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RESEARCH & KNOWLEDGE

Review Article

A brief history of superconductivity

Suthat Yoksan

Department of Physics, Srinakharinwirot University, Bangkok 10110, Thailand

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1. Introduction

This article begins with the discovery of superconductivity by Onnes in 1911, followed by the discovery of high-temperature superconductors by Müller and Bednorz in 1986 and ends with the discovery of iron-based superconductors by Hasono's group in 2008.

The major landmarks are covered and corresponding theories are presented. Some open questions are posed and a brief discussion on what new physics can be expected in the future.

2. The beginning

On 8th April 1911, a Dutch physicist named Heike Kamerlingh Onnes (Fig. 1) made an astonishingly unexpected discovery. He found that mercury completely loses its electrical resistance when cooled to 4.2 kelvins (4.2 degrees above absolute zero) and that an electric current could flow in the mercury forever without needing a battery to drive the current (Fig. 2) (see Onnes, 1911a;b;c).

No physicist had predicted this phenomenon and no one at that time could explain it. The effect was named superconductivity.

It took almost half a century to figure out how superconductivity occurs, and all through the years since, physicists have come to realize that we have not yet come to a full understanding of this complex and exotic phenomenon.

Figure 1. Kamerlingh Onnes (http://www.nobelprize.org).

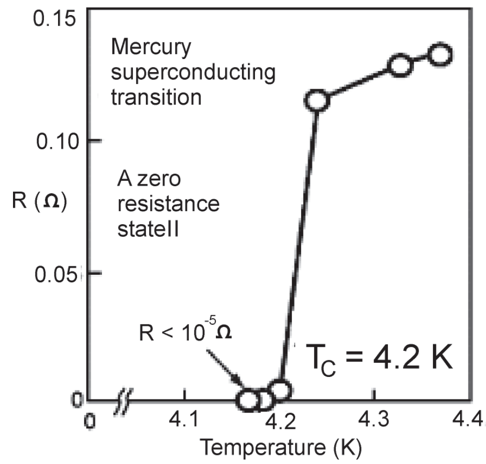

Figure 2. Sharp drop in resistance for mercury at 4.2 K (http://hyperphysics.phy-astr.gsu.edu).

3. The Meissner effect

In 1933, Walther Meissner and Robert Ochsenfeld did an experiment to investigate what happens to magnetic fields near a superconductor as it is cooled. They found that instead of passing through the superconductor, the field was expelled from the material (see Meissner and Ochsenfeld, 1933).

This Meissner effect is responsible for the ability of superconductors to float above magnets (Fig. 3). The hovering is due to currents that flow across its surfaces that produce their own magnetic field that repels an external one.

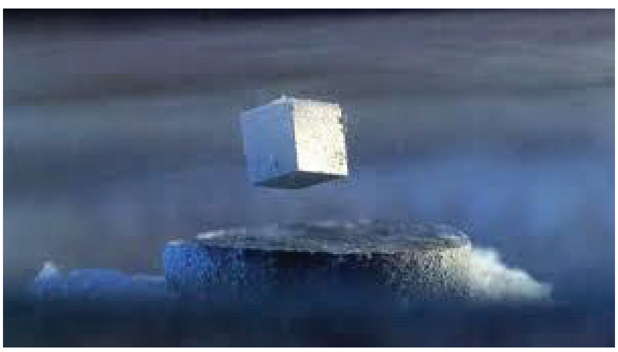

Figure 3. Meissner effect (http://web.physics.ucsb.edu).

Author for correspondence: suthat@swu.ac.th

4. The London theory

In 1934, Fritz and Heinz London (Figs. 4 and 5) proposed the first phenomenological theory of superconductivity (London and London, 1935). The London equations accounted for the properties of zero resistance and perfect diamagnetism. The solutions of the equations gave an expression for the magnetic penetration depth of a superconductor.

Figure 4. Fritz London (http://chemistry.bd.psu.edu).

Figure 5. Heinz London (http://www.spd-neuss.de).

5. The Ginzburg-Landau theory

In 1950, Vitaly Ginzburg (Fig. 6) and Lev Landau (Fig. 7) speculated that the superconducting electrons were in a macroscopic quantum state and a macroscopic wave function (or order parameter) exists. The London theory follows directly from this postulate. The Ginzburg-Landau theory now accounts for zero resistance and the Meissner effect in much more physical forms. The theory also accounted for the second order phase transition of a superconductor. It also provided a concept of the coherent length and a way to calculate the superconducting wave function.

