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Thermopower studies of a series of salts of tetramethyltetrathiafulvalene [(TMTTF)$_2X$, $X=$Br, ClO$_4$, NO$_3$, SCN, BF$_4$, AsF$_6$, and PF$_6$]

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Thermoelectric power measurements on a group of tetramethyltetrathiafulvalene (TMTTF)$_2X$ salts show a wide variety of behavior. In the range of temperatures $300 \geq T \geq 100$ K several of the salts ($X=$BF$_4$, ClO$_4$, NO$_3$, SCN) have a constant thermopower $S \simeq 35$ μV/K, while the PF$_6$ and AsF$_6$ salts have $S \propto 1/T$, and the Br salt has S increasing with T. Below ~ 100 K, S shows a steep increase or decrease with decreasing temperature for each salt which, with the exception of the SCN salt, is not associated with a phase transition. These materials had been identified as semiconductors below the maximum in conductivity σ vs T. We give arguments that the gap at the Fermi energy exists at temperatures above the maximum as well. The existence of a gap is good evidence that the material is characterized by Coulomb repulsion U for a second electron on a site larger than the bandwidth $4t$. However, the constant finite $S < 60$ μV/K found for several of the compounds above ~ 100 K suggests that U is not much larger than $4t$. The different behavior of S for the PF$_6$ and AsF$_6$ salts in the same temperature range and the sharp changes in S vs T at low temperatures (except for the SCN salt) are attributed to defects rather than, e.g., localization. In the SCN, ClO$_4$, and Br salts, features are seen at low temperatures that reflect known phase transitions in these materials.

I. INTRODUCTION

The discovery of superconductivity in a number of organic compounds based on the tetramethyltetraselenafulvalene (TMTSF) molecule and more recently on a single composition of the sulfur analog, tetramethyltetrathiafulvalene (TMTTF), has generated a great deal of interest in these compounds.[1] The compounds, with formulas (TMTSF)$_2X$ and (TMTTF)$_2X$, are isostructural, belonging to the $P\bar{1}$ space group.[2] The nearly planar TMTSF or TMTTF molecules, which form zig-zag stacks along the a direction, are slightly tilted relative to the stacking axis, resulting in dimerization. Charge transfer to the anions would result in $\frac{3}{4}$-filled bands, or $\frac{1}{4}$-filled hole bands, on the TMTSF or TMTTF stacks if we were to neglect the dimerization.[3]

Most of the studies so far have been focused on the (TMTSF)$_2X$ salts. These are quite good conductors along the chain direction, with typical conductivity $\sigma \simeq 600$ Ω^{-1}cm^{-1} at room temperature. This fact, plus the decrease in σ with temperature T over a wide range as T^{-2}, and many other properties, indicate that these salts are metallic at room temperature and over a wide range below.[3] The (TMTTF)$_2X$ salts are not as good conductors. Room-temperature conductivities are typically 20—100 Ω^{-1}cm^{-1} and $\sigma(T)$ shows a broad maximum at a temperature T_m between 200 and 250 K for $X=$NO$_3$, BF$_4$,

ClO$_4$, PF$_6$, and SCN, around 100 K for $X=$Br.[4,5] Below T_m, σ decreases more or less exponentially with temperature.[4,5] For $X=$PF$_6$, NO$_3$, and BF$_4$ an activation energy of ~ 600 K is found.[5] A similar activation energy is obtained for $X=$ClO$_4$ down to 50 K, the lowest temperature for which there are data, with the exception of a ~ 15-K-wide structure around 70 K which corresponds to the ordering of the anion sublattice.[5] The fact that sublattice ordering has only a small effect, which will be further documented later, eliminates the possibility that anion disorder is responsible for the nearly exponential decrease of σ with decreasing T for $T < T_m$. The decrease must therefore be due to a gap at the Fermi energy E_F.

The dimerization of the lattice causes a gap to open at what would have been the middle of the $\frac{3}{4}$-filled band. To simplify further discussion we will speak in terms of $\frac{1}{4}$-filled hole bands. If E_F were at the $\frac{1}{4}$-filled-band level, a gap at midband would clearly have little effect on σ since the bandwidth is much greater than kT. This is apparently the situation for the (TMTSF)$_2$ salts. The existence of a gap at E_F in the (TMTTF)$_2X$ salts can only be understood if they have strong electron correlations, i.e., Coulomb repulsion U for a second electron on a site larger than the bandwidth $4t$. X-ray studies have failed to show any other source of a gap at T_m or above. When $U > 4t$, as is well known, the Fermi wave vector is doubled. For (TMTTF)$_2X$ that brings E_F to midband, in coincidence

with the gap due to the dimerization. In the TMTSF salts $4t$ is expected to be larger, so that even if U had a value comparable to that in TMTTF, the condition $U < 4t$ could be satisfied. The proposal that a gap exists at E_F in the (TMTTF)₂X compounds due to large U was first made by Emery, Bruinsma, and Barisic.[6] Although the existence of a gap at E_F is the strongest evidence for $U > 4t$ in these compounds, additional evidence is provided by measurements of the magnetic susceptibility χ.[4,5] From the enhancement of χ, it was concluded that $U/4t \approx 2$.[4] The behavior of χ vs T is quite similar to that for quinolinium ditetracyanoquinodimethanide Qn(TCNQ)₂ (Ref. 7) and many other $\frac{1}{4}$-filled-band salts known to have large U.

