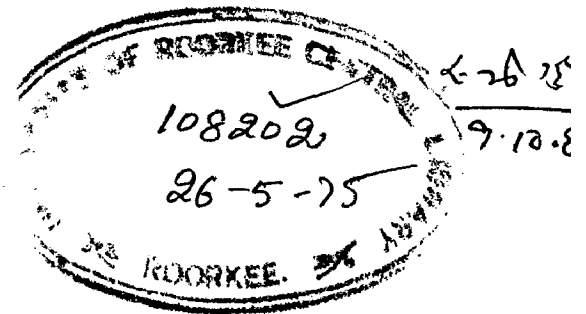


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IMPURITY AND FLUCTUATION EFFECTS IN SUPERCONDUCTORS

Thesis Submitted to
UNIVERSITY OF ROORKEE
FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
PHYSICS



by

PRAMOD KUMAR

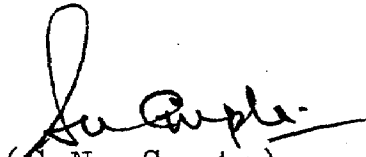


DEPARTMENT OF PHYSICS
UNIVERSITY OF ROORKEE
ROORKEE (India)
March, 1974

C E R T I F I C A T E

Certified that the thesis entitled "IMPURITY AND FLUCTUATION EFFECTS IN SUPERCONDUCTORS" which is being submitted by Shri Pramod Kumar in fulfilment for the award of the Degree of Doctor of Philosophy in Physics of University of Roorkee is a record of his own work carried out by him under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree.

This is further to certify that he has worked from October 1970 to February 1974, full time research, for preparing his thesis for Ph.D. Degree at this University.


(S.N. Gupta)

Dated 25.3.1974

Reader
Physics Department,
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Roorkee, India.

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The author is highly obliged to the Council of Scientific and Industrial Research, New Delhi for

the financial help.

Finally, I wish to dedicate this thesis to my parents who have continuously encouraged me to attain this goal. A great deal of credit for completing this work belongs to my parents.

PKullar
(Pramod Kumar)

(i)

R E S U M E

The theoretical explanation of the phenomenon of superconductivity, based fundamentally on Cooper's idea of the formation of bound singlet pairs of electrons near the Fermi surface under the action of phonon interaction, demands the existence of a spatial correlation between electrons at a distance of order ξ_0 ($\sim 10^{-4}$ cms, the coherence length) and of a superconducting order parameter governing the phase transition at the critical temperature. In an alloy, the electrons get scattered by impurities and since this scattering takes place at arbitrary angles, the correlation between electrons is very sensitive to the scattering process. Thus impurities must affect the properties of a metal in superconducting state. Different types of impurities, even when present in small concentration, have different effects on superconducting properties.

Furthermore, the order parameter governing the superconducting phase transition may have some thermal fluctuations in the region around the critical temperature. These thermal fluctuations cause in turn the Cooper pairs to fluctuate and thus drastically modify some of the superconducting properties. These fluctuations have been found to have a pronounced effect in dirty specimens of lower dimensions.

(ii)

The present thesis embodies some theoretical investigations on 'Impurity and Fluctuation Effects in Superconductors'. We have compared our results with experiments whenever the experimental data is available. The thesis is divided into seven chapters. Chapters II-V deal with the impurity effects in superconductors while the fluctuation effects in superconductors have been discussed in the last two chapters.

In the first chapter, a brief review of different theories of impurity and fluctuation effects in superconductors is presented, introducing basic facts and the mathematical techniques which have been used in the later six chapters.

In the second chapter, effects of nonmagnetic impurities on electronic thermal conductivity of superconducting transition metals (like Nb) has been studied using the Suhl-Matthias-Walker (abbreviated as SMW) two band model. Calculations have been carried out in the strong intraband electron-phonon coupling limit. Both the interband and intraband impurity scattering have been taken into account. The interband impurity scattering collision time τ_{sd} is taken to be $\approx 10^{-12}$ sec. Thermal conductivity is found to decrease with the increase in impurity concentration and has got a single slope when plotted with respect to temperature. The results are found to be in agreement qualitatively with

(iii)

the experimental results of Anderson et.al. This study provides a strong support for the validity of the SMW two band model (i.e. two energy gaps in Niobium).

The third chapter deals with the study of thermomagnetic effects in dirty transition metal superconductors (containing nonmagnetic impurities) in the vortex state near the upper critical field and in the temperature region $T_{cs} < T < T_{cd} (=T_c)$. We find that there is an anomalous increase in d-band thermomagnetic effects, due to interband impurity scattering, just in the vicinity of upper critical field, when the temperature region is restricted to $T_{cs} < T < T_c$. These results are analogous to those of Chow on Hall Effect. The results obtained by Caroli et.al. for the one d-band superconductor become a particular case of our general study.

The fourth chapter pertains to the study of the effects of paramagnetic impurities on Josephson current through SNS junctions. This study has been done both in the framework of Abrikosov-Gorkov theory (which treats the exchange interaction in lowest order Born approximation) and Shiba-Rusinov theory (which takes care of higher order scattering and deals with the classical spin case). This study is more general; the theoretical results obtained by Ishii for the pure case, follow in a natural manner from our results. In Abrikosov-Gor'kov model, the tunneling current is found to decrease

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(iv)

with the increase in impurity concentration for $\zeta < 1$, but in the gapless region ($\omega_g=0$) when $\zeta \gg 1$, the current is zero for $\zeta = 1$ and then becomes negative for $\zeta > 1$. However, when the current is calculated using Shiba-Rusinov model, the ratio of j^{impure} to j^{pure} is also found to depend on ϵ_0 (the position of localized state within the gap) in addition to ζ (a measure of impurity concentration).

In Chapter V, we again study the Josephson current through SNS junction but now in the presence of localized nonmagnetic transition metal impurities. The calculations have been done in the framework of Machida-Shibata theory. The ratio of the barrier supercurrent of impure SNS junction to that of the pure one, is found to decrease with the increase in impurity concentration. This behaviour is entirely different from that of nonlocalized nonmagnetic impurities where this ratio is exactly equal to one. At $\zeta = 0$ (which is a measure of impurity concentration) Ishii's result for the pure case follows from our more general study.

In the sixth chapter, using phenomenological Ginzburg-Landau theory, we have investigated the fluctuation enhanced diamagnetic susceptibility of dirty superconducting thin films below the critical temperature. The fourth order term in the GL free energy functional is included using Masker et.al. model. The diamagnetic

LIST OF PUBLICATIONS

1. Thermal Conductivity in the Two-Band Model of Superconducting Transition Metals containing Non-magnetic Impurities.
P.Kumar and S.N.Gupta, Phys.Rev.B6, 2642(1972).
2. Thermomagnetic Effects in Dirty Transition Metal Superconductors Near the Upper Critical Field.
P.Kumar and S.N. Gupta, Phys.Rev.B8,168(1973),
Erratum (to be published).
3. Effect of Paramagnetic Impurities on Josephson Current through Junctions with Normal Metal Barriers.
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4. Josephson Current through S-N-S junction containing Paramagnetic Impurities with Local States within the Gap.
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5. Effect of Resonance Scattering on Josephson Current Through a Superconductor-Normal Metal-Superconductor Junction.
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(to be published).
6. Fluctuation Enhanced Diamagnetic Susceptibility below T_c .
P.Kumar, Phys.Letters 42A, 475(1973).
7. Effect of Fluctuations on Diamagnetic Susceptibility of Zero Dimensional Superconductors Below T_c .
P.Kumar and G.C.Shukla, Phys.Letters 45A, 229(1973).
8. Effect of Fluctuations on Electrical Conductivity of Zero Dimensional Superconductors below T_c .
P.Kumar and G.C.Shukla (submitted to Phy.Lett).

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CHAPTER-I

I N T R O D U C T I O N

A. IMPURITY EFFECTS IN SUPERCONDUCTORS

(I) Statement and Importance of the Problem

The past two decades have witnessed an enormous activity, both theoretically and experimentally, in studying the effects of impurities in different fields of Physics from different view points. Impurities give rise to new effects in the host lattice which are easy to investigate, and help us in obtaining a great deal of valuable information. They play a leading role in finding out various thermodynamic and transport properties of metals. The studies of impurity effects thus help us in understanding the various complexities of many body problems in solids.

In the normal state, it is well known that these lattice defects i.e. impurities lead to the existence of residual resistance of metals. In the superconducting state (i.e. a state of infinite conductivity and perfect diamagnetism etc.), the impurities play an entirely different and crucial role. This problem of impurity effects in superconductors has been extensively investigated, both theoretically (1-5) and experimentally (6-9). Based on Cooper's idea (10) about the formation of bound singlet pairs of electrons near the Fermi surface under

susceptibility is found to increase sharply with the decrease of temperature below T_c .

Lastly, in Chapter VII, the problem of fluctuation effects in zero dimensional superconductors is investigated. We have studied the fluctuation enhanced diamagnetic susceptibility and electrical conductivity of zero dimensional superconductor below T_c . Calculations have been carried out, using again the phenomenological Ginzburg-Landau theory. It is found that both the diamagnetic susceptibility and electrical conductivity, increase more sharply with decrease of temperature, in contrast for the samples of higher dimensions. These results are consistent with the experimental observations that fluctuations strongly affect superconducting properties in lower dimensions than in higher ones.

the action of phonon interaction, Bardeen, Cooper and Schrieffer (11) successfully derived the electrodynamics of superconductors. This theory yielded a non-local character of the connection between current and field for the majority of pure superconductors. This nonlocal connection demanded that the dimensions of the bound pairs cause an existence of a correlation between electrons at distances of the order of $\xi_0 \sim 10^{-4}$ cms. It thus follows that the interactions between the electrons in a superconductor cause a definite spatial correlation between them. Put differently, we can say that the dependence of the various Green's functions in the coordinate representation on their spatial arguments at distances of order ξ_0 i.e. size of bound pair, undergoes an essential change when the metal makes a transition from the normal to superconducting state. In an alloy, the electrons are scattered by the impurities, and since this scattering takes place randomly, and as the scattered electrons have very small wavelengths, the correlation or coherence between the electrons is extremely sensitive to the scattering processes. This means that impurity scattering must decrease the spatial coherence between the electrons.

The impurities have got a little effect when present in very low concentrations, but an increase in the concentration leads to a decrease in the coherence distance of the electrons in the superconductor. At sufficiently

high impurity concentrations the role of the coherence length ξ_0 is taken over by the mean free path of the electrons. At these high concentrations one might expect new properties in the superconductor to appear which should, of course, depend on the nature of impurities and the type of scattering processes involved. It is important to notice here that this new behaviour occurs for concentrations that are still quite low ($\sim 1\%$). For large impurity concentrations, we are essentially dealing with a new substance, whose properties have nothing in common with the original superconductor. In particular, properties arising from electron-phonon interaction now change and so does the temperature at which the transition to superconducting phase occurs. These changes in the basic properties of the lattice can be neglected for sufficiently low concentrations. At the same time, it is interesting to note that the thermodynamic properties of the superconducting alloys are practically the same as those of the pure superconductor. The impurities are classified into the following three categories:

- (1) Nonmagnetic or spinless impurities,
- (2) Paramagnetic impurities, and
- (3) Localized nonmagnetic transition metal impurities.

The effects of the impurities of the first type are simplest to deal with and were studied in earlier theories (3,4) successfully in analogy to the case of a normal

metal. This type of impurity has got little effect on superconducting properties in contrast to the strong effects of second and third types. The second and third types of impurities also lead to the interesting aspects of gapless behaviour and existence of bound state inside the energy gap. These facts lead to an important conclusion that it is not the energy gap but the pairing correlation which is necessary for the existence of superconductivity. In this chapter, we give a brief review of the different theories in this field and introduce the basic formulation and concepts which will be used in the following four chapters. We shall use quantum field theoretical techniques (12) and Matsubara's formulation for finite temperature Green's function (13).

For the sake of completeness, we shall first discuss the case of normal metals containing spinless impurities.

(II). NONMAGNETIC IMPURITIES IN NORMAL METALS

Consider a free electron gas as a model of a normal metal. We assume that there are N_i impurity sites at the positions \vec{R}_1 --- \vec{R}_{N_i} . The Hamiltonian for the impure system is

$$H = H_0 + H_I \quad \dots (1.1)$$

where H_0 is the Hamiltonian for noninteracting electrons

and H_I corresponding to the interaction between the electrons and the impurity atoms, is of following form

$$\begin{aligned}
 H_I &= \sum_i \sum_{\alpha=1}^{N_i} u(\vec{X}_i - \vec{R}_\alpha) \\
 &= \sum_{\alpha=1}^{N_i} \int dx \psi^\dagger(x) u(\vec{X} - \vec{R}_\alpha) \psi(x) \\
 &= \sum_{\alpha=1}^{N_i} \sum_{\vec{k}q\sigma} c_{\vec{k}+q,\sigma}^\dagger c_{\vec{k},\sigma} u(\vec{q}) \exp(-i\vec{q} \cdot \vec{R}_\alpha) \dots (1.2)
 \end{aligned}$$

Here u is the impurity potential and is assumed to be spin-independent.

The interaction Hamiltonian H_I destroys the translational invariance and as such the single particle Green function $G(\vec{x}, \vec{x}'; \zeta_\rho)$ corresponding to (1.1) is not simply a function of $|\vec{x} - \vec{x}'|$. One recovers the translational invariance at a coarse level if the propagator corresponding to (1.1) is averaged over the impurity configurations. For a given distribution of impurities, we can expand the single particle Green's function in powers of the impurity potential u , using simple perturbation theory. The various terms contributing to $G(\vec{k}, \vec{k}', \zeta_\rho)$ (the double fourier transform of $G(\vec{x}, \vec{x}'; \zeta_\rho)$) are represented by diagrams given in Fig.1.1. The expansion represented by these diagrams is:

$$G(\vec{k}, \vec{k}', \zeta) = \frac{1}{\zeta \lambda^{-\epsilon \vec{k}}} (2\pi)^3 \delta(\vec{k} - \vec{k}') + \frac{1}{\zeta \lambda^{-\epsilon \vec{k}}} U(\vec{k} - \vec{k}') \frac{1}{\zeta \lambda^{-\epsilon \vec{k}'}} \\ + \int \frac{d^3 k''}{(2\pi)^3} \frac{1}{\zeta \lambda^{-\epsilon \vec{k}}} U(\vec{k}'' - \vec{k}) \frac{1}{\zeta \lambda^{-\epsilon \vec{k}''}} U(\vec{k}', -\vec{k}'') \frac{1}{\zeta \lambda^{-\epsilon \vec{k}'}} \\ \dots \quad (1.3)$$

where U is expressed as

$$U(\vec{q}) = \sum_{\alpha=1}^{N_i} \exp(-i\vec{q} \cdot \vec{R}_\alpha) u(\vec{q}) \quad \dots \quad (1.4)$$

Since the impurity atoms are randomly distributed throughout the metal, we have to average the expression over the position of each impurity atom. We use an important fact that the average distance between impurity atoms is much larger than the lattice spacing on account of low impurity concentration. Now we average the position of each impurity over the volume of the system; so that, for example,

$$\exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}_\alpha] \rightarrow \frac{1}{\text{vol.}} \int d^3 R \exp[-i(\vec{k} - \vec{k}') \cdot \vec{R}] = \delta_{\vec{k}, \vec{k}'} \\ \dots \quad (1.5)$$

Thus,

$$\langle U(\vec{k} - \vec{k}') \rangle = n_i u(0) (\text{vol.}) \delta_{\vec{k}, \vec{k}'} \rightarrow (2\pi)^3 n_i u(0) \delta(\vec{k} - \vec{k}') \\ \dots \quad (1.6)$$

where $n_i (= N_i / \text{vol.})$ is the density of impurities. Consider now the impurity average of two potentials. A distinction should now be made between second order scattering by a single impurity and two scatterings by differing impurities. The total contribution is

This is n_i times the relaxation rate in Born Approximation for scattering by a single impurity. Same is true for fig.(1.2c) also. Summing of all the diagrams for $\bar{\Sigma}$ with only one cross thus has the effect of replacing the Born approximation matrix element $u(\vec{k}-\vec{k}')$ in eq.(1.10) by the t-matrix element. The diagrams with more than one cross correspond to multiple scattering by more than one impurity. However it can be easily shown that contributions to $\bar{\Sigma}$ from higher order diagrams will be very small. Because of weak dependence of Γ on k and ω , we may make the replacement,

$$\begin{aligned} \bar{\Sigma}(\vec{k}, \zeta_\lambda \rightarrow \omega \mp i0) &= \Delta \pm \frac{i}{2} \Gamma(k_F, \mu) \\ &= \Delta \pm \frac{i}{2\tau} \end{aligned} \quad \dots (1.11)$$

The energy shift Δ , being essentially a constant, can also be absorbed into a shift of chemical potential. Taking $\bar{\Sigma}$ to be purely imaginary, we get

$$G(\vec{k}, \omega) = \frac{1}{\omega - \epsilon_{\vec{k}} \pm i/2\tau} \quad \dots (1.12)$$

Going over to the \vec{x} - representation, we easily see that the entire change in G as compared to $G^{(0)}$ (pure Green's function) reduces to multiplication by an exponentially damped factor ie:

$$G(\mathbf{x}-\mathbf{x}') = G^0(\mathbf{x}-\mathbf{x}') e^{-|\mathbf{x}-\mathbf{x}'|/2\lambda} \quad \dots (1.13)$$

where $\lambda = v_F \tau$.

$$G(\vec{k}, \vec{k}', \zeta) = \frac{1}{\zeta \chi^{-\epsilon \vec{k}}} (2\pi)^3 \delta(\vec{k} - \vec{k}') + \frac{1}{\zeta \chi^{-\epsilon \vec{k}}} U(\vec{k} - \vec{k}') \frac{1}{\zeta \chi^{-\epsilon \vec{k}'}} \\ + \int \frac{d^3 k''}{(2\pi)^3} \frac{1}{\zeta \chi^{-\epsilon \vec{k}}} U(\vec{k}'' - \vec{k}) \frac{1}{\zeta \chi^{-\epsilon \vec{k}''}} U(\vec{k}' - \vec{k}'') \frac{1}{\zeta \chi^{-\epsilon \vec{k}'}} \\ \dots (1.3)$$

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Thus,

$$\langle U(\vec{k} - \vec{k}') \rangle = n_i u(0) (\text{vol.}) \delta_{\vec{k}, \vec{k}'} \rightarrow (2\pi)^3 n_i u(0) \delta(\vec{k} - \vec{k}') \\ \dots (1.6)$$

where $n_i (= N_i / \text{vol.})$ is the density of impurities. Consider now the impurity average of two potentials. A distinction should now be made between second order scattering by a single impurity and two scatterings by differing impurities. The total contribution is

$$\begin{aligned}
 \langle U(\vec{q})U(\vec{q}') \rangle &= \left\langle \sum_{\alpha} u(\vec{q})u(\vec{q}') \exp\left[i(\vec{q}+\vec{q}') \cdot \vec{R}_{\alpha}\right] \right\rangle \\
 &+ \sum_{\alpha \neq \alpha'} u(\vec{q})u(\vec{q}') \exp(i\vec{q} \cdot \vec{R}_{\alpha}) \exp(i\vec{q}' \cdot \vec{R}_{\alpha'}) \\
 &= (2\pi)^3 n_i u(\vec{q})u(\vec{q}') \delta(\vec{q}+\vec{q}') \\
 &+ n_i \left(n_i - \frac{1}{vcl}\right) (2\pi)^6 u(\vec{q})u(\vec{q}') \delta(\vec{q}) \delta(\vec{q}') \dots (1.7)
 \end{aligned}$$

In the limit of large volume, the second term in eq.(1.7) is just the square of eq.(1.6). By averaging all terms of eq.(1.3) in this way one obtains a prescription for calculating the self energy part $\bar{\Sigma}$ corresponding to the averaged Green's function. These two quantities are related as below:

$$\langle G(\vec{k}, \vec{k}', \zeta_{\lambda}) \rangle = (2\pi)^3 \delta(\vec{k}-\vec{k}') \left[\zeta_{\lambda}^{-\varepsilon_{\vec{k}}} - \bar{\Sigma}(\vec{k}, \zeta_{\lambda}) \right]^{-1} \dots (1.8)$$

The terms in the expansion for $\bar{\Sigma}$ can be represented diagrammatically by bringing together at a single cross all scatterings from same impurity. Some terms are shown in fig.(1.2). The contribution from the first order diagram is $n_i u(c)$ (eq.(1.6)). The second order term is given

$$\begin{aligned}
 \bar{\Sigma}^{(2)} &= n_i \int \frac{d^3 k'}{(2\pi)^3} |u(\vec{k}-\vec{k}')|^2 \frac{1}{\zeta_{\lambda}^{-\varepsilon_{\vec{k}'}}} \\
 &= \int \frac{d\omega}{(2\pi)} \frac{\Gamma^{(2)}(\vec{k}, \omega)}{\zeta_{\lambda}^{-\omega}} \dots (1.9)
 \end{aligned}$$

where,

$$\Gamma^{(2)}(\vec{k}, \omega) = 2\pi n_i \int \frac{d^3 k'}{(2\pi)^3} |u(\vec{k}-\vec{k}')|^2 \delta(\omega - \varepsilon_{\vec{k}'}) \dots (1.10)$$

This is n_i times the relaxation rate in Born Approximation for scattering by a single impurity. Same is true for fig.(1.2c) also. Summing of all the diagrams for $\bar{\Sigma}$ with only one cross thus has the effect of replacing the Born approximation matrix element $u(\vec{k}-\vec{k}')$ in eq.(1.10) by the t-matrix element. The diagrams with more than one cross correspond to multiple scattering by more than one impurity. However it can be easily shown that contributions to $\bar{\Sigma}$ from higher order diagrams will be very small. Because of weak dependence of Γ on k and ω , we may make the replacement,

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The energy shift Δ , being essentially a constant, can also be absorbed into a shift of chemical potential. Taking $\bar{\Sigma}$ to be purely imaginary, we get

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$$G(x-x') = G^0(x-x') e^{-|x-x'|/2\lambda} \quad \dots (1.13)$$

where $\lambda = v_F \tau$.

(III). NONMAGNETIC IMPURITIES IN SUPERCONDUCTORS

We shall now generalize the discussion of last section to superconductors for treating the effects of dilute concentration of nonmagnetic impurities(3,4). Here, one should remember that the superconductor is described by two propagators and the order parameter Δ obeys a self-consistency condition. Nambu(14) introduced an ingenious way of two component space spanned by the field operator

$$\Psi(\vec{X}t) = \begin{pmatrix} \psi_{\uparrow}(\vec{X}, t) \\ \psi_{\downarrow}^{\dagger}(\vec{X}, t) \end{pmatrix} \quad \dots (1.14)$$

in order to take into account the two propagators simultaneously. The corresponding 2x2 matrix Green's function is given by

$$G_{ij}(\vec{X}t, \vec{X}'t') = -i \left\langle T \left[\psi_i(\vec{X}t) \psi_j^{\dagger}(\vec{X}'t') \right] \right\rangle \quad \dots (1.15)$$

Average values of the form $\langle \Psi\Psi \rangle$ and $\langle \Psi^{\dagger}\Psi^{\dagger} \rangle$ are interpreted as anomalous Green's functions i.e. F functions.

Writing out the matrix eq.(1.15) explicitly, we get

$$G_{ij}(\vec{X}t, \vec{X}'t') = \begin{pmatrix} G(\vec{X}t, \vec{X}'t') & F(\vec{X}t, \vec{X}'t') \\ \bar{F}(\vec{X}t, \vec{X}'t') & -G(\vec{X}'t', \vec{X}t) \end{pmatrix} \quad \dots (1.16)$$

A spin-independent potential in second quantized form is represented as

$$\sum_{i\alpha} u(\vec{X}_i - \vec{R}_{\alpha}) = \sum_{\alpha} \int d^3x u(\vec{X} - \vec{R}_{\alpha}) \text{Tr} \left[\Psi^{\dagger}(x) \tau_3 \Psi(x) \right] + \text{constt.} \quad \dots (1.17)$$

Here τ_3 is third Pauli matrix. In the two component language, the equation of motion for the matrix Green's function, given by eq.(1.16), for the pure system can be written as(15)

$$\begin{pmatrix} \zeta_{\lambda}^{-\epsilon_k} & -\Delta \\ -\Delta^* & \zeta_{\lambda}^{+\epsilon_k} \end{pmatrix} \begin{pmatrix} G(\vec{k}, \zeta_{\lambda}) & F(\vec{k}, \zeta_{\lambda}) \\ \bar{F}(\vec{k}, \zeta_{\lambda}) & -G(-\vec{k}, -\zeta_{\lambda}) \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ \dots & \dots \end{pmatrix} \quad \dots (1.18)$$

In matrix notation, eq.(1.18) now becomes

$$(\zeta_{\lambda}^{-\epsilon_{\vec{k}}} \tau_3 - \Delta \tau_1) \mathcal{G}_{\vec{k}}(\vec{k}, \zeta_{\lambda}) = 1 \quad \dots (1.19)$$

In coordinate space one then has

$$\left[\zeta_{\lambda} + \left(\frac{\nabla^2}{2m} + \mu \right) \tau_3 - \Delta \tau_1 \right] \mathcal{G}_{\vec{X}}(\vec{X}, \vec{X}'; \zeta_{\lambda}) = \delta^{(3)}(\vec{X} - \vec{X}') \quad \dots (1.20)$$

We can now generalize eq.(1.20) in the presence of a fixed distribution of impurities and get the following equation

$$\left\{ \zeta_{\lambda} + \left(\frac{\nabla^2}{2m} + \mu \right) \tau_3 - \left[\sum_{\alpha} u(\vec{X} - \vec{R}_{\alpha}) \right] \tau_3 - \Delta(\vec{X}) \tau_1 \right\} \mathcal{G}_{\vec{X}}(\vec{X}, \vec{X}', \zeta_{\lambda}) = \delta^{(3)}(\vec{X} - \vec{X}') \quad \dots (1.21)$$

After an average over the impurity configurations is performed $\langle \psi(\vec{X}) \psi(\vec{X}') \rangle$ will be independent of \vec{X} . However, the average will introduce correlations between Δ and $\mathcal{G}_{\vec{X}}$ because both quantities are strongly modified near the impurity sites. For a low concentration of impurities one may overlook these correlations. Then $\Delta(\vec{X})$ in eq.(1.20) can be replaced by $\bar{\Delta}$ - the average value

of the order parameter. Summing the diagrams as in previous section we get the following expression for self-energy:

$$\bar{\Sigma}(k, \zeta_\lambda) = n_i \int \frac{d^3q}{(2\pi)^3} u(\vec{q})^* \tau_3 \mathcal{E}(\vec{k}-\vec{q}, \zeta_\lambda) \tau_3 u(\vec{q}) \quad \dots (1.22)$$

This equation can be solved by making the following ansatz:

$$\bar{\Sigma}(k, Z) = Z - \tilde{Z} - (\bar{\Delta} - \tilde{\Delta}) \tau_1 \quad \dots (1.23)$$

where \tilde{Z} and $\tilde{\Delta}$ are unknown function of Z . Substituting this into the right hand side of eq.(1.22) and equating the coefficients of 1 and τ_1 on the left and right sides, we get,

$$Z - \tilde{Z} = n_i \int \frac{d^3q}{(2\pi)^3} |u(\vec{q})|^2 \frac{\tilde{Z}}{\tilde{Z}^2 - \epsilon_{\vec{k}-\vec{q}}^2 - \tilde{\Delta}^2} \quad \dots (1.24)$$

$$\bar{\Delta} - \tilde{\Delta} = n_i \int \frac{d^3q}{(2\pi)^3} |u(\vec{q})|^2 \frac{\tilde{\Delta}}{\tilde{Z}^2 - \epsilon_{\vec{k}-\vec{q}}^2 - \tilde{\Delta}^2} \quad \dots (1.25)$$

Changing the \vec{q} integral into energy integral and performing the ϵ -integration, gives:

$$Z - \tilde{Z} = - \frac{i}{2\tau} \frac{\tilde{Z}}{\sqrt{\tilde{Z}^2 - \tilde{\Delta}^2}} \quad \dots (1.26)$$

$$\bar{\Delta} - \tilde{\Delta} = - \frac{i}{2\tau} \frac{\tilde{\Delta}}{\sqrt{\tilde{Z}^2 - \tilde{\Delta}^2}} \quad \dots (1.27)$$

where τ is the normal-state life time. Equations (1.26) and (1.27) can be solved to give the following result

$$z/\bar{\Delta} = \tilde{z}/\tilde{\Delta} \quad \dots (1.28)$$

and with this equations (1.26) and (1.27) yield

$$\tilde{z} = z + \frac{i}{2\tau} \frac{z}{\sqrt{z^2 - \bar{\Delta}^2}} \quad \dots (1.29)$$

$$\tilde{\Delta} = \bar{\Delta} + \frac{i}{2\tau} \frac{\bar{\Delta}}{\sqrt{z^2 - \bar{\Delta}^2}} \quad \dots (1.30)$$

and $\bar{\Delta}$ is determined from the following self-consistency condition

$$\begin{aligned} \bar{\Delta} &= V \langle \psi_{\uparrow}(\vec{X}) \psi_{\downarrow}(\vec{X}) \rangle \\ &= -\frac{V}{\beta} \sum_{\vec{\lambda}} \int \frac{d^3 p}{(2\pi)^3} \frac{\tilde{\Delta}}{\tilde{\zeta}_{\vec{\lambda}}^2 - \epsilon_p^2 - \tilde{\Delta}^2} \quad \dots (1.31) \end{aligned}$$

$$= -\frac{V}{\beta} \sum_{\vec{\lambda}} \int \frac{d^3 p}{(2\pi)^3} \frac{\bar{\Delta}}{\zeta_{\vec{\lambda}}^2 - \epsilon_p^2 - \bar{\Delta}^2} \quad \dots (1.32)$$

Thus we see that $\bar{\Delta}$ obeys the same equation as the order parameter for pure superconductor. Hence a dilute concentration of spinless impurities does not change the transition temperature(16). The other interesting result is concerning the energy spectrum. The density of single particle states is

$$N(\omega) = -\int \frac{d^3 k}{(2\pi)^3} \frac{1}{\pi} \text{Im} \mathcal{E}_{11}(k, \omega + i\eta)$$

$$= N(0) \operatorname{Re} \left(\frac{Z}{\sqrt{Z^2 - \bar{\Delta}^2}} \right)_{Z=\omega+i\eta} \quad \dots (1.33)$$

Thus we get

$$\frac{N(\omega)}{N(0)} = \begin{cases} 0 & 0 < \omega < \bar{\Delta} \\ \omega / \sqrt{\omega^2 - \bar{\Delta}^2} & \omega > \bar{\Delta} \end{cases} \quad \dots (1.34)$$

This result is again the same as for a pure isotropic system. Other properties of impure system, however, get modified.

