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Organic Superconductors

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ABSTRACT

Superconductivity is a remarkable state of matter which does not have a clear explanation for the unconventional superconductors. This review focuses on organic superconductors, their properties, and proposed mechanism including the key ingredients for unconventional superconductivity. Most of the organic superconductors show a 2:1 stoichiometry; hence the carrier density of 0.5 is highlighted within this family. A New insulating state of Paired Electron Crystal (PEC), a mediator of the adjacent insulating state and the superconducting state, is introduced by the Hubbard model calculation for the strongly correlated electron-lattice systems. Also pointed out the coulomb enhanced pair-pair correlation compared to non-interacting limit is a signature for the superconducting state. The strong e-e correlation, a carrier density of 0.5 and the lattice frustration are the key ingredients for creating the spin singlets (PEC state) in strong electron systems such as the organic superconductors.

Key words: Organic superconductors, Hubbard model, Paired electron crystal

1. INTRODUCTION

Superconductivity (SC) is a fascinating state of matter discovered in the 20th century, which is having two main properties of zero resistance and diamagnetism (the Meissner effect). Superconductivity was first observed in mercury below a critical temperature (T_c) of 4.2 K by Kamerlingonnes in 1911 [1]. The BCS theory; this was the first satisfactory theoretical explanation of superconductivity. Basically, BCS theory describes a two-body interaction between either electrons or holes that leads to a Bose condensation of electron pairs (Cooper pairs) into a superconducting state. Coulomb repulsion between carriers of the same sign is overcome by an attraction mediated by vibration of the lattice, phonons. The formation of Cooper pairs follows the Pauli Exclusion Principle, so, two Cooper pairs can occupy the same wave-vector in momentum space. An energy gap (Δ) at the Fermi level, defined as the energy difference between lowest state of the quasi particle excitation and the superconducting ground state, is a signature of the superconducting state. For "conventional" superconductors, usually defined as those which can be well described by BCS theory, the energy gap is isotropic in momentum space. In 1986, discovered superconductivity in a perovskite structured lanthanum based cuprate at a T_c of 35 K [2]. This was the remarkable starting point for the High temperature superconductors (HTS). Later on, chemical substitutions in the cuprates lead to high transition temperature beyond the boiling point (77 K) of liquid nitrogen. A replacement of Lanthanum (L) by Yttrium (Y) gave $YBa_2Cu_3O_{7-x}$, which has an optimal T_c of 93 K [3]. Thallium and mercury base cuprates have T_c's of nearly 133 K [4]. Unlike the conventional superconductors, the BCS theory cannot explain the mechanism of high-T_c and other exotic superconducting materials. The superconductivity timeline (Figure 1) shows how much progress has been made in achieving high T_c's over the past 100 years. The black triangles represents the organic superconductors which are interested in this review. There are many more

superconductors synthesized other than the highlighted superconductors in this timeline. In 2015, sulfur hydride H_2S achieved a new record critical temperature of 203 K under the extremely high pressure of 150 G Pa [5]. They found enough experimental evidence for H_2S to be categorized under the conventional category, and this is the highest T_c record in this category. Theoretical interpretation suggests that the quantum behavior of hydrogen leads to such a high critical temperature [6].

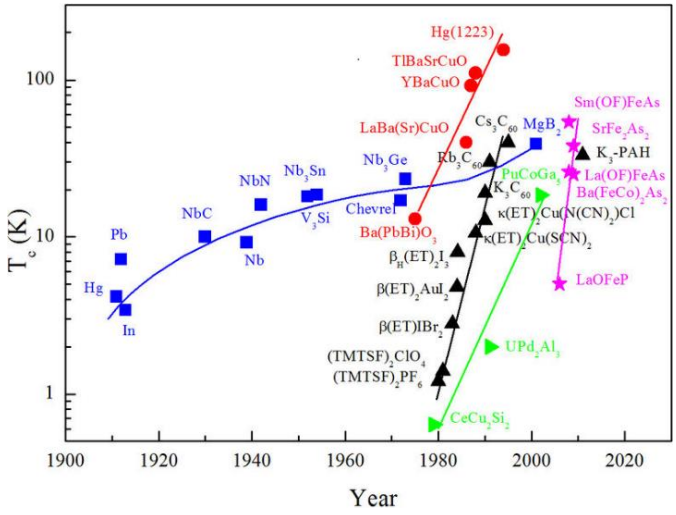

Figure 1: Superconductivity materials with their critical temperatures (T_c) and year of discovery.(D.Jerome, Superconductivity in New Materials, Volume 04)

2. ORGANIC SUPERCONDUCTORS

The investigation of organic superconductors with the intention of achieving a high T_c has been an active research area of modern condensed matter physics over the past thirty years. Organic superconductors show many strange phases and phenomena due to its properties of electronic correlations, dimensionality, and geometrical frustration. These properties can be tuned by magnetic field, temperature, and pressure.

