Critical Fields and Currents in Superconductors*

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I. INTRODUCTION

To determine critical fields and currents in small superconducting specimens, it has long been recognized that it is necessary to take into account the effect of a change in the order parameter with field or current. Pippard[1] discussed the problem in a qualitative way and showed that under some conditions the order parameter goes gradually to zero with increasing field, giving a second-order transition, while in others the transition is of first order. He suggested that the concentration of superconducting electrons n_s of the two-fluid model might be taken as the order parameter, and that an extra energy is involved if n_s changes appreciably over distances comparable to the coherence distance.

A phenomenological theory for treating such problems quantitatively was given by Ginzburg and Landau (G-L),[2] in which they introduced an effective wave function Ψ whose square is proportional to n_s. Their equations reduce to those of the London theory when space variations of n_s are ignored, and thus are not valid when the Pippard nonlocal theory must be used. Gor'kov[3] has shown that the present microscopic theory leads to the G-L theory near T_c where the London equations *do* apply. The only change is that the effective charge is $-2e$ rather than $-e$, a consequence of the pairing in the superconducting ground state. Gor'kov takes $\Psi(\mathbf{r})$ proportional to the energy gap parameter $\Delta(\mathbf{r})$. As we shall see, there is a close connection between this choice and the original concept of n_s as the order parameter.

In the present paper we shall be primarily concerned with small specimens of dimensions less than the coherence distance, so that changes in the energy gap with position may be neglected. One may then extend the theory to arbitrary temperatures by treating the gap as a variational parameter and finding the value which makes the free energy a minimum for given fields or currents.

Several calculations of critical currents and fields have been given, particularly by Ginzburg and Abrikosov,[4] on the basis of the original version of the G-L theory. This work can be taken over with little or no modification for application to temperatures near T_c. Douglass[5] has used the G-L equations to estimate the magnetic-field dependence of the energy gap, and finds good agreement between theory and experiments of Giaevar and Megerle.[6] By using the gap as a parameter, and by determining the dependence of free energy on gap at lower temperatures from a phenomenological two-fluid model, Tinkham[7] was able to get a significant improvement over the G-L theory in fitting his data on the dependence of thermal conductivity on magnetic field. Rogers[8] used the gap as a free parameter and determined how it changed with field or current. The present paper is an attempt to review this work, to put the theory on a more systematic basis, and to apply it to several problems.

In a few cases, more basic calculations have been made from the microscopic theory in which a modified equation for the gap has been obtained for a superconductor in the presence of fields or currents. Rogers[8] treated the case of a uniform current flow in a bulk specimen. Nambu and Tuan[9] have calculated the reduction in gap to the second order in field strength for a bulk superconductor with fields of arbitrary wavelength. Results obtained are equivalent to those obtained by the variational method in cases where they can be compared.

Section II is concerned with a general formulation of the thermodynamic relations when the gap is

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[1] A. B. Pippard, Phil. Mag. **43**, 273 (1952).
[2] V. L. Ginzburg and L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 1064 (1950).
[3] L. P. Gor'kov, J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 1918 (1959); **37**, 833 (1959); Soviet Phys.—JETP **9**, 1364 (1959); **10**, 593 (1960).
[4] V. L. Ginzburg, Doklady Akad. Nauk. S.S.S.R. **83**, 385 (1952); J. Expt. Theoret. Phys. (U.S.S.R.) **34**, 113 (1958); Soviet Phys.—JETP **7**, 78 (1958); A. A. Abrikosov, Doklady Akad. Nauk. S.S.S.R. **86**, 489 (1952).
[5] D. H. Douglass, Jr., Phys. Rev. Letters **6**, 346 (1961); IBM J. Research Develop. **6**, 44 (1962).
[6] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[7] M. Tinkham, IBM J. Research Develop. **6**, 49 (1962); D. E. Morris, Ph.D. thesis, University of California (Berkeley), 1962 (unpublished).
[8] K. T. Rogers, Ph.D. thesis, University of Illinois, 1960 (unpublished).
[9] Y. Nambu and S. F. Tuan, Phys. Rev. (to be published).

treated as a parameter, Sec. III with the Ginzburg-Landau equations, Sec. IV and Appendix C with explicit calculations of the free-energy difference between superconducting and normal states for general values of the gap parameter, and Sec. V deals with applications of the methods to the calculation of changes of gap with field or current in small specimens. Expressions for the magnetic moment of small specimens are listed in Appendix A and Appendix B gives Roger's calculation for uniform current flow.

II. THERMODYNAMIC RELATIONS

To discuss the thermodynamics of a superconductor in a magnetic field or with current flow, it is most convenient to take the external field H and the superfluid velocity v_s as independent variables. The latter is a significant variable only for thin films or wires of dimensions small compared with the coherence distance. In a bulk specimen, the current flow is confined to the penetration region near the surface and is determined by the magnetic field at the surface. The critical current is determined by the bulk critical field (Silsbee's hypothesis). In the discussion of thin films or wires, we shall assume that v_s is constant across the cross section.

We may take v_s to be the common velocity of the pairs in the ground state. More precisely, if the ground-state pairing[10] is $(\mathbf{k}+\mathbf{q}\uparrow, -\mathbf{k}+\mathbf{q}\downarrow)$, one may define $v_s = \hbar q/m$, where, in a periodic potential, m is an effective mass. In an electric field $\mathcal{E}$, the acceleration is given by

$$m dv_s/dt = -e\mathcal{E}\,. \tag{2.1}$$

The entire distribution of electrons, including the pairs, is displaced in momentum space by the electric field. Scattering of quasi-particles tends to reduce the current, but does not change the value of v_s. In a normal metal such scattering reduces the current to zero, but in a superconductor a net flow remains.

It is convenient to use rather than the electric current density, the density of mass flow defined by

$$J_s = m \sum \mathbf{v}_i/\mathcal{V}\,, \tag{2.2}$$

where $\mathcal{V}$ is the volume and $\mathbf{v}_i$ the velocity of the ith electron. The electric current density is then $-eJ_s/m$. When v_s is small, the equilibrium density J_s is proportional to v_s, and the ratio is the density ρ_s of the superfluid component of the two-fluid model.[11]

More generally, one may define ρ_s by the equation

$$\rho_s(v_s) = dJ_s(v_s)/dv_s\,, \tag{2.3}$$

so that

$$\frac{dJ_s}{dt} = \frac{dJ_s}{dv_s}\frac{dv_s}{dt} = -\frac{e\rho_s\mathcal{E}}{m}\,. \tag{2.4}$$

It is assumed that the variation with time is sufficiently slow, so that the quasi-particle distribution attains a steady-state distribution appropriate to the velocity v_s of the ground pairs.

One may use (2.2) and (2.4) to define v_s and ρ_s when impurity scattering is present so that the wave vector $\mathbf{k}$ is not a good quantum number. It is necessary to include effects of impurity scattering in thin films or other small specimens where electrons can be randomly scattered from the surface.

The displacement of the pairs causes an increase in free energy of the system which may be expressed simply in terms of J_s. The rate at which work is done per unit volume on the supercurrent by the electric field is

$$dW/dt = -e\mathcal{E}\cdot\sum \mathbf{v}_i = -e\mathcal{E}\cdot J_s\mathcal{V}/m = \mathcal{V}J_s(dv_s/dt)\,. \tag{2.5}$$

The net increase in free energy obtained by integrating with respect to t is

$$F_J = \mathcal{V}\int_0^{v_s} J(v_s')dv_s'\,. \tag{2.6}$$

In addition to the work associated with the superfluid component, there also will be a dissipation of energy from scattering of quasi-particles. By accelerating the electrons in a sufficiently small electric field, this ohmic energy dissipation can be made negligible with respect to F_J.

The increase in free energy as a result of an external magnetic field H is

$$F_H = -\int_0^H M(H')dH'\,, \tag{2.7}$$

where M is the total magnetic moment. This expression applies to a body of any shape. For a body of a simple shape such that there is no demagnetizing field,

$$M(H) = \mathcal{V}\chi H\,, \tag{2.8}$$

where χ is the susceptibility, equal to $-1/4\pi$ for a bulk superconductor.

For a specimen with dimensions small compared with the coherence distance, the magnetic moment

[10] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[11] J. Bardeen, Phys. Rev. Letters **1**, 399 (1959).

for small fields is given by an expression of the form

$$M = -\mathcal{V}aHN(0)\Delta_0\Delta \tanh(\tfrac{1}{2}\beta\Delta)\,, \qquad (2.9)$$

where a is a constant dependent on the shape of the body but independent of H and of the energy gap parameter Δ. Here $N(0)$ is the density of states of one spin in energy at the Fermi surface and Δ_0 the gap at $T = 0$ in the absence of fields. The method of derivation of (2.9) together with a list of values of the parameter a for different specimen shapes is given in Appendix A.

In large fields, the gap may depend on H and v_s. Further, for very large fields there may be strictly nonlinear effects not included in the change of Δ. The fact that there is only a very small change of penetration depth up to the critical field, indicates that such effects are unimportant for fields up to the usual bulk critical fields of a few hundred oersteds, but they may be important for specimens of small dimensions with critical fields of 10^4 or even 10^5 Oe. We shall ignore such effects here, and include only the dependence of Δ on H and v_s.

The procedure is to take Δ as an independent parameter along with H and v_s. This implies that calculations of the free energy are made with a set of quasi-particle states appropriate to a gap Δ, giving

$$F_s(\Delta,H,v_s) = F_{s0}(\Delta) - \int_0^H M(H',\Delta)dH' + \mathcal{V}\int_0^{v_s} J_s(v_s',\Delta)dv_s'\,, \qquad (2.10)$$

where $F_{s0}(\Delta)$ is the free energy in the absence of fields and currents, but with a gap which may differ from the usual value. One then finds the value of $\Delta(H,v_s)$ which makes the over-all free energy a minimum for given H and v_s by setting

$$(\partial F_s/\partial\Delta)_{H,v_s,T} = 0\,. \qquad (2.11)$$

When this value of $\Delta(H,v_s)$ is substituted in (2.10), one obtains an upper bound on the true free energy.

