THE SPIN FLUCTUATION MODEL AND ITS APPLICATION TO THE ACTINIDES

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Spin Fluctuations occur at low temperatures in narrow band systems that possess a high density of states and a strong exchange interaction. Such systems possess no localised moments, but rather exhibit a class of behaviour in the physical properties reminiscent of magnetic systems. The physical properties of the Actinides are anomalous at low temperatures. In particular, Pu has a negative magnetoresistivity, a $T^2$ term in the low temperature resistivity and other physical properties reminiscent of magnetic orderings at low temperatures. However, experiments have failed to detect any existence of localised moments in Pu. The high value of electronic specific heat constant and a highly exchanged enhanced magnetic susceptibility, indicative of a high density of states and a strong exchange interaction, in the Actinides favour the existence of Spin Fluctuations in these systems. In this thesis, we present a calculation of the magnetoresistivity in the Spin Fluctuation model and are able to account rather satisfactorily for the negative magnetoresistivity of Pu. Other physical properties of the Actinides are also discussed in the light of the Spin Fluctuation model, which while still imperfect and limited to low temperatures, provides a unified picture for the Actinides.
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Introduction

The existence of magnetism in the early members of the Actinide series, especially Plutonium, has long been the subject of controversy in this field of research. The high value of the electronic specific heat constant $\gamma$ and the highly enhanced magnetic susceptibility of the Actinides indicate a large density of states at the Fermi surface and hence the likelihood of magnetic ordering in these metals. In addition, various transport properties of Plutonium, e.g. the negative magnetoresistance, the anomalous Hall effect, the electrical resistivity which is highly reminiscent of that of $\alpha$-Mn, known to order antiferromagnetically, all add to the speculation of magnetic orderings in Pu in particular (for a review, see Lee 1971). However, various experiments designed to detect the existence of localised moments in the Actinides (Brodsky 1971 and references therein) have given negative results. On the other hand, the fact that a large number of compounds of the Actinides, e.g. UN, U$_2$C$_3$, UPt, NpAl$_2$, NpC, PuPd$_3$, PuN, Pu$_3$S$_4$, (e.g. Hill 1970) order magnetically at low temperatures, and that Actinides in dilute solid solution in Pd show either nearly magnetic behaviour (e.g. Pd-Pu) or form localised moments on the Actinide impurity atoms all point to the localisation of the 5f electrons on the Actinide atoms in the compounds and dilute alloys, giving rise to the magnetic or nearly magnetic properties in these systems. One would expect, on these grounds, magnetism to be highly likely in the Actinide metals, especially in Np and Pu where the density of states is high and a large number of their compounds and dilute alloys are magnetic. This, together with the failure of experiments to detect the existence of local moments in the pure Actinides, has led Brodsky (1971) and Arko et al (1972) to suggest that Np and Pu are nearly magnetic, or the
so-called Spin Fluctuation systems, i.e., systems that possess a highly exchange enhanced magnetic susceptibility, the enhancement (which increases with both the exchange interaction strength and the density of states) being sufficiently large to give rise to, at low temperatures, a class of behaviour reminiscent of magnetic systems. It is part of the purpose of this thesis, therefore, to discuss the properties of the Actinide metals in the light of the Spin Fluctuation model.

The main aim of this thesis is two-fold:

1) To calculate from first principles the magnetoresistivity in the Spin Fluctuation model and to apply the result to Pu,

2) To put together the available theoretical results of physical properties in the Spin Fluctuation model as well as the corresponding experimental results of the Actinides and to make a comparison between the two.

However, because of the close connection between 1) and 2), 1) is somewhat admixed into 2) in the presentation of this work.

In the first chapter, we shall attempt to explain what Spin Fluctuations are and the conditions under which they occur; we concentrate our discussion on the nearly ferromagnetic Spin Fluctuations, but we also discuss the possibility of nearly antiferromagnetic Spin Fluctuations by employing a band structure model used by T. M. Rice (1969) in his discussion on chromium. In chapter two, we present a calculation of the electrical resistivity and magnetoresistivity in the Spin Fluctuation model, and review on the other physical properties investigated theoretically by other authors. A review of the experimental results in the Actinides is given in chapter three. In chapter four, we review on and discuss the previous theoretical attempts.
at explaining the physical properties of the Actinides, we start off by reviewing on the results of band structure calculations performed by various authors. In chapter five, we apply the results of the magnetoresistivity calculation to Plutonium, agreement with experimental results is found to be satisfactory. Other physical properties of the Actinides are also discussed in the light of the theoretical predictions of the Spin Fluctuation model; the effect of temperature increase on the Spin Fluctuation system is discussed in the light of recent higher temperature models.
The Spin Fluctuation model: Introduction

The underlying principles of the Spin Fluctuation model can be best illustrated by considering a ferromagnetic system above the Curie temperature $T_C$. As is well known, a ferromagnetic spin system retains an appreciable amount of short range order above $T_C$, as the temperature of the system is lowered towards the magnetic transition at $T_C$, the spin-spin correlation time $\tau$ as well as the range of spin order increases, until both become infinite at $T = T_C$ and the system magnetic with all its spins aligned parallel to each other. By intuitive inference, we would expect similar behaviour to prevail in nearly magnetic systems at low temperatures where the spin-spin correlation time $\tau$ and the range of spin order have become considerable. In other words, the spins are aligned parallel to one another over a larger and larger distance in space, and these aligned 'clusters' as it were exist for longer and longer time as the magnetic instability is approached. Macroscopically, these 'long-lived' finite ranged orderings of spins give rise to fluctuations, in space and time, in the magnetization of the entire system, and hence the name 'Spin Fluctuations' (for a review, see Schrieffer 1968). These fluctuations are correlated, the correlation function being related to the imaginary part of the generalised susceptibility function which measures the response of the system to external disturbances.

The existence of Spin Fluctuations has been well established in various high susceptibility alloys and metals like Fe, where the non-local magnetic susceptibility function

$$\chi(\mathbf{r},0) \sim \int_0^\infty \left\langle [\mathbf{M}(\mathbf{r},t),\mathbf{M}(0,0)] \right\rangle \, dt$$  \hspace{1cm} (1.1)

where $\mathbf{M}(\mathbf{r},t)$ is the space and time dependent magnetization, $\left\langle \right\rangle$ denotes the thermal average of, has been observed to have a range of the order
by employing elastic neutron scattering techniques (Low 1964). This range would be expected to tend to infinity if the interaction strength responsible for the magnetic tendency were increased to the minimum required to produce ferromagnetism in the system at 0°K.

In the Spin Fluctuation model, the tendency towards magnetism is determined by the strength of the effective exchange interaction between electrons in a narrow band. The presence of the exchange interaction leads to an enhanced static susceptibility over that of the Pauli value predicted for a free electron gas. At T = 0°K, this enhancement factor, commonly known as the Stoner enhancement factor, is given by

\[ S = \frac{\chi}{\chi_p} = (1 - U_0 D(E_F))^{-1} \]  

(1.2)

where \( \chi_p \) is the unenhanced Pauli susceptibility, \( U_0 \) the strength of the exchange interaction, \( D(E_F) \) the density of states of the electrons system at the Fermi surface. As the system approaches the ferromagnetic instability at \( T = 0°K \), the factor \( S \rightarrow \infty \) (\( U_0 D(E_F) \rightarrow 1 \)) and hence the static susceptibility diverges. We see that both \( U_0 \) and \( D(E_F) \) play an important role in determining the tendency of the system towards magnetism. Thus a system is most prone to being ferromagnetic when it has a strong interaction among the electrons, i.e. a large \( U_0 \), and/or, a high density of states at the Fermi surface, which is only likely for narrow band systems.

The factor \( S \) was first obtained theoretically by Stoner (1938, 1939) in an attempt to rectify the poor agreement between the theoretical prediction of the Pauli susceptibility and the experimental values of the strongly paramagnetic alloys of the transition metals. Stoner postulated a phenomenological internal field, known as the molecular field \( H_M \), proportional to the magnetization \( M \) of the system, i.e. \( H_M = \lambda M \), where \( \lambda \) is the so called molecular field constant. The molecular field
enhanced the polarization of the d-band on top of that produced by an externally applied field \( H \) and thus resulting in an enhanced magnetic susceptibility \( \chi \)

\[
M = \chi^P_o (H + H_{\text{ext}}) = \chi H
\]

(1.3)
giving

\[
\chi = \chi^P_o / (1 - \chi^P_o) = SV\chi^P_o
\]

(1.4)
where \( \chi^P_o \) is the Pauli susceptibility and at finite temperature is given by the well known formula

\[
\chi^P_o = 2\mu_B^2 D(E_F) \left[ 1 + \frac{(\pi k_B T)^2}{6} \left[ \frac{1}{D(E_F)} \left( \frac{\partial^2 D(E)}{\partial E^2} \right)_{E_F} - \frac{1}{D(E_F)} \left( \frac{\partial D(E)}{\partial E} \right)^2_{E_F} \right] \right]
\]

(1.5)

At zero temperature, (1.4) is reduced to

\[
\chi(T = 0) = \chi^P_o (T = 0) / (1 - 2\mu_B^2 D(E_F)\lambda)
\]

(1.6)
and the susceptibility diverges as the strength of the molecular field increases to the minimum value required to produce ferromagnetism at \( T = 0^0K \). The factor \( (1 - 2\mu_B^2 D(E_F)\lambda)^{-1} \) may be identified with the factor in (1.2), and is related to the effective exchange interaction \( U_o \) by \( \lambda = U_o / 2\mu_B^2 \)

(1.7)
Attempts to clarify the physical origin of the enhancement first came from Izuyama et al (1963) and Hubbard (1963). In the work of Izuyama et al, the origin of the enhancement was represented within the framework of random phase approximation (RPA) by the presence of a short range repulsion between fermions. In their model, the system is assumed to be well described by a tight binding non-degenerate electron band.

The dynamics of the electrons in the band are then assumed to be completely described by the Hamiltonian

\[
\mathcal{H} = \mathcal{H}_o + \mathcal{H}_{\text{int}}
\]

(1.8)
where

\[
\mathcal{H}_o = \sum_{k,\sigma} \varepsilon(k) \mathbf{a}^+_k \mathbf{a}_k \sigma
\]

(1.9)
\[
\mathcal{H}_{\text{int}} = \frac{U_o}{N} \sum_{k k' \sigma} \mathbf{a}^+_k \mathbf{a}^+_k \mathbf{a}_k \sigma \mathbf{a}_k \sigma
\]

(1.10)
$H_0$ represents the ordinary band energy of the electrons, $H_{\text{int}}$ their interaction energy, $\varepsilon(k)$ is the kinetic energy of an electron having wave vector $k$ and is equal to $\frac{1}{2}k^2/2m$ for a parabolic band, $m$ being the band mass of the electron; $a_{k,\sigma}^+$ and $a_{k,\sigma}$ are respectively the creation and destruction operators for an electron state of wave vector $k$ and spin $\sigma$; $N$ is the number of atoms in the system.

In the interaction term $H_{\text{int}}$, the matrix element of electron interaction has been replaced by the constant $U_0$. This implies that the Coulomb repulsion between two electrons is only effective when the two electrons are within the same atomic orbital. This may be allowed as a first approximation to the real situation, since in practice, the Coulomb interaction is always screened by the presence of other electrons and hence has an effective short range. In this model, then, a further step has been taken and a zero-ranged interaction is assumed, i.e. the electrons are assumed to interact only via the intraatomic interaction $U_0$. Now since only the electrons occupying the same atomic orbital can interact, the Pauli Exclusion Principle further limits the interaction to be between electrons of opposite spins.

Assuming $z$ to be the axis of magnetization, then we can calculate two distinct components of the magnetic susceptibility function, namely, the transverse susceptibility function $\chi_{\perp}$ (which is a function of the raising and lowering operators $H_x(a,q,t) + iH_y(a,q,t)$, $H_x$ being the spin density operator along the $x$-direction) and the longitudinal susceptibility function which we denote by $\chi_{zz}$ (a function of $H_z$ only). In a ferromagnetic system, the two functions would be different due to the presence of magnetization along the $z$-axis, whereas in the paramagnetic phase and in the absence of external fields, the
three components \( \gamma_{xx}, \gamma_{yy}, \gamma_{zz} \) naturally coincide and equal \( \gamma_{zz} \) for a system having cubic symmetry.

In the tight binding approximation, the spin density operators are related to the creation and destruction operators \( a^+ \) and \( a \) by

\[
M_-(q,t) = (F(q)/N)^{1/2} \sum_k a^+_{k+q \downarrow}^\dagger(t) a_{k \uparrow}^\dagger(t) \tag{1.11}
\]

and

\[
M_+(q,t) = (M_-(q,t))^+ \tag{1.12}
\]

\[
M_z(q,t) = (F(q)/2N)^{1/2} \sum_k \left( a^+_{k+q \uparrow}(t) a_{k \uparrow}(t) - a^+_{k+q \downarrow}(t) a_{k \downarrow}(t) \right) \tag{1.13}
\]

with the Fourier component of the spin density correlation function being defined by

\[
S_{ab}(q,\omega) = \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \langle \hat{M}_a(q,t) \hat{M}_b(q,0) \rangle \tag{1.14}
\]

where \( a \) and \( b \) denote the components (+, −, or z in this case). The symmetrized function of the spin density correlation

\[
\overline{S}_{ab}(q,\omega) = \frac{1}{2} \left( S_{ab}(q,\omega) + S_{ba}(q,\omega) \right) \tag{1.15}
\]

is then related to the imaginary part of the generalized susceptibility by (Izuyama et al 1963)

\[
\overline{S}_{ab}(q,\omega) = \frac{1}{1 - \exp(-\beta \omega)} \, 2 \text{Im} \chi_{ab}(q,\omega) \left| F(q) \right|^2 \tag{1.16}
\]

where \( \chi_{ab}(q,\omega) \) is the Fourier transform of the susceptibility function in equation (1.1) and \( \beta = 1/k_B T \), \( F(q) \) is the atomic form factor normalised such that \( F(0) = 1 \).

\[
\chi_{ab}(q,\omega) = i \int_0^\infty e^{i\omega t} \left\langle \left[ \hat{M}_a(q,t), \hat{\rho}_b(q,0) \right] \right\rangle \, dt \tag{1.17}
\]

where \( \hat{\rho} \) has been taken to be one.

Within the Random Phase Approximation (RPA), Izuyama et al has shown that the transverse and longitudinal susceptibilities, for a system that can be described by the Hamiltonian (1.10), to be
given by
\[ \chi_{+}^{+}(q,\omega) = \frac{\Gamma_{+}^{+}(q,\omega)}{1 - U_{0} \Gamma_{+}^{+}(q,\omega)} \]  
(1.18)
where
\[ \Gamma_{+}^{+}(q,\omega) = \frac{1}{N} \sum_{k} \frac{f_{k \uparrow} - f_{k+q \downarrow}}{\varepsilon_{k+q}(k) - \varepsilon_{k} - \omega} \]  
(1.19)
and
\[ \chi_{zz}^{+}(q,\omega) = \frac{1}{4} \frac{\Gamma_{+}^{+}(q,\omega) + \Gamma_{-}^{-}(q,\omega) + 2U_{0} \Gamma_{+}^{+}(q,\omega) \Gamma_{+}^{-}(q,\omega)}{1 - U_{0} \Gamma_{+}^{+}(q,\omega) \Gamma_{+}^{-}(q,\omega)} \]  
(1.20)
where
\[ \Gamma_{\sigma}(q,\omega) = \frac{1}{N} \sum_{k} \frac{f_{k \sigma} - f_{k+q \sigma}}{\varepsilon_{k+q}(k) - \varepsilon_{k} - \omega} \]  
(1.21)
and
\[ \varepsilon_{\sigma}(k) = \varepsilon(k) + U_{0} n_{-\sigma}/N \]  
(1.22)
is the modified one-particle energy within the Hatree-Fock framework due to the presence of the intraatomic exchange interaction.

\[ n_{\sigma} = \sum \langle a_{k \sigma}^{+} a_{k \sigma} \rangle \]  
is the thermal averaged number of electrons having spin \( \sigma \); \( f_{k \sigma} \) is the Fermi-Dirac distribution function.

In the paramagnetic phase, we have the number of up spin electrons equalling that of down spin electrons, i.e. \( n_{\uparrow} = n_{\downarrow} \) and as can be seen from the equations (1.18) to (1.21), \( \Gamma_{+}^{+} \) and \( \Gamma_{+}^{-} \), \( \Gamma_{-}^{+} \) coincide, and \( \chi_{zz}^{+} = \chi_{zz}^{-} \). Hence it is only necessary to consider \( \chi_{-+}^{+}(q,\omega) \) in order to gain insight into the nature of the nearly magnetic spin fluctuations. As discussed earlier on, in a nearly ferromagnetic system, at low temperatures, spin fluctuations with long wavelength tend to persist for long periods of time. Hence we would expect the most significant part of the Fourier transform of the susceptibility function to reside in the low wave vector \( q \) and low energy \( \omega \) region of the spectrum. For a paramagnet, the function \( \Gamma_{-+}^{+} \) is complex
\[ \Gamma_{-+}^{+}(q,\omega) = \frac{1}{N} \sum_{k} \frac{f_{k} - f_{k+q}}{\varepsilon(k+q) - \varepsilon(k) - \omega} \]  
(1.23)
\[ = R(q,\omega) + iI(q,\omega) \]  
(1.24)
where $R$ and $I$ are respectively the real and imaginary parts given by

\begin{align*}
R(q, \omega) &= \text{P.P.} \sum_{k} \frac{f_k - f_{k+q}}{\epsilon(k+q) - \epsilon(k) - \omega} \\
I(q, \omega) &= \sum_{k} (f_k - f_{k+q})S(\epsilon(k+q) - \epsilon(k) - \omega)
\end{align*}

(P.P. denotes the Principal Part of)

For low $q$ and small $\omega$ such that $q \ll k_F$ and $\omega \ll q v F$ where $k_F$ and $v_F$ are respectively the Fermi wave vector and the Fermi velocity of the system of electrons, $R(q, \omega)$ and $I(q, \omega)$ can be expanded to give an approximate polynomial in $q$ and $\omega$ with temperature dependent coefficients. These coefficients are functions of the derivatives of the Fermi distribution function which for a nearly degenerate electron gas at low temperatures can be well approximated by their values at $T = 0^\circ K$. This has the advantage of simplifying the mathematics considerably without altering the essential features of the model. Moreover, the Spin Fluctuations are a low temperature effect, hence the approximation of the coefficients by their values at zero temperature is well justified. Within these limits, then, $R(q, \omega)$ and $I(q, \omega)$ are given by (Izuyama et al 1963)

\begin{align*}
R(q, \omega) &= R(0,0) - aq^2 - b(\omega/q)^2 \\
I(q, \omega) &= \begin{cases} 
B\omega/q & \text{for } |\omega| < q v F \\
0 & \text{for } |\omega| > q v F
\end{cases}
\end{align*}

with

\begin{equation}
R(0,0) = -\frac{1}{N} (2m)^{3/2} \left( \frac{v}{2\pi} \right)^2 \int_{0}^{\infty} (\epsilon(k))^{1/2} \frac{df}{d\epsilon} d\epsilon
\end{equation}

\begin{equation}
= \frac{1}{N} \sum_{k} S(\epsilon(k) - \epsilon_F) \quad \text{at } T = 0^\circ K, \text{ the density of states of the electrons at the Fermi surface}
\end{equation}

\begin{equation}
D(\epsilon_F) = \frac{V}{N} \left( \frac{mk_F}{2\pi^2} \right)
\end{equation}
\[ a = \frac{1}{N} (V(2m)^{1/2}/4\pi^2) \int_0^\infty \mathcal{E}^{-\frac{1}{2}} \left[ (2/9) f^2 + (1/2) f'' \right] \, d\mathcal{E} \]

\[ = \frac{1}{12} \frac{D(E_F)}{k_F^2} \quad \text{at } T = 0^\circ \text{K} \quad (1.28) \]

\[ b = - \frac{1}{N} (V(2m)^{1/2}/4\pi^2) \int_0^\infty \mathcal{E}^{-\frac{1}{2}} f' \, d\mathcal{E} \]

\[ = \frac{D(E_F)}{v_F^2} \quad \text{at } T = 0^\circ \text{K} \quad (1.29) \]

\[ B = \frac{\pi}{2} \frac{D(E_F)}{v_F} \quad (1.30) \]

\[ V = \text{volume of the system} \]

Hence the imaginary part of the generalised susceptibility \( \chi_{\perp}(q,\omega) \) is given by

\[ 2 \text{Im} \chi_{\perp}(q,\omega) = \frac{\pi D(E_F)}{v_F q} \left( \frac{\omega}{v_F q} \frac{\pi}{2} \right)^2 \left[ 1 - U_0 D(E_F) \left[ 1 - \frac{1}{12} (q/k_F)^2 - (\omega/v_F q)^2 \right]^2 + \frac{U_0 D(E_F) \omega}{v_F q} \frac{\pi}{2} \right]^2 \]

which for \( U_0 D(E_F) \sim 1 \), may be reduced to (Doniach and Engelsberg 1966)

\[ 2 \text{Im} \chi_{\perp}(q,\omega) = \frac{\pi D(E_F)}{v_F q} \left( 1 - U_0 D(E_F) \left[ 1 - \frac{1}{12} (q/k_F)^2 \right]^2 + \frac{U_0 D(E_F) \omega}{v_F q} \frac{\pi}{2} \right)^2 \]

(1.31)

This function shows a maximum at an energy \( \omega_q \) where

\[ \omega_q = \frac{1}{4} E_F \pi \frac{q}{k_F} \left[ 1 - \frac{U_0 D(E_F)}{U_0 D(E_F)} \right] \quad (1.32) \]

Hence to the extent that one can speak of the Spin Fluctuations as being excitations at low temperatures for which a energy - momentum relationship can be defined, we see that they are phonon-like with energy \( \omega_q \) proportional to the wave vector \( q \), having a phase velocity given roughly by

\[ \frac{\omega_q}{q} \approx \frac{\pi}{3} \left[ 1 - \frac{U_0 D(E_F)}{U_0 D(E_F)} \right] v_F \sim (1 - U_0 D(E_F)) v_F \quad (1.33) \]
for $U_o D(\xi_F)^2 \sim 1$, and hence very much smaller than $v_F$ the Fermi velocity. Such excitations are often referred to as paramagnons. The function $2 \text{Im} \chi(\mathbf{q}, \omega)$ in effect gives the weightings of the different energy Spin Fluctuations and is referred to as the spectral density of the Spin Fluctuation system, often denoted by $A(\mathbf{q}, \omega)$.