With the introduction of the Ginzburg-Landau theory, the classical period of superconductivity with Onnes, Meissner and the Londons came to an end, and the era of superconductivity as a macroscopic quantum phenomenon began. Yet the deeper origins of the Ginzburg-Landau theory based on the quantum theory were soon to be established (see Ginzburg and Landau, 1950).

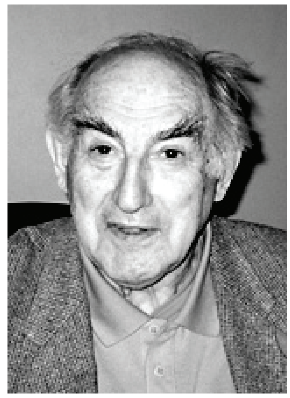

Figure 6. Vitaly Ginzburg (https://www.nobelprize.org).

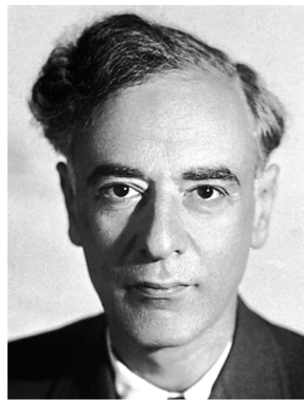

Figure 7. Lev Landau (http://www.nobelprize.org).

6. Type II superconductivity

In 1957, Alexei Abrikosov (Fig. 8) recognized that for a certain range of material parameters the Ginzburg-Landau equations gave a solution in which the magnetic field inside the superconductor was not zero-rather there were vortices inside the superconductor-regions of circulating currents with a peak in the magnetic field that decayed from the center. These vortices were found to form a regular lattice. Each contained exactly one quantum of flux. Such superconductors are called type II superconductors (see Abrikosov, 1957).

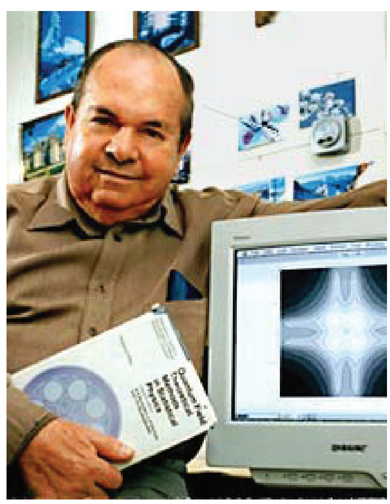

Figure 8. Alexei Abrikosov (http://www.nobelprize.org/nobel_prizes/physics/).

7. High-field, high-current superconductivity

While studying the properties of Nb_3Sn, Kunzler discovered that Nb_3Sn not only had a high transition temperature, but that it also sustained superconductivity to very high current densities and very high magnetic fields (Fig. 9) (Kunzler *et al.*, 1961). The practical field of superconducting magnets and large-scale applications of superconductivity grew out of these discoveries, and high-field superconductivity is possible because magnetic flux does penetrate the superconductor.

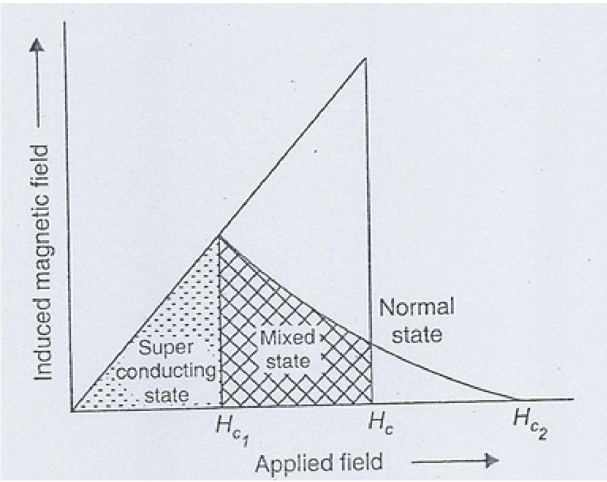

Figure 9. Type I and II superconductivity (http://ethesis.nitrkl.ac.in).

