

# Chapter One

## 1.1 Introduction:

Superconductivity is a phenomenon of exactly zero electrical resistance and expulsion of magnetic fields occurring in certain materials when cooled below a characteristic critical temperature. It was discovered by Dutch physicist Heike Kamerlingh Onnes on April 8, 1911 in Leiden. Like ferromagnetism and atomic spectral lines, superconductivity is a quantum mechanical phenomenon. It is characterized by the Meissner effect, the complete ejection of magnetic field lines from the interior of the superconductor as it transitions into the superconducting state. The occurrence of the Meissner effect indicates that superconductivity cannot be understood simply as the idealization of perfect conductivity in classical physics[1].

The electrical resistivity of a metallic conductor decreases gradually as temperature is lowered. In ordinary conductors, such as copper or silver, this decrease is limited by impurities and other defects. Even near absolute zero, a real sample of a normal conductor shows some resistance. In a superconductor, the resistance drops abruptly to zero when the material is cooled below its critical temperature. An electric current flowing through a loop of superconducting wire can persist indefinitely with no power source[1,2].

## 1.2 Research problem :

Applications of superconductors have been delayed in the field of electrical power transmission over large distances as an alternative to conventional cables made of copper or aluminum and is due to the reason that superconductors need a cooling to below the critical degree until it reaches the superconducting state. This was it constitutes a technical barrier huge because it was meant to reach the temperature to approximately the boiling point of

helium 4.2 K , and since that research on superconducting and the main concern for scientists is beginning to find a conductor super be critical degree higher what can preferably be close to room temperature

### **1.3 Aim of research :**

To obtain materials that behave as superconductors at unusually high temperatures.

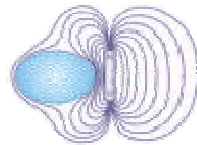
### **1.4 Research Significance :**

High temperature superconductivity is now very well understood, it's a field with many practical and theoretical aspects ,And is currently being very actively researched by universities, national laboratories , and companies around the world.

### **1.5 Literature review :**

Superconductors, materials that have no resistance to the flow of electricity, are one of the last great frontiers of scientific discovery. Not only have the limits of superconductivity not yet been reached, but the theories that explain superconductor behavior seem to be constantly under review. In 1911 superconductivity was first observed in mercury by Dutch physicist Heike Kamerlingh Onnes of Leiden University. When he cooled it to the temperature of liquid helium, 4 degrees Kelvin (-452 °F, -269 °C), its resistance suddenly disappeared. The Kelvin scale represents an "absolute" scale of temperature. Thus, it was necessary for Onnes to come within 4 degrees of the coldest temperature that is theoretically attainable to witness the phenomenon of superconductivity. Later, in 1913, he won a Nobel Prize in physics for his research in this area. The next great milestone in understanding how matter behaves at extreme cold temperatures occurred in 1933. German researchers Walther Meissner and Robert Ochsenfeld discovered that a superconducting material will repel a magnetic field . A magnet moving by a conductor induces currents in the conductor. This is the

principle on which the electric generator operates. But, in a superconductor the induced currents exactly mirror the field that would have otherwise penetrated the superconducting material - causing the magnet to be repulsed. This phenomenon is known as strong diamagnetism and is today often referred to as the "Meissner effect" (as shown in fig (1.1)). The Meissner effect is so strong that a magnet can actually be levitated over a superconductive material[1].



**Fig (1.1) Meissner effect**

In subsequent decades other superconducting metals, alloys and compounds were discovered. In 1941 niobium-nitride was found to superconduct at 16 K. In 1953 vanadium-silicon displayed superconductive properties at 17.5 K. And, in 1962 scientists at Westinghouse developed the first commercial superconducting wire, an alloy of niobium and titanium (NbTi). High-energy, particle-accelerator electromagnets made of copper-clad niobium-titanium were then developed in the 1960s at the Rutherford-Appleton Laboratory in the UK, and were first employed in a superconducting accelerator at the Fermilab Tevatron in the US in 1987.

The first widely-accepted theoretical understanding of superconductivity was advanced in 1957 by American physicists John Bardeen, Leon Cooper, and John Schrieffer. Their Theories of Superconductivity became known as the BCS theory - derived from the first letter of each man's last name - and won them a Nobel prize in 1972. The mathematically-complex BCS theory explained superconductivity at temperatures close to absolute zero for elements and simple alloys. However, at higher temperatures and with different superconductor systems, the BCS theory has subsequently become inadequate to fully explain how superconductivity is occurring[1].

Another significant theoretical advancement came in 1962 when Brian D. Josephson, a graduate student at Cambridge University, predicted that electrical current would flow between 2 superconducting materials - even when they are separated by a non-superconductor or insulator. His prediction was later confirmed and won him a share of the 1973 Nobel Prize in Physics. This tunneling phenomenon is today known as the "Josephson effect" and has been applied to electronic devices such as the SQUID, an instrument capable of detecting even the weakest magnetic fields[1].

The 1980's were a decade of unrivaled discovery in the field of superconductivity. In 1964 Bill Little of Stanford University had suggested the possibility of organic (carbon-based) superconductors. The first of these theoretical superconductors was successfully synthesized in 1980 by Danish researcher Klaus Bechgaard of the University of Copenhagen and 3 French team members.  $(\text{TMTSF})_2\text{PF}_6$  had to be cooled to an incredibly cold 1.2K transition temperature (known as  $T_c$ ) and subjected to high pressure to superconduct. But, its mere existence proved the possibility of "designer" molecules - molecules fashioned to perform in a predictable way.

Then, in 1986, a truly breakthrough discovery was made in the field of superconductivity. Alex Müller and Georg Bednorz (above), researchers at the IBM Research Laboratory in Rüschlikon, Switzerland, created a brittle ceramic compound that superconducted at the highest temperature then known: 30 K. What made this discovery so remarkable was that ceramics are normally insulators. They don't conduct electricity well at all. So, researchers had not considered them as possible high-temperature superconductor candidates. The Lanthanum, Barium, Copper and Oxygen compound that Müller and Bednorz synthesized, behaved in a not-as-yet-understood way. (Original article printed in *Zeitschrift für Physik Condensed Matter*, April 1986.) The discovery of this first of the superconducting copper-oxides (cuprates) won the 2 men a Nobel Prize the following year. It was later found

that tiny amounts of this material were actually superconducting at 58 K, due to a small amount of lead having been added as a calibration standard - making the discovery even more noteworthy[1].

Müller and Bednorz' discovery triggered a flurry of activity in the field of superconductivity. Researchers around the world began "cooking" up ceramics of every imaginable combination in a quest for higher and higher  $T_c$ 's. In January of 1987 a research team at the University of Alabama-Huntsville substituted Yttrium for Lanthanum in the Müller and Bednorz molecule and achieved an incredible 92 K  $T_c$ . For the first time a material (today referred to as YBCO) had been found that would superconduct at temperatures warmer than liquid nitrogen - a commonly available coolant. Additional milestones have since been achieved using exotic - and often toxic - elements in the base perovskite ceramic. The current class (or "system") of ceramic superconductors with the highest transition temperatures are the mercuric-cuprates. The first synthesis of one of these compounds was achieved in 1993 at the University of Colorado and by the team of A. Schilling, M. Cantoni, J. D. Guo, and H. R. Ott of Zurich, Switzerland. The world record  $T_c$  of 138 K is now held by a thallium-doped, mercuric-cuprate comprised of the elements Mercury, Thallium, Barium, Calcium, Copper and Oxygen. The  $T_c$  of this ceramic superconductor was confirmed by Dr. Ron Goldfarb at the National Institute of Standards and Technology-Colorado in February of 1994. Under extreme pressure its  $T_c$  can be coaxed up even higher - approximately 25 to 30 degrees more at 300,000 atmospheres[1]

The first high- $T_c$  superconductor was discovered in 1986 by IBM researchers Georg Bednorz and K. Alex Müller, who were awarded the 1987 Nobel Prize in Physics "for their important break-through in the discovery of superconductivity in ceramic materials".

In this study , high temperature superconductivity was explained again and the first compound to exhibit superconductivity above the boiling point of water was synthesized .

## **1.6 Research layout :**

This research has come into five chapters, Chapter one is introduction. Chapter two theoretical background of the superconductors, Chapter three explain the mechanism of superconductivity , Chapter four concerned with the high temperature superconductors ,while chapter five is devoted for discussion and conclusion .

## Chapter Two

### Superconductors

#### 2.1 Introduction

As if ceramic superconductors were not strange enough, even more mysterious superconducting systems have been discovered. One is based on compounds centered around the "Fullerene". The fullerene name comes from the late designer-author Buckminster Fuller. Fuller was the inventor of the geodesic dome, a structure with a soccer ball shape. The fullerene - also called a buckminsterfullerene or "buckyball" - exists on a molecular level when 60 carbon atoms join in a closed sphere. When doped with one or more alkali metals the fullerene becomes a "fulleride" and has produced Tc's ranging from 8 K for  $\text{Na}_2\text{Rb}_{0.5}\text{Cs}_{0.5}\text{C}_{60}$  up to 40 K for  $\text{Cs}_3\text{C}_{60}$ . In 1993 researchers at the State University of New York at Buffalo reported Tc's between 60 K and 70 K for C-60 doped with the interhalogen compound ICI[2,3].

Fullerenes, like ceramic superconductors, are a fairly recent discovery. In 1985, professors Robert F. Curl, Jr. and Richard E. Smalley of Rice University in Houston and Professor Sir Harold W. Kroto of the University of Sussex in Brighton, England, accidentally stumbled upon them. The discovery of superconducting alkali metal fullerides came in 1991 when Robert Haddon and Bell Labs announced that  $\text{K}_3\text{C}_{60}$  had been found to superconduct at 18 K.

Larger, non-spherical pure carbon fullerenes that will superconduct have only recently been discovered. In April of 2001, Chinese researchers at Hong Kong University found 1-dimensional superconductivity in single-walled carbon nanotubes at around 15 Kelvin. And in February 2006, Physicists in

Japan showed non-aligned, multi-walled carbon nanotubes were superconductive at temperatures as high as 12 K. Silicon-based fullerides like  $\text{Na}_2\text{Ba}_6\text{Si}_{46}$  will also superconduct. However, they are structured as infinite networks, rather than discrete molecules.

## **2.2 Uses for Superconductors:**

Magnetic-levitation is an application where superconductors perform extremely well. Transport vehicles such as trains can be made to "float" on strong superconducting magnets, virtually eliminating friction between the train and its tracks. Not only would conventional electromagnets waste much of the electrical energy as heat, they would have to be physically much larger than superconducting magnets. A landmark for the commercial use of MAGLEV technology occurred in 1990 when it gained the status of a nationally-funded project in Japan. The Minister of Transport authorized construction of the Yamanashi Maglev Test Line which opened on April 3, 1997. In December 2003, the MLX01 test vehicle (shown above) attained an incredible speed of 361 mph (581 kph)[3].

Although the technology has now been proven, the wider use of MAGLEV vehicles has been constrained by political and environmental concerns (strong magnetic fields can create a bio-hazard). The world's first MAGLEV train to be adopted into commercial service, a shuttle in Birmingham, England, shut down in 1997 after operating for 11 years. A Sino-German maglev is currently operating over a 30-km course at Pudong International Airport in Shanghai, China. The U.S. plans to put its first (non-superconducting) Maglev train into operation on a Virginia college campus.

An area where superconductors can perform a life-saving function is in the field of bio magnetism. Doctors need a non-invasive means of determining what's going on inside the human body. By impinging a strong superconductor-derived magnetic field into the body, hydrogen atoms that

exist in the body's water and fat molecules are forced to accept energy from the magnetic field. They then release this energy at a frequency that can be detected and displayed graphically by a computer. Magnetic Resonance Imaging (MRI) was actually discovered in the mid 1940's. But, the first MRI exam on a human being was not performed until July 3, 1977. And, it took almost five hours to produce one image! Today's faster computers process the data in much less time[3].

The Korean Superconductivity Group within KRISS has carried bio magnetic technology a step further with the development of a double-relaxation oscillation SQUID (Superconducting Quantum Interference Device) for use in Magneto encephalography. SQUID's are capable of sensing a change in a magnetic field over a billion times weaker than the force that moves the needle on a compass (compass:  $5e-5T$ , SQUID:  $e-14T$ ). With this technology, the body can be probed to certain depths without the need for the strong magnetic fields associated with MRI's.



**Fig (2.1) Super-Collider project planned for construction in Ellis county, Texas**

Probably the one event, more than any other, that has been responsible for putting "superconductors" into the American lexicon as shown in fig (2.1) above, was the Superconducting Super-Collider project planned for construction in Ellis county, Texas. Though Congress cancelled the multi-billion dollar effort in 1993, the concept of such a large, high-energy collider would never have been viable without superconductors. High-energy particle research hinges on being able to accelerate sub-atomic particles to nearly the

speed of light. Superconductor magnets make this possible. CERN, a consortium of several European nations, is doing something similar with its Large Hadron Collider (LHC) recently inaugurated along the Franco-Swiss border[3].

Other related web sites worth visiting include the proton-antiproton collider page at Fermilab. This was the first facility to use superconducting magnets. Get information on the electron-proton collider HERA at the German lab pages of DESY (with English text). And Brookhaven National Laboratory features a page dedicated to its RHIC heavy-ion collider.

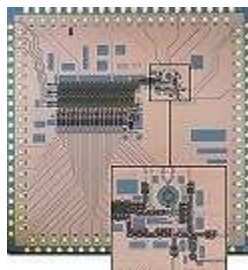
Electric generators made with superconducting wire are far more efficient than conventional generators wound with copper wire. In fact, their efficiency is above 99% and their size about half that of conventional generators. These facts make them very lucrative ventures for power utilities. General Electric has estimated the potential worldwide market for superconducting generators in the next decade at around 20-30 billion dollars. Late in 2002 GE Power Systems received \$12.3 million in funding from the U.S. Department of Energy to move high-temperature superconducting generator technology toward full commercialization. To read the latest news on superconducting generators.

Other commercial power projects in the works that employ superconductor technology include energy storage to enhance power stability. American Superconductor Corp. received an order from Alliant Energy in late March 2000 to install a Distributed Superconducting Magnetic Energy Storage System (D-SMES) in Wisconsin. Just one of these 6 D-SMES units has a power reserve of over 3 million watts, which can be retrieved whenever there is a need to stabilize line voltage during a disturbance in the power grid. AMSC has also installed more than 22 of its D-VAR systems to provide instantaneous reactive power support[3].

Recently, power utilities have also begun to use superconductor-based transformers and "fault limiters". The Swiss-Swedish company ABB was the first to connect a superconducting transformer to a utility power network in March of 1997. ABB also recently announced the development of a 6.4MVA (mega-volt-ampere) fault current limiter - the most powerful in the world. This new generation of HTS superconducting fault limiters is being called upon due to their ability to respond in just thousandths of a second to limit tens of thousands of amperes of current. Advanced Ceramics Limited is another of several companies that makes BSCCO type fault limiters. Intermagnetics General recently completed tests on its largest (15kv class) power-utility-size fault limiter at a Southern California Edison (SCE) substation near Norwalk, California. And, both the US and Japan have plans to replace underground copper power cables with superconducting BSCCO cable-in-conduit cooled with liquid nitrogen. (See photo below.) By doing this, more current can be routed through existing cable tunnels. In one instance 250 pounds of superconducting wire replaced 18,000 pounds of vintage copper wire, making it over 7000% more space-efficient[3].

An idealized application for superconductors is to employ them in the transmission of commercial power to cities. However, due to the high cost and impracticality of cooling miles of superconducting wire to cryogenic temperatures, this has only happened with short "test runs". In May of 2001 some 150,000 residents of Copenhagen, Denmark, began receiving their electricity through HTS (high-temperature superconducting) material. That cable was only 30 meters long, but proved adequate for testing purposes. In the summer of 2001 Pirelli completed installation of three 400-foot HTS cables for Detroit Edison at the Frisbie Substation capable of delivering 100 million watts of power. This marked the first time commercial power has been delivered to customers of a US power utility through superconducting wire. Intermagnetics General has announced that its IGC-SuperPower subsidiary has joined with BOC and Sumitomo Electric in a \$26 million

project to install an underground, HTS power cable in Albany, New York, in Niagara Mohawk Power Corporation's power grid. Sumitomo Electric's DI-BSCCO cable was employed in the first in-grid power cable demonstration project sponsored by the U.S. Department of Energy and New York Energy Research & Development Authority. After connecting to the grid successfully on July 2006, the DI-BSCCO cable has been supplying power to approximately 70,000 households without any problems. Currently the longest run of superconductive power cable was made in the AmpaCity project near Essen, Germany, in May 2014 as shown in fig (2.2). That cable was a kilometer in length.