The paramagnons behave much like heavily damped phonons and give rise to changes in the physical properties of the system in much the same way as damped phonons. However the scale on which these changes occur is determined by some characteristic temperature, in the case of paramagnons, a $T_{SF} \sim (1 - U_o D(\xi_F)) T_F$ which is very much smaller than the Fermi temperature $T_F$, whereas in the case of damped phonons, the characteristic temperature would be some effective Debye temperature which may be expected to be of the order of or larger than $T_F$. Hence at low temperatures such that $T \ll T_{SF}$, the Spin Fluctuation effects predominate, giving rise to the following contributions to the physical properties which will be reviewed and calculated in detail in the next chapter.

1) a term proportional to $T^2$ in the low temperature electrical resistivity due to the conduction electrons scattering off the paramagnons. These contributions have been calculated by M.J. Rice (1967) employing the Variational Principle technique and successfully applied to liquid He$^3$ and Pd-Ni alloys (Schindler and Rice 1967) which are highly exchange enhanced. A calculation employing a different method will be presented in Chapter 2.

2) a negative magnetoresistivity $(\rho_H - \rho_o)/\rho_o$ (where $\rho_o$ and $\rho_H$ are respectively the electrical resistivity in the absence and the presence of a magnetic field $H$) proportional to the square of the applied field $H$ at low fields. This calculation will be presented in Chapter 2.
3) a thermal resistivity proportional to $T$ at low temperatures, and a reduced Lorenz number.

4) a correction to the effective mass of the electrons and low temperature electronic specific heat due to the extra contributions to the single particle self-energy arising from the emission and reabsorption of the paramagnons. These effects have been calculated in detail by Doniach and Engelsberg (1966), Berk and Schrieffer (1966), Brinkman and Engelsberg (1968), where a divergence of electronic specific heat constant $\gamma$ with increasing enhancement as well as a $T^2 \log T$ term in the low temperature specific heat were found.

5) a susceptibility (magnetic) that decreases with increasing temperatures as $(T/T_{SF})^2$ at low temperatures such that $T < T_{SF}$.

So far, we have only discussed Spin Fluctuations in nearly ferromagnetic systems which occur around the zero wave vector $q = 0$. Spin Fluctuations in nearly antiferromagnetic systems, however, are much less well understood and relatively little work has been done. The main reason is that the only itinerant antiferromagnets that have been thoroughly studied theoretically and experimentally are Chromium and its alloys and the criterion for itinerant antiferromagnetism in these systems is believed to lie in the existence of the peculiar band structure in Chromium. Hence the possibility of the existence of antiferromagnetic Spin Fluctuations is debatable as the presence of highly specific band structure is necessary to give rise to the expected behaviour. However, for the sake of completeness, we shall pursue the issue a bit further and discuss it in slightly more detail.
Band structure calculations show that on the Fermi surface of Chromium, there are large electron and hole pockets similar in shape and size (Lomer 1962) and that the itinerant antiferromagnetism in Cr is believed to be due to the nesting of two such similar portions of the Fermi surface separated by a wave vector \( \mathbf{Q} \) approximately equal to half a reciprocal lattice vector, onto each other. Consequently, the itinerant antiferromagnetic ground state at low temperatures in Cr is stabilised by the formation of bound interband particle-hole pairs from the two portions of the Fermi surface. In systems that are nearly antiferromagnetic, i.e., systems that possess such or similar band structure but an insufficiently strong exchange interaction required to produce a stable antiferromagnetic state, then, in theory at low temperatures, the excitations of such interband particle-hole pairs (which manifest as fluctuations in the spin density of the system), or equivalently Spin Fluctuations, having wave vector close to \( \mathbf{Q} \), are possible, and the low temperature physical properties can be expected to be altered accordingly. The antiferromagnetic Spin Fluctuations differ from the ferromagnetic ones in that they occur around a finite wave vector \( \mathbf{Q} \) and not around the zero wave vector as is the case with the ferromagnetic ones. Hence one would expect interesting features in the generalized susceptibility \( \chi_{ab}(\mathbf{q},\omega) \) at \( \mathbf{q} = \mathbf{Q} \), \( \chi_{ab} \) being the interband susceptibility. In the paramagnetic state, a system of two bands interacting via some effective interband exchange interaction \( U \) would then have \( \chi_{ab} \), within the R.P.A., given by

\[
\chi_{ab}(\mathbf{q},\omega) = \frac{\Gamma_{ab}(\mathbf{q},\omega)}{1 - U \Gamma_{ab}(\mathbf{q},\omega)}
\]

where

\[
\Gamma_{ab}(\mathbf{q},\omega) = \sum_{\mathbf{k}} \frac{f(\epsilon^b_{\mathbf{k}+\mathbf{q}}) - f(\epsilon^a_{\mathbf{k}})}{\omega - (\epsilon^b_{\mathbf{k}+\mathbf{q}} - \epsilon^a_{\mathbf{k}})}
\]

is the interband susceptibility.
in the absence of interaction $U$; $\mathcal{E}^b$ and $\mathcal{E}^a$ are respectively the energies in the band corresponding to the hole surface and electron surface; the $f$'s are the corresponding Fermi-Dirac distribution functions. The system becomes unstable to an antiferromagnetic transition at $1 = U \pi_{ab}(Q, \omega)$ at which point $\chi_{ab}(Q, \omega)$ becomes infinite. However, in practice, $\chi(Q)$ is rather difficult to measure and what is usually measured in the susceptibility function at zero wave vector $\chi(0)$ which does not diverge as the antiferromagnetic instability is approached. Hence evidence for the existence of antiferromagnetic Spin Fluctuations is not as readily available, although the susceptibility function at finite $q$ vectors can be measured by neutron scattering techniques (Low and Holden 1966).

Attempts have been made to apply the theory to alloys of Cr like V-Cr and compounds like $V_{1-x}Cr_xB_2$, $Mn_{1-x}Cr_xB_2$, for $0 < x < 0.8$ atomic percent (Castaing et al 1970), highly specific band structures had to be employed in order to make the application feasible, and hence not very satisfactory. Also there has been disputes as to the kind of dispersion law these excitations obey, depending on the kind of band model employed. For a system with one spherical and one elliptical Fermi surface, Jerome (1970) has shown that the spectral density of the Spin Fluctuations has a maximum at an energy $\omega_q \sim \text{constant } q^2$ for $q \sim Q$, whereas Zuckermann (1971), employing a band model proposed by Rice for Cr (T.M. Rice 1970) that leads to a "cusp" type Kohn singularity in the susceptibility function at $q = Q$, has shown that a $\omega_q \sim q$ dispersion law is obeyed, similar to the nearly ferromagnetic case. For the sake of completeness, we shall discuss in slightly more detail the theory of antiferromagnetic Spin Fluctuations along the lines set out by T.M. Rice (1970) and Zuckermann (1971) by considering the following band structure due to T.M. Rice.
\[ \varepsilon^b(k+\mathbf{Q}) = \nu_F k_z + \nu_F |\mathbf{Q} - \mathbf{k}| + \frac{(k_x^2/2m_x)}{\mathbf{Q} - \mathbf{k}} - \frac{(k_y^2/2m_y)}{\mathbf{Q} - \mathbf{k}} \]

\[ \varepsilon^a(k) = -\nu_F k_z + \frac{(k_x^2/2m_x)}{\mathbf{Q} - \mathbf{k}} - \frac{(k_y^2/2m_y)}{\mathbf{Q} - \mathbf{k}} \]

where for convenience \((\mathbf{Q} - \mathbf{Q})\) is taken to be along the \(k_z\) direction, \(\varepsilon^b\) and \(\varepsilon^a\) being measured from the Fermi energy; and a model Hamiltonian of the form

\[ \mathcal{H} = \sum_{k\sigma} \sum_{a,b} \varepsilon^a(k) n^a_{k\sigma} + U \sum_{k,k',\mathbf{Q}} \sum_{\sigma\sigma'} \delta^a_{k+\mathbf{Q},\sigma} \delta^a_{k',\sigma'} \delta^b_{k',-\mathbf{Q},\sigma}, \delta^b_{k,\sigma} \]

where \(\delta^a\) and \(\delta^b\) are creation operators for electrons in the \(a\) and \(b\) pockets respectively, \(n\) is the number operator and \(U\) the Fourier transform of the effective Coulomb interaction which has been taken to be a constant as in the nearly ferromagnetic case. The Hamiltonian (1.36) is then assumed to describe completely the dynamics of the system, however the effects of intraband exchange has been ignored and assumed to be insignificant compared to the exchange interaction between the two bands. Within the R.P.A., then, the generalised susceptibility is given by

\[ \chi_{ab} = \frac{\Gamma_{ab}(\mathbf{Q},\omega)}{1 - U \Gamma_{ab}(\mathbf{Q},\omega)} \]

with

\[ \Gamma_{ab}(\mathbf{Q},\omega) = \sum_k \frac{\delta^b_{k+\mathbf{Q}} - \delta^a_k}{\omega - (\varepsilon^b_{k+\mathbf{Q}} - \varepsilon^a_k) + i\delta} \]

as defined earlier on. The interband susceptibility can be written in the following form for a general band structure (T.M. Rice 1970)

\[ \Gamma_{ab}(\mathbf{Q},\omega) = \int d\xi \int d\eta \ N_q(\xi,\eta) \frac{f(\eta+\xi) - f(\eta-\xi)}{\omega - 2\xi + i\delta} \]

(1.37)

where \(N_q(\xi,\eta)\) is the double density of states given by

\[ N_q(\xi,\eta) = \sum_k \delta[\xi - \gamma(\varepsilon^b_{k+\mathbf{Q}} - \varepsilon^b_k)] \delta[\eta - \gamma(\varepsilon^b_{k+\mathbf{Q}} + \varepsilon^a_k)] \]

(1.38)
which, for the band structure employed, has been shown by T. H. Rice (1970) to be given by

\[ N_q(\xi, \eta) = \varphi_0 \log \left[ \frac{\eta_0}{1 - \frac{\sqrt{2} \nu_F |q - \Delta|}{\sqrt{\eta_0}}} \right] \tag{1.39} \]

where \( \varphi_0 = (m_x m_y)^{3/2} / 4 \pi^3 \) and \( \eta_0 \) is the energy cutoff in the \( k_x - k_y \) plane. Employing (1.39) and (1.37), the real and imaginary parts of the susceptibility are then, for small \( |q - \Delta| \) and \( \omega \), given by

\[ \Gamma_{ab}(q, \omega) = R_{ab}(q, \omega) + i I_{ab}(q, \omega) \]

\[ R_{ab}(q, \omega) = \varphi_0 (A_0 - \frac{1}{2} \pi^2 \nu_F q') + O(\omega^2, q'^2) \tag{1.40} \]

\[ I_{ab}(q, \omega) = \frac{\pi \varphi_0}{2 \omega} \left[ \omega(\log \eta_0 - 1) + (\nu_F q'/2) \log \left| \frac{\omega - \nu_F q'}{\omega + \nu_F q'} \right| - \frac{\omega \log \left| \frac{\nu_F q'^2}{4} \right|}{2} \right] \tag{1.41} \]

where

\[ A_0 = 2 \eta_0 (2 + \log(\omega_0/\eta_0)) \tag{1.42} \]

and

\[ q' = |q - \Delta| \]

and \( \omega_0 \) is the energy cutoff in the \( k_z \) direction. We see from (1.40) that \( R_{ab}(q, 0) \) has a cusp type maximum at \( q = \Delta \) and this has important consequences on the dispersion relation obeyed by the antiferromagnetic paramagnons. The limiting form of \( I_{ab}(q, \omega) \) is given by

\[ I_{ab}(q, \omega) = \frac{\pi \varphi_0 \omega}{2} (\log(\frac{\omega_0}{\omega}) - 1), \quad \omega \gg \nu_F q' \tag{1.43} \]

\[ = \frac{\pi \varphi_0 \omega}{2} \log(\frac{\eta_0}{0.27 \nu_F q'}), \quad \omega \ll \nu_F q' \tag{1.44} \]

and the spectral density of these fluctuations in these limits are given by
\[ A(q, \omega) = 2 \text{Im} \chi_{ab}(q, \omega) \]

\[ = \frac{\pi \gamma_0^2 \omega \log \left( \frac{2 \eta_0}{\omega} - 1 \right)}{\left[ 1 - U \gamma_0 (A_0 - 2 \pi v_F q') \right]^2 + \left[ \frac{\pi}{2} \gamma_0 \omega \log \left( \frac{2 \eta_0}{\omega} - 1 \right) \right]^2} \]

for \( \omega \gg v_F q' \) \hspace{1cm} (1.45)

\[ = \frac{\pi \gamma_0^2 \omega \log \left( \frac{2 \eta_0}{\omega} - 0.27 v_F q' \right)}{\left[ 1 - U \gamma_0 (A_0 - 2 \pi v_F q') \right]^2 + \left[ \frac{\pi}{2} \gamma_0 \omega \log \left( \frac{2 \eta_0}{\omega} - 0.27 v_F q' \right) \right]^2} \]

for \( \omega \ll v_F q' \) \hspace{1cm} (1.46)

(1.45) then has a maximum at \( q \_q \) where the following dispersion relation is satisfied,

\[ \omega_q \left( \log \left( \frac{2 \eta_0}{\omega_q} - 1 \right) \right) = \frac{2}{U \gamma_0} \left[ 1 - U \gamma_0 A_0 + \frac{U \gamma_0}{4 \pi^2 v_F q'} \right] \]

(1.47)

Then assuming that for \( q' = |q - Q| \) small, \( \omega_q \) may be written as

\[ \omega_q = \omega_Q + \omega_{[q-Q]} \]

where the second term is much less than the first (Zuckermann 1971),

(1.47) can be expanded to give

\[ \omega_q = \pm \left( \alpha + \beta v_F q' \right) \]

(1.48)

where

\[ \alpha = \frac{2}{\pi \gamma_0 A_0 U} \left( \log \left( \frac{2 \eta_0}{\omega_q} - 1 \right) - 1 \right) \left( 1 - \gamma_0 A_0 \right) A_0 \]

\[ \beta = \frac{\pi}{2 \gamma_0 A_0 U} \left( \log \left( \frac{2 \eta_0}{\omega_q} - 1 \right) - 1 \right) \gamma_0 A_0 U v_F \]

Thus in the limit \( \omega \gg v_F q' \), the paramagnons are phonon-like and obey a dispersion relation similar to that of the ferromagnetic paramagnons.

Now we consider the limit when \( \omega \ll v_F q' \). In this limit, the
Spectral function will be given by (1.46) and this has a maximum at

$$
\omega_q = \pm \frac{2}{U \gamma_0 A_o} \left[ \frac{1 - U_0(A_o - j \pi^2 v_F q')}{\log(\eta_o/0.27 v_F q')} \right]
$$

$$
\omega_q = \pm \frac{2}{U \gamma_0 A_o} \left[ \frac{(1 - U_0 A_o) A_o}{\log(\eta_o/0.27 v_F q')} \right] \text{ for } v_F q' \ll A_o \quad (1.49)
$$

Hence in this limit, the paramagnons are not at all phonon-like, but rather obey the above dispersion law.

As in the case of nearly ferromagnetic Spin Fluctuations, we would expect the physical properties of a system to be altered somewhat by the existence of the nearly antiferromagnetic Spin Fluctuations. However, due to the difference in their behaviours near the critical point, we can expect some difference in their contributions to the physical properties.

It has been shown by Moriya (1970) on general grounds, employing a one-band model, that in a nearly antiferromagnetic system, as the magnetic instability is approached, no divergence of the electronic specific heat constant $\gamma$ occurs, neither is there a $T^3 \log T$ term in the low temperature specific heat, contrary to the case of nearly ferromagnets. Moriya's findings can be easily verified in this two-band model. Following the approach outlined by Moriya, we can write the dominant contribution of the Spin Fluctuations to the Free Energy as

$$
\Delta F = \frac{3}{2 \pi} \sum_q d \omega \coth(\omega/2k_B T) \tan^{-1} \left[ \frac{UI(q, \omega)}{1 - UR(q, \omega)} \right]
$$

(1.50)
At low temperatures, the most important contribution to $\Delta F$ comes from the form of $I(q, \omega)$ in the limit $\omega \gg v_F q'$ (Zuckermann 1971).

Substituting values of $R$ and $I$ from (1.40) and (1.41), we have

$$\Delta F = \frac{3}{2 \pi} \sum_{q'} \int_0^{\omega_c} d\omega \coth(\omega/2k_B T) \tan^{-1} \left[ \frac{\left( \frac{\pi}{2} \gamma_o A_o U(\omega/A_o) \log(2\eta_o/\omega) - 1 \right)}{1 - \gamma_o A_o U + (\pi/2)^2 \gamma_o A_o U(v_F q'/A_o)} \right]$$

(1.51)

For small $\omega$ such that $\omega/A_o \ll 1$ and for $\gamma_o A_o U \sim 1$, i.e. a system close to magnetic instability at $T = 0^\circ K$, (1.51) can be reduced to

$$\Delta F \simeq \frac{3}{4} \sum_{q'} \int_0^{\omega_c} d\omega \coth(\omega/2k_B T) \left[ \frac{(\omega/A_o)(\log(2\eta_o/\omega) - 1)}{1 - \gamma_o A_o U + (\pi/2)^2(v_F q'/A_o)} \right]$$

(1.52)

where a cutoff energy $\omega_c$ has been introduced to account for the inadequacy of the model at high energies, and the summation over $q'$ is from zero to some cutoff value $q'_c$. Then writing the summation over $q'$ as an integral,

$$\Delta F \simeq \int_0^{\omega_c} d\omega \int_0^{q'_c} dq' q'^2 \coth(\omega/2k_B T) \frac{(\omega/A_o) \log(2\eta_o/\omega) - 1}{1 - \gamma_o A_o U + (\pi/2)^2(v_F q'/A_o)}$$

(1.53)

(1.53) clearly does not diverge as $\gamma_o A_o U \rightarrow 1$, and hence the contribution of the nearly antiferromagnetic Spin Fluctuations to the Free Energy does not lead to anomalous behaviour in the specific heat at low temperatures as the magnetic instability is approached, in agreement with the findings of Moriya (1970).

At low temperatures, the main contribution to the electrical resistivity comes from long wave length Spin Fluctuations, i.e. those having small wave vectors, near $q = 0$. In a nearly anti-
ferromagnetic system, critical fluctuations occur around the wave vector $Q$ which is finite. Hence the major contribution to the electrical resistivity in a nearly antiferromagnetic system would come from the form of the spectral density in the limit $\omega \ll \sqrt{\frac{\mu}{|Q - \vec{Q}|}}$, i.e. small $Q(\ll Q)$ as given in equation (1.46). We see that the spectral density given in (1.46) has an $\omega$-dependence similar to that in the nearly ferromagnetic spectral density, i.e.

$$A(\omega) \sim \frac{\omega}{1 + \omega^2} \quad (1.54)$$

This form of spectral density leads to a temperature dependence of the resistivity at low temperatures going as $T^2$ as will be shown in the next chapter for the nearly ferromagnetic case.

To conclude, then, we have, in this chapter, presented a general description of the Spin Fluctuation model. We have outlined the contributions to the physical properties from the Spin Fluctuations both in the nearly ferromagnetic and the nearly antiferromagnetic case, where in the latter, we have presented a mathematical argument that discloses the essentially different nature of the antiferromagnetic paramagnon contribution to the low temperature specific heat (from that due to ferromagnetic paramagnons); the temperature dependence of the electrical resistivity was also discussed and concluded to be the same as in the nearly ferromagnetic case. However, due to the uncertainty in the existence of the antiferromagnetic paramagnons, we shall from now on center our discussion on the ferromagnetic paramagnons.
Chapter 2

The Spin Fluctuation model: Physical Properties

In the first part of this chapter, we shall present the calculation of the Spin Fluctuation contributions to the electrical resistivity and the magnetoresistivity. We begin by outlining the Boltzmann formalism for the general case of a system in the presence of a magnetic field and derive the general expression of conduction electron relaxation times and the scattering rates of the up and down spin conduction electrons. We then apply this to evaluate the electrical resistivity and the magnetoresistivity of a nearly magnetic system. In the second part of this chapter, we shall briefly review on the results obtained by other workers for various other physical properties in this model.

Part 1  Spin Fluctuation resistivity and magnetoresistivity

2.1 Boltzmann Formalism

a) The conduction electron relaxation times

For simplicity, we shall consider a system in which the conduction processes are carried out entirely by electrons in the s-band and consider only the scattering processes through which an s-electron flips its spin. We shall ignore the non-spin-flip processes since they are believed to make insignificant contribution to the resistivity compared to the former, especially at low temperatures (Mills and Lederer 1966). Spin dependent scatterings are in general inelastic, and in the presence of a magnetic field, lead to different relaxation times for the spin up and spin down conduction electrons ($\tau_+$ and $\tau_-$). Therefore it is necessary to consider the two separately.
Following Van Peski-Tinbergen and Dekker(1963), we shall assume a single parabolic band for the conduction electrons, assumed to be s in character, and define the zero of energy such that in the presence of an externally applied magnetic field \( H \), the one particle energy of an s-electron is given by

\[
E_{\pm}(k) = \pm \mu_B H + \hbar^2 k^2 / 2m_s
\]  

(2.1)

for the spin up (+) and the spin down (-) electrons, respectively, having a wave vector \( k \); \( \mu_B \) is the Bohr magneton, \( \hbar \) is the Plank's constant, and \( m_s \) is the effective mass of the s-electron.

In the absence of electric or any other non-uniform fields, the distribution function of the electrons is given by the Fermi-Dirac expression,

\[
f_{\pm} = \frac{1}{1 + \exp(-\beta (E_{\pm} \mp E_s))}
\]  

(2.2)

where \( \beta = (k_B T)^{-1} \), \( k_B \) is the Boltzmann's constant, \( T \) the absolute temperature; the subscript 0 signifies the equilibrium value of the distribution, and \( E_s \) is the Fermi energy of the s-electrons.

If we now apply to the system an electric field \( \mathcal{E} \) along the x direction say, the equilibrium distribution of the electrons will be disturbed and the rate of change of the electron distribution function \( f_{\pm}(k) \) (\( f_{\pm}(k) \) being the value in the presence of an applied field \( \mathcal{E} \)) with respect to time will be given by

\[
\frac{\delta f_{\pm}(k)}{\delta t} \left|_{\text{field}} \right. = - \left( e \mathcal{E} / \hbar \right) \left( \frac{\delta f_{\pm}}{\delta k} \right)
\]  

\[
= - \left( e \mathcal{E} k_x / m_s \right) \left( \frac{\delta f_{0\pm}}{\delta E_{\pm}} \right)
\]  

(2.3)
This rate of change must be balanced by the rate of change due to the scattering processes which restore the system back to equilibrium. Hence when equilibrium is re-established, i.e., in the steady state, we must have the total rate of change of \( f^+ \) vanishing, i.e.,

\[
\frac{df^+}{dt}_{\text{total}} = \frac{df^+}{dt}_{\text{field}} + \frac{df^+}{dt}_{\text{scattering}} = 0 \tag{2.4}
\]

Then employing the usual relaxation time approximation, we write

\[
\frac{df^+}{dt}_{\text{scatt.}} = -(f^+ - f_{0^+})/\tau^+ = -g_+(k)/\tau^+ \tag{2.5}
\]

\( \tau^+ \) being the relaxation times for the up and the down spin electrons respectively. Combining (2.3), (2.4) and (2.5), we arrive at

\[
f^+ - f_{0^+} = g_+(k) = -\tau^+ (e\xi k_x \mu^s)(\partial f_{0^+}/\partial E^+) \tag{2.6}
\]

\( g_+(k) \) being the shift in the Fermi distribution produced by the applied field \( \xi \).

