Review Paper

The Continuing Quest for High Tc – Superconductors: A Review

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ABSTRACT

Superconductors, perhaps a mirage in the eyes of most chemists for many years, was pushed to the forefront of chemical interest with the synthesis and characterization of the first ‘’high - temperature’’ superconductor (Sr-doped La_2CuO_4 or 2-1-4) in 1986. The first superconductor with a Tc above the boiling point of liquid nitrogen ($YBa_2Cu_3O_7$ which is often referred to as ‘’1-2-3’’ compound because of Y: Ba: Cu stoichiometry) was synthesized a year later.This was a time in which superconducting materials created unprecedented excitement in scientific community; it was a year in which the public was captivated by new vistas in technology. The title of the article reflects that there is a crave for superconducting materials. This paper attempts to elucidate the technological advantage of superconductors and reflects the notation that chemistry can have a positive impact upon our lives. Firstly, the historical background of superconductivity is presented then the theory of superconductivity and the description of physical and chemical principles upon which it rests is given. Finally, some prospects for the future applications of these new materials are discussed.

Keywords: High Tc superconductor, 1, 2, 3, compound; liquid nitrogen; Y:Ba:Cu; Phonons

1. INTRODUCTION

Superconductivity is the ability of certain metals, alloys and ceramic materials to let electrical current flow with no electrical resistance and energy dissipation [1]. A superconductor is generally considered as a conventional superconductor if it can be explained by Bardeen, Cooper and Schreiffer (BCS) theory. Conventional superconductors can be either type-**I** or type-**II**. Most of the elemental superconductors are conventional except Niobium and Vanadium which are type-**II**. While other elemental superconductors are type-**I** but the recently advanced high temperature superconductors are type **II** or unconventional [1].

Since the initial discovery of superconductivity in 1911 by KamerlinghOnnes [2], great advances have been made in both the understanding of the phenomenon and the materials which exhibit it. The materials which exhibit superconductivity have steadily grown in number and variety, but the number used in practical, commercial applications is still rather small. Even though few theories have been developed and widely accepted, extensive researches are underway regarding the deep understanding of the concept of superconductivity, the chemical composition of different superconductors, and to use them as a substitute of the normal conductors in the commercial world. But Understanding the mechanism of high-temperature super-conductivity has remained a subject of much interest since its experimental discovery in the cuprates in 1986 [3].

The most important characteristic of any superconductor, from the viewpoint of practical applications, is the maximum electrical transport current density that the superconductor is able to maintain without resistance. This statement is equally true for large-scale applications, such as power transmission lines, electromagnets, transformers, fault-current limiters and rotating machines, as well as for small-scale electronic applications [4].

Therefore in this review, the events in the historical developments of superconductivity including the theories, physical and chemical properties which describe the nature of superconductors, the recent advancement and challenges in the application of high temperature super conductors (HTSC) and the future perspectives of high temperature superconductors will be discussed in detail.

2. HISTORY OF SUPERCONDUCTIVITY

The history of superconductivity as a phenomenon is very rich, consisting of many events and discoveries. The first phenomenon of superconductivity was discovered in 1911 by the Dutch physicist H. KamerlinghOnnes and his assistant Gilles Holst in Leiden. They found that dc resistivity of mercury suddenly drops to zero below 4.2K [5]. In their subsequent experiment they cooled a mercury sample to 3K and again observed that the resistance was “practically zero”. As the temperature of the sample was slowly raised, near 4K, the resistance abruptly increased, by more than three orders of magnitude over a temperature interval much less than 0.1K.

Soon after two decades of the discovery of superconductivity, in 1933, W. Meissner and R. Ochsenfeld discovered in Berlin one of the most fundamental properties of superconductors: perfect diamagnetism. The applied magnetic field, below transition temperature, gets to magnetize the substance in an opposite direction, so it shows a negative magnetic susceptibility. They found that the magnetic flux is expelled from the interior of the sample that is cooled below its critical temperature in weak external magnetic fields. Thus, they found that no applied magnetic field is allowed inside a metal when it becomes superconducting. This phenomenon is known today as the Meissner effect [4, 5].

Following the discovery of the expulsion of magnetic flux by a superconductor (the Meissner effect) the brothers F. and H. London together proposed in 1935 two equations to govern the microscopic (local) electric and magnetic fields. These two equations provided a description of diamagnetism of superconductors in a weak external field. In the framework of the two-fluid model, the London equations, together with the Maxwell equations describe the behavior of superconducting electrons. The London equations explained not only the Meissner effect, but also provided an expression for the first characteristic length of superconductivity, namely what became known as *the London penetration depth* λL[5, 7].

Also in 1950, V. Ginzburg and L. Landau proposed an intuitive, phenomenological theory of superconductivity. The equations derived from the theory are highly non-trivial, and their validity was proven later on the basis of the microscopic theory. The Ginzburg-Landau theory played an important role in understanding the physics of the superconducting state. This theory is able to describe the behavior of superconductors (both conventional and unconventional) in strong magnetic fields. The Ginzburg-Landau theory provided the same expression for the penetration depth as the London equations and also an expression for the second characteristic length ξ GL, called the coherence length [5, 7, 8].

The first widely-accepted theoretical understanding of superconductivity was advanced in 1957 by American physicists John Bardeen, Leon Cooper, and John Schrieffer which is called the “BCS theory”. They described, in great detail, the unique electrical and thermal properties of the superconducting state. The central concept in the BCS theory are the cooper pair of electrons in which such electrons pass through a crystal lattice, the lattice deforms inward towards the electrons generating sound packets known as "phonons". These phonons produce a trough of positive charge in the area of deformation that assists subsequent electrons in passing through the same region in a process known as phonon-mediated coupling. For their pioneering work in developing their theory, they received the Nobel Prize in Physics in 1972 [4, 6, 7].

