Phase transition and non-Ohmic electrical transport in the spin-density-wave state of the organic conductor tetramethyltetraselenafalvinium hexafluorophosphate \((\text{TMTSF}_2\text{PF}_6)\)

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We report the electric field dependent conductivity in the spin-density-wave (SDW) state of the organic conductor \((\text{TMTSF}_2\text{PF}_6)\) using two different methods for making contacts. A new clamped-contact method reveals that the onset of the SDW transition of \((\text{TMTSF}_2\text{PF}_6)\) may be first order when the sample is strain free. A non-Ohmic behavior of the conductivity is observed above a threshold field in the range of 1–5 mV/cm. The temperature dependence of the threshold field agrees with a pinning mechanism due to commensurability between the SDW and the underlying lattice. The use of classical painted contacts leads to a smearing of the originally sharp transition and modifies the temperature dependence of the threshold field.

Tetramethyltetraselenafalvinium hexafluorophosphate \((\text{TMTSF}_2\text{PF}_6)\) is one of the most studied single-chain organic conductors. At ambient pressure it has a semiconducting spin-density-wave (SDW) state below 12 K whose presence has been clearly established by various magnetic measurements.\(^1\)\(^2\) X-ray studies show that it is a pure SDW state in which the \(2k_F\) scattering, which is the precursor of a charge-density-wave (CDW) instability, disappears below 50 K.\(^3\) Early experiments have shown the existence of an extra conductivity in the SDW state that depends on the applied electric field and the frequency.\(^4\)\(^5\)\(^6\) The electron-spin resonance signal was also restored by a large microwave field.\(^4\) However, no threshold field and no evidence for wide- or narrow-band noise or for a giant dielectric constant could be clearly identified.\(^5\) Subsequent studies were unable to reproduce the current carrying “spin-resurrected” state and also suggested that transport measurements were influenced by heating effects.\(^7\) Moreover, the observed non-Ohmic conductivity was correlated with the presence of irreversible jumps in the resistance associated with cracks developing on cooling down.\(^8\) However, conductivity measurements at microwave frequencies indicate the existence of a collective response associated with the SDW ground state.\(^8\)\(^9\)\(^10\)

In a recent Letter\(^1\)\(^1\) we have reported experiments on the electric field dependent conductivity in the SDW state of a related compound \((\text{TMTSF}_2\text{NO}_3)_2\). There was an evidence for increased conductivity above a finite threshold field \((E_T)\) and the sliding SDW mode was suggested as a plausible mechanism for the observed nonlinearity. While the value of \(E_T=40\) mV/cm is close to those found in CDW materials, it was found to be temperature independent below \(T_c/2\) in contrast to CDW systems where a slow increase \(\Delta E_T = A - BT\) is generally observed.\(^12\) In Ref. 11, we were unable to follow the \(T\) dependence of \(E_T\) between \(T_c/2\) and \(T_c\) or to check the sharpness of the threshold using continuous electric fields, because of heating.\(^13\)

In this Rapid Communication we report the observation of non-Ohmic conductivity above a finite threshold field associated with the SDW phase of \((\text{TMTSF}_2\text{PF}_6)\). We believe that this is an important result because in contrast to \((\text{TMTSF}_2\text{NO}_3)_2\) the complication of anion ordering is absent in \((\text{TMTSF}_2\text{PF}_6)\). As far as \((\text{TMTSF}_2\text{PF}_6)\) is concerned, the SDW phase has been studied in some detail by proton NMR experiments.\(^14\)\(^15\) Both studies have led to an estimate of the magnetic-distortion wave vector \(Q = (0.5a^*, 0.24 \pm 0.025\) \(b^*)\) (Ref. 14) and \((0.5a^*, 0.20\) \(\pm 0.056\) \(b^*)\);\(^15\) i.e., \(Q\) is close (or even equal) to the commensurate value \((0.5a^*, 0.25b^*)\), ignoring the third, weakly coupled \(c^*\) direction.

The measurements were performed on single crystals of \((\text{TMTSF}_2\text{PF}_6)\) from different batches with various lengths (0.5–2.5 nm) and typical cross sections of about 0.004 mm\(^2\). Gold pads were evaporated onto the samples. Two different mounting techniques were used. Electrical contacts were made either by silver paint or by mechanical clamping of fine gold wires.\(^16\) For samples with painted contacts, slow cooling rates (\(\approx 2\) K/h) were employed but all the samples measured showed some irreversible resistance jumps associated with microcracks. However, the non-Ohmic behavior disappeared above \(T_c\) and the threshold field observed for a given batch of samples was the same, irrespective of the resistance changes associated with jumps. Apart from the sharp jumps all samples measured showed the well-known metallic behavior down to the SDW transition at \(T_c=11.5\) \(\pm 0.25\) K as defined by the maximum of \(d\log\rho/dT\). We found a different resistivity ratio (RR) between 300 and 13 K ranging from 3.3 to 42. However, samples with clamped contacts did not show even the slightest visible crack in the whole temperature region. Transition temperatures were in the range 12 \(\pm 1\) K, and the RR was around 90.

