Story of Superconductivity

A Serendipitous Discovery

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Electricity is carried through metallic wires, called conductors. In the process, electrons move through metallic conductors that offer resistance (the value depends on the particular metal used), to the passage of electrons. This leads to the production of heat and loss of energy. This heating process is utilised in many electrical devices. However, for transmission of electrical energy from the power plants to the user and in many other applications, it would be a great boon if no energy was lost to resistance. The discovery of superconductivity by Heike Kamerlingh Onnes in 1911 at Leiden, offered a glimmer of hope to make this dream possible. It was a discovery totally unexpected at that time, and we owe this discovery to the painstaking and methodical investigations of Onnes – first to produce very low temperatures, and then measure properties of materials at these freezing temperatures.

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The story of the discovery of superconductivity is intertwined with the liquefaction of helium by Kamerlingh Onnes in 1908 that made his laboratory the coldest place on Earth to conduct experiments. It would not be out of place to briefly recount the story of his success in liquefying helium.

The element helium was identified by French astronomer Pierre Jules Cesar Janssen in the spectral lines of Sun‘s chromosphere on August 1868 while observing a solar eclipse in Guntoor, India. The English astronomer Joseph Norman Lockyer observed the same spectra in October 1868 and proposed the name ‘helium’ after the Sun (Helios). On the Earth, Sir William Ramsay found helium after treating cleveite, a uranium mineral from Norway with mineral acids in 1895.

Keywords
Superconductivity, superconductors, electrical resistance, liquefaction of helium, high field magnets, cryostats.

Box 1. Liquid Helium

Helium liquefies at the lowest temperature of all gases. Its inversion temperature itself is ~ 51 K . Its boiling point is 4.2 K at 1 atmosphere, lowest of all gases. Its latent heat of boiling is also quite small ~ 20 J/g. Hence helium has to be pre-cooled before Joule-Thomson expansion for cooling the gas can take effect. Kamerlingh Onnes pre-cooled helium to this low temperature using liquid hydrogen.

Ramsay sent the sample to Norman Lockyer who was thrilled to confirm it spectroscopically. Ramsay also extracted helium from the mineral thoronite received from India and Ceylon.

Kamerlingh Onnes started working on reaching low temperatures. He made liquefaction of helium (*Box* 1), the only permanent gas that remained to be liquefied, his goal when he joined the Leiden University. He built from scratch a cryogenic laboratory and established a school for instrument makers at the University in 1901. He built an oxygen liquefier by 1894 and succeeded in building a hydrogen liquefier after a protracted three-year long bureaucratic struggle to get a license for handling and storing hydrogen from the Leiden city council, in 1906. He was now ready to take on the challenge of building a helium liquefier. His liquefier machine was ready in the beginning of 1908. But helium was not available in large quantities at that time, and he began with small amounts sent to him by William Ramsay. With the help of his brother Onno, who was then Director of the Office of Commercial Intelligence in Amsterdam, he procured large quantities of monazite sand from USA and could extract about 360 litres of helium gas from it through a laborious process. Onnes finally succeeded in liquefying helium on 10th July 1908. It was the culmination of a heroic effort with painstaking attention to the details and the development of all the required technical skills in his laboratory. He had worked for more than 25 years from the time of his appointment to the Chair in Physics with his colleagues and students to achieve this result.

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Kamerlingh Onnes immediately set about systematically measuring the properties of matter at liquid helium temperature – a temperature that he alone in the world could then access. He concentrated first on the measurement of conductivity of pure metals as he was looking for a good thermometer material! He was using helium gas thermometers all the while and looked for a suitable metal with linear variation of resistance at low temperatures. But certainly, Onnes' interest in metallic resistance at low temperatures was much deeper. He had a long interest to understand the mechanism of variation of resistance at very low temperatures.

With lowering of temperature, the thermal agitations would decrease, thus reducing the scattering, and the resistance would keep falling down to zero as the absolute zero was approached.

The prevailing theories of electrical conductivity of metals during that period had different predictions for lowered temperatures. It was accepted that conduction of electricity was due to the flow of free conduction electrons in metals under the influence of an electric field, and resistance arose due to the scattering of electrons from the metal ions. With lowering of temperature, the thermal agitations would decrease, thus reducing the scattering, and the resistance would keep falling down to zero as the absolute zero was approached. However, according to Lord Kelvin, in addition to the lowering of resistance due to reduction of scattering at very low temperatures, the resistance would increase due to the decrease in free electron density (free electrons were assumed to be frozen around the ions at zero temperature).

