LUDWIG: SUPERCONDUCTIVITY AND THE KONDO EFFECT
SUPERCONDUCTIVITY AND THE KONDO EFFECT

by

A. Ludwig

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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"I've served this canon seven years and more,
Yet am no nearer science than before.
All that I ever had I've lost thereby,
And so, God knows, have many more than I.
Time was when I was fresh and fond of cheer,
Liked decent clothes and other handsome gear;
Now I might wear my hose upon my head,
And where my color was a lively red
My face is wan and wears a leaden look;
If you try science you'll be brought to book.
My eyes are bleared with work on preparations,
That's all the good you get from transmutations.
That slippery science stripped me down so bare
That I'm worth nothing, here or anywhere.
Added to that I am so deep in debt
From borrowing money, you can lay a bet
Long as I live I'll never pay it, never!
   Let every man be warned by me for ever;
Whoever tries his hand at such behavings,
If he goes on I say will lose his savings.
What's more, so help me God, his only gains
Are empty money-bags and addled brains.
And by the time the man's gone raging mad
And risked and lost whatever goods he had,
He then eggs others on and off they run
To lose their goods, as he himself has done.
    A spiteful wretch takes pleasure when he sees
That others suffer from the same disease,
So I was told once by a learned man.
But what's the odds? I'll on as I began...."

Prologue: The Canon's Yeoman's Tale
"The Canterbury Tales"
by Geoffrey Chaucer
ABSTRACT

In the first part of this thesis we have investigated the properties of superconductors that exhibit the Kondo effect in the normal state. An expression for the superconducting critical temperature as a function of the concentration of magnetic impurity is derived. We investigate the effect of magnetic impurities on the resistive transition of superconductors. The superconducting Proximity effect is used to study normal metals containing magnetic impurities. In the second part of this thesis we study the effect of electron correlations on the Falicov-Kimball model (1969) for the metal-insulator transition.
ACKNOWLEDGEMENTS

The author wishes to thank Professor M.J. Zuckermann for suggesting the problems on superconducting, Kondo alloys. The author also wishes to acknowledge the close cooperation of Dr. C.F. Ratto in the work on the metal-insulator transition problem.

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CHAPTER I
SUMMARY

This thesis reports work done in two topics in the field of phase transitions in solids. In the first part of this thesis we investigate the properties of superconducting alloys that exhibit the Kondo effect in the normal state. The second part of this thesis studies the effect of electron correlations on the metal-insulator transition.

Experimentally, it is found that the residual resistivity of metals containing magnetic impurities, i.e. impurities that have a net spin $S$ in the host matrix, increases as temperature is lowered. The Kondo effect is assumed to be due to a low temperature resonance in the scattering amplitude of the exchange interaction between the conduction electrons and the impurity spins $S$. If the host metal is a superconductor, the exchange scattering of conduction electrons is expected to change the superconducting properties of the host. In particular, we shall be interested in the superconducting critical temperature of the host as the concentration of magnetic impurity is increased.

In Chapter II, we review the theory of a single magnetic impurity in a metallic matrix. An outline of the derivation of Hamman's $t$-matrix for the exchange scattering of conduction electrons by the impurity spin $S$ is given. This $t$-matrix is used throughout our subsequent work on superconductivity.
Chapter III contains a review of the theories of superconductivity and the Kondo effect. We begin with a summary of the B.C.S. theory of superconductivity. A description of the work of Brink and Zuckermann (1965) introduces the topic of non-magnetic impurities in superconductors. This is generalized to the case of magnetic impurities in superconductors by a description of the work of Abrikosov and Gor'kov (1961). The chapter ends with a review of previous work on the initial decrease in the critical temperature of superconducting, Kondo alloys. The introductory chapters may seem unnecessarily long. However, it is felt that the number and complexity of the various formalisms warranted such an introduction.

In Chapter IV, we derive an expression for the critical temperature, $T_c$, of superconducting, Kondo alloys for increasing concentration of magnetic impurity. The exchange scattering of conduction electrons by the impurities is described by Hamman's $t$-matrix.

In Chapter V, we use the superconducting Proximity Effect to study normal metal films containing magnetic impurities. An expression for the superconducting critical temperature of the metal sandwich as a function of the thickness of the superconducting film is found.

Chapter VI considers the effect of magnetic impurities on the resistive transition of superconductors with short electron mean free path. We investigate the temperature dependence of
the resistivity for the characteristic behaviour of the various curves of $T_c$ versus magnetic impurity concentration found in Chapter IV.

The effect of electron correlations on the metal-insulator transition is investigated in part II of this thesis. Falicov and Kimball (1969) have proposed that the mechanism for the metal-insulator transition is the Coulomb interaction between electrons localized at atomic sites and itinerant electrons in the conduction band. However, they have only investigated this model in the Hartree approximation and thereby ignore the effect of correlations between the localized and itinerant electrons. We examine the effect of the correlations between electrons on the character of the transition using a variational approach.
CHAPTER II
THE KONDO EFFECT

I. Magnetic Moments on Metal Atoms with Filled Inner Shells

The valence electrons for metal atoms with filled inner shells couple to form states of total angular momentum \( J \) in the absence of spin-orbit coupling. For \( J \) different from zero each free atom possesses a magnetic moment. The paramagnetic susceptibility obeys a Curie Law. When the free metal atoms condense into a crystal, the valence electrons form a conduction band. Metal ions with closed inner shells do not have local magnetic moments. At low temperatures the paramagnetic susceptibility of the conduction electrons is temperature independent.

II. Magnetic Moments on Metal Atoms with Unfilled Inner Shells

(a) Rare Earths

Rare earth ions have unfilled inner 4f shells, e.g. Gadolinium. In the absence of spin-orbit coupling the ground state of the 4f electrons is predicted by Hund's theory of spectral terms. Hund's Rule tells us that for electrons from the same shell, the ground state has the maximum number of parallel electron spins consistent with the Pauli principle. The eigenvalue \( L \) of the total orbital angular momentum \( L \) is
the sum of the eigenvalues of $l_z$ for the occupied orbitals;  
the eigenvalue $S$ of the total spin $S$ is the sum of the eigenvalues of the $z$ component of each electron spin in the shell.  
The eigenvalue of the total angular momentum $J$ has the value  
$|L-S|$ when the shell is less than half filled and $L+S$ when  
the shell is more than half filled. The paramagnetic sus-
ceptibility $\chi$ of the free rare earth ions with $J \neq 0$ in the  
ground state obeys a Curie Law, i.e. $\chi \sim 1/T$ where $T$ is the  
temperature.

The 4f electron wave function is localized in coordinate  
space. In the rare earths the 4f electrons are shielded by  
5s and 5p electrons. For these reasons the 4f states will  
hardly mix with the conduction electron states when the  
atom is in a metallic environment (except Cerium). The rare  
earth ion in a crystal host retains its 4f atomic moment.  
The paramagnetic susceptibility is Curie-like at high enough  
temperatures.

(b) Transition Metals

Electrons in the unfilled d shells in free transition  
metal ions couple to form a ground state according to Hund's  
Rule. As expected for free spins the susceptibility is  
Curie-like.

In a transition metal ion the d electrons are the outer-
most electrons. Also, the d state wave functions are extended  
in coordinate space because the inner electrons screen the
nuclear charge. In a transition metal the d states from neighbouring ions will mix to form a d band.

Consider the situation of a transition metal ion dissolved in a simple metal (a metal whose ions have an inert gas configuration). The localized d state mixes with the host conduction electron states to form a virtual bound state (Freidel 1956, Anderson 1961). The wave functions for the mixed states are spatially extended.

To decrease their Coulomb energy, the electrons in these mixed states can correlate their motion to increase their spatial separation. This will happen for electrons of both spins. If the mixing is small (e.g. for narrow bands) the decrease in Coulomb energy for electrons of opposite spin is less than the energy gained from the Pauli principle by electrons of parallel spin. Hund's Rule for the ground state still applies. The local moment retains a value close to the free ion value. If the mixing is strong (e.g. wide bands) the decrease in Coulomb energy is large; the energy gained by the Pauli principle for electrons of parallel spin is not large enough to determine the ground state and Hund's Rule no longer applies. The local moment becomes non-integral since electrons of both spins occupy the virtual state. The value of the local moment can differ greatly from the free ion value and disappears in some alloys (e.g. Al-V). If the moment is maintained the paramagnetic susceptibility obeys a Curie or Curie-Weiss Law.
III. Exchange Interaction in Dilute Alloys Containing Rare
Earths or Transition Metals

The conduction electrons of a simple metal can interact in two ways with the electrons of a virtual bound state. There is the magnetic dipole-dipole interaction and the Coulomb interaction. The dipole-dipole interaction is proportional to \((1/r)^3\) and is dominated by the \((1/r)\) dependence of the Coulomb energy. Because of the Pauli principle, the Coulomb energy for a parallel alignment of local spin-conduction electron spin is lower than an anti-parallel alignment. This difference can be written

\[ -J \sigma \cdot \mathcal{S} \]  

where \(\mathcal{S}\) is the local spin, \(\sigma\) is the conduction electron spin and \(J\), the difference between the coulomb energies for the two spin alignments, is the exchange integral. \(J\) is usually positive. It is seen that the inner product \(\sigma \cdot \mathcal{S}\) describes the scattering of conduction electrons from the local spin.

The mixing of the localized d level and conduction band can lead to a negative exchange interaction as follows: a spin-down conduction electron can now occupy an empty spin-down d-orbital of an impurity with an occupied spin-up d-orbital. The Coulomb repulsion \(U\) between two d electrons of opposite spin makes it advantageous for the spin-up electron to jump into the conduction band via the s-d mixing
interaction. This describes the scattering of a spin-down conduction electron to a spin-up conduction electron. The resulting interaction can be written

$$-J_{\text{mix}} \mathbf{Q} \cdot \mathbf{S}$$

(2)

where $J_{\text{mix}} < 0$ (Schrieffer and Wolff 1966).

The total interaction between the conduction electrons and the local spin is then

$$-(J + J_{\text{mix}}) \mathbf{Q} \cdot \mathbf{S}$$

(3)

The sign of $(J + J_{\text{mix}})$ may be positive or negative. It is expected that for strong mixing between conduction electron and d electron states the sum is negative. If the mixing is weak, the sum is positive. The different signs of $(J + J_{\text{mix}})$ are expected to lead to different properties in the scattering rate for the exchange scattering of conduction electrons from the localized spin.

IV. Residual Resistance of Dilute Alloys

(a) Simple Metal Impurities

Consider a dilute alloy of two simple metals. Let the impurity ion valence differ from the valence of the host ions. Then the electrostatic potentials of the host and impurity ions will be different. The conduction electrons no longer move in a periodic potential as periodicity is destroyed by
the impurity. The conduction electrons are scattered by the effective potential $V(r)$ of the excess impurity charge $Ze$ ($Z$ may be positive or negative). We neglect the recoil of the impurity ion.

We wish to calculate the residual resistivity due to the scattering of electrons by $V(r)$ when the temperature $T$ is much less than the Fermi temperature. For simplicity we assume $V(r)$ is a contact potential $V_0(r)$. The scattering will be investigated in the first and second Born approximations. In the first Born approximation an electron of momentum $k$, spin $\sigma$ is scattered directly to a state of momentum $k'$, spin $\sigma'$. This scattering, shown in figure (1), has the matrix element $(V/N)$ where $N$ is the number of ions in the system.

In the second Born approximation, there are two scattering processes that take an electron from a state $(k,\sigma)$ to another state $(k',\sigma)$. These are shown in figures (2) and (3). Figure (2) shows an electron in state $(k,\sigma)$ being scattered into the empty intermediate state $(q,\sigma)$. The electron in the state $(q,\sigma)$ is then scattered into the final state $(k',\sigma)$. The matrix element for this is

\[
\left( \frac{V}{N} \right)^3 \sum_{k'q0} \frac{1 - \frac{\xi(q)}{\xi(k)}}{E_k - E_q}
\]
where $E_k = \frac{k^2}{2m}$ is the electron energy, $\tilde{f}(\varepsilon)$ is the Fermi function, and $m$ is the electronic mass. The process in figure (3) has a filled intermediate state $(q, \delta)$ scatter into the final state $(k', \delta)$. The initial state then scatters into the empty state $(q, \delta)$. The matrix element for this process is

$$ - \left( \frac{\hbar}{N} \right)^3 \sum_{q' + k'} \frac{\tilde{f}(\varepsilon_{q'})}{\varepsilon_q - \varepsilon_{k'}} \tag{5} $$

The minus sign arises from the antisymmetry of the Fermions.

The transition rate is

$$ W(k, \delta \rightarrow k', \delta) = 2\pi \delta(E_k - E_{k'}) \left( \frac{\hbar}{N} \right)^2 \left\{ 1 + \frac{V}{N} \sum_{q + k' - k} \frac{1}{\varepsilon_{k'} - \varepsilon_{q'}} \right\} \tag{6} $$

The transition rate is temperature independent. $W(k, \delta \rightarrow k', \delta)$ is temperature independent because we are considering the recoilless scattering of conduction electrons from a structureless potential $V(x)$. Since the state of the impurity is unchanged during a scattering event, the total scattering matrix element is independent of the order of the scattering processes. There is no distinction between the intermediate states being holes or particles. Since the probability of a state being empty or filled depends on temperature through the Fermi function, the scattering matrix element is temperature independent. The scattering of
electrons by a potential \( V(\mathbf{r}) \) can be hence treated as a one electron problem, the Pauli principle being neglected for the intermediate state.

For a small concentration \( c \) of impurities, the residual resistivity is

\[
\rho_i = c \frac{m e^2}{m} \int d\varepsilon \left( -\frac{\partial f(\varepsilon)}{\partial \varepsilon} \right) \frac{1}{\gamma(\varepsilon)}
\]

where \( m \) is the electron density, \( e \) the electronic charge and \( \gamma(\varepsilon) \) is the relaxation time for electrons of energy \( \varepsilon \) given by:

\[
\frac{1}{\gamma(\varepsilon)} = 2\pi \left( \frac{\varepsilon}{N} \right)^2 \left( 1 + \frac{\varepsilon}{N} \right) \int \frac{D(\varepsilon')}{\varepsilon - \varepsilon'} d\varepsilon'
\]

\( \Phi \) means the principle part and \( D(\varepsilon) \) is the density of states for conduction electrons. Although we have shown that \( \rho_i \) to the second Born approximation is temperature independent, it can be shown that this is true to all orders. Simple metal impurities give rise to temperature independent residual resistivities for \( T \ll \varepsilon_F/k \) where \( \varepsilon_F \) is the Fermi energy.

(b) Transition Metal Impurities: The Kondo Effect

For many alloys of simple metals with a small concentration \( c \) of transition metal impurities, the low temperature resistivity exhibits a minimum at a temperature \( T_{\text{min}} \). For
temperatures below \( T_{\text{min}} \) the resistivity \( \rho \) increases logarithmically with decreasing temperature (\( \rho \propto \ln T \)).

Kondo (1964) described the transition metal impurity-conduction electron interaction by

\[
\mathcal{H}(\mathbf{r}) + J \delta(\mathbf{r}) \mathbf{\sigma} \cdot \mathbf{S}
\]

where \( \mathcal{H}(\mathbf{r}) \) is an electrostatic potential and the exchange integral \( J \) may be positive or negative. The potential term will be neglected since it does not give rise to a temperature dependent residual resistivity. Kondo has shown that for a correct calculation of the residual resistivity, the impurity spin \( \mathbf{S} \) must be treated as a quantum mechanical operator with non-commuting components. The importance of the non-commuting spin components is demonstrated in the second Born approximation for the scattering rate since the first Born approximation consists of a single scattering event that contributes a temperature independent term to the residual resistivity.

Two simple processes illustrate the dynamical nature of the local spin. Let an electron of momentum \( \mathbf{k} \), spin-up [here denoted as \( (\mathbf{k},\uparrow) \)] scatter from the impurity into an empty intermediate state \( (\mathbf{q},\downarrow) \), changing the \( Z \) component of the local spin by +1. The state \( (\mathbf{q},\downarrow) \) then scatters from the impurity to the final state \( (\mathbf{k}',\downarrow) \), the \( Z \) component of the local spin changing by -1 (figure 4). The matrix element of such a scattering event is
where \( S_- \) and \( S_+ \) are the raising and lowering operators for the impurity spin. The second process for scattering \((K, \uparrow)\) to \((K', \uparrow)\) has an occupied state \((q, \downarrow)\) scattering into the final state \((K', \uparrow)\), the Z component of the local spin changing by -1. The initial state \((K, \uparrow)\) then scatters into the empty state \((q, \downarrow)\), the Z component of the local spin changing by +1 (figure 5). The matrix element is

\[
-S_\uparrow S_- \sum_{q \neq q'} \frac{\tilde{f}(\varepsilon_{q'})}{\varepsilon_{q'}}
\]

The final states in the above processes differ by a minus sign. Since we have \( \varepsilon_K = \varepsilon_{K'} \) for elastic scattering, the matrix elements combine to give

\[
S_- S_+ \sum_{q \neq q'} \frac{1}{\varepsilon_{q'} - \varepsilon_q} \left[ S_\uparrow S_- - S_- S_\uparrow \right] \sum_{q' \neq q} \frac{\tilde{f}(\varepsilon_{q'})}{\varepsilon_{q'} - \varepsilon_q}
\]

The temperature dependence arises from the quantum nature of the local spin; \([S_+ S_- - S_- S_+]\) is not zero. If the local spin were treated classically, \( S_+ \) and \( S_- \) would commute.

The local spin \( S \) has internal degrees of freedom; the Z component of the local spin is different in each intermediate state. The eigenvalue of \( S_z \) depends on the Pauli
Figure 4

Figure 5
exclusion principle for the intermediate electronic state. The sum of the two processes discussed above gives a temperature dependent scattering rate. These results may be put in a general form: electron scattering from a dynamical system must be treated as a many body problem.

In the second Born approximation, the residual resistivity due to exchange scattering is given by (Kondo 1964)

\[
\rho_{ex} = c \rho_m (1 + 4J N(0) \ln T)
\]  

(13)

where \(\rho_m = (2\pi N(0) m/2 Z N e^2) T^2 S (S+1)\), c is the impurity concentration, N is the number of atoms, Z is the number of conduction electrons per atom and N(0) is the density of states per atom per spin direction at the Fermi surface. The concentration c of the impurity is assumed to be sufficiently small enough so that the impurities do not interact.

We assume that the total resistivity can be expressed as the sum of the lattice resistivity, the residual resistivity due to the impurity potential \(\rho_I\), and the residual resistivity due to the exchange interaction \(\rho_{ex}(T)\). The low temperature lattice resistivity \(\rho_L(T)\) in a pure metal is proportional to \(T^5\). This temperature dependence arises because the angle of electron scatter is limited by the wave vector of the thermally excited phonons. The temperature independent residual resistivity \(\rho_I\) will be neglected. Then the resistivity \(\rho(T)\) is given by
\[ \rho(T) = \rho_l(T) + \rho_{ex}(T) = aT^s + c\rho_m(1 + 4JN(0)\ln T) \] (14)

\[ \rho(T) \text{ exhibits a minimum when } J < 0. \text{ Differentiation with respect to } T \text{ gives the temperature } T_{\text{min}} \text{ of the minimum} \]

\[ T_{\text{min}} = \left( \frac{4\rho_m N(0)|J|}{5a} \right)^{1/5} C^{1/5} \] (15)

For \( J > 0 \) no minimum occurs and \( \rho(T) \) increases monotonically with temperature. The \( C^{1/5} \) dependence of \( T_{\text{min}} \) has been observed experimentally (Pearson 1955). \( J \) is negative for many transition metal impurities in simple metals (e.g. AuFe, CuFe) indicating a large mixing of localized states and conduction band states.

The logarithmic term in the scattering rate has explained many features of transition metal impurities in simple metals. However, a divergence appears at \( T = 0 \). Although we have given \( \rho_{ex}(T) \) to the second Born approximation, it can be shown that the logarithmic divergence at \( T = 0 \) appears in all orders of perturbation series. This happens because the electrons can scatter into states with energies infinitesimally greater than the Fermi energy. To obtain the low temperature resistivity one must sum all the perturbation series or use non-perturbative techniques.
V. Removal of Low Temperature Divergence

(a) Abrikosov’s Method

Abrikosov (1965) attempted to find the low temperature form of the resistivity using perturbative methods. However, it is not possible to use standard diagram techniques because of the spin commutation relations. To overcome this, Abrikosov used a Holstein-Primakoff transformation (Holstein-Primakoff 1940) to define pseudo-Fermion operators. These pseudo-Fermion operators obey anti-commutation relations. Eigenstates of $S_z$ are represented by a pseudo-Fermion state being occupied, the remainder being empty. States where the sum of the occupation numbers is not one are unphysical. To eliminate these unphysical states from the spin average, Abrikosov assigns each pseudo-Fermion state an energy $\lambda' \gg KT$. Multiplying each term in the perturbation series by $(\exp (\lambda'/KT))/(2S + 1)$ and letting $\lambda' \to \infty$ one can project out the unphysical states.

Abrikosov uses this diagram technique to construct a perturbation series for the amplitude for exchange scattering of conduction electrons. In the $n^{th}$ order of the series he keeps the leading logarithmic term $[JN(0)]^{n+2} \ln^n nT$ where $N(0)$ is the density of conduction electron states per spin per atom. Summing this series he obtains for the residual resistivity due to exchange scattering

$$\rho(T) = c \rho_m (1 - 2JN(0) \ln(T/T_D))^{-a}$$

(16)
where $c$ is the concentration of transition metal impurity and $D$ is a bandwidth. This approach is used in Chapter IV for the calculation of the superconducting critical temperature.

For $J > 0$ the residual resistivity is monotonically increasing with temperature. If $J < 0$ the residual resistivity diverges at

$$T_K = D \cdot \exp \left\{ \frac{1}{2|J| N(0)} \right\}$$

(17)

Nagaoka suggested that at $T_K$ the conduction electrons at the impurity site form a bound state with the impurity spin. As the phenomena is basically a one-particle effect the thermal fluctuations would prevent a phase transition to a bound state. The divergence in Abrikosov's expression for the residual resistivity then comes from his not summing a lower order divergent series $[J N(0)]^{n+2+m} \ln^{n} n$ for $m > 1$. Since these terms become important at low temperatures, it is necessary to sum all these terms or use non-perturbative techniques.

