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Mortensen, Kell; Engler, E. M.

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Conductivity and thermopower studies of bis-tetramethyltetraselenafulvalenium hexafluorophosphide, bis-tetramethyltetrathiafulvalenium hexafluorophosphide, and their solid solutions, $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$

Kell Mortensen*
Physics Laboratory III, Technical University of Denmark, DK-2800 Lyngby, Denmark

E. M. Engler
IBM Research Laboratory, San Jose, California 95193

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The conductivity σ and the thermoelectric power S have been studied experimentally on the organic conductors bis-tetramethyltetraselenafulvalenium hexafluorophosphide $[(\mathrm{TMTSF})_2\mathrm{PF}_6]$ and bis-tetramethyltetrathiafulvalenium hexafluorophosphide $[(\mathrm{TMTTF})_2\mathrm{PF}_6]$ and their solid solutions: $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$. Dramatic effects are seen in σ already when dilute concentrations of TMTTF molecules are introduced in the TMTSF chains, and for $x=0.1$, σ shows generally activated behavior. The thermopower, on the contrary, remains basically unaffected for x at least as large as 0.25. These unusual findings are attributed to the small transverse transfer integral t_b associated with the TMTTF molecule, which leads to large on-site Coulomb repulsion. The parallel transfer integrals t_a appear to be very similar for the two constituent molecules. A slight x dependence of S, appearing below approximately 100 K, is attributed to enhanced one-dimensionality when the amount of TMTTF is increased. Close to and below the spin-density-wave ordering temperature, more marked x dependences appear, indicative of impurities. The $x=0.85$ salt behaves generally similar to the pristine TMTTF material, though dominated by additional impurity levels.

I. INTRODUCTION

The family of organic conductors, $(\mathrm{TMTSF})_2X$ and $(\mathrm{TMTTF})_2X$, based on, respectively, the tetramethyltetraselenafulvalene (TMTSF) and tetramethyltetrathiafulvalene (TMTTF) molecules and an inorganic monovalent anion ($X^-=\mathrm{PF}_6{}^-$, $\mathrm{ClO}_4{}^-$, $\mathrm{ReO}_4{}^-$, etc.), have generated a great deal of recent interest.[1] These compounds have shown a variety of novel features, including ground states ranging from superconducting to magnetic or nonmagnetic insulating. The compounds are isostructural, belonging to the $P\bar{1}$ (C_i^1) space group. The nearly planar TMTSF or TMTTF molecules form zigzag stacks along the a direction. A slight tilt relative to this stacking axis results in dimerized chains. Charge transfer to the anions results in $\frac{1}{2}$ hole ($\frac{3}{2}$ electrons) per TMTSF or TMTTF molecules, thus formally giving rise to half-filled bands. In an extended-zone scheme there would be a $\frac{3}{4}$-filled cosine band with a small dimerization gap at midband.

The hexafluorophosphide salts, $(\mathrm{TMTSF})_2\mathrm{PF}_6$ and $(\mathrm{TMTTF})_2\mathrm{PF}_6$, are among the most intensively studied compounds. $(\mathrm{TMTSF})_2\mathrm{PF}_6$ was the first discovered example of an organic material exhibiting superconductivity.[2] The superconducting state occurs under hydrostatic pressure greater than 6.5 kbar and at temperatures below 1 K. At ambient pressure, $(\mathrm{TMTSF})_2\mathrm{PF}_6$ shows metallic behavior to below 15 K.[3] The stacking-axis conductivity σ is $\sim 500\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at room temperature, and decreases with temperature T over a wide range as T^{-2}. The stacking-axis thermopower S is in the metallic region linear in temperature, though with a marked change in slope around 100 K, which is the temperature region attributed to one-dimensional—two-dimensional (1D-2D) crossover.[4] At 12 K an Overhauser-type instability causes a transition to a semiconducting, antiferromagnetic ordered spin-density-wave (SDW) ground state.[5]

The related sulphur compound, $(\mathrm{TMTTF})_2\mathrm{PF}_6$, differs distinctly from $(\mathrm{TMTSF})_2\mathrm{PF}_6$. Both the magnetic and the transport properties of the $(\mathrm{TMTTF})_2\mathrm{PF}_6$ salt have been interpreted as indicative of a relative large $U/4t_a$ ratio ($U/4t_a \sim 2$), U being the on-site Coulomb repulsion and t_a being the transfer integral.[6,7] As a result of this strong electron-electron correlation, the gap opened by the $4k_F$ potential is at the Fermi energy. Therefore, $(\mathrm{TMTTF})_2\mathrm{PF}_6$ is a magnetic semiconductor. Thermopower and magnetic studies suggest that some kind of impurities or defects play dominating roles for the physical properties of the salt. Close to 15 K, EPR investigations of the magnetic susceptibility discover a sharp anomaly, which from structural studies has been identified as a spin-Peierls transition.[6,8] In this paper we present experimental investigations of $(\mathrm{TMTSF})_2\mathrm{PF}_6$, $(\mathrm{TMTTF})_2\mathrm{PF}_6$, and their solid solutions $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$, $x=0.005$, 0.016, 0.03, 0.10, 0.25, and 0.85. The studies include stacking-axis dc conductivity and thermoelectric power.

Studies of transport parameters of alloys of organic conductors have previously been proven to be important tools for investigating the physical properties of organic conductors. For example, experiments with tetraselenafulvalene (TSeF) molecules doped into the tetrathiafulvalene (TTF) stack of TTF-TCNQ have given clear evidence of the metal-insulator transition as being driven by a Peierls distortion on the tetracyanoquinodimethane (TCNQ) stack.[9] It has, moreover, been shown that intrinsic transport parameters of each of the stacks of a conductor such as TTF-TCNQ can be determined experimentally since introduction of dopants into a single chain will suppress the corresponding mobility markedly, whereas that of the other chain remains approximately unaffected. As an example, a decomposition into intrinsic transport parameters (conductivity and thermopower) has been performed on TMTSF-DMTCNQ (DMTCNQ = dimethyltetracyanoquinodimethane).[10]

Some results on $(TMTSF)_2PF_6$ doped with dilute concentrations of TMTTF have already been published.[11,12] These studies showed that 3% TMTTF molecules in the TMTSF stacks give rise to dramatic effects on a variety of physical properties: A 40% rise in the metal-insulator -(MI) transition temperature (T_c), a 130% rise in the room-temperature spin susceptibility (χ_s) and a 30% decrease in the low-temperature g shift. It was speculated that the rise in T_c and χ_s are due to an increase in the density of states near the Fermi energy, upon which T_c depends exponentially. A similar mechanism has been applied in connection with the classical Overhauser unstable compound, chromium, when doped with, for example, aluminum. Another possible explanation for the rise in T_c can be improved nesting of the Fermi surface by doping.

