# Superconductivity

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The history of superconductivity is reviewed, beginning with its discovery in 1911. Various theoretical approaches are discussed and are compared with experiment. [S0034-6861(99)01602-5]

## I. DISCOVERY AND EARLY HISTORY

Superconductivity was discovered in 1911 by H. Kamerlingh Onnes (1911) in Leiden just three years after he first liquified helium, which made sufficiently low temperatures available. What he found was that the electrical resistance of some metals, such as lead, mercury, tin, and aluminum, disappeared completely in a narrow temperature range at a critical temperature $T_c$ (typically a few Kelvin) specific to each metal. Twenty-two years later, Meissner and Ochsenfeld (1933) discovered that these superconductors were perfectly diamagnetic (the "Meissner effect") as well as perfectly conducting. These remarkable properties were neatly described by the phenomenological theory of F. and H. London (1935). Their model postulated a density of "superconducting electrons" $n_s$ per unit volume, whose response to electromagnetic fields could be described by

$$\mathbf{J}_s=-(c/4\pi\lambda_L^2)\mathbf{A} \tag{1}$$

(with a specific "London gauge" choice for the vector potential). The time derivative of Eq. (1) implies that the superconducting electrons respond to an electric field $\mathbf{E}$ essentially as Drude free electrons with an infinitely long relaxation time. Combined with the Maxwell equations, this leads to a frequency-independent skin depth, called the London penetration depth:

$$\lambda_L=(mc^2/4\pi n_s e^2)^{1/2}. \tag{2}$$

The curl of Eq. (1) (with Maxwell's equations) implies the static flux expulsion of the Meissner effect, which cannot be interpreted in a classical way. Since $\lambda_L$ was found experimentally to diverge at $T_c$ roughly as $[1-(T/T_c)^4]^{-1/2}$, $n_s$ was presumed to go continuously to zero at $T_c$, as in a second-order phase transition.

Ginzburg and Landau (1950) extended the London phenomenology in a brilliant stroke based on Landau's theory of second-order phase transitions. They introduced as an order parameter, a complex "wave function of the superconducting electrons," $\psi(\mathbf{r})=|\psi(\mathbf{r})|e^{i\varphi(r)}$, such that $n_s\propto|\psi(\mathbf{r})|^2$. Their theory reproduced Eq. (1) in a gauge-invariant form,

$$\mathbf{J}=2e|\psi(\mathbf{r})|^2\mathbf{v}_s \tag{3}$$

where

$$m^*\mathbf{v}_s=\hbar\nabla\varphi-2e\mathbf{A}/c, \tag{3a}$$

with the effective mass $m^*$ usually taken to be $2m$. Moreover, this $\psi(\mathbf{r})$ was shown to be governed by a nonlinear differential equation, so that it could vary with position and field strength, in addition to the temperature dependence of $n_s$ in the London picture. For example, it provided a natural description for the interface between normal and superconducting phases in the presence of a critical magnetic field $H_c$. This theory was later shown by Gor'kov (1959) to be a limiting case of the BCS (Bardeen, Cooper, and Schrieffer, 1957a, 1957b) theory and remains today as the standard initial approach to problems with a spatially varying superconducting state.

Aided by wartime developments in high-frequency technology, Pippard was able to make very precise measurements of $\lambda_L$ to compare with Eq. (2), using parameters determined from similar measurements of the skin depth in the normal state. He found that, even at $T\approx0$, the fitted value of $n_s$ was less than the density of conduction electrons in the normal state, by a ratio that was larger for low-$T_c$ materials like Al($T_c\approx1$ K) than for metals like Pb ($T_c\approx7$ K). Building on Chambers' equation for the anomalous skin effect in normal metals, Pippard (1953) was able to explain this reduced value of $n_s$ by introducing a "coherence length"

$$\xi_0=a\hbar v_F/k_BT_c \tag{4}$$

into the London electrodynamics, where the coefficient $a$ was of order unity. In a review published in 1956, shortly before the discovery of the BCS microscopic theory of superconductivity, Bardeen (1956) was able to show that just such a "nonlocal" electrodynamics would be a consequence of an energy gap $\Delta$ in the electronic spectrum, if the energy gap was proportional to $T_c$. And, indeed, when the BCS theory was created, it predicted the nonlocal electrodynamics, with $\xi_0=\hbar v_F/\pi\Delta(0)$, in agreement with Pippard's brilliant conjecture.

