in levels with smaller ω_e values and hence larger r_e values than those of the ground state. This shows that collisions with the foreign gas the make molecules in the higher excited states go over into lower excited electronic states in the energy range 39131 to 47150 cm^{-1}, with larger r_e values and smaller ω_e values, in the manner discussed by Wieland.[6]

The author wishes to express his thanks to Dr. R. S. Mulliken and Dr. G. Herzberg for their kind interest in the work.

PHYSICAL REVIEW VOLUME 81, NUMBER 5 MARCH 1, 1951

Relation between Lattice Vibration and London Theories of Superconductivity

J. BARDEEN
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received November 2, 1950)

A gas of noninteracting electrons of small effective mass, m_{eff}, has a large diamagnetic susceptibility. It is shown that the London phenomenological equations of superconductivity follow as a limiting case when m_{eff} is so small that the Landau-Peierls theory yields a susceptibility $<-1/4\pi$. Justification is given for the use of an effective mass, $m_s \sim 10^{-4}\, m$, for superconducting electrons in the lattice-vibration theory of superconductivity. This value is sufficiently small to show that the theory gives the London equations and, as a consequence, the typical superconducting properties. The concentration of superconducting electrons, n_s, is smaller than the total electron concentration, n, by about the same ratio as the effective masses, so that $m_s/n_s \sim m/n$, and thus the penetration depth is of the same order as that given by the usual London expression.

I. INTRODUCTION

A THEORY of superconductivity based on interactions between electrons and lattice vibrations has been discussed in two previous communications.[1,2] The second of these (to be denoted by the letters WF), deals with wave functions for superconducting electrons. Fröhlich[3] has independently developed a theory along similar lines. These earlier papers have been concerned primarily with the energy of the lowest state of a superconductor and have not discussed in any detail how the electrodynamic characteristics of the superconducting state—perfect diamagnetism and infinite conductivity—follow from the model. We shall show here that the theory leads to the London phenomenological equations[4] in the manner indicated in our earlier papers.

The present theory is similar in many respects to one suggested some years ago by the author.[5] In the earlier theory it was proposed that in the superconducting state there is a small distortion of the lattice which produces Brillouin zone boundaries with small energy gaps, $\sim \kappa T_c$ (T_c = transition temperature) at the Fermi surface. There would be a resultant decrease in energy of electrons in states on the low energy side of the gap. Associated with the small energy gap is a small effective mass ratio, $\sim \kappa T_c/E_F$, for electrons with energies near the Fermi surface, E_F. It was shown that a sufficiently large diamagnetism for superconductivity will occur if there is a sufficient number of electrons of small effective mass. The difficulty with the theory as formerly proposed is that it appears that the energy required to distort the lattice and so to produce the zone boundaries is larger than the energy gained by the electrons.

In the present theory, zero-point vibrations replace the small permanent distortion of the lattice. The effective mass of the superconducting electrons is small as in the earlier theory, and we have suggested[1,2] that the explanation of the superconducting properties in terms of a large diamagnetic effect of the electrons is similar.

It has been recognized for some years that the Meissner effect ($\mathbf{B}=0$), is a more basic property of the superconducting state than infinite conductivity ($\mathbf{E}=0$), although, from a purely macroscopic point of view, neither one is a consequence of the other. Both follow from the London equations which can be derived most readily from a consideration of the magnetic properties.

From a formal point of view, a perfect diamagnetism can be described by a diamagnetic susceptibility equal to $-1/4\pi$. Landau[6] has shown that, as a consequence of quantum theory, a gas of free noninteracting electrons obeying Fermi-Dirac statistics has a diamagnetic susceptibility:

$$\chi_0 = -(n/2E_F)(e\hbar/2mc)^2 = -n\mu^2/2E_F, \qquad (1.1)$$

Here n is the number of electrons/cm^3, E_F is the

[1] J. Bardeen, Phys. Rev. **79**, 167 (1950).
[2] J. Bardeen, Phys. Rev. **80**, 567 (1950) (referred in the text as WF).
[3] H. Fröhlich, Phys. Rev. **79**, 845 (1950).
[4] F. and H. London, Physica **2**, 341 (1935).
[5] J. Bardeen, Phys. Rev. **59**, 928 (A) (1941). This work, done while the author was at the University of Minnesota, was interrupted by the war and was never published in full.
[6] L. Landau, Z. Physik **64**, 629 (1930).

