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Review Paper

Superconductivity in Organic Materials: A Fascinating Phenomenon

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Abstract

The organic superconductivity is a very interesting phenomenon. The highly anisotropy and other intriguing properties of organic superconductor (OSC) made them distinct from other superconductors. Due to hybridization, it does not leave any unfilled spots in the conduction and valence bands of organic molecules, as a result of which they normally act as insulator and do not exhibit the property of metals. Recent studies suggest that certain organic substances might be able to display metallic characteristics. 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. Recently, a number of hole doped fullerenes synthesized which shows superconductivity upto higher critical temperature i.e., 117K. So, replacement of non organic superconductors by these organic one may lead to various advantages accompanied with stability and durability. Further research in this area may lead to higher and higher Tc OSC. The present article reveals the phenomenon of organic superconductivity with its background, classes and applications.

Keywords: Fermi surface, superconductivity, cuprates, fullerene.

Introduction

Superconductivity is a fascinating and challenging field of science. Scientists and engineers throughout the world have been striving to develop an understanding of this remarkable phenomenon for many years. Superconductivity is being applied to many diverse areas such as: medicine, theoretical and experimental science, power production, electronics, as well as many other areas. In 1911 Kamerlingh and one of his assistants discovered the phenomenon of Superconductivity while studying the resistance of metals at low temperatures. They studied mercury which shows superconductivity at 4K. Till now, infinite researches have been done on nonorganic superconductor and right now, scientists have developed various cuprates superconductor having Tc upto 140K.

Organic Superconductor

An organic superconductor is an organic compound which exhibits superconductivity at low temperatures. The first organic superconductor, $(TMTSF)_2PF_6$ was synthesized by Klaus Bechgaard in 1980[1]. Here, TMTSF serve as electron donor and PF_6^- serve as electron acceptor. This discovery led to the creation of a wide range of related organic compounds, known as Bechgaard salts, which exhibit a vast array of unique properties. Following a 1964 paper by Little[2], it was hoped that organic conductors such as the Bechgaard salts would be high temperature superconductors, even superconducting at room temperature. However, Bechgaard salts have many other properties that make them very interesting subjects of research. For example, by varying both temperature and pressure, Bechgaard salts can be forced into almost any phase known to condensed matter physicists. Also, because Bechgaard salts are structurally so different from metallic superconductors, it seems 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.

Table-1
Various organic superconductor with their critical temperature

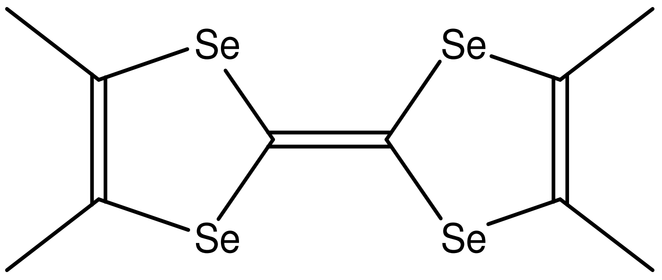
Organic superconductor	Critical temperature(Tc)
$(TMTSF)_2PF_6$	1.1K
$(TMTSF)_2ClO_4$	1.4K
$(BEDT\text{-}TTF)_2I_4$	3.3K
$\kappa\text{-}(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$	11.6K
β' $(BEDT\text{-}TTF)_2ICl_2$	14.2K
$\kappa\text{-}(ET)_2Cu[N(CN)_2]Cl$	13.1K
$RbCs_2C_{60}$	33K

Right now, the highest achieved critical temperature for an organic superconductor at ambient pressure is 33 Kelvin, observed in the alkali-doped fullerene $RbCs_2C_{60}$.

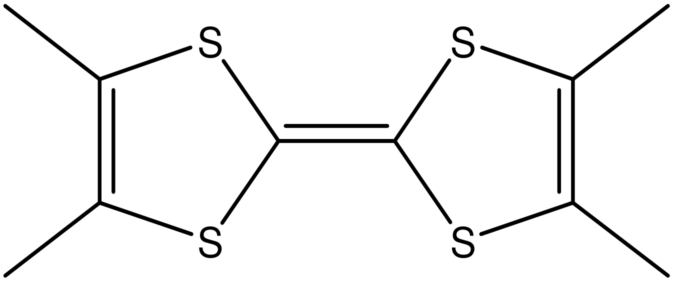
Classes of Organic Superconductors

There are four classes of organic superconductors on the basis of topology of fermi surface: i. Quasi one dimensional fabre- and Bechgaard-Salt, ii. Quasi two dimensional systems, iii. Doped Buckminster fullerene.

