

# 100 Years of Superconductivity

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This booklet has been published on the occasion of the symposium '100 Years of Superconductivity' on 8 April 2011 in Leiden, the Netherlands.

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Cover: charcoal drawing of Heike Kamerlingh Onnes, made by his brother Menso, 1909 (private collection)



Floating magnet above a superconductor: the Meissner effect

**O**n 8 April 2011 a symposium was organized in Leiden to commemorate the 100th anniversary of the discovery of superconductivity at the University of Leiden by Prof. Heike Kamerlingh Onnes and his colleagues, Cornelis Dorsman, Gerrit Jan Flim, and Gilles Holst. The most striking characteristic of a superconductor is that its electrical resistance is 'practically zero' (to quote Kamerlingh Onnes's notebook) at temperatures below some critical temperature, known as the superconducting transition temperature, which is unique for each superconductor.

To celebrate '100 Years of Superconductivity' the Institute of Electrical and Electronic Engineers has designated the discovery as an IEEE Milestone. The IEEE Milestones in Electrical Engineering and Computing program, established in 1983, recognizes technical achievements in these areas of science and technology. The Superconductivity Milestone is the 110th Milestone designated to date. Some of the Milestones previously approved by the IEEE include Maxwell's Equations, Alexander Graham Bell's Voice transmission over electric wire, the Invention of the Transistor at Bell Laboratories, the First Working Laser and the Birthplace of the Internet.

The discovery of the phenomena of superconductivity at the University of Leiden, by Prof. Kamerlingh Onnes and his colleagues in 1911, was a totally unexpected result, which opened a completely new area of research in the science and technology of electrical conduction in materials and in the development of energy efficient and high performance electrical and electronic devices and systems. During the 100 years since its discovery, the phenomena of superconductivity was observed in more than 10,000 elements, compounds and alloys, but, in all instances, the phenomena has only been observed at temperatures well below room temperature. The highest known superconducting transition temperature found to date is about 170 K (about -100°C).

During the first 50 years after the discovery of superconductivity most of the research effort was directed at identifying and investigating the very unique and exotic electric and magnetic behavior of superconductors and looking for materials with ever increasing transition temperatures, the temperature below which the 'zero' resistance characteristics was observed.

However, during the second 50 years, the emphasis has been focused on trying to exploit these very unique properties of the superconducting state in making devices and systems that can have a positive effect on society. Superconducting magnets have been the enabling technology for a number of medical diagnostic applications, such as Magnetic Resonance Imaging (MRI), for which more than 25,000 systems are currently in operation worldwide. Superconducting magnets operating at temperatures near 1.8 K are the enabling technology for most of the recent and future High Energy Physics particle accelerators such as the Large Hadron Collider at CERN (Geneva, Switzerland), which uses about 2,000 superconducting dipole and quadrupole magnets to bend and focus the beam of energetic particles and an additional 6,000 superconducting magnets for other beam correcting functions in the Collider. Superconducting materials are also currently under evaluation for improving the efficiency of electric power grids by enabling improved low loss power transmission, power transformation and fault current limiting, etc. and for use in the construction of energy efficient motors and generators.

For electronic applications of superconductivity, Josephson Junction devices are used in the internationally accepted voltage standard and in ultra sensitive magnetometers which have been used in geophysical exploration and in non-contacting, non-invasive magnetocardiography, magnetoencephalography, localization of focal epilepsy, cognitive neuroscience studies, etc. Furthermore, Josephson junction technology has the potential to provide digital logic chips with clock frequencies at least an order of magnitude faster than possible with current or projected semiconductor technology.

Thus a scientific study of the electrical behavior of pure metals at low temperatures by Prof. H. Kamerlingh Onnes and his colleagues, which lead to the discovery of the phenomena of superconductivity on 8 April 1911, has resulted in the developing of very energy-efficient electrical and electronic technologies which are beginning to play a role in improving the health and well being of society and which have the potential to play an ever increasing role in the future.

**Dr. Martin Nisenoff**

IEEE COUNCIL ON SUPERCONDUCTIVITY

# HEIKE KAMERLINGH ONNES AND THE ROAD TO LIQUID HELIUM

In 1908, Heike Kamerlingh Onnes first liquefied helium in a cryogenic laboratory whose excellence and scale were unparalleled. Creating, staffing and running the Leiden laboratory required more than just scientific skill.

On 10 July 1908, Heike Kamerlingh Onnes (1853-1926) liquified helium for the first time, briefly rendering his Dutch laboratory ‘the coldest spot on earth’. This paper tells the story of Leiden University’s famed cryogenics laboratory and the man behind it, whose scientific accomplishments earned him the Nobel Prize in Physics in 1913. The central question is how Kamerlingh Onnes was able to succeed so brilliantly in developing his cryogenics laboratory – undoubtedly an exceptional feat in terms of its scale and its almost industrial approach at the turn of the century. Key factors in his success were Kamerlingh Onnes’s organisational talent, his personality and his international orientation. The liquefaction of helium opened up unexplored territories of extreme cold and cleared the path for the eventual discovery of superconductivity on 8 April 1911.

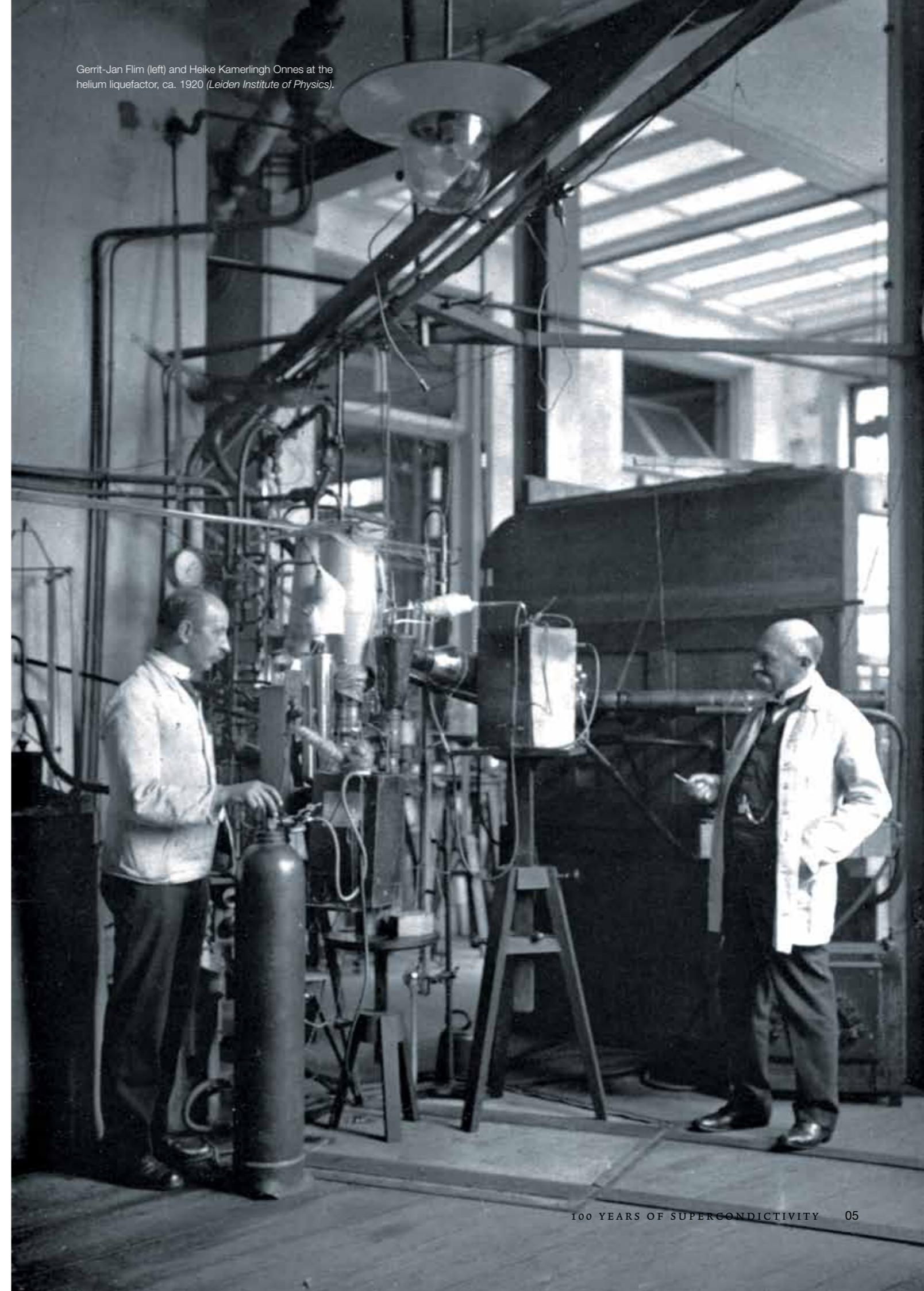
Heike Kamerlingh Onnes was born in the city of Groningen in 1853 [1]. His father owned a tile factory in a small village, a two hour drive on horseback. Heike studied at the University of Groningen. At the age of 17 he started studying chemistry, his favourite topic at high school. After passing his propædeutic exam he moved to Heidelberg, then famous for its international academic environment, for a *Wanderjahr* (year of travel). Why Heidelberg? Because of Robert Bunsen, in those days the most famous chemist in Europe. In his first semester, Heike enjoyed the chemistry lab very much. But when the time came to start some own research, Bunsen’s conservatism and aversion to mathematics got Heike to switch to the physics department, led by Gustav Kirchhoff. Important for Heike was that Kirchhoff was a modern physicist, in the sense that he propagated the

fruitful exchange between theory and experiment.

**MISSION**

When Kamerlingh Onnes started as a professor in experimental physics in Leiden in 1882, he immediately decided to transform the building into a research laboratory. Why this considerable effort? Because of his scientific mission: to test the molecular laws of Johannes Diderik van der Waals and in doing so to give international prestige to Dutch physics. Van der Waals had published his thesis on the continuity of the liquid and gas phase in 1873, a milestone in molecular physics – notice that molecules were not yet generally accepted in those days [2]. As a student in Groningen, Kamerlingh Onnes had been attracted to Van der Waals’ results and to the kinetic theory of Clausius, Maxwell and Boltzmann.

Gerit-Jan Flim (left) and Heike Kamerlingh Onnes at the helium liquefactor, ca. 1920 (Leiden Institute of Physics).



The Van der Waals equation of state posits the existence of a critical temperature for each gas. Above the critical temperature, condensation of the gas is impossible, even at the highest pressures. To verify Van der Waals' theories it was obviously best to start by using simple substances (and mixtures), which had low critical temperatures. Monatomic inert gases would have been ideal, but these did not become available until the 1890s, when Ramsay discovered them. So Kamerlingh Onnes started by using diatomic substances such as oxygen, hydrogen and nitrogen, as well as carbon dioxide ( $\text{CO}_2$ )

and methyl chloride ( $\text{CH}_3\text{Cl}$ ). The first few had critical temperatures far lower than  $0^\circ\text{C}$ , so there was no alternative but to create a cryogenic laboratory. This undertaking consumed almost all Kamerlingh Onnes's energy in the first few years of his professorship. A major piece of apparatus in Kamerlingh Onnes's cryogenic laboratory was the Cailletet vacuum pump, acquired in 1884 and transformed radically to suit Leiden's needs. The problem was that industrial standards were not good enough for scientific use. So Kamerlingh Onnes and his technicians spent lots of time dismantling the

pumps, improving parts, even changing essential structural components. During the first ten years of his professorship Kamerlingh Onnes did not publish a single article. All the time he was busy with the construction of his cryogenic installations. Kamerlingh Onnes lived in a world of grease, oil and fat. Nowadays, in the publish-or-perish era, a protracted preamble to a career such as that of Kamerlingh Onnes would be tantamount to academic suicide.

The liquid oxygen unit was completed in 1894. It consisted of a cascade. Each cycle was a refrigerator with a closed loop consisting of a compressor, an expansion tank and pumps. The end temperature of the first cycle was the starting point for the second one, et cetera. In the first cycle chloromethane was used, the second one consisted of ethylene and the third one had oxygen. In 1892 the Leiden cascade produced its first drops of liquid oxygen.

#### BIG SCIENCE

Heike's entrepreneurial abilities proved invaluable. Building up a cryogenic laboratory of international status, of a size and personnel unequalled anywhere in the world, called for more than a great talent for physics. Anyone who entered the Physics Laboratory, especially lab E and the surrounding area, and beheld the profusion of tubes, taps, gas flasks, gas holders, liquefiers, Dewar flasks, cryostats, clattering pumps and droning engines, glass-blowing and other workshops, instruments and appliances for scientific research, would have felt as if he had come to a factory. It was indeed a 'cold factory', with Professor Kamerlingh Onnes as its director, determining policy and exercising tight overall control. As the director of an enterprise, he also set up a well-oiled organisation presided over by an administrative supervisor, a research team including assistants and post-graduate students, a manager, instru-

Trainee instrument-makers ('blue-collar boys') at work in the garden of the Leiden Physics Laboratory (Leiden Institute of Physics).



ment-makers, glass-blowers, laboratory assistants, technicians, an engineer, an assistant supervisor, not to mention a small army of trainee instrument-makers to perform any number of odd jobs. Heike's project was Big Science.

