a third sample with a concentration ten times the first, the initial trace showed that a portion of the resonance is saturated but recovers within 0.03 second. In all crystals the trace made, as the field moves off resonance after the saturation, indicates a saturated width of several gauss. In the time the field remains off resonance the hole becomes less deep and about 10 gauss wide.

The external magnetic field inhomogenity, the microwave frequency fluctuation, and the bandwidth of the detection system do not account for the observed width. During the initial saturation, the rf power remains on the center of the resonance for a time which is sufficient for spin diffusion to take place. However, there is no change in the unsaturated region so the energy does not diffuse into the tails during the initial saturation or the later recovery.[5] The width of the saturated region is greater than the width of an individual multiplet (theoretically less than 1 gauss) indicating spin diffusion. The width of the saturated region is limited by the competition between spin diffusion and spin-lattice relaxation. A quantum of energy in the F center may either be exchanged with a neighbor or be absorbed by the lattice. The probability of energy transfer to a frequency neighbor is proportional to the difference in saturation at the two frequencies. The relaxation is proportional to the saturation. Spread of the saturation ceases when the gradient of the population difference is such that energy is transferred to the lattice before it diffuses to an unsaturated neighbor.

The concentration does not have a large effect on the width of the hole but the recovery rate is roughly proportional to the concentration. The recovery rate in the most dilute crystals is taken as a measure of the spin-lattice relaxation time, T_1. This may, however, still represent the time for heat conduction from the region of the F center and not the time which might be calculated for transfer of energy from spins to phonons. The hole has not been observed at 78°K so the large change in recovery time occurs above 4°K. The phonons in potassium chloride corresponding to the appropriate spin energy do not have an electromagnetic field associated with them. Therefore, the author believes that the spin interacts with two or more optical phonons instead of directly with one acoustical phonon.

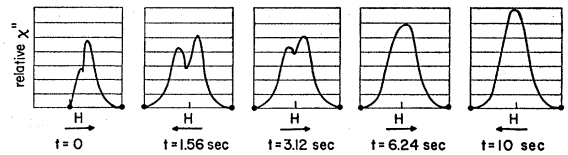

FIG. 2. A sequence of tracings made from a single photograph showing the recovery of the saturated portion of the resonance absorption at 4°K. The high-frequency field was 4.4×10^{-4} gauss. The sweep is 156 gauss between extremes and the center of the trace is near 3200 gauss. The concentration of F center was 4.8×10^{17} cm^{-3}.

The small peak in the bottom of the hole in the resonance observed in crystals of low concentration is possibly caused by cross relaxation.[4] Two saturated spins can exchange energy with two other spins having the same total energy. However, the process cannot proceed farther because of the absence of unsaturated pairs of systems whose absorption sufficiently overlaps that of the saturated systems.

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Transverse Collective Excitations in Superconductors and Electromagnetic Absorption*

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With use of the generalized random phase approximation an attempt is made to estimate the absorption of photons with energy less than the energy gap due to transverse collective excitations. The ratio of the surface resistance due to transverse collective excitations to that of normal metals in the extreme anomalous limit, calculated within the weak coupling theory, turns out to be too small to explain the observed data for superconducting lead and mercury. The interpretation of the collective excitations as bound pair states is briefly discussed.

I. INTRODUCTION

RECENTLY Ginsberg, Richards, and Tinkham measured the absorption of infrared radiation in bulk samples and the transmission through thin films of several superconductors.[1] The observed data were in good agreement with the result of the theory of Mattis and Bardeen, except for an interesting anomaly in the case of superconducting lead and mercury. For these

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[1] D. M. Ginsberg, P. L. Richards, and M. Tinkham, Phys. Rev. Letters 3, 337 (1959); D. M. Ginsberg, Ph.D. thesis, 1959 (unpublished); P. L. Richards, Ph.D. thesis, 1959 (unpublished).

two metals they observed some structure in the absorption curve for photons with energy less than the energy gap, indicating residual absorption in the gap. Similar structure was found in the transmissivity of the thin films. It seems likely that the structures observed in both cases are due to the same mechanism. It has been suggested that this phenomenon might be explained by an anisotropic energy gap, although it is rather difficult to account for the bump in the absorption curve by the anisotropy alone. An alternate explanation was proposed by Stern,[2] according to which the observed dip in the transmissivity of the thin films is due to the possible dielectric anomaly giving rise to a perfect reflection of the radiation not normally incident on the film. Apart from the value of the frequency at which this anomaly takes place, the frequency range where this effect is noticeable seems to be too narrow to explain the dip. He also discussed the effect of some surface collective oscillations as a separate mechanism for the case of a bulk sample. Another possibility pointed out by a number of people is to interpret the observed results as the absorption of radiation by low-lying levels of the transverse collective excitations discussed in the works of Anderson[3] and Bogoliubov, Tolmachev, and Shirkov.[4,5] It is the purpose of the present paper to investigate this latter possibility.

On the basis of the generalized random-phase approximation introduced by Anderson, Rickayzen discussed in detail the roles of collective excitations in the theory of superconductivity, including the effect of the transverse collective excitations on the Meissner effect.[6] Using his formulation we attempt to calculate the frequency spectrum of the excitations and to estimate the absorption of electromagnetic waves due to them. In so doing we have to assume a simple form for the matrix element of the two-body interaction because of the difficulties in determining it for actual metals. Because of this and other approximations used in the calculation the result is bound to be of a qualitative nature.

