

SUPERCONDUCTIVITY IN ORGANIC MATERIALS

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ABSTRACT:

In this paper, the development and present status of organic superconductors of charge-transfer salt based on electron donor molecules, electron acceptor molecules as well as polycyclic aromatic hydrocarbons ($T_c=33K$ at ambient pressure), graphite ($T_c=15.1K$ at 7.5GPa), carbon nanotube ($T_c=15K$ in zeolite), fullerene ($T_c=38K$ at 0.7GPa), Single component organic compound ($T_c \leq 2.3K$ at 58GPa), B doped diamond ($T_c=10K$) etc are discussed. The highest critical temperature obtained for an organic superconductor is 117 K which was found for hole doped C_{60} intercalated with $CHBr_3$. The search for higher critical temperatures in organic superconductors appears promising.

Index Terms: Bechgaard salts, fullerene, graphite, aromatic hydrocarbon.

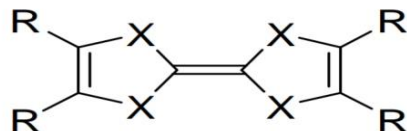
I. INTRODUCTION

The possibility of organic superconductors was first suggested theoretically by W. A. Little in 1964, who proposed an excitonic mechanism to obtain a high- T_c in organic superconductors [1]. Since then, several different types of organic superconductors have been identified such as the quasi-one-dimensional Bechgaard salts [2] and quasi-two-dimensional salts derived from the electron donor molecule [3] as well as tetracyanoquinodimethane (TCNQ) and fullerides from electron acceptor molecule. It was realized that conduction and valence bands in organic molecules can be made partially filled if planar organic molecules are combined with anions that are nonorganic. In such type of compound, organic molecule behave as electron donor and nonorganic molecule serve as electron acceptor. So, there is the formation of charge transfer complex with metal like characteristics. The first organic superconductor in a charge transfer salt $(TMTSF)_2PF_6$ with $T_c \sim 1.2K$ under pressure of 11Kbar [4] and with T_c rising to $\sim 13K$ in the ET salt $(ET)_2Cu[N(CN)_2]Cl$ were discovered. These materials which are typically made from stacks of organic molecules are highly anisotropic in electrical conductivity [8]. It is the unpaired electron residing in the π -orbital of the donor unit which is responsible for the electronic properties of these charge transfer salts.

Several superconducting materials were discovered including calcium intercalated graphite compounds [5], boron doped diamond [6], fullerenes, [7-9] nanotubes, [7] acenes, [8] polythiophene, [9] and oligomers of poly-phenylene-vinylene [10]. All the carbon polymorph with different covalent characters like, zero dimensional C_{60} , one dimensional carbon nanotubes, two dimensional graphite and three dimensional diamonds could provide superconductors either in themselves or by doping of metal atoms or by substitution of boron for carbon. Diamond can be engineered to exhibit superconductivity when doped with boron. It was pointed out that superconductivity in boron doped diamond is due to a phonon mediated pairing mechanism. Higher critical temperatures have been observed for hole doped C_{60} due to the higher density of states in the conduction band. The π -molecular orbital plays a very important role for superconductivity in C_{60} solid and graphite superconductors. In aromatic hydrocarbons, superconducting transition temperature was observed up to 33K. However the accurate amount of doped electrons and their positions have not been established experimentally, nor has any consensus reached for its superconducting mechanism.

II. QUASI ONE DIMENSIONAL SUPERCONDUCTORS

Quasi one dimensional superconductor contains one Fermi surfaces and having two parallel planes. The superconduction only occurs along a single axis. The first organic superconductor was discovered by K. Bechgaard [2]. The first organic superconductors consisted of planar tetramethyltetraselenafulvalene (TMTSF) donors and monovalent anion acceptors with the general formula $(\text{TMTSF})_2\text{X}$, where X is either an octahedral or tetrahedral anion. For the Bechgaard-salts important donors are TMTTF (Tetramethyltetrathiafulvalene) with sulfur and TMTSF (Tetramethyltetraselenfulvalene) with selenium.



