Nonlinear Electrical Transport Effects in Tetrathiafulvalene-Tetracyanoquinodimethane as Driven through Charge-Density-Wave Commensurability

R. C. Lacoe, J. R. Cooper,[a] D. Jérome, and F. Creuzet
Laboratorire de Physique des Solides, Université de Paris-Sud, 91405 Orsay, France

and

K. Bechgaard and I. Johannsen
H. C. Oersted Institute, DK-2100 Copenhagen, Denmark
(Received 3 July 1986)

Electric-field–dependent conductivity measurements in the organic two-chain conductor tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) are reported in the pressure (P) range $4 \le P \le 24$ kbar. Deviations from Ohm's law, with a threshold field E_T, are found at all P at temperatures below the upper Peierls transition. At low P, we find that the E_T temperature dependence approaches that found for $NbSe_3$. As TTF-TCNQ is driven through third-order commensurability at ~ 19 kbar, we observe a peak in E_T and a dip in the excess current at constant field. The results are discussed in terms of charge-density-wave and/or discommensuration transport.

PACS numbers: 72.80.Le, 72.15.Nj, 72.20.Ht

After the discovery of nonlinear (NL) electrical transport phenomenon in $NbSe_3$,[1] the search for and study of charge-density-wave (CDW) conduction shifted from organic to inorganic systems. In the inorganic materials[2] [e.g., TaS_3, $K_{0.3}MoO_3$, $(NbSe_4)_{10}I_3$,. . .] NL effects are generally interpreted as resulting from CDW depinning by moderate electric (E) fields. A CDW can be pinned by impurities[3,4] (impurity pinning), by the lattice potential[3] (commensurability pinning), or by Coulomb interactions between oppositely charged chains in two-chain systems[3] (Coulombic pinning). If the energy associated with an external E field coupled to the CDW is sufficient to overcome the pinning energy, the CDW will carry a current, and hence, contribute to the conductivity (σ).

Recently, it was shown[5] that there are deviations from Ohm's law at the onset of a Peierls transition in the one-dimensional two-chain organic conductor TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) at ambient pressure (P). The phase diagram of TTF-TCNQ, as derived from structural[6] and transport studies,[7,8] indicates that this system is unique in that by selecting the proper pressure-temperature (P,T) range, one can *select* either impurity, commensurability, or Coulombic pinning as the potential pinning mechanism. At ambient pressure, there are three successive phase transitions[6–9]; the upper transition at 54 K (T_H) involves distortion of the TCNQ (electronlike) stacks, while the lower two transitions at 49 and 38 K (T_M and T_L, respectively) involve the TTF (holelike) stacks. The wave vector of the periodic lattice distortion associated with the Peierls distortion, q_b, is related to the charge transfer ρ by $q_b = (\rho/2)b^*$, and is incommensurate with the undistorted lattice along the b (stacking) direction at 1 bar. Hence, at 1 bar, TTF-TCNQ is a single-chain incommensurate (SCI) CDW semimetal in the narrow T range $T_H > T > T_M$, while below T_M, one must consider Coulomb pinning.

The effect of pressure is to increase the charge transfer[6] from 0.59 at $P = 1$ bar to 0.66 at $P_c \sim 19$ kbar, corresponding to a third-order commensurate q_b. Hence, in the P range near 19 kbar, one expects commensurability pinning to be important. In the intermediate range $4 \lesssim P \lesssim 15$ kbar, $T_M = T_L$ (there is no phase corresponding to the sliding q_a seen at 1 bar), and the T range, where there is a SCI CDW system, is large compared with that at 1 bar.

In this Letter, we present measurements of the field-dependent conductivity of TTF-TCNQ in the range $4 \lesssim P \lesssim 24$ kbar. At all P, we find deviations from Ohm's law, with a threshold field E_T. At low P, where TTF-TCNQ is a SCI CDW semimetal over a large range of T, we find the T dependence of E_T approaches that found in $NbSe_3$. This confirms the suggestion[5] that the sharp rise in E_T below T_M at 1 bar is due to the development of the TTF CDW. At high P, as TTF-TCNQ is driven through third-order commensurability, we observe a peak in E_T at constant normalized T/T_p, where $T_p = T_H$ is the Peierls transition temperature, and a dip in the excess current $J_{ex} = J_{tot} - J_0$ at constant E field, where J_{tot} is the total current and J_0 is the normal current. The results near 19 kbar are discussed in terms of CDW transport and/or discommensuration transport.

