Heike Kamerlingh Onnes's Discovery of Superconductivity

The turn-of-the-century race to reach temperatures approaching absolute zero led to the unexpected discovery of electric currents that flowed with no resistance

by Rudolf de Bruyn Ouboter

Superconductivity—the disappearance of resistance in an electric current—is one of nature's stranger phenomena. Ten years ago this month, in what some called the "Woodstock of physics," hundreds of scientists crowded into a ballroom at the New York City Hilton to receive hurried reports of superconductivity at much higher temperatures than ever previously reported. Thirty years before that, John Bardeen, Leon N. Cooper and J. Robert Schrieffer established the theoretical foundations that best explained superconductivity. Almost forgotten in the search for theory, and for materials that superconduct at ever higher temperatures, is the work of the brilliant experimental physicist Heike Kamerlingh Onnes, superconductivity's discoverer.

Onnes was a man attracted to cold, which no doubt added to his enjoyment of the December day in Stockholm in 1913 when he received the Nobel Prize for Physics. His primary research goal was to quantify the behavior of gases at extremely low temperatures; the experimental program that allowed him to reach ever lower temperatures also led to the discovery of superconductivity.

Onnes was born in 1853 in Groningen, in the northeastern Netherlands. His father owned a roofing-tile factory, but his mother's more artistic temperament seems to have influenced the family. His brother and nephew became highly regarded painters, his sister married the well-known Leiden artist Floris Verster, and Onnes dabbled in poetry as a youth. A remnant of Onnes's poetic leanings can be found in his laboratory motto, *Door meten tot weten:* "Through measurement to knowledge." Onnes's passions, however, would be fully ignited only by his later pursuits in low-temperature physics.

