One-dimensional organic superconductivity: an investigation through electron Schottky tunnelling in N/GaSb-(TMTSF)$_2$PF$_6$ junctions under pressure (*)

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Résumé. — Un important effet de pseudo-gap dans la densité d'états au niveau de Fermi a été observé au moyen de l'effet tunnel de type Schottky entre GaSb (dopé N) et le supraconducteur organique (TMTSF)$_2$PF$_6$ sous pression de 11 kbar ($T_c = 1$ K). Ce phénomène permet de prouver expérimentalement sans ambiguïté les propriétés unidimensionnelles de la divergence supraconductrice et justifie la présence de fluctuations 1-D supraconductrices jusqu'aux températures élevées. Les résultats ont permis de mesurer une énergie de condensation de paires $2\Delta(0) = 3.6$ meV qui démontre bien la forte intensité de la divergence supraconductrice dans la famille des supraconducteurs organiques (TMTSF)$_2$X.

Abstract. — Observation of a large pseudo-gap at the Fermi level by Schottky tunnelling of electrons from N-doped-GaSb into the organic superconductor (TMTSF)$_2$PF$_6$ under a pressure of 11 kbar ($T_c = 1$ K) establishes, on an unambiguous experimental basis the one-dimensional character of the low temperature superconducting divergence and so justifies the presence of 1-D superconducting fluctuations to high temperatures. The intrachain pairing energy $2\Delta(0) = 3.6$ meV derived from tunnelling characteristics emphasizes the strength of the superconducting channel in the family of organic superconductors (TMTSF)$_2$X.

In the field of organic conductors the stabilization at low temperature of a high conductivity state was first achieved in the quasi-one-dimensional (Q-1-D) conductor TMTSF-DMTCNQ under high pressure [1]. At pressures above 10 kbar a conducting state exhibiting a metallic-like temperature dependence of the conductivity remains stable down to low temperature while longitudinal conductivity values exceed $10^7$ (Q.cm)$^{-1}$ at 1.2 K. Such conductivities were the largest ever reported in organic conductors at any temperature. Moreover, the high conductivity state can be destroyed by the application of a large magnetic field perpendicular to the chain axis.

It was thus suggested that the drastic increase of the conductivity below 50 K or so, could not be understood within the frame work of single particle electron behaviour but rather indicated the presence in such a temperature range of intrachain finite life time short range order contributing to the conduction in a collective manner the most likely collective mode being the establishment of 1-D Cooper pairing between $+k_F$ and $-k_F$ electron states. Subsequently a superconducting state exhibiting zero electrical resistance [2] and quasi complete diamagnetic shielding [3, 4] was detected in the organic salt (TMTSF)$_2$PF$_6$ and more recently seven other members of the (TMTSF)$_2$X [5, 6] family.

However, above the superconducting transition temperature at about $T_c = 1$ K under 10 kbar for (TMTSF)$_2$PF$_6$, the conductivity shows many features
identical to those already encountered in TMTSF-
DMTCNQ [1] namely: (i) a helium temperature conduc-
tivity exceeding $10^5 \, \text{cm}^{-1}$ and (ii) a strong
temperature dependence below 15 K, whereas in
the same temperature domain the resistance of
ordinary 3-D metals tends to saturate towards a
residual value limited by lattice imperfections or
impurities. For these reasons, a theoretical picture
was proposed, in which the transport properties of
(TMTSF)$_2$PF$_6$ at low temperatures are explained
in terms of dimensionality enhanced incipient super-
conducting pairing arising at temperatures much
larger than the 3-D ordering superconducting tem-
perature [7, 8]. Q-1-D conductors may undergo phase
transitions only if some interchain coupling between
order parameters exists [9], which implies low 3-D
ordered phase transition temperatures for weak
interchain couplings [10]. However, at the same time
One Dimensionality can lead to a drastic enhance-
ment $(\xi_\parallel / d)^2$ of the rms order parameter value
in domains of volume $\xi_\parallel d_\perp^2$ at $T > T_c$ [7] where $\xi_\parallel$ and
$d_\parallel$ are respectively the longitudinal temperature
dependent coherence length and the interchain dis-
tance. The incipient instability will also affect the
single-particle density of states, through the depression
of $N(E)$ below its high temperature value in an energy
range of width $2 \Delta$ at the Fermi level (the pseudo-gap
phenomenon) [11] where $2 \Delta$ is a measure of the
pairing energy within each isolated chains. Unlike
$T_c$, which for weakly coupled superconducting
chains [12] is proportional to $(J_\perp J_\parallel)^{1/2}$ where $J_\perp$ and
$J_\parallel$ are respectively the interchain and intrachain
superconducting coupling strengths, the value of
the pseudo-gap depends mainly on the intrachain
coupling.