Samples were mounted as previously described.[5] In order to minimize and compensate for heating, a pulse technique was used, with typical pulse durations of 10 μsec and repetition rates of 10 Hz. A bridge circuit was used to subtract the linear component of the conductivity, σ_0. By use of this technique, heating effects at the level of 1% could be clearly distinguished from the intrinsic NL contributions. The 4-kbar pressure was applied by ^{4}He gas, while higher pressures were obtained with use of isopentane as the pressure medium.

Measurements of the field-dependent σ were made at 4 and 8.9 kbar. At 4 (8.9) kbar, $T_H=54.8$ (54.8) K and $T_M=T_L=31$ (37.5) K. The normalized σ/σ_0 was roughly linear with log$E$ at all T in this P range. The T dependence of E_T, normalized to its minimum value of 0.125 (0.32) V/cm at 4 (8.9) kbar, vs T/T_p is shown in Fig. 1, along with that found previously[5] for TTF-TCNQ at 1 bar and that for $NbSe_3$ at the CDW transition[10] ($T_p=59$ K). At 4 kbar, after an initial drop in E_T just below T_p, which is a signature of E_T behavior in CDW systems,[11] E_T slowly increases, similar to that found in $NbSe_3$. At 4 kbar, typical σ/σ_0 values of 1.10–1.25 were obtained. At 8.9 kbar, σ/σ_0 vs log$E$ plots showed two regimes: a low-field regime where deviations from linearity were less than 2%, and a higher-field regime where $\sigma/\sigma_0 \propto \log E$. The maximum σ/σ_0 observed was ~ 1.10. The E_T is nearly T independent at 8.9 kbar.

In order to investigate the effect of commensurability on the field-dependent σ, measurements were made at 16.2, 16.5, 18.8 kbar (sample No. 7) and at 17.8, 21, and 24 kbar (sample No. 9). In this P range, there is only one transition, $T_H=T_M=T_L=T_p$, i.e., both chains undergo a Peierls transition at the same temperature. The deviations from linearity were found to be small: $\sim 5\%$ at 16.2 and 16.5 kbar; $\sim 2.3\%$ at 18.8 kbar.

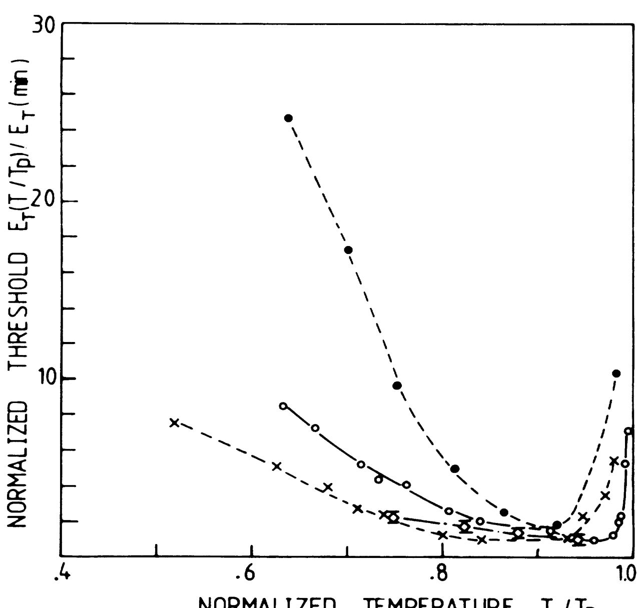

FIG. 1. Normalized threshold field [E_T/E_T(min)] vs normalized temperature (T/T_p) for TTF-TCNQ at 1 bar (Ref. 5) (filled circles), 4 kbar (open circles), and 8.9 kbar (lozenges), and for $NbSe_3$ at 1 kbar (crosses).

Figure 2 displays the normalized T dependence (T/T_p) of the E_T at various P. As P is applied, a peak is observed in T_H at ~ 19 kbar [inset (a)], consistent with previous measurements[7] and reflecting the added driving energy of the commensurate Peierls transition. The sharp peaking of T_p as a function of P allowed verification of the P with respect to P_c. As TTF-TCNQ is driven through commensurability, there is a peaking in E_T. This can be observed in inset (b), where E_T at constant $T/T_p=0.9$ is plotted versus P. The arrow in inset (b) indicates that no E_T was observed up to the field indicated. At commensurability, E_T(18.8 kbar) $\sim 10\,E_T$(13.7 kbar).