It should be noted that the moment $M(H,v_s)$ is given by the usual expression,

$$M(H,v_s) = -\left(\frac{dF_s}{dH}\right)_{v_s,T} = -\left(\frac{\partial F_s}{\partial H}\right)_{\Delta,v_s} - \left(\frac{\partial F_s}{\partial\Delta}\right)_{H,v_s}\left(\frac{\partial\Delta}{\partial H}\right)_{v_s}. \qquad (2.12)$$

Since the second term on the right vanishes by virtue of (2.11), one finds that $M(H,v_s) = M(\Delta(H,v_s),H)$. Integration of (2.12) gives the usual expression

$$F_s(H,v_s) = F_s(0,v_s) - \int_0^H M(\Delta(H',v_s),H')dH'\,. \qquad (2.13)$$

In Eq. (2.10), the dependence of F_{so}, M, and J_s on the gap has been indicated explicitly. Methods for determining these functions are discussed in the following sections.

If we assume that $\chi(\Delta)$ and $\rho_s(\Delta)$ are independent of H and v_s, we have

$$F_s = F_{s0}(\Delta) - \tfrac{1}{2}\mathcal{V}\chi(\Delta)H^2 + \tfrac{1}{2}\mathcal{V}\rho_s(\Delta)v_s^2\,. \qquad (2.14)$$

In this approximation, the gap is treated as an order parameter, and the dependence of χ and ρ_s on Δ is included, but other nonlinear effects are ignored. While this procedure can be justified for temperatures near T_c, and, in fact, gives the same results as the Gor'kov version of the Ginzburg-Landau theory, it may be in error for small specimens at low temperatures.

An equation similar to (2.14), but which ignores changes in χ and ρ_s with the gap or equivalent order parameter has sometimes been used to estimate critical fields or currents. The transition to the normal state would then occur when the added terms are equal to the free energy difference, $F_n - F_{so}$, between normal and superconducting states in the absence of fields and currents. The critical field for $v_s = 0$ would then be

$$H_c = H_{cb}(4\pi|\chi|)^{-1/2}\,, \qquad (2.15)$$

where H_{cb} is the bulk critical field, for which $\chi = 1/4\pi$. The critical current density for $H = 0$ would be

$$J_c = \rho_s v_c = (\rho_s/4\pi)^{1/2}H_{cb}\,. \qquad (2.16)$$

At $T = 0$°K, and in the absence of impurity scattering, $\rho_s = \rho = nm$ and $H_{cb} = H_0$ so that

$$J_c = (\rho/4\pi)^{1/2}H_0 = [nmN(0)\Delta_0^2]^{1/2} = (2/3)^{1/2}N(0)\Delta m v_F\,, \qquad (2.17)$$

where in the last form v_F is the velocity at the Fermi surface for a simple free electron model. We have used the relation $H_0^2/8\pi = \frac{1}{2}N(0)\Delta_0^2$, where H_0 and Δ_0 are the bulk critical field and gap parameter at $T = 0$°K, respectively. These expressions for H_c and J_c are equivalent to those which have been derived some years ago from the original London theory. When changes of Δ with field or current are taken into account, larger values are obtained for critical fields and somewhat smaller values for critical currents.

III. GINZBURG-LANDAU EQUATIONS FOR $T \sim T_C$

Gor'kov,[3] by use of a Green's-function method, has shown that the Ginzburg-Landau equations may be derived from the microscopic theory if the temperature is near T_c so that the local London theory applies. At these temperatures, ρ_s is proportional to the square of the gap, so that if one defines an effective wave function Ψ, such that

$$\Psi^2 = \rho_s/\rho , \tag{3.1}$$

Ψ will be proportional to the gap. Gor'kov used a somewhat different normalization for Ψ, one which is not as close to that of G-L. With our definition, the G-L equation may be written

$$-\frac{\hbar^2}{2m^*}\left[\frac{\partial}{\partial \mathbf{r}} - \frac{ie^*}{\hbar c}A(\mathbf{r})\right]^2\Psi - \alpha\Psi + \beta|\Psi|^2\Psi = 0 , \tag{3.2}$$

where $m^* = 2m$ and $e^* = -2e$, representing the mass and charge of a pair. With Gor'kov's definition of Ψ, m rather than $2m$ appears in the kinetic energy term. Equation (3.2) may be regarded as representing the center-of-mass motion of a bound pair; the wave vector for Ψ is $\mathbf{q}_p$, that of a pair.

The free-energy difference per unit volume is obtained by integrating over space and multiplying by $n/2$, the number of pairs per unit volume at $T = 0$:

$$F_s - F_n = \frac{n}{2}\int\left\{\frac{\hbar^2}{2m^*}\Psi^*\left[\frac{\partial}{\partial \mathbf{r}} - \frac{ie^*}{\hbar c}A(\mathbf{r})\right]^2\Psi - \alpha|\Psi|^2 + \tfrac{1}{2}\beta|\Psi|^4\right\}d\tau . \tag{3.3}$$

The density of mass flow is given by

$$\mathbf{J} = \frac{n}{2}\left\{-\frac{i\hbar}{2}\left(\Psi^*\frac{\partial\Psi}{\partial\mathbf{r}} - \Psi\frac{\partial\Psi^*}{\partial\mathbf{r}}\right) + \frac{e^*}{c}|\Psi|^2 A\right\}. \tag{3.4}$$

The kinetic-energy density for a wave vector $\mathbf{q}_p = 2\mathbf{q}$ for a pair is $\frac{1}{2}n(\hbar^2q_p^2/2m^*)|\Psi|^2$ and the density of flow $\mathbf{J} = \frac{1}{2}n\hbar\mathbf{q}_p|\Psi|^2$. Note that with $\mathbf{v}_s = \hbar\mathbf{q}_p/m^* = \hbar\mathbf{q}/m$ and $\rho_s = \rho|\Psi|^2 = nm|\Psi|^2$, these become $\frac{1}{2}\rho_s v_s^2$ and $\rho_s\mathbf{v}_s$, as they should.

The coefficients α and β are temperature-dependent parameters which were evaluated by Gor'kov from the microscopic theory. They also can be obtained directly from the equilibrium values of ρ_s/ρ and of $F_n - F_s = H_{cb}^2/8\pi$ in the absence of applied fields. The equilibrium value of $|\Psi|^2 = \alpha/\beta$, which is that which makes $-\alpha|\Psi|^2 + \frac{1}{2}\beta|\Psi|^4$ a minimum. The minimum free energy per unit volume for this value of $|\Psi|^2$ is

$$F_s - F_n = -n\alpha^2/4\beta = -H_{cb}^2/8\pi . \tag{3.5}$$

One may express ρ_s/ρ in terms of the penetration depth $\lambda(T)$ for the given temperature and $\lambda_L = (\rho c^2/4\pi n^2 e^2)^{1/2}$, the London penetration depth for density ρ:

$$\rho_s/\rho = \lambda_L^2/\lambda^2 = \alpha/\beta . \tag{3.6}$$

Thus

$$\alpha = H_{cb}^2\lambda^2/2\pi n\lambda_L^2 ; \quad \beta = H_{cb}^2\lambda^4/2\pi n\lambda_L^4 . \tag{3.7}$$

For temperatures near T_c such that $(T_c - T)/T = 1 - t \ll 1$, the model of Cooper, Schrieffer, and the author (BCS)[10] gives

$$\rho_s/\rho \simeq 2(1-t) . \tag{3.8}$$

One may also write for temperatures near T_c,

$$H_{cb}^2 \simeq (dH_{cb}/dt)_c^2(1-t)^2 . \tag{3.9}$$

The slope of the critical field curve near T_c may be expressed in terms of the jump in specific heat at T_c by use of Rutgers relation:

$$(1/8\pi)(dH_{cb}/dt)_c^2 = \tfrac{1}{2}T_c(C_s - C_n) . \tag{3.10}$$

For the BCS model, $T_c(C_s - C_n) = 6.2(H_0^2/8\pi)$ and

$$n\alpha = T_c(C_s - C_n)(1-t) . \tag{3.11a}$$

$$n\beta = \tfrac{1}{2}T_c(C_s - C_n) . \tag{3.11b}$$

Near T_c, the equilibrium gap is given by

$$(\Delta(T)/\Delta_0)^2 = 3.1(1-t) . \tag{3.12}$$

The expressions (3.7) are valid when impurity scattering is present, if the appropriate value of λ is used. Although H_{cb} and the equilibrium gap are not changed very much by scattering, λ is increased. According to Miller,[12] in the limit for which the mean free path l is much less than the coherence distance, $\xi_0 = \hbar v_F/\pi\Delta_0$,

$$\frac{\rho_s}{\rho} = \frac{\lambda_L^2}{\lambda^2} = \frac{\pi l\Delta\tanh(\frac{1}{2}\beta\Delta)}{\hbar v_F} , \tag{3.13}$$

where $\beta = 1/kT$. Equation (3.13) leads to values of α and β equivalent to those derived by Gor'kov for the limit $T \to T_c$. Note that (3.8) is no longer valid when impurity scattering is present. In the limit $T = 0$, $\Delta \to \Delta_0$, and

$$\rho_s = l\rho/\xi_0 = \pi\sigma m^2\Delta_0/(\hbar e^2) , \tag{3.14}$$

where $\lambda = ne^2\tau/m$ is the conductivity in the normal state.

