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CONCERNING SURFACE SUPERCONDUCTIVITY IN STRONG MAGNETIC FIELDS

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The question of surface superconductivity in fields above the critical field H_{c2} is examined. It is shown that the phenomenon exists at all temperatures below T_c. The critical field of thin films in a parallel field and the field dependence of the critical current for surface superconductivity of a bulk sample are determined.

In a recently published article[1] Saint-James and de Gennes showed that the existence of a thin superconducting sheath near the surface of a superconductor is possible in fields above H_{c2}, at which the beginning of the superconducting phase occurs (the upper critical field in superconductors of the second kind[2] and the critical super-cooling field for superconductors of the first kind, see [3]). Superconductivity vanishes in this sheath only when the external field becomes equal to $H_{c3} = 1.7\,H_{c2}$.

To begin with it is necessary to briefly explain the origin of this effect. As is well-known,[2,3] the field H_{c2} is the field at which for the first time a small layer of the superconducting phase may appear in a normal metal. In view of this, in order to determine H_{c2} it is necessary to examine the linearized equations for the energy gap Δ (or what is the same, the Ψ function of Ginzburg and Landau[4]). The eigenvalue of the field, at which this equation has a solution different from zero well inside the sample, is H_{c2}. Studying the Ginzburg-Landau equation for Ψ, Saint-James and de Gennes[1] noticed that if one requires $\Psi \neq 0$ not inside but near the surface, then the corresponding eigenvalue of the field turns out to be higher.

In fact, the Ginzburg-Landau equation has the following boundary condition for Ψ:

$$\mathbf{n}(-i\hbar\nabla\Psi - 2ec^{-1}\mathbf{A}\Psi) = 0,$$

where $\mathbf{n}$ is the normal to the surface. If the problem deals with a field parallel to a plane boundary, then one can choose $\mathbf{A} \perp \mathbf{n}$ so that the condition reduces to $\partial\Psi/\partial\mathbf{n} = 0$ on the boundary. The function $\Psi_0 = \exp[-\kappa^2 x^2/2\delta^2]$ satisfies the linearized Ginzburg-Landau equation and the boundary condition if the point $x = 0$ is far from the boundary (Fig. 1a). The corresponding eigenvalue of the field is $H_{c2} = \kappa\sqrt{2}\,H_{cm}$.[2] It is not difficult to see that if the point $x = 0$ is chosen on the boundary itself (Fig. 1b), then the function Ψ_0 will again satisfy both the equation and the boundary condition. If now the point $x = 0$ is chosen not on the surface itself but near it, then the function Ψ must be changed (Fig. 1c) and consequently the corresponding eigenvalue of the field must also change. It is easy to understand which way the change will go if it is remembered that the critical field is higher for thin films than for a bulk sample. It is clear from Fig. 1d how the Ψ function varies inside the sheath. Comparing with Fig. 1c, it is easy to see that in the case of Fig. 1c the critical field must turn out to be higher than in the cases of Figs. 1a and 1b. By selecting the position of the point $x = 0$, one can find the maximum field H_{c3}.

The presence of surface superconductivity must lead to a whole series of experimental consequences. Saint-James and de Gennes[1] mention such consequences as disagreement between the values of the critical field determined by the vanishing of the magnetic moment and the appearance of resistivity in superconductors of the second kind, an increase in the value of the supercooling field in superconductors of the first kind, etc.

Certain further aspects of this interesting phenomenon are considered in the present article.

1. SURFACE SUPERCONDUCTIVITY NEAR T_c AND AT LOW TEMPERATURES

In spite of the fact that the argument presented above makes the existence of surface superconductivity and the field H_{c3} quite certain at first glance, in reality a number of questions arise.

A. The boundary condition on the Ginzburg-Landau equation plays an extremely important role in this phenomenon. However, whereas the Ginzburg-Landau equation itself was obtained[5,6] from the microscopic theory, this did not occur with regard to the boundary condition.

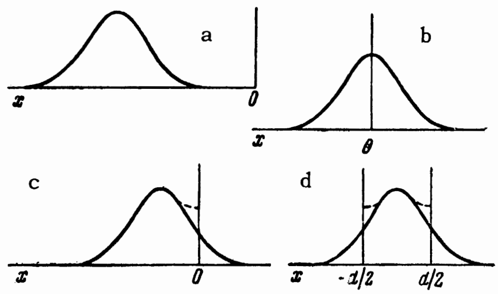

FIG. 1.

B. The region of applicability of the Ginzburg-Landau equations covers the temperatures at which all integral relations become local. This means that the penetration depth $\delta(T)$ and the characteristic length $\delta(T)/\kappa$ of superconducting structure must be considerably larger than the correlation parameter, which is of order $\delta(0)/\kappa$. In particular, it would be necessary that $(T_c - T)/T_c \ll 1$ in superconductors of the second kind with $\kappa > 1/\sqrt{2}$. If, however, $T_c - T \sim T_c$, then both the Ginzburg-Landau equation and the boundary condition on it become meaningless. The question arises of whether surface superconductivity is possible in this temperature range.

In order to answer these questions, we shall consider a general microscopic formulation of the problem where, for simplicity, we confine ourselves to an investigation of a pure unalloyed superconductor, and we assume specular reflection of electrons from the boundaries. The method which will be applied essentially follows the derivation of Gor'kov [7] for the critical supercooling field of pure superconductors. The difference is that we shall consider a semi-space instead of an infinite medium, and we require that

$$\mathfrak{G}_\omega(\mathbf{r}, 0) = \mathfrak{G}_\omega(0, \mathbf{r}') = 0, \quad \mathfrak{F}_\omega(\mathbf{r}, 0) = \mathfrak{F}_\omega(0, \mathbf{r}') = 0 \qquad (1)$$

(we shall use the temperature technique).