In 1894, when the Leiden cascade produced liquid oxygen very efficiently and was described by Nature as an 'extremely high performance apparatus' and as a 'model cryogenic laboratory', there was only one so-called 'permanent gas' to go: hydrogen (helium still had to be discovered on earth). But the cascade method was inadequate for the purposes of obtaining static liquid hydrogen - 'static' meaning gently boiling in a Dewar flask. With pumped-out liquid oxygen,  $54\text{ K}$  could be attained - any lower and the oxygen would freeze. Since the critical temperature of hydrogen was  $33\text{ K}$ , a gap of over  $20^\circ$  had to be bridged before any liquid hydrogen could start to form. This gap was bridged by the Joule-Thomson effect. When a gas is passing through a tube and encounters a porous plug, behind which it expands, there is a small temperature effect.

The race for liquid hydrogen was still undecided in 1895. Kamerlingh Onnes had developed ideas about building a hydrogen liquefier, but the problem was he could not get started. The Leiden Physics Laboratory was built on the very spot where in 1807 a gunpowder ship had exploded, with devastating effect. On 19 January 1895 Kamerlingh Onnes received a letter from the Leiden municipality that proved to be the opening move in a long drawn-out sparring match with the authorities.

The neighbourhood had been alerted about 'explosive substances' used by the physics professor and they wanted the laboratory moved out of town before another disaster could happen. Kamerlingh Onnes had to apply for a licence and to shut down his cryogenic laboratory for the time being. It was



Heike Kamerlingh Onnes, painted by his nephew Harm in 1920 (private collection).

only after a three-year struggle with the authorities that he was able to resume his cryogenic work.

At that time the race to liquefy hydrogen had just produced a winner: James Dewar. The British scientist had read out his 'Preliminary Note on the Liquefaction of Hydrogen and Helium' at the regular meeting of the Royal Society in London. Dewar said he had collected 20 cc of liquid hydrogen in a double-walled insulated glass flask in the basement laboratory of the Royal Institution in London. The liquid was clear and colourless and had a relatively high refractive index. Dewar had hoped to collect more, but after five minutes his unit had become clogged with freezing air in the pipes.

#### STRINGENT STANDARDS

The Leiden hydrogen liquefier was fully operational in 1906. It took this many years largely because Kamerlingh Onnes wanted his liquefier to meet stringent standards. Since Dewar's achievement in 1898, there was no point hastily assembling a piece of equipment that could produce a little

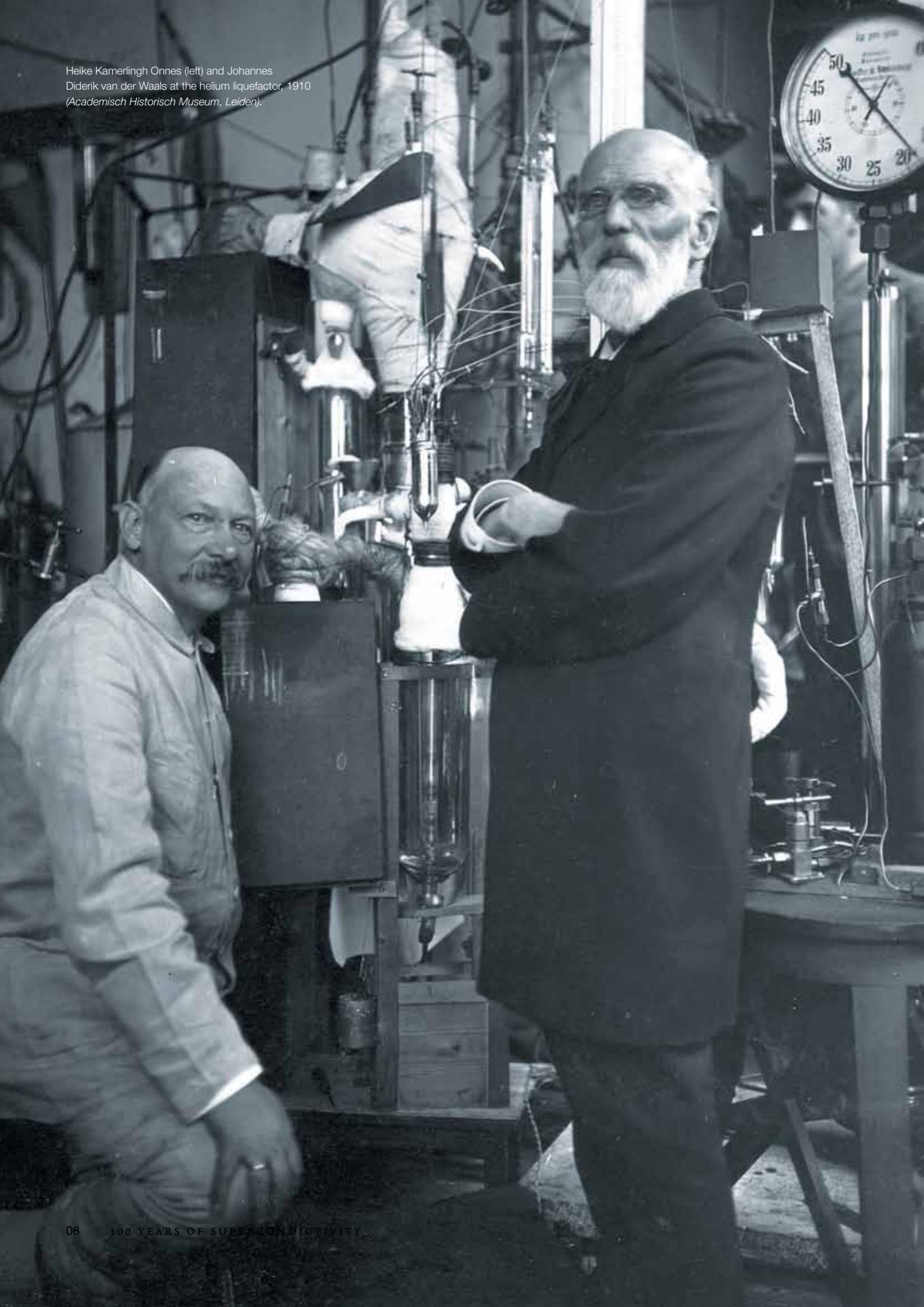
liquid hydrogen, and which would at best be useful for some small orientational experiments. Leiden had lost that race. What Kamerlingh Onnes wanted was a liquefier that produced several litres of liquid hydrogen per hour in a continuous process, with maximum economy. Van der Waals's law of corresponding states had told Kamerlingh Onnes how much liquid hydrogen he would need in his helium liquefier.

At that time, the race for liquid helium was still undecided. The biggest problem was collecting enough helium gas and purifying it. Kamerlingh Onnes first got some litres of gas from Ramsay, collected from wells. Later on his brother Onno mediated a shipment of tens of sacks of monazite sand, a mineral that contained helium (a product of radioactivity). Extracting the helium from the sand and purifying it constituted a mammoth task. Purification was extremely important because impurities like argon, neon or hydrogen froze in the cooling process and blocked pipes and valves.

On 10 July 1908, after a hard day's work in the Leiden cryogenic laboratory, the helium was liquefied. Early in the morning the work started with liquefying hydrogen. At half past one they had stored 20 litres in Dewar vessels. In the afternoon the helium gas started to circulate, being compressed by the Cailletet compressor to keep the gas pure. Kamerlingh Onnes had no time for lunch so his wife Betsy came along to feed him pieces of bread. A quote from Kamerlingh Onnes's report, 'The Liquefaction of Helium', to the Dutch Academy of Sciences:

'In the meantime the last bottle of the store of liquid hydrogen was connected to the apparatus: and still nothing had as yet been observed save for some slight wavering distortions of images near the cock. At first the thermometer even indicated an increase

Heike Kamerlingh Onnes (left) and Johannes Diderik van der Waals at the helium liquefactor, 1910 (Academisch Historisch Museum, Leiden).



in temperature with accelerated expansion from 100 atmospheres, which was an indication for us to lower the circulation pressure to 75 atmospheres. Nothing was observed in the helium space then either, but the thermometer began to be remarkably constant from this point on with an indication of less than 5 degrees Kelvin. [...]

It was, as Prof. Schreinemakers, who was present at this part of the experiment, observed, as if the thermometer was placed in a liquid. This proved genuinely the case. [...] The surface of the liquid was soon made clearly visible by reflection of light from below, and unmistakably so because it was clearly pierced by the two wires of the thermo-element. This was at 7.30 p.m. Once the surface had been seen, it remained in view. It stood out sharply defined like the edge of a knife against the glass wall. [...] At 9.40 only a few cm<sup>3</sup> of liquid helium were left. Then the work was stopped. Not only had the apparatus been strained to the uttermost during this experiment and its preparation, but the utmost had also been demanded from my assistants.' [3]

The temperature of the liquid helium – about 60 millilitres, a little teacup – was 4.2 Kelvin. By decreasing the pressure with a Burckhardt vacuum pump, the temperature was lowered to approximately 1.5 Kelvin, but helium refused to solidify. Decisive for Kamerlingh Onnes's success was his Big Science approach. Dewar struggled in the Royal Institution with impurities in his helium and had a shortage of liquid hydrogen. He lacked the technical support Kamerlingh Onnes had organised for himself and quarrelled with everybody. 'At the forefront of science assistants are a waste', Dewar once said. Kamerlingh Onnes proved him wrong. Leiden's cryogenic strength is clear from its long monopoly on liquid helium, which was not broken until 1923, by James McLennan in Toronto. Two years later, Walther Meissner in Berlin possessed the liquid too.

Heike Kamerlingh Onnes drove his



Flim, Kesselring and trainee instrument-makers at the helium liquefactor. Drawing by Harm Kamerlingh Onnes, ca. 1920 (Museum Boerhaave).

#### VISITORS

After the liquefaction of helium, the Leiden physics laboratory developed into an international facility for low temperature research. It attracted a lot of visitors and researchers from abroad. Kamerlingh Onnes was famous for his hospitality. Lots of great physicists – Albert Einstein, Marie Curie, Niels Bohr, Philip Lenard, William Ramsay, et cetera – stayed in his home 'Huizer Wetering', just outside Leiden and a meeting place for an artistic family that breathed a cosmopolitan atmosphere.

In 1913 Kamerlingh Onnes won the Nobel Prize for his low temperature work, resulting in the production of liquid helium. The Nobel committee did not mention the discovery two years earlier of superconductivity. Nevertheless, this enigmatic effect was the ultimate proof that the road to liquid helium had uncovered a landscape full of exciting physics.

people like the wind drove the clouds, said Pieter Zeeman, one of his students. The amazing thing is that a frail boy who missed a whole school year through illness when he was eleven (and sat at home reading Plutarch) and who was compelled to go to the Alps every summer for a health cure throughout his life, nonetheless possessed the energy and endurance to set up a large-scale enterprise such as his cryogenic laboratory and to make it such a great success.

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# Kamerlingh Onnes's Notebooks and the Discovery of Superconductivity

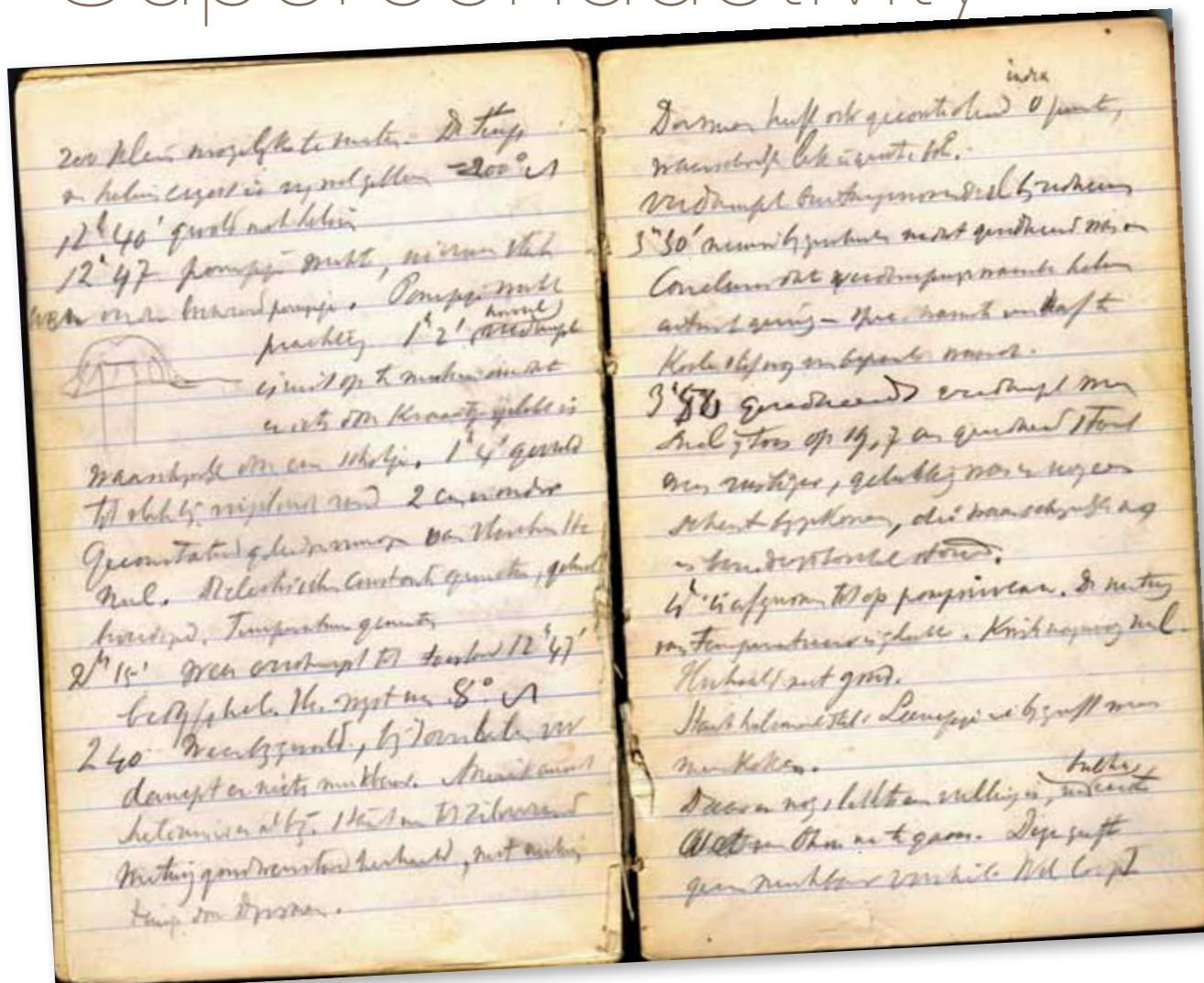


Fig.1. A crucial page from the entry for 8 April 1911 in Kamerlingh Onnes's notebook 56. On the 14th line the sentence *Kwik nagenoeg nul* means "Mercury [i's resistance is] practically zero [at 3.0K]" announcing the first observation of superconductivity. On the page left the sketch of the functioning stirrer is seen (Archive Museum Boerhaave, Leiden).

