The organic conductor TTF-TCNQ exhibits several experimental features characteristic of one-dimensional (1-D) metallic behaviour, such as: (i) satellite sheets at $\pm 2k_F$ away from Bragg reflections in X-ray diffuse scattering [1] as a result of fluctuating 1-D lattice distortions and (ii) magnetic field dependence of the nuclear relaxation rate induced by the electron motion [2], $T_1 \sim H^{1/2}$, connected to the singular behaviour of electron correlation functions at 1-D. Moreover, a 1-D model provides a satisfactory description of the metallic domain [3]. Large values of electron-electron interactions in TTF-TCNQ are necessary for the interpretation of the enhancements observed in nuclear relaxation rate [3, 4] and spin susceptibility [5]. However, the electron-phonon interaction reveals its presence through a moderate decrease of the density of states at the Fermi level below the interacting electrons (from e-e couplings) value [3]. This pseudo-gap phenomenon is limited to the low temperature domain of the metallic region [6] (at low pressure), namely $T \leq 150$ K.

High pressure studies [7] point out the contrast existing between the volume dependences which are (i) large, for all physical quantities related to Fermi level properties, (ii) small, when they are related to energy bandwidths, namely plasma frequency. Understanding of the dc metallic conductivity has however remained the great puzzle in the study of TTF-TCNQ and its derivatives [8, 9]. Bardeen [10] and co-workers [11] suggestion that long living fluctuating charge density waves (CDW) of the Fröhlich type [12] could reasonably contribute to the dc longitudinal conductivity of TTF-TCNQ has constituted a step forward. But the model in question has not received any clearcut experimental verification up to date. This letter intends to fill this gap.

The study of the TTF-TCNQ phase diagram [13] has shown the existence of a narrow pressure domain
in the vicinity of 20 kbar, where, as a result of the increase of the charge transfer, the wavelength of the low temperature periodic lattice distortion is commensurate with the lattice. The peaking of a single phase transition temperature (first order) around 20 kbar has suggested a commensurability \( \times 3 \) namely,

\[
2 k_F = b^*/3
\]

at this pressure [14]. This possibility has been confirmed recently by the measured change of \( 2 k_F \) under pressure by neutron diffraction [15]. The possibility of achieving commensurability in TTF-TCNQ happened to be an extremely important consideration for the understanding of the electronic properties of 1-D conductors.

Extensive resistivity measurements have been conducted on TTF-TCNQ single crystals

\[
(2 \times 0.3 \times 0.06 \text{ mm})
\]

up to 28 kbar. The \( b \)-axis resistivity was measured by standard 4-probe ac phase sensitive techniques at 70 Hz. High pressure was generated by He gas up to 12 kbar and by isopentane in a teflon capsule above. Readings of sample voltages and Cu-constantan thermocouple inside the pressure cell were digitized and automatically recorded during slow cooling and warming cycles at constant pressure. Samples used for this study showed conductivity peak ratios (CPR), at atmospheric pressure, ranging from 10 to 25. For all samples the unnormal voltage ratios were better than \( 10^2 \) at 300 K and exceeded 20 at \( T_{\text{peak}} \). No phase shifting or data irreproducibility after \( T \) and \( P \) cycles have been noticed within 2%. In the present study we have observed a single and sharp transition in the commensurability domain peaking at 74 K under

![Fig. 1. — Resistivity versus temperature at a pressure situated in the commensurability range. Experimental points have been displayed in the transition region. The lines drawn through these points (continuous = cooling, dotted = warming) indicate a 1 K hysteresis at \( T_{\text{RT}} \).](image1)

