THE CRITICAL SUPERCOOLING FIELD IN SUPERCONDUCTIVITY THEORY

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The magnitude of the critical supercooling field H_{c1} in superconductivity theory[1] is determined. It is found that the field H_{c1} is larger than or smaller than the critical field H_c, depending on whether the superconductor in a weak field is of the London or of the Pippard type. The superconductor in the first case must in a strong field display a behavior similar to that of alloys. The magnitude of the ratio H_{c1}/H_c depends weakly on the temperature in the whole temperature range.

It is well known that superconducting metals in a magnetic field undergo at some value of the field a phase transition from the normal to the superconducting phase. For a bulk specimen this transition is a first-order transition; the value of the critical magnetic field H_c can thus be obtained from thermodynamic considerations and was evaluated by Bardeen, Cooper, and Schrieffer (BCS) in their theory of superconductivity.[1] Along with the thermodynamic field there exist, apparently, for a given temperature, still two other critical field values corresponding to the so-called "superheating" field and the "supercooling" field H_{c1}. These fields determine a region of possible hysteresis: for fields above H_c, but below the superheating field the superconducting phase is metastable and, on the other hand, for field values below H_c, but above H_{c1} the normal phase is metastable. (We understand by metastability, as always, an instability with respect to a finite perturbation.) To determine the magnitude of these fields thermodynamic considerations are insufficient and one must turn to the microscopic theory of superconductivity. Using an earlier developed method[2] the existence in the BCS theory of a "supercooling" field is proved in the present paper and its magnitude is found.

In the method mentioned above, the superconductor is described by two Green functions $G(x, x')$ and $F^+(x, x')$, and equations for these in a magnetic field can in the usual manner be obtained from the field-free equations. We shall first consider the absolute zero. These equations are then of the form

$$\left\{i\frac{\partial}{\partial t}+\frac{1}{2m}\left(\frac{\partial}{\partial \mathbf{r}}-ie\mathbf{A}(\mathbf{r})\right)^2+\mu\right\}G(x,x')+i\Delta(\mathbf{r})F^+(x,x')=\delta(x-x'),$$

$$\left\{i\frac{\partial}{\partial t}-\frac{1}{2m}\left(\frac{\partial}{\partial \mathbf{r}}+ie\mathbf{A}(\mathbf{r})\right)^2-\mu\right\}F^+(x,x')-i\Delta^*(\mathbf{r})G(x,x')=0, \quad (1)$$

where

$$\Delta^*(\mathbf{r})=|g|F^+(x,x), \quad (2)$$

In a constant magnetic field $G(x, x')$ and $F^+(x, x')$ are functions of the difference in the time variables, $t-t'$; expanding all quantities in Fourier integrals in this difference we get for the Fourier components $G_\omega(\mathbf{r}, \mathbf{r}')$ and $F^+_\omega(\mathbf{r}, \mathbf{r}')$ the following set of equations

$$\left\{\omega+\frac{1}{2m}\left(\frac{\partial}{\partial \mathbf{r}}-ie\mathbf{A}(\mathbf{r})\right)^2+\mu\right\}G_\omega(\mathbf{r},\mathbf{r}')+i\Delta(\mathbf{r})F^+_\omega(\mathbf{r},\mathbf{r}')=\delta(\mathbf{r}-\mathbf{r}'),$$

$$\left\{-\omega+\frac{1}{2m}\left(\frac{\partial}{\partial \mathbf{r}}+ie\mathbf{A}(\mathbf{r})\right)^2+\mu\right\}F^+_\omega(\mathbf{r},\mathbf{r}')+i\Delta^*(\mathbf{r})G_\omega(\mathbf{r},\mathbf{r}')=0; \quad (1')$$

$$\Delta^*(\mathbf{r})=|g|(2\pi)^{-1}\int_{-\infty}^{+\infty}d\omega F^+_\omega(\mathbf{r},\mathbf{r}). \quad (2')$$

