THERMODYNAMICS OF ANISOTROPIC SUPERCONDUCTORS

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Results of the theory of anisotropic superconductors[3] are compared with the experimental data, and possible reasons of the discrepancy between the theory and experiments are analyzed. Several universal relations are desired for the thermodynamic quantities. The order of possible deviations from the universal relations of the isotropic model is considered. It is shown that Coulomb interaction of electrons and the possibility of formation of Cooper pairs in "nonsymmetric" states do not modify the results of the "anisotropic" theory. The contribution of higher approximation in the coupling constant is estimated, as well as the temperature range in which the theory may be wrong because of inapplicability of the free-quasiparticle concept. It is shown that in the low temperature region ($T \ll T_{cr}$) the theory is in good agreement with experiment. No such agreement is found at temperatures close to T_{cr}. This may be due to the fact that the quasiparticle concept is inapplicable near T_{cr}.

THE theory of superconductivity based on an isotropic model with weak coupling[1,2] leads to quantitative agreement with experiment, which is somewhat remarkable for so crude a model. One of the authors[3] developed a theory of anisotropic superconductors in the weak-coupling approximation and compared the results of the theory with experiment. In view of the lack of a sufficient number of good measurements of many quantities that are characteristic of semiconductors, the impression was gained that the agreement between theory and experiment became worse. Since that time, however, new experimental investigations were reported, in light of which it is advantageous to re-evaluate the agreement between the results of the theory of anisotropic superconductors with experiment. We consider, in addition, the possible reasons and probable orders of magnitude of deviations of experimental data from the results of the anisotropic theory, and we also estimate the order of the deviations of several thermodynamic quantities from the values predicted by the anisotropic model.

1. SUMMARY OF THE PRINCIPAL RESULTS OF THE THEORY[3] AND OF THE EXPERIMENTAL DATA

We recall first the principal results of the theory developed in [3] and derive some new relations that result from this theory. The principal equation of the theory is that of the energy gap $\Delta(\mathbf{p})$

$$\Delta(\mathbf{p}) = g\int U(\mathbf{p}, \mathbf{p}')\frac{\Delta(\mathbf{p}')}{\varepsilon(\mathbf{p}')}[1 - 2f(\beta\varepsilon(\mathbf{p}'))]\,d^3p'. \quad (1)$$

Here g — dimensionless coupling constant, $U(\mathbf{p}, \mathbf{p}')$ — interaction function of two Cooper pairs, $\epsilon(\mathbf{p}) = \sqrt{\xi^2(\mathbf{p}) + \Delta^2(\mathbf{p})}$, $\xi(\mathbf{p}) = \mathbf{v}_F \cdot (\mathbf{p} - \mathbf{p}_F)$, where $\mathbf{v}_F$ and $\mathbf{p}_F$ are the velocity and the momentum on the Fermi surface, and $f(x) = (e^x + 1)^{-1}$. The criterion of the applicability of Eq. (1) is apparently the smallness of the ratio c/v_F (c — velocity of sound), and not of g (see [2,4]).

In [3] this equation is solved for the anisotropic case under the assumption that the interaction occurs only in a narrow layer near the Fermi surface, with a thickness $\sim 2\omega_0$ (ω_0 = Debye frequency) and that in this layer $U(\mathbf{p}, \mathbf{p}')$ and $\Delta(\mathbf{p})$ depend only on the directions of the vectors p and p'. As a result of integration with respect to ξ we obtain for $\Delta(\mathbf{n})$ ($\mathbf{n} = \mathbf{p}/p$) the equation

$$\Delta(\mathbf{n}) = g\int U(\mathbf{n}, \mathbf{n}')\left[\ln\frac{2\omega_0}{\Delta(\mathbf{n}')} - F(\beta\Delta(\mathbf{n}'))\right]\Delta(\mathbf{n}')\frac{d\sigma'}{v_F'}, \quad (2)$$

$$F(x) = \int_{-\infty}^{\infty} dy\,(y^2 + 1)^{-1/2} f(x\sqrt{y^2 + 1}). \quad (3)$$

All further derivations of the theory are based on the solution of (2) or of the equation

$$\Delta(\mathbf{n}) = g\int U(\mathbf{n}, \mathbf{n}')\,\Delta(\mathbf{n}')\ln\frac{2\omega_0}{\Delta(\mathbf{n}')}\frac{d\sigma'}{v_F'} \quad (4)$$

with T = 0. In the zeroth approximation in g, the energy gap $\Delta(\mathbf{n})$ is given by the formula

$$\Delta(\mathbf{n}) = 2\omega_0 e^{-1/g}Q\psi(\mathbf{n}), \quad (5)$$

where $\psi(\mathbf{n})$ is the solution of the homogeneous Fredholm integral equation

$$\psi(\mathbf{n}) = \Lambda \int U(\mathbf{n}, \mathbf{n}')\psi(\mathbf{n}')\frac{d\sigma'}{v_F}, \quad (6)$$

normalized by the condition

$$\int \psi^2(\mathbf{n})\frac{d\sigma}{p_0 v_F} = 1 \quad (7)$$

(p_0 is a quantity of the order of the Fermi momentum, fixed by the condition

$$\int \frac{d\sigma}{p_0 v_F} = 1, \quad (8)$$

and Λ is the minimum positive eigenvalue of this equation). The value of Q (for T = 0) is determined by the formula

$$Q(0) = \exp\left[-\int \psi^2(\mathbf{n}) \ln\psi \frac{d\sigma}{p_0 v_F}\right] \leqslant 1. \quad (9)$$

It was shown in [3] that the thickness of the layer near the Fermi surface, in which the integration with respect to ξ is carried out, is a function of n and can therefore be replaced by a constant ω_0 defined by

$$\ln\omega_0 = \int \psi^2(\mathbf{n}) \ln\omega(\mathbf{n}) \frac{d\sigma}{p_0 v_F}. \quad (10)$$

