loosest bound electrons which largely determine the relative bond lengths, as is illustrated in simplified form in Fig. 4.

Theoretical estimates show that the lowest lying excited states involve the loosely bound electrons and are accompanied by a redistribution of bond lengths giving rise to a modification of the structure, see Fig. 4(b). In practice, the deformation is spread over several atoms but this simple picture is qualitatively correct. In any case, for such excitations to move, it is clear that there must be movement of the atoms. The mobility of the excited electron carriers is affected by the need to move massive atoms and may be limited, at high speeds, by their inability to follow the very rapid electron motions. This may be the explanation for the curious experimental results which show a high initial drift mobility for excited states but saturating at the velocity of sound.

Other Fields of Interest

Whereas research on the physics of very small electronic devices and the study of electronic properties of organic molecules are the two main programmes of the Long Range Research Laboratory of the GEC, there are two smaller programmes. One is in biotechnology where we are interested in the exact mechanisms whereby electrons taking part in biochemical reactions transfer to electrodes, and vice versa. We see an understanding of this as being crucial to any integration of biotechnology and electronics. The other is in perception where we have already advanced the theory of monocular depth perception from optical flow[3]) and are considering extending the studies to higher level visual processing.

Collaboration with other research workers within the GEC and at other research institutions, especially universities, is a particularly strong feature of our activities. Within the GEC there are many other research programmes which have a significant basic research content, but which, in most cases, have clearly identified and specific commercial objectives. There are no such specific objectives for the programmes of the Long Range Research Laboratory, but all four are are on topics where we expect scientific advances to occur over the next few years and those advances are likely to have commercial implications for the Company. By participation in the scientific research we shall be aware of those advances as soon as they occur and be ready to respond to them.

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SUPERCONDUCTIVITY IN ORGANIC SOLIDS

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Almost all the molecular conductors exhibiting superconductivity that have been found so far are derived from the molecule tetramethyltetraselenafulvalene (called TMTSF). When TMTSF, dissolved in an appropriate solvent containing a salt of a monovalent anion X, is oxidized on a platinum anode, high purity crystals of composition $TMTSF_2X$ separate directly on the electrode according to the reaction:

$$2n.\ TMTSF + n\ X^- \xrightarrow{-n.e^-} (TMTSF_2X)_n$$

In the triclinic crystal, the nearly planar TMTSF units are stacked in a zig-zag pattern along the a-axis (Fig. 1). X is typically a monovalent inorganic anion such as PF_6^-, ClO_4^- etc. and plays an essential role in the partial filling of the valence band, but otherwise does not contribute directly to electron transport. The anions do, however, in some cases affect the electronic properties of the $(TMTSF)_2X$ series via order-disorder phase transitions at low temperature. The conduction band derived from the overlapping π-type molecular orbitals is half filled rather than quarter filled as inferred from the 2:1 stoichiometry of the salt. This occurs due to the triclinicity and a slight dimerization of the TMTSF units (Fig. 1) which leads to an alternation of the band overlap integral $t_{//}$ along the a-axis.

The discovery of superconductivity in $(TMTSF)_2X$ salts is the result of an intense investigation of the electronic properties of molecular conductors which began about 10 years ago, with the preparation of the first stable highly conducting organic solids, namely those belonging to the TTF-TCNQ series. It was recognized quickly that the unusual properties of these conductors: existence of phase transitions towards non-magnetic insulating states at low temperature, and lattice precursor signs of these transitions observed at temperatures as high as about three times the actual phase transition temperature, required the use of one-dimensional (1-D) physics.

The concept of 1-D is relevant to most organic conductors as a result of the planar shape of the constituent molecules and of their particular arrangement in the crystal: namely the packing of molecules in stacks along a preferred direction. This results in a strong and weak overlap between the π-or-

