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Magnetoresistance of the organic conducting tetramethyltetraselenafulvalene salts $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$: Search for the coherent-diffusive transition or localization effects with increasing temperature

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In an attempt to detect the changeover from coherent to diffusive behavior in the transverse conductivity or phonon-induced localization, we have extended previous magnetoresistance measurements on single crystals of the organic conducting tetramethyltetraselenafulvalene salts $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ up to 200 and 125 K, respectively. For the geometry studied, namely current along the lowest conductivity axis and field along the intermediate axis, the magnetoresistance remains positive and of the same magnitude as expected from band theory. Surprisingly, although the transverse mean free paths become very small at higher temperatures and the transverse resistivity saturates, we did not detect any substantial changes in magnetoresistance corresponding to a change in the conductivity mechanism.

I. INTRODUCTION

In some recent papers[1-3] we have reported measurements of the electrical resistivity and magnetoresistance for single crystals of the linear-chain organic superconductor bis-tetramethyltetraselenafulvalenium perchlorate $(TMTSF)_2ClO_4$ at relatively low temperatures (2—22 K) in magnetic fields up to 7 T. For much of this work we have used an unconventional sample geometry; namely, current flow along the least-conducting axis ($\mathbf{c}^*$) and H along the intermediate conductivity axis ($\mathbf{b}'$) of the triclinic crystals. We have argued[2] that this is, in fact, the best geometry for magnetoresistance measurements on these extremely anisotropic conductors. Surprisingly, we found that the large magnetoresistance ($\Delta\rho/\rho$) obeyed Kohler's rule (KR) in the above field and temperature range. This observation led us to analyze the data in terms of the one-electron tight-binding band structure calculated by Grant[4] and standard transport theory involving the Boltzmann equation for an open Fermi surface (FS) with a constant relaxation time (τ). Within this picture several important transport parameters can be deduced from measurements of $\rho_\perp(T)$ (along $\mathbf{c}^*$) and $\Delta\rho_\perp/\rho_\perp$. For example, it turns out[1,2] that the magnitude of $\Delta\rho_\perp/\rho_\perp$ at low H is determined solely by the mean free path along the conducting chains and the (known) lattice parameters. As the on-chain tight-binding overlap integral ($t_{\parallel}$) is known quite well, both from optical measurements and band-structure calculations,[4,5] τ can then be obtained. Knowing τ, one can determine the magnitude of the overlap integral in the least-conducting direction $t_\perp^c$ from the measured value of ρ_{c*} and hence the (root-mean-square) mean free path $l_\perp$ along $\mathbf{c}^*$.

For $(TMTSF)_2ClO_4$, which we will refer to as C in the future, we found $t_\perp^c = 1.1 \pm 0.1$ meV,[2] for two different samples, which agrees well with a theoretical estimate for the ReO_4 salt.[6] $l_\perp$ values were $4c$ and $2c$ at 2 K falling to $0.4c$ at 20 K, where c is the transverse lattice parameter.[7]

We thought that it would be interesting to extend sucn magnetoresistance measurements to as high temperatures as possible with a view to detecting the coherent-diffusive transition[8] in the transverse conductivity via deviations from KR. According to the present level of understanding this occurs when the condition $\hbar/\tau_{\parallel} \gtrsim t_\perp^c$ is satisfied, where $\tau_{\parallel}$ is the on-chain scattering time.[8] If as here, τ is considered to be a constant, the above condition is the same as $l_\perp \lesssim c$. For isotropic conductors at any rate, the condition that the mean free path equals one lattice spacing has been generally accepted as marking the limit of validity of simple theories of band transport.

In anisotropic organic semiconductors such as napthalene this transition is referred to as the band-hopping transition[9] and has been studied both theoretically[10,11] using the Kubo formula and experimentally via measurements of drift velocity.[9] We note that the expressions given for the transverse mobility in Refs. 8, 10, and 11 are very similar; however, as far as we know the possible effect of a magnetic field has not been treated.

