Kamerlingh Onnes and the Discovery of Superconductivity: The Leyden Years, 1911-1914
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# Kamerlingh Onnes and the discovery of superconductivity: The Leyden years, 1911–1914

EARLY IN SEPTEMBER 1882 Heike Kamerlingh Onnes, not yet 29 years of age, was appointed to the chair of experimental physics at the University of Leyden. He was to hold this chair for 42 years. His inaugural address, and particularly his speech on taking office as Rector Magnificus two years later, stressed the extreme importance he attached to quantitative measurements, especially in low temperature investigations.[1] His dedicated drive, stimulated by J. D. van der Waals's theory of imperfect gases, made Leyden a center of low-temperature research. By 1900 it was successfully challenging the dominance earlier held by laboratories in Paris, Crakow, and London.

The first reduction of a so-called "permanent" gas, oxygen, to liquid form had been made by L. Cailletet in Paris five years before Onnes's appointment at Leyden. In 1883 S. F. Wroblewski and K. Olszewski of Crakow first produced liquid oxygen "boiling quietly in a test tube." Olszewski subsequently attempted to liquefy hydrogen in a race now joined by Onnes and by James Dewar at the Royal Institution of London. The race was won by Dewar in 1898, and the following year he also succeeded in solidifying hydrogen.[2] At that point only one

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The following abbreviations are used: *AP, Annalen der Physik;* KO, Kamerlingh Onnes Collection, Museum Boerhaave, Leyden; *PLC,* Leyden, University, Physical Laboratory, *Communications; PLS,* Leyden, University, Physical Laboratory, *Supplements to the Communications; PM, Philosophical magazine; PZ, Physikalische Zeitschrift; RN,* Akademie der Wetenschappen, Amsterdam, *Proceedings*; *RS*, Royal Society of London, *Proceedings*; *SB*, Akademie der Wissenschaften, *Sitzungsberichte*.

1. Reprinted in translation in "The importance of accurate measurements at very low temperatures," *PLS,* 9 (1904), 3–30.
2. F. E. Hoare, L. C. Jackson, and N. Kurti, eds., *Experimental cryophysics* (London,

permanent gas, helium, remained to be liquefied. The race continued between Olszewski, Dewar and Onnes, and was joined by William Ramsay. All but Onnes were severely hindered by lack of helium gas.

Onnes owed his advantage to careful planning and systematic expansion of his laboratory. By 1894 he had completed plants for liquefying oxygen, nitrogen, and air on a large scale, and he could embark on his program of low-temperature measurements in connection with van der Waals's equation of state. In 1906 he had an efficient hydrogen liquefier. Soon thereafter he secured a good supply of helium gas. From its equation of state Onnes inferred that helium gas could be cooled below its inversion point in hydrogen under reduced pressure. The attempt was made on July 10, 1908. It began at half past five in the morning. The climax came thirteen hours later:[3]

> It was a wonderful moment when the liquid, which looked almost immaterial, was seen for the first time. It had not been perceived when it flowed into the glass; its presence could be detected only when the glass had been filled. Its surface stood out sharply defined like the edge of a knife against the glass wall. I was overjoyed when I could show liquefied helium to my friend van der Waals, whose theory had been my guide in the liquefaction up to the end.

That very day Onnes's team tried to solidify helium by evaporation under reduced pressure. Although the experimental arrangement ensured "that the pressure could decrease even to one centimeter, the helium still [did not cease] to be a liquid." The next year, 1909, Onnes repeated his attempt by reducing the vapor pressure over the liquid to 2 mm. Although the liquid still refused to solidify, the attempt did yield a temperature of 1.38°K. In 1910 a further effort, with the vapor pressure diminished ten-fold, to 0.2 mm, again failed of its purpose and again created a new low in temperature, 1.15°K, later reevaluated as 1.04°K. Onnes later emphasized not the failure but the novel temperature: "this failure with regard to the solidification of helium mean[t] a gain: a new region of temperature, which on account of its extreme situation is especially important, was proved to be accessible to us."[4]

Since 0.2 mm (or around 1°K) appeared to be the lowest vapor pressure (or temperature) then attainable, Onnes decided that the time

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1961), give a brief historical summary and principal original publications from Paris, Crakow, and London.

3. E. Cohen, "Kamerlingh Onnes memorial lecture," Chemical Society, *Journal,* 1927:1, 1193–1209, on 1202; Onnes, "The liquefaction of helium," *PLC, 108* (1908). The helium liquefier is exhibited at the Rijksmuseum voor de Geschiedenis van de Natuurwetenschappen en van de Geneeskunde (Museum Boerhaave) in Leyden.

4. Onnes, "On the lowest temperature yet obtained," Faraday Society, *Transactions, 18* (1922), 145–174, on 149.

was ripe for concentrating instead on various physical investigations in the newly accessible temperature range. (It was a wise decision since not until 1922 could Onnes report a further important lowering of temperature to "some hundredths of a degree below 0.9°K."[5]) He placed highest priority on determining the electrical resistance of metals as a function of temperature. This was to continue into the new region investigations that Onnes and Jacob Clay had been carrying on at the temperature of liquid hydrogen to corroborate and extend earlier measurements by Dewar.[6] Dewar's researches had revealed that the resistance of an unalloyed metal continuously diminishes with temperature and appears to approach a definite asymptotic value, seemingly not reducible by further lowering of the temperature.

Onnes's discovery of superconductivity followed on his work with Clay and on the gradual uncovering of discrepancies between the theory that had guided their research and the outcome of experiments at liquid-helium temperatures. I begin with the theoretical and experimental equipment of Onnes's group around 1910. I continue with Onnes's adaptation of quantum theory and his recognition of superconductivity in 1911. The paper ends with accounts of the definitive work on superconductivity and its subtleties at low temperatures during the years just before the first world war.

## 1. THE EQUIPMENT OF 1910

### Theoretical

The first successful theory of the electrical and thermal properties of metals was started by Eduard Riecke and Paul Drude around 1900.[7]

5. Ibid., 173.

6. Onnes and Clay, "On the measurement of very low temperatures, XI. A comparison of the platinum resistance thermometer with the hydrogen thermometer," *RN, 9* (1907), 207–213 (*PLC, 95c,* 39–45); "On the measurement of very low temperatures, XII. Comparison of the platinum resistance thermometer with the gold resistance thermometer," *RN, 9* (1907), 213–216 (*PLC, 95d,* 49–52); "On the change of the resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures," *RN, 10* (1908), 207–215 (*PLC, 99c,* 17–26); "On the change of the resistance of pure metals at very low temperatures and the influence exerted on it by small amounts of admixtures," *RN, 11* (1909), 345–346 (*PLC, 107c,* 19–27); J. Dewar, "The nadir of temperatures, and allied problems," *RS, 68* (1901), 360–366, and "On electric resistance thermometry at the temperature of boiling hydrogen," *RS, 73* (1904), 244–251.

7. E. Riecke, "Zur Theorie des Galvanismus und der Wärme," *AP, 66* (1898) 353–389, 545–581; "Über das Verhältnis der Leitfähigkeiten der Metalle für Wärme und für Elektricität," *AP, 2* (1900), 835–842; P. Drude, "Zur Elektronentheorie der Metalle," *AP, 1* (1900) 566–613.

They treated an electric current in a metal as a drift of an electron "gas" under the influence of an electric field. Assuming that the electron drift velocity $u$ under the electric field $E$ is much less than the average electron velocity $v$ of thermal motion (the gas velocity), and that the electron loses all of its original momentum in colliding with a metal molecule, Riecke and Drude wrote $u = Eet/2m$, where $e$ and $m$ represent the electronic charge and mass, and $t$ the average time between successive collisions. The current density is $J = neu = nEe^2t/2m$, with $n$ the number of free electrons in unit volume. The time can be replaced by $\lambda/v$, $\lambda$ the mean free path, to give Ohm's law for the conductivity $\sigma$:

$$\sigma = \frac{J}{E} = \frac{e^2 n\lambda}{2mv} . \tag{1}$$

To obtain temperature dependence, the classical theorist supposed that the electrons are in thermal equilibrium with the metal atoms or molecules, and so could equate the kinetic energy of an electron to the mean translational kinetic energy of a gas molecule at the same temperature: $mv^2/2 = 3kT/2$, where $k$ is the Boltzmann constant. On substitution for $v$ in equation (1),

$$\sigma = \frac{1}{6}\frac{e^2 n\lambda v}{kT} . \tag{2}$$

This is Drude's celebrated expression for $\sigma$; it differs slightly from Riecke's in the numerical constant because of a difference of little consequence in kinematic treatment.

A temperature gradient in a metal will also cause an electron current to flow. Drude's expression for the coefficient of thermal conductivity is $K = nv\lambda k/2$, making the ratio between the thermal and electric conductivities the same for all metals at the same temperature, $K/\sigma = 3(k/e)^2T$, in agrement with the old rule of Wiedemann and Franz. Again Riecke's and Drude's expressions differ slightly in the numerical constant, which underwent several revisions in the ensuing years.

The most significant of these revisions resulted from H. A. Lorentz's refinement of the theory, which treated the velocity of the electrons as a statistical quantity in accordance with Maxwell's velocity distribution. His results differed little from Riecke's and Drude's, however, and did not remove the basic weakness of the earlier theory: neither provided basis for calculating a priori the variables $n$ and $\lambda$ as a function of temperature.[8]

8. H. A. Lorentz, "The motion of electrons in metallic bodies," *RN*, 7 (1905), 438–453, 585–593, 684–691; *The theory of electrons* (Teubner, 1909), 266–273.

The measurements of Onnes and Clay, and those of M. W. Travers and A. G. C. Gwyer in England,[9] who followed up Dewar's investigations, had confirmed an approximately linear depedence of resistance on temperature down to the temperature of liquid hydrogen. To fit these data the product $n\lambda\nu$ in equation (2) must be independent of temperature. Since, however, by assumption $\nu \propto \sqrt{T}$, the free-electron theory requires $n\lambda \propto 1/\sqrt{T}$. Returning to the problem in 1909, Riecke made the assumption, which he regarded as dubious, that $n$ is independent of temperature.[10] If so, $\lambda$ must be proportional to $1/\sqrt{T}$, a relation he justified by assuming closely-packed cubically-arranged atoms at the melting point. It would seem more plausible that $n\lambda$ should increase with temperature owing to increasing molecular dissociations and more space for the freely moving electrons. Moreover, the Thomson effect, the flow of heat caused by an electric current in a non-uniformly heated conductor, requires that $n$ go as $T^{1/2}$ or possibly as $T^{3/2}$, which would make $\lambda$ proportional to $1/T$ or $1/T^2$. In either case theory predicted that resistance would vary with temperature below the boiling point of hydrogen more slowly than indicated by the ongoing low-temperature measurements. Insight into this problem came with resolution of a much more serious difficulty in the classical electron theory: its conflict with measured specific heats of solids.[11]

Although neither the Riecke-Drude theory, nor its modifications, seemed able to account for the experimental data becoming available at the lowest temperatures, the Leyden effort seems to have been strongly driven by an assumption widely thought to be a natural consequence or inference from the theory: near absolute zero the density of the free electron gas should diminish, going to zero at absolute zero with the electrons condensing onto the atoms. On this assumption, metallic resistance should increase indefinitely as the temperature tends to zero. The asumption, which followed naturally from the notion of electrons as a substance characterized by an equation of state, was expressed repeatedly by Onnes and his co-workers between 1904 and 1908, and by many others including Lord Kelvin and J. Koeningsberger.[12] It

9. M. W. Travers and A. G. C. Gwyer, "On the comparison of the platinum scale of temperature with the normal scale at temperatures between 444° and -190°C., with notes on constant temperatures below the melting point of ice," *RS, 74* (1905), 528–538.