For the critical temperature we obtain the relation

$$T_{cr} = (\gamma/\pi)\, 2\omega_0 e^{-\Lambda/g}, \quad (11)$$

where $\ln\gamma$ is the Euler constant. Comparing (5) with (11) we get

$$\Delta(\mathbf{n}, T) = (\pi/\gamma)\, T_{cr} Q(T) \psi(\mathbf{n})$$

and by virtue of the inequality $Q(T) \leq Q(0) \ll 1$ we obtain

$$\Delta_{\min}(0)/T_{cr} \leqslant 1.76. \quad (12)$$

For the jump in the specific heat we obtain at $T = T_{cr}$ the relation

$$\Delta C/C_n(T_{cr}) = 1.4/B, \quad (13)$$

$$B = \int \psi^4(\mathbf{n}) \frac{d\sigma}{p_0 v_F} > 1, \quad (14)$$

hence [1)]

$$\Delta C/C_n(T_{cr}) < 1.4. \quad (15)$$

When $T \ll T_{cr}$ the critical magnetic field obeys the law

$$H_{cr}(T) = H_{cr}(0)\,(1 - \chi T^2/T_{cr}^2), \quad (16)$$

$$\chi = \gamma^2/3Q(0) = 1.06/Q(0). \quad (17)$$

From this we get

$$\chi > \chi_{is} = 1.06. \quad (18)$$

From the formulas in [3] we can obtain in simple fashion two additional universal relations:

$$H_{cr}^2(0)/C_n(T_{cr})\, T_{cr} = 6\pi\gamma^{-2} Q^2(0) \leqslant 6, \quad (19)$$

$$H_{cr}^2(0)\,\chi^2/C_n(T_{cr})\, T_{cr} = \frac{2\pi\gamma^2}{3} \cong 6.64. \quad (20)$$

[We note that only two of the three relations (18), (19), and (20) are independent.]

Using formula (27) from [3]

$$\frac{H_{cr}^2}{8\pi} = \frac{p_0}{16\pi^3}\left(\frac{\pi}{\gamma}T_{cr}\right)^2 Q^2(T) + \frac{T}{(2\pi)^3}\int\left[\Delta G(\beta\Delta) - \frac{\pi^2}{3}T\right]\frac{d\sigma}{v_F} \quad (21)$$

and substituting the asymptotic value of G(x) as $x \to 0$, we obtain an expression for $H_{cr}(T)$ at a temperature close to critical:

$$H_{cr}(T) = H_{cr}(0)\frac{1.8}{\sqrt{B}\,Q(0)}\left(1 - \frac{T}{T_{cr}}\right). \quad (22)$$

Since the quantity $\sqrt{B}Q(0)$ can be either larger or smaller than unity, the quantity $T_{cr}(dH_{cr}/dT)_{T_{cr}}/H_{cr}(0)$ can deviate to either side of 1.8.

Finally, using expressions (13) and (17) we obtain one more universal inequality

$$\tfrac{1}{2}(1.4C_n(T_{cr})/\Delta C - 1) \geqslant \ln(0.94\,\chi). \quad (23)$$

We now turn to a comparison of the obtained results and the experimental data. Table I lists the measured values of g/Λ, T_{cr}, $H_{cr}(0)$, $(dH_{cr}/dT)_{T_{cr}}$ and γ_e (γ_e is the coefficient of T in the electronic part of the normal specific heat $C_n = \gamma_e T$). Table II is a summary of the measured or calculated (from experimental data) values or combinations of values for which the universal relations were derived.

It can be seen from the presented data that the agreement between theory and experiment is generally satisfactory in the low-temperature region, with inequality (19) violated only for mercury and lead, and with a noticeable deviation from (20) existing for Tl. The situation is appreciably worse at temperatures close to T_{cr}, where the inequality (15) for the jump in the specific heat is violated for a whole series of elements. To save space, we do not present data on the inequality (23), which, as an obvious consequence of the violation of the inequality (15), is not satisfied in the majority of cases. The possible causes of this will be discussed in the following sections.

[1)] We take this occasion to correct an error in the abstract of [3], where the word "larger than" should be replaced by "smaller than."

TABLE I

Element	g/Λ [21]	T_{cr}	$\gamma_e \cdot 10^3$, J/mole-deg^2	$H_{cr}(0)$, Oe	$-\left(\frac{dH_{cr}}{dT}\right)_{T_{cr}}$, Oe/deg
Al	0.193	1.175 [5]	1.3 [5]; 1.44 [6]	104 [5]	163 [5]
Cd	0.196	0.56 [21]	0.71 [7]	28.8 [9]	100 [9]
Zn	0.200	0.84 [8]	0.66 [7]; 0.65÷0.67 [8]	52.5 [9]	83.5 [10]
Ga	0.206	1.09 [10]	0.63 [5]	59.5 [5]	92 [5] 99.5 [10]
V	0.274	5.03 [8]	8.83 [7]; 9.26 [8]	1200 [9]	400 [9]
Sn	0.296	3.72 [11]	1.96±0.1 [11] 1.75 [8]; 1.8 [12,13]	308.6±0.5 [11] 306 [13]	149 [12]
Ta	0.296	4.48 [11]	6.5±0.14 [11]; 6.0±0.2 [13]; 5.44 [8]	830±4 [11] 825 [14]	320 [9]
Tl	0.316	2.36 [8]	3.1 [7]; 2.55* [8]; 1.53** [8]	171 [9]	139 [9]
In	0.345	3.41 [11]	1.9±0.1 [11] 1.7±0.05 [13]; 1.81 [8]	285,7±0.5 [11]	156 [12]
Nb	0.357	9.17 [20]; 8.7 [8]	8.54 [8]	1944 [20]	
Hg_α	0.446	4.15 [13]	1.91±0.05 [13]; 2.1 ±0.15 [15]	412±1 [13] 413 [9]	185 [9]
Hg_β		3.94 [13]	1.37±0.04 [13]	339±1 [13]	
Pb	0.493	7.22 [21]	3.0 [7]; 3.09±0.05 [13]	805 [9]	200 [9]

*Calorimetric measurement data and values calculated from them.
**Values obtained from magnetic measurements.

