samples were prepared by melting together pieces of the very pure sodium with pieces of commercial grade pure sodium. The resulting resistivity ratios were measured using the eddy-current decay method.[20]

Figure 10 shows the results of the measurements on the width of the edge. The fractional width is plotted against the reciprocal of $\omega_c\tau$. $\omega_c\tau = RB_e/\rho_{4°\mathrm{K}}$. The resistivity at 4°K, $\rho_{4°\mathrm{K}}$, was determined using the room temperature resistivity (4.3×10^{-8} Ω-m for sodium and 6.1×10^{-8} Ω-m for potassium) and the measured resistivity ratio. The fractional width appears to be inversely proportional to $\omega_c\tau$. The solid line is $\Delta B/B_e = \pi/\omega_c\tau$.

V. SUMMARY

The properties of helicon waves have been investigated for the case when the helicon wavelength is smaller than the electron mean free path. Two experimental techniques have been used: One was the study of helicon waves propagating through a slab of metal; the other was the measurement of the surface impedance of the metal.

The free-electron theory predicts a deviation from the simple dispersion relation and a threshold field (the Kjeldaas edge) for the propagation of helicon waves. These predictions have been experimentally verified to within a few percent for polycrystalline sodium and potassium at 4°K. The values for the radius of the Fermi sphere deduced from the data are in excellent agreement with the theoretical values.

The measurement of the edge in polycrystalline indium shows that (a) the holes in indium behave very much like free holes with one hole/atom, and (b) an investigation of single crystals should yield valuable information about the indium Fermi surface.

The measurements on the fractional width of the edge demonstrated that it is inversely proportional to $\omega_c\tau$, and the empirical relation $\Delta B/B_e = \pi/\omega_c\tau$ fits the data reasonably well.

ACKNOWLEDGMENTS

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[20] C. P. Bean, R. W. DeBlois, and L. B. Nesbitt, J. Appl. Phys. **30**, 1976 (1959).

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Theory of the Thermal Conductivity of Superconducting Alloys with Paramagnetic Impurities

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The electronic thermal conductivity (K_s) of a weakly coupled, isotropic superconductor doped with a small concentration of paramagnetic impurities is computed. The theory of such superconducting alloys has been given by Abrikosov and Gor'kov, and is based on the assumption that the static magnetic impurities are randomly distributed and that their spins are uncorrelated. Starting from a Kubo formula, K_s is calculated by considering the electron-impurity interaction in the ladder approximation. A considerable simplification of the final expression for K_s obtains if the exchange scattering time τ_S is much larger than the total scattering time. Numerical calculations have been made of the ratio of the thermal conductivity in the superconducting and normal states as a function of the reduced temperature ($T/T_c \equiv t$) for different impurity concentrations. Abrikosov and Gor'kov have shown that the energy gap function $\omega_0(T)$ is quite different from the Gor'kov order parameter $\Delta(T)$ in such alloys. It is found, however, that K_s/K_n is less than unity even in the "gapless" region ($\Delta\tau_S<1$). Moreover, K_s/K_n as a function of t decreases with the paramagnetic-impurity concentration for $t \gtrsim 0.8$ and low concentrations. Some aspects of the Abrikosov-Gor'kov model are reviewed in an Appendix. The numerical values of Δ, ω_0, and the density of states that were used in the evaluation of K_s/K_n are given separately.

1. INTRODUCTION

THE prediction of "gapless" superconductivity in paramagnetic alloys by Abrikosov and Gor'kov,[1] and the confirmation of this prediction by Reif and Woolf[2] are significant recent developments. Although the theory is based on an approximate treatment of a simple model and more detailed experiments are needed,

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[1] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP, **12**, 1243 (1961)]. This will often be referred to as AG in the text.

[2] F. Reif and M. A. Woolf, Phys. Rev. Letters **9**, 315 (1962); Rev. Mod. Phys. **36**, 238 (1964).

the prediction is unambiguous and the confirmation convincing. The work of Abrikosov and Gor'kov (AG) is particularly interesting because it exhibits in a mathematically tractable form a possibility that has been admitted in principle for a long time. We refer to the possibility of an uniform system in which an infinitely reactive conductivity at zero frequency (acceleration current) occurs with merely a diminution, relative to the normal state, of the density of optical oscillator strength at small but finite frequencies.[3] The calculation of AG makes it clear that the key feature of the superconducting state is the condensation phenomenon. A gap in the single particle excitation spectrum is evidently not a necessary requirement for either the infinite conductivity or the perfect diamagnetism of the condensed state.

The experimental investigation of this phenomenon of superconductivity without an energy gap promises to improve our understanding both of superconductivity and of the effects of magnetic impurities in metals in general.[4] It has been known for some time that while nonmagnetic impurities have a relatively mild effect, paramagnetic impurities (i.e., magnetic impurities with well-defined localized spins) in small concentrations can produce a striking decrease[2,5] in the transition temperature T_c of a superconductor. It was first suggested by Herring[6] that this might be due to the existence of an exchange interaction between the localized spin of the impurity and the conduction electrons. By considering such an interaction and assuming that the "structureless" impurities were randomly distributed with uncorrelated spins, Suhl and Matthias[7] were able to show that the predicted reduction in T_c [$\delta T_c \propto n_i S(S+1)$, where S is the impurity spin, and n_i the impurity concentration] was in good agreement with experiment. The previously mentioned work of AG (see also Ref. 4) is based on the same model, but goes much further in drawing out its implications. Probably the most questionable steps in the calculation are the neglect of correlations between impurity spins,[8] and of multiple scattering by impurities. Very little seems to be known with certainty about the impurity concentrations at which corrections from these sources becomes significant, but there is indirect evidence[9] that they do become important even at very low concentrations. At high concentrations of paramagnetic impurities, it is possible that the alloy will become ferromagnetic owing to the interaction between two impurity atoms brought about by the exchange of conduction electrons.[4] It may happen that the specimen will still be superconducting, as verified experimentally in certain cases.[10] The possible coexistence of ferromagnetism and superconductivity has been demonstrated theoretically in some recent work by Gor'kov and Rusinov.[11] The present paper is mainly concerned with impurity concentrations such that the impurity spin correlations are small at the temperature of interest.

We might remark that the measurements reported in Ref. 2 have already been interpreted[2,3] to be in disagreement with a specific result of the AG theory. This theory predicts that at the absolute zero of temperature, the gap in the energy spectrum should vanish at $\exp(-\pi/4)\simeq 0.91$ of the concentration at which superconductivity disappears, whereas *linear* extrapolations in concentration (n_i) of the data for the energy gap (ω_0) and the critical temperature (T_c) lead to the conclusion that experimentally the former goes to zero at approximately 0.5 of the concentration at which the latter does. This apparent discrepancy is however largely due to an improper comparison. According to the AG theory, the curve of T_c versus n_i should be concave downward, while that of ω_0 versus n_i is concave upward and temperature-dependent. When the experimental points for T_c and ω_0 are compared with the predicted curves,[12] the agreement is not unsatisfactory, and it seems that one should keep somewhat of an open mind until more experimental information is available. The slight discrepancy with experiment could easily be due to the use of the BCS model for the effective electron-electron interaction, rather than the approximate treatment of the impurity scattering. Measurements of the differential conductance of tunneling junctions[13] and optical absorption will permit more detailed comparison with the theoretical densities of one and two particle states.

In this paper, we have calculated the thermal conductivity of superconductors containing paramagnetic impurities within the framework of the Abrikosov–Gor'kov theory. We start from the Kubo formula, and use the techniques of many-body theory to reduce the

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[3] Some remarks of this nature are contained in J. C. Phillips, Phys. Rev. Letters **10**, 96 (1963). Phillips however does not mention that the residue of the pole corresponding to the acceleration current [i.e., $\lim_{\omega\to 0}\omega\sigma(\omega)$, where $\sigma(\omega)$ is the long wavelength electrical conductivity] was explicitly calculated by Abrikosov and Gor'kov and is contained in Eqs. (38) and (39) of their paper.

[4] P. G. de Gennes and G. Sarma, J. Appl. Phys. **34**, 1380 (1963).

[5] See, for example, B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 93 (1958); J. Müller, Helv. Phys. Acta **32**, 141 (1959); K. Schwidtal, Z. Physik, **158**, 563 (1960); G. Boato, G. Gallinaro and C. Rizzuto, Rev. Mod. Phys. **36**, 162 (1964).

[6] C. Herring, Physica **24**, 184S (1958).

[7] H. Suhl and B. T. Matthias, Phys. Rev. **114**, 977 (1959). See also W. Baltensperger, Helv. Phys. Acta. **32**, 197 (1959).

[8] An attempt to explain gapless superconductivity on the basis of these correlations alone is contained in H. Suhl and D. R. Fredkin, Phys. Rev. Letters **10**, 131 (1963).

[9] For example, in dilute Zn-Mn alloys, there is observed a low-temperature resistance anomaly. See E. W. Collings, F. T. Hedgcock, and W. B. Muir, Phys. Rev. **134**, A1521 (1964), which contains further references.

[10] H. Suhl, B. T. Matthias, and E. Corenzwit, Phys. Chem. Solids **11**, 346 (1959).

[11] L. P. Gor'kov and A. I. Rusinov, Zh. Eksperim. i Teor. Fiz. **46**, 1363 (1964) [English transl.: Soviet Phys.—JETP **19**, 922 (1964)].

[12] Such a comparison was presented by S. Skalski, O. Betbeder-Matibet, and P. R. Weiss at the January 1964 meeting of the APS [Bull. Am. Phys. Soc. **9**, 30 (1964)]. In the course of our work, we found it easy to calculate these curves and some are given for completeness in Fig. 5.

[13] M. A. Woolf and F. Reif, Phys. Rev. **137**, A557 (1965).

conductivity to an integral involving frequency-dependent parameters introduced by Abrikosov and Gor'kov. The details of this calculation are the subject of Sec. 2.

A considerable simplification of the result occurs if we assume, as is reasonable, that the total single particle lifetime is much smaller than the exchange lifetime τ_S. With this assumption, we obtain in Sec. 3 an expression for the ratio of the thermal conductivity in the superconducting state and normal state of the form

$$\frac{K_s}{K_n}=\left(\frac{3}{2\pi^2}\right)\beta^3\int_0^\infty d\omega\omega^2\,\operatorname{sech}^2[\tfrac{1}{2}\beta\omega]h(\omega/\Delta,\alpha)\,. \quad (1.1)$$

Above[14] $\alpha\equiv(\tau_S\Delta)^{-1}$, Δ is the average order parameter, and $\beta\equiv(1/k_BT)$, where k_B is Boltzmann's constant and T is the temperature. For nonmagnetic impurities, one finds the usual result[15] that $h(\omega/\Delta<1)=0$ and $h(\omega/\Delta>1)=1$, the average order parameter $\Delta(T,\tau_S)$ being the energy gap in this case. For a paramagnetic alloy, the lower limit of integration is the physical energy gap $\omega_0(\Delta,\alpha)$ and not the average order parameter $\Delta(T,\tau_S)$. Moreover, the function $h(\omega)$ increases smoothly toward unity for $\omega>\omega_0$.

We have numerically evaluated the reduced conductivity K_s/K_n as a function of the temperature for various impurity concentrations. The integral in (1.1) can be done analytically for $T\simeq 0$°K and $T\simeq T_c$. The results are presented at the end of Sec. 3 and compared with the case of nonmagnetic impurities. Several features are simple enough to be worth mentioning here. Even in the gapless region ($\alpha>1$), the thermal conductivity is predicted to be lower than that in the normal state, because although the energy spectrum has no gap it is still distorted. In addition, the onset of gaplessness does not lead to an abrupt change in the thermal conductivity. Long before the gap actually vanishes, the BCS singularity in the density of states has been smoothed out by the impurity scattering. Finally it is found that K_s/K_n, considered as a function of the reduced temperature $t\equiv T/T_c$, has a characteristic concentration dependence. For $t\gtrsim 0.9$, K_s/K_n decreases for small n_i while for $t\lesssim 0.75$ it increases with n_i.

The authors hope, of course, that the predictions made in Sec. 3 will be experimentally tested. As has been indicated in the opening paragraphs of this section, one only has reason to expect good agreement with the theory for very low concentrations of impurities. Discrepancies at higher concentrations, if they are large, will serve as a useful test for a more inclusive theory.[11]

For nonmagnetic impurities in systems with weak electron-phonon interactions (to which we restrict ourselves), a simple calculation of the thermal conductivity using a Boltzmann equation is possible.[15] A justification of the need for the elaborate formalism of the next section seems therefore not to be out of place. First of all, in the interesting gapless region (which always obtains sufficiently close to T_c), it is not possible to associate a narrow band of energies with a state of momentum near the Fermi momentum. In other words, the quasiparticle approximation breaks down. In addition, the effects of the paramagnetic impurities in renormalizing the energy spectrum are crucial. Both these effects would cause difficulties in conventional transport theory, but they are easily taken into account in the Kubo formulation.

In the final section, we make some further comments on gapless superconductivity. In particular we briefly consider the relevance of our results to the study of the thermal conductivity of thin superconducting films (containing nonmagnetic impurities) in the presence of persistent currents, applied magnetic fields,[16–18] or rotations.

Two Appendices are included. In the main body of this paper, we assume some familiarity with the work of Abrikosov–Gor'kov.[1,4] Readers who are unfamiliar with the latter may find Appendix A of the present paper useful. Appendix B verifies a conjecture made in Sec. 2.

2. ANALYTICAL DEVELOPMENT

We take the Hamiltonian for the system of interest to be[1]

$$\begin{aligned}H=&\int d^3x\psi_\alpha^\dagger(\mathbf{x})\left(-\frac{\nabla^2}{2m}-\mu\right)\psi_\alpha(\mathbf{x})\\&-\frac{g}{2}\int d^3x\psi_\alpha^\dagger(\mathbf{x})\psi_\beta^\dagger(\mathbf{x})\psi_\beta(\mathbf{x})\psi_\alpha(\mathbf{x})\\&+\sum_n\int d^3x\psi_\alpha^\dagger(\mathbf{x})V_{\alpha\beta}(\mathbf{x}-\mathbf{R}_n)\psi_\beta(\mathbf{x})\,. \quad (2.1)\end{aligned}$$

Here $\psi_\alpha(\mathbf{x})$ is the annihilation operator for an electron of spin $\alpha(\alpha=\uparrow$ or $\downarrow)$ at the position $\mathbf{x}$, μ is the chemical potential with respect to which it is convenient to measure single-particle energies, and summation over repeated spin indices is implied. The phonon-induced attraction between electrons is approximated in the manner of Gor'kov.[19] The interaction of an electron with a paramagnetic atom of spin $\mathbf{S}$ at the position $\mathbf{R}_n$ is $V_{\alpha\beta}(\mathbf{x}-\mathbf{R}_n)$, where the short-ranged potential $V_{\alpha\beta}(\mathbf{x})$ is taken to be

$$V_{\alpha\beta}(\mathbf{x})=V_1(\mathbf{x})\delta_{\alpha\beta}+V_2(\mathbf{x})\left\{\mathbf{S}\cdot\frac{\boldsymbol{\sigma}_{\alpha\beta}}{2}\right\}\,. \quad (2.2)$$

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[14] We use units in which $\hbar=1$.

