Superconducting properties of metals

LECTURE 1

Basic properties of the superconducting state. Thermodynamics of superconductors. Intermediate state. The London theory.

<u>*Preamble*</u> The classical Boltzmann statistics predicts that all the mechanical motions should die up at the temperature of absolute zero ($T = 0°K$). Hence, considering electrons in a metal as the gas or fluid of charged particles (the Drude model of metals) one would expect growing viscosity at low temperatures, and therefore, increasing electric resistivity of metals when temperature decreases to zero.

Dutch physicist Kamerling-Onnes, who managed to cool the samples down to and even below the liquid helium-4 temperature ($4°K$), decided to check this general prediction of the Boltzmann's statistics. He discovered in 1911 that the mercury resistance disappears suddenly at $4°K$. Soon after this the same property has been found for several other metals. The new phenomenon was called "superconductivity", and the metals having this property were called "superconductors".

General properties of superconductors

The temperature at which the resistance disappears is called <u>*critical temperature*</u>, T_c , it varies for the different superconducting materials. Historical curve of the critical temperature time dependence, T_c (t), is presented in Fig. 1 and demonstrates step-like development.

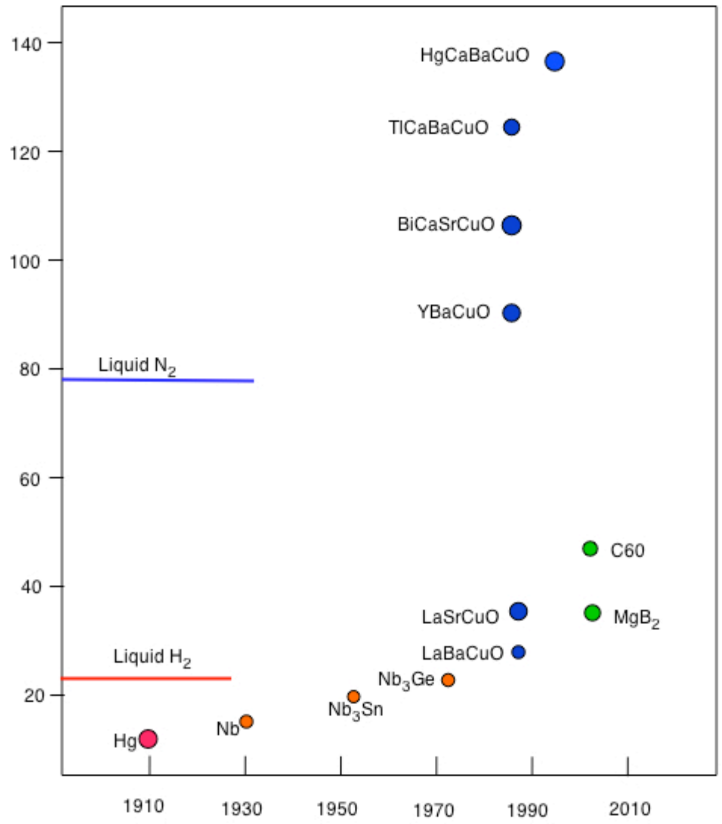

Fig. 1 *The history of experimental superconductivity.*

Nb_3Ge compound held the "title" of the highest T_c = 23 K material for about 15 years till the very end of the "common superconductors era" that lasted for 75 years and was characterized by an increase of

T_c from 4K to 23 K. The era ended with the famous discovery of the high superconducting temperature (T_c = 36 K), in cuprates by J.G. Bednorz and K.A. Müller in 1986, that was followed by an "explosive" increase of T_c by 100 K during the 7-year long course of discoveries, ended in so far highest T_c material HgCaBaCuO with T_c =136 K (April, 1993). The maximal critical temperature T_c = 9,25 K of all the single component metals has Nb, while the tungsten, W, has the smallest one T_c = 0,0154 K.

There are many examples of the practical hi-tech applications of the superconducting materials, the number of them would increase dramatically if/when their critical temperature will be increased up to room temperatures.

Phase diagram of the typical superconductor is sketched in Fig.2.

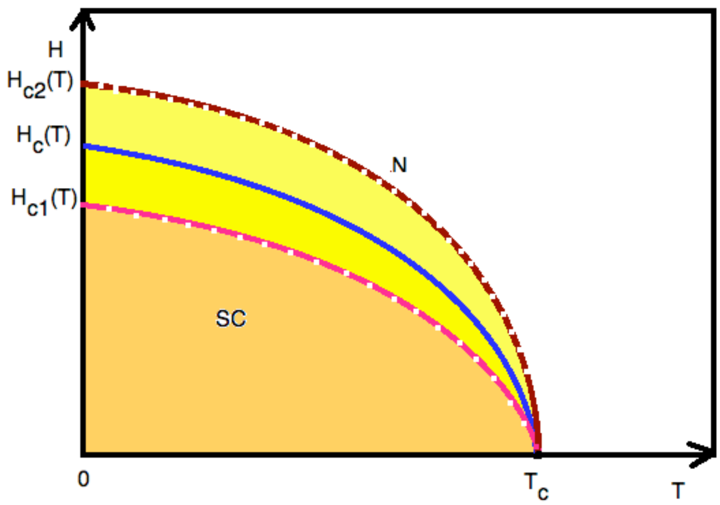

Fig.2 *Phase diagram of the typical superconductors: Type I (blue line); Type II (dashed lines).*

The superconductivity is destroyed by strong enough magnetic field (Kammerling-Onnes, 1914). It was established experimentally that *__the critical magnetic field__* $H_c(T)$ temperature dependence agrees well with the formula:

$$H_c(T) = H_c(0)[1 - (T/T_0)^2]. \qquad (1.1)$$

The breakdown of superconductivity also takes place when the critical current is applied, that according to *__the Silsbi rule__*, creates the magnetic field on the surface of superconductor equal to H_c.