The computations for \( \tau^- \) and \( \tau^- \) are very similar, we shall first consider \( \tau^+ \). The density of electrons corresponding to a volume element \( dk \) is given by \((2\pi)^{-3}f^+_{\frac{1}{2}}(k)dk\) in the steady state. Then summing over all the possible transitions into and out of the final state \( k' \), the rate of change of the distribution function with time is given by

\[
\frac{df^+}{dt}_{\text{scatt.}} = \frac{1}{(2\pi)^3} \int dk' \left[ - P(k\rightarrow k')f^+_+(1-f^-_1) + P(k\rightarrow k')f^-_+(1-f^+_1) \right] \tag{2.7}
\]

where \( P(k\rightarrow k') \) is the probability of transition from an initial
state \( k \) to a final state \( k' \), \( f \) being the probability that state \( k \) is being occupied, \( (1-f') \) the probability that state \( k' \) is vacant.

The principle of microscopic reversibility requires that in the absence of external fields,

\[
P(k' \rightarrow k) f'_o (1 - f'_o) = P(k \rightarrow k') f_o (1 - f'_o)
\]

\[
= Q(k \rightarrow k') \quad \text{say} \quad (2.8)
\]

where \( Q(k \rightarrow k') \) is the intrinsic transition rate. (2.8) implies that \( Q(k \rightarrow k') = Q(k' \rightarrow k) \), i.e. the transition rates both into and out of the final state \( k' \) must equal in the absence of perturbing fields.

After some straightforward algebra, we arrive at the following expression for the scattering rate,

\[
\frac{\delta f}{\delta t} = (2\pi)^{-3} \int \frac{dk}{2\pi^2} P(k \rightarrow k') f'_o (1 - f'_o) \left[ \frac{g'}{f_o (1 - f'_o)} - \frac{g}{f'_o (1 - f'_o)} \right]
\]

\[
= -g (2\pi)^{-3} \int \frac{dk}{2\pi^2} P(k \rightarrow k') \left( 1 - \frac{\tau}{\tau} \cos \theta \right) \frac{1}{f_o (1 - e^{-\beta (E_k - E_{k'})})}
\]

\[
= - \frac{g}{\tau} \quad (2.9)
\]

where we have made use of the following identities

\[
f_{o+} (1 - f_{o+}) = - k_B T \left( \delta f_{o+} / \delta E \right) \quad (2.10a)
\]

\[
f_{o-} (1 - f_{o-}) = - k_B T \left( \delta f_{o-} / \delta E \right) \frac{1}{1 - f_{o+} (1 - e^{-\beta (E_k - E_{k'})})} \quad (2.10b)
\]

\[
k' = k \cos \theta \quad , \quad \theta \text{ being the angle of scatter}.
\]
Then assuming spherical symmetry for the system, we can write the volume element $d\mathbf{k}'$ as

$$
\begin{align*}
    d\mathbf{k}' &= 2 \sin \theta \, d\theta \, k'^2 \, dk' = \left( \pi (2m_s/\hbar^2)^{3/2} \right) \sin \theta \, d\theta \, E'_s \, dE',
\end{align*}
$$

and obtain for $1/\tau_+$ the following expression:

$$
\begin{align*}
    \frac{1}{\tau_+} &= \frac{\pi (2m_s/\hbar^2)^{3/2}}{(2\pi \hbar)^3} \int \mathcal{F}(k \to k') E'_{s} \, dE' \left\{ \frac{1}{1 - f_+ (1 - \exp (\beta (E'_s - E')))} \right\} \\
    &\times \left( 1 - \frac{\tau_+}{\tau'_+} \cos \theta \right) \sin \theta \, d\theta \, (2.11)
\end{align*}
$$

Then following exactly the same procedure for the spin down conduction electrons, we have the following analogous expression for $1/\tau_-$:

$$
\begin{align*}
    \frac{1}{\tau_-} &= \frac{\pi (2m_s/\hbar^2)^{3/2}}{(2\pi \hbar)^3} \int \mathcal{F}(k \to k') E'_{s} \, dE' \left\{ \frac{1}{1 - f_- (1 - \exp (\beta (E'_s - E')))} \right\} \\
    &\times \left( 1 - \frac{\tau_+}{\tau'_-} \cos \theta \right) \sin \theta \, d\theta \, (2.12)
\end{align*}
$$

b) The scattering rates $Q(k \to k')$

Bearing in mind the intended application of this theory to the Actinide materials which are known to have a narrow band, $5f$ in character, that gives rise to their magnetic like behaviour, we shall assume for simplicity that our system consists of two bands, a broad conduction $s$-band, overlapping a narrow non-conducting $f$-band and that the spin-flip scattering processes are governed by an exchange interaction between the conduction electrons and the $f$-spin fluctuations. Following Hills and Lederer (1966), we write the interaction Hamiltonian in the form
\[ \mathcal{H}_{s-f} = VJ \int s(\mathbf{r}) \cdot M(\mathbf{r}) \, d^3 r \]  

(2.14)

where \( s(\mathbf{r}) \) = the spin density of the s-electrons (the s-electrons assumed to be described by plane waves)

\( M(\mathbf{r}) \) = spin density of the f-electrons which are assumed to be tightly bound

\( V \) = volume of an unit cell

\( J \) = exchange interaction between an s and a f electron

Retaining only the spin-flip terms in \( \mathcal{H}_{s-f} \), we have

\[ \mathcal{H}_{s-f} = \frac{VJ}{2} \int s_+(\mathbf{r}) M_-(\mathbf{r}) \, d^3 r + \frac{VJ}{2} \int s_-(\mathbf{r}) M_+(\mathbf{r}) \, d^3 r \]  

(2.15)

with

\[ s_+(\mathbf{r}) = \frac{1}{V} \sum_{kk'} c^+_{k'\uparrow} c^+_{k\downarrow} \exp( i \mathbf{r} \cdot (\mathbf{k'} - \mathbf{k})) \]  

(2.16)

\[ s_-(\mathbf{r}) = s_+(\mathbf{r})^* \]  

(2.17)

in the plane wave approximation for the s-electrons; \( c^+_{k'\uparrow} \) and \( c^+_{k\downarrow} \) are respectively the creation and destruction operators in the \( k'\uparrow \) and \( k\downarrow \) states, and \( M_+(\mathbf{r}) \) and \( M_-(\mathbf{r}) \) are defined by

\[ M_+(\mathbf{k}) = (N)^{-\frac{1}{2}} \int M_+(\mathbf{r}) \exp(-i\mathbf{k} \cdot \mathbf{r}) \, d^3 r \]  

(2.18)

\[ M_-(\mathbf{k}) = (N)^{-\frac{1}{2}} \int M_-(\mathbf{r}) \exp( i\mathbf{k} \cdot \mathbf{r}) \, d^3 r \]  

(2.19)

\[ = (N)^{-\frac{1}{2}F(\mathbf{k})} \sum_{\mathbf{k'}} a^+_{\mathbf{k'}\uparrow} a^+_{\mathbf{k}\downarrow} a^+_{\mathbf{k}\uparrow} \]  

in the tight binding approximation; \( a^+ \) and \( a \) are respectively the creation and annihilation operators for the f-electrons, \( F(\mathbf{k}) \) is the Fourier transform of the charge density associated with the Wannier functions of the
f-electrons, normalised so that $F(0) = 1$, $N$ being the total number of atoms.

Then in the first Born Approximation, the rate of scattering of an s-electron from state $k$ with spin up into state $k'$ with spin down, via the interaction $\mathcal{H}_{s-f}$, is given by

$$Q(k \rightarrow k') = \frac{2\pi}{\hbar} \sum_{\sigma=0} f_{o+}^{(1-f')_{o-}} |\langle F | \mathcal{H}_{s-f} | I \rangle|^2 P(I) \delta(E_F - E_I + E'_{+-} - E_{+-})$$  \hspace{1cm} (2.20)

where $\langle F |$ and $| I \rangle$ are the final and initial states respectively of the f-electron system; $P(I)$ denotes the probability of finding the f-electrons in the initial state $I$; the $\delta$ function takes care of the energy conservation of the scattering process. Then employing the form of $\mathcal{H}_{s-f}$ defined in (2.15) and the identities

$$2m\delta(\epsilon) = \int \exp(i\epsilon t) \, dt$$ \hspace{1cm} (2.21)

and

$$M(q,t) = \exp(i\mathcal{H}_f t) M(q) \exp(-i\mathcal{H}_f t)$$ \hspace{1cm} (2.22)

where $\mathcal{H}_f$ is the Hamiltonian of the f-electrons; the scattering rates for the up and the down spin s-electrons have been shown by Mills and Lederer (1966) to be

$$Q(k \rightarrow k') = \frac{j^2}{4N} f_{o+}^{(1-f')_{o-}} M_>(k_+ \rightarrow k'_- , E_{+-} - E_{+-})$$ \hspace{1cm} (2.23)

$$Q(k \rightarrow k') = \frac{j^2}{4N} f_{o-}^{(1-f')_{o+}} M_<(k'_+ \rightarrow k_- , E_{+-} - E_{+-})$$ \hspace{1cm} (2.24)

where

$$M_>(q,\omega) = \int_{-\infty}^{+\infty} \exp(i\omega t) \langle H_-(q,t)M_>(q,0) \rangle \, dt$$ \hspace{1cm} (2.25)

$$M_<(q,\omega) = \int_{-\infty}^{+\infty} \exp(i\omega t) \langle M_>(q,0)H_-(q,t) \rangle \, dt$$ \hspace{1cm} (2.26)
and \( \langle 0 \rangle = \text{the thermal average of the operator } O \)

\[ = \text{Tr}(\rho_f^0) \] where \( \rho_f \) is the density matrix describing the \( f \)-band, given by \( \rho_f = \exp(-\beta H_f)/\text{Tr}(\exp(-\beta H_f)) \).

This scattering of the \( s \)-electrons via the \( s-f \) interaction may then be viewed upon as the scattering by a set of elementary excitations in the fluctuating \( f \)-spin density having energy equal to the difference between the initial and final state energies of the \( s \)-electrons. Hence a gain in energy by the \( s \)-electron on being scattered to the final state (i.e. \( E' - E > 0 \)) would be due to the emission of such an excitation (paramagnon) of the spin system of the same amount of energy; conversely, an energy loss on being scattered would have been due to the absorption of a paramagnon. Hence the shape and energy range of the paramagnon spectrum, i.e. the spectral density \( A(q,\omega) \), will be the decisive factor governing the contribution to the resistivity. The spectral density \( A(q,\omega) \) is defined by

\[ M_q(q,\omega) = |F(q)|^2 (1 + n(\omega))A(q,\omega) \quad (2.27) \]

\[ M_<q(q,\omega) = |F(q)|^2 n(\omega)A(q,\omega) \quad (2.28) \]

where

\[ n(\omega) = \frac{1}{\exp(\beta \omega) - 1} \quad (2.29) \]

Hence the scattering rates in (2.23) and (2.24) can be written as

\[ Q(k_{-}\rightarrow k'_+) = \frac{J^2}{4N} f_{-}(1-f_0^-) \frac{1}{1 - \exp(\beta (E'_+ - E_-))} A(q,E'_+ - E_-) |F(q)|^2 \quad (2.30) \]

\[ Q(k_{-}\rightarrow k'_-) = \frac{J^2}{4N} f_{-}(1-f_0^+) \frac{1}{\exp(\beta (E'_+ - E_-)) - 1} A(-q,E'_+ - E_-) |F(q)|^2 \quad (2.31) \]

where we have written \( q = k'_+ - k'_- = k-k'_+ k-k'_- \)
2.2 Resistivity

The relaxation times for the up and down spin electrons are related to their respective conductivities, $\sigma_+$ and $\sigma_-$, by the well known formula

$$\sigma_\pm = -\frac{e^2}{(6\pi^2 m_s)} \int k_s^{3/2} \tau \left( \frac{\partial f_0}{\partial E} \right) \frac{dE}{E}$$  \hspace{1cm} (2.33)

However at low temperatures and small magnetic fields, $-\left( \frac{\partial f_0}{\partial E} \right)$ can be well approximated by the delta function $\delta(E-E_s)$ (see for example Mott and Jones 1936). This is in accordance with our assumption that $k_+ \sim k_- \sim k_s$ for small momentum transfer which is only possible for electrons residing near the Fermi surface. It is these small momentum transfer scatterings that give rise to the excitations of the long wavelength (i.e. small $q$) spin fluctuations at low temperatures. Therefore, the conductivities will be, to a good approximation given by their values at the Fermi surface

$$\sigma_\pm \approx \sigma_{\pm F} = \frac{e^2}{(6\pi^2 m_s)} k_s^{3/2} \tau_{\pm F}$$  \hspace{1cm} (2.34)

where the subscript $F$ denotes the Fermi surface value. Consequently the resistivity will be given by

$$\rho = (\sigma_{+F} + \sigma_{-F})^{-1}$$  \hspace{1cm} (2.35)

So now the problem reduces to that of evaluating $\tau_+$ and $\tau_-$ at the Fermi surface where $E_+ = E_s$. We shall first consider the case where the magnetic field is absent. In this case, we have $E_+ = E_-$, and as a result, $\tau_+ = \tau_-$ and the resistivity in the absence of magnetic field will be given by

$$\rho_0 = (2\sigma_F)^{-1} = \left( \frac{12\pi^2 m_s}{e^2 k_s} \frac{1}{\tau} \right)_{E=E_s}$$  \hspace{1cm} (2.36)

where the subscript $0$ denotes the value of $\rho$ in zero magnetic field.
Then it is straightforward to substitute the formula for \(1/T\) in (2.12) and the scattering rate in equation (2.30) into equation (2.36), taking \(n=1\), we have

\[
\rho_0 = \frac{12\pi^2 m_S}{e^2 k_S^3} \frac{(2m_S)^{3/2}}{(2\pi)^3} \frac{J^2}{4N} \int_0^\infty E' \frac{1}{\beta^2} dE' \frac{1}{1 - f_0(1-\exp(\beta(E'-E)))} \frac{1}{1 - \exp(\beta(E'-E))}
\]

\[
\times |F(q)|^2 A(q,E-E') \int (1 - \cos\theta) \sin\theta d\theta
\]

(2.37)
evaluated at \(E = E_s\).

In order to conserve energy and momentum in each scattering event, we must have

\[
E' - E = \omega
\]
and

\[
k' - k = q
\]
where \(\omega\) and \(q\) are respectively the energy and momentum of the emitted (or absorbed) paramagnon. Since we are dealing with scattering processes near the Fermi surface, we can, to a good approximation, write \(q = k'_s - k_s\) with the magnitude of \(q\) given by

\[
q = |k'_s - k_s| = |k_s - k'_s|
\]

\[
= 2\frac{\hbar}{k_s} \sqrt{1 - \cos\theta} \frac{1}{2}
\]

(2.39)

As a result, equation (2.37) can be rewritten as

\[
\rho_0 = \frac{3m_S}{8e^2 k_s^3} \frac{J^2}{N} \left(\frac{2m_S}{e^2 k_s^3}\right)^{3/2} \int (E_s + \omega)^{1/2} d\omega \frac{1}{1 + \exp(-\beta\omega)} \frac{1}{1 - \exp(\beta\omega)}
\]

\[
\times \frac{1}{2k_s} \int |F(q)|^2 \lambda(q,-\omega) q^3 dq
\]

(2.40)

where the integral is over all values of \(\omega\), positive and negative (corresponding to emitted and absorbed paramagnons, respectively),
and $A(q, \omega)$ is given by the formula derived in the previous chapter.

From equation (1.31), we have

$$A(q, \omega) = \frac{\pi D(\epsilon_f) \omega / v_f q}{\left[ 1 - U_0 D(\epsilon_f) \left( 1 - \frac{1}{12} (q/k_f)^2 \right) \right]^2 + \left[ U_0 D(\epsilon_f) \frac{\omega}{v_f q} \right]^2}$$

For small $q$ and $\omega$ such that $q/k_f \ll 1$ and $\omega \ll v_f q$, the above form of $A(q, \omega)$ can be simplified considerably. For nearly magnetic metals, $U_0 D(\epsilon_f)$ is approximately equal to one, now since $(q/k_f)^2$ and $(\omega/v_f q)^2$ are small compared to one, we can approximate $A(q, \omega)$ by

$$A(q, \omega) \approx \frac{\omega / v_f q}{(1 - U_0 D(\epsilon_f))^2}$$

(2.41)

In order to account for the inadequacy of the model at large $\omega$ and $q$, we shall introduce a cutoff wave vector $q_c$ in the spectrum. The corresponding cutoff in energy will then be $\omega_c = v_f q_c$ which would be of the order of the characteristic spin fluctuation energy

$$(1 - U_0 D(\epsilon_f)) \epsilon_f = k_B T_{SF}$$

where $T_{SF}$ is the characteristic temperature. This reduced form of the spectral density then in effect ignores the high frequency end of the spin fluctuation spectrum. At low temperatures such that $T \ll T_{SF}$, this approximation is well justified, as the Bose nature of these excitations in effect cuts off the spectrum at an energy $\omega \sim k_B T$.

Substituting equation (2.41) into equation (2.40) and making the transformation $y = \beta \omega$ under the integral, we have

$$P_0 = \frac{K}{\beta^2} \int_{-\beta \omega_c}^{\beta \omega_c} \frac{(E + \frac{y}{\beta})^{3/2} 2y dy}{1 + \exp(-y)} \frac{1}{1 - \exp(y)} \int_{-\beta \omega_c}^{\beta \omega_c} |q_c|^{-2} \frac{(q^2 / 2k_B T_{SF}) dq}{y / \beta v_f}$$
\[
\frac{K}{\beta^2} \int_0^{\beta \omega_c} (E_s + \frac{y}{\beta})^{1/2} \frac{2ydy}{1 + \exp(-y)} \frac{1}{1 - \exp(-y)} \int q_c |F(q)|^2 (q^2/2k_s^3) dq
\]

\[
+ \frac{K}{\beta^2} \int_0^{\beta \omega_c} (E_s - \frac{y}{\beta})^{1/2} \frac{2ydy}{1 + \exp(y)} \frac{1}{1 - \exp(-y)} \int -y/\beta v_f |F(q)|^2 (q^2/2k_s^3) dq \quad (2.42)
\]

where for convenience, we have written

\[
K = \frac{3 m_s}{8 \pi} \frac{(2m_s)^{3/2} \pi^2}{k_s^4} J_2 \frac{\pi}{v_f} \frac{D(\xi_f)}{v_f} (1 - U_0 D(\xi_f))^2
\]

\[
= \frac{3\pi m_s}{64 \pi} (E_s)^{-5/2} \frac{v_s}{v_f} \frac{v^2}{N} \frac{D(\xi_f)}{v_f} (1 - U_0 D(\xi_f))^2 \quad (2.43)
\]

At low temperatures, \( \beta \) is large, we can hence extend the upper limit of integration to infinity and the lower limit in \( q \) to zero. Expanding the square roots in the \( y \) integrals and performing the integration over \( q \), taking \( |F(q)|^2 \sim 1 \) (see for example Mills and Lederer 1966), we have

\[
\rho_0 = \frac{K}{\beta^2} \frac{q_c^3}{6k_s^3} \frac{E_s^{1/2}}{E_s} \left[ \int_0^\infty y \left( 1 + \frac{y}{2E_s \beta} - \frac{1}{3} \left( \frac{y}{E_s \beta} \right)^2 \cdots \right) \left( \frac{1}{\exp(-y) - 1} + \frac{1}{\exp(-y) + 1} \right) dy \right.
\]

\[
+ \int_0^\infty y \left( 1 - \frac{y}{2E_s \beta} - \frac{1}{3} \left( \frac{y}{E_s \beta} \right)^2 \cdots \right) \left( \frac{1}{\exp(-y) - 1} + \frac{1}{\exp(-y) + 1} \right) dy \left. \right]
\]

\[
= \frac{K}{\beta^2} \frac{q_c^3}{6k_s^3} \frac{\pi^2}{4} \frac{2E_s^{1/2}}{E_s} \frac{\pi^2}{4} \frac{2E_s^{1/2}}{E_s}
\]

\[
= \pi \frac{3}{64} \frac{q_c^3}{k_s} \frac{v_f \xi_f^2}{v_s \xi_f^2} \frac{m^2}{e^2 \nu \xi_f^2} D(\xi_f) \left( \frac{T}{\nu_0 \xi_f^2} \right)^2 \quad (2.44)
\]
Thus we see that at low temperatures the resistivity due to conduction electrons being scattered off Spin Fluctuations in the f-band goes as $T^2$. This result is in agreement with that obtained by other authors (e.g. M.J. Rice 1967, Mills 1973, Kaiser and Donicah 1971) for similar systems, where a variation method has been employed for the calculation. Recently Mills (1973) has shown that by employing the full form of the spectral density function as shown in equation (1.31), and expanding the denominator for small $T$, a correction to the $T^2$ term, initially proportional to $-(1 - U_0 D(\varepsilon_f))^{-1}(T/T_{SF})^4$, arises, causing the resistivity to deviate from the $T^2$ dependence as the temperature increases.

However, as pointed out by Mills, the expansion employed is only valid for limited range of temperatures due to the presence of the factor $(1 - U_0 D(\varepsilon_f))^{-1}$ in the expansion. In the low temperature region that we are concerned with, the $T^2$ term predominates over all the others, and we therefore feel that a simple model gives a reasonable representation of the overall picture of a Spin Fluctuation system. One immediate remark can be made concerning the result in equation (2.44): the Spin Fluctuation contribution to the electrical resistivity is inversely proportional to the square of the characteristic Spin Fluctuation temperature $T_{SF}$, that is to say, directly proportional to the square of the exchange enhancement factor $(1 - U_0 D(\varepsilon_f))^{-1}$. Thus the magnitude of this $T^2$ term in the electrical resistivity should increase as the tendency towards magnetism in the system increases.
2.3 Magnetoresistivity

We have seen in section (2.1) that the application of a magnetic field to the electron system under consideration leads to different scattering rates for the up and down spin conduction electrons, and thus a difference in their contributions to the electrical conductivities. That is to say, in the presence of a magnetic field $H$, $\sigma_+$ is no longer the same as $\sigma_-$, and in order to obtain the value to the electrical resistivity in the presence of $H$, it is necessary to evaluate the two separately. The scattering rates of the conduction electrons, in this case, are governed by the shape and range of the spectral density of the Spin Fluctuations in the f-band. The applied field $H$ imposes a definite magnetization in the f-band and thus alters the one-particle energy of the f-electrons. One would then expect this change in the f-electron energy to affect the scattering rates of the conduction electrons somewhat and thus lead to a resistivity value different from that in the zero magnetic field case.

