Fermi-Surface Instabilities in the Organic Conductor (TMTSF)$_2$NO$_3$: High-Pressure Studies.

W. Kang$^{1,2}$, K. Behnia$^1$, D. Jérome$^1$, L. Balicas$^1$
E. Canadell$^3$, M. Ribault$^1$ and J. M. Fabre$^4$

$^1$ Laboratoire de Physique des Solides (associé au CNRS)
Université Paris-Sud, 91405, Orsay, France
$^2$ Department of Physics - Ewha Womans University, Seoul 120-750, Korea
$^3$ Laboratoire de Chimie Théorique - Université Paris Sud, 91405, Orsay, France
$^4$ Laboratoire de Chimie Organique et Structurale, Université Montpellier II
Montpellier 34060, France

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Abstract. – The study of the magnetoresistance in the organic quasi-one-dimensional conductor (TMTSF)$_2$NO$_3$ at a pressure (8 kbar) exceeding the critical pressure required for the stabilization of a conducting state at low temperature has revealed the existence of quantum oscillations with a frequency of 190 T in good agreement with an extended Hückel-type calculation of the band structure. Unlike other members of the (TMTSF)$_2$X series the ambient pressure SDW ground state in (TMTSF)$_2$NO$_3$ can be understood in terms of an instability involving the nesting of 2D semi-metallic Fermi surfaces.

Quasi-one-dimensional conductors (Q-1D) such as (TMTSF)$_2$X, where TMTSF is the organic molecule tetramethyltetraselena fulvalene and X is an inorganic monoanion such as PF$_6$, ClO$_4$, NO$_3$, ... have been the subject of an intense activity in the last decade (see [1-3] for a review). Quite generally a competition between two ground states (superconductivity and spin density wave, SDW) is observed in these compounds. High pressure, increasing the interchain coupling of these Q-1D conductors suppresses the SDW ground state and superconductivity becomes observable below 1K [4]. Furthermore, under a magnetic field perpendicular to the high-conductivity axis (usually along c*), superconductivity is destroyed by the orbital effect of the magnetic field and a cascade of spin-density-wave transitions (known as FISDW) is induced [5-8]. The one remarkable exception to this general picture is (TMTSF)$_2$NO$_3$ where at pressures exceeding the critical pressure for the suppression of the SDW ground state, neither superconductivity nor FISDW phases could be detected [9,10]. These features lent some support to a theoretical model [11] which established a close link between superconductivity and FISDW phases in (TMTSF)$_2$X conductors.

In this paper, we present a magnetoresistance study performed under pressure above the critical value for the stabilization of the conducting state at low temperature. We report the first observation of quantum oscillations in (TMTSF)$_2$NO$_3$ under pressure with a fundamental frequency (190 T) which is in fair agreement with the tight-binding band structure. The angular dependences of both the Shubnikov-de Haas frequency and the oscillations amplitude

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could be understood supposing a peculiar corrugation along the axis of the quasi-cylindrical Fermi surface. Furthermore, the angular dependence of the magnetoresistance is very different from the situation in other Bechgaard salts. Unlike \((\text{TMTSF})_2\text{ClO}_4\) [12, 13] or \((\text{TMTSF})_2\text{PF}_6\) under pressure [14, 15], no signature of commensurability effects (known as Lebed oscillations) associated with Q-1D Fermi surface could be detected. This result can be understood if one takes into account the strong modification of the electronic structure brought about by the ordering of the \(\text{NO}_3^-\) anions (with \(\mathbf{Q} = (1/2, 0, 0)\)) below 45 K [16] which transforms the open Q-1D surface at high temperatures into the tubular one of a compensated 2D semi-metal [17, 4].

Resistivity measurements were performed using the standard four-probe a.c. technique with 17.5 µm gold wires silver-pasted on pre-evaporated gold contacts. A current of 100 µA was injected along the needle axis (\(a\)-axis). The sample was put under a pressure of 8 kbar using a standard Cu-Be clamp. The device described in [15] was used to cool the pressure cell down to 0.4 K and to rotate it in the hybrid magnet of the CNRS-MPI joint High Magnetic Field Laboratory at Grenoble. The actual orientation of the sample relative to the magnetic field was obtained using a Hall probe mounted on the pressure cell.

