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The Effects of Impurities on Superconductors with Kondo Effect

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The Green's functions of s- and d-electrons in superconductors are obtained on the basis of the interpolation theory[1),2)] which includes as impurity effects the pair breaking and the effective repulsive interaction between s-electrons. By the use of these Green's functions, the order parameter and the critical magnetic field at zero temperature in the presence of impurities and its initial decrease are given. The localized excited state in the gap is found and shown to be doublet, differently from that of Müller-Hartmann and Zittartz.

§ 1. Introduction

The effects of impurities on superconductors are qualitatively different between the cases of magnetic and nonmagnetic impurities. Magnetic impurities have striking effects even at small concentration,[3)] while the effects of nonmagnetic ones are moderate.

The condition for the presence or absence of localized moments on transition-metal impurities in normal metals was studied by Anderson.[4)] A self-consistent Hartree-Fock treatment shows that there is a sharp transition between the magnetic and the nonmagnetic states, depending on $U \gtrless \pi\Gamma$ in the case of half-filled d-levels, where U is the intra-atomic Coulomb repulsion and Γ the width parameter of d-level. Therefore, we can assume that the localized magnetic moments are well-defined in the case of $U \gg \pi\Gamma$ and investigate the effects of magnetic impurities in various metals on the basis of the s-d Hamiltonian. From this standpoint, Abrikosov and Gorikov (AG)[5)] discussed the effects of magnetic impurities on superconductors in the Born approximation. Müller-Hartmann and Zittartz (MZ)[6)] extended the AG theory to take account of the Kondo effect, and obtained fairly interesting results. Their theory, however, breaks down at low temperatures ($T < T_K$), where magnetic moments disappear. On the other hand, the theory based on the Anderson Hamiltonian can cover magnetic as well as nonmagnetic cases in the same framework. Shiba[7)] discussed the problem from this standpoint in the Hartree-Fock approximation, though it is still insufficient as the spin fluctuation is not taken into account.

Recently, Yamada and Yosida[8)] have developed a theory of impurities in normal metals on the basis of the Anderson model for the case of half-filled d-levels. Now we can say the problem in normal metals has been solved essentially. Thus, we extend their theory to the theory of impurities in superconductors. In the case $U/\pi\Gamma \gg 1$ on which we concentrate our attention here, we can divide the region of energy and temperature into two with respect to $|\omega|/T_K$ and/or $T/T_K \gtrless 1$. In the nonmagnetic region, $|\omega|/T_K < 1$ and $T/T_K < 1$, it is easy to extend the theory by Yamada and Yosida[8] in normal metals to superconductors.[9] In the magnetic region, $|\omega|/T_K$ and/or $T/T_K > 1$, it is necessary to take into account the effects of localized moments. Therefore, in this region, it is adequate to introduce an effective interaction $\tilde{J}(\omega)$ between spins of s-electrons and d-electrons, for which we can make use of the result of MZ, $\tilde{J}(\omega) = -\rho^{-1}[\ln^2 \pi|\omega|/4T_K + \pi^2 S(S+1)]^{-1/2}$.

On the basis of such considerations, the effects of impurities on superconductors were calculated in the previous paper[2] by Ichinose, Nagaoka and the present author (MIN) and some improvements were given on the dependence of the superconducting transition temperatures and the upper critical magnetic fields on the impurity concentration at low temperature ($T < T_K$) and at low magnetic field ($H < H_K$), respectively. The knowledge of the Green's functions in the normal state ($\Delta = 0$) was sufficient in this calculation. Extending this calculation we now attempt to obtain the Green's functions of the superconducting state ($\Delta \neq 0$) in the presence of impurities, and to investigate how the superconducting state is modified by the presence of them. We calculate the Green's functions, taking into account of the well-known fact[10] that, in the case $\Delta \neq 0$, the singularity at the Fermi level is suppressed by the presence of Δ. We, therefore, obtain another criterion for the magnetic (nonmagnetic) case that Δ is larger (smaller) than T_K.

The paper is arranged as follows: Section 2 is devoted to obtaining Green's functions in superconductors. In § 3 T_c and thermal properties near T_c, such as ΔC and C^* are discussed. Thermal properties at $T=0$, Δ, H_c, h^* and δ^* are found in § 4. In § 5 we study the single impurity problem and show the existence of a doublet as the localized state within the energy gap in the case $T_K \gg T_{c0}$.