The attention to details and the level of perfection that Onnes brought to his work is evident in the way he went on to build his equipment for these measurements. Since the cryostat in the liquefier itself lacked adequate space to house a platinum resistor, a separate cryostat totally made of glass was built (*Box* 2). It was ready for operation on 12th March 1910 as noted down in Onnes' notebook [1]. It describes the first attempt to transfer helium to a cryostat with a double-walled container and a smaller container connected with it which could be pumped using a series of vacuum pumps. He planned to transfer the liquid to the new cryostat and then reduce the pressure in the cryostat so that the vapour also condensed and pump further to a much lower pressure of 0.1 mm of Hg. The pumps worked well and a new low-temperature record of about 1.1 K was reached. In the next experiment, four months later, resistance of the platinum resistor that had previously been

Box 2. Cryostat

Cryostat is a container to hold a cold object so that its low temperature can be maintained over a long period of time. It is designed to reduce the influx of heat from the outside to the inside of the cryostat. There are three ways heat propagates, *viz.*, conduction, convection, and radiation. In a cryostat, care is taken to minimise all these three contributions to heat transfer. The material chosen for the container and all the support structures has low conductivity. The container is evacuated to eliminate the contribution of convection, and the radiation loss is minimised by the use of surfaces with low emissivity and also providing thermal shields at intermediate temperatures between outside and the cold surface. For example, if a surface at liquid helium temperature is exposed directly, in line of sight to a surface at room temperature ($\sim$ 300 K), the radiation heat transfer to the cold surface, Qr $\propto$ (300^4–4^4). Now if we insert a surface cooled at liquid nitrogen temperature (77 K), between the surface at liquid helium temperature and that at room temperature, then the radiation load, Qr $\propto$ (77^4–4^4) and is lower by about a factor of 16.

James Dewar invented the vacuum-insulated, silver-plated glass Dewar flask in 1892. This can be considered to be the first cryostat built in the world.

calibrated down to 14 K was to be measured. But the extra heat capacity of the resistor caused violent boiling of the small amounts of liquid helium that could be transferred using the existing transfer tubes and the experiment had to be abandoned.

So a completely new liquid helium transfer system to take care of the initial cooling of the resistor was designed. Since this design was taking a long time to implement, Onnes decided in the meanwhile to expand the original liquefier so that it could house a platinum resistor and continue the measurements at lower temperatures. On 2nd December 1910, he made the first measurement of R(T) for a metal at liquid helium temperatures. Cornelius Dorst, and Gerrit Jan Flim assisted Onnes with the measurements. Gilles Holst made the resistance measurements using a Wheatstone bridge and a mirror galvanometer [1]. The resistance measurement set-up was kept in a room far away from the liquefier, to prevent the large vibrations induced by the big pumps used in the liquefier.

Onnes correctly attributed the additional contribution to resistance to the impurities in the metals. So he looked for a metal that he could get in a purer form.

The resistance of a platinum wire became constant below 4.25 K, contrary to that predicted by Kelvin. The same behaviour was observed in the case of a gold wire. He found that by taking a specimen of gold with lower levels of impurity resulted in a lower value of resistance at these low temperatures. Onnes correctly attributed the additional contribution to resistance to the impurities in the metals. So he looked for a metal that he could get in a purer form. The choice fell on mercury (Hg) as it could be made in purest form in his laboratory. His assistant Gilles Holst had already perfected the art of purifying Hg. Hg would solidify at about −39°C (234 K) and would take the shape of a wire in capillary tubes.

Mercury practically zero!

