STABILIZED 1D METAL IN TTF(Ni(dmit)$_2$)$_2$ THROUGH VERY WEAK COUPLING BETWEEN PHONONS AND WEAKLY CORRELATED FERMIONS

M.L. Doublet[a], I. Malfant[b], S. Hebrard[c], E. Canadell[a], J. Gaultier[c],
D. Chasseau[c], J.P. Legros[b] and L. Brossard[d]

[a]Laboratoire de Chimie Theorique, URA CNRS 506, Université Paris-Sud
91405 Orsay, France
[b]Laboratoire de Chimie de Coordination du CNRS
205 route de Narbonne, 31077 Toulouse, France
[c]Laboratoire de Cristallographie et de Physique Cristalline
EFR CNRS 133, Université de Bordeaux
351 cours de la Liberation, 33405 Talence, France
[d]Laboratoire de Physique des Solides, URA CNRS 074
Complexe scientifique de Rangueil
31077 Toulouse, France

Extended Hückel band structure calculations derived from low temperature X-ray structural data, provide evidence, as temperature decreases, for an increasing 1D character of the multiparallel bands of the TTF(Ni(dmit)$_2$)$_2$ compound. This result is discussed within the monotonous metallic behaviour of the weakly correlated fermions gas, despite condensations of charge density wave instabilities.
PACS numbers: 71.20.Hk, 71.45.Lr, 61.66.Hq

1. Introduction

The π-donor–acceptor charge transfer salt TTF(Ni(dmit)$_2$)$_2$, where dmit^{2-} is (1,3-dithia-2thione-4,5-dithiolato), crystallizes in a monoclinic structure, characterized by uniform stacking along the b axis of the unit cell, of columns of TTF which alternate along a axis with sheets of plane molecules of Ni(dmit)$_2$ [1]. At ambient pressure, it displays a monotonous metallic resistivity behaviour from 300 K down to 50 mK [2]. Diffuse X-ray measurements performed above 27 K have evidenced structural fluctuations at $2k_F$, two of them very weak and a third weak one, which only condenses at 40 K into superlattice dots with a reduced wave vector $q = 0.4b^*$ [3]. Whereas an only small resistivity anomaly is displayed at 9 K in the

temperature dependence of the resistivity, not even partial breakdown of the Fermi surface is associated to the charge density wave (CDW) 3D ordering temperature, except for a very weak deviation of the $T^{1.65}$ power law of the resistivity around 40 K [2]. The energy dispersion $E(k)$ of the single electron conduction bands of this salt, as derived from 300 K X-ray refinements, is characterized by the overlap of three sets of parallel and partially filled bands. One set arises from the highest occupied molecular orbital (HOMO) of the TTF; the two others derive from the lowest unoccupied (LU) and the highest occupied (HO) molecular orbitals (MO) of the Ni(dmit)$_2$, respectively. The unusual feature that not only the LUMO but also the HOMO-based bands of the acceptor are partially filled, results from a Ni–S interaction which yields a HOMO–LUMO splitting (0.4 eV) in the monomer which is weak compared to the bandwidths W (0.6 eV) [4]. By tuning the three intersects of the bands by an adjusted Fermi level E_{F} to the wave vector q values of the three 1D structural fluctuations, yields (i) a charge transfer of about $0.75e^-$ per TTF molecule and (ii) a closed orbit around the center Γ of the first Brillouin zone [4]. This pocket has never been confirmed by any Shubnikov–de Haas (SdH) oscillations in the low temperature transverse magnetoresistance of needle-shaped single crystals. New X-ray structural refinements performed at 150 K and 12 K [5], as well as derived tight binding band structure calculations which are here reported, throw new light on this puzzling question.

2. Results

The first result is connected to kinks which appear at about 70 K in the decrease in the lattice parameters versus temperature [5]. This constitutes the first experimental result which may be directly correlated with thermopower data [6] showing that holes become the dominant carriers below this temperature. The fact that this occurs well above the condensation temperature (40 K) of the electron-like states of the LUMO bands, is closely related to the opening of a pseudo-gap in density of states (DOS) at the Fermi level [7].

The second point is related to the temperature dependence of the Fermi surfaces and of the tight-binding bands structure: they were derived from the relative strengths of the different interactions occurring in the salt. These interaction energies $\beta_{i,j}$ between molecular orbitals i and j can be written, within the effective one-electron H^{eff} Hamiltonian of the extended Hückel type, as

$$\beta_{i,j} = \sum_{\nu} \sum_{\mu} c_{\nu i} c_{\mu j} \langle \chi_\nu | H^{\mathrm{eff}} | \chi_\mu \rangle,$$

where $c_{\nu i}$ denotes the coefficient of atomic orbital χ_ν in the molecular orbital Ψ_i through $\Psi_i = \sum_\nu c_{\nu i} \chi_\nu$. Due to the lack of space, these values will be published elsewhere [5] and we will here focus on the results mainly related to the transfer integrals only.