One of the main properties of superconductors is *__the Meissner effect__* (Meissner and Oxenfield, 1933), which, as we shall see later in this course, is the workings of *__the Higgs mechanism__* in disguise. The superconducting metal expels magnetic field (which is less then H_c), so that in the bulk of the superconductor the magnetic field vanishes: $\boldsymbol{B} = 0$ (recall that the magnetic induction $\boldsymbol{B}$ is the average microscopic magnetic field). This is shown in the Fig. 3: *a* is the normal metal, *b* is the metal in the superconducting state. Some superconducting alloys behave in the magnetic field in a more complex way, in particular, the Meissner effect can be incomplete.

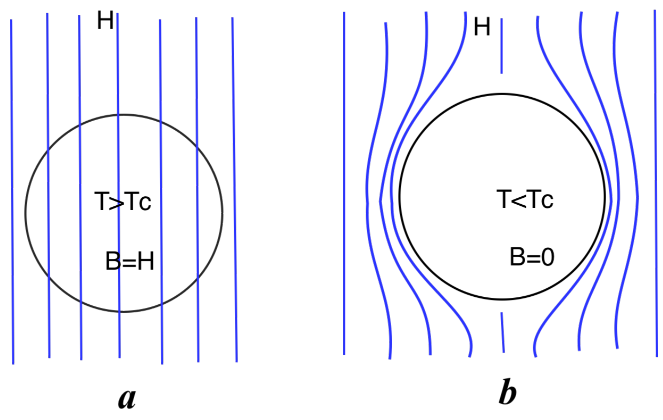

Fig. 3. *The Meissner and Oxenfeld effect.*

A more detailed investigation discovered that the magnetic field is equal to zero only inside the bulk of magnetic sample. The field in the thin layer near the superconductor surface vanishes gradually from the "vacuum field" value at the surface to zero field in the bulk. The thickness of this layer, called the penetration depth (δ_L), by the order of magnitude equals $10^{-5} - 10^{-6}$ cm.

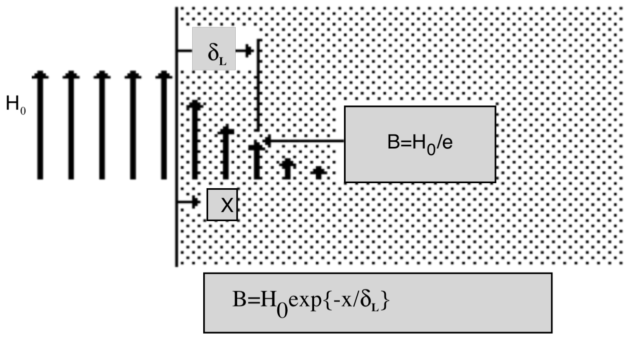

Fig. 4. *The London penetration depth describes magnetic field decay in the superconductor.*

<u>The F. London & G. London theory.</u>

The Meissner effect was explained first in the phenomenological theory of F. London and G. London (1935). The main experimental facts of zero resistance of the superconductor to electric current and the Meissner and Oxenfeld effect were incorporated into the theory directly. First, the absence of resistance was incorporated *via*, essentially, the Newtonian 2nd law equation:

$$d\Lambda\vec{j}/dt = \vec{E}; \quad \Lambda = m/\left(n_S e^2\right) \tag{1.2}$$

where n_S is the density of superconducting electrons, *m* and *e* are the electron mass and charge respectively. Next, from the Maxwell–Faraday equation:

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c}\frac{\partial \vec{H}}{\partial t}, \tag{1.3}$$

and Eq. (1.2) *<u>the London equation</u>* follows, that relates the curl of the current density $\vec{j}$ to the magnetic field:

$$\vec{\nabla} \times \vec{j} = -\frac{1}{c\Lambda}\vec{H}, \tag{1.4}$$

where the absence of the current and magnetic field in the bulk of superconducting sample was used to derive the last equation.

By relating the London equation to Maxwell's equation:

$$\vec{\nabla} \times \vec{H} = \frac{4\pi}{c}\vec{j} \tag{1.5}$$

and taking curl of both sides of (1.5) , then combining the result with (1.4), it can be shown directly that the Meissner effect arises with penetration length δ_L:

$$\nabla^2 \vec{H} = \frac{\vec{H}}{\delta_L^2}; \quad \delta_L^{-2} \equiv \frac{4\pi n_S e^2}{mc^2}. \tag{1.6}$$

This is one of the theoretical approaches to explanation of the Meissner effect. Another equivalent way to write down the London equation (1.4), very useful for calculations of diamagnetic moment, is to use the vector potential $\vec{A}$ instead of the magnetic field $\vec{H}$:

$$\vec{j} = -\frac{1}{c\Lambda}\vec{A}; \ \vec{\nabla} \cdot \vec{A} \equiv 0; \text{ where: } \nabla \times \vec{A} = \vec{H} \tag{1.4a}$$

Experimental data on the London penetration depth temperature dependence led to the following empiric formula:

$$\delta(T) = \delta(0)/[1 - (T/T_e)^4]^{1/2}. \tag{1.7}$$

that in essence prescribes the temperature dependence to the superconducting electron density n_S:

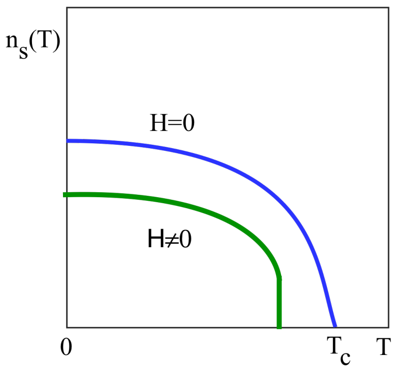

Fig. 5. *Superconducting electrons density in superconductor vs temperature at zero (2nd order transition) and finite (1st order transition) external magnetic fields.*

The thermodynamics of the superconducting transition.

