

of the value of the time constant  $T_2$  by relating it to critical parameters of the resonance curves. Four such parameters are: (a) the absorption at resonance, (b) the width of the absorption curve at half-maximum, (c) the peak-to-peak value of the frequency shift, (d) the separations in the peak-to-peak values. When this is done an over-all spread of about a factor 2 is obtained in the various determinations of  $T_2$ . Some of this spread is probably due to errors in the determination of some of the critical points, e.g., the positions of maximum positive and negative frequency shift. The spread may possibly be reduced by a better choice of  $Q_0$ . However, much of it appears to be inherent and to be related more sensitively to the frequency shift curve than to the absorption curve. At the present

time we are able to conclude only that the experimental methods used provide a rather stringent test of the phenomenological theory which may not be completely adequate for a precise quantitative description.

Other features of the resonance curves which remain unexplained are in the low field region. For example, in Figs. 2 and 4 we observe a second minimum in the frequency shift curve occurring at about 5700 gauss for nickel and 5500 gauss for supermalloy. Since these are perpendicular field cases, we are here in the region of unsaturated magnetization. The theory is consequently unable to explain the phenomena in question and it is for this reason that the data of Fig. 4 were replotted in Figs. 5 and 6 only for values of  $H_0$  greater than  $4\pi M_0$ .

## Theory of Boundary Effects of Superconductors\*

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An extension of the phenomenological London equations to take into account a space variation of the concentration of superconducting electrons is presented. The theory differs from that of Ginsburg and Landau in that it makes use of the Gorter-Casimir two-fluid model rather than an order parameter to derive an expression for the free energy. An effective wave function is used for the superconducting electrons. The theory is applied to calculate the boundary energy between normal and superconducting phases and the relative change  $\Delta\lambda/\lambda$  of penetration depth with magnetic field. Calculated values of boundary energies are somewhat larger, and of  $\Delta\lambda/\lambda$  somewhat smaller, than observed. It is suggested that additional nonlinear terms are required to account for the observed  $\Delta\lambda/\lambda$  at low temperatures. The connection of the theory with Pippard's ideas on range of order is discussed briefly.

### I. INTRODUCTION

TO estimate the energy of the boundary between normal and superconducting phases and for related problems, it is necessary to have a theory which takes into account a space variation in the effective concentration of superconducting electrons  $n_s$ . Across such a boundary,  $n_s$  changes from an equilibrium value on the superconducting side to zero on the normal side. We present here a theory based on the Gorter-Casimir<sup>1</sup> two-fluid model. It is an extension of the Ginsburg-Landau theory<sup>2</sup> so as to apply over the entire temperature range.

The theory of Ginsburg and Landau (denoted here

by G-L) applies for temperatures close to the critical temperature  $T_c$ . These authors identify  $n_s$  with an order parameter  $\eta$  which is small near  $T_c$ . The free energy is expanded in a power series in  $\eta$ . It is assumed that  $n_s$  (and thus  $\eta$ ) is given by the square of an effective wave function  $\Psi(x)$ , and that there is an energy term proportional to  $|\text{grad}\Psi|^2$ . The coefficient of  $|\text{grad}\Psi|^2$  is evaluated in terms of the critical field  $H_c$  and the penetration depth,  $\lambda$ , so that there are no undetermined parameters. In addition to the calculation of the boundary energy, the theory was applied to the magnetic and thermal properties of thin films and to estimate the change in  $\lambda$  with magnetic field.

Using a microwave method, Pippard<sup>3</sup> has shown that for tin the change in  $\lambda$  with field is no more than 3 percent for fields up to  $H=H_c$ . From these results he estimated that the ordered regions must extend over distances of the order of  $10^{-4}$  cm. Presumably the width of the normal-superconducting boundary is at least of this order.

The author<sup>4</sup> has pointed out that Pippard's result is

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<sup>1</sup> C. J. Gorter and H. B. G. Casimir, *Physik Z.* **35**, 963 (1934); *Z. tech. Phys.* **15**, 539 (1934). See D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), second edition, Chap. VI.

<sup>2</sup> V. L. Ginsburg and L. D. Landau, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **20**, 1064 (1950).

<sup>3</sup> A. B. Pippard, *Proc. Roy. Soc. (London)* **A203**, 210 (1950).

<sup>4</sup> J. Bardeen, *Phys. Rev.* **81**, 1070 (1951).

consistent with a model in which the superconducting electrons have small effective mass,  $m_s \sim 10^{-4}m$ . A localized electron is described approximately by a wave function  $U(x)$  whose square is the probability density. We showed that the energy

$$-\frac{\hbar^2}{2m_s} \int U \nabla^2 U d\tau$$

is of the order of  $\hbar^2/k_0 T_c$  if the electron is confined to a region  $< \sim 10^{-4}$  cm.

The same model was used to make some preliminary estimates of boundary energies. Before the results were published, the author learned about the G-L theory<sup>5</sup> and it was found that the two theories give very similar results. We shall show here the close connection between the two approaches. They both use an effective wave function for the superconducting electrons, but differ in how the free-energy difference between normal and superconducting phases depends on the wave function. Our earlier results should be better at low temperatures,  $T \ll T_c$ , and the G-L results should be better for  $T \sim T_c$ . The theory based on the Gorter-Casimir two-fluid model should be more satisfactory than either over the entire temperature range.

That the superconducting wave functions or the ordered regions should extend over large distances in space ( $\sim 10^{-4}$  cm) follows from rather general considerations, as has been pointed out on a number of occasions. Superconductivity arises from some sort of interaction, involving the lattice vibrations, between electrons which lie within  $\sim \Delta k$  of the Fermi surface,  $E_F$ . If it is assumed that

$$\Delta k/k_F \sim \hbar^2/k_0 T_c/E_F \sim 10^{-4}, \quad (1.1)$$

it follows from the uncertainty relation,

$$\Delta x \Delta k \sim 1,$$

that the ordered regions must extend over distances of the order of

$$\Delta x \sim 10^4/k_F \sim 10^{-4} \text{ cm}. \quad (1.2)$$

If the degree of order, or  $n_s$ , varies in space, an additional energy is involved. It is presumed by both G-L and ourselves that the energy can be obtained from the kinetic energy term for an effective wave function.

The real significance of the "order-parameter" or "effective wave function" is uncertain, so that at this stage the theory must be regarded as a semiempirical one.

In view of the uncertain theoretical foundation for the theory, it is perhaps best regarded as an extension of the London phenomenological theory to take into account a space variation of  $n_s$ .

<sup>5</sup> The author is indebted to Dr. Paul Marcus for bringing to his attention a translation of the Ginsburg-Landau article made by Dr. D. Shoenberg.

