

THE PROPERTIES OF FIVE HIGHLY CONDUCTING SALTS: $(\text{TMTSF})_2X$, $X = \text{PF}_6^-$, AsF_6^- , SbF_6^- , BF_4^- AND NO_3^- ,
DERIVED FROM TETRAMETHYLTETRASELENAFULVALENE (TMTSF)

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The properties of five new highly conducting salts of TMTSF, $(\text{TMTSF})_2X$, $X = \text{PF}_6^-$, AsF_6^- , SbF_6^- , BF_4^- and NO_3^- are reported. The measurements include d.c. and m.w. conductivity, thermopower, optical reflectivity, magnetic susceptibility and ^{19}F -NMR. Preliminary structural data indicate uniform donor stacks. Metal to insulator transitions in four materials occur below 20 K, where specific conductivities higher than $10^5 (\Omega\text{-cm})^{-1}$ are observed for two salts ($X = \text{PF}_6^-$ and NO_3^-).

1. INTRODUCTION

RECENTLY, it was shown that at temperatures below 15 K and at 10 kbar hydrostatic pressure, the two chain system TMTSF–DMTCNQ exhibits specific conductivities [1] in excess of $10^5 (\Omega\text{-cm})^{-1}$. Similarly in the one chain system $(\text{TSeT})_2\text{Cl}$ a phase transition [2] at pressures above 6 kbar takes the system into a highly [$\sigma > 10^5 (\Omega\text{-cm})^{-1}$] conducting state. Both solids at ambient pressure have charge-transfer $\frac{1}{2}$, $(\text{TSeT})_2\text{Cl}$ by stoichiometry and TMTSF–DMTCNQ as demonstrated by diffuse X-ray techniques [3]. However, the commensurability of the charge density wave (CDW) set up in these compounds with respect to the lattice, do not enhance T_C of the Peierls transition higher than to 42 and 24 K, respectively, at ambient pressure.

In this paper we report a series of five commensurate salts of TMTSF ($\Delta^{2,2'}$ -bi-(4,5-dimethyl)-1,3-diselenole) of the type $(\text{TMTSF})_2X$, four of which exhibit T_C well below 20 K, and two of which reproducibly exhibit conductivities in excess of $10^5 (\Omega\text{-cm})^{-1}$, the highest reported so far in organic compounds at ambient pressure.

Earlier, $(\text{TMTSF})_2^+$ halides and pseudohalides have been investigated [4], as well as some sulphur analogues [5] of the present compounds, both series being “metallic” only in a very narrow regime around room temperature.

The compounds reported and discussed are

$(\text{TMTSF})_2X$, X being PF_6^- , AsF_6^- , SbF_6^- , BF_4^- and NO_3^- (see Fig. 1).

2. EXPERIMENTAL RESULTS

Single crystals of the solids in question were prepared by electrochemical oxidation of neutral TMTSF in CH_2Cl_2 at constant current. The actual current used was sufficiently low to ensure that the crystallization rate was determined by diffusion, and not active transport of material to the electrode. Tetraalkylammonium or -phosphonium salts of the appropriate anions were used as supporting electrolyte. Since the stoichiometry of the new compounds in question is crucial for the commensurability, multiple microanalysis with standards between consecutive runs were obtained for each new salt, resulting in perfect 2:1 stoichiometry within experimental limits (0.5%).

The structure of $(\text{TMTSF})_2\text{PF}_6$ has been investigated in some detail (see Table 1 and Fig. 2). The structure is characterized by uniform donor stacks in sheets, separated by anion sheets. The donor molecules repeat by a pseudotranslation of period $a/2$ along a , and are nearly perpendicular to a (tilt angle 1.7°). In our preliminary data we find no indication of the slight dimerization in the donor stacks, which has been reported for a very similar sulphur compound $(\text{TMTTF})_2\text{Br}$ [5, 6]. In $(\text{TMTSF})_2\text{PF}_6$ the donor molecules are overlapping symmetrically giving rise to a

Table 1. Structural data for (TMTSF)₂PF₆

Triclinic $P\bar{1}$	
a : 7.297 Å	α : 83.39°
b : 7.711 Å	β : 86.27°
c : 13.522 Å	γ : 71.01°
Interplanar spacing along a : 3.65 Å.	
Tilt of donor plane relative to a : 1.7°.	

