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The metallic state of the organic conductor TMTSF-DMTCNQ at low temperature under pressure (*) (**)

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Résumé. — Nous présentons la mise en évidence d'un état de conductivité élevée ($\sigma > 10^5 (\Omega \cdot \text{cm})^{-1}$) à basse température, stabilisé sous haute pression ($P > 10$ kbar) dans le conducteur organique quasi unidimensionnel TMTSF-DMTCNQ. L'étude de la magnétoresistance suggère que parmi plusieurs interprétations de l'état métallique l'hypothèse d'une supraconductibilité quasi unidimensionnelle de type BCS persistant jusqu'à 30 K environ pourrait être retenue.

Abstract. — We present experimental evidences for a high conductivity state ($\sigma > 10^5 (\Omega \cdot \text{cm})^{-1}$) stabilized by high pressure ($P > 10$ kbar) at low temperature in the quasi one-dimensional organic conductor TMTSF-DMTCNQ. The magnetoresistance investigations suggest among several possible interpretations of the metallic state, the existence of a quasi 1-D BCS-like superconductivity remaining up to ≈ 30 K.

This note presents the finding in an organic conductor of a metallic-like high conductivity state stable under high pressure down to 1.2 K : the charge transfer compound TMTSF-DMTCNQ (tetramethyl tetraselenafulvalene-dimethyl tetracyanoquinodimethane).

The TMTSF-DMTCNQ structure [1, 2] exhibits the usual features of the TTF-TCNQ family, namely, the existence of segregated and uniform stacks of TMTSF and DMTCNQ molecules. Consequently, this compound presents pronounced quasi 1-D conductivity properties.

A sharp metal to insulator phase transition at 42 K has been revealed by transport properties [3]. As shown by ESR susceptibility [4] the acceptor chain (DMTCNQ) electron bandwidth is likely to be rather small. Moreover the pronounced 1-D character is suggested by both the crystal structure [2] and the narrowness of the ESR line [4].

Preliminary diffuse X-ray diffraction patterns show that the bands are 1/4 field [5], namely, a 0.5 charge transfer and a 4th order commensurability under atmospheric pressure. Consequently, the Fermi level in TMTSF-DMTCNQ lies closer to the band edge Van-Hove singularity than in TTF-TCNQ or in any other two-conducting chains compounds known up to date.

The transport properties under pressure have been looked at with the purpose of studying the influence of commensurability both on the phase diagram [6] and on the conductivity mechanism [7]. The goal was also the possibility of stabilization of a metallic state at low temperature under high pressure [8].

The longitudinal conductivity has been measured with the current techniques in our laboratory, on 29 single crystals of about $1 \times 0.05 \times 0.02 \text{ mm}^3$ in size. At 300 K the conductivity ranges around $700 (\Omega \cdot \text{cm})^{-1}$.

The phase transition temperature is only very weakly pressure dependent up to ≈ 10 kbar and drops sharply down to at least 1.2 K for all higher pressures. In the latter pressure domain the sample resistance exhibits a metallic character from ambient tempera-

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ture down to liquid helium temperature. Figures 1a, b display the resistance behaviour for two samples at $P = 13$ kbar.

In most samples the 4.2 K conductivity under pressure is bigger than $10^5 (\Omega \cdot \text{cm})^{-1}$ and can eventually reach $2 \times 10^5 (\Omega \cdot \text{cm})^{-1}$ in some cases. A

remarkable effect has been noticed with the application of a magnetic field perpendicular to the large conductivity axis of the sample, figure 1a. Under magnetic field (75 kOe), the temperature dependence of the resistivity shows the existence of a shallow metal to insulator transition around 12 K.

This behaviour is reminiscent of the case of HMTSF-TCNQ at atmospheric pressure, for which a structural phase transition at 24 K has been found to accompany the metal to insulator transition [8, 9].

The influence of a 75 kOe magnetic field parallel to the chains is far weaker as shown on figure 1b. Crudely speaking, it does not modify significantly the general trends of the resistance temperature dependence. Since the angle between the magnetic field and the chain axis cannot be zeroed with an accuracy better than $\approx 5^\circ$, the weak magnetoresistance effect, figure 1b, may be due to misalignment.

The stability of a metallic state at 1.2 K in a quasi 1-D conductor raises some serious problems. We shall suggest some possible interpretations for the results of figure 1 later in this note.