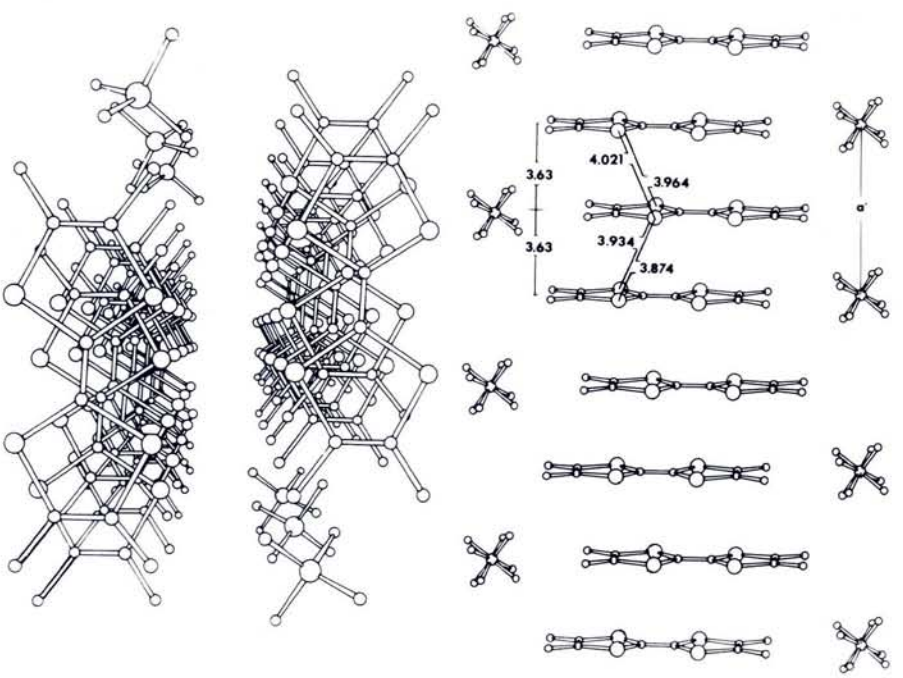


Fig. 1 — View of $(TMTSF)_2ReO_4$ along the stacking direction, a-axis (left). The ReO_4^- ions show alternative order along the a-axis ($T < 180$ K) leading to a 2a potential. Side-view of $(TMTSF)_2ClO_4$ (right). The dimerization is clearly visible in the Se-Se intermolecular contacts (after Thorup et al.).

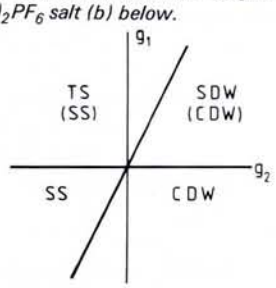
bitals of near neighbour molecules belonging to the same stacks and to adjacent stacks respectively. *The Peierls-Fröhlich nature* of the phase transition in TTF-TCNQ is just one of the particular features exhibited by a 1-D electron gas theoretically predicted to be unstable at low temperature. The nature of the instability depends on the interactions between the electrons within a given stack of molecules: direct coulombic interactions, or indirect electron-electron interactions mediated by phonons. The electric polarization of highly polarizable organic molecules may also be important. In the presence of interactions, the ground state of a 1-D electron gas is unstable against the formation of charge (or spin) density waves (CDW or SDW). This instability competes with another instability, superconductivity, which arises in the 1-D electron gas as well as in a usual 3-D gas.

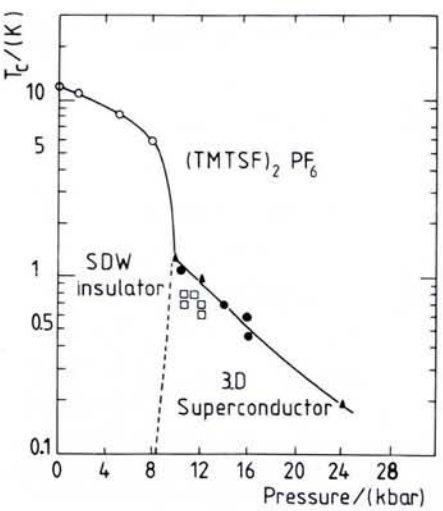
The interplay between spin (charge) density waves and superconducting instabilities of a 1-D electron gas becomes clear if the electron-hole (CDW-SDW channel) or the electron-electron (Cooper channel) response functions are calculated perturbatively. In the expansion of the superconducting response of a 1-D electron gas, divergent contributions from density fluctuations occur and *vice versa*, i.e. the two types of instability become coupled. Another problem in 1-D systems is the destruction of long-range order, i.e. the absence of phase transition, at any finite temperature by thermal fluctuations. Hence a treatment of phase transitions via a self consistent field acting on the order parameter which neglects possible deviations from its mean value (the so-called mean-field approximation) is inappropriate for a 1-D conductor. More elaborate treatments (beyond mean-field approximation) are required.

Keeping two specific features of a 1-D electron gas in mind (i) interplay between magnetism and superconductivity, (ii) possible existence of a strong fluctuation regime, we shall summarize here some of the fascinating properties of the organic superconductors.

A more thorough review of the properties of organic conductors and superconductors is given in references 1-3.

Fig. 2 — Most divergent response functions of the 1-D electron gas within the g_1/g_2 model (a) above. Experimental phase diagram of the $(TMTSF)_2PF_6$ salt (b) below.





Magnetism *Versus* Superconductivity

In the simplest theoretical treatment of the 1-D electron gas, the nature of the low temperature divergent response depends on the sign and spatial shape of the electron-electron interactions[4]). Approximating the Fourier transform of the electron-electron interaction by two constants g_1 and g_2 (related to scattering at wave vectors $q = 2k_F$ and $q = 0$ respectively) allows a derivation of a phase diagram in the g_1g_2 plane and establishing in which regions of the plane the correlation function of a given type is most strongly divergent. First order renormalization treatment gives a power law divergence of the static and uniform correlation functions ($q = \omega = 0$) and spin (charge) density waves or superconductivity at low temperature. As the inequality $g_1 < 2g_2$ is satisfied, the spin (charge) density wave divergence is predominant over the superconducting channel, whereas the opposite is predicted when $g_1 > 2g_2$. In addition, for $g_1 > 0$, triplet superconductivity (TS) and spin density wave (SDW) divergencies are logarithmically stronger than SS and CDW divergencies respectively (Fig. 2a).

