TRANSPORT PROPERTIES OF DILUTE ALLOYS

by

Veljko Zlatić

Thesis submitted for the Degree of Doctor of Philosophy of the University of London.

Physics Department
Imperial College of Science and Technology
London S.W.7

December, 1973

ABSTRACT

This thesis presents calculations of some properties of dilute alloys containing transition-metal impurities.

Simple-metal transition-metal alloys are described by the orthogonal Anderson Hamiltonian and the problem for the d electron spectral density is solved in the "single pole dominance" approximation for the transverse susceptibility, assuming that the most important contribution to the d electron self-energy comes from the scattering by the spin fluctuations. We find this spectral density to have all the features associated by various theories with localised magnetic and non-magnetic states in metals. The electrical resistivity of dilute alloys due to localised spin fluctuations is shown to be given by a universal function of the temperature, $\rho(T/T_K)$, where T_K is the characteristic temperature of the system. The resistivity is finite at T = 0, then <u>decreases</u> as T^2, T, lnT and 1/T, in agreement with the experimental data. Calculation of the low temperature thermoelectric power, in the same approximation, explains the anomalous behaviour of the TEP observed in the aluminium-based 3d-alloys.

In alloys in which both solvent and solute are transition metals, the relevant part of the impurity electronic structure is similar to that of the host. Such a system is described by the non-orthogonal Anderson Hamiltonian which in the case of isoelectronic alloys reduces to that of Wolff. Using this model we show that the electrical

resistivity due to scattering of conduction electrons from localized spin fluctuations is again given by a universal function of temperature. Resistivity is zero at T = 0, then increases as T^2, T and lnT, tending finally to the unitarity limit. Above the characteristic temperature T_K, the impurity behaves as if it had a well defined moment. This calculation accounts well for the unusual temperature dependence of the resistivity observed in Rh Fe and several similar dilute alloys.

ACKNOWLEDGEMENTS

It is a pleasure to thank Dr. Rivier for suggesting the topics of this thesis and for his helpful guidance and innumerable discussions during the course of this work.

I would also like to thank the members of the Imperial College Solid State Theory Group, especially K. Adkins, E. Balanovski, J. Bethell, M. Kahn, K. Mihill, Dr. F. Napoli, Dr. A. Nayyar, M. Rajan and Dr. D. Sherrington for their encouragement and many clarifying discussions.

I gratefully acknowledge Dr. E. Babić, Dr. J. Cooper, Professor B. Leontić, Dr. M. Miljak, Professor M. Paić and Dr. Z. Vucić from the University of Zagreb for their stimulating interest in all the phases of this work.

I would also like to thank Professors B. Coles, P. Lederer, C. Rizzuto and Drs. G. Grüner and A. Murani with whom I had a number of enlightening discussions.

My very special thanks go to my wife for her constant encouragement and patience.

Financial support for my stay at Imperial College was provided by a Scholarship from the Government of the SR Croatia.

PUBLICATIONS

Some of the material of this thesis appears in the following publications:

N. Rivier and V. Zlatić, 1972, Temperature dependence of the resistivity due to localised spin fluctuations, J. Phys. F: Metal Physics 2, L87.

N. Rivier and V. Zlatić, 1972, Temperature dependence of the resistivity due to localised spin fluctuations, II. Coles alloys, J. Phys. F: Metal Physics 2, L99.

V. Zlatić and N. Rivier, 1974, Low temperature thermoelectric power of Al-3d alloys, J. Phys. F: Metal Physics, in press.

V. Zlatić, G. Grüner and N. Rivier, 1974, Model calculation of the density of states of dilute alloys, Solid State Commun., in press.

TABLE OF CONTENTS

Page No.

INTRODUCTION

In general an isolated atom will have its spin and angular momentum determined by Hund's rule. But what about an isolated paramagnetic impurity in the metallic host? Does it have a "magnetic moment"? Experimentally, there are several ways of answering this question.

Susceptibility measurements provide direct evidence about the existence or non-existence of a local moment. In the case of "yes moment" systems a strongly temperature dependent, Curie like susceptibility is observed,

$$\chi = \frac{2\mu_{eff}^{2}}{3T}$$

characteristic of an assembly of isolated paramagnetic ions. The measured effective local magnetic moment is close to its free ion value, as seen for example in Au Mn and Cu Mn alloys. In the opposite case, the susceptibility is temperature independent, Pauli like, indicating that the magnetic moment of the impurity is completely lost in the metallic environment.

Equally, the response of the conduction electrons to an applied external electric field provides information about the magnetic character of the impurity. As known for a long time, the anomalous transport coefficients of some dilute alloys are related to the existence of a local moment at the impurity site. Kondo (1964) showed that the exchange scattering of the conduction electrons on the localised spin accounts for the deep minimum in the total resistivity of some alloys. On the other hand, the main effect of the non-magnetic impurity is to increase the residual resistivity.

However, careful experimental analysis (Caplin and Rizzuto, 1968; Narath, 1972; Rizzuto, 1974; Grüner, 1973) has shown that for most of the systems, the notion "magnetic" or "non-magnetic" is only a relative one. There are a number of alloys with only weakly temperature dependent Curie-Weiss susceptibility

$$\chi = \frac{C}{T + \theta}$$

where θ is of the order of a few hundred degrees, and alloys in which the enhanced Pauli like susceptibility is associated with the weak resistance minimum. Equally, if one looks at some of the alloys in a broad temperature range, it appears that one and the same alloy behaves as "magnetic" or "non-magnetic" depending on whether the temperature is below or above a certain characteristic temperature.

The theoretical framework in which the behaviour of such systems is usually studied is given by the Friedel-Anderson model. The problem of local moment formation has been solved by Friedel (1958) and Anderson (1961) in terms of a self-consistent polarisation of a virtual bound state, representing the impurity; the Hartree-Fock approximation gives the criterion according to which the impurity will or will not retain its moment in a given host.

Friedel-Anderson Theory.

Consider a transition metal impurity dissolved in a simple metal host. The conduction band of the host has an s-like character while the valence electrons of the impurity are s- and d-like. Due to the great band width of the conduction states, the energies of the impurity valence electrons will be, in general, above the bottom of the conduction band (Friedel, 1958; Friedel and Daniel, 1965). This means that the energy levels of the d-states will be broadened due to the mixing with the conduction states. If mixing is not too large, the perturbed d-electrons will still remain localized and a "virtual bound state" will be formed, which looks rather similar to the atomic d-state. Because the electrons in such a state are at least as localized as in a free atom (Anderson, 1968), one expects the exchange and correlation forces to play an important role. In certain situations this can give rise to the lifting of the spin degeneracy of the virtual state, i.e. the up- and down-spin virtual bound states will have differend energies. If, eventually, the virtual states are not too far away from the Fermi surface, the number of up and down-spin electrons will be different and a localized magnetic moment results (Friedel and Blandin, 1959; Daniel and Friedel, 1965). The condition for the spin splitting to occur is given by

$$U \left(\frac{\partial n}{\partial \varepsilon} \right)_{\varepsilon_F} > 1$$

where U is the exchange energy of local electrons and n(ε) is the number of local states at the Fermi level.

At temperatures close to T = 0, the transport properties of dilute alloys are determined by the phase shifts of conduction electrons due to their scattering on the virtual state.

In the case of the residual resistivities of Al-3d alloys, the agreement with the experimental data is rather remarkable (Fig. 1, Ch. III), while in the case of "magnetic" Cu based alloys the agreements is less good but we still see how the splitting of the virtual bound state is reflected in the residual resistivities as we move through the transition series.

The appropriate Hamiltonian to study the described physical situation is the Anderson Hamiltonian (Anderson, 1961)

$$H = H_{os} + H_{od} + H_{sd} + H_{dd} \tag{1}$$

In the standard notation

$$H_{os} = \Sigma_k \; \varepsilon_k \; a^{+}_{k\sigma} \; a_{k\sigma}$$

$$H_{od} = \Sigma_m \; E_d \; a^{m+}_{d\sigma} \; a^{m}_{d\sigma}$$

$$H_{sd} = \Sigma_{km} \; V^{m}_{kd} \; a^{+}_{k} \; a^{m}_{d} + \text{cc.}$$

$$H_{dd} = U \; \Sigma_m \; a^{m+}_{d\sigma} \; a^{m}_{d\sigma} \; a^{m+}_{d-\sigma} \; a^{m}_{d-\sigma} \; +$$

$$+ \; (U-J) \; \Sigma_{m\neq n} \; a^{m+}_{d\sigma} \; a^{m}_{d\sigma} \; a^{m+}_{n-\sigma} \; a^{n}_{n-\sigma}$$

Indices m and n denote the various d orbitals and U and J are Coulomb and exchange integrals between pairs of localized electrons. (Differences between the matrix elements $U_{mm'}$ and $J_{mm'}$ are neglected because they are small compared to the width of the virtual bound state; for the same reason the crystal field splitting of the d-level is neglected.) V^{m}_{kd} is the matrix element of the one-body s-d scattering potential.