10. Riecke, "Die jetzigen Anschauungen über das Wesen des metallischen Zustandes," *PZ, 10* (1909), 508–519.

11. J. J. Thomson, *The corpuscular theory of matter* (London, 1907), 79; E. F. Burton, *The phenomenon of superconductivity* (Toronto, 1934), 85–88; W. Hume-Rothery, *The metallic state* (Oxford, 1931), 175.

12. Onnes (ref. 1); J. Becquerel and H. Kamerlingh Onnes, "The absorption spectra of the compounds of the rare earths and the temperature obtainable with liquid hydrogen, and their change by the magnetic field," *RN, 10* (1908), 592–603, on 597 [*PLC 103*, 3–16]. Lord Kelvin, "Aepinus atomzied," *PM, 3* (1902), 257–283; J. Koeningsberger and

suggested that a minimum should occur somewhere in the curve of resistance versus temperature:[13]

> We may account for [the supposition that the resistance of metals near absolute zero should increase infinitely] by observing the actions which the dynamids [the electrical dipoles that constitute atoms in Lenard's model] exercise on the electrons, especialy on those which are deprived of their satellites. It seems as if the vapour of electrons which fills the space of the metal at a low temerature condenses more and more on the atoms. Accordingly, the conductivity, as Kelvin has first expressed it, will at a very low temperature reach a maximum and then diminish again till absolute zero is reached, at which point a metal would not conduct at all, any more than glass. The temperature of the maxima of conductivity [lies] probably some times lower than that of liquid hydrogen. At a much lower temperature still, there would not be any free electrons left, the electricity would be congealed, as it were, in the metal. As yet it does not seem possible to attain the temperature at which conductivity reaches a maximum, but the very great importance attached to observations of the conductivity of metals at extremely low temperatures—where also the investigation of the influence of small admixtures on the conductivity play[s] a part—urges on to numerous researches which may be said to lead to the equation of state of the electrons.

Dewar's resistance measurements in liquid hydrogen had indicated that in this temperature region the resistance of platinum, silver, gold, and even mercury dropped at a conspicuously slow rate. Indeed, measurements on mercury from below its melting point upward, going back to 1896, had shown that the "curve connecting [its] resistance...with temperature, throughout this range...was somewhat like the disused old English ʃ."[14] But Dewar could not decide whether the curve of resistance versus temperature goes through a minimum since he could not reach below the temperature of solid hydrogen, or approximately 16°K. The measurements of Onnes and Clay confirmed Dewar's results, again with no evidence for a re-rise in the resistance of platinum. Still, the flattening trend in the resistance curve strengthened Onnes's belief that the linear resistance of very pure metals observed at liquid-air temperatures and above could not reasonably prevail at very low temperatures; extrapolation of the available data would imply a negative resistance at absolute zero, or at least the equally implausible vanishing of resistance somewhere *above* absolute zero.

O. Reichenheim, "Über ein Temperaturgesetz der elektrischen Leitfähigkeit fester einheitlicher Substanzen und einige Folgerungen daran," *PZ, 7* (1906), 570–578; J. Koenigsberger and K. Schilling, "Über Elektrizitätsleitung in festen Elementen und Verbindungen," *AP, 32* (1910), 179–230.

13. Onnes (ref. 1), 28.

14. Dewar (ref. 6), 249.

## Experimental

In late fall of 1910 Onnes resumed his resistance measurements in collaboration with Cornelis Dorsman and Gilles Holst.[15] Their results, published the following February, were obtained using the liquefier-cryostat shown on the left of figure 1. The liquefier closely resembled the original one of 1908, and the cryostat was an integral part of it. The helium gas was cooled in stages: (1) in liquid air (upper part of far-left dewar), (2) successively in hydrogen abducted (pumped off) as vapor (Da) and in helium (Db), (3) in a liquid air-cooled charcoal air trap (lower part of far-left dewar), (4) refrigerating tubes cooled by liquid air and evaporated liquid hydrogen (upper and central sections of main right-hand dewar), and (5) a refrigerating tube in liquid hydrogen evaporating under reduced pressure (further down, main dewar). After following a regenerating coil (A) the gas was finally expanded, and the liquid collected in the inner silvered glass dewar of the multiple-walled cryostat ($E_A$) at the bottom of the figure. This inner vessel, also depicted to a larger scale, was thermally insulated, in turn, by liquid hydrogen, hydrogen gas, liquid air, and alcohol. In addition to serving as the liquid-helium reservoir, it contained a helium thermometer for measuring the bath temperature, the resistance element (denoted by $\Omega$), a dilatometer ($\Delta$), and a control dilatometer ($\delta$). Since stirring was not possible, a copper rod (Cu) conducted away heat to insure that the bath temperature remained as constant as possible.

Although the experimenters nevertheless had trouble maintaining a constant bath temperature, their arrangement allowed a maximum vapor-pressure gradient corresponding, at the lowest temperatures, to a temperature difference of only 0.06 degree. The helium thermometer, a conventional constant-volume thermometer with "zero" pressure equalling 14.5 cm, was accurate to about 0.1 degree, the limitation set by the low pressures at helium temperatures (approximately 1 mm). The apparatus at the far right in figure 1 regulated and measured the pressure; that in the center of the figure, connected to the dilatometer at the point marked $\Delta_3$, measured the mass of helium volumetrically in the cryostat, and is not of significance for the resistance measurements.[16] The resistance $\Omega$ was a fine platinum wire, previously

15. Onnes, "On the change in the resistance of pure metals at very low temperatures, etc., III. The resistance of platinum at helium temperatures," *PLC, 119b* (1911), 1–29.

16. It is worth noting, however, that density measurements performed in this series of experiments appeared to suggest that liquid helium reaches maximum density near 2.2°K. The result puzzled Onnes, who did not expect that a substance of such simple constitution as helium should have a maximum density (ibid., 15). They were observing a superfluid property elucidated much later at Leyden and elsewhere. Cf. F. London, *Superfluids* (2 vols., New York, 1954), esp. *2,* 1–17.

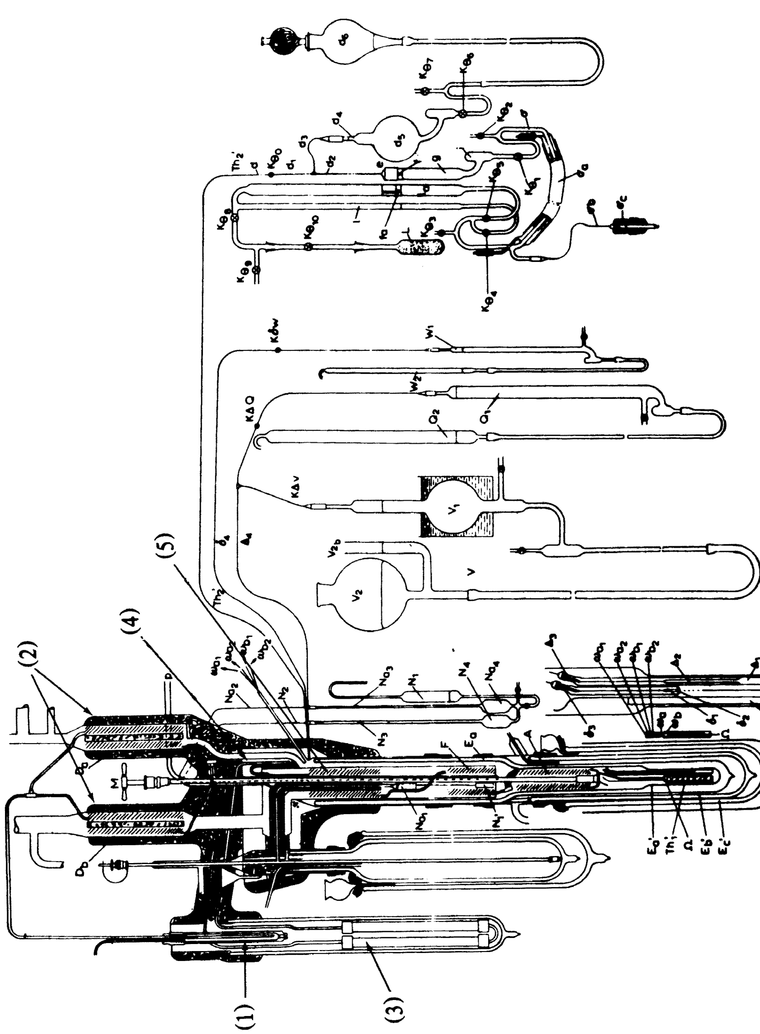

FIG. 1 Liquefier-cryostat arrangement for experiments with mercury in late 1910.

calibrated at hydrogen and higher temperatures, wound tightly on a glass cylinder by being wound while hot. A pair of double platinum leads ($Wa_1$, $Wa_2$, $Wb_1$, $Wb_2$) passed out of the cryostat (near the top of the figure).

TABLE 1

**Resistance** *W* of platinum wire PtB

| $T$ | $W_T/W_0$ |
|---|---|
| 273.09°K | 1 |
| 20.2 | 0.0171 |
| 14.2 | 0.0135 |
| 4.3 | 0.0119 |
| 2.3 | 0.0119 |
| 1.5 | 0.0119 |

The resistance values, measured with a Wheatstone bridge, are tabulated in Table 1 as ratios of the resistance at the temperature of observation to the resistance at 0° (assumed to be 273.09°K) versus absolute temperature. Far from approaching zero at absolute zero, much less rising after reaching a minimum, the resistance reached a constant but finite value extending down to at least 1.5°K. The results are also plotted as the curve designated PtB (denoting the reistance sample utilized in the experiment) in figure 2, which illustrates the striking asymptotical approach to a constant residual value.

The influence of impurities in the platinum specimen had to be evaluated before much significance could be attached to the results. Noting the similar departure from a linear dependence on temperature shown by several species of gold of different degrees of purity in earlier measurements, Onnes plotted these measurements (heavy dashed curves denoted AuV and AuIII) together with those on PtB.[17] The estimated percentage of impurities are indicated in the figure. Extrapolating these data to lower temperatures (light dashed curves) again suggested the onset of a constant residual resistance in the helium temperature range, whose value is lower the purer the specimen is. This tendency, which had been established in the hydrogen temperature range by Onnes and Clay as early as 1907, supported Onnes's conclusion of 1911: "the influence of admixtures can be represented with rough approximation even down to hydrogen temperatures by an additive resistance that is independent of the temperature."[18] (The

17. Onnes and Clay, *PLC, 99c* (ref. 6), 9–14. A comprehensive summary of resistance measurements at low temperatures up to 1911 is given in J. Clay, "Der galvanische Widerstand von Metallen und Legierungen bei tiefen Temperaturen," *Jahrbuch der radioaktivität und elektronik, 8* (1911), 383–406.