Quasi one Dimensional Bechgaard and Fabre Salt: Quasi one dimensional superconductor contains open Fermi surfaces and having 2 parallel planes. The first organic superconductors consisted of planar tetramethyltetraselenafulvalene (TMTSF) donors and monovalent anion acceptors with the general formula $(TMTSF)_2X$, where X is either an octahedral or tetrahedral anion such as PF_6-, AsF_6-, $SbPF_6$-, TaF_6-, NbF_6-, ClO_4-,or ReO_4-. These charge transfer salts, also known as the Bechgaard salts, consist of segregated, stacked sheets of donors and acceptors the TMTSF-salts are metals with a formally 3/4 filled conduction band[3]. Critical temperatures of 1-2 K have been reported for the Bechgaard salts. The critical temperature of a material (Tc) is the temperature below which a substance becomes superconducting. Only one Bechgaard-salt was found to be superconducting at ambient pressure which is $(TMTSF)_2ClO_4$[4] with a transition temperature of T_C = 1.4 K, while other salts become superconducting only under external pressure. The characteristic property of Bechgaard salt is their anisotropy which occurs primarily along the stacking axis of the donor molecules. The spacing between the molecules within a stack is smaller than the sum of the vander Waals radii of the Se atoms.



tetramethyltetraselenafulvalene



tetramethyltetrathiafulvalene

Scheme-1
Structures of TMTSF and TMTTF

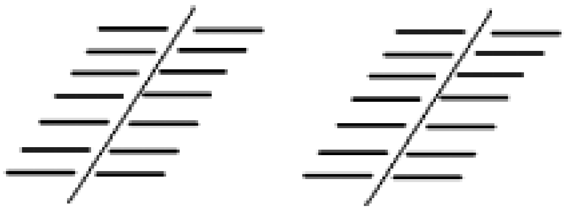


Figure-1
Donor stack interactions in a quasi 1D superconductor

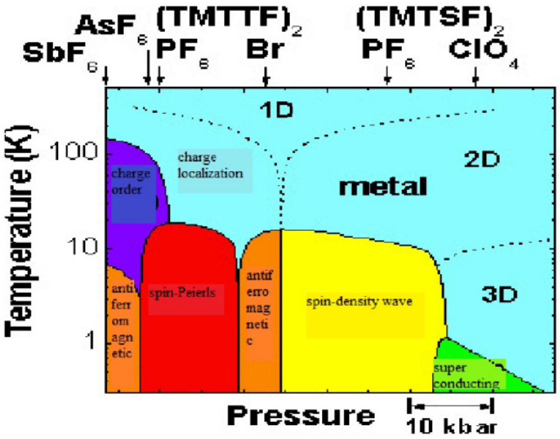
The molecules that comprise Bechaard salt are stacked into segregated sheets of electron acceptors and donors[5]. Due to their formation, electrical conductivity is extremely anisotropic. Conductivity is greatest along the axis upon which the donor molecules are stacked. Orbital overlap in each layer is poor and along the axis perpendicular to the stacking axis, electrical conductivity is reduced by several orders of magnitude. It is because superconduction can only occur along a single axis in Bechgaard salts that they are considered quasi-one dimensional materials.

Fabre-Salts are composed of tetramethyltetrathiafulvalene (TMTTF), for most of the Fabre-salts to show superconductivity there is requirement of external pressure[6]. The TMTTF-salts are metals with a formally 3/4 filled conduction band.

