

ORGANIC SUPERCONDUCTIVITY

Organic superconductivity refers to the regular phenomenon of superconductivity as it is observed in some metals and metallic inorganic compounds. However, what makes organic superconductivity so distinctive is that conduction in organic molecular conductors is linked to the transport of free charges (electrons or holes) between π -like molecular orbitals of neighbouring open shell molecules. In addition, these new materials reveal quasi one dimensional features of their electronic transport properties due to their peculiar crystal structure. They are considered as textbook examples for low dimensional physics. They have also been stimulating for the research on high T_c superconductors and pnictides.

Some definitions Superconductivity

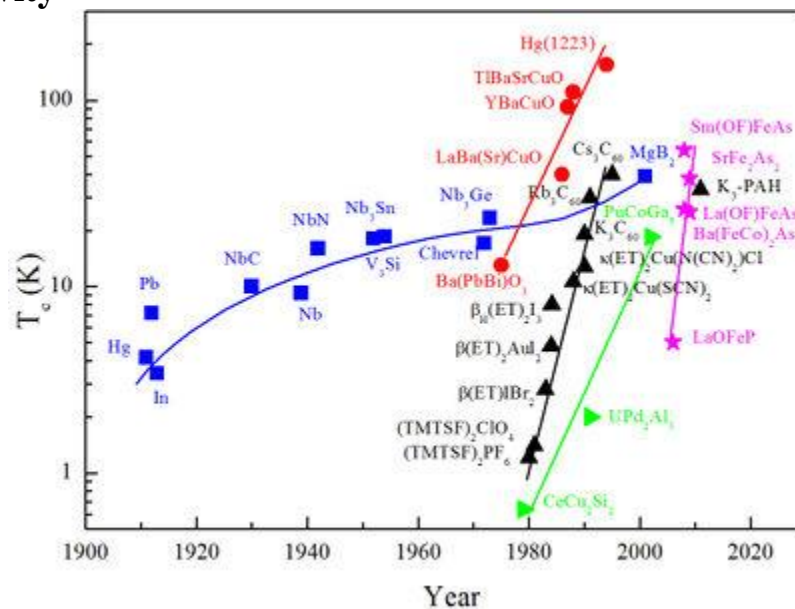


Figure 1: The figure displays the evolution of T_c in materials according to the date of the discovery of their superconducting properties. It clearly shows a renewed effort in superconductivity at the beginning of the eighties which triggered the research of novel materials with the discovery of organic superconductors in 1980 and high T_c cuprates in 1986.

Superconductivity (a new state of matter) is one of the major discovery in physics for the twentieth century given its experimental and theoretical impact on science. From an experimental point of view the finding by G. Holst in the laboratory of H. Kamerlingh Onnes [1] in 1911 of a current travelling without resistance through a metal cooled at very low temperature paved the way to a very large number of industrial applications. This experimental discovery happened long before the proposal of a satisfactory theoretical framework by Bardeen,

Cooper and Schrieffer ([BCS](#)) [2] in 1957 explaining the two basic properties of the superconducting ground state of a metal namely, the zero resistance state and the magnetic flux expulsion.

Superconductivity requires low temperature conditions to be observed in metals and intermetallic compounds, typically the helium temperature range as can be seen on fig(1). Until the years in the sixties, the critical temperature for superconductivity had been steadily rising as new intermetallic compounds were synthesized according to the paradigm of the BCS theory predicting an isotope effect namely, an electron-electron pairing in the superconducting ground state mediated by the electron-phonon interaction with the ionic mass dependence of the critical temperature, $T_c \propto M^{-1/2}$ [2].

Searching for new materials exhibiting the highest possible values of superconducting T_c was already a strong [motivation](#) in materials sciences in the early 70's, and the term high temperature superconductor was already commonly used referring to the intermetallic compounds of the A15 structure, namely, (Nb₃Sn or V₃Si) [3].

Expanding the successful idea of the isotope effect of the BCS theory other models were proposed in which excitations of the lattice responsible for the electron pairing had been replaced by higher energy excitations namely, electronic excitations, with the hope of new materials with T_c higher than those explained by the BCS theory. Consequently, the small electronic mass m_e of the polarizable medium would lead to an enhancement of T_c of the order of $(M/m_e)^{1/2}$ times the value which is observed in a conventional superconductor, admittedly a huge factor. V.L.Ginzburg [4,5] considered in 1964 the possibility for the pairing of electrons in metal layers sandwiched between polarizable dielectrics through virtual excitations at high energy.

