

MICROSCOPIC THEORIES OF SUPERCONDUCTIVITY

IV. 1 The BCS Theory

This theory was proposed by Bardeen, Cooper, and Schriefer in 1957 ¹ and is briefly reviewed in the following sections. The theory based on the idea of Cooper ² who showed, in 1956, that the effective attraction between electrons near the Fermi surface, due to electron-phonon interaction, must lead to bound pairs of electrons

IV.1.1 Instability of the Normal State in the Presence of an Attractive Interaction.

It has been observed 3 that the critical temperature of superconductors $^{\rm T}_{\rm c}$ varies with isotopic mass M. The experimental results may be fitted by a relation of the form

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¹Bardeen, J., L.N. Cooper and J.R. Schrieffer, "Theory of Superconductivity" Phys. Rev. , 108, 1175 (1957)

²Cooper, L.N., Bound Electron Pairs in a Degenerate Fermi Gas Phys. Rev., 104, 1189 (1956)

Maxwell, E., Isotope Effect in the Superconductivity of Mercury Phys. Rev., 78, 477 (1950); Reynolds, C.A., et al "Superconductivity of Isotopes of Mercury Phys. Rev., 78, 487 (1950)

(with the exception of several transition group which the isotope effect is much smaller or nearly absent)

The fact that the isotope effect is $M^{1/2}$ leads one to consider electron-phonon interaction as the mechanism responsible for superconductivity.

The indirect electron-electron interaction via phonon field can be written as 4

$$H'' = D^{2} \sum_{g \ kk'} \frac{\omega_{g}}{(\varepsilon_{k} - \varepsilon_{k-g})^{2} - \omega_{g}^{2}} C^{\dagger}_{k+g \ k'} C^{\dagger}_{k-g \ k} (4.2)$$

where

D = the interaction constant

W = energy of a phonon

 \mathcal{E}_{k} = energy of an electron.

This interaction is shown in Fig. 7.

The electron-electron interaction (4.2) is attractive (negative) for excitation energies $|\mathcal{E}_{k\pm g} - \mathcal{E}_k| < \mathcal{C}_{k}$; and repulsive otherwise. The screened Coulomb repulsion is less important if the interaction constant D is sufficiently large.

Assume for simplicity that in superconducting state the attraction is dominant when

$$\mathcal{E}_{F} - \mathcal{W}_{D} \langle \mathcal{E}_{K} ; \mathcal{E}_{K \pm g} \langle \mathcal{E}_{F} + \mathcal{W}_{D} ; \qquad (4.3)$$

where wo is Debye energy.

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⁴Kittel, C., <u>Quantum Theory of Solids</u>, John Wiley& Sons, Inc. 1967, p.152

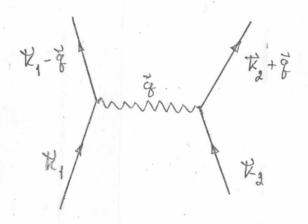


Fig. 7 Electron-Electron interaction through the lattice phonon

The repulsion region of (4.2) is of little interest, so it can be droped from the Hamiltonian and one can write (4.2) in the form

$$H'' = -V \sum_{q} \sum_{kk'} c^{\dagger}_{k'+q} c_{k'} c^{\dagger}_{k-q} c_{k}, \qquad (4.4)$$

where the summation over q is only in the region (4.3) and V is taken to be a positive constant.

The first suggestion that unusual properties would result from attractive interactions in a Fermi gas was made by Cooper⁵, who proved that the Fermi sea is unstable with respect to the formation of bound pairs.

The instability can be understood by considering two particular electrons of coordinates \vec{x}_1 and \vec{x}_2 . Consider only states where the center of gravity of the pair is at rest; the wave function of the two electrons, in unit volume, χ , is then only a function of $\vec{x}_1 - \vec{x}_2$.

Expand X in plane waves

$$\chi_{(x_1-x_2)} = \sum_{k} g_k e^{i\chi_*(x_1-x_2)}$$
; (4.5)

 g_{k} is the probability amplitude for finding one electron in the plane wave state of momentum $\hbar \vec{k}$ and the other electron in the state $-\hbar \vec{k}$.

