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The three dimensional stabilization of superconductivity at 12 K in the one dimensional organic superconductor (TMTSF)₂PF₆ under 11 kbar (*)

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Résumé. — Une étude sous haute pression de la résistance de contact entre le supraconducteur organique (TMTSF)₂PF₆ et une couche de GaSb évaporée démontre qu'un état supraconducteur de résistance nulle peut être stabilisé dans certaines régions de l'échantillon (TMTSF)₂PF₆ jusqu'à la température de 12 K.

Cette température est du même ordre de grandeur que la température qui détermine l'établissement des fluctuations supraconductrices quasi unidimensionnelles, comme l'indiquent les expériences d'effet tunnel.

Ces résultats expérimentaux sont interprétés par une augmentation du couplage interchaîne due à la diffusion d'atomes d'antimoine au voisinage de la surface de contact. En outre, ces résultats indiquent quelques procédés généraux permettant d'augmenter la température de supraconduction des conducteurs organiques à propriétés de transport quasi unidimensionnelles.

Abstract. — A study of the contact between the organic superconductor (TMTSF)₂PF₆ and an evaporated GaSb layer has shown that the zero resistance superconducting state of (TMTSF)₂PF₆ under pressure can be stabilized in some regions of the sample up to 12 K. This temperature is about the temperature fixing the development of the one dimensional superconducting fluctuations, as derived from the intrachain pairing energy *via* electron tunnelling experiments.

The experimental data have been explained by an increased interchain coupling in the vicinity of the contact *via* antimony atoms diffusion. These results indicate possible means of extending superconductivity in the quasi one dimensional organic conductors towards higher temperatures.

The recent observation [1] of a very large pseudo-gap in the quasiparticle density of states of the organic superconductor (TMTSF)₂PF₆ by the Schottky electron-tunnelling technique has established on a direct and unambiguous experimental basis the one dimensional character of organic superconductivity. Moreover, this experiment has led to the measurement of the pairing energy $2\Delta = 3.6$ meV under $P = 11$ kbar.

As a result of the 1-D character, the pseudo-gap structure is observed up to temperatures as high as 15 K or so, much larger than the 3-D ordering temperature, $T_{c3} = 1$ K, below which both a zero resistance state [2] and diamagnetic shielding are observed [3, 4].

The 1-D superconductor can be considered as an array of loosely coupled stacks of organic molecules, whose average transverse dimensions amount to a few Angström [5]. Consequently, the interchain coupling can be described by a weak Josephson-like coupling [6]. It is this small coupling which is responsible for the low T_{c3} of 1 K even though fluctuations of the order parameter develop up to much higher temperatures [7]

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and according to tunnelling data correspond to a mean field critical temperature, $T_{c1} \approx 12$ K, using for example the weak coupling limit of the BCS theory [1]. In the temperature range extending between 1 K and ≈ 30 K, the electronic properties of $(\text{TMTSF})_2\text{PF}_6$ i.e. conductivity, thermal conductivity, thermopower etc... can be described by a model of nearly uncoupled 1-D superconducting chains [6].

In the vicinity of the 3-D ordering temperature [8, 9, 6] T_{c3} given approximately by $T_{c3} \sim (J_{\parallel} J_{\perp})^{1/2}$ where $J_{\parallel}$ and $J_{\perp}$ are respectively the longitudinal and transverse superconducting coupling strengths, the 1-D superconductor crosses over to a more conventional 3-D highly anisotropic superconducting state.

The transverse coupling may be very small, less than 1 K or so in the case of $(\text{TMTSF})_2\text{PF}_6$. Consequently, it is natural to imagine that the strength of $J_{\perp}$ can be drastically modified by the proximity of a metallic surface or the diffusion of foreign atoms in between the organic stacks. Both effects are likely to occur near the interface of a degenerate semiconductor — organic conductor junction. As $J_{\perp}$ becomes very large the superconductor no longer behaves like a 1-D superconductor and T_{c3} can become of the order of T_{c1} . Very crudely, in case of strong transverse coupling the critical width of the superconducting 3-D transition, ΔT , is given by the Ginzburg criterion [7] $\Delta T/T_{c1} = 6.5 (k_F^2 A \chi)^{-2/3}$ where k_F is the Fermi momentum, χ the Gorkov function ($\chi \lesssim 1$) and A the cross sectional area of the superconducting strips formed by the bundles of strongly coupled organic chains. For the case of isolated chains the Ginzburg criterion leads to $\Delta T \sim 1.6 T_{c1}$ [6] i.e. there is no transition at finite temperature. However, using a crude scaling argument, one can easily show that bundles of strongly coupled chains containing about 10 chains in diameter present a narrow critical region around T_{c1} of about $\Delta T/T_{c1} \sim 1.6(10^2)^{-2/3} \approx 0.077$ (taking $k_F^2 A \sim 1$ for the single chain case).