It is easiest to solve this problem in the following manner. We shall consider the quasiclassical approximation. If we consider the vector potential $\mathbf{A}$ to be directed along the y axis and to depend on x (the field $\mathbf{H}_0$ is along the z axis), then according to [7] the quasiclassical function $\mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}')$ for the electrons in a normal metal occupying all space has the form

$$\mathfrak{G}_\omega^{(\infty)}(\mathbf{r}, \mathbf{r}') = \mathfrak{G}_{0\omega}(|\mathbf{r} - \mathbf{r}'|) \times \exp\{(ie/2\hbar c)[A(x) + A(x')](y - y')\}, \qquad (2)$$

where $\mathfrak{G}_{0\omega}$ is the field-free function. In order to satisfy condition (1) we write $\mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}')$ in the form

$$\mathfrak{G}_\omega(\mathbf{r}, \mathbf{r}') = [\mathfrak{G}_{0\omega}(|\mathbf{r} - \mathbf{r}'|) - \mathfrak{G}_{0\omega}(|\mathbf{r} - \bar{\mathbf{r}}'|)] \times \exp\{(ie/2\hbar c)[A(x) + A(x')](y - y')\}, \qquad (3)$$

where $\bar{\mathbf{r}}' = (-x', y', z')$. In order for this function to satisfy the same equation as $\mathfrak{G}_\omega^{(\infty)}(\mathbf{r}, \mathbf{r}')$ it is necessary that $A(-x') = A(x')$, i.e., that the vector potential be symmetrically continued across the boundary. It is quite possible to assume this, since we are only interested in the region $x' > 0$.

The equation for the gap Δ is written in a form similar to Eq. (6) of the article by Gor'kov: [7]

$$\Delta^*(\mathbf{r}) = -\frac{gT}{\hbar}\sum_\omega \int_{x'>0} d\mathbf{r}'\, \mathfrak{G}_{-\omega}(\mathbf{r}', \mathbf{r})\, \mathfrak{G}_\omega(\mathbf{r}', \mathbf{r})\, \Delta^*(\mathbf{r}'). \qquad (4)$$

In view of the fact that in the normal state the field inside a metal is homogeneous and equal to the external field, $A(x) = H_0(x - x_0)$. The constant x_0 corresponds to the possibility of movement of the center of the superconducting sheath relative to the boundary. The field H_{c3} should be defined as $\min_{x_0} H_c(x_0)$. Such an introduction of the constant x_0 is completely equivalent to the introduction of a phase factor e^{iky} into Δ, just as this done in [1].

Upon substitution of the function (3) into Eq. (4), one can immediately disregard the products $\mathfrak{G}_{0\omega}(|\mathbf{r} - \mathbf{r}'|)\mathfrak{G}_{0,-\omega}(|\mathbf{r} - \bar{\mathbf{r}}'|)$ since these terms are important only at distances from the boundary on the order of atomic distances and give a small contribution to the integral. Thus, we obtain

$$\Delta^*(\mathbf{r}) = -\frac{gT}{\hbar}\sum_\omega \int_{x'>0} d\mathbf{r}' [\mathfrak{G}_{0\omega}(|\mathbf{r}' - \mathbf{r}|)\, \mathfrak{G}_{0,-\omega}(|\mathbf{r}' - \mathbf{r}|) + \mathfrak{G}_{0\omega}(|\bar{\mathbf{r}}' - \mathbf{r}|)\, \mathfrak{G}_{0\omega}(|\bar{\mathbf{r}}' - \mathbf{r}|) \times \exp\left\{\frac{ieH_0}{\hbar c}(x + x' - 2x_0)(y - y')\right\}\Delta^*(\mathbf{r}'). \qquad (5)$$

Carrying out transformations similar to those performed in [7], we obtain

$$\Delta^*(\mathbf{r}) \ln\frac{\hbar v}{\pi T_c \sigma} = \frac{T}{2v}\int_{x'>0, R>\sigma} d\mathbf{r}' \times \exp\left\{\frac{ieH_0}{\hbar c}(y - y')(x + x' - 2x_0)\right\} \times \left[R^{-2}\left(\operatorname{sh}\frac{2\pi T R}{\hbar v}\right)^{-1} + \bar{R}^{-2}\left(\operatorname{sh}\frac{2\pi T \bar{R}}{\hbar v}\right)^{-1}\right]\Delta^*(\mathbf{r}'), \qquad (6)^*$$

where $R = |\mathbf{r} - \mathbf{r}'|$, $\bar{R} = |\mathbf{r} - \bar{\mathbf{r}}'|$, and σ is an infinitesimal number which does not appear in the final result. In what follows we shall look for a solution $\Delta^*(\mathbf{r})$ which depends only on the coordinate x.

First let us consider the case of temperatures in the neighborhood of T_c. As will be clear from what follows, $\Delta(x)$ varies over those same distances as the argument of the exponential in Eq.

*sh = sinh.

(6), i.e., over distances on the order of $(\hbar c/eH_c)^{1/2}$, where H_c is the critical field, proportional to $T_c - T$. In the neighborhood of T_c, this distance may become much larger than $\hbar v/\pi T_c$ —the characteristic distance for the kernel of Eq. (6) inside the square brackets. As a result, $\Delta(x)$ and the exponential factor may be expanded in powers of $\mathbf{r}' - \mathbf{r}$. Here we obtain

$$\Delta(x)\ln\frac{\hbar v}{\pi T_c\sigma} = \frac{T}{2v}\int_{-\infty}^{\infty} dy'\,dz'\int_{0}^{\infty} dx'\left[\Delta(x) + \frac{d\Delta(x)}{dx}(x'-x) + \frac{1}{2}\frac{d^2\Delta}{dx^2}(x'-x)^2 - \frac{1}{2}\left(\frac{2eH_0}{\hbar c}\right)^2 \times (y'-y)^2(x-x_0)^2\Delta(x)\right] \times\left[R^{-2}\,\mathrm{sh}^{-1}\frac{2\pi TR}{\hbar v} + \overline{R}^{-2}\,\mathrm{sh}^{-1}\frac{2\pi T\overline{R}}{\hbar v}\right]$$

[since we are dealing everywhere with real solutions, we shall write $\Delta(x)$].