In real systems, long range order is possible at low temperature because coupling between adjacent chains has to be taken into account. Using a mean-field approximation for the interchain coupling and exact results for the single chain problem, the transition temperature is given by:

$$1 - \alpha_\perp \chi_{1D}(0)\big|_{T=Tc} = 0$$

where $\chi_{1D}(q)$ is the order parameter susceptibility of a chain and $\alpha_\perp$ the transverse coupling.

Therefore the establishment of long-range order does not occur at a temperature which is of the order of the intrachain interaction $\alpha_{//}$, as for the mean-field approximation, but at a temperature which can be significantly lower, depending on the anisotropy of the interaction $\alpha_\perp/\alpha_{//}$.

For an order parameter with two components, the analogy with the ordering of a Heisenberg two-dimensional (XY) ferromagnet leads to the phase transition temperature:

$$T_c \approx (\alpha_\perp \alpha_{//})^{1/2} \qquad [1]$$

in the weak interchain coupling limit, *i.e.* $\alpha_\perp << \alpha_{//}$. Equation [1] provides two important results:

(i) the actual transition temperature of a quasi-one-dimensional (Q-1-D) conductor at T_c is lower than the transition which would be derived using a mean-field treatment of the 1-D problem in the ratio $(\alpha_\perp/\alpha_{//})^{1/2} < 1$.

(ii) the strengths of the inter and intrachain couplings have no necessary direct relation in any of the four instabilities (TS, SS, SDW, CDW) of a Q-1-D conductor.

The following may also be encountered: Consider for example two competing instabilities *A* and *B*, if

$$\alpha_{//}^A > \alpha_{//}^B \text{ and } \alpha_\perp^A < \alpha_\perp^B \qquad [2]$$

the instability *B* may appear below a 3-D ordering temperature T_c. But at temperatures well above T_c the divergence of the *A* instability will dominate.

This situation we think is relevant for $(TMTSF)_2PF_6$ at ambient pressure. The ground state is magnetic (SDW), but above T_c (12 K) we have suggested that the 1-D superconducting divergence is important.

Below we summarize some of the experimental results, which have led to this suggestion.

Pressure Dependence

Figure 2b shows the phase diagram of $(TMTSF)_2X$-like salts, when X is an anion of octahedral symmetry (PF_6, AsF_6, SbF_6, TaF_6...).

At low pressure, an itinerant antiferromagnetic ground state has been firmly established by magnetic measurements: anisotropic magnetic susceptibility, proton and selenium NMR and antiferromagnetic resonance (AFMR). The occurrence of a spin structure (SDW) is likely to double the periodicity of the electron potential along the a-direction and therefore triggers the opening of a gap at the Fermi level driven by exchange interactions. The stabilization of the SDW state below 12 K at ambient pressure is accompanied by a sharp drop of the conductivity. However, the imperfect nesting of the Q-1-D Fermi surface is probably responsible for a semi-metallic nature of the low temperature magnetic state, exhibiting a large and anisotropic magnetoresistance. Above 8 kbar or so, the ground state of $(TMTSF)_2PF_6$ and related compounds is superconducting as demonstrated by resistive and Meissner effect data. In the vicinity of 8 kbar the phase diagram is rather intricate: a re-entrance of the superconducting ground state is observed below the magnetic state, as shown by a pronounced upturn of the resistance around 4-5 K on cooling, followed by a subsequent transition towards a superconducting state around 1 K.