The new cryostat took nine months to build and was ready in the beginning of April 1911 for its first cool-down. It was a marvel of glass blowing skills of Onnes' laboratory evident from its complexity in *Figure* 1, (the bottom part of the cryostat is shown). It had 7 capillary U-tubes filled with pure Hg with Pt feedthroughs[1]

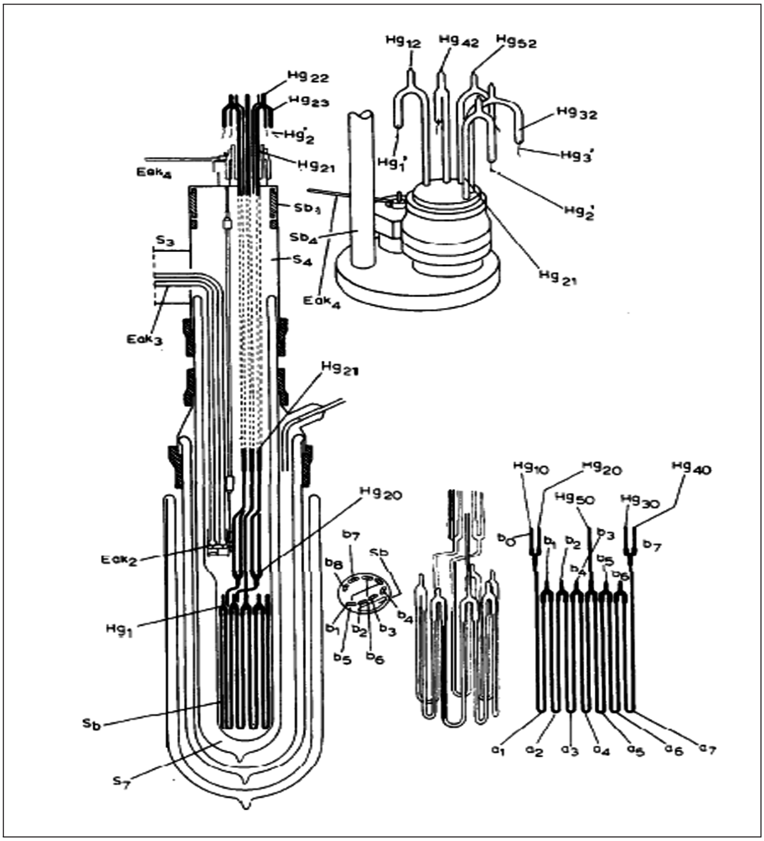

Figure 1. Bottom part of the cryostat in which resistance of Hg was determined. Reprinted with permission from [2] © The Nobel Foundation (1913).

and thin copper wires forming the connecting leads. A Wheatstone bridge and a mirror galvanometer were used for measuring the resistance. Small bulbs with Hg were attached to the top of the tubes, so that during freezing of Hg, there would be no discontinuity in the Hg wire in the capillary tubes. The transfer tube was a double walled glass tube with the annular region pumped to maintain vacuum and was cooled by liquid air circulating through a copper capillary coil wrapped around the outer tube. A stirrer connected to a magnet was provided so that a well defined temperature could be established inside the cryostat during the measurement.

[1] A conducting wire, vacuum sealed inside glass or ceramic insulators to carry current inside a vacuum chamber from outside.

The crucial experiment was performed on 8th April 1911 [1], when Onnes decided to transfer liquid He to the new cryostat. His assistants started the experiment at 7:00 AM, and it took almost the whole day for cooling the cryostat to about 5 K before liquid helium started to collect in the cryostat. Half an hour later, enough helium was collected so that the function of the stirrer could be checked. They made sure that liquid helium itself did not conduct electricity and determined its dielectric constant. Holst made precise measurement of resistance of Hg and gold (Au) and the temperature was measured by Dorsman.

The team then started to reduce the vapour pressure of helium, and it began to evaporate rapidly. They measured its specific heat and stopped at a vapour pressure of 197 mm Hg (0.26 atmospheres), corresponding to about 3 K. The resistances of the Hg and Au were determined again and exactly at 4:00 PM, Onnes noted in his book the historic entry – *Kwik nagenoeg nul* – in Dutch, meaning *mercury practically zero* [1]. Mercury was not offering any resistance to the passage of electrical current. It was such a surprising observation that the measurements were repeated with Au again to check that the system was behaving normally and there were no electrical shorts. The results obtained are shown in *Figure* 2 [2]. Measurements were continued at lower temperatures, and at the end of the day another curious phenomenon was observed. Dorsman, found the temperature surprisingly hard to control near the end of their experiment. They