The condition for the appearance of a local moment is obtained by calculating the average occupation, $\langle n^{m}_{d\sigma} \rangle$, of the spin up and down local levels. (Obviously, if $\Sigma_{m}(\langle n^{m}_{d\uparrow} \rangle - \langle n^{m}_{d\downarrow} \rangle \neq 0$, the system will have a moment.) The self-consistency condition is given by

$$\langle n^{m}_{d\sigma} \rangle = \int d\varepsilon \; n^{m}_{d\sigma}(\varepsilon) \tag{2}$$

where $n^{m}_{d\sigma}(\varepsilon)$ is the local density, defined as

$$n^{m}_{d\sigma}(\varepsilon) = -\frac{1}{\pi}\mathrm{Im}\; G^{m}_{d\sigma}(\varepsilon) \tag{3}$$

and G^{m}_{d} is the matrix element of the d-electrons Green function.

For a given set of parameters (U, J, E^{m}_{d}, etc.), a local moment will exist if the ground state energy of the system is at its minimum and the equation

$$\Sigma_{m}(\langle n^{m}_{d\uparrow} \rangle - \langle n^{m}_{d\downarrow} \rangle) = M \tag{4}$$

has a solution for $M \neq 0$, where M is the total moment of the local state. Equation (4) answers, in principle, the question about the existence of an impurity moment in the metallic host. In the Hartree-Fock approximation one obtains the condition

$$\frac{U + 4J}{\pi} \frac{\Delta}{(E_d - \varepsilon_F)^2 + \Delta^2} > 1 \qquad (5)$$

which in the symmetrical case reads

$$\frac{U}{\pi\Delta} > 1 \qquad (5')$$

where Δ is the width of the virtual bound state.

However, for the equality sign in the expression (5) equation (4) gives the sharp boundary between the magnetic and non-magnetic states, i.e. it defines the critical line between the "yes" and "no moment" regions in parameter space. Such a result, quite similar to what one finds when studying phase-transitions in extended systems (Stoner-Wolhfarth magnetism, for example), is not acceptable in a local system. It is hard to believe that one particle in some 10^{23} could cause the phase transition (time-reversal symmetry being destroyed). One already expects on the basis of the classical theory (Landau and Lifshitz, 1963), that in a finite system the fluctuations will destroy the possibility of a sharp transition.

Also, in the case of the Hartree-Fock magnetic impurity one can envisage a rather paradoxical situation in which the magnetic moment will be quenched at temperatures of the order of the splitting between the up-spin and down-spin virtual states.

LSF Concept.

To avoid these difficulties and to explain the above mentioned experimental data (in particular, "magnetic" behaviour above some characteristic temperature and "non-magnetic" below) one has to find a better approximation for the Anderson Hamiltonian than Hartree-Fock. Much of the theoretical work in this respect, in the past few years, has been done along the lines of the localised spin fluctuation (LSF) theory. Both the magnetic - non-magnetic transition and the "loss" of magnetic properties at sufficiently low temperatures are explained assuming that the behaviour of the system is dominated by the fluctuations of the local spin. The impurity is characterised by the lifetime τ of the LSF, and if τ is greater than the life-time of the thermal fluctuations, the system can show magnetic properties without necessarily having to sustain an infinitely long-lived magnetic moment, as predicted by the Hartree-Fock theory.

To introduce the localised spin fluctuations in the Anderson model, we first look at the magnetic properties of the Anderson Hamiltonian in the U=0 limit. In what follows we restrict our discussion to the case of the non-degenerate d-orbital, so that the Hamiltonian (1) reads

$$H = \Sigma_{k\sigma}\ \varepsilon_k\ a^+_{k\sigma}\ a_{k\sigma} + \Sigma_{k\sigma}(V_{kd}\ a^+_{k\sigma}\ a_{d\sigma} + V^*_{kd}\ a^+_{d\sigma}\ a_{k\sigma}) + Un_{d\uparrow}n_{d\downarrow}$$

If we assume that there is no correlation (U=0) between d-electrons of opposite spin, this Hamiltonian can be diagonalised exactly; all the Hartree-Fock results discussed in the previous section become rigorous in this limit. The d-electrons Green function is given by

$$G^o_d(\omega_n) = \frac{1}{\omega_n \pm i\Delta} \tag{6}$$

which means that the lifetime of a d-electron of a given spin is of the order of Δ^{-1}.

The rate of change from one spin to the other is related to the susceptibility by

$$\chi(\omega_m) = k_B T\ \Sigma_n\ G^o_d(\omega_m + \omega_n)\ G^o_d(\omega_n)\ , \tag{7}$$

from which it easily follows that the static susceptibility is given by

$$\chi^o_d(o) \sim \beta\psi'(\tfrac{1}{2} + \frac{\Delta\eta}{2\pi}) \tag{8}$$

where $\beta = 1/k_BT$ and $\psi'(z)$ is derivative of the digamma function (Abramovitz and Stegun, 1965). In the $T \rightarrow 0$ limit $\chi^o_d(0)$ tends to a constant while for $T \rightarrow \infty$ it behaves as $1/T$. Thus, for U=0, the static susceptibility varies from Pauli-like to Curie-like, with the change in regime occurring at a temperature of the order of Δ.

What is expected to happen if a non-zero correlation term appears? The new term in the Hamiltonian is $Un_{d\uparrow}n_{d\downarrow}$

and therefore the doubly occupancy of the d-orbital will be reduced on the average. A d-electron of a given spin tends to surround itself by a hole of the opposite spin: the lifetime of a given spin state will increase with increasing U. An alternative way of looking at such a state is to say that the impurity has got a magnetic moment which is of a finite lifetime $\tau(\tau > \Delta^{-1})$.

The static susceptibility of such a system is given by the same expression as eq. (8) (Rivier, 1968) but with Δ^{-1} replaced by τ; the transition temperature between the two regimes is shifted from Δ/k_B to T_K, where the characteristic temperature T_K is defined by

$$k_B T_K = \tau^{-1}$$

For temperatures below T_K the system is essentially non-magnetic, while above T_K it behaves as if the impurity had a well defined permanent spin. Thus, when the lifetime of the thermal fluctuations in the conduction band becomes shorter than $\lesssim\tau(T >> T_K)$, the conduction electrons can be spin-flip scattered on the impurity, which gives rise to the logarithmic temperature dependence of the resistivity.

Such a definition of the characteristic temperature T_K agrees well with the experimental and theoretical values of T_K deduced from the transport and thermodynamical properties of the dilute alloys. The transition between the "magnetic" and "non-magnetic" regime is smooth, as it should be in a system involving a limited number of degrees of freedom.

In a formal way, the localised spin fluctuations were introduced in the Anderson model by analogy with the critical fluctuations in the theory of nearly ferromagnetic metals (Berk and Schrieffer, 1966; Doniach and Engelsberg, 1966). The idea was to start with the Anderson Hamiltonian (assuming the ground state of the system to be non-magnetic) and evaluate quantities such as susceptibility, partition function, etc., by means of many-body techniques.

In the "random phase approximation" the fluctuation corrections to the d-electron self-energy have been calculated by Rivier and Zuckermann (1968) and in the RRPA by Suhl (1967), Levine and Suhl (1968) and Hamann (1969). Their aim was to solve simultaneously the set of equations for G_d, Σ_d and χ_d

$$G_d(i\,\varepsilon_n) = \frac{1}{i\,\varepsilon_n \pm i\Delta - \Sigma_d}$$

$$\Sigma_d(i\,\varepsilon_n) = \frac{1}{\beta}\,\Sigma_B\; G_d(i\,\varepsilon_m)\,\chi_d(i\,\varepsilon_m + i\,\varepsilon_n)$$

and

$$\chi_d(i\,\varepsilon_n) = \frac{\chi_o}{1 - U\,\chi_o}$$

where

$$\chi_o = -\frac{1}{\beta}\,\Sigma_F\; G_d(i\,\varepsilon_m + i\,\varepsilon_n)\; G_d(i\,\varepsilon_m)$$

and B and F denote the summation over Bose and Fermi frequencies.

Although in this approach the Hartree-Fock divergencies have been removed and a smooth transition between $U << \pi\Delta$ and $U >> \pi\Delta$ has been obtained, difficulties still remained in the magnetic ($U >> \pi\Delta$) limit. For example the flattening out of the susceptibility occurred at a temperature which is exponentially lower than that which is expected on the basis of Kondo theory. In addition, Beal-Monod and Mills (1970) have shown that for $U \simeq \pi\Delta$ vertex corrections which were not included in the theory of the above authors are at least as important as the self-energy corrections.