We shall now proceed to evaluate the spectral density of the f-Spin Fluctuations in the presence of a magnetic field $H$ and then apply it to evaluate the relaxation times $\tau_+$ and $\tau_-$ and thence the resistivity $\rho_H$ in the presence of a magnetic field $H$. Due to the dependence of $\tau_+$ and $\tau_-$ on the ratio $\tau_+ / \tau_-$, there is considerable difficulty in the precise evaluation of $\tau_+$ and $\tau_-$. Thus we have limited our calculation to the case of small fields, and made the corresponding approximations in the evaluation of the ratio $\tau_+ / \tau_-$. The Hamiltonian for the f-electrons will now take the form
\[ H_f = H_o + H_{\text{int}} + H_{\text{Zeeman}} \] (2.45)

\( H_o \) and \( H_{\text{int}} \) are as defined in Chapter 1 for the zero magnetic field case and are given by

\[ H_o = \sum_{k, \sigma} \varepsilon(k) \quad a_k^+ a_k \sigma \]

\[ H_{\text{int}} = \sum_i U_o n_i^\uparrow n_i^\downarrow \]

\( H_{\text{Zeeman}} \) is the Zeeman term and is given by

\[ H_{\text{Zeeman}} = (g \mu_B H/2) \sum_i (n_i^\uparrow - n_i^\downarrow) \]

where \( i \) denotes the \( i \)th atomic site; \( n_i^\sigma = a_i^+ a_i^\sigma \) is the number operator at atomic site \( i \) for an electron having spin \( \sigma \); \( a_i^+ \) and \( a_i^\sigma \) are respectively the creation and destruction operators for an electron of spin \( \sigma \) in the orbital state \( \phi(x - R_i) \), related to the momentum spin operators \( a_{k\sigma}^+ \) and \( a_{k\sigma} \) by

\[ a_{k\sigma}^+ = N^{-1/2} \sum_i \exp(-ik \cdot R_i) a_i^+ \quad a_{k\sigma} = (a_{k\sigma}^+)^+ \]

and \( g \) is the g-factor of the f-electrons, \( H \) is the magnetic field, all other symbols are as defined in Chapter 1.

Within the Hartree-Fock framework, the Hamiltonian in equation (2.45) then gives rise to the following one-particle energy for
the f-electrons having wave vector \( k \) and spin \( \sigma \),
\[
\mathcal{E}_\sigma(k) = \varepsilon(k) + U_0 (n_{-\sigma}/N) + \eta_\sigma (g\mu_B H/2)
\] (2.46)

where \( \eta_\sigma = +1 \) or \( -1 \) for \( \sigma = \uparrow \) or \( \downarrow \)

and \( n_\sigma = \sum_k \langle a_{k\sigma}^+ a_{k\sigma} \rangle \).

Within the random phase approximation, the transverse dynamic susceptibility \( \chi^{++}(q,\omega) \) for such a system interacting via the intra-atomic Coulomb interaction \( U_0 \) has been shown by Izuyama et al (1963) to be
\[
\chi^{++}(q,\omega) = \frac{\Gamma^{++}(q,\omega)}{1 - U_0 \Gamma^{++}(q,\omega)}
\] (2.47)

where \( \Gamma^{++}(q,\omega) \) is now given by
\[
\Gamma^{++}(q,\omega') = \frac{1}{N} \sum_k \frac{f_{k\uparrow} - f_{k+q\downarrow}}{\varepsilon(k+q) - \varepsilon(k) - \omega'}
\]
\[
= \frac{1}{N} \sum_k \frac{f_{k\uparrow} - f_{k+q\downarrow}}{\varepsilon(k+q) - \varepsilon(k) - (\omega' - \Delta)}
\] (2.48)

\[
= R(q,\omega') + iI(q,\omega')
\]

with \( \Delta = U_0 ((n_{\uparrow} - n_{\downarrow})/N) - g\mu_B H \) (2.49)

Since \( (n_{\uparrow} - n_{\downarrow}) \) is proportional to the magnetization \( M \) of the system, which for a paramagnet is directly proportional to the applied field \( H \) \( (M = \chi H \text{ where } \chi \text{ is the static susceptibility independent of the field } H \text{ and a function of temperature only}) \), \( \Delta \) is directly proportional to \( H \). Equation (2.49) can thus be rewritten as
\[
\Delta = -U_0 (M/\mu_B) - g\mu_B H
\]
\[
= -\mu_B H (U_0 \chi(T)/\mu_B^2 + g)
\] (2.50)
\( R(\mathbf{q}, \omega') \) and \( I(\mathbf{q}, \omega') \) are respectively the real and imaginary parts of \( \Gamma_{\pm}(\mathbf{q}, \omega') \) and are given by

\[
R(\mathbf{q}, \omega') = \text{P.P.} \sum_{k} \frac{f_{k\uparrow} - f_{k+\mathbf{q}\downarrow}}{\varepsilon(k+\mathbf{q}) - \varepsilon(k) - (\omega' - \Delta)}
\]

(2.51)

\[
I(\mathbf{q}, \omega') = \frac{\pi}{N} \sum_{k} \left( f_{k\uparrow} - f_{k+\mathbf{q}\downarrow} \right) \delta(\varepsilon(k+\mathbf{q}) - \varepsilon(k) - (\omega' - \Delta))
\]

(2.52)

where P.P. denotes the principle part of .

As before, we shall consider the low frequency and small wave vector end of the paramagnon spectrum and evaluate \( R \) and \( I \) in these limits. We shall also consider small \( \Delta \) (i.e. low fields) so that the limits we shall be dealing with are

\[
\frac{q}{k_F} < 1, \quad \text{and} \quad \omega' , \Delta \ll v_F q .
\]

Then writing for convenience the Fermi-Dirac function \( f_{k\uparrow} \) and \( f_{k+\mathbf{q}\downarrow} \) as

\[
f_{k\uparrow} = f(\varepsilon(k) + U_0 (n_e/N) + (g\mu_B H/2)) = f(\varepsilon'(k)) \quad \text{say}
\]

(2.53)

\[
f_{k+\mathbf{q}\downarrow} = f(\varepsilon(k+\mathbf{q}) + U_0 (n_e/N) - (g\mu_B H/2))
\]

\[
= f(\varepsilon(k+\mathbf{q}) + U_0 (n_e/N) + (g\mu_B H/2) + \Delta)
\]

\[
= f(\varepsilon'(k+\mathbf{q}) + \Delta)
\]

so that

\[
\frac{\delta f_{k\uparrow}}{\delta \varepsilon(k)} = \frac{\delta f(\varepsilon'(k))}{\delta \varepsilon'(k)}
\]

(2.54)

Equations (2.51) and (2.53) can be expanded for small \( q \), \( \omega' \) and \( \Delta \) to give values of \( R(\mathbf{q}, \omega') \) and \( I(\mathbf{q}, \omega') \) in a way similar to that employed by Izuyama et al (1963) for the zero field case. To keep the mathematics simple, we have assumed that the change in Fermi
energy imposed by the applied field is insignificant compared to the zero field value and hence can be ignored. This assumption is reasonable for small applied fields. As in the zero field case, all constants of expansion have been evaluated at zero temperature. This again is reasonable for a nearly degenerate system of f-electrons at low temperatures. \( R(q,\omega') \) and \( I(q,\omega') \) have been evaluated in the appendix and are given by

\[
R(q,\omega') = D(\epsilon_f) \left[ 1 - \frac{1}{12} \frac{q}{k_f} \right]^2 - \left( \frac{\omega'}{v_f q} \right)^2 - \frac{\omega' A}{(v_f q)^2} - \frac{q}{2k_f} \frac{A}{v_f q} \]  

(2.55)

for \( q \ll 2k_f \);

\[
I(q,\omega') = \frac{\pi}{2} D(\epsilon_f) \frac{\omega'}{v_f q} \text{ for } \omega' < v_f q  
\]

\[
= 0 \text{ for } \omega' > v_f q  
\]

(2.56)

The above two equations can be readily recognised to have a similar form to the ones in the zero field case, giving rise to a similar form of spectral function. In particular, we note that the form of the dissipative part of the unenhanced susceptibility, \( I(q,\omega') \), remains unchanged. By direct inference, we expect the form of the dissipative part of the enhanced susceptibility, \( \Im \chi(q,\omega') \), to be little affected by the small applied field. The spectral density of the system of paramagnons in a magnetic field is then given by

\[
A(q,\omega') = 2 \Im \chi^+(q,\omega') = \frac{\pi D(\epsilon_f) \omega'/v_f q}{\left[ 1 - U_0 D(\epsilon_f) \left( 1 - \frac{1}{12} \frac{q}{k_f} \right)^2 - \left( \frac{\omega'}{v_f q} \right)^2 - \frac{\omega' A}{(v_f q)^2} - \frac{q}{2k_f} \frac{A}{v_f q} \right]^2 + \frac{\pi^2}{2} \frac{D(\epsilon_f,\omega')}{v_f q}^2}  
\]

(2.57)

which for \( q \ll k_f \), \( \omega' \), \( A \ll v_f q \), can be to a good approximation reduced to
Hence as expected, the shape of the spectral density of the paramagnons is hardly altered by a small applied field, and can be well approximated by the value in zero field. However the energy $\omega'$ is now the total energy of a paramagnon in the presence of a magnetic field, and the paramagnons being spin one excitations, can be aligned either parallel or antiparallel to the magnetic field. Thus in a scattering event, in order for the energy to be conserved, the following must hold,

\[
E'_+ - E'_- = \omega' = (\omega + A)
\]  

(2.59)

where $\omega$ is the energy of the paramagnon in zero field. Then substituting (2.59) into equations (2.12) and (2.13), integrating over positive and negative values of $\omega'$ to take account of both emission and absorption processes, and introducing a cutoff energy $\omega_c = \sqrt{g_c}$ as before, we have

\[
\frac{1}{\tau'_\pm} = \frac{\pi (2m_e)^{3/2}}{(2\pi)^3} \frac{j^2}{4N} \left[ \int_{+\Delta}^{\omega_c} (E'_+ + \omega')^{1/2} d\omega' \cdot \int_{1 - \frac{1}{\exp(-\beta \omega')}}^{+1} \frac{1}{1 - \exp(-\beta \omega')} \cdot \frac{1}{1 - \exp(\beta \omega')} \right] 
\]

\[
x |F(q)|^2 A(q, \omega') \left[ \int_{+\Delta}^{\omega_c} d\omega' \right] (1 - \frac{\tau_{\pm}}{\tau_\pm} \cos \theta) \sin \theta d\theta
\]

(2.60)

As in the resistivity calculation in section (2.2), we retain in $(1/\tau'_\pm)$ only terms to those containing $T^2$ for low temperatures. Equation (2.60) is then reduced to
\[ \frac{1}{\tau_+} = 2\pi \frac{(2m_e)^{3/2}}{(2\pi)^3} \frac{j^2}{4N} \int_{+\Delta}^{\omega_c} \frac{d\omega'}{1 - \exp(-\beta \omega')} \left( \frac{1}{1 - \exp(-\beta \omega')} \right)^{+1} \times |F(q)|^2 A(q, \omega') \left( 1 - \frac{\tau_+}{\tau_+^{+}} \cos \theta \right) \sin \theta \delta \theta \] 

(2.61)

for \( E \sim E \sim E_s \), and \( f_{0+} \sim \frac{1}{2} \). Equation (2.61) can be slightly rearranged to give

\[ \frac{1}{\tau_+} = \frac{(2m_e)^{3/2}}{(2\pi)^3} \frac{j^2}{4N} \int_{+\Delta}^{\omega_c} \frac{d\omega'}{1 + \exp(-\beta \omega')} \left( \frac{1}{1 - \exp(\beta \omega')} \right)^{+1} \times |F(q)|^2 A(q, \omega') \left( 1 - \frac{\tau_+}{\tau_+^{+}} \cos \theta \right) \sin \theta \delta \theta \] 

(2.62)

For low temperatures and small momentum transfer, \( \nu \) is given by equation (2.32) and equation (2.39) as before, and \( \tau_+ \) are to a good approximation given by their values at the Fermi surface.

Substituting the value of \( A(q, \omega') \) from equation (2.58) , we have

\[ \frac{1}{\tau_+} = \frac{1}{\tau_{+F}} \frac{(2m_e)^{3/2}}{(2\pi)^3} \frac{j^2}{4N} \frac{D(\xi_F)}{(1 - U_0 D(\xi_F))^2 \nu_f} \int_{+\Delta}^{\omega_c} \frac{d\omega'}{1 + \exp(-\beta \omega')} \times \frac{\omega'/q}{\exp(\beta \omega') - 1} \frac{|F(q)|^2 q}{\nu_f} \left( \frac{q^2}{2k^2} \left( \frac{1}{2\nu_f^2} \right) \right) \left( 1 - \frac{\tau_+^{+}}{\tau_+} \right) \left( 1 - \frac{\tau_+^{+}}{2\nu_f^2} \right) \]

(2.63)
where

\[ \frac{1}{\tau_{+1F}} = K' \int_{\Delta}^{\omega_c} E_s^{1/2} d\omega' \frac{2}{1 + \exp(-\beta \omega')} \frac{\omega'/q}{\exp(\beta \omega') - 1} \int_{\Delta/v_f}^{q_c} |F(q)|^2 \frac{q^2}{k_s^2 2k_s^2} dq \]

\[ = \int_{0}^{\omega_c} - \int_{0}^{+\Delta} \]

\[ = \frac{1}{\tau_o} - \phi(\pm \Delta) \quad \text{say} \quad (2.64) \]

where \( \tau_o \) can be readily recognized to be the relaxation time in the absence of the magnetic field. This is also obvious from equation (2.63): in the absence of the magnetic field \( H \), \( \tau_+ = \tau_- \), i.e. the relaxation times for the up and down spin electrons are equal, and the second term in equation (2.63) vanishes so that \( \tau_+ = \tau_- = \tau_o \) since \( \omega = 0 \) for \( H = 0 \).

\[ \frac{1}{\tau_{+2F}} = K' \int_{\Delta}^{\omega_c} E_s^{1/2} d\omega' \frac{2}{1 + \exp(-\beta \omega')} \frac{\omega'/q}{\exp(\beta \omega') - 1} \int_{\Delta/v_f}^{q_c} |F(q)|^2 \left(1 - \frac{q^2}{2k_s^2} \right)^2 dq \]

\[ = \frac{1}{\tau_{+1F}} \frac{I_2}{I_1} \quad (2.65) \]

where

\[ K' = \frac{(2m_s)^{3/2}}{(2\pi)^2} \frac{J^2}{4N} \frac{\pi D(E_f)}{(1 - U_D(E_f))^2 v_f} \quad (2.66a) \]

\[ I_2 = \int_{\Delta/v_f}^{q_c} (1 - \frac{q^2}{2k_s^2})^1 |F(q)|^2 dq \]

\[ = \int_{0}^{q_c} (1 - \frac{q^2}{2k_s^2})^1 |F(q)|^2 dq \quad \text{for} \Delta \ll a_c v_f \quad (2.66b) \]
\[
I_q = \int_0^q \frac{q^2}{2k_s^2} \frac{1}{k_s^2} |F(q)|^2 \, dq \quad \text{for} \quad q \ll \frac{v_f}{c}
\] (2.66c)

\(I_1\) and \(I_2\) are both independent of \(\omega\) and hence of temperature. For the
ease of writing, we shall from now on omit the subscript \(F\) in \(\tau_{+1F}\)
and \(\tau_{+2F}\), and the implication of its presence understood.

As the relaxation times for the + and - conduction electrons
are interdependent, it is essential to obtain a value for the ratio
\(\tau_-/\tau_+\) in order to evaluate their absolute value. Solving the simult­
aneous equations in equations (2.63) for the ratios \(\tau_-/\tau_+\), we get

\[
\frac{\tau_-}{\tau_+} = \frac{(1/\tau_{+1}) + (1/\tau_{+2}) + (1/\tau_{-2})}{(1/\tau_{-1}) + (1/\tau_{-2}) + (1/\tau_{+2})} \quad \text{evaluated at} \quad E_+ = E_s
\]

\[
= \frac{(1/\tau_{+1}) + (I_2/I_1)(1/\tau_{+1}) + (1/\tau_{-1})}{(1/\tau_{-1}) + (I_2/I_1)(1/\tau_{+1}) + (1/\tau_{-1})}
\] (2.67)

Now making use of equation (2.64) and further assuming that
\(f(±\Delta)\) is small compared with \((1/\tau_0)\) so that terms of order higher
than \((f(±\Delta)/(1/\tau_0))^2\) can be ignored (i.e. we are considering the
low field limit), we have

\[
\frac{\tau_-}{\tau_+} = \frac{(1/\tau_0) - f(\Delta) + (I_2/I_1)((2/\tau_0) - (f(\Delta) + f(-\Delta)))}{(1/\tau_0) - f(-\Delta) + (I_2/I_1)((2/\tau_0) - (f(\Delta) + f(-\Delta)))}
\]

\[
= 1 + \tau_0 \frac{I_1}{2I_2 - I_1} (- f(\Delta) + f(-\Delta))
- \tau_0^2 \left( \frac{I_1}{2I_2 - I_1} \right)^2 \left( f(\Delta)f(-\Delta) + f(\Delta)^2 \left( \frac{I_2}{I_1} - 1 \right) - f(-\Delta)^2 \right) \] (2.68)
Similarly,

\[ \frac{\tau_+}{\tau_-} = 1 + \tau_0 \frac{I_1}{2I_2 - I_1} (-\phi(-\Delta) + \phi(\Delta)) \]

\[ - \tau_0^2 \left( \frac{I_1}{2I_2 - I_1} \right)^2 \left( \phi(\Delta)\phi(-\Delta) + \phi(-\Delta)^2 \left( \frac{I_2}{I_1} - 1 \right) - \phi(\Delta)^2 \frac{I_2}{I_1} \right) \]  

(2.69)

giving

\[ \frac{1}{\tau_+} = \frac{1}{\tau_0} - \phi(+\Delta) \frac{I_1}{2I_2 - I_1} - \phi(+\Delta) \frac{I_2 - I_1}{2I_2 - I_1} - \tau_0 \frac{I_2(I_2 - I_1)}{(2I_2 - I_1)^2} (\phi(-\Delta) - \phi(\Delta))^2 \]  

(2.70)

Hence

\[ \tau_+ = \tau_0 \left[ 1 + \tau_0 \left[ \phi(+\Delta) \frac{I_2}{2I_2 - I_1} + \phi(+\Delta) \frac{I_2 - I_1}{2I_2 - I_1} \right] \right. \]

\[ \left. + \tau_0^2 \left[ \phi(+\Delta)^2 \frac{I_2}{2I_2 - I_1} + \phi(+\Delta)^2 \frac{I_2 - I_1}{2I_2 - I_1} \right] \right] \]  

(2.71)

Then as before the total conductivity is given by

\[ \sigma_{\text{TOTAL}} = \sigma_+ + \sigma_- = \frac{e^2}{6\pi^2 m^*} k_s^3 (\tau_+ + \tau_-) \]

\[ = \frac{e^2}{6\pi^2 m^*} k_s^3 \tau_0 \left[ 1 + \tau_0 (\phi(\Delta) + \phi(-\Delta)) + \tau_0^2 (\phi(\Delta)^2 + \phi(-\Delta)^2) \right] \]  

(2.72)

The resistivity in the presence of a small magnetic field will then be

\[ \rho_H = \left( \sigma_{\text{TOTAL}} \right)^{-1} \]

\[ = \frac{6\pi^2 m^*}{e^2 k_s^3} \frac{1}{2\tau_0} \left[ 1 - \tau_0 (\phi(\Delta) + \phi(-\Delta)) + 2\tau_0^2 \phi(\Delta)\phi(-\Delta) \right] \]  

(2.73)
It is customary to write the magnetoresistivity as a dimensionless quantity \((\rho_H - \rho_0)/\rho_0\); from equation (2.73), it is obvious that this is just the second and the third terms within the square brackets,

\[
\frac{\rho_H - \rho_0}{\rho_0} = \frac{\xi_0}{\rho_0} = \tau_0 (\phi(\Delta) + \phi(-\Delta)) + 2\tau_0^2 \phi(\Delta)\phi(-\Delta) \tag{2.74}
\]

So now the problem of calculating the magnetoresistivity has been reduced down to that of evaluating the three integrals \((1/\tau_0)\), \(\phi(\Delta)\) and \(\phi(-\Delta)\) at the Fermi surface, the first of these having been evaluated in the resistivity section and is given by

\[
\frac{1}{\tau_0} = K' \frac{\hbar^2}{4} I_1 \varepsilon_s (\beta)^{-2} \quad \text{at low temperatures} \tag{2.75}
\]

In the evaluation of \(\phi(\pm\Delta)\), we shall limit ourselves to low temperatures and low magnetic fields such that the condition \(|\Delta\beta| \ll 1\) is satisfied. In this limit, \(\phi(\pm\Delta)\) can be readily evaluated and have a simple dependence on \(\Delta\) and \(\beta\). At higher fields, the dependence becomes complicated and cannot be evaluated analytically; also other complications of physical origin may arise and our previous approximations in the spectral density of the Spin Fluctuations may no longer be valid. The consequences of higher fields will be further discussed in chapter 5. Presently, we shall confine ourselves to the low field limit which is consistent with our previous assumptions. We have \(\Delta \sim \hbar v_B H \sim 10^{-20} \text{ erg/ gauss } \times H\)

\[
\beta = (k_B T)^{-1} = (1/1.381) \times 10^{16} \times T^{-1} \text{ (erg)^{-1}}
\]

Therefore, for \(T\) greater than, or of the order of a few degrees, the condition \(|\Delta\beta| \ll 1\) is satisfied for magnetic field values up to a few kilogauss. To sum up, then, the foregoing imposed condition has limited the validity of our calculation to be within the range
$10^6 K < T < 10^6 K$, possibly slightly higher, 

$H < 5$ kilogauss.