A century ago Heike Kamerlingh Onnes and his collaborators were the first to observe superconductivity. Although accidental, his retraced notebooks tell us today that this was the result of a well planned research program that was started after liquid helium temperatures were reached.

## LIQUID HELIUM TEMPERATURES

On 10 July 1908, in his laboratory at Leiden University, Heike Kamerlingh Onnes experienced the most glorious moment of his career. That day he first liquefied helium and thus opened an entirely new chapter in low temperature physics reaching temperatures between 1.5 and 4.2 kelvin (K). What happened next? The race for absolute zero must have taken a great deal of his energy, for it took until June 1909 before he could resume his experiments. The vapor pressure-temperature calibration was improved, but the truly important step to make was the transfer of helium from the liquefier, which lacked adequate space for experiments, to a separate cryostat. In those days, accomplishing that transfer was a real challenge. Thanks to his notebooks at the archives of Museum Boerhaave (see Fig.1 for an impression of such a notebook) and reading the Communications from the Physical Laboratory of the University of Leiden [1], we can follow quite closely the strategy followed by Kamerlingh Onnes; his technical manager of the cryogenic laboratory, Gerrit Jan Flim; and his master glassblower, Oskar Kesselring.

## THE FIRST ATTEMPT

A drawing of the first setup in which Kamerlingh Onnes attempted to transfer helium (12 March 1910) is reproduced in Fig.2. The cryostat consisted of a double walled glass container with an even smaller container inside which could be connected to an impressive battery of vacuum pumps. Because there was nothing else to cool, the transfer of liquid helium worked and a new low temperature record (1.1 K) could be registered. In next experiment, four months later, he wanted to measure the temperature dependence of a Pt resistor, but that experiment failed because the extra heat capacity of the built in resistor caused violent boiling and fast evaporation of the freshly transferred liquid helium. So it was decided to drastically change the transfer system. And that would take another nine months, till 8 April 1911.

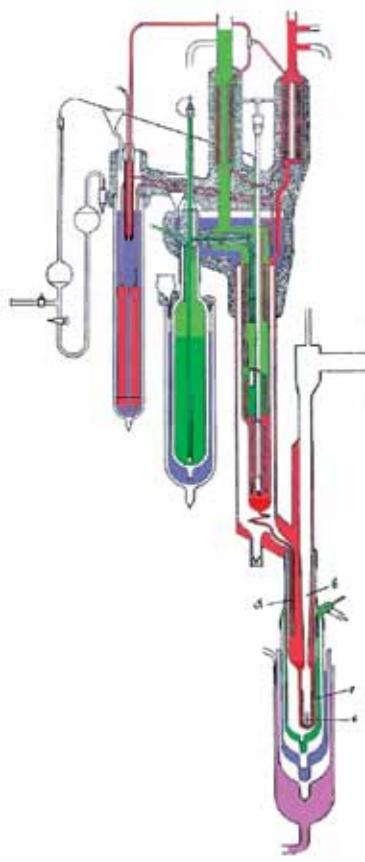
## MERCURY PRACTICALLY ZERO

The temperature dependence of the resistance, the R(T) behavior, of pure metals was a hot topic in those days. Before 1908 Kamerlingh Onnes and his assistant Clay had extensively studied the R(T) behavior of very pure gold and

platinum down to 14 K. They also investigated the effect of small admixtures of silver to the purest available gold and showed that improving the purity would make very low metal resistances possible. Kamerlingh Onnes didn't want to wait until the new transfer system was ready and he decided to extend the liquefier so that it could contain the Pt resistor. Thus, on 2 December 1910 he measured the first R(T) data of a metal below 4.2 K. Cornelis Dorsman assisted with the temperature measurements. Also Gilles Holst who just had arrived in Leiden was involved. His task was to operate the Wheatstone bridge with the ultra-sensitive galvanometer that had been placed on a vibration-proof column in a room at a safe distance from the thumping pumps of the cryogenic laboratory.

As shown in Fig.3 the Pt resistance became constant below 4.2 K, the residual resistance being determined by the amount of impurities. Evidently, the electron mobility did not freeze out near absolute zero. Kamerlingh Onnes concluded that the resistance of extremely pure metals should go to zero at T = 0, in accord with a model he had developed. And with the purification of mercury by repeated distillation they had very much experience in Leiden. So he planned to insert both a gold and mercury resistor into the cryostat.

At the beginning of April 1911, the new cryostat was ready for its first cooldown. It was a masterpiece, demonstrating the amazing level of glass-blowing skills and fine mechanical construction. A detailed drawing is reproduced in Fig.4. The transfer tube could now be closed by a valve which was operated from above. A stirrer was installed in the helium bath to guarantee uniform temperatures. The mercury resistor consisted of 7 U-shaped glass capillaries connected in series, each containing a small Hg reservoir to



**Fig.2** Set up used in the first attempt (March 12, 1910) to transfer helium from the liquefier to a separate cryostat in which experiments could be done. On the right a drawing is given of the cryostat consisting of several containers of glass fitting inside each other. Most of the containers are carried out in the form of a thermos bottle or Dewar (a double-walled glass container, pumped vacuum and usually covered with silver coatings on the inside walls. For visibility the coatings were not applied here). The outer vessel contained alcohol of 30–40 °C to prevent condensation of water vapor on the glass. The outer Dewar contained liquid air, the middle one liquid hydrogen, and the inner Dewar c was supposed to be filled with liquid helium coming from the liquefier on the left, entering through the double walled tube d. The bottom part of insert b was double walled and could be filled with liquid helium by condensation of helium gas. Subsequently, it could be evacuated to isolate the liquid helium inside b from the liquid helium in the cryostat. By pumping on the helium in b a new low temperature record was obtained. The left part of the drawing shows the liquefier with the Joule-Thompson valve clearly visible. Colors have been added to indicate various cryogenic fluids: alcohol (pink), liquid air (purple), liquid and gaseous hydrogen (dark and light green), and liquid and gaseous helium (dark and light red).

prevent the wire from breaking during the cooling process. In Fig.5 a similar design is shown that was used in October that year. To learn what happened on 8 April 1911, one just can follow the notes in his notebook. After the usual preparations the resistances of Hg and Au were measured (by Holst), as well as the temperature (by Dorsman). Then in the early afternoon, they started to reduce the vapor pressure, until a temperature of about 3 K was reached. Exactly at 4pm, says the notebook, the resistances of Hg and Au were determined again. The entry “Kwik nage noeg nul (Mercury practically zero)” marks the first resistance measurement on a superconductor.

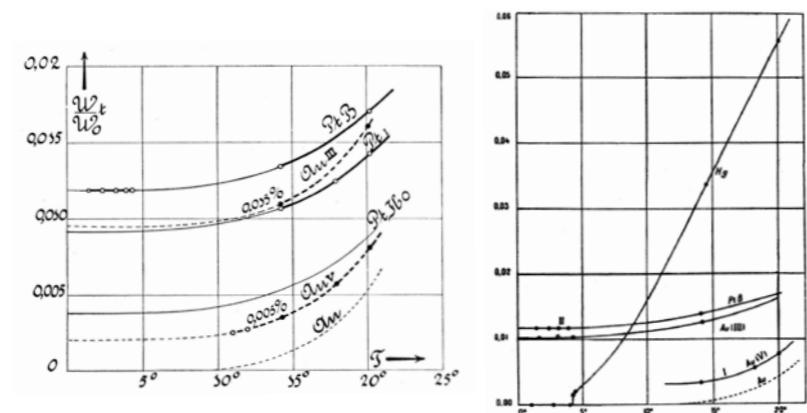
The experiments continued into the late afternoon. At the end of the day, Kamerlingh Onnes finished with an intriguing note: “Just before reaching the lowest temperature (about 1.8 K), the boiling suddenly stopped and was replaced by evaporation, in which the

liquid visibly shrank. So, a remarkable strong evaporation at the surface.” Two superfluid transitions had been seen for the first time, in one lab on one and the same day!

With only two data points in the liquid helium temperature range, Kamerlingh Onnes was not thinking of a new phenomenon but he rather thought that his predictions were justified, and a look at Fig.3 tells us that this was not unreasonable.

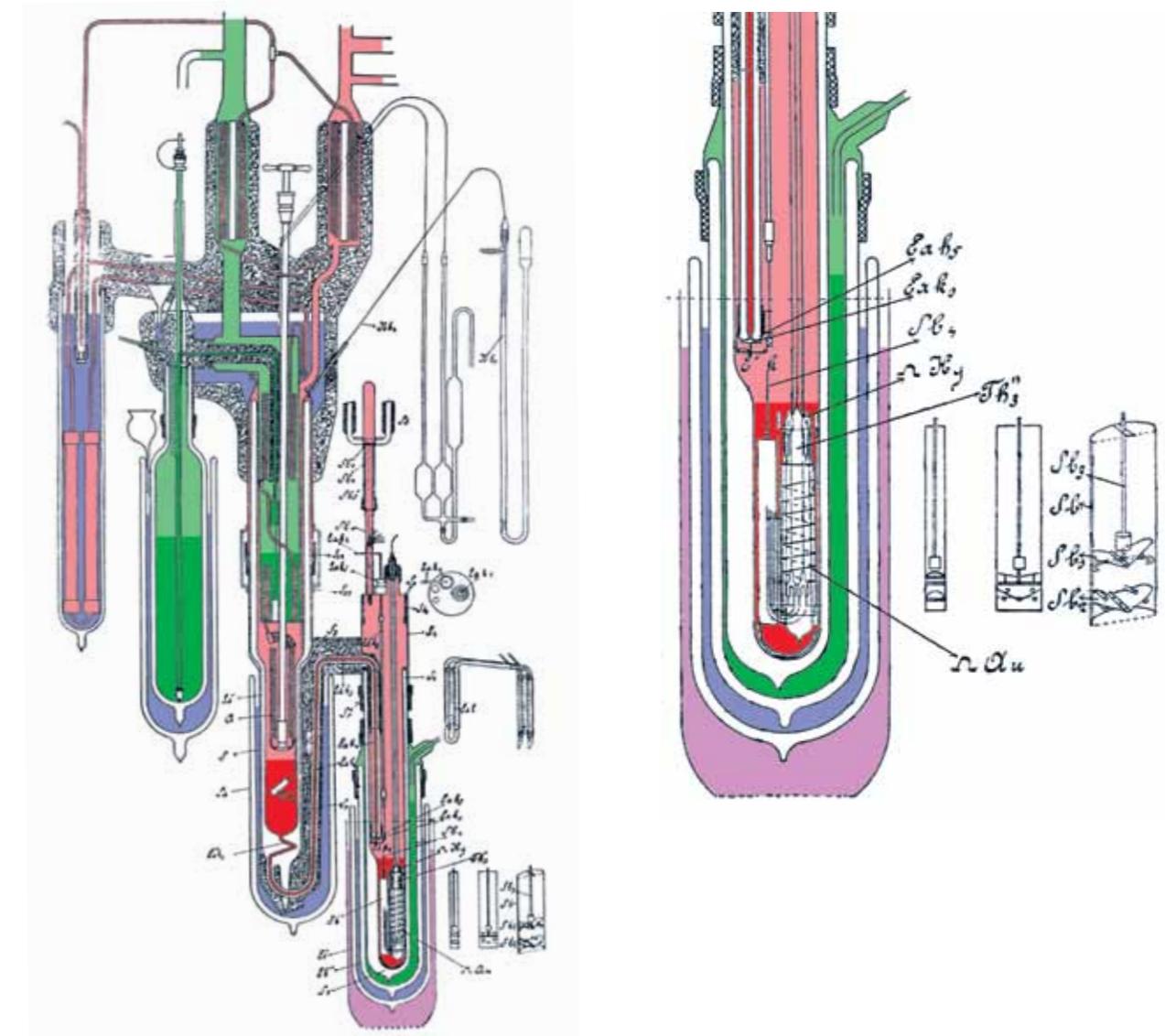
#### A NICE STORY

For the next experiment on 23 May 1911, the voltage resolution had been increased to about 30 nV, and the equipment was carefully checked for possible short circuits. After reducing the temperature to about 3 K, the Leiden team closed the valves to the liquefier and the vacuum pump so that the temperature could slowly rise. The notebook says: “At 4.00 K not yet anything to notice of up coming resist-



**Fig.3** Resistance ratios of some metals versus temperature  $T$  in kelvin. Left panel: Several platinum and gold resistors of various purities measured at different hydrogen temperatures. Pt-B was the first resistor ever to be cooled to helium temperatures in the experiment of 2 December 1910. The constant resistance below 4.3 K contradicted Kelvin's model for conductance; the electrons did not freeze onto the ion lattice at absolute zero. The remaining resistance was due to scattering of the electrons on impurities. By making the metal wires purer, both chemically and physically (by annealing out the lattice disorder), the resistance was shifted downwards over a constant value, demonstrating that Matthiessen's rule is valid down to the lowest temperatures. Right panel: The resistance ratio of Pt and Au compared to that of mercury (Hg). I denotes the temperature range of liquid hydrogen, II that of liquid helium.

