THE DISCOVERY OF SUPERCONDUCTIVITY

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One hundred years ago, on April 8, 1911, Heike Kamerlingh Onnes and his staff at the Leiden cryogenic laboratory were the first to observe superconductivity [1]. In a frozen mercury wire, contained in seven U-shaped capillaries in series (see Fig. 1), electrical resistance suddenly seemed to vanish at 4.16 kelvin [2]. Short-circuit – an apparently obvious explanation – was excluded, but the question exactly what was going on would only receive a satisfactory answer at the fundamental level with the publication of the BCS theory in 1957 [3].

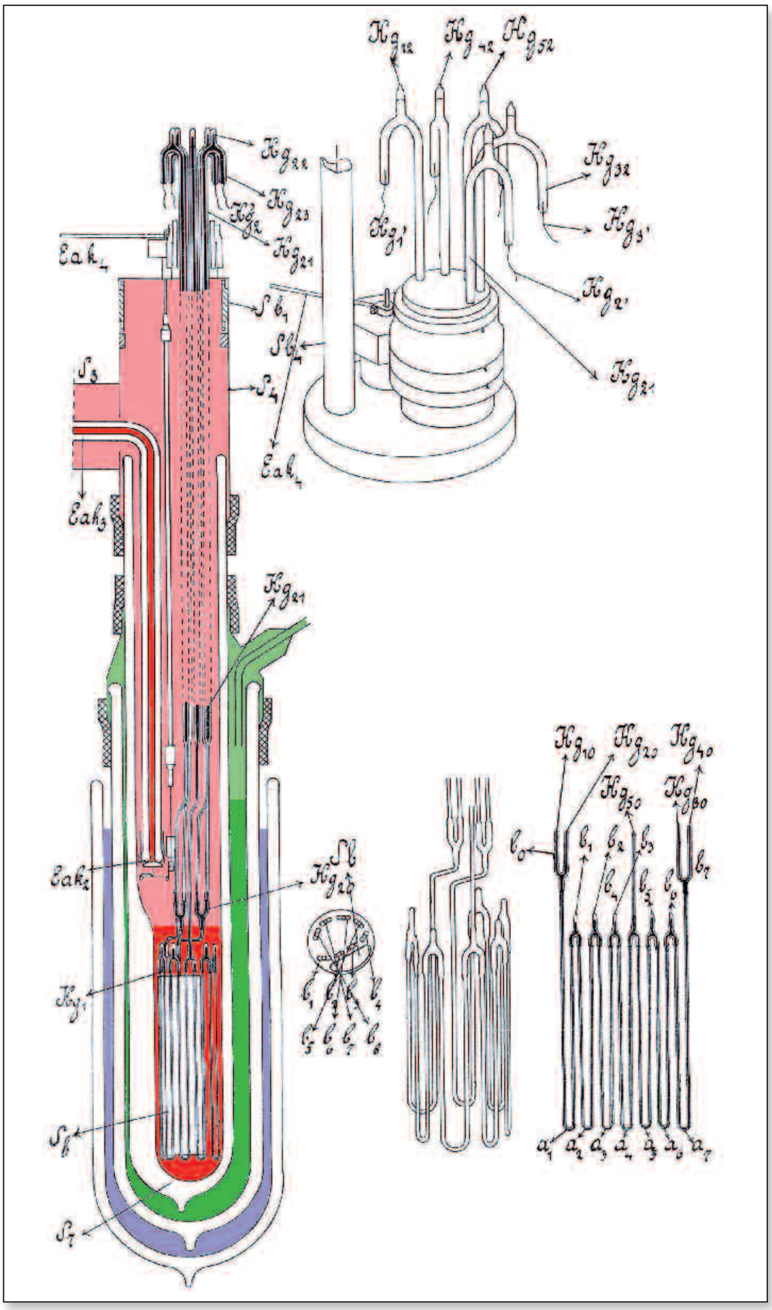
The discovery of superconductivity may have been accidental, but nonetheless the experiment was part of a carefully-considered research programme in Leiden. Studying the behaviour of the electrical resistance of metals (such as gold and platinum) at very low temperatures was interesting from both a practical and a theoretical point of view. Practical, because the fact that metal resistors were dependent on temperature made it possible to use them as (secondary) thermometers – thereby raising the possibility of a welcome addition to the (primary) gas thermometer which, although accurate, was cumbersome to use and slow in response. Theoretical, because Paul Drude had already applied the kinetic theory of gases to an electron gas in a metal in 1900, and on that basis had deduced the linear decrease in resistance with absolute temperature, while William Thomson (Lord Kelvin) had predicted one year later that at extremely low temperatures, the conducting electron would in fact become 'frozen solid' to the atoms, such that at absolute zero, resistance would become infinite [4].