The value H_{c1} of the supercooling field is the boundary itself of the metastability of the normal phase; at smaller fields the normal phase is absolutely unstable with respect to the appearance of a superconducting phase. We are, of course, not talking of the appearance of small layers of the superconducting phase but about the possibility that there appears that specific correlation between electrons which is caused by the interaction between them and which leads to the superconductivity phenomenon, and which finds an expression in the existence of a non-vanishing function $F^+(x, x')$. The metastability of the normal phase for fields $H > H_{c1}$ means instability with respect to the occurrence of finite values of $F^+(x, x')$ and $\Delta(\mathbf{r})$. In the point H_{c1} there occurs for the first time a solution with infinitesimal $\Delta(\mathbf{r})$ and $F^+(x, x')$. This makes it possible to simplify the set (1′) essentially, retaining in the equations only the first nonvanishing terms for small $\Delta(\mathbf{r})$. Furthermore, the magnetic field is uniform in the normal phase; it is convenient to take the vector potential $\mathbf{A}(\mathbf{r})$ in the form $A_x = -Hy$, $A_y = A_z = 0$. The second of Eqs. (1′) takes the following form

$$\left\{-\omega + \frac{1}{2m}\left[\left(\frac{\partial}{\partial x} - \frac{ieHy}{c}\right)^2 + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \mu\right\} F_\omega^+(\mathbf{r}, \mathbf{r}') - i\Delta^*(\mathbf{r})\widetilde{G}_\omega(\mathbf{r}, \mathbf{r}') = 0. \quad (3)$$

In this equation $\widetilde{G}_\omega(\mathbf{r}, \mathbf{r}')$ is the Green function of the electrons in the normal metal:

$$\left\{\omega + \frac{1}{2m}\left[\left(\frac{\partial}{\partial x} + \frac{ieHy}{c}\right)^2 + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right] + \mu\right\} \widetilde{G}_\omega(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (4)$$

If we rewrite (4) in such a way that the differentiation is with respect to the variables $\mathbf{r}'$:

$$\left\{\omega + \frac{1}{2m}\left[\left(\frac{\partial}{\partial x'} - \frac{ieHy'}{c}\right)^2 + \frac{\partial^2}{\partial y'^2} + \frac{\partial^2}{\partial z'^2}\right] + \mu\right\} \widetilde{G}_\omega(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (4')$$

we can use (4′) and (3) to write the function $F_\omega^+(\mathbf{r}, \mathbf{r}')$ in the following form

$$F_\omega^+(\mathbf{r}, \mathbf{r}') = -i\int \widetilde{G}_\omega(\mathbf{s}, \mathbf{r}')\widetilde{G}_{-\omega}(\mathbf{s}, \mathbf{r})\Delta^*(\mathbf{s})\, d^3s. \quad (5)$$

Substitution of (5) into (2) leads to an integral equation for $\Delta^*(\mathbf{s})$:

$$\Delta^*(\mathbf{r}) = -i|g|\frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega \int \widetilde{G}_\omega(\mathbf{s}, \mathbf{r})\, \widetilde{G}_{-\omega}(\mathbf{s}, \mathbf{r})\Delta^*(\mathbf{s})\, d^3s. \quad (6)$$

The value of the magnetic field for which there occurs for the first time (coming from large fields) a nonvanishing solution of this equation is then just the value of the supercooling field H_{c1} which interests us.

For what follows, it is necessary to determine the form of the function $\widetilde{G}_\omega(\mathbf{r}, \mathbf{r}')$. We perform the transformation

$$\widetilde{G}_\omega(\mathbf{r}, \mathbf{r}') = \exp\left\{-\frac{ieH}{2c}(y + y')(x - x')\right\}\widetilde{G}'_\omega(\mathbf{r} - \mathbf{r}'). \quad (7)$$

After substituting this expression into (4) the coefficients in the equation for $\widetilde{G}_\omega(\mathbf{r} - \mathbf{r}')$ are functions of the difference, namely,

$$\left\{\omega + \frac{1}{2m}\left(\frac{\partial}{\partial \mathbf{r}} - \frac{ie}{2c}\mathbf{H}\times[\mathbf{r} - \mathbf{r}']\right)^2 + \mu\right\}\widetilde{G}'_\omega(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \quad (8)$$

Thanks to this $\widetilde{G}'_\omega(\mathbf{r} - \mathbf{r}')$ clearly also depends only on the difference $\mathbf{R} = \mathbf{r} - \mathbf{r}'$. If there is no field the Green function $G_{0\omega}(R)$ is, as can easily be checked, of the form

$$G_{0\omega}(\mathbf{R}) = \begin{cases} -(m/2\pi R)\exp[ip_0R + i\omega R/v], & \omega > 0 \\ -(m/2\pi R)\exp[-ip_0R + i\omega R/v], & \omega < 0 \end{cases} \quad (|\omega| \ll \mu). \quad (9)$$