This was the state of our understanding of the electrodynamics of classic superconductors in the mid 1950s—a very satisfactory phenomenology, but no "explanation" in microscopic terms. What was the nature of the superconducting state that made it have these remarkable properties? This question was answered in one stroke by the classic paper of Bardeen, Cooper, and Schrieffer (1957a), which is the subject of the next section of this article.

## II. THE BCS MICROSCOPIC THEORY

The discovery of the isotope effect by Maxwell (1950) and Reynolds *et al.* (1950), namely, that $T_c\propto M^{-\alpha}$ where

$M$ is the ionic mass and $\alpha \approx 1/2$, gave strong support to the view that superconductivity is the result of the electron-phonon interaction. Prior to this discovery, Fröhlich (1950) had worked out a model based on this interaction but ran into formal difficulties and the approach did not describe the properties of a superconductor. In fact, Shafroth (1958) proved that the Meissner effect could only be obtained by going beyond perturbation theory in treating the effective interaction between electrons.

In 1955 Bardeen considered attacking the problem using the techniques of quantum field theory and invited Cooper to join the effort since Cooper's background was in particle physics. It soon became clear that since the existing field-theoretic methods were based on perturbation theory, another scheme would have to be devised.

Bardeen stressed the importance of an energy gap in the excitation spectrum and that superconductivity is due to a condensation in momentum space of a coherent superposition of normal-state configurations. A major difficulty existed in that the correlation energy in the normal phase is of order 1 eV per electron, while the energy distinguishing the normal and super phases is of order $10^{-6}$ eV per electron. Fortunately, Landau's theory of a Fermi liquid provided the necessary basis for treating the normal-state excitations in one-to-one correspondence with the free-electron gas so that the small condensation energy between the super and normal phases could be isolated.

Cooper (1956) studied the problem of two electrons interacting via an attractive effective potential above a frozen Fermi sea. He found that the normal state is unstable regardless of how weak the attraction is. Bardeen, Cooper, and Schrieffer (1957a, 1957b) then studied a reduced Hamiltonian which included interactions involving only paired states,

$$H_{\mathrm{red}} = \sum_{ks} \varepsilon_k n_{ks} + \sum_{kk'} V_{kk'} b_k^+ b_k , \tag{5}$$

where $b_k^+$ creates an electron pair in $(k\uparrow, -k\downarrow)$, and $\varepsilon_k$ is the normal-state quasiparticle energy measured relative to the chemical potential.

Bardeen argued on the basis of the uncertainty principle that the overlap of pair wave functions is extremely large because of the large ratio of the Fermi and critical temperatures. Thus one cannot think of the pairs as bosons since the Pauli principle plays a crucial role in the problem.

Schrieffer constructed a variational trial function in analogy with the Tomonaga (1947) approach to the pion nucleon problem,

$$\Psi = \prod_k (u_k + \nu_k b_k^+)|0\rangle, \tag{6}$$

where $u_k^2 + \nu_k^2 = 1$ for normalization, and the parameters $\nu_k$ are to be chosen to minimize the energy. This prescription describes pairing in a spin singlet and orbital $s$-wave state. One finds that the energy minimization leads to a self-consistency condition

$$\Delta_k = -\sum_{k'} V_{kk'} \Delta_{k'}/2E_{k'} \tag{7}$$

with

$$\nu_k^2 = \frac{1}{2}\left(1 - \frac{\varepsilon_k}{E_k}\right) \tag{8}$$

and

$$E_k = (\varepsilon_k^2 + \Delta_k^2)^{1/2}. \tag{9}$$

The excitation spectrum based on this state exhibits quasiparticles of energy $E_k$ with an energy gap $\Delta_k$. For $k$ far above the Fermi surface the excitations are electronlike, and far below $k_F$ they are holelike, while at $k_F$ they are an equal mixture of electron and hole, having charge zero but spin one-half. This is an example of charge-spin separation since the charge of an injected electron at the Fermi surface shifts the mean number of pairs by one-half with the spin remaining with the quasiparticle.

