MACROSCOPIC QUANTUM PHENOMENA FROM PAIRING IN SUPERCONDUCTORS

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by

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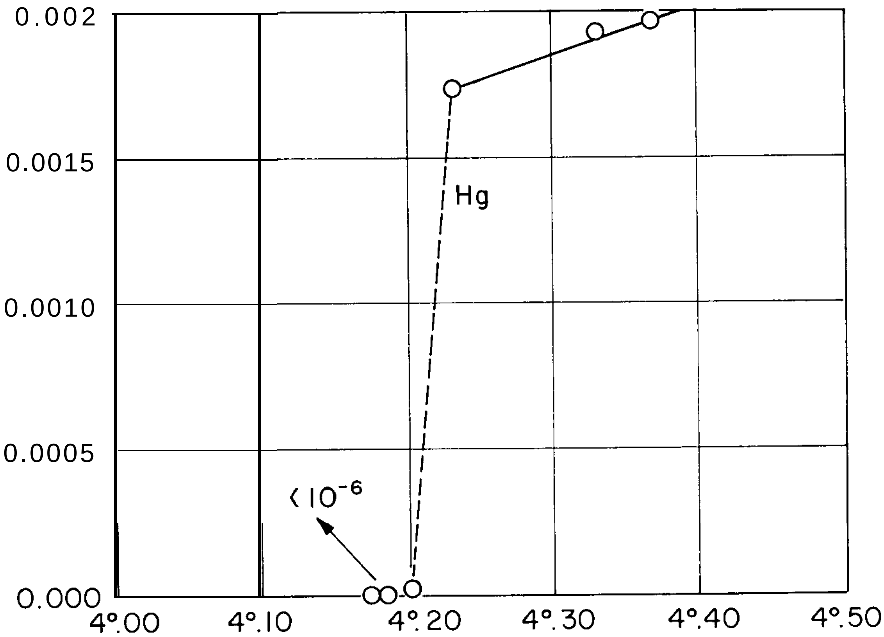
I. INTRODUCTION

It gives me great pleasure to have the opportunity to join my colleagues John Bardeen and Leon Cooper in discussing with you the theory of superconductivity. Since the discovery of superconductivity by H. Kamerlingh Onnes in 1911, an enormous effort has been devoted by a spectrum of outstanding scientists to understanding this phenomenon. As in most developments in our branch of science, the accomplishments honored by this Nobel prize were made possible by a large number of developments preceding them. A general understanding of these developments is important as a backdrop for our own contribution.

On December 11, 1913, Kamerlingh Onnes discussed in his Nobel lecture (1) his striking discovery that on cooling mercury to near the absolute zero of temperature, the electrical resistance became vanishingly small, but this disappearance "did not take place gradually but abruptly." His Fig. 17 is reproduced as Fig. 1. He said, "Thus, mercury at 4.2 K has entered a new state



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which owing to its particular electrical properties can be called the state of superconductivity." He found this state could be destroyed by applying a sufficiently strong magnetic field, now called the critical field H_c. In April - June, 1914, Onnes discovered that a current, once induced in a closed loop of superconducting wire, persists for long periods without decay, as he later graphically demonstrated by carrying a loop of superconducting wire containing a persistent current from Leiden to Cambridge.

In 1933, W. Meissner and R. Ochsenfeld (2) discovered that a superconductor is a perfect diamagnet as well as a perfect conductor. The magnetic field vanishes in the interior of a bulk specimen, even when cooled down below the transition temperature in the presence of a magnetic field. The diamagnetic currents which flow in a thin penetration layer near the surface of a simply connected body to shield the interior from an externally applied field are stable rather than metastable. On the other hand, persistent currents flowing in a multiply connected body, e.g., a loop, are metastable.

An important advance in the understanding of superconductivity occurred in 1934, when C. J. Gorter and H. B. G. Casimir (3) advanced a two fluid model to account for the observed second order phase transition at T_c and other thermodynamic properties. They proposed that the total density of electrons ϱ could be divided into two components

$$\varrho = \varrho_s + \varrho_n \tag{1}$$

where a fraction ϱ_s/ϱ_n of the electrons can be viewed as being condensed into a "superfluid," which is primarily responsible for the remarkable properties of superconductors, while the remaining electrons form an interpenetrating fluid of "normal" electrons. The fraction ϱ_s/ϱ_n grows steadily from zero at T_c to unity at $T = 0$, where "all of the electrons" are in the superfluid condensate.

