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J. Bardeen

Department of Physics, University of Illinois, Urbana-Champaign, Urbana, Illinois 61801, U.S.A.

Résumé.- On passe en revue les bases de la théorie microscopique des supraconducteurs publiée en 1957 et les développements expérimentaux et théoriques des années postérieures. Deux champs d'activité courants, la supraconductivité hors-équilibre et la recherche de supraconducteurs avec des températures de transition élevées seront traités brièvement.

Abstract.- A review is given of the basis for the microscopic theory of superconductivity introduced in 1957 and of the developments, both experimental and theoretical, in the years immediately following. Two currently active areas, nonequilibrium superconductivity and the search for superconductors with high transition temperatures are discussed briefly.

1. INTRODUCTION.- With the passage of more than 21 years since the basis for a microscopic theory of superconductivity was given by Cooper, Schrieffer and me, the theory has reached adulthood. From the work of a large number of people, both experimentalists and theorists, superconductivity has changed from a mystery into what has been called the best understood of all solid state phenomena. The period of rapid growth and development has been completed and superconductivity is making productive contributions to other branches of science and to society. Some of the concepts introduced have been used to help better understand nuclear structure and nuclear matter in neutron stars as well as problems of particle physics. An unexpected outcome was the precise measurement, through the Josephson frequency relation, of the ratio e/h, which brought about a revision of the values of the fundamental constants. Superconducting magnets and sensitive detecting devices, such as SQUIDS, are being used in laboratories throughout the world.

A large part of current basic research in superconductivity is inspired by potential applications, both large and small scale. Large scale applications such as to superconducting magnets, have stimulated the search for improved materials in regard to electrical and mechanical properties and particularly higher transition temperatures. Small scale applications, such as those bases on the Josephson effect, have stimulated much of the current activity on nonequilibrium phenomena.

The pairing theory is being applied sucessfully to account for the properties of superfluid ^{3}He. With triplet pairing, collective modes, textures analogous to those in liquid crystals, point and line singularities, this is an extraordinarily complex liquid. It is remarkable that such complex phenomena occur in a liquid constituted from spherical atoms with a very simple interaction between them. It gives hope that the very complex world we live in with its great variety of so-called elementary particles has a simple underlying structure.

The original BSC papers published in 1957 were concerned mainly with isotropic homogeneous systems. We derived the excitation spectrum of Fermi quasiparticles with energies, $E_k = (\varepsilon_k^2 + \Delta^2)^{1/2}$, in one-to-one correspondence with those of the normal metal, ε_k. The minimum energy required to create a pair of excitations is the energy gap, $E_g = 2\Delta$. Since the parameter Δ is also a measure of pairing, it is often called the pair potential and may be regarded as the order parameter of the theory. With the complete spectrum of excitations, we were able to work out the various thermal properties and response functions without much more difficulty than for normal metals. It was found that earlier phenomenological expressions, such as those for the temperature dependence of critical fields and penetration depths, followed approximately from the microscopic theory. Pippard's nonlocal version of the London expression for the current density in a magnetic field is also an approximate consequence, with a coherence distance $\xi_0 = \hbar v_F/\pi\Delta$, close to that found from experiment.

New, more general formulations of the theory were soon developed by others. Anderson gave the spin analogy, showed that there is broken gauge symmetry associated with long range order and how to give a gauge invariant formulation of the theory. Bogoliubov and Valatin independently introduced the well known quasiparticle transformation. Soon generalized to treat inhomogeneous problems. The powerful methods of thermal Green functions were first applied to superconductivity theory by Gor'kov. These allow one to treat not only inhomogeneous problems but also strong coupling superconductors for which quasiparticle lifetime effects are important. Gor'kov showed that the phenomenological Ginzburg-Landau theory is valid near T_c with the complex pair potential $\Delta(r)$ playing the role of an effective wave function to describe superfluid flow. It is these advances that provided the theoretical framework for future developments.

With a theory to interpret results of experiments and to suggest new experiments, there followed a period of rapid expansion of research in superconductivity. According to a count made by Pippard, the percentage of Physics Abstracts on superconductivity increased from about 0.7 % in 1957 to almost 2 % in 1965, which, with the general expansion of physics research, represented a ten-fold increase in number papers. Another measure is the attendence at international conferences on superconductivity, about 90 at Cambridge in 1959, 150 at IBM, Yorktown Heights, in 1961, 350 at Colgate in 1963 and 425 at Stanford in 1969.

