Study of Nonlinear Electric Field Effects in Tetramethyltetraselenefulvalene Hexafluorophosphate [$(TMTSF)_2PF_6$]

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Detailed field- and frequency-dependent conductivity measurements are reported in $(TMTSF)_2PF_6$. No threshold field and a small dielectric constant are found, implying the absence of restoring forces. No evidence is found for wide- or narrow-band noise in the nonlinear regime. This, together with the preliminary observation of a high mobility, suggests that single-particle effects are largely responsible for the nonlinear conductivity below the transition.

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Recently, Walsh *et al.*[1] reported the observation of nonlinear electric field effects (at very small fields) in the organic conductor *bis*-tetramethyltetraselenefulvalene hexafluorophosphate [$(TMTSF)_2PF_6$]. This material exhibits a number of other interesting properties that have attracted considerable attention: superconductivity under modest pressure,[2] a metal-insulator transition at rather low temperature ($T \sim 15$ K),[3] and an unusual magnetic response below $T = 15$ K.[4] Walsh *et al.*[1] suggest that their nonlinear dc conductivity results are similar to those observed in $NbSe_3$. They speculate, however, that it is a spin-density wave (SDW) rather than a charge-density wave (CDW) that is depinned by the small electric fields.

We report detailed experiments on electric-field- and frequency-dependent transport in $(TMTSF)_2PF_6$. We observe nonlinear conduction down to extremely low electric fields (10^{-4} V/cm) with the absence of a threshold field. The conductivity is independent of frequency up to 80 MHz with no out-of-phase component. Also, there is no noise associated with the nonlinear conductivity. These observations are dramatically different from those found in $NbSe_3$ and together with preliminary Hall measurements, which show high mobility below the transition, suggest that the nonlinear conductivity is due to single-particle effects below the transition.

The conductivity was measured by a four-probe pulse method to avoid heating effects at high electric fields. In the low-electric-field regime the derivative dV/dI was measured by an ac bridge technique as a function of dc bias. Figure 1(a) shows the resistance R as a function of electric

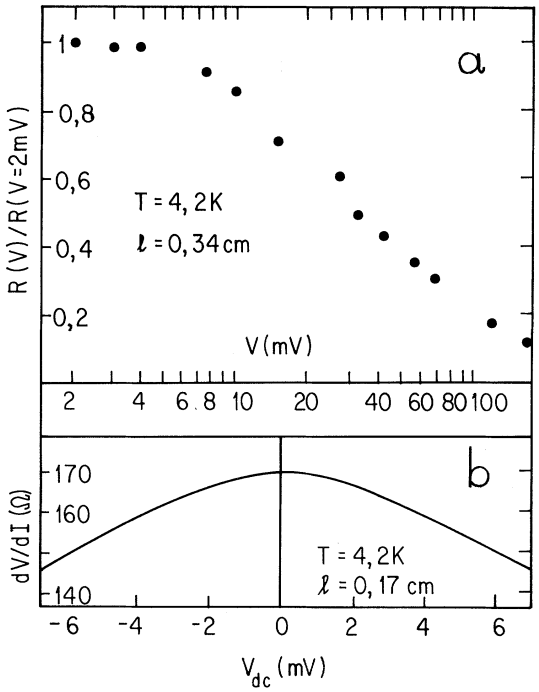

FIG. 1. (a) Electric field dependence of the resistance of $(TMTSF)_2PF_6$. (b) dV/dt vs electric field in the very-low-field regime. The sample length l is indicated in both cases.

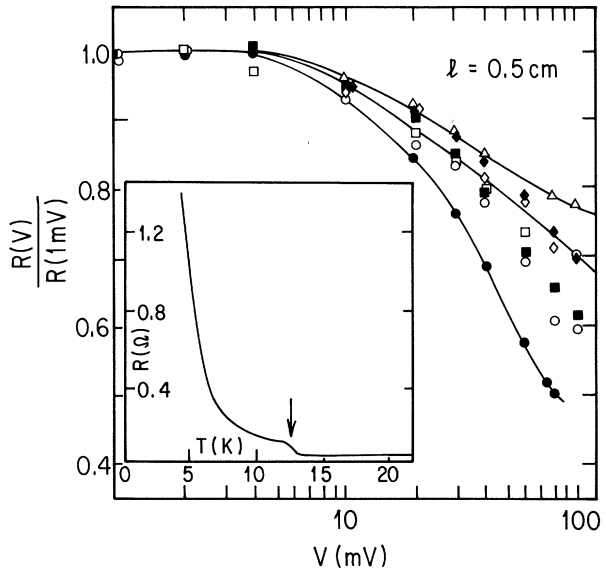

FIG. 2. Field dependence of the resistance at various temperatures. The full lines drawn through the experimental data at 4.2 K, 13 K, and 20 K are guides to the eye. Solid circles, 4.2 K; open circles 7 K; solid squares, 9 K; open squares, 11 K, solid diamonds, 13 K; open diamonds, 15 K; triangles 20 K. The inset shows the temperature dependence of the sample resistance for $V \to 0$.