maximum energy of the Fermi distribution and μ is the Bohr magneton. Landau's theory was later extended by Peierls[7] to apply to electrons with Bloch-type wave functions appropriate to motion in a periodic field of a crystal lattice. The effect of the periodic field is to introduce an appropriate effective mass instead of the ordinary mass in (1.1). If the effective mass is made sufficiently small, Eq. (1.1) will yield values for $\chi_0 < -1/4\pi$. If values of n and E_F characteristic of ordinary metals are inserted in (1), the expression gives values of χ_0 of the order of 10^{-7} to 10^{-6}, in agreement with observed susceptibilities. To get a value smaller than $-1/4\pi$ would require an effective mass of 10^{-3} m or smaller.

Wave functions for superconducting electrons (see WF) are linear combinations of Bloch states which lie within a small energy $\Delta \sim \kappa T_c$ of the Fermi surface. It has been pointed out that these wave functions correspond to a small effective mass, of the order of $(\Delta/E_F)m$. The concentration of superconducting electrons, n_s, is a small fraction, of the order of (Δ/E_F), of the total concentration, n, but the effective Fermi energy of the superconducting electrons, E_s, is of the order of Δ so that

$$n_s/E_s \sim n/E_F. \tag{1.2}$$

The condition for a perfect diamagnetism is then

$$(n_s\mu^2/2E_s)(m/m_{\text{eff}})^2 \sim (n\mu^2/2E_F)(E_F/\Delta)^2 > 1/4\pi. \tag{1.3}$$

In the derivation of (1.1) it is assumed that the magnetic field is uniform throughout the specimen. Actually, the magnetic field in a perfect diamagnetic or superconductor is confined to a thin surface layer. It is necessary to reinvestigate the problem with this in mind; we shall show that one is then led to the London phenomenlogical theory. In other words, we shall show that the London theory is the limiting case of a large diamagnetism of the Landau-Peierls type.

In the ordinary theory of diamagnetism, the electrons are in quantized states which correspond to the classical circular orbits of an electron in a magnetic field. Circular orbits in the interior of the specimen give a large diamagnetic moment which is cancelled to a large extent by electrons in boundary orbits whose moment is in the opposite direction.[8] We shall show that when (1.3) is fulfilled, the magnetic field and associated currents are confined to the penetration depth of the London theory and there are no quantum states which correspond to circular or to boundary orbits. The wave functions of the electrons are only slightly modified by the magnetic field.

The connection with the phenomenological theory follows the general approach anticipated by London.[9] London has pointed out that it is convenient to choose the gauge in the vector potential, $\mathbf{A}$, in such a way that the normal component vanishes at a free surface and such that the divergence of $\mathbf{A}$ vanishes everywhere:

$$\text{div}\mathbf{A}=0; \quad \mathbf{A}_\perp = 0 \text{ on the surface.} \tag{1.4}$$

These conditions determine $\mathbf{A}$ uniquely in a simply connected body. In a multiply connected body, such as a ring, an additional quantity, related to the flux through the ring, must be specified. This additional freedom permits the description of persistent currents by the theory. In a body of macroscopic size, $\mathbf{A}$ is confined to a thin surface layer and is parallel to the surface.[10]

In quantum theory, the average velocity of an electron of charge $(-e)$ is given by the average value of

$$\mathbf{v} = [(\mathbf{p} + e\mathbf{A}/c)/m]_{\text{Av}} \tag{1.5}$$

over the wave function. If it is assumed that the wave functions are not altered by the field (with the above choice of gauge), the average value of $\mathbf{p}$ will be zero and the current density at a position $\mathbf{R}$ will be given by[9]

$$\mathbf{j}(\mathbf{R}) = -n(\mathbf{R})e\mathbf{v}(\mathbf{R}) = -(e^2/mc)n(\mathbf{R})\mathbf{A}(\mathbf{R}), \tag{1.6}$$

where $n(\mathbf{R})$ is the concentration of electrons at $\mathbf{R}$. The curl of (1.5) gives the London phenomenological equation:

