

and are the only ones which join the measurements at higher temperatures. On the assumption that the correct heat capacity between 0.3 and 1.1°K is that obtained when no spontaneous heating was evident the heat capacity is very similar to that for $Y_{0.96}Gd_{0.04}Os_2$. With the extrapolation to $T=0$ shown in the figure the entropy in excess of that for pure lanthanum at 4.2°K is 95% of the expected $0.007 R \ln 8$. The superconducting transition is spread out between 1.4° and 1.8°K. The maximum decrease in heat capacity on application of

a magnetic field is 8 millijoules/mole deg and is consistent with the value 6.7 millijoules/mole deg² for γ for pure lanthanum.⁸ For each of the lanthanum-gadolinium samples the heat capacity maximum is in good agreement with an extrapolation of the T_c vs composition curve from above the point at which it crosses the T_s curve. Both samples are known to be superconducting at and below the maxima.²

⁸ D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

PHYSICAL REVIEW

VOLUME 121, NUMBER 1

JANUARY 1, 1961

Magnetic Field Dependence of Energy Gap in Superconductors*

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(Received July 20, 1960)

The dependence of energy gap in superconductors on static magnetic fields has been derived in a gauge-invariant way from the theory of Bardeen, Cooper, and Schrieffer. It has been shown that the gap width decreases with magnetic field approaching the critical value. Optimum conditions have been discussed for the observation of such an effect. The decrease in gap width has been calculated for two superconductors, Al and Sn, and it has been shown that for film thickness between 10^{-4} to 10^{-5} cm, the effect can be large enough to be observable.

1. INTRODUCTION

MUCH progress has been made in recent years in the theory of superconductivity proposed by Bardeen, Cooper, and Schrieffer.¹ Whereas the existence of an energy gap and the related thermal properties have been explained quite satisfactorily, the treatment of the electromagnetic properties of superconductors has not been quite unambiguous, mainly because of the question of gauge invariance.² A lot of work has appeared in the literature on the problem of gauge invariance,³⁻⁶ especially with a view to deriving the Meissner effect and the Pippard equation.⁷

In the present paper we consider another aspect of the magnetic behavior of a superconductor—the dependence of the energy gap on a static magnetic field. Since superconductivity is destroyed at a critical value of the magnetic field, one may expect that the energy gap would decrease with magnetic fields approaching the critical field. The purpose of the present

paper is to study this possibility, and to explore the conditions under which the gap decrease might be large enough to be observable.

Some experimental attempts have been made to study the effect of magnetic field on penetration depth and the gap width. Notable are the experiments of Pippard,⁸ and of Spiewak,⁹ and the more recent attempt of Ginsberg and Tinkham.¹⁰ Studying the behavior in a microwave field, Pippard found that for tin, in presence of a static magnetic field close to the critical field, the penetration depth increased by less than 3%. Spiewak's experiment also performed with tin wires (thickness $\sim 60\mu$) at a lower microwave frequency again indicated a very small effect for both longitudinal and transverse magnetic fields. Ginsberg and Tinkham, in contrast with the above experiments, used very thin superconducting films (thickness 12 Å), and with the technique of transmission of far infrared radiation through such specimens, found a very small effect again. One of the purposes of the present investigation is to understand these negative results on the BCS model of superconductivity. We shall see that according to our calculations, these experiments have been performed with films either too thick or too thin, while the optimum thickness for maximum effect lies somewhere in between the two.

* Work done under the auspices of the U. S. Atomic Energy Commission.

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¹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957), hereafter referred to as BCS.

² M. J. Buckingham, Nuovo cimento **5**, 1763 (1957).

³ P. W. Anderson, Phys. Rev. **110**, 827 (1958).

⁴ G. Wentzel, Phys. Rev. **111**, 1488 (1958).

⁵ G. Rickayzen, Phys. Rev. **115**, 795 (1959).

⁶ Y. Nambu, Phys. Rev. **117**, 648 (1960).

⁷ K. K. Gupta and V. S. Mathur, Phys. Rev. **115**, 75 (1959).

⁸ A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950).

⁹ M. Spiewak, Phys. Rev. **113**, 1479 (1959).

¹⁰ D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).

In this paper, the magnetic field will be treated as a perturbation, and the calculations will be carried out only in the lowest perturbation approximation. The electron-phonon interaction, on the other hand, shall be considered rigorously according to Bogoliubov's philosophy¹¹ of compensation of "dangerous graphs." The question of gauge invariance is an important one, but the various gauge invariant methods proposed involve approximations whose validity is not quite clear. In the present work we have used Wentzel's method; it has advantage in the ease with which it lends itself to Bogoliubov's elegant mathematical formulation. Since Wentzel's method is known to give penetration depths larger than the ones obtained by BCS and others, it is desirable to check the present calculations using one of the gauge-invariant techniques based on a random phase approximation. This work is in preparation now and will be published at a later date.

We start with Bloch-Fröhlich's Hamiltonian of a system of electrons and phonons in interaction in presence of a magnetic field. Wentzel's canonical transformation is then made to remove terms linear in the vector potential, so that the transformed Hamiltonian is explicitly gauge-invariant (Sec. 2). Next we apply Bogoliubov's quasi-particle transformation (in Sec. 3) extracting the "dangerous graphs" and mutually compensating for them (Sec. 4). The transformation parameters are now dependent on the magnetic field through the transverse vector potential, and so is the energy for a single-particle elementary excitation or the gap (Sec. 5). Section 6 is devoted to an application of these results to superconducting films. The decrease in the gap due to a static magnetic field is calculated separately for thick and thin films. Finally the possibility of observation of such an effect is discussed in Sec. 7.

Throughout the paper we have confined ourselves to temperature $T=0^\circ\text{K}$, and have neglected all Coulomb corrections. In view of the approximations made in simplifying the integrals encountered, the calculations should be considered only as a crude estimate of the result.

2. MANIFESTLY GAUGE-INVARIANT HAMILTONIAN

For our system of electron gas interacting with lattice vibrations in presence of a magnetic field, we adopt the well-known Bloch-Fröhlich Hamiltonian,

$$H = H_0 + H_g + H_A + H_{AA}. \quad (1)$$

Here

$$H_0 = \sum_{\mathbf{k}, s} E(\mathbf{k}) a_{\mathbf{k}s}^* a_{\mathbf{k}s} + \sum_{\mathbf{p}} \omega(\mathbf{p}) b_{\mathbf{p}}^* b_{\mathbf{p}} \quad (2)$$

is the energy of the free electron and phonon gas. $E(\mathbf{k}) = k^2/2m$ is the energy¹² of a single Bloch electron

of wave number k , $\omega(\mathbf{p})$ that of a phonon of momentum p . $a_{\mathbf{k}s}^*$, $a_{\mathbf{k}s}$ are the canonical creation and destruction operators for an electron of wave number k , spin s , satisfying the usual commutation relations. The electron-phonon interaction is given by

$$H_g = \frac{g}{(2V)^{\frac{1}{2}}} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{p}, s} \delta(\mathbf{k} - \mathbf{k}' - \mathbf{p}) \times \omega^{\frac{1}{2}}(\mathbf{p}) (b_{\mathbf{p}}^* + b_{-\mathbf{p}}) a_{\mathbf{k}s}^* a_{\mathbf{k}'s}, \quad (3)$$

where g is the coupling constant, and V the normalization volume. The delta function used in the summation is defined as

$$\begin{aligned} \delta(\mathbf{x}) &= 0 \quad \text{for } \mathbf{x} \neq 0, \\ \delta(0) &= 1. \end{aligned} \quad (4)$$

H_A and H_{AA} represent the linear and quadratic terms in the interaction of electrons with the external magnetic field. The magnetic field will be described by a general electromagnetic vector potential $\mathbf{A}(\mathbf{r})$, a specific form for which will not be chosen till Sec. 6.

$$H_A = -\frac{e}{2m} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, s} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}) \times \{(\mathbf{k} + \mathbf{k}') \cdot \mathbf{A}(\mathbf{q})\} a_{\mathbf{k}s}^* a_{\mathbf{k}'s}, \quad (5)$$

$$H_{AA} = \frac{e^2}{2m} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', s} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q} + \mathbf{q}') \times \{\mathbf{A}(\mathbf{q}) \cdot \mathbf{A}(\mathbf{q}')\} a_{\mathbf{k}s}^* a_{\mathbf{k}'s}, \quad (6)$$

where $\mathbf{A}(\mathbf{q})$ is the vector potential in momentum space, defined by the Fourier transformation

$$\mathbf{A}(\mathbf{r}) = \sum_{\mathbf{q}} \mathbf{A}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}}, \quad (7)$$

with the reality condition

$$\mathbf{A}(\mathbf{q}) = \mathbf{A}^*(-\mathbf{q}). \quad (8)$$

In order to have a manifestly gauge-invariant treatment, we follow Wentzel, and remove from the Hamiltonian (1) terms linear in \mathbf{A} by means of the canonical transformation:

$$H \rightarrow \bar{H} = e^{-L} H e^L, \quad (9)$$

with L satisfying the condition

$$[H_0 + H_g, L] = -H_A. \quad (10)$$

We shall then express L in a power series in g :

$$L = K_A + K_{gA} + K_{ggA} + \dots, \quad (11)$$

where the operators K_A , K_{gA} , K_{ggA} are the same as given by Eqs. (2), (4), (6), (7), and (8) of Wentzel's paper.