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[12] P. B. Miller, Phys. Rev. **113**, 1209 (1959). Equivalent results were obtained by a different method by A. A. Abrikosov and L. P. Gor'kov, J. Exptl. Theoret. Phys. (U.S.S.R.) **35**, 1558 (1958); **36**, 319 (1959); Soviet Phys.—JETP **8**, 1090 (1959); **9**, 220 (1959).

Changes in Ψ with applied fields or currents imply corresponding changes in the energy gap, since Ψ is proportional to the gap. At low temperatures, it is most convenient to take the gap itself as the order parameter. An alternative derivation which gives the change in gap directly when a current flow is present is given in Appendix B.

To determine Ψ and the critical current in the absence of magnetic fields, we have for minimum free energy

$$\rho v_s^2|\Psi|^2 - n\alpha|\Psi|^2 + n\beta|\Psi|^4 = 0\,,$$

or

$$|\Psi|^2 = \rho_s/\rho = (n\alpha - \rho v_s^2)/n\beta\,. \qquad (3.15)$$

The mass flow is

$$\rho_s v_s = [(n\alpha - \rho v_s^2)/n\beta]\rho v_s\,, \qquad (3.16)$$

which is a maximum for $v_s = (n\alpha/3\rho)^{1/2}$:

$$(\rho_s v_s)_{\max} = \tfrac{2}{3}\,(\alpha\rho/\beta)(n\alpha/3\rho)^{1/2}\,. \qquad (3.17)$$

The value of ρ_s/ρ at the maximum is

$$\rho_s/\rho = \tfrac{2}{3}\,(\alpha/\beta)\,, \qquad (3.18)$$

so that near T_c the gap at the current flow maximum is reduced to $(2/3)^{1/2} = 0.81$ of the normal value. The critical value of the mass flow is[4]

$$(\rho_s v_s)_{\max} = \frac{2}{3}\,\frac{\alpha}{\beta}\left(\frac{n\alpha\rho}{3}\right)^{1/2} = \left(\frac{2}{3}\right)^{3/2}\left(\frac{H_c^2\rho_s}{4\pi}\right)^{1/2}. \qquad (3.19)$$

which varies as $(1-t)^{3/2}$. A further discussion of critical currents is given in Sec. V.

IV. DEPENDENCE OF FREE ENERGY ON GAP

In this section, we shall derive expressions for $F_{s0}(T,\Delta)$, with the gap taken as a free parameter, not necessarily chosen to make the free energy a minimum. We use the model of Cooper, Schrieffer, and the author[10] in which there is a constant pair interaction $-V$ within an energy $|\epsilon| < \hbar\omega$ of the Fermi surface. If Δ is not chosen to satisfy the integral equation for the gap, Eq. (3.36) of reference 10 for the free-energy difference between superconducting and normal phases becomes

$$\begin{aligned} F_{s0} - F_{n0} &= -2N(0) \\ &\quad\times\int_0^{\hbar\omega}\{2Ef(E) - 2\epsilon f(\epsilon) - \epsilon(1-\epsilon/E)\}d\epsilon \\ &\quad - N(0)^2V\left[\int_0^{\hbar\omega}\frac{\Delta}{E}\,(1-2f(E))d\epsilon\right]^2, \end{aligned} \qquad (4.1)$$

where $N(0)$ is the density of states of one spin at the Fermi surface, f is the Fermi-Dirac (F-D) function and $E = (\epsilon^2 + \Delta^2)^{1/2}$. The last term is the interaction energy. If Δ satisfies the integral equation

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega}[1 - 2f(E)]\,\frac{d\epsilon}{E}\,. \qquad (4.2)$$

this term becomes $-\Delta^2/V$, and one recovers the BCS expression.

In general, one must evaluate (4.1) by numerical methods. When the gap is small compared with kT, it is possible to expand in powers of $(\beta\Delta)^2$, where $\beta = 1/kT$. This occurs near T_c, or perhaps in large magnetic fields at lower temperatures. At very low temperatures, one may expand the F-D function in powers of $e^{-\beta E}$ as discussed in Appendix C. We first consider the high-temperature expansion, for $\beta\Delta \ll 1$.

The integral needed in the second line of (4.1) may be written

$$\begin{aligned} \int_0^{\hbar\omega}[1-2f(E)]\,\frac{d\epsilon}{E} &= \int_0^{\hbar\omega}\left\{\frac{1-2f(E)}{E} - \frac{1-2f(\epsilon)}{\epsilon}\right\}d\epsilon \\ &\quad + \int_0^{\hbar\omega}\frac{1-2f(\epsilon)}{\epsilon}\,d\epsilon\,. \end{aligned} \qquad (4.3)$$

The integrand in first integral on the right-hand side of (4.3) converges sufficiently rapidly for large ϵ so that the upper limit $\hbar\omega$ may be replaced by ∞ without appreciable error. We change the variable of integration from ϵ to $x = \beta\epsilon$, let $x_0 = \beta\Delta$ and $X = \beta E = (x^2 + x_0^2)^{1/2}$. To expand in a power series in x_0^2, we need to take derivatives

$$\frac{\partial}{\partial x_0^2} = \frac{\partial(x^2 + x_0^2)^{1/2}}{\partial x_0^2}\,\frac{\partial}{\partial X} = \frac{1}{2X}\,\frac{\partial}{\partial X}\,.$$

In this way we find

$$\begin{aligned} g_1(x_0) &\equiv \int_0^{\infty}\left\{\frac{1-2f(\epsilon)}{\epsilon} - \frac{1-2f(E)}{E}\right\}d\epsilon \\ &= a_2x_0^2 + a_4x_0^4 + \cdots\,, \end{aligned} \qquad (4.4)$$

where

$$a_2 = -\int_0^{\infty}\frac{1}{2x}\,\frac{\partial}{\partial x}\left(\frac{1-2f(x)}{x}\right)dx = \frac{7\zeta(3)}{8\pi^2}\,. \qquad (4.5)$$

The second integral on the right-hand side of (4.3) becomes

$$\int_0^{\beta\hbar\omega}\frac{1-2f(x)}{x}\,dx \simeq \int_0^{\beta_c\hbar\omega}\frac{1-2f(x)}{x}\,dx + \int_{\beta_c\hbar\omega}^{\beta\hbar\omega}\frac{dx}{x}\,, \qquad (4.6)$$

where $\beta_c = 1/kT_c$ and it has been assumed that $f(\beta\hbar\omega)$ is vanishingly small. Making use of the integral equation (4.2) for the gap at $T = T_c$, we find that the first integral on the right-hand side of (4.6) is equal to $1/(N(0)V)$. Thus, we have

$$\int_0^{\hbar\omega} [1 - 2f(E)] \frac{d\epsilon}{E} = -g_1(\beta\Delta) + \frac{1}{N(0)V} + \ln \frac{\beta}{\beta_c} . \tag{4.7}$$

In the limit $T \to 0$, we may neglect f and find

$$g_1(\beta\Delta) \to \ln (\beta\Delta/\beta_c\Delta_0) .$$

The integral (4.7) set equal to $1/[N(0)V]$ is just the integral equation (4.2) for the gap. From previous calculations of $\beta\Delta$ as a function of $\beta/\beta_c = T_c/T$, one can determine $g_1(\beta\Delta)$. A direct evaluation is given in Appendix C.

The first line on the right-hand side of (4.1) may be written, after an integration by parts,

$$L_1 = 2N(0)\{(\hbar\omega)^2 - \hbar\omega[(\hbar\omega)^2 + \Delta^2]^{1/2}\} + 2N(0) \int_0^{\hbar\omega} \{E[1 - 2f(E)] - \epsilon[1 - 2f(\epsilon)]\}d\epsilon . \tag{4.8}$$

To get rapid convergence of the integrand of the second term, we may write it in the form

$$2N(0) \int_0^{\hbar\omega} \{E[1 - 2f(E)] - \tfrac{1}{2}(\Delta^2/\epsilon)[1 - 2f(\epsilon)] - \epsilon[1 - 2f(\epsilon)]\}d\epsilon + \Delta^2 N(0) \int_0^{\hbar\omega} \frac{1 - 2f(\epsilon)}{\epsilon} d\epsilon . \tag{4.9}$$

The upper limit of the first integral may now be replaced by infinity without appreciable error. In this way we find that L_1 may be expressed to a good approximation in the form

$$L_1 = N(0)\Delta^2\{1/N(0)V + \ln (\beta/\beta_c) - g_2(\beta\Delta)\} , \tag{4.10}$$

where

$$1 - g_2(x_0) \equiv 2x_0^{-2} \int_0^{\infty} \{X[1 - 2f(X)] - \tfrac{1}{2}(x_0^2/x) \times [1 - 2f(x)] - x[1 - 2f(x)]\}dx . \tag{4.11}$$

Again, g_2 may be expanded in a power series in x_0^2, the first term of which is

$$g_2(x_0) = \tfrac{3}{2} a_2 x_0^2 + \cdots , \tag{4.12}$$

with a_2 given by (4.5). In the low-temperature limit, x_0 large, we have by direct integration

$$g_2(x_0) \simeq \ln (x_0/\beta_c\Delta_0) + \tfrac{1}{2} - 2\zeta(2)/x_0^2 .$$

Plots of $g_1(x)$ and $g_2(x)$ as calculated by McMillan are given in Figs. 1 and 2.