For linear-chain conductors many theoretical papers take a completely different approach. They emphasize the importance of electron localization induced either by lattice defects at low temperature (T) or by electron-phonon scattering at high T. These theories have been reviewed by Abrikosov and Ryzhkin.[12] For static defects the breakdown of the three-dimensional (3D) band picture occurs when $\hbar/\tau_2 \gtrsim t_\perp$, where τ_2 is the characteristic time for backward scattering ($2k_F$ momentum change) on a given chain. Unfortunately, it is not clear to the present authors how to apply this condition in the present case, where $t_\perp^c : t_\perp^b : t_\parallel$ is 1:10:100,[4] i.e., the bandwidths in the two perpendicular directions are substantially different.[4] As reviewed in Ref. 12 above, the Debye temperature [which is of the order of 80 K for C (Ref. 13)] phonons may also cause localization. In this case the classical kinetic equation for the chain conductivity ($\sigma_\parallel$) is no longer valid. Instead $\sigma_\parallel$ is reduced by a factor of order $\omega_D \tau$, where ω_D is the Debye frequency and τ the scattering time.

However, in this context we should mention the counterargument of Kaveh, Weger, and Gutfreund,[14] who have suggested that localization effects are not important in linear-chain organic conductors such as $(TMTSF)_2X$ because of the large size of the molecule. The electron-defect and electron-phonon scattering potentials are thus long ranged, i.e., short ranged in **k** space, so that the backward scattering amplitudes responsible for localization are an order of magnitude smaller than the forward scattering amplitudes.

In this paper then we report new measurements of the magnetoresistance of single crystals of $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ (referred to as P) for $\mathbf{H} \| \mathbf{b}'$ and current flow along the least-conducting ($\mathbf{c}^*$) direction, up to temperatures approaching 200 K, as well as previously published resistivity measurements.[15] Some new data for the angular dependence of $\Delta\rho_\perp/\rho_\perp$ are also reported.

Although for both P and C the values of $l_\perp$ deduced by band theory become extremely small at higher temperatures, there is still a positive magnetoresistance of approximately the magnitude to be expected from band theory. For P there are substantial deviations from KR above 60 K but these seem to us to be due to an increase in $t_\perp^c$ with temperature rather than evidence for the coherent-diffusive transition or localization.

II. EXPERIMENTAL

Single-crystal samples were cut to the required length along the **a** axis with a razor blade, as indicated in the inset to Fig. 1, and four electrical contacts were made with silver paint. In the present work two additional samples of P and C were measured.

Their dimensions were $0.5 \times 0.45 \times 0.30$ mm^3 and $0.4 \times 0.1 \times 0.25$ mm^3 (C) and $0.25 \times 0.05 \times 0.15$ and $0.25 \times 0.20 \times 0.20$ mm^3 (P) along **a**, **b**′, and **c***, respectively.[7] Conductivity measurements were made using dc, at 10 or 50 μA, for several fixed fields up to 5.35 T. The increase in resistance was generally proportional to H^2. A new feature in this work was that the temperature was automatically stabilized to ±0.01 K during the field sweeps, by using a field-independent strontium titanate capacitance thermometer[16] and a capacitance bridge with lock-in detection of the balance point. The lock-in output controlled the current through a heater which was in good thermal contact with other resistance thermometers and the samples.

The samples were oriented by eye with $\mathbf{H} \| \mathbf{b}'$, i.e., perpendicular to both the direction of current flow $\mathbf{c}^*$ and the highly conducting **a** axis, and could be rotated about **a** at low T.

