Superconductivity until 1940 In Leiden and As Seen From There

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The organizers of this conference asked me to speak on superconductivity before 1940, and since Dr. Mendelssohn will treat the same subject I shall concentrate on the developments on the continent of Europe and, in particular, in Leiden, where Kamerlingh Onnes discovered superconductivity in 1911 and where a considerable fraction of the early developments took place. I have no personal recollections of the first 16 years. Working from 1927 to 1931 as a graduate student in the Kamerlingh Onnes Laboratory, I was fascinated by the researches carried out at that time by Sizoo, Voogd, and others under the supervision of De Haas. But I belonged to the paramagnetic group, which also stood under De Haas' supervision, with the equally fascinating future topic of adiabatic demagnetization in the background. I certainly followed the developments in the field of superconductivity and took a part in their discussions but it would have been contrary to the unwritten rules of the laboratory to meddle with the work of one's colleagues. It was only after my appointment at the small laboratory of Teyler's Foundation in Haarlem, 20 miles north of Leiden, that I started making small calculations on superconductivity, still profiting, however, from the contacts with the expert staff of the Leiden laboratory. Early in 1936, I was appointed at the University of Groningen in the north of the Netherlands, but already my main interest had switched back to paramagnetism: relaxations and attempts to observe nuclear and electronic resonances. I had been fortunate in that my Haarlem time had coincided with a period of rapid advance in our knowledge of superconductivity.

Let us turn back to the Leiden Communications of 1911. The discovery of the superconductivity of mercury was obviously a consequence of the liquefaction of helium, achieved by Kamerlingh Onnes 3 years earlier. A temperature interval reaching from 14° down to 1°K had then been opened for research. Onnes' collaborator Holst had improved the facilities for measuring small resistances, while, on the other hand, the necessity to keep the mercury in glass capillaries was an awkward complication. Incidentally, I may remind you that gold and platinum wire had been studied before and that, in 1910, Kamerlingh Onnes had claimed the resistance of very pure gold wires to be zero in the liquid-helium range within the limits of his, then, rather poor experimental accuracy. The theoretical background was formed by Lorentz' theory of electrons, according to which the electrical conductivity is proportional to the number of conduction electrons and to the time between consecutive scattering processes and Lord Kelvin's proposition that the conduction electrons would condense at very low temperatures on the atoms "to which they belong." Kamerlingh Onnes, at first, interpreted superconductivity as a quantum phenomenon leading to a very rapid decrease of the scattering probability with decreasing temperature, disengaging himself from Kelvin's proposition on the vanishing number of conduction electrons. But observing that, in lead and tin, superconductivity occurs in impure samples too, and noticing that the persistence of currents in a lead ring demonstrated the ratio between the resistances in normal metals and superconductors to be many orders of magnitude, he gave up premature theorizing and concentrated on experiments about the new phenomenon. He immediately had in mind the production of strong magnetic fields without dissipation of Joule heat. It was a great disappointment to him that longitudinal and transversal magnetic critical fields of a few hundred oersteds were found to destroy superconductivity. Though his supercurrent densities sometimes exceeded 10^5 A/cm^2, he also found that there was a maximum to the currents too. The state of the metals in large fields was found to be a continuation of the normal state above the transition. In connection with the superconductivity of films deposited on normal metal, he made the remark that apparently the superconducting electrons do not mix with those of the base metal.

During World War I, Kamerlingh Onnes had to stop almost all research with liquid helium. It was in that period that Silsbee made his suggestion that the disturbance of superconductivity by a current was due to the magnetic field at the surface of the wire, thus, making two phenomena merge into one. After the war, research was resumed by Tuyn who found the parabolic dependence on temperature of the critical field, and, thereupon, by Sizoo.

