



**HAL**  
open science

## The physics of organic superconductors

Denis Jérôme

► **To cite this version:**

Denis Jérôme. The physics of organic superconductors. *Science*, 1991, 252 (5012), pp.1509-1514.  
10.1126/science.252.5012.1509 . hal-04899301

**HAL Id: hal-04899301**

**<https://hal.science/hal-04899301v1>**

Submitted on 5 Feb 2025

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# The Physics of Organic Superconductors

D. JÉROME

The upper temperature for superconductivity in organic conductors has increased from 1 kelvin in 1980, when the phenomenon was discovered in the quasi-one-dimensional cation radical salt tetramethyltetraselenafulvalene phosphorus heptafluoride to 12 kelvin in a new series of organic salts that show nearly two-dimensional electronic properties. These superconductors are attracting interest because of the wide range of new phenomena that they exhibit, including the competition between various ground states, the influence of a magnetic field on a quasi-one-dimensional conductor, the quantization of the Hall effect in a three-dimensional material, the giant magnetoresistance effects related to the two-dimensional nature of the Fermi surface of some materials, and the coherent voltage oscillation of a spin-modulated ground state. Furthermore, there is reason to believe that organic conductors with high superconducting transition temperatures could be produced in the near future. The recent finding of superconductivity in "fullerene" doped with alkali metals supports this optimism.

IN A SEARCH FOR HIGH-TEMPERATURE SUPERCONDUCTIVITY, Little proposed an arrangement of chain conductors in a polarizable medium (1). The general idea was that a large polarization could induce over a wide frequency spectrum a large effective attraction between electrons on the chains, which could lead to superconductivity at temperatures much higher than those that had been reached in 1964. Little proposed that polarization could be attained by attaching lateral organic radicals that were polarizable and conjugated to the skeleton. He proposed that the chain could be organic, very much like polyacetylene. In view of Little's work, then, one can think of an organic conductivity (along the organic chain) together with a superconductivity not mediated by phonons (that is, polarization-mediated).

Although Little in 1964 had underestimated the impact of the Peierls prediction on actual chainlike conductors [that a one-dimensional (1-D) metal cannot exist at zero temperature], his proposal has boosted the search for organic conductors and superconductors (2) and has raised questions about a number of related problems, such as the role of fluctuations in low-dimensional conductors, the competition between electron-electron and electron-hole pairing in the 1-D regime, and the nature of the attractive interaction in organic superconductivity (3).

Twenty-five years after Little's initial proposal, organic materials

exist in which superconductivity can be stabilized at 12 K (Fig. 1). The nature of the electron-pairing mechanism is still not understood, but these new materials have contributed to the discovery of basic phenomena that is discussed in this article.

## Conduction in Molecular Solids

To create a conducting molecular solid, one must proceed along a long path with many pitfalls. First, a solid must exist in which the building blocks are charged, and secondly, these charges should be delocalized throughout the crystal. The first requirement can be fulfilled by taking a molecule that can be easily oxidized (or reduced) to form a stable cation (or anion) radical. Tetrathiafulvalene (TTF) is the prototype molecule that gives rise to a cation radical, whereas the counterpart for the formation of an anion radical is tetracyanoquinodimethane (TCNQ). Two kinds of potentially conducting molecular solids exist so far: (i) charge transfer compounds that contain both anion and cation radicals in the ratio 1:1 (such as TTF-TCNQ) and (ii) organic salts of an organic radical (cation or anion) with an appropriate closed-shell counterion, which can be a complex inorganic ion, such as  $\text{PF}_6^-$ ,  $\text{FSO}_3^-$ , and the like, or even an organic ion, such as quinolinium<sup>+</sup> or *n*-methylphenazinium (NMP<sup>+</sup>).

In order for the second requirement (charge delocalization) to be fulfilled, the Coulomb repulsion must not overcome the energy that is gained by the formation of energy bands in the solid. The Coulomb repulsion can be minimized by using large molecules, and the intermolecular overlap between molecular orbitals can be optimized by stacking planar molecules on top of each other like pancakes or by packing similar molecules in two-dimensional (2-D) conducting sheets (Fig. 2). Stacking planar molecules gives rise to a structure that is very likely to exhibit an overlap of the molecular orbitals that is greatest along the stacks of molecules and much

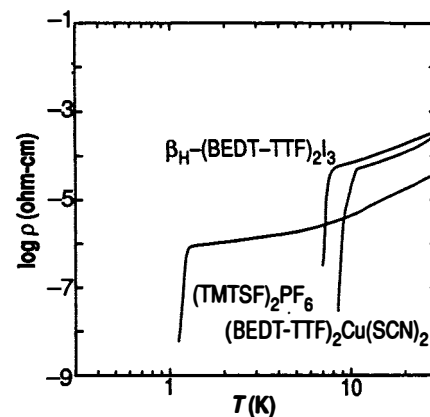


Fig. 1. The superconducting transition in various organic conductors.  $(\text{TMTSF})_2\text{PF}_6$  is under 8 kbar; both ET salts are at atmospheric pressure.

The author is in the Laboratoire de Physique des Solides, Université Paris-Sud, 91405, Orsay, France.

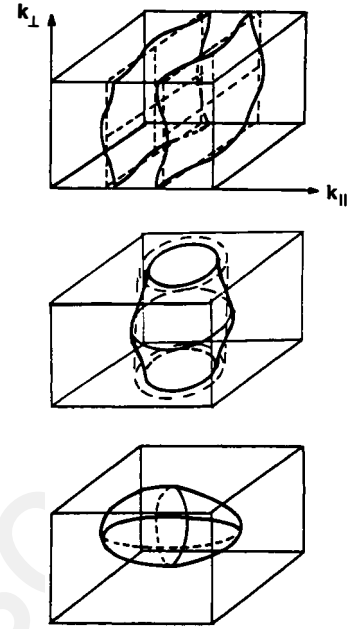
weaker between them. This overlap makes the conductivity greater along the stacking axis than in any other direction. Conductors in this family are thus quasi-one-dimensional (q-1-D) conductors.