![Fig. 2. — Pressure dependence of the conductivity of TTF-TCNQ at constant temperature. Results for three samples have been displayed, corresponding to CPR = 25, 16 and 11 for (a), (b) and (c) respectively. The sequence of temperatures is similar for the three samples. A \( T = 80 \text{ K} \) curve has been drawn only for sample (a) since for this sample \( T_{\text{peak}} \) at 19 kbar was situated below 80 K.](image2)
The constant temperature pressure dependence of the conductivity of three samples has been displayed on figure 2. The conductivity has been normalized at 400 (Ω cm)⁻¹ under ambient conditions for all samples [16]. The minimum temperature of 85 K, at which the pressure dependence of the conductivity has been studied for all samples, is already well into the metallic regime, (dρ/dT > 0), whatever the pressure is. The striking feature emerging from figure 2 is the loss of conductivity occurring around 19 kbar (when CDW and lattice become commensurate). The amplitude of the conductivity loss weakens in the case of a given sample as the temperature (say 85 K), as the CPR drops (CPR = 25, 16, 11 for samples a, b and c respectively). The overall pressure dependence of the conductivity becomes smaller at low temperature (d ln σ/dP ≈ 28 % kbar⁻¹ and 7 % kbar⁻¹ at 290 and 80 K respectively for sample (a) around atmospheric pressure) [17]. Figure 3 displays the behaviour of the transverse conductivity. To discuss the properties of the system at a pressure corresponding to a phase transition into the commensurate state x 3, it is essential to note that the effects of commensurability are described by a cubic term in the Landau free energy expansion [13, 18, 19, 20] similar to the Landau theory of the layered compounds [21]. Due to the cubic term, the phase transition into the commensurate CDW state is first order and the transition temperature Tc1 is higher than the temperature Tc2 of the second order transition occurring in the absence of cubic term (i.e., in the incommensurate case). According to the TTF-TCNQ phase diagram [13], a value Tc2 ≈ 60 K at 19 kbar provides an estimate of the commensurability induced transition temperature enhancement, Tc1 - Tc2 ≈ 15 K.

In the incommensurate case rigid translations of fluctuations into the CDW state (sliding mode conductivity) are possible since the energy of a fluctuation is independent of its phase [22]. In the commensurate case, however, the energy of a fluctuation does depend on its phase due to a phase-dependent cubic term [13, 18, 19]. Therefore, a finite restoring force prevents translations of the fluctuating CDW so that its phase is pinned to some equilibrium position thereby suppressing the sliding mode contribution to the conductivity [23]. Thus, a commensurability of low order is a drastic pinning mechanism for the fluctuating CDW and it can well explain the lowering of the conductivity in the commensurate case, as observed in the present study.

Changes in the single particle conductivity would constitute another possible explanation for figure 2. Fluctuations affect this part of the conductivity in essentially two ways: (i) fluctuations into a CDW state lead to the occurrence of a pseudo-gap at the Fermi level [24, 25, 26]. It has been shown experimentally that in TTF-TCNQ there is only a small reduction of the density of states near the Fermi level [6]. As the gap in the low temperature commensurate phase is larger than in the incommensurate phase [7] one might expect correspondingly larger pseudo-gap effects above the phase transition. However, the main effect of the cubic term in the free energy is to pin the phase of the fluctuations. The amplitude of the fluctuations which gives rise to the pseudo-gap is almost unaffected by the cubic term [20]. We can therefore preclude the possibility of an enhancement of the pseudo-gap contribution to the resistivity near the