The transformed Hamiltonian is then given by

$$\begin{aligned} \bar{H} = H_0 + H_g + H_{AA} + \frac{1}{2} [H_A, K_A + K_{gA} + K_{ggA}] \\ + O(A^3, gA^3, g^2A^3, \text{etc.}). \end{aligned} \quad (12)$$

Assuming the external field to be weak, we neglect terms of order A^3 and higher in the electromagnetic potential.

¹¹ N. N. Bogoliubov, *Nuovo cimento* **7**, 794 (1958).

¹² We use natural units $\hbar = 1$, velocity of light = 1.

The commutators in Eq. (12) can be calculated to be

$$\frac{1}{2}[H_A, K_A] + H_{AA} = -\frac{e^2}{m} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', s} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}' + \mathbf{q}) a_{ks}^* a_{k's} F_1(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}'), \quad (13)$$

$$\frac{1}{2}[H_A, K_{\theta A}] = -\frac{e^2}{2m} \frac{g}{(2V)^{\frac{1}{2}}} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}, s} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}' + \mathbf{q} + \mathbf{p}) \times \omega^{\frac{1}{2}}(\mathbf{p}) a_{ks}^* a_{k's} F_2(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}), \quad (14)$$

$$\begin{aligned} \frac{1}{2}[H_A, K_{\theta\theta A}] = & -\frac{e^2}{2m} \frac{g^2}{2V} \left\{ \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p}', s} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}' + \mathbf{q} + \mathbf{p} + \mathbf{p}') \times \omega^{\frac{1}{2}}(\mathbf{p}) \omega^{\frac{1}{2}}(\mathbf{p}') a_{ks}^* a_{k's} F_3(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p}') \right. \\ & \left. + \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}_1, \mathbf{k}_1', \mathbf{q}, \mathbf{q}', s, s'} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{k}_1' - \mathbf{k}_1 + \mathbf{q}' + \mathbf{q}) \times a_{ks}^* a_{k's} a_{k_1 s'}^* a_{k_1' s'} F_4(\mathbf{k}, \mathbf{k}', \mathbf{k}_1, \mathbf{k}_1', \mathbf{q}, \mathbf{q}') \right\}, \quad (15) \end{aligned}$$

where the functions F are complicated functions of the momenta, and have been listed in Appendix 1. It should be noted that F_1 and F_4 contain no phonon operators, F_2 is linear, and F_3 quadratic in them. Furthermore, it is clear from the Eqs. (13) to (15) that F 's are all quadratic in the vector potential. For a longitudinal vector potential, it can be seen immediately from the defining equations of the F functions that they are "manifestly" zero. The Hamiltonian (12) is then explicitly gauge-invariant. Without loss of generality we may now choose the vector potential to be transverse. The gauge $\nabla \cdot \mathbf{A} = 0$ will be adopted for further calculations.

3. BOGOLIUBOV'S TRANSFORMATION

It is well known that a straightforward perturbation theory cannot be applied to the Hamiltonian (12). We use here Bogoliubov's method of compensation of "dangerous graphs," and accordingly make the canonical transformation to the new Fermi amplitudes

$$\begin{aligned} \alpha_{k0} &= u_k a_{k, \frac{1}{2}} - v_k a_{-k, -\frac{1}{2}}^*, \\ \alpha_{k1} &= u_k a_{-k, -\frac{1}{2}} + v_k a_{k, \frac{1}{2}}^*, \end{aligned} \quad (16)$$

$$\begin{aligned} U = & 2 \sum_{\mathbf{k}} \{E(\mathbf{k}) - \lambda\} v_k^2 - \frac{2e^2}{m} \sum_{\mathbf{k}, \mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') F_1(\mathbf{k}, \mathbf{k}, \mathbf{q}, \mathbf{q}') v_k^2 + \frac{e^2}{2m} \frac{g^2}{2V} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') \\ & \times [2F_4(\mathbf{k}, \mathbf{k}', \mathbf{k}', \mathbf{k}, \mathbf{q}, \mathbf{q}') u_k^2 v_k^2 + \{F_4(\mathbf{k}, \mathbf{k}', -\mathbf{k}, -\mathbf{k}', \mathbf{q}, \mathbf{q}') + F_4(-\mathbf{k}, -\mathbf{k}', \mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}')\} u_k v_k u_{k'} v_{k'} \\ & + 2\{F_4(k, k, k', k', q, q') + F_4(k, k, -k', -k', q, q')\} v_k^2 v_{k'}^2], \quad (19) \end{aligned}$$

$$H_0 = \sum_{\mathbf{k}} \epsilon_1(\mathbf{k}) (\alpha_{k0}^* \alpha_{k0} + \alpha_{k1}^* \alpha_{k1}) + \sum_{\mathbf{p}} \omega_1(\mathbf{p}) b_p^* b_p, \quad (20)$$

where

$$\begin{aligned} \epsilon_1(\mathbf{k}) = & \{E_1(\mathbf{k}) - \lambda\} (u_k^2 - v_k^2) - \frac{e^2}{m} \frac{g^2}{2V} \sum_{\mathbf{k}', \mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') \\ & \times \{F_4(\mathbf{k}, \mathbf{k}', -\mathbf{k}, -\mathbf{k}', \mathbf{q}, \mathbf{q}') + F_4(-\mathbf{k}, -\mathbf{k}', \mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}')\} u_k v_k u_{k'} v_{k'}, \quad (21) \end{aligned}$$

$$\begin{aligned} E_1(\mathbf{k}) = & E(\mathbf{k}) - \frac{e^2}{m} \sum_{\mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') F_1(\mathbf{k}, \mathbf{k}, \mathbf{q}, \mathbf{q}') + \frac{e^2}{2m} \frac{g^2}{2V} \sum_{\mathbf{k}', \mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') \{F_4(\mathbf{k}, \mathbf{k}', \mathbf{k}', \mathbf{k}, \mathbf{q}, \mathbf{q}') u_k^2 \\ & + 2F_4(\mathbf{k}, \mathbf{k}, \mathbf{k}', \mathbf{k}', \mathbf{q}, \mathbf{q}') v_k^2 + 2F_4(\mathbf{k}, \mathbf{k}, -\mathbf{k}', -\mathbf{k}', \mathbf{q}, \mathbf{q}') v_{k'}^2 - F_4(\mathbf{k}', \mathbf{k}, \mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}') v_k^2\}, \quad (22) \end{aligned}$$

and

$$\omega_1(\mathbf{p}) = \omega(\mathbf{p}) + \frac{e^2}{2m} \frac{g^2}{2V} \sum_{\mathbf{k}, \mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') v_k^2 \times \{F_3(\mathbf{k}, \mathbf{k}, \mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p})\}_{\text{D.P.}}, \quad (23)$$

where u_k and v_k are real c numbers and satisfy the relation

$$u_k^2 + v_k^2 = 1. \quad (17)$$

The Hamiltonian (12) then transforms to

$$\bar{H}' = U + H_0 + H_{\text{int}} \quad (18)$$

where U is the constant part of the Hamiltonian; i.e., free of quasi-particle or phonon operators, H_0 is the diagonal part of the Hamiltonian, and H_{int} represents the interaction between quasi-particles and phonons.

Since Bogoliubov's quasi-particle transformation does not conserve the particle number, we first replace the Hamiltonian \bar{H} by $\bar{H} - \lambda N$, where N is the particle number operator $\sum_{\mathbf{k}, s} a_{ks}^* a_{ks}$, and λ is a parameter of the nature of a chemical potential. The transformation (16) can then be applied, and λ can be determined from the condition that the expectation value \bar{N} of the number operator in the Bogoliubov ground state should equal the actual number of particles N_F in the Fermi sphere.