18. Onnes (ref. 15), 20.

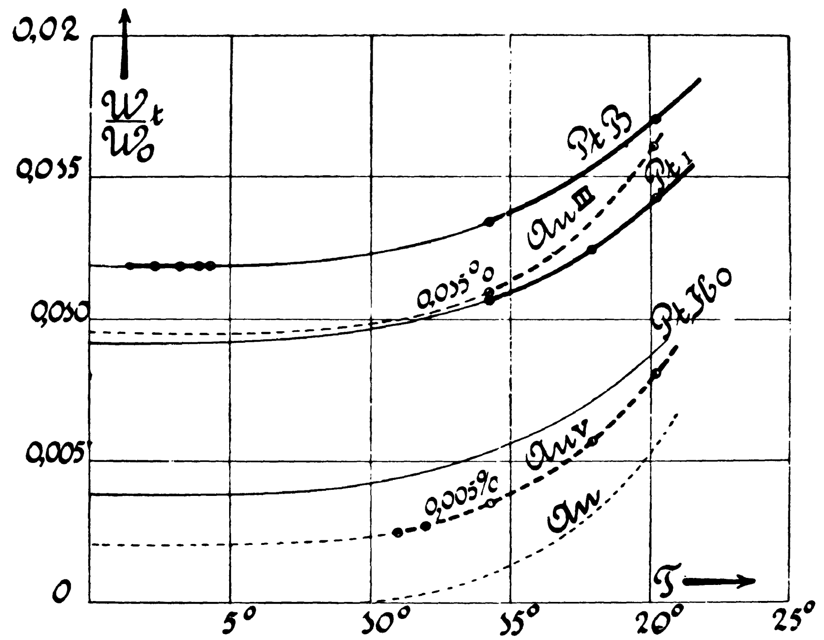

FIG. 2 Resistance versus temperature for several specimens of platinum and gold. Lightly drawn curves are extrapolations of the data.

conclusion was not very startling, having been known as Matthiessen's rule since 1864.) But that proposition did not allow calculation of the temperature at which the resistance of pure gold becomes constant. Assumption of a direct proportionality between amount of impurity and extra resistance led to an unintelligible negative constant resistance for pure gold. Onnes made the bold guess that he had reached the regime of constant residual resistance, and that the constant is zero: "within the limits of experimental error... the resistance of pure gold is already zero at helium temperatures" (lowest dashed curve in figure 2). He drew a similar conclusion for platinum by comparing the PtB results with those obtained from an earlier sample, PtI in figure 2.

## 2. QUANTUM THEORY AND SUPERCONDUCTIVITY

### The quantum of low temperature

At the time of the Leyden resistance measurements Walther Nernst was preoccupied with establishing his own cryogenic group in Berlin.

He hoped that measurement of specific heats as a function of temperature would confirm his heat theorem.[19] By 1911 Nernst's collaborators Arnold Eucken and F. A. Lindemann had extended the measurements down to liquid hydrogen temperatures.[20]

It had been known for years that the classic electron theory was quite unable to account for the specific heats of metals at room temperature: according to the theory the electrons should have a translational energy $3nkT/2$, which should contribute an amount $3nk/2$ to the specific heat $C_v$ per unit volume. If $n \approx N$, the number of atoms in unit volume, to which the theorem of equipartition of energy ascribed a heat capacity of $3Nk = 3R$, we have $C_v = 9R/2$, or about 9 calories/mole. At room temperature $C_v$ is about $3R$, the so-called law of Dulong and Petit. Apparently the electrons do not contribute much to $C_v$ at room temperature, an inference supported by the fact that there the specific heats of metals do not differ much from those of non-metals. Many exceptions were known to the law of Dulong and Petit, which in any case could only be an approximation because specific heats drop with temperature. In 1907 Einstein had calculated this drop by replacing the average energy of an atom as given by equipartition, $3kT$, with that deducible from Planck's radiation formula, $U = 3kTx/(e^x - 1)$, where $x \equiv h\nu/kT$.[21] We have for the specific heat of N such atoms,

$$C_v = \frac{d}{dx}(3U)\frac{dx}{dT} = 3Rx^2\frac{e^x}{(e^x-1)^2} . \tag{3}$$

At high temperatures ($x = h\nu/kT << 1$) this expression approaches $3R$; at low temperatures it has the exponential form $x^2e^{-x}$.

The first Berlin measurements appeared to agree with equation (3). The later values at liquid hydrogen temperatures, however, came out systematically higher than predicted by the theory. Nernst's group interpreted the discrepancy to mean that the eigenfrequency $\nu$ is not actually sharp, that a spectrum of frequencies is involved, a point that Einstein also realized. To pin down the spectrum required calibration,

19. W. Nernst, "Über die Berechnung chemischer Gleichgewichte aus thermischen Messungen," Akademie der Wissenschaften, Göttingen, *Nachrichten*, 1906:1, 1–40.

20. W. Nernst, "Untersuchungen über die spezifische Wärme bei tiefen Temperaturen, III," *SB*, 1911, 306–315.

21. A. Einstein, "Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wäme," *AP, 22* (1907), 180–190; Cf. M. J. Klein, "Einstein, specific heats, and the early quantum theory," *Science, 148* (1965), 173–180.

using the Onnes-Clay and Travers data, of the platinum and lead resistance thermometers employed from 20°K to 80°K. In the course of this calibration, Nernst was struck by the remarkable analogy in gross temperature dependence between specific heat and specific resistance, suggesting a similar quantum explanation. The available resistance data appeared to be expressible by a formula of the type

$$R = A/(e^x - 1) + B\ , \tag{4}$$

where $A$ and $B$ are constants characteristic of the metal ($B$ is a temperature-independent impurity contribution), and $\nu$ a parameter chosen to fit the data. The $\nu$-values thus obtained agreed rather well with those deduced from the specific heat data.[22]

Nernst's formula (4) for $R$ was, he admitted, purely empirical, a "convenient interpolation formula."[23] Whether $B$, in particular, approaches zero for pure metals, Nernst was unable to determine. Lindemann boldly attempted a derivation, starting with the theory of Riecke and Drude, but allowing for the square-root dependence of $n$ on temperature suggested by J. J. Thomson.[24] Unlike Riecke, who made $\lambda$ inversely proportional to the square of the atomic radius, he supposed $\lambda$ proportional to the square of the amplitude of atomic vibrations, the energy of which he took from Planck's formula. Substituting the value for $\lambda$ thus derived, Lindemann's formula for the resistance was

$$R = A^2(e^x - 1)^{-1} + 2AB(e^x - 1)^{-1/2} + B^2\ . \tag{5}$$

At high temperatures this formula agreed with the resistance data, approaching $(A^2k/h\nu)T + B^2$. At lower temperatures it also appeared to agree with the Leyden data on lead and silver, although failing (underestimating the observational data) at the very lowest temperatures (13.9°K in the case of silver), somewhat akin to the failure of Einstein's specific heat formula. For this reason, and because of the doubtful basic assumptions in the Riecke-Drude theory, Lindemann did not attach much significance to his theory.

Onnes followed the specific heat experiments in Berlin, and the adaptation of Planck's formula to the problem. Onnes considered that the new Leyden resistance measurements in liquid helium not only put to rest the notion of electrons' freezing to atoms, but also suggested that thermal agitation of Planckian vibrators might provide the resistance mechanism by limiting $\lambda$. Unaware of the Nernst-Lindemann speculations, Onnes also returned to Riecke's modified theory. He

22. W. Nernst, (ref. 20), 313.

23. Ibid.

24. F. A. Lindemann, "Untersuchungen über die spezifische Wärme bei tiefen temperaturen, IV," *SB*, 1911, 316–321; Thomson (ref. 11), 76.

recalled Riecke's arguments for a mean free path proportional to $1/\sqrt{T}$ and proposed to take $T$ proportional to the energy of a Planck oscillator. This curious mix of classical ideas and quantum formulas gave $\lambda \propto 1/\sqrt{U}$. Retaining the other features of the Riecke-Drude theory, in particular Riecke's assumption that $n$ is independent of $T$, Onnes computed for the ratio of the resistance $R_T$ at any temperature $T$ to the resistance $R_0$ at room temperature $T_0$ ($\equiv 273.1°K$):

$$R_T/R_0 = (TE_T/T_0E_0)^{1/2}. \tag{6}$$

Onnes's hypothesis, like Nernst's, was purely *ad hoc.*[25]

This formula seemed to give a qualitative explanation of the resistance data extrapolated to pure metals. With typical values for $\nu$ of around $10^{12}\,\mathrm{sec}^{-1}$, formula (6) indicates a resistance one ten-thousandth of that at room temperature at 4°K—practically vanishing resistance well above absolute zero. Also, since at room temperature $h\nu/kT$ is already small compared to unity, the exponential terms can be replaced by the first two terms in their expansions, to give

$$\frac{R_T}{R_0} \approx \frac{T - \mathrm{H}\nu/4k}{273.1 - \mathrm{H}\nu/4k} \approx \frac{T}{273.1}. \tag{7}$$

The specific resistance, $R_T/R_0$, at room temperature is to first approximation directly proportional to the absolute temperature. (At room temperature pure metals exhibit a temperature coefficient in the range 0.0039 to 0.0040, compared to 1/273.1 = 0.00366.) To fit the bend in the resistance curve in liquid helium—as well as to account for specific heats there—required a slight shift in frequency toward lower values.[26] Such a shift conflicted with Einstein's then ongoing investigation of the elastic constants of metals, which indicated an increase in frequency.[27] In the absence of definite values for $\nu$, but noting that Einstein's estimates were considerably higher than those of Nernst and Lindemann for lead (for silver agreement was closer), Onnes settled for a compromise, adopting half of Einstein's values, "as it is more a question of showing that the introduction of vibrators leads to a qualitative explanation." Calculations on this basis for platinum, silver, gold, and lead did indeed produce a qualitative correspondence with the Onnes-Clay measurements of the purest samples available down to 4.30°K.

25. Onnes (ref. 15), 23.
26. Onnes (ref. 15), 25.
27. A. Einstein, "Eine Beziehung zwischen dem elastischen Verhalten und der spezifischen Wärme bei festen Körpern mit einatomigem Molekül," *AP, 34* (1911), 170–174. Cf. W. Sutherland, "The mechanical vibrations of atoms," *PM, 20* (1910), 657–660; and E. Madelung, "Molekulare Eigenschwingungen," *PZ* (20), *11* (1910), 898–905.

To test the formula further, and to settle the question whether the resistance of an absolutely pure material might indeed vanish above absolute zero, a metallic conductor of even higher purity than gold was needed. Such a metal, albeit a liquid, was on hand: mercury. In his paper of 1911 on resistance of platinum at helium temperatures Onnes observed that with a "suitably" chosen value for $\nu$ the formula agreed quite closely with preliminary measurements on mercury, which, however, did not extend below 13.9°K. At this temperature the measured resistance ratio was 0.033; his formula indicated 0.027.[28]

This $\nu$-value was derived empirically, but with an eye to van der Waals's law of corresponding states, to fit the mercury data.[29] Onnes frequently generalized this law to metals, regarded as mechanically similar systems whose properties, when in corresponding states, are given by the same numerical values of the "natural units" appropriate to each metal. For the natural units of mass ($\mu$) and volume ($\phi^3$) he chose the atomic weight and the atomic volume, and for the unit of time ($\tau$) the reciprocal period of the resistance (atomic) vibrations. Moreover, since the curve of resistance versus temperature appeared to be strongly influenced by the melting point, Onnes chose to regard the melting temperature as a natural unit. Now the dimensions of energy are also proportional to those of temperature. Onnes accordingly related the melting points for two metallic substances, $\theta$ and $\theta'$, by his principle of similarity as follows:

$$\begin{aligned}\tau : \tau' &= \phi\mu^{1/2}\,\theta^{-1/2} : \phi'\mu'^{1/2}\,\theta'^{-1/2}\\ &= \rho^{-1/3}\mu^{5/6}\,\theta^{-1/2} : \rho'^{-1/3}\mu'^{5/6}\,\theta'^{-1/2}\,,\end{aligned}$$

where $\rho$ is the atomic density. Selecting the frequency for lead such that $xT = h\nu/k = 54$, Onnes deduced a frequency for mercury corresponding to $xT = 37$. A similar comparison with platinum yielding a value for mercury corresponding to $xT = 47$, Onnes felt justified, in view of the crudity of the analysis, in reducing $xT$ to 30, which agreed better with the measured resistance curve. With this value substituted in equation (6), the ratio of the resistance of mercury at 13.9K to the resistance at room temperature comes out to be 0.027; measurement gave 0.033, as noted.

