

can be applied successfully to "physical impurities," e.g., lattice defects in thallium, when they are introduced by virtually hydrostatic compression at 2.5°K.

At zero pressure, we find an extremely small gap-anisotropy parameter  $\lambda\langle a^2 \rangle = 0.0008$  (compared with  $\lambda\langle a^2 \rangle \approx 0.02$  for Sn and In). We also find that the anisotropy parameter of Tl increases strongly with pressure, reaching  $\lambda\langle a^2 \rangle = 0.007$  at 4 kbar, which explains quantitatively the anomalous pressure dependence of  $T_c$  in thallium.

#### ACKNOWLEDGMENTS

It is a pleasure to thank Professor Watt W. Webb for many discussions and for his hospitality. Discussions with Professor G. Boato, Professor B. Serin, Dr. Neil W. Ashcroft, and Dr. Gert Eilenberger are also gratefully acknowledged, as well as a discussion with Dr. J. Hasse, who kindly provided data prior to publication. Travel support from Carl Duisberg Stiftung and Karlsruher Hochschulvereinigung were essential for this work.

### Anomalous Scattering by Magnetic Impurities in Superconductors\*

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(Received 6 June 1966)

The effect of magnetic impurities in superconductors is studied by using the dispersion equations, which are simple extensions of those introduced by Suhl. In the case of a single impurity, we find that, if  $T_{c0} > T_r$  (where  $T_{c0}$  is the superconducting transition temperature and  $T_r$  is the Suhl-Abrikosov resonance temperature), a pair of bound states appear in the energy gap, while if  $T_{c0} < T_r$ , resonances appear at low temperatures. Also, self-consistent equations are constructed to treat the case of dilute concentration of impurity atoms. In the gapless region it is established that the Abrikosov-Gor'kov expressions are valid, except that  $\tau_s$  in their theory must be replaced by the exact frequency-dependent spin-flip lifetime  $\tau_s(\omega)$  in the normal state.

#### I. INTRODUCTION

AS Kondo<sup>1</sup> has recently pointed out, the spin-exchange scattering from magnetic impurities gives rise to an electron scattering amplitude in normal metals, which diverges logarithmically at low temperatures. Since Kondo's calculation is perturbational, his approach is valid only within two approximations. The impurity concentration must be small so that the spin correlation among impurity atoms is negligible, and the temperature must be relatively high, so that the logarithmic term (which comes from the second-order Born term) is still a small correction to the first-order Born term. Therefore there naturally arises a question concerning the convergence of the perturbation series at low temperatures, even if one still confines oneself to the dilute-concentration limit of magnetic impurities.<sup>2-5</sup>

Recently, Suhl<sup>2</sup> and Abrikosov<sup>4</sup> were able to show

that, if one sums up a certain class of the higher order effects [which essentially consist of diagrams containing only single-particle (or hole) states as intermediate states] than the second-order term, the logarithmic divergence in the scattering amplitude disappears, but the scattering amplitude develops a pair of poles at temperatures lower than  $T_r$ , the resonance temperature.  $T_r$  corresponds roughly to the temperature at which the second-order Born term becomes comparable with the first-order term and thus a simple perturbation calculation breaks down. In spite of the apparent success of Suhl and Abrikosov's theory [which not only gives a formal answer to the convergence problem of the perturbation series, but also allows one to calculate various equilibrium as well as inequilibrium properties of a dilute impurity system at low temperature ( $T \lesssim T_r$ )], a detailed study of the analytical behaviors of the scattering amplitude as a function of energy reveals a serious drawback: The poles are in the physical sheet (i.e., the first plane) of the complex energy plane, which is inconsistent with the principle of causality.<sup>2,3</sup> Fortunately, in a recent work Suhl and Wong<sup>6</sup> have succeeded in removing this difficulty in the framework of his dispersion theory.

It is well known that the spin-exchange scattering drastically modifies the electronic properties of super-

\* This work was partially supported by the U. S. Air Force, through Grant No. AF-AFOSR-610-64, Theory of Solids.

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<sup>1</sup> J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32**, 37 (1964).

<sup>2</sup> H. Suhl, *Phys. Rev.* **138**, A515 (1965); *Physics* **2**, 39 (1965); *Phys. Rev.* **141**, 483 (1966).

<sup>3</sup> Y. Nagaoka, *Phys. Rev.* **138**, A1112 (1965).

<sup>4</sup> A. A. Abrikosov, *Physics* **2**, 5 (1965).

<sup>5</sup> K. Yosida and A. Okiji, *Progr. Theoret. Phys. (Kyoto)* **34**, 505 (1965).

<sup>6</sup> H. Suhl and D. Wong, *Physics* (to be published).

conductors. In their now classic paper, Abrikosov and Gor'kov<sup>7</sup> treated the effect of magnetic impurities only in the first Born approximation, but nonetheless arrived at a number of striking theoretical predictions. For example they showed that the superconducting order parameter  $\Delta$  is no longer equivalent to the gap in the excitation spectrum, in contrast to the BCS case, which applies to pure metals. Moreover, in the case of strong exchange scattering the gap is completely suppressed, though the order parameter is still finite. This type of "gapless" superconductivity was confirmed recently by the beautiful experiment of Woolf and Reif.<sup>8</sup>