TABLE II

Element	$\frac{\Delta_{min}(0)}{T_{cr}}$ ($\leqslant 1.76$)	$\frac{\Delta C}{C_n(T_{cr})}$ ($\leqslant 1.4$)	$\chi - 1$ ($\geqslant 0.06$)	$\frac{H^2_{cr}(0)}{T_{cr}C_n(T_{cr})}$ ($\leqslant 6$)***	$\frac{H^2_{cr}(0)\,\gamma^2}{T_{cr}C_n(T_{cr})}$ ($\cong 6.64$)***	$-\frac{T_{cr}(dH_{cr}/dT)_{T_{cr}}}{H_{cr}(0)}$ (~ 1.8)****
Al	1.20 [8]	1.6 [5] 1.44 [6] 1.5 [19]	0.08 [5]	5.95 [5] 5.45 [6]	6.95 [5] 6.4 [6]	1.84
Cd	1.27 [20]	1.4 [8] 1.2 [20]		4.85 [7]		1.94
Zn	1.03 [8] 1.35 [16]	1.25±0.15 [8] 1.32 [19]		5.45 [7]		
Ga	1.18 [5] 1.32 [20]	1.41 [20]	0.11 [5]	5.65 [5]	6.95 [5]	1.7 [5] 1.84 [10]
V	1.7±0.1 [16] 1.5 [8]	1.7 [8] 1.52 [19]		5.85 [7] 5.6 [8]		1.68
Sn	1.8±0.1 [16] 1.65±0.1 [17] 1.35±0.05 [18] 1.5 [8]	1.82 [19] 1.4÷1.78 [9]	0.14 [11] 0.12 [13]	5.65 [11] 6.05 [13]	7.35 [11] 7.6 [13]	1.8
Ta	1.5 [16] 1.49 [8]	1.58 [8] 1.7 [20]	0.10 [11, 14]	5.75 [11]	6.96 [11]	1.7
Tl	1.3 [8]	1.72** [9, 8] 1.03* [9,8] 0.85* [9,7]	0.10 [11]	2.78* [7] 3.37* [8] 5.63** [8]	3.36* [7] 4.08* [8] 6.82** [8]	1.94
In	2.05±0.1 [16] 1.95±0.1 [17] 1.6 [8]	1.56 [11] 1.75 [13] 1.62 [20]	0.10 [11]	5.9 [8]	7.15 [8]	1.87
Nb	1.4±0.15 [16] 1.8 [8]	2.07 [19]		5.6 [8]		
Hg_α	2.3±0.1 [16]	2.1 [9]	—0.18 [9]	7.8 [13] 7.1 [15]	5.25 [13] 4.8 [15]	1.86
Pb	2.05±0.1 [16] 2.0±0.25 [17]	2.4 [9]		7.4 [7] 7 [13]		1.79

*Calorimetric measurement data and the values calculated from them.
**Values obtained from magnetic measurements.
***The published data refer to the value of γ, since the scatter of the values of $H_{cr}(0)$, T_{cr}, and χ is small.
****There are no references, since there is practically no scatter in the experimental data except for the case of Ga.

We note first that the previously developed theory[3] is quite dependent on the model; it considers neither the Coulomb interaction of the electrons nor the possible creation of Cooper pairs in states with symmetry different from the crystal symmetry. In the following sections we shall consider these effects and show that they do not change the results of the theory.

2. COULOMB INTERACTION

Let us examine the changes produced in the previously obtained result[3] by an account of the Coulomb interaction of the electrons. The content of the present section is a generalization of the Tolmachev method[2] to include the anisotropic case. The presence of a screened Coulomb interaction now causes the kernel of the integral equation (1) to consist of two terms. The first, $U_1(\mathbf{p}, \mathbf{p}')$, is due to the phonon pair interaction and differs from zero in a narrow energy interval near the Fermi surface with thickness $\sim 2\omega$ (we now consider the constant g to be included in U_1). The second term, $U_2(\mathbf{p}, \mathbf{p}')$, is the result of the screened Coulomb interaction and differs from zero in a wider energy range ($\sim\mu$). Thus, Eq. (1) assumes the form[2)]

$$c(\mathbf{p}) = \int [U_1(\mathbf{p}, \mathbf{p}') + U_2(\mathbf{p}, \mathbf{p}')] \frac{c(\mathbf{p}')}{\sqrt{(\xi')^2 + c^2(\mathbf{p}')}} d^3p'. \quad (24)$$

After integrating with respect to $\mathbf{p}'$ in the right half of this expression, we see that $c(\mathbf{p})$ is the sum of two terms, $c_1(\mathbf{p})$ and $c_2(\mathbf{p})$, which vanish when $\xi > \omega$ and $\xi > \mu$, respectively. When $\xi \ll \omega$, $c(\mathbf{p})$ is a function of the direction $\mathbf{n}$:

$$c(\mathbf{p})|_{\xi \ll \omega} = \Delta_1(\mathbf{n}). \quad (25)$$

Similarly, when $\omega \ll \xi \ll \mu$, $c(\mathbf{p})$ is another function of the direction

$$c(\mathbf{p})|_{\omega \ll \xi \ll \mu} = c_2(\mathbf{p})|_{\omega \ll \xi \ll \mu} = \Delta_2(\mathbf{n}). \quad (26)$$

Since the characteristic dimension of the function $c_2(\mathbf{p})$ is $\mu \gg \omega$ we have for $\xi \ll \omega$

$$c_2(\mathbf{p})|_{\xi \ll \omega} = \Delta_2(\mathbf{n}), \qquad c_1(\mathbf{p})|_{\xi \ll \omega} = \Delta_1(\mathbf{n}) - \Delta_2(\mathbf{n}). \quad (27)$$