$$\text{curl}\Lambda\mathbf{j} = -\mathbf{B}/c, \tag{1.7}$$

where the parameter Λ of the theory is evaluated to be:

$$\Lambda = m/ne^2. \tag{1.8}$$

The penetration depth, d, of the London theory is

$$d = (mc^2/4\pi e^2 n)^{\frac{1}{2}}. \tag{1.9}$$

As London points out,[9] the wave functions of the electrons will be modified by the field so that (1.6) is an over-simplification. He states that it would be "sufficient to show that a state would be established in which the eigenfunctions of a fraction of the electrons are prevented from coiling when the system is brought into a magnetic field, but stay essentially as they are without magnetic field, as if frozen." We may interpret this statement as being equivalent to the one made above: that in a superconductor "there are no quantum states which correspond to the classical circular or to the boundary orbits."

We shall show in (1.6) and (1.8), that the quantum states actually are modified by the field in such a manner as to introduce an effective mass instead of the ordinary electron mass. However, since m_{eff}/n_s is of the order of m/n, the values of Λ and of the penetration depth are of the same order as given by (1.8) and (1.9). It is well known that observed penetration depths are in general agreement with (1.9) as to order of magnitude.

[7] R. Peierls, Z. Physik **80**, 763 (1933).

[8] For an excellent discussion of this problem, see J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, England, 1932).

[9] F. London, Proc. Roy. Soc. (London) **A152**, 24 (1935); Phys. Rev. **74**, 562 (1948).

[10] For a justification for this choice of gauge, see J. Bardeen, Phys. Rev. **81**, 469 (1951).

II. RELATION BETWEEN THE LANDAU-PEIERLS AND THE LONDON THEORIES

We are concerned in this section with the relation between the Landau-Peierls theory[6,7] of diamagnetism and the London theory for a model in which we make the *ad hoc* assumption that the electrons have a small effective mass. The justification for the application to superconducting electrons will be given in following sections. We shall here assume simply that the electrons have an effective mass which is smaller than normal and work out the consequences.

In the Bloch theory, the effective mass is a tensor rather than a scalar. If the energy of an electron with wave vector $\mathbf{k}$ is $\epsilon(\mathbf{k})$, the effective mass is defined by[11]

$$1/m_{\text{eff}}=\hbar^{-2}\,\text{grad}_k\,\text{grad}_k\,\epsilon(\mathbf{k}). \tag{2.1}$$

For example, for motion in the x-direction,

$$(1/m_{\text{eff}})_{xx}=\hbar^{-2}\partial^2\epsilon(\mathbf{k})/\partial k_x{}^2. \tag{2.2}$$

For simplicity, we shall take a model for which

$$\epsilon(\mathbf{k})=(\hbar^2/2m)(\alpha_1 k_x{}^2+\alpha_2 k_y{}^2+\alpha_3 k_3{}^2). \tag{2.3}$$

The coefficients, α_i, are the effective mass ratios:

$$\alpha_1=m/(m_{\text{eff}})_{xx},\ \text{etc.} \tag{2.4}$$

Peierls' expression for the diamagnetic susceptibility for electrons with energies given by (2.3) is

$$\chi=-\tfrac{1}{2}n_s\mu^2\alpha_1\alpha_2/E_s, \tag{2.4'}$$

where n_s is the number of electrons per unit volume for which (2.3) holds and E_s is the maximum value of $\epsilon(\mathbf{k})$ in the Fermi distribution. It is assumed that the magnetic field is in the Z-direction.

If α is large, a Brillouin zone with energies given by (2.3) can accommodate only a small number of electrons; if the states are filled to a maximum energy E_s:

$$n_{\text{zone}}=(1/3\pi^2)(3mE_s/\hbar^2)^{\frac{3}{2}}(\alpha_1\alpha_2\alpha_3)^{-\frac{1}{2}}. \tag{2.5}$$

We shall not restrict n_s to the small value given by (2.5), but shall suppose that there is a sufficient number of zones to accommodate any desired number, n_s, of electrons.