The world of superconductivity in metals that has been explored in the past two decades is a vast one. Two large volumes were required in Parks' treatise to survey the work done in a little more than half of that time. It would be impossible in a single talk such as this to cover even the highlights. What I will attempt to do is to give some impressions of the exciting early days of the pairing theory and of the experiments that followed. I will then review briefly areas of current interest

2. DEVELOPMENT OF THE PAIRING THEORY : Since I have discussed the background for the pairing theory in a talk at LT8 in London in 1962 and elsewhere, I will say little about it here. However, I cannot fail to note the great insight of Fritz London that superconductivity is a quantum phenomena on macroscopic scale and that it involves some sort of condensation in momentum space. After 1950, with Fröhlich's suggestion and the independent discovery of the isotope effect, we knew that we had to look to electron-phonon interactions for an explanation of the phenomena. It was shown that these give an effective attraction between electrons which can be larger than the screened Coulomb repulsion for electrons with energies near the Fermi surface.

In 1956 Cooper showed that in the presence of an attractive interaction, the Fermi surface is unstable against the formation of bound pairs. To find the nature of the superconducting ground state and low-lying excitations required the solution of a many-body problem of large numbers of interacting electrons. We wanted to express the wave functions in terms of low-lying normal configurations so that we could concentrate on the differences between normal and superconducting states, differences which involve only a small amount of energy but have a profound effect on the properties.

Low-lying configurations of normal metals are defined by occupation numbers of quasiparticle and phonon states. These states are only approximate eigenstates since there are residual interactions between the normal quasiparticles ; it is these interactions that are responsible for superconductivity.

While the theory of superconductivity can be approched from several different points of view, I believe that the one we used in our original papers show most clearly the reason for pairing. The ground state wave function, ψ_s, of the superconductor is given by linear combinations of normal configurations, ψ_i, each defined by quasiparticle occupation numbers : $\psi_s = \sum a_i\psi_i$.

One may form a coherent non-perturbative low energy state of a Hamiltonian matrix if the off-diagonal matrix elements are predominantly negative. With Fermi-Dirac statistics, matrix elements between ψ_i of an attractive interaction can be made negative only for selected configurations for which the quasiparticle states are occupied in pairs such that if one of the pair is occupied the other is also. In all known superconducting metals there is singlet pairing so the paired states have opposite spin. To get a maximum number of matrix elements between the selected configurations, ψ_i, all paired states $(k_1\uparrow,k_2\downarrow)$ should have precisely the same total momentum, $p_s = \hbar(k_1 + k_2)$, so that any pair can be scattered into any other pair. The lowest energy corresponds to $p_s = 0$ with pairing $(k\uparrow,-k\downarrow)$. To derive the ground state energy we first tried to solve the reduced Hamiltonian which includes only the scattering of pairs of opposite spin and momentum.

The solution to this problem was found by Schrieffer in early February, 1957. Purely for mathematical convenience, he expressed ψ_s as product of creation operators which when expanded gives a series of terms with varying total number of pairs present :

$$\psi_s = \sum a_i \psi_i = \sum_N a_N e^{iN\chi} \psi_N .$$

We have introduced an arbitrary phase, χ. When the product is expanded, one may group together terms with the same total number of pairs, N, and ψ_N is the normalized wave function corresponding to a given N. As for a statistical ensemble, the coefficients a_N are sharply peaked about the mean number of pairs present.

There is often much more in a theory than is apparent even to the originators. This is certainly the case here, for this form for the wave function, chosen for mathematical reasons, is an eigenstate of phase, which we know to be an important variable to describe a superconductor. As pointed out by Anderson, χ and N may be regarded as conjugate variables, with $N_{op} = -i\partial/\partial\chi$. These have an uncertainty relation $\Delta N \Delta\chi \sim 1$, so that if the number of pairs is fixed, the phase is undetermined.

One can define the phase only for a superconductor coupled weakly with its surroundings so as to allows exchange of electrons. It was an attempt to see whether or not the phase really is a pertinent variable, after hearing lectures from Anderson, that led Josephson to the prediction of the Josephson effect. In the bulk, superfluid flow may be described by a slowly varying p_s as the gradient of space-varying phase : $p_s = \hbar$ grad χ, as follows, for example, from the Ginzburg-Landau theory. Phase plays the role for superfluid flow that voltage does for flow in normal metals.

