

ELECTRONIC BAND STRUCTURE AND POINT-CONTACT SPECTROSCOPY OF THE ORGANIC SUPERCONDUCTOR β -(BEDT-TTF) $_2$ I $_3$

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ELECTRONIC BAND STRUCTURE OF β -(BEDT-TTF) $_2$ I $_3$

Several band structure calculations of organic metals have been carried out, employing the extended Huckel (EH) method [1,2,3]. The molecular states are calculated using some quantum-chemistry method like CNDO, MINDO, etc. The overlap between states of neighboring molecules is then calculated in some approximation, and transfer integrals are evaluated from the overlap integrals using the Huckel approximation. From these transfer integrals the bandwidth and anisotropy are determined. This is illustrated in Fig. 1 for a case of one molecule per unit cell (a) and two molecules per unit cell (b). The EH method has been applied to β -BEDT-TTF $_2$ I $_3$ (ET) by Mori et al (5) and Whangbo et al (3). They obtain an (essentially) 2-dimensional band structure (Fig. 1c), with a closed, nearly cylindrical Fermi surface of holes around point Γ ($\vec{k} = (0,0,0)$).

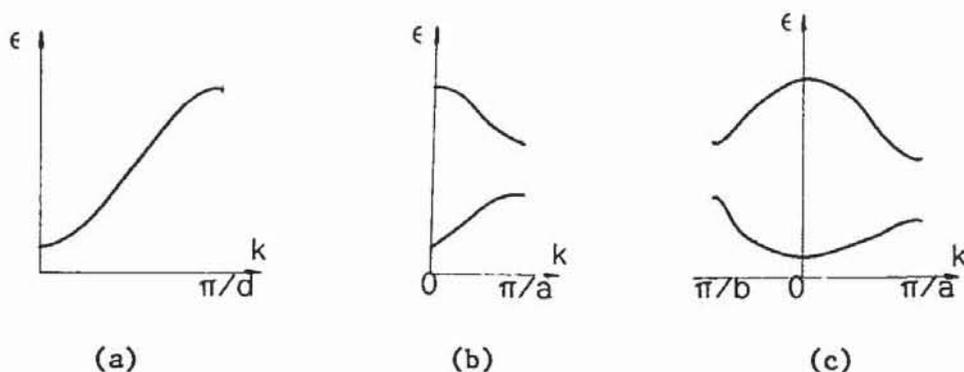


Figure 1

Electronic Band structure in the Extended Huckel Approximation, for one (a) and two (b) molecules per unit cell. (c) illustrates the band structure of β -(BEDT-TTF) $_2$ I $_3$ calculated by Mori et al [5].

The EH method, as well as the LCAO scheme on which it is based, assumes that the bandwidth W is small compared with the separation between the bands ΔE , so that admixture of states from neighboring bands can be ignored. The justification for this was given by a self-consistent calculation by Salahub et al [6] for TTF dimers, which showed that the splitting between dimer bonding and antibonding states is small compared with the separation $\Delta E \approx 2$ eV between the molecular levels. A bandwidth of $W \approx 0.2-0.5$ eV for TTF was estimated, and a similar value for TTF-TCNQ was estimated by Ladik [4]. Therefore, the assumption $W \ll \Delta E$ seemed to be justified. However, in one case [7] it was found necessary to consider admixtures from a neighboring band to account for the metallic conductivity of HMTSF-TCNQ at low temperatures.

We [8] carried out an ab-initio self-consistent electronic band structure calculation for ET, using the ASW method of Williams [9]. In this method it doesn't matter whether W is smaller or bigger than ΔE . This is a standard method that applies very well to metals, insulators, and crystalline solids in general. It is also well suited for loose structures, where the standard muffin-tin approximation for the potential (i.e. the assumption that the potential is constant outside the atomic spheres) is not good. The space between the atoms must be filled with spheres; the spheres overlap somewhat and their total volume equals the volume of the unit cell. The potential is calculated at each iteration from Poisson's equation, together with the local exchange-correlation term. A linearized basis set is employed, and this may introduce a slight error. Also, the correction terms for the overlaps between the spheres are not absolutely precise. However, the method is relatively fast and therefore suitable for large unit cells with a low symmetry, where the use of a larger basis set with present computers is not practical.