The condition that $\chi<-1/4\pi$, corresponding to a perfect diamagnetic, is:

$$n_s\mu^2\alpha_1\alpha_2/E_s>1/2\pi. \tag{2.6}$$

We shall show that (2.6) is equivalent to the condition for the validity of the London theory, and that the wave functions of the electrons are not modified very much by the magnetic field. When (2.6) applies, it is no longer permissible to assume that the magnetic field is uniform in the specimen. The current density and magnetic field should be determined by a self-consistent field procedure. The current flow depends on the magnetic field which in turn is determined in part by the current flow. We first calculate the current under the assumption that the wave functions are not altered very much by the field. The penetration of the field into the specimen then follows from the London theory. We shall then show that if (2.6) is satisfied, the wave functions are not significantly altered so that the initial assumption is justified.

We consider a metal whose surface is the plane $x=0$. The magnetic field, $\mathbf{B}$, has only a Z-component and decreases from a value B_0 at $x=0$ to zero in the interior in the case of a perfect diamagnetic. It is most convenient to choose the vector potential $\mathbf{A}$ in such a way that

$$A_x=A_z=0, \tag{2.7}$$

while $A_y(x)$ is independent of y and z. Then B, which depends only on x, is given by:

$$B_x=B_y=0,\quad B_z(x)=\partial A_y/\partial x. \tag{2.8}$$

The equation which determines $\mathbf{A}$ from the current density, $\mathbf{j}$, is:

$$d^2A_y/dx^2=-4\pi j_y/c. \tag{2.9}$$

We next consider how j_y depends on $\mathbf{A}$. The wave function, ψ_k, is of the form:

$$\psi_k=\exp[i(k_y y+k_z z)]\cdot f(x). \tag{2.10}$$

As the effective mass for motion in the y-direction is m/α_2, the y-component of current density for an electron in the state ψ_k is

$$-(\alpha_2 e/m)[\hbar k_y+(e/c)A_y]\psi_k{}^*\psi_k. \tag{2.11}$$

If the wave function for the state $+k_y$ does not differ appreciably from that for $-k_y$, the sum over k_y vanishes and the total current density is

$$j_y=-(\alpha_2 e^2/mc)n_s A_y, \tag{2.12}$$

where

$$n_s=\Sigma\psi_k{}^*\psi_k \tag{2.13}$$

is the concentration of electrons, which we shall assume to be constant.

When (2.12) is inserted into (2.9), there results an equation of the form:

$$\partial^2A_y/\partial x^2=A_y/d^2, \tag{2.14}$$

where d is the penetration depth of the London theory:

$$d=(mc^2/4\pi\alpha_2 e^2 n_s)^{\frac{1}{2}}. \tag{2.15}$$

The appropriate solution of (2.14) is:

$$A_y=-B_0 d e^{-x/d}. \tag{2.16}$$

Under what conditions is it valid to assume, as we have done above, that the wave function for the state $+k_y$ is nearly the same as that for $-k_y$? The wave equation for the electron is

$$(1/2m)[\alpha_1 p_x{}^2+\alpha_2(p_y+eA_y/c)^2+\alpha_3 p_z{}^2]\varphi=E\varphi. \tag{2.17}$$

We may set $p_y=\hbar k_y$ and $p_z=\hbar k_z$, so that (2.17) reduces

[11] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 316.

to an equation in x alone. The difference between the second term of (2.17) and $\alpha_2 p_y^2/2m$ is an effective potential, V_e, which is large only near the surface:

$$V_e=(\alpha_2/2m)[(p_y+eA_y/c)^2-p_y^2]. \quad (2.18)$$

The potential is negative (attractive) if p_y is opposite in sign to eA_y/c and is a minimum at a position $x=x_0$ such that

$$p_y+eA_y(x_0)/c=0. \quad (2.19)$$

In the usual theory of diamagnetism, the state corresponding to this value of p_y is localized near $x=x_0$. States localized very close to the surface correspond to boundary orbits whose moments nearly cancel those of states localized in the interior.[12] We shall show that if (2.6) is satisfied, there are no localized quantum states either at the boundary or in the interior, and that the wave function does not depend very much on the sign of k_y.