Lindemann's formula for determining the frequency, which Onnes was not aware of when he invented his argument from corresponding states, suggested a value of $xT = 46$ for mercury. Not only does this value, when substituted in equation (6), give worse agreement with the

28. Onnes (ref. 15), 26.

29. Onnes, "Further experiments with liquid helium, E. A helium cryostat," *RN, 14* (1912), 209–210.

measured resistance ratio at 13.9K (0.019) than Onnes's, but it predicted a lower resistance by an order of magnitude in the temperature range of liquid helium. At 3°K Onnes's value for $xT$ gave a ratio of $2.4 \cdot 10^{-4}$ against Lindemann's ratio of $2.1 \cdot 10^{-5}$.

### Detection of superconductivity

Between the announcement of the first resistance measurements in liquid helium in December 1910 and the next experiment, concentrating on mercury at these temperatures, Onnes's team modified their experimental arrangement significantly. They transferred the liquid helium from the liquefier to a separate helium cryostat, which permitted handling larger samples with greater ease and higher accuracy. And, having recognized that the electrical conductivity of liquid helium is negligible, they arranged to measure directly, on noninsulated wires. They used a differential galvanometer and the method of overlapping shunts, and they also made separate measurements of current and potential differences. Holst made the measurements, as he had done earlier.

Since mercury is a liquid at room temperature, it can easily be distilled repeatedly in vacuo to an even higher degree of purity than gold. From his formula Onnes had anticipated that its resistance in liquid helium would be much lower than at hydrogen temperatures, though not yet independent of temperature; and "that at very low temperatures such as could be obtained by helium evaporating under reduced pressure [it] would, within the limits of experimental accuracy, become zero."[30] An initial single experiment, reported "with all reserve" to a gathering of the Royal Academy on April 28, 1911, showed indeed that "while the resistance at 13.9°K is still 0.034 times the resistance of solid mercury extrapolated to 0°C, at 4.3°K it is only 0.00225, while at 3°K it falls to less than 0.0001."

This preliminary announcement came without details of data or description of the new cryostat arrangement. Onnes had taken his time building up his apparatus; its successful employment created a sense of urgency. As the announcement went to press, Onnes learned of Nernst's being "independently led to assume a connection between the energy of vibrations and electrical resistance" and of Lindemann's development of the hypothesis.

The preliminary mercury results thus seemed to confirm Onnes's expectation. However, the fit of the curve representing resistance as a

30. 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," *PLC, 120b* (1911), 17–19.

function of temperature between the melting point of hydrogen and the boiling point of helium was not as good as with gold. Worse, the rapidity of the transition from a finite value at the boiling point itself was very much a surprise. Therefore the experiment was repeated without delay.

They reported the new measurements in May 1911. Holst had checked and re-checked his calculations and instruments.[31] There was no doubting the results, "The disappearance of the resistance of mercury." At 4.3°K it had sunk to 0.0021 times what it would have been at 0°C; at 3°K the ratio had fallen to one ten-millionth, which remained the upper limit as the temperature sank to 1.5°K. The temperature at which the resistance first became measurable was found to be "slightly more than 4.2°K." The onset of measurable resistance was indeed much sharper than Onnes's formula suggested: a rise by two orders of magnitude between 4.2°K and 4.3°K, which he took for the boiling point of helium *(recte* 4.19°K at atmospheric pressure). A point of inflection, moreover, seemed to occur between the melting point of hydrogen and the boiling point of helium.

The experiments seemed worth continuing:[32]

> The more the upper limit which can be ascribed to the resistance remaining at helium temperatures decreases, the more important becomes the observed phenomenon that the resistance becomes practically zero. When the specific resistance of a circuit becomes a million times smaller than that of the best conductors at ordinary temperatures it will, in the majority of cases, be just as if electrical resistance no longer existed under those conditions. If conductors could be obtained which could be regarded as being devoid of resistance as long as their cross section was not excessively small, or conductors of the smallest possible sections, either cylindrical with diameters of the order of the wavelength of light,

31. Onnes, "Further experiments with liquid helium, D. On the change of the electrical resistance of pure metals at very low temperatures, etc. V. The disappearance of the resistance of mercury," *PLC, 122b* (1911), 13–15; A. de Kool, "Superconductivity. A discovery by Heike Kamerlingh Onnes," *Radio Nederland wereldomroep* (Hilversum, 1963), 5. It is not surprising that, in spite of Holst having been largely responsible for conducting the actual resistance measurements in these years, or from 1910 until his departure for the Philips Company in early 1914, his recognition by Onnes was limited to acknowledgements accompanying the various communications. Being of the old school and the one responsible for determining the research program at the laboratory, Onnes considered it only proper that all results appear in print under his own name only (co-authorships were reserved for more senior staff members). Eventually, after Holst had left Leyden, Holst did co-author several papers with Onnes, and in Onnes's confidential recommendation for Holst's membership in the Royal Netherlands Academy he emphasized Holst's important collaboration in the discovery of superconductivity. H. B. G. Casimir, *Haphazard reality: Half a century of science* (New York, 1983), 164–166.

32. Onnes (ref. 31), 14.

or films of molecular thickness, whose resistance would be but small, if there had no more to be reckoned with the Joule development of heat in increasing the current in a bobbin to exceedingly high values because the development of heat in a circuit of constant current strength could be made extremely small compared with the latent heat of vaporization of the liquid which can be used for cooling,—then further experiments in all possible directions would give the fullest promise, notwithstanding the great difficulties which are encountered when working with liquid helium. It is therefore all the more necessary to establish beyond all possibility of doubt the property of which advantage would be taken in such experiments. With this end in view modified measurements are now being made.

Onnes gave an account of his work on mercury, as completed in May, to the first Solvay Congress, which met in October.[33] Judging from the printed proceedings of the Congress, Onnes's report did not arouse much interest even though Nernst, one of the Congress organizers, dwelt in his report on the resistance measurements on platinum and lead at both Berlin and Leyden.[34] The discussion following Onnes's presentation was limited to his answers to two questions by Paul Langevin, who asked whether the large change in resistance was accompanied by any observable structural modification of the mercury, such as a change in volume, and whether the change in resistance might be a secondary result. Onnes replied that low-temperature measurements on thermal conductivity, specific heats, density, expansion and elastic properties of mercury appeared to support his theory. Perhaps Onnes was referring to the fact that the modified Riecke theory invokes a relationship between the coefficient of expansion and the mean free path, and the correlation of his modified formula with frequencies estimated from elastic constants.[35]

Onnes had drawn attention in his presentation, as he had done the previous April, to the work of Heinrich Rubens. In 1903 Rubens and E. Hagen had shown that the reflecting power of metals for radiation of very long wavelength may be accounted for on Drude's model of electrical conductivity.[36] The critical frequency that Onnes had deduced

33. Onnes, "Sur les résistances électriques," *La theorie du rayonnement et les quanta, rapports et discussions de la réunion tenue à Bruxelles, du 30 octobre au 3 novembre 1911 sous les auspices de M. E. Solvay*, ed. P. Langevin and M. de Broglie (Paris, 1912), 304–310. Hereafter referred to as *Rapports*.

34. Nernst, "Application de la théorie des quanta à divers problèmes physico-chimiques," ibid., 254–290.

35. Ibid., 311. No change in volume, in the absence of a magnetic field, has been observed at the superconducting transition, nor a change in elastic properties. D. Shoenberg, *Superconductivity* (Cambridge, 1965), 7.

36. E. Hagen and H. Rubens, "Über die Beziehungen zwischen dem Reflexionsvermögen der Metalle und ihrem elektrischen Leitvermögen," *SB*, 1903,

for mercury corresponds to a wavelength of 0.5 mm; Rubens had found that a mercury lamp emits radiation with a wavelength of about 3 mm. The order-of-magnitude similarity, and the Rubens-Hagen observation, suggested to Onnes a relationship between the resistance behavior and optical phenomena.

One thing was clear about wavelengths: to account for the abruptness of the change in resistance observed in the case of mercury would require a correspondingly rapid increase in frequency. Owing to the exponential in Planck's formula, only a small change, like doubling the frequency, can produce the enormous change in resistance. In his report to the Congress, Nernst discussed a revised specific-heat formula, published by Lindemann and himself in July of 1911,[37] which appeared to give better agreement with the measurements at very low temperatures and which offered a possible explanation of the rapid change in frequency Onnes needed:

$$C_v = (3R/2)[x^2e^x/(e^x-1)^2 + (x/2)^2e^{x/2}/(e^{x/2}-1)^2] . \qquad (8)$$

They associated the first term with the kinetic energy of the vibrating atoms, the second term, containing "half quanta," with their potential energy. Einstein, though unconvinced of the theoretical basis for the formula, inclined to view it as a step in the right direction, if an empirical one.[38] Nernst also discussed a formula derived a year earlier by Lindemann for calculating $\nu$ in terms of the melting temperature, molecular weight and density, on the assumption that melting occurs when the amplitude of vibration of the atoms at the melting point reaches some definite fraction of the spacing between atoms in the crystal.[39] Frequencies calculated by this formula agreed well with those estimated from the specific heats and from optical absorption measurements.

Planck discussed what became known as his "second quantum hypothesis," which brought the concept of "zero point energy" in connection with the problem of absorption of black-body radiation. He now gave for the mean energy of an oscillator,

$$U = xkT[(e^x-1)^{-1} + 1/2] . \qquad (9)$$

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269–277. See J. Mehra and H. Rechenberg, *The historical development of quantum theory* (4 vols., New York, 1982), *1*, 92; Niels Bohr, *Collected works, 1*, ed. J. Rud Nielsen (Amsterdam, 1972), 360–408; H. Kangro, "Ultrarotstrahlung bis zur grenze elektrisch erzeugter Wellen, das Lebenswerk von Heinrich Rubens," *Annals of science, 26* (1970), 235–259, and *27* (1971), 165–200.

37. W. Nernst and F. A. Lindemann, "Spezifische Wärme und Quantentheorie," *Zeitschrift für elektrochemie, 17* (1911), 817–827.

38. Einstein, in *Rapports* (ref. 33), 299.

39. F. A. Lindemann, "Über die Berechnung molekularer Eigenfrequenzen," *PZ, 11* (1910), 609–612.

In the ensuing discussion, Onnes pointed out the difficulty equation (9) posed for explaining the resistance data in terms of vibrators. The zero-point contribution implied an energy of vibration much too high to reconcile with experiment.[40]

## 3. MOPPING UP

In December 1911 Onnes reported measurements that narrowed the transition in mercury to a very small temperature range.[41] He took the occasion to describe the separate helium cryostat, which made it possible to maintain the bath at a uniform temperature by stirring and, moreover, to use a mercury resistance with mercury leads instead of platinum. The cryostat is depicted in figure 3 with an enlargement of the mercury resistance and leads.