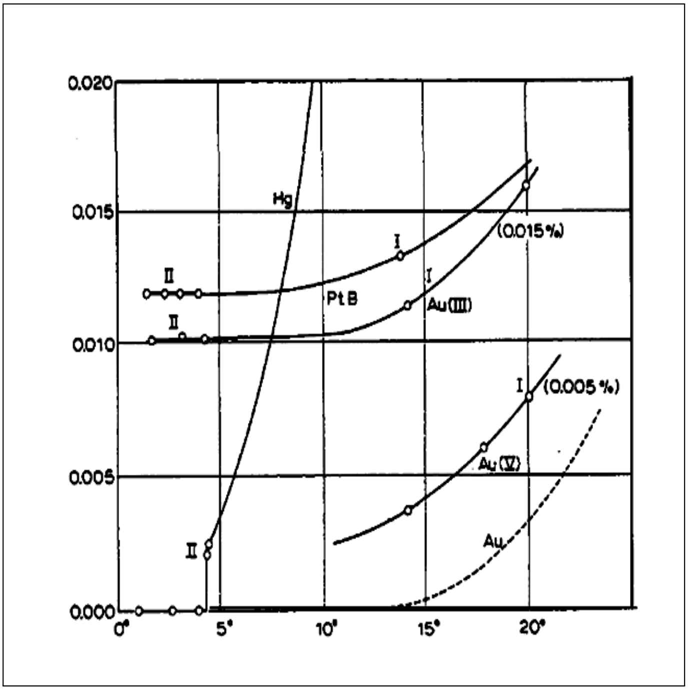

Figure 2. Data taken on 8 April, 1911. Reprinted with permission from [2]. © The Nobel Foundation (1913).

observed that just before the lowest temperature [about 1.8 K] was reached, the boiling suddenly stopped and was replaced by strong evaporation in which the liquid level shrank rapidly [1]. They did not pursue this aspect of the observation further. They had probably witnessed the phenomenon of 'superfluidity', but its significance eluded them.

Later measurements of resistance were performed on 23 May 1911 and 26 October 1911 [1] with improved voltage resolution of the system. Onnes wanted to find out how quickly the resistance changed with temperature near the transition. The team first measured resistance starting from 4.3 K down to 3.0 K and then went back up to higher temperatures. The increase of temperature could be done much slower than the decrease, and hence the temperature could be controlled more precisely. While increasing the temperature, they found that at 4.00 and 4.05 K, there was no rise but at 4.12 K, resistance begins to appear abruptly, and within 0.01 K the resistance jumps from less than 106 Ω to 0.1 Ω. The historic plot shown in *Figure* 3 (this is shown in most

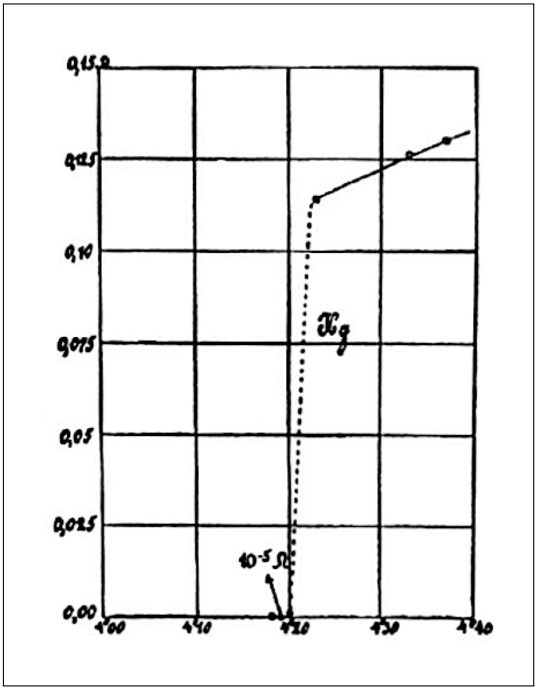

Figure 3. Graph showing the superconducting transition of Hg from [5]. © Huygens ING (KNAW) 2008–2012 under Creative Commons Licence, CC BY 2.0

text books), is from the data taken from this experiment and reported in the *Proceedings of Royal Netherlands Academy of Arts and Sciences* (KNAW), November 1911 [3]. Kammelingh Onnes called the phenomenon 'Supraconductivity'.

Onnes later took mercury that contained impurities like gold, cadmium or amalgam, and found that these were also superconducting so that it was not necessary to have pure mercury. Later trying other materials, they found that tin and lead also behaved as superconductors below temperatures of 3.7 K and 7.2 K, respectively.

The vanishing of resistance of the superconductors led Onnes to the thought of large magnetic fields using these materials, which could be used to 'destroy the atom by force' and hence increase our knowledge of matter.

