PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Anomalous Hall Effect and Magnetotransport Effects in the Organic Superconductor (TMTSF) $_{2}$ ClO$_{4}$ [and Discussion]

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Anomalous Hall effect and magnetotransport effects in the organic superconductor $(TMTSF)_2ClO_4$

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The organic conductor $(TMTSF)_2ClO_4$ exhibits unusual magnetotransport effects below 30 K. The resistivity and thermopower have large, anisotropic changes in a magnetic field, whereas the thermal conductivity is hardly affected. At lower temperature ($T \leqslant 5$ K) a magnetic field applied along the c^* direction causes a phase transition from a metallic, non-magnetic state to a semimetallic, magnetic state. This orbitally induced transition appears to be unique in nature. Above the threshold field for this transition steps in the Hall resistance are observed, suggestive of the quantum Hall effect. In this paper we review the magnetotransport experiment in these materials and discuss the possible origins of the unusual phenomena observed.

The Bechgaard salt, $(TMTSF)_2ClO_4$, exhibits many interesting properties, which have been described by other speakers in this symposium. In this short paper we review what is perhaps the most unusual aspect of this material: the anomalous behaviour of the transport properties in a magnetic field. We should remark at the outset that there is no completely satisfactory explanation for the magnetotransport at present. Therefore, we briefly summarize the experimental situation and discuss the possible origins of the magnetotransport. We only consider the effect of a magnetic field on the metallic state, which is produced by slow cooling through an anion-ordering transition at $T \approx 24$ K.

1. Magnetotransport

(*a*) *Field below threshold*

For temperatures below *ca.* 30 K, $(TMTSF)_2ClO_4$ exhibits a large and anisotropic transverse magnetoresistance (m.r.). With current (I) along the a-axis and the magnetic field (H) along the c^* direction the m.r. is non-saturating and the magneto-thermopower (m.t.) is large and temperature dependent (Choi *et al.* 1983). In this configuration the Kohler rule is not obeyed (Choi *et al.* 1983; Forró *et al.* 1984), whereas it is obeyed when current is along the c^* direction and magnetic field is along the b^* direction (Forró *et al.* 1984). Above a threshold magnetic field, oscillations in m.r. and m.t. are observed, but only for $I \parallel a$ and $H \parallel c^*$ (Kwak *et al.* 1982; Kajimura *et al.* 1983; Brusetti *et al.* 1983*a*; Choi *et al.* 1983).

The one-electron band structure of $(TMTSF)_2ClO_4$ shows that the Fermi surface consists of warped planes (Grant 1983), which allow only open orbits even in the presence of the anion ordering at 24 K. In the simplest approximation, such orbits will lead to a small saturating transverse m.r. for current perpendicular to the orbit ($I \parallel a$) and a non-saturating transverse m.r. for current along the orbit ($I \parallel b$). For $(TMTSF)_2ClO_4$, 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 can become a non-saturating function of H, an overlooked point, which may explain the observed transverse m.r. The violation of the Kohler rule and the magnetic-field-dependent thermopower suggest that the scattering time (τ) is not constant over the Fermi surface, a property that could also explain the non-saturating m.r. (Chaikin *et al.* 1983*a*). Qualitatively then, a one-electron model seems capable of explaining the magneto-transport properties below the threshold magnetic field (Forró *et al.* 1984) and many-body theories (Efetov 1983) are probably not necessary. However, a quantitative understanding of the magnetotransport is lacking and the phenomena are sufficiently large and complicated that the issue remains unresolved.