The mercury, distilled in vacuo at a temperature of 60°C to 70°C, was poured into a series of seven connecting U-shaped glass capillary tubes about 0.005 $mm^2$ in cross section and frozen in them during the experiment. At the upper end of each U stood a reservoir partially filled with mercury to accommodate the change in volume of the mercury during thawing or freezing without breaking the glass and without breaking the continuity of the mercury thread. The current entered and left the thread through the mercury leads $Hg_{10}$ and $Hg_{40}$; $Hg_{20}$ and $Hg_{30}$ could be used for the same purpose, or for measuring the potential difference between the ends of the thread. The potential at the point $b_4$ could be measured via $Hg_{50}$ in order to examine possible variation of resistance along the length of the thread.

To minimize the space they occupied in the cryostat and to fit alongside the stirring pump Sb, the mercury U-tubes, shown as mounted in a plane in the cryostat drawing, were actually arranged in a cylindrical configuration as shown in the lower middle insert to figure 3. The cryostat cover ($Sb_1$) appears in perspective at the top. Here too the leads had expansion volumes. Platinum wires, $Hg_1'$, $Hg_2'$, $Hg_3'$, $Hg_4'$ and $Hg_5'$, fused in the bent side pieces, provided connections to the measuring apparatus. Though Onnes's team shielded the junctions between the platinum wires and the copper leads of the measuring

40. M. Planck, "La loi du rayonnement noir," *Rapports* (ref. 33), 93–114, on 110–111, and Onnes, ibid., 129. Cf. T. S. Kuhn, *Black-body theory and the quantum discontinuity, 1894–1912* (Oxford, 1978), 236–246.

41. Onnes, "Further experiments with liquid helium, G. On the electrical resistance of pure metals, etc. VI. On the sudden change in the rate at which the resistance of mercury dissappears [*sic*]," *PLC, 124c* (1911), 21–27. Cryogenic details of the modified apparatus, particularly those pertaining to transferring liquid helium from the liquefier to the cryostat, are also described in Onnes, "Further experiments with liquid helium, E. A helium cryostat," *RN, 14* (1912), 204–210 *(PLC, 123a)*.

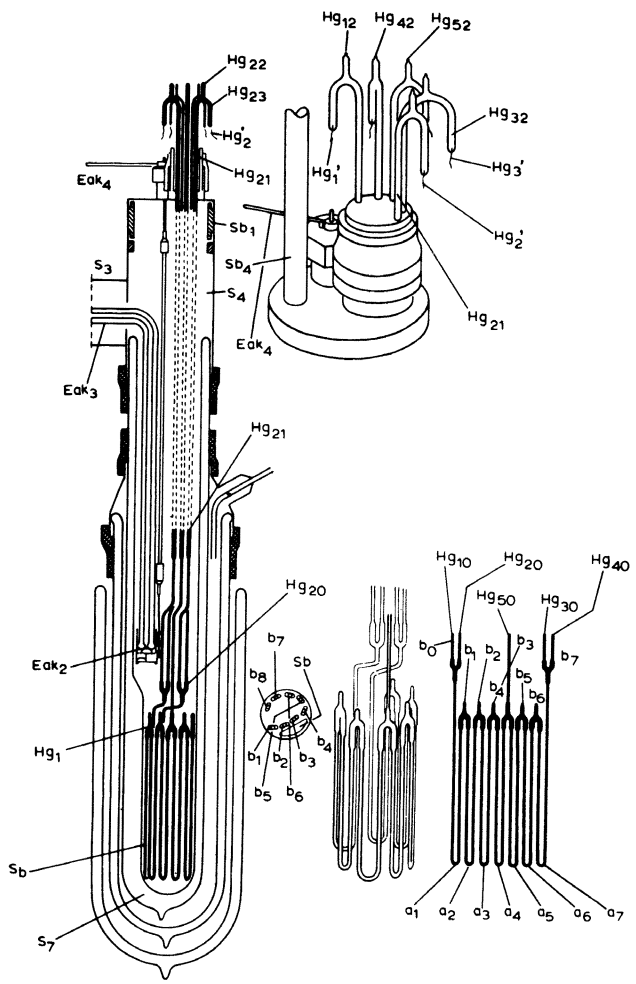


FIG. 3 Helium cryostat for experiments with mercury in the fall of 1911. The mercury resistance is shown drawn to an enlarged scale.

apparatus as well as they could from temperature variations, they could not eliminate a thermo-electric effect of about half a millivolt from the mercury resistance-lead circuit. Instead, they nullified its effect by an opposing EMF from an auxiliary circuit. They evaluated the resistance of the mercury thread by subtracting the deflection of a galvanometer placed in the circuit with $Hg_2$, $Hg_3$, and the compensating EMF, from the deflection in the same arrangement but with the main current reversed. This time the constant-volume thermometer had a "zero" pressure of 30 cm, or twice that utilized in the experiments of 1910.

Figure 4 displays the measured resistance in absolute ohms as a function of temperature. Onnes decided not to use ratios, as in figure 2, because the extrapolation to the resistance of solid mercury at 0°C (about 60 ohms) from the value at the melting point was not secure.[42] Figure 4 omits measurements extending up to the melting point of hydrogen; for these the Leyden group raised the bath temperature above the boiling point of helium (here given as 4.25°K) by allowing the pressure under which the liquid evaporated to increase (by closing the tap $Eak_2$ leading to the liquefier). Their purpose was to answer the question, raised originally in the experiments of 1906/7 and still not settled in the measurements reported in May 1911, whether a point of inflection occurs in the resistance curve somewhere between the melting point of hydrogen and the boiling point of helium. They showed, in fact, a smooth decrease in resistance in this temperature range, down to 4.21°K, essentially as described by Onnes's formula. But the capital point remained: between 4.21°K and 4.19°K—a temperature range no greater than 0.02°K—the resistance dropped from about 0.115Ω to less than $10^{-5}\Omega$. The value in figure 4 at 4.19°K was an upper limit. One could scarcely doubt that around 4.20°K the electrical character of mercury altered in a novel and profound way. To be sure, no more was known about the mechanism of transformation than when Langevin asked about it, whether properties other than resistance showed similar dramatic behavior.

Onnes concluded his report of December 1911 with a brief reference to an attempt at passing a comparatively strong current through the mercury thread below the transition temperature. The purpose was to attain more accurate potential measurements and thereby better estimates of the upper limit of the resistance. He did not find what he wanted: "the peculiarities of the phenomena which then occur make it desirable to experiment first with a modified apparatus before proceeding further." Before proceeding further, Onnes's group subjected tin to the same treatment as mercury and found that it too loses its measurable resistance, at a temperature they estimated to be 3.78°K. These interesting and important results, obtained on December 3, 1912, were announced in February and May 1913.[43]

42. A plot in terms of resistance ratios appears in Onnes's Nobel lecture, in *Nobel lectures..., physics, 1901–1921* (New York, 1967), 306–336, on 330.

43. Onnes, "Further experiments with liquid helium, H. On the electrical resistance of pure metals etc., VII. The potential difference necessary for the electric current through mercury below 4.19°K," *PLC, 133a* (1913), 3–26.

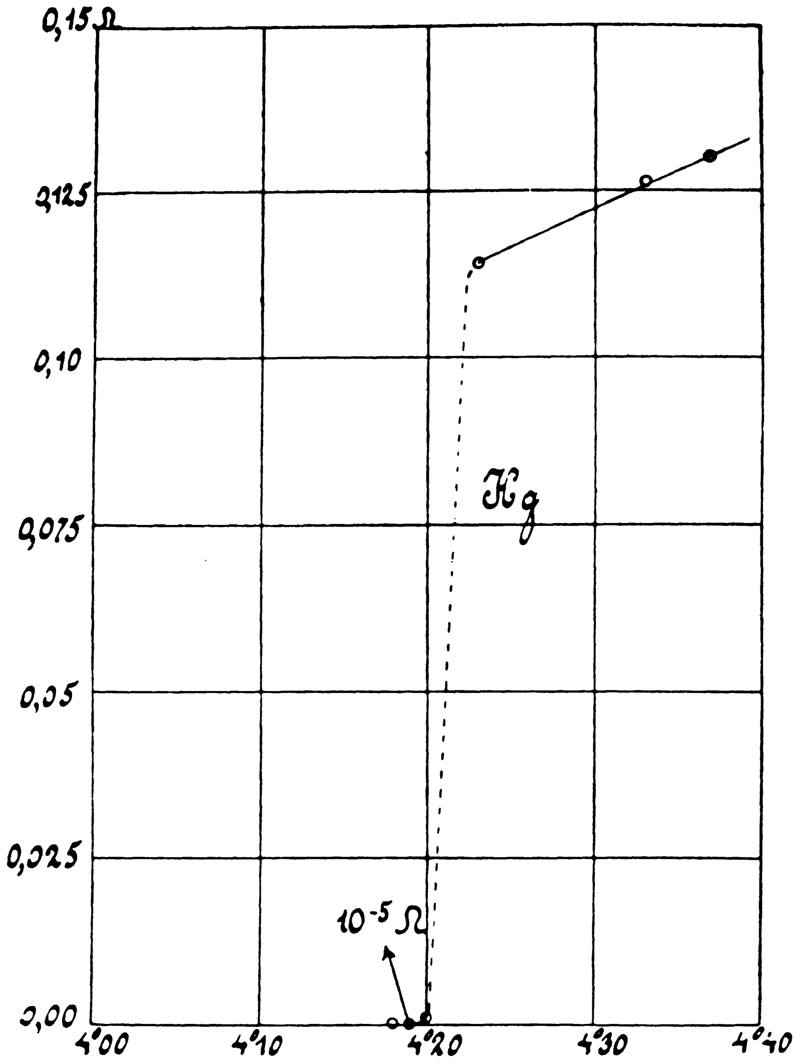


FIG. 4 Resistance of mercury versus temperature.

These papers belonged to the definitive four-part *Communication 133,* published in the spring of 1913. The first three parts close the investigation of mercury and the fourth moves on to tin and lead. These spring papers followed by over a year the description of the first mercury experiments presented to the Amsterdam Academy in December 1911. It had taken many months to investigate "difficulties" that Onnes's group had encountered the preceding October, just after the Solvay Congress. The first part of *Communication 133a* reveals that the difficulties were "special phenomena" that occurred when an electric current of great density passed through the mercury thread below 4.19°K:[44]

> At every temperature below 4.18°K for a mercury thread enclosed in a glass capillary tube a "*threshold value*" of the current density can be given, such that at the crossing of the "threshold value" the phenomena change. At current density below the "threshold value" the electricity goes through without any perceptable [*sic*] potential difference at the extremities of the thread being necessary. It appears therefore that the thread has no resistance, and for the residual resistance which it might possess, a higher limit can be given determined by the smallest potential difference which could be established in the experiments (here 0.03 x $10^{-6}$ V) and the "threshold value" of the current. At a lower temperature the threshold value becomes higher and thus the highest limit for the possible residual resistance can be pushed further back. As soon as the current density rises above the "*threshold value,*" a potential difference appears which *increases more rapidly than the current;* this seemed at first to be about proportional to the square of the excess value of the current above the initial [threshold] value, but as a matter of fact at smaller excess values it increases less and at greater excess values much more rapidly.