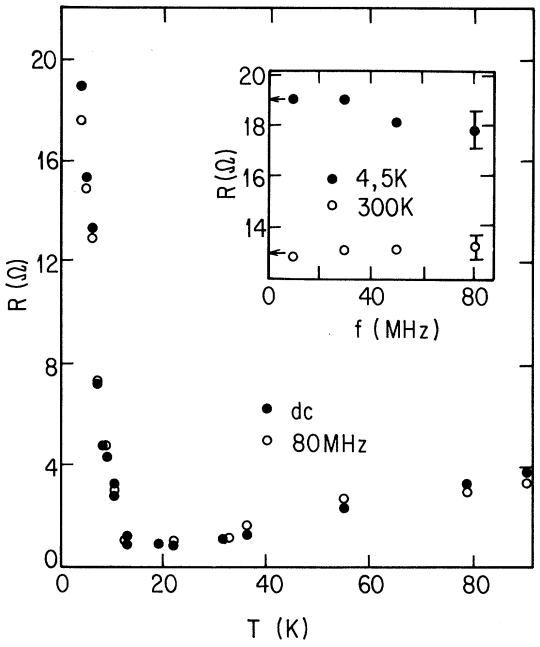

FIG. 3. Temperature dependence of the resistance at dc and at 80 MHz. The inset shows the frequency dependence below and above the transition.

field measured at 4.2 K. We have observed strong heating effects at voltages above 100 mV, pulsed, and conclude that dc experiments at much lower electric fields are heavily influenced by sample heating as Walsh *et al.*[1] suggested. At low electric field, heating effects are negligible and Fig. 1(b) shows the derivative of the resistance versus the applied voltage. It is obvious from Fig. 1(b) that the conductivity is non-Ohmic down to $E < 1$ mV/cm (further expanding the axis shows non-Ohmicity to 0.05 mV) and there is no evidence for a critical electric field E_c, which is observed[5] in $NbSe_3$. The resistance, measured by pulse technique at various electric fields, is shown in Fig. 2 for several temperatures. The transition temperature T_c as determined from the temperature dependence of dR/dT is 12.5 K. The conductivity is nonlinear both below and above T_c, but the nonlinearity strongly increases below the transition.

The frequency dependence of the conductivity was measured on several samples using a two-probe technique. The in-phase and out-of-phase components are balanced by a variable resistance and capacitance. Figure 3 shows the temperature dependence of R measured at (small) dc and at 80 MHz. The inset shows the conductivity versus frequency at two temperatures, one below and one above the transition. It is apparent from Fig. 3 that we do not find the strong frequency dependence observed in $NbSe_3$ where at 100 MHz the conductivity is already saturated at the high-field or high-frequency limit.[6]

While our experiments show negligible frequency dependence, the conductivity measured at 10^{10} Hz is higher than the dc conductivity. This would suggest that frequency-dependent transport sets in at frequencies much higher than in $NbSe_3$. We note, however, that the skin depth is comparable to the sample dimensions at microwave frequencies; this may lead to spurious high conductivities as observed in tetrathiafulvalene-tetracyanoquinodimethane.[7] What is perhaps more important is that we do not find an out-of-phase component, the sample capacitance below the transition is less than 1 pF. We have also searched, without success, for broad- and narrow-band noise[5,8] down to noise levels three orders of magnitude smaller than in $NbSe_3$ in the nonlinear conductivity region.

The above observations are in clear contrast to what has been observed in $NbSe_3$ where the depinning of charge-density waves (CDW) is responsible for the nonlinear conductivity. The

critical field E_c and giant dielectric constant reflect the restoring forces associated with pinning centers; the appearance of broad- and narrow-band noise is associated with the movement of the depinned collective mode. In $NbSe_3$, in the low-temperature ($T < 59$ K) CDW state, the minimum value of E_c is approximately 10 mV/cm,[5] with associated dielectric constant $\epsilon \sim 10^8$ at low frequencies.[6] Here we find no evidence for critical field E_c down to 0.1 mV/cm at 4.2 K. In any model in which charge carriers are pinned, the threshold electric field is proportional to the restoring force and there is a reactive component whose capacitance is inversely proportional to the restoring force. Thus E_c is approximately inversely proportional to the ϵ. An E_c smaller than 0.1 V/cm would suggest a dielectric constant much larger than that observed in $NbSe_3$, while our measurement sensitivity leads to an upper limit of 10^3, about five orders of magnitude smaller than that found in $NbSe_3$ in the low-temperature CDW state. Also, the absence of the noise in the nonlinear region is in clear contrast with observations made in the CDW state of $NbSe_3$.

Although pinning forces should be considerably weaker for an SDW than for a CDW, the basic transport properties of a sliding or pinned SDW and CDW are expected to be the same. The main differences are that the threshold field and noise will be scaled down and the dielectric constant scaled up by the reduced pinning force. The conductivity will also become frequency dependent at lower frequencies. Thus our measurements are not compatible with the depinning of a collective mode. We cannot, however, rule out some yet unknown collective phenomena which leads to nonlinear conductivity.