(*b*) *Field above threshold*

The origin of the threshold field (H_{th}) and the magnetotransport behaviour above it are far more puzzling. The oscillations observed above H_{th} in m.r. and m.t. do not appear to originate from the usual Shubnikov–de Haas effect since there is no well-established periodicity in $1/H$ and a magnetic field hysteresis is found for the higher field oscillations (Kajimura *et al.* 1983). The temperature dependence of H_{th} is shown in figure 1. N.m.r. measurements show that state

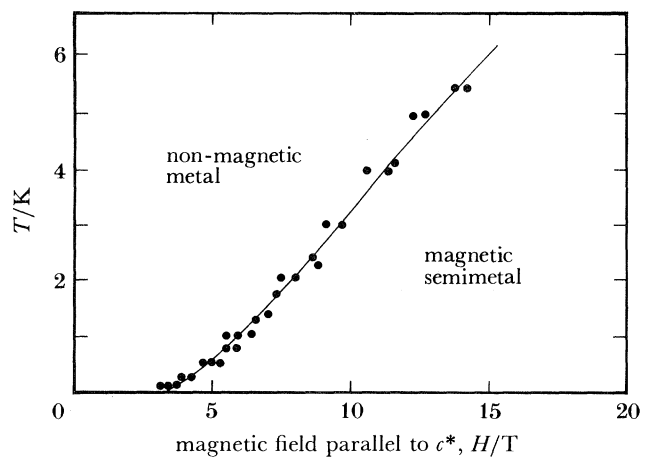

FIGURE 1. The phase diagram of $(TMTSF)_2ClO_4$ for a magnetic field (H) applied perpendicular to the *ab* plane (parallel to the c^* direction). The solid line is a guide for the eye through experimental data determined from resistivity measurements.

found below H_{th} is non-magnetic, whereas above H_{th} it is magnetic (Takahashi *et al.* 1983; Azevedo *et al.* 1983). The Hall resistance (ρ_{xy}) abruptly increases at H_{th} and continues to increase in a stepwise manner with increasing field, as shown in figure 2 (Chaikin *et al.* 1983*b*; Ribault *et al.* 1983). Evaluation of the Hall coefficient shows that this behaviour corresponds to a progressive decrease in the effective number of carriers and is consistent with the reduced electron density of states observed in the specific heat above H_{th} (Brusetti *et al.* 1983*b*). Thus, the magnetic field induces a transition from a metallic, non-magnetic state to a semimetallic, magnetic state. To our knowledge, there is no other example of such a transition in nature. A somewhat similar transition, without a change in magnetic state, occurs in graphite (Iye *et al.* 1982).

The threshold field depends uniquely on the component of the field along the c^* axis. Thus,

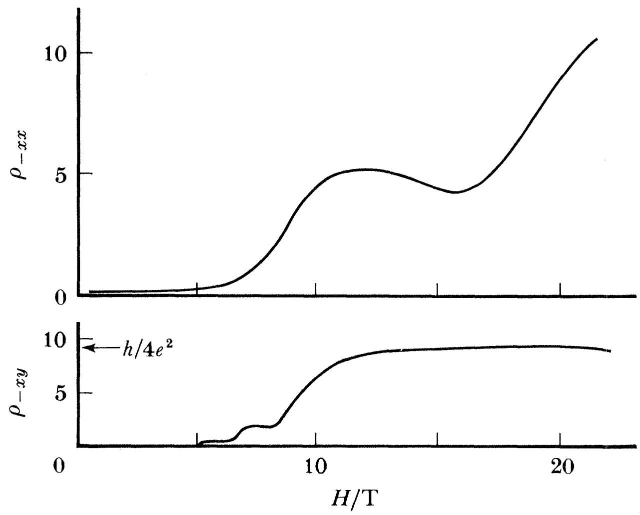

FIGURE 2. Magnetoresistance (ρ_{xx}) and the Hall resistance (ρ_{xy}) for $(TMTSF)_2ClO_4$ against magnetic field along c^* at 0.52 K. Resistance is labelled in terms of h/e^2 per conducting plane.