To circumvent these difficulties, another type of spin fluctuation was introduced by Hamann (1969a) and Schrieffer et al. (1969 and 1970). They calculate the partition function and susceptibility of the Anderson model using so called functional integral methods. (Review of various FI approaches to the Anderson model is given by Hassing and Esterling, 1973 and Morandi and Ratto, 1974). In this method the partition function of the system with two-body interactions ($Un_{d\uparrow}n_{d\downarrow}$) is replaced by a Gaussian average of the partition function for a system of particles interacting only with time varying external field (which couples to the system in the appropriate manner). The average is over all possible fictitious external fields and is expressed as a functional integral* (Stratonovich, 1958; Hubbard, 1959).

The FI methods enable one to treat the Anderson model for all values of $U/\pi\Delta$ within a single approximation, but presently neither in the $U/\pi\Delta >> 1$ nor in the $U \simeq \pi\Delta$ case do the FI results agree completely with certain well known limits obtained on the basis of the less sophisticated treatments (Hassing and Esterling, 1973; Morandi and Ratto, 1974).

Thus, although in the last few years considerable progress has been made in understanding the behaviour of dilute alloys, the relationship between experimentally determined properties (e.g. "simple power laws" or "spin fluctuation temperature", Star, 1971; Rizzuto, 1974) and parameters of fundamental Hamiltonians such as of Anderson or Wolff, is still not quite established.

In this respect, we believe that it would be of interest to look at a dilute alloy assuming that the transition metal impurity has got a magnetic moment which is of finite lifetime τ and calculate the properties of such a system, leaving the question of the exact relation between the LSF lifetime and parameters U, Δ and E_d open.

---

*Formulating the problem in field-theoretical language, it can be shown that the auxiliary field propagators have physical significance as higher order correlation functions of the original system (Sherrington, 1971). In the case of the Anderson Hamiltonian, the one-body auxiliary field propagator gives the frequency dependent local susceptibility.

CHAPTER 1

EFFECTS OF THE LOCALISED SPIN FLUCTUATIONS ON THE DENSITY OF STATES OF DILUTE ALLOYS

1.1 Single Pole Dominance Approximation

The LSF theory, discussed in the previous chapter, predicts the local susceptibility of the form

$$\chi_d = \frac{c}{T_K + i\varepsilon} \tag{1}$$

where T_K is a function of the parameters of the Anderson Hamiltonian and c some constant which depends on the particular model and approximation used to calculate χ_d. For example, in the RPA of the Anderson model one has $c = 2\mu_B^2/\pi$, for the non-degenerate d-level and $c = 2(2\ell+1)\mu_B^2/\pi$, for $(2\ell+1)$ - fold degenerate level. The static susceptibility, when calculated in the RRPA,(Hamann, 1969), varies from Pauli like to Curie-Weiss like as U goes from zero to infinity (retaining the finite value at T=0) so that the divergency in the local susceptibility is removed and a smooth transition from the magnetic to the non-magnetic state is obtained. However, the calculated values of χ_d are not in any agreement with the experimental data: calculated Curie constant is of the order of $(U/\Delta)^2$, while experimentally it is of the order of one. What is even worse, in the $U/\Delta \to \infty$ limit, RRPA values of T_K do not agree with the Kondo temperature obtained by the Schrieffer-Wolff transformation and the standard formula

$$T_K = T_F \exp(-\frac{1}{\rho_F J})$$

On the other hand, apart from the fact that experimentally established properties of dilute alloys vary smoothly with the local correlation energy (Rizzuto, Babic and Steward, 1973), the impurity NMR data show expression (1) for χ_d to be valid not just in the "non-magnetic" but in the "magnetic" regime as well (Narath, 1972; Narath and Weaver, 1969).

In this sense it is tempting to try and keep the expression (1) for the local susceptibility not as an ultimate goal of the fully renormalised theory but rather as a starting point of a phenomenological theory. Thus we calculate properties of a dilute alloy <u>assuming</u> the local dynamical susceptibility to be given by equation (1) and define the LSF propagator as

$$= \frac{\pi\ \Delta^2}{T_K + i\varepsilon} \qquad (2)$$

with T_K chosen as a phenomenological parameter and assume, following Suhl (1967), that the most important contribution to the d-electrons' self-energy Σ_d comes from the scattering by the spin fluctuations (Rivier, 1968; Hamann, 1969). In other words, we write for the self-energy

$$-i\Sigma_d =$$

$$. \qquad (3)$$

where as before, $\Rightarrow$ is the d-electrons Green function. Equations (2) and (3) form what we call the "single pole dominance" approximation.

In what follows we calculate, in the above defined "single pole dominance" approximation, some of the properties of a dilute alloy described by the Anderson Hamiltonian. We stress again that the validity of the calculations should not be connected to that of the RPA applied to the Anderson model but rather to that of the expression (1) for the local susceptibility. We believe that our results will remain the same within the frame of any approximation leading to such a susceptibility.

In the next section we derive first an expression for the d-electrons' spectral density and then look at the density of states as a function of temperature and parameters T_K, E_d and Δ. In the last section of this chapter we calculate the change in the excess specific heat of the alloy due to the presence of the local spin fluctuations.

1.2 Spectral Density of Local Electrons

By definition, the spectral density $A(\varepsilon)$ is obtained from the Green function by

$$A(\varepsilon) = -\frac{1}{\pi} \operatorname{Im} G_d(\varepsilon) \qquad (4)$$

and $G_d(\varepsilon)$ is determined by the Dyson equation

$$G_d(\varepsilon) = \frac{1}{\varepsilon - E_d \pm i_\Delta - \Sigma_d} \qquad (5)$$

Within the "single pole dominance" approximation we have for $\Sigma_d(\varepsilon)$ (Rivier, 1968)

$$- i\Sigma_d(i\varepsilon_n) = k_B T \; \Sigma_B \; \chi_d(i\varepsilon_m) \; G_d(i\varepsilon_m + i\varepsilon_n) \qquad (3')$$

where sum over B goes over all the Bose frequences $\Sigma_n = 2n\pi i k_B T$. Here, we restrict our discussion to the unrenormalized theory only, i.e. we replace $G_d(\Sigma)$ in the equation (3') with $G_d^o(\Sigma)$, believing that results obtained in such a way will give a physical insight in the modifications of the virtual bound state due to electron-hole correlations.

To calculate G_d for real frequencies we make the analytical continuation of the expression (3') from the imaginary on the real axes and obtain the integral (Rivier, 1968):

$$\Sigma_d(z) = \Delta^2 \int \frac{dx}{e^{x/\beta} - 1} \; \frac{x}{M^2 + x^2} \; \frac{1}{x + z - E_d \pm i\Delta} +$$

$$+ \int \frac{dx}{e^{x\beta} + 1} \; \frac{\Delta}{(x-E_d)^2 + \Delta^2} \; \frac{1}{M \mp i(z-x)} \qquad (5b)$$

where $M = k_B T_K$ is the inverse of the LSF life-time, and $\beta = 1/{}^{k}{}_{B}T$ is the inverse of the absolute temperature.

Evaluating this integral (mathematical details are given in the appendix I) we have for $\Sigma_d(\varepsilon)$

$$\Sigma_d(\varepsilon) = \Delta^2(I_1 + I_2 + I_3) \qquad (5c)$$

where

$$I_1 = \frac{1}{\varepsilon - E_d \pm i(M + \Delta)} \quad \frac{\pi}{M\beta}$$

$$I_2 = \frac{\varepsilon - E_d \pm i\Delta}{[\varepsilon - E_d \pm i(\Delta+M)][\varepsilon - E_d \pm i(\Delta-M)]} *$$

$$* \left\{ \psi\left(1 + \frac{\Delta\beta}{2\pi} \mp i\frac{(\varepsilon-E_d)\beta}{2\pi}\right) - \psi\left(1 + \frac{M\beta}{2\pi}\right) \right\}$$

$$I_3 = \frac{-i\Delta}{[(\varepsilon - E_d) + i(\Delta\mp M)][\varepsilon - E_d - i(\Delta\mp M)]} \psi\left(\tfrac{1}{2} + \frac{M\beta}{2\pi} \mp i\frac{\varepsilon\beta}{2\pi}\right) \mp$$

$$\mp \tfrac{1}{2} \left\{ \frac{\psi\left(\tfrac{1}{2} + \frac{\Delta\beta}{2\pi} + i\,\frac{E_d\beta}{2\pi}\right)}{\varepsilon - E_d \pm i M + i\Delta} - \frac{\psi\left(\tfrac{1}{2} + \frac{\Delta\beta}{2\pi} - i\frac{E_d\beta}{2\pi}\right)}{\varepsilon - E_d \pm i M - i\Delta} \right\}$$

In equation (5c) symbol $\psi(x)$ denotes the digamma function (Abramovitz and Stegun, (1965).