In the present case, there are 55 atoms in a unit cell with $\bar{P}1$ symmetry i.e. 28 atoms are inequivalent. In addition, 32 "empty spheres" were used to fill-up the space between the atoms (60% of the total volume). Each iteration takes about 4 hours "user time" on a very large computer (IBM 3090, ≈ 40 Mbytes effective CPU), and approximately 40 iterations are required to attain convergence. All "chemically" equivalent carbons, sulphurs, and hydrogens are assumed to possess the same charge; (thus there are 3 inequivalent carbons, 2 inequivalent sulphurs, 2 inequivalent iodines, and all hydrogens are assumed to be equivalent). The E vs. k curves are shown in Fig. 2. It is seen that some bands are approximately 0.5 to 1 eV wide, while the separation between bands is about 0.1 to 0.15 eV. Thus the condition for the validity of the extended Huckel approximation does not apply at all. The band structure looks more similar to that of a metal with a large unit cell, than that of a molecular crystal. The large density of bands is caused not only by the large size of the BEDT-TTF molecule, and the presence of 2 molecules per unit cell, but also there are additional states that are not molecular orbitals (LCAO's) but originate from the continuum (Fig. 3). These states are concentrated mainly in the "empty spheres" between the molecules. The location of these "empty spheres" for states with energies close to E_F is illustrated in Fig. 4. We were surprised to find that these "empty sphere" states sometimes form extremely narrow bands; in Fig. 5 we show a simplified partial density of states diagram, calculated assuming that all carbons, and all sulphurs, are equivalent. The narrow virtual state just above E_F corresponds to the empty sphere illustrated as a circle in Fig. 4. The value of the partial DOS of the empty spheres at E_F is very sensitive to details of the calculation; the value is smaller when we relax the condition that different carbons (and sulphurs) are inequivalent. Another surprising result of this calculation is the large partial DOS on the iodines at the FS. This suggests an appreciable participation of the iodines in the electronic properties of this compound.