A second important theoretical advance came in the following year, when Fritz and Hans London set down their phenomenological theory of the electromagnetic properties of superconductors, in which the diamagnetic rather than electric aspects are assumed to be basic. They proposed that the electrical current density $\mathbf{j}_s$ carried by the superfluid is related to the magnetic vector potential A at each point in space by

$$\mathbf{j}_s = -\frac{1}{\Lambda c}\mathbf{A} \tag{2}$$

where Λ is a constant dependent on the material in question, which for a free electron gas model is given by $\Lambda = m/\varrho_s e^2$, m and e being the electronic mass and charge, respectively. A is to be chosen such that $\nabla \cdot \mathbf{A} = 0$ to ensure current conservation. From (2) it follows that a magnetic field is excluded from a superconductor except within a distance

$$\lambda_L = \sqrt{\Lambda c^2/4\pi}$$

which is of order 10^{-6} cm in typical superconductors for T well below T_c. Observed values of λ are generally several times the London value.

In the same year (1935) Fritz London (4) suggested how the diamagnetic property (2) might follow from quantum mechanics, if there was a “rigidity” or stiffness of the wavefunction ψ of the superconducting state such that ψ was essentially unchanged by the presence of an externally applied magnetic field. This concept is basic to much of the theoretical development since that time, in that it sets the stage for the gap in the excitation spectrum of a superconductor which separates the energy of superfluid electrons from the energy of electrons in the normal fluid. As Leon Cooper will discuss, this gap plays a central role in the properties of superconductors.

In his book published in 1950, F. London extended his theoretical conjectures by suggesting that a superconductor is a “quantum structure on a macroscopic scale [which is a] kind of solidification or condensation of the average momentum distribution” of the electrons. This momentum space condensation locks the average momentum of each electron to a common value which extends over appreciable distance in space. A specific type of condensation in momentum space is central to the work Bardeen, Cooper and I did together. It is a great tribute to the insight of the early workers in this field that many of the important general concepts were correctly conceived before the microscopic theory was developed. Their insight was of significant aid in our own work.

The phenomenological London theory was extended in 1950 by Ginzburg and Landau (5) to include a spatial variation of ϱ_s. They suggested that ϱ_s/ϱ be written in terms of a phenomenological condensate wavefunction y(r) as $\varrho_s(r)/\varrho = |\psi(r)|^2$ and that the free energy difference ΔF between the superconducting and normal states at temperature T be given by

$$\Delta F = \int\left\{\frac{\hbar^2}{2\bar{m}}\left|\left(\nabla + \frac{\bar{e}}{c}A(r)\right)\psi(r)\right|^2 - a(T)|\psi(r)|^2 + \frac{b(T)}{2}|\psi(r)|^4\right\}d^3r \quad (3)$$

where $\bar{e}, \bar{m}$, a and **b** are phenomenological constants, with a(T_c) = 0.

They applied this approach to the calculation of boundary energies between normal and superconducting phases and to other problems.

As John Bardeen will discuss, a significant step in understanding which forces cause the condensation into the superfluid came with the experimental discovery of the isotope effect by E. Maxwell and, independently, by Reynolds, et al. (6). Their work indicated that superconductivity arises from the interaction of electrons with lattice vibrations, or phonons. Quite independently, Herbert Fröhlich (7) developed a theory based on electron-phonon interactions which yielded the isotope effect but failed to predict other superconducting properties. A somewhat similar approach by Bardeen (8) stimulated by the isotope effect experiments also ran into difficulties. N. Bohr, W. Heisenberg and other distinguished theorists had continuing interest in the general problem, but met with similar difficulties.

An important concept was introduced by A. B. Pippard (9) in 1953. On the basis of a broad range of experimental facts he concluded that a coherence length ξ is associated with the superconducting state such that a perturbation of the superconductor at a point necessarily influences the superfluid within a distance ξ of that point. For pure metals, $\xi \sim 10^{-4}$ cm. for $T \ll T_c$. He generalized the London equation (3) to a non-local form and accounted for the fact that the experimental value of the penetration depth is several times larger than the London value. Subsequently, Bardeen (10) showed that Pippard's non-local relation would likely follow from an energy gap model.