One can make the following substitution in the terms which do not contain derivatives of Δ:

$$\int_0^\infty dx'\left[R^{-2}\left(\mathrm{sh}\frac{2\pi TR}{\hbar v}\right)^{-1} + \overline{R}^{-2}\left(\mathrm{sh}\frac{2\pi T\overline{R}}{\hbar v}\right)^{-1}\right] = \int_{-\infty}^{\infty} dx'\,R^{-2}\,\mathrm{sh}^{-1}\frac{2\pi TR}{\hbar v}.$$

The integrals in such terms then become the same as for the case of infinite space. However, the terms with derivatives must be analyzed separately. Let us take the term with $d\Delta(x)/dx$ and change over from the variable x' to $x' - x$ in the term containing R and to $x' + x$ in the term containing $\overline{R}$. As a result we obtain

$$\frac{d\Delta(x)}{dx}\left[\int_{-x}^{\infty}\frac{X\,dX}{R^2\,\mathrm{sh}(2\pi TR/v)} + \int_{x}^{\infty}\frac{X\,dX}{R^2\,\mathrm{sh}(2\pi TR/\hbar v)} - 2x\int_x^\infty\frac{dX}{R^2\,\mathrm{sh}(2\pi TR/\hbar v)}\right],$$

where $R^2 = X^2 + (y-y')^2 + (z-z')^2$. Combining the three integrals, we obtain

$$2\frac{d\Delta}{dx}\int_x^\infty\frac{(X-x)\,dX}{R^2\,\mathrm{sh}(2\pi TR/\hbar v)}.$$

The coefficient of $d\Delta(x)/dx$ obviously differs from zero only at distances on the order of $\hbar v/\pi T_c$ from the boundary. Evaluating the integral of this coefficient with respect to x, we obtain

$$2\int_0^\infty dx\int_x^\infty\frac{(X-x)\,dX}{R^2\,\mathrm{sh}(2\pi TR/\hbar v)} = \int_0^\infty\frac{X^2dX}{R^2\,\mathrm{sh}(2\pi TR/\hbar v)} = \frac{1}{2}\int_{-\infty}^{\infty}\frac{X^2dX}{R^2\,\mathrm{sh}(2\pi TR/\hbar v)}.$$

Hence it follows that the term containing $d\Delta(x)/dx$ can be approximately written in the form

$$\frac{7}{12}\zeta(3)\left(\frac{\hbar v}{2\pi T}\right)^2\frac{d\Delta(x)}{dx}\delta(x-\sigma),\qquad \sigma\to+0.$$

Similarly transforming the term containing $d^2\Delta/dx^2$, we obtain

$$\frac{7}{12}\zeta(3)\left(\frac{\hbar v}{2\pi T}\right)^2\frac{d^2\Delta}{dx^2}[1-2x\delta(x-\sigma)],\qquad \sigma\to+0.$$

It is obvious that the second term inside the square brackets is simply equal to zero.

Thus, the term containing $d\Delta/dx$ turns out to be the only term having a δ-function structure. It can be isolated by integrating over a small neighborhood of the point $x = 0$. As a result, we obtain the condition $d\Delta(x)/dx\,|_{x=0} = 0$, which coincides with the Ginzburg-Landau boundary condition. After this, the equation for Δ takes the usual form of the linear approximation to the Ginzburg-Landau equation:

$$\frac{\hbar^2}{4m}\left[\frac{d^2\Delta}{dx^2} - \left(\frac{2eH}{\hbar c}\right)^2(x-x_0)^2\Delta(x)\right] + \frac{1}{\lambda}\frac{T_c - T}{T_c}\Delta(x) = 0,$$

$$\lambda = 7\zeta(3)\varepsilon_F/6(\pi T_c)^2.$$

Solving this equation, it is not difficult to see that Δ varies over distances on the order of $(\hbar c/eH_c)^{1/2}$, and H_c is proportional to $T_c - T$. Thus, in the neighborhood of T_c where Δ varies over distances which are large in comparison with $\hbar v/\pi T_c$, in fact not only the Ginzburg-Landau equation but also the boundary condition on it are valid.

The expansion in powers of $\mathbf{r} - \mathbf{r}'$ loses meaning at temperatures far from the critical temperature, because there Δ changes over distances on the order of $\hbar v/\pi T_c$; the same pertains to the argument of the exponential in Eq. (6) since the critical fields H_{c2} and H_{c3} are of order $(\hbar c/e)(T_c/\hbar v)^2$. Therefore, at such temperatures it is already impossible to use the Ginzburg-Landau equation, and it is necessary to solve the exact equation (6). This problem is very difficult, and therefore we shall only consider the case $T = 0$, and we confine ourselves to a demonstration that the surface superconductivity effect actually does exist in large fields.

At $T = 0$ Eq. (6) can be easily integrated with respect to $z - z'$ and $y - y'$. Also introducing a new dimension of length, namely $\xi = (2eH_0/\hbar c)^{1/2}x$, and putting $\eta = (2eH_0/\hbar c)^{1/2}x_0$, we obtain

$$\Delta(\xi)\ln\frac{v(2eH/\hbar c)^{1/2}}{\pi T_c\sigma_1}$$
$$=\frac{1}{2}\int_{\sigma_1}^{\infty}\left[\frac{\exp\{-{}^1/_2|\xi-\xi'||\xi+\xi'-2\eta|\}}{|\xi-\xi'|}+\frac{\exp\{-{}^1/_2(\xi+\xi')|\xi+\xi'-2\eta|\}}{\xi+\xi'}\right]\Delta(\xi')\,d\xi'. \qquad (7)$$