The excess current logJ_{ex} at $E=30$ V/cm vs P for $T/T_p=0.9$ and $T/T_p=0.7$ is plotted in Fig. 3. In many cases this required extrapolation of the low-field σ/σ_0 vs log$E$ curves. In the low-P range, J_{ex} is fairly constant; however, as driven through commensurability, there is a dip in J_{ex} by as much as three orders of magnitude. We previously developed a model[5] which qualitatively explained the features of the NL σ in TTF-TCNQ at 1 bar. In this model, we showed that because of the Coulombic coupling between the TCNQ (electronlike) and TTF (holelike) chains, it was not possible to excite

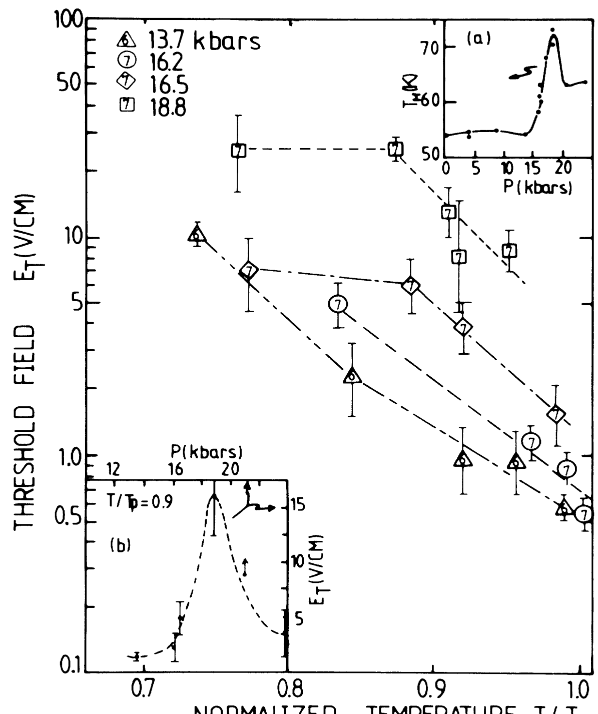

FIG. 2. logE_T vs T/T_p for TTF-TCNQ at (triangles) 13.7 (sample No. 6), (filled circles) 16.2, (lozenges) 16.5, and (open squares) 18.8 kbar (sample No. 7). Inset (a): Pressure dependence of T_H. Inset (b): The pressure dependence of E_T at $T/T_p=0.9$ near commensurability.

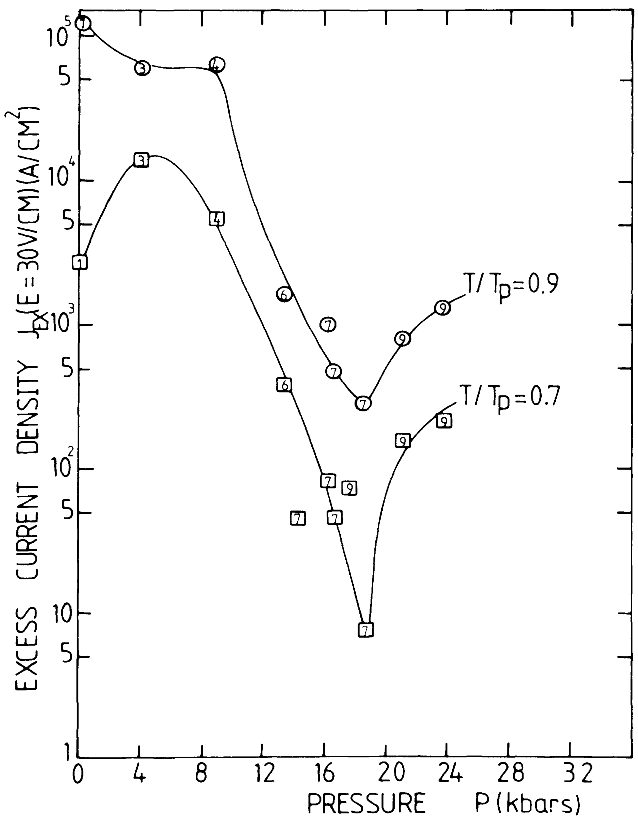

FIG. 3. $\log J_{ex}$ vs P for TTF-TCNQ at $E=30$ V/cm. Circles, $T/T_p=0.9$; squares, $T/T_p=0.7$. The number inside the symbol identifies the sample.