Quantum-mechanical tunneling of Cooper pairs through a thin insulating barrier (of the order of a few nanometers thick) between two superconductors was theoretically predicted by B. D. Josephson in 1962. The DC Josephson effect and AC Josephson effect collectively called the Josephson effects of mathematical predictions were later experimentally approved and played a special role in superconducting applications. [5, 9].

During the first 75 years after the discovery of superconductivity in mercury, more than 5,000 elements, compounds and alloys were discovered to exhibit superconductivity at a temperatures below about 23 K [6]. But the idea of High-Temperature Superconductivity was not still developed. In 1964 Little hypothesized that high-temperature super- conductivity can be realized in one-dimensional structures on the basis of the exciton mechanism. According to his hypothesis, the system should contain long linear conducting molecules(polyenes or polymers with metallic atoms in an organic matrix), and on each side of these molecules groups of atoms with a high electronic polarizability should be located. These side branches should guarantee the mutual attraction of the conducting electrons as a result of the exchange of molecular excitations of the electronic type [10].

The notable events in this regard were the discovery of Nb_3Sn in 1954 and its wire development in 1961. They were followed quickly the discovery of other A15 materials and NbTi, the currently most-used material. These enabled the construction of electromagnets which can produce much higher magnetic fields than conventional copper-wire electromagnets [11].

In 1977, Ginzburg and coworkers at the P. N. Lebedev Physical Institute in Moscow published a book entitled‘‘High-Temperature Superconductivity’’. In this book, they discussed the possibility of high-temperature superconductivity in many types of materials, including quasi-one and- two-dimensional materials. The appearance of this book excited scientists in many countries and the discovery of HTS materials aroused tremendous excitement, because many of them are superconducting and carry significant current above the boiling point of liquid nitrogen at 77.4 K (-196 ^{0}C) [10,12].

The true history of high Tc superconductors was began in 1986 with the discovery of superconductors on the system Ba-La-Cu-O having the critical temperature 36K by Karl Muller and Johannes Bednorz in IBM research laboratory. They studied the phenomenon of high-temperature superconductivity in the cuprateperovskites materials and they proposed high-Tc superconductivity is achieved when a moderate density of electrons or holes is introduced into the parent antiferromagnetic phases of the cuprate. This opened a new branch of high Tc superconductivity namely “High Tc superconductivity”[13,14]. Soon after this many other oxide based superconductors were discovered having transition temperatures (Tc) up to 138 K (164 K under pressure) [2].

In 1987, the groups at the Universities of Alabama and Houston under the direction of M. K. Wu and P. W. Chu, respectively, jointly announced the discovery of the 93 K superconductor Y-Ba-Cu-O. Electron-doped high-Tc cuprates were also first discovered by Tokura et al. in 1989 [5]. Pronounced features different from those in the hole-doped cupratesis not only the electron carrier, but also the reduction annealing, which is absolutely essential to obtain the superconductivity in the electron-doped cuprates [15].

In 1990, A. S. Davydov presented a theory of high-Tc superconductivity based on the concept of a moderately strong electron-phonon coupling which results in perturbation theory being invalid [5]. The theory utilizes the concept of bisolitons, or electron (or hole) pairs coupled in a singlet state due to local deformation of the -O-Cu-O-Cu- chain in the CuO_2 planes.

In 2005, a surprising result was obtained in thin films of the electron-doped cuprates with the Nd_2CuO_4-type structure (the so-called T' structure), in which the superconductivity appears without electron doping. Following observations of the undoped (Ce-free) superconductivity in the parent compounds and the suggestion of a new phase diagram opened a new era of research in the high-Tc superconductivity. Yet to date, the mechanism of the undoped superconductivity is unclear [15].

3. THEORY OF SUPERCONDUCTIVITY

Superconductivity is not a universal phenomenon. It shows up in materials in which the electron attraction overcomes the repulsion [5]. Even though the core concept of superconductivity is the above phenomenon, there are different theories regarding the nature, physics of conductivity, type of conductors, physical state of the superconductors etc.

3.1. London Theory

In 1935 F. London and H. London described the Meissner effect and zero resistivity of the superconducting material by taking E= 0 and B = 0 in the Maxwell's electromagnetic equation.

$$B(x)=B_0\exp(-x/\lambda_L)$$

This first London equation is consequence of the perfect magnetism [16]. According to this, the applied field does not suddenly drop to zero at the surface of the superconductor but decay exponentially according to the equation.

According to this theory a magnetic flux penetrating through a superconducting ring or a hollow superconducting cylinder can have values equal to nh/e, where n is an integer (Figure 1). The flux quantization has been confirmed experimentally, but the quantum of flux has been found to be h/2e rather than h/e .This unit of flux is called a fluxoid [14].

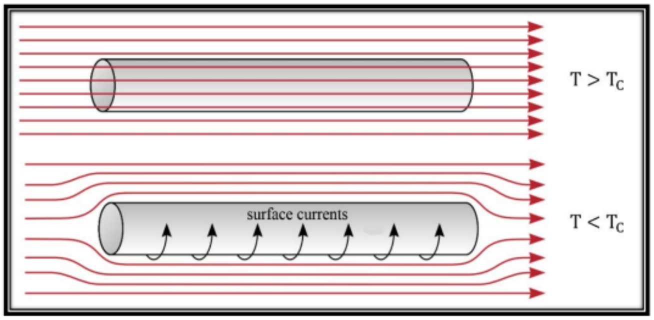

Fig.1. Meissner effect later approved by London theory [36]

3.2. Ginzburg - Landau Theory

In 1950, seven years before the microscopic theory of Bardeen, Cooper and Schrieer (BCS) was published, Ginzburg and Landau proposed a macroscopic, phenomenological theory of superconductivity to describe the properties of superconductors for temperatures near the critical temperature. There is no concept of the coherence length ξ in the London equation. Ginzburg and Landau proposed the phenomenological theory of the superconductor by using the order parameter $\psi = |\psi_0|\exp(i\theta)$ [4,16]. According to the Ginzburg–Landau theory, when ψ is small, the Helmholtz free energy per unit volume of the superconductor is expanded as a Taylor series of $|\psi|^2$. Thus we have

$$F_s = F_n + \alpha|\psi_0|^2 + (\beta/2)|\psi_0|^2$$

Where F_s and F_n are the Helmholtz free energies for the superconducting state and the normal conducting state, respectively, and α and β are the expansion coefficients.