Using equation (5) we can discuss the spectral density as a function of energy, temperature and parameters M, E_d and Δ. We have for the Im $G_d(\varepsilon)$

$$- \text{Im } G_d(\varepsilon) = \frac{(\Delta - \text{Im } \Sigma_d)}{(\varepsilon - E_d - \text{Re } \Sigma_d)^2 + (\Delta - \text{Im } \Sigma_d)^2} \qquad (6)$$

from which $A(\varepsilon)$ is easily obtained. The local density of states is obviously equal to the spectral density and in the next section we show that the d-electrons' density of states, $n_d(\varepsilon)$, is drastically changed with respect to its Hartree-Fock form, but it contains all the features associated by different theories with localised magnetic and non-magnetic states in metals.

1.3 Low Temperature Limit of the d-Electrons' Density of States

For temperatures close to zero we can greatly simplify expression (3') for $\Sigma_d(\varepsilon)$ and write $n_d(\varepsilon)$ in terms of usual analytical functions.

Let us first discuss the case $M \simeq \Delta$, i.e. the truly non-magnetic regime. Recalling that $k_B T \ll \Delta$ for any physical temperature and using the asymptotic expansion for ψ-functions

$$\psi(x) \to \ln(x) \text{ when } x \to \infty$$

Σ_d can be written as

$$\Sigma_d \sim \frac{1}{\varepsilon - E_d + 2i\Delta} \left\{ \frac{\pi}{\Delta\beta} + \frac{1}{2} \ln \frac{[\Delta - i(\varepsilon - E_d)](\Delta - i\varepsilon)}{\Delta(\Delta + i E_d)} \right\} +$$

$$+ \frac{1}{2} \frac{1}{\varepsilon - E_d} \ln \frac{[\Delta - i(\varepsilon - E_d)](\Delta - i E_d)}{\Delta(\Delta - i\varepsilon)}$$

The LSF contribution to the self-energy is such that $n_d(\varepsilon)$ is to a very good approximation Lorentzian of the width Δ, i.e. one recovers for the density of states the Hartree-Fock non-magnetic solution (Anderson, 1961). The position of the virtual bound state with respect to the Fermi level is fixed by the number of d-electrons which it has to accomodate.

The situation is different in the case when $M << \Delta$. Neglecting everywhere M against Δ and using the asymptotic form of ψ-functions we can write Σ_d as

$$\mathrm{Re}\,\Sigma \sim \frac{\Delta^2(\varepsilon-E_d)}{(\varepsilon-E_d)^2+\Delta^2}\,\ln\frac{\Delta^2+(\varepsilon-E_d)^2}{M^2} \quad \frac{\Delta^3}{(\varepsilon-E_d)^2+\Delta^2} \ast$$

$$\ast \left\{ \mathrm{tg}^{-1}\frac{\varepsilon}{M} + \mathrm{tg}^{-1}\frac{\varepsilon-E_d}{\Delta} \right\} \tag{7}$$

$$\mathrm{Im}\,\Sigma_d \sim -\tfrac{1}{2}\frac{\Delta^3}{(\varepsilon-E_d)^2+\Delta^2}\,\ln\frac{(M^2+\varepsilon^2)\left[(\varepsilon-E_d)^2+\Delta^2\right]}{M^2(\Delta^2+E_d^2)} -$$

$$\frac{\Delta^2(\varepsilon-E)}{(\varepsilon-E_d)^2+\Delta^2} \times \left\{ \mathrm{tg}^{-1}\frac{E_d}{\Delta} + \mathrm{tg}^{-1}\frac{\varepsilon-E_d}{\Delta} \right\}$$

At the Fermi level ($\varepsilon = 0$) one has:

$$\mathrm{Re}\,\Sigma_d(\varepsilon=0) = \frac{\Delta^2 E_d}{\Delta^2+E_d^2}\,\ln\frac{\sqrt{\Delta^2+E_d^2}}{M} + \frac{\Delta^3}{\Delta^2+E^2}\,\mathrm{tg}^{-1}\frac{E_d}{\Delta}$$

$$\mathrm{Im}\,\Sigma_d(\varepsilon=0) = 0 \tag{8}$$

and the density of states at the Fermi level can be written as

$$n_d(0) = \frac{1}{\pi}\,\frac{\Delta}{\tilde{E}_d+\Delta^2} \tag{9}$$

where the renormalised shift $\tilde{E}_d$ is defined as

$$\tilde{E}_d = E_d + \mathrm{Re}\,\Sigma_d \tag{10}$$

From the equations (9) and (10) it follows that the envelope of the Fermi level density of states is at its maximum in the symmetrical case ($\tilde{E}_d = E_d = 0$). Keeping Δ the same and changing M and E_d, i.e. changing impurity in the given host, we see that $n_d(0)$ decreases with increasing E_d in approximatively the same fashion as in the case of a non-magnetic virtual bound state. Now, it would be extremely nice if $\tilde{E}_d$ corresponded to the effective position of the virtual level as determined by the Friedel sum rule. However, in this unrenormalized theory it is E_d rather than $\tilde{E}_d$ which gives the effective position.

In the case of the symmetrical Anderson Hamiltonian, we can find an useful approximate expression for the Green function G_d and the density of states, valid in the energy region close to the Fermi level. From equation (7) we obtain, expanding *Σ_d for small ε and $T \simeq 0$,

$$\mathrm{Re}\ \Sigma_d \simeq \varepsilon \ln \frac{\Delta}{M} - \Delta \frac{\varepsilon}{M}$$

and $$\Sigma_d \simeq 0 + \theta(\varepsilon^2)$$

It follows that $G_d(\varepsilon)$ can be written as

$$G_d(\varepsilon) \simeq G_d^{eff} = \frac{M}{\Delta} \frac{1}{\varepsilon + iM} \tag{11}$$

and $n_d(\varepsilon)$ as

$$n_d(\varepsilon) \simeq \frac{1}{\pi\Delta} \frac{M}{\varepsilon^2 + M^2} . \tag{12}$$

---

*Up to logarithmic accuracy, i.e. $M/\Delta \ll |\ln(M/\Delta)|$

The density of states, close to the Fermi level, is given by narrow Lorentzian of width M, i.e. it is proportional to the inverse of the LSF life-time.

1.4 Temperature Dependence of $n_d(\varepsilon)$

To obtain the general structure of the density of states at finite temperatures and for any values of E_d, M and Δ, we have substituted expression (3) for $\Sigma_d(\varepsilon)$ in the expression (6) and made the numerical analysis. Properties of $n_d(\varepsilon)$ can be summarised as follows:

(i) For $M \ll \Delta$, $n_d(\varepsilon)$ has two broad peaks of width Δ, stable relative to the Fermi level and only weakly temperature dependent. They can be recognised as the Friedel-Anderson (Hartree-Fock) part of the density of states.

(ii) In addition, there is a narrow peak (width M) placed at the Fermi level which decreases rapidly with increasing temperature and disappears above T_K. The Fermi level density of states follows successively T^2, T and ln(T) temperature dependence.

Mathematically, this rapid change of $n_d(\varepsilon)$ for small values of its argument comes from the fact that the reduced temperature scale is defined by $\tilde{T} = (T/T_K)$. Also, we notice from the asymptotic behaviour of ψ-functions, that the initial quadratic energy dependence of $n_d(\varepsilon)$ is followed by logarithmic energy dependence ($\varepsilon < M$). The width, Γ, of the narrow peak follows the same temperature dependence as the inverse of the density of states at the Fermi level, i.e. one has (for $k_BT << M$) from eqs. (6), (7) and (8),

$$\Gamma(T) \simeq M \left[1 + \frac{\pi^2}{2} \left(\frac{k_BT}{M}\right)^2 \right] \qquad (13)$$

so that for $\varepsilon << M$ one can replace $n_d(\varepsilon)$ by an effective temperature dependent Lorentzian

$$n_d^{eff}(\varepsilon) = \frac{M}{\Delta} \frac{(T)}{\varepsilon^2 + \Delta^2} \qquad (14)$$

where $\Gamma(T)$ is the effective temperature dependent width and $\Gamma_{T=0}=M$. We repeat that at zero temperature the envelope of the many-body peak (for different impurities, i.e. different E_d) has approximately a Lorentzian shape, which has been associated by Friedel with the density of states around the 3d-impurity in non-magnetic alloys. Above T_K, the envelope of $-\frac{1}{\pi}\,\mathrm{Im}(G_d)_{\varepsilon=0}$ coincides with the density of states itself, so that one recovers the doubly peaked form, associated in the Hartree-Fock picture with the magnetic virtual bound state. The doubly peaked residual resistance of gold and copper based alloys (direct measure of the density of states at the Fermi level) is in fact measured above the respective Kondo temperatures of these alloys.

Splitting between two broad peaks increases with the decreasing M (i.e. T_K). However, we have not been able to obtain the quantitative relation between the splitting and T_K in the limit $M/\Delta \sim 0$. In the opposite limit the splitting disappears and one recovers the simple Lorentzian density of states of width Δ. In this limit the impurity is truly non-magnetic for any temperature smaller than the degeneracy temperature of the local Fermi gas, $T_{deg} \simeq \Delta$.