As in the TMTSF family, a wide variety of transitions is seen in the TMTTF group of compounds. At 160 K in (TMTTF)₂SCN there is a $4k_F$ structural transition, probably coupled with an order-disorder transition in the anion lattice.[8] This is correlated with a sharp decrease in σ with decreasing temperature, indicating the widening of the gap at the Fermi energy. A spin-Peierls transition has been observed at 15 K in (TMTTF)₂PF₆.[9,10] In (TMTTF)₂Br, which is the one of this group most like the TMTSF compounds, a spin-density-wave (SDW) transition, similar to that occuring in those compounds, is seen at 19 K.[10,11] This also widens the gap at E_F, as evidenced by the steeper slope of σ vs T below 19 K.[5] An order-disorder transition of the anions takes place around 70 K in the ClO₄ compound and around 40 K in the BF₄ compound.[5,9]

To further investigate the phase transitions, charge-carrier correlations, and other properties of these interesting compounds, we have measured the thermoelectric power of a group of them over a wide range of temperatures. In the next section we report our results. Discussion of the results is carried out in two sections, the first on high-temperature ($T \geq 100$ K) results, the second on low-temperature results. In the former we point out that the temperature variation of S and the magnetic susceptibility indicates there is no phase transition in this range. The maximum in σ is due to the competition between the number of carriers, which increases with T, and the mobility, which decreases with T. We derive a linear relation between T_m and the gap which enables us to deduce the value of the gap for the Br salt. It is suggested that the constant S, with a value less than the 60 μV/K predicted for intrinsic samples in the $U \to \infty$ limit, is due to U being not much larger than $4t$. The different behavior of S for the PF₆ and AsF₆ salts in this T range is attributed to defects. There is some evidence for greater defect concentration in the samples of these compounds. In the section on low-temperature results we are particularly concerned with the very rapid increase or decrease of S that appears below ~ 100 K for all but the SCN salts. After eliminating the possibilities that these sharp changes are due to phase transitions or disorder, we demonstrate that they could be due to defect levels. Finally, we summarize our results and conclusions.

II. MEASUREMENTS AND RESULTS

The samples were obtained by the electrochemical growing technique.[3] For the salts $X =$ ClO₄, NO₃, BF₄,

SCN, PF₆, and Br, the samples were taken from the same batches as those of Ref. 5. The thermopower data were obtained in a conventional apparatus using a slowly alternating temperature difference of typically 0.2 K. The samples were mounted on gold leads and contacts were made using silver paint.

The results are shown in Figs. 1—3. The data for (TMTTF)₂Br (Fig. 1) were separated because they differ distinctly from those for the other salts studied. At high temperatures, i.e., above ~ 100 K, S increases approximately linearly with T for this salt. As seen in Figs. 2 and 3, S at high temperatures for the ClO₄, SCN, BF₄, and NO₃ salts, in contrast, has a T-independent value between 30 and 35 μV/K (± 2 μV/K). The PF₆ and AsF₆ compounds have still a different T dependence, S varying approximately as $1/T$ at high temperatures. In the high-T limit, S for these two salts approaches a 30-μV/K value, suggesting they have similar characteristics to the other salts in that limit. For all of the salts (except AsF₆, for which data were not obtained to low enough temperatures) the quasilinear or constant behavior of S is replaced at some low temperature by a rapid increase or decrease with further decrease in T. It should be noted that we have obtained the same results on samples of (TMTTF)₂PF₆ and (TMTTF)₂Br made in other laboratories.
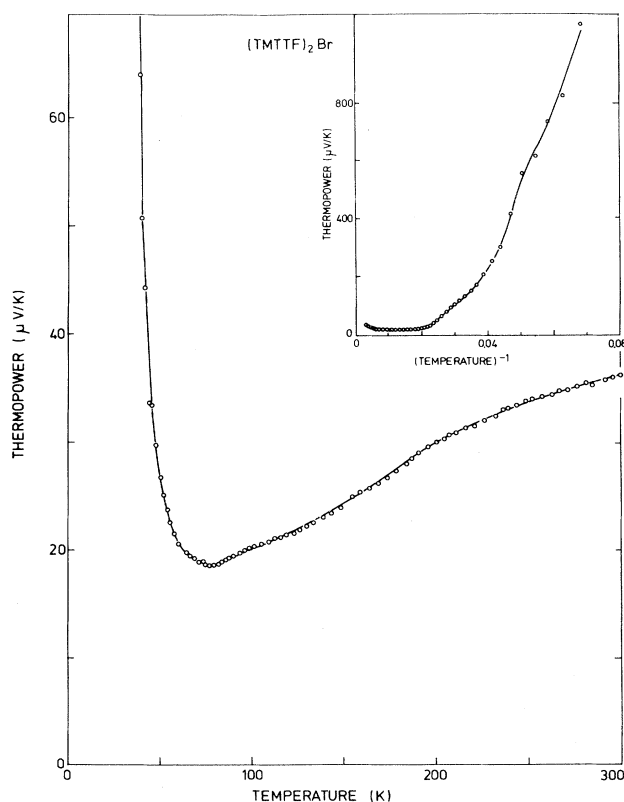