In this letter we present experimental results showing that a very large increase of T_{c3} up to 12 K has been achieved in tunnel junctions with $(\text{TMTSF})_2\text{PF}_6$.

We have studied various GaSb- $(\text{TMTSF})_2\text{PF}_6$ junctions under $P = 11$ kbar in the temperature range, 300 to 0.05 K using a technique similar to that already reported [1]. Due to the difficulty of preparing good quality Schottky barriers [10] we have obtained in several occasions junctions displaying strange but very interesting behaviours such as those shown on figures 1, 2. We have noticed similar characteristics for the junctions prepared on the same single crystal but different behaviours are usually observed for different crystals. In some junctions with low normal state resistance around 10Ω we have observed a zero-bias resistance decreasing at low temperature, figure 1. Between 30 and 15 K the resistance decreases in a manner similar to that of the bulk $(\text{TMTSF})_2\text{PF}_6$ resistance [6] whereas below 15 K the resistance drops abruptly and reaches a residual value of 0.2Ω at 12 K which corresponds approximately to that of the

Fig. 1. — Zero-bias differential resistance, dV/dI ($V = 0$) of a low resistance $(\text{TMTSF})_2\text{PF}_6$ -GaSb junction under 11 kbar. For this kind of junctions the Schottky barrier is by-passed by a direct contact between N doped GaSb and $(\text{TMTSF})_2\text{PF}_6$ (according to the situation 3 on figure 3). This contact becomes superconducting around 12 K and the residual resistance of 0.2Ω at lower temperatures corresponds to the series resistance of silver dag contacts and the remaining bulk $(\text{TMTSF})_2\text{PF}_6$ sample in a fluctuating superconducting state. Under 11 kbar, bulk $(\text{TMTSF})_2\text{PF}_6$ enters a zero resistance state only below 1 K.

Fig. 2. — The differential resistance dV/dI versus bias voltage of $(\text{TMTSF})_2\text{PF}_6$ -GaSb junctions in two different cases : State 1 corresponds to a conventional Normal conductor, Insulator, Superconductor (N-I-S) situation where the distance between the dV/dI minima corresponds approximately to 2Δ (the pseudo-gap of the 1-D fluctuating superconductor). State 2 which is obtained very often after an electric spike is applied to the junctions in state 1 shows two resistance extrema at $\pm\Delta$ and $\pm 2\Delta$. State 2 may correspond to a set of N-I-S and S-I-S junctions in parallel, as illustrated on figure 3. The N-I-S and S-I-S junctions give rise to resistance minima at $\pm\Delta$ and $\pm 2\Delta$ respectively, as shown in the insert (a) and (c). In addition (S-I-S) weak links give rise to resistance maxima at $\pm\Delta$ and $\pm 2\Delta$, situation (b) in the insert.

silver dag contacts since the measurements are performed with a 2-contact method. Thus, below 12 K the junction is in a zero resistance state, whereas at the same pressure superconductivity arises in the bulk sample below $T_{c3} \approx 1$ K only [2].

The observation of a superconductivity developing in the junction region at $T = 12$ K requires therefore

the stabilization of the 1-D fluctuations by some enhancement of the interchain coupling.

We may tentatively consider two possible ways which could lead to Josephson coupling reinforcement :

(i) Proximity effects between the organic chains at the junction interface and the metallic (doped semiconductor) layer [11]. This could be the situation if the insulating Schottky barrier is very thin. This possibility requires a stronger coupling between organic chains and individual Sb or Ga atoms than between two near neighbour organic chains. This is possible since Sb or Ga atoms are relatively small and can therefore come in close contact with the organic chains. Consequently, the first layer of organic chains in good contact with the metallic conductor is likely to show some enhanced interchain coupling. This increased coupling leads to the interesting possibility of forming a two dimensional superconductor similar to the one studied theoretically [12]. The zero resistance critical temperature can thus be increased with respect to $T_{c3} = 1$ K of organic chains in the bulk.

