INTRODUCTION

The organic charge-transfer salts based on the donor molecule TMTSF form one of the most physically interesting families yet studied.\(^1\) Although all of these salts have the same charge transfer and band filling, as well as virtually identical anisotropic band structures,\(^2\) the ground states which have been found range from metallic to spin-density wave\(^3\) (SDW) and anion order-induced charge-density-wave (CDW) insulators.\(^4\) Additionally, the first organic superconductor was discovered in the PF\(_6\) salt under a pressure of \(\sim 8\) kbar.\(^5\) There are also a number of transitions which involve the freezing of the rotational motion of the anion complexes,\(^6\) in some cases into an ordered structure with a particular wave vector and in other cases into a disordered state.\(^4,7,8\) The general phase diagram for many of these (TMTSF)\(_2\)X compounds involves a high-temperature metallic phase at ambient pressure, followed at lower temperature by a metal-insulator transition into a SDW or a CDW state usually driven by an anion ordering transition.\(^9\) Application of a moderate pressure \(\sim 10\) kbar suppresses the metal-insulator transition and the metallic state remains stable down to \(\sim 1\) K at which temperature the samples undergo a transition to the superconducting state. The great similarity of the electronic structure (and the electron-phonon interaction) in these salts is attested to by the observation that the superconducting transition temperatures are all \(1.2\) K (\(\pm 0.2\) K) at the pressure which just corresponds to the suppression of the insulating phase. (With the exception of the FSO\(_3\) salt which has an anion possessing a dipole moment and a \(T_c \sim 2-3\) K\(^4\).)

Band-structure calculations\(^2\) indicate that, in the metallic state, the Fermi surface should consist of two warped planes approximately parallel to each other and with warpage considerably less than their separation. The bandwidths are \(4\epsilon_F \sim 1\) eV, \(4\epsilon_F \sim 0.1\) eV, and \(4\epsilon_F < 0.01\) eV. Thus, there are no close orbits expected for the tight-binding-like bands. In contrast to what would be expected from the band structure, the magnetotransport properties of these compounds is quite remarkable. The first observation of the magnetoresistance in the PF\(_6\) (Ref. 10) salt indicated a large non saturating positive magnetoresistance corresponding to a doubling of the resistance in a field of 60 kG, while the sample remained in the metallic state at temperatures above 12 K. In the insulating phase below 12 K, the magnetoresistance increased still further but in a way that might be expected for a semiconductor.

The high anisotropy in the band parameters would indicate that the magnetotransport coefficients should also be highly anisotropic. The observed properties are consistent with this idea and the remarkable effects in high magnetic fields are seen with the magnetic field oriented along the \(c\) axis corresponding to orbital motion in the \(a-b\) plane which contains the highest conducting directions.\(^1\) One of the most striking observations was that the PF\(_6\) salt exhibited Schubnikov-de Haas oscillations\(^1\) at low temperatures and under sufficient pressure that it remained in the metallic and presumably open-orbit state.

The magnetic field dependent properties of the ClO\(_4\) salt have been more extensively studied, largely in relation to its superconductivity. (TMTSF)\(_2\)ClO\(_4\) and (BEDT-TTF)\(_2\)I\(_3\) are the only organic compounds to date which are superconducting at ambient pressure.\(^1\) When the samples are cooled slowly the metallic state is stable to low temperature and there is no density wave transition.\(^5\) Again the metallic state should consist of only open orbits.
on the Fermi surface, and yet quantum oscillations are observed in the resistance\textsuperscript{14} and the thermopower\textsuperscript{15} at temperatures below \( \sim 2 \) K. At higher temperatures a magnetic field directed along the \( c^* \) axis has also been shown to have strong effects on the specific heat,\textsuperscript{16} thermal conductivity,\textsuperscript{16} resistance,\textsuperscript{14} and thermopower.\textsuperscript{15}

The object of the present paper is twofold. It has often been suggested that the \( \text{ClO}_2 \) salt is very similar to the \( \text{PF}_6 \) salt under a pressure which stabilizes its metallic state and that even at ambient pressure the two are similar above the metal-insulator transition in \( \text{PF}_6 \). We will explore resistance and thermopower in this regime for the two salts as a function of magnetic field. We find that magnetic field effects are large but different in the two salts. Secondly, the temperature dependence of the thermopower of the \( \text{PF}_6 \) salt is quite anomalous in the region below the metal-insulator transition. Instead of showing a monotonic semiconducting-like thermopower, the reported thermopower increases to a positive maximum and then decreases and crosses zero as the temperature is lowered. The thermopower is very magnetic field dependent in this regime and in 80 kG the thermopower becomes monotonic and increases negatively as 1/\( T \).

