The unconventional riddle of paired electrons

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Iron based superconductor (FeSC) was discovered in 2008 as a new member to the group of unconventional high-temperature superconductors. Its discovery was first expected to put an end to the decades-long unsolved mystery of cuprates, but turned out to provide more questions than answers. The story of FeSC is not complete without mentioning cuprates and the story of cuprates begins with conventional superconductors. The purpose of this report is to equip the readers with the essential background to appreciate the complexity of this fascinating material, and what it means to our understanding about superconductivity.

Unconventional, literally implies there is something conventional. And knowing that "conventional" means electrons can attract each other, how mind-blowing can this unconventional world be? This report will follow the trajectory of how the scientific community gradually acquired the knowledge about superconductivity, from conventional superconductors to cuprates, and finally the Iron-based superconductors.

1. THE LIMIT OF THE CONVENTIONAL THEORY

Conventional superconductivity refers to the formation of Cooper pairs mediated by phonon-electron interactions as described by the BCS theory established in 1957 [1]. This is the first complete theory of superconductivity (although now almost taken for granted) after decades of extensive search for the mysterious attractive force that can overcome the electrons' repulsive coulomb potential. This is a fairly weak interaction that makes simple metals superconduct at no more than a few kelvin. The theory suggests that the superconductivity transition temperature T_c is proportional to Debye phonon frequency and electron-phonon coupling strength. However, clearly this interaction has a ceiling: the Debye frequency is inversely proportional to the mass of the ions, and the lightest possible ion would be metallic hydrogen[2]. The theory hence implies that materials with heavier ions are unlikely to have a high T_c if it is mediated by phonon.

1986 has been an unusual year for condensed matter physicists when the researchers at the IBM Research Laboratory reported a strange ceramic that can superconduct at the highest possible temperature that was then known: 30K[3] . The years that followed, several laboratories across the world discovered a family of similar materials with the record T_c at 164K under pressure[4]. Theoretical calculations all point to the same conclusion: phonon-electron coupling is no longer adequate. A new explanation needs to be established. This marks the beginning of the search for the unconventional theory of superconductivity.

2. THE CUPRATES FAMILY

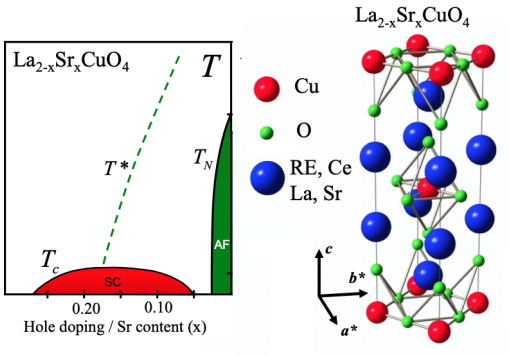

FIG. 1. (Right) Crystal structure of $La_{2-x}Sr_xCuO_4$. When x=0, the blue ions between the Copper-oxide layers are purely La^{3+}. To dope the compound with holes, some La^{3+} ions are replaced by Sr^{2+}. For each La^{3+}being replaced, an electron is removed from the p-orbital of oxygen (shown as light green), hence creating "holes". (Left) Schematic phase diagram as a function of hole doping. T_c is the transition temperature for superconductivity, T_N the AFM phase, T^* the pseudogap region [5]

Cuprate certainly is an unlikely candidate of superconductor for an obvious reason: it does not conduct electricity. To make it even more unusual: it is a Mott insulator, which means it would otherwise be a conductor, but the onsite repulsion is so strong that only one spin is allowed per site in an antiferromagnetic order (AFM), the energy band is completely filled in the reduced-Brillouin zone and hence an insulator. The family of cuprates shares a similar quasi-2D structure: layers of copper-oxide on a flat plane between inactive spacer ions. The Copper-oxide layer is believed to be responsible for superconductivity, while the spacer ions are charge reservoir and can be substituted for doping. Fig.1 shows a simple hole-doping example of La_2CuO_4 [6].Without doping, the Copper-oxide layers are separated by La-ions. The oxygen's p-orbital is completely filled, leaving one valance electron on Copper's $3d_{x^2-y^2}$ orbital per site. By substituting La^{3+}

with Sr^{2+}, holes are "doped" into the compound and spread over the p-orbitals of oxygen. Hopping of the holes will disturb the AFM order. As a result, the dynamics between the mobility of holes and the antiferromagnetic correlations can change the electronic property of the compound.

The ability to manipulate the material's property by doping is common among high-T_c superconductors. Therefore the phase diagram is usually represented as "temperature-vs-doping". For cuprates, the AFM phase is believed to be competing with the superconducting phase. When optimally doped, the AFM phase is suppressed and superconductivity emerges.

