BAND STRUCTURE OF $\beta$-(BEDT-TTF)$_2$PF$_6$.  
ONE-DIMENSIONAL METAL ALONG THE SIDE-BY-SIDE MOLECULAR ARRAY 

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(Received 22 October 1984 by W. Sasaki)  

The energy-band structures of isostructural organic conductors, $\beta$-(BEDT-TTF)$_2$PF$_6$ and (BEDT-TTF)$_2$AsF$_6$ are calculated (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene). The strong dimerization of the face-to-face array makes the Fermi surface open perpendicularly to the side-by-side array. This dimer model indicates that the phase transition around room temperature is associated with a $2k_F$ charge density wave.  

The compound $\beta$-(BEDT-TTF)$_2$PF$_6$ is the first organic conductor recognized one-dimensional along the side-by-side (transverse) array.$^1$ Its conductivity is largest along this array (the c-axis), it undergoes a metal-insulator transition at $T_C=297$ K, and below $T_C$ the lattice constant $c$ is doubled.$^2$ Recently Leung et al. have reported the crystal structure of (BEDT-TTF)$_2$AsF$_6$,$^3$ although its space group has been chosen differently, it is isostructural with $\beta$-(BEDT-TTF)$_2$PF$_6$. The AsF$_6$ salt also undergoes a similar phase transition at $T_C=273$ K.$^4$ In the present investigation, the tight-binding energy band structures of these compounds are calculated.  

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The intermolecular interactions of $\beta$-(BEDT-TTF)$_2$PF$_6$ is shown in Fig. 1 (space group Pnna).$^1$ The BEDT-TTF
molecules form sheets parallel to the ac-plane and electronic interaction between the different sheets is negligible. The AsF₆ salt (space group A2/a) has a similar molecular arrangement in the sheets; the c-axis of the PF₆ salt corresponds with the b-axis of the AsF₆ salt. There is only one crystallographically independent molecule.

In organic conductors, the molecular orbitals in solids are not largely different from the molecular orbitals of the independent molecule. Therefore the molecular orbitals of a single molecule are calculated by using the extended Hückel method. The Slater exponents and the ionization potentials (including sulfur 3d orbitals) are the same as those used in a previous report. ⁵)

\[
E(k) = 2t_c \cos k_c c \pm \sqrt{\Gamma + \Delta} \frac{1}{2}
\]

\[
\Gamma = (t_{a1} + 2t_p \cos k_c c)^2 + t_{a2}^2 + t_q^2 + 2t_{a1}t_{a2} \cos k_c c
\]

\[
\Delta = 2(t_{a1} + 2t_p \cos k_c c)(t_{a2}^2 + t_q^2 + 2t_{a1}t_{a2} \cos k_c c)^{1/2} \cos (k_a/2)
\]

The conduction band of cation radical salts consists of the highest occupied molecular orbitals (HOMO), from which the other energy levels are separated enough. The transfer integrals \(t\) of the conduction band are considered to be proportional to the intermolecular overlaps \(S\) of the HOMO. Hence the intermolecular overlaps of the HOMO are calculated (Table 1). Table 1 also shows the parameters \(\phi\) and \(D\), which describe the configuration of the neighbor molecules (Fig. 2). ⁵)

At first sight, the interactions are likely to show a small anisotropy. The face-to-face array is, however, strongly dimerized; the overlap \(a2\) is significantly smaller than \(a1\) (Table 1). In the configuration of \(a2\) (\(\phi = 60^\circ\), \(D = 0\, \text{Å}\)), the intermolecular overlap is small because the HOMO of the two molecules are overlapped so as to cancel the overlap of each atom. ⁵) On the contrary, it is evident from the crystal structure that the side-by-side array is uniform.

The energy dispersion relation derived from the tight-binding method is,

**Fig. 2. Definition of the parameters \(\phi\) and \(D\) shown in Table 1.**

**Table 1. Intermolecular overlaps in \((\text{BEDT-TTF})_2\text{PF}_6\) and \((\text{BEDT-TTF})_2\text{AsF}_6\).**

<table>
<thead>
<tr>
<th>((\text{BEDT-TTF})_2\text{PF}_6) Direction</th>
<th>(S / 10^{-3})</th>
<th>(\phi)</th>
<th>(D / \text{Å})</th>
<th>((\text{BEDT-TTF})_2\text{AsF}_6) S / 10⁻³</th>
<th>(\phi)</th>
<th>(D / \text{Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1) [100]</td>
<td>10.4</td>
<td></td>
<td></td>
<td>13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a_2) [100]</td>
<td>3.2</td>
<td>62°</td>
<td>0.1</td>
<td>-2.8</td>
<td>63°</td>
<td>0.2</td>
</tr>
<tr>
<td>(c) [001]</td>
<td>8.4</td>
<td>4°</td>
<td>1.7</td>
<td>10.3</td>
<td>4°</td>
<td>1.7</td>
</tr>
<tr>
<td>(p) [104]</td>
<td>2.8</td>
<td></td>
<td></td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(q) [104]</td>
<td>14.2</td>
<td>37°</td>
<td>1.6</td>
<td>16.5</td>
<td>36°</td>
<td>1.5</td>
</tr>
</tbody>
</table>
From this equation and the intermolecular overlaps in Table 1, the band structure and the shape of the Fermi surface is calculated (Fig. 3). In order to understand the energy dispersion of Eq. 1, it is instructive to consider a simplified model of the band structure. When $t_p=q=0$, the above energy dispersion is reduced to,

$$E(k) = 2t_c \cos k_c + (t_{a1}^2 + t_{a2}^2 + 2t_{a1}t_{a2} \cos (k_d a/2))^{1/2} \quad (2)$$

The band structure based on this relation is shown in Fig. 4. Although the largest overlap $q$ is neglected, Fig. 4 shows a similar feature to Fig. 3, because the role of the oblique interactions $p$ and $q$ can be to some degree substituted by the other interactions. The upper two energy bands are separated from the lower two by $2(|t_{a1}| - |t_{a2}|)$; this is the effect of the strong dimerization along the $a$-axis. Since the dispersion along $c$ ($4|t_c|$) is considerably larger than that along a ($2|t_{a2}|$), the Fermi surface is open perpendicularly to the $c$-axis.