§ 2. Formulation

Our model Hamiltonian is the same as Ratto-Blandin,[11] Kaiser[12] and Shiba's,[7] i.e.,

$$
\begin{aligned}
&H = H_{\mathrm{BCS}} + H_d + H_{sd} \,, \\
&H_{\mathrm{BCS}} = \sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}} a_{\boldsymbol{k}\sigma}^{+} a_{\boldsymbol{k}\sigma} - \sum_{\boldsymbol{k}} (\Delta a_{\boldsymbol{k}\uparrow}^{+} a_{-\boldsymbol{k}\downarrow}^{+} + \mathrm{h.c.}) \,, \\
&H_d = \sum_{i\sigma} E_d^{\,0} a_{di\sigma}^{+} a_{di\sigma} + U \sum_{i} n_{di\uparrow} n_{di\downarrow} \,, \qquad\qquad (2\cdot 1) \\
&H_{sd} = \sum_{i} \sum_{\boldsymbol{k}\sigma} (V e^{i\boldsymbol{k}\boldsymbol{R}_i} a_{\boldsymbol{k}\sigma}^{+} a_{di\sigma} + \mathrm{h.c.}) \,, \\
&n_{di\sigma} = a_{di\sigma}^{+} a_{di\sigma} \,,
\end{aligned}
$$

where $a_{\boldsymbol{k}\sigma}^{+}$ denotes the creation operator of a conduction electron of the host metal, and $a_{di\sigma}^{+}$ that of an electron in the resonance orbital of the i-impurity. $\xi_{\boldsymbol{k}}$ and

E_d^0 are measured from the Fermi energy. Here, following Yamada-Yosida,[8] we consider the half-filled resonance d-orbital and take $E_d^0 = -(U/2)$. H_{BCS}, H_d and H_{sd} represent the Hamiltonians of the host superconductor in the BCS approximation, the resonance orbitals and the s-d mixing, respectively. The sites of impurities are assumed to be randomly distributed.

We use the Green's function formalism extended to Nambu space. The temperature Green's functions for s- and d-electrons averaged over the spacial distributions and the spin directions of impurities are related to the self-energy parts by

$$G^{-1}(\boldsymbol{k}, \omega) = i\tilde{\omega} - \xi_{\boldsymbol{k}}\rho_3 - \tilde{\Delta}\rho_2\sigma_2 = i\omega - \xi_{\boldsymbol{k}}\rho_3 - \Delta\rho_2\sigma_2 - \Sigma_s(\omega), \tag{2·2}$$

$$G_d^{-1}(\omega) = i\tilde{\omega}_d - \tilde{\Delta}_d\rho_2\sigma_2 = i\omega - \Sigma_d(\omega), \tag{2·3}$$

where σ_i and ρ_i are Pauli matrices in spin space and in particle-hole space, respectively. Δ is the averaged order parameter of alloys. In normal metals, the density of states of d-levels has the central and side peaks at $\omega = 0$ and $\omega = \pm(U/2)$ respectively. In superconductors the same situation may be expected. In general contributions from both peaks are included in $G_d(\omega)$. We, however, regard $G_d(\omega)$ as the Green's function representing only the central peak of d-levels, as the contribution from the side peaks is appropriately expressed in terms of the spin dependent scattering. Then the scattering of s-electrons due to the central and side peaks can be represented by the s-d mixing and the spin dependent scattering terms, respectively. The former term is important in the nonmagnetic region, $|\omega|/T_K < 1$ and $\Delta/T_K < 1$, and the latter in the magnetic region, $|\omega|/T_K$ and/or $\Delta/T_K > 1$. From these considerations, self-energy parts are given by

$$\Sigma_s(\omega) = N_i V^2 \rho_3 G_d \rho_3 + \Sigma_s'(\omega), \tag{2·4}$$

$$\Sigma_d(\omega) = V^2 \rho_3 \overline{G}_s(\omega) \rho_3 + \Sigma_d'(\omega), \tag{2·5}$$

$$\overline{G}_s(\omega) = \sum_{\boldsymbol{k}} G(\boldsymbol{k}, \omega) = -\pi N\rho \frac{iu + \rho_2\sigma_2}{\sqrt{u^2+1}}, \tag{2·6}$$

where $u = \tilde{\omega}/\tilde{\Delta}$. The first terms of Eqs. (2·4) and (2·5) are due to the s-d mixing. $\Sigma_s'(\omega)$ comes from the effective spin dependent scattering part and is easily found if we take only the terms of order $\tilde{J}^2$:

$$\Sigma_s'(\omega) = \frac{-1}{2\tau_s} \frac{iu + \rho_2\sigma_2}{\sqrt{u^2+1}}, \tag{2·7}$$

where $1/\tau_s$ is the spin-flip scattering part for which we make use of the result of MZ's theory for $|\omega|$, Δ larger than T_K, and $N\rho$ the density of states of s-electrons at the Fermi energy. $\Sigma_d'(\omega)$ is due to the repulsive potential U and written as

$$\Sigma_d'(\omega) = -i\omega(\tilde{\chi}_{\text{even}} - 1) - \rho_2\sigma_2\Delta_d, \tag{2·8}$$

where $\tilde{\chi}_{\text{even}} = \pi\Gamma/4T_K$ and $\Gamma = \pi N\rho V^2$. The derivations of Eqs. (2·7) and (2·8) are given in the Appendix. Substitution of Eqs. (2·5) and (2·8) into Eq. (2·3) gives

$$G_d^{-1}(\omega)=\Gamma\left(i\bar{\omega}+i\frac{u}{\sqrt{u^2+1}}-\left(\frac{1}{\sqrt{u^2+1}}-\frac{\Delta_d}{\Gamma}\right)\sigma_2\rho_2\right), \tag{2·9}$$

$$\Delta_d=\frac{\pi\Gamma}{4T_K}\pi T\sum_\omega\frac{1}{(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2}\frac{1}{\sqrt{u^2+1}}, \tag{2·10}$$

where $\bar{\omega}\equiv\pi\omega/4T_K$.