(b) Nagaoka's Equation of Motion Technique

Nagaoka (1965) suggested that perturbational approaches to exchange scattering for $J < 0$ diverge because of the formation of a singlet bound state between the local spin and the conduction electrons. To investigate such correlations, Nagaoka used the method of retarded double-time Green's functions (Zubarev 1960) and the equation of motion technique
to obtain two coupled equations for the Fourier transform of the single particle retarded double-time Green's function. The decoupling scheme used by Nagaoka takes into account the correlation between the local spin and the conduction electron spin in the simplest manner. The important correlations are the spin conserving scattering of conduction electrons from the local spin. A simple example will exhibit this procedure:

\[ \langle C_{\mathbf{k}\uparrow} C_{\mathbf{k}\downarrow}^+ C_{\mathbf{k}\uparrow} S_- | C_{\mathbf{k}\downarrow}^+ \rangle = \langle C_{\mathbf{k}\uparrow} C_{\mathbf{k}\downarrow}^+ \rangle \langle C_{\mathbf{k}\downarrow}^+ S_- | C_{\mathbf{k}\downarrow}^+ \rangle + \langle C_{\mathbf{k}\downarrow}^+ C_{\mathbf{k}\downarrow} S_- \rangle \langle C_{\mathbf{k}\downarrow} | C_{\mathbf{k}\downarrow}^+ \rangle \]  

(18)

where \( C_{\mathbf{k}\uparrow}^+ \) is the creation operator for a conduction electron of momentum \( \mathbf{k} \), spin-up; \( \langle \cdots \rangle \) is a thermal average and \( \langle A | B \rangle \) denotes the Green's function for operators A and B. The term \( \langle C_{\mathbf{k}\uparrow} C_{\mathbf{k}\downarrow}^+ \rangle \) appears since it also conserves spin. The average \( \langle C_{\mathbf{k}\downarrow}^+ C_{\mathbf{k}\downarrow} S_- \rangle \) describes the spin flip scattering of a conduction electron by the magnetic impurity.

Nagaoka obtains an expression for the non-spin flip scattering amplitude \( t(\omega) \) for exchange scattering of conduction electrons from the magnetic impurity. \( t(\omega) \) has a resonance behaviour at the Fermi surface below the temperature \( T_K \) associated with the divergence of Abrikosov's perturbation series. The scattering resonance can be identified with the bound state. The residual resistivity calculated from \( t(\omega) \) does not diverge at \( T = T_K \). However, Nagaoka's expression for the residual resistivity does not give any physical insight into the temperature region \( \lesssim T_K \).
(c) **Hamman's Integral Equation**

The thermal averages that appear in equation (17) may be written as integrals over \( \omega \) with \( t(\omega) \) appearing in the integrand. Similarly, the \( t \) matrix \( t(\omega) \) is a functional of these averages. With these relations Hamman (1967) was able to construct an integral equation for \( t(\omega) \). Only the singular terms that are associated with the logarithmic divergences of the Kondo effect are retained in Hamman's integral equation. The further assumption that \( t(\omega) \) is large for energies less than \( K T_K \) (\( K T_K \ll \) bandwidth) leads to the integral equation

\[
\Psi(\omega+\xi) = \frac{1-\pi^2 S(S+1)(JN(0))^2+2JN(0)}{1+\pi^2 S(S+1)(JN(0))^2+2JN(0)} \int_{-\infty}^{\infty} \frac{\xi(\omega') - \frac{1}{2}a}{\omega - \omega' + i\delta} \Psi(\omega'+\xi) d\omega'
\]

where \( \Psi(\omega+\xi) = 1-2\pi i N(0) t(\omega+\xi) \) is the S matrix for non-spin flip scattering.

Hamman assumes the important contribution to the integrals in the numerator and denominator comes from the region of the Fermi surface \( \omega \approx 0 \). The solution to the approximate integral equation is

\[
t(\omega) = \frac{1}{2\pi i N(0)} \left[ 1 + \frac{X(\omega, T)}{(X^2(\omega, T)^2 \pi^2 S(S+1))^{1/2}} \right]
\]
where

\[ X(\omega, \Gamma) = \text{sign}(J) \ln \left( \frac{\omega + i \Gamma}{i \Gamma K'} \right), \]

\[ T_k' = D \cdot \exp \left\{ \frac{\text{sign}(J)}{2 \Gamma t N(\omega)} \left[ 1 - \frac{S(\omega t)}{\pi t N(\omega)} \right] \right\} \]

and \( \text{sign}(J) \) is positive if \( J > 0 \), negative if \( J < 0 \). One sees that the \( t \) matrix is analytic for all \( \omega \) in the upper half plane and all temperatures. The leading term in an expansion of \( t(\omega) \) for \( |X| \gg 1 \) is identical to the results of Abrikosov. The terms of higher order are important in removing unphysical divergences. Hamman and Bloomfield (1967) have solved the integral equation [equation (19)] exactly. We do not use the exact solution because it is a complicated function to compute with. The approximate \( t \) matrix [equation (20)] is simple to use for calculations and is correct for electrons near the Fermi surface (Müller-Hartmann 1969).

Hamman used his approximate solution for \( t(\omega) \) to calculate the residual resistivity and the local susceptibility. For a small concentration \( c \) of transition metal impurities the single particle relaxation time near the Fermi surface is given by

\[ \frac{1}{\tau_k} = -2 c \Im t(0 + i \delta) \]  

(21)

The residual resistivity \( \rho_{ex}(T) \) then becomes

\[ \rho_{ex}(T) = \frac{2\pi c}{m e^2 k_f} \left[ 1 + \frac{\text{sign}(J) \ln \left( \frac{T}{T_k'} \right)}{\left( \ln \left( \frac{T}{T_k'} \right) + \pi^2 S(\omega t) \right)^{\alpha/2}} \right] \] 

(22)
where \( n \) is the electron density and \( K_F \) the Fermi wave vector. \( \rho_{ex}(T) \) is a well behaved function of temperature. The expression for the local susceptibility predicts the disappearance of the local moment as \( T \to 0 \) for \( J < 0 \). This result is expected from Nagaoka's suggestion that the local spin and the conduction electron spin form a singlet bound state below \( T_K \). This picture is not clear since it has been noted (Silverstein and Duke 1967) that Hamman's \( t \) matrix is not correct for temperatures below \( T_K \).

(d) **Other Solutions**

(i) Müller-Hartmann and Zittartz (1968) have solved Nagaoka's equations exactly for a general density of conduction electron states and both signs of \( J \). They use the technique of singular integral equations (Muskhelishvilli 1953) to obtain the non-spin flip \( t \) matrix. In the limit of weak coupling \( |J|N(0) \ll 1 \) (\( J < 0 \)) and for energies near the Fermi surface the exact solution reduces to Hamman's approximate solution for \( t(\omega) \) (Müller-Hartmann 1969).

Müller-Hartmann and Zittartz have used their exact solution for the \( t \) matrix to calculate the singlet (\( J < 0 \)) ground state properties for the dilute alloy. They find that the conduction electrons overcompensate the local spin (they obtain a negative susceptibility) and for a spin 1/2 impurity the change in entropy is \( -k \ln \left( \frac{27}{16} \right) \) instead of \( -k \ln 2 \) as expected from a singlet state. Nagaoka's equations do not
have a spin singlet for a ground state.

(ii) Suhl (1965) studies the exchange scattering of conduction electrons by a local spin using Chew-Low scattering theory (1956). He obtains 2 coupled integral equations for the spin flip and non-spin flip scattering amplitudes. The exact solution of these equations is equivalent to the exact solution of Mueller-Hartmann and Zittartz and Bloomfield and Hamman's (1967) exact solution of Hamman's integral equation. If we use Hamman's approximate solution for $t(\omega)$ and Suhl's equations, the spin-flip scattering rate is given by

$$\frac{1}{\tau_S} = \frac{1}{2\pi N(0)} \left[ \frac{\pi^2 S(S+1)}{\ln^2(\sqrt{T/T_K}) + \pi^2 S(S+1)} \right]$$

(23)

In Chapter IV it will be shown that the superconducting critical temperature of an alloy containing magnetic impurities is determined by the spin flip scattering rate. In particular, equation (23) will be used to determine the critical temperature of superconducting, Kondo alloys.
CHAPTER III
SUPERCONDUCTIVITY AND THE KONDO EFFECT

PART ONE: SUPERCONDUCTIVITY

I. The Theory of Bardeen, Cooper and Schreiffer

When Onnes (1911) measured the resistivity of high purity mercury at liquid helium temperatures, he found the resistance dropped to a vanishingly small value over a narrow temperature range of .01°C. Onnes (1913) concluded that the mercury had entered a new state which he named the superconducting state. The assumption that a superconductor is fundamentally a perfect conductor is equivalent to the condition $\mathbf{\mathcal{B}} = 0$ i.e., the rate of change of the magnetic induction inside a superconductor is zero. This implies that the superconducting transition in a magnetic field is irreversible. However, Meissner and Ochsenfeld (1933) found experimentally that $\mathbf{\mathcal{B}} = 0$ inside a bulk superconductor i.e., that the flux is expelled from the interior of a bulk superconductor placed in a magnetic field. This experiment demonstrated that the superconducting transition in a magnetic field is reversible.

The possibility that superconductivity is a quantum effect was demonstrated by the discovery of the isotope effect (Maxwell 1950; Reynolds, Serin, Wright and Nesbitt 1950).
These experimenters showed that the superconducting critical temperature was strongly dependent on the isotopic mass of the constituent metal. Fröhlich (1950) related the isotope effect to the electron-phonon interaction from which he concluded that this interaction would lead to an energy gap in the single particle excitation spectrum for the electrons at the Fermi surface.

In spite of the realization that the electron-phonon interaction was responsible for superconductivity, a consistent microscopic theory was not available until Bardeen, Cooper and Schreiffer (B.C.S. 1957) proposed the following mechanism: electrons at the Fermi surface attract each other by the emission and absorption of virtual phonons. In a superconductor this phonon induced attractive interaction must be larger than the renormalized repulsive screened Coulomb interaction. Cooper (1956) showed that a pair of electrons interacting via an attractive interaction of this type will form a bound state of energy less than the sum of their kinetic energies. B.C.S. postulated that all the electrons at the Fermi surface in a superconductor formed such bound pairs. The Hamiltonian for the pairs of electrons is given by

\[ H = \sum_{\mathbf{k}, \mathbf{\sigma}} E_{\mathbf{k}} C_{\mathbf{k}\sigma}^+ C_{\mathbf{k}\sigma} + \sqrt{\sum_{\mathbf{g}, \mathbf{\sigma}} C_{\mathbf{g}\sigma}^+ C_{-\mathbf{g}\sigma}^+ C_{-\mathbf{g}\sigma} C_{\mathbf{g}\sigma}} \quad (1) \]
where $C_{\alpha}^+$ creates an electron of spin $\overrightarrow{\sigma}$, momentum $\mathbf{k}$ and energy $E_{\mathbf{k}}$, and $V$, the constant matrix element for the attractive electron-electron interaction, satisfies

$$V = -\frac{1}{\rho} \quad \text{if} \quad |E_k| < \omega_0$$

$$= 0 \quad \text{if} \quad |E_k| > \omega_0$$ (2a)

$$V = -\frac{1}{\rho} \quad \text{if} \quad |E_k| < \omega_0$$

$$= 0 \quad \text{if} \quad |E_k| > \omega_0$$ (2b)

with $\omega_0$ the Debye phonon frequency. The Fermi energy has been taken as the zero of energy.

A self-consistent approximation using the Hamiltonian in equation (1) gives the following results: the superconductor is described by a temperature dependent order parameter $\Delta(T)$ that has the following value at zero temperature

$$\Delta(0) = 2\omega_0 \cdot \exp\left\{- \frac{1}{|q| N(0)} \right\}$$ (3)

for $|q| N(0) \ll 1$ (weak coupling). $\Delta(T)$ vanishes at the superconducting critical temperature $T_{c0}$ which is given by

$$KT_{c0} = 1.14 \omega_0 \cdot \exp\left\{- \frac{1}{|q| N(0)} \right\}$$ (4)

For temperatures above $T_{c0}$, the metal is normal. The ratio of the order parameter at zero temperature to the superconducting critical temperature is

$$\frac{\Delta(0)}{KT_{c0}} = 3.5$$

This is the law of corresponding states. Superconductors that deviate strongly from this law are called strong coupling superconductors (e.g. Pb). In these cases one must
account for the phonons explicitly. The density of states for single particle excitations has an energy gap $\Delta(\tau)$ in the B.C.S. theory. This gap accounts for many properties of superconductors e.g., the Meissner Effect.

The B.C.S. theory of superconductivity has been formulated for pure metals. In Chapter IV, we shall calculate the critical temperature of B.C.S. superconducting alloys that exhibit the Kondo effect in the normal state.

II. The Perturbation Theory of Thouless

Thouless (1960) used a perturbational method to calculate the superconducting critical temperature for an isotropic B.C.S. superconductor. The Hamiltonian used by Thouless has normal electrons interacting by an attractive two body interaction with a non-zero matrix element between electrons of opposite spin. Thouless develops a perturbation series for the grand partition function of the interacting electrons in terms of ladder diagrams which represent the repeated scattering of a pair of electrons by the two body interaction. The Free Energy $\Omega_N$ of the normal electron system is given in terms of the sum of ladder propagators $\mathcal{L}(q, \omega_N)$ as

$$\frac{d\Omega_N}{d\Omega_1} = -KT \sum_{q, \omega} \left( \mathcal{L}(q, \omega_N) - \mathcal{L}_0(q, \omega_N) \right)$$  \hspace{1cm} (5)
where $\sum_{q\nu}L_0(q\nu)$ is the sum of ladder propagators when $|q| = 0$, $q$ is the momentum of an electron pair and $\omega_{\nu} = \frac{2\pi \nu kT}{\hbar}$ is their frequency (Matsubara 1955). The sum of ladder propagators $\sum_{q\nu}L(q\nu)$ is given by (Appendix A)

\[ L(q\nu) = L_0(q\nu) + \frac{1}{1 - iq} L_0(q\nu) \]

or

\[ L(q\nu) = L_0(q\nu) \left( 1 - \frac{1}{1 - iq} \right) \]

where

\[ L_0(q\nu) = N(0) \left\{ \ln \left( \frac{2\pi \omega}{\hbar kT} \right) - \frac{\pi \omega d}{8kT} - \frac{1}{3} \frac{\nu}{\hbar kT} \left( \frac{\nu}{\hbar kT} \right)^2 \right\} \]

\[ \chi = 0.5772, \quad \chi(3) = 1.202 \quad \text{and} \quad \omega_0 \quad \text{is the Debye frequency.} \]

Substituting equations (6b) and (6c) in equation (5), we integrate the resulting expression from 0 to $-|q|$ to obtain

\[ \omega_\nu(q) - \omega_\nu(0) = \frac{kT}{q\nu} \sum_{q\nu} \left\{ \ln \left( 1 - \frac{1}{1 - iq} \right) L_0(q\nu) + \frac{1}{1 - iq} L_0(q\nu) \right\} \]

Equation (7) was obtained by formally summing a perturbation series. It will be invalid if the series does not converge. Thouless' criteria for convergence is

\[ |q| L_0(q,0) < 1 \]

The series will diverge when

\[ 1 = |q| L_0(q,0) = |q| N(0) \ln \left( \frac{2\pi \omega_0}{\hbar kT} \right) \]

The normal state of the metal is unstable when the temperature is equal to the superconducting critical temperature $T_{co}$ of the
BCS theory. For temperatures below $T_{co}$ the expression equation (7) for the Free Energy is invalid; the metal is in the superconducting state.

We can generalize the repeated scattering of a pair of electrons by replacing the two body interaction by a $t$ matrix. The $t$ matrix is found from (Appendix A)

$$\mathcal{L}(q, \omega_r) = \mathcal{L}_0(q, \omega_r) + \mathcal{L}_0(q, \omega_r) t(q, \omega_r) \mathcal{L}_0(q, \omega_r)$$

(10)

Using equation (6b) we have

$$t(q, \omega_r) = \frac{\delta q}{1 - \delta q \mathcal{L}_0(q, \omega_r)}$$

(11)

Thouless' criteria for the convergence of the sum of ladder propagators is $t(0,0)$ is finite.

III. Non-Magnetic Impurities in Superconductors

Brink and Zuckermann (1965) extended Thouless' method to include non-magnetic impurities in an isotropic superconductor. The impurities are introduced by adding to Thouless' Hamiltonian the one body term (Rickayzen 1964)

$$H_I = \sum_{\mathbf{R}_i} \left( \sum_{\mathbf{q}} U(q) e^{i \mathbf{q} \cdot \mathbf{R}_i} \right) \mathbf{C}^\dagger_{\mathbf{p} \sigma} C_{\mathbf{p} \sigma + \mathbf{q} \sigma}$$

(12)

where $\mathbf{R}_i(n, N)$ are the positions of the impurities, and $U(q)$ is the potential of a single impurity. It is assumed the impurities lead only to electron scattering.

Impurity scattering destroys momentum conservation. The ladder diagrams and the sum of ladder propagators will
depend on the initial and final momenta of the electron pair and the position of the impurities. The frequency of the electron pair is conserved. Analogously to the pure superconductor, we have for the alloy

\[ \chi_{\text{imp}} = \chi_{\text{imp}}(q; q'; \omega_v; R_i) \]  
\[ \chi_0 = \chi_0(\omega_v; R_i) \]  

where \( q, q' \) are the initial and final momenta of the electron pair and \( \omega_v \) is the frequency of the electron pair.

If the impurities are assumed to be randomly distributed in the superconductor, all functions of \( R_i \) may be averaged as

\[ \langle F(R_1, R_2, \ldots, R_N) \rangle_{\text{av}} = \frac{1}{V} \int d^3R_1 d^3R_2 \ldots d^3R_N F(R_1, R_2, \ldots, R_N) \]  

where \( V \) is the volume of the superconductor. The averaging procedure restores translational invariance and therefore momentum conservation (Appendix B). Averaging \( \chi_{\text{imp}}(q; q'; \omega_v; R_i) \) and \( \chi_0(q; q'; \omega_v; R_i) \) gives

\[ \langle \chi_{\text{imp}}(q; q'; \omega_v) \rangle_{\text{av}} = \chi_{\text{imp}}(q; \omega_v) \delta_{q q'} \]  
\[ \langle \chi_0(q; q'; \omega_v) \rangle_{\text{av}} = \chi_0(q; \omega_v) \delta_{q q'} \]  

To lowest order in the impurity density \( \chi_{\text{imp}}(q; \omega_v) \) is given by

(Appendix B)

\[ \chi_{\text{imp}}(q; \omega_v) = \chi_{\text{imp}}(q; \omega_v) + 1g' \chi_{\text{imp}}(q; \omega_v) \chi_{\text{imp}}(q; \omega_v) \]  
\[ = \frac{\chi_{\text{imp}}(q; \omega_v)}{1 - g' \chi_{\text{imp}}(q; \omega_v)} \]
where
\[
\mathcal{L}_0^{\text{imp}}(q, \omega) = N(0) \left\{ \ln \left( \frac{2 \pi \omega}{\hbar c} \right) \cdot \frac{1}{\pi kT} \cdot \left[ \frac{1}{2} + \frac{\omega}{\pi kT} + \frac{\sqrt{1 + 4 \pi kT \omega}}{2 \pi kT} \right] - \frac{1}{2} \right\}
\]  
(18c)
and \( \Psi(z) \) is the digamma function.

The Free Energy for the normal electrons is given by
\[
\frac{d \Omega_n^{\text{imp}}}{dq} = -\kappa T \sum_q \left\{ \mathcal{L}_n^{\text{imp}}(q, \omega) - \mathcal{L}_0^{\text{imp}}(q, \omega) \right\}
\]  
(19)

The Free Energy \( \Omega_n^{\text{imp}} \) has the same form as equation (5) except \( \mathcal{L}_0(q, \omega) \) is replaced by \( \mathcal{L}_0^{\text{imp}}(q, \omega) \). We assume Thouless' criteria for the validity of equation (19) is the same as the pure system. Then the normal metal alloy becomes unstable when
\[
\mathcal{L}_0^{\text{imp}}(q, \omega) = \ln \left( \frac{2 \pi \omega}{\hbar c} \right)
\]  
(20)

The superconducting critical temperature is unchanged by nonmagnetic impurities.

The \( t \) matrix for two body scattering after impurity averaging can be defined in an analogous way to equation (10):
\[
\mathcal{L}^{\text{imp}}(q, \omega) = \mathcal{L}_0^{\text{imp}}(q, \omega) + \mathcal{L}_0^{\text{imp}}(q, \omega) \mathcal{T}^{\text{imp}}(q, \omega) \mathcal{L}_0(q, \omega)
\]  
(21)

From equation (18b) \( \mathcal{T}^{\text{imp}}(q, \omega) \) is given by
\[
\mathcal{T}^{\text{imp}}(q, \omega) = \frac{1}{1 - \mathcal{L}_0^{\text{imp}}(q, \omega)}
\]  
(22)
In Chapter VI we shall need the analogous matrix for magnetic impurities to study superconducting fluctuations in dilute magnetic alloys.

IV. Critical Temperature of Superconductors Containing Magnetic Impurities

The exchange interaction between a magnetic impurity and the conduction electrons of a simple, isotropic superconductor leads to a non-conservation of conduction electron spin. This decreases the correlation distance $\xi_0$ of a Cooper pair and may lead to a decrease in the superconducting critical temperature. It is assumed the magnetic impurities scatter the electrons elastically and do not change any other properties of the pure metal (e.g. density of conduction electron states).

The interaction between conduction electrons and magnetic impurities is introduced by adding to the B.C.S. Hamiltonian of equation (1) the term

$$\hat{V}(\mathbf{r}) = V_i(\mathbf{r}) + \mathbf{J} \hat{s} \cdot \hat{S}$$

(23)

where $\hat{s}$ is the impurity spin, $\hat{S}$ is the conduction electron spin, $\mathbf{J}$ is the exchange integral and $V_i(\mathbf{r})$ describes potential scattering from the magnetic impurity.

Abrikosov and Gor'kov (1961) have used a Green's function method to derive a self consistent equation for the order parameter $\Delta(\mathbf{r})$ of a superconductor containing a small concen-
Averaging over impurity positions gives

\[
\langle \Delta^*(T) \rangle_{av} \delta_{\mathbf{q}, \mathbf{q}'} = \frac{1}{Z} k T \sum_{\omega_m} K_{\omega_m}(T) \langle \Delta^*(T') \rangle_{av} d^3 r' \tag{24}
\]

where \(\langle \Delta^*(T) \rangle_{av}\) is the impurity averaged superconducting order parameter (Gor'kov 1958), \(\mathbf{q}_{\mathbf{q}, \mathbf{q}'} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\)

\[
K_{\omega_m}(T; T') \delta_{\mathbf{q}, \mathbf{q}'} = \langle G_{k \mathbf{q}}(T; T'; -\omega_m) \delta_{\mathbf{r}, \mathbf{r}'} G_{k \mathbf{q}}(T; T'; \omega_m) \rangle_{av} \tag{25}
\]

\(G_{k \mathbf{q}}(T; T'; \omega_m)\) is the Fourier transform of the single particle temperature Green's function and \(\mathbf{r}, \mathbf{r}'\) are spin indices. The rules for averaging over impurity positions are the same as in Appendix B. However, with the introduction of an exchange interaction it is necessary to average over the orientations of the impurity spin \(\mathbf{S}\). Abrikosov and Gor'kov treat the spin classically to obtain

\[
\langle \mathbf{S} \rangle_{av} = 0 \quad \langle S_i S_j \rangle_{av} = \frac{1}{3} S(S+1) \delta_{ij} \tag{26}
\]

for uncorrelated spins.