Prototypes of q-1-D organic superconductors are given by a salt of tetramethyltetraselenafulvalene:  $(\text{TMTSF})_2\text{PF}_6$  was the first case (4). However, the molecule with S atoms substituted for Se,  $(\text{TMTTF})_2\text{X}$  (5), provides materials with a similar 1-D structure and nonsuperconducting properties whose study is important for a complete understanding of the Se series (also called Bechgaard salts), in which superconductivity has been found. These conducting salts are known collectively as the  $\text{TM}_2\text{X}$  salts. In this series of organic conductors, the highest superconducting transition temperatures ( $T_c$ ) are around 2 K.

Noticeable improvements in  $T_c$  have been obtained over the last 5 years with a series of compounds in which the organic building block bis(ethylenedithio)-TTF (abbreviated ET) forms conducting sheets (instead of chains), such as in  $\beta\text{-(ET)}_2\text{I}_3$  (6) or the  $\kappa$ -phase  $\kappa\text{-(ET)}_2\text{X}$ , with complex anions  $\text{X}^- = \text{Cu}(\text{SCN})_2^-$  (7),  $\text{Cu}[\text{N}(\text{CN})_2]\text{Br}^-$  (8), or  $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}^-$  (9). The discovery of superconductivity in organic molecules containing S was achieved in the compound  $(\text{ET})_4(\text{ReO}_4)_2$  (10). However,  $T_c$  is less than 2 K in this material, probably because of its pronounced 1-D character.

In the  $\text{TM}_2\text{X}$  family the overlap ( $t$ ) between organic chains along the transverse  $b$ -direction amounts to  $t_\perp \approx 20$  to 30 meV, which is nearly one-tenth the intrastack overlap,  $t_\parallel \approx 150$  to 200 meV (the coupling along the  $c$ -direction is smaller than one-tenth of  $t_\perp$  and can be neglected in a first approximation). The pronounced anisotropy of the kinetic coupling causes the Fermi surface (FS) of  $\text{TM}_2\text{X}$  conductors to take a very particular shape (Fig. 3). The surface is characterized by a pair of quasi-planar sheets intersecting the  $k_\perp$ -axis at the wave vectors  $\pm k_F$ , where  $k_F$  for a 1-D conductor is related to the density of carriers ( $\rho$ ) per unit cell by the equation  $2k_F = \rho\pi/a$  ( $a$  is the unit cell length).

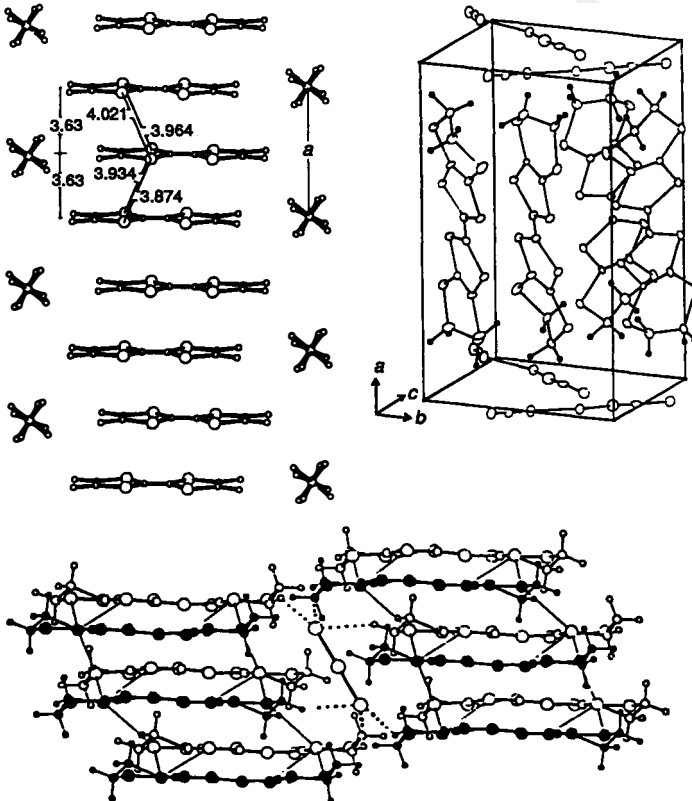
**Fig. 3.** Different shapes of Fermi surfaces: q-1-D (top), q-2-D (middle), and anisotropic 3-D (bottom).



## Instabilities in the 1-D Electron Gas

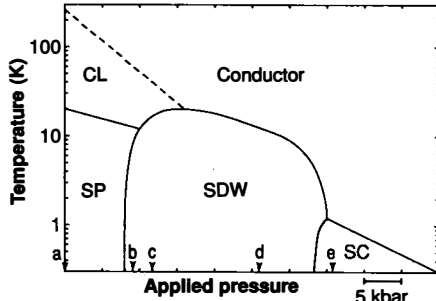
To create a superconducting phase that is stable below a certain  $T_c$ , one must overcome the strong tendency shown by low-dimensional electron gases (in particular, those with a pronounced 1-D character) to undergo a transition toward an insulating ground state exhibiting an additional periodic potential with wave vector  $\mathbf{Q}$ . The perturbing potential that is responsible for the insulating ground state can be either a mixed periodic lattice and charge modulation or a modulation of only the electron spin polarization, as predicted for 1-D conductors by Peierls (11) and Overhauser (12), respectively. The relative stability of these two modulated states depends on the energy balance between the interaction of electrons with the lattice and the Coulomb interaction.