In Sec. II the equations of motion for the collective variables in the presence of an external electromagnetic field are solved for a simple type of transverse collective excitations which can couple with radiation. In an attempt to get a physical interpretation of the transverse collective excitations it is explicitly shown in Sec. III that they can be viewed as bound states of a pair of quasi particles. In Sec. IV the correction to the BCS paramagnetic current density is calculated, from which we can determine the surface resistance $R_s(\Omega)$ of a bulk superconductor for frequencies below the energy gap. The ratio of $R_s(\Omega)$ to the normal resistance in the extreme anomalous limit is then computed and compared with the experimental data. We shall not discuss here the case of a thin film because it is not clear how the size affects the collective excitations, although we would expect more or less the same effect as in the bulk sample. In this work we consider only the case of zero temperature. The notation used here is the same as in Rickayzen's article. The basic equations and their derivations in Sec. II are almost the same as in Sec. VI of the latter article, so that we do not repeat them in detail.

II. EQUATIONS OF MOTION FOR COLLECTIVE VARIABLES

The Hamiltonian of the system is

$$H_0=\sum_{k,\sigma}\epsilon_k c_{k,\sigma}{}^* c_{k,\sigma} + \sum_{k,k',q,\sigma,\sigma'} V_D(k,k') c_{k',\sigma}{}^* c_{-k'+q,\sigma}{}^* c_{-k+q,\sigma} c_{k,\sigma'}, \quad (1)$$

where $V_D(k,k')$ includes the unscreened Coulomb interaction. In the following $V(k,k')$ denotes the interaction responsible for the superconducting transition, which is screened and is predominantly negative. In terms of quasi-particle operators introduced by Bogoliubov,

$$\gamma_{k0}=u_k c_{k\uparrow}-v_k c_{-k\downarrow}{}^*,\quad \gamma_{k1}=u_k c_{-k\downarrow}+v_k c_{k\uparrow}{}^*,$$
$$u_k=\tfrac{1}{2}(1+\epsilon_k/E_k)^{\frac{1}{2}},\qquad v_k=\tfrac{1}{2}(1-\epsilon_k/E_k)^{\frac{1}{2}},$$

the collective variables in a superconductor are defined as

$$\rho(Q)=\sum_k m(k,Q)(\gamma_{k+Q0}{}^*\gamma_{k1}{}^*+\gamma_{k+Q1}\gamma_{k0}),$$
$$B_K(Q)=\sum_k V(K,k)n(k,Q)(\gamma_{k+Q0}{}^*\gamma_{k1}{}^*+\gamma_{k+Q1}\gamma_{k0}),\quad (2)$$
$$A_K(Q)=-\sum_k V(K,k)l(k,Q)(\gamma_{k+Q0}{}^*\gamma_{k1}{}^*-\gamma_{k+Q1}\gamma_{k0}),$$

where

$$l(k,Q)=u_k u_{k+Q}+v_k v_{k+Q},$$
$$m(k,Q)=u_k v_{k+Q}+v_k u_{k+Q},$$
$$n(k,Q)=u_k u_{k+Q}-v_k v_{k+Q}.$$

In the definitions (2) we have omitted the parts involving $\gamma_{k+Q0}{}^*\gamma_{k0}$ and $\gamma_{k1}{}^*\gamma_{k+Q1}$ which, operating on physical states, always give zero. The interaction Hamiltonian with a transverse electromagnetic field,

$$\mathbf{a}(Q,\Omega)\exp[-i\mathbf{Q}\cdot\mathbf{X}-i\Omega t+\eta t] \quad (3)$$

satisfying $\mathbf{a}\cdot\mathbf{Q}=0$ (throughout this paper we put $\hbar=1$), is given by

$$H_1=-\alpha e^{-i\Omega t+\eta t}\sum_k \mathbf{a}(Q,\Omega)(2\mathbf{k}+\mathbf{Q}) \times p(k,Q)(\gamma_{k0}{}^*\gamma_{k+Q1}{}^*-\gamma_{k1}\gamma_{k+Q0}),\quad (4)$$

where

$$p(k,Q)=u_k v_{k+Q}-v_k u_{k+Q}$$

and $\alpha=e/2mc$. An infinitesimally small quantity η is introduced in order to ensure that the interaction is switched on adiabatically. With $H=H_0+H_1$ we calculate the equations of motion for the pair operators $\gamma_{k+Q0}{}^*\gamma_{k1}{}^*$ and $\gamma_{k+Q1}\gamma_{k0}$ with the help of the random-

[2] E. A. Stern, (unpublished).
[3] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).
[4] N. N. Bogoliubov, V. V. Tolmachev, and D. V. Shirkov, *A New Method in the Theory of Superconductivity* (English translation: Consultants Bureau, Inc., New York, 1959), Chap. 4.
[5] These possible explanations are discussed in detail by Richards and Ginsberg in their doctoral thesis (see reference 1).
[6] G. Rickayzen, Phys. Rev. **115**, 795 (1959).

phase approximation, linearizing them with respect to the BCS ground states:

$$\begin{aligned}[][H,\gamma_{k+Q0}{}^*\gamma_{k1}{}^*] &= (E_k+E_{k+Q})\gamma_{k+Q0}{}^*\gamma_{k1}{}^*+V_D(Q)\rho(Q)m(k,Q) \\ &\quad +\tfrac{1}{2}n(k,Q)B_k(Q)-\tfrac{1}{2}l(k,Q)A_k(Q) \\ &\quad +2\alpha p(k,Q)\mathbf{a}(Q,\Omega)\cdot\mathbf{k}e^{-i\Omega t+\eta t}, \qquad (5)\end{aligned}$$

$$\begin{aligned}[][H,\gamma_{k+Q1}\gamma_{k0}] &= -(E_k+E_{k+Q})\gamma_{k+Q1}\gamma_{k0}-V_D(Q)\rho(Q)m(k,Q) \\ &\quad -\tfrac{1}{2}n(k,Q)B_k(Q)-\tfrac{1}{2}l(k,Q)A_k(Q) \\ &\quad +2\alpha p(k,Q)\mathbf{a}(Q,\Omega)\cdot\mathbf{k}e^{-i\Omega t+\eta t}.\end{aligned}$$