The thermodynamics of the superconducting transition depends on magnetic field H. The experiments show that if the transition takes place at $H = 0$, i.e. at $T = T_c$, then this is the phase transition of *the second order*. In this case the latent heat of transition is zero, but specific heat has a discontinuity at T_c. If the transition takes place at $H \neq 0$, i.e. at $T < T_c$, then it is the phase transition of *first order*, which has finite latent transition heat. This change of the phase transition order can be related to the penetration depth behavior as it is sketched in Fig. 5.

In the "common superconductors", discovered before the HTS, the heat capacity at low temperatures was found to obey the exponential law:

$$C_{\exp} = a \cdot \exp\{-\Delta/k_B T\}. \tag{1.8}$$

The power law temperature dependence of the specific heat was discovered later for the HTS compounds and was explained as the result of the d-wave symmetry of the superconducting order parameter on the basisi of many different measured properties of these materials. For example, experiments show that in superconducting $La_{2-x}Sr_xCuO_4$ ($0.16 \le x \le 0.22$), the electronic specific heat C_{el} exhibits a T^2 dependence at $T << T_c$, and substitution of 0.3–0.5% Zn for Cu changes the T^2 dependence into one, that is described by the sum of T linear and T^3 terms. These features of C_{el} give convincing evidence for a clean superconductor with lines of nodes in the superconducting gap of the fermionic excitations.

The jump in the specific heat of the superconductor at T_c

Consider the bulk cylindrical sample in the longitudinal magnetic field. The condition of the superconducting transition implies the equality of the free energies:

$$F_s(H,T) = F_n(H,T); \quad (1.9)$$

where the indexes s and n denote the superconducting and normal phases respectively. The equality takes place only on the curve $H = H_c(T)$ in the H-T phase diagram, see e.g. Fig. 2.

The magnetic field penetrates into the superconductor only inside the layer of the penetration depth thickness, δ_L. In this layer the screening superconducting current flows in the presence of the magnetic field and provides the screening of the field in the bulk of the sample. This gives the contribution of order $\sim H_c^2/(8\pi)$ per unit volume of the surface layer of the thickness δ_L. Hence, the total contribution of the both the screening current and the field H into F_s is of the order $\sim \left(H_c^2/8\pi\right)\delta_L S/V << 1$ per volume V, where S is the surface area of the sample. This contribution can be neglected unless we deal with a very thin plate.

On the other hand, in the normal metal case, the magnetic field penetrates completely into the whole volume. Hence we obtain a detailed version of Eq. (1.9):

$$F_s(T) = F_n(0,T) - H_c^2/(8\pi). \quad (1.10)$$

Here we assume that the superconducting metals are not magnetic, i.e. they have $\mu \approx 1$.

After differentiating with respect to T, we can find the difference of entropies ($S = -\partial F/\partial T$):

$$S_n - S_s = -H_c\,(\partial H_c/\partial T)/(4\pi). \quad (1.11)$$

The quantity $q = T(S_n - S_s)$ gives the phase transition latent heat. As $dH_c/dT < 0$, (see Fig. 2) $q > 0$, i.e. the heat is absorbed in going from the superconducting phase to the normal phase, excluding the point $H_c=0$ at T_c, where transition is of the second order and, hence, $H_c=0$.

One more differentiation with respect to temperature gives the difference (jump) in heat capacities ($C_v = T(\partial S/\partial T)_v$):

$$C_n - C_s = -(4\pi)^{-1}[H_c d^2H_c/dT^2 + (dH_c/dT)^2]. \quad (1.12)$$

In particular at $T = T_c$, when $H_c = 0$, we have:

$$\Delta C = C_s(T_c) - C_n(T_c) = (4\pi)^{-1}\left(dH_c/dT\right)^2. \quad (1.13)$$

Remark₁ Here we mention, that this elementary derivation, that rests only on the experimental fact that there is the Meissner effect, allows one to obtain rigorous formula equating the critical magnetic field with the thermodynamic characteristic of the superconductor.

The intermediate state

The Meissner effect in the bulk sample may be incomplete due to the sample geometry that enhances the field intensity near its surface in the superconducting state. For an ellipsoid this enhancement effect is expressed in a most simple way via the single demagnetizing factor, *n*. The simplification comes from the fact that in case of the ellipsoid the Maxwell field H_i inside the sample is uniform, but differs from the external field at infinity, H_0 :

$$\vec{H}_i = \vec{H}_0 - 4\pi n\vec{M} \tag{1.14}$$

here $\vec{M}$ is the magnetization, n is the demagnetizing factor or equivalently the demagnetization coefficient.

The paradox

Assuume first that the metal is in the superconducting state, and the Meissner effect is complete, i.e. $\vec{B}=0$ inside the sample (neglecting the surface layer of order of the London penetration depth), i.e.

$$\vec{B} = \vec{H}_i + 4\pi n\vec{M} = \vec{H}_0 + 4\pi(1-n)\vec{M} \tag{1.15}$$

and hence:

$$\vec{M} = -\vec{H}_0/[4\pi(1-n)]; \quad \vec{H}_i = \vec{H}_0/(1-n) \tag{1.16}$$

According to the boundary conditions of the usual Maxwell theory of electromagnetism, both the normal component of ***B*** and the tangential component of ***H*** are continuous across the boundary between the two media. Outside of the superconductor ***B*** = ***H***. Hence, since ***B*** = 0 inside the superconductor, the ***H*** field has only tangential component at the boundary, i.e. the magnetic field force lines " circumflex" the superconductor (Fig. 3b).