the mode where the two chains move in opposite directions (which carries the maximum current) with the low E fields experimentally used. Instead, we suggested that the electric field depins both CDW's from impurities, but because of the strong Coulomb attraction between chains, both chains moved in the same direction. This is only possible when $(\rho_{cQ}-\rho_{cF})\neq 0$, i.e., the net charge of the two-chain system is nonzero, where[12] $\rho_{cQ}(F)$ is the fraction of carriers condensed in the TCNQ (Q) or TTF (F) chains. We found that, assuming the pinning is mainly due to the TCNQ chain,

$$E_T=E_{T0}\rho_{cQ}/(\rho_{cQ}-\rho_{cF}), \tag{1a}$$

where E_{T0} is the threshold field for an isolated chain, and

$$J_{ex}=J_{ex0}(1-\rho_{cF}/\rho_{cQ}), \tag{1b}$$

where $J_{ex}0$ is the single-chain excess current density; that is, as $\rho_{cF}\to\rho_{cQ}$, $E_{T0}\to\infty$ and $J_{ex}\to 0$.

As shown in Fig. 1, the T dependence of E_T at 1 bar increases much faster below the minimum in E_T in TTF-TCNQ at 1 bar than in $NbSe_3$.[10] Comparison is made to the lower transition in $NbSe_3$ because it is most similar to the case of TTF-TCNQ, where the Fermi surface is also partially gapped. It was suggested[5] that this reflected the growth of ρ_{cF} below T_M, resulting in the anomalous increase in E_T as predicted by (1a). At 4 and 8.9 kbar, where the T range where there is a SCI CDW system is large ($\rho_{cF}\sim 0$), we find that the T dependence of E_T approaches that of $NbSe_3$. This confirms that the rapid increase in E_T at 1 bar was due to the development of the TTF CDW.

Another feature of the E_T T dependence, which is a signature of CDW depinning,[11] is the initial drop in E_T below T_p. This can be seen in Fig. 1 for TTF-TCNQ at 1 bar and 4 kbar. This initial drop in E_T is probably due to the T dependence of ρ_{cQ} near T_p. Near T_p, the force acting on the CDW is proportional to $\Delta\times E$ where Δ is the order parameter.[12] Hence, below T_p, ρ_{cQ} is rapidly increasing, and the field necessary to produce a constant force is decreasing.

Figures 2 and 3 show that there is a peak in E_T and a dip in J_{ex} at P_c. There has been a great deal of both theoretical[13-18] and experimental[19-21] work on CDW systems near commensurability. For systems near commensurability, the ground state is not necessarily the incommensurate CDW, but rather commensurate CDW segments separated by discommensurations (DC).[13] These DC can be charged (and can carry a current) and the DC density depends on the deviation from commensurability. It follows that for a truly commensurate case, the DC density is zero. In principle, DC can be pinned, and hence, give NL transport effects.[17,18]

Interpretation of the behavior of E_T and J_{ex} is complicated by the fact that $T_H=T_M=T_L$ for $P\geq 15$ kbar. The source of nonlinear effects can be either from the depinning of (1) CDW's or (2) DC.

(1) In the range $15<P<24$ kbar, if the NL effects come from depinning the CDW (either from impurities or commensurability), it requires $\rho_{cQ}-\rho_{cF}$ to be nonzero (a peak in E_T and a dip in J_{ex} would occur if $\rho_{cQ}-\rho_{cF}$ goes toward zero at P_c). If the pinning mechanism is commensurability pinning, a peak in E_T can result from a peak in $E_{T0}(P)$ at commensurability. A calculation of E_{T0} from commensurability pinning[3] for TTF-TCNQ yields $E_{T0}\sim 10^4$ V/cm, larger than the E_T found here. However, in nearly third-order commensurate NbS_3,[19,20] $E_T\sim 2$ V/cm, while for the blue bronzes,[21] $E_T\sim 0.1$ V/cm. Also, a drop in E_T was found at the onset of commensurability in orthorhombic TaS_3.[20]

(2) If nonlinear effects come from DC depinning, the condition $(\rho_{cQ}-\rho_{cF})\neq 0$ is no longer imposed since it is not the CDW's which carry the current. The dip in J_{ex} is consistent with the DC density going to zero at P_c. The source of peaking of E_T is not evident in this picture. The behavior of the thermoelectric power[8] near P_c suggests DC transport is important in TTF-TCNQ.