## II. EXPRESSION FOR THE FREE ENERGY DENSITY

Ginsburg and Landau introduce an order parameter  $\eta$  in accord with a general theory of phase transitions of the second kind proposed by Landau and Lifshitz. The parameter  $\eta=0$  for the normal phase, and, at least for  $T$  near  $T_c$ , where  $\eta$  is small, the free energy difference  $f(T)$  per unit volume between superconducting and normal phases may be expressed as a quadratic function of  $\eta$ :

$$f(T) = F_s(T) - F_n(T) = \alpha(T)\eta + \frac{1}{2}\beta(T)\eta^2. \quad (2.1)$$

The equilibrium value of  $\eta$  in zero field is that which makes  $F_s$  or  $f$  a minimum:

$$\eta_e = -\alpha/\beta. \quad (2.2)$$

They identify  $\eta$  with the square of an effective wave function  $\Psi$  normalized in such a way that  $|\Psi|^2$  is equal to the concentration of superconducting electrons  $n_s$ .

We shall use a different normalization, and assume that  $\eta = |\Psi|^2 = 1$  at  $T = 0^\circ\text{K}$ , so that

$$n_s = n_0 |\Psi|^2, \quad (2.3)$$

where  $n_0$  is the equilibrium concentration at  $T = 0^\circ\text{K}$ . The free energy difference is then

$$f = \alpha |\Psi|^2 + \frac{1}{2}\beta |\Psi|^4. \quad (2.4)$$

The values of  $\alpha$  and  $\beta$  are determined from the critical field  $H_c$  and the penetration depth  $\lambda$ . The equilibrium free energy difference,  $-H_c^2/8\pi$  per unit volume, is obtained by inserting (2.2) into (2.1):

$$-f_e = \alpha^2/2\beta = H_c^2/8\pi. \quad (2.5)$$

The inverse relation between  $n_s$  and  $\lambda^2$  follows from the London theory and is also a consequence of the equations derived by G-L. From (2.5) and (2.6), it follows that

$$\alpha = -(H_c^2/4\pi)(\lambda^2/\lambda_0^2), \quad (2.7)$$

$$\beta = (H_c^2/4\pi)(\lambda^4/\lambda_0^4). \quad (2.8)$$

In addition to (2.1), G-L introduce an energy proportional to  $|\text{grad}\Psi|^2$ , corresponding to the density of kinetic energy in quantum mechanics. In a magnetic field defined by a vector potential  $\mathbf{A}$  the energy density becomes:

$$(n_0/2m_s) \left| -i\hbar \text{grad}\Psi + (e/c)\mathbf{A}\Psi \right|^2, \quad (2.9)$$

where  $m_s$  is an effective mass for the superconducting electrons. The charge on the electron is  $-e$ . Taking into account the field energy  $H^2/8\pi$  the total (Helmholz) free-energy difference is

$$F = \int \left\{ \frac{n_0}{2m_s} \left| -i\hbar \text{grad}\Psi + \frac{e}{c}\mathbf{A}\Psi \right|^2 + \frac{H^2}{8\pi} + \alpha |\Psi|^2 + \frac{\beta}{2} |\Psi|^4 \right\} d\tau. \quad (2.10)$$

Here  $H$  is the local value of the magnetic field. We could equally well use the symbol  $B$  for this quantity. The magnetic properties of the medium cannot be described in terms of a permeability. Equations for  $\Psi$  and  $\mathbf{A}$  such as to make  $F$  a minimum are derived by G-L. These will be discussed later, together with the boundary conditions which differ from the usual ones.

Our approach differs from G-L mainly in the way  $f(T)$  is assumed to depend on  $\Psi$ . It originated from a theory of superconductivity based on interactions between electrons and lattice vibrations as proposed by the author.<sup>6</sup> According to this picture, electrons with energies near the Fermi surface are lowered in energy by the interactions and have a small effective mass. It is the small effective mass which presumably accounts for the superconducting properties. In this formulation, the wave function for the electrons is approximated by determinants of one-electron wave functions, each of which may depend on the coordinates of the lattice vibrations. A transition from a superconducting to a normal region may be obtained by multiplying each of the wave functions of the superconducting electrons (i.e., those with energies near the Fermi surface) by a modulating factor  $U(x)$  which varies slowly from 1 to 0 across the boundary. The density of superconducting electrons is then proportional to  $U^2$ . It is assumed that the density of normal electrons varies as  $1-U^2$  so as to keep the total density of electrons approximately constant.

In our original calculation it was assumed that the free-energy difference

$$f(U) = -(H_0^2/8\pi)U^2. \quad (2.11)$$

We also assumed, according to the effective mass concept, that there is an additional energy density associated with  $\text{grad}U$ :

$$(n_e/2m_e) | -i\hbar \text{grad}U + (e/c)A U |^2, \quad (2.12)$$

where  $n_e$  is the equilibrium concentration. This latter expression is the same as that used by G-L since

$$n_e |U|^2 = n_0 |\Psi|^2. \quad (2.13)$$

Equations which we derived for  $U$  and  $\mathbf{A}$  are very similar to those derived by G-L. This is to be expected since the initial assumptions differ only in the expressions used for  $f(T)$ .

Expression (2.11) assumes that the energy associated with a variation of  $U$  comes entirely from the superconducting electrons. The term analogous to (2.12) for the normal electrons is negligible because the effective mass is so much larger. However, the increasing density of normal electrons with decrease in  $U$  should make an appreciable contribution to the free energy. This term is to a first approximation proportional to  $T^2$ .

Probably the best way to obtain a semiempirical ex-

pression for the free energy is from the Gorter-Casimir two-fluid model. This model was used by Pippard<sup>3</sup> in his estimates of the size of the ordered regions from the change in penetration depth with magnetic field. A parameter  $\omega$  is introduced which varies between unity at  $T=0^\circ\text{K}$  and zero at  $T=T_c$  and which represents the fraction of the electrons which are superconducting. The free-energy density  $F_s(T)$  is given in terms of  $F_n(0)$  (for  $T=0^\circ\text{K}$ ) as follows<sup>1</sup>:

$$F_s(T) = F_n(0) - (H_0^2/8\pi)[2t^2(1-\omega)^{1/2} + \omega]. \quad (2.14)$$

Here  $H_0$  is the critical field at  $T=0^\circ\text{K}$  and  $t=T/T_c$ . The term in  $t^2$  represents the contribution of the normal electrons and  $-(H_0^2/8\pi)\omega$  that of the superconducting electrons. The value of  $\omega$  which makes (2.14) a minimum is

$$\omega_e = 1 - t^4. \quad (2.15)$$

Since  $\omega \sim \lambda^{-2}$ , the observed dependence of penetration depth on temperature,  $\lambda^{-2} \sim (1-t^4)$  is obtained. A parabolic critical field curve also follows from the model:

$$f(T) = F_s(T) - F_n(T) = -H_c^2/8\pi, \quad (2.16)$$

with

$$H_c = H_0(1-t^2). \quad (2.17)$$

It has been pointed out to the author by P. Marcus that one can get a parabolic  $H_c-T$  curve from (2.1) by taking

$$\alpha(T) = -(H_0^2/4\pi)(1-t^2); \quad \beta = H_0^2/4\pi. \quad (2.18)$$

However,  $\eta$  then varies as  $1-t^2$  so that it cannot be interpreted as giving the relative concentration of superconducting electrons. The temperature dependence of  $\alpha$  and  $\beta$  given by (2.7) and (2.8) is more complicated. Following a suggestion of Marcus, it thus appears to be reasonable to identify  $\omega$  rather than  $\eta$  with  $|\Psi|^2$ .

