SCIENCE

# Electron-Phonon Interactions and Superconductivity

### John Bardeen

Our present understanding of superconductivity has arisen from a close interplay of theory and experiment. It would have been very difficult to have arrived at the theory by purely deductive reasoning from the basic equations of quantum mechanics. Even if someone had done so, no one would have believed that such remarkable properties would really occur in nature. But, as you well know, that is not the way it happened-a great deal had been learned about the experimental properties of superconductors and phenomenological equations had been given to describe many aspects before the microscopic theory was developed. Some of these have been discussed by Schrieffer (1) and by Cooper (2) in their talks.

My first introduction to superconductivity came in the 1930's, and I greatly profited from reading David Shoenberg's little book on superconductivity (3), which gave an excellent summary of the experimental findings and of the phenomenological theories that had been developed. At that time it was known that superconductivity results from a phase change of the electronic structure, and the Meissner effect showed that thermodynamics could be applied successfully to the superconductive equilibrium state. The two-fluid Gorter-Casimir model was used to describe the thermal properties, and the London brothers had given their famous phenomenological theory of the electrodynamic properties. Most impressive were Fritz London's speculations, given in 1935 at a meeting of the Royal Society in London (4), that superconductivity is a quantum phenomenon on a macroscopic scale. He also gave what may be the first indication of an energy gap when he stated that "the electrons be coupled by some form of interaction in such a way that the lowest state may be separated by a finite interval from the excited ones." He strongly urged, on the basis of the Meissner effect, that the diamagnetic aspects of superconductivity are the really basic property.

My first abortive attempt to construct a theory (5), in 1940, was strongly influenced by London's ideas, and the key idea was small energy gaps at the Fermi surface arising from small lattice displacements. However, this work was interrupted by several years of wartime research, and then after the war I joined the group at the Bell Telephone Laboratories where my work turned to semiconductors. It was not until 1950, as a result of the discovery of the isotope effect, that I again began to become interested in superconductivity and shortly after moved to the University of Illinois.

The year 1950 was notable in several respects for superconductivity theory. The experimental discovery of the isotope effect (6, 7) and the independent prediction of H. Fröhlich (8) that superconductivity arises from interaction between the electrons and phonons (the quanta of the lattice vibrations) gave the first clear indication of the directions along which a microscopic theory might be sought. Also in the same year the phenomenological Ginzburg-Landau equations appeared, which give an excellent description of supercon-

ductivity near the critical temperature  $T_{\rm c}$  in terms of a complex order parameter, as mentioned by Schrieffer (1) in his talk. Finally, it was in 1950 that Fritz London's book (9) on superconductivity appeared. This book included very perceptive comments about the nature of the microscopic theory that have turned out to be remarkably accurate. He suggested that superconductivity requires "a kind of solidification or condensation of the average momentum distribution." He also predicted the phenomenon of flux quantization, which was not observed for another dozen years.

The field of superconductivity is a vast one with many ramifications. Even in a series of three talks, it is possible to touch on only a few highlights. In this talk, I thought that it might be interesting to trace the development of the role of electron-phonon interactions in superconductivity from its beginnings in 1950 up to the present day, both before and after the development of the microscopic theory in 1957. By concentrating on this one area, I hope to give some impression of the great progress that has been made in the depth of understanding of the phenomena of superconductivity. Through developments by many people (10), electron-phonon interactions have grown from a qualitative concept to such an extent that measurements on superconductors are now used to derive detailed quantitative information about the interaction and its energy dependence. Further, for many of the simpler metals and alloys, it is possible to derive the interaction from first principles and calculate the transi-

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tion temperature and other superconducting properties.

The theoretical methods used involve the methods of quantum field theory as adapted to the many-body problem, including Green's functions, Feynman diagrams, Dyson equations, and renormalization concepts. Following Matsubara, temperature plays the role of an imaginary time. Even if you are not familiar with diagrammatic methods, I hope you will be able to follow the physical arguments involved.

In 1950, diagrammatic methods were just being introduced into quantum field theory to account for the interaction of electrons with the field of photons. It was several years before they were developed with full power for application to the quantum statistical mechanics of many interacting particles. After Matsubara, those prominent in the development of the theoretical methods include Kubo, Martin and Schwinger, and particularly the Soviet physicists Migdal, Galitski, Abrikosov, Dzyaloshinski, and Gor'kov (11). The methods were first introduced to superconductivity theory by Gor'kov (11) and a little later in a somewhat different form by Kadanoff and Martin (12). Problems of superconductivity have provided many applications for the powerful Green's function methods of many-body theory, and these applications have helped to further develop the theory.