Since we are looking for the linear response of the system in the ground state to the external field, we can treat the pair operators as c numbers and keep only the part varying as $e^{-i\Omega t+\eta t}$, thus replacing the left-hand side of the equations by $-(\Omega+i\eta)\gamma_{k+Q0}{}^*\gamma_{k1}{}^*$ and $-(\Omega+i\eta)\gamma_{k+Q1}\gamma_{k0}$, respectively. Then, it is easy to derive the equations of motion for the collective variables, which are the basis of the present analysis:

$$\begin{aligned}\rho(Q) &= \textstyle\sum_k\{V_D(Q)\rho(Q)m(k,Q)+\tfrac{1}{2}n(k,Q)B_k(Q)\} \\ &\quad \times m(k,Q)S_1(E_k+E_{k+Q}) \\ &\quad -\textstyle\sum_k\{-\tfrac{1}{2}l(k,Q)A_k(Q)+2\alpha p(k,Q)\mathbf{a}(Q,\Omega)\cdot\mathbf{k}\} \\ &\quad \times m(k,Q)S_2(E_k+E_{k+Q}), \qquad (6)\end{aligned}$$

$$\begin{aligned}B_K(Q) &= \textstyle\sum_k V(K,k)\{V_D(Q)\rho(Q)m(k,Q)+\tfrac{1}{2}n(k,Q)B_k(Q)\} \\ &\quad \times n(k,Q)S_1(E_k+E_{k+Q})-\textstyle\sum_k V(K,k) \\ &\quad \times\{-\tfrac{1}{2}l(k,Q)A_k(Q)+2\alpha p(k,Q)\mathbf{a}(Q,\Omega)\cdot\mathbf{k}\} \\ &\quad \times n(k,Q)S_2(E_k+E_{k+Q}), \qquad (7)\end{aligned}$$

$$\begin{aligned}A_K(Q) &= \textstyle\sum_k V(K,k)\{V_D(Q)\rho(Q)m(k,Q)+\tfrac{1}{2}n(k,Q)B_k(Q)\} \\ &\quad \times l(k,Q)S_2(E_k+E_{k+Q})-\textstyle\sum_k V(K,k) \\ &\quad \times\{-\tfrac{1}{2}l(k,Q)A_k(Q)+2\alpha p(k,Q)\mathbf{a}(Q,\Omega)\cdot\mathbf{k}\} \\ &\quad \times l(k,Q)S_1(E_k+E_{k+Q}), \qquad (8)\end{aligned}$$

where

$$S_1(x)=2x/[(\Omega+i\eta)^2-x^2],\quad S_2(x)=2\Omega/[(\Omega+i\eta)^2-x^2].$$

We first note that the inhomogeneous term in (6) is identically zero for a transverse field with $\mathbf{a}\cdot\mathbf{Q}=0$. As was pointed out by Rickayzen, if $V(k,k')$ is independent of the angle between $\mathbf{k}$ and $\mathbf{k}'$ the terms involving $\mathbf{a}$ in the above set of integral equations vanish and there will be no effect of transverse collective excitations. Physically $V(k,k')$ might be a complicated function of $\mathbf{k}-\mathbf{k}'$. We assume that $V(k,k')$ is only a function of the angle $\mu=\mathbf{k}\cdot\mathbf{k}'/kk'$, its dependence on k and k' being taken into account only as a cutoff at $\epsilon_k=\omega_c$, where ω_c is the average phonon frequency. Let us write $V(\mu)$ in the form,

$$V(\mu)=\sum_{n=0} V_n\mu^n. \qquad (9)$$

The driving term in Eq. (7) for $B_K(Q)$ is

$$-\alpha\epsilon_0\sum_k V(K,k)(\mathbf{a}\cdot\mathbf{k})\left(\frac{1}{E_{k+Q}}-\frac{1}{E_k}\right)S_2(E_k+E_{k+Q}).$$

If we replace the sum by integrals, it involves an integral over ϵ of the form,

$$\int_{-\omega_{\rm av}}^{\omega_{\rm av}} d\epsilon\left(\frac{1}{E_{k+Q}}-\frac{1}{E_k}\right)S_2(E_k+E_{k+Q}),$$

where we can approximate ϵ_{k+Q} by $\epsilon_k+(\mathbf{k}\cdot\mathbf{Q})/m$ to order Q/k_F. Since we are interested in the values of Q such that $v_0Q\ll\omega_c$, we can readily show that this integral vanishes because of the symmetry with respect to the Fermi surface. The driving term in Eq. (8) for $A_K(Q)$ is equal to

$$\alpha aQ\frac{\epsilon_0}{m}\sum_n\frac{V_n}{K^n}\sum_k\frac{(\mathbf{K}\cdot\mathbf{k})^n}{k^n}k_xk_z\frac{1}{E_kE_{k+Q}}S_1(E_k+E_{k+Q}),$$

where we took $\mathbf{a}$ in the z direction and $\mathbf{Q}$ in the x direction. To order Q/k_F, only the terms with even n ($\neq 0$) fail to vanish, and in general they take the following form:

$$a(Q,\Omega)(\mathbf{e}_1\cdot\mathbf{K})^{n_1}(\mathbf{e}_2\cdot\mathbf{K})^{n_2}(\mathbf{e}_3\cdot\mathbf{K})^{n_3}J(Q,\Omega),$$