[15] J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).

[16] D. E. Morris and M. Tinkham, Phys. Rev. Letters **6**, 600 (1961); Phys. Rev. **134**, A1154 (1964).

[17] H. Maki, Progr. Theoret. Phys. (Kyoto) **31**, 378 (1964).

[18] H. Maki, Progr. Theoret. Phys. (Kyoto) **29**, 10 (1963); **29**, 333 (1963); **29**, 603 (1963). We note that the relaxation time in these papers is twice the usual expression.

[19] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)].

Here $\boldsymbol{\sigma}$ is the Pauli spin matrix vector. Equation (2.1) permits the definition of a Hamiltonian density $h(\mathbf{x})$ in an obvious way. Using the equations of motion for the field operators, one can then verify that the operator $\mathbf{u}(\mathbf{x})$ defined by

$$\mathbf{u}(\mathbf{x})\equiv-\frac{1}{2m}[\dot{\psi}_\alpha{}^\dagger(\mathbf{x})\boldsymbol{\nabla}\psi_\alpha(\mathbf{x})+\boldsymbol{\nabla}\psi_\alpha{}^\dagger(\mathbf{x})\dot{\psi}_\alpha(\mathbf{x})] \tag{2.3}$$

obeys the equation

$$\dot{h}(\mathbf{x})+\boldsymbol{\nabla}\cdot\mathbf{u}(\mathbf{x})=0\,, \tag{2.4}$$

and may thus be interpreted as the energy current density.

For the thermal conductivity we are interested in the flow of energy with no flow of matter. We shall systematically neglect terms of order (k_BT/μ), and we shall verify that to this order the matter current accompanying an energy current is reduced to zero by measuring energies with respect to the chemical potential. The Kubo formula for the ratio of the energy current to the negative of the temperature gradient may be written in the form[20,21]

$$K=\frac{2}{3VT}\,\mathrm{Im}\int_{-\infty}^{0}dt_2t_2\int d^3x_1\int d^3x_2\langle\mathbf{u}(\mathbf{x}_1,0)\cdot\mathbf{u}(\mathbf{x}_2,t_2)\rangle\,. \tag{2.5}$$

Within our approximations, for the reason given above, it is consistent to take K to be the thermal conductivity. In Eq. (2.5), V is the volume of the system and the brackets denote an average over the positions and spins of the impurities as well as an average in the grand canonical ensemble. To assist in the evaluation of (2.5) it is convenient to introduce the correlation function,[21]

$$P(1,2)\equiv\langle T[\mathbf{u}(1)\cdot\mathbf{u}(2)]\rangle\,, \tag{2.6}$$

where 1, 2 denote space-time points, and T is Wick's time-ordering operator. In the region $\mathrm{Re}t_1=\mathrm{Re}t_2=0$, $0<\mathrm{Im}t_1$, $\mathrm{Im}t_2<-\beta$, one has the expansion[20,21]

$$P(1,2)=V\int\frac{d^3q}{(2\pi)^3}\frac{i}{\beta}\times\sum_m P(q,\nu_m)e^{i\mathbf{q}\cdot(\mathbf{x}_1-\mathbf{x}_2)}e^{-i\nu_m(t_1-t_2)}\,. \tag{2.7}$$

Here $\nu_m=2\pi mi/\beta$, m running over all integers, and $\beta=(k_BT)^{-1}$. The transport coefficient (2.5) is then related to the analytic continuation of the Fourier series coefficient $P(\mathbf{q},\nu_m)$ by

$$K=1/6T\times\lim_{\omega\to0}\frac{P(\mathbf{q}=0,\,\nu_m=\omega+i0^+)-P(\mathbf{q}=0,\,\nu_m=\omega-i0^+)}{\omega}\,. \tag{2.8}$$

[The details of the connection between (2.5) and (2.8) are contained, for example, in Eqs. (245) to (259) of the lecture notes referred to in footnote 20.]

In treating simultaneously the effect of the two interaction terms in (2.1) it is convenient to use a 4-component space[22]

$$\Psi(x)\equiv\begin{bmatrix}\psi_\uparrow(\mathbf{x})\\ \psi_\downarrow(\mathbf{x})\\ \psi_\uparrow{}^\dagger(\mathbf{x})\\ \psi_\downarrow{}^\dagger(\mathbf{x})\end{bmatrix};\quad \Psi^\dagger(\mathbf{x})\equiv(\psi_\uparrow{}^\dagger(\mathbf{x}),\psi_\downarrow{}^\dagger(\mathbf{x}),\psi_\uparrow(\mathbf{x}),\psi_\downarrow(\mathbf{x}))\,. \tag{2.9}$$

We write matrices in this space as direct products of (2×2) matrices. For example, we shall write

$$\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{bmatrix}=\left[\begin{array}{c|c}0&0\\\hline 1&-1\end{array}\right]=\tau_3\times1\,. \tag{2.10}$$

($\boldsymbol{\tau}$ denotes the Pauli matrices in the larger space.) We note in passing that the notation (2.9) is redundant because

$$\Psi_i{}^\dagger(x)=(\tau_1\times1)_{ij}\Psi_j(x)\,. \tag{2.11}$$

In this 4-component space, the energy current operator (2.3), apart from an irrelevant constant, takes the form

$$\mathbf{u}(1)=-\frac{1}{4m}\left(\frac{\partial}{\partial t_1}\boldsymbol{\nabla}_1{}'+\frac{\partial}{\partial t_1{}'}\boldsymbol{\nabla}_1\right)\times\Psi^\dagger(1')(\tau_3\times1)\Psi(1)|_{1'=1}\,. \tag{2.12}$$

The correlation function (2.7) is then[23]

$$P(1,2)=\frac{1}{16m^2}\left(\frac{\partial}{\partial t_1}\boldsymbol{\nabla}_1{}'+\frac{\partial}{\partial t_1{}'}\boldsymbol{\nabla}_1\right)\left(\frac{\partial}{\partial t_2}\boldsymbol{\nabla}_2{}'+\frac{\partial}{\partial t_2{}'}\boldsymbol{\nabla}_2\right)\times(\tau_3\times1)^{ij}(\tau_3\times1)^{kl}\times\langle T[\Psi_i(1)\Psi_k(2)\Psi_l{}^\dagger(2')\Psi_j{}^\dagger(1')]\rangle|_{\substack{1'=1^\dagger\\2'=2^\dagger}}\,. \tag{2.13}$$

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[20] For a review of the derivation of such formulas, see G. V. Chester, in *Reports on Progress in Physics*, edited by A. C. Stickland (The Physical Society, London, 1963), Vol. XXVI. The particular form used here is discussed by J. S. Langer, Phys. Rev. **128**, 110 (1962). See also V. Ambegaokar, in *Brandeis Lectures, 1962* (W. A. Benjamin, Inc., New York, 1963), Vol. 2.

[21] V. Ambegaokar and L. Tewordt, Phys. Rev. **134**, A805 (1964).

[22] This space has been used, for example, by G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 960 (1960) [English transl.: Soviet Phys.—JETP, **9**, 1385 (1959)]; R. Balian and N. R. Werthamer, Phys. Rev. **131**, 1553 (1963).

[23] In writing Eq. (2.13) we have neglected terms proportional to $\delta(t_1-t_2)$, which arise from the nonzero commutator of the time derivative and time ordering operations. This neglect does not affect the discontinuity of $P(\mathbf{q},\nu_m)$ to which the thermal conductivity is related. However, we shall see (see Ref. 25) that it leads to an apparently divergent sum over an intermediate frequency variable. Since the source of the difficulty will be immediately clear we prefer to proceed in this mathematically impure but algebraically more compact way.

We wish to evaluate (2.13) in the limit of a low concentration of impurities, neglecting the existence of any collective states. Calculations of this sort have been carried out in many contexts,[24] and we shall therefore omit some details. The effects of the attractive electron–electron interaction in (2.1) are taken into account by the existence of off-diagonal components of the single-particle Green's-function matrix,

$$\mathcal{G}_{ij}(12)\equiv -i\langle T[\Psi_i(1)\Psi_j^\dagger(2)]\rangle. \qquad (2.14)$$

These off-diagonal components have to be determined self-consistently[1] (see also Appendix A of this paper). The effect of scattering from impurities with spin is easily taken into account in our four-component notation. We treat in the Born approximation the scattering of single particles and particle-hole pairs from independent, randomly distributed impurities. The resulting expression for the Fourier series coefficient $P(\mathbf{q}=0,\nu_m)$ $[\equiv P(\nu_m)]$ is

$$P(\nu_m)=\frac{1}{8m^2}\left(\frac{i}{\beta}\right)\sum_{\xi_l} e^{\xi_l 0^+}\int\frac{d^3k}{(2\pi)^3}\mathbf{k}(2\xi_l+\nu_m)$$
$$\times\mathrm{Tr}\{(\tau_3\times 1)\mathcal{G}(\mathbf{k},\,\xi_l+\nu_m)\mathbf{\Gamma}_{\mathbf{k}}(\xi_l,\nu_m)\mathcal{G}(\mathbf{k},\xi_l)\}, \qquad (2.15)$$

where the vertex function $\mathbf{\Gamma}_{\mathbf{k}}$ satisfies the integral equation

$$\mathbf{\Gamma}_{\mathbf{k}}(\xi_l,\nu_m)=\mathbf{k}(2\xi_l+\nu_m)(\tau_3\times 1)+4n_i\int\frac{d^3k'}{(2\pi)^3}$$
$$\times\langle V(\mathbf{k}-\mathbf{k}')\mathcal{G}(\mathbf{k}',\,\xi_l+\nu_m)$$
$$\times\mathbf{\Gamma}_{\mathbf{k}'}(\xi_l,\nu_m)\mathcal{G}(\mathbf{k}',\xi_l)V(\mathbf{k}'-\mathbf{k})\rangle. \qquad (2.16)$$

Above $\xi_l=(2l+1)\pi i/\beta$ with l an integer and $\mathcal{G}(\mathbf{k},\xi_l)$ is the Fourier transform in space and imaginary time of the Green's function (2.14) which includes the effect of the scattering of single particles in the Born approximation (Appendix A). The density of impurities is n_i. The matrix $V(\mathbf{k}-\mathbf{k}')$ is the Fourier transform of the interaction potential in the four-component notation and is given by

$$V(\mathbf{k}-\mathbf{k}')=\tfrac{1}{2}V_1(\mathbf{k}-\mathbf{k}')(\tau_3\times 1)+\tfrac{1}{2}V_2(\mathbf{k}-\mathbf{k}')\left[(\tau_3\times\sigma_1)\frac{S_x}{2}\right.$$
$$\left.+(1\times\sigma_2)\frac{S_y}{2}+(\tau_3\times\sigma_3)\frac{S_z}{2}\right], \qquad (2.17)$$

where $\mathbf{S}\equiv(S_x,S_y,S_z)$. An over-all factor of 2 in Eq. (2.15) and the factor of 4 in the second term of (2.16) come from the redundancy (2.11). We have now to calculate the average over the impurity spins in Eq. (2.16). We assume, following Abrikosov and Gor'kov, that the impurity spins are unpolarized so that ($r, s=x, y, z$; n denotes a particular impurity spin)

$$\langle S_r^{\,n}\rangle=0;\quad \langle S_r^{\,n}S_s^{\,n'}\rangle=\tfrac{1}{3}S(S+1)\delta_{nn'}\delta_{rs}. \qquad (2.18)$$

Since there is no average polarization, the contribution to (2.16) of each component of **s** in (2.17) must be equal (one can explicitly verify this by keeping all terms to the end of the calculation). Thus, after averaging over spins, (2.16) may be written as

$$\mathbf{\Gamma}_{\mathbf{k}}(\xi_l,\nu_m)$$
$$=\mathbf{k}(2\xi_l+\nu_m)(\tau_3\times 1)+n_i\int\frac{d^3k'}{(2\pi)^3}|V_1(\mathbf{k}-\mathbf{k}')|^2(\tau_3\times 1)$$
$$\times\mathcal{G}(\mathbf{k}',\,\xi_l+\nu_m)\mathbf{\Gamma}_{\mathbf{k}'}(\xi_l,\nu_m)\mathcal{G}(\mathbf{k}',\xi_l)(\tau_3\times 1)$$
$$+n_i\frac{S(S+1)}{4}\int\frac{d^3k'}{(2\pi)^3}|V_2(\mathbf{k}-\mathbf{k}')|^2(\tau_3\times\sigma_1)$$
$$\times\mathcal{G}(\mathbf{k}',\,\xi_l+\nu_m)\mathbf{\Gamma}_{\mathbf{k}'}(\xi_l,\nu_m)\mathcal{G}(\mathbf{k}',\xi_l)(\tau_3\times\sigma_1). \qquad (2.19)$$

The obvious next step is to calculate (2.15) using the inhomogeneous term of (2.19) for $\mathbf{\Gamma}_{\mathbf{k}}$. It is well known from similar calculations that this corresponds to the neglect of "scattering-in" terms.

The single particle Green's function has been given by Abrikosov and Gor'kov.[1] We have rederived this result in Appendix A. In the next several equations we list the relevant results from this Appendix. The analytic continuation to the complex plane of the Fourier series coefficients of the single-particle Green's function has the form

$$\mathcal{G}(\mathbf{k},z)=\frac{zZ(z)(1\times 1)+\epsilon_k(\tau_3\times 1)-\varphi(z)(\tau_2\times\sigma_2)}{z^2Z^2(z)-\epsilon_k^{\,2}-\varphi^2(z)}, \qquad (2.20)$$

where ϵ_k is the normal state single-particle energy measured from the chemical potential. The complex functions $Z(z)$ and $\varphi(z)$ are given implicitly by the equations (z a complex variable)

$$zZ(z)=z+\frac{i}{2\tau^{(1)}}\frac{u(z)}{(u^2(z)-1)^{1/2}}, \qquad (2.21)$$

$$\varphi(z)=\Delta+\frac{i}{2\tau^{(2)}}\frac{1}{(u^2(z)-1)^{1/2}}, \qquad (2.22)$$

which can be combined to give

$$\frac{z}{\Delta}=u(z)-\frac{i}{\tau_S\Delta}\frac{u(z)}{(u^2(z)-1)^{1/2}}. \qquad (2.23)$$

We have defined $u(z)\equiv zZ(z)/\varphi(z)$. The appropriate branch of the radical is determined by the condition $\mathrm{Im}(u^2(z)-1)^{1/2}>0$. Above Δ is the temperature-dependent Gor'kov order parameter $\Delta\equiv g\langle\psi_\uparrow(\mathbf{x})\psi_\downarrow(\mathbf{x})\rangle$

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[24] S. F. Edwards, Phil. Mag. **3**, 1020 (1958); A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **35**, 1558 (1958); **36**, 319 (1959). [English transls.: Soviet Phys.—JETP **8**, 1090 (1959); **9**, 220 (1959)]. G. Rickayzen, in *The 1961 Bergen Lecture Notes on the Many Body Problem*, edited by C. Fronsdal (W. A. Benjamin, Inc., New York, 1962), p. 85.