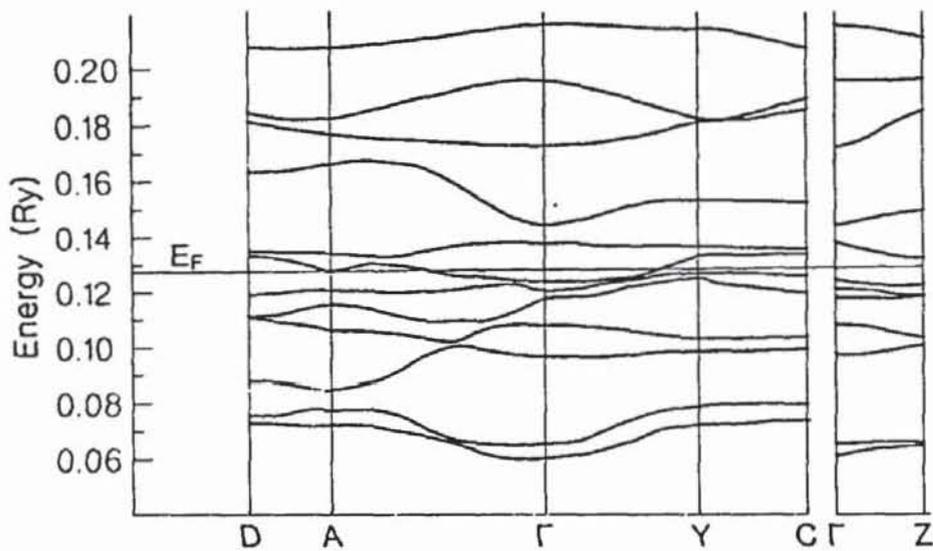


Figure 2
Energy vs. \vec{k} curves for β -(BEDT-TTF) $_2$ I $_3$

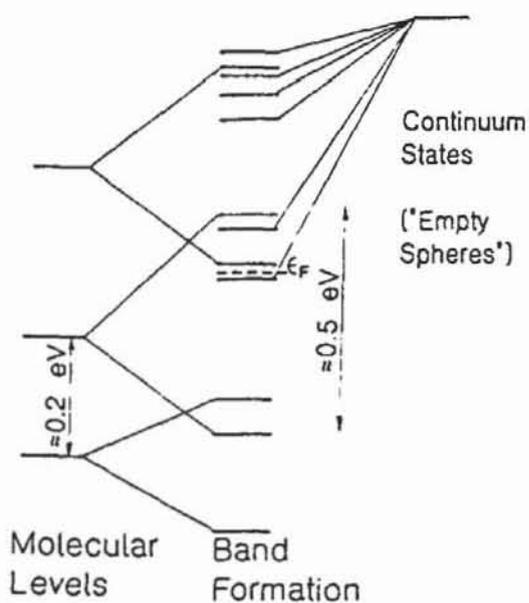


Figure 3

Illustration of the band formation from molecular and "empty sphere" states. The bandwidth greatly exceeds the distance between levels.

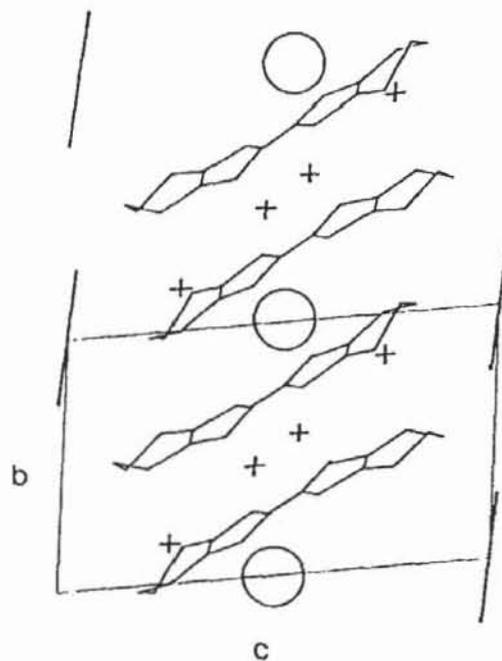
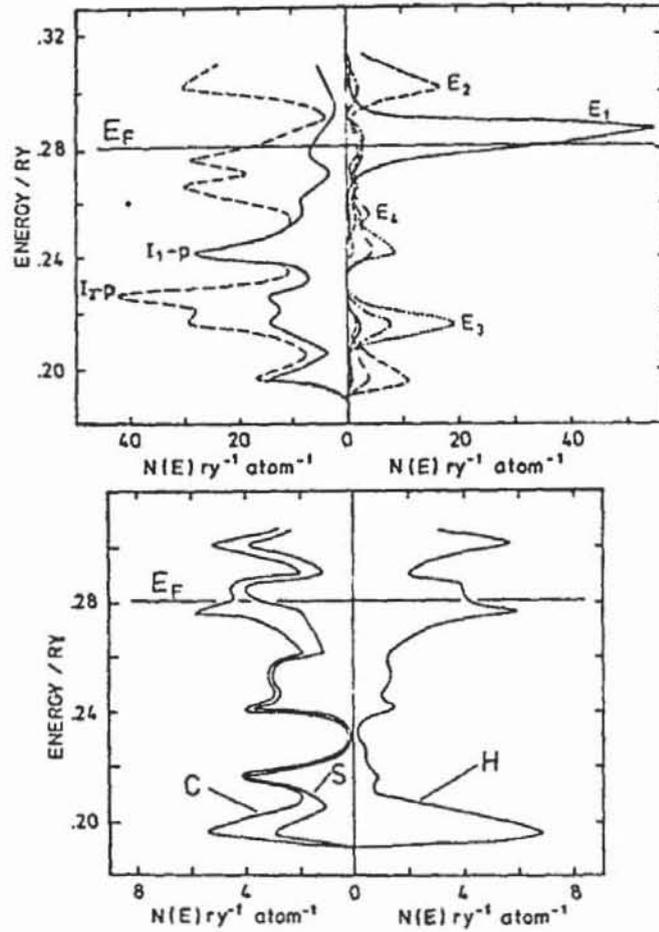


Figure 4

Illustration of the position of the empty spheres (Fig.5) E1 (circle), E2 and E3 (crosses) between the molecules.

Figure 5

Partial densities of states for the various atoms and empty spheres. The empty sphere states are narrow and close to the Fermi energy.