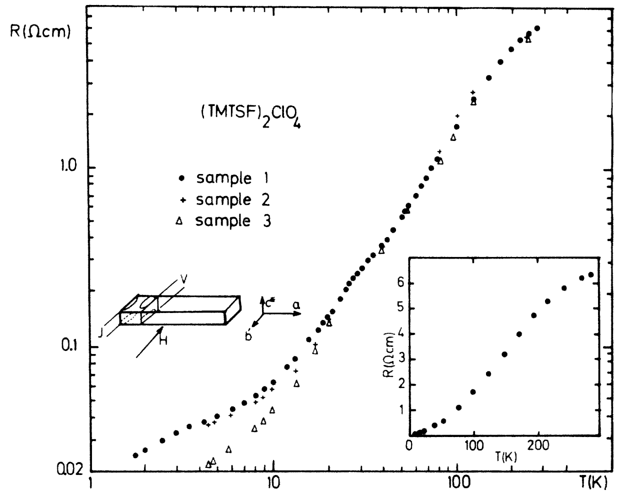


FIG. 1. Transverse (c^*) resistivity versus temperature for three crystals of $(TMTSF)_2ClO_4$ on log-log scale. Inset shows data on linear plot.

III. RESULTS

The average room-temperature resistivities along the $\mathbf{c}^*$ direction are 38 ± 10 Ω cm for P (four samples) and 6 ± 2 Ω cm for C (three samples). As shown in Figs. 1 and 2 the temperature dependences of ρ_{c^*} are also quite different. For C, ρ_{c^*} increases as T^n with $n = 1.7 \pm 0.05$ from 30–150 K, after which it starts to saturate, as shown more clearly by the inset of Fig. 1. On the other hand, for P, $n = 1.25$ to 1.6 from 25–70 K, depending on the residual resistance, and there is good overall agreement with data taken at microwave frequency.[17] However, in the latter measurements a somewhat larger value of n ($= 2$) was obtained, which we ascribe to the lower residual resistance, i.e., to the use of a higher-purity crystal. For P there is a maximum at 85 K after which ρ_{c^*} falls slightly. In all cases the T dependence was very reproducible and there were rarely any sharp resistance jumps which are usually a problem in resistivity measurements along the chain direction.

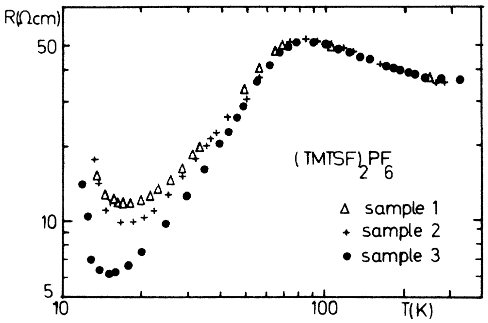


FIG. 2. Transverse (c^*) resistivity versus temperature for three crystals of $(TMTSF)_2PF_6$ on a log-log scale.

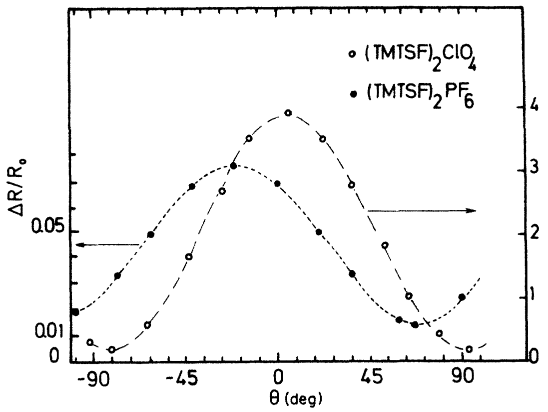


FIG. 3. Angular dependence of magnetoresistance for a sample of C at 4.5 K, $H=3$ T, and a sample of P at 25 K, $H=5.4$ T. θ is the angle between H and the **b**′ axis as determined by eye. The crystals were rotated about the **a** axis, i.e., $\theta=90°$ corresponds to **H**||**c***.