With the ground state wave function, we calculated the energy difference between normal and superconducting states and an energy gap at T = 0 K for creating a pair of quasiparticles in reasonable agreement with estimates from experiments on specific heats and from infrated absorption. We submitted the Letter of the Editor in mid-February and worked intensively on calculations of thermal and electromagnetic properties. It was a great thrill to find a second-order transition at T_c with a specific heat jump in agreement with experiment. Cooper gave the first public presentation of the theory in a post-deadline paper at the March meeting of the American Physical Society.

It took us a while to recognize that matrix elements for the scattering $k\uparrow \rightarrow k'\uparrow$ connect the same initial and final states as $-k'\downarrow \rightarrow -k\downarrow$ and so must be added coherently. Whether they add destructively or constructively depends on whether the interaction is symmetric or antisymmetric under time reversal. Since the latter applies to nuclear spin relaxation, we were able to account for the unexpected marked rise in relaxation rate below T_c observable by Hebel and Slichter. These experiments were being done at Illinois at the same time we were working out the theory. This confirmation gave us added confidence in the pairing theory.

An experiment being done at the time of great significance was that of Glover and Tinkham on far infrared transmission through thin superconducting films. These gave direct evidence for an energy gap corresponding to the frequency at which absorption sets in. The frequency dependence of the absorption above the gap is also approximately as predicted by the theory.

I spent part of the summer of 1957 at Berkeley where I was able to talk with Glover and Tinkham at first hand about their experiments. Also there was Freeman Dyson, with whom I had stimulating discussions about the pairing theory. He had shown that the ground state wave function for a fixed number of pairs N could be written as an antisymmetrized product of identical pair functions, as had been suggested earlier by Schafroth and Blatt. However, the latter too; the analogy with a Bose condensation of pairs too literally and had not determined the ground state energy, the excitation spectrum, or any superconducting properties.

3. EXPERIMENT AND THEORY AT LTV.- Later that summer the theory received its first exposure to an international audience at LTV, held at Madison, Wisconsin. Several of the experimental papers helped confirm the theory : Tinkham described the experiments on far infrared transmission through thin superconducting films of lead and tin, Slichter those on nuclear spin relaxation, Bömmel and R.W. Morse on ultrasonic attenuation, Biondi and Garfunkel on millimeter wave absorption in aluminium and tin. These gave evidence for the gap and its temperature dependence as well as the coherence effects predicted by theory. It was in a discussion with R.W. Morse on ultrasonic attenuation that I worked out the now familiar expression for the ratio of the attenuation between superconducting and normal states : $\alpha_s/\alpha_n = 2/[1 + \exp(\Delta(T)/k_BT)]$. This expression turned out to have far more general applicability than suggested by the initial derivation. Bohm and Morse and later others have used the expression to determine $\Delta(T)$ for several metals.

Also presented at LTV were some papers whose full significance was not appreciated until much later. One of these was by Hans Meissner who showed that a supercurrent could flow through a thin film of normal metal separating two superconductors. Another was on the properties of Nb_3Sn in the intermediate state. This compound had earlier been shown to be a high temperature superconductor by Matthias et al.

Reaction to the theory at the Madison meeting was mixed. Experimentalists were generally enthusiastic about it. Objections were raised mainly by theorists who had preconceived notions about the directions the theory should take and particularly about general principles that were thought to be violated.

Most skepticism was in regard to the theory of the Meissner effect. We carried out the response to static magnetic fields in the transverse or London gauge and used only the quasiparticle spectrum. The same procedures give incorrect results in a general gauge. In calculating response in a general gauge, one must take into account changes in Δ resulting from the field. When this is done, electromagnetic response may be calculated in a manifestly gauge invariant manner. Collective modes from longitudinal density fluctuations are pushed up to plasma frequencies by the long range Coulomb interaction.

4. RESEARCH IN THE USSR.- In 1957, exchange of information with Soviet scientists was not as free as it is today. Although the preprint of our paper, submitted in June, had wide circulation in the West, we were not allowed to send copies behind the iron curtain. In the summer of 1957 the only information available in Russia was the Letter to the Editor published in April. This Letter attracted the interest of Landau's group at the Institute for Physical Problems and a group under Bogoliubov at the Mathematics Institute in Moscow. Bogoliubov suggested the quasiparticle transformation which yielded an excitation spectrum identical to the one we used but in a form which was easier to apply. Bogoliubov later generalized the transformation to a space varying pair potential $\Delta(r)$ and gave coupled Schrödinger-like equations to determine the wave functions for the paired states in a self-consistent manner. Bogoliubov and co-workers also showed the Coulomb interactions are greatly reduced when renormalized to the same energy range as the phonons and could cause a departure of the exponent, α, in the isotope effect, $T_c \sim M^{-\alpha}$, from the value 1/2 expected for the electron-phonon interaction.