**Fig (2.2) Hypres Superconducting Microchip,  
Incorporating 6000 Josephson Junctions.**

The National Science Foundation, along with NASA and DARPA and various universities, are currently researching "petaflop" computers. A petaflop is a thousand-trillion floating point operations per second. Today's fastest computers have only recently reached these speeds. Currently the fastest is the U.S. Department of Energy "Sequoia" Supercomputer, operating at 16.32 petaflops per second. The fastest single processor is a Lenslet optical DSP running at 8 teraflops. It has been conjectured that devices on the order of 50 nanometers in size along with unconventional switching mechanisms, such as the Josephson junctions associated with superconductors, will be necessary to achieve the next level of processing speeds. TRW researchers (now Northrop Grumman) have quantified this further by predicting that 100 billion Josephson junctions on 4000 microprocessors will be necessary to reach 32 petabits per second. These Josephson junctions are incorporated into

field-effect transistors which then become part of the logic circuits within the processors. Recently it was demonstrated at the Weizmann Institute in Israel that the tiny magnetic fields that penetrate Type 2 superconductors can be used for storing and retrieving digital information. It is, however, not a foregone conclusion that computers of the future will be built around superconducting devices. Competing technologies, such as quantum (DELTT) transistors, high-density molecule-scale processors, and DNA-based processing also have the potential to achieve peta flop benchmarks. In the electronics industry, ultra-high-performance filters are now being built. Since superconducting wire has near zero resistance, even at high frequencies, many more filter stages can be employed to achieve a desired frequency response. This translates into an ability to pass desired frequencies and block undesirable frequencies in high-congestion rf (radio frequency) applications such as cellular telephone systems. ISCO International and Superconductor Technologies are companies currently offering such filters[3].

Superconductors have also found widespread applications in the military. HTSC SQUIDS are being used by the U.S. NAVY to detect mines and submarines. And, significantly smaller motors are being built for NAVY ships using superconducting wire and "tape". In mid-July, 2001, American Superconductor unveiled a 5000-horsepower motor made with superconducting wire (below). An even larger 36.5MW HTS ship propulsion motor was delivered to the U.S. Navy in late 2006.

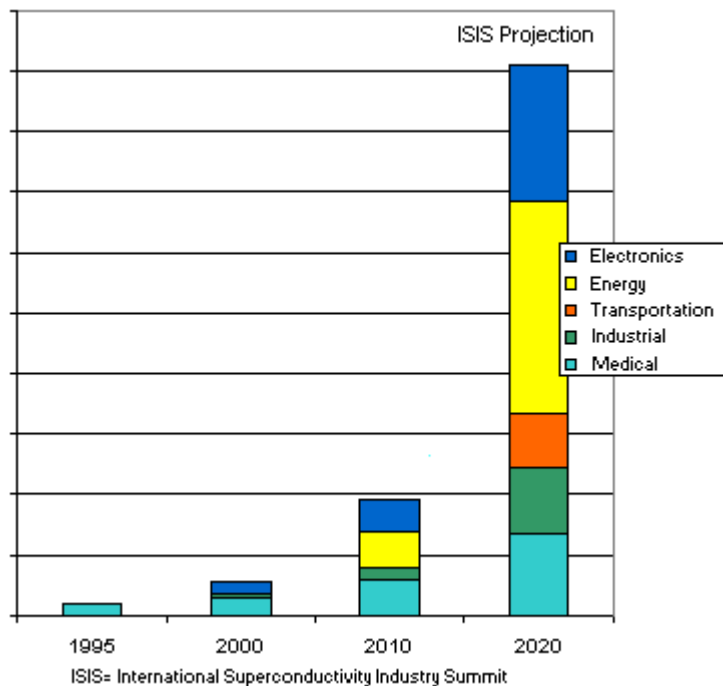
The newest application for HTS wire is in the degaussing of naval vessels. American Superconductor has announced the development of a superconducting degaussing cable. Degaussing of a ship's hull eliminates residual magnetic fields which might otherwise give away a ship's presence. In addition to reduced power requirements, HTS degaussing cable offers reduced size and weight.

The military is also looking at using superconductive tape as a means of reducing the length of very low frequency antennas employed on submarines. Normally, the lower the frequency, the longer an antenna must be. However, inserting a coil of wire ahead of the antenna will make it function as if it were much longer. Unfortunately, this loading coil also increases system losses by adding the resistance in the coil's wire. Using superconductive materials can significantly reduce losses in this coil. The Electronic Materials and Devices Research Group at University of Birmingham (UK) is credited with creating the first superconducting microwave antenna. Applications engineers suggest that superconducting carbon nanotubes might be an ideal nano-antenna for high-gigahertz and terahertz frequencies, once a method of achieving zero "on tube" contact resistance is perfected[3].

The most ignominious military use of superconductors may come with the deployment of "E-bombs". These are devices that make use of strong, superconductor-derived magnetic fields to create a fast, high-intensity electromagnetic pulse (EMP) to disable an enemy's electronic equipment. Such a device saw its first use in wartime in March 2003 when US Forces attacked an Iraqi broadcast facility.

Among emerging technologies are a stabilizing momentum wheel (gyroscope) for earth-orbiting satellites that employs the "flux-pinning" properties of imperfect superconductors to reduce friction to near zero. Superconducting x-ray detectors and ultra-fast, superconducting light detectors are being developed due to their inherent ability to detect extremely weak amounts of energy. Already Scientists at the European Space Agency (ESA) have developed what's being called the S-Cam, an optical camera of phenomenal sensitivity. And, superconductors may even play a role in Internet communications soon. In late February, 2000, Irvine Sensors Corporation received a \$1 million contract to research and develop a superconducting digital router for high-speed data communications up to 160

Ghz. Since Internet traffic is increasing exponentially, superconductor technology may be called upon to meet this super need. Irvine Sensors (as show in fig (2.3))speculates this router may see use in facilitating Internet2.



**Fig (2.3) ISIS projection**

According to June 2002 estimates by the Conectus consortium, the worldwide market for superconductor products is projected to grow to near US \$38 billion by 2020. Low-temperature superconductors are expected to continue to play a dominant role in well-established fields such as MRI and scientific research, with high-temperature superconductors enabling newer applications. The above ISIS graph gives a rough breakdown of the various markets in which superconductors are expected to make a contribution[3].

All of this is, of course, contingent upon a linear growth rate. Should new superconductors with higher transition temperatures be discovered, growth and development in this exciting field could explode virtually overnight.

Another impetus to the wider use of superconductors is political in nature. The reduction of green-house gas (GHG) emissions has becoming a topical issue due to the Kyoto Protocol which requires the European Union (EU) to

reduce its emissions by 8%. Physicists in Finland have calculated that the EU could reduce carbon dioxide emissions by up to 53 million tons if high-temperature superconductors were used in power plants.

The future melding of superconductors into our daily lives will also depend to a great degree on advancements in the field of cryogenic cooling. New, high-efficiency magnetocaloric-effect compounds such as gadolinium-silicon-germanium are expected to enter the marketplace soon. Such materials should make possible compact, refrigeration units to facilitate additional HTS applications[3].

### **2.3 Superconductor Terminology and the Naming Scheme**

**Anneal:** To heat and then slowly cool a material to reduce brittleness. Annealing of ceramic superconductors usually follows sintering and is done in an oxygen-rich atmosphere to restore oxygen lost during sintering. The oxygen content of a ceramic superconductor is critical. For example, YBCO with 6.4 atoms of oxygen will not superconduct. But YBCO with 6.5 atoms will[4,5].

**Anti-ferromagnetism:** A state of matter where adjacent ions in a material are aligned in opposite or "anti-parallel" arrays. Such materials display almost no response to an external magnetic field at low temperatures and only a weak attraction at higher temperatures. There is evidence that anti-ferromagnetism in the copper oxides plays a role in the formation of Cooper pairs and, thus, in facilitating a superconductive state in some compounds.

**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. This is analogous to rolling a bowling ball up the middle of a bed. 2 people, one lying on each side of the bed, will tend to roll toward the center of the bed, once the ball has created a depression in the mattress. And, a 2nd bowling ball, placed at the foot of the bed, will now, quite easily, roll toward the middle[4].

**Borocarbides:** Superconducting borocarbides are compounds containing both boron and carbon in combination with rare-earth and transition elements; some of which exhibit the unusual ability to return to a normal, non-superconductive state at temperatures below  $T_c$ .

**BSCCO:** An acronym for a ceramic superconductor system containing the elements Bismuth, Strontium, Calcium, Copper and Oxygen. Typically, a small amount of lead is also included in these compounds to promote the highest possible  $T_c$ . BSCCO has probably found the widest acceptance among high- $T_c$  superconductor applications due to its unique properties. BSCCO compounds exhibit both an intrinsic Josephson effect and anisotropic (directional) behavior.

**Ceramics:** Ceramic superconductors are inorganic compounds formed by reacting a metal with oxygen, nitrogen, carbon or silicon. The best-known of these are the copper-perovskites. Ceramics are typically hard, brittle, heat-resistant materials formed by a process known as solid-state reaction.

**Charge Reservoirs:** In superconductors, charge reservoirs are the layers that may control the oxidation state of adjacent superconducting planes (even though they themselves are not superconducting). In the layered cuprates, these consist of copper-oxide chains[4].

**Chevrel (phases):** A class of molybdenum chalcogenides (compounds containing Group VI elements S, Se or Te along with molybdenum and a

positively charged metal ion) - named for Roger Chevrel of the University of Rennes, whose research brought them to the attention of the scientific community in the early 1970's. Recently, the Superconductivity Group at the University of Durham (UK) reported a novel fabrication technique that increases  $H_{c2}$  (upper critical field) in the chevrel  $PbMo_6S_8$  from 50 T in bulk materials up to  $> 100$  T.

**Coherence Length:** The size of a cooper pair - representing the shortest distance over which superconductivity can be established in a material. This is typically on the order of  $1000\text{\AA}$ ; although it can be as small as  $30\text{\AA}$  in the copper oxides.

**Cooper Pair:** Two electrons that appear to "team up" in accordance with theory - BCS or other - despite the fact that they both have a negative charge and normally repel each other. (Named for Leon Cooper.) Below the superconducting transition temperature, paired electrons form a condensate - a macroscopically occupied single quantum state - which flows without resistance. However, since only a small fraction of the electrons are paired, the bulk does not qualify as being a "bose-einstein condensate".

**DAC:** An acronym for "diamond anvil cell". Often the  $T_c$  of a superconductor can be coaxed upward with the application of high pressure. The DAC is used to accomplish this in the laboratory. A DAC is composed of 2 specially-cut diamonds and a stainless steel gasket. The gasket goes between the diamonds and seals a small chamber in which a fluid is placed. Since neither the diamonds nor the liquid will compress, hydrostatic forces in excess of a million atmospheres can be brought to bear on a sample suspended within the fluid[4].

**Diamagnetism:** The ability of a material to repel a magnetic field. Many naturally-occurring substances (like water, wood and paraffin, and many of the elements) exhibit weak diamagnetism. Superconductors exhibit strong diamagnetism below  $T_c$ . In a few rare compounds, a material may become

superconductive at a higher temperature than the point at which diamagnetism appears. But, as a rule, the onset of strong diamagnetism is one of the most reliable ways to ascertain when a material has become superconductive.

**D-Wave:** A form of electron pairing in which the electrons travel together in orbits resembling a four-leaf clover. Wave functions help theoreticians describe (and predict) electron behavior. The d-wave models have gained substantial support recently over s-wave pairing as the mechanism by which high-temperature superconductivity might be explained[4].

**Energy Gap:** This is the energy required to break up a pair of electrons. According to BCS theory, the formula for determining the energy gap (in meV) is  $E_g = 7/2 K T_c$ . Where  $K$  = Boltzmann's constant ( $8.62 \times 10^{-5}$  eV/K). And where  $T_c$  is the critical transition temperature in Kelvin. Since electron-pairing is universally agreed to be the method by which superconductivity occurs, this is the amount of energy required to disrupt the superconducting state.

**Ferromagnetism:** A state wherein a material exhibits magnetization through the alignment of internal ions (neighboring magnetic moments). This contrasts with paramagnetism, which is temporary, much weaker and results from unpaired electrons.

**Flux-Lattice:** A configuration created when flux lines from a strong magnetic field try to penetrate the surface of a Type 2 superconductor. The tiny magnetic moments within each resulting vortex repel each other and a periodic lattice results as they array themselves in an orderly fashion.

**Fluxon:** The smallest magnetic flux (flux quantum) that exists in nature. Just as electrons are quantized charge, fluxons are a quantized flux. The term is used in association with vortices, which result from magnetic fields penetrating Type 2 superconductors in single fluxon quanta[4].

**Flux-Pinning:** The phenomenon where a magnet's lines of force (called flux) become trapped or "pinned" inside a superconducting material. This pinning binds the superconductor to the magnet at a fixed distance. Flux-pinning is only possible when there are defects in the crystalline structure of the superconductor (usually resulting from grain boundaries or impurities). Flux-pinning is desirable in high-temperature ceramic superconductors in order to prevent "flux-creep", which can create a pseudo-resistance and depress  $J_c$  and  $H_c$ [4].

**Four-point Probe:** The most common method of determining the  $T_c$  of a superconductor. Wires are attached to a material at four points with a conductive adhesive. Through two of these points a voltage is applied and, if the material is conductive, a current will flow. Then, if any resistance exists in the material, a voltage will appear across the other two points in accordance with Ohm's law (voltage equals current times resistance). When the material enters a superconductive state, its resistance drops to zero and no voltage appears across the second set of points. By using the four-point method, instead of just two points, resistance in the adhesive and wires can be ignored; as the second set of points do not themselves conduct any current and can, therefore, only reflect what voltage exists across the body of the material.

**Hall Effect:** When a magnetic field is applied perpendicularly to a thin metal film or semiconductor film that is conducting an electric current, a small voltage will appear perpendicular to the axis of both the film and the magnetic field. This voltage is proportional to the strength of the applied field. However, the output is typically not linear. The Hall resistance (the ratio of the Hall voltage to the current) changes in steps, pursuant to the laws of quantum mechanics. This is known as the Integral Quantum Hall Effect or just Quantum Hall Effect. Discovered in 1879, the Hall effect was named for its discoverer Edwin H. Hall, a graduate student at Johns Hopkins University.

H<sub>c</sub>: The scientific notation representing the "critical field" or maximum magnetic field that a superconductor can endure before it is "quenched" and returns to a non-superconducting state. Usually a higher T<sub>c</sub> also brings a higher H<sub>c</sub>[5].

Heavy Fermions: Compounds containing the elements cerium, ytterbium or uranium; whose (inner shell) conduction electrons often have effective masses (called quasiparticle masses) several hundred times as great as that of a "free" (normal) electron mass. This gives them what's known as a low "Fermi energy" and makes them unlikely - and unusual - superconductors. Research suggests cooper-pairing in heavy fermion systems arises from the magnetic interactions of the electron spins.

Hole: A positively-charged vacancy within a crystal lattice resulting from the shortage of an electron in that region. Holes are typically induced by doping a material with an impurity. However, they can also be synthesized electronically with devices like the field-effect transistor (FET). Modern electronic devices rely heavily on holes (as p-type semiconductors) to function. There is evidence that the holes of hypocharged oxygen in charge-reservoirs are, in fact, what makes possible high-temperature superconductivity in the layered cuprates[5].

