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On the band electronic structure of $X[M(dmit)_2]_2$
($X = \text{TTF}, (\text{CH}_3)_4\text{N} ; M = \text{Ni, Pd}$) molecular conductors
and superconductors

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Résumé. — Nous présentons les structures de bandes électroniques des conducteurs moléculaires $X[M(dmit)_2]_2$ ($X = \text{TTF}, (\text{CH}_3)_4\text{N} ; M = \text{Ni, Pd}$) calculée à 300 K et à 1 bar. Dans le cas de $\text{TTF}[\text{Ni}(dmit)_2]_2$, $\alpha$- et $\alpha'$-TTF[\text{Pd}(dmit)_2]_2, les résultats montrent que non seulement les bandes LUMO (orbitale moléculaire inoccupée la plus basse) mais aussi les bandes HOMO (orbitale moléculaire occupée la plus haute) des accepteurs sont partiellement remplies. Ces calculs indiquent que ces phases sont des métaux quasi-1D. Nos résultats sont confrontés aux vecteurs d'onde associés aux instabilités ODC (onde de densité de charge) expérimentalement observées. Le rôle crucial de la dimérisation dans les empilements des molécules acceptrices est souligné. Dans les systèmes dimérisés tels que $(\text{CH}_3)_4\text{N}[\text{Ni}(dmit)_2]_2$ et la phase $\beta$ de $\text{TTF}[\text{Pd}(dmit)_2]_2$, seule une bande des accepteurs est partiellement remplie d'après nos calculs. Nous suggérons que la transition métal-semiconducteur observée à 120 K dans la phase $\beta$ du sel de Pd pourrait résulter d'un emboîtement de la surface de Fermi.

Abstract. — The tight binding band electronic structures of the molecular conductors $X[M(dmit)_2]_2$ ($X = \text{TTF}, (\text{CH}_3)_4\text{N} ; M = \text{Ni, Pd}$) are reported. In the cases of $\text{TTF}[\text{Ni}(dmit)_2]_2$, $\alpha$- and $\alpha'$-TTF[\text{Pd}(dmit)_2]_2, it is shown that both the LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) bands of the acceptor are partially filled. Our calculations show that these phases are quasi-1D metals. The wave vectors of the experimentally observed CDW (charge density wave) instabilities are discussed on the basis of these results. The crucial role of dimerization within the acceptor stacks is emphasized. In dimerized systems like $(\text{CH}_3)_4\text{N}[\text{Ni}(dmit)_2]_2$ and $\delta$-TTF[\text{Pd}(dmit)_2]_2 only one band of the acceptor is partially filled according to our calculations. It is suggested that the metal-semiconductor transition at 120 K of the latter phase could be due to nesting of the Fermi surface.

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Introduction.

The physical and structural properties of molecular charge transfer salts $X[M(\text{dmit})_2]_2$, where $[M(\text{dmit})_2]$ (1) is the electron acceptor, face us with a series of very puzzling questions. For instance, for $X = \text{TTF}$, salts with either a 1:2 ($M = \text{Ni}$ and Pd) or a 1:3 ($M = \text{Pt}$) stoichiometries are found [1]. Whereas only one 1:2 phase has so far been isolated for $M = \text{Ni}$, three different ones ($\alpha$, $\alpha'$ and $\delta$) have been reported for $M = \text{Pd}$ [2, 3]. All these 1:2 phases are metallic at room temperature but the Pt 1:3 one is semiconducting [1, 3].

In spite of the isostructural character [1-3] of the $\alpha$ and $\alpha'$-TTF[$\text{Pd} (\text{dmit})_2]_2$ and TTF[$\text{Ni} (\text{dmit})_2]_2$ phases their physical behaviour are quite different. Whereas the latter is metallic down to 3 K [1c] at 1 bar and becomes superconducting at 1.6 K under 7 kbar [4-6], the Pd $\alpha'$ phase is metallic at room temperature, exhibits activated conductivity below 220 K and 1 bar and shows superconductivity under a 20 kbar pressure at 6.5 K [7, 8]. The Pd $\alpha$ phase, which structure at room temperature is almost identical with the $\alpha'$ one, shows an irreversible behaviour associated with a monoclinic ($\alpha$) to triclinic ($\beta$) phase transition near 240 K. By contrast, the $\alpha'$ phase presents a perfectly reversible behaviour [3, 8].

Several other $X[M(\text{dmit})_2]_n$ salts have been prepared [9-10]. Among them, it was reported that $(\text{CH}_3)_4\text{N}[\text{Ni}(\text{dmit})_2]_2$ is superconducting at 5.0 K under an applied pressure of 7 kbar [10b, c]. This result seems to be somewhat sample dependent. $(\text{CH}_3)_4\text{N}[\text{Ni}(\text{dmit})_2]_2$ presents an important structural difference with respect to TTF[$\text{Ni} (\text{dmit})_2]_2$: the stacks of Ni(dmit)$_2$ are slightly dimerized in the former [10a] but regular in the latter [1]. This dimerization was also found in $\delta$-TTF[$\text{Pd} (\text{dmit})_2]_2$ [3].

