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C. More, G. Roger, J.P. Sorbier, Denis Jérome ...+2 more authors

Institutions: University of Provence, University of Paris-Sud

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One-dimensional organic superconductivity : an investigation through electron Schottky tunnelling in N/GaSb-$(TMTSF)_2PF_6$ junctions under pressure (*)

C. More, G. Roger, J. P. Sorbier

Département d'Electronique, E.R.A. 375, Université de Provence, 13397 Marseille Cedex 4, France

D. Jérome, M. Ribault

Laboratoire de Physique des Solides (**), Université Paris-Sud, 91405 Orsay, France

and K. Bechgaard

H. C. Oersted Institute, Universtitetsparken 5, DK 2100 Copenhagen, Denmark

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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 $(TMTSF)_2PF_6$ 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 $(TMTSF)_2X$.

Abstract. — Observation of a large pseudo-gap at the Fermi level by Schottky tunnelling of electrons from N doped-GaSb into the organic superconductor $(TMTSF)_2PF_6$ 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 $(TMTSF)_2X$.

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 $10^5\ (\Omega.\text{cm})^{-1}$ 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 $(TMTSF)_2PF_6$ and more recently seven other members of the $(TMTSF)_2X$ [5, 6] family.

However, above the superconducting transition temperature at about $T_c = 1$ K under 10 kbar for $(TMTSF)_2PF_6$, the conductivity shows many features

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(**) Laboratoire associé au C.N.R.S.

identical to those already encountered in TMTSF-DMTCNQ [1] namely : (i) a helium temperature conductivity exceeding 10^5 $(\Omega.\text{cm})^{-1}$ 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 $(TMTSF)_2PF_6$ at low temperatures are explained in terms of dimensionality enhanced incipient superconducting pairing arising at temperatures much larger than the 3-D ordering superconducting temperature [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 enhancement $(\xi_{\parallel}/d_{\perp})^2$ of the rms order parameter value in domains of volume $\xi_{\parallel}\, d_{\perp}^2$ at $T > T_c$ [7] where $\xi_{\parallel}$ and $d_{\perp}$ are respectively the longitudinal temperature dependent coherence length and the interchain distance. 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 $(TMTSF)_2PF_6$ 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 superconductivity [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 obeying 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

$$N_T(E) = N(0)\,[\,|\,E\,|/(E^2 - \Delta^2)^{1/2}]$$

in the BCS model of superconductivity sharp resistance 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 determined 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].

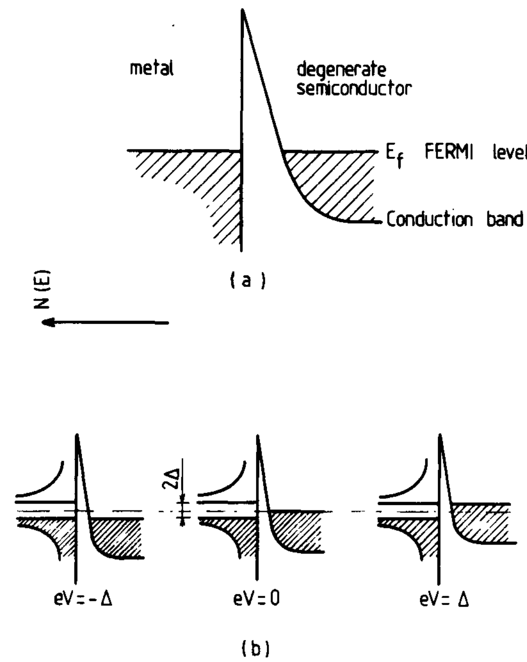

Fig. 1. — Band structure in the region of a contact between a metal and a N-type semiconductor. The bending of the bands in the semiconductor side results in the creation of a potential barrier (Schottky barrier). The upper diagram represents the situation of a normal metallic electrode and lower diagrams display schematically the energy density diagram of zero bias junction (middle) and $V = \pm\, e\Delta$ bias (left and right).