**Fig.4** Set up in which Heike Kamerlingh Onnes and coworkers carried out the 8 April 1911 experiment that first revealed superconductivity (same color scheme as in Fig.2). Left panel: On the left the liquefier with extended Dewar is schematically displayed. The liquid helium could be transferred through the double-walled vacuum-pumped siphon that at the end inside the cryostat could be closed with a valve (Ea k1). Right panel: Blow up of the lower part of the cryostat. Handwritten by Gerrit Jan Flim are labels for the mercury and gold resistors ( $\Omega$  Hg and  $\Omega$  Au), the gas thermometer (Th3), components at the end (Ea kn) of the transfer tube. On the right several cross sections of the stirrer are drawn.



ance. At 4.05 K not yet either. At 4.12 K the resistance begins to come into being”. That entry contradicts the oft-told anecdote about the key role of an apprentice of the instrumentmaker's school who assisted with the temperature control. The resistance jumped back to its normal value: within 0.1 K it

increased by a factor of about 400. Such a fast increase was much more than the model could account for, see Fig.3.

#### THE FAMOUS FIGURE

The next notebook starts on 26 October 1911 with “In helium apparatus mercury resistor (separate drawing made)

with mercury contact leads ....” This drawing, reproduced in Fig.5, reveals how the summer was used to replace the copper current and voltage leads by mercury wires in glass capillaries. This change was motivated by the wish to improve the voltage resolution. The idea was to minimize the thermoelec-

tric effect in the voltage leads by making everything of the same metal. It didn't work, because the transition from solid to liquid mercury turned out to be the source of a considerable thermoelectric voltage of 0.5 mV. Still, the October experiment produced the historic plot, shown in Fig.6, of the abrupt reappearance of the mercury resistance at 4.20 K. The part of the plot above the transition temperature ( $T_c$ ) is of particular interest because the gradual increase shows that the electrons at 4.2

Fig.5 Cryostat with mercury resistor and mercury leads for the 26 October 1911 experiment (same color scheme as in Fig. 2): seven U-shaped glass capillaries in series (inner diameter 0.07 mm), each with a mercury reservoir at the top and contact leads also made of glass capillaries filled with mercury. External contacts were made through Pt wires (denoted by Hgxx) shown in the top right drawing.

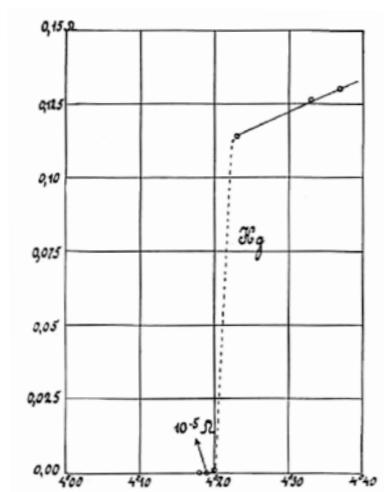
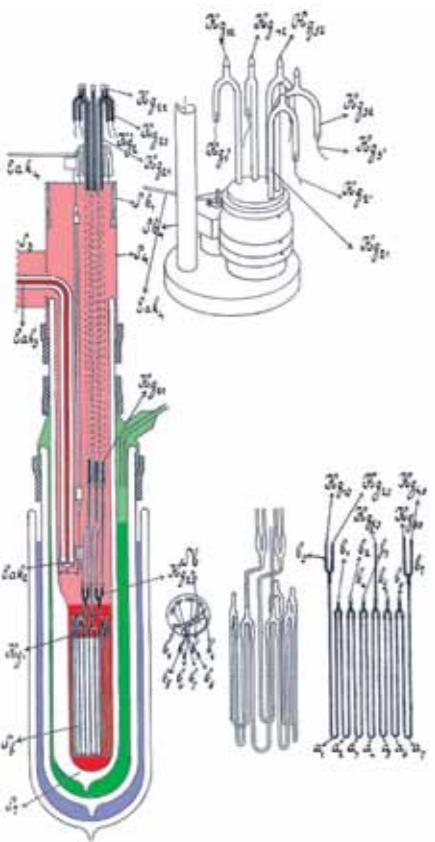


Fig.6 Historic plot of resistance ( $\Omega$ ) versus temperature (K) for mercury from the 26 October 1911 experiment showing the superconducting transition at 4.20 K. Within 0.01 K the resistance jumps from immeasurably small (less than  $10^{-5}\text{ }\Omega$ ) to 0.1  $\Omega$ .

K were still predominantly scattered by phonons (Planck vibrators). From the sudden jump it was clear that a totally new and unexpected phenomenon had been discovered, which Kamerlingh Onnes from thereon called 'superconductivity'.

#### MATERIALS AND MAGNETS

An interesting entry from 20 June 1912, "Discussed with Holst .... to alloy mercury with gold and Cd", indicates the first step to exploring other materials than pure mercury. Surprisingly, the resistance disappeared as before and Kamerlingh Onnes concluded that they could have saved a lot of time previously spent on the preparation of pure mercury. "Even with the amalgam used for the backing of mirrors, the resistance was found to be zero." In December 1912 also lead and tin were found to become superconducting at about 7 K and 3.8 K, respectively. Since then, the experiments were continued with these materials: no disasters any-

more with broken mercury threads! The generation of strong magnetic fields now became within reach. But the experiment, even announced in Kamerlingh Onnes's Nobel lecture and carried out on 17 January 1914, brought a great deception. The magnetic field generated with a lead coil turned out to destroy the superconductivity at 4.2 K already at 600 Gauss (60 mT). Gone were the dreams of producing magnetic fields as high as 10 T (100.000 Gauss): "An unforeseen difficulty is now found in our way, but this is well counterbalanced by the discovery of the curious property which is the cause of it".

#### PERSISTENT CURRENTS

The last notes about superconductivity in the archives are dealing with the persistent mode experiments carried out during the spring and summer of 1914. Kamerlingh Onnes concentrated on the question how small the resistance below  $T_c$  actually was and designed an elegant experiment using the lead coil in a closed-loop configuration. When this device is cooled through  $T_c$  in an applied magnetic field, any change in field will generate a current in the closed loop which, if the resistance is really zero, will circulate for ever. The magnetic field produced by that circulating current was probed by a compass needle and the current value followed from the compensating effect of the magnetic field from an almost identical copper coil positioned on the other side of the needle. In Fig.7 two sketches of the set up made by Gerrit Jan Flim are reproduced. The experiment worked well and Kamerlingh Onnes would have loved to demonstrate it to his colleagues at the monthly meeting of the KNAW, but he didn't have the means to do that. Although not possible in 1914, in 1932 Flim flew to London for the traditional Friday evening lecture of the Royal Institution bringing with him a portable dewar containing a ring of

Fig.7 Original drawing by Gerrit Jan Flim showing the setup for the persistent-current experiments of May 1914. Left: front view showing the lead coil in the helium cryostat and the copper compensation coil in the liquid air Dewar (actually, during the experiment, both coils were on the same height as the compass needle). Right: top view showing also the compass needle in the middle pointing north demonstrating good compensation of the fields from the Pb and the copper coils (Archive of the Museum Boerhaave, Leiden).

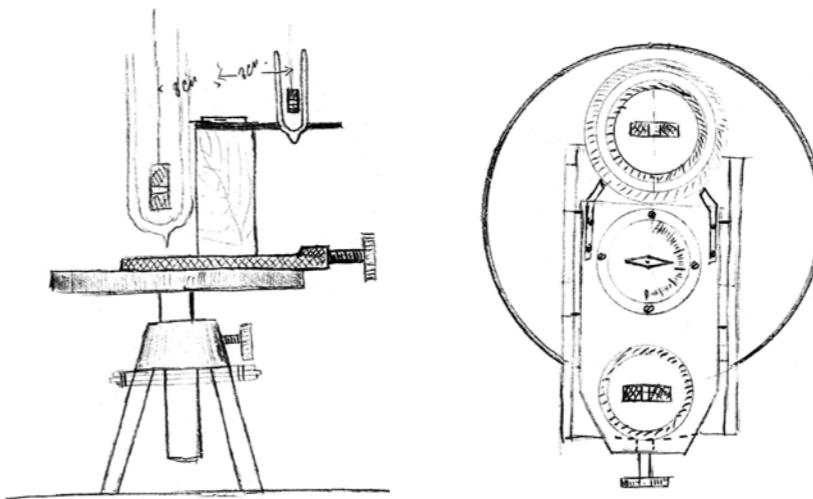
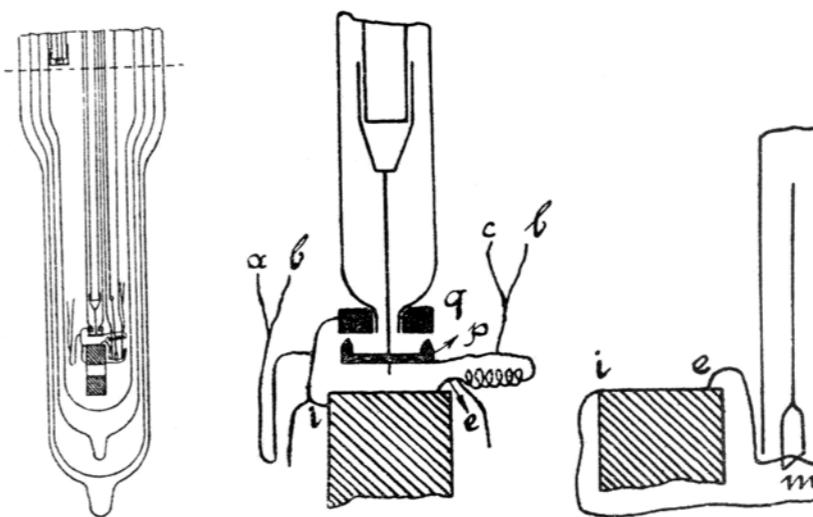


Fig.8 Design for the June 1914 experiment with (left) the cryostat with insert, (center) the mechanical persistent mode switch (superconducting "key") with p and q lead rings, and a, b, and c current leads and voltage leads, and (right) the cutting machine (Archive of the Museum Boerhaave, Leiden).



lead immersed in liquid helium and carrying a persistent current of 200 A. Today, the most compelling demonstration of persistent currents is the levitation of a permanent magnet by a superconductor.

The excitement about persistent currents on a macro scale spread quickly. Paul Ehrenfest, who witnessed the experiment, wrote in a letter to H.A. Lorentz: "Unsettling, to see the ring of electrons goes round and round and round [...] virtually without friction."

His colleague Kuenen proposed an experiment, depicted in Fig.8, in which the loop of lead could be interrupted, or even repeatedly opened and closed from outside, thus forming the first (mechanical) persistent mode switch. Upon Ehrenfest's suggestion Kamerlingh Onnes repeated the experiment with a single lead ring, which also worked. Still, Kamerlingh Onnes never believed that the "micro-residual resistance" was really zero, revealing that he was not aware of the new (quantum) state of matter he had discovered. That insight came in 1933 with the experiments of Meissner and Ochsenfeld in Berlin and the explanation by the young Gorter in Haarlem telling us that a superconductor actually is a perfect diamagnetic rather than a perfect conductor, and finally in 1957 with the microscopic explanation by Bardeen, Cooper and Schrieffer.

#### REFERENCES

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JOHAN OVERWEG, PHILIPS RESEARCH:

# “THERE IS STILL PLENTY OF DEVELOPMENT IN THE MRI SCANNER”

The only large-scale commercial application of superconductivity is the MRI scanner.

For more than twenty-five years, Philips Research have been active in this field.

Researcher Johan Overweg has been at the forefront of every development.