At the Solvay conferences of 1921 and 1924, Kamerlingh Onnes gave interesting progress reports. Because of Onnes' illness, Keesom replaced him at the latter conference. He had an interesting discussion with Bridgeman on the thermodynamics of the disturbance by a magnetic field. Keesom made the point that this disturbance was a typically irreversible phenomenon, since setting up an external magnetic field above the critical value H_c and thereupon reducing it to zero was leading to a situation different from the original one. Nevertheless, writing down Clapeyron's equation, replacing p by the magnetic field H and V by the magnetic moment M, he arrived at a relation between dH/dT along the transition line and the heat of transformation; which he confirmed with Van Laer a dozen years later.

In 1925, Mrs. De Haas—born Lorentz—published a note referring to the question, asked by her husband, how a variation of the external magnetic field could ever exert any influence on a superconductor if, according to Kamerlingh Onnes' view, it was completely screened off by a surface current. She pointed out that this so-called surface current should consist of n moving electrons per unit volume with charge e and mass m. In the usual reasoning on superconductivity, the kinetic energy $\frac{1}{2}mv^2$, where v is the average velocity of the electrons, was neglected in comparison with the electromagnetic energy. She computed at which size the two similar contributions would be equal and arrived at the statement that this would be at a few hundred Ångström, this being $(mc^2/4\pi ne^2)^{\frac{1}{2}}$. This important remark appeared in *Physica* in the Netherlands language and is therefore only rarely quoted. In 1933, Becker, Heller, and Sauter straightforwardly asked how thick the superconductive surface current would be if this consisted of free and frictionless electrons. Their expression for the current was proportional to $\exp(-x/\lambda)$, the same variation occurring for the magnetic field, x being the distance from the surface and the penetration depth λ again being $(mc^2/4\pi ne^2)^{\frac{1}{2}}$, which is now usually called London's penetration depth.

When Kamerlingh Onnes retired a few years before his death in 1926, Keesom and De Haas, as codirectors of the Kamerlingh Onnes Laboratory, divided the Leiden low-temperature research into two approximately equivalent parts. Keesom concentrated on liquid helium, molecular physics, and thermal properties, while De Haas took care of the electric and magnetic properties of matter. From time to time, minor friction occurred on competence in borderline subjects. After Keesom, with Clusius, had discovered the jump in the specific heat of liquid helium, he entered such a borderline subject, finding, with Van den Ende, a somewhat similar jump at the critical temperature of tin. This prompted Ehrenfest, in the last year of his life, to introduce the notion of phase transition of the second order. At the transition temperature not only the Gibbs functions of the phases are equal, but also their derivatives with respect to T—minus the entropy—and to p—minus the volume. Keesom, who had attracted Ehrenfest's attention to this problem, applied the formalism to the transition line between helium II and helium I and Rutgers suggested (at Ehrenfest's colloquium) its application to superconductivity. This induced me to consider this latter problem in some more detail. The difference in Gibbs function of a superconductive sample in zero magnetic field and of the same sample in the normal state, secured by a large magnetic field, could be computed by integrating down from a temperature above the critical temperature making use of the new specific-heat data.

Adding to the Gibbs function of the superconductor a magnetic term which is $1/8\pi$ times the square of the external field per unit volume if the sample is very oblong in the field direction, one can find at which field it reaches the value of the Gibbs function of the normal state. Making this simple calculation as a straightforward application of Keesom's excellent undergraduate course in thermodynamics, I obtained the field at which disturbance of superconductivity was thermodynamically possible, not entering into a discussion whether the mysterious irreversibility of the transition would considerably shift it to still higher fields. I suggested Rutgers join our efforts and that we write a paper together, but he was of the opinion that the time was not ripe and so I published my calculation in the Archives of the Teyler's Foundation at Haarlem to which I then had moved.