3.3. BCS Theory

The first widely-accepted theory to explain superconductivity put forth in 1957 by John Bardeen, Leon Cooper, and John Schreiffer. The theory asserts that, as electrons pass through a crystal lattice, the lattice deforms inward towards the electrons generating sound packets known as "phonons". These phonons produce a trough of positive charge in the area of deformation that assists subsequent electrons in passing through the same region in a process known as phonon-mediated coupling (Figure 2). The consequence is an attractive interaction between the two electrons. Now, the correlated pair of electrons is referred to as a Cooper pair. Cooper pairs occupy a collective state and move through the crystal lattice unimpeded [4,7,14].

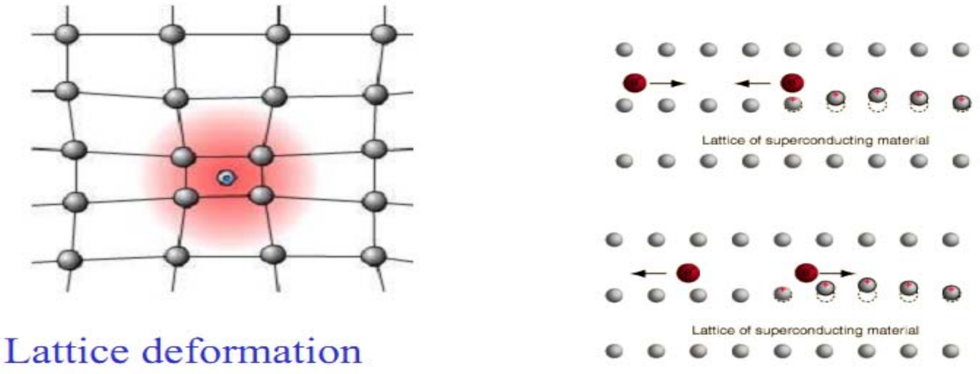

Fig.2. Schematic representation of phonon-electron attraction in a lattice [7]

When sufficient energy is supplied to Cooper pairs, they will decouple and the superconducting state ceases. Since the momentum is proportional to current density, the energy required to break Cooper pairs implies the existence of a critical current density Jc [18]. When Jc is exceeded, the Cooper pairs are destroyed. The energy required to break Cooper pairs also comes in the form of thermal energy from the vibrations of the crystal lattice and magnetic energy from magnetic fields. The former implies the existence of a critical temperature Tc, mentioned above, while the latter suggests the existence of a critical magnetic field H_c. The critical field depends on material and is temperature dependent according to the following equation

$$H_c= H_0[1-(T/T_c)]^2]$$

Where H_0 is the value of the critical field strength as T→0.

The BCS theory in its original form cannot be applied to the high temperature superconductors because the BCS predicted temperature are too low and because of non occurrence of the BCS predicted isotope effect [7,16].

3.4. Possible mechanism of conductivity in HTSC

Until Fe-based superconductors were discovered in 2008, the term high-temperature superconductor was used interchangeably with cuprate superconductor for compounds such as bismuth strontium calcium copper oxide (BSCCO) and yttrium barium copper oxide (YBCO) [17].

The question of how superconductivity arises in high-temperature superconductors is one of the major unsolved problems of theoretical condensed matter physics as of 2010 [7, 12]. The mechanism that causes the electrons in these crystals to form pairs is not known [5]. Despite intensive research and many promising leads, an explanation has so far eluded scientists. One reason for this is that the materials in question are generally very complex, multi-layered crystals (for example, BSCCO), making theoretical modeling difficult.

There have been two representative theories for HTS. Firstly, it has been suggested that the HTS emerges from antiferromagnetic spin fluctuations in a doped system [19]. According to this theory, the pairing wave function of the cuprate HTS should have a $d_x{}^2\text{-}y^2$ symmetry. Thus, determining whether the pairing wave function has d-wave symmetry is essential to test the spin fluctuation mechanism. That is, if the HTS order parameter (pairing wave function) does not have d-wave symmetry, and then a pairing mechanism related to spin fluctuations can be ruled out. Secondly, there was the interlayer coupling model, according to which a layered structure consisting of BCS-type (s-wave symmetry) superconductors can enhance the superconductivity by itself. By introducing an additional tunneling interaction between each layer, this model successfully explained the anisotropic symmetry of the order parameter as well as the emergence of the HTS [5, 7, 20, 21].

4. PROPERTIES OF SUPERCONDUCTING STATES

Among the many superconducting properties some basic and significant physical and chemical properties are discussed. Along with those properties,the superconducting property of cuprates particularly YBCO is presented.

4.1. Critical temperature

The most commonly known property of the superconducting state is that a superconductor is characterized by a critical temperature, below which the material exhibits “zero” resistance [6]. The critical temperature is mainly determined by chemical composition and structure, [22].Superconducting cuprate materials have higher transition temperatures. YBa_2Cu3O_{7-x} (YBCO) has a Tc of 93 K which is significant because it is greater than the boiling point of liquid nitrogen at atmospheric pressure as shown in Table 1. Bi-Sr-Ca-Cu-O, Tl-Ba-Ca-Cu-O, Hg-Ba-Ca-Cu-O and Hg-Tl-Ba-Ca-Cu-O compounds have higher critical temperatures as shown in the table [23]. All these high temperature superconductors have highly anisotropic crystal structures, containing layered CuO_2 planes in which the superconducting charge carriers are thought to be localized.