![Fig. 3. Temperature dependence of the longitudinal and transverse conductivities at commensurability (P = 19 kbar) and off commensurability (P = 12 kbar).](image)
commensurate phase transition with respect to the incommensurate case. (ii) Changes of the single electron scattering could lead to a reduction of the conductivity at commensurability. The proposed mechanisms for single electron scattering [27, 28, 29, 30] depend eventually on the amplitude of the order parameter fluctuations but in no case on its phase. On the other hand as mentioned above, the commensurability affects only slightly the amplitude fluctuations of the CDW and therefore the single electron scattering remains practically unchanged. It appears therefore that the single particle part of the conductivity is hardly affected by the commensurability. This agrees well with the results for the transverse conductivity which is clearly a single particle process [4] and which is independent of commensurability, as shown in figure 3a, b. It must be noticed that the normalized temperature dependence of $\sigma$ reveals nearly identical behaviour for both components of the conductivity at commensurability, figure 3a. Off commensurability because of the fluctuating 1-D contribution to $\sigma(T)$ both conductivities display very different temperature dependence, figure 3b. Thus, the lowering of the conductivity in the commensurate case is well explained by the commensurability pinning of fluctuating CDW's which contribute to the conductivity of the incommensurate case. At 19 kbar the resistivity is mainly due to single particle scattering and happens to be only weakly sample dependent (Figs. 2a, b, c). However, in the incommensurate case, for instance at $P \approx 12$ and 26 kbar and at low temperatures the large sample dependence noticed among various samples can be related to the pinning of fluctuations arising from impurities or crystal defects [31]. According to figure 2 the collective contribution to the conductivity at $P = 12$ kbar amounts to about 5 000 ($\Omega$ cm)$^{-1}$ at 80 K for sample (a). Accordingly we estimate for sample (a) that the collective mode contributes up to about half the total conductivity at 59 K ($\sigma_{\text{total}}^{(59K)} = 10.000$ ($\Omega$ cm)$^{-1}$). The large sample dependence of the conductivity at high pressure ($P \gtrsim 26$ kbar) indicates that the fluctuating conductivity contribution becomes increasingly important under pressure and presumably follows the increase of the electron-phonon coupling constant [3].

The temperature dependence of the fluctuating conductivity contribution $\sigma^*$ can be derived approximately at high pressure, interpolating the conductivity within the dip region at a given temperature and removing the single particle contribution. Thus it is found that $\sigma^*(T)$ follows at constant pressure a $(T-T_c)^x$ law whereby $I = (T - T_c)/T_c$ (with $T_c \approx 60$ K at 19 kbar) and $x$ varying from 1/2 for $T < 120$ K to 3/2 for $T > 120$ K. It should be noticed moreover that the dip in the conductivity at 19 kbar sets in at about 200 K, which is in fair agreement with the temperature at which $2k_F$ fluctuations are first seen in X-ray experiments under atmospheric pressure [32, 33].

The present study points out that in TTF-TCNQ fluctuation conductivity does not extend up to room temperature at pressures less than 25 kbar or so. Consequently the room temperature resistivity at low pressure is due to a single-particle scattering mechanism, probably enhanced by volume dependent correlation effects, as indicated by the large volume dependence of the resistivity [7]. Finally, preliminary experiments performed on the selenium analogue compound, TSeF-TCNQ, have shown a similar loss of conductivity around 7.5 kbar. According to the existence of maxima in both the low temperature gap and the ratio of the low temperature gap to transition temperature, a $\times 3$ commensurability is very likely to occur in TSeF-TCNQ around 7.5 kbar. No such behaviours have been observed in HMTTF and HMTSeF-TCNQ in the 30 kbar range since the charge transfer is already above 2/3 at atmospheric pressure [3].

In conclusion, this letter has reported an experiment which brings the clearcut evidence of the role played by the fluctuating collective mode of the Fröhlich type in incommensurate 1-D organic conductors. But it also defines the particular temperature domain in which this role comes into play. Around atmospheric pressure the fluctuating conductivity contributes to a large extent to the dc conductivity of good quality TTF-TCNQ single crystals in a temperature domain of about 100 K wide above the metal insulator transition.

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References


[14] A × 2 commensurability might come into mind, but it would not give rise to a first order phase transition as observed experimentally.
[16] We have not noticed in the present study any obvious correlation between measured values of the room temperature conductivity and the CPR at atmospheric pressure. Therefore, we believe that the scattering in σ (300 K) among various samples might be due to uncertainties in geometrical factors.
[18] Because of fluctuation effects a strictly 1-D system cannot be treated by mean-field theory. However, in a real system, there are always weak 3-D interactions. In the presence of such interactions, phase transitions can be well described by a renormalized mean-field theory, see for instance, Scalapino, D. J., Imry, Y. and Pincus, P., Phys. Rev. B 11 (1975) 2042; Menyhard, N., J. Phys. C 11 (1978) 2207 and ref. [3].