After averaging over impurity positions and spin orientation, Abrikosov and Gor'kov obtain an integral equation for the Fourier transform \(K_{\omega_m}(\mathbf{p}_1; \mathbf{p}_2)\). For a translationally invariant system, the solution to the integral equation is

\[
K_{\omega_m}(\mathbf{p}_1; -\mathbf{p}_1) = \hat{G}(\mathbf{p}_1, \omega_m) \hat{G}(-\mathbf{p}_1, -\omega_m) \left[ 1 + \frac{1}{2 \mathcal{V}_n \omega_m m_s} \right] \tag{27}
\]
where \( \hat{G}(p, \omega_n) = \left( \epsilon \omega_n + \frac{i}{2 \gamma} \frac{\omega_n}{|\omega_n|} - \epsilon_p \right)^{-1} \) is the impurity averaged single particle Green's function

\[
m_s = 1 + \frac{1}{\omega_n} \cdot \left( \frac{1}{\gamma_s} \right)^{A,s} \cdot \frac{1}{\epsilon} = \frac{m_s m p_F}{(2 \pi)^3} \int d \Omega_q \left\{ |V_q(q)|^2 - \frac{1}{4} J \gamma^s (S^s) \right\} \cdot \left( \frac{1}{\gamma_s} \right)^{A,s} = \frac{1}{\gamma} - \frac{1}{2 \gamma_0}
\]

(28)

\( m_s \) is the volume density of magnetic impurities and \( p_F \) is the Fermi momentum. The expression \( \left( \frac{\epsilon}{\gamma_s} \right)^{A,s} \to 0 \) is the conduction electron spin lifetime in the normal state.

Equation (27) for \( K w_n (P_0 - P_1) \) is used in equation (24) to obtain an equation for the critical temperature of a superconductor containing a small amount of magnetic impurity. Abrikosov and Gor'kov obtain

\[
\ln \left( \frac{T_0}{T_c} \right) = \psi \left( \frac{1}{2} \right) + \frac{1}{2 \pi K T_c} \left( \frac{1}{\gamma_s} \right)^{A,s} - \psi \left( \frac{1}{2} \right)
\]

(29)

where \( K T_{c0} = 1.14 |w_0| \exp \left\{ - \frac{1}{|q_0| N(\infty)} \right\} \) is the critical temperature of the pure metal and \( \psi(z) \), the digamma function, is the logarithmic derivative of Euler's Gamma function (Morse and Feshbach 1953).

Equation (29) predicts the decrease in the superconducting critical temperature as the concentration of magnetic impurity is increased. For \( m_s \ll 1 \) the initial decrease in the superconducting critical temperature is given by
As the concentration of magnetic impurity is increased, the correlation length \( \xi_0 \) of the Cooper pairs becomes smaller. This causes \( \langle \Delta'(\mathcal{T}) \rangle_0 \) to decrease. Eventually superconductivity is destroyed i.e. \( T_c \rightarrow 0 \) at a critical concentration \( m_1^c \) given by

\[
T_c = T_{c0} - \frac{\pi}{4} \left( \frac{1}{\xi_0} \right)^{A,G}.
\]  

(30)

where \( \Delta_o \) is the order parameter of the pure superconductor. Note \( \left( \frac{1}{\xi_0} \right)^{A,G} \) is directly proportional to \( m_1 \) [see equation (28)].

Abrikosov and Gor'kov used the first Born approximation for the scattering of conduction electrons from a classical spin to obtain the conduction electron exchange scattering rate \( \left( \frac{1}{\xi_0} \right)^{A,G} \). The first Born approximation does not distinguish between ferromagnetic and anti-ferromagnetic exchange. As already noted, the quantum mechanical treatment of the local spin leads to a temperature dependence in the exchange scattering rate in the second Born approximation. The inclusion of the temperature dependence and the distinction of ferromagnetic and anti-ferromagnetic exchange modifies Abrikosov and Gor'kov's results. This is important for a superconducting alloy that displays the Kondo effect in the normal state. This is described in Chapter IV.
PART TWO: SUPERCONDUCTIVITY AND THE KONDO EFFECT

I. Superconductivity as a Probe

One may look at superconductivity and the Kondo effect from two points of view. The first is to use the Kondo effect to probe the superconducting state of metals. The second is to use superconductivity as a probe to study the effects of exchange scattering (Kondo effect) in dilute magnetic alloys. We shall use the second point of view in our study of superconducting alloys.

II. Exchange and Potential Scattering

Suppose a superconductor contains a small amount of simple metal impurities. Each electron will be scattered by the impurity potential. Momentum is conserved after all quantities are averaged over impurity positions. A Cooper pair of electrons in states \( (\uparrow; \downarrow) \) will be scattered to another Cooper pair state \( (\uparrow'; \downarrow') \). There is no diminishing in the number of Cooper pairs. The superconducting critical temperature of the alloy is the same as that of the host metal.

Let the superconductor, still assumed to be a simple metal, contain magnetic impurities. The electrons in a Cooper pair undergo potential and exchange scattering from the impurities. Potential scattering causes no diminishing in the number of Cooper pairs. However, the exchange scattering leads to a
non-conservation of electron spin. The momenta of the final states of a Cooper may be \((\mathbf{k} + \mathbf{q}, -\mathbf{k} - \mathbf{q})\) after averaging all quantities over impurity position, but the spin of the pair may no longer form a singlet. The exchange interaction acts as a pair breaker. A decrease in the number of pairs lead, for example, to a depression in the superconducting critical temperature of the host metal and to the destruction of superconductivity at low impurity concentrations.

III. Quantum Mechanical Treatment of Exchange Scattering

(a) Normal State

The quantum mechanical treatment of a localized, impurity spin in a simple metal host leads to an anomalous temperature dependence in the conduction electron exchange scattering rate. These scattering rates, spin flip and non-spin flip, are given in equations II-(21) and II-(23) from Hamman's approximate t matrix.

(b) Initial Decrease in the Critical Temperature for Superconductors Containing Small Amounts of Magnetic Impurity

The initial decrease in the critical temperature of a superconductor containing a small amount of magnetic impurities depends on the conduction electron spin flip scattering rate at the critical temperature \(T'_c\) of the host metal. The spin flip scattering rate is maximum at the Kondo temperature \(T'_k\) [equation II-(20)] and is small for \(T'_k << T'_c\) and \(T'_k >> T'_c\).
The initial decrease in the superconducting critical temperature is largest for $T_{co} \approx T_k'$. Since the magnitude of $T_k'$ is proportional to $\exp \left\{ \frac{\text{Sign } J}{2|J|N(0)} \right\}$ for $|J|N(0) \ll 1$ we can determine which sign the exchange constant $J$ must have in order for $T_{co} \approx T_k'$. We note that $T_k' \approx T_k$ for $|J|N(0) \ll 1$.

(i) $J > 0$

For positive $J$ one sees that $\exp \left\{ \frac{1}{2|J|N(0)} \right\}$ is a very large number. The Kondo temperature $T_k'$ is expected to be very much larger than $T_{co}$. The thermal energy $K_{T_{co}}$ of the conduction electrons is much less than the energy $K_{T_k'}$ of the spin flip scattering resonance. At $T_{co}$ spin flip scattering will be small; the initial decrease in the superconducting critical temperature will be small.

(ii) $J < 0$ (Kondo Effect)

For negative $J$ such that $|J|N(0) \ll 1$, $\exp \left\{ -\frac{1}{2|J|N(0)} \right\}$ is a small number. Hence the Kondo temperature $T_k'$ can be the same order of magnitude as $T_{co}$. For some value of $|J|N(0)$, the thermal energy $K_{T_{co}}$ of the conduction electrons will equal the energy $K_{T_k'}$ of the spin flip scattering resonance. The initial decrease in the superconducting critical temperature will be large in this case.

(c) Decrease in the Superconducting Critical Temperature for a Finite Concentration of a Magnetic Impurity

We shall be interested in the superconducting critical temperature $T_c$ as a function of increasing magnetic impurity
concentration. It is assumed that there is no disruption of the host lattice. The situation of antiferromagnetic exchange will be the only one considered. The superconducting critical temperature depends on the spin flip scattering rate at $T_c$ (Griffin 1965). For simplicity, we use the spin flip scattering rate in the normal state [equation II-(23)] to obtain an understanding of the decrease in the superconducting critical temperature. This is reasonable since most conduction electrons are normal at $T_c$.

Suppose the superconducting critical temperature $T_{co}$ of the host metal is less than $T'_k$. The superconducting critical temperature $T_c$ of the alloy is expected to be a smoothly decreasing function of increasing magnetic impurity concentration. If $T'_k \gtrsim T_{co}$ the initial decrease in the superconducting critical temperature is large. As the concentration of magnetic impurity is increased the superconducting critical temperature decreases smoothly. When $T'_k < T_{co}$ there is some finite concentration of magnetic impurity where $T_c \gtrsim T'_k$. The decrease in the superconducting critical temperature as the concentration of magnetic impurity is increased will be enhanced by the spin flip scattering resonance at $T'_k$. For $T'_k \gg T_c$, the superconducting critical temperature decreases monotonically as the concentration of magnetic impurity is increased.
From these simple considerations of antiferromagnetic exchange we see that the critical temperature of a superconductor containing magnetic impurities can change in three ways depending on the ratio $T_k'/T_{co}$. This property is of central interest to this thesis.

In the next sections we shall outline several previous studies of superconductors containing magnetic impurities. These studies calculate the initial decrease in the superconducting critical temperature for $T_k'/T_{co} \gg 1$, $T_k'/T_{co} = 1$ and $T_k'/T_{co} \ll 1$. The results of these calculations will be very important to our study of the critical temperature of a superconductor containing a finite amount of magnetic impurity.

IV. Superconductivity and the Kondo Effect

We consider the system of a superconductor containing magnetic impurities. The Hamiltonian we use is written,

$$H = H_0 + H_{BCS} + H_{S-\Delta}$$

(32)

$H_0$ is the kinetic energy of the electron gas given by

$$H_0 = \sum_{\vec{g},\vec{s}} \epsilon_{\vec{k}} C^{\dagger}_{\vec{g}\vec{s}} C_{\vec{g}\vec{s}}$$

(33)

where $C^{\dagger}_{\vec{g}\vec{s}}$ is the creation operator for an electron of momentum $\vec{k}$, energy $\epsilon_{\vec{k}}$ and spin $\vec{\sigma}$. $H_{BCS}$ is the superconducting pairing interaction [equation (1)] given by
\[ H_{s.d.} = -J \sum_{i=1}^{N} \sum_{\ell \neq \ell'} C_{\ell \ell}^+ C_{\ell' \ell}^- C_{\ell' \ell}^- C_{\ell \ell}^+ \]  

(34)

\( H_{s.d.} \) describes the exchange interaction between the conduction electrons and the impurity spin \([\text{equation II-(3)}] \); Kondo 1969:

\[ H_{s-d} = -J \sum_{\ell=1}^{N} \sum_{i \neq j} C_{\ell \ell}^+ C_{\ell' \ell}^- (\mathbf{S} \cdot \mathbf{S}) e^{-i(\mathbf{K} - \mathbf{K}')} \]  

(35)

where \( \mathbf{R}_i (i=1, N) \) is the position of the magnetic impurities and \( J \), the exchange constant (Chapter II), is chosen to be negative. We neglect potential scattering from the impurity.

V. Initial Decrease in the Superconducting Critical Temperature

(a) Perturbation Technique

Solyom and Zawadowski (1969) have extended Abrikosov and Gor'kov's treatment of exchange scattering in superconductors to include the Kondo effect. Abrikosov's pseudo-Fermion representation (Chapter II) has been used to describe the interaction between the conduction electrons and the magnetic impurity. Solyom and Zawadowski have obtained for the Fourier transform of the kernel \( K_{\omega_m}(T, T') \) \([\text{equation (25)}] \) the following integral equation:

\[ K_{\omega_m}(p_1, p_2) = \mathcal{G}(p_1, \omega_m) \mathcal{G}(p_2, \omega_m) \int d^2p d^2p' \sum_{m'} V_{d\gamma \alpha p} (\omega_m, \omega_{m'}) \]  

\[ \times \mathcal{K}_{\omega_{m'}}(p_1, p_2, p_3, p_4) d^3p d^3p' \]  

(36)
\( \mathcal{G}(\varphi, \omega_m) \) is the impurity averaged normal electron Green's function given by

\[
\mathcal{G}(\varphi, \omega_m) = \left( \omega_m + \frac{1}{2\tau} \frac{\omega_m}{|\omega_m|} - \varepsilon_\varphi \right)^{-1} \tag{37}
\]

where the electron energy \( \varepsilon_\varphi \) is measured from the Fermi surface and \( \frac{1}{\tau} \) is the single particle relaxation rate due to exchange scattering. We have from Abrikosov (1965) to logarithmic accuracy \( T \gg T' \) (Chapter II, Abrikosov's Method).

\[
\frac{1}{2\tau} = m_0 J^2 S(St) \pi \left( \frac{2Z}{\Delta} \right) \left( 1 - \frac{2Z J}{\Delta^2} \ln \frac{T}{T_k} \right)^{-2} \tag{38}
\]

\( \nu_{\varphi \lambda \rho}(\omega_m, \omega_m') \) is an electron-electron interaction induced by the scattering of electrons from the magnetic impurity.

Solyom and Zawadowski approximate \( \nu_{\varphi \lambda \rho}(\omega_m, \omega_m') \) by an elastic scattering term \( \omega_m = \omega_m' \) (figure 6) and an inelastic scattering term \( \omega_m \neq \omega_m' \) (figure 7):

\[
\nu_{\varphi \lambda \rho}(\omega_m, \omega_m') = \left\{ \nu_{\varphi \lambda \rho}^{\text{elastic}}(\omega_m) \delta_{m,m'} + \nu_{\varphi \lambda \rho}^{\text{inelastic}}(\omega_m, \omega_m')(1 - \delta_{m,m'}) \right\} \tag{39}
\]

The exchange scattering vertex function \( \Gamma_T \) is given to logarithmic accuracy (Abrikosov 1965) by

\[
\Gamma_T = \frac{J}{\ln \frac{T}{T_k}} \ \hat{\sigma} \cdot \mathcal{S} \tag{40}
\]

where \( \hat{\sigma} \) is the host valence. Using this vertex one has \( \nu_{\varphi \lambda \rho}(\omega_m, \omega_m') \) to leading logarithmic order. This limits our consideration to the region \( T_{\text{co}} \gg T'_k \).
Figure 6

Figure 7
The elastic scattering was first studied by Abrikosov and Gor'kov (1961) in the Born approximation. Griffin (1965) extended the elastic scattering term to higher order to take into account the Kondo effect.

The superconducting critical temperature can be written from equation (24) as

$$\ln\left(\frac{T_\text{c}}{T_\text{c}}\right) = \sum \frac{\pi K T_\text{c}}{|\omega_m|^c} (1 - 2 |\omega_m|^c K_{\omega_m})$$

(41)

where $$\omega_m^c = (2m+1)\pi K T_\text{c}$$ and

$$K_{\omega_m} = \frac{1}{2\pi} \int K_{\omega_m}(p', -p) d\epsilon_p$$

(42)

Solyom and Zawadowski solve for $$K_{\omega_m}$$ to lowest order in the concentration $$\mathfrak{m}$$ of magnetic impurity. Their resulting equation for the superconducting critical temperature is the sum of contributions from the elastic and inelastic parts of $$V_{d\delta}$$ [equation (39)]. Since $$V_{d\delta}$$ is of higher order in $$J$$ than $$V_{\text{elastic}}$$, the superconducting critical temperature is determined by the elastic scattering of electrons from the magnetic impurity. This gives a linear decrease (to lowest order in impurity concentration $$\mathfrak{m}$$) in the superconducting critical temperature with increasing impurity concentration.

If we wish to study the region $$T_\text{c} \approx T_k$$ we must know the vertex function for exchange scattering to greater than logarithmic accuracy. This can be accomplished by the use
of Hamman's $t$ matrix [equation II-(20)] for the exchange scattering of conduction electrons.

(b) **Extension of Nagaoka's Green's Function Method to Include Superconductivity**

Zuckermann (1968) has extended Nagaoka's treatment of simple metals containing a single magnetic impurity to include the case of an isotropic superconducting host. The decoupling of the equations of motion for the retarded double-time Green's function (Zubarev 1960) is extended to include superconducting correlations. Such a term would be the quantity $\langle s c \gamma \gamma \rangle$ describing the breaking of a Cooper pair. The resulting equations of motion may be written using the Nambu-Schreiffer (1964) matrix formalism for superconductivity as

$$\hat{G}_{kk'}(\omega_m) = \hat{G}_{0k}(\omega_m) \left\{ \frac{\delta_{kk'}}{2\pi} + \hat{t}(\omega_m) \hat{G}_{0k'}(\omega_m) \right\}$$

where $\hat{G}_{kk'}(\omega_m)$ is the 2 x 2 matrix Green's function for superconducting electrons, $\hat{G}_{0k}(\omega_m) = (\omega_m \mathbb{1} - \varepsilon_k \gamma_3 - \Delta \gamma \gamma)^{-1}$, $\gamma_i$ is the $i$th Pauli matrix, $\mathbb{1}$ is a 2 x 2 unit matrix, $\hat{t}(\omega_m)$ is a 2 x 2 $t$-matrix for exchange scattering electrons from a single magnetic impurity and

$$\Delta = |q| \sum_k \langle \gamma \gamma \rangle \langle C^+_k \Delta C^+_{-k} \rangle$$

The off diagonal matrix elements of $\hat{G}_{kk'}$ represent Cooper pairing.
For a finite concentration $m_\text{z}$ of magnetic impurity the matrix Green's function $\hat{G}_{kk'}(\omega_\text{m})$ must be replaced by its average over impurity positions (Rickayzen 1964)

$$\langle \hat{G}_{kk'}(\omega_\text{m}) \rangle_\text{av} = \hat{G}_k(\omega_\text{m}) \delta_{kk'} = (\omega_\text{m} \mathbb{1} - \varepsilon_k \gamma_3 - \Delta \gamma_1 - m_\text{z} \hat{t}(\omega_\text{m}))^{-1} \delta_{kk'} \tag{45}$$

This form of $\langle \hat{G}_{kk'}(\omega_\text{m}) \rangle_\text{av}$ implies it is possible to write the matrix self-energy for exchange scattering as $m_\text{z} \hat{t}(\omega_\text{m})$.

Zuckermann uses the well known ansatz

$$\hat{G}_k(\omega_\text{m}) = (i \omega_\text{m} Z_\text{m} \mathbb{1} - \varepsilon_k \gamma_3 - \Delta_\text{m} \gamma_1)^{-1} \tag{46}$$

where $Z_\text{m}$ and $\Delta_\text{m}$ are functions of $\omega_\text{m}$. To obtain the correct $t$-matrix for a finite concentration of magnetic impurity, $\hat{t}(\omega_\text{m})$ must be expressed as a functional of $\hat{G}_k(\omega_\text{m})$.

This is simply done by replacing the functional dependence of $\hat{t}(\omega_\text{m})$ on $\hat{G}_{kk'}(\omega_\text{m})$ for the case of a single magnetic impurity by the same functional dependence on $\hat{G}_k(\omega_\text{m})$.

This substitution gives a set of self-consistent equations for $Z_\text{m}$ and $\Delta_\text{m}$ that may be summarized as

$$(\omega_\text{m}(Z_\text{m} - 1) \mathbb{1} + (\Delta_\text{m} - \Delta) \gamma_1 = m_\text{z} \hat{t}(\omega_\text{m}) \tag{47}$$

where $\hat{t}(\omega_\text{m})$ is a functional of $\hat{G}_\text{k}(\omega_\text{m})$.

Zuckermann finds $Z_\text{m}$ and $\Delta_\text{m}$ to lowest order in $m_\text{z}$. These lowest order solutions enable him to find the initial change in the superconducting critical temperature with increasing $m_\text{z}$. To find the change in the superconducting
critical temperature for all values of $T_k$, Zuckermann uses Hamman's matrix for exchange scattering in the normal state. He obtains

$$\ln \left( \frac{T_{c0}}{T_C} \right) = \frac{m^2}{2 \pi^2 k T_C N(0)} \sum_{m>0} \frac{(2m+1)^2 \pi^2 T_C N(0)}{m^2 (2m+1)^2} \left( \frac{2}{m^2} \right) \frac{X_m}{T_C} \left( \frac{T}{T_C} + \frac{1}{2} \right)$$

where $X_m = \frac{(2m+1)^2 \pi k T_C}{T_k}$ and $\Psi(2m+1) = \Psi(2m+1) - \Psi(\frac{1}{2})$

We see that the initial decrease is greatest for $T_{c0} = T_k$ and smallest for $T_{c0} < T_k$ or $T_{c0} > T_k$.

When $T_{c0} > T_k$ equation (48) reduces to the results of Solyom and Zawadowski if the lowest powers in $(\ln X_m)^{-1}$ are retained. The second term in the brackets of equation (48) is the contribution from the inelastic scattering of electrons from the magnetic impurities (figure 7). It is small compared to the first term arising from the elastic scattering of electrons (figure 6) for all ratios of $(T_{c0} / T_k)$.

For a finite concentration of magnetic impurity we expect that elastic electron scattering will dominate inelastic electron scattering. In Chapter IV we shall use the elastic scattering of electrons from magnetic impurities to obtain an expression for the superconducting critical temperature as a function of $m_x$.

VI. Solution of Nagaoka's Equations for Superconducting Host Below $T_C$

For temperatures below $T_C$, $\hat{\xi}(\omega_n)$ must be found by solving an integral equation constructed in the same manner as
Hamman's integral equation for the normal metal t-matrix.

Müller-Hartmann and Zittartz (1970) have solved this integral equation for the case of a single magnetic impurity.

