Theory of Superconducting Contacts

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The BCS theory of superconductivity is generalized to the case of a position-dependent energy gap (at the absolute zero of temperature and in the absence of magnetic fields). The BCS integral equation for the energy gap goes over into an integro-differential equation. The latter has nontrivial solutions (i.e., finite energy gap) even for the case of normal material ($V=0$). Expressions are obtained for the energy gap, for the volume energy density, and for the surface energy density at an interface, for both normal and superconducting material. These results are applied to a number of problems involving superconducting contacts. When a thin slice of normal material is sandwiched between bulk superconductors, it is found that the slice acts superconducting for thicknesses less than about 10^{-5} cm. When a thin slice of superconductor is sandwiched between bulk normal material, the slice acts like normal material for thicknesses less than about 10^{-5} cm. The energy gap at the free surface of a bulk superconductor may differ by as much as thirty percent from its constant value deep inside the material, the former being either larger or smaller than the latter, depending on the value of $N(0)V$, where $N(0)$ is the density of one-electron states of a given spin at the Fermi level in the normal metal.

I. INTRODUCTION

MEISSNER[1] has recently carried out a series of remarkable experiments on superconducting contacts. By measuring the contact resistance between plated superconducting wires, he has shown that a layer of metal like copper, ordinarily not a superconductor at any temperature, can be made superconducting by being sandwiched between bulk superconducting material such as tin. This can occur with layers as thick as 10^{-5} cm. In addition, Meissner has verified older work of Misener and others[2] by showing that a layer of tin sandwiched between or plated on the surface of bulk copper has finite electrical resistance at temperatures well below the superconducting transition temperature of bulk tin, here again for thicknesses as great as 10^{-5} cm. This is in sharp contrast with well-annealed tin films plated on an electrical insulator, since such films display the bulk transition temperature even when as thin as 5×10^{-7} cm.[3] Meissner has pointed out that these results are somewhat less startling when one remembers that electrons in a superconductor can be correlated with one another over distances as great as $\xi_0=10^{-4}$ cm, the Pippard coherence distance.[4]

In the present paper we shall develop the quantitative theory of these effects. In order to do this, it is first necessary to generalize the Bardeen-Cooper-Schrieffer theory of superconductivity[5] to include spatial dependence of the energy gap of the superconductor. The general formulation will be developed in the following section. This will be applied to normal material in Sec. III and to superconductive material in Sec. IV. In Sec. III we will see that a superconducting energy gap can indeed exist in a material such as copper which is usually thought to be never superconducting. In Sec. V we will calculate the volume energy density of a superconductor and in Sec. VI the surface energy density of both a superconductor and a normal metal. Section VII will furnish a discussion of boundary conditions. The final four sections will be devoted to the superconductor-vacuum contact, the superconductor-superconductor contact, the superconductor-normal-superconductor contact, and the normal-superconductor-normal contact, respectively.

Throughout the paper we shall assume that no magnetic field is present. In order to keep the analysis as simple as possible, we restrict ourselves to the absolute zero of temperature. Nevertheless, we will be able to draw certain conclusions concerning the superconducting transition temperature of the superconducting-normal-superconducting contact and of the normal-superconducting-normal contact. With regard to such contacts, it will be seen that theory and experiment are in good agreement, both in the size of the superconducting transition temperature T_c, and in the dependence of T_c on the thickness of the middle layer.

The theory predicts that the energy gap near the free surface of a bulk superconductor may differ somewhat from its value in the interior of the metal. The gap at the surface may be either larger or smaller than the gap in the interior, depending upon the strength of the effective electron-electron interaction. This effect is a manifestation of the presence of a surface energy density.

II. GENERAL FORMULATION

Consider the BCS theory of superconductivity[5] at the absolute zero of temperature. The superconducting

[1] H. Meissner, Phys. Rev. **109**, 686 (1958); Phys. Rev. Letters **2**, 458 (1959); Phys. Rev. **117**, 672 (1960).
[2] E. F. Burton, J. O. Wilhelm, and A. D. Misener, Trans. Roy. Soc. Can. **28**, 111, 65 (1934); A. D. Misener and J. O. Wilhelm **29**, 1 (1935); A. D. Misener, H. Grayson Smith, and J. O. Wilhelm **29**, 13 (1935); A. D. Misener, Can. J. of Research **14**, 25 (1936).
[3] A. I. Shalnikov, Nature **142**, 74 (1938).
[4] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).
[5] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957); henceforth this will be denoted BCS.

ground-state wave function is

$$\Psi_0=\prod_k [(1-h_k)^{\frac{1}{2}}+h_k^{\frac{1}{2}}c_{k\uparrow}^* c_{-k\downarrow}^*]\Phi_0.$$

Φ_0 is the vacuum-state wave function. The c_k's are the usual electron creation and destruction operators. The parameters h_k lie in the range $0\leqslant h_k\leqslant 1$. The normal-state wave function is

$$\Phi_N=\prod_{k<k_F} c_{k\uparrow}^* c_{-k\downarrow}^*\Phi_0,$$

k_F being the wave vector at the Fermi level. Thus we may write

$$\Psi_0=\prod_{k>k_F}[(1-h_k)^{\frac{1}{2}}+h_k^{\frac{1}{2}}c_{k\uparrow}^* c_{-k\downarrow}^*]\times\prod_{k<k_F}[h_k^{\frac{1}{2}}+(1-h_k)^{\frac{1}{2}}c_{-k\downarrow}c_{k\uparrow}]\Phi_N.$$

The energy density W_0 associated with the ground state is composed of the two terms $W_{\rm I}$ (interaction energy density) and $W_{\rm KE}$ (kinetic energy density).

$$W_{\rm I}=-\sum_{kk'} V_{kk'}[h_k(1-h_k)h_{k'}(1-h_{k'})]^{\frac{1}{2}}, \quad (2.1)$$

$$W_{\rm KE}=2\sum_{k>k_F}\epsilon_k h_k+2\sum_{k<k_F}|\epsilon_k|(1-h_k). \quad (2.2)$$

$V_{kk'}$ is the effective electron-electron interaction potential. The one-electron energy ϵ_k is measured relative to that of the Fermi level, i.e., on an effective-mass approximation

$$\epsilon_k=(\hbar^2/2m)(k^2-k_F^2),$$

m being the effective mass. W_0 is the energy density measured relative to that of the normal state.

We wish to generalize the theory to consider a spatially varying energy gap. This implies a spatial variation of the parameters h_k. Specifically, we assume that h_k is some function of the position of the center of mass of the two electrons occupying states $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$ when $k>k_F$, and that $(1-h_k)$ is some function of the center of mass of the two holes occupying states $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$ when $k<k_F$. We designate by $\nabla h_k^{\frac{1}{2}}$ the gradient of $h_k^{\frac{1}{2}}$ *with respect to its argument.* Thus the momentum operator of the ith electron acting on $h_k^{\frac{1}{2}}$ will give $-\frac{1}{2}i\hbar\nabla h_k^{\frac{1}{2}}$ when the ith electron occupies $\mathbf{k}\uparrow$ or $-\mathbf{k}\downarrow$, and will give zero otherwise. (Note the factor of one-half, which results from the argument of h_k being the center of mass of the electron pair.) We shall assume that h_k is essentially constant over distances of the order of the Fermi wavelength. (This assumption will later be corroborated.) Thus, for $k>k_F$, the term $\epsilon_k h_k$ must be replaced by

$$(\hbar^2/2m)[|(\mathbf{k}-\tfrac{1}{2}i\nabla)h_k^{\frac{1}{2}}|^2-k_F^2 h_k]=\epsilon_k h_k+(\hbar^2/8m)(\nabla h_k^{\frac{1}{2}})^2.$$

This represents the contribution of state $\mathbf{k}\uparrow$ to the kinetic energy density at x (x being the argument of h_k). Considering the pair of states $\mathbf{k}\uparrow$ and $-\mathbf{k}\downarrow$, the total *additional* contribution is

$$(\hbar^2/4m)(\nabla h_k^{\frac{1}{2}})^2.$$

This may be looked upon as the center-of-mass kinetic energy density of a Cooper pair of mass $2m$.