We studied the angular dependence of the magnetoresistance at 4.5 K for C and 25 K for P, by rotating the samples about the **a** axis, i.e., **H** was rotated from **b**′ to along the direction of current flow **c***. The results for two of the samples are shown in Fig. 3. In both cases $\Delta\rho_\perp/\rho_\perp$ follows a $\cos^2\theta$ law. The ratios of $\Delta\rho_{\max}/\Delta\rho_{\min}$ were 6.5 and 5.6 for two samples of P, and 6.3 and 22.2 for two samples of C.

Since the magnetoresistance is proportional to H^2 at low fields, then Kohler's rule takes the form $\Delta\rho/\rho_0 \propto H^2/\rho_0^2$. That is, for a fixed field, $\rho_0\Delta\rho$ should be independent of temperature if KR is obeyed. These plots are shown for all samples measured in Fig. 4, for a fixed field of 5.35 T (for C there are some deviations from an H^2 law below 12 K as $\Delta\rho/\rho_0$ becomes larger than unity, so in these cases we have obtained $\Delta\rho$ by extrapolating the low-field H^2 law to 5.35 T). As discussed in detail later, for P there are deviations from KR above 60 K where $\rho_0\Delta\rho$ falls approximately as T^{-3} and below 20 K where it rises due to the onset of the spin-density-wave transition at 12 K. For C, KR is obeyed approximately over the whole temperature range although there is an increase in $\rho_0\Delta\rho$ by a factor of 2 above 80 K, and a little T dependence ($\sim$20%) below 20 K.

IV. DISCUSSION

Initially[15] we thought that the $\rho_0\Delta\rho$ plots for P showed evidence for the breakdown of the band picture at high temperatures. However, when the data is plotted as $\Delta\rho_\perp/\rho_\perp$ versus T as in Fig. 5, a surprising result emerges. Namely, the data for C and P are very similar in spite of the completely different behavior of $\rho_{c^*}(T)$. $\Delta\rho_\perp/\rho_\perp$ obeys a T^{-3} power law (i.e., in the band picture $\tau\sim T^{-1.5}$) as shown by the straight lines in Fig. 5. Thus the deviations from KR for P in Fig. 4 seem to be due to changes in $\rho_{c^*}(T)$, but *not* in τ. The T dependence of τ is intermediate between that observed for the a axis conductivity of P and $C(T^{-2})$ and the **b**′ axis conductivity of $P^{17}(T^{-1})$.

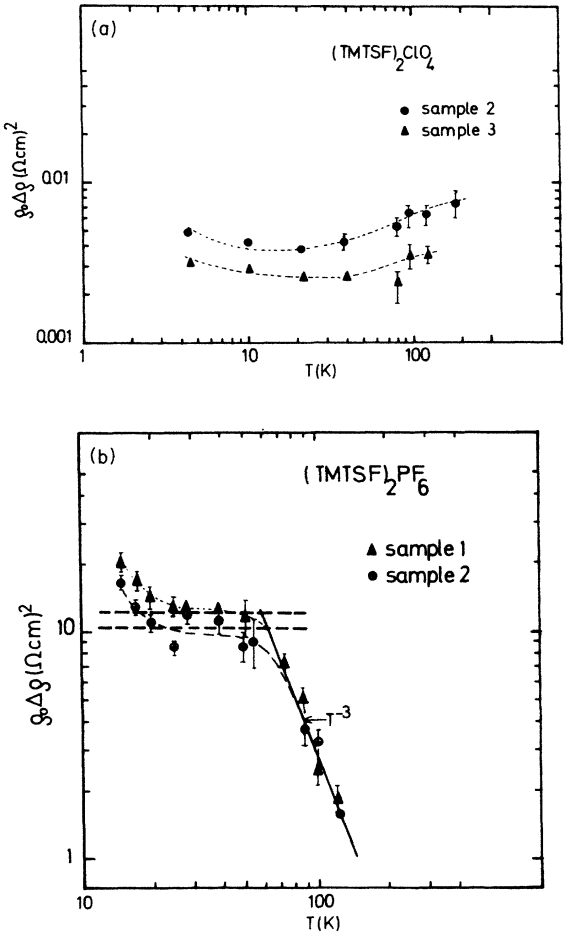
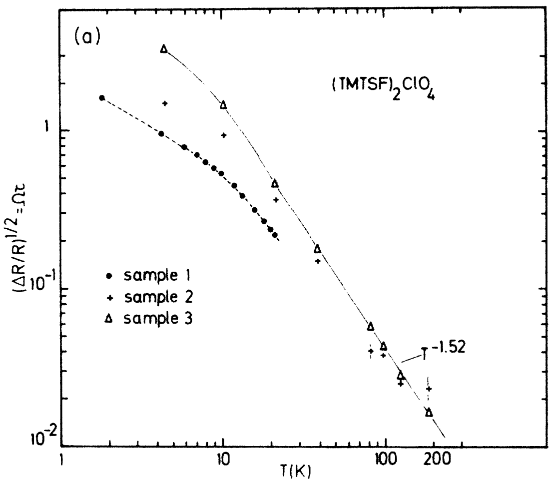