The t matrix they obtained has a pole for real energies \( \epsilon \) such that \(-\Delta \leq \epsilon \leq \Delta\). For \( J < 0 \), the pole appears near \( \Delta \) for \( T_k' \ll T_{co} \) and near \(-\Delta\) for \( T_k' \gg T_{co}\). When \( T_k' = T_{co} \) the pole appears at the Fermi surface (zero energy). The appearance of a pole in the t matrix signifies the existence of a collective bound state centered at the impurity. For a finite concentration of magnetic impurity it would appear as an impurity band (Shiba 1968). For \( T_k' \gg T_{co} \) and \( T_k' \ll T_{co} \) it would be near the gap edges. However, for \( T_k = T_{co} \) it would be in the center of the gap. This is the most striking aspect of the Kondo effect in superconductors.

Müller-Hartmann and Zittartz (1970) use their t matrix to calculate the initial decrease in the superconducting critical temperature. Their results are equivalent to Solyom and Zawadowski's perturbational treatment and Zuckermann's Green's function treatment.
CHAPTER IV
THE CRITICAL TEMPERATURE OF SUPERCONDUCTING ALLOYS

I. Introduction

Abrikosov and Gor'kov (1961) have treated the problem of magnetic impurities in superconductors for concentrations of magnetic impurity less than or equal to the critical concentration \(n^c_I\) [equation III-(31)] above which superconductivity vanishes. However, their Born approximation treatment omitted the Kondo effect. In Chapter III, we have seen that several authors (Griffin 1965, Solyom and Zawadowski 1969, Zuckermann 1968, Mueller-Hartmann and Zittartz 1970) extended the problem of magnetic impurities in superconductors to include the Kondo effect. These authors have evaluated the critical temperature of superconducting, Kondo alloys in the region of low impurity concentration. It is the purpose of this chapter to examine the critical temperature of superconducting, Kondo alloys as a function of increasing impurity concentration. The expression for the superconducting critical temperature is obtained by applying Abrikosov's diagrammatic method to superconductivity. The perturbation series for the impurity induced electron-electron interaction of Solyom and Zawadowski (1969) is extended to all values of \(T'_k\) by using Hamman's \(t\) matrix [equation II-(20)] for
the exchange scattering of conduction electrons by the impurity. The resulting expression for the superconducting critical temperature, valid for all values of $T'_k$, has the same form as the Born approximation result of Abrikosov and Gor'kov (1961), but the conduction electron scattering rate is frequency dependent as a consequence of the Kondo effect. Curves of the superconducting critical temperature versus magnetic impurity concentration are evaluated for several values of $(T'_c/T'_k)$ (see Chapter III) and compared to the experimental data on Th-U and Al-Mn (Maple et al. 1970, Caplin and Rizzutto 1968).

II. The Superconducting Critical Temperature

The Hamiltonian describing the magnetic alloy is given by

$$H = H_0 + H_{\text{B.C.S.}} + H_{s-d}$$  \hspace{1cm} (1)

where $H_0$ is the Hamiltonian for a free electron gas [equation III-(33)], $H_{\text{B.C.S.}}$ is the superconducting pairing Hamiltonian [equation III-(34)] and $H_{s-d}$ describes the conduction electron-impurity spin exchange interaction [equation III-(35)]. Using this Hamiltonian, Abrikosov and Gor'kov (1961) derived the following integral equation for the impurity averaged order parameter

$$\langle \Delta^a(\mathbf{r}) \rangle_{q_0} g_{q_0} = \frac{1}{q_0 ! K T} \int K_{\omega_n(\mathbf{r},\mathbf{r}')} g_{q_0} \langle \Delta^a(\mathbf{r}') \rangle_{q_0} d^3 \mathbf{r}'$$  \hspace{1cm} III-(24)
where \( \Phi_{AB} = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \) and

\[
K_{\omega m}(T;\Gamma')\Phi_{AB} = \left\langle G_\omega(\Gamma;\Gamma';-\omega_m)G_{\lambda\phi}(\Gamma;\Gamma';\omega_m) \right\rangle_{\alpha\nu}
\]

is the impurity averaged product of two single particle temperature Green's functions. Griffin (1965) and Solyom and Zawadowski (1969) have extended the work of Abrikosov and Gor'kov to higher order in perturbation theory to obtain the following integral equation for the Fourier transform \( K_{\omega m}(\phi_1;\phi_2) \):

\[
K_{\omega m}(\phi_1;\phi_2)\Phi_{AB} = \mathcal{G}(\phi,\omega_m)G(\phi_2-\omega_m)\Phi_{AB} + \frac{m\pi}{(2\pi)^3} KT \sum_{\omega_n} \int d^3p \left| V_{\phi\phi\phi}(\phi_1;\phi_2)\Phi_{AB} K_{\omega m}(\phi_1;\phi_2;\phi_2') \right|
\]

where \( \mathcal{G}(\phi,\omega_m) \) is the electron Green's function for a normal metal averaged over impurity sites [equation III-(37)] and \( V_{\phi\phi\phi}(\omega_m;\omega_m') \) is an electron-electron interaction induced by the exchange scattering of electrons from the magnetic impurity.

The dominant contribution to \( V_{\phi\phi\phi}(\omega_m;\omega_m') \) is given in figure (8) (Solyom and Zawadowski 1969). This diagram can be written as

\[
V_{\phi\phi\phi}(\omega_m;\omega_m') = \frac{\hbar}{\lambda S T} \sum_{\omega_n,\omega} G_{\text{imp}}(i\omega_n) G_{\text{imp}}(i\omega, i\omega_m - i\omega_m')
\]

\[
x \Gamma_{\phi\phi\phi}(i\omega_n; i\omega, i\omega_m - i\omega_m') \Phi_{\phi\phi\phi}(i\omega_n; i\omega_m - i\omega_m', i\omega', i\omega')
\]

\( G_{\text{imp}}(\omega_n) \) is the Green's function for the pseudo-Fermion representing the impurity spin (Abrikosov 1965). \( \Gamma_{\phi\phi\phi} \) is the total amplitude for scattering conduction electrons from a single magnetic impurity via the s-d exchange interaction [equation III-(35)].
Mattuck and Cheung (1970) have shown that Hamman's approximate solution to Nagaoka's equations (Chapter II) can be obtained from diagrammatic theory by renormalizing the electron Green's function $G(\omega_m)$ only. The pseudo-Fermion Green's function is unchanged in this renormalization scheme. In consequence, equation (2) for $V_{\delta m,\lambda}(\omega_m;\omega')$ can be used for $T < T'$ provided the scattering amplitude $\Gamma_{\delta m,\lambda}$ is evaluated using Hamman's approximation.

The electron-electron interaction $V_{\delta m,\lambda}(\omega_m;\omega')$ can be written as the sum of an elastic part $(\omega_m=\omega')$ and an inelastic part $(\omega_m \neq \omega')$:

$$V_{\delta m,\lambda}(\omega_m;\omega') = V_{\delta m,\lambda}^{\text{elastic}}(\omega_m)\delta_{m,m'} + V_{\delta m,\lambda}^{\text{inelastic}}(\omega_m;\omega')(1-\delta_{m,m'}) \tag{3}$$

Zuckermann's result [equation III-(48)] shows the inelastic contribution to the initial slope $\left(\frac{\partial T_c}{\partial m}\right)_{m=0}$ is small for all values of $T'$. We can, therefore, replace $V_{\delta m,\lambda}$ by $V_{\delta m,\lambda}^{\text{elastic}}$ in the integral equation [equation III-(36)] for $K_{\omega_m}(P_1;P_2)$. In this approximation equation (2) becomes

$$V_{\delta m,\lambda}^{\text{elastic}}(\omega_m) = \frac{-e}{2} kT \sum_{\omega_n} \left[G_{\text{imp}}(i\omega_n)\right]^2$$

$$\times \Gamma_{\delta m,\lambda}(\omega_m; i\omega_n) G_{\text{imp}}(-i\omega_n; i\omega_n) \Gamma_{\delta m,\lambda}(i\omega_n; i\omega_n) \Gamma_{\delta m,\lambda}(i\omega_n; i\omega_n)$$

where $G_{\text{imp}}(i\omega_n) = \left(i\omega_n-\lambda'\right)^{-2}$ and $\lambda'$ is the pseudo-Fermion energy. The total scattering amplitude $\Gamma_{\delta m,\lambda}$ can be written in terms of the non-spin flip scattering amplitude $\Gamma_\delta$ and the spin flip scattering amplitude $\Gamma_\lambda$ as
where the identity has been used.

In the regions where the analytic continuation \( i\omega \to z \) is valid the summation over imaginary frequencies \( i\omega \) in equation (6) can be transformed to a contour integral around the singularities of the summand (figure 9). Solyom and Zawadowski (1969) have shown the important contribution to \( V^{\text{elastic}}(\omega_m) \) comes from the double pole of \( G_{\text{imp}}(z) \) at \( z = \lambda' \).

Calculating the residue of this double pole gives

\[
V^{\text{elastic}}(\omega_m) = (KT(1+\text{e}^{-\lambda'\omega}))^{-1} \left\{ \Gamma_0(i\omega_m;\lambda) \Gamma_0(-i\omega_m;\lambda) \delta_{d\lambda} \delta_{q\phi} \right. \\
\left. + \Gamma_1(i\omega_m;\lambda) \Gamma_1(-i\omega_m;\lambda) \cdot \frac{1}{3} S(St) \delta_{d\lambda} \delta_{q\phi} \right\} 
\]

In order to project out the spurious pseudo-Fermion states we must take the limit \( \lambda' \to \infty \). Equation (8) then becomes

\[
V^{\text{elastic}}(\omega_m) = (KT)^{-1} \left\{ \Gamma_0(\omega_m) \delta_{d\lambda} \delta_{q\phi} \cdot \frac{1}{3} S(St) \Gamma_1(\omega_m) \delta_{d\lambda} \delta_{q\phi} \right\} 
\]
Figure 9
For future use we define the function $\mathcal{V}(\omega_m)$ as follows:

$$\mathcal{V}_{\text{elastic}}^{\text{total}}(\omega_m)q_{dq} = -(KT)^{-1} \mathcal{V}(\omega_m)q_{dq}$$

(10)

where

$$\mathcal{V}(\omega_m) = S(S+1) |\Gamma_{1}(\omega_m)|^2 - |\Gamma_{0}(\omega_m)|^2$$

(11)

and the identity $(\partial_{q_{d}} \cdot \partial_{q_{f}}) q_{dq} = -3q_{dq}$ has been used. Also define $K(\omega_m)$ as follows:

$$K(\omega_m) = \frac{1}{(2\pi)^3} \int K(\omega) \hat{q} \, d\varepsilon$$

III-(42)

Then from equations III-(36) and (10), $K(\omega_m)$ is given by:

$$K(\omega_m) = \frac{K_0(\omega_m)}{1 + 2\pi m \, N(0) \, \mathcal{V}(\omega_m) \, K_0(\omega_m)}$$

(12)

where

$$K_0(\omega_m) = \frac{1}{(2\pi)^3} \int |\mathcal{G}(\hat{q}, \omega_m)|^2 \, d\varepsilon$$

(13)

and $N(0)$ is the density of states of conduction electrons for one spin direction. $\mathcal{G}(\hat{q}, \omega_m)$ is given by

$$\mathcal{G}(\hat{q}, \omega_m) = (i\omega_m(1 + \frac{1}{\beta(\omega_m)} \cdot \frac{1}{\omega_m} - \varepsilon_\parallel)^{-1}$$

(14)

where $1/\beta(\omega_m)$ is the conduction electron exchange scattering rate given by Hamman's $t$ matrix, $\omega_m = (2m)(\pi KT)$ and $\varepsilon_\parallel$ is the kinetic energy of an electron of momentum $\hat{q}$ relative to the Fermi surface. Equations (13) and (14) give the following expression for $K(\omega_m)$:
Equation 111-(41) gives the following expression for the superconducting critical temperature:

\[
\ln \left( \frac{\tau_e}{T_c} \right) = \left[ \sum_{m>0} 2 \varphi(\omega_m) \left\{ (2m+1)(2m+1+\varphi(\omega_m)) \right\}^{-1} \right]_{T=T_c}
\]

where \( \varphi(\omega_m) \) is related to \( \nu_s(\omega_m) \) by:

\[
\varphi(\omega_m) = \left\{ \pi kT \nu_s(\omega_m) \right\}^{-1}
\]

Hence \( \varphi(\omega_m) \) is directly proportional to the impurity concentration. When \( \varphi(\omega_m) \) is determined from the first Born approximation we recover the results of Abrikosov and Gork'kov (1961).

The evaluation of the superconducting critical temperature as a function of \( m_e \) [equation (17)] requires the knowledge of \( \nu_s(\omega_m) \) and \( \sqrt{\nu_s(\omega_m)} \). These may be calculated from Mattuck and Cheung (1970). However, \( \nu_s(\omega_m) \) has been calculated by Zuckermann [equation III-(48)] using Hamman's \( t \) matrix. To lowest order in \( m_e \) equation (17) is

\[
\ln \left( \frac{\tau_e}{T_c} \right) = \frac{2}{\pi k T_c} \left[ \sum_{m>0} \frac{1}{\nu_s(\omega_m)} \frac{1}{(2m+1)^2} \right]_{T=T_c}
\]
Comparison of equation (19) with equation III-(48) gives the following results for $\varrho(\omega_m)$:

$$\varrho(\omega_m) = \frac{\mathcal{M}_\tau}{2\pi^2 K T N(0)} \left\{ \frac{\pi^3 S(S+1)}{\ln^2 \frac{\omega_m}{\sqrt{2}}} + \pi^2 S(S+1) \right\} \tag{20}$$

The behaviour of the superconducting critical temperature as a function of $\mathcal{M}_\tau$ is described by equations (17) and (20).

The simplest approximation is to replace $\varrho(\omega_m)$ by $\varrho(\omega_0)$ in equation (17). This gives

$$\ln\left(\frac{T_c}{T_c}\right) = \Psi\left(\frac{1}{2} + \frac{1}{2} \varrho\left(\frac{\mathcal{M}_\tau}{K T N(0)}\right)\right) - \Psi\left(\frac{1}{2}\right) \tag{21}$$

where $\Psi(z)$ is the digamma function (Morse and Feshbach 1953) and

$$\varrho\left(\frac{\mathcal{M}_\tau}{K T N(0)}\right) = \frac{\mathcal{M}_\tau}{2\pi^2 K T c N(0)} \left\{ \frac{\pi^3 S(S+1)}{\ln^2 \left(\frac{\mathcal{M}_\tau}{K T c}\right) + \pi^2 S(S+1)} \right\} \tag{22}$$

For large $\mathcal{M}_\tau$ we expect the superconducting critical temperature $T_c$ to approach zero (Abrikosov and Gor'kov 1961).

We can determine the behaviour of $T_c$ as a function of large $\mathcal{M}_\tau$ from the asymptotic behaviour $\Psi(z) \rightarrow \ln 2z$ for $z \rightarrow \infty$.

In the limit $T_c \ll \min \left( T_{co}, T_k \right)$, we obtain, for equation (21) from the asymptotic form of $\Psi(z)$ for $z \rightarrow \infty$, the expression

$$\ln\left(\frac{T_c}{T_c}\right) = \ln\left\{ \frac{\mathcal{M}_\tau}{2\pi^2 K T c N(0)} \left( \frac{\pi^2 S(S+1)}{\ln^2 \left(\frac{\mathcal{M}_\tau}{K T c}\right) + \pi^2 S(S+1)} \right) \right\} \tag{23}$$

We see that the $\ln T_c$ terms cancel on both sides of equation (23).
Solving for $\ln\left(\frac{\ell \gamma T_c}{T_k'}\right)$ from equation (23) we obtain

$$\Pi T_c = T_k' \cdot \exp\left\{-\left[\gamma S(S+1)\left(\frac{\gamma m_x}{2 \pi^2 K_{T_C} N(0)} - 1\right)^{1/2}\right]\right\}. \quad (24)$$

In consequence, $T_c$ is never identically zero for any finite concentration of magnetic impurity, but decays exponentially as $m_\downarrow \to \infty$. This is in contrast to the Born approximation result of Abrikosov and Gor'kov (1961) that predicts a critical concentration $m_x^c$ such that $T_c = 0$ for $m_\downarrow > m_x^c$.

We shall now analyze equation (21) for $T_c$ as a function of $m_x$ for different values of $(T_{co}/T_k)$ (see Chapter III). In particular, we shall be interested in $T_c$ as a function of $m_x$ for $T_{co}/T_k' > 1$. Also we shall fit equation (21) to the experimental results for the superconducting critical temperature of several non-magnetic alloys.

III. Numerical Results and Discussions

The variation of $T_c$ with magnetic impurity concentration shown in figure (10) was obtained by numerical methods from equations (21) and (22).

Curve A shows the results when $T_{k'}/T_{co} = 1$, curve B when $T_{k'}/T_{co} = 100$. The curves for $T_c$ are initially linear in $m_x$ after which they curve positively away from linearity. The above behaviour can be explained on the basis of Nagaoka's theory (Chapter II). For temperatures much less than $T_{k'}$, the impurity spin is compensated by a cloud of conduction electrons.
Figure 10
around the impurity site. The impurity can be regarded as essentially non-magnetic in this temperature regime. The compensation of the impurity spin results in the exponential tail in curves A and B [figure (10)] when $T_c/T_{co} \ll 1$.

When $T_k/T_{co} = 0.01$, the results are shown in curve C. $T_c$ versus $M_T$ is initially almost identical to the Born approximation result of Abrikosov and Gor'kov (1961) shown as the dashed line in figure (10). Both curves are initially linear in $M_T$ after which they curve negatively from linearity. However, when $T_c \approx T'_k$, curve C [figure (10)] exhibits a re-entrant behaviour and a small exponential tail when $T_c \ll T'_k$. The behaviour of curve C can be explained by Nagaoka's theory (Chapter II).

The Kondo temperature $T_k$ is energetically equivalent to the binding energy of the spin compensated state. In consequence for temperatures greater than $T_k$, the impurity spin is no longer compensated. The scattering of conduction electrons by the impurity spin then gives rise to the well known behaviour of dilute magnetic alloys, for example, the Kondo effect (logarithmic resistivity minimum) and the Born approximation theory of Abrikosov and Gor'kov (1961) for $T_c$ as modified by the Kondo effect (Griffin 1965). This explains the negative curvature deviation of curve C. When $T_c \approx T'_k$ (curve C), the resonance in the spin flip scattering leads to maximum in the breaking of Cooper pairs. In this temperature region, the metal becomes normal. The curve of $T_c$ versus $M_T$ exhibits a
re-entrant behaviour. When $T_c < T_k$ (curve C) we are again in the spin compensated (non-magnetic region). This results in the exponential tail in curve C when $T_c/T_c^o \ll 1$.

The above discussion suggests that the curves in figure (10) can be compared with experiment as follows:

(i) data for dilute, superconducting alloys whose impurities are magnetic can be analyzed in the limit $T_k/T_c^o < 1$ (curve C);

(ii) data for nearly magnetic alloys, that is, alloys exhibiting very weak magnetic effects, should be analyzed in the limit $T_k'/T_c^o \gg 1$ (curves A and B).

In figure (11) the variation of the superconducting critical temperature of Th-U with increasing Uranium concentration is shown (Th:$T_c^o = 1.36^0K$). The experimental curve (curve A) deviates positively from linearity with increasing Uranium concentration. A good fit to the experimental curve is obtained using equation (21). From our analysis we find that $S(S+1) = .72$ and $T_k = 42.5^0K$ (curve B). In figure (12), the variation of the superconducting critical temperature of Al-Mn with increasing Mn concentration is shown (Al:$T_c^o = 1.17^0K$). A good fit to the experimental curve (curve B) is obtained using equation (21). From our analysis we find $S(S+1) = .137$ and $T_k = 54.6^0K$ (curve A). Both of these alloys are in the spin compensated state ($T_k'/T_c^o \gg 1$). The normal state properties of these alloys exhibit weak magnetic effects. In
particular, their residual resistivities exhibit non-logarithmic behaviour (Caplin and Rizzutto 1968, Maple et al. 1970). Such non-magnetic properties may be explained by assuming the local spin is compensated.

An alternative description of these alloys is to assume they are in the non-magnetic limit of the Anderson model (Anderson 1961). Kaiser (1970) has derived an equation for $T_c$ in these circumstances that fits the experimental data for Al-Mn and Th-U (Maple 1970). In consequence, there are two explanations for nearly magnetic alloys:

(i) the Kondo temperature is very large and the impurity spin is compensated or

(ii) the non-magnetic limit of the Anderson model applies.

Further experimental work is required to distinguish between these models.
Figure 11

TH-U

IMPURITY CONCENTRATION

10  9  8  7  6  5  4  3  2  1

\frac{T_2}{T_1}
CHAPTER V
THE PROXIMITY EFFECT

I. Introduction

When a superconductor is placed in contact with a simple, normal metal, tunnelling of electrons through the interface leads to superconducting correlations in the normal metal electrons. In these systems the spatially varying order parameter prevents a complete solution for normal-superconducting metal sandwiches. De Gennes and Guyon (1963) and Werthamer (1963) have been able to calculate the superconducting critical temperature for dirty normal metal and superconducting films where the electron mean-free path $l$ is smaller than the superconducting coherence length $\xi$.

Mc Millan (1968) has introduced a completely soluble model of the proximity effect for clean normal metal and superconducting films, for which the electron mean free path $l$ in each film is of the order of the film thickness. The contact between the normal metal and superconducting films is simulated by a model in which the conduction electrons tunnel through a potential barrier separating the films. Mc Millan assumes the superconducting properties to be constant across each film. For this model to be applicable, the thickness of each film has to be less than the corres-
ponding coherence length. McMillan was then able to calculate the superconducting properties of the system, e.g. the quasi-particle spectrum and the superconducting critical temperature for the sample.

The advantage of the proximity effect is the ability to induce superconductivity into metals that are non-superconducting in the bulk. This is particularly useful for the study of alloys that exhibit the Kondo effect (logarithmic resistivity minimum) e.g. Cu-Fe, Au-Fe, but are not superconducting in the bulk. Kaiser and Zuckermann (1970) have extended McMillan's model to include magnetic impurities in the normal metal film. They have treated the scattering of conduction electrons by the magnetic impurities in the Born approximation. It is our intention to extend the treatment of Kaiser and Zuckermann (1970) to include the Kondo effect. We shall derive an expression for the superconducting critical temperature for the metal sandwich containing magnetic impurities in the normal metal. Abrikosov's diagrammatic technique shall be used to calculate the electron self-energy in the superconducting state self-consistently to second order in the tunnelling Hamiltonian and the conduction electron-impurity exchange interaction. As in Chapter IV, the exchange scattering of conduction electrons by the impurities will be described by Hamman's t matrix given by equation II-(20). The resulting expression
for the superconducting critical temperature $T_c$ will be valid for all values of $T_k'$. Curves of $T_c$ versus the thickness of the superconducting film for a fixed concentration of magnetic impurity and normal metal film thickness will be plotted. The value of doing proximity effect experiments to study the Kondo effect will be discussed.