In figures (1) and (2) we plotted the density of states as a function of energy and temperature for two different sets of parameters:

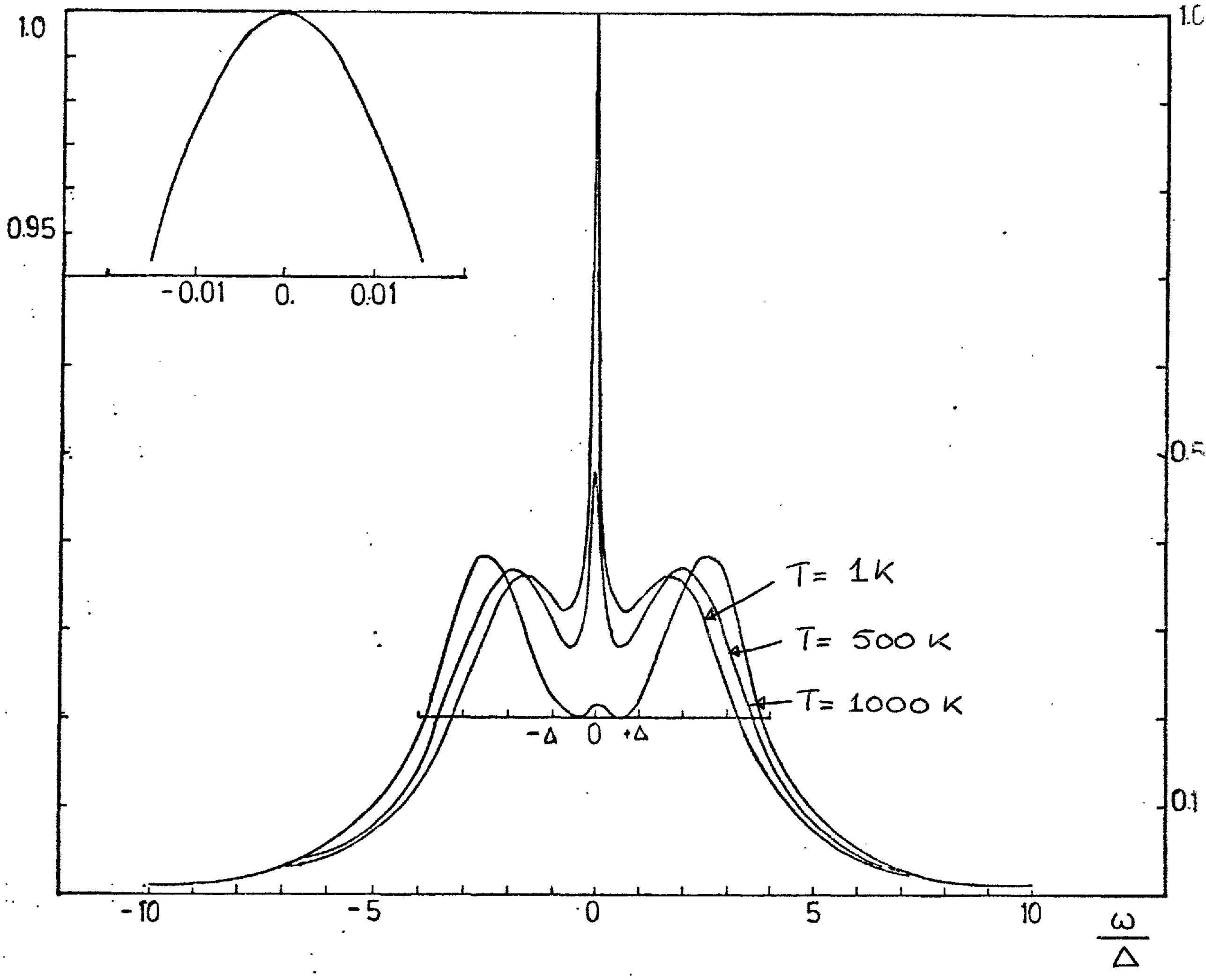
fig. (1); $E_d/\Delta = 0$, $M/\Delta = 0.07$,

fig. (2); $E_d/\Delta = -0.3$, $M/\Delta = 0.005$

In physical terms this would correspond to systems like <u>Al</u> Mn and <u>Cu</u> Fe. (E_d is chosen in such a way that the number of electrons in the virtual state is 5 and 6.5 respectively).

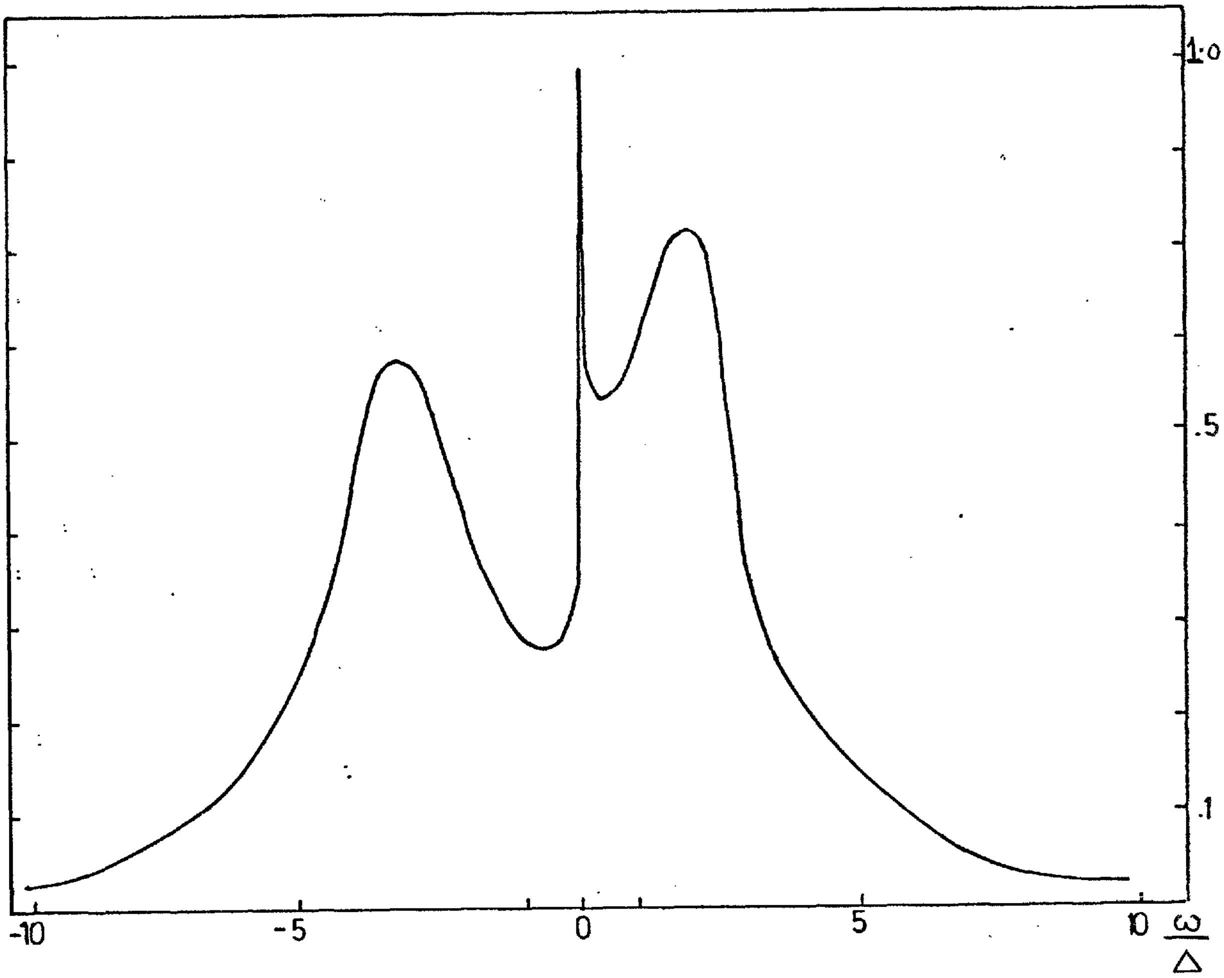
Finally, we mention that in order to give a plausible explanation of a number of experimentally observed properties of dilute alloys, Grüner and Zawadowski (1972) proposed that the d-electrons density of states should have basically the same form as our function $n_d(\varepsilon)$. Similarly, Schweitzer et al. (1972) postulated in their "heuristic treatment of the Anderson Hamiltonian" a spectral density of the same type as the one obtained here in the single pole dominance approximation. On the other hand, Larsen (1973) calculated the transport properties of a "magnetic" alloy starting from the Kondo Hamiltonian and in order to avoid the divergency of the scattering matrix at T=0, he assumed that the spectral density of a local spin has a finite temperature dependent width. The actual form of his spectral density is exactly the same as narrow many-body peak obtained here

Figure 1



The spectral density of the virtual bound state Im $G_d(\omega)$ at various temperatures, with parameters corresponding to <u>Al</u> Mn.

