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100 YEARS OF SUPERCONDUCTIVITY (1911-2011)

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In 1911 superconductivity was discovered in mercury having transition temperature at 4.2 K, during last 100 years transition temperature has been increased to 153 K. In this manuscript the major developments in experimental and theoretical fields have been reviewed. A summary of various applications of superconducting materials is also given and future prospects of superconductivity are discussed.

Keywords : Superconductivity, Meissner effect, Transition temperature, SQUID

1. Introduction

Superconductivity was first observed in 1911 by the Dutch physicist Heike Kamerlingh Onnes. When he cooled mercury to the temperature of liquid helium (4.2 K), its resistance suddenly disappeared [1]. Figure 1 shows the disappearance of electrical resistance in mercury at 4.2 K. This means that the material is able to conduct currents without any energy losses. Onnes also discovered that this dissipation-free state of matter, named superconductivity, was destroyed by high currents and external magnetic fields. The next milestone in understanding superconductivity occurred in 1933, when Walter Meissner and Robert Ochsenfeld discovered that a superconductor would repel an external magnetic field [2]. The currents induced in a surface layer of a superconductor by a magnet placed close to it exactly mirror the field that otherwise would have penetrated the superconducting material, creating a zero field inside the material. This means that a superconductor can be considered as a perfect diamagnet. The effect is usually referred to as the *Meissner effect*, this effect is so strong that a magnet can be levitated above the surface of a superconductor. The Meissner effect is more fundamental for a superconductor than the zero resistance.

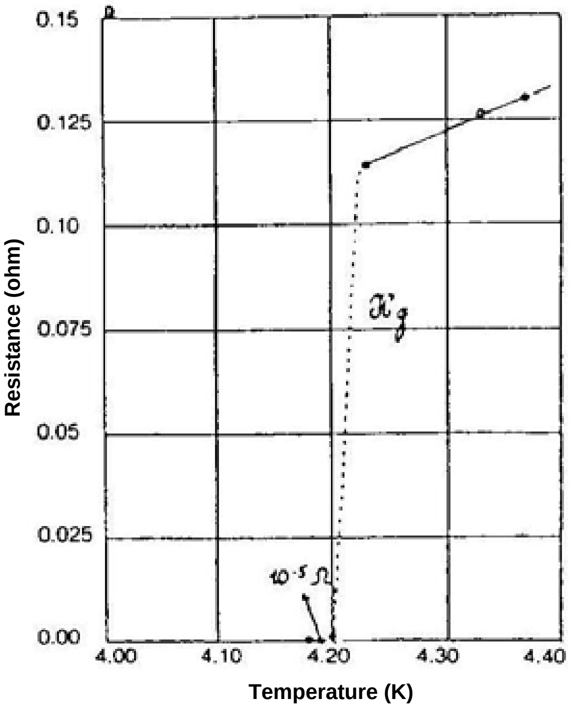

Figure 1. Resistance of mercury versus absolute temperature [1].

Since the discovery of superconductivity, scientists have tried to find new materials with even higher transition temperature T_c (the temperature below which the material becomes superconducting). Although a large number of the elements are superconductors, the highest T_c among the elements under normal conditions is only 9.2 K for Nb. The research for higher T_c in alloys and compounds resulted in the discovery of materials like NbN (T_c=16 K), NbTi (T_c=10 K), Nb_3Sn (T_c=18 K), and Nb_3Ge (T_c=23 K). Among the

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binary compounds, NbTi and Nb_3Sn have become the most important ones for fabricating superconducting wires; further details of earlier superconducting materials are reviewed by Roberts [3] and Scanlan [4].