The Hamiltonian (18) is then given by

$\{F_3(\mathbf{k}, \mathbf{k}, \mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p})\}_{\text{D.P.}}$ being the coefficient of the diagonal term $b_p^* b_p$ in $F_3(\mathbf{k}, \mathbf{k}, \mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p})$. The interaction between quasi-particles and phonons given by H_{int} is a complicated expression and we shall not write it in full. Schematically, however, it can be broken up as

$$H_{\text{int}} = H_1 + H_2 + H_3 + H_4, \quad (24)$$

where H_1 , H_2 , and H_3 are quadratic or biquadratic in α 's, and H_4 contains no quasi-particle operator. Now H_1 represents the creation (or destruction) of 2 quasi-particles, and is an operator of the form $\alpha^* \alpha^*$, $\alpha \alpha$, $\alpha^* \alpha^* \alpha^* \alpha$, \dots . With respect to the phonon operators, we may further subclassify H_1 as

$$H_1 = H_1' + H_1'', \quad (25)$$

where H_1' creates (or destroys) no phonons or 2 phonons, and H_1'' creates (or destroys) one phonon.

Next, H_2 is only quadratic in α 's, and represents no net creation or destruction of quasi-particles. It is an operator of the type $\alpha^* \alpha$. As before, we write

$$H_2 = H_2' + H_2'', \quad (26)$$

where H_2' and H_2'' have the same meaning as the corresponding primed quantities in Eq. (25), except that in the case no phonon is emitted (or absorbed) only the nondiagonal part (N.D.P.) of $\alpha^* \alpha$ is involved in H_2' , the diagonal part having been picked up in H_0 already.

The third term H_3 in the Hamiltonian (24) is wholly biquadratic in α 's, and contains no phonon operators. Note that the quasi-particle transformation gives rise to biquadratic terms in α 's only when there are no phonon operators with them. This is therefore also true for the biquadratic terms in H_1 . The biquadratic forms of α 's in H_3 are all those not contained in H_1 , e.g., of the type $\alpha^* \alpha^* \alpha^* \alpha^*$, $\alpha \alpha \alpha \alpha$, $(\alpha^* \alpha^* \alpha \alpha)_{\text{N.D.P.}}$, etc.

The last term H_4 contains no quasi-particle operators and is purely quadratic in the phonon operators. Thus it contains terms like $b^* b^*$, $b b$, $(b^* b)_{\text{N.D.P.}}$, etc.

We quote below the explicit forms of H_1' , H_1'' , and H_2'' , since these are the only terms which will be required in future.

$$\begin{aligned} H_1' = & 2 \sum_{\mathbf{k}} \{E(\mathbf{k}) - \lambda\} u_k v_k (\alpha_{k0}^* \alpha_{k1}^* + \alpha_{k0} \alpha_{k1}) - \frac{e^2}{m} \sum_{\mathbf{k}, \mathbf{k}'} \left\{ \sum_{\mathbf{q}, \mathbf{q}'} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}' + \mathbf{q}) F_1(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}') \right. \\ & - \frac{1}{2} \left(\frac{g^2}{2V} \right) \sum_{\mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p}'} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{q}' + \mathbf{q} + \mathbf{p}' + \mathbf{p}) F_3(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p}') \} \times \{ u_k v_{k'} \alpha_{k0}^* \alpha_{k'1}^* + u_{-k} v_{-k'} \alpha_{-k'0}^* \alpha_{-k1}^* \\ & + u_{k'} v_k \alpha_{k1} \alpha_{k'0} + u_{-k'} v_{-k} \alpha_{-k'1} \alpha_{-k0} \} + \frac{e^2}{2m} \frac{g^2}{2V} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{k}_1, \mathbf{k}_1', \mathbf{q}, \mathbf{q}'} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{k}_1' - \mathbf{k}_1 + \mathbf{q}' + \mathbf{q}) F_4(\mathbf{k}, \mathbf{k}', \mathbf{k}_1, \mathbf{k}_1', \mathbf{q}, \mathbf{q}') \\ & \times \{ (u_k u_{k'} \alpha_{k0}^* \alpha_{k'0} + v_k v_{k'} \alpha_{k1} \alpha_{k'1} + u_{-k} u_{-k'} \alpha_{-k1}^* \alpha_{-k'1} + v_{-k} v_{-k'} \alpha_{-k0} \alpha_{-k'0}^*) \\ & \times (u_{k1} v_{k1'} \alpha_{k10}^* \alpha_{k1'1}^* - u_{-k1} v_{-k1'} \alpha_{-k11}^* \alpha_{-k1'0}^* + v_{k1} u_{k1'} \alpha_{k11} \alpha_{k1'0} - v_{-k1} u_{-k1'} \alpha_{-k10} \alpha_{-k1'1}^*) \\ & + (u_k v_{k'} \alpha_{k0}^* \alpha_{k'1}^* - u_{-k} v_{-k'} \alpha_{-k1}^* \alpha_{-k'0}^* + v_k u_{k'} \alpha_{k1} \alpha_{k'0} - v_{-k} u_{-k'} \alpha_{-k0} \alpha_{-k'1}^*) \\ & \times (u_{k1} u_{k1'} \alpha_{k10}^* \alpha_{k1'0} + v_{k1} v_{k1'} \alpha_{k11} \alpha_{k1'1} + u_{-k1} u_{-k1'} \alpha_{-k11}^* \alpha_{-k1'1} + v_{-k1} v_{-k1'} \alpha_{-k10} \alpha_{-k1'0}^*) \}, \quad (27) \end{aligned}$$

$$\begin{aligned} H_1'' = & \frac{g}{(2V)^{\frac{1}{2}}} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{p} + \mathbf{q} + \mathbf{q}') \omega^{\frac{1}{2}}(\mathbf{p}) \{ b_p f(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) + b_{-p}^* g(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) \} \\ & \times \{ u_k v_{k'} \alpha_{k0}^* \alpha_{k'1}^* + u_{-k} v_{-k'} \alpha_{-k'0}^* \alpha_{-k1}^* + u_{k'} v_k \alpha_{k1} \alpha_{k'0} + u_{-k'} v_{-k} \alpha_{-k'1} \alpha_{-k0} \}, \quad (28) \end{aligned}$$

where

$$f(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) = \delta(\mathbf{q}) \delta(\mathbf{q}') - \frac{e^2}{2m} \{ \text{coeff. of } b_p \text{ in } F_2(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) \}, \quad (29)$$

$$g(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) = \delta(\mathbf{q}) \delta(\mathbf{q}') - \frac{e^2}{2m} \{ \text{coeff. of } b_{-p}^* \text{ in } F_2(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) \},$$

$$\begin{aligned} H_2'' = & \frac{g}{(2V)^{\frac{1}{2}}} \sum_{\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}} \delta(\mathbf{k}' - \mathbf{k} + \mathbf{p} + \mathbf{q} + \mathbf{q}') \omega^{\frac{1}{2}}(\mathbf{p}) \times \{ b_p f(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) + b_{-p}^* g(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) \} \\ & \times \{ u_k u_{k'} \alpha_{k0}^* \alpha_{k'0} + u_{-k} u_{-k'} \alpha_{-k1}^* \alpha_{-k'1} - v_k v_{k'} \alpha_{k'1}^* \alpha_{k1} - v_{-k} v_{-k'} \alpha_{-k'0}^* \alpha_{-k0} \}. \quad (30) \end{aligned}$$

4. THE COMPENSATION EQUATION

We now follow Bogoliubov's philosophy demanding compensation of "dangerous" graphs. Such "dangerous" graphs arise when two quasi-particles are created from

"vacuum" without the emission of phonons. Matrix elements for the creation of two quasi-particles, $\mathbf{k}0$ and $\mathbf{k}1$ say, can be written down in perturbation approximation. From the discussion on the form of the

interaction Hamiltonian (24), it is clear that only H_1' contributes in lowest order. In second order, the "dangerous" graph arises from a combined action of H_2'' and H_1'' . Equating the sum of these matrix elements to zero, we obtain the compensation equation, correct to second order,

$$\langle 0 | \alpha_{k0} \alpha_{k1} H_1' | 0 \rangle - \langle 0 | \alpha_{k0} \alpha_{k1} H_2'' (1/H_0) H_1'' | 0 \rangle = 0, \quad (31)$$

which together with Eq. (17) specifies u_k and v_k .