Similarly, for $k<k_F$, the term $|\epsilon_k|(1-h_k)$ is replaced by

$$|\epsilon_k|(1-h_k)+(\hbar^2/8m)[\nabla(1-h_k)^{\frac{1}{2}}]^2.$$

Thus

$$W_{\rm KE}=\sum_{k>k_F}[2\epsilon_k h_k+\tfrac{1}{4}\hbar^2 m^{-1}(\nabla h_k^{\frac{1}{2}})^2]+\sum_{k<k_F}\{2|\epsilon_k|(1-h_k)+\tfrac{1}{4}\hbar^2 m^{-1}[\nabla(1-h_k)^{\frac{1}{2}}]^2\}. \quad (2.3)$$

The terms involving $(\nabla h_k^{\frac{1}{2}})^2$ and $[\nabla(1-h_k)^{\frac{1}{2}}]^2$ give the modification of the BCS value of W_0 when h_k varies with position. These terms are reminiscent to those introduced by Ginzburg and Landau[6] in a generalization of the London theory of superconductivity. The Ginzburg-Landau theory suffers from the fact that it predates the BCS theory.

BCS obtained an equation for h_k by minimizing W_0 with respect to h_k, i.e., setting $\partial W_0/\partial h_k=0$. Because of the presence of the gradient terms, we must use the Euler-Lagrange equation,

$$[(\partial/\partial h_k)-\nabla\cdot(\partial/\partial\nabla h_k)]W_0=0. \quad (2.4)$$

For $k>k_F$, we get

$$2[\epsilon_k h_k-(\hbar^2/8m)h_k^{\frac{1}{2}}\nabla^2 h_k^{\frac{1}{2}}]=(1-2h_k)(1-h_k)^{-1}\sum_{k'}V_{kk'}[h_k(1-h_k)h_{k'}(1-h_{k'})]^{\frac{1}{2}}, \quad (2.5a)$$

as the integro-differential equation which h_k must satisfy. Similarly, for $k<k_F$, we get

$$2[|\epsilon_k|(1-h_k)-(\hbar^2/8m)(1-h_k)^{\frac{1}{2}}\nabla^2(1-h_k)^{\frac{1}{2}}]=(2h_k-1)h_k^{-1}\sum_{k'}V_{kk'}[h_k(1-h_k)\times h_{k'}(1-h_{k'})]^{\frac{1}{2}}. \quad (2.5b)$$

In the expression for W_0, we are free to replace the term

$$+(\hbar^2/4m)\sum_{k>k_F}(\nabla h_k^{\frac{1}{2}})^2 \text{ by } -(\hbar^2/4m)\sum_{k>k_F}h_k^{\frac{1}{2}}\nabla^2 h_k^{\frac{1}{2}}$$

and the term

$$+(\hbar^2/4m)\sum_{k<k_F}[\nabla(1-h_k)^{\frac{1}{2}}]^2 \text{ by } -(\hbar^2/4m)\sum_{k<k_F}(1-h_k)^{\frac{1}{2}}\nabla^2(1-h_k)^{\frac{1}{2}},$$

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[6] V. L. Ginzburg and L. D. Landau, J. Exptl. Theoret. Phys. U. S. S. R. **20**, 1064 (1950); V. L. Ginzburg, Nuovo cimento **2**, 1234 (1955).

provided that at the same time we introduce the surface energy density

$$W_{S0}=\tfrac{1}{4}\hbar^2m^{-1}\mathbf{n}\cdot[\sum_{k>k_F}h_k^{\frac{1}{2}}\nabla h_k^{\frac{1}{2}}+\sum_{k<k_F}(1-h_k)^{\frac{1}{2}}\nabla(1-h_k)^{\frac{1}{2}}]$$
$$=(\hbar^2/8m)\mathbf{n}\cdot[\sum_{k>k_F}\nabla h_k+\sum_{k<k_F}\nabla(1-h_k)], \quad (2.6)$$

$\mathbf{n}$ being the unit vector normal to the surface. W_{S0} will contribute to the total energy only at surfaces where there is a discontinuity in ∇h_k. Thus if ∇h_k is everywhere continuous, there is no surface energy. Replacing $(\nabla h_k^{\frac{1}{2}})^2$ by $-h_k^{\frac{1}{2}}\nabla^2 h_k^{\frac{1}{2}}$ and $[\nabla(1-h_k)^{\frac{1}{2}}]^2$ by $-(1-h_k)^{\frac{1}{2}}\times\nabla^2(1-h_k)^{\frac{1}{2}}$ in W_0, and making use of the integro-differential equation for h_k, we get

$$W_0=-\sum_{k>k_F}h_k^2[h_k(1-h_k)]^{-\frac{1}{2}}\sum_{k'}V_{kk'}[h_{k'}(1-h_{k'})]^{\frac{1}{2}}$$
$$-\sum_{k<k_F}(1-h_k)^2[h_k(1-h_k)]^{-\frac{1}{2}}\times\sum_{k'}V_{kk'}[h_{k'}(1-h_{k'})]^{\frac{1}{2}}. \quad (2.7)$$

Equation (2.7) is *formally* identical with the corresponding expression in the BCS theory, i.e., (2.7) contains no term involving ∇h_k.

III. ENERGY GAP IN NORMAL METALS

Throughout this paper, we make the assumption that a normal metal such as copper can be characterized by $V_{kk'}=0$ for all $\mathbf{k}$, $\mathbf{k}'$. This implies that W_0 vanishes for a normal metal irrespective of whether or not h_k varies with position. For a normal metal, the position-independent solutions of Eq. (2.5) are trivial, namely $h_k=0$ for $\epsilon_k>0$ and $h_k=1$ for $\epsilon_k<0$; the position-dependent solutions, however, are not trivial, there being two possible types. The first of these is

$$c_1\cosh[(x/\hbar)(8m|\epsilon_k|)^{\frac{1}{2}}]=[h_k(x)]^{\frac{1}{2}}, \quad \epsilon_k>0,$$
$$=[1-h_k(x)]^{\frac{1}{2}}, \quad \epsilon_k<0,$$

c_1 being some constant. The second type is

$$c_2\sinh[(x/\hbar)(8m|\epsilon_k|)^{\frac{1}{2}}]=[h_k(x)]^{\frac{1}{2}}, \quad \epsilon_k>0,$$
$$=[1-h_k(x)]^{\frac{1}{2}}, \quad \epsilon_k<0.$$

In general, we define the k-dependent energy gap ϵ_{0k} by means of the equation

$$h_k=\tfrac{1}{2}[1-\epsilon_k(\epsilon_k^2+\epsilon_{0k}^2)^{-\frac{1}{2}}]. \quad (3.1)$$

This implies

$$1-2h_k=\epsilon_k(\epsilon_k^2+\epsilon_{0k}^2)^{-\frac{1}{2}}, \quad (3.2)$$

$$2[h_k(1-h_k)]^{\frac{1}{2}}=\epsilon_{0k}(\epsilon_k^2+\epsilon_{0k}^2)^{-\frac{1}{2}}. \quad (3.3)$$