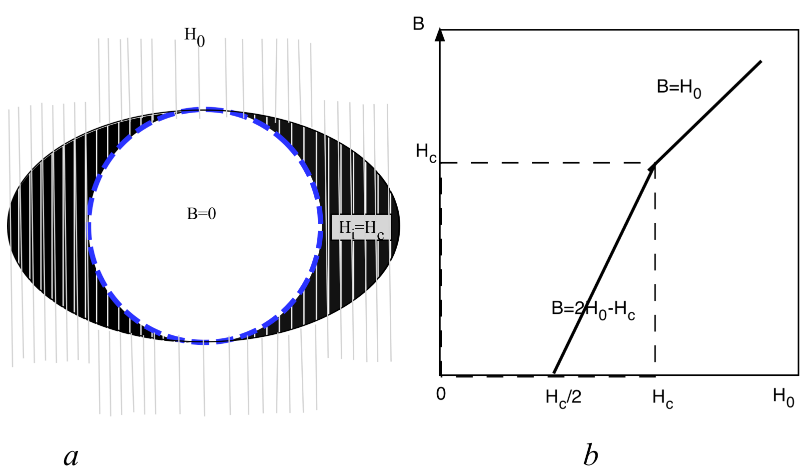

Fig.6 *Intermediate superconducting state: a) penetration of magnetic field in the ellipsoid. b) field distribution inside the cylinder with the axis perpendicular to the field (n=1/2).*

Since the tangential component of $\boldsymbol{H}$ is continuous at the boundary and hence, in those points where the directions of both $\boldsymbol{H}$ and $\boldsymbol{H}_0$ coincide the field at the boundary is maximal and equals $H_0/(1-n)$, i.e. it is greater than H_0. Therefore, there exists a possibility that the field H_i equals H_c in some regions, though away from the sample $H_0 < H_c$ is fulfilled.

But, this reasoning leads to a <u>*paradox*</u>. Suppose that $H_0 < H_c$ is fulfilled and that somewhere in the superconducting sample the field exceeds H_c, see e.g. hatched area in Fig. 6a. Then this region should become normal metal. But then the field returns to its value in the vacuum, $H_0 < H_c$, and hence, this region should be superconducting: <u>*a pradox*</u>!

The solution of the paradox is due to Peierls and London (1936), who advanced an idea of the "intermediate state". According to this idea, if the external field H_0 belongs to the following interval:

$$(1-n)H_c < H_0 < H_c \tag{1.17}$$

then the superconducting sample is described with the condition:

$$H_i = H_c. \tag{1.18}$$

In this case we obtain from (1.14) that the magnetization equals to:

$$M = -(H_c - H_0)/(4\pi n), \tag{1.19}$$

And consequently, B is not zero in the sample:

$$B = H_i + 4\pi M = H_0/n - H_c(1-n)/n. \tag{1.20}$$

Therefore, at $H_0 = (1-n)H_c$ the field $\boldsymbol{B} = 0$, and at $H_0 = H_c$ the field $B = H_c$, and in the interval between these values there is a linear dependence B on H_0, see Fig. 6b ($n = 1/2$) for the cylinder in the field perpendicular to its axis.

Remark₂ It was consequently shown by Landau that condition $H_i = H_c$ actually implies a superstructure of the alternating superconducting ($B=0$) and normal ($B=H_c$) layers in proportion determined by the positive surface energy (per unit area) of the boundary between the layers:

$$\sigma_{ns} = \left(H_c^2/8\pi\right)\xi\,(>0) \tag{1.21}$$

where ξ is the so-called (Landau)correlation length.

LECTURE 2

The main idea of the microscopic theory of superconductivity. Criterion of superfluidity. Phonon attraction. Cooper pairing. The Little's mechanism of high-temperature superconductivity in quasi one-dimensional molecular chains.

Preamble. The microscopic theory of superconductivity was developed by Bardin, Cooper and Schrieffer in 1956, and independently by Bogolyubov in 1957. It happened 46 years after the discovery of the superconductivity in Hg by Heike Kamerlingh Onnes. The logical root from 1911 to 1956 was as follows:

- *the superconducting phenomenon resembled much that of superfluidity of liquid helium, discovered by Kapitsa in 1938.*

- *the theory of the latter phenomenon was developed by Landau in 1941, who advanced the superfluidity criterion considering the helium flow through the capillaries with zero viscosity*
- *the superconductivity was interpreted as the superfluidity of the electronic liquid, but electrons are fermions and fermionic excitations of the Fermi liquid do not obey the Landau superfluidity criterion*
- *hence, electrons should form bose-particles via formation of pairs, but since electrons are equally charged and repel each other, the cause of pairing seemed mystique*
- *the isotope effect: dependence of T_c and H_c on the ion mass of the crystal lattice was discovered in 1950 (Maxwell, Reynolds et al.), that encouraged Fröhlich and Bardeen independently to forward a hypothesis of the phonon-based attraction between electrons in the metals*
- *but the Fermi energy (i.e. kinetic energy) possessed by conduction electrons is much greater than characteristic binding energy of superconducting pairs $k_B T_c \le \left(10^{-4} \div 10^{-2}\right)\cdot \varepsilon_F$; the solution to this paradox was found by* ***Cooper (1956)****, who calculated the binding energy of fermionic quasi-particles in the ground state of the Fermi liquid with attraction between the electrons in a narrow interval of energies around the Fermi level.*