Including the electron-electron interaction (4.4) in the Hamiltonian of the problem, we get

⁵ see Ref. 2

$$H = \frac{1}{2m} (p_1^2 + p_2^2) + H'' = \frac{p^2}{m} + H''$$

Now if > is the eigenvalue,

so that on taking a matrix element we have the secular equation; with $\mathcal{E}_{k} = k^{2}/m$,

$$(\xi_{k}-\lambda)g_{k} + \sum_{k'} g_{k'} \langle k,-k|H''|k',-k' \rangle = 0$$
 (4.6)
where $k = k'+q$; $-k = -k'-q$

If $f(\mathcal{E})$ is the density of two-electron states k, -k per unit energy range, the secular equation becomes

In agreement with (4.4) , we take, with V positive

for energy range $\pm \omega_{\rm D}$ of one electron relative to the other, outside this range the interaction is zero. Let us suppose the packet (4.5) is made up of one electron states above the top of the Fermi sea between \mathcal{E}_F and $\mathcal{E}_F + \omega_{\rm D}$, or between \mathbf{k}_F and $\mathbf{k}_{\rm m}$, where $\mathbf{k}_{\rm m}$ is defined by

$$\frac{1}{2m}(k_m^2 - k_F^2) = \mathcal{E}_m - \mathcal{E}_F = \omega_D$$

Then the secular equation becomes

$$(\xi-\lambda)g(\xi) = V \int_{2\xi_F}^{2\xi_m} d\xi' g(\xi') g(\xi') = G \qquad (4.7)$$

$$G = \text{constant, independent of } \xi;$$

$$1 - V \int_{2\xi_F}^{2\xi_m} d\xi' \frac{f(\xi')}{\xi' - \lambda} = 0 \qquad (4.8)$$

where the limits refer to the pair. Over the small energy range involved one may replace $f(\epsilon')$ by the constant f, the value at the Fermi level, so that

$$\frac{1}{P_F V} = \int_{2\mathcal{E}_F}^{2\mathcal{E}_m} \frac{d\varepsilon'}{\varepsilon' - \lambda} = \lim_{\Delta \mathcal{E}_m - \lambda} \frac{2\mathcal{E}_m - \lambda}{2\mathcal{E}_F - \lambda}$$

where we have written the lowest eigenvalue \ as

$$\lambda_o = 2\mathcal{E}_F - \Delta \tag{4.9}$$

Then

$$\Delta = \frac{2 cob}{e^{VP_F V} - 1} \tag{4.10}$$

This is the binding energy of the pair with respect to the Fermi level. We have thus found that for V positive (attractive interaction) and weak interaction limit, $\int_F V \ll 1$, we lower the energy of the system by exciting a pair of electrons above the Fermi level; therefore the Fermi sea is unstable.

IV.1.2 <u>Self-Consistent Solution for the BCS Hamiltonian</u> 6

The Hamiltonian which describes a superconducting state is in the form

Bogoliubov, N. "A New Method in the Theory of Superconductivity I" JETP, 7, 41 (1958)

$$H = \sum_{k\sigma} \epsilon_{k} c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{kk'} V_{kk'} c_{k'4}^{\dagger} c_{-k'4}^{\dagger} c_{-kb} c_{k4}$$
 (4.11)

If we write

the Hamiltonian becomes

$$H = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma} - \sum_{k\sigma} (\Delta_{k\sigma} c_{k\sigma}^{\dagger} c_{k\sigma}^{\dagger} + \Delta_{k\sigma}^{\dagger} c_{k\sigma}^{\dagger}) (4.12)$$

where we neglect the terms of products of four Fermi- operators (Hartree Fock approximation)

