

## Magnetic-Field-Induced Surface States in a Pure Type-I Superconductor\*

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We consider the problem of a bulk pure type-I superconductor in a static magnetic field ( $H < H_c$ ) applied parallel to the surface. We show that there may exist single-particle excitations of energy (relative to the Fermi energy) less than the zero-field energy gap, which are spatially bound to the surface region where the screening current flows. We then investigate the contribution of these localized states to the electromagnetic absorption of the superconductor at frequencies below the zero-field absorption edge ( $2\Delta$ ). Order-of-magnitude estimates seem to be in agreement with the observations in aluminum by Budzinski and Garfunkel.

### I. INTRODUCTION

THE purpose of this paper is to investigate the changes in the BCS<sup>1</sup> spectrum of electronic excitations, induced by the application of magnetic field, in a pure type-I (or Pippard) superconductor. We shall furthermore discuss the manner in which these modifications may affect the absorption of electromagnetic radiation by the superconductor.

It is by now well known that the spectrum of excitations (in zero field) for an ideal superconductor has the BCS form<sup>1</sup>

$$\epsilon_k^0 = (\xi_k^2 + \Delta^2)^{1/2}, \quad (1.1)$$

where  $\epsilon_k^0$  is the energy of a single-particle excitation of momentum  $\mathbf{k}$ ,  $\xi_k$  is the energy of the corresponding normal-state electron relative to the Fermi energy, and  $\Delta$  is the energy gap. There are no single-particle excitations with energy less than  $\Delta$ . This energy gap causes all effects that depend on thermally excited quasiparticles to decrease as  $\exp(-\Delta/k_B T)$  for  $k_B T < \Delta$ . Thus, for example, at sufficiently low temperatures the contribution of the thermal quasiparticles to the absorption of electromagnetic radiation may be arbitrarily small. The only allowed mechanism for the absorption of a photon is then the excitation of a pair of quasiparticles from the ground state. This process requires a minimum photon energy of  $2\Delta$  ( $\Delta$  for each quasiparticle). The detailed shape of this absorption edge has been calculated by Mattis and Bardeen<sup>2</sup> and there have been several experimental investigations of the electromagnetic absorption both in the infrared<sup>3</sup> and microwave<sup>4</sup> domains.

When a small magnetic field is applied parallel to the surface of a bulk type-I superconductor, Meissner

currents are set up along the surface perpendicular to the field in such a way so as to screen out the field in same characteristic penetration depth  $\lambda$ , which is given in the Pippard<sup>1</sup> limit by  $\lambda \simeq \lambda_L^{2/3} \xi^{1/3}$ , where  $\lambda_L = (mc^2/4\pi ne^2)^{1/2}$  is the London penetration depth and  $\xi = \hbar v_f/\pi\Delta$  is the coherence length. For aluminum, a typical Pippard superconductor, the parameters take on the values  $\lambda \simeq 500 \text{ \AA}$ ,  $\lambda_L \simeq 160 \text{ \AA}$ ,  $\xi = 16 \times 10^3 \text{ \AA}$ . It is important to notice that the condition for type-I behavior  $\lambda/\xi \ll 1$  is well satisfied in this case. The problem at hand is to study the effect of the surface currents on the excitation spectrum.

Let us first consider a superconductor in a state of *uniform* current flow of current density  $\mathbf{j} = ne\mathbf{v}_s$  where  $\mathbf{v}_s$  is the superfluid velocity. In this case the excitation spectrum (1.1) becomes<sup>1</sup>

$$\epsilon_k = \epsilon_k^0 + \hbar \mathbf{k} \cdot \mathbf{v}_s, \quad (1.2)$$

where  $\epsilon_k^0$  is given by (1.1). The gap function  $\Delta$  appearing in (1.2) must be determined self-consistently and is, in general, a function of  $\mathbf{v}_s$ . For quasiparticles traveling antiparallel to the current, the minimum excitation energy is then  $\Delta - P_f v_s$ , where  $P_f$  is the Fermi momentum. The current thus lowers the effective energy gap for single-particle excitations. This, however, does not imply electromagnetic absorption (at absolute zero temperature) for frequencies less than  $2\Delta/\hbar$ . In a uniform system, momentum conservation requires that the two quasiparticles excited from the ground state have equal and opposite  $\mathbf{k}$ . Thus, the reduction of the excitation energy for quasiparticles traveling antiparallel to the current is compensated by the corresponding increase for excitations directed parallel to the current. Indeed Maki<sup>5</sup> has calculated the microwave surface impedance for this uniform situation and his results appear to substantiate these remarks. Maki has also pointed out that when  $\Delta - P_f v_s$  becomes zero there exist thermal excitations at arbitrarily low temperatures and hence no frequency domain of vanishing electromagnetic absorption.

Our problem of a bulk type-I superconductor in a magnetic field and thus with a *nonuniform* current

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<sup>1</sup> P. G. de Gennes, *Superconducting Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966).

<sup>2</sup> D. C. Mattis and J. Bardeen, *Phys. Rev.* **111**, 412 (1958).

<sup>3</sup> See for example, the review article by M. Tinkham in F. Abelès, *Optical Properties and Electronic Structure of Metals and Alloys* (North-Holland Publishing Company, Amsterdam, 1966).

<sup>4</sup> See, for example, M. A. Biondi, M. P. Garfunkel, and W. A. Thompson, *Phys. Rev.* **136**, A1471 (1964).

<sup>5</sup> K. Maki, *Phys. Rev. Letters* **14**, 98 (1965).

distribution has some significant differences relative to the uniform current problem. (1) Because the currents flow only within a penetration depth of the surface, those excited states which have their excitation energies reduced as in (1.2) can only exist in this surface region, i.e., they are bound to the surface. Cyrot<sup>6</sup> has treated the somewhat similar problem of the quasiparticle excitation spectrum near an isolated vortex in a type-II superconductor. (2) Even at the absolute zero of temperature there may exist electromagnetic absorption at frequencies less than  $2\Delta/\hbar$  because the nonuniform nature of the field distribution breaks down the momentum conservation selection rule. Such an effect has been observed by Budzinski and Garfunkel<sup>7</sup> in pure aluminum.