TTF : X=S, R=H
TSF : X=Se, R=H
TTeF : X=Te, R=H
TMTSF : X=Se, R=Me
TMTTF : X=S, R=Me

Figure 1 Quasi one dimensional superconductor

The $(\text{TMTSF})_2\text{PF}_6$ was synthesized with a transition temperature of $T_c = 1.1$ K, at an external pressure of 6.5 kbar [1]. Here, TMTSF serve as electron donor and PF_6^- serve as electron acceptor. The ratio of donor and acceptor is generally 2:1 and the transition temperature is below 2 K which is depending on the acceptor. These charge transfer salts consist of segregated, stacked sheets of donors and acceptors. The TMTSF-salts are metals with a formally $3/4$ filled conduction band [3].

Table 1 Transition temperature (t_c) of quasi one-dimensional organic superconductors

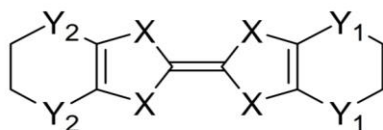
One Dimensional Organic Superconductor	T_c (K)
$(\text{TMTSF})_2\text{SbF}_6$	0.36
$(\text{TMTSF})_2\text{PF}_6$	1.1
$(\text{TMTSF})_2\text{AsF}_6$	1.1
$(\text{TMTSF})_2\text{ReO}_4$	1.2
$(\text{TMTSF})_2\text{TaF}_6$	1.35
$(\text{TMTTF})_2\text{Br}$	0.8
$(\text{TMTSF})_2\text{ClO}_4$	1.4

Only one Bechgaard-salt was found to be superconducting at ambient pressure which is $(\text{TMTSF})_2\text{ClO}_4$ [7] with a transition temperature of $T_c = 1.4$ K, while other salts become superconducting only under external pressure (5-12Kbar). Table 1 shows transition temperature of one-dimensional organic superconductors. The π -orbitals of the sulfur or selenium-atoms stretch perpendicular to the stacking direction and produce an overlap between the donor-molecules. Pressure increases the dimensionality and there is also an overlap with the neighbor atoms. Due to their formation, electrical conductivity is extremely anisotropic [8]. Conductivity is greatest along the axis upon which the donor molecules are stacked. Orbital overlap in each layer is poor and electrical conductivity is reduced by several orders of magnitude along the axis perpendicular to the stacking axis.

III. QUASI TWO DIMENSIONAL SUPERCONDUCTORS

In quasi two dimensional superconductors, the Fermi surface is cylindrical and the conductivity is isotropic in the plane of donor molecule. Here, a new donor BEDT-TTF [bis (ethylenedithio) tetrathiafulvalene [10], was synthesized which contains eight sulfur atoms whereas the TMTSF donor only contains four selenium atoms per donor. Four sulfur atoms are located at the peripheries of the donor, which provide better orbital overlap between stacks of donors compared to within the stacks [11]. These molecules form planes which are

separated by anions. A neutral BEDT-TTF molecule is non-planar and becomes almost flat on formation of the partial charge transfer complex except the terminal ethylene groups which are thermally disordered at high temperatures. Segregated packing of such molecules leaves cavities along the molecular long axis, where counter anions and sometimes solvent molecules occupy. It was pointed out that the ethylene conformation is one of the key parameters determining the physical and structural properties including the superconductivity [14]. The donor molecule is nonplanar due to the ethylene groups, which prevent good overlap along the stacking axis.



ET(BEDT-TTF) : $X=Y_1=Y_2=S$
BO(BEDO-TTF) : $X=S, Y_1=Y_2=O$
BETS(BEDT-TSF) : $X=Se, Y_1=Y_2=S$
EOET : $X=S, Y_1=S, Y_2=O$