HTS: An acronym for "High-Temperature Superconductor" (or Superconductivity). There is no widely-accepted temperature that separates HTS from LTS (Low-Temperature Superconductors). However, all the superconductors known before the 1986 discovery of the superconducting oxocuprates would be classified LTS. The barium-lanthanum-cuprate fabricated by Müller and Bednorz, with a T<sub>c</sub> of 30K, is generally considered to be the first HTS material. Certainly any compound that will superconduct above the boiling point of liquid nitrogen (77K) would be HTS.

Meissner Effect: Exhibiting diamagnetic properties to the total exclusion of all magnetic fields. (Named for Walther Meissner.) This is a classic hallmark of superconductivity and can actually be used to levitate a strong rare-earth magnet[5].

Mott Transition: The Mott transition is the shift from an insulating to a metallic state in a material. The high-temperature copper oxides are composed of CuO<sub>2</sub> planes that are separated from each other by ionic "blocking layers". Although it has one conduction electron (or hole) per Cu site, each CuO<sub>2</sub> plane is originally insulating because of the large electron correlation. That behavior is typical of the Mott insulator state, in which all the conduction electrons are tied to the atomic sites. The superconducting state emerges when holes from the blocking layers dope the CuO<sub>2</sub> layers in a way that alters the number of conduction electrons and triggers the Mott transition. Researchers believe that the strong antiferromagnetic correlation, which originates in the Mott-insulating CuO<sub>2</sub> sheets and persists into the metallic state, could be a possible mechanism of high-temperature superconductivity

Penetration Depth (also London Penetration Depth): This term relates to how deeply a magnetic field will penetrate the surface of a superconductor. An external magnetic field impinged upon a Type 2 superconductor will decay exponentially into the surface based on the paired electron density within the superconductor (only a small fraction of the electrons are in a superconductive state). The "London" name comes from brothers Fritz London and Heinz London, who in 1935 created a theoretical model of superconductivity[5].

Resistance: The opposition of a material to the flow of electrical current through it. Energy lost due to resistance is a result of vibrations at the molecular level and manifests itself as heat in proportion to the square of the current flow. In a superconductor all resistance disappears below a certain

temperature. However, this applies only to direct current (DC) electricity. Other types of losses result when transporting alternating current (AC). Examples of this include hysteresis, reactive-coupling and radiational losses. In the new high-temperature ceramic superconductors, the power loss in applications like transmission lines is inversely proportional to the critical current density for low magnetic field applications. This limitation can be compensated for to some degree by increasing the ratio of voltage to current. In Type 2 superconductors carrying high-frequency alternating current, "skin effect" losses also result as the energy tends to migrate to the surface where the conductive medium is inhomogeneous, producing a pseudo-resistance. In some materials the amount of resistance may also depend on the direction of current flow (anisotropic resistivity) and/or presence of an external magnetic field (hall effect)[4].

Room-temperature Superconductivity (RTSC): It has been theorized that a metallic form of hydrogen might be a room-temperature superconductor. In 1996 physicists at Lawrence Livermore Laboratory were able to briefly create metallic hydrogen. But, its existence was fleeting and no measurement of the Meissner effect was possible. Zero resistance has been observed at room temperatures in ballistic quantum wire. However, having one-dimensional geometry, this wire does not exhibit the Meissner effect, except when configured as a closed loop. Several copper-oxide superconductors have displayed signs of RTSC. But the volume fraction (percentage) of material was so low as to be unusable until a refinement method can be developed[5].

Superconductor: An element, inter-metallic alloy, or compound that will conduct electricity without resistance below a certain temperature. However, this applies only to direct current (DC) electricity and to finite amounts of current. All known superconductors are solids. None are gases or liquids. And all require extreme cold to enter a superconductive state. Once set in motion, current will flow forever in a closed loop of superconducting material -

making it the closest thing to perpetual motion in nature. Scientists refer to superconductivity as a "macroscopic quantum phenomenon". In addition to being classified Type 1 and Type 2, superconductors can be categorized further by their dimensionality. Most are 3-D. But some compounds, like surface-doped  $\text{NaWO}_3$  and some organic superconductors are 2-D.  $\text{Li}_2\text{CuO}_2$  and single-walled carbon nano-tubes have shown rare 1-D superconductivity. In addition to repelling magnetic fields, enhanced thermal conductivity, higher optical reflectivity and reduced surface friction are also properties of superconductors. The term "superconductor" is also used in some instances to refer to materials that have near infinite thermal conductivity - such as carbon nanotubes. However, on this website it is used in the context of electrical conductivity only[5].

**Susceptibility:** A measure of the relative amount of induced magnetism in a material. Magnetic susceptibility is often used in lieu of resistance measurements to determine the transition temperature of a superconductor. Although, on occasion, the two techniques produce very different  $T_c$ 's. In a typical superconductor, the (arbitrary) value of susceptibility will change from zero to a negative number as the temperature drops through  $T_c$ . However, in some materials it changes from positive to negative, as paramagnetism yields to diamagnetism[5].

**Unit Cell:** A unit cell is the smallest assemblage of atoms, ions, or molecules in a solid, beyond which the structure repeats to form the 3-dimensional crystal lattice.

**Vortices (plural of vortex):** Swirling tubes of electrical current induced by an external magnetic field into the surface of a superconducting material that represent a topological singularity in the wavefunction. These are particularly evident in Type 2 superconductors during "mixed-state" behavior when the surface is just partially superconducting. Superconductivity is completely suppressed within these volcano-shaped structures. Recent research suggests

that flux vortices may NOT possess quantum values (equal to multiples of Planck's constant divided by 2 times electron charge). But may instead have but a tiny fraction of the basic unit of magnetism. The movement of vortices can produce a pseudo-resistance and, as such, is undesirable. While superconductivity is a "macroscopic" phenomenon, vortices are a "mesoscopic" phenomenon.

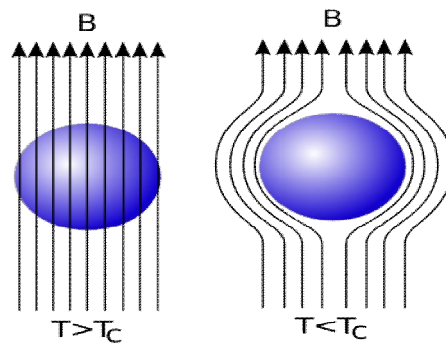
## Chapter Three

### 3.1 Introduction:

The London equations, developed by brothers Fritz and Heinz London in 1935, relate current to electromagnetic fields in and around a superconductor. Arguably the simplest meaningful description of superconducting phenomena, they form the genesis of almost any modern introductory text on the subject. A major triumph of the equations is their ability to explain the Meissner effect, wherein a material exponentially expels all internal magnetic fields as it crosses the superconducting threshold[6].

### 3.2 London equations:

A material drops below its superconducting critical temperature, magnetic fields within the material are expelled via the , as shown in fig(3.1).



**Fig (3.1) Meissner effect.**

There are two London equations when expressed in terms of measurable fields:

$$\frac{\partial \mathbf{j}_s}{\partial t} = \frac{n_s e^2}{m} \mathbf{E}, \quad \nabla \times \mathbf{j}_s = -\frac{n_s e^2}{mc} \mathbf{B}. \quad (3.1)$$

Here  $\mathbf{j}_s$  is the superconducting current density,  $E$  and  $B$  are respectively the electric and magnetic fields within the superconductor,  $e$  is the charge of an electron & proton,  $m$  is electron mass, and  $n_s$  is a phenomenological constant loosely associated with a number density of superconducting carriers. Throughout this article Gaussian (cgs) units are employed[6].

On the other hand, if one is willing to abstract away slightly, both the expressions above can more neatly be written in terms of a single "London Equation" in terms of the vector potential  $A$ :

$$\mathbf{j}_s = -\frac{n_s e^2}{mc} \mathbf{A}. \quad (3.2)$$

The last equation suffers from only the disadvantage that it is not gauge invariant, but is true only in the Coulomb gauge, where the divergence of  $A$  is zero. This equation holds for magnetic fields that vary slowly in space.

### 3.2.1 London Penetration Depth

If the second of London's equations is manipulated by applying Ampere's law,

$$\nabla \times \mathbf{B} = \frac{4\pi \mathbf{j}}{c}, \quad (3.3)$$

then the result is the differential equation

$$\nabla^2 \mathbf{B} = \frac{1}{\lambda^2} \mathbf{B}, \quad \lambda \equiv \sqrt{\frac{mc^2}{4\pi n_s e^2}}. \quad (3.4)$$

Thus, the London equations imply a characteristic length scale,  $\lambda$ , over which external magnetic fields are exponentially suppressed. This value is the London penetration depth.

A simple example geometry is a flat boundary between a superconductor within free space where the magnetic field outside the superconductor is a

constant value pointed parallel to the superconducting boundary plane in the  $z$  direction. If  $x$  leads perpendicular to the boundary then the solution inside the superconductor may be shown to be

$$B_z(x) = B_0 e^{-x/\lambda}. \quad (3.5)$$

From here the physical meaning of the London penetration depth can perhaps most easily be discerned[6].

### 3.2.2 Rationale for the London Equations

While it is important to note that the above equations cannot be formally derived, the Londons did follow a certain intuitive logic in the formulation of their theory. Substances across a stunningly wide range of composition behave roughly according to Ohm's law, which states that current is proportional to electric field. However, such a linear relationship is impossible in a superconductor for, almost by definition, the electrons in a superconductor flow with no resistance whatsoever. To this end, the London brothers imagined electrons as if they were free electrons under the influence of a uniform external electric field. According to the Lorentz force law

$$\mathbf{F} = e\mathbf{E} + \frac{e}{c}\mathbf{v} \times \mathbf{B} \quad (3.6)$$

these electrons should encounter a uniform force, and thus they should in fact accelerate uniformly. This is precisely what the first London equation states.

To obtain the second equation, take the curl of the first London equation and apply Faraday's law,

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad (3.7)$$

to obtain

$$\frac{\partial}{\partial t} \left( \nabla \times \mathbf{j}_s + \frac{n_s e^2}{mc} \mathbf{B} \right) = 0. \quad (3.8)$$

As it currently stands, this equation permits both constant and exponentially decaying solutions. The Londons recognized from the Meissner effect that constant nonzero solutions were nonphysical, and thus postulated that not only was the time derivative of the above expression equal to zero, but also that the expression in the parentheses must be identically zero. This results in the second London equation[6].

### 3.2.3 Canonical momentum arguments:

It is also possible to justify the London equations by other means. Current density is defined according to the equation

$$\mathbf{j}_s = n_s e \mathbf{v}. \quad (3.9)$$

Taking this expression from a classical description to a quantum mechanical one, we must replace values  $j$  and  $v$  by the expectation values of their operators. The velocity operator

$$\mathbf{v} = \frac{1}{m} \left( \mathbf{p} - \frac{e}{c} \mathbf{A} \right) \quad (3.10)$$

is defined by dividing the gauge-invariant, kinematic momentum operator by the particle mass  $m$ . We may then make this replacement in the equation above. However, an important assumption from the microscopic theory of superconductivity is that the superconducting state of a system is the ground state, and according to a theorem of Bloch's, in such a state the canonical momentum  $p$  is zero. This leaves

$$\mathbf{j}_s = -\frac{n_s e^2}{mc} \mathbf{A}, \quad (3.11)$$

which is the London equation according to the second formulation above.

### 3.3 Coherence length:

In physics, coherence length is the propagation distance over which a coherent wave (e.g. an electromagnetic wave) maintains a specified degree of coherence. Wave interference is strong when the paths taken by all of the interfering waves differ by less than the coherence length. A wave with a longer coherence length is closer to a perfect sinusoidal wave. Coherence length is important in holography and telecommunications engineering[6].

This article focuses on the coherence of classical electromagnetic fields. In quantum mechanics, there is a mathematically analogous concept of the quantum coherence length of a wave function.

In radio-band systems, the coherence length is approximated by

$$L = \frac{c}{n \Delta f}, \quad (3.12)$$

where  $c$  is the speed of light in a vacuum,  $n$  is the refractive index of the medium, and  $\Delta f$  is the bandwidth of the source.

In optical communications, the coherence length  $L$  is given by

$$L = \frac{2 \ln(2) \lambda^2}{\pi n \Delta \lambda}, \quad (3.13)$$

where  $\lambda$  is the central wavelength of the source,  $n$  is the refractive index of the medium, and  $\Delta \lambda$  is the spectral width of the source. If the source has a Gaussian spectrum with FWHM spectral width  $\Delta \lambda$ , then a path offset of  $\pm L$  will reduce the fringe visibility to 50%.

Coherence length is usually applied to the optical regime.

The expression above is a frequently used approximation. Due to ambiguities in the definition of spectral width of a source, however, the following definition of coherence length has been suggested:

The coherence length can be measured using a Michelson interferometer and is the optical path length difference of a self-interfering laser beam which corresponds to a  $1/e = 37\%$  fringe visibility, where the fringe visibility is defined as

$$V = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}, \quad (3.14)$$

where  $I$  is the fringe intensity.

In long-distance transmission systems, the coherence length may be reduced by propagation factors such as dispersion, scattering, and diffraction.

Multimode helium–neon lasers have a typical coherence length of 20 cm, while the coherence length of singlemode ones can exceed 100 m. Semiconductor lasers reach some 100 m. Singlemode fiber lasers with linewidths of a few kHz can have coherence lengths exceeding 100 km. Similar coherence lengths can be reached with optical frequency combs due to the narrow linewidth of each tooth. Non-zero visibility is present only for short intervals of pulses repeated after cavity length distances up to this long coherence length[6].

### **3.4 BCS theory:**

BCS theory is the first microscopic theory of superconductivity since its discovery in 1911. The theory describes superconductivity as a microscopic effect caused by a condensation of Cooper pairs into a boson-like state. The theory is also used in nuclear physics to describe the pairing interaction between nucleons in an atomic nucleus. It was proposed by John Bardeen,

Leon Cooper, and John Robert Schrieffer ("BCS") in 1957; they received the Nobel prize in physics for this theory in 1972[7].

Rapid progress in understanding superconductivity gained momentum in the mid-1950s. It began with the 1948 paper, "On the Problem of the Molecular Theory of Superconductivity", where Fritz London proposed that the phenomenological London equations may be consequences of the coherence of a quantum state. In 1953, Brian Pippard, motivated by penetration experiments, proposed that this would modify the London equations via a new scale parameter called the coherence length. John Bardeen then argued in the 1955 paper, "Theory of the Meissner Effect in Superconductors", that such a modification naturally occurs in a theory with an energy gap. The key ingredient was Leon Neil Cooper's calculation of the bound states of electrons subject to an attractive force in his 1956 paper, "Bound Electron Pairs in a Degenerate Fermi Gas".

In 1957 Bardeen and Cooper assembled these ingredients and constructed such a theory, the BCS theory, with Robert Schrieffer. The theory was first published in April 1957 in the letter, "Microscopic theory of superconductivity". The demonstration that the phase transition is second order, that it reproduces the Meissner effect and the calculations of specific heats and penetration depths appeared in the December 1957 article, "Theory of superconductivity". They received the Nobel Prize in Physics in 1972 for this theory. The 1950 Landau-Ginzburg theory of superconductivity is not cited in either of the BCS papers.

In 1986, high-temperature superconductivity was discovered (i.e. superconductivity at temperatures considerably above the previous limit of about 30 K; up to about 130 K). It is believed that BCS theory alone cannot explain this phenomenon and that other effects are at play. These effects are still not yet fully understood; it is possible that they even control superconductivity at low temperatures for some materials[7].

At sufficiently low temperatures, electrons near the Fermi surface become unstable against the formation of Cooper pairs. Cooper showed such binding will occur in the presence of an attractive potential, no matter how weak. In conventional superconductors, an attraction is generally attributed to an electron-lattice interaction. The BCS theory, however, requires only that the potential be attractive, regardless of its origin. In the BCS framework, superconductivity is a macroscopic effect which results from the condensation of Cooper pairs. These have some bosonic properties, while bosons, at sufficiently low temperature, can form a large Bose–Einstein condensate. Superconductivity was simultaneously explained by Nikolay Bogolyubov, by means of the so-called Bogoliubov transformations.