Since the spectrum exhibits a gap, it follows as Bardeen had argued, that the theory predicts a Meissner effect. The electrodynamics is nonlocal, involving a coherence length of a form [Eq. (4)] proposed by Pippard (1953).

The theory predicts a second-order phase transition at a temperature given by

$$k_B T_c \approx \hbar \overline{\omega}_0 e^{-1/N(0)V}, \tag{10}$$

with the gap vanishing at $T_c$ as $(T_c - T)^{1/2}$. Here $\hbar \overline{\omega}_0$ is the mean phonon energy and $V$ is the pair interaction. For weak-coupling superconductors, the ratio of the zero-temperature gap $2\Delta(0)$ and the transition temperature is predicted to be 3.52.

Magnetic flux trapped in a superconducting ring is predicted to be in units of $\Phi_0 = hc/2e$, reflecting the fact that the condensate is formed by electron pairs. This was observed experimentally by Deaver and Fairbank (1961) and by Doll and Näbauer (1961).

Gor'kov (1958) suggested the quantum field formulation of the BCS theory by making use of $\Delta_k$ as the "off-diagonal" long-range order parameter. By including spatial variation of the gap function $\Delta(r)$, he succeeded (Gor'kov, 1959) in deriving the Ginzburg-Landau phenomenological theory from the BCS theory.

Strong-coupling effects were explained by Eliashberg (1960) by extending the Gor'kov equations to include retardation effects in the pairing interaction and damping of the quasiparticles arising from phonon emission.

Shortly after the pairing theory was advanced, it was proposed (Bohr *et al.*, 1958) that the theory also described many features of atomic nuclei, such as the even vs odd effects on adding one nucleon to the nucleus. Moreover, the deviation of the moment of inertia from the rigid moment is the analog of the Meissner effect. $^3$He is another Fermi liquid, which was discovered by Osheroff *et al.* (1972) to undergo a transition to a superfluid state in which the pairing is in a spin-triplet state with orbital angular momentum one.

## III. EXPERIMENTAL CONFIRMATION OF THE BCS ENERGY GAP AND COHERENCE FACTORS

The BCS theory described a radically new vision of the nature of the superconducting state, which had eluded theorists for 46 years. Yet it was accepted by the great majority of physicists almost immediately. Why was that? For one thing, its predictions of the low-frequency electrodynamics essentially reproduced the results of the London and Pippard phenomenological theories, which were known to describe in detail the experimental data for the penetration depth. More decisive support for the new theory was provided by other experiments, which tested *new* predictions of the theory that went well beyond the general two-fluid models which had been available earlier.

One such prediction was the existence of an energy gap $2\Delta(T)$ for the creation of a pair of quasiparticle excitations. For weak-coupling superconductors, the theory predicted that $2\Delta = 3.52\ kT_c$ at $T=0$, falling continuously to zero at the second-order transition to the normal state at $T_c$. Such an energy gap was consistent with the exponential temperature dependence found in the latest specific-heat measurements (Corak *et al.*, 1954). It was supported more decisively by spectroscopic microwave absorption measurements (Biondi *et al.*, 1956) and spectroscopic far-infrared transmission experiments (Glover and Tinkham, 1956), the latter extending to frequencies well above the energy gap even at $T=0$. This allowed a quantitative test of the predictions of the BCS theory for the frequency-dependent complex conductivity $\sigma_1(\omega) - i\sigma_2(\omega)$ near the energy-gap frequency in the superconducting state. After the gap width was scaled up from 3.52 to $\sim 4.2kT_c$ for lead, which is not a weak-coupling superconductor, the transmission curve $T(\omega)$ predicted by the theoretical $\sigma_1(\omega) - i\sigma_2(\omega)$ was in excellent agreement with the experimental data, including the size and shape of a nontrivial *peak* in transmission near the energy-gap frequency, where both $\sigma_1(\omega)$ and $\sigma_2(\omega)$ are relatively small. In an elegant experiment, Hebel and Slichter (1957) observed a coherence peak in the NMR spectrum that probed details of the paired state and its excitations, in agreement with the BCS theory. The energy gap $\Delta(T)$ in the superconducting density of states was subsequently measured directly in an important pioneering experiment by Giaever (1960a, 1960b). in which he measured the minimum energy in $eV$ required to insert an electron into a superconductor by a tunneling process.