By setting  $\omega = |\Psi|^2$  in (2.14), we get

$$f(T) = F_s - F_n = (H_0^2/4\pi) \{ t^2 [1 - (1 - |\Psi|^2)^{1/2}] - \frac{1}{2} |\Psi|^2 \}. \quad (2.19)$$

For  $t$  small, this reduces to Eq. (2.11) which we have used, and for  $t$  near unity and  $\Psi$  small to

$$f(T) = -(H_0^2/8\pi) |\Psi|^2 (1-t^2) + (H_0^2 t^2/32\pi) |\Psi|^4. \quad (2.20)$$

This is in agreement with G-L, for it follows from (2.7) with  $H_c = H_0(1-t^2)$  and  $\lambda_0^2/\lambda^2 = 1-t^4$ , that

$$\begin{aligned} \alpha &= -(H_0^2/4\pi)(1-t^2)/(1+t^2), \\ \beta &= (H_0^2/4\pi)(1+t^2)^{-2}. \end{aligned} \quad (2.21)$$

As  $t \rightarrow 1$ ,  $\alpha$  approaches the coefficient of  $|\Psi|^2$  and  $\beta/2$  the coefficient of  $|\Psi|^4$  in (2.20). Thus the two-fluid model approaches that of Ginsburg and Landau near  $T=T_c$ .

### III. EQUATIONS FOR $\Psi$ AND $\mathbf{A}$

The Helmholtz free energy difference between the normal and superconducting phases may be written in

<sup>6</sup> J. Bardeen, Phys. Rev. **80**, 567 (1950); **81**, 829 (1951); **82**, 978 (1951); Revs. Modern Phys. **23**, 261 (1951).

the general form:

$$F = \int \left\{ \frac{n_0}{2m_s} | -i\hbar \text{grad}\Psi + (e/c)\mathbf{A}\Psi |^2 + \frac{H^2}{8\pi} + f(\Psi) \right\} d, \quad (3.1)$$

where  $f(\Psi)$  is one of (2.4), (2.11), or (2.19). It is assumed that  $\Psi$  is real when the gauge in  $\mathbf{A}$  is chosen appropriately ( $\text{div}\mathbf{A}=0$ ,  $A_{\perp}=0$ ). It is this reality requirement which gives the Meissner effect and which leads to the London equations for field penetration.

We shall be concerned only with examples for which  $\Psi(x)$  varies only in one dimension, which we take to be that of the  $x$  axis. The magnetic field is in the  $z$  direction so that the only component of  $\mathbf{A}$  is  $A_y(x)$ :

$$H_z = dA_y/dx. \quad (3.2)$$

To simplify the notation, we shall omit the subscript  $y$  in the following. With these simplifications, (3.1) becomes

$$F = \int \left\{ \frac{n_0\hbar^2}{2m_s} \left[ \left( \frac{d\Psi}{dx} \right)^2 + \left( \frac{eA\Psi}{\hbar c} \right)^2 \right] + \frac{1}{8\pi} \left( \frac{dA}{dx} \right)^2 + f(\Psi) \right\} dx. \quad (3.3)$$

Ginsburg and Landau derive equations for  $\Psi$  and  $A$  by requiring that  $F$  be a minimum.

Actually, it is the Gibbs free energy  $G$  which differs from (3.3) by a term  $-H_a M$  in the integrand, which should be minimized. Here  $H_a$  is the applied field and  $M = (H - H_c)/4\pi$  is the magnetization. The additional term makes  $H_a$  an independent variable, and the problem is to find  $A(x)$  such as to make  $G$  a minimum. This added term does not in general affect the differential equations for  $A$  and  $\Psi$  but it is important in determining the boundary conditions.

The equations for  $\Psi$  and  $A$  derived from (3.3) are:

$$\frac{d^2\Psi}{dx^2} = \frac{m_s}{n_0\hbar^2} \frac{df}{d\Psi} + \frac{e^2 A^2}{\hbar^2 c^2} \Psi, \quad (3.4)$$

$$\frac{d^2 A}{dx^2} = \frac{4\pi e^2 n_0 \Psi^2}{m_s c^2} A. \quad (3.5)$$

The boundary condition on  $\Psi$  at a free surface, as determined from the variational problem after an integration by parts, is  $d\Psi/dx=0$ . It is *not* required<sup>4</sup> that  $\Psi=0$  at the boundary. It is required that  $A \rightarrow 0$  in the interior of a superconducting region. As in the London theory, the current density is

$$\mathbf{j} = -\frac{n_0 e^2}{m_s c} \Psi^2 \mathbf{A}, \quad (3.6)$$

and the effective penetration depth is given by

$$\left( \frac{m_s c^2}{4\pi e^2 n_0 \Psi^2} \right)^{\frac{1}{2}}. \quad (3.7)$$

Equations (3.4) and (3.5) of G-L may be regarded as a generalization of the London phenomenological equations to allow for a variation in concentration of superconducting electrons in space.

#### IV. CALCULATION OF THE ENERGY OF THE BOUNDARY BETWEEN NORMAL AND SUPERCONDUCTING PHASES IN THE INTERMEDIATE STATE

The intermediate state of the superconductor consists of alternate layers of normal and superconducting phases.<sup>7</sup> The flux is carried by the normal regions in which the field is equal to the critical values  $H_c$ . According to a theory developed by Landau,<sup>8</sup> the layer thickness is determined by the surface energy  $\alpha_{ns}$  between the normal and superconducting phases. We shall derive here a value for  $\alpha_{ns}$  in terms of  $H_c$  and the penetration depth  $\lambda$ , and show that the values obtained in this way are in good agreement with those estimated from analysis of experimental data on the intermediate state. Our derivation differs somewhat from that in G-L, but the result is the same when the same expression is used for the free-energy difference.

We shall calculate the energy per unit area of the actual boundary relative to an ideal boundary for which there is an abrupt transition between normal and superconducting regions and for which  $H=H_c$  everywhere in the normal region and  $H=0$  everywhere in the superconducting region. This is the energy which enters into the theory of Landau and others and is designated by<sup>7</sup>

$$\alpha_{ns} = \Delta H_c^2 / 8\pi. \quad (4.1)$$

The parameter  $\Delta$  has the dimensions of a length.

The boundary energy is sometimes given relative to a boundary at which the field penetrates into the superconducting region with penetration depth  $\lambda$  as it would at a free surface. This energy is larger than (4.1) by  $\lambda H_c^2 / 8\pi$  or is equal to

$$\alpha_{ns}^{(1)} = \Delta_1 H_c^2 / 8\pi, \quad (4.2)$$

where

$$\Delta_1 = \Delta + \lambda. \quad (4.3)$$

Desirant and Shoenberg<sup>9</sup> have used the symbols  $\Delta$  for  $\Delta_1$  and  $\Delta'$  for  $\Delta$ .

