

EFFECT OF MAGNETIC IMPURITY
IN TWO-BAND MODEL OF SUPERCONDUCTOR

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Abstract: Perturbation theory is used to determine the change in transition temperature of a two-band superconductor due to the presence of magnetic impurity. Localized exchange interaction between the impurity spin and electron is considered. This interaction can lead to both inter-band and intra-band scattering. We find that the d-band transition temperature decreases more than the s-band transition temperature due to the addition of impurity. This distinction arises because the d-band gap is larger than the s-band gap.

1. Introduction

Suhl, Matthias and Walker¹⁾ proposed the two-band model of superconductor for transition metals like vanadium and niobium. In this model they allowed the formation of a Cooper pair not only within the same band (intra-band) but also between two different bands (inter-band). This model has received considerable attention within the last few years. By the use of Green's function, Chow²⁾ studied the effect of non-magnetic impurity on transition temperature. In the intra-band BCS coupling limit he found that the inter-band impurity scattering plays an important role in determining the change in transition temperature. In this paper we will study the effect of magnetic impurity in a two-band superconductor in the intra-band coupling limit.

We will use perturbation theory to determine the change in free energy in the normal and superconducting state. The method of calculating this change in free energy is the same as is used by Suhl and Matthias³⁾. This method is based on a

unitary transformation which eliminates the perturbation up to the first order from the total Hamiltonian. From this transformed Hamiltonian we then calculate the free energy and transition temperature by using Herring's differential equation method⁴⁾.

In Section 2 we will discuss the unperturbed Hamiltonian and the perturbation Hamiltonian. In Section 3 we will find the unitary transformation which will diagonalize the Hamiltonian up to the first order in perturbation. In Section 4 we will calculate the change in free energy and the change in transition temperature. Section 5 is the conclusion.

2. Hamiltonian of the system

The Hamiltonian of a two-band superconductor in the intra-band coupling limit looks like the following:

$$\begin{aligned}
 H^0 = & \sum_{k, \sigma} \varepsilon_k^{\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k, \sigma} \varepsilon_k^{\sigma} d_{k\sigma}^{\dagger} d_{k\sigma} - V_s \sum_{k, k'} c_{k\uparrow}^{\dagger} c_{-k\downarrow}^{\dagger} c_{-k'\downarrow} c_{k'\uparrow} - \\
 & - V_d \sum_{k, k'} d_{k\uparrow}^{\dagger} d_{-k\downarrow}^{\dagger} d_{-k'\downarrow} d_{k'\uparrow}, \quad (1)
 \end{aligned}$$

where the symbols have their usual meaning (see Ref. 1). We have assumed in writing this Hamiltonian that the inter-band coupling constant is zero. This means that we are not allowing for the inter-band Cooper pair formation. As a result of this assumption we will get two energy gaps one corresponding to each band, when the superconductor contains no impurity. This approximation^{7,8)} not only simplifies the calculation considerably but also in agreement with the experiment⁹⁾.

We diagonalize this Hamiltonian by Bogoliubov-Valatin transformation. This consists in replacing the operators c and d by new operators e and f related as follows:

$$\begin{aligned}
 c_{k\uparrow} &= \cos\left(\frac{\Theta_k}{2}\right) e_{k\uparrow} + \sin\left(\frac{\Theta_k}{2}\right) e_{-k\downarrow}^{\dagger} \\
 c_{k\downarrow} &= \cos\left(\frac{\Theta_k}{2}\right) e_{k\downarrow} - \sin\left(\frac{\Theta_k}{2}\right) e_{-k\uparrow}^{\dagger} \\
 d_{k\uparrow} &= \cos\left(\frac{\Phi_k}{2}\right) f_{k\uparrow} + \sin\left(\frac{\Phi_k}{2}\right) f_{-k\downarrow}^{\dagger} \\
 d_{k\downarrow} &= \cos\left(\frac{\Phi_k}{2}\right) f_{k\downarrow} - \sin\left(\frac{\Phi_k}{2}\right) f_{-k\uparrow}^{\dagger}, \quad (2)
 \end{aligned}$$

where

$$\begin{aligned}
 \sin \Theta_k &= \frac{\Delta_s}{\sqrt{\varepsilon_k^{\sigma 2} + \Delta_s^2}} \quad \text{for } |\varepsilon_k^{\sigma}| < \hbar \omega, \\
 &= 0 \quad \text{for } |\varepsilon_k^{\sigma}| > \hbar \omega,
 \end{aligned}$$

and

$$\begin{aligned} \sin \Phi_k &= \frac{\Delta_d}{\sqrt{\varepsilon_k^{d^2} + \Delta_d^2}} \quad \text{for } |\varepsilon_k^d| < \hbar\omega, \\ &= 0 \quad \text{for } |\varepsilon_k^d| > \hbar\omega. \end{aligned}$$