An even more provocative suggestion came from W.A.Little [6, 7] namely, a new mechanism for superconductivity which could lead to a drastic enhancement of the superconducting T_c to be observed in especially designed macromolecules. The idea of Little was still rooted in the extension of the isotope effect proposed by BCS replacing the mediating phonon by an electronic excitation which especially designed macromolecules could reveal. However a prerequisite to the model of Little was the achievement of metallic conduction in organic molecular crystals, not a trivial problem in the sixties.

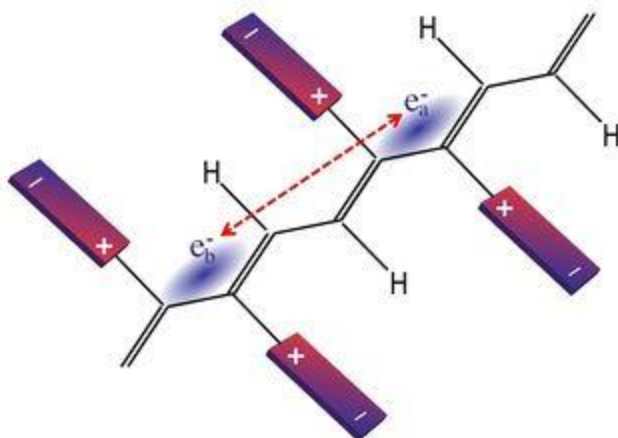


Figure 2: Schematic picture for the Little's suggestion. Charge carriers a and b forming a Cooper pair in the conducting spine are bound *via* a virtual electronic excitation of the polarizable side groups.

Organic conductors

Electronic conduction proceeds in organic molecular conductors through the transport of free charges (electrons or holes) between π -like molecular orbitals of neighbouring open shell molecules rather than between atomic orbitals in regular metallic conductors. One cannot find organic conductors in nature, unlike the metallic ones. The former must always be synthesized in a chemistry laboratory.

The first successful attempt to promote metal-like conduction between open shell molecular species came out in 1954 with the synthesis of the molecular salt of perylene oxidized with bromine [8] although this salt was unstable in air.

History

The idea of Little was based on the use of a long conjugated polymer such as a polyene molecule grafted by polarizable side groups [9]. Admittedly, this formidable task in synthetic chemistry did not reach its initial goal but the idea to link organic metallicity and one dimensionality was launched and turned out to be a very strong stimulant for the development of organic superconductors.

A major step was accomplished in 1970 towards the discovery of new materials for superconductivity with the synthesis by F.Wudl [10] of the new molecule tetrathiafulvalene, (TTF). This molecule containing four sulfur heteroatoms in the fulvalene skeleton can easily donate electrons when it is combined to electron accepting species.

From the charge transfer period to the first organic conductor

A short time later the synthesis of the first stable organic metal, the charge transfer complex TTF-TCNQ came out. This compound is made up of two kinds of flat molecules each forming segregated parallel conducting stacks. It fulfills the conditions for an organic conductor as the orbitals involved in the conduction (π -HOMO, highest occupied molecular orbital and π -LUMO, lowest unoccupied molecular orbitals for TTF and TCNQ respectively) are associated with the molecule as a whole rather than with a particular atom. Free carriers within each stacks are given by an interstack charge transfer *at variance* with other organic conductors such as the conducting polymers in which charges are provided by doping [11].

The announcement of a large and metal-like conduction in TTF-TCNQ was made in 1973, simultaneously by the Baltimore [12] and Pennsylvania groups [13]. The Pennsylvania group made a provocative claim announcing a giant conductivity peak of the order of $10^5 (\Omega\text{cm})^{-1}$ at 60 K arising just above a very sharp transition towards an insulating ground state at low temperature. This conductivity peak was attributed by their authors to precursor signs of an incipient superconductor.

