Observation of Nonlinear Electrical Transport at the Onset of a Peierls Transition in an Organic Conductor

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The *b*-axis conductivity was measured as a function of the electric field E for temperatures $T > 34$ K in the one-dimensional organic conductor TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane). Deviations from Ohm's law, with a threshold field E_T, have been observed for $T < 60$ K. E_T reaches a minimum of 0.25 V/cm just below the onset of the 54-K Peierls transition before increasing to 6.4 V/cm at 34 K. The results are discussed in terms of the depinning of the charge-density-wave condensate at high fields; the interaction between the two types of chains in TTF-TCNQ is included.

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Nonlinear electrical transport phenomena have been observed in a variety of organic[1-5] and inorganic[6] reduced-dimensional conductors and semiconductors. Both single-particle models (interrupted strand model,[7] hot electrons[3]) and many-body theories[6] [depinning of charge-density waves (CDWs), solitons, macroscopic quantum tunneling] have been employed to interpret the results. In the inorganic materials[6] (e.g., $NbSe_3$, TaS_3, $K_{0.3}MoO_3$, . . .), the nonlinear effects are generally interpreted as resulting from CDW depinning. The mechanisms which can pin a CDW are impurity pinning,[8,9] commensurability pinning,[8] and Coulomb interaction between oppositely charged chains in two-chain systems. If the energy associated with an external electric field is sufficient to overcome the pinning energy, the CDW will carry current and, hence, contribute to the conductivity.

Structural studies[10] indicate there are three successive phase transitions in the organic one-dimensional two-chain conductor TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane). EPR,[11] ^{13}C NMR,[12,13] thermoelectric-power,[14] and isotope-effect[15] measurements indicate that the TCNQ (electronlike) stacks distort at the upper Peierls phase transition at 54 K (T_H) while the lower two transitions at 49 and 38 K (T_M and T_L, respectively) involve the TTF (holelike) stacks. The periodic lattice distortion associated with the Peierls transitions is incommensurate with the underlying lattice along the *b* (stacking) direction. Hence, in the narrow temperature (T) range $T_H > T > T_M$, TTF-TCNQ is a single-chain incommensurate CDW semimetal and the only remaining pinning mechanism is impurity pinning.

Several low-temperature ($T < 20$ K) studies[1-3] indicate there are large non-Ohmic effects in TTF-TCNQ, and microwave experiments[16] indicate that nonlinear effects appear at the phase transition also. In this Letter we present measurements of the field-dependent conductivity of TTF-TCNQ in the range 34 K $< T <$ 300 K. We will show that the conductivity is field dependent below 60 K with a threshold field which reaches a minimum of 0.25 V/cm at 51.5 K. The results will be discussed in terms of a pinned CDW picture where the effect of oppositely charged CDW chains below T_M is included.

Single crystals of TTF-TCNQ with typical dimensions $4 \times 0.3 \times 0.03$ mm^3 and typical room-temperature conductivities $\sigma_{RT} \sim 520\ \Omega\ cm^{-1}$ were mounted in a four-probe configuration for conductivity measurements. 17.5-μm thermally annealed gold wires were attached to the samples with silver paint; contact resistances of $\sim 1\ \Omega$ were achieved. For several samples, gold pads were evaporated onto the samples before the application of silver paint. These yielded exactly the same results as silver-paint-only contacts.

In order to minimize and compensate for Joule heating of the samples, a short dc pulse technique was employed. Pulses with widths of 5–20 μsec were used with duty cycles between 10^4 and 10^5. Because of the high conductivity and relatively large cross sections of the samples, it was often necessary to use pulses corresponding to currents of 1 A in order to achieve high electric fields (~ 10 V/cm). Experiments were performed in a double-can cryostat which allowed temperature stabilization of better than 20 mK/h over the whole temperature range studied, while permitting several Torr of He^4 exchange gas in the sample space. During cooldown, sample resistance was monitored by use of standard low-frequency ac techniques to ensure that there were no microcracks, as reflected by jumps in the resistance, in the samples. We have seen here, as has been seen in other organics,[4] that associated with microcracks are anomalously large nonlinear effects. We have treated these effects as extrinsic and have discarded the results from such samples. Although measurements were made on seven samples of varying lengths of TTF-TCNQ, we present here the results for one sample. The results were qualitatively identical for all samples measured. The temperature dependence of the low-field resistivity ρ of our TTF-TCNQ samples is similar to that previously reported.[17] For $T > 60$ K, a T^2-type temperature dependence was observed, while below 54 K (T_H) ρ is activated with activation energy $\Delta \sim 331$ K in the range 49 K $> T_c > 38$ K. For the sample discussed, $\sigma_{\max}/\sigma_{\mathrm{RT}} = 15.7$.