Δ_s and Δ_d are the energy gaps of s -band and d -bands respectively. Under this transformation we obtain the Hamiltonian (1) as

$$H_0 = \sum_k E_k^s [e_{k\uparrow}^+ e_{k\uparrow} + e_{k\downarrow}^+ e_{k\downarrow}] + \sum_{k,\sigma} E_k^d f_{k\sigma}^+ f_{k\sigma} \quad (3)$$

where

$$E_k^s = \sqrt{\varepsilon_k^{s^2} + \Delta_s^2} \quad \text{etc.}$$

The effect of magnetic impurity scattering is equivalent to an exchange scattering of the conduction electron by the impurity spin. An electron in the s -band not only can get scattered to a state within s -band (intra-band scattering) but also can get scattered to a state in d -band (inter-band scattering). Such is true for the d -band electrons also.

If we assume the perturbation as perfectly localized around the impurity of spin S at the site R_i , then the perturbation Hamiltonian can be written as

$$H' = J\Omega_0 \sum_i \int \delta(\vec{r} - \vec{R}_i) \vec{S}_i \cdot s(\vec{r}) d^3 r,$$

where $\delta(\vec{r} - \vec{R}_i)$ is Dirac delta function and $s(\vec{r})$ is the spin density of the conduction electron at the space point \vec{r} .

Taking the Fourier transform in momentum space we can write the total perturbation for both intra-band and inter-band scattering as:

$$\begin{aligned} H' &= \frac{1}{2N} \left\{ J_1 \sum_{p,q} [S_{pq}^+ c_{p\downarrow}^+ c_{q\uparrow} + S_{pq}^- c_{q\uparrow}^+ c_{p\downarrow} + S_{pq}^z (c_{p\uparrow}^+ c_{r\uparrow} - c_{p\downarrow}^+ c_{q\downarrow})] + \right. \\ &+ J_2 \sum_{p,q} [S_{pq}^+ d_{p\downarrow}^+ d_{q\uparrow} + S_{pq}^- d_{q\uparrow}^+ d_{p\downarrow} + S_{pq}^z (d_{p\downarrow}^+ d_{q\uparrow} - d_{p\downarrow}^+ d_{q\downarrow})] + \\ &+ J_3 \sum_{p,q} [S_{pq}^+ c_{p\downarrow}^+ d_{q\uparrow} + S_{pq}^- d_{q\uparrow}^+ c_{p\downarrow} + S_{pq}^z (c_{p\downarrow}^+ d_{q\uparrow} - c_{p\downarrow}^+ d_{q\downarrow})] + \\ &+ J_3 \sum_{p,q} [S_{pq}^+ d_{p\downarrow}^+ c_{q\uparrow} + S_{pq}^- c_{q\uparrow}^+ d_{p\downarrow} + S_{pq}^z (d_{p\downarrow}^+ c_{q\uparrow} - d_{p\downarrow}^+ c_{q\downarrow})], \end{aligned} \quad (4)$$

where J_1 and J_2 are exchange integrals from intra-band scattering and J_3 is the exchange integral for inter-band scattering.