The Fermi surface (Fig.6) is in form of "warped planes" approximately perpendicular to the [110] direction. This is to be expected from the stacking of the molecules (Fig.7); however, the warping is very large and as a result the hole states form cylinders around points $A=(.5,0,k_c)$ and $Y=(0,.5,k_c)$. This FS is very different from that derived by the EH calculation; as a matter of fact, the states around Γ are electron states, rather than hole states. The hole cylinders around A and Y are approximately 2-dimensional, as predicted by the EH calculation, and also in agreement with the approximate 2-d nature of the conductivity and of H_{C2} . [10]

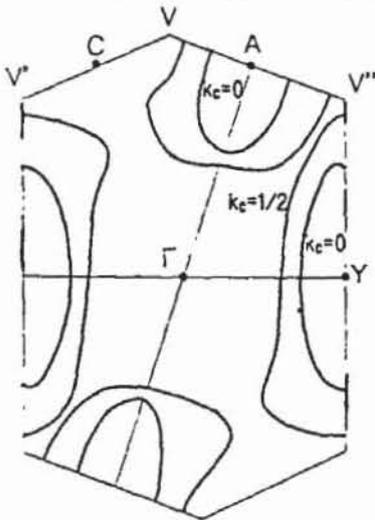


Figure 6

Cuts of the Fermi surface in the $k_a - k_b$ plane.

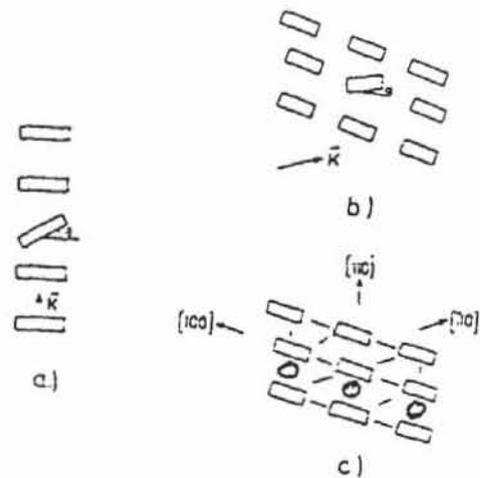


Figure 7

The stacking of the molecules (c), and illustration why the 2-d nature makes possible a linear electron-libron coupling (b), in contrast with 1-d stacks (a).

Superconductivity in organic metals was predicted on basis of the electron-phonon coupling theory, and the Eliashberg equations [11]. After the observation of superconductivity in TMTSF₂X, the question arose whether other mechanisms may be responsible for superconductivity [12], and if the electron-phonon mechanism is responsible, which phonons play the most important role: The high-frequency stretching modes, as suggested originally, the medium-frequency internal modes (bond twisting and bending) [13], or the low-frequency external modes (rigid translations and librations [14]). This question is also relevant nowadays, because of the new superconductors of the YBa₂Cu₃O₇ and La_{2-x}Sr_xCuO₄ families, where the Cu - O stretching mode may or may not play a rôle in the superconductivity mechanism.

This question can be investigated experimentally using the techniques of tunneling and point-contact spectroscopy to determine the Eliashberg function $\alpha^2(\omega)F(\omega)$ [15]. We used point-contact spectroscopy to determine the Eliashberg function, as well as tunneling to determine the superconducting gap. Preliminary results on α^2F were reported a year ago [16], and on the superconducting gap by the Argonne group [17]. They reported a value of $2\Delta/k_B T_c$ about 5 times larger than the BCS weak-coupling value of 3.52, and suggested that this is due to soft phonons.

We repeated the point-contact measurements using a contact between two crystals of ET in the a-b plane [18]. The d^2V/dI^2 curve is shown in Fig. 8, and the Eliashberg function $\alpha^2(\omega)F(\omega)$ derived from it is shown in Fig. 9.