The concept of moving electrons in a highly polarized organic polymers, proposed by W.A.Little in 1964 [7] was authorized to create room temperature superconductors. This idea had a strong impact on the synthesis of organic superconductors. Scientists have synthesized high conductivity organic materials that are quasi one dimensional (1D) and two dimensional (2D), in a novel research interface between Chemistry and Physics.

The first organic superconductor $(TMTSF)_2PF_6$ (bis-tetramethyl-tetraselenafulvalene-hexafluorophosphate $C_{10}Se_4H_{12}$ (abbreviated as TMTTF) was discovered with a T_c of 1.1 K under an external pressure of 6.5 kbar by K.Bechgaard, D.Jerome and other in 1979 [8]. Another two dimensional organic superconductor family was found based on the molecule BEDT-TTF (bisethylenedithio-tetrathia-fulvalene-$[(CH_2)_2]_2C_6S_8$ (abbreviated as ET)). $(ET)_4(ReO_4)_2$, was discovered as the first superconductor of the ET family with the critical temperature 2.0 K under an external pressure of 4.0 kbar in 1983 [9]. Both the $(TMTSF)_2X$ and $(BEDT\text{-}TTF)_2X$ are well known superconducting CTS families. The TMTSF and ET molecules have charge-carrying holes and the anions X have a closed shell structure [10].

2.1 Quasi 1D Organic Superconductors

The quasi 1D superconductor materials known as Bechgaard salts share the common formula $(TMTSF)_2X$. TMTSF molecules are stacked in columns along the a-axis which the highest conductivity occurs (Figure 2). $(TMTSF)_2X$ has 2:1 stoichiometry, and one electron is transferred from two TMTSF molecules to one X; therefore, the π band of TMTSF is ¾-filled. After the discovery of $(TMTSF)_2PF_6$, by replacing PF_6 by a variety of anion molecules, AsF_6, SbF_6, ClO_4, PF_4, ReO_4, and TaF_6, a series of superconducting materials was found. Among them, only $(TMTSF)_2ClO_4$ is superconducting at 1.2 K at ambient pressure with others superconducting under external pressure. Another 1D superconductor family of TMTTF (tetramethyltetrathiafulvalene) was discovered by replacing the Se in TMTTF by S (Figure 3-a).

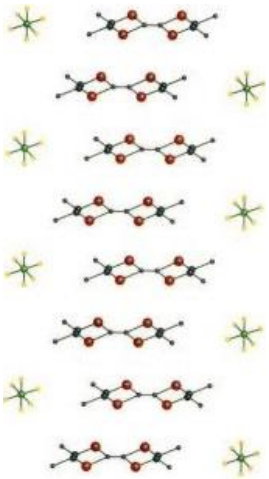

Figure 2: $(TMTSF)_2PF_6$ crystal structure [10].

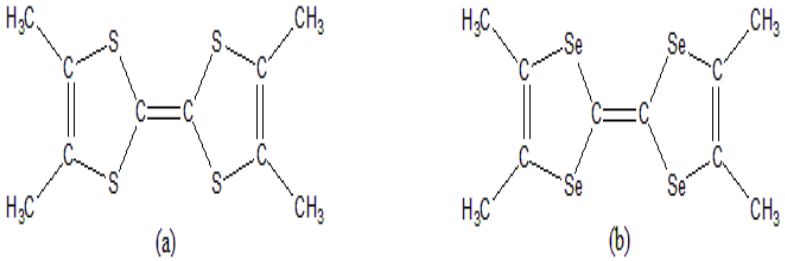

Figure 3: Molecular structure of the (a) TMTTF (b) TMTSF [10]

All the physical properties of TMTTF and TMTSF materials have been summarized in a temperature pressure phase diagram by Jerome et al. (see Figure 4). As an example, $(TMTSF)_2PF_6$ has a MI transition at around 10-20 K to a spin density wave (SDW) state as shown in Figure 4.These 1D organic materials serve as model systems for the study of spin-Peierls (SP) and SDW transition. It is speculated that magnetic ordering is related to the mechanism of superconductivity, since in the phase diagram these transitions occur in the vicinity of superconductivity.$(TMTTF)_2X$ lie on the low pressure side and $(TMTSF)_2X$ materials lie on the high pressure region in the phase diagram. Due to the changing external pressure or chemical pressure (due to different size anions), these materials have different ground state phases, including antiferromagnet (AFM), spin-Peierls, spin density wave, charge-order (CO), and superconductivity [8,11].

