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LANDMARK EXPERIMENTS IN SUPERCONDUCTIVITY

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SUPERCONDUCTIVITY is the phenomenon whereby certain elements, alloys, and compounds exhibit the startling property of losing all trace of electrical resistance quite abruptly at a definite and generally very low temperature—typically a few degrees above absolute zero. The phenomenon was discovered by the Dutch physicist Heike Kamerlingh Onnes at the University of Leiden in 1911, not by accident as is often asserted and, strictly speaking not by Kamerlingh Onnes himself. In this note, intended for those not particularly versed in the subject and its background, some of the elementary facts of superconductivity are introduced by way of a mostly nontechnical recounting of several classic experiments that established these facts.

Superconductivity owes its discovery to a classic scientific dispute that erupted at the turn of the century. The dispute centered on the behavior of the electrical resistance of pure metals at progressively lower temperatures. The work of Walther Nernst and his students in Berlin appeared to confirm the prevailing theoretical expectation that the resistance approaches zero near absolute zero. However, ongoing measurements by James Dewar in London gave troubling indications that, in the temperature domain of liquid hydrogen (near 20 degrees Kelvin), the resistance of platinum was dropping at an anomalously slow rate. This hinted at a contrary theory which held that near absolute zero the "free electrons" of a metal should condense onto the atoms. On this assumption a minimum in resistance should be encountered somewhere below 16 degrees Kelvin (the lowest temperature within reach in 1900), with the resistance increasing indefinitely at still lower temperatures. This implausible theory was mainly propounded by the omnipotent Lord Kelvin himself, whose opinions counted. For various reasons, Kamerlingh Onnes was sympathetic to this view as well.

Having succeeded in liquefying helium in 1908 (beating Dewar in a hotly contested race), Kamerlingh Onnes (Figure 1) was well positioned to pursue experimentally the resistance question to even lower temperatures, down to or below 4.2 degrees Kelvin (the boiling point of liquid helium). The actual measurements were entrusted to Gilles Holst, a graduate student. Preliminary measurements in late 1910 on platinum and gold to within 1.5 degrees of absolute zero (reached by pumping on the liquid helium bath) confirmed the tendency observed by Dewar. Far from approaching zero near absolute zero, much less rising after passing through a minimum, the resistance leveled off at a constant, temperature-independent "residual" value. The measurements also established (actually rediscovered a 50-year old rule known from room-temperature measurements) that the residual resistance decreases with increasing purity of the resistance sample, as shown in Figure 2. Moreover, extrapolation of the results to zero impurity suggested that the resistance might reach zero somewhere *above* absolute zero, not simply *at* $T = 0$. Kamerlingh Onnes even concocted a theory of sorts, invoking Planck's new quantum of action, to account for this possibility.

To settle the matter once and for all, Kamerlingh Onnes next turned to mercury with characteristic ingenuity: being a liquid metal at room temperature, mercury can be repeatedly distilled in vacuo to an even higher degree of purity than gold. The results, obtained during April–May of 1911, are also shown in Figure 2. Neither Nernst, Dewar, Kelvin, or Kamerlingh Onnes proved correct. To be sure, the resistance fell to an immeasurably low value well above zero, by happenstance nearly at the boiling point of liquid helium. Quite unforeseen, however, was the abruptness of the plunge in resistance, something which no theory—however implausible—could explain. Kamerlingh Onnes could scarcely doubt that he had encountered an entirely new state of matter.

Figure 1. H. Kamerlingh Onnes, as depicted in a well-known drawing by his nephew.