Until 1986, the highest transition temperature remained below 23.2 K, when a breakthrough was made by Alex Müller and Georg Bednorz at IBM Rüschlikon in Switzerland. They found that a ceramic compound of La, Ba, Cu and O became superconducting at 30 K [5]. The discovery of superconductivity near 30 K in La-Ba-Cu-O by Müller and Bednorz and later reconfirmation by other groups, Uchida et al. [6] and Takagi et al. [7], stimulated intense activity in this field around the world; the superconducting phase was identified as $La_{2-x}Ba_xCuO_4$ ($x = 0.05 - 0.2$) [7, 8]. The effect of pressure on $La_{2-x}Ba_xCuO_4$ was investigated and it was observed that T_c was raised up to 52.5 K by a pressure of 12 kbar [9, 10].

Intensive efforts were then initiated to substitute the component ions with similar elements on both La and Ba sites. Several groups independently observed that by replacing Ba with Sr, T_c increased up to 40 K [11-13]. In $La_{2-x}M_xCuO_4$ (M = Ba, Sr) superconductivity depends upon the nature and concentration of the dopants; the best results were obtained for $La_{1.85}Sr_{0.15}CuO_4$ when annealed in oxygen.

A major breakthrough came with the discovery of superconductivity above 90 K in the Y-Ba-Cu-O system [14], when La was substituted with Y; this successfully increased the transition temperature above liquid nitrogen (77 K), which encouraged the research for superconductivity in other related ceramic oxides, using a very common and cheap cryogen. The superconducting phase was identified as $YBa_2Cu_3O_7$ (Figure 2) having an orthorhombic structure [15] (referred as YBCO or Y(123)). Michel et al. [16] reported superconductivity in the Bi-Sr-Cu-O system with a transition temperature (T_c) up to 22 K. Although the superconductivity of this compound was relatively low, however this was an important development, as this system does not have any rare-earth element. The addition of Ca in the Bi-Sr-Cu-O system increased T_c to as high as 110 K [17]. It was found that the transition temperature becomes higher on increasing the number of CuO_2 layers up to three in the Bi-Sr-Ca-Cu-O (BSCCO) system. Structural studies revealed that there are three superconducting phases which are represented by the formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ (where n = 1, 2 and 3); these phases have T_c 22 K, 80 K and 110 K, respectively [18]. After that, the Bi was replaced with Tl and the superconductivity was increased up to 120 K in the Tl-Ca-Ba-Cu-O system [19, 20].

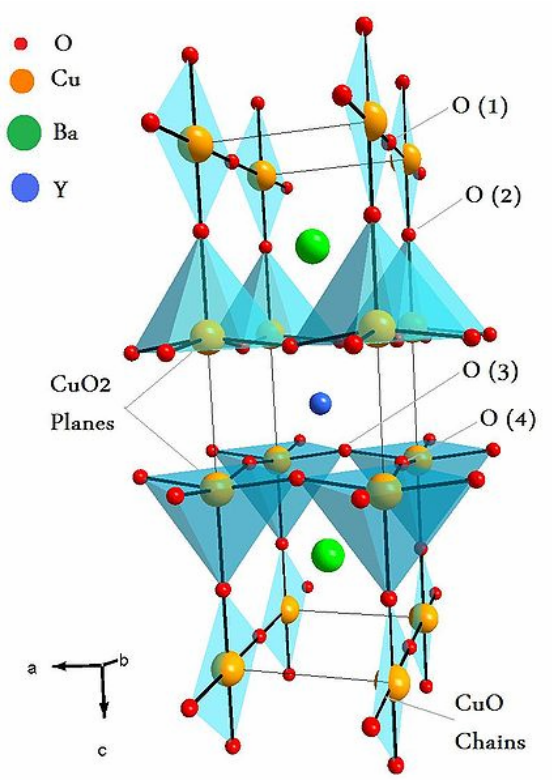

Figure 2. Crystal Structure of $YBa_2Cu_3O_7$ showing orthorhombic symmetry.