▲ The Atlas detector of the Large Hadron Collider at CERN, Geneva

Mercury

Using liquid hydrogen as a coolant, Jacob Clay and other students of Kamerlingh Onnes had succeeded in carrying out experiments down to 14 kelvin (the freezing point of hydrogen) at the Leiden Physics Laboratory, starting in 1906. It was noted during these experiments that, although the resistance of gold and platinum wire did fall with decreasing temperatures, at the same time it started to level out [5]. The successful liquefaction of helium on July 10, 1908 gave a massive boost to this research because at a stroke, temperatures as low as 1 kelvin had suddenly been made achievable [6]. The result of these new measurements was that at such very low temperatures, resistances reached a sort of residual value, that became lower the purer the platinum or gold could be made [7] (see Fig. 2). The expectation, therefore, was that with very pure metal, as absolute zero was approached, resistance would become equal to zero.

▼ **FIG. 1:** **Cryostat with mercury resistor and mercury leads for the 26 October 1911 experiment: 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. A similar design, but with copper contact leads, was used at the April 8 experiment. External contacts were made through Pt wires (denoted by Hg_{xx}) shown in the top right drawing. Colors have been added to indicate various cryogenic fluids: liquid air (purple), liquid and gaseous hydrogen (dark and light green), and liquid and gaseous helium (dark and light red).**

