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Nonlinear Transport in Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ) at Low Temperatures*

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(Received 15 July 1976)

An experimental study of electrical transport phenomena in TTF-TCNQ in the low-temperature ($T<4.2$ K) dielectric regime is reported. The current-voltage curves are nonlinear with conductance increasing with increasing voltage. The observed nonlinearity is insensitive to radiation-induced defects at the fraction of a percent level. The data are discussed in terms of electric field depinning of the incommensurate charge-density wave with a critical electric field of approximately 1.5×10^2 V/cm.

Extensive studies of the electrical conductivity of TTF-TCNQ have generally focused on two temperature ranges—the one-dimensional metal regime at $T>58$ K[1-6] and the region 38 K$<T<58$ K[7-9] in which a series of three electronic structural transitions have been observed.[10-14] In the dielectric regime below 38 K, the charge-density waves (CDW) are pinned by interchain coupling resulting in a three-dimensional superlattice with $a_s=4a$, $b_s=3.4b$, and $c_s=c$ (where a, b, and c are the lattice parameters of the undistorted structure).[10,12,14,15] However, the unusually large low-frequency dielectric constant[16] and the related low resonance frequency[17] for the coherent pinned phase mode imply relatively weak pinning forces. The question which we have approached experimentally is whether the application of an electric field at low temperatures ($T\ll38$ K) can cause the weakly pinned CDW condensate to depin (partially) and thereby become conducting. We report[18] in this Letter the results of an experimental study of nonlinear transport phenomena in TTF-TCNQ at low temperatures.

All measurements of the current-voltage characteristics were carried out on single crystals of TTF-TCNQ with use of the standard four-probe arrangement, with the sample immersed in the liquid-helium bath. Low current levels (<1 μA) were supplied by a simple dividing network using a battery source and were measured with a Kiethley 160B multimeter. At higher current levels, measurements were carried out in both controlled-current and controlled-voltage configurations with either an electronic measurements C612 constant current supply or a Hewlett-Packard dc power supply in series with a battery. In all cases, the voltage across the sample was measured using a Kiethley 610B electrometer as a high-impedance buffer (gain of one) connected to a Keithley 160 multimeter.

Figure 1 shows the I-V curves of a crystal of TTF-TCNQ measured along the principal conducting b axis. The I-V curves are nonlinear, with the dynamic conductance, dI/dV, increasing with increasing voltage. As the temperature is lowered, the low-field conductance decreases, but the degree of nonlinearity increases dramatically. The I-V curves qualitatively appear to be approaching an off-on situation at $T=0$ K where current is not generated until a "critical" electric field is reached. The degree of nonlinearity is illustrated in detail in the full logarithmic plot. The results shown in Fig. 1 represent current levels as low as 10^{-10} A and power inputs as low as 10^{-11} W. The solid line represents ohmic behavior and is shown for comparison. At the lowest temperatures, the I-V characteristics of TTF-TCNQ are nonlinear over the entire range meas-

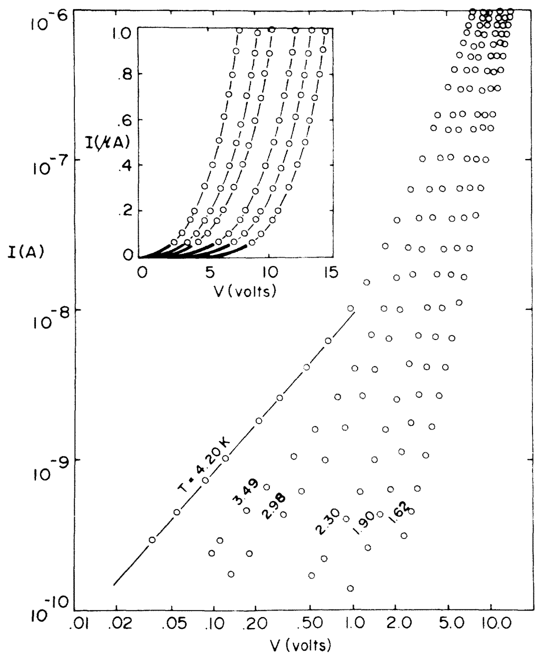

FIG. 1. Logarithmic plot of ***I*** vs ***V*** for TTF-TCNQ showing the nonlinear transport at low temperatures. The data are plotted as ***I*** vs ***V*** in the inset.

ured.

To clarify any possible role of crystalline defects or imperfections in these nonlinear transport phenomena, we have initiated a study of the effects of radiation damage on the electrical properties of TTF-TCNQ. Samples were bombarded with a total flux of 5×10^{14} cm^{-2} of 8-MeV deuterons from the University of Pennsylvania tandem accelerator. Crystals of TTF-TCNQ of typical thickness (50 μm) are essentially transparent to 8-MeV deuterons which lose approximately 100 KeV during passage.[19] The induced damage was monitored by observing the room-temperature resistance during irradiation; initial studies were on samples with room-temperature resistance increased by 20%. The electron spin resonance of the damaged samples at 4.2 K indicates an induced concentration of spin-$\frac{1}{2}$ impurities of order of 0.1%.