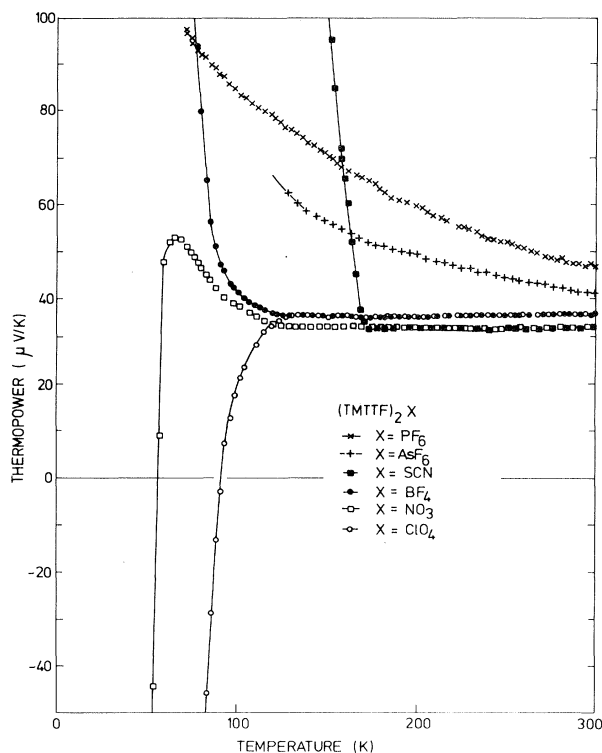FIG. 1. Thermopower vs temperature and inverse temperature for (TMTTF)₂Br.

FIG. 2. Thermopower vs temperature for $(TMTTF)_2X$, $X=BF_4$, NO_3, SCN, ClO_4, AsF_6, and PF_6.

FIG. 3. Thermopower vs inverse temperature for $(TMTTF)_2X$, $X=BF_4$, NO_3, SCN, ClO_4, AsF_6, and PF_6.

