important quantity in these calculations is, of course, the entropy. There is practically no experimental knowledge of its variation at the high energies here involved and the free particle model was used rather arbitrarily in the calculations.

Further experiments will be needed to fully justify the Li^8 production processes here advanced. For example, additional Li^8 cross sections for elements in the neighborhood of neon could verify the transition between the "residue" and evaporation reactions. Also more accurate and detailed excitation functions with light elements near the threshold should exhibit irregular features due to the fact that Li^8 can be reached from the compound nucleus by several alternate routes. These various routes will compete as they become energetically possible. For example, energetically Li^8 can be reached from C^{12} plus a proton most cheaply by emission of He^3 and two protons, more expensively by emission of a deuteron and three protons, and most expensively by emission of four protons and one neutron.

The production of Li^8 in nitrogen, a good cloud-chamber gas, may make it possible to test the conservation of momentum in the beta-decay of Li^8 more successfully than hitherto if the background difficulties can be circumvented.

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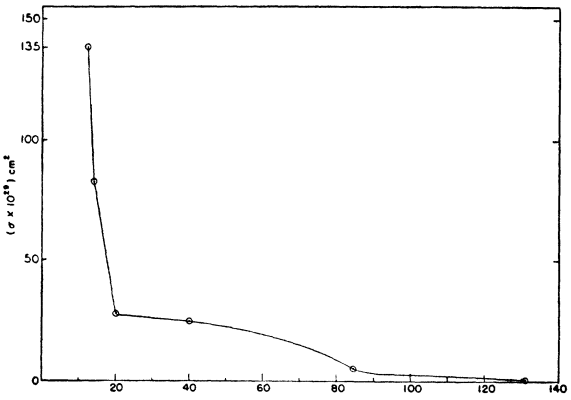

FIG. 13. Variation of the Li^8 cross section for 190-Mev deuterons as a function of A.

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Theory of the Superconducting State. I. The Ground State at the Absolute Zero of Temperature

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In Bloch's theory of electronic conductivity the scattering of electrons by lattice vibrations is connected with the absorption or emission of vibrational quanta. As in field theories this gives rise to a self-energy which can be calculated by application of perturbation theory. The most interesting term as a result of the Pauli principle has the form of an interaction between electrons in momentum (k) space. The interaction between two electrons whose energy difference is small compared with their energy has a most interesting angular dependence. Roughly speaking, it is repulsive for equal energies but different directions of $\mathbf{k}$, and attractive otherwise. If strong enough it leads in the ground state to a distribution in momentum space which is different from the normal (Fermi) distribution. If this is the case then excited states exist in which some (ΔZ) electrons in view of their interaction in momentum space are concentrated in a narrow region in $\mathbf{k}$-space. These states are stable in the sense that it requires energy to remove one of the electrons. Their energies are higher than the ground state by a term proportional to $(\Delta Z)^2$.

The condition that the above-mentioned ground state (identified with the superconducting state) is realized requires that the interaction between electrons and lattice vibrations exceeds a certain value. With the help of the theory of high temperature conductivity, this condition can be expressed in terms of the resistivity ρ at 0°C. It is found that $\rho n\nu^{5/3}$ ($1/n$ = atomic volume; ν = number of free electrons per atom) must exceed a value depending on universal constants only. If $\nu=1$ is assumed, all monovalent metals except lithium do not satisfy the required condition, but most superconductors do. The energy difference between the normal and the superconducting state at absolute zero is about ms^2 (s = velocity of sound) per electron. It has thus the correct magnitude corresponding to a temperature of a fraction of a degree absolute. No application to higher temperatures or to the influence of external fields has been made yet.

I. INTRODUCTION

IN the theory of the electric conductivity of metals first developed by Bloch[1] electrons are considered to move freely through the lattice except for occasional scattering by the lattice vibrations. This scattering is connected with the absorption or emission of a vibrational quantum. Anyone who is familiar with modern field theories will conclude at once that an electron will have a self-energy in this vibrational field since it

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[1] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

produces a lattice deformation which in turn reacts on the electron. In polar lattices this self-energy has recently been calculated with the use of the methods of field theory;[2] it arises from the interaction of the electron with the lattice polarization produced by the electron itself. In metals it will be necessary to consider all of the electrons together. It will be shown presently that through the influence of the Pauli principle the interaction energy between the electrons and the vibrational field depends on their distribution in momentum space, and if the interaction is strong enough it will be seen to lead to a new distribution which—subject to later confirmation—will be identified with the superconducting state. One should then expect the velocity of sound to play an important role, and it is not accidental that the energy of an electron moving with the velocity of sound is of a similar order as the energy per electron involved in the transition between the normal and the superconducting state. Nor is it accidental that very good conductors do not become superconductors, for the required relatively strong interaction between electrons and lattice vibrations gives rise to large normal resistivity.

In the following the properties at the absolute zero of temperature only will be considered; the extension to higher temperatures and to the presence of external fields will be made later.

II. INTERACTION BETWEEN ELECTRONS AND THE VIBRATIONAL FIELD

In the absence of interaction with the vibrational field the electrons will be considered as free. A one-electron wave function is then a plane wave whose wave vector will be denoted by $\mathbf{k}$ (or sometimes by $\mathbf{q}$). The corresponding energy is $\epsilon_k=\hbar^2k^2/2m$ (m=electronic mass, $2\pi\hbar$=Planck constant). In the lowest state these electrons fill a sphere in $\mathbf{k}$-space of radius k_0 where

$$2(4\pi k_0^3/3(2\pi)^3)=4k_0^3/3(2\pi)^2=n_{el}. \tag{2.1}$$

Here n_{el} is the number of electrons per unit volume. Use has been made of the condition that the number of one-electron states is $1/(2\pi)^3$ times the volume in $\mathbf{k}$-space, and that each state can be occupied by two electrons (spin). It is well known that the Fermi energy

$$\zeta=\hbar^2k_0^2/2m \tag{2.2}$$

has the magnitude 10 ev.

The vibrational field will also be described in terms of plane waves whose wave number be $\mathbf{w}$. The corresponding energy is $\hbar ws$ where the velocity of sound, s, is considered to be independent of w. We shall be interested in longitudinal waves only, since transverse waves do not interact with the electrons. In Debye's approximation the maximum value of w, denoted by w_0 satisfies the relation

$$2w_0^3/3(2\pi)^2=n, \tag{2.3}$$

where n is the number of atoms per unit volume. The temperature θ_l given by

$$K\theta_l=\hbar w_0 s \tag{2.4}$$

(K=Boltzmann constant) is the Debye temperature if the velocity of sound of longitudinal and transverse waves is assumed to be equal.

A number of quantities derived from combinations of electronic and of vibrational terms will be of importance. They are the number of electrons per atom,

$$\nu=n_{el}/n, \tag{2.5}$$

the wave number of an electron moving with the velocity of sound,

$$\sigma_0=ms/\hbar, \tag{2.6}$$

and the ratio

$$\sigma_0^2/k_0^2=ms^2/2\zeta=(2^{\frac{1}{3}}\nu^{\frac{2}{3}}/8)(K\theta_l/\zeta)^2, \tag{2.7}$$

of which the order of magnitude is 10^{-5}.

The interaction between the electrons and the vibrational field is completely determined by the matrix elements M_w for the absorption or emission of a vibrational quantum by an electron. They have been calculated by Bloch[1] in terms of an interaction constant C. In Bethe's notation[3]

$$|M_w|^2=\left(\frac{4C^2\hbar w}{9nVMs}\right)\begin{pmatrix} n_w \\ 1+n_w \end{pmatrix}. \tag{2.8}$$

Here n_w is the number of quanta with wave number $\mathbf{w}$. At absolute zero, $n_w=0$; V is the volume and M is the atomic mass. The two possibilities refer to absorption ($\propto n_w$) and emission of a quantum respectively. Conserving momentum the electron makes then a transition into the state $\mathbf{k}+\mathbf{w}$ or $\mathbf{k}-\mathbf{w}$.

The interaction constant C has the dimension of an energy and is of the order of 10 ev, similar to ζ. Its magnitude is of fundamental importance for the following. As it appears only in the ratio C^2/M, it is convenient to define a dimensionless constant of the order of magnitude of unity,

$$F=C^2/(3\zeta Ms^2). \tag{2.9}$$

It will be found later that the exact value of this constant decides whether a metal becomes superconducting.