We now integrate with respect to ξ' in the right half of (24). We first fix the value of $\xi \ll \omega$. In the term containing the kernel $U_1(\mathbf{p}, \mathbf{p}')$, the integration with respect to ξ' is effectively limited to the region $\xi \lesssim \omega$ and we have

$$\int U_1(\mathbf{p}, \mathbf{p}') \frac{c(\mathbf{p}')}{\sqrt{(\xi')^2 + c^2(\mathbf{p}')}} d^3p' = \int U_1(\mathbf{n}, \mathbf{n}') \Delta_1(\mathbf{n}') \ln \frac{2\omega(\mathbf{n}, \mathbf{n}'|c_1)}{\Delta_1(\mathbf{n}')} \frac{d\sigma'}{v_F'} = \hat{U}_1 \Delta_1 \Lambda,$$

$$\Lambda = \ln (2\omega(\mathbf{n}, \mathbf{n}'|c_1)/\Delta_1(\mathbf{n}')), \quad (28)$$

where $\omega(\mathbf{n}, \mathbf{n}'|c_1)$ is a function of $\mathbf{n}$ and $\mathbf{n}'$, while the functional c_1 is of the order of ω.

The integral containing the factor $U_2(\mathbf{p}, \mathbf{p}')c_1(\mathbf{p}')$ is sensitive also to small values of ξ, and we have

$$\int U_2(\mathbf{p}, \mathbf{p}') \frac{c_1(\mathbf{p}')}{\sqrt{(\xi')^2 + c^2(\mathbf{p}')}} d^3p' = \int U_2(\mathbf{n}, \mathbf{n}') [\Delta_1(\mathbf{n}') - \Delta_2(\mathbf{n}')] \ln \frac{2\omega(\mathbf{n}, \mathbf{n}'|c_2)}{\Delta_1(\mathbf{n}')} \frac{d\sigma'}{v_F'} = \hat{U}_2(\Delta_1 - \Delta_2)\Lambda.$$

(More accurately speaking, it is necessary to take into account the fact that the logarithm in the last formula differs from Λ by an amount of the order of unity. However, since this does not change the results, we assume these logarithms to be the same, to simplify the calculations.)

In the interval containing the factor $U_2(\mathbf{p}, \mathbf{p}')c_2(\mathbf{p}')$, the integration is effectively terminated at the upper limit $\sim\mu$:

$$\int U_2(\mathbf{p}, \mathbf{p}') \frac{c_2(\mathbf{p}')}{\sqrt{(\xi')^2 + c^2(\mathbf{p}')}} = \int U_2(\mathbf{n}, \mathbf{n}') \Delta_2(\mathbf{n}') \ln \frac{2\mu}{\Delta_1(\mathbf{n}')} \frac{d\sigma'}{v_F'}.$$

Ultimately we obtain for $\xi \ll \omega$

$$\Delta_1(\mathbf{n}) = (\hat{U}_1 + \hat{U}_2)\Delta_1\Lambda + \hat{U}_2\Delta_2\lambda, \quad (29)$$

$$\lambda = \ln \frac{\mu(\mathbf{n}, \mathbf{n}'|c_2)}{\omega(\mathbf{n}, \mathbf{n}'|c_1)}. \quad (30)$$

Similarly we get for $\omega \ll \xi \ll \mu$

$$\Delta_2(\mathbf{n}) = \hat{U}_2\Delta_1\Lambda + \hat{U}_2\Delta_2\lambda. \quad (31)$$

Solving the system (29) and (31) by perturbations, we set in the zeroth approximation Λ and λ equal to constants Λ_0 and λ_0 and seek $\Delta_i(\mathbf{n})$ in the form

$$\Delta_i(\mathbf{n}) = \Delta_i^{(0)} + \Delta_i^{(1)}. \quad (32)$$

The system of zeroth-approximation equations has the form

$$\Delta_1^{(0)} = \Lambda_0(\hat{U}_1 + \hat{U}_2)\Delta_1^{(0)} + \lambda_0\hat{U}_2\Delta_2^{(0)},$$

$$\Delta_2^{(0)} = \Lambda_0\hat{U}_2\Delta_1^{(0)} + \lambda_0\hat{U}_2\Delta_2^{(0)}. \quad (33)$$

Eliminating $\Delta_2^{(0)}$, we get

$$\Delta_1^{(0)} = \Lambda_0\hat{U}\Delta_1^{(0)}, \quad (34)$$

$$\hat{U} = \hat{U}_1 + \hat{U}_2(1 - \lambda_0\hat{U}_2)^{-1}. \quad (35)$$

Thus, Λ_0 and λ_0 assume the meaning of eigenvalues of a system of homogeneous integral equations for $\Delta_1^{(0)}$ and $\Delta_2^{(2)}$ and are by the same token

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[2)] To avoid confusion we use in the present section the symbol $c(\mathbf{p})$ in place of $\Delta(\mathbf{p})$.

uniquely defined. Since $U_2(\mathbf{n}, \mathbf{n}') < 0$, we see from (35) that the role of the Coulomb repulsion is effectively decreased by the presence of the large logarithm λ_0 in the denominator of the second term [see formula (38)]. This result agrees qualitatively with that of Tolmachev (see, for example, [2]).