where $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are the unit vectors in the directions of $\mathbf{a}$, $\mathbf{Q}$, and $\mathbf{a}\times\mathbf{Q}$, respectively, and $n_1+n_2+n_3=n$ is an even integer. Therefore we may suppose $A_K(Q)$ and $B_K(Q)$ to be of this form also. Then, by the same argument as we have used for the driving term in the equation for $B_K(Q)$, we can show that the cross terms connecting $B_K(Q)$ and $A_K(Q)$ vanish. Similarly the cross term connecting $\rho(Q)$ with $A_K(Q)$ in Eq. (6) vanishes when we sum over the angle of $\mathbf{k}$, provided that any one of n_1, n_2, and n_3 is odd. In this case $A_K(Q)$ are decoupled from the rest of the collective variables, $\rho(Q)$ and $B_K(Q)$. Because the driving terms in the equations of motion for $\rho(Q)$ and $B_K(Q)$ are small, we can put them equal to zero as in the static case. The equation of motion for $A_K(Q)$ is now reduced to

$$A_K(Q)=-\sum_k V(K,k)\left\{-\tfrac{1}{2}\left(1+\frac{\epsilon_k\epsilon_{k+Q}+\epsilon_0{}^2}{E_kE_{k+Q}}\right)A_k(Q)+2\alpha\frac{\epsilon_0(\epsilon_k-\epsilon_{k+Q})}{E_kE_{k+Q}}\mathbf{a}(Q,\Omega)\cdot\mathbf{k}\right\}S_1(E_k+E_{k+Q}). \qquad (10)$$

Since at present we do not have any detailed knowledge of $V(k,k')$ we have to proceed by assuming a simple model. As the odd-power terms in (9) do not contribute to the excitations which can couple with the transverse field, we take as our simple model,

$$-V(\mu)=V[1+\sigma P_2(\mu)], \qquad (11)$$

where $P_2(\mu)$ is the Legendre polynomial and σ is a parameter. For this form of $V(\mu)$ the inhomogeneous term in Eq. (10) becomes

$$3\alpha\sigma N(0)V\frac{\epsilon_F}{\epsilon_0}\cdot\frac{(\mathbf{a}\cdot\mathbf{K})(\mathbf{Q}\cdot\mathbf{K})}{K^2}L(Q,\Omega), \qquad (12)$$

where

$$L(Q,\Omega)=\frac{1}{2}\int_{-1}^{1} d\mu\, \mu^2(1-\mu^2)$$
$$\times\int_{-\omega_c/\epsilon_0}^{\omega_c/\epsilon_0} dx \frac{1}{yy'}\cdot\frac{y+y'}{(\omega+i\eta)^2-(y+y')^2}, \quad (13)$$

with $x=\epsilon_k/\epsilon_0$, $x'=\epsilon_{k+Q}/\epsilon_0$, $y=(x^2+1)^{\frac{1}{2}}$, and $\omega=\Omega/\epsilon_0$. From the expression (12) we suppose

$$A_K(Q)=(\mathbf{a}\cdot\mathbf{K})(\mathbf{Q}\cdot\mathbf{K})K^{-2}A(Q,\Omega), \quad (14)$$

as in the static case discussed by Rickayzen. Substituting this into (9) we get the equation for $A(Q,\Omega)$:

$$[1-G(Q,\Omega)]A(Q,\Omega)=3\alpha\sigma N(0)V(\epsilon_F/\epsilon_0)L(Q,\Omega), \quad (15)$$

where

$$G(Q,\Omega)=-\tfrac{3}{4}\sigma N(0)V\int_{-1}^{1}\frac{d\mu}{2}\mu^2(1-\mu^2)$$
$$\times\int_{-\omega_c/\epsilon_0}^{\omega_c/\epsilon_0} dx\left(1+\frac{1+xx'}{yy'}\right)$$
$$\times\frac{y+y'}{(\omega+i\eta)^2-(y+y')^2}. \quad (16)$$

The dispersion relation for this type of transverse collective excitation is hence given by

$$1-G(Q,\Omega)=0. \quad (17)$$

III. BOUND PAIR STATES

Before going into the calculation of the absorption of electromagnetic waves due to the transverse collective excitations, it would be desirable to get some physical understanding of their nature. Anderson pointed out that the transverse collective excitations could be regarded as bound pairs of the Cooper type in excited states.[3] In order to see this somewhat more clearly, let us consider a pair of quasi particles and set up an equation of the Bethe-Salpeter type for the pair. Starting from the quasi-particle vacuum $|0\rangle$, that is the BCS ground state,[7] we construct states with a pair of quasi particles present:

$$\Psi_{k'k}\rangle=\gamma_{k'0}{}^*\gamma_{k1}{}^*|0\rangle. \quad (18)$$

Let $\Psi\rangle$ be an eigenstate of the Hamiltonian with eigenvalue E (the energy of the ground state is taken to be zero):

$$H_0\Psi\rangle=E\Psi\rangle. \quad (19)$$

$\Psi\rangle$ can be expanded in terms of $\Psi_{k'k}\rangle$ as

$$\Psi\rangle=\sum_{k'k} f_{k',k}\Psi_{k'k}\rangle.$$

[7] When the collective excitations, $\rho(Q)$, $A_K(Q)$ and $B_K(Q)$ are taken into account, the true ground state is defined by $\mu_i|0\rangle=0$ where μ_i's are the normal modes including the collective excitations (see reference 6), and is no longer the BCS ground state. However, for the purpose of this section we may approximate it by the BCS ground state.