If we introduce the transformation equation (2) we obtain

$$\begin{aligned}
 H_1 = & \frac{J_1}{2N} \sum_{p,q} \left\{ S_{pq}^+ [\alpha_{pq} e_{p\uparrow}^+ e_{q\uparrow} + \frac{1}{2} \beta_{pq} (e_{p\uparrow}^+ e_{-q\downarrow}^+ + e_{-p\uparrow} e_{q\uparrow})] + \text{Herm. Conj.} + \right. \\
 & \left. + S_{pq}^- [\alpha_{pq} (e_{p\uparrow}^+ e_{q\uparrow} - e_{p\downarrow}^+ e_{q\downarrow}) + \beta_{pq} (e_{p\uparrow}^+ e_{-q\downarrow}^+ - e_{-p\downarrow} e_{q\uparrow})] + \right. \\
 & + \frac{J_2}{2N} \sum_{p,q} \left\{ S_{pq}^+ [\alpha'_{pq} f_{p\uparrow}^+ f_{q\uparrow} + \frac{1}{2} \beta'_{pq} (f_{p\uparrow}^+ f_{-p\downarrow}^+ + f_{-p\uparrow} f_{q\uparrow})] + \text{Herm. Conj.} + \right. \\
 & \left. + S_{pq}^- [\alpha'_{pq} (f_{p\uparrow}^+ f_{q\uparrow} - f_{p\downarrow}^+ f_{q\downarrow}) + \beta'_{pq} (f_{p\uparrow}^+ f_{-q\downarrow}^+ - f_{-p\downarrow} f_{q\uparrow})] \right\} + \quad (5) \\
 & + \frac{J_3}{2N} \sum_{pq} \left\{ S_{pq}^+ [\gamma_{pq} (f_{q\downarrow}^+ e_{p\uparrow} + f_{q\uparrow} e_{p\downarrow}^+) + \delta_{pq} (e_{p\downarrow}^+ f_{-q\downarrow}^+ - e_{-p\uparrow} f_{q\uparrow})] + \right. \\
 & \left. + \text{Herm. Conj.} + S_{pq}^- [\gamma_{pq} (e_{p\uparrow}^+ f_{q\uparrow} + f_{q\downarrow}^+ e_{p\downarrow} - f_{q\downarrow}^+ e_{p\downarrow} - e_{p\downarrow}^+ f_{q\downarrow}) + \right. \\
 & \left. + \delta_{pq} (e_{p\uparrow}^+ f_{-q\downarrow}^+ + e_{p\downarrow}^+ f_{-q\uparrow}^+ + e_{-p\downarrow} f_{q\downarrow} + e_{p\uparrow} f_{q\uparrow}) \right\},
 \end{aligned}$$

where

$$\begin{aligned}
 \alpha_{pq} &= \cos\left(\frac{\Theta_p - \Theta_q}{2}\right), & \beta_{pq} &= \sin\left(\frac{\Theta_q - \Theta_p}{2}\right), & \alpha'_{pq} &= \cos\left(\frac{\Phi_p - \Phi_q}{2}\right), \\
 \beta'_{pq} &= \sin\left(\frac{\Phi_q - \Phi_p}{2}\right), & \gamma_{pq} &= \cos\left(\frac{\Theta_p + \Phi_q}{2}\right), & \delta_{pq} &= \sin\left(\frac{\Theta_p + \Phi_q}{2}\right).
 \end{aligned}$$

The total Hamiltonian of the system in quasi-particle representation is

$$H_T = H_0 + H_1.$$

3. Diagonalizing the Hamiltonian

To calculate the free energy we need to know the trace of the Hamiltonian H_T . We diagonalize this Hamiltonian by a unitary transformation. We find a hermitian operator A such that

$$H_{\text{New}} = e^{-iA} H_T e^{iA} \quad (6)$$

is diagonal.

It is not possible to find a general form for operator A for the Hamiltonian H_T . From the study of Kondo effect it appears that the most important contribution to the scattering by an impurity spin comes from the term quadratic in the exchange integral. This term corresponds to the excitation and de-excitation by the same spin. So we keep in the new Hamiltonian the unperturbed Hamiltonian and a perturbation which is quadratic in exchange integral. Thus we write

$$H_{\text{New}} = H_0 + \frac{1}{2} i [H_1, A]_-,$$

where A is obtained from

$$H_1 = -i[H_0, A]_-.$$

It can be checked that the following operator A satisfies the condition

$$\begin{aligned} A = & \frac{i}{N} \sum_{p,q} \left[S_{pq}^+ \left\{ J_1 A_{pq} e_{p\downarrow}^+ e_{q\uparrow} + \frac{J_1 B_{pq}}{2} (e_{p\downarrow}^+ e_{-q\downarrow}^+ - e_{-p\downarrow} e_{q\uparrow}) + \right. \right. \\ & + J_2 A'_{pq} f_{pq}^+ f_{q\uparrow} + \frac{J_2 B'_{pq}}{2} (f_{p\downarrow}^+ f_{-q\downarrow}^+ - f_{-p\downarrow} f_{q\uparrow}) + J_3 C_{pq} (e_{p\downarrow}^+ f_{q\uparrow} - f_{q\downarrow}^+ e_{p\uparrow}) + \\ & \left. + J_3 D_{pq} (e_{p\downarrow}^+ f_{-q\downarrow}^+ - e_{p\downarrow} f_{q\uparrow}) \right\} + \text{Herm. Conj.} + \\ & + S_{x_{pq}} \left\{ J_1 A_{pq} (e_{p\downarrow}^+ e_{q\uparrow} - e_{q\downarrow}^+ e_{q\uparrow}) + J_1 B_{pq} (e_{p\downarrow}^+ e_{-q\downarrow}^+ + e_{-p\downarrow} e_{q\uparrow}) + \right. \\ & + J_2 A'_{pq} (f_{p\downarrow}^+ f_{q\uparrow} - f_{p\downarrow}^+ f_{q\downarrow}) + J_2 B'_{pq} (f_{p\downarrow}^+ f_{-q\downarrow}^+ + f_{-p\downarrow} f_{q\uparrow}) + \\ & + J_3 C_{pq} (e_{p\downarrow}^+ f_{q\uparrow} - e_{p\downarrow} f_{q\uparrow}^+ + e_{p\downarrow} f_{q\downarrow}^+ - e_{p\downarrow}^+ f_{q\downarrow}) + \\ & \left. + J_3 D_{pq} (e_{p\downarrow}^+ f_{-q\downarrow}^+ + e_{p\downarrow}^+ f_{-q\downarrow}^+ - e_{-p\downarrow} f_{q\uparrow} - e_{-p\downarrow} f_{q\downarrow}) \right\} \Big], \end{aligned}$$