Table.1. Some high Tc cuprate based superconductors [23]

Compounds	**Tc K**	**Compounds**	**Tc K**
$YBA_2CU_3O_7$	93	$TL_2CABA_2CU_2O_8$	119
$YBA_2CU_4O_8$	80	$TL_2CABA_2CU_2O_{10}$	128
$Y_2BA_4CU_7O_{15}$	93	$TLCABA_2CU_2O_7$	103
$BI_2CASR_2CU_2O_8$	92	$TLCA_2BA_2CU_3O_8$	110
$BI_2CA_2SR_2CU_3O_{10}$	110	$TL_{0.5}PB_{0.5}CA_2SR_2CU_3O_9$	120
$HGBA_2CA_2CU_3O_8$	135	$HG_{0.8}TL_{0.2}BA_2CA_2CU_3O_{8.33}$	138

4.2. Critical magnetic fields

Superconducting state can be destroyed by a sufficiently strong magnetic fields. But for type-II superconductor, there are two critical fields, the lower critical field H_{c1} and the upper critical field H_{c2}. In applied fields less than Hc_1, the superconductor completely expels the field, just as a type-I superconductor does below H_c. At fields just above H_{c1}, flux, however, begins to penetrate the superconductor.Type II superconductors are the most technologically useful because the second critical field can be quite high, enabling high field electromagnets to be made out of superconducting wire as shown in Figure 3. Wires made from say niobium-tin (Nb_3Sn) have a H_{c2} as high as 24.5 Tesla – in practice it is lower. This makes them useful for applications requiring high magnetic fields, such as Magnetic Resonance Imaging (MRI) machines, [5].

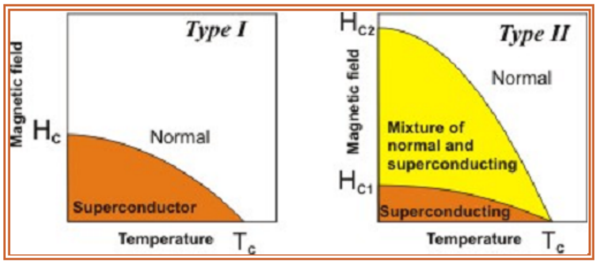

Fig. 3. Schematic plot of magnetic field vs temperature for type-I and type-II supercoductors.[36]

4.3. Critical current

Another important characteristic of a superconductor is the maximum transport current which can flow without dissipation. This is called the critical current, I_C. Its value is very sample dependent and can be affected by the sample shape and material quality. There is a criterion that says a superconductor loses its zero resistance when, at any point on the surface, the total magnetic field strength, due to the transport current and applied magnetic field, exceeds the critical field strength H_c. This quantity, I_C, is called the critical current. $I_C$depends on the external magnetic field experienced by the superconductor and has typical values of the order of 10^6-10^8 A cm^{-2} depending on the sample temperature [24].

4.4. Zero resistance

Every superconductor has zero resistivity, i.e. infinite conductivity, for a small-amplitude dc current at any temperature below T_c. This property of the superconducting state was demonstrated by inducing a small-amplitude dc current around a closed ring of a conventional superconductor. The experiment continued over two and a half years—there was no measurable decay of the current. This means that the resistivity of a superconductor is smaller than 10^{-24} Ωm. This value is 18 orders of magnitude smaller than the resistivity of copper ($1.7x10^{-6}$) at room temperature. Such a value of resistivity in a superconductor implies that the current lifetime in a super-conducting ring in zero magnetic field is not less than 10^5 years [5, 24].

4.5. Josephson Effects

As with semiconductor and thermocouple devices, there is the concept of a junction in a superconductor when it joins with an insulator. Two superconductors are separated by a thin insulating layer whose thickness is so small that Cooper pairs can pass through by the tunneling effect as given in Figure 4. This geometry is called the Josephson junction.

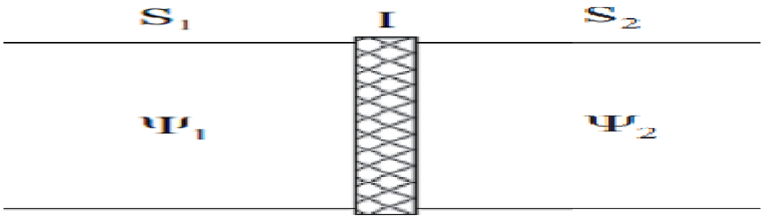

Fig. 4. Structure of Josephson junction (where s_1 and s_2 are two kinds of Superconductors, I is thin insulating layer) [36].

The Josephson Effect is the phenomenon of super current (A current that flows indefinitely long without any voltage applied) across a device which is known as Josephson junction. The Josephson Effect is an important basis of superconducting electronics applications and has widespread applications in many instruments such as voltage reference, superconducting cavities, superconducting filters and Superconducting Quantum Interference Devices (SQUIDs) [1].

4.6. Thermal property

4.6.1 Entropy

A marked decrease in entropy is observed during normal to superconductivity transition near the critical temperature; which indicates that the superconducting state is more ordered than normal state.

4.6.2 Specific heat

From the specific heat study of superconductor we can get the information about the existence of the band gap in superconductors. As we know specific heat of normal metal,

$$C_n = \gamma T + \beta T^3$$

Where, γT=specific heat term
βT^3=contribution of lattice vibration at low temp

Specific heat of superconductor shows a jump at Tc since the superconductivity affects electron mainly. So, the lattice vibration part remains unaffected. By this substitution the electronic specific heat Ces shows the exponential curve.

$$Ces(T) = A\exp(-\Delta_{/TK\beta})$$

And this indicates the existence of finite gap in the superconductor [14].

