

Theory of Superconductivity. II. Properties of the Modified Electron-Lattice States of Low Energy

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In addition to causing electron-phonon scattering, the electron-lattice interaction, considered in a previous paper, also modifies the structure of the stationary states, which become mixtures of the states considered in the adiabatic or Born-Oppenheimer approximation. The modified phonon and electron energies and electric current density are calculated. When a criterion depending on band structure is satisfied, the modified electronic configuration of lowest energy can be qualitatively different from the Fermi distribution of a normal metal, due to an effective interaction between electrons and holes of the same spin on each energy shell that arises from the electron-lattice interaction. Below a critical temperature there are two independent states of stationary free energy. The upper state has normal conductivity and heat ca-

capacity. The lower state has associated with it an electric current density that appears to have no dissipative resistance and that exhibits a Meissner effect with a resonance phenomenon at certain frequencies in an oscillatory field. In zero field the phase transition between these states is of second order, with a discontinuity in heat capacity at the transition temperature. An energy gap can occur, but it is not required in deriving the properties of the electric current density and of the phase transition between the two states. Various quantities calculated from the present theory for a simple model (effective mass, spherical Fermi surface, single conduction band) are in reasonable agreement with experimental values. Energies are generally an order of magnitude smaller than in the earlier theory of Fröhlich.

I. INTRODUCTION

IN a previous paper,¹ which will be referred to as I, the electron-lattice interaction responsible for electrical resistivity in ordinary metallic perfect crystals has been shown to be a form of the Jahn-Teller effect, arising as a correction to the Born-Oppenheimer or adiabatic approximation. The matrix elements that describe electron-phonon scattering are derived in I by a general argument that takes into account the Coulomb interaction between electrons and the electronic energy band structure. This argument leads qualitatively to the formalism usually assumed in the theory of metallic conductivity,² but it gives somewhat different values for the nonvanishing matrix elements.

Matrix elements of this interaction occur not only between degenerate Born-Oppenheimer states, leading to transitions between such states described as electron-phonon scattering, but also between nondegenerate states. Hence, the stationary states and energy spectrum are also modified, and the true stationary (or metastable) states are mixtures of the Born-Oppenheimer states. The present paper will examine this modification of the lowest electron-lattice states and of the energy spectrum. Since electron excitations are mixed with the pure phonon excitations of the Born-Oppenheimer approximation, the modified states can have a nonvanishing electric current density associated with the phonon states. Although this current density vanishes in the normal state of a metal or in the absence of a magnetic field, it will be shown that if a certain criterion depending on the energy band structure is satisfied, there is a state of different structure that is stable at low temperatures, and for which this current density is related to the magnetic induction by equations anal-

ogous to the London equations.³ This current density appears to be a true supercurrent, without electrical resistivity, and leads to an explanation of superconductivity as such and of the Meissner effect that appears to be qualitatively different from the generally accepted microscopic theory of Bardeen, Cooper, and Schrieffer (BCS)⁴ and of Bogoliubov and Valatin.⁵

The detailed derivations of the present paper are limited to the effective mass approximation, on the assumption that there is only one partially filled band and that the electron energy shells are spheres in the momentum space. The modified phonon and electron energies are derived in Secs. II and III, and the structure of the ground state is derived in Sec. IV. Up to this point the argument is very similar to the earlier work of Fröhlich,⁶ although certain results are quantitatively different as a result of the difference between the electron-phonon interaction assumed by Fröhlich and that derived in I. The present derivation has the very important advantage that as a result of the more careful treatment of singularities in I no singularities occur in the second-order perturbation theory as used here, and all results are found to be small finite corrections to the Born-Oppenheimer approximation. The qualitative change in the ground state that is found here results from a small change in energy that causes a change in the ground-state electronic configuration; the perturbed energy of an excited Born-Oppenheimer configuration becomes lower than the perturbed energy of the nominal Born-Oppenheimer electronic ground state.

³ F. and H. London, Proc. Roy. Soc. (London) **A149**, 71 (1935); *Physica* **2**, 341 (1935).

⁴ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

⁵ N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (Consultants Bureau Enterprises, Inc., New York, 1959); N. N. Bogoliubov, *Nuovo cimento* **7**, 794 (1958); J. G. Valatin, *ibid.* **7**, 843 (1958).

⁶ H. Fröhlich, Phys. Rev. **79**, 845 (1950); Proc. Phys. Soc. (London) **A64**, 129 (1951); Proc. Roy. Soc. (London) **A215**, 291 (1952).

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¹ R. K. Nesbet, Phys. Rev. **126**, 2014 (1962).

² A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed.

Thus, as in the BCS theory, the perturbed ground state cannot be obtained by perturbation theory from the unperturbed ground state. Nevertheless, it can be obtained by perturbation theory from what is nominally an excited configuration. Thus, the use of second-order perturbation theory appears to be justified.

In Sec. V it is shown that the present theory leads to a second-order phase transition in zero magnetic field, with reasonable values for the critical temperature and discontinuity in heat capacity derived from a rather crude model of the structure of the ground state. In nonzero magnetic field there is a contribution to the electric current density of the low-temperature phase that apparently exhibits no dissipative resistance and that leads to a Meissner effect. This current density is discussed in Sec. VI.

The present theory can lead to an energy gap by two different mechanisms. The first is that of the BCS theory—the second-order interaction between electron-hole excited states has the structure of an attractive electron-electron interaction. The second possibility might occur if there are overlapping electronic energy bands in the Born-Oppenheimer approximation. The energy gap is discussed in Sec. VII, although the derivations of the present paper must be generalized to the case of overlapping bands before a quantitative discussion can be given. A similar situation holds for the magnetic transition, discussed in Sec. VIII, since the upper state is more complex in structure than the ground state of a normal metal. A detailed derivation of the properties of this state in nonzero magnetic field becomes comparable in complexity to the theory of the de Haas-van Alphen effect.

The attenuation of an applied magnetic field in the low-temperature phase results from a field equation [Eq. (97) below] that has more structure than any of the earlier treatments of the Meissner effect. In particular, a resonance phenomenon is possible at certain values of the frequency of an applied field.

II. STATIONARY STATES

The matrix elements between zeroth-order Born-Oppenheimer states derived in I [Eq. (I-29)] are

$$\begin{aligned} & (\Phi_{ijk}^{abc\dots}(n)X(\dots n_k-1\dots), H\Phi_{jkl}^{bc\dots}(n)X(\dots n_k\dots)) \\ &= -(n_k\hbar\omega_k/2NM)^{\frac{1}{2}}\hbar\kappa(\epsilon_a-\epsilon_i-i\delta_i)^{-1} \\ & \quad \times (4\pi Ze^2/\kappa^2+\lambda^2)(N/V), \quad (1) \end{aligned}$$

where the electron wave vectors σ_a and σ_i are related by

$$\sigma_a = \sigma_i + \kappa. \quad (2)$$

The function $\Phi_{ijk}^{abc\dots}(n)$ is the Born-Oppenheimer electronic wave function (parametrically dependent on the nuclear coordinates) approximated by exciting electrons from orbitals $\phi_i, \phi_j, \phi_k, \dots$, occupied in the electronic ground state to excited orbitals $\phi_a, \phi_b, \phi_c, \dots$. $X(\dots n_k\dots)$ is the Born-Oppenheimer lattice wave function describing a state in which n_k phonons are in

the longitudinal normal mode with wave vector κ . It is assumed that the conduction electrons interact with ion cores of mass M and charge Ze , of which there are N in total volume V . The screening constant λ is estimated by the formula [Eq. (I-23)]

$$\lambda^2 = \frac{3}{2}(4\pi e^2 n_0 / \epsilon_F), \quad (3)$$

where n_0 is the density of conduction electrons and ϵ_F is the Fermi level measured from the bottom of the conduction band for conducting electrons or from the top for conducting holes. This formula follows from a semi-empirical argument that leads to an estimate of the velocity s of longitudinal acoustic waves [Eq. (I-27)],

$$s^2/v^2 = \frac{1}{3}mZ/M, \quad (4)$$

where m is the electron effective mass and v is the electron velocity at the Fermi surface. The quantity δ_i in Eq. (1) is found to be of the order $(s/v)\epsilon_i$.

The matrix element of Eq. (1) describes the scattering of an electron from σ_i with energy ϵ_i to σ_a with energy ϵ_a , while one phonon of mode κ is absorbed. There is an analogous matrix element, proportional to $(n_{-\kappa})^{\frac{1}{2}}$, that describes the same electronic transition, where one phonon of mode $-\kappa$ is emitted, leaving $n_{-\kappa}$ in the final state. These are the only matrix elements that occur between the Born-Oppenheimer states, if the electronic wave functions are expanded to first order in the nuclear displacement coordinates.