“Watch out for the stray field”, commented Johan Overweg, while revealing his key ring, and holding it up in front of the MRI scanner. In the research chamber, alongside a workroom bulging with soldering irons, electronic printed circuit boards, spare components, oscilloscopes and a huge selection of drawers and trays of parts, we are faced with a stripped-down MRI device. “They’ve put me in it on several occasions”, explained Overweg. “It is a 1.5-Tesla machine built in 1994, but the magnet is still in perfect working order, and we have kept the device completely up to date. It just doesn’t have a nice clean housing like the MRI scanners in hospitals. We use it for trials, placing standard objects in the opening, and every now and then a test subject.”

Overweg (straight hair, beige pullover, sandals) has been employed at Philips Research in Hamburg since 1994, and is head of the MR Front-End Hardware cluster of the Tomographic Imaging Group. After graduating in Technical Physics from the University of Twente, he has constantly been

working on the development of superconducting magnets and other major components of the MRI scanner. He started his career at Philips Medical Systems in Eindhoven, in 1984, just after the company had begun work on MRI scanners. In 1992, when Philips as a whole was suffering hard times, and even Medical Systems was facing stormy waters, Overweg switched to Siemens, where magnets were being developed for the Superconducting Super Collider (SCC). When the American particle accelerator was dropped due to cutbacks just eighteen months later, he returned to Philips. For personal reasons, he opted for Philips Research in Hamburg. There, on the Röntgenstrasse, he is above all in his element in the research lab. “Management isn’t really my thing.”

## MR SIGNAL

MRI stands for Magnetic Resonance Imaging. This imaging technique makes use of the fact that the human body is mainly made up of water. In a powerful magnetic field, created by



Philips experimental 2 Tesla scanner with a volunteer (Philips Research).

currents circulating in a coil, the hydrogen nuclei adopt specific energy states that can be manipulated using a high-frequency electromagnetic field (radio waves). If the high-frequency field is switched off, the manipulated hydrogen nuclei return to their normal state, emitting the same types of radio waves as those with which they were excited. Complicated digital processing of this MR signal then results in images of the soft internal parts of the patient, for example the brain or the heart. The major advantage of MRI over X-ray techniques or CT scans is that no ionising radiation is required.

In practice, an MRI scanner is made up of a number of coil systems. The outer coil generates a powerful magnetic field. The patient is placed in the cylindrical opening – for obese patients and patients suffering from claustrophobia, open MRI systems are available today. The large magnet makes use of superconductivity that in turn calls for a cryogenic system based on liquid helium. The measurement itself is carried

out with an RF coil, with a frequency in the radio range (15 to 200 MHz). The superconducting magnet houses the so-called gradient coil according to which the magnetic field strength in the patient is varied locally. This defines where the signal comes from. The computer converts the digitised signal into pictures.

The first MRI scan of a human being dates back to 1977. Three years previously, the mouse was the first subject to undergo MRI. Superconducting magnets were already available by that time, thanks to the discovery (in the early nineteen sixties) of an alloy of the metals Niobium and Titanium (NbTi) as a suitable wire material for producing powerful magnetic fields. Due to the low transition temperature of NbTi (9.2 Kelvin), a superconducting coil of this material cannot be achieved without cooling with liquid helium. MRI today is a widely used diagnostic technique and – to date – the only successful commercial application of superconductivity. Thanks to MRI, superconductivity made the leap from sci-



Experimental gradient coil, according to which the magnetic field strength in the patient is varied locally (Philips Research).

Scientific curiosity to a phenomenon that has a profound effect on our quality of life. Thirty years after the introduction of the technique, just under 30,000 MRI scanners have been installed worldwide (representing almost one hundred million examinations a year) and annual production at present is in excess of 2500 units. In the United States, there is one scanner for every 30,000 inhabitants. Half of all MRI shots are used for examination of the brain and spinal cord.

All in all, then, an interesting market in which Philips is a successful operator. The thing that attracts Overweg to the world of MRI is the fact that it brings together such diverse technologies. "You are dealing with magnet technology, high current electrical engineering, signalling technology, electromagnetic waves, signal processing – and all at extreme levels of precision. A magnet of this kind is a highly complex mechanical device. One typical problem is that the wire itself cannot be tested. You simply have to rely on specifications and strict quality and process controls. One magnet contains some 50 kilometres of wire, welded together in 10-kilometre sections. It is quite simply impossible to test whether all that wire retains its current at operating temperature and in the operating field. You only find out whether you have made any mistakes once the magnet is fully assembled."

The largest player in the field is Siemens, while General Elec-

tric and Japanese companies including Toshiba and Hitachi are also active on the MRI market. Overweg meets with the competition each year at the conference of the International Society of Magnetic Resonance in Medicine. "Particularly in respect of the magnets, very little is published. The reason is you cannot look at what is going on inside the magnet, and anything you keep to yourself is in principle secret. By contrast, a very great deal is published about the receiver coils placed on the patient. Even so, the internal secrets are less secret than they used to be. Researchers regularly switch from one company to the other. I have no illusions. I am certain for example that the people at General Electric, and probably Siemens know fairly precisely just how our magnets are made up."

#### STRAY FIELD

Designing an MRI scan is one huge optimisation problem. Overweg explained, "How powerful should the field be? How large should the volume be in which the field has the quality to produce images? How large should the opening be? Far and away the most expensive component is the magnet, followed by the system of the coil and amplifier for the gradient fields that are superimposed on the static field. Other parts, like the RF components and the digital electronics, are much cheaper."

The first MRI magnets were upscaled variants of laboratory magnets used for research into nuclear magnetic resonance. In Overweg's words, "But then with a larger hole in the middle and horizontal rather than vertical. In that period, the tank containing liquid helium was itself housed in another tank containing liquid nitrogen."

One major problem with the first generation MRI magnets was the stray field; the strength of the field outside the opening. Overweg continued, "The international agreement is that the stray field must be kept below 5 gauss, ten times the strength of terrestrial magnetism. The limit is based on pacemakers that can be programmed using magnets, and that if exposed to more than 5 gauss could be disrupted. The situation has now changed, and the 5 gauss limit is not particularly meaningful anymore. But it is still in place, and no one seems desperately keen to change the situation. To counteract the stray field, between 10 and 20 tonnes of iron shielding had to be installed in hospitals – a complicated procedure."

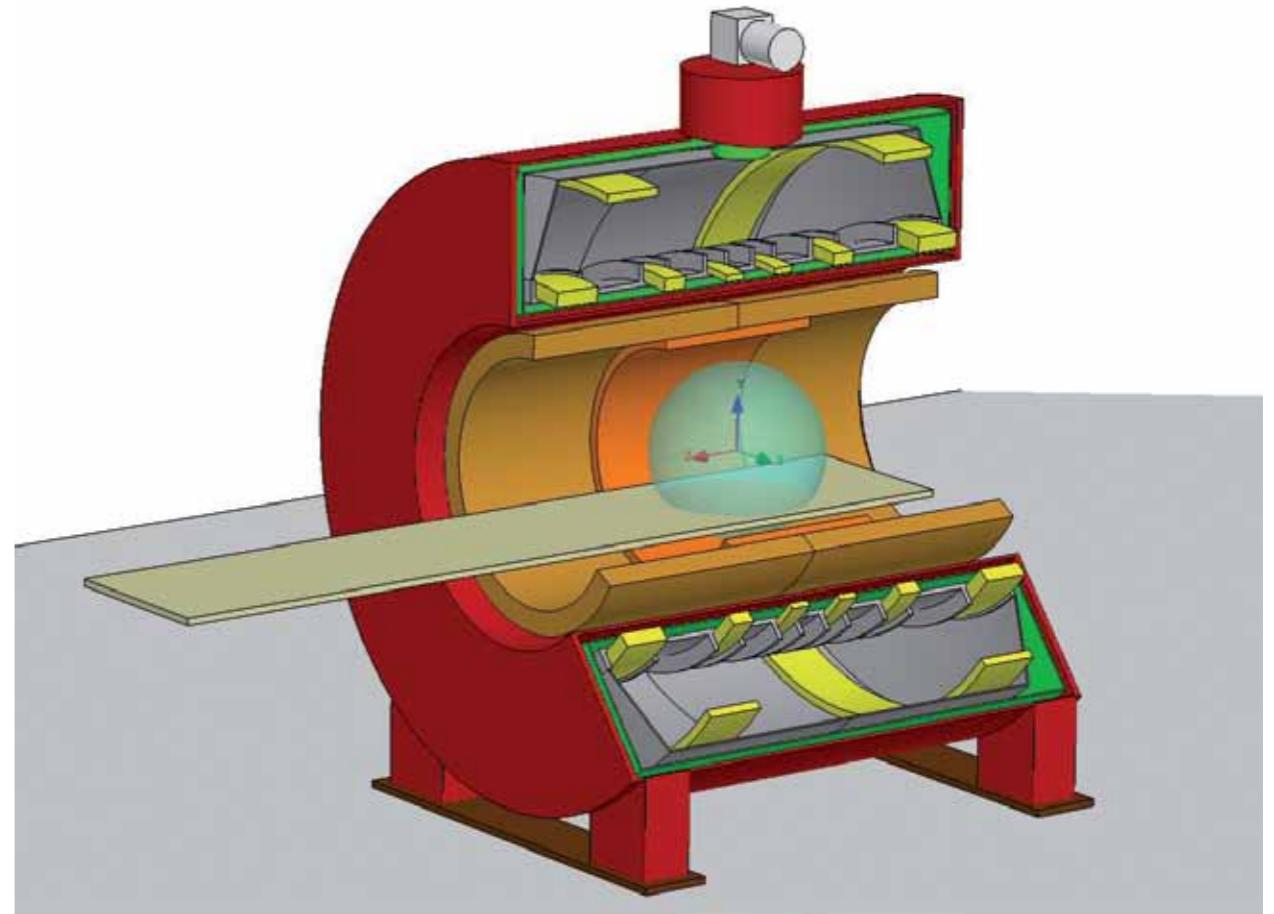
In 1986-87, the realisation grew that this situation could be optimised. The result was more compact magnets. Whereas in the first generation the hole was 1 metre or more in diameter, the opening has now been reduced to about 90 centimetres. The components in the hole were also made more compact, in order to leave as much space as possible for the patient.

One important improvement took place in the field of refrigeration engineering. In Overweg's words, "With a helium tank encased in a tank containing liquid nitrogen, approximately 0.5 litres of liquid helium were lost, every hour. During this period, compact refrigeration machines were introduced, developed for vacuum pump technology, but extremely compatible with the refrigeration capacity required by MRI. They are a variation on the Stirling machine, with a compressor and an expansion machine mounted directly on the magnet, which absorbs heat from the radiation shield around the magnet. As a result, the loss of liquid helium was reduced to 0.1 litre per hour, and following further design improvements, to 0.05 litres per hour."

The solution to the stray field problem is known as active

shielding. Overweg explained, "An actively-shielded magnet works with two concentric coil systems. Together they generate the required field in the centre, but outwardly they compensate for one another so that on balance, no field remains. The principle was not new, but the problem delaying introduction was the fact that the quantity of superconductive wire in the coil system is massively increased by this approach, and during the pioneering period of MRI, was considered too risky and too expensive. As NbTi wire became capable of withstanding more current, the situation changed. I was personally able to leave my mark on that development, namely making the system more compact, installing a refrigerating machine to replace the nitrogen tank and the active shielding. I was the trendsetter. The dimen-

A MRI-scanner is made up of a number of coil systems. The outer coil generates a powerful magnetic field. The patient is placed in the cylindrical opening. The large magnet makes use of superconductivity that in turn calls for a cryogenic system based on liquid helium. The measurement itself is carried out with an RF coil, with a frequency in the radio range (Philips Research).





Experimental gradient coil (Philips Research).

sions of the MRI magnet introduced to the market by Philips in 1988 have only changed by a few centimetres, since that time. On the other hand, we have succeeded in fitting ever more magnetic field into the housing, from 0.5 Tesla in 1988 via 1.5 Tesla in 1994 through to 3 Tesla since 2002. This increase in field strength has above all been made possible by an ever better understanding of the forces active in the coil. To give you an idea: in a 3 Tesla field, the ends of the magnet are drawn together with a force of 300 tonnes. And if you are not careful, the tensile forces in the wire can rise so high that the wire actually breaks."

A modern MRI magnet contains a maximum of 2000 litres of helium, and in operating situations, the tank is filled to between 40 and 90 percent. In other words, the system only has to be filled every one to two years. To top the system up,

Air Liquide or Air Products simply drive up with a few 250 or 500-litre containers, and a set of siphons. Absolutely no customer involvement is required. But there is still room for improvement. In the last ten years or so, MRI magnets have been introduced to the market, that re-condense all the evaporated helium. From a closed system of that kind, which has in fact now become the standard, except during maintenance, no helium escapes whatsoever."

