## Properties of Superconducting Alloys Containing Paramagnetic Impurities\*

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We have made some additional calculations on the effects of paramagnetic impurities in superconductors, using the Abrikosov-Gor'kov theory as our starting point and taking full advantage of the information contained in the Green's function of the system. The density of states in energy has been computed for different values of the inverse collision time for exchange scattering  $\Gamma$ . The (half) excitation energy gap  $\Omega_G$  (as distinguished from the order parameter  $\Delta$ ) is defined to be the energy at which the density of states vanishes. The temperature-dependent order parameter has been computed for different values of  $\Gamma$ , and from this, the behavior of  $\Omega_G(T)$  is determined. A comparison with tunneling experiments shows a disagreement of about 30%. The thermodynamic properties of the system follow from the density of states; the critical field and the discontinuity in the specific heat at the critical temperature are calculated in considerable detail. Expressions for the penetration depth and complex conductivity are obtained, and numerical results are presented for the case  $T=0^{\circ}$ . The real part of the conductivity at  $T=0^{\circ}$  is shown to be zero for frequencies less than  $2 \Omega_G$  and proportional to the square of the density of states for vanishingly small frequencies in the gapless region of impurity concentrations.

## I. INTRODUCTION

'N an interesting article<sup>1</sup> Abrikosov and Gor'kov investigated the effects of paramagnetic impurities on superconductors. They found first of all that the transition temperature decreases sharply with increasing impurity concentration and goes to zero at a critical concentration  $n_c^i$ . Furthermore, there exists a region of concentrations where the gap in the excitation energy spectrum is zero even though the substance is still a superconductor in the sense of having pair correlations and a nonzero transition temperature. This last result is striking because the BCS theory<sup>2</sup> contains only the single parameter  $\Delta$  which is at the same time the energy gap and a measure of the pair correlation. Measurements of the energy gap and of the transition temperature  $T_c$  as a function of the concentration of paramagnetic impurities<sup>3</sup> show that the gap decreases much more rapidly than does the critical temperature, thereby giving support to the results found by Abrikosov and Gor'kov (AG).

In contrast to the case of nonmagnetic impurities, paramagnetic impurities give rise to a real lifetime effect. Because of the spin-exchange scattering, the lifetime of a pair state is no longer infinite and this results in a rapid decrease in the ordering and therefore in the transition temperature. This can be understood when one realizes that the impurity-spin-electron-spin interaction Hamiltonian is not invariant under a time-reversal transformation. (The ordinary impurity interaction is invariant under time reversal and allows us to form pairs from time-reversed states with an essentially infinite lifetime.)

This fact was noted by de Gennes and Sarma<sup>4</sup> and Phillips.<sup>5</sup> The energy gap  $\Omega_G$  has a simple interpretation in the light of the density of states in energy of the states broadened by scattering, and it can be zero even though there exists an ordered state whose free energy is less than that of the normal state. In fact, if one defines a temperature  $T_c'$  for which the energy gap goes to zero, it turns out to be always smaller than the true critical temperature  $T_c$  so that for any value of the impurity concentration, there is a range of temperatures near  $T_c$ for which the energy gap is zero.

The problem of a superconductor containing paramagnetic impurities is very similar to the problem of an ordinary impure superconductor in the presence of an external current or magnetic field.<sup>6</sup> Here the timereversal invariance is removed by the external disturbance, and one again encounters a distinction between the energy gap  $\Omega_G$  and the ordering parameter  $\Delta$ .

We have extended the calculations of AG making fuller use of the Green's-function formalism to derive results that have more general validity than those of AG, and to derive new results for the electromagnetic properties. Section II is devoted to a derivation of the self-consistent equations for the self-energies in a way that differs slightly from AG and stresses the role of the time-reversal operation. In the next two sections we rederive some of the previous results for the critical temperature and order parameter and present the results of our numerical calculation of the density of states and order parameter together with a comparison with the experimental data of Reif and Woolf. Section V is devoted to the thermal properties, in particular, the specific heat and critical field. In the last section we evaluate the electromagnetic response-the presence of the Meissner effect for all impurity concentrations less

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<sup>39, 1781 (1960) [</sup>English transl.: Soviet Phys.-JETP 12, 1243

<sup>(1961)],</sup> hereafter referred to as AG. <sup>2</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

<sup>&</sup>lt;sup>3</sup> F. Reif and M. A. Woolf, Phys. Rev. Letters 9, 315 (1962).

<sup>&</sup>lt;sup>4</sup> P. G. de Gennes and G. Sarma, J. Appl. Phys. 34, 1380 (1963).
<sup>5</sup> J. C. Phillips, Phys. Rev. Letters 10, 96 (1963).
<sup>6</sup> K. Maki, Progr. Theoret. Phys. (Kyoto) 29, 10, 333, 603 (1963).

than  $n_c^i$ , the penetration depth, and the frequencydependent conductivity. The great advantage of our approach is the natural way in which the distinction between the energy gap  $\Omega_G$  and the order parameter  $\Delta$ arises when one emphasizes the effect of impurities on the density of states.

## **II. SELF-ENERGIES**

The paramagnetic impurities give rise to a perturbation

$$\mathcal{C}^{imp}(\mathbf{r}) = \sum_{i} \{ v_1(\mathbf{r} - \mathbf{R}_i) + v_2(\mathbf{r} - \mathbf{R}_i) \mathbf{S}_i \cdot \mathbf{s} \}, \quad (2.1)$$

where  $\mathbf{R}_i$  denotes the position of the impurity *i* with the free spin  $\mathbf{S}_{i}$ , and **s** is the electronic spin operator. The positions of the impurities are presumed to be random and the impurity spins are uncorrelated with each other. The first term describes collisions which do not involve the electron spin and would be the only perturbation present if the impurities were not paramagnetic. The second term describes the specific interaction between the electron and impurity spins and permits a reversal of the electron spin in a collision.

We use the Nambu<sup>7</sup> notation in the mathematical development, and in this notation, the impurities affect both the diagonal  $[M_0(k)]$  and the off-diagonal  $[M_1(k)]$ self-energies as shown in Figs. 1(a) and 1(b). The order parameter  $\Delta$  is in essence an off-diagonal self-energy as shown in Fig. 1(c). The intermediate propagators are the complete ones: that is to say, they include both the superconducting interaction V and the effects of impurities. It is essential that the three equations represented in Fig. 1 be solved as simultaneous equations, for it is only in this way that self-consistency can be achieved. We have been able to do this only in an approximate way; the propagators we use involve a (tensor) M averaged over the locations of the impurties and averaged over the orientations of the impurity spins  $S_i$ . We therefore are using an averaged propagator, and the principal limitation this imposes is that we cannot, with such propagators, investigate the possible fluctuations of the system. Within this limitation, we make some other and, we think, relatively minor approximations. The functions  $v_1$  and  $v_2$  are taken to be substantially Dirac  $\delta$  functions, which, in effect, means we neglect the dependence of the self-energies due to impurities on the propagation vectors. We also neglect crossing diagrams as making only a small correction. As a result of these simplifications, only collisions with the same impurity matter since all others vanish in averaging over the positions of the impurities. The two parts of the perturbing potential do not mix, so that they can be dealt with separately. This is advantageous because it helps illuminate the role played by time-reversal symmetry. We write the reciprocal of the tensor propagator (we use units in which  $\hbar = 1$ )

$$\mathbf{g}^{-1} = \boldsymbol{\epsilon}_{\mathbf{k}} \boldsymbol{\tau}_{3} - \boldsymbol{\omega} \boldsymbol{\tau}_{0} - M^{i} + \Delta \boldsymbol{\tau}_{1} \tag{2.2}$$



FIG. 1. Diagrams for evaluating the self-energy. (a) Diagonal part of the self-energy  $M_0^i(k)$ . (b) Off-diagonal part of the self-energy  $M_1^i(k)$ . (c) V is the superconducting interaction. This diagram defines the self-energy  $\Delta$ . The double line with arrows in the same direction represents the diagonal part of the propagator  $\mathcal{G}$ . The double line with arrows opposed is the off-diagonal part of the propagator. The X's denote a (double) interaction with the same impurity.

and

$$M^{i} = -(\omega - M_{0}^{i})\tau_{0} + (\Delta - M_{1}^{i})\tau_{1}, \qquad (2.3)$$

 $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are the usual Pauli matrices and  $\tau_0$  is the unit matrix. The superscript *i* denotes the contribution made by the impurities.

We rewrite (2.2) as

$$\mathbf{g}^{-1} = \boldsymbol{\epsilon}_{\mathbf{k}} \boldsymbol{\tau}_3 + \tilde{\Delta} \boldsymbol{\tau}_1 - \tilde{\omega} \boldsymbol{\tau}_0, \qquad (2.4)$$

and Figs. 1(a) and 1(b) yield, as contributions from the spin-independent part,

$$M_{(1)}{}^{i} = n^{i} \int \frac{d^{3}k'}{(2\pi)^{3}} v_{1}(\mathbf{k},\mathbf{k}') \tau_{3} \mathcal{G}(k') \tau_{3} v_{1}(\mathbf{k}',\mathbf{k}) \qquad (2.5)$$

$$= \frac{1}{2}i(\Gamma_1 + \Gamma_2)(\tilde{\omega}\tau_0 - \tilde{\Delta}\tau_1)/(\tilde{\omega}^2 - \tilde{\Delta}^2)^{1/2}, \quad (2.6)$$

where  

$$\frac{1}{2}(\Gamma_1 + \Gamma_2) = n^i \pi N_0 \langle |v_1(\mathbf{k}, \mathbf{k}')|^2 \rangle. \qquad (2.7)$$

Here  $n^i$  is the number density of impurities,  $N_0$  is the density of states of one spin at the Fermi surface, and the angular brackets denote an average over the solid angle between **k** and **k'**, and both propagation vectors lie substantially on the Fermi surface. In the contribution from the spin-dependent part the  $\tau_0$  component contains the matrix element

$$\langle k | v_2 \mathbf{S}_i \cdot \mathbf{s} | k' \rangle \langle k' | v_2 \mathbf{S}_i \cdot \mathbf{s} | k \rangle$$

whereas the  $\tau_1$  component contains the matrix element

$$egin{aligned} &\langle Tk \, | \, v_2 \mathbf{S}_i \!\cdot \! \mathbf{s} \, | \, Tk' 
angle \langle k' \, | \, v_2 \mathbf{S}_i \!\cdot \! \mathbf{s} \, | \, k 
angle \ &= - \langle k \, | \, v_2 \mathbf{S}_i \!\cdot \! \mathbf{s} \, | \, k' 
angle \langle k' \, | \, v_2 \mathbf{S}_i \!\cdot \! \mathbf{s} \, | \, k 
angle, \end{aligned}$$

that is to say, there is a sign reversal in the  $\tau_1$  component as compared to the  $\tau_0$  component. The average over the orientations of the impurity spin gives rise to the factor  $\frac{1}{4}S(S+1)$ . We let

$$\frac{1}{2}(\Gamma_1 - \Gamma_2) = n^i \pi N_0 \langle |v_2(\mathbf{k}, \mathbf{k}')|^2 \rangle \frac{1}{4} S(S+1), \quad (2.7')$$

then

$$M^{i} = \frac{i}{(\tilde{\omega}^{2} - \tilde{\Delta}^{2})^{1/2}} (\Gamma_{1} \tilde{\omega} \tau_{0} - \Gamma_{2} \tilde{\Delta} \tau_{1}). \qquad (2.8)$$

<sup>&</sup>lt;sup>7</sup> Y. Nambu, Phys. Rev. 117, 648 (1960).



FIG. 2. The critical temperature  $T_c$ , the order parameter  $\Delta(0)$ , and the half-excitation energy gap  $\Omega_G(0)$  at  $T=0^\circ$ , plotted as a function of the inverse collision time  $\Gamma$ . The superscript P refers to the value when  $\Gamma=0$ .

The diagram of Fig. 1(c) yields for the order parameter at  $T=0^{\circ}$ :

$$\Delta = \frac{N_0 V}{2} \int_{-\omega_{D'}}^{\omega_{D'}} \operatorname{Re} \frac{\dot{\Delta}}{(\tilde{\omega}^2 - \tilde{\Delta}^2)^{1/2}} d\omega, \qquad (2.9)$$

where we have introduced a cutoff at  $\omega_D'$  for the superconducting interaction. To make a connection with the BCS theory when the impurity interaction is turned off,  $\omega_D' = (\omega_D^2 + \Delta^2)^{1/2}$ , where  $\omega_D$  is the BCS cutoff. In our weak-coupling approximation, this will have a negligible effect on the solution of the integral equation for  $\Delta$ . However, it is important in the calculation of the freeenergy difference, which is proportional to  $\Delta^2$ .

The three equations contained in (2.8) and (2.9) are to be solved simultaneously, or, (2.9) is to be solved with

$$\tilde{\omega} = \omega + i\Gamma_1 \frac{\tilde{\omega}}{(\tilde{\omega}^2 - \tilde{\Delta}^2)^{1/2}}$$
(2.10)

and

$$\tilde{\Delta} = \Delta + i\Gamma_2 \frac{\tilde{\Delta}}{(\tilde{\omega}^2 - \tilde{\Delta}^2)^{1/2}}.$$
(2.11)

These equations can be simplified by introducing

$$u = \tilde{\omega} / \tilde{\Delta}$$
 (2.12)

and  $\Gamma = \Gamma_1 - \Gamma_2$  so that

$$u\Delta = \omega + i\Gamma \frac{u}{(u^2 - 1)^{1/2}}$$
 (2.13)

and

$$\Delta(0,\Gamma) = \frac{N_0 V}{2} \int_{-\omega_{D'}}^{\omega_{D'}} d\omega \operatorname{Re} \frac{1}{(u^2 - 1)^{1/2}}, \quad (2.14)$$

where Re means real part. In connection with (2.12) and (2.13) we take the positive square root for  $\omega \to \infty + i\delta$ and  $\omega \to -\infty - i\delta$ , where  $\delta$  is a small positive number. Before leaving this section we state the results for nonzero temperature. The usual factor of  $\tanh \frac{1}{2}\beta\omega$  occurs in (2.14) so that it reads

$$\Delta(T,\Gamma) = N_0 V \int_0^{\omega D'} d\omega \, \operatorname{Re} \frac{1}{(u^2 - 1)^{1/2}} \tanh \frac{1}{2} \beta \omega \,, \quad (2.15)$$

where  $\beta = (\kappa T)^{-1}$  and, in Eq. (2.13),  $\Delta$  occurring there is  $\Delta(T, \Gamma)$ .