unless there are enormous spin orbit effects, the transition is caused by an orbital effect of the magnetic field rather than a spin alignment. However, a detailed understanding of how a magnetic field causes this transition is lacking. One possibility is that the magnetic field causes a change from open orbits to closed orbits in the *ab* plane (Takahashi *et al.* 1983) or from very small closed orbits to somewhat larger ones (Kwak 1983). Below *ca.* 100 K, the band parameters show that coherent motion in the *ab* plane is expected, but Hall measurements (Ribault *et al.* 1983) and sound velocity measurements (Choi *et al.* 1984*a*) indicate that the low-temperature state below H_{th} consist primarily of open orbits. A transition to closed orbits may be aided by the very weak electronic coupling in the *c* direction (Chaikin *et al.* 1983*c*). When $\hbar\omega_c$ (the cyclotron energy) becomes greater than $4t_c$ (the bandwidth in the *c* direction) the electronic structure consists of a series of distinct Landau levels (separated by $\hbar\omega_c$) each described by the quasi-one-dimensional dispersion and density of state of the narrow *c*-axis band (Chaikin *et al.* 1983*a*). The system is then two-dimensional in the sense that only one Landau level is partially occupied at a time, and hence, the quantum Hall effect (q.H.e.) may be observed. However, each Landau level has a one-dimensional density of states rather than a delta function (as in two dimensions). The one-dimensional band structure is susceptible to an instability at $2k_F$ along *c*, which produces a gap over part of the Fermi surface. This model has recently been proposed to explain a similar transition in graphite, where the strongest instability was calculated to be a Coulomb induced charge density wave (c.d.w.) (Yoshioka & Fukuyama 1981). The dominant instability in $(TMTSF)_2ClO_4$ is probably a spin density wave (s.d.w.), in order to explain the magnetism observed above H_{th}. The temperature–magnetic field phase diagram shown in figure 1 is qualitatively predicted by this model.

Several interpretations have been given for the magnetotransport oscillations found above H_{th}; however, none of them can explain all the data quantitatively. One possibility follows from the model of H_{th} just discussed (Chaikin *et al.* 1983*b*). As the magnetic field is increased above H_{th}, the quasi-one-dimensional Landau levels move through the Fermi energy (ϵ_F), and for each new level at ϵ_F a gap-opening s.d.w. instability could occur. Thus, the steps in the Hall resistance and the oscillations in the m.r. (see figure 2) would correspond to a series of transitions approximately periodic in $1/H$, which progressively reduce the effective number of carriers. A somewhat similar interpretation (Ribault *et al.* 1983) proposes that a sequence of electron–hole instabilities (excitonic phases) could occur above H_{th}. As discussed above for $\hbar\omega_c > 4t_c$, the carriers in the *ab* plane behave as a system of two-dimensional (but anisotropic) carriers and some manifestation of the quantum Hall effect, such as plateaux in ρ_{xy} and drops in ρ_{xx} should accompany these transitions (Ribault *et al.* 1983; Chaikin *et al.* 1983*b*). A $(TMTSF)_2ClO_4$ crystal is then a multilayer structure of two-dimensional electron gas planes coupled together weakly. However, many features of the data do not follow that expected for the single carrier quantum Hall effect (Cage & Girvin 1983). Although the magnitude of the highest Hall resistivity plateau is very close to the quantized value $h/4e^2$ per conducting plane, the ratio of the plateaux in ρ_{xy} are not consecutive integers and the value of the Hall coefficient shows that the effective number of carriers is decreasing in a stepwise manner as H is increased. Moreover, the magnitudes of the ρ_{xy} plateaux are temperature dependent and although there are corresponding dips in ρ_{xx} they do not go to zero.

Since the band structure suggests that $(TMTSF)_2ClO_4$ is a compensated system we propose that a two-carrier version of the q.H.e. could explain the data. Consider a semimetal with equal numbers of electrons and holes. In the simplest case the Fermi energy is fixed and the electron Landau levels increase in energy as H increases. Correspondingly, the hole Landau levels decrease in energy. As electron and hole levels cross (as they will periodically in $1/H$) the number of carriers is decreased in a stepwise manner. At sufficiently high field an insulator will result for perfect compensation. This idea qualitatively agrees with the experimental data, but a quantitative theory is clearly needed.