At room temperature, no deviations from Ohm's law were seen for fields up to 8 V/cm. Figure 1 presents the conductivity normalized to the low-field Ohmic conductivity (σ_0) versus the logarithm of the electric field at various temperatures. At 90 K, σ is constant to within 2% for fields up to 10 V/cm. However, at 59 K σ is constant until a threshold field ($E_T = 2.5$ V/cm) is reached, above which σ increases. Similar behavior is seen down to 53 K. It is in this temperature range that the onset and stabilization of three-dimensional order between TCNQ CDW chains is established,[11-15] resulting in the observed precursor leveling of the low-field conductivity.

Below 53 K, the threshold field drops sharply (Fig. 2), reaching a minimum of 0.25 V/cm at 51.5 K, and rising only slightly down to 49 K. As shown in the Fig. 1 inset, the conductivity increases roughly linearly with the field. In this temperature range TTF-TCNQ is a single-chain CDW semimetal. It should be noted that the sample resistance at 90 K, where deviations from Ohm's law are less than 2%, is the same as that at 51.5 K, where large deviations from Ohm's law are observed.

Below 49 K, the threshold field increases rapidly down to the lowest temperature measured, 34.5 K, where $E_T = 6.4$ V/cm. The inset in Fig. 2 shows the threshold field normalized to the minimum threshold field versus the temperature normalized to the Peierls temperature T_{P} for TTF-TCNQ ($T_{\mathrm{P}} = 54$ K) and for the lower Peierls transition ($T_{\mathrm{P}} = 59$ K) of NbSe$_3$.[18] Near T_{P}, the threshold behavior is similar for the two materials, while below the minimum in E_T, E_T increases much more rapidly in TTF-TCNQ. Figure 3 shows the excess current associated with the extra conductivity [$J_{\mathrm{ex}} = (\sigma - \sigma_0)E$] versus electric field at 49.5 K.

The onset of non-Ohmic conductivity at the same temperature as the onset of three-dimensional CDW order strongly suggests that the nonlinearity is associated with the appearance of CDWs. Indeed, it is difficult to explain the low threshold fields at which deviations from Ohm's law are observed by models based on a single-particle picture.[2,4,19] For example, a hot-electron theory[3] requires mobilities of 10^5 cm^2/V·s and predicts a threshold field which increases with increasing temperature.

In the absence of any coupling between TTF and TCNQ chains, an electric field would lead to CDW motion in opposite directions on the two-chain system because of the electron (TCNQ) and the hole (TTF) character of the electronic bands. A nonzero coupling

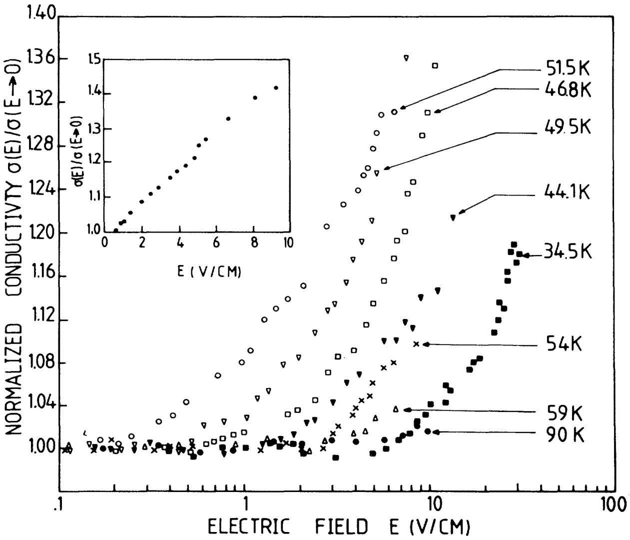

FIG. 1. Normalized conductivity $\sigma(E)/\sigma(E \rightarrow 0)$ vs log$E$ of TTF-TCNQ. The inset shows the linear behavior of $\sigma(E)/\sigma(E \rightarrow 0)$ vs E at $T = 49.5$ K.