Diagrammatic methods were first applied to a discussion of electron-phonon interactions in normal metals by Migdal (13), and his method was extended to superconductors by Eliashberg (14). A similar approach was given by Nambu (15). The theories are accurate to terms of order  $(m/M)^{\frac{1}{2}}$ , where m is the mass of the electron and M is the mass of the ion, and so give quite accurate quantitative accounts of the properties of both normal metals and superconductors.

I will first give a brief discussion of the electron-phonon interactions as applied to superconductivity theory from 1950 to 1957, when the pairing theory was introduced, then discuss the Migdal theory as applied to normal metals, and finally discuss Eliashberg's extension to superconductors and subsequent developments. I will close by saying a few words about applications of the pairing theory to systems other than those involving electron-phonon interactions in metals.

### Developments from 1950 to 1957

The isotope effect was discovered in the spring of 1950 by Reynolds *et al.* (6) at Rutgers University and by E. Maxwell (7) at the U.S. National Bureau of Standards. Both groups measured the transition temperatures of separated mercury isotopes and found a positive result that could be interpreted as  $T_c M^{\frac{1}{2}} \simeq \text{constant}$ , where *M* is the isotopic mass. If the mass of the ions is important, their motion and thus the lattice vibrations must be involved.

Independently, Fröhlich (8), who was then spending the spring term at Purdue University, attempted to develop a theory of superconductivity based on the self-energy of the electrons in the field of phonons. He heard about the isotope effect in mid-May, shortly before he submitted his paper for publication, and was delighted to find very strong experimental confirmation of his ideas. He used a Hamiltonian, now called the Fröhlich Hamiltonian, in which interactions between electrons and phonons are included but Coulomb interactions are omitted except as they can be included in the energies of the individual electrons and phonons. Fröhlich used a perturbation theory approach and found that there was an instability of the Fermi surface if the electron-phonon interaction was sufficiently strong.

When I heard about the isotope effect in early May in a telephone call from Serin, I attempted to revive my earlier theory of energy gaps at the Fermi surface, with the gaps now arising from dynamic interactions with the phonons rather than from small static lattice displacements (16). I used a variational method rather than a perturbation approach, but, like Fröhlich's, the theory was based on the electron self-energy in the field of phonons. Although we were very hopeful at the time, we soon found that both theories had grave difficulties, not easy to overcome (17). It became evident that nearly all of the self-energy is included in the normal state and is little changed in the transition. A theory involving a true man-body interaction between the electrons seemed to be required to account for superconductivity. Schafroth (18) showed that, starting with the Fröhlich Hamiltonian, one cannot derive the Meissner effect in any order of perturbation theory. Migdal's theory

(13), supposedly correct to terms of order  $(m/M)^{\frac{1}{2}}$ , gave no gap or instability at the Fermi surface and no indication of superconductivity.

Of course, Coulomb interactions really are present. The effective direct Coulomb interaction between electrons is shielded by the other electrons, and the electrons also shield the ions involved in the vibrational motion. David Pines and I (19) derived an effective electron-electron interaction starting from a Hamiltonian in which phonon and Coulomb terms are included from the start. As is the case for the Fröhlich Hamiltonian, the matrix element for the scattering of a pair of electrons near the Fermi surface from the exchange of virtual phonons is negative (attractive) if the energy difference between the electron states involved is less than the phonon energy. As discussed by Schrieffer (1), the attractive nature of the interaction was a key factor in the development of the microscopic theory. In addition to the phonon-induced interaction, there is the repulsive screened Coulomb interaction, and the criterion for superconductivity is that the attractive phonon interaction dominate the Coulomb interaction for states near the Fermi surface (20).

During the early 1950's there was increasing evidence for an energy gap at the Fermi surface. Also very important was Pippard's proposed nonlocal modification of the London electrodynamics which introduced a new length, the coherence distance,  $\xi_0$ , into the theory (21). In 1955 I wrote a review article (22) on the theory of superconductivity for the Handbuch der Physik. which was published in 1956. The central theme of the article was the energy gap, and I showed that Pippard's version of the electrodynamics would likely follow from an energy gap model. Also included was a review of electron-phonon interactions. I pointed out that the evidence suggested that all phonons are involved in the transition, not just the long-wavelength phonons, and that their frequencies are changed very little in the normal-superconducting transition. Thus one should be able to use the effective interaction between electrons as a basis for a true many-body theory of the superconducting state. Schrieffer and Cooper described in their lectures how we were eventually able to accomplish this goal.