Bearing these conditions in mind, we can now proceed to evaluate $\psi(\Delta)$. The expressions for $\psi(\Delta)$ and $\psi(-\Delta)$ are given by (2.64),

$$\psi(\Delta) = K'I_1 \int_0^{\Delta} \frac{E_s^{\frac{1}{2}} d\omega'}{\omega'} \exp(\beta \omega') - 1 - \frac{2}{\exp(-\beta \omega') + 1} \quad (2.76)$$

Making the substitution $y = \beta \omega'$ as before, we have

$$\psi(\Delta) = K'I_1(\beta)^{-2} \int_0^{\Delta \beta} \frac{E_s^{\frac{1}{2}} y dy}{\exp(y) - 1 - \frac{2}{\exp(-y) + 1}}$$

For $|\Delta \beta| \ll 1$, $y$ will be small compared to one throughout the entire range of integration. Hence we can write to a good approximation

$$\exp(y) = 1 + y + y^2/2 + 

\text{and} \quad \psi(\Delta) \text{ will be given by}

$$\psi(\Delta) = K'I_1(\beta)^{-2} \int_0^{\Delta \beta} \frac{E_s^{\frac{1}{2}} y dy}{\exp(y) - 1 - \frac{2}{\exp(-y) + 1}}$$

$$= K'I_1(\beta)^{-2} E_s^{\frac{1}{2}} (\Delta \beta) \quad (2.78)$$

Thus the low field magnetoresistivity in a Spin Fluctuation system is given by

$$\frac{\delta \rho}{\rho_o} = -\tau_0 (\psi(\Delta) + \psi(-\Delta)) + 2\tau_0^2 \psi(\Delta)\psi(-\Delta)$$

$$= -\frac{32}{\tau_0} (\Delta/k_B T)^2 \quad (2.79)$$
where $\Delta$ is a function of both the magnetic field and the interaction strength (and hence the exchange enhancement factor) of the Spin Fluctuation system and is given by equation (2.50). Therefore, we have found that the magnetoresistivity in a Spin Fluctuation system decreases with increasing magnetic field at low fields. As is directly proportional to the applied field $H$ and the exchange interaction $U_0$, the magnitude of this decrease increases with the interaction strength $U_0$ and decreases with increasing temperature. Thus for a nearly magnetic system with a high value of $U_0$, the value of $\rho/\rho_0$ will be large and negative at low values of applied fields where the results of this calculation are applicable. An application of the results of this calculation will be made to Pu in chapter 5 where the physical implications will be further discussed.

Part 2 Spin Fluctuation contributions to other physical properties

2.4 Thermal resistivity

In this and the following subsections, we shall attempt to give a brief review of the work performed by other authors employing a similar band structure to that discussed by us. We shall not go into the details of the mathematics involved, but rather give a general outline of the methods employed that led to the acquired results.

As in the case of electrical resistivity where in the presence of an externally applied electric field, the displaced conduction electrons re-establish equilibrium in the system by scattering off various available mechanisms, e.g. phonons, impurities, paramagnons, similar scatterings occur when the system is subjected to a thermal
gradient. In the presence of a thermal gradient, the distribution function of the conduction electrons is also changed, and a new equilibrium in the system is established when the rate of change of the distribution function due to the presence of the thermal gradient is balanced by the rate of change due to the conduction electrons scattering off the various mechanisms. Here of course, we are concerned only with the scatterings by Spin Fluctuations that give rise to the thermal resistivity component $\nu_{SF}$.

Schindler and Rice (1967), with the intention of applying their results to Pd-Ni alloys, employed the variational principle in their calculation and showed that the thermal resistivity can be expressed in the form

$$\nu_{SF} = \frac{1}{k_B} \left[ \frac{\int d^3k \int d^3k' V(k_+, k_-) (\phi(k_+) - \phi(k_-))^2}{\frac{2}{m_s} \int d^3k k (E(k) - E_S) \phi(k_-) \delta f_{o^+} \delta E_{o^+}} \right]^2$$

(2.80)

where

$$V(k_+, k_-) = \frac{(2\pi)^3}{N^2} \sum_q \int_{-\infty}^{+\infty} d\omega A(q, \omega) n(\omega) f_{o^+}(1 - f_{o^+}) \left[ (E_{o^+} - E_S) \delta(k_+ - k_- - q) \right]$$

(2.81)

and $\phi(k_+)$ is related to the deviation of the conduction electrons (assumed to be s-electrons only) distribution from equilibrium, $g_+$ by

$$g_+ = f_+ - f_{o^+} = - \left( \frac{\delta f_{o^+}}{\delta E_{o^+}} \right) \phi_+$$

and all the other symbols are as defined previously.

Then employing a trial function of the form $\phi(k_\sigma) = k_\sigma u(E(k_\sigma) - E_S) x$ a constant (where $\sigma$ denotes the spin direction and $u$ is a unit
vector in the direction of the thermal gradient) and a spectral density of the form

\[ A(q, \omega) = \alpha_0 \frac{\omega}{q} \quad \text{for } 0 \leq |\omega| \leq \omega_q \]

\[ = 0 \quad \text{for } |\omega| > \omega_q \]

with

\[ \omega_q = \frac{4}{\pi} \frac{1 - U_0 D(\xi_d)}{U_0 D(\xi_d)} \frac{q}{k_d} \xi_d \]

\[ = 0 \quad \text{for } q > q_c \]

\[ \alpha_0 = \frac{N}{2} \frac{\pi k_d}{\xi_d} \frac{D(\xi_d)}{(1 - U_0 D(\xi_d))^2} \]

where \( k_d \) and \( \xi_d \) are the Fermi wave vector and energy respectively of the d-electrons. Schindler and Rice have shown that at low temperatures such that \( T \ll T_{SF} \), the thermal resistivity has the form

\[ \rho_{SF} = (a T / T_{SF}^2) - b (T^2 / T_{SF}^3) + O(T / T_{SF})^4 \quad \text{.... (2.82)} \]

where \( T_{SF} \) is the characteristic Spin Fluctuation temperature defined by

\[ k_B T_{SF} = \frac{\omega}{q_c} = \frac{4}{\pi} \frac{1 - U_0 D(\xi_d)}{U_0 D(\xi_d)} \frac{q_c}{k_d} \xi_d \]

and the coefficients \( a \) and \( b \) are given by

\[ a/b = \left[ J_4 (1 - \frac{1/2}{3k_d^2}) + J_5 \pi^2 (q_c/3k_d^2)^2 \right] / J_5 \]

\( a \) is a constant independent of the enhancement factor \((1 - U_0 D(\xi_d))^{-1}\),

\( J_n \) are constants given by

\[ J_n = n! \sum_{s=1}^{\infty} (s)^{-n} \]
The form of $W_{SF}$ in equation (2.82) was intended for nearly ferromagnetic dilute Pd-Ni alloys having a narrow d-band. However it is perfectly general and applies to any Spin-Fluctuation system having a similar spectral density. At low temperatures, the thermal resistivity due to conduction electrons being scattered off Spin Fluctuations goes as $T$, this component should as in the case of electrical resistivity, dominate over the contribution from phonon scatterings which is proportional to $T^2$ at low temperatures. Therefore, provided that the other mechanism of heat conduction, namely the phonons, do not contribute significantly to the total conductivity (as is the case with most metals) this term linear in $T$ should be readily observable experimentally at low temperatures in a nearly ferromagnetic system.

2.5 The Lorenz number

The Lorenz number is the ratio of the electrical resistivity to the product of the electronic contribution to the thermal resistivity $W_e$ with the absolute temperature $T$,

$$L = \frac{\rho}{W_e T}.$$ 

$L$ is equal to a constant value $L_0$ given by

$$L_0 = \left(\frac{\pi k_B}{e}\right)^2/3 = 2.4453 \times 10^{-8} \text{ Watt units Ohm cm./°K}$$

so long as the electron scattering processes are elastic and the same relaxation time holds for both electrical and thermal resistivities. In a relatively pure metal whose resistivities arise mainly from conduction electrons being scattered off lattice vibrations, this situation is realized both in the very low temperature limit (or the so-called residual region) where impurity scatterings predominate and in the high temperature region where $T \gg \Theta_D$ the Debye temperature. In the high temperature region, the maximum amount of energy an electron can gain or lose is limited to $k_B \Theta_D$ which is much less than
\( k_B T \), the depth of the thermal layer of the d-electron distribution, with the result that all scatterings are essentially elastic. However, at somewhat lower temperatures where only long wavelength phonons are thermally excited, the electron distribution relaxes predominantly by small angle scatterings. The relaxation time for the electrical resistivity \( \rho \) becomes longer than that for the thermal resistivity \( \sigma \) due to the fact that small angle scatterings are less effective at checking the flow of electron current by a factor of \( \sim (\theta_B/T)^2 \) (Ziman 1960). This gives rise to a reduced Lorenz number that goes to zero as \( T \to 0^0K \). By analogy, in a system in the temperature region where electrons are predominantly scattered by long wavelength Spin Fluctuations, we would expect the Lorenz number to be somewhat reduced below the \( L_0 \) value.

Schriempf et al (1969) followed the s-d interaction formalism developed by Hills and Lederer (1966) and by employing the variational approach to the solution of Boltzman equation deduced the following value of Lorenz number for a system in which the spin density fluctuations in the narrow d-band serve as the dominant mechanism for scattering the s-electrons.

\[
L = L_0 \frac{s}{3 + 12\beta(1)/\beta(3)}
\]

where \( \beta(n) = \int_0^{2Q} d\eta \eta^2 \alpha(k_s\eta) |F(k_s\eta)|^2 \)

\[
2Q = 2^{\frac{1}{2}} (1 - \cos \theta_M)^{\frac{1}{2}} \quad \text{maximum value of } Q \text{ is one}
\]

\( \theta_M \) = maximum angle through which the s-electrons are scattered

\( F(k_s\eta) = \) form factor of the d-electrons, \( k_s \) being the Fermi wave vector of the s-electrons.
\( \alpha(q) \) is defined by \( A(q, \omega) = \omega \alpha(q) \), \( \hat{\alpha}(q, \omega) \) being the spectral density of the d-Spin Fluctuations.

\[
\alpha(q) = \text{constant} \times \frac{k_s/q}{[1 - U_o D(\varepsilon_d)(1 - (5q/k_s)^2)]^2}
\]

for a spherical band; \( \varepsilon \) is an adjustable parameter.

Taking \( |F(q)|^2 = 1 \), the \( \beta(n) \) integrals were evaluated to give for a pure metal the following Lorenz number

\[
L = L_o \left[ \frac{5q^2}{9 + 3q^2 + (96/5)U_o D(\varepsilon_d)q^2(1 - U_o D(\varepsilon_d))^{-1}} \right] \tag{2.84}
\]

It is apparent from equation (2.84) that the Lorenz number of a highly exchange enhanced metal is reduced below the value \( L_o \), and decreases rapidly with increasing magnitude of the enhancement factor. Hence in a system where scattering of conduction electrons from narrow band Spin Fluctuations predominates, we expect a reduced value of the Lorenz number that is independent of temperature in the low temperature region where \( \rho \propto T^2 \) and \( W \propto T \) hold true.

2.6 Specific heat

As the exchange enhancement increases, the corrections to the one-partical energy due to the emission and reabsorption of paramagnons become increasingly important. At \( T = 0^\circ K \) these corrections yield an enhanced effective mass for the electrons responsible for the Spin Fluctuations. Since the electronic specific heat coefficient 

\[
\gamma = \lim_{T \to 0} \frac{(C(T)/T)}{}
\]

is proportional to the effective mass \( m^* \), an enhanced \( \gamma \) results. At temperatures above zero, these corrections
modify the temperature dependence of the low temperature specific heat.

The calculation was performed concurrently by Doniach and Engelsberg (1966) and by Berk and Schrieffer (1966) where the correction to the ground state energy $\Delta E$ of the system due to the presence of the interaction represented by the Hamiltonian $H_{\text{int}}$ given by equation (1.10) was found to be

$$\Delta E = U_0 \langle n_i \rangle \langle n_j \rangle - i \int \frac{d\omega}{(2\pi)^{-1}} \sum_q \left[ \log(1 - U_0 \Gamma(q, \omega)) + U_0 \Gamma(q, \omega) \right]$$

(2.65)

where $\Gamma(q, \omega)$ is the generalised susceptibility function for a non-interacting Fermi gas. This expression for $\Delta E$ provides an approximation to the free energy at finite temperatures on employing temperature dependent Fermi functions.

The shift in entropy is given by

$$\Delta S = -\frac{\partial}{\partial T} \Delta E$$

leading to the following low temperature specific heat,

$$\frac{C_v}{C_{v_0}} = \frac{m^*}{m} + \alpha \left( \frac{T}{T_{SF}} \right)^2 \log \left( \frac{T}{T_{SF}} \right) + \ldots$$

(2.66)

where $\alpha = \frac{9}{2} \left( \frac{\pi U_0 D(\varepsilon_f)}{1 - U_0 D(\varepsilon_f)} \right)^2$

$$k_B^2 T_{SF} = \frac{4 \varepsilon_f}{\pi} \frac{(1 - U_0 D(\varepsilon_f))}{U_0 D(\varepsilon_f)}$$

$$C_{v_0} = \frac{2}{3} \pi^2 D(\varepsilon_f) k_B^2 T$$

the 'normal' electronic specific heat,

$$\frac{m^*}{m} = 1 + \frac{9}{2} U_0 D(\varepsilon_f) \log \left[ 1 + \frac{1}{12} \left( \frac{q_c/k_f}{1} \right)^2 \frac{U_0 D(\varepsilon_f)}{(1 - U_0 D(\varepsilon_f))} \right]$$

where $q_c$ is the cutoff wave vector in the paramagnon spectrum.
The temperature dependence of $C_v$ predicted by equation (2.86) has been observed in Ni-Rh alloys (Bucher et al. 1967) where the plot of $C_v T$ against $T^2$ shows an up turn at low temperatures as $T$ approaches zero.

### 2.7 Magnetic susceptibility

The contribution of Spin Fluctuations to the temperature dependence of the magnetic susceptibility of a nearly magnetic system has been calculated by Beal-Monod et al. (1968). The inverse of the uniform field spin susceptibility measures the second order energy cost of producing an infinitesimal spin polarization. If the ratio of the difference in number between the spin up and spin down electrons to the total number of electrons is denoted by $\frac{N_+ - N_-}{N}$, the susceptibility per unit volume can be expressed as

$$\chi = \frac{N}{V} \mu_B^2 \left( \frac{\partial^2 F}{\partial \xi^2} \right)^{-1}$$

(2.87)

where $N/V$ is the number of particles per unit volume, $\mu_B$ the Bohr magneton, $F$ the free energy per particle.

Then summing over all contributions to the free energy from the paramagnons, for low temperatures such that $T < T_{SF}$, the magnetic susceptibility was found to be given by

$$\frac{\chi(T)}{\chi(T=0)} = 1 - \frac{\pi^2}{4} \left( \frac{T}{T_{SF}} \right)^2 + O(T^4 \log T)$$

(2.88)

where

$$\chi(T=0) = \chi_{Pauli} \left( 1 - U_o D(\xi_{f}) \right)^{-1}$$

Equation (2.88) has been applied satisfactorily to data on He$^3$ by Beal-Monod et al.; He$^3$ is one of the well known 'paramagon systems'.
Chapter 3

Physical Properties of the Actinides: Experimental situation

3.1 Introduction

In this chapter, we shall review some of the known physical properties of the Actinides. This review is by no means exhaustive, however, we believe it would give an overall picture of the behaviour of the Actinide metals and enable a sensible comparison with existing theories to be made. At low temperatures, the physical properties of the Actinides are often anomalous and outside one's expectation, the anomalous behaviour progresses across the series, with Thorium, the first metal in the Actinide series, resembling most closely to a normal metal, and Plutonium, the furthest along the series that has been thoroughly investigated, being, so far, the most anomalous. This progression towards anomalous behaviour is evident in various physical properties like the electrical resistivity, the thermal conductivity, Lorenz number, the electronic specific heat constant, and the magnetic susceptibility, all of which will be reviewed in the following sections. We shall begin by reviewing on the electrical resistivity of these metals, where the progression towards anomalous behaviour is most evident.

3.2 Electrical Resistivity

We shall begin by giving an overall picture of the resistivity behaviour in the Actinides, and then review on the effects of various external parameters on the resistivity. Of all the transport properties of the Actinides, the electrical resistivity is the most extensively studied, both theoretically and experimentally. Figure 3.1 shows the electrical resistivity of all the Actinide metals so far measured. The progression towards higher and more
anomalous resistivity with increasing atomic number is apparent, with the behaviour in Thorium approximating most closely to a normal metal. Over a wide range of temperatures, the resistivity of Thorium is linearly proportional to the temperature as expected in a normal metal where the scattering of the conduction electrons by phonons constitutes the major part of the resistivity. However, at the lowest temperatures, i.e. the region immediately above the residual region, the ideal resistivity was found to obey a $T^3$ law rather than the $T^5$ law given by the Bloch-Gruneisen function for a simple metal (Haen and Meaden 1965, Peterson et al 1967). The next in the series, Protactinium, is also relatively normal, the resistivity is proportional to $T$ up to $100^0K$ where a change of slope occurs. Above about $200^0K$, a very slight curvature is apparent. Immediately above the residual region, the ideal resistivity was found to be proportional to $T^{2.8}$ (Mortimer 1972). Uranium is the first to show definite deviation from normal metal behaviour. A curvature in the $\rho$-$T$ curve throughout the measured temperature range is evident, with a $d\rho/dT$ decreasing with increasing temperatures. A change of slope also occurs in Uranium, at $43^0K$. This change of slope has been widely discussed in literatures and its cause has been attributed to a phase transition at that temperature, generally referred to as the $\alpha$-$\alpha'_0$ transition (Mortimer 1972 chapter 6). At the lowest temperatures, the ideal resistivity was found to be proportional to $T^{3.1}$ (Meaden 1963). The general trend followed by the resistivity of Uranium is much more pronounced and amplified in Neptunium, and it has been reported that its resistivity goes through a slight maximum at $\sim 500^0K$. At low temperatures, below $\sim 15^0K$, the resistivity of Neptunium was found by Arko et al (1972) to be proportional to $T^2$, Meaden (1963), however, found a $T^{3.12}$ dependence.
in the temperature region 3–32°K. The curvature in the ρ–T curve has developed into a well defined maximum at ~100°K in α-Plutonium. Above this temperature, the resistivity continues to slowly decrease with increasing temperature until the α-β phase transition. However, measurements on a single crystal of α-Pu (Arko and Brodsky 1970) indicate that along the b-axis of the crystal, the resistivity slope remains positive throughout the entire temperature range measured, while the maximum at 100°K was observed in all other directions. At low temperatures, below about 15°K, Arko et al (1972) found that the ideal resistivity in Pu, as in Np, obeys a T^2 law, while earlier results obtained by Meaden (1963) indicate that in the temperature range T = 8–27°K, the temperature dependence varies from T^2.3 to T^2.8, depending on the purity of the sample. The β-phase of Plutonium stabilised below room temperature by quenching shows a even sharper resistivity maximum at 25°K, however due to the high value of dρ/dT at the lowest temperatures measured (3µ cm deg^{-1} at 1.7°K), there has been considerable uncertainty as to the kind of power law followed by the ideal resistivity in the low temperature region. Hall and Purser (1971), with a reasonable choice of the residual resistivity, were able to fit the resistivity to a T^{1.55} dependence.

3.2a Effect of an externally applied magnetic field

Measurements of magnetoconductivity have been made on Thorium and Uranium in the temperature region between 1°K and 300°K (Berlin-court 1959), and on α and β Plutonium at various temperatures up to 53°K for α-Pu and to 78°K for β-Pu (Brodsky 1967). The resistivity of Thorium was found to increase on application of a magnetic field with the magnitude of the increase directly proportional to the square of the applied field H at all field strengths. This is in
accordance with the prediction of a simple two band theory for a system having equal numbers of positive and negative current carriers. However, in Uranium, the increase was found to be proportional to \( H^2 \) only at low field strengths; at high fields, the proportionality becomes linear. The results for Plutonium are anomalous. Both \( \alpha \) and \( \beta \) Plutonium show negative magnetoresistivity (i.e. a decrease in resistivity on applying a magnetic field) at low fields, with the magnitude of the decrease diminishing with increasing temperatures, until barely observable by 27\(^\circ\)K in \( \alpha \)-Pu and 21\(^\circ\)K in \( \beta \)-Pu. Above about 3 Kilogauss, both \( \alpha \) and \( \beta \)-Pu exhibit normal magnetoresistivity, i.e. a magnetoresistivity that is positive and increases as \( H^2 \) as predicted by simple theory. The results in Plutonium appear to suggest two separate contributions to the magnetoresistivity: a negative contribution which dominates at low fields, and a positive "normal" contribution which becomes dominant as the field strength increases.

3.2b Effect of Self-Irradiation Damage

Certain isotopes of the Actinides are unstable and decay by \( \alpha \)-particle emission. Both the emitted \( \alpha \)-particle and the recoil nucleus create interstitials and vacancies along their path lengths. At low temperatures, these defects are not mobile enough to migrate through the lattice and recombine, hence there is a gradual build-up of point defects with time at low temperatures and this in turn causes an increase of resistivity with time of damage. Self-irradiation damage experiments have been performed on Fa, \( \alpha \)-U, \( \alpha \)-Np and \( \alpha \) and \( \beta \)-Pu. In all cases, the samples were held at liquid helium temperature for \(~10^4\) hours and the resulting variation of resistivity with time examined (Griffin et al 1970 and references therein).

In the first three metals, the damage rates are considerably lower.
than in \( \alpha \) and \( \beta \)-Pu, the difference being too great to permit detailed comparisons with the latter two to be made. However, the initial rate of resistivity rise at 4.2 K, when normalised to comparable damage rates (i.e. rates of defect production) which for a first approximation was assumed to be proportional to the self-heat of the metal, was found to increase with increase in atomic number, the normalised rate of resistivity increase in \( \beta \)-Pu being \( \sim \) twice that of \( \alpha \)-Pu.

\[
\text{Table 3.1}
\]

<table>
<thead>
<tr>
<th>Element</th>
<th>((\text{initial } d\rho/dt) + (\text{self heat}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>231 Pa</td>
<td>(0.83 \times 10^{-5})</td>
</tr>
<tr>
<td>233 U</td>
<td>(2.8 \times 10^{-5})</td>
</tr>
<tr>
<td>237 Np</td>
<td>(10.9 \times 10^{-5})</td>
</tr>
<tr>
<td>239 (\alpha)-Pu</td>
<td>(24.0 \times 10^{-5})</td>
</tr>
<tr>
<td>239 (\beta)-Pu</td>
<td>(40.0 \times 10^{-5})</td>
</tr>
</tbody>
</table>

This led to the speculation that a correlation exists between the value of this ratio and the degree to which the temperature dependence of the resistivity (in the undamaged material) is anomalous, with the ratio in Pa being the smallest, corresponding to the near normal behaviour of its resistivity, while the highly anomalous resistivity of \( \beta \)-Pu corresponds to the highest value of the ratio in the series.