(which is independent of position as a result of the impurity average) and $\tau^{(1)}$, $\tau^{(2)}$, and τ_S are scattering lifetimes given by the formulas [$N(0)$ is the density of normal single-particle states at the Fermi surface],

$$\frac{1}{\tau^{(1)}}=2\pi n_i N(0)\int\frac{d\Omega}{4\pi}\times\left\{|V_1(k_F,\theta)|^2+\frac{S(S+1)}{4}|V_2(k_F,\theta)|^2\right\},\tag{2.24}$$

$$\frac{1}{\tau^{(2)}}=2\pi n_i N(0)\int\frac{d\Omega}{4\pi}\times\left\{|V_1(k_F,\theta)|^2-\frac{S(S+1)}{4}|V_2(k_F,\theta)|^2\right\},\tag{2.25}$$

$$\frac{1}{\tau_S}=\frac{1}{2}\left[\frac{1}{\tau^{(1)}}-\frac{1}{\tau^{(2)}}\right].\tag{2.26}$$

With this information we are in a position to carry out the evaluation of (2.15) with $\mathbf{\Gamma}_\mathbf{k}$ replaced by the leading term in the integral Eq. (2.16). It is convenient to note that $\mathcal{G}(z)$ is analytic everywhere except for a branch cut on the real axis. As a result there exists the following well-known spectral representation

$$\mathcal{G}(\xi_l)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{a(\omega)}{\xi_l-\omega},\tag{2.27}$$

where $a(\omega)=2\,\mathrm{Im}\,\mathcal{G}(z=\omega-i0^+)$. After substituting spectral representations for the two Green's functions in (2.15), we do the ξ_l sum.[25] The thermal conductivity may be evaluated according to the prescription (2.8). Calling the result $\tilde{K}_s$ to remind us that the "scattering-in" terms have still to be included, we find

$$\tilde{K}_s=\frac{1}{48m^2k_BT^2}\int\frac{d^3k\,d\omega}{(2\pi)^4}k^2\omega^2\,\mathrm{sech}^2(\tfrac{1}{2}\beta\omega)\times\mathrm{Tr}\{(\tau_3\times1)a(k,\omega)(\tau_3\times1)a(k,\omega)\}.\tag{2.28}$$

The integral over momenta can be converted into one over ϵ, and this integral can be done in a relatively straightforward way. (The integral is essentially identical to one which occurs in Ref. 21, and more details may be found there.) The result is

$$\tilde{K}_s=\frac{n}{8mk_BT^2}\int_0^\infty d\omega\frac{\omega^2\,\mathrm{sech}^2(\tfrac{1}{2}\beta\omega)}{\mathrm{Im}[\Omega+i/2\tau^{(1)}]}\times\left[1+\frac{|u|^2-1}{|u^2-1|}\right],\tag{2.29}$$

where n is the density of electrons, and

$$\Omega(z)\equiv\frac{z}{u(z)}(u^2(z)-1)^{1/2};\quad\mathrm{Im}(u^2(z)-1)^{1/2}>0.\tag{2.30}$$

The correct branch of $\Omega(z)$ has the properties

$$\begin{aligned}\Omega(z^*)&=-\Omega^*(z),\\\Omega(-z)&=\Omega(z).\end{aligned}\tag{2.31}$$

For real arguments, u and Ω are defined by $u(\omega)=u(z=\omega-i0^+)$ and $\Omega(\omega)=\Omega(z=\omega-i0^+)$.

Before proceeding we can check that (2.29) is correct in several interesting limits. For the normal metal $\Omega(\omega)\to-|\omega|\,\mathrm{sgn}\omega$, $u\to\infty$ and $\tilde{K}$ reduces to

$$\tilde{K}_n=\frac{n\tau^{(1)}}{2mk_BT^2}\int_0^\infty d\omega\omega^2\,\mathrm{sech}^2(\tfrac{1}{2}\beta\omega)=\frac{n\pi^2k_B{}^2\tau^{(1)}T}{3m}.\tag{2.32}$$

Except for the fact that the lifetime in (2.32) is the ordinary lifetime and not the transport lifetime, this is the correct answer for the normal state. (The "scattering-in" corrections will come, as we have remarked and will see shortly, from the vertex corrections.) Equation (2.29) also contains as a special case the result for nonparamagnetic impurities ($V_2\to0$). In this case $\Omega\to-\mathrm{sgn}\omega(\omega^2-\Delta^2)^{1/2}$, $u\to\omega/\Delta$, and $\tilde{K}$ becomes

$$\tilde{K}_s=\frac{n\tau^{(1)}}{2mk_BT^2}\int_\Delta^\infty d\omega\omega^2\,\mathrm{sech}^2[\tfrac{1}{2}\beta\omega].\tag{2.33}$$

(Compare Ref. 15.) Although a more complicated way of deriving the simple results (2.32) and (2.33) could scarcely be imagined, it is of course gratifying that these limits are correctly obtained. Moreover, it is to be noted that the Boltzmann equation approach of Bardeen, Rickayzen, and Tewordt (BRT) requires that the quasiparticle picture be valid, while our discussion does not. Equation (2.33) has been derived using Green's function techniques by Kadanoff and Martin[26] under the assumptions k_BT, $\Delta\gg1/\tau^{(1)}$, while very recently Maki[17] obtained it in the opposite limits. In contrast, our analysis requires no assumptions about the relative magnitudes of k_BT, Δ and $1/\tau^{(1)}$.

At this point we can also verify that the transport process we are calculating has no matter flow associated with it. If one uses the appropriate Kubo formula to calculate the matter flow, one obtains a formula similar to (2.28). The essential differences are that one factor of ω is missing and one matrix $(\tau_3\times1)$ is replaced by (1×1). We may now convert the momentum integration to an integration over ϵ. We neglect, as we have done in going from (2.28) to (2.29), the variation of the density of states and of the factor k^2 over the important region of integration. This neglect introduces errors of order (k_BT/μ). The remaining integration is then easily seen

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[25] The difficulty mentioned in footnote 23 occurs here. Because of the presence of the factor $(2\xi_l+\nu_m)^2$ in the numerator, the sum over ζ_l is apparently divergent. A more careful treatment of the time derivatives in $P(1,2)$ shows that the factor $(2\xi_l+\nu_m)^2$ should be replaced by $(\omega_1+\omega_2)^2$ where ω_1 and ω_2 are the integration variables of the spectral representations of $\mathcal{G}(\xi_l)$ and $\mathcal{G}(\xi_l+\nu_m)$. Thus, if one does the ξ_l sum by the standard contour integral technique (see, for example, the lecture notes referred to in Ref. 20) and ignores the large ξ contribution of the contour, one gets the correct answer.

[26] L. P. Kadanoff and P. C. Martin, Phys. Rev. **124**, 670 (1961).

using (2.20) and (2.27) to be odd in ϵ. The matter flow is thus zero to a sufficient accuracy.

To complete the calculation of the thermal conductivity we must properly treat[24] the integral Eq. (2.19). Since the only direction in which the vector $\mathbf{\Gamma}_\mathbf{k}$ can lie is $\mathbf{k}$, we write $\mathbf{\Gamma}_\mathbf{k}=\mathbf{k}\Gamma$. The two factors of $\mathcal{G}$ in the homogeneous terms ensure that the integral is a rapidly convergent function of $\epsilon_{k'}$. In addition, we are only interested in $\mathbf{\Gamma}_\mathbf{k}$ for k near k_F. As a result, the integral equation may be approximated by

$$\begin{aligned}\Gamma(\xi_l,\nu_m)&\\ &=(2\xi_l+\nu_m)(\tau_3\times 1)+\frac{1}{2\pi N(0)\tau'}\int\frac{d^3k'}{(2\pi)^3}\\ &\quad\times\{(\tau_3\times 1)\mathcal{G}(k',\,\xi_l+\nu_m)\Gamma(\xi_l,\nu_m)\mathcal{G}(k',\xi_l)(\tau_3\times 1)\}\\ &\quad+\frac{1}{2\pi N(0)\tau_S'}\int\frac{d^3k'}{(2\pi)^3}\{(\tau_3\times\sigma_1)\mathcal{G}(k',\,\xi_l+\nu_m)\\ &\qquad\times\Gamma(\xi_l,\nu_m)\mathcal{G}(k',\xi_l)(\tau_3\times\sigma_1)\}\,,\qquad(2.34)\end{aligned}$$

where τ' and τ_S' are given by

$$\frac{1}{\tau'}\equiv 2\pi n_i N(0)\int\frac{d\Omega}{4\pi}|V_1(k_F,\theta|^2\cos\theta \qquad(2.35)$$

and

$$\frac{1}{\tau_S'}\equiv 2\pi n_i N(0)\int\frac{d\Omega}{4\pi}|V_2(k_F,\theta)|^2\frac{S(S+1)}{4}\cos\theta. \qquad(2.36)$$

The quantity Γ is still a matrix in the 4-component space. Since the inhomogeneous term is proportional to $(\tau_3\times 1)$, we substitute the form $\Gamma=\Gamma_0(\tau_3\times 1)$ into the homogeneous terms. Then by performing the ϵ' integral, one sees that the only matrix which is generated by the inhomogeneous item is $(\tau_1\times\sigma_2)$. We are thus justified in making the ansatz

$$\Gamma=\Gamma_0(\tau_3\times 1)+i\Gamma_1(\tau_1\times\sigma_2)\,. \qquad(2.37)$$

When (2.37) is substituted with (2.34) and the coefficients of the two independent matrices are set separately equal to zero, one obtains two equations for the unknowns Γ_0 and Γ_1. The solution of these equations requires straightforward but tedious algebra which we shall omit here. The answer we obtain is

$$\Gamma_j(\xi_l,\nu_m)=\Gamma_j(z,z')\Big|_{\substack{z=\xi_l\\ z'=\xi_l+\nu_m}}\quad;\quad j=0,1\,, \qquad(2.38)$$

where

$$\begin{aligned}\Gamma_0&\left\{\left[\Omega+\Omega'+\frac{i}{\tau_{\mathrm{tr}}{}^{(1)}}\right]+\frac{i}{\tau_S'}\left[1+\frac{zz'}{\Omega\Omega'}\left(1-\frac{1}{uu'}\right)\right]\right\}\\ &=(z+z')\left\{\Omega+\Omega'+\frac{i}{\tau^{(1)}}-\frac{i}{2[\tau^{(2)}]'}\left[1+\frac{zz'}{\Omega\Omega'}\left(1-\frac{1}{uu'}\right)\right]\right\}\end{aligned}\qquad(2.39)$$

and

$$\begin{aligned}\Gamma_1&\left\{\left[\Omega+\Omega'+\frac{i}{\tau_{\mathrm{tr}}{}^{(1)}}\right]+\frac{i}{\tau_S'}\left[1+\frac{zz'}{\Omega\Omega'}\left(1-\frac{1}{uu'}\right)\right]\right\}\\ &=-\frac{i}{2[\tau^{(2)}]'}\frac{zz'}{\Omega\Omega'}\left[\left(\frac{1}{u}-\frac{1}{u'}\right)(z+z')\right],\end{aligned}\qquad(2.40)$$

with $\Omega\equiv\Omega(z)$ defined by Eq. (2.30) and $u=u(z)$ by Eq. (2.23); $u'\equiv u(z')$ and $\Omega'\equiv\Omega(z')$. The other new symbols in (2.39) and (2.40) are defined by

$$\begin{aligned}\frac{1}{\tau_{\mathrm{tr}}{}^{(1)}}\equiv 2\pi n_i N(0)\int\frac{d\Omega}{4\pi}&\Big\{|V_1(k_F,\theta)|^2\\ &+\frac{S(S+1)}{4}|V_2(k_F,\theta)|^2\Big\}(1-\cos\theta)\,,\end{aligned}\qquad(2.41)$$

$$\frac{1}{[\tau^{(2)}]'}\equiv\frac{1}{\tau'}-\frac{1}{\tau_S'}\,, \qquad(2.42)$$

τ' and τ_S' having been introduced in Eqs. (2.35) and (2.36), respectively.

We must now substitute (2.39) and (2.40) into (2.37) and use the resulting expression for $\mathbf{\Gamma}_\mathbf{k}(\xi_l,\nu_m)$ in (2.15). It is now convenient to do the momentum integral after converting it into one over energy according to the prescription $\int d^3k/(2\pi)^3=N(0)\int d\epsilon$. However, it is only after doing the ξ_l sum that the momentum integral is peaked about the Fermi surface.[27] We avoid this difficulty in the standard way by subtracting the expression for $P(\nu_m)$ in the normal state. The resulting expression for the difference has the form (in an obvious notation),

$$\begin{aligned}&P_s(\nu_m)-P_n(\nu_m)\\ &\quad=\frac{3\pi ni}{8m\beta}\sum_{\xi_l}e^{\xi_l 0^+}[F_s(\xi_l,\xi_{l'})-F_n(\xi_l,\xi_{l'})]\,,\end{aligned}\qquad(2.43)$$

where $\xi_l'\equiv\xi_l+\nu_m$. The quantity $F_n\equiv F_s(\Delta=0)$, and F_s is calculated to be

$$\begin{aligned}F_s(z,z')=2i(z+z')^2&\left[1-\frac{zz'}{\Omega\Omega'}\left(1-\frac{1}{uu'}\right)\right]\Big/\\ &\left\{\Omega+\Omega'+\frac{i}{\tau_{\mathrm{tr}}{}^{(1)}}+\frac{i}{\tau_S'}\left[1+\frac{zz'}{\Omega\Omega'}\left(1-\frac{1}{uu'}\right)\right]\right\}.\end{aligned}\qquad(2.44)$$

If we had neglected the vertex corrections, i.e., replaced Γ by $(z+z')\cdot(\tau_3\times 1)$, we would have obtained

$$\begin{aligned}\tilde{F}_s(z,z')=2i(z+z')^2&\left[1-\frac{zz'}{\Omega\Omega'}\left(1-\frac{1}{uu'}\right)\right]\Big/\\ &[\Omega+\Omega'+1/\tau^{(1)}].\end{aligned}\qquad(2.45)$$

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[27] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., New Jersey, 1963), p. 312; G. Rickayzen, *Theory of Superconductivity* (John Wiley & Sons, Inc., New York, to be published), Appendix 4.

In this case, we know the answer for the thermal conductivity. It is given by Eq. (2.29). Comparing (2.45) with (2.29) and using (2.31) we find the relation

$$\tilde{K}_s=\frac{n}{32mk_BT^2}\int_0^\infty d\omega\,\mathrm{sech}^2(\tfrac{1}{2}\beta\omega)\times\tilde{F}_s(\omega-i0^+,\omega+i0^+).\tag{2.46}$$

One is led to guess that this relation also holds for K_s and F_s, and indeed it can be shown (Appendix B) that for elastic scattering processes, such as those that concern us in this paper, the guess is correct.

