Superconductivity and Electron-Hole Superconductivity

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Abstract - After the discovery of superconductivity, it took some time to decide as to how very large currents of the order of $10^5$ Amperes start flowing when the temperature of the specimen is lowered in the limit $T \to 0$ K. Bardeen, Cooper and Schrieffer proposed a theory (BCS) based on the formation of Cooper pairs in which two electrons with spin and momentum in the opposite directions formed in which the exchanged phonon energy $\hbar \omega_p$ has to be more than the electronic energy states involved in the formation of Cooper pairs. The BCS theory could explain the properties of conventional superconductors and there was no mention of holes in the theory. Later studies, both theoretical and experimental, led to the conclusion that there exist holes that can form pairs like the Cooper pairs, and it is the holes that are responsible for superconducting currents in a variety of superconductors. Thus, we have tried to present a comparative analysis of what was conventional superconductivity and the hole superconductivity, along with the electron – hole superconductivity.

Keywords - Superconductivity, Cooper pairs, Phonon, Hole

I. INTRODUCTION

Superconductivity and superfluidity are two phenomena that were discovered unexpectedly in the last century. It took a few decades to understand the phenomena, and then to describe them within the fundamentals of microscopic theory.

Superconductivity was discovered in 1911 by Kamerlingh Onnes [1] in Leiden, Holland. He was studying the properties of frozen mercury when he found that at a temperature lower than $T_c = 4.15$ K, the electric resistance of mercury becomes zero, and this happens suddenly when the temperature is lowered below $T_c$. Currents of the order of $10^5$ amperes can flow through the materials in the superconducting state. A number of pure metals, alloys and doped semiconductors were found to have this property.

In 1933, W. Meissner and R. Ochsenfeld [2] discovered that a metal cooled in the superconducting state in a weak magnetic field (a metallic sample in a weak magnetic field is cooled to the superconducting state) expels the field from its interior. The relationship between the magnetic flux $\Phi$ and the magnetic field $\mathbf{H}$ is given by,

$$\Phi = M(1 + 4\pi \chi)$$  \hspace{1cm} (1)

where $\chi = -\frac{1}{4\pi} \frac{M}{\Phi}$ is the magnetic susceptibility (ability of the magnetic field to get through the material) and $M$ is the intensity of magnetization.

Flux exclusion in the superconducting state means $\Phi = 0$, for $T = T_c$, where $T_c$ is the transition temperature to the superconducting state. Eq. (1) then gives

$$\chi = -\frac{1}{4\pi}$$  \hspace{1cm} (2)

where $\chi$ is negative, a condition for a system to be in the diamagnetic state. Hence, such superconductors are diamagnetic. This is called Meissner effect.

The development of the microscopic theory of superconductivity took about 50 years. Still this long period was not sufficient to understand the key physical ideas that may constitute the microscopic theory of superconductivity. Along with the Meissner effect, another physical idea is that the current density $\mathbf{J}$ becomes very large, and the conductivity $\sigma \to \infty$ (infinity).

The current density is given by

$$\mathbf{J} = \sigma \mathbf{E}$$  \hspace{1cm} (3)

where $\mathbf{E}$ is the electric field inside the superconductor. For $\sigma$ to be infinity, eq. (3) gives that $\mathbf{E} = 0$ inside the superconductor. According to Maxwell’s equations

$$\frac{d\mathbf{B}}{dt} = -c(\nabla \times \mathbf{E}) = 0$$  \hspace{1cm} (4)

which means that $\mathbf{B} = \text{constant}$ inside such a material. According to Meissner effect, this constant could be zero. Since $\sigma \to \infty$, a ring of superconducting material could contain persistent electrical currents for years. The ratio of the resistance of the material in the normal state, $R_n$, to the resistance in the superconducting state, $R_s$, is of the order of

$$\frac{R_s}{R_n} < 10^{-15}$$  \hspace{1cm} (5)

The appearance of the superconducting state is accompanied by some drastic changes in the thermodynamic and thermal transport properties of a superconductor.

An important physical idea was proposed for pairing of electrons due to the presence of an attraction between the electrons by L. N. Cooper in 1956 [3]. There are two main
components of this idea. One is the source of attraction between electron pairs and the other is the possibility of formation of a bound state even with weak attraction. It was proposed that the quantized elastic vibrations of the ions, called phonons, mediate between the electrons leading to attraction between the electrons. The two electrons form a bound pair by the virtual exchange of a phonon between the electrons. If one electron is in the energy state $\varepsilon_{k1}$ and the other is in energy state $\varepsilon_{k2}$, then whenever $|\varepsilon_{k1} - \varepsilon_{k2}| < \hbar \omega_q$, the interaction between the pair of electrons will be attractive and it will form a bound pair. Here, $\hbar \omega_q$ is the energy of the phonon that is exchanged between the two electrons.