## Green's Function Method for Normal Metals

By use of Green's function methods, Migdal (13) derived a solution of Fröhlich's Hamiltonian,  $H = H_{e\ell} + H_{ph} + H_{e\ell-ph}$ , for normal metals which is valid for arbitrarily strong coupling and which involves errors only of order  $(m/M)^{\frac{1}{2}}$ . The Green's functions are defined by the thermal average of time-ordered operators for the electrons and phonons, respectively

$$G = -i < T\psi(1)\psi^{*}(2) > (1a)$$
  
$$D = -i < T\phi(1)\phi^{*}(2) > (1b)$$

Here  $\psi(r,t)$  is the wave field operator for electron quasi-particles and  $\phi(r,t)$ is the wave field operator for the phonons, the numerals 1 and 2 represent the space-time points  $(r_1, t_1)$  and  $(r_2, t_2)$ , and the brackets represent thermal averages over an ensemble.

Fourier transforms of the Green's functions for  $H_0 = H_{e\ell} + H_{ph}$  for non-interacting electrons and phonons are

$$G_{0}(P) = \frac{1}{\omega_{n} - \epsilon_{0}(k) + i\delta_{k}} \qquad (2a)$$
$$D_{0}(Q) = \left[\frac{1}{\nu_{n} - \omega_{0}(q) + i\delta} - \frac{1}{\nu_{n} + \omega_{0}(q) - i\delta}\right] \qquad (2b)$$

where  $P = (k\omega_n)$  and  $Q = (q,v_n)$  are four vectors,  $\varepsilon_0(k)$  is the bare electron quasi-particle energy referred to the Fermi surface,  $\omega_0(q)$  is the bare phonon frequency, and  $\omega_n$  and  $v_n$  are the Matsubara frequencies

$$\omega_n = (2n+1)\pi i k_{\rm B} T$$
$$\nu_n = 2n\pi i k_{\rm B} T \qquad (3)$$

for Fermi and Bose particles, respectively. Here  $k_{\rm B}$  is Boltzmann's constant and T is the absolute temperature.

As a result of the electron-phonon interaction,  $H_{\rm ph}$ , both electron and phonon energies are renormalized. The renormalized propagators, G and D, can be given by a sum over Feynman diagrams, each of which represents a term in the perturbation expansion. I shall use light lines to represent the bare propagators,  $G_0$  and  $D_0$ , heavy lines for the renormalized propagators G and D, straight lines for the electrons, and curly lines for the phonons.

The electron-phonon interaction is described by the vertex



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which represents the scattering of an electron or hole by the emission or adsorption of a phonon or the creation of an electron and hole by the absorption of a phonon by an electron in the Fermi sea. Migdal showed that renormalization of the vertex represents only a small correction, of order  $(m/M)^{\frac{1}{2}}$ , a result in accord with the Born-Oppenheimer adiabatic approximation. If terms of this order are neglected, the electron and phonon self-energy corrections are given by the lowest order diagrams, provided that fully renormalized propagators are used in these diagrams.

The electron self-energy  $\Sigma(P)$  in the Dyson equation:

 $G(P) \equiv G_0(P) + G_0(P)\Sigma(P)G(P) \quad (4$ 

is given by the diagram

$$\Sigma(P) = (a) \qquad (5)$$

The phonon self-energy,  $\pi(Q)$ , defined by

$$D(Q) = D_0(Q) + D_0(Q)\pi(Q)D(Q)$$
 (6)

is given by



Since to order  $(m/M)^{\frac{1}{2}}$  one can use an unrenormalized vertex function  $\alpha = \alpha_0$ , the Dyson equations form a closed system such that both  $\Sigma(P)$  and  $\pi(Q)$  can be determined. The phonon self-energy,  $\pi(Q)$ , gives only a small renormalization of the phonon frequencies. As to the electrons, Migdal noted that we are interested in states k very close to  $k_{\rm F}$ , so that to a close approximation  $\Sigma(k,\omega)$  depends only on the frequency. For an isotropic system,

$$\Sigma(k,\omega) \simeq \Sigma(k_{\rm F},\omega) \equiv \Sigma(\omega)$$
 (7)

The renormalized electron quasi-particle energy,  $\omega_k$ , is then given by a root of

$$\epsilon(k) \equiv \omega_k \equiv \epsilon_0(k) + \Sigma(\omega_k) \qquad (8)$$