Some of the theorists in Landau's group had been working with Feynman diagrams on problems of quantum electrodynamics and were extending the methods to statistical physics. As suggested by Matsubara, inverse temperature plays the role of an imaginary time. Gor'kov applied the methods to superconductivity theory and derived the ground state energy and excitation spectrum.

Pairing was introduced through the anomalous propagator (Green's function)

$$F(r_2,\ r_1\ ;\ t_2,\ t_1) = -i\ \langle N-1|T\psi(r_2,\ t_2)\psi(r_1,\ t_1)|N\rangle$$

where N is the number of pairs, the brackets represent a thermal average, T is a time ordering operator and $\psi(r_1, t_1)$ is the second quantized wave field operator for the electrons. In a homogeneous system, F depends only on the difference $r = r_2 - r_1$. Gor'kov gave coupled equations to determine the ordinary and anomalous propagators G and F.

The first papers of Bogoliubov and co-workers were submitted in October, 1957 and Gor'kov's first paper in November. Gor'kov refers to the preprint of the BCS paper published in the November issue of the Physical Review. Bogoliubov cites only the Letter published in the April, although in a footnote added in proof in December he refers to the preprint. Thus the preprint came to light in the Soviet Union sometiem between October and November. There is a story that a Soviet physicist working in a different field picked up a copy at a meeting held at Varenna, Italy, during the summer but, as many of us do, filled it away without reading it. After Bogoliubov's work became known, he looked up the preprint and found that we had already obtained, by a different method, the same ground state and spectrum of excitations and solved a number of problems.

Thermal Green's function methods were introduced independently by Martin and Schwinger and applied to problems of superconductivity by Kadanoff and Martin. Superconductivity has provided many problems which have aided in the development of the methods. Two of the most influential books have been those of Abrikosov, Gor'kov and Dzalashinskii and of Kadanoff and Baym.

5. EARLY DEVELOPMENT.- For two or three years following 1957, most experiments extended and refined measurements of properties that had been studied

earlier, such as heat capacity, critical fields, electromagnetic response, ultrasonic attenuation, thermal conductivity, etc. Derivations based on an isotropic, weak coupling model were given in BCS paper for thermal properties and for response to static magnetic fields. Mattis and I later extended the calculation of electromagnetic response to all frequencies and temperatures. Rickayzen, Tewordt and I derived a quasiparticle, Boltzmann equation and expressions for the electronic thermal conductivity for both impurity and phonon scattering and also the lattice conductivity when it is limited by electron scattering.

Agreement between theory and experiments was in general remarkably good. The BCS model gave departures from Tuyns' law, $H_c \cong H_o(1-t^2)$, where $t = T/T_c$, in the same direction and in approximately the same magnitude as most superconductors. Various experiments gave evidence for a temperature dependent energy gap in metals such Aℓ, In, Sn, in agreement with the model. The magnitude and temperature dependence of penetration depths also agreed well with theory. The metals that were found to depart most significantly from model, Hg and Pb, are those for which T_c/Θ_D is the greatest (~ 0.1). It was recognized that the discrepancies were probably due to quasiparticle life-time effects and that Gor'kov's method would be required to treat such "strong coupling" superconductors.

Abrikosov and Gor'kov applied Green's function methods to superconducting alloys, showing that magnetic impurities that cause spin-flip scattering are pair-breaking and cause a reduction in T_c. Just below the critical concentration at which T_c vanishes, there is a region where the gap vanishes. Thus a gap is not essential, but long range order exemptplified in a finite pair potential is required. In another application, they, together with Khalatnikov, worked out the electrodynamics of superconductors and obtained results for the response function at arbitrary frequencies and temperatures in agreement with those that Mattis and I had obtained by different methods. Abrikosov and Khalatnikov also derived a quasiparticle Boltzmann equation and applied it to thermal superconductivity.

Another important contribution of Soviet scientists was to derive by field theoretic methods essentially exact solutions of the Fröhlich Hamiltonian for both normal and superconducting metals. This Hamiltonian includes bare electrons and phonons and an interaction between them. Effects of Coulomb interactions are neglected except as they may modify the parameters of the theory. In a paper published in 1957 Migdal solved the Dyson equations for normal metals for renormalized electron and phonon propagators by showing that vertex corrections are small. Nambu and Eliashberg independently extended Migdal's methods to superconductors.