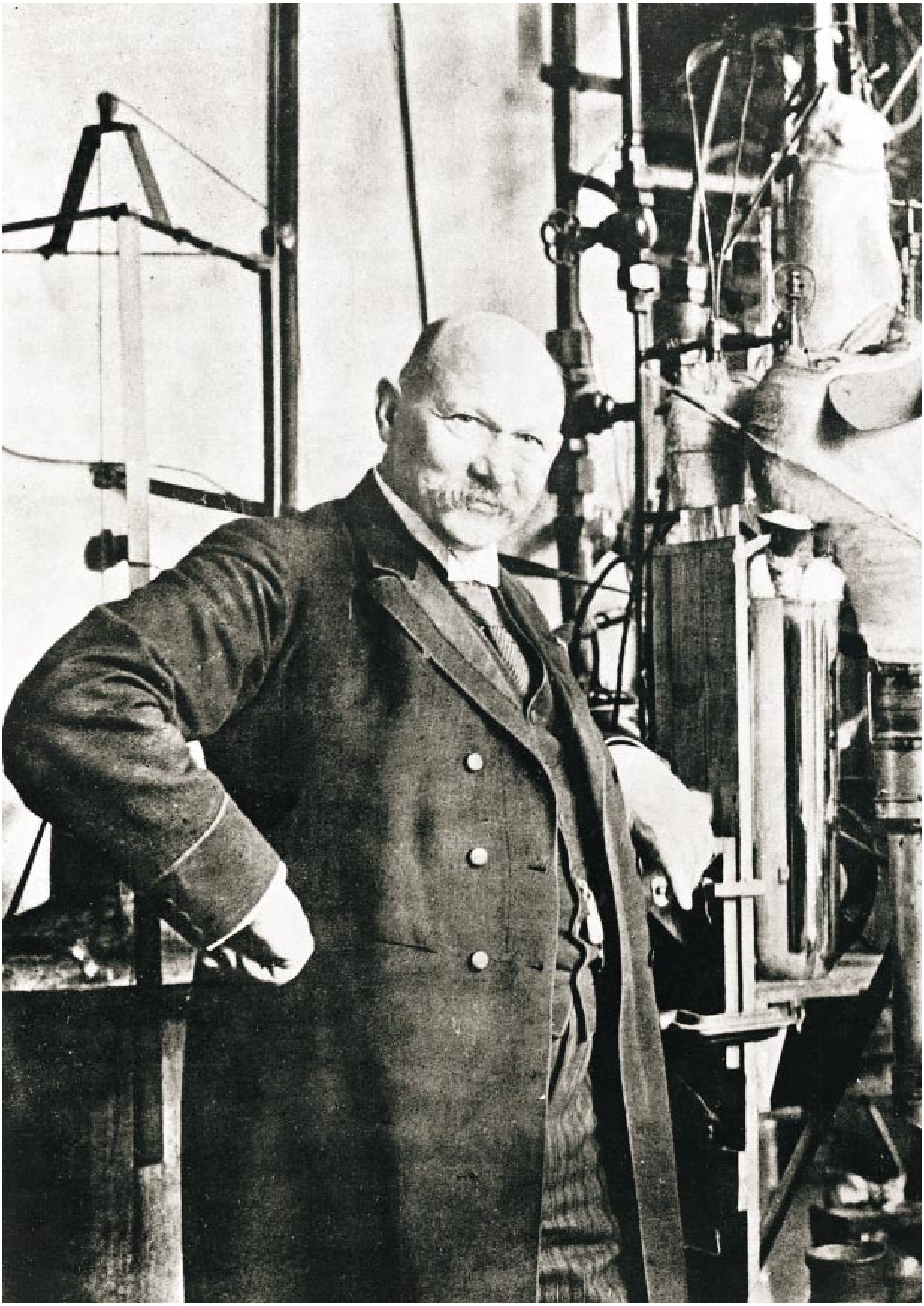
RON MAY

HEIKE KAMERLINGH ONNES stands in front of the apparatus he used to bring helium close to absolute zero and thereby liquefy it. As a by-product of this quest to reach extremely low temperatures, he serendipitously discovered the phenomenon he named "superconductivity." In recent years, superconductivity at ever increasing temperatures has raised expectations of expanding the market for devices that exploit the phenomenon. Above, a technician engaged in such research checks a coil submerged in inexpensive liquid nitrogen at a temperature of about 77 kelvins.