where

$$\begin{aligned} A_{pq} &= \frac{\alpha_{pq}}{E_p^s - E_q^s}, & B_{pq} &= \frac{\beta_{pq}}{E_p^s + E_q^s}, & A'_{pq} &= \frac{\alpha'_{pq}}{E_p^d - E_q^d}, \\ B'_{pq} &= \frac{\beta'}{E_p^d + E_q^d}, & C_{pq} &= \frac{\gamma_{pq}}{E_p^s - E_q^d}, & D_{pq} &= \frac{\delta_{pq}}{E_p^s + E_q^d}. \end{aligned}$$

With the knowledge of A we can calculate the new Hamiltonian. We find:

$$\begin{aligned} H_{\text{New}}^{\text{Diag.}} &= H_0 - S(s+1) \frac{N_t}{4N^2} \cdot \\ & \sum_{p,q} \left[\left\{ \frac{J_1^2 \alpha_{pq}^2}{E_p^s - E_q^s} - \frac{J_1^2 \beta_{pq}^2}{E_p^s + E_q^s} - \frac{J_3^2 \gamma_{pq}^2}{E_p^s - E_q^d} - \frac{J_3^2 \delta_{pq}^2}{E_p^s + E_q^d} \right\} (e_{p\downarrow}^+ e_{p\uparrow} + e_{p\downarrow}^+ e_{p\uparrow}) + \right. \\ & + \left\{ \frac{J_2^2 \alpha'_{pq}{}^2}{E_p^d - E_q^d} - \frac{J_2^2 \beta'^2}{E_p^d + E_q^d} + \frac{J_3^2 \gamma'_{pq}{}^2}{E_p^s - E_q^d} - \frac{J_3^2 \delta'_{pq}{}^2}{E_p^s + E_q^d} \right\} (f_{q\uparrow}^+ f_{q\uparrow} + f_{q\downarrow}^+ f_{q\downarrow}) + \\ & \left. + \frac{J_1^2 \beta_{pq}^2}{E_p^s + E_q^s} + \frac{J_2^2 \beta'{}^2}{E_q^d + E_p^d} + \frac{2J_3^2 \delta_{pq}^2}{E_p^s + E_q^d} \right], \end{aligned}$$

where we have multiplied by the number of impurity N_t .

4. The change in free energy

We define the free energy of the system as:

$$F = -\frac{1}{\beta} \ln \text{Tr. exp} [-\beta H_{\text{New}}^{\text{Diag.}}] = F_0 - n_i \delta F,$$

where F_0 is the free energy of the unperturbed system and N_i is the concentration of impurity (N_i/N). δF is the change in free energy due to the addition of impurity.

$$\begin{aligned} \delta F = & \frac{2s(s+1)}{4N} \sum_{p,q} \left\{ \left[J_1^2 \left(\frac{\alpha_{pq}^2}{E_p^s - E_q^s} - \frac{\beta_{pq}^2}{E_p^s + E_q^s} \right) - \right. \right. \\ & - J_3^2 \left(\frac{\gamma_{pq}^2}{E_p^s - E_q^d} + \frac{\delta_{pq}^2}{E_p^s + E_q^d} \right) \left. \right] F(E_p^s) + \left[J_1^2 \left(\frac{\alpha_{pq}^{\prime 2}}{E_p^d - E_q^d} - \frac{\beta_{pq}^{\prime 2}}{E_p^d + E_q^d} \right) - \right. \\ & \left. - J_3^2 \left(\frac{\gamma_{pq}^2}{E_p^s - E_q^d} - \frac{\delta_{pq}^2}{E_p^s + E_q^d} \right) \right] F(E_q^d) \left. \right\} + \\ & + \frac{s(s+1)}{4N} \sum_{p,q} \left[\frac{J_1^2 \beta_{pq}^2}{E_p^s + E_q^d} + \frac{J_2^2 \beta^{\prime 2}}{E_p^d + E_q^d} + \frac{2J_3^2 \delta_{pq}^2}{E_p^s + E_q^d} \right], \end{aligned}$$

where F etc. are the Fermi functions.