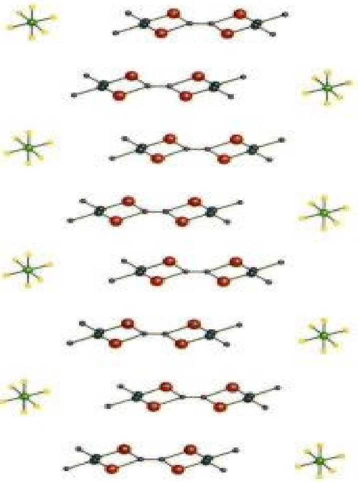
Table-2
Various Quasi one dimensional superconductors with their critical temperature

Organic superconductor (Fabre salt)	Tc(K)	Pex(Kbar)
$(TMTSF)_2SbF_6$	0.36	10.5
$(TMTSF)_2PF_4$	1.1	6.5
$(TMTSF)_2AsF_6$	1.1	9.5
$(TMTSF)_2ReO_4$	1.2	9.5
$(TMTSF)_2TaF_6$	1.35	11

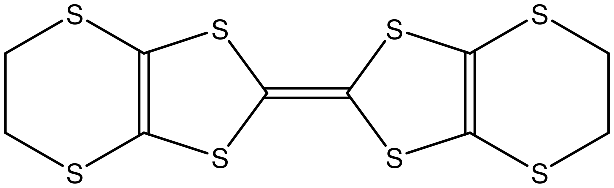
Quasi Two Dimensional Systems: In such superconductors, the Fermi surface is cylindrical and the conductivity is isotropic in the plane of donor molecule. It is a new class of organic superconductors. Here, a new donor BEDT-TTF [bis (ethylenedithio) tetrathiafulvalene][7], sometime abbreviated ET ,was 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[8]. These molecules form planes which are separated by anions. The requirement of external pressure for ET-salt is very small than those needed for Bechgaard-Salts.



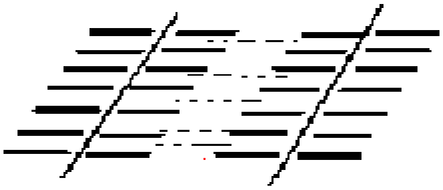
Phase diagram of $(TMTSF)_2X$ and $(TMTTF)_2X$.



$(TMTSF)_2X$-Structure: The planar organic molecules are stacked along the x-axis; in the z-direction they are separated by the X-anions



bis(ethylenedithio)tetrathiafulvalene
Scheme-2 (BEDT-TTF)



- - - - = S-S interaction

Figure-2
Donor stack interactions in a quasi 2D SC

The highest critical temperatures for the two dimensional charge transfer salts is $(ET)_2Cu[N(CN)_2]Cl$ (Tc= 12.8 K at 0.3 kbar)[9].

Doped Buckminster Fullerene: Fullerene is a 3 dimensional system; actually it is an insulator with a band gap of 1.7 eV, but on doping with alkali metals[10] produces superconductivity with critical temperatures up to 40 K. General formula for these superconductors is A_3C_{60} where A is an alkali metal. Superconductivity has also been observed in single-walled nanotubes with critical temperatures up to 15 K.

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.

Till now, the highest critical temperatures observed in organic superconductor in fullerene via a technique employing a field effect transistor to introduce charge or hole. Hole doped fullerenes exhibit higher critical temperature than electron doped fullerenes[11]. Recently, Schon et al. found a hole-doped C60 superconducting system $C_{60}/CHBr_3$, which exhibited very high critical temperature Tc = 117K at ambient pressure, it is the greatest Tc for an organic superconductor was achieved with a buckyball doped with holes and intercalated with CHBr3[12]. Field-effect doping exploits the fact that under a strong, static electric field, charge (electrons or holes) will accumulate at the surface of the material, effectively modifying the electronic density in that region. This type of doping avoids imperfections that cause the system to deviate locally[13].

Table-3
Various fullerene derivative superconductors with their critical temperature

Organic superconductor	Critical temperature(Tc) in K	Pex (Kbar)
K_3C_{60}	18	0
K_2CsC_{60}	24	0
$(NH_3)_4Na_2CsC_6$	29.6	0
Rb_3C_{60}	30.3	0
Cs_2RbC_{60}	33	0

Cs_3C_{60}	40	15
$C_{60}/CHBr_3$ (hole doped and intercalated)	117	0

It has been predicted that by hole doped and intercalated method very high Tc superconductor upto 150K can be develop. Some organic Superconductors have been predicted for being high Tclike $C_{60}/C_{12}H_{26}$, C_{60}/C_6H_5Cl, C_{60}/CHI_3 etc.