A particularly distinctive prediction of the BCS theory is the existence of coherence factors in the transition probabilities which distinguish processes, like ultrasonic absorption, that are even under time reversal from those, like nuclear relaxation, that are odd. This difference in coherence factors was predicted to cause the ultrasonic attenuation to drop very sharply on cooling through $T_c$, as confirmed by Morse (1959), while the nuclear relaxation rate was predicted to rise to a maximum above the normal-state value just below $T_c$, before dropping exponentially at lower temperatures, as was confirmed by Hebel and Slichter (1957). Since both of these processes depend on the density of quasiparticles, which correspond to the "normal electrons" of a two-fluid picture, the fact that the nuclear relaxation rate goes up while the ultrasonic attenuation rate goes down on cooling below $T_c$ is inexplicable without the coherence factors, which are a unique and specific feature of the BCS theory.

## IV. TYPE-II SUPERCONDUCTORS

In 1957, the same year as the BCS theory, Abrikosov (1957) also published a ground-breaking paper, based on the Ginzburg-Landau theory, in which he explored theoretically what would happen if the inequality $\lambda < \xi$ typical of superconductors like tin and lead were reversed. He found that when the ratio $\kappa = \lambda/\xi$ exceeded $1/\sqrt{2}$, the magnetic properties were completely different from the classic superconductors; he called these high-$\kappa$ materials "type-II superconductors." Instead of showing a first-order transition from superconducting flux exclusion (Meissner effect) to the normal state at a critical field $H_c$ like the classic, or type-I, superconductors, type-II superconductors above a lower critical field $H_{cl}$ were predicted to allow magnetic flux to penetrate in a regular array of quantum units of $\Phi_0 = hc/2e$, each flux tube being confined by a circulating vortex of current. These materials were predicted to remain superconducting until a second-order transition at an upper critical field $H_{c2} = \Phi_0/2\pi\xi^2 = \sqrt{2}\kappa H_c > H_c$. (Here $H_c$ is the thermodynamic critical field such that $H_c^2/8\pi$ equals the free-energy difference between superconducting and normal states of the metal.) Since for "dirty" metals, with short mean free path $\ell$, the BCS theory shows that $\xi^2 \approx \xi_0 \ell \approx \ell \hbar v_F/kT_c$, this $H_{c2}$ can be very high ($>10^5$ Oe) if $\ell$ is small and/or $T_c$ is high. These type-II materials thus made possible the fabrication of high-field superconducting magnets, which play an important role both in the laboratory and in large-scale applications of superconductivity.

Superconducting materials research was rejuvenated by the discovery by Bednorz and Müller (1986) of new classes of oxide-based high-temperature superconductors, some of which have $T_c$ in excess of 100 K and extremely high values of $H_{c2}$. The detailed origin of superconductivity in these materials is still unclear, but there is considerable evidence indicating that the pairing has a predominantly *d*-wave symmetry as opposed to the *s*-wave symmetry of conventional BCS superconductivity. This field remains one of vigorous research activity at the time of this writing.

## V. THE JOSEPHSON EFFECT

In 1962, Josephson (1962) made the remarkable prediction that a zero-voltage supercurrent of magnitude

$$I_s = I_c \sin(\Delta\varphi) \tag{11}$$

should flow between two superconducting electrodes separated by a thin tunnel barrier. Here $\Delta\varphi$ is the difference in the phase of the Ginzburg-Landau $\psi$ in the two electrodes. Although it was startling at the time, in retrospect this relation is now recognized as a general property of "weak links" between superconductors, and it can be derived as a discrete form of Eq. (3) for a short superconducting constriction. Josephson also predicted that if a voltage difference $V$ were maintained across the junction, the phase difference would evolve as

$$d(\Delta\varphi)/dt=2eV/\hbar. \tag{12}$$

Thus the current would be ac current of amplitude $I_c$ and frequency

$$f=2eV/h, \tag{12a}$$

consistent with the Planck-Einstein relation $E=hf$ relating frequency to the energy change associated with transfer of a Cooper pair from one electrode to the other. This fundamental relation is now used to define the standard volt in terms of a precise frequency.

