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Band-structure Parameters of Organic Conductors, $TSeT_2Cl$, TTT_2I_3, and $TSeT_2SCN$

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(Received March 24, 1983)

The band-structure parameters of organic conductors, $TSeT_2Cl$, TTT_2I_3, and $TSeT_2SCN$ (TSeT; 5,6:11,12-bis(diseleno)naphthacene; common name: tetraselenotetracene, and TTT; 5,6:11,12-bis(dithio)naphthacene; common name: tetrathiotetracene) were calculated using semiempirical molecular-orbital calculations. The longitudinal bandwidth W and the anisotropy parameter α of $TSeT_2Cl$ were obtained as 0.6 eV and 0.188 respectively. The shape of the Fermi surface, as calculated from the tight-binding theory and the large anisotropy parameter, agrees with its semimetallic nature at low temperatures. In TTT_2I_3, W=0.56 eV, and α=0.018. This compound was regarded as a one-dimensional metal. The semiconductive conduction of $TSeT_2SCN$ was interpreted in terms of the small bandwidth, W=0.26 eV.

A number of highly-conducting complexes containing tetrathiotetracene (TTT) or tetraselenotetracene (TSeT) have been known, and their solid-state properties have been studied in some detail.[1,2] Among these compounds, $TSeT_2Cl$, $TSeT_2Br$, and $TSeT_2I$ show a high conductivity *ca.* $10^3\,\Omega^{-1}\,cm^{-1}$ at room temperature and retain their metallic conductivity down to 26 K.[3,4] Below this temperature the magnitude of the resistivity increases, but there is a tendency for T→0 to a finite value on the order of the room-temperature value. TTT_2I_3 also shows a high conductivity *ca.* $10^3\,\Omega^{-1}\,cm^{-1}$ at room temperature, but it has a conductivity maximum and its conductivity follows an activation process at low temperatures.[5] However, there is a considerable range of nonstoichiometry on iodine, and its physical properties suffer a serious influence from the disorder of the iodine sublattice.[5-8]

It is widely believed that an organic metal has a quasi-one-dimensional conduction band resulting from the π-π interaction of the planar organic molecules. However, the density-wave instabilities inherent in one-dimensional metals tend to destroy the metallic states of these compounds. The present authors have previously calculated the band-structure parameters of $TMTSF_2X$ and $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$.[9-11] In the former, the authors concluded that the transverse transfer integrals, which are of the order of 0.1 of the longitudinal integrals, play an important role in the stabilization of the metallic states. On the other hand, $(BEDT\text{-}TTF)_2ClO_4(C_2H_3Cl_3)_{0.5}$ was regarded as a two-dimensional semimetal.

In the present investigation, the band-structure parameters of $TSeT_2Cl$ and TTT_2I_3 were calculated. To make a comparison, the calculation was also performed on an organic semiconductor, $TSeT_2SCN$. All these complexes have regular TSeT (or TTT) chains, and their conduction bands are three-quarters filled. In view of the calculated longitudinal bandwidths and the transverse interactions, their physical properties were also discussed.

Computation

The method of calculation was the same as has already been reported.[9-11] At first the molecular orbitals of a single molecule were calculated by the extended Hückel method using the parameters shown in Table 1.[12] Since the HOMO, which makes the conduction band in the crystal, is energetically separated enough from the other energy levels, as is shown in Fig. 1, only the overlaps of the HOMO's between the nearest-neighbor molecules were calculated. The transfer integrals t_i of the tight-binding theory are given from these overlaps S_i by the relation: $t_i=ES_i$, where E is a constant of the order of the ionization potential of the HOMO. From the energy level of the molecular orbital calculation (Fig. 1), in the present

TABLE 1. THE EXPONENTS ζ AND THE IONIZATION POTENTIALS ε (eV) FOR ATOMIC ORBITALS

		ζ	ε			ζ	ε
S	3 s	2.122	−21.6	C	2 s	1.625	−21.4
	3 p	1.827	−15.5		2 p	1.625	−11.4
Se	4 s	2.44	−20.5	H	1 s	1.0	−13.6
	4 p	2.07	−14.4				