We now introduce a constant ω_0, which has the same order as the Debye frequency and the exact value of which will be fixed later on, and a constant $\mu_0 \sim \mu$, and put

$$\Delta_0 = 2\omega_0 e^{-\Lambda_0}. \tag{36}$$

We then have

$$\Lambda = \ln \frac{2\omega(\mathbf{n}, \mathbf{n}' \mid c_1)}{\Delta_1(\mathbf{n}')} = \Lambda_0 - \ln \frac{\Delta_1(\mathbf{n}')}{\Delta_0} + \Gamma,$$
$$\lambda = \ln \frac{\mu(\mathbf{n}, \mathbf{n}' \mid c_2)}{\omega(\mathbf{n}, \mathbf{n}' \mid c_1)} = \lambda_0 - \Gamma_1, \tag{37}$$

where

$$\Gamma = \ln \frac{\omega(\mathbf{n}, \mathbf{n}' \mid c_1)}{\omega_0}, \quad \Gamma_1 = \ln \frac{\mu_0 \omega(\mathbf{n}, \mathbf{n}' \mid c_1)}{\omega_0 \mu(\mathbf{n}, \mathbf{n}' \mid c_2)}, \quad \lambda_0 = \ln \frac{\mu_0}{\omega_0}. \tag{38}$$

As in [3], we shall seek $\Delta_1^{(0)}$ and $\Delta_2^{(0)}$ in the form

$$\Delta_1^{(0)} = \Delta_0 Q\psi_1(\mathbf{n}), \qquad \Delta_2^{(0)} = \Delta_0 Q\psi_2(\mathbf{n}), \tag{39}$$

where $\psi_1(\mathbf{n})$ is the normalized solution of (34), and

$$\psi_2(\mathbf{n}) = \Lambda_0 (1 - \lambda_0 \hat{U}_2)^{-1} \hat{U}_2 \psi_1(\mathbf{n}).$$

The first-approximation equations then yield, after elimination of $\Delta_2^{(1)}$,

$$\Delta_1^{(1)} = \Lambda_0 \hat{U} \Delta_1^{(1)} - Q\Delta_0 \hat{U}\psi_1(\mathbf{n}) \ln (Q\psi_1(\mathbf{n}))$$
$$+ \Delta_0 Q [\hat{U}\Gamma_1\psi_1(\mathbf{n}) - (\hat{U} - \hat{U}_1)\Gamma_1\psi_2(\mathbf{n})]. \tag{40}$$

We now fix the choice of ω_0, stipulating the satisfaction of the equality

$$(\psi_1(\mathbf{n}), [\hat{U}\psi_1(\mathbf{n})\Gamma - (\hat{U} - \hat{U}_1)\psi_2(\mathbf{n})\Gamma_1]) = 0. \tag{41}$$

Then the condition that the inhomogeneous equation (40) be orthogonal to the solution of the homogeneous equation $\psi_1(\mathbf{n})$ yields

$$(\psi_1(\mathbf{n}), \hat{U}\psi_1(\mathbf{n}) \ln (Q\psi_1(\mathbf{n}))) = 0, \tag{42}$$

hence

$$Q = \exp\left\{-\int \psi_1^2(\mathbf{n}) \ln \psi_1(\mathbf{n}) \frac{d\sigma}{p_0 v_F}\right\}, \tag{43}$$

which agrees with the previous result[3].

Once we determine Q, we can solve Eq. (28), which can be rewritten

$$\iint \frac{d\sigma}{v_F} \frac{d\sigma'}{v_F'} \ln \frac{\omega(\mathbf{n}, \mathbf{n}' \mid 2\omega_0 e^{-\Lambda_0} Q\psi_1)}{\omega_0} K(\mathbf{n}, \mathbf{n}') = 0, \tag{44}$$

where

$$K(\mathbf{n}, \mathbf{n}') = \psi_1(\mathbf{n}) [U\psi_1(\mathbf{n}') - (\hat{U} - \hat{U}_1)\psi_2(\mathbf{n}')]$$

with respect to ω_0; this completes the determination of Δ_0 and of the function $\Delta_1(\mathbf{n})$.

Thus, the inclusion of the Coulomb interaction leads only to a finite renormalization of the kernel $U_1(\mathbf{n}, \mathbf{n}')$ and of the quantities $\psi_1(\mathbf{n})$, Λ_0, and $Q(0)$ associated with it, and consequently does not change the previously derived inequalities.

3. FORMATION OF COOPER PAIRS IN STATES WITH SYMMETRY OTHER THAN THAT OF THE CRYSTAL

Gor'kov and Galitskiĭ[22] have demonstrated within the framework of the isotropic model that if account is taken of the possible formation of electron pairs with angular momentum $\hbar l$ different from zero, then $\Delta(\mathbf{p})$ should be replaced by the set of $2l + 1$ quantities $\Delta_m(\mathbf{p})$ ($m = -l, \ldots l$), and the energy gap is determined by the equality $\Delta^2 = \Sigma |\Delta_m|^2$.

The values of $\Delta_m(\mathbf{p})$ for $T = 0°K$ are determined from the equation

$$\Delta_m(\mathbf{p}) = g \int U(\mathbf{p}, \mathbf{p}') \frac{\Delta_m(\mathbf{p}')}{\varepsilon(\mathbf{p}')} d^3p',$$
$$\varepsilon^2(\mathbf{p}) = \xi^2(\mathbf{p}) + \sum_m |\Delta_m(\mathbf{p})|^2. \tag{45}$$

The solutions of this equation are proportional to the associated Legendre polynomials $\Delta_m = a_m Y_{lm}(\theta, \varphi)$, and the equation is self-consistent (invariant under rotation) if and only if all the coefficients a_m are equal to one another: $a_m = a$.

It is of interest to consider the possible creation of pairs in states with symmetry other than the lattice symmetry in the anisotropic theory, and to show that in this case the equations remain self-consistent (invariant under transformation of the crystal symmetry group) and the ground state of the system has the same symmetry as the crystal.