Further interest in superconductivity was inspired by Cava et al. [21], when they reported that $Ba_{0.6}K_{0.4}BiO_3$ showed superconducting transition temperature near 30 K; as this discovery ruled out the speculation that copper was a vital element in high temperature superconductors (HTS). The development continued and in 1993 superconductivity was discovered at 94 K in $HgBa_2CuO_{4+x}$, a single CuO_2 layer compound, by Putlin et al. [22]; the addition of Ca increased T_c up to 135 K and this high-T_c phase was identified as $HgBa_2Ca_2Cu_3O_{8+x}$ [23]. This material had the highest known superconducting transition temperature and becomes superconducting at 153 K when subjected to an external pressure of 150 kbar [24]. Figure 3 shows the yearwise development leading to high temperature superconducting materials.

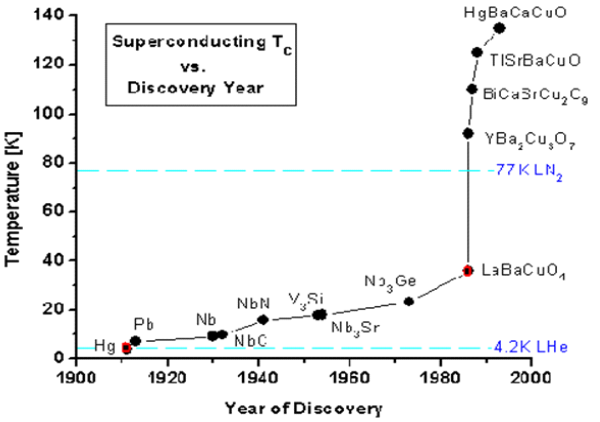

Figure 3. Yearwise development in search of high temperature superconductivity (HTS).

The first organic superconductor (TMTSF)$_2$PF$_6$ was discovered with relatively low T_c of 0.9 K under a pressure of 12 kbar [25]. In 1981, the first organic material (TMTSF)$_2$ClO$_4$ that was superconducting at ambient pressure was synthesized by Bechgaard et al. [26]. The discovery of superconductivity in alkali-metal-doped fullerenes (A_3C_{60}, where A= K or Rb), led to the discovery of a new sub-class of organic superconductors, with the transition temperature ~30 K [27-29].

The discovery of superconductivity in ruthenate-cuprate materials [30], which exhibit ferromagnetism and superconductivity at the same time, overturned a long-held belief that these properties were generally incompatible. An interesting discovery was made in 2001, when it was found that MgB$_2$ was superconducting at 39 K [31]; this was the highest T_c in a simple binary material. More recently another class of compounds referred as oxy-pnictide and characterized by the general formula RFeAsO (R= rare earth) has attracted much attention after the discovery of superconductivity with a transition temperature of 26 K in LaFeAs(O$_{1-x}$F$_x$) by Kamihara et al. [32].

2. Theoretical Description of Superconductivity

The phenomenon of high temperature superconductivity stimulated both experimentalists and theoreticians. Experimentalists can point to the phenomenal success in making an entire new class of superconducting material, while the theoretical excitement is posed by the need to explain the observation of superconductivity at such high temperatures. In addition to the total loss of electrical resistance to the passage of a direct current in these materials, there also occurs an unusual magnetic behaviour; the tendency to expel a magnetic field from its interior below T_c, this results in the formation of a perfect diamagnetic material, (Figure 4). This effect allows superconductors to repel magnets and act as magnetic shields with high efficiency.

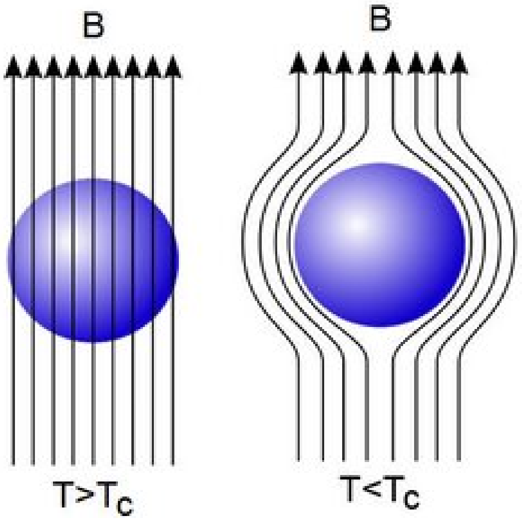

Figure 4. Expulsion of magnetic field due to Meissner effect on a superconducting material.