Another important experimental observation was the change of the transition temperature $T_c$ to the superconducting state when the superconductor is made of different isotopes. This is called isotope effect. Phonon frequency $\omega$ of energy $\hbar \omega$ depends on the mass of the particle or oscillating isotope, and since $T_c$ depends on isotopic mass, it is firmly established that the interaction (attraction) between the electrons is caused by phonons. However, the attraction is weak and the electrons are paired near or on the Fermi surface $\varepsilon_F$. The problem then reduces from three dimension to two dimension.

For practical applications of superconductors, the temperature of transition, $T_c$, to the superconducting state is very important. According to the BCS (Bardeen – Cooper – Shrieffer) theory, which is a complete microscopic theory of superconductivity [4], the critical temperature of transition to superconducting state is determined by the value of the electron pairing potential. In conventional superconductors, also called the BCS superconductors, electron pairing is a consequence of virtual exchange of phonons which are one type of quasi – particles. Pairing can also take place between the electrons by the exchange of other types of quasi – particles, such as plasmons. Different types of pairing were studied extensively theoretically for many years [5], but these studies could not result in the creation of new superconductors with high critical temperatures $T_c$. The experimental and theoretical studies on various high – temperature superconductors are being done, but the exact mechanism responsible for the electron pairing in such superconductors is not exactly known. The discovery of a new class of superconductors in 1986 [6], called the high – temperature superconductors led to the idea of some new type of pairing that may lead to high value of $T_c$.

It was in 1978 that John Bardeen expressed his convictions and intuition on the problem of high - temperature superconductors (HTS). His views were like this; ‘In view of the large number of experiments that have been done and the wide variety of materials tested, many have been pessimistic about the prospects of finding excitonic superconductivity. Whereas experiments do show that the conditions for observing it must be very exciting, they do not rule it out. The potential importance of high temperature superconductivity is so great. I feel that the research should be pursued vigorously even though the prospects of success may be small’. Ultimately, Bardeen’s view was correct, and when the ‘thunder struck’ in 1986 – 87, HTS was finally discovered.

II. CHARACTERISTICS OF HIGH – TEMPERATURE SUPERCONDUCTORS

The discovery of high – temperature superconductors in the initial stages was done via copper oxide based materials, such as Yttrium – Barium – Copper – Oxide (YBa – Cu – O, $T_c = 90K$) [6], Bismuth – Strontium – Calcium – Copper – Oxide (Bi – Sr – Ca – Cu – O, $T_c=105K$) [7] and Thallium – Barium – Calcium – Copper – Oxide (Tl – Ba – Cu – O, $T_c=110$ K) [8]. The three main characteristics of high – $T_c$ superconducting copper oxides are: (i) strong correlation on copper (ii) the well-known anisotropy (iii) large electron – phonon coupling.

A number of theories were proposed to explain the properties of HTS, but so far no successful theory is available. It is well known by now that in most of the high $T_c$ superconductors, Cu – O layers are sandwiched between layers of other materials [9]. For such superconductors, the charge carriers are electrons and the pairing mechanism between the electrons is exotic, that is the electron pairing is without any exchange of phonons as is the case in BCS (Bardeen – Cooper – Schrieffer Theory). In exotic superconductors, three electrons take part in the superconducting current and they interact with each other through harmonic forces [10]. Calculations showed that the high frequency vibrations of the apical oxygen atoms contribute to exotic pairing, and that exotic pairing and electron hopping affect the phenomena of transition to superconductivity.

III. HOLES IN THE NORMAL AND SUPERCONDUCTING STATE

1. Definition of a hole.

A hole is an electric charge carrier with a positive charge, equal in magnitude but opposite in sign to that of the charge on an electron. It is a massless quasi – particle with effective positive charge. It is also defined as absence of an electron in a particular place in an atom. Holes are created by the excitation of an electron and we can have electron – hole pairs just as in semiconductors.

2. Dressed holes in the Normal State.

Holes under the influence of electron – ion interaction are called dressed holes in the normal state.