If the interaction is now treated as a small quantity, perturbation theory leads in second order to a change E in energy. From a formal point of view this energy can be attributed to the virtual emission and re-absorption of vibrational quanta, just as in radiation theory. Thus an electron in a state $\mathbf{k}$ absorbs a quantum $\hbar ws$ and is transferred into an intermediate state with wave vector

$$\mathbf{q}=\mathbf{k}-\mathbf{w} \tag{2.10}$$

from which it is re-absorbed into the original state. To satisfy the Pauli principle the transition must be pro-

[2] Fröhlich, Pelzer, and Zienau, Phil. Mag. **41**, 221 (1950).

[3] A. Sommerfeld and H. Bethe, *Handbuch der Physik* **24**/2, 517 (1933).

portional to the probability $f_{\mathbf{k}}(\leq 1)$ that the state $\mathbf{k}$ is occupied, as well as to the probability $(1-f_{\mathbf{q}})$ that state $\mathbf{q}$ is empty. Thus by a well-known formula

$$E=-2\sum_{\mathbf{k}}\sum_{\mathbf{w}}\frac{|M_w|^2 f_{\mathbf{k}}(1-f_{\mathbf{q}})}{\epsilon_q-\epsilon_k+\hbar s w}, \tag{2.11}$$

or using (2.8), (2.9), and (2.6)

$$E=-\frac{16F\zeta\sigma_0}{3nV}\sum_{\mathbf{k}}\sum_{\mathbf{w}}\frac{w f_{\mathbf{k}}(1-f_{\mathbf{q}})}{q^2-k^2+\sigma_0 w}. \tag{2.12}$$

The sums go over all values of $\mathbf{k}$ and $\mathbf{w}$ and are practically integrals. The factor 2 in (2.11) accounts for the two spin systems which can be treated independently.

The energy can be written as the sum of two terms,

$$E_1=-\frac{16F\zeta\sigma_0}{3nV}\sum_{\mathbf{k}}\sum_{\mathbf{w}}\frac{w f_{\mathbf{k}}}{q^2-k^2+\sigma_0 w}, \tag{2.13}$$

and

$$E_2=+\frac{16F\zeta\sigma_0}{3nV}\sum_{\mathbf{k}}\sum_{\mathbf{w}}\frac{w f_{\mathbf{k}} f_{\mathbf{q}}}{q^2-k^2+\sigma_0 w}. \tag{2.14}$$

Calculation of the energy E_1 is simple and will be published on another occasion. This energy term is uninteresting from our point of view as it can be considered as simply giving rise to a small shift of the electronic energy levels. Its magnitude is of the order $\zeta\sigma_0/k_0\simeq 10^{-3}\zeta$ per electron.

The second energy term, however, E_2, has very interesting features. It will be noticed that $\mathbf{q}=\mathbf{k}-\mathbf{w}$ may be introduced as summation index instead of $\mathbf{w}$ so that there is complete symmetry in $\mathbf{k}$ and $\mathbf{q}$, since $w=|\mathbf{q}-\mathbf{k}|$. Then since

$$\sum_{\mathbf{k}}\sum_{\mathbf{q}}\frac{f_{\mathbf{k}} f_{\mathbf{q}} w}{q^2-k^2+\sigma_0 w}=\sum_{\mathbf{k}}\sum_{\mathbf{q}}\frac{f_{\mathbf{k}} f_{\mathbf{q}} w}{k^2-q^2+\sigma_0 w},$$

we find

$$E_2=\frac{8F\zeta\sigma_0}{3nV}\sum_{\mathbf{k}}\sum_{\mathbf{q}}\left\{\frac{w}{q^2-k^2+\sigma_0 w}-\frac{w}{q^2-k^2-\sigma_0 w}\right\}f_{\mathbf{k}} f_{\mathbf{q}}$$

$$=-\frac{16F\zeta{\sigma_0}^2}{3nV}\sum_{\mathbf{k}}\sum_{\mathbf{q}}\frac{f_{\mathbf{k}} f_{\mathbf{q}} w^2}{(q^2-k^2)^2-{\sigma_0}^2 w^2}. \tag{2.15}$$

From a formal point of view each term in this sum can be considered as representing an interaction between two points $\mathbf{k}$ and $\mathbf{q}$ in $\mathbf{k}$-space, occupied with densities $f_{\mathbf{k}}$ and $f_{\mathbf{q}}$, respectively. This interaction energy is positive when $(q^2-k^2)^2$ is small but it is negative when this quantity is large. It tends to make $q-k$ of the order σ_0.

The purpose of the following section will be to find a distribution $f_{\mathbf{k}}$ such that the total energy of our system has its smallest value. This will be done by starting with the distribution function f_0 which minimizes the total energy in zero order (sphere of radius k_0) and then introduce small alterations.

Clearly such alterations will take place near the surface of the distribution only. Therefore instead of $\mathbf{k}$ and $\mathbf{q}$ we shall frequently use the coordinates

$$x=k-k_0, \quad y=q-k_0 \tag{2.16}$$

together with the polar angles θ_k, θ_q and the azimuths φ_k, φ_q. Then

$$f_0(x)=1 \text{ if } -k_0\leq x\leq 0, \tag{2.17}$$

and $f_0(x)=0$ otherwise. Also an alteration $f(x)$ in the distribution will be defined by

$$f_{\mathbf{k}}=f_0(x)+f(x,\theta_k,\varphi_k); \quad f(x)\geq 0 \text{ if } x\geq 0; \quad f(x)\leq 0 \text{ if } x\leq 0, \tag{2.18}$$

where

$$\sum_{\mathbf{k}} f(x)=0. \tag{2.19}$$

For simplicity we shall often write $f(x)$ for $f(x,\theta_k,\varphi_k)$ but by this do not wish to imply necessarily independence of θ_k and φ_k. The range of x within which $f(x)$ is different from zero must be very small compared with k_0. The quantity x/k_0 will therefore be treated as small of the order $\sigma_0/k_0\simeq 10^{-3}$. Then in good approximation using (2.16) and (2.10),

$$q^2-k^2=2k_0(y-x), \quad w^2=4k_0^2\sin^2\theta/2, \tag{2.20}$$

where θ is the angle between $\mathbf{q}$ and $\mathbf{k}$. Furthermore, in calculating the change of E_2 energy caused by rearrangement in $\mathbf{k}$-space we have to replace $f_{\mathbf{k}} f_{\mathbf{q}}$ in (2.15) by (use (2.18))

$$f_{\mathbf{k}} f_{\mathbf{q}}-f_0(k)f_0(q)=f_0(x)f(y)+f_0(y)f(x)+f(x)f(y). \tag{2.21}$$

The change S per unit volume of the total energy due to a rearrangement of the lowest zero order configuration in $\mathbf{k}$-space (Fermi distribution) is then the sum of three terms

$$S=S_1+S_2+S_3 \tag{2.22}$$

where

$$S_1=-\frac{16F\zeta}{3nV^2}\sum_{\mathbf{k}}\sum_{\mathbf{q}} f_0(x)f(y)\psi(x,y) \tag{2.23}$$

and

$$S_2=-\frac{16F\zeta}{3nV^2}\sum_{\mathbf{k}}\sum_{\mathbf{q}}\tfrac{1}{2}f(x)f(y)\psi(x,y) \tag{2.24}$$

represent the change of E_2 per unit volume. There

$$\psi(x,y)=\frac{2{\sigma_0}^2\sin^2\theta/2}{(y-x)^2-{\sigma_0}^2\sin^2\theta/2}. \tag{2.25}$$

Use has been made of (2.15), (2.20), (2.21) and of the symmetry in x and y. S_3 represents the change per unit volume in zero order energy. Treating again x/k_0 as small and applying Eqs. (2.16), (2.18), (2.19) and (2.2) we have (factor 2 for spin)

$$S_3=(2/V)(\hbar^2/2m)\textstyle\sum_{\mathbf{k}} k^2 f(x)=(4\zeta/Vk_0)\sum_{\mathbf{k}} x f(x). \tag{2.26}$$