The Landau superfluidity condition

We start our study of the concepts listed above from the superfluidity criterion, that was introduced in Landau theory of superfluid ^{4}He. One can imagine helium flowing through the capillary at a speed of ***v***. If we go into the frame of reference connected with helium, it will rest, while the walls of capillary are moving with a speed of ***v***. If the viscosity arises then the moving tube will carry helium at rest away with it. This means helium gains momentum ***P*** and energy *E*. However we know that the homogeneous quantum system changes its momentum and energy by means of generation of quasi-particles. Let the quasi-particle appear with momentum ***p*** and energy ε(***p***). Back in the laboratory frame of reference bound with the tube the energy and momentum are equal:

$$\vec{P}' = \vec{P} + M\vec{\mathrm{v}}, \quad \mathrm{E}'=\mathrm{E}+\vec{P}\vec{\mathrm{v}}+M\mathrm{v}^2/2\,, \tag{2.1}$$

here *M* is the mass of the liquid. The energy change of the liquid when the quasi-particle appears equals:

$$\mathrm{E}+\vec{P}\vec{\mathrm{v}} \equiv \varepsilon\left(\vec{p}\right) + \vec{p}\vec{\mathrm{v}}\,. \tag{2.2}$$

For the quasi particle creation to be energetically favorable the inequality must be satisfied:

$$\varepsilon\left(\vec{p}\right) + \vec{p}\vec{\mathrm{v}} < 0\,. \tag{2.3}$$

The minimal value $\varepsilon\left(\vec{p}\right) + \vec{p}\vec{\mathrm{v}}$ is achieved when $\vec{p}$ and $\vec{\mathrm{v}}$ are antiparallel. Thus, at least:

$$\varepsilon\left(p\right) - p\mathrm{v} < 0 \ \text{, or:} \qquad \mathrm{v}>\mathrm{v}_c \equiv \left\{\varepsilon\left(p\right)/p\right\}_{\min}\,. \tag{2.4}$$

v_c is the minimum speed of the flow at which the quasi-particles with momentum ***p*** and energy ε(*p*) can appear.

Remark₁ Thus, the viscosity arises if the velocity exceeds v_c. It proved to be that the liquid helium has the energy spectrum that provides finite v_c. Hence, the liquid helium is a superfluid at velocities lower than v_c. But in the Fermi liquid the lowest excitation spectrum corresponds to the particle-antiparticle pair production. If they are produced just at the Fermi surface then the energy can be indefinitely small. At the same time the full change in the momentum can be up to $2p_F$ if the particle and antiparticle lay on the opposite sides of the Fermi sphere. *Therefore,* $v_c = 0$*, and the Fermi liquid has viscosity at any flow velocity. Hence, at least the electron pairing into bose-pairs is necessary to shut down the fermionic particle-antiparticle excitation channel that prohibits the superfluidity.*

The phonon attraction

In 1950 the isotope effect was discovered in the form of the dependence of T_c and H_c on the crystal lattice ion mass:

$$T_c \propto M^{1/2}, H_c \propto M^{1/2}, \tag{2.5}$$

The ion mass can manifest itself only when the crystal lattice is involved in superconductivity. Based on this fact, Fröhlich and Bardeen (1950) independently proposed that electrons can attract via the retarded crystal lattice deformation, as sketched in Fig. 7:

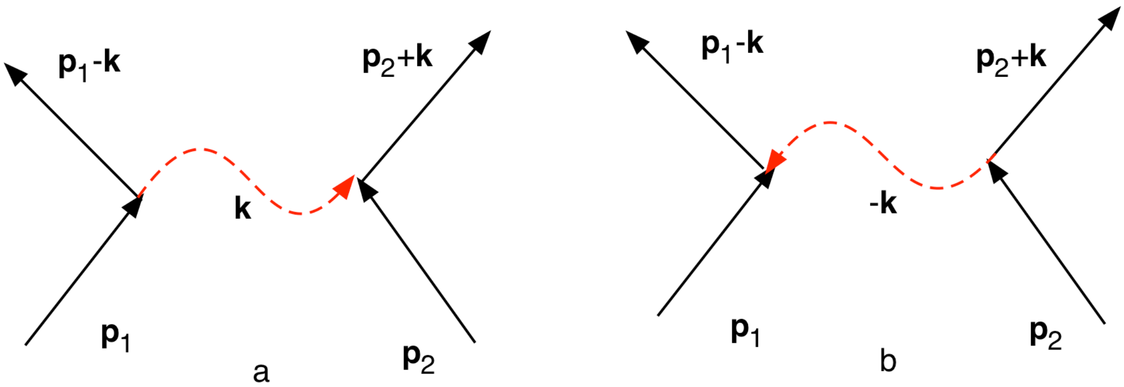

Fig. 7 The amplitudes of the phonon exchange between two electrons in a crystal lattice.

First, consider the diagram 7*a*. One electron with momentum $\boldsymbol{p}_1$ produces the phonon with momentum $\hbar\boldsymbol{k}$, hence, its own momentum becoming $\boldsymbol{p}'_1 = \boldsymbol{p}_1 - \hbar\boldsymbol{k}$. The phonon is absorbed by other electron, which had momentum $\boldsymbol{p}_2$ and after the absorption acquired the momentum $\boldsymbol{p}'_2 = \boldsymbol{p}_2 + \hbar\boldsymbol{k}$. The amplitude of this process, which is the second order perturbation in the electron-phonon interaction, is

$$\frac{|V_k|^2}{\varepsilon(p_1) - \varepsilon(p_1 - \hbar k) - \hbar\omega(k)}, \tag{2.6}$$

here $V_k = V_{\boldsymbol{p}-\hbar\boldsymbol{k},\boldsymbol{p}}$.