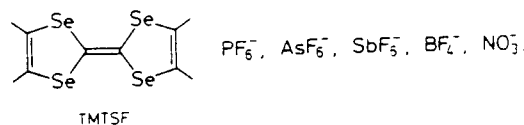


Fig. 1. Constituent molecules.

Table 2. Conductivity and dielectric constant data

X	σ_{\parallel} (d.c.)	σ_{\parallel} (35 GHz)	$\sigma_{\perp 1}$ (d.c.)	$\sigma_{\perp 1}$ (35 GHz)	$\sigma_{\perp 2}$ (d.c.)	T_C (K) [†]
	$\Omega^{-1} \text{ cm}^{-1}, T = 300 \text{ K}$					
PF ₆ ⁻	540	310	1.5	3.5	0.015	19
AsF ₆ ⁻	430	—	—	—	—	15
SbF ₆ ⁻	500	—	—	—	—	17
NO ₃ ⁻	780	240	—	—	—	12
BF ₄ ⁻	540	460*	—	—	—	39

* ϵ_1 (35 GHz, 20 K) = 250.

[†] As obtained from thermopower data.

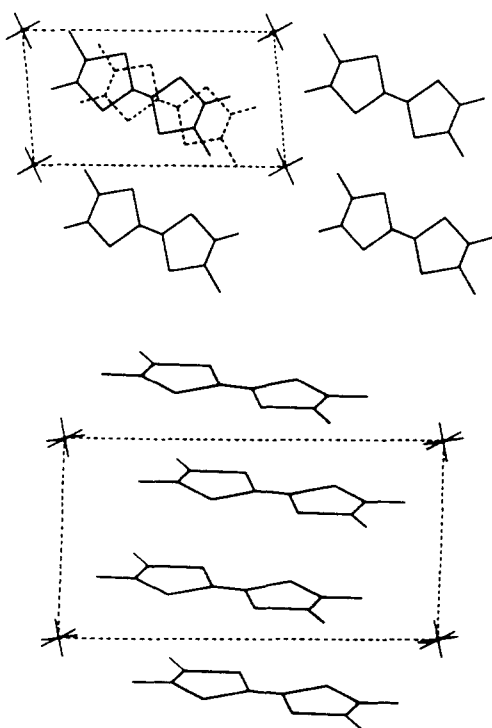


Fig. 2. (a) View along a . (b) View along b .

$\frac{3}{4}$ filled band, rather than a formally $\frac{1}{2}$ filled band in the dimerized situation. We do however wish to point out that such a weak dimerization, as claimed in the sulphur compounds [5], is only expected to influence the properties at very low temperature, where thermal motion is less important.

The present series of materials is remarkable in certain features: (1) the compounds are commensurate; (2) despite (1) the Peierls transitions in 4 materials are found below 20 K and (3) absolute values of conductivities in at least two materials are $> 10^5 (\Omega\text{-cm})^{-1}$ indicative of mean free paths in excess of 200 intermolecular spacings ($\sim 700 \text{ \AA}$).

In two materials (TMTSF)₂PF₆ and (TMTSF)₂NO₃ we infer, from the analysis of the transport data, that we have crystals of high quality. The AsF₆⁻ and the SbF₆⁻ are assumed to have the same inherent properties as the PF₆⁻ salt, but the crystal quality is probably not as good. (TMTSF)₂BF₄ is distinctly different from the other four materials. The crystal quality seems to be reasonable, but (TMTSF)₂BF₄ exhibits an extremely sharp phase transition at 39 K.

2.1. Conductivity

D.c. conductivity measurements were made using standard four probe techniques. In several runs minor contact problems occurred showing up as jumps into more resistive values. The best results were obtained using evaporated gold contacts. Figure 3 and Table 2 summarize the results.