These odd regularities were purchased at the price of considerable labor and vexation. Onnes allowed himself to vent his annoyance at the "various circumstances" that made "the investigation of the mercury enclosed in capillary tubes difficult:"[45]

> A day of experiments with liquid helium requires a great deal of preparation, and when the experiments treated of here were made, before the latest improvements in the helium circulation were introduced, there were only a few hours available for the actual experiments. To be able to make accurate measurements with the liquid helium then, it is necessary to draw up a program beforehand and to follow it quickly and methodically on the day of the experiment. Modifications of the experiments in connection with what one observes, must usually be postponed

44. Ibid., 3–4.
45. Ibid., 4–5.

> to another day on which experiments with liquid helium could be made. Very likely in consequence of some delay caused by the careful and difficult preparation of the resistance, the helium apparatus would have been taken into use for something else. And when we could go on with the experiment again, the resistance sometimes became useless... because in the freezing the fine mercury thread separated, and all our preparations were labour thrown away. Under these circumstances the detection and elimination of the causes of unexpected and misleading disturbances took up a great deal of time.

Mopping up the experiments of December 1911, which gave the upper limit for the resistance of mercury below the transition point as $10^{-9}$ that at 0°C at a bath temperature of 3.65°K, or two orders of magnitude less than their estimate of May 1911,[46] Onnes's group had pushed to $< 4.1 \cdot 10^{-10}$ in January 1913, and to $< 2.0 \cdot 10^{-10}$ in February. They still estimated that the transition occurred over 0.02°K, although Onnes suspected that it took place instantaneously, the small but detectable temperature interval between finite (normal) resistance and essentially zero resistance arising in fact from gradual cooling of the thread over its whole length.

Onnes understood the apparent breakdown of Ohm's law below the transition temperature as a consequence of the increase of the mean free path of electrons in super-cooled mercury to a size comparable with the dimensions of the conductor (100 cm). The drift velocity $u$ under the applied field might then no longer be small compared with the velocity $v$ of thermal agitation, and so violate a fundamental assumption of the simple electron model. There was of course no way of confirming Ohm's law in the new state; *above* the transition temperature it appeared to hold perfectly.

The main subject of concern in the spring of 1913 was, however, the phenomenon of the critical current. The Leyden group applied progressively higher current densities (up to 1000 A/mm$^2$) to improved mercury samples and found that the threshold current is inversely proportional to the bath temperature and increases approximately linearly with the difference between the bath temperature and the transition temperature, at least over a small temperature range. They ruled out one by one the obvious possible sources of error: Joule heating, Peltier effects, impurity admixtures, thermocurrents, uneven heating of the mercury thread, variations in its thickness from the freezing process, contact with ordinary conductors. Onnes had no place to locate the cause of the potential phenomena except the mercury resistance itself. Clearly heating took place somewhere in the circuit when the current

46. Ibid., 7, erroneously dates the experiments reported in *PLC, 122b* (ref. 31) to June instead of May 1911.

density exceeded the threshold value. The experiments in February 1913, for which the experimental arrangements had been sufficiently refined to eliminate the possibility of heat penetrating into the cryostat through the current leads, and probably from elsewhere, confirmed Onnes's suspicion: the heating at high current densities took place in the mercury thread itself. But the cause of the heat remained a mystery.

The second part of *Communication 133,* presented in March, pursues in greater depth the influence of possible impurities, which the group then still regarded as the most natural explanation for the potential effects and the residual resistance. Natural, perhaps, but somewhat unlikely since their experiments had demonstrated that "mercury could be so far freed from impurities as to make the resistance practically nothing." But an unwanted atom or two might have remained:[47]

> If one may judge by the additive resistance which even very pure gold exhibits, then with the residual resistance of mercury which is only perceptible at the threshold value of current density for the lowest temperatures, it would be a question of an impurity of the order of a millionth of the trace that could possibly be present in the most carefully purified gold. And it was a priori doubtful if the mercury could be procured in so much greater a state of purity than gold.

The Leyden experimenters therefore deliberately added trace impurities, gold in one case, cadmium in another. To Onnes's surprise this contamination did not appear to inhibit the drop in resistance; "much of the time spent on the preparation of pure mercury by distillation," he observed, "might therefore have been saved." No more did the introduction of an ordinary conductor, a steel capillary tube, affect what Onnes now called "the superconductivity of mercury."[48] Thus the new and lasting term for the phenomenon appeared in print for the first time.

In the third part of the spring bounty issued in May, Onnes discussed inhomogeneities in the form of different states of crystallization along the length of mercury thread.[49] Onnes settled for ascribing the disturbing potential phenomena to "bad places" in the thread. In view of the difficulties of working with mercury and, in particular, the impracticability of cooling the thread by direct contact with the liquid

47. Onnes, "Further experiments with liquid helium, H. On the electrical resistance of pure metals, etc., VII. The potential difference necessary for the electric current through mercury below 4.19°K (continuation)," *PLC, 133b* (1913), 29–32, on 29.

48. Ibid., 31.

49. Onnes, "Further experiments with liquid helium, H. On the electrical resistance of pure metals, etc., VII. The potential difference necessary for the electric current through mercury below 4.19°K (continued)," *PLC, 133c* (1913), 35–48.

(thus raising the threshold current, allowing more accurate measurements), other metals seemed more promising for further pursual of the matter. The obvious candidate was tin, which, as noted, had also been found to be superconducting.

### Magnets, and new surprises

The last part of the series is dated May 31, 1911. It deals not with mercury, but with tin and lead, which simplified the investigations very considerably by their greater ease in handling.[50] The discovery of the superconducting nature of lead must have occurred very soon after that of tin, in December 1912; the transition temperature for lead was then estimated to lie near 6.0°K. The samples were wound in coils to increase their length and sensitivity in order to clarify the potential phenomena, which, it was immediately apparent, also plagued tin and lead. These coils, several of which are preserved, may be regarded as the first superconducting magnets.[51] G. J. Flim, Chief of the Technical Department of the laboratory, prepared the solenoids by covering a steel core with pure tin or lead and cutting off thin spiral shavings. These he melted together into a longer wire, which he rewound upon glass cylinders between a spiral of insulating silk or piecin. This technique avoided the work hardening associated with drawing a wire, which could not practically be counteracted by annealing.

The experiments continued, as usual with the assistance of Holst, concentrating both on reducing the upper limit of any possible micro-residual resistance, and on explaining the potential differences above the current density threshold just below the point of vanishing resistance. They brought no substantive further progress in clarifying these questions, but great excitement about further possibilities:[52]

> A number of experiments with resistance free conductors of which several suggest themselves at once, now that we can use the readily workable super-conducting tin and lead, can be undertaken with good prospects of success. In this way the preparing of nonresistive coils of wire, with a great number of windings in a small space, changes from a theoretical possibility into a practical one. We come to new difficulties

50. Onnes, "Further experiments with liquid helium, H. On the electrical resistance, etc. (continued), VIII. The sudden disappearance of the ordinary resistance of tin, and the super-conductive state of lead," *PLC, 133d* (1913), 51–67.

51. Two coils, one wound with lead wire and one with tin, are in storage at the Museum Boerhaave, cataloged as items C12 and C13. In the catalog for the Lorentz-Kamerlingh Onnes Exhibition mounted at the Boerhaave in 1953, they are briefly described as item 130. KO, 113g.

52. Onnes (ref. 50), 62–63.

> [however] when we want not only to make a nonresisting coil but to supply it as a magnetic coil with a strong current.

Comparing the relative performance of several tin and lead coils of different geometries, Onnes concluded that the presence of "bad places" in the wire still offered the most likely explanation for the frustrating potential effects. "If we may therefore be confident that they can be removed (for instance by fractionising the wire) and if moreover the magnetic field of the coil itself does not produce any disturbance... then this miniature coil may be the prototype of magnetic coils without iron, by which in [the] future much stronger magnetic fields may be realized than are at present reached in the interferrum of the strongest electromagnets."

The allusion to the possible effect of a magnetic field perhaps hints that Onnes then had some evidence anticipating the results of crucial experiments only announced eight months later. He did in fact have a resolution of his difficulties. A sample of the tin wire was tested in liquid helium before winding the coil; 8 amp could be passed through the wire without exceeding the threshold current density. *After* coiling, the wire reached its current density threshold with only 1.0 amp. Lead wire behaved similarly.

In September 1913 Onnes attended the Third International Congress of Refrigeration in Washington and Chicago. He still seems to have regarded superconductivity as basically an extreme case of the normal mechanism of electrical conduction in metals: "There is little doubt that, if gold and platinum could be obtained absolutely pure, they would pass into the superconducting state at helium temperatures."[53] He held this view despite his strong evidence that adding impurities does not inhibit the drop to zero resistance, indicating that the superconducting state can not be reached by purity alone. (It was found, much later and at Leyden, that the degree of purity can affect the *breadth* of the transition: the purer the material the sharper it is.[54])

At the Congress Onnes discussed the exciting prospects for utilizing superconductors in very high-field electromagnets. Here he could go far beyond Jean Perrin's old suggestion of using air-core copper

53. Onnes, "Report on the researches made in the Leyden cryogenics laboratory between the second and third international congress of refrigeration," *PLC, 133–144: PLS, 34b,* presented at the congress of 1913. *(PLS, 34b* must have been published in or after February 1914 since it refers to *PLC, 139f,* dated February 1914.) Cf. *PLC, 133d* (ref. 50), 62: "Our results with tin and lead make it seem probable that all metals, or at least a class of them, if they can be procured sufficiently pure, pass into the superconducting state when reduced to a low enough temperature. Perhaps in all it would also be suddenly."

54. Shoenberg (ref. 35), 4.

magnets cooled with liquid air to produce fields of 100,000 gauss, which had not seemed to be very practical.[55] Approximately 1500 liters per hour of liquid air would be needed to carry away the heat generated; far more power would be needed for refrigeration than for the coil. Even more problematic was insuring adequate heat transfer between the supposedly compact coil and the coolant, which would, in fact, necessitate a coil of very large volume. Critics of the plan estimated the cost of implementing it at about that of building a cruiser. Prospects for silver coils, cooled by liquid hydrogen or even liquid helium, did not appear much brighter.

The potential for high-field superconducting coils, however, seemed exceedingly promising. Joule heating would no longer be a problem and, because they could handle high current densities, the coils could be of relatively modest dimensions. The possibility remained that a resistance might be developed in the superconductor, but Onnes did not regard it as likely. He wound a small coil with 1000 turns of lead wire within a section 1 cm deep and 1 cm long. It carried 0.8 amp without difficulty, and produced a field of several hundred gauss. Since Onnes still believed that "bad places" in the wire, not magneto-resistive heating, caused the severe degradation at the critical current densities (had not a stretched sample of the wire carried 8 amp?), he supposed that with better cooling to conduct the heat from the bad places the coil would operate at least close to the short sample performance, or 1000 gauss. He expected to realize improvement in cooling by using ordinary metal, which acts as insulator compared with superconductors, instead of silk, between the coil's turns.

Should this succeed, he calculated that a coil 30 cm in diameter should produce 100,000 gauss with a helium plant realizable at Leyden with relatively modest funding. But should the premature onset of resistance in superconductors charged above the current-density threshold prove to be intrinsic to pure metals, the hope of economical, large magnets would be difficult to sustain. The consolation, in this case, which Onnes regarded as unlikely, would be verification of electrical conduction in metals not obeying Ohm's law.