The boundary is taken normal to the  $x$  direction and the magnetic field is in the  $z$  direction. As in Sec. III, the only component of  $\mathbf{A}$  is  $A_y = A(x)$ . Let  $x = x_0$  be the position of the boundary in the ideal case, so that  $H = H_c$

<sup>7</sup> See, for example D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), second edition, Chap. IV.

<sup>8</sup> L. D. Landau, *Physik. Z. Sowjetunion* **11**, 129 (1937); *Nature* **141**, 688 (1938); *J. Phys. (U.S.S.R.)* **7**, 99 (1943).

<sup>9</sup> M. Desirant and D. Shoenberg, *Proc. Roy. Soc. (London)* **A194**, 63 (1948).

for  $x < x_0$  and  $H=0$  for  $x > x_0$ . The corresponding position of the actual boundary is determined by requiring the flux be the same as for the ideal boundary. If it is assumed that the transition region extends between  $x=0$  and  $x=a$ , we have:

$$x_0 H_c = \int_0^a H dx = \int_0^a (dA/dx) dx = -A(0). \quad (4.4)$$

It is assumed that  $A=0$  and  $H=0$  at  $x=a$ , as the vector potential vanishes in the interior of the superconducting regions. The position  $x=0$  is assumed to be in the normal region where  $H=H_c$ .

Relative to the ideal boundary, the energy difference per unit area is

$$\alpha_{ns} = \int_0^a \left\{ \frac{n_0 \hbar^2}{2m_s} \left[ \left( \frac{d\Psi}{dx} \right)^2 + \left( \frac{eA\Psi}{\hbar c} \right)^2 \right] + f(\Psi) + \frac{1}{8\pi} \left( \frac{dA}{dx} \right)^2 \right\} dx - x_0 \frac{H_c^2}{8\pi} + (a-x_0) \frac{H_c^2}{8\pi}. \quad (4.5)$$

The last two terms subtract off the energy of the ideal boundary,  $+H_c^2/8\pi$  in the normal and  $-H_c^2/8\pi$  in the superconducting regions. Equations for  $A$  and  $\Psi$  determined by the variational method are those given in Sec. III, Eqs. (3.4) and (3.5). The variations  $\delta A$  and  $\delta\Psi$  are required to vanish at both limits, the former by consequence of Eq. (4.4). Because the flux is the same for the ideal and actual boundaries, there is no difference between using Helmholtz or Gibbs free energies.

There is an integral of Eqs. (3.4) and (3.5) which can be used to simplify the expression for the energy:

$$\frac{n_0 \hbar^2}{2m_s} \left( \frac{d\Psi}{dx} \right)^2 + \frac{1}{8\pi} \left( \frac{dA}{dx} \right)^2 = f(\Psi) + \frac{e^2 n_0 \Psi^2 A^2}{2m_s c^2} + \frac{H_c^2}{8\pi}. \quad (4.6)$$

The constant of integration  $H_c^2/8\pi$  is chosen to give the proper values outside of the transition zone. In the normal region,

$$\Psi = d\Psi/dx = f(\Psi) = 0, \quad (4.7)$$

$$dA/dx = H = H_c. \quad (4.8)$$

In the superconducting region,

$$A = dA/dx = d\Psi/dx = 0, \quad (4.9)$$

$$f(\Psi) = -H_c^2/8\pi. \quad (4.10)$$

Equations (4.7) to (4.10) are the boundary conditions for the differential equations.

Equation (4.6) may be used to eliminate the derivatives in (4.5), and there results

$$\alpha_{ns} = 2 \int_0^a \left[ f(\Psi) + \frac{e^2 n_0 \Psi^2 A^2}{2m_s c^2} \right] dx + 2(a-x_0) \frac{H_c^2}{8\pi}. \quad (4.11)$$

Equations (3.4) and (3.5) are nonlinear and it is not possible to get general integrals. We shall derive an expression for  $\alpha_{ns}$  which applies when the width of the transition region is large compared with the penetration depth so that most of the energy comes from the transition region in the superconducting phase where  $H \ll H_c$ .

The expression for  $\alpha_{ns}$  derived by use of the two-fluid model for  $f(\Psi)$  [Eq. (2.19)] agrees with a similar limiting expression derived by Ginsburg and Landau from (2.4) in the high-temperature limit ( $t=T/T_c \sim 1$ ) and with a result we had derived earlier from (2.11) in the low-temperature limit ( $t \ll 1$ ). The expression for  $\alpha_{ns}$  derived from (2.4) and (2.11) differs by less than 20 percent, so that it does not make a great deal of difference which form is taken for  $f(\Psi)$ .

We shall also give results obtained from a numerical integration of the equations by use of a differential analyzer at the Bell Telephone Laboratories and by the digital computer at the University of Illinois. Equation (2.11) was used for  $f(\Psi)$  in this calculation, so that the results apply strictly only in the low-temperature limit. It is not believed that the two-fluid model would give results which are very different. This numerical calculation is not restricted to the limiting case of a wide transition region.

### Two-Fluid Model

Equations (3.4) and (3.5) may be simplified by use of the following reduced variables:

$$U = \Psi/\Psi_e, \quad \xi = x/\lambda, \quad (4.12)$$

$$V = eA\lambda/\hbar c, \quad s = eH\lambda^2/\hbar c,$$

in which  $\lambda$  is the usual penetration depth as given by

$$\lambda^2 = m_s c^2 / (4\pi n_0 e^2 \Psi_e^2), \quad (4.13)$$

and  $\Psi_e$  is the equilibrium value of  $\Psi$  in the superconducting state:

$$\Psi_e^2 = 1 - t^4. \quad [\text{See Eq. (2.15).}]$$

With this notation, Eqs. (3.4) and (3.5) become:

$$\frac{d^2 U}{d\xi^2} = s^2 \frac{4\pi}{H_c^2} \frac{df}{dU} + V^2 U, \quad (4.14)$$

$$\frac{d^2 V}{d\xi^2} = U^2 V. \quad (4.15)$$

In (2.19) we replace  $\Psi$  by  $U\Psi_e$  and obtain:

$$(4\pi/H_c^2) f(U) = (H_0^2/H_c^2) t^2 [1 - (1 - U^2 \Psi_e^2)^{\frac{1}{2}}] - \frac{1}{2} U^2 \Psi_e^2. \quad (4.16)$$

It is to be recalled that for this model,  $H_c/H_0 = 1 - t^2$  [see Eq. (2.17)]. From (4.16), it follows that

$$\frac{4\pi}{H_c^2} \frac{df}{dU} = -\frac{1+t^2}{1-t^2} \left( 1 - \frac{t^2}{(1-U^2 \Psi_e^2)^{\frac{1}{2}}} \right) U. \quad (4.17)$$

### Limiting Cases

The limiting forms of (4.14) for low and high temperatures are:

$$d^2U/d\xi^2 = (V^2 - s^2)U, \quad t \rightarrow 0; \quad (4.18)$$

$$d^2U/d\xi^2 = [V^2 - 2s^2(1 - U^2)]U, \quad t \rightarrow 1. \quad (4.19)$$

Equation (4.19) is equivalent to the one used by Ginsburg and Landau, while we have used (4.18) for the numerical integration which will be discussed later.