Computing the expectation values in Eq. (31), we obtain the compensation equation in the form:

$$\xi(\mathbf{k}) u_k v_k = \frac{1}{2} c(\mathbf{k}) (u_k^2 - v_k^2), \quad (32)$$

where

$$\xi(\mathbf{k}) = \{ \bar{E}(\mathbf{k}) - \lambda \} - \frac{e^2}{m} \sum_{\mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') F_1(\mathbf{k}, \mathbf{q}, \mathbf{q}'), \quad (33)$$

$$c(\mathbf{k}) = \frac{g^2}{2V} \sum_{\mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{q}_1, \mathbf{q}_1', \mathbf{p}} \delta(\mathbf{k} - \mathbf{k}' + \mathbf{p} + \mathbf{q} + \mathbf{q}') \delta(\mathbf{k}' - \mathbf{k} - \mathbf{p} + \mathbf{q}_1 + \mathbf{q}_1') \times \frac{\omega(\mathbf{p})}{\epsilon_1(\mathbf{k}') + \epsilon_1(\mathbf{k}) + \omega_1(\mathbf{p})} \\ \times \{ f(-\mathbf{k}, -\mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) g(\mathbf{k}, \mathbf{k}', \mathbf{q}_1, \mathbf{q}_1', -\mathbf{p}) + f(\mathbf{k}, \mathbf{k}', \mathbf{q}_1, \mathbf{q}_1', -\mathbf{p}) g(-\mathbf{k}, -\mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) \} u_{k'} v_{k'} \\ - \frac{e^2}{2m} \frac{g^2}{2V} \sum_{\mathbf{k}', \mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') \{ F_4(\mathbf{k}, \mathbf{k}', -\mathbf{k}, -\mathbf{k}', \mathbf{q}, \mathbf{q}') + F_4(-\mathbf{k}, -\mathbf{k}', \mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}') \} u_{k'} v_{k'}, \quad (34)$$

with

$$\bar{E}(\mathbf{k}) = E(\mathbf{k}) - \frac{g^2}{2V} \sum_{\mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{q}_1, \mathbf{q}_1', \mathbf{p}} \delta(\mathbf{k} - \mathbf{k}' + \mathbf{p} + \mathbf{q} + \mathbf{q}') \delta(\mathbf{k}' - \mathbf{k} - \mathbf{p} + \mathbf{q}_1 + \mathbf{q}_1') \times \frac{\omega(\mathbf{p})}{\epsilon_1(\mathbf{k}') + \epsilon_1(\mathbf{k}) + \omega_1(\mathbf{p})} \\ \times \{ f(\mathbf{k}, \mathbf{k}', \mathbf{q}_1, \mathbf{q}_1', -\mathbf{p}) g(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}) u_{k'}^2 - f(\mathbf{k}', \mathbf{k}, \mathbf{q}, \mathbf{q}', \mathbf{p}) g(\mathbf{k}, \mathbf{k}', \mathbf{q}_1, \mathbf{q}_1', -\mathbf{p}) v_{k'}^2 \} \\ + \frac{e^2}{2m} \frac{g^2}{2V} \sum_{\mathbf{k}', \mathbf{q}, \mathbf{q}'} \delta(\mathbf{q} + \mathbf{q}') [u_{k'}^2 F_4(\mathbf{k}, \mathbf{k}', \mathbf{k}', \mathbf{k}, \mathbf{q}, \mathbf{q}') + v_{k'}^2 \{ 2F_4(\mathbf{k}, \mathbf{k}, \mathbf{k}', \mathbf{k}', \mathbf{q}, \mathbf{q}') \\ + 2F_4(\mathbf{k}, \mathbf{k}, -\mathbf{k}', -\mathbf{k}', \mathbf{q}, \mathbf{q}') - F_4(\mathbf{k}', \mathbf{k}, \mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}') \}], \quad (35)$$

$\epsilon_1(\mathbf{k})$ and $\omega_1(\mathbf{p})$ being given by Eqs. (21) and (23). Equation (32) is formally similar to Bogoliubov's compensation equation and indeed becomes identical to it in the absence of the electromagnetic field. From Eqs. (17) and (32), we can solve for u_k and v_k in terms of $c(\mathbf{k})$ and $\xi(\mathbf{k})$ to obtain

$$u_k^2 = \frac{1}{2} \left[1 + \frac{\xi(\mathbf{k})}{\{c^2(\mathbf{k}) + \xi^2(\mathbf{k})\}^{\frac{1}{2}}} \right], \quad (36)$$

$$v_k^2 = \frac{1}{2} \left[1 - \frac{\xi(\mathbf{k})}{\{c^2(\mathbf{k}) + \xi^2(\mathbf{k})\}^{\frac{1}{2}}} \right],$$

whence

$$u_k v_k = - \frac{1}{2} \frac{c(\mathbf{k})}{\{c^2(\mathbf{k}) + \xi^2(\mathbf{k})\}^{\frac{1}{2}}}. \quad (37)$$

Substituting for $u_k v_k$ from Eq. (37) in the expression (34), one obtains an integral equation for $c(\mathbf{k})$. The first term on the right-hand side of Eq. (34) can be written out fully using the defining Eqs. (29) for f , g . The term $2\delta(\mathbf{q})\delta(\mathbf{q}')\delta(\mathbf{q}_1)\delta(\mathbf{q}_1')$ in the expression inside the curly brackets is the one that contains Bogoliubov's result. Within the limits of our approximation, the remaining terms that we need consider inside the curly brackets are the ones proportional to $g^2 e^2$. These can be shown to be negligible as follows. If we write out these terms in full using the definition (A-2) of the F_2 function, we can interchange the variables

suitably to group them into expressions like

$$\left\{ \frac{\omega(\mathbf{k} - \mathbf{k}')}{E(\mathbf{k}') - E(\mathbf{k} + \mathbf{q}') - \omega(\mathbf{k} - \mathbf{k}')} - \frac{\omega(\mathbf{k} - \mathbf{k}')}{E(\mathbf{k}' + \mathbf{q}') - E(\mathbf{k}) - \omega(\mathbf{k} - \mathbf{k}')} \right\}. \quad (38)$$

Now, the maximum contribution comes from k , k' close to the Fermi momentum k_F , so that for

$$\omega \gg |E(\mathbf{k}_F) - E(\mathbf{k}_F + \mathbf{q}')| \quad (39)$$

these terms are negligible. The first term on the right-hand side of Eq. (34) in our approximation then reduces to

$$\frac{g^2}{V} \sum_{\mathbf{k}', \mathbf{p}} \delta(\mathbf{k}' - \mathbf{k} - \mathbf{p}) \frac{\omega(\mathbf{p})}{\epsilon_1(\mathbf{k}') + \epsilon_1(\mathbf{k}) + \omega_1(\mathbf{p})} u_{k'} v_{k'}. \quad (40)$$

This has been evaluated in Appendix 2. Note that here we have to take into account terms in $\epsilon_1(\mathbf{k})$ which are proportional to e^2 . However, these can be shown to be negligible, so that integral (40) reduces to

$$\frac{2g^2 m k_0}{(2\pi)^2} c \ln(2\tilde{\omega}/c), \quad (41)$$

where k_0 is defined by the equation

$$E(k_0) - \lambda = 0. \quad (42)$$

Note that in the above evaluation $c(\mathbf{k})$ has been taken to be a constant as an approximation, and $\omega(\mathbf{p})$ has been replaced by a certain mean phonon energy $\bar{\omega}$. The parameter k_0 defined in terms of the "chemical potential" λ , can be evaluated from the condition that the particle number is conserved. Following Bogoliubov's field-free case, it is simple to show that $k_0 \simeq k_F$.

In the second term on right-hand side of Eq. (34), substituting for F_4 from Eq. (A-4) and rearranging the terms, we find expressions like

$$\left\{ \frac{\omega(\mathbf{k}-\mathbf{k}')}{E(\mathbf{k}')-E(\mathbf{k}+\mathbf{q})+\omega(\mathbf{k}-\mathbf{k}')} + \frac{\omega(\mathbf{k}-\mathbf{k}')}{E(\mathbf{k}+\mathbf{q})-E(\mathbf{k}')+\omega(\mathbf{k}-\mathbf{k}')} \right\}, \quad (43)$$

which under assumption (39) can be replaced by 2. The result, after some algebra, becomes

$$-\frac{2e^2}{m} \frac{g^2}{V} \sum_{\mathbf{q}, \mathbf{k}'} u_{\mathbf{k}, \mathbf{k}'} v_{\mathbf{k}'} \times \left[\frac{\mathbf{k} \cdot \mathbf{A}(\mathbf{q}) \mathbf{k} \cdot \mathbf{A}^*(\mathbf{q})}{\{E(\mathbf{k})-2E(\mathbf{k}')+E(\mathbf{k}+\mathbf{q})\} \{\mathbf{q} \cdot (\mathbf{k}+\mathbf{q}/2)\}} - \frac{\mathbf{k}' \cdot \mathbf{A}(\mathbf{q}) \mathbf{k}' \cdot \mathbf{A}^*(\mathbf{q})}{\{2E(\mathbf{k})-E(\mathbf{k}'+\mathbf{q})-E(\mathbf{k}')\} \{\mathbf{q} \cdot (\mathbf{k}'+\mathbf{q}/2)\}} \right]. \quad (44)$$