From the other hand, the same final momentum occurs if the electron having the momentum $\boldsymbol{p}_2$ emits phonon with the momentum $-\hbar\boldsymbol{k}$, which will be then absorbed by the electron with momentum $\boldsymbol{p}_1$ (Fig. 7b). The amplitude of this process is

$$\frac{|V_k|^2}{\varepsilon(p_1)-\varepsilon(p_1+\hbar k)-\hbar\omega(k)}. \qquad (2.7)$$

Here we took into account that ω($\boldsymbol{k}$) and V_k are invariant to the change of the sign of $\boldsymbol{k}$. The sum of the two amplitudes (2.6) and (2.7), accounting for the conservation of energy:

$$\varepsilon(\boldsymbol{p}_1) + \varepsilon(\boldsymbol{p}_2) = \varepsilon(\boldsymbol{p}'_1) + \varepsilon(\boldsymbol{p}_2'), \qquad (2.8)$$

gives the final amplitude:

$$-\frac{2|V_k|^2\hbar\omega(k)}{\left[\hbar\omega(k)\right]^2-\left[\varepsilon(p_1)-\varepsilon(p_1-\hbar k)\right]^2}. \qquad (2.9)$$

Taking into account the expression for V_k following from the electron - acoustic phonon emission-absorption Hamiltonian (6.12) in the Lecture 6, and estimating it as:

$$|V_k|^2 \sim \frac{\hbar^4\omega(k)}{p_F mV},$$

we estimate the amplitude (2.9) by an order of magnitude:

$$-\frac{\hbar^3}{p_F mV}\frac{\left[\hbar\omega(k)\right]^2}{\left[\hbar\omega(k)\right]^2-\left[\varepsilon(p_1)-\varepsilon(p_1-\hbar k)\right]^2}. \qquad (2.10)$$

Remark$_2$ The amplitude of electron-electron scattering via the phonon exchange (2.10) _is negative when_ $|\varepsilon(p_1)-\varepsilon(p_1-\hbar k)| \le \hbar\omega(k)$, _hence, manifesting attraction between electrons_ . Besides, in the limit $|\varepsilon(p_1)-\varepsilon(p_1-\hbar k)| \ll \hbar\omega(k)$ the amplitude does not depend on $\boldsymbol{k}$. Hence, this attraction between electrons can be approximated by a local potential $U = U_0\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)$, neglecting the retardation effects manifested by the frequency dependence in (2.10). This potential is isotropic and called s-wave scattering amplitude with zero orbital momentum $l = 0$ of the two electrons in the center of their mass. Therefore the coordinate wave-function of the interacting electrons is symmetrical relative to permutation of the particles. However, since the electrons are fermions, their complete wave-function is antisymmetrical relative to permutation of particles. Thus, the spin part of the wave function must be antisymmetrical, i.e. _the pair of electrons is in the singlet state_. This is actually the Pauli principle in disguise: the attraction of the two electrons with coinciding coordinates is not zero only when their spins are opposite.

Assuming that the phonon density of states is proportional to $k^2(dk/d\omega)$, i.e. it decreases quickly when k is small, and the attraction amplitude is k - independent, one concludes that the main contribution to the electron-electron attraction amplitude bring the Debye phonons with: $k \propto k_D \propto \pi/a$ and $\hbar\omega \propto \hbar\omega_B$.

Remark$_3$ When $|\varepsilon(\boldsymbol{p}_1) - \varepsilon(\boldsymbol{p}_1')| >> \hbar\omega_D$ the inter-electron interaction decreases steeply. Hence, the electrons are attracted only in the vicinity of the Fermi surface: the width of the attraction layer being $\hbar\omega_D$ on the energy scale and $\Delta p \propto \hbar\omega_D/\mathrm{v}_F$ on the momentum scale. Allowing for the uncertainty principle one estimates the attraction radius Δr in the real space as follows:

$$\Delta r \propto v_F/\omega_D \propto a\left(v_F/s\right) \propto \left(M/m\right)^{1/2} a \tag{2.11}$$

where M is the ion mass, m is the electron mass, and thus: $\left(M/m\right)^{1/2} \sim 10^2 \div 10^3$, i.e. $\Delta r \propto 10^{-6} \div 10^{-5} cm$. Therefore, _the phonon interaction is the long-ranged_ one: $\Delta r \propto \left(p_F m/\hbar^3\right)^{-1}$. At the same time the Coulomb repulsion, owing to the Debye screening, acts within the Debye screening radius r_D which is of the order of the metallic crystal's lattice spacing a: $r_D \propto \hbar/p_F \sim a$. Therefore, the screened _Coulomb potential is short-ranged_ and can be approximated with the Dirac's delta-function:

$$U_C \approx e^2 a^2 \delta(\vec{r}_1 - \vec{r}_2). \tag{2.12}$$

The ratio of the amplitudes of the phonon attractive and Coulomb repulsive effective potentials is, according to (2.10) and (2.12), is approximately *1*:

$$e^2a^2/(\hbar^2/p_0 m) \propto (e^2\hbar^2/p_0 m/\hbar^3) \propto 1. \tag{2.13}$$

Nevertheless, the phonon attraction can dominate, in some metals, the Coulomb repulsion due to, so-called, dynamic factor: $1/\ln(M/m) << 1$, that depletes effectively the Coulomb repulsion at longer times.

In most cases these interactions differ significantly, and thus, for the studying of the superconductivity, one can account solely for the phonon attraction. Instead of the exact formula (2.10) we can represent this attractive potential via its matrix elements in the momentum space of the fermionic quasi-particles:

$$U_{p,p'} = \begin{cases} -g, \ \mu - \hbar\omega_D < \varepsilon(p), \varepsilon(p') < \mu + \hbar\omega_D; \\ 0, \qquad |\varepsilon(p) - \mu|, |\varepsilon(p') - \mu| > \hbar\omega_D. \end{cases} \tag{2.14}$$

Here $g \propto \hbar^3/p_0 m \propto [\nu(\mu)]^{-1}$.