More recently, some equivalent solid solutions, $(TMTSF_{1-x}TMTTF_x)_2$-ClO_4 with $x \leq 0.3$, have been studied.[13] The experimental findings (conductivity and EPR magnetism) of these compounds are qualitatively similar to those of the PF_6^- salts, showing dramatic effects for concentrations less than $\sim 5\%$. For larger concentrations, however, only minor change was observed. It was therefore proposed that a crossover from a magnetic to a nonmagnetic low-temperature ground state occurs for $x \sim 0.05$.

The experimental data presented below disclose, however, that the solid solutions are not simply ascribed to a $x = 0.05$ crossover, as caused by competition between TMTSF properties (i.e., metallic at high T and a low-T SDW ground state) and TMTTF properties (semiconducting already at high T and a low-T spin-Peierls ground state). In contrast to all previously studied physical parameters, including the conductivity which is presented below, the thermopower shows basically no changes at $x = 0.05$. Furthermore S remains unaffected (i.e., TMTSF-like) for at least 25% TMTTF molecules in the conducting chains.

II. EXPERIMENTAL

Single crystals of $(TMTSF)_2PF_6$, $(TMTTF)_2PF_6$, and their solid solutions were grown from the purified constituents by the electrochemical technique.[12] The applied potential, which was kept constant at a voltage lower than the first oxidation potentials of either TMTSF or TMTTF (typically 0.25—0.35 V), was controlled using a reference electrode. Current levels were typically 2—8 μA. The ratio of TMTTF molecules versus TMTSF molecules was controlled by the initial admixture of TMTSF and TMTTF, and was analyzed using the electron-microprobe technique. Such analysis of multiple 1-μm regions along the length of the crystals gave a constant value of x within the accuracy of the measurements ($\pm 5\%$). Moreover, a number of x-dependent physical properties were, within experimental error, equal for different crystals taken from the same batch. The samples must therefore be relatively homogeneous, not only within a single crystal, but within the whole assembling of crystals of a batch.

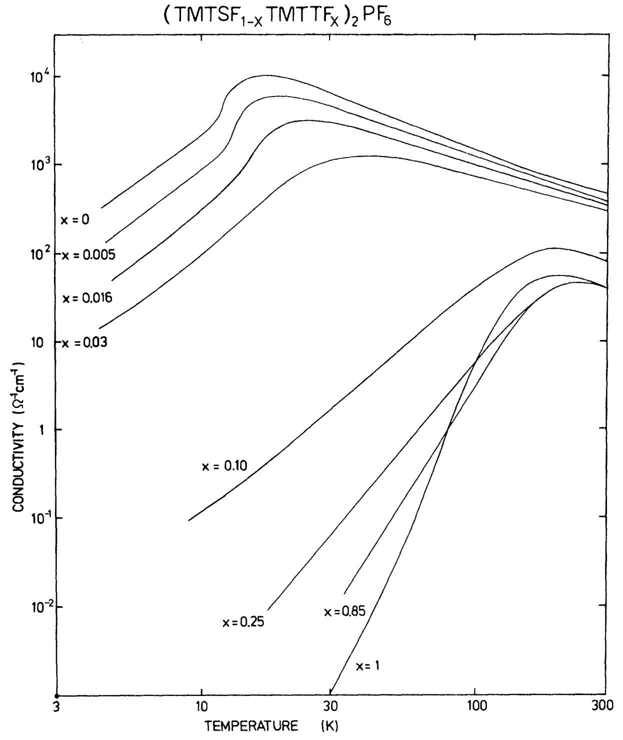

FIG. 1. Conductivity vs temperature of

$(TMTSF_{1-x}TMTTF_x)_2PF_6$.

$x = 0$, 0.005, 0.016, 0.03, 0.10, 0.25, 0.85, and 1. Note the log-log plot.

The longitudinal conductivity was measured by the standard four-probe technique using a lock-in amplifier of ~ 40 Hz. The samples were mounted on 25-μm gold wires supported at one end only. Contacts were made using silver paint. As it is often observed in salts of TMTSF or TMTTF, the conductivity measurements are drastically disturbed by numerous erratic jumps in the $\sigma(T)$ curves, as caused by some kinds of microcracks. For this reason, each of the $\sigma(T)$ curves presented in Fig. 1 is not a reflection of the crude data of $\sigma(T)$ of one single sample. Each curve represents, on the contrary, average values of data obtained from several crystals issued from the same batch. Before making the average $\sigma(T)$ curve, all erratic jumps were removed by assuming that the only effect of a microcrack is to destroy parts of the conduction path.

The longitudinal thermopower (S) was measured in a conventional apparatus using a slow alternating temperature difference of typical 0.2 K. The samples were mounted on 25-μm gold wires and contacts were made using silver paint. Measurements performed in this way have an accuracy of about $\pm 5\%$. Within this experimental errorbars, we found in the whole temperature region studied the same values of S for crystals issued from the same batches. While the conductances, as mentioned above, were drastically affected by interruptions in the crystals, no corresponding effects could be observed in the thermopower. These features, which have been verified by simultaneously measurements of σ and S,[14] is to be expected if the microcracks act as breaks of the conducting chains, and only negligible temperature drops occur across these breaks.

III. RESULTS

A. Conductivity

In Fig. 1 are shown the conductivity versus temperature of $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$, $x=0$, 0.005, 0.016, 0.03, 0.1, 0.25, 0.85, and 1. The pristine materials exhibit the well-known properties.[3,6] $(\mathrm{TMTSF})_2\mathrm{PF}_6$ shows, at high-temperature, metallic behavior, with a conductivity equal to 500 $\Omega^{-1}\mathrm{cm}^{-1}$ at room temperature and a T^{-2} temperature dependence. At 17 K, σ reaches a maximum of about 10^4 $\Omega^{-1}\mathrm{cm}^{-1}$. At 11.5 K, the $\sigma(T)$ curve clearly reflects the MI transition, which is a result of the SDW formation. The width of the transition, defined as the width at half maximum of $-d(\ln\sigma)/d(1/T)$, is of the order of 1–1.5 K. Below 10 K, σ exhibits activated behavior with an activation energy E_a/k_B equal 24 K.