Note that the first term in (44) gives a dependence on the orientation of \mathbf{k} . In the present work, we shall not discuss this angular dependence, and will confine ourselves only to the magnitude of the effect caused by the extra terms (49). Averaging out the angular dependence, it is easy to see that the two terms in (44) become equal in magnitude within the limits of our approximation, so that for $k \sim k_F$, (44) reduces to

$$-\frac{e^2}{2} \frac{g^2 c}{(2\pi)^2} k_F^2 \sum_{\mathbf{q}} \frac{|\mathbf{A}(\mathbf{q})|^2}{q} \int_{-1}^{+1} \frac{(1-u^2) du}{(u+\gamma/2)} I(u, q), \quad (45)$$

where

$$\gamma = q/k_F, \quad (46)$$

$$I(u, q) = \int_{-\omega}^{+\omega} \frac{d\eta'}{(c^2 + \eta'^2)^{3/2}} \frac{1}{\eta' + \alpha'}, \quad (47)$$

$$\alpha' = (c/\beta)(u + \gamma/2), \quad (48)$$

$$\beta = 2mc/k_F q, \quad (49)$$

and η' is related to k' by the equation

$$\eta' = \bar{E}(\mathbf{k}') - \lambda. \quad (50)$$

It is understood that at singularities one takes the principal values of the integrals. The maximum contribution to $I(u, q)$ comes from small values of

$\eta' (\eta' \sim c)$, and for $|\eta'| > \omega$ the factor (43) becomes very small. The limits for η' integration have therefore been chosen as $-\omega < \eta' < \omega$. The η' integral is straightforward, but the resulting u integral in (45) cannot be done exactly. We estimate this integral in the following way. Split the range of integration of q in the following two domains: (i) $v_F q < c$, (ii) $v_F q > c$, where v_F is the Fermi velocity. In Appendix 3, we have evaluated the u integral in these two regions, so that (45) can be written approximately as

$$-\frac{2}{3} \frac{e^2}{m} \frac{g^2}{(2\pi)^2} \frac{k_F^3}{c} \sum'_{\mathbf{q}} |\mathbf{A}(\mathbf{q})|^2 - 5.4 \frac{e^2}{(2\pi)^2} \frac{g^2}{k_F^2} \sum''_{\mathbf{q}} \frac{|\mathbf{A}(\mathbf{q})|^2}{q}, \quad (51)$$

where the single and the double primes on the summation sign indicate the respective domains (i) and (ii).

With the help of (41) and (51), the integral equation (33) can be solved to yield

$$c = c_0 [1 - \sum_{\mathbf{q}} f(\mathbf{q})], \quad (52)$$

where

$$f(\mathbf{q}) = \frac{1}{3} \frac{e^2}{m^2} \frac{k_F^2}{c_0^2} |\mathbf{A}(\mathbf{q})|^2 \quad \text{for } v_F q < c, \quad (53)$$

$$f(\mathbf{q}) \simeq 2.7 \frac{e^2}{m} \frac{k_F}{c_0} \frac{|\mathbf{A}(\mathbf{q})|^2}{q} \quad \text{for } v_F q > c, \quad (54)$$

and c_0 is Bogoliubov's field-free solution, given by

$$c_0 = 2\bar{\omega} e^{-1/\rho}, \quad (55)$$

with

$$\rho = (g^2/2\pi^2) m k_F. \quad (56)$$

In deriving Eq. (52) we have assumed $\sum_{\mathbf{q}} f(\mathbf{q}) \ll 1$, so that Eq. (52) is not valid for strong magnetic fields that violate this condition.

5. ENERGY OF AN ELEMENTARY EXCITATION

Consider a state with one quasi-particle

$$|\mathbf{k}0\rangle = \alpha_{\mathbf{k}0}^* |0\rangle. \quad (57)$$

In our approximation, the energy of this state is

$$E_e(\mathbf{k}) = \langle \mathbf{k}0 | H_0 | \mathbf{k}0 \rangle - \left\langle \mathbf{k}0 \left| H_2'' \frac{1}{H_0 - \epsilon_1(\mathbf{k})} H_2'' \right| \mathbf{k}0 \right\rangle + \left\langle 0 \left| H_1''(\mathbf{k}0) \frac{1}{H_0} H_1''(\mathbf{k}0) \right| 0 \right\rangle, \quad (58)$$

where $H_1''(\mathbf{k}0)$ refers to that part of the Hamiltonian H_1'' which creates (or destroys) the quasi-particle, $\mathbf{k}0$, while creating (or destroying) a pair. The last term in Eq. (58) thus arises due to inhibition imposed by Pauli's exclusion principle. Since we are interested in the excitation spectrum for electrons very close to the

top of Fermi sphere, we have for such electrons $\epsilon_1(\mathbf{k}) \sim 0(g^2, g^2 e^2, e^4)$. Consistent with our approximation, we neglect terms of order $g^2 \epsilon_1(\mathbf{k})$. Writing Eq. (58) in an expanded form and using some symmetry properties for the f and g functions, we get

$$E_e(\mathbf{k}) = \epsilon_1(\mathbf{k}) + 2c_1(\mathbf{k})u_k v_k - \frac{g^2}{2V} \sum_{\mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{q}_1, \mathbf{q}_1', \mathbf{p}} \delta(\mathbf{k} - \mathbf{k}' + \mathbf{p} + \mathbf{q} + \mathbf{q}') \frac{\omega(\mathbf{p})}{\epsilon(\mathbf{k}') + \omega(\mathbf{p})} \times \{f(-\mathbf{k}, -\mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p})g(-\mathbf{k}', -\mathbf{k}, \mathbf{q}_1, \mathbf{q}_1', -\mathbf{p}) \times u_{k'}^2 - g^2(\mathbf{k}, \mathbf{k}', \mathbf{q}_1, \mathbf{q}_1', -\mathbf{p}) \times f(\mathbf{k}', \mathbf{k}, \mathbf{q}, \mathbf{q}', \mathbf{p})v_{k'}^2\} (u_k^2 - v_k^2), \quad (59)$$

where $c_1(\mathbf{k})$ is the first term on the right-hand side of the integral Eq. (33) for $c(\mathbf{k})$. Now with the help of Eqs. (35), (21), (34), and (32), it is easy to reduce this to

$$E_e(\mathbf{k}) = \xi(\mathbf{k})(u_k^2 - v_k^2) + 2c(\mathbf{k})u_k v_k = \{c^2(\mathbf{k}) + \xi^2(\mathbf{k})\}^{\frac{1}{2}}, \quad (60)$$

so that the minimum energy required for an elementary excitation or the energy gap is given by $c(\mathbf{k})$.

6. LONDON AND PIPPARD SOLUTIONS FOR $A(q)$ INSIDE A SUPERCONDUCTING MATERIAL

So far the magnetic field \mathbf{B} , or its vector potential was undetermined, but now we shall specify it, in accordance with what is known about the magnetic response of a superconductor. We do this for the simple case of a plane-parallel plate of thickness L , say $-L/2 \leq z \leq L/2$, with $\mathbf{A} = (0, A(z), 0)$, $\mathbf{B} = (B(z), 0, 0)$, $B(\pm L/2) = B$. Now L may be large or small compared with the coherence distance⁷ $\xi_0 = v_F/\pi^2 c$. We first treat the former case ($L \gg \xi_0$) because it is simpler for two reasons: (1) The main contribution to Eq. (52) will come from $q < c/v_F$, and the error in adopting Eq. (53) for *all* values of q will be small. (2) The magnetic response is given by the simple London equation, the modification due to nonlocal effects (Pippard) being irrelevant. It is well known¹³ that in this case the solution of London equation with appropriate boundary conditions is

$$B(z) = B \frac{\cosh \mu z}{\cosh(\mu L/2)}, \quad A(z) = -\frac{B}{\mu} \frac{\sinh \mu z}{\cosh(\mu L/2)}, \quad (61)$$

for $|z| \leq L/2$, where μ^{-1} is the penetration depth. Using

¹³ F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1.

the Fourier transformation defined in Eq. (7), we get

$$\sum_{\mathbf{q}} |\mathbf{A}(\mathbf{q})|^2 = \frac{1}{L} \int_{-L/2}^{+L/2} |A(z)|^2 dz = \frac{B^2}{2L\mu^3} \frac{(\sinh \mu L - \mu L)}{\cosh^2(\mu L/2)}, \quad (62)$$

so that for $L \gg \mu^{-1}$ (which follows from the condition $L \gg \xi_0$, since in general $\xi_0 \gg \mu^{-1}$)

$$c = c_0 \left(1 - \frac{1}{3} \frac{e^2}{m^2} \frac{k_F^2}{c_0^2} \frac{B^2}{\mu^3 L} \right). \quad (63)$$

The L dependence makes it clear that the effect calculated here is *not* responsible for the breakdown of superconductivity at higher than critical field strengths in bulk material.