As mentioned, the scattering amplitude is anomalous in normal metals if one treats the exchange scattering to higher order. We expect similar features in the superconducting state. A discussion of the spin-exchange scattering up to third order in the exchange constant  $J$  (which is the same approximation as used by Kondo for normal metals) has been given by Liu.<sup>9</sup> He concluded that, within the above approximation, there is no serious modification of the original results of AG.<sup>7</sup> However, the Born approximation to the spin-flip lifetime  $\tau_s$  in AG theory has to be replaced by a new lifetime, which contains a term proportional to  $\rho J \ln(E_F/kT_{c0})$ . Here  $\rho$ ,  $E_F$ , and  $T_{c0}$  are the density of states at Fermi energy, the Fermi energy itself, and the superconducting transition temperature of the pure metal, respectively. More recently, using the diagram technique developed by Abrikosov,<sup>4</sup> Griffin<sup>10</sup> calculated the shift of the superconducting transition temperature due to magnetic impurities. His result (which included terms to all orders in  $J$ ) gives a small deviation from the result due to AG.

The purpose of the present paper is to give a systematic way to treat the effect of the spin exchange scattering on the electronic properties of superconductors. The dispersion-theoretical technique of Suhl<sup>2</sup> for a normal metal is suitably generalized to deal with a superconductor. This equation involves not only scattering amplitudes of particle to particle and hole to hole, but also of particle to hole and hole to particle. Two simple applications of the above equation are discussed. First, we study the effect of a single impurity atom in a superconductor. We find that the complex poles still appear in the scattering amplitude at low temperature, if the superconducting transition temperature  $T_{c0}$  is low ( $T_{c0} \leq T_r$ , where  $T_r$  is the Suhl-Abrikosov resonance temperature). However, a pair of poles (which can be interpreted as bound states) appear in the energy gap of the excitation spectrum, when the superconductor has a high transition temperature ( $T_{c0} \geq T_r$ ). Second, we consider the effect of impurity scattering in the gapless

region (the temperature region close to  $T_c$  where the order parameter  $\Delta$  is small) by using a self-consistent dispersion equation for the case of finite concentration of impurity atoms. An additional complication, foreign to a normal metal, arises in the case of a superconductor because the exchange scattering strongly modifies the density of states. In the gapless region this self-consistent equation is solved rigorously and we establish that to a good approximation AG expressions hold, except that  $\tau_s$ , the spin-flip lifetime has to be replaced by  $\tau_s(\omega)$ , the exact spin-flip lifetime in the normal metal. The above result is not trivial, since we can show that the above substitutional law is valid only in the gapless region. Thus we can quite naturally reproduce the shift of the transition temperature previously obtained by Griffin.<sup>10</sup> The explicit form of the density of states is also given, which can be measured by a tunneling experiment.

As already mentioned, Suhl and Wong<sup>6</sup> have recently obtained a solution of his dispersion equation free from the unphysical complex pole. The same technique has to be used in the present case in order to avoid an unphysical conclusion for the case of a single impurity atom with  $T_{c0} \leq T_r$ . The other results, stated above, are unchanged in this new formulation.

## II. DISPERSION EQUATION FOR SINGLE-IMPURITY PROBLEM

We shall here consider the effect of a single magnetic impurity in a superconductor. The interaction between the impurity atom and conduction electrons is given by

$$H_I = \int \psi^*(\mathbf{r})(V(\mathbf{r}) + \frac{1}{2}J(\mathbf{r})\mathbf{S} \cdot \boldsymbol{\sigma})\psi(\mathbf{r})d^3r, \quad (1)$$

where  $\mathbf{r}$  is the distance from the impurity atom. Here  $\mathbf{S}$ ,  $\boldsymbol{\sigma}$ , and  $\psi$  are the spin operator of the magnetic impurity, the Pauli matrix, and the field operator (two components) of conduction electrons, respectively. In the following we shall assume that the interaction is local [i.e.,  $V(\mathbf{r}) = V\delta(\mathbf{r})$  and  $J(\mathbf{r}) = J\delta(\mathbf{r})$ ] for simplicity. The method we shall expound here is a straightforward generalization of that employed by Suhl in a normal metal. In the superconducting state there is an additional degeneracy in the energy of the quasiparticles and we have to treat a four-channel scattering problem even if we confine ourselves to a single-particle (or -hole) state. Therefore it is convenient to introduce a four-dimensional space<sup>11</sup> in which the electron field operators are written as

$$\Psi(\mathbf{r}) = \begin{pmatrix} \psi_{\uparrow}(\mathbf{r}) \\ \psi_{\downarrow}(\mathbf{r}) \\ \psi_{\uparrow}^{\dagger}(\mathbf{r}) \\ \psi_{\downarrow}^{\dagger}(\mathbf{r}) \end{pmatrix}, \quad \Psi^{\dagger}(\mathbf{r}) = (\psi_{\uparrow}^{\dagger}(\mathbf{r}), \psi_{\downarrow}^{\dagger}(\mathbf{r}), \psi_{\uparrow}(\mathbf{r}), \psi_{\downarrow}(\mathbf{r})). \quad (2)$$

In this space the interaction Hamiltonian (1) is

<sup>11</sup> V. Ambegaokar and A. Griffin, Phys. Rev. **137**, A1151 (1965).

<sup>7</sup> A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 178 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)], hereafter referred to as AG.

<sup>8</sup> M. A. Woolf and F. Reif, Phys. Rev. **137**, A557 (1965).

<sup>9</sup> S. H. Liu, Phys. Rev. **137**, A1209 (1965).