(IV). MAGNETIC IMPURITIES IN SUPERCONDUCTORS

(i) Abrikosov-Gorkov Model

Magnetic impurities have a pronounced effect on superconducting properties(17) and cause a rapid decrease of transition temperature in contrast to nonmagnetic impurities. The first monumental theory of magnetic impurities in superconductors was given by Abrikosov and Gorkov(18) (abbreviated as A.G.Theory). On the basis of experimental information Herring(19) proposed the following Hamiltonian describing the exchange interaction between impurity atoms and conduction electrons

$$\hat{U} = U_1 \rho_3 + U_2 \vec{S} \cdot \vec{\alpha} \quad \dots (1.35)$$

where ρ_3 is the Pauli matrix which operates on the space composed of the electron and hole states. Here, the first term is the ordinary impurity scattering potential while

the second term is the so-called exchange interaction. \vec{S} denotes the spin operator of the localized magnetic moments. The spin exchange interaction breaks the time reversal invariance and thus may inhibit the appearance of the superconducting correlations. A rigorous calculation was first given by Abrikosov and Gorkov(18) who were able to obtain the Green's function, describing equilibrium as well as nonequilibrium properties of the system. In particular, they predicted an existence of gapless region in which the excitation spectrum starts from zero energy. The following assumptions are made in the AG theory:

- (1) The correlations among the impurity spins are neglected.
- (2) Spatial variations of the order parameter in the vicinity of the impurities have not been taken into account.
- (3) The exchange interaction is treated in Born approximation and the effect of the anomalous exchange scattering (Kondo effect (20)) has been neglected.

Using the standard technique outlined in sections II and III, the Green's function is obtained by taking eq.(1.35) as the interaction between impurity atoms and the conduction electrons. After averaging over the random distribution of impurity atoms, the Green's function recovers the translational invariance. Hence, the renormalized Green's function which describes the electron

in the environment of randomly distributed impurity of concentration n , is given by

$$G_{\omega}(\vec{p}) = (i\tilde{\omega} - \xi \rho_3 - \tilde{\Delta} \rho_1 \sigma_2)^{-1} \quad \dots (1.36)$$

where $\tilde{\omega}$ and $\tilde{\Delta}$ are the renormalized frequency and order parameters respectively and are determined from the equation

$$G_{\omega}^{-1}(\vec{p}) = \left[G_{\omega}^0(\vec{p}) \right]^{-1} - \Sigma_{\omega}(\vec{p}) \quad \dots (1.37)$$

Here,

$$G_{\omega}^0(\vec{p}) = (i\omega - \xi \rho_3 - \Delta \rho_1 \sigma_2)^{-1} \quad \dots (1.38)$$

is the Green's function in the absence of impurities, and Δ has to be determined self-consistently as in sections II and III. In the Born approximation $\Sigma_{\omega}(\vec{p})$ is given as

$$\Sigma_{\omega}(\vec{p}) = n \int \frac{d^3 p'}{(2\pi)^3} \left[\hat{U}(\vec{p} - \vec{p}') G_{\omega}(\vec{p}') U(\vec{p} - \vec{p}') \right] \quad \dots (1.39)$$

where

$$\hat{U}(\vec{p} - \vec{p}') = U_1(\vec{p} - \vec{p}') \rho_3 + U_2(\vec{p} - \vec{p}') \vec{S} \cdot \vec{\alpha} \quad \dots (1.40)$$

Using eq.(1.36) for the Green's function and performing the integration over \vec{p}' one can easily obtain

$$\Sigma_{\omega}(\vec{p}) = - \frac{1}{2\tau_1} \frac{i\tilde{\omega} - \tilde{\Delta} \rho_1 \sigma_2}{\sqrt{\tilde{\omega}^2 + \tilde{\Delta}^2}} - \frac{1}{2\tau_2} \frac{i\tilde{\omega} + \tilde{\Delta} \rho_1 \sigma_2}{\sqrt{\tilde{\omega}^2 + \tilde{\Delta}^2}} \quad \dots (1.41)$$

where

$$\frac{1}{\tau_1} = nN(0) \int |u_1(\vec{p} - \vec{p}')|^2 d\Omega$$

$$\frac{1}{\tau_2} = nN(0)S(S+1) \int |u_2(\vec{p}-\vec{p}')|^2 d\Omega \quad \dots (1.42)$$

Substituting eq.(1.41) into eq.(1.37) and then comparing the coefficient of 1 and $\rho_1 \sigma_2$, one gets the following two equations:

$$\begin{aligned} \tilde{\omega} &= \omega + \frac{1}{2} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \frac{\tilde{\omega}}{\sqrt{\tilde{\omega}^2 + \tilde{\Delta}^2}} \\ \tilde{\Delta} &= \Delta + \frac{1}{2} \left(\frac{1}{\tau_1} - \frac{1}{\tau_2} \right) \frac{\tilde{\Delta}}{\sqrt{\tilde{\omega}^2 + \tilde{\Delta}^2}} \quad \dots (1.43) \end{aligned}$$

Here τ_2 is the spin life time of electrons due to impurities. Introducing an auxiliary parameter u defined by $u = \tilde{\omega}/\tilde{\Delta}$, Equation (1.43) then reduces to

$$\frac{\omega}{\Delta} = u \left(1 - \zeta \frac{1}{\sqrt{1+u^2}} \right) \quad \dots (1.44)$$

where $\zeta = \frac{1}{\tau_2 \Delta}$

To study the energy spectrum of the superconductor containing magnetic impurities, we shall first write eq.(1.44) in terms of ordinary frequencies by doing an analytical continuation to real frequencies, i.e.,

$$\frac{\omega}{\Delta} = u \left(1 - \zeta \frac{1}{\sqrt{1-u^2}} \right) \quad \dots (1.45)$$

Let us first consider the case for $\zeta \ll 1$. If we plot the eq.(1.45) in ω -plane, then we will see that the curve starts from origin and initially ω increases

as u increases. As u further increases, ω goes through a maximum and then decreases. At $u = 1$, ω is negative and diverges. Maximum value of ω in the region $0 < u < 1$ is called as the energy gap ω_g and is determined by the following condition:

$$0 = \frac{1}{\Delta} \frac{\partial \omega}{\partial u} = 1 - \zeta (1-u^2)^{-3/2} \quad \dots (1.46)$$

This equation gives us

$$\begin{aligned} u_0 &= (1 - \zeta^{2/3})^{1/2} \\ \omega_g &= \Delta (1 - \zeta^{2/3})^{3/2} \end{aligned} \quad \dots (1.47)$$

We can now make an expansion of eq.(1.45) around u_0 to obtain

$$\frac{\omega - \omega_g}{\Delta} = - \frac{3}{2} \zeta^{-2/3} (1 - \zeta^{2/3})^{1/2} (u - u_0)^2 \quad \dots (1.48)$$

In the second case of $\zeta > 1$, the asymptotic expression for u at small values of ω is given by

$$u = i \sqrt{\zeta^2 - 1} + \zeta^2 (\zeta^2 - 1)^{-1} \left(\frac{\omega}{\Delta}\right) + \frac{3}{2} i \zeta^2 (\zeta^2 - 1)^{-5/2} \left(\frac{\omega}{\Delta}\right)^2 + \dots \quad \dots (1.49)$$

The density of states in terms of the Green's function is given by

$$\begin{aligned} N_s(\omega) &= \frac{1}{2\pi} \text{Im} \left[\frac{d^3 p}{(2\pi)^3} \text{Tr} \left[G_\omega(p) \right] \right]_{\omega=i\omega} \\ &= N(0) \text{Im} \left(\frac{u}{\sqrt{1-u^2}} \right) \\ &= N(0) \zeta^{-1} \text{Im}, u \end{aligned} \quad \dots (1.50)$$

Let us first consider the case for $\zeta < 1$. Solving equation (1.48) for u and substituting into eq.(1.50), one obtains

$$N_s(\omega) = \begin{cases} 0 & \text{for } \omega < \omega_g \\ N(0)\zeta^{-2/3}(1-\zeta^{2/3})^{-1/4} \left[\frac{2}{3} \frac{\omega-\omega_g}{\Delta} \right] & \text{for } \omega > \omega_g \end{cases} \dots (1.51)$$

Thus we see that ω_g gives the threshold frequency for the density of states. Similarly for $\zeta > 1$, we obtain

$$N_s(\omega) = N(0) \left[(1-\zeta^{-2})^{1/2} + \frac{3}{2}\zeta^4(1-\zeta^{-2})^{-5/2} \left(\frac{\omega}{\Delta}\right)^2 \right] \dots (1.52)$$

Here we see that $N_s(\omega)$ is finite at $\omega = 0$ i.e. the energy spectrum starts continuously from zero energy level. Here gap ω_g in the energy spectrum vanishes i.e. it is the gapless region. =1

For the special case of $\zeta=1$ one gets

$$N_s(\omega) = N(0) \frac{\sqrt{3}}{2} \left[\left(\frac{2\omega}{\Delta}\right)^{1/3} - \frac{1}{24} \left(\frac{2\omega}{\Delta}\right)^{5/3} \right] \dots (1.53)$$

(ii) Shiba-Rusinov Model

Tunneling experiments of Reif and Woolf(21,22) confirmed somewhat later that there are some disagreements in their experimental results and the predictions of AG(18) theory which was based on the assumption of weak interaction of conduction electrons with a magnetic

impurity. In order to reach an agreement between theory and experiment, Shiba⁽²³⁾ and Rusinov⁽²⁴⁾ generalized the AG theory to the case when the conduction electron-magnetic impurity interaction is strong. Their calculations lead to the appearance of local impurity levels inside the energy gap. This can be traced to the appearance of Kondo Anomaly⁽²⁰⁾ (quantum mechanical effect of spin) when we go beyond the Born approximation to treat the strong interaction. We write the interacting potential in the form

$$V_i = U(\vec{r}-\vec{r}_i) + \vec{\sigma} \cdot \vec{S} J(\vec{r}-\vec{r}_i) \quad \dots (1.54)$$

In the AG theory, where V_i is treated in Born Approximation, the final result actually does not depend on whether we regard the spin \vec{S} as a classical vector or as an operator. In contrast to this the above result is no more valid at higher order approximations as a result of the well known Kondo effect (which essentially comes into the picture due to the noncommutativity of spin operators⁽²⁵⁾). As such, inclusion of Kondo effect is a difficult problem and studies were restricted^(23,24) to the classical spins in superconductors. By classical we mean that $J \rightarrow 0$, $S \rightarrow \infty$ and $\vec{J} \cdot \vec{S}$ is finite. Actually this assumption is apparently allowed if the impurity spin is sufficiently large (i.e. $\vec{S} \gg 1$). However, Maki^(26,27), Fowler and Maki⁽²⁸⁾, Fowler⁽²⁹⁾, Zittartz and Muller-Hartmann^(30,31) have also successfully investigated Kondo effect in superconductors and found the effect on

localized impurity levels. But it has been also shown (30,31) that in the pole approximation, Kondo effect can be incorporated in the Shiba-Rusinov model by assuming that $\epsilon_0^2 = v^2 \left[v^2 + \pi^2 S(S+1) \right]^{-1}$ where $v = \lambda n(T_K/T)$ (ϵ_0 is the position of bound state for isotropic scattering inside the gap and T_K is the Kondo temperature of the alloy.)

Therefore, it is convenient and simpler to work within the framework of Shiba(23)-Rusinov(24) model which apply to alloys in which conduction electron-impurity interaction is strong and also to superconducting Kondo alloys. Here we present a brief review of this theory.

Let us assume that magnetic impurities are distributed randomly in a superconductor and their concentration is low enough so that impurity-impurity interaction is negligible. Here again the calculations can be done as in previous sections except with the difference that we have to calculate the self-energy in higher order approximations. This has been done in detail by Shiba(23) and Rusinov(24) and we will only quote their results. Rusinov Green's function of the superconducting alloy, averaged over the positions and the spin directions of the impurities is given as

$$\hat{G}(\vec{p}, \omega_n) = \left[i\tilde{\omega}_n \rho_3 - \epsilon_p + i\tilde{\Delta}_n \rho_1 \sigma_2 \right]^{-1} \quad \dots (1.55)$$

With $u_n = \tilde{\omega}_n / \tilde{\Delta}_n$ satisfying the following equations:

$$\frac{\omega_n}{\Delta(\alpha, T)} = u_n \left[1 - \sum_{\lambda=0}^{\infty} (2\lambda+1) \left[\tau_{s\lambda} \Delta(\alpha, T) \right]^{-1} (1+u_n^2)^{1/2} (u_n^2 + \epsilon_\lambda^2)^{-1} \right] \dots (1.56)$$

$$(\tau_{s\lambda})^{-1} = C_i \left[2\pi N(o) \right]^{-1} (1 - \epsilon_\lambda^2) \dots (1.57)$$

$$\epsilon_\lambda = \cos(\delta_\lambda^+ - \delta_\lambda^-) \dots (1.58)$$

$$\omega_n = \pi T(2n+1) \dots (1.59)$$

Here $\Delta(\alpha, T)$ is the temperature dependent order parameter for impure superconductor, $\tau_{s\lambda}$ the spin flip scattering life time, δ_λ^\pm are the phase shifts describing the scattering of an electron by the impurity with orbital momentum λ and spin projections $\pm(1/2)$ in normal metal, $N(o) = mp_F/2\pi^2$ and ϵ_λ is the position of the bound state inside the gap brought about by treating the scattering of electrons by magnetic impurity in exact way. The different quantities can be calculated in a closed form if we deal with the physical situation of isotropic scattering (i.e. $\lambda=0$) (as also done by Shiba(24)). Then eq.(1.56) reduces to

$$\frac{\omega_n}{\Delta(\alpha, T)} = u_n \left[1 - (\alpha/\Delta(\alpha, T)) (1+u_n^2)^{1/2} (\epsilon_o^2 + u_n^2)^{-1} \right] \dots (1.60)$$

where,

$$\alpha = (\tau_{so})^{-1} = C_i \left[2\pi N(o) \right]^{-1} (1 - \epsilon_o^2) \dots (1.61)$$

$$\epsilon_o = \cos(\delta_o^+ - \delta_o^-) \dots (1.62)$$

According to Shiba(24) ϵ_0 is given by

$$\epsilon_0 = \left| \left\{ \left(1 - \left[JS\pi N(o)/2 \right]^2 \right) / \left(1 + \left[JS\pi N(o)/2 \right]^2 \right) \right\} \right| \dots (1.63)$$

and is independent of temperature and of the sign of J.

It is found(23) that a localized excited state appears inside the energy gap if we deal with a single impurity problem. For finite concentration this state grows into an impurity band. The impurity band is found to be separated from the continuum for a low concentration of impurities(23) but for higher concentration, it is not possible to distinguish between the 'impurity band' and the continuum.

(V). LOCALIZED NONMAGNETIC TRANSITION METAL IMPURITIES IN SUPERCONDUCTORS

Transition metal impurities are categorised in two classes, nonmagnetic and magnetic (i.e. having no localized magnetic moment and finite localized magnetic moment, respectively). The possibility of the existence or nonexistence of localized magnetic moments on such impurities when dissolved in nonmagnetic metals was first explained by Friedel(32) and Anderson(33). There are two different approaches for treating the effects of these two types of impurities. The Abrikosov-Gorkov(18) theory based on the s-d exchange interaction (Kondo Hamiltonian) is usually applied to paramagnetic impurities (discussed in the Sec.III), while for

nonmagnetic impurities having no localized magnetic moment such as iron group elements (Fe, Co, Ni, Cr, Mn) in aluminium, the normagnetic resonance orbital model (34-38) is regarded to be most appropriate. Zuckermann (36,38) first studied the effect of nonmagnetic transition metal impurities on superconductivity using Anderson model with $U=0$ (U the Coulomb repulsion). The Coulomb repulsion was neglected for the sake of simplicity since it was found that its inclusion does not drastically influence the qualitative behaviour (34,35). These different theoretical investigations which were also confirmed experimentally (39,40,41,42) showed that there exists bound state in the energy gap which grows to a impurity band as impurity concentration increases. The appearance of these bound states is due to presence of resonance scattering of conduction electrons of the host metal with the localized d-electron of impurity ions. It is this resonance scattering which gives rise to relatively large changes in various properties of non-transition metals such as Cu, Al or Zn when they are added with small amounts of transition metal impurities.

(i) Single Impurity Case

We first consider the single impurity problem: The Hamiltonian of the system under consideration can be written as

$$\begin{aligned}
 H = & \sum_{\vec{k}\sigma} \epsilon_{\vec{k}} c_{\vec{k}\sigma}^{\dagger} c_{\vec{k}\sigma} + \sum_{\vec{k}d} v_{\vec{k}d} (c_{\vec{k}\sigma}^{\dagger} a_{\sigma} + a_{\sigma}^{\dagger} c_{\vec{k}\sigma}) + E \sum_{\sigma} n_{d\sigma} \\
 & - \Delta \sum_{\vec{k}} (c_{\vec{k}\uparrow}^{\dagger} c_{-\vec{k}\downarrow}^{\dagger} + c_{-\vec{k}\downarrow} c_{\vec{k}\uparrow}) \quad \dots (1.64)
 \end{aligned}$$

where Δ is to be determined self-consistently from the following equation

$$\Delta = |g| \sum_{\vec{k}} \langle c_{\vec{k}\uparrow}^{\dagger} c_{-\vec{k}\downarrow}^{\dagger} \rangle \quad \dots (1.65)$$

For the sake of convenience, we shall work in Nambu space and define the double time Green's function as

$$G_{\vec{k}\vec{k}'}(\omega) = \begin{pmatrix} \langle\langle c_{\vec{k}\uparrow}; c_{\vec{k}'\uparrow}^{\dagger} \rangle\rangle & \langle\langle c_{\vec{k}\uparrow}; c_{-\vec{k}'\downarrow} \rangle\rangle \\ \langle\langle c_{-\vec{k}\downarrow}^{\dagger}; c_{\vec{k}'\uparrow}^{\dagger} \rangle\rangle & \langle\langle c_{-\vec{k}\downarrow}^{\dagger}; c_{-\vec{k}'\downarrow} \rangle\rangle \end{pmatrix} \quad \dots (1.66)$$

Solving the equation of motion for Green's function one obtains the following result(43)

$$G_{\vec{k}\vec{k}'}(\omega) = \frac{1}{2\pi} (G_{\vec{k}}^0(\omega) \delta_{\vec{k}\vec{k}'} + G_{\vec{k}}^0(\omega) t(\omega) G_{\vec{k}'}^0(\omega)) \quad \dots (1.67)$$

where,

$$G_{\vec{k}}^0(\omega) = (\omega - \epsilon_{\vec{k}} \tau_3 + \Delta \tau_1)^{-1}, \quad \dots (1.68)$$

$$\text{and } t(\omega) = v_{kd}^2 \tau_3 (\omega - E \tau_3 - v_{kd}^2 \tau_3 F(\omega) \tau_3)^{-1} \tau_3 \quad \dots (1.69)$$

$$\text{with } F(\omega) = \sum_{\vec{k}} G_{\vec{k}}^0(\omega) \quad \dots (1.70)$$

For $\frac{|\omega|}{\Delta} \ll 1$, we have

$$V_{\vec{k}d}^2 F(\omega) = -\Gamma \frac{\omega - \Delta \tau_1}{\sqrt{\Delta^2 - \omega^2}} \quad \dots (1.71)$$

with $\Gamma = \pi \rho V_{\vec{k}d}^2 \quad \dots (1.72)$

where ρ is the density of states at the Fermi surface.

It can be easily seen by the poles of eq.(1.69) that there always exists a bound state inside the energy gap(45).

(ii) Finite Impurity Concentration Problem

Here we shall make use of the conventional approximation that the self energy part $\bar{\Sigma}(\omega)$ is connected to the t-matrix by the following equation:

$$\bar{\Sigma}(\omega) = C \bar{t}(\omega) \quad \dots (1.73)$$

where $\bar{t}(\omega) = (\omega - E \tau_3 - V_{\vec{k}d}^2 \tau_3 \bar{F}(\omega) \tau_3)^{-1} \quad \dots (1.74)$

with $\bar{F}(\omega) = \sum_{\vec{k}} \bar{G}_{\vec{k}\vec{k}}(\omega) \quad \dots (1.75)$

The above equations can be easily solved if we substitute:

$$\bar{G}_{\vec{k}\vec{k}}(\omega) = (\omega - \epsilon_{\vec{k}} \tau_3 + \Delta \tau_1 - \bar{\Sigma}(\omega))^{-1} = (\tilde{\omega} - \tilde{\epsilon}_{\vec{k}} \tau_3 + \tilde{\Delta} \tau_1)^{-1} \quad \dots (1.76)$$

We then obtain the following self-consistent equations for ω and Δ :

$$\tilde{\omega} = \omega - CV_{\vec{k}d}^2 \left(\omega + \frac{\tilde{\omega} \Gamma}{\sqrt{\tilde{\Delta}^2 - \tilde{\omega}^2}} \right) \left\{ \omega^2 + \frac{2\Gamma \omega \tilde{\omega}}{\sqrt{\tilde{\Delta}^2 - \tilde{\omega}^2}} - (E^2 + \Gamma^2) \right\}^{-1}$$

$$\tilde{\Delta} = \Delta - CV^2 \frac{\tilde{\Delta} \Gamma}{k_d \sqrt{\tilde{\Delta}^2 - \tilde{\omega}^2}} \left\{ \omega^2 + \frac{2 \Gamma \omega \tilde{\omega}}{\sqrt{\tilde{\Delta}^2 - \tilde{\omega}^2}} - (E^2 + \Gamma^2) \right\}^{-1} \dots (1.77)$$

If we define, $u = \tilde{\omega}/\tilde{\Delta}$ and $v = \omega/\Delta$, eq.(1.77) reduces to

$$v = u + \zeta \frac{v}{v^2 + 2 \bar{\Gamma} (uv / \sqrt{1-u^2}) - \bar{\epsilon}^2} \dots (1.78)$$

For small concentration ($C \ll 1$), the above equation can be solved easily by iteration. The first iteration gives

$$v = u \left(1 + \zeta \frac{1}{u^2 + 2 \bar{\Gamma} (u^2 / \sqrt{1-u^2}) - \bar{\epsilon}^2} \right) \dots (1.79)$$

where,

$$\zeta = \frac{C}{\Delta} \frac{v^2}{k_d}, \quad \bar{\Gamma} = \Gamma / \Delta$$

and

$$\bar{\epsilon}^2 = (E/\Delta)^2 + (\Gamma/\Delta)^2 \dots (1.80)$$

It is found that this equation has qualitatively the same behaviour (43) as eq.(1.60) of Sec.IV(ii). The qualitative analysis of eq.(1.79) yields the following form for density of states:

$$N_s(\omega) = \rho \operatorname{Im} \frac{u}{\sqrt{1-u^2}} \dots (1.81)$$

B. FLUCTUATION EFFECTS IN SUPERCONDUCTORS

Since a part of the work reported in this thesis concerns fluctuation effects in superconductors, we will now give a brief introduction to the phenomenon

of fluctuation effects in superconductors. Since the estimates of the effects of thermodynamic fluctuations by Pippard(44), Ginzburg(45) and Thouless(46), most of the solid state physicists held the view that fluctuation effects in superconductors would be unobservable experimentally. However, in 1967 the experimental(47) and theoretical(48) studies revealed that superconducting thin films exhibit an excess conductivity in an observable magnitude due to the presence of Cooper pairs created by thermal fluctuations. Since then, many fluctuation effects in superconductors have been observed in a variety of properties. The study of fluctuation effects has provided much stimulus in the development of the theory of superconductivity. The extreme sharpness of the superconducting phase transition in the absence of a magnetic field was supposed to be an evidence that the superconducting state is an ordered state with a coherence length much larger than atomic dimensions. This exceedingly long coherence length of a superconductor, about $10^3 \sim 10^4$ Å makes the critical phenomenon in superconductors apparently different from those in other systems like superfluid helium or magnetic systems where it is only few angstroms. The coherence length, which is determined by the range of spatial variations of fluctuations, is a most fundamental parameter in the investigations of critical phenomenon. Ginzburg(45) discussed the fluctuation effects in materials showing the second order phase transition on the basis of Landau theory(49).

This theory takes the form of the Ginzburg-Landau (GL) theory (50) in the case of superconductors. In particular, superconductivity is the only phenomenon to which Landau's theory applies so well that deviations from it had not been observed and had been given also a firm support from the microscopic basis (51). An outline of the GL theory is given below:

(i) Phenomenological Ginzburg-Landau Theory

In the framework of the GL theory, a state of the specimen is represented by a superconducting order parameter $\Psi(\vec{r})$, $\Psi(\vec{r})$ being a complex function of the space coordinate \vec{r} . If \vec{A} is the vector potential representing the magnetic flux density $\vec{H} = \vec{\nabla} \times \vec{A}$, the probability $\rho_A[\Psi(\vec{r})]$ of the appearance of a state represented by $\Psi(\vec{r})$ and $\vec{A}(\vec{r})$ is supposed to be given by (52)

$$\rho_A[\Psi(\vec{r})] = \exp \left\{ -F_A[\Psi(\vec{r})] / T \right\} \quad \dots (1.82)$$

where $F_A[\Psi(\vec{r})]$ is the GL free-energy functional:

$$F_A[\Psi(\vec{r})] = \int d^3r \left[-\alpha |\Psi(\vec{r})|^2 + \frac{\beta}{2} |\Psi(\vec{r})|^4 + \frac{1}{2m} |(-i\vec{\nabla} - e^* \vec{A}) \Psi(\vec{r})|^2 + H^2 / 8\pi \right] \quad \dots (1.83)$$

Here, e^* is the unit of electric charge carried by the supercurrent, m is the mass of an electron, and $\alpha[\alpha(T_c - T)]$ and β are the GL parameters. If the thermal

fluctuations are neglected, the equilibrium state is realized at one of the minima of the GL functional $F_A[\Psi(\vec{r})]$, so that $\Psi(\vec{r})$ and \vec{A} at equilibrium satisfy the following equations:

$$\frac{1}{2m}(-i\vec{\nabla}-e^*\vec{A})^2\Psi-\alpha\Psi+\beta|\Psi|^2\Psi = 0 \quad \dots (1.84)$$

$$\nabla^2\vec{A} = -4\pi\vec{j} \quad \dots (1.85)$$

$$\vec{j} = -\frac{ie^*}{2m}(\Psi^\dagger\nabla\Psi-\Psi\nabla\Psi^\dagger)-\frac{(e^*)^2}{m}|\Psi|^2\vec{A} \quad \dots (1.86)$$

with the boundary condition

$$\hat{n}\cdot(-i\vec{\nabla}-e^*\vec{A})\Psi(\vec{r}) = 0, \quad \dots (1.87)$$

\hat{n} being a unit vector perpendicular to the boundary surface.