Because the FS of  $\text{TM}_2\text{X}$  compounds is open, the major concepts of 1-D physics should apply to these materials, namely (i) the absence (or at least the severe suppression) of long-range order at finite temperature (13), (ii) the existence of equally divergent electron-electron correlations leading to superconducting pairing, and (iii) electron-hole correlations leading to density wave pairing [either spin density waves (SDWs) or charge density waves (CDWs)] (14). The mixture of these diverging pairing channels is, however, limited at low temperature by the existence of the finite coupling  $t_\perp$ , which gives rise to a crossover temperature  $T_{x1}$ , below which 1-D physics no longer applies (15). The experimental data and the theory suggest that  $T_{x1}$  is indeed smaller than the value  $t_\perp/\pi$ , which is expected for a q-1-D noninteracting electron gas. Furthermore, it has been argued that the crossover can be renormalized by the Coulombic interactions in the 1-D electron gas (16). In the  $(\text{TMTSF})_2\text{X}$  series,  $T_{x1}$ , as derived from the interpretation of nuclear magnetic resonance (NMR) data, is about 10 K. This is one-tenth the bare value, which can be inferred from the coupling  $t_\perp$  in band structure calculations. This low value for  $T_{x1}$  is a sign of the strongly developed 1-D character of the electron gas; for example, phase transitions accompanied by the establishment of 3-D ordering are suppressed to the low-temperature region. Above 50 K or so, 1-D theory should be a good starting point for understanding the temperature dependencies of physical properties, such as optics, magnetism, and transport.



**Fig. 2.** Crystal structure of  $(\text{TMTSF})_2\text{ClO}_4$  (upper left),  $\kappa\text{-(ET)}_2\text{Cu}(\text{SCN})_2$  (upper right), and  $\beta\text{-(ET)}_2\text{I}_3$  (bottom).

**Fig. 4.** Generalized phase diagram for the  $\text{TM}_2\text{X}$  series. The notations SP, SDW, and SC refer to spin-Peierls, spin density wave, and superconducting ground states, respectively. The dotted line marks the limit between conducting and charge-localized (CL) behavior. The lowercase letters designate compounds and indicate their location at atmospheric pressure in the generalized diagram: a,  $(\text{TMTTF})_2\text{PF}_6$ ; b,  $(\text{TMDTDSF})_2\text{PF}_6$ ; c,  $(\text{TMTTF})_2\text{Br}$ ; d,  $(\text{TMTSF})_2\text{PF}_6$ ; and e,  $(\text{TMTSF})_2\text{ClO}_4$ .



## Phase Diagram

A direct consequence of the pronounced 1-D character of the  $\text{TM}_2\text{X}$  series is the existence of a wide variety of ground states that can be observed, depending on parameters such as the chemical composition of the organic molecule or the inorganic anion and the hydrostatic pressure, in various members of the family. The long-range order that is stabilized at low temperature depends on the nature of the incipient instabilities that develop at high temperature on a short-range scale along each stack without any transverse correlation.

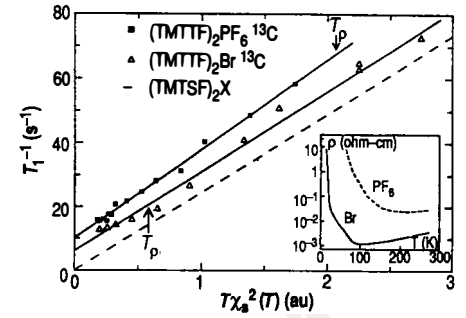
The generic diagram in Fig. 4 displays the variety of ground states that can be observed in the  $\text{TM}_2\text{X}$  series. At the left side of the diagram,  $\text{TM}_2\text{X}$  compounds exhibit metal-like properties at high temperature, but below the temperature  $T_\rho$ , where the resistivity exhibits a minimum, a loss of the charge degrees of freedom is observed, although the spin susceptibility is unaffected (1-D quantum antiferromagnet). Coulomb correlations are believed to be responsible for this localization (Wigner-like localization)(17). In the same temperature range the electron-phonon interaction gives rise to a 1-D lattice modulation at the wave vector  $2\mathbf{k}_F$  (that is, periodicity  $2a$ ). Below about 20 K these 1-D lattice fluctuations order in three dimensions and the system undergoes a phase transition with the loss of the spin degrees of freedom. The ground state is a spin-Peierls (SP) phase in which the lattice is tetramerized and the localized spins are coupled in a spin singlet state (18). Toward the right side of the diagram the role of the electron-phonon interaction becomes less dominant, but electron-electron interactions remain important, as shown by the temperature dependence of the spin susceptibility, which is similar to that of the 1-D antiferromagnet. In this region of the phase diagram, the new order established below 12 to 19 K is characterized by a modulation of the spin density with a characteristic wave vector  $2\mathbf{k}_F$  (19). This additional periodicity in the exchange potential is responsible for the opening of a gap at the Fermi level accompanied by a metal-insulator transition. At the far right of the diagram the SDW ground state itself is suppressed by an enhanced transverse coupling, and superconductivity becomes stable.

Superconductivity has also been discovered in a family of charge-transfer compounds based on the transition metal compound 1,3-dithia-2-thione-4,5-dithiolato  $[\text{M}(\text{dmit})_2]$ , where  $\text{M} = \text{Ni}$  or  $\text{Pd}$  with  $T_c = 1.6$  K under 7 kbar (20). In this series, structural and NMR studies support the picture of a 1-D FS and show that the ground state competing with superconductivity is a CDW modulation driven by the  $\text{Ni}(\text{dmit})_2$  stacks.