4.7. Superconducting Energy Gap

According to the BCS theory, the Cooper pairs are bound together with an energy E given by the relationship

$$E = hv = 3.52k_BT_c$$

Where h is Planck's constant (h = 6.6262 x10^{-34} Joule-sec), is the frequency, k_B is Boltzmann constant (k_B =1.3806 x 10^{23} Joules/Kelvin) and T_c is the superconducting transition temperature. The photon frequency corresponding to the energy gap of a superconductor with a T_c = 1 K is about 73 GHz. Thus the energy gap of most superconductors corresponds to photons in the terahertz or far infrared frequency regions of the spectrum [6]. Absorption of energy in that region may cause promotion of electron from supper conducting state to metallic state. Additional evidence for reduced free energy in supper conducting state comes from heat capacity measurements. These show the superconducting state to have lower entropy and hence to be more ordered than the metallic state [25].

5. SUPERCONDUCTIVITY IN CUPRATE OXIDES

Since 1987, cuprate superconductors with Tc > 77K have been the centre of intense interest. One of the first to be discovered was $YBa_2Cu_3O_7$ made by reaction given below. The oxygen content of the final material depends on reaction conditions (e.g. temperature and pressure).

$$4BaCO_3 + Y_2(CO_3)_3 + 6CuCO_3 \xrightarrow{1220K} 2YBa_2Cu_3O_{7-x} + 13CO_2$$ [23,26]

It is related to the perovskite structure as follows: by tripling the perovskite (ABO_3) unit cell and substituing one yttrium atom for every third barium atom, the formula $Y_1Ba_2Cu_3O_9$ results. Hovewer, a little more than two oxygen vacancies are required for superconductivitythere are position of nine atoms of O in the unit cell but only 7 are occupied [27,28].

There are systematic oxygen atom vacancies in the unit cell compared to stack of simple perovskite unit cells. These occur between adjacent copper atoms along the *c*axis. The vacancies are in the yittruim atom plan.There are also vacancies between copper atoms along the a axis in the copper-and-oxygen planes that lie between the planes of barium atoms [26]. This non-stoichiometry is denoted by the x in the chemical formula $YBa_2Cu_3O_{7-x}$. When $x = 1$, the O(1) sites in the Cu(1) layer are vacant and the structure is tetragonal. The tetragonal form of YBCO is insulating and does not superconduct. Increasing the oxygen content slightly causes more of the O(1) sites to become occupied. For $x < 0.65$, Cu-O chains along the *b* axis of the crystal are formed. Elongation of the *b* axis changes the structure to orthorhombic, with lattice parameters of a = 3.82, b = 3.89, and c = 11.68 Å. Optimum superconducting properties occur when $x \approx 0.07$, i.e., almost all of the O(1) sites are occupied, with few vacancies.

In experiments where other elements are substituted on the Cu and Ba sites, evidence has shown that conduction occurs in the Cu(2)O planes while the Cu(1)O(1) chains act as charge reservoirs, which provide carriers to the CuO planes. However, this model fails to address superconductivity in the homologue Pr123 (praseodymium instead of yttrium). This (conduction in the copper planes) confines conductivity to the *a*-*b* planes and a large anisotropy in transport properties is observed (Figure 5). Along the *c* axis, normal conductivity is 10 times smaller than in the *a*-*b* plane. For other cuprates in the same general class, the anisotropy is even greater and inter-plane transport is highly restricted [29].

The oxidation state of copper in $Y_1Ba_2Cu_3O_7$ is unusual .If we assume that Y,Ba and O have their usual oxidation state +3,+2 and -2 respectively,for charge balance,the copper must have an average of +2.33.This may be rationalized interms of one third of the copper is Cu^{3+} and the remainder is Cu^{2+} [1,23,25,26,28].

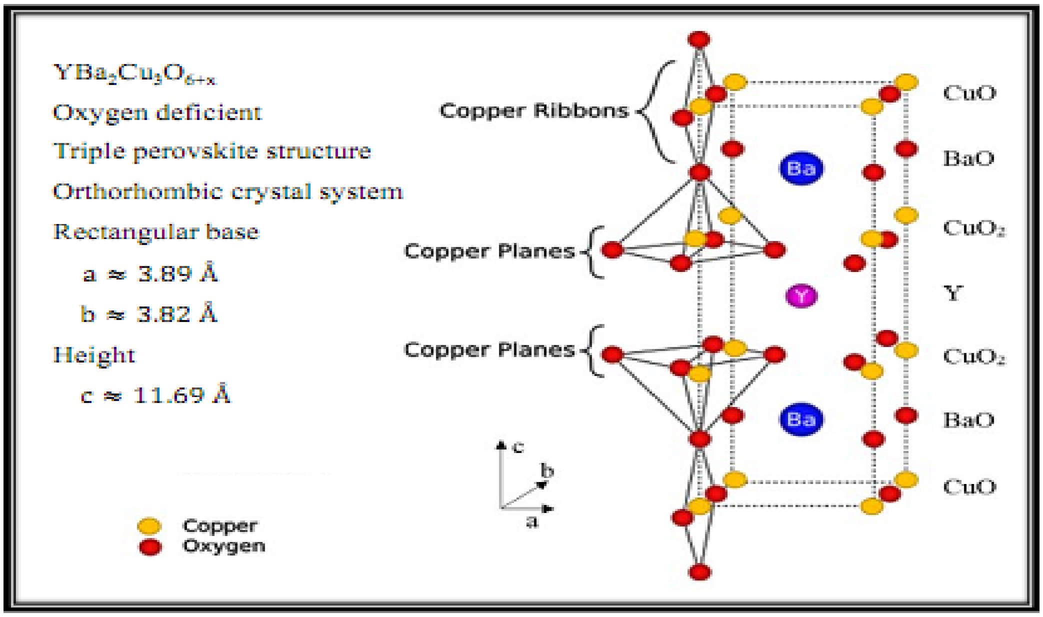

Fig. 5. The crystal structure of $YBa_2Cu_3O_7$ oxygen deficient compound [36]

6. APPLICATION OF SUPERCONDUCTORS

Due to the unique properties of high temperature superconducting materials, their applications are becoming attractive continuously with the improvement in properties of superconductors. The search for applications has always been a driving force for superconductor material science. Right from the discovery, it had been envisioned that superconducting coils with high persistent current might be used to produce strong magnetic field.