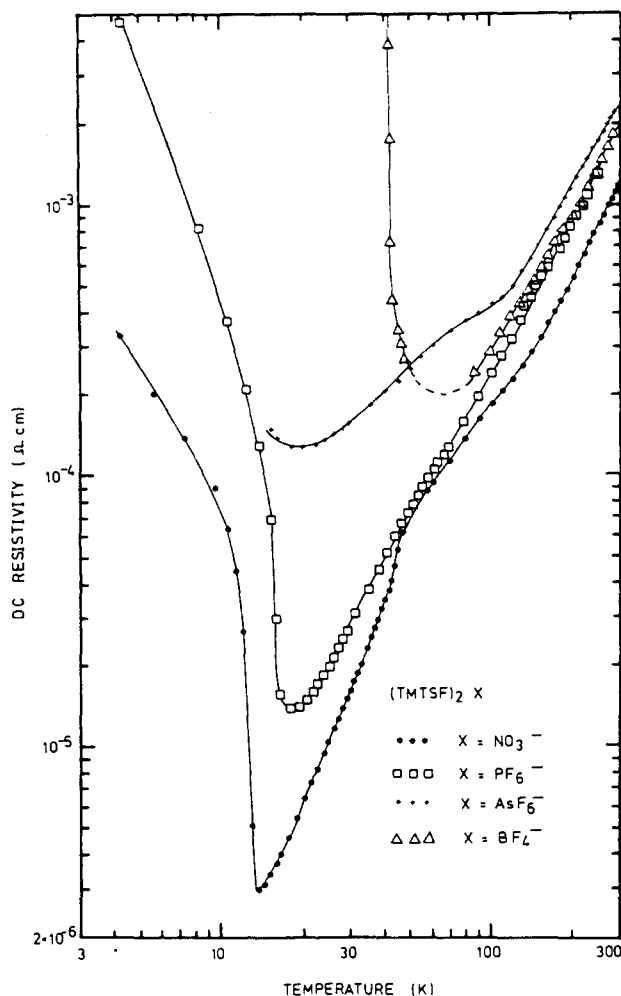


Fig. 3. D.c. resistivity vs temperature for typical samples of $(\text{TMTSF})_2X$. Note the logarithmic temperature and resistivity scales.

The d.c. results were confirmed by microwave (m.w.) measurements at 35 GHz [7], in which also thermal contraction as well as the temperature dependence of the anisotropy was determined. In the insulating state of $(\text{TMTSF})_2\text{BF}_4$ the dielectric constant ϵ_1 was estimated. Results are given in Fig. 4 and Table 2.

Room temperature conductivities range from $500\text{--}800 (\Omega\text{-cm})^{-1}$. In Fig. 3 we show resistivity data for typical crystals of each material.

The resistivity of $(\text{TMTSF})_2\text{PF}_6$ decreases monotonically 130–200 X from the room temperature values to the minimum at 18 K. From the maximum slope of the curve we infer that a phase transition occurs at 15 K. This transition probably reflects the opening of a Peierls gap. The crystals do not go insulating, but retain resistivities well below the room temperature value down to the lowest measured temperatures (4 K). This is very likely caused by impurity states in the very narrow gap. At high temperature (> 100 K) the

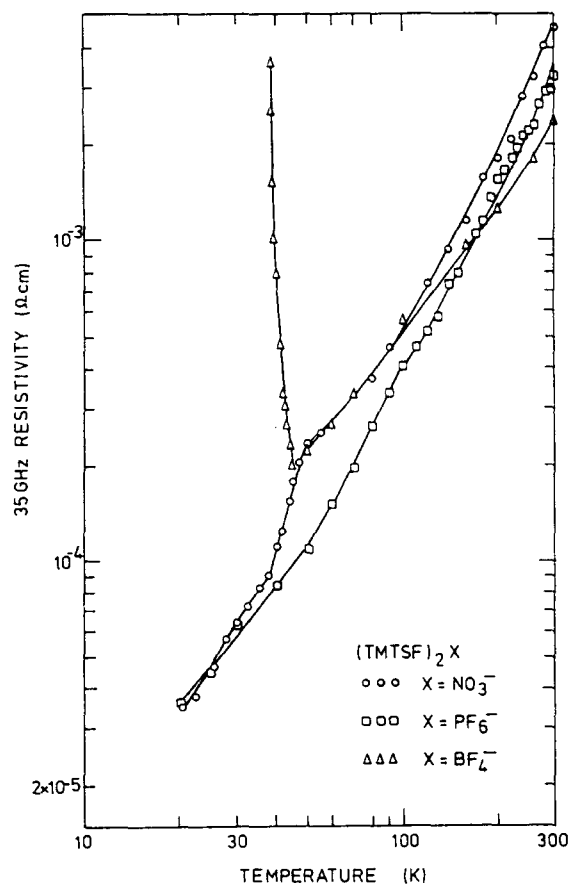


Fig. 4. Microwave resistivity vs temperature for typical samples of $(\text{TMTSF})_2X$. Note the logarithmic temperature and resistivity scales.