One final answer for the thermal conductivity then follows directly from (2.44) and is

$$K_s=\frac{n}{8mk_BT^2}\int_0^\infty\frac{d\omega\omega^2\,\mathrm{sech}^2(\tfrac{1}{2}\beta\omega)\left[1+\dfrac{|u|^2-1}{|u^2-1|}\right]}{\mathrm{Im}\left\{\Omega+\dfrac{i}{2\tau_{\mathrm{tr}}^{(1)}}+\dfrac{i}{2\tau_S'}\left[1-\dfrac{|u|^2-1}{|u^2-1|}\right]\right\}}.\tag{2.47}$$

Equation (2.47) forms the basis for the discussion and calculations of the next section.

3. APPROXIMATIONS AND NUMERICAL CALCULATIONS

Our first task is to comment on the qualitative features of the basic result of the preceding section, Eq. (2.47). Note that the correct formulas for a normal metal and for a superconductor with nonparamagnetic impurities are obtained from (2.47) in the same manner as (2.32) and (2.33) were obtained from (2.29). In the latter case, K_s/K_n is unaffected by the vertex corrections. Further, if the impurity potentials are assumed to be delta functions in coordinate space [so $V(q)$ is independent of q], then K_s reduces to $\tilde{K}_s$ in (2.29).

In discussing K_s, it is convenient to rewrite it as follows:

$$K_s=\frac{n}{4mk_BT^2}\int_0^\infty d\omega\times\frac{\omega^2\,\mathrm{sech}^2(\tfrac{1}{2}\beta\omega)h(\omega/\Delta,\alpha)}{\mathrm{Im}\left\{\Omega(\omega)+\dfrac{i}{2\tau_{\mathrm{tr}}^{(1)}}+\dfrac{i}{\tau_S'}[1-h(\omega/\Delta,\alpha)]\right\}},\tag{3.1}$$

where we have introduced the new function

$$h(\omega/\Delta,\alpha)\equiv\tfrac{1}{2}[1+(|u(\omega/\Delta,\alpha)|^2-1)/|u^2(\omega/\Delta,\alpha)-1|],\tag{3.2}$$

with $\alpha\equiv(\tau_S\Delta)^{-1}$, a parameter which will play a leading role in the discussion which follows.

Finally, we have from Eqs. (2.23) and (2.30),

$$(\omega/\Delta)=u(\omega/\Delta,\alpha)\{1-[i\alpha/(u^2(\omega/\Delta,\alpha)-1)^{1/2}]\},\tag{3.3}$$

$$\frac{\Omega(\omega)}{\Delta}=\frac{\omega}{\Delta}\frac{1}{u(\omega/\Delta,\alpha)}[u^2(\omega/\Delta,\alpha)-1]^{1/2}=(u^2(\omega/\Delta,\alpha)-1)^{1/2}-i\alpha.\tag{3.4}$$

We have numerically solved Eq. (3.3) to obtain $u(\omega/\Delta,\alpha)$ as a function of ω/Δ for some representative values of α. We have then obtained curves for $h(\omega/\Delta,\alpha)$ and these are plotted in Fig. 1. As was pointed out by Abrikosov and Gor'kov,[1] the desired solution of (3.3) is complex for $\omega\geq\omega_0$, where

$$\begin{aligned}\omega_0&=\Delta(1-\alpha^{2/3})^{3/2}\quad\text{for}\quad\alpha<1,\\&=0\quad\text{for}\quad\alpha>1.\end{aligned}\tag{3.5}$$

As a result $h(\omega/\Delta,\alpha)$ is finite for $\omega>\omega_0$. It can be easily verified using (3.3) that at $\omega=0$,

$$h(0,\alpha)=1-\alpha^{-2}\quad\text{for}\quad\alpha>1\tag{3.6}$$

and that the maximum value of $h(\omega/\Delta,\alpha)$ is unity. In Fig. 2, we have plotted the other quantity of interest in (3.1), namely the imaginary part of $\Omega(\omega)$, as a function of α. For $\alpha<1$, "cusps" appear at ω_0, where

$$\mathrm{Im}\left[\frac{\Omega(\omega_0)}{\Delta}\right]=\left(\frac{\omega_0}{\Delta}\right)^{2/3}\left[1-\left(\frac{\omega_0}{\Delta}\right)^{2/3}\right]^{1/2}=\alpha^{1/3}(1-\alpha^{2/3}),\tag{3.7}$$

the maximum height of the cusp occurring for α_M

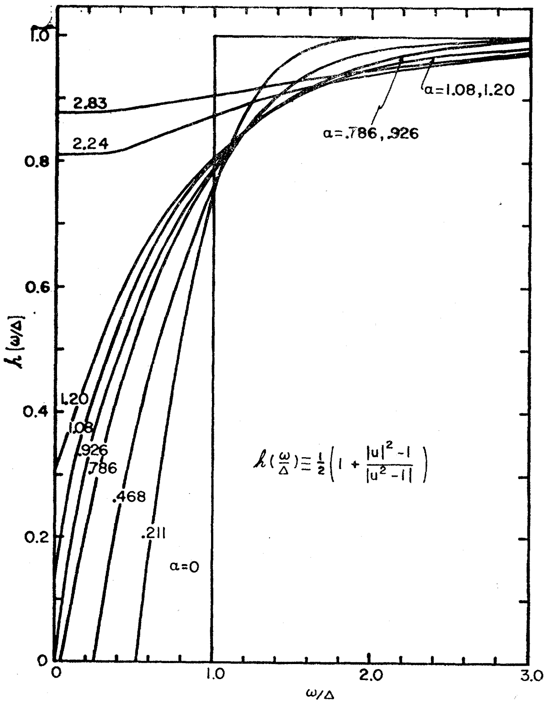

FIG. 1. The function $h(\omega/\Delta,\alpha)$ versus ω/Δ for various values of $\alpha=(\tau_S\Delta)^{-1}$; τ_S and $\Delta(T,\tau_S)$ are the exchange scattering time and temperature-dependent, impurity averaged Gor'kov order parameter, respectively.

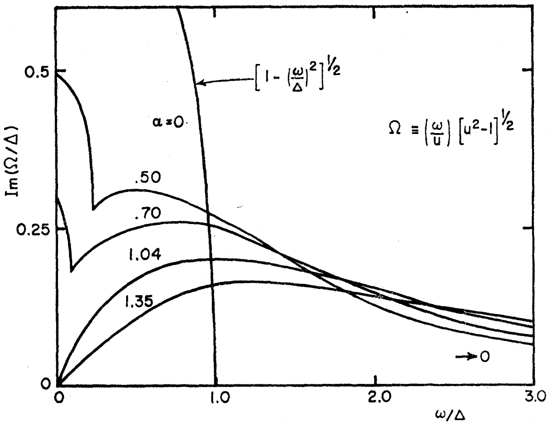

FIG. 2. The imaginary part of $\Omega(\omega)/\Delta$ vs ω/Δ, for various values of α. This function occurs in the denominator of the integrand of (3.1) and is defined in (2.30).

$=3^{-3/2}\simeq 0.192$. Finally, we note that

$$\operatorname{Im}\left[\frac{\Omega(\omega=0)}{\Delta}\right]=(1-\alpha) \quad \text{for} \quad \alpha<1,$$
$$=0 \qquad \text{for} \quad \alpha>1$$

and that the maximum value of $\operatorname{Im}(\Omega(\omega)/\Delta)$ is unity.

We now want to show that the first and last terms in the denominator of (3.1) are negligible if we make the reasonable assumption

$$\tau_{\text{tr}}^{(1)} \ll \tau_S \leq \tau_S' . \tag{3.8}$$

It is clear that

$$\frac{1}{2\tau_{\text{tr}}^{(1)}} \gg \frac{1}{\tau_S'}[1-h(\omega/\Delta,\alpha)] \tag{3.9}$$

follows directly from (3.8). This approximation reduces (3.1) to a form identical to (2.29), except for the replacement of the scattering cross section by the correct transport cross section. We next want to show that (3.8) generally implies

$$\frac{1}{2\Delta\tau_{\text{tr}}^{(1)}} \gg \operatorname{Im}\left[\frac{\Omega(\omega)}{\Delta}\right] \quad \text{for} \quad \omega \geq \omega_0 . \tag{3.10}$$

We need only consider the region $\omega \geq \omega_0$ as a result of the function $h(\omega/\Delta,\alpha)$ in the numerator of (3.1). For large α (say $\alpha \gtrsim 0.1$), it is clear from Fig. 2 and (3.7) that (3.8) implies (3.10). For very small α, however, (3.10) may not be satisfied. The inverse of the first two terms in the denominator of (3.1) plays the role of a frequency-dependent mean free path. While we shall not consider the third term any further in this paper, we would like to emphasize that the analytic approximations for K_s/K_n which we discuss later in this section do include the decrease in the generalized mean free path if it is significant.

In general, the exchange potential $V_2(x)$ is somewhat smaller than the direct potential $V_1(x)$—estimates[1,4,11] range from 3 to 10 times smaller. Even a factor of 3 would amply ensure the correctness of our basic approximation (3.8). However, one can almost always assume the latter to be valid due to the presence of nonmagnetic impurities in addition to the paramagnetic impurities of interest. Thus, the total direct scattering would be the sum of the contributions from both kinds of impurities while the exchange scattering would be unaffected by nonmagnetic impurities. It seems significant that at the critical concentration, $(1/\tau_S)_{\text{cr}} = \frac{1}{2}\Delta_p(0)$, and hence the "critical exchange mean free path" is of the same order as the coherence distance in a pure metal ($\xi_0 \simeq 10^{-4}$ cm).

In summary then, we have shown that if the exchange scattering is much smaller than the nonexchange scattering, the electronic thermal conductivity of a superconducting alloy with paramagnetic impurities is given by

$$K_s = \frac{n2\tau_{\text{tr}}^{(1)}}{4mk_BT^2}\int_{\omega_0(\Delta,\alpha)}^{\infty} d\omega\omega^2 \operatorname{sech}^2(\tfrac{1}{2}\beta\omega)h(\omega/\Delta,\alpha) , \tag{3.11}$$

where the function h is defined in (3.2). Actually the terms omitted in the denominator of (3.1), though small, are positive and hence K_s given by (3.11) is in the nature of an "upper limit" approximation to (3.1). We hasten to add that (3.11) is actually an extremely good approximation to (3.1), given (3.8). A very crude, but still useful, estimate of a lower bound may be obtained by multiplying our upper bound by the factor

$$(1+2\tau_{\text{tr}}^{(1)}\Delta)^{-1}, \tag{3.12}$$

since the maximum value of $\operatorname{Im}(\Omega(\omega)/\Delta)$ is unity. What is of special interest is the ratio of K_s to K_n (the normal state electronic thermal conductivity) which is given by (1.1) of the introduction. This ratio is a function of the exchange scattering time τ_S and hence will not be a universal curve as in the case of nonmagnetic impurities. While the derivation of (1.1) requires no assumption (compare Ref. 17) about the relative magnitude of k_BT, $\Delta(T,\tau_S)$ and $1/\tau_{\text{tr}}^{(1)}$, we might note that in the interesting "gapless" region [$\alpha>1$, for which $\omega_0(\Delta,\alpha)=0$], one is effectively in the "dirty limit" [where $\Delta(T,\tau_S)\tau_{\text{tr}}^{(1)} \ll 1$] as a result of (3.8).

It should be clear that even in the "gapless" region, K_s/K_n is still less than unity. Indeed, this can be studied analytically in the somewhat academic region of 0°K (academic because the main heat carriers at such temperatures are phonons and the main dissipative mechanism for the latter are the specimen boundaries). Since $\omega^2 \operatorname{sech}^2(\frac{1}{2}\beta\omega)$ is peaked around $\omega \simeq 2.5k_BT$, for sufficiently low temperatures the main contribution of the integral in (3.12) will come from the neighborhood of ω_0. Thus following the lead of Abrikosov and Gor'kov[1] in their evaluation of the electronic specific heat, it is useful to expand the right-hand side of (3.3) in a power series in $u-u_0$ if $\alpha<1$, with $u_0\equiv u(\omega_0/\Delta,\alpha)=(1-\alpha^{2/3})^{1/2}$. To lowest order, we find

$$u=u_0-i[(\omega-\omega_0)/\Delta]^{1/2}(\tfrac{2}{3})^{1/2}\alpha^{1/3}u_0^{-1/2}. \qquad (3.13)$$

Now for the purposes of using (3.13), a slightly more practical version of (3.2) is

$$h(\omega/\Delta,\alpha)=\left\{\mathrm{Re}\frac{u(\omega/\Delta,\alpha)}{[u^2(\omega/\Delta,\alpha)-1]^{1/2}}\right\}^2 - \left\{\mathrm{Re}\frac{1}{[u^2(\omega/\Delta,\alpha)-1]^{1/2}}\right\}^2. \qquad (3.14)$$

Combining (3.3) with (3.14), and using (3.13) consistently to lowest order, we find for $\omega\gtrsim\omega_0$

$$h(\omega/\Delta,\,\alpha<1)=(2/3\Delta)\alpha^{-2/3}(1-\alpha^{2/3})^{-1/2}(\omega-\omega_0). \qquad (3.15)$$

For $\alpha>1$, a low temperature expansion may be found by expanding (2.23) in a power series in $[u-i(\alpha^2-1)^{1/2}]$. To lowest order,

$$u=i(\alpha^2-1)^{1/2}-(\omega/\Delta)\alpha^2(1-\alpha^2)^{-1} \qquad (3.16)$$

and proceeding as for the case $\alpha<1$, we find for $\omega\gtrsim 0$

$$h(\omega/\Delta,\,\alpha>1)=(1-\alpha^{-2})+0(\omega^2/\Delta^2). \qquad (3.17)$$

Inserting (3.15) and (3.17) into (2.29), we conclude (see also Ref. 17) that in the limit of $T\to 0$,

$$K_s/K_n=\frac{4}{\pi^2}(\alpha^{-2/3}-1)\frac{\omega_0}{k_BT}e^{-\omega_0/k_BT}\left[\frac{\tau^{(1)}}{\tau^{(2)}}+\frac{2\tau^{(1)}}{\tau_S}\alpha^{-2/3}\right]^{-1} \quad \text{for } \alpha<1, \qquad (3.18a)$$

$$K_s/K_n=(1-\alpha^{-2}) \quad \text{for} \quad \alpha>1. \qquad (3.18b)$$

The omission of the $\Omega(\omega)$ term in (3.1) is equivalent to setting the last factor in (3.18a) to unity. Actually the expansion around ω_0 in (3.13) is only a good approximation if $k_BT/\Delta\ll\alpha^{2/3}$. Since (3.18a) assumes $k_BT/\Delta\ll(1-\alpha^{2/3})^{3/2}$ as well, we see that it is only correct for intermediate impurity concentrations. This is the reason we do not obtain the well-known result for $1/\tau_s=0$.