In Sec. II, within the framework of a simplified model of the field distribution, we calculate the excitation spectrum for these magnetic field induced surface states. Section III is devoted to a qualitative discussion of the effect of these surface states on the electromagnetic absorption at energies less than  $2\Delta$ .

## II. SURFACE STATES

We consider a semi-infinite type-I superconductor as depicted in Fig. 1, with a magnetic field,  $\mathbf{H}$ , directed along the  $z$  axis in the surface of the specimen and the Meissner currents therefore flowing along the  $y$  axis. We shall restrict our discussion to such fields that any intermediate state structure occurs over macroscopic distances and thus may be neglected in any discussion of surface phenomena. This is not a stringent requirement and is satisfied if  $H$  is only slightly less than the critical field  $H_c$ .

The excitation energies  $\epsilon$  are determined from the Bogoliubov equations,<sup>1</sup>

$$\begin{aligned} \epsilon u(\mathbf{r}) &= [(2m)^{-1}[(\hbar/i)\nabla - (e/c)\mathbf{A}]^2 - E_f]u(\mathbf{r}) \\ &\quad + \Delta(\mathbf{r})v(\mathbf{r}), \\ \epsilon v(\mathbf{r}) &= -[(2m)^{-1}[-(\hbar/i)\nabla - (e/c)\mathbf{A}]^2 - E_f]v(\mathbf{r}) \\ &\quad + \Delta^*(\mathbf{r})u(\mathbf{r}), \end{aligned} \quad (2.1)$$

where  $u(\mathbf{r})$  and  $v(\mathbf{r})$  are respectively the electron-like and hole-like amplitudes of the quasiparticle wavefunction. In (2.1), the standard Hartree-Fock potential has been omitted. It plays no central role in our simple model and could be included without difficulty. The self-consistent gap function (or pair potential)  $\Delta(\mathbf{r})$  is given by

$$\Delta(\mathbf{r}) = V \sum_n v_n^*(\mathbf{r}) u_n(\mathbf{r}) (1 - 2f_n), \quad (2.2)$$

where  $V$  is the strength of the separable BCS electron-electron interaction,  $f_n$  is the Fermi distribution function for the  $n$ th state, and the sum is over all states. By means of the Landau-Ginsburg theory, Caroli<sup>8</sup> has shown that a magnetic field suppresses  $\Delta(\mathbf{r})$  near the

<sup>6</sup> M. Cyrot, *Physik Kondensierten Materie* **3**, 374 (1965).

<sup>7</sup> W. V. Budzinski and M. Garfunkel, *Phys. Rev. Letters* **16**, 1100 (1966); **17**, 24 (1966).

<sup>8</sup> C. Caroli, *Ann. Inst. Henri Poincaré* **4**, 159 (1966).

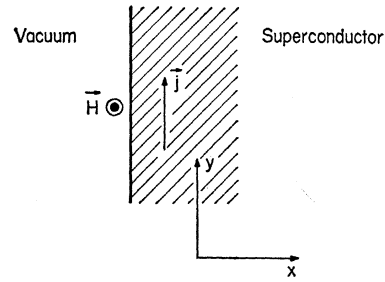


FIG. 1. The geometry under consideration: a semi-infinite superconducting slab with a static magnetic field applied along the  $z$  axis in the plane of the surface; the screening current  $j$  is also in the surface plane but perpendicular to the field; the  $x$  direction is perpendicular to the surface which is taken to be at  $x=0$ . The impinging electromagnetic wave is taken to be polarized with its electric field directed along the  $y$  axis.

surface only slightly from the BCS value in the absence of a field. In fact, she finds

$$\Delta(0) \simeq \Delta(1 - \kappa/2\sqrt{2}), \quad (2.3)$$

where  $\Delta$  is the zero-field energy gap,  $\Delta(0)$  is the value of the gap parameter at the surface for  $H=H_c$ , and the Landau-Ginsburg parameter  $\kappa \simeq \lambda_L/\xi$ . For the type-I situation of interest here  $\kappa \ll 1$ , and thus  $\Delta(0) \simeq \Delta$ . Furthermore we expect that the principal spatial variation of  $\Delta(\mathbf{r})$  occurs on the scale of  $\xi$ . Thus, since we are mainly interested here in phenomena which take place within a few penetration depths of the surface we may assume that  $\Delta(\mathbf{r})$  is spatially constant and maintains its zero-field value. It has been implicitly assumed that the gap parameter is real. In the presence of magnetic fields, this is the case if the vector potential  $\mathbf{A}$  is chosen in the London gauge, i.e.,  $\text{div } \mathbf{A} = 0$  and the component of  $\mathbf{A}$  normal to the surface is zero. We shall employ this gauge throughout. In principal, the vector potential must also be determined self-consistently. However, for our purpose, it is sufficient to approximate the exact field distribution by an exponential decay of the form

$$h(x) = H e^{-x/\lambda}, \quad (2.4)$$

where  $H$  is the applied field and  $x$  is the distance from the surface of the specimen. This distribution is generated from the vector potential

$$A_x = A_z = 0, \quad A_y = A(x) = -H\lambda e^{-x/\lambda} \quad (2.5)$$

which indeed satisfies the London gauge.