resistivity can be fitted to $\rho = \rho_0 + bT^2$ with ρ_0 close to zero, indicative of good crystal quality. $(\text{TMTSF})_2\text{NO}_3$ exhibits the same general features. $\rho_{\text{RT}}/\rho_{\text{min}}$ range from 130–400. The phase transition occurs at an even lower temperature (~ 12 K). Again $\rho = \rho_0 + bT^2$ is observed at high temperature with ρ_0 close to zero. Interestingly, a distinct change of slope is seen in all crystals of the NO_3^- salt (both by d.c. and m.w.) at 45 K, indicative of a transition into a more conductive state.

Preliminary magnetoresistance data in a field of 4 T perpendicular to a were obtained for $(\text{TMTSF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{NO}_3$. At 20 K (still in the metallic regime) the resistivity is enhanced 20%.

$(\text{TMTSF})_2\text{AsF}_6$ and $(\text{TMTSF})_2\text{SbF}_6$ are less interesting so far. Both exhibit Peierls transitions around 15 K (as the PF_6^- salt), but the high residual resistivities obtained in the $\rho = \rho_0 + bT^2$ analysis as well as the lower resistivity ratios ($\sim 20\text{--}50$) indicate that the crystal quality is moderate compared to the materials described above.

$(\text{TMTSF})_2\text{BF}_4$ exhibits an extremely sharp metal to

Table 3. Drude parameters for $(\text{TMTSF})_2\text{PF}_6$

ϵ_b	ω_p cm^{-1}	Γ cm^{-1}
2.54	10,050	1220

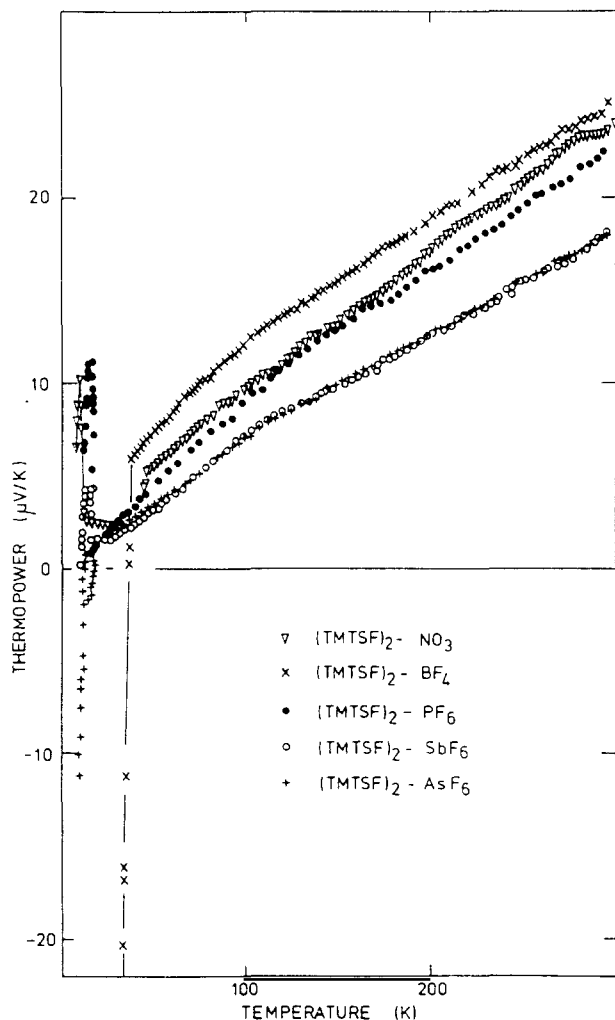


Fig. 5. Thermopower vs temperature for typical $(\text{TMTSF})_2X$ samples.

insulator transition at 39 K. From the m.w. data the dielectric constant, ϵ_1 , was obtained from 20–35 K. A nearly constant value of 250 is found. We emphasize that this value is an order of magnitude smaller than in TTF–TCNQ [8]. At present we await crystallographic information of $(\text{TMTSF})_2\text{BF}_4$ which appears to be distinctly different from the other 4 materials. However, the high temperature resistivity is again described by a $\rho = \rho_0 + bT^2$ relation.

