



HAL
open science

Organic superconductors

Denis Jérôme

► **To cite this version:**

Denis Jérôme. Organic superconductors. *Advanced Materials*, 1990, 2 (6-7), pp.321-324. <10.1002/adma.19900020613>. <hal-04944348>

HAL Id: hal-04944348

<https://hal.science/hal-04944348v1>

Submitted on 3 Apr 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.



HAL Authorization

about 450–500 °C as in the glass case, leading to improved performance of the device. In the coating examples cited, the glass-ceramic coatings can withstand temperatures up to about 900 °C and so are capable of withstanding the firing-on of thick film circuitry at temperatures in the region of 850 °C.

Further developments are taking place which will allow these structures to be used and/or processed at temperatures in excess of 1000 °C.

Glass-ceramics have also been developed for the joining together of ceramic and glass parts. For example, glass-ceramic joining media are available for alumina ceramics which will enable high quality, complex shapes to be built up from relatively simple shapes and so eliminate the need for complicated machining procedures. Interestingly, glass-ceramic bonding media are also used to bond glass face plates onto the glass conical sections of TV tubes and other CRTs—in these cases bonding temperatures in the region of 500 °C are employed thus avoiding distortion of the glass.

In further developments, improved understanding of interfacial regions is being generated together with the development of means of testing the strength of glass-ceramic bonds to metals, both as methods of optimizing given combinations and as aids in the development of new systems. The possibility of developing glass-ceramic bonding media which exhibit a gradation of thermal expansion across the system to enable materials of widely different thermal expansion characteristics to be joined by glass-ceramics is being investigated.

3. Conclusions

Glass-ceramic joins to other materials such as glasses, ceramics and metals are now well established and new materials and combinations are being developed. This technology in many instances, offers an attractive and more readily realizable alternative to other bonding techniques such as brazing or diffusion bonding.

- [1] Y. Ishida (Ed.): *Fundamentals of Diffusion Bonding*, Proc. 1. Seiken Int. Symp. Interface Structure, Properties and Diffusion Bonding, Tokyo, Japan, 2–4 December 1985. *Series Studies in Physical and Theoretical Chemistry*, 48, Elsevier, Amsterdam 1987.
- [2] S. D. Peteves (Ed.): *Designing Interfaces for Technological Applications: Ceramic-Ceramic; Ceramic-Metal Joining*, Proc. Europ. Colloq. Petten, The Netherlands, 20–21 April 1988, Elsevier, Amsterdam 1989.
- [3] W. Kraft (Ed.): *Joining Ceramics, Glass and Metal*. Int. Conf. Joining Ceramics, Glass and Metal, Bad Nauheim, FRG, 26–28 April 1989. Dtsch. Gesell. Materialkunde, Oberursel 1989.
- [4] M. G. Nicholas: *Joining Structural Ceramics* in Ref. [1], pp. 49–76.
- [5] G. Partridge, S. V. Phillips: *New Developments in Glasses and Ceramics for the Electrical Industry*, *GEC J. Sci. Tech.* 45 (1) (1978) 11–20.
- [6] J. Pask, *Chemical Reactions and Adherence at Glass-Metal Interfaces*. *Proc. Porcelain Enamel Inst. Tech. Forum* 33 (1971) 1–16.
- [7] G. Partridge: *Joining Glass-Ceramics to Metals* in M. G. Nicholas (Ed.): *Ceramic Joining* Chapman and Hall, London 1990, in press.
- [8] G. Partridge, C. A. Elyard, E. A. Logan, D. Holland, *Glass-Ceramic Bonds to Metals*, in Ref. [3], p. 163–170.
- [9] S. C. Kunz, R. E. Lochman, *Thermal Expansion Mismatch Produced by Interfacial Reactions in Glass-Ceramic to Metal Seals*, *Adv. Ceram. Mater.* 2 (1) (1987) 69–73.
- [10] G. Partridge: *New Glass-Ceramic Coated Metal Substrates for Use in Electronic Applications*. Ceramic composites and coatings, recent developments and applications, IBC Technical Services Ltd, 8–9 September 1989, to be published, Elsevier, Amsterdam 1990.

Research News

Organic Superconductors

By Denis Jérôme*

Over the past decade there has been much activity in research into organic superconductivity, particularly in two directions: the improvement of superconducting properties through the elaboration of new materials, and the study of new basic phenomena in selected systems.