A few months later, the Meissner effect was discovered. Its background was a paper of Von Laue in which he ascribed Sizoo's result that the first trace of resistance in a superconductive wire appears in a transversal field, which is only about half the longitudinal critical field H_c, to the squeezing of the magnetic field lines which are supposed not to penetrate into the superconducting wire. To test this suggestion, De Haas and Voogd investigated the disturbance in a wire of ellipsoidal cross section and confirmed Laue's picture. Meissner and Ochsenfeld then studied the local magnetic field by small induction coils at different spots near large superconductive samples. While Tuyn's Leiden experiments of the early twenties had led to the conclusion that, upon decreasing a large field, the critical field would be frozen into a superconductor, Meissner found that a large fraction of magnetic field lines often were pushed out of the sample when the field was reduced to a low value. A sphere of pure tin behaved as if it had a very small permeability, almost as if the situation had been reached by increasing the external field from zero. I immediately reacted, in *Nature*, suggesting $B = 0$ to be a general characteristic for superconductivity, ascribing Tuyn's result to the formation of superconductive rings enclosing normal-state matter. Casimir and I then discussed the whole matter again in *Physica*, emphasizing the character of the magnetic energy, the decisive role of the parallel local field at the boundary between the phases, and the splitting of samples which are not very oblong in the external field direction into thin normal and superconductive regions in a range of external fields below the critical field H_c.

F. London later told me that, after reading Meissner and Ochsenfeld's note, his brother and he had immediately made the thermodynamical analysis too and then were disappointed to find that its result had already been published in what he was right to consider a rather obscure journal. Later he was, however, faster than we in publishing—simultaneously with Peierls—a formal description of the "intermediate state," occurring in the not very oblong samples, between the field strength at which the first flux enters and the critical field H_c. The paper which Casimir and I had prepared on the same subject had been retarded by our doubts on the shape of the phase boundaries near the surface of the sample. Later, Landau and the Cambridge school grappled with that question.

At that time, only a few German physicists had been influenced by the Nazi ideology which had politically taken over in Germany, and after some hesitation Keesom, as well as I, decided to attend the meeting of the German Physical Society in Bad Pyrmont in September 1934 at which low-temperature physics was a main subject. In the several interesting discussions, Meissner left the statement that the magnetic induction in pure superconductors was zero at my responsibility. With Laue, Keesom and I had rather tenacious discussions. Laue and Justi had attacked the possibility of Ehrenfest's transitions of the second order arguing that the free energies, or Gibbs functions, of the two phases would osculate in the transition point so that above and below the osculation point the same phase would be stable. Now this question was just answered by a short communication of Casimir and myself in which we introduced an internal parameter indicating a degree of superconductivity. With rising temperature this degree would decrease gradually—this could be described as a sort of evaporation of superconductive electrons into the normal state—until with the disappearance of the last superconductive electrons the superconductive properties would disappear. It is clear that in this model there is no place for Laue and Justi's objection since the number of superconductive electrons could not become negative. There was also a difference of opinion with Laue on the tricky matter of the magnetic contribution to the Gibbs function.

When it was later found by Pontius, Misener, Shalnikov, Shoenberg, and others that the penetration depth increases with rising temperature, and by H. London that high-frequency electric losses occur approximately as expected for a mixture of superconductive electrons, this so-called two-fluid model obtained a similar temporary popularity as Tisza and Landau's two-fluid model of helium II. In the fifties, the internal parameter was reincarnated in the order parameters of Landau–Ginsburg and Pippard, which can vary with the coordinates and the local field, while the parameter may also be considered as an ancestor of the actual temperature-dependent energy gap. The exponential dependence of the specific heat of a superconductor far below the transition temperature has sometimes been used as an argument for the replacement of the two-fluid model by an energy-gap model. I feel that this was hardly relevant. In order to agree with Tuyn's simple critical field curve and with Keesom and Kok's T^3 behavior of the specific heat of a superconductor, we proposed a rather queer dependence of the free energy on the internal parameter. A more natural choice of this free energy would have yielded an exponential temperature dependence of the specific heat and to a corresponding small deviation from Tuyn's curve.