These equations have been justified by Gorkov(51). He finds, the parameters α, β and e^* to be explicitly given by

$$\alpha = -\epsilon/\lambda_\tau \quad \dots (1.88)$$

$$\beta = \frac{2}{N\lambda_\tau\chi(\rho_\tau)} \quad \dots (1.89)$$

and $e^* = 2e$, e being the electronic charge. Here,

$$\epsilon = T-T_c/T_c \quad \dots (1.90)$$

$$\lambda_\tau = \frac{7\zeta(3)E_F\chi(\rho_\tau)}{12\pi^2T_c^2} \quad \dots (1.91)$$

$$\chi(\rho_\tau) = \frac{1}{7\zeta(3)\rho_\tau} \left\{ \frac{\pi^2}{8} + \frac{1}{2\rho_\tau} \left[\Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + \frac{\rho_\tau}{2}\right) \right] \right\} \quad \dots (1.92)$$

where N is number density, E_F is the Fermi energy, $\rho_\tau = (2\pi T_c \tau)^{-1}$, τ being mean free time of electrons due to normal impurity scattering, and $\psi(Z)$ and $\zeta(Z)$ are di-gamma and the zeta functions, respectively.

In the absence of magnetic field, the average order parameter $\bar{\Psi}_0$ is given by

$$|\bar{\Psi}_0| = \begin{cases} \sqrt{\alpha/\beta} & T < T_c \\ 0 & T > T_c \end{cases} \quad \dots (1.93)$$

If $F[\bar{\Psi}(\vec{r})]$ is used as a thermodynamic free energy, one obtains a classical second order phase transition. Deviations from such behaviour are presumably described by fluctuations about $|\bar{\Psi}_0|$. It is very difficult to calculate the effects of such fluctuations, but one might attempt to make an estimate of the temperature region in which they are large (45). Retaining terms quadratic in $|\bar{\Psi} - \bar{\Psi}_0|$ one gets

$$\langle |\bar{\Psi}_k|^2 \rangle \equiv \frac{\int \delta\bar{\Psi} \exp\left[-F/T\right] |\bar{\Psi}_k|^2}{\int \delta\bar{\Psi} \exp\left[-F/T\right]} \approx \begin{cases} \sum_k T/k^2 + \alpha, & T > T_c, \\ \sum_k T/k^2 - 2\alpha & T < T_c, \end{cases} \quad \dots (1.94)$$

where k is the wave number of fluctuations and T is the temperature in energy units. The criterion for small fluctuations, namely that the fluctuations should explore regions of $\bar{\Psi}$ space small compared to the region over which F varies quadratically, is

$$\frac{1}{\text{volume}} \sum_{\mathbf{k}} \frac{T}{k^2 + \xi^{-2}(T)} \ll \frac{|\alpha|}{\beta} \quad \dots (1.95)$$

where we have now introduced a temperature dependent coherence length $\xi(T)$ given by

$$\xi^2(T) = \xi^2(0)/\varepsilon = \begin{cases} 1/\alpha, & T > T_c, \\ -1/2\alpha, & T < T_c. \end{cases} \quad \dots (1.96)$$

where,

$$\varepsilon = |T - T_c|/T_c.$$

It is known from the microscopic theory that $\xi(0)$ depends upon the purity of the system. In the pure limit ($\xi_0 \ll \lambda$) $\xi(0) = \xi_0 \sim hv_F/T_c$, whereas in the dirty limit ($\xi_0 \gg \lambda$) $\xi(0) = (\xi_0 \lambda)^{1/2}$, where λ is the electronic mean free path.

A general concept in the theory of second order phase transition is that macroscopic-critical phenomenon are dominated by fluctuations with small wave number k , i.e. $|k|$ smaller than a certain cut-off value. In fact, important contributions arise from the range $|k| < 1/\xi_T$. Taking all these considerations into account, it is easy to derive the formulae for the transformation of sums over k into integrals, as follows:

$$\frac{1}{\text{vol}} \sum_{\mathbf{k}} = \begin{cases} \frac{1}{(2\pi)^3} \int_{|k| < k_c} d^3k & d = 3 \\ \frac{1}{(2\pi)^2} \int_{|k| < k_c} d^2k & d = 2 \\ \frac{1}{2\pi S} \int dk & d = 1 \end{cases} \quad \dots (1.97)$$

where d is the dimensionality of a specimen; t is the thickness of a film specimen, and S is a cross sectional area of a whisker. Now, one can estimate $\langle |\psi|^2 \rangle$ appearing in eq.(1.94), and compare with $|\psi_0|^2$ and obtain the temperature region where Landau's theory offers a good approximation, i.e., $|\psi_0|^2 \gg \langle |\psi|^2 \rangle$, as

$$\epsilon > \epsilon_c \quad \dots (1.98)$$

where,

$$\epsilon_c \equiv \begin{cases} \frac{1}{k_F^4 \xi_0^4} & d=3 \\ (k_F \xi_0)^{-2} (k_F t)^{-1} & d=2 \\ (k_F \xi_0)^{-4/3} (\xi_0^2/S)^{2/3} & d=1 \end{cases} \quad \dots (1.99)$$

($\xi(0) = \xi_0$)
(pure limit)

and

$$\epsilon_c \equiv \begin{cases} (k_F \xi_0)^{-1} (k_F \lambda)^{-3} & d=3 \\ (k_F t)^{-1} (k_F \lambda)^{-1} & d=2 \\ (\xi_0/S^2 (k_F^4))^{1/3} & d=1 \end{cases} \quad \dots (1.100)$$

[$\xi(0) = (\xi_0 \lambda)^{1/2}$]
(dirty limit)

From the above equations, one sees that relatively large fluctuation effects are expected in dirty alloy specimen ($\lambda \ll \xi_0$). This was first pointed by Ferrel and Schmidt.(53). This speculation led Glover(47) to make the first experimental studies of superconducting critical phenomenon above T_c . We can also ascertain from above equations that lower the dimensionality of specimen the larger are the fluctuation effects, which also follows from the microscopic Green's function theory

of Aslamazov and Larkin(48) of fluctuation effects above T_c .

(ii) Behaviour of Fluctuations of Superconducting Order Parameter in different ranges of Temperature

There are different temperature regions in which fluctuations have got different behaviour and correspondingly different theories have been developed to deal with them. Broadly, there are three temperature regions known as 'classical' (above T_c), critical (around T_c) and 'below T_c ' regions. We had given a brief description of classical region in last section in order to understand basic concepts of the fluctuation phenomenon. In this region, the density of fluctuation modes is very low and they can be easily treated to be independent. On the other hand, in the temperature region below T_c , the density of fluctuation modes becomes very high and they are no more independent. It then becomes necessary to include the fourth order term in GL free energy functional which describes the interaction between fluctuation modes below T_c .

A different type of success emerged in extending the studies of Aslamazov et al (48). This was the explanation by Marcelja(54) of the resistive transition of thin films in the temperature region lower than the one where AL's (48) result agrees with observations. This temperature region is slightly below T_c where the

excess conductivity is more than normal state conductivity. The essential point of Marcelja's idea is the linearization of the quartic term in the GL free energy in the sense of Hartree approximation. The microscopic theory of this was given by Schmid (55) and experimental investigations were done by Masker, Marcelja and Parks (56,57).

(C) PRESENT WORK

The present thesis deals with the investigations of the impurity and fluctuation effects in superconductors. The effects of impurities on superconducting properties are studied in the following four chapters while remaining two chapters are devoted to the investigations concerning the fluctuations phenomenon in superconductors. The plan of presentation chapterwise is described below.

In Chapter II, effect of nonmagnetic impurities on electronic thermal conductivity of superconducting two band transition metals, has been discussed using Suhl, Matthias and Walker (SMW) model (58). The calculations have been done by applying Chow's theory⁽⁵⁹⁾ which is an extension of one band theory presented in Section III of Chapter IA. The existence of two energy gaps in Niobium is also critically analysed.

In Chapter III, thermomagnetic effects in dirty

transition metals having nonmagnetic impurities have been investigated near the upper critical field and in the temperature region $T_{CS} < T < T_{Cd}$. Here we have again made use of the Chow's theory for impure two band superconductors. An enhancement of thermomagnetic effects just below the upper critical field is found to occur and needs experimental verification.

In Chapter IV, the effect of paramagnetic impurities on Josephson current through SNS junction is studied within the frameworks of both the Abrikosov-Gorkov Model and of Shiba-Rusinov Model which have been described in Section IV (Chapter IA).

Chapter V again deals with the study of the effect of localized nonmagnetic transition metal impurities on Josephson current through SNS junctions. The calculations have now been done using Resonance scattering model discussed in Sec.V (Chapter IA).

Chapters VI and VII are devoted to the study of effects of fluctuations of superconducting order parameter on superconducting properties. In Chap. VI, an expression has been derived for the fluctuation enhanced diamagnetic susceptibility below T_c using phenomenological Ginzburg-Landau Theory, outlined in Section I (Chap.IB). The sharp increase in the diamagnetic susceptibility below T_c is discussed.

In the last chapter VII, we have studied the effect of fluctuations on the superconducting properties of zero dimensional superconductors below T_c , using again the phenomenological Ginzburg-Landau theory. The behaviour of both diamagnetic susceptibility and electrical conductivity in the presence of fluctuations is discussed and analysed.

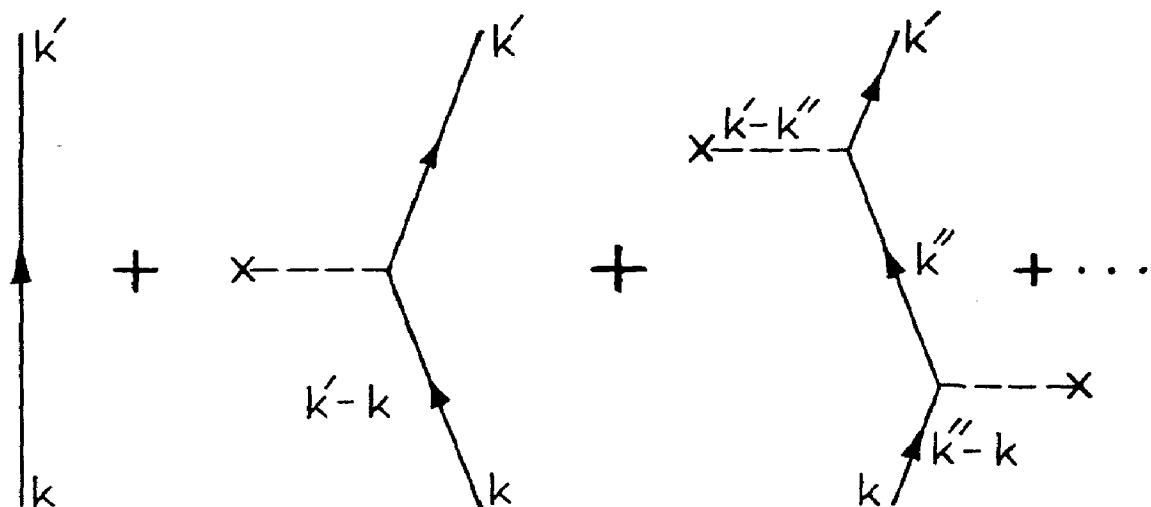


FIG.1.1 - Diagrams representing different terms in the expansion of $G(\vec{k}, \vec{k}'; \zeta_l)$.

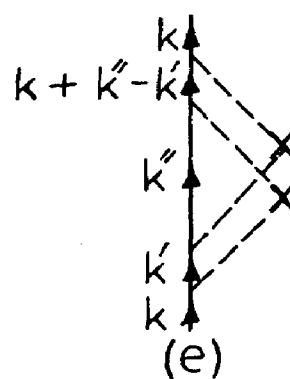
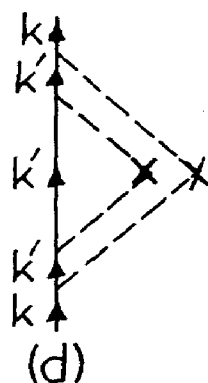
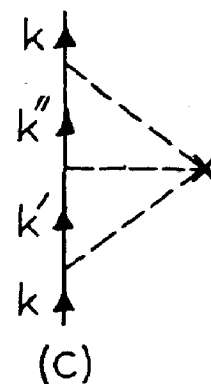
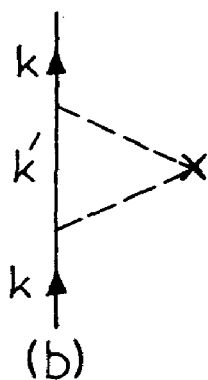
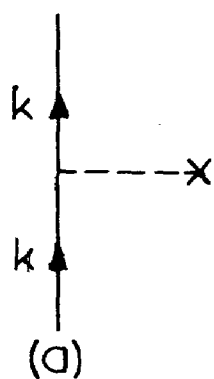


FIG.1.2 - Diagrams representing some terms in the expansion of self energy $\vec{\Sigma}(\vec{k}, \zeta_l)$.

CHAPTER II

THERMAL CONDUCTIVITY IN TWO BAND MODEL OF SUPERCONDUCTING TRANSITION METALS CONTAINING NONMAGNETIC IMPURITIES

(I). INTRODUCTION

Two band model was first proposed by Suhl, Matthias and Walker(58) (referred as SMW model). They showed that at low temperatures, both the s-band and d-band electrons in the transition metals can be in the superconducting phase. Some recent experimental investigations also show evidence for the existence of a second energy gap(60,61) and this has given rise to great interest in the study of this model(59,62,63). It has been found that this model quite successfully explains various physical properties of superconducting transition metals. Chow(62), for example, has recently studied the effect of nonmagnetic impurities on the specific heat of superconducting transition metals within the framework of the two band model, assuming a strong intraband-phonon-coupling limit, and has been able to explain the effect of impurities and the two slope behaviour of the specific heat of Niobium, observed by Shen et al.(64).

Guided by these successes, we extend the SMW(58) two-band model to study the thermal conductivity of

of superconducting transition metals containing non-magnetic impurities as a function of temperature, using Green's-function formulation(65). Starting from the Kubo formula for thermal conductivity, we use the technique employed by Ambegaoker et.al(66). Calculations are carried out on the assumption of strong intraband-phonon-coupling limit. We make use of the 4x4 matrix formulation of the Green's function, which becomes diagonal in the above coupling limit (59). As far as the effects of impurities are concerned, both the interband and intraband impurity scattering have been taken care of.

In Section II we write the Hamiltonian of the impure two band superconductor and the other basic equations of two-band model(59). In Section III an expression for the thermal conductivity K has been derived using the matrix Green's functions given in Section II. This is followed by a discussion of the results of numerical computation and a comparison with the recent experiment of Anderson et al(67) on impure Niobium.

II. BASIC TWO-BAND EQUATIONS IN THE STRONG INTRABAND-PHONON-COUPLING LIMIT

The Hamiltonian of the system under consideration can be written as (59)

$$H = H_0 + H_{\text{sup.}} + H_{\text{imp.}} \quad \dots (2.1)$$

where H_0 is the free Hamiltonian, $H_{\text{sup.}}$ is the Hamiltonian

due to interactions giving rise to superconductivity, and H_{imp} is the Hamiltonian due to interactions with nonmagnetic impurities.

In the second quantised form these terms are given below:

$$H_0 = \sum_{\sigma} \int d^3x \psi_{s\sigma}^{\dagger}(\vec{X}) \left(-\frac{\hbar^2}{2m_s} - \mu \right) \psi_{s\sigma}(\vec{X}) \\ + \sum_{\sigma} \int d^3x \psi_{d\sigma}^{\dagger}(\vec{X}) \left(-\frac{\hbar^2}{2m_d} - \mu \right) \psi_{d\sigma}(\vec{X})$$

$$H_{\text{sup.}} = -g_s \int d^3x \psi_{s\uparrow}^{\dagger}(\vec{X}) \psi_{s\downarrow}^{\dagger}(\vec{X}) \psi_{s\downarrow}(\vec{X}) \psi_{s\uparrow}(\vec{X}) \\ -g_d \int d^3x \psi_{d\uparrow}^{\dagger}(\vec{X}) \psi_{d\downarrow}^{\dagger}(\vec{X}) \psi_{d\downarrow}(\vec{X}) \psi_{d\uparrow}(\vec{X}) \\ -g_{sd} \int d^3x \left[\psi_{d\uparrow}^{\dagger}(\vec{X}) \psi_{s\downarrow}^{\dagger}(\vec{X}) \psi_{s\downarrow}(\vec{X}) \psi_{d\uparrow}(\vec{X}) \right. \\ \left. + \psi_{s\uparrow}^{\dagger}(\vec{X}) \psi_{d\downarrow}^{\dagger}(\vec{X}) \psi_{s\downarrow}(\vec{X}) \psi_{d\uparrow}(\vec{X}) \right],$$

$$H_{\text{imp.}} = \sum_i \sum_{\sigma} \int d^3x v_s(\vec{X}-\vec{R}_i) \psi_{s\sigma}^{\dagger}(\vec{X}) \psi_{s\sigma}(\vec{X}) \\ + \sum_i \sum_{\sigma} \int d^3x v_d(\vec{X}-\vec{R}_i) \psi_{d\sigma}^{\dagger}(\vec{X}) \psi_{d\sigma}(\vec{X}) \\ + \sum_i \sum_{\sigma} \int d^3x v_{sd}(\vec{X}-\vec{R}_i) \left[\psi_{s\sigma}^{\dagger}(\vec{X}) \psi_{d\sigma}(\vec{X}) + \psi_{d\sigma}^{\dagger}(\vec{X}) \psi_{s\sigma}(\vec{X}) \right]$$

where $\psi_{s(d)\sigma}(\vec{X})$ and $\psi_{s(d)\sigma}^{\dagger}(\vec{X})$ are, respectively, the annihilation and creation operators for an electron in the s(d) band, of spin σ ($\sigma = \uparrow$ or \downarrow), at the position \vec{X} .

μ is the chemical potential and m_s and m_d are, respectively, the effective masses of electrons in the s and d bands.

V_s and V_d are the intraband and V_{sd} is the interband impurity-scattering potentials. Similarly, g_s , g_d are the intraband and g_{sd} the interband electron phonon coupling constants.

An exact treatment should take into account both the intraband and interband phonon couplings, but then it becomes tedious and the calculation is very much involved. However, the cases which are easily tractable are:

- (i) the strong intraband-phonon coupling limit (i.e. g_s and g_d are nonzero and $g_{sd}=0$), and
- (ii) the strong interband-phonon coupling limit (i.e., g_{sd} is nonzero and both g_s and g_d are equal to zero.).

The approximation made in the first case is quite justified as the intraband phonon coupling constants are fairly large and play an appreciably significant role in determining the physical properties of superconducting transition metals(59). Keeping this feature in mind, we shall restrict ourselves to the situation of strong intraband-phonon coupling limit. In this limit, the 4x4 matrix Green's function \mathcal{G}_j is rendered diagonal (59) and is expressed by

$$\mathcal{G}_j = \begin{pmatrix} G_s & 0 \\ 0 & G_d \end{pmatrix} \dots (2.2)$$

Here G_s and G_d are 2×2 matrix Green's functions for s and d bands, respectively, and are given by (59)

$$G_s(\vec{p}, z_\nu) = \frac{\tilde{z}_{sv} 1 + \epsilon_{sp} \tau_3 + \tilde{\Delta}_{sv} \tau_1}{\tilde{z}_{sv}^2 - \epsilon_{sp}^2 - \tilde{\Delta}_{sv}^2} \dots (2.3)$$

$$G_d(\vec{p}, z_\nu) = \frac{\tilde{z}_{dv} 1 + \epsilon_{dp} \tau_3 + \tilde{\Delta}_{dv} \tau_1}{\tilde{z}_{dv}^2 - \epsilon_{dp}^2 - \tilde{\Delta}_{dv}^2} \dots (2.4)$$

The calculations of these Green's functions for a two band superconductor containing nonmagnetic impurities were first done by Chow(59) by simply extending the theory of one band superconductor containing nonmagnetic impurities, presented in Section III of Chapter I.

The τ_i 's are the usual 2×2 Pauli spin matrices and 1 is the 2×2 unit matrix. Furthermore, we have

$$\begin{aligned} z_\nu &= i\omega_\nu = (\pi i / \beta)(2\nu + 1) \\ \tilde{z}'_{sv} &= i\tilde{\omega}_{sv}, \quad \tilde{z}'_{dv} = i\tilde{\omega}_{dv}, \quad \dots (2.5) \\ \beta &= 1/k_B T, \end{aligned}$$

where k_B is the Boltzmann constant and ν is any +ve or -ve integer.

Here the quantities $\tilde{\omega}_{sv}$, $\tilde{\Delta}_{sv}$, $\tilde{\omega}_{dv}$ and $\tilde{\Delta}_{dv}$ are related to the corresponding ones for a pure two-band superconductor through the following equations:

$$\tilde{\omega}_{sv} = \omega_v + \frac{1}{2\tau_s} \frac{\tilde{\omega}_{sv}}{(\tilde{\omega}_{sv}^2 + \tilde{\Delta}_{sv}^2)^{1/2}} + \frac{1}{2\tau_{sd}} \frac{\tilde{\omega}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} \dots \quad (2.6)$$

$$\tilde{\Delta}_{sv} = \bar{\Delta}_s + \frac{1}{2\tau_s} \frac{\tilde{\Delta}_{sv}}{(\tilde{\omega}_{sv}^2 + \tilde{\Delta}_{sv}^2)^{1/2}} + \frac{1}{2\tau_{sd}} \frac{\tilde{\Delta}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} \dots \quad (2.7)$$

$$\tilde{\omega}_{dv} = \omega_v + \frac{1}{2\tau_d} \frac{\tilde{\omega}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} + \frac{1}{2\tau_{ds}} \frac{\tilde{\omega}_{sv}}{(\tilde{\omega}_{sv}^2 + \tilde{\Delta}_{sv}^2)^{1/2}} \dots \quad (2.8)$$

$$\tilde{\Delta}_{dv} = \bar{\Delta}_d + \frac{1}{2\tau_d} \frac{\tilde{\Delta}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} + \frac{1}{2\tau_{ds}} \frac{\tilde{\Delta}_{sv}}{(\tilde{\omega}_{sv}^2 + \tilde{\Delta}_{sv}^2)^{1/2}} \dots \quad (2.9)$$

$\bar{\Delta}_{s(d)}$ is the order parameter of the s(d) band of a pure two-band superconductor. The τ 's are the impurity-scattering relaxation times and are given by the following equations:

$$\frac{1}{2\tau_s} = \pi n_i N_s(0) \langle |V_s(\vec{p})|^2 \rangle_{\Omega} , \quad \dots \quad (2.10)$$

$$\frac{1}{2\tau_d} = \pi n_i N_d(0) \langle |V_d(\vec{p})|^2 \rangle_{\Omega} , \quad \dots \quad (2.11)$$

$$\frac{1}{2\tau_{sd}} = \pi n_i N_d(0) \langle |V_{sd}(\vec{p})|^2 \rangle_{\Omega} , \quad \dots \quad (2.12)$$

$$\frac{1}{2\tau_{ds}} = \pi n_i N_s(0) \langle |V_{sd}(\vec{p})|^2 \rangle_{\Omega} , \quad \dots \quad (2.13)$$

where n_i is the density of impurities, $N_{s(d)}(0)$ is the density of states for the s(d) band at the Fermi surface, $V_{s(d)}(\vec{p})$ is the fourier transform of the s(d) intraband impurity-scattering potential, $V_{sd}(\vec{p})$ is similarly the Fourier transform of the interband impurity-scattering

potential and $\langle \dots \rangle_{\Omega}$ denotes the solid angle average.

For a Niobium superconductor, the density of states $N_d(o)$ is very large compared to $N_s(o)$ and we assume that all impurity-scattering potentials are of same strength. With this approximation, equations (2.6)-(2.9) reduce to the following equations:

$$\tilde{\omega}_{sv} = \omega_v + \frac{1}{2\tau_{sd}} \frac{\tilde{\omega}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} \quad \dots (2.14)$$

$$\tilde{\Delta}_{sv} = \bar{\Delta}_s + \frac{1}{2\tau_{sd}} \frac{\tilde{\Delta}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} \quad \dots (2.15)$$

$$\tilde{\omega}_{dv} = \omega_v + \frac{1}{2\tau_{sd}} \frac{\tilde{\omega}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} \quad \dots (2.16)$$

$$\tilde{\Delta}_{dv} = \bar{\Delta}_d + \frac{1}{2\tau_{sd}} \frac{\tilde{\Delta}_{dv}}{(\tilde{\omega}_{dv}^2 + \tilde{\Delta}_{dv}^2)^{1/2}} \quad \dots (2.17)$$

III. ANALYTICAL TREATMENT

The Kubo formula for thermal conductivity is given as

$$K = \frac{2}{3VT} \text{Im} \int_{-\infty}^0 dt_2 \, t_2 \int d^3x_1 \int d^3x_2 \langle \vec{u}(\vec{x}_1, 0) \cdot \vec{u}(\vec{x}_2, t_2) \rangle , \quad \dots (2.18)$$

where V is the volume of the system, T is the temperature and the brackets denote an average over positions and spins of impurities as well as an average in the grand canonical ensemble.

Here the heat current operator $\vec{u}(\vec{x})$ is

$$\vec{u}(\vec{X}) \equiv -\frac{1}{2} \sum_{i,\sigma} \frac{1}{m_i} \left[\dot{\psi}_{i\sigma}^{\dagger}(\vec{X}) \vec{\nabla} \psi_{i\sigma}(\vec{X}) + \vec{\nabla} \psi_{i\sigma}^{\dagger}(\vec{X}) \psi_{i\sigma}(\vec{X}) \right], \quad \dots (2.19)$$

where the dot over ψ denotes the time derivative and i denotes the band indices s and d .

For the sake of simplicity, we redefine the creation (and annihilation) operator for the s and d bands as

$$\psi_{s\sigma}^{\prime\dagger}(\vec{X}) = \frac{1}{(m_s)^{1/2}} \psi_{s\sigma}^{\dagger}(\vec{X}) \quad \dots (2.20)$$

$$\psi_{d\sigma}^{\prime\dagger}(\vec{X}) = \frac{1}{(m_d)^{1/2}} \psi_{d\sigma}^{\dagger}(\vec{X}) \quad \dots (2.21)$$

In terms of the primed creation and annihilation operators, the heat-current operator $\vec{u}(\vec{X})$ takes the form

$$\vec{u}(\vec{X}) = -\frac{1}{2} \sum_{i,\sigma} \left[\dot{\psi}_{i\sigma}^{\prime\dagger}(\vec{X}) \vec{\nabla} \psi_{i\sigma}^{\prime}(\vec{X}) + \vec{\nabla} \psi_{i\sigma}^{\prime\dagger}(\vec{X}) \psi_{i\sigma}^{\prime}(\vec{X}) \right] \quad \dots (2.22)$$

In order to treat simultaneously the effect of the two interaction terms and two bands in eq.(2.1) it is convenient to work in a four-component space(59,68,69).

$$\underline{\Psi}^{\prime}(\vec{X}) \equiv \begin{pmatrix} \psi_{s\uparrow}^{\prime}(\vec{X}) \\ \psi_{d\uparrow}^{\prime}(\vec{X}) \\ \psi_{s\downarrow}^{\prime}(\vec{X}) \\ \psi_{d\downarrow}^{\prime}(\vec{X}) \end{pmatrix} \quad \dots (2.23)$$

$$\underline{\Psi}^{\prime\dagger}(\vec{X}) \equiv (\psi_{s\uparrow}^{\prime\dagger}(\vec{X}), \psi_{d\uparrow}^{\prime\dagger}(\vec{X}), \psi_{s\downarrow}^{\prime}(\vec{X}), \psi_{d\downarrow}^{\prime}(\vec{X})) \quad \dots (2.24)$$

In this four-component space the heat current operator (eq.2.22) takes the form

$$\vec{u}(1) = -\frac{1}{4} \left(\frac{\partial}{\partial t_1} \vec{\nabla}_1 + \frac{\partial}{\partial t_1} \vec{\nabla}_1 \right) \Psi'^{\dagger}(1') (\tau_3 \times 1) \Psi'(1) \Big|_{1'=1} \dots (2.25)$$

where we have denoted by 1 and 1' the space-time points (\vec{X}, t) and (\vec{X}', t') , respectively.