The width of the transition region is determined by the dimensionless parameter  $s$ . If  $s \ll 1$ , the width is large compared with  $\lambda$  and  $V$  is appreciable only where  $U$  is small. For this limiting case it is possible to derive a general expression for the boundary energy, but we shall first consider the simpler equation (4.18) which applies for  $t \ll 1$ . If  $V^2$  is neglected in comparison with  $s^2$ , the approximate solution which vanishes at the boundary  $x = x_0 = 0$  and for which  $dU/d\xi \rightarrow 0$  as  $U \rightarrow 1$  is

$$U = \sin s\xi. \quad (4.20)$$

This solution joins with the solution  $U = 1$  in the body of the superconducting region  $\xi = \pi/2s$ , or  $x = a = \pi\lambda/2s$ .

We shall use (4.11) to calculate  $\alpha_{ns}$ . With (4.20),

$$f(U) = - (H_c^2/8\pi)U^2 = - (H_c^2/8\pi) \sin^2 s\xi. \quad (4.21)$$

The term in  $\Psi^2 A^2$  gives a negligible contribution in this limiting case, so that

$$\begin{aligned} \alpha_{ns} &= (H_c^2/8\pi) \left[ 2a - 2 \int_0^a \sin^2(sx/\lambda) dx \right] \\ &= (H_c^2/8\pi)a = (\pi/2)(\lambda H_c^2/8\pi s) \\ &= H_c \hbar c / 16\lambda e, \quad (t \rightarrow 0). \end{aligned} \quad (4.22)$$

The corresponding expression derived by Ginsburg and Landau from (4.19) is

$$\alpha_{ns} = (4/3)(\lambda H_c^2/8\pi s) = H_c \hbar c / 6\pi\lambda e, \quad (t \rightarrow 1), \quad (4.23)$$

which is smaller by less than 20 percent.

### General Expression for Small $s$

A general expression for  $\alpha_{ns}$  for the limiting case of small  $s$  may be derived from the two-fluid model by use of the integral (4.6) and the expression (4.11) for the energy. We again take the boundary for  $x = x_0 = 0$  and neglect the contributions from the magnetic field. Equation (4.11) then becomes

$$\alpha_{ns} = 2 \int_0^a [f(x) + (H_c^2/8\pi)] dx, \quad (4.24)$$

and (4.6) becomes, for  $x > 0$ ,

$$\frac{n_0 \hbar^2}{2m_s} \frac{(d\Psi)^2}{dx} = f(\Psi) + \frac{H_c^2}{8\pi}, \quad (4.25)$$

so that

$$\alpha_{ns} = (n_0 \hbar^2 / m_s) \int_0^a (d\Psi/dx)^2 dx. \quad (4.26)$$

The variable of integration can be changed from  $x$  to  $\Psi$ :

$$\alpha_{ns} = (n_0 \hbar / m_s) \int_0^{\Psi_e} (d\Psi/dx) d\Psi. \quad (4.27)$$

Equation (4.25) may now be used to express  $d\Psi/dx$  in terms of  $\Psi$ . Using (2.19) for  $f(\Psi)$ , we find

$$f(\Psi) + H_c^2/8\pi = (H_c^2/8\pi) [(1 - \Psi^2)^{\frac{1}{2}} - t^2]^2. \quad (4.28)$$

Therefore, from (4.25),

$$\frac{d\Psi}{dx} = \left( \frac{m_s H_c^2}{4\pi n_0 \hbar^2} \right)^{\frac{1}{2}} [(1 - \Psi^2)^{\frac{1}{2}} - t^2]. \quad (4.29)$$

When this result is inserted into (4.27) and the integration is carried out, we find

$$\begin{aligned} \alpha_{ns} &= (\hbar c H_c / 8\pi \lambda_0 e) (\sin^{-1} \Psi_e - t^2 \Psi_e), \\ &= \frac{\lambda H_c^2}{8\pi} \frac{(\Psi_e^{-1} \sin^{-1} \Psi_e - t^2 \Psi_e)}{s(1 - t^2)}, \end{aligned} \quad (4.30)$$

where  $\Psi_e = (1 - t^2)^{\frac{1}{2}}$ . This expression reduces to (4.22) and (4.23) in the two limiting cases and changes smoothly from one limit to the other as  $t$  varies between 0 and 1. Since the over-all change in the coefficient multiplying  $(\lambda H_c^2/8\pi s)$  is less than 20 percent, either limiting form of the theory will probably give reasonably satisfactory results for all  $t$ .

### Numerical Integration for Small $t$

Equations (4.18) and (4.15), which apply for  $t \ll 1$ , have been integrated numerically to obtain  $\alpha_{ns}$  as a function of  $s$ . Integration for  $s > 0.2$  was carried out early in 1951 with the aid of the differential analyzer of the Bell Telephone Laboratories.<sup>10</sup> Because of the large variation in magnitude of the functions, this method was not satisfactory for smaller values of  $s$ . A second numerical integration, carried out later with the aid of the digital computer at University of Illinois,<sup>10</sup> was more accurate for smaller values of  $s$ . The two integrations are in reasonable agreement for values of  $s$  larger than about 0.3.

It is convenient to express  $\alpha_{ns}$  in the form

$$\alpha_{ns} = g(s) (\lambda H_c^2 / 8\pi s), \quad (4.31)$$

or

$$\Delta = (\lambda/s) g(s),$$

<sup>10</sup> The author is indebted to Dr. R. W. Hamming for aid with the computations on the differential analyzer at the Bell Telephone Laboratories, and to Dr. D. J. Wheeler for aid with work done with the digital computer at the University of Illinois.

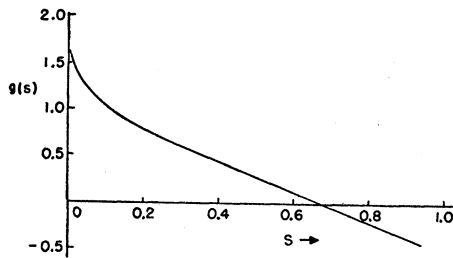


FIG. 1. Plot of  $g(s)$  versus  $s$  [see Eqs. (4.12) and (4.31)].

where  $g(s)$  is a numerical coefficient. Figure 1 is a plot of  $g(s)$  as a function  $s$ . As  $s \rightarrow 0$ ,  $g(s) \rightarrow \pi/2$ , in accordance with Eq. (4.22). As  $s$  increases,  $g(s)$  decreases and goes through zero and becomes negative for values of  $s$  larger than about 0.68. Ginsburg and Landau find, using their value for the free energy, that  $\alpha_{ns}$  goes through zero at  $s=0.5$ . A Meissner effect would not be observed if the boundary energy is negative, as it then would be favorable to form alternating lamina of normal and superconducting regions.<sup>11</sup> Between  $s=0.1$  and 1.0,  $g(s)$  varies almost linearly with  $s$  and is approximately equal to

$$g(s) \sim (1.1 - 1.6s). \quad (4.32)$$

It should be noted that  $g(s)$  decreases rapidly from the limiting value  $\pi/2$ , corresponding to  $s=0$ , and is down by a factor of about 2 at  $s=0.2$ .