Integrating in (45) over a layer of thickness 2ω (under the same assumptions as before), we obtain

$$\Delta_m(\mathbf{n}) = g \int U(\mathbf{n}, \mathbf{n}') \ln [2\omega (\sum_l |\Delta_l|^2)^{-1/2}] \Delta_m(\mathbf{n}') \frac{d\sigma'}{v_F} \tag{46}$$

We seek a solution of this equation in the form

$$\Delta_{mk}(\mathbf{n}) = 2\omega e^{-\lambda_k/g} Q_k \psi_{mk}(\mathbf{n}). \tag{47}$$

In the zeroth approximation we have for the functions ψ_{mk} the equations

$$\psi_{mk}(\mathbf{n}) = \lambda_k \int U(\mathbf{n}, \mathbf{n}') \psi_{mk}(\mathbf{n}') \frac{d\sigma'}{v_F'}. \tag{48}$$

The functions ψ_{mk} form a multi-dimensional representation of the crystal symmetry group with

order equal to the degree of degeneracy of the eigenvalue λ_k. It is easy to see that

$$\sum_l |\Delta_{lk}|^2 = 4\omega^2 e^{-2\lambda_k/g} Q_k^2 \sum_l |\psi_{lk}|^2$$

transforms in accord with the unitary representation of this group. Consequently, Eq. (46) for the gap is a self-consistent equation — any transformation from the crystal symmetry leaves this equation invariant.

As shown in [3], the ground state of a superconductor corresponds to the solution (48) with the minimal positive eigenvalue. It is easy to see that in the case of a Froehlich Hamiltonian the interaction function $U(\mathbf{n}, \mathbf{n}')$ is positive everywhere on the Fermi surface. For positive symmetrical kernels there exists a theorem (see [23]), by which the smallest positive eigenvalue of (48), Λ, is not degenerate and the corresponding eigenfunction $\psi(\mathbf{n})$ has no zeroes. Consequently, the energy gap $\Delta(\mathbf{n})$ does not vanish anywhere on the Fermi surface and all the results previously obtained remain in force (it is easy to see that if the gap were to vanish at some point on the Fermi surface, the specific heat $C_S(T)$ would vary in the low-temperature region not exponentially, but in accordance with a power law, which would apparently be in contradiction with the experimental data). Unfortunately, we cannot point to a necessary criterion for the absence of zeroes in the function $\psi(\mathbf{n})$. Thus, an account of the possible creation of "asymmetrical" pairs does not change the results of the theory. In particular, all the universal relations given in Sec. 1 remain in force.

4. OTHER POSSIBLE CAUSES OF DISAGREEMENT BETWEEN EXPERIMENT AND THEORY

The contradictions between the predictions of the theory and the results of the experiment may also be due to the fact that the theory uses essentially the concept of free quasiparticles. This concept is suitable only for temperatures at which the average energy of the quasiparticles is considerably higher than the damping. On approaching T_{cr}, the gap decreases, on the one hand, but damping due to collisions of the quasiparticles with one another, with phonons, and with impurities increases, on the other. Consequently, at a certain temperature the concept of quasiparticles ceases to correspond to reality (in the case of a polycrystalline superconductor, additional damping is produced also by the boundaries of the crystallites, which assume the same role as impurities). For collisions with phonons, the temperature interval in which the quasiparticle concept ceases to be suitable was estimated by Éliashberg[4] and was found to be quite small [$\sim (\Delta/\omega_0)^4 T_{cr}$].

It is easy to present also a more general estimate, based directly on the experimental data. From the measurements of the specific heat of superconductors[8,18] it follows that for typical specimens the collision frequency is

$$\tau^{-1} \sim 10^{10} - 10^{11}\,\text{sec}^{-1}.$$

The concept of free quasiparticles becomes meaningless when $1/\tau$ becomes of the same order of magnitude as Δ. From this we have at temperatures close to critical

$$\Delta = \Delta_0 \sqrt{1 - T_{cr}/T} \sim 10^{10} - 10^{11},$$

$$(T - T_{cr})/T_{cr} \sim 10^{-1} - 10^{-3}.$$

The experimental data presently available do not make it possible to ascertain whether an excess increase in specific heat occurs in the narrow temperature interval near T_{cr}. From the proposed explanation for the disparity between the experimental data on the specific-heat jumps and the theory it follows that $\Delta C/C_n$ is highly dependent on the degree of purity of the sample. Nor do the available experimental data enable us to judge whether such a dependence exists.

The discrepancy between experiment and the theoretical results can in principle be attributed also to the contribution of the higher approximations in the coupling constant and also to the fact that the quantity ω_0 (or ω in [3]) is in fact a function of the temperature. Let us consider first the influence of the second effect. Integration with respect to ξ in the right half of (1) yields at $T = 0$, accurate to ω/μ, the expression

$$\int_{-\infty}^{\infty} U(\mathbf{p}, \mathbf{p}') \frac{\Delta(\mathbf{p}')}{\varepsilon(\mathbf{p}')} d\xi' = U(\mathbf{p}, \mathbf{n}') \ln \frac{2\omega(\mathbf{p}, \mathbf{n}')}{\Delta(\mathbf{n}')}, \qquad (49)$$

where $\omega(\mathbf{p}, \mathbf{n}')$ is of the order of the Debye frequency.

It can be proved (see the appendix) that, accurate to quantities $\sim \Delta/\omega$, $\omega(\mathbf{p}, \mathbf{n}')$ depends functionally only on the ratios $U(\mathbf{p}, \mathbf{p}')/U(\mathbf{p}, \mathbf{n}')$ and $\Delta(\mathbf{p}')/\Delta(\mathbf{n}')$, but is independent of $\Delta(\mathbf{n})$.