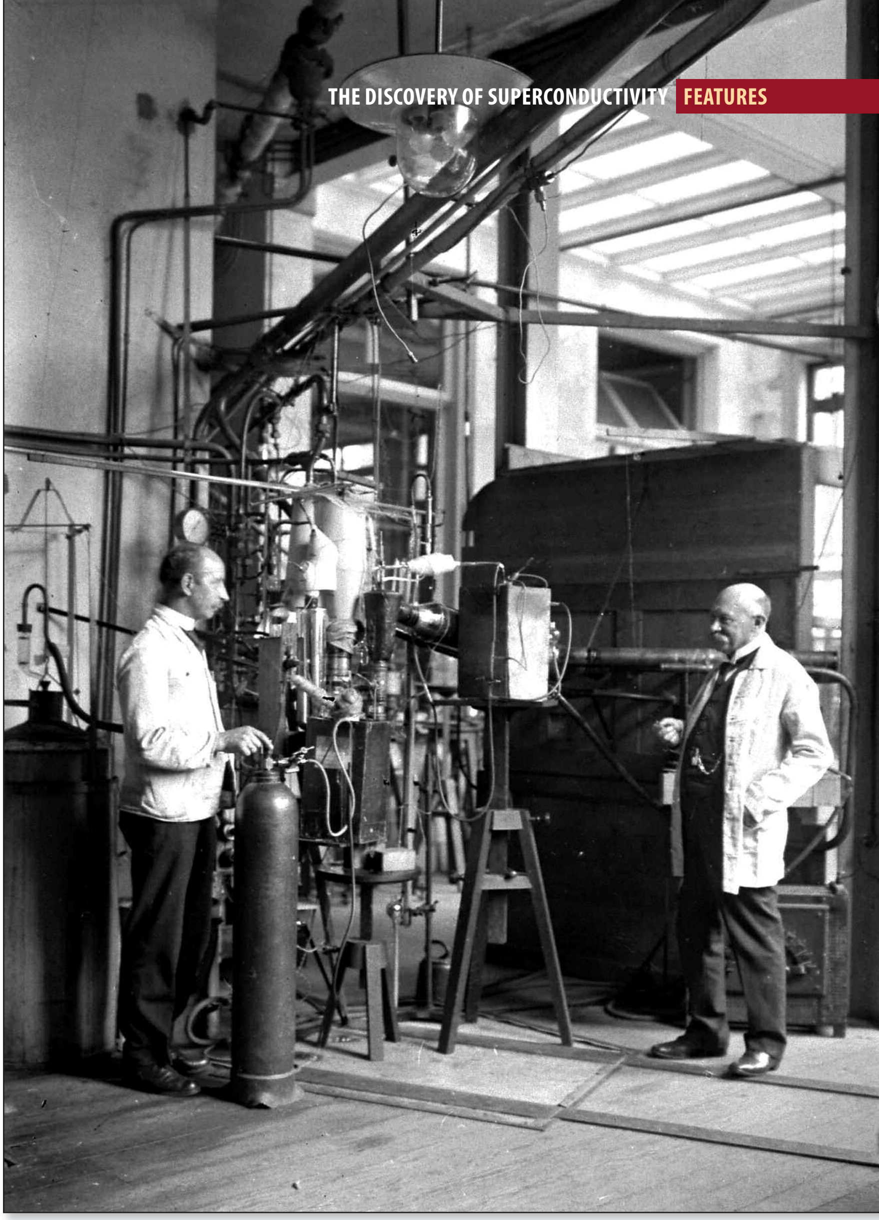


The logical next step was the choice of mercury since, via distillation, the metal could be made extremely pure. The capillary construction, a masterpiece of the Leiden-based glass blower Kesselring, was installed in the helium cryostat next to the liquefactor. The actual goal of the experiment was the test of the transfer system for liquid helium. During the decisive experiment on the 8th of April, 1911, Kamerlingh Onnes and Gerrit Jan Flim, head of the cryogenic laboratory and master instrument maker, were responsible for the cryogenic installations (see Fig. 3). Measuring the temperature (using a gas thermometer) was the task of Cornelis Dorsman, while the resistance of the mercury wire (and of gold) was determined via an electrical bridge circuit with a mirror galvanometer. The galvanometer was placed in a room at a safe distance from the throbbing pumps, on a vibration-proof column, and was monitored by Gilles Holst (who communicated via a speaking tube). The result of these experiments was that the mercury resistance did indeed fall to zero (see Figs. 4 and 5). However, the result was complicated by the occurrence of a transition temperature that could not be explained by theory [8].

New superconductors

In December 1912, mercury as a superconductor was joined by tin and lead, metals with a transition temperature of 3.8 and 7.2 kelvin, respectively. From then on, there was no need to experiment with fragile mercury capillaries. Experiments could now be carried out with handy coils of wire. The wires were cut from a cylinder jacket in tin or lead, using a chisel, a method that clearly generated better results than the mechanical drawing of wires. Using sections of wire soldered together to form a total length of 1.75 metres, a coil consisting of some 300 windings, each with a cross-section of 1/70 mm^2, and insulated from one another with silk, was wound around a glass core (see Fig. 6). One major stumbling block was that the critical current (threshold current) in a tin or lead wire, above which the superconductivity disappeared, was far lower in a coil than in a straight wire. Whereas in a straight tin wire the threshold current was 8 ampère, in the case of the coil, it was just 1 ampère. A similar situation applied to lead. Initially, Kamerlingh Onnes attributed this effect to poor welding or other extrinsic effects [9].