8. Superconducting materials

Since its discovery, superconductivity has been explored systematically throughout the elements of the periodic table (Fig. 10). Particular fascination concerns the transition temperature of a superconductor and how one might increase it. Physicists began to look at binary systems including both alloys and compounds. The discovery of superconductivity in V_3Si by J. Hulm and G. Hardy opened up the era of A15 compounds and the transition temperature was increased to 18 kelvins with the discovery of superconductivity in Nb_3Sn (Hardy and Hulm, 1954).

Despite all this success, these developments had little impact on the basic understanding of superconductivity and they had virtually no impact on the technology of the time.

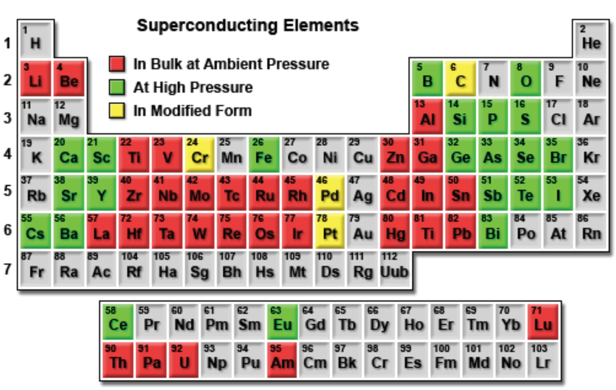

Figure 10. Superconducting elements (https://nationalmaglab.org).

9. The mechanism of superconductivity

In the 1950's, some physicists examined the effect of changing the isotopic mass of a superconductor on its transition temperature and found that the transition temperature went up as did the inverse square root of the isotopic mass of the element. This suggested that vibrations of the ionic lattice (or phonon) were playing a role in the superconductivity. The implication was that the electron-phonon interaction might cause the superconductivity (Fig. 11) (see Serin, 1950).

H. Fröhlich then showed that when an electron moves through a crystal it polarizes the lattice, leaving a positive potential for a second electron coming along later. This is the attractive electron-phonon interaction between two electrons (see Fröhlich, 1954).

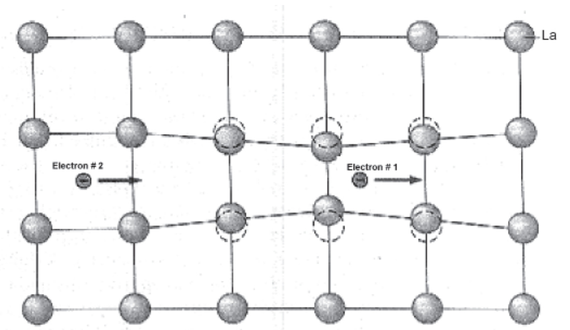

Figure 11. Electron-phonon interaction (http://ffden-2.phys.uaf.edu).

10. The BCS theory

In the presence of an attractive interaction, between electrons no matter how small, L. Cooper showed that the two independent electrons above a filled Fermi sphere are unstable toward the existence of a Cooper pair. Using this idea, Bardeen, Cooper and Schrieffer (Fig. 12) solved the many body problems for all the conduction electrons in a solid. The theory shows that the phases of the BCS wave function are locked to the same value (Bardeen *et al.*, 1957).

Figure 12. John Bardeen (left), Leon Cooper (center) and John Schrieffer (right) (http://www.nobelprize.org).

The resulting overall phase of the BCS wave function is just the phase of the Ginzburg-Landau wave function. This shows the connection between the two theories and it demonstrates that the BCS theory contains the macroscopic quantum nature of superconductivity.

The BCS theory also predicts that there is an energy gap in the density of states of a superconductor with a sharp peak just above the gap followed by a smooth decrease to the normal state value.

11. Superconducting tunneling

In 1960, I. Giaever discovered superconducting for electron tunneling. In particular, he found that it was possible for electron to tunnel from a normal metal through an insulating barrier into a superconductor. The resulting differential conductance of the junction, dI/dV, as a function of bias voltage has a shape of the thermally-smeared density of states in the superconductor. Giaver's work confirmed the existence of an energy gap and provided a method to measure the density of states of a superconductor (see Giaever, 1960).

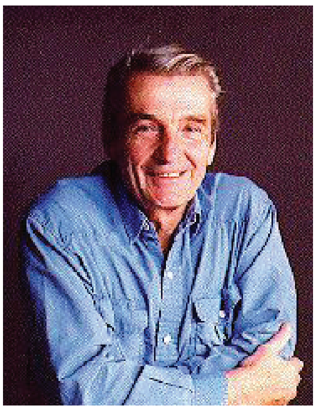

Figure 13. Ivar Giaver (http://homepages.rpi.edu).