## Coulombic Interactions

Direct evidence for the role of electron-electron interactions in this low-dimensional conducting electron gas is given by the interpretation of the nuclear spin-lattice relaxation rate  $T_1^{-1}$  in-

**Fig. 5.** Plot of the  $^{13}\text{C}$  spin-lattice relaxation rate (inverse relaxation time  $T_1^{-1}$ ) versus  $T\chi_S^2(T)$  for three compounds in the  $\text{TM}_2\text{X}$  series. The temperature at which the charges become localized (see inset) is indicated by  $T_\rho$ . No localization is observed for Se compounds.



duced by the modulation of the hyperfine fields (which does not follow the behavior expected for noninteracting 1-D particles) in terms of the temperature dependence of the susceptibility,  $\chi_S(T)$ . For all members of the  $\text{TM}_2\text{X}$  series,  $T_1^{-1}$  follows the experimental temperature dependence:

$$[T_1(T)]^{-1} = C_0\chi_S^2(T) + C_1 \quad (1)$$

(where  $C_0$  and  $C_1$  are constants) which can be fairly well understood within the 1-D theory (16). The first term in Eq. 1 is related to the uniform ( $q = 0$ ) spin correlations of the 1-D electron gas, whereas the second term probes the  $q = 2\mathbf{k}_F$  contribution. Figure 5 shows that for those compounds exhibiting a Coulomb-assisted localization,  $(\text{TMTTF})_2\text{PF}_6$  or  $(\text{TMTTF})_2\text{Br}$ , and behaving like a 1-D quantum antiferromagnet, the weight of  $2\mathbf{k}_F$  spin correlations is very important even up to room temperature. The  $2\mathbf{k}_F$  contribution is not visible for Se salts (Fig. 5). However, another presentation of the data, namely  $T_1^{-1}$  versus  $T$ , reveals the existence of active 1-D antiferromagnetic correlations in  $(\text{TMTSF})_2\text{PF}_6$  up to  $\sim 100$  K and in  $(\text{TMTSF})_2\text{ClO}_4$  up to  $\sim 30$  K, despite the presence in this latter compound of a superconducting ground state. The analysis of the temperature dependence of  $T_1^{-1}$  below 30 K has given quantitative information about the divergence of the  $2\mathbf{k}_F$  antiferromagnetic response, which is expected to be governed by a power law in one dimension, namely  $\chi \approx (T/E_F)^{-\gamma_{1D}}$ . The interpretation of the NMR data leads to  $\gamma_{1D} \approx 0.6$  for  $(\text{TMTSF})_2\text{PF}_6$  and  $(\text{TMTSF})\text{-ClO}_4$ , and  $\gamma_{1D} = 1$  for  $(\text{TMTTF})_2\text{PF}_6$ , which agrees with the case of a 1-D quantum antiferromagnet (21). The analysis of the NMR data leads to the intermediate coupling regime for  $\text{TM}_2\text{X}$  salts, that is, on-site Coulomb repulsion over bandwidth ratio  $g_1/2\pi\nu_F \approx 0.6$  and 0.5 for Se and S compounds, respectively, where  $g_1$  is the gyromagnetic ratio factor and  $\nu_F$  is the electron velocity at the Fermi level (22).

## High-Field Properties

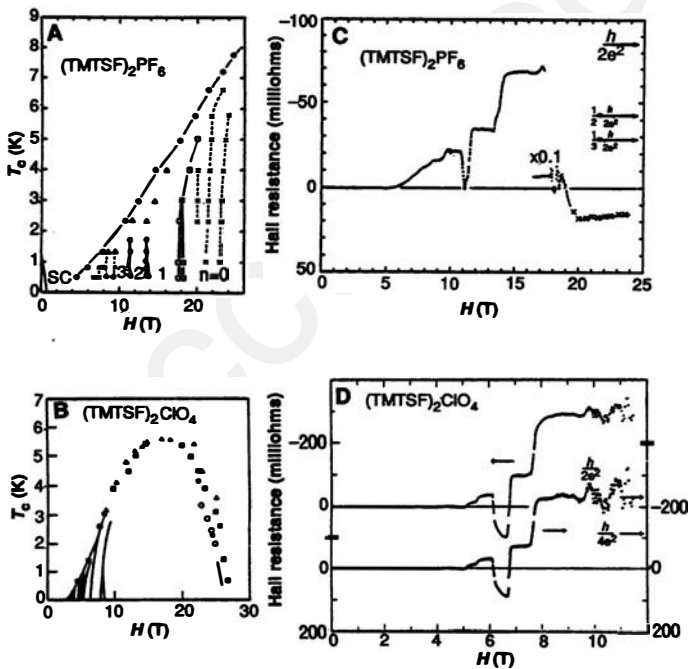
Organic superconductors have had a strong impact on physics in a context that is linked to the remarkable shape of their Fermi surface (Fig. 3). In a q-1-D situation (such as the  $\text{TM}_2\text{X}$  series), the electron dispersion  $E(\mathbf{k})$ , where  $\mathbf{k}$  is the wave vector, can be described in a simple model by the equation:

$$E(\mathbf{k}) = E_0 + \nu_F(|\mathbf{k}_x| - k_F) + 2t_\perp \cos(\mathbf{k}_y b) + 2t'_\perp \cos(2\mathbf{k}_y b) \quad (2)$$

where the dispersion around the Fermi level is linearized along the chain direction with a repeat distance  $b$  and  $t'_\perp \approx t_\perp^2/t_\parallel$  (23). As long as the transverse coupling remains small ( $t'_\perp$  typically smaller than the mean field temperature  $T_0$  for the onset of a SDW state), nesting of the Fermi surface occurs over a large fraction of its area. The spin susceptibility  $\chi(\mathbf{q})$  becomes large near  $\mathbf{Q} = (2k_F, \pi/b)$  as  $T$  approaches zero, although it is not strictly divergent and an SDW order is established below  $T_N$ . As  $t'_\perp$  is increased (by applying