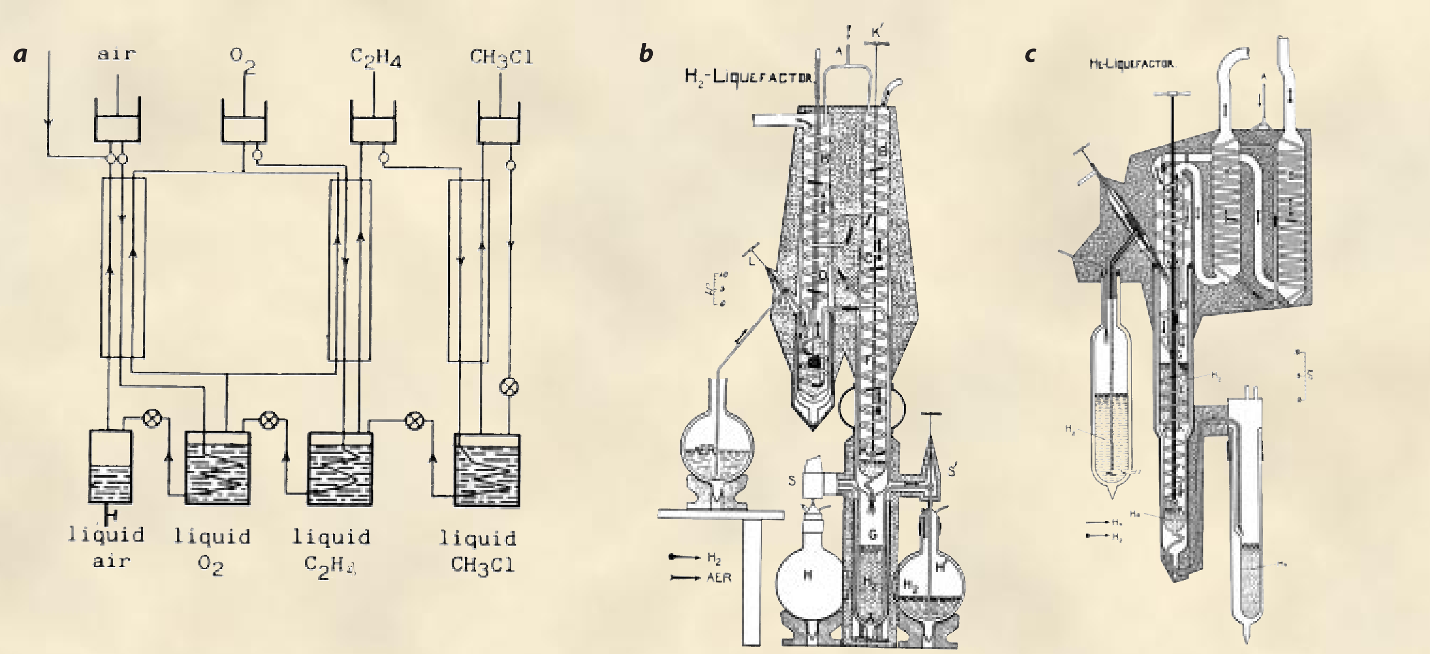
In 1870 Onnes enrolled at the University of Groningen to study physics. He apparently had a bit of wanderlust, as he transferred the following year to the University of Heidelberg in Germany, where he studied with the chemist Robert Bunsen (whose last name is familiar to everyone who has lit a burner in a high school chemistry laboratory course) and with the physicist Gustav Kirchhoff. In 1873 he returned to Groningen, where five years later he defended his doctorate on the influence of the earth's rotation on a short pendulum. Accounts allege that at the conclusion of that defense his examiners burst into applause.

Toward the end of his doctoral work, Onnes became acquainted with Johannes Diderik van der Waals, then professor of physics at the University of Amsterdam. The behavior of gases had been approximately known since the late 17th century, when Anglo-Irish scientist Robert Boyle showed that pressure was inversely proportional to volume at any given temperature. The resulting equations describing the behavior of gas pertained to a mythical perfect gas, whose molecules occupied no volume and exerted no forces on one another. As measuring techniques improved, however, chemists and physicists began to notice deviations from the perfect comportment of gases.

Van der Waals set about to develop a coherent description of real gases, taking into account the actual space occupied by real gas molecules, along with the forces they exert on one another. In 1873 he succeeded in formulating the van der Waals law, describing real gas behavior for individual gases; seven years later he published his law of corresponding states: a single equation accounting for the behavior of all real gases. Although Onnes's work in mechanics was exemplary, he found himself far



COURTESY OF THE KAMERLINGH ONNES LABORATORY, LEIDEN UNIVERSITY, THE NETHERLANDS



CASCADE APPARATUS (*a*) constructed by Onnes in 1892 could produce 14 liters of liquid air per hour. Liquid air was essential for operating the hydrogen liquefier (*b*) he perfected in 1906. The hydrogen gas travels through the system to a liquid air bath and ultimately to an expansion valve, which permits hydrogen gas to expand and liquefy. The liquid hydrogen is collected, while gas returns to the compressor. Onnes developed the first helium liquefier (*c*) in 1908. He posed with his mentor, Johannes Diderik van der Waals, in front of the device in 1911 (*d*) and, a decade later, with his chief assistant, Gerrit Flim (*e*).

more interested in following van der Waals's lead and exploring the behavior of gases.

Cascading toward Liquid Hydrogen

In 1882 Onnes was appointed professor in physics at Leiden University. Although quantitative techniques were the rule in mechanics and electromagnetic research, studies of matter, rather than forces, could still often be quite qualitative. Onnes set about to make quantitative analyses universal; mathematical rigor was essential for the scientific problems concerning him.

