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Electronic structure of di-tetramethyltetraselenafulvalene-X [$(\mathrm{TMTSF})_2X$]: An extended Hückel calculation

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Using the extended Hückel method, the band structure and Fermi surface for a di-tetramethyltetraselenafulvalene-X [$(\mathrm{TMTSF})_2X$] sheet have been studied. The band topology near the Fermi level is found to be far from that of a simple single-band picture. Both heavy- and light-mass electrons coexist. The electronic structure shows strong two-dimensional characteristics. The Fermi surface possesses both closed and open orbits for the structural model considered. A density wave along the [11] direction is suggested.

In this paper we report a theoretical study of the electronic structure of an idealized two-dimensional TMTSF crystal. The calculations were carried out using an extended Hückel scheme. The crystal structure is taken to be the in-sheet atomic positions determined by Bechgaard *et al.*[1] for $(\mathrm{TMTSF})_2\mathrm{ClO}_4$. For simplicity we have idealized the molecular geometry by replacing the four methyl (CH_3) groups with hydrogen ligands. The two-dimensional unit cell thus contains two molecular units which stack into chains along the direction ($\hat{a}$) of high conductivity.

The synthesis[2] of the organic charge-transfer salts $(\mathrm{TMTSF})_2X$ with X denoting the anions (PF_6, ClO_4, AsF_6, etc.) has led to some major recent discoveries in the field of quasi-one-dimensional organic conductors. Some of the remarkable physical properties of this family of compounds are (1) very high conductivity,[2] (2) a metal-insulator transition at low temperature which has been shown to be a manifestation of a spin-density-wave ground state,[3] and (3) superconductivity.[4,5] These are the first such observations in highly anisotropic organic metals. Recent experiments have further shown that multidimensionality effects may be important in determining these novel properties.[5-8] The present work is aimed at providing a theoretical understanding for the electronic structure[9] of these materials. Our results show that the band structure near the Fermi level, E_F, is very different from that of a single band picture which has been heretofore used in many experimental analyses. A band complex including both light- and heavy-mass bands cuts across E_F. Interchain interactions are substantial leading to an overall two-dimensional band structure.

The method employed for the present calculation is a crystalline extension of the standard extended Hückel method.[10] The parameters which enter into the calculations are listed in Table I. The Slater exponents, α, for the atomic orbitals for C and H are standard values found in the literature. Our choice of $\alpha = 1.473$ for Se is an extrapolated value from considering the known values for O ($\alpha = 2.275$) and S ($\alpha = 1.817$). To account for the changes in the electronegativity of the atoms in the molecular environment, the diagonal Hamiltonian matrix elements, H_{ii}, have been iterated to their self-consistent values using the scheme of Basch, Viste, and Gray.[11] As a result, the Se atoms are significantly more electronegative than the C atoms. The off-diagonal Hamiltonian matrix elements, H_{ij}, are subsequently derived from the diagonal elements and the overlap matrix elements, S_{ij}, using the weighted formula method.[12]

In addition to the full band structure, we have performed calculations for the various size building blocks to elucidate the formation of bands and the physical origins of the states near the Fermi level. We find that the states near E_F are predominantly combinations of the two highest of the five possible molecular orbitals in the π system of the five-member ring fragments. Figure 1 illustrates the formation of various states. The lower of the two molecular orbitals (labeled S in Fig. 1) has its wave function mainly localized on the Se atoms as expected from their larger electronegativity. Conversely the higher orbital (labeled A) is localized mostly on two

TABLE I. Atomic parameters for extended Hückel calculations. Slater exponents and the valence-state ionization potentials (in electron volts) for the atomic orbitals resulting from a self-consistent charge iteration.

	Slater exponent α	H_{ii}^s	H_{ii}^p
H	1.3	−12.43 to −12.72	
C	1.625	−18.35 to −19.03	−8.55 to −9.23
Se	1.473	−25.27 to −25.69	−14.40 to −14.73