The maximum negative potential at the surface occurs when p_y has its maximum value given by

$$\alpha_2 p_y^2/2m=E_s. \quad (2.20)$$

The value of V_e is then $-E_s$ at $x=0$, and the negative potential extends over a distance of the order of the penetration depth, d. This potential will not affect the wave function very much, and there will be no stationary state if

$$\int p_x dx<\hbar, \quad (2.21)$$

where p_x is computed classically for an energy $E=E_s$. If (2.21) is satisfied, the change in phase of the wave function in the W.K.B. approximation is less than one radian. The value of p_x is 0 for $x>\sim d$ and is

$$p_x\sim(2mE_s/\alpha_1)^{\frac{1}{2}} \text{ for } x<\sim d. \quad (2.22)$$

Condition (2.21) is then approximately

$$(2mE_s/\alpha_1)^{\frac{1}{2}}d<\hbar,$$

or

$$\alpha_1\hbar^2/2mE_sd^2>1. \quad (2.23)$$

With use of (2.15) for d, this relation becomes

$$n_s\mu^2\alpha_1\alpha_2/E_s>1/8\pi, \quad (2.24)$$

which, except for a numerical factor, is the same as (2.6).

We have thus shown that when the Landau-Peierls theory indicates a perfect diamagnetism, there are no bound states and the wave functions of the electrons are not altered very much by the field near the surface. The conditions for the London theory are satisfied.

III. EFFECTIVE MASS OF SUPERCONDUCTING ELECTRONS

We have shown in WF that the wave functions of the superconducting electrons are linear combinations of Bloch states, ψ_k, which have energies in the range between $E_F-\epsilon_1$ and $E_F+\epsilon_1$ where E_F is the energy of the Fermi surface of the normal metal at $T=0°$K. In WF they were taken to be of the form

$$\Psi_k=c_k\psi_k+\Sigma_{k'}c_{k'}[q_{kk'}/(q_{kk'})_{rms}]\psi_{k'}. \quad (3.1)$$

Here, $q_{kk'}$ is the amplitude of the normal mode whose wave vector connects the states $\mathbf{k}$ and $\mathbf{k}'$. The states ψ_k have energies in the range between E_F and $E_F+\epsilon_1$, and the states $\psi_{k'}$ have energies between $E_F-\epsilon_1$ and E_F. There is one superconducting state for each ψ_k. The value of ϵ_1 is chosen to make the energy a minimum when interactions between electrons and normal modes are taken into account and is presumably of the order of kT_c.

The equations which determine the coefficients c_k and $c_{k'}$ are Eqs. (3.20) of WF:

$$c_k\epsilon_k+\Sigma_{k'}c_{k'}M_{k'k}=E_kc_k, \quad (3.2a)$$

$$c_{k'}(\epsilon_{k'}+\hbar\omega_{kk'})+c_kM_{kk'}=E_kc_{k'}, \quad (3.2b)$$

in which ϵ_k and $\epsilon_{k'}$ are the energies of the Bloch states, E_k is the energy of the superconducting state, Ψ_k, and $M_{kk'}$ is the matrix element and $\omega_{kk'}$ the angular frequency for the normal mode kk'. Equation (3.2b) can be solved for $c_{k'}$:

$$c_{k'}=M_{kk'}c_k/(E_k-\epsilon_{k'}-\hbar\omega_{kk'}). \quad (3.3)$$

When (3.3) is inserted into (3.2a), there results an equation for E_k:

$$\Sigma\frac{|M_{kk'}|^2}{E_k-\epsilon_{k'}-\hbar\omega_{kk'}}=E_k-\epsilon_k. \quad (3.4)$$

In order to get an approximate solution of (3.4) we shall replace $\epsilon_{k'}+\hbar\omega_{kk'}$ by an average value, ϵ'. Equation (3.4) then reduces to

$$(E_k-\epsilon_k)(E_k-\epsilon')=\Delta^2, \quad (3.5)$$

where

$$\Delta^2=\Sigma_{k'}(M_{kk'})^2. \quad (3.6)$$

The solution of (3.5) is familiar from the theory of nearly free electrons in metals:

$$E_k=\tfrac{1}{2}(\epsilon_k+\epsilon')\pm\tfrac{1}{2}[(\epsilon_k-\epsilon')^2+4\Delta^2]^{\frac{1}{2}}. \quad (3.7)$$

The low energy state, which is the one of interest, is that with the negative sign. For $|\epsilon_k-\epsilon'|<2\Delta$, the approximate solution of (3.7) is[13]

$$E_k=\tfrac{1}{2}(\epsilon_k+\epsilon')-\Delta-[(\epsilon_k-\epsilon')^2/8\Delta]. \quad (3.8)$$

[12] E. Teller, Z. Physik **67**, 311 (1931).