**EXPERIMENTAL RESULTS**

The experiments reported below were performed in an apparatus consisting of a brass sample holder connected to the bottom of a \( ^3 \text{He} \) pot. The holder and pot were situated in an indium-sealed stainless-steel vacuum can so that the temperature could be varied from room temperature to \( \sim 0.5 \) K. Sample leads were heat sunk to the vacuum-can top and then to the sample holder. Since the thermopower measurement requires the establishment of a temperature gradient, it was necessary to have the samples surrounded by vacuum. In order to prevent the samples from equilibrating to a temperature other than that of the sample holder, a split copper can was placed around the sample holder and screwed to the \( ^3 \text{He} \) pot. The use of this arrangement provided ample temperature uniformity, while allowing for a moderately rapid cycling of the magnetic field without producing a large amount of eddy current heating.

Temperatures were measured with a germanium resistance thermometer and a carbon glass thermometer which were also used to calibrate a capacitance thermometer used to control the temperature during magnetic field sweeps.

Contacts were made to the sample with silver paint. Leads were 1 mil or \( \frac{1}{4} \) mil Au wires. Resistance measurements were four probe ac (\( \sim 103 \) Hz) and checked occasionally by dc. Although there was considerable sample cracking, as observed by resistance jumps, during the cooldown\textsuperscript{17} the resistance showed no such jumps below 60 K. The thermopower was measured using the technique of Ref. 18 with the following adaptations: the quartz blocks were replaced by thin sapphire slides sandwiching a thin heater wire to reduce the thermal cycling time to \( \sim 10 \) s; the data were taken by continually applying an offset square wave to one heater; and the voltage from the differential thermocouple and the sample were plotted continuously on the \( Y \) axis of two separate \( x-y \) plotters with the \( X \) axis being either the output of a temperature sensor or the output of a current sensor measuring the magnetic field. The peak-to-peak change in the thermocouple and sample voltages then supply the necessary information for the calculation of the thermopower. It is necessary to observe the relative phase of the motion of the two pens to determine a sign change in the thermopower. We find that these modifications lead to considerably more sensitive measurements of small changes as well as allowing for a quasiconstant monitoring of the thermopower as a function of either temperature or magnetic field.

The magnetic field was generated with a superconducting magnet with a quench field of 106 kG at 1.5 K. The samples were aligned with their axes at particular orientations to the field by mounting them in different configurations at room temperature. The alignment is nominal but probably accurate to \( \sim 5^\circ \) since adjustments were made visually using the needle axis as parallel to \( a \), and the plane of the platelet as perpendicular to c \( \sim c^* \).

The temperature dependence of the thermopower is shown in Fig. 1. The results for zero field are qualitatively consistent with previous studies.\textsuperscript{1,19} At temperatures above the SDW transition the thermopower is small and positive as expected from the band filling and bandwidth. The deviations from linearity in the metallic region have been associated with fluctuations preceding the SDW transition.\textsuperscript{19} The transition itself is marked by the sharp positive rise of the thermopower at 12.5 K. The thermopower then increases positively, reaches a maximum, and then becomes increasingly negative as the sample is cooled. As yet, there is no conclusive interpretation of the thermopower below \( T_{\text{SDW}} \).

The temperature dependence of the thermopower in an applied field of 80 kG along the \( c^* \) direction is also shown in Fig. 1. There are striking differences in comparing this curve with that obtained in zero applied magnetic field. The transition is not evident and the data appears as one continuous curve. There is no hint of the positive thermopower region seen below \( T_{\text{SDW}} \) in the zero field results. When the data is plotted as \( S \) versus 1/\( T \) [Fig. 1(a)], the thermopower in 80 kG shows the characteristic semiconducting behavior, \( S \sim -E_c/2k\_B\_T + B \cdot \) The gap obtained from the slope of this curve is 35 K, similar to that observed in the zero-field resistance.

The presence of a magnetic field clearly effects the thermopower above the transition as well as below. The metallic state thermopower shifts to a more negative value and the difference with the zero-field result increases as the transition is approached. The drop in the \( H=0 \) thermopower near \( T_{\text{SDW}} \) is still present in \( H=80 \) kG. Shown for comparison in this figure are curves of the thermopower for \((\text{TMTSF})_2\text{ClO}_2\) in the same temperature range and for the same magnetic fields. Note that the \( \text{ClO}_2 \) salt has a thermopower that increases positively in the presence of a magnetic field,\textsuperscript{20} opposite to the effect in the \( \text{PF}_6 \) salt.