III. DISCUSSION OF RESULTS FOR $T > 100$ K

It was suggested in Ref. 6 that the metal-semiconductor transition in these materials occurs around T_m due to a rapid increase in dimerization there. The constant value of the thermopower for BF_4, NO_3, and ClO_4 salts over the T range $\sim 100-300$ K and for the SCN salt from 170 to 300 K indicates, however, that there is no phase transition in this range for these materials. The lack of structure in the magnetic susceptibility versus T in this range[4,5] is further evidence to this effect. Thus the gap at the Fermi energy must exist throughout the range (as well as outside it), although of course it may vary with temperature. This is not unexpected for a gap that arises from the dimerization and the potential due to the anions on the TMTTF stacks. There is no reason why the anion potential should vanish, although its effect might be somewhat decreased at high T's due to lattice vibrations, and there is no evidence that the dimerization vanishes in this temperature range. The existence of a gap at all temperatures in the range is not inconsistent with the observation that the conductivity has a shallow maximum within this range for all these materials. The conductivity σ is proportional to the product of carrier concentration n and mobility μ. The former increases with temperature in a one-dimensional (1D) case as $T^{1/2}\exp(-E_G/2k_BT)$ where E_G is the gap, while the latter decreases with temperature as $T^{-\alpha}$, where the value of α depends on the scattering mechanism. When $E_G \sim k_BT$ the rate of increase of n with T is not rapid and
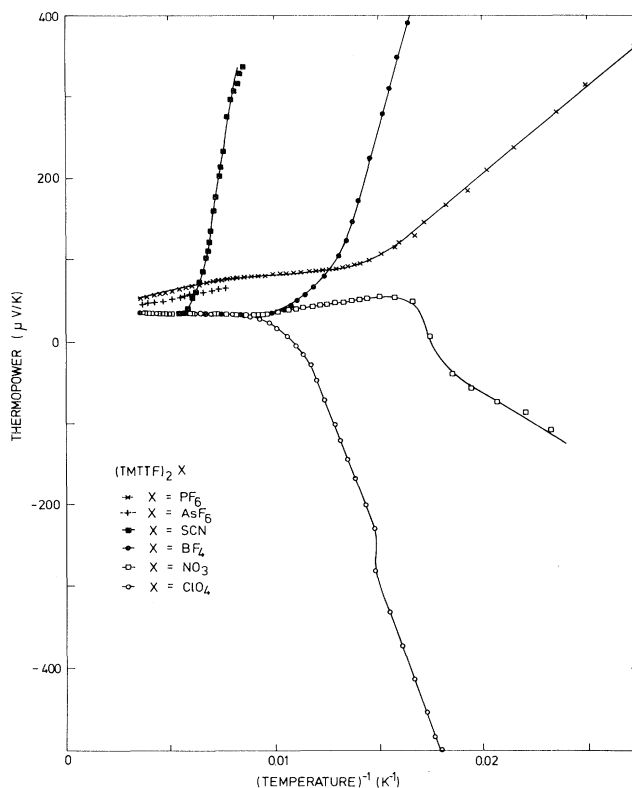
can well be smaller than the rate of decrease of μ with T, making the net change in σ with increasing T a decrease. It has been shown that a combination of these two factors can account well for σ vs T of $Qn(TCNQ)_2$ and other $\frac{1}{4}$-filled-band materials over a wide range of temperatures including a similar shallow maximum.[12] In fact, the maximum of $Qn(TCNQ)_2$ is around 250 K, about the same as those for several of the $(TMTTF)_2X$ salts, and $E_G/2$ required for a fit to σ vs T in the $Qn(TCNQ)_2$ case was ~ 600 K,[12] the value found experimentally for $X=PF_6$, NO_3, BF_4, and ClO_4 in the "semiconducting region,"[5] i.e., the region in which E_G is sufficiently greater than $2k_BT$ that the exponential T variation of n dominates σ. Thus parameters similar to those for $Qn(TCNQ)_2$ should result in a good fit for σ vs T of $(TMTTF)_2X$ with $X=BF_4$, NO_3, and ClO_4 from ~ 100 to 300 K. Below that the situation is probably different, as evidenced by the sharp change in S vs T. In the case of the SCN salt the fit would only cover the region $\sim 170-300$ K due to the phase transition at ~ 169 K which apparently greatly widens the gap.

Conductivity versus T of the Br compound is also consistent with a gap at the Fermi energy existing up to 300 K and beyond, but the gap must be considerably smaller than for the compounds discussed above since the temperature of the maximum, T_m, in σ is much lower. We can calculate the gap from the measured value of T_m.

With n and μ having the T dependences specified above, the maximum in σ occurs at $T_m = (E_G/2k_B)/(\alpha - \frac{1}{2})$. Thus, if we make the reasonable assumption that α is about the same for all members of this group of compounds, with T_m for the Br compound about half as large as that for the others its gap must be about half as large, i.e., the gap in the Br compound is ~ 600 K. We note that for $T_m \simeq 200$ K and $E_G \simeq 1200$ K, or equally for $T_m \simeq 100$ K and $E_G \simeq 600$ K, the relation between T_m and E_G requires $\alpha \simeq 3.5$. Interestingly, this is close to the values of α obtained by fitting σ vs T for (N-methylphenazinium) (tetracyanoquinodimethanide) (NMP)(TCNQ), Acridizinium(TCNQ)$_2$ [Adz(TCNQ)$_2$], etc.[12] (Note that α in Ref. 12 is smaller by $\frac{1}{2}$ than the value used here.) Such values of α, in contrast to the value of ~ 2 obtained for metallic compounds in this family, are accounted for by internal-mode scattering being dominant.[12] The smaller effect of acoustic-phonon scattering in the semiconducting state, as compared to the metallic state, is due to the much smaller size of phonons with which the carriers interact in a semiconductor. Since coupling to the internal modes is strong, they easily dominate the scattering in the semiconductor once the temperature is high enough for them to be excited. With the known internal phonon frequencies and coupling constants, α values of 3.5—4 were obtained for conduction along TCNQ chains in the temperature range concerned.[12] Even higher values were obtained for TTF chains due to very strong coupling to a mode with relatively high energy, 475 cm^{-1}.[12] No detailed information is available on internal modes in TMTTF, but it is reasonable to expect that there are comparable modes, and that these, with perhaps some admixture of acoustic mode or libron scattering, could account for an α of 3.5. It should also be noted that α values are not precise. For one thing, in fitting to obtain α we neglect the possibility that the gap may be somewhat temperature dependent. Nevertheless, $\alpha = 3.5$ leads for the Br compound, to a ratio between σ at 100 K and σ at 300 K of 3.7, in good agreement with the data of Coulon et al.[5] The higher room-temperature σ of the Br compound, 240 Ω^{-1}cm^{-1} vs 40—50 for the SCN, PF$_6$, ClO$_4$, and BF$_4$ compounds,[5] is partly due to the smaller gap, which results in carrier concentration 2.7 times as large as for the other compounds. The remaining difference is attributable to larger μ, expected due to the greater overlap.