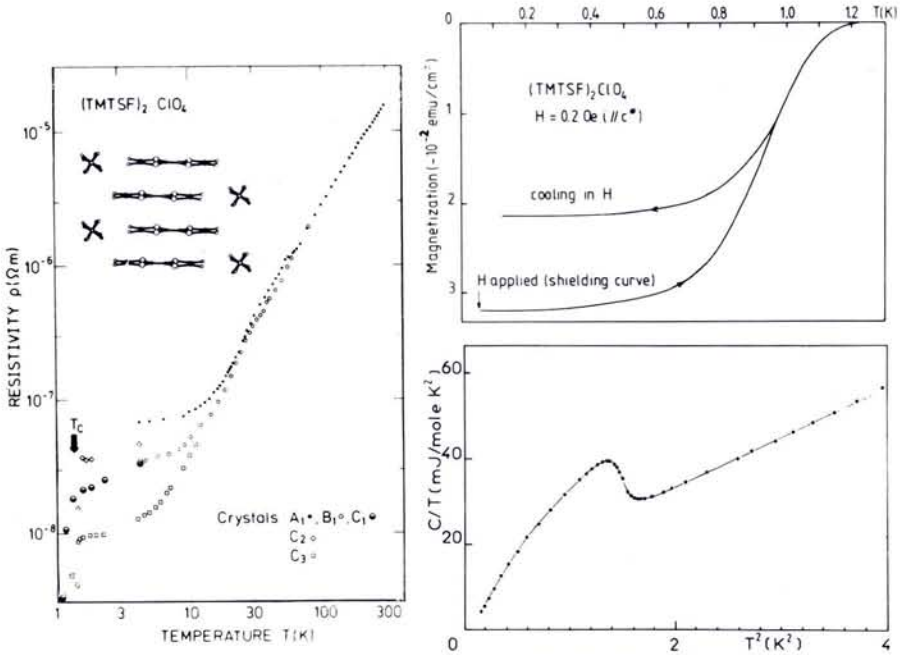


Fig. 3 — Observation of organic superconductivity in $(TMTSF)_2ClO_4$ via different techniques: resistive transition of several crystals, Meissner effect and molar specific heat for the R-state.

The compounds $(TMTSF)_2X$ in which the anions have tetrahedral symmetry (X = ReO_4, ClO_4) show similar behaviour, namely insulating or superconducting ground states depending on the applied pressure.

The stable ground state ($T_{M\text{-}I}$ = 180 K) in $(TMTSF)_2ReO_4$ is non-magnetic and insulating. X-ray investigation has clearly shown alternate ordering of anions along the a-, b- and c-directions giving rise to a gap at the Fermi level. Above about 8 kbar this ordering is suppressed, and the material becomes metallic and superconducts below T_c = 1.4 K. $(TMTSF)_2ClO_4$ is an interesting system since superconductivity can be observed without external pressure. Fig. 3 summarizes the superconducting transition of $(TMTSF)_2ClO_4$ as observed by resistive, DC magnetization and specific heat techniques. The Meissner effect shown here was measured on one single crystal cooled through the transition in a small magnetic field of 0.2 Oe aligned with the c*-axis. It was also found, by comparison with a tin reference sample, the shielding of an external vanishing field, namely $H \approx 0.01$ Oe, is complete for all three crystallographic axes, once $(TMTSF)_2ClO_4$ has been cooled to 50 mK in a "zero" applied field.

The Meissner signals, which are 80% and 55% of the shielding for the c* and b* directions respectively, in low field and at low temperature, indicate the bulk and 3-D nature of the superconducting state. However, as far as the Meissner effect along the a-direction is concerned, only 1% of the shielding signal is observed. Following the Meissner experiments one can expect qualitatively that the longitudinal overlap $t_{//}$ is larger than both transverse integrals $t_\perp^{c^*}$ and $t_\perp^{b^*}$. Although the exact ratios between the electronic coupling along the main crystallographic directions are still somewhat uncertain we believe that a fair compromise using, optical data, H_{c2} critical field anisotropy and conductivity anisotropy is given by 10:1:1/15 for the sequence t_a:t_{b^*}:t_{c^*}. Considering the above determination of the band parameters, the Fermi surface of the conducting phase of $(TMTSF)_2X$ salts is open, although some warping is expected from finite transverse overlaps. Hence, the magnetoresistance of this phase should not present any de Haas-Shubnikov oscillations. This quasi 1-D character by no means prevents the transverse electron motion from being coherent (band-like) at low temperature, with the concomitant existence of a transverse plasma edge in the optical reflectance spectrum.

Additional interesting information related to the superconducting state below 1.2 K is given by the interpretation of the specific heat anomaly. The condensation energy and the thermodynamical critical field are 2 x 10^{16} eV/mol and 44 Oe respectively. The approximate determination of the gap at the Fermi level below T_c is 2δ = 0.35 meV. Notice the ratio $2\delta/T_c$ equals approximately the BCS weak coupling value. Heat capacity measurements have also revealed a behaviour of the electronic properties at low temperature which seems up to now, specific to $(TMTSF)_2ClO_4$.

A fast-cooled crystal of $(TMTSF)_2ClO_4$ below 40 K undergoes a superconducting transition at 0.9 K instead of at 1.2 K as when the sample is cooled slowly at a rate about 0.1 K/minute. This varying behaviour is due to a phase transition (at 24 K) as shown by resistive, EPR and NMR measurements. Furthermore, X-ray investigations have shown that below 24 K a 3-D superlattice structure is observed with no change of the periodicity along a and c, but a doubling along b. A careful study of the dynamics of this structural transition shows that it probably corresponds to the ClO_4 ions ordering ferroelectrically along the a-axis below 24 K. While slow cooling results in quasi perfect ordering at low temperature (called the relaxed R-state), rapid cooling below 30 K (≥ 10 K/minute) leads to a partially ordered (quenched-Q state) exhibiting excess entropy in the superconducting state in comparison with the R-state. This excess entropy has been attributed to frozen-in lattice (ClO_4 ions) disorder. It is remarkable, however, that in spite of a lowering of T_c in the Q-state, no marked change of $N(E_F)$ in the temperature domain 1.2 - 2 K can be detected via c_v data. Therefore, unless an important reorganization of the phonon spectrum is associated with the 24 K structural transi-