In the last 20 years, many applications of high temperature superconductors have been developed in very diverse fields. Applications of superconductivity can be found in transportation (maglev trains), marine and military (propulsion motors, degaussing systems and EMP weapons), particle research (large hadron collider, proton-antiproton collider and electron proton collider etc.), power generation and distribution (fault current limiters, superconducting wires, superconducting magnetic energy storage systems and superconducting transformers etc.), information technology & computing (quantum computers, quantum cryptography and high performance computers etc), electronics & telecommunications (Superconducting Quantum Interference Device (SQUID), single-quantum flux devices (SFQ devices), and cellular filters etc.) and medical diagnostic systems (magnetic resonance imaging (MRI))[30]. In this section some typical applications of high temperature superconductors are discussed.
The fundamental technologies for applications of superconductivity are discussed here with the classifications of Superconducting bulks, Superconducting tapes and Superconducting devices.

6.1. Superconducting bulk and its applications

Materials for superconducting bulk are $REBa_2Cu_3O_7$ where RE is Sm, Nd, Gd or Y. The bulk is made using the oxygen controlled melt growth (OCMG) method under a low partial pressure of oxygen except for YBCO where the quenched melt growth (QMG) method is used, here the superconducting bulk YBCO is grown using half-melt materials at a high temperature of nearly 1000 ^{0}C, followed by a very slow cooling. The bulk almost has a single-crystal like structure, and a large critical current of more than 10^5A/cm^{2}is obtained at liquid-nitrogen temperature [12,31].

The special feature of the bulk is that the introduction of pinning centres is easily carried out by controlling the density of fine Y_2BaCuO_5 particles as pinning centres in the bulk. The most distinguishing characteristic is that it is possible to trap a strong magnetic field of 2 to 3 T, even at liquid-nitrogen temperature. This value is much higher than the magnetic field of an ordinary permanent magnet. Recently, the mechanical strength of bulk has been increased by polymer impregnation, and this bulk has trapped a very high magnetic field of 17 T at 30K. The applications of the bulk are of two types:

(i). As the pining force of the magnetic flux is so strong, the outside magnetic field cannot penetrate the bulk in the superconducting state. This results in strong levitation force of about 15 Kg/cm^2 when the bulk is close to an ordinary permanent magnet at 77 K. This phenomenon is exploited to make Flywheel electric storage systems that can store about 10 KW/h, based on frictionless superconductor bearings. Using bulk HTS self-cantering bearings allows levitation and rotation in a vacuum, thereby reducing friction losses. Conventional flywheels suffer energy losses of 3-5% per hour, whereas HTS based flywheels operate at <0.1% loss per hour. Large and small demonstration units are in operation and development [1,12,31].

(ii). When the bulk is in normal state, a magnetic field applied from outside is uniformly distributed throughout the bulk. But after the bulk is cooled to below the critical temperature the magnetic field is quantized and quantized flux is pinned by strong pinning centres. Then when the external field is removed the quantized flux is left inside and behaves like a permanent magnet. One fruit full application of this bulk is in water cleaning using the magnetic separation effect. The impurity particles in water join magnetic particles, and they are removed from the filter by the strong magnetic field of the bulk. The operation can be continuous and results have been impressive which is 100 times efficient than the present cleaning system available today. Other opportunities are in materials manufacturing such as semiconductor production in high magnetic field and induction heating [1, 12, 31, 32].

6.2. Superconducting tapes

6.2.1. First-generation superconducting tapes

The first generation of superconducting tape using high temperature superconductors is the so-called Silver-sheathed Bi-compound Tape. The Bi-compound usually used is $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223). The tape is 4mm in width and 0.25mm in thickness, and inside the sheath there are 55 filaments of Bi-2223 superconductor. Recently, Sumitomo has succeeded in producing higher-quality tapes by introducing a heat-treatment process under a high pressure of 300 atmospheric pressures, and has obtained a critical current of 200A at 77 K [12,31,33].

6.2.2. Second-generation superconducting tapes

Although mechanical properties of the first generation wires are reasonably robust and the critical current values have reached more than 10^4 A/cm^2 at 77K and at commercial lengths, there are several weak points in this system in that high critical current density decreases rapidly with increasing magnetic field at liquid nitrogen temperature. Therefore, recent developments in the second generation coated conductors to improve the magnetic field dependence, where a thin film of $(RE)Ba_2Cu_3O_y$ superconductors is deposited on an appropriate substrate with specifications required by the specific application, gain a lot of interest [33]. YBCO tape consists of a thin metal plate, a buffer layer and a superconducting layer has developed with critical current density of 3 x 10^6 A/cm^2 in a magnetic field of 20 T at approximately 20 K that have law dependence in magnetic field [1, 12, 31].

6.2.3. Electric Power

6.2.3.1 Superconducting electric power cable

A possibility of electric energy transportation without loss is the most attractive property of superconductors. A high transition temperature of the cuprate HTS has enabled their practical applications by development of HTS power cables which are able to carry up to ten times greater current and power capacity per cross section than conventional copper cables. HTS coated conductor tapes are used in fabricating power cables. American Superconductor Company (AMSC) produces a single phase power cable using GdBCO tapes that are fabricated by using pulsed laser deposit technique and having greater current density than YBCO tapes. To reduce HTS cable cost three phase power cables were developed by AMSC, Where three 2G wires are concentrically placed around the common central core surrounded by a copper shield. The Triax HTS cable was developed jointly by Southwire and nkt cables companies. This compact construction has several advantages over the single-phase cable: in the three-phase cable, only about one-half of the quantity of HTS wire is needed and the cables cold surface area is reduced, which lower the cost associated with cryogenic cooling equipment. A single HTS Triax cable operating at 13 kV carries 3,000 A, which is equivalent of 18 conventional underground cables [1,32, 34].

