Superconductivity in a synthetic organic conductor (TMTSF)2PF 6

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Classification
Physics Abstracts
74.10 — 74.40 — 72.15N

Superconductivity in a synthetic organic conductor $(TMTSF)_2PF_6$ (†)

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(*Reçu le 19 décembre 1979, accepté le 3 janvier 1980*)

Résumé. — Nous avons observé le phénomène de supraconductibilité dans le conducteur organique quasi-unidimensionnel di-(tétraméthyltétraselénofulvalène)-hexafluorophosphate, $(TMTSF)_2PF_6$, par mesures résistives sous pression hydrostatique de 12 kbar à une température de 0,9 K. Nous présentons aussi l'effet de champs magnétiques perpendiculaires à l'axe des chaînes.

Abstract. — Superconductivity has been observed by resistive measurements in the quasi-one dimensional organic conductor di-(tetramethyltetraselenafulvalene)-hexafluorophosphate, $(TMTSF)_2PF_6$ under a hydrostatic pressure of 12 kbar with a transition temperature of 0.9 K. The effect of magnetic fields perpendicular to the chain axis is also reported.

We have discovered the existence of superconductivity in the organic conductor $(TMTSF)_2PF_6$, (di-($\Delta^{2,2'}$-bi-4,5-dimethyl-1,3-diselenole)-hexafluorophosphate), with a transition temperature of 0.9 K at a pressure of 12 kbar.

Previous investigations [1] have shown that $(TMTSF)_2PF_6$ (and related salts) exhibits low temperature conductivities in excess of 10^5 $(\Omega.cm)^{-1}$, which were the highest reported so far in organic solids at ambient pressure. In $(TMTSF)_2PF_6$ a sharp metal to insulator transition occurs at 15 K (T_P). The structure of $(TMTSF)_2PF_6$ consists of nearly uniform stacks of TMTSF molecules ordered in sheets separated by anion sheets (Fig. 1). A very slight dimerization of the TMTSF molecules is observed at room temperature, but contrary to the isomorphous sulfur analogues $(TMTTF)_2X$ [2] this does not seem to influence the electronic properties, as judged from the very high conductivity observed at low temperature.

The one dimensional nature of the solid inferred from the structure was confirmed by the anisotropy of both DC and microwave conductivity (anisotropies are > 300 and 10^4 respectively at room temperature) and by the existence of a plasma edge at

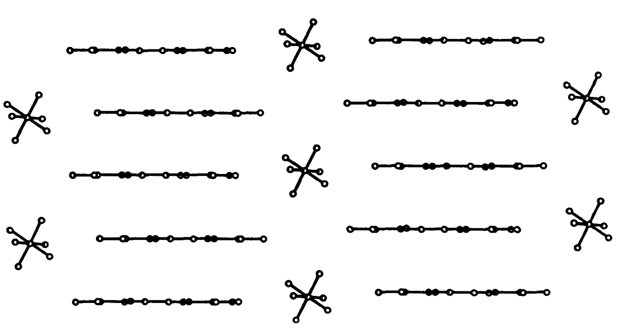

Fig. 1. — Side view of the TMTSF stacks.

10 050 cm^{-1} for light polarized along the conducting axis. For a perpendicular polarization the reflectance remains small and constant throughout the region measured (5 000-16 000 cm^{-1}). We wish to point out that the charge transfer in the one chain system $(TMTSF)_2PF_6$ is fixed by stoichiometry = 1/2, considering the enormous electron affinity of the PF_6-radical, in contrast to the related two chain materials f.ex.TTF-TCNQ where it may change on substitutions of the molecules or by pressure.

The single crystals used in the present study have been obtained from ultrapure constituents by an electrochemical technique [3]. Typical sizes were $4 \times 0.2 \times 0.1$ mm^3. Good electrical contacts have been obtained with gold paste contacts. The AC current ($\nu \approx 79$ or 88 Hz) is usually kept low ($I \lesssim 100$ µA) in this $\rho(T, P)$ investigation. Conven-

(†) La version française de cet article a été acceptée aux Comptes Rendus de l'Académie des Sciences et est insérée dans le n° du 14 janvier 1980.

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tional four contacts and lock-in techniques have been used, with unnested voltages always lower than 10 %.