## **III. CRITICAL TEMPERATURE**

The critical temperature  $T_c$  is the solution of (2.15) in the limit  $\Delta(T,\Gamma) \rightarrow 0$  or  $u\Delta \rightarrow \omega + i\Gamma$ . This is

$$1 = N_0 V \int_0^{\omega_D} d\omega \operatorname{Re} \frac{1}{\omega + i\Gamma} \tanh \frac{1}{2} \beta_c \omega$$

$$= N_0 V \int_0^{\omega_D} d\omega \frac{\omega}{\omega^2 + \Gamma^2} \tanh \frac{1}{2} \beta_c \omega.$$
(3.1)

This reduces to the usual expression in the absence of the spin-dependent scattering when  $\Gamma \rightarrow 0$ . That is, in the presence of the paramagnetic impurities, the highly singular factor  $\omega^{-1}$  in the equation for the critical temperature is replaced by the broadened function  $\omega/(\omega^2 + \Gamma^2)$ —indicating a true lifetime effect. For finite  $\Gamma$ ,  $\beta_c$  must be larger than it is when  $\Gamma=0$ . The presence of the impurities lowers the critical temperature. Moreover there is a critical concentration for which the critical temperature  $T_c$  vanishes. One recalls that

$$1/N_0 V = \ln(2\omega_D/\Delta^P(0)),$$
 (3.2)

where  $\Delta^{P}(0)$  is the gap at  $T=0^{\circ}$  for the pure material. Consequently, at the critical value of  $\Gamma$ ,  $\Gamma_{er}$ ,

$$rac{1}{N_0 V} = \ln rac{2 \omega_D}{\Delta^P(0)} = rac{1}{2} \ln \left( 1 + rac{\omega_D^2}{\Gamma^2} 
ight) pprox \ln rac{\omega_D}{\Gamma_{
m or}} \, .$$

Therefore,

$$2\Gamma_{\rm er} = \Delta^P(0) \,. \tag{3.3}$$

For values of  $\Gamma < \Gamma_{er}$  one can express  $T_e$  in terms of  $\psi$  functions  $\psi(x) = (d/dx) \ln \Gamma(x)$ :

$$\ln(T_{c}^{P}/T_{c}) = \psi(\frac{1}{2} + \rho) - \psi(\frac{1}{2})$$
 (3.4)

with  $\rho = \Gamma/2\pi\kappa T_c$ . This is shown in Fig. 2 in the curve labeled  $T_c/T_c^P$  and, as shown there, this quantity vanishes when  $\Gamma/\Delta^P(0)=0.50$ . The order parameter  $\Delta(T=0, \Gamma)=\Delta(0,\Gamma)$  may be calculated from (2.14) by using the contour shown in Fig. 3. One readily establishes that the contribution to the integral from the arc is purely imaginary so that we need integrate only along the imaginary axis. The result is, in agreement with that stated by Abrikosov and Gor'kov,<sup>1</sup>

$$\ln \frac{\Delta(0,\Gamma)}{\Delta^{P}(0)} = -\frac{\pi}{4} \frac{\Gamma}{\Delta(0,\Gamma)} \quad \text{for} \quad \Gamma \leq \Delta(0,\Gamma) ,$$
  
$$\ln \frac{\Delta(0,\Gamma)}{\Delta^{P}(0)} = -\ln[\bar{\Gamma} + (\bar{\Gamma}^{2} - 1)^{1/2}] + \frac{1}{2\bar{\Gamma}} (\bar{\Gamma}^{2} - 1)^{1/2} \quad (3.5)$$

$$-\frac{1}{2}\overline{\Gamma} \arctan(\overline{\Gamma}^2-1)^{-1/2}$$
 for  $\Gamma \geq \Delta(0,\Gamma)$ ,

and

and  $\bar{\Gamma} = \Gamma/\Delta(0,\Gamma)$ . The behavior of  $\Delta(0,\Gamma)/\Delta^{P}(0)$  as a function of  $\Gamma/\Delta^{P}(0)$  is shown in Fig. 2. One sees the very important result: the order parameter  $\Delta(0,\Gamma)$  vanishes at the critical concentration. Before considering the temperature-dependent function  $\Delta(T,\Gamma)$ , it is useful to introduce the density of states, which we do in the next section.

## IV. DENSITY OF STATES

It is customary to work with the density of states in k space, but here it is much more convenient to consider the density of states in  $\omega$  space. The reason is this: because of collision broadening, the energy of a given momentum state is spread throughout a region in k space whose width in k is  $\Gamma_1/v_F$ . On the other hand, the energy  $\omega$  is conserved in each collision so that there is no broadening. We therefore evaluate the density of states  $N(\omega)$  as

$$N(\omega) = \frac{1}{2} \frac{N_0}{\pi} \int_{-\infty}^{\infty} d\epsilon \operatorname{Tr}[\operatorname{Im} \mathfrak{g}(\mathbf{k}, \omega)]. \quad (4.1)$$

Here  $N_0$  is the density of states at the Fermi surface and the factor of  $\frac{1}{2}$  is inserted to define the density of states for a single spin. The path of integration can be deformed so that one encircles the positive real axis in a negative sense. One finds

$$N(\omega) = N_0 \operatorname{Re} \frac{u}{(u^2 - 1)^{1/2}}.$$
 (4.2)

In the limit as  $\Gamma \rightarrow 0$  this reduces to

$$N^{P}(\omega) = N_{0} \frac{|\omega|}{(\omega^{2} - \Delta^{2})^{1/2}} \text{ for } |\omega| > \Delta$$
  
= 0 otherwise, (4.3)

which is the same as that described by the BCS theory. This is the result whatever the size of  $\Gamma_1$ . We find, accordingly, that nonparamagnetic impurities do not affect the parameter  $\Delta$ , the critical temperature, or the density of states. The very small change in critical temperature observed in the nonparamagnetic case is attributable to a smearing out of anisotropic interaction. The equations (4.2) and (2.13) must be solved simultaneously to determine  $N(\omega)$ . This, it should be remarked, depends on temperature by way of the







FIG. 4. The density of states in energy plotted as a function of the reduced energy for several values of the reduced inverse collision time  $\Gamma/\Delta$ .  $\Delta(T)$  is to be understood as  $\Delta(T,\Gamma)$ .

parameter  $\Delta$ . The solution is a numerical one and is achieved by setting

$$u = \cosh z = \cosh(x + iy), \qquad (4.4)$$

where x and y are real. This substitution yields the cubic equation

$$\sin^{3}2y + (\bar{\omega}^{2} + \bar{\Gamma}^{2} - 1) \sin^{2}2y - 2\bar{\omega}\bar{\Gamma} = 0$$
 (4.5)

for y, where  $\bar{\omega}$  and  $\bar{\Gamma}$  are the corresponding quantities measured in units of  $\Delta(T,\Gamma)$ . The quantity x is determined by

$$\cosh x \cos 2y = \bar{\omega} \cos y - \bar{\Gamma} \sin y$$
 (4.6)

$$N(\omega) = N_0 \sinh 2x (\cosh 2x - \cos 2y)^{-1}.$$
 (4.7)

The results of these numerical computations are shown in Fig. 4 where  $N(\omega)/N_0$  is plotted against  $\omega/\Delta(T,\Gamma)$ . The asymptotic curve is  $N(\omega)/N_0=1$ , achieved when  $\omega/\Delta(T,\Gamma) \to \infty$ ; the dotted curve is that given by the BCS theory and corresponds to  $\Gamma=0$ . The curves for  $\Gamma \neq 0$  start from zero at a value  $\omega < \Delta$  and, for small  $\Gamma$ , rise steeply to a maximum and then approach the BCS curve. The value of the energy  $\Omega_G$  at which the curve rises from a zero value is the half-energy gap, the minimum energy for excitations. As the concentration of the paramagnetic impurities increases,  $\Omega_{G}$  decreases and so does the size of the maximum.  $\Omega_{\mathcal{G}}$  is zero when  $\Gamma/\Delta=1$  and this value of  $\Gamma$  is another critical  $\Gamma$ ,  $\Gamma_{er}'$ . The curves drawn by Phillips<sup>5</sup> are a remarkably good estimate of those shown here. One essential point revealed in these curves is that a distinction must be made between the gap  $\Omega_G$  and the order parameter  $\Delta(T,\Gamma)$ . The relation between these quantities can be obtained as follows: For a fixed value of  $\Gamma/\Delta < 1$ , Eq. (2.13) has real solutions for u which are less than unity for  $\omega/\Delta$ sufficiently small. In this range of  $\omega$ , the density of states is zero, as can be seen from Eq. (4.2). The density of states departs from zero at the value of  $\omega(\Omega_G)$  at which



FIG. 5. The order parameter plotted as a function of temperature for several values of the inverse collision time. The superscript Prefers to the value when  $\Gamma=0$ . The dashed curve is a boundary curve separating the gapless region from the region with a gap.

u first becomes complex. Rewriting Eq. (2.13) as

$$\bar{\omega} = u - \bar{\Gamma} \frac{u}{(1-u^2)^{1/2}}$$

one sees that the maximum value of the right-hand side occurs at  $u_0 = (1 - \overline{\Gamma}^{2/3})^{1/2}$  and that this point yields the gap

$$\Omega_G(T,\Gamma) = \Delta(T,\Gamma) \left[ 1 - \left( \frac{\Gamma}{\Delta(T,\Gamma)} \right)^{2/3} \right]^{3/2}.$$
 (4.8)

The ratio  $\Omega_G/\Delta^P$  is plotted in Fig. 2 at zero temperature as a function of  $\Gamma/\Delta^P(0)$ . There is another critical concentration or another critical value of  $\Gamma$ ,  $\Gamma_{er}'$ , the one for which  $\Omega_G(\Gamma_{er}')=0$ . This is

$$\Gamma_{\rm cr}' = \Delta(0, \Gamma_{\rm cr}'), \qquad (4.9)$$

$$\Gamma_{\rm cr}' = e^{-\pi/4} \Delta^P(0) = e^{-\pi/4} 2 \Gamma_{\rm cr} = 0.91 \Gamma_{\rm cr}. \quad (4.10)$$

At any temperature there is a region of concentration (or a region of  $\Gamma$ ) in which the material is superconducting but the excitation energy gap is zero.

A numerical evaluation of  $\Delta(T,\Gamma)$  for various values of  $\Gamma$  yielded the results shown in Fig. 5. The dotted curve in this figure is a boundary curve; the intersection with a full curve, for a particular value of  $\Gamma$ , gives the temperature at which the energy gap vanishes for that value of  $\Gamma$ , so that in the interval from this temperature to the corresponding critical temperature, the energy gap remains zero in magnitude.

In determining the curves of Fig. 5, explicit use was made of the BCS relation between critical temperature and order parameter at zero temperature for the pure material. That is,  $\Delta^P(0)/\kappa T_c{}^P$  was taken to be 1.76. One can see from the curves of Fig. 5 that the critical temperature changes faster with impurity concentration than the order parameter at zero temperature. Thus, the ratio  $\Delta(0,\Gamma)/\kappa T_c$  is no longer a constant, but depends on the impurity concentration. The value of this ratio, normalized to its value in the pure material, is plotted in Fig. 6. The limiting value of  $\Delta(0)/\kappa T_c$  when  $\Gamma = \Gamma_{\rm er}$ is  $\sqrt{2}\pi$ . Therefore, it is incorrect to assume the constancy of this ratio in any theory to explain the effects of paramagnetic impurities.<sup>8</sup>

Before proceeding further, it is of some interest to look at the integral equation for  $\Delta(T,\Gamma)$  for nonzero but small temperatures to see how the solution changes qualitatively as one passes from the region with gap to the gapless region. If in Eq. (2.15) one uses  $\tanh \frac{1}{2}\beta\omega$  $= 1-2(e^{\beta\omega}+1)^{-1}$ , the term involving unity can be evaluated in the same way as was done in obtaining Eq. (3.5). The remainder is

$$-2N_0V \int_0^{\omega_D'} d\omega \operatorname{Re}(u^2 - 1)^{-1/2} (e^{\beta\omega} + 1)^{-1}. \quad (4.11)$$

For  $\Gamma/\Delta(T,\Gamma) < 1$ , u is real and less than unity up to  $\Omega_G$  so that the lower limit becomes  $\Omega_G$ . For sufficiently low temperatures, we can replace the temperaturedependent factor in (4.11) by  $e^{-\beta\omega}$ . Because of the rapidly decreasing exponential factor, a good approximation is obtained by using the value of  $\operatorname{Re}(u^2-1)^{-1/2}$ in the neighborhood of  $\Omega_G$ . A straightforward but involved expansion of Eqs. (4.5) and (4.6) gives

$$\operatorname{Re}\frac{1}{(u^2-1)^{1/2}} \approx (\frac{2}{3})^{1/2} \frac{\Omega_G^{1/6}}{\Gamma^{2/3}} (\omega - \Omega_G)^{1/2}. \quad (4.12)$$

Substitution in Eq. (4.11) and use of Eq. (3.5) gives finally

 $\Delta(0) - \Delta(T) = (2\pi/3)^{1/2} \frac{\Omega_G^{1/6}}{\Gamma^{2/3}\beta^{3/2}} \left(1 - \frac{\pi}{4} \frac{\Gamma}{\Delta(0)}\right)^{-1} e^{-\beta\Omega_G}.$  (4.13)

For  $\Gamma/\Delta(T,\Gamma) > 1$ ,  $\Omega_G = 0$ , the lower limit on the integral is 0 and  $\operatorname{Re}(u^2-1)^{-1/2}$  now rises linearly with  $\omega$  and is in fact  $(\omega/\Gamma)[(\Gamma/\Delta)^2-1]^{-1/2}$ . Again relying on the rapid drop in the remainder of the integrand to cut out the large  $\omega$  contribution to the integral (4.11), we



<sup>8</sup> See, for example, H. Suhl and B. T. Matthias, Phys. Rev. 114, 977 (1959).

or



FIG. 7. Critical temperature and half-energy gap at  $T/T_c=0.25$  as a function of  $\Gamma/\Delta^P(0)$ . The open circles and triangles are the experimental points for the critical temperature and half-energy gap respectively as measured by Reif and Woolf. The dashed curve is their linear extrapolation of the low-impurity-concentration points. The triangle at  $\Gamma/\Delta^P(0)=0.3$  is roughly the concentration at which no gap is observed.

get using Eq. (3.5)

$$\Delta(0) - \Delta(T) = \frac{\pi^2}{6} \frac{(\kappa T)^2}{\Delta(0)} \left[ \bar{\Gamma}_0 (\bar{\Gamma}_0^2 - 1)^{1/2} \right]^{-1} \\ \times \left[ 1 - \frac{(\bar{\Gamma}_0^2 - 1)^{1/2}}{2\bar{\Gamma}_0} - \frac{\bar{\Gamma}_0}{2} \arctan(\bar{\Gamma}_0^2 - 1)^{-1/2} \right]^{-1}, \quad (4.14)$$

for  $\Gamma/\Delta(T,\Gamma) > 1$  with  $\overline{\Gamma}_0 = \Gamma/\Delta(0)$ .