<sup>10</sup> A. Griffin, Phys. Rev. Letters **15**, 703 (1965).

recast as

$$H_I = \int \Psi^\dagger(\mathbf{r})(V(\mathbf{r})\rho_3 + \frac{1}{2}J(\mathbf{r})\mathbf{S} \cdot \boldsymbol{\alpha})\Psi(\mathbf{r})d^3r, \quad (3)$$

where

$$\boldsymbol{\alpha} = \frac{1}{2}(1 + \rho_3)\boldsymbol{\sigma} + \frac{1}{2}(1 - \rho_3)\sigma_2\boldsymbol{\sigma}\sigma_2. \quad (4)$$

Here  $\rho_1 \cdots \rho_3$  and  $\sigma_1 \cdots \sigma_3$  denote the Pauli spin matrices acting on different spaces. The product  $\rho_i \sigma_j$  is defined, for example, as

$$\rho_3 \sigma_j = \begin{pmatrix} \sigma_j & 0 \\ 0 & -\sigma_j \end{pmatrix}. \quad (5)$$

The Green's function in the superconducting state is given as

$$G(p, \omega) = (\omega - \xi p^2 - \Delta \rho_1 \sigma_2)^{-1}, \quad (6)$$

where  $\xi = p^2/2m - \mu$  and  $\mu$  is the chemical potential. As we shall see, the introduction of four-dimensional space enables us to obtain the dispersion relations for the scattering amplitude in the superconducting state in close parallel to those in the normal state.

Following Suhl,<sup>2</sup> we make the following assumptions:

(1) At an infinite distance from the impurity, the ground-state vector approaches weakly the ground-state vector of the BCS state.

(2) There are an even number of conduction electrons, and the value of the impurity spin is  $S$ , so the ground state of the target is  $(2S+1)$ -fold degenerate.

(3) Low-lying excitations of the target (with energies infinitesimally above the ground-state energy) are described with wave functions which asymptotically approach the vector of electron-hole pairs at an infinite distance from the impurity.

The last assumption is crucial in the present problem, since it allows us to treat the dynamical character of the impurity by a spin operator.

A single-quasiparticle (or -hole) state is generated from the ground state by applying a creation operator  $A_k^\dagger$  (which is  $4 \times 4$  matrix operator):

$$A_k^\dagger |\Omega, M\rangle, \quad (7)$$

where  $M$  is the  $z$  component of the impurity spin. Furthermore  $A_k^\dagger$  has to satisfy the equation

$$[H_0, A_k^\dagger] = z A_k^\dagger, \quad (8)$$

where

$$H_0 = (p^2/2m - \mu)\rho_3 + \Delta \rho_1 \sigma_2,$$

and

$$z = \pm \epsilon_k = \pm (\xi_k^2 + \Delta_k^2)^{1/2}.$$

In the presence of an impurity atom the total Hamiltonian is given by

$$H = H_0 + H_I. \quad (9)$$

We shall first find the exact incoming and outgoing scattering eigenstates

$$|k, \Omega\rangle^\pm = A_k^\dagger |\Omega\rangle + |\chi\rangle^\pm, \quad (10)$$

which satisfies the Schrödinger equation

$$(H - z) |k, \Omega\rangle^\pm = 0. \quad (11)$$

(We hereafter drop the obvious index  $M$  indicating the ground state.) The solution is easily written as

$$|k, \Omega\rangle^\pm = A_k^\dagger |\Omega\rangle + (H - z \pm i\delta)^{-1} J_k |\Omega\rangle, \quad (12)$$

where

$$J_k = [H_I, A_k^\dagger].$$

The scattering matrix from a single-quasiparticle (or -quasihole) state  $k$  to another state  $k'$  is defined as

$$S_{k'\Omega'; k\Omega} \equiv -\langle k'\Omega' | k\Omega \rangle^+, \quad (13)$$

which is reduced to a  $4 \times 4$  matrix. Making use of the relation

$$|k\Omega\rangle^+ - |k\Omega\rangle^- = -2\pi i \delta(z - H) J_k |\Omega\rangle, \quad (14)$$

which follows from Eq. (12), we obtain

$$S_{k'\Omega'; k\Omega} = \delta_{kk', \Omega\Omega'} - 2i\delta(z - \epsilon_{k'}) \langle k'\Omega' | J_k |\Omega\rangle. \quad (15)$$

Now let us introduce the  $T$  matrix which is given by

$$\begin{aligned} T_{k'\Omega'; k\Omega} &\equiv -\langle k'\Omega' | J_k |\Omega\rangle \\ &= \langle \Omega' | A_{k'} J_k |\Omega\rangle + \langle \Omega' | J_{k'}^\dagger (z' - H + i\delta)^{-1} J_k |\Omega\rangle. \end{aligned} \quad (16)$$

We note here that the  $S$  matrix is expressed in term of the  $T$  matrix as

$$S_{k'\Omega'; k\Omega} = \delta_{kk', \Omega\Omega'} - 2\pi i \delta(\epsilon_k - \epsilon_{k'}) T_{k'\Omega'; k\Omega}. \quad (17)$$

