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Organic superconductors: low-dimensional conductors and anomalous superconductors

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Organic superconductors belonging to the $(TMTSF)_2X$ series are quasi-one-dimensional conductors in the sense that their Fermi surface is open. The strong sensitivity of the superconducting state to pressure and non-magnetic impurities is probably a direct consequence of the low-dimensionality of the electron energy dispersion. We discuss the remarkable stabilization of semimetallic (magnetic) states observed under high magnetic fields in $(TMTSF)_2ClO_4$ in terms of recently proposed theoretical models. These models suggest the existence of a sequence of phase transitions between spin density wave sub-phases and the quantization of the Hall resistance within each of these sub-phases as observed experimentally.

Introduction

$(TMTSF)_2X$ salts (Bechgaard *et al.* 1980) have been the first among organic conductors to show superconductivity at low temperature (Jérome *et al.* 1980). More recently superconductivity has also been discovered in another series of organic conductors, namely the sulphur-based family $(BEDT\text{-}TTF)_2X$, first under pressure with $X = ReO_4$ (Parkin *et al.* 1983) and subsequently at ambient pressure with $X = I_3$ (Yagubskii *et al.* 1984).

In common with all other organic conductors known up to now these conducting salts show a strong anisotropy in their transport properties. Such an anisotropy is provided by the packing of flat molecules along a direction (the *a*-axis for the TMTSF series) in which the overlap between molecular orbitals of neighbouring molecules is stronger than between molecules belonging to adjacent stacks. Furthermore, the $(TMTSF)_2X$ crystal structure is special in the sense that short interchain Se ... Se contacts make the molecular overlap significant along the transverse *b*-direction as well. However, the transverse *c*-direction along which stacks of TMTSF molecules are separated from each other by X anions represents a direction of weak interchain coupling. Because of the intermediate coupling along the *b*-axis, $(TMTSF)_2X$ salts have been the subject of intense controversies; some groups (Greene *et al.* 1982) claiming that $(TMTSF)_2X$ should not be treated on the same footing as materials of the TTF-TCNQ series so far as one-dimensional properties are concerned, while the Orsay group (Schulz *et al.* 1981) was inclined to believe that one dimensionality (namely the existence of an 'open' Fermi surface) is the clue to all their physical properties. As more and more experiments have accumulated over the past few years it seems now more obvious that one-dimensional models are the only ones that account for the numerous exotic properties of these conductors.

The purpose of this survey is to review some of these exotic physical properties and to show how they can be related to the basis of low-dimensional physics. An overview of the $(TMTSF)_2X$ series has been written recently by the author (Jérome 1984*a*).

Anisotropic properties

The anisotropy of the electron dispersion law is revealed in a large number of transport or optical properties. There have been several reports of σ_a/σ_b anisotropy data ranging from 25, the smallest in $(TMTSF)_2ClO_4$ (Greene *et al.* 1982), up to 2×10^2–4×10^2 in other salts (Jacobsen *et al.* 1981). When the conductivity proceeds via a coherent motion along the chain and a diffusive process from chain to chain (which is probably the situation at room temperature) the anisotropy of conductivity is given by the relation (Soda *et al.* 1977)

$$\sigma_a/\sigma_b = (at_a/bt_b)^2, \tag{1}$$

where $a(b)$ and $t_a(t_b)$ are, respectively, the lattice parameters and the overlap integrals along the $a(b)$-axis. The experimental value of σ_a/σ_b together with (1) leads to $t_a/t_b \geqslant 10$.

Infrared reflectance studies (Jacobsen *et al.* 1983) have shown the existence at low temperature of plasma edge features for $(TMTSF)_2X$ with light polarized along the transverse b-axis at about a ten times lower energy than the chain axis edge.

For an open Fermi surface the conversion of plasma frequencies into bandwidths is linear and therefore the ratio $t_a/t_b \approx 10$ is recovered again. The experiment that allows an unambiguous determination of the Fermi surface topology (i.e. closed or open Fermi surface) is indeed provided by the low-field Hall effect of $(TMTSF)_2ClO_4$ (Ribault *et al.* 1983). As shown in figure 1, the Hall voltage is linear against magnetic field up to 30 kOe†, (with a Hall constant $R_H = +4\times10^{-9}$ m^3/(A s)) and temperature independent from 0.1 K up to at least 5 K. The experimental Hall constant is in fairly good agreement with the standard expression for the low-field Hall coefficient in a one-dimensional tight-binding model (Cooper *et al.* 1977). $R_H = (1/nec)\,(k_F a/tgk_F a)$, which implies that $R_H = 3.4\times10^{-9}$ m^3/(A s), given $k_F = 3\pi/4a$ (the slight dimerization in the organic stack does not modify the energy band near k_F) and n corresponding to one hole for two TMTSF molecules. With closed Fermi surfaces it would be unlikely to expect both a field-independent Hall constant as displayed in figure 1 and a very good agreement with the one-dimensional tight-binding model.