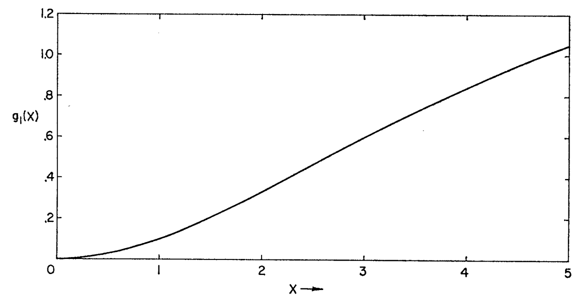

FIG. 1. Plot of the function $g_1(X)$, as defined by Eq. (4.4).

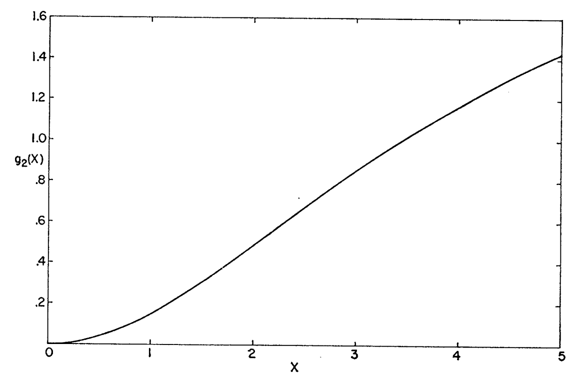

FIG. 2. Plot of the function $g_2(X)$, as defined by Eq. (4.11).

The second line of (4.1) may be evaluated with use of (4.7). We thus find

$$\begin{aligned} F_{s0} - F_n &= +N(0)\Delta^2\{1/N(0)V + \ln (\beta/\beta_c) - g_2(\beta\Delta) - N(0)V[-g_1(\beta\Delta) + 1/N(0)V + \ln (\beta/\beta_c)]^2\} \\ &= -N(0)\Delta^2\{[-2g_1 + \ln (\beta/\beta_c)][1 + N(0)V \ln (\beta/\beta_c)] + N(0)Vg_1^2 + g_2\} . \end{aligned} \tag{4.13}$$

Expanding to order Δ^4, we find

$$F_{s0} - F_n = N(0)\Delta^2\{\ln t[1 - N(0)V \ln t] + a_2(\beta\Delta)^2[1 - 4N(0)V \ln t] + \cdots\} , \tag{4.14}$$

where $t = \beta_c/\beta = T/T_c$.

The limiting expression as $T \to 0$ is

$$F_{s0} - F_n = -N(0)\Delta^2 \times \{\tfrac{1}{2} - \ln (\Delta/\Delta_0) + N(0)V[\ln (\Delta/\Delta_0)]^2\} . \tag{4.15}$$

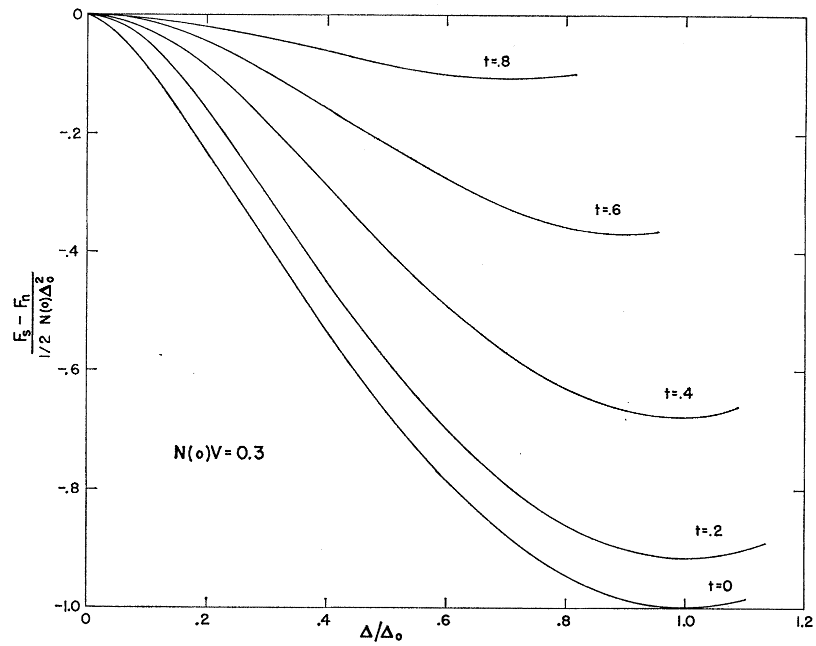

FIG. 3. Free-energy difference $(F_{so}(\Delta) - F_n)$ in units of $\frac{1}{2}N(0)\Delta_0^2 = H_0^2/8\pi$ as a function of Δ/Δ_0 for several reduced temperatures. The minima of these curves correspond to the usual equilibrium gap for the corresponding temperatures. The curves apply to a coupling strength $N(0)V = 0.3$.

A plot of $(F_{so} - F_n)/[\frac{1}{2}N(0)\Delta_0^2]$ as a function of Δ/Δ_0, for several different reduced temperatures, based on calculations of McMillan, is given in Fig. 3.

V. APPLICATION TO SMALL SPECIMENS

In this section we consider the application of the theory to a thin film or filament with thickness small compared with the penetration depth. We suppose that the magnetic field is either transverse or parallel to the filament or is in the plane of the film. Scattering at the boundaries may be taken into account by use of an effective mean free path l, which by our assumptions, is such that $l/\xi_0 \ll 1$. We shall use (2.14) for the free energy, which takes into account the dependence of χ and ρ_s on Δ but neglects other nonlinear effects. This approximation is valid when $\beta\Delta \ll 1$, and probably also at lower temperatures when $l \ll \xi_0$, since critical currents and fields may then not be so large as to get into the true nonlinear range. It is certainly not valid when $\beta\Delta > 1$ and $l > \xi_0$. As shown in Appendix B, for the latter case one may still use the concept of a gap varying with v_s, but the current density is not given by $\rho_s(\Delta)v_s$ as assumed in (2.14). Whereas a calculation similar to that of Appendix B could be made for small specimens for a boundary condition corresponding to specular reflection, it is difficult to treat the case of large fields or currents with random scattering at the surface or that corresponding to $l \ll \xi_0$.

We shall use (2.9) for the magnetic moment and (3.13) for ρ_s. Since the dependence on Δ is the same for both, we have for unit volume

$$F_s = F_{s0} + \tfrac{1}{2}\,(aH^2 + bv_s^2)N(0)\Delta_0\Delta \tanh\left(\tfrac{1}{2}\,\beta\Delta\right), \tag{5.1}$$

where a is the symbol in (2.9) and, from (3.13)

$$b = l\rho/[\xi_0 N(0)\Delta_0^2]\,.$$

The equilibrium value of Δ is that which makes the free energy a minimum. Analytic solutions can be obtained only for the limits $\beta\Delta \ll 1$ and $\beta\Delta \gg 1$. For the former, we use (4.14) and for the latter (4.15).

In the limit $\beta\Delta \ll 1$, we have

$$\begin{aligned} F_s - F_n = N(0)\Delta^2\{&\ln t[1 - N(0)V\ln t] \\ &+ a_2(\beta\Delta)^2[1 - 4N(0)V\ln t]\} \\ &+ AN(0)\Delta_0(\tfrac{1}{2}\,\beta\Delta^2 - \tfrac{1}{12}\,\beta^3\Delta^4)\,, \end{aligned} \tag{5.2}$$

where $A = \frac{1}{2}(aH^2 + bv_s^2)$. The equilibrium value of Δ is given by

$$(\beta\Delta)^2 = \frac{-\{\ln t[1 - N(0)V\ln t] - \frac{1}{2}\,\beta A\Delta_0}{2a_2[1 - 4N(0)V\ln t] - \frac{1}{6}\,\beta A\Delta_0}\,. \tag{5.3}$$

With increasing magnetic field, there is a second-order transition if Δ gradually goes to zero. This means that there must exist a solution of (5.3) as $\Delta \rightarrow 0$, which would occur for

$$\beta\Delta_0 A = -2\ln t[1 - N(0)V\ln t] . \quad (5.4)$$

It is necessary that the denominator remain positive for this value of A, or that t be such that

$$2a_2[1 - 4N(0)V\ln t] > -\tfrac{1}{3}\ln t[1 - N(0)V\ln t] . \quad (5.5)$$

The reduced temperature t_1, above which the transition is second order, is given by the solution of the quadratic equation

$$6a_2[1 + 4N(0)Vy] = y[1 + N(0)Vy] , \quad (5.6)$$

where $y = -\ln t_1$. A plot of t_1 as a function of $N(0)V$ is given in Fig. 4.

At reduced temperatures above t_1, such that (5.4) applies, the critical field H_c is given by

$$A = \tfrac{1}{2}aH_c^2 = \frac{-2\ln t[1 - N(0)V\ln t]}{\beta\Delta_0} . \quad (5.7)$$

Near T_c, this expression reduces to:

$$H_c^2 = 4(1-t)/\beta_c\Delta_0 a . \quad (5.8)$$

Values of a for various specimen shapes are given in Appendix A.

In the opposite limit of low temperatures, ρ_s and χ are proportional to Δ. With $y = \Delta/\Delta_0$, as in (4.15),

$$F_s = F_{n0} - \tfrac{1}{2}N(0)\Delta_0^2 y^2 \times \{1 - 2\ln y[1 - N(0)V\ln y]\} + AN(0)\Delta_0\Delta . \quad (5.9)$$

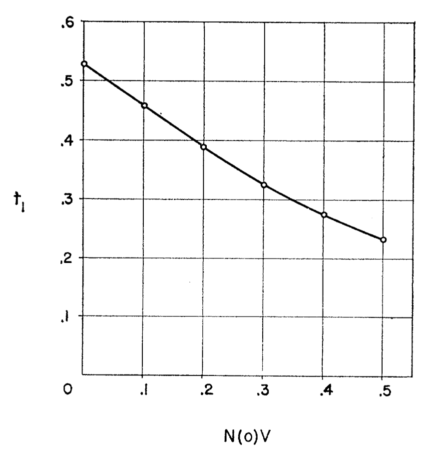

FIG. 4. Reduced temperatures t_1, which mark the change from a first- to a second-order transition of small specimens in a magnetic field as a function of the coupling strength, $N(0)V$.