The first term in Eq. (16) is further rewritten as

$$\begin{aligned} \langle \Omega' | A_{k'} J_k |\Omega\rangle &= \langle \Omega' | \{A_{k'} J_k\}_+ |\Omega\rangle - \langle \Omega' | J_k A_{k'} |\Omega\rangle \\ &= \langle \Omega' | \mu_{k'k} |\Omega\rangle + \langle \Omega' | J_k (H + z')^{-1} J_{k'}^\dagger |\Omega\rangle, \end{aligned} \quad (18)$$

where

$$\mu_{k'k} = \{A_{k'} J_k\}_+.$$

Here we have made use of the equations

$$A_{k'} |\Omega\rangle = -(H + z')^{-1} J_{k'}^\dagger |\Omega\rangle,$$

and

$$[H_0, A_{k'}] = -z' A_{k'}. \quad (19)$$

From Eqs. (16) and (18), we finally obtain

$$\begin{aligned} T_{k'\Omega'; k\Omega} &= \langle \Omega' | \mu_{k'k} |\Omega\rangle \\ &+ \sum_n \langle \Omega' | J_{k'}^\dagger | n \rangle^- \langle n | G_0(z') | n \rangle^- - \langle n | J_k |\Omega\rangle \\ &+ \sum_n \langle \Omega' | J_k | n \rangle^- \langle n | G_0(-z') | n \rangle^- - \langle n | J_{k'}^\dagger |\Omega\rangle. \end{aligned} \quad (20)$$

The above equation is formally equivalent to the one obtained by Suhl, except that now  $T$ ,  $\mu_{k'k}$ ,  $J_k$ , and  $G_0$  are matrices operating in 4-dimensional space. In the following we further assume that the important intermediate states  $|n\rangle^-$  are exhausted by single-particle (or -hole) states. Introducing an analytical function  $T(z)$  which is related to  $T_{k'\Omega'; k\Omega}$  by

$$(1 + \rho_3) T_{k'\Omega'; k\Omega} = (1 + \rho_3) \mathbf{T}(z) \Big|_{z = \epsilon_k + i\delta}, \quad (21)$$

$$(1 - \rho_3) T_{k'\Omega'; k\Omega} = (1 - \rho_3) \mathbf{T}(z) \Big|_{z = -\epsilon_k - i\delta}, \quad (22)$$

we can write Eq. (20) as

$$\begin{aligned} \mathbf{T}(z) = & \mathbf{V} + \int \frac{d^3 p'}{(2\pi)^3} \mathbf{T}^*(z') G(p', z) \mathbf{T}(z') \delta(\epsilon_{p'} - z') \\ & + \int \frac{d^3 p'}{(2\pi)^3} \mathbf{T}^{*t}(z') G(p', -z) \mathbf{T}^t(z') \delta(\epsilon_{p'} - z'), \end{aligned} \quad (23)$$

where

$$\mathbf{V} = V\rho_3 + J(\mathbf{S} \cdot \boldsymbol{\alpha})/2.$$

Here we made use of the fact that  $\epsilon_{k'} = \epsilon_k$ .

From the above equation we see that the crossing relation holds:

$$\mathbf{T}(z) = \mathbf{T}^t(-z), \quad (24)$$

which is a simple generalization of that in the normal state.

In order to solve the above equation for  $\mathbf{T}(z)$ , we decompose the scattering matrix as follows:

$$\begin{aligned} \mathbf{T}(z) = & t(z) + \tau(z)(\mathbf{S} \cdot \boldsymbol{\alpha}/2) + \rho_3(L + \Lambda(\mathbf{S} \cdot \boldsymbol{\alpha}/2)) \\ & + \rho_1 \sigma_2(u + v(\mathbf{S} \cdot \boldsymbol{\alpha}/2)) + \rho_1 \sigma_2 \rho_3(N + H(\mathbf{S} \cdot \boldsymbol{\alpha}/2)). \end{aligned} \quad (25)$$

Substituting Eqs. (6), (24), and (25) into Eq. (23), and after a straightforward but rather lengthy calculation, we obtain

$$\begin{aligned} t_{\pm}(z) = & t(z) \pm u(z) \\ = & \int_{-\infty}^{\infty} \rho \frac{dx}{z-x} [(g \pm f)(|t_{\pm}|^2 + \frac{3}{16}|\tau_{\pm}|^2) \\ & + (g \mp f)(|L_{\mp}|^2 + \frac{3}{16}|\Lambda_{\mp}|^2)] \\ \tau_{\pm}(z) = & \tau(z) \pm v(z) = J + \int_{-\infty}^{\infty} \rho \frac{dx}{z-x} \\ & \times \left[ (g \pm f) \left( t_{\pm}^* \tau_{\pm} + \tau_{\pm}^* t_{\pm} - \frac{\eta(x)}{2} |\tau_{\pm}|^2 \right) \right. \\ & \left. + (g \mp f) \left( L_{\mp}^* \Lambda_{\mp} + \Lambda_{\mp}^* L_{\mp} - \frac{\eta(x)}{2} |\Lambda_{\mp}|^2 \right) \right], \\ L_{\pm}(z) = & L(z) \pm N(z) = V + \int_{-\infty}^{\infty} \rho \frac{dx}{z-x} \\ & \times [(g \pm f)(t_{\pm}^* L_{\pm} + \frac{3}{16}(\tau_{\pm}^* \Lambda_{\pm})) \\ & + (g \mp f)(L_{\mp}^* t_{\mp} + \frac{3}{16}(\tau_{\mp}^* \Lambda_{\mp}))], \\ \Lambda_{\pm}(z) = & \Lambda(z) \pm H(z) = \int_{-\infty}^{\infty} \rho \frac{dx}{z-x} \\ & \times \left[ (g \pm f) \left( t_{\pm}^* \Lambda_{\pm} + \tau_{\pm}^* L_{\pm} - \frac{\eta(x)}{2} (\tau_{\pm}^* \Lambda_{\pm}) \right) \right. \\ & \left. + (g \mp f) \left( t_{\mp}^* \Lambda_{\mp} + \tau_{\mp}^* L_{\mp} - \frac{\eta(x)}{2} (\tau_{\mp}^* \Lambda_{\mp}) \right) \right], \end{aligned} \quad (26)$$