The Bogoliubov equations (2.1), for this problem, are separable in Cartesian coordinates, and can be reduced to a one dimensional form by the transformation

$$\begin{aligned} u(\mathbf{r}) &= u(x) \exp[i(k_y y + k_z z)]; \\ v(\mathbf{r}) &= v(x) \exp[i(k_y y + k_z z)]. \end{aligned} \quad (2.6)$$

The quadratic term in the vector potential in (2.1) can be shown to be negligible relative to the linear term

as follows: The ratio of these terms, using (2.6), is

$$\frac{(eA/c)^2}{(2e\hbar k_y A/ic)} = \frac{eA}{2\hbar c k_y} = \frac{1}{2}(\pi) \frac{A}{\phi_0 k_y}, \quad (2.7)$$

where  $\phi_0 = ch/2e$  is the flux quantum. Then using (2.4) and the relation for the critical field

$$H_c = (\frac{3}{2})^{1/2} (\phi_0/\pi^2 \xi \lambda_L),$$

the ratio in (2.7) becomes approximately

$$(2\pi)^{-1} (\frac{3}{2})^{1/2} (H/H_c) (\lambda/\lambda_L) (\xi k_y)^{-1} \ll 1 \text{ for } \xi k_y \gg 1;$$

but, because we are principally interested in electrons traveling along the  $y$  axis  $k_y \simeq k_f$ , the ratio is much less than unity and we are able to drop the  $A^2$  term in (2.1). Under these conditions, the Bogoliubov equations become

$$\begin{aligned} \epsilon u(x) &= \left[ K_t - E_f - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \frac{e\hbar}{mc} A(x) k_y \right] u(x) + \Delta v(x), \\ \epsilon v(x) &= \left[ -K_t + E_f + \frac{\hbar^2}{2m} \frac{d^2}{dx^2} - \frac{e\hbar}{mc} A(x) k_y \right] v(x) + \Delta u(x), \end{aligned} \quad (2.8)$$

where  $K_t = (\hbar^2/2m)(k_y^2 + k_z^2)$  is the transverse kinetic energy. Using (2.5), the vector-potential term in (2.8) can be treated as the velocity-dependent potential

$$V(x) = (e\hbar/mc) k_y \lambda H e^{-x/\lambda}. \quad (2.9)$$

This potential is attractive or repulsive depending on the sign of  $k_y$ , i.e., electrons traveling antiparallel to the current experience an attractive potential, while the parallel moving electrons are repelled from the surface.

At this point we must decide how to treat the surface, i.e., what boundary condition is to be imposed on  $u(x)$  and  $v(x)$  at the surface  $x=0$ . For simplicity, we shall assume an ideal surface in the sense that we replace the semi-infinite slab by an infinite sample and symmetrizing the potential  $V(x)$  with respect to the plane  $x=0$ . There will then be symmetric and anti-symmetric solutions for  $u(x)$  and  $v(x)$ . While the details of the excitation spectrum depend on the exact choice of boundary conditions we hope that the qualitative nature of the results are unchanged.

Even with this simplified choice of boundary conditions, the Bogoliubov equations (2.8) with  $V(x)$  given by (2.9) are rather messy to handle. In order to make the problem more tractable, we approximate  $V(x)$  by a rectangular potential  $\bar{V}$ . This is accomplished in an arbitrary way by choosing the width of the well to be  $\lambda$  and adjusting its depth (or height) to be such that its area is the same as that given by (2.9), i.e.,

$$\bar{V} \lambda = \int_0^\lambda V(x) dx \simeq (e\hbar/2mc) k_y \lambda^2 H. \quad (2.10)$$

For electrons traveling antiparallel to the drift current, the form of this potential is given in Fig. 2. Of course the sign of the potential for the holes is opposite to

that for the electrons. The equations (2.8) now reduce to a pair of coupled Schrödinger equations for a one-dimensional square well: One equation describes the electronic excitation, the other is for the holes, and the coupling is via the gap parameter  $\Delta$ . These equations are now solved by the standard technique of forming solutions in the two regions (I and II of Fig. 2) and requiring that the wave-functions [in this case  $u(x)$  and  $v(x)$ ] be continuous and have continuous derivatives across the boundary at  $x=\lambda$ . The coupled equations are now

$$\begin{aligned} \epsilon u(x) &= [-\alpha - (\hbar^2/2m)(d^2/dx^2) - V]u(x) + \Delta v(x), \\ \epsilon v(x) &= [\alpha + (\hbar^2/2m)(d^2/dx^2) - V]v(x) + \Delta u(x), \end{aligned} \quad (2.11)$$

where  $\alpha = E_f - K_t$  and  $\bar{V} = 0$  for  $|x| > \lambda$  and  $V = \bar{V}$  for  $|x| < \lambda$ . Now assuming that  $u(x)$  and  $v(x)$  vary as  $e^{iqx}$ , we find from (2.11) for  $|x| > \lambda$ ,

$$\epsilon = (\xi_q^2 + \Delta^2)^{1/2}, \quad (2.12)$$

where  $\xi_q = (\hbar^2 q^2/2m) - \alpha$  is the total kinetic energy relative to the Fermi energy. Formally this is identical to the BCS spectrum (1.1). However, there is no longer translational symmetry along the  $x$  axis and therefore  $q$  need not be real. Indeed as we are interested in states of energy less than  $\Delta$ , it is necessary that  $\xi_q$  be imaginary.<sup>9</sup> This implies a complex  $q$ , which is given by

$$\begin{aligned} q = (2m/\hbar^2)^{1/2} \{ \pm [\frac{1}{2}((\alpha^2 + |\xi_q|^2)^{1/2} + \alpha)]^{1/2} \\ + i[\frac{1}{2}((\alpha^2 + |\xi_q|^2)^{1/2} - \alpha)]^{1/2} \}, \end{aligned} \quad (2.13)$$

where the  $(\pm)$  refer to right and left traveling waves, respectively. Thus, if there exist bound states with  $\epsilon < \Delta$  the electron and hole amplitudes for these states are exponentially decreasing oscillating functions in the forbidden region. For  $0 < \epsilon < \Delta$  the characteristic extent

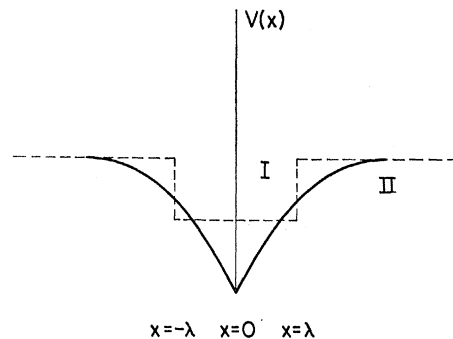


Fig. 2. The solid line represents schematically the effective one-dimensional potential experienced by quasiparticles traveling antiparallel to the screening current. The dashed line represents our square-well approximation. In the figure, the potential is symmetrized with respect to the surface, thus determining the boundary conditions.