II. McMillan Model for Critical Temperature of the Superconducting Proximity Effect for Dilute Magnetic Alloys

(a) Self-Energy Equations

The physical system under consideration is shown in figure (13). The superconducting film is usually a high critical temperature superconductor: e.g. Pb. The normal metal film is a dilute magnetic alloy. Each film must be considered clean, i.e. the electron mean free path $\ell$ is of the same order as the film thickness and the coherence length $\xi$ is larger than the film thickness. In experiments, the films are made of the order $1000 \, \AA$ (Minnigerode 1966). It is now our purpose to derive self-consistent equations for the renormalized superconducting energy-gap functions in each film. The linearized solutions to these equations will help us determine the superconducting critical temperature of the sandwich.

The Hamiltonian for the above system is given by the McMillan tunnelling model as
\[ H = H_S + H_N + H_T \]  \hspace{1cm} (1)

(i) \( H_S \) is the Hamiltonian for the superconducting film given by

\[ H_S = H_{os} + H_{B.C.S}. \]  \hspace{1cm} (2)

where \( H_{os} \) is the kinetic energy of the conduction electrons in the superconducting film and \( H_{B.C.S.} \) is the superconducting interaction equation III-(34).

(ii) \( H_N \) is the Hamiltonian for the normal metal given by

\[ H_N = H_{ON} + H_{sd} \]  \hspace{1cm} (3)

where \( H_{ON} \) is the kinetic energy of the conduction electrons in the normal metal film and \( H_{sd} \) describes the exchange scattering of conduction electrons by the impurities [equation III-(35)]. The normal metal film is assumed to exhibit the Kondo effect in the bulk.

(iii) \( H_T \) is the transfer Hamiltonian (Cohen et al. 1962) describing the contact of the two films:

\[ H_T = T \sum_{m,m'} (c_{m \up}^+ b_{m' \up} + b_{-m \up}^+ c_{-m' \up}^+ ) + h.c. \]  \hspace{1cm} (4)

where \( c_{m \up}^+ \) creates an electron in state \( m \) and spin \( \up \) in the normal metal film and \( b_{m' \up}^+ \) creates an electron in state \( m' \) and spin \( \up \) in the superconducting film. The transfer matrix element \( T \) is assumed independent of the initial and final states \( m \) and \( m' \).
The Hamiltonian equation (1) is treated self-consistently to second order in both the transfer matrix element $T$ and the exchange constant $J$ [equation III-(35)] in the Nambu-Schreiffer (1964) formalism for superconductivity. The equations for the $2 \times 2$ matrix self-energies $\widehat{\Sigma}_N(i\omega_n)$ and $\widehat{\Sigma}_S(i\omega_n)$ for superconducting electrons in the normal and superconducting films are shown in figure (14). The double lines represent the full matrix propagators $\widehat{G}_N(i\omega_n)$ and $\widehat{G}_S(i\omega_n)$ for electrons in the normal and superconducting films and are given by

$$\widehat{G}_N(i\omega_n) = \left[ i\omega_n Z_N(i\omega_n) - \varepsilon_m \gamma_3 - \phi_N(i\omega_n) \gamma_1 \right]^{-1}$$

$$\widehat{G}_S(i\omega_n) = \left[ i\omega_n Z_S(i\omega_n) - \varepsilon_m' \gamma_3 - \phi_S(i\omega_n) \gamma_1 \right]^{-1}$$

where $I$ is the $2 \times 2$ unit matrix, $\gamma_1$ and $\gamma_3$ are Pauli matrices, $Z(i\omega_n)$ is the renormalization function, $\phi(i\omega_n)$ is the unrenormalized gap function and $\varepsilon_m$ is the energy of the $n^{th}$ one electron state. The exchange scattering of conduction electrons by the impurities in the normal film will be described by Hamman's $t$ matrix [equation II-(20)]. After averaging over impurity sites in the normal metal film, the equations for the matrix self-energies $\widehat{\Sigma}_N(i\omega_n)$ and $\widehat{\Sigma}_S(i\omega_n)$ [figure (14)] become

$$\widehat{\Sigma}_N(i\omega_n) = -\frac{me^{2}z_{r}}{(2\pi T)^{3}} \sum_{\omega_n} \int \frac{d\theta}{(2\pi)^{3}} \gamma_3 \Gamma_{5\gamma}(i\omega_n,i\omega) G_{\gamma}(i\omega_n \varepsilon_{x}) \left( \gamma_3 \right)^{2} \sum_{\delta=1}^{N_{d}} \gamma_1 G_{\delta}(i\omega_n \varepsilon_{\delta}) \gamma_3$$

$$\chi \Gamma_{\delta\gamma\alpha}(i\omega_n,i\omega) \gamma_{3} \left[ G_{\gamma\alpha}(i\omega_n) \right]^{2} \gamma_3 T^{2} \sum_{\kappa} \widehat{G}_{\kappa}(i\omega_n \varepsilon_{\kappa}) \gamma_3$$
\[ \sum_{S}^{\wedge} (\omega_m) = \hat{D}_S(\omega_m) \]

\[ \sum_{N}^{\wedge} (\omega_m) = \hat{G}_N(\omega_m) \]

Figure 13

Figure 14
\[ \sum_{s}^{\text{PHONON}} (\omega_m) = \sum_{s}^{\text{PHONON}} (i\omega_m) + \gamma_3 T^2 \sum_{k} \hat{G}_{1} \left( (\omega_m \epsilon_k) \gamma_3 \right) \]  

(7-b)

where \( \sum_{s}^{\text{PHONON}} \) is the self energy arising from the B.C.S. pairing interaction, \( \Gamma_{\text{pairing}} \) is the amplitude for the exchange scattering of conduction electrons by a single impurity and \( G_{\text{imp}} (\omega) \) is the Green's function for the pseudo-Fermion representing the impurity spin (Abrikosov 1965).

We have followed Chapter IV in keeping only the elastic scattering of conduction electrons from the magnetic impurities to determine the superconducting critical temperature.

The summation over imaginary frequency \( i\omega_n \) in equation (7-a) is calculated as in Chapter IV. Using the analytic continuation \( (\omega_n \rightarrow \mathcal{Z}^2) \), we can transform the summation over \( i\omega_n \) to a contour integral \([\text{figure (9)}]\). Only the contribution of the double pole of \( \left\{ G_{\text{imp}} (\mathcal{Z}) \right\}^2 \) at \( \mathcal{Z} = \lambda' \) is retained in calculating the contour integral (Chapter IV).

After projecting out spurious pseudo-Fermion states by taking the limit \( \lambda \rightarrow \infty \) equation (7-a) is given by

\[ \sum_{m}^{\text{PHONON}} (\omega_m) = \left\{ \frac{d^3 \kappa}{(2\pi)^3} \left\{ \frac{(\omega_m A_{\parallel} m_0 (2\pi)^3)}{\omega_m^2 (\omega_m + \epsilon_k^2 + \Omega_{m}^2 (\omega_m))} \right\} \frac{\gamma_3 - \delta_{m}(\omega_m) B \gamma_1}{\gamma_3 - \delta_{m}(\omega_m) B \gamma_1} \right\} \]

\[ + \gamma_3 T^2 \sum_{k} \hat{G}_{1} (\omega_m \epsilon_k) \gamma_3 \]

(8)

where equation IV-(5) has been used in the spin summation.

The terms A and B in equation (8) are given in terms of
equation IV-(5) as

\[ A = n_x \left\{ |\Gamma_0(w_m)|^2 + S(S+1)|\Gamma_1(w_m)|^2 \right\} \]

\[ B = n_x \left\{ |\Gamma_0(w_m)|^2 - S(S+1)|\Gamma_1(w_m)|^2 \right\} \]  

where \( n_x \) is the concentration of magnetic impurity in the normal metal film. Completing the summation over single particle states in equations (7-a) and (7-b), we obtain the following self-consistent equations for \( Z_N((w_m)), Z_S((w_m)) \)

\[ \Phi_N((w_m)) \text{ and } \Phi_S((w_m)): \]

\[ Z_N((w_m)) = 1 + \frac{1}{2 \epsilon((w_m)) \left( \omega_m^2 Z_N^2((w_m)) + \Phi_N^2((w_m)) \right)^{1/2}} \]

\[ \frac{\Gamma_N Z_N((w_m))}{(\omega_m^2 Z_N^2((w_m)) + \Phi_N^2((w_m))^{1/2}} \]

\[ \Phi_N((w_m)) = \frac{1}{2 \epsilon((w_m)) \left( \omega_m^2 Z_N^2((w_m)) + \Phi_N^2((w_m)) \right)^{1/2}} \]

\[ \frac{\Gamma_N \Phi_N((w_m))}{(\omega_m^2 Z_N^2((w_m)) + \Phi_N^2((w_m))^{1/2}} \]

\[ Z_S((w_m)) = 1 + \frac{\Gamma_S Z_N((w_m))}{(\omega_m^2 Z_N^2((w_m)) + \Phi_N^2((w_m))^{1/2}} \]

\[ \Phi_S((w_m)) = \Delta_{\text{PHONON}} + \frac{\Gamma_S \Phi_N((w_m))}{(\omega_m^2 Z_N^2((w_m)) + \Phi_N^2((w_m))^{1/2}} \]

where

\[ \frac{1}{2 \epsilon((w_m))} = \prod_x N_x((w_m)) \left\{ |\Gamma_0(w_m)|^2 + S(S+1)|\Gamma_1(w_m)|^2 \right\} \]

is the relaxation rate for the exchange scattering of the
conduction electrons by the impurities,

\[ \frac{1}{2\gamma_2'(\omega_m)} = \pi m_+ N_v(\omega) \left\{ \left| \Gamma_0(\omega_m) \right|^2 - S(S+1) \left| \Gamma_1'(\omega_m) \right|^2 \right\} \] (16)

\( N(0) \) is the density of states per atom per spin at the Fermi surface for the corresponding film and \( \Delta_{S^{\text{Phonon}}} \) is the order parameter for the superconducting film given self-consistently by

\[ \Delta_{S^{\text{Phonon}}} = g \pi kBN_s(0) \sum_{\omega_m} \frac{\phi_s'(\omega_m)}{(\omega_m^2 Z_s^2(\omega_m) + \phi_s^2(\omega_m))^{1/2}} \] (17)

The parameters \( \Gamma_N \) and \( \Gamma_S \) appearing in equations (11) through (14) are defined in terms of the transfer matrix element \( T \) as follows

\[ \Gamma_N = \pi T^2 d_s A D_s(0) = \frac{1}{2\gamma_N} \] (18)

\[ \Gamma_S = \pi T^2 d_n A D_N(0) = \frac{1}{2\gamma_S} \] (19)

where \( D_s(0) \) and \( \gamma_s \) are the density of states per unit volume for one spin direction at the Fermi level and the relaxation time for electrons in the superconducting film of thickness \( d_s \) and area \( A \), and similarly for the normal metal film. The relation

\[ \frac{\Gamma_N}{\Gamma_S} = \frac{d_s D_s(0)}{d_n D_N(0)} \] (20)

implies the number of electrons crossing the barrier in opposite directions is the same.
The relaxation time is given by (Mc Millan 1968)

\[ \gamma_N = 2B^2 \frac{\Delta d_N}{(\nu_{FN} \sigma')} \]  

(21)

where \( \nu_{FN} \) is the Fermi velocity in the normal metal, \( \sigma' \) is the probability that an electron incident on the barrier will be transmitted and \( 2B^2 d_N \) is the path length between successive collisions with the barrier. For clean films, Mc Millan (1968) suggests \( B \sim 2 \). Therefore, both \( \Gamma_N \) and \( \Gamma_S \) are inversely proportional to \( d_N \) and \( d_S \) respectively. We now calculate the dependence of the superconducting critical temperature of the sandwich on film thickness.

We define the renormalized energy-gap functions \( \Delta_S(\omega_m) \) and \( \Delta_N(\omega_m) \) as follows:

\[ \Delta_N(\omega_m) = \Phi_N(\omega_m)/Z_N(\omega_m) \] \[ \Delta_S(\omega_m) = \Phi_S(\omega_m)/Z_S(\omega_m) \]

From equations (11), (12), (13) and (14) we obtain the following equations for \( \Delta_N(\omega_m) \) and \( \Delta_S(\omega_m) \):

\[ \Delta_N(\omega_m) = \frac{\Gamma_S \Delta_S(\omega_m)}{(\omega_m^2 + \Delta_S^2(\omega_m))^{1/2}} \left[ \frac{\Gamma_N}{(\omega_m^2 + \Delta_S^2(\omega_m))^{1/2}} + \frac{\Gamma(\omega_m)}{\Delta_N^2(\omega_m)} \right]^{-1} \]  

(22)

\[ \Delta_S(\omega_m) = \Delta^{\text{PHONON}} + \frac{\Gamma_S \Delta_N(\omega_m)}{(\omega_m^2 + \Delta_N^2(\omega_m))^{1/2}} \left[ \frac{\Gamma_S}{(\omega_m^2 + \Delta_N^2(\omega_m))^{1/2}} \right]^{-1} \]  

(23)
where
\[
\Gamma'(\omega_m) = \frac{1}{2\gamma'(\omega_m)} - \frac{1}{2\gamma''(\omega_m)}
\]  

(24)

From equations IV-(11), (15) and (16), \(\Gamma'(\omega_m)\) is equal to the spin flip scattering rate for conduction electrons \(\frac{1}{\gamma'(\omega_m)}\) [equation IV-(16)]. Since we are using Hamman's \(t\) matrix equation II-20 to describe the exchange scattering of conduction electrons by the impurity, we have from equations IV-(18) and IV-(20).

\[
\Gamma'(\omega_m) = \frac{m^*}{2\pi N(0)} \left\{ \frac{\Pi^2 S(S+1)}{\ln^2 (\frac{\omega}{\Delta}) + \Pi^2 S(S+1)} \right\}
\]  

(25)

(b) The Superconducting Critical Temperature

The equation for the superconducting critical temperature for the metal sandwich is obtained by linearizing equations (17), (22) and (23) with respect to \(\Delta^\text{PHONON}_S\), \(\Delta_N(i\omega_m)\) and \(\Delta_S(i\omega_m)\). Equations (22) and (23) become:

\[
\Delta_N(i\omega_m) = \Delta_S(i\omega_m) \Gamma_N \left\{ |\omega_m| + \Gamma_N + \Gamma'(\omega_m) \right\}^{-1}
\]  

(26)

\[
\Delta_S(i\omega_m) = \left\{ |\omega_m| \Delta^\text{PHONON}_S + \Delta_N(i\omega_m) \Gamma_S \right\} \cdot \left\{ |\omega_m| + \Gamma_S \right\}^{-1}
\]  

(27)

The linearized equation for \(\Delta^\text{PHONON}_S\) is (Kaiser and Zuckermann 1970)
Kaiser and Zuckermann (1970) show that the superconducting critical temperature for the metal sandwich can be written as

\[
\Delta_{S}^{\text{phonon}} = \int g_{\pi} N_{\pi}(0) kT \sum_{\omega_{m}} \frac{\Delta_{S}(\omega_{m})}{|\omega_{m}|}
\]

(29)

\[
\ln \left( \frac{T_{c0}}{T_{c}} \right) = \pi kT_{c} \sum_{\omega_{m}} \left\{ \frac{1 + \frac{\Gamma(\omega_{m})}{|\omega_{m}|}}{|\omega_{m}|^{2} + (\Gamma_{u}^{+} + \Gamma_{s}^{+} + \Gamma(\omega_{m}))|\omega_{m}| + \Gamma(\omega_{m}) \Gamma_{s}} \right\}_{T = T_{c}}
\]

(30)

where \( T_{co} \) is the critical temperature of the bulk superconductor. The simplest approximation is to replace \( \Gamma(\omega_{m}) \) by \( \Gamma(\omega_{0}) \) in equation (30). This gives (Kaiser and Zuckermann 1970)

\[
\ln \left( \frac{T_{c0}}{T_{c}} \right) = \frac{\Gamma_{s}}{A_{+} - A_{-}} \left\{ \left[ 1 - \frac{\Gamma(\prod \frac{T_{c}}{kT_{c}^{2}})}{A_{+}} \right] \Psi \left( \frac{1}{2} + \frac{A_{+}}{2 \pi kT_{c}} \right) \right. \\
\left. - \left[ 1 - \frac{\Gamma(\prod \frac{T_{c}}{kT_{c}^{2}})}{A_{-}} \right] \Psi \left( \frac{1}{2} + \frac{A_{-}}{2 \pi kT_{c}} \right) \right\} - \Psi \left( \frac{1}{2} \right)
\]

(31)

where

\[
\Gamma(\prod \frac{T_{c}}{kT_{c}^{2}}) = \frac{2 \pi N_{\pi}(0)}{\prod \frac{T_{c}}{kT_{c}^{2}}} \left[ \frac{\prod^{2} S(S+1)}{\ln^{2} \left( \frac{\prod \frac{T_{c}}{kT_{c}^{2}}}{\prod^{2} S(S+1)} \right) + \prod^{2} S(S+1)} \right]
\]

(32)

\[
A_{\pm} = \frac{1}{2} \left[ \Gamma(\prod \frac{T_{c}}{kT_{c}^{2}})^{2} \Gamma_{u}^{+} + \Gamma_{s}^{+} \right]^{2} \left[ \frac{1}{4} \left( \Gamma(\prod \frac{T_{c}}{kT_{c}^{2}})^{2} \Gamma_{u}^{+} + \Gamma_{s}^{+} \Gamma_{N}^{2} - \Gamma(\prod \frac{T_{c}}{kT_{c}^{2}})^{2} \Gamma_{s}^{+} \Gamma_{N} \right)^{2} \right]^{-1/2}
\]

(33)

and \( \Psi(z) \) is the digamma function.
For the case of bulk superconducting, Kondo alloys we have shown that for large concentrations of magnetic impurity the critical temperature decreases exponentially with \( m_\pi \) [equation IV-(24)]. We shall use equation (31) to find a similar behaviour for the superconducting critical temperature of the metal sandwich as a function of the concentration of magnetic impurity in the normal metal film. In the limits 
\[
\Gamma(\frac{\Gamma N}{\Gamma K}) \ll m_\pi m_0 (\Gamma_{\pi 0} \Gamma_{\pi N}) \quad \text{and} \quad T_c \ll \min(T_{co}, T'_{k})
\]
we use the asymptotic form \( \psi(z) \rightarrow \log 2 \gamma z \) for \( z \rightarrow \infty \) in equation (31) to obtain
\[
\log(2\pi K T_{co}) \approx \frac{\Gamma S}{\Gamma S + \Gamma N} \left[ \log \left( 2 \gamma \Gamma (\frac{\Gamma N}{\Gamma S}) \right) + \frac{\Gamma S}{\Gamma S + \Gamma N} \log \left( \frac{2 \gamma \Gamma S}{\Gamma S + \Gamma N} \right) \right]
\]
(34)
We see the \( \log(T_c) \) terms have cancelled on both sides of equation (34). Solving for \( \log(\frac{\pi T_c}{\Gamma K}) \) from equation (34) we obtain
\[
\pi T_{c'} = T_{K'} \exp \left\{ - \left( \frac{N^2 S (5+1)}{2 \pi N (2 \pi K T_{co}) (\Gamma_{N} + \Gamma_{N'}) (\Gamma_{S} + \Gamma_{S'}) (\Gamma_{N} - \Gamma_{S}) (\Gamma_{S'} - \Gamma_{N'}) / \Gamma_{N'} \right) \right\}
\]
(35)
For fixed \( d_s, d_N > 0 \), \( T_c \) for the sandwich is never identically zero for a finite concentration of magnetic impurity in the normal metal film, but decays exponentially with increasing \( m_\pi \).

We shall now analyze equation (31) for \( T_c \) as a function of \( d_s \) for fixed \( m_\pi \) and \( d_N \) for different values of \( (T_{co}/T'_{K}) \).
Also we shall comment on the experimental results for (Cu-Fe)-Pb and (Cu-Mn)-Pb sandwiches.

Curves of $T_c$ versus superconducting film thickness, $d_s$, for a fixed concentration of magnetic impurity ($M_T = 0.005$ atomic percent), a fixed normal metal film thickness, $d_N = 250.0 \, \text{Å}$ and for various values of $T'_{k}/T_{co}$ are shown in figure (15). In figure (15) curve M shows the variation of $T_c$ with $d_s$ for a normal metal film with no magnetic impurities. Curves A, B and C are the curves of $T_c$ versus $d_s$ when the normal metal film contains magnetic impurities.

Curves A and B of figure (15) are obtained when $T'_{k}/T_{co} = 100$ and $T'_{k}/T_{co} = 1$ respectively. In this case $T_c$ is always less than $T_k$ and $T_c$ is a monotonically decreasing function of $d_s$. This can be explained in terms of Nagaoka's theory (Chapter II) because the impurity spin is compensated by a cloud of conduction electrons around the impurity when $T < T_k$. The impurity is essentially non-magnetic for $T_c \ll T_{co}$ and the curves tend toward the non-magnetic curve M.

Curve C shows the case when $T_k/T_{co} = 0.01$, the impurity spin is no longer compensated. This leads to the Born approximation result of Kaiser and Zuckermann (1970) [dashed line in figure (15)]. For $T_c \gg T_k$, the Born approximation result (dashed line) and curve C give the same results for the variation of the superconducting critical temperature of the sandwich with superconducting film thickness. However,
for $T_c \approx T_{c'}$, the decrease in $T_c$ for the curve labelled C [figure (15)] is steeper than the Born approximation curve [dashed line in figure (15)]. The enhanced decrease in $T_c$ is a manifestation of the Kondo effect.

We shall now give a qualitative analysis of the experimental data of Hauser et al. (1971) for (Cu-Fe)-Pb sandwiches [figure (16)] and (Cu-Mn)-Pb sandwiches [figure (17)]. No attempt was made to fit the experimental data for the following reasons:

(a) the normal film containing the magnetic impurities was dirty,

(b) the metal sandwiches had many metallurgical problems, e.g., some Cu films did not have the structure of bulk Cu.

Figure (16) shows the experimental data for the variation of $T_c$ with $d_s$ for (Cu-Fe)-Pb sandwiches [crosses on figure (16)] and Cu-Pb sandwiches [dots on figure (16)]. The solid line averages the data for both sandwiches. The Cu-Fe film appears to be non-magnetic. This is to be expected since the range of temperatures is well below the Kondo temperature of Cu-Fe ($14^\circ$K).

