# Compared ( T, P ) Phase Diagrams, Electronic Instabilities & Band Structures of Molecular Superconductors TTF(M(dmit)$_2$)$_2$

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**Abstract.** *The pressure-temperature phase diagrams of the molecular superconductors TTF(M(dmit)$_2$)$_2$ (M= Pd, Ni) are compared. These conductors show low pressure $2k_F$ CDW instabilities which wave vector can be well accounted for by an unusual conduction band structure involving both the HOMO's and the LUMO's of the acceptor. In the Pd salt, the CDW insulating ground state vanishes under pressure and a superconducting phase, with a $T_C$ maximum at the borderline with the former phase, is stabilized. In the Ni salt, an original phase diagram is observed with the successive stabilisation of a CDW insulating ground state then of a superconducting phase in weak competition with CDW.*

Below are reviewed some physical properties of the donor-acceptor compounds TTF(M(dmit)$_2$)$_2$ (M= Pd or Ni). These molecular conductors adopt the $C2/c$ monoclinic symmetry [1, 2], with b as the one dimensional (1D) direction of electronic properties. Both materials exhibit superconductivity under pressure [3, 4], however their (P, T) phase diagram as well as their electronic properties at ambient pressure differ sizeably.

**At ambient pressure**, the Pd salt ($\sigma_b$= 770 $\Omega$cm$^{-1}$ at 300K) shows a resistivity minimum at 240K and a metal-insulator transition, at 110K, characterized by an inflexion point (where $d\mathrm{Ln}\sigma/d(1/T)$ is maximum) of its resistivity [4]. On the other hand, the Ni salt ($\sigma_b$= 300 $\Omega$cm$^{-1}$ at 300K) remains metallic down to 3K, temperature below which a slight increase of the resistivity is observed [5]. Recent resistivity measurements [6] show a deviation from the power law dependence $T^n$ (n= 1.5-1.65) between 90K and 20K and a weak bump below 10K. Magnetoresistance measurements [5] at 4.2K reveal departure from 1D electronic behaviour.

X ray diffuse scattering studies performed down to about 20K on both materials, reveal 1D structural fluctuations [7] which were associated to $2k_F$ charge density wave (CDW) instabilities, taking place in a complexe 1D band structure, where the LUMO's bands of the acceptors and the HOMO's bands of both the TTF and the acceptors cut the Fermi energy [8] (Fig 1 and 2). From structural data, the charge transfer is estimated between 0.75 and 1 hole per TTF, which leads to a Fermi energy close to $E_F$" in Fig 1 and 2. In the Pd salt two main structural instabilities, associated with the Pd(dmit)$_2$ species, are observed at the reduced wave vectors $q_1$=0.5b$^*$ and $q_2$=0.31b$^*$. They can be assigned respectively to CDW instabilities within the bunch of HOMO's and within the bunch of LUMO's of the acceptors (see Fig 1). They drive smeared Peierls transitions at $T_1$= 150K and $T_2$= 105K respectively [7], this last tempera-
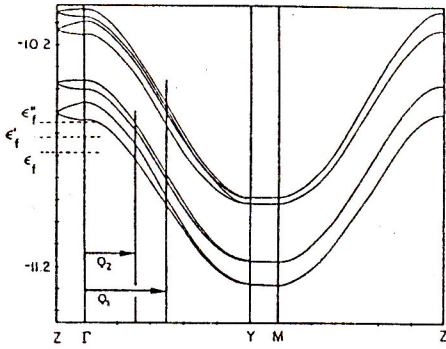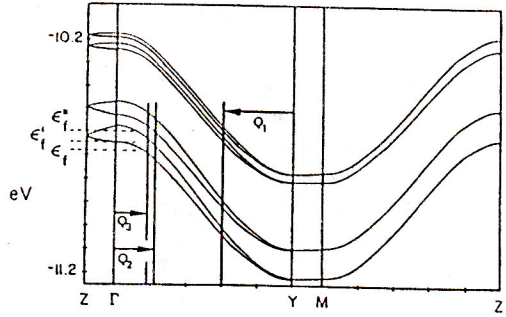
**Fig 1 ( M = Pd )**          **Fig 2 ( M = Ni)**