FIG. 4. (a) Plots of $\rho_0\Delta\rho$ versus T for two samples of C. $\Delta\rho$ is the increase in resistivity produced by a field of 5.35 T, ρ_0 is the zero-field resistivity along **c***. (b) Plots of $\rho_0\Delta\rho$ versus T for two samples of P.

We wish to emphasize that use of the band formulas for ρ_{c^*} and $\Delta\rho_\perp/\rho_\perp$ gives very short mean free paths along c^* for both P and C. Examples are shown at some selected temperatures in Table I, the parameters having been determined with the aid of Eqs. (2)—(4) of Ref. 2. For C the mean free path $l_\perp$ varies from $4c$ at 2 K (Ref. 2) down to $0.01c$ at 190 K. For P the $l_\perp$ values are even smaller since the τ values are nearly the same while $t_\perp^c$ is about a factor 8 smaller. Within the band picture the saturation in resistivity of (TMTSF)$_2$ClO$_4$, the resistivity maximum observed in (TMTSF)$_2$PF$_6$ at 85 K, and the deviations from KR for P above 60 K can only be interpreted as arising from an increase in $t_\perp^c$ as T increases. We note that increases of transverse bandwidth with temperature have also been proposed for napthalene,[11] due to lattice vibrations. However, for P there is a frequency-independent maximum in the proton relaxation rate at 58 K, indicating a structural rearrangement[18] of the PF$_6$ and methyl groups which may also lead to changes in $t_\perp^c$.

The theoretical treatments based on hopping[8,10,11] give a similar expression for $\rho_\perp^{c^*}$ to that from band theory,



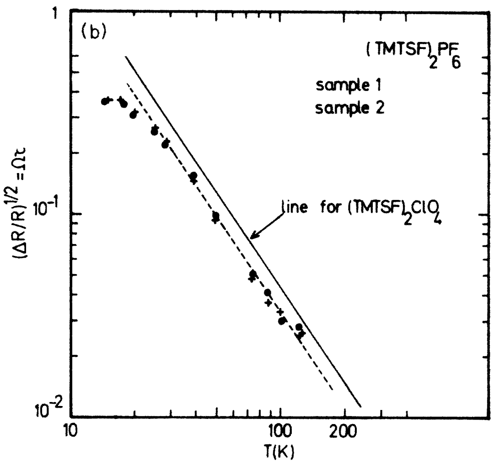


FIG. 5. (a) Plots of $(\Delta R/R)^{1/2}$, i.e., $(\Delta\rho/\rho_0)^{1/2}$ versus T for the same three samples of C in Fig. 1. (b) Plots of $(\Delta R/R)^{1/2}$, i.e., $(\Delta\rho/\rho_0)^{1/2}$ versus T for two samples of P (samples 1 and 2 of Fig. 2).

TABLE I. Parameters deduced from band description of magnetoresistance (taking $t_{\parallel}=0.3$ eV, $a=3.63$ Å, $b=7.68$ Å, $c=13.3$ Å).