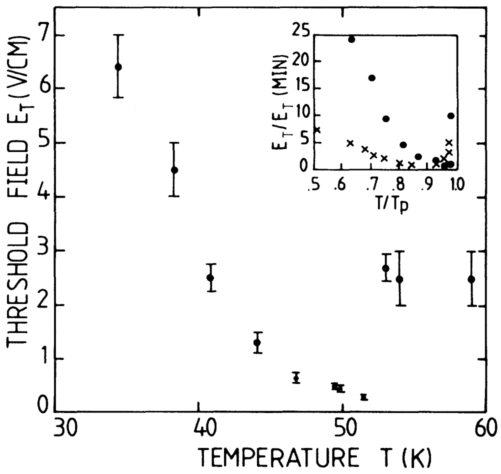

FIG. 2. Threshold field E_T vs T of TTF-TCNQ. The inset shows E_T normalized by the minimum threshold field E_T(min) vs T normalized to the Peierls temperature T_{P} for TTF-TCNQ ($T_{\mathrm{P}} = 54$ K) (crosses), and NbSe$_3$ ($T_{\mathrm{P}} = 59$ K) (filled circles).

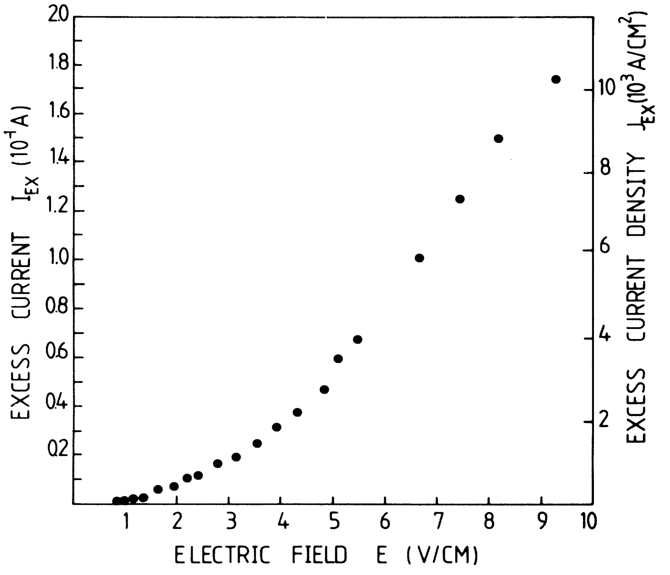

FIG. 3. Excess current vs E of TTF-TCNQ at $T = 49.5$ K.

then leads to an effective commensurability pinning[8, 20] and the resulting net current depends on the intervening CDW charge densities, as discussed below. On the other hand, impurity pinning is expected to act equally on both chain systems.

In order to understand the role of different pinning mechanisms in the nonlinear transport, especially in a temperature region where the CDWs have quite different temperature dependences on the TTF and TCNQ chains, we use a Landau-type free energy[21] for the coupled system of CDWs:

$$f = f_0 + \lambda\rho_Q\rho_F\cos 2\phi_- + (eE/\pi) \times [(\rho_{cQ} - \rho_{cF})\phi_+ + (\rho_{cQ} + \rho_{cF})\phi_-], \qquad (1)$$

where ρ_F (ρ_Q) is the CDW amplitude of the TTF (TCNQ) chain, $\phi_\pm = (\phi_Q \pm \phi_F)/2$ where ϕ_F and ϕ_Q are the CDW phases, and ρ_{cF} and ρ_{cQ} are the fraction of carriers condensed into the CDW. The CDW current is given by

$$J = (e/\pi)[(\rho_{cQ} - \rho_{cF})\dot{\phi}_+ + (\rho_{cQ} + \rho_{cF})\dot{\phi}_-]. \qquad (2)$$