The low-temperature I-V curves were measured before and after irradiation with several important results. The low-field ohmic conductance at 4.2 K was increased by more than two orders of magnitude and was sample-independent. This defect contribution to the low-temperature transport is *ohmic* and described by $\sigma_d = \sigma_d^0 \exp(-E_d/T)$, with $E_d = 20$ K. The previously observed nonlinearity is masked at 4.2 K by the larger defect contribution. At 1.6 K, where σ_d is small and unimportant, the nonlinearity shows up clearly with identical curvature as a function of applied voltage. The absolute current density was reduced by a constant factor of 3 because of the irradiation-induced defects. The effect of radiation-induced damage on the full range of electronic properties of TTF-TCNQ is of significant interest and is being actively pursued. For the purposes of this Letter, the preliminary results outlined above bear directly on the question of the origin of the observed nonlinearity.

A trivial source of nonlinearity in a semiconductor sample is self-heating.[20] The ohmic behavior of the irradiated samples at 4.2 K when combined with the measured temperature dependence of σ_d allows an upper limit for self-heating of order 0.1 K at an input power level of 10^{-3} W. Since the data of Fig. 1 are restricted to power levels below 10^{-5} W, the maximum sample heating is less than 10^{-3} K, or completely negligible. This experimental upper limit is consistent with independent estimates based on values of the thermal conductivity as inferred from thermal time constants observed in low-temperature heat capacity measurements.

Transport studies of TTF-TCNQ have revealed the existence of contact resistance at the silver-paint–sample interface.[21] Although the contacts have been shown to be ohmic at higher temperatures,[2-4] nonlinearity resulting from rectifying contacts at low temperatures must be considered. We have repeated the measurements in a two-probe configuration using all possible combinations of the four leads. Because of the high input impedance of the measuring circuit ($>10^{14}$ Ω), only 10^{-5} of the measuring current passes through the voltage contacts in the four-probe configuration whereas all the current passes through the volatge contacts in the two-probe measurement. In all cases, the two-probe and four-probe data were identical with the magnitude of the voltage scaling with the intercontact spacing (i.e., an electric-field effect). Since a factor-of-10^5 change in current through the voltage contacts caused no change in I-V characteristics, we conclude that the observed data do not result from contact rectification.

The I-V characteristics of a semiconductor can be nonlinear if the number of carriers is determined by the applied electric field through injection, impact ionization by accelerated carriers, or field ionization of neutral impurities. Each of these mechanisms can be ruled out on theoretical grounds. To achieve the measured current densities by injection would require a mobility in excess of 10^3 cm^2/V sec.[22] Similarly, impact ionization at the observed electric field of order 10^2 V/cm of carriers with activation energy or order 20 K would require $\mu > 10^3$ cm^2/V sec.[23] These values are three to four orders of magnitude greater than found in even the purest single-crystal organic semiconductors. Moreover, defects and chain breaks are especially important in quasi-one-dimensional systems and will limit the mobility. Field ionization is a tunneling process and the available energy is determined by the applied electric field integrated over the length of the impurity wave function. To ionize carriers with binding energy of order 20 K with $E \simeq 10^2$ V/cm would require that the impurity wave function extend over lengths of order 10^3 Å. Direct experimental evidence that these traditional mechanisms are not involved in the present observations comes from the relative insensitivity of the low-temperature nonlinearity to induced defects at the fraction-of-a-percent level.

The I-V characteristics of more than twenty-five samples have been studied. In all cases, nonlinear I-V curves were observed. The data from Fig. 1 are replotted in Fig. 2 as $\ln I$ versus $1/T$ at fixed electric field (fixed voltage). The general features are those of a thermally activated conductivity, with the activation energy, Δ/k_B, decreasing with increasing electric field. The field-dependent activation energy as obtained from the slopes of the curves is plotted in the inset to Fig. 2, which shows Δ decreasing approximately linearly with increasing field and extrapolating to zero at $E_0 \simeq 125$ V/cm. Thus for $E < E_0$, the data are adequately described by an expression of the form $j/E = \sigma_0 \exp[-(1 - E/E_0)\Delta/T]$. The value for E_0 as obtained from several samples is 150 ± 50 V/cm, with the variation from sample to sample consistent with the errors involved in determining the distance between voltage contacts on the small samples. The activation energy is approximately $\Delta/k_B = 14$ K with little variation (± 1 K) from sample to sample. The prefactor, σ_0, is somewhat sample-dependent, ranging from 5×10^{-5} to 3×10^{-4} (Ω cm)$^{-1}$ with a typical value of 10^{-4} (Ω cm)$^{-1}$. The irradiation experiments suggest that σ_0 is dependent on sample perfection as described above. For $E < E_0$, the prefactor is only weakly field-dependent, with σ_0 increasing by less than a factor of 2 whereas j/E changes by three orders of magnitude at the lowest temperatures (Fig. 2). Preliminary evidence suggests that at higher fields ($E \geq E_0$) the prefactor increases more rapidly, approximately exponentially, with increasing electric field. Pulsed measurements are underway to characterize fully this high-current regime.