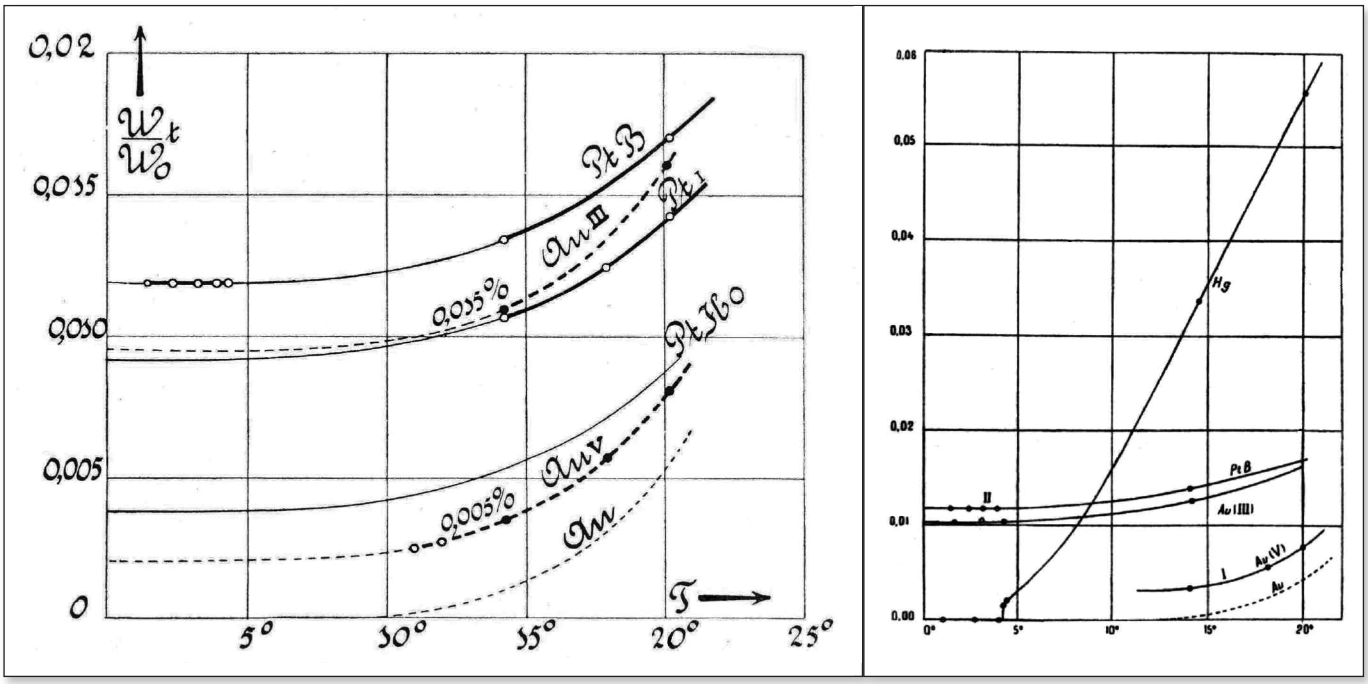
The wish was the father of the thought. The stakes were high: nothing less than a compact, powerful superconducting magnet. At the start of the century, Jean Perrin had already put forward the idea of a liquid-nitrogen-cooled magnet of copper wire, with a magnetic field of 100,000 gauss. Further quantitative analysis indicated that a giant magnet of this kind would require 100 kilowatt of power. The timely discharge of the heat would require at least 1500 litres of liquid air per hour, making this 'dream magnet' as expensive to build as a battle cruiser. The situation with superconductivity was different. At the third International Congress of Refrigeration in Chicago, in the autumn of 1913, Kamerlingh Onnes once again raised the issue of the super magnet. 'The solution to the problem of obtaining a field of 100,000 gauss could be obtained by a coil of, say, 30 centimetres in diameter, and the cooling with helium would require a plant which could be realized in Leiden with a relatively modest financial support', he wrote in his summary of the cryogenic work in Leiden. 'Since we may confidently expect an accelerated development of experimental science, this future ought not to be far away' [10]. In Chicago, George Claude, founder of Air Liquide, promptly took the initiative of providing financial