The Cooper pairs

An application of the effective potential (2.14) to the _fermionic quasi-particles_ and _not the bare electrons_ of the FL anabled Leon Cooper to solve the paradox, mentioned above, of the smallness of the binding energy of the Cooper pair with respect to the Fermi energy of the electrons.

We will consider isotropic case for simplicity, with the linearized quasi-particle spectrum $|\xi(p)|$, where $\xi = v_F(p - p_F)$, as is sketched in Fig. 8: the right branch refers to the quasi-particles of the "particle" type, the left one refers to the quasi-particles of the "antiparticle" type with the positive charge.

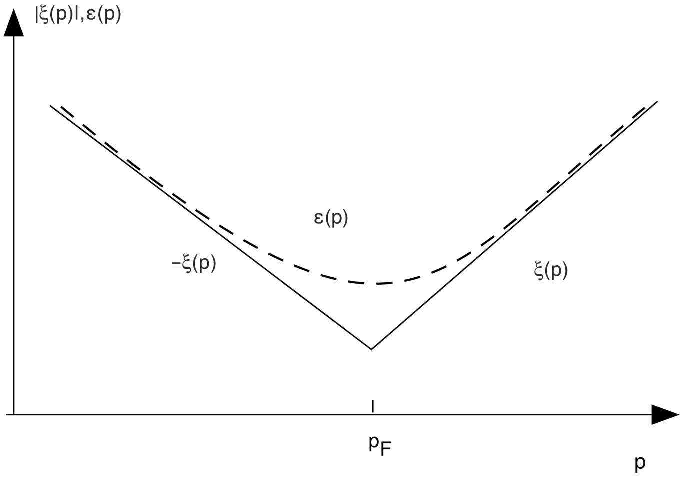

Fig.8

It will be seen below that the most important for the superconductivity is the interaction of the quasi-particles with the same $|\boldsymbol{p}|$, i.e. the interaction of either two particles or two antiparticles with the center of mass at rest. Then, from (2.9) it follows that in both cases the phonons perform the attraction.

Let us write the Schrödinger equation for two quasi-particles:

$$[H_0(\boldsymbol{r}_1) + H_0(\boldsymbol{r}_2) + U(\boldsymbol{r}_1, \boldsymbol{r}_2)]\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2); \qquad (2.16)$$

here $H_0(\boldsymbol{r}_1)$ is the free quasi-particle Hamiltonian, i.e.

$$H_0(\boldsymbol{r}_1)\psi_p(\boldsymbol{r}_1) = |\xi(\boldsymbol{p})|\psi(\boldsymbol{r}_1) \qquad (2.17)$$

($\psi_{\boldsymbol{p}} = V^{-1/2}e^{ipr/\hbar}$, i.e. plane wave in the free quasi-particle approximation). Both the total momentum and the spin of the bound pair in the ground state must be zero. Hence, the wave function of the pair will be the superposition of two states of two free quasi-particles having both the opposite momenta and spins, i.e.

$$\Psi(r_1, r_2) = \sum_p c_p \psi_{p,+}(r_1)\psi_{-p,-}(r_2), \qquad (2.18)$$

here the indexes plus and minus mean the ± 1/2 spin projections. Substituting this in the equation (2.16) we obtain

$$2|\xi(\boldsymbol{p})|c_{\boldsymbol{p}} + \sum U_{\boldsymbol{pp'}}c_{\boldsymbol{p'}} = Ec_{\boldsymbol{p}}. \qquad (2.19)$$

Suppose

$$U_{pp'} = \begin{cases} -g, \; p_F - \hbar\omega_D / \mathrm{v}_F < |p|, |p'| < p_F + \hbar\omega_D / \mathrm{v}_F, \\ 0 \;\; \text{outside this interval} \end{cases} \qquad (2.20)$$

and solve (2.19) for $c_{\boldsymbol{p}}$:

$$c_{\boldsymbol{p}} = gI/[2|\xi(\boldsymbol{p})| - E], \qquad (2.21)$$

where

$$I = \sum_{|p'| = p_0 - \hbar\omega_D / v}^{|p'| = p_0 + \hbar\omega_D / v} c_{p'} \,. \qquad (2.22)$$

We have to take into account that we are seeking for the negative energy eigenvalue. Let us denote $E = -2\Delta$ and substitute c_p from (2.21) in the condition (2.22). We find in this case:

$$I = (gI/2)\sum_{|p'|=p_0-\hbar\omega_D/v}^{|p'|=p_0+\hbar\omega_D/v}\left[|\xi(p)|+\Delta\right]^{-1}. \qquad (2.23)$$

Going to the integration over ξ and taking into account that the integral is taken over the vicinity of the Fermi surface, we obtain:

$$1 = [g\nu(\mu)/2]\ln(\hbar\omega_D/\Delta) \qquad (2.24)$$

(the multiplier 1/2 arises since we sum over the states of a quasi-particle with the given spin projection, whereas previously defined density of states $p_0 m/(\pi^2\hbar^3)$ accounted for the both spin projections). Solving for Δ, we obtain:

$$\Delta = \hbar\omega_D \exp[-2(g\nu(\mu))]; \quad E=-2\Delta \qquad (2.25)$$

Thus, the pair of the quasi-particles has finite binding energy -2Δ. Such pairs are called the Cooper pairs, by the name of the author of this derivation. At $T = 0$ the Cooper pairs form the Bose condensate. This self-consistent derivation nevertheless does not take into consideration that the spectrum of the quasi-particles possesses the gap Δ at $T = 0$, then, corrected value of Δ is twice the one in (2.25).