The absence of resistivity anomalies in TTF[$\text{Ni} (\text{dmit})_2]_2$ until very low temperatures, was initially related to the existence of relatively short S...S contacts [1] in the directions perpendicular to the stacking axis of the TTF and Ni(dmit)$_2$ chains. It was thought that these contacts will help to suppress the inherent instability of one-dimensional (1D) systems. Nevertheless, a qualitative band electronic structure study by Kobayashi et al. [11] suggests that the system is 1D. A $^1\text{H}$ NMR study of the TTF stacks in the same system supports the idea that a 1D model is appropriate for the TTF chains [12].

Although the actual degree of charge transfer is not known in these TTF salts, the observation of superconductivity in $(\text{CH}_3)_4\text{N}[\text{Ni}(\text{dmit})_2]_2$ provides reasonable evidence for considering the acceptor molecules as driving the instability. Furthermore, a recent X-ray study [13] of TTF[Ni(dmit$_2$)$_2$]$_2$ at ambient pressure reported the observation of 1D structural fluctuations under the form of diffuse lines at the reduced wave vectors $\pm 0.4 b^*$, providing evidence of charge density wave (CDW) instability. This scattering couples tridimensionally below about 40 K. The X-ray study [13] of $\alpha'$-TTF[Pd(dmit)$_2$)$_2$ shows two sets of diffuse lines at the reduced wave vectors $q_1 = 0.5 b^*$ and $q_2 = \pm 0.31 b^*$. These two scatterings, related to two different 1D CDW instabilities which probably originate from the acceptor stacks, condense in satellite reflections at $T_1 \approx 150$ K and $T_2 \approx 105$ K respectively. At low temperatures, additional satellite reflections at the reduced wave vectors $2q_2$ and $q_2 \pm q_1$ are also observed. The change in the conductivity regime observed below 220 K in $\alpha'$-TTF[Pd(dmit)$_2$)$_2$ [7, 8] can be associated with the development of these CDW
instabilities. This indicates that the acceptor molecules could drive CDW and superconductivity instabilities in these TTF salts.

As mentioned, the $\delta$-TTF[$\text{Pd} (\text{dmit})_2$]$_2$ phase also presents a transition from a metallic to a semiconducting regime at about 120 K although its origin has not yet been studied. Single crystal resistivity measurements show that this system is a quasi-isotropic metal in the $a$-$c$ plane [3].

In the present work we try to answer several questions related to the band electronic structure of these TTF[$M (\text{dmit})_2$]$_2$ phases. First, what is the real dimensionality of these compounds? Second, can we understand the value of the wave vector of the observed CDW instabilities? Third, is there any strong difference in the band electronic structures which can be related to the different physical behaviour of TTF[$\text{Ni} (\text{dmit})_2$]$_2$ and $\alpha'$-TTF[$\text{Pd} (\text{dmit})_2$]$_2$ at ambient pressure? Fourth, how their band electronic structures are related to that of the superconducting (CH$_3$)$_4\text{N}[$Ni(dmit)$_2$]$_2$? Fifth, what is the likely origin of the metal-semiconductor transition reported [3] in $\delta$-TTF[$\text{Pd} (\text{dmit})_2$]$_2$?

**Method of calculation.**

The tight binding band structure calculations reported in this work are based upon the effective one-electron Hamiltonian, $H_{\text{eff}}$, of the extended Hückel method [14]. The off-diagonal matrix elements of the effective Hamiltonian were calculated according to the modified Wolfsberg-Helmholz approximation [15]. All valence electrons were explicitly considered in the calculations. The basis set consisted of Slater type orbitals ($\chi_v$) of double-zeta quality for M and of either single or double-zeta [16] quality for C and S. A double-zeta orbital is given by a linear combination of a diffuse and a contracted orbital. Single-zeta orbitals were used for H. Since for any practical reason the results obtained with the single and double-zeta basis for C and S were equivalent, only results obtained with the single-zeta orbitals will be reported in the following. The exponents, contraction coefficients and atomic parameters used in the calculations are summarised in table I [17]. In all cases the calculations have been performed on the presently available experimental structures at ambient pressure and room temperature.

