A STUDY ON SUPERCONDUCTING MATERIALS
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ABSTRACT
In this work, a comprehensive study of superconductor materials has been studied since its discovery, and th classification according to certain bases, as well as the important applications in daily life.

I. INTRODUCTION

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 [1, 2]. In 1911 superconductivity was first observed in mercury by Dutch physicist Heike Kamerlingh Onnes of Leiden University (shown above). 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 (above left) and Robert Ochsenfeld (above right) discovered that a superconducting material will repel a magnetic field (below graphic). 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 [3, 4]. This phenomenon is known as strong diamagnetism and is today often referred to as the ”Meissner effect” (an eponym). The Meissner effect is so strong that a magnet can actually be levitated over a superconductive material.

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 Fermi lab 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 (above). 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[5,6]. 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. Another significant theoretical
advancement came in 1962 when Brian D. Josephson (above), 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. (Below SQUID graphic courtesy Quantum Design.)

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 three French team members. (TMTSF)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 [7, 8]. 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. 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 Tc'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 [9, 10]. For more than 20 years the mercury copper-oxides held the record for highest transition temperature at 138 K. However, recently the thallium copper-oxides have moved into the lead. When incorporated into a 3212 structure, thallium, barium, tellurium, copper and oxygen will produce a T$_c$ near 147K with purity comparable to the mercuric cuprates. The first company to capitalize on high-temperature superconductors was Illinois Superconductor (today known as ISCO International), formed in 1989. This amalgam of government, private-industry and academic interests introduced a depth sensor for medical equipment that was able to operate at liquid nitrogen temperatures (~ 77K). In recent years, many discoveries regarding the novel nature of superconductivity have been made [11, 12]. In 1997 researchers found that at a temperature very near absolute zero an alloy of gold and indium was both a superconductor and a natural magnet. Conventional wisdom held that a material with such properties could not exist! Since then, over a half-dozen such compounds have been found. Recent years have also seen the discovery of the first high-temperature superconductor that does NOT contain any copper (2000), and the first all-metal perovskite superconductor (2001). Also in 2001 a material that had been sitting on laboratory shelves for decades was found to be an extraordinary new superconductor. Japanese researchers measured the transition temperature of magnesium diboride at 39 Kelvin - far above the highest T$_c$ of any of the elemental or binary alloy superconductors. While 39 K is still well below the Tc's of the "warm" ceramic superconductors, subsequent refinements in the way MgB$_2$ is fabricated have paved the way for its use in industrial applications. Laboratory testing has found MgB$_2$ will outperform NbTi and Nb$_3$Sn wires in high magnetic field applications like MRI. Though a theory to explain high-temperature superconductivity still
eludes modern science, clues occasionally appear that contribute to our understanding of the exotic nature of this phenomenon. In 2005, for example, Superconductors.ORG discovered that increasing the weight ratios of alternating planes within the layered perovskites can often increase $T_c$ significantly. Further increases in transition temperatures were then noticed when high dielectric constant alloys were used. This has led to the discovery of more than 130 new high-temperature superconductors, including a candidate for a new world record. The most recent "family" of superconductors to be discovered is the "pnictides". These iron-based superconductors were first observed by a group of Japanese researchers in 2006[13, 14, and 15]. Like the high-$T_c$ copper-oxides, the exact mechanism that facilitates superconductivity in them is a mystery. However, with $T_c$'s over 50K, a great deal of excitement has resulted from their discovery.

II. TYPES I AND II SUPERCONDUCTORS
There are thirty pure metals which exhibit zero resistivity at low temperatures and have the property of excluding magnetic fields from the interior of the superconductor (Meissner effect). They are called Type II superconductors. The superconductivity exists only below their critical temperatures and below a critical magnetic field strength. Type I superconductors are well described by the BCS theory. Starting in 1930 with lead-bismuth alloys, a number of alloys were found which exhibited superconductivity; they are called Type II superconductors. They were found to have much higher critical fields and therefore could carry much higher current densities while remaining in the superconducting state. The variations on barium-copper-oxide ceramics which achieved the superconducting state at much higher temperatures are often just referred to as high temperature superconductors and form a class of their own.