The growing shortage of helium is a major problem. Overweg again, "Of the tens of thousands of MRI scanners currently in use worldwide, a large proportion are not zero boil-off. They all have to be topped up. And every new magnet first has to be filled. The MRI market takes around 20 percent of the world's helium supply – far and away the world's largest

consumer of helium, on the other hand, is welding engineering. New magnet designs with far less helium than required today, will have to offer the eventual solution. The disadvantage is that without a buffer of liquid helium, the system becomes more susceptible to disruptions. If the refrigerating system breaks down, and you have no buffer, the magnet has to be switched off within a few hours, or it quenches." A quench is the sudden loss of the superconducting state. In the NbTi wire, the normal resistance returns, bringing with it the heat development that comes with the current. In next to no time, all the helium is evaporated. Overweg added, "It happens occasionally, but I am sworn to secrecy. Such a situation is entirely without risk to the patient. It is above all a shame to lose the helium; it is simply boiled off into the outside air, via a pipe. Just like a steam boiler venting its steam."

#### CLINICAL

The more powerful the magnetic field, the more detailed the resultant image. But Overweg is still not convinced of the large-scale clinical value of 7-Tesla scanners. "The standard today is 1.5 Tesla. When 3-Tesla systems became available, the question arose: should we at Philips follow the trend? Is it just a research gadget or will there be real clinical applications? Today we are able to build a 3-Tesla magnet for an acceptable price, and there is a market for 3-Tesla systems. At 7 Tesla, the situation is more difficult. A magnet that powerful brings you close to the field in which our standard superconductors become less effective. To generate 7 Tesla, you are stuck with an inefficient magnet, that is disproportionately more expensive than a 3-Tesla model, particularly if you also want to employ active shielding. Passive iron shielding would require hundreds of tonnes of iron – itself an expensive option – and one that cannot be installed in every situation. Using 7 Tesla you can produce brilliant images of the head, but it is still uncertain whether such precise imagery is of real value for other parts of the body. One problem is that the RF frequency is so high that the signal no longer easily penetrates the body. In addition, heat development increases quadratically with the frequency, and you have to be careful not to fry your patient. For research purposes, on the other hand, 7 Tesla is excellent."

One project in which Overweg is closely involved is the integration of an MRI scanner with radiotherapy; in other words tackling tumours with ionising radiation (from an accelerator or radioactive source) from outside the body. "The idea was suggested by Lagendijk, professor of clinical physics in Utrecht. I was involved in the implementation of the system right from the start. Developing this combination was too much of a financial risk for Philips, on its own, and during the first few years, the project was financed by the Technol-

ogy Foundation STW. It is a fascinating project. The technical concept of the system currently installed in Utrecht was my brainchild. During a brainstorming session at Philips in 2002, I came up with the idea of passing the beam clear through the magnet. And it works. Since 2009, a prototype has been installed in Utrecht. A machine is currently being designed in which patients can actually undergo radiation therapy."

Are there still challenges for researchers in MRI? Overweg's response is clear. "In the mid-nineteen nineties it was feared that developments had reached their peak, and there was little left to discover. That turns out to have been a major misconception. Integrating MRI with therapy offers numerous opportunities. There is still plenty of development in the MRI scanner."

MRI-scanner (Philips Research).



# SUPER CONDUCTIVITY AND THE FUNDAMENTALS OF PHYSICS IN THE 21ST CENTURY

It is perhaps surprising that in 2011, hundred years after its discovery, research in superconductivity is still intensely pursued in the world. It is regarded as a central subject of modern fundamental physics research and it is represented in the majority of prominent physics laboratories. The outlook has however changed much. Although the superconducting state itself is quite well understood, in the last 25 years or so a zoo of materials have been discovered being home to quite mysterious quantum mechanical electron systems. As a rule these tend to form sturdy superconductors with unconventional order parameters while the origin of this superconductivity is part of the mystery. The king of the hill is the family of copper oxide superconductors as discovered in 1986 [1], famous for its superconductivity at a high temperature ("high  $T_c$ "). Although these are still stand-alone with regard to their capacity to superconduct at "very" high temperature (150 Kelvin), in the intervening years a number of systems have been identified that are believed to be governed by a similar unknown general mechanism: the family of heavy fermion systems, a number of organic systems including the 'buckyballs', cobaltates, ruthenates and especially the recently discovered iron superconductors [2]. Given the length limitations of this exposition I will mostly focus here on the copper oxides. These are in a way the extremists of the family, while they have been at the center of this intense research effort.

What is the greater context of this research? It would be surely of great benefit to humanity when materials would be discovered supporting large supercurrents at room temperature. Although this quest for room temperature superconductor is the main energizer in the engineering corners of the pursuit, one encounters a greater ambition on the physics floors. As I will discuss in the next section, at stake is our understanding of the fundamental nature of matter. Fundamental physics finds itself in an era where it is becoming increasingly clear that there is much more to the notion of "matter" than we used to realize. Superconductivity research has played in the past a key role in supplying key insights for the "material" side of high energy physics, but this role is intensifying in the present era. Fundamental physics is on a steep learning curve regarding the awareness that forms of

"quantum matter" exist that are utterly different from the stuffs that we encounter in daily life. In this regard, this research is just a branch of a cocktail that also involves the high energy accelerators and the telescopes of modern astronomy. Its special merit is its empirical richness. Rapid progress has been made due to the experimental techniques of condensed matter physics leaping forward: the 'telescopes' that make possible to observe the quantum physical electrons worlds formed in solids have improved dramatically. Metaphorically it is like the Voyager mission in the solar system: viewing matters from close by reveals a richness and colorfulness that nobody expected. The theorists were actually left behind, struggling to find the proper mathematical language to understand what is really going on [3]. Being very aware of this handicap I will do my best to get across the excitement of the empirical research: after discussing some high  $T_c$  generalities in section 2, I will turn to the wild and colorful quantum matter world encountered in the "pseudogap regime" in section 3, to hopefully climax in section 4 with the austere beauty of the strange metals that are believed to be the secret of the best superconductors. These strange metals represent more than anything else the point of contact with fundamental physics. It appears that the phenomenon of quantum criticality is at work and in the last years this has become a major research subject in string theory. As I will explain at the very end, the remarkable mathematics of string theory

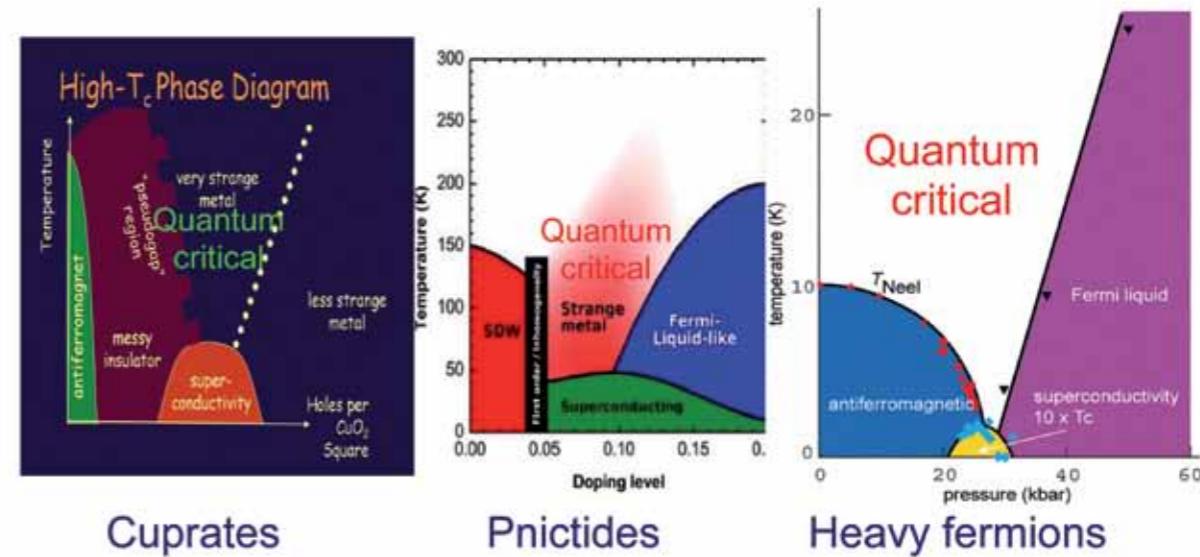
suggests that high  $T_c$ 's strange metals are directly linked to the material attitudes of post-modern hairy black holes.

## 1. QUANTUM PHYSICS AND THE EMERGENCE OF EVERYTHING

It is an old physics wisdom that when large numbers of simple microscopic things like water molecules are packed together they form 'states of matter' like steam, water and ice, showing behaviors completely detached from the properties of the constituents. Although underappreciated, the statistical physics of the twentieth century triumphed in enumerating in a tight mathematical language the emergence principles governing the nature of classical matter. The historical significance of superconductivity has been to demonstrate how this wisdom can be extended to the realms of quantum physics.

Electrons are the most quantum mechanical entities that are readily available under earthly conditions in the form of the "free" electrons found in metals. The superconducting state discovered by Kamerlingh Onnes played a key role in demonstrating how the quantum physics of the electrons can survive in the macroscopic realms. The secret of superconductivity is that the supercurrents are unstoppable by classical means because every electron in the superconducting state is literally "everywhere at the same time", referring to the delocalization property that quantum particles are not allowed

Fig.1 The universal phase diagram believed to underlie the strange superconductors. As function of a zero temperature "control parameter" (charge density in case of cuprates and pnictides, pressure in case of heavy fermions) some electronic order is subjected to a zero temperature phase transition. A quantum critical metal is realized right at the quantum phase transition, and this is somehow a very beneficial circumstance for the appearance of very sturdy superconductivity.



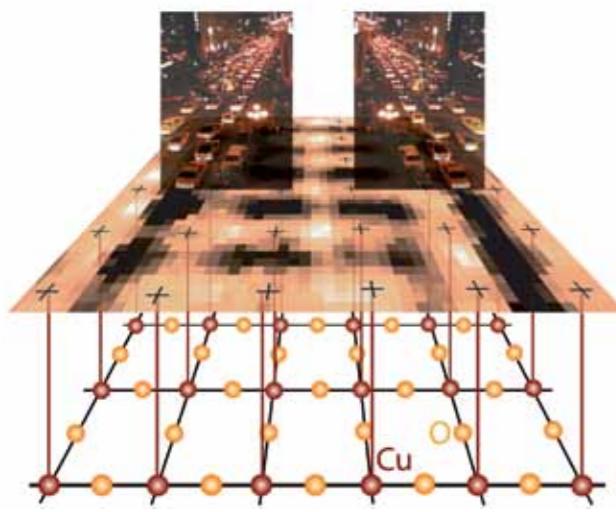


Fig.2 A good metaphor for the strongly interacting electron world in the copperoxide layers is as if they form a dense traffic that keeps moving due to the quantum fluctuations. Coherent “stop and go” patterns emerge corresponding with “rivers of charge” separated by domains where the electrons are completely localized: the stripes. This physics is directly measured by scanning tunneling spectroscopy on the surface of these systems (the blurred pattern in the middle).

to have a preference for any particular location in a homogeneous space. Confusingly, the superconductor is at the same time a “hard” state, like a piece of ice, as is manifested by the way it imposes its will on for instance magnetic fields. This revolves around the notion of Bose condensation, described mathematically by the Ginzburg-Landau theory, showing how the particle-wave duality works in many particle quantum physics. The hardness of normal crystals is rooted in the fact that the atoms turn into particles, telling each other where they want to be in normal space. In a superconductor the electrons take the form of quantum waves, that now prescribe each other where they want to be in the place where quantum waves live: momentum space.

The Ginzburg-Landau theory describes the collective properties of the quantum liquid, regardless the detailed properties of the constituents. Resting on this trait it has played a hidden but decisive role in the greatest paradigm shift of twentieth century physics.

When the standard model of elementary particles physics was nailed down, in the 1970’s it was immediately clear that it is just like a Ginzburg-Landau theory fancied up by larger symmetry principles. In fact, the famous Higgs mechanism responsible for the mass of the elementary particles is literally the same thing as the hardness of the superconductor. The bottom line is that the fields that were first believed to be fundamental turned out to represent “collective vibra-

tions” of a material “quantum vacuum”, quite like the superconductor except that it is formed from primordial stuff of an unknown kind [4].

The focus in fundamental physics shifted to the problem of quantum gravity and here the central role of quantum emergence becomes even more obvious. Space and time (and perhaps even quantum physics itself) are emergent representing collective properties of a primordial physics which is completely in the dark because its traits got lost completely in the collectivization process. The most developed mathematical theory dealing with quantum gravity is string theory. In hindsight, the change from the reductionist to the emergence view was most dramatic in this community. Initially the string theory pursuit was aimed at the unique equation explaining everything. However, spurred by mathematical consistency requirements a complete reorientation took place in the mid 1990’s where it was reinterpreted in terms of a very fanciful system of emergence principles (the “second string revolution”). The main result was the discovery of mathematical transformations (holographic dualities) [5] demonstrating that the physics of fanciful universes governed by Einstein’s general relativity can be precisely encoded in the properties of strange forms of quantum matter. As I will discuss at the end, very recently evidences started to accumulate that this is precisely the kind of stuff that is realized in the unconventional superconductors! Before getting there, let us first step back 25 years to find out how it all started.