In the thermal Green's function formalism, one may make an analytic continuation from the imaginary frequencies,  $\omega_n$ , to the real  $\omega$  axis to determine  $\Sigma(\omega)$ . Although  $\Sigma(\omega)$  is small compared with the Fermi energy,  $E_{\rm F}$ , it changes rapidly with energy and so can affect the density of states at the Fermi surface and thus the low-temperature electronic specific heat. The mass renormalization factor  $m^*/m$ , at the Fermi surface may be expressed in terms of a parameter  $\lambda$ :

$$m^*/m = Z(k_{\mathbf{F}}) = 1 + \lambda = (d\epsilon_0/dk)_{\mathbf{F}}/(d\epsilon/dk)_{\mathbf{F}} \quad (9)$$

In modern notation, the expression for  $\lambda$  is

$$\lambda = 2 \int_{0}^{\infty} d\omega \, \frac{\alpha^{2}(\omega) F(\omega)}{\omega} \qquad (10)$$

where  $F(\omega)$  is the density of phonon states in energy and  $\alpha^2(\omega)$  is the square of the electron-phonon coupling constant averaged over polarization directions of the phonons. Note that  $\lambda$  is always positive so that the Fermi surface is stable if the lattice is stable. Values of  $\lambda$  for various metals range from about 0.5 to 1.5. The parameter  $\lambda$  corresponds roughly to the  $N(0)V_{\rm ph}$ of the Bardeen-Cooper-Schrieffer (BCS) theory (20). Here N(0) is the density of states of one spin at the Fermi surface and  $V_{\rm ph}$  is an average of the electron-phonon interaction potential [see (1) and (20)].

# Nambu-Eliashberg Theory for Superconductors

Migdal's theory has important consequences that have been verified experimentally for normal metals, but gave no clue as to the origin of superconductivity. After the introduction of the BCS theory, Gor'kov showed that pairing could be introduced through the anomalous Green's function

$$F(P) = -i < T\psi \uparrow \psi \downarrow >$$
 (11)

Nambu showed that both types of Green's functions can be conveniently included with use of a spinor notation

$$\Psi = \begin{pmatrix} \psi \uparrow (r,t) \\ \psi \downarrow (r,t) \end{pmatrix}$$
(12)

where  $\psi \uparrow$  and  $\psi \downarrow$  are, respectively, wave field operators for up-spin and downspin electrons and a matrix Green's function with components

$$\tilde{G}_{\alpha\beta} = -i < T \Psi_{\alpha} \Psi_{\beta}^{+} > \qquad (13)$$

Thus  $G_{11}$  and  $G_{22}$  are, respectively, the single-particle Green's functions for

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Fig. 1 (left). Schematic diagram illustrating tunneling from a normal metal into a superconductor near  $T = 0^{\circ}$ K. Shown in the lower part of the diagram is the uniform density of states in energy of electrons in the normal metal, with the occupied states shifted by an energy eV



cupied states shifted by an energy eVfrom an applied voltage V across the junction. The upper part of the diagram shows the density of states in energy in the superconductor, with an energy gap  $2\Delta$ . The effect of an increment of voltage  $\delta V$  giving an energy change  $\delta \omega$  is to allow tunneling from states in the range  $\delta \omega$ . Since the tunneling probability is proportional to the density of states  $N_s(\omega)$ , the increment in current  $\delta I$  is proportional to  $N_s(\omega)\delta V$ . Fig. 2 (right). Conductance of a lead-magnesium junction as a function of the applied voltage [from (26)]. [Courtesy of the American Institute of Physics. New York]

up-spin and down-spin particles and  $G_{12} = G_{21}^* = F(P)$  is the anomalous Green's function of Gor'kov.

There are two self-energies,  $\Sigma_1$  and  $\Sigma_2$ , defined by the matrix

$$\widetilde{\Sigma} = \begin{pmatrix} \Sigma_1 & \Sigma_2 \\ \Sigma_2^* & \Sigma_1 \end{pmatrix}$$
(14)

Eliashberg noted that one can describe superconductors to the same accuracy as normal metals if one calculates the self-energies with the same diagrams that Migdal used, but with Nambu matrix propagators in place of the usual normal state Green's functions. The matrix equation for  $\tilde{G}$  is

$$\widetilde{G} = \widetilde{G}_0 + \widetilde{G}_0 \widetilde{\Sigma} \widetilde{G}$$
(15)

The matrix equation for  $\tilde{\Sigma}$  yields a pair of coupled integral equations for  $\Sigma_1$ and  $\Sigma_2$ . Again  $\Sigma_1$  and  $\Sigma_2$  depend mainly on the frequency and are essentially independent of the momentum variables. Following Nambu (15), one may define a renormalization factor  $Z_s(\omega)$  and a pair potential,  $\Delta(\omega)$ , for isotropic systems through the equations:

$$\omega Z_{s}(\omega) = \omega + \Sigma_{1}(\omega) \qquad (16)$$
  
$$\Delta(\omega) = \Sigma_{2}(\omega)/Z_{s}(\omega) \qquad (17)$$

Both  $Z_s$  and  $\Delta$  can be complex and include quasi-particle lifetime effects. Eliashberg derived coupled nonlinear integral equations for  $Z_s(\omega)$  and  $\Delta(\omega)$ which involve the electron-phonon interaction in the function  $\alpha^2(\omega)F(\omega)$ .