We see that near the absolute zero of temperature, the deviation from  $\Delta(0)$  is exponential in temperature but becomes quadratic in the gapless region. Note that (4.13) does not go over smoothly into (4.14) since as  $\Omega_G \rightarrow 0$  for some values of T,  $\beta\Omega_G$  is no longer large and therefore the Fermi function cannot be replaced by the exponential. Furthermore the expansion (4.12) is not valid for very small  $\Gamma$  and one cannot recover the purematerial value from (4.13).

An expression for  $\Delta(T,\Gamma)$  near the transition temperature for arbitrary value of  $\Gamma$  can also be obtained by an expansion of Eq. (2.15) in powers of  $\Delta$ . However, it is easier to obtain an expression for  $\Delta$  directly by minimizing the free energy; we shall return to this point later.

## Comparison with Experiment

To date, the most definitive experiment to test the theory has been the tunneling measurements of Reif and Woolf.<sup>3</sup> A comparison with their results can be made using Eq. (4.8) for the excitation energy gap, obtaining  $\Delta(T,\Gamma)$  from Eq. (2.15) and using the observed depression of the critical temperature to evaluate  $\Gamma$ . For any given sample, the initial slope of the critical temperature curve determines  $\Gamma/\Delta^P(0)$ . For this value of  $\Gamma/\Delta^P(0)$ , and for the desired temperature  $(T/T_c{}^P \approx 0.25$  for their experiment),  $\Delta(T,\Gamma)$  is determined from the solution of the integral equation and substituted in Eq. (4.8) to obtain the energy gap. The result is shown

in Fig. 7 as the curve labeled  $\Omega_G/\Delta^P(0)$  along with the curve of  $T_c/T_c^P$ . The experimental points for the transition temperature are shown by open circles and the points for the gap by triangles. A linear extrapolation of the low-impurity-concentration points is shown as the dotted line. The lowest point at  $\Gamma/\Delta^P(0) \approx 0.3$  is roughly the concentration at which no gap is measured. One sees that the quantitative agreement, although not good, is probably all that can be expected. Clearly it would be very desirable to do tunneling on a normal-superconductor junction, preferably at a low temperature to reduce temperature broadening effects, so that a direct comparison can be made with the density of states given by Eq. (4.2).

Recall that the pure material was assumed to be an ideal BCS superconductor, that is,  $\Delta^{P}(0)/\kappa T_{o}{}^{P}=1.76$ . This value is not observed in the thin films used in the tunneling experiments, but is about 1.90, a difference of about 8%. If the measured value of this ratio is introduced into the theory, the curves for  $T_{o}$  and  $\Delta(T,\Gamma)$  are depressed and bring the theory into somewhat better agreement with the experiment.

## V. THERMAL PROPERTIES

In this section we derive expressions for the specific heat and critical field of an alloy containing paramagnetic impurities. These can easily be obtained from the free energy. One method of obtaining the free energy is to use the well-known relation involving an integral over the coupling constant for the superconducting interaction. This is, however, difficult to perform at arbitrary temperatures and impurity concentrations. Instead, we will derive an expression for the expectation value of the total energy using the previously derived Green's function. Then, using the fact that the essential effect of the impurities is to alter the density of states, we get an expression for the entropy and thus the free energy.

In an approximation of a delta-function interaction with a strength V, the superconducting interaction energy is just  $-\Delta^2/V$ . We derive in Appendix A the following expression for the total energy  $E_S$  in the superconducting state:

$$E_{S} - \frac{\Delta^{2}}{V} = 4N_{0} \int_{-\infty}^{\infty} d\epsilon \left\{ \int_{\Omega_{G}}^{\omega_{D'}} \frac{d\omega}{2\pi} \omega f(\omega) \operatorname{Im} \mathcal{G}_{11}(\mathbf{k}, \omega) + \int_{\Omega_{G}}^{\omega_{D'}} \frac{d\omega}{2\pi} \omega (1 - f(\omega)) \operatorname{Im} \mathcal{G}_{11}(\mathbf{k}, -\omega) \right\}, \quad (5.1)$$

where  $g_{11}(\mathbf{k},\omega) = (\tilde{\omega}+\epsilon)(\epsilon^2+\tilde{\Delta}^2-\tilde{\omega}^2)^{-1}$  is the (1,1) component of the tensor Green's function and we have introduced the cutoff  $\omega_D' = (\omega_D^2 + \Delta^2)^{1/2}$  to make the connection with the BCS theory in the absence of any impurities. Substituting in this expression for  $\mathcal{G}$  and carrying out the integration over  $\epsilon$ , dropping terms odd n  $\epsilon$ , we obtain

$$E_{S} - \frac{\Delta^{2}}{V} = -2N_{0} \int_{\Omega_{G}}^{\omega_{D'}} d\omega \operatorname{Im} \frac{\omega \tilde{\omega}}{(\tilde{\Delta}^{2} - \tilde{\omega}^{2})^{1/2}} \operatorname{tanh}_{2}^{1} \beta \omega$$
$$= -2N_{0} \int_{\Omega_{G}}^{\omega_{D'}} d\omega \operatorname{Re} \frac{u}{(u^{2} - 1)^{1/2}} \omega \operatorname{tanh}_{2}^{1} \beta \omega$$
$$= -\int_{0}^{\omega_{D'}} d\omega N(\omega) 2\omega \operatorname{tanh}_{2}^{1} \beta \omega.$$
(5.2)

The density of states enters in a natural way, but because the energy  $\omega$  contains not only the kinetic energy contribution but also the effects of the interaction, there is an additional term  $\Delta^2/V$ . The impurity effects come in only through the altered density of states  $N(\omega)$  and the self-energy  $\Delta$ . The normal-state energy is obtained by setting  $\Delta=0$  in (5.2). Since the integration over  $\omega$  in the normal state extends only up to  $\omega_D$  rather than  $\omega_D'$ , we add and subtract

$$N_0 \int_{\omega_D}^{\omega_D} d\omega 2\omega \tanh \frac{1}{2} \beta \omega \approx N_0 \Delta^2,$$

and obtain for the total energy difference between the superconducting and normal states

$$E_{\mathcal{S}} - E_{N} = -N_{0} \int_{0}^{\omega_{D}'} d\omega \left(\frac{N(\omega)}{N_{0}} - 1\right)$$
$$\times 2\omega \tanh \frac{1}{2}\beta \omega + \frac{\Delta^{2}}{V} - N_{0}\Delta^{2}. \quad (5.3)$$

It is absolutely necessary for the upper limit to be  $\omega_D'$ rather than  $\omega_D$  if we are to count correctly all terms of order  $\Delta^2$  which are important in the free-energy difference.

The entropy is

$$S = -2\kappa \sum_{k} \{ n_{k} \ln n_{k} + (1 - n_{k}) \ln(1 - n_{k}) \}, \quad (5.4)$$

where  $\kappa$  is Boltzmann's constant,  $n_k$  is the Fermi function, and the factor of 2 is for spins. Converting to an integral over  $\epsilon_k$  and then to an integral over  $\omega$  using  $N_0 d\epsilon_k = N(\omega) d\omega$ , we obtain

$$S_{S} = 4\kappa \int_{0}^{\omega_{D}'} d\omega N(\omega) \left[ \ln(1 + e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega} + 1} \right], \quad (5.5)$$

where we have used the evenness of the integrand to write it as an integral over positive energies only. Thus, the only difference from the case of no impurities is in the density of states. After subtracting off the normalstate value, the free energy difference  $\Delta F = \Delta E - T \Delta S$  is

$$F_{S}-F_{N} = -N_{0} \int_{0}^{\omega_{D}'} d\omega \left(\frac{N(\omega)}{N_{0}}-1\right)$$

$$\times 2\omega \tanh^{\frac{1}{2}}\beta\omega + \frac{\Delta^{2}}{V} - N_{0}\Delta^{2}$$

$$-\frac{4N_{0}}{\beta} \int_{0}^{\omega_{D}'} d\omega \left(\frac{N(\omega)}{N_{0}}-1\right)$$

$$\times \left[\ln(1+e^{-\beta\omega}) + \frac{\beta\omega}{e^{\beta\omega}+1}\right]. \quad (5.6)$$

Note that in our approximation, the normal state is not affected by impurities. The critical field for a bulk specimen of unit volume is then given by the usual formula

$$H_c^2/8\pi = F_N - F_S,$$
 (5.7)

and the specific-heat difference by

$$C_{S} - C_{N} = T(\partial/\partial T)(S_{S} - S_{N}).$$
(5.8)

The expression for the free energy cannot be simplified any further and one must work out the integral numerically. We have not done this although it would not be difficult to do using the previous results of the calculation of  $N(\omega)$  and  $\Delta$ . Instead, we have concentrated on the limiting cases of T near absolute zero and T near the critical temperature for arbitrary values of the impurity concentration (or equivalently  $\Gamma$ ).

# Low Temperatures

We can evaluate the free energy at  $T=0^{\circ}$  by the same device employed in calculating  $\Delta(0,\Gamma)$ . In using the contour in Fig. 3, the integral over the arc does not contribute and the integral over the imaginary axis can be converted to an integral over the variable *iu* using (2.13). Then

$$F_{S}(0) - F_{N}(0) = -\frac{1}{2}N_{0}\Delta^{2}(0,\Gamma)\left[1 - \frac{1}{2}\pi\bar{\Gamma} + \frac{2}{3}\bar{\Gamma}^{2}\right] \quad \text{for} \quad \bar{\Gamma} \leq 1$$
  
$$= -\frac{1}{2}N_{0}\Delta^{2}(0,\Gamma)\left\{1 - \bar{\Gamma} \arcsin(\bar{\Gamma})^{-1} + \bar{\Gamma}^{2}\left[1 - (\bar{\Gamma})^{-1}(\bar{\Gamma}^{2} - 1)^{1/2}\right] - \frac{1}{3}\left[1 - (1 - \bar{\Gamma}^{-2})^{3/2}\right]\right\}$$
  
for  $\bar{\Gamma} \geq 1$ , (5.9)

where  $\overline{\Gamma} = \Gamma/\Delta(0,\Gamma)$ . For T > 0, the free-energy difference is

$$F_{S}-F_{N}=D_{0}(T,\Gamma)-\frac{4}{\beta}N_{0}\int_{0}^{\omega_{D}^{*}}d\omega\left(\frac{N(\omega)}{N_{0}}-1\right)$$
$$\times\ln(1+e^{-\beta\omega}),\quad(5.10)$$

where  $D_0(T,\Gamma)$  is just the right-hand side of Eq. (5.9) but with  $\Delta(0,\Gamma)$  replaced by  $\Delta(T,\Gamma)$ . In the gap region,  $\Omega_G \neq 0$ , we can replace the logarithm above by the exponential itself and therefore this correction term will be exponential in T. Furthermore, using (4.13),  $D_0(T,\Gamma)$ will be just  $D_0(0,\Gamma)$  plus a term that is also exponential in T. Therefore the leading term in the correction for finite temperature will come from the change in the normal-state free energy with temperature. On the other hand, in the gapless region, the contribution from the integral and from  $D_0(T,\Gamma)$  will be of order  $T^2$  just as is the contribution from  $F_N(T)$ . In fact, to a fairly good approximation, we can replace the factor  $N(\omega)/N_0$  in the integral above by its value at  $\omega=0$ , namely,  $(\Gamma^2 - \Delta^2)^{1/2}/\Gamma$  and get

$$\begin{bmatrix} F_{S}(T) - F_{N}(T) \end{bmatrix} - \begin{bmatrix} F_{S}(0) - F_{N}(0) \end{bmatrix} = D_{0}(T,\Gamma) - D_{0}(0,\Gamma) + \begin{bmatrix} (\Gamma^{2} - \Delta^{2})^{1/2} / \Gamma - 1 \end{bmatrix} F_{N}(T).$$
(5.11)

In either case the critical field for small temperatures will be of the form

$$H_c^2(T,\Gamma) = H_c^2(0,\Gamma) [1 - a(\Gamma)(\kappa T/\Delta(0,\Gamma))^2], \quad (5.12)$$

where the function  $a(\Gamma)$  can be deduced from (5.11), (5.10), (5.9), and (3.5). We shall not go into this any further but go on to consider the specific heat at low temperatures.

It is most convenient to obtain the specific heat from the entropy (5.5). First, consider the region where the gap is not zero. In this case  $N(\omega)$  is zero up to  $\Omega_G$  and therefore if  $\Gamma$  is not too large,  $\beta \omega$  will always be large and

$$\ln(1+e^{-\beta\omega})+\beta\omega/(e^{\beta\omega}+1)\approx e^{-\beta\omega}(1+\beta\omega).$$

Furthermore, because of the rapidly decreasing exponential factor, we can replace  $N(\omega)$  by its value in the vicinity of  $\Omega_G$ . Again using (4.5) and (4.6) it is possible to show that

$$N(\omega) \approx N_0(\frac{2}{3})^{1/2} \frac{(\omega - \Omega_G)^{1/2}}{\Omega_G^{1/6} \Gamma^{2/3}} \Delta^{1/3}.$$

Therefore,

$$\begin{split} S_{\mathcal{S}} &= 4\kappa N_{0}(\frac{2}{3})^{1/2} \Delta^{1/3} (\Omega_{G}^{1/6} \Gamma^{2/3})^{-1} \\ & \times \int_{\Omega_{G}}^{\infty} d\omega (\omega - \Omega_{G})^{1/2} (1 + \beta \omega) e^{-\beta \omega} \\ &= 4\kappa N_{0}(\frac{2}{3})^{1/2} \Delta^{1/3} (\Omega_{G}^{1/6} \Gamma^{2/3})^{-1} e^{-\beta \Omega_{G}} \\ & \times \int_{0}^{\infty} d\omega' \omega'^{1/2} (1 + \beta \omega' + \beta \Omega_{G}) e^{-\beta \omega'}, \end{split}$$

where because of the rapid convergence we have replaced the upper limit by infinity. Keeping only the leading term in T we obtain

$$C_{S} = (8\pi/3)^{1/2} \kappa N_{0} \frac{\Delta^{1/3} \Omega_{G}^{11/6}}{\Gamma^{2/3}} \frac{e^{-\beta \Omega_{G}}}{(\kappa T)^{1/2}} \,. \tag{5.13}$$

The gap in the excitation spectrum shows up as an exponentially varying specific heat in the superconducting state, as one would expect. Again note that this expression does not go over into the pure material value because of the inapplicability of the expansion of  $N(\omega)$  for very small  $\Gamma$ .

