INTRODUCTION TO SUPERCONDUCTIVITY

Second Edition

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ABOUT THE AUTHOR

A native of Wisconsin, **Michael Tinkham** received an A. B. degree from Ripon College and his M. S. and Ph.D. from MIT. After a postdoctoral year at the Clarendon Laboratory in Oxford, he spent 11 years teaching at the University of California, Berkeley, before moving to Harvard in 1966, where he is now the Rumford Professor of Physics and Gordon McKay Professor of Applied Physics. Over the years, he has spent sabbatical leaves at MIT and at the University of Paris, Orsay, as a Guggenheim Fellow; at the Cavendish Laboratory in Cambridge University as an NSF Senior Postdoctoral Fellow; at the Institute for Theory of Condensed Matter in Karlsruhe, Germany, as a Humboldt Prize Fellow; at the University of California in Berkeley as a Visiting Miller Professor; and as a Visiting Professor at the Technical University of Delft, the Netherlands.

He is a Member of the National Academy of Sciences and a Fellow of the American Academy of Arts and Sciences, of the Amercian Physical Society, and of the American Association for the Advancement of Science. Honors from the American Physical Society include the Richtmyer lectureship and the Buckley Solid State Physics Prize for his research on the electromagnetic properties of superconductors. In 1976 he was awarded an honorary Sc.D. from Ripon College. He has also served on the US National Committee of IUPAP and as chairman of the Fritz London Award Committee.

Author of over 200 research publications, he has written three previous books: *Group Theory and Quantum Mechanics, Superconductivity*, and the first edition of *Introduction to Superconductivity*, which has been translated into Russian, Japanese, and Chinese.

CONTENTS

CHAPTER 1

HISTORICAL OVERVIEW

Superconductivity was discovered in 1911 by H. Kamerlingh Onnes[1] in Leiden, just 3 years after he had first liquefied helium, which gave him the refrigeration technique required to reach temperatures of a few degrees Kelvin. For decades, a fundamental understanding of this phenomenon eluded the many scientists who were working in the field. Then, in the 1950s and 1960s, a remarkably complete and satisfactory theoretical picture of the classic superconductors emerged. This situation was overturned and the subject was revitalized in 1986, when a new class of high-temperature superconductors was discovered by Bednorz and Müller.[2] These new superconductors seem to obey the same general phenomenology as the classic superconductors, but the basic microscopic mechanism remains an open and contentious question at the time of this writing.

The purpose of this book is to introduce the reader to the field of superconductivity, which remains fascinating after more than 80 years of investigation. To retard early obsolescence, we shall emphasize the aspects which seem to be reasonably securely understood at the present time.

The goal of this introductory chapter is primarily to give some historical perspective to the evolution of the subject. All detailed discussion is deferred to later chapters, where the topics are examined again in much greater depth. We start by reviewing the basic observed electrodynamic phenomena and their early

[1] H. Kamerlingh Onnes, *Leiden Comm.* **120b**, **122b**, **124c** (1911).

[2] G. Bednorz and K. A. Müller, *Z. Phys.* **B64**, 189 (1986).

phenomenological description by the Londons. We then briefly sketch the subsequent evolution of the concepts which are central to our present understanding. This quasi-historical review of the development of the subject is probably too terse to be fully understood on the first reading. Rather, it is intended to provide a quick overview to help orient the reader while reading subsequent chapters, in which the ideas are developed in sufficient detail to be self-contained. In fact, some readers have found this survey more useful to highlight the major points *after* working through the details in subsequent chapters.

1.1 THE BASIC PHENOMENA

What Kamerlingh Onnes observed was that the electrical resistance of various metals such as mercury, lead, and tin disappeared completely in a small temperature range at a critical temperature T_c, which is characteristic of the material. The complete disappearance of resistance is most sensitively demonstrated by experiments with persistent currents in superconducting rings, as shown schematically in Fig. 1.1. Once set up, such currents have been observed to flow without measurable decrease for a year, and a lower bound of some 10^5 years for their characteristic decay time has been established by using nuclear resonance to detect any slight decrease in the field produced by the circulating current. In fact, we shall see that under many circumstances we expect absolutely no change in field or current to occur in times less than $10^{10^{10}}$ years! Thus, *perfect conductivity* is the first traditional hallmark of superconductivity. It is also the prerequisite for most potential applications, such as high-current transmission lines or high-field magnets.