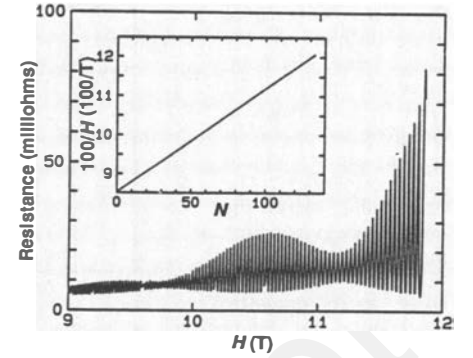
pressure or changing the anion chemically), the low-temperature increase of  $\chi(\mathbf{q})$  is smeared out, and a situation may be reached in which it is no longer possible for the SDW ordering to be stable at any finite temperature (when  $t_{\perp} \approx T_c$ ). This scenario would explain the suppression of  $T_N$  close to the border with superconductivity in Fig. 4. The divergence of  $\chi(\mathbf{q})$  at low temperature can, however, be reactivated as soon as a magnetic field is applied to this q-1-D electron gas along the direction  $c^*$  of lowest conductivity (24). The spin susceptibility  $\chi(\mathbf{q}, H)$  thus displays logarithmically divergent peaks as  $T$  approaches zero for the set of different wave vectors defined by  $Q_x = 2k_F + NeHb/h$ , where  $N$  is an integer,  $e$  is the charge of the electron, and  $h$  is Planck's constant (25). Crudely speaking, the field restores enough 1-D character in the energy dispersion for the SDW distortion to become stable at a nonzero temperature.

The observation of magnetic field-induced transitions in  $(\text{TMTSF})_2\text{PF}_6$  has been inferred from the early work of Kwak *et al.* (26). However, the experimental data of  $(\text{TMTSF})_2\text{PF}_6$  show that the problem is slightly more sophisticated than was originally thought. A sequence of phases must be crossed before the “ $N = 0$ ” phase (which is believed to correspond to the insulating SDW ground state, which is stable at ambient pressure) can be reached above 18 T (Fig. 6) (27, 28). The variable  $N$ , which is related to the deviation of  $Q_x$  from  $2k_F$ , labels the phase containing  $N$  fully occupied Landau levels.  $N = 0$  means no density of states at the Fermi level; that is, a gap has opened over the whole FS. Phases with  $N = 1, 2, 3$ , and so forth, which are observed below 18 T, correspond to semimetallic phases with a very low density of carriers ( $\sim 10^{-2}$  per unit cell) and a tubular FS along the  $c^*$ -axis. In these subphases  $N$  Landau levels are completely filled. The situation where the Fermi level falls between completely filled and completely empty levels minimizes the diamagnetic energy of the 2-D carriers. This situation prevails in a finite range of magnetic fields as long as the wave vector of the magnetic modulation within a given subphase can vary linearly with the field. First-order phase transitions are



**Fig. 6.**  $T$ - $H$  diagram (A and B) and quantized Hall resistance (C and D) for two superconductors belonging to the  $\text{TM}_2\text{X}$  series. The magnetic field is along the axis of lowest conductivity.  $(\text{TMTSF})_2\text{PF}_6$  is at a pressure of 8 kbar (27), and  $(\text{TMTSF})_2\text{ClO}_4$  is at atmospheric pressure (29, 30).

**Fig. 7.** Giant oscillations of the transverse magnetoresistance of  $\beta_{\text{H}}(\text{ET})_2\text{I}_3$ . The inset shows that the field corresponding to extrema is periodic versus  $1/H$ . The low frequency beating is due to the finite but small inter-layer coupling.



expected between various subphases; these transitions are in agreement with the hysteresis shown in Fig. 6.

A direct consequence of the field dependence of the  $\mathbf{Q}$  vector is the quantization of the Hall resistance at  $\rho_{xy} = h/2Ne^2$  (where the factor of 2 comes from the spin degeneracy). The  $(\text{TMTSF})_2\text{PF}_6$  Hall data (Fig. 6) agree quantitatively with the quantized nesting theory (25). The almost perfect agreement between the data and the standard model is not, however, observed in other members of the  $(\text{TMTSF})_2\text{X}$  series with  $\text{X}^- = \text{ClO}_4^-$  or  $\text{ReO}_4^-$ . The  $\text{ClO}_4^-$  compound is interesting for several reasons (Fig. 6). First, the Hall resistance exhibits well-defined plateaus when plotted versus magnetic field, and these plateaus can be indexed by the quantum numbers  $N = 1, 3, 6$ , and so forth (29). The plateau  $N = 2$  is clearly missing in the data of Fig. 6, and a sign reversal of the Hall resistance is observed between  $N = 3$  and  $N = 6$ . Other investigators have attributed a fractional number  $N = 1/3$  to the phase that is remarkably stable in a magnetic field above 8 T (30). Second, the standard quantized nesting model does not provide an interpretation for the destruction of the SDW ordering in a very high field with the reappearance of the undistorted phase. This reappearance is not understood so far, although a non-mean field approach has been proposed (31).

The quantization of the Hall resistance in the field-induced SDW (FISDW) phases is reminiscent of the quantum Hall effect in the 2-D electron gas. There is, however, an important difference between these two phenomena. In both cases the quantization requires a reservoir of nonconducting electronic states. This reservoir is provided by localized states in the gap between conducting Landau levels or the electron-hole (spin modulation) condensate for the 2-D electron gas and the FISDW of organics, respectively.