The other extreme case, that of very thin films, $L \ll \xi_0$, is much more complicated. The main contribution to the q summation in Eqs. (51) or (52) comes from q values $> c/v_F$, and the London equation must be replaced by an equation similar to the Pippard equation. Instead of solving Pippard's equation explicitly with the approximate boundary condition, we proceed as follows: We consider a superconducting medium of infinite thickness and apply the surface current

$$\mathbf{j}^{\text{ext}}(\mathbf{r}) = \mathbf{J} \{ \delta(z - \frac{1}{2}L) - \delta(z + \frac{1}{2}L) \}, \quad (64)$$

where $\mathbf{J} = (0, J, 0)$. Alternatively, the external magnetic field ($|z| > L/2$) may be thought to be generated by this surface current, and the field inside the thickness L will be the same in the two pictures. The value of J will be fixed by the condition that the field generated by (64) has the value B at $z = \pm L/2$. The desired expression for $\mathbf{A}(\mathbf{q})$ can then be obtained from the Fourier transform of the Maxwell equation

$$\nabla^2 \mathbf{A}(\mathbf{r}) = -4\pi [\mathbf{j}^{\text{ext}}(\mathbf{r}) + \mathbf{j}^s(\mathbf{r})], \quad (65)$$

where $\mathbf{j}^s(\mathbf{r})$ is the supercurrent induced by the magnetic field. The Fourier transform of $\mathbf{j}^s(\mathbf{r})$ may be written as

$$\mathbf{j}^s(\mathbf{q}) = -\frac{1}{4\pi} K(q) \mathbf{A}(\mathbf{q}), \quad (66)$$

where the expression for the Kernel $K(q)$ in Pippard's case has been derived in an earlier study⁷ (based on the same approximation as the one used in Sec. 2 and Sec. 3).

$$K(q) = \frac{\pi \rho}{2} \frac{3\pi^2 c}{4\lambda^2 v_F} \frac{1}{|q|}, \quad v_F |q| > c. \quad (67)$$

Using the fact that in Wentzel's theory the penetration depth μ^{-1} and coherence length ξ_0 are given by

$$\mu^2 = \frac{1}{2} \rho / \lambda^2, \quad \xi_0 = v_F / \pi^2 c,$$

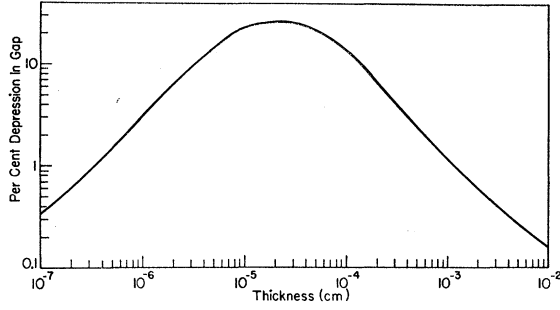


FIG. 1. Percentage depression in the gap width for superconducting aluminum plotted against the thickness of aluminum foil on a log-log scale.

the Pippard kernel becomes

$$K(q) = \frac{3\pi}{4} \frac{\mu^2}{\xi_0} \frac{1}{|q|}, \quad (68)$$

which is formally the same as the BCS expression for the kernel, and identical to it if we use experimental values for the penetration depth μ^{-1} and coherence distance ξ_0 .

Unfortunately the evaluation of J and the summation over \mathbf{q} in Eq. (52) can be performed only in a crude approximate way. Defining

$$q_0 = \left(\frac{3\pi}{4} \frac{\mu^2}{\xi_0} \right)^{\frac{1}{2}} \quad (69)$$

the final result can be stated for two different cases. For $1/q_0 < L < \xi_0$,

$$\frac{(c-c_0)}{c_0} \simeq -2.7 \frac{e^2 k_F B^2}{m c_0 q_0^3} \left(\frac{2}{q_0^3 L^3} \right)^{\frac{1}{2}} \chi(\nu L), \quad (70)$$

where

$$\nu = (q_0^3 L/2)^{\frac{1}{2}}, \quad (71)$$

and

$$\chi(\nu L) = [1 - e^{-\nu L}(1 + \nu L)] / (1 + e^{-\nu L})^2, \quad (72)$$

which tends to unity for $\nu L \gg 1$. For $L < 1/q_0$,

$$\frac{(c-c_0)}{c_0} \simeq -0.4 \frac{e^2 k_F B^2 L}{m c_0 q_0^2} \phi(q_0 L), \quad (73)$$

where

$$\phi(q_0 L) = (2/q_0^2 L^2) \{1 - e^{-q_0 L}(1 + q_0 L)\}, \quad (74)$$

which tends to unity for $q_0 L \ll 1$.

It should be noted that the London case could also be treated by this method using the appropriate value for the London kernel $K(q)$. In this case, however, the straightforward method we have adopted is much simpler.

Notice also that the magnetic field generated by the current (64) is periodic in $2L$ and not in L , as has been assumed in deriving Eq. (62). Care should therefore be taken in the Fourier expansions used for the two cases.

At this point we would like to emphasize that the

results deduced in this section are *independent* of the Bogoliubov parameter ρ defined by Eq. (56). The situation is therefore different from one that obtains in the calculation of penetration depths in Wentzel's theory where the result is different for different superconductors because of the dependence on ρ . The disappearance of ρ from our final result can be traced to its cancellation in deriving Eq. (52), and also because we have chosen to use experimental values for the kernels (64) and (65). The depression of the gap can be calculated for various superconductors, the difference in the result for different metals entering in two ways: firstly through the quantity kF/mc_0 , and secondly through the quantity μ in Eq. (63) and q_0 in Eqs. (70) and (73). Experimental values for these quantities have been used from the data quoted in Table IV of BCS.

7. POSSIBILITY OF OBSERVATION

The decrease in the gap width due to the magnetic field has been calculated from Eqs. (63), (70), and (73) for two superconductors, aluminum and tin, and the results have been plotted in Figs. 1 and 2. It is clear that the effect is quite sensitive to the thickness of the film. It is also evident that the optimum thickness for maximum effect is independent of the strength of the field and is of the order of $1/q_0$. For tin the gap depression for fields near the critical field is quite small ($\sim 8\%$), but for aluminum the result predicted ($\sim 25\%$) seems large enough to be observable. The sensitivity of the effect to the thickness of the film explains why the experiments of Pippard, of Spiewak, and of Ginsberg and Tinkham give a very small effect. Our result indicates that the superconducting specimens of Pippard and of Spiewak were too thick, and those of Ginsberg and Tinkham too thin compared with the optimum thickness $1/q_0$ ($\sim 10^{-5}$ cm).

Superconducting films of optimum thickness are neither thin films nor bulk superconductors, and so the experimental detection of the effect may present some difficulties. Infrared or microwave transmission experiments may not be feasible because of the opacity of such films. Experiments involving specific heat, thermal conductivity, or ultrasonic attenuation are not likely to give enough information. However, measurement of absorptivity of far infrared or microwave

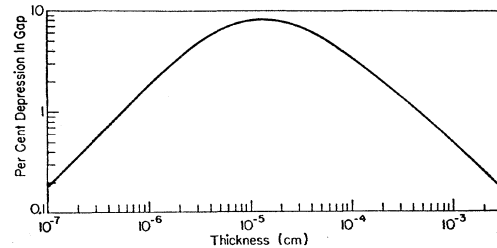


FIG. 2. Percentage depression in the gap width for superconducting tin plotted against the thickness of tin foil on a log-log scale.

radiation in such specimen appears feasible. A possible way of doing this is to look for the absorption edge in the reflected radiation as the frequency is increased to correspond to the gap width. Such an experiment has been recently described by Richards and Tinkham^{14,15} who used it to determine the gap energy in bulk superconductors. It is perhaps also possible to detect the effect by experiments involving nuclear spin relaxation.

We would like to emphasize at this point again that, in view of the approximate mathematical technique used, the calculations should at best be treated only as an order of magnitude result. The dependence of the effect on the thickness of the superconducting material is, however, quite reliable. The use of Wentzel's gauge invariant technique does not appear to be very crucial to the result. In fact, the final result is independent of the Bogoliubov parameter ρ which is characteristic of Wentzel's results.