The expression of $G_d(\omega)$ in Eq. (2·9) is valid only when $|\bar{\omega}|<1\,(\bar{\omega}\equiv\pi\omega/4T_K)$ and $\bar{\Delta}<1$ $(\bar{\Delta}\equiv\pi\Delta/4T_K)$. When we consider the magnetic region, $\bar{\Delta}>1$ and/or $|\bar{\omega}|>1$, $G_d(\omega)$ corresponding to the central peak is expected to vanish since it arises from the anomaly due to the sharp Fermi surface which does not exist in this case on account of the presence of the gap Δ and/or ω. $G_d(\omega)$ in Eq. (2·9) satisfies this expectation. We use this Green's function of d-electron as an extrapolation to all region of $\bar{\omega}$ and $\bar{\Delta}$. From Eqs. (2·2), (2·4), (2·7) and (2·9), we obtain

$$\Sigma_s(\omega)=\frac{-1}{2\tau_s}\frac{iu+\rho_2\sigma_2}{\sqrt{u^2+1}}+\frac{n}{\pi\rho}$$
$$\times\frac{-i(\bar{\omega}+(u/\sqrt{u^2+1}))+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))\rho_2\sigma_2}{(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2}, \tag{2·11}$$

where n is the concentration of impurities. The following expression is verified by setting up the equations for $\tilde{\omega}$ and $\tilde{\Delta}$:

$$\frac{\omega}{\Delta}=u\left[1-\frac{1}{\tau_s\Delta}\frac{1}{\sqrt{u^2+1}}-\frac{n}{\pi\rho}\frac{\Delta_d}{\Delta\Gamma}\frac{1}{(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2}\right]$$
$$-\frac{n}{\pi\rho}\frac{\bar{\omega}}{(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2}. \tag{2·12}$$

Equation (2·12) coincides with Shiba's essentially if we replace the factor $4T_K/\pi$ in the definition of $\bar{\omega}$ and Δ_d by Γ and ignore the difference of the treatment of the spin scattering.

§ 3. Thermal properties near T_c

The average order parameter is determined by

$$\Delta=|g|N\rho\pi T\sum_\omega\frac{1}{\sqrt{u^2+1}}, \tag{3·1}$$

where $\omega=\pi T(2n+1)$. By substituting into Eq. (3·1) the expansion of u and Δ_d in powers of Δ

$$u=\frac{a_{-1}}{\Delta}+a_1\Delta+\cdots, \tag{3·2}$$

$$\Delta_d=\frac{\pi\Gamma}{4T_K}(\Delta d_1+\Delta^3 d_3+\cdots), \tag{3·3}$$

and equating the coefficients of equal powers of Δ on both sides of Eq. (3·1), we obtain, with the use of Eq. (2·12),

$$\ln\frac{T_{c0}}{T}=B_0(n,T)+\frac{1}{2}B_1(n,T)\left(\frac{\Delta}{2\pi T}\right)^2+\cdots, \tag{3·4}$$

$$B_0(n,T)=-2\pi T\sum_{\omega>0}\left(\frac{1}{a_{-1}}-\frac{1}{\omega}\right), \tag{3·5}$$

$$B_1(n,T)\cong(2\pi T)^3\sum_{\omega>0}\frac{1}{a_{-1}^4}\,\omega\left(1+\frac{n}{4\rho T_K}\frac{1}{(1+\bar{\omega})^2}\right), \tag{3·6}$$

where

$$\frac{1}{a_{-1}}=\frac{1-(n/4\rho T_K)\,(d_1/(1+|\bar{\omega}|)^2)}{|\omega|+(1/\tilde{\tau}_s)}, \tag{3·7}$$

$$d_1=\frac{\Phi_1(T)}{1+(n/4\rho T_K)\,\Phi_2(T)}, \tag{3·8}$$

$$\Phi_n(T)=2\pi T\sum_{\omega>0}\frac{1}{(1+\bar{\omega})^{2n}}\,\frac{1}{\omega+(1/\tilde{\tau}_s)}. \tag{3·9}$$

In Eqs. (3·7) and (3·9), we make use of an interpolation formula:[2]

$$\frac{1}{\tilde{\tau}_s}=\frac{1}{\tau_s}+\frac{n}{4\rho T_K}\frac{\omega}{(1+\bar{\omega})^2}=\frac{n}{2\pi\rho}\gamma(\bar{\omega})=\frac{n}{2\pi\rho}$$
$$\times\begin{cases}2\bar{\omega}-\bar{\omega}^2 & ;\ 0<\bar{\omega}<1,\\[2mm] \dfrac{\pi^2 S(S+1)}{\ln^2|\bar{\omega}|+\pi^2 S(S+1)} & ;\ \bar{\omega}>1.\end{cases} \tag{3·10}$$

When we derive Eq. (3·6), we neglect the terms which are of order $(T_c/T_K)^n$ $(n\geq 1)$ in the case $T_K\gg T_c$ and $(T_K/T_c)^n$ $(n>0)$ in $T_c\gg T_K$. Therefore it is quantitatively insufficient in the region $T_c/T_K\cong 1$.