In many superconductors, the attractive interaction between electrons (necessary for pairing) is brought about indirectly by the interaction between the electrons and the vibrating crystal lattice (the phonons). Roughly speaking the picture is the following:

An electron moving through a conductor will attract nearby positive charges in the lattice. This deformation of the lattice causes another electron, with opposite spin, to move into the region of higher positive charge density. The two electrons then become correlated. Because there are a lot of such electron pairs in a superconductor, these pairs overlap very strongly and form a highly collective condensate. In this "condensed" state, the breaking of one pair will change the energy of the entire condensate - not just a single electron, or a single pair. Thus, the energy required to break any single pair is related to the energy required to break all of the pairs (or more than just two electrons). Because the pairing increases this energy barrier, kicks from oscillating atoms in the conductor (which are small at sufficiently low temperatures) are not enough to affect the condensate as a whole, or any individual "member pair" within the condensate. Thus the electrons

stay paired together and resist all kicks, and the electron flow as a whole (the current through the superconductor) will not experience resistance. Thus, the collective behavior of the condensate is a crucial ingredient necessary for superconductivity[7].

BCS theory starts from the assumption that there is some attraction between electrons, which can overcome the Coulomb repulsion. In most materials (in low temperature superconductors), this attraction is brought about indirectly by the coupling of electrons to the crystal lattice (as explained above). However, the results of BCS theory do *not* depend on the origin of the attractive interaction. For instance, Cooper pairs have been observed in ultracold gases of fermions where a homogeneous magnetic field has been tuned to their Feshbach resonance. The original results of BCS (discussed below) described an s-wave superconducting state, which is the rule among low-temperature superconductors but is not realized in many unconventional superconductors such as the d-wave high-temperature superconductors. Extensions of BCS theory exist to describe these other cases, although they are insufficient to completely describe the observed features of high-temperature superconductivity.

BCS is able to give an approximation for the quantum-mechanical many-body state of the system of (attractively interacting) electrons inside the metal. This state is now known as the BCS state. In the normal state of a metal, electrons move independently, whereas in the BCS state, they are bound into Cooper pairs by the attractive interaction. The BCS formalism is based on the reduced potential for the electrons attraction. Within this potential, a variational ansatz for the wave function is proposed. This ansatz was later shown to be exact in the dense limit of pairs. Note that the continuous crossover between the dilute and dense regimes of attracting pairs of fermions is still an open problem, which now attracts a lot of attention within the field of ultracold gases[7].

### 3.4.1 Underlying evidence:

The hyper physics website pages at Georgia State University summarize some key background to BCS theory as follows:

- Evidence of a band gap at the Fermi level (described as "a key piece in the puzzle") - the existence of a critical temperature and critical magnetic field implied a band gap, and suggested a phase transition, but single electrons are forbidden from condensing to the same energy level by the Pauli exclusion principle. The site comments that "a drastic change in conductivity demanded a drastic change in electron behavior". Conceivably, pairs of electrons might perhaps act like bosons instead, which are bound by different condensate rules and do not have the same limitation.
- Isotope effect on the critical temperature, suggesting lattice interactions. The Debye frequency of phonons in a lattice is proportional to the inverse of the square root of the mass of lattice ions. It was shown that the superconducting transition temperature of mercury indeed showed the same dependence, by substituting natural mercury  $^{202}\text{Hg}$  with a different isotope  $^{198}\text{Hg}$ .
- An exponential rise in heat capacity near the critical temperature for some superconductors - An exponential increase in heat capacity near the critical temperature also suggests an energy bandgap for the superconducting material. As superconducting vanadium is warmed toward its critical temperature, its heat capacity increases massively in a very few degrees; this suggests an energy gap being bridged by thermal energy.
- The lessening of the measured energy gap towards the critical temperature - this suggests a type of situation where some kind of binding energy exists but it is gradually weakened as the

critical temperature is approached. A binding energy suggests two or more particles or other entities that are bound together in the superconducting state. This helped to support the idea of bound particles - specifically electron pairs - and together with the above helped to paint a general picture of paired electrons and their lattice interactions.

### **3.4.2 Successes of the BCS theory**

BCS derived several important theoretical predictions that are independent of the details of the interaction, since the quantitative predictions mentioned below hold for any sufficiently weak attraction between the electrons and this last condition is fulfilled for many low temperature superconductors - the so-called weak-coupling case. These have been confirmed in numerous experiments:

- The electrons are bound into Cooper pairs, and these pairs are correlated due to the Pauli exclusion principle for the electrons, from which they are constructed. Therefore, in order to break a pair, one has to change energies of all other pairs. This means there is an energy gap for single-particle excitation, unlike in the normal metal (where the state of an electron can be changed by adding an arbitrarily small amount of energy). This energy gap is highest at low temperatures but vanishes at the transition temperature when superconductivity ceases to exist. The BCS theory gives an expression that shows how the gap grows with the strength of the attractive interaction and the (normal phase) single particle density of states at the Fermi level. Furthermore, it describes how the density of states is changed on entering the superconducting state, where there are no electronic states any more at the Fermi level. The energy gap is most directly observed in tunneling experiments and in reflection of microwaves from superconductors.

- BCS theory predicts the dependence of the value of the energy gap  $\Delta$  at temperature  $T$  on the critical temperature  $T_c$ . The ratio between the value of the energy gap at zero temperature and the value of the superconducting transition temperature (expressed in energy units) takes the universal value

$$\Delta(T = 0) = 1.764 k_B T_c, \quad (3.15)$$

independent of material. Near the critical temperature the relation asymptotes to

$$\Delta(T \rightarrow T_c) \approx 3.07 k_B T_c \sqrt{1 - (T/T_c)} \quad (3.16)$$

which is of the form suggested the previous year by M. J. Buckingham<sup>[11]</sup> based on the fact that the superconducting phase transition is second order, that the superconducting phase has a mass gap and on Blevins, Gordy and Fairbank's experimental results the previous year on the absorption of millimeter waves by superconducting[7].

- Due to the energy gap, the specific heat of the superconductor is suppressed strongly (exponentially) at low temperatures, there being no thermal excitations left. However, before reaching the transition temperature, the specific heat of the superconductor becomes even higher than that of the normal conductor (measured immediately above the transition).
- BCS theory correctly predicts the Meissner effect, i.e. the expulsion of a magnetic field from the superconductor and the variation of the penetration depth (the extent of the screening currents flowing below the metal's surface) with temperature. This had been demonstrated experimentally by Walther Meissner and Robert Ochsenfeld in their 1933 article *Ein neuer Effekt bei Eintritt der Supraleitfähigkeit*.

- It also describes the variation of the critical magnetic field (above which the superconductor can no longer expel the field but becomes normal conducting) with temperature. BCS theory relates the value of the critical field at zero temperature to the value of the transition temperature and the density of states at the Fermi level.
- In its simplest form, BCS gives the superconducting transition temperature  $T_c$  in terms of the electron-phonon coupling potential  $V$  and the Debye cutoff energy  $E_D$ :

$$k_B T_c = 1.13 E_D e^{-1/N(0) V}, \quad (3.17)$$

where  $N(0)$  is the electronic density of states at the Fermi level. For more details, see Cooper pairs.

- The BCS theory reproduces the isotope effect, which is the experimental observation that for a given superconducting material, the critical temperature is inversely proportional to the mass of the isotope used in the material. The isotope effect was reported by two groups on 24 March 1950, who discovered it independently working with different mercury isotopes, although a few days before publication they learned of each other's results at the ONR conference in Atlanta. The two groups are Emanuel Maxwell, who published his results in Isotope Effect in the Superconductivity of Mercury and C. A. Reynolds, B. Serin, W. H. Wright, and L. B. Nesbitt who published their results 10 pages later in Superconductivity of Isotopes of Mercury. The choice of isotope ordinarily has little effect on the electrical properties of a material, but does affect the frequency of lattice vibrations. This effect suggests that superconductivity is related to vibrations of the lattice. This is incorporated into BCS theory, where lattice vibrations yield the binding energy of electrons in a Cooper pair.

### 3.5 Bardeen-Cooper-Schrieffer theory:

The BCS theory or Bardeen-Cooper-Schrieffer theory is the theory of superconductivity developed by John Bardeen, Leon N Cooper and John R. Schrieffer in 1957.

### **3.5.1 Electron correlations that produce superconductivity:**

The superconducting phase exhibits correlations absent in the normal metal. It is believed that any attractive interaction between fermions in a many-fermion system can produce a superconducting-like state and this is thought to be the case, in addition to metals, in nuclei, neutron stars and He. Thus the BCS theory focuses on the consequences of an attractive two-body interaction without enquiring too much further about its origin[7].

The fundamental difference between the superconducting and normal ground state wave functions is produced when the large degeneracy of single-particle electron levels in the normal state is removed. If one visualizes the Hamiltonian matrix that results from an attractive two-body interaction in the basis of normal metal configurations, one finds sub-matrices in which all single-particle states except for one pair of electrons remain unchanged. These two electrons can scatter via their interaction to all states of the same total momentum. Such pair may be thought to “wend its way” over all states unoccupied by other electrons. It is known as a Cooper pair and plays the central role in BCS.

Since every such state is connected to every other, one is presented with submatrices of the entire Hamiltonian corresponding to an  $M$ -dimensional space of two-particle excited states on top of the Fermi sea. The origin of Cooper pairs can be understood from the following simplified example: all off-diagonal elements are set equal to  $-V$  and all diagonal terms are set equal to 0 as though all the initial electron levels were completely degenerate. Diagonalizing this matrix results in an energy level structure with  $M-1$  levels with energy  $V$  and one level with the energy  $E=-(M-1)V$ . The latter level is a

superposition of all original levels. The number of levels  $M$  is proportional to the volume of the system while the scattering matrix element  $V$  is inversely proportional to the volume. Hence,  $E$  is independent of the volume. In other words, the removal of the degeneracy produces a single level separated from the others by a volume independent gap.

To incorporate this into a solution of the full Hamiltonian, one must devise a technique by which all electron pairs can scatter while obeying the exclusion principle. In the BCS wave function that accomplishes this, an inspired guess of Robert Schrieffer, each pair gains an energy due to the removal of the degeneracy as above and one obtains the maximum correlation of the entire wave function if all pairs have the same total momentum. For a combination of statistical and dynamical reasons, this gives a coherence to the wave function with a preference for momentum zero, singlet spin correlations. Formation of the superconducting state is a phase transition, and is characterized by an order parameter. Gor'kov showed that the superconducting symmetry parameter is proportional to the wave function of the Cooper pair[7].

### **3.5.2 Thermodynamic properties of the ideal superconductor**

The thermodynamic properties of the superconductor follow from the excitation spectrum discussed in the previous section. The free energy of the superconductor is given by

$$F[h,\phi,f]=W(T)-TS, \tag{3.18}$$

where  $T$  is the temperature and  $S$  is the entropy;  $f(k)$  is the probability that the state  $k$  is occupied by a quasiparticle (a superconducting Fermi function). The entropy of the system comes entirely from the excitations as the correlated portion of the wave-function is not degenerate. Since a portion of the phase space is occupied by excitations at finite temperatures, making it unavailable

for the transitions of bound pairs, the energy is a function of the temperature  $W(T)$ . As  $T$  increases,  $|W(T)|$  and at the same time  $\Delta$  decrease until the critical temperature is reached and the system reverts to the normal phase[7].

The minimization of the free energy with respect to the variational parameters  $h$  and  $f$  gives the Fermi-Dirac expression for  $f$ :

$$f = \frac{1}{1 + \exp(E/kT)} \quad (3.19)$$

where  $E$  is given by Eq. (1) and the gap  $\Delta$  satisfies the fundamental integral equation of the theory

$$\Delta k(T) = -12 \sum_q V_{kq} \Delta q(T) E q(T) \tan \frac{h E q(T)}{2kT}. \quad (3.20)$$

This equation has a nonzero solution for the gap  $\Delta(T)$  below a critical temperature  $T_c$ . At  $T < T_c$  the properties of the system are qualitatively different from the normal metal.

In the simplified model used in the original formulation of the BCS theory, the scattering potential was approximated as

$$V_{kq} = -V, |\epsilon| < \hbar\omega D \quad (3.21)$$

$$V_{kq} = 0, |\epsilon| > \hbar\omega D \quad (3.22)$$

where  $\omega D$  is the Debye frequency of the material. The energy-dependent density of states was replaced by its value at the Fermi surface  $N(0)$ . In this approximation the second-order transition temperature in zero magnetic field

$$kT_c = 1.14 \hbar\omega D \exp(-1/N(0)V) \quad (3.23)$$

At zero temperature the gap

$$\Delta(0) = 1.76 kT_c. \quad (3.24)$$

The Cooper pair size can be estimated as  $\xi = \hbar v_F / [\pi \Delta]$ , where  $v_F$  is the Fermi velocity in the normal state. The gap approaches zero as

$$\Delta(T) = 1.74 \Delta(0) \left(1 - T/T_c\right) \quad (3.25)$$

near the critical temperature. The specific heat is discontinuous at the transition point. Right below the transition it is 2.43 times greater than immediately above it. At low temperatures the specific heat is exponentially small as a function of the inverse temperature.

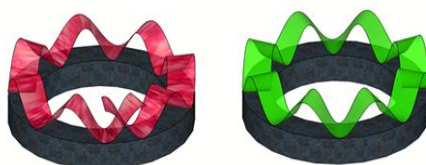
### **3.6 Flux quantization:**

The “huge” size of the quantum wave that describes superconductivity has a surprising consequence: the quantization of the magnetic field. Indeed, when an object becomes superconducting, the quantum wave describing the electron properties covers the entire object, however big the latter might be. This is what is original in these collective modes, where a single wave corresponds to all the electrons in the system. This superconducting wave has a “phase”. The notion of phase is very general: the phase of a wave for instance, consists in knowing whether we are in the trough or on the crest of the wave[7].

In classical physics, a wave corresponds to something that oscillates; to know the phase, you have to check at which place of the oscillation you are: the value of the phase enables to know whether we are at the beginning, in the middle or at the end of that oscillation. For a quantum wave, the definition of phase is more complicated, because no object is oscillating. Nevertheless, this phase has a determined value that can be constant or that can vary in the superconducting object.

When the superconducting object has a hole (in the case of a ring for instance), the phase variation must follow certain rules. Indeed, when you have reached a complete turn of the ring, the phase value needs to go back to

the same value, because the phase cannot be discontinuous. Some variations are hence forbidden. Yet, when a magnetic flux is applied to a ring, this flux modifies the phase along the ring. In order for the phase to go back to its initial value after a complete turn, only certain values of magnetic flux are allowed to go through the ring. The flux is “quantized”, which means it only proceeds by stages and only takes integer multiple values of a basic value called flux quantum,  $\Phi_0$ , equal to  $2,07 \cdot 10^{-15} \text{ Tm}^2$  (or Weber)[7]. The phase variation of the condensate along the ring is represented by a colour oscillation. The left image cannot exist, because the phase is not continuous (no joint after a turn of the ring). The right image corresponds to an acceptable situation as shown in fig (3.2).



**Fig (3.2) Schematic representation of a superconducting ring**

To summarize, since the quantum wave is defined on the entire superconducting object, its phase must do an integer number of “oscillations” when we follow a full turn of the ring. Consequently, the magnetic flux in this ring is quantized, which means it must be a multiple of a minimum value,  $\Phi_0$ . This value is very small, but it was possible to measure it with experiments! Theoretically, the value of  $\Phi_0$  depends on the electric charge of the bosons that form the superconducting condensate: the value we get for  $\Phi_0$  corresponds to a charge twice as high as that of an isolated electron. Measuring  $\Phi_0$  is hence a way to confirm that the quantum objects forming the superconducting condensate are electron pairs and not isolated electrons.

Flux quantization also enables to understand why, in a mixed state, one magnetic flux quantum goes through each vortex, whatever the chemical composition of the superconductor and whatever the precise value of the temperature and the magnetic field.

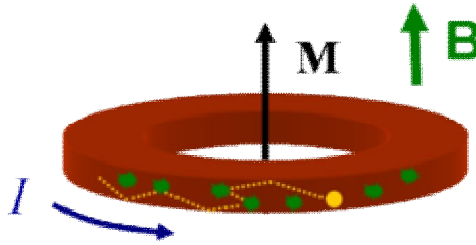
Another consequence of the existence of the phase of the condensate is the Josephson effect[7].