The salient effect of high pressure, as displayed on figure 2, is to shift smoothly the metal to insulator transition down in temperature. Above 10 kbar a high conductivity state is stabilized down to 1.2 K (at least). The conductivity of the pressure stabilized conducting state exceeds 10^5 $(\Omega.\text{cm})^{-1}$ at helium temperature.

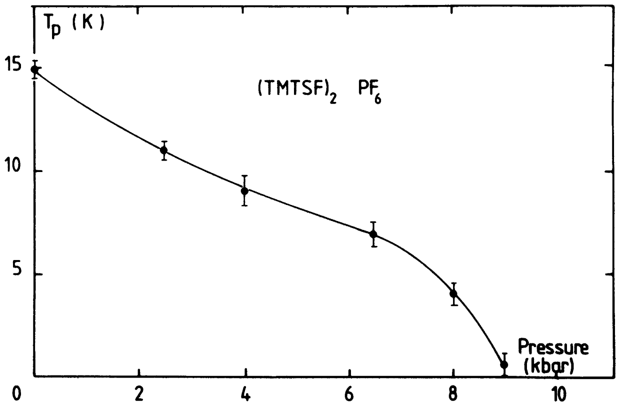

Fig. 2. — Phase diagram T_P *vs.* P showing the suppression of the semiconducting state at high pressure.

A similar behaviour has recently been reported in the related two-chain conductor TMTSF-DMTCNQ [4] where a 10 kbar pressure removes *suddenly* the low temperature dielectric Peierls state. However, the unusual behaviour of the resistivity of the metallic state in $(\text{TMTSF})_2\text{PF}_6$ is the quasi-linear temperature dependence noticed in the temperature domain 4.2-1.2 K. In TMTSF-DMTCNQ the resistivity has been found to saturate below 5 K.

High pressure investigations have been performed at lower temperature with a beryllium-copper pressure vessel holding two samples and cooled by a ^3He-^4He dilution refrigerator. The temperature is measured by means of platinum thermometers and carbon or germanium [5] thermometers below 10 K. The pressure vessel is in tight thermal contact with the mixing chamber and the thermometers are mounted on the outside wall of the vessel. The resistance of two samples has been measured with two independent electric circuits.

The resistance between the voltage contacts amounts to 4 mΩ and 55 mΩ at 1.2 K for samples I and II respectively under 12 kbar. In spite of the difference of resistance between both samples, their temperature dependence is fairly similar between 4.2 K and 200 K with a ratio $\rho(200\text{ K})/\rho(4.2\text{ K}) \approx 100$. The temperature dependence of the resistance normalized to the 4.6 K value shows a sharp transition towards a superconducting state at 0.9 K in both samples, figure 3. Although the resistance at 1.2 K and the temperature dependence between 4.2 and 1.2 K are

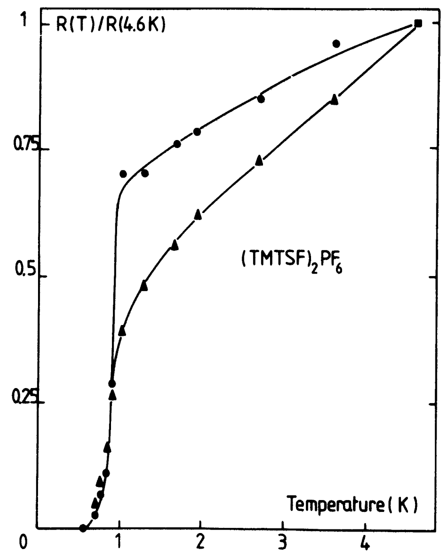

Fig. 3. — Temperature dependence of the resistance normalized to the 4.6 K-value for 2 samples at 12 kbar. (Sample I : ▲, Sample II : ●.)

significantly different in the two samples, the same critical temperature is observed using the criterion $R(T_c) = R(1.2\text{ K})/2$ for the two samples.