Organic superconductivity (SC) was first found in the tetramethyltetraselenafulvalene (TMTSF) radical cation compound $(\text{TMTSF})_2\text{PF}_6^{[1]}$ which belongs to the broader family $(\text{TMTTF}-\text{TMTSF})_2\text{X}$, where X is an inorganic anion

such as PF_6^\ominus , AsF_6^\ominus , ClO_4^\ominus , ReO_4^\ominus , FSO_3^\ominus , etc.^[2] and TMTTF is tetramethyltetrafulvalene. The selenium series, $(\text{TMTSF})_2\text{X}$, is characterized by a strong intermolecular overlap of the π orbitals along the stacking axis of the organic molecules. This feature is the origin of the metal-like conducting behavior of these molecular compounds. Furthermore, these materials exhibit a quasi one-dimensional (Q-1-D) energy dispersion based on the highest occupied molecular orbital (HOMO) levels of the donor molecule with a Fermi surface comprising two open sheets.

According to the physics of low-dimensional systems, two important features can be expected in a theoretical 1-D con-

[*] Dr. D. Jérôme
Laboratoire de Physique des Solides (associé au CNRS),
Université Paris-Sud, F-91405 Orsay (France)

ductor.^[3] First, equally divergent behavior of the superconducting and dielectric correlations on cooling, and second the absence of long-range order at low temperature due to the easy excitation of one-dimensional thermodynamic fluctuations. In actual materials (Q-1-D), such as those giving rise to organic superconductivity, the non-zero transverse coupling makes the establishment of long-range order (magnetism or superconductivity) possible in the temperature domain $T < 20$ K.

A direct consequence of the 1-D character of the (TMTTF-TM-TSF)₂X series is the existence of a wide variety of ground states depending on the chemical composition of the compound in the series and also on the hydrostatic pressure.^[4] The phase diagram shown in Figure 1 applies.

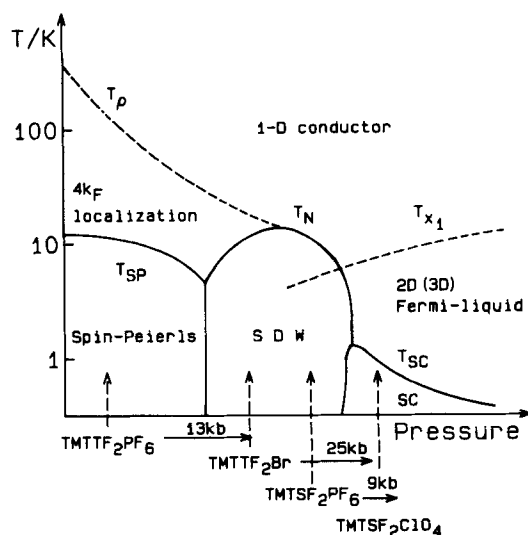


Fig. 1. Universal phase diagram for the (TMTTF-TM-TSF)₂X series. T_{x1} is the dimensionality cross-over 1D-2D.

The all-sulfur compound (TMTTF)₂PF₆ exhibits a smooth charge localization below 200 K which is not accompanied by any symmetry change and which has been attributed to on-site Coulomb repulsions boosted by the Umklapp scattering existing in the half-filled band. The localized spins then undergo a 3-D non-magnetic lattice distorted spin-Peierls (SP) transition around 19 K. Under pressure, the Coulomb-driven charge localization is suppressed and the ground state evolves through a first-order phase transition from the non-magnetic SP to the spin density wave (SDW) above 10 Kbar. Charge localization is no longer observed in the selenium material (TMTSF)₂PF₆, which undergoes a SDW transition below 12 K. In turn, the SDW state is suppressed by the application of a high pressure ($P > 8$ kbar in (TMTSF)₂PF₆) and the superconducting state then becomes the most stable ground state.

Figure 1 shows that SP/SDW and SDW/SC competitions are the highlights of the (TMTTF-TM-TSF)₂X series. Furthermore, this competition is a property which is characteris-

tic of the organic stack even though it can be obscured in some cases by the occurrence of an insulating ground state driven by the ordering of non-centrosymmetric anions.^[5]

A necessary requirement for the existence of an SDW ground state in a low-dimensional conductor is the existence of a unique vector \mathbf{Q} connecting the two sides of the Fermi surface which provides a good nesting of both sheets. The nesting is preserved even in the presence of transverse coupling as long as the shape of the surface does not depart from sinusoidality, i.e. when the transverse dispersion remains negligible compared to the longitudinal one ($t_{\perp} \ll t_{\parallel}$). According to a mean-field theory of the SDW transition in Q-1-D materials there exists a critical value of the interchain overlap beyond which the ground state becomes a superconductor, in agreement with the experimental findings (Fig. 1).