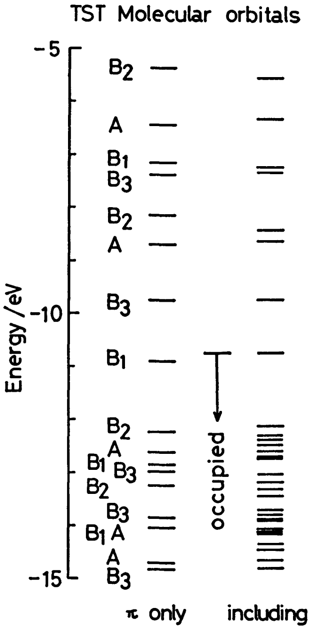

Fig. 1. Molecular orbital energy levels of TSeT. The left is the calculation including π-orbitals only, and the orbital symmetry of D_2 point group is shown.

paper E was assumed to be -10 eV. This value was also used in the calculations for the radical cation salts of TTF and BEDT–TTF when sulfur 3d orbitals were not included; it gave realistic magnitudes of transfer integrals which agrees well with the experimental results.[11] As will be discussed in the present paper, it also agrees consistently with various experiments on the salts of TTT and TSeT. The structural data were taken from the literature.[16–18]

Results and Discussion

$TSeT_2Cl$. The crystal structure of $TSeT_2Cl$ is shown in Fig. 2.[16] Because of the tetragonal symmetry, there are only two kinds of intermolecular interactions: the longitudinal interaction along the c axis, and the transverse interaction along the a axis. The calculated overlaps S, the bandwidth, and the anisotropy parameter α $(=t_{\mathrm{i}}/t_{//})$ of the HOMO are shown in Table 2. The longitudinal bandwidth has been experimentally obtained as 0.6 eV from the magnetism.[3] This estimation agrees well with the results of the present calculation.

From the anisotropy of the conductivity, the anisotropy parameter can be roughly estimated using the following relation:[19]

$$\alpha=\left(\frac{t_{\perp}}{t_{//}}\right)\gtrsim\left(\frac{\sigma_{\perp}}{\sigma_{//}}\right)^{1/2}. \tag{1}$$

From the observed anisotropy of $TSeT_2Br$, $(\sigma_{//}/\sigma_{\perp})=60$,[20] one obtains $\alpha=0.129$ $(t_{\mathrm{a}}=0.077\ \mathrm{eV})$. The magnitude of the calculated $|\alpha|$ is slightly larger than this value.

From a standard tight-binding theory,[21] we obtained the following seqular equation for the conduction band.

$$\begin{vmatrix} \lambda & \cos\frac{kb}{2}\cos\frac{kc}{2} & 0 & \cos\frac{ka}{2}\cos\frac{kc}{2} \\ \cos\frac{kb}{2}\cos\frac{kc}{2} & \lambda & \cos\frac{ka}{2}\cos\frac{kc}{2} & 0 \\ 0 & \cos\frac{ka}{2}\cos\frac{kc}{2} & \lambda & \cos\frac{kb}{2}\cos\frac{kc}{2} \\ \cos\frac{ka}{2}\cos\frac{kc}{2} & 0 & \cos\frac{kb}{2}\cos\frac{kc}{2} & \lambda \end{vmatrix}=0, \tag{2}$$

$$\lambda=\frac{2t_{\mathrm{c}}\cos kc-\varepsilon}{4t_{\mathrm{a}}}.$$

This equation yields the dispersion relation:

$$\varepsilon(k)=2t_{\mathrm{c}}\left[\cos kc\pm2\alpha\left(\cos\frac{ka}{2}\cos\frac{kc}{2}\pm\cos\frac{kb}{2}\cos\frac{kc}{2}\right)\right], \tag{3}$$