It should be pointed out that the DC's can be pinned by Coulomb interactions on oppositely charged chains which can result in very large values of E_T.[22]

In summary, we have presented the first results of field-dependent measurements in TTF-TCNQ in the range $4 < P < 24$ kbar. Deviations from Ohm's law are seen at low fields. We show that at low P, the T dependence of E_T approaches that of $NbSe_3$, confirming that the two-chain nature of TTF-TCNQ is important in influencing the E_T. As driven through commensurability, we observed a strong peak in E_T and a marked dip in J_{ex}. We presented different frameworks, including depinning of the CDW and/or DC, by which the results can be interpreted.

The authors wish to acknowledge the skillful technical assistance of J. C. Ameline and L. Legoupil. One of us (R.C.L.) wishes to thank the National Science Foundation—Centre National de la Recherche Scientifique Exchange of Scientists Program and two of us (R.C.L. and J.R.C.) wish to thank Centre National de la Recherche Scientifique for temporary positions.

---

[a]Permanent address: Institute of Physics, University of Zagreb, YU-41001 Zagreb Yugoslavia.

[1]P. Monceau, N. P. Ong, A. M. Portis, A. Meerschaut, and J. Rouxel, Phys. Rev. Lett. **37**, 161 (1976).

[2]See, for example, *Charge Density Waves in Solids,* Lectures Notes in Physics Vol. 217, edited by Gy. Hutiray and J. Solyom (Springer Verlag, 1985).

[3]P. A. Lee, T. M. Rice, and P. W. Anderson, Solid State Commun. **14**, 703 (1974).

[4]H. Fukuyama and P. A. Lee, Phys. Rev. B **17**, 535 (1978).

[5]R. C. Lacoe, H. J. Schulz, D. Jérome, K. Bechgaard, and I. Johannsen, Phys. Rev. Lett. **55**, 2351 (1985).

[6]For a review of x-ray and neutron diffraction experiments see R. Comés and G. Shirane, in *Highly Conducting One-Dimensional Solids,* edited by J. T. Devreese (Plenum, New York, 1978).

[7]R. H. Friend, M. Miljak, and D. Jérome, Phys. Rev. Lett. **40**, 1048 (1978).

[8]C. Weyl, D. Jérome, P. M. Chaikin, and K. Bechgaard, Phys. Rev. Lett. **47**, 946 (1981).

[9]S. Etemad, Phys. Rev. B **13**, 2254 (1976).

[10]M. C. Saint-Lager, Third Cycle Thesis, Université de Grenoble, 1983 (unpublished).

[11]P. Monceau, M. Renard, J. Richard, M. C. Lager, and Z. Z. Wang, in Ref. 2, p. 279.

[12]P. A. Lee and T. M. Rice, Phys. Rev. B **19**, 3970 (1978); T. M. Rice, P. A. Lee, and M. C. Cross, Phys. Rev. B **20**, 1345 (1979).

[13]W. L. McMillan, Phys. Rev. B **12** 1187 (1975), and **14**, 1496 (1976).

[14]M. J. Rice, A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Phys. Rev. Lett. **36**, 432 (1976).

[15]W. P. Su, J. R. Schrieffer, and A. J. Heeger, Phys. Rev. Lett. **42**, 1698 (1979), and Phys. Rev. B **22**, 2099 (1980); W. P. Su and J. R. Schrieffer, Phys. Rev. Lett. **46**, 738 (1981).

[16]M. Weger and B. Horovitz, Solid State Commun. **43**, 583 (1982).

[17]J. A. Wilson, Phys. Rev. B **19**, 6456 (1979).

[18]S. E. Burkov and V. L. Pokrovsky, Solid State Commun. **46**, 609 (1983).

[19]C. Roucau, R. Ayrolles, H. Salva, Z. Z. Wang, P. Monceau, L. Guemas, and A. Meerschaut, to be published.

[20]H. Salva, Z. Z. Wang, P. Monceau, J. Richard, and M. Renard, Philos. Mag. B **49**, 385 (1984).

[21]C. Schlenker and J. Dumas, *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures* (D. Reidel, Dordrecht, 1986) p. 135.

[22]S. Barsic, in *Low-Dimensional Conductors and Superconductors,* edited by L. Caron and D. Jérome (Plenum, New York, 1987). We thank S. Barisic for making this remark.