### **3.6.1 Persistent currents in superconductors:**

In superconductors, charge can flow without any resistance. It is possible to make pieces of superconductor with a large built-in persistent current, either by creating the superconducting state (cooling the material) while charge is flowing through it, or by changing the magnetic field around the superconductor after creating the superconducting state. This principle is used in superconducting electromagnets to generate sustained high magnetic fields that only require a small amount of power to maintain. The persistent current was first identified by Onnes, and attempts to set a lower bound on their duration have reached values of over 100,000 years.

### **3.6.2 Persistent currents in resistive conductors:**

The green arrow as shown in fig (3.3) indicates the direction of static applied magnetic field  $B$  which allows a net current  $I$  (blue arrow) to flow and create a magnetization  $M$  (black arrow) by breaking the symmetry between clockwise and counterclockwise currents. The yellow dot represents an electron traversing the disordered material of the ring (green stars) without dissipation. A typical ring current is 1 nanoampere for a ring diameter of 0.6 micrometer at a temperature below 0.5 kelvin[7].



**Fig (3.3) Persistent current schematic**

Surprisingly, it is also possible to have tiny persistent currents inside resistive metals that are placed in a magnetic field, even in metals that are nominally "non-magnetic". The current is the result of a quantum mechanical effect that influences how electrons travel through metals, and arises from the same kind of motion that allows the electrons inside an atom to orbit the nucleus forever.

This type of persistent current is a mesoscopic low temperature effect: the magnitude of the current becomes appreciable when the size of the metallic system is reduced to the scale of the electron quantum phase coherence length and the thermal length. Unlike with superconductors, these persistent currents do not appear at zero magnetic field, as the current fluctuates symmetrically between positive and negative values; the magnetic field breaks that symmetry and allows a nonzero average current. Although the persistent current in an individual ring is largely unpredictable due to uncontrolled factors like the disorder configuration, it has a slight bias so that an average persistent current appears even for an ensemble of conductors with different disorder configurations.

This kind of persistent current was first predicted to be experimentally observable in micrometer-scale rings in 1983 by Markus Büttiker, Yoseph Imry, and Rolf Landauer. Because the effect requires the phase coherence of electrons around the entire ring, the current cannot be observed when the ring is interrupted by an ammeter and thus the current must be measured indirectly through its magnetization. In fact, all metals exhibit some magnetization in magnetic fields due a combination of de Haas–van Alphen effect, core

diamagnetism, Landau diamagnetism, Pauli paramagnetism, which all appear regardless of the shape of the metal. The additional magnetization from persistent current becomes strong with a connected ring shape, and for example would disappear if the ring were cut[7].

Experimental evidence of the observation of persistent currents were first reported in 1990 by a research group at Bell Laboratories using a superconducting resonator to study an array of copper rings. Subsequent measurements using superconducting resonators and extremely sensitive magnetometers known as superconducting quantum interference devices (SQUIDs) produced inconsistent results. In 2009, physicists at Stanford University using a scanning SQUID and at Yale University using micro electro mechanical cantilevers reported measurements of persistent currents in nano scale gold and aluminum rings respectively that both showed a strong agreement with the simple theory for non-interacting electrons.

## Chapter Four

### High-temperature superconductivity

#### 4.1 Introduction

High-temperature superconductors (abbreviated high- $T_c$  or HTS) are materials that behave as superconductors at unusually high temperatures. Whereas "ordinary" or metallic superconductors usually have transition temperatures (temperatures below which they superconduct) below 30 K ( $-243.2\text{ }^\circ\text{C}$ ), HTS have been observed with transition temperatures as high as 138 K ( $-135\text{ }^\circ\text{C}$ )[8].

Until 2008, only certain compounds of copper and oxygen (so-called "cuprates") were believed to have HTS properties, and 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). However, several iron-based compounds (the iron pnictides) are now known to be superconducting at high temperatures.

The phenomenon of superconductivity was discovered by Kamerlingh Onnes in 1911, in metallic mercury below 4 K ( $-269.15\text{ }^\circ\text{C}$ ). For seventy-five years after that, researchers attempted to observe superconductivity at higher and higher temperatures. In the late 1970s, superconductivity was observed in certain metal oxides at temperatures as high as 13 K ( $-260.1\text{ }^\circ\text{C}$ ), which were much higher than those for elemental metals. In 1986, J. Georg Bednorz and K Alex Müller, working at the IBM research lab near Zurich, Switzerland were exploring a new class of ceramics for superconductivity. Bednorz encountered a barium-doped compound of lanthanum and copper oxide

whose resistance dropped down to zero at a temperature around 35 K ( $-238.2\text{ }^{\circ}\text{C}$ ). Their results were soon confirmed by many groups, notably Paul Chu at the University of Houston and Shoji Tanaka at the University of Tokyo[8].

Shortly after, P. W. Anderson, at Princeton University came up with the first theoretical description of these materials, using the resonating valence bond theory, but a full understanding of these materials is still developing today. These superconductors are now known to possess a d-wave pair symmetry. The first proposal that high-temperature cuprate superconductivity involves d-wave pairing was made in 1987 by Bickers, Scalapino and Scalettar, followed by three subsequent theories in 1988 by Inui, Doniach, Hirschfeld and Ruckenstein, using spin-fluctuation theory, and by Gros, Poilblanc, Rice and Zhang, and by Kotliar and Liu identifying d-wave pairing as a natural consequence of the RVB theory. The confirmation of the d-wave nature of the cuprate superconductors was made by a variety of experiments, including the direct observation of the d-wave nodes in the excitation spectrum through Angle Resolved Photoemission Spectroscopy, the observation of a half-integer flux in tunneling experiments, and indirectly from the temperature dependence of the penetration depth, specific heat and thermal conductivity.

The superconductor with the highest transition temperature that has been confirmed by multiple independent research groups (a prerequisite to be called a discovery, verified by peer review) is mercury barium calcium copper oxide ( $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ) at around 133 K.

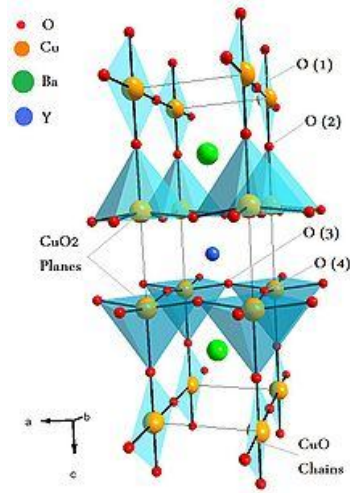
After more than twenty years of intensive research the origin of high-temperature superconductivity is still not clear, but it seems that instead of electron-phonon attraction mechanisms, as in conventional superconductivity, one is dealing with genuine electronic mechanisms (e.g. by antiferromagnetic correlations), and instead of s-wave pairing, d-waves are substantial. One goal of all this research is room-temperature superconductivity[8].

## **4.2 Crystal structures of high-temperature ceramic superconductors:**

The structure of high- $T_c$  copper oxide or cuprate superconductors are often closely related to perovskite structure, and the structure of these compounds has been described as a distorted, oxygen deficient multi-layered perovskite structure. One of the properties of the crystal structure of oxide superconductors is an alternating multi-layer of  $\text{CuO}_2$  planes with superconductivity taking place between these layers. The more layers of  $\text{CuO}_2$  the higher  $T_c$ . This structure causes a large anisotropy in normal conducting and superconducting properties, since electrical currents are carried by holes induced in the oxygen sites of the  $\text{CuO}_2$  sheets. The electrical conduction is highly anisotropic, with a much higher conductivity parallel to the  $\text{CuO}_2$  plane than in the perpendicular direction. Generally, Critical temperatures depend on the chemical compositions, cations substitutions and oxygen content. They can be classified as superstripes; i.e., particular realizations of superlattices at atomic limit made of superconducting atomic layers, wires, dots separated by spacer layers, that gives multiband and multigap superconductivity[8].

## **4.3 YBaCuO superconductors:**

The first superconductor found with  $T_c > 77$  K (liquid nitrogen boiling point) as shown in fig (4.1) is yttrium barium copper oxide ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ); the proportions of the three different metals in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  superconductor are in the mole ratio of 1 to 2 to 3 for yttrium to barium to copper, respectively. Thus, this particular superconductor is often referred to as the 123 superconductor[9].



**Fig(4.1) YBCO unit cell**

The unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  consists of three pseudocubic elementary perovskite unit cells. Each perovskite unit cell contains a Y or Ba atom at the center: Ba in the bottom unit cell, Y in the middle one, and Ba in the top unit cell. Thus, Y and Ba are stacked in the sequence [Ba–Y–Ba] along the c-axis. All corner sites of the unit cell are occupied by Cu, which has two different coordinations, Cu(1) and Cu(2), with respect to oxygen. There are four possible crystallographic sites for oxygen: O(1), O(2), O(3) and O(4). The coordination polyhedra of Y and Ba with respect to oxygen are different. The tripling of the perovskite unit cell leads to nine oxygen atoms, whereas  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has seven oxygen atoms and, therefore, is referred to as an oxygen-deficient perovskite structure. The structure has a stacking of different layers: (CuO)(BaO)(CuO<sub>2</sub>)(Y)(CuO<sub>2</sub>)(BaO)(CuO). One of the key features of the unit cell of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) is the presence of two layers of CuO<sub>2</sub>. The role of the Y plane is to serve as a spacer between two CuO<sub>2</sub> planes. In YBCO, the Cu–O chains are known to play an important role for superconductivity.  $T_c$  is maximal near 92 K when  $x \approx 0.15$  and the structure is orthorhombic. Superconductivity disappears at  $x \approx 0.6$ , where the structural transformation of YBCO occurs from orthorhombic to tetragonal[9].

### 4.3 Bi-, Tl- and Hg-based high- $T_c$ superconductors

The crystal structure of Bi-, Tl- and Hg-based high- $T_c$  superconductors are very similar.<sup>[22]</sup> Like YBCO, the perovskite-type feature and the presence of  $\text{CuO}_2$  layers also exist in these superconductors. However, unlike YBCO, Cu–O chains are not present in these superconductors. The YBCO superconductor has an orthorhombic structure, whereas the other high- $T_c$  superconductors have a tetragonal structure.

The Bi–Sr–Ca–Cu–O system has three superconducting phases forming a homologous series as  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n+x}$  ( $n = 1, 2$  and  $3$ ). These three phases are Bi-2201, Bi-2212 and Bi-2223, having transition temperatures of 20, 85 and 110 K, respectively, where the numbering system represent number of atoms for Bi, Sr, Ca and Cu respectively. The two phases have a tetragonal structure which consists of two sheared crystallographic unit cells. The unit cell of these phases has double Bi–O planes which are stacked in a way that the Bi atom of one plane sits below the oxygen atom of the next consecutive plane. The Ca atom forms a layer within the interior of the  $\text{CuO}_2$  layers in both Bi-2212 and Bi-2223; there is no Ca layer in the Bi-2201 phase. The three phases differ with each other in the number of  $\text{CuO}_2$  planes; Bi-2201, Bi-2212 and Bi-2223 phases have one, two and three  $\text{CuO}_2$  planes, respectively. The  $c$  axis of these phases increases with the number of  $\text{CuO}_2$  planes (see table below). The coordination of the Cu atom is different in the three phases. The Cu atom forms an octahedral coordination with respect to oxygen atoms in the 2201 phase, whereas in 2212, the Cu atom is surrounded by five oxygen atoms in a pyramidal arrangement. In the 2223 structure, Cu has two coordinations with respect to oxygen: one Cu atom is bonded with four oxygen atoms in square planar configuration and another Cu atom is coordinated with five oxygen atoms in a pyramidal arrangement[9].

Tl–Ba–Ca–Cu–O superconductor: The first series of the Tl-based superconductor containing one Tl–O layer has the general formula  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ ,<sup>[25]</sup> whereas the second series containing two Tl–O layers has a formula of  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  with  $n = 1, 2$  and  $3$ . In the structure of  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  (Tl-2201), there is one  $\text{CuO}_2$  layer with the stacking sequence (Tl–O) (Tl–O) (Ba–O) (Cu–O) (Ba–O) (Tl–O) (Tl–O). In  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  (Tl-2212), there are two Cu–O layers with a Ca layer in between. Similar to the  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  structure, Tl–O layers are present outside the Ba–O layers. In  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (Tl-2223), there are three  $\text{CuO}_2$  layers enclosing Ca layers between each of these. In Tl-based superconductors,  $T_c$  is found to increase with the increase in  $\text{CuO}_2$  layers. However, the value of  $T_c$  decreases after four  $\text{CuO}_2$  layers in  $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ , and in the  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  compound, it decreases after three  $\text{CuO}_2$  layers[9].

Hg–Ba–Ca–Cu–O superconductor: The crystal structure of  $\text{HgBa}_2\text{CuO}_4$  (Hg-1201),  $\text{HgBa}_2\text{CaCu}_2\text{O}_6$  (Hg-1212) and  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$  (Hg-1223) is similar to that of Tl-1201, Tl-1212 and Tl-1223, with Hg in place of Tl. It is noteworthy that the  $T_c$  of the Hg compound (Hg-1201) containing one  $\text{CuO}_2$  layer is much larger as compared to the one- $\text{CuO}_2$ -layer compound of thallium (Tl-1201). In the Hg-based superconductor,  $T_c$  is also found to increase as the  $\text{CuO}_2$  layer increases. For Hg-1201, Hg-1212 and Hg-1223, the values of  $T_c$  are 94, 128 and the record value at ambient pressure 134 K,<sup>[28]</sup> respectively, as shown in table below. The observation that the  $T_c$  of Hg-1223 increases to 153 K under high pressure indicates that the  $T_c$  of this compound is very sensitive to the structure of the compound.

Critical temperature ( $T_c$ ), crystal structure and lattice constants of some high- $T_c$  superconductors

Formula	Notation	$T_c$ (K)	No. of Cu-O planes in unit cell	Crystal structure
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Critical temperature ( $T_c$ ), crystal structure and lattice constants of some high- $T_c$  superconductors

Formula	Notation	$T_c$ (K)	No. of Cu-O planes in unit cell	Crystal structure
$\text{YBa}_2\text{Cu}_3\text{O}_7$	123	92	2	Orthorhombic
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	Bi-2201	20	1	Tetragonal
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$	Bi-2212	85	2	Tetragonal
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_6$	Bi-2223	110	3	Tetragonal
$\text{Tl}_2\text{Ba}_2\text{CuO}_6$	Tl-2201	80	1	Tetragonal
$\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$	Tl-2212	108	2	Tetragonal
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	Tl-2223	125	3	Tetragonal
$\text{TlBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11}$	Tl-1234	122	4	Tetragonal
$\text{HgBa}_2\text{CuO}_4$	Hg-1201	94	1	Tetragonal
$\text{HgBa}_2\text{CaCu}_2\text{O}_6$	Hg-1212	128	2	Tetragonal
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$	Hg-1223	134	3	Tetragonal

#### 4.4 Preparation of high- $T_c$ superconductors:

The simplest method for preparing high- $T_c$  superconductors is a solid-state thermochemical reaction involving mixing, calcination and sintering. The appropriate amounts of precursor powders, usually oxides and carbonates, are mixed thoroughly using a ball mill. Solution chemistry processes such as coprecipitation, freeze-drying and sol-gel methods are alternative ways for preparing a homogeneous mixture. These powders are calcined in the

temperature range from 800 °C to 950 °C for several hours. The powders are cooled, reground and calcined again. This process is repeated several times to get homogeneous material. The powders are subsequently compacted to pellets and sintered. The sintering environment such as temperature, annealing time, atmosphere and cooling rate play a very important role in getting good high- $T_c$  superconducting materials. The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound is prepared by calcination and sintering of a homogeneous mixture of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  in the appropriate atomic ratio. Calcination is done at 900–950 °C, whereas sintering is done at 950 °C in an oxygen atmosphere. The oxygen stoichiometry in this material is very crucial for obtaining a superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  compound. At the time of sintering, the semiconducting tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  compound is formed, which, on slow cooling in oxygen atmosphere, turns into superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . The uptake and loss of oxygen are reversible in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . A fully oxidized orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample can be transformed into tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_6$  by heating in a vacuum at temperature above 700 °C[9].