Pristine $(\mathrm{TMTTF})_2\mathrm{PF}_6$ has, at room temperature, a chain-axis conductivity approximately equal to 40 $\Omega^{-1}\mathrm{cm}^{-1}$. Upon cooling, σ rises to a broad maximum around 200 K with $\sigma \sim 60$ $\Omega^{-1}\mathrm{cm}^{-1}$. From the $\sigma(T)$ plot there are no indications of a MI phase transition. A plot of $\log\sigma$ vs $1/T$ shows curvature in the whole temperature region studied (4–300 K). Thus, a well-defined activation energy (E_a) cannot be deduced. With the use of the slope around 100 K, however, a value of E_a/k_B equal to ~ 600 K is calculated.

The solid solution $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ with $x=0.005$ behaves generally similar to the pristine $(\mathrm{TMTSF})_2\mathrm{PF}_6$ salt. The room-temperature conductivity is slightly depressed, namely a value of 400 $\Omega^{-1}\mathrm{cm}^{-1}$, and the maximum value is also smaller than that of the pristine material. The temperature of maximum conductivity (T_m), the MI transition temperature (T_c), and the width of the transition are all enhanced by approximately 1°. The changes in behavior compared to those of pristine TMTSF become more marked when $x=0.016$ and 0.03. The room-temperature values are 350 and 300 $\Omega^{-1}\mathrm{cm}^{-1}$, respectively, and the T dependences are less pronounced. Most remarkable is that the MI transitions change drastically in character. The value of T_c has risen to 14 and 16 K for the $x=0.016$ and 0.03 salts, respectively, and the transitions have broadened substantially.

The $x=0.1$, 0.25, and 0.85 compounds show all $\sigma(T)$ properties, which, to some extent, approach that of pure $(\mathrm{TMTTF})_2\mathrm{PF}_6$, i.e., relatively low room-temperature conductivities and maxima of σ around 200 K. The high-T conductivity of the $x=0.1$ salt is about twice the value of $(\mathrm{TMTTF})_2\mathrm{PF}_6$, and at low T, the activation energy $E_a(T)$, as defined from the slope of $\log\sigma$ vs $1/T$, is only half of the TMTTF value. Generally, the $E_a(T)$ value increases with the amount of TMTTF in the donor stacks.

B. Thermopower

In Figs. 2 and 3 we show the thermopower of $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_4\mathrm{PF}_6$, $x=0$, 0.005, 0.03, 0.10, 0.25, 0.85, and 1, versus temperature and reciprocal temperature, respectively. The data of the pristine materials are equal to that previously published.[4,7] The thermopower of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ shows, at high temperature, the linear T dependence which is characteristic of metallic properties. The room-temperature value is 30 μV/K. Close to 100 K there is, however, a significant change in slope of S vs T. A few degrees above the MI transition temperature, S exhibits peculiar properties which result in a singularity in the slope of S vs T at T_c. Below T_c, S rises to a sample-dependent maximum of approximately 4 μV/K around 10 K, and upon further cooling S decreases as $1/T$.

The thermopower of pristine $(\mathrm{TMTTF})_2\mathrm{PF}_6$ differs markedly from that of pure $(\mathrm{TMTSF})_2\mathrm{PF}_6$.[7] No metallic, i.e., $S \propto T$, region is seen. Upon cooling, S rises as $1/T$ in the whole temperature region studied ($30<T<300$ K), although it does so with changes in slope around both 125 and 66 K. No anomalous properties have been observed at the temperature of maximum conductivity ($T_m=200$ K). The room-temperature value of S is 42 μV/K.

While the conductivity (and magnetism) shows dramatic changes in characteristics when x is varied from 0 to 0.1, the high-temperature ($T>100$ K) thermopower remains effectively unchanged for at least a 25% concentration of TMTTF molecules in the conducting chains. Only the $x=0.25$ sample has an absolute value which relative to that of pure $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is enhanced with an amount slightly over the experimental accuracy. At room temperature the thermopower is 32 μV/K.

In the low-temperature region ($T<100$ K), however, only the $x=0.005$ sample exhibits all the characteristics known from the pristine TMTSF salt, i.e., the relative sharp change in slope of S vs T around 100 K and the peculiar properties around T_c. In accordance with the conductivity measurement, the thermopower study of this alloy shows that T_c has risen to 12.5 K. In the semiconducting ground state, the slope of S vs $1/T$ of the $x=0.005$ salt is somewhat larger than that of pristine $(\mathrm{TMTSF})_2\mathrm{PF}_6$.

The low-temperature thermopower of

$$(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$$

with $x=0.03$, 0.10, and 0.25 appears to have quite similar features which differ significantly from those of $(\mathrm{TMTSF})_2\mathrm{PF}_6$. Compared to $(\mathrm{TMTSF})_2\mathrm{PF}_6$, the $\sim$100-K crossover, seen as a rise in slope of S vs T, has become less pronounced in the $x=0.03$ compound, and in the

