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D. Jaccard, H. Wilhelm, Denis Jerome, J. Moser, C. Carcel, et al.. From spin-Peierls to superconductivity: (TMTTF) 2 PF 6 under high pressure. *Journal of Physics: Condensed Matter*, 2001, <10.1088/0953-8984/13/4/104>. <hal-04989020>

**HAL Id: hal-04989020**

**<https://hal.science/hal-04989020v1>**

Submitted on 17 Mar 2025

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## LETTER TO THE EDITOR

## From spin-Peierls to superconductivity: (TMTTF)<sub>2</sub>PF<sub>6</sub> under high pressure

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Received 14 December 2000

### Abstract

The nature of the attractive electron–electron interaction, leading to the formation of Cooper pairs in unconventional superconductors, has still to be fully understood and is subject to intensive research. Here we show that the sequence spin-Peierls, antiferromagnetism, superconductivity observed in (TMTTF)<sub>2</sub>PF<sub>6</sub> under pressure makes the (TM)<sub>2</sub>X phase diagram universal. We argue that the suppression of the spin-Peierls transition under pressure, the close vicinity of antiferromagnetic and superconducting phases at high pressure, as well as the existence of critical antiferromagnetic fluctuations above  $T_c$  strongly support the intriguing possibility that the interchain exchange of antiferromagnetic fluctuations provides the pairing mechanism required for bound charge carriers.

The existence of a common border between the superconducting (SC) ground state and the insulating phase of spin density wave (SDW) nature [1], was recognized as a remarkable property of the phase diagram of the Bechgaard salt (TMTSF)<sub>2</sub>PF<sub>6</sub>. It belongs to a broad family of isostructural compounds (TM)<sub>2</sub>X, where the flat organic molecule TM is either tetramethyltetraselenafulvalene (TMTSF) or tetramethyltetrathiafulvalene (TMTTF). Here X denotes a monovalent anion such as PF<sub>6</sub>, AsF<sub>6</sub>, ClO<sub>4</sub> or Br [2]. In the crystal, these molecules form stacks separated by chains of anions X. The overlap between the electron clouds of neighbouring TM molecules along the stacking direction (parallel to the *a* axis) is about 10 (500) times larger than that between the stacks in the transverse *b* (*c*) direction. Provided that the longitudinal overlap is large compared with the on-site Coulomb repulsion, these organic materials become conducting with a pronounced one-dimensional (1D) character.

The 1D character of the Fermi surface of (TM)<sub>2</sub>X, the presence of a spin-Peierls (SP) transition instead of the usual Peierls instability [3, 4] as well as the existence of enhanced antiferromagnetic (AF) fluctuations at low temperature, evidenced by NMR relaxation experiments, raised several questions about the mechanism responsible for superconductivity in organic conductors [5]. Since 1D physics is a relevant concept in these low-dimensional

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systems, SDW and electron–electron pairing can develop simultaneously at low temperature in the interacting electron gas [1]. A cross-over from SDW to SC correlations could possibly be achieved through a small variation of the coupling constants either by applying pressure or changing  $X$  [6]. Furthermore, the nuclear spin-lattice relaxation rate data of  $(\text{TMTSF})_2\text{PF}_6$  suggest that SDW correlations prevail at low temperature even under pressure when superconductivity is stabilized [5]. Therefore, the mere existence of a SC instability in the quasi-1D  $(\text{TM})_2X$  series is a non-trivial phenomenon on account of the repulsive character of the electron–electron interaction [1].

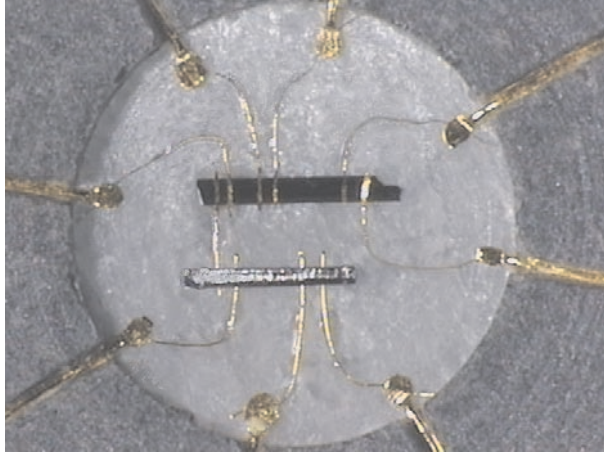
In the generic phase diagram proposed for the  $(\text{TM})_2X$  family [7] the sequence of ground states (SP, AF/SDW and SC) can be observed for different members of the series if they are placed according to their ambient pressure properties. However, only parts of the sequence can be found for a given member of the series if pressure is applied. For instance, the SDW ground state of  $(\text{TMTTF})_2\text{Br}$  can be suppressed and at a pressure  $p = 2.6$  GPa a SC phase appears [8]. However, starting from a SP ground state, which is observed only for  $(\text{TMTTF})_2X$  with  $X=\text{PF}_6$  or  $\text{AsF}_6$  [3, 9, 10], no superconductivity had been observed.

