Non-Ohmic Electrical Transport in the Spin-Density-Wave State of Tetramethyltetraselenafulvalinium Nitrate, $(TMTSF)_2NO_3$

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Electric-field–dependent measurements are reported in the spin-density-wave state of the organic conductor $(TMTSF)_2NO_3$. Nonlinearity appears in the longitudinal conductivity above a finite threshold field of about 40 mV/cm. No temperature dependence is detectable up to at least half of the transition temperature. The excess conductivity is smaller in samples with a lower resistance ratio. The sliding spin-density-wave mode might be responsible for the observed electric-field–dependent response.

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A substantial number of highly anisotropic conductors, both inorganic and organic, have been discovered and studied in the past fifteen years. Depending on the material and the applied pressure, there is usually a phase transition to a superconducting, a charge-density-wave (CDW), or a spin-density-wave (SDW) ground state at low temperatures.

For CDW materials such as $NBSe_3$, TaS_3, $K_{0.3}MoO_3$, and tetrathiafulvalinium-tetracyanoquinodimethanide (TTF-TCNQ) it is now well established that below the Peierls transition the coupled electron-phonon collective mode contributes to the electrical conductivity as originally proposed by Fröhlich.[1] However, because the CDW is pinned by impurities a finite threshold field is needed for CDW conductivity[2] (in TTF-TCNQ the Coulomb interaction between oppositely charged chains and, under pressure, the lattice commensurability are also sources of pinning). Hence, nonlinear current-voltage characteristics accompanied by broad- and narrow-band noise, with sharp threshold fields of the order of 10–1000 mV/cm, are a signature of CDW motion.

Theoretically, similar behavior might be expected for a SDW state,[3] because collective transport does not depend on the nature of the underlying interaction mechanism (electron-electron rather than electron-phonon). Furthermore, a SDW can be regarded as two CDW's of opposite phase and spin. The SDW model systems are some members of the $(TMTSF)_2X$ family in which the SDW nature of the ground state has been firmly established by magnetic measurements.[4,5] Frequency-dependent conductivity measurements in the SDW state of $(TMTSF)_2PF_6$ can be interpreted in terms of a collective SDW mode with pinning as for a CDW.[6] Attempts to measure the electric-field-dependent response have failed to identify nonlinear effects up to now, because of experimental problems related to contacts and heating effects. In $(TMTSF)_2PF_6$ samples nonlinear conduction was found with no threshold field and its magnitude was correlated with resistance jumps developed during cooling.[6,7] Recently, non-Ohmic transport was reported in the magnetic-field-induced SDW state in $(TMTSF)_2ClO_4$ and interpreted as the first evidence for SDW sliding due to the applied voltage exceeding a threshold value.[8] However, because the measured resistance actually increased with voltage, it was suggested that the nonlinearity occurred only in the transverse component of the conductivity. The measured threshold field was very small and undetectable in some samples.

$(TMTSF)_2NO_3$ appears to be somewhat special among the extensively studied members of the $(TMTSF)_2X$ family. At ambient pressure a metallic state persists down to about 10 K, where a phase transition to a semiconducting SDW state takes place.[9,10] Structural investigations show a superstructure $(2a,b,c)$ below 45 K due to the ordering of noncentrosymmetric NO_3 anions.[11] This superstructure corresponds to a $(2k_F,0,0)$ wave vector which does not give nesting and hence does not give a gap over the whole Fermi surface.[12] Indeed, the electrical resistivity actually falls at the anion ordering transition. In contrast, the SDW wave vector is presumably very near to the optimal nesting vector and therefore leads to a gap over the whole Fermi surface. Under pressure, the SDW transition is suppressed, but superconductivity has not been observed up to 24 kbars.[13]

In this Letter we report the results of experiments on the electric-field–dependent conductivity in the SDW state of (TMTSF)$_2$NO$_3$. We find that the conductivity becomes field dependent above a threshold field of about 40 mV/cm. This threshold field is temperature independent below 6 K. Furthermore, the magnitude of the nonlinearity is smaller in samples with a lower resistance ratio. We will show that such behavior might well be explained in the framework of recent theories for a sliding SDW mode pinned to nonmagnetic impurities.