Other spectacular effects of the low dimensionality are observed in the series of  $(\text{ET})_2\text{X}$  conductors with a 2-D tubelike FS. Figure 7 displays magnetoresistance data in the phase of  $\beta_{\text{H}}(\text{ET})_2\text{I}_3$  that can be stabilized at low temperature after a special procedure is used. Unlike the phase  $\beta_{\text{L}}$  ( $T_c = 1.2$  K), obtained after normal cooling, the  $\beta_{\text{H}}$  phase, which can be stabilized at atmospheric pressure after the special cooling procedure (32) under pressure, is free from incommensurate lattice modulation, and  $T_c$  rises to 8.1 K. The oscillation of extremely large amplitude that appears above 9 T in the  $\beta_{\text{H}}$ -phase is periodic in  $1/H$  with a fundamental field  $H_0 = 3730$  T, which corresponds to the cross section of the tubular FS by a plane perpendicular to the field ( $H$  is thus perpendicular to the conducting sheets), in agreement with a density of carriers of  $\sim 1$  per formula unit (33). In addition, the low-frequency beating is related to the deviation from perfect two dimensionality. The low-frequency  $H_1 = 36.8$  T provides an estimate for the interlayer coupling, namely  $t_c \approx 0.5$  meV (if  $t_{\parallel} = 70$  meV). With the value of  $t_c$  derived from the experiment, the discrete Landau levels are actually broadened into minibands of width  $4t_c = 2$  meV because of the energy dispersion along the  $k_z$  direction. It has been recognized that the

discrete splitting can be restored if the magnetic field is no longer perpendicular to the conducting planes (that is,  $H \parallel c^*$ ) but tilted by an angle  $\phi$  from the  $c^*$  axis (34), such as  $ck_F \tan\phi = \pi(n - 1/4)$ ,  $n = 1, 2, 3$ , and so on. At the angles given by this relation, the area of the cross section of the FS normal to the magnetic field becomes independent of the  $k_z$  coordinate; the minibands are nearly separated (the width of each miniband becomes smaller than the splitting between Landau levels). This model has explained the angle-dependent magnetoresistance oscillations that are observed in several 2-D (ET)<sub>2</sub>X salts (35).

## Superconductivity

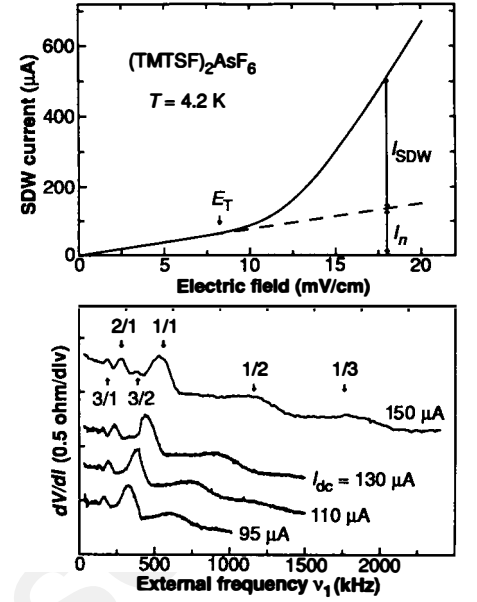
The differences between the superconducting properties of the TM<sub>2</sub>X and (ET)<sub>2</sub>X series are clear-cut. A salient feature of superconductivity in the q-1-D TM<sub>2</sub>X series is the common border existing between superconducting and magnetic phases;  $T_c$  is always limited to values smaller than 2 K and drops quickly under pressure. This upper limit for  $T_c$  is apparently independent of the anion symmetry. Attempts to force the stabilization of superconductivity at lower pressures in the hope for an increased  $T_c$  in the compound (TMTSF)<sub>2</sub>ReO<sub>4</sub> (where a pressure of 10 kbar is necessary to prevent ReO<sub>4</sub><sup>-</sup> anion ordering at low temperature) from an opened gap at the Fermi level have failed to raise  $T_c$  above 1.2 K (36). The (TMTSF)<sub>2</sub>ReO<sub>4</sub> behavior shows the deeply rooted competition that exists between superconductivity and magnetism in the TM<sub>2</sub>X series. It is widely believed that the low value of  $T_c$  in this series is a direct consequence of the 1-D character of the FS. In this situation fluctuations are very efficient in suppressing the superconducting long-range order to low temperature. If the latter argument is reasonable,  $T_c$  values higher than 1 or 2 K should be looked for in materials in which FS is less favorable for the stabilization of antiferromagnetism. The (ET)<sub>2</sub>X series, with Fermi surfaces in which the 2-D character is supported by studies, has indeed provided higher  $T_c$  values (37), up to 8.1 K for  $X^- = I_3^-$  and 10 to 12 K for  $X^- = \text{Cu}(\text{SCN})_2^-$  or  $\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}^-$ . The parameters describing the superconducting state of the  $\text{Cu}(\text{SCN})_2^-$  salt are as follows:  $T_c \approx 10$  K,  $H_{c2}^{\parallel(\perp)} = 20$  T (2.5 T),  $H_{c1}^{\parallel(\perp)} = 1$  Oe (45 Oe),  $\xi_{\parallel}^{b(c)} \approx 174$  Å (118 Å), and  $\xi_{\perp} \approx 7.8$  Å. It is not yet clear whether these layered superconductors should be considered 3-D anisotropic superconductors or 2-D superconductors, in which the long-range ordering at  $T_c^{\text{3D}}$  results from a Josephson coupling between the layers.