Choosing $\mathbf{p}$ also on the Fermi surface, we obtain from (1) the equations

$$\Delta(\mathbf{n}) = g \int U(\mathbf{n}, \mathbf{n}') \Delta(\mathbf{n}') \ln \frac{2\omega(\mathbf{n}, \mathbf{n}')}{\Delta(\mathbf{n}')} \frac{d\sigma'}{v_F'}, \qquad T = 0. \qquad (50)$$

$$\Delta(\mathbf{n}) = g \int U(\mathbf{n}, \mathbf{n}') \Delta(\mathbf{n}') \left[\ln \frac{2\omega(\mathbf{n}, \mathbf{n}')}{\Delta(\mathbf{n}')} - F(\beta\Delta(\mathbf{n}')) \right] \frac{d\sigma'}{v_F'}, \qquad T \neq 0. \qquad (51)$$

If we now seek, following [3], a solution of (50) or (51) in the form

$$\Delta(\mathbf{n}) = 2\omega_0 e^{-\Lambda/g}[Q\psi(\mathbf{n}) + \varphi_1(\mathbf{n})], \quad (52)$$

where $\varphi_1(\mathbf{n})$ is a correction of the order of g, and define the constant ω by means of

$$\ln\omega_0 = \frac{\Lambda}{p_0}\int U(\mathbf{n},\mathbf{n}')\,\psi(\mathbf{n})\,\psi(\mathbf{n}')\ln\omega(\mathbf{n},\mathbf{n}')\frac{d\sigma}{v_F}\frac{d\sigma'}{v_F'}, \quad (53)$$

then all the results obtained in [3] remain in force.

Since $\omega(\mathbf{n},\mathbf{n}')$ depends functionally on $\Phi(\mathbf{p}) = \Delta(\mathbf{p})/\Delta(\mathbf{n})$, both $\omega(\mathbf{n},\mathbf{n}')$ and ω_0 are functions of the temperature. Let us show, however, that $\omega_0(T_{cr})$ and $\omega_0(0)$ coincide in the isotropic model, with relative accuracy $\sim\Delta/\omega$. Indeed, in the isotropic model $\Delta(\xi)$ is determined from the formulas

$$\Delta(\xi) = g\Delta(0)\int U(\mathbf{p},\mathbf{n}')\ln\frac{2\omega(\mathbf{p},\mathbf{n}')}{\Delta_0}\frac{d\sigma}{v_F} \qquad (T=0), \quad (54)$$

$$\Delta(\xi) = g\Delta(0)\int U(\mathbf{p},\mathbf{n}')\ln\frac{2\omega(\mathbf{p},\mathbf{n}')\gamma}{\pi T_{cr}}\frac{d\sigma}{v_F} \qquad (T\approx T_{cr}). \quad (55)$$

The equation for the energy gap has at T = 0 the form

$$1 = gU_0\ln(2\omega_0(0)/\Delta_0). \quad (56)$$

The critical temperature is determined by the relation

$$1 = gU_0\ln(2\omega_0(T_{cr})\gamma/\pi T_{cr}), \quad (57)$$

where ω_0 is determined, independently of the temperature, from the equation

$$\ln\omega_0 = \frac{1}{U_0}\int U(\mathbf{n},\mathbf{n}')\ln\omega(\mathbf{n},\mathbf{n}')\frac{d\sigma}{v_F}\frac{d\sigma'}{v_F'},$$

$$U_0 = \iint U(\mathbf{n},\mathbf{n}')\frac{d\sigma}{v_F}\frac{d\sigma'}{v_F'}. \quad (58)$$

From (54) — (58) we get

$$\Phi(\xi) \equiv \frac{\Delta(\xi)}{\Delta(0)} = \frac{1}{U_0}\int U(\mathbf{p},\mathbf{n}')\frac{d\sigma'}{v_F'} + g\int U(\mathbf{p},\mathbf{n}')\ln\frac{\omega(\mathbf{p},\mathbf{n}')}{\omega_0}\frac{d\sigma'}{v_F'} \quad (59)$$

both when T = 0 and when $T = T_{cr}$. Since $\omega(\mathbf{p},\mathbf{n}')$ depends, apart for terms $\sim\Delta/\omega$, only on $\Phi(\xi)$ and not on Δ, the values of $\omega(\mathbf{n},\mathbf{n}')$ for $T = 0$ and $T = T_{cr}$ coincide with the same degree of accuracy. Consequently $[\omega_0(T_{cr}) - \omega_0(0)]/\omega_0(0)$ is of the order of Δ/ω_0 in the isotropic model. One of the main relations of the theory, $\Delta(0)/T_{cr} = 1.76$, is obviously satisfied with the same accuracy.

In view of the fact that $[\omega_0(T_{cr}) - \omega_0(0)]/\omega_0$ does not contain in the isotropic model terms proportional to g, it is natural to assume that in the anisotropic theory this quantity will be at least of order ag, where a is the anisotropy parameter, which we define by means of the formula

$$a^2 = \int(\psi-1)^2\frac{d\sigma}{p_0 v} = 2\left(1 - \int\psi\frac{d\sigma}{p_0 v_F}\right). \quad (60)$$

A calculation, which is too cumbersome to present here, confirms this assumption. (In the intermediate range of temperatures ω_0 differs from $\omega_0(0)$ and $\omega_0(T_{cr})$ by an amount $\sim g\omega_0$ in both the isotropic and the anisotropic theory.)

Let us estimate the deviation of Q(0) from unity, assuming the parameter a to be small. We have

$$1 - Q \cong -\ln Q = \int\psi^2\ln\psi\frac{d\sigma}{p_0 v_F}$$

$$\cong \int\psi^2(\psi-1)\frac{d\sigma}{p_0 v_F} = \frac{3}{2}a. \quad (61)$$

Let us examine, finally, the contribution made to Eq. (2) by higher approximations in g. At temperatures close to T_{cr}, using the asymptotic expression for the function F(x) (see [19]), we obtain for the gap $\Delta(\mathbf{n})$ the equation

$$\Delta(\mathbf{n}) = \left(\Lambda + g\ln\frac{T_{cr}}{T}\right)\int U(\mathbf{n},\mathbf{n}')\Delta(\mathbf{n}')\frac{d\sigma'}{v_F'}$$

$$- g\int U(\mathbf{n},\mathbf{n}')\Delta(\mathbf{n}')\left[-\lambda\frac{\Delta^2(\mathbf{n}')}{T^2} + \ldots\right]\frac{d\sigma'}{v_F'}, \quad (62)$$

from which we see that as $T \to T_{cr}$ the actual expansion is not in the coupling constant g, but in $(T - T_{cr})/T_{cr}$. Consequently the contribution of the higher approximations is always small at sufficiently small $T - T_{cr}$. When $T \ll T_{cr}$, account of the higher approximations in the coupling constant can be readily carried out and leads to an effective increase in Q(0) by an amount $\sim ga^2$.