In the gapless region,  $\Gamma > \Delta(T, \Gamma)$ , the density of states is finite at  $\omega = 0$  and is in fact given by

$$N(\omega) = N_0 (\Gamma^2 - \Delta^2)^{1/2} / \Gamma.$$

Since the remainder of the integrand contributes principally for small values of  $\omega$ , a good approximation consists of retaining only the constant term in the density of states evaluated at  $T=0^{\circ}$ , and extending the upper limit to  $\infty$ . The net result is to change the entropy and therefore the specific heat in the normal state by a constant factor:

$$C_{S} = [(\Gamma^{2} - \Delta^{2})^{1/2} / \Gamma] C_{N}.$$
 (5.14)

Therefore, in the gapless region, the specific heat depends linearly on the temperature as in the normal state but with an altered density of states. These results for the specific heat at low temperatures were obtained previously in AG.

#### Temperatures Near $T_c$

We have already shown that the order parameter  $\Delta$  goes smoothly to zero at the critical temperature for all values of the impurity concentration. Therefore we can use the theory of second-order phase transitions to expand the free energy in a power series in  $\Delta$  around the critical point. To do this we expand the integrand in (5.6) in powers of  $\Delta$  up to order  $\Delta^4$ . It is easily shown that odd powers do not contribute.

$$\frac{N(\omega)}{N_0} - 1 = \operatorname{Re} \frac{u}{(u^2 - 1)^{1/2}} - 1$$
$$= \operatorname{Re} \frac{1}{2} \left\{ \frac{\Delta^2}{(\omega + i\Gamma)^2} + \frac{3}{4} \frac{\Delta^4}{(\omega + i\Gamma)^4} - i\Gamma \frac{\Delta^4}{(\omega + i\Gamma)^5} \right\},$$

where we have used the fact that as  $\Delta$  goes to zero,  $u\Delta$  goes to  $(\omega+i\Gamma)$ . Thus the free-energy difference near the critical point is

$$F_{S}-F_{N} = \Delta^{2} \left\{ \frac{1}{V} - N_{0} - N_{0} \int_{0}^{\omega_{D}'} d\omega \left[ \omega \tanh \frac{1}{2} \beta \omega + \frac{2}{\beta} \ln(1 + e^{-\beta \omega}) + \frac{2\omega}{e^{\beta \omega} + 1} \right] \operatorname{Re} \frac{1}{(\omega + i\Gamma)^{2}} \right\} - \Delta^{4} N_{0} \int_{0}^{\infty} d\omega \left[ \omega \tanh \frac{1}{2} \beta \omega + \frac{2}{\beta} \ln(1 + e^{-\beta \omega}) + \frac{2\omega}{e^{\beta \omega} + 1} \right] \operatorname{Re} \left( \frac{3}{4} \frac{1}{(\omega + i\Gamma)^{4}} - \frac{i\Gamma}{(\omega + i\Gamma)^{5}} \right).$$
(5.15)

Again, the upper limit in the last term has been replaced by infinity because of the rapid convergence of the ntegrand. Doing an integration by parts on the first term above gives as the coefficient of  $\Delta^2$ :

$$\frac{1}{V} - N_0 \int_0^{\omega_D'} d\omega \frac{\omega}{\omega^2 + \Gamma^2} \tanh \frac{1}{2} \beta \omega \,.$$

Note that this vanishes at the critical temperature as would be expected. The remaining integral can be evaluated in terms of the generalized Riemann zeta functions. Thus (5.15) becomes

$$F_{S} - F_{N} = \Delta^{2} \left( \frac{1}{V} - N_{0} \int_{0}^{\omega_{D'}} d\omega \frac{\omega}{\omega^{2} + \Gamma^{2}} \tanh^{\frac{1}{2}} \beta \omega \right) + \Delta^{4} \frac{N_{0}}{4} \left( \frac{\beta}{2\pi} \right)^{2} \left[ \zeta(3, \frac{1}{2} + \lambda) - \lambda \zeta(4, \frac{1}{2} + \lambda) \right]$$
$$\equiv \Delta^{2} \alpha_{1}(T, \Gamma) + \Delta^{4} \alpha_{2}(T, \Gamma) , \qquad (5.16)$$

where  $\zeta(s,z) = \sum_{n=0}^{\infty} (n+z)^{-s}$ , and  $\lambda = \Gamma \beta / (2\pi)$ . This expression is valid for all values of  $\Gamma$  for a suitable temperature interval near the critical temperature for which  $\Delta$  is small. It reduces to the BCS expression for  $\Gamma = 0$ .

The order parameter is now obtained by minimizing (5.16) with respect to  $\Delta$ . Thus

$$\Delta^2(T,\Gamma) = -\frac{1}{2} \left[ \alpha_1(T,\Gamma) / \alpha_2(T,\Gamma) \right].$$

Substituting in (5.16) for  $\alpha_1(T,\Gamma)$ , we see that the free-energy difference is proportional to  $\Delta^4$ , and therefore to  $(T_c-T)^2$ .

Expanding  $\alpha_1(T,\Gamma)$  to second order in the small quantity  $(T_c-T)$ , and evaluating  $\alpha_2(T,\Gamma)$  at  $T_c$  we obtain

$$\Delta^{2}(T,\Gamma) = \frac{2(1 - T/T_{c})\{1 - \lambda_{c}\zeta(2, \frac{1}{2} + \lambda_{c}) + \frac{1}{2}(1 - T/T_{c})[1 - 2\lambda_{c}(\zeta(2, \frac{1}{2} + \lambda_{c}) - \lambda_{c}\zeta(3, \frac{1}{2} + \lambda_{c}))]\}}{(\beta_{c}/2\pi)^{2}[\zeta(3, \frac{1}{2} + \lambda_{c}) - \lambda_{c}\zeta(4, \frac{1}{2} + \lambda_{c})]}, \quad (5.17)$$

where  $\lambda_c = \lambda(T = T_c)$ .

In the extreme gapless region,  $\lambda_c \gg 1$ , we recover the AG result, since

$$\begin{aligned} &\alpha_1(T,\Gamma) \to -N_0 \kappa^2 2\pi^2 (T_c^2 - T^2)/12\Gamma^2, \\ &\alpha_2(T,\Gamma) \to N_0/24\Gamma^2, \end{aligned}$$

and therefore

and

$$F_{S}-F_{N}=-N_{0}\Delta^{4}/24\Gamma^{2}$$

$$\Delta^2(T,\Gamma) = 2\pi^2 \kappa^2 (T_c^2 - T^2)$$

One should be extremely careful in using these last expressions since they are valid over only a very limited range of values of  $\Gamma$ . In fact,  $\lambda_c$  is still almost unity for  $\Gamma/\Delta^P(0)=0.49$ , i.e., within 2% of the critical value of 0.5. Contributions from higher orders in  $(\lambda_c)^{-1}$  would not be negligible.



FIG. 8. The discontinuity in the specific heat at the critical temperature. Note that the horizontal scale is chosen so that the impurity concentration increases towards the right. The superscript P refers to the value when  $\Gamma=0$ . If we keep only the  $(T_c - T)$  term, the critical field as obtained from (5.16) is

$$\frac{H_c^2}{8\pi} = N_0 \left(1 - \frac{T}{T_c}\right)^2 \times \frac{\left[1 - \lambda_c \zeta(2, \frac{1}{2} + \lambda_c)\right]^2}{(\beta_c/2\pi)^2 \left[\zeta(3, \frac{1}{2} + \lambda_c) - \lambda_c \zeta(4, \frac{1}{2} + \lambda_c)\right]}.$$
 (5.18)

We shall be interested only in the linear term in the specific heat near the critical temperature, and therefore we need retain only the term in  $\Delta^2$  in the entropy (5.5), evaluating the coefficient at  $T = T_c$  (the upper limit can be set equal to infinity with negligible error):

$$S_{S} - S_{N} = \frac{2\Delta^{2}N_{0}}{\beta_{c}} \int_{0}^{\infty} d\omega \left[ \ln(1 + e^{-\beta_{c}\omega}) + \frac{\beta_{c}\omega}{e^{\beta_{c}\omega} + 1} \right] \operatorname{Re} \frac{1}{(\omega + i\Gamma)^{2}}$$
$$= -\Delta^{2}N_{0}\kappa\beta_{c}(1 - \lambda_{c}\zeta(2, \frac{1}{2} + \lambda_{c})).$$
(5.19)

$$C_{S} - C_{N} = 12\gamma T \frac{\lfloor 1 - \lambda_{c} \zeta(2, \frac{1}{2} + \lambda_{c}) \rfloor^{2}}{\lfloor \zeta(3, \frac{1}{2} + \lambda_{c}) - \lambda_{c} \zeta(4, \frac{1}{2} + \lambda_{c}) \rfloor}, \qquad (5.20)$$

where  $\gamma = \frac{2}{3}N_0\pi^2\kappa^2$ . The jump in the specific heat at the critical temperature is given by the right-hand side of (5.20) evaluated at  $T_c$ . This jump, normalized to its value in the pure material, is plotted in Fig. 8 as a function of the reduced critical temperature.

The specific heat has been measured in the La-Gd system<sup>9,10</sup> and indeed shows a well-defined jump at the critical temperature that decreases as the concentration of Gd is increased. Unfortunately the interpretation of these measurements is clouded by the possible presence of both phases of La, and the theory may be in very good or rather poor agreement with experiment depending on the interpretation.

## VI. ELECTROMAGNETIC PROPERTIES

A basic property of a superconductor is its ability to exclude a static magnetic field from its interior-the Meissner effect. We shall show that superconductors containing paramagnetic impurities display this property for all concentrations up to the critical value  $n_c^i$  where the order parameter  $\Delta$  goes to zero. The penetration depth increases with increasing impurity concentration, rising very sharply in the gapless region. We also calculate the complex conductivity as a function of frequency, displaying explicitly the gap  $2\Omega_G$  in the excitation spectrum. We expect that most samples of these alloys will have short mean free paths so that we can assume an essentially local relation between field and current, and therefore have neglected the dependence of the response function on the wave number q. Our results will in general be in the form of integrals that must be done numerically; however, for  $T=0^{\circ}$ , we do the calculation in detail or give numerical results.

The response to a weak transverse field is most conveniently described in terms of the wave-number and frequency-dependent kernel  $K(\mathbf{q},q_0)$ :

 $j(\mathbf{q},q_0) = K(\mathbf{q},q_0)A(\mathbf{q},q_0)$ ,

where

$$\mathbf{A}(\mathbf{q},q_0)\cdot\mathbf{q}=\mathbf{0}$$
,

(6.1)

and

$$K(\mathbf{q},q_0) = K_p(\mathbf{q},q_0) - Ne^2/mc$$
.

For the existence of a Meissner effect it is sufficient to show that

$$\lim_{n\to\infty} K_p(\mathbf{q},0) < Ne^2/mc.$$

We consider the function  $K_p(\mathbf{q},\Omega_n)$  with  $\Omega_n = 2\pi n/-i\beta$ and  $n=0, \pm 1, \cdots$ . The analytic continuation of  $K(q,\Omega_n)$ , which is defined for isolated points along the imaginary frequency axis, to real frequencies will be just the temperature-dependent function  $K_p(\mathbf{q},q_0)$ . In general, K is determined by a two-particle Green's function. We shall work only in the Hartree-Fock approximation where the two-particle Green's function is a product of single-particle Green's functions:

$$K_{p}(\mathbf{q},\Omega_{n}) = i \frac{e^{2}}{m^{2}c} \sum_{\mathbf{k},\mathbf{k}'} \frac{1}{-i\beta} \\ \times \sum_{\nu} \operatorname{Tr} \langle \mathcal{G}(\mathbf{k}+\mathbf{q},\mathbf{k}',z_{\nu}) \mathcal{G}(\mathbf{k}'-\mathbf{q},\mathbf{k},z_{\nu}-\Omega_{n}) \rangle_{\mathrm{av}} \\ \times (\mathbf{k} \cdot \hat{a}) (\mathbf{k}' \cdot \hat{a}), \quad (6.2)$$

where  $z_{\nu} = (2\nu + 1)\pi/-i\beta$ ,  $\nu = 0, \pm 1, \pm 2, \cdots$ , and  $\hat{a}$  is a unit vector in the direction of A. The average of the product of G's is over the impurity distributions. The average of the product is not equal to the product of the averages; the difference can be expressed in terms of the vertex corrections. It is well known that in the case of nonmagnetic impurities, the major effect of the vertex corrections is to replace the inverse collision time  $\Gamma_2$  by the correct transport value  $\Gamma_2^{tr}$  which is defined in terms of the average of the scattering potential weighted by a factor  $(1 - \cos \alpha)$ , where  $\alpha$  is the angle between k and k'. Although we have not worked out these vertex corrections in the general case, we show in Appendix B for K(0,0) at  $T=0^{\circ}$ , that this is also the case for magnetic impurities to a very good approximation. Therefore, we will not make a distinction, in what follows, between the averaged product and the product of the averages, and will consider  $\Gamma_2$  to be an experimentally determined parameter. Alternatively, we can assume that only swave scattering from the impurities is important.