However, an accurate determination of the bandwidth is more difficult to obtain. The Drude analysis of the parallel reflectance data gives a one-dimensional tight-binding bandwidth of

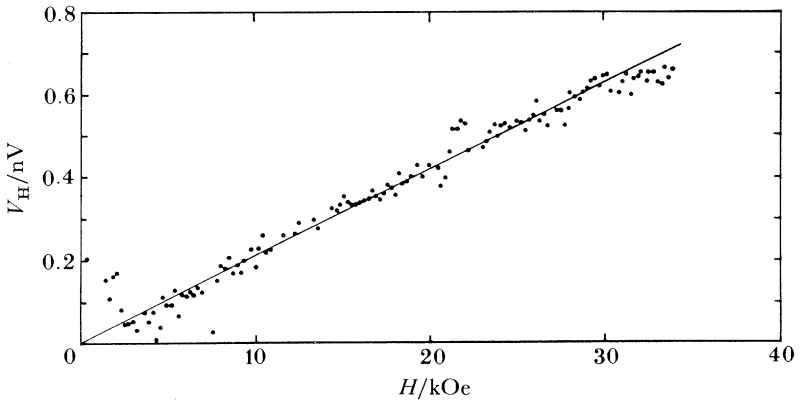


Figure 1. The Hall voltage of $(TMTSF)_2ClO_4$ in the low-field régime. The sample is in the R-state.

† 1 Oe ≈ 79.5775 A m^{-1}.

ca. 1 eV (i.e. $t_a \approx 0.25$ eV) (Jacobsen *et al.* 1983). Somewhat larger values have been obtained by Grant (1983) ($t_a \approx 0.37$ eV) using a semi-empirical molecular orbital calculation.

The anisotropy of the electron dispersion is also responsible for the recent observation of the magnetic field dependence of the proton spin-lattice relaxation rate in $(TMTSF)_2PF_6$ at room temperature (Stein 1985). When the electron Larmor frequency ω_e becomes larger than the electron hopping rate along the transverse b-direction the relaxation induced by the hyperfine coupling to the electrons is field dependent ($1/T_1 \approx H_0^{-\frac{1}{2}}$). A comparison between the n.m.r. data of $(TMTSF)_2X$ and those obtained earlier for the TTF-TCNQ system (Soda *et al.* 1977) leads to the qualitative conclusion that the transverse coupling of $(TMTSF)_2X$ is about twice that of the TCNQ chain in TTF-TCNQ (i.e. $t_b^{TM} \approx 10$ meV). This value is admittedly smaller than the estimate derived either from the Drude analysis of the reflectance data or from the band parameter calculation. However, according to transport, optical and n.m.r. results we feel justified in stating that the Fermi surface of $(TMTSF)_2X$ is quasi-one-dimensional at all temperatures provided the conducting state is stable. But transverse coherent motion may very well coexist with an open Fermi surface. The condition to be fulfilled is qualitatively $\hbar/\tau_\parallel \lesssim 2\pi t_\perp$ (Soda *et al.* 1977), where $\tau_\parallel$ is the intra-chain electron scattering time. A t_b of about 10 meV is enough to guarantee a transverse coherent picture provided $\tau_\parallel > 10^{-14}$ s. This is likely to explain the occurrence of the b-axis plasma edge below 100 K in $(TMTSF)_2X$.

The various experimental results are in fairly good agreement with ratios for $t_a : t_b ; t_c$ such as $10 : 1 : \frac{1}{30}$. Furthermore, reasonable figures for t_a are in the range 0.10 to 0.25 eV. To summarize, we have seen that the Fermi surface of the conducting state of $(TMTSF)_2X$ is open. Hence, we are entitled to ask what is the influence of one-dimensional phenomena on the electronic properties, in particular (i) the role of fluctuations depressing the occurrence of three-dimensional long-range order at low temperature and (ii) the interplay between electron–electron and electron–hole instabilities in an interacting quasi-one-dimensional electron gas?

However, it appears clearly from the previous survey of the anistropy properties that organic conductors belonging to the $(TMTSF)_2X$ series are less anisotropic than the TTF-like charge transfer compounds. The purpose of the rest of this article is to show that in spite of their moderate anisotropy, $(TMTSF)_2X$ conductors exhibit characteristic behaviour typical of one-dimensional physics. In this paper we shall emphasize the interplay between ground states of different natures. The present situation concerning the role of fluctuations is discussed in the proceedings of another conference (Jérome 1984*b*).

Theoretical outline

The theory of the one-dimensional interacting electron gas has been extensively reviewed in other publications (Solyom 1979; Jérome & Schulz 1982) and here we present only the principal features.

It is well known that when treated in the mean field approximation (i.e. neglecting fluctuations of the order parameter around its mean value (Friedel & Jérome 1982)) the ground state of a one-dimensional electron gas is described by a phase stability diagram that depends on the values of the interaction parameters g_1 and g_2 (related to scatterings at wavevectors $2k_F$ and $q = 0$, respectively). However, the mean-field approximation suffers from a serious drawback: it predicts long-range order at finite temperature, whereas in a one-dimensional

system fluctuations are known to destroy long-range order (Jérome & Schulz 1982). But a perturbation theory going beyond mean-field diagrams encounters the problem of the one-dimensional electron gas, which was first treated by Bychkov *et al.* (1966). At low temperatures, the divergence of the electron–hole channel (spin density or charge density wave, s.d.w., c.d.w.) is strongly mixed with the divergence of the Cooper channel. Renormalization group methods thus provide a fairly complete picture of the properties of the one-dimensional interacting electron gas (Jérome & Schulz 1982).

The most divergent correlation functions at low temperature can be determined according to g_1 and g_2 values (figure 2). When $g_1 < 2g_2$, electron hole instabilities are dominant (s.d.w.