Such a choice of the solutions of (8) without a field was made in accordance with the requirement that the imaginary part of the Green function changes sign when the frequency changes sign.[3] We shall show that the function $\widetilde{G}'_\omega(\mathbf{R})$ in (7) is the same as its value (9) without a field. Looking ahead we note that in the following we require distances R of the order of ξ_0 where ξ_0 is the parameter in the BCS theory which is connected with the value Δ_0 of the gap in the spectrum at $T = 0$ and which is equal to $\xi_0 \sim \hbar v/\Delta_0$. It turns out that one can neglect at those distances the term quadratic in the field in (8), or in other words, that the curving of the electrons in the fields of interest to us is very small. Under those conditions it is convenient, because of the large value of p_0, to look for solutions of (8) in the form $\exp\{i\varphi(R)\}G_{0\omega}(R)$, where $G_{0\omega}(R)$ is the Green function (9) when there is no field present. Substituting this expression into (8) leads to the following equation for $\varphi(R)$, which contains only quadratic terms in the field:

$$\mp p_0\partial\varphi/\partial R - (e^2/4c^2)([\mathbf{H}\times\mathbf{R}])^2 = 0,$$

[the ± sign in this equation depends on the sign of the frequency in accordance with (9)]. As will become clear below, the fields of interest to us are such that $eH\xi_0^2/c \sim 1$. Therefore, $\varphi(R)$ which is determined by this equation will give a correction in the phase factor in (7) of the order of $1/p_0\xi_0$, i.e., an insignificant quantity of the order 10^{-4}.

Substituting (7) and (9) into (6) and integrating over the frequency we get the following equation

$$\Delta^*(\mathbf{r}) = \frac{mp_0}{2\pi^2}\frac{|g|}{2\pi}\int\frac{\exp\{(ieH/c)(y + y')(x - x')\}}{|\mathbf{r} - \mathbf{r}'|^3}\Delta^*(\mathbf{r}')\, d^3r'. \quad (10)$$

The kernel of this equation leads to a logarithmic divergence when we integrate the right hand side for $\mathbf{r} = \mathbf{r}'$, which is connected with the fact that the relation (2) determines the gap $\Delta(\mathbf{r})$ as the value of the function F^+ for equal arguments. This definition is somewhat inaccurate. The fact is that in the BCS model the interaction Hamiltonian which leads to superconductivity was chosen in the form

$$H_{int} = \frac{g}{2} \sum_{p_1+p_2=p_3+p_4} a^+_{p_1\sigma_1} a^+_{p_2\sigma_2} a_{p_3\sigma_2} a_{p_4\sigma_1} \tag{11}$$

with a constant coupling constant for all electrons with energies in a narrow layer $\hbar\tilde{\omega}$ in the neighborhood of the Fermi surface. This cutting off is realized in (11) by the functions θ_p:

$$\theta_p = \begin{cases} 1, & |\varepsilon_p - \varepsilon_F| < \tilde{\omega} \\ 0, & |\varepsilon_p - \varepsilon_F| > \tilde{\omega} \end{cases}.$$

The quantity $\tilde{\omega}$ enters logarithmically in the determination of the gap Δ_0, in the Fermi spectrum:

$$1 = |g|(mp_0/2\pi^2)\ln(2\tilde{\omega}/\Delta_0).$$

To the cut-off in momentum representation there corresponds, in coordinate space, some spreading out over distances of the order $\hbar v/\tilde{\omega}$. Using (11) for the interaction Hamiltonian and repeating the derivation of the equations in reference 2, we find easily that the quantity $\Delta^*(\mathbf{r})$ is connected with the function $F^+(x, x')$ in the following manner:

$$\Delta^*(\mathbf{r}) = \iint \theta(\mathbf{r}-\mathbf{s})\,\theta(\mathbf{r}-\mathbf{m})\,F^+(t, \mathbf{s}; t, \mathbf{m})\,d^3s\,d^3\mathbf{m}, \tag{2''}$$

where $\theta(R)$ is a smearing out function corresponding to the cut-off function θ_p in the momentum representation:

$$\theta(\mathbf{R}) = (2\pi)^{-3}\int e^{i\mathbf{p}\mathbf{R}}\theta_p d^3p = \frac{p_0}{\pi^2}\frac{\sin p_0 R}{R}\frac{\sin(\tilde{\omega}R/v)}{R}. \tag{12}$$