With this point of view

$$K_{p}(\mathbf{q},\Omega_{n}) = \frac{ie^{2}}{m^{2}c} \sum_{\mathbf{k}} \frac{1}{-i\beta} \\ \times \sum_{\mathbf{k}} \operatorname{Tr} \left[ \mathbf{Q}(\mathbf{k},z_{\mathbf{k}}) \mathbf{Q}(\mathbf{k}-\mathbf{q},z_{\mathbf{k}}-\Omega_{n}) \right] (\mathbf{k}\cdot\hat{d})^{2}, \quad (6.3)$$

where the Green's functions here contain the impurities, since they are determined from the set of self-consistent equations of Sec. II. Putting  $\mathbf{q} = 0$  in (6.3), carrying out the angular integration, and replacing the **k** integration by an integration over  $\epsilon_{\mathbf{k}}$ , we obtain

$$K_{p}(0,\Omega_{n}) = i \frac{Ne^{2}}{2mc} \int_{-\infty}^{\infty} d\epsilon \frac{1}{-i\beta} \times \sum_{\nu} \operatorname{Tr}[\Im(\mathbf{k}, z_{\nu})\Im(\mathbf{k}, z_{\nu} - \Omega_{n})], \quad (6.4)$$

where N is the number density of electrons. We must be careful in what follows to do the summation over  $\nu$  (or integration over  $\omega$  after we convert the sum to a contour integral), before the integration over  $\epsilon$ , since only then will the contributions far from the Fermi surface be negligible and allow us to replace k in the integral by  $k_{F}$ .<sup>11</sup>

## Zero Temperature

At  $T=0^{\circ}$ , the summation over  $\nu$  goes into an integration over  $\omega$  over a contour that follows the real  $\omega$  axis below for  $\omega < 0$  and above for  $\omega > 0$ . The continuation of  $K_p(0,\Omega_n)$  to real frequencies  $q_0$  is accomplished by just putting  $\Omega_n = q_0$ . Substituting in (6.4) for G, the trace

<sup>&</sup>lt;sup>9</sup> D. K. Finnemore, D. L. Johnson, J. L. Ostenson, F. H. Spedding, and B. J. Beauduy, Bull. Am. Phys. Soc. 9, 267 (1964). <sup>10</sup> D. K. Finnemore (private communication).

<sup>&</sup>lt;sup>11</sup> See, for example, A. A. Abrikosov, L. P. Gor'kov, and I. E Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

brings in a factor of 2 and we get

$$K_{p}(0,q_{0}) = i\frac{Ne^{2}}{mc} \int_{-\infty}^{\infty} d\epsilon \int_{C} \frac{d\omega}{2\pi} \frac{\tilde{\omega}\tilde{\omega}_{-} + \epsilon^{2} + \tilde{\Delta}\tilde{\Delta}_{-}}{(\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2})(\epsilon^{2} + \tilde{\Delta}_{-}^{2} - \tilde{\omega}_{-}^{2})}$$
$$= i\frac{Ne^{2}}{mc} \int_{-\infty}^{\infty} d\epsilon \int_{C} \frac{d\omega}{2\pi} \left\{ \frac{1}{\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2}} + \frac{\tilde{\omega}\tilde{\omega}_{-} + \tilde{\Delta}\tilde{\Delta}_{-} + \tilde{\omega}_{-}^{2} - \tilde{\Delta}_{-}^{2}}{(\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2})(\epsilon^{2} + \tilde{\Delta}_{-}^{2} - \tilde{\omega}_{-}^{2})} \right\}, \quad (6.5)$$

$$\tilde{\omega}_{-} = \omega - q_{0} + i\Gamma_{1} \frac{v_{-}}{(v_{-}^{2} - \Delta^{2})^{1/2}},$$

$$\tilde{\Delta}_{-} = \Delta + i\Gamma_{2} \frac{\Delta}{(v_{-}^{2} - \Delta^{2})^{1/2}},$$

$$v_{-} = (\tilde{\omega}_{-}/\tilde{\Delta}_{-})\Delta = u_{-}\Delta.$$
(6.6)

Now it is the first term in (6.5) that gives rise to a formal divergence and must be done in the proper order:  $\omega$  first, then  $\epsilon$ . The second term is well behaved and we can interchange the order of integration.

Consider the first term above. If we do a formal integration by parts on  $\omega$ , the integrated term behaves like  $\omega^{-1}$  and contributes nothing. The integral is, therefore,

$$\begin{split} i \int_{-\infty}^{\infty} d\epsilon \int_{C} \frac{d\omega}{2\pi} \frac{1}{\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2}} \\ &= i \int_{-\infty}^{\infty} d\epsilon \int_{C} \frac{d\omega}{2\pi} \frac{\omega}{(\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2})^{2}} \frac{\partial}{\partial \omega} (\tilde{\Delta}^{2} - \tilde{\omega}^{2}). \end{split}$$

Now this integral goes as  $\epsilon^{-4}$  for large  $\epsilon$  and thus we can interchange the order of the  $\omega$  and  $\epsilon$  integrations to get

$$\frac{i}{2\pi} \int_{C} d\omega \omega \frac{\partial}{\partial \omega} (\tilde{\Delta}^{2} - \tilde{\omega}^{2}) \frac{\pi}{2} \frac{1}{(\tilde{\Delta}^{2} - \tilde{\omega}^{2})^{3/2}}$$
$$= -\frac{i}{2} \int_{C} d\omega \omega \frac{\partial}{\partial \omega} \frac{1}{(\tilde{\Delta}^{2} - \tilde{\omega}^{2})^{1/2}}$$
$$= -\frac{i}{2} \int_{C} d\omega \frac{\partial}{\partial \omega} \frac{\omega}{(\tilde{\Delta}^{2} - \tilde{\omega}^{2})^{1/2}} + \frac{i}{2} \int_{C} d\omega \frac{1}{(\tilde{\Delta}^{2} - \tilde{\omega}^{2})^{1/2}}$$

Next, distort the contour so that it surrounds the positive real axis since there are no singularities in the lower half-plane. The first term is

$$\begin{split} &-\frac{i}{2}\int_{c}d\omega\frac{\partial}{\partial\omega}\frac{\omega}{(\tilde{\Delta}^{2}-\tilde{\omega}^{2})^{1/2}}\\ &=-\frac{i}{2}\lim_{\omega\to\infty}\left\{\left[\frac{\omega}{(\tilde{\Delta}^{2}-\tilde{\omega}^{2})^{1/2}}\right]_{\rm above}-\left[\frac{\omega}{(\tilde{\Delta}^{2}-\tilde{\omega}^{2})^{1/2}}\right]_{\rm below}\right\}\\ &=-\frac{i}{2}\lim_{\omega\to\infty}\left\{\left[\frac{i\omega}{(v^{2}-\Delta^{2})^{1/2}+i\Gamma_{2}}\right]_{\rm above}-\left[\frac{i\omega}{(v^{2}-\Delta^{2})^{1/2}+i\Gamma_{2}}\right]_{\rm below}\right\},\end{split}$$

and the square root goes into its complex conjugate as we cross the real axis, and has the limiting value  $\omega + i\Gamma$ above for large  $\omega$ . Therefore, this term just gives unity. And

$$i\!\int_{-\infty}^{\infty} d\epsilon\!\int_C \!\frac{d\omega}{2\pi} \frac{1}{\epsilon^2 \!+\! \tilde{\Delta}^2 \!-\! \tilde{\omega}^2} \!=\! 1 \!+\! \frac{i}{2}\!\int_C \!d\omega \frac{1}{(\tilde{\Delta}^2 \!-\! \tilde{\omega}^2)^{1/2}}\,.$$

The term unity just combines with the left-hand side to give the total  $K(0,q_0)$  and thus

$$K(0,q_{0}) = i\frac{Ne^{2}}{2mc} \int_{C} d\omega \left\{ \frac{1}{(\tilde{\Delta}^{2} - \tilde{\omega}^{2})^{1/2}} + \int_{-\infty}^{\infty} \frac{d\epsilon}{\pi} \frac{\tilde{\omega}\tilde{\omega}_{-} + \tilde{\Delta}\tilde{\Delta}_{-} + \tilde{\omega}_{-}^{2} - \tilde{\Delta}_{-}^{2}}{(\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2})(\epsilon^{2} + \tilde{\Delta}_{-}^{2} - \tilde{\omega}_{-}^{2})} \right\}$$
$$= -\frac{1}{2} \frac{Ne^{2}}{mc} \int_{C} d\omega \frac{1}{(v^{2} - \Delta^{2})^{1/2} + (v_{-}^{2} - \Delta^{2})^{1/2} + 2i\Gamma_{2}}}{\times \left[ 1 - \frac{vv_{-} + \Delta^{2}}{(v^{2} - \Delta^{2})^{1/2}(v_{-}^{2} - \Delta^{2})^{1/2}} \right], \quad (6.7)$$

after carrying out the integration and expressing the result in a concise form using (6.6).

We now have our result in a form with which we can calculate the penetration depth and absorption.

## Meissner Effect and Penetration Depth

We need to evaluate K(0,0). Setting  $q_0=0$  in (6.7) we get

$$K(0,0) = \frac{Ne^2}{mc} \frac{\Delta^2}{2} \int_C d\omega \frac{1}{(v^2 - \Delta^2)^{1/2} + i\Gamma_2} \frac{1}{v^2 - \Delta^2}$$
$$= \frac{Ne^2}{mc} \frac{\Delta^2}{2} \int_{-i\infty}^{i\infty} d\omega \frac{1}{(v^2 - \Delta^2)^{1/2} + i\Gamma_2} \frac{1}{v^2 - \Delta^2}, \quad (6.8)$$

where the contour has been deformed to run along the imaginary axis. Making the substitution  $\omega \rightarrow iy$  and

 $v \rightarrow ix$  in (6.8) and (6.6), Eq. (6.8) can be written as

$$K(0,0) = -\frac{Ne^2}{mc} \Delta^2 \int_0^\infty dy \frac{1}{(x^2 + \Delta^2)^{1/2} + \Gamma_2} \frac{1}{x^2 + \Delta^2}.$$

Using (6.6) to convert the integral over y to one over x,

$$dy = dx [1 - \Gamma \Delta^2 / (x^2 + \Delta^2)^{3/2}],$$

and being careful to notice that the lower limit  $x_0$  when y=0 depends on the relative size of  $\Gamma$  and  $\Delta$  and is in fact

$$x_0 = 0$$
 for  $\Gamma \leq \Delta$   
 $x_0 = (\Gamma^2 - \Delta^2)^{1/2}$  for  $\Gamma \geq \Delta$ ,

as can be easily established using (6.6), we finally obtain

$$K(0,0) = -\frac{Ne^2}{mc} \Delta^2 \int_{x_0}^{\infty} dx \frac{1}{(x^2 + \Delta^2)((x^2 + \Delta^2)^{1/2} + \Gamma_2)} \times \left[1 - \frac{\Gamma \Delta^2}{(x^2 + \Delta^2)^{3/2}}\right].$$
 (6.9)

In Appendix B we derive the result including vertex corrections which is just the above but with the factor

$$[(x^2+\Delta^2)((x^2+\Delta^2)^{1/2}+\Gamma_2)]^{-1}$$

replaced by

$$\left[(x^2+\Delta^2)((x^2+\Delta^2)^{1/2}+\Gamma_2^{\mathrm{tr}})+\Gamma^t\Delta^2\right]^{-1}.$$

One can assume that the exchange scattering is much weaker than the direct scattering, making  $\Gamma \ll \Gamma_2$ . The term in  $\Gamma^t$  above will therefore contribute negligibly to the integral and so can be dropped. The only other effect of the vertex corrections is to redefine  $\Gamma_2$ . This is the principal justification for the remarks made earlier in which we agreed to interpret  $\Gamma_2$  as an experimentally determined parameter.

The integral in Eq. (6.9) can now be done, and the result depends on both  $\Gamma$  and  $\Gamma_2$ . Since  $\Gamma < \Gamma_2$ , we need to consider three cases: (I)  $\Gamma$ ,  $\Gamma_2 < \Delta$ ; (II)  $\Gamma < \Delta$ ,  $\Gamma_2 > \Delta$ , and (III)  $\Gamma$ ,  $\Gamma_2 > \Delta$ . The results for  $K(0,0)/(Ne^2/mc)$  are:

Case I:

$$-(\eta\bar{\Gamma})^{-1}\left[1+\bar{\Gamma}(\eta\bar{\Gamma})^{-3}\right]\left[\frac{\pi}{2}-\frac{\arccos\eta\bar{\Gamma}}{(1-(\eta\bar{\Gamma})^2)^{1/2}}\right]$$
$$+\bar{\Gamma}(\eta\bar{\Gamma})^{-3}\left[\frac{2}{3}\eta^2\bar{\Gamma}^2-\frac{\pi}{4}\eta\bar{\Gamma}+1\right].$$

FIG. 9. The penetration depth at  $T=0^{\circ}$  in units of the London penetration depth, plotted as a function of  $\Gamma/\Delta^{P}(0)$ . The sharp rise occurs at about the value 0.45 where the energy gap vanishes.

Case II:

$$\left[ (\eta \bar{\Gamma})^{-1} \left[ 1 + \bar{\Gamma} (\eta \bar{\Gamma})^{-3} \right] \left[ \frac{\pi}{2} - \frac{\operatorname{arccosh} \eta \bar{\Gamma}}{((\eta \bar{\Gamma})^2 - 1)^{1/2}} \right] \right]$$

10

<u>></u>

 $\Gamma_2/\Gamma$ 

10

2 50

$$+\bar{\Gamma}(\eta\bar{\Gamma})^{-3}\left[\frac{2}{3}\eta^{2}\bar{\Gamma}^{2}-\frac{\pi}{4}\eta\bar{\Gamma}+1\right].$$
 (6.10)

Γ/Δ (0)

$$-(\eta\bar{\Gamma})^{-1} [1+\bar{\Gamma}(\eta\bar{\Gamma})^{-3}] \left\{ \frac{\pi}{2} - \frac{2(\bar{\Gamma}-1)}{(\bar{\Gamma}^{2}-1)^{1/2}} - [(\eta\bar{\Gamma})^{2}-1]^{-1/2} \right. \\ \left. \times \left( \operatorname{arccosh} \eta\bar{\Gamma} - 2 \operatorname{arctanh} \left[ \frac{(\bar{\Gamma}-1)(\eta\bar{\Gamma}-1)}{(\bar{\Gamma}+1)(\eta\bar{\Gamma}+1)} \right]^{1/2} \right) \right\} \\ \left. + (\eta\bar{\Gamma})^{-3} \left\{ (\frac{2}{3}\eta^{2}\bar{\Gamma}^{2}+1)(\bar{\Gamma}-(\bar{\Gamma}^{2}-1)^{1/2}) \right. \\ \left. (\pi - [\bar{\Gamma}-1] ) \right\} \right\}$$

 $-\frac{1}{2}\eta(\bar{\Gamma}^{2}-1)^{1/2}(\frac{2}{3}\eta-1)-\eta\bar{\Gamma}^{2}\left(\frac{\pi}{4}-\frac{\lfloor 1-1\rfloor}{(\bar{\Gamma}^{2}-1)^{1/2}}\right)\right\},$ 

where we have used the notation  $\eta = \Gamma_2/\Gamma$  and  $\overline{\Gamma} = \Gamma/\Delta$ . Note that here  $\Delta = \Delta(0, \Gamma)$ .