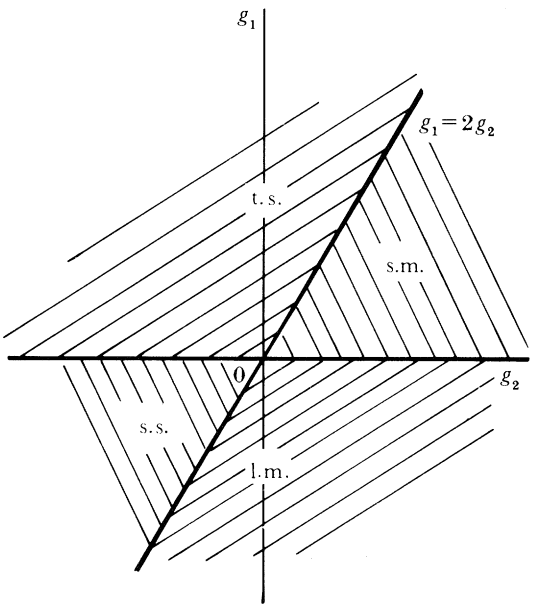


FIGURE 2. Most divergent response functions in a one-dimensional electron gas: spin modulation (s.m.), lattice modulation (l.m.), triplet superconductivity (t.s.) and singlet superconductivity (s.s.). L.m. and s.s. are also secondary divergences in the s.m. and t.s. sections of this diagram, respectively. This diagram is also indicative of the ground states within the mean-field approximation.

or c.d.w. for $g_1 > 0$ and $g_1 < 0$, respectively). The Cooper channel is dominant when $g_1 > 2g_2$. If $g_1 > 0$ the triplet pairing (triplet superconductivity) is more divergent than the usual singlet pairing. Furthermore, three-dimensional long-range order at low temperature exists in a real quasi-one-dimensional conductor. This is due to the finite interchain coupling $t_\perp$. The nature of the ground state depends on two parameters: (i) the nature of the most divergent correlation function for given g_1 and g_2 parameters and (ii) the magnitude of the transverse coupling related to the specific nature of the ground state (Friedel & Jérome 1982). The ground state of a quasi-one-dimensional conductor is thus either superconducting or s.d.w. (c.d.w.). Schulz (1983) has recently predicted that for particular Coulomb interactions a non-distorted one-dimensional conducting state could remain stable at zero temperature. There exists as yet no experimental evidence of such a behaviour at low temperature in one-dimensional conductors free from impurities.

The superconducting state

Superconductivity is observed below 1.2 K in the six salts X = ClO_4, ReO_4, PF_6, AsF_6, TaF_6, SbF_6 of the $(TMTSF)_2X$ series (Jérome *et al.* 1980; Parkin *et al.* 1981). For all salts but the first one high pressure is required to stabilize the superconducting state. Superconductivity has also been found in the sulphur-based molecular crystals $(BEDT\text{-}TTF)_2X$, with X = ReO_4 under pressure (Parkin *et al.* 1983), and X = I_3 at ambient pressure (Yagusbskii *et al.* 1984).

The superconducting state is suppressed by the application of a magnetic field exceeding the critical field $H_{c_2} \approx 1$ kOe for H parallel to c^*.

Effect of disorder

Non-magnetic impurity potentials have usually very little effect on the superconductivity of metals. However, they have a suprisingly important effect on the stability of superconductivity in organic superconductors, a topic that is briefly reviewed below.

(i) *Anion ordering in* $(TMTSF)_2ClO_4$

X-ray investigations (Pouget *et al.* 1983) have clearly established that non-centrosymmetric ClO_4 ions order below 24 K with no change of the lattice periodicity along the a and c-axis and a doubling along b. Samples that are slowly cooled through the 24 K transition (R-state) exhibit long-range ion ordering and a very sharp superconducting transition at 1.15 K (Ribault 1984). However, rapid cooling below 30 K down to 4.2 K leads to a partly ordered state (Q-state) exhibiting both lattice disorder (Kagoshima *et al.* 1983) and excess entropy (Garoche *et al.* 1983). Increasing the cooling rate strongly destabilizes superconductivity (Ribault 1984; Garoche *et al.* 1983). Instead, a magnetic insulating state identified by resistivity and e.p.r. (Tomic *et al.* 1982), n.m.r. (Takahashi *et al.* 1982) and antiferromagnetic e.p.r. (Walsh *et al.* 1982) is established below 3.5–4 K.

(ii) *Alloying* $(TMTSF)_2ClO_4$

$(TMTSF)_2ClO_4$ and $(TMTSF)_2ReO_4$ are both superconductors at around 1.2 K, the latter compound requiring a pressure of over 10 kbar† (Parkin *et al.* 1981). However, mixing of the two superconductors, namely $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$, leads to a magnetic insulating ground state at $x > 3\%$ (Tomic *et al.* 1983) (figure 3). A similar stabilization of a magnetic state is observed when a solid solution is made on the organic stack in $[(TMTSF)_{1-x}(TMTTF)_x]_2ClO_4$ at $x > 2\%$ (Coulon *et al.* 1982).

It is important to notice that the s.d.w., which is stabilized by disorder instead of superconductivity, can be removed by the subsequent application of a high pressure. A reasonably highly conducting state is thus restored at low temperature *but* superconductivity can no longer be obtained (at least down to 0.1 K). A similar stabilization of a s.d.w. state has also been obtained in the R-state of $(TMTSF)_2ClO_4$ with the substitution of *ca.* 0.3% (by mass) of S to the Se atom in the organic molecule (A. Moradpour, personal communication (1984)).

To summarize, we have seen how non-magnetic disorder can govern the balance between

† 1 bar = 10^5 Pa.