Let us assume that $\eta \gg 1$. In such a case it is convenient to introduce the integration variable $\xi-\eta$. If in addition we also suppose, and this is confirmed below, that $\Delta(\xi)$ will be large only for $\xi-\eta\sim 1$, then the lower limit with regard to the variable $\xi-\eta$, equal to $-\eta$, can be regarded as equal to $-\infty$. As a result we obtain

$$\Delta(\xi)\ln\frac{v(2eH_0/\hbar c)^{1/2}}{\pi T_c\sigma_1}$$
$$=\frac{1}{2}\int_{\substack{-\infty\\|\xi-\xi'|>\sigma_1}}^{\infty}\left[\frac{\exp(-{}^1/_2|\xi^2-\xi'^2|)}{|\xi-\xi'|}+\frac{\exp(-\eta|\xi+\xi'|)}{2\eta}\right]\Delta(\xi')\,d\xi'. \qquad (8)$$

In the second term of the kernel of the integral equation, we have neglected ξ in comparison with η. If this second term were not present, then Eq. (8) would coincide with Gor'kov's equation[7] for the field H_{c2} at $T = 0$. This term is exponentially small for $\eta \gg 1$. Values of $|\xi+\xi'|\sim\eta^{-1}$, in other words, $\xi\approx-\xi'$, are important in the evaluation of the integral containing the second term of the kernel. This gives the possibility of substituting $\Delta(\xi')\approx\Delta(\xi)$ in this integral and transferring this term to the left side.

As a result of evaluating the integral with respect to $\xi+\xi'$ we obtain

$$\Delta(\xi)\left[\ln\frac{v(2eH_0/\hbar c)^{1/2}}{\pi T_c\sigma_1}-\frac{1}{2\eta^2}\right]$$
$$=\frac{1}{2}\int_{-\infty}^{\infty}\frac{\exp(-{}^1/_2|\xi^2-\xi'^2|)}{|\xi-\xi'|}\Delta(\xi')\,d\xi'. \qquad (9)$$

This equation coincides exactly with the equation for H_{c2} if we make the replacement

$$H_0=H_c(\eta)=H_{c2}(1+\eta^{-2}). \qquad (10)$$

From here it follows that the critical field for nucleation increases as the nucleation center approaches the surface. This completely proves the existence of surface superconductivity beyond the region of applicability of the equations of Ginzburg and Landau.

It is unusually difficult to evaluate the field H_{c3} in the general case. However, on the basis of well-known properties of superconductors we can, it seems to us, draw the following conclusion. All experimental data indicates that the Ginzburg-Landau equations provide a good description of the magnetic properties of superconductors over the entire temperature interval, if it is assumed that the constants of this theory are slowly varying functions of the temperature. Of course, this is only an empirical fact. However, if we take such a viewpoint, then the ratio H_{c3}/H_{c2} must depend on temperature far more weakly than H_{c2}/H_{cm} does. Since the latter ratio only changes by 20% in the interval from T_c to absolute zero, we can assume that the relation

$$H_{c3}(T)=1.7H_{c2}(T), \qquad (11)$$

derived in [1] for the neighborhood of $T = T_c$, will be satisfied over this entire range of temperatures.

In concluding this section, we note the following circumstance. Saint-James and de Gennes already showed[1] that near the field H_{c3}, in spite of the presence of a surface superconducting layer, a total surface current shielding the inside of the sample from the external field is not created in the superconductor. This is not completely trivial, since the current density in the surface layer does not vanish; however, it changes sign upon going deeper inside the sample, so that on the whole no surface current is present. It is not difficult to see that this will be valid over the entire range of surface superconductivity, i.e., from the field H_{c2} up to H_{c3}. In fact, upon the appearance of a total surface current, the field well inside the sample is different from the external field. If the energy is measured from the normal state, then a positive increment to it appears, proportional to the volume of the sample:

$$\int\frac{(H-H_0)^2}{8\pi}\,dV.$$

At the same time, the change of the electron state occurs only near the surface, so the associated change of the energy is proportional to the surface area. Thus, one must necessarily have $H = H_0$ in bulk samples. Below (see Sec. 3) we shall demonstrate directly the absence of total current within the limits of the Ginzburg-Landau approximation (but far from H_{c3}).

2. CRITICAL FIELD OF THIN FILMS OF TYPE II SUPERCONDUCTORS

It follows from what has been said above that the magnetic moment of a bulk superconductor of the second kind must vanish at $H = H_{c2}$. However, if the critical field is defined by the appearance of electrical resistivity, then H_{c3} must be the critical field. The critical field of thin films[8] is measured in precisely this way, and in this connection the dependence of H_{c3} on the thickness of the film is of interest. A similar problem was considered by Saint-James and de Gennes[1] for a film located in a perpendicular field; however, having a comparison with the experimental data of Khukhareva[8] in mind, we shall investigate here the case of a parallel field.

In contrast our earlier determination of the critical field,[9] we must take into consideration here the effect of surface superconductivity, which is manifest in the fact that at sufficiently large thicknesses it may turn out that an asymmetric solution of the energy gap equation (with respect to the center of the film) can exist at larger fields than the symmetric solution (considered in [9]). In the same way as in [9], we confine ourselves to the neighborhood of T_c and use the Ginzburg-Landau equation.

Introducing the variable[1)] $\xi = \delta^{-1}(\kappa H_0/\sqrt{2}H_{cm})^{1/2}x$, where x is normal to the surface of the film, and $\beta = \kappa\sqrt{2}H_{cm}/H_0 = H_{c2}/H_0$, we obtain the equation

$$d^2\Psi / d\xi^2 + [\beta - (\xi - \eta)^2]\Psi = 0. \tag{12}$$

The boundary condition corresponds to $d\Psi/d\xi = 0$ for $\xi = \pm s/2$, where

$$s = \frac{1}{\delta}\left(\frac{\varkappa H_0}{\sqrt{2}H_{cm}}\right)^{1/2} d = \frac{\varkappa}{\delta}\left(\frac{H_0}{H_{c2}}\right)^{1/2} d = \frac{\varkappa d}{\delta\sqrt{\beta}},$$

d is the thickness of the film. The quantity η in Eq. (12) corresponds, as in the preceding section, to a choice of the arbitrary constant in the vector potential such that Ψ is a function of only one coordinate. The problem consists in a determination of the minimum eigenvalue β of Eq. (12) as a function of s and η, and then minimization of β with respect to η in order to determine the final quantity $H_{c3}(d)$.