The Eliashberg equations have been used with great success to calculate the

properties of strongly coupled superconductors for which the frequency dependence of Z and  $\Delta$  is important. They reduce to the BCS theory and to the nearly equivalent theory of Bogoliubov (23) based on the principle of "compensation of dangerous diagrams" when the coupling is weak. By weak coupling I mean that the significant phonon frequencies are very large compared with  $k_{\rm B}T_{\rm c}$ , so that  $\Delta(\omega)$  can be regarded as a constant independent of frequency in the important range of energies extending to at most a few  $k_{\rm B}T_{\rm e}$ . In weak coupling one may also neglect the difference in quasi-particle energy renormalization and assume that  $Z_{\rm s} = Z_{\rm n}$ .

The first solutions of the Eliashberg equations were obtained by Morel and Anderson (24) for an Einstein frequency spectrum. Coulomb interactions were included, following Bogoliubov, by introducing a parameter  $\mu^*$  which renormalizes the screened Coulomb interaction to the same energy range as the phonon interaction. In weak coupling,  $N(0)V = \lambda - \mu^*$ . Morel and And erson estimated  $\lambda$  from electronic specific heat data and  $\mu^*$  from the electron density and thus the transition temperatures,  $T_c$ , for a number of metals. Order-of-magnitude agreement with experiment was found. Later work, based in large part on tunneling data, has yielded precise information on the electron-phonon interaction for both weak and strongly coupled superconductors.

### Analysis of Tunneling Data

From the voltage dependence of the tunneling current between a normal metal and a superconductor one can derive  $\Delta(\omega)$  and thus get direct information about the Green's function for electrons in the superconductor. It is possible to go further and derive empirically from tunneling data the electron-phonon coupling,  $\alpha^2(\omega)F(\omega)$ , as a function of energy. That electron tunneling should provide a powerful method for investigating the energy gap in superconductors was suggested by I. Giaever (25), and he first observed the effect in the spring of 1960.

The principle of the method is illustrated in Fig. 1. At very low temperatures, the derivative of the tunneling current I with respect to voltage V is proportional to the density of states in energy in the superconductor. Thus the ratio of the density of states in the metal in the superconducting phase,  $N_{\rm s}$ , to that of the same metal in the normal phase,  $N_{\rm n}$ , at an energy eV(e is the electronic charge) above the Fermi surface is given by

$$\frac{N_{\rm s}(eV)}{N_{\rm n}} = \frac{(dI/dV)_{\rm ns}}{(dI/dV)_{\rm nn}} \qquad (18)$$

The normal density is essentially independent of energy in the range involved (a few millielectron volts). In weak-coupling superconductors, for a voltage V and energy  $\omega = eV$ ,

$$\frac{N_{s}(\omega)}{N_{n}} = \frac{\omega}{(\omega^{2} - \Delta^{2})^{\frac{1}{2}}}$$
(19)

As  $T \to 0^{\circ}$ K, no current flows between the normal metal and the superconductor until the applied voltage reaches  $\Delta/e$ , when there is a sharp rise in dI/dV followed by a drop. This is illustrated in Fig. 2 for the case of lead.

The first experiments of Giaever were on aluminum, which is a weakcoupling superconductor. Good agreement was found between theory and experiment. In later measurements on tunneling into lead, a strongly coupled superconductor, Giaever *et al.* (26) observed anomalies in the density of states that appeared to be associated with phonons, as shown in Fig. 2. These results were confirmed by more complete and accurate tunneling data on lead by Rowell *et al.* (27).

In the meantime, in the summer of 1961, Schrieffer, working with a group engaged in developing methods for computer control using graphical display methods, had derived numerical solutions of the Eliashberg equations (28). He and his co-workers calculated

the complex  $\Delta(\omega)$  for a Debye frequency spectrum. Later, at the University of Pennsylvania, he, together with D. J. Scalapino and J. W. Wilkins (29), continued work on the problem with a view to explaining the observed anomalies on lead. They showed that for the general case of a complex  $\Delta(\omega)$ 

$$\frac{(dI/dV)_{\rm ns}}{(dI/dV)_{\rm nn}} = \frac{N_{\rm s}(\omega)}{N_{\rm n}} = Re \left\{ \frac{\omega}{[\omega^2 - \Delta^2(\omega)^{\frac{1}{2}}]} \right\}$$
(20)

where Re represents the real part. From measurements of the ratio over the complete range of voltages, one can use the Kramers-Krönig relation to obtain both the real and imaginary parts of  $\Delta(\omega) = \Delta_1(\omega) + i\Delta_2(\omega)$ . From analysis of the data, one can obtain the Green's functions which in turn can be used to calculate the various thermal and transport properties of superconductors. This has been done with great success, even for such strongly coupled superconductors as lead and mercury.