We also show the experimental data in figure (17) for the variation of $T_c$ versus $d_s$ of (Cu-Mn)-Pb sandwiches. The experimental data is fitted using the Born approximation for the exchange scattering of conduction electrons by the impurity. The Born approximation curve in figure (17) deviates strongly from the experimental data for $T_c \approx 2^\circ$K. The sharp decrease in
\( T_c \) is a manifestation of the Kondo effect. The Kondo temperature of random Mn impurities in Cu is estimated to be 0.05\(^{0}K\) (Lee and Heeger 1969). For temperatures greater than \( T_k \), the exchange scattering of conduction electrons by the Mn spin leads to a sharp decrease in \( T_c \). Further experiments using clean films are necessary for a quantitative analysis using equation (31).
Figure 16
Figure 17
CHAPTER VI
SUPERCONDUCTING FLUCTUATIONS AND THE KONDO EFFECT

I. Introduction

Experiment (Glover 1967, Strongin et al. 1968) shows that the resistive transition of superconductors is continuous at the critical temperature. For pure crystalline superconductors the width of the transition region is \( \sim 10^{-17} \text{ K} \). On the other hand, the width of the transition region is much greater for dirty superconductors, e.g. for dirty films the width of the transition region is \( \sim 0.01 \text{ K} \).

The temperature dependence of the resistivity in the transition region has been calculated by using an extension of the phenomenological Landau-Ginzberg equations for superconductivity to temperatures above the superconducting critical temperature (Ambegaokar 1967, Abrahams and Woo 1968).

The resistive transition of superconductors can also be further investigated by using the B.C.S. theory of superconductivity. Above the superconducting critical temperature the equilibrium density of electron pairs is zero. However, fluctuations will lead to a deviation in the number of electron pairs from its equilibrium value. These electron pairs will decay as \( \exp\{-t/\gamma_t\} \) where \( \gamma_t \) is the relaxation time for the process. At the superconducting critical temperature \( \gamma_t \) is infinite for electron pairs of zero momentum.
For temperatures above the superconducting critical temperature electron pairs with a finite life-time \( \gamma_T > 10^{-8} \text{sec.} \) will contribute to the supercurrent. This will lead to a lowering of the resistivity for temperatures above the superconducting critical temperature. In particular, Aslamasov and Larkin (1968) have shown that the conductivity of a two dimensional superconductor with short mean free path is given by

\[
\sigma = \frac{e^2}{16 \pi d} \left( \frac{T}{T - T_c} \right)
\]

(1)

for temperatures \( T > T_c \) where \( d \) is the film thickness.

The effect of magnetic impurities on the resistive transition has been studied in the Born approximation by H. Schmidt (1968). The temperature dependence in equation (1) remains valid, but the transition is broadened by pair breaking effects. We shall study the influence of the Kondo effect on the resistive transition of a superconductor containing magnetic impurities. Only the case of a dirty superconducting host will be considered. Abrikosov's diagrammatic technique will be used to calculate the excess conductivity due to electron pair fluctuations for temperatures above the superconducting critical temperature of the alloy (Chapter IV).

The exchange scattering of conduction electrons by the magnetic impurities will be described by Hamman's \( t \)-matrix given by equation II-(20). The resulting expression for the excess con-
ductivity will be considered separately for the ratios $T_k / T_{co} \geq 1$ and $T_k / T_{co} < 1$ where $T_{co}$ is the superconducting critical temperature of the host. From these separate treatments of the excess conductivity due to electron pair fluctuations we shall obtain two expressions for the resistivity of superconducting, Kondo alloys. Their temperature dependence will be discussed.

II. **Contribution of Superconducting Fluctuations to the Conductivity**

(a) **The Response Function**

The physical system we shall consider is a superconductor containing a small amount of magnetic impurities. In the absence of magnetic impurities the host metal is assumed to be a disordered system with a short electron mean free path. The superconductor containing magnetic impurities exhibits the Kondo effect in the normal state. There is assumed to be no interference between the magnetic and non-magnetic scattering effects of conduction electrons. This has been shown to be valid at non-zero temperatures (Everts and Keller 1970). Therefore, the scattering rate for conduction electrons is the sum of the magnetic and non-magnetic scattering rates. It is our intention to obtain an expression for the excess conductivity due to electron pair fluctuations in a temperature range near the superconducting critical temperature where the number of electron pair fluctuations is small.
In a weak, homogeneous, fluctuating field described by a vector potential \( A(q\omega_v) \), the current density \( j(q\omega_v) \) is given by

\[
j(q\omega_v) = -Q(q\omega_v) A(q\omega_v)
\]

where \( Q(q\omega_v) \) is the linear response function (Kubo 1957) and \( \omega_v = 2\pi v KT \). For small frequencies the conductivity \( \sigma \) is related to the response function \( Q(q\omega_v) \) by

\[
\sigma(q\omega_v) = -i\omega \sigma
\]

where we have analytically continued the complex frequency \( \omega \) onto the real axis. Once the pair fluctuation contribution to the response function \( Q(q\omega_v) \) is known, equation (3) can be used to obtain the pair fluctuation conductivity.

For the temperature range under consideration, the electron pair fluctuations may be treated as a perturbation on the normal state properties. After averaging over impurities the lowest order contributions of pair fluctuations to \( Q(q\omega_v) \) are shown in figure (18) (Aslamasov and Larkin 1968). We follow Aslamasov and Larkin (1968) and retain figure (18)-(d) to calculate \( Q(q\omega_v) \). This gives

\[
Q_{4\sigma}(q\omega_v) = \frac{2e^2kT}{\pi m^2} \sum_{\omega_m} \int \frac{d^3r}{(2\pi)^3} t^{\text{imp}}(\rho\omega_v;\omega_m,\omega_v) t^{\text{imp}}(\rho\omega_m)
\]

\[
\times F_{\sigma}(\rho\omega_m; q\omega_v) F_{\sigma}(\rho\omega_v; q\omega_v)
\]

where \( t^{\text{imp}}(\rho\omega_m) \) is the propagator for superconducting fluctuations in the presence of impurities, \( \frac{e}{m} F_{\sigma}(\rho\omega_m; q\omega_v) \) is
Figure 18
the renormalized electromagnetic vertex with

\[ F_{\alpha}(P, Q; q) = -\frac{\pi}{\alpha} \sum_{\omega} \left\{ \frac{dP'}{dP_\alpha} \right\} \langle G(P', P, \omega) G(Q - P, Q - P', \omega') G(Q, Q') \rangle \]

\[ \langle \ldots \rangle_{av} \] is the average over impurity sites [equation III-(15)] and \( G(P, Q) \) is the single particle temperature Green's function. For future use let us define \( \tilde{G}(P, Q) \), the impurity averaged single particle Green's function, given by

\[ \tilde{G}(P, Q) = \left( i\omega_n + \frac{\omega_m}{\omega_n} \left( \frac{1}{2\gamma_o} + \frac{1}{2\gamma_m(\omega_n)} \right) - \varepsilon_P \right)^{-1} \]

In equation (6), \( \frac{1}{\gamma_o} \) is the scattering rate of conduction electrons in the host superconductor in the absence of magnetic impurities and \( \frac{1}{\gamma_m(\omega_n)} \) is the conduction electron exchange scattering rate given by Hamman's t-matrix [equation II-(20)]. The electron mean free path for non-magnetic scattering effects is much smaller than the electron mean free path for magnetic scattering effects, i.e. we take

\[ \frac{1}{\gamma_o} \gg \frac{1}{\gamma_m(\omega_n)} \]

(b) Calculation of the Fluctuation Propagator

The fluctuation propagator is given by the impurity averaged t-matrix describing the repeated scattering of a pair of conduction electrons of net momentum \( q \) and net frequency \( \omega_n \) by the B.C.S. pairing interaction [equation III-(34)]. The impurity averaged t matrix is given by [equation III-(22)].
where

\[ I^{\text{imp}}(q,\omega) = \frac{|q|^{2}}{1 - |q|^{2}} \hat{I}^{\text{imp}}_{0}(q,\omega) \]  \hspace{1cm} (7)

\[ \hat{I}^{\text{imp}}_{0}(q,\omega) = kT \sum_{\omega_{m}} \int \frac{d^{3}p}{(2\pi)^{3}} K(p+q;p,\omega_{m};\omega_{i}-\omega_{m}) \]  \hspace{1cm} (8)

and

\[ K(p+q;p,\omega_{m};\omega_{i}-\omega_{m}) g_{q} = \langle G_{01}(p+q,\omega_{m};\omega_{i}) g_{q} G(-p,\omega_{m}) \rangle_{av} \]  \hspace{1cm} (9)

is the Fourier transform of the impurity averaged product of two single particle temperature Green's functions [equation III-(25)]. The impurity average must now be taken over the sites of both the magnetic and non-magnetic impurities. From equations III-(36) and B-(2) the integral equation for \( K(p+q;p,\omega_{m};\omega_{i}-\omega_{m}) \) is

\[
K(p+q;p,\omega_{m};\omega_{i}-\omega_{m}) g_{q} = \hat{G}(p+q,\omega_{m};\omega_{i}) \hat{G}(-p,\omega_{m}) \{ g_{q} + \int \frac{d^{3}p}{(2\pi)^{3}} V_{d\alpha\lambda}(\omega_{m};\omega_{i}) g_{q} K(p+q;p,\omega_{m};\omega_{i}-\omega_{m}) \} \]

where \( \hat{G}(p,\omega_{m}) \) is given by equation (6),

\[
V_{d\alpha\lambda}(\omega_{m};\omega_{i}) = m|U_{o}|^{2} \delta_{\alpha\lambda} \delta_{\phi\phi} - \frac{m^{2}}{(2S+1)} \sum_{\omega} \left[ \frac{G_{i\phi}(\omega)}{2\omega} \right]^{2} \times \Gamma_{d\alpha\lambda}(\omega_{m};\omega_{i}) \Gamma_{\phi\lambda}(-\omega_{m};\omega_{i}) \]

\( U_{o} \) is the amplitude for scattering electrons from the non-magnetic impurities and \( \Gamma_{d\alpha\lambda}(\omega_{m};\omega_{i}) \) is the amplitude for scattering conduction electrons from a single magnetic impurity via the s-d exchange interaction [equation III-(35)].
\(n_x\) and \(n\) are the concentrations of magnetic and non-magnetic impurities. Only the elastic scattering of conduction electrons by the magnetic impurities is retained as in Chapter IV.

Using the analytic continuation \( (\omega) \to z \) we can transform the summation over \( \omega \) in equation (11) to a contour integral [figure (9)]. Only the double pole of \( \{G_{\alpha \rho p}(z)\}\) at \( z = \lambda' \) is retained in calculating the contour integral. After projecting out spurious pseudo-Fermion states by taking the limit \( \lambda' \to \infty \) equation (11) becomes

\[
\lambda_{\alpha \rho p}(\omega_m, \omega_v) = m |U_0|^2 \delta_{\alpha \lambda} \delta_{\rho \rho} \Gamma_0(\omega_m + \omega_v) \Gamma_o(-\omega_m) \delta_{\lambda \lambda} \delta_{\rho \rho} \\
+ \frac{1}{3} S(S+1) \Gamma_o(\omega_m + \omega_v) \Gamma_o(-\omega_m) \delta_{\lambda \lambda} \cdot S_{\rho \rho}
\]

where equation IV-(7) has been used. We define the function \( \lambda(\omega_m, \omega_v) \) as follows

\[
\lambda_{\alpha \rho p}(\omega_m, \omega_v) = (m |U_0|^2 - n_x \lambda(\omega_m, \omega_v)) g_{\alpha \rho p}
\]

where

\[
\lambda(\omega_m, \omega_v) = S(S+1) \Gamma_o(\omega_m + \omega_v) \Gamma_o(-\omega_m) - \Gamma_o(\omega_m + \omega_v) \Gamma_o(-\omega_m)
\]

and the identity \((\delta_{\alpha \lambda} \cdot \delta_{\rho \rho}) g_{\alpha \rho p} = -3 g_{\alpha \rho p}\) has been used. The dependence of equation (14) on \( \omega_m + \omega_v \) can be shown from perturbation theory.

Define \( K(q, \omega_m + \omega_v - \omega_m) \) as follows

\[
K(q, \omega_m + \omega_v - \omega_m) = \int d^3 p \ K(p + q, \omega_m + \omega_v - \omega_m)
\]
Then from equations (10) and (13) \( K(q_i; \omega_m + \omega_v; -\omega_m) \) is given by

\[
K(q_i; \omega_m + \omega_v; -\omega_m) = \frac{K_0(q_i; \omega_m + \omega_v; -\omega_m)}{1 + (m^2 V(\omega_m + \omega_v) - m |U_0|^2)K_0(q_i; \omega_m + \omega_v; -\omega_m)} \tag{16}
\]

where

\[
K_0(q_i; \omega_m + \omega_v; -\omega_m) = \frac{1}{(2\pi)^3} \mathcal{G}(p \cdot q, \omega_m + \omega_v) \mathcal{G}(-p \cdot \omega_m), \tag{17}
\]

where

\[
\frac{1}{2\gamma_0} = m\pi N(0) |U_0|^2 \tag{18}
\]

and \( \mathcal{G}(p \cdot \omega_m) \) is given by equation (6).

Near the superconducting critical temperature the important electron pair fluctuations will have small momenta and frequency. Therefore, \( K(q_i; \omega_m + \omega_v; -\omega_m) \) must be expanded to lowest order in \( q_i \) and \( \omega_v \). In this limit equations (16) and (17) give the following expression for \( K(q_i; \omega_m + \omega_v; -\omega_m) \):

\[
K(q_i; \omega_m + \omega_v; -\omega_m) = \frac{\pi N(0)}{|\omega_m| \cdot d(\omega_m; \omega_v; q_i)} \tag{19}
\]

where

\[
d(\omega_m; \omega_v; q_i) = \frac{1}{a} \left\{ \frac{2}{\gamma_s(\omega_m)} + |\omega_v| + \frac{1}{3} V_F^2 \gamma'(\omega_m) q_i^2 \right\}, \tag{20}
\]

\[
\frac{1}{\gamma'(\omega_m)} = \frac{1}{\gamma_a} + \frac{1}{\gamma(\omega_m)} \tag{21}
\]
is the total electron relaxation rate for magnetic and non-magnetic scattering effects and \( \frac{1}{\gamma_\epsilon}(\omega_m) \) is given by equation IV-(16). Equations (7), (8), (15), (19) and (20) give the following expression for \( t^{\text{imp}}(q, \omega_v) \):

\[
t^{\text{imp}}(q, \omega_v) = \left[ N(\omega) \left\{ \ln\left(\frac{T}{T_c}\right) + \frac{2}{\pi \hbar k T} \sum_{m=\pm \omega_0} \gamma((\omega_m; \omega_v; q) \right\} \right]^2 \tag{22}
\]

where the identity 
\[
\ln\left(\frac{1 + \frac{1}{4} \omega_0}{\omega_0}\right) = 2\pi k T \sum_{m=\pm \omega_0} \frac{1}{\omega_m}
\]
has been used. The simplest approximation is to replace \( \gamma((\omega_m; \omega_v; q) \) by \( \gamma((\omega_0; \omega_v; q) \) in equation (22). This gives

\[
t^{\text{imp}}(q, \omega_v) = \left[ N(\omega) \left\{ \ln\left(\frac{T}{T_c}\right) + \Psi\left(\frac{1}{2} + \frac{1}{4\pi k T} + \frac{\gamma\epsilon}{2\pi k T} + \frac{1}{2\pi k T \gamma_\epsilon}\right) - \Psi(1) \right\} \right]^2 \tag{23}
\]

where \( \Psi(z) \) is the digamma function,

\[
\frac{1}{\gamma_\epsilon} = \frac{1}{\gamma_0} + \frac{m_\epsilon}{\pi N(\omega)} \left\{ 1 - \frac{\ln(\gamma_\epsilon)}{\ln^2(\gamma_\epsilon/\nu) + \pi \gamma_\epsilon^2(\Gamma + 1)\gamma_\epsilon} \right\} \tag{24}
\]

and

\[
\frac{1}{\gamma_\epsilon} = \frac{m_\epsilon}{2\pi N(\omega)} \left\{ \frac{\pi \gamma_\epsilon^2(\Gamma + 1)}{\ln^2(\gamma_\epsilon/\nu) + \pi \gamma_\epsilon^2(\Gamma + 1)} \right\} \tag{25}
\]

are found from Hamman's t-matrix equation II-(20).

(c) The Calculation of \( F_4(q, \omega_m; q, \omega_v) \)

The vertex \( F_4(q, \omega_m; q, \omega_v) \) describes the coupling of the external field to the electrons. Near the superconducting critical temperature, the important electron pair
fluctuations have small frequency and momentum. Therefore, we need the vertex $F_\alpha (\mathbf{q} \omega_n; \mathbf{q} \omega_n')$ for small $\mathbf{q}$. In order to calculate $F_\alpha (\mathbf{p} \mathbf{0}; \mathbf{q} \omega_n)$, we can set the external frequency $\omega_n$ and momentum $\mathbf{q}$ to zero (H. Schmidt preprint). This gives

$$F_\alpha (\mathbf{p} \mathbf{0}; 00) = i \hbar T \sum_{\omega_n} \frac{d^3 \mathbf{q}}{(2 \pi)^3} \mathbf{p} \cdot \langle \mathbf{G}(\mathbf{p} \omega_n') \mathbf{G}(\mathbf{p} \omega_n') \mathbf{G}(\mathbf{p} \mathbf{p}' \omega_n') \rangle_{ov} (26)$$

The impurity averaged product of three single particle temperature Green's functions is given for small $\mathbf{p}$ by (Gor'kov 1960)

$$\langle \mathbf{G}(\mathbf{p} \omega_n') \mathbf{G}(\mathbf{p} \omega_n') \mathbf{G}(\mathbf{p} \mathbf{p}' \omega_n') \rangle_{ov} = \frac{2}{2[\omega_n' + \tilde{\chi}'(\omega_n)]^2} \left[ \frac{2[\omega_n' + \frac{1}{\tilde{\chi}'(\omega_n)}]}{2[\omega_n' + \frac{1}{\tilde{\chi}'(\omega_n)}]} \right]$$

$$\times \tilde{\chi}(\mathbf{p} \omega_n') \tilde{\chi}(\mathbf{p} \omega_n') \tilde{\chi}(\mathbf{p} \mathbf{p}' \omega_n')$$

(27)

where $\tilde{\chi}(\mathbf{p} \omega_n')$ is given by equation (6), $1/\chi'(\omega_n)$ is given by equation (21) and $1/\chi_s(\omega_n)$ by equation IV-(16).

Equations (26) and (27) give the following expression for $F_\alpha (\mathbf{p} \mathbf{0}; 00)$:

$$F_\alpha (\mathbf{p}) \triangleq F_\alpha (\mathbf{p} \mathbf{0}; 00) = \frac{i \mathbf{p} \cdot \mathbf{p}^3 K T}{3 \pi} \sum_{\omega_n > 0} \frac{\chi'(\omega_n)}{[\omega_n + \frac{1}{\chi_s(\omega_n)}]^2}$$

(28)

The simplest approximation we can make is to replace $\chi'(\omega_n)$ and $\chi_s(\omega_n)$ by $\chi'(\omega_0)$ and $\chi_s(\omega_0)$ in equation (28). This gives

$$F_\alpha (\mathbf{p}) \triangleq F_\alpha (\mathbf{p} \mathbf{0}; 00) = \frac{i \mathbf{p} \cdot \mathbf{p}^3 K T}{12 \pi^3} \psi' \left( \frac{1}{2} \psi \frac{1}{2 \pi K T \chi_s} \right)$$

(29)
where $\frac{1}{\gamma'}$ is given by equation (24), $\frac{1}{\gamma_s'}$ is given by equation (25) and $\psi'(z)$ is the first derivative of the digamma function.

We now calculate the fluctuation contribution to the conductivity for different values of the ratio $T'_k/T_{co}$ where $T'_k$ is the Kondo temperature and $T_{co}$ is the superconducting critical temperature of the pure host metal.

III. **Fluctuation Conductivity for $T'_k \gg T_{co}$**

When $T'_k/T_{co} \gg 1$ the superconducting critical temperature $T_c$ is a monotonic decreasing function of the concentration of magnetic impurity [figure (10)]. For a fixed concentration of magnetic impurity and the corresponding superconducting critical temperature, we shall calculate the excess conductivity due to electron pair fluctuations for $T-T_c \ll T_c$.

In the region $T \gtrsim T_c$, the first-order expansion of $L^{imp}(g, \omega)$ in $(T-T_c)/T_c$ is given from equation (23) as

$$L^{imp}(g, \omega) = \left[ N(\omega) \left( 1 - \bar{\rho}_s \psi'(\frac{\omega}{2} + \rho_s) \right) \left[ \frac{T-T_c}{T_c} + C \frac{\pi \Omega}{\partial T_c} + 2 \frac{\sqrt{\pi \gamma_s T_{co}}}{\pi} \right] \right]^{-1}$$

where

$$\bar{\rho}_s = \frac{1}{2\pi K T_{co}}$$

$\rho_s$ at $T = T_c$.

$$\rho_{co} = \rho_s - \frac{1}{2\pi} \left[ \frac{\partial}{\partial T} \frac{1}{\gamma_s} \right]_{T = T_c}$$

(30)
and

$$C = \frac{\psi\left(\frac{1}{2}\right) \psi'\left(\frac{1}{2} + \rho^c_s\right)}{\left[1 - \rho^c_s \psi'\left(\frac{1}{2} + \rho^c_s\right)\right]}$$

The quantity $\rho^c_s$ satisfies equation IV-(21)

$$\ln\left(\frac{T_o}{T_c}\right) = \psi\left(\frac{1}{2} + \rho^c_s\right) - \psi\left(\frac{1}{2}\right) \quad \text{IV-(21)}$$

With this expression for $\Im \rho(q, \omega_r)$ we can calculate the singular part of the response function $Q_{ab}(q, \omega_r)$.