This observation supports the fact that a current of 100 μA is lower than the critical current in both samples despite their large differences in cross sections. Moreover, this has been checked using 10 μA currents. Below 0.6 K no signal can be detected for both samples, which means that the resistances are less than 10^{-7} Ω for both samples, taking into account the instrumental limit. The application of a magnetic field perpendicular to the chain direction brings the most conclusive evidence for the superconducting nature of the 0.9 K transition, figure 4. The effect of the magnetic field is to shift the R *versus* T curves

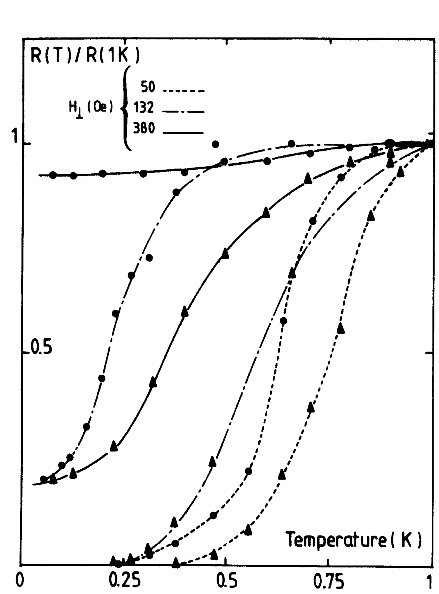

Fig. 4. — Temperature of the resistance in perpendicular magnetic fields for sample I (▲) and II (●).

down in temperature the response being somewhat different for the two samples.

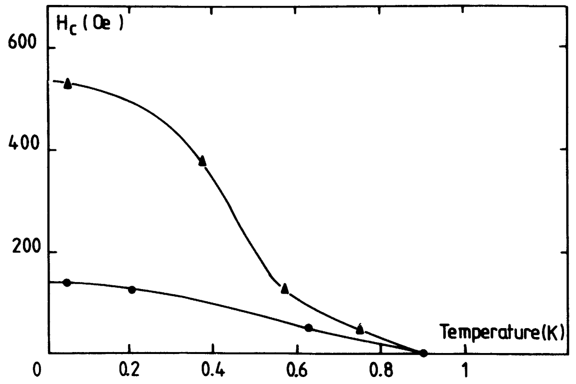

Fig. 5. — Temperature dependence of $H_{c_2}^{\perp}$ for sample I (▲) and II (●).

Figure 5 displays the temperature dependence of the critical field derived from the inflection point in $R(T)$ of figure 4. According to the data of figure 5 the behaviour of the critical field *versus* temperature appears fairly normal for a type II superconductor [6] as far as sample II is concerned. The low temperature value of the critical field of sample II is $H_{c_2}^{\perp} = 140$ Oe, for a current of 100 μA (as displayed on figure 5). However at lower currents a slight increase of the low temperature $H_{c_2}^{\perp}$ has been detected, 200 Oe at 10 μA and 223 Oe at 1 μA. All these $H_{c_2}^{\perp}$ values are larger than thermodynamic critical fields, H_c, of type I superconductors. In zinc, for instance, $T_c = 0.88$ K [6] and H_c equals 53 Oe. The result of $H_{c_2}^{\perp}$ in $(TMTSF)_2PF_6$ (at 1 μA) leads to a

$$\kappa_{\perp} = H_{c_2}/\sqrt{2}\,H_c$$

of 3, using the same thermodynamic critical field as Zn. Moreover, we should notice that the $H_{c_2}^{\perp}$ may also be related to the possible fibrous nature of the crystal.

The situation is somewhat different for the sample I in which an upward curvature of the $H_{c_2}^{\perp}$ *versus* temperature curve is clearly observed below ≈ 0.6 K [7]. It may be possible to relate this phenomenon with the decrease of the transverse coherence length, $\xi_{\perp}$, at low temperature. A Ginzburg-Landau theory [8] of coupled superconducting filaments has been worked out recently. The upward curvature occurs at low temperature ($T < T_c$) when $\xi_{\perp} \approx$ the interchain distance. The possibility of upward curvature of $H_{c_2}^{\perp}$ and consequently of large $H_{c_2}^{\perp}$ could arise from lattice defects of impurities. Therefore, it is likely that sample II is the cleanest of the two samples available, despite its large 4.2 K resistance which is probably due to a small effective cross section. In sample II, $\xi_{\perp}$ probably remains larger than the interchain distance at $T < T_c$ preventing the observation of large upward curvature. Admittedly the critical fields and Landau-Ginzburg parameters are likely to show very large anisotropy. A study of this effect is in progress and will be reported in the near future. For both samples near T_c,

$$\mathrm{d}H_{c_2}^{\perp}/\mathrm{d}T \approx 222\ \mathrm{Oe.K^{-1}}$$

and therefore $(\xi_{\parallel}(0)\ \xi_{\perp}(0))^{1/2}$ derived from the experiment through the Ginzburg-Landau relation [9]

$$\mathrm{d}H_{c_2}^{\perp}/\mathrm{d}T = \varphi_0/2\pi\ \xi_{\parallel}(0)\ \xi_{\perp}(0)\ T_c\,;$$

($\varphi_0 = 2 \times 10^{-7}$ Oe.cm^2) becomes 2 240 Å. The above determination of $(\xi_{\parallel}\ \xi_{\perp})^{1/2}$ is much larger than a reasonable estimate of the electron mean free path at low temperature [10], $l \approx 80$ Å, and confirms the influence of impurities or lattice imperfections on the superconductivity properties [6].