First of all we note that the final result must obviously have the form $H_{c3}/\kappa\sqrt{2}H_{cm} = f(\delta/\kappa d)$. Putting $\kappa = (2\sqrt{2}e/\hbar c)H_{cm}\delta^2$ and defining $\theta = (2e/\hbar c)^{1/2}H_{cm}\delta$, we obtain a dependence of the type

$$\frac{H_{c3}(d)}{2\theta^2} = f\left(\frac{1.29\cdot 10^{-4}}{\theta d}\right). \tag{13}$$

The same kind of dependence was obtained in [9], but in our case the function f is different (we also considered the doubling of the charge). It is characteristic that one parameter θ determines the complete curve $H_{c3}(d)$.

In the region of very small thicknesses, $s \ll 1$, the funtion Ψ will be close to constant. With increase of the thickness, it is obvious that the symmetric solution (i.e., $\eta = 0$) will correspond for some of the time to the largest field. This means that in the region of small thicknesses, the curve $H_{c3}(d)$ will coincide with $H_{c2}(d)$ found in [9], namely

$$H_{c3}(d) / H_{cm} \approx 2\sqrt{6}\,\delta / d, \quad d\varkappa / \delta \ll 1. \tag{14}$$

However, at some value $s \sim 1$, η now becomes unequal to zero, and the curve $H_{c3}(d)$ will deviate from the curve found in [9]. An exact consideration of such thicknesses is unusually complicated. But we shall use the fact that in the region where values of $\eta \neq 0$ first appear, the formula for small thicknesses still gives a very good approximation for $H_{c3}(d)$. This will be clear from what follows.

If we change over from the variable ξ to $\xi - \eta$, then Eq. (12) coincides with the same equation which was solved in [9] and the boundary condition will be $d\Psi/d\xi = 0$ for $\xi = (s/2) - \eta$ and $\xi = -(s/2) - \eta$. Here the general solution of the equation will be

$$\Psi = \exp\left(-\frac{\xi^2}{2}\right)\left[C_1 F\left(\frac{1-\beta}{4}, \frac{1}{2}, \xi^2\right) + C_2\xi F\left(\frac{3-\beta}{4}, \frac{3}{2}, \xi^2\right)\right] \tag{15}$$

(F is the confluent hypergeometric function). Expanding the function Ψ in powers of ξ and substituting into the boundary conditions, we obtain the following expression for β:

$$\beta = \frac{1}{3}\left(\frac{s}{2}\right)^2 - \frac{8}{35\cdot 27}\left(\frac{s}{2}\right)^6 + \eta^2\left[1 - \frac{8}{15}\left(\frac{s}{2}\right)^4\right] + \eta^4\frac{26}{63}\left(\frac{s}{2}\right)^6. \tag{16}$$

From here it follows that for $(s/2)^4 < 15/8$ the coefficient of the η^2 term is positive and the smallest value of β corresponds to $\eta = 0$. We note that on the boundary of this region, the second term in expression (16) amounts to only $1/21$ of the first. In reality, in the expression for H_{c3} the correction is smaller by another factor of two.

Using the expression for s and substituting $\beta \approx 1/3\,(s/2)^2$, we obtain the critical thickness

$$d_c = \sqrt{5/2}\,\delta / \varkappa. \tag{17}$$

At larger thicknesses the coefficient of η^2 is negative. From the minimum of β with respect to η^2, with use of the term containing η^4, we obtain, substituting all the quantities,

[1)]This variable coincides with ξ in the preceding section. In fact, according to Gor'kov,[5] $k = 2\sqrt{2}\,e\,H_{cm}\delta^2/\hbar c$, where H_{cm} is the thermodynamic critical field, δ is the penetration depth.

$$\frac{H_{c3}(d)}{H_{cm}} = \frac{2\sqrt{6}}{d}\delta\left\{1+\frac{d^2\varkappa^2}{105\delta^2}+\frac{84}{325}\left[\left(\frac{d}{d_c}\right)^2-1\right]^2\right\}. \quad (18)$$

The difference from the curve obtained in [9] lies in the last term.

One can obtain another limiting formula for large thicknesses. Since even for an infinite sample the calculation of H_{c3} is a difficult problem requiring numerical calculation, we employ the following method. The determination of the minimum value of β from Eq. (14) is equivalent to the variational problem of finding the minimum of the expression

$$\beta = \left[\int_0^s \left(\frac{d\Psi}{d\xi}\right)^2 d\xi + \int_0^s (\xi-\eta)^2\Psi^2 d\xi\right] \Big/ \int_0^s \Psi^2 d\xi \quad (19)$$

(here we measure ξ and η from one of the boundaries). Let us assume that the solution of the variational problem is known as $s \to \infty$, where Ψ usually falls off with a characteristic distance on the order of unity. Then one can show that the difference between β of the variational problem (19) and β of the case $s \to \infty$ has the form

$$\beta = \beta_0 + \left(\frac{d\Psi_0^2}{d\xi}\right)_{\xi=s} \Big/ \int_0^\infty \Psi_0^2 d\xi, \quad (20)$$

where Ψ_0 and β_0 correspond to the problem with $s \to \infty$. The exact function Ψ_0 cannot be simply written. However, one can use the fact that the trial function $\Psi = \exp(-b\xi^2/2)$ gives, for $b = [1-(2/\pi)]^{1/2}$, a value

$$\beta_0 = b = (1-2/\pi)^{1/2}, \quad (21)$$

differing from the true value by 2%. Substituting the approximate function Ψ_0 into (20), we obtain

$$H_{c3}(d) = H_{c3}(\infty)\left[1+\frac{4}{\sqrt{\pi}}\frac{\varkappa d}{\delta}\exp\left\{-\left(\frac{\varkappa d}{\delta}\right)^2\right\}\right]. \quad (22)$$

If the experimental data are reduced to the form (13), then it is useful to keep in mind that the new function f is very similar to the old function found in [9]. In the limiting cases it has the form $f(x) \to 1.7$ as $x \to 0$ (in contrast to unity in [9]) and $f(x) \approx 2\sqrt{3}x$ as $x \to \infty$ (the same as in [9]).