5. COMPARISON OF THE THEORETICAL AND EXPERIMENTAL RESULTS

We now turn to an examination of Tables I and II and continue the comparison of the theoretical conclusions with the experimental results. We start with an examination of the quantity $\Delta_{min}(0)/T_{cr}$ and see what deviations from inequality (12) can be expected for real superconductors. We have already seen that inclusion of the next approximation in the coupling constant leads to an effective increase of Q by an amount $\sim ga^2$, which makes the inequality "worse." Another possible cause of the violation of inequality (12) is the temperature variation of ω_0. This change is of indefinite sign and has, as we have seen, an order of magnitude ga.

Since the deviation of Q from unity is $\sim a^2$ [see (61)], the satisfaction of inequality (12) could be assured for all superconductors for which

$g \ll a$. No such superconductors exist in nature, so that we can speak only of the probable satisfaction of inequality (12) for rigid superconductors with maximum values $\omega/T_{cr} \sim e^{\Lambda/g}$ and with anisotropy a.

Measurements of $\Delta_{min}(0)$ have been made on the basis of two different principles: 1) determination of the absorption threshold of infrared radiation in superconductors, and 2) measurement of the specific heat of the superconductor at $T \ll T_{cr}$. As can be seen from Table II, measurements of the infrared absorption threshold were made by Richards and Tinkham for superconductors with large values of g and have led to the conclusion that inequality (12) is violated in many cases (Pb, Hg, In, Sn). Although, as shown above, failure to satisfy inequality (12) does not strictly speaking contradict the theory, nevertheless in the case of Hg, and particularly in the case of In, which has an almost spherical Fermi surface, the deviation of $\Delta_{min}/1.76\, T_{cr}$ from unity is exceedingly large. Thus, to obtain agreement with experiment, it becomes necessary to assign to In a parameter $a \sim 0.4$, which is of little likelihood.

Possible reasons of these discrepancies will be analyzed elsewhere. Unlike the threshold measurements, measurements of the specific heat in the low temperature region[8,18,20] yield for all superconductors, with the exception of Nb, a value of $\Delta_{min}(0)/T_{cr}$ which agrees with inequality (12).

Let us consider further the data pertaining to the critical magnetic field. According to estimates of the preceding section, $\chi - 1.06 \sim a^2$. The main reason for the possible failure to satisfy inequality (18) is the difference between $\omega_0(0)$ and $\omega_0(T_{cr})$. This leads to an effective change in χ by a factor $[\omega_0(T_{cr})/\omega_0(0)]^2 = 1 \pm bga$ (b — constant on the order of unity). Thus, inequality (18) should be satisfied also for superconductors with $g/a < 1$. There are only a few exact measurements of χ. As can be seen from Table II the values of χ obtained for Ga, Al, In, Sn, and Tl agree with inequality (18). This inequality, according to Shoenberg[9], is violated for Hg, but the deviation can be attributed to the difference between $\omega_0(T_{cr})$ and $\omega_0(0)$ for reasonable values of the anisotropic coefficient a.

Inequality (19) is noticeably violated for mercury and lead. This is not at all strange, in view of the large values of g of these metals.

What is striking is the unexpectedly small value of $H_{cr}^2(0)/T_{cr}C_n(T_{cr})$ for Tl,[7,8] and the associated violation of inequality (20). However, the value of $C_n(T_{cr})$ for Tl, determined by calorimetric means, is utterly unreliable, since when $T \sim T_{cr} = 2.39°K$ the electronic part of the specific heat amounts to less than 3% of the lattice part. Magnetometric data[8] are apparently much more reliable. They lead to satisfactory agreement with relations (19) and (20).

APPENDIX

We consider the integral

$$P = \int_0^\infty \frac{f(\xi)\, d\xi}{\sqrt{\xi^2 + \Delta^2}}, \tag{A.1}$$

Assuming that $f(\xi)$ decreases rapidly when $\xi \gtrsim \omega$, with $\omega \gg \Delta$. Integrating by parts, we obtain

$$P = -\int_0^\infty f'(\xi) \ln \frac{2\xi}{\Delta}\, d\xi - \int_0^\infty f'(\xi) \ln\left(\frac{1}{2} + \frac{1}{2}\sqrt{1 + \frac{\Delta^2}{\xi^2}}\right) d\xi. \tag{A.2}$$

It is easy to show that the second integral in the right half of (A.2) has the order Δ/ω. Actually, the substitution $\Delta/\xi = y$ reduces it to the form

$$\Delta \int_0^\infty f'\left(\frac{\Delta}{y}\right) \ln\left(\frac{1}{2} + \frac{1}{2}\sqrt{1 + y^2}\right) \frac{dy}{y^2}, \tag{A.3}$$

where the integral with respect to y converges as $\Delta \to 0$. From this we have

$$P = f(0) \ln \frac{2\omega}{\Delta}, \qquad \ln \omega = -\int_0^\infty \frac{f'(\xi)}{f(0)} \ln \xi\, d\xi, \tag{A.4}$$

i.e., ω is functionally dependent only on the ratio $f(\xi)/f(0)$, but not on Δ.

We have assumed so far that $\Delta = \text{const}$. The derivation remains in force also if $\Delta = \Delta(\xi)$ is a slowly varying function of ξ. Indeed, the difference from the case $\Delta = \text{const}$ reduces to the appearance in the integrand of (A.2) of a factor

$$[(\xi^2 + \Delta_0^2)/(\xi^2 + \Delta^2(\xi))]^{1/2} \qquad (\Delta_0 = \Delta(0)),$$

which is quite close to unity at both small and large ξ. In this connection, the result remains the same accurate to $(\Delta_0/\omega)^2$.

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