We have checked that the critical currents for both samples are larger than 1 mA, corresponding to critical current densities in excess of ≈ 0.2 A/mm^2. However, careful measurements of the high current characteristics require a better control of possible heating effects occurring in the gold paste contacts. They will be reported in forthcoming articles.

Besides the existence of 3-D superconducting ordering at 0.9 K in $(TMTSF)_2PF_6$ the most interesting feature displayed on figure 2 is the behaviour of the resistivity between 4.2 K and T_c, contrasting significantly with the residual resistivity behaviour observed in the vast majority of metals in the same temperature domain. We believe that this is the sign of significant superconducting fluctuations above T_c, giving rise to paraconductivity and extending up to fairly high temperatures. This is corroborated by the effect of a transverse magnetic field of amplitude much larger than $H_{c_2}^{\perp}$. A field of 60 kOe at 40 mK produces a magnetoresistance $\Delta\rho/\rho(400\ \mathrm{Oe}) \approx 8$. Following the theory of superconducting paraconductivity it seems reasonable to expect the more impure sample (I) to show the stronger fluctuations, since the paraconductivity is related to the electron mean free path by the relation $\sigma \sim 1/\sqrt{l}$ (in 3-D superconductors). Moreover, large magnetoresistance effects have been observed at 12 kbar up to about 20 K in a field of 60 kOe. A similar enhancement of the resistance at 20 K have been reported at atmospheric pressure [11]. Therefore, we suggest that already at 1 bar, the conductivity of $(TMTSF)_2PF_6$ is influenced by paraconductive superconducting fluctuations at low temperature.

Some estimate of the 3-D ordering temperature can be derived from the quantity $t_{\perp}^2/t_{\parallel}$, which is the interchain Josephson coupling [12], where $t_{\perp}$ and $t_{\parallel}$ are respectively the interchain and intrachain overlap integrals. Thermal fluctuations destroy the 3-D interchain coherence whenever $kT > t_{\perp}^2/t_{\parallel}$. Therefore, the Josephson coupling gives an order of magnitude upper limit of T_c. In the present situation $t_{\parallel} \approx 2\,000$ K can be derived from optical reflectance studies. Consequently, $t_{\perp}^2/t_{\parallel} = 0.9$ K leads to $t_{\perp} = 40$ K a value which is in good agreement with the previous NMR determination [13] of the tunnelling coupling in TTF-TCNQ.

In summary, we have established conclusively that superconductivity exists in the organic solid state. From now on, it seems clear that the two competing channels leading to low temperature instabilities in 1-D conductors, namely insulating and superconducting channels, must be taken into account in theoretical developments [14]. So far, it is not clear why the superconducting channel has *won* in $(TMTSF)_2PF_6$. Besides $(TMTSF)_2PF_6$, high pressure has allowed the stabilization of the metallic state at low temperature in already a fair number of 1/4 filled band selenium charge transfer salts : TMTSF-DMTCNQ [4], $(TSeT)_2I$ [15], $(TSeT)_2Cl$ [16] and $(TMTSF)_2NO_3$ [17]. Since the present discovery strongly suggests that the large conductivity observed at low temperature under pressure in TMTSF-DMTCNQ is also the result of large superconducting fluctuations up to ≈ 30 K, we believe that chemical engineering can lead to molecular conductors showing higher values of T_c.

Acknowledgments. — We wish to acknowledge the very skilful help of G. Benedek and A. Andrieux during this work. We have had numerous discussions related to the theoretical implications of this work with H. J. Schulz. We wish to thank J. P. Pouget for a discussion of his preliminary diffuse X-ray, N. Thorup, C. S. Jacobsen, K. Mortensen and H. Pedersen for the collaboration on the ambient pressure state of this new material. We acknowledge P. G. de Gennes for a fruitful discussion and J. Friedel for his constant encouragements during the development of this work.

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