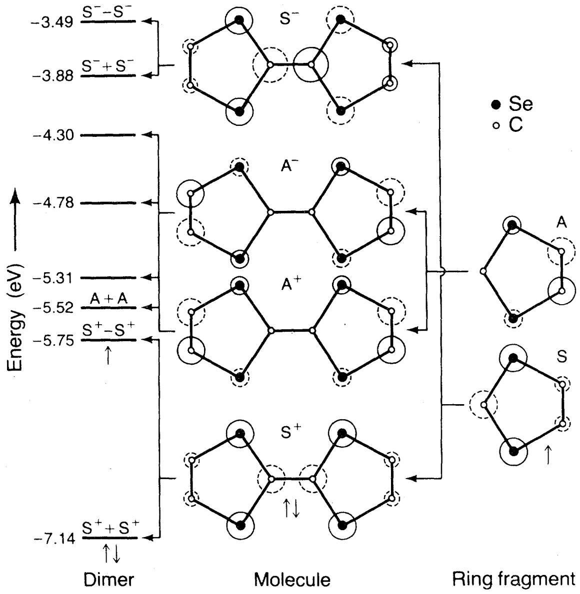

FIG. 1. Schematic diagram illustrating the molecular orbitals and sequence of steps in the formation of energy bands of $(TMTSF)_2X$ near E_F.

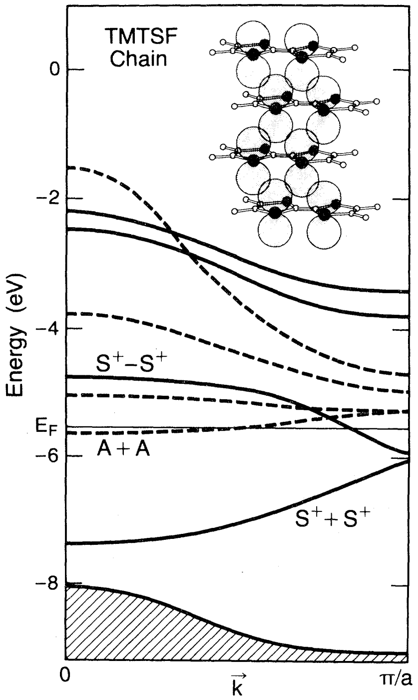

FIG. 2. Calculated energy band structure near E_F for a TMTSF chain.

adjacent carbon atoms. For a neutral ring, the orbital S is occupied by one electron.

As the two ring fragments are joined to form the molecule, four levels are generated near E_F. Owing to the symmetry of the ring orbitals, the bonding (S^+) and antibonding (S^-) levels resulting from the interaction of the S ring orbitals show a large energy separation whereas similar levels $(A^+$ and $A^-)$ resulting from the interaction of the A orbitals are nearby. We next form a molecular dimer in the structure corresponding to the unit cell basis of $(TMTSF)_2ClO_4$. The intermolecular interactions give rise to eight levels in which three electrons have to be placed for the salts under consideration. The bonding-antibonding energy separations are predominantly from the interactions between overlapping Se orbitals from the two molecules since the C orbitals are much more contracted. As the dimers are joined to form the TMTSF chains, these interactions broaden the levels into a one-dimensional band structure as shown in Fig. 2.

In Fig. 2 only the eight bands derived from the eight levels shown in Fig. 1 are depicted since all other bands are well separated from this complex. The solid lines denote states which mainly arise from the S level of the ring fragment and the dashed lines denote states which mainly arise from the A levels. The two groups of bands have different symmetry respect to a mirror plane passing through the molecular axis. We note that the Fermi level crosses two very different types of bands. The S^+-S^+ band is dispersive whereas the $A+A$ band is very flat. An analysis of the wave functions shows that the amplitude on the Se atoms is three times higher for the S^+ bands. As shown in the inset in Fig. 2, electron conduction along the chain is expected to result mainly from hopping along the Se-Se connections. Thus we have the peculiar arrangement (somewhat similar to that of transition metals) that the light-mass S^+-S^+ band contributes predominantly to the conductivity while the heavy-mass $(A+A)$ band gives rise to a high density of states at E_F. The conventional expectation is that a high state density at E_F would favor superconductivity.

The energy bands near E_F for the full two-dimensional sheet are presented in Fig. 3. As in the single chain case, the two-dimensional crystal retains the important feature that there are both heavy- and light-mass electrons at E_F. An examination of the mass tensor for the whole Brillouin zone shows that there is a strong anisotropy with the light mass being along the chain direction. This is thus consistent with the observed anisotropy in the conductivity for these materials. The calculated bands nevertheless show strong interchain interactions for bands with appreciable wave-function amplitude on the Se atoms. The dispersions seen in Fig. 3 along the Γ-Y direction arise from overlaps among the π orbitals of the neighboring chains. This is not unexpected since the interchain Se-Se distances between Se atoms on neighboring chains are virtually the same as the intra-