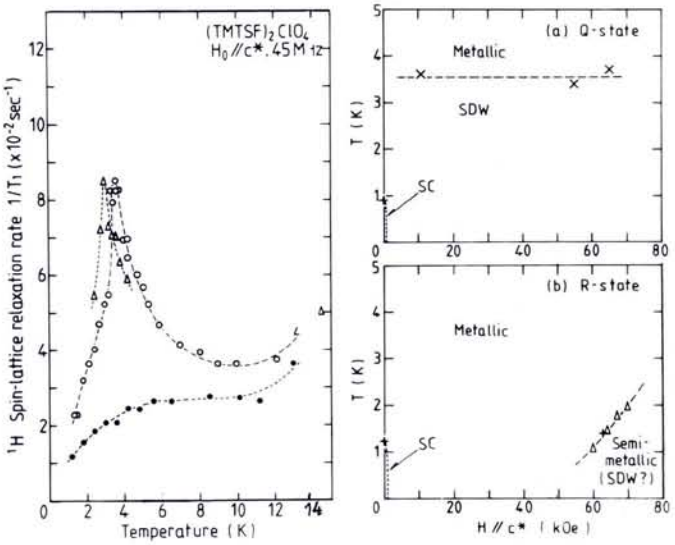


Fig. 4 — Proton spin-lattice relaxation rate of $(TMTSF)_2ClO_4$ versus temperature in the Q-state (O), partially annealed (Δ) and R-state (●) (left). Proposed phase diagram of $(TMTSF)_2ClO_4$: Q-state (a) and R-state (b). The data of specific heat under high field (+) and threshold of de Haas-Shubnikov oscillations, Δ, (after Azevedo et al.) are also included.

tion, the lowering of T_c can be attributed to the residual (non-magnetic) disorder of the Q-state.

Effects of High Magnetic Field

Proton and selenium NMR and high field c_ν data performed on the R-state of $(TMTSF)_2ClO_4$ enable us to map the *T-H* phase diagram (Fig. 4). As far as the R-state is concerned, superconductivity is observed below 1.2 K in zero field and up to a critical field $H_{c2}\perp \approx 1$ kOe at $T = 0$ K for H // c*. Experiments on c_ν under higher field have revealed the existence of a transition at $T_c \cong 1.4$ K ($H = 63$ kOe) between a high $N(E_F)$ state at $T > 1.4$ K and a small $N(E_F)$ state at lower temperatures (possibly a semi-metallic state). Furthermore, ^{77}Se NMR data strongly support the occurrence of SDW's in the high field induced semi-metallic state of $(TMTSF)_2ClO_4$.

The phase line between the metallic and the high-field induced semi-metallic state of $(TMTSF)_2ClO_4$ is in remarkable agreement with the threshold field necessary for the observation of de Haas-Shubnikov oscillations, a fact which is proof of the two-dimensional nature of the Fermi surface (closed orbits) at fields larger than the threshold field.

Recent de Haas-Shubnikov data obtained at Tokyo University give a threshold field of 50 kOe at 0.5 K and at the Electrotechnical Laboratory in Tsukuba, a field of 43 kOe was observed at 25 mK. We may emphasize that a similar high field restoration of a semi-metallic (magnetic) state is also observed in $(TMTSF)_2PF_6$ under pressure.

Effects of Lattice Disorder in the Q-state of $(TMTSF)_2ClO_4$

The onset of a phase transition around 3.5 K in the Q-state of $(TMTSF)_2ClO_4$ is best demonstrated by a sharp peaking of the spin lattice (^1H and ^{77}Se) relaxation rates at that temperature. Below 3.5 K an increase of the NMR linewidth is also observed. Consequently, a state showing SDW characteristics is stabilized below 3.5 K in agreement with the observation of an AFMR signal at the helium temperature.

In the same temperature domain, a significant drop of the conductivity is observed at low temperature, whereas $N(E_F)$ measured by specific heat does not seem to be strongly affected by the onset of magnetism. Superconductivity arises at a temperature lower than in the R-state, namely $T_c < 0.9$ K. Annealing the Q-state at a temperature $T > 30$ K, followed by a slow cooling allows the restoration of the R-state which is not showing any onset of magnetism prior to the superconducting transition at 1.2 K.