In this context  $(\text{TMTTF})_2\text{PF}_6$  is of particular interest because the existence of the pressure-dependent SP ordering can be used for a quantitative estimate of the pressure dependence of the pairing force, mediated by acoustic phonons [11]. The coupling between electrons and the lattice manifests itself by a divergence of the  $2k_F$  lattice susceptibility below 100 K [3] and by opening a pseudo-gap in the uniform spin susceptibility ( $\chi(q = 0)$ ) at  $T_{\text{SP}}^0 \approx 40$  K [12]. The latter evolves towards a true SP gap at  $T_{\text{SP}} = 19$  K [3]. When 1D  $2k_F$  phonon softening occurs in the presence of fully developed 1D AF correlations in the Mott localized phase at  $T < T_\rho$  (where  $T_\rho$  represents the temperature below which the 1D Mott localization produces an insulating behaviour of the electrical resistivity) bond charge correlations couple to  $2k_F$  acoustic phonons and a SP instability sets in at low temperature [11]. The knowledge of the parameters related to the SP instability (occurrence of the pseudo-gap at  $T_{\text{SP}}^0$  and of a true SP gap at  $T_{\text{SP}}$ ) makes it possible to determine the bare electron–electron attraction produced by the exchange of phonons at the wavevector  $2k_F$  [11]. These are the same scattering processes which are known to contribute predominantly to the attraction between electrons in a 1D BCS scheme [13]. From the pressure dependence of the SP ordering known experimentally up to 0.9 GPa, it can be inferred that the bare electron–electron attraction mediated by phonons should be severely depressed at elevated pressure; a reduction by a factor three is anticipated at 4.5 GPa in  $(\text{TMTTF})_2\text{PF}_6$  [11]. In addition, x-ray scattering experiments performed on different compounds of the  $(\text{TM})_2X$  series at ambient pressure reveal a strong enhancement of the electron–phonon-vertex part in  $(\text{TMTTF})_2\text{PF}_6$  when the SP ground state is stable but no particular enhancement whenever either a SDW or a SC ground state become stable in the selenide compounds [14]. Consequently, a relevant question to be raised is whether a traditional phonon-driven BCS mechanism can still remain strong enough to stabilize superconductivity in  $(\text{TMTTF})_2\text{PF}_6$  at very high pressure. This has been a great stimulus for the search and subsequent discovery of superconductivity in  $(\text{TMTTF})_2\text{PF}_6$  at pressures beyond 4 GPa.

The influence of pressure on the longitudinal electrical resistivity  $\rho_a$  of  $(\text{TMTTF})_2\text{PF}_6$  single crystals grown by electrocrystallization [15] was studied with a piston-cylinder clamped cell capable of reaching pressures of  $p_{\text{max}} \approx 4$  GPa and a Bridgman anvil cell for higher pressures ( $p_{\text{max}} \approx 10$  GPa) designed for temperatures as low as  $T = 25$  mK [16]. The sample chamber of the latter apparatus is shown in figure 1<sup>5</sup>.

The pressure effect on  $\rho_a$  at room temperature is quite strong:  $\rho_a$  decreases from

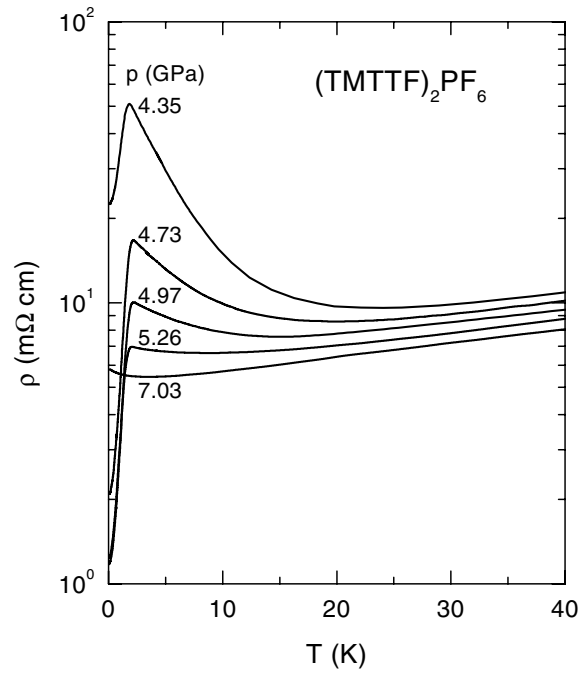
<sup>5</sup> The pressure dependent SC transition temperature of Pb yields the pressure. The upper limit for the inevitable, but small pressure gradient is estimated from the width of the Pb transition to be about 0.1 GPa.