where we have assumed that the spin of the magnetic impurity is  $\frac{1}{2}$  [or  $(\mathbf{S} \cdot \boldsymbol{\alpha}/2)^2 = \frac{3}{16} + \frac{1}{2}(\mathbf{S} \cdot \boldsymbol{\alpha}/2)$ ] for simplicity. Here  $g(z)$  and  $f(z)$  are given by

$$g(z) = \text{Re}[z/(z^2 - \Delta^2)^{1/2}]$$

and

$$f(z) = \text{Re}[\Delta/(z^2 - \Delta^2)^{1/2}], \quad (27)$$

respectively.  $\eta(z)$  is given by

$$\begin{aligned} \eta(z) = & +1, \quad \text{for } z > 0; \\ = & 0, \quad \text{for } z = 0; \\ = & -1, \quad \text{for } z < 0. \end{aligned} \quad (28)$$

It is not difficult to show that at finite temperatures  $\eta(z)$  is replaced simply by  $\tanh(\frac{1}{2}\beta z)$  with  $\beta = 1/T$ .<sup>2</sup> The above results are exact within two approximations: (1) The important intermediate states must be exhausted by single particle states; (2) the impurity concentration must be extremely dilute (i.e.,  $c \rightarrow 0$  where  $c$  is the density of impurity atoms). In the case of a finite concentration of impurities, the self-energy correction due to impurity scattering modifies both  $g(z)$  and  $f(z)$  and we have a more complicated set of equations (for discussion, see Secs. IV and V).

### III. BOUND STATES IN THE ENERGY GAP

Before going into the solution of the above equations, we note the fact that  $L$ ,  $\Lambda$ ,  $N$ , and  $H$  vanish identically if  $V=0$ , while  $\tau$ ,  $v$ ,  $\Lambda$ , and  $H$  vanish if  $J=0$ . Since Eq. (26) is too complicated to be tractable, we confine ourselves in the following to the case  $V=0$ , where we can deduce some rigorous conclusions. In this case we have

$$\begin{aligned} t_{\pm}(z) = & \int_{-\infty}^{\infty} \rho \frac{dx}{z-x} (|t_{\pm}|^2 + \frac{3}{16}|\tau_{\pm}|^2)(g \pm f), \\ \tau_{\pm}(z) = & J + \int_{-\infty}^{\infty} \rho \frac{dx}{z-x} \left( t_{\pm}^* \tau_{\pm} + t_{\pm} \tau_{\pm}^* - \frac{\eta(x)}{2} |\tau_{\pm}|^2 \right) \\ & \times (g \pm f). \end{aligned} \quad (29)$$

The above set of equations has the same mathematical structure as the one discussed by Suhl [Eq. (3) in Ref. 2], if one replaces  $t_{\pm}$ ,  $\tau_{\pm}$ , and  $\rho(g \pm f)$  by  $t$ ,  $\tau$ , and  $\rho$ , respectively. The solution is written as

$$\begin{aligned} \pi \rho(g \pm f) t_{\pm}(z) = & -(1/2i)(e^{2i\delta_{\pm}} - 1), \\ \tau_{\pm}(z) e^{-2i\delta_{\pm}(z)} = & \tau_{\pm}(z) / [1 - 2\pi i \rho(g \pm f) t_{\pm}(z)] \equiv F_{\pm}(z), \\ e^{-4\delta_{\pm}(z)} = & 1 - a_{\pm}(z) |\tau_{\pm}(z)|^2 = [1 + a_{\pm}(z) |F_{\pm}(z)|^2]^{-1}, \end{aligned}$$

and

$$\begin{aligned} F_{\pm}(z) = & 4 \left( \frac{4}{J} - 2 \int_{-\infty}^{\infty} dx \rho(g \pm f) \frac{\eta(x)}{x-z} \right)^{-1} \\ = & J(1 - \rho J I_{\pm}(z))^{-1}, \end{aligned} \quad (30)$$

where we have put

$$\begin{aligned}\delta(z) &= \delta'(z) + i\delta''(z), \\ a_{\pm}(z) &= 12\pi^2\rho^2(g \pm f).\end{aligned}\quad (31)$$

Here  $I_{\pm}(z)$  are given as

$$\begin{aligned}I_{\pm}(z) &= \frac{1}{2} \int_{-D}^D \frac{dx}{x-z} \eta(x) (g(x) \pm f(x)) \\ &= \int_{\Delta}^D \frac{dx}{(x^2 - \Delta^2)^{1/2}} \frac{(x \pm \Delta)}{x^2 - z^2} \\ &= \operatorname{arccosh}\left(\frac{D}{\Delta}\right) + \frac{z \pm \Delta}{(\Delta^2 - z^2)^{1/2}} \operatorname{arcsin}\left(\frac{z}{\Delta}\right), \\ &\quad \text{for } |z| \leq \Delta; \\ &= \operatorname{arccosh}\left(\frac{D}{\Delta}\right) - \frac{z \pm \Delta}{(z^2 - \Delta^2)^{1/2}} \left\{ \operatorname{arccosh}\left(\frac{z}{\Delta}\right) - \frac{\pi}{2}i \right\}, \\ &\quad \text{for } |z| \geq \Delta.\end{aligned}\quad (32)$$