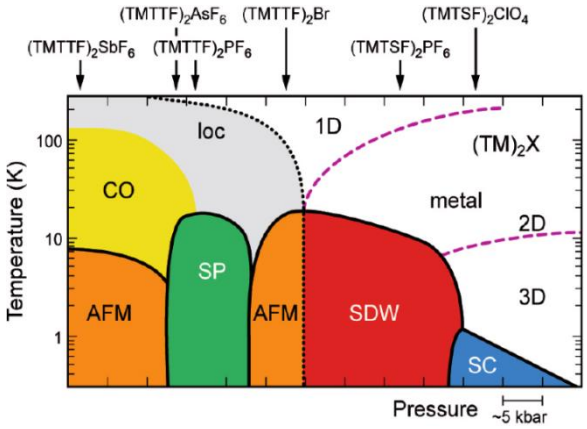

Figure 4: Phase diagram for TM salts.

2.2 Quasi 2D Organic Superconductors

Next generations of organic superconductors were discovered, based on the bisethylenedithio-terathiafulvalene (BEDT-TTF-abbreviated as ET) molecule as shown in Figure 5. The composition ratio of ET superconductors is 2:1 $((ET)_2X)$ with alternating layers of anionic X^- and cationic $ET^{+1/2}$ (Figure 5) whose π band is $\frac{3}{4}$-filled.

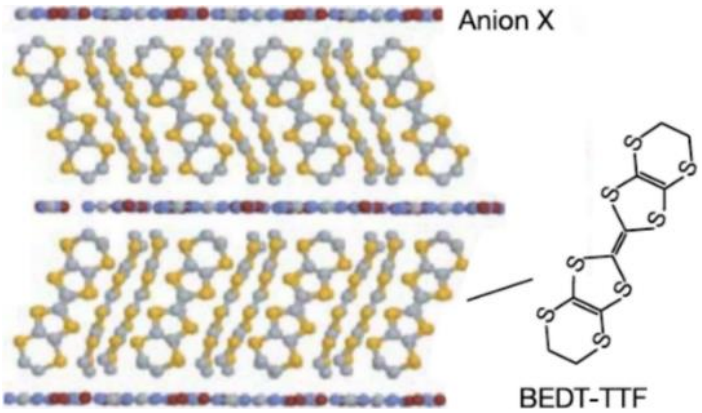

Figure 5: Layered crystal structure of the $(BEDT\text{-}TTF)_2X$ [10].

Increasing pressure tends to decrease the distance of adjacent molecules, so that the side-by-side overlap integrals between molecules are increased. The first ET superconductor, $\beta-(BEDT\text{-}TTF)_2ReO_4$ is superconducting under pressure of 0.4 GPa with T_c of 2 K [9]. Many anions (such as $I_3^-, Cu(NCS)_2^-, Cu[N(CN)_2]Br^-$, and $SF_6CH_2CF_2SO_3^-$) give different crystal structures with different electronic properties [10,12]. There is no universal phase diagram fits for all superconducting materials in the ET family due to their two dimensionality. Like the TMTTF/TMTSF materials, ET materials show several unusual ground states other than the superconducting state, such as antiferromagnetic, Charge Ordered, Quantum Spin Liquid (QSL), etc.

3. THEORETICAL MODEL

Many theoretical works contributed to the mechanism of superconductivity for different families of materials. Also all strongly correlated systems are not superconducting. Therefore it is very important to investigate the common ingredients for all correlated superconductivity other than strong e-e interaction.

Strongly correlated-electron systems are modeled using Hubbard Hamiltonian in Equation (1).

$$H = \sum_{\sigma=\uparrow\downarrow} \sum_{<i,j>} -t_{ij}\left(c_{i\sigma}^{\dagger} c_{j\sigma} + c_{j\sigma}^{\dagger} c_{i\sigma}\right) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V \sum_{<ij>} n_i n_j \qquad (1)$$

In Equation (1),t_{ij} is the transfer integral which shows kinetic energy of the electron via electron hopping between the sites. U and$V$ are local coulomb interaction and nearest neighbor interaction respectively. The fermionic operator $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$ are creation and annihilation of an electron at the site i with spin σ. $n_{i\sigma} = c_{i\sigma}^{\dagger} c_{i\sigma}$is the number operator for spin σ at site i. The order parameter of SC pair-pair correlations (Equation (2)) between two sites was calculated by solving this Hamiltonian. As an example *d*-wave pairing shown in Figure 6.

The equal time pair-pair correlation is defined as

$$P_{ij} = < \Delta\alpha_i^{\dagger} \Delta\alpha_j > \qquad (2)$$

The singlet pair creation operator ($\Delta\alpha_i^{\dagger}$) on site i is define as

$$\Delta^{\dagger}\alpha_i = \sum_v g(v) \frac{1}{\sqrt{2}} (c_{i,\uparrow}^{\dagger} c_{i+\bar{r}_v,\downarrow}^{\dagger} - c_{i,\downarrow}^{\dagger} c_{i+\bar{r}_v,\uparrow}^{\dagger}) \qquad (3)$$

In equation (3) $g(v)$ is the phase factor (+ or -), which is determined the pairing symmetry.