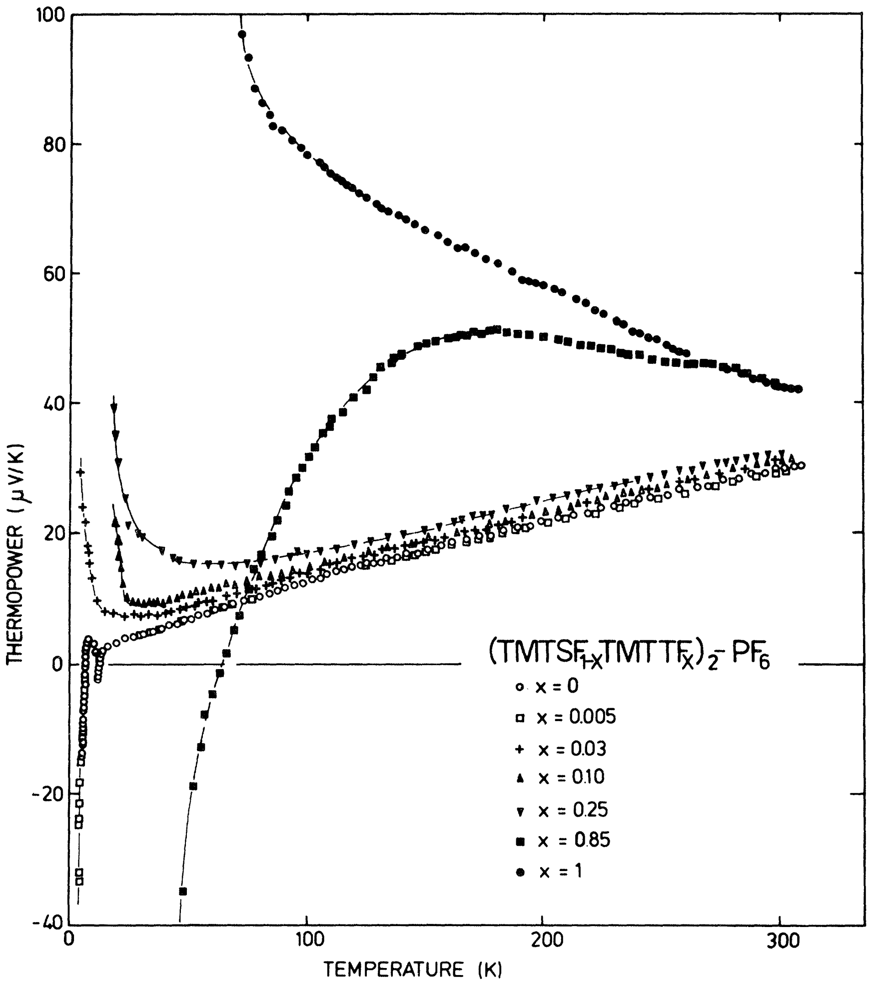

FIG. 2. Thermopower vs temperature of $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$, $x=0$, 0.005, 0.03, 0.10, 0.25, 0.85, and 1.

$x=0.10$ and 0.25 materials, no crossover could be observed. The temperature associated with this rise in slope of the $x=0.03$ salt is reduced to approximately 80 K. None of the three salts show indications of the divergent rise in slope of S vs T as T approaches T_c. On the contrary, upon cooling the thermopower approach a constant value before showing the low-temperature $1/T$ dependence. For $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$, $x=0.03$, a constant value of $S \sim 5$ μV/K is seen in the temperature region 17—40 K. At the $x=0.03$ transition temperature ($T_c=16$ K), as defined from the maximum of $-d(\ln\sigma)/d(1/T)$, the $S(T)$ curve exhibits a relative sharp kink (Fig. 3). Both the $x=0.10$ and 0.25 materials also show such kinks. It is therefore a reasonable assumption that these kinks are associated with phase transitions, which would yield T_c's of 30 and 80 K for the $x=0.10$ and 0.25 salts, respectively. There is, however, at the present time, no independent experimental results which confirm the temperature of phase transitions of these solid solutions.

The solid solution, $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$, $x=0.85$, exhibits a thermopower which differs distinctly from that of both pristine $(\mathrm{TMTSF})_2\mathrm{PF}_6$ and the compositions discussed above. It does, however, to some extent, approach that of $(\mathrm{TMTTF})_2\mathrm{PF}_6$. Above approximately 260 K, the thermopower of the $x=0.85$ and 1 salts are equal. While S of pure $(\mathrm{TMTTF})_2\mathrm{PF}_6$ remains positive upon cooling, the thermopower of the $x=0.85$ salt reaches a maximum of ~ 50 μV/K at approximately 180 K. Upon further cooling, $S(T)$ shows $1/T$ proportionally with negative slope. At ~ 65 K, S crosses zero.

IV. DISCUSSION

The binary alloys of the form $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ display dramatic changes in electrical properties for dilute concentrations of TMTTF molecules. On contrast, the thermopower remains basically unaffected for concentrations as large as 25%. Figure 4 shows some of the characteristics of