This perfect diamagnetic behaviour is called the *Meissner effect* (Meissner and Ochsenfeld, 1933) [2]. The Meissner effect is responsible for the levitation phenomenon in superconductors (Figure 5). Because certain superconductors can carry high electrical currents, coils with several

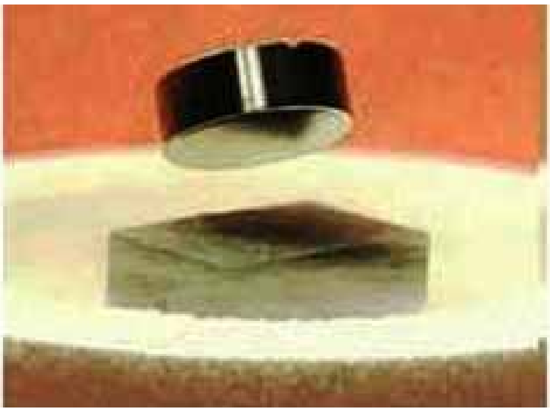

Figure 5. Levitation of a magnet by a superconductor due to Meissner effect.

turns of superconducting wire can generate very strong magnetic fields, strong enough to levitate an entire train for high-speed travel on a magnetic track.

The phenomenon of superconductivity was for a long time an unresolved problem. A phenomenological and macroscopic theory of superconductivity was proposed by the London brothers in 1935 [33]. In 1950 Ginzburg-Landau theory was proposed, it was a mathematical theory used to model superconductivity [34]. It did not explain the microscopic mechanisms giving rise to superconductivity; instead, it examined the macroscopic properties of a superconductor with the aid of general thermodynamic arguments. The microscopic theory by John Bardeen, Leon Cooper, and Robert Schrieffer (known as the BCS theory), was published in 1957, where general agreement on the theory of superconductivity for metals and alloys was obtained [35]. This theory has been successful in explaining essentially all of the phenomena associated with the conventional superconductors. The BCS theory postulates that when an electron is moving through the lattice of positive ions, the negative field of the electron polarizes and distorts the lattice of positive ions which, in turn, attracts the second electron and yields an effective attractive interaction between the two electrons. This weak attractive force binds the two electrons into pairs known as *Cooper pairs* (Cooper, 1956) [36]. The Cooper pairs have opposite spins but equal and opposite momenta, so that the net spin and net momentum are both zero. A Cooper pair is more stable than the two unpaired electrons by the amount of the binding energy. The Cooper pairs are broken up when energy is supplied to the system; for example, application of an external magnetic field or by increasing the temperature. If the attractive interaction is greater than the Coulomb repulsion, then superconductivity results.

The BCS theory has worked well in predicting the behaviour of conventional superconductors, which operate near absolute zero. It appears that the BCS theory may hold for the superconductors up to 40 K. But for superconductors above liquid nitrogen temperature (77 K), the applicability of the BCS theory is uncertain. Lattice vibrations, are suggested, to become too great to interact with superconducting electrons, suggesting there must be some other interaction involved. A number of theoretical models have been discussed to explain the possible mechanisms of high temperature superconductivity [37-40]; however, there is still no explicit theoretical explanation for this phenomenon.

In 1962 Brian Josephson, made a remarkable prediction that an electrical current could flow between two superconducting materials, even when they are separated by a non-superconductor or insulator [41]. His prediction was later confirmed and this tunneling phenomenon is known as the *Josephson effects* and has been applied to electronic devices.

The superconducting state is defined by three very important factors: critical temperature (T_c), critical field (H_c), and critical current density (J_c); each of these parameters is very dependant on the other two properties. Maintaining the superconducting state requires that the magnetic field and the current density, as well as the temperature, remain below the critical values, all of which depend on the material.