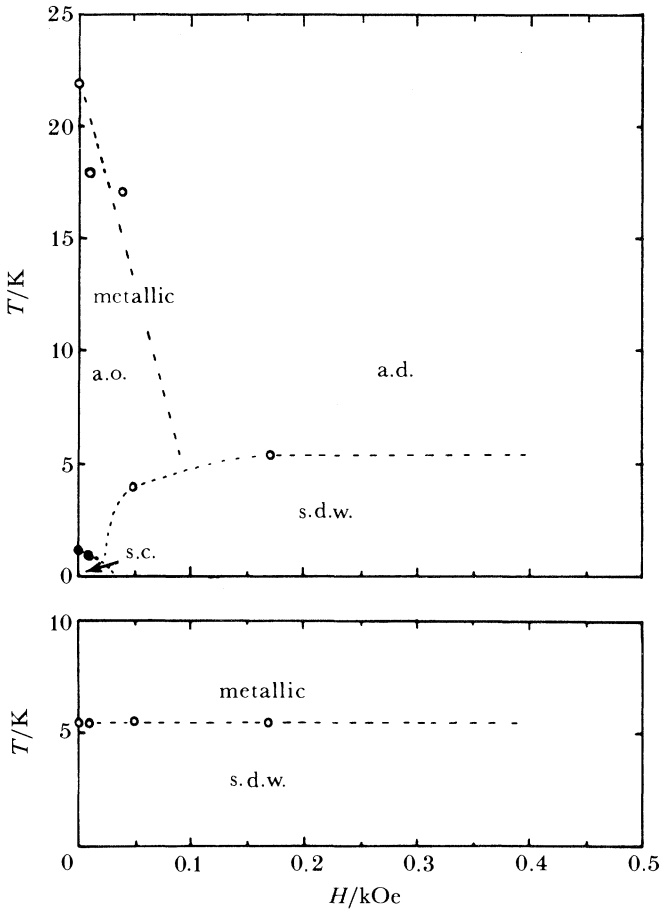


FIGURE 3. Phase diagram of the solid solution $(TMTSF)_2ClO_{4(1-x)}ReO_{4x}$ in R (top) and Q (bottom) states $(0 < x < 0.2)$.

superconductivity and magnetism in the $(TMTSF)_2X$ series. We wish to emphasize that the influence of non-magnetic impurities on the superconducting ground state is highly anomalous since no similar influence is observed at such low concentrations of defects in ordinary superconductors, especially when we consider that the restoration of a s.d.w. state at a large concentration of defects suggests that the Fermi surface is not significantly smeared by a possible shortening of the electron scattering time. Any theoretical attempt to understand organic superconductivity must take into account the observed sensitivity to disorder.

MAGNETIC STATES

$(TMTSF)_2PF_6$ or $(TMTSF)_2AsF_6$ are typical examples of antiferromagnetic insulators at low temperature. The magnetic nature of the ambient pressure ground state has been firmly established by various magnetic measurements: single crystal susceptibility (Mortensen 1982), n.m.r. (Andrieux *et al.* 1981) and antiferromagnetic e.p.r. (Torrance *et al.* 1982). The insulating or semiconducting character of the ground state implies that the periodicity of the electron potential along the *a*-axis is doubled by the onset of magnetic long-range order. So far, the spin structure has not been observed by diffraction techniques.

High pressure suppresses the s.d.w. state of $(TMTSF)_2PF_6$-like conductors, allowing the stabilization of superconductivity above 8–9 kbar (Jérome *et al.* 1980). However, close to the critical pressure the phase diagram (figure 4), exhibits a re-entrance of the superconducting state below the magnetic phase (Brusetti *et al.* 1982). In the re-entrance region the transition between the s.d.w. and the superconducting state is especially sharp. It has been noticed by

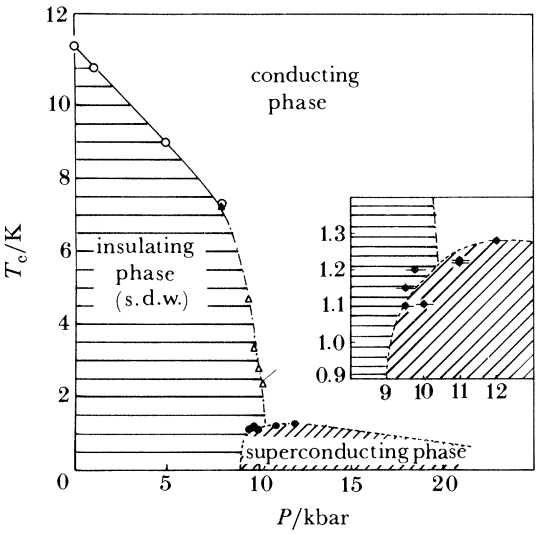


FIGURE 4. Phase diagram of $(TMTSF)_2AsF_6$, showing the re-entrance of the superconducting state below the s.d.w. phase in the pressure range $P \approx 10$ kbar.

Yamaji (1983) that this transition must be first order. Furthermore, the re-entrance has been explained very easily from free-energy considerations using the mean-field approximation (Yamaji 1983). Along the coexistence curve separating the s.d.w. and normal states, $F_{s.d.w.}$ is equal to F_n. However in the re-entrant pressure domain, say at zero temperature, the free energy of the superconducting state, F_{sup} is lower than F_n by the amount $N(E_F)\,\delta^2$ where $N(E_F)$ and δ are the density of states of the normal phase and the zero-temperature superconducting gap, respectively. Thus the superconducting phase must extend into the s.d.w. state over a finite pressure range since the coexistence curve between s.d.w. and superconductivity is defined by $F_{s.d.w.} = F_{sup}$.