The value of y which makes F_s a minimum is given by the solution of

$$-\tfrac{1}{2}4y\ln y[1 - N(0)V - N(0)V\ln y] = A . \quad (5.10)$$

If A is larger than a critical value A_c, the free energy in the normal state will be lower than that of the superconducting state. To determine the critical value of $y = y_c$, we substitute the value of A given by (5.10) into (5.9), set $F_s = F_{no}$, and solve for $\ln y_c$:

$$\ln y_c = \frac{1 - 2N(0)V - \{1 - 2N(0)V + 4[N(0)V]^2\}^{1/2}}{2N(0)V} . \quad (5.11)$$

For $N(0)V = 0.3$, $\ln y_c \simeq -0.80$ and

$$A_c = 0.68 . \quad (5.12)$$

For a value of A less than A_c, the minimum in F_s will be less than F_{n0} and for larger values of A greater than F_{n0}. At this critical value, a first-order transition to the normal state will occur. Such a transition has not been observed in small specimens of dimensions of the order of the penetration depth or less.

Numerical calculations are required to determine the variation of the gap with field for the complete range of temperatures. Figure 5 is a plot of (Δ/Δ_0) vs the parameter A for several reduced temperatures for $N(0)V = 0.3$, based on the free energy plots of Fig. 3. For this case, the gap gradually goes to zero,

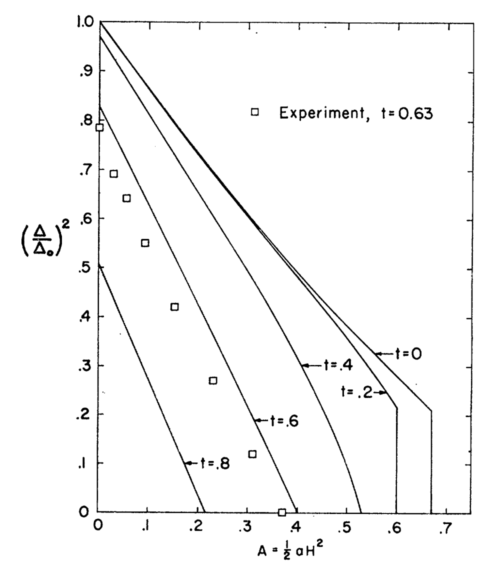

FIG. 5. Change in gap parameter with $A = \frac{1}{2}aH^2$ for coupling strength $N(0)V = 0.3$ at several reduced temperatures. the plotted points are deduced from data of Tinkham and Morris (reference 7) on thermal conductivity of a thin ($\sim$650Å) film of indium for $t = 0.63$.

giving a second-order transition, if $t > 0.325$, and the transition is of first order for $t < 0.325$. At the higher reduced temperatures, $t = 0.6$ and 0.8, $(\Delta/\Delta_0)^2$ is very close to a linear function of A or of H^2. Even at $t = 0.4$, the departures are not very large. An asymptotic behavior of this sort is to be expected from (5.3) near $t = 1$, when the first term of the numerator as well as the ln t term in the denominator can be neglected. It also follows from the Ginzburg-Landau theory, as shown by Douglass.[5] However, it is surprising that this limiting behavior is approximately valid at reduced temperatures as low as $t = 0.6$, or even 0.4.

In Fig. 6 is plotted, again for $N(0)V = 0.3$, the

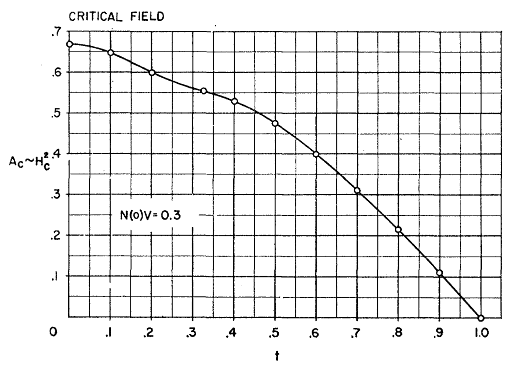

FIG. 6. Critical values of $A_c = \frac{1}{2}\, aH_c^2$ at which the transition from superconducting to normal state occurs for $N(0)V = 0.3$. Below about $t = 0.325$, the transition is of first order, above it is second order.

critical value of A, denoted by A_c, at which the transition from superconducting to normal behavior occurs. Below the inflection point near $t = 0.325$, the transition is of first order, above of second order.

Experimental evidence for a change in gap with field and a second order transition comes from (1) tunneling experiments of Giaevar and Megerle,[6] (2) changes of thermal conductivity in thin films with field as measured by Tinkham,[7] and (3) changes in the specific heat curves of high field superconductors, which presumably have superconducting domains of very small size. Morin and his coworkers[13] have measured the specific heat of V_3 Ga in fields of 40 kG and of 70 kG, and find that T_c decreases with increasing field, but the transition apparently remains one of second order, contrary to the behavior expected in bulk specimens which exhibit a Meissner effect. Their data indicate that H_c varies as $(1 - t)$ while the theory [Eq. (5.8)] for small specimens of uniform size predicts H_c^2 rather than H_c is linear in t near T_c. The reason for this discrepancy is not known. From the plot of Fig. 6, one might expect that at very high fields, such that $t < 0.3$, the transition would change to one of first order. To date, no such first order transition has been observed, although measurements on lead[7] have been made at temperatures as low as $t = 0.2$.

Values of $\Delta(H)/\Delta(0)$ deduced by Tinkham and Morris[7] from measurements of thermal conductivity in thin ($\sim$650Å) films of indium in high magnetic fields are compared with theory in Fig. 5. The reduced temperature for the experimental run is $t = 0.63$. Agreement between theory and experiment is excellent. Data taken at $t = 0.36$ (not shown) are in much poorer agreement with theory.

Klukhara[14] has measured critical fields of deposited mercury films with thickness d, varying from about 1 to 10×10^{-5} cm. The fields were parallel to the plane of the films. Measurements made near T_c were found to be in good quantitative agreement with predictions of the Gor'kov version of the Ginzburg-Landau theory as modified to take impurity scattering into account (see Sec. III). Susceptibilities were calculated by use of the local London theory for a mean free path $l < d$ (Appendix A). The theory predicts, as observed, that H_c varies inversely with d. In the Pippard nonlocal limit with $l > d$, one would expect H_c to vary as $d^{-3/2}$ when d is very small. While measurements were made on annealed films with longer mean free path, the film thicknesses were too large to expect this limit to apply. It was found that critical fields of the annealed films as well as of the unannealed films varied as d^{-1}.

We next consider the application of the equations to a calculation of critical currents. As noted in Sec. III, the current density $\rho_s v_s$ increases to a maximum and then decreases with increasing v_s, as the decrease in ρ_s with decreasing gap more than compensates for the increase in v_s. Only the values up to the maximum can be realized in practice. Since at the maximum there is only a moderate decrease in the gap, large changes in gap cannot be obtained simply by increasing the current. A magnetic field is necessary. We shall first derive the expression for the critical current when a magnetic field is present for the limit $\beta\Delta \ll 1$, which may apply either near T_c or in high magnetic fields near H_c.

[13] F. J. Morin, J. P. Maita, H. J. Williams, R. C. Sherwood, J. H. Wernick, and J. E. Kunzler, Phys. Rev. Letters (to be published).

[14] I. S. Khukhareva, J. Exptl. Theoret. Phys. (U.S.S.R.) **41**, 728 (1961); Soviet Phys.—JETP **14**, 526 (1962).

Using (5.3) and (3.13), we may express ρ_s in the form

$$\rho_s = \frac{3bN(0)\Delta_0}{2\beta}\left\{\frac{c_1 - v_s^2}{c_2 - v_s^2}\right\}, \tag{5.13}$$

where

$$c_1 = -(4/\Delta_0\beta b)\{\ln t[1 - N(0)V\ln t]\} - aH^2/b \tag{5.14}$$

$$c_2 = (12a_2/\Delta_0\beta b)[1 - 4N(0)V\ln t] - aH^2/b\,. \tag{5.15}$$

The value of $v_s = v_{sc}$ which makes $\rho_s v_s$ a maximum is given by setting

$$\frac{d}{dv_s}\left\{\frac{v_s(c_1 - v_s^2)}{c_2 - v_s^2}\right\} = 0\,, \tag{5.16}$$

which gives

$$v_{sc}^2 = \tfrac{1}{2}\{3c_2 - c_1 - [(9c_2 - c_1)(c_2 - c_1)]^{1/2}\}\,. \tag{5.17}$$

The value of $(\beta\Delta)^2$ for this critical velocity is

$$(\beta\Delta)_c^2 = 3\left\{\frac{(9c_2 - c_1)^{1/2} - 3(c_2 - c_1)^{1/2}}{(9c_2 - c_1)^{1/2} - (c_2 - c_1)^{1/2}}\right\}. \tag{5.18}$$

The solution is valid only when $(\beta\Delta)_c \ll 1$, which, in turn, implies $c_1 \ll c_2$. In this limit, $v_s^2 \simeq c_1/3$ and $(\beta\Delta)_c^2 \simeq 2c_1/c_2$. The critical current is

$$J_c = \rho_s v_{sc} \simeq [bc_1N(0)\Delta_0/\beta c_2](c_1/3)^{1/2}\,. \tag{5.19}$$