First of all we see that even in the gapless region,  $K \neq 0$ , and in fact it becomes zero only when  $\Gamma = \Gamma_{\rm cr}$ ; there is a Meissner effect for all values of  $\Gamma < \Gamma_{\rm cr}$ . Also we recover the nonmagnetic-impurity result of Abrikosov and Gor'kov<sup>12</sup> in the limit  $\Gamma = 0$ .

In our approximation, the penetration depth is given by

$$\lambda = [-(4\pi/c)K(0,0)]^{-1/2}.$$
 (6.11)

This quantity is plotted in Fig. 9 as a function of the parameter  $\Gamma/\Delta^P(0)$  for two different values of the parameter  $\Gamma_2/\Gamma$  which one might encounter in an actual sample of such alloys. Note that the curves are not extended to very small impurity concentrations since we would not expect (6.11) to be valid here; in this region it is necessary to calculate the **q** dependence of  $K(\mathbf{q}, \mathbf{0})$  explicitly.

<sup>&</sup>lt;sup>12</sup> A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 35, 1558 (1958) [English transl.: Soviet Phys.—JETP 8, 1090 (1959)].



FIG. 10. Contours used in evaluating the integral in Eq. (6.12): (a)  $q_0 < 2\Omega_G$ , (b)  $q_0 > 2\Omega_G$ , where  $\Omega_G$  is the impurity-concentrationdependent function  $\Omega_G(0,\Gamma)$ .

#### Absorption

We now calculate the frequency dependence of the kernel K. The real part of the complex conductivity, and therefore the absorption, is related to the imaginary part of K. Rewritten in a more symmetrical form that will facilitate further work, Eq. (6.7) becomes

$$K(0,q_{0}) = -\frac{1}{2} \frac{Ne^{2}}{mc} \int_{C} d\omega \frac{1}{(v_{+}^{2} - \Delta^{2})^{1/2} + (v_{-}^{2} - \Delta^{2})^{1/2} + i2\Gamma_{2}} \times \left[1 - \frac{(v_{+}v_{-} + \Delta^{2})}{(v_{+}^{2} - \Delta^{2})^{1/2}(v_{-}^{2} - \Delta^{2})^{1/2}}\right], \quad (6.12)$$

where  $\omega_{\pm} = \omega \pm q_0/2$ , etc. Now v has a cut along the real  $\omega$  axis from  $-\infty$  to  $-\Omega_G$  and from  $\Omega_G$  to  $\infty$ . Now  $v \to \omega + i\Gamma$  as  $\omega \to \infty + i\delta(\delta > 0)$ , and  $v \to \omega - i\Gamma$  as  $\omega \to \infty - i\delta$ , so that v goes into its complex conjugate as the cut is crossed. Using (6.6) for the case  $q_0 = 0$  it is



FIG. 11. The real part of the conductivity for q=0, at  $T=0^{\circ}$  plotted as a function of frequency for several values of the impurity concentration.  $\Delta$  is to be understood as  $\Delta(0,\Gamma)$ .

then possible to show that as the cut is crossed,

$$v \to v^{*},$$

$$(v^{2} - \Delta^{2})^{1/2} \to -[(v^{2} - \Delta^{2})^{1/2}]^{*},$$

$$(v^{2} - \Delta^{2})^{-1/2} \to -[(v^{2} - \Delta^{2})^{-1/2}]^{*},$$

$$(6.13)$$

$$\frac{v}{(v^{2} - \Delta^{2})^{1/2}} \to -\left[\frac{v}{(v^{2} - \Delta^{2})^{1/2}}\right]^{*}.$$

Let us write  $A_{\pm} = v_{\pm}/(v_{\pm}^2 - \Delta^2)^{1/2}$ ,  $B_{\pm} = \Delta/(v_{\pm}^2 - \Delta^2)^{1/2}$ ,  $C_{\pm} = (v_{\pm}^2 - \Delta^2)^{1/2}$ . Then (6.12) becomes

$$K(0,q_0) = -\frac{1}{2} \frac{Ne^2}{mc} \int_C d\omega \frac{1 - A_+ A_- - B_+ B_-}{C_- + C_+ + i2\Gamma_2}$$

It is convenient to give  $q_0$  a small imaginary part so as to separate the cuts for  $v_+$  and  $v_-$ .

For the case  $q_0 < 2\Omega_G$ , the contour is shown in Fig. 10(a). Over the interval  $\Omega_G - q_0/2$  to  $\Omega_G + q_0/2$ , we have  $A_- \rightarrow (1/i)\tilde{A}_-, B_- \rightarrow (1/i)\tilde{B}_-, C_- \rightarrow i\tilde{C}_-$ , where, for example,  $\tilde{C}_- = (\Delta^2 - v_-^2)^{1/2}$ , and because  $v_-$  is real in this interval, the quantities  $\tilde{A}_-, \tilde{B}_-$ , and  $\tilde{C}_-$  are all real. Then

$$K(0,q_{0}) = -\frac{Ne^{2}}{mc} \int_{\Omega_{G}+q_{0}/2}^{\infty} d\omega \operatorname{Re}\left\{\frac{1-A_{+}A_{-}-B_{+}B_{-}}{C_{-}+C_{+}+i2\Gamma_{2}}\right\} -\frac{Ne^{2}}{mc} \int_{\Omega_{G}-q_{0}/2}^{\Omega_{G}+q_{0}/2} d\omega \operatorname{Re}\left\{\frac{1-(1/i)\widetilde{A}_{-}A_{+}-(1/i)\widetilde{B}_{-}B_{+}}{i\widetilde{C}_{-}+C_{+}+i2\Gamma_{2}}\right\}.$$
(6.14)

We immediately have that  $\text{Im}K(0,q_0)$  and therefore  $\text{Re}\sigma(0,q_0)$  is zero for  $q_0 < 2\Omega_G$ .  $2\Omega_G$  again plays the role of a gap in the excitation spectrum—there is no absorption of electromagnetic radiation until enough energy is supplied to cause a transition into states above the gap.

When  $q_0 > 2\Omega_G$ , the contour is that shown in Fig. 10(b). Incidentally, this is also the case to consider in the gapless region of impurity concentrations. Then

$$K(0,q_{0}) = -\frac{Ne^{2}}{mc} \int_{\Omega g + q_{0}/2}^{\infty} d\omega \operatorname{Re} \left\{ \frac{1 - A_{+}A_{-} - B_{+}B_{-}}{C_{-} + C_{+} + i2\Gamma_{2}} \right\} - \frac{Ne^{2}}{mc} \int_{-\Omega g + q_{0}/2}^{\Omega g + q_{0}/2} d\omega \operatorname{Re} \left\{ \frac{1 - (1/i)\tilde{A}_{-}A_{+} - (1/i)\tilde{B}_{-}B_{+}}{i\tilde{C}_{-} + C_{+} + i2\Gamma_{2}} \right\} - \frac{Ne^{2}}{mc} \frac{1}{2} \int_{\Omega g - q_{0}/2}^{-\Omega g + q_{0}/2} d\omega \left\{ \frac{1 + A_{+}A_{-}^{*} + B_{+}B_{-}^{*}}{-C_{-}^{*} + C_{+} + i2\Gamma_{2}} - \frac{1 - A_{+}^{*}A_{-}^{*} - B_{+}^{*}B_{-}^{*}}{-C_{-}^{*} - C_{+}^{*} + i2\Gamma_{2}} \right\}.$$
 (6.15)

The last term is complex so that there is a contribution to  $\text{Im}K(0,q_0)$  for  $q_0 > 2\Omega_G$ . We shall be interested only in the real part of the complex conductivity

$$\operatorname{Re}\sigma(0,q_0) + i \operatorname{Im}\sigma(0,q_0) = (c/iq_0)K(0,q_0).$$

Furthermore, for values of  $q_0$  that are not too large  $[q_0\tau\ll 1]$ , where  $\tau$  is essentially  $(2\Gamma_2)^{-1}$  with the reservation noted previously concerning vertex corrections], we can neglect all terms in the denominator of the third term above compared to  $\Gamma_2$ . Then

$$\operatorname{Im}K(0,q_{0}) = \frac{1}{4} \frac{Ne^{2}}{mc\Gamma_{2}} \int_{\Omega_{G}-q_{0}/2}^{-\Omega_{G}+q_{0}/2} d\omega \operatorname{Re}\{A_{+}A_{-}*+A_{+}*A_{-}*+B_{+}B_{-}*+B_{+}*B_{-}*\}$$
$$= \frac{\sigma_{N}}{c} \int_{\Omega_{G}-q_{0}/2}^{-\Omega_{G}+q_{0}/2} d\omega \left\{ \operatorname{Re}\frac{v_{+}}{(v_{+}^{2}-\Delta^{2})^{1/2}} \operatorname{Re}\frac{v_{-}}{(v_{-}^{2}-\Delta^{2})^{1/2}} + \operatorname{Re}\frac{\Delta}{(v_{+}^{2}-\Delta^{2})^{1/2}} \operatorname{Re}\frac{\Delta}{(v_{+}^{2}-\Delta^{2})^{1/2}} \right\},$$

where we have used  $\Gamma_2 = (2\tau)^{-1}$  and  $\sigma_N \approx N e^2 \tau / m$ . Finally,

$$\frac{\operatorname{Re}\sigma(0,q_0)}{\sigma_N} = \frac{1}{q_0} \int_{\Omega_G - q_0/2}^{-\Omega_G + q_0/2} d\omega \{ n(\omega + q_0/2)n(\omega - q_0/2) + m(\omega + q_0/2)m(\omega - q_0/2) \},$$
(6.16)

for  $q_0 > 2\Omega_{\sigma}$  and zero otherwise, and  $n(\omega) = \operatorname{Rev}/(v^2 - \Delta^2)^{1/2}$  and  $m(\omega) = \operatorname{Re\Delta}/(v^2 - \Delta^2)^{1/2}$ . These functions are just the density-of-states function and the kernel of the integral equation for  $\Delta$ , respectively. Notice that  $n(\omega)$  is an even function and  $m(\omega)$  an odd function of  $\omega$ , and therefore the two terms above come in with opposite signs since the range of integration is over negative arguments. However,  $n(\omega) > m(\omega)$  so that the result is positive. For the case of nonmagnetic impurities,  $\Gamma=0$ , and (6.16) reduces to the result of Abrikosov and Gor'kov<sup>12</sup> and Mattis and Bardeen.<sup>13</sup> Note that the ratio  $\operatorname{Re}\sigma_s/\sigma_N$  has the same form in both the dirty limit  $\ell \ll \xi$  of Abrikosov and Gor'kov and the extreme anomalous limit of Mattis and Bardeen. This comes about because in both cases we can approximate the kernel  $I(\omega, R, T)$  of Mattis and Bardeen by  $I(\omega, 0, T)$ .

Equation (6.16) is plotted in Fig. 11 for different impurity concentrations. In the gapless region, the conductivity is proportional to the square of the density of states as  $q_0 \rightarrow 0$ .

## Nonzero Temperature

For temperatures greater than zero it is convenient to write Eq. (6.4) in terms of an integral over  $\omega$  following a contour that encircles the imaginary axis in the positive sense. Then Eq. (6.4) becomes, after substitution for G,

$$K_{p}(0,\Omega_{n}) = -i\frac{Ne^{2}}{mc} \int_{-\infty}^{\infty} d\epsilon \int_{C'} \frac{d\omega}{2\pi} f(\omega) \left\{ \frac{1}{\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2}} + \frac{\tilde{\omega}\tilde{\omega}_{-} + \tilde{\Delta}\tilde{\omega}_{-} + \tilde{\omega}_{-}^{2} - \tilde{\omega}_{-}^{2}}{(\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2})(\epsilon^{2} + \tilde{\Delta}_{-}^{2} - \tilde{\omega}_{-}^{2})} \right\},$$
(6.17)

where  $\tilde{\omega}_{-}$  and  $\tilde{\Delta}_{-}$  are defined as in (6.6) but with  $\Omega_n$  replacing  $q_0$  and,  $f(\omega)$  is the Fermi function. We must handle the formally divergent first term above by first doing an integration by parts over  $\omega$ . Proceeding in the same way as in the  $T=0^{\circ}$  case, the first term becomes

$$\frac{Ne^2}{mc} \left\{ \frac{i}{2} \int_{C'} d\omega \frac{\partial}{\partial \omega} \left[ \frac{\omega f(\omega)}{(\tilde{\Delta}^2 - \tilde{\omega}^2)^{1/2}} \right] - \frac{i}{2} \int_{C'} d\omega \frac{f(\omega)}{(\tilde{\Delta}^2 - \tilde{\omega}^2)^{1/2}} \right\}$$

On distorting the contour in the first term so as to surround the real  $\omega$  axis from  $\Omega_G$  to  $\infty$  and from  $-\Omega_G$  to  $-\infty$ , and using the properties of  $(v^2 - \Delta^2)^{1/2}$  as one crosses the cut and  $f(-\omega) = 1 - f(\omega)$ , the terms containing the Fermi function give zero and the remainder is just  $Ne^2/mc$ . Again, this combines with  $K_p$  on the left-hand side to give K, and the result is

$$K(0,\Omega_{n}) = -i\frac{Ne^{2}}{mc} \int_{C'} \frac{d\omega}{2\pi} f(\omega) \left\{ \frac{\pi}{(\tilde{\Delta}^{2} - \tilde{\omega}^{2})^{1/2}} + \int_{-\infty}^{\infty} d\epsilon \frac{\tilde{\omega}\tilde{\omega}_{-} + \tilde{\Delta}\tilde{\Delta}_{-} + \tilde{\omega}_{-}^{2} - \tilde{\Delta}_{-}^{2}}{(\epsilon^{2} + \tilde{\Delta}^{2} - \tilde{\omega}^{2})(\epsilon^{2} + \tilde{\Delta}_{-}^{2} - \tilde{\omega}_{-}^{2})} \right\}$$
$$= \frac{1}{2} \frac{Ne^{2}}{mc} \int_{C'} d\omega f(\omega) \frac{1}{(v^{2} - \Delta^{2})^{1/2} + (v_{-}^{2} - \Delta^{2})^{1/2} + i2\Gamma_{2}} \left[ 1 - \frac{vv_{-} + \Delta^{2}}{(v^{2} - \Delta^{2})^{1/2}(v_{-}^{2} - \Delta^{2})^{1/2}} \right].$$
(6.18)

<sup>13</sup> D. C. Mattis and J. Bardeen, Phys. Rev. 111, 412 (1958).