We may consider $f_{k',k}$ as a wave function for the pair in momentum space. Rewriting (19) in the form

$$\sum_{k'k} f_{k'k}\{[H_0,\gamma_{k'0}{}^*\gamma_{k1}{}^*]-\gamma_{k'0}{}^*\gamma_{k1}{}^*H_0\}|0\rangle=E\Psi\rangle,$$

and then making a projection into the two-body Fock space, we get an integral equation for $f_{k',k}$:

$$\sum_{k',k}\langle\Psi_{K'K}|[H_0,\gamma_{k'0}{}^*\gamma_{k1}{}^*]|0\rangle f_{k',k}=Ef_{K',K}. \quad (20)$$

Now the commutator has already been calculated with the random phase approximation. Substituting (5) into (20) we find

$$V_D(Q)m(K,Q)\sum_k m(k,Q)f_{k+Q,k}+\tfrac{1}{2}\sum_k V(k,K)$$
$$\times\{n(K,Q)n(k,Q)+l(K,Q)l(k,Q)\}f_{k+Q,k}$$
$$=(E-E_K-E_{K+Q})f_{K+Q,K} \quad (21)$$

with the help of Eqs. (2).

A bound state is possible only for transverse waves, that is, for $f_{K+Q,K}$ proportional to the component of $\mathbf{K}$ perpendicular to $\mathbf{Q}$, for which the first direct term vanishes, and the left-hand side of (21) is negative. Introducing a new quantity defined by

$$f_{K+Q,K}=l(K,Q)(E-E_{K+Q}-E_K)^{-1}F_{K+Q,K}, \quad (22)$$

we rewrite Eq. (20) in the form

$$\tfrac{1}{2}n(K,Q)\sum_k V(k,K)n(k,Q)l(k,Q)(E-E_k-E_{k+Q})^{-1}F_{k+Q,k}$$
$$+l(K,Q)[\tfrac{1}{2}\sum_k V(k,K)l^2(k,Q)$$
$$\times(E-E_k-E_{k+Q})^{-1}F_{k+Q,k}-F_{K+Q,K}]=0, \quad (23)$$

where we have omitted the direct term. Let us make the following ansatz for $F_{K+Q,K}$:

$$F_{K+Q,K}=(\mathbf{e}_\lambda\cdot\mathbf{K})(\mathbf{Q}\cdot\mathbf{K})^nK^{-n-1}Q^{-n}F_n(Q), \quad (24)$$

where $\mathbf{e}_\lambda$ ($\lambda=1, 2$) are the unit vectors perpendicular to $\mathbf{Q}$. As we shall see below, $n=0$ corresponds to p wave and $n=1$ to d wave (that is the same form as considered in Sec. II). For this form of $F_{K+Q,K}$ one can show that the first term in (23) is zero to order Q/k_F (corresponding to $B_K(Q)$ being negligible). Therefore we are left with the equation for $F_n(Q)$:

$$[1-\tfrac{1}{2}\sum_k V(k,K)l^2(k,Q)(\mathbf{e}_\lambda\cdot\mathbf{k})$$
$$\times(\mathbf{Q}\cdot\mathbf{k})^nk^{-n-1}Q^{-n}(E-E_k-E_{k+Q})^{-1}]F_n(Q)=0. \quad (25)$$

This determines the eigenvalue E for each value of Q and $F_n(Q)$ is a delta function. This is a consequence of the random-phase approximation. It should be noted that this equation is slightly different from the one for $A_K(Q)$ [Eq. (10) without the driving term]; because of our approximate ground state the pole, $E=-(E_k+E_{k+Q})$, is missing in (25).

If we introduce the center-of-mass coordinate $\mathbf{R}=\frac{1}{2}(\mathbf{x}_1+\mathbf{x}_2)$ and the relative coordinate $\mathbf{r}=\mathbf{x}_2-\mathbf{x}_1$ where $\mathbf{x}_1$ and $\mathbf{x}_2$ are the positions of two quasi particles, the wave function for the pair in configuration space is given by

$$\psi_n(\mathbf{r},\mathbf{R})=\exp(-i\mathbf{Q}\cdot\mathbf{R})\sum_k \exp[i(\mathbf{k}+\mathbf{Q}/2)\cdot\mathbf{r}] \times\frac{(\mathbf{e}_\lambda\cdot\mathbf{k})(\mathbf{Q}\cdot\mathbf{k})^n}{k^{n+1}Q^n}\frac{l(k,Q)}{E-E_k-E_{k+Q}}F_n(Q). \quad (26)$$

The wave function for relative motion is simply

$$\psi_n(\mathbf{r})=C\sum_k \exp[i(\mathbf{k}+\mathbf{Q}/2)\cdot\mathbf{r}] \times\frac{(\mathbf{e}_\lambda\cdot\mathbf{k})(\mathbf{Q}\cdot\mathbf{k})^n}{k^{n+1}Q^n}\frac{l(k,Q)}{E(Q)-E_k-E_{k+Q}}, \quad (27)$$

where $E(Q)$ is the solution of (25) for a given Q and C is a constant. In the limit of $Q\rightarrow 0$ the p and d wave take the following forms,

$$\psi_1(\mathbf{r})=C_1\frac{(\mathbf{e}_\lambda\cdot\mathbf{r})}{r}\left(\frac{r}{k_F}\right)\left(\frac{1}{r}\frac{d}{dr}\right)\frac{\sin k_F r}{k_F r}f(r), \quad (28)$$

$$\psi_2(\mathbf{r})=C_2\frac{(\mathbf{e}_\lambda\cdot\mathbf{r})(\mathbf{e}_0\cdot\mathbf{r})}{r^2}\left(\frac{r}{k_F}\right)^2\left(\frac{1}{r}\frac{d}{dr}\right)^2\frac{\sin k_F r}{k_F r}f(r), \quad (29)$$