Figure 2



The spectral density of the virtual bound state Im $G_d(\omega)$ with parameters corresponding to <u>Cu</u> Fe, at T=0.

on the basis of the Anderson Hamiltonian. In this sense we believe that the spectral density given by equations (4) and (6) demonstrates that there is no basic difference between Kondo and LSF description of the localised "magnetic" state of spin 1/2.

1.5 Discussion of the Experimental Data Related to Density of States

Direct evidence about the structure of the broad resonance and its position with respect to the Fermi level comes from optical and photo emission data.

Experiments of these kinds enable one to study electronic properties of an alloy over an energy range of several eV.

In the case of the optical absorption one usually studies the imaginary part of the dielectric constant $\varepsilon_2(\omega)$, which is proportional to

$$\varepsilon_2(\omega) \sim \int n_f(\omega')n_i(\omega'-\omega)d\omega'$$

Here, $n_i(\omega)$ and $n_f(\omega)$ are the densities of the initial and final electronic states. The presence of the virtual bound state is going to modify the interband transitions so that one expects the absorption peaks at energies E_d.

Using the method due to Kjöllerström (1969), it is possible to relate the results of the optical experiments to the parameters of the Anderson model. In the case of a non-magnetic alloy one has (Kjöllerström, 1969)

$$\frac{\Delta\varepsilon_2(\omega)}{c} = \frac{5}{\omega}\left(\frac{\omega_p^2 V^2}{\omega^2} + \omega_d^2\right)\left(tg^{-1}\frac{E_d + \omega}{\Delta} + tg^{-1}\frac{E_d - \omega}{\Delta}\right) \quad (15)$$

where $\Delta\varepsilon_2$ is the difference in the imaginary part of the dielectric function between the dilute alloy and pure metal at frequency ω, C is the concentration of impurities, ω_p the plasma frequency of the metal, ω_d an oscillator strength for interband transition from the impurity and E_d, V and Δ the usual parameters of the Anderson model. The shape of $\Delta\varepsilon_2$ is thus determined by E_d and Δ, while the amplitude contains two terms, one due to conduction electron resonant potential scattering proportional to V^2 and the other due to interband transition proportional to ω_p.

Fig. (3) shows the results of the measurements by Callender and Schnetterly (1972) on low concentration Ag Pd alloys. One sees a pronounced peak at about 2.4 eV, whose position is independent of the concentration, suggesting that one is dealing with the single impurity effect. Such structure of the density of states is in accord with the non-magnetic character of palladium in silver, i.e. with the unsplit virtual bound state. Using eq. (15), the estimates of the parameters E_d and Δ give: $E_d = -1.9$ eV and $\Delta = 0.24$ eV. These results agree quite well with the earlier measurements on more concentrated alloys (Myers et al. 1968) and $E_d = -1.6$ eV, $\Delta = 0.18$ eV given by Kjöllerström (1969). A negative value of E_d, i.e. virtual bound state bellow the Fermi level, is expected for Pd which

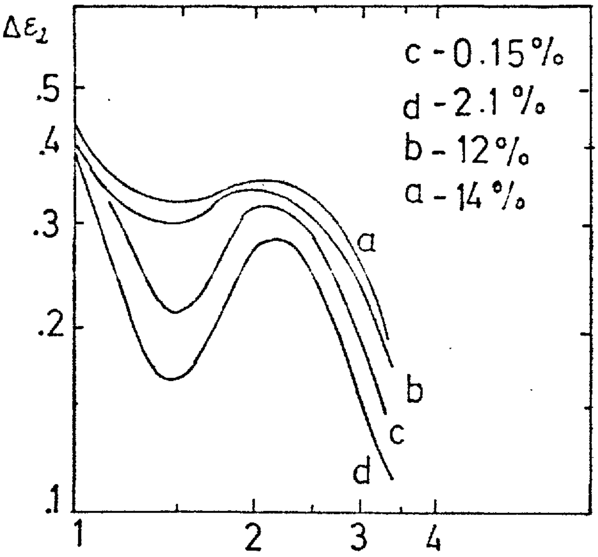


Figure 3: The optical absorption as a function of energy for different concentration of Pd in Ag. (Callender and Schnatterly, 1973)

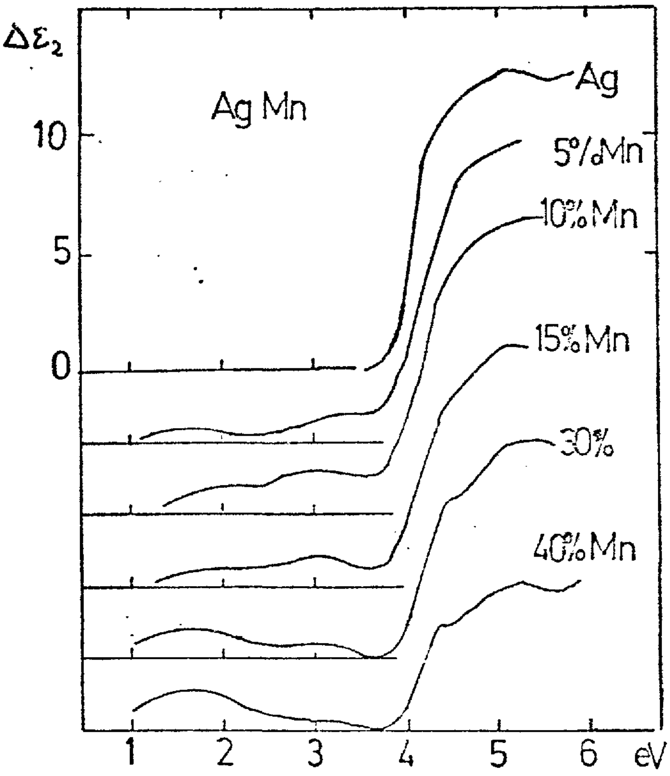


Figure 4: The optical absorption as a function of energy in the case of Au Mn. (Myers et al., 1968)

has a nearly filled d-shell.

Evaluating the scattering potential V^2 from the amplitude of the expression (15) and using an estimated value for the conduction electrons density of states, $\rho(\omega_F) \simeq 0.23\ (eV)^{-1}$, the width of the virtual bound state is about $\tilde{\Delta} = \pi V^2 \rho(\omega_F) \simeq 0.45$ eV; almost a factor of 2 larger than Δ estimated from the shape of eq. (17). This discrepancy is not really unexpected since eq. (17) was derived assuming that only the resonant ($\ell=2$) phase-shifts are different from zero. However, one knows that in order to get the quantitative agreement with the experimental data, d-phase shifts only are not sufficient. s- and p- phase shifts have to be taken into account as well, as can be seen from the example of residual resistivities or thermopower of dilute alloys (see Chapter 3).

We notice that in such a way the conduction electron's phase shifts are becoming almost uniquely determined. (The strongest condition upon the phase shifts is the Friedel sum rule). It would be interesting to see whether it is possible to find unique a set of phase shifts which would give a good agreement between this simple one-electron theory and experiments, as different as e.g. optical absorption and thermopower measurements.

In the case of the magnetic impurities one expects to see a doubly-peaked structure in the absorption spectra corresponding to the spin-split virtual bound state. Figure (4) shows two peaks observed in the interband absorption in the Ag Mn alloys. Estimating the parameters of the virtual bound state (Grüner, 1973) one has approximately: $E_d \simeq 0$, $\Delta = 0.5$ eV and $(U + 4J) \simeq 5$ eV. These values are consistent with the magnetic character of the manganese in silver and with the Friedel-Anderson condition $(U + 4J)/\pi\Delta > 1$. A similar spin split virtual bound state is observed in Au Mn and Cu Mn alloys. The splitting energy is about 5 eV, suggesting that U + 4J as an intra-atomic property of the impurity is independent of the host.

A detailed description of the optical and photoemission properties of dilute alloys and the values of the parameters of the Anderson model deduced from those properties is given in the review paper by G. Grüner (1973).

In the case of the aluminium based alloys the experimental situation, as regards the optical properties, is still not quite clear. However, the existing Al Mn data provide an interesting example. Measuring the optical reflectivity of several Al Mn alloys, Beaglehole and Will (1973) observed some extra absorption due to the interband transitions from the manganese d-states, spread over several eV. The total intensity is that of about five d-electrons, placed symmetrically below and above the Fermi level, but no doubly peaked structure in the local density of states is observed. (We notice that the optical experiments cannot give any information about the electronic structure close to the Fermi level, because of "Drude" absorption. However, strong energy variation of the density of states close to the Fermi level will show up in rapid temperature variations of the transport and thermal properties.)