The junctions have been prepared by evaporating tellurium doped GaSb ($N_D > 3 \times 10^{18}\ \text{cm}^{-3}$) on a natural face of $(TMTSF)_2PF_6$ 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 contacts 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 ($\nu = 750$ Hz) and the corresponding AC voltage is measured with a phase sensitive detector. Modulation currents of

$$\Delta I = 10^{-7}\ \text{A} \quad \text{or} \quad 5 \times 10^{-9}\ \text{A}$$

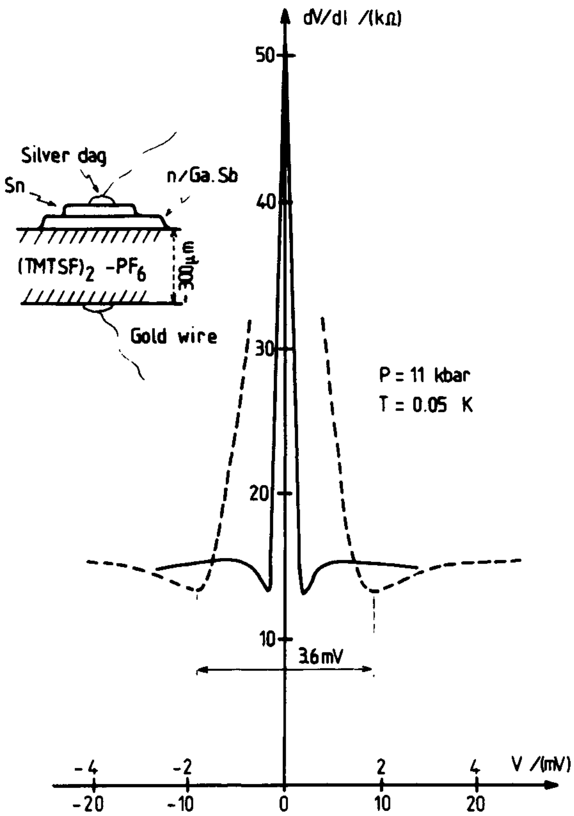

Fig. 2. — dV/dI *versus* bias voltage for a $(TMTSF)_2PF_6$-N/GaSb tunnel contact at $T = 0.05$ K and $P = 11$ kbar with a modulation current of 5×10^{-9} A. The dashed curve represents data obtained with a voltage axis sensitivity increased by a factor 5. The tunnel junction resistance is about 5 to 10 kΩ under ambient conditions. The insert sketches the junction geometry.

were used, depending on the temperature domain. The smallest modulation amplitude of 5×10^{-9} A used at $T = 50$ mK led to detected voltages of less than 100 µV, 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-$(TMTSF)_2PF_6$ 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 3*a* plotted as $(R_{max}/R_{min}) - 1$

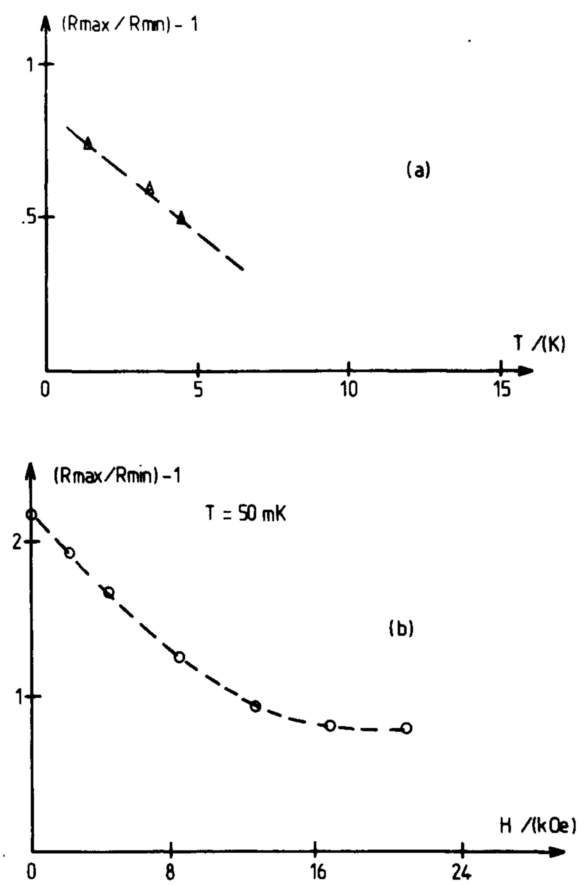

Fig. 3. — Temperature dependence of the zero bias tunnel resistance (*a*) with $\Delta I = 10^{-7}$ A and magnetic field dependence at $T = 0.05$ K, with $\Delta I = 5 \times 10^{-9}$ A (*b*).

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 2Δ 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 3*a* (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 3*b*. 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 kŒ 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 $T = 50$ mK, increases the value of the zero bias incremental resistance by a factor 2. Thus it is very likely that for $T \ll T_c$ the tunnelling characteristics appears 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. 3*b*) 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, 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 kŒ 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 $2\,\Delta(0) \approx 3.6$ 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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