Figure 2 Quasi two dimensional superconductors

The electronic properties of the BEDT-TTF -based crystals are determined by its growing phase, its anion and by the external pressure applied. Table 2 shows quasi two dimensional organic superconductors with T_c (K). The external pressure needed to drive a BEDT-TTF-salt with insulating ground state to a superconducting one is much smaller than those needed for Bechgaard salts. κ -(ET)₂Cu[N(CN)₂]Br becomes superconducting at $T_c = 11.8$ K at ambient pressure, and a pressure of 300 bar drives deuterated κ -(ET)₂Cu[N(CN)₂]Cl from an antiferromagnetic to a superconducting ground state with a transition temperature of $T_c = 13.1$ K. Complexes such as β -(BEDT-TTF)₂X where X is I₃⁻, Br-I-Br⁻, and I-Au-I⁻ have all shown superconductivity with critical temperatures of 1.5, 2.7, and 4.9 K, respectively. When X is I-I-Br⁻, superconductivity is not detected, possibly due to a more disordered system.[15] Disorder within charge transfer salts appears to suppress superconductivity. Critical temperature of the BEDT-TTF salts increase with increasing anion length. This trend has been attributed to a higher density of states caused by less interaction between the donor molecules. Other donors have been synthesized including oxygen-containing donors such as BEDO-TTF [8] [(bisethylenedioxy) tetrathiafulvalene] and unsymmetrical donors like DODHT [9] [(1, 4-dioxane-2, 3-diylidithio) dihydrotetrathiafulvalene]. Although lighter atoms (compared to selenium or sulfur) were predicted to yield higher T_c superconductors, none of the oxygen containing donors has yielded high critical temperatures.

Table 2 Quasi two dimensional organic superconductors with T_c (K)

Material	T_c (K)
β_H -(ET) ₂ I ₃	1.5
k -(ET) ₂ I ₃	3.6
α -(ET) ₂ KHg(SCN) ₄	1.2
κ (ET) ₂ Cu[N(CN) ₂]Cl	13.1
κ (ET) ₂ Cu[N(CN) ₂]Br	11.6
κ -(ET) ₂ Cu(NCS) ₂	10.4
κ -(ET) ₄ Hg _{2.89} Cl ₈	1.8
κ_H (ET) ₂ Cu(CF ₃) ₄ ·TCE	9.2

Unfortunately, no further advancements have been made in the search for a higher critical temperature for quasi two dimensional organic superconductors. Even more superconductors can be found by changing the BEDT-TTF molecules slightly either by replacing the sulfur atoms by selenium (BEDT-TSF) or by oxygen (BEDO-TTF).

IV. FULLERENE SUPERCONDUCTOR

Superconducting fullerenes are fairly different from other organic superconductors were discovered in 1985[16]. C_{60} fullerene molecule composed of 20 hexagons and 12 pentagons has diameter of 0.7nm. The pure C_{60} grows in a fcc-lattice with a lattice constant of 14.17Å at room temperature [17].

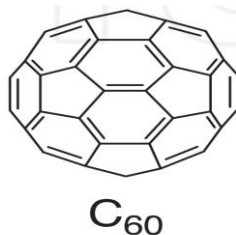


Figure 3 Fullerene superconductor

Fullerene molecules is highly electronegative and a three dimensional insulator with a band gap of 1.7 eV, but on doping with electron donating alkali metals[18] produces superconductivity with critical temperatures up to 40K. General formula for these superconductors is A_3C_{60} where A is an alkali metal. K_3C_{60} and Rb_3C_{60} show superconductivity with the onset T_c of 18K and 28K. $C_{60}I_4$ is the first example of a fullerene intercalation compound with no charge transfer. The highest measured transition temperature up to 1995 for an organic superconductor in Cs_3C_{60} pressurized with 15 kbar to be $T_c = 40$ K. Hole doped fullerenes exhibit higher critical temperature than electron doped fullerenes[19]. A hole-doped C_{60} superconducting system $C_{60}/CHBr_3$, exhibited very high critical temperature $T_c = 117$ K at ambient pressure is the greatest T_c for an organic superconductor achieved with a buckyball doped with holes and intercalated with $CHBr_3$ [8, 20]. Table 3 shows various fullerene derivative superconductors with their critical temperature. Unfortunately C_{60} crystals are not stable at ambient atmosphere. They are grown and investigated in closed capsules, limiting the measurement techniques possible. Superconducting phase was observed below 19 K for the potassium-doped compounds prepared by a vapor-solid reaction [21], immediately after the isolation of macroscopic quantities of C_{60} solid [22]. Superconductivity in alkali metal doped fullerene nanowhiskers ($C_{60}NWs$) was observed in $K_{3.3}C_{60}NWs$, $Rb_{3.0}C_{60}NWs$ and $Cs_{2.0}Rb_{1.0}C_{60}NWs$ with transition temperatures at 17, 25 and 26K respectively [23]. They showed large superconducting volume fraction, as high as 80%.