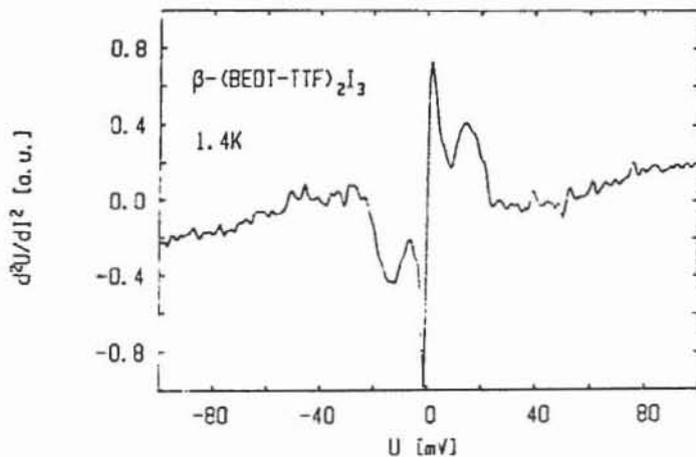


Figure 8

Second derivative of the point-contact spectroscopy I-V curve for ET.

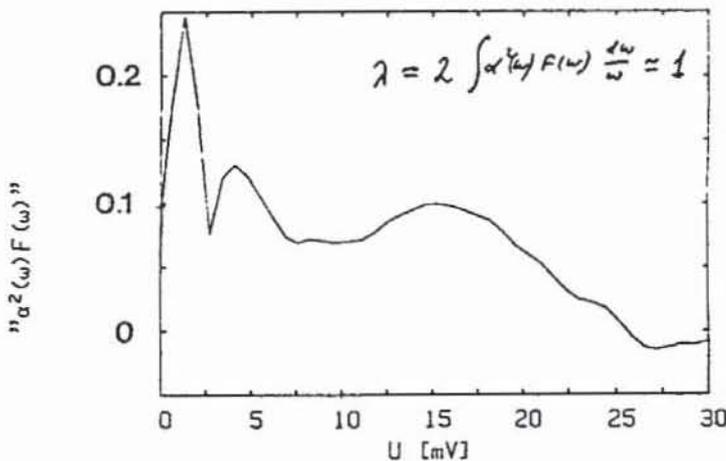


Figure 9

The Eliashberg function $\alpha^2 F$ derived from the I-V curves (Fig. 8) with no adjustable parameters.

It is seen that phonons with energies of ≈ 1 meV and 4 meV are strongly coupled with the electrons, as well as a broad band of phonons around 15 meV, up to 25 meV, above which frequency α^2F vanishes. The 1 meV phonon is exceedingly soft, and such phonons have not been seen before in organic metals (but predicted by Hawley et al [17]). The phonon at 4 meV fits well with a Raman line observed at 35 cm^{-1} [19]. The band around 15 meV is probably due mostly to external modes of the BEDT-TTF molecule, though a stretching mode of the I_3 molecule is observed around 120 cm^{-1} by Raman spectroscopy [20].

Integration of the observed $\alpha^2(\omega)F(\omega)$ curve using the Eliashberg equations, and the Bergmann-Rainer algorithm [21] yields a value of T_c in the range of the observed value of $T_c=1.35 \text{ K}$; the absolute precision of such a measurement is not very high, because of uncertainties concerning the surfaces of the crystals that actually touch [15]. Nevertheless, the value of $\lambda = 2 \int \alpha^2(\omega)F(\omega) d\omega/\omega$ (we find $\lambda \approx 1$) is probably reliable to better than a factor of 2. This leads strong support to the electron-phonon theory of the superconductivity of organic metals.

The value of $2\Delta/k_B T_c$ determined by the point-contact method is somewhat uncertain, since the shape of the d^2V/dI^2 curve is "gaussian" (Fig.10a) and does not agree precisely with the theoretical curve [22]. Measurements were carried out by U. Poppe using the vacuum-tunneling technique, in which the surfaces of the crystals do not touch, and therefore there is no stress on them [18]. This yields curves closer to the theoretical one (Fig.10b). For this curve, the value of $2\Delta/k_B T_c \approx 4.0 \pm 0.2$ is close to the BCS value, or more precisely, close to the value of strong-coupling superconductors like Pb, (and agrees with the value we expect for the value $\lambda \approx 1$ obtained from the integration of α^2F). Also, a theoretical determination, from the Eliashberg equations, using the Bergmann-Rainer algorithm, and the α^2F function of Fig.9 with the soft phonon at 1 meV strongly coupled to the electrons, yields this value, and not the very large value reported by Hawley et al [17]. Various other curves, and values of $2\Delta/k_B T_c$, are given in ref [18], and large values of $2\Delta/k_B T_c$ are indeed observed under certain experimental conditions.