Beagleholes result is hard to understand in the same Hartree-Fock picture which we used to explain the data on systems like Au Mn or Ag Pd. If, on one hand, we assume that $n_d(\varepsilon)$ is a simple Lorentzian placed at ε_p (and of the width Δ), the optical data would suggest that Δ is extremely large (few eV). On the other hand, from the specific heat or the transport properties one would conclude that, close to ε_F, the density of states is well represented by a very narrow Lorentzian (of width $\simeq 0.1$ eV) symmetrical with respect to the Fermi level. Thus, most of the d-electrons should not be observable in the optical measurements.

In order to reconcile these two experimental observations, i.e. that

(i) there is a narrow peak in the density of states close to ε_F;

(ii) most of the d-electrons are far away from ε_F, Grüner and Zawadowski (1972) suggested that the density of states should have basically the same form as function $n_d(\varepsilon)$ obtained here in the "single pole dominance" approximation ((eq. 6) and fig. 1).

1.6 Remark on the Specific Heat Due to the LSF

In this section we discuss the LSF contribution to the electronic part of the specific heat of a simple-metal transition-metal alloy. We show that in the zero temperature limit this contribution gives rise to a linear behaviour and that it is only the width of the narrow peak in the spectral density (inverse of the LSF temperature) which enters the expression for the specific heat.

At low temperatures the specific heat of a metal can be expressed by

$$C(T) = \gamma T + \alpha T^3 \tag{16}$$

where the linear and cubic terms describe the electron and phonon contributions respectively. Since we are interested in the low temperature properties ($T < \theta_D$) the higher order terms have been neglected.

In general, when the transition metal impurity is added to the host one can expect that it will not just change the coefficients of the two terms in the expression (1) but also give rise to new "magnetic" terms which, though electronic in nature, can be non-linear in temperature. However, it is often difficult to single those terms out because of different spurious contributions to the specific heat coming, e.g. from phonons or concentration effects (Rizzuto, 1974). Thus we shall primarily be concerned with the increase in the linear term, $\Delta\gamma/c$, due to the interactions between electrons and isolated impurity.

The Hartree-Fock approximation of the Anderson Hamiltonian (Klein and Heeger, 1966) gives in the zero temperature limit $\Delta\gamma/c$ simply proportional to the density of local states at the Fermi level. One has

$$\frac{\Delta\gamma}{c} = \frac{\pi^2 k_B^2}{3} \Sigma_\sigma \rho_d^\sigma(\varepsilon_F) \tag{17}$$

and this expression works satisfactorily for alloys in which the LSF effects can be neglected. However, in systems like Cu Fe or Al Mn one finds $\Delta\gamma/c$ to be greatly enhanced over the values predicted by the Hartree-Fock theory. Measurements by Aoki and Otsuka (1969) give $\Delta\gamma/c = 0.44$ (mJ/mol K^2) for Al Mn and $\Delta\gamma/c = 0.3$ (mJ/mol K^2) for Al Cr, which would imply that the width of the virtual bound state is one order of magnitude smaller than what is expected on the basis of the Friedel-Anderson theory.

To obtain the contribution to the electronic specific heat due to the spin fluctuations, we follow a method of Abrikosov, Gorkov and Dzyaloshinskii (1964, § 19.5). We calculate the entropy of an interacting Fermi liquid at non-zero temperature from which the coefficient $\Delta\gamma/c$ is simply given by

$$\frac{\Delta\gamma}{c} = \left.\frac{dS}{dT}\right|_{T=0} \tag{18}$$

In what follows, we outline the main steps of the calculation.

The starting point is the observation that the knowledge of the total number of particles in a system enables one to determine the entropy, from the thermodynamic relation

$$\left(\frac{\partial N}{\partial T}\right)_\mu = \left(\frac{\partial S}{\partial \mu}\right)_T , \tag{19}$$

where $N(\mu, T)$ is the total number of particles at a given chemical potential μ and temperature T. In the case of the Anderson Hamiltonian we have (at finite temperatures)

$$N(\mu,T) = 2Tk_B \Sigma_n G(\varepsilon_n) e^{i\varepsilon_n \tau} \tag{20}$$

and the notation is the same as in Chapter 1.

Since we are concerned mostly with the low temperature properties (low with respect to the degeneracy temperature of the local Fermi gas) we expand $N(\mu,T)$ up to terms linear in T and obtain the difference

$N(\mu,T) - N(\mu,0)$,

$$N(\mu,T) - N(\mu,0) = -2Tk_B \Sigma_n \frac{\partial}{\partial\mu} \ln G(0,\varepsilon_n) + \text{(terms independent of temperature)} \tag{21}$$

Differentiating with respect to temperature (with constant μ) and comparing it with the expression (4) we have the entropy

$$S = -2 \frac{\partial}{\partial T} Tk_B \Sigma_n \ln G(\varepsilon_n) \tag{22}$$

Evaluating the sum over imaginary frequencies in a standard way, we obtain for $\Delta\gamma/c$

$$\frac{\Delta\gamma}{c} = \frac{\pi^2 k_B^2}{3} \Sigma_\sigma \frac{1}{\pi} \text{Im} \frac{1}{G^R_{d\sigma}} \frac{\partial}{\partial\varepsilon} G^R_{d\sigma} \tag{23}$$

where $G^R_{d\sigma}(\omega)$ is the Fourier transform of the retarded local Green function evaluated at zero temperature.

Here we would like to point out that the above derivation of the specific heat enhancement should be equally valid in the case of an alloy described by the Wolff Hamiltonian. The only difference is that in the final expression (eq. 23) one replaces the d-electron Green function $G^R_{d\sigma}(\omega)$ by a local function $G^R_{o\sigma}(\omega)$ which, in the Wolff model, describes an electron localised at the impurity site $R_i=0$, rather than an electron in a well defined angular state ($\ell=2$ in our case).

Going back to the Anderson model we recall first that $G^R_{d\sigma}$ is given by eq. (4) with positive sign in front of Δ, i.e.

$$G^R_d = \frac{1}{\omega - E_d + i\Delta - \Sigma_d}$$

and secondly, if we assume that it is the scattering on spin fluctuations which gives the most important contribution to the self-energy Σ_d, we can write an approximate expression for $G_{d\sigma}$ which is valid in the zero temperature limit and for energies close to Σ_F. We have from equation (11)

$$G_d \simeq \frac{M}{\Delta} \frac{1}{\omega + iM}$$

so that finally we obtain $\Delta\gamma/c$ (for $2\ell+1$ times degenerate level)

$$\frac{\Delta\gamma}{c} = \frac{2\pi^2\, k_B^2}{3}\;\frac{(2\ell + 1)}{\pi\, M} \tag{24}$$

The low temperature specific heat depends linearly on temperature and we notice that it is not the Hartree-Fock width Δ which enters the expression (24) but rather it is M, the width of the narrow peak in the density of states which develops at the Fermi level as the result of the interactions between local electron and spin fluctuations (Hargita and Coradi, 1969; Caroli et al., 1969).

From the data of Aoki and Otsuka (1969) we obtain M=0.17 (eV) and M=0.28 (eV) for Al Mn and Al Cr respectively, values which are consistent with M determined from different kinds of experiments (e.g. T^2 dependence of the resistivity).

At higher temperatures we were not able to calculate the LSF contribution in a rigorous way. However, if we assume that the main effect comes from the temperature dependence of the spectral density, we can speculate that equations (23) and (24) are still valid at $T \neq 0$ but with M replaced by the effective width $\Gamma(T)$. From equation (13) we would then have

$$\Gamma(T) = M\left[1 + \frac{\pi^2}{2}\left(\frac{k_B\, T}{M}\right)^2\right]$$

and the specific heat would deviate from the linear law as

$$C_V = \frac{2\ell+1}{M}\;\frac{2\pi^2 kT}{3}\left[1 - \frac{\pi^2}{2}\left(\frac{RT}{M}\right)^2\right] \tag{25}$$