Figure 1 presents the angular dependence of the magnetoresistance for various fields at \(T = 0.45\) K. The magnetic field was rotated in the least-conducting plane \((b', c^*\)). Here, \(\theta\) is the tilt angle of the field off the \(c^*\)-axis. At low fields, the very moderate magnetoresistance presents no features apart from a shallow minimum around \(\theta = 90^\circ\) which was taken as the \(b'\)-direction. We now comment on the angular dependence of the magnetoresistance as shown in fig. 1. With increasing field a clear structure consisting of two broad peaks at \(\theta = 56^\circ\) and \(\theta = -48^\circ\) plus an additional weaker peak for \(\theta = 18^\circ\) appears. Essentially the same result was obtained at a higher temperature \((T = 4.2\) K). Comparing the \(R(\theta)\) curves for a given field at these two temperatures, we found that the broad peaks are the genuine features of the \(R(\theta)\) structure. The magnetoresistance is virtually unchanged as a function of temperature for all field orientations except in the vicinity of the peaks where it increases with decreasing temperature. Besides the peaks already discussed above, two minima are observed at \(\theta = +3.1^\circ\) and \(+28.9^\circ\) in fields larger than 14 T and merging into one broad minimum below 10 T. Minima of magnetoresistance have been observed at low fields (metallic regime) in Q-1D
conductors such as (TMTSF)$_2$ClO$_4$ [12, 13] and (TMTSF)$_2$PF$_6$ under pressure [15, 14]. They correspond to particular angles with electron trajectories on the quasi-planar Fermi surface of these materials which are commensurate with the reciprocal lattice. Considering the triclinic structure of (TMTSF)$_2$NO$_3$, the Lebed's magic-angle formula reads $\tan \theta = (p/q) \cdot \left( \frac{b}{c} \sin \gamma / \sin \beta \sin \alpha^* \right) - \cot \alpha^*$ and predicts minima at $\theta = -29.3^\circ (p/q = -1)$, $-0.3^\circ (p/q = 0)$ and $+28.8^\circ (p/q = 1)$, where $p$ and $q$ are arbitrary integers. The absence of minima at low fields in the vicinity of the $c^*$-axis and the missing minimum at $\theta = -29.3^\circ$ make the data of fig.1 difficult to understand within the Lebed's formalism for a Q-1D Fermi surface.

Figure 2 presents the magnetoresistance for a field oriented along the direction $\theta = -19^\circ$. As more clearly seen in the inset, oscillations with $1/H$ periodicity gradually appear for fields stronger than 12 T. We have detected such oscillations for fields orientations in the vicinity of the $c^*$-axis direction ($-49^\circ < \theta < +50^\circ$).

The angular dependence of the frequency and amplitude are shown in fig.3. The frequency deviates slightly from a $1/\cos \theta$ law. The deviation (about 7%) is positive and larger than the experimental inaccuracy. The variation of the amplitude with the field orientation is, however, more puzzling. As seen in the inset, the amplitude is largest when the magnetic field is oriented along $\theta = -20^\circ$. A weaker maximum is also observed at $\theta = +20^\circ$.

The above-mentioned discrepancy is not too surprising since the anion ordering at $T_{\lambda_0} = 45$ K renders (TMTSF)$_2$ClO$_4$ different from conductors exhibiting either no anion ordering or an ordering which does not affect the longitudinal periodicity. This is the situation encountered in (TMTSF)$_2$ClO$_4$ at 24 K. (TMTSF)$_2$NO$_3$ instead, undergoes a Fermi-surface instability at the anion ordering transition between a conductor with a nearly flat Fermi surface at high temperature and a 2D semi-metal at low temperature. This Fermi-surface modification has been detected in the temperature dependence of the thermopower[18]. Above 45 K, the Seebeck coefficient shows a linear $T$ dependence corresponding to 1D hole carriers while the sharp drop of the coefficient noticed below 45 K can be attributed to the anion ordering transition with a Seebeck coefficient becoming the weighted average of the coefficients related to electrons and holes pockets, namely $S = (\sigma_e S_e + \sigma_h S_h) / (\sigma_e + \sigma_h)$, where $S_e$ and $S_h$ have opposite signs. Consequently, the stabilization of the SDW phase at 9 K cannot be explained by the regular model based on the nesting of Q-1D Fermi surfaces. What