In Fig. 3, we give numerical results for K_s/K_n as a function of the reduced temperature T/T_c (where T_c is the transition temperature for a given concentration of paramagnetic impurities) and the paramagnetic impurity concentration n_i. We have found it instructive to give the latter in terms of the critical concentration (n_{cr}) required to destroy superconductivity completely. It should, of course, be understood that what comes into all the relevant formulas is the exchange scattering time τ_S defined by (2.26),

$$\frac{1}{\tau_S}=n_i2\pi N(0)\int\frac{d\Omega}{4\pi}|V_2(k_F,\theta)|^2\frac{S(S+1)}{4}.$$

In our numerical calculations, we have used the BCS expression for the order parameter $\Delta_p(T)$ at 0°K, namely, $\Delta_p(0)=1.76k_BT_{cp}$, where T_{cp} is the transition temperature for $n_i=0$. AG evaluated the temperature and impurity-dependent Gor'kov order parameter $\Delta(T,n_i)$ only at $T=0$°K. We have derived in Appendix A a useful expansion which enables one to compute $\Delta(T,n_i)$ for $(\Delta/\pi T)\ll 1$, i.e., near T_c. The computed order parameters for various concentrations are plotted in Fig. 4 as a function of T/T_{cp}. From the point of view of Fig. 3, which gives K_s/K_n as a function of T/T_c, the order parameters increase with impurity concentration—each Δ in Fig. 4 being scaled up by a factor (T_{cp}/T_c). Some values of the true energy gap $\omega_0(T,n_i)$ are plotted in Fig. 5, based on (3.5) and the curves in Fig. 4.

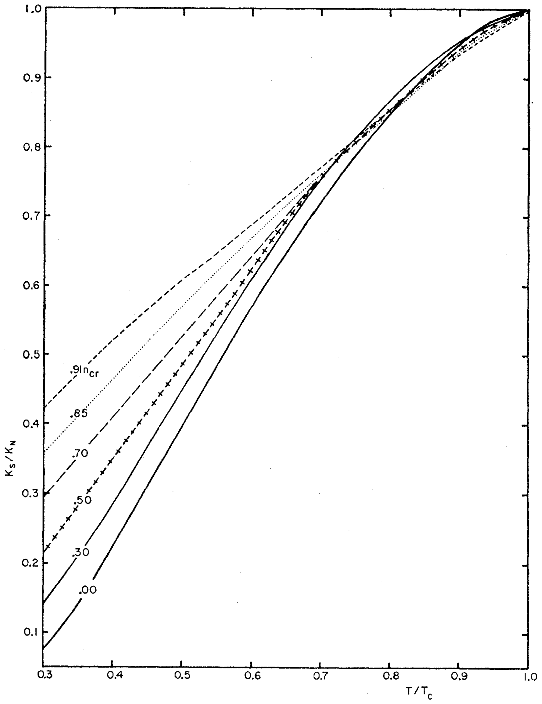

FIG. 3. The ratio of the electronic thermal conductivity in the superconducting and normal states (K_s/K_n) vs $t\equiv T/T_c$ for various paramagnetic impurity concentrations. T_c is the transition temperature for the relevant impurity concentration, the latter being expressed in terms of n_{cr}, the concentration required to completely destroy superconductivity. The curve for nonmagnetic impurities alone is denoted by $n_i=0.00n_{\mathrm{cr}}$. The $n_i=0.70n_{\mathrm{cr}}$ curve is almost identical to the 0.85 curve for $t\gtrsim 0.7$ and is not shown explicitly in this region. These results are based on (1.1) or (3.11).

In examining Fig. 3, one should use the curve corresponding to nonmagnetic impurities as a guide (this curve is independent of concentration in our isotropic, BCS-type superconductor). Undoubtedly the most interesting feature of these curves is the crossover in paramagnetic impurity concentration dependence. We note that for $t\equiv T/T_c\gtrsim 0.9$, K_s/K_n decreases with n_i. (All the curves drawn in Fig. 3 go to zero for $t=0$.) This odd dependence merits a few more words. As we previously noted, by normalizing our results to $T_c(n_i)$, we are effectively scaling the order parameter $\Delta(n_i)$ in Fig. 4 by a factor (T_{cp}/T_c). We shall denote this

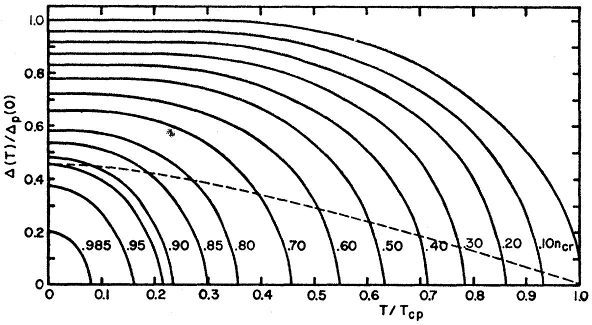

FIG. 4. The Gor'kov order parameter $\Delta(T,\tau_S)$ for a paramagnetic alloy (relative to its value in a pure metal at $T=0$°K) as a function of the temperature (relative to the transition temperature of a pure metal). The dashed curve is defined by $\Delta(T,\tau_S)\tau_S=1$, τ_S^{-1} being proportional to the impurity concentration n_i [see (2.26)]. For a given value of n_i, the gapless region occurs for temperatures $T_g \leq T < T_c$, where T_c is the transition temperature for that concentration and T_g is the temperature at which the dashed curve crosses $\Delta(T,n_i)$. The minimum value of n_i at which gaplessness occurs down to 0°K is $\exp(-\pi/4)n_{\mathrm{cr}} \simeq 0.91 n_{\mathrm{cr}}$, assuming the relation $\Delta_p(0)=1.76T_{cp}$. The curve for this concentration is not labeled.

"effective" order parameter by $\Delta'(t)=\Delta(T/T_{cp})T_{cp}/T_c$. In addition, let us make the useful change of variable $\omega \longrightarrow \beta\omega$ in (1.1), with the result

$$\frac{K_s}{K_n}(t)=\frac{3}{2\pi^2}\int_0^\infty d\omega\omega^2 \operatorname{sech}^2(\tfrac{1}{2}\omega)h\left(\frac{\omega}{\phi'},\alpha=\frac{1}{\tau_S\Delta(T/T_{cp})}\right),$$

where $\phi'(t)\equiv\Delta'(t)t^{-1}(k_BT_{cp})^{-1}$. This equation has the advantage that the dependence of $K_s/K_n(t)$ on t and n_i is completely contained in $h(\omega/\phi',\alpha)$, which is plotted in Fig. 1. As one builds up the impurity concentration (or, more precisely, $1/\tau_S$) from zero, both $\phi'(t)$ and α increase [note $\Delta'(t)$ increases but $\Delta(T/T_{cp})$ decreases]. However, the increase in $\phi'(t)$ will tend to *decrease* K_s/K_n, while the increase in α will tend to *increase* K_s/K_n. A careful investigation of the criterion under which the former dominates leads to the conclusion that $\phi'(t, n_i=0)$ must be somewhat less than unity. When $\phi'(t, n_i=0)$ is small, any increase is important. When it is large ($\gg1$), an increase in $\phi'(t)$ is less significant. Note that for sufficiently large concentrations, $\phi'(t)$ becomes independent of n_i [see (A37′)] and hence K_s/K_n *must* increase.

Actually, one may study analytically the odd concentration dependence discussed in the preceding paragraph by making use of the fact that $\alpha\gg1$ for T sufficiently close to T_c. With the expansion of u in (A24) of Appendix A, we find from (2.29)

$$\frac{K_s}{K_n}=1-\left(\frac{3}{2\pi^2}\right)\beta^3\int_0^\infty d\omega\omega^2 \operatorname{sech}^2(\tfrac{1}{2}\beta\omega) \times\frac{\alpha^2}{\left[\left(\frac{\omega}{\Delta}\right)^2+\alpha^2\right]^2}, \tag{3.19}$$

where we have neglected terms $0(\Delta^4)$ and higher. For low impurity concentrations $0<\rho_{Sc}=(\pi\tau_Sk_BT_c)^{-1}\ll1$, we may set $\operatorname{sech}^2(\frac{1}{2}\beta\omega)$ to unity in (3.19), and hence

$$K_s/K_n=1-(3/8\pi)(\Delta/k_BT)^3\alpha. \tag{3.20}$$

Combining this result[17] with (A36′), we find

$$K_s/K_n(t)=1-[3\pi^2/14\zeta(3)\gamma](n_i/n_{\mathrm{cr}})[(1-t)/t], \tag{3.21}$$

and hence $K_s/K_n(t)$ *decreases* with n_i for low concentrations with t sufficiently close to 1. If $\rho_{Sc}\gg1$, we may omit $(\omega/\Delta)^2$ in the denominator of (3.19) with the result that K_s/K_n is given by (3.18b) again. Upon using (A37′) and (A34′), this reduces to

$$K_s/K_n(t)=1-12\ln(n_{\mathrm{cr}}/n_i)(1-t^2). \tag{3.22}$$

Actually (3.22) is valid for low temperatures as well. We note that for sufficiently high concentrations [such that (3.22) is valid], $K_s/K_n(t)$ *increases* with n_i. Eventually the anomalous concentration dependence of $K_s/K_n(t)$ must reverse itself.

As we remarked in the Introduction, the onset of gaplessness does not give rise to any "structure" in K_s/K_n. For example, ω_0 first vanishes at $t=0.616$ for $n_i=0.85n_{\mathrm{cr}}$ in Fig. 3.

4. CONCLUDING REMARKS

The Abrikosov-Gor'kov description of a superconductor with a small concentration of paramagnetic impurities has been used in this paper to work out the electronic thermal conductivity of such alloys. We believe that a comparison of our results (as summarized

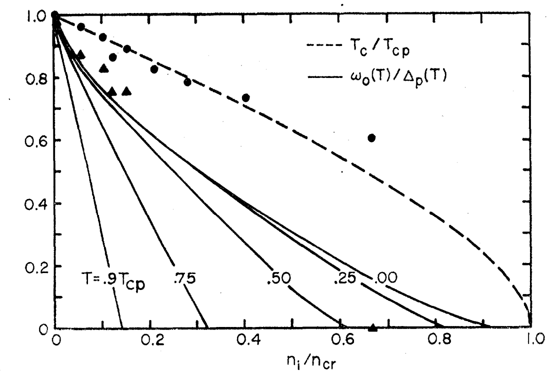

FIG. 5. The transition temperature T_c and energy gap ω_0 as a function of paramagnetic impurity concentration (both normalized to unity, i.e., a pure metal). The energy gap is given for various fractions of the transition temperature of the pure metal. The closed circles and triangles are the data points of Reif and Woolf (Ref. 2) (T_c and ω_0, respectively) for Fe impurities in quenched In films. The energy gap was measured by tunneling techniques at 1°K, which would correspond to the $T=0.25T_{cp}$ curve. Since experimentally $\Delta_p(0)=1.9T_{cp}$, the correct ω_0 curves for comparison would decrease slightly slower than those shown. The initial reduction in T_c was fitted to the theoretical curve of AG and from this the relation between percent Fe impurities and percent critical concentration found ($0.70n_{\mathrm{cr}}\simeq1\%$ Fe). The experimental values of the energy gap could then be plotted. According to Ref. 2, the tunneling curves are those of a normal metal for Fe impurity concentrations greater than 0.85%, or $n_i\simeq0.6n_{\mathrm{cr}}$.

in Fig. 3) with experimental observations will provide a useful test of the basic correctness of the AG theory. Conversely, these theoretical results may be used to estimate the value of the exchange scattering time τ_S and the energy gap $\omega_0(T,\tau_S)$ from experimental data.

One may think of the paramagnetic impurities as modifying both the superfluid condensate [due to the change in $\Delta'(t)$] as well as the excitation spectrum (through the change in α). In this sense, the initial decrease and final increase in K_s/K_n at high temperatures gives graphic evidence of how transport properties in superconductors may separately depend on the superfluid condensate as well as on the normal fluid.

Although calculations of transport properties in the AG[28] model are easy, as the preceding sections have shown, we believe that some light remains to be shed on the physical basis of the theory. The central point that emerges from our calculation is that the condensation phenomenon is the essential characteristic of the superconducting state. It would thus appear that for persistent currents with or without an energy gap the key requirement is that pair states, whose average momentum cannot be changed by single particle scattering, be macroscopically occupied. The reduced thermal conductivity in the gapless superconducting state is evidently also due to the macroscopic occupation, the paired states carrying no entropy. The stability of the paired states in the presence of a gapless excitation spectrum is however something for which a simple physical explanation seems to us to be lacking. In this connection, a study of the spatial variations of the order parameter would be useful. If, for example, "depairing" occurs only in the vicinity of paramagnetic impurities, the superflow may simply be circumventing these obstacles.[29] A study of these questions is planned.

That the Gor'kov parameter $\Delta(T)$ is not equivalent to the energy gap $\omega_0(T)$ in the excitation spectrum has been realized in other contexts as well. Even though one cannot in general define a single particle excitation spectrum from the poles of such expressions as (2.20), one may always define an energy gap as the lowest frequency ω_0 at which the diagonal component of $\mathcal{G}(k,\omega)$ has a discontinuity on the real ω axis. This generalized concept of an energy gap has been extensively discussed in the case of pure, strongly coupled superconductors[21,30] and for anisotropic superconductors with nonmagnetic impurities.[31–33] What is peculiar to paramagnetic impurities is not so much the degree to which they decrease ω_0 relative to Δ—with ω_0 even vanishing—but the sharpness of the threshold. The density-of-states increases rapidly as soon as ω passes ω_0 in paramagnetic alloys.

The effect of the indirect impurity spin interaction brought about by the polarization effect of the conduction electrons has not been considered in this paper. As we mentioned in the Introduction, this coupling may lead to ferromagnetism at sufficiently high impurity concentrations.[11] However, it may also be of some importance at lower concentrations.[34] We plan to return to these questions. Of course, even these refinements are a long way from a complete theory which would discuss the dynamics of the impurity spins as well as that of the conduction electrons. Again we reiterate that the AG approximation should be quite good at low enough concentrations of paramagnetic impurities.

It is perhaps worth remarking that the Hartree-Fock approximation to the electronic thermal conductivity is given by (2.29) for a wide class of superconductors. The function $u(z)$ which occurs in (2.29) and (2.30) is defined by $zZ(z)/\varphi(z)$, with $Z(z)$ and $\varphi(z)$ being given by the single particle Green's function matrix (2.20). In the problem considered in detail in this paper, $u(z)$ was determined by (2.23). In a previous paper[21] by Tewordt and one of the authors (V.A.), the coupled integral equations for $Z(z)$ and $\varphi(z)$ were given for a pure superconductor with strong electron-phonon coupling in the weak momentum approximation (Z and φ have no momentum dependence). If one wished to compute the electronic thermal conductivity of an anisotropic, weakly coupled superconductor with nonmagnetic or even paramagnetic impurities, (2.29) would again hold except that $u(z,\hat{\Omega})$ would now depend on the direction $\hat{\Omega}$ and there would be an angular integration $\int d\Omega/4\pi$ in addition to the frequency integral. [See Eqs. (A18′) and (A19′) in Appendix A of this paper.] Gor'kov and Rusinov[11] have determined the analog of (2.23) if the concentration of paramagnetic impurities is large enough to warrant consideration of the resulting constant exchange field.