III. TYPE I SUPERCONDUCTORS AND A PERIODIC CHART COMPARISON

The Type I category of superconductors is mainly comprised of metals and metalloids that show some conductivity at room temperature. They require incredible cold to slow down molecular vibrations sufficiently to facilitate unimpeded electron flow in accordance with what is known as BCS theory. BCS theory suggests that electrons team up in "Cooper pairs" in order to help each other overcome molecular obstacles - much like race cars on a track drafting each other in order to go faster. Scientists call this process phonon-mediated coupling because of the sound packets generated by the flexing of the crystal lattice[16,17]. Type I superconductors - characterized as the "soft" superconductors - were discovered first and require the coldest temperatures to become superconductive. They exhibit a very sharp transition to a superconducting state (see above graph) and "perfect" diamagnetism - the ability to repel a magnetic field completely. Below is a list of known Type I superconductors along with the critical transition temperature (known as $T_c$) below which each superconducts. The 3rd column gives the lattice structure of the solid that produced the noted $T_c$. Surprisingly, copper, silver and gold, three of the best metallic conductors, do not rank among the superconductive elements[18].
IV. CRITICAL MAGNETIC FIELD

The superconducting state cannot exist in the presence of a magnetic field greater than a critical value, even at absolute zero. This critical magnetic field is strongly correlated with the critical temperature for the superconductor, which in turn correlates with the band gap. Type II superconductors show two critical magnetic field values, one at the onset of a mixed superconducting and normal state and one where superconductivity ceases.

![Type I vs Type II Critical Magnetic Field](image)

It is the nature of superconductors to exclude magnetic fields (Meissner effect) so long as the applied field does not exceed their critical magnetic field. This critical magnetic field is tabulated for 0K and decreases from that magnitude with increasing temperature, reaching zero at the critical temperature for superconductivity. The critical magnetic field at any temperature below the critical temperature is given by the relationship

\[ B_c \approx B_c(0) \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right] \]

V. TYPE II SUPERCONDUCTORS

Except for the elements vanadium, technetium and niobium, the Type II category of superconductors is comprised of metallic compounds and alloys. The recently-discovered superconducting "perovskites" (metal-oxide ceramics that normally have a ratio of 2 metal atoms to every 3 oxygen atoms) belong to this Type II group. They achieve higher Tc's than Type I superconductors by a mechanism that is still not completely understood. Conventional wisdom holds that it relates to the planar layering within the crystalline structure (see above graphic). Although, other recent research suggests the holes of hypocharged oxygen in the charge reservoirs are responsible. (Holes are positively-charged vacancies within the lattice.) The superconducting cuprates (copper-oxides) have achieved astonishingly high Tc's when you consider that by 1985 known Tc's had only reached 23 Kelvin. To date, the highest Tc attained at ambient pressure for a material that will form stoichiometrically (by direct mixing) has been 147 Kelvin. And the highest Tc overall is 202 Celsius for a material which does not form stoichiometrically. It is almost certain that other, more-synergistic compounds still await discovery among the high-temperature superconductors. The first superconducting Type II compound, an alloy of lead and bismuth, was fabricated in 1930 by W. de Haas and J. Voogd. But, was not recognized as such until later, after the Meissner effect had been discovered. This new category of superconductors was identified by L.V. Shubnikov at the Kharkov Institute of Science and Technology in the Ukraine in 1936 when he found two distinct critical magnetic fields (known as \( H_{c1} \) and \( H_{c2} \)) in PbTl. The first of the oxide superconductors was created in 1973 by DuPont researcher Art Sleight when Ba(Pb,Bi)O3 was found to have a Tc of 13K. The superconducting oxocuprates followed in 1986. Type II superconductors - also known as the “hard” superconductors - differ from Type I in that their transition from a normal to a superconducting state is gradual across a region of "mixed state" behavior. Since a Type II will allow some penetration by an external magnetic field into its surface, this creates some rather novel mesoscopic phenomena like superconducting "stripes" and "flux-lattice vortices". While there are far too many to list in totality, some of the more interesting Type II superconductors are listed below by similarity and with descending Tc's. Where available, the lattice structure of the system is also noted [19,20,21].
VI. SUPERCONDUCTOR APPLICATIONS