12. The Josephson effect

In 1962, B. D. Josephson (Fig. 14) found that not only could single electrons tunnel, but that Cooper pairs could tunnel as well. This discovery of the Josephson effect led to the Josephson effect devices of superconductive electronics. The effect can be viewed as a phase coupling of two weakly-coupled superconductors, and it demonstrates explicitly the connection to the quantum nature of superconductivity (Fig. 15) (see Josephson, 1962).

The development of superconductivity research up to now is that the mechanism of superconductivity was established. The large-scale electrical and electronic applications were pursued rigorously, but there were always some scientists who persisted and said that there had to be a new body of knowledge, new materials and new theories in order to achieve room-temperature superconductivity.

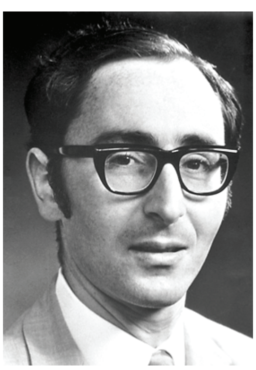

Figure 14. Brian Josephson (http://www.nobelprize.org).

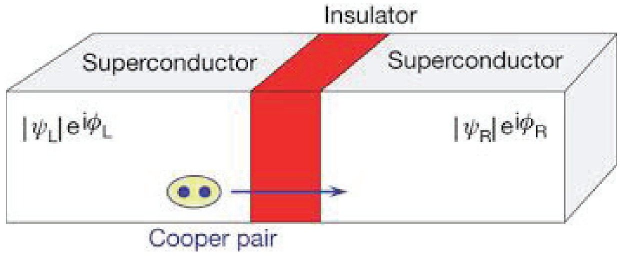

Figure 15. Josephson Junction (http://csp2015.ac.ru).

13. Novel mechanisms and exotic superconductors

The BCS theory is based on the electron-phonon interaction, but it does not explicitly depend on it. Any attractive interaction will do. Some bold theorists turned their attention to novel, non-electron phonon mechanisms and to exotic superconductors when there was a reason to believe the underlying physics might be different.

Theorists therefore thought of new pairing interactions: polarons, excitons, plasmons, spin-fluctuations-all kinds of things. Experimentalists at the same time sought higher transition temperatures and superconductivity in unusual materials. Out of this came organic superconductors and heavy fermion superconductors, etc.

14. High-temperature superconductivity

Since 1973, the highest transition temperature (T_c) of 23.3 K in Nb_3Ge alloy had not been enhanced. However, at IBM's Zurich Research Laboratory, where J.G. Bednorz and K.A. Müller (Fig. 16) worked on structural and ferroelectric properties of insulating oxides, the pair observed that $BaPb_{1-x}Bi_xO_3$ perovskite exhibited superconductivity with T_c's of 13 K. No one expected to see the effect in an oxide, because oxidation means rust or tarnishing. A. Müller therefore began to suspect that a big discovery was a possibility. He and G. Bednorz subsequently prepared various oxides and studied them.

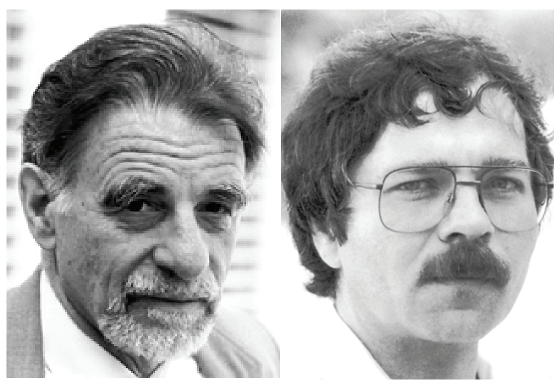

Figure 16. Karl Alexander Müller (left) and J. Georg Bednorz (right) (https://www.nobelprize.org).

The breakthrough came when they saw a report from a French research group on an oxide compound containing barium, lantanum and copper. The French team found that their sample conducted like a metal, which was unusual for an oxide, but they did not study its properties at low temperatures, because they were more interested in its possible use as a catalyst.

Bednorz and Müller immediately prepared samples containing the same elements with different compositions and cooled them to low temperatures. By January 1986, they had found superconductivity in the perovskite Ba-La-Cu oxide system at 35 K (Bednorz and Müller, 1986).