The function $[-\psi(x,y)]$ plays the role of an interaction between two electrons in $\mathbf{k}$-space. It has a remarkable angular dependence: It is positive (repulsive in $\mathbf{k}$-space) if $\sin^2\theta/2>(y-x)^2/{\sigma_0}^2$ and negative (at-

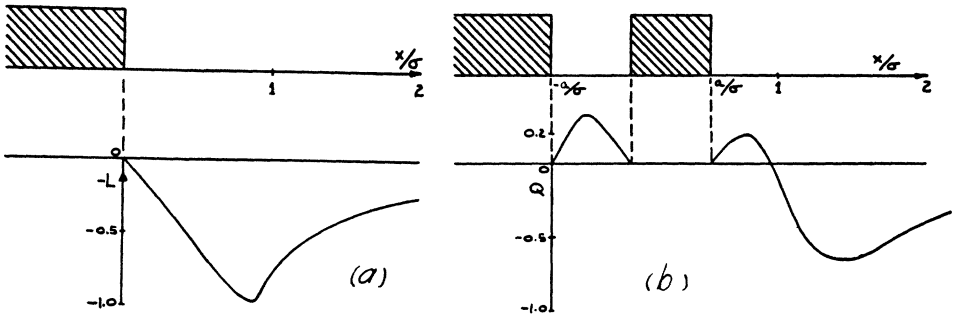

FIG. 1. (a) The energy required to remove an electron from the surface of a normal f_0 distribution ($\propto -L$). (b) The same for the f_1 distribution ($\propto Q$). Occupied x-values are indicated by shading.

tractive) otherwise. This tends to concentrate electrons into similar direction of motion provided $(y-x)^2<\sigma_0^2$.

Before evaluating the above expressions a word should be said about the use of perturbation theory. The denominator in the sums in equation (2.12) will vanish for certain values of $\mathbf{q}$ and $\mathbf{k}$. Integration can, however, always be carried out if principal values are used, and the final expressions converge. A vanishing denominator means that in zero order of approximation a transition into a different $f_\mathbf{k}$ distribution would be possible from an energetic point of view. Taking the energy in second order, however, these transitions are excluded energetically for the distribution with the lowest energy. For this case perturbation theory should be expected to yield reasonably good results. The same should be expected of metastable $f_\mathbf{k}$ distributions where no energy can be gained by shifting a few electrons only into different k-values.

III. INTEGRATIONS

In the present section the integrations required for the calculation of the energy will be carried out, but all essential discussions of the consequences are left to the next section. Since all important contributions to expressions (2.23) and (2.24) come from very small x- and y-values we can use the approximation $k^2dk=k_0^2dk$. Hence the transformation from sum to integral is

$$\sum_\mathbf{k}\{\cdots\}=[Vk_0^2/(2\pi)^3]\int dxd\cos\theta_k d\varphi_k\{\cdots\}. \quad (3.1)$$

In expression (2.23) for S_1, where $f_0(x)$ is independent of θ_k and φ_k one can use $\mathbf{q}$ as axis if the $\mathbf{k}$-integration is carried out first. Then with

$$u=\sigma_0\sin\theta/2, \quad (3.2)$$

one finds (see (2.25))

$$\sum_k \psi f_0(x)=[4k_0^2V/(2\pi)^2\sigma_0^2]\int_{-k_0}^{0}dx\int_0^\sigma \psi u du. \quad (3.3)$$

Since θ is the angle between $\mathbf{k}$ and $\mathbf{q}=\mathbf{k}-\mathbf{w}$ the upper limit σ is σ_0 if $w_0>2k_0$. Usually, however, $2k_0>w_0$ and the range of θ has then to be restricted so that $\sigma=\sigma_0 w_0/2k_0$, or using (2.1), (2.3) and (2.5)

$$\begin{aligned}&\sigma_0^3/\sigma^3=4n_{el}/n=4\nu, \text{ if } (4\nu>1);\\ &\sigma_0^3/\sigma^3=1 \text{ otherwise.}\end{aligned} \quad (3.4)$$

Normally this would influence the limits in the radial integrations, but in our case of a very small range the effect of this is negligible. Then with the use of[4] (2.25)

$$\begin{aligned}-\int_\alpha^\beta dx\int_0^\sigma \psi u du&=-\int_\alpha^\beta dx\int_0^\sigma \frac{2u^3du}{(y-x)^2-u^2}\\ &=\int_\alpha^\beta\left[\sigma^2+(y-x)^2\ln\left(1-\frac{\sigma^2}{(y-x)^2}\right)\right]dx\\ &=\frac{1}{3}\Big[\sigma^2x+(x-y)^3\ln\left(1-\frac{\sigma^2}{(y-x)^2}\right)\\ &\qquad -\sigma^3\ln\frac{k-y-\sigma}{x-y+\sigma}\Big]_{x=\alpha}^{\beta}, \end{aligned} \quad (3.5)$$

if $\beta=0$ and $\alpha=-k_0(\to-\infty)$ are used. Thus

$$-\sum_\mathbf{q} f(y)\sum_\mathbf{k} f_0(x)\psi=-\frac{4k_0^2V\sigma^3}{(2\pi)^2\sigma_0^2}\sum_\eta L(y)f(y), \quad (3.6)$$

where

$$L(y)=\frac{1}{3}\left\{\frac{y}{\sigma}+\frac{y^3}{\sigma^3}\ln\left(1-\frac{\sigma^2}{y^2}\right)+\ln\left(\frac{y+\sigma}{y-\sigma}\right)\right\}. \quad (3.7)$$

It follows from (2.23) that $-L(y)$ gives the y-dependence of the interaction energy when removing an electron a distance y from the k_0 surface. From Fig. 1a it is seen to be negative, thus tending to expel electrons from the surface. We shall therefore now calculate the change S of energy when all electrons in the shell between $x=-a$ and $x=0$ are moved outward into the shell between $x=0$ and $x=a$, as shown in Fig. 2a. Thus

$$f(x)=-1 \text{ if } -a\le x\le 0; \quad f(x)=1 \text{ if } 0\le x\le a. \quad (3.8)$$

It will be noticed then that

$$\begin{aligned}\int_{-a}^{a}\psi f(x)dx&=\left(-\int_{-a}^{0}+\int_0^a\right)\psi dx\\ &=\left(\int_0^a+\int_0^{-a}\right)\psi dx \end{aligned} \quad (3.9)$$

[4] Absolute values of the arguments of the logarithmic function are always to be used.

holds. Since the angular integration can be carried out as for S, we require again the integral (3.5) but with the limits α and β as indicated by (3.9). Thus from (2.24), similar to (3.6), we require

$$-\frac{1}{2}\sum_{\mathbf{q}} f(y)\sum_{\mathbf{k}} f(x)\psi=+\frac{4k_0^2V}{(2\pi)^2}\frac{\sigma^3}{\sigma_0^2}\sum_{\mathbf{q}} J(y)f(y) \quad (3.10)$$

where

$$J(y)=\frac{1}{3}\Big\{-\frac{1}{2}\frac{(y-a)^3}{\sigma^3}\ln\Big(1-\frac{\sigma^2}{(y-a)^2}\Big)-\frac{1}{2}\frac{(y+a)^3}{\sigma^3}\ln\Big(1-\frac{\sigma^2}{(y+a)^2}\Big)-\frac{1}{2}\ln\frac{(y+\sigma)^2-a^2}{(y-\sigma)^2-a^2}+y^3\ln\Big(1-\frac{\sigma^2}{y^2}\Big)+\ln\Big(\frac{y+\sigma}{y-\sigma}\Big)\Big\}. \quad (3.11)$$