The next hallmark to be discovered was *perfect diamagnetism*, found in 1933 by Meissner and Ochsenfeld.[3,4] They found that not only a magnetic field is *excluded* from entering a superconductor (see Fig. 1.2), as might appear to be

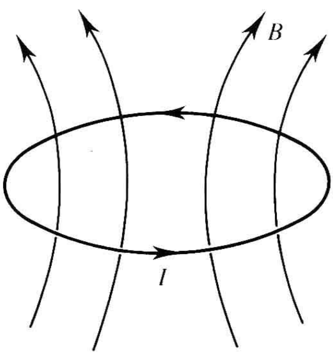

FIGURE 1.1
Schematic diagram of persistent current experiment.

[3]W. Meissner and R. Ochsenfeld, *Naturwissenschaften* **21**, 787 (1933).

[4]Actually, the diamagnetism is perfect only for *bulk* samples, since the field does penetrate a finite distance λ, typically approximately 500 Å.

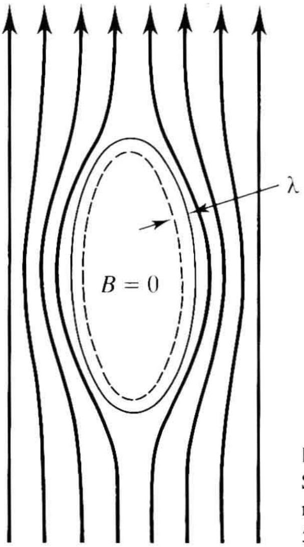

FIGURE 1.2
Schematic diagram of exclusion of magnetic flux from interior of massive superconductor. λ is the penetration depth, typically only 500 Å.

explained by perfect conductivity, but also that a field in an originally normal sample is *expelled* as it is cooled through T_c. This certainly could *not* be explained by perfect conductivity, which would tend to trap flux *in*. The existence of such a reversible *Meissner effect* implies that superconductivity will be destroyed by a critical magnetic field H_c, which is related thermodynamically to the free-energy difference between the normal and superconducting states in zero field, the so-called condensation energy of the superconducting state. More precisely, this *thermodynamic critical field* H_c is determined by equating the energy $H^2/8\pi$ per unit volume, associated with holding the field out against the magnetic pressure, with the condensation energy. That is,

$$\frac{H_c^2(T)}{8\pi} = f_n(T) - f_s(T) \tag{1.1}$$

where f_n and f_s are the Helmholtz free energies per unit volume in the respective phases in zero field. It was found empirically that $H_c(T)$ is quite well approximated by a parabolic law

$$H_c(T) \approx H_c(0)[1 - (T/T_c)^2] \tag{1.2}$$

illustrated in Fig. 1.3. While the transition in zero field at T_c is of second order, the transition in the presence of a field is of first order since there is a discontinuous change in the thermodynamic state of the system and an associated latent heat.

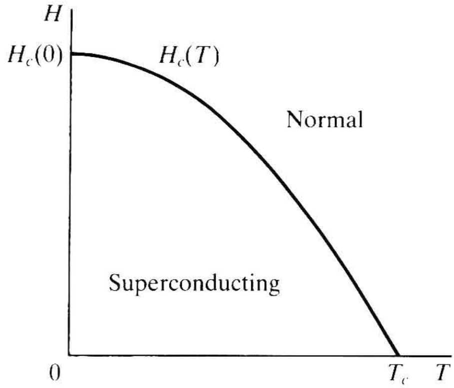

FIGURE 1.3
Temperature dependence of the critical field.

1.2 THE LONDON EQUATIONS

These two basic electrodynamic properties, which give superconductivity its unique interest, were well described in 1935 by the brothers F. and H. London,[5] who proposed two equations to govern the microscopic electric and magnetic fields

$$\mathbf{E} = \frac{\partial}{\partial t}(\Lambda \mathbf{J}_s) \tag{1.3}$$

$$\mathbf{h} = -c \text{ curl } (\Lambda \mathbf{J}_s) \tag{1.4}$$

where

$$\Lambda = \frac{4\pi\lambda^2}{c^2} = \frac{m}{n_s e^2} \tag{1.5}$$

is a phenomenological parameter. It was expected that n_s, the *number density of superconducting electrons*, would vary continuously from zero at T_c to a limiting value of the order of n, the density of conduction electrons, at $T \ll T_c$. In (1.4), we introduce our notational convention of using **h** to denote the value of the flux density on a microscopic scale, reserving **B** to denote a macroscopic average value. Although notational symmetry would suggest using **e** for the microscopic local value of **E** in the same way, to avoid constant confusion with the charge e of the electron, we shall do so only in the few cases[6] where it is really useful. These notational conventions are discussed further in the appendix.