![Fig. 2.](image1.png)

**Fig. 2.** - Magnetoresistance for a field which makes $\theta = -19^\circ$ relative to the $c^*$-axis. Note the quantum oscillations appearing at high fields. The inset shows the oscillating part of the magnetoresistance as a function of $1/H$.

![Fig. 3.](image2.png)

**Fig. 3.** - Angular dependence of the frequency of the quantum oscillations. The line represents the $1/\cos \theta$ behaviour expected from a perfectly bidimensional Fermi surface. The inset shows the angular dependence of the oscillations amplitude.
should be considered instead is an exciton-like transition driven by the nesting between the 2D pockets of a semi-metal [4,19]. In order to make these considerations more quantitative, the band structure of (TMTSF)$_2$NO$_3$ has been revisited. Tight-binding band structure calculations for the donor slabs of (TMTSF)$_2$NO$_3$ were carried out using the room temperature and ambient pressure crystal structure [20]. An extended Hückel-type Hamiltonian [21] was used and the non-diagonal matrix elements were calculated according to the modified Wolfsberg-Helmoltz formula [22]. All valence electrons were explicitly considered and the basis set consisted of double-$\tilde{\zeta}$-type Slater orbitals [23]. The exponents, contraction coefficients and $H_{ij}$ values were taken from previous work [24]. The calculated Fermi surface for the TMTSF slabs is shown in fig. 4a. The Fermi surface corresponding to the slabs in the (1/2, 0, 0) superstructure was approximated by folding the Fermi surface of fig. 4a, i.e. the potential of the anions was not explicitly taken into account, and is shown in fig. 4b). For pressures exceeding the critical pressure, i.e. in the absence of Spin Density Wave transition, fig. 4b) represents the cross-section of the low-temperature Fermi Surface. This represents three per cent of the original first Brillouin zone at high temperature and would yield a fundamental frequency for quantum oscillations of 266 T, using the room temperature structure. It is conceivable that the Fermi surface of fig. 4b) is unstable against a density wave transition with a nesting vector which leads to the configuration displayed on fig. 4c). The area covered by the unannealed electron and hole pockets is about one-third of the area before nesting. We suggest fig. 4c) to be a fair representation of the Fermi surface of (TMTSF)$_2$NO$_3$ at ambient pressure in the SDW phase. We notice that the nesting vector in fig. 4b) is incommensurate with the underlying lattice. The particular ordering vector of NO$_3$ anions seems to make a qualitative difference between the Fermi surface of metallic (TMTSF)$_2$NO$_3$ at low temperature as compared to other Bechgaard salts.

The first outcome of our experiment is to confirm this qualitative difference: unlike other quasi-one-dimensional conductors of the same family, the angular dependence of the
magneto resistance in this compound shows no signature of Lebed commensurability effects. For the moment, we lack an appropriate theoretical approach to explain in detail this angular dependence. Apparently, there is no simple way to attribute the high-field structure of magneto resistance to resonant effects frequently reported in two-dimensional conductors [25].