In order to evaluate the thermal conductivity, it is convenient to first introduce a correlation function (70),

$$P(1,2) \equiv \langle T \left[\vec{u}(1) \cdot \vec{u}(2) \right] \rangle \dots (2.26)$$

where 1,2 denote the space-time points, and T is Wick's time ordering operator. In the region $\text{Ret}_1 = \text{Ret}_2 = 0$, $0 < \text{Im } t_1, \text{Im } t_2 < -\beta$, the fourier transform of P(1,2) is defined by the expression

$$P(1,2) = V \int \frac{d^3 q}{(2\pi)^3} \frac{i}{\beta} \sum_m P(\vec{q}, v_m) e^{i\vec{q} \cdot (\vec{X}_1 - \vec{X}_2) - i v_m (t_1 - t_2)} \dots (2.27)$$

where $v_m = 2\pi m i / \beta$, m running over all integers, and $\beta = (k_B T)^{-1}$. The thermal conductivity (2.18) is then related to the analytically continued fourier series coefficient $P(\vec{q}, v_m)$ by (66, 71-73)

$$K = \frac{1}{6T} \lim_{\omega \rightarrow 0} \frac{P(\vec{q}=\vec{0}, v_m = \omega + i0^+) - P(\vec{q}=\vec{0}, v_m = \omega - i0^+)}{\omega} \dots (2.28)$$

The correlation function is now evaluated assuming

a low concentration of impurities and neglecting the existence of any collective states(74,75). The scattering from independent, randomly distributed impurities is treated in Born approximation. Thus proceeding in a manner analogous to that of Ambegaoker(70), we get the following expression for the Fourier series coefficient $P(\vec{q}=0, \nu_m) [\equiv P(\nu_m)]$ in our case:

$$P(\nu_m) = \frac{1}{8} \left(\frac{i}{\beta}\right) \sum_{\xi_\lambda} e^{\xi_\lambda 0^+} \int \frac{d^3 k}{(2\pi)^3} \vec{k}(2\xi_\lambda + \nu_m) \\ \times \text{Tr} \left[(\tau_3 \times 1) \mathcal{G}'(\vec{k}, \xi_\lambda + \nu_m) \Gamma'_k(\xi_\lambda, \nu_m) \mathcal{G}'(\vec{k}, \xi_\lambda) \right] \\ \dots (2.29)$$

where $\Gamma'_k(\xi_\lambda, \nu_m)$ is the vertex function satisfying the integral equation:

$$\Gamma'_k(\xi_\lambda, \nu_m) = \vec{k}(2\xi_\lambda + \nu_m) (\tau_3 \times 1) + n_i \int \frac{d^3 k'}{(2\pi)^3} |v_1(\vec{k} - \vec{k}')|^2 \\ \times (\tau_3 \times 1) \mathcal{G}'(\vec{k}', \xi_\lambda + \nu_m) \Gamma'_k(\xi_\lambda, \nu_m) \mathcal{G}'(\vec{k}', \xi_\lambda) (\tau_3 \times 1) \\ \dots (2.30)$$

with $\xi_\lambda = (2\lambda + 1)\pi i / \beta$ and λ being an integer. $\mathcal{G}'(\vec{k}, \xi_\lambda)$ is the Fourier transform in space and imaginary time of the following Green's function:

$$\mathcal{G}'_{ij}(1, 2) = -i \langle T [\bar{\Psi}'_i(1) \Psi'_j{}^\dagger(2)] \rangle \dots (2.31)$$

To simplify the calculations, we shall take the first leading term of the right-hand side for the vertex function. Consequently we get for $P(\nu_m)$:

$$P(\nu_m) = \frac{1}{8} \left(\frac{i}{\beta} \right) \sum_{\xi_\lambda} e^{\xi_\lambda 0^+} \int \frac{d^3 k}{(2\pi)^3} \vec{k} (2\xi_\lambda + \nu_m)^2$$

$$\times \text{Tr} \left[(\tau_3 x_1) \mathbf{e}_j'(\vec{k}, \xi_\lambda + \nu_m) (\tau_3 x_1) \mathbf{e}_j'(\vec{k}, \xi_\lambda) \right]$$

... (2.32)

Since in the strong-intraband-phonon-coupling limit, the 4x4 matrix Green's function is diagonal, as given by eq.(2.2) in section II, and the matrix $(\tau_3 x_1)$ is also a diagonal matrix, it is obvious that the resulting 4x4 matrix under the trace sign in eq.(2.32) is also diagonal. The correlation function $P(\nu_m)$ can thus be written as the sum of two correlation functions $P_1(\nu_m)$ and $P_2(\nu_m)$ which involve the Green's functions G'_S and G'_d , respectively, and given by:

$$P_1(\nu_m) = \frac{1}{8} \left(\frac{i}{\beta} \right) \sum_{\xi_\lambda} e^{\xi_\lambda 0^+} \int \frac{d^3 k}{(2\pi)^3} \vec{k} (2\xi_\lambda + \nu_m)^2$$

$$\times \text{Tr} \left[\tau_3 G'_S(\vec{k}, \xi_\lambda + \nu_m) \tau_3 G'_S(\vec{k}, \xi_\lambda) \right], \quad \dots (2.33)$$

$$P_2(\nu_m) = \frac{1}{8} \left(\frac{i}{\beta} \right) \sum_{\xi_\lambda} e^{\xi_\lambda 0^+} \int \frac{d^3 k}{(2\pi)^3} \vec{k} (2\xi_\lambda + \nu_m)^2$$

$$\times \text{Tr} \left[\tau_3 G'_d(\vec{k}, \xi_\lambda + \nu_m) \tau_3 G'_d(\vec{k}, \xi_\lambda) \right] \quad \dots (2.34)$$

The primed Green's functions can now be changed into unprimed ones with the help of following evident relations:

$$G'_S = G_S / m_S \quad \dots (2.35)$$

$$G'_d = G_d / m_d \quad \dots (2.36)$$

and equations (2.33) and (2.34) reduce to following form:

$$P_1(v_m) = \frac{1}{8m_s^2} \left(\frac{i}{\beta}\right) \sum_{\xi_\lambda} e^{\xi_\lambda 0^+} \int \frac{d^3 k}{(2\pi)^3} \vec{k} (2\xi_\lambda + v_m)^2 \times \text{Tr} \left[\tau_3 G_s(\vec{k}, \xi_\lambda + v_m) \tau_3 G_s(\vec{k}, \xi_\lambda) \right] \dots (2.37)$$

$$P_2(v_m) = \frac{1}{8m_d^2} \left(\frac{i}{\beta}\right) \sum_{\xi_\lambda} e^{\xi_\lambda 0^+} \int \frac{d^3 k}{(2\pi)^3} \vec{k} (2\xi_\lambda + v_m)^2 \times \text{Tr} \left[\tau_3 G_d(\vec{k}, \xi_\lambda + v_m) \tau_3 G_d(\vec{k}, \xi_\lambda) \right] \dots (2.38)$$

G_s and G_d are the 2x2 matrix Green's functions already introduced by equations (2.3) and (2.4).

Further, $G_s(Z)$ is analytic everywhere except for a branch cut on the real axis and hence it can be expressed through the following well-known spectral representation:

$$G_{s(d)}(\vec{k}, \xi_\lambda) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{a_{s(d)}(\omega)}{\xi_\lambda - \omega} \dots (2.39)$$

where,

$$a_{s(d)}(\omega) = G_{s(d)}(Z=\omega - i0^+) - G_{s(d)}(Z=\omega + i0^+) \dots (2.40)$$

After substituting the spectral representations for the two Green's functions in equations (2.37) and (2.38), the ξ_λ sum is carried out (73). The thermal conductivity is then calculated from the formula (2.28). K is thus found to be the sum of two terms, K_1 and

K_2 arising from the two correlation functions $P_1(v_m)$ and $P_2(v_m)$, respectively, and have the following form:

$$K_1 = \frac{1}{48m_s^2 k_B T^2} \int \frac{d^3 k d\omega}{(2\pi)^4} k^2 \omega^2 \operatorname{sech}^2\left(\frac{1}{2}\beta\omega\right) \times \operatorname{Tr} \left[\tau_3 a_s(\vec{k}, \omega) \tau_3 a_s(\vec{k}, \omega) \right] \quad \dots (2.41)$$

and

$$K_2 = \frac{1}{48m_d^2 k_B T^2} \int \frac{d^3 k d\omega}{(2\pi)^4} k^2 \omega^2 \operatorname{sech}^2\left(\frac{1}{2}\beta\omega\right) \times \operatorname{Tr} \left[\tau_3 a_d(\vec{k}, \omega) \tau_3 a_d(\vec{k}, \omega) \right] \quad \dots (2.42)$$

The integration over momentum variable k is performed with relative ease by converting it to an integral over the energy ϵ (70); the expressions for K_1 and K_2 then become

$$K_1 = \frac{n_s}{8m_s k_B T^2} \int_0^\infty d\omega \frac{\omega^2 \operatorname{sech}^2\left(\frac{1}{2}\beta\omega\right)}{\operatorname{Im} \left[(\tilde{Z}_s^2 - \tilde{\Delta}_s^2)^{1/2} \right]} \left(1 + \frac{|\tilde{Z}_s|^2 - |\tilde{\Delta}_s|^2}{|\tilde{Z}_s^2 - \tilde{\Delta}_s^2|} \right) \quad \dots (2.43)$$

$$K_2 = \frac{n_d}{8m_d k_B T^2} \int_0^\infty d\omega \frac{\omega^2 \operatorname{sech}^2\left(\frac{1}{2}\beta\omega\right)}{\operatorname{Im} \left[(\tilde{Z}_d^2 - \tilde{\Delta}_d^2)^{1/2} \right]} \left(1 + \frac{|\tilde{Z}_d|^2 - |\tilde{\Delta}_d|^2}{|\tilde{Z}_d^2 - \tilde{\Delta}_d^2|} \right) \quad \dots (2.44)$$

where $n_{s(d)}$ is the density of electrons in the $s(d)$ band.

Let us now define

$$u_s = \frac{\tilde{Z}_s}{\tilde{\Delta}_s} = \frac{i\tilde{\omega}'_s}{\tilde{\Delta}_s} \quad \dots (2.45)$$

and
$$u_d = \frac{\tilde{z}_d}{\tilde{\Delta}_d} = \frac{i\tilde{\omega}_d}{\tilde{\Delta}_d} \dots (2.46)$$

We can now rewrite equations (2.14)-(2.17) in terms of u_s and u_d as:

$$\tilde{z}_s = z + \frac{i}{2\tau_{sd}} \frac{u_d}{(u_d^2 - 1)^{1/2}} \dots (2.47)$$

$$\tilde{\Delta}_s = \bar{\Delta}_s + \frac{i}{2\tau_{sd}} \frac{1}{(u_d^2 - 1)^{1/2}} \dots (2.48)$$

$$\tilde{z}_d = z + \frac{i}{2\tau_{sd}} \frac{u_d}{(u_d^2 - 1)^{1/2}} \dots (2.49)$$

$$\tilde{\Delta}_d = \bar{\Delta}_d + \frac{i}{2\tau_{sd}} \frac{1}{(u_d^2 - 1)^{1/2}} \dots (2.50)$$

Substituting equations (2.45), (2.46), (2.48) and (2.50) into equations (2.43) and (2.44), we have

$$K_1 = \frac{n_s}{8m_s k_B T^2} \int_0^\infty d\omega \frac{\omega^2 \operatorname{sech}^2(\frac{1}{2}\beta\omega)}{\operatorname{Im} \left\{ \bar{\Delta}_s (u_s^2 - 1)^{1/2} + i\Gamma \left[(u_s^2 - 1)^{1/2} / (u_d^2 - 1)^{1/2} \right] \right\}} \times \left(1 + \frac{|u_s|^2 - 1}{|u_s^2 - 1|} \right) \dots (2.51)$$

$$K_2 = \frac{n_d}{8m_d k_B T^2} \int_0^\infty d\omega \frac{\omega^2 \operatorname{sech}^2(\frac{1}{2}\beta\omega)}{\operatorname{Im} \left[\bar{\Delta}_d (u_d^2 - 1)^{1/2} + i\Gamma \right]} \left(1 + \frac{|u_d|^2 - 1}{|u_d^2 - 1|} \right) \dots (2.52)$$

where,

$$\Gamma = \frac{1}{2\tau_{sd}} \dots (2.53)$$

From equations (2.49) and (2.50) it is easy to see that

$$u_d = \frac{\tilde{z}_d}{\tilde{\Delta}_d} = \frac{z}{\Delta_d} = \frac{i\omega}{\Delta_d} \quad \dots (2.54)$$

Similarly, the two equations (2.47) and (2.48) can now be combined to give

$$u_s = \left[\frac{i\omega}{\Delta_s} \left(1 + \frac{\Gamma}{(\omega^2 + \Delta_d^2)^{1/2}} \right) \right] / \left(1 + \frac{\Delta_d}{\Delta_s} \frac{\Gamma}{(\omega^2 + \Delta_d^2)^{1/2}} \right) \quad \dots (2.55)$$

Further, as argued by Chow(59), $\Delta_d \gg \Delta_s$ and we can neglect the factor $1 + \left[\Gamma / (\omega^2 + \Delta_d^2)^{1/2} \right]$ in comparison to

$1 + (\Delta_d / \Delta_s) \left[\Gamma / (\omega^2 + \Delta_d^2)^{1/2} \right]$ and can approximate equation (2.55) as

$$u_s \cong \frac{i\omega / \Delta_s}{\left\{ 1 + (\Delta_d / \Delta_s) \left[\Gamma / (\omega^2 + \Delta_d^2)^{1/2} \right] \right\}} \quad \dots (2.56)$$

Substituting for u_s and u_d from equations (2.54) and (2.56), respectively, we finally get

$$K_1 = \frac{n_s}{4m_s k_B} \int_0^\omega d\omega \frac{\omega^4 \operatorname{sech}^2(\frac{1}{2}\beta\omega)}{T^2 \left\{ \omega^2 + \Delta_s^2 \left[1 + (\Delta_d / \Delta_s) \left(\Gamma / (\omega^2 + \Delta_d^2)^{1/2} \right) \right]^2 \right\}^{3/2}} \quad \dots (2.57)$$

and

$$K_2 = \frac{n_d}{4m_d k_B} \int_0^\omega d\omega \frac{\omega^4 \operatorname{sech}^2(\frac{1}{2}\beta\omega)}{T^2 (\omega^2 + \Delta_d^2) \left[(\omega^2 + \Delta_d^2)^{1/2} + \Gamma \right]} \quad \dots (2.58)$$

We can write the above equations also in the

following form:

$$K_1 = \frac{n_s}{m_s k_B} I_1 \quad \dots (2.59)$$

$$K_2 = \frac{n_d}{m_d k_B} I_2 \quad \dots (2.60)$$

where,

$$I_1 = \int_0^{\infty} d\omega \left\{ \omega^4 / T^2 (2 + e^{\beta\omega} + e^{-\beta\omega}) \left[\omega^2 + \bar{\Delta}_s^2 \left(1 + \frac{\bar{\Delta}_d}{\bar{\Delta}_s} \frac{\Gamma}{(\omega^2 + \bar{\Delta}_d^2)^{1/2}} \right) \right]^2 \right\}^{3/2} \quad \dots (2.61)$$

$$I_2 = \int_0^{\infty} d\omega \left\{ \omega^4 / T^2 (2 + e^{\beta\omega} + e^{-\beta\omega}) (\omega^2 + \bar{\Delta}_d^2) \left[(\omega^2 + \bar{\Delta}_d^2)^{1/2} + \Gamma \right] \right\} \quad \dots (2.62)$$

As the integrals I_1 and I_2 can not be solved analytically, their values have been computed numerically, in the temperature range 0.04-0.90°K for various values of the parameter Γ (which is a measure of impurity concentration) ranging from 50×10^{-17} ergs to 60×10^{-17} ergs. The calculations have been done using the following BCS expressions for the two energy gaps $\bar{\Delta}_s$ and $\bar{\Delta}_d$:

$$\bar{\Delta}_s = 3.1 k_B T_{cs} \left(1 - \frac{T}{T_{cs}} \right)^{1/2} \quad \dots (2.63)$$

$$\bar{\Delta}_d = 3.1 k_B T_{cd} \left(1 - \frac{T}{T_{cd}} \right)^{1/2} \quad \dots (2.64)$$

The values of the critical temperatures T_{cs} and T_{cd} due to the s and d bands are taken to be 0.926 and 9.26 °K, respectively, as we know that $T_{cd} = T_c$ of Niobium and $T_{cs} \approx 10^{-1} T_{cd}$ (59,62) and T_c for Niobium

is 9.26 °K. Calculations have been done by taking units of energy in eV.

One can make a qualitative estimate of K_1 and K_2 in this model, if information about the parameters n_s , n_d , m_s , and m_d is available. However, as no information seems to be available at present for the case of Niobium, we investigate the behaviour of $I_1(2)$ vs temperature T . Since, $n_{s(d)} / m_{s(d)} k_B$ is a constant factor, it will only scale the values of $K_1(2)$ and will not affect the behaviour of $K_1(2)$ vs temperature T .

As a result of numerical computation, we find that I_2 is about 10^{-7} times smaller than I_1 . Furthermore, since $n_s / m_s k_B$ is greater than $n_d / m_d k_B$ because $n_s > n_d$ and $m_s < m_d$, the contribution of the K_2 term will be far smaller than that of the K_1 term and it can be neglected to a fairly good degree of approximation. Thus, thermal conductivity K will be equal to K_1 . The quantity $K / (n_s / m_s k_B)$ is plotted on log-log graph paper against temperature T for two values of parameter Γ , as shown in Fig.2.1.

IV DISCUSSION

Working in the two-band model, we find that the thermal conductivity K is the sum of two parts K_1 and K_2 . The interesting feature is that while K_2 depends only on the single energy gap parameter $\bar{\Delta}_d$, K_1 depends on both the energy gap parameters $\bar{\Delta}_s$ and $\bar{\Delta}_d$, and this

dependence manifests itself in a rather complicated manner- it seems impossible to further split K_1 in terms of $\bar{\Delta}_s$ and $\bar{\Delta}_d$ separately. Further, since $K_2 \simeq 10^7 K_1$, the thermal conductivity $K \simeq K_1$. A log-log plot of the quantity $K/(n_s/m_s k_B)$ vs temperature T for two values of the parameter Γ (which is a measure of impurity concentration) is shown in Fig.2.1. The general and broad features of this study are as follows:

(a) For $\Gamma = 31.25 \times 10^{-5}$ eV, we find that for the temperature range $0.04-0.20^\circ$ K, the points lie on one straight line. The slope thereafter decreases slightly i.e., the thermal conductivity shows a mild decrease.

(b) For $\Gamma = 37.50 \times 10^{-5}$ eV, a similar behaviour is observed, but the change in slope now starts slightly earlier, viz., at around $T = 0.16^\circ$ K.

(c) The thermal conductivity is found to decrease with the increase in impurity concentration. This result is in agreement qualitatively with the experiment (67). Moreover, the result is analogous to the case of one band BCS superconductor, where also the nonmagnetic impurities decrease slightly the thermal conductivity. Furthermore, we see that it is the inter-band impurity scattering which affects the thermal conductivity in our calculations.

(d) The thermal conductivity is found to vary with temperature as $T^{3.1}$ or $T^{3.2}$.

While comparing our results with experiments we observe that two sets of experimental data are available on the thermal conductivity of superconducting Niobium. In the first, Carlson and Satterthwaite (76) have observed anomalous increase in thermal conductivity below 0.6°K , which they attribute to electrons associated with a second small energy gap. However, in the other experiment, reported recently by Anderson et al., (67) they find no such evidence for an anomalously large thermal conductivity near 0.5°K . These authors, while offering an explanation (on the basis of their own unpublished data and of Rowell's (77)) for the anomalous behaviour observed by Carlson and Satterthwaite (76) as the effects of physical strains in the sample, interpret the lack of an anomalous behaviour in their own experiment to mean that there is no contribution to the thermal transport due to the second energy gap, concluding thereby that their experiment gives negative evidence against the SMW two-band model.

It is obvious from our results plotted in Fig.2.1 that a theory based on the two-band model of SMW does not predict any anomalous increase in the thermal conductivity, and as such the interpretation by Carlson and Satterthwaite (76) of the anomalous behaviour which they observed is not correct. Similarly, the inference drawn by Anderson et al (67), based on the absence of any large anomalous behaviour in thermal conductivity measurements,

that it provides a negative evidence against the two-band model of SMW, is not at all substantiated by the theoretical predictions of this model. In this context, it is important to notice that the nature of the theoretical curves in Fig.2.1 in fact agrees with the ones reported by Anderson et al.(67). For example, the curve D, of Fig.1 of Ref.(67), is a straight line and shows a depression, though very slight, at around 0.2°K .

To sum up, our calculations, based on the SMW two-band model, show that the thermal conductivity of superconducting Niobium decreases with the increase in impurity concentration and does depend on both the energy gap parameters in a rather peculiar manner; this is corroborated by experiments and thus gives a positive evidence in favour of this model.

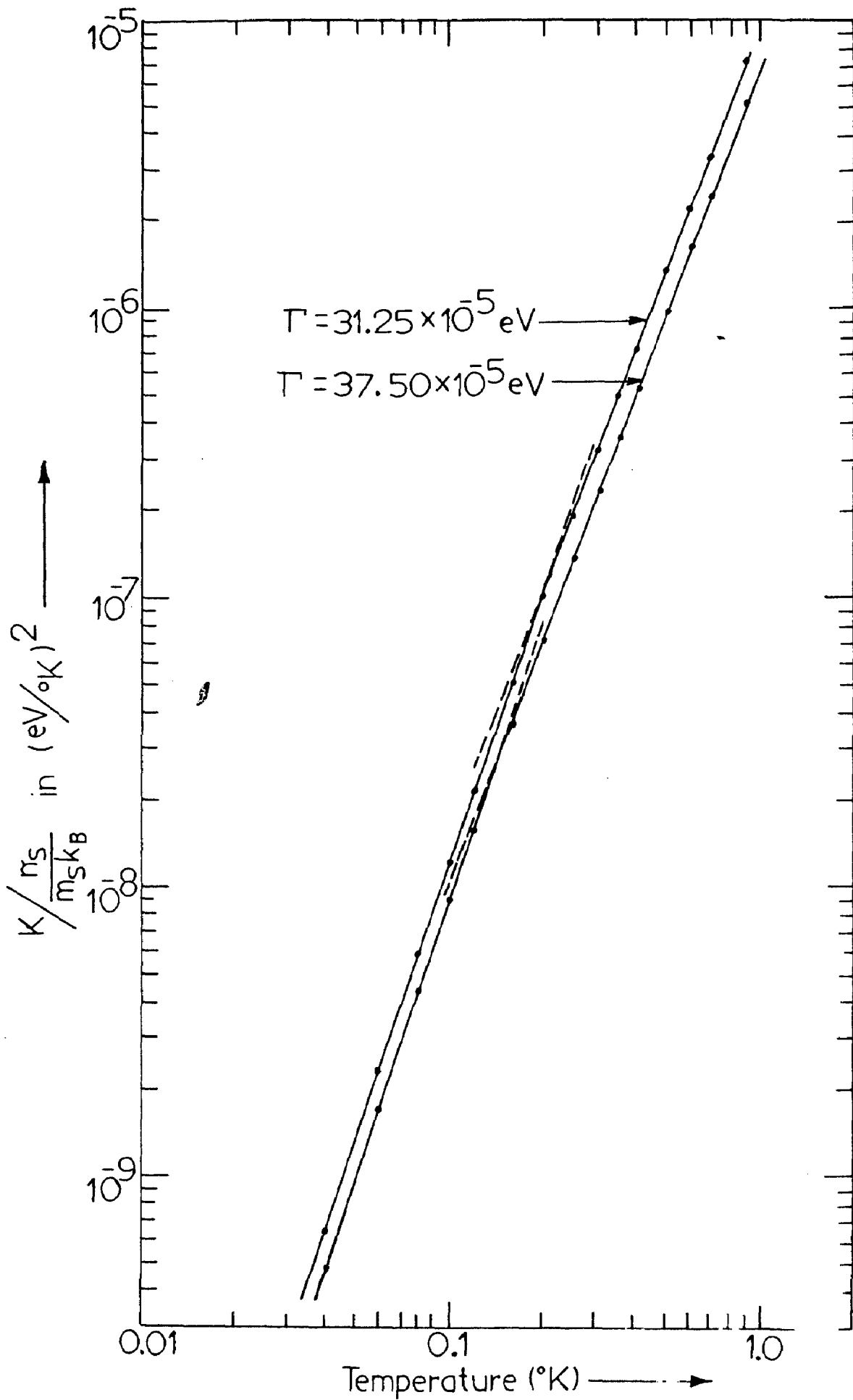


FIG.2.1-A log-log plot showing the variation of the quantity $\left(\frac{K/n_s}{m_s k_B}\right)$ versus temperature T for two values of parameter Γ .

CHAPTER III

THERMOMAGNETIC EFFECTS IN DIRTY TRANSITION METAL SUPERCONDUCTORS NEAR THE UPPER CRITICAL FIELD

I INTRODUCTION

In the preceding chapter we had extended the SMW two-band model (58) to study the thermal conductivity of superconducting transition metals containing nonmagnetic impurities. Now we shall use this model to study the Thermomagnetic Effects in dirty ($\lambda < \xi_0$) transition metal superconductors containing nonmagnetic impurities near the upper critical field. It has been confirmed by previous investigations (78-80) that it is the pair-breaking mechanism due to the interband impurity scattering which is responsible for the anomalous changes in various physical properties of dirty transition metal superconductors near the critical temperature. Very recently, Chow (80) has investigated how the interband impurity scattering would influence the Hall effect in the dirty type-II transition metal superconductors in a magnetic field immediately below the upper critical field $H_{c_2}(T)$ and in the temperature region $T_{cs}^{(0)} < T < T_{cd}(=T_c)$. In this region the s-band electrons are in the normal phase and the d-band electrons are in the superconducting mixed phase. In the present chapter, we extend (81) this

study to investigate the influence of the interband impurity scattering on the thermomagnetic effects (such as the Etingshausen, Nernst, and Peltier effects) of dirty type-II transition metal superconductors under similar conditions of magnetic field and temperature. Thermomagnetic effects in the mixed state of a superconductor arise from normal electron flow in the cores of the vortex lines (82) and to a much greater extent from the existence of localized excitations- and hence an entropy- in the cores of the vortex lines (83). The calculations have been done following closely the Caroli-Maki theory (84) for the thermomagnetic effects of dirty one-band type-II superconductors. The pinning effects on the motion of the order parameter may be completely disregarded which is a quite plausible assumption and is confirmed by experiments in the high field region ($H < H_{c2}$).

In the calculations presented here, we assume that the Fermi surface is spherical (which may be true for dirty Niobium). Further as in Chapter II the intraband BCS coupling constants, g_s and g_d , are assumed to be non-zero and the interband coupling constant g_{sd} is put equal to zero. Another important point which should be noticed is that the interband impurity scattering only slightly changes the upper critical field in the temperature region $T_{cs}^{(0)} < T < T_c$ (85). In Section II,

a theoretical formulation of thermomagnetic effects in dirty transition metal superconductors is given. Results are summarized in Section III., and conclusions are drawn in Section IV.

II THEORETICAL FORMULATION

A Heat Current Density in Dirty Limit

We adopt the procedure followed by Caroli and Maki(84) for calculating the heat current density in the dirty limit ($\lambda < \xi_0$). In the high field region and at the temperatures of interest, $T_{cs}^{(0)} < T < T_c$, there will be only a small percentage of the electrons in the s band, and so the heat current density (hence the thermomagnetic effects) of the two-band system should mainly be due to the d-band electrons. Therefore, we will be interested here in calculating the d-band heat current density.