3. CRITICAL CURRENT IN THE CASE OF SURFACE SUPERCONDUCTIVITY

Since, as already mentioned, one can detect the critical field H_{c3} by the appearance of resistivity, the question arises: what limitation must be imposed on the magnitude of the measuring current? The critical current is also of interest from the point of view of the possibility of technological utilization of surface superconductivity. As in the preceding section, we shall confine ourselves to the approximation of Ginzburg and Landau, i.e., to the case when T is close to T_c.

First let us consider the neighborhood of $H = H_{c3}$. We assume that the current is parallel to the magnetic field. In this connection, the function Ψ acquires the factor e^{ikz}. If the current density is expressed in units of $cH_{cm}\sqrt{2}/4\pi\delta$, and the function Ψ, as usual, refers to the value for a bulk sample at the same temperature and without a magnetic field, then the expression for the current density has the form

$$j = q|\Psi|^2, \quad (23)$$

where $q = k\delta/\kappa$. The total current per unit length of contour of the transverse cross section, expressed in units of $cH_{cm}\sqrt{2}/4\pi$, is obviously equal to

$$J = \frac{\sqrt{\beta}}{\varkappa}\int_0^\infty j\, d\xi, \quad (24)$$

where ξ is the variable introduced earlier: $\xi = \kappa x/\delta\sqrt{\beta}$.

The equation in the linear approximation determines Ψ to within an arbitrary constant factor. In order to determine it, let us consider the complete equation for Ψ, where we take the factor e^{ikz} into consideration. Using the general equation for Ψ (see [4]) and changing over to the units introduced here, we obtain an equation for the correction of the first approximation with respect to Ψ^2, $\beta - \beta_0$, and q^2:

$$\frac{d^2\Psi_1}{d\xi^2} + [\beta_0 - (\xi-\eta)^2]\Psi_1 = \beta_0\left[\Psi_0^3 + \frac{2}{\varkappa^2}(\xi-\eta)\Psi_0(\xi) \times \int^{\xi} d\xi_1 \int_0^{\xi_1} \Psi_0^2(\xi_2)(\xi_2-\eta)\, d\xi_2\right] - (\beta-\beta_0-\beta_0 q^2)\Psi_0. \quad (25)$$

Here the correction to the vector potential (in the usual units),

$$\frac{d^2\mathbf{A}_1}{dx^2} = \frac{4\pi(2e)^2}{2mc^2}|\Psi|^2\mathbf{A}_0,$$

which is obtained from the equation for **A**, has been taken into consideration.

Ψ_0 is that solution of the homogeneous equation corresponding to (25) which satisfies the boundary conditions. The right side must be orthogonal to this solution. Hence we obtain the condition

$$(\beta-\beta_0-\beta_0 q^2)\int_0^\infty \Psi_0^2 d\xi = \beta_0 \int_0^\infty \left(\Psi_0^4 - \frac{2}{\varkappa^2}Q^2\right)d\xi,$$

$$Q(\xi) = \int_\xi^\infty (\xi-\eta)\Psi_0^2(\xi)\, d\xi, \quad (26)$$

which also determines the normalization of the function Ψ_0.

In order to establish the magnitude of the critical current, we substitute the found value of Ψ_0 into formula (26) and determine the unknown number q from the condition that J be a maximum. We have:

$$J = \frac{\sqrt{\beta_0}\, q}{\varkappa} \int_0^\infty \Psi_0^2 d\xi = \frac{\sqrt{\beta_0}\, q\,(\beta - \beta_0 - \beta_0 q^2)}{\varkappa \beta_0} \frac{\left[\int_0^\infty \Psi_0^2 d\xi\right]^2}{\int_\infty^0 \left(\Psi_0^4 - \frac{2}{\varkappa^2} Q^2\right) d\xi}. \qquad (27)$$

The ratio of the integrals in (27) no longer contains normalization coefficients. Therefore, one can evaluate the maximum of only the preceding factor with respect to $\sqrt{\beta_0}\, q$. Performing this, we obtain

$$J_c = \frac{2}{3\sqrt{3}} \frac{\sqrt{\beta_0}}{\varkappa} \left(1 - \frac{\beta_0}{\beta}\right)^{3/2} \frac{\left[\int_0^\infty \Psi_0^2 d\xi\right]^2}{\int_0^\infty \left(\Psi_0^4 - \frac{2}{\varkappa^2} Q^2\right) d\xi}. \qquad (28)$$

Now let us assume that the current flows along the surface but in a direction perpendicular to the field. This can occur only when η deviates from the value corresponding to the maximum field. As already mentioned in the preceding section, the determination of the smallest eigenvalue β_c is equivalent to the variational problem (19) (in the present case $s = \infty$). Since β_c is minimized with respect to η, the expansion of β_c in powers of $\eta - \eta_0$ begins with the quadratic term. Moreover, from (19) we obtain

$$\beta_c = \beta_0 + {}^1/_2 (\eta - \eta_0)^2 (\partial^2 \beta / \partial \eta^2)_{\eta_0} = \beta_0 + (\eta - \eta_0)^2. \qquad (29)$$

The current density in the usual units would be $-(2e^2/mc)\mathbf{A}|\Psi|^2$. In our units it equals

$$j = -(\delta / \sqrt{\beta})(\xi - \eta)|\Psi|^2. \qquad (30)$$

But since the total current vanishes for $\eta = \eta_0$, then according to (24) we have

$$J = \frac{1}{\varkappa}(\eta - \eta_0) \int_0^\infty |\Psi|^2 d\xi. \qquad (31)$$

