Diamagnetic AC susceptibility in the quasi-one dimensional organic conductor : \((\text{TMTSF})_2\text{PF}_6\)

M. Ribault, G. Benedek, D. Jérome

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

and K. Bechgaard

H.C. Oersted Institute, Universitetsparken 5, DK 2100, Copenhague, Denmark

(Reçu le 19 mai 1980, révisé le 26 juin, accepté le 1er juillet 1980)

Résumé. — Les mesures de la susceptibilité alternative du conducteur organique quasi-unidimensionnel \((\text{TMTSF})_2\text{PF}_6\) sous pression hydrostatique de 12 kbar indiquent l’existence d’un fort diamagnétisme au-dessous de 0,9 K. L’amplitude de la variation de la composante réelle de la susceptibilité suggère une expulsion pratiquement complète du champ magnétique hors de l’échantillon. Nous présentons aussi les effets de l’application d’un champ magnétique statique. Ces résultats permettent d’établir l’existence d’une supraconduction de type II dans \((\text{TMTSF})_2\text{PF}_6\).

Abstract. — Measurements of the AC susceptibility of the quasi-one dimensional organic conductor, \((\text{TMTSF})_2\text{PF}_6\), under hydrostatic pressure of 12 kbar show the occurrence of a large diamagnetic contribution below 0.9 K. The amplitude change of the real part of the susceptibility suggests nearly complete magnetic flux expulsion. The effects of the application of a DC magnetic field are also reported. The existence of superconductivity of the second kind is thus firmly established in the organic conductor \((\text{TMTSF})_2\text{PF}_6\).

Superconductivity has been recently reported in the organic 1-D conductor \(\text{di-tetramethyltetrahiafulvalene, hexafluorophosphate (TMTSF)}_2\text{PF}_6\), using resistive measurements [1]. However, there was still a lack of data concerning the characterization of superconductivity in the organic state via magnetic measurements.

This letter reports an investigation of the complex AC susceptibility of \((\text{TMTSF})_2\text{PF}_6\) under a pressure of 12 kbar. The data provide the clear evidence of a diamagnetic susceptibility corresponding to a quasi complete expulsion of the magnetic flux, namely Meissner effect, below \(T_c = 0.9\) K.

Moreover, the typical behaviour of a type II superconductor is observed when a DC magnetic field is superimposed to the oscillating field.

The experiment consists in measuring the voltage induced on a coil containing the sample which is surrounded by an independent coaxial coil producing an oscillating magnetic field (\(\gamma = 68\) Hz) of small amplitude. The real part \(\chi’\) of the susceptibility is given by the induced voltage in phase quadrature with the modulating magnetic field, while the imaginary part \(\chi’’\) is provided by the in-phase component. Both coils are located in the teflon cap of beryllium-copper pressure vessel similar to that used for resistive measurements [1]. The pressure vessel is in tight thermal contact with the mixing chamber of a \(^3\text{He}-{^4}\text{He}\) dilution refrigerator. The temperature is measured by means of platinum thermometers and carbon or germanium thermometers below 10 K. The limited space which is available in the pressure cell prevents so far the use of the more sensitive double pick-up coil circuit as normally used in de Haas-van Alphen measurements. The organic sample consists in single crystals, which have been roughly oriented in the pick-up coil with their high conductivity axis perpendicular to the AC field. The \((\text{TMTSF})_2\text{PF}_6\) crystals have been obtained from ultrapure constituents by an electrochemical technique [2]. Typical sizes were \(2 \times 0.2 \times 0.1\) mm\(^3\). Together with the sample, a small piece of niobium has been put for the purpose of equipment, sensitivity calibration. The masses of \((\text{TMTSF})_2\text{PF}_6\) and Nb specimen are respectively 13.7 mg and 5 mg leading to a volume ratio

\[
\frac{V((\text{TMTSF})_2\text{PF}_6)}{V(\text{Nb})} = 9.6
\]

(*) Laboratoire associé au C.N.R.S.
given the calculated density of 2.42 g/cm³ for (TMTSF)$_2$PF$_6$.

When the whole pressure vessel is cooled or heated in earth magnetic field a large response occurs on the induced voltage of the pick-up coil when crossing the superconducting transitions, figure 1. No hysteresis of X has been observed with temperature sweeps. The peak amplitude of the AC field for the results shown on figure 1 is about 0.03 Oe. We have also checked that increasing the magnitude of the AC field by a factor 100 increases the X response accordingly. The comparison between the ($\chi'$) responses of (TMTSF)$_2$PF$_6$ and Nb specimen shows that below 0.9 K the organic sample is strongly diamagnetic. The relative amplitude of the change of $\chi'$ signals at $T_c$ for both Nb and (TMTSF)$_2$PF$_6$ samples leads, strictly speaking, to a diamagnetic contribution at low temperature which is about 1/3 of the full diamagnetic value ($-\frac{1}{4}\pi$) of a complete Meissner effect [3]. However we do not believe that the above derived factor 1/3 bears much significance for various reasons:

(i) A large fraction of the sample volume lies at both ends of the receiving coil and therefore contributes less efficiently to flux expulsion than niobium (located at the coil centre).