$$\alpha=t_{\mathrm{a}}/t_{\mathrm{c}}.$$

Since the conduction level is three-quarters filled, when $\alpha=0$ the Fermi surface consists of two pleces of four-fold degenerated planes at $k_{\mathrm{F}}=\pm\pi/4c$. The shape of the Fermi surface depends only on the anisotropy parameter α. We numerically calculated their shapes for several values of α, as is shown in Fig. 3. When

$$\alpha=t_{\mathrm{a}}/t_{\mathrm{c}}=\frac{2}{8}\left(1-\cos\frac{\pi}{4c}c\right)=0.07322,$$

one of the Fermi surfaces touches the $k_{\mathrm{c}}=0$ plane, and if α is larger, a closed Fermi surface appears. At the calculated value of $\alpha=0.188$, two of the Fermi surfaces are closed, and though the other two remain open, they are seriously distorted. On the other hand, at the value of $\alpha=0.129$ obtained from the anisotropy of the conductivity of $TSeT_2Br$, one is closed, while the other three remain open. It is worth noting that, though the anisotropy parameter α of $TSeT_2Cl$ is only slightly larger than that of $TMTSF_2X$ (*ca.* 0.1),[9] the three-dimensional alignment and the larger number (8) of the neighbor molecules than that (4) of $TMTSF_2X$ effectively distort the Fermi surface.

From the anomaly of the magnetic susceptibility and the specific heat,[3,22] many authors have treated the transition at 26 K as of a Peierls type. Shchegolev and Yagubskii proposed a model where two of the four pairs of Fermi surfaces are nested, but the other two are unnested.[1] However, not only ideally planar Fermi surfaces, but also slightly distorted Fermi surfaces, can be effectively nested by a proper transfer vector.[23] Delhaes and his co-workers interpreted the properties below 26 K as a semimetallic state resulting from an imperfectly nested quasi-one-dimensional Fermi surface.[4] The observation of the anisotropic magnetoresistance also supports this interpretation.[20] The highly distorted Fermi surfaces in Fig. 3(d) agree with such semimetallic states. However, we are not certain whether a simple Peierls-type phase transition may occur on such a highly distorted Fermi surface as is shown in Fig. 3(d). A quantitative relation between the anisotropy and the Peierls transition in such a multi-band conductor remains unsolved.

In conclusion, we consider $TSeT_2Cl$ to be placed

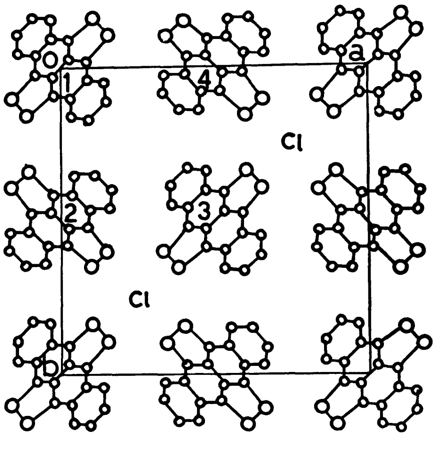

Fig. 2. Crystal structure of $TSeT_2Cl$, projection along c. The numbering of the molecules was used to derived Eq. 2.

TABLE 2. BAND-STRUCTURE PARAMETERS OF $TSeT_2Cl$

Direction	Overlap	$4t_{\mathrm{i}}$/eV	$\lvert\alpha_{\mathrm{i}}\rvert$
c	-15.0×10^{-3}	0.60	
a	2.8×10^{-3}	-0.11	0.188