**Table I. — Parameters and exponents used in the calculations.**

<table>
<thead>
<tr>
<th>atom</th>
<th>orbital</th>
<th>$H_{ii}$ (eV)</th>
<th>$\zeta_1$</th>
<th>$\zeta_2$</th>
<th>$c_1 (\times 10^{-3})$</th>
<th>$c_2 (\times 10^{-3})$</th>
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<td>S</td>
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<td>1.817</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3p</td>
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<td>1.817</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>1.625</td>
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<td></td>
<td></td>
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<tr>
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<td>1s</td>
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<td>1.30</td>
<td></td>
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<td>5s</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5p</td>
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<td>2.15</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>4d</td>
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<td>2.613</td>
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<td>0.6372</td>
</tr>
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<td>2.10</td>
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<td></td>
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<tr>
<td></td>
<td>4p</td>
<td>-5.15</td>
<td>2.10</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>3d</td>
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<td>5.75</td>
<td>2.30</td>
<td>0.5798</td>
<td>0.5782</td>
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</table>

(*) Contraction coefficients used in the double-$\zeta$ expansion.
In order to evaluate the relative strength of the different interactions occurring in the TTF[M(dmit)₂]₂ salts, we have calculated the interaction energies involving the LUMO (lowest unoccupied molecular orbital) of M(dmit)₂ and the HOMO (highest occupied molecular orbital) of TTF and M(dmit)₂. The interaction energy between orbitals \(i\) and \(j\) (\(\beta_{i,j}\)) can be written as

\[
\beta_{i,j} = \sum_{\nu} \sum_{\mu} c_{\nu i} c_{\mu j} \langle \chi_\nu | H_{\text{eff}} | \chi_\mu \rangle
\]

where \(c_{\nu i}\) denotes the coefficient of atomic orbital \(\chi_\nu\) in the molecular orbital \(\Psi_i\). These interaction energies have been extensively used by Whangbo et al. [18] to discuss the electronic structure of molecular conductors.

### Results and discussion.

#### A. TTF[Ni(dmit)₂]₂.

Figure 1a shows a projection on the \(ac\) plane of the TTF[Ni(dmit)₂]₂ structure [1a]. Slabs of Ni(dmit)₂ alternate with slabs of TTF. Every Ni(dmit)₂ slab is built from four stacks as shown in figure 1b. As shown in figure 1 there are four different types of interactions between Ni(dmit)₂ molecules of a slab: those of type 1, 2 and 9 involve lateral (interstacks) contacts and can be responsible for departure from one-dimensionality. There are no short contacts

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![Crystal structure of TTF[Ni(dmit)₂]₂](image-url)  
Fig. 1. — Crystal structure of TTF[Ni(dmit)₂]₂: a) projection onto the (010) plane, and b) parallel view along [010] of the Ni(dmit)₂ slabs. The different types of interactions reported in table I are numbered from 1 to 9.
between the TTF molecules other than along the $b$ direction (type 5 interactions). TTF-Ni(dmit)$_2$ interactions are labeled 6, 7 and 8 in figure 1a and are associated with S...S contacts of 3.38, 3.48 and 3.59 Å respectively. Finally, there is a contact of 3.61 Å between Ni(dmit)$_2$ molecules of different slabs (type 4).

Our computed values for the different $\beta_{i,j}$ interaction energies involving the LUMO of Ni(dmit)$_2$ and/or the HOMO of TTF are reported in table II. Those concerning the intrastack interactions for TTF (type 5) and Ni(dmit)$_2$ (type 3) are comparable and of the same order as for most organic metals examined so far [18]. The TTF-Ni(dmit)$_2$ ones as well as the Ni(dmit)$_2$-Ni(dmit)$_2$ of type 4 are very small. It is clear that the influence of these interactions on the band structure will be extremely small. More interesting are the results concerning the interactions within the slab. They are also very small and particularly those of type 2 are about 40 times smaller than the intrastack ones (type 3). This will preclude any delocalization perpendicular to the stacks. The value corresponding to interaction type 9 is even smaller. On the basis of these results one comes to the conclusion that TTF[Ni(dmit)$_2$]$_2$ should be described as a series of almost independent 1D systems. In this respect these results are in agreement with those reported by Kobayashi et al. [11]. One could argue that the small interaction values are the result of an inadequate basis set for the S and C atoms. In order to test this possibility we repeated the calculations using the double-zeta basis for S and C. The results are very similar to those reported in table I and, since this basis set contains fairly diffuse orbitals on sulfur, we are led to the conclusion that these small interaction energies are the result of some very fundamental structural feature.

Table II. — Interaction energies ($\beta_{i,j}$) for TTF[Ni(dmit)$_2$]$_2$.

<table>
<thead>
<tr>
<th>interaction</th>
<th>type (*)</th>
<th>interaction energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO$_{Ni(dmit)<em>2}$-LUMO$</em>{Ni(dmit)_2}$</td>
<td>1</td>
<td>0.0362</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td></td>
<td>3</td>
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<tr>
<td></td>
<td>4</td>
<td>-0.0063</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>-0.0015</td>
</tr>
<tr>
<td>HOMO$<em>{TTF}$-HOMO$</em>{TTF}$</td>
<td>5</td>
<td>0.2964</td>
</tr>
<tr>
<td>HOMO$<em>{TTF}$-LUMO$</em>{Ni(dmit)_2}$</td>
<td>6</td>
<td>0.0176</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.0092</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-0.0038</td>
</tr>
<tr>
<td>HOMO$_{Ni(dmit)<em>2}$-HOMO$</em>{Ni(dmit)_2}$</td>
<td>1</td>
<td>-0.1078</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.0229</td>
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<tr>
<td></td>
<td>3</td>
<td>0.3402</td>
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<tr>
<td></td>
<td>4</td>
<td>-0.0044</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.0206</td>
</tr>
<tr>
<td>HOMO$<em>{TTF}$-HOMO$</em>{Ni(dmit)_2}$</td>
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<td>-0.0279</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-0.0146</td>
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<tr>
<td></td>
<td>8</td>
<td>-0.0026</td>
</tr>
</tbody>
</table>