In the computation of  $I_{\pm}(z)$  we have cut off the integration at a frequency  $D$  which corresponds roughly to the Fermi energy. The location of the pole in  $\tau_{\pm}(z)$  is determined by

$$1 - \rho J I_{\pm}(z) = 0. \quad (33)$$

Equation (33) is written in a more convenient form as

$$\ln(T_r/T_{c0}) + f_{\pm}(z) = 0, \quad (34)$$

where

$$\begin{aligned}f_{\pm}(z) &= \frac{z \pm \Delta}{(\Delta^2 - z^2)^{1/2}} \operatorname{arcsin}\left(\frac{z}{\Delta}\right), \quad \text{for } |z| \leq \Delta; \\ &= -\frac{z \pm \Delta}{(z^2 - \Delta^2)^{1/2}} \left\{ \operatorname{arccosh}\left(\frac{z}{\Delta}\right) - \frac{\pi}{2}i \right\}, \\ &\quad \text{for } |z| \geq \Delta.\end{aligned}\quad (35)$$

Here  $T_r = (\gamma D/\pi)e^{-1/\rho J}$  is the Suhl-Abrikosov resonance temperature. One can easily see that Eq. (34) has a real solution for  $|z| < \Delta$  if  $T_r/T_{c0} \leq 1$ , while Eq. (34) has a complex root if  $T_r/T_{c0} > 1$ . Therefore we conclude that there appear a pair of bound states below the energy gap for  $T_r \lesssim T_{c0}$ , while the complex poles remain even in the superconducting state for  $T_r > T_{c0}$ . The latter poles have to be treated by a more elaborate method,<sup>6</sup> which will not be discussed here. As the resonance temperature decreases, the complex poles approach the real axis and at  $T_r = T_{c0}$  the poles of the bound states appear at  $z = 0$ . Further decrease in  $T_r$  is accompanied by the increase of  $|z|$  along the real axis, and finally the bound states merge into the continuum for  $T_r = 0$ . Asymptotic solutions of Eq. (34) are given as

$$z = \pm \Delta \left\{ \left(1 - \frac{T_r}{T_{c0}}\right) - \frac{1}{2} \left(1 - \frac{T_r}{T_{c0}}\right)^2 \right\}, \quad \text{for } \frac{T_r}{T_{c0}} \lesssim 1; \quad (36)$$

and

$$z = \pm \Delta \left( \frac{1 - \frac{1}{4}\pi^2 [2 - \ln(T_r/T_{c0})]^{-2}}{1 + \frac{1}{4}\pi^2 [2 - \ln(T_r/T_{c0})]^{-2}} \right), \quad \text{for } \frac{T_r}{T_{c0}} \ll 1. \quad (37)$$

As one sees from the relation

$$|\tau_{\pm}|^2 = |F_{\pm}|^2 / (1 + a_{\pm} |F_{\pm}|^2), \quad (38)$$

$\tau_{\pm}$  has poles at the same places as  $F_{\pm}$  has for  $T_r/T_{c0} \leq 1$ , since  $a_{\pm} = 0$  for  $|z| \leq \Delta$ . On the other hand,  $t_{\pm}(z)$  does not have corresponding poles, as can be seen from Eq. (30). The equation for  $t_{\pm}(z)$  reduces in the case of weak scattering ( $\rho J \ll 1$ —the usual case) to

$$\begin{aligned}t_{\pm}(z) &= -\frac{3\rho}{(g \pm f)} \int (g \pm f)^2 \frac{dx}{x-z} |F_{\pm}|^2 \\ &= -\frac{3\rho J^2}{(g \pm f)} \int (g \pm f)^2 \frac{dx}{x-z} |1 - \rho J I_{\pm}(z)|^{-2}.\end{aligned}\quad (39)$$

#### IV. SELF-CONSISTENT EQUATION FOR THE CASE OF FINITE CONCENTRATION OF IMPURITIES

We have restricted ourselves so far to the effect of a single impurity atom on the conduction electrons in the superconducting phase. We found in certain cases ( $T_{c0} > T_r$ ) that the impurity induces a pair of bound states below the energy gap in the quasiparticle excitation. We shall next consider the case of a finite concentration, though we still assume that the concentration of impurity atoms is so low that the correlation between spins of different impurity atoms is negligible. The present case is more complicated than that in the normal state, where we could assume that the density of states was not changed by the presence of the magnetic impurities. This situation is related to the fact that in the normal state the effect of scattering from many random impurities gives rise to a renormalization of energy only. This amounts to the introduction of a finite lifetime for the electron, but no change in the density of states. [More precisely, there is a small change in the density of states of the order of  $(c \operatorname{Re}t(\omega))/E_F$  due to the shift of the energy of excitation, where  $c$  is the density of impurity atoms.] In the case of a superconductor, the asymptotic BCS state is replaced by a uniformly disturbed state, which is described by the renormalized Green's function.<sup>7</sup> Since the exchange scattering breaks the time-reversal symmetry of the electronic system, the renormalization factors for the frequency and the order parameter are different, which causes nontrivial changes for both  $g(z)$  and  $f(z)$  in Eq. (27). The renormalized Green's function is given now by

$$G(p, \omega) = (\tilde{\omega} - \xi_p \rho_3 - \tilde{\Delta} \rho_1 \sigma_2)^{-1}, \quad (40)$$

where

$$\begin{aligned}\tilde{\omega} &= \omega = ct(\omega); \\ \tilde{\Delta} &= \Delta + cu(\omega).\end{aligned}\quad (41)$$