The transition temperature is determined, by taking only $B_0(n,T_c)$, by

$$1=|g|N\rho\left[\Phi_0(T_c)-\frac{n}{4\rho T_K}\frac{\Phi_1^2(T_c)}{1+(n/4\rho T_K)\,\Phi_2(T_c)}\right], \tag{3·11}$$

which is the same equation as obtained in MIN. The numerical results of Eq. (3·11) are given there. The jump of the specific heat ΔC at the superconducting transition temperature and its initial decrease C^* are given by

$$\frac{\Delta C}{\Delta C_0}=\frac{T_c}{T_{c0}}\frac{B_1(0,T_{c0})}{B_1(n,T_c)}\left(1+T_c\frac{\partial B_0(n,T_c)}{\partial T_c}\right)^2, \tag{3·12}$$

$$C^*=\lim_{n\to 0}\frac{(\Delta C-\Delta C_0)/n\Delta C_0}{(T_c-T_{c0})/nT_{c0}}. \tag{3·13}$$

In both of the limiting cases $T_K/T_{c0}\ll 1$ and $T_K/T_{c0}\gg 1$, these results reduce to the AG's[5] for magnetic cases and Takanaka and Nagashima's[13] and Shiba's[7] for nonmagnetic ones, respectively. However, for the quantitative improvement in the region $T_c \cong T_K$, we must take account of more complicated graphs of the self-energy.*)

§ 4. Thermal properties at $T=0$K

The concentration dependence of the average order parameter at 0K was studied by Kaiser[12] for nonmagnetic cases and Shiba[7] for magnetic cases, respectively. On the other hand we can discuss both cases. The order parameter is given by

$$\varDelta = |g| N\rho \int_0^{\omega_D} d\omega \frac{Y}{\sqrt{Z^2+Y^2}}, \tag{4·1}$$

where

$$Z=\omega+\frac{1}{\tau_s \varDelta}\frac{u}{\sqrt{u^2+1}}+\frac{n}{4\rho T_K}\frac{\omega}{(\varpi+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\varDelta_d/\Gamma))^2},$$

$$Y=\varDelta\left\{1-\frac{nd}{4\rho T_K}\frac{1}{(\varpi+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\varDelta_d/\Gamma))^2}\right\}$$

and

$$d \equiv \frac{4T_K}{\pi\Gamma}\frac{\varDelta_d}{\varDelta}. \tag{4·2}$$

In the nonmagnetic case ($\varDelta \ll T_K$), $\varDelta$ is determined ignoring the terms of $\varDelta(\varDelta/T_K)^2$ by

$$\varDelta \cong |g|N\rho\left\{\int_0^{\omega_D} d\omega \frac{\varDelta}{\sqrt{\omega^2+(\varDelta f)^2}}+\varDelta\kappa\right\} = |g|N\rho\left\{\varDelta f \ln\frac{2\omega_D}{\varDelta f}+\varDelta\kappa\right\}, \tag{4·3}$$

$$\kappa = \int_0^{\omega_D} d\omega\left(\frac{1}{a_{-1}}-\frac{f}{\omega}\right), \tag{4·4}$$

where

$$f=\frac{1-(n/4\rho T_K)d}{1+(n/4\rho T_K)}, \quad \frac{1}{a_{-1}}=\frac{1-(n/4\rho T_K)d(1/(1+|\varpi|)^2)}{\omega+(1/\tilde{\tau}_s)}$$

and

$$d \simeq f \ln\frac{2\omega_D}{\varDelta f}+\int_0^{\omega_D} d\omega\left(\frac{1}{(1+\varpi)^2}\frac{1}{a_{-1}}-\frac{f}{\omega}\right). \tag{4·5}$$

Comparing Eq. (4·5) with Eq. (4·3), we find

$$d=\frac{(1/|g|N\rho)-(\varPhi_0(0)-\varPhi_1(0))}{1-(n/4\rho T_K)(\varPhi_1(0)-\varPhi_2(0))}. \tag{4·6}$$

*) This problem will be discussed by S. Ichinose in a forthcoming paper by a different approach.