As indicated by (3.13), ρ_s is proportional to Δ^2 near T_c, and near $T = 0$ is independent of Δ for $l \gg \xi_0$ and proportional to Δ for $l \ll \xi_0$. In Fig. 5 is shown how ρ_s varies with A. Note that in the absence of a magnetic field, A is proportional to v_s^2. Thus, near T_c, ρ_s decreases linearly with v_s^2. Near $T = 0$, for $l \ll \xi_0$, Δ and thus ρ_s drop roughly linearly with A or v_s^2 until a critical field is reached at which an abrupt first-order change to the normal state occurs. The slope in the limit $A \to 0$, $T \to 0$, is

$$\frac{1}{\Delta}\frac{d\Delta}{dA} = \frac{1}{\rho_s}\frac{d\rho_s}{dA} = -\frac{1}{2[1 - N(0)V]}\,. \tag{5.20}$$

The current density, proportional to $\rho_s v_s$, increases to a maximum and then decreases with increasing v_s; the critical current density is given by the maximum of the curve. Several limiting forms for the critical current density, $J_c = (\rho_s v_s)_{\max}$, are of interest. It is convenient to normalize in terms of the critical density $J_{\mathrm{F.E.}}$ given by the free-energy criterion for a bulk specimen as given in (2.13). The corresponding electrical current density is obtained by multiplying by e/m:

$$I_{\mathrm{F.E.}} = \frac{H_{cb}}{4\pi}\left(\frac{4\pi\rho_s e^2}{m^2}\right)^{1/2} = \frac{H_{cb}}{4\pi\lambda_L}\,,\ \text{(emu.)} \tag{5.21}$$

where λ_L is the London penetration depth. Equation (5.21) may be used to estimate critical current densities at temperatures different from zero, if $H_{cb}(T)$ and $\rho_s(T)$ are the temperature dependent quantities. The dependence of ρ_s on scattering mean free paths should be taken into account, with use of (3.13) if $l \ll \xi_0$. The values obtained from (5.21) are somewhat too large because this expression does not take into account the dependence of the gap on v_s.

Near T_c, when $\beta\Delta \ll 1$, we have from (3.19)

$$I_c/I_{\mathrm{F.E.}} = (2/3)^{3/2} = 0.545\,. \tag{5.22}$$

Near $T = 0$, with $l \ll \xi_0$, we have from (4.15) and (5.1)

$$I_c/I_{\mathrm{F.E.}} = \tfrac{2}{3}\{\tfrac{4}{3}[1 - N(0)V]\}^{1/2} \simeq \tfrac{2}{3}\,. \tag{5.23}$$

Near $T = 0$, with no scattering, we have from (B12)

$$I_c/I_{\mathrm{F.E.}} = 1.017(2/3)^{1/2} \simeq 0.82\,. \tag{5.24}$$

An approximate formula valid for all temperatures may be obtained by using the relations $H_{cb}(t) = H_0(1 - t^2)$, $\lambda_L(t) = \lambda(0)/(1 - t^4)^{1/2}$, so that

$$H_{cb}(t)/\lambda(t) = [H_0/\lambda_L(0)](1 - t^2)^{3/2}(1 + t^2)^{1/2}\,. \tag{5.25}$$

To obtain a useful approximation valid for all temperatures one may express ρ in terms of the conductivity, $\sigma = ne^2l/mv_F$, of the normal state, and find for $l \ll \xi_0$ (the usual situation for thin films):

$$I_c \simeq \tfrac{2}{3}H_0(\sigma/\xi_0)^{1/2}(1 - t^2)^{3/2} = \tfrac{1}{2}H_0\left(\frac{\Delta(0)\sigma}{\hbar}\right)^{1/2}(1 - t^2)^{3/2}\,. \tag{5.26}$$

Since H_0 is proportional to Δ_0 and ξ_0 to Δ_0, I_c varies as $T_c^{3/2}$. A rough formula based on a free-electron model is

$$I_c \simeq 3(l/\xi_0)^{1/2}T_c(1 - t^2)^{3/2} \times 10^6\ \mathrm{A/cm^2}\,. \tag{5.27}$$

The best experimental observations of critcial currents in thin film are in fair agreement with (5.26), both as regards temperature dependence and magnitude. Care must be taken to avoid effects of magnetic fields produced by the current on the current distribution by use of a compensated geometry, and also as pointed out particularly by Bremer and

Newhouse[15] to avoid heating effects by use of short pulses. As far as the writer is aware, no experiments have been done in which both precautions have been taken. Ginzburg and Shalnikov[16] and Alekseevskii and Mikheeva[17] have used a compensated geometry with a specimen in the form of a thin film deposited on the outside of a circular cylinder. They found that I_c varies as $(1 - t)^{3/2}$ near T_c, as predicted by the G-L theory. However, they used direct currents, and so may have had heating effects and observed the critical current for propagation of a normal-superconducting boundary rather than a true critical current.[15] Mercereau and Hunt[18] have observed the flux trapped in thin film rings of tin of very small dimensions. With films less than 700Å in thickness, they find current densities greater than 10^6 A/cm^2 and near T_c the predicted temperature dependence of critical current. A plot of their data is given in Fig. 7. Observations with pulses so as to avoid heat effects have been made by a number of workers[13,19] on planar film strips, mainly in connection with cryotron studies. This geometry is unfavorable for basic studies because the current distribution may be altered by the magnetic field and not be uniform across the film. Nevertheless, results have generally been in qualitative accord with theory.

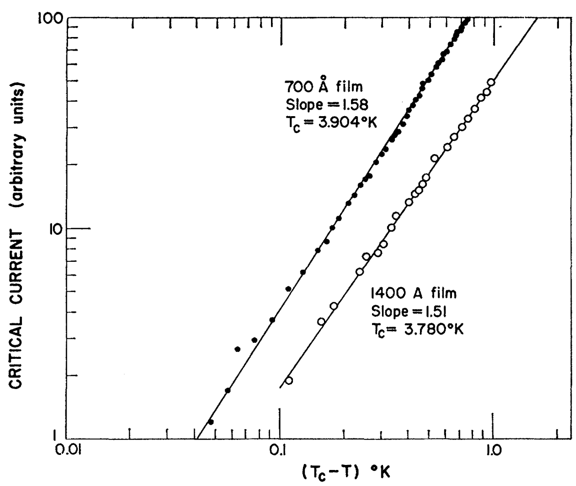

FIG. 7. Critical currents of thin (~700Å) films of tin as a function of $T_c - T$, from data of Mercereau and Hunt (reference 18). Theory predicts a slope of 1.50.

VI. CONCLUDING REMARKS

The discussion has been confined to specimens with at least one dimension small in comparison with the coherence distance, so that the variation of the gap parameter Δ with position may be neglected. To determine changes in gap with applied fields and currents, we use a variational method and treat Δ as a free parameter, chosen to make the over-all free energy a minimum. As discussed in Sec. II, there are three contributions to the free energy: (1) that from the pairing interaction, which is a minimum for the value of Δ determined from the usual gap equation; (2) that from the magnetization, which decreases as Δ decreases, allowing further penetration of the field; and (3) that from the kinetic energy of the supercurrents. Section IV and Appendix C are concerned with the calculation of the first of these, the free energy difference $F_{s0} - F_n$ between superconducting and normal states for general values of Δ.

To determine the magnetization, $M(H,\Delta)$, and the supercurrent density, $J_s(v_s,\Delta)$, for a velocity, v_s, of the ground-state pairs, we have generally taken the first nonvanishing terms, those proportional to H^2 and v_s^2, respectively. Thus, we take into account effects of changes of gap, but neglect other specifically nonlinear effects. This procedure is justified for temperatures near T_c, and, in fact, gives results equivalent to those derived from the Gor'kov version of the Ginzburg-Landau theory. This latter theory is reviewed in Sec. III. It is likely that the method gives reasonably satisfactory results at all temperatures for fields and currents up to the critical values if the mean free path of the electrons is much less than the coherence distance, the usual situation in small specimens. Applications of the theory to various problems and comparisons of theory and experiment are discussed in Sec. V.

While agreement between theory and experiment is good in general, there are some discrepancies. Further experiments on well-defined specimens are desirable. In particle, it would be of interest to study combined effects of field and current on specimens of simple geometry. Measurements of the change of gap with field at very low reduced temperatures ($t < 0.3$) are required to see whether or not the predicted first-order transition occurs.

Rather than use the variational method, one could,

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[15] J. W. Bremer and V. L. Newhouse, Phys. Rev. **116**, 309 (1959).

[16] N. I. Ginzburg and A. I. Shalnikov, J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 399 (1959); Soviet Phys.—JETP **10**, 285 (1960).

[17] N. E. Alekseevskii and M. N. Mikheeva, J. Exptl. Theoret. Phys. (U.S.S.R.) **38**, 292 (1960); Soviet Phys.—JETP **11**, 211 (1960).

[18] J. E. Mercereau and T. K. Hunt, Phys. Rev. Letters **8**, 243 (1962).

[19] The problems encountered are discussed in A. M. Kolchin, Yu. G. Mikhailov, N. M. Reinov, A. V. Runyantreva, A. P. Smirnov, and V. N. Totubaliv, J. Exptl. Theoret. Phys. **40**, 1543 (1961); Soviet Phys.—JETP **13**, 1083 (1961), where other references to the literature may be found.

from a more basic point of view, rederive an integral equation for the gap in the presence of fields and currents, and thus determine changes in Δ with H and v_s directly from an integral equation. This latter method is applied in Appendix B to determine changes in gap with a uniform current flow. In more general cases, the integral equation may be derived from the general Gor'kov equations, valid for all temperatures, or directly from microscopic theory. In the few cases where comparisons can be made, results obtained by the more general methods are equivalent to those obtained by the variational method. It would be desirable to make further calculations by the more general methods, particularly in cases where nonlinear effects other than those represented by changes in gap are important.