The preparation of Bi-, Tl- and Hg-based high- $T_c$  superconductors is difficult compared to YBCO. Problems in these superconductors arise because of the existence of three or more phases having a similar layered structure. Thus, syntactic intergrowth and defects such as stacking faults occur during synthesis and it becomes difficult to isolate a single superconducting phase. For Bi–Sr–Ca–Cu–O, it is relatively simple to prepare the Bi-2212 ( $T_c \approx 85$  K) phase, whereas it is very difficult to prepare a single phase of Bi-2223 ( $T_c \approx 110$  K). The Bi-2212 phase appears only after few hours of sintering at 860–870 °C, but the larger fraction of the Bi-2223 phase is formed after a long reaction time of more than a week at 870 °C. Although the substitution of Pb in the Bi–Sr–Ca–Cu–O compound has been found to promote the growth of the high- $T_c$  phase, a long sintering time is still required.

## 4.5 Properties of high temperature superconductors:

"High-temperature" has two common definitions in the context of superconductivity:

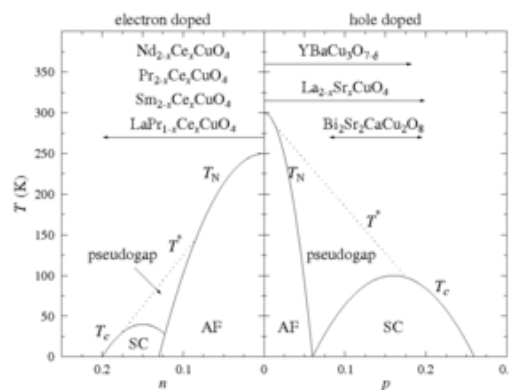
1. Above the temperature of 30 K that had historically been taken as the upper limit allowed by BCS theory.
2. 1973 record of 23 K that had lasted until copper-oxide materials were discovered in 1986.
3. Having a transition temperature that is a larger fraction of the Fermi temperature than for conventional superconductors such as elemental mercury or lead. This definition encompasses a wider variety of unconventional superconductors and is used in the context of theoretical models.

The label high- $T_c$  may be reserved by some authors for s materials with critical temperature greater than the boiling point of liquid nitrogen (77 K or  $-196\text{ }^\circ\text{C}$ ). However, a number of materials – including the original discovery and recently discovered pnictide superconductors – had critical temperatures below 77 K but are commonly referred to in publication as being in the high- $T_c$  class.

Technological applications could benefit from both the higher critical temperature being above the boiling point of liquid nitrogen and also the higher critical magnetic field (and critical current density) at which superconductivity is destroyed. In magnet applications the high critical magnetic field may prove more valuable than the high  $T_c$  itself. Some cuprates have an upper critical field of about 100 tesla. However, cuprate materials are brittle ceramics which are expensive to manufacture and not easily turned into wires or other useful shapes[9].

After two decades of intense experimental and theoretical research, with over 100,000 published papers on the subject, several common features in the properties of high-temperature superconductors have been identified. As of 2011, no widely accepted theory explains their properties. Relative to conventional superconductors, such as elemental mercury or lead that are adequately explained by the BCS theory, cuprate superconductors (and other unconventional superconductors) remain distinctive. There also has been much debate as to high-temperature superconductivity coexisting with magnetic ordering in YBCO, iron-based superconductors, several ruthenocuprates and other exotic superconductors, and the search continues for other families of materials. HTS are Type-II superconductors, which allow magnetic fields to penetrate their interior in quantized units of flux, meaning that much higher magnetic fields are required to suppress superconductivity. The layered structure also gives a directional dependence to the magnetic field response[9].

#### 4.6 Cuprates:



**Fig(4.2) Simplified doping dependent phase diagram of cuprate superconductors for both electron (n) and hole (p) doping.**

The phases shown in fig (4.2) above, are the antiferromagnetic (AF) phase close to zero doping, the superconducting phase around optimal doping, and the pseudogap phase. Doping ranges possible for some common compounds are also shown. After.

Cuprate superconductors are generally considered to be quasi-two-dimensional materials with their superconducting properties determined by electrons moving within weakly coupled copper-oxide ( $\text{CuO}_2$ ) layers. Neighbouring layers containing ions such as lanthanum, barium, strontium, or other atoms act to stabilize the structure and dope electrons or holes onto the copper-oxide layers. The undoped 'parent' or 'mother' compounds are Mott insulators with long-range antiferromagnetic order at low enough temperature. Single band models are generally considered to be sufficient to describe the electronic properties.

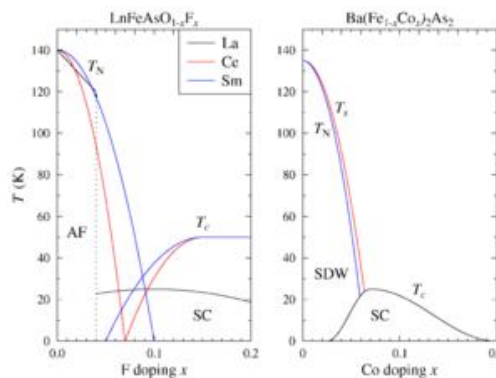
The cuprate superconductors adopt a perovskite structure. The copper-oxide planes are checkerboard lattices with squares of  $\text{O}^{2-}$  ions with a  $\text{Cu}^{2+}$  ion at the centre of each square. The unit cell is rotated by  $45^\circ$  from these squares. Chemical formulae of superconducting materials generally contain fractional numbers to describe the doping required for superconductivity. There are several families of cuprate superconductors and they can be categorized by the elements they contain and the number of adjacent copper-oxide layers in each superconducting block. For example, YBCO and BSCCO can alternatively be referred to as Y123 and Bi2201/Bi2212/Bi2223 depending on the number of layers in each superconducting block ( $n$ ). The superconducting transition temperature has been found to peak at an optimal doping value ( $p = 0.16$ ) and an optimal number of layers in each superconducting block, typically  $n = 3$ .

Possible mechanisms for superconductivity in the cuprates are still the subject of considerable debate and further research. Certain aspects common to all materials have been identified. Similarities between the antiferromagnetic low-temperature state of the undoped materials and the superconducting state that emerges upon doping, primarily the  $d_{x^2-y^2}$  orbital state of the  $\text{Cu}^{2+}$  ions, suggest that electron-electron interactions are more significant than electron-phonon interactions in cuprates – making the superconductivity

unconventional. Recent work on the Fermi surface has shown that nesting occurs at four points in the antiferromagnetic Brillouin zone where spin waves exist and that the superconducting energy gap is larger at these points. The weak isotope effects observed for most cuprates contrast with conventional superconductors that are well described by BCS theory[9].

Similarities and differences in the properties of hole-doped and electron doped cuprates:

- Presence of a pseudogap phase up to at least optimal doping.
- Different trends in the Uemura plot relating transition temperature to the superfluid density. The inverse square of the London penetration depth appears to be proportional to the critical temperature for a large number of underdoped cuprate superconductors, but the constant of proportionality is different for hole- and electron-doped cuprates. The linear trend implies that the physics of these materials is strongly two-dimensional.
- Universal hourglass-shaped feature in the spin excitations of cuprates measured using inelastic neutron diffraction.
- Nernst effect evident in both the superconducting and pseudogap phases.



**Fig(4.3) Simplified doping dependent phase diagrams of iron-based superconductors for both Ln-1111 and Ba-122 materials**

The phases shown are the antiferromagnetic/spin density wave (AF/SDW) phase close to zero doping and the superconducting phase around optimal doping. The Ln-1111 phase diagrams for La and Sm were determined using muon spin spectroscopy, the phase diagram for Ce was determined using neutron diffraction. The Ba-122 phase diagram is based on.

Iron-based superconductors contain layers of iron and a pnictogen—such as arsenic or phosphorus—or a chalcogen. This is currently the family with the second highest critical temperature, behind the cuprates. Interest in their superconducting properties began in 2006 with the discovery of superconductivity in LaFePO at 4 K and gained much greater attention in 2008 after the analogous material LaFeAs(O,F) was found to superconduct at up to 43 K under pressure.<sup>[43]</sup> The highest critical temperatures in the iron-based superconductor family exist in thin films of FeSe, where a critical temperature in excess of 100 K has recently been reported[9].

Since the original discoveries several families of iron-based superconductors have emerged:

- LnFeAs(O,F) or LnFeAsO<sub>1-x</sub> (Ln = lanthanide) with T<sub>c</sub> up to 56 K, referred to as 1111 materials. A fluoride variant of these materials was subsequently found with similar T<sub>c</sub> values.
- (Ba,K)Fe<sub>2</sub>As<sub>2</sub> and related materials with pairs of iron-arsenide layers, referred to as 122 compounds. T<sub>c</sub> values range up to 38 K. These materials also superconduct when iron is replaced with cobalt
- LiFeAs and NaFeAs with T<sub>c</sub> up to around 20 K. These materials superconduct close to stoichiometric composition and are referred to as 111 compounds.
- FeSe with small off-stoichiometry or tellurium doping.

Most undoped iron-based superconductors show a tetragonal-orthorhombic structural phase transition followed at lower temperature by magnetic

ordering, similar to the cuprate superconductors. However, they are poor metals rather than Mott insulators and have five bands at the Fermi surface rather than one.<sup>[55]</sup> The phase diagram emerging as the iron-arsenide layers are doped is remarkably similar, with the superconducting phase close to or overlapping the magnetic phase. Strong evidence that the  $T_c$  value varies with the As-Fe-As bond angles has already emerged and shows that the optimal  $T_c$  value is obtained with undistorted  $\text{FeAs}_4$  tetrahedra. The symmetry of the pairing wavefunction is still widely debated, but an extended s-wave scenario is currently favoured.

## **4.7 Other materials sometimes referred to as high-temperature superconductors**

Magnesium diboride is occasionally referred to as a high-temperature superconductor<sup>[57]</sup> because its  $T_c$  value of 39 K is above that historically expected for BCS superconductors. However, it is more generally regarded as the highest  $T_c$  conventional superconductor, the increased  $T_c$  resulting from two separate bands being present at the Fermi level.

Fulleride superconductors where alkali-metal atoms are intercalated into  $\text{C}_{60}$  molecules show superconductivity at temperatures of up to 38 K for  $\text{Cs}_3\text{C}_{60}$ .

Some organic superconductors and heavy fermion compounds are considered to be high-temperature superconductors because of their high  $T_c$  values relative to their Fermi energy, despite the  $T_c$  values being lower than for many conventional superconductors. This description may relate better to common aspects of the superconducting mechanism than the superconducting properties[9].

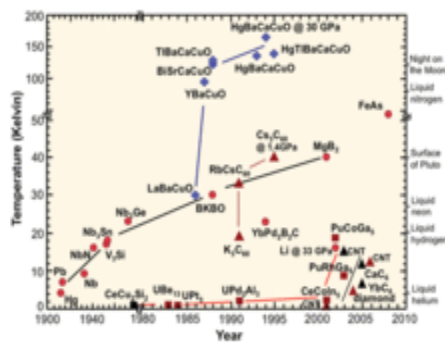
Theoretical work by Neil Ashcroft in 1968 predicted that solid metallic hydrogen at extremely high pressure should become superconducting at approximately room-temperature because of its extremely high speed of

sound and expected strong coupling between the conduction electrons and the lattice vibrations. This prediction is yet to be experimentally verified.

All known high- $T_c$  superconductors are Type-II superconductors. In contrast to Type-I superconductors, which expel all magnetic fields due to the Meissner effect, Type-II superconductors allow magnetic fields to penetrate their interior in quantized units of flux, creating "holes" or "tubes" of normal metallic regions in the superconducting bulk called vortices. Consequently, high- $T_c$  superconductors can sustain much higher magnetic fields.

#### 4.8 Ongoing research

The question of how superconductivity arises in high-temperature superconductors is one of the major unsolved problems of theoretical condensed matter physics. The mechanism that causes the electrons in these crystals to form pairs is not known. 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 modelling difficult as shown in fig(4.4).



**Fig (4.4) Superconductor timeline**

Improving the quality and variety of samples also gives rise to considerable research, both with the aim of improved characterisation of the physical properties of existing compounds, and synthesizing new materials, often with the hope of increasing  $T_c$ . Technological research focuses on making HTS

materials in sufficient quantities to make their use economically viable and optimizing their properties in relation to applications.

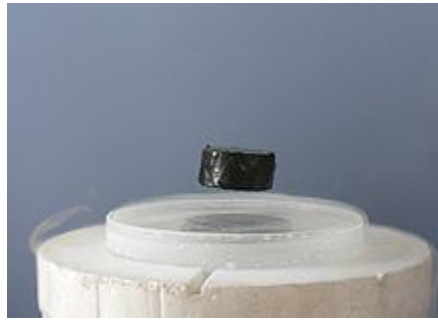
#### **4.9 Possible mechanism**

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. According to this theory, the pairing wave function of the cuprate HTS should have a  $d_{x^2-y^2}$  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, then a pairing mechanism related to spin fluctuations can be ruled out. (Similar arguments can be made for iron-based superconductors but the different material properties allow a different pairing symmetry.) 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 tunnelling interaction between each layer, this model successfully explained the anisotropic symmetry of the order parameter as well as the emergence of the HTS. Thus, in order to solve this unsettled problem, there have been numerous experiments such as photoemission spectroscopy, NMR, specific heat measurements, etc. But, unfortunately, the results were ambiguous, some reports supported the d symmetry for the HTS whereas others supported the s symmetry. This muddy situation possibly originated from the indirect nature of the experimental evidence, as well as experimental issues such as sample quality, impurity scattering, twinning, etc[9].

#### **4.10 Junction experiment supporting the d symmetry**

There was a clever experimental design to overcome the muddy situation as shown in fig (4.5). An experiment based on flux quantization of a three-grain

ring of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBCO) was proposed to test the symmetry of the order parameter in the HTS. The symmetry of the order parameter could best be probed at the junction interface as the Cooper pairs tunnel across a Josephson junction or weak link. It was expected that a half-integer flux, that is, a spontaneous magnetization could only occur for a junction of d symmetry superconductors. But, even if the junction experiment is the strongest method to determine the symmetry of the HTS order parameter, the results have been ambiguous. J. R. Kirtley and C. C. Tsuei thought that the ambiguous results came from the defects inside the HTS, so that they designed an experiment where both clean limit (no defects) and dirty limit (maximal defects) were considered simultaneously[10].



**Fig (4.5) The Meissner effect or a magnet levitating above a superconductor (cooled by liquid nitrogen)**

In the experiment, the spontaneous magnetization was clearly observed in YBCO, which supported the d symmetry of the order parameter in YBCO. But, since YBCO is orthorhombic, it might inherently have an admixture of s symmetry. So, by tuning their technique further, they found that there was an admixture of s symmetry in YBCO within about 3%.<sup>[65]</sup> Also, they found that there was a pure  $d_{x^2-y^2}$  order parameter symmetry in the tetragonal  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ .

## 4.11 Qualitative explanation of the spin-fluctuation mechanism

Despite all these years, the mechanism of high- $T_c$  superconductivity is still highly controversial, mostly due to the lack of exact theoretical computations on such strongly interacting electron systems. However, most rigorous theoretical calculations, including phenomenological and diagrammatic approaches, converge on magnetic fluctuations as the pairing mechanism for these systems. The qualitative explanation is as follows:

In a superconductor, the flow of electrons cannot be resolved into individual electrons, but instead consists of many pairs of bound electrons, called Cooper pairs. In conventional superconductors, these pairs are formed when an electron moving through the material distorts the surrounding crystal lattice, which in turn attracts another electron and forms a bound pair. This is sometimes called the "water bed" effect. Each Cooper pair requires a certain minimum energy to be displaced, and if the thermal fluctuations in the crystal lattice are smaller than this energy the pair can flow without dissipating energy. This ability of the electrons to flow without resistance leads to superconductivity[10].