It has been shown that a large interchain tunnelling coupling can at low temperature stabilize a metallic state instead of the insulating Peierls state [10]. This effect has actually been observed in impure HMTSF-TCNQ samples [8] under pressure. However, the conductivity of the metallic state thus stabilized does not grow significantly above $10^4 (\Omega \cdot \text{cm})^{-1}$. Moreover, the temperature dependence of the HMTSF-TCNQ resistivity at $P > 4$ kbar is not modified by the application of a transverse magnetic field of 28 kOe [11]. Most electronic properties of HMTSF-TCNQ have been satisfyingly explained with a semi-metallic band model [12].

Incommensurate CDW's can also contribute significantly to the electronic conduction of 1-D conductors [13].

For TTF-TCNQ this has been proved thanks to the measurements of the longitudinal [7] and transverse [14] conductivity in the vicinity of the $\times 3$ commensurability under pressure.

However the collective Fröhlich fluctuating contribution is proportional to the CDW coherence length [13] and its rise towards low temperature is limited by the interchain Coulomb pinning mechanism leading to an insulating state [15]. As far as TTF-TCNQ is concerned, the conductivity maximum of Fröhlich-like origin reaches $\approx 2 \times 10^4 (\Omega \cdot \text{cm})^{-1}$ at 60 K. This value is nevertheless 10 times smaller than the value $\sigma(4.2 \text{ K})$ in TMTSF-DMTCNQ, figure 1a.

The last possibility which we shall investigate has not been observed up to now. The existence of a superconducting BCS-like state could explain both the large values found for $\sigma(4.2 \text{ K})$ and the influence of a magnetic field. With such a picture the superconducting transition can conceivably be substantially broadened by the pronounced 1-D character of the conduc-

Fig. 1. — Temperature dependence of the longitudinal resistivity of 2 different samples of TMTSF-DMTCNQ at 13 kbar : a) $H = 0$ and $H_{\perp} = 75$ kOe, b) $H = 0$ and $H_{\parallel} = 75$ kOe.

tor [2, 4]. The growth of the conductivity below 4.2 K might possibly be limited by some breaks in the chains which are always present on a macroscopic scale in imperfect crystals, as observed in superconducting SN_x [16].

Considering the curvature of the resistivity temperature dependence between 40 and 10 K, figure 1, the resistivity might possibly reach a zero value below, say, 10 K in perfect samples, if real 3-D ordering takes place.

The interchain coupling, necessary for the establishment of a superconducting state in charge transfer compounds, is not negligible as shown in TTF-TCNQ by the 3-D behaviour of the elastic coefficients [17]. Consequently, the superconducting transition temperature might be higher than 10 K.

Assuming the model of an anisotropic type II superconductor (used for SN_x [18]) to be valid for TMTSF-DMTCNQ, a 75 kOe transverse field is presumably larger than $H_{c2}^\perp$, and therefore breaks the superconducting pairs. This pair-breaking effect allows the establishment of a low temperature Peierls state [19], figure 1a. Under transverse magnetic field, the conductivity reaches $\approx 3 \times 10^4 (\Omega \cdot \text{cm})^{-1}$ around 22 K, figure 1a.

Preliminary studies of the pressure dependence of the conductivity at $T > 42$ K and of the transverse conductivity suggest a collective Fröhlich fluctuating origin for the conductivity at high temperature, say

$T \gtrsim 42$ K. Thus we are tempted to believe that under strong transverse magnetic field the large value reached by the conductivity at 22 K is due to the fluctuating Fröhlich contribution. The only weak effect of a parallel field on the resistance indicates the existence of a large value for $H_{c2}^\parallel$ (this value may even be larger than the paramagnetic limit of ≈ 200 kOe, for $T_c \approx 10$ K).

Finally, the proximity between the Fermi level and a Van-Hove singularity [20] on the one hand and a weaker covalency interchain effect as compared to the neighbouring compounds TSF-TCNQ or TTF-TCNQ on the other hand might increase the superconducting transition temperature.

In conclusion, this work has conclusively established the existence of a very high conductivity state of metallic character in TMTSF-DMTCNQ under pressure. We have suggested among several explanations, the possibility of a quasi 1-D BCS-like mechanism contributing to the conductivity below 30 K. More high pressure studies are in progress : ac susceptibility, thermoelectric power and tunnelling.

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