The additional resistivity due to build-in damage in Pa, \( \alpha \)-U and \( \alpha \)-Np shows tendency to saturate at high levels of damage, and the experimental results could be fitted to a single exponential term of the form

\[
\rho - \rho_0 = A \left[1 - \exp(\alpha t)\right]
\]
where $A = \rho_S - \rho_0$, and $\rho$, $\rho_0$ and $\rho_S$ are the resistivities at time $t$, initially, and at saturation respectively; $\alpha$ being the time constant for the build-in of the defects giving rise to the additional resistivity. The situations in $\alpha$ and $\beta$-Pu are much more complex. For holding time in excess of $6 \times 10^3$ hours at $4.2^\circ K$, the additional resistivity of $\alpha$-Pu goes through a maximum (King et al 1965, Griffin 1968, Oslen and Elliot 1964). The results of $\alpha$-Pu were analysed into three terms given by (Hall and Mortimer 1971, Griffin et al 1970)

$$\rho - \rho_0 = A[1 - \exp(-\alpha t)] + A_\circ[1 - \exp(-\alpha_\circ t)] + B[1 - \exp(-\beta t)]$$

where the $A$ term corresponds to the degree of anomalous behaviour in the resistivity - temperature curve, the $A_\circ$ term, which is negative, relates to the small time dependent term seen in the low temperature thermal resistivity of $\alpha$-Pu, and finally, the $B$ term, which is also negative, has a time dependence which is controlled by defect saturation. The coefficients $\alpha$, $A_\circ$ and $B$ are functions of the purity of the specimen, while the time constants are the same in various samples of different purities,

$\alpha \sim 0.6 \times 10^3$/hour, $\alpha_\circ \sim 0.19 \times 10^{-2}$/hour, $\beta \sim 0.17 \times 10^{-3}$/hour.

The results for $\beta$-Pu were also fitted to a similar equation having only the $A$ and the $B$ term which is positive (Griffin et al 1970), the resistivity increase in $\beta$-Pu does not go through a maximum with time.

Earlier work by King et al (1965) indicated that the additional resistivity in Pu due to accumulation of damage is strongly temperature dependent. The failure of Matthiesen's rule points to the fact that the damage is affecting the "anomalous" scattering mechanism.
(which causes the anomalous behaviour in the resistivity in the undamaged state) rather than simply acting as extra point-defect scatterers, though the latter effect could well be present. On the whole, the effect of damage is to greatly increase the resistivity over the undamaged value below \( \sim 50^\circ K \), while slightly decreasing it at temperatures greater than \( 50^\circ K \). A heavily damaged sample thus has an essentially temperature independent resistivity. This was indeed found to be the case when an \( \alpha \)-Pu sample kept at \( 4.2^\circ K \) for 8200 hours was warmed up fairly quickly so as to minimise the effect of annealing (of the accumulated defects). The results showed that up to \( 119^\circ K \), the resistivity remains essentially temperature independent and has the same value as the undamaged material at \( \sim 50^\circ K \). A rapid annealing then occurred between \( 119^\circ K \) and \( 152^\circ K \), above which the resistivity regained its undamaged values. The situation in \( \beta \)-Pu is further complicated by the fact that the temperature at which the resistivity maximum occurs was shifted to a lower value by increasing damage at \( 4.2^\circ K \), and the saturation value of the additional resistivity is above that at the maximum of the undamaged resistivity curve.

3.2c Effect of alloying

Olsen and Elliott (1965) investigated the effect of Neptunium addition on the temperature dependence of the resistivity of \( \alpha \)-Pu between \( 4.2^\circ K \) and \( 300^\circ K \) and found that the resulting additional resistivity deviates considerably from Mattheisen's rule. Up to a few atomic percent of Np in solid solution, the effect is to greatly increase the resistivity over the value in pure Pu below \( \sim 60^\circ K \) while only slightly decreasing it above this temperature. Thus the low temperature decline in the pure Pu resistivity curve
was completely eliminated by addition of 7 at.\% Np. It was also found that the resistivity of these alloys at 4.2^0\text{K} increases with Np content at first, then passes through a maximum at \sim 7 at.\% Np; this compares well with the self-irradiation damage results where the additional resistivity due to damage passes through a maximum at \sim 7000 hours of damage at 4.2^0\text{K}. Later work by Griffin (1968) on the effect of Np addition on the self-irradiation dependence of the resistivity clearly indicated that the changes induced by the two processes are closely related, with 1 at.\% Np addition approximately equivalent to 1000 hours of damage at 4.2^0\text{K} up to high levels of damage and high Np concentration. Hall and Purser (1971) extended the work to \beta-Pu. Here the rapid decline in the resistivity of the pure metal below \sim 20^0\text{K} is suppressed by a smaller concentration of Np, \sim 2 at.\%, compared to \sim 7 at.\% for \alpha-Pu. This again is in accord with the self-irradiation damage measurements where the low temperature decline in the resistivity of the undamaged sample was eliminated after about 2000 hours of damage at 4.2^0\text{K}. The resistivity of the \beta-Pu alloys measured at 4.2^0\text{K}, however, contrary to that of \alpha-Pu alloys which increases with Np content and reaches a maximum at \sim 7 at.\% Np, does not go through a maximum with increasing Np content: it rises rapidly with Np addition up to \sim 2 at.\% Np concentration and then increases more slowly above this concentration, again reflecting the apparent link with the self-irradiation damage results.

The effect of Plutonium addition on the resistivity of Uranium has also been investigated (Mortimer 1972). It was again found that the additional resistivity deviates from Matthiesen's rule, with its magnitude decreasing with increasing temperatures. Thus the addition of 5f electrons to Uranium has the effect of increasing
the curvature of the resistivity-temperature curve and causing it to tend towards that of Neptunium, although the curvature is still much smaller.

### 3.2d Effect of Pressure

Resistivity measurements on \(\alpha\)-Uranium at various pressures up to 40.7 kbars (Mortimer 1972) form a regular progression, an increase in pressure produces a reduction in the resistivity as expected in the case of a normal metal. The curvature in the resistivity-temperature curve, however, remains, and appears to be hardly altered by the increase in pressure, contrary to the effect of Pu addition.

Measurements on \(\alpha\)-Pu were carried out at pressures up to 13.1 kbars (Mortimer 1972) and the results are shown in figure 3.2. The difference in the low temperature behaviour of the 13.1 kbar resistivity is due to the presence of considerable strain introduced during the compression process and is not an intrinsic effect of the pressure. After correcting for the effect of strain, the results represented by the curves again fall in a progression. It is immediately apparent from figure 3.2 that the negative temperature coefficient above the resistivity maximum in \(\alpha\)-Pu is progressively reduced in magnitude by increasing pressure, whereas the low temperature decline remains relatively unchanged. There is also no change in the residual resistivity with pressure. This again is in contrast with the results produced by Np additions where the affected regions of the resistivity-temperature curve are reversed.

### 3.2e Concluding remarks

It appears from the experimental results reviewed that the
resistivity-temperature curve of Pu can be divided into two regions in its response to various external parameters. In the temperature region above the resistivity maximum, the resistivity is highly sensitive to pressure variation while relatively insensitive (or, in the case of an applied magnetic field, has normal response) to Np additions, self-irradiation damage, and external magnetic field. However, below the maximum, the resistivity is rather insensitive to pressure, yet changes dramatically with all the other parameters. This seems to point to two totally different scattering mechanisms being operative in Pu: one in the low temperature region below the resistivity maximum, responsible for the $T^2$ dependence below about $150^\circ$K and the rapid rise with increasing temperature; the second mechanism is operative (or predominant) in the temperature region above the resistivity maximum, responsible for the negative slope in the resistivity-temperature curve. Unfortunately, there is insufficient data to permit a comparison with the other Actinides; however, if one could associate the increasing curvature in the resistivity-temperature curves from Th to Np with the same mechanism that operates in Pu below the temperature of the resistivity maximum, our conclusion then ties in with the pressure measurements on U where the curvature in the resistivity-temperature curve is also unaffected by pressure application.

3.3 Thermal Conductivity

The thermal conductivity measurements across the Actinide series are shown in figure 3.3, a gradual decrease in magnitude with increasing atomic number is evident, with the value for Pu the lowest reported so far for any pure metal. Lattice conduction plays an important role in the Actinides (Hall and Lee 1970) especially in Pu where the lattice component forms a significant
fraction of the whole owing to the small value of the total conductivity. In an ordinary metal, lattice conduction forms only a small part of the whole, this is because at high temperatures, the phonons are scattered by thermal vibrations of the lattice and at low temperatures, by the conduction electrons; thus in a normal metal, the thermal conductivity is largely electronic in nature, and tends to a constant value at high temperatures. This behaviour is still qualitatively followed by Thorium and to some extent by Uranium. However, beginning with Uranium, there is an increasing tendency for the higher temperature thermal conductivity (above ~400 K) to rise with increasing temperature. This appears to be a reflection of the increasingly negative curvature in the resistivity-temperature curves of the Actinides, the effect of which at low temperatures is being masked by the size of the lattice component.

3.4 Lorenz number

The Lorenz ratio \( L = \frac{K}{\rho T} \) relates the electrical resistivity to the electronic thermal conductivity \( K \) of a metal. The values of \( L \) derived using the measured values of the thermal conductivity for Thorium, Uranium and Plutonium are as follows:

1. Thorium: \( L \) starts with the free electron value of \( L_0 = 2.45 \times 10^{-8} \frac{V^2}{K} \) at low temperatures, goes through a minimum at 150 K and then rises to a high value of \( 3 \times 10^{-8} \frac{V^2}{K} \). This behaviour resembles a normal metal, the high value of \( L \) was attributed to the presence of a significant lattice component in the thermal conductivity (Schettler et al 1969).

2. Uranium: \( L \) starts with a value of \( 3.9 \times 10^{-8} \frac{V^2}{K} \) at 50 K, rising to a sharp maximum of \( 5.3 \times 10^{-8} \frac{V^2}{K} \) at 150 K and then falls to a sensibly constant level of between 3.2-3.5 \( 10^{-8} \frac{V^2}{K} \).
over the range 25-100°K (Hall and Lee 1970).

(3) Plutonium: L rises from a value of $3.4 \times 10^{-8} V^2 K^{-2}$ at $0^\circ K$ to a high maximum of $8 \times 10^{-8} V^2 K^{-2}$ at $50^\circ K$ and then decreases gradually to $5.7 \times 10^{-8} V^2 K^{-2}$ at $100^\circ K$ (Hall and Lee 1970).

These figures above appear to indicate a highly anomalous behaviour of the Lorenz number. However, Hall and Lee (1970), citing the fact that in self-irradiation damage experiments, the thermal resistivity of Plutonium changes comparatively little with time and that the changes are of the same order throughout the entire temperature range (unlike the case of the electrical resistivity where below $50^\circ K$ the additional resistivity $\Delta \rho$ due to damage is very temperature dependent, $\Delta \rho \sim 0$ at $50^\circ K$), they argued that the electronic thermal conductivity in Plutonium is a relatively smooth function of temperature, resulting in a Lorenz number that begins with a value below $L_0$, and increases steadily with temperature to $L_0$ at about the Debye temperature. This behaviour of L resembles that of a normal metal, therefore they extended their arguments to other actinides and concluded that the Lorenz number behaves normally in the Actinides, and that the observed anomalous values are a result of the lattice component increasing across the series and the anomalous electrical resistivity.

3.5 Specific heat

All the known data derived from the specific heat measurements on the Actinides are summarised in figure 3.4. This figure is taken from a review article by Lee et al (1970) and the numbers in the diagram refer to the references in that article. There is a marked increase in $C_p$ across the series from Th to Fu, and the room temperature values are as plotted. This increase can be adequately
accounted for by a similar increase in the dilation term \((C_p - C_v)\)
and an increase in the electronic specific heat coefficient \(\gamma\).

The Debye temperature, however, shows no sign of following any
particular trend across the series. The increase in dilation term
reflects the increase in the volume thermal expansion coefficient
across the series while the increase in the electronic \(\gamma\) reflects
an increase in the density of states at the Fermi surface of the
system. The value of density of states derived from values of
shall be listed in Table 3.2 together with the values derived from
magnetic susceptibility measurements on these metals so that a
comparison can be made.

A small anomaly is present in the specific heat curve of Uranium
at 45\(^\circ\)K related to the \(\alpha - \alpha\) phase transition (Lee et al 1969).
A similar anomaly in Pu\(^{239}\) at 60\(^\circ\)K was also reported in the same
paper, however later measurements on Pu\(^{242}\) (Sandenaw 1972) have
failed to confirm this finding.

3.6 Magnetic susceptibility

The magnetic susceptibility of the Actinides again shows a
progression across the series. Results reported by Brodsky and
co-workers (Brodsky 1971) are shown in figure 3.5. Measurements
on Pa (not included in the figure) have also been carried out
(Bansal 1966) and the results fit in well with the progression
across the Actinide series, exhibiting the same general behaviour.
The magnetic susceptibilities of the Actinides, from Np onwards,
are high, and vary little with temperature, including that of
Pa and U, an indication of the non-magnetic nature of the actinide
metals. The upturn at low temperatures in the Am data is a consequence
of Np impurities in the sample (Brodsky 1971). There has long been
the contention of a small magnetic moment present in Pu, however numerous experiments (Mossbauer effect, Neutron diffraction, Nuclear magnetic resonance) have failed to confirm the presence of any moment on the Pu atom. Furthermore, differential susceptibility measurements by Arko and Brodsky (1970) on single crystal α-Pu have set an upper limit of a net moment to be 0.01 μB per Pu atom.

In simple theory, the magnetic susceptibility of a paramagnet is proportional to the density of states at the Fermi surface at zero temperature. Thus a large susceptibility indicates a high density of states; the values derived from susceptibility measurements and those derived from the electronic Y have been evaluated by Jullien et al. (1972) and shown in Table 3.2, where the former are clearly several order of magnitude higher than the latter, indicating the presence of some enhancement effect present in the magnetic susceptibility, originating from some interaction between the electrons.

<table>
<thead>
<tr>
<th>element</th>
<th>density of states (from specific heat)</th>
<th>density of states (from susceptibility)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>1 per ev atom</td>
<td></td>
</tr>
<tr>
<td>Pa</td>
<td>---</td>
<td>4.1</td>
</tr>
<tr>
<td>U</td>
<td>2</td>
<td>5.8</td>
</tr>
<tr>
<td>Np</td>
<td>3</td>
<td>8.6</td>
</tr>
<tr>
<td>Pu</td>
<td>3</td>
<td>8.1</td>
</tr>
<tr>
<td>Am</td>
<td>---</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Thus a theory that seeks to explain the physical properties of the Actinides must provide for this enhancement effect, which increases across the Actinide series and is probably the underlying
cause for the increasing electrical and thermal resistivities with atomic number. The Spin Fluctuation model, which predicts an exchange enhanced magnetic susceptibility, a $T^2$ dependence in the electrical resistivity at low temperatures and a reduced Lorenz number, appears to have considerable advantage over the previous theories (which are more or less centered on the anomalous electrical resistivity of Fu) in providing a unified picture for the Actinides, though at present, the Spin Fluctuation model is only applicable at low temperatures, and a lot of questions concerning the higher temperature region, particularly the electrical resistivity of Fu, remain unanswered. Both recent suggestions, outlined in chapter 5, and previous theories may provide some answers. In the following chapter, the previous theories will be reviewed and discussed in some detail.
FIG. 3.1 ELECTRICAL RESISTIVITY OF ACTINIDE METALS.
FIG. 3.2  ELECTRICAL RESISTIVITY OF FU UNDER PRESSURE
FIG. 3.3 THERMAL CONDUCTIVITY OF ACTINIDE METALS
FIGURE 3.4
FIG. 3.5 MAGNETIC SUSCEPTIBILITIES OF THE ACTINIDES.
Chapter 4

Physical properties of the Actinides: Theoretical situation

4.1 Introduction

Theoretical attempts at explaining the physical properties of the Actinides have been centered on the resistivity of Lu. Up to ~1970, the unusual temperature dependence of the Lu resistivity have been attributed to either interband scattering effects similar to those discussed by Mott and Jones (1936) for the transition metals, or to some magnetic transition occurring around 600 K, neither being wholly satisfactory and will be discussed in more details below. Numerous band structure calculations have also been performed in an attempt to gain insight into the electronic distribution in these metals, as well as to provide a basis for theoretical calculations. However, due to the complicated crystal structures of the low temperature phases in the early Actinides, existing calculations are limited to those on the high temperature phases. A general framework has now emerged from all these calculations though the band picture of these metals to date is by no means a complete one. We shall now discuss in some details the band structures of the Actinides.

4.2 Band Structure

The Actinides in the atomic state are typified by the gradual filling of the 5f electronic shell outside a radon core with 86 electrons, and have two to four valence electrons in the 6d and 7s states. The first two elements in the series, Actinium and Thorium, having respectively the configuration 6d\(^1\)7s\(^2\) and 6d\(^2\)7s\(^2\), resemble most closely to transition metals with a partially filled
6d shell. In the metallic state, there is a pronounced 6d character at the Fermi surface and a negligible 5f character (Kmetko and Hill 1970 and references therein). Thus these two Actinides are for all practical purposes "transition-like", and can be described by the same s-d model utilized for the transition metals (Hott and Jones 1936). The population of 5f states begins in Pa, the next element along the series, and due to the considerable radial extent of the 5f orbitals, in the metallic state, the itinerant nature of these electrons causes them to hybridize strongly with the 6d and 7s bands. Thus in Pa and the several elements following, the Fermi surface has a marked hybridized 5f character, the hybridized bandwidth having a value compatible with the 3d-band in the first transition series. The amount of overlap of 5f wave functions between neighbouring atomic sites is still appreciable as far into the series as Bk, however, in Am and the elements beyond, the 5f band has become sufficiently narrow to resemble the situation in the rare earths where the narrowness of the 4f band is responsible for the magnetic behaviour in many of these metals. This transition across the Actinide series from "transition-like" behaviour to "rare earth-like" behaviour is also reflected in the crystal structures of these metals, summarised in figure 4.1. Actinium and Thorium, having negligible 5f character in their energy bands, assume crystal structures favoured by the transition metals, while Am and the elements beyond assume close-packed structures favoured by the rare earths. However, in the intermediate elements, Pa, U, Np, and Pu, where the 5f as well as the 6d and 7s electrons participate in the bonding, the crystal structures are complex and neither "transition-like" nor "rare earth-like". The elements U, Np and Pu have several crystallographic phases, in particular, Pu has six, pointing to the complex situation in these metals.
Results of the calculations by Kmetko and Hill (1970) employing the augmented plane wave method carried out on the high temperature phases of the Actinides are shown in table 4.1. They indicate the general behaviour described above, with the width of the hybridized f band increasing with atomic number in the first instance, reaching a maximum value of ~3 ev in Uranium, then decreases steadily to a value of ~0.6 ev in Curium. The value of 3 ev in Uranium compares well to the width of the 3d band of ~3.5 ev in Nickel, while the value of ~0.6 ev in Am is the same as the width of the 4f band in Y-Ce, an early rare earth metal. The number of s-electrons per atom is small compared to both d and f-electrons from Pa through the series to Am, suggesting that conduction processes in these metals are carried out mainly by the 6d electrons.

<table>
<thead>
<tr>
<th>element</th>
<th>&quot;f&quot;-bandwidth</th>
<th>number of f-electrons per atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ac</td>
<td>2.7ev</td>
<td>0.2</td>
</tr>
<tr>
<td>Th</td>
<td>3.0ev</td>
<td>0.5</td>
</tr>
<tr>
<td>&quot;β-Pa&quot;</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>γ-U</td>
<td>1.3ev</td>
<td>5.3</td>
</tr>
<tr>
<td>γ-Np</td>
<td>1.3ev</td>
<td>6.6</td>
</tr>
<tr>
<td>γ-Pu</td>
<td>0.6ev</td>
<td>7.6</td>
</tr>
<tr>
<td>γ-Am</td>
<td>0.6ev</td>
<td>8.6</td>
</tr>
<tr>
<td>γ-Cm</td>
<td>0.6ev</td>
<td></td>
</tr>
</tbody>
</table>

(N.B. "β-Pa" is a hypothetical high temperature phase for Pa)

The results of the calculation also show that the number of 5f electrons per atom increases steadily across the series and that the density of states in γ-U as a function of energy shows a
double-peak in the vicinity of the Fermi energy $E_F$, as a result of the hybridized $f$-band. The general features of the density of states curve of $\delta$-$U$ are also present in all the metals from Pa to Fu in the Actinide series, i.e. a narrow double-peaked hybridized band of mainly $5f$ nature overlapping a broad band of $6d$-$7s$ character, and a high density of states at the Fermi surface.

The results of this and various other calculations (Koelling et al. 1970, Ridley 1958, Lehman 1959, 1960) are in qualitative agreement and confirm the intuitive deduction of Friedel (1956, 1958) summarised in the first paragraph of this section. More recently Julien et al. (1972), expanded on the ideas of Friedel, and by employing the Anderson formalism (Anderson 1961), accounted for the "delay" of magnetism in the Actinides until Curium and elements beyond by the inclusion of a phenomenological $f$-$d$ hybridization term in the Hamiltonian of the system. With a suitable choice of parameters, Julien et al. were able to reconcile their theoretical predictions with the band calculation results of Kmetko and Hill (1970) on the hybridized $f$-band with, as well as the value of the density of states at the Fermi surface deduced from specific heat measurements. Unfortunately, it is not clear what the transport and other physical properties would be in such a model, and its applicability is rather limited.