3. THE CUPRATES' ODD COUSIN

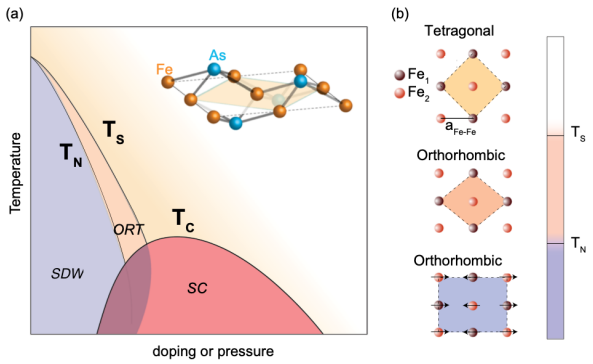

FIG. 2. (a) (Top) Superconducting layer of FeSC, Fe is bonded with As in a tetragonal structure, with the As-ion either being above or below the Fe-ion plane. (Bottom) Schematic phase diagram of FeSC. T_N: transition temperature to the spin density wave phase (SDW). T_S: tetragonal to orthorhombic structural change (ORT), together with a nematic phase change. T_c: superconducting phase. In the dark purple region in the middle, all phase can co-exist. (b) There are 2 Fe-ions in a unit cell. Below T_S the unit cell changes from tetragonal to orthorhombic. Below T_N a long-range magnetic order emerges: antiferromagnetic order from left to right; ferromagnetic order from top to bottom [7]

In 2008, more than 20 years after discovering the cuprates without solving the riddle, the scientists saw a new hope in the discovery of another high-T_c superconducting material that at-first-glance showed striking similarities to the cuprates [8]. The Iron-based superconductors (FeSCs) has a similar layered structure. Analogous to the superconducting Copper-oxide layer in cuprates, FeSCs consist of iron bonded with either group 15 pnictogen (arsenic) or group 16 chalcogens (selenium), on a buckled instead of a flat plane (Fig.2 a (top)), between the inactive spacer ion layers. The phase diagram of FeSCs also shows a superconductiviting phase next to a magnetic order phase (Fig.2 a (bottom)). Without doping, the parent compound of FeSCs is a metal, despite being a bad one. Nonetheless it may imply the coulomb repulsion between electrons is weaker than that of cuprates, making it an easier problem to solve, or is it?

4. IRON-BASED SUPERCONDUCTORS

As it turns out, the physics of FeSCs is far richer than it seems. First of all, the orbital in cuprates that is responsible for the electronic state near the fermi surface is almost certainly $3d_{x^2-y^2}$ on the Copper ion. However for FeSC, all 5 of the 3d orbital of Fe-ion contributed differently. Magnetic order of the Iron compound added another dimension to the complexity (Fig.2a). When the temperature is above T_S, the compound is paramagnetic. When it is cooled below T_S, a tetragonal-to-orthorhombic structural change is accompanied by a nematic phase. It means that the spins have a tendency to align with their neighbours but the direction can change. As a result the rotational symmetry is broken but the magnetization is still zero. The origin of the nematic transition is not known and is an active area of debate. When the temperature falls below T_N, a long range magnetic order is formed in the SDW phase (Fig.2b). The SDW, nematic and superconducting phase can coexist, making it unclear what is the role of the long range magnetic order to superconductivity. It is noteworthy that unlike the case of cuprates where doping certainly happens in the inactive spacer ion layer, doping in FeSC can substitute the Fe ion in the superconducting layer as well. The substituted "dopants", apart from being passive charge carrier donors, can potentially change the compound's electronic structure or dilute the magnetic spin, making it challenging to fully understand its effect [9].

5. THE GAP FUNCTION AND SUPERCONDUCTIVITY

To proceed with the discussion of how strong repulsion between electrons in high T_C superconductors can lead to formation of Cooper pairs, we need to go back to the original BSC theory and get a deeper understanding of the gap function. Recall the BCS Hamiltonian constructed from a fermi gas model. A pair of electrons with opposite momentum close to the fermi surface can condense into Cooper pair and lower their energy. The energy difference can be interpreted as the Cooper pair binding energy, which also serves as a self-consistent condition for the Hartree-Fock approximation.

$$\Delta_k = \frac{1}{2V}\sum_{\vec{k}'} V_{\vec{k},\vec{k}'}\,\langle\psi_o|c_{-\vec{k}'\downarrow}c_{\vec{k}'\uparrow}|\psi_o\rangle \tag{1}$$

$$\langle\psi_o|c_{-\vec{k}'\downarrow}c_{\vec{k}'\uparrow}|\psi_o\rangle = -\frac{\Delta_{\vec{k}'}}{E(\vec{k}')} \tag{2}$$