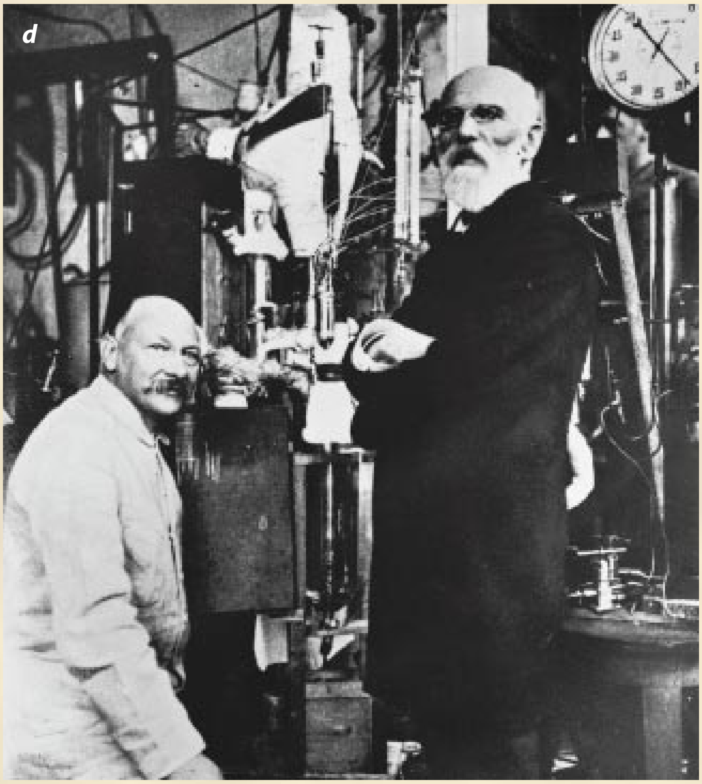
The only way to test van der Waals's ideas was to measure gaseous behavior at extreme conditions. At exceedingly low temperatures, for example, a particular gas deviates ever more greatly from the ideal gas laws, following instead van der Waals's predictions for real gases. The need for extremely cold conditions led Onnes to establish a cryogenic laboratory at Leiden. (The facility was renamed the Kamerlingh Onnes Laboratory in 1932.) The correspondent need for trained craftsmen to create the complex and delicate instruments necessary for cryogenic work led him to establish the Society for the Promotion of the Training of Instrument Makers. This school within the university churned out highly skilled technicians, including glassblowers, who would create devices for him and many other researchers around the world.

In 1877 French physicist Louis P. Cailletet and Swiss scientist Raoul P. Pictet independently succeeded in liquefying both oxygen and nitrogen. Before that achievement, many in the scientific community assumed that those gases, along with hydrogen, were perhaps beyond liquefaction. (Although helium had been seen in solar spectra, that gas would not be discovered on the earth until 1895.) The problem lay in achieving the exceedingly low temperatures required to condense these gases. The quantities of liquid that Cailletet and Pictet could produce were extremely small. Onnes, however, needed large amounts to conduct his research.

By 1892 Onnes had succeeded in developing an apparatus for producing those large amounts. The system took advantage of what became known as the cascade process—a series of gases with ever lower condensation temperatures are compressed, cooled to their liquefaction point and then expanded. The vapor coming from the evaporating liquid cools the next compressed vapor in the series. Starting with methyl chloride, which condenses at +21 degrees Celsius under five atmospheres (atm) of pressure, Onnes sequentially condensed ethylene (–87 degrees C at 3 atm), then oxygen (–145 degrees C at 17 atm), and finally air (–193 degrees C at 1 atm).