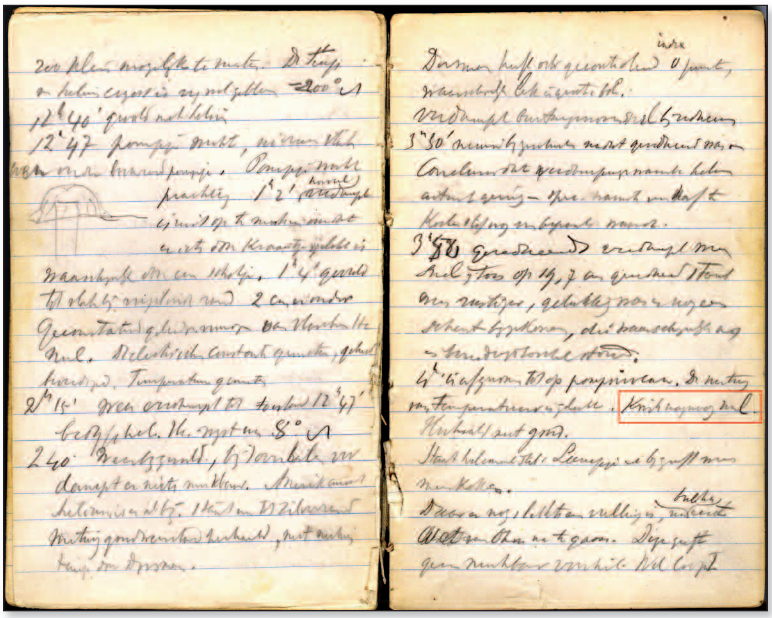


▲ **FIG. 3:** Gerrit Jan Flim (left), head of the Leiden cryogenic laboratory, and Heike Kamerlingh Onnes at the helium liquefier. Ca. 1920.

> **"The capillary construction was a masterpiece of the Leiden-based glass blower Oskar Kesselring"**

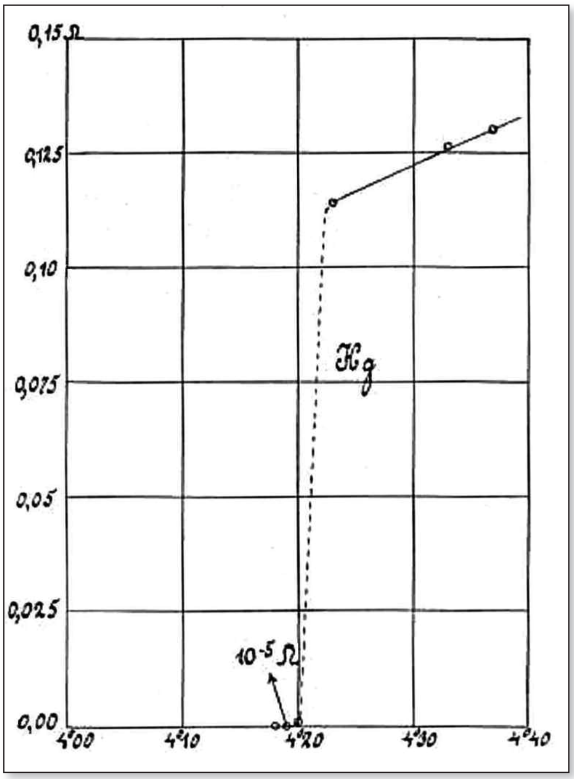
▼ **FIG. 2:** Resistance ratios of some metals versus temperature *T* in kelvin. Left-hand panel (a): Several platinum and gold resistors of various purities measured at different hydrogen temperatures. Pt-B was the first resistor ever to be cooled to helium temperatures in the experiment of 2 December 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 by a constant value, demonstrating that Matthiessen's rule is valid down to the lowest temperatures. Right-hand panel (b): The resistance ratio of Pt and Au compared to that of mercury (Hg, steep curve). Here, I denotes the temperature range of liquid hydrogen, II that of liquid helium.