We imagine a slice of normal metal lying in the range $-X\leqslant x\leqslant+X$, with $\epsilon_{0k}(x)$ assuming the value $\epsilon_{0k}(X)\neq0$ at $x=\pm X$. Thus the first of the above solutions for h_k becomes

$$h_k(x)=\tfrac{1}{2}\{1-\epsilon_k[\epsilon_k^2+\epsilon_{0k}^2(x)]^{-\frac{1}{2}}\}$$
$$=\frac{1}{2}\left(1-\frac{\epsilon_k}{[\epsilon_k^2+\epsilon_{0k}^2(X)]^{\frac{1}{2}}}\right)\left(\frac{\cosh(x/\hbar)(8m\epsilon_k)^{\frac{1}{2}}}{\cosh(X/\hbar)(8m\epsilon_k)^{\frac{1}{2}}}\right)^2, \quad \epsilon_k>0,$$
$$=1-\frac{1}{2}\left(1+\frac{\epsilon_k}{[\epsilon_k^2+\epsilon_{0k}^2(X)]^{\frac{1}{2}}}\right)\times\left(\frac{\cosh(x/\hbar)(8m|\epsilon_k|)^{\frac{1}{2}}}{\cosh(X/\hbar)(8m|\epsilon_k|)^{\frac{1}{2}}}\right)^2, \quad \epsilon_k<0. \quad (3.4)$$

Solving for $\epsilon_{0k}(x)$, we find, in the limit of small $|\epsilon_k|$, that

$$\frac{1}{\epsilon_{0k}(x)}=\frac{1}{\epsilon_{0k}(X)}+\frac{8m}{\hbar^2}(X^2-x^2)$$
$$=\frac{1}{\epsilon_{0k}(0)}-\frac{8m}{\hbar^2}x^2. \quad (3.5)$$

Thus we have the remarkable situation of a finite energy gap at the Fermi level in a slice of normal material. As a result, the slice will have the electrical properties of a superconductor.

On the other hand, let us take the second type of solution for h_k where

$$h_k(x)=\tfrac{1}{2}\{1-\epsilon_k[\epsilon_k^2+\epsilon_{0k}^2(x)]^{-\frac{1}{2}}\}$$
$$=\frac{1}{2}\left(1-\frac{\epsilon_k}{[\epsilon_k^2+\epsilon_{0k}^2(X)]^{\frac{1}{2}}}\right)\left(\frac{\sinh(x/\hbar)(8m\epsilon_k)^{\frac{1}{2}}}{\sinh(X/\hbar)(8m\epsilon_k)^{\frac{1}{2}}}\right)^2, \quad \epsilon_k>0,$$
$$=1-\frac{1}{2}\left(1+\frac{\epsilon_k}{[\epsilon_k^2+\epsilon_{0k}^2(X)]^{\frac{1}{2}}}\right)\times\left(\frac{\sinh(x/\hbar)(8m|\epsilon_k|)^{\frac{1}{2}}}{\sinh(X/\hbar)(8m|\epsilon_k|)^{\frac{1}{2}}}\right)^2, \quad \epsilon_k<0. \quad (3.6)$$

Solving for $\epsilon_{0k}(x)$, we find, in the limit of small $|\epsilon_k|$, that

$$\epsilon_{0k}(x)=|\epsilon_k|[1-(x/X)^2]^{-1}, \quad x^2<X^2. \quad (3.7)$$

Thus the gap vanishes at the Fermi level where $\epsilon_k=0$, i.e., there is no gap separating the ground state of the system from excited states. The electrical properties will be essentially the same as in a bulk normal metal.

IV. ENERGY GAP IN SUPERCONDUCTORS

In general

$$h_k^{\frac{1}{2}}\nabla^2h_k^{\frac{1}{2}}=\tfrac{1}{2}\nabla^2h_k-\tfrac{1}{4}h_k^{-1}(\nabla h_k)^2,$$
$$(1-h_k)^{\frac{1}{2}}\nabla^2(1-h_k)^{\frac{1}{2}}=-\tfrac{1}{2}\nabla^2h_k-\tfrac{1}{4}(1-h_k)^{-1}(\nabla h_k)^2.$$

Equation (3.1) gives

$$\nabla h_k=-\tfrac{1}{2}\epsilon_k\epsilon_{0k}^3(\epsilon_k^2+\epsilon_{0k}^2)^{-\frac{3}{2}}\nabla(1/\epsilon_{0k}), \quad (4.1)$$

so that

$$\lim_{\epsilon_k\to 0}\nabla h_k=-\tfrac{1}{2}\epsilon_k\nabla(1/\epsilon_0), \tag{4.2}$$

$$-\lim_{\epsilon_k\to 0}(1-h_k)^{\frac{1}{2}}\nabla^2(1-h_k)^{\frac{1}{2}}=\lim_{\epsilon_k\to 0}h_k^{\frac{1}{2}}\nabla^2 h_k^{\frac{1}{2}}$$
$$=-\tfrac{1}{4}\epsilon_k\nabla^2(1/\epsilon_0), \tag{4.3}$$

where we have defined

$$\epsilon_0=\lim_{\epsilon_k\to 0}\epsilon_{0k}. \tag{4.4}$$

In this limit, Eq. (2.5), the integro-differential equation for h_k, becomes (for both positive and negative values of ϵ_k)

$$\sum_{k'}\tfrac{1}{2}(\epsilon_{0k'}/\epsilon_0)V_{kk'}(\epsilon_{k'}^2+\epsilon_{0k'}^2)^{-\frac{1}{2}}$$
$$-(\hbar^2/16m)\nabla^2(1/\epsilon_0)=1. \tag{4.5}$$

As in BCS, we now approximate $\epsilon_{0k'}$ by ϵ_0 inside the summation over k', we replace the summation by the equivalent integration; and we we set $V_{kk'}$ equal to the constant V for $|\epsilon_k|$, $|\epsilon_{k'}|<\hbar\omega$ (the mean phonon energy) and equal to zero otherwise. We get

$$N(0)V\,\mathrm{arcsinh}(\hbar\omega/\epsilon_0)-(\hbar^2/16m)\nabla^2(1/\epsilon_0)=1,$$

$N(0)$ being the density of one-electron states (of a single spin) per unit energy at the Fermi level in the metal in the normal state. Since under all conditions $\epsilon_0\ll\hbar\omega$, we may approximate

$$\mathrm{arcsin}(\hbar\omega/\epsilon_0)\quad\text{by}\quad\ln(2\hbar\omega/\epsilon_0).$$

Thus,

$$N(0)V\ln(2\hbar\omega/\epsilon_0)-(\hbar^2/16m)\nabla^2(1/\epsilon_0)=1. \tag{4.6}$$

In case $V=0$, we immediately get the solution

$$[1/\epsilon_0(x)]=[1/\epsilon_0(0)]-(8m/\hbar^2)x^2,$$

obtained previously for a slice of normal material.