Near $T_c$ the dominant contribution to $Q_{ab}(q, \omega_r)$ comes from the summand with $\omega_m = 0$ in equation (4). From equations (29) and (30) we have

$$Q_{ab}(0, \omega_r) = -\frac{2e^2}{m^2 \hbar T} \left\{ \frac{\rho^2 \gamma'}{2 \pi^2} \right\}^2 T \left\{ \frac{\psi'\left(\frac{1}{2} + \frac{1}{2\pi \hbar \kappa \gamma}\right)}{N(0)\left(1 - \frac{1}{2}\psi\left(\frac{1}{2} + \rho^c_s\right)\right)} \right\}^2$$

$$\times \int \frac{d^3 p}{(2\pi)^3} p_a p_b \left\{ m + C \left[ \frac{\Omega_k^2}{\hbar T_c} + \frac{\pi D^2 p^2}{\hbar T_c} \right] \right\}^2 \left\{ m + \frac{\pi D p^2}{\hbar T_c} \right\}^2$$

where $m = (T - T_c)/T_c$ and $D = \frac{1}{3} V^2 \gamma' T \left. \right|_{T = T_c}$

and $\psi' \gamma'$ is given by equation (25). Analytic continuation of $\omega_r$ to real frequencies gives

$$Q_{ab}(0, \omega) = -\frac{2e^2}{m^2 \hbar T} \left\{ \frac{\rho^2 \gamma'}{2 \pi^2} \right\}^2 T \left\{ \frac{\psi'\left(\frac{1}{2} + \frac{1}{2\pi \hbar \kappa \gamma}\right)}{N(0)\left(1 - \frac{1}{2}\psi\left(\frac{1}{2} + \rho^c_s\right)\right)} \right\}^2$$

$$\times \int \frac{d^3 p}{(2\pi)^3} p_a p_b \left\{ m + C \left[ -\frac{\omega \pi}{\hbar T_c} + \frac{\pi D^2 p^2}{\hbar T_c} \right] \right\}^2 \left\{ m + \frac{\pi D p^2}{\hbar T_c} \right\}^2$$

Equation (33) gives the following expression for the excess conductivity

...
We shall now calculate the excess conductivity for bulk superconductors and thin films.

(a) **Bulk Superconductors**

For a 3-dimensional superconductor where the superconducting coherence length is less than the sample dimensions, integration of equation (34) gives

\[
\sigma_{\phi} = \frac{2e^2}{m^2 kT} \left[ \frac{\rho_F^2}{16\pi^3} \right] \cdot \left\{ \frac{\psi'(\frac{1}{2} + \frac{1}{2\pi kT \rho_s^c})}{N(0) (1 - \rho_s^c \psi'(\frac{1}{2} + \frac{1}{2\pi kT \rho_s^c}))} \right\}^2
\]

\[
\times \int \frac{d^3p}{(2\pi)^3} \rho_0^c P_c \left\{ m + \frac{\pi C D P^2}{8kT_c} \right\}^{-3}
\]

(34)

In the absence of magnetic impurities, equation (35) reduces to the results of Aslamasov and Larkin (1968):

\[
\sigma_{\phi} = \frac{e^2}{16\pi^3} \left( \frac{T_c}{\rho_F^2} \right) \cdot \left\{ \frac{1}{1 - \rho_s^c \psi'(\frac{1}{2} + \frac{1}{2\pi kT \rho_s^c})} \right\}^2 \cdot \frac{1}{m \gamma_a} + O(\gamma_a^2)
\]

(35)

Equation (35) shows that the square root divergence of the excess conductivity due to electron pair fluctuations is unchanged by the Kondo effect. However, pair breaking effects lead to a greater broadening of the resistive transition of a superconductor.
(b) Films

For a film whose thickness $d$ is the same order of magnitude as the superconducting coherence length, the integral in equation (34) is replaced by a discrete sum:

$$\begin{align*}
\sigma_{\theta} &= \frac{2e^2}{m^2kT} \left[ \frac{p^3}{(2\pi)^3} \right] \frac{\Psi' \left( \frac{1}{2} + \frac{e^c}{2} \right)}{N(0) \left( 1 - \frac{e^c}{\Psi' \left( \frac{1}{2} + \frac{e^c}{2} \right) } \right)} \\
&\times \frac{1}{d} \sum_{p_x} \left[ \frac{d^2}{(2\pi)^2} p_x \right] \left[ \frac{m + \pi C D \gamma - \frac{1}{8T_c}}{m} \right]^3
\end{align*}$$

The excess conductivity parallel to the surface of the film is given by

$$\sigma_{\parallel} = \frac{e^2}{8\pi d} \left[ \frac{\Psi' \left( \frac{1}{2} + \frac{e^c}{2} \right)}{1 - \frac{e^c}{\Psi' \left( \frac{1}{2} + \frac{e^c}{2} \right) } } \right] \frac{1}{m} + \text{terms } O(m)$$

If the exchange scattering of conduction electrons is treated in the Born approximation, equation (38) reduces to the results of Schmidt (1968). In the absence of magnetic impurities equation (38) reduces to the results of Aslamasov and Larkin (1968) for thin films

$$\sigma_{\parallel}^{\text{AsL}} = \frac{e^2}{16d} \cdot \frac{1}{m}$$

The Kondo effect does not change the linear divergence of the pair fluctuation contribution to the conductivity of thin films. As in the case of a 3-dimensional superconductor, pair breaking effects lead to a broadening of the resistive transition.
We shall now study the excess conductivity due to electron pair fluctuations for thin films when \( \frac{T'_k}{T'_{co}} < 1 \). In particular, we shall be interested in the region where the curve \( T_c \) versus concentration of magnetic impurity is re-entrant [figure (10)].

### IV. Fluctuation Conductivity for \( \frac{T'_k}{T'_{co}} < 1 \)

The manner in which the superconducting critical temperature decreases with increasing magnetic impurity concentration \( m_z \) depends on the ratio \( \frac{T'_k}{T'_{co}} \). In particular, the curve of \( T_c \) versus \( m_z \) is re-entrant for \( \frac{T'_k}{T'_{co}} < 1 \) [figure (19)]. Preliminary experiments indicate the possibility of such behavior for \((La_{1-x}Ce_x)Al_2\) (Ribbet and Winzer 1971). Let \( T_o \) and \( m_{z_0} \) be the superconducting critical temperature and concentration, respectively, at which the curve \( T_c \) versus \( m_z \) becomes re-entrant [figure (19)]. We will study the effect of pair fluctuations on the temperature dependence of the resistivity in the regime

\[
(m_z - m_{z_0}) \ll m_{z_0} (m_z > m_{z_0}) \text{ for temperatures } |T - T_0| \ll T_0.
\]

Fulde and Maki (1970) have pointed out that the critical field as a function of temperature may have a maximum at the second order phase transition point \((H^m_o, T^m_o)\). They further show that the excess conductivity of a thin film in a parallel magnetic field exhibits a maximum for fields \( H \approx H^m_o \) and temperatures \( T \approx T^m_o \) in the presence of pair fluctuations. Hence,
Figure 19

$\frac{T_c}{T_{c0}}$ vs. Impurity concentration (at %)
a minimum can be expected in the resistivity of superconducting films exhibiting a re-entrant 'Kondo' behaviour for temperatures \( T \gtrsim T_0 \) and concentrations \( m_x > m_0^2 \).

We expand the t-matrix equation (23) in the region \( m_x > m_0^2 \) and \( T \gtrsim T_0 \) by analogy with Fulde and Maki (1970). To this purpose we define the function \( \epsilon_o(T) \) as follows

\[
\ln \left( \frac{T_{ef}}{T_c} \right) = \psi \left( \frac{1}{2} + \frac{\epsilon_o(T)}{2 \pi KT} \right) - \psi \left( \frac{1}{2} \right) \tag{40}
\]

where \( \psi(z) \) is the digamma function. The equation for \( T_c \) is given in terms of \( \epsilon_o(T_c) \) by \( \epsilon_o(T_c) = \left\{ \frac{1}{2} \right\} \frac{1}{T_0 + T_c} \), where \( \frac{1}{2} \gamma' \) is given by equation (25). When \( m_x \approx m_0^2 \) we have

\[
\epsilon(T, m_x) = \frac{1}{\gamma'^2} - \epsilon_o(T) \ll KT_c \tag{41}
\]

To first order in \( \epsilon(T, m_x) \) the t-matrix equation (23) is given by

\[
\{t^{\text{mp}}(0, \omega_v)\} = \frac{4\pi KT}{N(0)\psi\left(\frac{1}{2} + \frac{\epsilon_o(T)}{2 \pi KT}\right)} \left\{ \frac{1}{3} V_F^3 \gamma' Q_0^2 + \omega_v + 2 \epsilon(T, m_x) \right\}^{-1} \tag{42}
\]

Equations (3), (4), (29) and (42) give the following expression for the excess conductivity

\[
\sigma_{\text{ex}} = \frac{32 e^2}{\pi m^2} \left[ \frac{P_F^3 \gamma'}{12 \pi^2} \right]^2 \frac{KT}{N(0)} \left\{ \frac{d \theta}{(\Delta n)^3} \frac{P_0}{P_F^2} \right\}^3 \tag{43}
\]
where $\frac{4}{\nu'}$ is given by equation (24).

For a thin film the excess conductivity is

$$\sigma'' = \frac{e^2 T}{4\pi d} \frac{1}{E(T, m_x)}$$

(44)

where $d$ is the film thickness. Expansion of $E(T, m_x)$ in the region $T_o$ and $m_x^0$ gives

$$\sigma'' = \frac{e^2 T}{4\pi d} \left\{ A(m_x - m_x^0) + B(T - T_o) + D(m_x - m_x^0)(T - T_o) \right\}^{-1}$$

(45)

where

$$A = \frac{\partial}{\partial m_x} \left( \frac{1}{\nu_s'} \right) \bigg|_{m_x = m_x^0, T = T_o}$$

$$B = \left\{ \frac{\partial^2}{\partial T^2} E(T, m_x) \right\} \bigg|_{m_x = m_x^0, T = T_o}$$

$$D = \frac{\partial^2}{\partial T \partial m_x} \left( \frac{1}{\nu_s'} \right) \bigg|_{m_x = m_x^0, T = T_o}$$

(46)

and $\frac{1}{\nu_s'}$ is given by equation (25). $\sigma''$ diverges quadratically in temperature as $T \rightarrow T_o$ and $m_x \rightarrow m_x^0$. This is analogous to Fulde and Maki (1970). The linear divergence of Aslamasov and Larkin (1968) is no longer present. In particular, $\sigma''$ as a function of temperature exhibits a maximum at $T = T_o$ for concentrations $m_x > m_x^0$.

The resistance per square is given by

$$R = \frac{\pi}{e^2 \xi_F} \cdot \frac{1}{\nu'} \cdot \left[ 1 + \frac{T}{E_F} \cdot \frac{1}{\nu'} \cdot \frac{1}{E(T, m_x)} \right]$$

(47)
where $\mathcal{E}_F$ is the Fermi energy; $\frac{1}{T^*}$ is given by equation (24).

Figure (20) shows the resistance per square as a function of $T$ for various values of $m_\Sigma > m^o_\Sigma$ where $m^o_\Sigma = 0.19$ atomic percent and $T_k'/T_{co} = 0.03$. Curve D shows the variation of the resistance per square with temperature when the effects of superconducting fluctuations are negligible ($m_\Sigma > m^o_\Sigma$). Curves A, B and C show the variation of the resistance per square with temperature in the region of impurity concentration $m_\Sigma \approx m^o_\Sigma$. Each of these curves shows a minimum at $T = T_o$. The minimum is a consequence of the existence of superconducting fluctuations in the region $m_\Sigma \approx m^o_\Sigma$. In the region of temperature near $T_o$, supercurrents caused by the superconducting fluctuations lead to a decrease in the resistance per square of the film. At $T = T_o$ the density of superconducting fluctuations is a maximum and decreases as $|T - T_o|$ increases. This leads to a maximum in the supercurrent and a minimum in the resistance per square of the film at $T = T_o$. The minimum in the resistance per square is largest for curve A ($m_\Sigma = 0.1901$ atomic percent) since for $m_\Sigma \approx m^o_\Sigma$ and $T$ near $T_o$ the system is in a region of critical superconducting fluctuations. When $m_\Sigma$ is increased (curve B, $m_\Sigma = 0.191$ atomic percent; curve C, $m_\Sigma = 0.2$ atomic percent) the system is no longer in this critical region. The minimum in the resistance per square will become less pronounced and will eventually vanish for $m_\Sigma > m^o_\Sigma$ (curve D).

The observation of a minimum in the resistance per square of thin film containing magnetic impurities would provide a
further confirmation of the re-entrant behaviour of the curve $T_c$ versus $M_L$ in dilute superconducting, Kondo alloys.
The resistivity $\rho$ as a function of temperature in the neighbourhood of the re-entrant point $(C_0^M, T_0)$ for various magnetic impurity concentrations $C_M > C_0^M$. Here $T_0 = 2.7 \text{ K}$, $C_0^M = 0.19 \text{ at.} \%$. The concentrations are: A, 0.1901 at.\%; B, 0.191 at.\%; C, 0.2 at.\%; D, 0.225 at.\%. The specimen is a thin film.
CHAPTER VII

EFFECT OF ELECTRON CORRELATIONS IN THE FALICOV-KIMBALL
MODEL FOR THE METAL-INSULATOR TRANSITION

I. Introduction

Transition metal oxides and sulfides are ideal subjects to study because of the diversity of electrical properties of apparently similar materials. Most of these materials that are pure, stoichiometric crystals are either insulators or metals at all temperatures. The metals are characterized by a low resistivity, of the order $10^{-2}$ - $10^{-6}$ ohm-cm at room temperature and a linear increase in resistivity as the temperature is raised. Some of these materials are TiO, CrO$_2$ and ReO$_3$. The insulators and semiconductors have resistivities of the order $10^3$ - $10^{17}$ ohm-cm at room temperature and an exponentially decreasing resistivity as temperature increases. Some of the good insulators are NiO, CoO and MnO.

The materials which we are concerned with do not fall into either of the above categories. These are semiconducting or insulating at low temperatures, but at a given temperature or over a range of temperature their resistivity decreases by a factor as great as $10^{17}$ and at higher temperatures are metallic. The wide variety in the properties of materials that undergo the metal-insulator transition can be exhibited in four examples: V$_2$O$_3$, VO$_2$, Ti$_2$O$_3$ and NiS.
\( V_2O_3 \) undergoes a first order phase transition at 150°K from a high temperature metal to a low temperature semiconductor. At the transition \( V_2O_3 \) orders antiferromagnetically and undergoes a 3.5% volume expansion. The application of pressure decreases the transition temperature until it reaches zero at 26 kilobars (Rice and McWhan 1969).

\( NiS \) undergoes a first order phase transition from a metal to a semi-metal at 264°K. At the transition temperature, anti-ferromagnetic ordering sets in and there is a volume change of less than 1%.

\( VO_2 \) exhibits a first order phase transition from a metallic to a semiconducting state at 340°K. The semiconducting gap is temperature dependent. At the transition temperature the crystal distorts, but there is neither a volume change nor magnetic ordering.

Similarly, \( Ti_2O_3 \) exhibits a phase transition accompanied by a crystalline symmetry change without magnetic ordering. Here the phase transition is second order and the high temperature behaviour is not that of a simple metal. For \( Ti_2O_3 \), the experimental situation is somewhat unclear.

There are several physically different theoretical models for the metal-insulator phase transition. One which exhibits, in the Hartree approximation, a wide range of behaviour is a model introduced by Falicov and Kimball (1969). We discuss this model in the next section.
II. The Model of Falicov and Kimball

Falicov and Kimball (1969) have proposed a model that is applicable to any material that exhibits a metal-insulator transition. The model is characterized by:

1. a conduction band (to be called an "s" band) provided by uncorrelated, extended states.

2. a very narrow band (to be called a "d" band) provided by highly localized and correlated states; the correlations are important enough to prevent the occupancy by electrons of the opposite spin of the same localized state.

3. a Coulomb repulsion between the localized "d" electron and the "s" electron centered on the same atom; this interaction is the mechanism responsible for the metal-insulator transition.

The insulating ground state of the system has the localized "d" states singly occupied and the "s" band empty. Quasi-particle excitations correspond to the excitation of electrons into the "s" band.

The Hamiltonian we consider is

\[
H = \sum_{ij\sigma} E_{ij} c_{i\sigma}^+ c_{j\sigma} + \sum_{\alpha} E d_{\alpha}^+ d_{\alpha} + \lambda \sum_{\alpha \beta} c_{i\alpha}^+ c_{i\beta}^+ d_{i\alpha}^+ d_{i\beta} + H_d'
\]  

where \( c_{i\sigma}^+ \) is the creation operator in the Wannier representation for an "s" electron of spin \( \sigma \) at the ionic site \( R_i \), \( d_{i\alpha}^+ \) is the creation operator for a localized "d" electron
of spin $\sigma$ at the ionic site $R_i$, and $\lambda$ is the Coulomb interaction constant. The term $H_d^i$ describes the overlap between neighbouring "d" states or between "d" states and extended states. This interaction provides a mechanism for the number of "d" electrons to fluctuate. However, the number of electrons in a localized "d" state can never be two.

Falicov et al. (1970) treat the Hamiltonian [equation (1)] in the Hartree approximation. They replace the operator

$$\sum_i d_{i^0}^d d_{i^0}^d = \sum_i \langle d_{i^0}^d d_{i^0}^d \rangle = m_d$$

where $m_d$ is the average number of "d" electrons for each ion. The number of "d" electrons in the equilibrium configuration is found from the minima of the Free energy as a function of $m_d$. When the strength of the electron-electron Coulomb interaction is varied the number of "d" electrons (or "s" electrons) in the equilibrium configuration has the following behaviours:

(a) stable metal,
(b) stable insulator,
(c) first order metal-insulator transition, and
(d) a gradual metal to insulator transition.

In the Hartree approximation the "s" electrons move in the average Coulomb field of the "d" electrons on a site $R_i$. This approximation is most valid if the excited states are delocalized throughout the crystal (wide bands). It is not expected to be valid if the excited states are localized at
the ionic site. In this case the "s" electron moves in the 
Coulomb field of one "d" electron and not the Coulomb field 
of the average number of "d" electrons for each ion. Also 
there is the intermediate case of the electronic excited 
states being delocalized over several unit cells (narrow 
bands). These electrons will interact with each localized 
"d" electron in the unit cell. We see that the Hartree ap-
proximation incorrectly gives the electron-electron Coulomb 
energy for strongly correlated systems. Since the Coulomb 
energy determines the phase transitions of the system we 
must go beyond the Hartree approximation to include the 
effects of correlations on the metal-insulator phase transi-
tion.

III. The Atomic Limit

The Hamiltonian (1) can be solved in the atomic limit; 
that is, in the limit of negligible overlap between the wave 
functions on different atoms. The only effect of the sur-
rounding atoms on the considered atom is to allow fluctua-
tions in the number and spin direction of the electrons 
(provide a Fermi surface). For simplicity we take the con-
duction band infinitely narrow with

\[ \epsilon_{ij} = \epsilon_{0} \delta_{ij} \]
The interaction $H_d$ in the Hamiltonian equation (1) allows the number of "s" and "d" electrons on each ionic site to fluctuate. In the atomic limit each "s" electron is localized on an ionic site. Each of the possible ionic configurations is an eigenstate of the Hamiltonian equation (1). There are 12 eigenstates of the Hamiltonian:

(a) 2 with 3 electrons: $d_{-\beta}^+ a_{-\beta}^+ a_{-\beta}^0 \rangle$, $d_{-\beta}^+ a_{-\beta}^0 a_{-\beta}^0 \rangle$; 
(b) 5 with 2 electrons: $d_{-\beta}^+ a_{-\beta}^0 a_{-\beta}^0 \rangle$, $d_{-\beta}^+ a_{-\beta}^0 a_{-\beta}^0 \rangle$, $d_{-\beta}^+ a_{-\beta}^+ a_{-\beta}^+ \rangle$ and $a_{-\beta}^+ a_{-\beta}^+ \rangle$; 
(c) 4 with 1 electron: $d_{-\beta}^+ a_{-\beta}^0 \rangle$, $a_{-\beta}^+ a_{-\beta}^0 \rangle$ and $\beta \rightarrow -\beta$; 
(d) 1 with no electrons: $|0\rangle$

where $|0\rangle$ is the vacuum state and $\beta$ is the electron spin.

Since the Hamiltonian [equation (1)] is rotationally invariant, some of the eigenstates have a spin degeneracy. Taking account of the degenerate states in the usual manner, the wave function for an arbitrary atom is written as

$$|\Psi\rangle = [\omega^{(m_1 n_1 a_{s^1}^0)} (\mu^0 n_1 a_{s^1}^0)(p^0 q_1 a_{s^1}^0)(p^0 q_1 a_{s^1}^0)] |0\rangle \tag{3}$$

where $a_{s^1}^0$ creates an electron of spin $\beta$ in the "s" state, $d_{d^1}^0$ creates an electron of spin $\beta$ in the "d" state and $\mu^0 = \rho^0 = \omega^2 = 2z^2 = 1$ for $|\Psi\rangle$ to be normalized to unity. The density matrix that describes the considered atom is

$$\rho = \sum_i P_i |i\rangle \langle i| \tag{4}$$
where the sum is over the non-degenerate atomic eigenstates of the Hamiltonian (1) and $P_i$ is the probability of finding the atom in the non-degenerate eigenstate $|i\rangle$. From equation (3) the probability $p(S^4, d^0)$ of having $d$ "s" electrons and $d$ "d" electrons are

$$p(S^4, d') = Z^2 q^4$$  
$$p(S^4, d) = (1 - 2Z^2) n^4$$  
$$p(S', d') = Z^2 q^2(1 - q^2)$$  
$$p(S', d) = (1 - 2Z^2) n^2(1 - n^2)$$  
$$p(S^0, d') = Z^2 (1 - q^2)^2$$  
$$p(S^0, d) = (1 - 2Z^2)(1 - n^2)^2$$

where $Z^2$ is the probability of having a "d" state occupied by an electron of either spin direction, $q^2$ is the probability of having an "s" state occupied by an electron of either spin direction when there is an electron in the localized "d" state and $n^2$ is the probability of having an "s" state occupied by an electron of either spin direction when the "d" state is empty. The entropy $S$, energy $E$ and number of electrons $N$ for each atom are

$$S = -K \sum_i P_i \ln (P_i)$$

$$= -K \left\{ (1 - 2Z^2) [3n^2 \ln n^2 + 2(1 - n^2) \ln (1 - n^2) + \ln (1 - 2Z^2)] \right\} + 2Z^2 [q^2 \ln q^2 + 2(1 - q^2) \ln (1 - q^2) + \ln q^2]$$

$$E = \sum_i P_i E_i$$

$$= \varepsilon_0 \left\{ (1 - 2Z^2) [2n^2 + 2Z^2 q^2] + \varepsilon (2Z^2) + 2 (2Z^2) (2q^2) \right\}$$
where $\langle \psi | \mathbf{H} | \psi \rangle = E \langle \psi | \psi \rangle$ and

$$
N = \sum_l P_l N_l = (1-2z^2)2n^2 + (2z^2)(2q^2) + 2Z^2
$$

Since the number of "s" electrons and "d" electrons for each atom are

$$
\begin{align*}
\mathbf{m}_s &= (1-2z^2)2n^2 + (2z^2)(2q^2) \\
\mathbf{m}_d &= 2z^2
\end{align*}
$$

the average energy for each atom can be written

$$
E = \varepsilon_0 \mathbf{m}_s + \varepsilon \mathbf{m}_d + \lambda \mathbf{m}_d \mathbf{m}_s
$$

where $\lambda = \frac{2q^2}{m_s}$ is the fraction of "s" electrons that interact with a localized "d" electron.