In these calculations, only the normal-phase Green's functions will be needed, as shown by Caroli and Maki (84). They can be easily obtained for our case (85) from eq.(2.3) and (2.4) of Chapter II and are given as,

$$G_s^{(0)}(\vec{p}, z_\nu) = (\tilde{Z}_{sv} - \epsilon_{sp} + e \vec{V}_{Fs} \cdot \vec{A})^{-1} \quad \dots (3.1)$$

$$G_d^{(0)}(\vec{p}, z_\nu) = (\tilde{Z}_{dv} - \epsilon_{dp} + e \vec{V}_{Fd} \cdot \vec{A})^{-1} \quad \dots (3.2)$$

where $z_\nu = i(2\nu+1)\pi T$, with ν being an integer. Further, $\tilde{Z}_{sv} (=i\tilde{\omega}_{sv})$ and $\tilde{Z}_{dv} (=i\tilde{\omega}_{dv})$ are given by

$$\tilde{\omega}_{sv} = \omega_v + \text{sgn } v(1/2\tau_s + 1/2\tau_{sd}) \quad \dots (3.3)$$

$$\tilde{\omega}_{dv} = \omega_v + \text{sgn } v(1/2\tau_d + 1/2\tau_{ds}) \quad \dots (3.4)$$

where τ_s and τ_d are intraband-impurity-scattering relaxation times and τ_{sd} and τ_{ds} are interband-impurity-scattering relaxation times for the s-d and d-s processes respectively, and are given by equations (2.10)-(2.13) in Chapter II. It has been shown by Chow(85), that the inclusion of interband-impurity-scattering relaxation times τ_{ds} modifies the upper critical field equation

$$\log(T/T_{c0}) + \psi\left[\frac{1}{2} + (\tau_{tr,d} v_{Fd}^2 / 6\pi T) eH_{c2}\right] - \psi\left(\frac{1}{2}\right) = 0 \quad \dots (3.5)$$

to the following correct equation:

$$\log(T/T_{c0}) + \psi\left[\frac{1}{2} + \frac{\epsilon_{d0}}{4\pi T} + \frac{1}{4\pi T\tau_{ds}}\right] - \psi\left[\frac{1}{2}\right] = 0 \quad \dots (3.6)$$

where $\epsilon_{d0} = 2D_d eH_{c2}(T)$ with $D_d = \frac{1}{3}\tau_{tr,d} v_{Fd}^2$.

Here $\tau_{tr,d}$ is the d band intraband-transport relaxation time, $\psi(x)$ is the digamma function, $H_{c2}(T)$ is the temperature dependent upper critical field, D_d is the d-band diffusion coefficient and v_{Fd} is the Fermi-velocity of d-band electrons.

The equations of motion governing the order parameter in a two-band superconductor, in the presence of

an external magnetic field and electric field, are given by (84):

$$(\Omega + D_d q^2) \Delta_d^*(\vec{q}, \zeta_m) = \epsilon_{d0} \Delta_d^*(\vec{q}, \zeta_m) \quad \dots (3.7)$$

$$(\Omega + D_d q^2) \Delta_d(\vec{q}, \zeta_m) = \epsilon_{d0} \Delta_d(\vec{q}, \zeta_m) \quad \dots (3.8)$$

where, in equation (3.7), Ω and \vec{q} are to be replaced as below

$$\Omega \Rightarrow \Omega_m + 2ie\phi(\vec{r}) \quad \dots (3.9)$$

$$\vec{q} \rightarrow \vec{q} - 2e\vec{A}(\vec{r}) \quad \dots (3.10)$$

when operating on Δ_d^*

and in equation (3.8), Ω and \vec{q} are to be replaced as below

$$\Omega \rightarrow \Omega_m - 2ie\phi(\vec{r}) \quad \dots (3.11)$$

$$\vec{q} \rightarrow \vec{q} + 2e\vec{A}(\vec{r}) \quad \dots (3.12)$$

when operating on Δ_d .

Here, $\phi(\vec{r}) = -Ex$ and $\vec{A} = (0, Hx, 0)$ and the d-band order parameter $\Delta_d^*(\vec{q}, \zeta_m)$ is given by

$$\Delta_d^*(\vec{r}, t) = T \sum_{\zeta_m} \int \frac{d^3q}{(2\pi)^3} e^{i\vec{q} \cdot \vec{r} - i\zeta_m t} \Delta_d^*(\vec{q}, \zeta_m) \quad \dots (3.13)$$

with $\zeta_m = i\Omega_m = i2\pi mt$, m being an integer.

We shall now calculate the d-band heat current density which is expressed (using the standard notation)

as (84)

$$\vec{j}_d^h(\vec{r}, t) = \vec{j}_{d1}^h(\vec{r}, t) + \vec{j}_{d2}^h(\vec{r}, t) \quad \dots (3.14)$$

with

$$\vec{j}_{d1}^h(\vec{r}, t) = -ie \int_{-\infty}^t dt' \int d^3r' \left\langle \left[\vec{j}_d^h(\vec{r}, t), n_d(\vec{r}', t') \right] \right\rangle \phi(\vec{r}', t') \quad \dots (3.15)$$

$$\begin{aligned} \vec{j}_{d2}^h(\vec{r}, t) = & \frac{1}{2} \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 \int d^3r \int d^3m \\ & \times \left\{ \left\langle \left[\left[\vec{j}_d^h(\vec{r}, t), \bar{\Psi}_d(\vec{r}, t_1) \right], \bar{\Psi}_d^\dagger(\vec{m}, t_2) \right] \right\rangle \right. \\ & \left. + \left\langle \left[\left[\vec{j}_d^h(\vec{r}, t), \bar{\Psi}_d^\dagger(\vec{m}, t_2) \right], \bar{\Psi}_d(\vec{r}, t_1) \right] \right\rangle \right\} \Delta_d^*(\vec{r}, t_1) \Delta_d(\vec{m}, t_2) \quad \dots (3.16) \end{aligned}$$

where $\vec{j}_d^h(\vec{r}, t)$ is the d-band heat current density operator

$$\begin{aligned} \vec{j}_d^h(\vec{r}, t) = & -\frac{1}{2m_d} \sum_{\sigma} \left[(\vec{\nabla} - ie\vec{A}) \left(\frac{\partial}{\partial t} - ie\phi \right) + (\vec{\nabla}' + ie\vec{A}') \left(\frac{\partial}{\partial t} + ie\phi \right) \right] \\ & \times \psi_{d\sigma}^\dagger(\vec{r}', t') \psi_{d\sigma}(\vec{r}, t) \Big|_{\vec{r}'=\vec{r}, t'=t} \quad \dots (3.17) \end{aligned}$$

and $\bar{\Psi}_d$ and $\bar{\Psi}_d^\dagger$ are d-band pair annihilation and creation operators:

$$\bar{\Psi}_d(\vec{r}, t) = \psi_{d\uparrow}(\vec{r}, t) \psi_{d\downarrow}(\vec{r}, t) \quad \dots (3.18)$$

$$\bar{\Psi}_d^\dagger(\vec{r}, t) = \psi_{d\downarrow}^\dagger(\vec{r}, t) \psi_{d\uparrow}^\dagger(\vec{r}, t) \quad \dots (3.19)$$

Now $\vec{j}_{d1}^h(\vec{r}, t)$ is just the d-band heat current density in the normal phase and we have (84)

$$\vec{j}_{d1x}^h = ST\sigma_d (1+\eta_d^2)^{-1} E, \quad \dots (3.20)$$

$$J_{dly}^h = -ST\sigma_d \left[\eta_d / (1 + \eta_d^2) \right] E, \quad \dots (3.21)$$

where $\sigma_d = e^2 \tau_{tr,d} n_d / m_d$, the electrical conductivity of a one-d-band normal metal in zero magnetic field, $\eta_d = (e \tau_{tr,d} / m_d C) H$, and $S (\approx \pi^2 T / 2e\mu$ for a spherical Fermi Surface), the thermoelectric-power coefficient.

$\vec{J}_{d2}^h(\vec{r}, t)$, defined in equation (3.16), is the contribution due to the motion of the vortex structure (i.e., that of the order parameter) which is of main interest here. It is calculated with the help of the standard temperature Green's function technique (86). We have kept here only the lowest order term in $\Delta(\vec{r}, t)$, since we are interested in the region near the upper critical field. In order to evaluate the retarded product in eq. (3.16), we first calculate the corresponding thermal product,

$$\begin{aligned} \vec{J}_{d2}^h(\vec{r}, \Omega_1 + \Omega_2) &= \frac{1}{m_d} \left(\frac{\partial}{\partial t}, \vec{\nabla} + \frac{\partial}{\partial t} \vec{\nabla}' \right) T \sum_{\nu=-\infty}^{\infty} \int d^3 \lambda d^3 m \\ &\times \langle G_d^{(0)}(\vec{r}, \vec{\lambda}; \zeta_1 - Z_\nu) G_d^{(0)}(\vec{m}, \vec{\lambda}; Z_\nu) G_d^{(0)}(m, \vec{r}'; -\zeta_2 - Z_\nu) \\ &\times \Delta_d(\vec{\lambda}; \Omega_1) \Delta_d^*(\vec{m}; \Omega_2) \Big|_{\vec{r}=\vec{r}', t=t'} \quad \dots (3.22) \end{aligned}$$

where $\zeta_1 = i\Omega_1 = i2\pi m_1 t$ and $\zeta_2 = i\Omega_2 = i2\pi m_2 t$, with m_1 and m_2 being integers in the absence of external fields. In the presence of external fields, $\phi(\vec{r})$ should be included in Ω_1 and Ω_2 according to the convention given in equations (3.9) and (3.11). $\langle \dots \rangle_i$ represents the

impurity-scattering vertex corrections. Now, with vanishing Δ_d and Δ_d^* , the only vertex corrections to be included would be the intraband impurity-scattering vertex corrections, which have been treated in Ref.84. It should be emphasized here that the Green's functions in equation (3.22) are now given by eq.(3.2) with interband impurity scattering in self-energies included.

Further, confining ourselves to the case $\Omega_1, \Omega_2 > 0$, as we are interested in the retarded product, we obtain

$$\begin{aligned}
 J_{d2}^h(\vec{q}, \Omega_1 + \Omega_2) = & \frac{n_d \tau_{tr,d}}{4m_d} (\vec{q}_1 - \vec{q}_2) \left\{ \Psi\left(\frac{1}{2} + \frac{\Omega_2 + D_d q_2^2}{4\pi T} + \frac{1}{4\pi T \tau_{ds}}\right) \right. \\
 & - \Psi\left(\frac{1}{2} + \frac{2\Omega_1 + \Omega_2 + D_d q_2^2}{4\pi T} + \frac{1}{4\pi T \tau_{ds}}\right) \\
 & + \frac{\Omega_2 - D_d q_1^2 - 1/\tau_{ds}}{\Omega_1 + \Omega_2 - D_d (q_1^2 - q_2^2)} \left[\Psi\left(\frac{1}{2} + \frac{2\Omega_1 + \Omega_2 + D_d q_2^2}{4\pi T} + \frac{1}{4\pi T \tau_{ds}}\right) \right. \\
 & \left. - \Psi\left(\frac{1}{2} + \frac{\Omega_1 + D_d q_1^2}{4\pi T} + \frac{1}{4\pi T \tau_{ds}}\right) \right] \\
 & + \frac{\Omega_2 + D_d q_1^2 + 1/\tau_{ds}}{\Omega_1 + \Omega_2 + D_d (q_1^2 - q_2^2)} \left[\Psi\left(\frac{1}{2} + \frac{2\Omega_2 + \Omega_1 + D_d q_1^2}{4\pi T} + \frac{1}{4\pi T \tau_{de}}\right) \right. \\
 & \left. - \Psi\left(\frac{1}{2} + \frac{\Omega_2 + D_d q_2^2}{4\pi T} + \frac{1}{4\pi T \tau_{ds}}\right) \right] \left. \right\} \\
 & \times \Delta_d(\vec{q}_1, \Omega_1) \Delta_d^*(\vec{q}_2, \Omega_2) \dots \quad (3.23)
 \end{aligned}$$

Using equations (3.7) and (3.8) we get

$$\begin{aligned}
 \vec{J}_{d2}^h(\vec{q}, \Omega_1 + \Omega_2) &= \frac{n_d \tau_{tr,d}}{4m_d} (\vec{q}_1 - \vec{q}_2) \left\{ \frac{(\Omega_2 - \Omega_1) - \epsilon_{do} - \frac{1}{\tau_{ds}}}{2\Omega_1} \right. \\
 &\times \left[\psi\left(\frac{1}{2} + \rho + \frac{2\Omega_1}{4\pi T} + \frac{1}{4\pi T \tau_{ds}}\right) - \psi\left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}}\right) \right] \\
 &+ \frac{(\Omega_2 - \Omega_1) + \epsilon_{do} + \frac{1}{\tau_{ds}}}{2\Omega_2} \left[\psi\left(\frac{1}{2} + \rho + \frac{2\Omega_2}{4\pi T} + \frac{1}{4\pi T \tau_{ds}}\right) \right. \\
 &\left. \left. - \psi\left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}}\right) \right] \right\} \Delta_d(\vec{q}_1, \Omega_1) \Delta_d^*(\vec{q}_2, \Omega_2) \dots (3.24)
 \end{aligned}$$

where $\rho = \frac{\epsilon_{do}}{4\pi T} = 2D_d eH_{c2}/4\pi T$. Now Ω_1 and Ω_2 can be treated as small quantities as we essentially make the analytical continuation $i(\Omega_1 + \Omega_2) = \zeta_1 + \zeta_2 \rightarrow (\omega_1 + \omega_2) + i0^+$ where ω_1 and ω_2 are real frequencies and then take the limit $\omega_1 + \omega_2 \rightarrow 0$. Also, at sufficiently high temperatures, to which we have restricted ourselves, $1/4\pi T \tau_{ds}$ will be a small quantity for most dirty superconductors. Here in our case of $T > T_{cs}^{(0)}$, we would only require $1/\Delta_s(0) \tau_{ds} \approx 1/\Delta_s(0) \tau_s$ to be a small quantity. It is well known that for small x , we have the following expansion:

$$\psi\left(\frac{1}{2} + \rho + x\right) = \psi\left(\frac{1}{2} + \rho\right) + x\psi^{(1)}\left(\frac{1}{2} + \rho\right) + \frac{1}{2}x^2\psi^{(2)}\left(\frac{1}{2} + \rho\right) \dots (3.25)$$

where,

$$\psi^{(1)}\left(\frac{1}{2} + \rho\right) = \frac{\partial}{\partial \rho} \psi\left(\frac{1}{2} + \rho\right) = \sum_{v=0}^{\infty} \frac{1}{(v + \frac{1}{2} + \rho)^2} > 0 \dots (3.26)$$

$$\psi^{(2)}\left(\frac{1}{2} + \rho\right) = \frac{\partial^2}{\partial \rho^2} \psi\left(\frac{1}{2} + \rho\right) = -2 \sum_{v=0}^{\infty} \frac{1}{(v + \frac{1}{2} + \rho)^3} < 0 \dots (3.27)$$

Using Eq.(3.25), \vec{J}_{d2}^h can be approximated by,

$$\vec{J}_{d2}^h(\vec{q}=\vec{q}_1+\vec{q}_2, \omega_1+\omega_2)$$

$$\begin{aligned} &= \frac{n_d \tau_{tr,d}}{8\pi m_d T} (\vec{q}_1 - \vec{q}_2) (\omega_2 - \omega_1) \Delta_d(\vec{q}_1, \omega_1) \Delta_d^*(\vec{q}_2, \omega_2) \\ & \times \left[\psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right) + \left(\frac{\rho}{2} + \frac{1}{8\pi T \tau_{ds}} \right) \psi^{(2)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right) \right] \\ & \dots (3.28) \end{aligned}$$

After doing the analytical continuation and taking the limit $\omega_1 + \omega_2 \rightarrow 0$, we obtain

$$\begin{aligned} \vec{J}_{d2}^h(\vec{r}, t) &= \frac{n_d \tau_{tr,d}}{8\pi m_d T} (\vec{q}_1 - \vec{q}_2) (\omega_2 - \omega_1) \Delta_d(\vec{r}_1, t_1) \Delta_d^*(\vec{r}_2, t_2) \Big|_{\vec{r}_1 = \vec{r}_2 = \vec{r}} \\ & \times \psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right) \left[1 + \left(\frac{\rho}{2} + \frac{1}{8\pi T \tau_{ds}} \right) \right. \\ & \left. \psi^{(2)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right) \right] \\ & \times \frac{\psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)}{\psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)} \\ & \dots (3.29) \end{aligned}$$

where $\vec{q}_1, \vec{q}_2, \omega_1$ and ω_2 should now be understood as operators in the sense

$$\begin{aligned} \vec{q}_1 &= \frac{1}{i} \vec{\nabla}_1 - 2e\vec{A}(1), \quad \vec{q}_2 = \frac{1}{2} \vec{\nabla}_2 + 2e\vec{A}(2) \\ \omega_1 &= i \frac{\partial}{\partial t_1} - 2e\phi(1), \quad \omega_2 = i \frac{\partial}{\partial t_2} + 2e\phi(2) \\ & \dots (3.30) \end{aligned}$$

Taking the space average (84), we have

$$\langle \vec{J}_{d2x}^h \rangle = 0 \quad \dots (3.31)$$

$$\begin{aligned}
 J_{d2y}^h &= - \frac{n_d \tau_{tr,d}}{4\pi m_d T} \psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right) \langle |\Delta_d|^2 \rangle eE \\
 &\quad \times \left[2 + \left(\rho + \frac{1}{4\pi T \tau_{ds}} \right) \frac{\psi^{(2)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)}{\psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)} \right] \\
 &= M_d E \left[2 + \left(\rho + \frac{1}{4\pi T \tau_{ds}} \right) \frac{\psi^{(2)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)}{\psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)} \right] \dots (3.32)
 \end{aligned}$$

which can be written as

$$\langle J_{d2y}^h \rangle = M_d E \left[2 - Z(t) \left(1 + \frac{1}{\epsilon_{do} \tau_{ds}} \right) \right] \dots (3.33)$$

where

$$Z(t) = -\rho \frac{\psi^{(2)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)}{\psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right)} \dots (3.34)$$

is always a positive quantity, as is evident from equations (3.26) and (3.27). Here M_d is the spatially averaged d-band magnetization of a very dirty type-II two band superconductor, and is given by the following expression

$$\begin{aligned}
 M_d &= - \frac{e \tau_{tr,d} n_d}{4\pi m_d T} \langle |\Delta_d|^2 \rangle \psi^{(1)} \left(\frac{1}{2} + \rho + \frac{1}{4\pi T \tau_{ds}} \right) \\
 &= - \frac{1}{4\pi} \frac{H_{c2}(T) - H}{\left[2K_2^2(t) - 1 \right] \beta_A}, \quad H < H_{c2}(T) \dots (3.35)
 \end{aligned}$$

where $K_2(t)$ is the second Landau-Ginzburg parameter with t denoting T/T_c and $\beta_A = 1.16$.

Using eq.(3.35) and including also the heat

current due to the magnetization current ($= -H \vec{J}_d^M = -HM_d \frac{E}{H} = -M_d E$) associated with Vortex motion (87) we finally get the following expression for heat current density;

$$\langle J_{d2y}^h \rangle = \frac{E \sigma_d D_d H_{c2} 4K_1^2(o)}{(2K_2^2(t) - 1) \beta_A} \left(1 - \frac{H}{H_{c2}}\right) \left[Z(t) \left(1 + \frac{1}{\epsilon_{do} \tau_{ds}}\right) - 1 \right] \dots (3.36)$$

Here we have used the relation

$$(4\pi\sigma_d D_d)^{-1} = 4K_1^2(o)$$

where $K_1(t)$ is the first Ginzburg-Landau parameter.

B. Transport Equations in Resistive State

The ratio of the heat and electric current (80) is given by

$$\frac{\langle J_{d2y}^h \rangle}{\langle J_{d2x} \rangle} = -D_d H_{c2} \frac{1 - Z(t) \left(1 + \frac{1}{\epsilon_{do} \tau_{ds}}\right)}{1 - \frac{X(t)}{\epsilon_{do} \tau_{ds}}} \dots (337)$$

This result suggests that a temperature gradient (perpendicular to the magnetic field) produces the reciprocal effect (i.e., a heat current parallel to the temperature gradient and an electric current perpendicular to it), so that the complete set of transport equations is

$$J_{dy}^h = \alpha_d E - K_{sd} (\vec{\nabla} T)_y \dots (3.38)$$

$$J_{dx} = \sigma_{sd} E + \beta (\vec{\nabla} T)_y \dots (3.39)$$

with

$$\alpha_d = \frac{\sigma_d D_d H_{c2} 4K_1^2(o)}{e [2K_2^2(t) - 1] \beta_A} \left(1 - \frac{H}{H_{c2}}\right) \left[Z(t) \left(1 + \frac{1}{\epsilon_{do} \tau_{ds}}\right) - 1 \right] \dots (3.40)$$

and $\beta = \alpha_d / T$

Here, we have considered the normal value of α_d to be negligible as suggested by Caroli and Maki(84).

C Etingshausen Effect and Delivered Entropy

When an electric field is applied along the x direction, an electric current along the x axis and a finite temperature gradient along the y axis are induced and are given by

$$J_{dx} = \left[\sigma_{sd} + \alpha_d^2 / T K_{sd} \right] E , \dots (3.41)$$

and

$$(\vec{\nabla} T)_y = (\alpha_d / K_{sd}) E , \dots (3.42)$$

as

$$J_{dy}^h = 0 \dots (3.43)$$

Hence, we get from Eqs.(3.40) and (3.42)

$$\frac{(\vec{\nabla} T)_y}{E} = \frac{4\sigma_d D_d H_{c2} K_1^2(o)}{e K_{sd} [2K_2^2(t) - 1] \beta_A} \left(1 - \frac{H}{H_{c2}}\right) \left[Z(t) \left(1 + \frac{1}{\epsilon_{do} \tau_{ds}}\right) - 1 \right] \dots (3.44)$$

This equation might be interpreted by saying that each vortex line carries an amount of entropy, given by

$$S_d = - \frac{\pi K_{sd}}{eT} \frac{(\nabla T)_x}{E}$$

$$= - \frac{\sigma_d D_d H_{c2}}{e^2 T} \frac{4\pi K_1^2(o)}{[2K_2^2(t)-1] \beta_A} \left(1 - \frac{H}{H_{c2}}\right) \left[Z(t) \left(1 + \frac{1}{\epsilon_{do} \tau_{ds}}\right) - 1 \right]$$

... (3.45)

It should be noted here that this entropy vanishes at $H=H_{c2}$ (as it should be at a second-order phase transition).

D. Nernst Effect

This is just the reciprocal of the Ettingshausen effect. When a finite temperature gradient is applied along the y-axis, a heat current along the y axis and a finite electric field in the x direction are induced. These are given by

$$J_{dy}^h = [K_{sd} + \alpha_d^2 / T \sigma_{sd}] (-\nabla T)_y \quad \dots (3.46)$$

$$\text{and } E = (\alpha_d / T \sigma_{sd}) (\nabla T)_y \quad \dots (3.47)$$

We can rewrite Eq.(3.47) as

$$\frac{E_x}{(\nabla T)} \approx \frac{D_d H_{c2}(t) 4K_1^2(o)}{eT [2K_2^2(t)-1] \beta_A} \left(1 - \frac{H}{H_{c2}}\right) \left[Z(t) \left(1 + \frac{1}{\epsilon_{do} \tau_{ds}}\right) - 1 \right]$$

... (3.48)

E. Peltier Effect

The Peltier coefficient is given by

$$\pi_d = \frac{J_{dx}^h}{J_{dx}} \quad \dots (3.49)$$

Neglecting higher-order terms in η_d , we obtain with the help of Equations (3.20) and (3.31), the following expression for J_{dx}^h :

$$J_{dx}^h = \sigma_d \text{EST} \quad \dots (3.50)$$

Hence equations (3.49) and (3.50) combined with the following expression of Maki(80)

$$J_{dx} = \sigma_d E \left[1 - \frac{4K_1^2(o) [1 - H/H_{c2}(T)]}{[2K_2^2(t) - 1] \beta_A} \left(\frac{X(t)}{\epsilon_{do} \tau_{ds}} - 1 \right) \right] \quad \dots (3.51)$$

give the following expression for Peltier coefficient

$$\pi_d = ST \left[1 + \frac{4K_1^2(o) (1 - H/H_{c2})}{[2K_2^2(t) - 1] \beta_A} \left(\frac{X(t)}{\epsilon_{do} \tau_{ds}} - 1 \right) \right] \quad \dots (3.52)$$

where, $X(t) = -\rho \psi^{(2)} \left(\frac{1}{2} + \rho \right) / \psi^{(1)} \left(\frac{1}{2} + \rho \right) \quad \dots (3.53)$

III RESULTS

We can now apply the above results to Niobium for which $T_c = 9^\circ\text{K}$. The temperature region in which we are interested corresponds to $0.15 < t < 0.45$. At these temperatures, the maximum values of both $X(t)$ and $Z(t)$ will always be less than unity. Furthermore, the quantity $\epsilon_{do} \tau_{ds}$ can be explicitly written as $\frac{1}{3} \tau_{ds} \tau_{tr,d} v_{Fd}^2 H_{c2}^2(T)$. It has already been shown (85) that in the dirty limit, $H_{c2}(T)$ is independent of the density of impurities.

Further, one would expect that for a sufficiently dirty transition metal superconductor $\tau_{ds} \epsilon_{do} \ll 1$. Therefore, we note that as the magnetic field decreases from the upper critical field $H_{c_2}(T)$, the correction factor due to interband impurity scattering increases. This implies that the d-band thermomagnetic effects in dirty type-II transition metal superconductors show an anomalous increase, in the magnetic field region immediately below $H_{c_2}(T)$ and in the temperature region $T_{cs}^{(0)} < T < T_c$. The validity of all these results is limited to the high field region, just as in the case of the one-band Caroli-Maki theory(84).

IV CONCLUDING REMARKS

We have shown that it is chiefly the interband impurity scattering (corresponding to interband impurity scattering relaxation time τ_{ds}) which causes the anomalous increase in the thermomagnetic effects immediately below H_{c_2} in dirty type-II Transition metal superconductors. It leads to the general conclusion that the influence of s-band electrons on the transport properties of the d-band electrons is through interband impurity scattering.

We should like to emphasize that this behaviour in d-band thermomagnetic effects of dirty two-band transition

metal superconductors is quite similar in nature to the d-band Hall angle(80). Moreover, for dirty one-d-band superconductor, our results exactly reduce to those of Caroli et al.(84).

At present, no experimental information seems to be available on the measurements of these effects in dirty two-band transition metal superconductors below H_{c2} and in the temperature region $T_{cs}^{(0)} < T < T_c$. It is hoped that the experimental information would be forthcoming in the near future, to make it possible to check the results presented here.

CHAPTER IV

EFFECT OF PARAMAGNETIC IMPURITIES ON JOSEPHSON
CURRENT THROUGH A SUPERCONDUCTOR-NORMAL
METAL-SUPERCONDUCTOR JUNCTION

I INTRODUCTION

Since the discovery of the famous Josephson effect (88), the supercurrent due to Cooper pair tunneling through superconductor-insulator-superconductor (SIS) junctions has been widely studied both theoretically and experimentally. However, much of the theoretical and experimental work done in this direction pertains to junctions with insulating barriers, and there exist standard techniques, like the Green's function approach (89) and the tunneling Hamiltonian method (88,90), for theoretical study of these junctions. However, not much attention has been given to the theoretical study of the junctions with normal-metal barriers. In such junctions, the usual technique of treating the tunneling Hamiltonian as a small perturbation can not be applied for the following reasons:

- (1) In the thin-barrier limit, the proximity effects play the dominant role which makes the effective tunneling matrix elements too large to be regarded as a small perturbation.

(2) In the thick barrier limit, the normal barrier offers by itself a bulky region for the electronic motion, which cannot be described by the naive tunneling Hamiltonian.

One must thus adopt the Green's-function technique Ishii(91) has recently applied this technique and determined ~~the one~~ particle Green's function for pure superconductor-normal metal-superconductor (SNS) junctions in the thick-barrier limit. Choosing a simple model for the junction (92), he calculated the dc Josephson current at $T = 0^{\circ}\text{K}$, using the Green's functions for the superconducting and normal regions.

Ishii does not take into account the effect of impurity scattering in either barrier or superconducting regions. The object of the present study is to investigate the effect of paramagnetic impurities in the barrier and superconducting regions on Josephson current through junction with normal metal barriers, using both the Abrikosov-Gorkov model(18) and Shiba-Rusinov model(23,24). (An outline of these models has already been given in Sec.IV of Chapter I). For simplicity, we shall restrict ourselves to the case of zero temperature, since all fundamental properties of the Josephson effect are already included in this case. Furthermore, we shall consider the potential difference V between the superconductors to be zero, i.e. we are concerned only with the dc Josephson effect. Interest in the study of the effect

of paramagnetic impurities is linked with the circumstance (as shown by Abrikosov and Gorkov(18)) that while the energy gap ω_g in the spectrum of single-particle states vanishes in superconductors in such cases, the ordering parameter is nonzero, i.e., the metal still remains a superconductor.

In Section II an analytical treatment is given for the calculation of Josephson current through impure SNS junctions, taking the renormalized Green's function for both the barrier and superconducting region. In Section IIA and IIB, we have used the renormalized Green's functions given by Abrikosov-Gorkov(18) and Shiba-Rusinov(23,24), respectively, to treat the effect of paramagnetic impurities on Josephson current. This is followed by a discussion of results in Section III.