<sup>9</sup> This is in contradistinction to the ordinary Schrödinger equation square-well problem where the bound states have negative kinetic energies in the classically forbidden region.

of the amplitudes  $u(x)$  and  $v(x)$  in this forbidden region is from (2.13),  $(\xi\lambda_f)^{1/2}$  where  $\lambda_f$  is the Fermi wavelength. In the case of aluminum,  $\xi \approx 16 \times 10^3 \text{ \AA}$  and  $\lambda_f \approx 3 \text{ \AA}$ , this distance is approximately  $200 \text{ \AA}$  and is therefore of the same order of magnitude as the penetration depth  $\lambda$ .

In the interior region  $|x| < \lambda$ , (2.11) gives

$$\epsilon = (\Delta^2 + \xi k^2)^{1/2} - \bar{V}, \quad (2.14)$$

which is the analog of (1.2) for this problem. In this case the two wave vectors are given by

$$k = (2m/\hbar^2)^{1/2} \{ \alpha \pm [(\epsilon + \bar{V})^2 - \Delta^2]^{1/2} \}. \quad (2.15)$$

Notice that if the second term in the curly bracket is larger than  $\alpha$ , one value of  $k$  is pure imaginary while the other is always real.

It is now necessary to match the solutions in the two regions at their mutual boundaries  $|x| = \lambda$ . There exist two types of solutions: symmetric with respect to the surface [zero slope at  $x=0$  for  $u(x)$  and  $v(x)$ ] and antisymmetric [ $u(x)$  and  $v(x)$  are zero at the surface]. We shall consider the symmetric solutions in some detail. The antisymmetric solutions have the same general behavior. For the even solutions in the interior region we may take

$$\begin{aligned} u(x) &= \mu_0 \cos k_0 x + \mu_1 \cos k_1 x, \\ v(x) &= \nu_0 \cos k_0 x + \nu_1 \cos k_1 x, \end{aligned} \quad (2.16)$$

where  $k_0$  and  $k_1$  correspond to the two expressions for the wave vector given in (2.15). The coefficients  $\mu_i$  and  $\nu_i$  are related by (2.11):

$$\Delta \nu_{0,1} = (\epsilon \mp \xi k \pm \bar{V}) \mu_{0,1}, \quad (2.17)$$

where the minus sign corresponds to the zero subscript. In the exterior region, we may express  $u(x)$  and  $v(x)$  by

$$\begin{aligned} u(x) &= u_0 \exp(iq|x|) + u_1 \exp(-iq^*|x|), \\ v(x) &= v_0 \exp(iq|x|) + v_1 \exp(-iq^*|x|), \end{aligned} \quad (2.18)$$

where  $q$  is that solution (2.13) with  $\text{Re}q > 0$  and  $\text{Im}q > 0$ . Again  $u_{0,1}$  and  $v_{0,1}$  are related (2.11) by

$$\Delta v_{0,1} = (\epsilon \mp i | \xi_q |) u_{0,1}, \quad (2.19)$$

where the zero subscript corresponds to the minus sign. We now match (2.16) and (2.17) at the boundary  $|x| = \lambda$  in the usual way and find, with the aid of (2.17) and (2.19), the secular equation

$$\begin{aligned} 4i\xi k | \xi_q | |q|^2 - 2\xi k | \xi_q | (q - q^*) (k_1 \tan k_1 \lambda + k_0 \tan k_0 \lambda) \\ + i(q + q^*) (\xi k^2 - | \xi_q |^2 - \bar{V}^2) (k_1 \tan k_1 \lambda - k_0 \tan k_0 \lambda) \\ + 4ik_0 k_1 \tan k_0 \lambda \tan k_1 \lambda \xi k | \xi_q | = 0, \end{aligned} \quad (2.20)$$

where  $\xi k$  and  $\xi_q$  are the kinetic energies relative to the Fermi level in the interior and exterior regions, respectively. This eigenvalue equation has been solved numerically for the excitation energy  $\epsilon$  as a function of the effective well depth  $\bar{V}$  for several values of the parameter  $\alpha$ . This parameter together with the kinetic

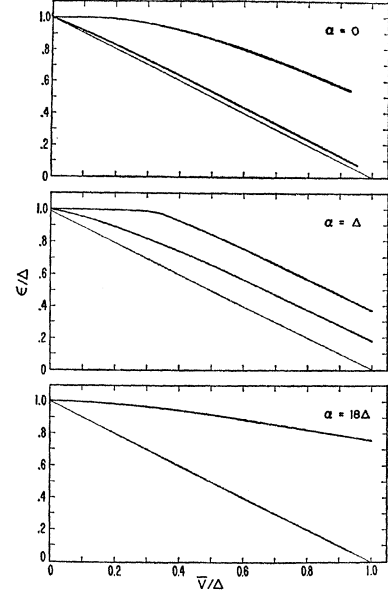


FIG. 3. Some examples of the bound-state spectrum as a function of the well depth  $\bar{V}$  for three values of the parameter  $\alpha$  defined in the text.