[5] F. and H. London, *Proc. Roy. Soc.* (London) **A149**, 71 (1935).

[6] The fundamental basis for our notational asymmetry in treating **E** and **B** is in the Maxwell equations curl $\mathbf{h} = 4\pi\mathbf{J}/c$ and curl $\mathbf{e} = -(1/c)\partial\mathbf{h}/\partial t$. Superconductors in equilibrium can have nonzero $\mathbf{J}_s$, as described by the London equations, causing **h** to vary on the scale of λ. But in equilibrium, or even steady state, $\partial\mathbf{h}/\partial t = 0$, so that **e** is zero, or at least constant in space, so the use of both **e** and **E** offers no advantage. The distinction is useful only in discussing time-dependent phenomena such as motion of flux-bearing vortices in type II superconductors.

The first of these equations (1.3) describes perfect conductivity since any electric field *accelerates* the superconducting electrons rather than simply sustaining their velocity against resistance as described in Ohm's law in a normal conductor. The second London equation (1.4), when combined with the Maxwell equation curl $\mathbf{h} = 4\pi\mathbf{J}/c$, leads to

$$\nabla^2\mathbf{h} = \frac{\mathbf{h}}{\lambda^2} \tag{1.6}$$

This implies that a magnetic field is exponentially screened from the interior of a sample with penetration depth λ, i.e., the Meissner effect. Thus, the parameter λ is operationally defined as a penetration depth; empirically, the temperature dependence of λ is found to be approximately described by

$$\lambda(T) \approx \lambda(0)[1 - (T/T_c)^4]^{-1/2} \tag{1.7}$$

The implications of the London equations are illustrated much more thoroughly in Chap. 2.

A simple, but unsound, "derivation" of (1.3) can be given by computing the response to a uniform electric field of a perfect normal conductor, i.e., a free-electron gas with mean free path $\ell = \infty$. In that case, $d(m\mathbf{v})/dt = e\mathbf{E}$, and since $\mathbf{J} = ne\mathbf{v}$, (1.3) follows. But this computation is not rigorous for the spatially nonuniform fields in the penetration depth, for which (1.3) and (1.4) are most useful. The fault is that the response of an electron gas to electric fields is nonlocal; i.e., the current at a point is determined by the electric field averaged over a region of radius $\sim\ell$ about that point. Consequently, only fields that are uniform over a region of this size give a full response; in particular, the conductivity becomes *infinite* as $\ell \to \infty$ *only* for fields filling all space. Since we are dealing here with an interface between a region with field and one with no field, it is clear that even for $\ell = \infty$, the effective conductivity would remain finite. For the case of a high-frequency current, this corresponds to the extreme anomalous limit of the normal skin effect, in which the surface resistance remains finite even as $\ell \to \infty$.

A more profound motivation for the London equations is the quantum one, emphasizing use of the vector potential **A**, given by F. London[7] himself. Noting that the canonical momentum **p** is $(m\mathbf{v} + e\mathbf{A}/c)$, and arguing that in the absence of an applied field we would expect the ground state to have zero net momentum (as shown in a theorem[8] of Bloch), we are led to the relation for the local average velocity in the presence of the field

$$\langle\mathbf{v}_s\rangle = \frac{-e\mathbf{A}}{mc}$$

[7]F. London, *Superfluids*, vol. I, Wiley, New York, 1950.

[8]This theorem is apparently unpublished, though famous. See p. 143 of the preceding reference.

This will hold if we postulate that for some reason the wavefunction of the superconducting electrons is "rigid" and retains its ground-state property that $\langle \mathbf{p} \rangle = 0$. Denoting the number density of electrons participating in this rigid ground state by n_s, we then have

$$\mathbf{J}_s = n_s e \langle \mathbf{v}_s \rangle = \frac{-n_s e^2 \mathbf{A}}{mc} = \frac{-\mathbf{A}}{\Lambda c} \tag{1.8}$$

Taking the time derivative of both sides yields (1.3) and taking the curl leads to (1.4). Thus, (1.8) contains both London equations in a compact and suggestive form.[9]

This argument of London leaves open the actual value of n_s, but a natural upper limit is provided by the total density of conduction electrons n. If this is inserted in (1.5), we obtain

$$\lambda_L(0) = \left(\frac{mc^2}{4\pi n e^2} \right)^{1/2} \tag{1.9}$$

The notation here is chosen to indicate that this is an ideal theoretical limit as $T \to 0$. Note that n_s is expected to decrease continuously to zero as $T \to T_c$, causing $\lambda(T)$ to diverge at T_c as described by (1.7). Careful comparisons of the rf penetration depths of samples in the normal and superconducting states have shown that the superconducting penetration depths λ are always larger than $\lambda_L(0)$, even after an extrapolation of the data to $T = 0$. The quantitative explanation of this excess penetration depth required introduction of an additional concept by Pippard: the coherence length ξ_0.