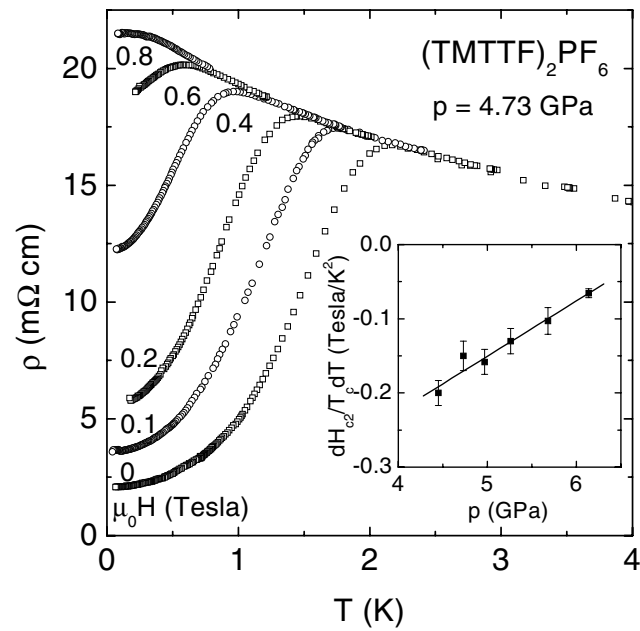
**Figure 1.** The sample chamber of the high-pressure device before pressurization. In the cylindrical gasket (pyrophyllite) the  $(\text{TMTTF})_2\text{PF}_6$  single crystal (black bar) is placed on a disc of a soft pressure medium (steatite,  $\varnothing = 2$  mm). Thin Au wires ( $\varnothing = 5$   $\mu\text{m}$ ) on the sample and the pressure gauge (Pb foil) are attached to thicker Au wires ( $\varnothing = 50$   $\mu\text{m}$ ) which establish the electrical contact across the gasket. The cell is closed with a second disc of steatite on top of this arrangement and then pressurized between the two Bridgman anvils.

400 m $\Omega$  cm at ambient pressure to  $\rho_a = 11$  m $\Omega$  cm for  $p = 4.05$  GPa. At this pressure, temperature has a similar strong influence on  $\rho_a(T)$ : it decreases by a factor of 40 upon cooling to temperatures of the order of 10 K. Here,  $\rho_a(T)$  passes through a minimum at  $T_{\min}$  and the upturn in  $\rho_a(T)$  is related to a transition into an insulating state, attributed to the onset of itinerant antiferromagnetism (SDW) [17]. In this temperature region the AF fluctuations, related to the insulating state, start to develop. The phase transition temperature  $T_{\text{SDW}}$  is deduced from the  $\rho_a(T)$  curves using either the maximum of  $\partial \ln \rho(T)/\partial T$  (for the low-pressure curves) or the criterion  $\rho_a(T) = 2 \times \rho_a(T_{\min})$ . Both criteria have been found to be equivalent for the large transitions into the SDW phase [1]. Beyond  $p = 4$  GPa the strong increase of  $\rho(T)$  at low temperature is disrupted by the onset of a sharp drop in  $\rho(T)$  at  $T_c = 1.8$  K (see curve at  $p = 4.35$  GPa in figure 2). At  $p = 4.73$  GPa  $\rho(T)$  already starts to decline at  $T_c = 2.2$  K and has decreased by one order of magnitude at 1 K. The temperature  $T_c$  as well as the magnitude of the drop in  $\rho(T)$  decrease as pressure increases further. The residual resistivity  $\rho_0$ , measured at the lowest temperature reached in each run, amounts to 1–2 m $\Omega$  cm. Beyond 7 GPa no evidence of a drop in resistivity is found above 50 mK.