2. Thermal conductivity

The thermal conductivity ($\mathscr{K}$) of $(TMTSF)_2ClO_4$ along the *a*-axis was first measured by Djurek *et al.* (1982). They found a roughly constant $\mathscr{K}$ between room temperature and 60 K, while below 60 K, $\mathscr{K}$ decreased by up to a factor of five at 4 K. The behaviour of $\mathscr{K}$ in a magnetic field was very anomalous; a large increase in $\mathscr{K}$ was observed below *ca.* 30 K such that $\mathscr{K}$ became approximately constant below 30 K. This increase in $\mathscr{K}$ cannot be explained by the Wiedemann–Franz law since the electrical resistivity is enhanced (not decreased) by a magnetic field. The drop in $\mathscr{K}$ below 30 K was attributed to the opening of a superconducting pseudo-gap and taken as further evidence in favour of the model of superconducting fluctuations in the $(TMTSF)_2X$ salts (Jerome & Schultz 1982). In a magnetic field, the pseudo-gap is suppressed and thus $\mathscr{K}$ increases.

A more recent measurement of $\mathscr{K}$ is shown in figure 3 (Choi *et al.* 1984*b*). Below 60 K, this data is completely different from the earlier results. The thermal conductivity increases strongly below the anion ordering transition at 24 K and then decreases below a maximum at *ca.* 10 K. An 8 T magnetic field applied parallel to the c^* direction decreased $\mathscr{K}$ by about 20% at temperatures below 24 K. Since the electrical resistivity is strongly increased in a field of 8 T, this result suggests that $\mathscr{K}$ is dominated by the phonon contribution below 24 K. The large increase in $\mathscr{K}$ below 24 K shows that a superconducting pseudo-gap is not being formed. Moreover, the magnetic field dependence is consistent with a partial contribution to $\mathscr{K}$ from normal electrons.

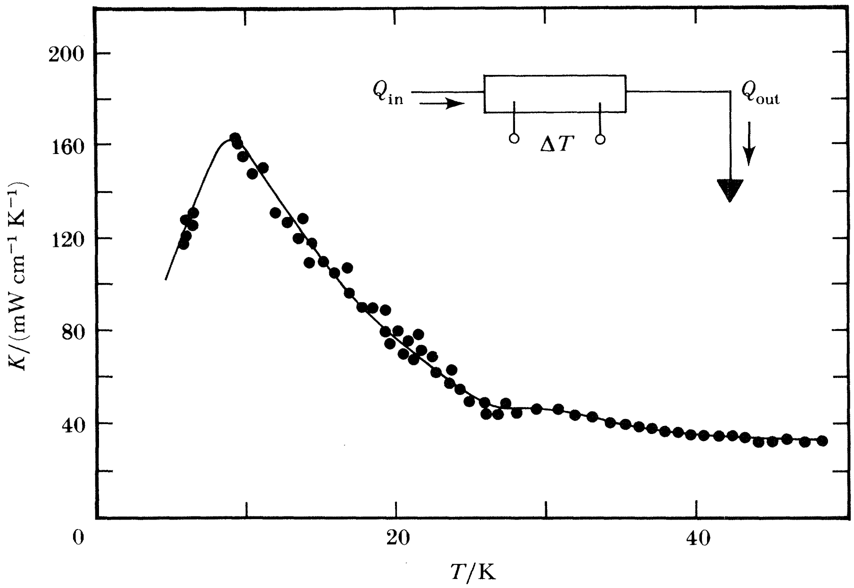

FIGURE 3. The thermal conductivity of $(TMTSF)_2ClO_4$ for a temperature gradient along the a-axis. The inset shows the six-probe geometry used to measure the heat into the sample (Q_{in}), the heat out (Q_{out}) and the temperature gradient (ΔT) across the sample. Thermal ground is indicated by the large arrow.

Why are these two measurements of the thermal conductivity so different below 60 K? The measurement of thermal conductivity on small samples is notoriously difficult at low temperatures. One must be very careful to avoid spurious heat losses from the sample. The measurement by Choi *et al.* (1984*b*) was made using the six-probe configuration shown schematically in figure 3. This allowed us to measure the heat into the sample (Q_{in}), the heat out (Q_{out}) and the temperature gradient across the sample (ΔT). By this technique, the temperature-dependent heat loss from the sample could be determined and an accurate value for $\mathcal{K}(T)$ could be calculated. The earlier determination of $\mathcal{K}$ (Djurek *et al.* 1982) was essentially a two-probe measurement and therefore susceptible to error, since the heat loss was not known.