Onnes's next important appearance on the international scene after the Congress on Refrigeration came in Stockholm, where, on December 10, 1913, he received the Nobel Prize in physics "for his investigations on the properties of substances at low temperatures, which investigations, amongst other things, have led to the liquefaction of helium." In a note added to the proofs of his Nobel lecture early in 1914 Onnes

55. Perrin had discussed his scheme at a meeting of the French Physical Society on April 19, 1907. See C. Fabry, "Production de champs magnétiques intenses au moyen de bobines sans fer," *Journal de physique,* 9 (1910), 129–134.

explained why, when he gave the lecture the previous December, the Leyden group considered that the effect of a magnetic field on the superconducting state could only be minor. In December, he wrote, they had rejected the possibility that the threshold value of the current might be connected with a perceptible magnetic resistance to the field of the current: "we had then no reason to think of a law of increase of the resistance with the field other than proportional to it, or to the square of it, and the law of increase of the potential differences at currents above the threshold value could not be reconciled with either supposition."[56] They expected that even if a field effect existed, it would not be significant at fields under 10 kG (10,000 gauss); and since they had no magnet stronger than 2 kG, they did not then pursue the possibility.

A magnet that could reach 10 kG became available in January 1914. It had been built for the Leyden laboratory by Maschinenfabrik Oerlikon in Zurich according to a design by Pierre Weiss.[57] Coils placed in the aperture of the magnet showed considerable resistance in the presence of an applied field between 5 and 10 kG; but since some doubt about the superconducting character of the coils existed, the experiment produced nothing definite. In February the experiment continued with non-inductively wound coils known to be superconducting. A lead coil mounted with the plane of its winding parallel to the applied magnetic field again indicated considerable resistance at 10 kG, somewhat less at 5 kG, and none at all beginning with a sudden onset of the superconducting state between 500 and 700 gauss. "The curve, which represents the change of the resistance with the field is closely analogous to that which represents the change of the resistance with the temperature." Figure 5 shows curves of resistance as a function of field for bath temperatures of 4.25°K and 2.0°K, both well below the transition temperature. Onnes concluded: "The sudden change in the resistance moves at low temperatures towards higher fields; beyond this point the resistance increases at lower temperatures (2°K) almost in the same way as at higher ones,...as if *the introduction of the magnetic field has the same effect as heating the conductor.*" The tin coil showed essentially the same behavior, but a much lower threshold (200 gauss). Studies made with a flat coil of lead showed that the sudden change in

56. Onnes, "Further experiments with liquid helium, I. The Hall effect, and the magnetic change in resistance at low temperatures, IX. The appearance of galvanic resistance in supra-conductors which are brought into a magnetic field, at a threshold value of the field," *PLC, 139f* (1914), 65–71, on 65.

57. KO, 56. The magnet is in storage at the Museum Boerhaave; a similar magnet, of uncertain vintage, may be seen in the Kamerlingh Onnes Laboratory of the University of Leyden.

resistance took place at about the same threshold value of the field independent of the orientation of the windings to the field, although the longitudinal effect was weaker than the transverse.[58]

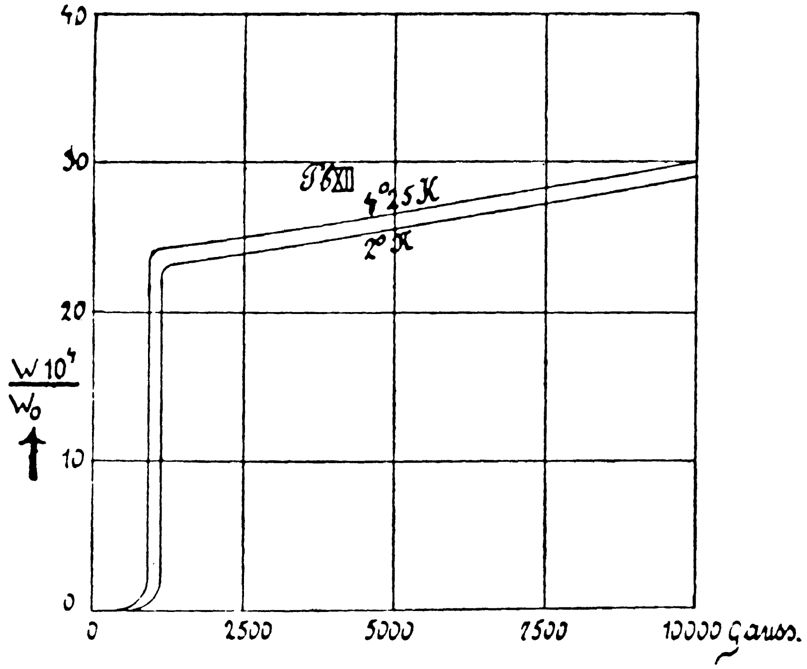

FIG. 5 Resistance of a lead coil as a function of magnetic field, for two different helium bath temperatures.

Onnes did not draw any inference regarding a relationship between the threshold current and the threshold field. He entertained no doubt, however, that the field effects related closely to the abrupt onset of resistance in superconductors at a certain temperature: "The analogy between the influence of heating upon the resistance and that of the introduction of the magnetic field, is so far complete."

Onnes's group had time for only one more set of superconducting experiments before the first world war forced a halt to essentially all work with liquid helium. Although throwing little further light on the phenomenon itself, they did demonstrate the superconducting state, and Onnes's experimental talents, in a most elegant way. The objective

58. Onnes (ref. 56), 69.

was to pin down a still more accurate value for the micro-residual resistance below the transition point by measuring the time constant (the time for the current to fall to $1/e$ times its initial value) in a superconducting circuit. This constant is given by $\tau = L/R$, where $L$ is the self-inductance of the circuit and $R$ the resistance. The lead coil they worked with had $R = 734\Omega$, $L = 10m\text{H}$, at room temperature, whence $\tau = 1.4 \cdot 10^{-5}$ sec, a time too short for Onnes to measure. But in the superconducting state with a resistance one ten-billionth that at room temperature, $\tau \approx$ one day. The first attempt at measuring $\tau$ was made in April 1914.[59]

The coil with its leads fused together to form a closed superconducting loop (Onnes had satisfied himself that the joint resistance was negligible) was mounted in its cryostat between the poles of an electromagnet, the plane of its winding perpendicular to the field. The critical current of the coil, at 1.8°K, had been determined to be 0.8 A, and the critical field approximately 1000 gauss. When the coil had become superconducting by filling the cryostat with liquid helium, the applied field was reduced from 400 to 200 gauss, and then the magnet was removed entirely. A magnetic needle outside the cryostat indicated that a "persistent" current had been induced in the coil. To evaluate the magnitude of the current, the experimenters placed a coil geometrically similar to the superconducting one equidistant from the compass needle and adjusted the current through it to annul the action of the superconducting coil on the needle. They measured the compensating current as approximately 0.6 A, below the critical current of the superconductor. For about an hour, until the helium bath warmed up from 1.8°K to the normal boiling point of 4.25°K, they observed no fall in current. And even when it became perceptible at the higher temperature, they judged that "the observations might have continued much longer without much diminution of the current." That suggested the possibility of transporting current-carrying loops:[60]

> A coil cooled in liquid helium and provided with current at Leyden, might, if kept immersed in liquid helium, be conveyed to a considerable distance and there be used to demonstrate the permanent magnetic

59. Onnes, "Further experiments with liquid helium, J. The imitation of an Ampère molecular current or of a permanent magnet by means of a supra-conductor," *PLC, 140b* (1914), 9–18.

60. Ibid., 15. Superconducting lead rings with persistent currents initiated at Leyden were eventually transported not only to Amsterdam but even to England. On June 3, 1932, J. C. McLennan exhibited before the Royal Institution such a ring carrying more than 200 amp. The current had been initiated in Leyden six hours earlier. McLennan, "Electrical phenomena at extremely low temperatures," *Report on progress in physics, 1934* (Cambridge, 1934), 198–227, on 206.

> action of a superconductor carrying a current. I should have liked to show the phenomenon in this meeting (Royal Academy of Amsterdam), in the same way as I brought liquid hydrogen here in 1906, but the appliances at my disposal do not yet allow the transportation of liquid helium.

It was therefore necessary to go to Leyden to see the miracle. It made a great impression. Paul Ehrenfest wrote Lorentz after visiting Onnes's laboratory: "It is uncanny to see the influence of these 'persistent' currents on a magnetic needle. You can feel almost tangibly how the ring of electrons in the wire turns around, around, around—slowly, and almost without friction."[61]

In a repetition of the experiment, reported in May, the current fell by less than one percent per hour, indicating a time constant of at least four days.[62] Assuming that Ohm's law is still obeyed below the threshold (and Onnes could only note that the experiments provided no ground for contradicting this supposition), he could reduce the upper limit on the micro-resistance from $0.5 \cdot 10^{-10}$ to $0.2-0.3 \cdot 10^{-10}$ times the resistance at room temperature. Having performed control experiments to rule out possible spurious explanations (magnetic effects of the apparatus, external fields, etc.), Onnes summarized the results: "Taken together...they may be said to confirm the main experiment which shows that it is possible in a conductor without electromotive force or leads from outside to maintain a current permanently and thus approximately to imitate a permanent magnet or better a molecular current as imagined by Ampère."

## 4. EPILOGUE

The experiments in January and February 1914 decisively dashed Onnes's dream of exploiting superconductors in high-field magnets with their enormous potentials for fundamental and practical applications. In spite of this disappointment and the interruption of the war, Leyden continued to maintain a leading role in superconducting investigations well into the 1920s.[63] The elegant experiments on persistent currents

61. P. Ehrenfest to H. A. Lorentz, 11 Apr 1914, quoted in M. J. Klein, *Paul Ehrenfest, Volume I: The making of a theoretical physicist* (Amsterdam, 1970), 214.

62. Onnes, "Further experiments with liquid helium, J. The imitation of an Ampère molecular current or of a permanent magnet by means of a supra-conductor," *PLC, 140c* (1914), 21–26. One of the lead coils used in the 1914 experiments, preserved in the Museum Boerhaave, is described briefly as item 132 in KO, 113g (ref. 51).

63. Cf. C. A. Crommelin, "Zusammenfassende Bearbeitungen: Der supraleitende zustand von metallen," *PZ, 21* (1920), 274–280, 300–304, 331–336; C. J. Gorter, "Superconductivity until 1940 in Leyden and as seen from there," *Reviews of modern physics, 36* (1964), 3–7.

were repeated and refined many times,[64] steadily depressing the upper limit on resistance below the critical temperature.[65] The Leyden group further showed that, under certain conditions, the transition to superconductivity occurs discontinuously; the experimentally observed slight knee in the curve of resistance against temperature at the transition point is an artifact of the sample purity and the finite measuring current. In addition to mercury, tin and lead, thallium, indium and gallium were soon found to be superconducting. A very long time elapsed, however, before the several effects frustrating Onnes's dream were fully understood.

In retrospect, one of the most interesting aspects of the researches at Leyden up to 1914 is that the true relationship between the critical current and the critical field apparently eluded Onnes. That they are indeed identical effects—that a critical current restores the resistance of a wire by the surface magnetic field it produces—was first explicitly suggested by Francis Briggs Silsbee of the National Bureau of Standards in Washington in 1916. A decade later the Leyden group confirmed Silsbee's hypotheses that the critical current derives from the critical field, and that superconductivity is destroyed when the sum of the applied field and the "self field" of the transport current exceeds the critical field.[66] Equally noteworthy is Onnes's discovery of superconductivity following upon his quest for ever purer substances—a poignant illustration that experimental advances come often by circuitous paths.