On this basis we must, strictly speaking, write Eq. (6) in the form

$$\Delta^*(\mathbf{r}) = i|g|\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\int \overline{G_\omega(\mathbf{s}, \mathbf{r})}\,\overline{G_{-\omega}(\mathbf{s}, \mathbf{r})}\,\Delta^*(\mathbf{s})\,d^3s, \tag{6'}$$

denoting by $\tilde{G}_\omega(\mathbf{r}, \mathbf{r}')$ the integral over the Green function (7):

$$\overline{G_\omega(\mathbf{r}, \mathbf{r}')} = \int \theta(\mathbf{r}-\mathbf{s})\,G_\omega(\mathbf{s}, \mathbf{r}')\,d^3s.$$

The field dependent phase factor in (7) can be taken out from under the integral sign in the last expression since $\theta(\mathbf{r}-\mathbf{s})$ has the character of a δ-function. It amounts thus practically to replacing $G_{0\omega}(R)$ in the previous calculations [see Eq. (9)] by

$$\overline{G_{0\omega}(R)} = (2\pi)^{-3}\int e^{i\mathbf{p}\mathbf{R}} G_{0\omega}(\mathbf{p})\,\theta_p d^3p.$$

Following this, all expressions stay finite. We have succeeded in eliminating the cut-off quantity using the relation (2″), which determines the gap in the energy spectrum at $T = 0$ when there is no field. One verifies easily, by evaluating the corresponding function $F_0^+(t, \mathbf{r}; t, \mathbf{r}')$ through the Fourier components found in reference 2, that

$$F_0^+(t, \mathbf{r}; t, \mathbf{r}') = \frac{m\Delta_0}{2\pi^2}\frac{\sin p_0 R}{R} K_0\left(\frac{R\Delta_0}{v}\right), \tag{13}$$

where K_0 is a Bessel function of imaginary argument which tends logarithmically to infinity for small R.

Substituting (13) into (2″) and noting that the function $\theta(\mathbf{r})$ possesses the following δ-function property

$$\int \theta(\mathbf{r}-\mathbf{s})\,\theta(\mathbf{s})\,d^3s = \theta(\mathbf{r})$$

(this equation can be most easily checked by the Fourier components) we get, using the form (12) for the function $\theta(\mathbf{R})$ and averaging the fast oscillating factors:

$$1 = |g|\frac{mp_0}{4\pi^4}\int K_0\left(\frac{R\Delta_0}{v}\right)\frac{\sin(\tilde{\omega}R/v)}{R^3}d^3R$$

$$= \frac{m^2|g|}{4\pi^4}\int\left(\int_0^{\tilde{\omega}}\frac{\cos(R\xi/v)}{R^2}d\xi\right)K_0\left(\frac{R\Delta_0}{v}\right)d^3R.$$

Integrating over $d|\mathbf{R}|$ in the last expression by parts we find

$$\frac{1}{|g|} = -\frac{m^2\Delta_0}{4\pi^4}\int_0^{\tilde{\omega}}\frac{d\xi}{\xi}\int\frac{\sin(R\xi/v)}{R^2}K_1(R\Delta_0/v)\,d^3R.$$

This expression for $1/|g|$ is convenient because the integral over d^3R posssesses the same singularity as Eq. (10) when $\tilde{\omega} \to \infty$.

After substituting this expression into (6) we get an equation in which the logarithmically diverging terms are cancelled after which $\tilde{\omega}$ can tend to infinity. Omitting the intermediate calculations we shall give the final form of (10), taking into account that the function $\Delta^*(\mathbf{r})$ depends on the coordinate y only:

$$\Delta^*(y)\ln\left(\frac{e\gamma\Delta_0}{v}\varepsilon\right)$$

$$= -\frac{1}{2}\int_{-\infty}^{\infty}\frac{\exp\{-|(eH/c)(y^2-y'^2)|\}}{|y-y'|}\Delta^*(y')\,d_\varepsilon y'.$$

[We shall show below that the general form of the function $\Delta^*(\mathbf{r})$ corresponding to a given value of H_{c1} can be found by a simple method in terms of the solution of this equation.] Here γ is Euler's constant, ϵ an infinitesimal constant introduced to cause the integration on the right hand side to be performed only over a distance $|y - y'| \geq \epsilon$. Thanks to the logarithmic character of the singularity on the right hand side, ϵ disappears from the final results. It is convenient to introduce dimensionless variables $\xi = y\sqrt{eH/c}$ in which the equation becomes

$$\Delta^*(\xi)\ln\left(\frac{e\gamma\Delta_0\delta}{v\sqrt{eH/c}}\right) = -\frac{1}{2}\int_{-\infty}^{\infty}\frac{\Delta(\xi')\exp\{-|\xi^2-\xi'^2|\}}{|\xi-\xi'|}d\xi'. \quad (14)$$