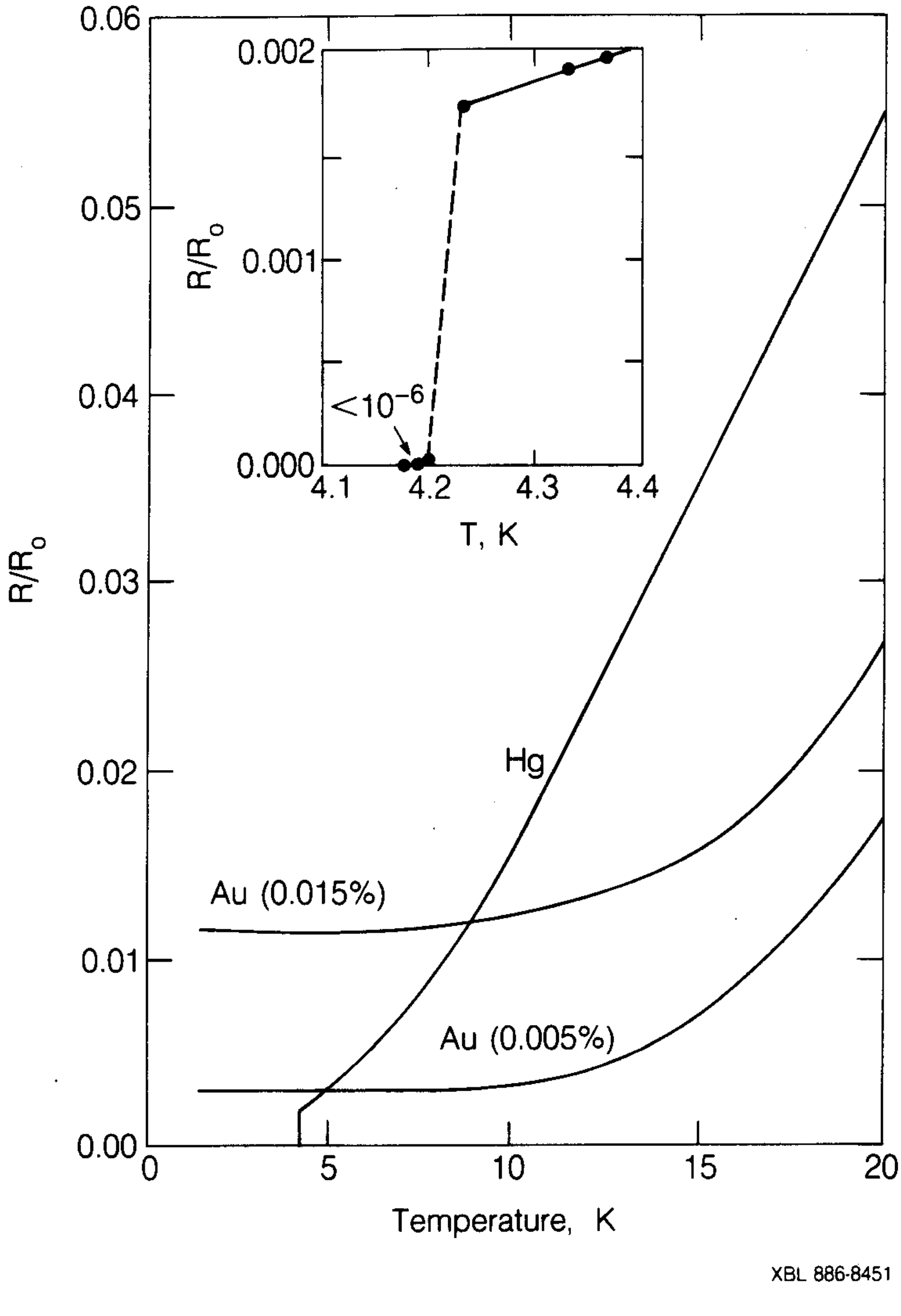

Figure 2. Resistance vs. temperature for two gold samples of different degrees of purity (as measured in 1910) and for pure mercury (1911). The insert shows the actual data points for mercury, plotted to a finer scale.