For the liquefaction of hydrogen, however, the temperature necessary would be significantly closer to absolute zero, making the construction of the apparatus more delicate. According to the laws governing the behavior of an ideal gas, at constant volume, the pressure falls with falling temperature. In theory, the pressure becomes zero at –273.15 degrees C (although real gases would already have liquefied). This temperature defines zero on the Kelvin scale and is called absolute zero because it is the lowest temperature attainable.

In 1898 James Dewar, the Scottish low-temperature physicist, beat Onnes to liquid hydrogen by taking advantage of a thermodynamic effect known as Joule-Thomson expansion: the temperature of a gas changes, usually going down, as it expands through a valve. Joule-Thomson expansion was used as part of the cascade process; Dewar made it central to his effort for liquefying hydrogen, because if hydrogen is first cooled to below –80 degrees C and then expanded, its temperature drops further.



COURTESY OF THE KAMERLINGH ONNES LABORATORY, LEIDEN UNIVERSITY (*a–e*)

(Curiously, above –80 degrees C, hydrogen warms if it expands, which is why this point is known as its inversion temperature.) In this way, Dewar drove hydrogen down to its liquefaction temperature of about –253 degrees C, or 20 kelvins.

Dewar's apparatus produced only small amounts of liquid hydrogen. That result was probably not a disappointment to him, however. Whereas Onnes seems to have been motivated by observations of gas behavior at low temperatures, Dewar's objective was simply to achieve temperatures approaching absolute zero. Nevertheless, it was Onnes who became known as "the gentleman of absolute zero."

Onnes was interested in producing much larger amounts of liquid hydrogen than Dewar had, which is one reason why he did not liquefy hydrogen until eight years after Dewar did. Another factor was a frightened Leiden community. In 1807, during the Napoleonic occupation of the Netherlands, an ammunition ship exploded in a canal in the center of Leiden. The Onnes laboratory was built on the ruins of the destroyed section of town. In 1896, when the town council learned that the laboratory housed considerable quantities of compressed hydrogen, a wildly combustible gas, the historical memory of the ship's explosion drove them into a panic. The authorities appointed a commission to study the matter, but even with the presence of van der Waals on that commission and a letter from Dewar imploring the council to permit the research to continue, Onnes's hydrogen work was shut down for two years.

Helium Becomes the Prize

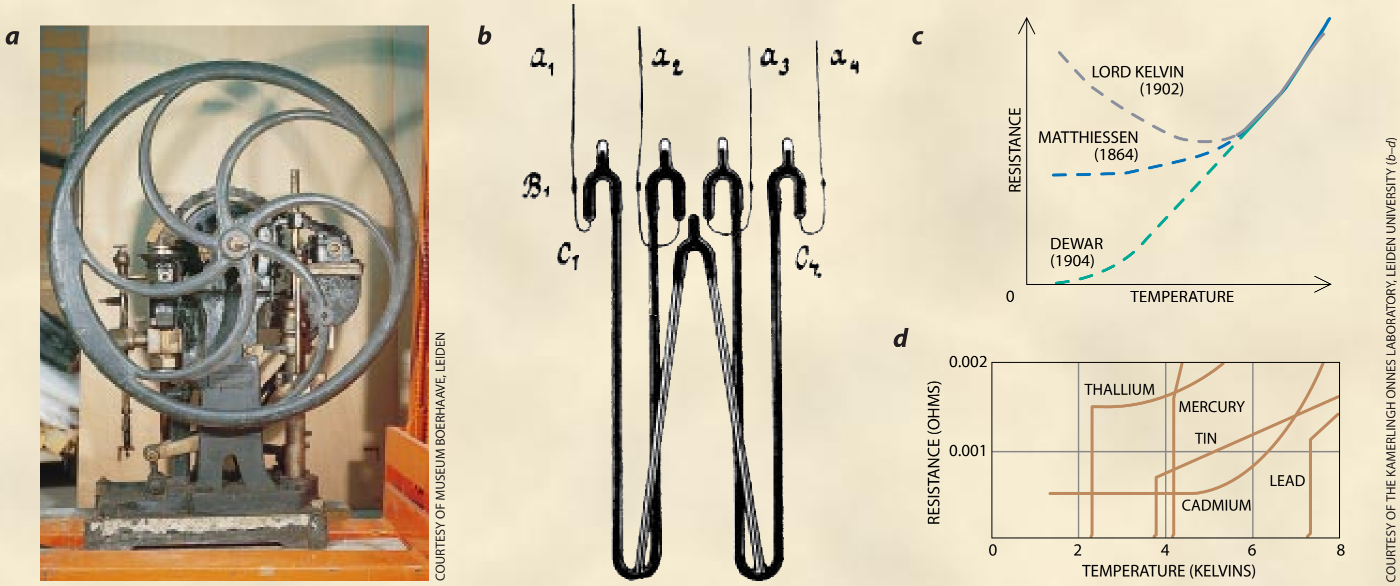
By 1906 Onnes and his team had developed an apparatus capable of producing relatively large amounts of liquid hydrogen via Joule-Thomson expansion. The liquefier compressed hydrogen gas, passed it through a region chilled by liquid air and then allowed it to expand, thereby cooling the hydrogen enough to liquefy at least some of it. Any remaining gaseous hydrogen was captured and returned to the system for another attempt. The apparatus could produce four liters of liquid hydrogen an hour at first and up to 13 liters with later improvements.