(*) See figure 1 for definition.
It is interesting to argue why the Ni(dmit)$_2$ slabs containing many S...S short contacts should exhibit a 1-D behaviour. This can be easily done on the basis of the structure of the LUMO of Ni(dmit)$_2$ which is shown in figure 2a. This orbital is antisymmetric with respect to the pseudo-symmetry plane 1. Because of the type of interaction shown in figure 1a and this antisymmetric character, the five contacts implicated in interaction type 2 are effectively reduced to one. By the same reason, three of the S$_\alpha$...S$_\alpha$ contacts (see Fig. 2 for notation) implicated in interaction type 1 are reduced to one. The remaining four contacts involve $S_\beta$ which has a small coefficient in the LUMO and consequently, the interaction although greater than that of type 2 cannot be strong. Interaction type 9 is very small because two of the three contacts involve $S_\beta$ and the orientation of the orbitals is not quite good. However the essential result is that interaction type 2 is very weak. This is the reason why electronic delocalization perpendicular to the stacks is almost completely prevented.

Figure 2. — LUMO (a) and HOMO (b) of an ideal M(dmit)$_2$ molecule. Hatched and non-hatched lobes refer to positive and negative contributions, respectively.

Figure 3 presents the calculated band electronic structure for an Ni(dmit)$_2$ slab. The surprising result is that the LUMO-based bands overlap appreciably with the HOMO-based ones. On that point our results contrast with the report of Kobayashi et al. [11] which only considered the LUMO bands. The reason for this is easy to understand. In contrast with what happens in other molecules used as acceptors in molecular conductors, the HOMO and LUMO of Ni(dmit)$_2$ are close in energy (0.4 eV). Since the overlap along the chain is good it leads to band dispersions which more than compensate for the initial energy difference. The schematic drawings of figure 2 show why these orbitals are close in energy. They are essentially the in-phase and out-of-phase combinations of one of the $\pi$ orbitals of the dmit ligand. The three symmetry planes of the ideal dmit ligand do not allow the metal d orbitals to mix into the HOMO. The nodal properties of the ligand orbital produce only a modest overlap, and hence relatively small mixing of the Ni $d_{xz}$ orbital into the LUMO. Thus, the energy gap between these orbitals cannot be great. The interaction energy $(\beta_{i,j})$ values corresponding to the HOMO are also included in table II. As follows from our previous arguments the lateral interactions are somewhat greater which lead to some more lateral dispersion and separation of the four HOMO bands.

The degree of charge transfer on this compound is not presently known so that it is difficult to estimate the Fermi level appropriate for figure 3. We have reported there the $\epsilon_f$ values for charge transfers corresponding to TTF$^{0+}$, TTF$^{0.5+}$ and TTF$^+$. The transport study [1] has shown that, although a CDW 3D ordering develops under $\sim 40$ K at $q = 0.4 b^\ast$, the system is still metallic and does not present any resistivity anomaly. This suggests that not all the bands crossing the Fermi level undergo a CDW instability. On the
other hand, $^1$H NMR measurements [12] show that there is no gap on the TTF band until low temperature. It is thus tempting to associate the CDW to the Ni\((\text{dmit})_2\) bands.

Our calculations allow us to propose the three following assignements (see Fig. 3). First, the CDW instability originates from the perfect nesting of the bunch of four LUMO bands by the \(2k_F = 0.6b^*\) wave vector, leading to the observation of diffuse lines at \(q = b^* - 2k_F = 0.4b^*\) in the X-ray pattern. In that case the charge transfer would be \(\sim +1\). Second, the CDW instability is due to nesting of some of the HOMO bands on the LUMO ones by the \(q = 0.4b^*\) wave vector, leading, from our calculations to a charge transfer near to 1. Third, the instability comes from the nesting of the upper pair of HOMO bands by the \(2k_F = 0.4b^*\) wave vector, with a charge transfer near to zero.