The magnetic field dependence of the thermopower is highly anisotropic. In Fig. 2 we show the thermopower as a function of temperature for 0 and 80 kG for a sample which aligned so that its needle (\( a \)) axis was parallel to
dependence to previous results, the alignment of the $c^*$ axis sample is readily verified. The $a$ axis sample shows little magnetic field dependence in either study (Fig. 3). The small effects observed, $\Delta R \sim 5\%$, probably correspond to a disalignment of $\sim 0.3^\circ$.

In Fig. 4 we show a more detailed study of the thermopower of another crystal of (TMTSF)$_2$PF$_6$ using the technique of Ref. 18. The strong negative increase in thermopower at low fields and the saturation at high fields are evident in this data as is the increase in the characteristic field as the temperature is increased.

A more meaningful presentation of the magnetoresistance data is shown in Fig. 5. The Kohler plots $\ln(\Delta \rho/\rho_0)$ versus $H/\rho_0$ are taken from the temperature dependence of the resistance in zero field and in 80 kG, as well as from fixed temperature sweeps of the magnetic field. Also shown for comparison are similar data obtained from the $H||c^*$ magnetoresistance of (TMTSF)$_2$ClO$_4$.

FIG. 3. Thermopower and resistance vs magnetic field along the $a$ axis.

FIG. 4. Magnetic field dependence of the thermopower of (TMTSF)$_2$PF$_6$ for several temperatures.
COMPARISON WITH PREVIOUS TRANSPORT DATA

There have been several previous studies of the magneto-transport properties of both the PF₆ and the ClO₄ salts of TMTSF₃. For (TMTSF)₂PF₆ the transport coefficients measured include the conductivity along a, b, and c axes; the magneto-resistance with the field along the principle axes and the current along a; the Hall coefficient; and the thermopower in zero field along the a and the b axes. For (TMTSF)₂ClO₄ the x axis conductivity and thermopower and their magnetic field dependences have been investigated. Some work on the anisotropic conductivity has also been reported.

The magneto-resistance and zero-field thermopower reported in this paper are qualitatively consistent with previous data. The absolute value of the magneto-resistance with the field along c* is very sensitive to the scattering rates and therefore varies appreciably (up to a factor of 4 at low temperatures) even in nominally pure samples. The general aspects are quite similar and involve a Dr/p ~ 1 at 80 kG in the metallic phase below about 30 K, with a good fit to an H² behavior, and a much larger non-saturating field dependence with Dr(80 kG)/p ~ 10 and a lower power in H at high fields for the semiconducting phase.

The zero-field thermopower is the same in the metallic state (to within ~ 20% for results from different groups, samples, and techniques), but there seems to be a larger variation in the absolute value of the positive anomaly directly below the metal-insulator transition temperature. This suggests that the anomaly may also be impurity dependent.

Since it has often been suggested that the ClO₄ salt is similar to the PF₆ salt in the metallic phase, from the Kohler plots shown in Fig. 5 the field dependences are different with a H² behavior for the PF₆ salt and a H dependence for the ClO₄ salt. The differences in transport are also seen in Fig. 1 anticipating the lower-temperature behaviors.

Another of the surprising features of the magnetotransport has already been noted in Ref. 22. The Hall coefficient of the PF₆ salt in the semiconducting phase has been measured as large and positive for temperatures down to 2 K. The zero-field thermopower becomes negative below ~ 8 K. However, the thermopower measured along the b axis remains positive at all temperatures. Thus the sign of the carriers is ambiguous in any simple model.

DISCUSSION

The unusually large magneto-resistance of the TMTSF salts, especially in the metallic state, is a matter of considerable interest. We review briefly previous interpretations. The magnitude of the magneto-resistance was so large in these salts that it suggested to some researchers that the origin was in the quenching of superconducting fluctuations. The initial interpretation of the magneto-resistance in the PF₆ salt suggested that there might be anomalous scattering from pieces of the Fermi surface which were almost nested.