II ANALYTICAL TREATMENT

The supercurrent through the junction is calculated from the following expression derived by Josephson(89):

$$j = 2ie \frac{L_{11}^2}{(2\pi)^2} \int d^2 k_{11} \left(\int_{x \in V_1} dx \int_{x' \in V_2} dx' - \int_{x \in V_2} dx \int_{x' \in V_1} dx' \right) \\ \times T \sum_{\omega_n} G_{i\omega_n}^{(1,1)S'S} (x, x') e_{jN, i\omega_n}^{(2,2)} (x, x') \Delta^*(x) \Delta(x') \dots (4.1)$$

where the regions V_1 and V_2 simply stand for the two superconducting regions S and S' and L_{11} denotes the

linear dimensions of the junction in the y or z direction.

The expressions, derived by Ishii(91) for the (1,1) component of $G^{S'S}(x,x')$ and the (2,2) component of $C_{N,i\omega_n}^N(x,x')$, for the case of pure-SNS junction, are

$$G_{i\omega_n, k_{11}}^{(1,1)S'S}(x,x') = \sum_{\sigma} \tilde{G}_{i\omega_n, k_{11}}^{\sigma} \exp(i\sigma k^{\sigma} |x-d| + i\sigma k^{\sigma} |x'+d|),$$

$$\tilde{G}_{i\omega_n, k_{11}}^{\sigma}(s',s) = d_s 2i\Omega_n \frac{i\omega_n + i\sigma\Omega_n}{i\omega_n + i\Omega_n} \exp(2i\sigma K^{\sigma} d) X_{\sigma}(\phi) \times \begin{cases} 1 & , \sigma=+ \\ e^{2\phi} & , \sigma=- \end{cases}$$

... (4.2)

where,

$$k^{\sigma} = \text{sgn } \omega_n \left[2n(\mu_{Fx} + i\sigma\Omega_n) \right]^{1/2}, \quad \text{Im } k^{\pm} > 0$$

$$i\Omega_n = \left[(i\omega_n)^2 - (\Delta)^2 \right]^{1/2},$$

$$K^{\sigma} = \text{sgn } \omega_n \left[2n(\mu_{Fx} + i\sigma\omega_n) \right]^{1/2}, \quad \text{Im } K^{\pm} > 0$$

$$d_s^{\sigma} = - \frac{n}{2\Omega_n k^{\sigma}}$$

$$X_{\sigma}(\phi) = \left[1 - \frac{i\omega_n - i\Omega_n}{i\omega_n + i\Omega_n} \exp\left(-\frac{4|\omega_n|d}{v_{Fx}} + i\sigma\phi\right) \right]^{-1}, \dots (4.3)$$

with $2d$ being the thickness of the barrier, ϕ the phase difference between the two superconductors, and

$$C_{N,i\omega_n}^{(2,2)}(x,x') = d_N \exp(-iK^- |x-x'|) \quad \dots (4.4)$$

with

$$d_N^\sigma = \frac{n}{iK^\sigma}$$

Using the Green's functions given by eqs.(4.2) and (4.4), the final expression for the current through pure-SNS junction at absolute zero temperature is given by [91].

$$j_{T=0}^{\text{pure SNS}}(\phi) = \sum_{n=1}^{\infty} j_n^{\text{pure SNS}(T=0)} \left(\frac{2d}{\xi}\right) \sin n\phi \dots (4.5)$$

where $\xi = v_F/\pi\Delta$ (v_F is the Fermi velocity and Δ is the energy gap for a pure superconductor) and the coefficient j_n (which is a function of the thickness of N layer scaled by the coherence length of the pure bulk S or S' metal) is given by

$$j_n^{\text{pure SNS}}\left(\frac{2d}{\xi}\right) = 2ie \frac{L_{11}^2}{(2\pi)^2} (-4ik_F^2) \int_0^1 d \cos\theta \tilde{j}_n^{\text{pure SNS}}(\cos\theta) \dots (4.6)$$

θ is defined by $v_{Fx} = v_F \cos\theta$ and

$$\tilde{j}_n^{\text{pure SNS}}(\cos\theta) = \int_0^\infty d\omega \left[\frac{\omega - (\omega^2 + \Delta^2)^{1/2}}{\omega + (\omega^2 + \Delta^2)^{1/2}} \exp\left(-\frac{2d}{\xi} \frac{\omega}{\Delta} \frac{1}{\cos\theta}\right) \right]^n \dots (4.7)$$

Now, in the presence of random distribution of impurity atoms, the Green's function gets renormalized (18,23,24) and the renormalized Green's functions (describing the electrons in the presence of randomly distributed impurities) are obtained in a simple manner by replacing ω and Δ in Eqs.(4.2) and (4.4) by their renormalized values

i.e., $\tilde{\omega}$ and $\tilde{\Delta}$, respectively. [The renormalized values $\tilde{\omega}$ and $\tilde{\Delta}$ are different in different models and depend on the types of impurities as we shall see in this chapter and later in the next chapter]. We thus obtain

$$\begin{aligned} \tilde{G}_{i\tilde{\omega}_n, k_{11}}^{(1,1)S'S} (x, x') &= \sum_{\sigma} \tilde{G}_{i\tilde{\omega}_n, k_{11}}^{\sigma(S'S)} \exp(i\sigma\tilde{k}^{\sigma}|x-d| + i\sigma\tilde{k}^{\sigma}|x'+d|), \\ \tilde{G}_{i\tilde{\omega}_n, k_{11}}^{\sigma(S'S)} &= \tilde{d}_s 2i\tilde{\omega}_n \frac{i\tilde{\omega}_n + i\sigma\tilde{\omega}_n}{i\tilde{\omega}_n + i\tilde{\omega}_n} \exp(2i\sigma\tilde{K}^{\sigma}d) \tilde{X}_{\sigma}(\emptyset) \times \begin{cases} 1 & , \sigma = + \\ e^{i\emptyset} & , \sigma = - \end{cases} \\ &\dots (4.8) \end{aligned}$$

where \tilde{k}^{σ} , $\tilde{\omega}_n$, \tilde{K}^{σ} , \tilde{d}_s , and $\tilde{X}_{\sigma}(\emptyset)$ will be given by an equation similar to (4.3) on replacing ω by $\tilde{\omega}$ and Δ by $\tilde{\Delta}$.

Similarly,

$$\tilde{G}_{N, i\tilde{\omega}_n}^{(2,2)} (x, x') = \tilde{d}_N^{\sigma} \exp(-i\tilde{K}^{-}|x-x'|), \quad \dots (4.9)$$

with

$$\tilde{d}_N^{\sigma} = m/i \tilde{K}^{\sigma}$$

Thus, analogously, the supercurrent through the impure-SNS junction is found to be given by

$$\begin{aligned} j^{\text{impure SNS}}(\emptyset) &= 2ie \frac{L_{11}^2}{(2\pi)^2} (-4ik_F^2) \sum_{n=1}^{\infty} \sin n\emptyset \int_0^1 d \cos\theta \\ &\times \tilde{j}_n^{\text{impure SNS}}(\cos\theta) \quad \dots (4.10) \end{aligned}$$

where,

$$J_n^{\text{impure SNS}}(\cos\theta) = \int_0^\infty d\omega \left[\frac{\tilde{\omega} - (\tilde{\omega}^2 + \tilde{\Delta}^2)^{1/2}}{\tilde{\omega} + (\tilde{\omega}^2 + \tilde{\Delta}^2)^{1/2}} \exp\left(-\frac{2d}{\xi} \frac{\tilde{\omega}}{\tilde{\Delta}} \frac{1}{\cos\theta}\right) \right]^n \dots (4.11)$$

(A) Abrikosov-Gorkov Model

We shall first apply the Abrikosov-Gorkov model to treat the effect of paramagnetic impurities on Josephson current through SNS junctions(94). Abrikosov and Gorkov(18) assumed the interaction between conduction electrons and magnetic impurities to be very weak and thus treated the exchange scattering in lowest order Born approximation. According to this theory (as shown in Section IV(i) of Chapter IA), in the presence of a random distribution of paramagnetic impurity atoms, the renormalized frequency $\tilde{\omega}$ and order parameter $\tilde{\Delta}$ of the renormalized Green's function are given by the following equations:

$$\tilde{\omega} = \omega + \frac{1}{2} \left(\frac{1}{\tau_1} + \frac{1}{\tau_2} \right) \frac{\tilde{\omega}}{(\tilde{\omega}^2 + \tilde{\Delta}^2)^{1/2}} \dots (4.12)$$

$$\tilde{\Delta} = \Delta + \frac{1}{2} \left(\frac{1}{\tau_1} - \frac{1}{\tau_2} \right) \frac{\tilde{\Delta}}{(\tilde{\omega}^2 + \tilde{\Delta}^2)^{1/2}}$$

where τ_1 and τ_2 are the two relaxation times corresponding to two types of scattering, without and with spin flip, respectively and are given by expression(1.42) of Chapter I. It is convenient here to introduce a new auxiliary parameter u defined by $u = \tilde{\omega}/\tilde{\Delta}$. In terms

of real frequencies , Eq.(4.12) then leads to (93)

$$\frac{\omega}{\Delta} = u(1-\zeta \frac{1}{(1-u^2)^{1/2}}) \quad \dots (4.13)$$

where,

$$\zeta = \frac{1}{\tau_2 \Delta} \quad \dots (4.14)$$

An important feature which follows from this relation is that ω increases as u increases. At $u = 1$, ω is negative and diverges. The maximum value of ω is in the region $0 < u < 1$.

In terms of the auxiliary parameter u , expression (4.11) now reduces to

$$\tilde{j}_n^{\text{impure SNS}}(\cos\theta) = \int_0^\infty d\omega \left[\frac{u-(1+u^2)^{1/2}}{u+(1+u^2)^{1/2}} \exp(-\frac{2d}{\xi} \frac{u}{\cos\theta}) \right]^n \quad \dots (4.15)$$

Putting $u = \sinh \alpha$, Eq.(4.15) reduces to

$$\tilde{j}_n^{\text{impure SNS}}(\cos\theta) = (-)^n \int_0^\infty d\omega \exp(-2n\alpha - n\frac{2d}{\xi} \frac{\sinh\alpha}{\cos\theta}) \quad \dots (4.16)$$

The integral over ω can be transformed into an integral over α with the help of the following equation,

$$\frac{\omega}{\Delta} = \sinh\alpha(1-\zeta \frac{1}{(1-\sinh^2\alpha)^{1/2}}) \quad \dots (4.17)$$

Remembering that $u^2 (= \sinh^2\alpha) \ll 1$, the transformation equation (4.17) after a simple calculation gives

$$d\omega = d\alpha \left[\cosh\alpha - \zeta \left(\frac{3}{8} \cosh 3\alpha + \frac{5}{8} \cosh\alpha \right) \right] \quad \dots (4.18)$$

Substituting Eq.(4.18) into Eq.(4.16) we have

$$\begin{aligned}
 \tilde{j}_n^{\text{impure SNS}}(\cos\theta) &\equiv \Delta(-)^n \int_0^\infty d\alpha \left[\cosh\alpha - \zeta \left(\frac{3}{8} \cosh 3\alpha + \frac{5}{8} \cosh\alpha \right) \right] \\
 &\quad \times \exp\left(-2n\alpha - n \frac{2d}{\xi} \frac{\sinh\alpha}{\cos\theta}\right) \\
 &= \Delta(-)^n \left\{ \frac{1}{2} \left[B_{2n+1}\left(n \frac{2d}{\xi \cos\theta}\right) + B_{2n-1}\left(n \frac{2d}{\xi \cos\theta}\right) \right] \right. \\
 &\quad \left. - \zeta \frac{3}{16} \left[B_{2n+3}\left(n \frac{2d}{\xi \cos\theta}\right) + B_{2n-3}\left(n \frac{2d}{\xi \cos\theta}\right) \right] \right. \\
 &\quad \left. - \zeta \frac{5}{16} \left[B_{2n+1}\left(n \frac{2d}{\xi \cos\theta}\right) + B_{2n-1}\left(n \frac{2d}{\xi \cos\theta}\right) \right] \right\} \dots (4.19)
 \end{aligned}$$

The function $B_m(Z)$ given by

$$B_m(Z) \equiv \int_0^\infty d\alpha \exp(-m\alpha - Z \sinh\alpha) \dots (4.20)$$

is the associated Bessel function and has asymptotic form(95)

$$B_m(Z) \simeq \frac{1}{Z} - \frac{m}{Z^2} + \dots, \quad |Z| \rightarrow \infty \dots (4.21)$$

Using this we find the following expression for

$\tilde{j}_n^{\text{impure SNS}}(\cos\theta)$:

$$\tilde{j}_n^{\text{impure SNS}}(\cos\theta) \sim \Delta \frac{(-)^n}{n} \left[\left(\frac{\xi}{2d} \right) \cos\theta - 2 \left(\frac{\xi}{2d} \right)^2 \cos^2\theta \right] (1-\zeta) \dots (4.22)$$

Finally the expression for the total supercurrent through the impure-SNS junction, is obtained with the help of Eq.(4.10) and we get:

$$j^{\text{impure SNS}}(\phi) = -(2ev_F) \left(\frac{mk_F}{2\pi} \right) \Delta \left[\frac{1}{2} \left(\frac{\xi}{2d} \right) - \frac{2}{3} \left(\frac{\xi}{2d} \right)^2 \right] (1-\zeta) S(\phi) \quad \dots (4.23)$$

where,

$$S(\phi) = 2 \sum_{n=1}^{\infty} (-)^{n+1} \frac{\sin n\phi}{n} \quad \dots (4.24)$$

We recall that for pure SNS junction, Ishii (91) has derived the following expression:

$$j^{\text{pure SNS}}(\phi) = -(2ev_F) \left(\frac{mk_F}{2\pi} \right) \Delta \left[\frac{1}{2} \left(\frac{\xi}{2d} \right) - \frac{2}{3} \left(\frac{\xi}{2d} \right)^2 \right] S(\phi) \quad \dots (4.25)$$

Eqs.(4.23) and (4.25) combine to give finally the simple result

$$\frac{j^{\text{impure SNS}}(\phi)}{j^{\text{pure SNS}}(\phi)} = 1-\zeta \quad \dots (4.26)$$

which is valid for all values of ζ .

B. Shiba-Rusinov Model

In the preceding section, the effect of paramagnetic impurities was discussed within the framework of the Abrikosov-Gorkov model (18). We shall now study in this section the effect of paramagnetic impurities on Josephson current through SNS junction using the Shiba-Rusinov model(96). Shiba (23) and Rusinov(24) have generalized the AG theory assuming that the interaction of the conduction electrons with the magnetic impurities

is strong and thus treated the exchange scattering beyond the Born approximation but in a simpler classical spin case.

The Josephson current through impure SNS junction is to be calculated with the help of equations (4.15) and (4.10). The auxiliary parameter in this model (i.e. the ratio of renormalized frequency $\tilde{\omega}$ and the renormalized order parameter $\tilde{\Delta}$) is now given by the following equation

$$\frac{\omega}{\Delta} = u \left[1 - \zeta (1 - u^2)^{1/2} (\epsilon_0^2 - u^2)^{-1} \right] \dots (4.27)$$

$$\text{with } \zeta = \frac{1}{\tau_2 \Delta} = C_1 \left[2\pi N(0) \Delta \right]^{-1} (1 - \epsilon_0^2) \text{ and } \epsilon_0 = \cos(\delta_0^+ - \delta_0^-) \dots (4.28)$$

All other parameters are the same as defined in Chapter I.

Putting again $u = \sinh \alpha$ in equations (4.15) and (4.27), we get,

$$\tilde{j}_n^{\text{impure SNS}}(\cos\theta) = (-)^n \int_0^\infty d\omega \exp(-2n\alpha - n \frac{2d}{\xi} \frac{\sinh\alpha}{\cos\theta}) \dots (4.29)$$

and

$$\frac{\omega}{\Delta} = \sinh\alpha \left[1 - \zeta (1 - \sinh^2 \alpha)^{1/2} (\epsilon_0^2 - \sinh^2 \alpha)^{-1} \right] \dots (4.30)$$

The integral over ω in eq.(4.29) can be transformed into an integral over α with the help of equation (4.30). Since $u^2 (= \sinh^2 \alpha) \ll 1$ and $\epsilon_0^2 \ll 1$, the

transformation equation after a simple calculation gives

$$dw = \Delta \left[\cosh \alpha - \left(\frac{\zeta}{\epsilon_0^2} - \frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{8\epsilon_0^6} \right) \cosh 2\alpha - \left(\frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{4\epsilon_0^6} \right) \cosh 4\alpha - \frac{\zeta}{8\epsilon_0^6} \cosh 6\alpha - \frac{\zeta}{4\epsilon_0^4} \right] d\alpha \dots (4.31)$$

Substituting eq.(4.30) into eq.(4.28), we have

$$\begin{aligned} \tilde{J}_n^{\text{impure SNS}}(\cos\theta) &= \Delta (-)^n \int_0^\infty d\alpha \left[\cosh \alpha - \left(\frac{\zeta}{\epsilon_0^2} - \frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{8\epsilon_0^6} \right) \cosh 2\alpha - \left(\frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{4\epsilon_0^6} \right) \cosh 4\alpha - \frac{\zeta}{8\epsilon_0^6} \cosh 6\alpha - \frac{\zeta}{4\epsilon_0^4} \right] \\ &\quad \times \exp\left(-2n\alpha - n \frac{2d}{\xi} \frac{\sinh \alpha}{\cos \theta}\right) \\ &= \Delta (-)^n \left\{ \frac{1}{2} \left[B_{2n+1} \left(n \frac{2d}{\xi \cos \theta} \right) + B_{2n-1} \left(n \frac{2d}{\xi \cos \theta} \right) \right] - \frac{1}{2} \left(\frac{\zeta}{\epsilon_0^2} - \frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{8\epsilon_0^6} \right) \left[B_{2n+2} \left(n \frac{2d}{\xi \cos \theta} \right) + B_{2n-2} \left(n \frac{2d}{\xi \cos \theta} \right) \right] - \frac{1}{2} \left(\frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{4\epsilon_0^6} \right) \left[B_{2n+4} \left(n \frac{2d}{\xi \cos \theta} \right) + B_{2n-4} \left(n \frac{2d}{\xi \cos \theta} \right) \right] - \frac{1}{2} \frac{\zeta}{8\epsilon_0^6} \left[B_{2n+6} \left(n \frac{2d}{\xi \cos \theta} \right) + B_{2n-6} \left(n \frac{2d}{\xi \cos \theta} \right) \right] - \frac{\zeta}{4\epsilon_0^4} B_{2n} \left(n \frac{2d}{\xi \cos \theta} \right) \right\} \dots (4.32) \end{aligned}$$

$B_m(Z)$ is again the associated Bessel function defined

by equation (4.19). Using the asymptotic expansion given by eq.(4.20) we get

$$\begin{aligned} \tilde{j}_n^{\text{impure SNS}}(\cos\theta) \simeq \Delta \frac{(-)^n}{n} \left[\left(\frac{\xi}{2d}\right) \cos\theta - 2\left(\frac{\xi}{2d}\right)^2 \cos^2\theta \right] \\ \times \left[1 - \zeta \left(\frac{1}{\epsilon_0^2} + \frac{1}{4\epsilon_0^4} - \frac{1}{4\epsilon_0^6} \right) \right] \\ \dots (4.33) \end{aligned}$$

From eq.(4.33) and eq.(4.10), we finally obtain the following expression for the total supercurrent through impure SNS junction:

$$\begin{aligned} j^{\text{impure SNS}}(\phi) = -2ev_F \left(\frac{mk_F}{2\pi^2} \right) \Delta \left[\frac{1}{2} \left(\frac{\xi}{2d} \right) - \frac{2}{3} \left(\frac{\xi}{2d} \right)^2 \right] \\ \times \left[1 - \zeta \left(\frac{1}{\epsilon_0^2} + \frac{1}{4\epsilon_0^4} - \frac{1}{4\epsilon_0^6} \right) \right] S(\phi) \\ \dots (4.34) \end{aligned}$$

where $S(\phi)$ is given by eq.(4.24).

Combining eq.(4.34) and eq.(4.25) for the pure SNS junction we get

$$\frac{j^{\text{impure SNS}}(\phi)}{j^{\text{pure SNS}}(\phi)} = \left[1 - \zeta \left(\frac{1}{\epsilon_0^2} + \frac{1}{4\epsilon_0^4} - \frac{1}{4\epsilon_0^6} \right) \right] \dots (4.35)$$

III RESULTS AND DISCUSSION

(A) Results in Abrikosov-Gorkov Model

The important features which emerge using Abrikosov-Gorkov Model, are the following

- (i) It is obvious from eq.(4.26) that the barrier supercurrent through the impure-SNS junction is nonzero and positive for $\zeta < 1$ (low concentration of impurities) and decreases with the increase in impurity concentration.
- (ii) In the gapless region ($\omega_g=0$) when $\zeta \gg 1$, the current becomes zero at $\zeta = 1$ and becomes negative as ζ is further increased.
- (iii) For $\zeta = 0$, we get the result, derived by Ishii(91) for the pure-SNS junctions.
- (iv) For purely diamagnetic impurities, having no localized magnetic moments, there will be no spin-flip scattering of electrons by the impurities, i.e., $\tau_2=\infty$. It then follows from eq.(4.13) that $u = \omega/\Delta$, implying that the frequency and order parameter will not be renormalized. In other words, the Green's functions will be the same as in the absence of impurities. As a result, the diamagnetic impurities have no effect on the magnitude of Josephson currents through junctions with normal-metal barriers.

We may here refer to a parallel work done by
by Kulik(97) on the effects of paramagnetic impurities on

SIS-junction supercurrents who obtained the following relation:

$$\frac{j_{\text{SIS}}^{\text{impure}}}{j_{\text{SIS}}^{\text{pure}}} = \begin{cases} 1 - \frac{4}{3\pi} \zeta & ; \quad \zeta < 1 \\ 1 - \frac{4}{3\pi} \zeta - \frac{4}{3\pi} \zeta \left(\frac{1}{2} (1 - \zeta^{-2}) \right)^{3/2} - \frac{3}{2} (1 - \zeta^{-2})^{1/2} - \frac{2}{\pi} \tan^{-1} (\zeta^2 - 1)^{1/2} & ; \quad \zeta > 1 \end{cases} \quad \dots (4.36)$$

It is interesting to note the similarity between our result [Eq.(4.26)] and that of Kulik [Eq.(4.36)]. The only-difference is in the constant coefficient of ζ . Further, in the case of SIS junctions, the current becomes negative for $\zeta \geq 3\pi/4$. Thus, broadly speaking, the qualitative behaviour of the Josephson current through SNS and SIS junctions, in the presence of paramagnetic impurities, is similar in character.

(B). Results in Shiba-Rusinov Model

We may now draw some important conclusions from the calculations in Shiba-Rusinov Model.

It is evident from the Eq.(4.35) that when the conduction electron-magnetic impurity interaction is strong, $j^{\text{impure SNS}}(\phi)$ depends on two parameters ϵ_0 and ζ ; ϵ_0 is the renormalized position of the bound state inside the energy gap and ζ is the measure of impurity

concentration. Compared to the AG model, Josephson current through SNS junction is strongly affected when the impurity scatterings are treated in Shiba-Rusinov model.

It is important to notice that for $\epsilon_0 \rightarrow 1$ (i.e. when conduction electron-magnetic impurity interaction is weak) equation (4.35) reduces exactly to the result obtained in previous section in the framework of Abrikosov-Gorkov Model.

For $\zeta = 0$ this result (eq.4.35) again agrees exactly with that of Ishii (91) for pure case. The validity or otherwise of these studies has to await future experiments.

CHAPTER V

EFFECT OF LOCALIZED NONMAGNETIC TRANSITION
METAL IMPURITIES ON JOSEPHSON CURRENT
THROUGH SNS JUNCTION

I. INTRODUCTION

In the preceding chapter we had studied (94,96) the effect of paramagnetic impurities on dc Josephson current through SNS junction, using Abrikosov-Gorkov (18) and Shiba-Rusinov (23,24) theories. Very recently, Machida and Shibata (MS) (43) have studied the effect of resonance scattering due to localized nonmagnetic transition metal impurities on superconductivity, using Anderson model (33) in the superconductors with $U=0$ (as the inclusion of the Coulomb repulsion U does not affect the qualitative behaviour of final results (43)). A brief description of this theory has been given in Section V of Chapter IA. In this chapter we shall apply this theory to study the effect of resonance scattering due to localized nonmagnetic impurities on dc Josephson current through SNS junctions (98). The interest in the study of the effect of resonance scattering due to localized impurities arises from the fact that there appears a bound state inside the energy gap and the energy gap vanishes here too just as it does for the

paramagnetic impurities(18)

In Section II, the ratio of zero bias Josephson current through the impure SNS junction, to that of pure SNS junction, is calculated using MS theory (43). This is followed by a discussion of results in Section III.

II THEORETICAL ANALYSIS

It has been shown in earlier chapters that in the presence of impurities, the Green's function gets renormalized due to the renormalization of the frequency and the order parameter. The supercurrent through the impure SNS junction is to be calculated in a similar way using the expressions (4.15) and (4.10) of Chapter IV. As discussed in Section V of Chapter IA, Machida and Shibata have shown, that for a small concentration of localized nonmagnetic impurities (i.e., for $C \ll 1$ or $\zeta \ll 1$) the auxiliary parameter u ($= \tilde{\omega}/\tilde{\Delta}$) appearing in equation (4.15) is given by the following expression

$$\frac{\omega}{\Delta} = u \left(1 + \zeta \frac{1}{u^2 + 2 \sqrt{\left(\frac{u^2}{\sqrt{1-u^2}} \right) - \bar{\epsilon}^2}} \right) \dots (5.1)$$

where all other parameters are the same as defined by eq.(1.80) in Chapter I. It is important to note here that ω has got its maximum value only for values of u lying between 0 and 1 (43).