1.3 THE PIPPARD NONLOCAL ELECTRODYNAMICS

Pippard[10] introduced the coherence length while proposing a nonlocal generalization of the London equation (1.8). This was done in analogy to Chambers's nonlocal generalization[11] of Ohm's law from $\mathbf{J}(\mathbf{r}) = \sigma \mathbf{E}(\mathbf{r})$ to

$$\mathbf{J}(\mathbf{r}) = \frac{3\sigma}{4\pi \ell} \int \frac{\mathbf{R}[\mathbf{R} \cdot \mathbf{E}(\mathbf{r}')] e^{-R/\ell}}{R^4} \, d\mathbf{r}'$$

[9] Since (1.8) is evidently not gauge-invariant, it will only be correct for a particular gauge choice. This choice, known as the London gauge, is specified by requiring that div $\mathbf{A} = 0$ (so that div $\mathbf{J} = 0$), that the normal component of $\mathbf{A}$ over the surface be related to any supercurrent through the surface by (1.8), and that $\mathbf{A} \to 0$ in the interior of bulk samples.

[10] A. B. Pippard, *Proc. Roy. Soc.* (London) **A216**, 547 (1953).

[11] This approach of Chambers is discussed, e.g., in J. M. Ziman, *Principles of the Theory of Solids*, Cambridge University Press, New York (1964), p. 242.

where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$; this formula takes into account the fact that the current at a point $\mathbf{r}$ depends on $\mathbf{E}(\mathbf{r}')$ throughout a volume of radius $\sim\ell$ about $\mathbf{r}$. Pippard argued that the superconducting wavefunction should have a similar characteristic dimension ξ_0 which could be estimated by an uncertainty-principle argument, as follows: Only electrons within $\sim kT_c$ of the Fermi energy can play a major role in a phenomenon which sets in at T_c, and these electrons have a momentum range $\Delta p \approx kT_c/v_F$, where v_F, is the Fermi velocity. Thus,

$$\Delta x \gtrsim \hbar/\Delta p \approx \hbar v_F/kT_c$$

leading to the definition of a characteristic length

$$\xi_0 = a\frac{\hbar v_F}{kT_c} \tag{1.10}$$

where a is a numerical constant of order unity, to be determined. For typical elemental superconductors such as tin and aluminum, $\xi_0 \gg \lambda_L(0)$. If ξ_0 represents the smallest size of a wave packet that the superconducting charge carriers can form, then one would expect a weakened supercurrent response to a vector potential $\mathbf{A}(\mathbf{r})$ which did not maintain its full value over a volume of radius $\sim\xi_0$ about the point of interest. Thus, ξ_0 plays a role analogous to the mean free path ℓ in the nonlocal electrodynamics of normal metals. Of course, if the ordinary mean free path is less than ξ_0, one might expect a further reduction in the response to an applied field.

Collecting these ideas into a concrete form, Pippard proposed replacement of (1.8) by

$$\mathbf{J}_s(\mathbf{r}) = -\frac{3}{4\pi\xi_0\Lambda c}\int\frac{\mathbf{R}[\mathbf{R}\cdot\mathbf{A}(\mathbf{r}')]}{R^4}e^{-R/\xi}d\mathbf{r}' \tag{1.11}$$

where again $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ and the coherence length ξ in the presence of scattering was assumed to be related to that of pure material ξ_0 by

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{\ell} \tag{1.12}$$

Using (1.11), Pippard found[12] that he could fit the experimental data on both tin and aluminum by the choice of a single parameter $a = 0.15$ in (1.10). [We shall see in Chap. 3 that the microscopic theory of Bardeen, Cooper, and Schrieffer[13] (BCS) confirms this form, with the numerical constant $a = 0.18$.] For both metals, λ is considerably larger than $\lambda_L(0)$ because $\mathbf{A}(\mathbf{r})$ decreases sharply over a distance $\lambda \ll \xi_0$, giving a weakened supercurrent response, and hence an increased field penetration. Moreover, the increase of λ with the decreasing mean free path predicted by (1.11) and (1.12) was consistent with data on a series

[12]T. E. Faber and A. B. Pippard, *Proc. Roy. Soc.* (London) **A231**, 336 (1955).

[13]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).