2.2. Anisotropy

The anisotropy of $(\text{TMTSF})_2\text{PF}_6$ was measured by

both d.c. and m.w. techniques. At room temperature d.c. reveals $\rho_{\perp 1}/\rho_{\parallel} = 300$ and $\rho_{\perp 2}/\rho_{\parallel} = 3 \times 10^4$. The m.w. anisotropy was measured as a function of temperature. $\rho_{\perp 1}/\rho_{\parallel}$ increase from 100 to more than 1500 at 20 K, thus confirming the one dimensional nature of the solid in accordance with the structural features.

2.3. Optical results

Polarized single crystal spectra in the range from 5000–16,000 cm^{-1} have been recorded for $(\text{TMTSF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{NO}_3$. The spectra are nearly superimposable. In the highly conducting direction, R_{\parallel} drops rapidly from the infrared to a minimum at 8200 cm^{-1} . We interpret this reflectivity edge as a metallic plasma edge. At higher energy the reflectance rises monotonically as we enter the region of molecular transitions. Perpendicular to the stacks R_{\perp} is nearly constant throughout the region measured. The features in the vicinity of the plasma edge are analyzed in a Drude model for the dielectric function:

$$\epsilon_{\parallel}(\omega) = \epsilon_b - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}$$

where ω_p is the plasma frequency, ϵ_b the background dielectric constant and Γ the relaxation rate. Since the present materials are simple 1-chain salts of charge transfer $\rho = \frac{1}{2}$, ω_p can be used to estimate the bandwidth W . Assuming a uniform chain we get for a cosine band [9]:

$$\omega_p^2 = \frac{e^2 a^2 \sin(\frac{1}{2}\rho\pi)}{2\pi\epsilon_0 h^2 V_c} \frac{W}{2}$$

where V_c is the unit cell volume.

A value of approximately 1 eV for W is obtained in the analysis. This value is substantially larger than the estimated bandwidths in most TTF–TCNQ salts (~ 0.5 eV) [9, 10]. Table 3 summarizes the optical data.

2.4. Thermopower

In Fig. 5 we show the thermopower (S) of all the materials. In the metallic region small positive values of S falling linearly with temperature and extrapolating to zero are found. We notice, however, a slight curvature against smaller S in all materials. This could be indicative of collective phenomena. If we for simplicity assume a single particle approach we find for a highly anisotropic free electron gas, a band structure contribution to the thermoelectric power [11] in a $\frac{3}{4}$ filled band:

$$S = \frac{2\sqrt{2}}{3} \pi^2 \frac{k_B}{e} \frac{k_B T}{W}$$

From the slope of $S(T)$ we estimate bandwidths of 1.0 eV in accordance with the optical results. In the plot of S vs $1/T$ (Fig. 6) anomalies indicative of phase