This paper presents experimental evidence for the
existence of a well developed pseudo-gap in
(TMTSF)$_2$PF$_6$ above $T_c$.

The pairing energy can be determined by several
techniques in ordinary metallic superconductors [13]
but as it was claimed by a specialist in superconduc-
tivity [14] « Tunnelling is by far our most sensitive
probe of the superconducting state ».

As electrons tunnel between two metallic electrodes
separated by a thin insulating barrier, the M-I-M
geometry, the transition probability of carriers obey-
ing Fermi statistics is proportional to the energy level
density of final states. Thus, provided one of the
electrodes is in a superconducting state the transition
probability of electrons through the barrier remains
small (the junction resistance is large) as long as the
bias voltage does not exceed $V = \pm \Delta / e$. For $V < \Delta / e$
the electrons find no available energy states in the
superconducting electrode to tunnel into. Since the
density of tunnelling states $N_T$ is given by

$$N_T(E) = N(0) \left[ \frac{E}{(E^2 - \Delta^2)^{1/2}} \right]$$

in the BCS model of superconductivity sharp resis-
tance minima are expected for a junction bias of $V = \pm \Delta / e$.

Although there are several types of tunnel junctions
which may be used to determine a superconducting
energy gap [16] we have chosen the Schottky metal-
semiconductor contact geometry (Fig. 1). In particular
since the intrinsic properties of the barrier are deter-
mined at the contact between a degenerate doped
semiconductor and a metal electrode, the Schottky
junction is more resistant to the application of high
pressure than usual M-I-M junctions [17, 18].

This junction has been prepared by evaporating
tellurium doped GaSb ($N_D > 3 \times 10^{18} \, \text{cm}^{-3}$) on
a natural face of (TMTSF)$_2$PF$_6$ single crystals parallel
to the chain axis at room temperature [19]. The size of
the semiconducting evaporated « dot » is typically
0.3 mm in diameter and 5 000 Å in thickness. Ohmic
contacts on the semiconductor are subsequently
made by evaporating a circular layer of tin 500 Å
thick and 0.15 mm in diameter. Finally, ohmic con-
tacts on tin and on the organic conductor are made
with a drop of silver dag (Fig. 2).

The current flowing through the tunnel junction is
AC modulated at low frequency ($v = 750$ Hz) and the
corresponding AC voltage is measured with a phase
sensitive detector. Modulation currents of

$$\Delta I = 10^{-7} \, \text{A} \quad \text{or} \quad 5 \times 10^{-9} \, \text{A}$$
were used, depending on the temperature domain. The smallest modulation amplitude of $5 \times 10^{-9}$ A used at $T = 50$ mK led to detected voltages of less than 100 mV, so ensuring no modulation broadening. The incremental resistance of the tunnel junction $dV/dI$ is thus investigated as a function of the applied bias. Typical zero bias junction resistances amount to 5 to 10 kΩ under ambient conditions. Destructions of the junctions occurred for large bias voltages so preventing the application of voltage drops larger than 15 mV.

The use of GaSb for the semiconducting electrodes is limited to pressures lower than approximately 12 kbar, at which pressure GaSb transforms from a direct band gap to an indirect gap semiconductor (at $P > 12$ kbar) with a concomitant dramatic increase in the zero bias incremental resistance [20]. The present study was performed at 11 kbar with high pressure and low temperature equipment similar to that described previously [2].