Tentatively the behaviour of the Q-state can be rationalised following the theory of Larkin and Melnikov on the effect of disorder on phase transitions in Q-1-D conductors. In the framework of this theory, weak impurity potentials may induce independent (and non-coherent) phase shifts of the electron wavefunction on each filament, resulting in a decrease of the amplitude for hopping of a Cooper pair from chain to chain. It therefore follows that with an increase of the concentration of impurity scattering potentials, T_c decreases, but the 1-D divergence of the superconducting response function is more weakly affected.

As far as $(TMTSF)_2ClO_4$ is concerned, the smearing of the 1-D SC divergent channel in the Q-state may be large enough to allow the establishment of a SDW on the nested portions of the Fermi surfaces below 3.5 K or so. We notice that intermediate situations between Figs. 4a and b can be achieved varying the annealing time or (and) the cooling rate below 30 K. However, we believe that figure 4b represents the behaviour of an R-state in which the only external parameter governing the balance between the 1-D divergences is the magnetic field.

Since band parameters are obviously unchanged by the magnetic field, the competition between superconductivity and magnetism at low temperature in $(TMTSF)_2ClO_4$ (and in $(TMTSF)_2PF_6$ under pressure) cannot be attributed to a variation of the interchain tunnelling coupling, as it could be inferred from the pressure dependent phase diagram of $(TMTSF)_2PF_6$ in zero field. We suggest instead an interpretation relying on the 1-D character of the electronic properties: after an easy removal of the 3-D ordered superconducting state by a small magnetic field ($H_{c2}^{c^*} \approx$ 1 kOe at $T = 0$), the 1-D superconducting divergence is weakened by larger fields and finally, when the field reaches the threshold value (H // c* $\approx$ 63 kOe at 1.4 K) the balance between 1-D superconducting divergence and 3-D SDW instability turns in favour of the second which condenses

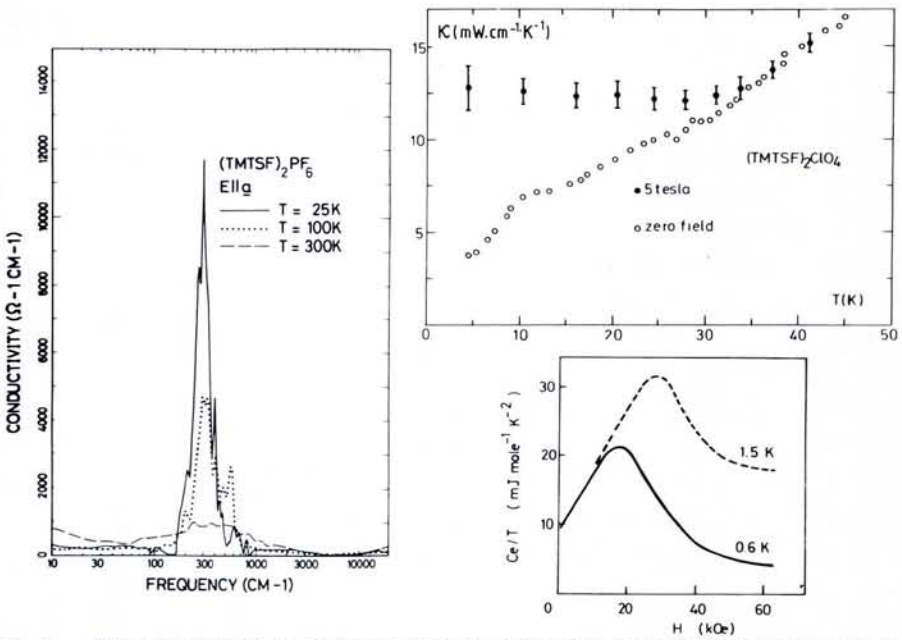


Fig. 5 — Frequency dependence of the conductivity of $(TMTSF)_2PF_6$ at 25 K under atmospheric pressure (left) (after C.S. Jacobsen et al). Temperature dependence of the thermal conductivity of $(TMTSF)_2ClO_4$ and influence of a magnetic field (top right). Field dependence of the electronic specific heat of $(TMTSF)_2ClO_4$ at 0.6 and 1.5 K (H // c) (bottom right).*