(ii) For type (a) junctions the Sb atoms in excess are likely to diffuse into the organic conductor within a finite (but still unknown) thickness of 10 to 500 Å. For that reason the 3-D coupling is enhanced in the layer and its critical temperature may reach the value derived from the pseudo-gap amplitude, namely $T_{c3} \approx T_{c1} = 2 \Delta / 3.5$.

As already noticed above the large decrease of the critical region width leads to a concomitant increase of T_{c3} . This is obtained even with relatively small bundles of about 30 Å in diameter. We may notice however that the T_{c3} of these bundles is probably a very sensitive function of the bundle size and foreign atoms concentration. We may also expect a rather heterogeneous structure for superconducting

domains in contact with the GaSb film leading therefore to strange properties due to Josephson coupling between different regions of the interface with different critical temperatures.

In fact, as shown in figure 2, with some junctions exhibiting somewhat higher resistance (≈ 1 k Ω) we have observed interesting behaviours. These junctions can be switched between two states according to external current spikes (provided by the switching on and off of a recorder or a liquid helium sensor). State 1 in figure 2 represents the typical characteristics of normal conductor to superconductor electron tunnelling with resistance minima at $V = \pm \Delta$. In state 2 however we observe two sets of resistance extrema at $V = \pm \Delta$ and $V = \pm 2 \Delta$ with Δ corresponding to the same voltage as for state 1. The occurrence of a resistance maximum at 2Δ can be explained by superconducting pair tunnelling between two superconducting regions with the same pseudo-gap through weak links [13].

Various possibilities are illustrated schematically in figure 3. Let us first remark that the initially good Schottky barrier (3.1) can be degraded in some places of the interface (in particular after large transients) by atomic diffusion as shown in 3.2 and 3.3. Consequently, local precipitation of Sb atoms leads to strongly conducting contacts between (TMTSF)₂PF₆ and metallic spots of Ga_{1-x}Sb_x ($x \approx 1\%$). The various « local » junctions at the interface present resistance extrema at $V = \pm \Delta$ and $V = \pm 2 \Delta$. N-I-S and S-I-S junctions display resistance minima at $V = \pm \Delta$ and $V = \pm 2 \Delta$ respectively, whereas weak superconducting links (see insert on figure 2) are likely to show resistance maxima. Therefore the overall characteristics of all these junctions in parallel is likely to show resistance extrema at $\pm \Delta$ and $\pm 2 \Delta$. In addition we have noticed through a microscopic examination of the sample surface the existence of

Fig. 3. — Schematic picture of the junction interface leading to the state 2 characteristics. Regular Schottky barrier 10-30 Å thick giving rise to a N-I-S contact (1) state 1, figure 2. The barrier is locally degraded by the diffusion or the precipitation of an excess of Sb atoms (2). In the shaded area individual TMTSF stacks become more strongly coupled via Sb atoms in between. For that reason the 1-D fluctuating superconductivity is three dimensionalized in the shaded area with a possible concomitant increase of T_{c3} up to T_{c1} . The 3-D stabilized superconducting spots induce small superconducting area (shaded) inside GaSb by proximity effects through the very thin insulating barrier. As a result junction 2 behaves like a Josephson (S-I-S) junction. In case (3) the Schottky barrier behaves like a weak link between two superconducting spots with resistance maxima at $\pm \Delta$ and $\pm 2 \Delta$. Strands sticking out of the sample surface (4) leading to S-I-S junctions or weak links with near neighbour superconducting spots.

small strands sticking out of the surface with an angle around 30 or 60 degrees, as shown in figure 3.4. It is likely that the Schottky barrier vanishes near the end of such strands since Sb atoms for instance can easily diffuse between the organic chains.

All the preceding remarks, illustrated by figure 3, show that the obtention of a well characterized uniform surface state is probably very difficult to achieve with $(\text{TMTSF})_2\text{PF}_6$ and related compounds. The actual junction behaves like a mosaic of individual junctions in parallel (N-I-S, S-I-S and weak links) giving rise to the characteristics displayed on figure 2.