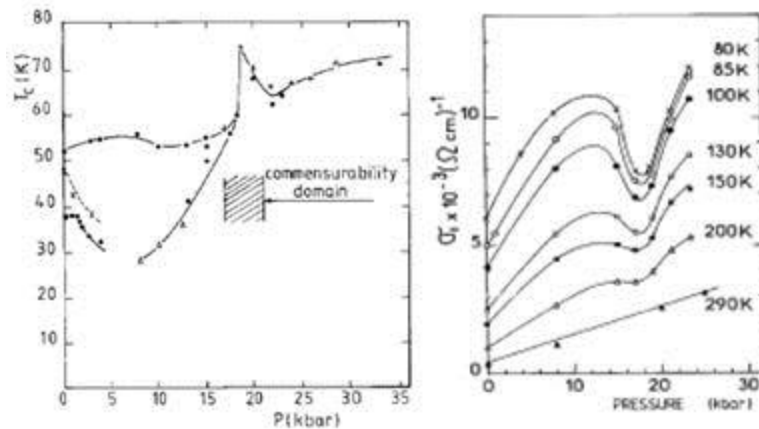


Figure 3: Isothermal pressure dependence of the longitudinal conduction of TTF-TCNQ, showing a drop of the conduction in the commensurability ($\times 3$) domain of the fluctuating Fröhlich contribution due to pinning by the lattice [15]. The ratio $\sigma(80\text{K})/\sigma(290\text{K})$ is evolving from 18 to 3 from ambient pressure up to 18 kbar and rising again at higher pressures.

Thanks to pressure studies it has been shown that the very large conductivity peak exhibited by TTF-TCNQ at 59K is actually the contribution of collective Fröhlich [fluctuations](#) in a 1D regime adding to the conduction coming from single particles [14]. Driving the charge transfer through a commensurate value $\rho=2/3$ under the pressure of ≈ 18 kbar provided in turn the proof for collective Fröhlich fluctuations existing in the 1D regime under ambient pressure, leading to a large enhancement of the ordinary single particle conduction since the wave length of these *CDW* fluctuations is not commensurate with the underlying lattice, in particular under ambient pressure [14], *see*, fig(3). Furthermore high pressure experiments performed recently in Japan managed to partly suppress the onset of the Peierls instability in TTF-TCNQ [16] after an initial increase up to 30 kbar confirming the early Orsay work [14] but failed to reveal any sign of superconductivity which had

been anticipated by Horowitz *et-al* [17] when phonons become soft in the vicinity of the Peierls transition, hence enhancing T_c according to the traditional electron-phonon mechanism. Furthermore, the $4k_F$ signature in X-ray diffuse scattering experiments [18] have pointed out that 1D electron-electron repulsive interactions cannot be ignored in these kinds of molecular compounds. Hence, new charge transfer compounds with the acceptor TCNQ were synthesized using other heteroatoms for the donor molecule, *i.e.* substituting sulfur for selenium in the TTF skeleton thus leading to the TSF molecule where S stands for selenium. Much [attention](#) was devoted to the tetramethylated derivative of the TSF molecule which, when combined to the dimethylated TCNQ gave rise to TMTSF-DMTCNQ [19]. The outcome of the high pressure study of this latter compound has been truly decisive for the quest of organic superconductivity [19, 20, 21]. First, the metal insulator transition located at 42 K has been identified by X-ray diffuse scattering experiments [22] as a Peierls transition driven by the TMTSF chain and a quarter filling of both donor and acceptor bands of this charge transfer compound has been derived from the measurement of the wave vector $2k_F$ in the Peierls state. Second, for the first time the metallic state of an organic compound could be stabilized down to 1.2 K under pressure *albeit* without superconductivity [23]. Although the reason for the stability of a metallic state in TMTSF-TCNQ above the pressure of 9 kbar is not yet understood, emphasizing the role of the donor stack (TMTSF) for conduction has been a strong motivation for the synthesis of new organic conductors with structures even simpler than those of the two stacks charge transfer compounds. This is how $(\text{TMTSF})_2\text{PF}_6$, the so-called Bechgaard salt [24], came out of the Copenhagen chemistry laboratory in 1979 inspired by a series of isomorphous radical cationic conductors based on TMTTF previously synthesized at Montpellier

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