#### Comparison with Experimental Values of $\alpha_{ns}$

These calculations were made with use of the free energy expression (2.11) which is valid for  $t$  small. Calculations have not been carried out using the general form of the free energy (2.19) derived from the two-fluid model. However, the errors involved in using (2.11) over the entire temperature range are probably not very large. We have seen that for  $s$  small, the various expressions for the free energy give values of  $\alpha_{ns}$  differing by less than 20 percent.

If we assume a parabolic critical field curve, and assume that

$$\lambda^2 = \lambda_0^2 / (1 - t^2), \quad (4.33)$$

TABLE I. Values of  $s_0 = eH_0\lambda_0^2/\hbar c$  for various metals.

Metal	$\lambda_0$ (cm $\times 10^6$ )	$H_0$ (gauss)	$T_0$ ( $^\circ$ K)	$s_0$
Sn	5.0	305	3.7	0.115
In	6.4	270	3.35	0.17
Pb	3.9	535	4.24	0.13
Hg	4.5	415	4.15	0.125

<sup>11</sup> See F. London, *Superfluids* (John Wiley and Sons, New York, 1950), p. 128.

we find that  $s$  varies as

$$s = s_0 / (1 + t^2). \quad (4.34)$$

Thus  $s$  changes by a factor of two between  $T=0$  and  $T=T_0$ .

Table I gives values of  $s_0$  as calculated from  $\lambda_0$  and  $H_0$  for Sn, In, Hg, and Pb. These are the only metals for which values of  $\lambda$  are known. Values of  $\lambda$  for Sn, In, and Pb are from Lock<sup>12</sup> and for Hg from Laurmann and Shoenberg.<sup>13</sup> It is to be noted that the values of  $s_0$  are all rather small.

The width of the boundary region is of the order of  $\lambda/s$ . The small values of  $s$  indicate a wide transition region of the order of  $10^{-4}$  cm. This distance is consistent with Pippard's estimate of the range of order in superconducting tin.

Our value of the boundary energy should probably be regarded as an upper limit attained only for an ideal specimen. If imperfections in the crystal limit the range of order to something less than  $10^{-4}$  cm, the width of the boundary region and the boundary energy will both be smaller than the theoretical limit.<sup>14</sup>

There are as yet no reliable measurements of  $\alpha_{ns}$ . Estimates have been made by comparing the magnetization curves obtained in the intermediate state with theory. Landau's branching model is the one most often used, but it is known that the normal lamina do not actually branch as envisaged in the theory. Further, there is evidence that the transitions in the intermediate state are not always reversible. Kuper<sup>15</sup> has made some estimates from a nonbranching model, but finds large differences in values of  $\Delta$  estimated from different parts of the magnetization curve and there are doubts about the validity of the theory. A review of the problem is given in Shoenberg's book.<sup>7</sup>

We give in Table II a comparison of observed and calculated values of  $\Delta/\lambda$  for Sn and in Table III for Hg. Other estimates of  $\Delta/\lambda$ , both larger and smaller, can be found in Shoenberg's book. The values ( $L$ ) given in Tables II and III are estimated from the slope of the falling part of the magnetization curve for transverse cylinders, as observed by Desirant and Shoenberg<sup>9</sup> and by Andrew,<sup>16</sup> and are based on Landau's branching model. Another estimate for Sn can be obtained from the measured thicknesses of the lamina in the intermediate state in a sphere. This gives<sup>11</sup>  $\Delta \sim 5 \times 10^{-5}$  cm and  $\Delta/\lambda \sim 7.5$  for  $T \sim 3^\circ$ K.

The calculated values are larger than most of those estimated from experiment. It is comforting that the general trend with temperature is given correctly by the theory. It would, of course, be very desirable to have more reliable measurements of boundary energies.

<sup>12</sup> J. M. Lock, Proc. Roy. Soc. (London) A208, 391 (1951).

<sup>13</sup> E. Laurmann and D. Shoenberg, Proc. Roy. Soc. (London) A198, 560 (1949).

<sup>14</sup> A. B. Pippard, reference 3, and Proc. Roy. Soc. (London) A216, 547 (1953).

<sup>15</sup> C. G. Kuper, Phil. Mag. 42, 961 (1951).

<sup>16</sup> E. R. Andrew, Proc. Roy. Soc. (London) A194, 98 (1948).

### V. CHANGE IN SUPERCONDUCTING PENETRATION DEPTH WITH FIELD<sup>17</sup>

By use of a microwave method, Pippard<sup>8</sup> has measured the change in penetration depth with applied magnetic field. His measurements, shown by the dotted curve in Fig. 2, apply to tin and give the relative change in penetration depth between zero field and the critical field as function of temperature. The critical field itself, of course, varies with temperatures from a maximum as  $T=0^\circ\text{K}$  to zero at  $T=T_c$ .

It is noteworthy that the change is very small, less than 3 percent. This suggests that a linear theory should be a good approximation. The minimum near  $T=3^\circ\text{K}$  is also significant. It suggests that there are two factors affecting the penetration depth, one largest at low temperatures, becoming small near  $T=T_c$  and the other large only near  $T=T_c$ , and dropping rapidly as the temperature is decreased.

Pippard himself accounted for the rise near  $T=T_c$  as coming from a decrease in  $n_s$  near the surface. Such a

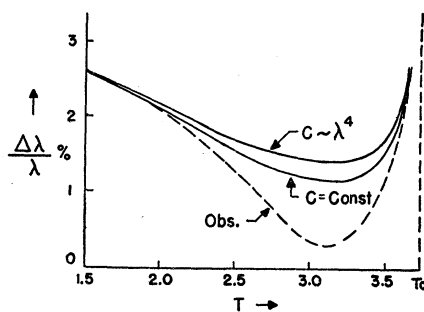


FIG. 2. Observed and calculated values of relative change in penetration depth for magnetic field  $H=H_c$ . Observed values from Pippard, reference 3; calculated from Eqs. (5.11) and (5.12).

decrease would allow a larger penetration of the field and a consequent decrease in free energy. The fact that the change is small suggests a rigidity or long-distance order of the superconducting electrons, and Pippard estimated that the order extends over distances of the order of  $10^{-4}$  cm. We shall give later an estimate of this effect based on the modified Ginsburg-Landau theory.

It is believed that the increase in  $\Delta\lambda/\lambda$  at low temperatures comes from essentially nonlinear terms which are left out of both the London theory and the modified theory presented here. The fact that  $\Delta\lambda/\lambda$  is small indicates that the wave functions of the electrons are only slightly modified by the field. F. London suggested many years ago that superconductivity follows from such a model. He assumed that if the gauge in  $\mathbf{A}$  is chosen appropriately, the wave functions are not modified at all by the field. The current density  $\mathbf{j}$  is

<sup>17</sup> Material in this section was presented at the Washington meeting of the American Physical Society, May, 1952. See Phys. Rev. **87**, 192 (1952).