Here  $c$  is the concentration of impurities and  $t$  and  $u$  are components of the scattering amplitude. The dispersion equations in the present case are still given by Eq. (23), but the old  $G(\mathbf{p}, \omega)$  has to be replaced by the one in Eq. (40). After carrying out the same reductions as given before, we arrive at the set of Eq. (29), where now  $g(z)$  and  $f(z)$  are given by

$$\begin{aligned} g(z) &= \text{Im} \left\{ \frac{\tilde{\omega}}{(\tilde{\Delta}^2 - \tilde{\omega}^2)^{1/2}} \right\} \Big|_{\omega=z}, \\ f(z) &= \text{Im} \left\{ \frac{\tilde{\Delta}}{(\tilde{\Delta}^2 - \tilde{\omega}^2)^{1/2}} \right\} \Big|_{\omega=z}. \end{aligned} \quad (42)$$

The set of equations thus obtained allows us to discuss the effect of magnetic impurities at finite concentration in considerable generality (though we still neglect the spin correlation between impurity atoms). The mathematical structure of the equations is, however, quite complicated, since we should solve self-consistently for both the  $T$  matrices and the single-particle Green's functions. We shall see, however, in the next section that the above set of equations will be solved in gapless superconductors, where the order parameter  $\Delta$  is small.

### V. EFFECT OF ANOMALOUS SCATTERING IN GAPLESS SUPERCONDUCTORS

By "gapless superconductors" we mean superconductors in which thermodynamical quantities as well as transport coefficients can be expanded in powers of  $\Delta$ . In particular we know from the AG theory that, in the presence of magnetic impurities, the superconductor becomes gapless at temperatures close to the transition temperature. The present technique offers a powerful method for approaching the problem of gapless superconductors in the presence of magnetic impurities. We shall solve the self-consistent equation here by expanding all quantities involved in powers of the order parameter  $\Delta$ . First, let us consider the renormalization of the energy. By putting  $\Delta=0$  in Eq. (41), we have

$$\tilde{\omega} = \omega + ic \text{Im} t_n(\omega) \quad (43)$$

where  $t_n(\omega)$  is the non-spin-flip scattering amplitude<sup>12</sup> in the normal metal. According to Suhl,  $t_n(\omega)$  is given by

$$t_n(\omega) = -\frac{1}{2\pi\rho i} \left\{ \exp \left[ \frac{i}{2\pi} \int \frac{dx}{x-z} \ln(1+a|F|^2) \right] - 1 \right\}, \quad (44)$$

where

$$a = 12\pi^2\rho^2$$

and

$$F = J \left( 1 - \rho J \int \frac{dx'}{x'-x} \tanh \frac{x'}{2} \right)^{-1}. \quad (45)$$

<sup>12</sup> Since the real part of  $t_n(\omega)$  depends weakly on frequency and the constant part has to be absorbed in the shift of the chemical potential, we only consider the imaginary part given in Eq. (41).

Here we neglect for simplicity the term due to the ordinary scattering (i.e., we assume  $V=0$ ). We can recast the above equation into the form

$$\tilde{\omega} = \omega \left( 1 + \frac{1}{2\tau_s(\omega)} \frac{i}{|\omega|} \right) \quad (46)$$

where

$$\tau_s(\omega)^{-1} = c \text{Re} \left\{ \frac{1}{2\pi\rho} \left[ \exp \left( \frac{1}{2\pi} \int \frac{dx}{x-z} \times \ln(1+a|F|^2) \right) - 1 \right] \right\} \quad (47)$$

which is proportional to  $\frac{3}{4}(\pi|\tau|^2)$ ,<sup>13</sup> the square of the spin-flip amplitude. Second, we shall set up a self-consistent equation for the renormalization factor of  $\Delta$ .  $\tilde{\Delta}$  is defined by the second equation in Eq. (41):

$$\tilde{\Delta} = \Delta + ic \text{Im} u(\omega), \quad (48)$$

where

$$u(\omega) = \frac{1}{2} \{ t_+ - t_- \}, \quad (49)$$

and

$$t_{\pm} = -\frac{1}{2\pi i \rho (1 \pm \Delta \phi_0)} \times \left\{ \exp \left[ \frac{i}{2\pi} \int \frac{dx}{x-z} \ln(1+a_{\pm}|F_{\pm}|^2) \right] - 1 \right\}. \quad (50)$$

Here

$$a_{\pm} = 12\pi^2\rho^2(1 \pm \Delta\phi_0')^2$$

and

$$F_{\pm} = J \left\{ 1 - \rho J \int \frac{dx'}{x'-x} (1 \pm \Delta\phi_0') \tanh \frac{\beta x'}{2} \right\}^{-1}. \quad (51)$$