For the case V finite, it pays to define the constants

$$\epsilon_0(\infty)=2\hbar\omega e^{-1/N(0)V}, \tag{4.7}$$

$$\delta=\frac{1}{8}\left(\frac{\hbar}{N(0)Vm\omega}e^{1/N(0)V}\right)^{\frac{1}{2}}, \tag{4.8}$$

and the variable

$$z(x)=\epsilon_0(\infty)/\epsilon_0(x), \tag{4.9}$$

so that Eq. (4.6) becomes

$$2\delta^2\nabla^2 z=\ln z. \tag{4.10}$$

In the one-dimensional case (which we consider exclusively henceforth), this can be immediately integrated once

$$\delta(dz/dx)=\pm[K+z(\ln z-1)]^{\frac{1}{2}}, \tag{4.11}$$

K being an integration constant. Thus

$$x=\pm\delta\int_{z_0}^{z}[K+z'(\ln z'-1)]^{-\frac{1}{2}}dz', \tag{4.12}$$

z_0 being the arbitrary value of z at $x=0$. The constant $\epsilon_0(\infty)$ is just the constant value of ϵ_0 to be found in the interior of a bulk superconductor [i.e., $\epsilon_0(\infty)$ is the BCS value of ϵ_0]. Thus in such a bulk superconductor we want $z\to 1$ as $x\to\infty$. At the same time we want $(dz/dx)\to 0$. This means that for a bulk superconductor we must take

$$K=1. \tag{4.13}$$

For this case, a plot of $1/z$ versus $\pm x/\delta$ can assume the two possible forms diagrammed in Fig. 1. The constant δ can be written in terms of the Fermi wavelength

$$\lambda_F=2\pi/k_F \tag{4.14}$$

and the BCS form of the Pippard coherence distance

$$\xi_0=[\hbar v_F/\pi\epsilon_0(\infty)], \tag{4.15}$$

v_F being the velocity of electrons at the Fermi level. We have

$$\delta=\tfrac{1}{8}[\xi_0\lambda_F/N(0)V]^{\frac{1}{2}}. \tag{4.16}$$

Taking as representative values $\xi_0=10^{-4}$ cm, $\lambda_F=4\times10^{-8}$ cm, $N(0)V=\frac{1}{4}$, we get $\delta=\frac{1}{2}\times10^{-6}$ cm, smaller than ξ_0 by a factor of two hundred. The energy gap in a superconductor can thus change appreciably over distances of the order of 10^{-6} cm.

V. VOLUME ENERGY DENSITY

Let us return to Eq. (2.7), the expression for W_0. Expressing h_k in terms of ϵ_0, and making the same approximation we made in the last section in solving the integro-differential equation, we get

$$W_0=-\tfrac{1}{4}V\sum_{kk'}[(\epsilon_k^2+\epsilon_0^2)^{\frac{1}{2}}-|\epsilon_k|]^2$$
$$\times[(\epsilon_k^2+\epsilon_0^2)(\epsilon_{k'}^2+\epsilon_0^2)]^{-\frac{1}{2}}$$
$$=-[N(0)]^2V\left(\int_0^{\hbar\omega}(\epsilon^2+\epsilon_0^2)^{-\frac{1}{2}}d\epsilon\right)$$
$$\times\left(\int_0^{\hbar\omega}[2(\epsilon^2+\epsilon_0^2)^{\frac{1}{2}}-2\epsilon-\epsilon_0^2(\epsilon^2+\epsilon_0^2)^{-\frac{1}{2}}]d\epsilon\right)$$
$$=-[N(0)]^2V\hbar\omega\{[(\hbar\omega)^2+\epsilon_0^2]^{\frac{1}{2}}-\hbar\omega\}$$
$$\times\mathrm{arcsinh}(\hbar\omega/\epsilon_0)$$
$$\cong-\tfrac{1}{2}V[N(0)\epsilon_0]^2\ln(2\hbar\omega/\epsilon_0). \tag{5.1}$$

We designate by $W_0(\infty)$ the value of W_0 when $\epsilon_0=\epsilon_0(\infty)$. Thus $W_0(\infty)$ is the energy density in the interior of a bulk superconductor (i.e., the value computed by BCS). We have

$$W_0(\infty)=-\tfrac{1}{2}N(0)[\epsilon_0(\infty)]^2, \tag{5.2}$$

and

$$W_0-W_0(\infty)=z^{-2}[z^2-N(0)V\ln z-1]|W_0(\infty)|. \tag{5.3}$$

As a result of the smallness of $N(0)V$ in practice, W_0

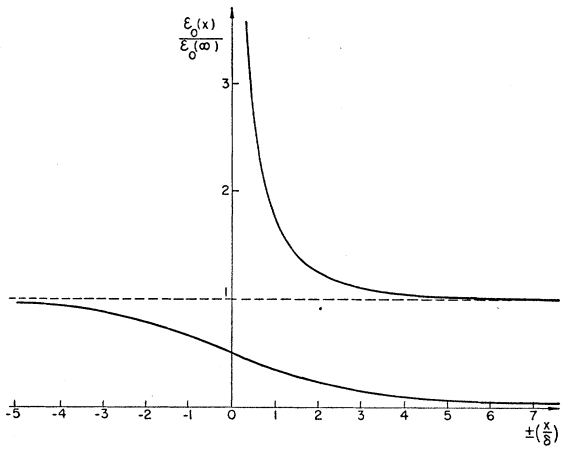

FIG. 1. Energy gap versus position for a bulk superconductor.

becomes larger (more positive) than $W_0(\infty)$ whenever ϵ_0 becomes smaller than $\epsilon_0(\infty)$.

VI. SURFACE ENERGY DENSITY

Let us return to Eq. (2.6), the expression for W_{S0}. Expressing h_k in terms of ϵ_0, and making the same approximations we made in solving the integro-differential equation, we get

$$\begin{aligned}W_{S0}&=-(\hbar^2/16m)[(d/dx)\epsilon_0^{-1}]\epsilon_0^3\sum_k|\epsilon_k|(\epsilon_k^2+\epsilon_0^2)^{-\frac{3}{2}}\\&=-(\hbar^2/16m)[(d/dx)\epsilon_0^{-1}]\epsilon_0^3N(0)\\&\qquad\times\int_0^{\hbar\omega}2\epsilon(\epsilon^2+\epsilon_0^2)^{-\frac{3}{2}}d\epsilon\\&=-(\hbar^2/8m)[(d/dx)\epsilon_0^{-1}]\epsilon_0^3N(0)\\&\qquad\times\{\epsilon_0^{-1}-[(\hbar\omega)^2+\epsilon_0^2]^{-\frac{1}{2}}\}\\&\cong-(\hbar^2/8m)[(d/dx)\epsilon_0^{-1}]\epsilon_0^2N(0).\end{aligned}\tag{6.1}$$

For superconductive material ($V\neq0$)

$$\begin{aligned}(d/dx)\epsilon_0^{-1}&=[1/\epsilon_0(\infty)](dz/dx)\\&=\pm[\delta\epsilon_0(\infty)]^{-1}[K+z(\ln z-1)]^{\frac{1}{2}},\end{aligned}$$

so that

$$\begin{aligned}W_{S0}&=\mp\hbar^2\epsilon_0(\infty)N(0)(8m\delta z^2)^{-1}[K+z(\ln z-1)]^{\frac{1}{2}}\\&=\mp8N(0)V|W_0(\infty)|\delta z^{-2}[K+z(\ln z-1)]^{\frac{1}{2}}.\end{aligned}\tag{6.2}$$

The sign of W_{S0} is the same as the sign of $(d\epsilon_0/dx)$ at the surface. Thus if ϵ_0 decreases as the surface is approached, then W_{S0} will be negative.

For a slice of normal material ($V=0$) with a finite gap

$$(d/dx)\epsilon_0^{-1}=-16m\hbar^{-2}X\quad\text{(boundary at } x=X),$$

so that

$$W_{S0}=2N(0)X\epsilon_0^2(X).\tag{6.3}$$

Let us imagine a hypothetical superconducting material characterized by a bulk gap $\epsilon_0(\infty)$, bulk energy density $W_0(\infty)$, and in addition having the *same* $N(0)$ as does the normal material under consideration. Then (6.3) may be written

$$W_{S0}=4|W_0(\infty)|Xz^{-2},\tag{6.4}$$

where $z=\epsilon_0(\infty)/\epsilon_0(X)$. (It will later be convenient to specify that the effective mass m of our hypothetical superconducting material is the same as that of the normal material.)