$V_{\vec{k},\vec{k}'}$ is the Fourier transform of the attractive interaction between the electrons. It is assumed to be small and independent to $\vec{k}$ and hence $V_{\vec{k},\vec{k}'} = -V_o$, where V_o is positive. This gives:

$$\Delta = \frac{\hbar\omega_D}{sinh\frac{1}{V_o N(\mu)}} \tag{3}$$

ω_D is the Debye frequency and $N(\mu)$ is electron density. Instead of binding energy, Δ is more often called the gap function. Look at what happens at the Fermi surface.

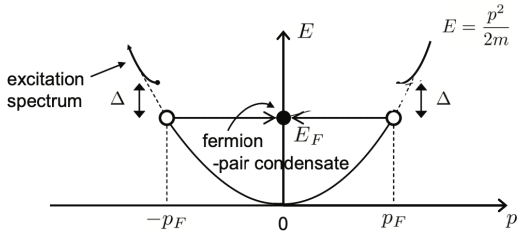

FIG. 3. A pair of electrons with opposite momentum close to the Fermi surface condense into Cooper pair with zero total momentum. The formation of Cooper pair lower their energy, resulting in a gap at the Fermi surface of the size Δ. This is the reason why superconductivity is sometimes referred to as "Fermi surface instability"

Conventional superconductivity refers to a gap function just like equation (3): postive and independent to $\vec{k}$. Is it therefore called the "S-wave" making reference to its spherical symmetry.

We can plot the wavefunction of Cooper pair from conventional superconductivity, see Fig. 4:

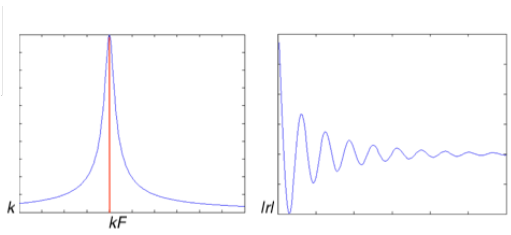

FIG. 4. (Left) Wavefunction of Cooper pair in momentum space $\psi(k)$ is a sharp peak at k_F. (Right)Wavefunction of Cooper pair in real space $\psi(|r|)$. $|r|$ is the distance between the pair. Note that the amplitude is maximum at $|r| = 0$.[10]

What conventional superconductivity actually suggests is that the screening of the coulomb repulsion is the result of retardation in time. The electrons in simple metals are loosely bound (hence Fermi "gas") and can move much faster than the ions. After an electron moves away from a location, the lattice stays polarized and attracts another electron to occupy the same site. It can be seen from the wavefunction of Cooper pair in (Fig.4) is non-zero at the origin. The electrons can occupy the same space because they avoided each other in time. But this mechanism almost certainly does not work for unconventional superconductors. Their electrons are more localized, and hence move at the similar time scale as the lattice. But it turns out, phonon is not the only way to bind electrons together. Interestingly, the theoretical framework was already established in 1965 which states that a stronger, but repulsive interaction can also do the job under one condition: the gap function changes sign [11]. Equation (3) is derived using a Fermi gas model, under the assumption that V_o is small and positive. The generalization of BCS theory to lattice models with more complex pairing mechanism is beyond the scope of the report. But we can follow the logic by asking a hypothetical question: what does equation (3) look like if V is strong and repulsive, can we get a Δ_k that is negative?

It is often helpful to visualize the gap function by plotting it out on a 2D Brillouin-zone (Fig.5).

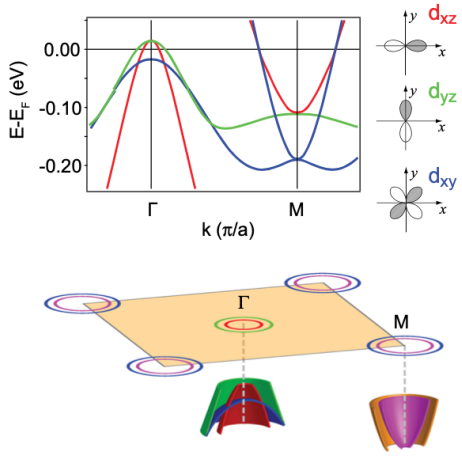

FIG. 5. (Top) Band structure of FeSC. Γ is located at (0,0) of the BZ; M at $(\pi, 0)$ and $(0, \pi)$. When temperature is below T_C, a gap opens at the Fermi level. A horizontal cut at Fermi energy therefore gives information about the location of the gap in momentum space. (Bottom) This graph is often seen in literature. It shows the location of hole-pocket and the electron-pocket of FeSC. The hole-pocket (at Γ) refers to an energy band shaped like a dome that crosses the Fermi level: a small area in k-space that is not occupied by electrons (hence occupied by holes). Vice versa for "electron pockets" [7]