3. Undressed holes.

Holes that are not under the influence of electron – ion interaction become undressed from the electron – ion interaction and behave like undressed carriers in the superconducting state. There is enough experimental evidence to show that dressed hole carriers in the normal state become undressed electron carriers in the superconducting state [11]. How this happens can be understood in the following experimental set up. For instance, if a superconductor rotates in a uniform manner with angular velocity $\omega$, then it develops a uniform magnetic field, $H$, in the interior of the superconductor [12] such that

$$H = -\frac{2 \pi e}{c} \omega$$

where $c$ is the velocity of light, $m$ is the mass of free electron and $e$ is the charge on the electron. This magnetic field has been measured for conventional superconductors [13,14], for heavy fermion superconductors [15] and high – $T_c$ cuprate superconductors [16,17]. The magnetic field direction is always
parallel to the angular velocity as shown in eq. (6). It is never anti-parallel to \( \omega \), showing that the superfluid / superconducting carriers are negatively charged carriers [18]. This is what happens when a superconducting system is rotating.

If on the other hand, a magnetic field \( H \) is suddenly applied to a superconductor at rest, then the whole body of the superconductor starts rotating with angular momentum \( L_e \), such that,

\[
L_e = \frac{mc}{2\pi} U H
\]

where \( U \) is the volume of the superconductor [12]. The direction of the angular momentum is always antiparallel to the applied magnetic field \( H \).

Another quantity of importance is Bernoulli potential. Such a potential is created due to creation of electric field when there is spatial variation of superfluid velocity. The expression of the electric field is

\[
E = \frac{1}{2} V \left( \frac{m e v}{\varepsilon} \right)
\]

where \( v_s \) is the superfluid velocity. The sign of the measured Bernoulli potential corresponds to negative charge carriers [13]. The study of Hall co-efficient also shows that the charge carriers change from hole – like to electron – like charge carriers in the superconducting state [14]. In general, Hall co-efficient is positive in the normal state and this is due to hole carriers [15]. But its sign changes from positive to negative at temperatures somewhat below the transition temperature \( T_c \) (transition from normal to superconducting state), and this shows that the charge carriers change from hole – like to electron – like in the transition from normal to superconducting state.

The above mentioned experimental observations and some of the theoretical considerations emphatically confirm that, the carriers of the electric current in the normal state (dressed hole carriers) transform into undressed electron – like carriers in the transformation from normal to the superconducting state.

By now, it is well known that many of the significant electronic properties of the high – \( T_c \) cuprate superconductors depend on the number of charge carriers put into the copper – oxygen planes (called doping). As per the theory of semiconductors, these charge carriers can be either holes or electrons. In the superconductor \( \text{La}_{2-x} \text{Sr}_x \text{CuO}_4 \), holes are doped, and in \( \text{Pr}_{2-x} \text{Ce}_x \text{CuO}_4 \), electrons are doped. It is found experimentally [16,17,18] that the normal state properties of these materials are determined by both electrons and holes.

IV. ELECTRON – HOLE SUPERCONDUCTIVITY

In condensed matter physics, the problem of formation of bound state between a hole and an electron has been studied for quite some time. Such an electron – hole bound pair is known as exciton. There are superconductors in which there exists electron – hole interaction. It is found that the anti-ferromagnetic spin fluctuations in cuprates such as \( \text{YBa}_2\text{Cu}_3\text{O}_6 \) results in the Cu – O layer which contains singly ionized \( \text{Cu}^+ \) ions. These ions do not have a magnetic moment. Oxygen doping places \( O^{2-} \) ions along the \( b \) axis resulting in the change of \( \text{Cu}^+ \) to \( \text{Cu}^{2+} \). Hence, holes are created in the 3 d shell of \( \text{Cu}^+ \) ions. Simultaneously, \( \text{Cu}_2 \) in \( \text{YBa}_2\text{Cu}_3\text{O}_6 \) have \( \text{Cu}^{2+} \) ions. Each Cu gives two electrons, one from the 4s shell and the other from the 3d orbitals resulting in net magnetic moment of the \( \text{Cu}^{2+} \) ions in this layer. In this case the oxygen can only be varied in the CuO and not in the CuO2. Beyond a certain required amount of oxygen more holes are created in the CuO2 planes because oxygen atoms trap two electrons to become \( O^{2-} \) ions. Thus, there could exist electrons and holes simultaneously in the copper oxide planes, and they can form pairs to carry current in a superconductor. Within the Cu – O chain in the CuO2 planes, electrons or holes can move in the vertical direction from the d orbitals of Cu atoms to the \( O^{2-} \) ions. Hence, the electron – hole pairs may move parallel to the CuO2 planes and perpendicular to the CuO2 planes, and superconducting current may exist parallel and perpendicular to the CuO2 planes. The magnitude of the currents may not be the same. There may also exist inter – layer electron – hole pairing interaction.

V. SUPERCONDUCTIVITY FROM UNDRESSING

For superconductivity from undressing, literature is full of experimental observations and theories and some of them are briefly described below.