TABLE II. Values of  $\Delta$  for Sn, calculated and estimated from experiments on the intermediate state.

$T$ ( $^\circ\text{K}$ )	$t$	$\lambda$ ( $\text{cm} \times 10^6$ )	$s$	$g(s)$	$\Delta/\lambda$ (calc)	$\Delta/\lambda$ ( $L$ )
2.1	0.56	0.53	0.0875	1.06	12	3.8
3.0	0.81	0.66	0.0695	1.14	16.5	5.6
3.5	0.94	1.06	0.061	1.17	19	6.0

then proportional to  $\mathbf{A}$ :

$$\mathbf{j} = -(n_s e^2 / m_s c) \mathbf{A}, \quad (5.1)$$

and one is led to the London equations.

To be consistent, one should include in a linear energy terms of the first order in  $\mathbf{A}$ , rather than assume that  $\Psi$  is unchanged. This leads in general to an integral relation between  $\mathbf{j}$  and  $\mathbf{A}$ :

$$\mathbf{j}(\mathbf{r}) = \int g(\mathbf{r}, \mathbf{r}') \mathbf{A}(\mathbf{r}') d\mathbf{r}'. \quad (5.2)$$

Pippard<sup>14</sup> has recently proposed a generalization of this sort for the London theory.

Terms linear in  $A$  give an energy varying quadratically with the applied field  $H_a$ . If one expands the free energy as a power series in  $H_a$ , the next higher terms will be of fourth order. These fourth-order terms come from second-order changes in the wave functions. We suggest that it is true nonlinear terms of this sort which give the change in penetration depth with field at low temperatures.

Let us then expand the free energy  $F$  in a power series in  $H_a$  and keep terms to the fourth order:

$$F = F_0 + (a - \lambda)(H_a^2/8\pi) - CH_a^4, \quad (5.3)$$

where  $C$  may depend on the temperatures. We consider the penetration terms on only one plane surface of a superconducting lamina of thickness  $a \gg \lambda$ , and  $F$  is energy per unit area. The magnetic moment per unit area of surface is:

$$M = -F/H_a = (H_a/4\pi)(-a + \lambda + 16\pi CH_a^2). \quad (5.4)$$

The effective penetration depth is

$$\lambda_{\text{eff}} = \lambda + 16\pi CH_a^2. \quad (5.5)$$

The change is quadratic in the field, as observed by Pippard.<sup>3</sup> This effective change in  $\lambda$  from the fourth-order terms is in addition to changes in  $\lambda$  resulting from changes in  $n_s$ .

TABLE III. Values of  $\Delta$  for Hg, calculated and estimated from experiments on the intermediate state.

$T$ ( $^\circ\text{K}$ )	$t$	$\lambda$ ( $\text{cm} \times 10^6$ )	$S$	$g(s)$	$\Delta/\lambda$ (calc)	$\Delta/\lambda$ ( $L$ )
2.1	0.505	0.46	0.0985	1.02	10.3	2.6
3.7	0.89	0.74	0.0675	1.14	17	2.85
3.97	0.96	1.24	0.063	1.15	18	2.25



The relative change in  $\lambda$  at  $H_a = H_c$  is

$$\Delta\lambda/\lambda = 16\pi C H_c^2/\lambda. \quad (5.6)$$

If it is assumed that  $C$  is temperature independent,  $\Delta\lambda/\lambda$  will vary with the reduced temperature  $t$  as

$$(\Delta\lambda/\lambda)_1 \sim (1-t^2)^2(1-t^4)^{\frac{1}{2}}, \quad (H_a = H_c), \quad (5.7)$$

the first factor coming from  $H_c^2$  and the second from  $\lambda$ . If it is assumed that it is the magnitude of the vector potential rather than the field which is important,  $C$  will vary as  $\lambda^4$ , since according to the London theory,

$$A = -\lambda H = -\lambda H_c \exp(-x/\lambda). \quad (5.8)$$

This would introduce an extra factor  $(1-t^4)^{-2}$  into (5.7), so that

$$(\Delta\lambda/\lambda)_1 \sim (1+t^2)^{-2}(1-t^4)^{\frac{1}{2}}, \quad (H_a = H_c). \quad (5.9)$$

Both (5.7) and (5.9) give a rapid drop in  $\Delta\lambda/\lambda$  as  $t$  increases. As shown in Fig. 2, the difference between using (5.7) and (5.9) for the low-temperature contribution to  $\Delta\lambda/\lambda$  is not very large.

To estimate the high-temperature contribution from the change in  $n_s$ , Pippard assumed that  $n_s$  changes uniformly in a slab of depth  $a$  adjacent to the surface. Making use of the Gorter-Casmiri two-fluid model, he found

$$\left(\frac{\Delta\lambda}{\lambda}\right)_2 = \frac{\lambda}{2a} \frac{t^4}{(1-t^2)^2}, \quad (H_a = H_c). \quad (5.10)$$

To get agreement with experiment, it was found necessary to take  $a \sim 10^{-4}$  cm.

We have attempted to fit Pippard's data by adding expressions of the form (5.10) to [(5.7) or (5.9)]. Shown in Fig. 2 are plots of the following functions:

$C = \text{const.}$

$$\frac{\Delta\lambda}{\lambda} = \frac{2.9t^4}{(1-t^2)^2(1-t^4)^2} + 3.6(1-t^2)^2(1-t^4)^{\frac{1}{2}}; \quad (5.11)$$

$C \sim \lambda^4$ ,

$$\frac{\Delta\lambda}{\lambda} = \frac{2.65t^4}{(1+t^2)^2(1-t^4)^{\frac{1}{2}}} + \frac{3.35(1-t^2)^{\frac{1}{2}}}{(1+t^2)^2}. \quad (5.12)$$

The only significance that can be attached to the comparison between observed and calculated values of  $\Delta\lambda/\lambda$  is that the minimum occurs at about the right temperatures. Dr. Pippard has informed the author that, because of experimental uncertainties, the minimum on the observed curve may not actually be as deep as indicated.

The change in  $n_s$  near  $T = T_c$  may also be estimated from the theory of Secs. II and III, but when this is done it is found that the calculated values are too small. This may indicate that because of imperfections the range of order may be less than the theoretical limit.