**Band structure of M(dmit)$_2$ slabs of TTF(M(dmit)$_2$)$_2$ from ref. [8]: half the 1D critical wavevectors (Q$_i$= q$_i$/2) measured by X-ray diffuse scattering are shown.**

ture corresponding to the inflexion point of the resistivity curve. The increase of resistivity observed below 240K can be attributed to the presence of strong $q_1$ and $q_2$ CDW fluctuations. On the other hand, the Ni salt exhibits only one main 1D structural instability at $q_1$= 0.40b* [7]; it drives a structural transition around 40K which affects weakly the resistivity. The $q_1$ CDW instability can be associated to the bunch of the LUMO's bands of the acceptor slabs (Fig 2). This assignment is in agreement with thermopower data [9] showing that holes are the dominant carriers at low temperature. Recently two other weaker quasi 1D diffuse scatterings at $q_2$= 0.22b* and $q_3$= 0.18b* were detected [10]. They could be associated with $2k_f$ CDW instabilities within the bunch of the HOMO's (Fig 2). Their possible condensation at low temperature could explain the bump observed at 10K in the resistivity. The (semi)metallic [6] and magnetoresistive [5] behaviour thus observed could be due to imperfect nesting and/or to the 2D character of the sheets of Fermi surface derived from the HOMO's bands of the acceptors (see Fig 2 around the Γ point). This interpretation does not contradict ^{1}H NMR measurements which do not reveal the opening of a gap in the electronic excitations of the TTF down to 1.5K [11]. Finally, the greater dispersion along ΓY of the band structure of the Pd salt compared with the Ni one results from the surprising shortening of the unit cell parameter b when Pd is substituted to Ni [1]: the Pd salt is more anisotropic than the Ni one.

 **Under pressure** the electrical conductivity of the Pd and Ni salts shows sizeable differences: from its temperature behaviour, the phase diagrams displayed by Fig 3 and 4 were respectively derived.

 The simplest phase diagram is shown by the Pd derivative [4]. The electronic ground state changes from a CDW insulator to a superconductor above 16 kbar. The temperatures of the minimum $T_m$ (line 1) and of the inflexion point $T_I$ (line 2) of the resistivity decrease exponentially with pressure up to 12 kbar, then vanish under pressure at about 20 kbar, where the superconducting temperature $T_C$ is maximum at 6.5K. Above this pressure, $T_C$ (line 3) decreases at the same rate as $T_m$ and $T_I$. These features suggest that the Pd salt constitutes the first example among the molecular complexes of a strong competition between superconductivity and CDW ( instead of SDW in the quasi 1D

organic Bechgaard salts $(TMTSF)_2PF_6$ or $AsF_6$).

At ambient temperature, the conductivity of the Ni salt increases rapidly until 5 kbar [4], pressure at which it recovers the ambient pressure value of its Pd counterpart, as well as its relative increase $(dLn\sigma/dP= .11/kbar)$.