A major problem in constructing a first principles theory was the fact that the physically important condensation energy ΔF amounts typically to only 10^{-8} electron volts (e.V.) per electron, while the uncertainty in calculating the total energy of the electron-phonon system in even the normal state amounted to of order 1 e.V. per electron. Clearly, one had to isolate those correlations peculiar to the superconducting phase and treat them accurately, the remaining large effects presumably being the same in the two phases and therefore cancelling. Landau's theory of a Fermi liquid (11), developed to account for the properties of liquid He^3, formed a good starting point for such a scheme. Landau argued that as long as the interactions between the particles (He^3 atoms in his case, electrons in our case) do not lead to discontinuous changes in the microscopic properties of the system, a "quasi-particle" description of the low energy excitations is legitimate; that is, excitations of the fully interacting normal phase are in one-to-one correspondence with the excitations of a non-interacting fermi gas. The effective mass m and the Fermi velocity v_F of the quasi-particles differ from their free electron values, but aside from a weak decay rate which vanishes for states at the Fermi surface there is no essential change. It is the residual interaction between the quasi-particles which is responsible for the special correlations characterizing superconductivity. The ground state wavefunction of the superconductor ψ_0 is then represented by a particular superposition of these normal state configurations, Φ_n.

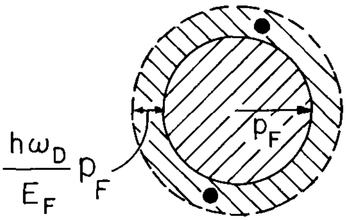
A clue to the nature of the states Φ_n entering strongly in ψ_0 is given by combining Pippard's coherence length ξ with Heisenberg's uncertainty principle

$$\Delta p \sim \hbar/\xi \sim 10^{-4} p_F \tag{4}$$

where p_F is the Fermi momentum. Thus, Ψ_0 is made up of states with quasi-particles (electrons) being excited above the normal ground state by a momentum of order Δp. Since electrons can only be excited to states which are initially empty, it is plausible that only electronic states within a momentum $10^{-4} p_F$ of the Fermi surface are involved significantly in the condensation, i.e., about 10^{-4} of the electrons are significantly affected. This view fits nicely with the fact that the condensation energy is observed to be of order 10^{-4}. $k_B T_c$. Thus, electrons within an energy $\sim v_F \Delta p \simeq kT_c$ of the Fermi surface have their energies lowered by of order kT_c in the condensation. In summary, the problem was how to account for the phase transition in which a condensation of electrons occurs in momentum space for electrons very near the Fermi surface. A proper theory should automatically account for the perfect conductivity and diamagnetism, as well as for the energy gap in the excitation spectrum.

II. THE PAIRING CONCEPT

In 1955, stimulated by writing a review article on the status of the theory of superconductivity, John Bardeen decided to renew the attack on the problem.



He invited Leon Cooper, whose background was in elementary particle physics and who was at that time working with C. N. Yang at the Institute for Advanced Study to join in the effort starting in the fall of 1955. I had the good fortune to be a graduate student of Bardeen at that time, and, having finished my graduate preliminary work, I was delighted to accept an invitation to join them.

We focused on trying to understand how to construct a ground state Ψ_0 formed as a coherent superposition of normal state configurations Φ_n,

$$\Psi_0 = \sum_n a_n \Phi_n \tag{5}$$

such that the energy would be as low as possible. Since the energy is given in terms of the Hamiltonian H by

$$E_0 = (\Psi_0, H\psi_0) = \sum_{n,n'} a_{n'}{}^* \, a_n \, (\Phi_{n'}, H\Phi_n) \tag{6}$$

we attempted to make E_0, minimum by restricting the coefficients a_n so that only states which gave negative off-diagonal matrix elements would enter (6). In this case all terms would add in phase and E_0 would be low.