Each Born-Oppenheimer state is characterized by a set of occupation numbers n_κ for the longitudinal lattice modes, by a choice of N occupied electronic orbitals, and by occupation numbers for the transverse lattice modes, omitted here since they are not affected by the interaction of Eq. (1) unless Umklapp transitions are taken into account. The difference in energy between two states such as those of Eq. (1) is

$$\epsilon_a - \epsilon_i - \hbar\omega_\kappa \quad (5a)$$

when a phonon of mode κ is absorbed, and is

$$\epsilon_a - \epsilon_i + \hbar\omega_{-\kappa} \quad (5b)$$

when a phonon of mode $-\kappa$ is emitted. There are no diagonal elements of Eq. (1), which arises from an operator proportional to the normal mode momentum $p_{-\kappa} = p_\kappa^*$.

The energy correction for a Born-Oppenheimer state, to second order of the Rayleigh-Schrödinger perturbation theory, follows from Eq. (1). If it is assumed that $\omega_{-\kappa} = \omega_\kappa$, and if occupied electron orbitals are described by occupation numbers $f_s(\sigma_i)$, where s refers to spin orientation, the energy correction is

$$\begin{aligned} \Delta E = & - \sum_s \sum_i \sum_a \hbar\omega_\kappa I_{ai}^2 f_s(\sigma_i) [1 - f_s(\sigma_a)] \\ & \times \left[\frac{n_\kappa}{\epsilon_a - \epsilon_i - \hbar\omega_\kappa} + \frac{n_{-\kappa} + 1}{\epsilon_a - \epsilon_i + \hbar\omega_\kappa} \right], \quad (6) \end{aligned}$$

where, if $Z=1$,

$$I_{ai}^2 = (N/MV^2) \{ 8\pi^2 e^4 \hbar \kappa^2 / (\kappa^2 + \lambda^2)^2 [(\epsilon_a - \epsilon_i)^2 + \delta_i^2] \}. \quad (7)$$

The phonon wave vector κ in Eq. (6) is determined by Eq. (2).

For states of physical interest it is reasonable to assume that

$$n_{-\kappa} = n_{\kappa}. \quad (8)$$

This condition, which is compatible with the detailed structure of the present theory, simplifies Eq. (6) to give

$$\Delta E = \Delta E_{\text{ph}} + \Delta E_{\text{el}}, \quad (9)$$

where

$$\Delta E_{\text{ph}} = - \sum_i \sum_a (n_{\kappa} + \frac{1}{2}) \hbar \omega_{\kappa} \left[\frac{2(\epsilon_a - \epsilon_i) I_{ai}^2}{(\epsilon_a - \epsilon_i)^2 - \hbar^2 \omega_{\kappa}^2} \right] \times \sum_s f_{si} (1 - f_{sa}) \quad (10)$$

and

$$\Delta E_{\text{el}} = \sum_i \sum_a \left[\frac{\hbar^2 \omega_{\kappa}^2 I_{ai}^2}{(\epsilon_a - \epsilon_i)^2 - \hbar^2 \omega_{\kappa}^2} \right] \sum_s f_{si} (1 - f_{sa}). \quad (11)$$

III. MODIFIED PHONON AND ELECTRON ENERGIES

The energy correction given by Eq. (10) is obviously of the form of a renormalization of the phonon energies. From the constraint of Eq. (2), one of the two summations over electron wave numbers can be replaced by summation over the phonon wave number κ . Thus the energy associated with each longitudinal normal mode becomes

$$E(n_{\kappa}) = (n_{\kappa} + \frac{1}{2}) \hbar \omega_{\kappa} [1 - \alpha(\kappa)], \quad (12)$$

where, if the contributions from both electron spins are the same,

$$\alpha(\kappa) = \sum_i 4f_i (1 - f_a) (\epsilon_a - \epsilon_i) I_{ai}^2 / [(\epsilon_a - \epsilon_i)^2 - \hbar^2 \omega_{\kappa}^2]. \quad (13)$$

As before, σ_a is fixed by Eq. (2). This expression is estimated in Appendix A for the normal electron Fermi distribution at absolute zero, and $\alpha(\kappa)$ is found to be of the order (s/v) if κ is less than the diameter of the Fermi surface. This formula exhibits the anomaly discussed by Kohn⁷ since α must decrease abruptly as κ increases beyond this value. The result is, except for this anomaly, a small renormalization of the phonon frequencies, with no observable consequences.

The energy correction given by Eq. (11) does not contain the phonon occupation numbers n_{κ} . Hence, it describes an additional electronic energy due to the electron-lattice interaction. Formally, since it is quadratic in the electron occupation numbers, it leads to correlation between electron momentum states. This formula has the same qualitative significance as that derived by Fröhlich⁶ and used by him to develop a microscopic theory of superconductivity. The argument

⁷ W. Kohn, Phys. Rev. Letters 2, 393 (1959).

used here (developed in I) is intended to meet various theoretical objections to Fröhlich's derivation. The present formula differs from Fröhlich's primarily in the structure of the quantity I_{ai}^2 of Eq. (7). This will be shown to have important consequences.

A well-known representation of the Dirac δ function is

$$\pi \delta(\epsilon_a - \epsilon_i) = \lim_{\delta_i \rightarrow 0} \delta_i / [(\epsilon_a - \epsilon_i)^2 + \delta_i^2]. \quad (14)$$

Hence, I_{ai}^2 of Eq. (7), which contains a factor of this form, concentrates the electron-hole interaction given by Eq. (11) primarily to an interaction between states on the same energy shell. To examine the effect of this it is convenient to define a chemical potential function

$$\mu_s(\sigma) = \partial E / \partial f_s(\sigma) = \epsilon(\sigma) + \epsilon'_s(\sigma), \quad (15)$$

where E includes the electronic Hartree-Fock energy in addition to the correction ΔE . Thus, from Eq. (11),

$$\epsilon'_s(\sigma_i) = \sum_j I_{ji}^2 (2f_{sj} - 1) \quad (16)$$

if the δ -function property of I_{ai}^2 is used to simplify Eq. (11) by omitting $(\epsilon_a - \epsilon_i)^2$ in the denominator. For the Fermi distribution at absolute zero Eq. (16) implies that $\epsilon'(\sigma)$ has a finite discontinuity at σ_F , the Fermi surface,

$$\epsilon'(\sigma_F -) = \sum_j I_{ji(F)^2}, \quad (17)$$

$$\epsilon'(\sigma_F +) = - \sum_j I_{ji(F)^2}. \quad (18)$$

This is, however, an oversimplification, since it is not correct to use the limiting form of Eq. (14) when $f(\sigma)$ is discontinuous. Since δ_i is finite [$\sim (s/v)\epsilon_i$] in the present case, the function $\epsilon'(\sigma)$ is continuous at the Fermi surface but it has a sharp zigzag of the form

$$- \tan^{-1} [2v(\sigma - \sigma_F) / s\sigma_F]. \quad (19)$$

Using Eqs. (3), (4), and (7), near σ_F ,

$$\epsilon'(\sigma) \cong - (s/v) \epsilon(\sigma) \left[\tan^{-1} \left(\frac{2v(\sigma - \sigma_F)}{s\sigma_F} \right) \right] \left(\frac{\sigma_F^3 V}{6\pi^2 N} \right) \left(\frac{2\lambda^4}{\sigma_F^4} \right) \times \int_0^{2\sigma} \frac{\kappa^3 d\kappa}{(\kappa^2 + \lambda^2)^2}. \quad (20)$$

The summation over σ_j has been replaced by integration in bicentric coordinates,

$$\sum_j \sim \frac{V}{4\pi^2 \sigma} \int_0^{\infty} \kappa d\kappa \int_{|\sigma - \kappa|}^{\sigma + \kappa} \rho d\rho, \quad (21)$$

where σ, ρ are, respectively, the magnitudes of σ_i, σ_j in Eq. (16). The near singularity in the integrand effectively restricts the range of κ to values for which $|\sigma - \kappa| \leq \rho \leq \sigma + \kappa$, so that the energy shell, $\rho = \sigma$, falls within the limits of integration. Hence, the upper limit of κ is taken to be 2σ .

The quantity $\sigma_F^3 V / 6\pi^2 N$ is the ratio of the volume of the Fermi sphere to that of the first Brillouin zone.

This is just $\frac{1}{2}$ for simple monovalent metals. The other factors in Eq. (20) are of the order of magnitude of unity when $|\sigma - \sigma_F| > (s/v)\sigma_F$, except for $(s/v)\epsilon(\sigma)$. Hence, asymptotically,

$$\epsilon'(\sigma_F \mp) \sim \pm (s/v)\epsilon_F, \quad (22)$$

and the effect is a small renormalization of the one-electron energies which should be insignificant at normal temperatures.