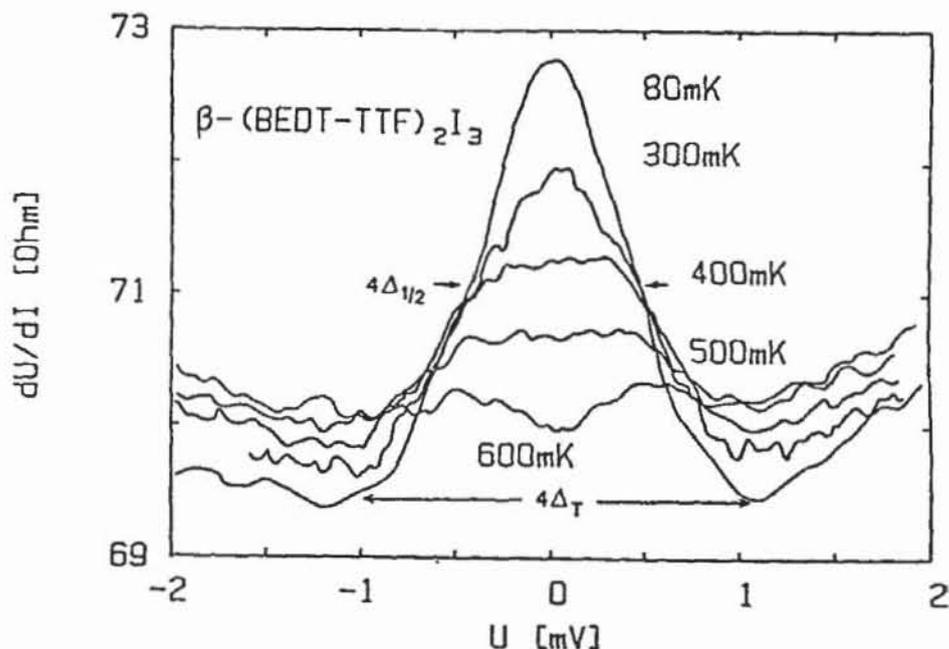


Figure 10 a

Tunneling data at various temperatures for two touching β -(BEDT-TTF) $_2I_3$ crystals. $\Delta_{1/2}$ is close to the BCS value for $T_c=1.35 \text{ K}$, while Δ_T is considerably larger.

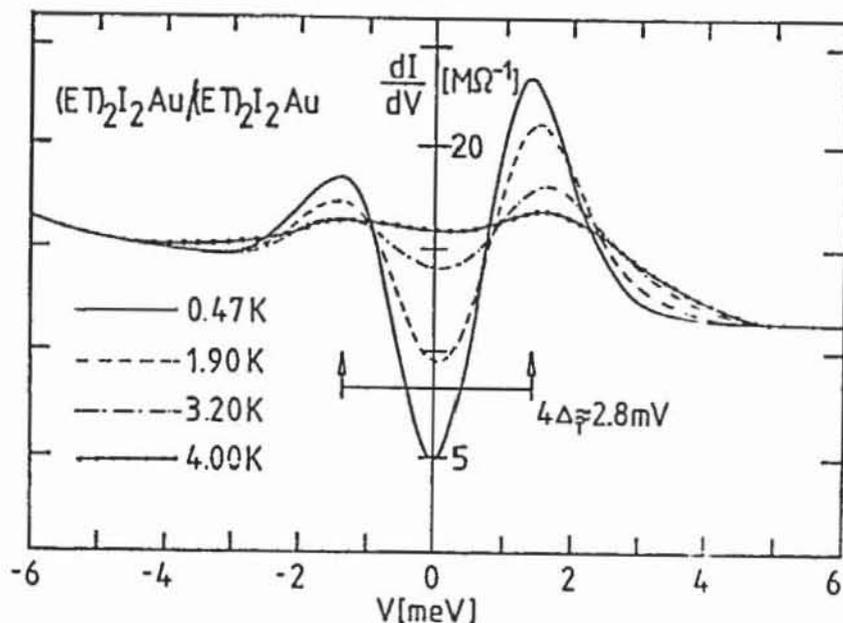


Figure 10 b

Vacuum tunneling data for $(\text{BEDT-TTF})_2\text{IAuI}$ ($T_c = 4.1 \text{ K}$).
Here $2\Delta_T/k_B T_c \approx 4$.