Table 3. Various fullerene derivative superconductors with their critical temperature

Fullerene derivative superconductors	T_c (K)
K_3C_{60}	18
Rb_3C_{60}	30.7
K_2CsC_{60}	24
K_2RbC_{60}	21.8
K_5C_{60}	8.4
Sr_6C_{60}	6.8
$(NH_3)_4Na_2CsC_{60}$	29.6
$(NH_3)K_3C_{60}$	28
$RbCs_2C_{60}$	33
Cs_3C_{60}	40
$C_{60}/CHBr_3$	117

The superconductivity has been observed for many M_3C_{60} (M: alkali metal), e.g., Rb_3C_{60} ($T_c = 29$ K [24]), Rb_2CsC_{60} ($T_c = 31$ K [25]), and $RbCs_2C_{60}$ ($T_c = 33$ K) [26]. The T_c varies monotonously with lattice constant, independently of the type of the alkali dopant.

V. POLYCYCLIC AROMATIC HYDROCARBON SUPERCONDUCTORS

The discovery of superconductivity above 30K in aromatic hydrocarbons has been an exciting event in condensed matter physics. Doping of alkali metals in picene has a wider band gap (3.3 eV) than 1.8 eV for pentacene, introduced superconductivity [27]. The bulk superconducting phase was observed at 18 K for K_3 picene (hydrocarbon consisting of five fused benzene). Considering the fact that $Ca_{1.5}$ picene also shows a superconducting phase below 7 K [28], three-fold charge transfer from dopants to one picene molecule would be responsible for emergence of the superconductivity. After the discovery of the picene-based superconductors, several superconductors have been found for alkali metal ($T_c = 7$ K) [29] and alkaline-earth metal ($T_c \sim 5.5$ K) [30] doped phenanthrene, potassium-doped 1, 2:8, 9-dibenzopentacene ($C_{30}H_{18}$) ($T_c = 33$ K; partially decomposed) [31], and potassium-doped coronene ($T_c < 15$ K) [25]. Among them, a phenanthrene-based superconductor shows an enhancement of T_c with increasing pressure, which is indicative of the non-BCS behavior. In particular Sm doped phenanthrene, chrysene and picene show superconductivity around $T_c \sim 5$ K [41]. The superconductivity in these systems cannot be explained by considering only the electron-phonon interaction [18].

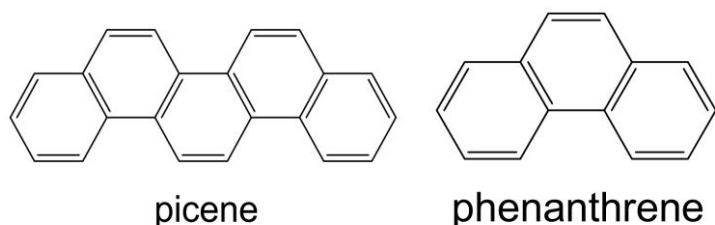


Figure 4 Hydrocarbon superconductor

VI. CARBON NANOTUBES SUPERCONDUCTORS

The first superconducting carbon nanotubes were discovered for ropes of single walled carbon nanotubes with diameters of the order of 1.4 nm ($T_c = 0.4$ K) [32], and immediately after that a single walled nanotubes with diameters of 0.4 nm embedded in a zeolite matrix ($T_c = 15$ K) [10,34] shows that the drop in magnetic susceptibility is more gradual than expected for three-dimensional superconductors, and superconducting gap estimated from the I-V plot shows the temperature dependency characteristic of one-dimensional fluctuations. It is apparent that the isolation of carbon nanotubes from each other is responsible for the realization of the almost ideal one-dimensional system. Multi-walled carbon nanotubes with diameters of 10–17 nm that were grown in nanopores of alumina templates was found to show superconductivity with $T_c = 12$ K [35].

VII. GRAPHITE SUPERCONDUCTORS

Graphite has a layered structure composed of infinite benzene-fused π -planes (graphenes) with sp^2 character. First-stage alkali metal doped graphite intercalation compound were known to superconduct with $T_c = 0.15$ K for KC_8 [36] and $T_c = 0.023$ K for RbC_8 .