As displayed in Table I, the thermal contraction induces a decrease in the b parameter and a corresponding increase in the bandwidths $W = 4t_b$, where t_b is the transfer integral along the stack. Concerning the acceptor stack, it is worth to note that at each T, the bandwidth of the HOMO is slightly greater than the bandwidth of the LUMO. The thermal contraction should similarly affect the

TABLE I

Temperature dependence of the bandwiths W of the
HOMO and LUMO bands, of the b parameter and of
the volume V of the unit cell.

W	TTF	Ni(dmit)₂		b	V
[eV]	HOMO	HOM O	LUMO	[Å]	[Å³]
$T = 295$ K	0.7	0.6	0.56	3.732	3439
$T = 150$ K	0.79	0.7	0.67	3.664	3348
$T = 12$ K	0.83	0.73	0.72	3.638	3308

transverse integrals t_c and t_a. These partial DOS were derived via [5], but their respective increases are relatively smaller than for t_b, which induces an increasing 1D character of the salt as T decreases. By assuming that the charge transfer remains constant, this will in turn already suppress at 150 K the suggested 2D hole pocket around the Γ point [5]. This may be one of the reasons for the absence of any low temperature SdH oscillations.

3. Discussion

The previous increasing in the 1D character of TTF(Ni(dmit)₂)₂ as T decreases, while the CDW condensations at 40 and probably also 9 K do not affect its overall metallic character, raises some discussion on the interplay between the respective strengths of the electron correlations and the electron–phonon coupling. In the random phase approximation (RPA), the intensity I of the X-ray diffuse lines equals $\lambda\chi_\rho$, where λ is the electron–phonon coupling; the CDW polarizability χ_ρ equals $\lambda\chi_e/(1 - \lambda\chi_e)$, where χ_e is the electronic one. Hence, either a small λ or a weak divergence of χ_e at $q = 2k_F$ may lead to the experimental weak I. Besides, the Pd counterpart compound, which is characterized by a strong electron–phonon coupling [3], shares with the Ni salt very similar bands structure and Fermi surfaces [4]. Hence, a weak divergence of χ_e seems very unlikely in the Ni salt which may be characterized by a very weak λ.

The partial DOS $n(0)$ displayed in Table II are the contributions to the total DOS $N(0)$ from the different atoms of TTF and of Ni(dmit)₂. They were derived via a Mulliken population analysis of the crystal orbitals and yield the calculated non-interacting Pauli spin susceptibility χ_P [7]. By comparing this value with the room temperature experimental spin susceptibility χ_S enable to evaluate, in the small U limit, the Stoner α parameter which measures the enhancement of the Pauli χ_P by the short range on site Coulomb repulsion U. With $1 - \alpha = \chi_P/\chi_S$, we got $\alpha = 0.52$ [7]. In Table II, the calculated values U are derived in the random phase approximation from $U = \alpha/n(0)$, instead of $\alpha/N(0)$ as misleading done in [7]. The small U limit is insured ($U < W$) and the ratio U/E_F (= 0.7) is close to the value (= 1) of $g_1/\pi V_F$, determined [8] by NMR spin–lattice relaxation rate analysis on the ^{1}H of the TTF chain (g_1 is the backward scattering potential and V_F — the Fermi velocity).

TABLE II

Calculated W, partial DOS $n(0)$ at the Fermi level E_F, and intramolecular electron correlations U for the HOMO and LUMO bands.

$T = 295$ K		W [eV]	$n(0)^*$	U [eV]	U/W	U/E_F
TTF	HOMO	0.70	2.066	0.25	0.36	0.7
Ni(dmit)$_2$	HOMO	0.60	3.063	0.17	0.28	0.34
Ni(dmit)$_2$	LUMO	0.56	2.499	0.20	0.36	1

* In units of e^-/eV chemical entity.

We believe that these rather weak electron correlations as well as the very weak electron–phonon coupling are the key to understand, despite the CDW condensation, the stabilization as the temperature decreases, of an enhanced 1D character of the metallic behaviour of $TTF(Ni(dmit)_2)_2$.

Acknowledgments

References

[1] M. Bousseau, L. Valade, J.P. Legros, P. Cassoux, M. Garbauskas, L.V. Interrante, *J. Am. Chem. Soc.* **108**, 1908 (1986).

[2] L. Brossard, M. Ribault, L. Valade, P. Cassoux, *Phys. Rev. B* **42**, 3935 (1990).

[3] S. Ravy, E. Canadell, J.P. Pouget, in: *The Physics and Chemistry of Organic Superconductors*, Springer-Verlag, Berlin 1990, p. 252.

[4] E. Canadell, I.E.I. Rachidi, S. Ravy, J.P. Pouget, L. Brossard, J.P. Legros, *J. Phys. (Paris)* **50**, 2967 (1989).

[5] S. Hebrard, M.L. Doublet, I. Malfant, J. Gaultier, J.P. Legros, D. Chasseau, E. Canadell, to be published.

[6] W. Kang, D. Jerome, L. Valade, P. Cassoux, *Synth. Met.* **42**, 2343 (1991).

[7] L. Brossard, E. Canadell, L. Valade, P. Cassoux, *Phys. Rev. B* **47**, 1647 (1993).

[8] C. Bourbonnais, P. Wzietek, D. Jerome, F. Creuzet, L. Valade, P. Cassoux, *Europhys. Lett.* **6**, 177 (1988).