The first two explanations seem to be in agreement with the thermopower measurements [19] which suggest that the holes are the major carriers at low temperature. It could be argued that a charge transfer close to 1 is in conflict with the fact that the central C--C bondlength in TTF, which usually correlates very well with the charge transfer degree [20], was found to be very short (1.33 Å). Nevertheless, it should be remarked that this short distance is even shorter than in TTF itself (1.34 Å) [21]. In view of the low reliability factor (\(R_N \sim 9.7\%\)) obtained in the TTF\[Ni(\text{dmit})_2\] refinement [1], we believe this distance could be incorrect. A reexamination of this structure with that of the Pd salt, for which a good reliability factor was obtained, suggests that the intermolecular distances should be basically correct, but that certain intramolecular ones are certainly inaccurate. However, after a careful consideration of the different interactions to which the band structure is sensitive, we believe that the essential features of the band structure of the Ni\((\text{dmit})_2\) slabs should be accurately accounted for by the present calculations. The structural redetermination is essential in order to have a better estimation of the charge transfer. On the absence of such an estimation we cannot seriously discriminate between the different possibilities. We will further discuss this point later.

**B. \(\alpha'\)-TTF\[Pd(\text{dmit})_2\].**

As mentioned, this salt presents the same structure as TTF\[Ni(\text{dmit})_2\]. The overlap between the HOMO and LUMO bands in the later led us to suspect that the two sets of CDW instabilities observed for \(\alpha'\)-TTF\[Pd(\text{dmit})_2\] could result from the same phenomenon. In

Fig. 3. — Band structure for the Ni\((\text{dmit})_2\) slabs in TTF\[Ni(\text{dmit})_2\] [1a]. \(\Gamma, Y, Z\) and \(M\) refer to the wave vectors \((0,0), (b^*/2,0), (0,c^*/2)\) and \((b^*/2, c^*/2)\) respectively. The Fermi levels noted \(\varepsilon_f, \varepsilon_f^1\) and \(\varepsilon_f^2\) are those appropriate for charge transfers of 0, 1/2 and 1 respectively.

[Diagram of band structure]
addition, it was found in the X-ray study that the two sets of CDW instabilities should be associated with the Pd(dmit)$_2$ slabs. This reinforced our suspicion that two sets of bands should be cut by the Fermi level. Consequently, we studied the band electronic structure of this salt following the same approach used in the previous section. Similar results concerning the dimensionality of the salt were obtained.

The band structure of a Pd(dmit)$_2$ slab as found in $\alpha'$-TTF[Pd(dmit)$_2$]$_2$ [3] is shown in figure 4. Analogous results were obtained for the $\alpha$-TTF[Pd(dmit)$_2$]$_2$ phase. It shows qualitatively the same features as that of figure 3 except for a greater dispersion. This is a consequence of the shorter intrastack contacts [3]. The $\varepsilon_f$ values for charge transfers corresponding to TTF$^{0+}$, TTF$^{0.5+}$ and TTF$^+$ have been marked in figure 4.

The dc resistivity measurements [22] have shown that, at low temperature, there are no more carriers in the system. This can be explained only by the appearance of energy gaps at the Fermi level in all the conduction bands of the system: the HOMO and LUMO bands of Pd(dmit)$_2$ and the TTF band. It can be seen in figure 4 that, whatever the charge transfer is, the LUMO bands are cut near $k_F^L \sim 0.25 b^*$ and the HOMO ones near $k_F^H \sim 0.15 b^*$. Let us recall that for such 1D multi sheets Fermi surface system with $n$ bands, the charge transfer conservation rule is:

$$\sum_{i=1}^{n} \gamma_i \left(4 \frac{k_F^L}{b^*}\right) = \text{number of holes per unit cell}$$

$LUMO$ bands), where $i$ indexes the bands, $\gamma_i$ is their degeneracy, and $k_F^i$ is their Fermi wave vector. We thus propose the following possible assignments for the CDW wave vectors observed in the X-ray study [13]:

i) the bunch of the LUMO bands are nested by $2k_F^L = 0.5 b^* = q_1$ and the HOMO ones by $2k_F^H = 0.31 b^* = q_2$. The charge conservation rule gives, if $k_F^T$ is the Fermi vector of the doubly degenerate TTF bands,

$$4\left(4 \frac{k_F^L}{b^*}\right) + 4\left(4 \frac{k_F^H}{b^*}\right) + 2\left(4 \frac{k_F^T}{b^*}\right) = 4 \times 2 = 8,$$

from which we obtain the charge transfer $\rho = 4 \frac{k_F^T}{b^*} = 0.76$. A distortion at $b^* - 2k_F^T = 2$
\[ b^* - 0.38b^* = 0.62 b^* = 2 q_2, \] which is experimentally observed, will thus also induce a gap on the TTF chains, leading to the destruction of all the carriers;

ii) the bunch of the LUMO bands are nested by the \[ 2 k_F^\perp = 0.5 b^* = q_1 \] and the upper pair of the HOMO ones by \[ 0.31 b^* \]. In addition the lower pair of HOMO bands can be nested by the \[ q_1 - q_2 = 0.19 b^* \] wave vector which leads to \[ \rho = 4 k_F^\perp/b^* = 1 \] by the charge conservation rule. A gap would thus be open in the TTF band at the \[ 2 k_F^\perp = 0.5 b^* \] wave vector except if its ground state is of a Mott-Hubbard type with a \[ 4 k_F \] charge localization [23] which is likely for \[ \rho = + 1 \].