By studying the eigenvalue spectrum of a class of matrices with off-diagonal elements all of one sign (negative), Cooper discovered that frequently a single eigenvalue is split off from the bottom of the spectrum. He worked out the problem of two electrons interacting via an attractive potential-V above a quiescent Fermi sea, i.e., the electrons in the sea were not influenced by V and the extra pair was restricted to states within an energy $\hbar\omega_D$ above the Fermi surface, as illustrated in Fig. 2. As a consequence of the non-zero density of quasi-particle states $\mathcal{N}(0)$ at the Fermi surface, he found the energy eigenvalue spectrum for two electrons having zero total momentum had a bound state split off from the continuum of scattering states, the binding energy being

$$E_B \cong \hbar\omega_D e^{-\frac{2}{\mathcal{N}(0)V}} \tag{7}$$

if the matrix elements of the potential are constant equal to V in the region of interaction. This important result, published in 1956 (12), showed that, regardless of how weak the residual interaction between quasi-particles is, if the interaction is attractive the system is unstable with respect to the formation of bound pairs of electrons. Further, if E_B is taken to be of order $k_B T_c$, the uncertainty principle shows the average separation between electrons in the bound state is of order 10^{-4} cm.

While Cooper's result was highly suggestive, a major problem arose. If, as we discussed above, a fraction 10^{-4} of the electrons is significantly involved in the condensation, the average spacing between these condensed electrons is roughly 10^{-6} cm. Therefore, within the volume occupied by the bound state of a given pair, the centers of approximately $(10^{-4}/10^{-6})^3 \cong 10^6$ other pairs will be found, on the average. Thus, rather than a picture of a dilute gas of strongly bound pairs, quite the opposite picture is true. The pairs overlap so strongly in space that the mechanism of condensation would appear to be destroyed due to the numerous pair-pair collisions interrupting the binding process of a given pair.

Returning to the variational approach, we noted that the matrix elements $(\Phi_{n'}, H\Phi_n)$ in (6) alternate randomly in sign as one randomly varies n and n' over the normal state configurations. Clearly this cannot be corrected to obtain a low value of E_0, by adjusting the sign of the a_n's since there are N^2 matrix elements to be corrected with only N parameters a_n. We noticed that if the sum in (6) is restricted to include only configurations in which, if any quasi-particle state, say k, s, is occupied ($s = \uparrow$ or $\downarrow$ is the spin index), its "mate" state $\bar{k}, \bar{s}$ is also occupied, then the matrix elements of H between such states would have a unique sign and a coherent lowering of the energy would be obtained. This correlated occupancy of pairs of states in momentum space is consonant with London's concept of a condensation in momentum.

In choosing the state $\bar{k}, \bar{s}$ to be paired with a given state k, s, it is important to note that in a perfect crystal lattice, the interaction between quasi-particles conserves total (crystal) momentum. Thus, as a given pair of quasi-particles interact, their center of mass momentum is conserved. To obtain the largest number of non-zero matrix elements, and hence the lowest energy, one must choose the total momentum of each pair to be the same, that is

$$k + \bar{k} = q. \tag{8}$$

States with $q \neq 0$ represent states with net current flow. The lowest energy state is for $q = 0$, that is, the pairing is such that if any state $k\uparrow$ is occupied in an admissible Φn, so is $-k\downarrow$ occupied. The choice of $\downarrow\uparrow$ spin pairing is not restrictive since it encompasses triplet and singlet paired states.

Through this reasoning, the problem was reduced to finding the ground state of the reduced Hamiltonian

$$H_{\text{red}} = \sum_{ks} \epsilon_k n_{ks} - \sum_{kk'} V_{k'k}\, b_{k'}^{+} b_k. \tag{9}$$

The first term in this equation gives the unperturbed energy of the quasi-particles forming the pairs, while the second term is the pairing interaction in which a pair of quasi-particles in $(k\uparrow, -k\downarrow)$ scatter to $(k'\uparrow, -k'\uparrow)$. The operators $b_k^{+} = c_{k\uparrow}^{+} c_{-k\downarrow}^{+}$, being a product of two fermion (quasi-particle) creation operators, do not satisfy Bose statistics, since $b_k^{+2} = 0$. This point is essential to the theory and leads to the energy gap being present not only for dissociating a pair but also for making a pair move with a total momentum different from the common momentum of the rest of the pairs. It is this feature which enforces long range order in the superfluid over macroscopic distances.