In 1985, new superconductors appeared in the series of radical cations based on the molecule BEDT-TTF (bis(ethylenedithio)tetrathiofulvalene, ET) coupled to various anions such as I₃⁻, IBr₂⁻ and more recently^[6] Cu(SCN)₂⁻.

The peculiarity of ET molecules is to generate structural arrangements in which the intermolecular overlap is large along two directions: the stacking direction and one transverse direction as well. Hence, two dimensionality of the Fermi surface results from the crystal structure. This property can be clearly observed in Shubnikov-de Haas experiments as oscillations with extraordinarily large amplitudes have been detected in the β_H phase of (ET)₂I₃ free from the incommensurate distortion.^[7] The critical temperatures of the ET series range from 1.4 K in β_L -(ET)₂I₃ up to 8.1 K and even 10 K in β_H -(ET)₂I₃ and κ -(ET)₂Cu(SCN)₂ respectively (Fig. 2). No sign of competition between magnetism and superconductivity is apparently present in these 2-D conductors.

In addition to the regular Shubnikov-de Haas oscillations, angular oscillations have been detected in some Q-2-D ET

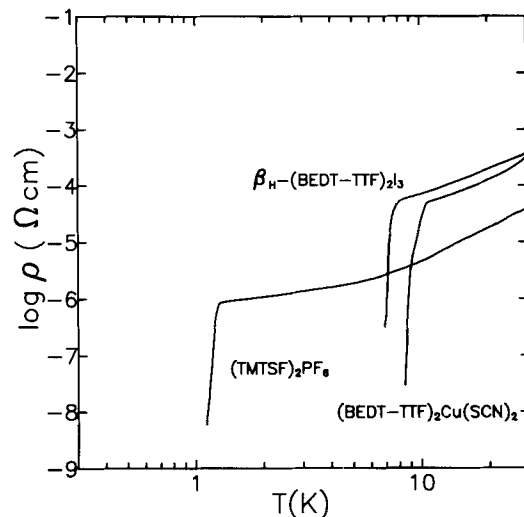


Fig. 2. The superconducting transition in various organic conductors. (TMTSF)₂PF₆ is under 8 kbar, both ET salts are at atmospheric pressure.

salts at constant field. At special angles between the magnetic field and the axis of the 2D Fermi surface the magnetoresistance displays sharp maxima. At these angles, the cross section of the Fermi surface perpendicular to the magnetic field becomes independent (in first order approximation) of the position along the c^* axis.^[6]

Another aspect of the competition between SC and SDW is observed at low temperature in Q-1-D compounds when a high magnetic field is applied to the conducting phase of some organic conductors, $(\text{TMTSF})_2\text{ClO}_4$ or $(\text{TMTSF})_2\text{PF}_6$, under pressure. The magnetic field one-dimensionalizes the trajectory of Q-1-D electrons and one-dimensional instabilities (SDW) can thus be restored under high field. The stabilization of a SDW semimetallic phase at high fields has been observed in several organic conductors belonging to the $(\text{TMTSF})_2\text{X}$ family. However, the semimetallic SDW state is more subtle than it seems at first sight. According to theory, the wave vector Q of the magnetic modulation must be field dependent in order to maintain a complete filling of N Landau levels over some range of magnetic field corresponding to the stability domain of the SDW phase labeled by the quantum number N . This is the configuration which minimizes the diamagnetic energy.^[8]

This model predicts a sequence of first-order transitions between SDW phases labeled by successive integers N . A field dependence of the density of unnested carriers $n = NeH/h$ and the quantization of the Hall voltage $R_H = H/ne = h/Ne^2$ are direct consequences of this model. The finding of a field independent Hall voltage in $(\text{TMTSF})_2\text{ClO}_4$ was the first stimulus for the development of the theory. However, the latter compound suffers from an additional