It has been shown by Suhl and Matthias³⁾ that the terms containing the Fermi function contributes negligibly to the change in free energy. So we will calculate terms in the last bracket only.

$$\delta F \approx \frac{s(s+1)}{4N} \sum_{p,q} \left[\frac{J_1^2 \beta_{pq}^2}{E_p^s + E_q^d} + \frac{J_2^2 \beta^{\prime 2}}{E_p^d + E_q^d} + \frac{2J_3^2 \delta_{pq}^2}{E_p^s + E_q^d} \right].$$

We obtain the change in free energy in the superconducting and normal states as

$$\begin{aligned} \delta F_s = & \frac{s(s+1)}{4N} \sum_{\epsilon_p, \epsilon_q > 0} \left[2J_1^2 \frac{E_p^s E_q^s - \Delta_s^2}{(E_p^s + E_q^s) E_p^s E_q^s} + \right. \\ & \left. + 2J_2^2 \frac{E_p^d E_q^d - \Delta_d^2}{(E_p^d + E_q^d) E_p^d E_q^d} + 4J_3^2 \frac{E_p^s E_q^d + \Delta_s \Delta_d}{(E_p^s + E_q^d) E_p^s E_q^d} \right], \\ \delta F_n = & \frac{s(s+1)}{4N} \sum_{\epsilon_p, \epsilon_q > 0} \left[\frac{2}{\epsilon_p^s + \epsilon_q^s} + \frac{2}{\epsilon_p^d + \epsilon_q^d} + \frac{4}{\epsilon_p^s + \epsilon_q^d} \right]. \end{aligned}$$

The first two terms of each δF_s and δF_n have been calculated by Suhl and Matthias³⁾. The third term of δF_n can be calculated directly. The third term of δF_s can be calculated by using the substitution

$$\varepsilon_p^s = \Delta_s \text{Cosh } \Theta_p,$$

and

$$\varepsilon_p^d = \Delta_d \text{Cosh } \Theta_p,$$

and approximating

$$\text{Cosh } \Theta \simeq \frac{e^\Theta}{2}$$

we obtain

$$\delta F_n - \delta F_s + \frac{s(s+1)}{4N} [N_s^2(0) J_1^2 \pi^2 \Delta_s + N_d^2(0) J_2^2 \pi^2 \Delta_d + 4 N_s(0) N_d(0) \Delta_d J_3^2],$$

where we have neglected the quadratic terms of the order-parameter and have assumed $\Delta_d > \Delta_s$ near the transition temperature^{5,6)}.

If we write Herring's differential equation for two-band model as

$$\frac{d\Delta_s}{dn_t} = -\frac{\delta F_n - \delta F_s}{N_s(0)\Delta_s}, \quad \frac{d\Delta_d}{dn_t} = -\frac{\delta F_n - \delta F_s}{N_d(0)\Delta_d},$$

we obtain the change in the transition temperature of s- and d-band as

$$kT_{cs} = kT_{cs}^0 - \frac{S(s+1)}{4N} n_t \frac{J_1^2 \pi^2 N_s(0)}{1.75},$$

$$kT_{cd} = kT_{cd}^0 - \frac{S(s+1)}{4N} n_t \left\{ \frac{J_2^2 \pi^2 N_d(0) + 4 J_3^2 N_s(0)}{1.75} \right\}.$$

Due to the inter-band scattering the d-band transition temperature decreases more than the s-band transition.

Experimentally available information for niobium that $N_d(0) > N_s(0)$ implies that the change in transition temperature of s-band is negligible in comparison to the change in d-band transition temperature, unless J_1 is too large in comparison to J_2 and J_3 .

5. Conclusion

The change in transition temperature due to inter-band scattering is asymmetric with respect to density of states. This asymmetry arises because near the transition temperature $\Delta_d > \Delta_g$. Validity of the use of perturbation theory needs to be checked against the experimental result. No experimental result so far is available to check this validity.

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