Putting $u = \sinh \alpha$, equations (4.15) and (5.1) simplify to the following:

$$\tilde{j}_n^{\text{impure SNS}}(\cos\theta) = (-)^n \int_0^\infty d\omega \exp(-2n\alpha - n \frac{2d}{\xi} \frac{\sinh\alpha}{\cos\theta}) \dots (5.2)$$

and

$$\frac{\omega}{\Delta} = \sinh \alpha \left(1 + \zeta \frac{1}{\sinh^2 \alpha + 2 \bar{\Gamma} \left(\frac{\sinh^2 \alpha}{1 - \sinh^2 \alpha} \right) - \bar{\epsilon}^{-2}} \right) \dots (5.3)$$

Now, the integral over ω can be transformed into an integral over α with the help of equation (5.3). Remembering that $u^2 (= \sinh^2 \alpha) \ll 1$, equation (5.3) after some straightforward and lengthy algebra gives

$$\begin{aligned} d\omega = \Delta \left[\cosh\alpha \left(1 - \frac{\zeta}{\bar{\epsilon}^2} + \frac{\zeta}{2\bar{\epsilon}^4} - \frac{\zeta}{4\bar{\epsilon}^6} + \frac{3}{4} \frac{\zeta}{\bar{\epsilon}^4} \bar{\Gamma} - \frac{1}{16} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma} \right. \right. \\ \left. \left. + \frac{7}{16} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma}^2 \right) \right. \\ \left. + \cosh 3\alpha \left(-\frac{1}{2} \frac{\zeta}{\bar{\epsilon}^4} + \frac{3}{4} \frac{\zeta}{\bar{\epsilon}^6} - \frac{5}{4} \frac{\zeta}{\bar{\epsilon}^4} \bar{\Gamma} + \frac{21}{16} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma} + \frac{1}{2} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma}^2 \right) \right. \\ \left. + \cosh 5\alpha \left(-\frac{1}{4} \frac{\zeta}{\bar{\epsilon}^6} - \frac{1}{4} \frac{\zeta}{\bar{\epsilon}^4} \bar{\Gamma} - \frac{1}{16} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma} + \frac{1}{4} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma}^2 \right) \right. \\ \left. + \cosh 7\alpha \left(-\frac{3}{16} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma} - \frac{5}{32} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma}^2 \right) \right. \\ \left. + \cosh 9\alpha \left(-\frac{1}{32} \frac{\zeta}{\bar{\epsilon}^6} \bar{\Gamma}^2 \right) \right] d\alpha \dots (5.4) \end{aligned}$$

Substituting eq.(5.4) into equation (5.2) and performing the integration over α , we get:

$$\begin{aligned}
 \tilde{j}_n^{\text{impure SNS}}(\cos\theta) \equiv \Delta(-)^n & \left[\frac{1}{2} \left(1 - \frac{\zeta}{\epsilon^2} + \frac{\zeta}{2\epsilon^4} - \frac{\zeta}{4\epsilon^6} + \frac{3}{4} \frac{\zeta}{\epsilon^4} \bar{\Gamma} \right. \right. \\
 & \left. \left. - \frac{1}{16} \frac{\zeta}{\epsilon^6} \bar{\Gamma} + \frac{7}{16} \frac{\zeta}{\epsilon^6} \bar{\Gamma}^2 \right) \left\{ B_{2n+1}(Z) + B_{2n-1}(Z) \right\} \right. \\
 & + \frac{1}{2} \left(-\frac{1}{2} \frac{\zeta}{\epsilon^4} + \frac{3}{4} \frac{\zeta}{\epsilon^6} - \frac{5}{4} \frac{\zeta}{\epsilon^4} \bar{\Gamma} + \frac{21}{16} \frac{\zeta}{\epsilon^6} \bar{\Gamma} \right. \\
 & \left. + \frac{1}{2} \frac{\zeta}{\epsilon^6} \bar{\Gamma}^2 \right) \left\{ B_{2n+3}(Z) + B_{2n-3}(Z) \right\} \\
 & + \frac{1}{2} \left(-\frac{1}{4} \frac{\zeta}{\epsilon^6} - \frac{1}{4} \frac{\zeta}{\epsilon^4} \bar{\Gamma} - \frac{1}{16} \frac{\zeta}{\epsilon^6} \bar{\Gamma} + \frac{1}{4} \frac{\zeta}{\epsilon^6} \bar{\Gamma}^2 \right) \\
 & \times \left\{ B_{2n+5}(Z) + B_{2n-5}(Z) \right\} \\
 & + \frac{1}{2} \left(-\frac{3}{16} \frac{\zeta}{\epsilon^6} \bar{\Gamma} - \frac{5}{32} \frac{\zeta}{\epsilon^6} \bar{\Gamma}^2 \right) \left\{ B_{2n+7}(Z) + B_{2n-7}(Z) \right\} \\
 & + \frac{1}{2} \left(-\frac{1}{32} \frac{\zeta}{\epsilon^6} \bar{\Gamma} \right) \left\{ B_{2n+9}(Z) + B_{2n-9}(Z) \right\} \\
 & \dots \quad (5.5)
 \end{aligned}$$

where $Z = (n 2d/\xi \cos\theta)$ and $B_m(Z)$ is the associated Bessel function defined by equation (4.19) of Chapter IV. Using the asymptotic form of $B_m(z)$ we get

$$\begin{aligned}
 \tilde{j}_n^{\text{impure SNS}}(\cos\theta) \simeq \frac{\Delta(-)^n}{n} & \left[\left(\frac{\xi}{2d} \right) \cos\theta - 2 \left(\frac{\xi}{2d} \right)^2 \cos^2\theta \right] \\
 & \times \left[1 + \zeta \left\{ \frac{1}{\epsilon^6} (\bar{\Gamma}^2 + \bar{\Gamma} + \frac{1}{4}) - \frac{3}{4} \frac{\bar{\Gamma}}{\epsilon^4} - \frac{1}{\epsilon^2} \right\} \right] \\
 & \dots \quad (5.6)
 \end{aligned}$$

Substituting eq.(5.6) into eq.(4.10) of Chapter IV, we finally get the following expression for the total supercurrent through impure SNS junction

$$j_{\text{impure SNS}}(\phi) = -(2ev_{\text{F}}) \left(\frac{mk_{\text{F}}}{2\pi^2} \right) \Delta \left[\frac{1}{2} \left(\frac{\xi}{2d} \right) - \frac{2}{3} \left(\frac{\xi}{2d} \right)^2 \right] S(\phi) \\ \times \left[1 + \zeta \left\{ \frac{1}{\bar{\epsilon}^6} (\bar{\Gamma}^2 + \bar{\Gamma} + \frac{1}{4}) - \frac{3}{4} \frac{\bar{\Gamma}}{\bar{\epsilon}^4} - \frac{1}{\bar{\epsilon}^2} \right\} \right] \dots (5.7)$$

where $S(\phi)$ is the same as given by eq.(4.24) in Chapter IV.

Thus, dividing eq.(5.7) with that of Ishii's expression (4.24) for $j_{\text{pure SNS}}(\phi)$ we finally obtain:

$$\frac{j_{\text{impure SNS}}(\phi)}{j_{\text{pure SNS}}(\phi)} = \left[1 + \zeta \left\{ \frac{1}{\bar{\epsilon}^6} (\bar{\Gamma}^2 + \bar{\Gamma} + \frac{1}{4}) - \frac{3}{4} \frac{\bar{\Gamma}}{\bar{\epsilon}^4} - \frac{1}{\bar{\epsilon}^2} \right\} \right] \dots (5.8)$$

III INTERPRETATION OF RESULTS

To interpret our results we note that for small concentration of impurities, $\zeta \ll 1$ and $\bar{\Gamma} \ll 1$. Further, it can be shown that the value of $\bar{\epsilon}^2$ will be far greater than unity(43) as the bound state or impurity band will be much nearer to the gap edge. Hence, it follows from equation (5.8) that Josephson current through SNS junction decreases with the increase in concentration of localized nonmagnetic transition metal impurities (i.e. Resonance scattering). This in fact is an expected feature since the density of states decreases with the increase in concentration of localized non-magnetic impurities. We wish to emphasize here that this behaviour is completely different from that of

nonlocalized nonmagnetic impurities, where the barrier supercurrent through SNS junction remains unaffected by the impurities (94) as has been seen in Chapter IV. Further, in the limit $\zeta = 0$ (i.e., pure case) our result agrees with Ishii (91) for pure SNS junctions. It should be remarked here that due to very less solubility of transition metals in nontransition ones, there seems to be no experimental information available at the moment for the verification of our results.

CHAPTER VI

FLUCTUATION ENHANCED DIAMAGNETIC SUSCEPTIBILITY
OF DIRTY SUPERCONDUCTING THIN FILMS
BELOW CRITICAL TEMPERATURE

I INTRODUCTION

The effect of thermodynamic fluctuations of superconducting order parameter on various physical properties of superconductors in different regions of temperature, has been the subject of active research in recent years (48,52,56,99-101). These fluctuations give divergent contributions to various properties like electrical conductivity, ultrasonic attenuation and diamagnetic susceptibility for $T > T_c$. It is found that for $T < T_c$, the contribution of the fluctuation to electrical conductivity is again divergent. In the present chapter, we study the effect of fluctuations on diamagnetic susceptibility of dirty superconducting thin films below T_c (102). The calculations have been done here within the framework of the phenomenological Ginzburg-Landau theory (discussed in Chapter IB), which not only yields the same results as the microscopic theory (103-105) but has the advantage of being a direct and more general approach. We have chosen here a dirty superconducting thin film since fluctuations show a prominent effect in dirty samples of lower dimensions (as is already mentioned in Chap.IB).

The fourth order term in GL free energy functional has been included following the Masker, Marcelja and Parks model (56).

Details of calculations for a dirty superconducting thin film are given in Section II. This is followed by a discussion of results in Section III.

II THEORETICAL FORMULATION

The phenomenological Ginzburg-Landau free energy functional is written as:

$$F_{GL}[\Psi(\vec{r})] = \int d^3r \left[\alpha |\Psi(\vec{r})|^2 + \frac{\beta}{2} |\Psi(\vec{r})|^4 + \frac{1}{2m} \left| \left(\frac{\hbar \nabla}{i} - \frac{2e}{c} \vec{A} \right) \Psi(\vec{r}) \right|^2 \right] \quad \dots (6.1)$$

The fourth order term has been included here to take into account the interaction between fluctuation modes below T_c , which becomes important as the density of fluctuation modes increases. The phenomenological constants appearing in equation (6.1) are given by (56):

$$\alpha = \frac{\hbar^2}{2m} \frac{1}{\xi_{GL}(0)^2} \frac{(T-T_c)}{T_c}; \quad \dots (6.2)$$

$$\beta = \frac{1.02 \hbar^2}{mN\lambda_{eff}}; \quad \dots (6.2)$$

with $\xi_{GL}(0)$ being GL coherence length of the dirty sample; N , the electron density; and λ_{eff} , the effective mean free path of the electrons.

If we now introduce

$$\underline{\Psi}(\vec{r}) = \sum_{\vec{k}} a_{\vec{k}} e^{i\vec{k} \cdot \vec{r}} \quad \dots (6.3)$$

then integration over \vec{r} in Eq.(6.1), for the case of a homogenous magnetic field yields:

$$F_{GL} = \sum_{\vec{k}, n} \left[\alpha + E(\vec{k}, n + \frac{1}{2}) \right] a_{\vec{k}}^{\dagger} a_{\vec{k}} + \frac{\beta}{2} \sum_{\vec{k}, \vec{k}', \vec{Q}} a_{\vec{k} + \vec{Q}}^{\dagger} a_{\vec{k}' - \vec{Q}}^{\dagger} a_{\vec{k}} a_{\vec{k}'} \quad \dots (6.4)$$

where, $E(\vec{k}, n + \frac{1}{2})$ is the energy of electron states, expressed as the sum of translational energy, together with the quantization energy of the **cyclotron** motion in the magnetic field, and is given by (106)

$$E(\vec{k}, n + \frac{1}{2}) = \frac{\hbar^2 k^2}{2m} + (n + \frac{1}{2}) \left(\frac{2e\hbar}{mc} \right) B \quad \dots (6.5)$$

with, $n = 0, 1, \dots$

In the language of second quantization, $a_{\vec{k}}^{\dagger}$, $a_{\vec{k}}$ may be regarded as creation and annihilation operators for the fluctuation modes. Since it is impossible to calculate the exact partition function when the fourth order term is in its original form, we resort to the approximation scheme as suggested by Masker et al(56). For any general state, described by the occupation number $n_{\vec{k}} (= a_{\vec{k}}^{\dagger} a_{\vec{k}})$, the expectation value of the fourth order term is (56):

$$\begin{aligned} & \left\langle \dots n_{\vec{k}_2} n_{\vec{k}_1} \left| \frac{\beta}{2} \sum_{\vec{k}, \vec{k}', \vec{Q}} a_{\vec{k} + \vec{Q}}^{\dagger} a_{\vec{k}' - \vec{Q}}^{\dagger} a_{\vec{k}} a_{\vec{k}'} \right| n_{\vec{k}_1} n_{\vec{k}_2} \dots \right\rangle \\ & = \beta \sum_{\vec{k}} n_{\vec{k}} \sum_{\vec{k}'} n_{\vec{k}'} \quad \dots (6.6) \end{aligned}$$

Here, we have now to make a Hartree-like approximation and replace the sum over $n_{\vec{k}}$ by its average value; thus

$$\sum_{\vec{k}'} n_{\vec{k}'}, \sum_{\vec{k}} n_{\vec{k}} \approx n \sum_{\vec{k}} n_{\vec{k}} = \langle |\Psi|^2 \rangle \sum_{\vec{k}} n_{\vec{k}} \quad \dots (6.7)$$

Equation (6.4) now gets simplified to the following form

$$F_{GL} = \sum_{\vec{k}} \left[\alpha + E(k, n + \frac{1}{2}) + \beta \langle |\Psi|^2 \rangle \right] n_{\vec{k}} \quad \dots (6.8)$$

If we write

$$n_{\vec{k}} = \sum_{q, n} |C(q, k, n)|^2 \quad \dots (6.9)$$

then $C(q, k, n)$ are to be considered as the expansion coefficients of $\Psi(\vec{r})$ with respect to the normalized eigen-functions of a particle in a magnetic field (106). Then eq. (6.8) takes the form:

$$F_{GL} = \sum_{q, k, n} |C(q, k, n)|^2 \left[\alpha + E(k, n + \frac{1}{2}) + \beta \langle |\Psi|^2 \rangle \right] \quad \dots (6.10)$$

Now, the Ginzburg-Landau free energy is $(-k_B T)$ times the logarithm of a restricted partition function in which the sum over states is restricted to those states of the whole system in which the order parameter takes on the values of a prescribed function $\Psi(\vec{r})$. Therefore, in order to obtain the unrestricted partition function,

we have to sum up $\exp\left[-F_{GL}/k_B T\right]$ over all possible $\Psi(\vec{r})$, i.e.,

$$Z = \int \prod_{q,k,n} d^2C(q,k,n) \exp\left(-\frac{F_{GL}}{k_B T}\right) = \prod_{k,n} \frac{\pi k_B T}{E(k, n+\frac{1}{2}) + \alpha + \beta \langle |\Psi|^2 \rangle}$$

The number of single particle states of energy $E(k, n+\frac{1}{2})$ is $eB/\pi\hbar C$ times the cross-section of the sample perpendicular to the magnetic field (106). Thus we obtain the following expression of free energy

$$\begin{aligned} F &= -k_B T \log Z \\ &= -V k_B T \frac{2eB}{\pi\hbar C} \int \frac{dk}{2\pi} \sum_{n=0}^{\infty} \log \frac{\pi k_B T}{E(k, n+\frac{1}{2}) + \alpha + \beta \langle |\Psi|^2 \rangle} \end{aligned} \quad \dots (6.12)$$

where V is the volume of the sample. Using Poisson's sum formula (106) we obtain the following expression for free energy:

$$\begin{aligned} F &= F^{(0)} - V \frac{k_B T e B}{\pi\hbar C} \sum_{s=1}^{\infty} \int \frac{dk}{2\pi} (-1)^s \\ &\quad \times \int_0^{\infty} dx \log \frac{\pi k_B T}{E(k, x) + \alpha + \beta \langle |\Psi|^2 \rangle} \cos 2\pi x s \end{aligned} \quad \dots (6.13)$$

where $F^{(0)}$ is the free energy in the absence of a magnetic field. The integration over x can be done by parts twice and in the limit of small magnetic field is approximately given by

$$\int_0^{\infty} dx \dots = \frac{2e\hbar B}{mC} \frac{1}{\frac{\hbar^2 k^2}{2m} + \alpha + \beta \langle |\Psi|^2 \rangle} \frac{1}{(2\pi s)^2} \dots \quad (6.14)$$

For a film of thickness d smaller than the coherence length and in a magnetic field \perp to the surface of the film (where the integral $\int dk/2\pi$ can be replaced by $1/d(k=0)$) we finally get

$$F = F^{(0)} + V \frac{k_B T}{48\pi^2 md} \left(\frac{eB}{C}\right)^2 \frac{1}{\alpha + \beta \langle |\Psi|^2 \rangle} \dots \quad (6.15)$$

It can be easily seen following Masker et al (56) that for a dirty thin film in a magnetic field

$$\alpha + \beta \langle |\Psi|^2 \rangle \approx k_B T \exp\left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{(\alpha - E(0, 0 + \frac{1}{2}))}{\beta}\right) \dots \quad (6.16)$$

Substituting expression (6.16) in eq.(6.15) we get finally the expression

$$F = F^{(0)} + V \frac{1}{48\pi^2 md} \left(\frac{eB}{C}\right)^2 \exp\left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{(E(0, 0 + \frac{1}{2}) - \alpha)}{\beta}\right) \dots \quad (6.17)$$

for the free energy.

The diamagnetic susceptibility is now easily calculated from the well known formula

$$\chi = - \frac{1}{V} \frac{\partial^2 F}{\partial B^2}$$

and we get

$$\chi = - \frac{1}{48\pi^2 md} \left[\frac{2e^2}{c^2} + \frac{4e^2}{c^2} \left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{e\hbar}{mC\beta} B \right) + \frac{e^2}{c^2} \left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{e\hbar B}{mC\beta} \right)^2 \right] \exp\left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{e\hbar}{mC\beta} B \right) \times \exp\left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{\hbar^2}{2m\beta\xi^2(o)} \frac{(T_c - T)}{T_c} \right) \dots (6.17)$$

The above expression can be rewritten as

$$\chi = -\chi_0 \exp\left[\lambda(T_c - T)\right] \dots (6.18)$$

where,

$$\chi_0 = \frac{1}{48\pi^2 md} \left[\frac{2e^2}{c^2} + \frac{4e^2}{c^2} \left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{e\hbar}{mC\beta} B \right) + \frac{e^2}{c^2} \left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{e\hbar B}{mC\beta} \right)^2 \right] \exp\left(\frac{2\pi\hbar^2 d}{mk_B T} \frac{e\hbar B}{mC\beta} \right) \dots (6.19)$$

and

$$\lambda = \frac{2\pi\hbar^2 d}{mk_B T} \frac{\hbar^2}{2m\beta\xi^2(o)} \dots (6.20)$$

It is evident from eq.(6.2), that both χ_0 and λ are positive and independent of $(T_c - T)$.

When the demagnetization effects, which are very important for a thin film in a perpendicular magnetic field (107), are included, the susceptibility χ' is given by $\chi = \chi' (1 + 4\pi\chi')^{-1}$ with χ defined by eq.(6.18).

Thus,

$$\chi' = - \frac{1}{\left[\frac{1}{\chi_0} \exp\left\{-\lambda(T_c - T)\right\} + 4\pi \right]} \dots (6.21)$$

The factor $\exp\left\{-\lambda(T_c - T)\right\} / \chi_0$ in the above equation

has been estimated for an aluminium film of thickness $d = 170 \text{ \AA}$ at $T = 1.0^\circ\text{K}$ and in a magnetic field of 50 Gauss. Its value was found to be $\approx 4.3 \times 10^{-12}$. At $T = 0^\circ\text{K}$, the diamagnetic susceptibility $\chi' = -\frac{1}{4\pi}$ while at $T = T_c$, it has got a finite value.

III RESULTS AND DISCUSSION

We find that the fluctuation enhanced diamagnetic susceptibility χ' increases with the decrease of temperature approaching $-1/4\pi$ at $T = 0^\circ\text{K}$ and remains finite at $T = T_c$. This behaviour of diamagnetic susceptibility (arising due to fluctuating Cooper pairs) is quite similar to the behaviour observed in fluctuation enhanced electrical conductivity of dirty superconducting thin films below T_c (56). Hence we conclude that fluctuations of order parameter give an appreciable contribution to the various properties of superconducting thin film below T_c .

CHAPTER VII

EFFECT OF FLUCTUATIONS ON DIAMAGNETIC SUSCEPTIBILITY
AND ELECTRICAL CONDUCTIVITY OF ZERO DIMENSIONAL
SUPERCONDUCTORS BELOW CRITICAL TEMPERATURE

I. INTRODUCTION

In the preceding chapter we had discussed the effect of fluctuations on diamagnetic susceptibility of a dirty superconducting thin film below T_c , using phenomenological Ginzburg Landau theory. In recent years, there has been great interest in studying the effect of fluctuation on various superconducting properties of very small dimensional superconductors both above and below T_c (108,109,110). For example, Parkinson(108) has calculated the specific heat of zero dimensional superconductors using Ginzburg Landau theory, and an exact thermal averaging procedure. In this chapter we extend this work and study the contribution of fluctuations to diamagnetic susceptibility(111) and electrical conductivity(112) of zero dimensional superconductors below critical temperature. Fluctuation enhanced diamagnetic susceptibility of zero dimensional superconductor has also been studied earlier(109) but with an altogether different and tedious functional integral method. In this particular case, the two approaches yield an identical behaviour. Details of

calculations have been given in section II. The results are discussed in Section III.

II. THEORETICAL FORMULATION

(i) Fluctuation Enhanced Diamagnetic Susceptibility

The usual Ginzburg-Landau free energy functional, in the presence of a magnetic field below T_c is given by Eq.(6.1) in Chapter VI. Fourier transforming eq.(6.1), one gets:

$$F_{GL} = \sum_{\vec{k}, n} (\alpha + E(\vec{k}, n + \frac{1}{2})) |\psi_{\vec{k}}|^2 + \frac{\beta'}{2} \sum' \psi_{\vec{k}_1}^* \psi_{\vec{k}_2}^* \psi_{\vec{k}_3} \psi_{\vec{k}_4} \dots \quad (7.1)$$

where $\beta' = \beta V^{-1}$ and $E(\vec{k}, n + \frac{1}{2})$, α and β are the same as given by Eqs. (6.5) and (6.2) in Chapter VI. Here, the prime on the summation implies that $\vec{k}_1 + \vec{k}_2 = \vec{k}_3 + \vec{k}_4$.

For a rectangular specimen of sides $\lambda_1, \lambda_2, \lambda_3$ the components \vec{k} are given as, for example, $k_x = \frac{2\pi n_1}{\lambda_1}$ where n_1 is any integer. Thus, for a zero dimensional sample (i.e., a sample of very small dimension), significant fluctuation effects will be prominent for $\vec{k}=0$ states only. Further, we presume that only $n=0$ Landau level will contribute to free energy on account of very small size (comparable to ξ_0 - the coherence length of the superconductor). Keeping all these facts in view, the expression (7.1) for Free Energy functional reduces to,

$$F_{GL}^{(0)} = \left(\alpha + \frac{e\hbar}{mC} B\right) x + \frac{1}{2}\beta' x^2 \quad \dots (7.2)$$

where,

$$x = |\psi_0|^2 \quad \dots (7.3)$$

Now, the average value of free energy is given by

$$\langle F_{GL}^{(0)} \rangle = \left(\alpha + \frac{e\hbar}{mC} B\right) \langle x \rangle + \frac{1}{2}\beta' \langle x^2 \rangle \quad \dots (7.4)$$

The average value of x can be calculated from eq.(7.2) by weighting the fluctuations with the free energy associated with them in the following usual way:

$$\langle x \rangle = \frac{\int_0^\infty x \exp \left\{ -F_{GL}^{(0)} / k_B T \right\} dx}{\int_0^\infty \exp \left\{ -F_{GL}^{(0)} / k_B T \right\} dx} \quad \dots (7.5)$$

Substituting Eq.(7.2) into Eq.(7.5) we have

$$\langle x \rangle = \frac{\int_0^\infty x \exp \left[\left\{ -\left(\alpha + \frac{e\hbar}{mC} B\right)x - \frac{1}{2}\beta' x^2 \right\} / k_B T \right] dx}{\int_0^\infty \exp \left[\left\{ -\left(\alpha + \frac{e\hbar}{mC} B\right)x - \frac{1}{2}\beta' x^2 \right\} / k_B T \right] dx} \quad \dots (7.6)$$

These integrals can be performed analytically very easily and in the limit of small magnetic field we obtain

$$\langle x \rangle = \frac{\left(\alpha + \frac{e\hbar}{mC} B\right)}{\beta'} \left[1 - \frac{\sqrt{k_B T \beta'} \exp \left[-\frac{1}{2} \left(\alpha^2 + \frac{2e\hbar}{mC} \alpha B\right) / k_B T \beta' \right]}{\left(\alpha + \frac{e\hbar}{mC} B\right) \sqrt{2\pi} F \left[-\frac{1}{\sqrt{k_B T \beta'}} \left(\alpha + \frac{e\hbar}{mC} B\right) \right]} \right] \quad \dots (7.7)$$

$\langle x^2 \rangle$ can similarly be calculated

and we obtain

$$\langle F_{GL}^{(0)} \rangle = \frac{1}{2} k_B T \left[\frac{(\alpha + \frac{e\hbar}{mC} B)}{\sqrt{2\pi k_B T \beta'}} \frac{\exp\left[-\frac{1}{2}(\alpha^2 + \frac{2e\hbar}{mC} \alpha B)/k_B T \beta'\right]}{F\left[-\frac{1}{\sqrt{k_B T \beta'}}(\alpha + \frac{e\hbar}{mC} B)\right]} - \frac{(\alpha^2 + \frac{2e\hbar}{mC} \alpha B)}{k_B T \beta'} + 1 \right] \dots (7.8)$$

where F stands for normal probability function and we have assumed that the magnetic field is small so that the second order terms may be neglected.

The total diamagnetic susceptibility is calculated from the formula

$$\chi_{total} = \chi V = - \frac{\partial^2 \langle F_{GL}^{(0)} \rangle}{\partial B^2} \dots (7.9)$$

where V is the volume of the sample.

Using equations (7.8) and (7.9), we finally obtain

$$\chi_{total} = -A \left[\frac{\exp(-C'B)}{F(-D-EB)} \left\{ C'^2 \left(\alpha + \frac{e\hbar}{mC} B \right) - \frac{2e\hbar}{mC} C' \right\} + \sqrt{\frac{2E}{\pi}} \frac{\exp\left[-(C'B + \frac{D^2}{2} + EBD)\right]}{F^2(-D-EB)} \times \left\{ \frac{e\hbar}{mC} - \left(\frac{ED}{2} + C' \right) \left(\alpha + \frac{e\hbar}{mC} B \right) \right\} + \frac{E^2}{\pi} \frac{\exp\left[-(C'B + D^2 + 2EBD)\right]}{F^3(-D-EB)} \left(\alpha + \frac{e\hbar}{mC} B \right) \right], \dots (7.10)$$

where,

$$A = \frac{1}{2\sqrt{2\pi}} \exp\left[-\frac{\alpha^2}{2k_B T \beta'}\right] \sqrt{\frac{k_B T}{\beta'}} \quad \dots (7.11)$$

$$C' = \frac{e\hbar\alpha}{mCk_B T \beta'} \quad \dots (7.12)$$

$$D = \frac{\alpha}{\sqrt{k_B T \beta'}} \quad \dots (7.13)$$

$$E = \frac{e\hbar}{mC\sqrt{k_B T \beta'}} \quad \dots (7.14)$$

We have estimated χ_{total} for an aluminium sample of volume $1.25 \times 10^{-16} \text{ cm}^3$ for different values of temperature below T_c ($T_c = 1.2^\circ \text{K}$ for Al) and in a magnetic field of 0.2 Gauss. The phenomenological constants α and β' are taken to be the same as in Ref.(108). A semi log plot of χ_{total} versus $(T - T_c)$ is shown in figure (7.1).

(ii) Fluctuation Enhanced Electrical Conductivity

We shall now calculate the effect of fluctuations on electrical conductivity of zero dimensional superconductor below T_c following again the same exact averaging procedure of Parkinson(108). It is easily seen from eq.(7.2) that in the absence of magnetic field, the Free Energy functional for a zero dimensional superconductor is given by

$$F_{GL}^{(0)} = \alpha |\psi_0|^2 + \frac{1}{2} \beta' |\psi_0|^4 \quad \dots (7.15)$$

Using the exact averaging procedure (108), the average value of $|\psi_0|^2$ is given by

$$\langle |\psi_0|^2 \rangle = -\frac{\alpha}{\beta'} \left(1 - \frac{1}{q} h(q)\right) \quad \dots (7.16)$$

where,

$$h(q) = \frac{\exp(-\frac{1}{2}q^2)}{\sqrt{2\pi} F(-q)} \quad \dots (7.17)$$

$$q = \frac{\alpha}{\sqrt{k_B T \beta'}},$$

and $F(-q)$ is the normal probability function.

The fluctuation enhanced electrical conductivity σ'_0 of zero-dimensional superconductor is given by the expression

$$\sigma'_0 = \frac{e^2}{m} n_0 \tau_0 \quad \dots (7.18)$$

where $n_0 = \langle |\psi_0|^2 \rangle$ and τ_0 is the relaxation time for the zero dimensional superconductor.

In order to calculate τ_0 we write the time dependent Ginzburg-Landau equation for the order parameter $\psi_0(X, t)$ as

$$\hbar\gamma \frac{\partial}{\partial t} \psi_0(x, t) = (\alpha + \beta \langle |\psi_0|^2 \rangle) \psi_0(x, t) \quad \dots (7.19)$$

where,

$\gamma \left[= \frac{\pi \hbar^2}{16 m k_B T \xi^2(0)} \right]$ has been calculated in Ref.(114).

Assuming the following functional form of $\psi_0(x, t)$

$$\psi_0(x, t) = \psi_0(x) e^{-t/\tau_0} \quad \dots (7.20)$$

we get for τ_0 , the expression

$$\tau_0 = \frac{\pi \hbar^3}{16 m k_B T \xi^2(0)} \frac{1}{\alpha + \beta \langle |\psi_0|^2 \rangle} \quad \dots (7.21)$$

Combining equations (7.16), (7.18) and (7.21) we obtain the desired expression for the fluctuation enhanced electrical conductivity of zero dimensional superconductor below T_c to be:

$$\sigma'_0 = \frac{\pi e^2 \hbar^3}{16 m^2 k_B T \xi^2(0)} \left[1 - \sqrt{2\pi} q F(-q) \exp\left(\frac{q^2}{2}\right) \right] \quad \dots (7.22)$$

III RESULTS AND DISCUSSION

The following interesting features emerge from the above two calculations:

(i) Diamagnetic Susceptibility

In this calculation, firstly, the fluctuation enhanced diamagnetic susceptibility χ_{total} has a finite value at $T=T_c$ and it increases exponentially as T decreases (as seen from Fig.7.1). This behaviour is qualitatively in agreement with the previous work of Takayama(109) who had obtained a similar behaviour using an altogether different technique viz. the functional integral method. A similar behaviour is also observed in both the bulk samples (115) and thin films(102). Secondly, it also seems that χ_{total} does not increase so sharply in the region farther away from T_c as it does in the vicinity of T_c .