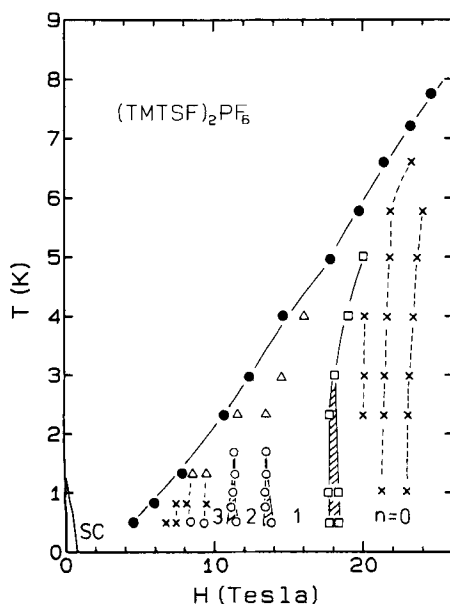


Fig. 3. Phase diagram T-H of $(\text{TMTSF})_2\text{PF}_6$ under 8 kbar. The field is aligned along the direction of lowest conductivity (c^*). The critical field H_{c2} is not represented on the correct scale but is of the order of 1 kOe. FISDW states are labeled according to the number N of filled Landau levels.

complexity which is the ordering of ClO_4^- ions, opening small gaps on the Fermi surface at $(\pm k_F, \pm \pi/2b)$.

No such complication exists in the case of $(\text{TMTSF})_2\text{PF}_6$ although all experiments must be performed under high pressure.^[9, 10]

Well defined Hall plateaus (Fig. 3) whose heights are in the ratio 1, 1/2, 1/3, 1/4, 1/5 are observed at fields below 18 T. The absolute value of 11 k Ω /molecular layer found for the largest plateau is rather close to the prediction of the quantized Hall value, $h/2e^2 = 12.9$ k Ω /layer for $N = 1$ in the presence of spin degeneracy. The data in Figure 3 clearly prove that the quantized Hall effect can exist in a bulk crystal made up of about 10^5 weakly interacting layers. Above 18 T, the magnetoresistance increases rapidly by a factor $\approx 10^4$ and therefore the $H > 18$ T ground state is probably similar to the low-temperature semiconducting state at ambient pressure ($N = 0$) in which a finite gap exists over the entire Fermi surface. Figure 4 displays the phase diagram (obtained from galvanomagnetic data) of $(\text{TMTSF})_2\text{PF}_6$ ($P = 8$ Kbar) under high fields.

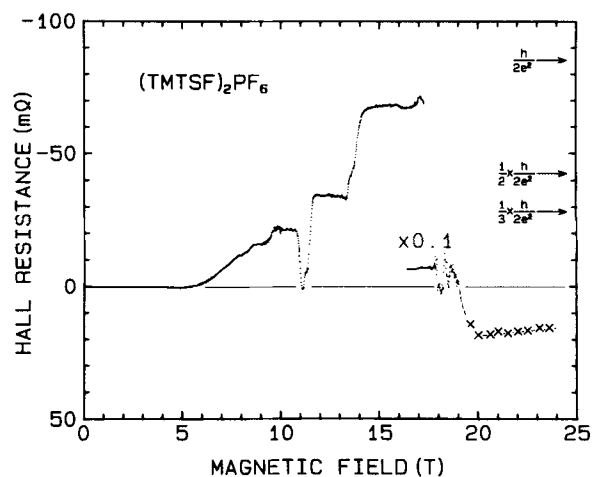


Fig. 4. Hall resistance V_H/I versus magnetic field H/c^* in $(\text{TMTSF})_2\text{PF}_6$ at $P = 8$ kbar and $T = 0.5$ K. The quantized values $h/2ne^2$ (12.9/n) k Ω per molecular layer are marked with arrows for $n = 1, 2$ and 3.

The recent finding of a similar Hall quantization in the system $(\text{TMTSF})_2\text{ReO}_4$ suggests that the small gaps due to the ordered anions have very little (if any) effect on the stabilization of SDW phases at high fields.^[11]

Above 20 T another new phenomenon has been found in $(\text{TMTSF})_2\text{ClO}_4$, namely a decrease of the SDW ordering temperature at increasing field. The theory of this "reentrant" behavior is not yet fully established. Among several possibilities, a Wigner crystallization of a low-dimensional electron gas is an attractive prospect.

Summarizing, the close cooperation between synthetic organic chemists and solid state physicists has provided a number of new conducting compounds which have led to

superconductivity and to a wealth of new fundamental phenomena. Much work remains to be done, for example understanding the interplay between the nature of the pairing interaction, the dimensionality of the electron gas and the strength of the Coulombic repulsion. Superconductivity has also been stabilized in multi Fermi surface molecular solids based on the acceptor molecule $M(dmit)_2$, $M = Ni, Pd$, and $dmit = 1,3$ -dithia-2-thione-4,5-dithiolato. New areas of research have been opened with the study of the Fröhlich conductivity in the SDW state of organics. In terms of record-breakers, organic superconductors still show some promise in spite of competition from the high-temperature ceramic superconductors, since the T_c of the former materials has grown by a factor 10 in less than one decade.