Angular integration in the now remaining $\mathbf{q}$-integration yields 4π, as there are no angular dependent terms left. Then with the help of (3.1) and with (3.8) and (3.6),

$$-\sum_{\mathbf{q}}\sum_{\mathbf{k}} f(y)(f_0(x)+\tfrac{1}{2}f(x))\psi$$
$$=-2[2k_0^2V/(2\pi)^2]^2(\sigma^4/\sigma_0^2)\int[L(y)-J(y)]dy/\sigma \quad (3.12)$$

with the same integration limits as in (3.9). The value of this integral is

$$P(\xi)=\tfrac{1}{3}\Big\{\tfrac{1}{2}\xi+\tfrac{3}{4}\ln(1-4\xi)-\tfrac{3}{2}\ln(1-\xi)+4\xi^2\ln\Big(1-\frac{1}{4\xi}\Big)-\frac{1}{2}\xi^2\ln\Big(1-\frac{1}{\xi}\Big)+2\sqrt{\xi}\ln\frac{1+2\sqrt{\xi}}{1-2\sqrt{\xi}}\frac{1-\sqrt{\xi}}{1+\sqrt{\xi}}\Big\}, \quad (3.13)$$

where

$$\xi=a^2/\sigma^2. \quad (3.14)$$

Hence by inserting (3.12) into (2.23) and (2.24)

$$S_1+S_2=-\frac{16F\zeta}{3n}2\Big(\frac{2k_0^2}{(2\pi)^2}\Big)^2\frac{\sigma^4}{\sigma_0^2}P(\xi). \quad (3.15)$$

Integration of expression (2.26) for S_3 is straightforward using (3.8). It yields

$$S_3=(4\zeta/k_0)(2k_0^2/(2\pi)^2)\sigma^2\xi. \quad (3.16)$$

By making use of Eqs. (2.1), (3.4), and (2.7) we obtain the total energy S from (2.22), (3.15) and (3.16), (per unit volume)

$$S=S(\xi)=\frac{3}{2}\frac{ms^2n_{el}}{\nu^{\frac{1}{2}}2^{\frac{1}{2}}}[-F(4\nu)^{\frac{1}{2}}P(\xi)+\xi]$$
$$[=3ms^2n_{el}(-4\nu FP(\xi)+\xi),\ \text{if } 4\nu<1]. \quad (3.17)$$

From Fig. 3 it will be seen that $S_1+S_2\propto -P(\xi)$ has a minimum at $\xi=\xi_0$, with

$$\xi_0=0.3, \quad \text{or} \quad \frac{a_0}{\sigma}=\sqrt{0.3}\simeq 0.55. \quad (3.18)$$

Also since $P(\xi)=\xi$ if $\xi\ll 0.3$, the total energy has a minimum only if

$$(4\nu)^{\frac{1}{2}}F>1; \quad [4\nu F>1, \text{ if } 4\nu<1]. \quad (3.19)$$

If this important condition is fulfilled then the distribution (Fig. 2a)

$$f_1(x)=f_0(x)+f(x) \quad (3.20)$$

has a lower energy than the $f_0(x)$ distribution.

We shall now calculate the energy required to remove an electron from the $f_1(x)$ distribution. This implies replacement of $f_0(x)$ in (2.23) by $f_1(x)$. The same integration as that leading to (3.6) has to be carried out but with x-limits $-k_0\leq x\leq -a$ and $0\leq x\leq a$. Inserting these limits into (3.5) we find

$$-\sum_{\mathbf{k}} f_1(x)\psi=+(4k_0^2V\sigma^3/(2\pi)^2\sigma_0^2)Q(y), \quad (3.21)$$

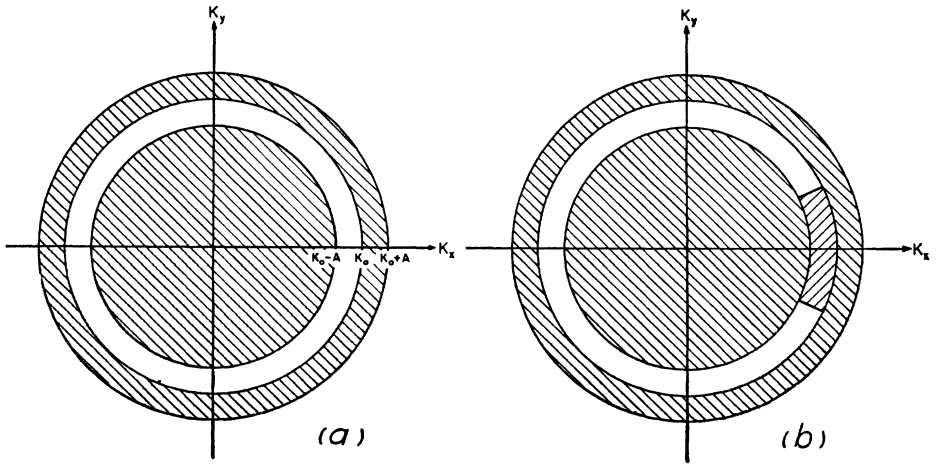

FIG. 2. (a) Distribution of electrons of a superconductor in $\mathbf{k}$-space, ground state. (b) Distribution in a nonsymmetrical excited state.

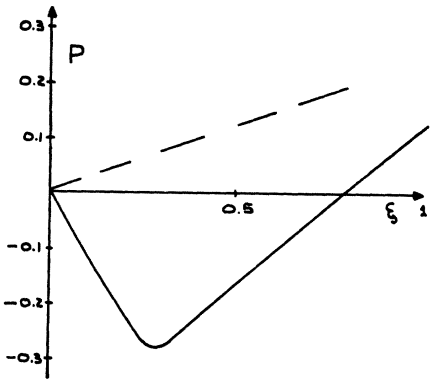

FIG. 3. Energy of an f_1 distribution as a function of gap width.

where

$$Q(y)=\frac{1}{3}\left\{-\frac{y}{\sigma}+\frac{y^3}{\sigma^3}\ln\left(1-\frac{\sigma^2}{y^2}\right)-\frac{(y+a)^3}{\sigma^3}\ln\left(1-\frac{\sigma^2}{(y+a)^2}\right)-\frac{(y-a)^3}{\sigma^3}\ln\left(1-\frac{\sigma^2}{(y-a)^2}\right)-\ln\frac{(y+a)^2-\sigma^2}{(y-a)^2-\sigma^2}\right\}. \quad (3.22)$$

Since

$$\frac{dP}{d\xi}=\frac{1}{3}\left\{1+8\xi\ln\left(1-\frac{1}{4\xi}\right)-\xi\ln\left(1-\frac{1}{\xi}\right)+\frac{1}{\sqrt{\xi}}\ln\frac{1+2\sqrt{\xi}}{1-2\sqrt{\xi}}\frac{1-\sqrt{\xi}}{1+\sqrt{\xi}}\right\} \quad (3.23)$$

it will be seen that $Q(0)=Q(a)=Q(-a)=0$ if $\xi=\xi_0$. Also, in contrast to the $f_0(x)$ distribution, energy must now be spent to remove an electron from either of the surfaces as is shown in Fig. 1b. Beyond a certain distance outward from the outer surface the function $Q(y)$ decreases again, reaches a minimum and then approaches zero. In this latter part it thus behaves similar to $-L(y)$, but its minimum is not so deep as that of $-L(y)$ (ratio 2:3). Also, since it is separated by a potential hill from occupied levels so that relatively more zero order energy must be spent to move electrons from the f_1 distribution than was required to move them from the f_0 distribution. For simplicity we shall consider only cases in which either the f_0 or the f_1 distribution is that with lowest energy. If this is not the case then f_2, f_3, $\cdots$ distributions must be constructed with 2, 3 or more shells until stability is reached. This would of course lead to an increase in the magnitude of the total energy $|S|$ over the value (3.17) by a factor $G\gtrsim 1$. I should expect that at most G is of the order $(4\nu)^{\frac{1}{4}}F$. The existence of more than one shell does not alter condition (3.19), however, because this is the condition that f_1 has a lower energy than f_0.