The nature of the pairing mechanism has obviously been a matter of conjecture and still remains an open question. Organic superconductivity is strongly sensitive to the presence of impurities and even to nonmagnetic lattice defects observed in both families of superconductors (the latter being unusual in conventional superconductors), which could point toward the existence of an anisotropic gap in the superconducting state. Pairing of carriers through the exchange between neighboring chains of an antiferromagnetic fluctuation is a possibility for gap anisotropy in the TM<sub>2</sub>X series. The absence of an anomaly in the spin-lattice relaxation time at  $T_c$  in the TM<sub>2</sub>X series can also support the existence of an anisotropic gap (38).

## Spin Density Wave Collective Conduction

The broken symmetry ground state characterized by the magnetic modulation (SDW) of wavevector  $\mathbf{Q}$  is responsible for the activated behavior of the conductivity in the semiconducting phase of (TMTSF)<sub>2</sub>X,  $X^- = \text{PF}_6^-$  or  $\text{NO}_3^-$ , through the single particle gap  $2\Delta$ . Moreover, two kinds of collective excitations arise in the SDW

**Fig. 8.** Current-voltage characteristics in the SDW state of (TMTSF)<sub>2</sub>AsF<sub>6</sub> (top). Differential resistance versus frequency of the applied ac current for constant dc current  $I_{dc}$  [from (46)] (bottom).



condensate. They are (i) the magnon excitations that manifest themselves in the antiferromagnetic resonance (39), and (ii) the phase mode of the condensate, which is gapless provided the spin modulation is not commensurate with the underlying lattice. In (TMTSF)<sub>2</sub>PF<sub>6</sub>, the wave vector corresponding to the optimum nesting of the Fermi surface is probably incommensurate, although it is very close to the commensurate value (0.5, 0.25, 0) (40, 41).

As long as  $\mathbf{Q}$  is incommensurate, a rigid motion of the density wave can be achieved without any cost in energy. This translational invariance gives rise to a collective contribution to the conductivity:

$$\sigma(\omega) = (ne^2/m^*) \delta(\omega - \omega_0) \quad (3)$$

where  $n$  is the density of condensed carriers in the SDW state and  $\omega_0$  is either zero, in an ideally pure material, or a finite frequency when the collective mode is pinned by impurities. The effective mass of the condensate is  $m^*$ .

The interaction between a SDW and nonmagnetic impurities provides a finite pinning energy. A threshold electric field  $E_T$  must be reached, therefore, before the condensate can contribute to the conduction at zero frequency. In all SDW phases of the (TMTSF)<sub>2</sub>X series,  $E_T$  lies in the millivolt per centimeter range (Fig. 8) (42). Furthermore, the linear increase of  $E_T$  versus the density of lattice defects  $n_i$  suggests that the phase of the spin modulation is locally adjusted at each defect site to provide the largest pinning energy (strong pinning limit) (43).

The finite frequency response of the SDW phase is dominated by a strong resonance in  $\sigma(\omega)$  centered around  $0.1 \text{ cm}^{-1}$  (3 GHz) in (TMTSF)<sub>2</sub>PF<sub>6</sub>, which has been attributed to the oscillation of the pinned phase mode (44). A weaker resonance at about  $30 \text{ cm}^{-1}$  comes from the single particle excitation across the gap  $2\Delta$ . In the clean limit situation ( $1/\tau \ll \Delta$ ), which is fulfilled in these materials, nearly all of the oscillator strength is associated with the collective mode resonance at  $\omega_0$ , namely:

$$\int_0^\infty \sigma_{SDW} d\omega = \pi ne^2/2m_0 \quad (4)$$

where  $m_0$  is the effective mass. Experimentally, the oscillator strength is about  $10^{-2}$  times the value given by Eq. 4. It has been suggested that this difference could be attributed to a strong effect of Coulomb interactions on the electrostatics of an SDW state rather than a large enhancement of the effective mass condensate with respect to the free electron value (45).

Perhaps the most direct evidence for an SDW transport is the detection of voltage oscillations with a frequency proportional to the current carried collectively. The recent observation of voltage oscillations and harmonic and subharmonic locking of this voltage oscillation to an external ac source (Fig. 4) has provided firm evidence for the existence of a novel collective transport in an SDW condensate (46).

## Conclusions

The study of the new class of synthetic conductors in which superconductivity has been discovered has contributed to a better experimental and theoretical understanding of the physics in low-dimensional electron gases (1-D or 2-D), although there is still no firm explanation for the driving mechanism leading to attractive pairing in organic superconductors. The interplay between antiferromagnetic and superconducting ground states in the  $\text{TM}_2\text{X}$  series, the role of Coulombic interactions in the magnetic properties of the low-dimensional electron gas above  $T_c$ , and the strong sensitivity of  $T_c$  to nonmagnetic impurities in both 1-D and 2-D organic superconductors are all factors that contribute to a nonconventional superconducting mechanism. However, it is still premature to establish a close connection between the mechanism of superconductivity in existing organic superconductors and the model proposed 25 years ago by Little. Moreover, the stabilization of SDW phases at high magnetic fields and the coherent motion of a SDW state under high electric fields are remarkable products of the developments of these new low-dimensional compounds. From past and present activity we can expect that  $T_c$  values may continue to increase and that a number of basic phenomena may be understood in these prototype materials and possibly used for applications. The recent discovery of superconductivity in fullerene ( $\text{C}_{60}$ ) doped with alkali metals is very encouraging for the future of new superconducting materials in which conductivity is governed by the formation of  $\pi$ -orbitals (47).

## REFERENCES AND NOTES

1. W. A. Little, *Phys. Rev. A* **134**, 1416 (1964).
2. D. Jérôme, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett.* **41**, L95 (1980).
3. D. Jérôme and H. J. Schulz, *Adv. Phys.* **31**, 299 (1982).
4. K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, N. Thorup, *Solid State Commun.* **33**, 1119 (1980).
5. G. Brun *et al.*, *C.R. Acad. Sci.* **284**, 211 (1977).