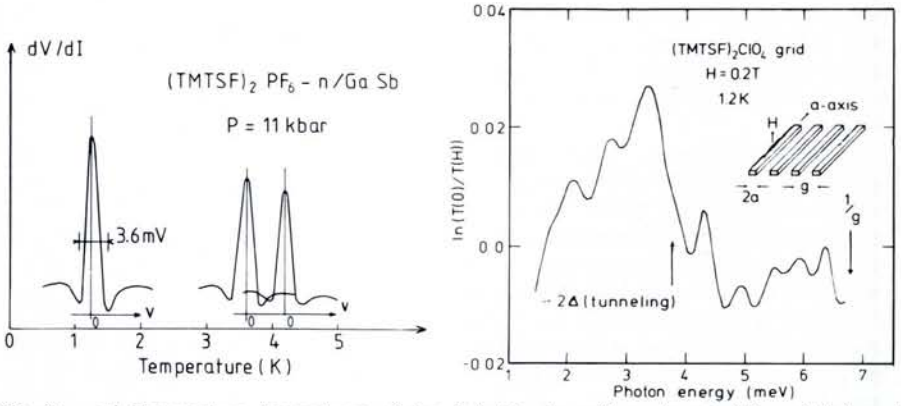


Fig. 6 — a) Temperature dependence of the Schottky tunnelling characteristics of N-doped GaSb/$(TMTSF)_2PF_6$ junctions under 11 kbar. — b) Magnetoabsorption of a $(TMTSF)_2ClO_4$ grid. There is a pronounced onset of magnetoabsorption below $\approx$ 3.6 meV. The electromagnetic radiation is polarized along the a-axis and the magnetic field is normal to this axis.

and gives rise to a semi-metallic state accompanied by quantum oscillations of the magnetoresistance.

Fluctuating Regime

This section gives a brief survey of experimental results suggesting that the superconducting channel is the dominating divergence in the 1-D regime (transverse coherence length < interchain distance) up to high temperature, 30 K or so, for the $(TMTSF)_2X$ series. All the results of this section refer to the low temperature behaviour of either $(TMTSF)_2ClO_4$ (R-state) under ambient pressure or $(TMTSF)_2PF_6$ -AsF_6 at $P > P_c$ when the T domain lower than 25 K is considered.

Electrical Conductivity

The longitudinal DC conductivity becomes larger than 10^4 $(\Omega cm)^{-1}$ at low temperature reaching 10^5 - 10^6 $(\Omega cm)^{-1}$ at helium temperatures (Fig. 3), a value which in terms of a single-particle interpretation suggests an electron mean free path of 1000 Å or more. σ_{DC} is also greatly diminished by the application of a magnetic field (the magnetoresistance is strongest when the field is aligned with the c* direction). However, optical reflectance data point towards a drastic frequency dependence of the conductivity in the very far infrared domain. In both $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ at ambient pressure, the optical electron life-time increases by a factor 3 at most between 300 K and low temperature ($T \approx 25$ K) (Fig. 5), whereas the corresponding increase of the DC conductivity exceeds a factor 50. Furthermore, the FIR conductivity of $(TMTSF)_2PF_6$ is about 400 $(\Omega cm)^{-1}$ at $T = 25$ K, $\omega = 10$ cm^{-1} i.e. $\approx$ 100 times smaller than DC or microwave conductivites. Therefore, FIR conductivity data imply the existence of a long life time collective mode at 25 K (10^{-12} s $< \tau_c < 2 \times 10^{-11}$ s).

Thermal Conductivity of $(TMTSF)_2ClO_4$

The study of the thermal conductivity of $(TMTSF)_2ClO_4$ and $(TMTSF)_2PF_6$ ($P = 12$ kbar) shows a significant drop below 50 K (Fig. 5). Such behaviour is very striking for two reasons:

i) In the same T-domain σ_{DC} is strongly T-dependent and therefore one could expect heat to be carried by the electrons when σ_{DC} reaches 10^5 $(\Omega cm)^{-1}$, following the Wiedemann-Franz proportionality relation between κ_e and σ.

ii) The drop of κ is greatly suppressed, especially below 25 K, by the application of a magnetic field. This latter behaviour is again in contradiction with the Wiedemann-Franz law, which would predict a decrease of κ (and not an increase) under magnetic field, according to the large positive magnetoresistance observed at low temperature. The drop of κ at low temperature must be attributed to a change in the electronic structure (typically a decrease of $N(E_F)$ at low temperature) which is sensitive to magnetic field.

Field Dependence of the Specific Heat

At low temperature ($T < 3$ K), the specific heat of $(TMTSF)_2ClO_4$ is well described by the typical law $c_v = \gamma T + \beta T^3$ where γ and β are related to $N(E_F)$ and the phonon spectrum respectively. However a striking field dependence of $N(E_F)$ is observed at low temperature (Fig. 5) up to 20 kOe or so after the suppression of the superconducting state above $H_{c2}^{c^*} \leq 1$ kOe. The 70% increase of $N(E_F)$ in a field of 20 kOe at helium temperature is a remarkable effect which agrees qualitatively with the field of the thermal conductivity and which suggests a field-induced restoration of $N(E_F)$. The study of the field dependence of $N(E_F)$ has not yet been performed above 3 K since at higher temperatures the electronic contribution becomes very much smaller than the lattice contribution.

Summarizing: (i) the density of states at the Fermi level is depressed at low temperature below its value at high temperature ($T \geq 40$ K) and (ii) the depression is partly suppressed by the application of a large magnetic field.