The measurements were performed on single crystals of (TMTSF)$_2$NO$_3$ of varying lengths and with typical dimensions $2\times0.5\times0.03$ mm^3. Gold pads were evaporated onto the samples and 17-μm thermally annealed gold wires were attached to the pads with silver paint in the four-probe configuration. Samples were cooled slowly from room temperature (RT) at 2 to 6 K per hour in order to avoid resistance jumps which are known to appear in all (TMTSF)$_2X$ compounds. We observed very few cracks as reflected by only one or two small resistance jumps near 100 K. The total increase in resistance caused by the cracks never exceeds 0.5% of the sample resistance at 100 K. The temperature dependence of the low-field resistance of two (TMTSF)$_2$NO$_3$ samples is shown in Fig. 1. There is a clear change in slope at 45 K revealing the onset of the anion ordering. A plot of log$R$ vs $1/T$ below the SDW transition at $T_c\approx11$ K is shown in the inset of Fig. 1. The activation energy is small, of order 10^{-3} eV at 4.2 K, but the curvature of the log$R$ vs $1/T$ plot indicates that the ground state may be semimetallic, as for NbSe$_3$, rather than semiconducting.

To search for electric-field–dependent transport in the SDW state, we used a short-dc-pulse technique together with a bridge circuit to subtract the Ohmic component of the conductivity, similar to that used previously for TTF-TCNQ.[14] The standard pulse length was 40 μsec with a dead time of about 5 μsec and a repetition time of 23 msec. Care was taken to avoid the influence of heating. As usual two tests for sample heating were made. Possible heating during a single pulse could be detected by monitoring the out-of-balance signal from the bridge versus time on the oscilloscope, from 5 to 40 μsec after the start of the pulse. If this signal increased linearly with time, corrections for heating could be made by extrapolating back to the onset of the pulse. However, above certain fields (of the order of 100 mV/cm at 4.2 K and less than 40 mV/cm above 6 K, depending on the contact resistances) the heating after 20 μsec became too large for this procedure to be accurate. Consequently we could not obtain data outside this field and temperature range. Any overall increase in the sample temperature was ruled out by varying the repetition rate of the pulses. As a further check for intrinsic nonlinearity, I-V characteristics were also measured in the metallic region between 80 and 100 K, where the sample resistance was close to that at 4.2 K. Here we report results for three samples with different resistivity ratios (RR) $\rho_{\mathrm{RT}}/\rho_{\mathrm{min}}$, where ρ_{RT} and ρ_{min} are the resistivities measured at RT and at 11 K, respectively.

Figure 2(a) shows the field-dependent conductivity for sample 1 (which has an extremely high RR, ≈750) normalized to the low-field Ohmic conductivity (σ_0) versus the logarithm of the electric field at various temperatures. At 100 K the conductivity stays constant ($\sigma=\sigma_0$)

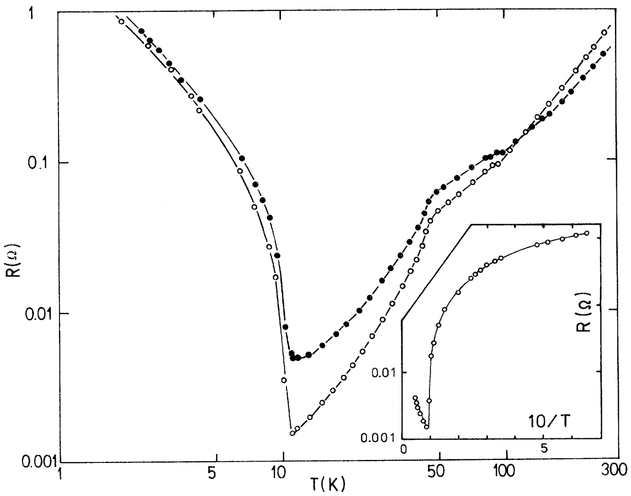

FIG. 1. Log-log plot of resistance vs temperature for two (TMTSF)$_2$NO$_3$ samples. Open and filled circles are for samples 1 and 2, respectively. Inset: plot of log$R$ vs $1/T$ for sample 1.