64. Onnes demonstrated that a persistent current could be initiated by a battery and made to disappear by breaking the circuit. For this purpose the Leyden group devised a superconducting switch consisting of two lead blocks, one of which had three small conical points on its surface. By pressing these blocks together under liquid helium a contact of negligible resistance could be readily opened or closed, allowing the superconducting coil to be short-circuited at will in the helium bath. Onnes, "Further experiments with liquid helium, L. The persistence of currents without electromotive force in supraconducting circuits," *PLC, 141b* (1914), 15–21. Recently physicists at MIT kept a persistent current running for several years until they found it impractical to maintain the liquid-helium level in the dewar.

65. No modern experiment has succeeded in revealing any trace of resistance. The known upper limit is $10^{-14}$ times that of the purest copper at close to absolute zero. D. Dew-Hughes, "Introduction to superconducting materials" in T. Luhman and D. Dew-Hughes, eds., *Metallurgy of superconducting materials* (New York, 1979), 1.

66. F. B. Silsbee, "Electrical conduction in metals at low temperatures," Washington Academy of Sciences, *Journal, 6* (1916), 597–602; W. Tuyn and H. Kamerlingh Onnes, "Further experiments with liquid helium, AA. The disturbance of supra-conductivity by magnetic fields and currents. The hypothesis of Silsbee," *PLC, 174a* (1926), 13–39. This paper, which demonstrated the parabolic dependence on temperature of the critical magnetic field, was a reworking of Tuyn's doctoral thesis of 1924.

## Guesses at the mechanism

In summing up his experiments on mercury in 1913, Onnes insisted that they decisively disproved the validity of the old electron theory at low temperatures even in connection with the law of Wiedemann and Franz, which had been one of its greatest successes. This failure, he wrote, "indicates a difference between the super-conducting and the ordinary conducting state, which may be regarded as a *characteristic* difference of both." Perhaps, he suggested, the entire approach—the hypothesis of the movement of free electrons through metals—would have to give way to "an essentially different one for the superconducting condition, according to which the movement of the electrons is carried by the current for considerable distances, but each separate electron which takes part in the progress, only moves one molecular distance."[67]

Onnes noted that Johannes Stark had suggested such a theory to explain the dependence of electrical conductivity on temperature.[68] He assumed that each atom in a metal releases a valence electron, and that these electrons form a regular lattice maintaining the atoms in position. An electron in a lattice can be displaced only on certain shearing surfaces of the metal crystal and only in unison with the simultaneous movement of other electrons. Stark's model was unable to account for thermal conductivity. However promising Stark's approach might appear if regarded as a forerunner of lattice theories, Onnes—and most other physicists of the time—considered that Wilhelm Wien had come closer to the mark. Wien's theory addressed the problem of fitting Planck's formulas to the data on superconductivity. Quite apart from the trouble with the zero-point energy, which Onnes had mentioned at the Solvay Congress, was the difficulty that to get a quick onset of superconductivity the frequency $\nu$ in Planck's formula must increase slightly at the vanishing point, whereas to make the formula agree even qualitatively with the course of the resistance curve at higher temperatures, the frequency must drop as the temperature falls.

Wien took equation (1) as his starting point, but from the evidence furnished by specific heats, that electrons do not appear to contribute significantly to the thermal energy of a metal, he discarded the most fundamental assumption of the free electron theory, namely, that the kinetic energy of the electrons is proportional to the absolute temperature.[69] He ignored the classic problem of thermal conductivity and the

67. Onnes (ref. 49), 42–43.

68. J. Stark, "Über electrische und mechanische Schubflächen in Metallen," *PZ, 13* (1912), 585–589.

69. W. Wien, "Zur Theorie der elektrischen Leitung in Metallen," *SB, 5* (1913), 184–200. According to K. F. Herzfeld, "Zur Elektronentheorie der Metalle," *AP, 41*

Wiedemann-Franz law. He assumed with Riecke and Onnes that the electron density is independent of temperature, and so had only the mean free path to vary in his theory. He connected with Planck's formula by the relationship then usually supposed between the frequency of collisions (and hence mean free path) and the square of the amplitude of atomic vibrations, which he justified by demonstrating that this is the only relationship that makes the frequency of collisions independent of the exact distribution of energy among the atoms. To get resistance as a function of temperature, he integrated Planck's first expression for oscillator energy over a spectrum of frequencies.[70] At high temperatures, Wien's formula gives $R \propto k\nu_M T/h$, where $\nu_M$ is an upper limit in the frequency spectrum; when expressed as a quadratic ratio of resistances, this formula reduces to equation (7). At low temperatures, Wien got $R \propto (kT/h)^2$; this quadratic dependence on $T$ is not sufficiently fast to describe most metals at the lowest temperatures, and, of course, it could not account for the behavior of superconductors. Like Onnes, Wien regarded Planck's hypothesis of zero-point energy as problematic for the resistance theory, and vice versa.[71]

During the war Lindemann tried his hand at explaining the Leyden results via a lattice theory, and Thomson proposed a characteristically ingenious and implausible model. Lindemann treated electrical conduction as a drift of the electron lattice as a whole through the atomic lattice; below a certain temperature the amplitude of atomic vibrations no longer hinders the motion of the electron lattice and superconductivity results. He could not derive an explicit dependence of resistance on temperature, but he was able from dimensional arguments to suggest behavior in broad agreement with modern theories. Thomson regarded metal atoms as electrical doublets normally aligned at random. In an electric field they tend to align in chains bound together by both the field and forces between the dipoles. Superconductivity occurs when the forces between the dipoles exceed the lattice forces. Thermal vibrations and the lattice forces eventually combine to exceed the dipole-restoring forces above a certain temperature.[72] Thomson's theory had

(1913), 27–52, on 29, J. Koeningsberger, Deutsche Physikalische Gesellschaft, *Verhandlungen, 13* (1911), 934, was the first to suggest that the electron energy might differ from $3kT/2$.

70. Cf. P. Debye, "Zur theorie der spezifischen Wärmen," *AP, 39* (1912), 789–839. In Debye's treatment, $\nu$ is not a frequency of atomic vibrations, but of elastic waves in a solid.

71. Cf. Kuhn (ref. 40), 246–247, 319. The reception of the hypothesis of zero-point energy deserves study. An important view by one close to Onnes is W. H. Keesom, "Zur theorie der freien elektronen in metallen," *PZ, 14* (1913), 670–675 (*PLS, 30b* [1913], 17–26), and in the correpondence between Keesom and Wien, May 1913, in KO, 93.

72. F. A. Lindemann, "Note on the theory of the metallic state," *PM, 29* (1915), 127–140; J. J. Thomson, "Conduction of electricity through metals," *PM, 30* (1915), 192–202.

considerable popularity among physicists unfriendly to quantum theory. As for the father of quantum theory, he had no explanation to propose of Onnes's "remarkable discovery of a discontinuity in resistance."[73]

In 1922 the other chief architect of the quantum theory, Einstein, reviewed the problem of superconductivity and admitted that it still defied explanation.[74] It could not, in his view, depend on *free* electrons moving under the influence of thermal agitation, in light of Onnes's demonstration that normal threads coated with superconductors are also superconducting. Conduction would have to be associated with peripheral atomic electrons involved in "closed molecular chains" analogous to Onnes's Amperian currents. (A similar mechanism had been suggested by Fritz Haber in 1919.) But Onnes's further discovery that a junction between two different superconductors (tin and lead) is also superconducting undermined the approach since it seemed improbable that two different types of atoms could form chains with each other. Einstein put the dilemma back in the hands of the experimentalists: "with our considerable ignorance of complicated quantum-mechanical systems we are far from being able to formulate these ideas in a comprehensive theory. We can only attack the problem experimentally."[75]

For several decades, the superconducting state was synonymous with metals with zero electrical resistance. But in 1933 Walther

73. Planck to Onnes, 10 Mar 1915 (KO, 8).

74. A. Einstein, "Theoretische Bemerkungen zur Supraleitung der Metalle," *Het natuurkundig laboratorium der Rijksuniversitetet te Leiden in de jaren 1904–1922* (Leyden, 1922), 429–435. For a review of the experimental situation to 1920 see J. Koeningsberger, "Metallische Leitung," *Handbuch der Elektrizität und des Magnetismus, 3* (Leipzig, 1923), 597–724. Superconductivity came up for discussion at the third Solvay conference (1921), where Onnes discussed superconducting "filaments," or macroscopic paths along which peripheral atomic electrons pass without transferring energy to neighboring atoms, and expressed confidence in the Rutherford-Bohr atom and the quantum theory. Onnes, "Le paramagnétisme aux basses températures...," *Atomes et électrons* (Paris, 1923), 131–157. (*PLS, 44a* [1921], 30–50). Onnes reiterated his views on filaments at the fourth Solvay Congress (1924): "Nouvelles expériences avec les supra conducteurs," *Conductibilité électrique des métaux et problèmes connexes* (Paris, 1927), 251–281.

75. In a letter to Maria Rooseboom, 27 Feb 1953 (KO, 113), Einstein gave the following assessment of Onnes's scientific personality: "I knew Kamerlingh Onnes very well, but mainly on a personal basis. His warm and kind personality concealed a tanacity and energy such as is only rarely encountered. We were naturally less close scientifically, and thus we rarely entered into points of discussion. Discussions with him were on the whole not easy. Inasmuch as he was indeed extraordinarily accurate in his intuitive reasoning, he was less able to express himself rigorously in abstract matters, and was also not very open to the reflections of others—a psychologically extremely interesting personality, into which, however, I was not able to gain adequate insight in order to venture a characterization."

Meissner and Robert Ochsenfeld demonstrated that an external field is excluded from the interior of a conductor cooled below the critical temperature in the presence of the field.[76] This diamagnetic behavior was a surprise against all expectations for a metal of infinite conductivity based on firmly rooted principles of electromagnetism. The discovery sparked several phenomenological theories reproducing the observed gross macroscopic behavior of superconductivity. New centers of research, first in Toronto, Berlin, Cambridge, and Oxford, then in the United States, collectively eclipsed Leyden in this field. A genuine microscopic theory, at least for a certain class of superconductors, appeared in the United States in the 1950s. Practical application in high field magnets became possible only some years later.[77]

Superconductivity has been described as "the kind of phenomenon that every physicist would like to have discovered; it is very striking and easy to verify."[78] However, the exciting events of 1911–1914 were the reward of years of systematic investigation and, indeed, the culmination of twenty years of preparatory cryogenic effort. Well over half a century would be required to complete the unravelling of the phenomenon firmly established by Onnes and his colleagues before the first world war.

76. W. Meissner and R. Ochsenfeld, "Ein neuer Effekt bei Eintritt der Supraleitfähigkeit," *Naturwissenschaften, 21* (1933), 787–788.

77. See R. D. Parks, *Superconductivity,* (2 vols., New York, 1969); D. M. Ginsberg, "Resource letter SCY-1 on superconductivity," *American journal of physics, 32* (1964), 85–89, and "Resource letter SCY-2 on superconductivity," ibid., *38* (1970), 949–955; and, for technical applications of superconductors, *Metallurgy* (ref. 65).

78. M. and B. Ruhemann, *Low temperature physics* (Cambridge, 1937), 270.