III. THE GROUND STATE

In constructing the ground state wavefunction, it seemed clear that the average occupancy of a pair state $(k\uparrow, -k\downarrow)$ should be unity for k far below the Fermi surface and 0 for k far above it, the fall off occurring symmetrically about kF over a range of momenta of order

$$\Delta k \sim \frac{1}{\xi} \sim 10^4\ \mathrm{cm}^{-1}.$$

One could not use a trial Ψ_0 as one in which each pair state is definitely occupied or definitely empty since the pairs could not scatter and lower the energy in this case. Rather there had to be an amplitude, say v_k, that $(k\uparrow, -k\downarrow)$ is occupied in Ψ_0 and consequently an amplitude $u_k = \sqrt{1-v_k^2}$ that the pair state is empty. After we had made a number of unsuccessful attempts to construct a wavefunction sufficiently simple to allow calculations to be carried out, it occurred to me that since an enormous number ($\sim 10^{19}$) of pair states $(k'\uparrow, -k'\downarrow)$ are involved in scattering into and out of a given pair state $(k\uparrow, -k\downarrow)$, the "instantaneous" occupancy of this pair state should be essentially uncorrelated with the occupancy of the other pair states at that "instant". Rather, only the average occupancies of these pair states are related.

On this basis, I wrote down the trial ground state as a product of operators - one for each pair state-acting on the vacuum (state of no electrons),

$$\Psi_0 = \pi_k\ (u_k + v_k b_k)\ |0>, \tag{10}$$

where $u_k = \sqrt{1-v_k^2}$. Since the pair creation operators b_k^+ commute for different k's, it is clear that Ψ_0 represents uncorrelated occupancy of the various pair states. I recall being quite concerned at the time that Ψ_0 was an admixture of states with different numbers of electrons, a wholly new concept to me, and as I later learned to others as well. Since by varying v_k the mean number of electrons varied, I used a Lagrange multiplier μ (the chemical potential) to make sure that the mean number of electrons ($\mathcal{N}_{\mathrm{op}}$) represented by Ψ_0 was the desired number $\mathcal{N}$. Thus by minimizing

$$E_0 - \mu\mathcal{N} = (\Psi_0, [H_{\mathrm{red}} - \mu\mathcal{N}_{\mathrm{op}}]\Psi_0)$$

with respect to v_k, I found that v_k was given by

$$v_k^2 = \tfrac{1}{2}\left[1 - \frac{(\epsilon_k - \mu)}{E_k}\right] \tag{11}$$

where

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2} \tag{12}$$

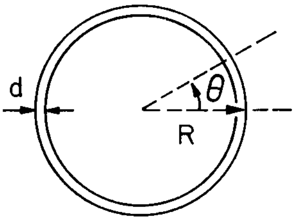
and the parameter Δ_k satisfied what is now called the energy gap equation:

$$\Delta_k = -\sum V_{k'k} \frac{\Delta_{k'}}{2E_{k'}} \tag{13}$$

From this expression, it followed that for the simple model

$$V_{k'k} = \begin{cases} V, & |\epsilon_k - \mu| < \hbar\omega_D \text{ and } |\epsilon_{k'} - \mu| < \hbar\omega_D \\ 0, & \text{otherwise} \end{cases}$$

$$\Delta = \hbar\,\omega_D e - \frac{1}{\mathcal{N}(0)V} \tag{14}$$



and the condensation energy at zero temperature is

$$\Delta F = \tfrac{1}{2}\mathcal{N}(0)\Delta^2 \tag{15}$$

The idea occurred to me while I was in New York at the end of January, 1957, and I returned to Urbana a few days later where John Bardeen quickly recognized what he believed to be the essential validity of the scheme, much to my pleasure and amazement. Leon Cooper will pick up the story from here to describe our excitement in the weeks that followed, and our pleasure in unfolding the properties of the excited states.

IV. QUANTUM PHENOMENA ON A MACROSCOPIC SCALE

Superconductors are remarkable in that they exhibit quantum effects on a broad range of scales. The persistence of current flow in a loop of wire many meters in diameter illustrates that the pairing condensation makes the superfluid wavefunction coherent over macroscopic distances. On the other hand, the absorption of short wavelength sound and light by a superconductor is sharply reduced from the normal state value, as Leon Cooper will discuss. I will concentrate on the large scale quantum effects here.