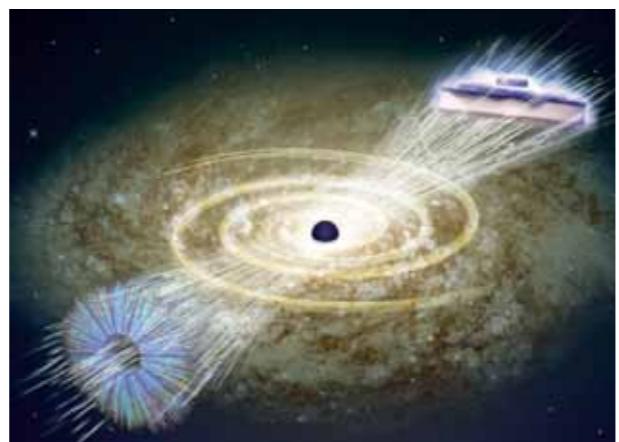


Fig.3 According to modern string theory, the physics of the quantum critical metals and superconductors is “holographically” encoded in the properties of a black hole located in the center of an Anti-de-Sitter universe. The quantum matter of modern condensed matter physics can be viewed as a fanciful form of Hawking black hole radiation, and from this perspective there is not much of a difference with the perfect fluid behavior of the quark-gluon plasma created at high energy accelerators (the “little bang”, lower left).

## 2. HOW HIGH $T_c$ SUPERCONDUCTIVITY STARTED

An earthquake rumbled through physics in 1987 due to the Bednorz-Mueller discovery of superconductivity at temperatures up to 150 Kelvin [1], much higher than was deemed possible. Some thirty years earlier the Bardeen-Cooper-Schrieffer (BCS) theory seemed to have explained everything that matters in conventional superconductors [6]. The crucial first step of the BCS theory is the assumption that the electrons in the metal above the superconducting transition form a “Fermi-liquid”, the state of electrons in normal metals. The key ingredient of this remarkable piece of 1950’s physics [7] is that electrons are fermions subjected to the Pauli principle, insisting that every single particle state can only be occupied once. For delocalized, non-interacting fermions this implies that the particles have to occupy states of increasing kinetic energy with the effect that at the high electron densities found in metals the system as a whole has an enormous ( $10^4$ - $10^5$  Kelvin) quantum zero point motion energy (Fermi energy). Electrons do interact strongly via electrostatic repulsions but since the Fermion statistics renders this system to be extremely liquid it also has an enormous screening power, with the effect that the electrostatic repulsions are diminished to a degree that the macroscopic system behaves as if the electrons form a perfect, non-interacting Fermi-gas. The other wheel of the BCS theory is the Cooper instability, a mathematical construct showing that when the fermi-gas is subjected to a small attractive interaction the electrons have to form pairs at low enough temperature. The remainder of the story is straightforward: pairs of fermions are bosons and bosons condense forming the superconducting state.

The required attractive action is the tricky part since electrons naturally repel each other. BCS pointed out that the quantum mechanical exchange of quantized lattice vibrations (phonons) will induce such attractions and this “phonon glue” got well established as the driving force of conventional superconductivity. However, this is a rather feeble affair and it surely falls short to pair electrons at “high” temperature: it is now believed that a  $T_c$  of 40K should be the absolute bound, based on the “optimal” BCS superconductor MgB<sub>2</sub> discovered in 2001. The superconducting state of the high  $T_c$  and other ‘exotic’ superconductors do look similar to the BCS superconducting state in the regard that they are Bose condensates of electron pairs. However, an obvious unconventional property of the superconductivity is that the Cooper pairs possess more internal structure. The ‘phonon glue’ of the conventional superconductors strongly favors featureless pairs, but invariably the pairs in the new superconductors carry a magnetic moment and/or an angular momentum: the cuprate pairs are in a non-magnetic “d-wave” angular momentum state.

A view that has been popular all along is that the essence of BCS is still at work, but that instead of phonons some other, more muscular glue is at work [3]. Given that the cuprates and other new superconductors tend towards antiferromagnetism (next section), a natural candidate are then transient “precursor” magnetic fluctuations taking the role of the phonons, having the added benefit that these can explain the unconventional pairing state. However, despite a concentrated search compelling evidence for the existence of such



Fig.4 The so called ‘mirror ovens’ that are used to produce large single crystal of the complicated oxides and other materials that form the environments where the “quantum matter” electron systems are found.

a “spin fluctuation superglue” mechanism never substantiated. To the contrary, there is now much evidence that the starting assumption of the BCS theory is violated: there is no evidence whatever that any of the non-superconducting metallic states realized in the cuprates has anything to do with the non-interacting fermion gas. To the contrary, the superconducting state is exceptional since it seems to comply to established principle while everything non-superconducting in cuprates is just weird and mysterious: the subject of the remainder of this story.

The crystal structure of the cuprates consists of simple square lattices of CuO<sub>2</sub> unit cells where all the action takes places, which are separated by electronically dead ionic spacer layers. The way that these layers are stacked together has a substantial (and poorly understood) influence on the maximal T<sub>c</sub> but in other regards the different cuprate families behave in very similar ways. There is actually much going on in the cuprates, as summarized in the iconic “phase diagram” of Fig.1, also highlighting the similarities with the heavy fermions and iron pnictides. It starts out with stoichiometric “parent” compounds that are insulating. By chemical substitutions in the spacer layers, carriers are injected in the CuO<sub>2</sub> layers (the x-axis of Fig.1a) having similar effects as doping a semiconductor: the system becomes more conductive and at a carrier density of 5% the superconductivity sets in. The T<sub>c</sub> is rising in the “underdoped” regime up, to go through a maximum around 20% (“optimally doped”) to decrease at higher doping (“overdoped”). At very high dopings the “normalcy” of the Fermi-liquid seems to re-establish itself with detrimental effects for the superconductivity. In the next section the special nature of the insulating state and the rich pseudogap state will be in the spotlights, while the last section is dedicated to the strange metal found at optimal doping.

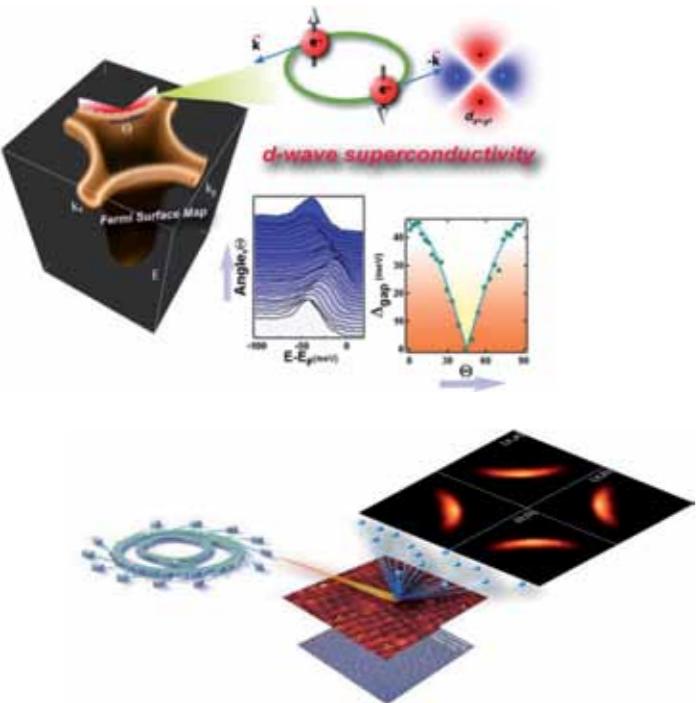


Fig.5 Photoemission measures directly the wave like properties of the electrons. A cartoon of how the technique measures directly the energy gap in the wave spectrum of the electrons associated with the presence of superconductivity (top), but also how the stripe patterns are reflected in this wave vector space in the form of the “pseudogap” (bottom). See <http://arpes.stanford.edu/index.html>

### 3. DOPING THE MOTT INSULATOR AND THE COMPLEXITIES OF THE PSEUDOGAP PHASE

The state of the “parent” compounds is quite interesting since it is insulating because of the domination of the electron repulsions: this “Mott insulator” is precisely the opposite of the Fermi-liquid. The active electrons in the copper oxide layers are derived from the rather localized 3d states of the Cu ions, impeding the itinerant motions of the electrons, with the effect that the “delocalization drive” of the electrons loses out against the electron repulsions. An electron world is now realized that has more dealings with rush hour traffic than with the eerie quantum fog found in conventional metals. In the parent compound there are just as many “parking spaces” (states per unit cell) as there are electrons and the effect is that the electron traffic comes to a standstill in a perfect traffic jam - the Mott insulator. Doping has now the influence of removing here and there an electron from the cuprate planes and one enters a regime being the electronic version of stop and go traffic on the congested highway. Although the completely localized Mott insulator has no secrets, this stop and go regime is the theorist’s hell [3]. None of the great mathematical weaponries of theoretical physics dedicated to strongly interacting quantum many body systems makes any difference when fermions are in the game. The Fermi-Dirac statistics introduces a kind of many particle entanglements (“fermion sign problem”) that cannot be handled by available field theoretical methods when one is away from either the non-interacting Fermi gas or the completely localized Mott insulator.

For the experimentalists it turned however into a paradise to try out their new “electron world telescopes”. Early on it became clear that in underdoped cuprates the density of electronic excitations are depleted below a characteristic temperature that is itself decreasing for increasing doping. Initially it was speculated that this “pseudogap temperature” (Fig.1) signalled the formation of “preformed” pairs while their Bose condensation was suppressed to a much lower superconducting transition temperature due to thermal fluctuations. Around 2000 thermal transport (“Nernst effect”) experiments showed that such fluctuation effects indeed do happen, but they set in at much lower temperatures, while their doping dependence is quite different from the pseudogap [8]. Instead, it became clear that the pseudogap temperature signals the onset of a whole zoo of “quantum matter” phenomena, coexisting with the (fluctuating) superconductivity and with each other. These were all unknown in 1986: (static-, fluctuating) stripes, quantum liquid crystal order and spontaneous diamagnetic currents.

The stripes were the first to be identified, in fact when my

person was taken by surprise staring at a computer output on a Friday afternoon in October 1987. I was playing with a quite imperfect computer simulation of a doped Mott insulator finding out that the “electron stop and go traffic” wanted to organize itself in interesting “striped” patterns corresponding with domains where the traffic is completely stuck interrupted by “rivers of charge” where the quantum motions are relatively free (Fig.2) [9]. Mottness goes hand in hand with magnetism since the spins of the localized electrons have plenty of room to organize themselves. In stripe phases this turns into a special form of “incommensurate” antiferromagnetism and in the 1990’s neutron scattering experiments that directly probe magnetic order revealed that these stripe phases are ubiquitous in non-superconducting doped Mott insulators (like Nickelates, cobaltates, manganites). In 1995 it was discovered that such “static stripes” also occur in special cuprates which are particularly bad superconductors [10]. Much later it was confirmed by the brand new technique of resonant soft X-ray scattering that the “rivers of charge” envisioned by the stripe picture do indeed form as well.

The community had to get used to the idea that such intricate organizations can occur in electron systems. The notion got fashionable after the arrival of the revolutionary scanning tunneling spectroscopy (STS) technique developed by Seamus Davis and coworkers early this century. With this technique the electronic excitations are measured by tunneling spectroscopy with a subatomic spatial resolution. The first results showed that although the electron system appears to be very homogeneous at energies that are low compared to the gaps, the magnitude of the pseudogap (directly seen in the tunneling) varies greatly on a length scale of 4-5 unit cells [11]. In 2006 a special energy integrated mode was developed through which the “Mott traffic jams” are directly probed, and with this technique the stripes became quite literally directly visible (see Fig.2).

In generic underdoped cuprates evidence for static stripe order in the bulk is missing. However, in its inelastic mode neutron scattering can also keep track of spins that are quantum fluctuating, and such measurements indicate that stripes are still formed at “short” (nanosecond) time scales. However, at longer times collective quantum fluctuations get increasingly stronger with the effect that at macroscopic times the stripes are completely delocalized: the “dynamical” stripes [12]. Although not obvious to the naked eye, the STS patterns of Fig.2 show that besides the stripish features the electron system tends to render the two directions in the lattice to be inequivalent. This in turn relates to yet another

form of order that was first identified by neutron scattering: it appears that the quantum fluctuating electron matter behaves differently in the two directions in the lattice. It signals that a quantum liquid is formed that has a spontaneous preference for one particular direction in the lattice. A similar ordering phenomenon occurs in classical liquids where it is called a nematic liquid crystal, employed on a large scale in displays (LCD = liquid crystal display). The orientationally ordered quantum liquid formed in the underdoped cuprates is therefore called “quantum nematic” [13].

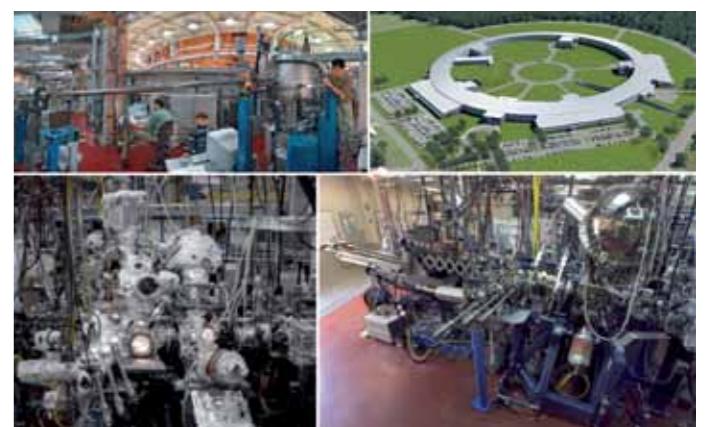


Fig.6 Photoemission uses synchrotrons as a light source (top), while the spectrometers themselves have become highly sophisticated machines.