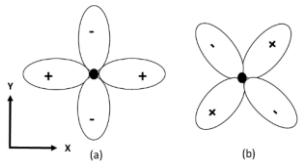

Figure 6: (a) $d_{x^2-y^2}$ pairing symmetry (b) d_{xy} pairing symmetry

Superconducting pair-pair correlations provide an accurate assessment of the presence of SC. Two criteria must be satisfied within this model if a SC state mediated by e-e interaction present (i) the pair-pair correlation must be enhanced by Hubbard *U* compared to *U=0*, and (ii) at $T = 0$, the pair-pair correlations must extrapolate to a finite value to indicate long range order [13].

In this review pointed out two ingredients responsible for many correlated-electron superconductors are (i) Carrier density (ρ) of 0.5 (electrons or holes is 1/2 per atom or unit cell) and (ii) Lattice frustration (t'). The materials which are satisfied these two ingredients show a strong tendency to arrange in a local spin-singlets. The formation of spin-singlets are the Bosonicpseudomolecules in Schafroth's theory of SC [14].

3.1 Paired Electron Crystals (PEC)

Clay *et al*. have introduced a novel spin singlet state known as Paired Electron Crystal (PEC). The density of 0.5 is the key requirement for the PEC state [11,15,16]. The formation of the PEC is independent of dimensionality, and driven by charge-spin-lattice coupling. Clay *et al*. showed that the formation of spin singlet in 1D, zigzag ladder and 2D triangular lattice [11,15,16,17,18].

The effect of frustration (t')(t' is a bond considered along x+y direction in a square lattice as shown in figure 7.) is investigated for a quarter filled ($\rho = \frac{1}{2}$) 2D square lattice with the parameters of finite U and V<Vc, using charge densities, bond orders, and spin-spin correlations [18]. The figures in real paper [18] show distortion of AFM order due to frustration and formation of local spin singlets.

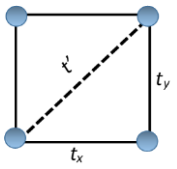

Figure 7: Frustration (t') introduced along the diagonal for a square lattice.

The numerical works of Clay *et al*. showed that d_{xy} and $d_{x^2-y^2}$pair-pair correlations are enhanced for frustrated triangular lattice systems at the $\rho \sim 0.5$ as shown Figure (8) [13]. Frustrated triangular lattices describe 2D CTS like $(BEDT\text{-}TTF)_2X$ materials. The numerical calculations on 32 and 64 site frustrated triangular lattices for κ-$(ET)_2Cl$ and κ-$(ET)_2CN$ [19] confirmed that this pairing enhancement of superconductivity is not related to the presence of AFM order and QSL in these two materials respectively

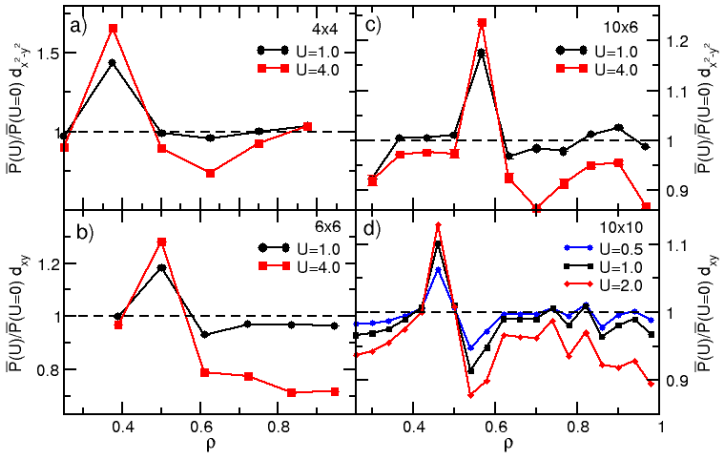

Figure 8: Coulomb - enhanced pair correlations as a function of σ for anisotropic triangular lattice systems [13].

4. CONCLUSIONS

Organic superconductors, a subset of the strongly correlated electron superconductors, were studied to understand the mechanism of superconductivity using advanced numerical calculation. Clay *et al.* found that key ingredients of (i) the strong e-e interaction (ii) the carrier density exact/near 0.5 and (iii) the frustration are responsible for the PEC state which shows spin-singlet pairing. The unified state of PEC was introduced, where the superconducting state in CTS is mediated by a coupled charge-spin and independent from the adjacent semiconducting state.

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