Table 4: Graphitic superconductors with their critical temperature (T_c)

Materials	T_c (K)
CaC_6	11.5
$Li_3Ca_2C_6$	11.15
BaC_6	0.065
SrC_6	1.65
YbC_6	6.5
SrC_6	1.65
KC_8	0.14
RbC_8	0.025

Further efforts were poured to synthesize graphite intercalation compound with higher T_c , such as LiC_2 with $T_c = 1.9$ K [37]. The discovery of CaC_6 with T_c was found as high as 11.5 K at ambient pressure [38],

which goes up to 15.1 K under pressures up to 7.5 GPa [39]. The superconductivity in CaC_6 is due to an electron-phonon mechanism and carriers are mostly electrons in the Ca Fermi surface which couples with in plane Ca-Ca phonon and out of plane C-C phonons [40]. There is importance of Ca fermi surface for the superconductivity. The graphite $\text{Ca}_x\text{K}_{1-x}\text{C}_y$ [46] for $0.33 \leq x \leq 1$ shows $T_c \sim (6.5-11.5\text{K})$. In other alkaline-earth metal doped graphite intercalation compounds, the maximum T_c onset were 7.1K at 1.8GPa for YbC_6 [41], 2K at 1GPa for SrC_6 [42], and 1.7 K at 1.5 GPa for KC_8 . The graphite superconductor prepared by alkali earth or lanthanide atom are BaC_6 [45] with $T_c = 0.065\text{K}$. Table 4 shows graphitic superconductors with their critical temperature (T_c)

The pressure dependence is the characteristics of graphite superconductors. The apparent reduction of T_c strongly suggests that the interlayer states of graphite have an impact on the electronic state of graphite intercalation compound, which was supported by theoretical calculations [43]. Some binary elements intercalated graphite superconductors were realized such as RbHgC_8 ($T_c = 1.44\text{K}$), $\text{KT}_{1.5}\text{C}_4$ ($T_c = 2.7\text{K}$), $\text{CsBi}_{0.55}\text{C}_5$ ($T_c = 4.05\text{K}$) and $\text{Li}_3\text{Ca}_2\text{C}_6$ ($T_c = 11.15\text{K}$) [44].

VIII. BORON DOPED DIAMOND SUPERCONDUCTORS

Superconductivity in diamond was achieved through heavy p-type doping by boron with critical temperature $T_c = 4 \text{ K}$ [6]. Enhanced $T_c = 11\text{K}$ has been achieved in homoepitaxial CVD films [47]. Doped boron introduces an acceptor level with a hole binding energy of 0.37 eV and results in a metallic state above a critical boron concentration in the range of a few atoms per thousand. The T_c varies between 1 and 10 K with the doping level [48]. Superconducting gap estimated from STM [49] and isotopic substitution of boron and carbon [50] follow the BCS picture. Regarding the origin of superconductivity in diamond, three alternative theories exist at the moment: conventional BCS theory based on phonon-mediated pairing, correlated impurity band theory [51] and spin-flip-driven pairing of holes weakly localized in the vicinity of the Fermi level [52].

IX. SINGLE COMPONENT SUPERCONDUCTORS

There are two single-component superconductors under extremely high pressure, p-iodanil ($T_c \sim 2 \text{ K}$ at 52 GPa) [53, 54] and hexaiodobenzene ($T_c = 0.6-0.7 \text{ K}$ at around 33 GPa and 2.3 K at 58 GPa) [55].



Figure 5 One dimensional superconductor

The pressure dependence of resistivities of a single component molecular conductor Nickel bis (trifluoromethyl) tetrathiafulvalenedithiolate [$\text{Ni}(\text{hfdt})_2$], show that at the low temperature insulating phase was suppressed above 7.5GPa and resistivity dropped, indicating the superconducting transition occurred around 7.5-8.7 GPa with a maximum T_c (onset temperature) of 5.5 K with clear evidence that a single component molecular superconductor has been discovered [56]. Search for superconductivity in various materials [33] with increasing transition temperature is going on.

IX. CONCLUSION

Although the critical temperature of organic superconductors is still fairly modest, these materials have provided a wealth of new physical phenomena. Organic superconductor exhibits different contrasting properties which separate them from other superconductors. Bechgaard salts are structurally so different from metallic superconductors, that the standard explanation for superconductivity given by the BCS theory of Bardeen, Cooper, and Schrieffer does not apply very well, and as a result there is a lot of work to be done to understand the mechanism behind superconductivity in these materials. Organic superconductors provide good system to study the interplay of strong electron-electron and electron-phonon interactions in low dimensional system.

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