1. Superconducting Magnets
Type II superconductors such as niobium-tin and niobium-titanium are used to make the coil windings for superconducting magnets. These two materials can be fabricated into wires and can withstand high magnetic fields. Typical construction of the coils is to embed a large number of fine filaments (20 micrometers diameter) in a copper matrix. The solid copper gives mechanical stability and provides a path for the large currents in case the superconducting state is lost. These superconducting magnets must be cooled with liquid helium. Superconducting magnets can use solenoid geometries as do ordinary electromagnets. Most high energy accelerators now use superconducting magnets [22]. The proton accelerator at Fermi lab uses 774 superconducting magnets in a ring of circumference 6.2 kilometers. They have also found wide application in the construction of magnetic resonance imaging (MRI) apparatus for medical imaging.

2. Superconducting Transmission Lines
Since 10% to 15% of generated electricity is dissipated in resistive losses in transmission lines, the prospect of zero loss superconducting transmission lines is appealing. In prototype superconducting transmission lines at Brookhaven National Laboratory, 1000 MW of power can be transported within an enclosure of diameter 40 cm. This amounts to transporting the entire output of a large power plant on one enclosed transmission line. This could be a fairly low voltage DC transmission compared to large transformer banks and multiple high voltage AC transmission lines on towers in the conventional systems. The superconductor used in these prototype applications is usually niobium-titanium, and liquid helium cooling is required [22]. Current experiments with power applications of high-temperature superconductors focus on uses of BSCCO in tape forms and YBCO in thin film forms. Current densities above 10,000 amperes per square centimeter are considered necessary for practical power applications, and this threshold has been exceeded in several configurations.

3. Superconducting Maglev Trains
While it is not practical to lay down superconducting rails, it is possible to construct a superconducting system onboard a train to repel conventional rails below it. The train would have to be moving to create the repulsion, but once moving would be supported with very little friction. There would be resistive loss of energy in the currents in the rails[23]. Ohanian reports an engineering assessment that such superconducting trains would be much safer than conventional rail systems at 200 km/h. A Japanese magnetically levitated train set a speed record of 321 mi/h in 1979 using superconducting magnets on board the train. The magnets induce currents in the rails below them, causing a repulsion which suspends the train above the track.

4. Fault-Current Limiters
High fault-currents caused by lightning strikes are a troublesome and expensive nuisance in electric power grids. One of the near-term applications for high temperature superconductors may be the construction of fault-current limiters which operate at 77K. The need is to reduce the fault current to a fraction of its peak value in less than a cycle (1/60 sec). A recently tested fault-current limiter can operate at 2.4 kV and carry a current of 2200 amperes. It was constructed from BSCCO material.

5. Superconductors in NMR Imaging
Superconducting magnets find application in magnetic resonance imaging (MRI) of the human body. Besides requiring strong magnetic fields on the order of a Tesla, magnetic resonance imaging requires extremely uniform fields across the subject and extreme stability over time. Maintaining the magnet coils in the superconducting state helps to achieve parts-per-million special uniformity over a space large enough to hold a person, and ppm/hour stability with time[24].

6. SQUID Magnetometer
The superconducting quantum interference device (SQUID) consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions. The device may be configured as a magnetometer to detect incredibly small magnetic fields -- small enough to measure the magnetic fields in living organisms. Squids
have been used to measure the magnetic fields in mouse brains to test whether there might be enough magnetism to attribute their navigational ability to an internal compass[25].

Threshold for SQUID: $10^{14}$ T
Magnetic field of heart: $10^{10}$ T
Magnetic field of brain: $10^{13}$ T

The great sensitivity of the SQUID devices is associated with measuring changes in magnetic field associated with one flux quantum. One of the discoveries associated with Josephson junctions was that flux is quantized in units

$$\Phi_o = \frac{2\pi h}{2e} = 2.0678 \times 10^{-15} \text{tesla} \cdot \text{m}^2$$

If a constant biasing current is maintained in the SQUID device, the measured voltage oscillates with the changes in phase at the two junctions, which depends upon the change in the magnetic flux. Counting the oscillations allows you to evaluate the flux change which has occurred.