A comparison between curves \(a\) and \(b\) in Fig. 1 reveals a marked difference between painted and clamped contacts as far as the temperature dependence of the resistance is concerned. For the clamped contact technique an extremely sharp metal-insulator (MI) transition is observed and in the temperature domain 12–5 K a nearly temperature-independent gap can be derived from the data in Fig. 1, curve \(a\) (\(\Delta = 23\) K). In addition, a resistance increase is clearly observed below 4 K or so. On the other hand, using the painted contact technique, a temperature dependence close to the classical BCS behavior was
found with a similar value for $2\Delta$ (28 K).

The experimental apparatus used to search for electric field dependent transport was similar to the one in Ref. 11 with pulse durations of about 40 $\mu$s and a repetition rate of 50 ms. We also performed regular checks for sample heating to rule out spurious effects and made additional measurements in the metallic region, at about 25 K, and between 80 and 100 K.

Figure 2(a) shows the field dependent conductivity for clamped contact samples at various temperatures versus the applied pulsed electric field. The pulse method avoids most sample heating problems but only has a resolution of $\approx 1\%$. Thus data in Fig. 2(a), e.g., those at 4.6 K, reveal an Ohmic character of the conductivity, $\sigma = \sigma_0$ at low fields in a broad field domain and a threshold field at $E_T = 5.5$ mV/cm, which we define as the intercept between $\sigma_0$ and the extrapolation of the field dependence above $E_T$. Furthermore, under favorable circumstances, e.g., a thin sample at low temperatures or one directly immersed in superfluid helium we were able to observe a flat, field independent conductivity with the much more sensitive dc technique which implies that the threshold field must be finite (of the order of 5 mV/cm or so). However, at higher temperatures sample heating becomes important even below $E_T$ as higher currents must be passed through the sample. Then there is a curvature below $E_T$ but we were still able to see a well-defined effect near to $E_T$ by plotting the apparent sample temperature (as determined from the conductivity itself) versus power. In the latter case the continuous curvature of $\sigma(V)$ vs $V$ was similar to that reported in Ref. 5. Therefore, in our opinion, heating is one possible reason for the absence of a clear threshold reported in Ref. 5. However, we have also found that samples with very low RR values ($\approx 1$) due to microcracks do not show a well-defined threshold.

The non-Ohmic conductivity behavior of painted contact samples is displayed in Fig. 2(b). At 24 and 100 K the conductivity remains constant over two decades of electric field. Below 12 K a non-Ohmic field dependence is observed above a certain threshold field ranging from 20 to 7.5 mV/cm at 12 and 2 K, respectively. As indicated in the inset of Fig. 2(b), dc measurements at 4.2 K confirm the existence of the threshold field and the value obtained corresponds fairly well to the pulsed data also shown in the inset. We have also noted that the magnitude of the excess conductivity is smaller for samples with smaller RR as already observed for (TMTSF)$_2$NO$_3$ and that samples from another batch with a broader MI transition have much larger $E_T$ values ($\approx 140$ mV/cm at 1.7 K). The observation that $E_T$ can be 15–30 times larger for crystals with broad MI transitions is important since it implies that $E_T$ is very sensitive to the impurity content and this could explain why some previous investigators have failed to detect any threshold behavior. Note that if there are microcracks the RR is not a good indicator of the impurity content.

The onset of non-Ohmic conductivity at the temperature of three-dimensional SDW order strongly suggests that the nonlinearity is associated with the establishment of a SDW. Indeed, as was previously argued, it is difficult to explain the observed effects using models based on a single-particle picture. Moreover, another highlight of the present data is the behavior of the low electric field conductivity versus temperature in samples studied using the clamped contact technique. The sharpness of the
resistive transition as shown in Fig. 1, curve $a$ is somewhat suggestive of the establishment of three-dimensional magnetic ordering via a first-order transition with the magnetic order parameter jumping from zero to a finite value at the transition. Indeed, a similar behavior of the order parameter (e.g., non-BCS temperature dependence) has already been observed in the study of the temperature dependence of the magnetic broadening of the proton NMR spectrum which jumps from zero to half the zero-temperature value at 12 K.\(^{17}\)