Before going on to calculate the frequency- and temperature-dependent conductivity, we derive an expression for the temperature-dependent penetration depth. Putting  $\Omega_n = 0$  in (6.18) and deforming the contour to encircle the real axis from  $\Omega_G$  to  $\infty$  and from  $-\Omega_G$  to  $-\infty$ , we obtain

$$K(0,0) = \frac{1}{2} \frac{Ne^2}{mc} \int d\omega f(\omega) \frac{1}{(v^2 - \Delta^2)^{1/2} + i\Gamma_2} \left[ 1 - \frac{v^2}{v^2 - \Delta^2} \right]$$
$$= \frac{1}{2} \frac{Ne^2}{mc} \int d\omega f(\omega) \frac{1}{C + i\Gamma_2} [1 - A^2].$$
(6.19)

Using the properties of v and  $(v^2 - \Delta^2)^{1/2}$  as the cut is crossed, this can be written as

$$K(0,0) = -\frac{1}{2} \frac{Ne^2}{mc} \int_{\Omega_G}^{\infty} d\omega (1 - 2f(\omega)) \left[ \frac{1 - A^2}{C + i\Gamma_2} - \frac{1 - (A^*)^2}{-C^* + i\Gamma_2} \right]$$
$$= -\frac{Ne^2}{mc} \int_{\Omega_G}^{\infty} d\omega \tanh \frac{1}{2} \beta \omega \operatorname{Re} \left\{ \frac{-\Delta^2}{(v^2 - \Delta^2)((v^2 - \Delta^2)^{1/2} + i\Gamma_2)} \right\}.$$
(6.20)

We can evaluate this integral in the limit of temperatures close to the transition temperature as was done earlier with the free energy. That is, we retain only the leading term in  $\Delta^2$ . Since K is already proportional to  $\Delta^2$ , the remainder of the integral can be evaluated at  $\Delta=0$ ,  $T=T_c$ .

$$K(0,0) = \frac{Ne^2}{mc} \Delta^2 \int_0^\infty d\omega \tanh \frac{1}{2} \beta_c \omega \operatorname{Re} \left[ \frac{1}{(\omega + i\Gamma)^2 (\omega + i\Gamma_1)} \right],$$

with  $\Gamma_1 = \Gamma + \Gamma_2$ . The result is

$$K(0,0) = -\frac{Ne^2}{mc} \frac{\beta_c^2 \Delta^2}{4\pi^2} \sum_{n=0}^{\infty} \left[ \left( n + \frac{1}{2} + \frac{\Gamma_1 \beta_c}{2\pi} \right) \left( n + \frac{1}{2} + \frac{\Gamma_2 \beta_c}{2\pi} \right)^2 \right]^{-1}.$$

In the limit of large  $\Gamma_1$  (short mean free path), we can neglect  $n+\frac{1}{2}$  compared to  $\Gamma_1\beta_c/2\pi$  in the denominator and then

$$K(0,0) = -\frac{Ne^2}{mc} \frac{\Delta^2 \beta_c}{2\pi \Gamma_1} \zeta \left(2, \frac{1}{2} + \frac{\Gamma \beta_c}{2\pi}\right)$$
$$= -\frac{\sigma_N \beta_c}{\pi c} \Delta^2 \zeta \left(2, \frac{1}{2} + \frac{\Gamma \beta_c}{2\pi}\right), \qquad (6.21)$$

with  $2\Gamma_1 \approx (\tau)^{-1}$  and  $\beta_c$  and  $\Delta$  are the values in the presence of the magnetic impurities. The penetration depth follows from Eq. (6.11). It reduces to the usual result for  $\Gamma = 0$ . In the extreme gapless limit,  $\Gamma\beta_c \gg 1$ , (6.21) reduces to

$$K(0,0) = -(4\pi^{2}/c\Gamma)\sigma_{N}\kappa^{2}(T_{c}^{2} - T^{2})$$

$$\lambda = \frac{c}{4\pi\kappa T_{c}} \left[ \frac{\pi\sigma_{N}}{\Gamma} \left( 1 - \frac{T^{2}}{T_{c}^{2}} \right) \right]^{-1/2},$$
(6.22)

and the penetration depth is

the result obtained previously in AG. Note that this relation is true for all temperatures provided  $\Gamma\beta_c \gg 1$  because then  $T_c$  itself is small. Unfortunately, as remarked earlier, the condition  $\Gamma\beta_c \gg 1$  is not satisfied except over an extremely limited range of impurity concentrations close to the critical value.

To conclude this section, we simply state the results for the temperature-dependent kernel  $K(0,q_0)$ ; the conductivity follows from  $\sigma(0,q_0) = (c/iq_0)K(0,q_0)$ . The details of the calculation are given in Appendix C. For positive

 $q_0$ , in our usual notation,

$$K(0,q_{0}) = \frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}}^{\infty} d\omega \frac{1 + AA_{+}^{*} + BB_{+}^{*}}{-C_{+}^{*} + C + i2\Gamma_{2}} \{ \tanh^{\frac{1}{2}}\beta(\omega + q_{0}) - \tanh^{\frac{1}{2}}\beta\omega \}$$

$$-\frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}}^{\infty} d\omega \left\{ \left[ \frac{1 - AA_{+} - BB_{+}}{C + C_{+} + i2\Gamma_{2}} \right] \tanh^{\frac{1}{2}}\beta(\omega + q_{0}) + \left[ \frac{1 - AA_{+} - BB_{+}}{C + C_{+} + i2\Gamma_{2}} \right]^{*} \tanh^{\frac{1}{2}}\beta\omega \right\}$$

$$-\frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}-q_{0},-\Omega_{G}}^{\Omega_{G}} d\omega 2 \operatorname{Re} \left\{ \frac{1 - (1/i)\tilde{A}A_{+} - (1/i)\tilde{B}B_{+}}{i\tilde{C} + C_{+} + i2\Gamma_{2}} \right\} \tanh^{\frac{1}{2}}\beta(\omega + q_{0})$$

$$-\frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}-q_{0}}^{\Omega_{G}} d\omega \left\{ \frac{1 + A^{*}A_{+} + B^{*}B_{+}}{-C^{*} + C_{+} + i2\Gamma_{2}} - \frac{1 - A^{*}A_{+}^{*} - B^{*}B_{+}^{*}}{-C^{*} - C_{+}^{*} + i2\Gamma_{2}} \right\} \tanh^{\frac{1}{2}}\beta(\omega + q_{0}), \qquad (6.23)$$

where the lower limit on the third term is  $\Omega_G - q_0$  for  $q_0 < 2\Omega_G$ , and  $-\Omega_G$  for  $q_0 > 2\Omega_G$ , and the fourth term appears only for  $q_0 > 2\Omega_G$ . Note that in contrast to the case at  $T=0^\circ$ , the first two terms have an imaginary part even for  $q_0 < 2\Omega_G$ . Therefore there will be absorption even in the gap when  $T > 0^\circ$ , This is just the contribution from the thermal excitations across the gap which are not present at  $T=0^{\circ}$ . The integrals themselves must be done numerically. We remark that  $\Omega_{G}$  is the impurity-concentration and temperature-dependent function  $\Omega_{G}(T,\Gamma)$ .

## VII. CONCLUSIONS

These detailed calculations show clearly that the essential feature of superconductivity is the correlation of the electrons rather than the existence of a gap in the excitation energy spectrum. For even in the absence of a gap, so long as correlations persist there is an ordered state below a certain critical temperature which displays the usual properties of a superconductor. We have not discussed persistent currents, although this can be done without difficulty with the use of the sum rule for the conductivity. This shows that such currents are possible in spite of the absence of a gap, but we leave this for a later report.

#### APPENDIX A

In this appendix we derive Eq. (5.1) for the total energy. The Hamiltonian is

$$3C = -\frac{1}{2m} \sum_{\sigma} \int d^{3}r \psi_{\sigma}^{\dagger}(x) \nabla^{2} \psi_{\sigma}(x) - \frac{1}{2} V \sum_{\sigma} \int d^{3}r \psi_{\sigma}^{\dagger}(x) \psi_{-\sigma}^{\dagger}(x) \psi_{-\sigma}(x) \psi_{\sigma}(x) + \sum_{\sigma} \sum_{i} \int d^{3}r v_{1}(\mathbf{r} - \mathbf{R}_{i}) \psi_{\sigma}^{\dagger}(x) \psi_{\sigma}(x) + \sum_{i} \int d^{3}r v_{2}(\mathbf{r} - \mathbf{R}_{i}) \{S_{i}^{-} \psi_{\uparrow}^{\dagger}(x) \psi_{\downarrow}(x) + S_{i}^{+} \psi_{\downarrow}^{\dagger}(x) \psi_{\uparrow}(x) + S_{i}^{z} (\psi_{\uparrow}^{\dagger}(x) \psi_{\downarrow}(x) - \psi_{\downarrow}^{\dagger}(x) \psi_{\downarrow}(x))\}$$

$$= 3C_{K} + 3C_{V} + 3C_{1} + 3C_{2}, \qquad (A1)$$

 $=3C_K+3C_V+3C_1+3C_2$ 

where  $x = (\mathbf{r}, t)$ ,  $S_i^{\pm} = S^x(\mathbf{R}_i) \pm iS^y(\mathbf{R}_i)$  are the impurity spins and we have assumed a local superconducting interaction of strength (-V). The equation of motion for the operators  $\psi_{\uparrow}(x)$  and  $\psi_{\uparrow}^{\dagger}(x)$  are

$$\left(i\frac{\partial}{\partial t} + \frac{\nabla^2}{2m} - V_1(\mathbf{r})\right) \psi_{\dagger}(x) = \left[\psi_{\dagger}(x), 3\mathcal{C}_V\right] + \sum_i v_2(\mathbf{r} - \mathbf{R}_i) \left(S_i - \psi_{\dagger}(x) + S_i \psi_{\dagger}(x)\right),$$
(A2)

$$\left(-i\frac{\partial}{\partial t'}+\frac{\nabla'^2}{2m}-V_1(\mathbf{r}')\right)\psi_{\dagger}^{\dagger}(x') = \left[\psi_{\dagger}^{\dagger}(x')\ \Im \mathcal{C}_{V}\right] + \sum_{i} v_2(\mathbf{r}-\mathbf{R}_i)(-S_i^{\dagger}\psi_{\dagger}^{\dagger}(x')-S_i^{z}\psi_{\dagger}^{\dagger}(x')),$$
(A3)

with a corresponding pair of equations for  $\psi_{\dagger}(x)$  and  $\psi_{\dagger}^{\dagger}(x)$ , and where  $V_1(\mathbf{r}) = \sum_i v_1(\mathbf{r}-R_i)$ . Now multiplying through (A2) on the left by  $\psi_{\uparrow}^{\dagger}(x')$  and (A3) on the right by  $\psi_{\uparrow}(x)$ , integrating over **r** or **r'** and similarly for the spin-down equations, and adding all four equations together setting x = x' at the end, we get

$$\int d^3r \left\{ \left( \frac{\partial}{\partial t} - i \frac{\partial}{\partial t'} \right) (\psi_{\dagger}^{\dagger}(x') \psi_{\dagger}(x)) + \left( \frac{\partial}{\partial t} - i \frac{\partial}{\partial t'} \right) (\psi_{\downarrow}^{\dagger}(x') \psi_{\downarrow}(x)) \right\}_{x=x'} = 25 \mathcal{C}_K + 23 \mathcal{C}_1 + 25 \mathcal{C}_2 + 45 \mathcal{C}_V.$$

Carrying out the average over the impurity distributions, and the ensemble average, this becomes

$$2i \int d^3r \left\{ \left( i \frac{\partial}{\partial t} - i \frac{\partial}{\partial t'} \right) g_{11} < (x - x') \right\}_{x = x'} = 2 \langle \mathfrak{IC} \rangle + 2 \langle \mathfrak{IC}_V \rangle,$$

where  $G_{11} \leq (x - x') = -i \langle \psi_{\uparrow}^{\dagger}(x') \psi_{\uparrow}(x) \rangle$ , and  $\langle \mathfrak{IC} \rangle = E_s$  is the total energy. Furthermore,  $\langle \mathfrak{IC} \rangle_V$  is  $-\Delta^2/V$ , so that

$$E_{S} - \frac{\Delta^{2}}{V} = i \int d^{3}r \left\{ \left( i \frac{\partial}{\partial t} - i \frac{\partial}{\partial t'} \right) g_{11} < (x - x') \right\}_{x = x'}.$$
 (A4)

Introducing the Fourier transform

$$g_{11}(x-x') = \sum_{k} \frac{1}{-i\beta} \sum_{\nu} g_{11}(\mathbf{k}, z_{\nu}) e^{-iz_{\nu}(t-t')+i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')},$$
$$E_{S} - \frac{\Delta^{2}}{V} = -\frac{2}{\beta} \sum_{k} \sum_{\nu} z_{\nu} g_{11}(\mathbf{k}, z_{\nu}) e^{-iz_{\nu}0^{-}},$$

we get

where  $z_{\nu} = (2\nu+1)\pi/-i\beta$ ,  $\nu=0, \pm 1, \cdots$ . Converting the sum over  $\nu$  to an integral over a contour enclosing the imaginary  $\omega$  axis in the positive sense we have

$$E_{s} - \frac{\Delta^{2}}{V} = -2i \sum_{\mathbf{k}} \int_{C} \frac{d\omega}{2\pi} \omega \mathcal{G}_{11}(\mathbf{k}, \omega) f(\omega) e^{\omega 0^{+}},$$

and  $f(\omega) = (e^{\beta\omega} + 1)^{-1}$ . Using the fact that G is analytic except for a cut along the real axis from  $-\infty$  to  $-\Omega_{q}$  and from  $\Omega_{q}$  to  $\infty$ , and the fact that ImG changes sign as we cross the cut, the contour can be converted to one surrounding the real axis to get

$$E_{S} - \frac{\Delta^{2}}{V} = 4 \sum_{\mathbf{k}} \left\{ \int_{\Omega_{G}}^{\infty} + \int_{-\Omega_{G}}^{-\infty} \right\} \frac{d\omega}{2\pi} \omega \operatorname{Im} \mathcal{G}_{11}(\mathbf{k}, \omega) f(\omega) e^{\omega 0^{+}}.$$
(A5)

Putting  $\omega \to -\omega$  in the second integral and dropping the  $e^{\omega 0^+}$  (which merely assured convergence) we get Eq. (5.1).