3. Applications of Superconducting Materials

It is the remarkable physical properties of superconductors that have driven commercial interest in these materials. Superconductors allow loss less electrical conduction and can carry current densities over 1000 times greater than copper wires. They are also used in a wide range of microwave and electronic devices and in medical and geological scanners to detect magnetic fields less than a billionth of the size of the Earth's field.

Electric generators made with superconducting wire are far more efficient than conventional generators wound with copper wire. In fact, their efficiency is above 99% and their size about half that of conventional generators. These facts make them very lucrative ventures for power utilities.

Applications currently being explored are mostly extensions of technology used with the low temperature superconductors. Current applications of high temperature superconductors include: magnetic shielding devices, medical imaging systems, superconducting quantum interference devices (SQUIDs), infrared sensors, analog signal processing devices and microwave devices.

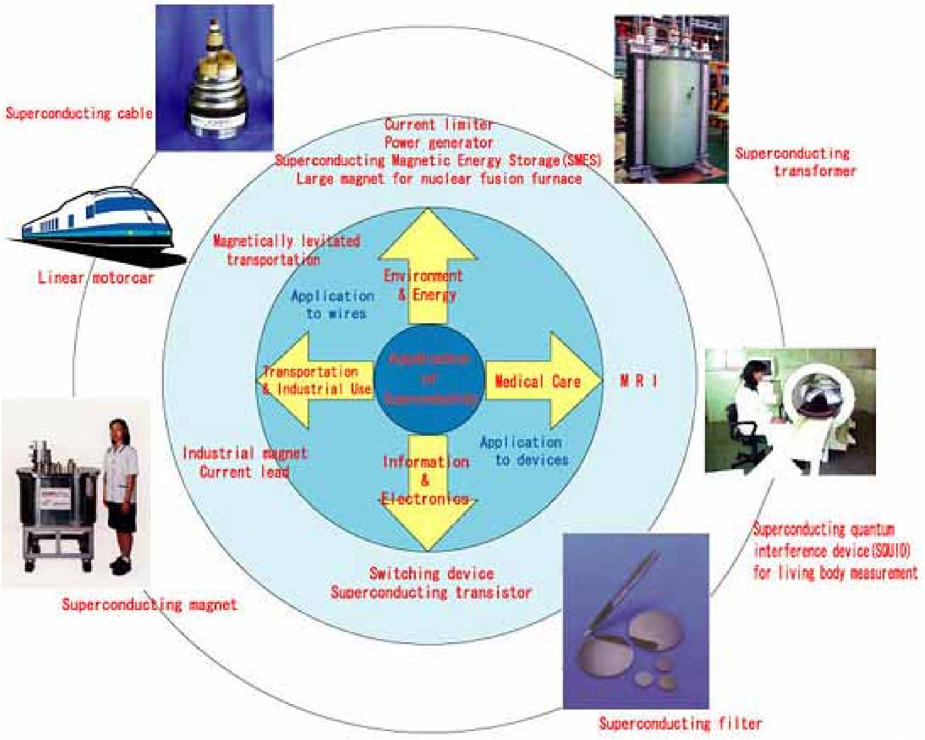

Figure 6. Various applications of superconductors taken from Ref. [42].

New applications of superconductors will increase with the increase of critical temperature. Liquid nitrogen based superconductors have provided industry more flexibility to utilize superconductivity as compared to liquid helium superconductors. As our understanding of the properties of superconducting material increases, applications such as; power transmission, superconducting magnets in generators, energy storage devices, particle accelerators, levitated vehicle transportation, rotating machinery, fault current limiters and magnetic separators will become more practical. The following are some of the major fields where superconductors are being used at present; various applications of superconducting materials are summarized in Figure 6 [42].

3.1. *Superconducting Transmission Lines*

Superconducting cables can provide 2 to 5 times more power than the conventional cables of the same size. Since 10% to 15% of generated electricity is dissipated in resistive losses in transmission lines, the prospect of zero loss superconducting transmission lines is tempting. The superconductor used in these prototype applications is usually niobium-titanium, and liquid helium cooling is required. Current experiments with power applications of high-temperature superconductors focus on uses of BSCCO in tape forms and YBCO in thin film forms [43].