[13] *Note added in proof.*—It has been pointed out to the author by J. H. Van Vleck (private communication) that a lower energy is obtained if the ψ_k are taken in the range between $E_F-\epsilon_1$ and E_F and the $\psi_{k'}$ in the range between E_F and $E_F+\epsilon_1$. The difference is small when $|\epsilon_k-\epsilon'|<2\Delta$ so that (3.8) may be used. This condition is equivalent to the criterion for superconductivity given by Eq. (4.17) of WF and is required to get a small effective mass for the superconducting electrons. The approximation $(E_k)_{AV}=(1/2)(\epsilon_k+\epsilon')_{AV}-\Delta$ used in WF is independent of whether the states ψ_k are taken in the high energy or the low energy range.

We shall see in Sec. IV that the effective mass should be computed from energy changes which involve shifts of $\mathbf{k}$ and all the $\mathbf{k}'$ by the same small vector displacement $\mathbf{K}$ in $\mathbf{k}$-space. The normal modes which connect $\mathbf{k}$ and $\mathbf{k}'$ are then unchanged, since they depend only on the vector displacement between $\mathbf{k}$ and $\mathbf{k}'$. We also want to consider virtual shifts in which it is assumed that the matrix elements $M_{kk'}$ are independent of $\mathbf{K}$. The effective mass tensor is defined by

$$[(m_{\text{eff}})^{-1}]_{ij}=\hbar^{-2}(\partial^2 E_k/\partial K_i \partial K_j)_{K=0}. \quad (3.9)$$

In differentiating (3.8), with respect to K to get the effective mass, we therefore assume that Δ and $(\hbar\omega_{kk'})_{\text{Av}}$ are independent of $\mathbf{K}$. The largest contribution comes from differentiation of the third term of (3.8);

$$[(m_{\text{eff}})^{-1}]_{ij}\sim\frac{\hbar^{-2}}{4\Delta}\left[\frac{\partial\epsilon_k}{\partial K_i}-\left(\frac{\partial\epsilon_{k'}}{\partial K_i}\right)_{\text{Av}}\right]\left[\frac{\partial\epsilon_k}{\partial K_j}-\left(\frac{\partial\epsilon_{k'}}{\partial K_j}\right)_{\text{Av}}\right]. \quad (3.10)$$

We can use the free electron approximation,

$$\epsilon_k=\hbar^2k^2/2m, \quad (3.11)$$

to estimate the order of magnitude of (3.10). Since the angles between $\mathbf{k}$ and $\mathbf{k}'$ are in general large, each of the factors is of the order of

$$\left[\frac{\partial\epsilon_k}{\partial K}-\left(\frac{\partial\epsilon_{k'}}{\partial K}\right)_{\text{Av}}\right]\sim\frac{\partial\epsilon_k}{\partial K}\sim\frac{\hbar^2k_0}{m}, \quad (3.12)$$

where k_0 is the magnitude of $\mathbf{k}$ on the Fermi surface. Thus we have

$$(m_{\text{eff}})^{-1}\sim(\hbar^2/4\Delta)(\hbar^2k_0/m)^2\sim m^{-1}(E_F/2\Delta). \quad (3.13)$$

As $\Delta\sim kT_c\sim10^{-4}$ ev and E_F is several ev, $(m_{\text{eff}})^{-1}$ is of the order of $10^{-4}\,m$. A similar estimate was obtained by a slightly different procedure in WF.

IV. CURRENT FLOW IN THE LONDON THEORY

It is not at once evident that an effective mass should be used in the expression (1.5) for the current density in the London theory, because it is the ordinary mass which appears in the expression (1.4) for the average velocity. We shall derive an expression for the current density, sufficiently general to apply to superconducting as well as to Bloch wave functions, in order to show why the effective mass appears.