It is worth pointing out that, the charge transfer close to 1 associated with both possibilities is in agreement with the reported central C=\(\text{C}\) bondlength of 1.39 Å [3], obtained from a well resolved structure (\(R = 3\%\)), which typically corresponds to a TTF\(^+\) [21\]. In addition, both possibilities are consistent with our calculated band structure. The comparison of the calculated results with the previous analysis suggests an error of \(\pm 0.05\) eV, which seems quite reasonable.

At this point we would like to stress the fact that nesting wave vectors are generally incommensurate. Thus, the finding of a simple commensurate value \(q_1 = 0.5 b^*\) is puzzling. It could be that the nesting of the LUMO bands gives a wave vector close to \(1/2\) and that additional effects, like Umklapp terms or many body interactions, drive its locking at the commensurate value.

In short, we suggest that the band electronic structure of figure 4 contains the main features needed to build a tentative explanation of the puzzling behaviour of \(\alpha\)'-TTF[Pd(dmit)\(_2\)]\(_2\) if one assumes TTF molecules in an oxidation state close to \(+1\). Needless to say, the electronic structure of the salt results from a very subtle balance and can be easily altered, by pressure changes for instance. Two possible pressure induced changes with important consequences for the scenario described above include: a) modification of the lateral interactions (types 1 and 2) which can lead to decreased one-dimensionality, and b) compression along the intrastack direction which, as a result of the overlap of the HOMO and LUMO bands, will subtly affect the Pd(dmit)\(_2\) interband charge transfer and so, the different Fermi wave vectors. Structural work under pressure would be of invaluable help in the study of these materials.

However, the more puzzling result is that although TTF[Ni(dmit)\(_2\)]\(_2\) and \(\alpha\)'-TTF[Pd(dmit)\(_2\)]\(_2\) have a similar band structure, the former salt exhibits one CDW instability [32] whereas the latter one exhibits two. In the case of \(\alpha\)'-TTF[Pd(dmit)\(_2\)]\(_2\) the \(q_1 = 0.5 b^*\) and \(q_2 = 0.31 b^*\) CDW instabilities can be assigned to the bunch of LUMO and HOMO bands respectively. This assignment is ambiguous in the case of the single \(q = 0.4 b^*\) CDW instability of TTF[Ni(dmit)\(_2\)]\(_2\). However, whatever the assignment is, the crucial question is why all the bands do not develop a CDW instability. A possible answer is that the bands of lower energy do not have a well defined 1D character and thus, can not be nested. It is particularly true for the two HOMO bands of lower energy, which for a charge transfer between 0.5 and 1 have a closed Fermi surface (see Fig. 3 near the \(\Gamma\) point). This interpretation, suggested by our calculations, is also conforted by the observation of a low anisotropy of the magnetoresistance at \(T = 4.2\) K [1c]. A unique feature of TTF[Ni(dmit)\(_2\)]\(_2\) compared to \(\alpha\)'-TTF[Pd(dmit)\(_2\)]\(_2\) seems to be the presence of a closed portion of the Fermi surface in the former material, where the anomalously large value of the \(b\) parameter [1a, b] leads to a smaller band dispersion along \(\Gamma \rightarrow Y\). The shift of the Fermi level induced by the shortening of the \(b\) parameter under pressure, could be a clue to understand the highest pressure dependence of the electrical resistivity of TTF[Ni(dmit)\(_2\)]\(_2\) compared to \(\alpha\)'-TTF[Pd(dmit)\(_2\)]\(_2\) [8].

Finally, let us point out that although \(\alpha\)'-TTF[Pd(dmit)\(_2\)]\(_2\) is related to NbSe\(_3\) [25] in the sense that there are two CDW instabilities, there is a fundamental difference between these
two systems. In NbSe₃, the two CDW instabilities are associated with bands originating from different fragments of the structure whereas in α'-TTF[Pd(dmit)₂]₂, the two sets of bands are associated with the same part of the crystal.