It has been pointed out that T_m in these compounds is correlated with the degree of dimerization.[6] The linear relation given above between T_m and E_G establishes the connection between E_G and the degree of dimerization.

We consider now what to expect for the variation of thermoelectric power with temperature in the range ~ 100—300 K. For a single type of carrier,

$$S_{\mp} = \mp \frac{k_B}{|e|} \left[\frac{|E_F - E_b|}{k_B T} + \frac{|\Delta E_T|}{k_B T} \right] , \tag{1}$$

where the upper sign is for electrons, the lower for holes, $|E_F - E_b|$ is the distance of the Fermi energy from the conduction- or valence-band edge, and $|\Delta E_T|$ is a weighted average of the energy transported per carrier (across unit area in unit time) relative to the band edge.

When the concentration of electrons in the conduction band is n, of holes in the valence band p, the thermopower for the sample is[13]

$$S = \frac{S_n \sigma_n + S_p \sigma_p}{\sigma_n + \sigma_p} . \tag{2}$$

Since we are dealing with a $\frac{3}{4}$-filled band it is not unreasonable to expect the two Hubbard subbands to be symmetric in the sense that bandwidths and scattering processes are the same. In the intrinsic temperature region, where $n = p$, the kinetic-energy contributions to S of the two bands would then cancel and

$$S = \frac{k_B}{2|e|} \left[-\frac{E_C - E_F}{k_B T} + \frac{E_F - E_V}{k_B T} \right]$$

$$= \frac{k_B}{|e|} \left[\frac{E_F - E_G/2}{k_B T} \right] . \tag{3}$$

Here E_c and E_v denote conduction- and valence-band edges and $E_F - E_G/2$ is the distance of the Fermi energy from midgap. Thus in the intrinsic region when the bands are symmetric we will obtain S independent of T over a range of temperatures provided that

$$E_F - E_G/2 = \gamma k_B T , \tag{4}$$

γ being a constant in this range. This condition is clearly satisfied in the $U = 0$ limit, where $\gamma = 0$. It is also satisfied in the $U \to \infty$ limit when $E_G > k_B T$ provided the bands are symmetric.[14] We show now that (4) will not be satisfied if the bands are not symmetric. When $E_G \gg k_B T$, which should apply in this T range for all but the Br salt, Maxwell-Boltzmann statistics may be used. In the large-U limit, for the $\frac{3}{4}$-filled band, we obtain[14]

$$n = (\pi a)^{-1} F(E_0^{(c)}) \exp[-(E_c - E_F)/k_B T] ,$$
$$p = (4\pi a)^{-1} F(E_0^{(v)}) \exp[-(E_F - E_v)/k_B T] , \tag{5}$$

where a is the lattice constant, E_0 is the bandwidth, and

$$F(E_0^{(i)}) \equiv \int_0^{E_0^{(i)}} e^{-E/k_B T} [E(E_0^{(i)} - E)]^{-1/2} dE . \tag{6}$$

Equating n to p we obtain for the Fermi energy

$$E_F = E_G/2 \mp k_B T \ln 2 + (k_B T/2)\ln[F(E_0^{(v)}/F(E_0^{(c)})] , \tag{7}$$

the upper and lower signs holding for the $\frac{1}{4}$- and $\frac{3}{4}$-filled bands, respectively. Inserting (7) in Eqs. (1) and (2) we obtain

$$S = -\frac{k_B}{|e|} \left[\frac{E_G}{2k_B T} \frac{\sigma_n - \sigma_p}{\sigma_n + \sigma_p} \pm \ln 2 - \frac{1}{2} \ln \left(\frac{F(E_0^{(v)})}{F(E_0^{(c)})} \right) \right.$$

$$\left. + \frac{\sigma_n |\Delta E_T|_n - \sigma_p |\Delta E_T|_p}{(\sigma_n + \sigma_p)k_B T} \right] . \tag{8}$$