The final surprise occurred in 2006. Following suggestions by the theorist Varma yet another completely unrelated form of order was identified by neutron scattering [14]. At the pseudogap temperature a pattern emerges of spontaneous quantum mechanical currents where the electrons move around on the bonds between the copper and oxygen atoms inside the unit cell. There is no precedent for such “spontaneous diamagnetic current order” elsewhere in physics. These circulating currents leave their mark on experiments in unexpected places and therefore it took so long to identify this rather sturdy order, but the evidences for it to be real have been accumulating rapidly in the last years.

Alltogether it took around 15 years for the empirical picture as sketched in the above to settle. It took time to get used to the new rules. The mathematically well understood conventional electron systems behave very differently in the sense that these tend to pick one or the other very simple order. The physics behind the occurrence of the pseudogap brew of coexisting, complex organizational phenomena is still quite mysterious. This enigma is further amplified by the results of

angular resolved photoemission measurements. The resolution of this technique improved by a factor of 1000 over the last twenty years and it has turned into a mighty telescope that is exquisitely sensitive to the quantum side of electron matter. Since it “lives” on the wave side of the particle-wave duality, it probes directly the quantum coherence properties of the electrons in momentum space. Photoemission reveals a very strange organization of this coherence in the pseudogap regime [15]. In some (‘nodal’) regions of momentum space the electrons behave quite wave-like, showing signatures of a conventional BCS gap developing with the superconducting order. However, in other (‘antinodal’) parts of momentum space the electrons seem to know everything about the competing orders and here the spectra indicate a complete absence of the quantum mechanical, wave like behavior of the electronic excitations. The theoretical explanation for this behavior is still completely in the dark.

#### 4. QUANTUM CRITICALITY AND THE BLACK HOLES OF STRING THEORY

Because there is much to study the pseudogap regime has been the main focus of the experimental research in the last decade. However, for the superconductivity it is just bad news. For increasing doping the pseudogap physics gradually fades away and there is little, if anything left of it at optimal doping. A new state takes over at temperatures above the superconducting transition. This “strange” metal is radically opposite to the “complex” pseudogap stuff since it behaves in very simple ways. In fact, this simplicity is just very unreasonable when viewed from a conventional reference point, but this is in turn greatly appealing to the physicist’s mind. The remarkable nature of the strange metal was recognized already in the late 1980’s [16]. Its simplicity imprints on all its physical properties, including the electrical resistivity which has become particularly iconic. Although the Fermi liquid is also very simple, the temperature evolution of its resistivity is still interesting. The quasiparticles are like balls scattering against obstacles, and the character of this pin ball machine is strongly dependent on temperature. At zero Kelvin it is about lattice imperfections, at low temperatures the quasiparticles scatter against each other, and at higher temperatures the thermal disorder in the lattice becomes important. The result is that the resistivity of a normal metal is an interesting function of temperature, with bums and wiggles revealing the temperature dependence of the pin ball machine. How different is the resistivity of the strange metal! The resistivity is as function of temperature a perfectly boring straight line, setting in at the melting point of the crystal at a searing hot 1000 degrees, until it suddenly drops down to zero at the superconducting transition.

At present it is widely believed that this simplicity finds its origin in a quantum mechanical clash between the pseudogap stuff at low doping and a normal Fermi-liquid metal that is re-established in the overdoped regime. This clash takes the form of a quantum version of the familiar thermal phase transitions found in classical matter [17]. In analogy with the critical state established at continuous thermal transitions, the system becomes scale invariant precisely at the critical point at optimal doping, but now it pertains to the quantum physics: the system quantum fluctuates in the same way on all scales from microscopic dimensions up to the macroscopic scale. Since this “quantum criticality” is associated with the fermionic electrons, it is quite different from the classical critical state because of the “fermion sign” entanglements. Precisely this aspect establishes the contact with string theory. Before turning to this aspect, why is it so that the quantum criticality idea got on the foreground in the condensed matter world?

The suspicion that the bad metal has dealings with quantum criticality was born in the early 1990’s. Since scale invariance is a potent symmetry principle in quantum physics, simple heuristic scaling arguments can be employed to explain aspects of the “unreasonable simplicity” [17]. It got new impetus recently by the developing consensus that the pseudogap does refer to a separate state of quantum matter that can therefore come to an end at a quantum phase transition. However, already in the early 1990’s the idea was used with great effect to “quantum-engineer” new superconductors. The Cambridge group of Lonzarich realized that in the family of so-called “heavy fermion” metals, containing 4f and 5f elements, one finds examples of magnetic transitions at a very low temperature. By applying (chemical) pressure or magnetic fields one can now attempt to press the transition temperature to zero, thereby “manufacturing” a quantum phase transition between a magnetic and non-magnetic heavy fermion metal. The outcome was glorious: right at the quantum critical point cuprate type strange metals do occur, while at low temperatures a “dome” of unconventional superconductivity appears “hiding the singularity” (Fig. 1) [16]. Since then a zoo of such ‘quantum critical’ heavy fermion superconductors have been discovered. The superconducting  $T_c$ ’s are in the single digit Kelvin range, but one can argue that the overall energy scales descending from the “chemistry” at the lattice scale are just much smaller in these 4f/5f systems compared to the 3d oxides. The last addition to this club of quantum critical systems might be the iron pnictides as discovered in 2007 with the second best  $T_c$ ’s after the cuprates (55 K). Although they are different from the cuprates, especially in the regard that these do not form Mott-insula-

tors, the most recent experimental findings point at some striking similarities: in their underdoped regime that starts with simple antiferromagnetism (Fig. 1) indications of complex pseudogap physics have been detected, while evidences are accumulating for bad metal behavior (including linear resistivities) in the optimally doped iron superconductors.

I have repeatedly emphasized that the theorists have played a rather marginal role, lacking apparently the capacity to mobilize truly powerful mathematics. Simple but incomprehensible physics as in the strange metal is then good news since it signals that there is such mathematics at work. A most fanciful mathematics-for-physics has been developed by the string theorists and since a few years the case has been developing that it is precisely this type of math that is at work in the high  $T_c$  problem. This is a quite serious affair: it is too early to claim victory but it has triggered a large research effort in the string theory community.

String theory is a highly mathematical affair and during its forty year history it has been driven forward by mathematical consistency requirements. Although the traditional aim of string theory has been to shed light on the quantum origin of space and time and so forth, it produced mathematical machines that are accomplishing breath taking feats. Although it is clear that these have somehow dealings with physics, the precise relation with phenomena observed in laboratories tends to be less obvious. Three years ago it was suddenly realized that their best machine (the so-called AdS/CFT correspondence) is actually directly addressing the nature of strongly coupled quantum critical matter which is of the kind discussed in this treatise [5]. The way it works sounds as far fetched science fiction when one hears it for the first time: the physics of quantum critical metals is encoded in the quantum physics of special black holes with the ramification that high  $T_c$  superconductivity should be viewed as a fancy version of Hawking’s black hole radiation! According to the correspondence the “fermionic entanglements” change completely the rules associated with conventional critical states and the theory predicts intriguing “hybrids” of Fermi-liquids and quantum critical states that have striking resemblances with experimental observations in the strange metals [18]. Such quantum critical matter becomes extremely unstable at low temperatures, while the black hole physics suggests that it represents a versatile building material to construct a variety of orderly and stable states. Although still under construction, the mathematics signals that quantum critical matter can be the origin of many competing states, including the Fermi liquid of the overdoped state and the exotic orders of the pseudogap phase. It is however already

firmly established that it codes for a mechanism causing superconductivity that is completely different from BCS [19]. The black hole version of the ‘naked’, zero temperature quantum critical state is in an absolute sense the most unstable of all collective quantum states in existence and the black hole physics demonstrates that the system has to get out of this mess already at a high temperature by adopting a stable superconducting ground state instead. This is accomplished without a manifest need for glue. Nothing is sure yet and it might all turn out to be nonsense. However, inspired by Einstein’s good example, I want to bet that Our Lord could not resist this particular opportunity to employ such breathtakingly beautiful mathematics in his creation.

#### REFERENCES

- Instead of references to the research literature I have included here a number of News and Views (N&V) and Perspective commentaries as they appeared in Nature and Science, respectively. These are intended to be easy to comprehend for the non-experts while they also form excellent entries to the research literature.
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On April 8, 2011 an IEEE Milestone Award (above) and a Dutch plaque presented by Philips Research, both commemorating 100 years of superconductivity, were presented to the president of Leiden University. They will be placed on the spot where the heliumliquefier was located and where superconductivity was discovered.

## COMMUNICATIONS

FROM THE

## PHYSICAL LABORATORY

OF THE

UNIVERSITY OF LEIDEN

BY

H. KAMERLINGH ONNES,  
*Director of the Laboratory.*

N°. 120<sup>b</sup>.

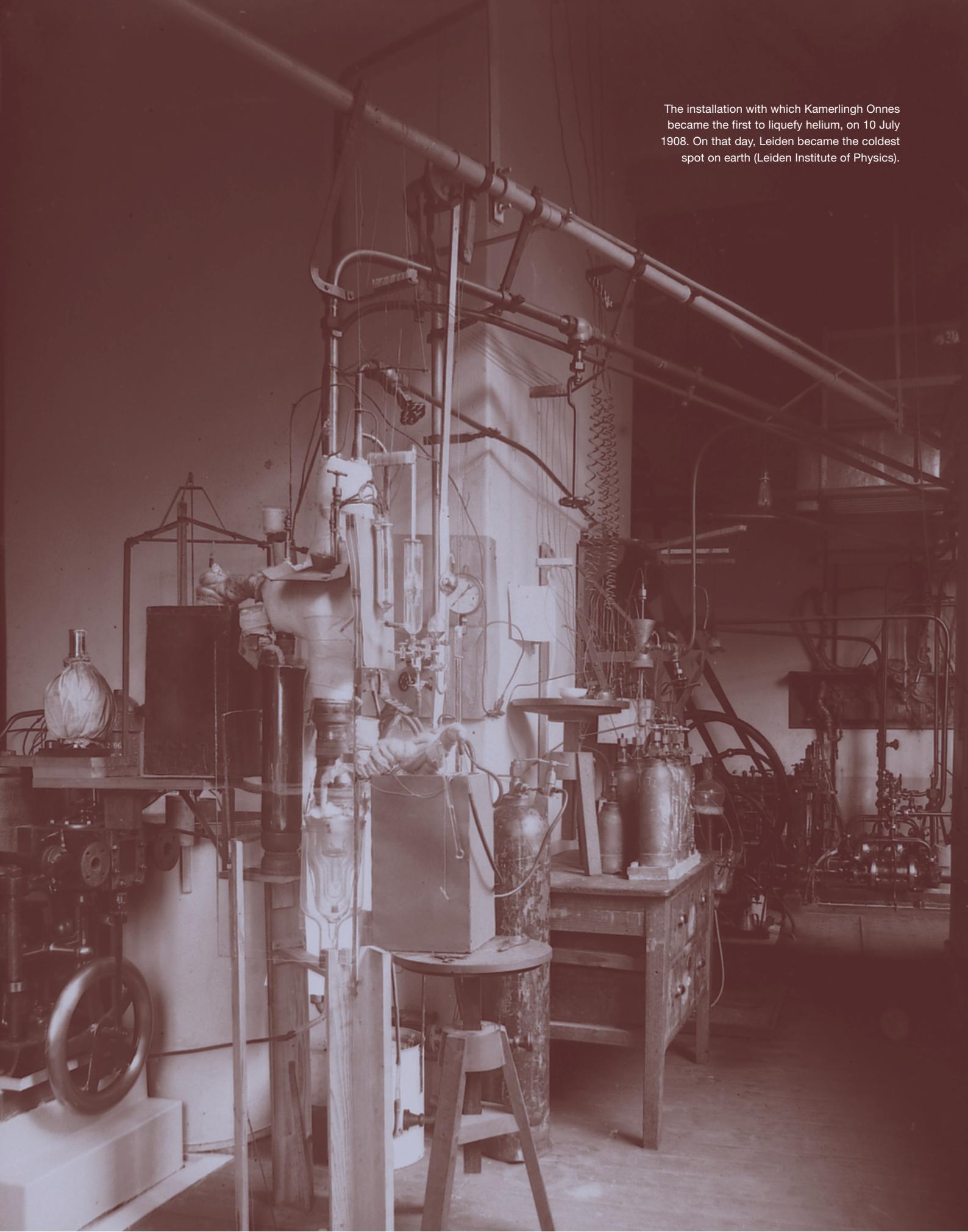
(REPRINT.)



**H. KAMERLINGH ONNES.** Further experiments with liquid helium. C. On the change of electric resistance of pure metals at very low temperatures etc. IV. The resistance of pure mercury at helium temperatures.

(Translated from: *Verslag van de Gewone Vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akad. van Wetenschappen te Amsterdam, 28 April 1911, p. 1479—1481.*)

EDUARD IJDO — PRINTER — LEIDEN.



The installation with which Kamerlingh Onnes became the first to liquefy helium, on 10 July 1908. On that day, Leiden became the coldest spot on earth (Leiden Institute of Physics).



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