At very low temperatures, unless the term ϵ' is large enough to cause the one-electron potential function $\mu(\sigma) = \epsilon(\sigma) + \epsilon'(\sigma)$ to turn over, the point of inflection due to ϵ' will increase the observed effective mass but will not qualitatively change the properties of the system. If ϵ' is large enough, however, the function $\mu(\sigma)$ can have a relative maximum just inside the Fermi surface, followed by a relative minimum just outside. This is the situation considered by Fröhlich⁶ in his theory of superconductivity, since superseded by the Bardeen-Cooper-Schrieffer theory. Because the effects considered here, derived from the matrix elements of Eq. (1), are somewhat different from those obtained in the earlier theory, it is worthwhile to re-examine their implications.

If the unperturbed energy $\epsilon(\sigma)$ is expanded in powers of $(\sigma - \sigma_F)$ the modified one-electron potential near the Fermi surface is

$$\mu(\sigma) = \epsilon_F + \hbar v(\sigma - \sigma_F)[1 - \beta] + \dots \quad (23)$$

There will be a subsidiary maximum and minimum if the quantity in square brackets is negative. This criterion is $\beta > 1$, where by Eq. (20),

$$\beta = \left(\frac{\sigma_F^3 V}{6\pi^2 N} \right) \left(\frac{2\lambda^4}{\sigma_F^4} \right) \int_0^{2\sigma_F} \frac{\kappa^3 d\kappa}{(\kappa^2 + \lambda^2)^2}. \quad (24)$$

For simple monovalent metals the first factor is just $\frac{1}{2}$. If the integral is estimated by the trapezoidal rule,

$$\beta \cong 8\lambda^4 / (4\sigma_F^2 + \lambda^2)^2, \quad (27)$$

which will be less than unity if $\lambda \leq \sigma_F$. Since λ is the screening constant for the perturbed effective Hartree-Fock potential in a metal, it cannot be much larger than $2/r$ where r is the effective radius of the unit cell. But this gives $\lambda \cong \sigma_F$, indicating that simple monovalent metals should not satisfy the criterion. A relatively small change in the constants would suffice to make β exceed unity, particularly since, by Eq. (3), λ^2 is proportional to ϵ_F .

The existence of this subsidiary maximum and minimum implies a qualitative change in the nature of the electronic ground state. If, following Fröhlich, this is taken to be the criterion for superconductivity, then the present result is compatible with the fact that the alkali metals are not superconductors, but that metals with more complex band structure are. It should be noted that the parameter s/v , which measures the

strength of the electron-lattice interaction in the present work, does not enter into the criterion constant β , which depends only on the electronic energy band structure.

Comparison of Eqs. (17), (18), and (22) gives the following approximate formula, which will be used in the derivation of thermodynamic properties,

$$\sum_j I_{ji}^2 \cong (s/v)\epsilon(\sigma_i). \quad (25)$$

IV. STRUCTURE OF THE GROUND STATE

To consider the structure of the ground state when $\beta > 1$, it is convenient to pass to the limit in Eq. (14), thus confining the interaction of Eq. (11) to particles and holes of the same spin in the same energy shell. This is reasonable when the electron distribution function $f_s(\sigma)$ varies smoothly with σ , as it is found to do for the modified ground state. For consistency, if this is done, it is necessary to require that $f_s(\sigma)$ have well-defined derivatives with respect to components of σ , except possibly for a bounding surface in the limit of $T=0^\circ\text{K}$. The one-electron energy $\epsilon(\sigma)$ is taken to be a Hartree-Fock energy appropriate to the Born-Oppenheimer electronic ground state. As is well known, although this does not imply that the total Hartree-Fock energy is the sum of the $\epsilon(\sigma)$, it does imply that $\epsilon(\sigma)$ is the derivative of this energy, as indicated in Eq. (15). Hence, for small displacements from the Fermi distribution the total electronic energy, except for a macroscopic constant, can be obtained by integrating Eq. (15). By Eq. (16) this becomes

$$E_{e1} = \sum_s \sum_i f_{si}(\epsilon_i - \sum_a I_{ai}^2(1 - f_{sa})). \quad (26)$$

If $f_s(\sigma_i)$ is independent of spin and also independent of the direction of σ_i , the approximation of Eq. (25) gives

$$E_I = 2 \sum_i f_i \epsilon_i \left(1 - \frac{s}{v}(1 - f_i) \right). \quad (27)$$

The suffix I will be used to denote the state of lowest energy (or free energy) which has these properties of spin and momentum isotropy. The corresponding property for a real metal is the requirement that f_i should depend only on ϵ_i .

The entropy associated with state I is given by the usual formula

$$-TS_I = 2kT \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)]. \quad (28)$$

The number of conduction electrons is

$$N = 2 \sum_i f_i. \quad (29)$$

These formulas are subject to the exclusion principle, so $0 \leq f_i \leq 1$, treating f_i as a statistical function to be determined by the condition of minimum free energy. Expressed as a potential per electron this condition is

$$\frac{1}{2} \partial(E - \zeta N - TS) / \partial f_i = \mu_i - \zeta + kT \ln[f_i / (1 - f_i)] = 0, \quad (30)$$

subject to $0 < f_i < 1$. When $f_i = 0$ or 1 , Eq. (30) does not hold. Here

$$\mu_i = \frac{1}{2} \partial E / \partial f_i = \epsilon_i [1 - (s/v)(1 - 2f_i)]. \quad (31)$$

When $T > 0$, Eq. (30) is equivalent to

$$f_i = \{1 + \exp[(\mu_i - \zeta)/kT]\}^{-1}. \quad (32)$$

This automatically satisfies the condition $0 < f_i < 1$.

So far this is completely analogous to the derivation of the normal Fermi distribution function, and would be identical if μ_i were not a function of f_i . This dependence, however, leads to a new result for very low temperatures. This results from the fact that Eq. (30), when $T = 0$, has a solution with $0 < f_i < 1$ over a *finite* interval of energy. This solution is determined by

$$\mu_i = \epsilon_i [1 - (s/v)(1 - 2f_i)] = \zeta, \quad (33)$$

if $0 < f_i < 1$. Clearly, this determines the distribution function at $T = 0$,

$$\begin{aligned} f_i^I &= 1, & (\epsilon_i - \zeta) < -(s/v)\epsilon_i \\ &= \frac{1}{2} - \frac{1}{2} [(\epsilon_i - \zeta)/(s/v)\epsilon_i], & -(s/v)\epsilon_i < (\epsilon_i - \zeta) < (s/v)\epsilon_i \\ &= 0, & (\epsilon_i - \zeta) > (s/v)\epsilon_i. \end{aligned} \quad (34)$$

The solution f_i of Eq. (32), in which f_i occurs implicitly on the right-hand side, approaches Eq. (34) as $T \rightarrow 0$.

If terms of second order in (s/v) are neglected, then

$$\zeta \cong \epsilon_F \quad (35)$$

and

$$\begin{aligned} f_i^I &\cong \frac{1}{2} - \frac{1}{2} [(\epsilon_i - \epsilon_F)/(s/v)\epsilon_F], \\ - (s/v)\epsilon_F &< (\epsilon_i - \epsilon_F) < (s/v)\epsilon_F. \end{aligned} \quad (36)$$

Qualitatively, as a result of the electron-lattice interaction, the Fermi distribution has been modified in a shell of finite thickness enclosing the Fermi surface; the distribution function goes continuously from 1 to 0; and the one-electron effective potential μ of Eq. (33) is constant throughout this shell. This state has stationary free energy, in fact minimum, subject to momentum isotropy, but it is a state of finite entropy at $T = 0$, and it is not the true ground state of the system.

To make further progress it is necessary to examine states for which $f_i(\sigma)$ depends on the direction as well as magnitude of σ . From general symmetry arguments, such as Bloch's theorem, this discussion can be limited to states with time-reversal symmetry,

$$f_+(\sigma) = f_-(-\sigma), \quad (37)$$

where the subscript denotes spin direction. This condition implies that $M_S = 0$ and that total linear momentum vanishes in the absence of external fields.

An important property of the quantity I_{ai}^2 of Eqs. (7) and (26) is that it vanishes quadratically as κ approaches zero. It reaches a very flat maximum for $\kappa = \lambda$, where λ is of the order of $\sqrt{2}\sigma_F$ for ordinary metallic conductors and is not likely to be of a different order of magnitude for superconductors. Hence, an electron

interacts with holes throughout the opposite hemisphere of its energy shell with comparable strength. This is in striking disagreement with the interaction postulated in the BCS theory, which restricts the interaction to diametrically opposite electron-hole pairs (of opposite spin).