The hamiltonian for an electron interacting with the normal modes can be expressed in the form (WF):

$$(H_e+H_L+H_I)\psi=E\psi, \quad (4.1)$$

where H_e is the hamiltonian for the electrons with the ions in their equilibrium positions, H_L is that for the vibrations and H_I represents the interaction terms between the electron and normal modes.

We again consider a metal with a surface at $x=0$ subject to a magnetic field in the Z-direction. The vector potential may be defined as in (2.7), so that

$$H_e=(1/2m)[p_x^2+(p_y+eA_y/c)^2+p_z^2]+V(r), \quad (4.2)$$

where the subscript i represents the ith electron. Since A_y is a function only of the x coordinate, the periodicity in the y and z-directions is not destroyed.

A typical term of H_I is of the form

$$q_sV_s(r), \quad (4.3)$$

where q_s is the amplitude of a mode with wave vector s and $V_s(r)$ gives the interaction for unit amplitude.

The superconducting states can still be designated by k_y and k_z, but it is in general necessary to replace k_x by a different quantum number which need not be specified. The wave function is then of the form

$$\psi(r, q_s)=\exp[i(k_yy+k_zz)]\cdot U_k(r, q_s). \quad (4.4)$$

Owing to the interaction terms, the complete hamiltonian is not periodic, so that $U(r)$ is not periodic, as it would be for Bloch functions. There are, however, various ways in which U_k may be so specified as to express a wave function in the form (4.4). One might require, for example, that when U is expanded in a power series in the q_s's, the term independent of the q_s's be periodic. In other words, U_k should be periodic when all the q_s's are set equal to zero.

If (4.4) is substituted into (4.1), the following equation is obtained for U_k:

$$\left[\frac{\hbar^2}{2m}(k_y^2+k_z^2)+\frac{e\hbar k_y}{m}\left(p_y+\frac{e}{c}A_y\right)\right]U+\left[\frac{\hbar^2p^2}{2m}+V+H_L+H_I\right]U=EU. \quad (4.5)$$

Let us now change k_y to $k_y+\Delta k_y$, and treat the terms in Δk_y as a perturbation. Terms linear in Δk_y are

$$(\hbar\Delta k_y/m)(\hbar k_y+p_y+eA_y/c). \quad (4.6)$$

We suppose that the interaction terms remain unchanged. The change in energy, ΔE, corresponding to the change Δk_y can be obtained by first-order perturbation theory. It is required that U_k be of the form specified above so that k_y does not enter into the boundary conditions for U_k. There results:

$$\Delta E/\Delta k_y=(\hbar/m)\int U_k^*(\hbar k_y+p_y+eA_y/c)U_k d\tau,$$

$$=(\hbar/m)\int\psi_k^*(p_y+eA_y/c)\psi_k d\tau. \quad (4.7)$$

The term on the right is just $\hbar$ times the average velocity v_y. Thus, just as for ordinary Bloch functions, we have

$$v_y=\partial E/\hbar\partial k_y. \quad (4.8)$$

This equation is valid if the change in energy is computed by assuming that the interaction terms remain

unchanged. This requires that when k_y in a wave function of the form (3.1) is changed to $k_y+\Delta k_y$, k_y' must be increased to $k_y'+\Delta k_y$. The normal modes will then be unchanged. Furthermore, in computing the change in energy, it must be assumed that $M_{kk'}$ depends only on the vector displacement between $\mathbf{k}$ and $\mathbf{k}'$. Even if this latter condition is not satisfied, we can consider virtual displacements in which it is. Equation (4.8) will then be valid if the energy is calculated for such virtual displacement.

We shall now suppose that $A_y(x)$ is such that the wave functions are not altered very much by the field. The conditions for the London theory are then satisfied. We may then treat the terms in A_y as a perturbation and calculate the energy, E_{k1}, arising from the magnetic field by first-order perturbation theory. The total energy is

$$E_k=E_{k0}+E_{k1}+\cdots, \tag{4.9}$$

where E_{k0} is the energy for a wave function Ψ_{k0} corresponding to zero field and

$$E_{k1}=\frac{1}{2m}\int\Psi_{k0}^*\left[\frac{2e}{c}p_yA_y+\frac{e^2}{c^2}A_y^2\right]\Psi_{k0}d\tau. \tag{4.10}$$

The average velocity of the electron can be obtained by use of (4.8)

$$v_y=[(\partial E_{k0}/\partial k_y)+(\partial E_{k1}/\partial k_y)]/\hbar. \tag{4.11}$$

The change in energy with k_y is to be computed as required for (4.8) to hold. This expression is accurate to terms of the second order in the wave function.