The oxide opened up the field of high-temperature superconductivity research. The basic formula for the high T_c materials seemed to be to keep a structure with planes of copper and oxygen and vary other atoms. By following this, new superconductors were discovered that worked at higher and higher temperatures.

Within a year, yttrium barium copper oxide-known as YBCO was found to superconduct at 92 K. The temperature record hit 138 K by 1995 and even 164 K when the compound $HgBa_2Ca_2Cu_3O_8$ was squeezed to high pressure.

The era of high-temperature superconductivity had begun (Fig. 17).

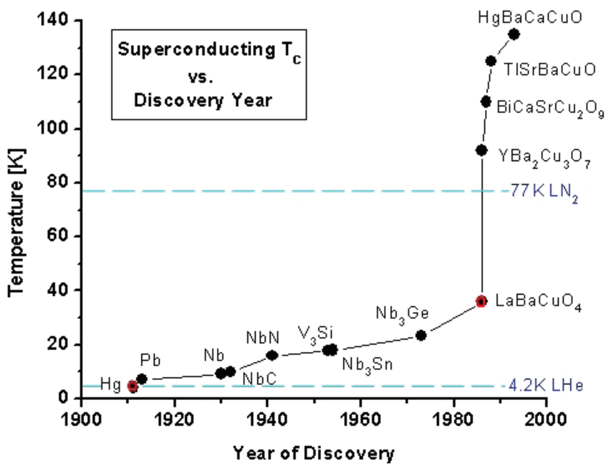

Figure 17. Superconducting T_c vs. Discovery Year (http://users.humboldt.edu).

To review our understanding so far, in conventional superconductors, electrons move in quantum waves of distinct energies. Since quantum mechanics forbids two electrons from occupying the same state, they stack into the states from the lowest energy on up. The electrons start to lower their total energy by pairing like ballroom dancers. That partnership produces superconductivity.

The pairing changes the spacing of the energy levels, creating a gap near the top of the stack. To break from its partner, and electron must jump the gap to an empty state. However, there is not enough energy around to do that, so the pairs glide along unperturbed. According to the BCS theory, phonon is the glue that binds the two electrons.

Now, high-temperature materials are different, structurally. The compounds contain planes of copper and oxygen ions that resemble chess boards, with a copper ion at every corner of a square and an oxygen ion along each side (Fig. 18). Electrons hop from copper ion to copper ion. Between the planes lie elements such as lanthanum, strontium, yttrium, bismuth, and thallium. However, it is along the copper-and-oxygen planes that the electrons pair and glide.

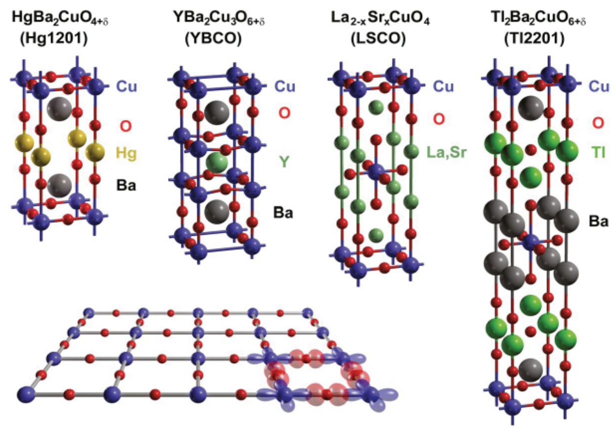

Figure 18. High-temperature superconducting materials (http://www.pnas.org).

How that happens is a big problem, because the electrons in high-temperature superconductors repel one another vigorously, so that they tend to end up with one electron on each copper ion. The deadlock can be broken by the creation of positively charged "holes", a process called doping.

The challenge is to explain how electrons that fiercely repel each other manage to pair. Some physicists argue that a wave of magnetism plays a similar role as one phonon plays in low-temperature superconductors.

Some believe that stripes of electric charge on the planes in some materials trigger the pairing. Still others say that high temperature superconductivity may not have one root cause, for example, the existence of loops of current flowing inside each copper-and-oxygen square may be another key.

As of present, we can say that three decades after discovery, physicists still do not agree on how electrons within them pair to glide through the materials effortlessly at temperatures as high as 138 K.