HIGH MAGNETIC FIELD EFFECTS IN $(TMTSF)_2ClO_4$

Perhaps the most spectacular behaviour of $(TMTSF)_2ClO_4$ besides the existence of a superconducting state at low temperature is the response of the electron gas to the application of a magnetic field. When the field is applied, say at $T < 1$ K, the three-dimensional ordered superconduction is destroyed at a critical field H_{c_2}, which depends on the orientation of the magnetic field with respect to the crystal axis. Roughly speaking $H_{c_2}(0)$ amounts to 1 and 15 kOe for the c and b directions, respectively. The low-field Hall data (figure 1) have shown that above H_{c_2} the conductor behaves like an open Fermi surface quasi-one-dimensional conductor. This topology of the Fermi surface does not last for ever at higher fields because the Hall coefficient ($H \parallel c^*$, $I \parallel a$) begins to increase very sharply above a temperature-dependent onset field (H_0) (figure 5). H_0 is about 65 kOe at $T = 1.3$ K. Such a large increase of R_H is

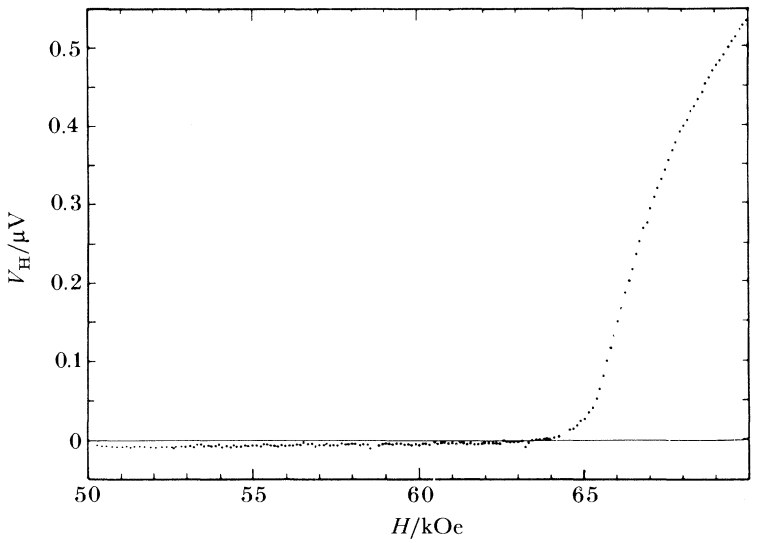
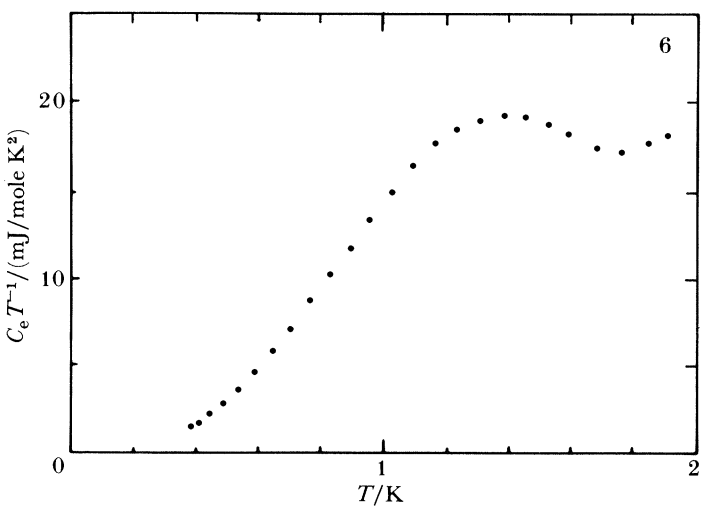


FIGURE 5. Field dependence of the Hall voltage of $(TMTSF)_2ClO_4$, showing the onset of the semimetallic state at 65 kOe ($T = 1.3$ K).

the signature of a reorganization of the Fermi surface, which implies a drastic reduction of the number of carriers at $H > H_0$. At high fields ($H > H_0$) the Hall effect is electron-like. Oscillations of the resistance have been detected in $(TMTSF)_2ClO_4$ above H_0 (Kwak *et al.* 1982). First they were attributed to Shubnikov–de Haas oscillations on a Fermi surface consisting of small compensated tubes of electrons and holes parallel to the c^*-axis, namely a two-dimensional semi-metallic Fermi surface implying the existence of very small closed orbits in the (a–b) plane, corresponding to only *ca.* 1 % of a Brillouin zone cross section perpendicular to the c^* direction.

Another confirmation of the semimetallic character of the high-field ($H > H_0$) Fermi surface came from electronic specific heat measurements made under high field (Garoche *et al.* 1982), revealing a large decrease of C_V below 1.4 K at $H = 63$ kOe parallel to c^* (figure 6). Further ^{77}Se n.m.r. experiments (Takahashi *et al.* 1982) led to the conclusion that $(TMTSF)_2ClO_4$ exhibits itinerant magnetism under high fields (figure 7). So far, the behaviour of $(TMTSF)_2ClO_4$ against magnetic field can be summarized by saying that the field induces a Fermi surface transformation at an onset field H_0, from an open metal-like Fermi surface at $H < H_0$ to a semi-metal-like Fermi surface related to a s.d.w. state at $H > H_0$. The orientation dependence of H_0, namely $H \cos\theta$, where θ is the angle between the magnetic field and the c^* direction, suggests that the stabilization of the s.d.w. field is related to the anisotropy of the electron trajectories of the quasi-one-dimensional phase: it is an orbital effect.