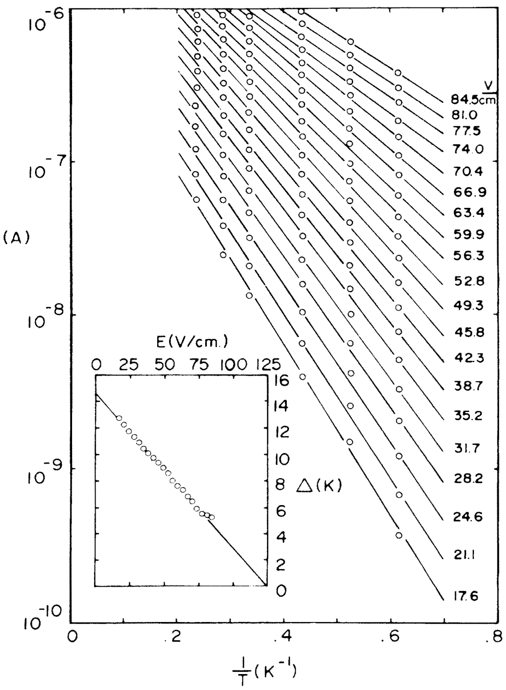

FIG. 2. $\ln I$ vs T^{-1} at various values of the applied electric field. The solid lines represent least-squares fits to the data at each field. The field-dependent activation energy is shown in the inset.

The critical field for depinning the CDW at $T = 0$ K can be estimated from the following argument. We assume a pinning potential $V(\varphi) = V_0 f(\varphi)$, where $f(\varphi)$ is periodic in φ. The real-space periodicity would depend on the pinning mechanism.[24] If the pinning is due to high-order commensurability for example, the potential would be periodic in the equilibrium lattice constant, $\varphi = (2\pi/b)x$. If the pinning arises from interchain Coulomb interactions, the potential would be periodic in the superlattice constant [i.e., $\varphi = (2\pi/\lambda_s)x$, where $\lambda_s = 3.4b$ for TTF-TCNQ]. In order to depin, the electric field energy in moving the CDW a periodicity length (l) must be greater than V_0; thus, $E_c \sim V_0/l$. In the simplest case, $f(\varphi) = 1 - \cos\varphi$ and V_0 can be related to the fundamental pinning frequency, ω_F, and the Fröhlich effective mass M^* by expanding about the pinned equilibrium and retaining only the harmonic term.[25] We have then

$$E_c = \frac{M^* \omega_F^2}{el} \left(\frac{d\varphi}{dx} \bigg|_0 \right)^{-2}. \quad (1)$$

Using values of M^* and ω_F^2 from infrared studies,[17] we obtain E_c of order several hundred volts per centimeter (a rough estimate due to uncertainties in the values of the parameters) and, more importantly, the actual form of $f(\varphi)$. For a rigid CDW, the nonlinear current density would be zero at $T=0$ K for $E<E_c$. Inhomogeneous pinning or phase-soliton excitations[24] will allow thermally activated precursor effects to show up below the critical field. We therefore identify E_c with the field needed to reduce the activation energy to zero; $E_c \simeq 1.5\times10^2$ V/cm. From this point of view, the CDW conductivity in this regime ($E \gtrsim E_c$) is itself nonohmic, increasing approximately exponentially with applied field.

In summary, we have presented an initial experimental study of the nonlinear electrical transport in TTF-TCNQ at low temperatures. The insensitivity of the I-V nonlinearity to induced defects argues against traditional semiconductor mechanisms. The results were discussed in terms of the onset of electric-field depinning of the charge-density wave.

We are grateful to Professor J. Krumhansl, Dr. A. Bishop, and Dr. S. Trullinger for important discussions and considerable encouragement. The irradiation experiments could not have been done without the help of Professor R. Zurmuhle and Mr. L. Mulligan. We thank Mr. William Gunning, Mr. L. Scott Smith, and Mr. Fred Klinker for help on several aspects of the problem.

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*Work supported by the National Science Foundation under Grant No. DMR-74-22923 and through the Laboratory for Research on the Structure of Matter (under Grant No. DMR-72-03025), and by the Advanced Research Projects Agency under Grant No. DAHC-15-72-C-0174.

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