The largest value of the magnetic field, for which a solution that decreases at infinity exists for (14), is just the value of the critical field H_{c1}, the "supercooling" field. Equation (14) can only be solved numerically. We shall show that (14) has a maximum eigenvalue for the magnetic field and we shall estimate its magnitude. To do this we add to and subtract from $\Delta(\xi')$ under the integral on the right hand side of (14) the value $\Delta(\xi)$. After this (14) is transformed to the following form, which no longer contains the infinitesimal constant δ:

$$\Delta^*(\xi)\ln\left(\frac{\Delta_0 e}{v}\sqrt{\frac{\gamma c}{eH}}\right) = \Phi(\xi)\Delta^*(\xi) - \frac{1}{2}\int_{-\infty}^{\infty}\frac{\exp\{-|\xi^2-\xi'^2|\}}{|\xi-\xi'|}[\Delta^*(\xi')-\Delta^*(\xi)]d\xi'. \quad (15)$$

The function $\Phi(\xi)$ is here equal to

$$\Phi(\xi) = e^{-\xi^2}\int_0^{|\xi|}e^{\xi'^2}\xi'\ln\frac{|\xi|+\xi'}{|\xi|-\xi'}d\xi'.$$

Multiplying (15) by $\Delta(\xi)$ and integrating over ξ we get

$$|\Delta|^2\ln\left(\frac{e\Delta_0}{v}\sqrt{\frac{\gamma c}{eH}}\right) = \int_{-\infty}^{\infty}\Phi(\xi)|\Delta(\xi)|^2d\xi + \frac{1}{4}\int\int_{-\infty}^{\infty}\frac{\exp\{-|\xi^2-\xi'^2|\}}{|\xi-\xi'|}|\Delta(\xi)-\Delta(\xi')|^2d\xi'd\xi. \quad (15')$$

Since $\Phi(\xi) > 0$ it follows from the fact that the right-hand side is positive that

$$eH/c \leqslant \Delta_0^2 e^2\gamma/v. \quad (16)$$

We can obtain the value of H_{c1} approximately (and conceivably with great accuracy) by a variational method if we choose $\Delta(\xi)$ in the form of $\exp(-\alpha\xi^2)$. With such a form for $\Delta(\xi)$ all integrals in the variational principle for (14) can be evaluated and the maximum value of H arises when $\alpha = 1$ and is equal to

$$H_{c1} \approx (e^2\gamma/2)(c\Delta_0^2/ev).$$

One can show that a lower limit is then obtained for the value of H_{c1}. The theory gives for the thermodynamic critical field H_c at $T = 0$

$$H_c = \Delta_0\sqrt{2mp_0/\pi}.$$

The ratio of the two fields is

$$H_{c1}/H_c = 1.77(3\pi T_c mc/e)(2\pi m/7\zeta(3)p_0^5)^{1/2} \quad (17)$$

[$\zeta(x)$ is Riemann's zeta-function; $\vartheta(3) = 1.202$]. It is convenient to write this quantity as follows. We have shown earlier[4] that in a sufficiently narrow region of temperatures near T_c the equations of the phenomenological Ginzburg-Landau theory[5] with a double charge follow from the theory of superconductivity. The phenomenological constant κ of this theory was defined microscopically and turned out to be equal to

$$\varkappa = (3\pi T_c mc/e)(2\pi m/7\zeta(3)p_0^5)^{1/2}. \quad (18)$$

If the ratio (17) is expressed in terms of this constant it can be written as follows

$$H_{c1}/H_c = 1.77\varkappa. \quad (19)$$

Near T_c the result of the Ginzburg-Landau theory[5] must hold, i.e.,

$$H_{c1}/H_c = \sqrt{2}\varkappa. \quad (20)$$

We see that the change in the ratio H_{c1}/H_c is small in the whole of the temperature range and does not exceed 25%.