The stabilization of a s.d.w. state by a magnetic field applied to a quasi-one-dimensional conductor is already a remarkable property, but recent Hall effect data have revealed that the phenomenon may be even more subtle that it looks at first glance. At very low temperature the Hall coefficient shows a series of steps and flat plateaux (Ribault *et al.* 1983) (figure 8). The value of the Hall resistance for a given plateau is temperature dependent, increasing on cooling and reaching a T-independent value of about 6 kΩ below 0.3 K for the 64–80 kOe plateau. Hall effect measurements extended to a higher range of fields have shown that more steps and plateaux are obtained above 100 kOe (Chaikin *et al.* 1983).



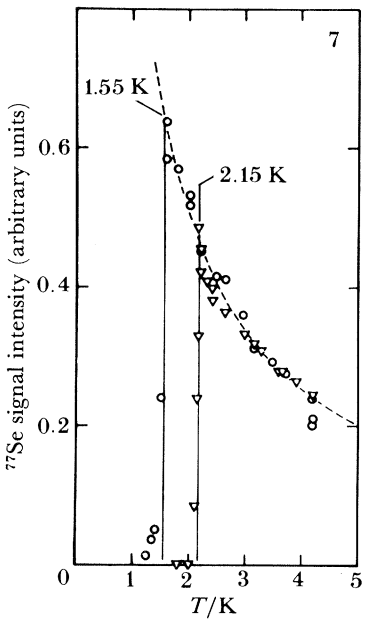


FIGURE 6. Temperature dependence of the electronic specific heat C_e/T, showing the onset of the semimetallic state at $T \approx 1.4$ K; the magnetic field is 63 kOe parallel to c^*.

FIGURE 7. Temperature dependence of the ^{77}Se n.m.r. intensity. The broken line represents the Curie-like behaviour, which is expected in a paramagnetic phase. The vanishing of the n.m.r. signal is the signature of the s.d.w. state: ▽, 7.39T parallel to c^*; ○, 6.4T parallel to c^*.

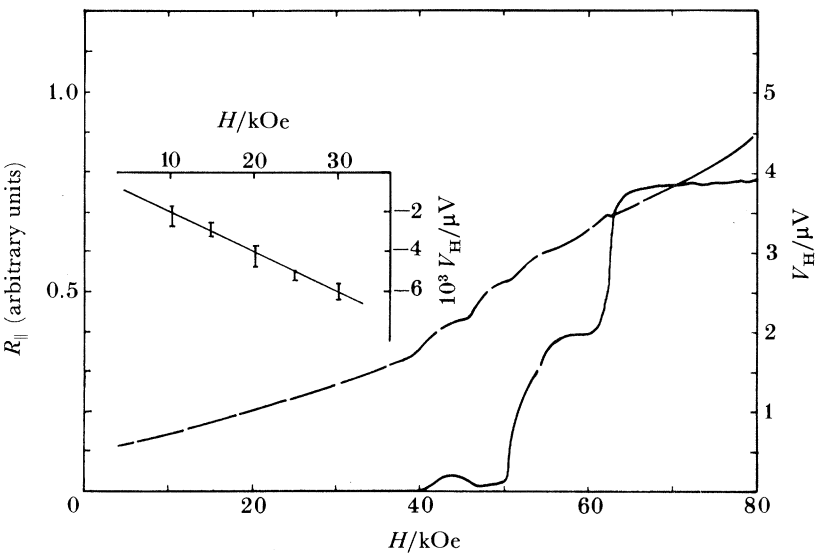


FIGURE 8. Hall voltage of $(TMTSF)_2ClO_4$ in the high-field régime (right scale, line with one break) and magnetoresistance (left scale, line with multiple breaks). The inset shows the field dependence in the low-field régime. The sign of the Hall constant is positive (hole) and negative (electrons) at low and high fields respectively.

The existence of the Hall plateaux has been related to the quantum Hall effect of two-dimensional electron gases (Klitzing *et al.* 1980; Tsui & Gossard 1981). The suggestion was based on the idea that $(TMTSF)_2ClO_4$ may be considered as a packing of conducting $(a–b)$ planes along the c-direction (Ribault *et al.* 1983). In the high-field limit, the orbits are closed in the $(a–b)$ plane in spite of a very pronounced anisotropy. As t_c is likely to be smaller than the energy separation between Landau levels at high fields when H is parallel to c^*, the warping of the tubular Fermi surface along c^* can be neglected. So, the carriers in the $(a–b)$ planes behave as a system of two-dimensional carriers. Hence, in the high-field state, $(TMTSF)_2ClO_4$ could mimick the situation of a multilayer structure with a very large number of identical two-dimensional layers (about 10^5 in a crystal of thickness 0.2 mm electrically connected in parallel by the Hall probes). This is the situation where the Hall voltage adopts a quantized behaviour against magnetic field instead of the usual linear relation (observed at $H < H_0$ (figure 1)): the Hall resistance ρ_{xy} becomes h/e^2i, where i is the number of filled Landau levels. It is tempting to establish an order of the magnitude for the connection between the Hall voltage plateaux of $(TMTSF)_2ClO_4$ and the quantum Hall effect, since the measured Hall resistance of *ca.* 6 kΩ per layer at $H \geqslant 60$ kOe is close to the quantized value of the Hall resistance $(h/4e^2 = 6453\ \Omega)$ for $i = 4$.

However, several features of the $(TMTSF)_2ClO_4$ Hall data cannot be readily understood in terms of quantum Hall effect: (i) both the value of the Hall plateaux and the values of the magnetic field corresponding to the steps are considerably temperature dependent, especially above 0.5 K; (ii) in the data displayed on figure 8 the diagonal resistance does not vanish in the Hall plateau regions as it should for a quantum Hall effect (Stormer & Tsui 1983); (iii) the Hall resistance steps do not show a perfect periodicity in $1/H$, even at very low temperature; (iv) some magnetic field hysteresis has been detected at the position of the Hall resistance steps or in the high-field magnetoresistance (Ishiguro *et al.* 1983).