Another possible source of nonlinearity in highly anisotropic conductors is random large barriers, associated with impurities or breaks in the sample.[9] The increasing conductivity with increasing electric field results from large potential drops across the non-Ohmic barriers. The accumulation of charge at the barriers leads to polarization, which shows up in the dielectric constant and leads to a frequency-dependent conductivity.[10] The absence of capacitance and of frequency-dependent conductivity strongly suggests that break effects do not play an important role in $(TMTSF)_2PF_6$.

We note that the observed nonlinear conductivity is distinctively different from that expected for a Zener tunneling across a small single-particle gap. The field dependence of σ cannot be fitted with a formula $\sigma = \sigma_0 \exp(E_0/E)$ with $E_0 = \text{const}$. Also, the Zener mechanism leads to a temperature-independent contribution to the conductivity, while it is clear from Fig. 2 that the nonlinear conductivity has a strong temperature dependence.

Another mechanism which must be considered in discussing nonlinear conductivity is the acceleration of electrons to nonthermal states. If the mean free path is sufficiently long, an electron may attain a large kinetic energy equal to the voltage drop across the distance between inelastic scatterings. When this energy becomes comparable to the semiconducting gap, one relaxation process is the creation of electron-hole pairs. Such a non-Ohmic effect would produce no significant periodic noise and the low-field conductivity would be independent of frequency with no reactive component.[7]

The possibility of high mobility at low temperatures is suggested both by the fact that the conductance in the normal metallic state is very high at ~20 K and by preliminary Hall measurements which give a mobility $\gtrsim 10^4$ cm^2/V sec from a single-carrier analysis and higher mobility for several carriers. With such high mobilities, it is natural to begin thinking about the traditional non-Ohmic mechanisms known in conventional semiconductors such as impact ionization and other "hot-electron" effects.[11]

One problem with such interpretation is the observation of non-Ohmic behavior above the metal insulator transition where it is, of course, much smaller than the nonlinearity seen at lower temperatures. This may result from the partial condensation of the conduction electrons below a fluctuating gap which is present above the three-dimensional ordering temperature. The resistivity measurements clearly indicate resistive fluctuations for several degrees kelvin above the observed metal insulator transition.

In conclusion, we have found strongly non-Ohmic conductivity in $(TMTSF)_2TF_6$ in the temperature region 1.1–20 K. The nonlinear behavior is distinguished from that observed in $NbSe_3$ by the absence of a threshold field, a strongly frequency-dependent conductivity, a dielectric constant, and periodic noise. We suggest that the non-Ohmicity is related to the high mobility of this unusually "clean" organic quasi-one-dimensional conductor.

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Substrate-Dependent C(1*s*) Shape Resonance in CO Overlayers on Ni(111) and Ni(001)

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A large resonance was observed in the C(1*s*) angle-resolved photoemission cross section of CO overlayers on Ni(111) and Ni(001), with use of synchrotron radiation at the Stanford Synchrotron Radiation Laboratory, while none was observed for O(1*s*). Energy-, angular-, and polarization-dependence measurements showed that the C(1*s*) resonance, which is peaked at $h\nu = 311$ eV, is closely related to the shape resonance predicted for the C(1*s*) level in isolated CO. However, the surface potential introduces strong substrate-dependent deviations from gas-phase theory.

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The study of the structure of molecular overlayers on metal surfaces by valence-band angle-resolved photoemission (ARP) has recently received considerable attention.[1] The primary result has usually been the determination of molecular axis ($\vec{M}$) orientation with respect to the crystal normal ($\vec{n}$), as inferred from comparison of experimental ARP intensities with gas-phase data and theory. Examples include the prototype systems CO-Ni(111)[2] and CO-Ni(001).[3-5] In the latter system, an intensity resonance in the overlayer level derived from the 4σ molecular orbital[4] has been assigned to the adsorbed-molecule analog of the well-known gaseous CO valence-shell shape resonance.[6-8] It has been pointed out that the angular peaking of photoelectrons along the molecular axis at the shape resonance energy could serve as a direct "beacon" identifying the molecular adsorbate orientation,[7,9] provided that adsorbed molecules possess resonances similar to those predicted for free molecules.[7,10] In this connection, adsorbate core levels[10] possess distinct advantages for orientation studies, because their spatial localization eliminates ambiguities due to initial-state substrate effects.[11] Recently, the advantages of core levels have been exploited in ARP studies of CO-Ni(001) with use of Al $K\alpha$ radiation.[5] In this Letter, we report the first observation of adsorbate core-level ARP resonances, for the C(1*s*) level in CO-Ni(111) and CO-Ni(001). Although these resonances are similar to the predicted oriented-molecule shape resonance,[9] there is strong evidence for both substrate perturbations and substrate specificity.

The ARP experiments employed soft x rays from beam line I-1 at the Stanford Synchrotron Radiation Laboratory, in the energy range 300 eV $\leq h\nu \leq$ 360 eV. Our spectrometer, described elsewhere,[12] employs a 5.40-cm mean radius hemispherical analyzer with independent two-circle rotation. In these experiments, the relative orientations of the radiation vector potential ($\vec{A}$), the outgoing photoelectron direction ($\vec{p}$), and the crystal normal ($\vec{n}$) were independently varied in