Around this time, I made my first visit to the new and dynamic low-temperature research group of refugees from Germany which had formed in Oxford. Though it was not hidden from me that the contacts maintained by the Netherlands scientists with their colleages in Germany were hardly appreciated by Simon and his colleagues, immediately a spirit of understanding and friendship developed among us. I greatly enjoyed those cordial and stimulating contacts with the Oxford group. Our lively and fertile exchange of ideas by correspondence was repeatedly mentioned in the papers from both sides.

In 1935, F. and H. London proposed their wellknown equation according to which the curl of the supercurrent density is proportional to the local magnetic field. Though the elegance of the treatment was certainly recognized, I am afraid that its importance was underestimated somewhat in Holland. It was sometimes considered as a completion of Becker, Heller, and Sauter's formalism by fixing the integration constant of the magnetic field according to the Meissner effect. The discussion of the implications and the background of the equation gave emphasis to the diamagnetic aspect of superconductivity, while the complete disappearance of the electrical resistance at most appeared as a secondary quality, a shift of values which was not immediately appreciated everywhere. But it cannot be denied that the London equation has proved to be the basis for further understanding of the nature of superconductivity as well as for the formal description of the magnetic and electric behavior of superconductive bodies. That this was, in the long run, also appreciated in Holland was demonstrated when in 1953 F. London was awarded the Lorentz medal for theoretical physics. The confirmation of his prediction of flux quantization was a late demonstration of the width of his vision. The application of the London formula to the distribution of fields and currents in films and small particles was made by H. London.

Let us finally consider the early work on supraconductive compounds and alloys. Meissner, in his Berlin time, was—so to say—the Matthias of the late twenties and early thirties and discovered the superconductivity of several transition metals, compounds, and alloys. In Toronto, MacLennan and collaborators also investigated many alloys, while, in Leiden, the Belgian physicist and metallurgist Van Aubel participated in such research. In 1930, De Haas and Voogd observed that the destruction of superconductivity in some alloys required very high magnetic fields. In connection with Rutgers' equation, Van Alphen remarked that this ought to be accompanied by an enormous jump in the specific heat. A large part of the following experimental investigations on alloys was carried out in Oxford and Charkov by Mendelssohn and Schubnikov and their collaborators. The large jump in the specific heat was found to be absent and the magnetic field was found to penetrate at much lower fields than were required for the destruction of superconductivity. I tried to reconcile these results with the thermodynamical and electromagnetic argument by proposing the splitting up of the alloys in thin superconductive and normal regions parallel to the field. The difference with the "intermediate state" occurring below the critical field in common superconductors of not very oblong shape was that the superconductive regions should be thinner than, or anyhow of the order of, the penetration depth λ. This would reduce the magnetic term in the Gibbs function so that superconductivity could persist in high fields. The problem remained why this behavior did not occur in common superconductors too. H. London went into these matters in a more quantitative way using the formula for field penetration in thin layers and the notion of structural surface energy between the two phases. In the fifties, Pippard demonstrated that in alloys the reduced mean free path of the superconductive electrons was responsible for the smallness of structural surface energy, while still later Abrikosov's analysis showed that also the Ginzburg–Landau dependence of the order parameter on the coordinates was required to account for the data on the magnetization in the alloys and for its two critical fields, observed by Schubnikov and by Mrs. Casimir more than 20 years earlier. Simultaneously to the work of H. London and myself, Mendelssohn called attention to the inhomogenities of the alloys concerned which ought to lead to a rapid variation of the difference in free energy and therefore to a sponge structure in which magnetic induction passes through, and is captured in, the meshes of a superconductive sponge. Mendelssohn also had, in particular, his observations on hysteresis phenomena in mind, observations which require the existence of considerable local current densities. In fact, recent research has shown the essential role of the irregularities and impurities in superconductors of the second kind for their hysteresis and current-carrying capacity. It may be noted here that Mendelssohn, as well as Keesom, investigated the possibility of making use of the alloys concerned for the construction of superconductive coil magnets. The attempts failed due to their low current-carrying capacity. It was only 25 years later that Kunzler and others observed that certain compounds and alloys of the transition elements have much higher current-carrying capacity even at very high magnetic fields and thereby made possible the realization of Kamerlingh Onnes' dream of producing a strong magnetic field without dissipation of Joule heat.