We have not discussed the closely related problem of changes of gap with rotation in nuclei. To first order, the Coriolis force in the rotating frame is equivalent to a magnetic field. As pointed out first by Mottelson and Valaten,[20] one expects, as for the corresponding magnetic case, that the gap will decrease with increasing rotational velocity, and eventually go to zero. These authors derived a modified gap equation valid to second order for the rotational velocity. Recently Grin[21] has treated the problem from the general Gor'kov equations.

ACKNOWLEDGMENTS

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[20] B. R. Mottelson and J. G. Valatin, Phys. Rev. Letters **5**, 511 (1960).
[21] Yu T. Grin', J. Exptl. Theor. Phys. (U.S.S.R.) **41**, 410 (1961); Soviet Phys.—JETP **14**, 320 (1962).

APPENDIX A. MAGNETIC MOMENTS FOR VARIOUS SPECIMEN SHAPES

Here we shall tabulate results of calculations which have been made of the magnetic moment of specimens whose smallest dimension d is less than the coherence distance ξ_0 (typically of the order of 10^{-5} to 10^{-4} cm). Different methods have been used to make such calculations. The London theory, with a penetration depth λ given by (3.13), may be used when the mean free path $l \ll d$. When $l > d$, a nonlocal theory must be used to determine the current density from the vector potential. In this case the results depend to some extent on the boundary condition assumed for scattering of electrons from the surface. May and Schafroth[22] have given a general method by which the magnetic moment of a specimen of any shape can be determined for the case of specular reflection. Random scattering is more difficult to treat; a method suggested by Pippard can be used for specimens of simple shape.

Recently, Hauser and Helfand[23] have given calculations for several specimen shapes according to the London theory and also for the nonlocal theory with use of the method of May and Schafroth. Included were a sphere, a cylinder in a transverse field, a cylinder in a parallel field, and a thin plate in a parallel field. They took into account effects of a mean free path in the expression for the current density. Earlier calculations have been made with use of the random scattering boundary condition for a sphere by Whitehead and for a thin plate by Schrieffer. In Table I are given the results of these

TABLE I. Coefficients for calculation of magnetization of small specimens from Eqs. (A6) and (A7).

Specimen geometry	Random scattering g	Specular reflection g	London limit g_L
I Thin film parallel field	0.376[a,b]	0.500[d]	0.333[d]
II Cylinder parallel field	0 100[g]	0.122[d]	0.125[d]
III Cylinder transverse field	0.200[g]	0.316[d]	0.250[d]
IV Sphere	0.0625[c]	0.0845[d,e]	0.100[d,f]

[a] J. R. Schrieffer, Phys. Rev. **106**, 47 (1957).
[b] K. T. Rodgers, Ph.D. Thesis, University of Illinois (1960) (unpublished).
[c] C. S. Whitehead, Proc. Roy. Soc. (London) **A238**, 175 (1956).
[d] J. J. Hauser and E. Helfand, reference 23.
[e] R. M. May and M. R. Schafroth, Proc. Phys. Soc. (London) **74**, 153 (1959).
[f] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950).
[g] Hitherto unpublished calculations of W. L. McMillan.

[22] R. M. May and M. R. Schafroth, Proc. Phys. Soc. (London) **74**, 153 (1959).
[23] J. J. Hauser and E. Helfand, Phys. Rev. **127**, 386 (1962).

calculations for the limit $d \ll \xi_0$, together with hitherto unpublished calculations of McMillan for a cylinder in a transverse field and in a parallel field.

The general expression for the current density, including the effect of a scattering mean free path is[10,12]:

$$j(\mathbf{r}) = -\frac{3}{4\pi c\Lambda_T\xi_0}\int \frac{\mathbf{R}[\mathbf{R}\cdot\mathbf{A}(\mathbf{r}')]J(R,T)e^{-R/l}}{R^4}d\tau' \,, \tag{A1}$$

where $\mathbf{R} = \mathbf{r} - \mathbf{r}'$. For specimens with $d \ll \xi_0$, one may replace $J(R,T)$ by $J(0,T)$ without appreciable error, where

$$J(0,T) = (\Lambda_T/\Lambda)(\Delta/\Delta_0)\tanh(\beta\Delta/2) \,. \tag{A2}$$

When in addition $l \ll d$, so that $\mathbf{A}(\mathbf{r})$ does not vary much over a mean free path, one may replace $\mathbf{A}(\mathbf{r}')$ by $\mathbf{A}(\mathbf{r})$, carry out the integration, and find the London relation

$$j(r) = -(c/4\pi\lambda^2)A(r) \,, \tag{A3}$$

with the penetration depth λ given by (3.13).

For the case of random scattering with simple specimen shapes such as those considered here, one simply carries out the integration over the specimen. In the limit $d/\lambda \to 0$, the field in the specimen is little changed from the applied field, so that one takes for $\mathbf{A}(\mathbf{r})$ the vector potential of the external field H. The magnetic moment is

$$\begin{aligned}\mathbf{M} &= \frac{1}{2c}\int \mathbf{r}\times\mathbf{j}(\mathbf{r})d\mathbf{r}\\ &= -\frac{3\Delta\tanh(\frac{1}{2}\beta\Delta)}{8c^2\Lambda\hbar v_F}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{(\mathbf{r}\times\mathbf{R})[\mathbf{R}\cdot\mathbf{A}(\mathbf{r}')]}{R^4}\,,\end{aligned} \tag{A4}$$

in which we have assumed $l \gg d$, and replaced $e^{-R/l}$ by unity. Comparing (A3) and (2.9), and using the relations $H_0^2/8\pi = \frac{1}{2}N(0)\Delta_0^2$, $\xi_0 = \hbar v_F/\pi\Delta_0$, $\Lambda = 4\pi\lambda_L^2/c^2$, we find for the coefficient a of (2.9):

$$a = \frac{3}{8\pi\lambda_L^2\xi_0H_0^2HV}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{(\mathbf{r}\times\mathbf{R})[\mathbf{R}\cdot\mathbf{A}(\mathbf{r}')]}{R^4}\,, \tag{A5}$$

which is the expression used by McMillan for his calculations.

The four specimen geometrics considered are (I) a thin film of thickness $2r$ in a parallel magnetic field, (II) a small cylinder of radius r in a parallel field, (III) a small cylinder of radius r in a transverse field, and (IV) a small sphere of radius r. For the nonlocal theories, the coefficient a may be expressed in the form

$$a = gr^3/\lambda_L^2\xi_0H_0^2 \,, \tag{A6}$$

where g is a dimensionless geometrical factor. Values for g are listed in Table I for both random scattering and specular reflection.

In the London limit, a is proportional to r^2 rather than r^3 and may be expressed in the form

$$a = g_Lr^2/\lambda^2H_0^2 \,. \tag{A7}$$

Values of the dimensionless coefficient g_L are also listed in Table I, prepared by McMillan.

APPENDIX B. DIRECT CALCULATION OF CHANGE OF GAP WITH CURRENT[24]

We discuss in this section a direct calculation of the change in gap with current flow which applies for all T. The problem is an idealized one because we disregard effects of magnetic fields and assume, contrary to fact, that one can have a uniform current flow in a bulk specimen. It is of interest because the calculation goes back to first principles and because the change in gap is determined directly from an integral equation. Results near T_c are equivalent to those obtained from the G-L theory.

The calculation is similar to that required for the two-fluid model, but is extended to arbitrarily large currents. We consider first a situation in which the ground-state pairs have zero net momentum, but for which there is a distribution of quasi-particle excitations giving a net current J. Let $f_{k\uparrow}$ be the probability of an excitation in the state $\mathbf{k}\uparrow$ and $f_{-k\uparrow}$ that in $-\mathbf{k}\downarrow$. Then the mass flow is

$$J_x = \sum \hbar k_x(f_{k\uparrow} - f_{-k\downarrow}) \,. \tag{B1}$$

We want to determine the f_k to give a minimum free energy subject to a given J. We use the BCS model for which the pair interaction is $-V$ in an energy zone $|\epsilon_k| < \hbar\omega$ about the Fermi surface, where $\epsilon_k = \hbar^2k^2/2m - \mu$. If v is a Lagrange multiplier for J_x, we have [cf. Eq. (3.16) of reference 9].