Energy Width of the Pseudo-Gap

Two different techniques, electron quantum tunnelling and FIR absorption experiments performed on $(TMTSF)_2ClO_4$ and in $(TMTSF)_2PF_6$ under pressure allow a determination of the energy width at the vicinity of the Fermi energy over which the density of states is depressed at low temperature. The energy dependence of the transition probability of electrons which obey Fermi statistics to tunnel between two metallic

electrodes separated by a thin insulating barrier can reproduce to some extent the energy dependence of the density of states in the vicinity of the Fermi level of the electrodes. This technique is largely used to derive quantities such as energy gaps in the quasi-particle density of states if one or both electrodes are superconductors. Schottky-type electron tunnelling using N-doped evaporated GaSb on $(TMTSF)_2PF_6$ or $(TMTSF)_2ClO_4$ performed under 11 kbar and ambient pressure for the two organic compounds respectively, supports the existence of a depression of $N(E_F)$ in the organic superconductor over an energy width $2\Delta \approx 3.6$ meV centred at the Fermi energy (Fig. 6a). The FIR reflectance of $(TMTSF)_2ClO_4$ studied at helium temperature reveals a drop of 5% around 3.8 meV. As shown by magneto-absorption experiments (Fig. 6b), this optical absorption threshold can be observed without significant shift of its energy up to 15 K or so. The vanishing of the absorption threshold occurs between 20 and 50 K [5]).

The experimental results presented in this section suggest the existence of a pseudo-gap of width 3.6 - 3.8 meV at the Fermi level. This pseudo-gap is suppressed by a large magnetic field and remains visible up to temperatures which are about ten times the temperature for the onset of long range superconducting order. Since organic conductors are Q-1-D conductors, precursor signs of the low temperature instabilities are expected to occur at temperatures larger than the 3-D ordering temperature. Thus, we must consider precursor effects of two different kinds: SDW or superconductivity.

We may rule out the SDW origin of the pseudo-gap for several reasons (i) no sign of magnetism has been detected (via NMR experiments) up to the temperature domain in which the pseudo-gap is observed; (ii) whenever a SDW gap is observed, it is stabilized and not suppressed by a magnetic field; (iii) there is no SDW state stable at low temperature in $(TMTSF)_2PF_6$ under pressure; (iv) electron tunnelling characteristics related to an SDW gap which have been observed in $(TMTSF)_2PF_6$ below 12 K at ambient pressure do not show the typical resistance minima on both sides of the zero bias; (v) commensurability would prevent the fluctuating SDW from contributing to the DC conduction.

Superconducting Fluctuations and Conclusion

The discussion in the previous section shows that superconductivity probably originates from the strongly developed precursor regime. However, how can one reconcile a precursor domain extending about 30 K, with a superconducting transition which behaves very much like phase transition within the mean-field theory (Fig. 3). The small critical width of the superconducting transition seen by specific heat ($\Delta T/T_c \leq 10\%$) does not support the existence of fluctuations up to $T \approx 10\ T_c$ unless the point of view of phase transitions in Q-1-D conductors is taken. In this case for a two degrees of freedom order parameter (amplitude and phase) some decoupling of the two components occurs at $T >> T_c$. The spatial correlation function of the order parameter is given by:

$$< \Delta(x)\, \Delta(0) = |\Delta|^2 \exp(-x / \xi(T))$$

where $\xi(T) \approx \alpha_{//}/kT$. Consequently, at $T > 0$, the short range order which arises with a coherence length $\xi(T)$, digs a pseudo-gap of width $2\Delta \approx \alpha_{//}$ at the Fermi level. The amplitude of the order parameter reaches a significant value ($\approx \alpha_{//}$) already below the 1-D mean-field temperature, $T_1 \approx \alpha_{//}$, whereas the phase is still free to take any value until T_c is reached. At T_c inter-chain locking of the phases occurs. If the zero point motion of the phase (quantum fluctuations) is taken into account a true gap develops below T_c. Its value at $T = 0$ amounts to a real gap $2\Delta(T=0) = 3.5\ T_c$, a value much smaller than the amplitude of the pseudo-gap. For strong quantum fluctuations Schulz and Bourbonnais [6]) have derived $2\Delta(T=0) = 3.5\ T_c$; i.e. the mean-field behaviour is recovered for the phase locking transition (onset of 3-D order). Furthermore with reasonable values of the intrachain coupling ($g_1 - 2g_2 \approx 0.6$) and of the band structure anisotropy ($t_{//}/t_{\perp} = 10$), the same authors have calculated, using $T_c = 1.2$ K, that the superconducting precursor region will extend up to about 30 K.

In conclusion, organic superconductors of the $(TMTSF)_2X$ series exhibit several characteristic features of quasi-1-D electron gas and, in addition, a narrow 3-D ordering transition satisfying approximately mean-field rules is observed. Superconductivity of organic conductors is, very likely, not at its optimum in the $(TMTSF)_2X$ series. It may be possible to take advantage of the strong 1-D divergence at higher temperature and an increase of the inter-chain coupling could therefore allow a substantial increase of the critical temperature.

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