15. Mapping out the mysteries

On the experimental side, in 1994, John Kirtley and Chang Tsuei studied the shape of the quantum wave that describes the paired electrons (Fig. 19) (Tsuei *et al*., 1994). In a low-temperature superconductor, electrons can pair in any direction so the wave is a sphere, s-wave. In high-temperature superconductors, the cloud is shaped like a four-leaf clover. That d-wave shape means that paired electrons sit on adjacent copper ions and never on the same ion.

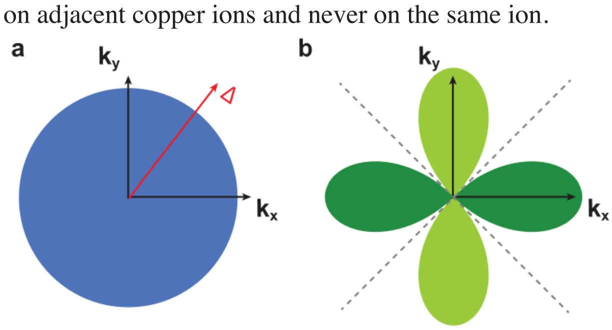

Figure 19. Shape of quantum waves for paired electrons: a. s-wave symmetry b. d-wave symmetry (http://www.2physics.com).

In spite of the discord among theorists, experimentalists have agreed upon the properties common to all the high T_c materials, which change with the amount of doping. That is, start with an undoped material, it is an antiferromagnetic insulator, then dope it to draw between 6% and 22% of the electron out of the planes, and it is a superconductor. Dope it more, and it becomes an ordinary metal.

The properties indicate that to solve this problem, one needs to understand the whole phase diagram of the material. Since one finds that at low doping and at temperatures far above T_c, pseudogap appears. This leads many theorists to speculate that these may be two different gaps: pseudogap and real gap and the theory that explains the pseudogap may explain the superconductivity.

Even without a theory to explain the phenomenon, physicists agree that the pursuit of high temperature superconductivity has led to the discovery of new materials, of new states of matter and of new concepts. In the quest to find high Tc superconductors, experimentalists have refined their techniques to new levels of sensitivity, precision, and speed.

At the same time, condensed matter theorists have come to see high temperature superconductivity as the gateway to a new study of strongly correlated electrons.

High temperature superconductivity has thus completely changed the landscape of condensed matter physics and led physicists to new realms.

16. Applications of superconductors

Superconductivity is not only fascinating, it is also incredibly useful. Many superconductors are already used in applications as diverse as nuclear magnetic resonance and particle accelerators.

16.1 Hunting the Higgs particle

Particle accelerators need strong magnets to bend beams of high energy particles. As the energy of the beams increase, so the need for stronger magnetic fields increase, and hence the necessity to have large superconducting magnets.

In the Large Hadron Collider (LHC) at CERN, beams of protons are accelerated in opposite directions around a circular tunnel 27 kilometers long (Fig. 20). To steer the protons requires very strong magnetic fields all the way around the ring. The LHC comprises 1232 superconducting magnets, each 15 meters long and weighing 35 tonnes. The magnet contain coils of superconducting wires made from niobium and titanium that are cooled to just above 1 kelvin using 100 tonnes of liquid helium.

In 2012, the LHC, as the world most powerful accelerator, discovered the Higgs particle.

16.2 Levitation

Magnetic fields are usually quite content to pass through any material, but as soon as the temperature falls low enough for superconductivity to occur, the magnetic field is expelled from the material. It is forced to pass around the superconductor. This Meissner effect is responsible for the ability of a superconductor to levitate above magnets. As a consequence, a superconductor coil if attached to a train can keep it floating above the magnetic track, thus avoiding friction. We then have a maglev train that can reach a speed of 600 kilometers per hour (Fig. 21).

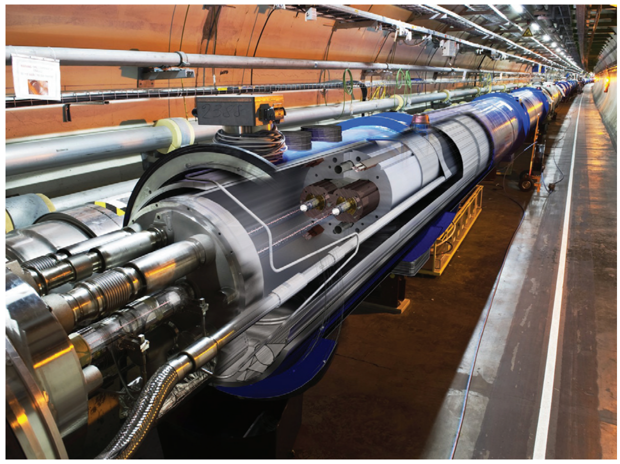

Figure 20. Large Hadron Collider (LHC) at CERN (http://www.ep.ph.bham.ac.uk).