Eliashberg derived a pair of coupled nonlinear integral equations for the mass renormalization factor, $Z_s(\omega)$, and the gap, $\Delta(\omega)$, both in general complex. The electron-phonon interaction enters in the form $\alpha^2(\omega)\ F(\omega)$, where α is the vertex function and F the energy density of states. These equations have been widely used in calculations of superconducting properties, including T_c, from first principles and to derive $\alpha^2F(\omega)$ from tunneling data.

The period 1960-62 marked several striking advances in superconductivity that opened up new areas in experiment, theory and applications. These are (1) quasiparticle tunneling by Giaever in 1960, (2) flux quantization by Deaver and Fairbank and Doll and Näbauer in 1961, (3) superconductors that withtand very large magnetic fields by Kunzler and associates in 1961, (4) pair tunneling and other effects predicted by Josephson and first observed by Anderson and Rowell in 1962. In their Nobel lectures, Giaever and Josephson give interesting accounts of their research.

It is remarkable how much has come from the tunneling discoveries in both science and applications. Quasiparticle tunneling has led, with theoretical advances by Schrieffer, Scalapino, McMillan and others and experimental advances by Giaever, Rowell and others to tunneling spectroscopy. With use of McMillan's computer program and the Eliashberg equations, one can derive $\alpha^2F(\omega)$ directly from tunneling data. Pair tunneling has led to quantum interference devices as very sensitive detectors, to computer components and to the use of tunnel junctions as a pair potential probe. Tunnel junctions to thin film superconductors and to microbridges have been widely used in studies of nonequilibrium phenomena.

The discovery of high field superconductors stimulated not only a vast amount of research on the properties of type II superconductors, but also the search for high T_c superconductors. Abrikosov's phenomenological theory based on the Ginzburg-Landau equations, published in 1957, has received strong experimental support, including the beautiful pictures of vortex arrays by Essman and Trauble. Kim observed resistive effects when the transport current exceeded a critical value, interpreded by Anderson in terms of motion of vortices transverse to the current.

Orsay has been a major center for both theory and experiment on type II materials. De Gennes and co-workers made extensive use of the generalized Bogoliubov equations. Later an improved microscopic theory was made possible by Eilenberger's formulation of the Gor'kov equations. The problem of vortex structure and motion is a difficult one and many questions are still under investigation.

The discovery that A-15 compounds are high-temperature superconductors, as well as of many other superconducting compounds, including NbTi, came about as an outgrowth of a research program initiated at the University of Chicago in 1950. Matthias and Hulm were both young staff members, Matthias coming from Bell Labs where his main interest had been ferroelectric materials and Hulm from Cambridge with a background in low temperature physics. It was Fermi who suggested that they join forces to look for new superconducting materials. Matthias returned to Bell Labs in 1951, where he introduced low temperature methods and with Geballe and others continued the work. It was in 1954 that Nb_3Sn was discovered to have a high T_c. Before that, Hulm and co-workers at Chicago had discovered the first A-15 superconductor, V_3Si. Although many new superconducting compounds have been discovered over the years, it is the A-15 compounds that have been studied most intensively. Recent developments will be reviewed at this conference by Testardi.

6. CURRENT PROBLEMS.- In spite of the success of the Eliashberg theory and of tunneling spectroscopy, the search for high T_c superconductors is still largely empirical. It is much easier to measure T_c than to calculate it. Although it is hard to give a rigorous upper bound, many feel that T_c can be no larger than 30-40 K for phonon-induced superconductivity, except perhaps for metallic hydrogen. Many suggestions have been made for other mechanisms for an effective attraction and high T_c : Exchange of excitons (or creation of virtual electron-hole pairs), exchange of plasmons, a Wigner lattice of electrons and heavy holes, etc. Thus far results have been disappointing. A notable exception is the large diamagnetism observed in CuCℓ under pressure, which may be related to superconductivity. Ginzburg has called the search for high T_c superconductivity the most outstanding problem in solid state physics.

Another active field in both experiment and theory is nonequilibrium phenomena. This subject was reviewed by Langenberg at LT 15 and by Schmid at this Conference. As in semiconductors the quasiparticle distribution can depart substancially from that for thermal equilibrium by radiation of current flow from a junction, causing related changes in the pair potential and phonon distribution. This is a large field which is just beginning to be explored.

It seems impractical to give specific references. Good sources are Superconductivity, R.D. Parks, ed. (Marcel Dekker, New York), 1969 ; Solymar, L. Superconductive Tunneling and Applications (Chapman and Hall, London), 1972 and LT Conference proceedings.