THE ELECTRON-PHONON COUPLING

In the 1-d organic metals TTF-TCNQ, TMTSF₂X, etc. the resistivity follows a T^2 law, indicating quadratic electron-phonon coupling [23]. A T^2 law was recently observed also in polyacetylene [24]. In ET the resistivity does not seem to follow a T^2 law; at low temperatures, $\rho = \rho_0 + aT + bT^2$ with a significantly large value of a , indicating an electron-phonon coupling constant $\lambda \approx 1$ [25]. Thus, the strong linear electron-phonon coupling differs from the other organic metals.

The cause for the large linear coupling may be the 2-d electronic band structure, which makes it possible for librions to couple linearly with the electrons (Fig. 7; see also ref. 16).

Another possibility is the virtual state close to E_F (Fig. 5). A linear matrix element $\langle \psi_M | \partial V / \partial \theta | \psi_L \rangle \neq 0$ is allowed by symmetry; here ψ_M indicates a molecular state, ψ_L a localized state ("empty sphere" state), and θ a libration angle. Thus, if ψ_L has a contribution at E_F , a linear electron-phonon coupling is allowed by symmetry (Fig. 11a). We may say that the degeneracy of ψ_M and ψ_L makes possible a band Jahn-Teller effect. If the localized state does not have a contribution at E_F , but its energy E_L is still close to E_F , a second-order term

$$\langle \psi_M | \partial V / \partial \theta | \psi_L \rangle^2 / (E_F - E_L)$$

gives rise to a strong quadratic electron-phonon coupling (Fig. 11b). This may be the case in TTF-TCNQ, TMTSF₂X, etc. where this quadratic coupling is exceedingly large [23, 26]. A direct evidence for this is provided by X-ray determinations of the charge density, that shows maxima in the region between the molecules [27].

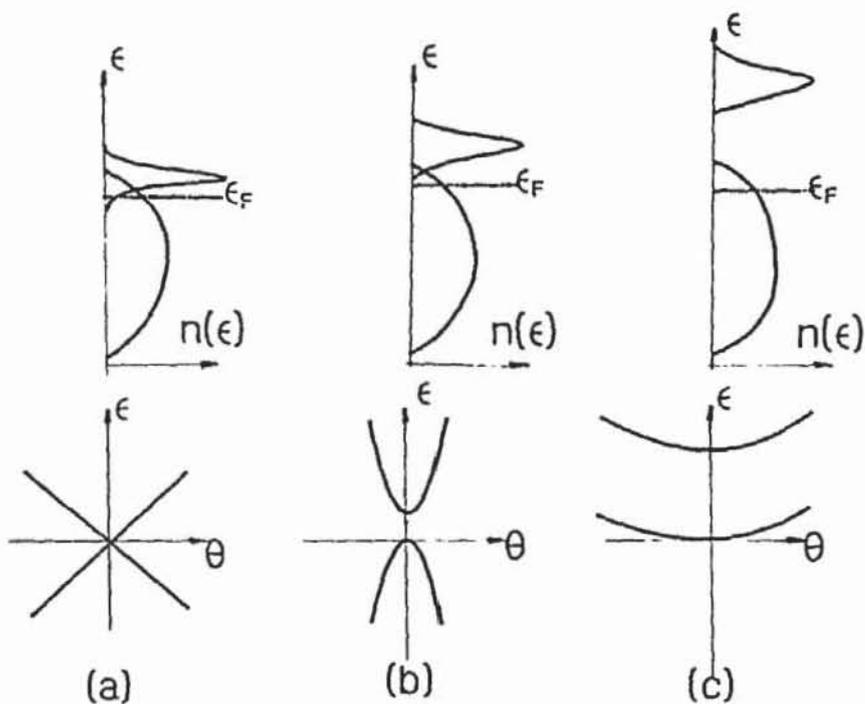


Figure 11

Illustration how a narrow "empty sphere" state at E_F (a) can give rise to linear electron-libron coupling, and near E_F (b) to a large quadratic electron-libron coupling.

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