Figure 21. High speed train (Murakami, 2015).

16.3 Sensors: SQUID

Electrical engineers know that circuits containing a superconductor will provide unprecedented sensitivity to tiny magnetic fields. Any magnetic field passing through the coil will generate a screening current that subsequently alters the current flowing in the circuit.

This is the working principle of SQUIDs (superconducting quantum interference devices) which are used to detect the very small magnetic fields generated by currents in the heart and brain, hence they can be used to locate the positions of tumors in organs (Fig. 22). SQUIDs have also been used to capture exotic particles, such as dark matter.

16.4 Electrical transmission

The lack of electrical resistance means that superconductivity has applications in power transmission. Several companies have made cables out of high-temperature superconductors that can carry currents of 3000 amperes without any losses. Similar resistance-free cables are used in electrical circuits in computers and radio telescopes (Fig. 23).

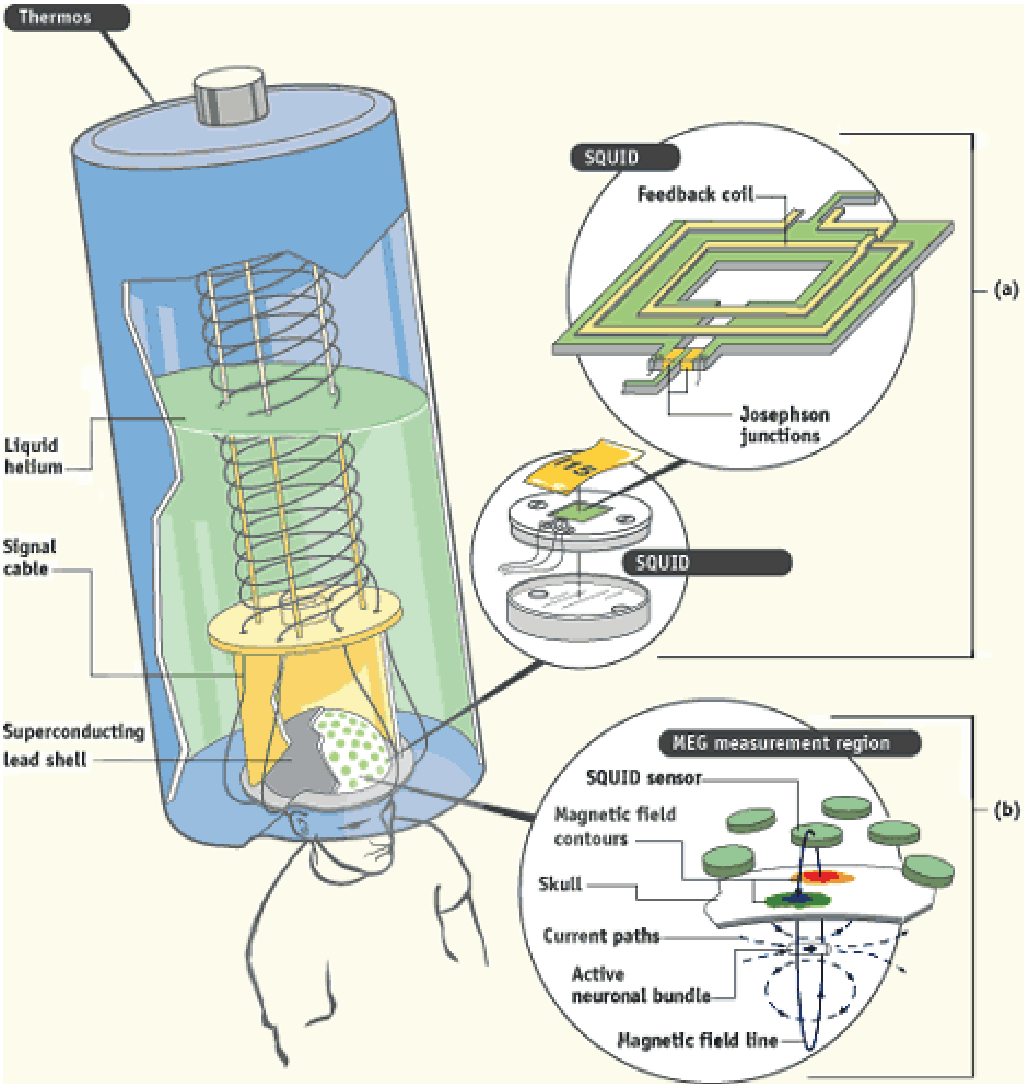

Figure 22. SQUID (http://www.lanl.gov).