For lead, Schrieffer et al. (29) used a phonon spectrum consisting of two Lorentzian peaks, one for transverse waves and one for longitudinal waves, and obtained a good fit to the experimental data for  $T \ll T_c$ . The calculations were extended up to  $T_c$  for lead, mercury, and aluminum by Scalapino et al. (30), who also found good agreement with the experiment.

In the analysis of tunneling data, one would like to find a phonon interaction spectrum,  $\alpha^2(\omega)F(\omega)$ , and a Coulomb interaction parameter,  $\mu^*$ , which, when inserted into the Eliashberg equations, will yield a solution consistent with the tunneling data. W. L. McMillan (31) devised a computer program such that one could work backwards and derive  $\alpha^2(\omega)F(\omega)$ and  $\mu^*$  directly from the tunneling data. His program has been widely used since then and has been applied to a number of superconducting metals and alloys, including aluminum, lead, tin, the transition elements tantalum and niobium, a rare earth, lanthanum, and the compound Nb<sub>3</sub>Sn. In all cases it has been found that the phonon mechanism is dominant with reasonable values of  $\mu^*$ . Peaks in the phonon spectrum agree with peaks in the phonon density of states as found from neutron scattering data, as shown in Fig. 3 for the case of lead. Figure 4 shows the real and imaginary parts of  $\Delta(\omega)$  for lead as derived from tunneling data.

One can go further and calculate the various thermodynamic and other properties. Good agreement with ex-28 SEPTEMBER 1973

periment is found for strongly coupled superconductors even when there are significant deviations from the weak coupling limits. For example, the weakcoupling BCS expression for the condensation energy at  $T = 0^{\circ}$ K is

$$E_{\rm BCS} \equiv \frac{1}{2}N(0)Z_{\rm n}\Delta_0^2$$
 (21)

where  $N(0)Z_n$  is the phonon-enhanced density of states and  $\Delta_0$  is the gap parameter at  $T = 0^{\circ}$ K. The theoretical expression with  $Z_s(\omega)$  and  $\Delta(\omega)$  derived from tunneling data, again for the case of lead, gives (31, 32)

$$E_{\rm theor} = 0.78 \, E_{\rm BCS} \tag{22}$$



Fig. 3 (left). Density of states versus energy for lead. (Solid line) Calculated by Schrieffer et al. (29); (long dashed line) observed from tunneling; (short dashed line) BCS weak-coupling theory. Fig. 4 (right). Real and imaginary parts of  $\Delta(\omega) =$  $\Delta_1(\omega) + i\Delta_2(\omega)$  versus energy for lead [after McMillan and Rowell (31)]. [Courtesy of Marcel Dekker, Inc., New York]



Fig. 5. Comparison of  $\alpha^2 F$  for lead derived from tunneling data with phonon density of states from neutron scattering data of Stedman et al. (39).





Fig. 6 (left). A plot of  $\alpha^2 F$  versus energy for indium [after McMillan and Rowell (31)]. [Courtesy of Marcel Dekker, Inc., New York] Fig. 7 (right). A plot of

 $\alpha^2 F$  versus energy for lanthanum [after Lou and Tomasch (33)]. [Courtesy of the American Institute of Physics, New York]

in excellent agreement with the experimental value

$$E_{\rm exp} = (0.76 \pm 0.02) E_{\rm BCS}$$
 (23)

In Figs. 5-8 are shown other examples of  $\alpha^2(\omega)F(\omega)$  derived from tunneling data for lead, indium (31), lanthanum (33), and Nb<sub>3</sub>Sn (34). In all cases the results are completely consistent with the phonon mechanism. Coulomb interactions play only a minor role, with  $\mu^*$  varying only slowly from one metal to another, and generally in the range 0.1 to 0.2.