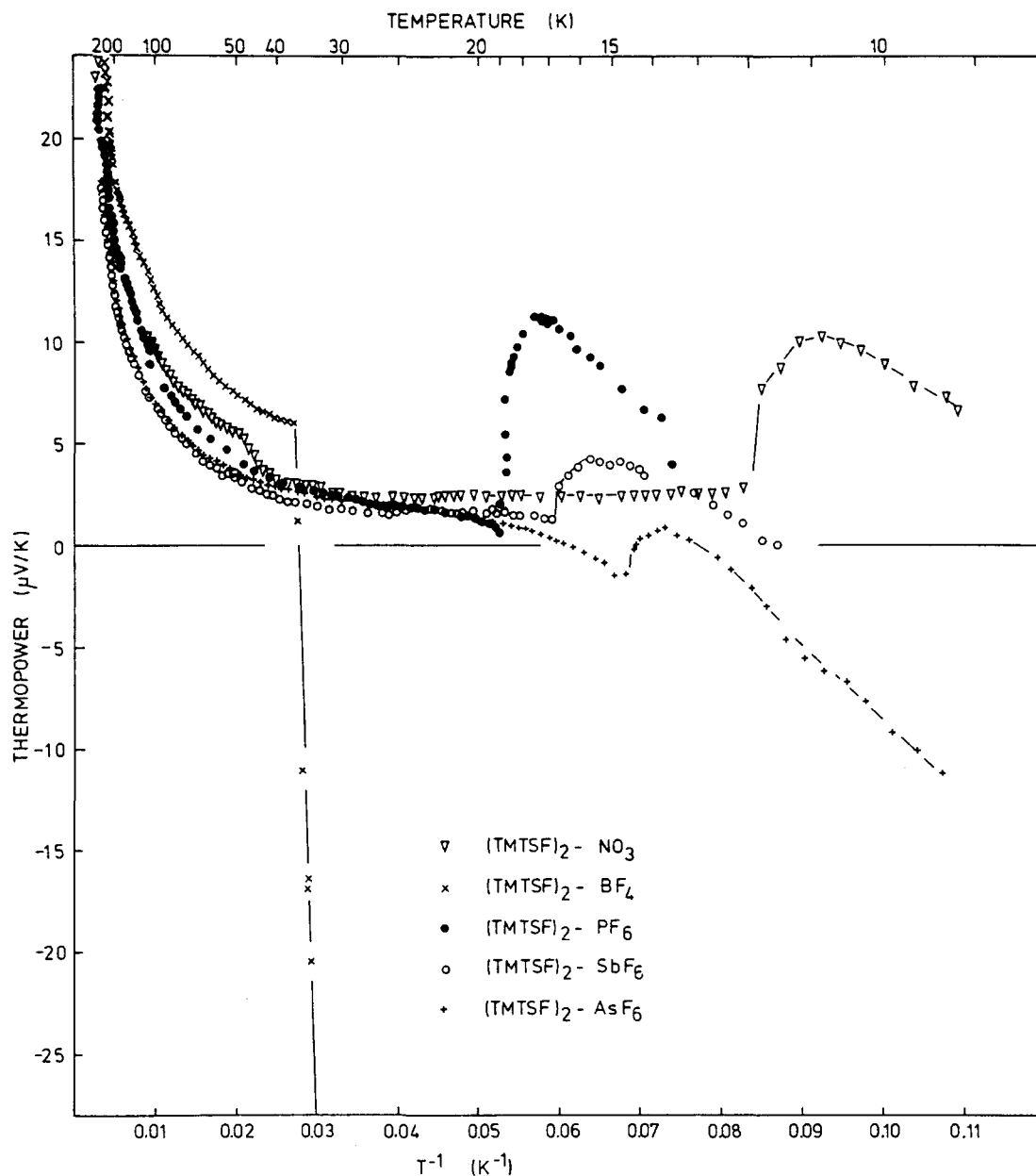


Fig. 6. Thermopower vs inverse temperature for the same samples as in Fig. 5.

transitions are clearly seen at the same temperatures as in the resistivity data. Below T_c the thermopower is indicative of semiconducting behaviour. The resistivities obtained in this region can be interpreted similarly since in the small-gap materials quite few impurities may give rise to deviations from ideal semiconducting behaviour.

2.5. Magnetic susceptibility

The magnetic susceptibility of $(\text{TMTSF})_2\text{PF}_6$ was measured by the Faraday method. A rather high, temperature independent value of approximately 4.2×10^{-4} emu per formula unit is found. Below 30 K a persistent, sample dependent Curie tail is observed.

The actual susceptibility of the material depends somewhat on aging, as it was found in the sulphur series [5]. The high susceptibility is somewhat confusing. The value is 3–4 times the Pauli value as calculated from the bandwidth estimated above, and certainly more experimental information is needed.

The magnetic behaviour of highly conducting quasi one-dimensional systems is diverse. TMTSF-DMTCNQ [12] and HMTSF-TCNQ [13] are strongly diamagnetic at low temperature, whereas the nearly temperature independent paramagnetism of $(\text{TSeT})_2\text{Cl}$ [2] agrees reasonably well with the estimated Pauli value.