The above expression holds only when the quantity

$$u=X\hbar^{-1}[8m\epsilon_0(X)]^{\frac{1}{2}}=\tfrac{1}{2}[N(0)Vz]^{-\frac{1}{2}}(X/\delta),\tag{6.5}$$

is sufficiently small. The error at large u results from assuming ϵ_0 is independent of $\mathbf{k}$ in the normal metal. To see this, we note that $\Delta h_k(k>k_F)$ and $\nabla(1-h_k)\times(k<k_F)$ are both given by

$$\frac{1}{X}\left(1-\frac{|\epsilon_k|}{[\epsilon_k^2+\epsilon_0^2(X)]^{\frac{1}{2}}}\right)\left(\frac{X}{\hbar}(8m|\epsilon_k|)^{\frac{1}{2}}\right)\times\tanh\left(\frac{X}{\hbar}(8m|\epsilon_k|)^{\frac{1}{2}}\right),$$

at $x=X$. Thus W_{S0} is,

$$\begin{aligned}W_{S0}&=\frac{\hbar^2}{8mX}\sum_k\left(1-\frac{|\epsilon_k|}{[\epsilon_k^2+\epsilon_k^2(X)]^{\frac{1}{2}}}\right)\\&\qquad\times\left(\frac{X}{\hbar}(8m|\epsilon_k|)^{\frac{1}{2}}\right)\tanh\left(\frac{X}{\hbar}(8m|\epsilon_k|)^{\frac{1}{2}}\right)\\&=\frac{\hbar^2}{4mX}N(0)\int_0^{\hbar\omega}\left(1-\frac{\epsilon}{[\epsilon^2+\epsilon_0^2(X)]^{\frac{1}{2}}}\right)\\&\qquad\times\left(\frac{X}{\hbar}(8m\epsilon)^{\frac{1}{2}}\right)\tanh\left(\frac{X}{\hbar}(8m\epsilon)^{\frac{1}{2}}\right)d\epsilon.\end{aligned}\tag{6.6}$$

For a slice of normal material with no gap (i.e., $h_k^{\frac{1}{2}}$ is a hyperbolic sine rather than a hyperbolic cosine), the expression for W_{S0} is modified by replacing the tanh by a coth,

$$\begin{aligned}W_{S0}&=\frac{\hbar^2}{4mX}N(0)\int_0^{\hbar\omega}\left(1-\frac{\epsilon}{[\epsilon^2+\epsilon_0^2(X)]^{\frac{1}{2}}}\right)\\&\qquad\times\left(\frac{X}{\hbar}(8m\epsilon)^{\frac{1}{2}}\right)\coth\left(\frac{X}{\hbar}(8m\epsilon)^{\frac{1}{2}}\right)d\epsilon.\end{aligned}\tag{6.7}$$

Comparing Eqs. (6.6) and (6.7), we see that they become equal in the limit of large u where both tanh and coth can be replaced by unity. In this limit W_{S0} is independent of u or X. Still considering the case of no gap, when u is sufficiently small we may replace the hyperbolic cotangent times its argument by unity, so that

$$W_{S0}=\hbar^2(4mX)^{-1}N(0)\int_0^{\hbar\omega}\{1-\epsilon[\epsilon^2+\epsilon_0^2(X)]^{-\frac{1}{2}}\}d\epsilon$$
$$=\hbar^2(4mX)^{-1}N(0)\{\epsilon_0(X)+\hbar\omega-[(\hbar\omega)^2+\epsilon_0^2(X)]^{\frac{1}{2}}\}$$
$$\cong\hbar^2(4mX)^{-1}N(0)\epsilon_0(X). \quad (6.8)$$

In terms of a hypothetical superconducting material having the same $N(0)$ and m as does the normal material under consideration, Eq. (6.8) may be rewritten as

$$W_{S0}=(4\delta)^2N(0)V|W_0(\infty)|(Xz)^{-1}. \quad (6.9)$$

We note that Eqs. (6.4) and (6.9) assume the common value,

$$W_{S0}=8\delta[N(0)V]^{\frac{1}{2}}|W_0(\infty)|z^{-\frac{1}{2}}, \quad (6.10)$$

when $u=1$; while (6.4) is smaller than (6.9) for $u<1$. We shall henceforth make the assumption that Eqs. (6.4) and (6.9) hold for the gap and no-gap solutions, respectively, whenever $u<1$, while Eq. (6.10) holds for both solutions when $u\gtrsim 1$.

VII. BOUNDARY CONDITIONS

It is appropriate at this point to summarize briefly the rather formal developments of the past five sections. If the parameters h_k of the BCS theory of superconductivity are allowed to vary with position, then the BCS expression for the kinetic-energy density is modified to that given by Eq. (2.3). This converts the BCS integral equation for h_k into an integro-differential equation, Eq. (2.5). Its solutions for a superconductor are given implicitly by Eq. (4.12). For a slice of normal metal ($V=0$) there are two possible solutions, given by Eqs. (3.4) and (3.6), respectively. For the first of these solutions, there is an energy gap at the Fermi level, so that the slice has the electrical properties of a bulk superconductor. For the second solution, there is no gap, and the electrical properties are "normal." The volume energy density W_0 of a superconductor is given by Eq. (5.1); W_0 vanishes for a normal metal, irrespective of whether or not there is a gap. The surface energy density W_{S0} of a superconductor is given by Eq. (6.2). For a slice of normal metal characterized by the parameter u of Eq. (6.4), the surface energy density is given by Eq. (6.10) for $u\gtrsim 1$, and by either (6.4) (gap) or (6.9) (no gap) for $u<1$.

Before we can apply these results to specific physical problems, we must discuss the boundary conditions which h_k must satisfy. This is the topic of the present section. We consider a plane interface between two metals. The electron trajectories making contact with the interface can be divided into two classes: penetrating trajectories which pass through the interface; nonpenetrating trajectories which do not pass through the interface. The latter represent reflection at the interface; the former in general represent a certain amount of refraction at the interface resulting from the simultaneous conservation of energy and of momentum parallel to the interface. Let one of the metals be characterized by effective mass m_1, and Fermi wave vector k_{F1}, the other metal by m_2 and k_{F2}. We assume $k_{F2}>k_{F1}$ (i.e., the conduction-electron density is greater in metal No. 2). Let $\mathbf{k}_1$ and $\mathbf{k}_2$ be the wave vectors associated with a penetrating trajectory, $\mathbf{k}_1$, characterizing that part of the trajectory lying in metal No. 1 and $\mathbf{k}_2$ that part lying in metal No. 2. Given either $\mathbf{k}_1$ or $\mathbf{k}_2$, the other member of the pair is specified by the conservation conditions

$$(\hbar^2/2m_1)(k_1^2-k_{F1}^2)=(\hbar^2/2m_2)(k_2^2-k_{F2}^2),$$
$$k_{1\|}=k_{2\|},$$

the subscript $\|$ denoting the component parallel to the interface. When $\mathbf{k}_1$ and $\mathbf{k}_2$ lie at the Fermi level, the orientation by $\mathbf{k}_1$ is arbitrary, but the orientation of $\mathbf{k}_2$ is limited by the restriction

$$\sin\theta_2\leqslant(k_{F1}/k_{F2}), \quad (7.1)$$

θ_2 being the angle between $\mathbf{k}_2$ and the normal to the interface.

We shall assume the two following boundary conditions for the h_k associated with a *penetrating* trajectory.