As a further check, it is possible to derive the phonon density of states,  $F(\omega)$ , from neutron scattering data and use pseudopotential theory to calculate the electron-phonon interaction parameter  $\alpha_{q}(\omega)$ . From these values, one can use the Eliashberg equations to calculate  $Z_s(\omega)$  and  $\Delta(\omega)$  and the various superconducting properties, including the transition temperature,  $T_{c}$ . Extensive calculations of this sort have been made by J. P. Carbotte and his co-workers (35) for several of the simpler metals and alloys. For example, for the gap edge,  $\Delta_0$ , in aluminum at  $T = 0^{\circ}$ K they find 0.19 millielectron volt as compared with an experimental value of 0.17. The corresponding values for lead are 1.49 millielectron volts from theory as compared with 1.35 millielectron volts from experiment. These are essentially first-principles calculations and give convincing evidence that the theory as formulated is essentially correct. Calculations made for a number of other metals and alloys give similar good agreement.

### Conclusions

In this talk I have traced how our understanding of the role of electronphonon interactions in superconductivity has developed from a concept to a precise quantitative theory. The selfenergy and pair potential, and thus the Green's functions, can be derived either empirically from tunneling data or directly from microscopic theory with use of the Eliashberg equations. Physicists, both experimental and theoretical, from different parts of the world have contributed importantly to these developments.

All evidence indicates that the electron-phonon interaction is the dominant mechanism in the cases studied so far, which include many simple metals, transition metals, a rare earth, and various alloys and compounds. Ex-



Fig. 8. A plot of  $\alpha^2 F$  versus energy for Nb<sub>3</sub>Sn [after Shen (34)]. [Courtesy of the American Institute of Physics, New York]

cept possibly for the metallic form of hydrogen (36), which is presumed to exist at very high pressures, it is unlikely that the phonon mechanism will vield substantially higher transition temperatures than the present maximum of about 21°K for a compound of niobium, aluminum, and germanium.

Other mechanisms have been suggested for obtaining higher transition temperatures. One of these is to get an effective attractive interaction between electrons from an exchange of virtual excitons, or electron-hole pairs. This requires a semiconductor in close proximity to the metal in a layer or sandwich structure. At present, one cannot say whether or not such structures are feasible and in no case has the exciton mechanism been shown to exist. As Ginzburg (37) has emphasized, this problem (as well as other proposed mechanisms) deserves study until a definite answer can be found.

The pairing theory has had wide application to Fermi systems other than electrons in metals. For example, the theory has been used to account for many aspects of nuclear structure. It is thought that the nuclear matter in neutron stars is superfluid. Very recently, evidence has been found for a possible pairing transition in liquid <sup>3</sup>He at very low temperatures (38). Some of the concepts, such as that of a degenerate vacuum, have been used in the theory of elementary particles. Thus pairing seems to be a general phenomenon in Fermi systems.

The field of superconductivity is still a very active one in both basic science and applications. I hope that these lectures have given you some feeling for the accomplishments and the methods used.

#### References

- 1. J. R. Schrieffer, Science 180, 1243 (1973).
- L. N. Cooper, *ibid.* 181, 908 (1973).
   D. Shoenberg, Superconductivity (Cambridge)

Univ. Press, Cambridge, 1938; ed. 2, 1951). F. London, Proc. Roy. Soc. Ser. A Math. Univ. Press, Cambridge, 1938; ed. 2, 1951).
4. F. London, Proc. Roy. Soc. Ser. A Math. Phys. Sci. 152, 24 (1935).
5. J. Bardeen, Phys. Rev. 59, 928A (1941).
6. C. A. Reynolds, B. Serin, W. H. Wright, L. B. Nesbitt, *ibid.* 78, 487 (1950).
7. E. Maxwell, *ibid.*, p. 477.
8. H. Fröhlich, *ibid.* 79, 845 (1950); Proc. Roy.
6. C. Macher Phys. Sci. 213, 201 (1952).