The stability of persistent currents is best understood by considering a circular loop of superconducting wire as shown in Fig. 3. For an ideal small diameter wire, one would use the eigenstates $e^{im\theta}$, (m = 0, ± 1, ± 2, . . .), of the angular momentum L_z about the symmetry axis to form the pairing. In the ground state no net current flows and one pairs $m\uparrow$ with $-m\downarrow$, instead of $k\uparrow$ with $-k\downarrow$ as in a bulk superconductor. In both cases, the paired states are time reversed conjugates, a general feature of the ground state. In a current carrying state, one pairs $(m+\nu)\uparrow$ with $(-m+\nu)\downarrow$, (ν = 0, ±1, ±2 . . .), so that the total angular momentum of each pair is identical, $2\hbar\nu$. It is this commonality of the center of mass angular momentum of each pair which preserves the condensation energy and long range order even in states with current flow. Another set of flow states which interweave with these states is formed by pairing $(m+\nu)\uparrow$ with $(-m+\nu+1)\downarrow$, ($\nu = 0, \pm 1, \pm 2$ . . .), with the pair angular momentum being $(2\nu+1)\hbar$. The totality of states forms a set with all integer multiples n of $\hbar$ for allowed total angular momentum of pairs. Thus, even though the pairs greatly overlap in space, the system exhibits quantization effects as if the pairs were well defined.

There are two important consequences of the above discussion. First, the fact that the coherent condensate continues to exist in flow states shows that to scatter a pair out of the (rotating) condensate requires an increase of energy.

Crudely speaking, slowing down a given pair requires it ot give up its binding energy and hence this process will occur only as a fluctuation. These fluctuations average out to zero. The only way in which the flow can stop is if all pairs simultaneously change their pairing condition from, say, v to v - 1. In this process the system must fluctate to the normal state, at least in a section of the wire, in order to change the pairing. This requires an energy of order the condensation energy ΔF. A thermal fluctuation of this size is an exceedingly rare event and therefore the current persists.

The second striking consequence of the pair angular momentum quantization is that the magnetic flux Φ trapped within the loop is also quantized,

$$\Phi_n = n \cdot \frac{hc}{2e} \qquad (n = 0, \pm 1, \pm 2 \ldots). \tag{16}$$

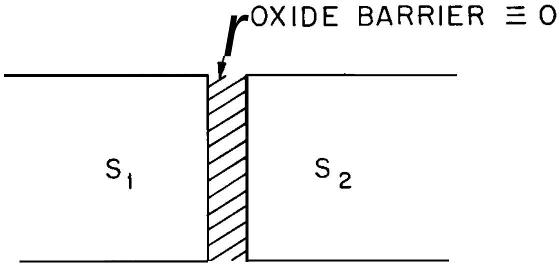
This result follows from the fact that if the wire diameter d is large compared to the penetration depth λ, the electric current in the center of the wire is essentially zero, so that the canonical angular momentum of a pair is

$$L_{\text{pair}} = \frac{2e}{c} r_{\text{pair}} \times A \tag{17}$$

where r_{pair} is the center of mass coordinate of a pair and A is the magnetic vector potential. If one integrates L_{pair}, around the loop along a path in the center of the wire, the integral is nh, while the integral of the right hand side of (17) is $\frac{2e}{c}\Phi$.

A similar argument was given by F. London (4b) except that he considered only states in which the superfluid flows as a whole without a change in its internal structure, i.e., states analogous to the $(m+\nu)\uparrow, (-m+\nu)\downarrow$ set. He found $\Phi z = n \cdot hc/e$. The pairing $(m+\nu)\uparrow, (m+\nu+1)\downarrow$ cannot be obtained by adding ν to each state, yet this type of pairing gives an energy as low as the more conventional flow states and these states enter experimentally on the same basis as those considered by London. Experiments by Deaver and Fairbank (13), and independently by Doll and Näbauer (14) confirmed the flux quantization phenomenon and provided support for the pairing concept by showing that 2e rather than e enters the flux quantum. Following these experiments a clear discussion of flux quantization in the pairing scheme was given by Beyers and Yang (15).

The idea that electron pairs were somehow important in superconductivity has been considered for some time (16, 17). Since the superfluidity of liquid He^4 is qualitatively accounted for by Bose condensation, and since pairs of electrons behave in some respects as a boson, the idea is attractive. The essential point is that while a dilute gas of tightly bound pairs of electrons might behave like a Bose gas (18) this is not the case when the mean spacing between pairs is very small compared to the size of a given pair. In this case the inner structure of the pair, i.e., the fact that it is made of fermions, is essential; it is this which distinguishes the pairing condensation, with its energy gap for single pair translation as well as dissociation, from the spectrum of a Bose con-



densate, in which the low energy exictations are Bose-like rather than Fermi-like as occurs in acutal superconductors. As London emphasized, the condensation is an ordering in occupying momentum space, and not a space-like condensation of clusters which then undergo Bose condensation.