It is clear, as stated above, that Eq. (8) will not lead to a temperature-independent S unless $\sigma_n = \sigma_p$ and scattering processes and bandwidths are the same for the two bands. When those conditions are satisfied it is seen from (8) that, for $U \to \infty$, γ in Eq. (4) is $-\ln 2$ for a $\frac{1}{4}$-filled band, $+\ln 2$ for a $\frac{3}{4}$-filled band. The latter leads to $S = +60$

μV/K for the $\frac{3}{4}$-filled band in the $U \rightarrow \infty$ limit. As noted earlier, the magnitude of $U/4t$ deduced from the susceptibility for these compounds is ~ 2. It is reasonable that the behavior of E_F and S for this case be similar to what has been described for $U \rightarrow \infty$. However, since $\gamma = 0$ in the limit $U \ll 4t$, it is likely that γ decreases when $U/4t$ is not infinite, i.e., $\gamma < \ln 2$ for the $\frac{3}{4}$-filled band when $U/4t$ is not ∞. This could account for a constant value of $S < 60$ μV/K being seen for the BF$_4$, ClO$_4$, NO$_3$, and SCN salts for a wide range of temperatures below 300 K. It was seen from Eq. (8) above that lack of symmetry between conduction and valence bands would not account for this. We note that thermopower data exist for at least one case in which $U \sim 4t$, (NMP)$_x$(Phen)$_{1-x}$TCNQ, where Phen represents phenazine, with $x = 0.63$.[15] S in this case $\simeq -55$ μV/K for $300 > T > 80$ K, as compared with -65 μV/K for a sample with $x = 0.54$, for which $U > 4t$. The decrease in S, however, cannot be uniquely assigned to the decrease in $U/4t$ since the additional doping in the 0.63 sample may also affect E_F. A small piece of evidence in favor of this explanation is that the BF$_4$ and ClO$_4$ compounds, which have larger values of χ and thus larger U than the NO$_3$ salt,[5] have slightly larger values of S than the NO$_3$ salt. χ data are not available for the SCN salt.

In light of the above discussion, S for the PF$_6$ salt, which has a gap as large as or larger than that of the SCN, ClO$_4$ salts, etc., should also have a constant value at high temperatures. Indeed, it does appear to be approaching a constant value of the order of that for SCN, ClO$_4$, BF$_4$, etc., in the high-T limit above 300 K. This would indicate that conduction band and valence band are symmetric in that limit. A $1/T$ dependence from 300 down to 100 K or lower could be accounted for by the $E_G/2k_BT$ term in Eq. (8) since the terms in $F(E_0^{(i)})$ and ΔE_T are weakly T dependent. However, this would require that the symmetry of these bands be lost somewhere above 300 K. It is possible to conceive of a complex band structure that makes the bands nonsymmetric for $T \lesssim 300$ K while they appear symmetric for $T > 300$ K, but it is difficult to explain why such a band structure would be seen in the PF$_6$ salt and not in the others. A more likely explanation is that there are defects or impurities present in the PF$_6$ salt. The detailed variation of E_F and S with T is then determined by the number and location of defect levels. A $1/T$ dependence of S can result, as will be shown in the next section. Evidence that the PF$_6$ samples have more defects than the others comes from the magnetic susceptibility. χ begins to rise with decreasing T for this salt at ~ 80 K,[5] a much higher temperature than for the other salts in the group. Although the rise is interrupted around 20 K, presumably due to the phase transition that occurs in that neighborhood,[6] it undoubtedly represents a Curie tail, indicating that the number of defect spins is much larger in this material than in the others. Another piece of evidence for significant defect concentration is the fact that $\ln\sigma$ vs $1/T$ shows no region of constant slope in the entire T range. The gradual rise of S vs T suggests that the defect level is close to midgap. The similar behavior of S vs T for the AsF$_6$ salt may have the same origin. The available crystals of that salt were of very poor quality.

Large numbers of cracks made low-temperature thermopower studies impossible.

The Br salt differs from the others in having smaller dimerization[2] and a smaller gap, as we have seen. Owing to the greater overlap of S atoms on adjacent chains it is also more 3D than the other salts of this group.[5] It is also likely, as noted earlier, that t is larger, making $U/4t$ smaller. In any case, a number of its properties are intermediate between those of the TMTTF salts we have been discussing and those of a typical TMTSF salt such as (TMTSF)$_2$PF$_6$, and this is also true of the thermopower for $T \gtrsim 100$ K. S for (TMTSF)$_2$PF$_6$ decreases linearly by a factor of 3 in the range $300 > T > 100$ K,[3,16] while the decrease for (TMTTF)$_2$Br is by less than a factor of 2 in this range.