energies  $\xi k$  describes the angle between the directions of propagation of the excitation and the surface of the sample; e.g.,  $\alpha=0$  describes motion antiparallel to the Meissner current. In Fig. 3 we have plotted the bound-state excitation energies as a function of the potential  $\bar{V}$ . For values of  $\alpha \gtrsim 20\Delta$ , the bound states have excitation energies only very slightly less than  $\Delta$ . Therefore  $\alpha \approx 20\Delta$ , for aluminum, is approximately the maximum value of that parameter for which there is an appreciable reduction in the minimum excitation energy. For electrons at the Fermi surface, this corresponds to an angle  $\theta \approx (\alpha/E_f)^{1/2} \approx (k_f \xi)^{-1/2} \approx 10^{-2}$  between the surface and the propagation direction of the electrons. Thus only very few electrons become bound to the surface. However, these states have large amplitudes near the surface and may therefore play an important role in surface phenomena. The eight amplitudes  $u_{0,1}, v_{0,1}, \mu_{0,1}, \nu_{0,1}$  can be determined by (2.17), (2.19), three of the four matching equations, and the normalization condition

$$\int_0^\infty [ |u(x)|^2 + |v(x)|^2 ] dx = 1. \quad (2.21)$$

For electronic states with  $k_y$  parallel to the screening current the potential  $\bar{V}$  is repulsive and thus there are no states bound to the surface. Nevertheless for our subsequent discussion of electromagnetic absorption we must give a discussion of at least the lowest-lying excitations of this type. We shall particularly focus on those states in the energy range  $\Delta + \bar{V} > \epsilon > \Delta$  because only these play an important role for absorption with  $\hbar\omega < 2\Delta$ . In the exterior region  $|x| > \lambda$ , Eq. (2.12) still applies. However, there is now no possibility for excitations with energies less than  $\Delta$ , and the kinetic energy  $\xi_q$  is real. In the interior region we find

$$\epsilon = (\Delta^2 + \xi k^2)^{1/2} + | \bar{V} |. \quad (2.22)$$

This implies imaginary kinetic energies  $\xi k$  for states

with  $\Delta + \bar{V} > \epsilon > \Delta$  and consequently exponentially damped waves in the surface region. These excitations are thus states which tunnel into the region of Meissner current flow. They form a continuum whose density of levels is roughly the BCS density of states. We shall not discuss these tunneling states in more detail here because their description is algebraically rather complex.

### III. ELECTROMAGNETIC ABSORPTION

Budzinski and Garfunkel<sup>4</sup> have demonstrated by microwave experiments in pure bulk aluminum that the absorption of electromagnetic energy at frequencies below  $(2\Delta/\hbar)$  is strongly enhanced when a static magnetic field (less than the critical field) is applied parallel to the surface. In this section, we shall show that the surface states discussed in Sec. II may be responsible for this field-induced absorption. We shall develop some general expression for the absorption and then make some very crude estimates of the effects of the surface states.

We shall begin by treating the electromagnetic field as a perturbation:

$$\mathcal{H}' = - (e/2mc) \sum_i [\mathbf{P}_i \cdot \mathbf{A}'(\mathbf{r}_i) + \mathbf{A}'(\mathbf{r}_i) \cdot \mathbf{P}_i], \quad (3.1)$$

where the sum is over all electrons and  $\mathbf{A}'$  is the vector potential associated with the oscillating electric field. Clearly the coupling of the electromagnetic field to the surface states will be greatest if the electric field is polarized along the direction of the Meissner current, i.e., along the  $y$  axis. In fact Budzinski and Garfunkel<sup>4</sup> have indeed observed a strong anisotropy in the microwave absorption when the polarization direction of the

electric field vector is rotated in the plane of the surface. For these reasons and to simplify the notation we shall restrict the electric field to the  $y$  axis, and then

$$\mathbf{A}' = A_y \hat{y} = - (c/i\omega) e^{i\omega t} E(x) \hat{y}, \quad (3.2)$$

where  $\omega$  is the applied frequency and  $E(x)$  is the electric field amplitude which, because of the surface screening currents, falls off to zero in the interior of the sample over distances of the order of the penetration depth  $\lambda$ . The coupling Hamiltonian may be written in second-quantized form<sup>1</sup> by

$$\mathcal{H}_{\text{eff}} = \sum_{\alpha} \int \Psi^*(\mathbf{r}, \alpha) \mathcal{H}' \Psi(\mathbf{r}, \alpha) d\mathbf{r}, \quad (3.3)$$

where  $\alpha$  denotes the spin index and the field operators  $\Psi$  are given in terms of the creation and annihilation operators for quasiparticles in the state  $n$ ,  $\gamma_n^\dagger$ , and  $\gamma_n$  by

$$\begin{aligned} \Psi(\mathbf{r}, \uparrow) &= \sum_n [\gamma_n^\dagger u_n(\mathbf{r}) - \gamma_n v_n^*(\mathbf{r})], \\ \Psi(\mathbf{r}, \downarrow) &= \sum_n [\gamma_n v_n(\mathbf{r}) + \gamma_n^\dagger v_n^*(\mathbf{r})]. \end{aligned} \quad (3.4)$$

The second-quantized coupling Hamiltonian may be written as

$$\mathcal{H}_{\text{eff}} = \mathcal{H}_0 + \mathcal{H}_1, \quad (3.5)$$

where  $\mathcal{H}_0$  and  $\mathcal{H}_1$  describe, respectively: (a) the absorption of a photon accompanied by the creation of a pair of quasiparticles (or the inverse process); (b) the absorption of a photon by a thermal quasiparticle which is then scattered into another quasiparticle state. Substituting (3.4) into (3.3), we find

$$\mathcal{H}_0 = \sum_{n,p} \gamma_n^\dagger \gamma_p \int [u_p^*(\mathbf{r}) \mathcal{H}' v_n^*(\mathbf{r}) d\mathbf{r} + \int u_n^*(\mathbf{r}) \mathcal{H}' v_p^*(\mathbf{r}) d\mathbf{r}] + \text{H.c.}, \quad (3.6a)$$

$$\mathcal{H}_1 = \sum_{n,p} (\gamma_n^\dagger \gamma_p + \gamma_n v_p^\dagger) \left[ \int u_n^*(\mathbf{r}) \mathcal{H}' u_p(\mathbf{r}) d\mathbf{r} - \int v_p(\mathbf{r}) \mathcal{H}' v_n^*(\mathbf{r}) d\mathbf{r} \right]. \quad (3.6b)$$

