CHEMISTRY LETTERS, pp. 1923-1926, 1982.

BAND STRUCTURE OF THE ORGANIC SUPERCONDUCTOR: $(TMTSF)_2X$

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Energy band calculation of the organic superconductor $(TMTSF)_2X$ was carried out. The ratio of the intermolecular overlap integrals of the highest occupied molecular orbitals parallel and perpendicular to the chain axis is more than ten times smaller than that of TTF-TCNQ. The Fermi surface is a slightly waving plane.

Recently, the dimensionality of the organic superconductor $(TMTSF)_2X$ ($X=PF_6$, AsF_6, SbF_6, TaF_6, and ClO_4) has been actively discussed. $(TMTSF)_2X$ is considered as a one-dimensional metal from the anisotropy of the conductivity and the optical reflectance,[1)] as well as the studies on charge density wave or spin density wave.[2)] However the importance of the interchain interaction has been indicated from the short interchain Se-Se distances,[3,4)] the observation of the plasma edge by the light polarized perpendicular to the stacking axis,[5)] and the closed two-dimensional orbit expected from the Shubnikov-de Haas resistance.[6)]

In this paper we report energy band calculation of $(TMTSF)_2BF_4$.[7)] The ratio of the intermolecular overlap integrals of the highest occupied molecular orbitals (HOMO) parallel and perpendicular to the chain axis $S_{/\!/}/S_{\perp}$ is obtained to be about 10, which is considerably smaller than that in TTF-TCNQ; the order of 10^2.[8)] Whereas the shape of the Fermi surface is a plane, which indicates a one-dimensional conductor along the chain.

We adopted tight-binding approximation and the Bloch functions are constructed from atomic orbitals $\phi_a(r)$,

$$\Psi_a(r)=\frac{1}{\sqrt{N}}\sum_n e^{inka}\phi_a(r-na). \tag{1}$$

The overlap integrals and the Fock integrals are given as,

$$\begin{aligned} S_{ij}(k)&=S_{ij}^{(0)}+\sum_L (S_{ij}^{(L)}+S_{ji}^{(L)})\cos ka_L+i\sum_L (S_{ij}^{(L)}-S_{ji}^{(L)})\sin ka_L \\ H_{ij}(k)&=H_{ij}^{(0)}+\sum_L (H_{ij}^{(L)}+H_{ji}^{(L)})\cos ka_L+i\sum_L (H_{ij}^{(L)}-H_{ji}^{(L)})\sin ka_L \ , \end{aligned} \tag{2}$$

where,

$$S_{ij}^{(L)}=\int\phi_i(r)\,\phi_j(r-a_L)d\tau, \qquad H_{ij}^{(L)}=\int\phi_i(r)\hat{H}\phi_j(r-a_L)d\tau \ , \tag{3}$$

and the summations are taken for all nearest neighboring pairs illustrated in Fig. 1. The $S_{ij}^{(L)}$'s were calculated from Slater type orbitals with the parameter ζ's Se 4s; 2.112, 4p;1.827, 4d;1.5, C 2s;1.625, 2p; 1.625, and H 1s;1.00.[9] The $H_{ij}^{(L)}$'s were estimated from the equation,

$$H_{ij}^{(L)}=\frac{(K-(K-1)\Delta^2)}{2}[(1+\Delta)H_{ii}+(1-\Delta)H_{jj}] \times S_{ij}^{(L)} \qquad (4)$$

$$\Delta=\frac{H_{ii}-H_{jj}}{H_{ii}+H_{jj}}$$

where K=1.75.[10] $H_{ii}=\varepsilon_i$'s are ionization potentials with the values, Se 4s;-20.0, 4p;-11.0, C 2s;-21.4, 2p;-11.4, and H 1s;-13.6eV. ε for Se 4d was changed from -2.7 to -8.0eV and the calculation excluding Se 4d orbitals was also performed to investigate the influence of Se 4d orbitals. After the calculation of the H and S matrices, the secular equation,

$$|H_{ij}(k) - \varepsilon S_{ij}(k)| = 0 \qquad (5)$$

was solved for various values of k's.