(ii) We have neglected the shadow effect due to flux expulsion in the niobium piece and experienced by the crystals surrounding the niobium specimen.

(iii) Changes of volume occurring under pressure have not been taken into account.

The peaking of $\chi''$ observed at $T_c$ for both samples is a well known phenomenon. It corresponds to the development of filamentary superconducting structures in the vicinity of $T_c$ [4]. We can also verify on figure 1 that the losses ($\chi''$) are smaller below than above $T_c$, in agreement with the AC field expulsion. Hence, the data of figure 1 together with the previous remarks indicate essentially a complete flux expulsion in (TMTSF)$_2$PF$_6$ below $T_c$. This phenomenon is well established in type I superconductors exhibiting complex metallurgical structures, for example cold-worked tin wires [4]. A $\chi'$ peaking can also result from the presence of vortices in the mixed state of a type II superconductor, close to the superconducting transition.

While the sample is kept at $T = 160$ mK, a DC magnetic field parallel to the AC field is slowly increased. The shape of $\chi'$ and $\chi''$ versus field is displayed on figure 2 for the (TMTSF)$_2$PF$_6$ sample.

We notice that $\chi'$ departs from its zero field value at a field of about 30 Oe, and a maximum of $\chi''$ is observed at 330 Oe. No marked field hysteresis effects have been detected. The behaviours of $\chi'$ and $\chi''$ as shown on figure 1 have also been observed in typical type II superconductors such as niobium [5]. Consequently, 30 and 330 Oe correspond roughly to the lower ($H_{c1}$) and upper ($H_{c2}$) critical fields. If the magnetic field is further increased, signals similar to those shown on figure 2 are observed around 1000 Oe and 4000 Oe corresponding to $H_{c1}$ and $H_{c2}$ of the marker sample. Consequently the effects on $\chi$ of the niobium superconductivity do not affect the results of figure 2. Admittedly the above determination of the critical fields from figure 2 is crude, since in particular, demagnetization coefficients have not been taken into account [6], but the value of $H_{c2}$ thus derived is in fairly good agreement with resistive measurements [1]. We cannot discard the possibility of surface superconductivity above $H_{c2}$. Results such as those of figure 1 indicate nearly complete AC Meissner effect:
this does not prove necessarily that a DC Meissner effect exists. As a matter of facts there are several cases where that situation has been observed for either filamentary conductors $\text{SN}_n$ [7] and $\text{NbSe}_3$ [8] or layered conductors $\text{TaS}_2$ [9]. However as far as the organic conductor is concerned we have a reason to believe that the supercurrents take place in practically the entire sample volume and not only on the surface or in small fibers. ($\text{TMTSF})_2\text{PF}_6$ single crystals have about the same cross sections as those of ($\text{SN})_n$ or $\text{NbSe}_3$ where currents in excess of 10 $\mu$A are enough to shift the transition temperature down [10] whereas we have been able [1] to pass currents of 1 mA in the organic superconductor without changing $T_c$. Moreover, we have checked that the sample is driven towards its normal state for currents larger than 1 mA not because of critical currents but because of self heating in the contact resistance. Consequently, we think that superconductivity is indeed a bulk phenomenon in ($\text{TMTSF})_2\text{PF}_6$ and therefore it cannot be attributed either to metal inclusions or surface superconductivity. Moreover, the sharpness of the $\chi'$ drop below 0.9 K is indicative of the homogeneous nature of the superconducting state. Measurements of the DC magnetization curve are planned in the future; they will allow a deeper understanding of the superconductivity properties under magnetic field. A rough estimate of the Landau-Ginzburg parameter, $K_L^2 = H_{c2}/2 H_{c1}$, derived from figure 2 is $\kappa_\perp = 2.35$. It is also clear from the value of $H_{c2}$ that the dirty limit is relevant for the superconductivity of ($\text{TMTSF})_2\text{PF}_6$, since

$$(\zeta_0(0), \xi(0))^{1/2} = \left(\varphi_0/2 \pi H_{c2}\right)^{1/2} \approx 10^3 \text{ Å}$$

much larger than a reasonable electron mean free path of $\approx 30$ Å or so. We have failed to detect precursor effects on the susceptibility above $T_c$, although effects of some importance are expected for fluctuations in quasi-1-D conductors [11]. However the present failure to detect very large fluctuation diamagnetism above $T_c$ is not in contradiction with the observation of very strong paraconductivity in a temperature domain extending up to 40 K [12]. Preliminary calculations show that the effects of superconducting fluctuations must be more easily visible on transport than on magnetic properties [13]. It is also very likely that the large diamagnetic susceptibility observed in the parent compound TMTSF-DMTCNQ at low temperature [14], as the conducting state is stabilized by high pressure is provided similarly by diamagnetic fluctuations.

In conclusion, the AC susceptibility results reported in this letter establish definitively the superconductivity of ($\text{TMTSF})_2\text{PF}_6$ first observed by resistive measurements. They suggest a strong expulsion of the magnetic flux from the sample and illustrate the type II nature of the bulk superconductivity.

We benefited from fruitful discussions with J. Friedel and H. J. Schulz.

References