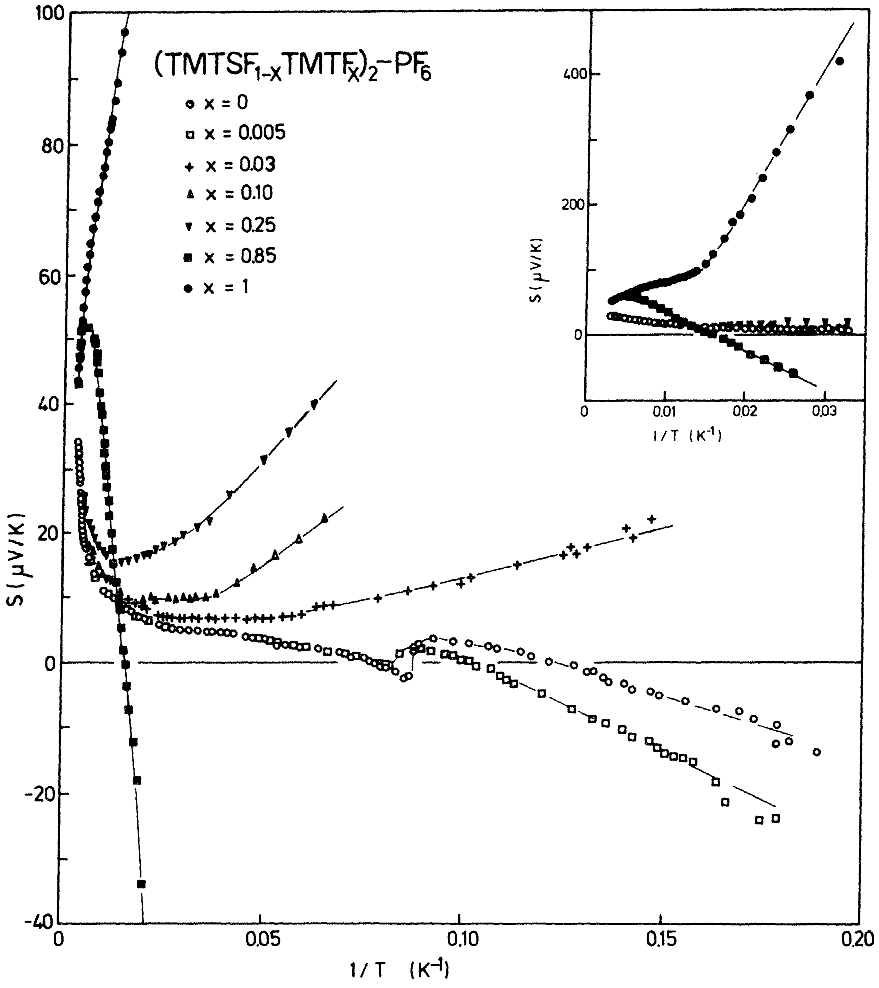

FIG. 3. Thermopower vs inverse temperature of $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$, $x=0$, 0.005, 0.03, 0.10, 0.25, 0.85, and 1. Inset shows expansion of the region with $T > 30$ K, making the data of the $x=0.85$ and 1 salts more clear.

$(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ as a function of x: Resistivity $\rho(300\ \mathrm{K})$, temperature of maximum conductivity T_m, transition temperature T_c [defined by the anomaly in $S(T)$ as discussed above], spin susceptibility $\chi_s(300\ \mathrm{K})$, and thermopower $S(300\ \mathrm{K})$. It appears that ρ, T_m, and χ_s show basically similar x dependences, namely dramatic changes for $x < 0.1$ and only minor changes for $x > 0.1$. T_c increases approximately linear with x for x up to 0.25. The room-temperature value of S, as well as the slope of S vs T, remain approximately unchanged for x up to 0.25, and only the $x=0.85$ salt shows features comparable with those of pristine $(\mathrm{TMTTF})_2\mathrm{PF}_6$. Before going into a discussion on these unusual findings of a solid solution, we will consider some of the relevant properties of the pristine materials.

$(\mathrm{TMTSF})_2\mathrm{PF}_6$ should, above the SDW transition temperature $(T_c = 11.5\ \mathrm{K})$, be treated as a metallic system in which the band properties near the Fermi level are expected to be basically unaffected by the structurally induced midband gap. Assuming a tight-binding band with bandwidth W (transfer integral $t_a = W/4$), Boltzmann-transport theory then gives the thermopower on the form

$$S = -\frac{2\pi^2}{3}\frac{k_B}{e}\frac{k_B T}{W}\left[\frac{\cos(k_F a)}{\sin^2(k_F a)} + \frac{W}{2}\frac{d(\ln\tau)}{d\epsilon}\bigg|_{\epsilon=\epsilon_F}\right], \tag{1}$$

where τ is the single-particle scattering time. The first term of the bracket in Eq. (1), the so-called "band" term, is for the $\frac{3}{4}$-filled TMTSF band equal to $\sqrt{2}$. The latter term of Eq. (1) is called the scattering term.

From optical studies the bandwidth is known to be approximately 1 eV.[15] Application of Eq. (1) to the experimental $S(T)$ curve for $T > 100$ K, which gives $(W/2)d(\ln\tau)/d\epsilon \simeq 0.3$, suggests that the thermopower of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is dominated by the band term. On the basis of a simple perturbation theory, first-order coupling between electrons and external modes leads to a τ given

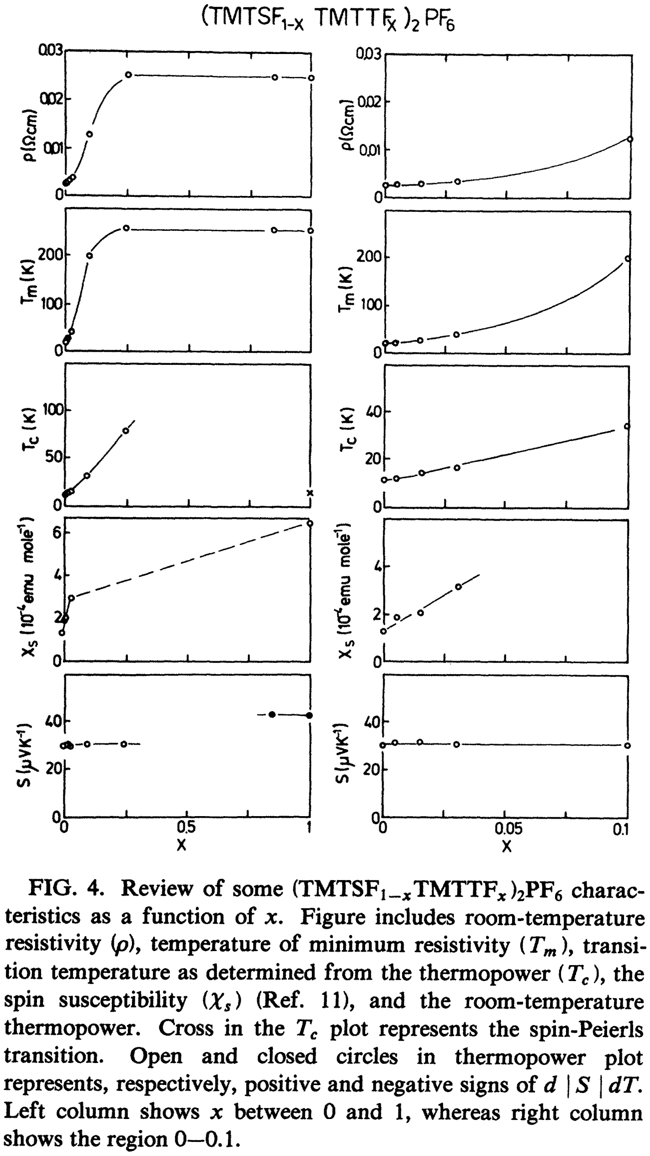

FIG. 4. Review of some $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ characteristics as a function of x. Figure includes room-temperature resistivity (ρ), temperature of minimum resistivity (T_m), transition temperature as determined from the thermopower (T_c), the spin susceptibility (χ_s) (Ref. 11), and the room-temperature thermopower. Cross in the T_c plot represents the spin-Peierls transition. Open and closed circles in thermopower plot represents, respectively, positive and negative signs of $d\,|S\,|\,dT$. Left column shows x between 0 and 1, whereas right column shows the region 0—0.1.