C. (CH₃)₄N[Ni(dmit)₂]₂.

As shown in figure 5, this salt contains slabs of dimerized [Ni(dmit)₂]⁻¹/₂ separated by slabs of (CH₃)₄N⁺. The band electronic structure for a Ni(dmit)₂ slab is shown in figure 6. The HOMO and LUMO bands do not overlap anymore and the problem becomes that of a half-filled single band. The reason why there is no band overlap as in the previous salts is clear. Because of the dimerization along the stacks, both the HOMO and LUMO orbitals will give a bonding combination (Ψ⁺) of lower energy and an antibonding combination (Ψ⁻) of higher energy. Since Ψ⁺ and Ψ⁻ are associated with transfer integrals of opposite sign, the Ψ⁺ and Ψ⁻ bands will have different slopes. Because of the low symmetry of the system, the two bands are allowed to mix and they stay separate. This mixing, which is already clear near X and S in figure 6, can be evaluated by decomposing the Ψ⁺ and Ψ⁻ wavefunctions at different points of the Brillouin Zone in terms of the HOMO and LUMO orbitals of each slab.
monomer. The HOMO contribution has increased from only 7% at \( \Gamma \) to 26% and 30% at X and S respectively. Because of these mixings, which will increase with the strength of the interactions along the stack, the Fermi surface acquires some irregular warping although it remains 1D. Even if the need for inclusion of both HOMO and LUMO orbitals of \( \text{M(dmit)}_2 \) is less crucial in this case, the details of the Fermi surface can be affected by the neglect of the HOMO one.

The results of sections A, B and C make clear that it is absolutely necessary to include both the HOMO and LUMO orbitals in the band structure calculations, every time there are regular \( \text{M(dmit)}_2 \) stacks in a crystal structure. In that sense the electronic structure of systems like (DBTTF)[Ni(dmit)_2] [26] should be reconsidered.

D. \( \delta \)-TTF[\( \text{Pd(dmit)}_2 \)]_2.

The structure of this new TTF[\( \text{Pd(dmit)}_2 \)]_2 phase has been reported recently [3] and as in the latter case the acceptor slabs contain dimerized stacks (Fig. 7). The extent of dimerization is stronger in the present case and there are obvious metal-metal interactions. Interestingly, the acceptor slabs here are similar to those of TTF[Pt(dmit)_2] except for the fact that, in the latter there occurs trimerization except of dimerization. The existence of metal-metal interactions (Pd-Pd = 3.11 Å) leads to a sizeable bending of the Pd(dmit)_2 molecules.

At first sight it can be surprising that \( d^8 \) complexes like these have a tendency to form metal-metal bonds [27]. In fact the system is not \( d^8 \) but \( d^8 + \chi \), because of the charge transfer and consequently the LUMO of the system which contains some contribution of the Pd \( d_{xz} \) orbital is partially filled. The bending allows the mixing of the p and d orbitals of Pd in order to maximize the intradimer metal-metal overlap as schematically shown in figure 9 while avoiding excessive intradimer S...S repulsive interactions. Because of the repulsions associated with the four occupied mainly metal orbitals of these \( d^8 \) complexes, the Pd-Pd distance is kept relatively long, far from a typical Pd-Pd metal bond distance (2.7-2.8 Å) [28]. Nevertheless, the interaction is strong enough to raise the energy of the antibonding combination of the monomer HOMO's higher than that of the bonding combination of the

![Fig. 7. — Two projections of the Pd(dmit)_2 slabs in \( \delta \)-TTF[\( \text{Pd(dmit)}_2 \)]_2 [3] showing the S...S contacts shorter than 3.7 Å.](image_url)
monomer LUMO’s. The d orbitals of Ni are more contracted and consequently, the formation of these incipient metal-metal bonds will produce severe S...S repulsions. We believe 6-type structures are not likely for Ni(dmit)₂.

Since the dimerization is stronger than in (CH₃)₄N[Ni(dmit)₂]₂ one should expect again a half-filled single band situation. Bending of monomers and, more importantly, slipping of the successive dimers of a stack (see Fig. 8) cause the interdimer overlap along the stacks to become small. In fact there are only two interdimer S...S contacts along the stacks smaller than 3.6 Å. These contacts are not very effective in creating a strong interaction because they involve one S₂ atom (see Fig. 2), with a small coefficient in the HOMO. There are also eight S...S contact smaller than 3.85 Å but only two of them do not involve such S₂ atoms. As a result there are only two S...S of 3.80 Å which are really contributing to the interdimer overlap. The corresponding interaction energy is relatively small. There are however numerous S...S short contacts between parallel stacks. Because of the nature of both the monomer orbital (HOMO) and of the lateral S...S contacts, which as shown in figure 7b are somewhat different from those in the a’ phase, the lateral overlaps should not be as small as in the a’ phase. On the basis of this analysis it is expected that the dispersion of the half-filled band of this system should be similar along both a* and c*.

These expectations are confirmed by the calculated band electronic structure. The dispersion relations of the only partially filled band of the system are reported in figure 10a. However, the Fermi level corresponding to a + 1 charge transfer does not cut this band along a*. Consequently, the system has an open Fermi surface. Let us note that an identical result is obtained by using the double-zeta basis set which contains more diffuse S orbitals. The assumed charge transfer is again reasonable on the basis of the TTF structure (central C≡C bondlength = 1.39 Å) which is very similar to other characterized TTF⁺ systems [24]. The computed Fermi surface is shown in figure 10b. It is clear from there that the conductivity should be good along c and a, although better along c. These results are in good agreement with previously reported resistivity measurements which indicate that the conductivity along c

Fig. 8. — Overlap between the Pd(dmit)₂ molecules a) within a dimer and, b) between dimers along the stack.