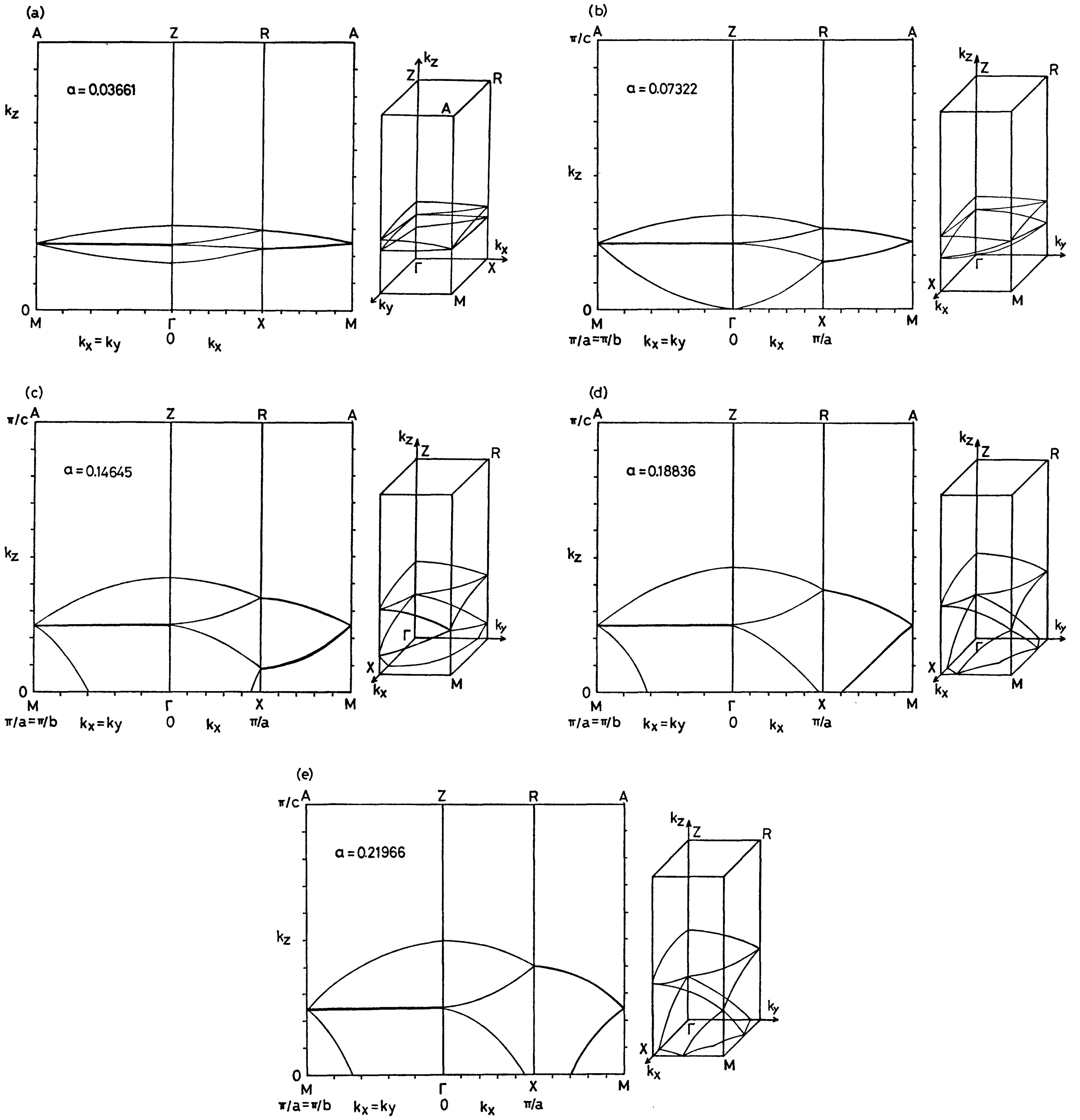

Fig. 3. Shape of the Fermi surfaces for various anisotropy parameters α, based on the dispersion of Eq. 3.

on the boundary between a one-dimensional metal and a three-dimensional metal.