Excited States

If the f_1 distribution leads to the lowest energy state, then distributions with a different sized single shell exist which are stable in the sense that energy must be expended to remove single electrons. In these distributions the gap and the shell are no longer of equal width and they have a higher energy than the distribution with equal width. They can be obtained from the original f_1 distribution by adding to (or removing from) the surfaces thin (compared with a) spherically symmetrical layers. The interaction $A(y-x)$ of such a layer at x with a single electron at y is proportional to expression (3.5) with $|\beta-\alpha|\ll a$, so that except for a numerical factor of order unity,

$$A(y-x)=\frac{16F\zeta}{3n}\left[1+\frac{(y-x)^2}{\sigma^2}\ln\left(1-\frac{\sigma^2}{(y-x)^2}\right)\right]t, \quad (3.24)$$

where t is the number of electrons contained in the layer. $A(y-x)$ is an even function of $(y-x)$, and is positive nearly up to $y-x\simeq\sigma$. The existence of these excited states can easily be proved. Let A_0t, A_1t and A_2t be the values of $A(y-x)$ at distance $y-x=0$, $\pm a$, $\pm 2a$, respectively. Also let the number of electrons in the three layers deposited on the three surfaces $(x=-a, 0, a)$ be z_1, z_2, z_3, respectively. We then require that the total change of interaction B with a single electron is the same near each of the three surfaces. This requires that

$$(A'+A_0)z_1+A_1z_2+A_2z_3=B \quad (3.25a)$$

for the surface $x=-a$, and similarly

$$A_1z_1+(A'+A_0)z_2+A_1z_3=B \quad (3.25b)$$

and

$$A_2z_1+A_1z_2+(A'+A_0)z_3=B, \quad (3.25c)$$

where A' is the change of interaction energy of an electron with the rest of the electrons (S_1-type). This quantity is determined by the slope of the function $Q(y)$ (3.22) which through (3.21) and (2.23) gives the required change of energy. This function behaves near each surface y_0 approximately as $2(y-y_0)/3a$ as can be seen from Fig. 1b. Also according to (3.1) the number of electrons in a shell of width $y-y_0$ is $8\pi k_0^2(y-y_0)/(2\pi)^3$. Thus

$$A'\simeq\frac{16F\zeta}{3n}\frac{1}{2}\frac{\sigma^2}{a\sigma_2}t\simeq\frac{16F\zeta}{3n}\frac{t}{2}, \quad (3.26)$$

where Eq. (3.4) has been used and $\nu=1$, $a^2/\sigma^2=0.3$ have been assumed. Inserting this value for a^2/σ^2 in (3.24) solution of (3.25) yields

$$z_1=z_3,\quad z_2/z_1=1+\frac{A_2-A_1}{A_0+A'-A_1}\simeq-9z_1. \quad (3.27)$$

Clearly if we start in the ground state these

$$\Delta z = z_1 + z_2 + z_3 = -7z_1 \tag{3.28}$$

electrons must be removed from the surfaces and placed in a different way. One possibility which will be of importance when dealing with higher temperatures is to put them out of the range of forces near the surfaces. The other case leaving them near the surfaces leads to cluster formation as will be shown presently. In both cases the total change in energy is composed of the contribution R_0 connected with removal from the surfaces, and R the contribution due to replacing the electrons. The value of R_0 is independent of the way of replacing the electrons because with (3.25) to (3.27)

$$R_0 = \tfrac{1}{2}(A_0 + A' - 9A_1 + A_2) z_1 \Delta z \simeq \frac{16F\zeta}{3n} (\Delta z)^2. \tag{3.29}$$

Non Symmetrical States*

In contrast to $S(\xi)$, the following calculations [as (3.29)] are intended to be accurate only up to a numerical factor of order one. Assume now the Δz electrons to be equally distributed over the whole (or a fraction) of the width of the gap, but let $\Delta z < z$ where (see (2.1))

$$z = 4k_0^2 a/(2\pi)^2 = 3n_{el}(a/k_0) \tag{3.30}$$

is the number of places available in the gap. Assume first that the distribution is spherically symmetrical. Then in contrast to all previously discussed distributions the average occupation number per level is neither zero nor unity, but $\Delta z/z < 1$. We shall now show that the angular dependence of the ψ interaction tends to concentrate the electrons into as small a volume as is compatible with the Pauli principle. The energy contribution R of such a distribution $g(x)$ is obtained from S (see (2.23), (2.24) and (2.26)) by replacing the distributions $f_0(x)$ and $f(x)$ by $f_1(x)$ and $g(x)$. The only term depending on the angular distribution is obtained from S_2 and will now be denoted as

$$R_2 = -(16F\zeta/3n)\tfrac{1}{2} \sum_{\mathbf{q}} g(y) \sum_{\mathbf{k}} g(x)\psi. \tag{3.31}$$

For simplicity assume $g(x)$ to be independent of x. We then require

$$-\frac{1}{2} \sum_{\mathbf{q}} \sum_{\mathbf{k}} g(y)g(x)\psi = \frac{1}{2}\left(\frac{z}{4a}\frac{1}{2\pi}\right)^2 \int d\cos\theta_k d\cos\theta_q d\varphi_k d\varphi_q \times \int_0^a dxdy \frac{(-2)u^2}{(y-x)^2 - u^2}. \tag{3.32}$$

* Not required for the discussion of the ground state.

The x, y integration yields

$$-\int_0^a \frac{2u}{(y-x)^2-u^2} dxdy = 2u^2 \ln\left(1 - \frac{a^2}{u^2}\right) - 2au \ln\left(\frac{u-a}{u+a}\right) \simeq 2 \times 1.6ua \text{ if } u < 0.9a. \tag{3.33}$$

By inspection it is found that the exact expression approximately rises as $2\times 1.6ua$ up to $u \simeq 0.9a$ then decreases and approaches $2a^2$ as $u > a$. There is thus a tendency to concentrate electrons into as narrow an angular range as permissible by the Pauli principle. This can be verified by calculating the energy for such a distribution $g(x)$ as a function of its angular spread γ. Let thus $g(x)$ be constant in the range $0 \leq \theta \leq \theta_1$ and define

$$\gamma = \frac{1}{2}\int_{\cos\theta_1}^{1} d\cos\theta = \frac{1}{2}(1 - \cos\theta_1) < 1. \tag{3.34}$$

Since according to (3.2), $u = \sigma_0 \sin\theta/2$ we shall require

$$\int_{1-2\gamma}^{1} d\cos\theta_k d\cos\theta_q \int_0^{2\pi} d\varphi_k d\varphi_q [1 - \cos\theta_k \cos\theta_q - \sin\theta_k \sin\theta_q \cos(\varphi_k - \varphi_q)]^{\frac{1}{2}} = (2\pi)^2(8/3)\gamma^3 \text{ if } \gamma < 1. \tag{3.35}$$

Then using the approximation $1.6ua$ in (3.33) which holds if $\gamma < a/\sigma$, we find with (3.31) to (3.35), and with $\Delta z = \gamma z$,

$$R_2 = (\Delta z)^2 \frac{\sigma_0}{a} 1.6 \times \frac{8}{3}\gamma \frac{16F\zeta}{3n} \simeq \frac{16F\zeta}{3n} 4(\Delta z)^2\gamma, \quad \text{if } \gamma < a/\sigma. \tag{3.36}$$

For constant particle number Δz, this expression thus decreases as the angular spread is reduced.

If we had assumed the distribution to extend only over a width $b \ll a$ instead of over the full gap width we would have found

$$\Delta z/z = b\gamma/a, \quad b \ll a. \tag{3.37}$$

In Eq. (3.33), a must then be replaced by b. With the use of (3.37), Eq. (3.36) is seen to obtain a factor a/b so that with a further use of (3.37)

$$R_2 = (16F\zeta/3n)4(\Delta z)^2\gamma a/b = (16F\zeta/3n)4z\Delta z\gamma^2. \tag{3.38}$$

The R_1 contribution corresponding to S_1 can be found in a similar way as A', (3.26). With the help of (2.23), (3.21) and (3.30) (using again $\nu = 1$, i.e. $\sigma^2/\sigma_0^2 \simeq 0.4$ and $a^2/\sigma^2 = 0.3$),

$$R_1 = (16F\zeta/3n)(\sigma^3/\sigma_0^2 a) z\Delta z\bar{Q} \simeq (16F\zeta/3n) z\Delta z\bar{Q}, \tag{3.39}$$

where $\bar{Q}$ is the average of $Q(y)$ (see (3.22) or Fig. 1b) over the occupied range. From Fig. 1b we see that

approximately (use (3.37))

$$\bar{Q}\simeq 0.2 \text{ if } b=a, \quad \bar{Q}\simeq b/2a=\Delta z/2z\gamma \text{ if } b\ll\tfrac{1}{2}a. \quad (3.40)$$

Finally the R_3 contributions, corresponding to S_3 are of the same type as R_1. They lead to a factor $(1\pm 1/(4\nu)^{\frac{1}{2}}F)$ if $b<a$ (+ near the lower, − near the upper surface) and thus vanish on an average. For $b=a$, R_1 vanishes exactly. Thus with (3.29), (3.36), (3.38) and (3.39) the total energy required to form the cluster of Δz electrons is

$$R=R_0+R_1+R_2\simeq(16F\zeta/3n)(\Delta z)^2\chi, \quad (3.41)$$

where χ is a factor depending on the shape. In particular (see 3.40)

$$\chi=1+(4\gamma^2 z/\Delta z)+(1/2\gamma) \text{ if } b\ll a \quad (3.42)$$

and

$$\chi=1+4\gamma+z/\Delta z=1+(4\Delta z/z)+z/\Delta z \text{ if } b=a. \quad (3.43)$$

It will be noticed that if $b\ll a$, R has a minimum for given Δz when $16\gamma^3=\Delta z/z$ or using (3.37) when $16\gamma^2=b/a$. But if b becomes larger, then the value of γ leading to the smallest value for R is $\gamma=\Delta z/z$.