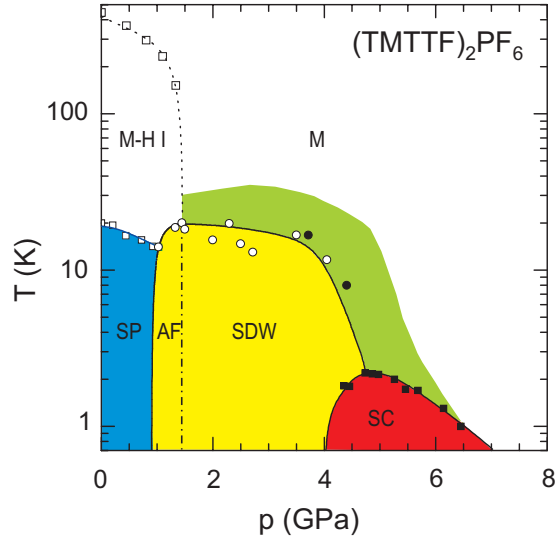
The influence of an external magnetic field along the  $c$  axis is shown in figure 3. The drop in  $\rho(T)$  is completely suppressed in a field of  $\mu_0 H = 0.8$  T. This is taken as a strong argument to identify  $T_c$  as a SC transition temperature despite the finite value of  $\rho_0$  which can be attributed (above 4.7 GPa) to microcracks related to the extreme sample brittleness and possible non-hydrostatic components in the Bridgman anvil cell. The value of the critical field  $H_{c2}^c$ , determined by the recovery of the normal state resistivity, increases together with  $T_c$  as pressure decreases. Within the framework of clean type-II superconductors, which is justified in most  $(\text{TMTSF})_2X$  salts since the electron mean free path is of the order of  $10^4 \times a$ , with  $a$  the lattice parameter,  $dH_{c2}^c/dT = -\frac{A}{t_a t_b} T_c$  for  $T \rightarrow T_c$ , where  $A$  is a constant independent of the field orientation and pressure [18]. The variation of  $dH_{c2}^c/T_c dT$  between 4.45 and 6.14 GPa leads to a pressure dependence of 2.0% kbar $^{-1}$  for  $(t_a t_b)^{1/2}$  which is in fair agreement with the optical measurements of the bare band parameters of organic conductors under pressure [1].



**Figure 2.** Electrical resistivity  $\rho(T)$  of  $(\text{TMTTF})_2\text{PF}_6$  at various pressures and low temperature.



**Figure 3.** Magnetic field dependence of  $\rho(T)$  at  $p = 4.73$  GPa for a field direction along the crystallographic  $c$  axis. In zero field the critical temperature is as high as  $T_c = 2.2$  K. The inset shows  $\partial H_{c2}/T_c \partial T_c$  versus pressure.



**Figure 4.**  $(T, P)$  phase diagram of  $(\text{TMTTF})_2\text{PF}_6$ . The spin-Peierls (SP) [17], an antiferromagnetic (AF), and the spin density wave state (SDW) are suppressed by pressure and a superconducting (SC) phase emerges above 4 GPa. Over a wide pressure range AF spin fluctuations (green region) are present. At high temperature a Mott–Hubbard insulating (M–H I) and a metallic (M) state are observed. Open symbols represent data taken from [17].

Our data provide the missing information enabling the  $(T, P)$  phase diagram of  $(\text{TMTTF})_2\text{PF}_6$  shown in figure 4 to be constructed and establish its truly universal character. After the suppression of the SP phase [5, 19] the AF (Néel and SDW) ground states are stable up to about 4 GPa [17]. The SC region extends from slightly above 4 GPa to almost 7 GPa with a SC transition temperature as high as  $T_c = 2.2$  K at  $p = 4.73$  GPa. It is worth noting that close to this pressure three phase lines meet. The green region in figure 4 indicates the presence of AF spin fluctuations. This region has an upper bound in temperature defined by  $T_{\min}$  and a lower limit given by either  $T_{\text{SDW}}$  or  $T_c$ . In this temperature interval  $\rho(T)$  shows an upturn. The width in temperature of this interval increases with decreasing pressure and is largest where  $T_c(P)$  reaches its optimum value. Thus,  $T_{\min}$  appears to be closely linked to the critical temperature  $T_c$ . Critical AF fluctuations seem to be enhanced when the SDW ground state is approached from high pressure, i. e. where the system is close to the border between the SDW and SC phases. At slightly lower pressure the decrease of  $T_c$  is clearly related to the occurrence of the SDW phase at a higher temperature. Similar behaviour is encountered in the competition between charge density wave and SC instabilities in layered conductors [20]. The correlation between the fall of  $T_{\text{SDW}}$  and the rise in  $T_c$  reflects the suppression of the SDW gap with pressure. This restores areas of the Fermi surface lost by the creation of magnetic gaps, thereby increasing the density of states at the Fermi level and hence  $T_c$ .