To obtain the thermodynamic properties of our system, we calculate the Free energy $F = E - TS$ for a fixed number of electrons for each atom from equations (6) and (7). Minimizing the Free energy with respect to $\mathbf{m}$ and $\mathbf{m}_d$ we obtain the following coupled equations:

$$
\begin{align*}
\mathbf{m}_d \mathbf{m}_d (N - m_d) (1 - e^{-\mathbf{m}_d}) + &m_2 + (e^{-\mathbf{m}_d} - 1)(N + m_d) - 2e^{-\mathbf{m}_d} = 0 \\
\frac{K T}{2} &\left\{ - \sum \mathbf{m}_d \ln (m_d (1-m_d)) - \sum \mathbf{m}_d \ln (1-m_d) - \sum \mathbf{m}_d \ln (N - m_d) \\
+ (1 - m(N - m_d)) \ln (1 - m(N - m_d)) &+ m(N - 2m_d) \ln m - m \ln 2 \\
- (1 - m(N - 2m_d)) \ln (1 - 2N - m_d + m m_d (N - m_d)) \right\} = \varepsilon_0 - \varepsilon - m \lambda (N - 2m_d)
\end{align*}
$$
The solutions to equations (12) and (13) give the number of "d" electrons and "s" electrons in the equilibrium configuration for a given energy level separation ($\mathcal{E} - \mathcal{E}_0$) and Coulomb interaction $\lambda$. For the sake of simplicity we consider only the case with $\mathcal{E}_0 > \mathcal{E}$ and $N = 1$.

For all values of $\mathcal{E}, \mathcal{E}_0, \lambda$ and $T$, equations (12) and (13) have one solution for $m_d$ and $m_s > 0$. We shall follow Falicov et al. (1970) and choose $m_d = 0 (m_s = 1)$ for the metallic state and $m_d = 1 (m_s = 0)$ for the insulating state. In figure (21) we show the variation of $m_s = 1 - m_d$ with $\left(\frac{\mathcal{E} - \mathcal{E}_0}{\lambda}\right)$ for several values of temperature. The number of "s" electrons is seen to be a continuous function of $\left(\frac{\mathcal{E} - \mathcal{E}_0}{\lambda}\right)$. If we plot for each temperature $T$ the variation of $m_s$ with $\left(\frac{\mathcal{E} - \mathcal{E}_0}{\lambda}\right)$ we can obtain the variation of $m_s$ with $\lambda/T$ for fixed $\left(\frac{\mathcal{E} - \mathcal{E}_0}{\lambda}\right)$. This is shown in figure (22). We see from figure (22) that it is difficult to thermally excite "d" electrons to the "s" state if the energy difference $\mathcal{E} - \mathcal{E}_0$ is large (compare curves A and D). From the dependence of $m_s$ on $\lambda/T$ [figure (22)] we see that there is not a first order phase transition from an insulating state to a metallic state. Rather there is a continuous change in the number of "s" electrons as the temperature is changed. This behaviour is similar to the change in the conductivity of SmB$_6$ (Menth et al. 1969) with temperature.
Figure (23) shows the variation of $\mathcal{M}$ (the fraction of "s" electrons interacting with "d" electrons) with $\mathcal{M}_d$ for various values of temperature. For all values of $\mathcal{M}_d$, the value of $\mathcal{M}$ increases as temperature increases [figure (23)]. This is expected since the occupation of "s" states increases with temperature. Figure (24) (curves a, b, and c) show the variation of $\mathcal{M}$ with $\lambda/\tau$ for fixed $\mathcal{M}_d$. These curves have the same behaviour as the curves of $\mathcal{M}$ versus $\mathcal{M}_d$ in figure (23).

IV. Case of Increasing Overlap of the "s" Electronic States

We now consider the situation in which the overlap between "s" orbitals on different atoms is not negligible. The "s" eigenstates of the Hamiltonian [equation (1)] will be

$$|\psi_i\rangle = \sum_j \lambda_{ij} |\varphi_j\rangle$$
Figure 21
Figure 22
Figure 23
where \( i \) and \( j \) refer to the atoms at sites \( R_i \) and \( R_j \), \( \psi_j \) is an atomic like orbital centered on an ion at \( R_j \) and \( d_{ij} = \delta_{ij} \) in the atomic limit. In general, \( d_{ij} \) is a function of the hopping term \( \xi_{ij} \), the Coulomb interaction \( \lambda \) in the Hamiltonian equation (1) and the distribution of "d" electrons.

An "s" electron with wave function \( |\psi_i\rangle \) (centered on site \( R_i \)) interacts with a "d" electron on the same site. It will also move in the Coulomb field of the "d" electrons on neighbouring atoms. Likewise the "d" electron at \( R_i \) will interact with a fraction \( |d_{ii}|^2 \) of the electron described by \( |\psi_i\rangle \) plus a fraction \( \sum_j |d_{ji}|^2 \) of the electrons described by \( |\psi_i\rangle \).

The Coulomb energy for a "d" electron at atomic site \( R_i \) and an "s" electron whose wave function is \( |\Psi_i\rangle \) will depend on \( |d_{ii}|^2 \). When \( |d_{ii}|^2 = 1 \) the Coulomb energy is maximum. For \( |d_{ii}|^2 < 1 \), the Coulomb energy decreases since the "s" electron is no longer localized at \( R_i \). It is expected that the change in the Coulomb energy with \( |d_{ii}|^2 \) will effect any possible phase transitions. Initially, we assume that \( |d_{ii}|^2 \) and \( \sum_j |d_{ji}|^2 \) do not depend on \( i \).

As in the atomic limit \( m_s \) and \( m_d \) are the average number of "s" electrons and "d" electrons for each atom. The probability that the "s" state centered on an ion with no "d" electron is occupied by an electron of one spin direction is \( \mathcal{N}^a \); if the "d" state is occupied, the probability
that the "s" state is occupied by an electron of one spin direction is \( q^2 \). The average number of "s" electrons not interacting with "d" electrons is given by \( 2(1-m_d)X^2 \); the average number of "s" electrons interacting with "d" electrons is given by \( 2m_dy^2 \) where

\[
2X^2 = 2v^2y^2 + (1-f)m_s
\]

\[
2Y^2 = 2q^2y^2 + (1-f)m_s,
\]

\( f = \frac{1}{4} \) and

\[
m_s = 2(1-m_d)X^2 + 2m_dy^2 = 2(1-m_d)/v^2 + 2m_d q^2
\]

In the next approximation, the conduction band energy is replaced by an average kinetic energy \( E_0 \).

The average total energy, number of electrons and entropy for each atom are

\[
E = (1-m_d)(2X^2)E_0 + m_d(2Y^2)E_0 + \lambda m_d(2Y^2) + \varepsilon m_d
\]

\[
= m_s E_0 + \varepsilon m_d + \lambda m_d m_s (m_f + 1-f)
\]

\[
N = m_d + m_s
\]

\[
S = -k\left[ m_d \left\{ 2q^2 \ln q^2 + 2(1-q^2) \ln (1-q^2) + \ln \left( \frac{m_d}{x} \right) \right\} + (1-m_d) \left\{ 2v^2 \ln v^2 + 2(1-v^2) \ln (1-v^2) + \ln (1-m_d) \right\} \right]
\]
where \( m = \frac{2q^2}{m_s} \). The effective Coulomb interaction \((1-f+m f)\lambda\) cannot be smaller than \((1-f)\lambda\). It is noted that only the energy for each atom depends on \( f \).

The thermodynamic properties of the system are found by minimizing the Free energy \( F = E - TS \) for a fixed number of electrons for each atom with respect to \( m \) and \( m_d \). The resulting coupled equations for \( m \) and \( m_d \) are

\[
\begin{aligned}
\lambda m_d (N-m_d)(1-e^{-f\lambda})(1-e^{-f\lambda})m_d (2+f-e^{-f\lambda})(N+m_d)-2e^{-f\lambda}=0
\end{aligned}
\]


\[
\begin{aligned}
\varepsilon - \varepsilon_0 + [(1-f+m f)\lambda (N-2m_d)+kT[ln(m_d (1-m_d))-ln(N-m_d)]
\end{aligned}
\]

\[
\begin{aligned}
-(1+m(N-m_d))ln(1-m_d)+(2-m(N-2m_d))ln(2-m(N-m_d))-ln2
\end{aligned}
\]

\[
\begin{aligned}
+m(N-2m_d)ln m -(1-m(N-2m_d))ln(2-N-m_d+m m_d (N-m_d)] = 0
\end{aligned}
\]

We shall now obtain the values of \( m_d \) and \( m \) in the equilibrium configuration from the solutions of equations (20) and (21) as \( f \) is changed.

(a) The Atomic Limit: \( f = 1 \)

In the atomic limit the overlap of "s" states on adjacent atoms is negligible. The fraction \( f \) of an "s" electron with wave function \( |\psi_i\rangle \) remaining at the atomic site \( R_i \) is one. In this limit we recover equations (6), (7) and (8) for the entropy, energy and number of electrons for each atom. These equations have been discussed previously.
The transcendental equations (20) and (21) give one value of \( O \) and one or three values of \( m_d \) [figure (26)]. In the case of three solutions for \( m_d \), two give relative minima for the Free Energy and one gives a maximum for the Free Energy. To find which value of \( m_d \) corresponds to an absolute minima we must calculate the Free Energy. In figure (25) we show the Free Energy as a function of \( \frac{E - \varepsilon_0}{\lambda} \) for \( T/\Lambda = 0.2 \) and \( f = 0 \). From figure (25) we see that the Free Energy is a minimum along the curve ABE. Using these values of the Free Energy along this curve we shall now find the equilibrium electronic configurations of our system.

Figure (26) shows the variation of \( m_d \) with \( \frac{E - \varepsilon_0}{\lambda} \) for \( T/\Lambda = 0.2 \) and \( f = 0 \). The Free Energy corresponding to the electronic configurations having the values of \( m_d \) along the curve AB'CDB'E [figure (26)] is given by the curve ABCDBE in figure (25). The values of \( m_d \) indicated by B' and B'' correspond to the same Free Energy [indicated by B in figure (25)]. The values of the Free Energy given by the curve ABE [figure (25)] correspond to values of \( m_d \) given by the curves AB' and B''E [figure (26)]. When the value of \( m_d \) in the equilibrium configuration is given by the curve AB' [figure (26)], the system is in the insulating state \( m_d > 0, m_s = 0 \). When the value of \( m_d \) in the equilibrium configuration is given by the curve B''E [figure (26)], the system is in the metallic state \( m_d < 0, m_s = 1 \). We see that
Figure 25
Figure 26
Figure 27
Figure 28
the system undergoes a first order phase transition from an insulator to a metal at a value of \((\frac{\epsilon - \epsilon_0}{\lambda})\) corresponding to the point B' [figure (26)]. If we repeat this analysis for different temperatures and different values of \(f\) we can construct a phase diagram for the metal-insulator transition. This is shown in figure (27) where we have plotted the variation of the temperature for the first order transition with \((\frac{\epsilon - \epsilon_0}{\lambda})\).

The region marked M is the metallic state; the region marked I is the insulating state. Comparing the phase diagrams for \(f = 0\) and \(f = .5\) in figure (27) for the same value of \((\frac{\epsilon - \epsilon_0}{\lambda})\) we see that increasing \(f\) has decreased the temperature at which the first order phase transition takes place. In fact, for some values of \((\frac{\epsilon - \epsilon_0}{\lambda})\) there is a first order phase transition when \(f = 0\), but no first order phase transition when \(f = 0.5\).

These effects can be seen in figures (29) and (30) where we have plotted the variation of the number of "s" electrons

\[ m_s = N - m_d \quad \text{with} \quad \gamma / T \quad \text{for} \quad f = 0 \quad \text{[figure (29)]} \quad \text{and} \quad f = 0.5 \quad \text{[figure (30)].} \]

Each figure shows the three values of \(m_s\) found from equations (20) and (21). The dashed lines represent the unphysical solutions; the solid lines are the number of "s" electrons in the equilibrium configuration for a fixed \((\frac{\epsilon - \epsilon_0}{\lambda})\). Each of figures (29) and (30) shows a first order phase transition from a low temperature insulator \(m_s \approx 0\) to a high temperature metal \(m_s \approx 1\). The transition temperature decreases from \(T_p = .14 \lambda\) for \(f = 0\) [figure (29)] to \(T_p = .1 \lambda\) for \(f = .5\).
Figure 29

\[ N = 1 \quad \varepsilon - \varepsilon_0 = -0.1 \lambda \]

\[ f = 0 \]
Figure 30

N=1  \( \epsilon - \epsilon_o = -0.1 \lambda \)

\( f = 0.5 \)
When \( f = 1 \) we have already seen there is no first order phase transition from an insulator to a metal.

The suppression of the first order metal insulator transition can be seen from the following. For a two level system of fixed energy difference the Free Energy can be decreased by increasing the electron entropy. This can be accomplished by thermally exciting "d" electrons into "s" states. However, there will be an accompanying increase in the electron energy, in particular, the Coulomb energy. In our model the Coulomb interaction is between "d" and "s" electrons at the same site \( \mathbf{R}_1 \). We have said that \( f \) is the fraction of an electron whose wave-function is centered on \( \mathbf{R}_1 \), that is localized at the site \( \mathbf{R}_1 \). Increasing \( f \) will then increase the Coulomb energy for the "s" and "d" electrons at the site \( \mathbf{R}_1 \). For a fixed \( (E - E_0) \), this will increase the energy needed to excite a "d" electron into an "s" state. If the increase in the electron energy is large enough it will offset any decrease in the Free Energy caused by an increase in the entropy. This will lead to a suppression of the first order metal-insulator transition. The first order metal-insulator phase transition disappears when \( f = 1 \) because the "s" state is localized at the atomic site \( \mathbf{R}_1 \). This gives the largest value for the Coulomb energy.

A consequence of this is the expectation that \( \eta \), the fraction of "s" electrons interacting with "d" electrons, will
increase as \( f \) decreases. This is shown by comparing figure (28) \((f = .5)\) and figure (23) \((f = 1)\) for the variation of \( m \) with \( m_d \) at a fixed temperature. Comparing the curves of \( m \) versus \( m_d \) for the same temperature shows that \( m \) increases as \( f \) decreases. Figure (24) shows the curves of \( m \) versus \( \lambda/\Gamma \) for some values of \( m_d \) for \( f = 1 \) and \( f = .5 \). These curves reflect the same general behaviour as was exhibited by figures (23) and (28).

The \( f = 0 \) solution is particularly interesting. In this case, \( \lambda^2 = q^2, m = 1 \) and \( X^2 = Y^2 \). This is clearly the Hartree approximation: the probability of having an "s" electron on a particular site is independent of the presence of a "d" electron. Using the notation of section (III), we have
\[
p(s^d d^0) = p(s^0) p(d^0).
\]
The Coulomb interaction has its full value \( \lambda \). This is the approximation used by Falicov et al. (1970).

The Falicov and Kimball model (1969) has been treated in the C.P.A. approximation by Plischke (1972) who found, at least in a significant range of parameters, the phase transition is an artifact of the Hartree approximation. Our calculation is qualitatively different from the C.P.A. approximation. The C.P.A. approximation treats the Coulomb interaction as a random variable with value 0 or \( \lambda \) on each atomic site. For our translationally invariant system, we have an effective Coulomb interaction which we treat as a thermodynamic variable. Unlike the C.P.A. approximation our solution exhibits a wide variety of
electrical properties. However, the effect of correlations between the localized and itinerant electrons is to change the character of the metal-insulator phase transition predicted by the Hartree treatment of Falicov et al. (1970).
APPENDIX A

We shall outline the derivation of equation III-(6a). The perturbation series for the ladder propagator is shown in figure (a-1). The integral equation for the ladder propagator is

\[ G_s(p+K_j-p; \omega_m+\omega_j-\omega_m) = G_0(p+K_j-p; \omega_m+\omega_j-\omega_m) \left[ 1 + \frac{1}{i\omega_m - \xi F} \right] G_0(-p - \omega_m) \]

where \( G_0(\omega_m) = (i\omega_m - \xi F)^{-1} \) and \( \omega_m = (2m+1)\pi FT \)

The sum of ladder propagators \( \mathcal{L}(k\omega_r) \) and \( \mathcal{L}_0(k\omega_r) \) are defined as

\[ \mathcal{L}(k\omega_r) = \kappa T \sum_{\omega_m} \int \frac{d^3q}{(2\pi)^3} G_s(q+K_j-q; \omega_m+\omega_j-\omega_m) \]

\[ \mathcal{L}_0(k\omega_r) = \kappa T \sum_{\omega_m} \int \frac{d^3q}{(2\pi)^3} G_0(q+K_j-q; \omega_m+\omega_j-\omega_m) G_0(-p - \omega_m) \]

Multiplying equation A-1 by \( \kappa T \) and summing over \( \omega_m \) we obtain equation III-(6a).

\[ \mathcal{L}(k\omega_r) = \mathcal{L}_0(k\omega_r) + ig \mathcal{L}_0(k\omega_r) \mathcal{L}(k\omega_r) \]

The perturbation series for the \( t \) matrix is shown in figure (a-2). The integral equation for the matrix is

\[ t(q\omega_r) = ig \left\{ 1 + \sum_m \int \frac{d^3q}{(2\pi)^3} G_0(q+q\omega_m,\omega_r) G_0(-q - \omega_m) t(q\omega_r) \right\} \]

\[ = ig \left\{ 1 + \mathcal{L}_0(q\omega_r) t(q\omega_r) \right\} \]
One may also write the integral equation for the ladder propagator in terms of $t(q\omega)$:

$$G_s(p + p_i - p_f, \omega_n + \omega_i - \omega_m) = G_0(p + q, \omega_n + \omega_f) G_0(-p - \omega_m)$$

$$A-6$$

$$\times \{1 + t(q, \omega_f) KT \sum_{\omega_n} \left( \frac{d^3k}{(2\pi)^3} \right) G_0(p + k, \omega_n + \omega_f) G_0(-p - \omega_m) \}$$

Summing equation $A-6$ over $(p, \omega_n)$ gives equation $III-(10)$. 
APPENDIX B

In the presence of impurities each ladder diagram in the perturbation series for the ladder propagator depends on the position of the impurities because each scattering of an electron by an impurity leads to a factor $U(q) e^{iq \cdot a}$. If the analytic expression for a ladder diagram is averaged over impurity position $R_i$, the result will be zero unless there are pair scatterings from the same impurity with momentum transfers $q$ and $-q$ [see fig. (a-3)]. Each pair scattering gives a term $m_x |U(q)|^2$ to the averaged term in the perturbation series. $m_x$ is the volume density of impurities. As the averaging has restored momentum conservation, we have

$$\langle G_{5}^{\text{imp}}(p+q_1-p_1, \omega_m, \omega_{v_1}; \omega_m) \rangle_{av} = G_{5}^{\text{imp}}(p+q_1-p_1, \omega_m, \omega_{v_1}; \omega_m) e^{ip \cdot a} \quad B-1$$

Some impurity averaged ladder diagrams that appear in the perturbation series for $G_{5}^{\text{imp}}(p+q_1-p_1, \omega_m, \omega_{v_1}; \omega_m)$ are shown in figure (a-3). The pair scattering from the same impurity is shown by a dashed line joining two crosses. We neglect all higher terms in figures (a-3-i) and (a-3-ii) (Brink and Zuckermann 1965). Only impurity averaged ladder diagrams such as figure (a-3-iii) are retained in the perturbation series for $G_{5}^{\text{imp}}(p+q_1-p_1, \omega_m, \omega_{v_1}; \omega_m)$. The integral equation for $G_{5}^{\text{imp}}(p+q_1-p_1, \omega_m, \omega_{v_1}; \omega_m)$ is now given by
\[ G_{s}^{\text{imp}}(k + \rho, \rho; m + \omega, \omega) = K(p + \rho; m + \omega, \omega) \{ 1 + iq \} KT \]

\[ \sum_{\omega} \left[ \frac{d^3 \rho}{(2\pi)^3} G_{s}^{\text{imp}}(p + \rho; m + \omega, \omega) \right] \]

where \( K(p + \rho; m + \omega, \omega) \) is the impurity averaged product of two single particle Green's functions.

One can obtain a power series expansion in \( m_{2} |U(q)|^{2} \)

for \( K(p + \rho; m + \omega, \omega) \). The terms in the series are the impurity averaged ladder diagrams figure (a-4). Higher order expressions corresponding to figures (a-4-i) and (a-4-ii) are neglected (Gor'kov 1960). Dashed lines joining crosses on the same electron line give the impurity averaged single particle Green's function [figure (a-4-iii)].

\[ \hat{G}(p, \omega) = (i\omega_{m} + \frac{1}{2\tau} \cdot \frac{\omega_{m}}{|\omega_{m}|} - \varepsilon_{p})^{-1} \]

where

\[ \frac{1}{2\tau} = m_{2} \frac{m_{p} e}{(2\pi)^{3}} \int |U(q)|^{2} \, d\Omega \]

is the single particle scattering rate.

The ladder series [figure (a-4-iv)] for \( K(p + \rho; m + \omega, \omega) \)

may be summed using the integral equation (Gor'kov 1960)

\[ K(p + \rho; m + \omega, \omega) = \hat{G}(p + \rho; m, \omega) \hat{G}(p, \omega) \]

\[ \times \left[ 1 + m_{2} \left( \frac{d^3 \rho}{(2\pi)^3} |U(q)|^{2} K(q + \rho; m + \omega, \omega) \right) \right] \]

The definitions of \( \chi^{\text{imp}}(q, \omega) \), \( \chi^{\text{imp}}_{0}(q, \omega) \) and \( \chi^{\text{imp}}_{0}(q, \omega) \) are the same as in Appendix A except one uses the impurity averaged ladder propagators.
\[ G_s = \frac{k+q}{\omega_m + \omega_r} + \frac{k+q}{\omega_m + \omega_r} + \frac{k'+q}{\omega_m' + \omega_r} \]

Figure a-1

\[ t = \left\{ \frac{k+q}{\omega_m + \omega_r} + \frac{k+q}{\omega_m + \omega_r} + \frac{k'+q}{\omega_m' + \omega_r} \right\} \]

Figure a-2
Figure a-3

Figure a-4
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