It is interesting that according to (18) — (20) the magnitude of the field H_{c1} does by no means have to be less than H_c, not even for pure superconductors. Moreover, it is well known that in the new theory we can distinguish among the pure superconductors two classes depending on their properties in a weak magnetic field. For superconductors of the first class the penetration depth δ is at all temperatures appreciably larger than the parameter ξ_0 of the BCS theory. Such superconductors satisfy the electrodynamics of the Londons and may be called London superconductors (see the survey by Abrikosov and Khalatnikov[6]). The criterion for this case $\delta \gg \xi_0$ can be written as the condition $\kappa \gg 1$ (more accurately $\kappa \gg 0.4$). The opposite case may be called the Pippard case. Here, the penetration depth is in the whole of the temperature range, except in the immediate vicinity of T_c, much less than ξ_0, and the London equation is replaced by a more complicated nonlocal relation. The corresponding criterion will be $\kappa \ll 1$. The majority of the known pure superconductors belongs to the last or to an intermediate type. It is clear from (18) and (20) that if a superconductor belongs to the Pippard class the condition $H_{c1} \ll H_c$ is sure to be satisfied. In the London case, however, H_{c1} must be larger than H_c. In other words, a metal the behavior of which in a weak field shows the London character must display in a strong field the characteristic properties of alloys: a negative surface energy, a smeared out transition, and so on. Abrikosov[7] studied alloys in the phenomenological Ginzburg-Landau theory from this point of view and showed that superconductors with $\kappa > 1/\sqrt{2}$ possess such properties.

Apart from T_c, the combination of quantities that make up the constant κ according to (18) contains also the effective electron mass m at the Fermi surface and the Fermi momentum p_0; expressing κ in terms of the density of the number of "free electrons" $n = p_0^3/3\pi^2$ we get

$$\varkappa = 0.485\, kT_c c m^{3/2} / e\hbar^2 n^{5/6}.$$

To determine m and n from experimental data we choose as one of the quantities the value of the critical magnetic field H_{c0} at $T = 0$, which is expressed as follows in terms of m and n:

$$H_{c0} = 2{,}48\, \hbar^{-1} m^{1/2} n^{1/6} kT_c.$$

We can take as the second quantity, for instance, data on the anomalous skin-effect in the normal state. The magnitude of the active part of the resistance R yields n directly:[8]

$$n = (\pi^{5/2} 3^{5/4} \omega^3 \hbar^{3/2} / c^6 e^3)\, R^{-9/2}.$$

When we evaluate the processed data on the specific heat in the normal state and the magnitude of R for the anomalous skin effect in reference 1 (see reference 9) we find $\kappa = 0.011$ for aluminum and $\kappa = 0.135$ for tin. At the same time we must note that this method is rather unreliable, since the result is very sensitive to a change in the magnitude of R (R^6 enters into κ). It is therefore advisable to use other data. The evaluation must proceed differently for Pippard and for London superconductors.

It is convenient to use for London superconductors the fact that the equations of the Ginzburg-Landau theory hold for them over a wide range near the critical temperature. We can thus use the well-known relation[5] with the doubled charge[4]

$$\varkappa = (\sqrt{2}2e / \hbar c)(H_{cT} \delta_T^2)_{T=T_c}, \qquad (21)$$

where H_{cT} is the critical field at the given temperature and δ_T the penetration depth. We can also use this relation for metals intermediate between London and Pippard types, since in that case the region of applicability of (21) is sufficiently wide. The majority of the most studied superconductors belongs apparently to the intermediate type. Tin[10] ($\kappa = 0.158$), lead[11] ($\kappa = 0.234$) and indium[11] ($\kappa = 0.22$) are, for instance, such superconductors.

The Ginzburg-Landau equations are, finally, applicable also for Pippard metals in the immediate vicinity of T_c, but this neighborhood is very small ($\Delta T/T_c \sim \kappa^2$). For aluminum the London temperature region begins at $\Delta T/T_c \sim 10^{-4}$. Equation (21) can therefore not be used to determine κ in the range of temperatures which is easily accessible. The value of κ can in that case be determined from data on the magnitude of the magnetic field H_{c0} and the penetration depth δ_0 at $T = 0$. The theoretical expression for δ_0 in the Pippard case is according to the BCS theory of the following form:

$$\delta_0 = (\sqrt{3}/2)(\pi^2 p_0^2 kT_c / \gamma \hbar^4 c^3)^{-1/3}.$$

Expressing the constant κ in terms of δ_0 and H_{c0} we get

$$\varkappa = 213\, (eH_{c0} / c\hbar)^3 \delta_0^6. \qquad (22)$$

For aluminum we find in this way $\kappa \approx 0.012$.

The available experimental data of Faber's on the magnitude of the supercooling field refer to a temperature range near T_c.[12] For tin, the value of H_{c1}/H_c as given by (20), with $\kappa = 0.16 - 0.226$, agrees very well with the experimental[12] value 0.232. For indium with $\kappa = 0.22$ the theoretical value $H_{c1}/H_c = 0.32$ is nearly twice as large as the experimental[12] one, 0.16. It is difficult to understand the causes of such a discrepancy.