Establishment of a cluster in the gap leads to a change of the energy of an electron near the outer surface by approximately (see (2.25))

$$-\frac{16F\zeta}{3n}\Delta z\frac{\sigma_0^2\sin^2\bar{\theta}/2}{(3a/2)^2-\sigma_0^2\sin^2\bar{\theta}/2} \quad (3.44)$$

if $\bar{\theta}$ is its average angle with the position of the cluster, and $3a/2$ its average distance. This quantity is negative (attractive) if

$$\sin\bar{\theta}/2<3a/2\sigma_0\simeq\tfrac{1}{2}. \quad (3.45)$$

Some energy can be gained therefore by removing a fraction of the Δz electrons to the outer surface within an angle $\bar{\theta}$. This will not change appreciably the energy R; in the form (3.41) for R it only leads to a slightly different definition of the form factor χ.

It might be expected that if $\Delta z/z\ll 1$ the form factor χ should be independent of Δz for the shape at which R has its minimum, so that $R\propto(\Delta z)^2$. That this is not true for the two cases (3.42) and (3.43) shows that we have not found the best shape. In fact one should hardly expect that this shape has sharp edges as have our models. Improvements will decrease the energy R_1+R_2; but since R_0 is independent of shape, always $\chi>1$. Equation (3.41) therefore represents the correct order of the energy R.

IV. DISCUSSION OF THE ENERGY

The results of the calculations of the previous section are based on the interaction energy $-\psi$ in k-space [Eq. (2.25)]. This quantity exhibits two tendencies as can also be seen from Fig. 4: for small energy difference $[(x-y)^2<\sigma^2]$ it tends to concentrate electrons into a narrow angular range in $\mathbf{k}$-space. If this is impossible because all states are filled then the second tendency comes into play. It attempts to place electrons at distances of the order $x-y=\sigma$. In fact by averaging $-\psi$ over the angles we obtain, as in (3.5),

$$-\bar{\psi}=1+((y-x)^2/\sigma^2)\ln[1-\sigma^2/(y-x)^2]. \quad (4.1)$$

As can be seen from Fig. 5 this function is positive nearly up to σ, has a (negative) minimum just beyond it and then approaches zero.

For a first orientation on the influence of interaction on the distribution function it is useful to see that according to Eqs. (3.6) and (3.7), or to Fig. 1a, interaction energy can be gained by removing an electron from the surface of a normal (Fermi) distribution f_0. This suggests calculation of the change $S_1(\xi)+S_2(\xi)$ of interaction energy when a shell of width a is shifted outward from the surface leaving a gap of width a as shown in Fig. 2a. The change of interaction energy due to the establishment of this distribution depends on the interaction parameter $\xi=a^2/\sigma^2$ (see Eq. (3.13) and (3.14)) as illustrated in Fig. 3. It has a minimum at $\xi=\xi_0\simeq 0.3$. Zero order energy $S_3(\xi)$ on the other hand increases linearly with ξ as indicated by the dotted line. It follows that the total change in energy $S(\xi)$, [Eq. (3.17)] has a minimum only if condition (3.19) is fulfilled. Otherwise no minimum exists and the f_0 distribution remains stable. Again as before we can now investigate the change in interaction energy when a single electron is removed from one of the surfaces. Figure 1b drawn according to Eq. (3.22) shows the result if $\xi=\xi_0=0.3$. In contrast to the f_0 distribution the energy of interaction now increases near the surfaces. At a larger distance from the outer surface, however, a similar decrease to that found near the f_0 surface is repeated; again interaction energy can be gained when removing an electron from the surface to the minimum. But now the depth of the minimum is only about $\frac{2}{3}$ of what it was in the f_0 case, and the distance from the surface is larger by a factor two, approximately. Therefore the increase in zero order energy when removing an electron from the surface is larger than in the f_0 case. If the interaction parameter F (see (2.9)) is very large, removal of a second shell (f_2 distribution) from the surface may lead to a further decrease in total energy. We shall assume here that this is not the case. Its main effect would be to increase the magnitude of the total energy $S(\xi)$ by a factor smaller than two.

If condition (3.19) is not fulfilled little doubt can exist that in the approximation used here the f_0 distribution (normal state) has the lowest energy. If however (3.19) is fulfilled, then on the assumptions made it seems likely that the f_1 distribution leads to the lowest energy. A general proof has not been attempted, however, and would probably be very difficult.

In metals for which the f_0 distribution forms the lowest state excited states must exist in which electrons from near the surface are moved to higher energies similar to the case in which the interaction is neglected completely. It should be expected then that when the

thermal energy of the electrons is larger than S, ($\xi \simeq \xi_0$), these metals behave as in zero order, but that below this temperature deviations of a quantitative but not qualitative nature occur.

In case the f_1 distribution forms the lowest state there will also be excited states in which single electrons have been removed from the surfaces. This alters the energy and gap width of the remaining f_1 distribution as discussed in connection with Eq. (3.25). One should again expect that at temperatures sufficiently high, the metal behaves as in zero order. Below this temperature, however, changes of a qualitative nature occur because of the qualitative difference between the f_1 and f_0 distributions.

It was not intended in the present paper to deal quantitatively with excited states required for questions of temperature dependence. Another type of excited states may be of importance, however, even at the absolute zero of temperature. In these states denoted in Sec. III as non-symmetrical states electrons are clustered in the gap of the f_1 distribution as shown in Fig. 2b (or possibly near the outer surface). The energy of such a cluster was found in Sec. III by minimizing the energy, and it can be seen then that it is stable in the sense that energy must be expended to divide it into smaller parts or to remove single electrons. To return to the ground state would require, therefore, that the cluster be first dissolved. This would be impossible by processes acting on single electrons like scattering on lattice imperfections. In view of this stability the number Δz of electrons contained in the cluster which according to Eq. (3.41) determines its energy can be used as a parameter of the system. Then from (3.41) and (3.17) the total energy per unit volume is given by

$$S(\xi)+R(\Delta z)=S(\xi)+(16F\zeta/3n)\chi(\Delta z)^2. \quad (4.2)$$

The formation of stable clusters can be understood in a qualitative way immediately from the interaction $-\psi$ [Eq. (2.25) and Figs. 4 and 5]. This interaction tends to concentrate electrons within the gap as far as is permissible by the Pauli principle. The opposite tendency, dispersal over all angles, would manifest itself only at sufficiently high energy differences requiring $(x-y)^2>\sigma_0^2$, and would thus require energy. The most important energy term (R_2) leading to cluster formation is derived from S_2 in Eq. (2.24) by replacing there the distribution $f(x)$ by the distribution function $g(x)$ of the cluster, according to (3.31). This term which might be denoted as the self-energy of the cluster is proportional to $(\Delta z)^2$, and to the average value $-\langle\psi\rangle_{Av}$ obtained by averaging the interaction $-\psi$ between two electrons in $\mathbf{k}$-space for both electrons over the cluster. Then consider two limiting cases on the assumption that Δz is very small: (i) a spherically symmetrical distribution in which the electrons fill a very thin shell. Then from (4.1), $-\langle\psi\rangle_{Av}=1$ if Δz is so small that the width of the shell is small compared with σ_0. On the other hand for a thin needle in radial direction $\langle\sin^2\theta/2\rangle_{Av}\to 0$ and $\langle(x-y)^2\rangle_{Av}\to\infty$ so that $-\langle\psi\rangle_{Av}\to 0$, showing that the needle shaped cluster has the lower self-energy. Other energy terms, however, behave in the opposite way and the result is a more regularly shaped cluster.