On the basis of Eq. 2, the condition that the Fermi surface is open perpendicularly to the $c$-axis, is obtained,

$$|t_{a1}| - |t_{a2}| + (t_{a1}^2 + t_{a2}^2)^{1/2} > 2|t_c| > |t_{a2}| \quad (3)$$

The overlaps in Table 1 satisfy this condition. In general, this condition is fulfilled when $|t_{a1}|c|t_c|||t_{a2}|$. In this dimer model the upper bands are half-filled ($k_F \approx |2c|/2c$). On the other hand, in a simple one-dimensional band along the $c$-axis ($|t_c| >> |t_{a1}|, |t_{a2}|$), the Fermi surface is also open and the whole bands are 3/4-filled ($k_F \approx 3\pi/4c$). Between these two regions, the Fermi surface shows a complicated form.

The large anisotropy of the conductivity ($\sigma_c/\sigma_a \approx 50$, above $T_c$) agrees with the one-dimensional nature of the band structure in Fig. 3. According to Kwak's derivation, it is obtained that in a metal with an open Fermi surface the anisotropy of the conductivity is proportional to the square of the ratio of the band widths, thus $\sigma_c/\sigma_a = (2t_c/t_{a2})^2$ in this compound. The calculated values give $\sigma_c/\sigma_a \approx 28$ for the

\[PF_6\text{ salt and } \sigma_c/\sigma_a \approx 54 \text{ for the AsF}_6\text{ salt. In view of the large error in measuring the anisotropy of conductivity, these values agree with the experimental values }\sigma_c/\sigma_a = 20 \text{ to } 50.\]

As shown in Fig. 3, it is possible that the Fermi surfaces are nested by the transfer vector $\vec{v} = (1, 0, 0.5)$ = (0, 0, 0.5). This vector corresponds to the doubling of the $c$ lattice below $T_c$ found in the X-ray investigation. Horovitz et al. have derived the condition that the nesting of the Fermi sur-
The optical conductivity includes the 'interband transition' between the dimers as well as the transition within one energy band.

The effect of the strong dimerization is, in the real space, schematically represented in Fig. 5. Above $T_c$ the dimers form a half-filled uniform metallic chain along the c-axis. Below $T_c$ the lattice constant c is doubled by accompanying a $2k_F$ charge density wave.

It has been considered in an earlier investigation that the transition at $T_c$ is due to a $4k_F$ modulation in a highly correlated band. Above $T_c$ this compound shows relatively large temperature-independent thermoelectric power $60 \mu V K^{-1}$. This value is too large to be interpreted by the one-electron Boltzmann transport theory and was attributed to strong Coulomb correlation, because the spin entropy $(k/e) \ln 2 = 60 \mu V K^{-1}$ in a highly correlated $3/4$-filled band is equal to the observed thermoelectric power. In a $3/4$-filled band the doubling of the lattice means the development of a $4k_F$ charge density wave. The $4k_F$ modulation is consistent with the large thermoelectric power, because such a modulation develops in a highly correlated band.

With regard to the optical reflectance, however, the oscillator strength of the a/ and the c/-spectra have been estimated to be almost equal. This is not surprising, because the energy scale observed in the optical measurement is much larger than that of the dc conductivity; the
In this interpretation, the simple one-dimensional band along the c-axis ($|t_c| >> |t_{al}|, |t_{a2}|$) is tacitly assumed. This assumption is, however, inconsistent with the results of the present calculation and the observation of the optical reflectance. Like the strong Coulomb repulsion, in the dimer model the dimer structure divides the energy band into two, and enables the two-fold modulation to make the Fermi surface nested. The difference between the $2k_F$ and the $4k_F$ models appears in the magnetic properties. For the $4k_F$ modulation, the electron spin survives below $T_C$. On the contrary, a $2k_F$ charge-density-wave state is nonmagnetic. Recently the decrease in the EPR signal, following the expression $\chi_P = (C/T)e^{-E_g/T}$ and $E_g = 1000$ K, has been observed in the AsF$_6$ salt. This observation indicates the development of a $2k_F$ charge density wave. The large thermoelectric power is interpretable by the entropy of electrons in a comparatively narrow band regardless of the magnitude of the Coulomb repulsion.\(^{10}\)

In conclusion, the band calculation shows that $\beta$-(BEDT-TTF)$_2$PF$_6$ is not a simple one-dimensional metal where $|t_c| >> |t_{al}|, |t_{a2}|$. Nevertheless the Fermi surface is open perpendicularly to the side-by-side array because of the strong dimerization, $|t_c| >> |t_{al}|, |t_{a2}|$. The dimer model indicates that the phase transition at $T_C$ is associated with a $2k_F$ charge density wave.

REFERENCES

9) R. Tajima, private communication.