In the presence of a magnetic field, $\Delta\varphi$ in these expressions must be generalized to a gauge-invariant phase difference, consistent with the general expression (3a). The resulting sensitivity of the Josephson current to magnetic fields stems from the fact that a single quantum of flux $\Phi_0=hc/2e$ enclosed in a superconducting circuit shifts $\Delta\varphi$ by a full $2\pi$. This has made possible the development of SQUID (Superconducting QUantum Interference Device) magnetometers of extreme sensitivity $\sim 10^{-6}\,\Phi_0$, which are approaching the ultimate limit set by the quantum-mechanical uncertainty principle.

## VI. PHASE AND NUMBER VARIABLES

In its canonical form (6), the BCS ground-state wave function is a superposition of states with many different numbers of pairs in a grand canonical ensemble. In reality, because the electrons carry a charge, there is a Coulomb energy $(\delta N)^2E_c$ associated with any imbalance $(\delta N)$ between the number of electrons and the number of positive nuclear charges in the sample. Here $E_c=e^2/2C$ is the charging energy associated with a single electronic net charge on a system with self-capacitance $C$. Since the capacitance scales with physical size, $E_c$ is small for macroscopic superconductors, and this energy term can usually be neglected. However, in mesoscopic superconductors $E_c$ can become the dominant energy term, and the electron number must be precisely fixed in the ground state of the system. As pointed out by Anderson (1967), this can be accomplished by associating a Ginzburg-Landau-like phase variable with each pair in the BCS ground state and then projecting out the part with a definite number of pairs. More explicitly, if we generalize Eq. (6) to the form

$$\Psi_\varphi=\prod_k\,(u_k+v_k e^{i\varphi}b_k^+)|0\rangle, \tag{13}$$

where $u_k$ and $v_k$ are taken to be real, then we can obtain an eigenfunction containing $N$ electrons ($N/2$ pairs) by writing

$$\Psi_N=\int_0^{2\pi} e^{-iN\varphi/2}\Psi_\varphi d\varphi. \tag{14}$$

This Fourier transform relation between eigenfunctions of phase and number has the same form as that between eigenfunctions of position and momentum for a particle. Accordingly, it also implies an uncertainty relation between phase and number of the form

$$\Delta N\Delta\varphi\geqslant 1. \tag{15}$$

In dealing with macroscopic superconductors, for example in the Josephson effect, it is more appropriate to use eigenfunctions of the form of Eq. (13), in which the phase variable $\varphi$ is well defined and identified with the phase variable in the Ginzburg-Landau equations. However, for describing small isolated superconducting particles, the $\Psi_N$ of Eq. (14) is more appropriate.

An interesting illustration of the use of superconducting eigenstates of number rather than of phase is offered by the superconducting single-electron tunneling transistor. This device consists of a nanoscale superconducting island connected to two leads by high-resistance, low-capacitance tunnel junctions and capacitively coupled to a gate electrode. If the tunnel resistance is greater than $R_Q\sim h/e^2$, the number of electrons on the island is a good quantum number, and if the capacitance is small enough that $E_c=e^2/2C\gg kT$, a unique choice of electron number is energetically favored. If one measures the current through the device for a fixed small-bias voltage between the leads while sweeping the charge $C_gV_g$ induced by a voltage $V_g$ on the gate, one finds periodic current peaks spaced $2e$ apart in gate charge (Tuominen *et al.*, 1992). These peaks occur at values of $V_g$ at which states with successive integer numbers of pairs on the island are degenerate, allowing pairs to be transferred without an energy barrier. This phenomenon provides a rather direct demonstration of the paired nature of the superconducting ground state.

In conclusion, we point out that the above discussion is necessarily incomplete, due to length limitations. Instead of attempting a brief review of the entire field, we have focused on the development of the pairing theory, together with some key points in the prehistory and later consequences of the theory.

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