Conference Reports

Cu Alloys in Anaheim

By Wolfgang Kaysser*

The TMS Structural Materials and Powder Metallurgy Committee organized a one and a half day symposium on High Performance Copper-Based Alloys. The symposium was part of the 119th TMS Annual Meeting held from the 20th to the 23rd of February in Anaheim, California.

Copper-based alloys have been used for a number of years as cooled first-wall materials in high performance rocket propulsion systems on account of their good combination of strength and thermal conductivity. Most prominent examples are space-shuttle components such as the main combustion chamber or the high-pressure turbo pumps for the fuel. Due to their outstanding heat conductivity the copper alloys even perform better than unreinforced superalloys or W-fiber-reinforced superalloys. The high thermal conductivity lowers the transient thermal stresses which occur at the start and after shut off of the systems to values which the high-strength Cu alloys can deal with.

Other applications, such as heat exchangers or high-performance switches are envisaged. The high strengths at RT and at elevated temperatures are obtained from multiphase filament or layer structures with extremely fine filament spacing. Recently, efforts to further refine composite microstructures, which are basically generated by extensive deformation processing, have been directed towards the optimization

- [1] D. Jérôme, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett. (Paris)* 41 (1980) L-95.
- [2] K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, N. Thorup, *Solid State Commun.* 33 (1980) 1119.
- [3] (Review article) D. Jérôme, H. J. Schulz, *Adv. Phys.* 31 (1982) 299.
- [4] D. Jérôme, L. G. Caron (Eds.): *Low Dimensional Conductors and Superconductors*, NATO ASI. Series No. 155, Plenum, New York 1987.
- [5] S. Tomic, D. Jérôme, *J. Phys. Cond. Matter* 1 (1989) 4451.
- [6] T. Ishiguro, K. Yamaji, *Organic Superconductors*, Springer Series in Solid State Sciences 88, Springer-Verlag, Heidelberg 1990.
- [7] W. Kang, G. Montambaux, J. R. Cooper, D. Jérôme, P. Batail, C. Lenoir, *Phys. Rev. Lett.* 62 (1989) 2559.
- [8] G. Montambaux, in [4] p. 233.
- [9] J. R. Cooper, W. Kang, P. Auban, G. Montambaux, D. Jérôme, K. Bechgaard, *Phys. Rev. Lett.* 63 (1989) 1984.
- [10] S. T. Hannahs, J. S. Brooks, W. Kang, L. Y. Chiang, P. M. Chaikin, *Phys. Rev. Lett.* 63 (1989) 1988.
- [11] Orsay group, unpublished.

of the starting microstructures. *K. P. Cooper*, from the Naval Research Laboratory, Washington, D.C., reported on the use of fine gas atomized Cu (7.7 wt.-%) Cr (2.2 wt.-%) Ag powders which showed a homogeneous distribution of primary Cr precipitates with a mean size of 0.5 μm . The powders were hot isostatically pressed (HIPed) at 750 °C, swaged into rods 0.673 cm in diameter and drawn into fibrous composite wires 150 μm in diameter. From the as HIPed to the final wire state the strength of the material increased by a factor of four.

In general, the Cu-composites are produced from material initially containing bcc dispersoids of Nb, Ta, Cr or Fe. The ultimate tensile strength (UTS) increases linearly with the true processing strain factor, $\ln \{ \text{initial wire diameter} / \text{final wire diameter} \}$, from 500 MPa at a strain factor of 2 to over 1000 MPa at a strain factor of 7. The relationship between microstructure refinement and increasing UTS was explained by *Spitzig* and coworkers from Iowa State University. A failure mechanism is proposed which starts by the formation of voids in the fcc-Cu areas between the bcc-fibrous filaments. Void growth and void coalescence lead to dimple sizes related to the fiber separation. Final failure occurs through the fracture of the bcc filaments.

P. B. Krotz from the Rocketdyne Division of Rockwell, CA, described the production of fine layered Cu (15 wt.-%) Nb sheets by rolling. When dynamic recrystallization during hot rolling is suppressed, the single layers can be reduced to thicknesses of less than 1 μm . The ultimate yield strength

[*] Dr. W. A. Kaysser
Max-Planck-Institut für Metallforschung
Heisenbergstrasse 5, D-7000 Stuttgart (FRG)