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A. Andrieux, H.J. Schulz, D. Jérôme, K. Bechgaard. Fluctuation conductivity in 1-D conductor tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ). *Journal de Physique Lettres*, 1979, 40 (15), pp.385-389. 10.1051/jphyslet:019790040015038500 . jpa-00231650

HAL Id: jpa-00231650

<https://hal.science/jpa-00231650>

Submitted on 1 Jan 1979

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Classification
 Physics Abstracts
 72.15N

Fluctuation conductivity in 1-D conductor tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) (*)

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(Reçu le 17 mai 1979, révisé le 11 juin 1979, accepté le 12 juin 1979)

Résumé. — Nous présentons l'existence d'une chute de la conductibilité longitudinale de TTF-TCNQ qui, à température constante, apparaît dans un domaine étroit de pressions, centré sur 19 kbar. Aucun effet n'a été remarqué sur la conduction transversale dans le même domaine de pressions.

La chute de conduction a été reliée à la possibilité d'une commensurabilité d'ordre 3 entre la distorsion structurale et le réseau. Le comportement de la conduction apporte la preuve qu'une importante fraction de la conduction métallique de TTF-TCNQ incommensurable est due aux fluctuations du mode collectif.

Abstract. — We report an important drop in the longitudinal conductivity of TTF-TCNQ occurring at constant temperature in the metallic phase and in a narrow pressure domain located around 19 kbar. No change of the transverse conductivity has been noticed in the same pressure region.

The conductivity drop has been related to the $\times 3$ commensurability of the longitudinal distortion with the lattice. It brings the proof that a significant fraction of the metallic conductivity of incommensurate TTF-TCNQ at low temperature is due to the fluctuating collective mode.

The organic conductor TTF-TCNQ exhibits several experimental features characteristic of one-dimensional (1-D) metallic behaviour, such as : (i) satellite sheets at $\pm 2 k_F$ away from Bragg reflexions 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 $T \lesssim 150$ 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

(*) This work was supported in part by the Délégation Générale à la Recherche Scientifique et Technique, contract n° 78-7-0313.

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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,

$$2k_F = b^*/3$$

at this pressure [14]. This possibility has been confirmed recently by the measured change of $2k_F$ 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 *unmested voltage* ratios were better than 10^2 at 300 K and exceeded 20 at T_{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_{c1} .

19 kbar. The first order character of the transition in the commensurability pressure domain is clearly shown by the hysteresis of about 1 K observed at the transition, figure 1. The transverse conductivity along the a -axis has been measured *versus* temperature, using the direct 4-probe method at 19 kbar (commen-

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 $T = 80$ K curve has been drawn only for sample (a) since for this sample T_{peak} at 19 kbar was situated below 80 K.

surate situation) and 12 kbar (incommensurate situation).

The constant temperature pressure dependence of the conductivity of three samples has been displayed on figure 2. The conductivity has been normalized at $400 (\Omega \cdot \text{cm})^{-1}$ 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, ($d\rho/dT > 0$), 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 ($d \ln \sigma / dP \approx 28 \% \text{ kbar}^{-1}$ and $7 \% \text{ kbar}^{-1}$ 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 $\times 3$, 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 T_{c1} is *higher* than the temperature T_{c2} 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 $T_{c2} \approx 60 \text{ K}$ at 19 kbar provides an estimate of the commensurability induced transition temperature enhancement, $T_{c1} - T_{c2} \approx 15 \text{ K}$.

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 reduc-

Fig. 3. — Temperature dependence of the longitudinal and transverse conductivities at commensurability ($P = 19 \text{ kbar}$) and off commensurability ($P = 12 \text{ kbar}$).

tion 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

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 σ reveals nearly identical behaviour for both components of the conductivity at commensurability, figure 3a. Off commensurability because of the fluctuating 1-D contribution to $\sigma_{\parallel}(T)$ 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 $5\,000 (\Omega \cdot \text{cm})^{-1}$ 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 ($\sigma_{\text{total}}^{(59\text{K})} = 10\,000 (\Omega \cdot \text{cm})^{-1}$). 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 σ' 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 $t^{-\alpha}$ law whereby $t = (T - T_{c2})/T_{c2}$ (with $T_{c2} \approx 60$ K at 19 kbar) and α 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.

Acknowledgments. — We wish to acknowledge the contribution of R.H. Friend towards the understanding of the electronic properties of TTF-TCNQ at an early stage of this work. We thank S. Barišić, P. Chaikin and J. Friedel for useful discussions and G. Malfait for the maintenance of the high pressure equipment.

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