Heike Kamerlingh Onnes received the Nobel Prize in 1913 "for his investigations on the properties of matter at low temperatures which led, inter alia, to the production of liquid helium". The vanishing of resistance of the superconductors led Onnes to the thought of large magnetic fields using these materials, which could be used to 'destroy the atom by force' and hence increase our knowledge of matter. During his visit to USA, while lecturing at the Third International Congress of Refrigeration at Chiacgo in September 1913, Kamerlingh Onnes had said, "the solution of the problem of obtaining a field of 100,000 Gauss could then be obtained by a coil of say 30 cm in diameter and the cooling with a plant which could be realized in Leiden with a relatively modest financial support."

Figure 4. The world's first superconducting magnet, consisting of a wire coil made of lead, was manufactured in the Leiden (The Netherlands) Physics Laboratory in 1912. Reprinted with permission from [6].

The world's first superconducting magnet, consisting of a wire coil made of lead, was manufactured in the Leiden (The Netherlands) Physics Laboratory in 1912, and is shown in *Figure* 4 [4].

But Onnes was disappointed that the coil lost its superconducting property as the magnetic field was increased to the modest value of 600 Gauss at 4.2 K. In his Nobel lecture [2], Onnes acknowledged this saying, "thus an unexpected difficulty in the production of magnetic field with coils without iron faced us. The discovery of the strange property which causes this made up for the difficulties involved."

The discovery of superconductivity spurred research in many laboratories in the world as low temperatures were made available to them. Further understanding of superconductivity came with the discovery by Meissner and Ochsenfeld in 1933 [5], that magnetic flux was totally excluded from superconductors making them perfect diamagnets in addition to being perfect conductors (*Box* 3). Efforts to generate large magnetic fields with superconductors had to wait for the discovery of type II superconductors by Lev Shubnikov at Kharkov, Ukraine, in 1937 [6], which had two critical magnetic fields (*Box* 4). He found that in some alloys, the magnetic field was expelled from the bulk up to a lower critical value beyond which the magnetic field could penetrate the material without loss of superconductivity till the higher critical field was reached.

Magnetic flux is totally excluded from superconductors making them perfect diamagnets in addition to being perfect conductors.

Many stalwarts worked to find the theory of superconductivity including Einstein, Bloch, Pauli, Landau, Bohr, Heisenberg, Brillouin, and Feynman without success. Finally, John Bardeen, Leon Cooper, and Robert Schrieffer were able to explain superconductivity in 1957 [7], a full 46 years after the phenomenon was dis-

Box 3. Meissner Effect

As a superconductor is cooled through its critical temperature, it expels totally the magnetic flux from its interior. This property was discovered by Walther Meissner and Robert Ochsenfeld working at Berlin in 1933 [5], who measured the field outside two cylindrical single crystals of tin as they were cooled in a magnetic field. The effect was completely reversible, showing that superconductivity is an equilibrium thermodynamic state which does not depend on the history of the superconductor. The brothers Fritz and Heinz London, working in Oxford, wrote down the equation bearing their name to describe how the electrons respond to magnet field in a cooperative way, screening the interior of the sample such that the magnetic field inside is always zero. However, the magnetic field penetrates at the surface of the superconductor decaying over a short distance, known as the London penetration depth.

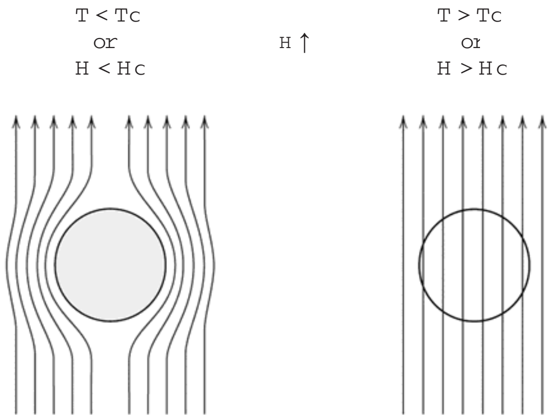

Figure A(a) (left). Magnetic lines of flux avoiding the superconductor.
Figure A(b) (right). Magnetic flux lines penetrating the material in its non-superconducting state.

covered. It led to the Nobel Prize in 1972 for Bardeen (second Nobel in Physics), Cooper, and Schrieffer. The successful theory incorporating thermodynamic basis of superconductivity was worked out by Ginzburg, Landau, Abrikosov, and Gorkov.