In 1960, Ivar Giaever (19) carried out pioneering experiments in which electrons in one superconductor (S,) tunneled through a thin oxide layer (~ 20-30 A) to a second superconductor (S,) as shown in Fig. 4. Giaever's experiments were dramatic evidence of the energy gap for quasi-particle excitations. Subsequently, Brian Josephson made a highly significant contribution by showing theoretically that a superfluid current could flow between S_1 and S_2 with zero applied bias. Thus, the superfluid wavefunction is coherent not only in S_1 and S_2 separately, but throughout the entire system, S_1-0-S_2, under suitable circumstances. While the condensate amplitude is small in the oxide, it is sufficient to lock the phases of S_1 and S_2 together, as has been discussed in detail by Josephson (20) and by P. W. Anderson (21).

To understand the meaning of phase in this context, it is useful to go back to the ground state wavefunction Ψ_0, (10). Suppose we write the parameter v_k as $|v_k|$ exp $i\varphi$ and choose u_k to be real. If we expand out the k-product in Ψ_0, we note that the terms containing N pairs will have a phase factor exp (i $N\varphi$), that is, each occupied pair state contributes a phase φ to Ψ_0. Let this wavefunction, say $\Psi_0^{(1)}$ represent S_1, and have phase φ_1. Similarly, let $\Psi_0^{(2)}$ represent S_2 and have phase angle φ_2. If we write the state of the combined system as a product

$$\Psi_0^{(1,2)} = \Psi_0^{(1)}\ \Psi_0^{(2)} \tag{18}$$

then by expanding out the double product we see that the phase of that part of $\Psi_0^{(1,2)}$ which has N_1 pairs in S_1 and N_2 pairs in S_2 is $N_1\varphi_1 + N_2\varphi_2$. For a truly isolated system, $2(N_1+N_2)$ = 2N is a fixed number of electrons; however N_1 and N_2, are not separately fixed and, as Josephson showed, the energy of the combined system is minimized when $\varphi_1 = \varphi_2$ due to tunneling of electrons between the superconductors. Furthermore, if $\varphi_1 = \varphi_2$, a current flows between S_1 and S_2

$$j = j_1 \sin(\varphi_1 - \varphi_2) \tag{19}$$

If $\varphi_1 - \varphi_2 = \varphi$ is constant in time, a constant current flows with no voltage applied across the junction. If a bias voltage is V applied between S_1 and S_2, then, according to quantum mechanics, the phase changes as

$$\frac{2eV}{\hbar}=\frac{d\varphi}{dt} \tag{20}$$

Hence a constant voltage applied across such a junction produces an alternating current of frequency

$$\nu=\frac{2eV}{\hbar}=483\ \mathrm{THz/V}. \tag{21}$$

These effects predicted by Josephson were observed experimentally in a series of beautiful experiments (22) by many scientists, which I cannot discuss in detail here for lack of time. I would mention, as an example, the work of Langenberg and his collaborators (23) at the University of Pennsylvania on the precision determination of the fundamental constant e/h using the frequency-voltage relation obeyed by the alternating Josephson supercurrent. These experiments have decreased the uncertainty in our experimental knowledge of this constant by several orders of magnitude and provide, in combination with other experiments, the most accurate available value of the Sommerfeld fine structure constant. They have resulted in the resolution of several discrepancies between theory and experiment in quantum electrodynamics and in the development of an “atomic” voltage standard which is now being used by the United States National Bureau of Standards to maintain the U.S. legal volt.

V. CONCLUSION

As I have attempted to sketch, the development of the theory of superconductivity was truly a collaborative effort, involving not only John Bardeen, Leon Cooper and myself, but also a host of outstanding scientists working over a period of half a century. As my colleagues will discuss, the theory opened up the field for many exciting new developments, both scientific and technological, many of which no doubt lie in the future. I feel highly honored to have played a role in this work and I deeply appreciate the honor you have bestowed on me in awarding us the Nobel prize.

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