by[4,16]

$$\tau_1(\epsilon)=4\left[\frac{dt_a}{du}\right]^2\frac{\sin(ka)}{Mt_a\omega_q}(2n_q+1)\bigg|_{q=2k}\,, \tag{2}$$

where M is the molecular mass, ω_q is the phonon frequency, and n_q is the phonon occupancy number. dt_a/du describes the coupling from modulation of t_a due to a photon displacement u. If equipartition is valid, $2n_q+1\simeq 2k_BT/\hbar\omega_q$, and only one-phonon branch, for simplicity, is taken into account, the corresponding scattering term of Eq. (1) is

$$\frac{W}{2}\frac{d(\ln\tau)}{d\epsilon}=\frac{2}{\sin(k_Fa)}\frac{d(\ln\omega_{2k})}{d(ka)}\bigg|_{k=k_F}-\frac{\cos(k_Fa)}{\sin^2(k_Fa)}\,, \tag{3}$$

which substituted into Eq. (1) gives

$$S=-\frac{4\pi^2}{3}\frac{k_B}{e}\frac{k_BT}{W\sin(k_Fa)}\frac{d(\ln\omega_{2k})}{d(ka)}\bigg|_{k=k_F}\,. \tag{4}$$

If optical modes dominate τ, it is evident from Eq. (4) that S vanishes as $d\omega/dk\simeq 0$. If, on the other hand, acoustic modes dominate, the scattering term makes precisely the same contribution to S as the band term, assuming that the harmonic approximation $\omega_{2k}=\omega_0\sin(ka)$, is valid. The charge-carrier scattering of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is believed to be dominated by acoustic modes.[17] The dimerization cause, however, a Brillouin-zone boundary exactly at the relevant phonon wave vector, $q=2k_F$. The $\omega_{2k}=\omega_0\sin(ka)$ relation therefore markedly overestimates the scattering term, and it is not unlikely that the term actually will be rather small when acoustic modes dominate. A further discussion of the origin of the band-term-dominated thermopower must await more experimental knowledge about vibrational modes.

The change in slope of S vs T around 100 K has been interpretated as being related to the crossover from one dimensionality to two dimensionality. More directly, this dimensionality crossover has been observed in studies of the b-axis thermopower, which shows a change from hopping to metallic behavior around 100 K.[4] Theoretically it has been shown that a relatively sharp 1D-2D crossover should occur at $T_D\simeq t_b/\pi$ (Ref. 18), which with the transverse transfer integral $t_b=22$ meV (Ref. 15) is 80 K, in good agreement with the experiments. More recently, it has, however, been suggested that the 100-K crossover arises from a structural change with is presumably related to the anions.[19]

The thermopower anomaly observed in the vicinity of the SDW ordering temperature $(T\gtrsim T_c)$ is characterized by a singularity in the temperature derivative of S. This singularity is believed to originate in interactions between the charge carriers and the spin waves.[4] As T approaches T_c, the SDW fluctuations will diverge, thereby giving rise to the $S\propto|T-T_c|^{-\nu}$ term. In the region below T_c, the transport properties of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ are dominated by the gap, which is induced by the new Brillouin zone associated with the SDW vector. In general the thermopower of semiconductors can be expressed in the form

$$S=-\frac{k_B}{e}\left[\frac{\epsilon_a}{k_BT}+A\right]\,, \tag{5}$$

where the T dependence of A, which is related to the detailed band properties, can usually be neglected. In the case of intrinsic conduction, ϵ is a weighted sum of the activation energy,

$$\epsilon_a=[(\sigma_n-\sigma_p)/(\sigma_n+\sigma_p)]E_a\,.$$

For an extrinsic semiconductor dominated by a single defect or impurity level, ϵ_a is equal to the activation energy given by the difference between the defect level and the Fermi energy. For $(\mathrm{TMTSF})_2\mathrm{PF}_6$, ϵ_a/k_B is found to be 2.5 K. From the conductivity, which can be described by $\sigma\propto\exp(-E_a/k_BT)$, E_a is found to be 24 K. Thus, the transport properties of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ cannot be dominated by a single defect level in the temperature region 4—10 K. Assuming intrinsic properties, the experimental values of ϵ_a and E_a give $\sigma_n/\sigma_p\simeq 1.2$. For a $\frac{3}{4}$-filled, simple, tetramized tight-binding band, the ratio σ_n/σ_p should, however, be less than 1. It is, though, possible to conceive of a more complex band structure that makes $\sigma_n/\sigma_p > 1$. Another explanation of the S-vs-T^{-1} relation can be related to the T dependence of E_F if the (4—10)-K region represents a crossover from intrinsic to extrinsic dominance. As T decreases the number of intrinsic carriers decreases and the presence of levels in the lower part of the gap cause E_F to go down toward the valence band. It has in relation to such a model been speculated that the relevant defect level of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is the soliton band, which is expected to exist in 1D commensurate systems.[20] Since the material is at least 2D, however, a shallow hydrogenic level might be more appropriate.[20]

In contrast to the selenium salt, $(\mathrm{TMTTF})_2\mathrm{PF}_6$ should be treated as a system with relatively strong electron correlations, i.e., Coulomb repulsion U for a second electron on a site larger than the bandwidth $4t_a$ (Ref. 7). When $U/4t_a > 1$, as is well known, the Fermi wave vector is doubled. For the $\frac{3}{4}$-filled bands of $(\mathrm{TMTTF})_2\mathrm{PF}_6$ that brings E_F to midband in coincidence with the gap due to dimerization. $(\mathrm{TMTTF})_2\mathrm{PF}_6$ is therefore semiconducting in the whole temperature region studied (4—300 K). In the $U/4t_a \rightarrow \infty$ limit, the high-T thermopower should approach $(k_B/e)\ln 2 \simeq 60$ μV/K, provided that the two Hubbard subbands are symmetric, which is not unreasonable to expect of the $\frac{3}{4}$-filled band. However, the $T \rightarrow \infty$ converging thermopower of $(\mathrm{TMTTF})_2\mathrm{PF}_6$ is only 35 μV/K (see Fig. 3). As discussed in detail by Mortensen, Conwell, and Fabre (Ref. 7), this suggests that, although $U/4t_a > 1$, U is not much larger than $4t_a$. Analysis of magnetic data yields $U/4t_a \simeq 2$ (Ref. 21).