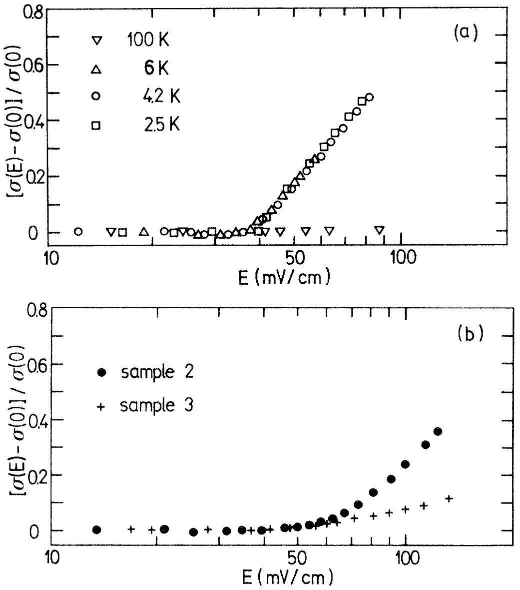

FIG. 2. Non-Ohmic conductivity $\sigma(E)-\sigma(E\rightarrow0)/\sigma(E\rightarrow0)$ vs logarithm of electric field (E) for (TMTSF)$_2$NO$_3$: (a) at various temperatures for sample 1 (RR ≈750) and (b) at 4.2 K for sample 2 (RR ≈130) and sample 3 (RR ≈30).

to within 1% for fields up to 0.7 V/cm. However, at 4.2 K σ is constant until a threshold field is reached, above which it increases sharply. For electric fields equal to twice the threshold field, the field dependence of the conductivity $(\sigma-\sigma_0)/\sigma_0$ reaches 50% of the low-field value. Experiments made at different temperatures from 1.6 to 6 K yield essentially the same result: $E_T=38\pm2$ mV/cm and the magnitude of the excess conductivity keeps the same value to within 10%.

For samples with smaller resistivity ratios (RR $\approx$ 130 and 30 for sample 2 and sample 3, respectively) the field dependence of the conductivity is smoother and its magnitude for a particular electric field is smaller [Fig. 2(b)]. Again, no temperature dependence of either E_T or $[\sigma(E)-\sigma_0]/\sigma_0$ was observed below 6 K. Figure 3 shows the excess current associated with the field-dependent conductivity, $j_{\mathrm{ex}}=(\sigma-\sigma_0)E$, as a function of electric field at 4.2 K.

We note that an electric field of about 40 mV/cm provides much smaller energy (ϵ) on a microscopic length scale than k_BT, namely, $\epsilon/2kT<10^{-2}$. This can be estimated as follows. The electronic mean free path of the $(\mathrm{TMTSF})_2X$ salts is typically 7 Å at RT. The highest values reported at low temperatures (just above the superconducting transition temperature of the $\mathrm{ClO_4}$ salt) are about 2000 times larger, i.e., 14000 Å. Thus the maximum energy obtainable from the electric field is 0.06 K. Provided the inelastic electron mean free path is not substantially larger than the above value in the range 6 to 1.6 K, electron heating effects can be ruled out as the source of substantial nonlinearity. In any case the latter would be expected to be strongly temperature dependent in contrast to the experimental findings. Electron heating effects were discussed in detail for $(\mathrm{TMTSF})_2\mathrm{PF}_6$.[15] It was found that the usual type of hot-electron effects cannot give more than a 10% increase in conductivity, which is consistent with the above argument. However, we cannot entirely rule out the additional hot-electron mechanism proposed in Ref. 15 involving a spatially inhomogeneous gap, although again one might expect this to be temperature dependent, in contrast to the behavior found experimentally. The threshold fields are also far too low for Zener breakdown to be relevant. Therefore, we conclude that the observed nonlinearity cannot be attributed to hot-electron effects or to the destruction of the condensed state by the electric field. Furthermore, our results are reminiscent of those in the charge-density-wave systems where the nonlinearities have been attributed to the sliding CDW becoming depinned in high enough electric fields, although one important difference is that in the present case E_T has been found to be temperature independent.

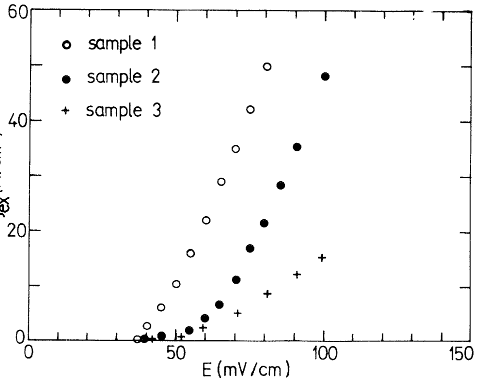

FIG. 3. Excess current (J_{ex}) vs electric field (E) for three samples of $(\mathrm{TMTSF})_2\mathrm{NO}_3$ at 4.2 K.