Finally we wish to comment briefly on the thermal conductivity of thin superconducting films (containing nonmagnetic impurities) in the presence of uniform persistent currents or a constant magnetic field parallel to its surface. Maki has suggested, in a series of papers,[18] that these latter systems (in the dirty limit $\tau^{(1)}\Delta\ll 1$) formally resemble superconductors with paramagnetic impurities[1] if one makes the appropriate reinterpretation of the parameter α. In the case of a uniform supercurrent Maki's theory is quite straightforward and leads to the result that α is proportional to the square of the flow momentum. Our numerical results for K_s/K_n should be directly applicable, care being taken that in measuring the thermal conductivity, a "compensated geometry"

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[28] Calculations of ultrasonic attenuation and the nuclear spin relaxation time have been completed by one of the present authors (AG); see *Proceedings of the Ninth International Conference on Low Temperature Physics* (Plenum Press, New York, to be published).

[29] We gratefully acknowledge several discussions with G. Rickayzen on this question.

[30] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963).

[31] T. Tsuneto, Progr. Theoret. Phys. (Kyoto) **28**, 857 (1962).

[32] D. Markowitz and L. P. Kadanoff, Phys. Rev. **131**, 563 (1963).

[33] P. Hohenberg, Zh. Eksperim. i Teor. Fiz. **45**, 1208 (1963) [English transl.: Soviet Phys.—JETP **18**, 834 (1964)].

[34] P. W. Anderson and H. Suhl, Phys. Rev. **116**, 898 (1959).

be used to minimize screening effects due to the supercurrents (for example, a thin film on the outside of a hollow cylinder). We might remark that one can easily generalize Maki's analysis to cover the case of paramagnetic impurities. If the center-of-mass velocity of the Cooper pairs is v, one has

$$\frac{\omega}{\Delta}=u\left[1-\frac{i(\alpha+\zeta)}{(u^2-1)^{1/2}}+0(\zeta\tau^{(2)}\Delta)\right], \qquad (4.1)$$

where $u=\tilde{\omega}/\tilde{\Delta}$, $\alpha=1/\tau_S\Delta$, and

$$\zeta\equiv\tfrac{2}{3}(vk_F)^2\frac{[\tau^{(2)}]^2}{\tau^{(1)}\Delta}. \qquad (4.2)$$

The derivation of (4.1) requires, just as in the special case $1/\tau_S=0$, that the impurities give rise to pure s-wave scattering, that Δ is spatially independent and, finally, terms of order $\tau^{(2)}\Delta$ and higher are negligible. The similarity between persistent currents and paramagnetic impurities comes from the breakdown of time reversal invariance of the single particle Hamiltonian in both cases; the Cooper pairs are hindered from forming as a result.[4] Finally we note that our Hartree-Fock calculation of K_s/K_n is somewhat more accurate than Maki's since it includes the decrease in the generalized mean free path. However this leads only to corrections of order $(\tau^{(1)}\Delta)$.

Maki's analysis of the effect of a constant magnetic field parallel to the surface of a very thin film leads to the conclusion that α is now proportional to the square of the magnetic field. This case is of some interest in view of the extensive experimental work of Morris and Tinkham.[16] These authors reduced their thermal conductivity data by using the well-known formula of Bardeen, Rickayzen, and Tewordt[15] [see (2.33) of the present paper] and hence found, supposedly, the magnetic field dependence of the energy gap. While Maki's discussion is suggestive, there seems to be some question as to the correct point in the calculation to average over the vector potential $\mathbf{A}(\mathbf{x})$.[35] Maki's procedure is to use volume-averaged self-energies. We might remark that Maki's analysis should also apply to a rotating cylindrical film.

On the whole, Morris and Tinkham's (MT) results for indium films are in agreement with what one would expect *if* Maki's theory were correct. Considering that MT used a step function instead of the correct $h(\omega/\Delta,\alpha)$ given in Fig. 1, their value of ω_0 should be and is slightly larger than the predicted value—further, both *decrease* with T for a given value of $H^2/H_c^2(T)$. The field $H_c(T)$ destroys superconductivity at the temperature T, and may be read from Fig. 5, since $n_i/n_{cr}\Rightarrow H^2/H_c^2(0)$. Indeed, if we expand the horizontal scale of $\omega_0(T)$ by $H_c^2(T)/H_c^2(0)$, we automatically have $\omega_0(T)$ as a function of $H^2/H_c^2(T)$. We might remark that for $T=0.9T_{cp}$, Maki's approach gives $\omega_0(H)/\Delta p(T)\simeq[1-H^2/H_c^2(T)]$. We should point out that Meservey and Douglass[36] have determined the magnetic field dependence of ω_0 for thin aluminum films using tunneling experiments and though their results are in qualitative agreement with Maki's predictions, there is the important difference that ω_0 *decreases* as T increases, ω_0 being considered as a function of $H^2/H_c^2(T)$.

ACKNOWLEDGMENTS

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APPENDIX A

The main purpose of this Appendix is to sketch the derivation of Eqs. (2.20)–(2.23), while incidentally reviewing some salient features of the Abrikosov-Gor'kov theory of superconducting alloys. We shall use the same notation as in Sec. 2, the Hamiltonian of the "alloy" being given in (2.1).

The single particle Green's function matrix defined by (2.14) may be written more explicitly as

$$\mathcal{G}(\mathbf{x},\mathbf{x}';\zeta_l)=\begin{pmatrix} G_{\alpha\beta}(\mathbf{x},\mathbf{x}';\zeta_l) & -iF_{\alpha\beta}(\mathbf{x},\mathbf{x}';\zeta_l) \\ -i\bar{F}_{\alpha\beta}(\mathbf{x},\mathbf{x}';\zeta_l) & -\tilde{G}_{\alpha\beta}(\mathbf{x},\mathbf{x}';\zeta_l) \end{pmatrix}, \qquad (A1)$$

where we have already Fourier transformed over the time-difference variables along the imaginary time axis and $\tilde{G}_{\alpha\beta}(\mathbf{x},\mathbf{x}';\zeta_l)\equiv G_{\beta\alpha}(\mathbf{x}',\mathbf{x};-\zeta_l)$. A straightforward investigation of the equations of motion for $G_{\alpha\beta}$ and $F_{\alpha\beta}$ shows that they may be summarized by the matrix equation

$$\begin{pmatrix} \zeta_l-h_{\alpha\beta}(\mathbf{x}) & -\Delta_{\alpha\beta}(\mathbf{x}) \\ \Delta_{\alpha\beta}^*(\mathbf{x}) & \zeta_l+h_{\alpha\beta}{}^t(\mathbf{x}) \end{pmatrix}\mathcal{G}(\mathbf{x},\mathbf{x}';\zeta_l)=\delta(\mathbf{x}-\mathbf{x}')\begin{pmatrix} 1_{\alpha\beta} & 0 \\ 0 & 1_{\alpha\beta} \end{pmatrix}, \qquad (A2)$$

where we have made use of the relation $F_{\alpha\beta}(\mathbf{x},\mathbf{x}';\zeta_l)=-F_{\beta\alpha}(\mathbf{x}',\mathbf{x};-\zeta_l)$. We have also introduced the abbreviations $\Delta_{\alpha\beta}(\mathbf{x})=g\langle\psi_\alpha(\mathbf{x})\psi_\beta(\mathbf{x})\rangle$ and

$$h_{\alpha\beta}(\mathbf{x})=\delta_{\alpha\beta}\left[-\frac{\nabla^2}{2m}-\mu+\Sigma_n V_1(\mathbf{x}-\mathbf{R}_n)\right] +\Sigma_n V_2(\mathbf{x}-\mathbf{R}_n)\mathbf{S}\cdot\frac{\boldsymbol{\sigma}_{\alpha\beta}}{2}\equiv h_{\beta\alpha}{}^t(\mathbf{x}). \qquad (A3)$$

At this stage, we have not made any average over the positions of the random, static impurities. However we shall and as a result homogeneity will be restored (momentum will be conserved at each impurity vertex in the scattering diagrams in momentum space) and the Fourier transform of (A1) will be $\mathcal{G}(\mathbf{k},\mathbf{k}';\zeta_l)=\mathcal{G}(\mathbf{k};\zeta_l)\delta(\mathbf{k}-\mathbf{k}')$.

If we could assume that the order parameter $\Delta(\mathbf{x})$ was essentially unchanged from its value in a pure metal by the presence of the impurities, we could solve (A2) by iterating it in the impurity potential and making the usual impurity average.[24] However, the presence of the exchange term in (A3), which leads to large changes in Δ, requires that a slightly different procedure be used. One way of proceding is to go back one step and introduce the original electron-phonon interaction (in our 4×4 space) which

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[35] This was first suggested to the authors by G. Rickayzen in a discussion of the magnetic field dependence of the transition temperature of thin films.

[36] R. Meservey and D. H. Douglass, Jr., Phys. Rev. **135**, A24 (1964).

gives rise to the effective electron-electron interaction in (2.1). Then we may treat the electron-phonon and electron-impurity coupling on an equal footing and look for nonperturbative solutions of the equations of motion. This procedure is essentially a generalization to a 4×4 space of the approach used by Nambu[37] in a pure metal and by others to discuss the effect of nonmagnetic impurities (see, for example, the recent paper by Markowitz and Kadanoff[32]). Our major concern in this Appendix is to understand the effects of the impurity exchange interaction and we shall consequently content ourselves with a very crude model of the electron-phonon coupling—one consistent with (2.1).

We define a matrix self-energy $\mathbf{\Sigma}(\mathbf{k},\zeta_l)$ in a formally identical fashion as one does in a 1-component space,

$$\mathcal{G}^{-1}(\mathbf{k};\zeta_l)=\zeta_l 1\times 1-\epsilon_{\mathbf{k}}\tau_3\times 1-\mathbf{\Sigma}(\mathbf{k},\zeta_l)\equiv\mathcal{G}_0^{-1}(\mathbf{k},\zeta_l)-\mathbf{\Sigma}(\mathbf{k},\zeta_l)\,. \tag{A4}$$

Infinite-order perturbation theory of the usual kind may be used to expand $\mathbf{\Sigma}(\mathbf{k},\zeta_l)$ in the electron-phonon interaction and

$$V=\begin{pmatrix} V_{\alpha\beta} & 0 \\ 0 & -V_{\alpha\beta}{}^t \end{pmatrix} \tag{A5}$$

[see (A2)], using $\mathcal{G}_0(\mathbf{k},\zeta_l)$ as the unperturbed propagator. We shall determine $\mathbf{\Sigma}(\mathbf{k},\zeta_l)$ self-consistently by equating an "ansatz" with the lowest order diagrams [expressed in terms of the true propagator $\mathcal{G}'(\mathbf{k},\zeta_l)$] contributing to the self-energy. We shall neglect all contributions of order $(k_Fl)^{-1}$, where $l=v_F\tau^{(1)}$, and hence assume that the density of impurities is not too large ($l\gg a$, where a is the interatomic lattice spacing).

To lowest order, then, the 4×4 matrix self-energy is the sum of two self-energy diagrams. The interaction leading to superconductivity gives rise to the off-diagonal component of

$$\mathbf{\Sigma}_s(k,\zeta_l)=-i\left(\frac{1}{-i\beta}\right)\Sigma_{l'}\int\frac{d^3k'}{(2\pi)^3}g\tau_3\times 1\mathcal{G}(\mathbf{k}-\mathbf{k}',\zeta_l-\zeta_{l'})\tau_3\times 1 \tag{A6}$$

or

$$\Sigma_s|_{\text{o.d.}}=g\left(\frac{-1}{\beta}\right)\Sigma_l\int\frac{d^3k}{(2\pi)^3}\mathcal{G}(\mathbf{k},\zeta_l)|_{\text{o.d.}}\,. \tag{A7}$$

We remark that this will turn out to be proportional to $\tau_2\times\sigma_2$, and the impurity averaged order parameter $\bar{\Delta}$ will be defined by

$$\Sigma_s|_{\text{o.d.}}=-\bar{\Delta}\tau_2\times\sigma_2\,. \tag{A8}$$

Since the paramagnetic impurities are randomly distributed, the self-energy due to electron-impurity scattering will be given by the usual Born approximation. This contribution to $\mathbf{\Sigma}(\mathbf{k},\zeta_l)$ is[27]

$$\Sigma_i(\mathbf{k},\zeta_l)=4\int\frac{d^3k'}{(2\pi)^3}\langle V_T(\mathbf{k}')\mathcal{G}(\mathbf{k}-\mathbf{k}',\,\zeta_l)V_T(-\mathbf{k}')\rangle_I\,, \tag{A9}$$

where $\langle\cdots\rangle_I$ denotes an impurity position average and the Fourier transformed impurity potential in our 4-component space is [see (A5)]

$$\begin{aligned}2V_T(\mathbf{q})=1\times\frac{\sigma_2}{2}\,&\Sigma_n\,V_2(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{R}_n)S_y{}^n\\ &+\tau_3\times 1\,\Sigma_n\,V_1(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{R}_n)\\ &+\tau_3\times\frac{\sigma_1}{2}\,\Sigma_n\,V_2(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{R}_n)S_x{}^n\\ &+\tau_3\times\frac{\sigma_3}{2}\,\Sigma_n\,V_2(\mathbf{q})\exp(-i\mathbf{q}\cdot\mathbf{R}_n)S_z{}^n.\end{aligned} \tag{A10}$$

In calculating $\mathbf{\Sigma}_i(\mathbf{k},\zeta_l)$, we shall further assume that there is no impurity spin-spin correlation. Inserting (A10) into (A9) and making use of (2.18), we find

$$\begin{aligned}\Sigma_i(k,\zeta_l)=n_i\int\frac{d^3q}{(2\pi)^3}\frac{S(S+1)}{3.4}&|V_2(\mathbf{q})|^2(1\times\sigma_2\mathcal{G}1\times\sigma_2)\\ &+n_i\int\frac{d^3q}{(2\pi)^3}\frac{S(S+1)}{3.4}|V_2(\mathbf{q})|^2\\ &\times(\tau_3\times\sigma_3\mathcal{G}\tau_3\times\sigma_3+\tau_3\times\sigma_1\mathcal{G}\tau_3\times\sigma_1)\\ &+n_i\int\frac{d^3q}{(2\pi)^3}|V_1(\mathbf{q})|^2(\tau_3\times 1\mathcal{G}\tau_3\times 1)\,,\end{aligned} \tag{A11}$$

where $\mathcal{G}\equiv\mathcal{G}(\mathbf{k}-\mathbf{q},\,\zeta_l)$. Of course, due to the assumed isotropic nature of the exchange interaction, we really need only consider one component of $\mathbf{S}$ explicitly. An obvious generalization is to consider the possibility that, say, $\langle\Sigma_n\,S_z{}^n\rangle$ is a nonzero constant.[11] If so, we should also have considered the contribution of the constant exchange field to $\mathbf{\Sigma}_i(\mathbf{k},\zeta_l)$, which is not included in (A9).