The existence of a gap at the Fermi level is not inconsistent with the observation that the conductivity has a shallow maximum around 200 K since σ is proportional to the product of carrier concentration (n) and mobility (μ). While the former increases with temperature as $T^{1/2}\exp(-E_a/k_B T)$, the latter decreases with temperature as $T^{-\alpha}$, thereby leading to a maximum of σ at $T_m = E_a(\alpha - \frac{1}{2})$. A fit to the experimental curve leads to $E_a/k_B = 600$ K and $\alpha = 3.5$ (Ref. 7). The same value of α is derived for the other $(\mathrm{TMTTF})_2X$ materials, thus indicating that the same kind of scattering mechanism is dominant in that series of compounds. As it appears from the thermopower discussed below, defect levels cause, however, the activation energy to be T dependent. This should be included in a more detailed analysis of $\sigma(T)$.

The thermopower of $(\mathrm{TMTTF})_2\mathrm{PF}_6$ increases by lowering the temperature, as expected for a semiconductor. The slope of S vs $1/T$ is, however, T dependent, thus indicating that both defect-donated and intrinsic band carriers take part in the conduction process. Below approximately 60 K the regular S-vs-$1/T$ dependence suggest that a single defect level has become dominant. The $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ alloys exhibit transport properties which suggest that the compositions with advantage can be separated into three groups. The first group, containing salts with $x \leq 0.03$, exhibits, in general, properties similar to those of pure $(\mathrm{TMTSF})_2\mathrm{PF}_6$. The second group, which is represented by the salts of $x = 0.10$ and 0.25, shows metallic thermopower but activated conductivity. The last group ($x = 0.85$) is dominated by the TMTTF properties.

The salts with $x \leq 0.03$ should be treated as metals of dilute binary alloys. The transport properties of such compositions are commonly analyzed in terms of the Nordheim-Gorter relations

$$\sigma^{-1} = \sigma_0^{-1} + \sigma_1^{-1} , \tag{6a}$$

$$S = S_1 + (\sigma/\sigma_0)(S_0 - S_1) , \tag{6b}$$

where σ_0 and S_0 are the parameters of the pure material [i.e., $(\mathrm{TMTSF})_2\mathrm{PF}_6$ in the present case] and σ_1 and S_1 represent those parameters that would be obtained in a material with the same band structure as that of the solvent, but with the charge-carrier scattering dominated by impurities such as those introduced by the solutes (i.e., TMTTF molecules). The Nordheim-Gorter rule thus predicts a linear relation between the resulting thermopower and conductivity of the alloys. The measurements on $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ indeed show such a linear S-vs-σ relationship for T above approximately 100 K. The behavior is, however, rather abnormal as the slope of S vs σ is zero. According to the Nordheim-Gorter rule this implies that the thermopower is independent of whether the charge-carrier scattering is dominated by phonons or impurities. Although it is questionable whether the Nordheim-Gorter rule in the simple linear S-vs-σ form applies to quasi-1D conductors, it is reasonable to believe that this conclusion applies to the present alloys. The result is also in perfect agreement with the analysis above, showing that the band term dominates the thermopower of pristine $(\mathrm{TMTSF})_2\mathrm{PF}_6$ [cf. Eq. (1)]. The composition-independent thermopower, moreover, suggests that the band properties in the state of dominating 1D properties ($T > 100$ K) are not seriously affected by the introduction of TMTTF molecules into the conducting chain. This is in agreement with recent optical-reflection measurements showing that the transfer integral (t_a) of $(\mathrm{TMTTF})_2\mathrm{PF}_6$ is reduced by only 20% compared to that of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ (Ref. 15).

Below approximately 100 K some deviations in the thermopower of the alloys compared to the pristine TMTSF salt appear. The change in slope of S vs T becomes less pronounced and the temperature associated with the change is somewhat suppressed. Since this anomaly in S of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is attributed to the 1D-2D crossover, it is likely that the observations on S reflect enhanced one dimensionality upon doping with TMTTF. Pure $(\mathrm{TMTTF})_2\mathrm{PF}_6$ is certainly more 1D than the selenium analogs, and preliminary studies of the anisotropic conductivity of dilute alloys have indicated similar conclusion.[11] The enhanced one dimensionality can, moreover, explain the rise in T_c if it causes improved nesting of the Fermi surface.

The dilute alloys show suppression of the $(T - T_c)^{-\nu}$-dependent thermopower term near the SDW ordering temperature. As shown above this T dependence probably reflects some interactions between the charge carriers and the spin waves. The detailed mechanism is though still unknown. It may simply be a magnon-drag effect. The suppression of the associated thermopower can then easily be understood as the impurities will dominate the spin-wave scattering. This is analogous to the well-known effect on the phonon-drag thermopower of classical metals incorporated with impurities.

The $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ alloys with $x=0.1$ and 0.25 show anomalous behavior: The thermopower displays metallic characteristics while the conductivity appears to be basically semiconducting. The high degree of similarity between the thermopower of these two intermediate alloys and that of the salts with more dilute concentrations of TMTTF suggests that the band properties are not seriously affected by the large amount of TMTTF molecules substituted into the conducting chains. Especially, there cannot be any gap at the Fermi level. These findings are in accordance with expectations when only the transfer integrals (t_a) are taken into account. The semiconducting character of the conductivity must then be a result of the mobility being activated and not the number of charge carriers. The more or less activated mobility can be understood when the electronic properties of the TMTTF molecules beyond the t_a integral are taken into account. The transverse transfer integrals (t_b) are very small and may lead to a large Coulomb repulsion (U) on the TMTTF molecules. Each of these molecules allow, therefore, even when situated in the TMTSF surroundings, occupation by only one charge carrier. The TMTTF molecules may act as ionic scattering centers which prevent the metallic mobility. This model also explains the disproportionally large TMTTF contribution to the magnetic properties of the alloys found experimentally[11] since the majority of the TMTTF sites contain exactly one spin.