The effect of an interaction of this kind is to favor distributions in which the electrons on an energy shell are bunched together in a compact region (or several such regions) with a compact distribution of holes in complementary regions, determined by the detailed form of I_{ai}^2 . Since continuity between adjacent energy shells is required, the state of lowest energy can be expected to have a distribution described by a new kind of potential surface dividing regions in which $f_i = 1$ and 0 , obtained by superimposing hills and valleys on the normal Fermi surface. This surface is a level surface of the one-electron effective potential given by Eqs. (26) and (31), without the constraint of isotropy,

$$\mu_{si} = \epsilon_i - \sum I_{ji}^2 (1 - 2f_{js}). \quad (38)$$

Equation (37) implies that the potential surfaces for the two different spin directions should be related to each other by inversion. Hence, in the absence of external fields, it is necessary to consider electrons of one spin only, multiplying calculated thermodynamic functions by two to account for the other spin direction.

If the limiting potential surface is determined by $\mu_i = \zeta$, then $f_i = 1$ for $\mu_i < \zeta$ and $f_i = 0$ for $\mu_i > \zeta$. This surface will intersect each energy shell ($\epsilon = \text{const}$) in a curve determined from Eq. (38) by

$$- \sum_{j(\text{occ})} I_{ji}^2 + \sum_{a(\text{unocc})} I_{ai}^2 = \epsilon_i - \zeta, \quad (39)$$

for σ_i , σ_j , and σ_a on the energy surface ϵ_i , subject to the normalization condition

$$\sum_s \sum_i f_{si} = N. \quad (40)$$

The ground state is that distribution which has minimum energy subject to Eqs. (39) and (40). This will be referred to as state II, which is to be determined by minimizing the free energy, without the constraint of isotropy, for $T > 0^\circ\text{K}$.

It is convenient to use the limiting case of Eq. (14) and to expand I_{ji}^2 in spherical harmonics,

$$I_{ji}^2 = \delta(\epsilon_j, \epsilon_i) \sum_{n=0}^{\infty} I_n P_n(\cos\omega_{ji}), \quad (41)$$

where, since I_{ji}^2 vanishes when $\kappa = 0$,

$$\sum_n I_n = 0. \quad (42)$$

If $x = \cos\theta$, where θ is the polar angle for a spherical polar coordinate system in momentum space (axial symmetry is assumed for convenience), then let $f_l(\sigma)$ be defined by

$$f^{\text{II}}(\sigma, x) = \sum_{l=0}^{\infty} (2l+1) f_l(\sigma) P_l(x) \quad (43)$$

Thus for the isotropic component,

$$f_0(\sigma) = \frac{1}{2} \int_{-1}^{+1} f^{\text{II}}(\sigma, x) dx. \quad (44)$$

To simplify the following discussion it will be assumed that f^{II} can be approximated by redistributing f^{I} on the energy shells, without changing the net number of electrons in each shell. This implies that

$$f_0(\sigma) \cong f^{\text{I}}(\sigma). \quad (45)$$

Then Eq. (38) becomes (dropping the spin index)

$$\mu^{\text{II}}(\sigma, x) = \mu^{\text{I}}(\sigma) + \text{const} \sum_{n>0} I_n f_n(\sigma) P_n(x), \quad (46)$$

where, approximately, by Eq. (25)

$$\text{const} I_0 = 2(s/v)\epsilon(\sigma), \quad (47)$$

and, from Eq. (31),

$$\mu^{\text{I}}(\sigma) = \epsilon(\sigma) [1 - (s/v)(1 - 2f_0(\sigma))]. \quad (48)$$

The functions $f_n(\sigma, T)$ can be treated as independent thermodynamic variables, subject to the condition of continuity in σ required in passing to the limit in Eq. (14). In terms of these functions, the internal energy difference between states I and II is obtained from Eq. (26). Expressed as an average energy per particle in momentum shell σ ,

$$U_{\text{I}}(\sigma, T) - U_{\text{II}}(\sigma, T) = -\frac{1}{2} \text{const} \sum_{n>0} I_n f_n^2(\sigma, T) \quad (49)$$

The heat capacity difference per particle in shell σ is

$$\Delta C(\sigma, T) = d(U_{\text{II}}(\sigma, T) - U_{\text{I}}(\sigma, T))/dT \\ = \frac{1}{2} \text{const} \sum_{n>0} I_n (\partial f_n^2(\sigma, T)/\partial T). \quad (50)$$

The condition for minimum free energy, Eqs. (30) or (32), becomes a set of integral equations

$$f_n(\sigma, T) \\ = \frac{1}{2} \int_{-1}^{+1} \left\{ P_n(x) / \left[1 + \exp\left(\frac{\mu^{\text{II}}(\sigma, x, T) - \zeta}{kT} \right) \right] \right\} dx, \quad (51)$$

where μ^{II} depends on the functions f_n through Eq. (46). It should be noted that $f_n = 0$ for $n > 0$ is always a solution of these equations. Thus, the isotropic distribution $f^{\text{I}}(\sigma, T)$ corresponds to a definite thermodynamic state of the system. It will be shown that a second solution can exist below a certain transition temperature, becoming the distribution $f^{\text{II}}(\sigma, x)$ described by Eq. (39) at $T = 0^\circ\text{K}$.

The approximation of Eq. (45) amounts to the initial stage of an iterative procedure that might be used to determine solutions of Eq. (51). Given estimates of f_m for $m < n$, retain only the terms with $m \leq n$ in

Eq. (46), substituted on the right-hand side of Eq. (51). This gives an integral equation to be solved for the single function f_n . Then in turn each of the f_m , $m \leq n$, should be recalculated from the equation with μ expanded out to order n . This cycle can then be repeated with n increased by unity.

V. ENERGY, HEAT CAPACITY, AND CRITICAL TEMPERATURE

In this section the simplest possible nontrivial example will be considered. Suppose that only the $n=0$ and $n=1$ terms occur in the Legendre series of Eq. (41). Then Eqs. (42) and (47) imply that

$$\text{const} I_1 = -\text{const} I_0 = -2(s/v)\epsilon(\sigma). \quad (52)$$

Then $\mu^{\text{II}}(\sigma, x, T)$ is linear in x with at most a single root $x_0(\sigma, T)$.

At $T = 0^\circ\text{K}$, $x_0(\sigma)$ determines the intersection of the limiting potential surface $\mu = \zeta$ and the energy shell $\epsilon(\sigma)$, by Eq. (39). Thus, if $x_0(\sigma)$ is unique the energy shell is divided into two compact regions. Suppose for spin $+\frac{1}{2}\hbar$ the region containing $x=1$ is that of the occupied energy states. Then for consistency, $x_0(\sigma)$ must be determined by Eq. (44) if Eq. (45) is assumed. Then by Eq. (51),

$$f^{\text{I}}(\sigma) = f_0(\sigma) = \frac{1}{2} \int_{x_0}^1 P_0(x) dx = \frac{1}{2}(1 - x_0), \quad (53)$$

or

$$x_0(\sigma) = 1 - 2f^{\text{I}}(\sigma) = 1 - 2f_0(\sigma). \quad (54)$$

Also

$$f_1(\sigma) = \frac{1}{2} \int_{x_0}^1 P_1(x) dx = \frac{1}{4}[1 - x_0^2(\sigma)] \\ = f_0(\sigma)[1 - f_0(\sigma)]. \quad (55)$$

This could also be obtained directly by minimizing the energy expression, Eq. (26). The $f_n(a)$ with $n > 1$ do not vanish, but are determined by equations analogous to Eq. (55). By Eq. (46) they do not affect the integrand of Eq. (51) when $I_n = 0$ for $n > 1$. Thus the only approximation made here, assuming this truncation, is that of fixing the number of electrons in a given energy shell by Eq. (45).

By Eqs. (49) and (52) the internal energy difference per electron in shell σ is

$$U_{\text{I}}(\sigma, 0) - U_{\text{II}}(\sigma, 0) = -\frac{1}{2} \text{const} I_1 f_1^2(\sigma, 0) \\ = (s/v)\epsilon(\sigma) f_0^2(1 - f_0)^2. \quad (56)$$

Then using the approximate formulas, Eqs. (36) and (45), the excitation energy per unit volume of the upper state is

$$U_{10} = 2 \int_{-\infty}^{+\infty} [U_{\text{I}}(\sigma, 0) - U_{\text{II}}(\sigma, 0)] N(\epsilon) d\epsilon \\ \cong (2/15) N(\epsilon_F) (s/v)^2 \epsilon_F^2. \quad (57)$$

This should be equal to $H_0^2/8\pi$ if states I and II are identified with the "normal" and "superconducting"

states, respectively, of superconductors, by the usual thermodynamic argument. Equation (57) is an order of magnitude smaller than the corresponding result in Fröhlich's theory,⁶ which is empirically too large by at least an order of magnitude. Thus, Eq. (57) is consistent with empirical values of critical magnetic field H_0 at absolute zero, if the crudeness of the various approximations made here is taken into account.