where $\mathbf{e}_0=\mathbf{Q}/Q$ and

$$f(r)=\int_0^{\omega_c/\epsilon_0} dx\,[(x^2+1)^{\frac{1}{2}}-E(0)/2\epsilon_0]^{-1}\cos tx$$

with $t=r/\pi\xi_0$. Note that this is a function similar to the one appearing in the correlation function of electrons of opposite spin in the BCS ground state.[8] Following the same argument as in the case of the correlation function one can show that for large r the function $f(r)$ falls off in the same way as

$$I(r)\equiv\int_0^\infty dx\,[(x^2+1)^{\frac{1}{2}}-E(0)/2\epsilon_0]^{-1}\cos tx = (\pi)^{\frac{1}{2}}\sum_{n=0}^\infty\left[\left(\frac{t}{2}\right)^{\frac{1}{2}}\frac{E(0)}{2\epsilon_0}\right]^n\frac{K_{n/2}(t)}{\Gamma[(n+1)/2]},$$

where $K_{n/2}(t)$ is a modified Bessel function. It can be shown that $I(r)$ falls off like $\exp\{-t[1-(E(0)/2\epsilon_0)^2]^{\frac{1}{2}}\}$ for $r\gg\pi\xi_0$, whereas the correlation function behaves like e^{-t}. From this one can see that the bound-state wave functions spread out as E approaches $2\epsilon_0$. For finite Q the wave functions are deformed and the corresponding energy eigenvalues become larger.

If we expand $\psi_1(\mathbf{r})$ and $\psi_2(\mathbf{r})$ in terms of spherical harmonics, they are just linear combinations of $Y_1^{\pm1}(\theta,\varphi)$ and $Y_2^{\pm1}(\theta,\varphi)$, respectively. We may note that the p-wave state does not contribute to the absorption of radiation since the matrix element of current density in terms of the quasi-particle operators is

$$\langle\Psi_n|\mathbf{j}(Q)|0\rangle = -\alpha c\sum_k(2\mathbf{k}+\mathbf{Q})p(k,Q)\langle\Psi_n|\gamma_{k+Q0}{}^*\gamma_{k1}{}^*|0\rangle, \quad (30)$$

which vanishes for $n=1$ because of the factor $p(k,Q)$ that is proportional to $\mathbf{k}\cdot\mathbf{Q}$ for a small Q. In general only even parity waves contribute to the absorption of radiation.

IV. CALCULATION OF SURFACE RESISTANCE

In this section we shall calculate the correction to the BCS paramagnetic current due to the transverse collective excitation $A_K(Q)$ and determine the surface resistance of a bulk superconductor for frequencies less than the gap.

The paramagnetic part of the current density is

$$\mathbf{j}_p(Q)=-c\alpha\sum_k(2\mathbf{k}+\mathbf{Q})p(k,Q)(\gamma_{k+Q0}{}^*\gamma_{k1}{}^*-\gamma_{k+Q1}\gamma_{k0}).$$

From Eqs. (5) one can easily derive the expression for the current density to first order in $\mathbf{a}(Q,\Omega)$ (see reference 6):

$$\mathbf{j}_p(Q,\Omega)=-4\alpha^2\sum_k(2\mathbf{k}+\mathbf{Q})\mathbf{a}(Q,\Omega)\cdot\mathbf{k}p^2(k,Q)\frac{E_k+E_{k+Q}}{(\Omega+i\eta)^2-(E_k+E_{k+Q})^2} +\tfrac{1}{2}c\alpha\sum_k(2\mathbf{k}+\mathbf{Q})A_k(Q)\times\frac{\epsilon_0(\epsilon_k-\epsilon_{k+Q})}{E_kE_{k+Q}}\frac{E_k+E_{k+Q}}{(\Omega+i\eta)^2-(E_k+E_{k+Q})^2}. \quad (31)$$

The first term yields the BCS paramagnetic current density which, together with the London diamagnetic current, we write

$$\mathbf{j}_0(Q,\Omega)=-(c/4\pi)K_0(Q,\Omega)\mathbf{a}(Q,\Omega). \quad (32)$$

Substituting $A_K(Q)$ given by (14) we can calculate the second term:

$$j_{\mathrm{coll}}(Q,\Omega)=-2c\alpha a(Q,\Omega)QA(Q,\Omega)\sum_k\frac{k_z{}^2k_x}{k^2}\times\frac{\epsilon_0(\epsilon_k-\epsilon_{k+Q})}{E_kE_{k+Q}}\frac{E_k+E_{k+Q}}{(\Omega+i\eta)^2-(E_k+E_{k+Q})^2}, \quad (33)$$

where the x and z axis are chosen in the directions of $\mathbf{a}$ and $\mathbf{Q}$, respectively. Let us define the kernel relating $\mathbf{j}_{\mathrm{coll}}$ and $\mathbf{a}$ as

$$\mathbf{j}_{\mathrm{coll}}(Q,\Omega)=-(c/4\pi)K_{\mathrm{coll}}(Q,\Omega)\mathbf{a}(Q,\Omega). \quad (34)$$

[8] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957), Appendix D.

With the aid of (15) we get

$$K_{\mathrm{coll}}(Q,\Omega)=-\frac{9\pi^2}{16}\sigma N(0)V\left(\frac{\xi_0}{\lambda_L}\right)^2 Q^2\frac{L^2(Q,\Omega)}{1-G(Q,\Omega)},\quad (35)$$

where $\xi_0=v_0/\pi\epsilon_0$ is the correlation length and $\lambda_L^2=mc^2/4\pi ne^2$. Because G contains an imaginary quantity $i\eta$, the kernel K_{coll} has an imaginary part given by

$$\mathrm{Im}K_{\mathrm{coll}}(Q,\Omega)=\frac{9\pi^3}{16}\sigma N(0)V\left(\frac{\xi_0}{\lambda_L}\right)^2 Q^2L^2(Q,\Omega)\times\left|\frac{\partial G}{\partial\Omega}\right|^{-1}\delta[\Omega-\Omega(Q)],\quad (36)$$

where $\Omega(Q)$ is the solution of $1-G(Q,\Omega)=0$.