IV. DISCUSSION OF RESULTS FOR $T \lesssim 100$ K

A feature of considerable interest in the thermopower of these materials is the very rapid increase or decrease observed at some temperature below 100 K, except for the SCN salt where it is observed at ~ 170 K. In the latter case the temperature at which the rapid increase occurs more or less coincides with that at which σ drops rapidly. This temperature has been associated with a phase transition involving a superstructure formation and probably an anion ordering with perhaps an accompanying change in the TMTTF stack dimerization.[8] In any case, it is reasonable that there is a relatively abrupt increase in gap accompanying this transition, explaining the rapid decrease in σ that occurs around the transition temperature. The rapid increase in S with T could be due to a small asymmetry of the conduction and valence bands arising from this transition. Analysis of the data according to Eq. (8), under the assumption that the bands are close enough to symmetry that the terms involving $|\Delta E_T|$ and $F(E_0)$ are small, yields an effective gap, $E_G(\sigma_p - \sigma_n)/(\sigma_p + \sigma_n)$, of 1450 K.

In no case other than that of the SCN salt is the beginning of the sharp change in S close enough to a phase transition to be associated with it. No structure in σ vs T or χ vs T or in x-ray investigations has been observed around the temperature at which the rapid increases or decreases in S occur. Similar sharp changes from constant S vs T, not associated with phase transitions, have been observed in many $\frac{1}{4}$-filled-band compounds with large U, e.g., Qn(TCNQ)$_2$,[17] (NMP)$_x$(Phen)$_{1-x}$TCNQ for various x,[15] and (TEA)(TCNQ)$_2$,[18] where TEA represents triethylammonium, and it has been argued, at least in the Qn case, that the drop arises from localization of the conduction electrons due to disorder on the anion chains. It is clear that there is no such effect in this group of compounds. As noted earlier, in the ClO$_4$ salt σ vs T has essentially the same T dependence above and below the anion ordering temperature of ~ 75 K; the only effect of the ordering is a wiggle in σ vs T over a (10–15)-K range around 75 K.[5] For two salts with centrosymmetric ions, I and PF$_6$, σ vs T differs little over the entire measurement range, $300 \geq T \geq 50$ K, from that of the NO$_3$ salt, where the ions are disordered throughout the range; the only difference is that the PF$_6$ salt has lower σ's at high tem-

peratures.[5] Thus these rapid changes in S below ~ 100 K are not due to the effects of localization nor, as reasoned earlier, to phase transitions. The fact that in the low-temperature limit S goes negative for two of the salts (ClO$_4$ and NO$_3$) while it stays positive for the others is evidence that the behavior is due to impurities or other defects. Such rapid changes occur when the number of electrons or holes that can cross the gap becomes smaller than the number of carriers contributed by defects. Particularly if the defect level is much closer to one of the band edges than E_F in intrinsic material, the Fermi level must move a considerable distance and S_n and S_p no longer essentially cancel each other. The steep increase in S for the BF$_4$ salt and the decrease for ClO$_4$ below 100 K should be attributable to just this transition from intrinsic to extrinsic conduction, and in fact S vs T looks similar to what is seen in this transition region for germanium, for example.[19] The differing behavior of the NO$_3$ salt, where S increases somewhat before plunging steeply to negative values, could be due to competing acceptor and donor levels. As noted above, there is no evidence from other properties for a phase transition in this temperature range.

The nature of the defect levels in these materials is still a matter of speculation. Since they are commensurate a soliton model might be applicable. There is evidence from low-temperature conductivity and thermopower data that there are shallow levels in (TMTSF)$_2$PF$_6$ and it has been suggested that a soliton model might apply there.[20] That material is at least 2D, however, and a shallow hydrogenic level might be more appropriate.[20] The (TMTTF)$_2$X compounds are considerably more 1D than the (TMTSF)$_2$X compounds,[5] making a soliton model more likely in the former case than in the latter.

To write an expression for S in the temperature range where $n \neq p$ and Maxwell-Boltzman statistics are valid, we may use in Eq. (5) for n or p the low-temperature approximation of Eq. (6),

$$F(E_0) = \pi a (2\pi m k_B T / h^2)^{1/2} , \qquad (9)$$

where E_0 has been expressed in terms of m, the effective mass of an electron or hole at the bottom of the band. With (5) and (9) substituted in (1) and (2) we may obtain a general and and unwieldy expression for S vs T when $n \neq p$ for the $\frac{1}{4}$-filled band in the large-U limit. A simplification occurs in the limit that one type of carrier is much less numerous than the other and may be neglected. In that case S for electrons is

$$S_- = -\frac{k_B}{|e|} \left[\frac{1}{2}\ln \left| \frac{2\pi m k_B T}{h^2} \right| - \ln n + \frac{|\Delta E_T|}{k_B T} \right] , \qquad (10)$$