Its low temperature behaviour, whose preliminary analysis [6] gives the phase diagram of Fig 4, is more complex. The metallic resistivity still exhibits a weak bump between 100 K and 50 K (vertical - - -) under pressure. This bump is affected by increasing current density, suggesting some CDW depinning. Between few hundred of bars and 5.3 kbar, the ground state is that of an insulator: the resistivity shows a minimum at $T_m$ (- — —) and an inflexion point at $T_I$ (·········); further studies are needed to elucidate the puzzling dispersion of the $T_m$ and the $T_I$ values with pressure. Between 5.3 and 5.5 kbar, the insulating state abruptly disappears and enters (- - · - - -) [6] the superconductivity whose $T_C$ increases slowly with pressure (- - - -): this unusual dependence corroborates previous low field ESR measurements [12] in spite of a shift of
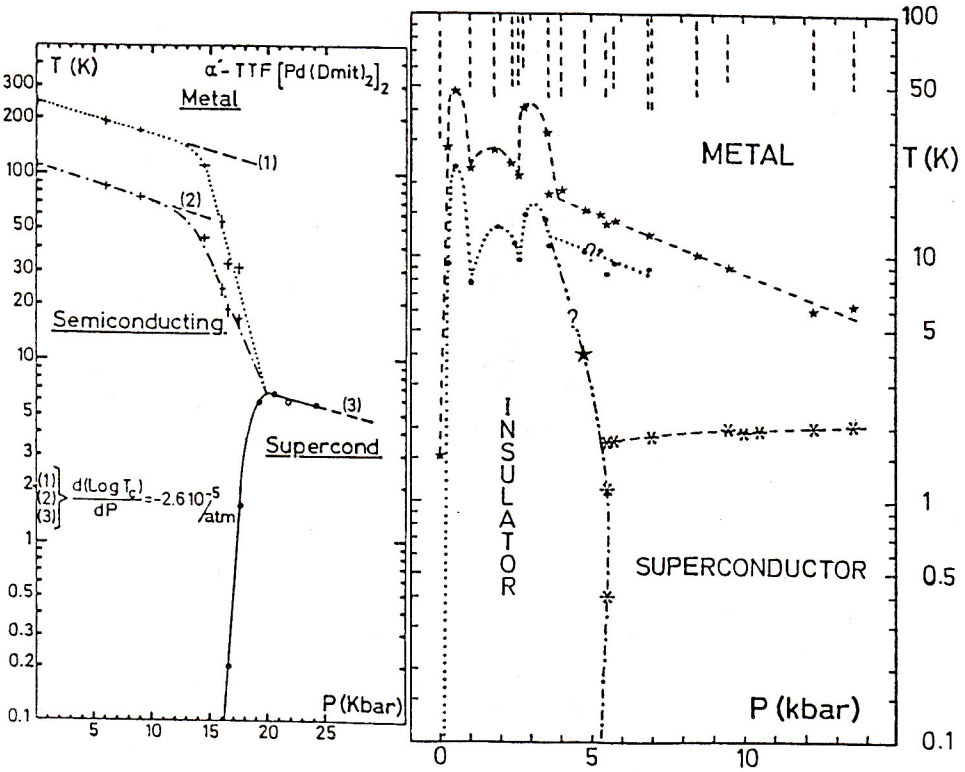


Fig 3 (M= Pd)          Fig 4 (M= Ni)

**Phase diagrams of TTF(M(dmit)$_2$)$_2$ derived from resistivity measurements**

2.3 kbar between the pressure scales. Above $T_C$, the resistivity still exhibits a minimum, but $T_m$ as well as the rate of increase of the resistivity below $T_m$ gradually vanish under pressure; consequently it becomes meaningless to assign a defined value to $T_I$ above 7 kbar. A weak anomaly of resistivity at 4.8 kbar around 4K suggests some extension (-·-·-·-) towards higher temperature of the entrance line (-·-·-·-) [6]. Nevertheless, some difficulties remain to define the high pressure boundary of the insulating phase above $T_C$ (see question marks in Fig. 4).

At variance with the behaviour of the Pd salt, where the simultaneous vanishing of $T_m$ and $T_I$ under pressure suggests a disappearance of the $q_1$ and $q_2$ CDW ground states, the anomalous features exhibited by the Ni derivative could be related to the presence of CDW's which behave under pressure in a quite decoupled way. Actually, the major difference between the band structures of the two compounds at ambient conditions concern the HOMO's bands. In the Ni salt, the position of the Fermi level near the top of the HOMO's bands makes the dimensionality of the system very sensitive to any change of the relative filling of the bands. Compared to the Pd salt, this situation could lead to an unexpected behaviour of the CDW's under pressure. The existence of anomalies of resistivity in the pressure range where the superconductivity is stabilized suggests, contrary to the Pd salt i) from the observation of a high temperature bump, the persistence of the $q_1$ CDW and ii) from the pressure dependences of $T_m$ and $T_C$, a weak competition between superconductivity and CDW. In this respect, the successive stabilization of (semi)metallic, insulating and superconducting phases could be associated to changes in the dimensionality of the Fermi surface associated to the HOMO's and its CDW instabilities.

We thank J. Friedel, M. Ribault, P. Chaikin, J. P. Ulmet and P. Cassoux for fruitful discussions or close collaborations.

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