To determine $\mathcal{G}(\mathbf{k},\zeta_l)$, we make the ansatz

$$\mathcal{G}^{-1}(k,\zeta_l)=\tilde{\zeta}_l(1\times 1)-\epsilon_k(\tau_3\times 1)+\tilde{\Delta}_l(\tau_3\times\sigma_2)\,. \tag{A12}$$

Here the c-number functions $\tilde{\zeta}_l$ and $\tilde{\Delta}_l$ are assumed to depend only on ζ_l and not on k. If we rationalize the denominator of (A12) using the well-known properties of the Pauli matrices, we find

$$\mathcal{G}(k,\zeta_l)=\frac{\tilde{\zeta}_l 1\times 1+\epsilon_k\tau_3\times 1-\tilde{\Delta}_l\tau_2\times\sigma_2}{\tilde{\zeta}_l{}^2-\epsilon_k{}^2-\tilde{\Delta}_l{}^2} \tag{A13}$$

which upon insertion into (A11) gives

$$\begin{aligned}\Sigma_i(k,\zeta_l)=n_i\int\frac{d^3k'}{(2\pi)^3}&|V_1(\mathbf{k}-\mathbf{k}')|^2\frac{\tilde{\zeta}_l 1\times 1+\epsilon_{k'}\tau_3\times 1+\tilde{\Delta}_l\tau_2\times\sigma_2}{\tilde{\zeta}_l{}^2-\epsilon_{k'}{}^2-\tilde{\Delta}_l{}^2}\\ &+n_i\int\frac{d^3k'}{(2\pi)^3}|V_2(\mathbf{k}-\mathbf{k}')|^2\frac{S(S+1)}{12}\\ &\quad\cdot 3\frac{\tilde{\zeta}_l 1\times 1+\epsilon_{k'}\tau_3\times 1-\tilde{\Delta}_l\tau_2\times\sigma_2}{\tilde{\zeta}_l{}^2-\epsilon_{k'}{}^2-\tilde{\Delta}_l{}^2}\end{aligned} \tag{A14}$$

$$\begin{aligned}=n_i\int\frac{d^3k'}{(2\pi)^3}&\left\{|V_1(\mathbf{k}-\mathbf{k}')|^2+\frac{S(S+1)}{4}\right\}|V_2(\mathbf{k}-\mathbf{k}')|^2\\ &\times\frac{\tilde{\zeta}_l 1\times 1+\epsilon_{k'}\tau_3\times 1}{\tilde{\zeta}_l{}^2-\epsilon_{k'}{}^2-\tilde{\Delta}_l{}^2}\\ &+n_i\int\frac{d^3k'}{(2\pi)^3}\left\{|V_1(\mathbf{k}-\mathbf{k}')|^2-\frac{S(S+1)}{4}\right\}\\ &\times|V_2(\mathbf{k}-\mathbf{k}')|^2\frac{\tilde{\Delta}_l\tau_2\times\sigma_2}{\tilde{\zeta}_l{}^2-\epsilon_{k'}{}^2-\tilde{\Delta}_l{}^2}\,.\end{aligned} \tag{A15}$$

In terms of (A13), (A7) becomes

$$\Sigma_s|_{\text{o.d.}}=g\left(-\frac{1}{\beta}\right)\Sigma_l\int'\frac{d^3k}{(2\pi)^3}\frac{\tilde{\Delta}_l}{\tilde{\zeta}_l{}^2-\epsilon_k{}^2-\tilde{\Delta}_l{}^2}(-\tau_2\times\sigma_2)$$

which vindicates (A8), with

$$\bar{\Delta}\equiv g\left(-\frac{1}{\beta}\right)\Sigma_l\int'\frac{d^3k}{(2\pi)^3}\frac{\tilde{\Delta}_l}{\tilde{\zeta}_l{}^2-\epsilon_k{}^2-\tilde{\Delta}_l{}^2}\,. \tag{A16}$$

Actually the sum and integral in (A16) diverge—however, this divergence is removed by noting that we must introduce a cutoff in momentum space (hence the prime) when we use (2.1). If we assume that the impurity potential $V(\mathbf{k}-\mathbf{k}')$ depends only on the angle between $\mathbf{k}$ and $\mathbf{k}'$, owing to its short-range character, we may do the integrals over the kinetic energy in (A15). Referring to Ref. 32 for details, to this approximation we find

$$\Sigma_i(k,\zeta_l)\simeq\Sigma_i(\zeta_l)\simeq\frac{i}{\tau^{(1)}}\frac{\tilde{\zeta}_l 1\times 1}{(\tilde{\zeta}_l{}^2-\tilde{\Delta}_l{}^2)^{1/2}}+\frac{i}{\tau^{(2)}}\frac{\tilde{\Delta}_l\tau_2\times\sigma_2}{(\tilde{\zeta}_l{}^2-\tilde{\Delta}_l{}^2)^{1/2}}\,, \tag{A17}$$

where $\tau^{(1)}$ and $\tau^{(2)}$ are defined in (2.24) and (2.25). Considered as a function of the complex variable $\tilde{z}$, the appropriate branch of the square root is determined by $\mathrm{Im}(\tilde{z}^2-\tilde{\Delta}^2)^{1/2}>0$.

If we now analytically continue our result for $\mathcal{G}^{-1}(k,\zeta_l)$ [see (A4), (A8), and (A17)] to the whole complex plane z,

$$\mathcal{G}^{-1}(k,z)=z(1\times 1)-\epsilon_k\tau_3\times 1+\bar{\Delta}\tau_2\times\sigma_2-\Sigma_i(z)$$

and compare it with the ansatz (A12), we find

$$\tilde{z}=z+\frac{i}{2\tau^{(1)}}\frac{\tilde{z}}{(\tilde{z}^2-\tilde{\Delta}^2)^{1/2}}\,, \tag{A18}$$

$$\tilde{\Delta}=\bar{\Delta}+\frac{i}{2\tau^{(2)}}\frac{\tilde{\Delta}}{(\tilde{z}^2-\tilde{\Delta}^2)^{1/2}}\,, \tag{A19}$$

with $\bar{\Delta}$ being self-consistently defined by (A16) (we shall generally

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[37] Y. Nambu, Phys. Rev. **117**, 648 (1960).

drop the bar on Δ). If we define $u(z)=\tilde{z}/\tilde{\Delta}$, then (A18) gives

$$\tilde{z}=z+\frac{i}{2\tau^{(1)}}\frac{u(z)}{(u^2(z)-1)^{1/2}},$$

while (A19) leads to the alternate form

$$\tilde{z}=u(z)\Delta+\frac{i}{2\tau^{(2)}}\frac{u(z)}{(u^2(z)-1)^{1/2}}.$$

Subtracting the latter equation from the former, we have

$$(z/\Delta)=u(z)-\frac{i}{\Delta}\left[\frac{1}{2\tau^{(1)}}-\frac{1}{2\tau^{(2)}}\right]\frac{u(z)}{(u^2(z)-1)^{1/2}}.$$

This essentially completes the derivation of Eqs. (2.20)–(2.23), apart from some notational changes. It should be clear that in the lowest order approximation used to derive (A18) and (A19), the presence of several kinds of impurities (whether paramagnetic or nonmagnetic) will simply give rise to total scattering times of the kind

$$\frac{1}{\tau_T{}^{(1)}}=\Sigma_j\frac{1}{\tau_j{}^{(1)}};\quad \frac{1}{\tau_T{}^{(2)}}=\Sigma_j\frac{1}{\tau_j{}^{(2)}},$$

where j denotes the impurity species.

If we were dealing with a superconductor with an anisotropic effective electron-electron interaction, an essentially identical discussion would lead to

$$\tilde{z}(z)=z+\frac{i}{2\tau^{(1)}}\int\frac{d\Omega'}{4\pi}\frac{u(z,\hat{\Omega}')}{(u^2(z,\hat{\Omega}')-1)^{1/2}},\tag{A18$'$}$$

$$\tilde{\Delta}(z,\hat{\Omega})=\Delta(\hat{\Omega})+\frac{i}{2\tau^{(2)}}\int\frac{d\Omega'}{4\pi}\frac{1}{(u^2(z,\hat{\Omega}')-1)^{1/2}},\tag{A19$'$}$$

where $u(\hat{\Omega})\equiv\tilde{z}/\tilde{\Delta}(\hat{\Omega})$ and $\hat{\Omega}$ is a unit vector in the direction $\mathbf{k}$. The consequences of (A18′) and (A19′) have been discussed at length by several authors[31–33] for nonmagnetic scattering ($V_2=0$). In the latter case, the anisotropy is crucial since $u=\omega/\Delta$ if $\Delta(\hat{\Omega})$ is independent of orientation.

The spectral density $a(k,\omega)$ of the ordinary single particle Green's function, defined by (2.27), is of particular interest since it is directly related to the probability that a particle put into the system will have energy ω and momentum k. We note that, as defined here, $a(k,\omega)$ satisfies the sum rule

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}a(k,\omega)=1.$$

In general, one has

$$a(k,\omega)=2\,\mathrm{Im}\left\{\frac{\tilde{z}(z)}{\tilde{z}^2(z)-\epsilon_k{}^2-\tilde{\Delta}^2(z)}\right\}\bigg|_{z=\omega-i0^+},\tag{A20}$$

but for simplicity we shall restrict ourselves to the Fermi surface ($k=k_F$) where

$$\begin{aligned}a(k_F,\omega)&=2\,\mathrm{Im}\left\{\frac{u(z)}{[u^2(z)-1]\tilde{\Delta}(z)}\right\}\bigg|_{z=\omega-i0^+}\\&=a(k_F,-\omega).\end{aligned}\tag{A20$'$}$$

The last equality (which of course holds only for $k=k_F$) follows from the easily verified relations

$$\mathrm{Re}u(-\omega+i0^+)=-\mathrm{Re}u(\omega+i0^+),$$
$$\mathrm{Im}u(-\omega+i0^+)=\mathrm{Im}u(\omega+i0^+).$$

We now consider $a(k_F,\omega)$ for several special cases. For a pure superconductor, $u=\omega/\Delta$ and $\tilde{\Delta}=\Delta$ and hence (A20′) gives the well-known result

$$a(k_F,\omega)=\pi[\delta(\omega-\Delta)+\delta(\omega+\Delta)].$$

For a superconducting alloy with nonmagnetic impurities, we find the more complicated expression

$$\begin{aligned}a(k_F,\omega)=&\frac{1}{\omega^2-\Delta^2+\left[\dfrac{1}{2\tau^{(1)}}\right]^2}\times\frac{\omega\,\mathrm{sgn}\omega}{\tau^{(1)}(\omega^2-\Delta^2)^{1/2}}\\&+\frac{\omega^2-\Delta^2}{\omega^2-\Delta^2+\left[\dfrac{1}{2\tau^{(1)}}\right]^2}\times\pi[\delta(\omega-\Delta)+\delta(\omega+\Delta)],\ \text{for }|\omega|\geq\Delta,\\=&0,\quad\text{for}\quad|\omega|<\Delta.\end{aligned}\tag{A21}$$

While there are no states within the energy gap, which is Δ in this example, the delta functions at $|\omega|=\Delta$ have decreased weight due to the broadening for $|\omega|>\Delta$. In the case of paramagnetic impurities, we find

$$\begin{aligned}\Delta a(k_F,\omega)&\simeq2\tau^{(2)}\Delta[1-2\tau^{(2)}/\tau^{(1)}]\rho(\omega),\quad\text{for}\quad\omega\lesssim\Delta\quad\text{and}\quad\tau_S\gg\tau^{(2)}\\&\simeq2\left(\frac{\Delta}{\omega}\right)^2,\quad\text{for}\quad\omega\gg\Delta,\end{aligned}$$

where $\rho(\omega)$ is the density of states to be discussed next.

The single particle density of states[22,30] is defined, relative to the density of states at the Fermi surface in a normal metal, by

$$\begin{aligned}\frac{N_s(\omega)}{N(0)}&=\frac{1}{\pi}\int_0^\infty d\epsilon_k\,\mathrm{Im}G(k,z=\omega-i0^+)\\&=\frac{1}{2\pi}\int_0^\infty d\epsilon_k a(k,\omega).\end{aligned}\tag{A22}$$

It is quite easy to show from (2.20) that

$$\frac{N_s(\omega)}{N(0)}=-\mathrm{Re}\left(\frac{u(z)}{[u^2(z)-1]^{1/2}}\right)\bigg|_{z=\omega-i0^+}\tag{A23}$$

and further, using (2.23),

$$\frac{N_s(\omega)}{N(0)}=-(\tau_S\Delta)\,\mathrm{Im}u(z=\omega-i0^+).\tag{A23$'$}$$

In Fig. 6 we have plotted some examples of the density of states curves for paramagnetic alloys.[38] These curves may be useful in tunneling experiments since the differential conductance of a normal superconducting junction is directly proportional to the

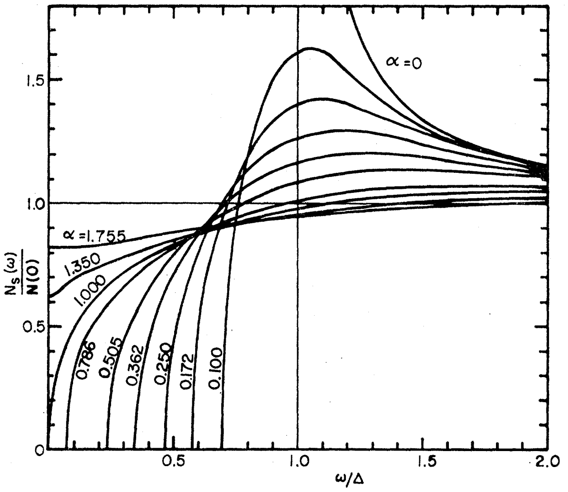

FIG. 6. The density of states $N_s(\omega)$ in a paramagnetic alloy function of the excitation frequency ω (we have normalized the former with respect to a normal metal and the latter with respect to the Gor'kov order parameter Δ). The density of states for nonmagnetic impurities is also shown [$\alpha\equiv(\tau_S\Delta)^{-1}=0$].