Now let us consider the equation for Ψ. In the present case q = 0, but η differs from η_0. We transfer the term containing Ψ^3, and also the term containing the difference between β and the new critical value (30), to the right side. We have

$$\frac{d^2\Psi_1}{d\xi^2} + [\beta_c - (\xi - \eta)^2]\Psi_1 = \beta_0 \Big[\Psi_{01}^3 + \frac{2}{\varkappa^2}(\xi - \eta)\Psi_{01}(\xi) \times \int^\xi d\xi_1 \int_0^{\xi_1} \Psi_0^2(\xi_2)(\xi_2 - \eta)\, d\xi_2\Big] - [\beta - \beta_0 - (\eta - \eta_0)^2]\Psi_{01}.$$

The solution Ψ_{01} of the homogeneous equation (for $\eta \neq \eta_0$) differs little from Ψ_0. The problem, as it is easy to see, reduces to the previous problem, except that $\eta - \eta_0$ appears instead of $\sqrt{\beta_0}\, q$. Thus, the critical current coincides in this case with (28). One can generalize this derivation without difficulty to the case of an arbitrary angle between field and current. Thus, the critical current is isotropic.

As already stated, the function $\Psi_0 = \exp(-\beta_0 \xi^2/2)$ gives a value of β_0 in good agreement with the result of the exact calculation. Substituting this function into (28), we find

$$J_c = \frac{1}{3}\sqrt{\frac{2\pi}{3}} \frac{(1 - H/H_{c3})^{3/2}}{\varkappa(1 - 0.156/\varkappa^2)}. \qquad (32)$$

The fact that a trial function of the type $\exp(-b\xi^2/2)$ satisfies the variational procedure well makes it realistic to attempt to obtain the critical current in the general case of fields ranging between H_{c2} and H_{c3}. We confine ourselves here to the case $\kappa \gg 1$. In this connection, we can neglect the deviation of the vector potential from $A_0 = H_0(x - x_0)$. It is necessary for us to find the exact solution of the equation for Ψ (the current is along the z axis):

$$d^2\Psi / d\xi^2 + [\beta - \beta q^2 - (\xi - \eta)^2]\Psi - \beta\Psi^3 = 0. \qquad (33)$$

Instead of this, we can look for the minimum of the integral

$$F = \int_0^\infty \left(\frac{d\Psi}{d\xi}\right)^2 d\xi + \int_0^\infty [(\xi - \eta)^2 - \beta + \beta q^2]\Psi^2 d\xi + \frac{\beta}{2}\int_0^\infty \Psi^4 d\xi. \qquad (34)$$

This expression in fact corresponds to the free energy, and it is necessary to interpret its minimization more broadly than simply as a formal way of obtaining Eq. (33). In particular, it is also necessary to minimize F with respect to η. From here and from expression (31) we immediately find that the transverse screening current is equal to zero, which is natural, as indicated earlier.

First let us consider the case when no current is present, i.e., q = 0. We choose a trial function in the form $\Psi = C\exp(-b\xi^2/2)$ and we determine the minimum of expression (34) with respect to η, C, and b. As a result we obtain

$$b = -{}^1/_3\beta + [{}^1/_9\beta^2 + {}^5/_3(1 - 2/\pi)]^{1/2},$$

$$C^2 = (4\sqrt{2}/5\beta)\{{}^4/_3\beta - [{}^1/_9\beta^2 + {}^5/_3(1 - 2/\pi)]^{1/2}\}. \qquad (35)$$

As it should, $C^2 = 0$ for $\beta = \beta_0 = [1 - (2/\pi)]^{1/2}$. Here $b = \beta_0$. As $\beta \to \infty$ (a case which in fact is

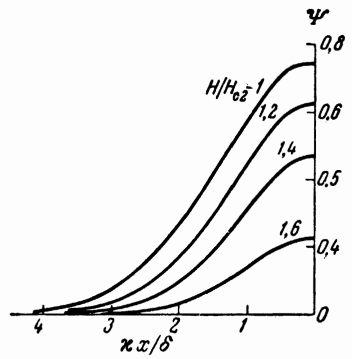

FIG. 2

not realized) $C^2 \to 4\sqrt{2}/5$ and $b \to 5\beta_0^2/2$. The form of Ψ for various values of the magnetic field H_0/H_{c2} is shown in Fig. 2.

In that case when a current exists in the z direction, it is necessary to make the substitution $\beta \to \beta(1-q^2)$ in the expression for b and in the numerator of the expression for C^2. According to (23) and (24) we obtain

$$J = \frac{1}{2}\sqrt{\frac{\pi}{b}}\frac{\sqrt{\beta}q}{\varkappa}C^2 = \frac{\sqrt{\pi}}{5\beta\varkappa b^2}(2b\beta - 3\alpha + 3b^2)^{1/2}(3\alpha - 5b^2), \quad (36)$$

where $\alpha = \frac{5}{3}[1-(2/\pi)] = \frac{5}{3}\beta_0$. Here for simplicity we have expressed q in terms of b. In this form it is more convenient to determine the maximum of J. The condition for a maximum gives the following equation:

$$t^4 + {}^1/_3\mu t^3 + t^2 + \mu t - {}^{10}/_3 = 0, \quad (37)$$

where $t = b/\beta_0$, $\mu = \beta/\beta_0$. In turn, the expression for the current can be written in the form

$$J_c = (\sqrt{2\pi}/\varkappa)Q(H_{c3}/H);$$

$$Q(\mu) = (\mu t + {}^3/_2 t^2 - {}^5/_2)^{1/2}(1-t^2)/\mu t^2. \quad (38)$$

Here one should express t in terms of μ with the aid of Eq. (37). These formulas give a complete determination of the dependence of J_c on H. Near H_{c3} we obtain $1-t \approx (\mu-1)/6$, $Q \approx (\mu-1)^{3/2}/3\sqrt{3}$, i.e., expression (32). For $H \to 0$, i.e., for $\mu \to \infty$, $t \approx 10/3\mu$, $Q(\mu) \approx (3/10)^{3/2}\mu/2$, i.e., $J_c \propto H^{-1}$. Of course, this case is actually not realized. The

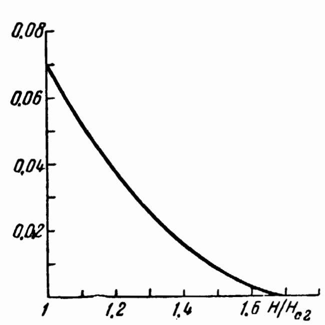

FIG. 3

dependence of J_c on (H/H_{c2}) in the region $H_{c2} < H < H_{c3}$ is plotted in Fig. 3.