Near T_c, $\rho_{ci} \propto \rho_i$, but for low temperatures $\rho_{ci} \approx 1$, independent of ρ_i.[20] In Eq. (1) f_0 describes the TTF and TCNQ chains separately, the second term is the coupling between them (mainly due to the Coulomb interaction), and the last term describes the coupling to the electric field. It is important to note that because of the electron (hole) character of the TCNQ (TTF) bands, the two types of chains intervene with opposite signs in Eqs. (1) and (2).

As a function of ϕ_-, f has a stable minimum as long as

$$eE < eE_T = \frac{2\pi\lambda\rho_Q\rho_F}{(\rho_{cQ} + \rho_{cF})}. \qquad (3)$$

In a purely classical picture, only for $E > E_T$ is a dc current *with nonzero* ϕ_- possible. Saub, Barisic, and Friedel[22] found $\lambda = e^2 K_0(2k_F d)$, where d is the interchain distance. With the assumption that at low temperatures $\rho_Q\rho_F \sim 10^{-2}$ (molecule)$^{-2}$ (see Berlinsky[23]) and $\rho_{ci} = 1$, one finds $E_T \sim 5\times 10^4$ V/cm. This value is consistent with the optically observed phase-mode frequency.[24] A similar order of magnitude is found for E_T from Maki's soliton-pair-creation model.[25] From these estimates, it seems clear that the motion of the TTF and TCNQ CDWs *in opposite directions,* which carries the maximum CDW current [Eq. (2)], cannot be responsible for the nonlinear effects found here with $E_T \sim 1$–10 V/cm. On the other hand, in TTF-TCNQ for $T_H > T > T_M$, there is a CDW only on the TCNQ chains, and even below T_M the initial growth of the TTF CDW is quite slow. Consequently, there is a fairly wide temperature range where $\rho_{cQ} - \rho_{cF}$ differs appreciably from zero, so that the motion of both TCNQ and TTF chains *in the same direction* carries a net current (and couples to the field). The main pinning mechanism will be impurity pinning, giving typical $E_T \sim 1$ V/cm for a single chain. Assuming the pinning is mainly due to the TCNQ chain, one would find in our model $E_T = E_{T0} \times [\rho_{cQ}/(\rho_{cQ} - \rho_{cF})]$, where E_{T0} is the impurity-induced threshold field for the single-chain system, and, hence, a steeper increase in E_T with decreasing temperature than for a single-chain system (which will be even steeper if impurity pinning to the TTF chain is included). This may well explain the threshold-field dependence on temperature found in TTF-TCNQ, as shown in Fig. 2, where we see that E_T increases much faster than in the single-chain system NbSe$_3$.[18] Also, from Eq. (2) one sees that the CDW current decreases with decreasing temperature (decreasing $\rho_{cQ} - \rho_{cF}$), again in qualitative agreement with our results. This decrease is much steeper than is seen for the trichalcogenides. For example, for TaS$_3$ [26]

$$J_{\mathrm{ex}}(T/T_\mathrm{P} = 0.70)/J_{\mathrm{ex}}(T/T_\mathrm{P} = 0.95) = 0.56$$

at $E - E_T = 8$ V/cm, while for TTF-TCNQ it equals $\sim 2\times 10^{-2}$.

In conclusion, we have shown that there are strong deviations from Ohm's law in TTF-TCNQ for $T < 60$ K, the temperature at which three-dimensional CDW order sets in. To our knowledge, this is the first observation of nonlinear transport at the onset of a Peierls transition in an organic conductor. The threshold field reaches a minimum in the temperature range where TTF-TCNQ is a single-chain (TCNQ) CDW semimetal, and increases rapidly with the development of CDWs on the second (TTF) chain. We suggest a model which qualitatively explains the temperature dependence of the threshold field and the excess current.

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