The gap function gives several crucial information about the pairing mechanism 1) if $\Delta_{\vec{k}}$ changes sign at some $\vec{k}$, it indicates a repulsive interaction. 2) The relative location of the hole and electron pockets gives hints about how the charge carriers can interact. 3) the symmetry of the gap function inherits the symmetry the the lattice and the Cooper pair wavefunction. For example, if the gap function of FeSC is conventional, it would look like Fig. 6.

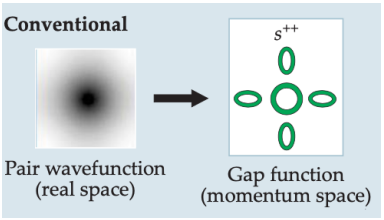

FIG. 6. The gap structure of FeSC being conventional S-wave, the corresponding wavefucntion of the Cooper pair is non-zero at the origin (non-zero probabiliy for the electrons to be at the same location). S^{++} means both the hole and the electron pocket are of the same sign [12]

It is considered an unlikely solution for a system with strong electron-electron repulsion, because it indicates a high probability for the electrons to be close to each other. This arrangement is less likely to be stable. Now consider unconventional gap functions.

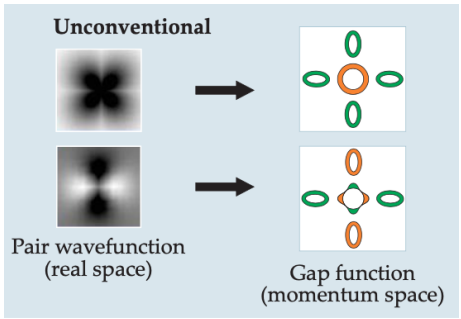

FIG. 7. Unconventional gap structure (Top) s^{+-} channel. It means the gap has rotational symmetry, but the electron and hole pocket has different signs. (Bottom) $d_{x^2-y^2}$ channel refers to the lower rotational symmetry. The gap changes sign every 90^o rotation. Note that the pair wavefunction has the same symmetry as the gap function [12]

As shown in Fig.7, repulsive pairing interaction is possible only when the gap function changes sign in the BZ because it corresponds to the Cooper pair wavefunction that is zero at the origin. It eliminates the probability of electrons being at the same location and hence avoids repulsion. One of the possible interaction is mediated by spin. It is analogous to electron polarizing the lattice in phonon-mediated pairing. Electron can also polarize the spin of the electrons around it, resulting in magnon-mediated pairing. This interesting mechanism has been discussed in detail in literature. Curious readers can refer to [6] and [13] for good overview.

6. THE CHALLENGES

Cuprates are now commonly believed to have a d-wave gap determined by a series of phase sensitive experiments [14]. However, determining the features of FeSCs' gap function is a surprisingly difficult task. Unlike cuprates that show relatively consistent properties within the family, different members of the FeSC family can have different gap symmetry. In fact, even for the same compound, some believe different doping can change the gap structure as well. This can be attributed to FeSCs' multi-band structure, or "orbital degree of freedom"[7]. As mentioned earlier, for cuprates there is only one band crossing the Fermi surface, corresponds to the $d_{x^2-y^2}$ on Copper. For FeSCs, as shown in Fig. 5, 3 bands correspond to the d_{xz}, d_{yz} and d_{xy} orbitals on Iron are close to the Fermi surface. Experimentally it is challenging to distinguish the effect of individual bands. It is also stretching the limit of theoretical calculations and modeling. This added degree of freedom creates a lot of possibilities in gap symmetry, pairing mechansim and doping that is not observed in cuprates, waiting for scientists to explore.

7. CONCLUSIONS

First introduced as a close cousin to cuprates, FeSCs have demonstrated to be a unique class of their own. Their research value does not reside on the race of higher superconducting transition temperature. In fact, their non-universality on one hand creates challenges, on the other hand opens up opportunities beyond what cuprates' (relatively) simple single band one-orbital structure can provide. What FeSCs bring to the scientific community is the extended views towards superconductivity. They coordinate efforts among experimentalists, theorists and computational physicists to find a way out of the fascinating unconventional riddle of paired electrons.

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