I. h_k is a continuous function of position along a penetrating trajectory; i.e.,

$$h_{k1}=h_{k2} \text{ at the interface.} \quad (7.2)$$

II. A penetrating trajectory makes no contribution to the surface energy density W_{S0}; i.e.,

$$(\hbar^2/8m_1)(\partial h_{k1}/\partial n)$$
$$=(\hbar^2/8m_2)(\partial h_{k2}/\partial n) \text{ at the interface.} \quad (7.3)$$

We shall assume the following boundary condition for the h_k *never* associated with a penetrating trajectory [e.g., h_{k2} when $\mathbf{k}_2$ is such that (7.1) is *not* satisfied].

III. The boundary value of an h_k never associated with penetrating trajectories is chosen to minimize the total energy of the system. It might be thought that condition III is already automatically satisfied by the integro-differential equation for h_k. Such is not the case, since Eq. (2.4) represents a minimization of W_0 subject to arbitrary, *specified* boundary values of h_k.

Although the above boundary conditions appear eminently reasonable to the writer, it is by no means obvious to him that they can be rigorously justified. They should best be considered plausible assumptions. As a practical matter, these boundary conditions are in general too difficult to apply. The reason is easy to see. The boundary value of h_k is determined by conditions I and II for some orientations of $\mathbf{k}$ [those orientations which satisfy Eq. (7.1)] and by condition III for other orientations [those which fail to satisfy Eq. (7.1)]. This implies an orientation dependence of h_k at the boundary. However, in the past five sections we have assumed that h_k is independent of the orientation of $\mathbf{k}$, an assumption which is necessary in order to make Eq.

(2.5), the integro-differential equation, practicable to solve. In order to avoid this difficulty, we will make the drastic simplification of considering only interfaces where the trajectories are either all penetrating or all nonpenetrating. This implies either that the metals on both sides of the interface have identical values of m, k_F, and $N(0)$ (all penetrating trajectories) or that the interface is one separating a metal from an insulator or vacuum (all nonpenetrating trajectories). We will make the additional simplification of assuming $\hbar\omega$ is the same on both sides of a metal-metal interface. This is necessary in order to satisfy condition I between two superconductors. The difficulty arises from the approximation made in solving the integro-differential equation that $\epsilon_{0k}=\epsilon_0$ for $|\epsilon_k|<\hbar\omega$ and $\epsilon_{0k}=0$ otherwise. This last approximation also makes it impossible to satisfy condition II between a superconductor and a normal metal even when $\hbar\omega$ is the same for both. Thus we shall replace condition II by the weaker condition:

II′. The sum of the contributions of all penetrating trajectories to the surface energy must vanish. Therefore at the interface between two metals the net surface energy vanishes; i.e.,

$$W_{S01}+W_{S02}=0, \tag{7.4}$$

W_{S01} and W_{S02} being the surface energy densities associated with each of the two metals forming the interface. Note that because of the simplifications already made, conditions II and II′ are equivalent for an interface separating two superconductors.

Summing up, we may say that only two types of interfaces will be considered:

(1) Metal-vacuum (or metal-insulator) interfaces.

(2) Metal-metal interfaces where the two metals differ only in the interaction potential V. Condition III specifies the boundary conditions for (1); Conditions I and II′ specify them for (2).

Before concluding this section, it should be pointed out that we are assuming that bulk properties of a metal like m, $\hbar\omega$, $N(0)$, and V are constants independent of position inside a given metal. Any position dependence of these quantities is probably restricted to regions within a few lattice spacings of the interface, i.e., distances small compared to δ, so that it is a good approximation to ignore their position dependence within a given metal; ergo we assume they change discontinuously at an interface.

VIII. SUPERCONDUCTOR-VACUUM CONTACT

For our purpose, a metal-insulator contact is no different from a metal-vacuum contact. Furthermore, a normal metal-vacuum contact is not of interest. We therefore restrict the discussion of the present section to superconductor-vacuum contacts. For simplicity, we consider the interface between vacuum and a *bulk* superconductor (as contrasted with a superconducting film). We assume the superconductor occupies the half-space characterized by $x<0$; i.e., the interface lies at $x=0$, with superconductor to the left and vacuum to the right.

We define W_{B0}, the boundary surface energy density, as the difference (per unit surface area) between the total energy of the superconductor and its energy if $\epsilon_0(x)$ were equal to $\epsilon_0(\infty)$ throughout the superconductor. Thus

$$W_{B0}=\int_{-\infty}^{0}[W_0(x)-W_0(\infty)]dx+W_{S0}. \tag{8.1}$$

Making use of Eqs. (4.11), (4.13), (5.3), and (6.2), we get,

$$W_{B0}=[\mathrm{sgn}(z-1)]\delta|W_0(\infty)| \times\left(\int_1^z\frac{[z'^2-N(0)V\ln z'-1]}{z'^2[1+z'(\ln z'-1)]^{\frac{1}{2}}}dz' -8N(0)Vz^{-2}[1+z(\ln z-1)]^{\frac{1}{2}}\right), \tag{8.2}$$

where z is the value of $z'=\epsilon_0(\infty)/\epsilon_0(x)$ at the surface of the superconductor, and $\mathrm{sgn}(z-1)$ is the signature of $(z-1)$. When ϵ_0 at the surface differs only slightly from $\epsilon_0(\infty)$, i.e.,

$$\epsilon_0(0)=\epsilon_0(\infty)(1+\kappa), \quad |\kappa|\ll 1, \tag{8.3}$$

we have

$$W_{B0}=\sqrt{2}\delta|W_0(\infty)|\{-\kappa[2-5N(0)V] +\tfrac{1}{6}\kappa^2[4+29N(0)V]\}. \tag{8.4}$$

Condition III of the previous section is equivalent to the requirement that W_{B0} be minimized with respect to z (or κ). If we set $\partial W_{B0}/\partial\kappa=0$, we find

$$\kappa=3[2-5N(0)V][4+29N(0)V]^{-1}, \tag{8.5}$$

$$W_{B0}=-\tfrac{3}{2}\sqrt{2}\delta|W_0(\infty)| \times[2-5N(0)V]^2[4+29N(0)V]^{-1}. \tag{8.6}$$

According to the work of Pines,[7] $N(0)V$ lies in the range 0.2–0.5 for most superconductors. Thus, from (8.5), κ ranges from $+0.3$ to -0.08. This suggests that (8.3) is not too bad an approximation. We see that the energy gap on the surface of a bulk superconductor will be either smaller or larger than the gap in the interior when $N(0)V$ is either larger or smaller, respectively, than 0.4.

IX. SUPERCONDUCTOR-SUPERCONDUCTOR CONTACT

Consider an interface at $x=0$ between bulk superconductors No. 1 and No. 2. The two superconductors have differing values of V [and thus of $\epsilon_0(\infty)$ and δ].

[7] D. Pines, Phys. Rev. **109**, 280 (1958).