In the $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$, $x=0.85$ sample, the large U has become a dominant band property and is no longer localized to the individual TMTTF molecules. Therefore, the Mott-Hubbard insulating properties dominate the alloy in a way similar to the situation in pristine $(\mathrm{TMTTF})_2\mathrm{PF}_6$. At high temperatures the transport properties seem to be dominated by the same kind of defect or impurity levels as in the pure salt. Below approximately 250 K, however, the S and σ of the alloy deviate from that of $(\mathrm{TMTTF})_2\mathrm{PF}_6$, thus indicating that new defect levels have been introduced by the TMTSF dopant.

One may argue for an alternative explanation of the transport properties of the intermediate alloys that is based on a model of variable-range hopping. The conductivity varies basically as $\exp[-(T_0/T)^{1/4}]$ in such a system, whereas the thermopower has a square-root dependence, $S \propto T^{1/2}$ (Ref. 22). Although the experimental S-vs-T dependence appears very linear, suggesting diffusion transport [cf. Eq. (1)], we cannot ignore the fact that the variable-range-hopping model will fit the experimental data when more detailed analyses are worked out. However, one should expect to see some significant changes in the thermopower when the conduction process crosses over from diffusion to hopping, in contrast to the experimental findings.

V. SUMMARY

The studies of the transport properties of solid solutions of the form $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ have provided some new insights on these unusual materials based on, respectively, the TMTSF and the TMTTF molecules. In spite of the structural similarities between the two pristine salts, $(\mathrm{TMTSF})_2\mathrm{PF}_6$ and $(\mathrm{TMTTF})_2\mathrm{PF}_6$, behave very differently. While $(\mathrm{TMTSF})_2\mathrm{PF}_6$ is metallic down to the SDW ordering at 11.5 K, $(\mathrm{TMTTF})_2\mathrm{PF}_6$ is already semiconducting at ambient temperature. The experimental study of $(\mathrm{TMTSF}_{1-x}\mathrm{TMTTF}_x)_2\mathrm{PF}_6$ have shown that the semiconducting properties of $(\mathrm{TMTTF})_2\mathrm{PF}_6$ are not due to a small bandwidth. On the contrary, W is approximately the same as that of the metallic selenium analogous. The semiconductivity is a result of a large on-site Coulomb correlation which gives rise to a Mott-Hubbard insulator. Presumably, the large U is caused by a rather small interchain transfer integral. The dramatic effects on a number of physical properties of $(\mathrm{TMTSF})_2\mathrm{PF}_6$ when doped with dilute concentrations of TMTTF are also attributed to the large U and small t_b associated with the TMTTF molecule. The studies of alloys with $x \leq 0.25$ show that the thermopower is dominated by the band properties and that the scattering term plays a minor role. The studies show moreover that the materials become more 1D upon doping. The impurities or defects introduced by the TMTTF molecules in the conducting chains cause suppression of the thermopower term associated with charge-carrier interactions with the spin waves. In the semiconducting states, the impurities or defects introduce new levels in the energy gap. These levels dominate the transport properties.

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*Permanent address: Physics Department, Risø National Laboratory, DK-4000 Roskilde, Denmark.

[1] For recent reviews, see Proceedings of the International Conference on Low Dimensional-Conductors, Boulder, Colorado, 1981 [Mol. Cryst. Liq. Cryst. 79 (1982)]; Proceedings of Le Colloque International du CNRS sur la Physique et la Chimie des Métaux Synthétiques et Organiques, Les Arcs, France, 1982 [J. Phys. (Paris) Colloq. C3 (1983)].

[2] D. Jerome, A. Mazaud, M. Ribault, and K. Bechgaard, J. Phys. Lett. 41, L95 (1980).

[3] K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, Solid State Commun. 33, 1119 (1980).

[4] K. Mortensen, Solid State Commun. 44, 643 (1982).

[5] K. Mortensen, Y. Tomkiewicz, T. D. Schultz, and E. M. Engler, Phys. Rev. Lett. 49, 1234 (1981).

[6] C. Coulon, P. Delhaes, S. Flandrois, R. Lagnier, E. Bonjour, and J. M. Fabre, J. Phys. (Paris) 43, 1059 (1982).

[7] K. Mortensen, E. M. Conwell, and J. M. Fabre, Phys. Rev. B 28, 5856 (1983).

[8] J. P. Pouget, R. Moret, R. Comes, K. Bechgaard, J. M. Fabre,

and L. Giral, Mol. Cryst. Liq. Cryst. 79, 485 (1982).

[9] For a review of the organic alloys $(\mathrm{TTF}_{1-x}\mathrm{TSeF}_x)(\mathrm{TCNQ})$, see T. D. Schultz and R. A. Graven, in *Highly Conducting One-Dimensional Solids*, edited by J. T. Devreese, R. P. Evrard, and V. E. van Doren (Plenum, New York, 1979).

[10] K. Mortensen, C. S. Jacobsen, J. R. Andersen, and K. Bechgaard, *Lecture Notes in Physics* (Springer, Berlin, 1979), Vol. 96, p. 159.

[11] K. Mortensen, Y. Tomkiewicz, T. D. Schultz, E. M. Engler, V. V. Patel, and A. R. Taranko, Solid State Commun. 40, 915 (1981).

[12] E. M. Engler, R. Greene, P. Haen, Y. Tomkiewicz, K. Mortensen, and J. Berendzen, Mol. Cryst. Liq. Cryst. 79, 371 (1982).

[13] C. Coulon, P. Delhaes, J. Amiell, J. P. Manceau, J. M. Fabre, and L. Giral, J. Phys. (Paris) 43, 1721 (1982).

[14] K. Mortensen, unpublished results.

[15] C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, Phys. Rev. Lett. 46, 1142 (1981); J. Phys. (Paris) Colloq. C3, 859 (1983); Phys. Rev. B 28, 7019 (1983).

[16] E. M. Conwell, Phys. Rev. B 22, 1761 (1980).

[17] E. M. Conwell and C. S. Jacobsen, Solid State Commun. 40, 203 (1981).

[18] V. J. Emery, J. Phys. (Paris) Colloq. C3, 977 (1983).

[19] A. Maaroufi, C. Coulon, S. Flandrois, P. Delhaes, K. Mortensen, and K. Bechgaard, Solid State Commun. 48, 555 (1983).

[20] E. M. Conwell, Phys. Rev. B 27, 7654 (1983).

[21] P. Delhaes, Mol. Cryst. Liq. Cryst. (in press).

[22] See, e.g., N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).