The re-entrance of superconductivity below the SDW ordering appears to be a general behaviour among  $(\text{TM})_2X$  superconductors. It has also been identified with a finite value of  $\rho(T)$  in the ‘superconducting’ state in  $(\text{TMTSF})_2\text{AsF}_6$  [1, 21] although less clear due to a larger compressibility. The enhanced  $\rho_0$  values reported here cannot be attributed to pressure inhomogeneity. They support furthermore the picture of an inhomogeneous SC ground state between 4.2 and 4.5 GPa where SC islands are dispersed in a SDW insulating background. In such a scenario the non-percolating SC domains could contribute to a finite resistivity below  $T_c$ .

Given the inability for the traditional electron–phonon mechanism to promote SC in  $(\text{TMTTF})_2\text{PF}_6$  under very high pressure in the range of 2 K other approaches such as magnetically mediated pairing can be considered. The correlation between the  $T_c$ -value and the (insulating) spin fluctuation regime is taken as a strong experimental argument in favour of a pairing mechanism involving AF fluctuations. It is also remarkable to notice that the maximum value of  $T_c$  is about twice as large in  $(\text{TMTTF})_2\text{PF}_6$  as in the parent selenium compound [1]. This is in agreement with the more developed AF fluctuation regime observed in the former compound and provides an additional support for the involvement of AF fluctuations in the microscopic pairing mechanism. Such a scenario was also considered for Ce- and U-based strongly correlated electron multiband systems where deviations from the canonical quadratic temperature dependence of the Fermi liquid model are observed at the border between superconductivity and antiferromagnetism [22, 23].

The use of SDW fluctuations to form bound states of charge carriers is another possibility considered by Emery and worked out in the context of nearly AF itinerant fermion systems [24]. As far as 1D organic conductors are concerned, it was shown that the exchange of SDW fluctuations between carriers belonging to the same stack does not lead to attractive pairing and thus the development of a 1D attractive pairing appears to be hopeless. In addition, in 1D systems the electron–phonon coupling is opposed to the Coulomb repulsion of carriers moving in a restricted phase space.

A conventional approach using the spin fluctuation exchange model in quasi-1D organic superconductors has predicted  $d$ -wave pairing in the vicinity of the SDW phase [25]. However, this theory does not take fully into account the entire temperature regime and in particular the non-Fermi liquid features, observed in DC transport [17, 26] and optical conductivity [27] at high temperature, which persist down to low temperature. An attractive interstack pairing can be the outcome of the exchange of AF spin fluctuations between electrons located on neighbouring stacks [28]. Such a mechanism would lead to an anisotropic SC gap. In this picture, the attractive interaction is accounted for by the growth of electron–hole pair tunnelling generated in the 1D regime at temperatures larger than the 1D to 2D dimensionality crossover [11].

To summarize, we have reported pressure-induced superconductivity in  $(\text{TMTTF})_2\text{PF}_6$  *in spite of* its SP ground state at ambient pressure. This important result establishes the universality of the  $(\text{TM})_2X$  phase diagram. Furthermore, the suppression of the SP ground state makes the traditional phonon-mediated Cooper-pair formation unlikely to explain the existence of superconductivity at temperatures as high as  $T_c = 2.2$  K at  $p = 4.73$  GPa. The manifestation of critical AF spin fluctuations above the onset of superconductivity and the close connection between their amplitude and the value of  $T_c$  speaks strongly in favour of an interstack pairing mechanism mediated by the exchange of these fluctuations between neighbouring stacks. Thus, our findings supply an important input for theoretical models of magnetic coupling in quasi-1D conductors and may even shed light on superconductivity in strongly correlated electron systems including high-temperature superconductors<sup>6</sup>.

Useful discussions with C Bourbonnais, C Pasquier and P Auban-Senzier as well as the technical help of M Nardone are acknowledged. The work carried out in Geneva was supported by the Swiss National Science Foundation. We thank R Cartoni and A Holmes for technical assistance.

<sup>6</sup> During preparation of this manuscript a confirmation of the pressure-induced superconductivity in  $(\text{TMTTF})_2\text{PF}_6$  was reported by Adachi *et al* [29].

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