3.2. *Power Applications*

Power applications of high temperature superconductors would have the major advantage of being able to operate at liquid nitrogen temperature. The biggest barrier to their application has been the difficulty of fabricating the materials into wires and coils. Current development focuses on BSCCO and YBCO materials [44].

3.3. *Fault-Current Limiters*

High fault-currents caused by lightning strikes are a troublesome and expensive nuisance in electric power grids. One of the near-term applications for high temperature superconductors may be the construction of fault-current limiters which operate at 77K. The need is to reduce the fault current to a fraction of its peak value in less than a cycle (1/60 sec). A fault-current limiter, constructed from BSCCO material, can operate at 20 kV and carry a current of 1600 amperes [45].

3.4. Superconducting Motors

Superconducting motors and generators could be made with a weight of about one tenth that of conventional devices for the same output. In future, it may be possible to build very large capacity generators for power plants where structural strength considerations place limits on conventional generators.

3.5. Superconducting Maglev Trains

Magnetically levitated (MAGLEV) trains can be made to "float" on strong magnets, virtually eliminating friction between the train and the tracks. The non-contact configuration of the train makes it possible to attain very high speeds. Although MAGLEV trains can be made by conventional electromagnets, superconducting magnets are competitive due to their small size (and thus small weight of the vehicle).

3.6. Superconducting Magnets

Superconducting alloys such as niobium-tin and niobium-titanium are used to make the coil windings for superconducting magnets. These two materials can be fabricated into wires and can withstand high magnetic fields. Typical construction of the coils is to embed a large number of fine filaments in a copper matrix. The solid copper gives mechanical stability and provides a path for the large currents in case the superconducting state is lost.

3.7. SQUID Magnetometer

The superconducting quantum interference device (SQUID) consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions. The device may be configured as a magnetometer to detect incredibly small magnetic fields, small enough to measure the magnetic fields in living organisms. By using SQUID, it is possible to detect the small magnetic signals created by human brain activity (senses the neuronal ionic currents) and by the heart (senses the ionic depolarizing currents which generate the heart beat). The magnetic fields that are measured are extremely low, several tens of a pT for the heart and around 100 fT for the brain.

3.8. Magnetic Resonance Imaging

Superconducting magnets find application in magnetic resonance imaging (MRI) of the human body. In medicine, doctors need an easy-to-use method to determine what's going on inside the human body. By applying a strong magnetic field from a superconducting magnet across the body, hydrogen atoms inside the body are forced to take up energy from the magnetic field. They then release this energy at a frequency that can be detected and displayed on a computer. This method is called Magnetic Resonance Imaging (MRI) and is widely used in hospitals all over the world.

4. Discussion and Future Prospects

While a great effort has been made to discover new high temperature superconductors, a large scale parallel effort has been made to determine the fundamental properties of these fascinating new materials.

Future research must contain a strong effort towards the synthesis of some very high T_c materials. New synthesis methods have to be found, replacing the actual laboratory methods by industrial techniques. Further efforts are also needed with respect to current limiting mechanisms in HTS and possible materials-related solutions. Although it is well established that both grain boundaries and flux line dynamics are two important limiting factors, these issues are needed to tackle on a nanometer scale.

The development of the processing techniques for bulk HTS of complex shape and composite components and with very low resistivity is essential. The relevant properties for these materials are the current densities, the magnetic fields, their distributions, the levitation force, the losses, the mechanical and the thermal properties.

For HTS electronics, less expensive processing routes and cheaper buffered substrates are needed. Many circuits will incorporate other materials, e.g. ferroelectrics, ferrites or colossal magnetoresistive materials. Completely new technologies may have to be developed to achieve the necessary reproducibility for HTS junctions. This will require new material engineering for understanding the limiting factors for the performance of junctions and for providing the necessary characterization tools. The fabrication of thin films and devices should be considered with a micron or less lithography.

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