The expression for E_{k1} can be simplified if it is assumed that A_y is a slowly varying function which can be treated as a constant while the integration is carried out over a unit cell. We can then use (4.8) to replace p_y/m by v_y for zero field, and obtain

$$E_{k1}=\int\left(\frac{e}{c}\frac{\partial E_{k0}}{\partial k_y}A_y+\frac{e^2}{2mc^2}A_y^2\right)\Psi_{k0}^*\Psi_{k0}d\tau. \tag{4.12}$$

If we now make the reasonable assumption that the average value of $\Psi_{k0}^*\Psi_{k0}$ over a cell is independent of changes in k_y, we find

$$v_y=\frac{1}{\hbar}\frac{\partial E_{k0}}{\partial k_y}+\int\frac{e}{\hbar^2c}\frac{\partial^2E_{k0}}{\partial k_y^2}A_y\Psi_{k0}^*\Psi_{k0}d\tau. \tag{4.13}$$

The first term gives the normal current which averages to zero, and the second term is that arising from the magnetic field. It is similar to that used by London except that an effective mass, given by

$$(m_{\text{eff}})^{-1}=\hbar^{-2}\partial^2E_{k0}/\partial k_y^2, \tag{4.14}$$

replaces the ordinary electron mass. The current density which arises from the magnetic field is

$$j_y=-(e^2/\hbar^2c)(\partial^2E_{k0}/\partial k_y^2)A_y\sum\Psi_{k0}^*\Psi_{k0}, \tag{4.15}$$

where the sum is over all occupied states. This completes the proof that an effective mass should be used in London expressions for the current density.

V. JUSTIFICATION FOR USE OF EFFECTIVE MASS

There remains to discuss the justification for using an effective mass, m/α_1, in the condition for the validity of the London theory, (2.3), which came from Eq. (2.17) and following. The method of the effective mass has been used for the discussion of the motion of electrons in a slowly varying potential, V_s, superimposed on the periodic potential of the crystal lattice. In an energy band in which the energies are given by an expression of the form (2.3) it is possible to omit the periodic potential and calculate a wave function from the equation:

$$[(2m)^{-1}(\alpha_1p_x^2+\alpha_2p_y^2+\alpha_3p_z^2)+V_s]\varphi=E\varphi. \tag{5.1}$$

To a close approximation, the true wave function is

$$\psi=\varphi(r)\psi_0(r), \tag{5.2}$$

where $\psi_0(r)$ is the Bloch function for $k=0$. The method can be applied to slowly varying magnetic fields, in which case φ is a solution of (2.17).

One way to get the appropriate effective mass for motion, say, in the x-direction is to compare the energy of a Bloch function with a sinusoidal modulation with that of the corresponding plane wave. Such a function is

$$\psi=-\tfrac{1}{2}i(\psi_{k+a}-\psi_{k-a})\simeq\sin ax\psi_k, \tag{5.3}$$

for which the energy is approximately:

$$\begin{aligned}E&=\tfrac{1}{2}[\epsilon(k+a)+\epsilon(k-a)]\\&=\epsilon(k)+\tfrac{1}{2}a^2\partial^2\epsilon/\partial kx^2.\end{aligned} \tag{5.4}$$

If the added energy is compared with $\hbar^2a^2/2m$, it can be seen that the effective mass is $\hbar^{-2}\partial^2\epsilon(k)/\partial kx^2$, as given by (2.2).

The added energy is that required to localize a wave function centering about ψ_k within a distance π/a. The above argument can be extended without modification to apply to superconducting wave functions. The change in energy with k should then be computed on the assumption that the interaction terms remain unchanged, as discussed below (4.7) for application to the calculation of average velocity. It should be noted that in our model the effective mass is negative so that the hole theory should be used for the superconducting electrons.