We have suggested (Ribault *et al.* 1983) that the Hall data of $(TMTSF)_2ClO_4$ is not to be understood *stricto sensu* within the framework of the quantum Hall effect. Instead, a combination of a sequence of field-induced phase transitions and Hall quantization within each phase may be more appropriate. The mechanism of field-induced transitions might bear some resemblance to the model of nested excitonic instabilities (Jérome *et al.* 1967; Kohn 1967) where first an Overhauser-like transition takes place between a non-magnetic conducting state and a magnetic semimetallic state. Subsequent phases are also magnetic with a concomitant decrease in the number of carriers at increasing magnetic fields.

A clue seems to have been given by recent theoretical studies of the phase stability of a quasi-one-dimensional electron-gas at low temperature including the effect of a magnetic field (Gorkov & Lebed 1984) extended by Héritier *et al.* (1984). Gorkov & Lebed (1984) have proposed a model based on the open Fermi surface of a quasi-one-dimensional conductor, taking into account near-neighbour (*ca.* $t_b \cos k_b b$) *and* next near-neighbour ($t'_b \cos 2k_b b$) interactions between chains in the transverse energy dispersion where $t'_b \ll t_b$. Furthermore, they have studied the stability of the electron gas by looking at the poles of the generalized susceptibility $\chi(\boldsymbol{Q})$, which includes parameters such as T, P or H.

In the standard random phase approximation for the susceptibility, which is valid at low temperature *close enough* to three-dimensional ordering, $\chi(\boldsymbol{Q})$ reads

$$\chi(\boldsymbol{Q}) = \chi_0(\boldsymbol{Q})/(1-\lambda\chi_0(\boldsymbol{Q})),$$

where λ is the interaction constant of the mean-field approximation and $\chi_0(\boldsymbol{Q})$ is the response for non-interacting electrons at given P, T, H.

By taking into account the effect of the magnetic field, substituting $\boldsymbol{k}-e\boldsymbol{A}/\bar{c}$ for $\boldsymbol{k}$ in the calculation of $\chi_0(\boldsymbol{Q})$, Gorkov & Lebed (1984) have reached the following conclusions.

(i) For $\boldsymbol{Q}=(2k_F, \pi/b, \pi/c)$, s.d.w. states are stabilized under high field (supposed to be parallel to the c-axis) at low temperature.

(ii) A sequence of phase transitions between s.d.w. states characterized by different number of carriers is given *approximately* by the fields H_n, which satisfy the zeros of the Bessel function $J_0(z)$:

$$J_0(2\bar{c}t_b'/v_F\, eH_n\, b) = 0,$$

where $\bar{c}$ is the velocity of light.

(iii) The phase transition temperatures between the quasi-one-dimensional non-magnetic conductor and the various s.d.w. sub-states is given approximately by

$$T_{\text{s.d.w.}} \approx \mathrm{e}^{-n},$$

where n is an integer increasing with magnetic field. The above-mentioned argument explains fairly well the stabilization of the s.d.w. state at high fields and the sequence of phase transitions detected by the steps of the Hall constant or increased radio frequency energy absorption (Azevedo *et al.* 1984). However, it does not account either for the flatness of the Hall resistance within each phase or for the drop of longitudinal resistance within the Hall plateau domain, which has been detected in a very high quality $(TMTSF)_2ClO_4$ sample (figure 9).

Héritier *et al.* (1984) have extended the argument of Gorkov & Lebed (1984) by allowing some leeway in the definition of the wavevector in the s.d.w. states, namely

$$\boldsymbol{Q}=\left(2k_F+q_x, \frac{\pi}{b}+q_y, \frac{\pi}{c}+q_z\right). \tag{2}$$

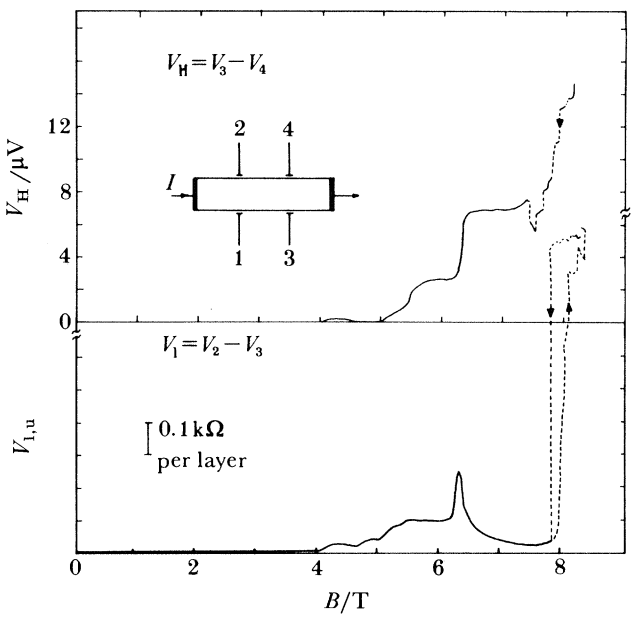


FIGURE 9. Field dependence of the Hall voltage (upper part) and of the longitudinal resistance (lower part) measured at $T=0.15$ K in a $(TMTSF)_2ClO_4$ sample exhibiting a resistivity ratio $R(300\text{ K})/R(4.2\text{ K}) \approx 1600$.