3. Conclusion

The low-field (below H_{th}) magnetotransport properties of $(TMTSF)_2ClO_4$ can be qualitatively explained by a conventional (one-electron) Boltzmann equation approach (Forró *et al.* 1984), but a quantitative theory is still lacking. The origin of the threshold magnetic field and the subsequent high-field oscillations in the magnetotransport are not completely understood at present. One promising model was briefly discussed. This model requires coherent electron motion in the *ab* plane and weak coupling between the planes. Collective (many-body) effects are probably involved, being responsible for either a series of s.d.w. or electron–hole (excitonic) transitions accompanied by a two-carrier version of the quantum Hall effect. New thermal conductivity data was reported, which is very different from previous results. The new data shows that the low temperature thermal conductivity of $(TMTSF)_2ClO_4$ has both lattice and electron contributions with no observable contribution from superconducting fluctuations.

We appreciate the major contributions made by M. Y. Choi to the work reviewed here and the expert sample preparation of E. M. Engler and V. Y. Lee.

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Discussion

R. Pethig (*School of Electronic Engineering Science, University College of North Wales, Bangor, U.K.*). The Hall voltages that Dr Greene has measured are quite small, so I wonder if it is of relevance to know whether or not voltages arising from the Ettinghausen effect possibly influenced his results. For materials that exhibit thermoelectric effects or whose thermal conductivity arises from both lattice and electronic contributions, the Ettinghausen effect can be a significant one. Is it known whether his materials have such physical characteristics? The effect is a thermoelectric one arising essentially from the Lorentz force separating the fast from the slow moving charge carriers, and it is indistinguishable from the Hall effect in that (unlike the Nernst, Righi–Leduc or Hall probe misalignment voltage) it is not cancelled out by the averaging of the four results obtained on reversing the applied magnetic field and the current in the test sample. The effect does, however, become vanishingly small for a.c. Hall effect measurements made at sufficiently high frequency. Although none of this alters the fact that he has observed very interesting and unique effects, I suppose I am asking if all the relevant magnetotransport effects have been fully considered.

R. L. Greene. The Hall voltages that we have measured are definitely not caused by the Ettingshausen effect since we have been careful to keep our sample completely isothermal during the experiment. There was no possibility of thermal gradients developing across the sample in any direction and therefore no possibility of thermoelectric effects of any kind. Thus we have measured the Hall effect and nothing more. The origin of the threshold magnetic field for the Hall effect and the unusual stepwise behaviour (see figure 2) has become more clear from a recent theory of P. M. Chaikin (1985). The essence of the theory is that an electron in a magnetic field (along c^*) is forced to move on the open orbit Fermi surface. In real space this corresponds to electron motion with an approximately constant velocity along the a direction and an oscillatory motion in the b direction. As the magnetic field is increased the excursion in the b direction is reduced until eventually the electron is localized on a single conducting chain. Thus the magnetic field drives the system from two-dimensional to one-dimensional behaviour. The one-dimensional system is then unstable against a Fermi surface instability (c.d.w. or s.d.w.), which Chaikin shows will occur at a wavevector (Q) with component $2k_F$ along a and zero along b. This nesting Q will gap part of the Fermi surface but will leave an electron and hole pocket. The Landau levels in these compensated pockets are then responsible for the large magnetoresistance oscillations and Hall steps above H_{th} as described briefly in §2 of the paper. Chaikin's model is different from the model proposed for graphite (Yoshioka & Fukuyama 1981) since in the $(TMTSF)_2ClO_4$ case distortions along the c^* direction do not appear to dominate. Another theory for the magnetic field induced transition (due to L. P. Gorkov) was discussed by Dr Jérome (this symposium). An understanding of the similarities and differences of these theories and the accuracy of their predictions for the physical properties in the $(TMTSF)_2X$ materials must await future work.

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