The effect of decrease in gap width in presence of a magnetic field may have some interesting consequences; a brief speculation on the problem of Knight shift will be made here. It is known that the temperature dependence of the paramagnetic susceptibility of a

superconductor, calculated from the BCS theory,¹⁶ is at variance with the experimental results of Reif¹⁷ and Knight¹⁸; the theoretical curve falling off too rapidly with decreasing temperature. It is easy to see that if the decreased gap width due to magnetic field is taken into account the theoretical curve would shift in the *right direction* towards the experimental points. Of course, such a shift would depend on the size of the superconducting specimen. A quantitative calculation of the magnitude of this shift cannot be made without extending the calculations of this paper to finite temperatures—a generalization by no means trivial. Note that the above argument does not help in the problem of the vanishing of paramagnetic susceptibility at absolute zero; it is intended only for the temperature region $0 < T < T_c$.

ACKNOWLEDGMENTS

Thanks are due to Professor G. Wentzel for suggesting the problem and for his valuable advice at all stages of the work. One of us (V.S.M.) would like to gratefully acknowledge a fellowship from the Ministry of Education, Government of India.

APPENDIX 1

$F_1(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}')$

$$= \frac{1}{4} \left\{ \frac{[(\mathbf{k} + \mathbf{k}' + \mathbf{q}') \cdot \mathbf{A}(\mathbf{q})][(\mathbf{2k}' + \mathbf{q}') \cdot \mathbf{A}(\mathbf{q}')] - [(\mathbf{k} + \mathbf{k}' - \mathbf{q}') \cdot \mathbf{A}(\mathbf{q})][(\mathbf{2k} - \mathbf{q}') \cdot \mathbf{A}(\mathbf{q}')] }{\mathbf{q}' \cdot (\mathbf{2k}' + \mathbf{q}')} - \frac{[(\mathbf{k} + \mathbf{k}' - \mathbf{q}') \cdot \mathbf{A}(\mathbf{q})][(\mathbf{2k} - \mathbf{q}') \cdot \mathbf{A}(\mathbf{q}')] }{\mathbf{q}' \cdot (\mathbf{2k} - \mathbf{q}')} \right\} - \frac{1}{2} \mathbf{A}(\mathbf{q}) \cdot \mathbf{A}(\mathbf{q}'), \quad (\text{A-1})$$

$F_2(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p})$

$$= \frac{1}{2} \left\{ [(\mathbf{2k} - \mathbf{q}) \cdot \mathbf{A}(\mathbf{q})][\mathbf{A}(\mathbf{q}') \cdot \mathbf{X}(\mathbf{k}' + \mathbf{p} + \mathbf{q}', \mathbf{k}', \mathbf{q}', \mathbf{p})b_p + \mathbf{A}(\mathbf{q}') \cdot \mathbf{Y}(\mathbf{k}' + \mathbf{p} + \mathbf{q}', \mathbf{k}', \mathbf{q}', \mathbf{p})b_{-p}^*] \right. \\ \left. - [(\mathbf{2k}' + \mathbf{q}) \cdot \mathbf{A}(\mathbf{q})][\mathbf{A}(\mathbf{q}') \cdot \mathbf{X}(\mathbf{k}, \mathbf{k} - \mathbf{p} - \mathbf{q}', \mathbf{q}', \mathbf{p})b_p + \mathbf{A}(\mathbf{q}') \cdot \mathbf{Y}(\mathbf{k}, \mathbf{k} - \mathbf{p} - \mathbf{q}', \mathbf{q}', \mathbf{p})b_{-p}^*] \right\}, \quad (\text{A-2})$$

$F_3(\mathbf{k}, \mathbf{k}', \mathbf{q}, \mathbf{q}', \mathbf{p}, \mathbf{p}')$

$$= \frac{1}{2} \left\{ [(\mathbf{2k} - \mathbf{q}) \cdot \mathbf{A}(\mathbf{q})] \left[\mathbf{A}(\mathbf{q}') \cdot \mathbf{X}(\mathbf{k} - \mathbf{q} - \mathbf{p}', \mathbf{k}', \mathbf{q}', \mathbf{p}) \left(\frac{b_{p'} b_p}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') - \omega(\mathbf{p}') - \omega(\mathbf{p})} \right. \right. \right. \\ \left. \left. + \frac{b_{-p'}^* b_p}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') + \omega(\mathbf{p}') - \omega(\mathbf{p})} \right) - \mathbf{A}(\mathbf{q}') \cdot \mathbf{X}(\mathbf{k} - \mathbf{q}, \mathbf{k}' + \mathbf{p}', \mathbf{q}', \mathbf{p}) \left(\frac{b_{p'} b_p}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') - \omega(\mathbf{p}') - \omega(\mathbf{p})} \right. \right. \\ \left. \left. + \frac{b_{-p'}^* b_p}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') + \omega(\mathbf{p}') - \omega(\mathbf{p})} \right) + \mathbf{A}(\mathbf{q}') \cdot \mathbf{Y}(\mathbf{k} - \mathbf{q} - \mathbf{p}', \mathbf{k}', \mathbf{q}', \mathbf{p}) \left(\frac{b_{-p'}^* b_{p'}}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') - \omega(\mathbf{p}') + \omega(\mathbf{p})} \right. \right. \\ \left. \left. + \frac{b_{-p'}^* b_{-p}^*}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') + \omega(\mathbf{p}') + \omega(\mathbf{p})} \right) - \mathbf{A}(\mathbf{q}') \cdot \mathbf{Y}(\mathbf{k} - \mathbf{q}, \mathbf{k}' + \mathbf{p}', \mathbf{q}', \mathbf{p}) \left(\frac{b_{-p'}^* b_{p'}}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') - \omega(\mathbf{p}') + \omega(\mathbf{p})} \right. \right. \\ \left. \left. + \frac{b_{-p'}^* b_{-p}^*}{E(\mathbf{k} - \mathbf{q}) - E(\mathbf{k}') + \omega(\mathbf{p}') + \omega(\mathbf{p})} \right) \right] - [(\mathbf{2k}' + \mathbf{q}) \cdot \mathbf{A}(\mathbf{q})] \right\}$$

¹⁴ P. L. Richards and M. Tinkham, Phys. Rev. Letters **1**, 318 (1958).

¹⁵ P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

¹⁶ K. Yosida, Phys. Rev. **110**, 769 (1958).

¹⁷ F. Reif, Phys. Rev. **106**, 208 (1957).

¹⁸ G. M. Androes and W. D. Knight, Phys. Rev. Letters **2**, 386 (1959).

$$\begin{aligned}
& \times \left[A(q') \cdot X(k-p', k'+q, q', p) \left(\frac{b_{p'} b_p}{E(k) - E(k'+q) - \omega(p') - \omega(p)} + \frac{b_{-p'}^* b_p}{E(k) - E(k'+q) + \omega(p') - \omega(p)} \right) \right. \\
& - A(q') \cdot X(k, k'+p'+q, q', p) \left(\frac{b_p b_{p'}}{E(k) - E(k'+q) - \omega(p') - \omega(p)} + \frac{b_{-p'}^* b_p}{E(k) - E(k'+q) + \omega(p') - \omega(p)} \right) \\
& + A(q') \cdot Y(k-p', k'+q, q', p) \left(\frac{b_{-p'}^* b_{p'}}{E(k) - E(k'+q) - \omega(p') + \omega(p)} + \frac{b_{-p'}^* b_{-p}^*}{E(k) - E(k'+q) + \omega(p') + \omega(p)} \right) \\
& \left. - A(q') \cdot Y(k, k'+p'+q, q', p) \left(\frac{b_{-p'}^* b_{p'}}{E(k) - E(k'+q) - \omega(p') + \omega(p)} + \frac{b_{-p'}^* b_{-p}^*}{E(k) - E(k'+q) + \omega(p') + \omega(p)} \right) \right] \Bigg\}, \quad (A-3)
\end{aligned}$$

$$F_4(k, k', k_1, k_1', q, q')$$

$$\begin{aligned}
& = \frac{1}{2} \left\{ \frac{-(2k_1 - q) \cdot A(q)}{E(k) - E(k') + E(k_1 - q) - E(k_1')} [\omega(k_1' - k_1 + q) A(q') \cdot X(k, k', q', p) - \omega(k - k') A(q') \cdot Y(k_1 - q, k_1', q', p)] \right. \\
& + \frac{(2k_1' + q) \cdot A(q)}{E(k) - E(k') + E(k_1) - E(k_1' + q)} [\omega(k_1' - k_1 + q) A(q') \cdot X(k, k', q', p) - \omega(k - k') A(q') \cdot Y(k_1, k_1' + q, q', p)] \\
& - \frac{(2k - q) \cdot A(q)}{E(k - q) - E(k') + E(k_1) - E(k_1')} [\omega(k_1' - k_1) A(q') \cdot X(k - q, k', q', p) - \omega(k - q - k') A(q') \cdot Y(k_1, k_1', q', p)] \\
& \left. + \frac{(2k' + q) \cdot A(q)}{E(k) - E(k' + q) + E(k_1) - E(k_1')} [\omega(k_1' - k_1) A(q') \cdot X(k, k' + q, q', p) - \omega(k - q - k') A(q') \cdot Y(k_1, k_1', q', p)] \right\}, \quad (A-4)
\end{aligned}$$

$$X(k, k', q, p) = \left(\frac{(k' + q/2)}{q \cdot (k' + q/2)} - \frac{(k - q/2)}{q \cdot (k - q/2)} \right) \frac{1}{E(k') - E(k) + \omega(p)}, \quad (A-5)$$

$$Y(k, k', q, p) = \left(\frac{(k' + q/2)}{q \cdot (k' + q/2)} - \frac{(k - q/2)}{q \cdot (k - q/2)} \right) \frac{1}{E(k') - E(k) - \omega(p)}. \quad (A-6)$$