For an incommensurate SDW there also exists a translational spin-density-wave mode which theoretically is expected to give a collective conductivity similar to the CDW case.[16,17] To first order the SDW has a uniform charge density and one would expect the pinning to nonmagnetic impurities to be negligibly weak. However, recent theories developed independently by several authors suggest that there is a broad range of SDW pinning energies which could easily attain the values found for a CDW or could be even larger.[18,19] The starting idea is that an unperturbed, linearly polarized SDW can be decomposed into two out-of-phase CDW's formed by spin-up and spin-down electrons. Nonmagnetic impurities will pin the SDW by inducing a distortion of the total electron density near the impurity sites. This happens because the up- and down-spin components of the charge spin density deform differently to yield the net local charge. Basically, the problem is reduced to the coupling of the nonmagnetic impurities to the second-order harmonic CDW that coexists with the SDW.[18,19]

In a recent Letter, Tütto and Zawadowski[20] treat the same problem as a competition between the SDW and an impurity-induced CDW using the quantum-theory result that the pinning energy is a nonsinusoidal function of the phase. Again, the pinning is due to the mismatch of charge and spin oscillations, but the phase dependence is not canceled. Their calculation clearly shows that the SDW pinning energy can reach the values typically found in CDW systems.

Since the distortion produced by nonmagnetic impurities on the condensate appears to be qualitatively the same as for the CDW case, the existence of a threshold field and of narrow-band noise is expected. Recently, Maki and Virosztek[19] derived the following expression for the SDW threshold field in the strong-pinning limit, within the Fukuyama-Lee-Rice model, by treating the SDW pinning energy up to second order:

$$E_T(0)=(Q/e)(n_i/n_e)(\pi N_0 V)^2\Delta(0)\,, \qquad (1)$$

where $Q=2k_F$ is the SDW wave vector, e is the electronic charge, n_e is the electron concentration, and N_0 is the electronic density of states. V, n_i, and $\Delta(0)$ are the impurity potential, the impurity concentration, and the SDW gap, respectively. Taking $N_0V=0.1$, $\Delta(0)=10^{-3}$

eV, $Q = 2k_F = \pi/2a$, and n_i/n_e to be a few ppm, one gets $E_T(0) \approx 10$ mV/cm, which is close to the value we observe in $(\mathrm{TMTSF})_2\mathrm{NO}_3$. The temperature dependence is given by

$$\frac{E_T(T)}{E_T(0)} = \frac{\Delta(T)}{\Delta(0)} \tanh\left[\frac{\Delta(T)}{2T}\right] \frac{\rho}{\rho_s(T)}, \qquad (2)$$

where ρ is the total electron density and $\rho_s(T)$ is the density of electrons condensed in the SDW. From this equation, $E_T(T)/E_T(0)$ increases monotonically from unity at $T=0$ to 1.33 at $T=T_c$. However, in the temperature range over which we have been able to study the nonlinearity experimentally $(T_c/8 < T < T_c/2)$, Eq. (2) predicts that E_T is constant to within 10%. This agrees perfectly well with the experimental observation that E_T is temperature independent (Fig. 2). In contrast, within the same theoretical framework, E_T for a CDW exhibits a divergence at $T=T_c$ of the form $(1-T/T_c)^{-1/2}$ and a minimum slightly below T_c which results from an increase in E_T at low temperature due to phase fluctuations. This behavior is indeed observed in a number of experiments on CDW systems.

In conclusion, we have observed for the first time non-Ohmic electrical transport above a finite threshold field in the spin-density-wave state of an organic conductor. The threshold field is temperature independent at least below $T_c/2$. The magnitude of the field dependence is strongly sensitive to the resistance ratio and probably to the defect concentration. We suggest the sliding SDW mode as a plausible mechanism of the observed nonlinear effects. The recent model by Maki and Virosztek explains the magnitude and temperature dependence of the threshold field. More work needs to be done to establish the sharpness of the threshold using continuous electric fields, the influence of the pinning centers on E_T, and the behavior close to the transition temperature.

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