Regardless of the physical mechanism at work (which would remain obscure for half a century), Kamerlingh Onnes realized at once the potential practical significance of their discovery:

> The more the upper limit which can be ascribed to the resistance remaining at helium temperature 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 ..., 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 ..., then further experiments in all possible directions would give the fullest promise, notwithstanding the great difficulties which are encountered when working with liquid helium.[1]

Unfortunately, mercury was at best an awkward material. The resistances had to be prepared by an elaborate procedure, pouring distilled mercury into a series of U-shaped glass capillary tubes and freezing it during each experiment. Great must have been the excitement with the discovery, in late 1912, of superconductivity in lead and tin (and in not particularly pure samples at that!). Prospects for exploiting superconductors in high-field electromagnets brightened at once. Two benefits beckoned, as Kamerlingh Onnes had emphasized. First, the power consumption in resistive heating plaguing conventional copper windings was virtually eliminated. Second, since the superconductors could evidently support high current densities, high magnetic fields should be possible in coils of relatively modest dimensions.

Alas, Kamerlingh Onnes's hope was soon dashed. In fact, indications of something amiss had cropped up soon after the original discovery with mercury. To obtain better estimates for the upper limit on the "micro-residual" resistance, if any, below the transition temperature, they had steadily raised the strength of the current passed through the samples, hoping thereby to improve the accuracy of measurements of potential difference along the mercury threads. It gradually dawned on them that the superconducting state is "quenched" if the current density exceeds a certain threshold or critical value; this value was disappointingly low for mercury, tin or lead. An equally nasty surprise awaited them when they wound the first small coils of lead or tin: a threshold for the magnetic field (typically a few hundred gauss), above which the conductor again reverts to the normal (resistive) state.

At the time Kamerlingh Onnes failed to see any connection between the threshold current (which he vaguely blamed on "bad places" in the wire or mercury thread) and the threshold field (the effect of which he perceptively likened to that of heating the conductor). The connection was correctly deduced by Francis B. Silsbee of the U.S. National Bureau of Standards in 1916. According to "Silsbee's hypothesis," the two effects are in fact one and the same thing: "The threshold value of the current," in Silsbee's words, "is that at which the magnetic field due to the current itself is equal to the critical magnetic field."

Kamerlingh Onnes's team found time for one more, particularly elegant experiment before the first world war intervened. (Holland remained neutral during WWI, but they ran out of helium.) To further pin down the upper limit on resistance, they (actually the indispensable technical supervisor G. J. Flim) prepared a small lead coil with its leads fused together to form a closed electrical circuit (the joint resistance having previously been found to be negligible). The coil in its helium vessel (cryostat) was cooled down while exposed to an external magnetic field (weaker than the threshold field) by filling the vessel with liquid helium with the vessel placed between the pole pieces of a laboratory magnet. The field was then removed by rolling the magnet away on casters. In so doing, a "persistent current" was automatically induced in the coil (decreed by the laws of electrodynamics to compensate for the change in magnetic flux linking the circuit). The existence of the current was shown by its effect on a magnetic needle adjacent to the cryostat. For about an hour, or until the helium bath evaporated, they observed no diminution in current strength, indicating that the resistance had to be at least ten billion times smaller than its room temperature value.

In a modern repetition of this experiment at the Massachusetts Institute of Technology, a persistent current ran for over two years with no sign of weakening (stopped only by a strike that interrupted the supply of helium). Though it cannot be established unequivocally by experiment, it seems reasonable to assume (from even more persuasive measurements) that the electrical resistance in the superconducting state is truly zero.

For 22 years it was tacitly assumed by almost everybody that the only essential property of superconductors is that of zero electrical resistance. Thus, superconductivity was perceived essentially as an extreme case of classical electromagnetic behavior subject to the laws of Maxwell. This assumption could have been put to a rather simple test. If the superconducting state is simply one of infinite electrical conductivity then, on cooling a *solid* specimen below the transition temperature while in a magnetic field, the sample, once superconducting, should trap the field in its interior. On subsequently removing the external field, persistent currents should be induced in the superconductor such as to leave the specimen with a permanent "frozen-in" flux, easily measured. An experiment by Walther Meissner and his assistant Robert Ochsenfeld, carried out in Berlin in 1933, revealed this *not* to be the case; when a superconductor is cooled in a magnetic field the field is actually expelled from its interior the moment it enters the superconducting state.