When the crystal lattice structure is taken into account it is to be expected that the anisotropic distribution function of state II will have at most a small finite number of possible orientations with respect to the reciprocal lattice, and hence that the entropy per unit volume vanishes. Any finite degeneracy of the ground state would be resolved by an "infra-Jahn-Teller" effect due to weak interactions not taken into account here and probably not leading to easily observable phenomena.

In the absence of an electromagnetic field, the entropy of the upper state is finite. This does not imply, however, that the entropy of this state does not vanish in the critical magnetic field H_c . Without further analysis, no conclusion can be drawn about the thermodynamic properties of the upper state for the transition associated with the Meissner effect, except at $T=0^\circ\text{K}$ or $H=0$. When $T=0$ and $H=0$, the entropy of state I is determined by Eqs. (28) and (36) to be

$$\begin{aligned} S_{I0} &= 2k \int_{-\infty}^{+\infty} [f_0 \ln f_0 + (1-f_0) \ln(1-f_0)] N(\epsilon) d\epsilon \\ &= 2k \int_0^1 [f_0 \ln f_0 + (1-f_0) \ln(1-f_0)] \\ &\quad \times N(\epsilon) (-d\epsilon/df_0) df_0 \\ &\cong 2kN(\epsilon_F)(s/v)\epsilon_F. \end{aligned} \quad (58)$$

The iterative method discussed in Sec. IV can be used to evaluate the distribution function at finite temperatures. In the first cycle of this process, the $n=0$ approximation to the potential function is

$$\begin{aligned} \mu(\sigma, x, T) - \zeta &= \epsilon(\sigma) - \epsilon_F - (s/v)\epsilon(\sigma)[1 - 2f_0(\sigma, T)] \\ &= kTB(\sigma, T)g(\sigma, T), \end{aligned} \quad (59)$$

where

$$B(\sigma, T) = 2(s/v)\epsilon(\sigma)/kT \quad (60)$$

and

$$g(\sigma, T) = f_0(\sigma, T) - f_0(\sigma, 0). \quad (61)$$

Equations (34), (35), and (48) have been used here. The approximate integral equation for g derived from Eq. (51) is

$$f_0(\sigma, T) = f_0(\sigma, 0) + g = (1 + \exp Bg)^{-1}. \quad (62)$$

When Bg is small the right-hand side of Eq. (62) can be replaced by $(2 + Bg)^{-1}$, and this equation has an approximate solution, using Eqs. (34) and (45),

$$\begin{aligned} Bg &= \ln\{[1 - f_0(\sigma, T)]/f_0(\sigma, T)\} \\ &\cong (\epsilon - \epsilon_F)[kT + \frac{1}{2}(s/v)\epsilon]. \end{aligned} \quad (63)$$

Bg will be reasonably small for all states of interest even for temperatures below T_c , since the most important region for the distribution function falls within $\frac{1}{2}(s/v)\epsilon$ of the Fermi surface. Equations (60) and (63), in agreement with the definition of g , imply that $g(\sigma, 0)$ vanishes.

The heat capacity per unit volume of the upper state, from Eqs. (28) and (30), is

$$C_I = TdS_I/dT \quad (64)$$

$$= 2k \int_{-\infty}^{+\infty} [\mu(\sigma, T) - \zeta][df_0(\sigma, T)/kdT]_{\sigma} N(\epsilon) d\epsilon. \quad (65)$$

Then from Eq. (62),

$$df_0 = -f_0(1-f_0)d(Bg). \quad (66)$$

Hence, using Eq. (63),

$$(df_0/kdT)_{\sigma} = f_0(1-f_0)(\epsilon - \epsilon_F)/[kT + \frac{1}{2}(s/v)\epsilon]^2, \quad (67)$$

$$(d\epsilon/df_0)_{T} = -[kT + \frac{1}{2}(s/v)\epsilon]/f_0(1-f_0). \quad (68)$$

Then Eq. (65) becomes

$$C_I \cong 2k^2TN(\epsilon_F) \int_0^1 \left[\ln\left(\frac{1-f_0}{f_0}\right) \right]^2 df_0 = \gamma_n T, \quad (69)$$

where

$$\gamma_n = \frac{2}{3}\pi^2N(\epsilon_F)k^2 \quad (70)$$

is the same constant that is obtained for the electronic heat capacity of a normal metal, despite the qualitative difference between $f^I(\sigma, T)$ and the normal Fermi distribution function.

The $n=1$ approximation to the potential function, in the first cycle of the iterative solution of Eq. (51), is

$$\begin{aligned} \mu(\sigma, x, T) - \zeta &= \epsilon(\sigma) - \epsilon_F - (s/v)\epsilon(\sigma) \\ &\quad \times [1 - 2f_0(\sigma, T) + 2f_1(\sigma, T)x], \end{aligned} \quad (71)$$

again using Eqs. (35) and (48). The approximate integral equation for f_1 , with B given by Eq. (60), is

$$f_1(\sigma, T) = F(x_0; Bf_1) \quad (72)$$

where

$$F(x_0; Bf_1) = \frac{1}{2} \int_{-1}^{+1} \frac{x dx}{[1 + \exp Bf_1(x_0 - x)]}, \quad (73)$$

where x_0 is the root of Eq. (71). For consistency with the equation for f_0 , x_0 must be approximately equal to the value determined by Eq. (53) for $T > 0$. Then

$$x_0(\sigma, T) \cong 1 - 2f_0(\sigma, T). \quad (74)$$

This value of x_0 always satisfies

$$x_0^2 \leq 1. \quad (75)$$

When Bf_1 is large, Eq. (73) has the asymptotic form

$$\begin{aligned} F(x_0; Bf_1) &\sim \frac{1}{4}(1 - x_0^2) \{ [1 + \exp Bf_1(x_0 - 1)]^{-1} \\ &\quad - [1 + \exp Bf_1(x_0 + 1)]^{-1} \}. \end{aligned} \quad (76)$$

Thus, Eq. (72) agrees with Eq. (55) as $T \rightarrow 0^\circ\text{K}$. The general behavior of $F(x_0; Bf_1)$ as a function of Bf_1 is that it rises from zero with monotonically decreasing slope and approaches a constant value $\frac{1}{4}(1-x_0^2)$ exponentially. It follows that Eq. (72) always has a solution $f_1=0$, corresponding to the isotropic state I. In addition, if the initial slope $BdF/d(Bf_1)$ exceeds unity there will be a second solution with finite f_1 . Hence, there will be a critical value of B and, by Eq. (60), a critical value of T below which the anisotropic state II exists.

The initial slope of $F(x_0; Bf_1)$ can be obtained by a Taylor expansion of Eq. (73),

$$F(x_0; Bf_1) \cong (1/12)Bf_1 - (1/240)(1+5x_0^2) \times (Bf_1)^3 + \dots \quad (77)$$

Hence, the condition for a second solution of Eq. (72) is

$$B > 12. \quad (78)$$

Since this is independent of x_0 , and since B depends only on ϵ , not on $\epsilon - \epsilon_F$, the critical temperature T is a slowly varying function of σ near σ_F . Hence, for all energy shells for which f_1 is appreciable the transition temperatures will be nearly the same, and the critical value of T at the Fermi surface can be identified with T_c , the transition temperature for a superconductor in zero magnetic field. The transition is clearly of second order since the distribution functions f^I and f^{II} coincide at T_c .

From Eqs. (60) and (78), the transition temperature is

$$kT_c = \frac{1}{6}(s/v)\epsilon_F. \quad (79)$$

This is an order of magnitude smaller than the corresponding quantity in the theory proposed by Fröhlich. Although the constants for the alkali metals would lead to unusually large values of T_c , those metals do not satisfy the criterion indicated by Eqs. (23) and (25). For the actual superconducting metals ϵ_F is considerably smaller, since they tend to have nearly filled or nearly empty bands, while by Eq. (4), s/v must be of comparable magnitude for metals of comparable atomic mass. This could make the quantity given by Eq. (79) considerably smaller than in the case of the alkali metals and could put T_c in the range of experimental values.