In 1895, while Onnes and Dewar had been attempting to liquefy hydrogen, William Ramsay in England discovered helium on the earth. Helium is the lightest of the inert gases; its atoms exert extremely weak forces among themselves. Those weak interactions contribute to an exceptionally low condensation temperature. Where the grail had been liquid hydrogen, it now became liquid helium. "I resolved to make reaching the end of the road my purpose immediately," Onnes wrote.

The first step was acquiring a sufficient amount of the recently discovered helium gas. Fortunately, Onnes's brother was director of the Office of Commercial Intelligence in Amsterdam, and he was able to arrange for large amounts of monazite sand, which contains helium, to be purchased from North Carolina. Onnes was able to extract about 300 liters of helium gas (at 1 atm) from the sand shipment.

The availability of a steady supply of liquid hydrogen was the key to the attempt to liquefy helium. Onnes designed a new apparatus, using liquid air and finally liquid hydrogen as the coolants. Again, a Joule-Thomson expansion would be tried to condense helium and obtain a few precious drops of liquid. The system was up and running on July 10, 1908, and word spread throughout the university. A small audience of scientists gathered to watch.

By midafternoon, helium gas flowed through the circuit, but no helium liquid was apparent by early evening, and the



COURTESY OF MUSEUM BOERHAAVE, LEIDEN

COURTESY OF THE KAMERLINGH ONNES LABORATORY, LEIDEN UNIVERSITY (*b–d*)

CAILLETET COMPRESSOR (*a*), invented by Louis P. Cailletet, who liquefied oxygen and nitrogen, was extremely useful to Onnes throughout his research. Because no gas is lost during compression or expansion, the device was suitable for working with pure and costly gases. A W-shaped capillary tube (*b*) carried the mercury wire used in the tests for mercury's resistance at low temperatures. Before Onnes began his investigations, the predicted behavior of metals (*c*) was quite different from what he actually found. He discovered that sharp drops in resistance (*d*) accompany decreasing temperatures for mercury and a number of other metals.

thermometer refused to go any lower than 4.2 kelvins. A chemistry professor who happened by, Fransiscus Schreinemakers, suggested that perhaps the thermometer reading had stopped declining because liquid helium was in fact already there but was simply hard to see. Onnes proceeded to illuminate the collection vessel from below. He later recounted that this was a wonderful moment, with the surface of liquid helium suddenly becoming clear against the glass wall of its vessel like the edge of a knife, and that he was overjoyed to be able to show liquid helium to van der Waals. By reducing the pressure, Onnes brought the temperature down to 1.7 kelvins, tantalizingly close to absolute zero for those days. They used helium gas thermometers to measure these extremely low temperatures. (At constant volume and low pressure, helium in the thermometer behaves closely enough to the mythical ideal gas to allow for temperature measurement: because pressure times volume is proportional to temperature, measuring the pressure at constant volume reveals the temperature.)