Let us assume for the sake of simplicity the boundary condition of specular reflection. Then the instantaneous field inside a bulk superconductor is given by the spectrum

$$a(Q,\Omega)=-[H(0)/\pi][Q^2-\Omega^2/c^2+K(Q,\Omega)]^{-1},\quad (37)$$

where $H(0)$ is the magnetic field at the surface. Because we are interested in the infrared region we can neglect Ω^2/c^2. Furthermore, for our purpose of crude estimation we may neglect K_{coll} in the denominator[9]; in other words we consider the field inside the superconductor to be largely determined by the ordinary kernel K_0. The rate of absorption of a wave with frequency Ω is equal to

$$2(2\pi)^2\int^{\infty}\mathrm{Re}[\mathbf{j}(Q,\Omega)\cdot\mathbf{E}(Q,\Omega)]dQ=-\frac{2\Omega}{\pi}\int_0^{\infty}\mathrm{Im}[K(Q,\Omega)\mathbf{a}^2(Q,\Omega)]dQ.\quad (38)$$

Substituting (37) for $\mathbf{a}(Q,\Omega)$, one can find the resistance $R_s(\Omega)$ of a superconductor for $\Omega<2\epsilon_0$:

$$R_s(\Omega)=-\frac{2\Omega}{\pi}\int_0^{\infty}\frac{\mathrm{Im}K_{\mathrm{coll}}(Q,\Omega)}{[Q^2+K_0(Q,\Omega)]^2}dQ.\quad (39)$$

The problem now is to evaluate the integrals $G(Q,\Omega)$ and $L(Q,\Omega)$. By suitable transformations $G(Q,\Omega)$ can be brought into the following form,

$$G(Q,\Omega)=\sigma'-(15/4)\sigma'N(0)VI(q,\omega)-(3/14)\sigma'N(0)V(q/\omega)^2,\quad (40)$$

where $\sigma'=\sigma/5$, $q=v_0Q/\epsilon_0$, $\omega=\Omega/\epsilon_0$, and

$$I(q,\omega)=\frac{1}{8}\int_{-1}^{1}d\mu\,\mu^2(1-\mu^2)\times\int_{-\infty}^{\infty}\frac{dx}{y}\frac{2q\mu x+q^2\mu^2-\omega^2}{x^2+q\mu x+(q^2\mu^2-\omega^2)/4+\omega^2/(\omega^2-q^2\mu^2)}.$$

In deriving this expression the use has been made of the relation $N(0)V\sinh^{-1}(\omega_c/\epsilon_0)=1$, and the limits of integration in $I(q,\omega)$ are extended to infinity from $\pm\omega_c/\epsilon_0$, which is allowed in the weak coupling case. Although the first integral over x can be carried out explicitly, it is rather complicated and we are compelled to make an approximation that is valid only for small values of q. Since, as we shall see below, the collective excitations with frequencies below $2\epsilon_0$ can occur only for small values of Q, it will, at least partly, serve our purpose. If $q\ll 2$ and $q^2\ll 4-\omega^2$, we get

$$I(q,\omega)=-\frac{4}{15}\frac{\omega}{(4-\omega^2)^{\frac{1}{2}}}\sin^{-1}\frac{\omega}{2}+\frac{2q^2}{35}\left\{\frac{1}{4-\omega^2}+\frac{4}{(4-\omega^2)^{\frac{3}{2}}}\sin^{-1}\frac{\omega}{2}\right\}.\quad (42)$$

In this case the dispersion relation of the excitation is given by

$$\beta=\frac{\omega}{(4-\omega^2)^{\frac{1}{2}}}\sin^{-1}\frac{\omega}{2}-\frac{3}{14}q^2\left\{\frac{1}{\omega^2}+\frac{1}{4-\omega^2}+\frac{4}{(4-\omega^2)^{\frac{3}{2}}}\sin^{-1}\frac{\omega}{2}\right\},\quad (43)$$

where β is defined as

$$\beta\equiv(1-\sigma')/\sigma'N(0)V.\quad (44)$$

In particular the minimum value of ω corresponding to $q=0$ is simply given by the solution of

$$\beta=\omega_0(4-\omega_0^2)^{-\frac{1}{2}}\sin^{-1}(\omega_0/2).\quad (45)$$

The value of ω_0 depends rather sensitively on the value of σ, the parameter of the angular dependence of $V(\mu)$. For small σ, the frequency ω_0 approaches very close to 2, where the continuum of single particle excitation starts. It may be noted here that the maximum value of q for which $\omega=2$, is determined by

$$\beta=\frac{15\pi}{8q_{\max}}-1+\frac{7}{4}q_{\max}^2,\quad (46)$$

if $q_{\max}$ is still small compared to 1. Unfortunately, for a

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[9] Strictly speaking, this procedure is not correct because K_{coll} contains a singularity. In order to avoid this difficulty, we have to start from the Maxwell equation for the vector potential with the boundary condition of specular reflection:

$$[Q^2+K_0(Q,\Omega)+K_{\mathrm{coll}}(Q,\Omega)]a(Q,\Omega)=-H(0)/\pi.$$

Let us take an average over a small range of Q around $Q(\Omega)$, a solution of $G=1$, assuming $a(Q,\Omega)$ varies smoothly with Q. If, for sufficiently small $\Delta Q/Q$,

$$\int_{-\Delta Q12}^{-\Delta Q12}(Q^2+K_0)dQ\sim\Delta Q/\lambda_L^2\ll\left|\int_{-\Delta Q12}^{\Delta Q12}K_{\mathrm{coll}}(Q,\Omega)dQ\right|$$

holds, we may neglect K_{coll} in determining the field. One can show that this is the case here {The above inequality reduces to $\Delta Q/Q\gg(4\pi/5)q\beta^2/\omega^4|g|$, [see Eq. (48)].}

reasonably strong angular dependence $q_{\max}$ would not be within the limit of applicability of our approximation.