Next we transforms Eq. (4.12) by using the Bogoliubov transformation defined as followings,

$$C_{k1} = U_{k} Y_{k0} + U_{k}^{*} Y_{k1}^{+}$$

$$C_{-kt}^{+} = -U_{k} Y_{k0} + U_{k}^{*} Y_{k1}^{+}$$
(4.13)

where γ_k are Fermion operators, and where the coefficients U_k , V_k are chosen to make the Hamiltonian diagonal, that is, they are chosen to make the coefficients of $\gamma_{ko}^{\dagger} \gamma_{kl}^{\dagger}$ and $\gamma_{kl}^{\dagger} \gamma_{ko}^{\dagger}$ in the Hamiltonian vanish. This latter condition requires that

$$2\mathcal{E}_{k}U_{k}v_{k} + \Delta_{k}V_{k}^{2} - \Delta_{k}^{\dagger}U_{k}^{2} = 0 \qquad (4.14)$$

Since the Eq. (4.13) represent a canonical transformation, the commutation relations between the γ 's being the same as those between the C's, we have the further constraints on the constants U_k , V_k that

$$|U_k|^2 + |V_k|^2 = 1$$
 (4.15)

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Eq. (4.14) and (4.15) are sufficient to determine V_k and V_k in terms of Δ . From the imaginary part of eq. (4.14) we find that $\Delta V/U$ is real, and hence eq. (4.14) can be written

$$2 \in_{k} \left| U_{k} U_{k} \right| + \left| \Delta_{k} \left| \left| \left| U_{k} \right|^{2} - \left| V_{k} \right|^{2} \right| = 0$$

From this and eq. (4.15) we then find

$$|U_{k}|^{2} = \frac{1}{2}(1 + \varepsilon_{k}/\varepsilon_{k})$$

$$|U_{k}|^{2} = \frac{1}{2}(1 - \varepsilon_{k}/\varepsilon_{k})$$
(4.16)

where

$$E_k = (\epsilon_k^2 + |\Delta_k|^2)^{\frac{1}{2}}$$
 (4.17)

Now

$$H = \sum_{k} E_{k} (y_{ko}^{\dagger} y_{ko} + y_{kl}^{\dagger} y_{kl}) + \text{constant with no}$$
operators

(4.18)

Since the operators γ_{ko} , γ_{kl} obey the Fermi-Dirac commutation relations, this Hamiltonian describes independent fermions with excitation energies E_k .

The physical observed quantities are the statistical average,

so that

$$\langle \Delta_k \rangle = -\sum_{k'} V_{kk'} T_r \left[\exp(-\beta H) \left(C_{-kl} C_{kl} \right) \right] T_r \exp(-\beta H)$$

$$= -\sum_{k'} V_{kk'} T_r \left[\exp(-\beta H) \left(-V_k V_k \gamma_{ko}^{\dagger} \gamma_{ko} + V_k O_k^{\dagger} \gamma_{kl}^{\dagger} \gamma_{kl}^{\dagger} \right) \right]$$

$$= k' \sum_{k'} \left[\exp(-\beta H) \left(-V_k V_k \gamma_{ko}^{\dagger} \gamma_{ko} + V_k O_k^{\dagger} \gamma_{kl}^{\dagger} \gamma_{kl}^{\dagger} \right) \right]$$

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$$\Delta_{k} = -\sum_{k'} V_{kk'} \frac{\Delta_{k'}}{2E_{k'}} (1 - 2f_{CE_{k'}})$$
 (4.19)

where f(E) is the Fermi-Dirac distribution function,

$$f(E) = [E \times P (BE) + 1]^{-1}$$
 (4.20)

From eq. (4.19) and the assumption

= 0 otherwise,

one gets the equation for T

N(0) = density of state at Fermi level

Aluso one can get the gap parameter

$$\Delta (T) = 1.74 (1-T/T_c)^{1/2}$$
 (4.22)

Since the energy of an excitation is E_k , for the simple model we have been discussing there is a minimum energy required to create a new excitation, namely, \triangle . The new excitations are created in pairs, thus the minimum energy required to create excitation from the ground state is

$$E_g = 2\Delta$$

IV.1.3 The Green Function Method (T = 0)