6.2.3.2 Fault Current Limiters

As new generators are added to the network, many local grids face a rising risk of unacceptably high power surges that result from “faults” or short circuits. A fault current occurs in the event of a short circuit caused by lightning, accidental contact between the lines or the ground, etc. In this case, the power current flowing through a local network can increase enormously damaging electrical equipment. To protect the transmission or distribution of electric systems from outages caused by fault currents a special device – a fault current limiter (FCL) is installed in the transmission grid. Conventional line reactors widely used as FCLs have high AC losses and can produce voltage drop in the grid in the case of a fault current. HTS technology enables a new solution: compact, “smart” fault current limiters (FCLs) that operate, passively and automatically, as power “safety valves” to ensure system reliability when individual circuits are disrupted. Taking advantage of the inherent properties of superconductors, they sense such dangerous over currents and reduce them to safe levels by changing state instantaneously, from “super” conductors to resistors when the electric current exceeds the materials critical current.

The HTS FCL represents a coated conductor consisted of layers of HTS material within layers of resistive materials. Under normal operating conditions, the current in the cable flows through the HTS layers in the FCL. In the case of a fault, the current exceeds the HTS material’s critical current and the HTS layers become normal. In that case, the current is automatically shunted within a millisecond to flow through the higher resistance layers, effectively quenching the fault current amplitude. The very rapidly operated HTS FCLs greatly reduce damage to electrical equipment caused by system faults. They are fail-safe since they require no external sensing of the current to initiate the transition [1, 32].

6.2.4. Transportation

6.2.4.1 Superconducting Magnet for Maglev Trains

Expulsion of magnetic field by superconductors in superconducting state is useful in magnetically levitated trains, called as Maglev trains, which are operational in a few countries. Themagnet for maglev train has been made by using Bi-2223 superconducting tape. This magnet has a racetrack shape and consists of twelve pancake coils, of 1m length and 50 cm height. This magnet is operated at 20k and generates a magnetic field of 2.5 T at the center of the magnet. The huge magnetic field that can be sustained by the superconductors is used to levitate and propel the trains. Furthermore, the rate of decay of the persistent current is only 0.5% a day. This magnet is very successful and recently a train using this magnet reached a speed of 500 km/h [1,35].

6.2.5. Marine

6.2.5.1 Superconducting Motor for Ships

The ship propulsion system is undergoing a revolution. In the new system, propellers and the electric motor are directly connected and they are outside the body of the ship and this propulsion system is called a “pod motor”. By employing such a system, freedom of boat design is very much improved, and as a result, energy saving becomes possible.

The large size and heavy weight of conventional copper-based electrical propulsion motors and generators has been a barrier to broad adoption of electric propulsion. A HTS motor is most suitable for this pod motor system, because the superconducting motor generates a large torque even at a slow rotating propeller speed of about 100 rpm; furthermore, it is much smaller and much lighter than ordinary motors using Medical Imaging and Diagnostics copper wire. In the United States, various types of superconducting motors are being developed; all of them use Bi-2223 superconducting tape. In Japan, a superconducting motor using YBCO tape has been recently developed, and this is the first such motor in the world [1,32].

6.2.6. Medical application

6.2.6.1 Magnetic Resonance Imaging (MRI)

One of the largest commercial power applications of superconductors at present is magnetic resonance imaging (MRI), with thousands of units in hospitals and global sales of several billion US dollars per year. The superconducting portion consists of a “basic” solenoid, which creates the background strong magnetic field that forces hydrogen atoms that exist in the body’s water and fat molecules to accept energy from the magnetic field. These species then release this energy at a certain frequency which can be detected and displayed in the form of an image by a computer [1,2,35].

6.3. Superconducting electronic devices

One of the most prominent phenomena of superconductors is the Josephson tunnelling effect and most of the applications of superconductors in electronics and sensors are based on this phenomenon. Applications of superconductors have arisen in areas other than electromagnets, more specifically in electronics and sensors, wherein the materials required are often small thin films which are much easier to produce in highly perfect forms, especially from HTS. [2].

6.3.1 Superconducting Quantum Interference Devices (SQUID)

SQUIDs are superconducting loops with integrated Josephson junctions which can be used as the most sensitive measurement for magnetic fields, voltage, and related electromagnetic quantities based on the Josephson tunnelling phenomena. The magnetic field resolution of HTS SQUIDs operating at 77 K temperature is about 10 times lower than the commercial LTS SQUIDs operating at 4K [1]. However, a large commercial impact is only expected for HTS SQUID systems that are able to observe magnetic signals even in the presence of disturbing background fields without the burden of magnetic shielding [36]. SQUID magnetometers may be the most sensitive measurement device known. The threshold for SQUID is of the order of 1 fT,(100 billion times smaller than the Earth's field), making it capable of measuring extremely feeble magnetic fields. Because of their extreme sensitivity, SQUIDs have established themselves as very accurate devices for both Magnetocardiography and Magnetoencephalography. The application of high temperature SQUIDs to a magnetocardiography has been made recently by Hitachi, Ltd. It consists of 51 SQUIDs on one plate and is used for the diagnosis of human heart diseases [1].

6.3.2 Microwave filters

The simplest applications of high-quality high-temperature superconducting films with commercial availability are HTS passive RF and microwave filters for wide-band communications and radar. These are based on conventional microstrip and cavity designs with superconductors used for the microstrips or to line the metal cavity. They have the advantages of very low noise and much higher selectivity and efficiency than conventional filters [12]. In early stages of development it was hoped that many filtering systems would be used in the base stations of portable telephone systems. However, at present, only several thousand filters are employed in the world, because of the cost of the cooling system [10].