Meissner's experiment was in fact performed to test a somewhat different but related question, and succeeded by a fortuitous accident. He wished to confirm what had been generally suspected for some time, that a current passed through a superconductor flows exclusively in a very thin surface layer. The experimental arrangement consisted of a pair of long side-by-side cylindrical rods (single crystals) of tin, connected electrically in series and to an external current source. The idea was to measure the magnetic field between the two cylinders with a small current flowing down one rod and back up the other, first at room temperature and then with the cylinders cooled below the transition temperature; the field would depend on the detailed current distribution in the rods. (Note that a *single* current-carrying cylinder would not have sufficed for this particular test, since by the symmetry the external field produced by it would have been the same whether the current flowed in a surface layer or uniformly over the whole cross section.) It happened that in one of the experimental runs the Earth's magnetic field was not cancelled with an auxiliary coil (normally a routine procedure), and it was observed that this field was spontaneously expelled from the tin cylinders as soon as they became superconducting. In deference to the principal experimenter this effect, which has no classical analogue, is known as the Meissner effect. (Subsequent experiments by Meissner also confirmed the superficiality of the current distribution in superconductors.)

In closing, it should be emphasized that the superconducting properties discussed here, zero resistance, perfect diamagnetism (exclusion of magnetic flux), and finite but low threshold field (or current) applies mainly to one class of superconductors known in the modern parlance as Type I superconductors. These include virtually all of the superconducting elements in the periodic table (about two dozen) except niobium. In the early 1930's a second group of superconductors was uncovered at Leiden and in Berlin, consisting of compounds and alloys—notably lead-bismuth. These had much more promising critical fields (tens of thousands of gauss). However, the revived optimism for practical application again proved short-lived with the subsequent determination that their current-carrying capacity remained too poor to be of other than academic interest.

Another thirty years elapsed before the first practical high-field superconductors were developed by industry, exemplified by the ductile alloy niobium-titanium which is the workhorse of today's superconducting technology. These belong to a second and much larger class of superconductors, those of Type II, that derive their high field *and* current capability from the very fact that they possess a rather intricate structure which has the effect of inhibiting the properties of "ideal" (Type I) superconductors—i.e., those of zero resistance and complete field exclusion. Quite recently, much national attention has focused on a new and startling variety of Type II superconductors: the so-called high-T_c or oxide superconductors. As implied by the dual phraseology, these materials exhibit unparalleled high transition temperatures (≥ 100 K), but their current capacity remains uncertain and, being oxides of metals, their mechanical properties are definitely problematic! Only time will tell the significance of these recent developments from both a fundamental and a practical point of view.

References

[1] H. Kamerlingh Onnes, "On the change of the electrical resistance of pure metals at very low temperatures, etc. The disappearance of the resistance of mercury," *Communications from the Physical Laboratory of the University of Leiden, 122b* (1911), 13-15.

Further Reading

For a more technical account of the early experiments at Leiden, with references, see R. de Bruyn Ouboter, "Superconductivity: Discoveries during the early years of low temperature research at Leiden, 1908-1914," *IEEE Trans. on Magnetics*, *MAG-23* (1987), 355-370. The best semitechnical introduction to superconductivity and the development of low-temperature physics generally remains K. Mendelssohn's *The Quest for Absolute Zero* (McGraw Hill Book Co., New York and Toronto, 1966); Mendelssohn cites most of the classical sources. A standard text is A. C. Rose-Innes and E. H. Rhoderick, *Introduction to Superconductivity*, 2nd Ed. (Pergamon Press, New York, 1977).