▲ FIG. 4: A crucial page from the entry for 8 April 1911 in Kamerlingh Onnes's notebook. The highlighted sentence Kwik nagenoeg nul means "Mercury['s resistance is] practically zero [at 3.0 K]" announcing the first observation of superconductivity. On the page left the sketch of the functioning stirrer is seen. (Archive of the Boerhaave Museum, Leiden).

► support for Kamerlingh Onnes' superconducting magnet project to the tune of 100,000 francs (the outbreak of World War One threw a spanner in the works). Unfortunately, the disastrous effect of a magnetic field on superconductivity was rapidly revealed. On a lead coil at 4.25 kelvin, superconductivity disappeared when a field of just 600 gauss was applied [11]. As a consequence of this magnetically induced return of the resistance, the superconducting variant of Perrin's dream was totally shattered. It was not until the nineteen sixties that the powerful superconducting magnet was finally introduced, thanks to niobium titanium wire. This is a conventional superconducting material with a high threshold field, a large current density, and a transition temperature (T_c) of 9 kelvin. MRI scanners and deflection magnets in particle accelerators still make use of magnets of this kind. All we are now waiting for is suitably high T_c superconductors from which wires can be drawn in a technically manageable way, thereby eradicating the need for cooling by liquid helium.



► FIG. 5: Historic plot of resistance (Ω) 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 unmeasurably small (less than 10^{-5} Ω) to 0.1 Ω.

Applications

In fact, such wires already exist, but they are still relatively expensive and therefore they are only used in applications where best performance prevails over costs. For instance, the current leads from the room-temperature power supplies to the deflection magnets of the LHC at CERN are made of BiSrCaCuO. High T_c cables for electric power transport operating at liquid nitrogen temperature are currently being tested in several pilot projects. When successful, those cables will replace the high-voltage power lines of copper in urban areas and perhaps, in the near future, a world-wide net of such high T_c power lines will transport energy from durable energy power plants to big consumer concentrations.

The present situation is that superconductivity is mainly utilized for medical diagnostics (MRI systems) and for scientific purposes (particle accelerators and detectors, high-field NMR). These applications are based on the very high current densities without losses in magnetic fields of over 20 tesla which have been obtained in materials such as Nb-Ti and Nb_3Sn. This property makes these materials very suitable for the construction of a large variety of superconducting magnets. There is also an important market for low current superconducting electronics, predominantly based on the tunnelling of Cooper pairs (the Josephson effect , predicted and first observed in 1962) and the quantization of magnetic flux combined in Superconducting Quantum Interference Devices (SQUIDs). Very sensitive measuring equipment based on SQUIDs can be found nowadays in almost every solid state or materials physics laboratory.

One may thus conclude that today's utilization of superconductors has been made possible by the great discoveries and developments in the fifties and sixties of the last century. Just to name a few: the discovery of the isotope effect, the purity dependence of the penetration depth, the phenomenological Ginzburg-Landau theory, the Abrikosov theory of type II superconductors, the microscopic BCS theory and its extensions by Gor'kov, Bogoliubov, De Gennes, Anderson and Eliashberg, electron-phonon spectroscopy, the observation of flux quantisation, the prediction and discovery of the Josephson effect, the observation of flux line lattices, and so on [12, 13]. The latter demonstrated the existence of flux lines containing a single quantum of magnetic flux, as predicted by Abrikosov. Without flux lines and the pinning of flux lines, high critical currents would not be possible, and consequently high current applications would not exist. One can safely state therefore that the application of superconductors relies on superconductivity being a macroscopic quantum phenomenon. And one can also state that conventional superconductors are completely understood. A nice example is the recently discovered "high-temperature" MgB_2 ($T_c \approx 40$ K). Within a year of its discovery the conventional BCS-Eliashberg framework could tell us why this simple metal has such a surprisingly high critical temperature.