Using (3.1) and (3.2) for the electromagnetic perturbation together with (2.6), the pair-breaking and quasiparticle scattering terms become

$$\mathcal{H}_0 = \sum_{n,p} \gamma_n^\dagger \gamma_p \int M_{pn} \delta_{k_{nz}, -k_{pz}} \delta_{k_{ny}, -k_{py}} + \text{H.c.}, \quad (3.7a)$$

$$\mathcal{H}_1 = \sum_{n,p} (\gamma_n^\dagger \gamma_p + \gamma_n v_p^\dagger) N_{pn} \delta_{k_{nz}, k_{pz}} \delta_{k_{ny}, k_{py}}, \quad (3.7b)$$

where the matrix elements  $M_{pn}$  and  $N_{pn}$  are given by

$$M_{pn} = (e\hbar k_{ny}/im\omega) \left[ \int u_p^*(x) E(x) v_n^*(x) dx - \int u_n^*(x) E(x) v_p^*(x) dx \right], \quad (3.8a)$$

$$N_{pn} = (e\hbar k_{ny}/im\omega) \left[ \int u_n^*(x) E(x) u_p(x) dx + \int v_n^*(x) E(x) v_p(x) dx \right]. \quad (3.8b)$$

The formulas (3.7a) and (3.7b) exhibit explicitly the conservation of electronic momentum in the plane of the surface when the photon momentum is negligible.

The electromagnetic power absorbed is given quite generally by

$$W = 2\pi\omega \sum_{i,f} |\langle f | \mathcal{H}_{\text{eff}} | i \rangle|^2 \delta(\epsilon_f - \epsilon_i - \hbar\omega), \quad (3.9)$$

where  $i$  and  $f$  denote initial and final electronic states, respectively.

### A. Absolute Zero

We shall first restrict our discussion to absolute zero where there are rigorously no excited states occupied. Then only  $\mathcal{H}_0$  is operative, i.e., the only absorption mechanism is the excitation of a pair of quasiparticles. The energy conservation condition is then

$$\hbar\omega = \epsilon_n + \epsilon_p. \quad (3.10)$$

Furthermore, the momentum conservation selection rule requires that the two excitations have wave vectors whose  $y$  components are equal in magnitude and oppositely directed. Therefore only one of these quasiparticles can belong to the quasidecrete spectrum of surface states (described in the last section) with energies less than  $\Delta$ . Since we are interested in absorption at frequencies less than  $(2\Delta/\hbar)$ , we must excite one surface state with  $\Delta > \epsilon_n > \Delta - \bar{V}$  and one tunneling state with  $\Delta + \bar{V} > \epsilon_p > \Delta$ . It is interesting to note that no such mechanism can occur in a superconductor with a *uniform* current. In that case the momentum conserving quasiparticle pairs would have a minimum total energy of  $2\Delta$ .

In principle, the absorption (2.9) could be explicitly calculated using the results of the previous section. This would, however, be rather tedious and we shall therefore content ourselves here with making some very crude order of magnitude estimates. First of all the oscillating electric field extends into the metal a characteristic distance  $\delta$  which is typically of the same order of magnitude as the effective penetration depth  $\lambda$ . Thus, the domain of integration in the matrix elements (3.8) is limited to  $\delta$ . In order to calculate the matrix element  $M_{pn}$ , we need the amplitudes  $u_i(x)$  and  $v_i(x)$

for both the surface and tunneling states. Near the surface, from Sec. II, we can determine roughly that

$$u_n(x), v_n(x) \sim \lambda^{-1/2} \exp[-x(\xi\lambda_f)^{-1/2}] \quad (3.11)$$

for the surface states. The factor  $\lambda^{-1/2}$  is a result of the normalization condition (2.21). Notice that in our rough approximation we have lost the distinction between the hole-like and electron-like amplitudes. This does not imply a cancellation of the two terms in  $M_{pn}$ . A more exact treatment keeping the phases of the  $u$ 's and  $v$ 's indeed shows that no such cancellation occurs. Similarly the tunneling-state amplitudes in the surface region,  $x \lesssim \delta$ , can be given by

$$u_p(x), v_p(x) \sim L^{-1/2} \exp[x(\xi\lambda_f)^{-1/2}], \quad (3.12)$$

where  $L$  is the thickness of the sample. Then the matrix element  $M_{pn}$  is of order

$$M_{pn} \sim (eE\hbar k_y/im\omega)\delta(\lambda L)^{-1/2}. \quad (3.13)$$

The power absorbed then becomes

$$W \simeq 2\pi\omega \sum_{p,n} |M_{pn}|^2 \delta(\epsilon_p + \epsilon_n - \hbar\omega). \quad (3.14)$$