Before we explain how undressing leads to superconductivity, we have to understand the meaning of dressing and undressing with reference to electrons and holes. The electrons in metals are said to be ‘dressed’ by a cloud of other electrons with which they interact. Thus, dressing caused by the interaction between the electrons leads to increase in the effective mass of the electrons, and when the dressing is large, the metal cannot conduct electricity easily. If on the other hand the temperature of the metal is lowered, and the electrons manage to undress (not interact with the surrounding cloud of electrons), their effective mass will be reduced, and electricity can flow easily. When electricity can flow easily, that will mean reduction in the resistance of metal, and hence this can lead to the flow of large electric currents, and this is how superconductivity arises. This process can occur only if the carriers in the metal in its normal state are ‘holes’ rather than electrons, and undressing takes place when two hole carriers of opposite spin form a pair. The absence of electron is described as a hole; and it carries positive charge.

In metals electrons are also dressed by electron – ion interaction. Such an interaction reduces the electrical conductivity in the normal state and more electrons can occupy the band. If, however there are too many electrons in a band such that there are more than half as many as can fit in, then some of them do not contribute to the electrical conductivity, and hence move in the wrong direction due to electron – ion scattering – it is here that the conduction is due to the movement of holes. Thus, undressing occurs from the electron – ion interaction such that all the electrons may contribute to the conduction of electric current in the superconducting state. However, it is well known that all the electrons cannot contribute to the current in the superconducting state; only a very small fraction of electrons \( \sim 0.01 \) percent or
The model of hole superconductivity, therefore postulates that the mobility of a hole carrier increases as the concentration of holes increases in the system. The carrier concentration increases as the temperature is lowered, and hence the system becomes superconducting [19].

The ability of the charge carriers (electrons, holes or their pairs) to move freely (without resistance) leads to the flow of large currents in a material and this is superconductivity. So the question is under what condition they can flow without scattering.

There is also experimental evidence to show that in high – Tc cuprates superconducting transition is an undressing transition [20]. It is found that a single parameter, say \( \epsilon \), describes the strength of the undressing process and hence drives the transition to superconductivity. It is found that in the normal state, the spectral function evolves from predominantly incoherent to partly coherent pairing as the hole concentration increases. It is found that when \( \epsilon \neq 0 \) (non – zero), the resulting contribution to the spectral function is positive for hole extraction, and negative for hole injection. It is found that such results explain the observation of sharp quasi – particle states in the superconducting states of cuprates. Such studies lead to the assertion that superconductivity can occur only when ‘hole’ carriers exist in the normal state of the matter. Since a ‘hole’ is described as the absence of an electron, and hole carries exist when an electron energy band is almost full, holes are not the same as electrons. In a full band, hole has difficulty in propagating due to its surroundings. Thus, superconductivity is caused due to pairing of hole carriers that can propagate more easily (since they have smaller effective mass) compared to the propagation of single holes. Lowering the effective mass leads to lowering of the kinetic energy and hence the holes pairing becomes predominant, whereas single electrons move fast and hence do not pair. Thus, electrons and holes have different natures. The mobility of holes increases since holes undress on pairing, and turn into electrons. This leads to a new understanding and concept in superconductivity. If these ideas are accepted, then the electron – phonon interaction in superconductivity, especially BCS theory, becomes irrelevant. It is emphasized that the high temperature superconductivity of the cuprates, whether hole - doped and or electron – doped, the arsenides, magnesium diboride, elements under high pressure, transition metal elements can be explained via the theory of hole superconductivity [21-27].

There are two types of excitons. One is called Frenkel excitons [28] and the other is called Wannier excitons [29]. Frenkel excitons are intermolecular excitations that propagate along a crystal. They propagate as a wave and not by diffusion. Frenkel excitons have a small radius., whereas the Wannier excitons are bound pair of electrons from the conduction band and a hole from the filled valence band. In this case, the size of an exciton is of the order of the Bohr radius \( a = \frac{\hbar^2}{me^2 \epsilon} \), where \( m \) is the effective mass of an electron – hole pair, \( \epsilon \) is the dielectric permeability of the environment in which the electron – hole pair moves. Since the value of \( \epsilon \) is large and \( m \) is small, the size of the Wannier exciton sufficiently exceeds the interatomic distance. The coupling energy of an exciton is of the order of the effective Rydberg \( R_y = \left( \frac{m_e}{m_0} \epsilon^2 \right) R_y \), where \( m_e \) is the mass of the free electron. The coupling energy can even reach 10^3 K (energy = \( kT = 1.38 \times 10^{-16} \) ergs K\(^{-4} \times 10^5 K = E_c = 1.38 \times 10^{12} \) erg, the \( E_c = 0.8625 \times 10^{-1} \) ev = 0.08625 ev).