4.3 Interband Scattering model

The interband scattering mechanism was originally proposed by Mott (1936) and later refined by Wilson (1938) to account for the high electrical resistivity in the transition metals. Smoluchowski (1962) extended the application of this model to explain the observed resistivity behaviour in Plutonium. Mott suggested that considerable
additional resistivity can be caused by interband scatterings mediated by phonons or impurities (whereby, in the case of transition metals, an electron in the conduction band gets scattered into the narrow non-conducting d-band and hence giving rise to considerable resistivity) in a metal where there is a large difference in the effective mass or in the density of states at the Fermi level in two or more bands. This condition is best satisfied in systems which have one (or more) narrow band which has electrons of high effective mass, and a broad conduction band containing free electrons with normal electronic mass. For a simplified system consisting of two such bands, the temperature dependence of the Fermi level is given by

$$\mu = E_F - \left(\frac{\pi^2}{6}\right)(k_B T)^2 \frac{1}{D} \frac{dE}{dE} E_F$$

(4.1)

for $T \ll T_F$, where $E_F = k_B T_F$ is the Fermi energy at $T = 0^0K$; $D$ is the density of states function of the system. This temperature dependence then leads to the following variation of the resistivity with temperature at not too low temperatures,

$$\rho(\mu, T) = \rho(E_F, T) \left[1 - \frac{\pi^2}{6} (k_B T)^2 \left[ -\frac{d^2 D}{D dE^2} + 3 \left(\frac{1}{D} \frac{dD}{dE}\right)^2 \right] E_F \right]$$

(4.2)

where $\rho(E_F, T)$ is the resistivity the system would have if the narrow band were also broad and is a linear function of temperature. On differentiating (4.2) with respect to temperature, it can be shown that if the expression within the smaller square brackets has a value between $2(\pi k_B T)^{-2}$ and $6(\pi k_B T)^{-2}$, then the resistivity is positive while its temperature derivative is negative. Thus depending on the shape of the density of states curve at the Fermi level, the interband scattering mechanism could give rise to a resistivity
that decreases with increasing temperature. Smoluchowski suggested that this could be responsible for the negative slope in the in resistivity in the temperature region above the resistivity maximum. Citing that the measured value of the absolute thermoelectric power of Pu is positive (Lee and Hall 1959), and employing the approximation derived by Friedel (1956) relating the slope of the density of states curve to the absolute thermoelectric power $S$, 

$$\frac{1}{D} \frac{dD}{dE} = \frac{(3e^2)}{\pi^2} S/k_B^2 T$$

he concluded that $dD/dE$ is also positive in Pu. However, the value of $S$ is too small to account for the observed resistivity decrease above the maximum, thus the value of $(1/D)d^2D/dE^2$ in Pu had to be large and negative. This condition is readily satisfied in the kind of density of states curve proposed by Friedel (1956) for Uranium and by Lee and Hall (1959) for Pu. Thus employing a double-peaked density of states curve for the narrow f-band of the order of two to three tenths of an electron volt wide, Smoluchowski was able to reconcile the theoretical value with the experimentally observed value of $(1/\rho)d\rho/dT$ in $\alpha$-Pu as well as the value of the density of states at the Fermi surface deduced from specific heat measurements.

The main arguments against the validity of this model in Pu have been that similar resistivity behaviour is also present in other allotropic phases of Pu as well as dilute alloys of the $\delta$-phase, thus a very similar density of states curve would be required for all these different phases of Pu for this model to be valid; however in view of the highly different crystal structures assumed by these phases, this requirement was considered to be unlikely to be met (Arko et al 1972). However, band structure calculations by Kmetko and Hill (1970) have indicated that a similar density of states
curve holds for all the Actinides from Pa through to Pu with the characteristic double-peaked narrow band overlapping a broad one, while the relative positions of the two bands as well as the Fermi level vary slightly from element to element. It seems reasonable then to expect that this is also the case in the different phases of Pu. Due to the different positions occupied by the Fermi level (caused by the difference in the number of 5f electrons per ev per atom in the phases), the value of the expression in the smaller square brackets of equation (4.2) varies in the different phases of Pu, giving rise to differing values of \( \frac{d\rho}{dT} \). Employing the same characteristic band structure, Smoluchowski was also able to reconcile the theory with the observed values of \( \frac{1}{\rho} \frac{d\rho}{dT} \) in stabilised dilute 6-Pu alloys. Thus this model, despite its simple nature, provides a satisfactory explanation for the negative resistivity slope in Pu.

The low temperature behaviour, however, was less satisfactorily explained, and the expected temperature dependence could not be observed experimentally. Wilson (1938) has pointed out that the interband scattering is limited by the selection rule

\[
 k - k' + q = 0
\]  

(4.4)

where \( k \) is the wave vector of the electron in the initial state and \( k' \) that in the final state, \( q \) being the wave vector of the phonon that mediates the transition of the electron from its initial state to its final state. However, for an electron to undergo an interband transition from a broad band (band 1 say) to a narrow band (band 2), in its initial state it must have \( |k| = k_1 \), and in its final state \( |k'| = k_2 \), where \( k_1 \) and \( k_2 \) are the respective Fermi wave vectors for the two bands. Since in general \( k_1 \neq k_2 \),
(4.4) then imposes a considerable restriction on the number of possible transitions. A minimum value of $|q| \sim |k_1 - k_2|$ is thus required to effect an interband transition. At high temperatures, all the lattice vibrations are thermally excited and therefore interband transitions are frequent. However, at low temperatures, only long wavelength phonons (i.e. small $q$) are thermally excited, and most of the interband transitions are forbidden, thus one expects a rather rapid drop in the resistivity in the temperature region around $\Theta'$ where $k_B \Theta' = \pm \omega(q_{\text{min}})$, $q_{\text{min}} \sim |k_1 - k_2|$, and $\omega$ is the phonon frequency, a function of $q$. At low temperatures such that $T \ll \Theta'$ and for $\Theta' \ll \Theta_D$ the Debye temperature, Wilson has shown that the probability of interband transitions approaches zero as $\exp(-\Theta'/T)$. Smoluchowski estimated a value of $\Theta' = 55^0K$ for $\alpha$-Pu and commented that in $\alpha$-Pu, if it were not for the phonon-cut-off at low temperatures, the residual resistivity would be comparable to the value at the maximum of the resistivity-temperature curve. However, this exponential dependence was deliberately sought for but failed to be found (Wigley 1963). Thus either this model is not appropriate for $\alpha$-Pu, or, additional mechanisms become operative at low temperatures giving rise to a resistivity whose stronger temperature dependence and larger magnitude have the effect of masking the relatively slow temperature variation of the exponential term due to interband scatterings. The Spin Fluctuation model, while not conflicting with the assumptions in the interband scattering model at high temperatures, gives rise to a $T^2$ term in the resistivity at low temperatures. The interband model, together with the Spin Fluctuation model could provide a satisfactory explanation for the resistivity behavior in Pu.
4.4 Magnetic Ordering

The similarity of the plutonium resistivity-temperature curve to that of α-Manganese which is known to be antiferromagnetic has led Lee, Meaden and Mendelssohn (1960) to suggest that Pu may be antiferromagnetic at low temperatures; the low temperature decline in the resistivity curve being indicative of the onset of long range orderings of magnetic moments, while the negative slope above the resistivity maximum is due to the presence of short range magnetic order. Later measurements on the magnetoresistivity by Brodsky (1967) (the values of $\delta \rho/\rho_0$ being negative at low temperatures and low fields), and the specific heat peak at 600 K reported by Lee et al. (1969) provide further support to this hypothesis. Rocher and Friedel (1961) pursued this idea further and interpreted this magnetic order-disorder transition in the de Gennes-Friedel formalism employed for the description of magnetic behaviour in the rare earth metals (de Gennes and Friedel, 1953) assuming that the 5f electrons in Pu can be treated in the same way as the localized 4f electrons in the rare earths. Within this framework, the resistivity due to the scatterings of conduction electrons by disordered localised spins, in the vicinity of the transition, is given by

$$\rho_m = (1 - \Phi^2) \left[ 1 + (1 - \Phi^2)f(k_FD)T_C/T \right] \rho_{mo}$$  \hspace{1cm} (4.5)

where $\rho_{mo}$ is the resistivity in the presence of complete spin disorder, $\Phi$ is the long range order parameter, equal to zero above the transition temperature $T_C$, while below $T_C$, it is a function of temperature; $k_F$ is the Fermi wave vector and $D$ is the distance between neighbouring magnetic ions; $f(k_FD)$ is the oscillating function given by

$$f(k_FD) = \frac{3}{2(k_FD)^2} \left[ \cos(2k_FD) - \frac{\sin(2k_FD)}{k_FD} + \frac{1 - \cos(2k_FD)}{2(k_FD)^2} \right]$$
At $T = T_c$, the resistivity in this model is given by

$$\rho_m(T) = (1 + f(k_F D))\rho_{mo}$$

(4.6)

while in the temperature region immediately above the transition, this model predicts a resistivity that decreases with increasing temperature as the reciprocal of the temperature,

$$\rho_m(T > T_c) = (1 + f(k_F D) T_c/T)\rho_{mo}$$

(4.7)

This temperature dependence of $\rho_m$ above $T_c$ is due to the presence of short range order of the magnetic moments.

Rocher and Friedel (1961) also calculated the expected change of slope in the thermoelectric power $S$ at the transition temperature, this is given by

$$\Delta \left( \frac{dS}{dT} \right) = -\frac{\pi^2 k_B^2}{16 e |e|} \left[ \frac{\rho_{mo}}{\rho_A + \rho_{mo}} (1 + 2f(k_F D)) \right]$$

(4.8)

where $\rho_A$ is the resistivity due to scattering by impurities, $\rho_{mo}$ and $\rho_A$ both assumed to be very much larger than the resistivity due to scatterings by phonons; $e$ is the electronic charge. A change of slope in the thermoelectric power of Pu at 65°K has been reported by Lallement (1962, 1965). However, the validity of equation (4.8) in the case of Pu is questionable, as the formula relating the thermoelectric power to the resistivity due to Kott and Jones (1936)

$$S = \frac{\pi^2 k_B^2}{3 |e|} \frac{\delta \log \rho}{\delta E_F}$$

employed in the calculation, is strictly valid only for temperatures
above the Debye temperature, which for Pu is about $160^\circ K$, while the 'transition' temperature is $\sim 60^\circ K$.

The absence of confirming evidence of a magnetic transition from both magnetic susceptibility measurements and neutron diffraction experiments was attributed to the smallness of the moment that lies beyond the limit of detection. To reconcile the assumption of the existence of small moments with the high value of $\rho_{mo}$ in Pu, Rocher (1962) proposed that the 5f electrons in Pu occupy two virtual bound levels (Friedel 1962) of a fraction of an electron volt wide, each capable of holding seven electrons of one spin direction. These virtual bound levels are split in energy by the exchange interaction between the up and down spin electrons, the splitting being very much less than the width of the levels, and the difference in the numbers of the up and down spin f-electrons occupying these two virtual bound levels gives rise to a small localised moment at each atomic site. The resistivity due to spin disorder scattering in Rocher's model is then given by

$$\rho_{mo} = \frac{14\pi}{2k_F} (\sin^2 \delta_\uparrow + \sin^2 \delta_\downarrow)$$  \hspace{1cm} (4.9)

where $\delta_\uparrow$ and $\delta_\downarrow$ are phase shifts at the Fermi level resulting from the coupling of the conduction electrons to the 5f electrons and are related to the number of up and down spin 5f electrons by

$$\delta_\uparrow, \downarrow = n_\uparrow, \downarrow \pi/2$$

where $n_\uparrow$ and $n_\downarrow$ are respectively the number of 5f electrons in the up and down spin virtual bound level, $Z$ is the number of conduction electrons. Thus this model predicts a large resistivity due to disordered spins scattering for a small magnetic moment, (4.9)
also predicts a large $\rho_m$ in the limit of vanishing magnetic moment, i.e. $n^+ - n^\Lambda = 0$, which appears unlikely to be true in practice.

4.5 Concluding Remarks

Despite the attractiveness of the magnetic ordering model, its application to $\text{Pu}$ has suffered various setbacks. Besides the fact that the temperature dependence of $\rho_m$ above the assumed "transition" temperature predicted by equation (4.7) was not observed experimentally as pointed by Lallement (1963), it is difficult to understand in this model why the negative slope in the resistivity curve persists over such a long temperature range, goes through two phase transitions and is still present in the $\gamma$-phase at high temperatures. Perhaps the soundest reason for rejecting the hypothesis of magnetic ordering in $\text{Pu}$ is the negative results presented by neutron diffraction and various other experiments carried out to detect the presence of magnetic moment on $\text{Pu}$ atoms as mentioned in the Introduction of this thesis. However, the high density of states at the Fermi surface of the Actinide metals as revealed by both the specific heat and magnetic susceptibility measurements, as well as the negative magnetoresistivity reported by Brodsky (1967) for $\text{Pu}$, seem to favor the presence of some magnetic effect in these metals.

The interband scattering model, which account well for the negative slope in the $\rho$-$T$ curve of $\text{Pu}$, and the progressively higher resistivity across the Actinide series, and which probably contributes to both effects, fails to account for the low temperature resistivity behaviour. Also if the variation of the Fermi level with temperature were entirely responsible for the negative slope in the high temperature $\rho$-$T$ curve in $\text{Pu}$, then we would expect a similar temperature dependence in the magnetic susceptibility to be present, this, however is not observed. The Spin Fluctuation model, the application
of which to the Actinides will be discussed in the following chapter. While not in conflict with the assumptions of the interband model, thus appears to provide a plausible alternative to the description of the low temperature properties of these metals.
U: $\alpha = \text{orthorhombic}$ $\beta = \text{tetragonal}$

Np: $\alpha = \quad \beta = \quad$

Pu: $\alpha = \text{monoclinic}$ $\beta = \text{B.C. monoclinic}$

$\gamma = \text{orthorhombic}$

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**FIG. 4.1 PHASE TRANSITIONS AND CRYSTAL STRUCTURES OF THE HEAVY ELEMENTS.**
Chapter 5

The Spin Fluctuation model: Application to the Actinides

5.1 Magnetoresistivity: application to Plutonium

The negative magnetoresistivity in Pu had been taken as the strongest evidence for magnetic ordering at low temperatures in this metal. However, as we have seen in Chapter 2, the existence of Spin Fluctuations in the system also leads to a negative magnetoresistivity at low fields; the magnitude of which (at a fixed field value) decreases with increasing temperature, in qualitative agreement with the experimental results obtained by Brodsky (1967), summarised in Chapter 3. To a first approximation, physically, the effect of an externally applied magnetic field $H$ of magnitude such that $|Δ| ≪ k_B T$, where $Δ$ is as defined in equation (2.50), can be viewed as partially suppressing the spin-flip scattering processes that occur via paramagnons (which contribute significantly to the electrical resistivity of the system at zero magnetic field), and thus resulting in a reduction in the resistivity of the system. If we consider a scattering process in which a down spin conduction electron with initial energy $E_-$, on being scattered by a paramagnon, flips its spin and emerges with final energy $E_+^'$ in the spin up state; in the presence of a magnetic field, a minimum energy difference (between $E_-$ and $E_+^'$) of $|Δ|$ is required for this transition from $E_-$ to $E_+^'$ of the conduction electron to occur via a paramagnon, $|Δ|$ corresponds to the energy of a zero wave vector ($q = 0$) paramagnon of spin one in the presence of a magnetic field. However, since only electrons initially within $\pm k_B T/2$ of the Fermi surface are able to take part in the transport processes, the final states of the conduction electrons...
will then have energies less than the Fermi energy by at least $|\Delta| - k_B T/2$ and at most by $|\Delta| + k_B T/2$. The latter is not allowed by the Exclusion Principle for any value of $\Delta$. But since the magnetic field is applied in the positive direction, more transitions will be of the type $E_\rightarrow E'_+$ rather than the reverse which is allowed by the Exclusion Principle. Hence the scatterings via Spin Fluctuations are effectively quenched, leading to a decrease in the resistivity. If the spin-flip scatterings via the Spin Fluctuations were the dominant mechanism contributing to the resistivity in zero magnetic field, then any reduction in the resistivity resulting from low values of applied magnetic field could be to a good approximation attributed entirely to the partial quenching out of the spin-flip scatterings via paramagnons. It is possible, however, for spin wave type collective excitations to exist within the energy gap $\Delta$. But for small values of applied magnetic field, and hence small $\Delta$, these excitations only constitute a small portion of the phase space and we can ignore their contribution to the resistivity compared to the resistivity decrease due to the "quenching out" of the spin-flip scatterings.

From equations (2.50) and (2.79), we have $\Delta$ and the magneto-resistivity $\delta \rho/\rho_0$ in the Spin Fluctuation model given by

$$\Delta = -\mu_B h \left( U_0 \chi(T)/\mu_B^2 \right) + g$$

(5.1)

$$\delta \rho/\rho_0 = -\left( 32/\pi^4 \right) (\Delta/k_B T)^2$$

(5.2)

where $\mu_B$ is the Bohr magneton, $\chi(T)$ the static magnetic susceptibility (function of temperature $T$), $g$ the Landé $g$-factor for the f-electrons. In our calculation, we have, for convenience,
assumed a simple system consisting of a broad conducting s band and a narrow, non-conducting f band. This of course is not the exact situation in the Actinides, as band calculations have shown, the conduction band is mainly s-d in nature, with possibly some f character due to the hybridization of the f band with the s and the d bands. However, we believe that our simplifications have not altered the results too significantly, as our expression for $\delta \rho / \rho_o$, as shown in equation (5.2), is dependent on $\Delta$, which is a function of the susceptibility $\chi$, and the intraatomic interaction strength $U_o$ only, both being intrinsic properties of the 5f band (in the Spin Fluctuation model, it is assumed that the contribution to $\chi$ from the narrow 5f band dominates over all other contributions, due to the high density of states and the exchange enhancement effect in the 5f band) and the parameters of the conduction band are not involved. At low temperatures such that $T \ll T_{SF}$, where $T_{SF}$ is the characteristic Spin Fluctuation temperature, $\chi(T)$ is given by equation (2.88)

$$\chi(T) = \frac{2\mu_B^2 D(\xi_f)}{1 - U_o D(\xi_f)} \left[ 1 - \frac{2}{\Pi} \left( \frac{T}{T_{SE}} \right)^2 \ldots \ldots \right] \quad (5.3)$$

where $D(\xi_f)$ is the density of states of the f-electrons at the Fermi surface. Substituting (5.3) into equation (5.1), we have

$$\Delta = -\mu_B^2 \left[ \frac{2U_o D(\xi_f)}{1 - U_o D(\xi_f)} \left( 1 - \frac{2}{\Pi} \left( \frac{T}{T_{SE}} \right)^2 \right) + g \right] \quad (5.4)$$

Employing the value of the enhancement factor $(1 - U_o D(\xi_f))^{-1}$ of $\sim 2$ estimated by Arko et al (1972) for Pu, and further assuming that the g-factor of the f-electrons can be taken to be the same as that of the free electrons i.e. 2, we have for Pu,
In figure (5.1), we have plotted the prediction of equation (5.6) for small values of temperatures and for field strengths up to 5 kilogauss. The experimental data available are too sparse to permit a detailed comparison with the theory and hence have not been included in the graphs. However, a few values of $\delta \rho/\rho_o$ can be drawn from the results of Brodsky (1967) for $\alpha$-Pu; at 50 K, the values at 0.5 kilogauss, 1 kilogauss and 1.5 kilogauss are respectively $-0.3 \times 10^{-3}$, $-0.5 \times 10^{-3}$ and $-0.65 \times 10^{-3}$; these values compare with the corresponding theoretical values of $-0.3 \times 10^{-3}$, $-0.94 \times 10^{-3}$ and $-2.0 \times 10^{-3}$. It can be seen that while the values at 0.5 kilogauss and 1 kilogauss show reasonable agreement, the theoretical value at 1.5 kilogauss is far larger than the value observed experimentally. In general, at higher fields, our theory predicts a variation of $\delta \rho/\rho_o$ with $H$ that is far too rapid. This is perhaps not surprising in view of the crude nature of our approximations and the fact that our calculation is only valid for $|H| \ll k_B T$. Also in applying our theoretical results to Pu we have assumed that the experimentally observed magnetoresistivity is due entirely to the presence of the Spin Fluctuations in the system. This can be expected to be a valid assumption at low fields for reasons discussed earlier on. However, as the field increases, the situation becomes complex and extends beyond the validity of our calculation. As mentioned previously, there is the possibility of spin wave type excitations being present. These excitations
become increasingly important as the field increases, and would act as extra scattering mechanism for the conduction electrons and tend to increase the resistivity. This increase would then partly or totally cancel the decrease due to the quenching out of spin flip scatterings via paramagnons, and thus resulting in a $\delta \rho/\rho_0$ decreasing with $H$ slower than $H^2$ predicted by our low field calculation. There is of course the normal positive contribution to the magnetoresistivity due to the $\nu A H$ term in the Boltzmann equation ($\nu$ being the velocity of the conduction electron), i.e. the deflection of the conduction electron from its straight path by the Lorenz force. This gives a positive $\delta \rho/\rho_0$ that is in general proportional to $H^2$ and obeys Kohlar's rule (see for example Ziman 1960), and has been shown by Brodsky (1967) to be the dominant term above 3 kilogauss in his Pu measurements.

To sum up, then, we have shown that the presence of Spin Fluctuations in Pu could account reasonably well for the initial decrease of resistivity with increase in magnetic field when external magnetic fields are applied to the system. The magnetic nature of these spin one excitations, in the presence of a magnetic field, imposes a minimum energy of $|A|$ on the difference between the initial and final energies of the conduction electrons for the transition to occur via them. Some of these transitions are forbidden by the Exclusion Principle and thus partial "quenching out" of the spin flip scatterings is resulted, leading to a decrease in the resistivity, or equivalently a negative magnetoresistivity. The Spin Fluctuation model thus offers a plausible alternative to the magnetic ordering model in providing an explanation for the magnetoresistivity results in Plutonium.
5.2 Other physical properties of the Actinides in the Spin Fluctuation model

The investigation into the effect of Spin Fluctuations on the physical properties of metals in general is by no means complete. However, the results of theoretical work available so far seem to lend support to this model in providing, at least qualitatively, a reasonable basis for the interpretation of the low temperature physical properties of the Actinides. A unified picture seems to emerge if we consider the exchange enhancement factor, a function both of the intraatomic exchange interaction $U_o$ within the narrow 5f band and the density of states at the Fermi surface, given by $(1 - U_o D(\varepsilon_f))^{-1}$ increases across the Actinide series, and that by the time we arrive at Neptunium and Plutonium, the interaction strength $U_o$ has become sufficiently strong and/or the density of states at the Fermi surface has become sufficiently large for these metals to be considered as nearly magnetic, and the Spin Fluctuations play an important role in their electronic properties at low temperatures. The progressive increase of the magnetic susceptibility $\chi$ across the Actinide series can be explained satisfactorily in the Spin Fluctuation model which predicts, from equation (2.88)

$$\chi(T) = \frac{2\mu_B^2 D(\varepsilon_f)}{1 - U_o D(\varepsilon_f)} \left[ 1 - \frac{4}{\pi^2} \left( \frac{T}{T_{SF}} \right)^2 \ldots \ldots \right]$$

This equation is valid only for low temperatures such that $T \ll T_{SF}$, thus the second term is, in practice, negligible. We then have in this model, at low temperatures, a magnetic susceptibility that is essentially temperature independent and proportional to both the density of states and the enhancement factor. The nearly constant magnetic susceptibilities of the Actinides at low temperatures...
are indeed observed experimentally, and the increase of $\chi$ with atomic number would in this model be due to the increase in both $D(E_f)$ and the enhancement factor $(1 - U_0 D(E_f))^{-1}$ with atomic number across the series. The results on electronic specific heat constant $\gamma$ of the Actinides also find an explanation in the Spin Fluctuation model on similar grounds. From equation (2.86) of chapter 2, in the Spin Fluctuation model, $\gamma$ is given by

$$\gamma = \frac{2}{3} (\pi k_B)^2 D(E_f) \frac{m^*}{m}$$

with

$$m^*/m = 1 + \frac{9}{2} U_0 D(E_f) \log \left[ 1 + \frac{1}{12} (q_{\chi}/k_f)^2 U_0 D(E_f) / (1 - U_0 D(E_f)) \right]$$

where the symbols are as defined in chapter 2. The experimentally observed increase in $\gamma$ across the series could then be attributed to the increase in $D(E_f)$, the density of states, as well as the increase in $m^*/m$, the electronic mass enhancement which is a function of the exchange enhancement factor $(1 - U_0 D(E_f))^{-1}$.