Note that these functions have some symmetry properties that have been used in the text of the paper:

$$X(-k', -k, q, p) = Y(k, k', q, p), \quad (A-7)$$

$$F_1(k, k', q, q') = F_1(-k', -k, q, q'), \quad (A-8)$$

$$F_4(k, k', k_1, k_1', q, q') = F_4(-k_1', -k_1, -k', -k, q, q'), \quad (A-9)$$

$$F_4(k, k, k_1, k_1, q, q') = F_4(k_1, k_1, k, k, q, q'). \quad (A-10)$$

APPENDIX 2

Using Eq. (37) and summing over p , the integral (40) can be written as

$$I = \frac{1}{2} \frac{g^2}{(2\pi)^3} \int d\mathbf{k}' \frac{\tilde{\omega}}{\epsilon_1(\mathbf{k}) + \epsilon_1(\mathbf{k}') + \omega_1(\mathbf{k} - \mathbf{k}')} \frac{c}{[c^2 + \xi^2(\mathbf{k}')]^{\frac{1}{2}}}, \quad (A-11)$$

where we have taken $c(\mathbf{k}')$ to be independent of \mathbf{k}' as an approximation, and have replaced $\omega(\mathbf{k} - \mathbf{k}')$ by a mean phonon energy $\tilde{\omega}$. Substituting for ϵ_1 , ω_1 , and ξ from Eqs. (21), (23) and (33), we obtain with the help of Eqs. (22) and (35), the following result, consistent with our approximations:

$$I = \frac{1}{2} \frac{g^2}{(2\pi)^3} \int d\mathbf{k}' \frac{\tilde{\omega}}{(\eta - \Gamma)^2 / [c^2 + (\eta - \Gamma)^2]^{\frac{1}{2}} + (\eta' - \Gamma')^2 / [c^2 + (\eta' - \Gamma')^2]^{\frac{1}{2}} + \tilde{\omega}} \times \frac{c}{[c^2 + (\eta' - \Gamma')^2]^{\frac{1}{2}}}, \quad (A-12)$$

where

$$\eta \equiv \eta(\mathbf{k}) = \tilde{E}(\mathbf{k}) - \lambda, \quad (\text{A-13})$$

$$\eta' \equiv \eta(\mathbf{k}'),$$

$$\Gamma \equiv \Gamma(\mathbf{k}) = -\frac{e^2}{m} \int d\mathbf{q} d\mathbf{q}' \delta(\mathbf{q} + \mathbf{q}') F_1(\mathbf{k}, \mathbf{k}, \mathbf{q}, \mathbf{q}'), \quad (\text{A-14})$$

and

$$\Gamma' \equiv \Gamma(\mathbf{k}'). \quad (\text{A-15})$$

Expanding the integrand in powers of e^2 , we get

$$I = \frac{g^2 m}{2(2\pi)^3} \int k' d\eta' d\Omega' \frac{\tilde{\omega}}{[\eta^2(c^2 + \eta^2)^{-\frac{1}{2}} + \eta'^2(c^2 + \eta'^2)^{-\frac{1}{2}} + \tilde{\omega}]} \frac{c}{(c^2 + \eta'^2)^{\frac{1}{2}}} \times \left\{ 1 - \frac{1}{[\eta^2(c^2 + \eta^2)^{-\frac{1}{2}} + \eta'^2(c^2 + \eta'^2)^{-\frac{1}{2}} + \tilde{\omega}]} \right. \\ \left. \times \left[\frac{\Gamma \eta^3}{(c^2 + \eta^2)^{\frac{3}{2}}} - \frac{2\Gamma \eta}{(c^2 + \eta^2)^{\frac{1}{2}}} + \frac{\Gamma' \eta'^3}{(c^2 + \eta'^2)^{\frac{3}{2}}} - \frac{2\Gamma' \eta'}{(c^2 + \eta'^2)^{\frac{1}{2}}} \right] - \frac{\Gamma' \eta'}{(c^2 + \eta'^2)} \right\}. \quad (\text{A-16})$$

Note that the maximum contribution to the integral comes when $\eta' \sim 0$, i.e., $k' \sim k_0$. We, therefore, replace k' in the integrand by k_0 , so that Γ' is replaced by Γ_0 . Now we are interested in $k \sim k_F$, and since $\eta_F \sim 0(e^2)$, the terms involving $\Gamma \eta$ are negligible. Furthermore the integrand is small for large η' , and negligible for $|\eta'| > \tilde{\omega}$. The limits of integration for η' may thus be taken from $-\tilde{\omega}$ to $+\tilde{\omega}$. It follows that the terms proportional to Γ_0 are zero. Finally the integral reduces to

$$I = \frac{g^2 m}{(2\pi)^2} k_0 \int_{-\tilde{\omega}}^{+\tilde{\omega}} d\eta' \frac{c}{(c^2 + \eta'^2)^{\frac{1}{2}}}, \quad (\text{A-17})$$

which gives Eq. (41), i.e.,

$$I = \frac{2g^2 m k_0}{(2\pi)^2} c \ln(2\tilde{\omega}/c). \quad (\text{A-18})$$

APPENDIX 3

Here we evaluate the integral in the expression (45):

$$J = \int_{-1}^{+1} \frac{(1-u^2)du}{(u+\gamma/2)} I(u, q), \quad (\text{A-19})$$

where

$$I(u, q) = \int_{-\tilde{\omega}}^{+\tilde{\omega}} \frac{d\eta'}{(c^2 + \eta'^2)^{\frac{1}{2}}} \frac{1}{\eta' + \alpha'} \\ = \frac{1}{(c^2 + \alpha'^2)^{\frac{1}{2}}} \ln \left(\frac{c^2 - \alpha' \omega - (c^2 + \alpha'^2)^{\frac{1}{2}} (c^2 + \omega^2)^{\frac{1}{2}} \omega - \alpha'}{c^2 + \alpha' \omega - (c^2 + \alpha'^2)^{\frac{1}{2}} (c^2 + \omega^2)^{\frac{1}{2}} \omega + \alpha'} \right).$$

Case (a). For $v_F q \ll c$, $\beta \gg 1$, we have $\alpha' \ll c$ and $\tilde{\omega}$, and $I(u, q)$ reduces to the simple form

$$I(u, q) = (2/c\beta)(u + \gamma/2). \quad (\text{A-21})$$

The integral J in this case is therefore simply

$$J = \frac{4}{3} (k_F q / mc^2). \quad (\text{A-22})$$

Case (b). For $v_F q \gg c$, $\beta \ll 1$, note that in the subsequent q integration, the integrand decreases as q increases. For simplicity we shall consider $v_F q < \{cE(k_F)\}^{\frac{1}{2}}$, which implies $\beta > \gamma/2$. The integral

$$J = \int_0^1 (1-u^2) du \left\{ \frac{I(u, q)}{(u + \gamma/2)} - \frac{I(-u, q)}{(u - \gamma/2)} \right\} \quad (\text{A-23})$$

can then be estimated by splitting the range of u integration into three domains $0 \leq u \leq \gamma/2$, $\gamma/2 \leq u \leq \beta$, $\beta \leq u \leq 1$. If we call the corresponding integrals J_1 , J_2 , and J_3 , a straightforward integration yields

$$J_1 \simeq 2\gamma/c\beta, \\ J_2 \simeq 4/c, \\ J_3 \simeq 6.8/c.$$

Consistent with our approximation $J_1 < J_2$ and J_3 , so that finally

$$J \simeq 10.8/c. \quad (\text{A-24})$$

Using (45) with Eqs. (A-22) and (A-24), result (51) follows immediately.