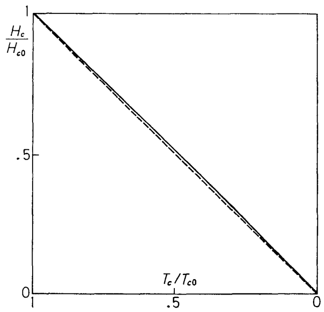

Fig. 1. The reduced critical field H_c/H_{c0} at 0K versus reduced critical temperature T_c/T_{c0}. The dashed line represents the BCS law of corresponding states and the solid lines our result for $50 \lesssim (T_K/T_{c0}) < 10^3$.

From Eq. (4·3), we easily obtain

$$\frac{\Delta}{\Delta_0}=\frac{1}{f}\exp\left[\frac{1}{|g|N\rho}\left(1-\frac{1}{f}\right)+\frac{\kappa}{f}\right]. \tag{4·7}$$

This result coincides with Kaiser's[12] if we replace the factor $4T_K/\pi$ in the definition of f and κ by Γ and assume $\Gamma \gg T_{c0}$. The free energy difference between the normal and the superconducting states is easily obtained by

$$\Omega_s-\Omega_n=\int_0^\Delta d\Delta'\Delta'^2\frac{d}{d\Delta'}\left(\frac{1}{|g|}\right)=-\frac{1}{2}N\rho f\Delta^2. \tag{4·8}$$

The critical magnetic field H_c at zero temperature is determined by

$$\Omega_s-\Omega_n=-\frac{1}{2}N\rho f\Delta^2=-\frac{H_c^2}{8\pi}$$

and

$$\frac{H_c}{H_{c0}}=\frac{1}{\sqrt{f}}\exp\left[\frac{1}{|g|N\rho}\left(1-\frac{1}{f}\right)+\frac{\kappa}{f}\right]. \tag{4·9}$$

Figure (1) shows some examples of the numerical results for $S=1/2$ obtained.

In general case, we introduce the following approximations in Eq. (4·1); i.e., we substitute u by ω/Δ in the terms proportional to the impurity concentration n of the denominator and $(\bar{\omega}+u/\sqrt{u^2+1})^2+(1/\sqrt{u^2+1}-\Delta_d/\Gamma)^2$ by $(1+\sqrt{\bar{\omega}^2+\bar{\Delta}^2})^2$. The first substitution is reasonable because of the dilute impurity. The incorrectness of the second at $|\omega|\lesssim\Delta$ is not important, since it does not affect much on the result of the summation. Thus, we get the following equations of the order parameter as an interpolation formula:

$$\frac{1}{|g|N\rho}\cong\Psi_0-\frac{nd}{4\rho T_K}\Psi_1, \tag{4·10}$$

where

$$d\cong\Psi_1-\frac{nd}{4\rho T_K}\Psi_2, \tag{4·11}$$

$$\Psi_n \equiv \int_0^{\omega_D} d\omega \frac{1}{(1+\sqrt{\bar{\omega}^2+\bar{\varDelta}^2})^{2n}}$$

$$\times \frac{1}{\sqrt{\omega^2(1+(1/\tilde{\tau}_s(\sqrt{\omega^2+\varDelta^2})\sqrt{\omega^2+\varDelta^2}))^2+\varDelta^2(1-(nd_0/4\rho T_K)(1/(1+\sqrt{\bar{\omega}^2+\bar{\varDelta}^2})^2))^2}} \tag{4·12}$$

and

$$d_0 \equiv \int_0^{\omega_D} d\omega \frac{1}{(1+\sqrt{\bar{\omega}^2+\bar{\varDelta}^2})^2} \frac{1}{\sqrt{\omega^2+\varDelta^2}}. \tag{4·13}$$

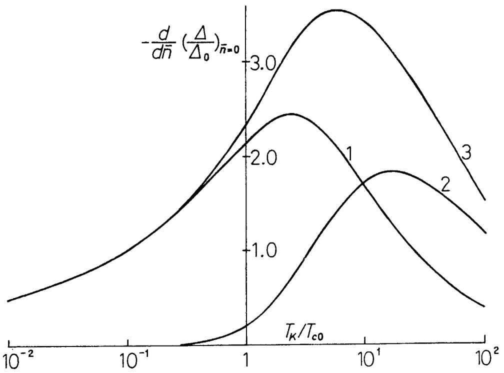

Fig. 2. The initial decrease of the reduced order parameter at 0K $\varDelta/\varDelta_0$ versus the reduced Kondo temperature T_K/T_{c0}. Numbers attached to each curve denote 1) the contribution from the pair-breaking effects, 2) the effective repulsive potential and 3) the total value, respectively.

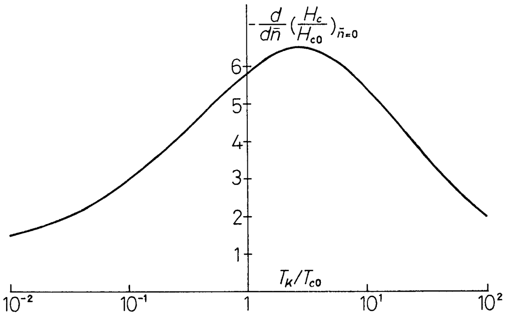

Fig. 3. The initial decrease of the reduced critical field at 0K versus the reduced Kondo temperature T_K/T_{c0}.