(ii) Electrical Conductivity .

Similar to the case of χ_{total} , σ'_0 also increases sharply with the decrease of temperature below T_c exponentially and is proportional to $\exp\left[\frac{A}{T}(T_c-T)^2\right]$, where A is a constt. (Note that this particular contribution to σ'_0 dominates over the first contribution which is inversely proportional to T). This is reminiscent of the physical observation that the fluctuation shows pronounced effects in the physical superconducting properties when the dimensionality of the superconductor is lowered. For example, in one- and, two-dimensional

superconductors(56), σ' have the following dependence on $(T_c - T)$, namely, $\sigma' \propto -\epsilon^3$ and $\sigma' \propto \exp(-\epsilon T_c / \epsilon_c T)$ [ϵ_c is a sample-dependent parameter and $\epsilon = T - T_c / T_c$] respectively.

We have to await future experiments to check the validity of these calculations.

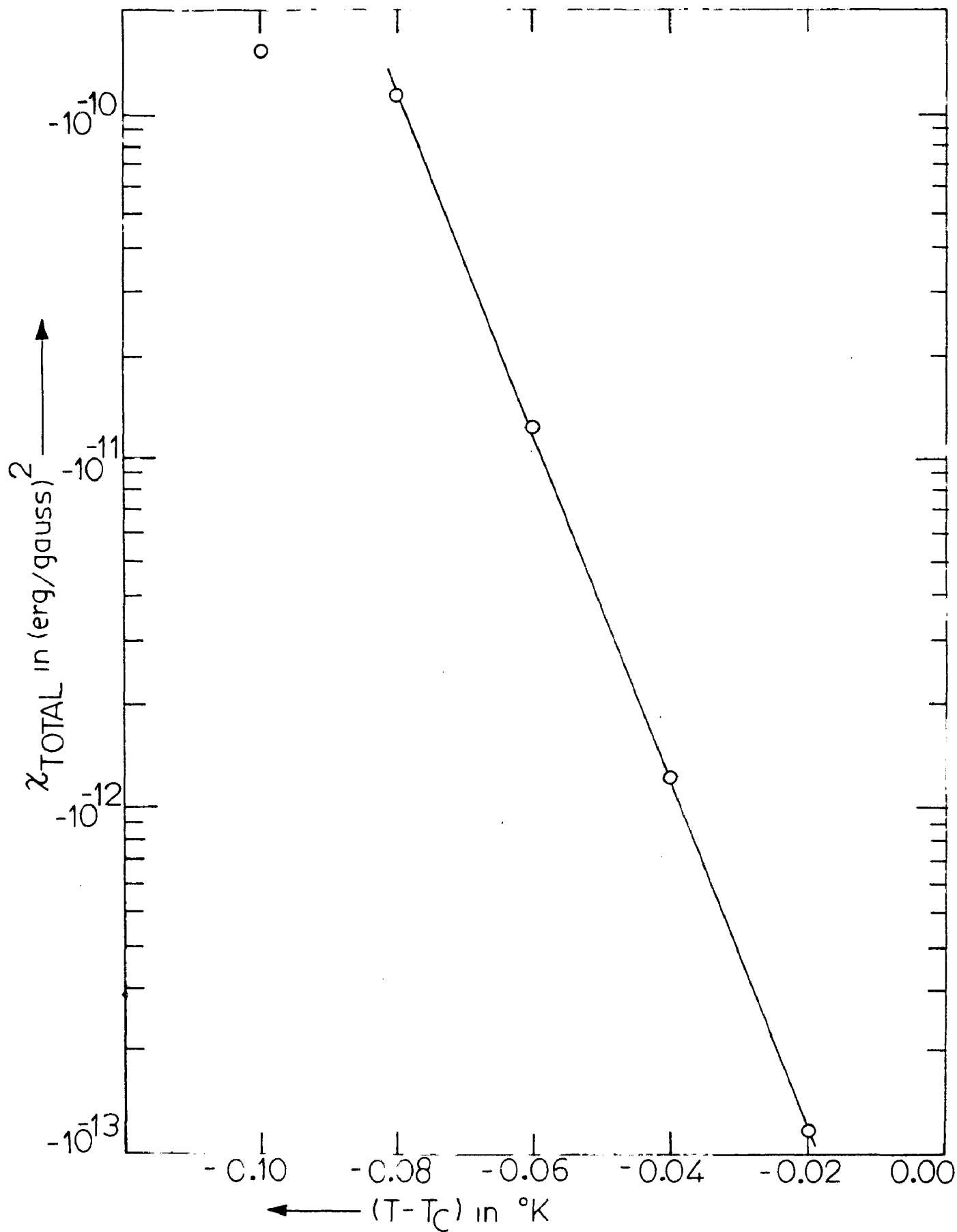


FIG.7.1- A Semi-log plot of χ_{total} versus $(T - T_C)$ for a small aluminium sample of volume $1.25 \times 10^{-16} \text{ cm}^3$.

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FLUCTUATION ENHANCED DIAMAGNETIC SUSCEPTIBILITY BELOW T_c

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The effect of fluctuating Cooper pairs on the diamagnetic susceptibility of dirty superconducting thin films is investigated, for temperature $T < T_c$. The susceptibility decreases with the decrease in temperature, approaching $-1/4\pi$ at $T = 0^\circ\text{K}$ and remains finite at $T = T_c$.

The effect of fluctuations of the order parameter on various physical properties of superconductors in different ranges of temperatures, has been the subject of active studies in recent years [1-6]. These fluctuations give divergent contributions to electrical conductivity, ultrasonic attenuation and diamagnetic susceptibility for $T > T_c$. For $T < T_c$, the contribution of the fluctuation to electrical conductivity is again divergent. The purpose of the present letter is to study theoretically the effect of fluctuations on the diamagnetic susceptibility below T_c , using the phenomenological approach as followed by Schmid [5].

The Ginzburg-Landau free energy functional is:

$$F_{\text{GL}}[\Psi(\mathbf{r})] = \int d^3r \left[\alpha |\Psi(\mathbf{r})|^2 + \frac{1}{2} \beta |\Psi(\mathbf{r})|^4 + \frac{1}{2m} \left| \left(\frac{\hbar \nabla}{i} - \frac{2e}{c} A \right) \Psi(\mathbf{r}) \right|^2 \right] \quad (1)$$

Here the fourth order term has been included to take into account the interaction between fluctuation modes below T_c and the phenomenological constants α and β are given by [6]:

$$\alpha = \frac{\hbar^2}{2m} \frac{1}{\xi_{\text{GL}}^2(0)} \frac{T - T_c}{T_c}, \quad \beta = \frac{1.02 \hbar^2}{mN l_{\text{eff}}} \quad (2)$$

with ξ_{GL} being GL coherence length; N the electron density and l_{eff} the effective mean free path of the electrons.

If we now introduce

$$\Psi(\mathbf{r}) = \sum_{\mathbf{k}} a_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (3)$$

then integration over \mathbf{r} in eq. (1), for the case of a homogeneous magnetic field yields:

$$F_{\text{GL}} = \sum_{\mathbf{k}, n} [\alpha + E(\mathbf{k}, n + \frac{1}{2})] a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \frac{\beta}{2} \sum_{\mathbf{k}, \mathbf{k}', Q} a_{\mathbf{k}+Q}^\dagger a_{\mathbf{k}'-Q}^\dagger a_{\mathbf{k}} a_{\mathbf{k}'} \quad (4)$$

where,

$$E(\mathbf{k}, n + \frac{1}{2}) = (\hbar^2 k^2 / 2m) + (n + \frac{1}{2}) (2e\hbar / mc) B \quad (5)$$

with $n = 0, 1, \dots$

In the language of second quantization, $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$ may be regarded as creation and annihilation operations for the fluctuation modes. For any general state described by the occupation number $n_{\mathbf{k}}$ ($= a_{\mathbf{k}}^\dagger a_{\mathbf{k}}$) the expectation value of the fourth order term is [6]:

$$\langle \dots n_{\mathbf{k}_2} n_{\mathbf{k}_1} \left| \frac{\beta}{2} \sum_{\mathbf{k}, \mathbf{k}', Q} a_{\mathbf{k}+Q}^\dagger a_{\mathbf{k}'-Q}^\dagger a_{\mathbf{k}} a_{\mathbf{k}'} \right| n_{\mathbf{k}_1} n_{\mathbf{k}_2} \dots \rangle = \beta \sum_{\mathbf{k}} n_{\mathbf{k}} \sum_{\mathbf{k}'} n_{\mathbf{k}'} \approx \beta n \sum_{\mathbf{k}} n_{\mathbf{k}} = \beta \langle |\Psi|^2 \rangle \sum_{\mathbf{k}} n_{\mathbf{k}} \quad (6)$$

Eq. (4) now gets simplified to the following form

$$F_{\text{GL}} = \sum_{\mathbf{k}} [\alpha + E(\mathbf{k}, n + \frac{1}{2}) + \beta \langle |\Psi|^2 \rangle] n_{\mathbf{k}} \quad (7)$$

If we write

$$n_{\mathbf{k}} = \sum_{q, n} |c(q, \mathbf{k}, n)|^2 \quad (8)$$

then $c(q, \mathbf{k}, n)$ are to be considered as the expansion coefficients of $\Psi(\mathbf{r})$ with respect to the normalised eigen-functions of a particle in a magnetic field [7] and eq. (7) becomes

$$F_{\text{GL}} = \sum_{q, \mathbf{k}, n} |c(q, \mathbf{k}, n)|^2 [\alpha + E(\mathbf{k}, n + \frac{1}{2}) + \beta \langle |\Psi|^2 \rangle] \quad (9)$$



The partition function is

$$Z = \prod_{q,k,n} \int d^2 c(q, k, n) \exp [-F_{GL}/k_B T]$$

$$= \prod_{q,k,n} \frac{\pi k_B T}{E(k, n + \frac{1}{2}) + \alpha + \beta \langle |\Psi|^2 \rangle} \quad (10)$$

The number of single particle states of energy $E(k, n + \frac{1}{2})$ is $eB/\pi\hbar c$ times the cross section of the sample perpendicular to the magnetic field [7]. Using Poisson's sum formula [7] we now obtain the following expression for the free energy;

$$F = -k_B T \ln Z = F^{(0)} - V \frac{k_B T eB}{\pi\hbar c} \sum_{s=1}^{\infty} \int \frac{dk}{2\pi} (-1)^s$$

$$\times \int_0^{\infty} dx \ln \frac{\pi k_B T \cos 2\pi xs}{E(k, x) + \alpha + \beta \langle |\Psi|^2 \rangle} \quad (11)$$

where $F^{(0)}$ is the free energy in the absence of a magnetic field. For a film of thickness d smaller than the coherence length and in a magnetic field perpendicular to the surface of the film, (where the integral $\int dk/2\pi$ can be replaced by $1/d$ ($k=0$)) we finally get

$$F = F^{(0)} + V \frac{k_B T}{48\pi^2 md} \left(\frac{eB}{c}\right)^2 \frac{1}{\alpha + \beta \langle |\Psi|^2 \rangle} \quad (12)$$

Now, for the dirty film in a magnetic field [6]

$$\alpha + \beta \langle |\Psi|^2 \rangle \approx k_B T \exp \left[\frac{2\pi\hbar^2 d}{mk_B T} \frac{\alpha - E(0, 0 + \frac{1}{2})}{\beta} \right] \quad (13)$$

Using $\chi = -(1/V) \partial^2 F / \partial B^2$, we get

$$\chi = - \frac{1}{48\pi^2 md}$$

$$\times \left[\frac{2e^2}{c^2} + \frac{4e^2}{c^2} \left\{ \frac{2\pi\hbar^2}{mk_B T} \frac{e\hbar B}{mc\beta} \right\} + \frac{e^2}{c^2} \left\{ \frac{2\pi\hbar^2}{mk_B T} \frac{e\hbar B}{mc\beta} \right\}^2 \right]$$

$$\times \exp \left\{ \frac{2\pi\hbar^2}{mk_B T} \frac{e\hbar B}{mc\beta} \right\} \cdot \exp \left\{ \frac{2\pi\hbar^2}{mk_B T} \frac{\hbar^2}{2m\beta\xi^2(0)} \frac{T_c - T}{T_c} \right\} \quad (14)$$

It now follows from eqs. (2) and (14) that

$$\chi = -\chi_0 \exp [\lambda (T_c - T)] \quad (15)$$

where χ_0 and λ are positive and independent of $(T_c - T)$.

When the demagnetisation effects, which are very important for a thin film in a perpendicular magnetic field [8] are included, the susceptibility χ' is given by $\chi = \chi' (1 + 4\pi\chi')^{-1}$ with χ defined by eq. (15). Thus,

$$\chi' = - \frac{1}{\chi_0} \exp \{-\lambda (T_c - T) + 4\pi\}^{-1} \quad (16)$$

The factor $\exp \{-\lambda (T_c - T)\} / \chi_0$ in above equation has been estimated for an aluminium film of thickness $d = 170 \text{ \AA}$ at $T = 1.0^\circ \text{K}$ and in a magnetic field of 50 gauss and is $\approx 4.3 \times 10^{-12}$. At $T = 0^\circ \text{K}$, the diamagnetic susceptibility $\chi' = -1/4\pi$.

Thus, the diamagnetic susceptibility χ' decreases with the decrease in temperature, approaching $-1/4\pi$ at $T = 0^\circ \text{K}$ and remains finite at $T = T_c$. However, an experimental check of our calculations must await future experiments as no such data is available at the moment.

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JOSEPHSON CURRENT THROUGH S-N-S JUNCTION CONTAINING PARAMAGNETIC IMPURITIES WITH LOCAL STATES WITHIN THE GAP

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The ratio of zero bias, zero temperature Josephson current through SNS (superconductor-normal metal-superconductor) junction containing paramagnetic impurities with local states within the gap, to that of the pure-SNS junction, is studied and found to be $1 - \xi [(1/\epsilon_0^2) + (1/4 \epsilon_0^4) - (1/4 \epsilon_0^6)]$, where ξ is a measure of impurity concentration and ϵ_0 is the normalized position of a local state within the gap.

In earlier paper [1], a study was made to investigate the effect of paramagnetic impurities on zero bias Josephson current through junctions with normal metal barriers at $T = 0^\circ\text{K}$, using Ishii [2] and Abrikosov-Gorkov theory [3]. However, Abrikosov and Gorkov have assumed a weak interaction between the conduction electrons and the magnetic impurities and thus treated the exchange scattering in the lowest order Born approximation. On the other hand, Shiba [4] and Risonov [5] have generalised the A-G theory assuming that the interaction of the conduction electrons with the magnetic impurities is strong, and show that an exact calculation leads to the appearance of local states within the gap. The object of the present paper is to generalize the result obtained in ref. [1] and we calculate the ratio of the zero temp, zero bias Josephson current through impure SNS junction containing paramagnetic impurities with local states within the gap, to that of pure SNS junction, using Shiba-Rusinov model.

For isotropic scattering, Rusinov Green's function of the superconducting alloy, averaged over the positions and spin directions of the impurities, is given by

$$\hat{G}(P, \omega) = [i \tilde{\omega} \rho_3 - \epsilon_p + i \tilde{\Delta} \rho_1 \sigma_3]^{-1} \quad (1)$$

where the renormalized frequency $\tilde{\omega}$ and the renormalized order parameter $\tilde{\Delta}$ for impure superconductor are related to that for the pure, through the following equation

$$\omega/\Delta = u [1 - \xi (1 - u^2)^{1/2} (\epsilon_0^2 - u^2)^{-1}] \quad (2)$$

with $u = \tilde{\omega}/\tilde{\Delta}$, $\xi = 1/\tau_2 \Delta = C_1 [2\pi N(0)\Delta]^{-1} (1 - \epsilon_0^2)$ and $\epsilon_0 = \cos(\delta_0^+ - \delta_0^-)$.

Here τ_2 is the time taken by an electron spin to flip during scattering, C_1 is the concentration of the impurities, δ_0^\pm are the phase shifts describing the scattering of an electron by the impurity with orbital momentum $l=0$ and spin projections $\pm \frac{1}{2}$ in normal metal, $N(0) = mp_F/2\pi^2$ (p_F is Fermi momentum) and ϵ_0 is the position of the bound state inside the gap arising due to the strong scattering of electrons by the magnetic impurity [6].

Following Ishii [2], it has been shown in ref. [1] that the total supercurrent through the impure SNS junction is given by

$$j_{T=0}^{\text{impure SNS}}(\phi) = 2ie \frac{L_{\parallel}^2}{(2\pi)^2} (-4ip_F^2) \sum_{n=1}^{\infty} \sin n\phi \int_0^1 d\cos\theta \int_0^{\infty} \tilde{j}_n^{\text{impure SNS}}(\cos\theta) d\omega \quad (3)$$

with

$$\tilde{j}_n^{\text{impure SNS}}(\cos\theta) = \int_0^{\infty} d\omega \left[\frac{u - (1+u^2)^{1/2}}{u - (1+u^2)^{1/2}} \exp\left(-\frac{2d}{\xi} \frac{u}{\cos\theta}\right) \right]^n \quad (4)$$

where ϕ , L_{\parallel} and ξ have been defined in ref. [2].

We shall now apply the Shiba-Rusinov model to calculate Josephson current through impure SNS junction with the help of eqs. (3), (4) and (2). Putting $u = \sinh \alpha$, eqs. (2) and (4) reduce to the following:

$$\tilde{j}_n^{\text{impure SNS}}(\cos\theta) = \int_0^\infty d\omega \exp\left(-2n\alpha - n \frac{2d \sinh \alpha}{\xi \cos\theta}\right) \quad (5)$$

$$\text{and } \omega/\Delta = \sinh \alpha [1 - \zeta(1 - \sinh^2 \alpha)^{1/2} (\epsilon_0^2 - \sinh^2 \alpha)^{-1}]. \quad (6)$$

The integral over ω in eq. (5) can be transformed into an integral over α with the help of eq. (6). Since $u^2 (= \sinh^2 \alpha) \ll 1$ and $\epsilon_0^2 < 1$, the transformation eq. after a simple calculation gives

$$\frac{d\omega}{d\alpha} = \Delta \left[\cosh \alpha - \left(\frac{\zeta}{\epsilon_0^2} - \frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{8\epsilon_0^6} \right) \cosh 2\alpha - \left(\frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{4\epsilon_0^6} \right) \cosh 4\alpha - \frac{\zeta}{8\epsilon_0^6} \cosh 6\alpha - \frac{\zeta}{4\epsilon_0^4} \right]. \quad (7)$$

Substituting eq. (7) into eq. (5), we have

$$\begin{aligned} \tilde{j}_n^{\text{impure SNS}}(\cos\theta) = \Delta (-)^n & \left\{ \frac{1}{2} \left[B_{2n+1} \left(n \frac{2d}{\xi \cos\theta} \right) + B_{2n-1} \left(n \frac{2d}{\xi \cos\theta} \right) \right] \right. \\ & - \frac{1}{2} \left(\frac{\zeta}{\epsilon_0^2} - \frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{8\epsilon_0^6} \right) \left[B_{2n+2} \left(n \frac{2d}{\xi \cos\theta} \right) + B_{2n-2} \left(n \frac{2d}{\xi \cos\theta} \right) \right] \\ & - \frac{1}{2} \left(\frac{\zeta}{2\epsilon_0^4} - \frac{\zeta}{4\epsilon_0^6} \right) \left[B_{2n+4} \left(n \frac{2d}{\xi \cos\theta} \right) + B_{2n-4} \left(n \frac{2d}{\xi \cos\theta} \right) \right] \\ & \left. - \frac{1}{2} \frac{\zeta}{8\epsilon_0^6} \left[B_{2n+6} \left(n \frac{2d}{\xi \cos\theta} \right) + B_{2n-6} \left(n \frac{2d}{\xi \cos\theta} \right) \right] - \frac{\zeta}{4\epsilon_0^4} B_{2n} \left(n \frac{2d}{\xi \cos\theta} \right) \right\}. \quad (8) \end{aligned}$$

$B_m(Z)$, the associated Bessel function, has the well known asymptotic behaviour

$$B_m(Z) \sim 1/Z - m/Z^2 + \dots, \quad |Z| \rightarrow \infty \quad (9)$$

Using eqs. (9), (8) and (3), we finally obtain the following expression for the total supercurrent through SNS junction

$$j^{\text{impure SNS}}(\phi) = -2ev_F (mp_F/2\pi^2) \Delta \left[\frac{1}{2} (\xi/2d) - \frac{2}{3} (\xi/2d)^2 \right] [1 - \zeta(1/\epsilon_0^2 + 1/4\epsilon_0^4 - 1/4\epsilon_0^6)] S(\phi) \quad (10)$$

where, $S(\phi) = 2 \sum_{n=1}^{\infty} (-1)^{n+1} \sin n\phi/n$. Combining eqs. (10) and Ishii's expression for $j^{\text{pure SNS}}(\phi)$

$$j^{\text{impure SNS}}(\phi)/j^{\text{pure SNS}}(\phi) = [1 - \zeta(1/\epsilon_0^2 + 1/4\epsilon_0^4 - 1/4\epsilon_0^6)]. \quad (11)$$

It is important to note here that when the conduction electron-magnetic impurity interaction is strong, $j^{\text{impure SNS}}(\phi)$ depends on ϵ_0 - the renormalised position of the bound state inside the gap. For $\epsilon_0 \rightarrow 1$ (i.e. when conduction electron-magnetic impurity interaction is weak) eq. (11) reduces exactly to the result obtained in ref. [1], derived in the framework of A-G theory. Further, for $\zeta = 0$ this result again agrees exactly with that of Ishii [2] for pure case. As has been pointed out earlier [1], there is no experimental data available at the moment for the verification of the aboven result.

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EFFECT OF FLUCTUATIONS ON DIAMAGNETIC SUSCEPTIBILITY OF ZERO DIMENSIONAL SUPERCONDUCTORS BELOW T_c

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The effect of fluctuations of superconducting order parameter on the diamagnetic susceptibility χ of a zero dimensional superconductor is studied below T_c , using the phenomenological Ginzburg–Landau theory. χ is found to increase exponentially with the decrease of temperature below T_c and has a finite value at the critical temperature.

In the past few years, there has been great interest in studying the effect of fluctuations of superconducting order parameter on various superconducting properties of small dimensional superconductors both above and below T_c [1–4]. Very recently, Parkinson [1] has calculated the specific heat of small dimensional superconductors using Ginzburg–Landau theory and exact thermal averaging procedure. We extend this work and study the effect of fluctuations on the diamagnetic susceptibility of zero dimensional superconductors below T_c , which has also been studied [2] earlier but with an altogether different and tedious functional integral method. In this particular case, the two approaches yield an identical behaviour.

The usual Fourier transformed Ginzburg–Landau free energy functional, in the presence of a magnetic field below T_c , is written as [1, 3]:

$$F_{GL} = \sum_{k,n} (\alpha + E(k, n + \frac{1}{2})) |\Psi_k|^2 + \frac{\beta'}{2} \sum' \Psi_{k_1}^* \Psi_{k_2}^* \Psi_{k_3} \Psi_{k_4}, \quad (1)$$

where $\beta' = \beta V^{-1}$ and the prime on the summation implies that $k_1 + k_2 = k_3 + k_4$ and

$$E(k, n + \frac{1}{2}) = \hbar^2 k^2 / 2m + (n + \frac{1}{2}) (2e\hbar/mc)B; \quad n = 0, 1, 2, \dots \quad (2)$$

For a zero dimensional sample (i.e. a sample of very small dimension), significant fluctuation effects will be prominent for $k = 0$ states only [1]. Further, we presume that only $n = 0$ Landau level will contribute to free energy on account of very small size (comparable to ξ_0 , the coherence length of superconductor). Keeping these facts in view, the free energy reduces to

$$F_{GL}^{(0)} = (\alpha + e\hbar B/mc) x + \frac{1}{2} \beta' x^2; \quad x = |\Psi_0|^2. \quad (3)$$

It is easy to show that the average value of free energy is given by

$$\langle F_{GL}^{(0)} \rangle = \frac{1}{2} k_B T \left[\frac{(\alpha + e\hbar B/mc) \exp[-\frac{1}{2}(\alpha^2 + 2e\hbar \alpha B/mc)/k_B T \beta']}{\sqrt{2\pi k_B T \beta'}} \frac{1}{F[-(\alpha + e\hbar B/mc)/\sqrt{k_B T \beta}]} - \frac{\alpha^2 + 2e\hbar \alpha B/mc}{k_B T \beta'} + 1 \right], \quad (4)$$

where F stands for normal probability function and we have assumed that the magnetic field is small so that second order terms may be neglected.

The total diamagnetic susceptibility is defined as

$$\chi_{\text{total}} = \chi V = -\partial^2 \langle F_{GL}^{(0)} \rangle / \partial B^2 \quad (5)$$

where V is the volume of the sample.

Using eqs. (4) and (5), we get

$$\chi_{\text{total}} = -A \left[\frac{\exp[-C'B]}{F(-D-EB)} \left\{ C'^2 \left(\alpha + \frac{e\hbar}{mc} B \right) - \frac{2e\hbar}{mc} C' \right\} + \frac{\sqrt{2E} \exp[-(C'B+D^2/2+EBD)]}{\sqrt{\pi} F^2(-D-EB)} \right. \\ \left. \times \left\{ \frac{e\hbar}{mc} - \left(\frac{ED}{2} + C' \right) \left(\alpha + \frac{e\hbar}{mc} B \right) \right\} + \frac{E^2}{\pi} \frac{\exp[-(C'B+D^2+2BED)]}{F^3(-D-EB)} \left(\alpha + \frac{e\hbar}{mc} B \right) \right]; \quad (6)$$

$$A = \exp[-\alpha^2/(2k_B T\beta')] \sqrt{[(k_B T)/\beta']/(2\sqrt{2\pi})}; \quad C' = e\hbar\alpha/mck_B T\beta'; \quad D = \alpha/\sqrt{k_B T\beta'} \text{ and } E = e\hbar/mc\sqrt{k_B T\beta'}.$$

We estimate χ_{total} for an aluminium sample of volume $1.25 \times 10^{-16} \text{ cm}^3$ for different values of temperature below T_c ($T_c = 1.2^\circ\text{K}$ for Al). The phenomenological constants α and β' are taken to be the same as in ref. [1].

A semi log plot of χ_{total} versus $(T-T_c)$ is shown in fig. 1. We note few interesting features of the present calculation. Firstly χ_{total} has a finite value at $T = T_c$ and it increases exponentially as T decreases. This behaviour is qualitatively in agreement with the previous work of Takayama [2]. A similar behaviour is also observed in both the bulk samples [5] and thin films [3]. Secondly, it also seems that χ_{total} does not increase so sharply in the region farther away from T_c as it is in the vicinity of T_c .

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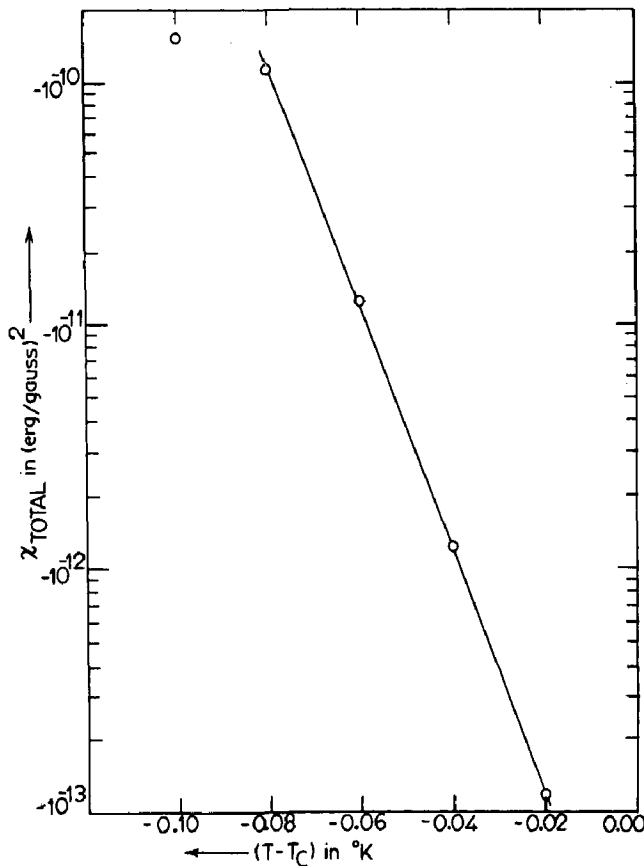


Fig. 1. A semi-log plot of χ_{total} versus $(T-T_c)$ for a small aluminium sample of volume $1.25 \times 10^{-16} \text{ cm}^3$.

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