Here we shall not carry out the derivation for current flowing at an angle to the field. This derivation is completely analogous to the preceding and leads to the conclusion that the critical current is isotropic.

4. EXPERIMENTAL DATA

Some of the experimental consequences of surface superconductivity were already discussed in the article by Saint-James and de Gennes.[1] The fundamental consequence, of course, is the fact that the vanishing of the magnetic moment of a bulk superconductor of the second kind and the appearance of resistivity in such superconductors occur at different values of the field. In experiments in which the moment is measured, surface superconductivity does not manifest itself in any way. However, in the extensive investigation of the critical fields of type II superconductors carried out by Berlincourt and Hake,[10] not the magnetic moment but the appearance of resistivity was observed. Therefore, one would think that they must have observed not H_{c2} but H_{c3}. At the same time, a comparison of data with the theoretical value of the field H_{c2} revealed agreement in this region of concentrations of alloys, where the mean free path was not overly small, and therefore the theory was applicable. In this same region, where the mean free path became too small, the theoretical field H_{c2} was above and not below the observed field.

It may be possible to attribute this clear contradiction to the large measuring current. In the experiments of Berlincourt and Hake, bars of length 1.3 cm, width from 0.02 to 0.08 cm, and thickness 0.005 cm were used. The current, relative to the cross sectional area, amounted to 10 A/cm^2. If we assume that surface superconductivity did exist, then the current must have flowed only on the surface. Recalculating, we obtain 2.5×10^{-2} A/cm. In order to estimate the critical current, we use formula (32). Changing over to the usual units, we obtain

$$J_c = \frac{5H_{cm}}{3\sqrt{3\pi\varkappa}}\left(1 - \frac{H}{H_{c3}}\right)^{3/2} \text{ A/cm}. \quad (39)$$

If the most unfavorable numbers are substituted here, namely $H_{cm} = 100$ Oe and $\kappa = 100$, then we find that the current used in [10] should shift the field by only 16%. In fact, however, H_{cm} is closer to 1000 Oe and κ is hardly larger than 10 in the region where the quantitative theory is applicable. Therefore, we must admit that for some reason surface superconductivity was absent in the experiments of Berlincourt and Hake. It is possible that the reason was the inhomogeneity of the surface layers of the samples.

The experiments of Khukhareva[8] on the determination of the critical field of thin films condensed at low temperature, were more favorable for the observation of surface superconductivity. The method of preparation of these films would most likely give homogeneous samples. Khukhareva compared her data with theory[9] and observed quite good agreement. However, as we shall show, her results not only do not contradict, but perhaps are even in better agreement with the formulas of Sec. 2 of the present article.

In fact, the experimental data were reduced with the aid of a formula of type (13). Formula (13) exhibits two characteristic regions: the region of small relative thicknesses (neighborhood of T_c) where $H_{c3}(d)/2\theta^2 = (2\sqrt{3})\,1.29 \times 10^{-4}/\theta d$, and the region of large relative thicknesses where $H_{c3}/2\theta^2 \approx 1.7$. Since an incorrect relation $H_{c3}/2\theta_1^2 \approx 1$ was used by Khukhareva for large thicknesses, the value of θ_1 thus found was $\sqrt{1.7}$ times larger than the true value. Khukhareva recalculated from the value of θ, the coefficient δ_{00} in the temperature dependence of the penetration depth. $\delta_{00} = (22.6 \pm 2.3) \times 10^{-6}$ cm was obtained for mercury. A theoretical determination from the normal-state conductivity gives $\delta_{00} = 16 \times 10^{-6}$ cm. Since θ is proportional to δ_{00}, it follows that it is necessary to decrease the experimental value of δ_{00} by $\sqrt{1.7}$ times. This yields $\delta_{00} = (17.3 \pm 1.7) \times 10^{-6}$, in excellent agreement with the theoretical value.

To be sure, it is necessary to show that a decrease in θ leads, according to the relation in the region of small relative thicknesses, to the fact that one should regard the thickness of the films as 30% less than assumed earlier. This is apparently quite permissible. The point is that Khukhareva[8] determined the thickness of the films by two methods: a) from the amount of evaporated metal with assumption of a cosine law distribution on the surface, and b) by direct weighing of the collected evaporated substance (in one experiment). The first method gave a thickness 20% smaller than the second. A previous determination of the thickness of the film according to the curve of $H_c(d)$[9] agreed with the larger value obtained by the second method. Thus, a decrease of the thickness by 30% is in any case a change of the data in the right direction and by an amount of permissible order.

From everything that has been said, and also from the discussion of experimental data given by Saint-James and de Gennes,[1] it follows that at the present time there is still no clear experimental confirmation of surface superconductivity, and new more thorough experiments are necessary.

Remark (May 27, 1964). Recently a whole series of articles devoted to the measurement of the field H_{c3} have appeared in print. Surface superconductivity has been observed for a large number of different superconducting alloys.[11] The majority of these measurements well confirm the relationship $H_{c3} = 1.7\,H_{c2}$ of Saint-James and de Gennes. It is of interest that surface superconductivity is observed even in superconductors of the first kind, for which $1/\sqrt{2} > \kappa > (1/\sqrt{2})/1.7$ (i.e., $H_{c2} < H_c < H_{c3}$[12]).

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