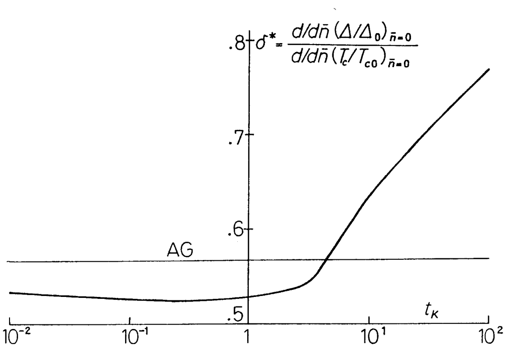

Fig. 4. The initial slope of $\varDelta/\varDelta_0$ at 0K versus T_c/T_{c0} against T_K/T_{c0}. The line AG represents the AG value.

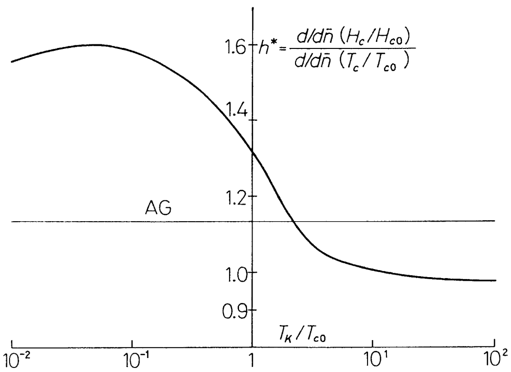

Fig. 5. The initial slope of H_c/H_{c0} at 0K versus T_c/T_{c0} against T_K/T_{c0}. The line AG represents the AG value.

From these equations, we find

$$\frac{1}{|g|N\rho}=\Psi_0-\frac{n}{4\rho T_K}\frac{\Psi_1^2}{1+(n/4\rho T_K)\Psi_2}\,. \tag{4·14}$$

This equation of the order parameter is analogous to that of the critical temperature. The critical magnetic field H_c at zero temperature is defined by

$$\begin{aligned} h_c^2=\left(\frac{H_c}{H_{c0}}\right)^2 &= \frac{2}{\varDelta_0^2}\int_0^{\varDelta_0} d\varDelta_0'\varDelta_0'\left(\frac{\varDelta'}{\varDelta_0'}\right)^2 \\ &= 2t_K^2\int_{t_K}^{\infty}dt_K'\,\frac{1}{t_K'^3}\left[\frac{\varDelta}{\varDelta_0}\right]^2(t_K'), \end{aligned} \tag{4·15}$$

where $\varDelta/\varDelta_0$ of the integrand is the function of $t_K'=T_K/T_{c0}'$ and H_{c0} is the critical field of the host superconductor.

The initial decrease of $\varDelta$ and H_c is easily written, by the use of Eqs. (4·14) and (4·15) as

$$\begin{aligned} -\frac{d}{d\bar{n}}\left(\frac{\varDelta}{\varDelta_0}\right) &= \frac{\pi^2}{2t_K}\int_{\bar{\varDelta}_0}^{\bar{\omega}_D}dx\frac{\sqrt{x^2-\bar{\varDelta}_0^2}}{x^3}\,\gamma(x)+\frac{\pi^2}{t_K} \\ &\times\int_{\bar{\varDelta}_0}^{\bar{\omega}_D}dx\,\frac{1}{(1+x)^2}\,\frac{1}{\sqrt{x^2-\bar{\varDelta}_0^2}}\int_{\bar{\varDelta}_0}^{\bar{\omega}_D}dx\,\frac{1}{(1+x)^2}\,\frac{\sqrt{x^2-\bar{\varDelta}_0^2}}{x^2}, \end{aligned} \tag{4·16}$$

$$-\frac{d}{d\bar{n}}\left(\frac{H_c}{H_{c0}}\right)=2t_K\int_{t_K}^{\infty}dt_K'\,\frac{1}{t_K'^2}\left[-\frac{d}{d\bar{n}}\left(\frac{\varDelta}{\varDelta_0}\right)\right](t_K'), \tag{4·17}$$

where the integrand is the function of t_K' and $\bar{n}=n/(2\pi)^2\rho T_{c0}$. We illustrate $-(d/d\bar{n})(\varDelta/\varDelta_0)_{\bar{n}=0}$, $-(d/d\bar{n})(H_c/H_{c0})_{\bar{n}=0}$, $\delta^*=\{(d/d\bar{n})(\varDelta/\varDelta_0)/(d/d\bar{n})(T_c/T_{c0})\}$ and $h^*=\{(d/d\bar{n})(H_c/H_{c0})/(d/d\bar{n})(T_c/T_{c0})\}$ in Figs. (2), (3), (4) and (5), respectively. These results are reasonable in comparison with the experimental ones given in the review article of Takayanagi and Sugawara.[14] δ^* and h^* are different from that of Müller-Hartmann and Shiba.[15]