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[38] Such curves have been also discussed in Ref. 12. See also A. Baratoff, thesis, Cornell University, 1964 (unpublished).

density of states in the superconductor.[30] We remark that $N_s(\omega)$ always has its maximum for $\omega \geq \Delta$. If we expand $u(\omega/\Delta)$ in inverse powers of $(\omega/\Delta - i\alpha)$ and determine the coefficients by putting the series in (2.23), we find

$$u = (\omega/\Delta - i\alpha) - \frac{i\alpha}{2}(\omega/\Delta - i\alpha)^{-2} + \cdots . \tag{A24}$$

Thus if we may cut off the expansion as shown,

$$\frac{N_s(\omega)}{N(0)} \simeq 1 + \frac{1}{2}\frac{(\omega/\Delta)^2 - \alpha^2}{[(\omega/\Delta)^2 + \alpha^2]^2} + O(\Delta^4). \tag{A25}$$

This result is valid in two situations. For $\omega \gg \Delta$, we see quite generally that

$$N_S(\omega)/N(0) \simeq 1 + \tfrac{1}{2}(\Delta/\omega)^2 \tag{A25$'$}$$

and hence there always is a "peaking" in the density-of-states. Secondly we note that for $T \simeq T_c$, $\alpha \gg 1$ and therefore (A25) is a good approximation for all ω. Here the "peaking" occurs at $\omega = \Delta\alpha \gg \Delta$. More generally, we note that for ω near the threshold $\omega_0(\alpha < 1)$, (3.13) inserted in (A23′) gives

$$\frac{N_s(\omega)}{N(0)} = \alpha^{-2/3}\left(\frac{\omega - \omega_0}{\Delta}\right)^{1/2}\left(\frac{\omega_0}{\Delta}\right)^{-1/6}\left(\frac{2}{3}\right)^{1/2}. \tag{A26}$$

One sees that the threshold is sharp. For $\alpha > 1$, $\omega_0 = 0$ and in this case [see (3.16)] we find

$$N_s(\omega = 0)/N(0) = (1 - \alpha^{-2})^{1/2} + O(\omega/\Delta)^2. \tag{A26$'$}$$

Hohenberg[33] has recently published a careful analysis of the effect of anisotropy on $N_s(\omega)$ for the case of nonmagnetic impurities. The interesting corrections he finds would probably be swamped if one repeated his calculations using (A18′) and (A19′). Indeed when one reflects that $\alpha \to \infty$ for $T \to T_c$ no matter how small the paramagnetic impurity concentration, it is obvious that great care must be taken that there be no trace of paramagnetic impurities in samples used to study the effects of anisotropy on the density-of-states near T_c.

We now turn to the question of an energy gap. Consider (2.23) as defining ω/Δ as a function of real $u \equiv u_R$. Obviously for $\alpha < 1$, ω will increase with u_R, reach a maximum equal to ω_0 at $u_R = u_0$ and then decrease, with $\omega = 0$ for $u_R = (1 - \alpha^2)^{1/2}$. For $\alpha > 1$, ω always decreases with increasing u_R. Therefore u, as a function of ω/Δ and $\alpha < 1$, will have a real solution for $\omega \leq \omega_0$ and be complex for all $\omega > \omega_0$. It is clear that ω_0 plays the role of an energy gap, the latter being the minimum frequency at which either u takes on an imaginary value or equals unity. Some representative values of $\omega_0(T, n_i)$ are given in Fig. 5 and compared with the tunneling data of Reif and Woolf.[2]

The last point we must discuss is the determination of the Gor'kov order parameter $\Delta(T, \tau_S)$, which according to (A16) is given by the self-consistent integral equation[1] [$\tilde{z}$ and $\tilde{\Delta}$ are defined by (A18) and (A19)]

$$\bar{\Delta} = gk_BT \sum_{l=-\infty}^{\infty} N(0) \int_{-\omega_D}^{\omega_D} d\epsilon \frac{\tilde{\Delta}_l}{\tilde{\omega}_l^2 + \epsilon^2 + \tilde{\Delta}_l^2}, \tag{A27}$$

where $\tilde{\omega}_l = -i\tilde{z}(\omega_l)$, $\tilde{\Delta}_l = \tilde{\Delta}(\omega_l)$ and $\omega_l = (2l+1)\pi/\beta$, l an integer. We have introduced the usual BCS cutoff at the Debye phonon frequency ω_D. Now, as in the BCS theory,[27]

$$\ln\left(\frac{2\gamma\omega_D}{\pi k_BT}\right) = k_BT \sum_{l=-\infty}^{\infty} \int_{-\omega_D}^{\omega_D} \frac{d\epsilon}{\omega_l^2 + \epsilon^2} \tag{A28}$$

holds as an identity for arbitrary T, where $\ln\gamma$ is Euler's constant. This follows from combining the usual integral equation which determines the transition temperature T_{cp} with the relation $[N(0)g]^{-1} = \ln(2\gamma\omega_D/\pi T_{cp})$. If we subtract a term $\bar{\Delta}(\omega_l^2 + \epsilon^2)^{-1}$ from the integrand on the right-hand side of (A27) and use (A28), we find

$$\ln(T/T_{cp}) = \frac{k_BT}{\Delta} \sum_{l=-\infty}^{\infty} \int_{-\omega_D}^{\omega_D} d\epsilon \left(\frac{\tilde{\Delta}_l}{\tilde{\omega}_l^2 + \epsilon^2 + \tilde{\Delta}_l^2} - \frac{\bar{\Delta}}{\omega_l^2 + \epsilon^2}\right). \tag{A29}$$

There are no divergence difficulties in the integral on the right-hand side and we may extend the limits of integration to infinity, with the result[18]

$$\ln(T/T_{cp}) = 2x_0 \sum_{l=0}^{\infty} \left(\frac{1}{(1 + u_l^2)^{1/2}} - \frac{1}{x_l}\right), \tag{A30}$$

where $x_l \equiv (2l+1)\pi k_BT/\bar{\Delta}$ and

$$x_l = u_l[1 - \alpha(1 + u_l^2)^{-1/2}]. \tag{A31}$$

We have made use of $u_l^2 = u_{-l-1}^2$ and $\omega_l^2 = \omega_{-l-1}^2$ in reducing the sum over l. Since $u_l \simeq x_l + \alpha$ for $x_0 \gg 1$ (which is the case we are interested in), it is useful from the point of view of improving convergence to add and subtract $(x_l + \alpha)^{-1}$ from the right-hand side of (A30). If in addition we make use of (A31) to rewrite $(1 + u_l^2)^{-1/2}$, we have

$$\ln\left(\frac{T}{T_{cp}}\right) = 2x_0 \sum_{l=0}^{\infty} \left[\frac{1}{\alpha} - \frac{1}{\alpha}\frac{x_l}{u_l} - \frac{1}{x_l + \alpha}\right] - \chi(\rho_S), \tag{A32}$$

where $\rho_S \equiv (\pi k_BT\tau_S)^{-1}$ and

$$\chi(x) \equiv 2 \sum_{l=0}^{\infty} \left(\frac{1}{2l+1} - \frac{1}{2l+1+x}\right) = \psi\left(\frac{1+x}{2}\right) - \psi(\tfrac{1}{2}), \tag{A33}$$

with $\psi(x)$ being the well-known digamma function (the logarithmic derivative of the Γ function). We note in passing that at T_c, the transition temperature of the paramagnetic alloy, (A32) reduces to the simple result[1]

$$\ln(T_{cp}/T_c) = \chi(\rho_{S_c}). \tag{A34}$$

For $\rho_{S_c} = (\pi k_BT_c\tau_S)^{-1} \ll 1$, we have

$$T_c = T_{cp} - (\pi/4k_B\tau_S), \tag{A34$'$}$$

while for $\rho_{S_c} \gg 1$,

$$T_c^2 = 6/\pi^2\tau_S^2 \ln(\pi k_BT_{cp}\tau_S/2\gamma). \tag{A34$''$}$$

This last result predicts that when $(1/\tau_S)_{\text{cr}} = \pi k_BT_{cp}/2\gamma = \Delta_p(0)/2$ (using the BCS relation $\Delta_p(0) = 1.76T_{cp}$), superconductivity is destroyed. We have plotted T_c vs n_i in Fig. 5. If one fits (A34′) to the experimental results, one finds (A34) to be in good agreement with experiment,[5] and furthermore the value of the exchange potential so found is consistent[9] with other investigations.

As mentioned, we are interested in finding $\Delta(T, \tau_S)$ for T near T_c, and shall use the inverse power series the first terms of which are given in (A24). This is an expansion in powers of Δ, which is small in the region of interest. After a little algebra, we find

$$\begin{aligned}\ln(T_{cp}/T) = \chi(\rho_S) &+ x_0^{-2} \sum_{l=0}^{\infty} \left\{\frac{+1}{(2l+1+\rho_S)^3} - \frac{\rho_S}{(2l+1+\rho_S)^4}\right\} \\ &- \tfrac{3}{4}x_0^{-4} \sum_{l=0}^{\infty} \left\{\frac{1}{(2l+1+\rho_S)^5} - \frac{3\rho_S}{(2l+1+\rho_S)^6} + \frac{2\rho_S}{(2l+1+\rho_S)^7}\right\} + 0(x_0^{-6}).\end{aligned} \tag{A35}$$

This is a quadratic equation in x_0^{-2} which can be used to find $\Delta(T, \tau_S)$ for $x_0 \gg 1$. Some special limiting cases of (A35), which is valid for $(\Delta/\pi k_BT) \ll 1$, are of interest. For low impurity concentrations ($\rho_{S_c} \ll 1$), one has[18]

$$\ln\left(\frac{T_{cp}}{T}\right) = \ln\left(1 + \frac{\pi^2}{4}\rho_S\right) + \tfrac{7}{8}\zeta(3)\left(\frac{\Delta}{\pi k_BT}\right)^2 \tag{A36}$$

and hence

$$\Delta^2 = \frac{8\pi^2 k_B^2 T^2}{7\zeta(3)}\left(\frac{T_c - T}{T_c}\right). \tag{A36$'$}$$

This reproduces the usual BCS expression for $T_c \to T_{cp}$.[39] In con-

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[39] We might remark that according to (A36′), the jump in the electronic specific heat in a superconductor with a small ($\rho_{S_c} \ll 1$) concentration of paramagnetic impurities is T_c/T_{cp} as large as that in a pure superconductor.

trast, for high concentrations ($\rho_{Sc} \gg 1$), (A35) reduces to

$$\ln\left(\frac{T_{cp}}{T}\right)=\ln(2\gamma\rho_S)+\frac{1}{6\rho_S^2}+\frac{1}{12\rho_S^2}\left(\frac{\Delta}{\pi k_BT}\right)^2, \qquad \text{(A37)}$$

and therefore

$$\Delta^2=2\pi^2[(k_BT_c)^2-(k_BT)^2]. \qquad \text{(A37}')$$

We note that Δ has an infinite slope at T_c for all impurity concentrations. In addition, we might remark that if use is made of Maki's expression[17] for $\Delta(T)$ when $(\Delta/\pi k_BT) \gg 1$, one finds that $\Delta(T)$ is given by (A37′) once again for $\rho_{Sc} \gg 1$. That (A37′) is correct for all temperatures in the large concentration limit was first noted by Abrikosov and Gor'kov.[1]

AG have considered the other limit $x_0 \ll 1$, that is, near $T=0$°K. In particular, they find

$$\ln[\Delta(T=0)/\Delta_p(T=0)]=-\pi/4\tau_S\Delta(T=0) \quad \text{for} \quad \Delta(T=0)\tau_S>1.$$

Thus if $\Delta(0)\tau_S=1$, then $\Delta(0)=\Delta_p(0)e^{-\pi/4}$ and hence

$$1/\tau_S=\Delta(0)=2e^{-\pi/4}(1/\tau_S)_{\mathrm{cr}}.$$

This result means that for paramagnetic impurity concentrations $0.912n_{\mathrm{cr}} \leq n_i \leq n_{\mathrm{cr}}$, the gapless region exists for *all* temperatures.

By combining (A35) and AG's low temperature calculations, we have computed $\Delta(T,n_i)$ for several impurity concentrations. These results are plotted in Fig. 4.

APPENDIX B

The subject of this Appendix is the proof of Eq. (2.46). A convenient starting point is a spectral representation for the quantity $P(\nu_m) \equiv P(\mathbf{q}=0, \nu_m)$ as defined in Eqs. (2.6) and (2.7). An examination of Eqs. (2.15) and (2.16) shows that for the problem at hand one has the representation

$$P(\nu_m)=\frac{i}{\beta}\Sigma_l\, e^{\zeta_l 0^+}\int\frac{d^3k}{(2\pi)^3}\int\frac{d\omega_1 d\omega_2}{(2\pi)^2}\frac{f_k(\omega_1,\omega_2)}{(\zeta_l-\omega_1)(\zeta_l+\nu_m-\omega_2)}. \qquad \text{(B1)}$$

[It should be emphasized that (B1) is not completely general. The general spectral representation has been derived in Ref. 21, where it was shown that there are two independent spectral functions, and not one as in (B1). The second independent denominator can be chosen to be either $(\zeta_l-\omega_1)(\nu_m-\omega_2)$ or $(\zeta_l+\nu_m-\omega_1)(\nu_m-\omega_2)$. However, no such denominators occur with integral equation (2.16) because the scattering is elastic. Thus (B1) is sufficiently general for the present problem.] Using (B1), we can express the thermal conductivity as an integral over the spectral function $f_k(\omega_1,\omega_2)$. First we carry out the sum over l and then use the prescription (2.8) to get

$$K=\frac{1}{24k_BT^2}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int\frac{d^3k}{(2\pi)^3}f_k(\omega,\omega)\,\mathrm{sech}^2(\tfrac{1}{2}\beta\omega). \qquad \text{(B2)}$$

To get a result of the form (2.46) we have to show that $\int d^3k\, f_k(\omega,\omega)$ is simply related to the summand of (B1). Here again we encounter the "order of operations" problem mentioned above (2.43) (see Ref. 27). The difficulty is again avoided by subtracting the expression in the normal state. Then we write

$$P_s(\nu_m)-P_n(\nu_m)=\frac{3\pi ni}{8m\beta}\Sigma_{\zeta_l}\, e^{\zeta_l 0^+}[F_s(\zeta_l,\zeta_l')-F_n(\zeta_l,\zeta_l')], \qquad \text{(B3)}$$

with

$$\frac{3\pi ni}{8m}F_s(\zeta_l,\zeta_l')=\int\frac{d\omega_1 d\omega_2}{(2\pi)^2}\int\frac{d^3k}{(2\pi)^2}\frac{f_k^s(\omega_1,\omega_2)}{(\zeta_l-\omega_1)(\zeta_l'-\omega_2)}, \qquad \text{(B4)}$$

where $\zeta_l' \equiv \zeta_l+\nu_m$.

It follows directly from (B4) that

$$\int\frac{d^3k}{(2\pi)^3}f_k^s(\omega_1,\omega_2)=\frac{3\pi n}{4}[F_s(\omega+i0^+,\omega-i0^+) -\mathrm{Re}F_s(\omega-i0^+,\omega-i0^+)]. \qquad \text{(B5)}$$

An examination of the explicit form of F_s [Eq. (2.44)] using (2.30) shows that the second term in the square bracket in (B5) is zero. This term is therefore also zero in the normal state since $F_n \equiv F_s(\Delta=0)$. One can also verify using Eq. (2.8) that the contribution to the thermal conductivity of F_n is just the thermal conductivity of the normal state. Putting all these facts together, we obtain

$$K=\frac{n}{64mk_BT^2}\int_{-\infty}^{\infty}d\omega\,\mathrm{sech}^2\left(\frac{\beta\omega}{2}\right)F_s(\omega-i0^+,\omega+i0^+). \qquad \text{(B6)}$$

Combining (2.44) and (2.31), one can show that the integrand of (B6) is even in ω, and Eq. (2.46) follows at once.