We would like to mention in passing that Julien et al (1973) have suggested that by including the mass enhancement effect which had been ignored by Arko et al (1972) in evaluating the value of the exchange enhancement factor of Pu (by comparing the values of the density of states obtained from magnetic susceptibility measurements, $D(E_f)_\chi$, with that from specific heat measurements $D(E_f)_\gamma$), the exchange enhancement factor of Pu would be of the order of 10 rather than the value of 2.1 obtained by Arko et al. However, we found that the mass enhancement in Pu is relatively small, although not negligible, and the exchange enhancement factor is close to 2 rather than 10 as suggested by Julien et al.
We shall briefly present our arguments below:

Including the mass enhancement factor $m^*/m$, we have for Pu

$$\frac{D(\xi_f)}{D(\xi_f)_0} = \frac{(1 - U_0 D(\xi_f))^{-1}}{m^*/m} = 2.1$$

then employing the Spin Fluctuation value of $m^*/m$ given by equation (2.86) we have

$$(1 - U_0 D(\xi_f))^{-1} = 2.1 \left(1 + \frac{q_c}{2} U_0 D(\xi_f) \log \left[1 + \frac{1}{12} \frac{(q_c/k_f)^2 U_0 D(\xi_f)}{1 - U_0 D(\xi_f)}\right]\right)$$

This equation has a solution at $U_0 D(\xi_f) \approx 0.53$, for $q_c \approx k_f$, giving a mass enhancement factor a value of $\approx 1.13$, and an exchange enhancement factor a value close to 2.

The Spin Fluctuation model also predicts a term proportional to $(T/T_{SF})^3 \log(T/T_{SF})$ in the low temperature specific heat (equation (2.86)), this would show up as an up turn in the low temperature region as $T \to 0$ in a plot of $C_V T$ against $T^2$ where $C_V$ is the measured specific heat. It would be interesting to see if this up turn exist in Np and Pu when low temperature data become available in the future (present specific heat data of Np are limited to those above $8^\circ K$ (Lee et al 1970) and Pu to those above $10^\circ K$ (Lee et al 1970). The low temperature resistivity of both Np and Pu obey a $T^n$ law where $n \approx 2$, again in agreement with the prediction of the model, which predicts a dominant $T^2$ term in the low temperature electrical resistivity arising from the spin flip scatterings of the conduction electrons via paramagnons. The comparison between theoretical prediction and experimental results is, however, less obvious in the thermal resistivity. It is made difficult by the important role played by phonons in thermal conduction in the Actinides, especially in Pu, where the majority of the heat is carried by
phonons (Hall, Mortimer and Lee 1973), contrary to the case of an ordinary metal where heat conduction is almost entirely due to electrons. Therefore, it has not been possible to single out satisfactorily the electronic component in the thermal resistivity for meaningful comparison with the theory to be made.

5.3 Recent models for the higher temperature resistivity of \( Np \) and \( Pu \)

The Spin Fluctuation model appears to provide a reasonable explanation for the physical properties of the Actinides at low temperatures. However, there is one obvious question that one can ask: what happens to the Spin Fluctuation system when the temperature is raised? Kaiser and Doniach (1970) and Mills (1973) extended the resistivity calculation to higher temperatures by employing the zero temperature form of spectral density of the Spin Fluctuations. The results show that the electrical resistivity changes gradually from a \( T^2 \) dependence at low temperatures to a \( T \) dependence at a temperature of the order of \( J_TSF \), and then the resistivity continues to increase linearly with \( T \) indefinitely.

The transfer of the resistivity from a \( T^2 \) to a \( T \) dependence calculated this way may be a good first approximation to the effect of temperature increase on the Spin Fluctuation system; however, at higher temperatures, the zero temperature form of the spectral density is no longer a good approximation. As shown by Julien et al (1973), the peak in the spectral density of the Spin Fluctuations that exists at low temperatures broadens out as the temperature is increased, due to the temperature variation of the function \( R(q, \omega) \), the real part of the dynamic susceptibility for a non-interacting electron gas. At temperatures such that \( T \sim T_f \), the degeneracy temperature of the narrow f-band, the spectral
density of the Spin Fluctuations, which is proportional to $\text{Im}\chi(q,\omega)$ the imaginary part of the susceptibility function, has become small and flat. Thus the peak characteristic of the paramagnons at low temperatures gets levelled out by temperature increases, and one can no longer speak of enhanced Spin Fluctuations at high temperatures. Julien et al (1973) computed the temperature dependence of both $\text{Im}\chi(q,\omega)$ and $R(q,\omega)$ over the entire temperature range and used the results to account for the resistivity behaviour in Np and Pu. However, in order to fit the experimental data, degeneracy temperatures of the same order of magnitude for both the conduction band and the narrow f-band had to be employed, and this, as pointed out by Doniach (1973), seems unlikely to be the case in practice. Moreover, the results of Julien et al (1973) predict a strongly temperature dependent static susceptibility that obeys a Curie-Weiss law at temperatures $>100^\circ K$, such temperature dependence has not been observed experimentally for Np and Pu.

The different effects of self-irradiation damage on the two temperature regions of the resistivity curve, namely, the region below the resistivity maximum and the region above it, appears to point to separate mechanisms being operative in these regions. This led Doniach (1971) and Arko et al (1972) to suggest that the 5f electrons, which are well hybridized and hence have well defined bands at low temperatures, are no longer completely hybridized at high temperatures, but become partially localised leading to a situation similar to disordered alloy systems. Between the two temperature regions, the behaviour of the resistivity-temperature curve would then depend considerably on the purity and state of damage of the specimen and would be unpredictable. At low temperatures,
the scattering of conduction electrons off the Spin Fluctuations of the narrow 5f band gives rise to the $T^2$ term in the resistivity. At high temperatures such that $T > T_{SF}$, it was suggested that because of the high concentration of the Actinide atoms, the scatterings of the conduction electrons have the effect of broadening the energy level with of the hybridized f-electrons, making the f-band Bloch functions lose their coherence and thus tending to de-hybridize them. Doniach then showed that when the energy level width of the f-electrons have been broadened to be of the order of the width of the narrow f-band, the scattering and hence the resistivity becomes self-limiting. The reduction of the exchange enhancement factor with increasing temperature could then lead to a reduction in magnetic scattering and hence a negative slope in the resistivity-temperature curve at higher temperatures. However, under these circumstances, one would expect a corresponding decrease in the magnetic susceptibility should the exchange enhancement factor decrease with increasing temperatures. The magnetic susceptibilities of the Actinides are, however, almost temperature independent. Doniach's theory, therefore, while qualitatively accounting for the resistivity behaviour of Np and Pu at high temperatures, again fails to predict the observed temperature dependence of the magnetic susceptibilities of these metals.

5.4 Concluding remarks

Thus the low temperature properties of the Actinides can be explained reasonably satisfactorily within the Spin Fluctuation or equivalently paramagnon model. However, the almost temperature independent magnetic susceptibility and the strongly temperature
dependent electrical resistivity of in particular Np and Pu, which are believed to be nearly magnetic, have presented considerable difficulties in attaining a consistent theory at higher temperatures.

Existing theories for the high temperature negative slope of the resistivity-temperature curve of Pu, namely the interband model discussed in chapter 4, and the models due to Julien et al (1973) and Doniach (1971) mentioned above, while accounting well for the high temperature resistivity behaviour, all suffer the draw-back of predicting a temperature dependent magnetic susceptibility which is not observed in the Actinides. Thus, one is led to conclude that were the existing high temperature theories applicable, there must be some extra mechanism being operative in Np and Pu, giving rise to a magnetic susceptibility that increases with temperature in such a way as to balance the decrease due to either the temperature variation of the Fermi level (in Smoluchowski's theory, chapter 4 or the decrease in magnetic scattering with temperature increase (Doniach's theory, this chapter), or both, resulting in a magnetic susceptibility that is almost independent of temperature. Thus to explain both the observed electrical resistivity and magnetic susceptibility of the Actinides, Np and Pu in particular, existing high temperature theories had to be supplemented by bringing in an extra mechanism that causes a temperature dependence in the magnetic susceptibility that is equal and opposite to that due to the mechanism responsible for the high temperature behaviour in the electrical resistivity while having little or no effect on it. Unfortunately, such a mechanism seems difficult to be conceived. An alternative conclusion that one can draw is that at low temperatures the physical properties of the Actinides, particularly Np and Pu, are dominated by Spin Fluctuations in these
systems. As the temperature increases, the Spin Fluctuations lose their significance and some extra mechanism becomes operative at higher temperatures. This extra mechanism would be non-magnetic in nature, thus leaving the magnetic susceptibility little changed while strongly affecting the electrical resistivity and causing it to increase much less rapidly in the case of Np, and in Pu, to decrease with increasing temperature. Owing to the complicated crystal structure of these earlier Actinides, this mechanism could possibly originate from some lattice effects. However, the Actinides are complicated systems and detailed investigations are necessary before firm conclusion can be drawn.
FIG. 5.1 SPIN FLUCTUATION MAGNETORESISTIVITY OF Pu
APPENDIX: Calculation of $R(\mathbf{q}, \omega')$ and $I(\mathbf{q}, \omega')$

A.1 $R(\mathbf{q}, \omega')$

Taking $\mathbf{q}$ to be along the $z$-axis, we can extend the denominator and the numerator of $R(\mathbf{q}, \omega')$ for $q/k_\perp << 1$ and $\omega', \Delta \ll v_f q$. From (2.51) and (2.53), we have

$$R(q, \omega') = \frac{1}{N} \sum_k \frac{f_{k\uparrow} - f_{k+q\downarrow}}{\epsilon(k+q) - \epsilon(k) - (\omega' - \Delta)}$$

$$= \frac{1}{N} \sum_k \frac{f(\epsilon'(k)) - f(\epsilon'(k+q) + \Delta)}{k_z q/m + q^2/2m - (\omega' - \Delta)}$$

$$= \frac{1}{N} \sum_k \frac{f(\epsilon'(k)) - f(\epsilon'(k+q)) - \Delta f' \epsilon'(k+q) - \Delta^2 f''}{k_z q/m + q^2/2m - (\omega' - \Delta)}$$

(1)

where $f'(\epsilon') = \frac{d f(\epsilon')}{d \epsilon'}$ from (2.53).

As the expansion of the numerator is fairly tedious, we shall consider it separately. Expanding for small $q$, we have

$$\text{numerator} = -\left[ q \frac{\partial f}{\partial k_z} + \frac{q^2}{2!} \frac{\partial^2 f}{\partial k_z^2} + \frac{q^3}{3!} \frac{\partial^3 f}{\partial k_z^3} + \frac{q^4}{4!} \frac{\partial^4 f}{\partial k_z^4} + \frac{q^5}{5!} \frac{\partial^5 f}{\partial k_z^5} + \cdots \right] + \Delta f' \epsilon'(k+q) + \frac{\Delta^2 f''}{2!}$$

$$+ \frac{\Delta^2}{2!} \left( f'' + q \frac{\partial f''}{\partial k_z} + \frac{q^2}{2!} \frac{\partial^2 f''}{\partial k_z^2} + \cdots \right)$$

$$+ \frac{\Delta^3}{3!} \left( f''' + q \frac{\partial f'''}{\partial k_z} + \frac{q^2}{2!} \frac{\partial^2 f'''}{\partial k_z^2} + \cdots \right)$$

$$+ \frac{\Delta^4}{4!} \left( f'''' + q \frac{\partial f''''}{\partial k_z} + \cdots \right)$$

(2)
Employing the following identities

\[
\frac{\partial}{\partial k_z} = \frac{\partial}{\partial k_z} = (k_z / m) \frac{\partial}{\partial k_z} = (k_z / m) \frac{\partial}{\partial k_z} , \text{ where } k_z = k_x
\]

\[
\frac{\partial^2}{\partial k_z^2} = (1 / m) \frac{\partial}{\partial k_z} + (k_z^2 / m^2) \frac{\partial^2}{\partial k_z^2}
\]

\[
\frac{\partial^3}{\partial k_z^3} = (3k_z / m^2) \frac{\partial^2}{\partial k_z^2} + (k_z^3 / m^3) \frac{\partial^3}{\partial k_z^3}
\]

\[
\frac{\partial^4}{\partial k_z^4} = (3k_z^2 / m^3) \frac{\partial^3}{\partial k_z^3} + (k_z^4 / m^4) \frac{\partial^4}{\partial k_z^4}
\]

\[
\frac{\partial^5}{\partial k_z^5} = (15k_z / m^3) \frac{\partial^4}{\partial k_z^4} + (10k_z^2 / m^4) \frac{\partial^5}{\partial k_z^5} + (k_z^5 / m^5) \frac{\partial^6}{\partial k_z^6}
\]

and rearranging the terms, we have

\[
\text{numerator} = -q \left[ (kx / m + q / 2m + \Delta / q - \omega / q + \omega / q) f' + (q/2)(kx / m + q / 2m + \Delta / q - \omega / q + \omega / q)^2 f'' + (q^2/6)(kx / m + q / 2m + \Delta / q - \omega / q + \omega / q)^3 f''' + \ldots \right] \quad (3)
\]

Writing the sum over k as an integral, we have

\[
R(q, \omega') = \frac{-1}{N} \frac{V}{4\pi} \int_0^\infty k^2 dk \int_{-1}^{+1} dx \left[ f' + \frac{(\omega / q)f'}{kx / m + q / 2m + (\Delta - \omega) / q} + \frac{(\omega / q)^2}{kx / m + q / 2m + (\Delta - \omega) / q} \right.
\]

\[
\left. + \frac{(\omega / q)^3}{kx / m + q / 2m + (\Delta - \omega) / q} \right] + \quad (4)
\]
Terms containing $q^1 \left( \frac{\omega}{q} \right)^m \left( \frac{\Delta}{q} \right)^n$ with $l+m+n \geq 4$ are being omitted because the contribution of these terms to $R(q, \omega)$ has the factors

$$0 \left[ \frac{q}{k_f} \right]^4 + O \left[ \frac{q}{v_f q} \right]^2 \omega^2 + O \left[ \frac{\Delta}{v_f q} \right]^4 + O \left[ \frac{q}{k_f} \right]^2 \frac{\Delta}{v_f q}^2 + \ldots$$

which are negligible in the limits being considered.

Integrating over $x$ and rearranging, we have

$$R(q, \omega') = -\frac{1}{N} \frac{V}{4\pi^2} \int_0^\infty k^2 dk \left[ 2f' + \frac{q f''}{2m} + \frac{\Delta}{q} + \omega' \right]$$

$$\left. \left( \frac{\omega'}{q} \right)^2 f'' + \frac{a}{2} \frac{\omega'}{q} f'' \right] \left[ \frac{k}{m} \frac{q}{2m} + \frac{\Delta}{q} \frac{\omega'}{q} \right]$$

$$\left. \left( \frac{\omega'}{2} \frac{q}{q} f'' + \frac{a}{b} \frac{\omega'}{q} f'' \right) \left[ \frac{m}{2m} + \frac{\omega'}{q} \frac{\Delta}{q} \right] \right]$$

Expanding the log term for small $q$ and $(\Delta - \omega')$, we have

$$R(q, \omega') = -\frac{1}{N} \frac{V}{4\pi^2} \int_0^\infty k^2 dk \left[ 2f' + \left( f'' \left( \frac{k}{2m} \right)^2 + \frac{f''}{2m} \right) q^2 + (\Delta + \omega') f'' \right]$$

$$+ \frac{m}{k} \frac{\omega'}{q} f' + \frac{a}{b} \frac{\omega'}{q} f'' \log \left[ \frac{1 + \frac{a}{2k} \left( \frac{\Delta - \omega'}{q} \right)}{1 - \frac{a}{2k} \left( \frac{\Delta - \omega'}{q} \right)} \right]$$

Expanding the log term for small $q$ and $(\Delta - \omega')$, we have

$$R(q, \omega') = -\frac{1}{N} \frac{V}{4\pi^2} \int_0^\infty k^2 dk \left[ 2f' + \left( f'' \left( \frac{k}{2m} \right)^2 + \frac{f''}{2m} \right) q^2 + (\Delta + \omega') f'' \right]$$

$$+ \frac{m}{k^2} \omega' f' + \frac{2 \omega' \Delta}{q^2} \frac{m^2}{k^2} f' - \frac{2 \omega'^2 m^2}{q^2} \frac{m^2}{k^2}$$

$$= R(0, 0) - aq^2 - b \left( \frac{\omega^2}{q^2} - \frac{\omega' \Delta}{q^2} \right) - c \Delta \quad (5)$$
where

\[ R(0,0) = -\frac{V}{N} \int_{0}^{\infty} k^2 dk \, 2f', \]

\[ = -\frac{V}{N} \frac{1}{2\pi^2} (2m)^{3/2} \int_{0}^{\infty} (\varepsilon(k))^{3/2} \frac{d\varepsilon}{d\varepsilon} \, \varepsilon \, d\varepsilon \]

\[ = \frac{V}{N} \frac{mk_f}{2\pi^2} = D(\varepsilon_f) \quad \text{at } T = 0^\circ K. \]

\[ a = \frac{V}{N} \frac{(2m)^{3/2}}{4\pi^2} \int_{0}^{\infty} \varepsilon^{1/2} \left[ \varepsilon f'' + \frac{1}{2} f'' \right] d\varepsilon \]

\[ = \frac{1}{12} \frac{D(\varepsilon_f)}{k_f^2} \quad \text{at } T = 0^\circ K. \]

\[ b = -\frac{V}{N} \frac{(2m)^{3/2}}{4\pi^2} m^2 \int_{0}^{\infty} \varepsilon^{-3/2} f'' d\varepsilon \]

\[ = \frac{D(\varepsilon_f)}{\varepsilon_f^2} \quad \text{at } T = 0^\circ K. \]

\[ c = \frac{V}{N} \frac{1}{4\pi^2} \int_{0}^{\infty} k^2 dk \, f'' \]

\[ = \frac{V}{N} \frac{(2m)^{3/2}}{4\pi^2} \int_{0}^{\infty} \varepsilon^{-3/2} f'' d\varepsilon \]

\[ = \frac{D(\varepsilon_f)}{4\varepsilon_f^2} \quad \text{at } T = 0^\circ K. \]

Therefore, at \( T = 0^\circ K \), \( R(\mathbf{q}, \omega') \) is given by

\[ R(\mathbf{q}, \omega') = D(\varepsilon_f) \left[ 1 - \frac{1}{12} \frac{\mathbf{q}^2}{k_f^2} - \left( \frac{\omega'^2}{v_f^2} \right) \frac{\omega^2}{v_f^2} \frac{\Delta}{v_f^2} \right] \quad (6) \]
From (2.52), we have
\[ I(q, \omega') = \frac{\pi}{N} \sum_k \left[ f(k) - f(k+\Delta) \right] \delta \left( \varepsilon(k+q) - \varepsilon(k) - (\omega' - \Delta) \right) \]
\[ = \frac{\pi}{N} \sum_k \left[ f(\varepsilon'(k)) - f(\varepsilon'(k+\Delta)) \right] \delta \left( \frac{kzq}{m} + \frac{q^2}{2m} - (\omega' - \Delta) \right) \]

From (3), and writing sum over \( k \) as integral, we have
\[ I(q, \omega') = \frac{\pi}{N} \frac{V}{4\pi^2} \int_0^{\infty} k^2 dk q \left[ f' \left( \frac{2m+q}{2m+\Delta} \right) + f'' \frac{2m+q}{2m+\Delta} \right]^2 \]
\[ + f' \frac{2}{q} \left( \frac{2m+q}{2m+\Delta} \right)^3 + \ldots \ldots \ldots \ldots \ldots \ldots \ldots \]
\[ \times \frac{m}{kq} \left[ \int_{-1}^{+1} dx \delta \left( x - \left[ \frac{(\omega' - \Delta)}{kq/m} - \frac{q}{2m} \right] \right) \right] \]
\[ = \frac{\pi}{N} \frac{V}{4\pi^2} \int_0^{\infty} mk \left[ f' \left( \frac{\omega' - \Delta}{q} - q/2m + q/2m + \Delta/q \right) \right] \]
\[ + f'' \frac{(q/2)^2}{q} \left( \frac{\omega' - \Delta}{q} - q/2m + q/2m + \Delta/q \right)^2 \]
\[ + f' \left( \frac{q^2/6}{q} \right) \left( \frac{\omega' - \Delta}{q} - q/2m + q/2m + \Delta/q \right)^3 \ldots \ldots \]
\[ = \frac{\pi}{N} \frac{V}{4\pi^2} \int_0^{\infty} mk \left[ f' \frac{\omega'}{q} + f'' \frac{\omega'}{2q} \left( \frac{\omega'}{q} \right)^2 + f' \frac{\omega'}{3q} \left( \frac{\omega'}{q} \right)^3 \ldots \ldots \ldots \right] \]
\[ = \frac{\pi}{N} \frac{V}{4\pi^2} m^2 \frac{\omega'}{q} = \frac{\pi}{2} D(\xi_f) \frac{\omega'}{v_f q} \]

(7)
REFERENCES

BANSAL B.K. (1966) Thesis, University of California, Berkeley,


BRODSKY M.B. (1971) Proc. of Conference on Rare Earths and Actinides,
Durham 1971, pg. 75.


CASTAING J., Costa P., Heritier K., Lederer P. (1972)

DONIACH S. (1971) Proceedings of 17th conference on magnetism and
magnetic materials (A.I.P. 1972) Pg. 549.

(1973) Lecture notes, Mont Tremblant international summer
school on 'Transition metals, alloys and magnetism', Canada


Nuclear Metallurgy 17, 635.


Nuclear Metallurgy 17, 194.
Nuclear Metallurgy 17, 58.