The Frenkel excitons were first observed experimentally by Prikhot’ko [30] and McChure [31], whereas Wannier excitons were observed by Gross [32]. The movement of these excitons was observed by Thomas and Hopfield [33]. It is important to understand that these excitons, being composed of electrons and holes which are fermions, will behave like bosons. It is this boson character of excitons that can lead to the boson condensation.

The excitons do not transfer either mass or charge, then it needs to be explained as to how their superfluidity is exhibited. However, excitons do not transfer energy without dispersion, and this will lead to the superfluidity of excitons.

It was found that the life time of excitons can be appreciably increased, and even made infinite, in systems which are bilayer, and the conductivity of each layer is different. In such systems, the separated electrons and holes (electrons in one layer and holes in another layer) can be paired spatially, and this can lead to superfluidity of electrons – hole pairs [34-36]. It should be understood that the bilayer systems are sand – wich type systems in which electron and hole conductive layers are separated by a thin dielectric layer of thickness \( d \) say. This means that the electrons flow in one layer and the holes flow in another layer, the two layers are separated, and the spatially separated carriers form pairs. This type of pairing is of great advantage when compared with the systems in which the holes and electrons are not separated in space. The first advantage is that in such systems, the tunneling between layers is a consequence of interzonal transitions. The amplitude of tunneling varies exponentially with the thickness \( d \) of the dielectric layer that lies between the two layers. The value of \( d \approx 10^{-6} \) cm, whereas in the case of GaAs heterostructures, the value of \( d \approx a_0 \) (Bohr radius). The values of \( d \) are generally small, and are said to be negligibly small. It is found that the coupling energy of the pair for \( d < a_0 \) remains almost constant, but for large \( d \) values, the coupling energy of the pair decreases exponentially. The second advantage is that the electron – hole pairs in the bilayer systems are dipoles that repel each other. Consequently, this prevents the combination of pairs into drops. Simultaneously, the spatial separation of the components of the pairs is confirmed by the fact that, as the pairs move in the conduction layers, we get electric currents that are equal in magnitude but opposite in direction, and these currents can be measured. Hence, superfluidity of pairs with spatially separated components is known as special type of superconductivity and is known as counter – flow electron – hole superconductivity. Another name for such process is superfluidity of electron – hole pairs, and the transition is called superfluid transition.
It is appropriate to point out that many articles and reviews have been published to study the Bose condensation and superfluidity of excitons in bilayer systems with spatially separated charge carriers [37 - 40]. In such systems, the study of superfluidity with pairing of spatially separated charge carriers continues to be an important problem for investigation in condensed matter Physics. The importance of this study lies in the fact that it can lead to the possibility of obtaining superfluidity and superconductivity at comparatively high temperatures. Particularly, such systems are known as graphene systems, for which critical temperature up to room temperature have been predicted theoretically. However, some critical problems remain to be solved. For instance, the critical temperature of superfluid transition decreases both for small d and large d of the dielectric layer. Even the phenomena of electron – hole superconductivity is poorly understood. It will be worthwhile to study the phenomenon of electron – hole superconductivity in bilayer quantum Hall systems, and the work devoted to bilayer systems based on graphene [41 - 43].

Studies have also been done to understand if the electron or hole pairs in copper oxide layers of LBCO (Lanthanum – Barium – Copper – Oxide) may survive efforts to kill superconductivity [36]. Similarly, mechanisms of superconductivity and electron – hole doping asymmetry in k – type molecular conductors has been studied to understand the correlation among metal insulators (MI) transition, magnetism and superconductivity [44 - 51]. It seems new concepts about charge carrier pairing have to be proposed to explain superconductivity in different types of materials and this effort will go on

REFERENCES
[1]. Kamerlingh H. Onnes, Leiden Commun. 122a, 124c (1911)
[2]. Meissner, W and Oschenfeld R. Naturwiss 21 (1933) 787
[28]. Frankel, J. Phys. Rev. 37, 17 (1931)
[29]. Wannier, G. H. Phys. Rev. 52, 191 (1937)
[32]. Gross, E. F. and Karryer, H. A. Dan SSSR 84, 471 (1952)
[34]. Lozovik, Yu E. and Yudson, V. I. PismaZhETF, 22, 556 (1975)
[42]. Narozlony, B. Nand Levhenko, A. Mod. Phys. 88, 025003(2016)
[46]. Hildebrand A. F. Phys. Rev. Lett. 8, 190 (1964)