Then assuming  $M_{pn}$  is constant and replacing the sum over the continuum states by an integral with the BCS density of states, we find

$$W \simeq 2\pi\omega |M|^2 N(0) \sum_n (\hbar\omega - \epsilon_n) [(\hbar\omega - \epsilon_n)^2 - \Delta^2]^{-1/2}, \quad (3.15)$$

where the BCS density of states is

$$N(\epsilon) = N(0)\epsilon [ \epsilon^2 - \Delta^2 ]^{-1/2}, \quad (3.16)$$

and  $N(0)$  is the normal metal density of states at the Fermi surface. The sum over the bound states of the quasidecrete spectrum is now estimated in the following way. Given  $k_y$  and  $k_z$ , the eigenvalue problem determines  $k_x$ . If we now assume that the states of interest lie very close to the Fermi surface, we may use (2.14) in the form

$$\epsilon_n \simeq \Delta - V_0 \cos\phi, \quad (3.17)$$

where  $V_0$  is the value of  $\bar{V}$  for  $k_y = k_f$  and  $\cos\phi = (k_y/k_f)$ . Then the sum is rewritten as an integration over  $k_y$  and  $k_z$ , which in cylindrical coordinates is

$$\sum_n (\hbar\omega - \epsilon_n) [(\hbar\omega - \epsilon_n)^2 - \Delta^2]^{-1/2} \simeq [k_f S / (2\pi)^2] \iint dk d\phi (\hbar\omega - \epsilon_n) [(\hbar\omega - \epsilon_n)^2 - \Delta^2]^{-1/2}, \quad (3.18)$$

where  $S$  is the surface area of the sample. The  $k$  integral is restricted by the condition that the angle  $\theta$  between the quasiparticle propagation direction and the surface must be small, i.e., the limits on the  $k$  integral are  $k_f(1 - \cos\theta)$  and  $k_f$ . The  $\phi$  integral is limited by the fact that the minimum continuum energy is  $\Delta$ , i.e.,

$$\hbar\omega - \epsilon_n \geq \Delta, \quad (3.19)$$

or using (3.17), the maximum value of  $\phi$  is given by

$$\phi_{\text{max}} = \cos^{-1}[(2\Delta - \hbar\omega)/V_0]. \quad (3.20)$$

The absorbed power then becomes

$$W \simeq \omega |M|^2 N(0) S k_f^2 (\theta^2/4\pi) \int_0^{\phi_{\text{max}}} d\phi (\hbar\omega - \epsilon_n) [(\hbar\omega - \epsilon_n)^2 - \Delta^2]^{-1/2}. \quad (3.21)$$

If we form the ratio of this to the normal-metal absorption in the usual way, we find

$$W_S/W_n \simeq (\hbar k_f \theta^2 / 2m\omega\lambda) \int_0^{\phi_{\max}} d\phi (\hbar\omega - \epsilon_n) [(\hbar\omega - \epsilon_n)^2 - \Delta^2]^{-1/2}, \quad (3.22)$$

where we have used the free-electron expression for the density of states

$$N(0) = mk_f / 2\pi^2 \hbar^2. \quad (3.23)$$

For aluminum we have seen in the previous section that  $\theta^2 \sim 10(k_f \xi)^{-1}$ . Rewriting (3.22), we have

$$W_S/W_n \simeq 5\pi(\Delta/\hbar\omega)(k_f \lambda)^{-1} I(\hbar\omega/\Delta, V_0/\Delta), \quad (3.24)$$

where  $I$  is the  $\phi$  integral. In the frequency regime where absorption can occur ( $\hbar\omega > 2\Delta - V_0$ ),  $I$  is a slowly varying function of  $\omega$  and is of order unity. For aluminum  $H \sim (\frac{1}{2})H_c$  gives  $V_0 \sim \Delta$  and thus  $\hbar\omega_{\min} \sim \Delta$  as observed by Budzinski and Garfunkel. In this case  $k_f \lambda \sim 10^8$  which gives a relative absorption  $W_S/W_n \sim 10^{-2}$ . This seems to be about a factor of 5 smaller than the observed absorption below  $2\Delta$ . We must emphasize that these estimates are very crude.

### B. Finite Temperature

At a finite temperature  $T$  ( $< T_c$ ), aside from the temperature dependence of the energy gap, there exists a further modification of the electromagnetic absorption caused by thermally excited bound-state excitations. In particular, a thermally excited surface state can absorb a photon and be excited into the continuum

preserving the initial values of  $k_y$  and  $k_z$ . Of course in addition there may be transitions between bound states. We shall neglect such processes because of their low density of states. However, they may play an important role in low-frequency ( $\hbar\omega \ll 2\Delta$ ) microwave absorption such as performed by Richards.<sup>10</sup>

The matrix elements  $N_{pn}$  for the microwave-induced transitions from a bound state to the continuum are enhanced over the quasiparticle pair excitation mechanism considered in the last section by the fact that the continuum states with energies of the order of  $\Delta$  do not now tunnel into the surface region but are more nearly plane-wave-like, i.e., they involve quasiparticles traveling antiparallel to the screening current, for which there is no potential barrier at the surface. The power absorbed from the electromagnetic wave is then

$$W \simeq 2\pi\omega \sum_{p,n} |N_{pn}|^2 (f_n - f_p) \delta(\epsilon_p - \epsilon_n - \hbar\omega), \quad (3.25)$$

where the states  $n$  are the surface states and  $p$  labels the continuum states with the same values of  $k_y$  and  $k_z$ . The factors  $f_p$  and  $f_n$  are the corresponding Fermi distribution functions, and

$$N_{pn} \sim M_{pn} \exp[x(\xi\lambda_f)^{-1/2}]. \quad (3.26)$$

The analog of (3.15) is now

$$W \simeq 2\pi\omega |N|^2 N(0) \sum_n (\hbar\omega + \epsilon_n) [(\hbar\omega + \epsilon_n)^2 - \Delta^2]^{-1/2} [f(\epsilon_n) - f(\epsilon_n + \hbar\omega)]. \quad (3.27)$$