7. **Superconducting Motors**

Superconducting motors and generators could be made with a weight of about one tenth that of conventional devices for the same output. This is the appeal of making such devices for specialized applications. Motors and generators are already very efficient, so there is not the power savings associated with superconducting magnets. It may be possible to build very large capacity generators for power plants where structural strength considerations place limits on conventional generators[26]. In 1995 the Naval Research Laboratory demonstrated a 167 hp motor with high-$T_c$ superconducting coils made from Bi-2223. It was tested at 4.2K and at liquid neon temperature, 28K with 112 hp produced at the higher temperature.

VII. **CONCLUSION**

**Advantage One: Transforming the Electricity Grid**

The electric power grid is among the greatest engineering achievements of the 20th century. Demand, however, is about to overwhelm it. For example, the North American blackout of 2003, which lasted about four days, affected over 50 million persons and caused about $6$ billion in economic loss. Superconductor technology provides loss-less wires and cables and improves the reliability and efficiency of the power grid. Plans are underway to replace by 2030 the present power grid with a superconducting power grid. A superconducting power system occupies less real estate and is buried in the ground, quite different from present day grid lines.

**Advantage Two: Improving Wide-Band Telecommunication**

Wide-band telecommunications technology, which operates best at gigahertz frequencies, is very useful for improving the efficiency and reliability of cell phones. Such frequencies are very difficult to achieve with semiconductor-based circuitry. However, they have been easily achieved by Hypres's superconductor-based receiver, using a technology called rapid single flux quantum, or RSFQ, integrated circuit receiver. It operates with the aid of a 4-kelvin cry cooler. This technology is showing up in many cell phone receiver transmitter towers.
Advantage Three: Aiding Medical Diagnosis

One of the first large-scale applications of superconductivity is in medical diagnosis. Magnetic resonance imaging, or MRI, uses powerful superconducting magnets to produce large and uniform magnetic fields inside the patient's body. MRI scanners, which contain liquid helium refrigeration systems, pick up how these magnetic fields are reflected by organs in the body. The machine eventually produces an image. MRI machines are superior to x-ray technology in producing a diagnosis. Paul Leuterbur and Sir Peter Mansfield were awarded the 2003 Nobel prize in physiology or medicine, "for their discoveries concerning magnetic resonance imaging," underlying the significance of MRI, and by implication superconductors, to medicine.

Disadvantages of Superconductors

Superconducting materials superconduct only when kept below a given temperature called the transition temperature. For presently known practical superconductors, the temperature is much below 77 Kelvin, the temperature of liquid nitrogen. Keeping them below that temperature involves a lot of expensive cryogenic technology. Thus, superconductors still do not show up in most everyday electronics. Scientists are working on designing superconductors that can operate at room temperature.

VIII. RECOMMENDATIONS

- Successfully used for high energy physics, MRI, laboratory magnets.
- For electric power, many demonstrations: cables, motors, and generators.
- Enhancing Efficiency in the Electric Power Grid: 7-10% of 1 Terawatt US electric power now lost in grid, superconductor equipment could cut this by half, save 50 Gigawatts!
- Superconductor cables bringing 50%-efficient generation to cities, replacing 30%-efficient “reliability-must-run” generators: super grid: a radical leap in grid efficiency.
- Reduced $I^2R$ loss by efficient transformers, high voltage superconductor break this paradigm: $I^2R = 0$ enables high Dc current, low voltage.
- Superconductors - “smart” materials, switch to resistive state above critical current.
- Superconducting power equipment avoids use of oil a contaminant and fire hazard.
- Superconductor’s high efficiency reduces unnecessary pollution and CO$_2$ emission at energy source.
- Most desired superconductor functionalities (high current density, robust mechanical properties) have already been achieved, but still at too low a temperature with processes which could be simplified. The main challenge is the cost.

Summary

Superconductivity is in the right place at the right time to address grand challenges of energy delivery and use:
- Major increase in energy efficiency and capacity.
- Higher efficiency grid equipment.
- Electrification of transport.
- Breaking power bottlenecks for reorganization.
- Environmentally green and clean technology

REFERENCES

9. (The displacement is ignored because it is assumed that electric field only varies slowly with respect to time, and the term is already suppressed by a factor of c.)