When Bf_1 is small, Eqs. (72) and (77) can be solved for f_1 ,

$$f_1^2(B) \cong 20(B-12)/B^3(1+5x_0^2), \quad 0 < B-12 \ll 1. \quad (80)$$

The steepness of the increase of f_1 to its asymptotic value is indicated by the fact that for $x_0=0$, $B=12.7$ gives $Bf_1=3$, obviously already in the range of the asymptotic formula, not Eq. (77), and $f_1=0.236$, compared with its asymptotic value 0.250. Thus, B must be very close to 12 for Eq. (80) to hold.

In the limit as $T \rightarrow T_c$ from below, $B \rightarrow 12$ from

above, and from Eqs. (60), (74), and (80),

$$(df_1^2/dT)_c = -\frac{5}{36(1+5x_0^2)T_c} = -\frac{5k}{6(1+5x_0^2)(s/v)\epsilon}. \quad (81)$$

It follows from this that the jump in heat capacity per unit volume at T_c , given by Eqs. (50), (67), and (74), is

$$\begin{aligned} (\Delta C)_c &= -2 \int_{-1}^{+1} \frac{s}{v} \epsilon N(\epsilon) (df_1^2/dT)_c (d\epsilon/dx_0) dx_0 \\ &\cong -\frac{5s}{9v} \epsilon_F N(\epsilon_F) \left[\left(kT_c + \frac{1}{2} \frac{s}{v} \epsilon_F \right) / kT_c \right] \int_{-1}^{+1} \frac{dx_0}{1+5x_0^2} \\ &= 2.29N(\epsilon_F)(s/v)\epsilon_F k. \end{aligned} \quad (82)$$

From Eqs. (69) and (84), the ratio of ΔC to C_I at T_c is given by

$$(\Delta C)_c / \gamma_n T_c = 2.07. \quad (83)$$

This ratio is in good agreement with the value 2.00 of the Gorter-Casimir two-fluid model⁸ and the value 1.52 in the BCS theory.⁴ Experimental values lie within this range.

Another nondimensional ratio, the law of corresponding states, follows from Eqs. (57), (70), and (79). This is

$$\gamma_n T_c^2 / H_0^2 = \gamma_n T_c^2 / 8\pi U_{10} = 0.055. \quad (84)$$

This ratio is 0.159 in the Gorter-Casimir theory and 0.170 in the BCS theory. A factor of three could easily be accounted for by including higher terms in the Legendre polynomial expansions used to derive Eq. (57), and by improving other rather crude approximations made here. Since U_{10} depends on an angular distribution in momentum space in the present theory, it should be more sensitive to details of the band structure than is kT_c .

The isotope effect is a consequence of Eqs. (4) and (79) which imply the relationship

$$T_c M^{\frac{1}{2}} = \text{const} \quad (85)$$

for isotopes with the same electronic energy band structure.

VI. CURRENT DENSITY AND THE MEISSNER EFFECT

In the present theory, since no canonical transformation has been carried out, the electric current density is given by the usual formula derived from the non-relativistic Schrödinger equation.⁹ This is

$$\mathbf{j}(\mathbf{x}) = \sum_{\alpha} \text{Re} \int \Psi^* [(q_{\alpha} \hbar / im_{\alpha}) \text{grad}_{\alpha} - (q_{\alpha}^2 / m_{\alpha} c) \mathbf{A}(\mathbf{x})] \Psi d\tau_{\alpha}', \quad (86)$$

⁸ C. J. Gorter and H. B. G. Casimir, *Z. Physik* **35**, 963 (1934); *Z. Tech. Phys.* **15**, 539 (1934).

⁹ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), pp. 221-223.

where $\int \cdots d\tau_\alpha'$ denotes integration over all coordinates except those of particle α , whose coordinates are set equal to \mathbf{x} . The quantities q_α , m_α are the charge and mass, respectively, of particle α . This current density is gauge invariant when the usual gauge-dependent phase transformation of the Schrödinger wave function Ψ is associated with a gauge transformation of the vector potential \mathbf{A} . By the equation of continuity, $\text{div} \mathbf{j}$ must vanish under stationary conditions. This places a condition on $\text{div} \mathbf{A}$ when Ψ is specified, and, together with boundary conditions and the definition $\text{curl} \mathbf{A} = \mathbf{B}$, should suffice to determine \mathbf{A} uniquely.

For the Born-Oppenheimer zeroth order wave functions indicated by Eq. (1), the principal contribution to the current density arises from the terms for which α denotes an electron, since the nuclear masses are very large compared with the electron mass. It is a reasonable approximation to replace Eq. (86) by the corresponding expression summed over the electrons only. Even so, there will be a term linear in the nuclear displacement coordinates to the approximation considered in deriving Eq. (1). For diagonal matrix elements, since the lattice vibrational quantum numbers do not change, these terms vanish when the full wave function (integration over nuclear displacement coordinates) is taken into account. The usual statement that phonons do not carry electric current follows to the same order of approximation from Eq. (86), since the phonon momenta also occur only to first order in the current density operator. Thus, the phonon contribution to the first term in Eq. (86) vanishes exactly for the zeroth order wave functions considered here, while the second term (dependent on \mathbf{A}) is small in the ratio of electron to nuclear mass. The momentum due to this second term cannot be neglected, since for a material medium at rest it is equal in magnitude to the net electron momentum. This should be taken into account in considering the problem of flux quantization in multiply-connected superconductors.¹⁰ A discussion of this point will be given in a separate paper.

The wave functions that interact with a given Ψ_0 though the matrix elements of Eq. (1) all differ from Ψ_0 by both an electron transition and a phonon transition. Since the current density operator contains the individual particle operators additively, it has no nondiagonal matrix elements for wave functions of this kind.

For states Ψ_μ that interact with a given state Ψ_0 , if an operator \mathbf{j} has this property,

$$\mathbf{j}_{\mu 0} = 0, \quad \text{for all } \mu, \quad (87)$$

then to second order the mean value of \mathbf{j} is

$$\langle \mathbf{j} \rangle = \mathbf{j}_{00} + \sum'_\mu \frac{H_{0\mu}^2}{(H_{\mu\mu} - H_{00})^2} (\mathbf{j}_{\mu\mu} - \mathbf{j}_{00}). \quad (88)$$

The first term, \mathbf{j}_{00} , of Eq. (88), for the electric current density given by Eq. (86), is the usual expression for the electronic current density in the theory of normal metals. Unless there is an energy gap (which has not yet appeared in the present theory), this first term should lead to normal electrical conductivity and magnetic susceptibility.² For an applied magnetic field, if there is no energy gap, the first term can be made to vanish by a shift of the distribution function in momentum space under which to lowest order the electronic energy remains equal to its value in the absence of a magnetic field. If there is an energy gap of the kind that occurs in nonconducting crystals, the Brillouin zones are either completely full or completely empty at $T=0^\circ\text{K}$ and an infinitesimal shift in the distribution function cannot occur. In either case the term \mathbf{j}_{00} leads to normal magnetic susceptibilities and electrical conductivity.

For the current density operator of (86) the second term of Eq. (88) will be denoted by \mathbf{j}_s , in anticipation of the discussion given below. If terms of opposite spin and momentum are related by the time-reversal symmetry condition, Eq. (37), then

$$\begin{aligned} \mathbf{j}_s = & -\frac{e}{m} \sum_i \sum_a \frac{I_{a_i}^2}{\hbar\omega_k} \left\{ \left[\left(\hbar\boldsymbol{\sigma}_a + \frac{e}{c}\mathbf{A} \right) |\phi_a|^2 - \left(\hbar\boldsymbol{\sigma}_i + \frac{e}{c}\mathbf{A} \right) |\phi_i|^2 \right] (n_k + n_{-k} + 1) f_+(\boldsymbol{\sigma}_i) [1 - f_+(\boldsymbol{\sigma}_a)] \right. \\ & \left. + \left[\left(-\hbar\boldsymbol{\sigma}_a - \frac{e}{c}\mathbf{A} \right) |\phi_{-a}|^2 - \left(-\hbar\boldsymbol{\sigma}_i - \frac{e}{c}\mathbf{A} \right) |\phi_{-i}|^2 \right] (n_k + n_{-k} + 1) f_-(-\boldsymbol{\sigma}_i) [1 - f_-(-\boldsymbol{\sigma}_a)] \right\} \quad (89) \end{aligned}$$

$$= -2 \frac{e^2}{mc} \mathbf{A} \sum_i \sum_a \frac{I_{a_i}^2}{\hbar\omega_k} (2n_k + 1) (|\phi_a|^2 - |\phi_i|^2) f_i (1 - f_a). \quad (90)$$

If ϕ_a and ϕ_i are Bloch waves rather than plane waves, the terms arising from the gradient operator still cancel exactly if Eq. (37) holds.