6. V. N. Laukhin, E. E. Kostyuchenko, Y. V. Susko, I. F. Schegolev, E. B. Yagubskii, *JETP Lett.* **41**, 81 (1985); K. Murata *et al.*, *J. Phys. Soc. Jpn.* **54**, 1236 (1985).
7. H. Urayama *et al.*, *Chem. Lett.* **1988**, 55 (1988).
8. A. M. Kini *et al.*, *Inorg. Chem.* **29**, 2555 (1990).
9. J. M. Williams *et al.*, *ibid.*, p. 3272.
10. S. S. Parkin *et al.*, *Phys. Rev. Lett.* **50**, 270 (1983).
11. R. E. Peierls, *Quantum Theory of Solids* (Oxford Univ. Press, Oxford, 1955), p. 108.
12. A. W. Overhauser, *Phys. Rev. Lett.* **4**, 462 (1960).
13. L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1950), p. 482.
14. Y. Byschkov, L. P. Gorkov, I. E. Dzyaloshinskii, *Sov. Phys. JETP* **23**, 489 (1966).
15. V. J. Emery, *J. Phys. (Paris) C3* **44**, 977 (1983).
16. C. Bourbonnais, in *Low Dimensional Conductors and Superconductors*, D. Jérôme and L. G. Caron, Eds. (North Atlantic Treaty Organization Advanced Study Institutes Series, Plenum, New York, 1987).
17. V. Emery, R. Bruinsma, S. Barisic, *Phys. Rev. Lett.* **48**, 1039 (1982).
18. J. P. Pouget *et al.*, *Mol. Cryst. Liq. Cryst.* **79**, 129 (1982).
19. A. Maaroufi *et al.*, *J. Phys. (Paris) C3* **44**, 1091 (1983).
20. L. Brossard, M. Ribault, M. Bousseau, L. Valade, P. Cassoux, *C.R. Acad. Sci.* **302**, 205 (1986).
21. C. Bourbonnais *et al.*, *Phys. Rev. Lett.* **62**, 1532 (1989).
22. P. Wzietek *et al.*, *J. Phys. (Paris)*, in press; P. Wzietek, thesis, University of Paris-Sud (1990).
23. G. Montambaux, in (16), p. 233; K. Yamaji, *Mol. Cryst. Liq. Cryst.* **119**, 105 (1985).
24. L. P. Gor'kov and A. G. Lebed', *J. Phys. (Paris) Lett.* **45**, L433 (1984).
25. M. Héritier, G. Montambaux, P. Lederer, *ibid.*, p. L943.
26. J. F. Kwak *et al.*, *Phys. Rev. Lett.* **46**, 1296 (1981).
27. J. R. Cooper *et al.*, *ibid.* **63**, 1984 (1989).
28. S. T. Hannahs, J. S. Brooks, W. Kang, L. Y. Chiang, P. M. Chaikin, *ibid.*, p. 1988.
29. W. Kang and D. Jérôme, *J. Phys. (Paris)* **1**, 449 (1991).
30. M. J. Naughton *et al.*, *Phys. Rev. Lett.* **61**, 2276 (1988).
31. V. M. Yakovenko, *ibid.* (comment), p. 2276.
32. W. Kang, G. Creuzet, D. Jérôme, C. Lenoir, *J. Phys. (Paris)* **48**, 1035 (1987).
33. W. Kang *et al.*, *Phys. Rev. Lett.* **62**, 2559 (1989).
34. K. Yamaji, *J. Phys. Soc. Jpn.* **58**, 1520 (1989).
35. T. Osada *et al.*, *Synth. Met.*, in press.
36. S. Tomic and D. Jérôme, *J. Phys. Condens. Matter* **1**, 4451 (1989).
37. For details of the superconducting properties of  $(\text{ET})_2\text{X}$  salts, see the *Proceedings of the International Conference on Science and Technology of Synthetic Metals 1988* [*Synth. Met.* **27** (nos. 1 and 2) (1988)].
38. M. Takigawa, H. Yasuoka, G. Saito, *J. Phys. Soc. Jpn.* **56**, 873 (1987).
39. J. B. Torrance, H. J. Pedersen, K. Bechgaard, *Phys. Rev. Lett.* **49**, 881 (1982).
40. T. Takahashi, Y. Maniwa, H. Kawamura, G. Saito, *J. Phys. Soc. Jpn.* **55**, 1364 (1986).
41. J. M. Delrieu, M. Roger, Z. Toffano, A. Moradpour, K. Bechgaard, *J. Phys. (Paris)* **47**, 839 (1986).
42. S. Tomic, J. R. Cooper, K. Bechgaard, *Phys. Rev. Lett.* **62**, 462 (1989).
43. W. Kang, S. Tomic, J. R. Cooper, D. Jérôme, *Phys. Rev. B* **43**, 1264 (1991).
44. D. Quinlivan *et al.*, *Phys. Rev. Lett.* **65**, 1816 (1990).
45. K. Maki and G. Grüner, *ibid.* **66**, 782 (1990).
46. G. Kriza, G. Quirion, O. Traetteberg, W. Kang, D. Jérôme, *ibid.*, p. 1922.
47. A. F. Hebard *et al.*, *Nature* **350**, 600 (1991).
48. I gratefully acknowledge the help of all my colleagues who have contributed to the research in organic conductors at Orsay, Copenhagen, Sherbrooke, and Zagreb. This work is presently supported by the European Strategic Programme for Research and Development in Information Technology Basic Research Action 3121.