The effective Hamiltonian

may be written in the form

$$H = \int [-(\Psi^{\dagger} \nabla^{2} \Psi) + \bigvee_{\alpha} (\Psi^{\dagger} (\Psi^{\dagger} \Psi) \Psi)] dV,$$

where $(\psi^{\dagger}\psi) = \psi^{\dagger}\psi_{d}$, and the particle field operators $\psi(\vec{r})$, $\psi^{\dagger}(\vec{r})$ in the Schrodinger representation satisfy the usual commutation relations

$$\left\{ \begin{array}{l} \psi(\vec{r}), \psi(\vec{r}') \\ \psi(\vec{r}), \psi(\vec{r}') \\ \end{array} \right\} = \left\{ \begin{array}{l} \psi(\vec{r}), \psi(\vec{r}') \\ \psi(\vec{r}), \psi(\vec{r}') \\ \end{array} \right\} = \left\{ \begin{array}{l} \psi(\vec{r}), \psi(\vec{r}') \\ \end{array} \right\} = 0$$

Next, we go over to the Heisenberg representation, in which the operators ψ^{\dagger} and ψ^{\dagger} depend on time and obey the Tollowing operator equations :

The propagator G(x,x) is defined by

⁷Abrikosov, A.A., L.R. Gorkov and I.Y. Dzyaloshinskii, Quantum Field Theoretical Methods In Statistical Physics, 2nd Ed., Pergamon Press, Oxford (1965) Chapter 7.

$$G_{\mu\beta}(x,x') = -i \langle T \{ \hat{\psi}_{(x)} \hat{\psi}_{\beta}^{\dagger}(x') \} \rangle$$
 (4.27)

where T is the Wick chronological operator and $\langle \cdot \cdot \cdot \cdot \rangle$ indicates an ensemble average over the ground state.

The anomalous Green's function is defined by

$$F(x,x) = e \qquad \langle T \left\{ \tilde{\psi}(x) \; \tilde{\psi}_{\rho}(x) \right\} \rangle$$

$$F_{\alpha\beta}^{\dagger}(x,x) = e \qquad \langle T \left\{ \tilde{\psi}_{\alpha}^{\dagger}(x) \; \tilde{\psi}_{\beta}^{\dagger}(x) \right\} \rangle$$

$$\left\{ T \left\{ \tilde{\psi}_{\alpha}^{\dagger}(x) \; \tilde{\psi}_{\beta}^{\dagger}(x) \right\} \rangle$$

$$\left\{ T \left\{ \tilde{\psi}_{\alpha}^{\dagger}(x) \; \tilde{\psi}_{\beta}^{\dagger}(x) \right\} \rangle$$

M = chemical potential (in our case M = Fermi energy)

The ensemble average over ground state means an N - particle ground state on the right and an N + 2 - particle (N - 2 - particle) ground state on the left for F^+ (F).

Since we are dealing with Heisenberg operators, we have, for any operator A, the relation

Also we have

$$-i \langle T \quad \widetilde{\Psi}_{a}(x) \quad \widetilde{\Psi}_{\beta}^{\dagger}(x) \rangle = -i \quad \widetilde{\Psi}_{a}(x) \quad \Psi_{\beta}^{\dagger}(x) \quad \Theta c t - t' \rangle$$
and
$$+i \quad \Psi_{\beta}(x) \quad \Psi_{a}(x) \quad \Theta c t - t' \rangle$$

$$= -\delta c t' - t' \rangle$$

$$= -\delta c t' - t' \rangle$$

So we can get the equation for G and F as following (assume that it is a homogeneous problem, G(x,x)) depends only on the coordinate difference x-x')

$$(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m})G_{(x-x')} - iVF_{(x-x')} F_{(x-x')}^{\dagger} = G_{(x-x')}$$

$$(i\frac{\partial}{\partial t} - \frac{\nabla^2}{2m} - 2\mu)F_{(x-x')} + iVF_{(x-x')}^{\dagger}G_{(x-x')} = 0$$

$$(4.29)$$

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$$F_{ab}^{\dagger}(o^{\dagger}) = e^{-ai\mu t} \langle N+2| \psi_{a}^{\dagger}(x) \psi_{b}^{\dagger}(x) | N \rangle$$