§ 5. Single impurity

In the case of a single impurity located at $R=0$, we replace u by $\omega/\varDelta$ in Eq. (2·9) and perform the analytic continuation, $i\omega\to\omega$. Thus we obtain

$$G_d^{-1}(\omega)=\Gamma\left[\bar{\omega}+\frac{\omega}{\sqrt{\varDelta^2-\omega^2}}-\left(\frac{\varDelta}{\sqrt{\varDelta^2-\omega^2}}-\frac{\varDelta_d}{\Gamma}\right)\sigma_2\rho_2\right], \tag{5·1}$$

$$\varDelta_d=\frac{\pi\Gamma}{4T_K}\,T\sum_{\omega}\frac{1}{(\bar{\omega}+(\omega/\sqrt{\omega^2+\varDelta^2}))^2+((\varDelta/\sqrt{\omega^2+\varDelta^2})-(\varDelta_d/\Gamma))^2}\frac{\varDelta}{\sqrt{\omega^2+\varDelta^2}}\,. \tag{5·2}$$

Equation (5·1) has a pole in the case $|\omega|<\varDelta$ and $\varDelta/T_K\ll 1$. Because the pole locates near the gap edge, we can derive

$$G_d(\omega)\simeq\frac{1}{\Gamma}\left[\frac{\omega}{\sqrt{\Delta^2-\omega^2}}-\left(\frac{\Delta}{\sqrt{\Delta^2-\omega^2}}-\frac{\Delta_d}{\Gamma}\right)\rho_2\sigma_2\right]^{-1}$$

$$=\frac{1}{\Gamma}\;\frac{-(\omega/\sqrt{\Delta^2-\omega^2})-((\Delta/\sqrt{\Delta^2-\omega^2})-\alpha)\sigma_2\rho_2}{\left(\sqrt{\dfrac{\Delta-\omega}{\Delta+\omega}}-\alpha\right)\left(\sqrt{\dfrac{\Delta+\omega}{\Delta-\omega}}-\alpha\right)}\,, \tag{5·3}$$

where

$$\alpha=\frac{\Delta_d}{\Gamma}\simeq\frac{\pi\Delta}{4T_K}\ln\left(\frac{4T_K}{\pi\Delta}e\right). \tag{5·4}$$

The position of the pole is given by

$$\omega_0=\pm\Delta\frac{1-\alpha^2}{1+\alpha^2}\,, \tag{5·5}$$

which is the same result obtained by Machida and Shibata[16] if we substitute $4T_K/\pi$ by Γ in the definition of α.

The retarded Green's function $G_{\boldsymbol{k}\boldsymbol{k}'}(\omega)$ for the s-electrons in the single impurity case is determined by

$$G_{\boldsymbol{k}\boldsymbol{k}'}(\omega)=G_{\boldsymbol{k}}{}^0(\omega)\delta_{\boldsymbol{k}\boldsymbol{k}'}+G_{\boldsymbol{k}}{}^0(\omega)t(\omega)G_{\boldsymbol{k}'}{}^0(\omega), \tag{5·6}$$

with the BCS Green's function

$$G_{\boldsymbol{k}}{}^0(\omega)=[\omega-\xi_{\boldsymbol{k}}\rho_3-\Delta\sigma_2\rho_2]^{-1}. \tag{5·7}$$

The matrix of the scattering due to an impurity has the form

$$t(\omega)=V\rho_3G_d(\omega)\rho_3V=\frac{1}{\pi\rho}\;\frac{-(\omega/\sqrt{\Delta^2-\omega^2})+((\Delta/\sqrt{\Delta^2-\omega^2})-\alpha)\rho_2\sigma_2}{(\sqrt{(\Delta-\omega/\Delta+\omega)}-\alpha)(\sqrt{(\Delta+\omega/\Delta-\omega)}-\alpha)}\,. \tag{5·8}$$

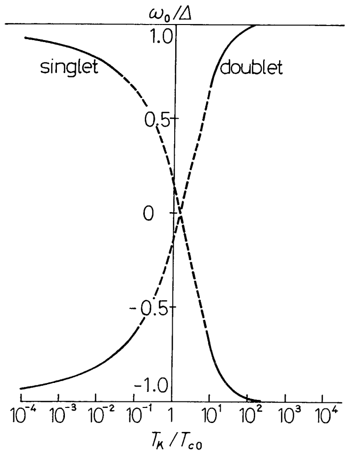

Fig. 6. The position of the LES versus the reduced temperature T_K/T_{c0}.