In the above derivation we have put

$$\begin{aligned} \hat{g}(z) &= \tilde{\omega} / (\tilde{\omega}^2 - \tilde{\Delta}^2)^{1/2} = 1 + O(\Delta^2), \\ \hat{f}(z) &= \tilde{\Delta} / (\tilde{\omega}^2 - \tilde{\Delta}^2)^{1/2} = \phi_0(z) \Delta + O(\Delta^3), \end{aligned} \quad (52)$$

and

$$\phi_0' = \text{Re} \phi_0.$$

As we shall see later,  $\phi_0'$  vanishes as  $\omega$  at the Fermi surface (in the gapless case). Thus we can further neglect  $\phi_0'$  in the integrands in Eqs. (50) and (51), which develop at most the singularity  $T \ln T$  for small  $T$ . Finally we have

$$t_{\pm}(z) = \frac{1}{(1 + \Delta\phi_0)} t_n(z). \quad (53)$$

Inserting this into Eq. (49), we obtain

$$u(\omega) = -\Delta\phi_0 t_n(\omega). \quad (54)$$

Noting the relation

$$\phi_0(z) = \frac{\tilde{\Delta}}{\tilde{\omega} \Delta},$$

<sup>13</sup> Precisely speaking, it also contains terms proportional to  $|t|^2$  [which is of the order of  $(\rho J)^4$ ].

we have from Eq. (48)

$$\bar{\omega}\phi_0(z) = 1 - i\phi_0(z)c \operatorname{Im}t_n(z),$$

or

$$\phi_0(z) = (\bar{\omega} + ic \operatorname{Im}t_n(z))^{-1} = (\omega + i2c \operatorname{Im}t_n(\omega))^{-1}. \quad (55)$$

From Eq. (55) we obtain

$$\phi_0'(\omega) = \omega/(\omega^2 + \tau_s^{-2}(\omega)) \quad (56)$$

which vanishes linearly in  $\omega$  at Fermi surface.

Summarizing the results, in the gapless region, more rigorous treatment of the exchange scattering amounts to the AG theory with the exact spin-flip lifetime [i.e.,  $\tau_{sB}^{-1}$  in the AG theory should be replaced by  $\tau_s^{-1}(\omega)$  in Eq. (47)]. For example, the shift of the superconducting transition temperature due to a magnetic impurity is given by

$$\ln \frac{T_c}{T_{c0}} + 2\pi T_c \sum \left\{ \frac{1}{|\omega_n|} - \frac{1}{|\omega_n| + \tau_s^{-1}(\omega_n)} \right\} = 0, \quad (57)$$

where

$$\omega_n = 2\pi(n + \frac{1}{2})T_c$$

and

$$\tau_s(\omega_n)^{-1} = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\tau_s(z)^{-1}}{z - i\omega_n} dz. \quad (58)$$

The above equation has been derived previously by Griffin,<sup>10</sup> by using the diagrammatical method proposed by Abrikosov.<sup>4</sup> The tunneling density of states in the gapless region is given by the usual expression<sup>14</sup>:

$$\frac{N(\omega)}{N(0)} = 1 - \frac{\Delta^2}{2} \frac{\tau_s^{-2}(\omega) - \omega^2}{(\omega^2 + \tau_s^{-2}(\omega))^2}, \quad (59)$$

with the exact  $\tau_s^{-1}(\omega)$ .

It is interesting to note that this frequency dependence of  $\tau_s^{-1}(\omega)$  might account for discrepancies between the AG theory and the observation by Woolf and Reif<sup>8</sup> for alloys contaminated with Fe and Cr, though it is too early to draw a definite conclusion. It is not difficult to calculate various transport coefficients in the same limiting case.

<sup>14</sup> By using Abrikosov's diagram technique, Griffin obtained, up to the third order in  $(\rho J)$  an expression for  $N(\omega)/N(0)$ , which agrees with the present results (private communication).

## VI. CONCLUSION

We have treated the effect of magnetic impurities on superconducting properties. Using the technique developed by Suhl for normal metals, we have discussed some limiting cases in superconductors.

First, the effect of a single impurity atom was considered. If the transition temperature  $T_{c0}$  is large ( $T_{c0} > T_c$ ), a pair of bound states appears in the energy gap. It is not clear at present how the bound states affect various electronic properties.

Second, in the gapless region ( $\Delta$  small), the self-consistent equation in the presence of randomly distributed magnetic impurities was solved. It was shown to a good approximation that the results of AG theory (which essentially treated the spin-exchange interaction in Born approximation) still hold, if one replaces  $\tau_s$  by the exact scattering amplitude in the normal state. We expect that, under favorable conditions, the measurement of the tunneling density of states will reveal an observable deviation from the AG theory on the low-frequency side.

The case of a finite concentration of impurities in a more general situation (for arbitrary value of  $\Delta$ ) is more difficult to analyze and will be left for the future.

Very recently Suhl and Wong succeeded in removing the difficulty associated with the complex poles by introducing a pair of Castillejo-Dalitz-Dyson poles in the expression for the  $F$  function. The revised treatment is easily extended to the case of superconductors. We can show that the result concerning the appearance of bound states in the case of a single impurity is not affected in this new version. Also we find that the results concerning the properties of gapless superconductors still hold.

## ACKNOWLEDGMENTS

The author thanks Professor H. Suhl, Dr. A. Griffin, and Dr. Y. Nagaoka for interesting discussions and helpful suggestions in the course of this work.

The author is happy to express his gratitude to Professor P. G. de Gennes and the Service de Physique des Solides of the University of Paris (Orsay) for their hospitality extended to him while this work was completed.