Under ambient pressure conducting $(\text{TMTSF})_2\text{PF}_6$ undergoes at $T_{\text{MI}} = 11.5$ K a transition towards a semiconducting state [5] which has been shown to exhibit magnetism [14] and antiferromagnetic ordering [15]. At $T < T_{\text{MI}}$ the tunnel junctions with $(\text{TMTSF})_2\text{PF}_6$ exhibit a very pronounced peak of width ≈ 6 mV between inflexion points [16]. However at $T > T_{\text{MI}}$ namely between 11.5 K and 50 K, several features of the conductivity (strong temperature and magnetic field dependences and value approaching $10^5(\Omega\text{cm})^{-1}$ at 11.5 K are reminiscent of the behaviour under a pressure of 11 kbar [6]. Therefore, it is reasonable to assume that 1-D superconducting fluctuations exist also under ambient pressure in $(\text{TMTSF})_2\text{PF}_6$ and give rise to a drastic conductivity enhancement above 11.5 K [17]. It is thus conceivable to stabilize superconductivity in $(\text{TMTSF})_2\text{PF}_6$ in some regions of the sample *via* a local increase of the interchain coupling. In fact, as shown in figure 4, we have observed for some $(\text{TMTSF})_2\text{PF}_6$ junctions beside a large bump of resistance related to the development of the bulk semiconducting gap of width ≈ 6 mV, sharp resistance peaks similar to those observed under 11 kbar, figure 2, and separated by $4\Delta = 14$ mV. Such a value of the pseudo-gap, namely $2\Delta = 7$ mV under ambient pressure, leads to $T_{\text{c}} = 23$ K (according to the BCS relation). The asymmetry of the tunnelling characteristics together with some hysteresis effects (*versus* applied bias) are likely related to hysteresis of the bulk antiferromagnet [18].

Although the critical temperature of these superconducting spots was about $T_{\text{c}} = 3$ K, the data under ambient pressure show that the local stabilization of superconductivity is possible despite the existence of a bulk insulating antiferromagnetic state. Moreover, the pressure dependence of the pseudo-gap varying between $2\Delta = 7$ mV and $2\Delta = 3.6$ mV from ambient to 11 kbar pressure indicates that the negative pressure coefficient of T_{c} observed between 11 and 24 kbar [19] is indeed a result of an intrinsic property of the individual organic stacks.

In conclusion a spectacular enhancement of the

Fig. 4. — Differential resistance of a $(\text{TMTSF})_2\text{PF}_6$ -GaSb junction at ambient pressure. Usually a bump of width ≈ 6 mV (between inflexion points) is observed at low temperature, corresponding to the establishment of the insulating spin density wave state below 11.5 K. However in several occasions two sharp peaks separated by ≈ 14 mV are observed superimposed to the SDW bump. They could be related to the existence of superconducting spots near the junction interface provided high temperature 1-D superconducting fluctuations are stabilized by increased interchain coupling.

critical temperature for superconductivity up to $T_{\text{c}} = 12$ K has been achieved in $(\text{TMTSF})_2\text{PF}_6$ under a pressure of 11 kbar. The value of the enhanced critical temperature is in good agreement with the independent measurement of a 3.6 mV one dimensional pseudo-gap. We have suggested that the observed T_{c} increase related to the $t_{\perp}$ [20] enhancement could be explained by the diffusion of antimony atoms between organic stacks and proximity effects at the interface between the $(\text{TMTSF})_2\text{PF}_6$ crystals and an evaporated Ga-Sb layer. Finally, we believe that the model for superconductivity in quasi one dimensional conductors based on the existence of bare repulsive electron-electron [21] interactions ($g_1 > 0$) together with a finite $t_{\perp}$ [22] constitutes a good starting point for the interpretation.

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- [10] GaSb is evaporated on to the (TMTSF)₂PF₆ crystals following two methods : (a) A 15 s evaporation of a 5 000 Å thick GaSb layer. Due to the larger vapour pressure of Sb relative to Ga it seems very likely that the proximity of the (TMTSF)₂PF₆ surface is richer in Sb atoms than Ga atoms i.e. the evaporated GaSb is non stoichiometric at the interface. (b) Better stoichiometry is used with successive flash evaporations. Very often junction failure occurs under high pressure through the separation of the GaSb film from the (TMTSF)₂PF₆ surface. However, as far as the resistance to thermal and pressure effects is concerned type (a) junctions have led to more satisfying results. The junction resistance at $P = 1$ atm., $T = 300$ K amounts to 10-500 Ω and 10-50 kΩ for type (a) and (b) respectively. For type (a) junctions the excess Sb at the interface can favour a diffusion of Sb inside the organic conductor and lead to a better adhesion of the semi-conducting film. Since the Sb excess is equivalent to an increased donor concentration the Schottky barrier can be significantly reduced and even suppressed. It is the situation which is encountered for the low resistance, type (a) junctions.
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