The degeneracy of the pole (localized excited state) is found, following the paper by Nagaoka and the present author[17] as

$$\frac{1}{\pi}\operatorname{Im}T_r\int_{-\infty}^{\infty}\sum_{\boldsymbol{k}}G_{\boldsymbol{k}\boldsymbol{k}}(\omega+i\delta)\,|_{\rm pole}d\omega=2\,. \tag{5·9}$$

Equation (5·9) shows the LES is doublet. This fact is apparent since the LES is accompanied by the half-filled singlet d-electron. We plot the position of the LES in Fig. 6. The LES at $\pi\Delta/4T_K\ll 1$ is completely different from MZ.[6] In the case $J<0$, it seems the LES changes from the singlet states[17] to doublet at the point of $\Delta\pi/4T_K\simeq 1$. In the region $\Delta\pi/4T_K\ll 1$ or $\Delta\pi/4T_K\gg 1$, the LES is understood easily as one particle state.

§ 6. Conclusion

The Green's functions of *s*-electrons and *d*-electrons in superconductors were obtained on the basis of the interpolation theory which includes as impurity effects the pair breaking and the effective repulsive interaction between *s*-electrons. By the use of these Green's functions, the equations to determine the effects of magnetic impurities on thermal properties at $T=T_c$ (T_c, ΔC and C^*) and at $T=0$K (Δ and H_c) were derived. That of T_c was the same as MIN's. We calculated numerically Δ and H_c at $T=0$K in the nonmagnetic case and its initial decrease δ^* and h* in both of magnetic and nonmagnetic cases. The localized excited state in the gap is found in the case $T_K/T_{c0}\gg 1$ without the interpolation and shown to be doublet.

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Appendix

(i) $\Sigma_s'(\omega)$

The term corresponding to Fig. A·1 is given by

$$N_i\left(\frac{\tilde{J}(\omega)}{2N}\right)^2 S(S+1)(-\pi N\rho)\frac{iu+\rho_2\sigma_2}{\sqrt{u^2+1}} \equiv \frac{-1}{2\tau_s}\frac{iu+\sigma_2\rho_2}{\sqrt{u^2+1}}, \tag{A·1}$$

where $\tilde{J}(\omega)=-(1/\rho)\{\ln^2(\pi\sqrt{\omega^2+\Delta^2}/4T_K)+\pi^2 S(S+1)\}^{-1/2}$. To discuss the jump of the specific heat ΔC at the transition temperature, we need to obtain the self-energy up to the terms of order Δ^3.

(ii) $\Sigma_d'(\omega)$

$\Sigma_d'(\omega)$ comes from the repulsive potential U. The normal part is given by following Yamada-Yosida:[8)]

$$-i\omega(\tilde{\chi}_{\rm even}-1), \tag{A·2}$$

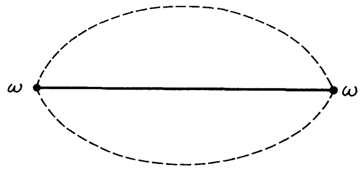

Fig. A·1. The solid and dashed lines represent the propagators of the *s*-electron and pseudo Fermions. The points represent the effective interaction between the *s*-electron and pseudo Fermions and are given as $-\tilde{J}(\omega)/2N((1+\rho_3/2)\sigma+(1-\rho_3/2)\sigma_2\boldsymbol{\sigma}\sigma_2)\cdot\boldsymbol{S}$.

where we ignore the term $\Gamma(\omega/T_K)^2$.

For the off-diagonal part, we only keep the term corresponding to the induced d-pairing,

$$-\Delta_d\sigma_2\rho_2 = UT\sum_\omega \rho_3 G_d(\omega)\rho_3|_{O.D}\ . \tag{A·3}$$

Substituting Eq. (2·9) into Eq. (A·3), Δ_d is given by

$$\Delta_d = \frac{U}{1+(U/\Gamma^2)T\sum_\omega\{1/(\bar{\omega}+(1/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2\}}$$
$$\times\frac{1}{\Gamma}T\sum_\omega\frac{(u^2+1)^{-1/2}}{(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2}\ . \tag{A·4}$$

Taking the limit $U\to\infty$, we obtain

$$\Delta_d = \frac{1}{(1/\Gamma^2)T\sum_\omega\{1/(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2\}}$$
$$\times\frac{1}{\Gamma}T\sum_\omega\frac{1/\sqrt{u^2+1}}{(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2}\ . \tag{A·5}$$

The effective potential is approximated, when $T=0$ and $\Delta=0$, by

$$\frac{1}{(1/\Gamma^2)T\sum_\omega\{1/(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2\}}\cong\frac{\pi^2\Gamma^2}{4T_K}\equiv\tilde{U}\ . \tag{A·6}$$

The right-hand side of Eq. (A·6) is the same as given by Yamada-Yosida.[8] We therefore find within the above approximation,

$$\Sigma_d'(\omega)\simeq -i\omega(\tilde{\chi}_{\text{even}}-1)-\rho_2\sigma_2\tilde{U}T\sum_\omega\frac{1}{\Gamma}$$
$$\times\frac{1}{(\bar{\omega}+(u/\sqrt{u^2+1}))^2+((1/\sqrt{u^2+1})-(\Delta_d/\Gamma))^2}\frac{1}{\sqrt{u^2+1}}\ . \tag{A·7}$$

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