The second outcome of our experiment is the first detection of quantum oscillations in the magneto resistance at high pressure. Such oscillations have already been observed only in the ambient pressure SDW state of (TMTSF)$_2$NO$_3$. The frequency of the oscillations at ambient pressure (75 T [10] or 63 T [26,27]) is, however, about one-third of our fundamental frequency (190 T). These results are consistent with our band calculation. As seen in fig. 4c, the SDW transition would reduce to one third the area of the Fermi surface. It is thus reasonable to expect quantum oscillations in the metallic state under pressure to exhibit a frequency three times larger than that of the SDW state. Quantitatively, the band calculation, using ambient pressure room temperature crystal data, predicts a fundamental frequency of 266 T for the metallic state corresponding to fig. 4b) which is somewhat higher than our experimental result (190 T) measured under pressure. However, the band calculation in fig. 4b) does not take into consideration the existence of a finite anion potential inducing a further reduction of the orbit's area.

The frequency of the large orbits increases a little faster than 1/cos θ when the magnetic field is tilted away from the c*-axis. Such a deviation can be explained by the existence of a finite transverse coupling which would introduce a small corrugation along the axis of the quasi-cylindrical Fermi surface. In this picture, its order of magnitude should be comparable to $t_c/t_b$ (= 1/20) which is the case. The carrier trajectories which can be stabilized at low temperature under pressure are somehow similar to those observed at ambient pressure albeit only under large fields. The modest difference of frequencies (248 T at $P = 1$ bar and 190 T under pressure) could be ascribed to a pressure-induced deformation of the structure. Figure 4d) provides an illustration for the small orbits in the SDW phase ($X'$ is an inversion centre for the orbits). At high fields, carriers may jump from one orbit to the symmetric one and the resulting orbit becomes about three times larger.

The magnitude of the small axis of the ellipsoidal Fermi-surface cross-section as shown in fig. 4b) allows a derivation of the band structure anisotropy, $t_b/t_a = 0.075$, given the experimental frequency of 190 T.

The unusual angular dependence of the resistance, fig. 1, is also reminiscent of the data observed for the high-frequency oscillations at ambient pressure where two maxima at θ = ±20° are observed [27,28]. To explain such an effect, it is tempting to propose a Fermi surface as shown in fig. 5 where the warping along the c*-axis is asymmetrical. The particular orientation which gives the maximal orientation is associated with a stationary extremal cross-section of the Fermi surface, namely, $\delta^2 A/\delta k_z^2 = 0$. Given the triclinic symmetry of the crystal, such a configuration is not forbidden. This asymmetrical warping may probably survive after the second nesting associated to the SDW transition, hence similar angular dependences for the amplitude of the oscillations in ambient pressure SDW and high-pressure metallic states may be expected.

The observation in the semi-metallic state stabilized at low temperature under pressure of a magneto resistance oscillating at the frequency related to the interchain coupling as suggested in [4] is now established. It shows that the anion ordering at 45 K transforms the 1D Fermi surface at high temperature into a 2D semi-metallic surface at low temperature. The frequency of the oscillations is in fair agreement with the extended Hückel calculation of the Fermi surface. Furthermore, the onset of the SDW state below 9 K at ambient pressure should be considered as arising from the nesting of electron and hole tubes with a cross-section of 190 T. In spite of the hybridization between electron and hole pockets, some smaller pockets are left in the SDW state due to the nested areas. These portions give rise to the semi-
metallic behaviour[29] and to the low-frequency oscillations. The excitonic model which is proposed for \((\text{TMTSF})_2\text{NO}_3\) at ambient pressure takes advantage of the 2D nesting whereas in the original excitonic instability proposed for a 3D semimetal[30] the transition temperature was restricted to a very low-temperature regime (with \(T_c\) less than the exciton binding energy).

The angular dependence of the amplitude of the rapid oscillations is still lacking a proper explanation. It cannot be explained by a purely 2D model of the Fermi surface. We suggest that a model following the idea proposed initially for the angular dependence of the Shubnikov–de-Haas oscillations in BEDT-TTF salts[31] is probably more appropriate. However, this model would depend on details of the Fermi surface which are beyond the present capabilities of our calculations. The failure of[10] to observe rapid oscillations can be understood considering the data on fig.3. Although no mention of the field direction was made in[10], we notice that the amplitude is maximum only in a narrow range of angles around \(-20^\circ\).

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