TTT$_2$*I*$_3$. The crystal structure of $\mathrm{TTT_2I_3}$ is shown in Fig. 4.[17] There are three kinds of intermolecular interactions. The calculated band-structure parameters are shown in Table 3. Since the magnetic susceptibility of $\mathrm{TTT_2I_3}$ shows some temperature dependence, we cannot estimate the bandwidth directly from the magnetic data. However this fact qualitatively suggests that $U/4t$ in $\mathrm{TTT_2I_3}$ is larger than that in $\mathrm{TSeT_2Cl}$, and if the on-site Coulomb repulsion U is assumed to be unchanged, in $\mathrm{TTT_2I_3}$ a slightly smaller bandwidth than that of $\mathrm{TSeT_2Cl}$ is to be expected. There are some discrepancies as to the thermoelectric power because of the influence of disorder, but the bandwidth is estimated as 0.64 eV by Isett,[7] as 0.67 eV by Chaikin *et al.*,[24] as 0.7 eV by Khanna *et al.*,[8] and as 1.0 eV by Mihaly *et al.*[6] Since the magnitude of the thermoelectric power decreases with an increase in disorder,[8,24] we consider that the smallest *W* is the value free from the influence of disorder. Therefore, our calculated value agrees with the experimental results and can be regarded as the 'intrinsic' bandwidth free from disorder.

Though the shortest transverse S–S distance, 3.373 Å, along c is considerably smaller than the shortest longitudinal distance, 3.73 Å,[17] the calculated transverse overlap is much smaller than the longitudinal

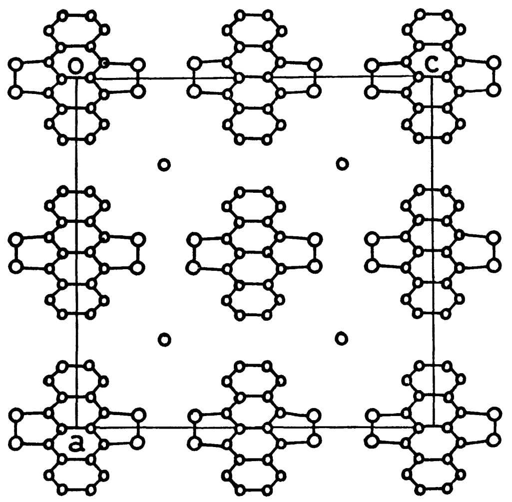

Fig. 4. Crystal structure of TTT_2I_3, projection along b.

Table 3. Band-structure parameters of TTT_2I_3

Direction	Overlap	$4t_i$/eV	$\|\alpha_i\|$
b	13.9×10^{-3}	-0.56	
c	-0.25×10^{-3}	0.010	0.018
a	0.064×10^{-3}	-0.0026	0.005

overlap and the anisotropy parameter, $\alpha=0.018$, is very small. It has been observed in the transverse interaction of TTF that the magnitude of the orbital overlap crosses zero between the σ-like and π-like overlap of the sulfur p-orbitals.[11] Because of the two similar sulfur atoms on the side of the molecule and the π-character of the HOMO, the change in the overlap between the two TTT molecules with side-by-side orientation is not very different from the case of TTF. Since the orientation between the two TTT molecules along c in TTT_2I_3 satisfies the crossover condition ($\phi=10°$ by the notation in Ref. 11, where ϕ is the angle between the molecular plane and the intermolecular transfer vector), t_c similarly happens to be small. Therefore, despite the relatively short transverse S–S distance, TTT_2I_3 has a highly-anisotropic band structure. This large anisotropy, $\alpha=0.018$, corresponds to that of the well-known organic metal, TTF–TCNQ ($\alpha=0.015$, for the largest transverse overlap).[19,25]

There are many pieces of evidence which suggest that the phase transition of TTT_2I_3 at 50 K is of a Peierls type. The magnetic susceptibility follows an exponential law with a gap 190 K below 50 K,[5,7] and the specific heat shows an anomaly of magnitude consistent with a mean-field model for a Peierls phase transition with correction for fluctuations.[26] The lack of the observation of distortion by X-ray scattering can be interpreted by the large scattering factor of iodine.[27] Though the influence of disorder seriously modifies the properties, especially those such as electrical conductivity and thermoelectric power, we regard TTT_2I_3 as essentially a quasi-one-dimensional metal, in which the bandwidth and the anisotropy parameter α are of about the same order as, or slightly larger than, those of TTF–TCNQ.