In a high- $T_c$  superconductor, the mechanism is extremely similar to a conventional superconductor. Except, in this case, phonons virtually play no role and their role is replaced by spin-density waves. As all conventional superconductors are strong phonon systems, all high- $T_c$  superconductors are strong spin-density wave systems, within close vicinity of a magnetic transition to, for example, an antiferromagnet. When an electron moves in a high- $T_c$  superconductor, its spin creates a spin-density wave around it. This spin-density wave in turn causes a nearby electron to fall into the spin depression created by the first electron (water-bed effect again). Hence, again, a Cooper pair is formed. When the system temperature is lowered, more spin density waves and Cooper pairs are created, eventually leading to

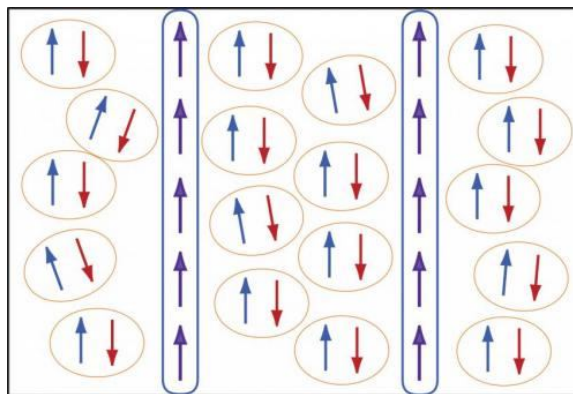
superconductivity. Note that in high- $T_c$  systems, as these systems are magnetic systems due to the Coulomb interaction, there is a strong Coulomb repulsion between electrons. This Coulomb repulsion prevents pairing of the Cooper pairs on the same lattice site. The pairing of the electrons occur at near-neighbor lattice sites as a result. This is the so-called d-wave pairing, where the pairing state has a node (zero) at the origin[10].

#### **4.12 Superconductivity without cooling:**

Superconductivity is a remarkable phenomenon: superconductors can transport electric current without any resistance and thus without any losses whatsoever. It is already in use in some niche areas, for example as magnets for nuclear spin tomography or particle accelerators. However, the materials must be cooled to very low temperatures for this purpose. But during the past year, an experiment has provided some surprises[10].

#### **4.13 New evidence for an exotic, predicted superconducting state:**

A research team led by a Brown University physicist has produced new evidence for an exotic superconducting state, first predicted a half-century ago, that can arise when a superconductor is exposed to a strong magnetic field. Magnetism breaks electron Cooper pairs that enable superconductivity. The new research shows that those unpaired electrons congregate into discrete bands along the superconducting material. Those bands remain capable of conducting supercurrent as shown in fig (4.6).



**Fig (4.6) evidence for an exotic superconducting state**

Superconductors and magnetic fields do not usually get along. But a research team led by a Brown University physicist has produced new evidence for an exotic superconducting state, first predicted a half-century ago, that can indeed arise when a superconductor is exposed to a strong magnetic field.

Superconductors and magnetic fields do not usually get along. But a research team led by a Brown University physicist has produced new evidence for an exotic superconducting state, first predicted a half-century ago, that can indeed arise when a superconductor is exposed to a strong magnetic field[10].

"It took 50 years to show that this phenomenon indeed happens," said Vesna Mitrovic, associate professor of physics at Brown University, who led the work. "We have identified the microscopic nature of this exotic quantum state of matter."

The research is published in Nature Physics.

Superconductivity—the ability to conduct electric current without resistance—depends on the formation of electron twosomes known as Cooper pairs (named for Leon Cooper, a Brown University physicist who shared the Nobel Prize for identifying the phenomenon). In a normal conductor, electrons rattle around in the structure of the material, which creates

resistance. But Cooper pairs move in concert in a way that keeps them from rattling around, enabling them to travel without resistance[10].

Magnetic fields are the enemy of Cooper pairs. In order to form a pair, electrons must be opposites in a property that physicists refer to as spin. Normally, a superconducting material has a roughly equal number of electrons with each spin, so nearly all electrons have a dance partner. But strong magnetic fields can flip "spin-down" electrons to "spin-up", making the spin population in the material unequal.

"The question is what happens when we have more electrons with one spin than the other," Mitrovic said. "What happens with the ones that don't have pairs? Can we actually form superconducting states that way, and what would that state look like?"

In 1964, physicists predicted that superconductivity could indeed persist in certain kinds of materials amid a magnetic field. The prediction was that the unpaired electrons would gather together in discrete bands or stripes across the superconducting material. Those bands would conduct normally, while the rest of the material would be superconducting. This modulated superconductive state came to be known as the FFLO phase, named for theorists Peter Fulde, Richard Ferrell, Anatoly Larkin, and Yuri Ovchinniko, who predicted its existence[10].

To investigate the phenomenon, Mitrovic and her team used an organic superconductor with the catchy name  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(NCS)<sub>2</sub>. The material consists of ultra-thin sheets stacked on top of each other and is exactly the kind of material predicted to exhibit the FFLO state.

After applying an intense magnetic field to the material, Mitrovic and her collaborators from the French National High Magnetic Field Laboratory in Grenoble probed its properties using nuclear magnetic resonance (NMR).

What they found were regions across the material where unpaired, spin-up electrons had congregated. These "polarized" electrons behave, "like little particles constrained in a box," Mitrovic said, and they form what are known as Andreev bound states.

"What is remarkable about these bound states is that they enable transport of supercurrents through non-superconducting regions," Mitrovic said. "Thus, the current can travel without resistance throughout the entire material in this special superconducting state."

Experimentalists have been trying for years to provide solid evidence that the FFLO state exists, but to little avail. Mitrovic and her colleagues took some counterintuitive measures to arrive at their findings. Specifically, they probed their material at a much higher temperature than might be expected for quantum experiments[10].

"Normally to observe quantum states you want to be as cold as possible, to limit thermal motion," Mitrovic said. "But by raising the temperature we increased the energy window of our NMR probe to detect the states we were looking for. That was a breakthrough."

This new understanding of what happens when electron spin populations become unequal could have implications beyond superconductivity, according to Mitrovic.

It might help astrophysicists to understand pulsars—densely packed neutron stars believed to harbor both superconductivity and strong magnetic fields. It could also be relevant to the field of spintronics, devices that operate based on electron spin rather than charge, made of layered ferromagnetic-superconducting structures.

"This really goes beyond the problem of superconductivity," Mitrovic said. "It has implications for explaining many other things in the universe, such as behavior of dense quarks, particles that make up atomic nuclei[10].

## Chapter Five

### 5.1 Introduction :

The question of whether room-temperature superconductivity (RTSC) is possible in the copper-oxides has been answered. Superconductors.ORG herein reports the observation of superconductivity near 28 Celsius (83F, 301K) in a binary oxycuprate[11].

Normally, extreme cold is required to cool even a "high temperature" superconductor below its critical transition temperature ( $T_c$ ). To make this discovery, no cooling was required. For the first time a cryostat actually had to be heated to witness a superconductive phase transition.

### 5.2 Room-Temperature Superconductivity in a Copper-oxide:

The hallmark of superconductivity is a sudden resistance drop to zero ohms and strong diamagnetism (the Meissner effect) near the same temperature. In numerous tests a small amount of the compound  $(Tl_5Pb_2)Ba_2Mg_2Cu_9O_{17+}$  consistently produced sharp resistive transitions near 28.5 Celsius (see above graphics), and diamagnetic transitions also near 28.5C (see below)<sup>1</sup>. The transitions were unambiguous, repeatable, and at ambient pressure, making this the first observation of true room-temperature superconductivity in a copper-oxide. Unfortunately, like the 18C superconductor discovered in March 2011, these transitions occurred in a noisy environment, suggesting the volume fraction is very low[12].

As such, any plans for immediate commercialization will have to wait for a refinement method to be developed.

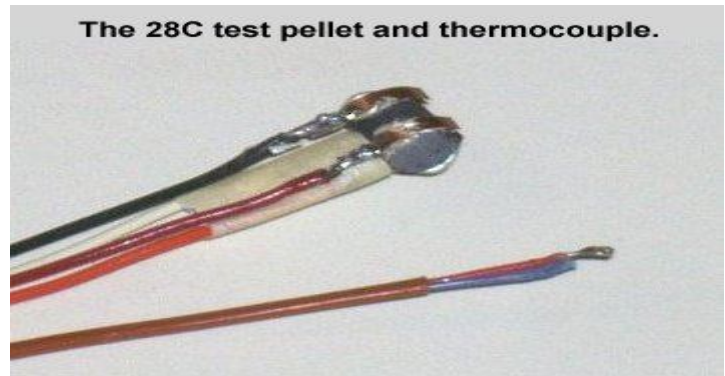
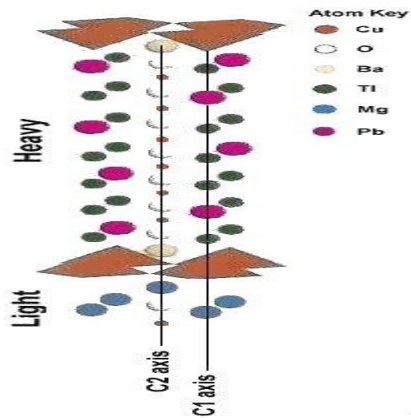
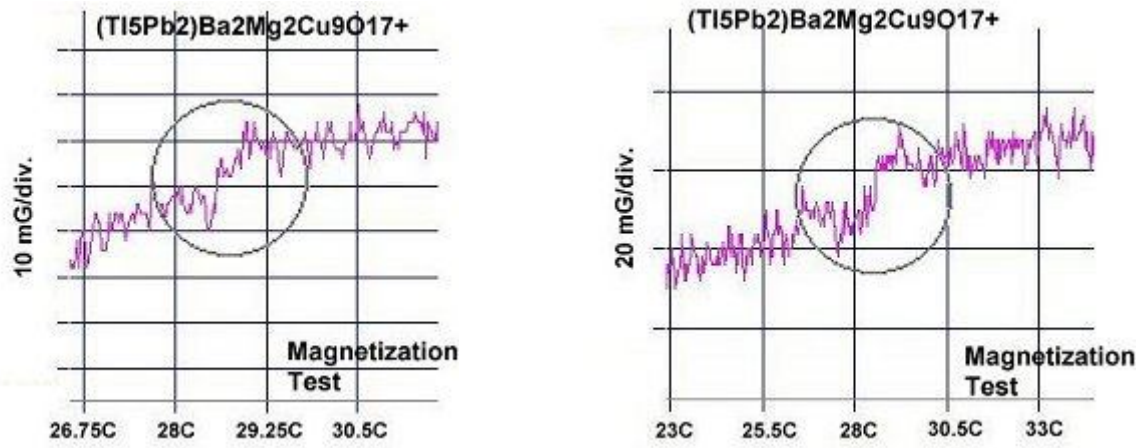


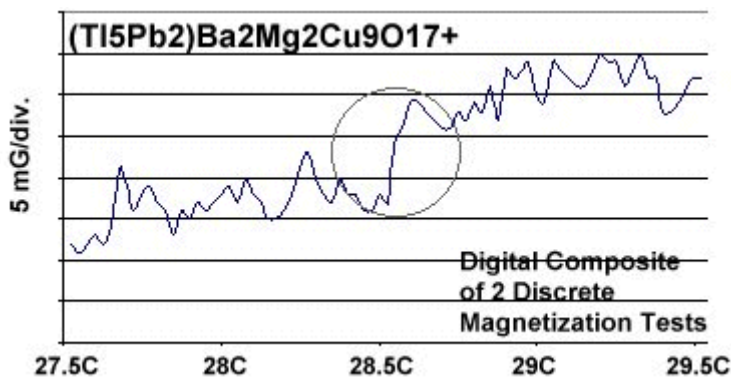
Fig (5.1) result of efforts to reformulate the 18C superconductor discovered in March 2011. The key to improving that material was substitution of a magnesium atom into one of the C2 copper sites (see "LIGHT" region of D223 graphic at left). By doing this the planar weight ratio (PWR) of the C2 axis increases, while the PWR of the C1 axis remains unchanged. Research since 2005 has confirmed a direct correlation between PWR and  $T_c$ .

Logically, the next evolutionary step might be to place magnesium atoms into both C2 copper sites. But, experience has shown every metallic non-copper layer must have a copper layer adjacent to it on at least one side. 2 Mg atoms in the LIGHT C2 would necessitate a copper in the LIGHT C1 to meet this requirement. However, since Cu is over 2.5 times as heavy as Mg, that would significantly lower the C1 PWR, causing a drop in  $T_c$ .



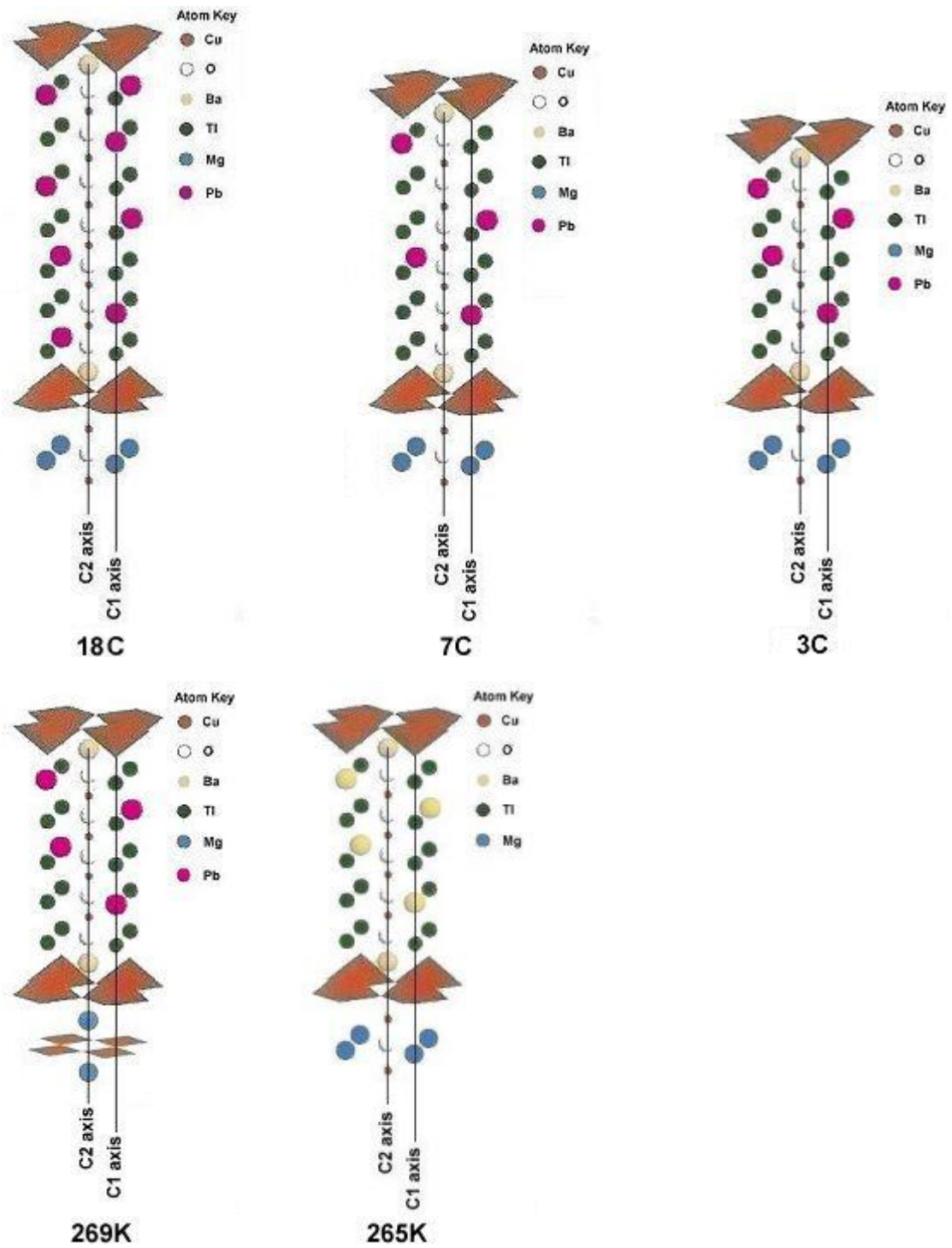
**Fig (5.2) plots of two sequential magnetization tests**

The Meissner transition in the plots represents about 10 milli-Gauss with a -10db noise floor. The signal-to-noise ratio can be improved 3db by digitally summing these plots together, producing the below composite. The flashing lines represent the average of the noise component, skewing apart at 28.5C.