However, the magneto-resistance of the ClO₄ salt attains values of Dr/p ~ 10. Extensions of the above model suggest that such large values are possible if the scattering is extremely strong in very small regions of the open orbit. In such a case the magneto-resistance does not saturate until o_anomalous ~ 1, where o_anomalous is the scattering time in the region of the anomalously large scattering. Moreover, the field dependence of the magneto-resistance for this mechanism has a large linear region (Dr/p ~ H) and hence may be particularly appropriate for the ClO₄ salt. Although this is a viable explanation there is a more direct one. For the TMTSF salts, the a and b axes are not orthogonal. Therefore the a axis conductivity has a component along the direction of the open orbit. In this case the a axis resistance becomes a non-saturating function of H and is related to the b axis magneto-resistance by

\[ R_a = R_b \cos^2 \theta, \]

where \( \theta \) is the angle between the current direction and the open-orbit direction.

In the semiconducting state of the PF₆ salt, the interpretation of the large nonsaturating magneto-resistance with values of Dr/p ~ 10—100 involved the existence of closed, compensated electron and hole bands with a large mobility. The Hall mobility from these studies was ~ 10⁴ cm²/volt.s. Moreover, the dependence on scattering rate was checked by radiation damage studies which showed that Dr/p ~ (o,t)². However, the deviations from H² dependence are not easily explained. Parameters characterizing the electron and hole bands suggest that for fields above ~ 60 kG at temperatures below 5 K, one is entering the quantum regime.

Some general comments are necessary before trying to interpret the new field-dependent thermopower results. In a semiconductor in the quantum regime, the thermopower and magneto-resistance are nonsaturating functions of field. Since, in the present case, with the PF₆ salt the thermopower is definitely saturating at low fields (Fig. 4), we are probably not in the quantum regime.

On the other hand, the classical treatment of the high-field thermopower, for both metals and semiconductors, gives a saturating thermopower independent of whether...
the magnetoresistance is saturating or not. Therefore
the observation of a saturating thermopower is to be
expected.
Thermoelectric effects arise from two contributions:
diffusion thermopower from the energy dependence of
the density and mobility of the carriers, and boson drag
thermopower from the electron-boson (phonon-magnon)
interaction and the heat of the boson gas. Both of these
contributions can change in the presence of a magnetic
field as carriers are swept across the Fermi surface and
experience different mobilities and different interactions
with the bosons. The fact that no identifiable phonon-
drag contribution is observed in the zero-field thermo-
power suggests that this is not the dominant effect. How-
ever, studies of the magnetic field dependent thermopower
in noble metals have shown that the phonon-drag thermo-
power may be enhanced in the presence of a magnetic
field. One of the usual features of the magnetothermal-

pot in the metallic phase is that it has a different sign for the
ClO$_4$ salt than for the PF$_6$ salt. This may result from the
slightly different low-temperature band structures of the
two materials. The former compound has an anion-
ordering transition at 24 K which splits the two sides of the
Fermi surface into two pieces each but leaves only
open orbits. Also, the PF$_6$ salt presumably has a contribu-
tion to its thermopower from fluctuations into the
SDW state at temperatures just above 12.5 K.

We now turn to an interpretation of the new results.
The most striking and unusual effect that we see in the
magnetotransport properties is the change in the thermo-
power of the PF$_6$ salt when a field is applied along the $c^*$
axis. The characteristic temperature dependences for met-
als and insulators are

\[
S = (k_B/e)(k_B T/E_F) \quad \text{for metals,} \tag{2a}
\]

\[
S = (k_B/e)(E_g/2k_B T) \quad \text{for insulators.} \tag{2b}
\]

Since $k_B/e \approx 87 \mu$V/K, a metal should have a consider-
ably lower thermopower than 87 $\mu$V/K, while a semicon-
ductor should have a comparable or larger thermopower.
Moreover, a semiconductors thermopower should vary as
$1/T$.

Thus the thermopower of (TMTSF)$_2$PF$_6$ is not charac-
teristic of the semiconducting behavior which is seen in
the resistance. Although the zero-field data in itself
would not be considered striking, and could be explained
in terms of a particular set of parameters for the band
structure, energy dependent scattering, and donor or ac-
ceptor concentration, the fact that a much more charac-
teristic semiconducting behavior is restored with applica-
tion of a magnetic field is quite striking. The effect of a
magnetic field on an SDW transition is quite small as is
known both theoretically and experimentally. Note, for
example that the transition temperature has changed by
less than 0.1 K in the presence of a field of 80 kG.

It should be emphasized at this point that the large ef-
fects which are seen are only present for the configuration
in which the field is aligned with the $c^*$ axis (compare
Figs. 1 and 2). This orientation causes the electrons to
circulate in the $a$-$b$ plane, in which the transfer integrals
and bandwidths are maximum. Thus it appears clear that
the effects which are observed are orbital in origin. In the
absence of strong spin-orbit coupling we would expect
spin effects to be isotropic.