Let $\epsilon_0(0)$ be the common value of $\epsilon_0(x)$ at the interface, and let z_1 and z_2 be the values of z for the two superconductors at the interface. Condition I of Sec. VII implies that

$$\epsilon_0(0)=\epsilon_{01}(\infty)/z_1=\epsilon_{02}(\infty)/z_2. \tag{9.1}$$

Condition II′ implies, with the aid of Eq. (6.2), that

$$V_1\delta_1[1+z_1(\ln z_1-1)]^{\frac{1}{2}}=V_2\delta_2[1+z_2(\ln z_2-1)]^{\frac{1}{2}}. \tag{9.2}$$

For the metal with the larger $\epsilon_0(\infty)$, we must take $z>1$; for the other metal, $z<1$; so that $\epsilon_0(0)$ is bracketed between $\epsilon_{01}(\infty)$ and $\epsilon_{02}(\infty)$. This is necessary in order that W_{S0} for the two metals be opposite in sign so that the net surface energy density can vanish. These two equations serve to determine z_1 and z_2, and thus $\epsilon_0(0)$. For example, when

$$\epsilon_{02}(\infty)/\epsilon_{01}(\infty)=1+\kappa, \quad |\kappa|\ll 1, \tag{9.3}$$

we have

$$\begin{aligned}\epsilon_0(0)&=\epsilon_{01}(\infty)[1+V_1\delta_1(V_1\delta_1+V_2\delta_2)^{-1}\kappa]\\&=\epsilon_{02}(\infty)[1-V_2\delta_2(V_1\delta_1+V_2\delta_2)^{-1}\kappa].\end{aligned} \tag{9.4}$$

X. SUPERCONDUCTOR-NORMAL-SUPERCONDUCTOR CONTACT

Consider a slice of normal metal of thickness $2X$ sandwiched between bulk superconductor (of the same type on both sides). We recall that there are two solutions to the integro-differential equation for the slice of normal metal, one where there is a gap at the Fermi level, the other where there is none. For the former solution, a vanishing net surface energy density at either normal-superconductor interface requires that

$$\begin{aligned}&8N(0)V|W_0(\infty)|\delta z^{-2}[1+z(\ln z-1)]^{\frac{1}{2}}\\&\quad=4|W_0(\infty)|Xz^{-2}, \qquad u<1,\\&\quad=8\delta[N(0)V]^{\frac{1}{2}}|W_0(\infty)|z^{-\frac{3}{2}}, \quad u\gtrsim 1,\end{aligned} \tag{10.1}$$

where u is given by Eq. (6.5). The case $u\gtrsim 1$ corresponds to $X\gtrsim X_c$ and $z=z_c$, where X_c and z_c are constants which will be determined momentarily. The case $u<1$ corresponds to $X<X_c$ and $z<z_c$, where z is the solution to the equation

$$(X/2\delta)=N(0)V[1+z(\ln z-1)]^{\frac{1}{2}}. \tag{10.2}$$

The constant z_c is given by

$$z_c=N(0)V[1+z_c(\ln z_c-1)], \tag{10.3}$$

which, to an excellent approximation, may be rewritten

$$z_c=N(0)Vz_c(\ln z_c-1),$$

or

$$z_c=e^{1+1/N(0)V}. \tag{10.4}$$

Combining (10.2), (10.3), and (10.4), we get

$$X_c=2\delta[N(0)Ve^{1+1/N(0)V}]^{\frac{1}{2}}. \tag{10.5}$$

For the no-gap solution, a vanishing net surface energy density requires that

$$\begin{aligned}&8N(0)V|W_0(\infty)|\delta z^{-2}[1+z(\ln z-1)]^{\frac{1}{2}}\\&\quad=(4\delta)^2N(0)V|W_0(\infty)|X^{-1}z^{-1}, \quad u<1,\\&\quad=8\delta[N(0)V]^{\frac{1}{2}}|W_0(\infty)|z^{-\frac{3}{2}}, \quad u\gtrsim 1.\end{aligned} \tag{10.6}$$

The case $u\gtrsim 1$ corresponds to $X\gtrsim X_c$ and $z=z_c$, just as before. In contrast to the previous situation, however, the case $u<1$ does *not* correspond to $X<X_c$, but rather to $X>X_c$. This can be seen as follows. For $u<1$, we have

$$(X/2\delta)=z[1+z(\ln z-1)]^{-\frac{1}{2}}<[N(0)Vz]^{\frac{1}{2}}, \tag{10.7}$$

or

$$1+1/N(0)V<z^{-1}+\ln z\cong\ln z,$$

so that $z>z_c$ while $X\cong 2\delta[z/(\ln z-1)]^{\frac{1}{2}}>X_c$. We conclude that there is no solution to Eq. (10.6) for $X<X_c$; while there are two solutions for $X>X_c$, namely $z=z_c$ and z given by Eq. (10.7). Of these two solutions, $z=z_c$ is the stable solution since it corresponds to the lower energy of the system.

For X larger than X_c, the total energy of the system is independent of whether we use the gap or the no-gap solution in the slice of normal metal (since in either case $z=z_c$). However, at any finite temperature the no-gap solution will have the greater entropy and thus the lower free energy. This means that the no-gap solution is the stable one for $X>X_c$. In contrast, for $X<X_c$, the gap solution is the only one which satisfies boundary conditions, so that the slice has the electrical properties of a superconductor. The slice will exhibit normal resistivity only when the bulk superconductor on either side of the slice reverts to the normal phase. This implies that the superconducting transition temperature of the slice is the same as that of the bulk superconductor for $X<X_c$. Since the transition temperature of the slice is zero for $X>X_c$, we see that the transition temperature is a discontinuous function of thickness (at the critical thickness $2X_c$). This discontinuity is probably an artifact of the approximation embodied in assuming that Eqs. (6.4), (6.9), and (6.10) are correct in the intermediate range of $u\approx 1$. A more accurate expression for W_{S0} in this range would undoubtedly lead to the conclusion that, for X in the vicinity of X_c, both the gap and the no-gap solutions can satisfy boundary conditions with, at the same time, the former having the lower energy. This would probably remove the discontinuity in transition temperature as a function of thickness. The essential results would remain unchanged, however, these being that for X appreciably greater than X_c the transition temperature vanishes, while for X appreciably less than X_c it is equal to the bulk transition temperature. The critical thickness $2X_c$ can be written in terms of the Fermi energy E_F, the phonon energy $\hbar\omega$, and the Pippard coherence distance ξ_0, i.e.,

$$2X_c=\pi(e/2)^{\frac{1}{2}}\xi_0(\hbar\omega/E_F)^{\frac{1}{2}}. \tag{10.8}$$

Taking $E_F=400\hbar\omega$ and $\xi_0=10^{-4}$ cm, we get $2X_c=1.8$

$\times 10^{-5}$ cm$\cong\frac{1}{6}\xi_0$, in good agreement with the experimental work of Meissner.

At the critical thickness, the gap at either interface is smaller than the bulk gap by a factor of z_c, while the gap at the center of the slice is still smaller by a factor of two. Thus the gap in the slice of metal is a couple oders of magnitude smaller than the bulk gap. However, the gap in the slice rises quite rapidly as X becomes smaller than X_c. To see this, take

$$z=z_c(1-\kappa), \quad \kappa\ll 1, \tag{10.9}$$

and substitute into Eq. (10.2). We find

$$\kappa=[1+N(0)V]^{-1}[1-(X/X_c)^2]. \tag{10.10}$$

Although (10.10) applies only when $X\approx X_c$, it indicates that $\epsilon_0(X)$ may be considerably greater than $\epsilon_0(X_c)$ when X is appreciably smaller than X_c.

In concluding this section, we point out that in the limit $X=\infty$ we get the behavior of an interface between bulk normal and bulk superconducting materials, the gap at the interface being smaller than the bulk gap by a factor of z_c.

XI. NORMAL-SUPERCONDUCTOR-NORMAL CONTACT

Consider a slice of superconducting metal of thickness $2X$ sandwiched between bulk normal metal (of the same type on both sides). A vanishing net surface energy density at either normal-superconducting interface requires that

$$8N(0)V|W_0(\infty)|\delta z^{-2}[z(\ln z-1)-z_0(\ln z_0-1)]^{\frac{1}{2}} = 8\delta[N(0)V]^{\frac{1}{2}}|W_0(\infty)|z^{-\frac{3}{2}}, \tag{11.1}$$

where z is the value of $\epsilon_0(\infty)/\epsilon_0(x)$ at either interface, and z_0 is the value at the center of the slice (where $d\epsilon_0/dx$ vanishes). Since the normal metal is assumed to be infinitely thick, we have used Eq. (6.10) for determining the contribution of the normal metal to the net surface energy density. Equation (11.1) becomes

$$1/N(0)V=\ln z-1-(z_0/z)(\ln z_0-1). \tag{11.2}$$

This, when combined with

$$X=\delta\int_{z_0}^{z}[z'(\ln z'-1)-z_0(\ln z_0-1)]^{-\frac{1}{2}}dz', \tag{11.3}$$

serves to determine z_0 and z for a given value of X.