#### APPENDIX B

We derive an expression for K(0,0) including vertex corrections at  $T=0^{\circ}$ . The major contribution will come from the ladder diagrams and we consider only these. In this approximation, the equation for the vertex part is

$$\Lambda_{\rho}(\mathbf{k},\omega) = \tau_0 k_{\rho} + \sum_{\mathbf{k}'} \langle \mathfrak{U}(\mathbf{k}-\mathbf{k}') \mathfrak{G}(\mathbf{k}',\omega) \Lambda_{\rho}(\mathbf{k}',\omega) \mathfrak{G}(\mathbf{k}',\omega) \mathfrak{U}(\mathbf{k}'-\mathbf{k}) \rangle_{\mathrm{av}}, \qquad (B1)$$

where  $\rho = x, y, z$ , and the average is over the impurity distributions. The interaction matrix  $\mathfrak{U}(\mathbf{k}-\mathbf{k}')$  will have the following form

$$\mathfrak{U}(\mathbf{k}-\mathbf{k}') = \sum_{i} \left[ v_1(\mathbf{k}-\mathbf{k}')\tau_3 + v_2(\mathbf{k}-\mathbf{k}')\mathbf{S}_i \cdot \mathbf{s}\tau_0 \right] e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_i}.$$
(B2)

Now it is not at all obvious that the exchange interaction term will just be proportional to  $\tau_0$ . In general it will not be. However, for the particular case we are considering  $(q=0, q_0=0)$ , a more detailed calculation (which is faciliated by using the Éliashberg<sup>14</sup> four-component spinor notation) shows that the spin-dependent effects can be represented in the above form.

Now the vector  $\Lambda_{\rho}$  must be directed along **k**; therefore, on introducing the function

 $k_{\rho}\phi(\omega) = \sum_{\mathbf{k}'} \langle \mathfrak{U}(\mathbf{k} - \mathbf{k}') \mathfrak{G}(\mathbf{k}', \omega) \Lambda_{\rho}(\mathbf{k}', \omega) \mathfrak{G}(\mathbf{k}', \omega) \mathfrak{U}(\mathbf{k}' - \mathbf{k}) \rangle_{\mathrm{av}},$ 

the equation satisfied by  $\phi(\omega)$  is

$$k_{\rho}\phi(\omega) = \sum_{\mathbf{k}'} \langle \mathfrak{U}(\mathbf{k} - \mathbf{k}') \mathfrak{g}(\mathbf{k}', \omega) k_{\rho}'(\tau_0 + \phi(\omega)) \mathfrak{g}(\mathbf{k}', \omega) \mathfrak{U}(\mathbf{k}' - \mathbf{k}) \rangle_{\mathrm{av}}.$$
(B3)

Using the assumption that  $\mathfrak{U}(\mathbf{k}-\mathbf{k}')$  is essentially independent of the magnitudes of  $\mathbf{k}$  and  $\mathbf{k}'$ , and carrying out the average over impurities we get

$$\phi(\omega) = n^{i} \sum_{k'} |v_{1}(\alpha)|^{2} \cos\alpha\tau_{3} \Im(\mathbf{k}', \omega) (\tau_{0} + \phi(\omega)) \Im(\mathbf{k}', \omega) \tau_{3} + n^{i} \frac{\Im(\Im + 1)}{4} \sum_{k'} |v_{2}(\alpha)|^{2} \cos\alpha\Im(\mathbf{k}', \omega) (\tau_{0} + \phi(\omega)) \Im(\mathbf{k}', \omega),$$
(B4)

<sup>14</sup> G. M. Éliashberg, Zh. Eksperim. i Teor. Fiz. 38, 966 (1960) [English transl.: Soviet Phys.-JETP 11, 696 (1960)].

where  $k_{F^2} \cos \alpha = \mathbf{k} \cdot \mathbf{k}'$ . Making the ansatz  $\phi(\omega) = \gamma(\omega)\tau_0 + \delta(\omega)\tau_1 + \mu(\omega)\tau_1$  and doing the integration over  $\epsilon_{\mathbf{k}'}$ , it is easy to show that  $\delta(\omega) = 0$  and we get coupled equations for  $\gamma(\omega)$  and  $\mu(\omega)$  whose solutions are

$$1+\gamma(\omega) = 1 + \frac{\Gamma_1{}^t}{\tilde{\Delta}(1-u^2)^{3/2} + \Gamma_2{}^t u^2 - \Gamma_1{}^t}, \quad \mu(\omega) = \frac{-\Gamma_2{}^t u}{\tilde{\Delta}(1-u^2)^{3/2} + \Gamma_2{}^t u^2 - \Gamma_1{}^t}, \tag{B5}$$

where  $\Gamma_1{}^t$ , and  $\Gamma_2{}^t$  are defined exactly as  $\Gamma_1$  and  $\Gamma_2$  were except that the angular average is weighted by a factor  $\cos \alpha$ . Now

$$K_{p}(0,0) = \frac{ie^{2}}{m^{2}c} \sum_{\mathbf{k}} \int_{C} \frac{d\omega}{2\pi} \operatorname{Tr}[\mathcal{G}(\mathbf{k},\omega)(\tau_{0}+\phi(\omega))\mathcal{G}(\mathbf{k},\omega)](\mathbf{k}\cdot\hat{\alpha})^{2}.$$

Substituting for  $\phi(\omega)$  and G and carrying out first a partial integration over  $\omega$  and then the integration over  $\epsilon_k$  just as in the body of the text, we get an expression for K(0,0):

$$K(0,0) = \frac{Ne^2}{mc} \frac{\Delta^2}{2} \int_{c} d\omega \frac{1}{(v^2 - \Delta^2) [(v^2 - \Delta^2)^{1/2} + i\Gamma_2 tr] + i\Gamma' \Delta^2},$$
 (B6)

where  $\Gamma_2^{\text{tr}}$  is defined in terms of the angular average weighted by the factor  $(1 - \cos \alpha)$ . We see comparing Eq. (6.8), that the effect of the ladder diagrams is to change  $\Gamma_2$  to  $\Gamma_2^{\text{tr}}$  and to add the factor  $i\Gamma^t\Delta^2$  in the denominator.

## APPENDIX C

The contour in Eq. (6.18) can be deformed to that shown in Fig. 12, where the cuts for v and  $v_{-}$  are displaced by the purely imaginary "frequency"  $\Omega_n$ . The function  $K(0,q_0)$ , extended to all values of the complex frequency  $q_0$ , will have singularities, since the contours  $C_2$  and  $C_4$  can pass through the points  $\omega = (2n+1)\pi/-i\beta$  where the function  $f(\omega)$  becomes infinite. Therefore, to continue the function  $K(0,\Omega_n)$  analytically, we must avoid these singularities. This is accomplished by noting that  $f(\omega) = f(\omega \pm 2n\pi/(-i\beta))$ , so that by using the transformation  $\omega - \Omega_n \rightarrow -\omega'$ , the integral over  $C_2$  combines with the integral over  $C_1$ , and similarly for the contours  $C_3$  and  $C_4$ , For example,

$$C_{2} = \frac{1}{2} \frac{Ne^{2}}{mc} \int_{-\Omega_{G} + \Omega_{n}}^{-\infty + \Omega_{n}} d\omega \left\{ \frac{1 - AA_{-} - BB_{-}}{C + C_{-} + i2\Gamma_{2}} - \frac{1 + AA_{-}^{*} + BB_{-}^{*}}{C - C_{-}^{*} + i2\Gamma_{2}} \right\} f(\omega)$$

$$\equiv \frac{1}{2} \frac{Ne^{2}}{mc} \int_{-\Omega_{G} + \Omega_{n}}^{-\infty + \Omega_{n}} d\omega f(\omega) \{ h(A, A_{-}, B, B_{-}, C, C_{-}) - h(A, -A_{-}^{*}, B, -B_{-}^{*}, C, C_{-}^{*}) \}$$

$$= \frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}}^{\infty} d\omega' (1 - f(\omega')) \{ -h(-A_{-}, -A, B_{-}, B, C_{-}, C) + h(-A_{-}, A^{*}, B_{-}, -B^{*}, C_{-}, -C^{*}) \}, \quad (C1)$$

where we have used the fact that  $v \to -v_{-}$  and  $v_{-} \to -v$  as  $\omega - \Omega_n \to -\omega'$ , and  $f(-\omega' + \Omega_n) = f(-\omega') = 1 - f(\omega')$ . But

$$C_{1} = \frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}}^{\infty} d\omega' \{h(A, A_{-}, B, B_{-}, C, C_{-}) - h(-A^{*}, A_{-}, -B^{*}, B_{-}, -C^{*}, C_{-})\} f(\omega').$$
(C2)





FIG. 12. The contour used in evaluating the integral in Eq. (6.18).  $\Omega_G$  means  $\Omega_G(T,\Gamma)$ .

FIG. 13. Contours used in evaluating the temperature-dependent function  $K(0,q_0)$ : (a)  $q_0 < 2\Omega_G$ , (b)  $q_0 > 2\Omega_G$ , where  $\Omega_G$  means  $\Omega_G(T,\Gamma)$ .

Therefore, Eqs. (C1) and (C2) can be combined to give a single integral over the contour  $C_1$ . In exactly the same way, the integral over  $C_4$  combines with the integral over  $C_3$  to give a single integral over the contour  $C_3$ . After substituting back for A, B, C in terms of v, etc., the result for the function  $K(0,q_0)$  analytically continued for all  $q_0$  is

$$K(0,q_0) = -\frac{1}{2} \frac{Ne^2}{mc} \int_{C_1+C_3} d\omega \tanh \frac{1}{2} \beta \omega \frac{1}{(v^2 - \Delta^2)^{1/2} + (v_-^2 - \Delta^2)^{1/2} + i2\Gamma_2} \left[ 1 - \frac{vv_- + \Delta^2}{(v^2 - \Delta^2)^{1/2} (v_-^2 - \Delta^2)^{1/2}} \right].$$
(C3)

Consider  $q_0$  real and positive. As at  $T=0^\circ$ , two cases arise,  $q_0 < 2\Omega_G$  and,  $q_0 > 2\Omega_G$ , because in following the contour, different values for the phase of v and  $(v^2 - \Delta^2)^{1/2}$  will come in for the two possibilities. (See Fig. 13.) For  $q_0 < 2\Omega_G$ ,

$$K(0,q_{0}) = -\frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}+q_{0}}^{\infty} d\omega' \tanh^{\frac{1}{2}}_{2} \beta\omega' \left\{ \frac{1-AA_{-}-BB_{-}}{C+C_{-}+i2\Gamma_{2}} - \frac{1+A^{*}A_{-}+B^{*}B_{-}}{-C^{*}+C_{-}+i2\Gamma_{2}} \right\} \\ -\frac{1}{2} \frac{Ne^{2}}{mc} \int_{-\Omega_{G}}^{-\infty} d\omega' \tanh^{\frac{1}{2}}_{2} \beta\omega' \left\{ \frac{1+AA_{-}^{*}+BB_{-}^{*}}{C-C_{-}^{*}+i2\Gamma_{2}} - \frac{1-A^{*}A_{-}^{*}-B^{*}B_{-}^{*}}{-C^{*}-C_{-}^{*}+i2\Gamma_{2}} \right\} \\ -\frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}}^{\Omega_{G}+q_{0}} d\omega' \tanh^{\frac{1}{2}}_{2} \beta\omega' \left\{ \frac{1-(1/i)A\tilde{A}_{-}-(1/i)B\tilde{B}_{-}}{i\tilde{C}_{-}+C_{-}^{*}+i2\Gamma_{2}} - \frac{1+(1/i)A^{*}\tilde{A}_{-}+(1/i)B^{*}\tilde{B}_{-}}{i\tilde{C}_{-}-C^{*}+i2\Gamma_{2}} \right\}.$$
(C4)

If in the first and third integrals one makes the transformation  $\omega' \to \omega + q_0$ ,  $(v \to v_+, v_- \to v)$ , and in the second integral the transformation  $\omega' \to -\omega$ ,  $(v \to -v, v_- \to -v_+)$ , and then combines terms, (C4) becomes

$$K(0,q_{0}) = \frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}}^{\infty} d\omega \frac{1 + AA_{+}^{*} + BB_{+}^{*}}{-C_{+}^{*} + C + i2\Gamma_{2}} \{ \tanh \frac{1}{2}\beta(\omega + q_{0}) - \tanh \frac{1}{2}\beta\omega \} - \frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G}}^{\infty} d\omega \left\{ \left[ \frac{1 - AA_{+} - BB_{+}}{C + C_{+} + i2\Gamma_{2}} \right] \tanh \frac{1}{2}\beta(\omega + q_{0}) + \left[ \frac{1 - AA_{+} - BB_{+}}{C + C_{+} + i2\Gamma_{2}} \right]^{*} \tanh \frac{1}{2}\beta\omega \right\} - \frac{1}{2} \frac{Ne^{2}}{mc} \int_{\Omega_{G} - q_{0}}^{\Omega_{G}} d\omega 2 \operatorname{Re} \left\{ \frac{1 - (1/i)\widetilde{A}A_{+} - (1/i)\widetilde{B}B_{+}}{i\widetilde{C} + C_{+} + i2\Gamma_{2}} \right\} \tanh \frac{1}{2}\beta(\omega + q_{0}).$$
(C5)

For  $q_0 > 2\Omega_G$ , in exactly the same way, we get (C5) again except the lower limit on the third term is  $-\Omega_G$  instead of  $\Omega_G - q_0$ , and there is an additional term

$$-\frac{1}{2}\frac{Ne^2}{mc}\int_{\Omega_{G-q_0}}^{-\Omega_G}d\omega \left\{\frac{1+A^*A_++B^*B_+}{-C^*+C_++i2\Gamma_2}-\frac{1-A^*A_+^*-B^*B_+^*}{-C^*-C_+^*+i2\Gamma_2}\right\} \tanh \frac{1}{2}\beta(\omega+q_0).$$

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