Finally it should be mentioned that the establishment of a stable configuration can also be understood in terms of the spontaneous transitions of electrons connected with the emission of lattice quanta. Whenever such transitions are possible, occupation of the final states by electrons leads to a decrease in ψ-interaction energy. On the other hand, it can be seen from Fig. 4 that once a cluster has been formed in the gap, transitions into other directions within the gap would require energy. Thus changes due to transitions will not spread the cluster over the gap.

It should also be pointed out here that the change from a f_0 to a f_1 distribution leads to an alteration of the distance correlation of two electrons in ordinary space. Its main effect is to increase the probability of finding two electrons at a distance smaller than $1/a$. The decrease in interaction is understandable in an elementary way because one electron can benefit from the lattice deformation produced by another one if it remains sufficiently close (in ordinary space) to it.

V. REMARK ON THE ELECTRODYNAMIC PROPERTIES

In Secs. III and IV it has been shown that in metals in which the f_1 distribution is realized in the ground state stable non-symmetrical states exist which lead to cluster formation in $\mathbf{k}$-space. In these clusters a number Δz of electrons move in a similar direction giving thus rise to an electric current in the absence of an electric field. We shall therefore identify the f_1 distribution with the superconducting state. It should be remembered that according to Eq. (4.2) the energy of these current carrying states is higher than the ground level by a term proportional to $(\Delta z)^2$.

The existence of such stable currents has often been postulated as an alternative phenomenological hypothesis to postulation of the London equations[5] and had first thought that the two are closely related. For if we assume clusters of a very small size so that all electrons move practically in the same direction with velocity $\hbar k_0/m$ the density of the electric current is

$$j=(e\hbar k_0/m)\Delta z. \quad (5.1)$$

Inserting from here into Eq. (4.2) with the use of (2.2), the energy per unit volume is found as

$$S(\xi)+\tfrac{1}{2}\lambda j^2, \quad (5.2)$$

where

$$\lambda=(16F\chi/3)(m/e^2n). \quad (5.3)$$

From our discussion at the end of Sec. III it seemed likely that for small Δz the form factor χ is independent

[5] F. and H. London, Proc. Roy. Soc. **A149**, 71 (1935); also M. von Laue, Theorie der Supraleitung (Springer, 1947).

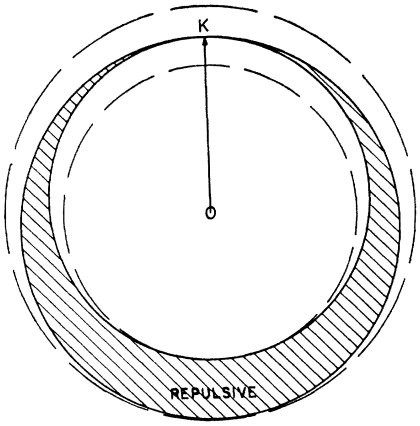

FIG. 4. The $-\psi$ interaction in $\mathbf{k}$-space. It is repulsive between an electron in the shaded region and the electron $\mathbf{k}$. Otherwise it is attractive. At the boundary it is singular.

of Δz and hence of j. Also $\chi \gtrsim 1$ and hence since condition (3.19) must be fulfilled,

$$16F\chi/3>4. \tag{5.4}$$

It must now be remembered that we have not yet taken account of the magnetic interaction energy between electrons connected with the current. Tentatively this might be done macroscopically by adding a term $H^2/8\pi$ representing the energy of the magnetic field H, where

$$\text{curl}\mathbf{H}=4\pi\mathbf{j}/c, \quad \text{div}\mathbf{H}=0. \tag{5.5}$$

Thus with (5.2) the total energy per unit volume is

$$U=U_0+S(\xi)+\frac{1}{2}\lambda j^2+\frac{H^2}{8\pi} \tag{5.6}$$

The existence of an energy term proportional to j^2, in addition to the H^2 term is characteristic of the London equations. The term U_0 represents the energy of the normal state, and $S(\xi)$ it will be remembered is the energy difference between the superconducting and the normal state in the absence of a current.

The above outlined procedure holds only for very thin layers, however, where the magnetic interaction is very small. Otherwise (5.1) becomes invalid. It will then be necessary to introduce the magnetic field at an earlier stage. (See *Notes added in proof.*)

VI. COMPARISON WITH EXPERIMENTS

The calculations of the previous sections were based on a free electron model. According to the electron theory of metals, permitted energy levels have a band structure. When such an energy band is not too highly filled the free electron model is sound. On the other hand, when a band is nearly filled a similar model applies if holes (empty levels) instead of electrons are considered. It can easily be seen that in this case all our previous results hold. For by introducing a hole distribution function $h_\mathbf{k}=1-f_\mathbf{k}$ we find that in our basic expression (2.11) we replace $f_\mathbf{k}(1-f_\mathbf{q})$ by $h_\mathbf{q}(1-h_\mathbf{k})$ thus interchanging k and q. In going to Eq. (2.12) the same interchange has to be carried out in the denominator, thus leaving the whole expression unaltered. From the experience gained in the theory of metals it appears that our calculations should apply reasonably well to most metals except for the transition metals and metals of the Bi group.

The Condition for Superconductivity

It has been assumed in the previous sections that in superconductors the distribution in the ground state is of the f_1 type shown in Fig. 2a. This condition is realized if the interaction between the electrons and the vibrational field is sufficiently strong to fulfill condition (3.19). Using (2.9),

$$(4\nu)^{\frac{1}{3}}F=(4\nu)^{\frac{1}{3}}C^2/3\zeta Ms^2>1, \quad (\text{if } 4\nu<1) \tag{6.1}$$

is thus the condition which must be fulfilled by a metal to make it a superconductor. Since the required strong interaction also leads to high normal resistivity ρ at high temperatures T where $\rho \propto T$ one should expect that condition (6.1) can be written in terms of ρ. In fact it is found that[6]

$$KT/\rho=(4\nu M/\pi^3 m)(\zeta/C)^2(K\theta_l)^2/k_0\hbar a_0, \tag{6.2}$$

where a_0 is the Bohr radius. By using the identities expressed by Eqs. (2.4), (2.3), (2.2), and (2.1), together with the definition of the number ν of free electrons per atom we obtained

$$KT/\rho=(12\nu^{4/3}/2^{\frac{1}{3}}\pi)(\hbar^3/m^2a_0)(Ms^2\zeta/C^2)n. \tag{6.3}$$

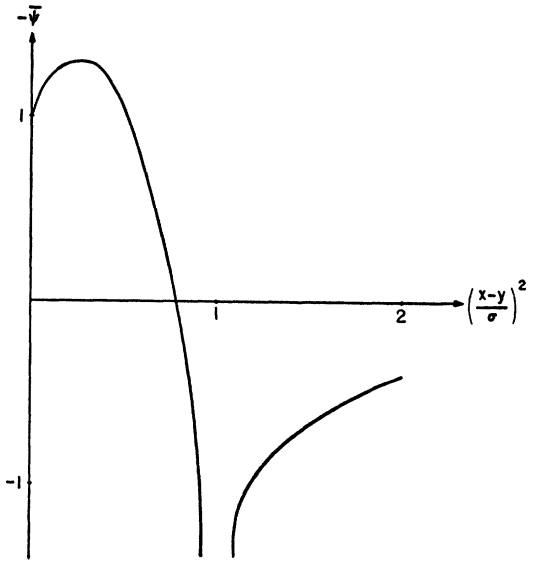

FIG. 5. Angular average $-\bar{\psi}$ of the $-\psi$ interaction.

[6] See Eq. (36.12) of reference 3. Replace there $(K_0 dE/dK_0)^2$ by $4\zeta^2$, n_0 by ν, θ by θ_l and k by K.

TABLE I. Data for normal metals.