If we now assume  $\hbar\omega > k_B T$ , the second Fermi factor appearing in (3.27) is approximately zero, and in a similar way to the last section the analog of (3.22) is

$$W_S/W_n \simeq (\hbar k_f \theta^2 / 2m\omega\lambda) \exp[2\delta(\xi\lambda_f)^{-1/2}] \int_{\phi_{\min}}^{\phi_{\max}} d\phi (\hbar\omega + \epsilon_n) [(\hbar\omega + \epsilon_n)^2 - \Delta^2]^{-1/2}, \quad (3.28)$$

where  $\phi_{\max}$  is now determined by the condition  $\epsilon_n \lesssim k_B T$  which is

$$\phi_{\max} = \cos^{-1}[(\Delta - k_B T)/V_0]. \quad (3.29)$$

The minimum value  $\phi_{\min}$  is determined by the condition that the state  $p$  be in the continuum, i.e.,  $\epsilon_p \geq \Delta$ . This gives

$$\phi_{\min} = \cos^{-1}(\hbar\omega/V_0), \quad (3.30)$$

provided that  $\hbar\omega < \Delta$ . If  $\hbar\omega > \Delta$ ,  $\phi_{\min}$  is zero. Again analogously to (3.24), we have

$$W_S/W_n \simeq 5\pi(\Delta/\hbar\omega)(k_f \lambda)^{-1} \times \exp[2\delta(\xi\lambda_f)^{-1/2}] J(\hbar\omega/\Delta, V_0/\Delta, k_B T/\Delta). \quad (3.31)$$

For example, for  $V_0 \sim \Delta$ ,  $k_B T \sim \Delta/3$ ,  $\hbar\omega \sim (\frac{3}{2})\Delta$ ,  $J$  is of order unity, the exponential term is of the order 10

and we see then that this mechanism may dominate the pair-creation term calculated before. The rough orders of magnitude are consistent with Budzinski's and Garfunkel's observations in aluminum and may therefore provide the physical mechanism for the absorption below the gap. Better surface-impedance calculations should be able to prove or disprove the conjectures given here.

### IV. CONCLUSIONS

We have shown that in a pure type-I superconductor in a static magnetic field  $H$  ( $< H_c$ ) there may exist quasiparticle excitations, bound to the surface, which have energies less than the zero-field energy gap.

<sup>10</sup>P. L. Richards, Phys. Rev. 126, 912 (1962).

Assuming that (1) the order parameter is independent of field and spatially constant (which is not self-consistent), and (2) approximating the vector potential by a square well (or barrier) we have calculated the spectrum of these excited states. The bound states occur for electrons traveling rather accurately antiparallel to the screening current. It would seem difficult to observe the bound states by single-particle tunneling because such experiments are most sensitive to quasiparticles traveling perpendicular to the surface.

The bound states give rise to electromagnetic absorption at frequencies  $\hbar\omega < 2\Delta$  even at absolute zero. The mechanism is the excitation of a bound state and a continuum state from the condensate. At finite temperatures, such that the thermal energy is greater than some typical bound-state energies, there exists the somewhat stronger mechanism of the scattering of a bound state by a photon into the continuum. Very approximate order-of-magnitude estimates of these processes seem to be in rough agreement with the

microwave absorption in aluminum. Furthermore at low frequencies ( $\hbar\omega \ll 2\Delta$ ) the electromagnetic waves may induce transitions between bound states. This is possibly related to Richards'<sup>10</sup> observations in tin.

In addition to more precise calculations of the phenomena discussed here, further studies should include a consideration of the important effects of nonmagnetic impurities as observed in aluminum.<sup>7</sup>

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### Ferromagnetism of an Electron Gas

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The ferromagnetic stability of an electron gas (with uniform positive charge background) interacting through a Yukawa potential with an arbitrary screening parameter has been examined previously. Here three evaluations of the screening parameter based on Thomas-Fermi, self-consistency, and plasma-cutoff considerations are given and the corresponding ferromagnetic stability is discussed. It is concluded that for  $r_s > 9.4$ , where  $\frac{4}{3}\pi r_s^3$  is the volume per electron, such a system may become ferromagnetic for the third type of screening, while the other two do not exhibit ferromagnetism at all.

**T**HE first to point out that an electron gas with a compensating positive background becomes ferromagnetic in the Hartree-Fock approximation if  $r_s > 5.45$  when bare Coulomb interaction is assumed to exist between the electrons was Bloch.<sup>1</sup> Here  $r_s$  is the radius of the sphere whose volume equals the volume per electron and is measured in units of Bohr radius. Wigner<sup>2</sup> pointed out that this calculation is not quite reliable because of the neglect of Coulomb correlations. Pines<sup>3</sup> showed from his collective description of this system that as a result of long-range Coulomb correlations, the electron-electron interaction is reduced to an interaction of range  $k_e^{-1}$ , where  $k_e$  is the cutoff momentum beyond which plasma oscillations do not exist as stable excitations of the system. Assuming  $k_e$  to be independent of magnetization, he surmised that

the tendency towards ferromagnetism is absent in such a system. A more detailed calculation based on these ideas was made by Shimuzu,<sup>4</sup> confirming the conclusions of Pines. Very recently, Hedin<sup>5</sup> and, in more detail, Misawa,<sup>6</sup> used the Gell-Mann-Brueckner formalism to compute the tendency towards ferromagnetism. This calculation takes into account more fully the dynamical correlations in the system and it was surmised by Hedin and more conclusively by Misawa that ferromagnetism could occur for  $r_s > 10$ . A detailed discussion of the various calculations as well as a conjecture that for  $r_s > 10$  ferromagnetism may occur, one may refer to the recent book of Herring.<sup>7</sup> It seems to be of some interest to investigate the effects of correlations in the form of Yukawa interaction as a model.<sup>7</sup> Such a model, however, overlooks completely the dynamical correlations such as plasma

<sup>1</sup> F. Bloch, *Z. Physik* **57**, 545 (1929).

<sup>2</sup> E. P. Wigner, *Trans. Faraday Soc.* **34**, 678 (1938).

<sup>3</sup> D. Pines, *Elementary Excitations in Solids* (W. A. Benjamin, Inc., New York, 1964); and in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 427.

<sup>4</sup> M. Shimuzu, *Proc. Phys. Soc. Japan* **15**, 376 (1960).

<sup>5</sup> L. Hedin, *Phys. Rev.* **139**, A796 (1965).

<sup>6</sup> S. Misawa, *Phys. Rev.* **140**, A1645 (1965).

<sup>7</sup> C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. 4, p. 29.