This expression can be simplified by noting that only the antisymmetric part $\frac{1}{2}(f_i - f_a)$ of the term $f_i(1 - f_a)$ contributes to Eq. (90), since the other factors under the double summation are symmetric in indices i and a .

¹⁰ F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. I, p. 152; J. B. Keller and B. Zumino, *Phys. Rev. Letters* **7**, 164 (1961); B. S. Deaver and W. M. Fairbank, *ibid.* **7**, 43 (1961); R. Doll and M. Näbauer, *ibid.* **7**, 51 (1961).

Then Eq. (90) reduces to

$$\begin{aligned} \mathbf{j}_s(\mathbf{x}) &= -\frac{e^2}{mc} \mathbf{A}(\mathbf{x}) \sum_i \sum_a \frac{I_{ai}^2}{\hbar\omega_k} (2n_k + 1) \\ &\quad \times (|\phi_a|^2 - |\phi_i|^2) (f_i - f_a), \\ &= - (e^2/mc) R(\mathbf{x}) \mathbf{A}(\mathbf{x}), \end{aligned} \quad (91)$$

where the density function $R(\mathbf{x})$ defined by these equations is periodic with the structure of the crystal space lattice. Since ϕ_a and ϕ_i are Bloch waves, both normalized to N^{-1} in the unit cell, it follows that $R(\mathbf{x})$ integrates to zero over each unit cell.

The current density \mathbf{j}_s has several remarkable properties which justify the hypothesis that it should be identified with the superconducting current density. Since I_{ai}^2 is an interaction effectively confined to electrons and holes within the same energy shell, \mathbf{j}_s vanishes when f_i is constant on each energy shell, as is the distribution function for state I. Hence this current density is a property of state II only and vanishes above the transition temperature. The magnetic susceptibility of a normal metal is small because the distribution function can shift in momentum space so that the gradient terms in Eq. (86) cancel the vector potential terms.¹¹ This applies to \mathbf{j}_{00} , as mentioned above, unless there is an energy gap, but not to the current density of Eq. (91), which depends only on *relative* momenta and thus cannot be affected by a simple translation of the distribution function in momentum space. The energy due to the interactions that produce this current density, given by the perturbation formula, Eq. (11), depends only on relative energies, for which the effect of the vector potential \mathbf{A} cancels out. Hence, the electron-lattice interaction introduces a current density with no change in the energy of the material system, which plays a passive role in providing the coupling density function $R(\mathbf{x})$.

The energy associated with this current density can be thought of as an addition to the energy density of the electromagnetic field. An energy density of this kind occurs in the derivation by London¹² of the energy conservation law that follows when the London equations, relations between \mathbf{j}_s and the electromagnetic field of the same nature as Eq. (91), are adjoined to Maxwell's equations. Following exactly the derivation by London, neglecting any time dependence of $R(\mathbf{x})$, this energy density is found to be

$$(e^2/2mc^2) R(\mathbf{x}) \mathbf{A}^2(\mathbf{x}) = \frac{1}{2} \Lambda(\mathbf{x}) \mathbf{j}_s^2(\mathbf{x}). \quad (92)$$

The function

$$\Lambda(\mathbf{x}) = m/e^2 R(\mathbf{x}) \quad (93)$$

¹¹ R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955), pp. 144-150; A. H. Wilson, reference 2, pp. 160-176.

¹² F. London, reference 10, pp. 65, 66.

has been defined in analogy to the London constant

$$\Lambda_L = 4\pi\lambda_0^2/c^2, \quad (94)$$

where λ_0 is the penetration depth. Since $\Lambda(\mathbf{x})$ is not positive definite the present theory is not equivalent to the London theory. In fact, Eq. (93) implies that $\Lambda(\mathbf{x})$ is singular, while $R(\mathbf{x})$ as defined by Eq. (91) is regular. Thus, a formulation in terms of R and \mathbf{A} appears to be more appropriate than a formalism analogous to the London theory, based on equations

$$\text{curl}(\Lambda(\mathbf{x}) \mathbf{j}_s(\mathbf{x})) = -(1/c) \mathbf{B}(\mathbf{x}), \quad (95)$$

$$\partial(\Lambda(\mathbf{x}) \mathbf{j}_s(\mathbf{x}))/\partial t = \mathbf{E}(\mathbf{x}), \quad (96)$$

derived from Eq. (91) when there is no electrostatic potential.

As mentioned above, in discussing the gauge invariance of Eq. (86), the vector potential is determined here by: its curl, the magnetic induction; by the equation of continuity for $\mathbf{j}(\mathbf{x})$; and by boundary conditions (\mathbf{A} and its first derivatives must be continuous), thus fixing a particular gauge. Under stationary conditions the present theory leads to $\text{div}(R\mathbf{A}) = 0$ instead of the London gauge, $\text{div}\mathbf{A} = 0$. Thus \mathbf{A} can be treated as a field variable.

In the presence of an electrostatic field there is an additional potential gradient term in Eq. (96), and a corresponding dissipative current density. The usual derivation of electrical resistivity, when applied to \mathbf{j}_s as defined by Eq. (91), leads to a null result. This occurs because the acceleration term in the Boltzmann equation vanishes, since an electrostatic field leads to a uniform rate of translation of the electronic distribution function in momentum space,¹³ whereas Eq. (91) depends only on relative momenta and energies and is not affected by a displacement in momentum space. Thus, \mathbf{j}_s as derived here appears to be a true supercurrent, with no electrical resistivity.

From this argument, the dissipative current \mathbf{j}_n in superconductors (observed at high frequencies) must be attributed to the first term \mathbf{j}_{00} of Eq. (88), as applied to Eq. (86). This term behaves as a normal metallic current if there is no energy gap, and as the normal electronic current density of an intrinsic semiconductor if there is an energy gap in state II.

When combined with Maxwell's equations, Eq. (91) leads to an equation for the amplitude of an oscillatory vector potential field of frequency ω . This equation, in Cartesian coordinates, if ϵ_0 and ω are taken to be unity, is

$$[-c^2\nabla^2 + (4\pi e^2/m)R(\mathbf{x})]\mathbf{A}(\mathbf{x}) = (\omega^2 + 4\pi i\omega\sigma)\mathbf{A}(\mathbf{x}). \quad (97)$$

Since $R(\mathbf{x})$ is real and periodic, Eq. (97) is analogous to the Schrödinger equation for a Bloch electron in a periodic lattice. Its solutions are wavelike in character,

¹³ N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936), pp. 93-96.

damped only by the electrical resistivity through the imaginary term on the right, if ω^2 is near an eigenvalue of the operator on the left-hand side. The eigenvalues ω_0^2 of the operator in Eq. (97) consist for each propagation vector \mathbf{k} of a discrete set of real numbers, bounded below. Thus $\omega_0^2(\mathbf{k})$, the set of eigenvalues, will have a band structure analogous to the energy band structure. When ω lies in a gap between these eigenvalue bands the vector potential must decay exponentially from values at an external boundary, with a penetration depth determined solely by the function $R(\mathbf{x})$ if ω is sufficiently small. Since $R(\mathbf{x})$, from Eq. (91), is a thermodynamic function of the material, this provides a qualitative explanation of the Meissner effect as the reversible expulsion of a static magnetic field during the transition from state I to state II.

When ω is near an eigenvalue of Eq. (97) there should be a peak in the dissipative part of the complex conductivity since partial penetration of the field can occur. This might be the explanation of the absorption peak observed in thin film experiments on Hg and Pb.¹⁴ If it were possible to carry out similar experiments at the surface of single crystals, Eq. (97) indicates that the effect should be anisotropic in a manner characteristic of the eigenvalue band structure of this equation.

VII. THE ENERGY GAP

Experimental data on electron tunneling across a thin insulating film between superconducting layers¹⁵ and on microwave and infrared absorption¹⁶ provide direct evidence for an energy gap in superconductors. The present theory can lead to such an energy gap, although its existence is not required, as shown by the argument developed here, to account for many of the most important thermodynamic and electromagnetic properties of superconductors.

The argument developed so far in this paper has been concerned with effects of first order in the electron-lattice wave functions, treating the Born-Oppenheimer states as zeroth order states. The calculated second-order energy changes are finite, and lead to the various results considered above. There is another effect that must still be considered, since the modified electron-lattice states will in general form a continuum, and any interaction between states in a continuum can lead to a collective state separating off below or above, depending on the sign of the interaction. It can easily be seen that the residual interaction between the modified electron-lattice states characterized by electron-hole excitations (coming from Born-Oppenheimer states all

with the same lattice wave function) is just the electron-electron interaction Hamiltonian assumed in the BCS theory, with matrix elements modified only because of the difference between Eq. (7) above and the matrix element for electron-phonon interaction that is usually assumed. The result is that the interaction is important only for electrons on an energy shell, and, thus, the Hamiltonian analogous to that used by BCS becomes purely attractive, since the second-order interaction matrix element is negative on the electron energy shell. An energy gap for modified electron excitations should follow from this, exactly as in the BCS theory. The present formalism does not require the *ad hoc* assumption of a limiting electron energy difference made by BCS. A more complete discussion will be given in a later paper.