Normal	Li	Na	K	Rb	Cs	Cu	Ag	Au	Be	Mg	Ca	Sr	Ba
$n\times10^{22}$ (cm^{-3})	4.63	2.56	1.33	1.08	0.87	8.50	5.90	5.93	12.5	4.34	2.33	1.80	1.59
ρ^{-1}(Ω^{-1} cm^{-1}, 273°)	12	24	16	8.6	5.6	65	67	49	18	25	24	3.3	1.7
$4^{\frac{1}{3}}F$	2.2	0.60	0.47	0.71	0.88	0.74	0.50	0.68	4.0	1.0	0.55	3.1	5.3

TABLE II. Data for superconducting metals.

Superconducting	Zn	Cd	Hg	Al	Ga	In	Tl	Sn	Pb
n	6.60	4.66	4.40	6.06	5.13	3.86	3.52	3.74	3.32
ρ^{-1}	18	15	4.4	34	1.9	12	7.1	10	5.2
$4^{\frac{1}{3}}F$	2.1	1.8	5.6	1.0	15	1.7	2.8	2.1	3.6

Consequently condition (6.1) becomes

$$(4\nu)^{\frac{1}{3}}F=(\rho n\nu^{5/3}/KT)D, \tag{6.4}$$

where

$$D=(2^{\frac{1}{3}}\times4/\pi)(\hbar^3/m^2a_0) \tag{6.5}$$

is a universal constant. The simplest way to find F for various metals is to take one metal, say silver, as a standard. Here according to Bethe[3] (p. 524), $(C/\zeta)_{Ag}=1.2$. Furthermore, from (2.2) and (2.1), $\zeta_{Ag}=5.5$ ev is obtained with $\nu=1$ (which follows from optical and Hall effect measurements). With the value $s=2.7\times10^5$ cm/sec. for the velocity of sound, and $\nu=1$ we find according to (6.1),

$$4^{\frac{1}{3}}F_{Ag}=(4^{\frac{1}{3}}/3)(C^2/\zeta Ms^2)_{Ag}=0.50<1, \tag{6.6}$$

which shows that silver does not fulfill the condition for superconductivity. With this value we can now express the condition (6.4) for superconductivity in the form

$$(4\nu)^{\frac{1}{3}}F=4^{\frac{1}{3}}F_{Ag}(\rho n\nu^{5/3}/\rho_{Ag}n_{Ag})$$
$$=0.50(\rho n/\rho_{Ag}n_{Ag})\nu^{5/3}>1. \tag{6.7}$$

In this condition the only quantity that brings some uncertainty is the number ν of free electrons per atom. This number is for most metals (not only for monovalent ones) of the order $\nu=1$ although accurate values are difficult to obtain. Tables I and II show the striking result that for none of the superconductors is $4^{\frac{1}{3}}F$ smaller than unity, and only for four (Li, Be, Sr, Ba) of thirteen normal metals is it larger than unity. It is of interest to see that this quantity is small for alkali metals because of their small value for n, but for noble metals because of their low resistivity. It should not be forgotten, however, that the uncertainty of the number ν of free electrons per atom reflects on the above results. Furthermore, the resistivity at 273° abs. used in the tables need not in all cases be in the high temperature range where $\rho\propto T$. It may also happen that electrons fill two energy bands, only one of which goes into the superconductive state. In this case (6.7) would be invalid. Finally, it should be of interest to see how the superconductivity condition (6.1) varies with the number of free electrons when other parameters are not altered. According to (2.1) and (2.2), $\zeta\propto n_{el}^{\frac{2}{3}}$. Thus if ζ_0 is defined as the value of ζ if $n_{el}=n$ ($\nu=1$) then (6.1) becomes

$$(1/\nu^{\frac{1}{3}})(4^{\frac{1}{3}}C^2/3\zeta_0Ms^2)>1;\quad(4\nu>1). \tag{6.8}$$

This shows that to make a normal metal superconducting the number of free electrons per atom, ν, should be reduced, providing this can be done without reducing C^2/Ms^2. It seems likely that an effect of this type occurs when alloys of normal metals become superconductive. It suggests the formation of an alloy between a monovalent metal and a transition metal in such a way that most electrons of the monovalent metal are used to fill up the incomplete shell of the transition metal. This occurs, for example, in Pd-Au with up to 40 percent Pd, as has been shown by Mott;[7] but the variation of the other parameters should be taken into account before making definite predictions.

TABLE III. Critical magnetic fields for superconductors.

	s (cm/sec.)	H_c (theory) ($\nu=1$)	H_c (exp. extrapolated to $T=0$), (gauss)
Zn	3.7	4100	
Sn	2.6	2800	300
Pb	1.3	1700	800

Critical Magnetic Field

On application of a magnetic field larger than a critical field, H_c, a superconductor is transferred into the normal state. It is shown in the phenomenological theory[8] that this is a thermodynamic consequence of the magnetic properties, and that $H_c^2/8\pi$ is the difference between the free energies of the metal in the normal and in the superconducting state. This energy difference has been calculated in Sec. III, Eq. (3.17)

[7] N. F. Mott, Proc. Phys. Soc. London **47**, 571 (1935).
[8] C. J. Gorter and H. Casimir, Physica **1**, 306 (1934).

and is denoted by $-S(\xi)$. Thus at $T=0$, using $\nu=n_{el}/n$, and (2.9)

$$\frac{H_c^2}{8\pi}=\frac{3\times 4^{\frac{1}{3}}F}{2\times 2^{\frac{1}{3}}}ms^2n\nu^{\frac{1}{3}}\left[P(\xi)-\frac{\xi}{F(4\nu)^{\frac{1}{3}}}\right]$$

$$=\frac{C^2}{\zeta}\frac{m}{M}n_{el}\left[P(\xi)-\frac{\xi}{(4\nu)^{\frac{1}{3}}F}\right]. \tag{6.9}$$

The expression in the bracket refers to the value of ξ at which it has its minimum. Its value is always less than 0.3 as can be seen from Fig. 3. It is close to 0.15 for values of $(4^{\frac{1}{3}}F)=2$, but 0.2 if $(4^{\frac{1}{3}}F)=3.6$ (Pb). To find H_c requires only the root which for both values will be equated to 0.4 which involves an error of only 10 percent. Thus from (6.9)

$$H_c=2.2\times(4^{\frac{1}{3}}F)^{\frac{1}{2}}(nms^2)^{\frac{1}{2}}\nu^{\frac{1}{2}}. \tag{6.10}$$

Values of $4^{\frac{1}{3}}F$ and of n are given in Table II. With $\nu=1$, Table III shows values of the order of 1000 gauss in agreement with the magnitude obtained experimentally, though somewhat larger. It follows that the energy difference calculated in Sec. III has the correct absolute magnitude. Finer details would no doubt be very sensitive to deviations from the free electron model.

Notes added in proof: (1) The isotope effect [see Reynolds *et al.*, Phys. Rev. **78**, 487 (1950); Maxwell, Phys. Rev. **78**, 477 (1950)] which has recently come to my notice follows quantitatively from the proportionality of $|S|$ with the inverse isotopic mass $1/M$ [see e.g. Eq. (6.9) where F depends on Ms^2 only and is hence independent of the isotopic mass] as was stated in a recent note [Frölich, Proc. Phys. Soc. **A63**, 778 (1950)]. This agreement provides a direct check for the fundamental assumptions of the theory.

(2) Dr. Kun Huang has checked the integrations without making the approximations $(q-k)^2\ll k_0^2$. He confirmed the values for S_1 and S_2; but the repulsive energy S_3 has to be reduced by a factor two. We have also found that the change of Coulomb exchange energy provides a further repulsive term; together with S_3 it leads approximately to a total increase in repulsive terms by a factor three. This reduces all F values of the table by about a factor 3 and thus does not essentially alter the conclusions. It reduces H_c for lead to about 1200 gauss thus improving the agreement with experiment.

(3) I have now been able to show that the assumption of a homogeneous magnetic field H, however weak, in a sufficiently extended metal would lead to a reduction of the magnitude of the S-interaction by a value independent of H. Such a field can therefore not exist in a superconductor as required by the Meissner effect. The calculations are not yet sufficiently advanced to decide whether the presence of a field always leads to the normal state or whether an intermediate state may occur.