The voltage dependence of the incremental resistance of N/GaSb-(TMTSF)$_2$PF$_6$ junctions displayed in figure 2 shows typical behaviour, expected for the situation of a superconducting electrode with a well developed gap at the Fermi level. The separation of the two minima in figure 2 defines the pairing energy, $2\Delta = 3.6$ meV at $T = 0.1$ K. As the temperature is increased even above, $T_c = 1$ K, the characteristic tunnelling behaviour of figure 2 is only weakly affected. The temperature dependence of the tunnelling characteristics shown on figure 3a plotted as $(R_{max}/R_{min}) - 1$ versus temperature, defining $R_{max}$ and $R_{min}$ as respectively the maximum of $dV/dI$ at $V = 0$ and the minimum at $V = \pm \Delta/e$ respectively. A 20% increase of the peak to peak voltage difference $2\Delta$ is seen on warming between 0.2 and 5 K. The tunnelling characteristics such as shown on figure 2 have been observed on several junctions, emerging above the background level below 15 K or so. A linear extrapolation of the temperature dependence on figure 3a (the junction failed at temperatures $T > 5$ K on warming) would lead to $T \approx 11$ K for the disappearance of the resistance anomaly. However, we do not attach too much physical significance to such a linear extrapolation, particularly for this case of 1-D superconductivity.

The application of a magnetic field perpendicular to the plane of the junction (and also to the chain axis) decreases markedly the amplitude of the resistance anomaly, as shown on figure 3b. The resistance anomaly however is not totally wiped out under the high magnetic field used in the present study. Figures 2
and 3 show that the tunnelling characteristics can be attributed to the formation of a superconducting pseudo-gap in the organic superconductor. The magnetic field dependence shows in addition that the pseudo-gap is related to the intrachain pairing energy and not to the 3-D ordered state, since the zero resistance superconducting state of (TMTSF)_2PF_6 is completely destroyed by perpendicular magnetic fields weaker than 1 kOe or so. We therefore claim that the pseudo-gap observed in (TMTSF)_2PF_6 reflects the establishment of short range ordered one-dimensional superconducting pairing.

However, we have noticed that decreasing the amplitude of the modulating current by a factor 20 at \( T = 50 \text{ mK} \), increases the value of the zero bias incremental resistance by a factor 2. Thus it is very likely that for \( T < T_c \), the tunnelling characteristics appear as that given by a very narrow real gap, three-dimensional in nature, establishing below \( T_c \) at the centre of the 1-D pseudo-gap.

The stability of the pseudo-gap with respect to the application of an external magnetic field requires a more elaborate interpretation. First, it seems possible that a fluctuating short range ordered superconducting state might be stable with respect to any external magnetic field even those applied along a transverse direction since the weakness of the interchain coupling impedes the formations of closed loops leading to magnetic shielding of orbital origin [7].

Secondly, the high field saturation of the pseudo-gap (Fig. 3b) could possibly imply a contribution from a triplet-paired spin state to the 1-D superconductivity [21]. In such a situation an external magnetic field would not destroy the pairing of electrons with spins aligned along the field axis, namely \( \langle S_z \rangle = 1 \).

Finally, we must keep in mind that the conductivity of (TMTSF)_2PF_6 is strongly affected by a large transverse magnetic field [8] and that under 55 kOe some kind of « weakly » insulating state is restored at helium temperature. The saturation of the pseudo-gap may hence be related to the low temperature magnetoresistance.

In conclusion, the success of these first preliminary experiments of electron tunnelling into an organic superconductor constitutes a significant step towards a better understanding of Organic Superconductivity. The most important points are the following : (i) The pseudo-gap in the single particle density of states which can be detected for temperatures up to about 10 times \( T_c \) confirms conclusively the 1-D nature of the superconducting instability in (TMTSF)_2PF_6. Moreover, it supports the interpretation of the low temperature conduction properties in terms of « the dominant role of superconducting fluctuations in (TMTSF)_2PF_6 up to about 40 K », (ii) the tendency towards the establishment of superconductivity is very strong for (TMTSF)_2PF_6 under 11 kbar, since 2 \( A(0) \approx 3.6 \text{ meV} \) (or 40 K) is larger than the value of the pairing energy encountered in any elementary superconducting metals. Consequently, this may explain the dominance of the superconducting divergence of (TMTSF)_2PF_6 with respect to its competition with other kinds of divergence, exemplified by the dielectric instability [22].

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