Fig. 9. — d-p mixing as a result of the M(dmit)₂ bending.
is 5 times greater [29]. In order to clearly probe the anisotropy of the system measurements along c and a* should be carried out. Although the detailed features of the Fermi surface can not be determined without knowing the actual charge transfer, the two pieces of the surface in figure 10b, which should not be far from the real one, are reasonably well nested by one of the two wave vectors shown. In consequence, we suggest that this nesting can be at the origin of the metal-semiconductor transition at 120 K reported for this salt [3].

Concluding remarks.

The main result of the present work is that both the HOMO and LUMO of the acceptor must be considered in the conduction band structure of TTF[Ni(dmit)$_2$]$_2$ and $\alpha'$-TTF[Pd(dmit)$_2$]$_2$. This is a unique situation never found so far in the field of quasi-1D molecular conductors. The multi sheets Fermi surface which results explains satisfactorily the critical wave vector of the CDW instabilities observed in these materials [13]. A second important result of the present calculations, is that the electronic structure at ambient pressure and room temperature is quasi-1D. This is again in agreement with the observation of 1D CDW instabilities [13]. However, the dimensionality of these phases results from a subtle balance between lateral interactions. It can be substantially altered under pressure. This could be a key feature to understand the phase diagram. Moreover, the deterioration of the nesting properties of the Fermi surface could be invoked as leading to the destabilization of the CDW condensate state under pressure and the stabilization of a low temperature metallic and superconducting ground state. In this respect the phase diagram of $\alpha'$-TTF[Pd(dmit)$_2$]$_2$ under pressure recalls those of quasi-1D conductors NbSe$_3$ (competition with a CDW semimetallic state) [30] and (TMTSF)$_2$AsF$_6$ (competition with a spin density wave (SDW) state) [31]. TTF[Ni(dmit)$_2$]$_2$ shows a more subtle behavior under pressure whose study is now under way. A third key feature of the present work is to show the subtle role of the dimerization of the acceptor stacks on the band structure. Calculations performed for the dimerized materials (CH$_3$)$_4$N[Ni(dmit)$_2$]$_2$ and $\delta$-TTF[Pd(dmit)$_2$]$_2$ show that the HOMO and LUMO bands no longer overlap, leading to the more conventional situation of a single acceptor conduction band. In addition, it was found that although the Fermi surface remains open, its shape is significantly warped because of substantial lateral interaction, especially in the case of $\delta$-TTF[Pd(dmit)$_2$]$_2$. The nesting properties of such a Fermi surface could explain

Fig. 10. — Dispersion relations (a) and Fermi surface (b) for the partially filled band of the Pd(dmit)$_2$ slab in $\delta$-TTF[Pd(dmit)$_2$]$_2$ [3]. $\Gamma$, X, Z and S refer to the wave vectors (0, 0), $(a^*/2, 0)$, $(0, c^*/2)$ and $(-a^*/2, c^*/2)$ respectively. The Fermi level in (a) and the associated Fermi surface (b) are those appropriate for a charge transfer of 1.
the metal-insulator phase transition observed in $\delta$-TTF$[\text{Pd (dmit)}_2]_2$. Finally, let us point that in this paper we have just presented a one-electron description of the electronic structure of $X[\text{M (dmit)}_2]_2$ phases. At this stage, the discussion of the competition of the low temperature instabilities (CDW, superconductivity, and eventually SDW) is beyond the scope of our work because, as it is generally agreed, many body effects should be explicitly included. However our calculations give parameters of the 1D electron gas ($2k_F$ critical wave vectors, number of conduction bands, existence of a dimerization gap, etc.) which remain of great importance to discuss the mechanism of the low temperature instabilities, even in the presence of electron-electron interactions.

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References


The exponents \( \xi_{\mu} \) and contraction coefficients \( c_{\mu} \) used in the double-zeta calculations were respectively: 2.662, 1.688, 0.5564, 0.4874 for S 3s; 2.338, 1.333, 0.5212, 0.5443 for S 3p; 1.831, 1.153, 0.7616, 0.2630 for C 2s and 2.730, 1.257, 0.2595, 0.8025 for C 2p.


Kang K., private communication.


Ribault M., Brossard L., unpublished results.


The conductivities along a and c were unfortunately inverted in the original report [3] due to the use of different axis during the initial structural determination.


Very recent X-ray experiments on TTF[Ni(dmit)$_2$]$_2$ at ~25 K show additional very weak diffuse lines at wave vectors 0.18 (3) \( b^* \) and 0.22 (3) \( b^* \). These new features, which must be studied more carefully, could make a link between the apparently different behaviour of TTF[Ni(dmit)$_2$]$_2$ and \( \alpha'\)-TTF[Pd(dmit)$_2$]$_2$. 

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