6.3.3 Single-Quantum Flux (SFQ) Devices

Another important application of, High Temperature Super Conductors, HTSC is the single quantum flux device (SFQ). The principle operation of SFQ device is that in a superconductor ring of a SQUID the magnetic field is quantized, and by applying a current pulse to the ring, the Josephson junction reaches a normal state for a short duration, and the quantized flux appears or disappears in the ring depending on the original state. The state of the flux in the ring is 0 or 1, and responds to the 0 or 1 of an information signal and so logical circuits can be made by combining SFQ devices [10,31]. The electricity consumption of the SFQ circuits is very small, 0.1 mW per one logic gate, and this is about one hundredth that of semiconductor circuits. The operation speed is about 100 GHz, and this is one hundred times faster than that of semiconductor circuits [1].

In the past fifteen years, the circuit technology of SFQ circuits using Nb-based SFQs has made a good progress, the integration of more than 10^4 junctions has become possible, high-speed shift registers and high-speed switching systems have been developed. Special feature of SFQ circuits based on high-temperature superconductors are a high-speed operation of over 100 GHz and a high-temperature operation at approximately 40 K. On the other hand, the integration is more difficult than that of Nb-based SFQ circuits owing to the complexity of process technology (Figure 6). A high-speed sampler and a toggle flip-flop circuit are examples of SFQ circuits with about twenty Josephson junctions and operating at about 40 K. The high-speed sampler is very useful for observing waveforms of a very short pulse greater than 40 GHz, which will be popular in future, communication systems. And the toggle flip-flop circuit generates two output pulses for one input, and can be used as demultiplexer and this circuit is operates faster than 370 GHz [10]. At present, the integration of a high-temperature SFQ circuit is limited to about 100 junctions, but it is hoped that this will reach to more than 500 junctions.

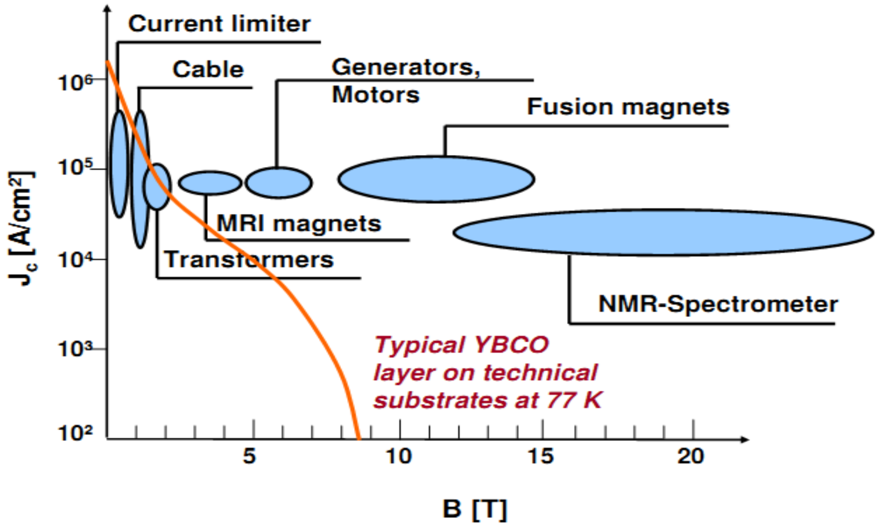

Fig.6. Required properties for different power applications of HTSC[36].

6.4 Future perspective of HTS

The last ~30 years have seen the development of a number of prototypes of new high temperature superconducting power and electronic equipment's that are mentioned above and many others. But, so far only few of them are successfully commercialized. The problem has usually been the cost of the HTS version versus other LTS and non-superconducting solutions. Superconducting motors and generators are one strong example; a number of prototypes have been successfully built and tested to full function, but the economics have not allowed commercialization [2]. High temperature superconductivity does not necessarily require correlated electron systems with complex competing or coexisting orders. Instead, it may be achieved in a phonon-mediated classical superconductor having a high Debye temperature and large electronic density of states at the Fermi level in a material with light atoms and strong covalent bonds [37-39].

The future of HTS applications and commercialization is a persistent question and can only be answered once the scientific and technological challenges hindering the large-scale application of HTS are addressed. First, the geometrical shapes of HTS wire are limited. It is mostly available in tape format. Fabrication of HTS wire (tape) requires an expensive and special technology and process machinery.

The second challenge has to deal with the material properties that result in high values of TC and HC. These properties include high normal state resistance, proximity of superconductivity to competing Anti-Ferromagnetic (AF) state, large anisotropic ratios and sensitivity of superconducting properties to local nonstoichiometry. These lead to the lack of widespread applications of HTS. In addition, absence of any validated microscopic theory of superconductivity in HTS materials means we cannot predict new superconducting materials with higher TC values.

If these challenges of HTS are addressed, then the HTS will bring the features of save energy, compact, lightweight, high performance and save resources, and could play a trump on forthcoming low-carbon society in our life.

7. CONCLUSION

One of the most brilliant events in the 20th century was the discovery of ceramic-type HTS materials that led to extensive research for new discoveries and theories. The physics of HTS is complicated, that the theoretical basis is uncertain yet, and it may be in the far front of solid state physics. Till this moment high temperature superconducting properties has been discovered with in many types of materials and research will continue to synthesize new materials that may expose these new phases in an experimental sense or improve on those already known. We have studied historic view of HTS, theories of superconductivity, and characteristics and different properties of HTS materials. We also studied the application of HTS in different sectors. As the properties of HTS continue to improve, more applications are expected to become a commercial reality. Steady improvement of the HTS materials basis will surely widen this spectrum of applications within near future.

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