Many people have asked why the advance of our knowledge in this part of the science of superconductivity slowed down around 1936 so that in some respects quite a new start had to be made in recent years. I do not know a simple answer. One might, however, find a few more or less accidental and personal reasons besides the vague more general causes.

Among the first is the fact that the number of research workers in the field was small and that some of them almost simultaneously left it. Schubnikov disappeared, Mendelssohn concentrated a large part of his attention on the superfluid properties of helium II while—as already mentioned—I returned to magnetism. As to the properties of alloys, I feel that the lack of metallurgical facilities and experience also weighed heavily. The rapid advance of the years 1932–1936 was consolidated by the appearance of Shoenberg's excellent monograph. But, though much further valuable work, not discussed in the present rapid and personal review, was carried out, this consolidation did not lead to a concentrated attack on the remaining problems before the outbreak of war. The rapid development during the war of high-frequency electronics led to developments in new directions, mainly achieved in Cambridge and the U.S.A. But it is not my task to describe those or to discuss the important advances made by Landau, Ginzburg, and by a number of British and U.S.A. theorists after the war.

Prewar Work on Superconductivity as Seen from Oxford

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My own recollections, like those of Professor Gorter, are of necessity subjective and personal. They cannot, and should not, claim to provide a complete and balanced account.

In 1933, just thirty years ago, I went from Breslau to Oxford to install the first helium liquefier in England. The liquefier, incidentally, was one of a race of small scale devices which were being developed by Simon and his school in Berlin and, later, in Breslau. Nowadays, it is not generally appreciated that one of the main reasons for making these miniature liquefiers was the scarcity of helium gas, which had to be extracted laboriously from Monazite sand. The arrival of the first American helium from gas wells was an important event, and I went down to the Berlin Customs House to open the crate. But then the official wanted to open the cylinder too, to see whether it contained liquor. He only relented when I assured him that I should be most disappointed if it did.

At the same time that we set up small scale liquefiers at Berlin University in the late twenties, Meissner at the Physikalisch Technische Reichstanstalt installed a conventional type of helium plant, and it was agreed that the field of research should be divided up. Meissner would concentrate on superconductivity, while we were to continue the thermodynamic work of the Nernst Laboratory. Thus, my only excursion into superconductivity before 1933 was a thermodynamic one, and it did not turn out too well. The idea was to look for a discontinuity in the specific heat at the transition point. Unfortunately we chose lead, because it already becomes superconductive at 7.2°K. Not unnaturally (we were then looking for something of the order of RT), we found that it was not there.[1] The small discontinuity which must be there was completely swamped by the enormous lattice specific heat, and has not been observed by direct experiment to this day.[2]

When, a little later, Keesom and van den Ende[3] discovered such a discontinuity in tin, I therefore read their paper with special interest. My attention was drawn to two low specific heat values just below T_c which they ascribed to the accidental presence of a magnetic field. This immediately suggested to me that there must exist a magnetocaloric effect which might be useful for making temperatures below 1°K. That was, of course, before the first paramagnetic cooling experiments.

As I was leaving the University library after reading Keesom's paper, I had to duck a few bullets which were flying through the streets of Breslau, heralding the approach of Nazi rule, and it became clear that the cooling experiment would have to be deferred a little. In fact, it was eventually carried out at Oxford in 1934.

However, my first experiment in Oxford dealt with

[1] K. Mendelssohn and F. Simon, Z. Physik. Chem. **B16**, 72 (1932).

[2] After my talk I was informed by Dr. C. Shiffman that, together with J. F. Cochran and M. Garber, he had just measured this anomaly directly.

[3] W. H. Keesom and J. N. van den Ende, Comm. Phys. Lab. Univ. Leiden, No. 219b (1932).