Applications

Organic superconductor may have higher advantage over nonorganic superconductor. For example, they have reduced weight and potential versatility having ability to modify their electrical attributes via chemical methods.

Current applications of high temperature organic superconductors include; magnetic shielding devices, medical imaging systems, superconducting quantum interference devices (SQUIDS), infrared sensors, analog signal processing devices, and microwave devices[14].

Some other uses of it include energy storage devices, particle accelerators, levitated vehicle transportation, rotating machinery, and in magnetic separators.

Conclusions

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. The discriminating property of p-triplet and d-singlet pairings and anisotropy are not explained by standard superconductivity theories. Final answers and explanations for these criminating properties should await more experimental studies.

Organic conductors gather most of the relevant problems in modern condensed matter physics. This 25 years old subject still holds a very promising future.

Acknowledgement

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References

1. Jérome D., Mazaud A. and Ribault M., Superconductivity in a synthetic organic conductor (TMTSF) 2PF6 (+), *J. Physique - LETTRES.*, **41**, 95-98 **(1980)**

2. Little W.A., Superconductivity at Room Temperature, *Sci. Am..,* **212**, 21-27 **(1965)**

3. Hackl R. and Hanke W., Towards a better understanding of superconductivity at high transition temperatures, *Eur. Phys. J. Special Topics.,***188,** 3–14 **(2010)**

4. Gabovich A.M., Voitenko A.I. and Ausloos M., Charge and spin-density waves in existing superconductors: competition between Cooper pairing and Peierls or excitonic instabilities*, Physics Reports.,* **367**, 583–709 **(2002)**

5. Bechagaard K., Jacobsen, Mortensen C.S., Pedersen K. and Thorup N., The Properties of Five Highly Conducting Salts: (TMTSF)2X, X=PF6-, AsF6-, SbF6-,BF4 and NO3-, derived from Tetramethyltetraselenafulvalene (TMTSF), *Solid State Commun.*, **33**, 1119-1125 **(1980)**

6. Jerome D., Organic superconductivity, *Physica B+C.*, **109(3**), 1447–1460 (1982)

7. Ersan Demiralp and William A. Goddard., Vibrational Analysis and Isotope Shifts of BEDT-TTF Donor for Organic Superconductors., *J. Phys. Chem. A.*, **102**, 2466-2471 **(1998)**

8. Senthil Kumar A.P., Karthikeyan P., Prabhu Raja V., Ramu M., Somasundharam S. and Vasudevan V., Empirical Correlation of Various Inclusions on the Effect of Primary and Secondary Parameters for Estimation of Effective Thermal Conductivity (ETC) of Two Phase Materials, *Res. J. Recent Sci.,* **1(1),** 22-32 **(2012)**

9. Williams J.M., Ferraro J.R., Thorn R.J., Corlson K.D., Geiser U., Wang H.H., Kini A.M. and Whangbo M.H., *Organic Superconductors (including Fullerenes)*; *Prentice Hall: Englewood Cliffs*, NJ. **(1992)**

10. Shukur Majid M., Kadhim F. Al-Sultani and Hassan Mohammed N., Preparation of Alkali Lead Glass and Glass – Ceramic Compositions as Electrical Insulators**,** *Res. J. Chem. Sci.,* **2(2**), 28-34 **(2012)**

11. Szasz A., Fullerene superconductivity by short-range order instability, *Journal Of Superconductivity*, **6(2),** 99-106 **(1993)**

12. Anju S.G., Jyothi K.P., Sindhu Joseph, Suguna Y. and Yesodharan E.P., Ultrasound assisted semiconductor mediated catalytic degradation of organic pollutants in water: Comparative efficacy of ZnO, TiO2 and ZnO-TiO2, *Res. J. Recent Sci*., **1(ISC-2011),** 191-201 **(2012)**

13. Senthil Kumar A.P., Karthikeyan P., Selvakumar B. Jagadheeshwaran M., Dinesh J. and Kandasamy, Influence of Density and Concentration on Effective Thermal Conductivity of two Phase Materials using Square Guarded hot plate Apparatus S., *Res. J. Recent Sci.,* **1(8),** 42-47 **(2012)**