Over the next three years, Onnes devoted himself to developing better apparatus for using liquid helium in research. Merely moving the liquid from the vessel in which the helium condenses into a storage vessel presented great technical challenges. Finally, in 1911, a helium cryostat, which could maintain the liquid at a constant low temperature, was ready for investigating the behavior of other substances at the liquid-helium temperatures.

Cold and Currents

It was well known by this time that the electrical resistance in a metal decreased with temperature. Exactly what would happen to resistance at temperatures approaching absolute zero, however, was hotly debated. Lord Kelvin believed that the flow of electrons, which seemingly improved with decreasing temperatures as the lower resistance indicated, might actually stop altogether, the electrons becoming frozen in place. The resistance at absolute zero would thus be infinitely high. Others, including Onnes and Dewar, assumed that the decrease in resistance with falling temperature would continue in an orderly fashion, ultimately reaching zero at the zero temperature point. (In 1905 Walther H. Nernst of Germany showed that the laws of thermodynamics prohibit reaching absolute zero experimentally. Temperatures of 0.3 kelvin have since been reached using the rare isotope helium 3, and the demagnetization of atomic nuclei has produced temperatures as low as 0.00001 kelvin.) What actually happened was stunning and, given the understanding of matter at the atomic level in 1911, completely unpredictable.

Because impurities in a metal might disturb an electric current and confuse experimental results, Onnes decided to work with mercury. He could repeatedly distill liquid mercury at room temperature, thus producing a very pure sample for his low-temperature experiments. The mercury was incorporated into a U-shaped glass capillary tube with electrodes on both ends so that current could be measured passing through it while still liquid. Finally, the mercury was cooled to a solid wire. At all measured temperatures, the Onnes team found the expected regular decrease in resistance. At liquid-helium temperatures still measurably higher than absolute zero, however, the resistance already appeared to have completely vanished.

Onnes, Gerrit Flim, chief of the technical staff, and their co-workers Gilles Holst and Cornelius Dorsman performed the experiments. Onnes and Flim looked after the cryogenic apparatus in which the mercury was cooled, while Holst and Dorsman sat in a dark room 50 meters away, recording the resistance readings from the galvanometer.

Jacobus de Nobel, a researcher in the cryogenic laboratory of Leiden, recently recounted the story that he heard from Flim on arriving there as a young man in 1931. (Of course, one must be careful in taking these accounts too literally, for much time has passed, and the story is thirdhand.) Repeated trials all indicated zero resistance at the liquid-helium temperatures. The workers assumed that some kind of short circuit was responsible and replaced the U-tube with a W-shaped tube with electrodes at both ends and at the kinks, presenting four different segments for measurement. Again, the resistance was zero, and no short circuits could be found in any of the segments.

They continued to repeat the experiment. A student from the instrument-makers school was charged with watching the readings of a pressure meter connected to the apparatus. The helium vapor pressure in the cryostat needed to be slightly lower than the atmospheric pressure so that air would rush into any tiny leaks, freeze, and seal them. During one experimental run, the youngster nodded off. The pressure slowly rose, as did the temperature. As it passed near to 4.2 kelvins, Holst saw the galvanometer readings suddenly jump as resistance appeared.

According to de Nobel's story, Holst had unwittingly witnessed, in reverse, the transition at which mercury went from its normal conductive behavior into the state that Onnes would call "superconductivity." Repeated trials convinced Onnes that the sudden loss of mercury's resistance at about 4.2 kelvins was real. He published the finding in November 1911 as "On the Sudden Change in the Rate at Which the Resistance of Mercury Disappears." Subsequent tests of tin and lead showed that superconductivity was a property of numerous metals if they were cooled sufficiently.