Finally, taking the Fourier components of these equations, we obtain

$$(\omega - P^{2}/2m) G_{c}\rho \omega - iV F_{cot})F_{c}\rho \omega = 1$$

$$(\omega + P^{2}/2m - 2\mu) F_{c}\rho \omega + iV F_{cot})G_{c}\rho \omega = 0$$
(4.30)

Since we measure energies relative to the Fermi level, we make the transformations

$$\omega' = \omega - u ; = \frac{p^2}{2m} - u = , (4.31)$$

to get

$$(cw - \S) G_{ipw} + iV F_{io} + F_{cpw} = 1$$

$$(cw + \S) F_{cpw} + iV F_{(o)} G_{cpw} = 0$$

$$(4.32)$$

(the prime on co has been dropped)

Solving (4.32), we obtain

$$G(\rho\omega) = \frac{\omega + 3}{\omega^2 - 3^2 - 4^2}.$$

$$F(\rho\omega) = \frac{-iVF(cot)}{\omega^2 - 3^2 - 4^2}.$$
where $\Delta^2 = V^2 |F(cot)|^2$
(4.34)

The positive pole of the propagator give the energy spectrum of the system, so that

$$E_{p} = \sqrt{3^2 + 4^2}$$
 (4.35)

This spectrum has a gap

$$\Delta_{o} = 2 \hbar \omega_{0} e^{-i/N},$$
 where
$$= V = V \frac{mP_{0}}{2\pi} = VN_{(0)},$$
 (4.36) which is the same as (4.23)

IV. 2 SMW Theory

Experimental investigations of the specific heats by Sung and Shen⁸ led a number of workers to postulate the existence of two energy gaps in transition metals as a mean of explaining their findings. Later, two gaps were observed in tunneling and other experiments by several workers⁹.

To take into account the two-band structure of the transition metals Suhl, Matthias and Walker 10 had proposed a two-band model of superconductivity (SMW theory) and it was shown that two energy gaps would we sult. If these two bands do not interact the problem is separable since each band can be treated individually. So superconductivity can result if either band possesses a mechanism giving pairing, in the BCS manner. Two transition temperatures, and two

Sung, C.C. and L.Y.L. Shen, The Specific Heat of Superconducting Transition Metals, Phys. Lett., 19, 101 (1965)

⁹Hafstrom, J.W., R.M. Rose and M.L.A. Mac Vicar, Phys. Lett.
30 A, 379 (1969); Hafstrom, J.W. and M.L.A. Mac Vicar, Phys. Rev.
B 2, 4511 (1970); Mac Vicar, M.L.A., and R.M. Rose, Phys. Lett.,
26 A, 510 (1968) and Tang, I.M., Phys. Lett., 35 A, 39 (1971)

¹⁰ Suhl, H., B.T. Matthias and L.R. Walker, "Bardeen-Cooper-Schrieffer Theory of Superconductivity in the Case of Overlaping Bands", Phys. Rev. Lett., 3, 552 (1959).

energy gaps, can result from such a model if both bands can form pairs. However, if the two bands interact, even if slightly, the lower transition temperature disappears 10.

To apply these ideas to transition metals, one must note that these metals have two bands; the d-band, which is narrow and hence the density of states at its Fermi surface is large, and the s-band, which is wide and hence the density of states at its Fermi surface is small. In the SMW model, which seems most appropriate to the transition metal superconductors, we find two energy gaps, $\triangle_{\rm S}$ and $\triangle_{\rm d}$, such that $\triangle_{\rm d} > \triangle_{\rm S}$, but only one transition temperature since there are non-zero interband interaction present.

It is important to note here that the two-band ideas do not smoothly go over to the one band model. In transition metals, measurements of mean free paths in the normal state are generally made by observing transport properties. This means that these measurements yield values for the electronic mean free path of the s-band, the lighter electrons. However, when a transition metal superconductor is analysed within the one-band model, the energy gap which is computed must be the larger of the two gaps, the d-gap. Hence it is not suitably to use values of the mean free path deduced from transport properties in conjunction with value of the energy gap deduced from properties of the superconductor, as these quantities do not belong to the same electrons.