- Soc. Ser. A Math. Phys. Sci. 213, 291 (1952).
   F. London, Superfluids (Wiley, New York, 1950).
- 1950). For recent review articles with references, see the chapters by D. J. Scalapino (pp. 449-560) and by W. L. McMillan and J. M. Rowell (561-613) in *Superconductivity*, R. D. Parks, Ed. (Dekker, New York, 1969), vol. 1. An 10. Ed. (Dekker, New York, 1969), vol. 1. An excellent reference for the theory and earlier experimental work is J. R. Schrieffer, *Theory* of *Superconductivity* (Benjamin, New York, 1964). The lecture presented here is based in part on a chapter by the author in Co-operative Phenomena, H. Haken and M. Wagner, Eds. (Springer-Verlag, New Y in press). York. in press).
- in press). See A. A. Abrikosov, L. P. Gor'kov, I. E. Dzyałoshinski, Methods of Quantum Field Theory in Statistical Physics (Prentice-Hall, Englewood Cliffs, NJ., 1963). The first ap-plication of the Green's function methods of superconductivity theory is found in L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 34, 735 (1958) [English translation in Sov. Phys. JETP 7, 505 (1959)] 11. See A. 505 (1958)]. 12. L. P. Kadanoff and P. C. Martin, Phys. Rev.
- L. P. Kadanoff and P. C. Martin, Phys. Rev. 124, 670 (1961).
   A. B. Migdal, Zh. Eksp. Teor. Fiz. 34, 1438 (1958) [English translation in Sov. Phys. JETP 7, 996 (1958)].
   G. M. Eliashberg, Zh. Eksp. Teor. Fiz. 38, 966 (1960) [English translation in Sov. Phys. JETP 11, 606 (1960).
- JETP 11, 696 (1960)].
- JETP 11, 696 (1960)].
  15. Y. Nambu, Phys. Rev. 117, 648 (1960).
  16. J. Bardeen, ibid. 79, 167 (1950); ibid. 80, 567 (1950); ibid. 81, 829 (1951).
  17. ——, Rev, Mod. Phys. 23, 261 (1951).
  18. M. R. Schafroth, Helv. Phys. Acta 24, 645 (1951); Nuovo Cimento 9, 291 (1952).
  10. J. Berdeen and D. Binor, Phys. Rev. 99

- 19. J. Bardeen and D. Pines, Phys. Rev. 99, 1140 (1955).

- 1140 (1955).
   J. Bardeen, L. N Cooper, J. R. Schrieffer, *ibid.* 108, 1175 (1957).
   A. B. Pippard, Proc. Roy. Soc. Ser. A Math. Phys. Sci. 216, 547 (1953).
   J. Bardeen, in Encyclopedia of Physics, S. Flugge, Ed. (Springer-Verlag, Berlin, 1956), vol. 15, p. 274.
   See N. N. Bogoliubov, V. V. Tolmachev, D. V. Shirkov, A New Method in the Theory of Superconductivity (Consultants Bureau, New York, 1959).
- New York, 1959). 24. P. Morel and P. W. Anderson, *Phys. Rev.* 125, 1263 (1962).
- L. Giaever, Phys. Rev. Lett. 5, 147 (1960);
   *ibid.*, p. 464.
   H. R. Hart, K. Megerle, Phys. Rev.

- —, H. R. Hart, K. Megerle, *Phys. Rev.* 126, 941 (1962).
   J. M. Rowell, P. W. Anderson, D. E. Thomas, *Phys. Rev. Lett.* 10, 334 (1963).
   G. J. Culler, B. D. Fried, R. W. Huff, J. R. Schrieffer, *ibid.* 8, 339 (1962).
   J. R. Schrieffer, D. J. Scalapino, J. W. Wilkins, *ibid.* 10, 336 (1963); D. J. Scalapino, J. R. Schrieffer, J. W. Wilkins, *Phys. Rev.* 148 263 (1966).

- Wilkins, Did. & Sob (1997) E. F. W. Wilkins, Phys. Rev. 148, 263 (1966).
  30. D. J. Scalapino, Y. Wada, J. C. Swihart, Phys. Rev. Lett. 14, 102 (1965); *ibid.*, p. 106.
  31. See W. L. McMillan and J. M. Rowell in (10).
  32. G. M. Eliashberg, Zh. Eksp. Teor. Fiz. 43, 1005 (1962) [English translation in Sov. Phys. JETP 16, 780 (1963)].
  33. L. F. Lou and W. J. Tomasch, Phys. Rev. Lett. 29, 858 (1972).
  34. L. Y. L. Shen, *ibid.* 29, 1082 (1972).
  35. J. P. Carbotte, Superconductivity, P. R. Wallace, Ed. (Gordon & Breach, New York, 1969), vol. 1, p. 491; and R. C. Dynes, Phys. Rev. 172, 476 (1968); C. R. Leavens and J. P. Carbotte, Can. J. Phys. 49, 724 (1971).
  36. N. W. Ashcroft, Phys. Rev. Lett. 21, 1748 (1968).
- (1968). 37. See V. L. Ginzburg, Annu. Rev. Mater. Sci.
- 663 (1972).
   D. D. Osheroff, W. J. Gully, R. C. Richardson, D. M. Lee, *Phys. Rev. Lett.* 29, 1621
- 1972).
- figure is derived from data of R. 39. This Stedman, L. Almquist, and G. Nilsson in-cluded in the chapter by D. J. Scalapino, in *Superconductivity*, R. D. Parks, Ed. (Dekker, New York, 1969), vol. 1, p. 511.

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