while S for holes is similar with n replaced by $p/4$. The dominant temperature dependence in this expression is usually that of the carrier concentration. At low enough temperatures when a single defect level dominates $n \propto \exp(-E_d/k_B T)$, where E_d is the energy difference between the defect level and the band edge. In that situation S again has a $1/T$ dependence and the slope of S vs $1/T$ is $\sim E_d/k_B$ since $|\Delta E_t| \sim k_B T$. The PF$_6$ salt is apparently in this range below ~ 60 K, where its thermopower shows

a $1/T$ dependence with a slope of 340 K. If we assume that the BF$_4$ and ClO$_4$ salts are in the range where (10) is applicable we obtain E_d values of 900 and 800 K, respectively. These make no sense since they are larger than half the gap. Alternatively if we were to assume these salts are still intrinsic in this range and apply Eq. (8) we would find that $(E_G/2)(\sigma_n - \sigma_p)/(\sigma_n + \sigma_p)$ is larger than $E_G/2$. Similar contradictory results are found for the Br salt, where the low-temperature slope corresponds to E_d or a half-gap of 350 K, larger than we have estimated the gap to be. This reinforces our previous assignment of this steeply changing region to the transition between intrinsic and extrinsic conductivity. The behavior of the PF$_6$ salt is different since, according to our earlier statements, it is already extrinsic at temperatures well above 100 K.

Interestingly, the thermopower does exhibit some anomalies associated with the phase transitions. Close to 70 K there is a slight but distinct shift in the S-vs-$1/T$ curve for the ClO$_4$ salt. This is the same temperature around which anomalies are seen in σ,[5] and an order-disorder transition of the anions has been identified by x rays.[9] The rather weak effect on S, as well as the almost identical behavior of σ above and below the transition, indicate, as noted earlier, that the anion ordering (corresponding to a $4k_F$ potential) has little influence on the already existing gap. Despite the scatter of experimental points, a small shift of S vs T is also seen for the Br salt around 19 K, where the SDW transition takes place.[10,11]

V. SUMMARY

To account for the (TMTTF)$_2$X salts ($X=$Br, ClO$_4$, BF$_4$, NO$_3$, SCN, AsF$_6$, and PF$_6$) being semiconductors when the isostructural (TMTSF)$_2$X salts are not requires that $U > 4t$ for the former. With $\frac{3}{4}$-filled bands and $U > 4t$ the gap opened up by the chain dimerization and the anion potential is at the Fermi energy. The lack of structure in the thermopower data around and above the temperature T_m where σ peaks shows that gaps persist in these salts to $T > T_m$, in fact to the highest temperatures measured. The maximum occurs in σ due to the competition between the increasing member of carriers $[n \propto T^{1/2}\exp(-E_G/2k_B T)]$ and the decreasing mobility ($\mu \propto T^{-\alpha}$). The value of half-gap required to fit σ vs T is ~ 600 K for the BF$_4$, ClO$_4$, PF$_6$, and NO$_3$ salts, in agreement with the experimental determination of Coulon et al.[5] The value of T_m is $(E_G/2k)(\alpha - \frac{1}{2})$. Using this, we obtain a gap of ~ 600 K for the Br salt.

At high temperatures we expect these materials to be in the intrinsic range. The constant, finite value of S over a wide temperature range ($300 \geq T \gtrsim 100$ K) for a number of these salts ($X=$NO$_3$, ClO$_4$, BF$_4$, and SCN) is expected for large-U materials with symmetric conduction and valence bands (same width and scattering processes). We attribute the fact that the constant value of S is less than 60 μV/K, the value predicted for a $\frac{3}{4}$-filled-band material in the limit $U \to \infty$, to U being not much larger than $4t$ in these materials. The dependence of S on $1/T$ for the PF$_6$ and AsF$_6$ salts in the range where the other salts have constant S suggests that their properties are not intrinsic, but dominated by impurities even at high temperatures. The fact

that S for the Br salt behaves more like the $(TMTSF)_2X$ compounds is due to its being more 3D and probably having smaller $U/4t$.

The rapid increases or decreases in S with T seen below ~ 100 K are attributed to extrinsic behavior, i.e., impurities or defects, for all but the SCN salt where the increase coincides with a phase transition. With that exception, the constant high-T value of S is maintained until T has decreased to the point that the intrinsic number of carriers is comparable to the number of electrons or holes contributed by impurities. Below that temperature the location of E_F and the value of S are increasingly determined by the number of location of defect levels. With the possible

exception of the PF_6 salt, the data have not been carried to low enough temperature so that the slope of S vs $1/T$ represents an activation energy, in this case the distance from the band edge of a single dominant defect level.

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