According to (2) the nesting vector can be incommensurate in all three directions. Then, the criterion for the stability of the s.d.w. states requires

$$S(q_x)/S_0 = n, \tag{3}$$

where $S(q_x) = 2\pi q_x/b$ is the area in momentum phase space that is enclosed between the original Fermi surface and this surface translated by $\boldsymbol{Q}$; $S_0 = eH2\pi/\bar{c}$ is the quantum of momentum space area in the presence of a field H, n is an integer.

The variable nesting wavevector theory predicts that the Fermi surface cross section $S(q_x)$ must increase with H. However, when $S(q_x)$ in (3) reaches a maximum possible value the integer n jumps to $n-1$. At this stage $S(q_x)$ diminishes suddenly since the number of filled Landau orbits decreases by one unit. The whole process starts again at higher field with the quantum number $n-1$. As the area $S(q_x)$ encloses the unpaired charge carriers N contributing to the Hall effect, the Hall resistivity $\rho_H = H/Ne\bar{c}$ becomes

$$\rho_H \approx h/e^2 n$$

in the s.d.w. sub-phase characterized by the given integer n.

The physical reason for the plateaux in the Hall constant is that the s.d.w. wavevector can adapt to the field variation in such a way that the quantization of the Fermi surface nesting expressed by (3) is preserved. Furthermore, an integral number of Landau levels are completely filled within each s.d.w. sub-phase, as for the interpretation of the usual quantum Hall effect.

Héritier *et al.* (1984) have predicted a series of first-order phase transitions between s.d.w. sub-phases accompanied by discontinuities of the nesting wavevector and a drop of the electron scattering (i.e. drop of resistivity) along Hall plateaux. The possibility of coexistence of phase transitions and quantization of the Hall resistance has also been proposed independently by Ribault *et al.* (1983, 1984).

Conclusion

This article has been devoted to a description of phenomena occurring in organic conductors $(TMTSF)_2X$ at low temperature. All experiments show that superconducting and magnetic states are very close in energy. Indeed, when submitted to a small perturbation (pressure, presence of non-magnetic defects) these compounds undergo a phase transition from a three-dimensional ordered superconducting state to a magnetic (semiconducting) ground state. This interplay between electron–electron and electron–hole pairing is very much in the essence of the theory of one-dimensional conductors. We have not discussed the insulating state at low temperature coming from the alternation of non-centrosymmetric anions (ReO_4, FSO_3, etc.) in this paper. Such conducting to semiconducting transitions require a one-dimensional structure for the energy dispersion spectrum, but the transition itself is not driven by the properties of the single-chain electron gas.

One dimensionality manifests itself also in the existence of a wide domain in temperature where one-dimensional response functions reach large values and influence many experimental properties. There was no attempt to review this aspect of organic superconductors in the present article (see Jérome 1984*a*, *b*). Perhaps the most spectacular effect of the quasi-one-dimensionality of the Fermi surface is the existence of a sequence of phase transitions towards s.d.w. states in $(TMTSF)_2ClO_4$, and probably also in other members of the $(TMTSF)_2X$ series, induced by a large magnetic field.

The experimental phase diagram of $(TMTSF)_2ClO_4$ under high field is summarized in figure 10. Recent theories based on the effect of the magnetic field on the orbital motion of carriers moving on a quasi-one-dimensional Fermi surface explain very elegantly practically all experimental features known at present. They explain in particular the transition from a quasi-one-dimensional conductor to nearly two-dimensional semimetallic phases and the quantization of the Hall resistance in the field-induced s.d.w. phases.

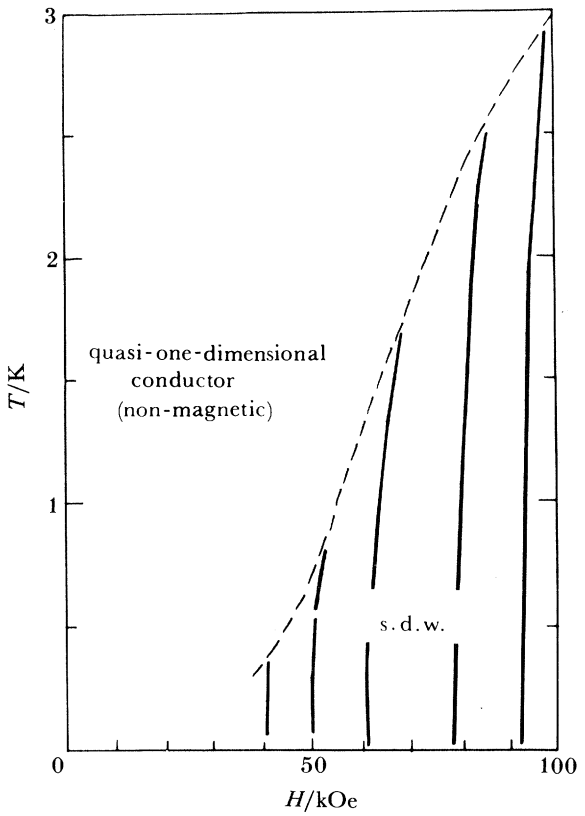


FIGURE 10. Phase diagram of $(TMTSF)_2ClO_4$, R-state with magnetic field aligned along c^*. This diagram has been obtained from Hall effect, specific heat, ^{77}Se and ^1H n.m.r. data. The broken line corresponds to the second-order transition between the quasi-one-dimensional conductor and two-dimensional magnetic states. The solid lines indicate first-order phase transitions between s.d.w. sub-phases. The superconducting state is practically invisible in this diagram since $H^*_{c_2} = 1$ kOe.

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