By 1914 Onnes established a permanent current, or what he called a "persistent supercurrent," in a superconducting coil of lead. The coil was placed in a cryostat at low temperature, with the current being induced by an external magnetic field. With no resistance, the electrons in the coil were free to continue to flow indefinitely. After seeing the current, Austrian-Dutch physicist Paul Ehrenfest wrote to Nobel physicist Hendrik Lorentz in the Netherlands, "It is uncanny to see the influence of these 'permanent' currents on a magnetic needle. You can feel almost tangibly how the ring of electrons in the wire turns around, around, around—slowly, and without friction."

COURTESY OF THE KAMERLINGH ONNES LABORATORY, LEIDEN UNIVERSITY

DRAWING OF ONNES was done by his nephew, Harm Kamerlingh Onnes, in 1922.

Onnes was disappointed, however, to discover that even a minor magnetic field could quench superconductivity. This sensitivity meant that only small amounts of current could pass through superconducting materials despite the lack of resistance—the magnetic fields associated with currents of sufficient strength extinguished the superconductivity. This issue remained the biggest impediment toward practical applications of Onnes's discovery during his lifetime. Half a century would pass before materials were discovered and processed in ways allowing for large currents and associated magnetic fields. The magnetic resonance imaging (MRI) devices that have become mainstays of modern diagnostic medicine have been the best-known important practical application of the advances in superconductivity made in the second half of this century.

Heike Kamerlingh Onnes died in 1926. His accomplishments are all the more remarkable given that he suffered from a bronchial condition that forced him away from the laboratory for long periods of recovery in Switzerland. His physical absence apparently did not prevent Onnes from piloting his laboratory workers—even death did not stop him. According to Leiden legend, his funeral service lasted longer than expected, forcing the procession to rush through town to be on time for the scheduled burial in the nearby village of Voorschoten. As the procession hurried along, Gerrit Flim is said to have remarked, "That is the old man all right—even now he keeps us running."

Although superconductivity remained an esoteric scientific research area during his lifetime, Onnes firmly believed that the resistance-free current would eventually allow for the creation of many practical devices. Levitating trains and superconducting electrical transmission lines are two of the most frequently mentioned potential applications. The ongoing drive to discover materials that superconduct at more convenient temperatures may yet make Onnes's discovery a part of everyday life. SA

The Author

RUDOLF DE BRUYN OUBOTER is professor of experimental physics at the Kamerlingh Onnes Laboratory of Leiden University in the Netherlands. His research field is low-temperature physics, in particular the properties of superconductors, superfluid helium and mesoscopic Josephson junction devices. When not conducting research or teaching physics, he devotes himself to the history of science.

Further Reading

THE QUEST FOR ABSOLUTE ZERO: THE MEANING OF LOW-TEMPERATURE PHYSICS. Kurt Mendelssohn. Taylor and Francis, 1977.

SUPERCONDUCTIVITY: DISCOVERIES DURING THE EARLY YEARS OF LOW TEMPERATURE RESEARCH AT LEIDEN 1908–1914. Rudolf de Bruyn Ouboter in *IEEE Transactions on Magnetics,* Vol. Mag-23, No. 2, pages 355–370; March 1987.

THE PATH OF NO RESISTANCE: THE STORY OF THE REVOLUTION IN SUPERCONDUCTIVITY. Bruce Schechter. Simon & Schuster, 1989.

SUPERCONDUCTIVITY: THE NEXT REVOLUTION? Gianfranco Vidali. Cambridge University Press, 1993.

THE DISCOVERY OF SUPERCONDUCTIVITY. Jacobus de Nobel in *Physics Today,* Vol. 49, No. 9, pages 40–42; September 1996.