[24] Based on the thesis of K. T. Rogers, reference 8.

$$\begin{aligned}F + v\cdot J = {}& \sum \epsilon_k(f_{k\uparrow} + f_{-k\downarrow}) + 2\sum_{|\epsilon_k|<\hbar\omega}\epsilon_k h_k(1 - f_{k\uparrow} - f_{-k\downarrow})\\ &+ \hbar^{-1}v\sum\frac{\partial\epsilon_k}{\partial k}(f_{k\uparrow} - f_{-k\downarrow}) - V\sum_{|\epsilon_k|<\hbar\omega}[h_k(1-h_k)h_{k'}(1-h_{k'})]^{1/2}(1 - f_{k\uparrow} - f_{-k\downarrow})\\ &\times(1 - f_{k'\uparrow} - f_{-k'\downarrow}) + k\beta^{-1}\{\sum f_{k\uparrow}\ln f_{k\uparrow} + (1-f_{k\uparrow})\ln(1-f_{k\uparrow})\\ &+ f_{-k\downarrow}\ln f_{-k\downarrow} + (1-f_{-k\downarrow})\ln(1-f_{-k\downarrow})\}\,,\end{aligned} \tag{B2}$$

where $\beta = (k_BT)^{-1}$ and h_k is the probability of a pair in k. The values of f_k and h_k are determined so as to make $F + \mathbf{v}\cdot\mathbf{J}$ a minimum. The solution is similar to that for $\mathbf{v} = 0$:

$$h_k = \tfrac{1}{2}(1 - \epsilon_k/E_k) \tag{B3}$$

$$E_k^2 = \epsilon_k^2 + \Delta^2 \tag{B4}$$

$$f_{k\uparrow} = \frac{1}{1 + \exp[\beta(E_k + \mathbf{v}\cdot\hbar\mathbf{k})]},$$

$$f_{-k\downarrow} = \frac{1}{1 + \exp[\beta(E_k - \mathbf{v}\cdot\hbar\mathbf{k})]}. \tag{B5}$$

To get a state corresponding a velocity v_s of the ground pairs and a normal component of current equal to zero, one may displace the above configurations in momentum space by mv_s and then take $v = -v_s$. An equivalent solution can be obtained from the general Gor'kov equations for the thermal Green's function, valid for all temperatures.[25]

We may write to a close approximation

$$\mathbf{v}\cdot\mathbf{k} = vk_F\cos\theta = vk_Fx, \tag{B6}$$

where k_F is the magnitude of the wave vector of the Fermi surface, θ is the angle between v and k and $x = \cos\theta$. The equation for the energy gap then becomes

$$\frac{1}{N(0)V} = \frac{1}{2}\int_0^{\hbar\omega}\frac{d\epsilon}{E}\int_{-1}^{1}dx \times\left\{1 - \frac{1}{1+e^{\beta(E+ax)}} - \frac{1}{1+e^{\beta(E-ax)}}\right\}, \tag{B7}$$

where $a = \hbar k_FV_s$. The integration over angles may be carried out explicitly to give

$$\frac{1}{N(0)V} = \int_0^{\hbar\omega}\left\{1 - \frac{1}{\beta a}\ln\frac{e^{\beta E_k}+e^{\beta a}}{e^{\beta E_k}+e^{-\beta a}}\right\}\frac{d\epsilon_k}{E}. \tag{B8}$$

In the limit $\mathbf{v} = a = 0$, this equation reduces to the usual equation for the gap. At temperatures near T_c such that $\beta a \ll 1$ and $\beta\epsilon_0(T) \ll 1$, one may expand in a series in $(\beta a)^2$ and $(\beta\epsilon_0)^2$. To terms of order v^2, one gets

$$[\beta_c\Delta(T)]^2 = [8\pi^2/7\zeta(3)](1-t) - \tfrac{2}{3}(\beta_c\hbar k_F)^2v_s^2, \tag{B9}$$

which is in agreement with (3.15)

In the low temperature limit, $\beta \to \infty$, there are no excitations formed and thus no change in Δ until the velocity v_s reaches the value for which it is favorable to form pairs of excitations, corresponding to transfer of an electron from one side of the Fermi sea to the other. This criterion is (depairing condition)

$$\tfrac{1}{2}m(\hbar k_F/m + v_s)^2 - \tfrac{1}{2}m(\hbar k_F/m - v_s)^2 > 2\Delta, \tag{B10}$$

or

$$\hbar k_Fv_s > \Delta.$$

The gap decreases very rapidly when v_s exceeds the critical value. The maximum in the flow occurs for

$$v_m = 1.03\,\epsilon_0/\hbar k_F, \tag{B11}$$

with the maximum being only slightly greater than that corresponding to the depairing condition:

$$J_{\max} = 1.017\,N\epsilon_0(0)/v_F. \tag{B12}$$

This is roughly $(2/3)^{1/2}$ or about 80% of the value corresponding to the free-energy criterion.

APPENDIX C

In order to find the free energy as a function of Δ, we must evaluate the functions $g_1(x_0)$ and $g_2(x_0)$ numerically. It is convenient to expand the F-D function $f(X)$ in powers of e^{-X}. From (4.4)

$$\begin{aligned} g_1(x_0) &\equiv \int_0^\infty\left[\frac{1-2f(x)}{x} - \frac{1-2f(X)}{X}\right]dx \\ &\cong \int_0^{\beta_c\hbar\omega}\left[\frac{1-2f(x)}{x} - \frac{1}{X}\right]dx + 2\int_0^\infty\frac{f(X)}{X}dx \\ &= \ln\frac{x_0}{\beta_c\Delta_0} + 2\sum_{n=1}^{\infty}(-1)^{n+1} \\ &\quad\times\int_0^\infty\frac{\exp[-n(x^2+x_0^2)^{1/2}]}{(x^2+x_0^2)^{1/2}}dx. \end{aligned} \tag{C1}$$

Here $X = (x^2 + x_0^2)^{1/2}$, and we make weak coupling approximations, $[(\Delta_0/\hbar\omega)^2 \ll 1;\ f(\beta_c\hbar\omega) \ll 1]$, throughout.

Substituting $x = x_0\sinh y$, we find

$$\int_0^\infty\frac{\exp[-n(x^2+x_0^2)^{1/2}]}{(x^2+x_0^2)^{1/2}}dx = \int_0^\infty e^{-nx_0\sinh y}dy = K_0(nx_0).$$

$K_0(x)$ is the Hankel function of order zero.[26] Thus, we find

$$g_1(x_0) = \ln\frac{x_0}{\beta_c\Delta_0} + 2\sum_{n=1}^{\infty}(-1)^{n+1}K_0(nx_0). \tag{C2}$$

[25] K. Maki and T. Tsuneto, Progr. Theoret. Phys. (Kyoto) **27**, 228 (1962).

[26] W. Magnus and F. Oberhetinger, *Formulas and Theorems for the Functions of Mathematical Physics* (Chelsea Publishing Company, New York, 1954), p. 27.

We may evaluate $g_2(x_0)$ in a similar way. From (4.11)

$$g_2(x_0) \equiv 1 - \frac{2}{x_0^2}\int_0^\infty \left\{X[1-2f(X)] - \frac{x_0^2}{2x}[1-2f(x)] - x[1-2f(x)]\right\}dx$$
$$\cong 1 - \int_0^{\beta_c\hbar\omega}\left[\frac{2X}{x_0^2} - \frac{1-2f(x)}{x} - \frac{2x}{x_0^2}\right]dx + \frac{4}{x_0^2}\int_0^\infty [Xf(X) - xf(x)]dx\,. \qquad \text{(C3)}$$

We again expand $f(X)$ in powers of e^{-X}

$$\frac{4}{x_0^2}\int_0^\infty Xf(X)dx = \frac{4}{x_0^2}\sum_{n=1}^\infty (-1)^{n+1} \times \int_0^\infty \exp\{-n[(x^2+x_0^2)]^{1/2}\}[(x^2+x_0^2)]^{1/2}dx\,.$$

Substituting $x = x_0 \sinh y$

$$\frac{4}{x_0^2}\int_0^\infty Xf(X)dx = 4\sum_{n=1}^\infty (-1)^{n+1} \times \int_0^\infty \exp(-nx_0\sinh y)(1+\sinh^2 y)dy$$
$$= 4\sum_{n=1}^\infty (-1)^{n+1}\left[K_0(nx_0) + \frac{K_1(nx_0)}{nx_0}\right],$$

where $K_1(x)$ is the Hankel function of order one. The remaining integrals of (C3) are easily evaluated. We find

$$g_2(x_0) = \tfrac{1}{2} + \ln(x_0/\beta_c\Delta_0) - 2\zeta(x)/x_0^2 = 4\sum_{n=1}^\infty (-1)^{n+1}\left[K_0(nx_0) + \frac{K_1(nx_0)}{nx_0}\right], \qquad \text{(C4)}$$

where $\zeta(x)$ is the Riemann zeta function.[27] The Hankel functions $K_\nu(x)$ are related to the Bessel functions of the third kind[28] $H_\nu(x)$ by

$$K_\nu(x) = (\pi i/2)e^{\nu\pi i/2}H_\nu^{(1)}(ix)\,.$$

The Hankel functions decrease exponentially for large values of the argument allowing the summations to be truncated at $n \sim 5/x_0$. The functions $g_1(x_0)$ and $g_2(x_0)$, calculated from (C2) and (C4) are given in Figs. 1 and 2. Using these functions and (4.13), we can calculate the free energy as a function of Δ in the absence of external fields or currents. The free energy as a function of Δ for $N(0)V = 0.3$ is given in Fig. 3. Finally, we can find the free energy as a function of Δ when both a magnetic field and current flow are present, and minimize this free energy with respect to Δ to determine the gap Δ in the presence of the field and current. The energy gap as a function of the field has been determined, for $N(0)V = 0.3$, with the free energy given by (4.13) and (5.1), and is given by the solid lines in Fig. 5.

[27] E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, Inc., New York, 1945), p. 236.

[28] These functions are tabulated in reference 27, p. 236 and elsewhere.

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Note on the Interactions between the Spins of Magnetic Ions or Nuclei in Metals

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The coupling between spins of magnetic ions, or of nuclei, which results indirectly from the interaction of such spins with those of conduction electrons in metals has been the subject of a number of papers. Zener[1] proposed that this indirect mechanism is the cause of ferromagnetism. The corresponding calculation for nuclear spins was made still earlier by Fröhlich and Nabarro.[2] The resulting nuclear coupling is, of course, very weak, but capable of detection in some metals by nuclear resonance. Calculations of the Zener-Fröhlich-Nabarro (ZFN) type are incomplete because they neglect the effect, essentially a second-order or polarization one, of the matrix elements which are nondiagonal in the

[1] C. Zener, Phys. Rev. **81**,440 (1951).

[2] H. Fröhlich and F.R.N. Nabarro, Proc. Roy. Soc. (London) **A175**, 382 (1940).