We shall give a brief outline of the theory. The difference between the Gibbs free energy in the superconducting and normal states is

$$G_s - G_n = \int_0^a \left\{ \frac{n_0 \hbar^2}{2m_s} \left[ \left( \frac{d\Psi}{dx} \right)^2 + \left( \frac{eA\Psi}{\hbar c} \right)^2 \right] + f(\Psi) + \frac{1}{8\pi} \left( \frac{dA}{dx} \right)^2 - \frac{H_a^2}{8\pi} - H_a \cdot M \right\} dx, \quad (5.13)$$

where the magnetization is

$$M = (H - H_a)/4\pi. \quad (5.14)$$

The boundary conditions are

$$H = H_a \text{ at } x = 0, \quad (5.15)$$

$$\Psi \rightarrow \Psi_s \text{ and } A \rightarrow 0 \text{ for } x \text{ large.} \quad (5.16)$$

We assume, and this will be justified by the results, that  $\Psi$  does not change much when  $A$  has an appreciable value and may be taken to be a constant  $\Psi_s$  equal to the value of  $\Psi$  at the surface  $x = 0$ . The solutions for  $A$  and  $H$  are then

$$A = -\lambda_s H_a \exp(-x/\lambda_s), \quad (5.17)$$

$$H = H_a \exp(-x/\lambda_s), \quad (5.18)$$

where  $\lambda_s$  is the value of  $\lambda$  at the surface,

$$\lambda_s = \lambda_0/\Psi_s. \quad (5.19)$$

The terms dependent on the magnetic field then give

$$(a - \lambda_s) H_a^2 / 8\pi, \quad (5.20)$$

so that

$$G = \int_0^a \left[ \frac{n_0 \hbar^2}{2m_s} \left( \frac{d\Psi}{dx} \right)^2 + f(\Psi) \right] dx + (a - \lambda_s) \frac{H_a^2}{8\pi}. \quad (5.21)$$

The variation of  $G$  with  $\Psi$  after an integration by parts gives

$$\delta G = \delta \Psi_s \left[ -\frac{n_0 \hbar^2}{2m_s} \left( \frac{d\Psi}{dx} \right)_s + \frac{\lambda_0}{\Psi_s^2} \frac{H_a^2}{8\pi} \right] + \int_0^a \delta \Psi \left[ -\frac{n_0 \hbar^2}{2m_s} \frac{d^2 \Psi}{dx^2} + \frac{df}{d\Psi} \right] dx. \quad (5.22)$$

Setting  $\delta G = 0$ , we have

$$\left( \frac{d\Psi}{dx} \right)_s = \frac{\lambda_0}{\Psi_s^2} \frac{m_s H_a^2}{8\pi n_0 \hbar^2}, \quad (5.23)$$

$$\frac{d^2 \Psi}{dx^2} = \frac{df}{d\Psi} \frac{m_s}{n_0 \hbar^2}. \quad (5.24)$$

The equations can be simplified by using the reduced variables  $U, s, \xi$  [see Eqs. (4.12)]. With  $H_a = H_c$ , we

have

$$\left(\frac{dU}{d\xi}\right)_s = \frac{s^2}{2}, \quad (5.25)$$

$$\frac{d^2U}{d\xi^2} = \frac{4\pi s^2}{H_c^2} \frac{df}{dU}. \quad (5.26)$$

A first integral of (5.26) which satisfies the boundary conditions for  $\xi$  large is

$$(dU/d\xi)^2 = (8\pi s^2/H_c^2)[f(U) - f(\Psi)]. \quad (5.27)$$

Since  $U$  is nearly equal to unity, we may write

$$U_s = 1 - \delta U_s. \quad (5.28)$$

From (5.25) and (5.27), we have to the first order in  $U$ ,

$$\delta U_s = \frac{\Delta\lambda}{\lambda} = \frac{s_0 t^2}{2(1+t^2)}. \quad (5.29)$$

It will be recalled (Table I) that  $s_0$  for tin is about 0.115. At  $t=1$ , we then have  $\delta U_s \sim 0.015$ . The observed values of  $\Delta\lambda/\lambda$  are at least two or three times larger, and perhaps more serious, the observed rise in  $\Delta\lambda/\lambda$  as  $T$  approaches  $T_c$  is more rapid than indicated by (5.29).

## VI. CONCLUDING REMARKS

### Thin Films

Ginsburg and Landau apply their theory to magnetization of thin films. If the film thickness is very small,  $n_s$  will not vary much across the film, but in the presence of a magnetic field may differ from the equilibrium value for bulk material. They show that in such a case the thermal transition in a magnetic field may be second order rather than first order. The value of  $n_s$  then starts at 0 as the critical temperature is reached and increases gradually as the temperature is lowered.

Our theory would yield results equivalent to those obtained by Lock by a direct application of the Gorter-Casimir two-fluid model to thin films. Lock found that allowing  $n_s$  to vary did account for some features of the observed magnetization curves, but that other non-linear effects are probably present as well. Pippard has applied a similar analysis to small spheres and has used the results to explain some aspects of the colloid experiments of Shoenberg.

### Connection with Range of Order

Pippard<sup>14</sup> has suggested a modification of the London equations so as to take into account a range of order of the superconducting electrons. In a pure metal, such as tin, the range is about  $10^{-4}$  cm, but is less in an

impure metal or alloy. He suggests an integral relation, such as (5.2), for the connection between current density and vector potential, and points out that such a modification of the London theory would require a corresponding modification of the Ginsburg-Landau theory. The same remarks would apply to our theory as well. Earlier,<sup>18</sup> Pippard discussed boundary energies in a qualitative way from the same point of view. Some of his conclusions differ from those of the Ginsburg-Landau theory.

It appears to the author that such a modification of the London equations is required, and is, in fact, suggested by quantum-mechanical approach of Sec. V. However, there do not seem to be strong reasons for taking for  $g(\mathbf{r}, \mathbf{r}')$  in (5.2) the particular expression chosen by Pippard. While it would not be difficult to modify our theory along similar lines, it is probably not worth while to do so until more is known about the correct form of  $g(\mathbf{r}, \mathbf{r}')$ .

On the whole, our theory, as well as that of Ginsburg and Landau, gives values for the boundary energy which are too large and for the change in penetration depth with field which are too small. Both indicate that the "range of order" given by the theory is too large. It is possible that the theoretical results apply to ideal crystals as a result of imperfections of one sort or another. It is more likely, however, that it is the theory which is defective. It is uncertain whether or not a modification along the lines of the preceding paragraph would give better results. Pippard suggests that the "range of order" should be determined by the uncertainty relations (1.1) and (1.2), and that  $\Delta$  should be roughly inversely proportional to  $T_c$ , and thus large for metals with low  $T_c$ , such as Al, and small for metals with large  $T_c$ , such as Pb. Faber<sup>19</sup> has proposed a test to distinguish between the Ginsburg-Landau type of theory and the suggestion of Pippard.

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<sup>18</sup> A. B. Pippard, Proc. Cambridge Phil. Soc. **47**, 617 (1951).

<sup>19</sup> In a talk at the Third International Conference on Low-Temperature Physics and Chemistry, Rice Institute, Houston, Texas, 1953, R. Faber suggested a method for testing the phenomenological theory. From Eq. (4.31) and the expression for  $s$  in (4.12), it follows that  $\Delta H_c \lambda = (\hbar c/e)g(s)$ . Since the quantity  $g(s)$  does not vary much when  $s$  is small, the right-hand side and thus the product  $\Delta H_c \lambda$  should be nearly the same for different superconductors. He plans to compare values of the product for Al and Sn, for which  $H_c$  differs by a factor of about 3.