For small values of q the integral $L(Q,\Omega)$ can be expressed in terms of $I(q,\omega)$; the lowest order term is just $(2/\omega^2)I(q,\omega)$. Hence, for Q and Ω such that $G(Q,\Omega)=1$, we get

$$L(Q,\Omega)\simeq -8\beta/15\omega^2, \tag{47}$$

because of (40). If we substitute this into (36) and rewrite the expression, expecting an integral over Q, we find

$$\mathrm{Im}K_{\mathrm{coll}}(Q,\Omega)=\tfrac{4}{5}\cdot\frac{\beta^2 q^2}{\lambda_L{}^2\xi_0\omega^4}\frac{\delta[Q-Q(\Omega)]}{g(q,\omega)}, \tag{48}$$

where $Q(\Omega)$ is the solution of $G=1$ for a given Ω and $g(q,\omega)$ is defined as

$$g(q,\omega)\equiv\frac{1}{\sigma' N(0)V}\left|\frac{\partial G}{\partial q}\right|.$$

For small $q\ll 2$ the denominator of (39), $Q^2+K_0(Q,\Omega)$, can be approximated by $1/\lambda_L{}^2$. Then, we get from (39) and (48) an expression for the surface resistance due to the transverse collective excitation:

$$R_s(\Omega)=\frac{8}{5\pi}\beta^2\epsilon_0\frac{\lambda_L{}^2}{\xi_0}\frac{q^2(\omega)}{\omega^4 g[q(\omega),\omega]}. \tag{49}$$

The ratio of this to the resistance of normal metals in the extreme anomalous limit,

$$R_\infty(\Omega)=3^{1/6}(\omega\lambda_L/4)^{2/3}\xi_0{}^{1/3}\epsilon_0$$

is equal to

$$\frac{R_s(\Omega)}{R_\infty(\Omega)}=\frac{32}{5\pi(4\sqrt{3})^{1/3}}\beta^2\left(\frac{\lambda_L}{\xi_0}\right)^{4/3}\frac{q^2(\omega)}{\omega^{11/3}g[q(\omega),\omega]}. \tag{50}$$

With the help of (42) we can evaluate this ratio for frequencies not too close to $2\epsilon_0$. The result for various values of σ is shown in Fig. 1.

V. CONCLUSION

The observed data of Ginsberg, Richards, and Tinkham seem to indicate that the absorption in the gap starts from a frequency near half the gap frequency and its maximum lies around $\frac{3}{4}$ of $2\epsilon_0$. According to our calculation, in order that the absorption due to the transverse collective excitations can occur considerably below the gap, the angular dependence of $V(k,k')$ must be quite strong; in our model $\omega_0=1$ requires $\sigma\sim 4$. Otherwise they fall very close to the gap. As one can see from Fig. 1, the ratio $R_s(\Omega)/R_\infty(\Omega)$ obtained here is apparently too small to account for the observed structure, although it shows a maximum for a frequency below the gap. For example, if we take ξ_0/λ_L for lead equal to 4, the maximum value of the ratio is only about 0.02, whereas the observed bump is at least of order 0.1. Therefore it seems unlikely that within the framework of the weak coupling theory the transverse collective excitation can explain the observed structure in the gap. However, we cannot exclude the possibility especially because of the fact that lead and mercury, the only metals so far known to possess this anomaly, have both relatively small values of Θ_D/T_c, so that our calculation based on the weak coupling limit is probably inadequate. It is possible that corrections due to the strong coupling would enhance the effect of the collective excitations.

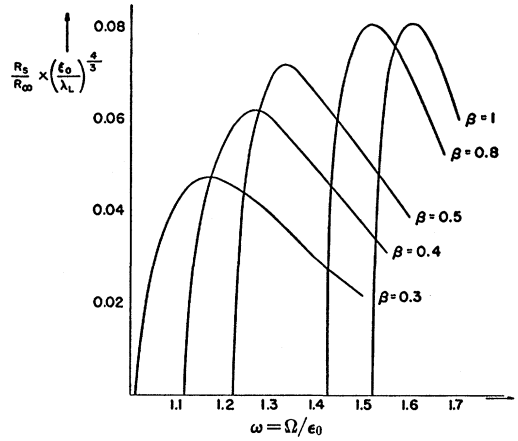

FIG. 1. The ratios of the surface resistance for a superconductor to the normal resistance in the extreme anomalous limit, $R_s(\Omega)/R_\infty(\Omega)$, as a function of frequency, calculated for various values of $\beta=(1-\sigma')/\sigma' N(0)V$, where σ' is the parameter of the angular dependence of $V(k,k')$.

It may be added that according to the expression (50) the absorption due to the transverse collective excitations is not likely to be observed in superconductors with large values of ξ_0/λ_L. This is consistent with the fact that the structure has not been found in aluminum.[10]

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[10] M. A. Biondi and M. P. Garfunkel, Phys. Rev. Letters 2, 143 (1959).