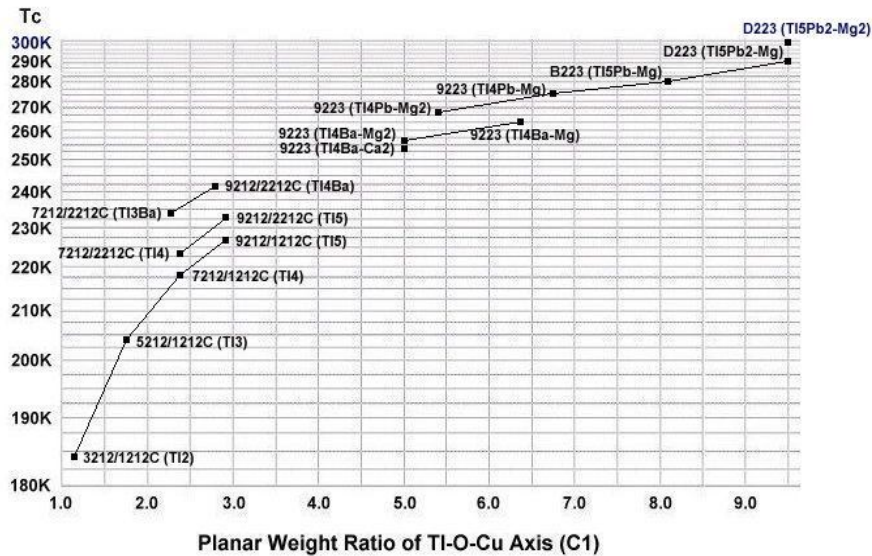
**Fig(5.3) parent structures**

Parent structures that previously established world records in this family of perovskites are shown below for comparison. The resistive  $T_c$  produced by each structure is noted below it as a Celsius or Kelvin temperature.



**Fig (5.4) Dots have been placed within the C1**

Plot below, depicting where D223(Tl<sub>5</sub>Pb<sub>2</sub>-Mg<sub>2</sub>) lies relative to the other high performance thallium-cuprates. Temperatures plotted (in Kelvin) are resistive. The C2 plot of PWR-v-T<sub>c</sub> is not shown.



**Fig (5.5) As with prior discoveries that advanced high Tc through asymmetry along the C axis,  $(\text{TI}_5\text{Pb}_2)\text{Ba}_2\text{Mg}_2\text{Cu}_9\text{O}_{17+}$  does not form stoichiometrically (by conventional mixing of chemicals)**

It must be synthesized using the layer cake method, as shown below. The prototype pellets each had roughly 50 to 60 interference layers. And, even using this technique, the volume fraction is low, requiring very sensitive test equipment.

**5.3 The below stoichiometric ratios were used for the ODD layers:**

$\text{Ti}_2\text{O}_3$	99.99%	(Alfa Aesar)	7.366	grains
$\text{PbO}$	99.99%	(Alfa Aesar)	2.88	grains
$\text{BaCO}_3$	99.95%	(Alfa Aesar)	2.546	Grains
$\text{CuO}$	99.995%	(Alfa Aesar)	4.106	grains

and the below ratios for the EVEN layers.

$\text{MgO}$	99.95%	(Alfa Aesar)	2.08	grains	(4x stoichiometric)
$\text{CuO}$	99.995%	(Alfa Aesar)	2.05	grains	(4x stoichiometric)

The chemical precursors were pelletized at 70,000 PSI and sintered for 35-36 hours at 865C. The pellet was then annealed for 10 hours at 500C in flowing O<sub>2</sub>. The 4-point probe was bonded to the pellet with CW2400 silver epoxy and used 7 volts on the primary, with a 50-ohm series resistor. Temperature was determined using an Omega type "T" thermocouple and precision OP77 DC amplifier. The magnetometer employed twin Honeywell SS94A1F Hall-effect sensors with a tandem sensitivity of 50 mv/Gauss.

#### **5.4 first computer-designed superconductor:**

A Binghamton University scientist and his international colleagues report this week on the successful synthesis of the first superconductor designed entirely on the computer. Their findings were published in Physical Review Letters, the leading journal in the field[13].

"Paradigm-shifting superconducting materials have so far been discovered experimentally, and oftentimes accidentally,".

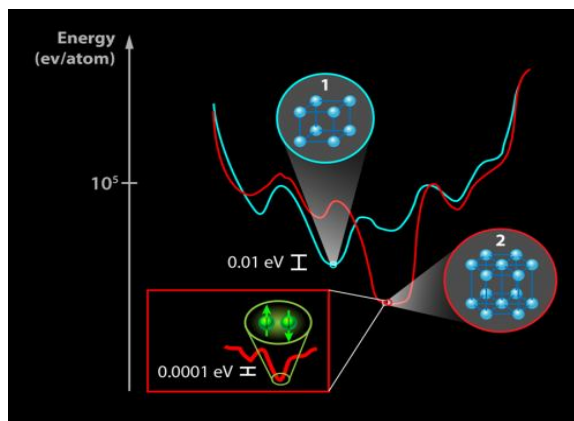
Until now, theory has been used primarily to investigate superconducting mechanisms and, in rare cases, suggest ways that existing materials might be modified to become superconductors. But many proposed superconducting materials are not stable enough to form and those that do form are poor superconductors.

Superconductors, which conduct electric current without any resistance when cooled below a certain temperature, have many interesting applications. For instance, power lines made out of superconducting materials can significantly reduce the energy lost in transmission. Superconducting magnets are also used in high-speed levitating trains and could improve wind turbines.

The phenomenon of superconductivity was discovered more than 100 years ago, with breakthroughs in the 1960s bringing it into practical application in a variety of technologies. The critical temperature, or T<sub>c</sub>, for superconductors

discovered to date is between 0 and 136 Kelvin (-460 and -214 degrees Fahrenheit). This means that most superconductors require expensive cooling mechanisms. Scientists are still searching for new materials that are superconductors at higher temperatures and can be mass produced.

More than five years ago, Kolmogorov, then at Oxford University, began studying boron-based materials, which have remarkably complex structures and a wide range of applications. He developed an automated computational tool to identify previously unknown stable crystal structures without any input from experiment. His "evolutionary" algorithm emulates nature, meaning it favors more stable materials among thousands of possibilities. (Kolmogorov is a computational physicist, but he also dreams of holding a compound in his hands that he predicted in silico as shown in fig (5.6).



**Fig (5.6) A schematic free energy landscape for different crystallographic configurations is given by the blue line**

Note the small difference in energy between various structures compared with the total energy of a crystal demanding high computational accuracy. The application of pressure as done by Gou et al. will modify the energy landscape (red curve), potentially stabilizing new structures. The ground state (such as superconductivity, magnetism, or other forms of order) for a given structure is determined at even lower energy scales, as depicted in the inset. The addition of strong electronic correlations in some materials will further

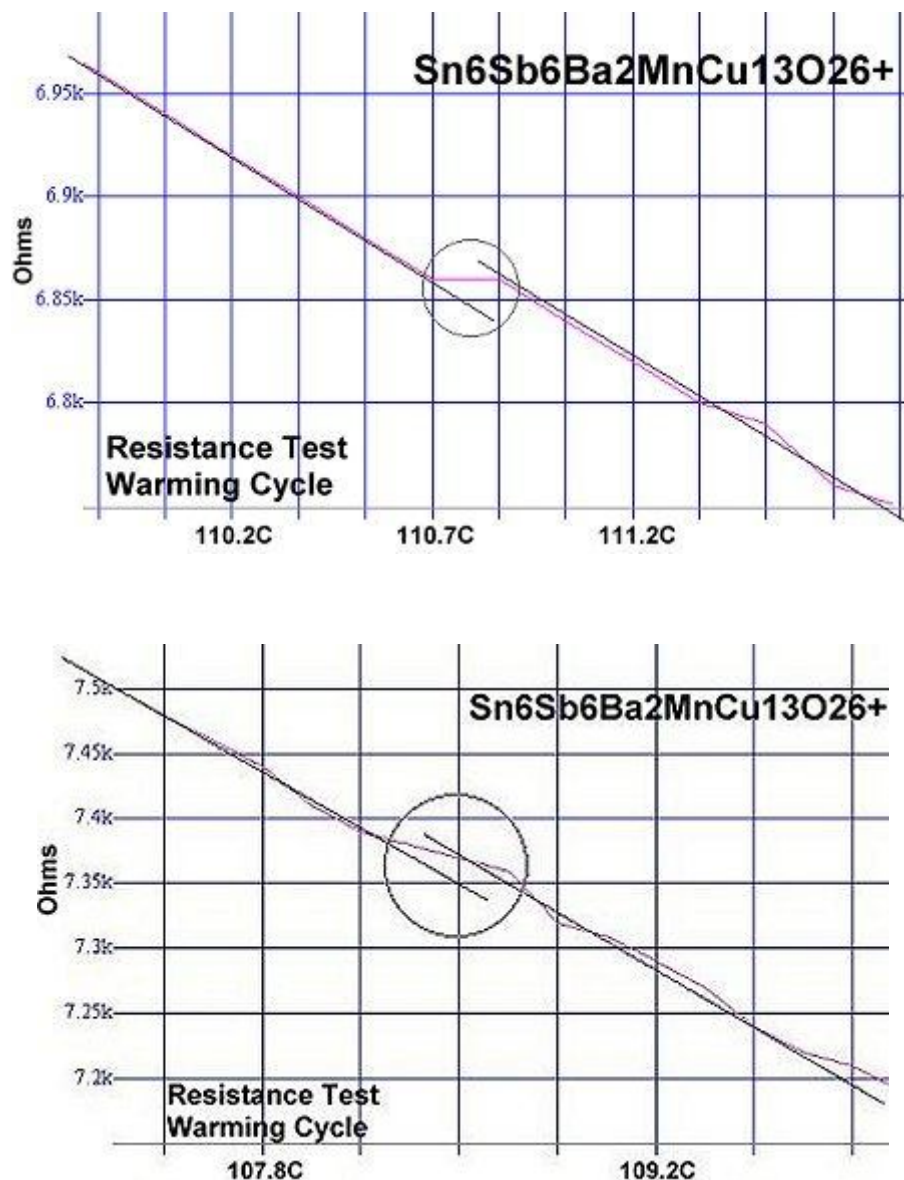
modify the landscape over large energy scales up to 10eV, making predictions even more challenging.

## **5.5 Milestone Superconductivity Above 100 Celsius:**

Superconductors.ORG herein reports the successful synthesis of the first compound to exhibit superconductivity above the boiling point of water.  $\text{Sn}_6\text{Sb}_6\text{Ba}_2\text{MnCu}_{13}\text{O}_{26+}$  displays a critical transition temperature near 110 Celsius (230F, 383K). This brings to 21 the number of compounds found to display superconductivity above room temperature[14].

Confirmation of superconductivity was made using a magnetometer and direct resistance tests of two pellets. Ten magnetization tests produced sharp diamagnetic transitions at an average temperature of 110.0C. Then thirteen resistance tests revealed companion resistance drops at an average temperature of 109.7C. The two plots at page top show examples of the Meissner transitions. The straight lines approximate the average of the data points, skewing apart at  $T_c$ , the critical transition temperature.

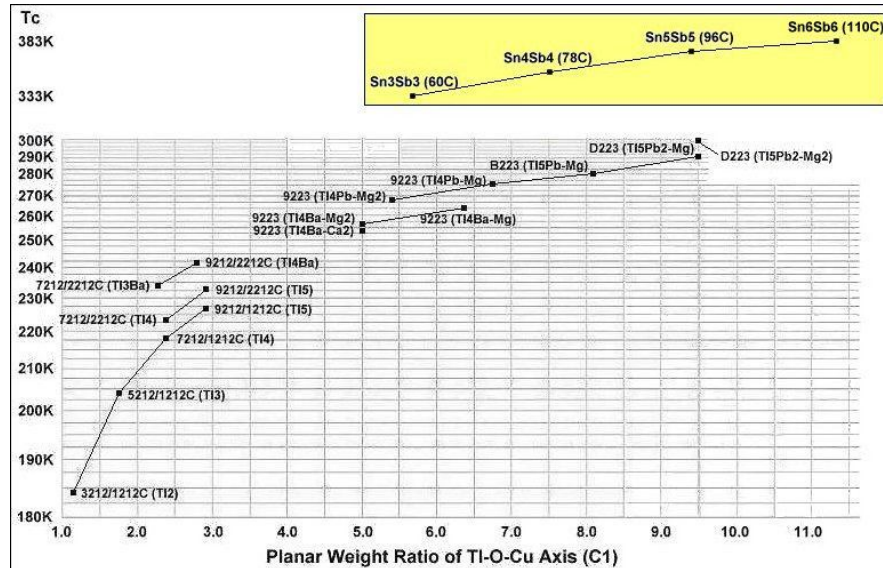
Like the 95C superconductor announced in Octob2014, this copper-oxide ceramic exploits a high dielectric constant (K) in both the  $\text{MnO}_2$  anion and SnSb cation layers to complement a high planar weight ratio (PWR) along the C axis. This new formulation features longer chains of tin-antimony in the C1 axis as well as longer copper-oxygen chains in the C2 axis than were used in the J212 structure of the 95C prototype. This results in an exceptionally large unit cell. Using the standard naming convention, the target structure would be classified N212 (shown at left)<sup>2</sup>. Below are two of the thirteen direct resistance plots.



**Fig (5.7) the associated diamagnetic transitions**

The above resistance plots confirm that the associated diamagnetic transitions are Meissner transitions. In the physical sciences there is no phenomenon other than superconductivity that can produce a sharp diamagnetic transition and a resistance drop at the same temperature. Note that the bulk has a negative temperature coefficient, sloping the opposite direction as the superconductive transitions. All of the plots on this page exhibit a low signal-to-noise ratio due to a low volume fraction of superconductive material and a high thermal noise level inherent to these temperatures.

The below graph illustrates how influential dielectric constant (relative permittivity) is in promoting  $T_c$ . The dots within the grid are copper-oxides that have a low K. While those in the yellow box are copper-oxides that have a high K. At the same PWR, the curve with the high K compounds features transition temperatures 60 to 70 degrees higher as shown in fig (5.8).



**Fig (5.8) the curve with the high K compounds features transition temperatures 60 to 70 degrees higher.**

In order to maximize formation of the N212 structure, this compound was synthesized using the layer cake method, as shown below. The pellet had approximately 100 interference layers. And, even using this layering technique, the volume fraction is low, requiring very sensitive test equipment[15].

## 5.6 Discussion :

All materials that behave as superconductors at unusually high temperatures are called High-temperature superconductors.

It have been observed with transition temperatures as high as 138 K ( $-135^{\circ}\text{C}$ ).

mercury barium calcium copper oxide ( $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ) is the highest transition temperature that has been confirmed at around 133 K.

the unique crystal structure of high- $T_c$  copper oxide or cuprate superconductors causes a large anisotropy in normal conducting and superconducting properties, since electrical currents are carried by holes induced in the oxygen sites of the  $\text{CuO}_2$  sheets. The electrical conduction is highly anisotropic, with a much higher conductivity parallel to the  $\text{CuO}_2$  plane than in the perpendicular direction.

In a high- $T_c$  superconductor, the mechanism is extremely similar to a conventional superconductor. Except, in this case, phonons virtually play no role and their role is replaced by spin-density waves.

### **5.7 Conclusion :**

The superconductivity near 28 Celsius (83F, 301K) was observed in the copper-oxides superconductors . Also superconductivity above the boiling point of water was observed in  $\text{Sn}_6\text{Sb}_6\text{Ba}_2\text{MnCu}_{13}\text{O}_{26+}$  displays a critical transition temperature near 110 Celsius (230F, 383K).

### **5.8 Recommendation:**

To prepare superconductor that require special labs to procedure the thermo electrical interactions that take place at high temperatures of 800 C to 950 ° C that cannot found under normal circumstances.

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