High magnetic fields became accessible only using type II superconductors. The alloy Nb_3Sn was discovered by B Matthias at Bell Laboratories to have a critical temperature of 18.6 K [8] and NbTi was discovered by J Hulm and R Blaugher at Westinghouse laboratory with a T_c of 11 K [9]. With these alloys, the dream of

Box 4. Type I and Type II Superconductors

There are two basic types of superconductors, aptly termed type I and type II superconductors. Type I superconductors are usually metals (e.g., Hg, Sn, Pb, Nb) and are known as ‘soft’ superconductors since their transition temperatures are much lower than those of type II. Type I superconductors (*Figure* B(a)) show perfect diamagnetism below their critical magnetic field. When a magnetic field greater than the threshold is applied to a type I superconductor, its superconducting state ceases abruptly.

Type II superconductors are usually referred to as ‘hard’ superconductors. They are composed of metallic alloys (e.g., NbTi, Nb_3Sn, V_3Ga), metal oxides and ceramics (e.g., $YbBa_2Cu_3O_7$, BiSrCaCuO). Type II superconductors (*Figure* B(b)) have higher critical temperature than the type I superconductors. They show perfect diamagnetism till a lower critical magnetic field and maintain the superconducting properties in the presence of higher magnetic fields till a higher critical value is reached.

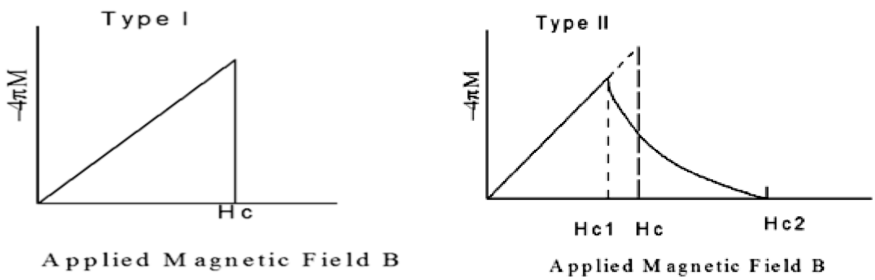

Figure B(a) (left).
Figure B(b) (right).

reaching Onnes’ dream of magnetic fields greater than 10 Tesla could be achieved. Today, most of the high field magnets in use employ these two alloys of Nb, while other alloys are also being explored. Large scale applications of superconductivity happen in particle accelerators in the form of magnets and superconducting radio frequency cavity resonators. High field magnets are used in Magnetic Resonance Imaging (MRI) for medical diagnostics and recently Superconducting QUantum Interference Device (SQUID) arrays are being employed for brain mapping.

There has been a constant search for materials that would be superconducting at higher and higher temperatures and in 1986, Georg Bednorz and Alex K Mueller of IBM Zurich Research Laboratory discovered a lanthanum-based material that became superconducting at 35 K [10], which was then a record high temperature. In 1987, Paul Chu of the University of Houston substituted yttrium in Bednorz and Mueller's compound and produced yttrium-barium-copper-oxide with a transition temperature of 92 K [11]. This was a big breakthrough as liquid helium was no longer necessary to cool the superconductors, and liquid nitrogen would suffice for these high temperature superconductors (HTS), making them much cheaper. Efforts are now on to find materials which become superconductor at higher temperatures with the goal of finding a room temperature superconductor. Already, HTS materials are being increasingly employed in different applications in the form of filters for cell phone stations, connecting of power lines to networks, etc.

Kamerlingh Onnes dream of destroying atoms by the force of magnets has not been realised, but large accelerators employing giant superconducting magnets are providing ever increasing details of innermost constituents of matter. The discovery of superconductivity exemplifies the dictum of Louis Pasteur – "Chance favours the prepared mind".

Suggested Reading

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[2] **Heike Kamerlingh Onnes – Nobel Lecture: *Investigations into the Properties of Substances at Low Temperatures, Which Have Led, amongst Other Things, to the Preparation of Liquid Helium*, Nobelprize.org. Nobel Media AB 2014. ¡http://www.nobelprize.org/nobel_prizes/physics/laureates/1913/onnes-lecture.html¿.**

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