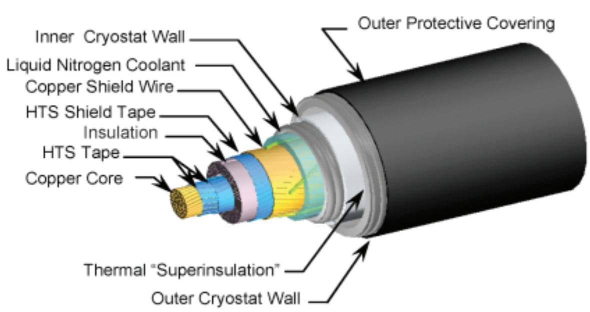

Figure 23. Superconducting wire (http://energy.gov/sites/prod/files/oeprod/DocumentsandMedia/LIPA__5_16_08.pdf).

16.5 Magnetic Resonance Imaging (MRI)

Applications of superconducting magnets in magnetic resonance MRI are tantalizing, because MRI is the best way to see inside the body without invasive surgery (Fig. 24).

Presently MRI is used to examine the body's soft tissues and is valuable for detecting tumors and revealing disorders in joints, muscles and blood vessels. It shows the water content of tissue, which is altered by diseases inside the body.

In an MRI scanner, a superconducting magnet provides the magnetic field that starts the hydrogen nuclei in water molecules precessing. Then a second electromagnetic field, whose frequency is tuned to match the precession frequency is applied. When this happens, the nuclei absorb energy, allowing a doctor to work out how much water is present and where.

To produce high-resolution images, a MRI machine requires a field of between 1 and 3 tesla, and the magnet must be large enough for a person to slide inside its bore.

There are now many variants of MRI, including functional MRI (fMRI) that monitors blood flow in the brain in response to particular drugs.

Superconductors have therefore given several million patients each year a much better medical diagnosis.

As important as these achievements are, their promise for future technology may be even greater. Looking back after the discovery of superconductivity, what have we learned? One lesson is that the time from the discovery to significant applications was very long. It looks almost 50 years to know how to make superconductivity magnet and about 25 years to develop the magnetic resonance imaging technique. The long timescale is due to the fact that to get the correct concepts and appropriate technology for an application is very difficult.

Yet superconductivity still hides many surprises despite its discovery 105 years ago. In 2008, iron the iron-based superconductors were discovered unexpectedly (Kamihara *et al*., 2008) and this highlights how little we have learned and how much more we have to know.

Figure 24. MRI machine (http://mnc.umd.edu).

17. Superconducting milestones

Finding materials that exhibit zero resistance at increasingly higher temperatures has been a persistent and continuing goal of condensed matter physicists since superconductivity was discovered in 1911.

1911, Hg mercury was found to be the first superconductor by Heike Kamerlingh Onnes at 4.2 kelvins.

1971, Nb_3Ge niobium germanium alloy was found to be superconducting at 23 kelvins, this material held the record for highest transition temperature from 1971 to 1986.

1986, $La_{2-x}Sr_xCuO$ the first recognized copper oxide with superconducting properties at 35 kelvins, and this ceramic material was the first that could be cooled with liquid nitrogen at 77 kelvins.

1987, $YBa_2Cu_3O_{6.95}$ yttrium copper oxide superconductor was found to operate at 92 kelvins.

1991 C_{60} solid crystals made of buckyballs superconducted at 33 kelvins when doped with alkali metal atoms such as potassium, rubidium and cesium.

1995, $Hg\,Ba_2\,Ca_2\,Cu_3\,O_8$ thallium doped mercuric cuprate recorded the highest temperature for any superconductor at 138 kelvins at atmospheric pressure. At high pressure it superconducts at up to 164 kelvins.

2001, MgB_2 magnesium diboride superconducts at up to 39 kelvins.

2008, Sm Fe As O recorded as having highest critical temperature for iron-based superconductor, at 56 kelvins.

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