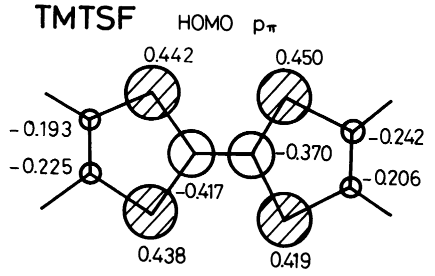

Fig. 2. Coefficients of the HOMO.

It has been well known that the HOMO of TTF analogue is a total symmetry molecular orbital constructed from p_π orbitals of carbon and chalcogen atoms. Figure 2 shows the coefficients of the HOMO of the TMTSF molecule in $(TMTSF)_2BF_4$ obtained by extended Hückel molecular orbital calculation.[4] Because the energy level of the HOMO is far from the other levels, the energy band structure near the Fermi level can be studied by calculating the intermolecular overlap integrals of the HOMO. The transfer integrals are proportional to the overlap integrals from Eq. 4; $t_i=E\ S_i$ where E is a constant of the order of ionization potential of the HOMO. The intermolecular overlap integrals of the HOMO illustrated in Fig. 1. are shown in Table 1. S_1 and S_2, which are parallel to the chain axis, are about ten times larger than the others. This small ratio $S_{/\!/}/S_{\perp}$ compared to that of the order of 10^2 in TTF-TCNQ,[7] indicates the importance of interchain interaction

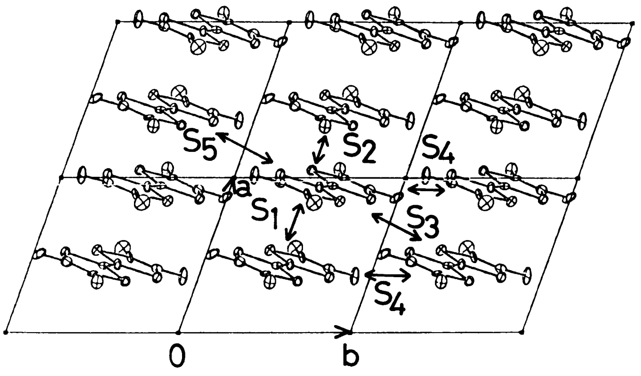

Fig. 1. Intermolecular interaction of TMTSF.

Table 1. Overlap integrals of the HOMO illustrated in Fig. 1.

	Direction	$\times 10^{-3}$
S_1	[100]	34.766
S_2	[100]	38.455
S_3	$[1\bar{2}0]$	-3.556
S_4	[010]	-3.959
S_5	$[1\bar{2}0]$	-1.607