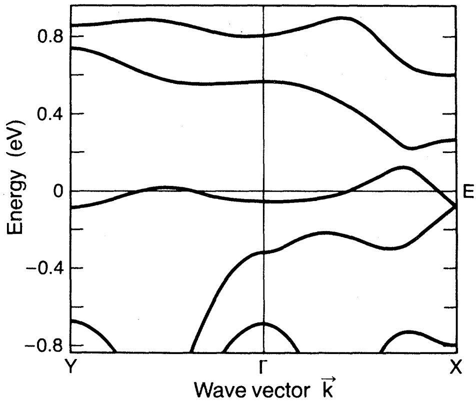

FIG. 3. Calculated energy band structure near E_F for a TMTSF sheet along two symmetry directions.

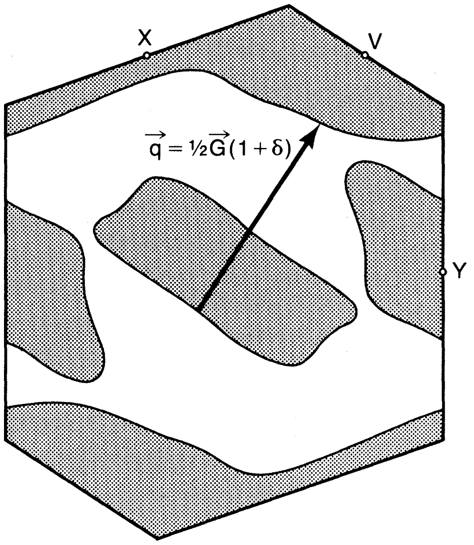

FIG. 4. Calculated Fermi surface of a TMTSF sheet in the charge configuration corresponding to one-half of an electron transferred from each molecule.

chain separations. Moreover there are appreciable $pp\sigma$ interactions among the π orbitals of the TMTSF from neighboring chains because of the geometry. The lattice vector $\vec{b}$[13] is not orthogonal to the lattice vector $\vec{a}$ and progression along the $\vec{b}$ direction also partially implies stacked molecules. This gives rise to a band dispersion for all the π states, but as before the $A+A$ band (because of the localized nature of the C atomic orbitals) remains flat relative to the other bands.

Figure 4 depicts the calculated Fermi surface for the two-dimensional sheet. The theoretical result shows very rich structure. Both closed electron orbits and open orbits are present. In the calculation we have assumed that half of an electron per TMTSF molecule has been transferred to the anions. The exact amount will have to be determined from a full three-dimensional calculation and will make small changes in the exact position of the Fermi lines in Fig. 4. The two-dimensional nature of the calculated Fermi surface is qualitatively consistent with the experimental properties of this class of materials. In particular the work of Greene and co-workers has shown that multidimensional electronic structure is required to interpret their $(TMTSF)_2PF_6$ data consistently.[5,6,8]

As seen from Fig. 4, there exist "flat" pieces of the Fermi surface which are necessary for the formation of spin-density waves. Conspicuously two pieces of the Fermi surface are spanned by a wave vector $\vec{q}$ which is nearly $(\vec{G}_a + \vec{G}_b)/2$ along the Γ-V direction. This Fermi surface topology coupled with the fact that the bands are flat at E_F strongly suggests a single nearly commensurate density wave along the [11] direction for our TMTSF sheet. If we choose $q = (|\vec{G}_a + \vec{G}_b|/2)(1+\delta)$, then δ is ~ 0.1 from the present calculation. There are, however, some sizable uncertainties in δ because of many simplifying assumptions made in the calculation. Similarly, a slightly different potential or a shift in E_F arising from interactions with the anions might close the neck in the Fermi surface in the upper right quadrant of Fig. 4. This would result in a closed hole orbital in addition to the closed electron orbital at the zone center, leading to the nearly compensated Fermi surface topology which was observed for $(TMTSF)_2PF_6$ under pressure.[6]

In summary we have calculated the energy band structure of a two-dimensional TMTSF sheet. Our results can be considered as generic to all the $(TMTSF)_2X$ compounds because of the nearly identical in-plane structure and very small interplane coupling. The theory is in qualitative agreement with many of the experimental properties. In particular the complexity of the calculated band near E_F provides a possible explanation for the richness in behavior for this class of materials upon changes in chemical composition of the anions, pressure, temperature, and other parameters.

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[13] We use the same notation as in Ref. 1.