Preliminary EPR measurements indicate a g -value of 2.033 typical of g_{\perp} in a TMTSF-stack [14]. A rather broad line, 250 G, is found at room temperature.

2.6. NMR

Measurements of ^{19}F -NMR linewidths [15] of solid $(\text{TMTSF})_2\text{PF}_6$ indicate that above 70 K the PF_6^- ions are disordered. Below 70 K the measurements indicate some ordering, but still free rotation. At even lower temperatures the measurements are obscured by the paramagnetic impurities. It is not clear to what effect dynamic disorder of the anions may have on the transport properties of $(\text{TMTSF})_2\text{PF}_6$ but we do notice a slight S -shape at 70 K in the resistivity plots. Similarly the anomaly at 45 K in $(\text{TMTSF})_2\text{NO}_3$ could arise from freezing of the NO_3^- ions.

We do however note a discrepancy between the NMR-data and the structural results, which indicates that the PF_6^- ions are ordered at room temperature. Alternatively a change of electronic states at 70 K could influence the NMR-linewidth.

3. CONCLUSION

In the class of pseudo one dimensional conductors the one dimensional electron lattice instability at $2k_F$ is a dominant feature in most examples leading to 3-D order at lower temperature and semiconducting behaviour due to a static energy gap at the Fermi surface. In certain cases impurity states in the gap or a transition into a semimetallic state [2, 16] can lead to fairly conducting solids below T_C . In the present salts we observe a lowering of T_C relative to other reported materials and especially relative to the nearly isostructural sulphur analogues [5]. The large bandwidth ($\sim 1.0\text{eV}$) and long mean free paths place the present materials in the metallic regime, where Coulomb correlations are presumably unimportant. The phase transitions observed may be Peierls transitions at temperatures which, due to the high anisotropies, are suppressed strongly from the mean field values. We note that T_C is apparently not enhanced by commensurability, i.e. by the fact that the $2k_F$ -CDW's have wavelengths equal to 2 crystallographic units (or 4 intermolecular spacings). Similar conclusions come from studies of TTF-TCNQ where a pressure induced incommensurate-commensurate transition [17] only enhances T_C about 20%.

The present experimental results raises some theoretical questions. (a) There is an apparent inconsistency between the large bandwidth estimated from the thermopower and the optical results and the high, temperature-independent susceptibility. The present system is, to our knowledge the only one to possess this feature. (b) We observe an extremely low residual

resistivity in $(\text{TMTSF})_2\text{PF}_6$ and $(\text{TMTSF})_2\text{NO}_3$. TMTSF-DMTCNQ under pressure also exhibits this feature. In that material a cross over from 1-D to 3-D [1, 12], and that a moderate range defect potential can suppress multiple scattering [12], was suggested, or alternatively, that a collective effect is important [1]. (c) There is no obvious commensurability effects observed in the present materials. There is, however, some theoretical work indicating that CDW's are not necessarily strongly locked to the underlying lattice [18, 19]. (d) At high temperature ($> 150\text{K}$) the investigated materials show strong similarities. The resistivity is reasonably well fitted to $\rho = \rho_0 + bT^2$. The systems should thus be attractive in testing various existing transport theories [20, 21] as they have only one conducting chain and exhibit very high conductivities. Especially in the investigation of thermal conductivity it should be possible to distinguish electronic from lattice contributions at lower temperature. (e) The strong effect of the transverse magnetic field is unexpected. In $(\text{TSeT})_2\text{Cl}$ a minor effect was observed [2]. The two-chain system TMTSF-DMTCNQ (20 K, 13 kbar) behave quantitatively very similar to the present material. In TMTSF-DMTCNQ it was suggested that the strong effect is the result of a break-down of a collective state [1].

Additional studies of diffuse X-ray scattering, magnetoresistance, magnetic characteristics and pressure dependence of the transport properties should help to give us a better understanding of these intriguing new materials.

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Note added in Proof: It has recently been shown that $(\text{TMTSF})_2\text{PF}_6$ goes superconducting at 0.9 K under a hydrostatic pressure of 12 kbar [22].