T (K)	$l_{\parallel}$ (Å)	τ (10^{-14} s)	$t_{\perp}^{c*}$ (meV)	$l_{\perp}^{c*}/c$
		(TMTSF)$_2$ClO$_4$		
4.5	2778	113	0.85	2.17
21	412	16.8	0.90	0.34
39	159	6.46	0.88	0.13
82	50.2	2.04	0.83	0.038
189	14.2	0.58	0.78	0.010
		(TMTSF)$_2$PF$_6$		
21	272	11	0.10	0.025
39	133	5.4	0.10	0.012
74	45	1.8	0.119	0.005
125	25	1.0	0.167	0.004

since the hopping rate between chains (or planes) is determined by the on-chain[8] (or in-plane[10,11]) scattering time $\tau_{\parallel}$. So even using the diffusive theory ($l_{\perp} \ll c$) $\rho_{\perp}$ remains inversely proportional to $t_{\perp}^2\tau_{\parallel}$, and thus the maxima in $\rho_{\perp}$ seem to require an increase in $t_{\perp}^c$.

We think that a magnetic field along **b**$'$ cannot have similar effects in the band and diffusive regions, but in the absence of appropriate calculations (for example, along the lines of Refs. 19 and 20 for the Hall mobility) this possibility cannot be excluded.

In either case there seems to be no doubt that $l_{\perp} \gtrsim c$ for (TMTSF)$_2$ClO$_4$ below 10 K, so that band theory should apply there. Thus one concrete prediction of this work is that there should also be a plasma edge in the optical reflectivity of (TMTSF)$_2$ClO$_4$ even for light polarized with the electric field along **c***. According to the parameters given in Table I the plasma frequency $\omega_p^c=112$ cm^{-1} and $\omega_p^c\tau=15$ at 4.5 K. Such measurements seem to be technically feasible[21] and would perhaps provide the best test of the band interpretation given here and in previous papers.[1-3]

A trivial explanation of our results would be that because of the unusual sample geometry the Hall field induces a transverse current flow and there is thus a contribution to $\Delta\rho_{\perp}/\rho_{\perp}$ of the order of $(R_H H)^2/\rho_{\parallel}^2$ (where R_H is the low-field Hall coefficient[22]), arising from field-induced curvature of the lines of current flow. We have examined this possibility using the analysis of Van der Pauw[23] but find no evidence for such a contribution which is anyway a factor 5 too small to account for the observed values of $\Delta\rho_{\perp}/\rho_{\perp}$ at 100 K.

V. CONCLUSION

We have made magnetoresistance measurements on single crystals of the organic conductors (TMTSF)$_2$ClO$_4$ and (TMTSF)$_2$PF$_6$ up to higher temperatures expecting to see deviations from Kohler's rule associated with the coherent-diffusive transition or localization.

Although the effective mean free paths perpendicular to the conducting chains (c^*) become very small, and there are some deviations from KR, we did not observe significant reductions in the magnetoresistances. There is evidence that the transverse resistivity of both compounds reaches a maximum whose origin is not understood, as the temperature is raised. However, it seems that in the present cases, where the electronic structure is very anisotropic and scattering is by lattice vibrations, the classical band formulas give an adequate description of the magnetoresistance even though the perpendicular mean free paths are much smaller than the interchain spacing.

ACKNOWLEDGMENTS

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[7] The crystal structure is triclinic (see, e.g., Ref. 4), but only one angle ($\mathbf{a}<\mathbf{b}$) is appreciably different from 90°. Thus we do not distinguish between the directions of the lattice parameter **c**, the reciprocal-lattice vector $\mathbf{c}^*$ and the projection of **c** perpendicular to $\mathbf{a},\mathbf{c}'$. However, $\mathbf{b}'$, the projection of $\mathbf{b}\perp$ to **a**, is substantially different from **b**.

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