An energy gap of the same nature as that in a normal intrinsic semi-conductor can also occur in state II if the normal Fermi surface cuts across two overlapping energy bands. As a result of the electron-hole interaction that leads to the modified potential function of Eq. (38), the limiting potential surface defined by Eq. (39) could lie between the two bands. The excitation energy is determined by the potential function $\mu(\sigma)$ rather than by the one-electron energy $\epsilon(\sigma)$. According to Eqs. (22) and (79) such a gap would be limited to

$$2\epsilon_0 < 12kT_c, \quad (98)$$

since this is the maximum amount by which two bands originally tangent at the Fermi surface could be displaced.

The present theory indicates that in principle it should be possible to have superconductors without an energy gap. Then the dissipative component of the current density of the superconducting state should have the properties of the current density of a normal metal. A superconductor of this kind would exhibit the behavior indicated by the London theory of microwave absorption (summarized by Schafroth¹⁷), which postulated an electrical conductivity ρ_n comparable to that of the normal metal.

It is interesting to note that most superconductors probably have overlapping bands. This is related to their property of being relatively poor metallic conductors. In fact some time ago Born and Cheng¹⁸ proposed that this property by itself might account for superconductivity.

The density function $R(x)$ of Eq. (91) will also be considerably larger when orbitals ϕ_a and ϕ_i come from two overlapping bands than in the case of a single band. By Eqs. (93) and (94) superconductors without an energy gap would have exceptionally large penetration depths, since $R(\mathbf{x})$ would then be relatively small.

¹⁷ M. R. Schafroth, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 10, pp. 324-337.

¹⁸ M. Born and K. C. Cheng, *Nature* **161**, 968, 1017 (1948); K. C. Cheng, *ibid.* **163**, 247 (1949).

¹⁴ D. M. Ginsberg and M. Tinkham, *Phys. Rev.* **118**, 990 (1960); P. L. Richards and M. Tinkham, *ibid.* **119**, 575 (1960).

¹⁵ I. Giaver, *Phys. Rev. Letters* **5**, 147, 464 (1960); J. Nicol, S. Shapiro, and P. H. Smith, *ibid.* **5**, 461 (1960).

¹⁶ M. A. Biondi, A. T. Forrester, M. P. Garfunkel, C. B. Satterthwaite, *Revs. Modern Phys.* **30**, 1109 (1958); M. A. Biondi and M. P. Garfunkel, *Phys. Rev. Letters* **2**, 143 (1959); R. E. Glover, III, and M. Tinkham, *Phys. Rev.* **108**, 243 (1957); D. M. Ginsberg, P. L. Richards, and M. Tinkham, *Phys. Rev. Letters* **3**, 337 (1959).

VIII. THE MAGNETIC TRANSITION

Equation (58) indicates that state I is degenerate at $T=0^\circ\text{K}$. However, this state is not observed except in a magnetic field, since state II has lower free energy below the critical temperature. It is known from the theory of the electronic diamagnetic susceptibility¹¹ that the electronic wave functions cannot be represented by Bloch waves (approximate momentum eigenfunctions) when a magnetic field is present. From the degenerate perturbation theory, it is to be expected that the correct zeroth-order orbitals could be constructed as linear combinations of Bloch waves on the same energy shell, translated in momentum space by an amount proportional to the vector potential. The energy of these orbitals should then depend on the magnetic field, which would remove the degeneracy of state I.

An accurate evaluation of the critical magnetic field at temperatures between 0 and T_c will be left for a later paper. This requires a detailed treatment of state I in a magnetic field and would be comparable in difficulty to the theory of electronic susceptibility and the de Haas-van Alphen effect. It would also be necessary to extend the argument for the field-independent heat capacity difference given by Eq. (82) into the intermediate temperature range.

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APPENDIX A

It is required to estimate the magnitude of Eq. (13) for the Fermi distribution:

$$\alpha(\mathbf{k}) = \sum_i 4(\epsilon_a - \epsilon_i) I_{a_i^2} [(\epsilon_a - \epsilon_i)^2 - \hbar^2 \omega_{\mathbf{k}}^2], \quad (\text{A1})$$

where $\sigma_a = \sigma_i + \mathbf{k}$. In spheroidal coordinates, with

$$\xi = (\sigma_a + \sigma_i)/\kappa, \quad \eta = (\sigma_a - \sigma_i)/\kappa, \quad (\text{A2})$$

the summation over the Fermi distribution, $\sigma_i < \sigma_F < \sigma_a$, is

$$\sum_i \sim \frac{V}{4\pi^2} \frac{\kappa^3}{8} \int_0^1 d\eta \int_{(2\sigma_F/\kappa)-\eta}^{(2\sigma_F/\kappa)+\eta} d\xi (\xi^2 - \eta^2), \quad \xi \geq 1. \quad (\text{A3})$$

In these variables,

$$\epsilon_a - \epsilon_i = (\hbar^2 \kappa^2 / 2m) \xi \eta \quad (\text{A4})$$

and the integral to be evaluated is

$$C \int_0^1 d\eta \int_{(2\sigma_F/\kappa)-\eta}^{(2\sigma_F/\kappa)+\eta} \frac{d\xi (\xi^2 - \eta^2) \xi \eta}{(\xi^2 \eta^2 + D^2)(\xi^2 \eta^2 - F^2)}. \quad (\text{A5})$$

When $(2\sigma_F/\kappa) > 1 + \eta$, the lower limit for the ξ integration is just 1. Here,

$$C = (s^2/v^2) [\sigma_F \lambda^4 / 2\kappa (\kappa^2 + \lambda^2)^2], \quad (\text{A6})$$

from Eqs. (3), (4), and (7). The relation

$$\sigma_F^3 V / 6\pi^2 N = \frac{1}{2}, \quad (\text{A7})$$

valid for half-filled bands (alkali metals) has also been used. The other constants in Eq. (A5) are

$$D = 2m\delta / \hbar^2 \kappa^2 = (s/v) (\sigma_F^2 / \kappa^2), \quad (\text{A8})$$

if

$$\delta = (s/v) \epsilon_F = (s/v) (\hbar^2 \sigma_F^2 / 2m), \quad (\text{A9})$$

and

$$F = 2m\hbar\omega_{\mathbf{k}} / \hbar^2 \kappa^2 = (s/v) (2\sigma_F / \kappa). \quad (\text{A10})$$

The dominant contribution to the integral (A5) comes from the singularity in the integrand along the curve

$$\eta = F/\xi. \quad (\text{A11})$$

Hence η can be considered to be small for the region near this singularity. When $(2\sigma_F/\kappa) > 1$, the inner integration can be approximated by setting $\xi = 2\sigma_F/\kappa$ and multiplying the integrand by 2η , the interval of ξ . This reduces the integral (A5) to the form,

$$(\kappa C / \sigma_F) \int_0^1 \eta^2 d\eta \{ [\eta^2 - (s^2/v^2)] \times [\eta^2 + (s/v)^2 (\sigma_F / 2\kappa)^2] \}^{-1}, \quad (\text{A12})$$

where $\xi^2 - \eta^2$ has been replaced by ξ^2 .

The dominant term in the principal value of this integral gives

$$\alpha(\mathbf{k}) \cong (v/s) \pi C \kappa^4 / \sigma_F^2 (\sigma_F^2 + \kappa^2) \quad (\text{A13})$$

$$= (s/v) \pi \kappa^3 \lambda^4 / \sigma_F (\sigma_F^2 + \kappa^2) (\kappa^2 + \lambda^2)^2 \quad (\text{A14})$$

$$\cong (s/v) \quad (\text{A15})$$

when $\kappa \cong \lambda \cong \sigma_F$.

If κ exceeds $2\sigma_F$, the singularity in the integrand is no longer within the region of integration. The integral then becomes of the order of magnitude of the constant C , smaller than (A14) by a factor s/v . The condition $\kappa = 2\sigma_F$ corresponds to the diameter of the Fermi surface. This is the Kohn anomaly,⁷ since the abrupt change in phonon energy must cause a similar change in phonon occupation number when the phonon momentum equals the Fermi surface diameter in a given direction. An effect of this kind has been observed in Pb.¹⁹

¹⁹ B. N. Brockhouse, K. R. Rao, and A. D. B. Woods, Phys. Rev. Letters **7**, 93 (1961).