Numerical solution of these two equations leads to the following results. For all values of X, there is the solution $z_0=z=\infty$, corresponding to the slice being in the normal phase. For X smaller than a critical length X_c, there are no other solutions. For X larger than X_c, there are two additional solutions. If X is appreciably larger than X_c, then these two solutions are $z_0\approx 1$, $z\approx e^{1+1/N(0)V}$ and $z_0\approx z=$ large number, the latter having the higher total energy of the two. In the limit as X approaches infinity, this latter solution coalesces with the normal-phase solution $z_0=z=\infty$. For X appreciably greater than X_c, the lower-energy solution is characterized by $\epsilon_0(x)\cong\epsilon_0(\infty)$ over most of the volume of the superconducting slice, so that the superconducting transition temperature of the slice is presumably nearly that of a bulk superconductor of the same material. As X approaches X_c from above, the two superconducting solutions coalesce and disappear. A plot of X_c (and of z and z_0 at $X=X_c$) as a function of $1/N(0)V$ is given in Fig. 2. Over the range of values of $1/N(0)V$ of interest (i.e., 2–5), this X_c is quite comparable with the critical distance computed in the previous section for the superconductor-normal-superconductor contact, as can be seen by comparing Fig. 2 with Eq. (10.5). This is in agreement with the experimental results of Meissner.

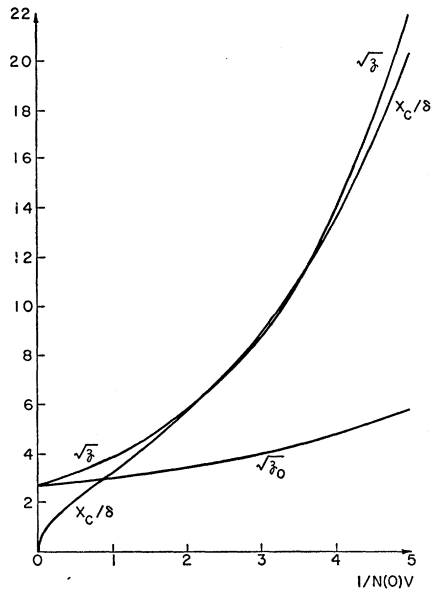

FIG. 2. Critical half thickness X_c of superconducting slice (and corresponding values of $z^{\frac{1}{2}}$ and $z_0^{\frac{1}{2}}$) as a function of $1/N(0)V$.

Although it appears impossible to get an analytic expression for X_c as a function of $N(0)V$, it is possible to show analytically that there is an X_c, i.e., to show that no superconducting solution exists if X is sufficiently small. Let us assume for the moment that $z=z_0+p$ where $p\ll z_0$. Thus

$$[z(\ln z-1)-z_0(\ln z_0-1)]^{\frac{1}{2}}\cong[p\ln z_0]^{\frac{1}{2}}, \tag{11.4}$$

$$(X/\delta)\cong\int_0^p[p'\ln z_0]^{-\frac{1}{2}}dp'=2[p/\ln z_0]^{\frac{1}{2}}, \tag{11.5}$$

$$(p/z_0)\cong(X/2\delta)^2(\ln z_0)/z_0, \tag{11.6}$$

$$1/N(0)V\cong(X/2\delta)^2(\ln z_0)^2/z_0. \tag{11.7}$$

Equation (11.6) shows that our assumption $p\ll z_0$ is indeed correct in the limits $z_0\to 1$ and $z_0\to\infty$. Equation (11.7) shows that $1/N(0)V$ increases from zero as

z_0 increases from one or decreases from infinity. This strongly suggests that there is some maximum value of $1/N(0)V$ as a function of z_0. This maximum represents the value of $1/N(0)V$ for which X is the critical length X_c. For any value of $1/N(0)V$ smaller than the maximum, there will be two corresponding values of z_0, representing the two possible superconducting solutions. For any value of $1/N(0)V$ greater than the maximum, there corresponds no value of z_0, indicating that no superconducting solution exists.

Let us assume that Eq. (11.7) holds for all values of z_0. Then we clearly see that there is a maximum value of $1/N(0)V$ equal to $(X/e\delta)^2$, occurring at $z_0=e^2$. This gives

$$X_c=e\delta[N(0)V]^{-\frac{1}{2}}, \tag{11.8}$$

and

$$p/z_0=1/2N(0)V. \tag{11.9}$$

Equation (11.9) shows that when $1/N(0)V\ll\frac{1}{2}$, it is indeed true that $p\ll z_0$ (so that Eq. (11.7) holds true) for all values of z_0. Figure 2 shows that X_c varies as $[N(0)V]^{-\frac{1}{2}}$ and $z\to z_0\to e^2$ as $1/N(0)V\to 0$. However, over the range of interest of $1/N(0)V$ (i.e., 2–5), Eq. (11.8) is not a good approximation to X_c.

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Band Structure of Aluminum

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Calculations of the band energies at symmetry points in aluminum by Heine are extended into the zone using the pseudopotential interpolation scheme in order to obtain constant-energy curves in the neighborhood of the Fermi surface. In conjunction with this calculation, the lines of contact between various bands are found in detail. The de Hass-van Alphen effect, cyclotron-resonance effect, anomalous skin effect, and low-temperature specific heat are discussed in terms of these constant-energy curves and the results compared with experiment. It appears from this comparison that the geometry of the Fermi surface is given quite well by the band calculations, but that there is a discrepancy of a factor of order two between the derived and measured effective masses. A "single orthogonalized-plane-wave approximation" is compared with the more exact treatment and found to be a good starting approximation, suitable for semiquantitative treatment of the electronic structure.

I. INTRODUCTION

FOLLOWING the remarkable success of Gold[1] in understanding extensive de Haas-van Alphen data on lead in terms of a "nearly-free-electron approximation", the author[2] applied the same method to existing data on aluminum. Again, the data seemed to fit quite closely that to be expected on the basis of this very simple model. In view of the success of this model in understanding the de Haas-van Alphen effect, it is desirable to consider the band structure of one of these metals in detail in order to see to what extent the simple model describes the actual band structure.

In the following sections the orthogonalized-plane-wave (OPW) calculations for aluminum by Heine[3] are extended to obtain constant-energy curves in wave-number space. These are compared with a "single-OPW approximation," the latter being equivalent to the "nearly-free-electron approximation" in its application. Finally, the descriptions of the de Haas-van Alphen effect, cyclotron-resonance effect, anomalous skin effect, and low-temperature specific heat derived from the two points of view are compared with each other and with experiment.

II. ENERGY-BAND CALCULATIONS

Heine[3] has calculated the energies of the bands at several points of high symmetry in the band using the orthogonalized-plane-wave method. In order to consider the behavior of the electron gas in aluminum, we require knowledge of the energy bands at more general points in the zone, and in particular near the Fermi surface. Heine[4] has indicated that in the first two bands the energy is quite close to the free-electron value except near the zone faces. This suggests[5] that in most of the band the wave functions may be fairly well described by a single OPW. This further suggests that near a zone face only two are necessary; near a zone edge, three; and near a zone corner, four. Finally, consideration of the zones in aluminum indicates that the mixing of OPW's in the region of interest should be describable in terms of only two independent off-diagonal matrix elements of the Hamiltonian. Thus

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