The Hamiltonian of SMW theory is of the form

$$H = \sum_{ks} \epsilon_{ks} c_{ks}^{\dagger} c_{ks} + \sum_{ks} \epsilon_{kd} d_{ks}^{\dagger} d_{ks} - V_{ss} \sum_{kk'} c_{k\uparrow}^{\dagger} c_{-k\downarrow}^{\dagger} c_$$

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where \mathcal{E}_{ks} , \mathcal{E}_{kd} are s- and d- band kinetic energies, and \mathcal{E}_{ks} , and \mathcal{E}_{kd} are s- and d- band kinetic energies, and \mathcal{E}_{ks} , and \mathcal{E}_{kd} are the averaged interaction energies resulting from phonon emission and absorption by s-s, d-cl, and s-d processes, minus the corresponding shielded Coulomb interaction terms.

Assume, as in the BCS theory, that the summations extend only over \not E values corresponding to energies within a distance $\pm \hbar \omega$ of the Fermi surface. ($\hbar \omega$ is of the order of the maximum available phonon energy) SMW showed that for this model the energy spectrums are,

$$E_{ks} = (\epsilon_{ks}^2 + A^2)^{1/2},$$

$$E_{kd} = (\epsilon_{kd}^2 + B^2)$$
(4.38)

where the energy gaps

$$A = V_{sd} D + V_{ss} S$$

$$B = V_{sd} D + V_{sd} S$$

$$(4.39)$$

and

$$D = \frac{1}{2} \sum_{k} \sin \varphi_{k} \left[1 - 2 f_{d} \left(E_{kd} \right) \right] \qquad (4.40)$$

$$S = \frac{1}{2} \sum_{k} sin \Theta_{k} [1 - 2f_{S}(E_{ks})]$$
 (4.41)

The transition temperatures are given by the equation

$$k_{8}T_{c} = 1.14 \text{ for exp} \left\{ - \left[\frac{[N_{8}N_{A}V_{sd} + \frac{1}{4}(N_{d}V_{dd} - N_{8}V_{8S})^{2}]^{2}}{(V_{sd}^{2} - V_{88}V_{dd})N_{8}N_{d}} - \frac{\frac{1}{2}(N_{d}V_{dd} + N_{8}V_{8s})}{N_{8}N_{d}(V_{sd}^{2} - V_{88}V_{dd})} \right] \right\}$$

$$(4.42)$$

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where N_s , N_d are the densities of state in the s- and d- bands near the Fermi level.

The variation of energy gaps with temperature is shown schematically in the Fig. 8 .

The SMW model of superconductivity is however not generally accepted. The objections to the SMW model by most theoriest in the field centers on the question of what are the mechanisms responsible for the strong attraction between the s-electrons. Since the density of states of the s-band is very small at the Fermi surface, the interactions V_{ss} , V_{sd} , and V_{ds} must be very large. Otherwise $N_s V_{ss}$ in Eq. (4.42) can be neglected in comparision with the $N_d V_{dd}$ term. Thus we need $V_{ss} \gg V_{dd}$.

At the present time, none of the proposed interaction mechanism will lead to an interaction which will give $V_{\rm SS} > V_{\rm dd}$.

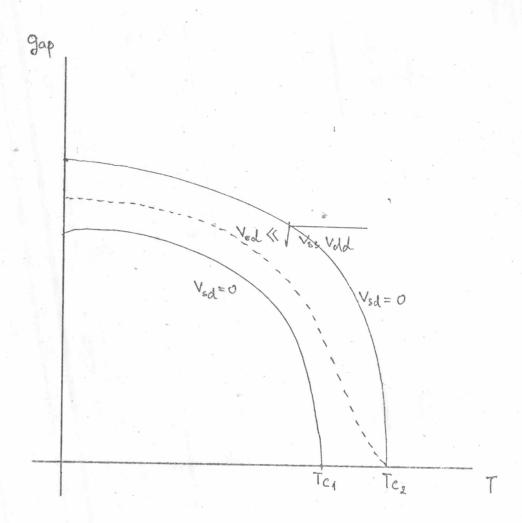


Fig. 8 Variation of Energy Gaps with Temperature

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