On the other hand, experiments sensitive to the lattice dynamics have not shown any measurable discontinuity in either the lattice parameter\(^{18}\) or the sound velocity.\(^{19}\) Consequently, the first-order character of the MI transition appears to be due to this magnetization (e.g., the spin-phonon coupling is small). At this stage we can think of one possibility for the first-order character of the transition if the wave vector of the magnetic modulation is commensurate, i.e., $Q = (0.5a^* , 0.25b^*)$ an hypothesis which is compatible with the present knowledge of NMR properties. A similar first-order transition between a normal state and a commensurate CDW state has already been encountered in the study of the phase diagram of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).\(^{20}\) In a narrow domain around of 19 kbar the CDW of TTF-TCNQ becomes commensurate ($\times 3$) with the underlying lattice and the MI transition becomes first order instead of second order. A temperature hysteresis ($\approx 1.5\%$) is thus observed at the transition of TTF-TCNQ. However, in case of the SDW transition we have failed so far to detect any hysteresis between cooling and warming runs. The existence of a first-order SDW transition is also reminiscent of that reported in unstrained chromium at $T_N \approx 311.5$ K.\(^{21, 22}\)

In addition, the resistive anomaly which is located around 4 K in Fig. 1, curve $a$ may be related to the transition towards a “more insulating” state detected by NMR at the same temperature.\(^{23, 24}\) The difference in behavior between clamped and painted contacts is still unclear. However, we tend to believe that the method which guarantees the absence of microcracks during cooling down is more likely to provide an intrinsic behavior.

Finally, we come to the discussion of the threshold field $E_T$ which displays different behavior with temperature depending on the contact technique (inset of Fig. 1). For painted contacts the increase of $E_T$ close to $T_c$ is qualitatively reminiscent of the behavior found in the CDW system. However, the threshold field does not diverge at $T_c$, as for most CDW materials.\(^{12}\) Furthermore, the negative temperature coefficient of $E_T$ below $T_c$ which has been observed for CDW is clearly absent here. Data in the inset of Fig. 1, curve $b$, are consistent with those obtained in (TMTSF)$_2$NO$_3$ using the painted contact technique\(^{11}\) with $E_T$ constant below $T_c/2$. The inset of Fig. 1, curve $b$, shows $E_T(T_c)/E_T(1.7$ K)$\approx 2.5$ in fair agreement with the theory of Maki and Virostek\(^{25}\) predicting an increase of $E_T$ of 3.13 and 1.77 for the weak pinning limit in $D = 3$ and 2 dimensions, respectively. However, in samples with clamped contacts $E_T$ display a minimum below $T_c$ and a steep divergence at $T_c$. The different behavior of $E_T$ vs $T$ may again be understood in terms of commensurability (or incommensurability) of the SDW. There exist two limiting situations: In a clean sample the SDW is pinned by a commensurability potential leading to a temperature dependence of $E_T$ as shown in Fig. 1 of Ref. 26; on the other hand, for a sample containing more defects (possibly introduced by microcracks) the impurity potential may be the dominant pinning mechanism. It is worth noting that if this interpretation is correct, it implies that the fourfold-commensurate SDW considered here still has a small threshold field. This can be understood within the theoretical model of Maki and Virostek.\(^{26}\) In contrast, for the CDW mentioned above, there was a large increase in $E_T$ in the region of commensurability.\(^{27}\)

In conclusion, using a new method for electrical contacts, the resistive transition at the onset of the SDW of (TMTSF)$_2$PF$_6$ appears to be first order. A careful examination of the thermodynamic properties at the SDW transition of a strain-free (TMTSF)$_2$PF$_6$ crystal should be enlightening. A non-Ohmic behavior of the conductivity is observed above a threshold field in the range of 1–5 mV/cm. The temperature dependence of the threshold field agrees with a pinning mechanism due to commensurability between the SDW and the underlying lattice. The use of classical painted contacts leads to a smearing of the originally steep transition and modifies the temperature dependence of the threshold field.

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Recently for (TMTSF)$_2$NO$_3$ a sharp threshold was observed in the differential resistance at 1.8 K using continuous electric fields (S. Tomić et al., in Proceedings of the First Institute for Solid State Physics International Symposium on the Physics and Chemistry of Organic Superconductors, 1989, edited by G. Saito (Springer-Verlag, Berlin, in press)).

T. Takahashi, in Low-Dimensional Conductors and Superconductors, Ref. 11, p. 195.