At first sight Eq. (20) for aluminum pertains only to that temperature range where the Ginzburg-Landau equations are applicable. This range is very narrow, but we shall see in the following that the region of applicability of (20) is for a Pippard metal appreciably wider than the London temperature region* near T_c. It is, in particular, helpful to note that at $T = 0$ the character of the solution of (14) does not depend on whether the metal is a Pippard or a London metal in a weak field. With the value of κ found above for aluminum near T_c we have $H_{c1}/H_c \approx 0.017$ while the experimental[12] value is 0.036, i.e., larger than the theoretical one by a factor two. Such a discrepancy should not cause any surprise for a Pippard metal if we take into account how rough the model is and the high powers of the experimental quantities which enter into (22). At the same time Eq. (20) can itself serve to determine κ for Pippard metals. The smallness of the ratio H_{c1}/H_c (or, what is the same, the large magnitude of the surface energy) is a criterion for a metal being of the Pippard type.

In conclusion we wish to discuss some additional points. First we touch upon the general form of the solution of (6). Up to now we assumed that the magnitude of the gap $\Delta(\mathbf{r})$ depended only on y. Such an assumption is permissible, since an appropriate choice for the vector potential $\mathbf{A}$ had been made in the equations of the basic set (1′). It is also

*This fact was already noted by Ginzburg.[13]

rather obvious from uniformity considerations that the value of the field equal to H_{c1} will correspond to a constant solution $\Delta(x, y)$ in the direction of the field. At the same time the problem is degenerate in the x,y plane, i.e., many solutions $\Delta(x,y)$ correspond to one value of H_{c1}. One can easily verify with the aid of (3) and (4) that if $\Delta(y)$ is a solution of (6) the function

$$\Delta(x, y) = \exp(ieHax/c)\,\Delta(y-a)$$

is also a solution, and the general form of the function which corresponds to a given value of H_{c1} will thus be

$$\Delta(x, y) = \sum_j \exp(ieHxa_j/c)\,A_j\Delta(y-a_j)$$

with arbitrary a_j and A_j.

We shall finally dwell on the problem of the temperature dependence of the field H_{c1}. If the temperature is different from absolute zero, one must use instead of (1′) the appropriate thermodynamic technique.[14] We applied this technique earlier[4] to a superconductor; we shall here only indicate to what differences from the foregoing results it leads. The mathematical change in the formalism used above consists of the following: it is sufficient to replace ω by $i\omega_n$ [where $\omega_n = \pi T(2n+1)$, n is an integer] in all equations, beginning with (4), and to replace the integration over $d\omega$ by summation over n, as follows:

$$-\frac{i}{2\pi}\int_{-\infty}^{\infty} d\omega\,(\ldots)_\omega \to T\sum_{-\infty}^{+\infty}(\ldots)_{i\omega_n}.$$

The field dependence of the Green functions remains as before, and the further calculations lead instead of to Eq. (14) to

$$\Delta_T(\xi)\ln\left(\frac{e\gamma\Delta_0}{v}\sqrt{\frac{c}{eH}}\,\delta\right) = -\frac{1}{2}\int_{-\infty}^{\infty} K_T(\xi,\xi')\,\Delta_T(\xi')\,d\xi', \quad (23)$$

where

$$K_T(\xi,\xi') = \frac{2\pi T}{v}\sqrt{\frac{c}{eH}}\int_1^{\infty}\frac{J_0[(\xi^2-\xi'^2)\sqrt{u^2-1}]}{u\sinh(2\pi Tv^{-1}\sqrt{c/eH}\,u\,|\xi-\xi'|)}\,du. \quad (24)$$

Because of the complexity of this kernel one can in the general case only obtain the dependence of H_{c1} on T by a numerical integration. We shall consider limiting expressions.