Conclusions: the main consequences of the BCS theory of superconducting pairing

1. The bound state with the binding energy -2Δ exists at an arbitrary small value of the attraction *g due to filled up Fermi surface.*
2. The greater is the coupling energy per quasi-particle eigen state, $g\nu(\mu)$, the higher is the superconducting transition temperature $T_c \sim \Delta/k_B$. Usual superconductors (i.e. discovered before 1986) obey inequality: $g\nu(\mu) < 1$, which leads to an estimate: $T_c/\hbar\omega_D \le 10^{-2}$.
3. The conclusion 1) stems from the fact demonstrated by Cooper, that the involved in *the pairing quasi-particles occupy essentially one-dimensional space when the Fermi sphere is filled up*: the integrals over the momenta transform according to the rule $\int d^2p/(2\pi\hbar)^2 \to (\nu/2)\int d\xi$, and in the one-dimensional system any attraction is enough to bind the particles.
4. $\Delta(T)$ decreases with temperature and at $T_c \sim \Delta(0)/k_B$ it turns to zero.

Thus we see that the presence of filled Fermi sphere plays an important role in the Cooper pairs formation in the weak coupling limit studied in the BCS theory.

The Little's mechanism of high-temperature superconductivity in quasi one-dimensional molecular chains (the exciton mechanism in superconductivity)

The exciton mechanism of the superconductivity proposed by W.A. Little (1964) is expressed in the following citation from his paper: "The excitonic mechanism is a proposed mechanism in which an electronically polarizable entity is used instead of the polarizable ionic lattice. Here, instead of the ionic mass (*M*) the much smaller electronic mass (*m*) would appear, and the superconducting transition temperatures would be expected to be of the order of $(M/m)^{1/2}$ times greater than those of conventional superconductors. This is the basis of the hope for achieving superconductivity at liquid nitrogen temperatures or perhaps even room temperature. Life is not that simple though and our problem is to try to devise a real system to utilize this mechanism. " The estimate made above is based on the isotope effect (2.5), assuming that the effective coupling constant etc. is preserved as in the phonon assisted attraction case considered above. The realization of the "electronically polarizable entity" is sketched in Fig. 9.

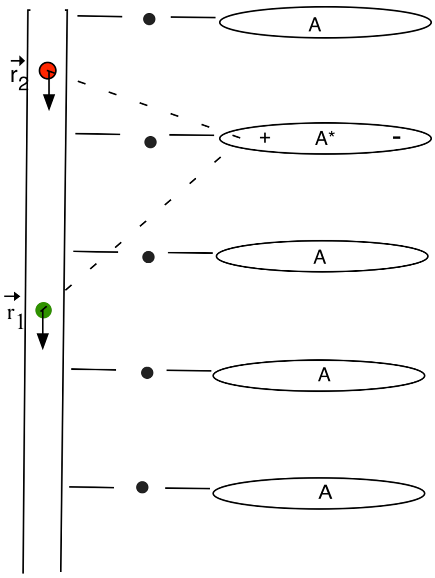

Fig. 9. The exciton mechanism of the superconductivity (W.A. Little, 1964).

In Fig. 9 the one-dimensional (1D) conducting structure is a long conducting channel (e.g. a polymer) which is attached by a series of insulating bonds to a series of side chains *A*. These side chains should constitue some highly polarizable molecules, such as an intensely colored dye. An electron at $\vec{r}_1$ moving along the channel induces a charge separation in the side chain, A^*, but because of the finite frequency of oscillation of the charge in the side chain the maximum induced charge appears some distance behind this electron. A second electron at $\vec{r}_2$ could then be attracted to it, so that a superconducting state would occur here as in a metal, but with the excitons of the side chains, $A \rightarrow A^*$, playing the role of the phonons:

$$e_1 + A \rightarrow e_1' + A^*, \quad e_2 + A^* \rightarrow e_2' + A\,. \tag{2.26}$$

Then, in analogy with the derivation for the phonon-assisted superconductivity (2.9)-(2.25), one finds:

$$g_{ex} \sim -\frac{2|V_{SA}|^2 E_{ex}}{[E_{ex}]^2 - [\varepsilon(p_1) - \varepsilon(p_1')]^2} \Rightarrow T_c \sim E_{ex} \exp[-2/(\tilde{g}_{ex}\nu(\mu))]; \quad \tilde{g}_{ex} \approx |V_{SA}|^2 / E_{ex} \tag{2.27}$$

where we have considered a single exciton state for the side chain, A^*, having an energy E_{ex} and coupled to the conducting channel electron via a matrix element V_{SA}. If the net energy for producing the charge separation in the side chains becomes negative, the system will be unstable to the formation of electron (Cooper) pairs. This mechanism would work "for achieving superconductivity at liquid nitrogen temperatures or perhaps even room temperature", if not for the phase ϕ fluctuations of the superconducting order parameter $\Psi = |\Psi| e^{i\phi}$, that ruin the superconducting long-range order in 1D conductors (T.M. Rice, 1964):

$$\left\langle \Psi(x_1)\Psi(x_2)\right\rangle \sim \exp\left[-|x_1-x_2|\, mT/\Psi_0^2\hbar^2\right]\Big|_{|x_1-x_2|\to\infty} \to 0 \tag{2.28}$$

Namely, as it follows from (2.28), the superconducting long-range order is absent in 1D conductor since the correlation function of the superconducting order parameter tend to zero in the long distance limit. The attempts to synthesize the higher-dimensional conductors with excitonic mechanism of superconductivity led (until 1986) to the failure in obtaining the high superconducting T_c. Nevertheless, it is very well possible that in the HTS compounds discovered since 1986 this mechanism does work in disguise.