The "true" high-temperature superconductors are a totally different story. Life changed with the discovery of superconductivity in what essentially are doped insulators. As Beasley expresses it in his contribution to [13]: "Historically [...] there are clearly two epochs: *From Onnes to Bednorz and Müller*, and *After Bednorz and Müller*". The understanding of those strongly correlated, quasi two-dimensional electron systems like the doped cuprates or the recently discovered doped Fe pnictides is still evolving. It is an extremely exciting field with many deep questions that still wait for an answer. A nice and profound review of the progress made in the last two decades is given in [14].

From March 1, 2011 to April 1, 2012, Museum Boerhaave in Leiden will host the special exhibition 'Mercury practically zero. A hundred years of superconductivity'. See www.museumboerhaave.nl. ■

About the authors

Dirk van Delft is director of Museum Boerhaave, the

Dutch museum for the history of science and medicine, and extraordinary professor 'Heritage of the Sciences' at Leiden University. In 2007 he published *Freezing Physics. Heike Kamerlingh Onnes and the Quest for Cold* (Edita, Amsterdam).

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▲ **FIG. 6: Coil of lead wire (viewed along coil axis), used in 1912 by Kamerlingh Onnes and his co-workers and now in Museum Boerhaave.**

References

[1] The date 8 April 1911 emerged from Kamerlingh Onnes' own notebooks, and was recently confirmed. See Dirk van Delft and Peter Kes, *Physics Today* (September 2010) 38.

[2] H. Kamerlingh Onnes, *Proceedings* **13** II (1911) 1274. Also published as *Communications of the Physical Laboratory of the University of Leiden*, no 120b.

[3] J. Bardeen, L.N. Cooper and J.R. Schrieffer, *Physical Review* **108** (1957) 1175-1204.

[4] For an overview of experimental and theoretical advances in relation to conductivity, see Per Fridtjof Dahl, *Superconductivity, its Historical Roots and Development from Mercury to the Ceramic Oxides* (New York 1992) 13-49.

[5] H. Kamerlingh Onnes and J. Clay, *KNAW Proceedings* **10** I (1907), 207. *Comm.* **99c**.

[6] H. Kamerlingh Onnes, *KNAW Proceedings* **11** (1909),168. *Comm.* **108**.

[7] H. Kamerlingh Onnes, *KNAW Proceedings* **13** (1911), 1093. *Comm.* **119**.

[8] It becomes clear from this presentation of the course of events during the experiment, that the regularly recurring claim that Holst in fact discovered superconductivity is entirely unfounded. Holst, in 1914 appointed as first director at Philips Research, in fact never claimed that position.

[9] H. Kamerlingh Onnes, *KNAW Proceedings* **16** II, (1914), 987. *Comm.* **139f**.

[10] H. Kamerlingh Onnes, *Comm.* Supplement **34a**.

[11] See note 9.

[12] H. Kamerlingh Onnes *Symposium on the Origins of Applied Superconductivity – 75th Anniversary of the Discovery of Superconductivity* at the 1986 APPLIED SUPERCONDUCTIVITY CONFERENCE, September 28-October 3, 1986, Baltimore, Maryland, IEEE Transactions on Magnetics, MAG-23 (1987) 354.

[13] A book project "100 Years of Superconductivity" is underway with many (personal) scientific contributions which both give an account of the historic developments in the passed 100 years, but also the present view on the perspectives of superconductivity and its applications. See www.eucas2011.org the link "Book Project" for actual information.

[14] 'J. Zaanen, 'A modern, but way too short history of the theory of superconductivity at a high temperature', to appear in [13]. See also http://arxiv.org/abs/1012.5461