The kernel (24) can for low temperatures be written in the following form:

$$K_T(\xi,\xi') = K_0(\xi,\xi') - \frac{2\pi^2T^2c^2}{3eH_{c1}v^2}\,\frac{\exp\{-|\xi^2-\xi'^2|\}}{|\xi+\xi'|}, \quad (25)$$

where $K_0(\xi, \xi')$ is the kernel of (14). This expansion loses its validity in the neighborhood of $\xi = -\xi'$, where the temperature dependent correction term in (25) has a singularity. In that point one cannot expand the hyperbolic sine in (24) in powers of T since it just guarantees the convergence of (24) for large u. One sees easily that the width of the region $\Delta\xi = |\xi+\xi'|$ where (25) is inapplicable is of the order $\Delta\xi \sim (2\pi T/v)\sqrt{c/eH_{c1}}$. We rewrite (23) in the following form:

$$\lambda(\xi)\ln\left(\frac{e\gamma\Delta_0}{v}\sqrt{\frac{c}{eH_{c1}}}\,\delta\right) + \frac{1}{2}\int_{-\infty}^{+\infty} K_0(\xi,\xi')\,\lambda(\xi')\,d\xi' = \Delta_0(\xi)\frac{\delta H_T}{H_{c1}} - \frac{1}{2}\int_{-\infty}^{+\infty}\delta K_T(\xi,\xi')\,\Delta_0(\xi')\,d\xi',$$

where

$$\lambda(\xi) = \Delta_T(\xi) - \Delta_0(\xi).$$

One must determine $\delta H_T/H_{c1}$ from the condition that the right hand side be orthogonal to the solution of the homogeneous Eq. (14). If we use an approximate solution for $\Delta_0(\xi) \sim \exp(-\xi^2)$ we can find the main term in the additional term in H_{c1}/H_{cT} at low temperatures, using (25), which is of the form $(T^2/T_c^2)\ln(T/T_c)$. Integrating with logarithmic accuracy, we get

$$H_{c1}/H_{cT} = 1.77\times[1 + 0.65(T/T_c)^2\ln(\text{const}\cdot T/T_c)] \quad (26)$$

with an unknown constant [if $T \ll T_c$ we have:[6] $H_{cT} = H_{c0}(1-\gamma^2T^2/3T_c^2)$].

Near the transition temperature the field H_{c1} is small, and the equation becomes considerably simpler. It is clear from (23) and (24) that in that case in the integration the essential $|\xi-\xi'|$ are of the order of $\xi_0\sqrt{eH/c}$ because of the exponential character of the kernel (24), while it is natural to assume that $\Delta(\xi)$ changes little over those distances. Using this, it turns out that near T_c the integral equation (23) is changed into a differential equation which to a first approximation is the same as the corresponding equation for the same problem in the Ginzburg-Landau theory with a doubled charge,[4,5] the known solution of which leads to (20).

Taking the next terms into account, we can find after some calculations the temperature dependence of the ratio H_{c1}/H_c near T_c:

$$H_{c1}/H_c = \sqrt{2}\varkappa(1+0.41t);\quad t = 1 - T/T_c. \quad (27)$$

We should like to note here that the condition for the applicability of (20) and (27) follows from the derivation: $\Delta T \ll T_c$, whereas the applicability of the general equations of the Ginzburg-Landau theory obtained in reference 4 near T_c was confined to a much narrower temperature range near T_c. In discussing the penetration depth problem, for instance, for these equations to be applicable it is necessary that not only $\Delta T/T_c$ be small, but also that the superconductor be in the London region at the temperatures considered, i.e., that the penetration depth be large compared to ξ_0. For this it is necessary that the condition $\sqrt{\Delta T/T_c} \ll \kappa$ is satisfied which for superconductors with a small κ (Pippard superconductors) may be an appreciably stronger restriction. In the problem of the supercooling field, therefore, the question whether a superconductor belongs to the Pippard or to the London class is not a decisive factor over the whole temperature range.

We saw already that the change in the ratio H_{c1}/H_c is small in the whole of the temperature range. We can thus believe that an interpolation formula, combining (26) and (27) can represent adequately the variation of H_{c1}/H_c over the whole temperature range. Since the logarithm in (26) is a slowly-varying function, we can take simply for such a formula the polynomial

$$H_{c1}/H_c = \varkappa\,[1.77 - 0.43\,(T/T_c)^2 + 0.07\,(T/T_c)^4].$$

Returning, in conclusion, to the problem of the possibility whether there exist pure superconductors with alloy properties, i.e., with $\kappa > 0.56$, we note that among the best studied superconductors, lead and indium, have the largest κ, about 0.23. To increase κ it is necessary to have a larger value of H_c and a larger penetration depth. From this point of view, La, V, U, and Nb are worthy of attention. Unfortunately there are, apparently, no data about the penetration depth for these superconductors. There are in reference 11 some indications about the anomalous properties of these metals which are similar to the properties of alloys, although it is not clear whether these anomalies are caused by the presence of impurities. There is at any rate considerable interest in clarifying the problem of the existence of pure superconductors with $\kappa > 0.56$, since they should possess all anomalous properties of alloys.

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