The general behavior of the thermopower suggest that
there are at least two types of carriers present. Predomi-
nantly positive carriers with energy close to the chemical
potential at temperatures just below the transition and in
the absence of a magnetic field, and negative carriers with
higher energy at low temperatures or in the presence of a
magnetic field.

Since the properties of quasi-one-dimensional systems
have proven to be a very attractive topic for theoretical
physicists, there are many possibilities to be explored.
Aside from the thermally excited band carriers, there have
been various suggestions that transport may have sizable
contributions from sliding SDW, fractionally charged sol-
itons related to the SDW transition, and the presence of
superconducting fluctuations. In addition, there are more
mundane explanations possible in terms of an impurity
band, localized impurity states, and phonon drag. Anoth-
er possibility is antiferromagnon drag from the magnetic
excitations below the SDW transition.

The case for fluctuating superconductivity is the weak-
est since the supercurrent should have no thermopower of
its own and should not participate in interactions with the
other carriers. Likewise, the sliding SDW contribution
should also have no entropy term unless there were strong
interactions with normal carriers or other elementary exci-
tations.

Conwell$^{22}$ has suggested that the discrepancy in sign be-
tween the Hall coefficient and the $a$ axis thermopower (at
zero field) may result from the presence of solitons. In
her model the solitons are of sufficiently high concentra-
tion that they overlap along a single chain and thus have
their dominant conductivity along the $a$ axis with little
conductivity along the $c$ or $b$ axis. The Hall effect sees
only the band carriers and remains positive as does the $b$
axis thermopower. The thermopower sees the solitons and
the band carriers. At low temperature the Fermi level lies
below the soliton states so that they appear as electron-
like (i.e., negative) carriers. If this model is correct, then
its extension to the present observations would go approxi-
mately as follows. The band carriers producing a posi-
tive contribution are frozen out by the magnetic field.
This leaves only the solitons with negative effective
charge to contribute to the thermopower.

The freeze out of the normal carriers may be due to the
classical magnetoresistance effects or to Landau quantiza-
tion raising the energy of the band states. What is unusu-
al in this picture is that the thermopower should have a
similar field dependence to the magnetoresistance.$^{27}$ Also,
the solitons must be thermally activated to give the ex-
ponential resistance that is observed and the soliton states
must be close to the band-gap edge in order to give a ther-

mopower with a $1/T$ dependence and a value consistent
with the gap that one expects from the observed transition
temperature.

While an explanation in terms of phonon drag is prob-
ably inappropriate simply because the temperatures are
too low (phonon drag peaks usually occur at about
The magnetothermopower of the (TMTSF)$_2$X compounds points out two major characteristics: the high mobility of the band carriers at low temperature and the quasi-two-dimensional nature of the band structure. Although these properties can account qualitatively for the similarity in the magnetoresistance in the different salts, we see that the thermopower behavior is different specifically between the PF$_6$ and the ClO$_4$ salts even in the metallic state.

The most unusual discovery revealed in this paper is the strong dependence of the thermopower in the semiconducting state on applied magnetic field along the $c^*$ direction. Unless the band structure and scattering mechanisms have conspired to produce unexpected results, the straightforward interpretation of our findings is that low energy (that is residing close to the Fermi energy) positive carriers dominate the transport at temperatures just below the metal-insulator transition. These carriers freeze out upon lowering the temperature or applying a magnetic field along the $c^*$ direction. What remains are negative carriers with relatively large energy (distance to $E_F$ large compared to $k_B T$). Comparison with Hall measurements and transverse thermopower measurements indicate that only the positive carriers are mobile in the perpendicular ($b$) direction.

Another possibility deserving further investigation is that the thermopower indicates a drag effect with the relevant dragged bosons being the excitations from the spin-density-wave state.

CONCLUSIONS

The magnetotransport measurements on the (TMTSF)$_2$X compounds points out two major characteristics: the high mobility of the band carriers at low temperature and the quasi-two-dimensional nature of the band structure. Although these properties can account qualitatively for the similarity in the magnetoresistance in the different salts, we see that the thermopower behavior is different specifically between the PF$_6$ and the ClO$_4$ salts even in the metallic state.

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Another possibility deserving further investigation is that the thermopower indicates a drag effect with the relevant dragged bosons being the excitations from the spin-density-wave state.

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