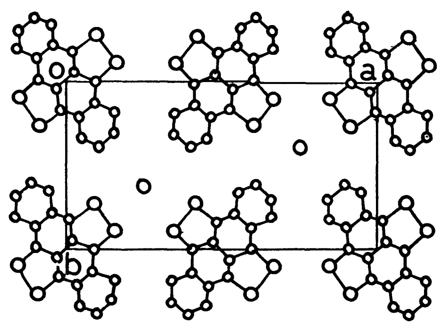

Fig. 5. Crystal sturcture of $TSeT_2SCN$, projection along c.

Table 4. Band-structure parameters of $TSeT_2SCN$

Direction	Overlap	$4t_i$/eV	$\|\alpha_i\|$
c	-6.6×10^{-3}	0.26	
a	-0.22×10^{-3}	0.0087	0.033
b	0.18×10^{-3}	-0.007	0.027

$TSeT_2SCN$. The crystal structure of $TSeT_2SCN$ is shown in Fig. 5.[18] Here again there are three kinds of intermolecular interactions. The calculated overlap and the bandwidths are shown in Table 4.

Though the degree of the occupancy of the TSeT chain is the same as that in $TSeT_2Cl$, its longitudinal conductivity is 20 Ω^{-1} cm^{-1} at room temperature and decreases with a lowering of the temperature.[18] This difference has been attributed to the larger interplanar separation (3.53 Å in $TSeT_2SCN$, and 3.37 Å in $TSeT_2Cl$), and to the pronounced anisotropy in the packing of the TSeT molecules which comes from the difference in the angle between the molecular plane and the chain direction.[18] The calculated small bandwidth and the small α reflect these structural differences. Though this anisotropy is large enough to produce a Peierls gap, it is more likely that the diffusive conduction occurs due to the larger electronic correlation in a narrowband conductor.

General Discussion. In the present paper, we neglected the interaction through anions. Since the Se–Cl distance, 3.024 Å, in $TSeT_2Cl$[16] and the Se–S distance, 3.160 Å, in $TSeT_2SCN$[18] are much shorter than the sum of the van der Waals radii, a considerable overlap of their orbitals is to be expected. These overlaps may contribute to the transport of electrons. Shchegolev and Yaguskii considered it as the dominant mechanism of the transverse interaction in $TSeT_2Cl$.[1] The contribution of such a transport to the transfer integral can be represented by a second-order perturbation theory as follows:

$$H_{ij} = \frac{H_{ia}H_{aj}}{E_a - E_o}, \tag{5}$$

where i and j represent the different organic molecules; E_a, the energy of the highest occupied level of the anion, and E_o, the energy of the HOMO. $E_a - E_o$ is estimated to be usually of the order of several electron volts. In $TSeT_2Cl$, even if H_{ia} is assumed to be 10 times larger than the direct interaction, $W_a=0.01$ eV, H_{ij} is less than 0.05 eV. It is possible that this second-order effect makes a considerable contribution to the transverse transport. However, it is unlikely that the calculated, not-small direct interaction is negligible compared with the indirect transport.

In summary, using semiempirical molecular orbital calculations, the present authors calculated the band-structure parameters of $TSeT_2Cl$, TTT_2I_3, and $TSeT_2SCN$. The bandwidth and the anisotropy parameter of $TSeT_2Cl$ are obtained as 0.6 eV and 0.188 respectively; this compound is considered to be on the boundary between a one-dimensional metal and a three-dimensional metal. In TTT_2I_3, the bandwidth is 0.56 eV and $\alpha=0.018$, and this compound is regarded essentially as a one-dimensional metal. On the contrary, the small bandwidth 0.26 eV of $TSeT_2SCN$ is considered to be responsible for the diffusive conduction.

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