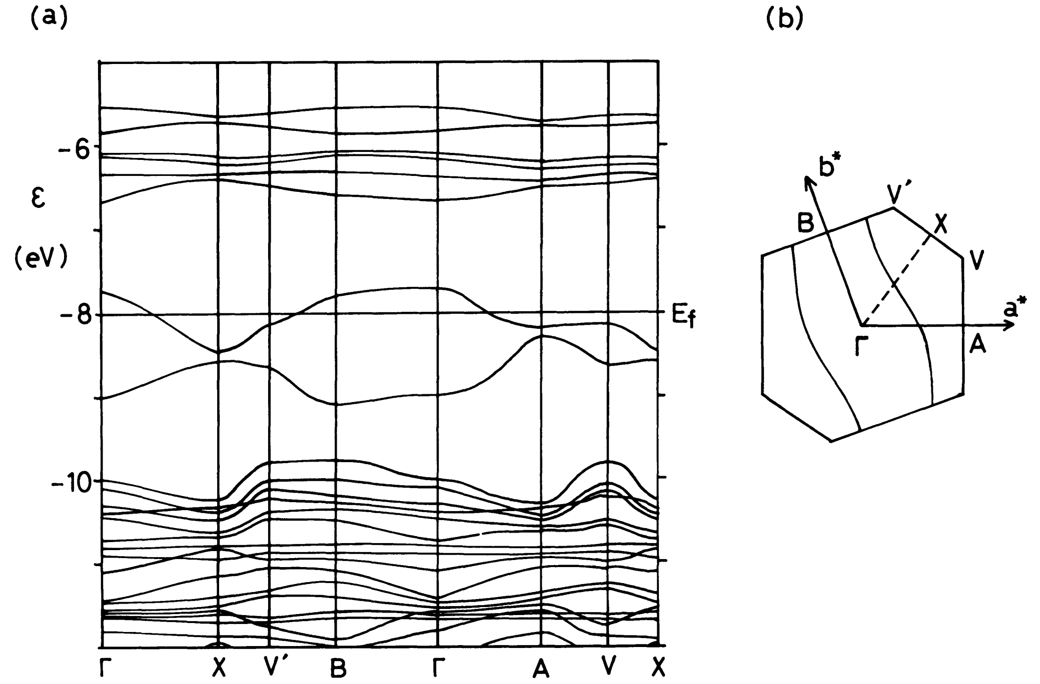

Fig. 3. Energy band structure of $(TMTSF)_2X$.

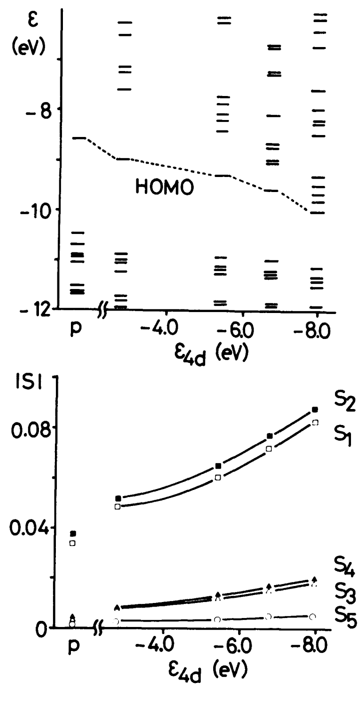

Fig. 4. Influence of Se 4d orbitals. (a) Energy levels of molecular orbitals. (b) Change of the intermolecular overlap integrals.

along the b axis. The overlap integrals along the c axis are negligible due to the large separation between TMTSF molecules. It is worth noting that in spite of the short Se-Se distances along the [1$\bar{2}$0] direction,$^{3)}$ the interaction S_4 along the [010] direction is larger than S_3 and S_5.

The energy band structure obtained from Eq. 5. is shown in Fig. 3, in which Se 4d orbitals are not included. The stoichiometry of the complex indicates that one quarter of the electrons of the HOMO is removed. Therefore the Fermi level crosses the upper energy level around $k_a=0.5\pi/a$. If one runs from $k_b=0$ to $k_b=\pi/b$ on the Fermi surface, the ripple of k_a is within $0.1\pi/a$ (Fig. 3b). Thus the Fermi surface is a slightly waving plane. This result seems to conflict with the observation of the magnetic quantum oscillations. Then we investigated the influence of Se 4d. Figure 4 shows the change of energy levels of molecular orbitals and the variation of the intermolecular overlap integrals of the HOMO with changing ε_{4d}. Both overlap integrals parallel and perpendicular to the chain axis increase when ε_{4d} is lowered. Therefore the ratio $S_{/\!/}/S_{\perp}$ and the shape of the Fermi surface calculated from the HOMO suffers very little change. However the HOMO is no longer energetically far from the other levels. From the band calculation including Se 4d (ε_{4d}=-8.0eV), we obtained a wide energy band constructed from a number of energy levels, which continues from about -14eV to -5eV. This wide band is partially-filled and the Fermi level crosses at least two different levels. In this extreme case there is no trace of one-dimensionality. However we cannot consider this picture plausible because of the many one-dimensional properties of $(TMTSF)_2X$.

We conclude that $(TMTSF)_2X$ is essentially a one-dimensional metal. Enhanced ripple of the planar Fermi surface caused by the smaller $S_{/\!/}/S_{\perp}$ ratio than that of TTF-TCNQ, is considered to inhibit the Peierls transition. In this sence the two-dimensionality of $(TMTSF)_2X$ is important. However closed two-dimensional Fermi surface is not resulted straightfowardly in spite of the relatively large inter-chain couplings. It was pointed out by Horovitz et al. that if spin (or charge) density waves are present, shifting one of the two sheets of the quasi-one-dimensional Fermi surface by the nesting vector results in small electron and hole pockets.[11)] Thus the spin density waves observed in $(TMTSF)_2PF_6$ show that the slightly waving Fermi surface obtained by the present calculation is not necessarily in conflict with the two-dimensionality of $(TMTSF)_2X$.[12)]

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(Received September 13, 1982)