Finally, we want to mention some preliminary results for the specific heat obtained following the method suggested by Kjöllerström, Scalapino and Schrieffer (1966). They derive an expression for the ground state energy of the Anderson Hamiltonian,

$$E(T) = -\frac{1}{\pi}\int_{-\infty}^{\varepsilon_F} d\varepsilon \; f(\varepsilon) \; \mathrm{Im}\{(\varepsilon - i\Delta)\; G_d(\varepsilon + i\delta)\} \qquad (26)$$

from which the specific heat is obtained as

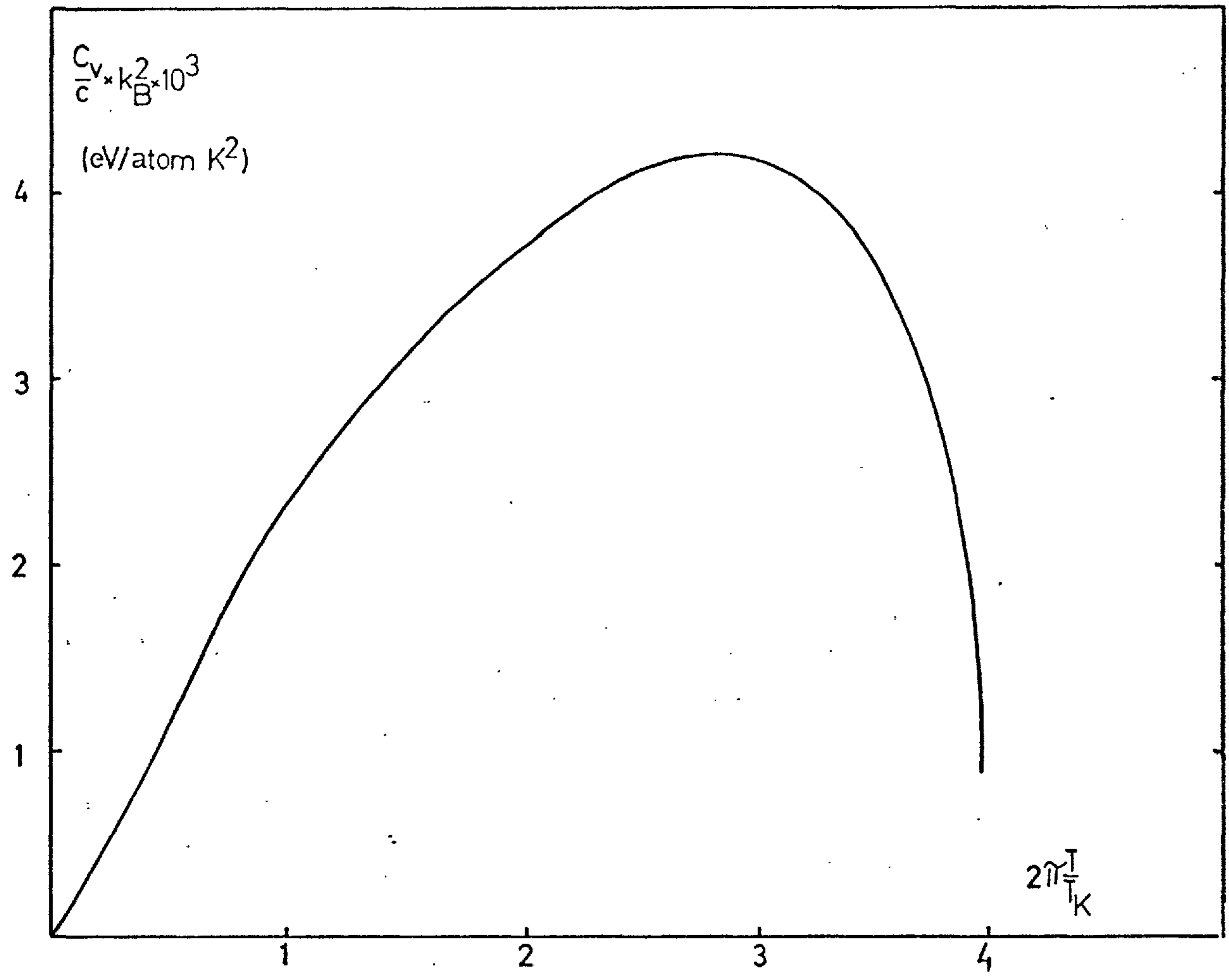
$$C_V = \frac{\partial E}{\partial T} \qquad (27)$$

However, we notice that the expression (26) for the ground state energy is not convergent, even in the case of a truly "non-magnetic" virtual bound state, hence one has to introduce a cutoff in the energy integration before making the derivative with respect to temperature. (Derivation of equations (57) and (61) in paper by Kjöllerström et al. is incorrect since operations $\frac{\partial}{\partial T}\int d\varepsilon$ and $\int d\varepsilon \frac{\partial}{\partial T}$ are not commutable in general).

Choosing the cutoff energy of the order of Δ and substituting for $G_d(\varepsilon)$ in equation (26) our expression (5), we have evaluated C_V numerically. The result of the calculation is shown in Figure (5).

For temperatures below 0.1 $\tilde{T}$ ($\tilde{T} = 2\pi\, T/T_K$) numerical values agree well with those obtained from equation (24). At higher temperatures, the specific heat exhibits the characteristic "hump" with maximum at about $3\tilde{T}$, but for temperatures large enough, we obtain the unphysical result

Figure 5



The specific heat obtained from the equation (26) in the text, plotted as a function of the reduced temperature $\tilde{T} = 2\pi\ T/T_K$.

that the specific heat becomes negative. Also, at present, we are not certain how the effect of choosing different cutoffs will influence the shape of the specific heat curves.

Appendix A

We have to evaluate the expression

$$I = I_1 + I_2$$

where

$$I_1 = \int_{-\infty}^{\infty} d\varepsilon \; b(\varepsilon) \frac{\varepsilon}{\varepsilon^2 + M^2} \frac{1}{\varepsilon - E_d + z \pm i\Delta}$$

and

$$I_2 = \int_{-\infty}^{\infty} d\varepsilon \; f(\varepsilon) \frac{\Delta}{(\varepsilon - E_d)^2 + \Delta^2} \frac{1}{M \mp i(z - \varepsilon)}$$

and where b(ε) and f(ε) are Bose and Fermi functions

$$b(\varepsilon) = \frac{1}{e^{\varepsilon/\beta} - 1}$$

$$f(\varepsilon) = \frac{1}{e^{\varepsilon/\beta} - 1}$$

Integrals of such a form are often encountered when dealing with the finite temperature Green functions, i.e. when evaluating sums over Bose and Fermi imaginary frequencies.

To evaluate I we expand the meromorphic functions b(ε) and f(ε) in the series around their simple poles (Lavrentiev and Chabat, 1972, p. 433),

$$b(\varepsilon) = -\frac{1}{2} + \frac{1}{\varepsilon\beta} + \frac{2}{\beta}\sum_{n=1} \frac{\varepsilon}{\varepsilon^2 + Y_n^2}$$

$$f(\varepsilon) = \frac{1}{2} - \frac{2}{\beta}\sum_{n=0} \frac{\varepsilon}{\varepsilon^2 + X_n^2}$$

where

$$Y_n = \frac{2n}{\beta}\pi \qquad \text{and } X_n = \frac{2n+1}{\beta}\pi$$

In such a way we can write for I

$$I = A + B + C$$

where

$$A = -\frac{1}{2}\int_{-\infty}^{\infty} d\varepsilon \left(1 - \frac{2}{\varepsilon\beta}\right)\frac{\varepsilon}{\varepsilon^2 + M^2}\,\frac{1}{\varepsilon - E_d + z \pm i\Delta}$$

$$+ \frac{1}{2}\, d\varepsilon\, \frac{\Delta}{(\varepsilon - E_d)^2 + \Delta^2}\,\frac{1}{M \mp i(z - \varepsilon)}$$

$$B = -\frac{2}{\beta}\sum_{n=0}\int d\varepsilon\, \frac{\varepsilon}{\varepsilon^2 + X_n^2}\,\frac{\Delta}{(\varepsilon - E_d)^2 + \Delta^2}\,\frac{1}{M \mp i(z - \varepsilon)}$$

$$C = \frac{2}{\beta}\sum_{n=1}\int d\varepsilon\, \frac{\varepsilon}{\varepsilon^2 + Y_n^2}\,\frac{\varepsilon}{\varepsilon^2 + M^2}\,\frac{1}{\varepsilon - E_d + z \pm i\Delta}$$

Using Jordan's lemma we can calculate A, B and C making the contour integration along the real axis and semicircle in the upper (or lower) half-plane. From the theory of residues we then have for A

$$A = \frac{1}{z - E_d \pm i(M + \Delta)} \; \frac{\pi}{M\beta}$$

To evaluate B (and C) we decompose the integral as follows

$$B = \pm \frac{1}{\beta} \; \frac{1}{E_d - z + i\Delta \mp iM} \sum_{n=0} \int d\varepsilon \frac{\varepsilon}{\varepsilon^2 + X_n^2} \left[\frac{1}{\varepsilon - E_d - i\Delta} - \frac{1}{\varepsilon - z \mp iM} \right]$$

$$\pm \frac{1}{\beta} \; \frac{-1}{E_d - z - i\Delta \mp iM} \sum_{n=0} \int d\varepsilon \; \frac{\varepsilon}{\varepsilon^2 + X_n^2} \left[\frac{1}{\varepsilon - E_d + i\Delta} - \frac{1}{\varepsilon - z \mp iM} \right]$$

Using now Jordan's lemma we have for the integral in the first term

$$\pi \sum_{n=0} \left[\frac{1}{\frac{2n+1}{\beta}\pi + \Delta - iE_d} - \frac{1}{\frac{2n+1}{\beta}\pi + M \mp iz} \right]$$

and an analogous expression for the second integral.

Comparing this with the definition of the ψ-functions (Abramovitz and Stegun, 1965)

$$\psi(1 + z) = -\gamma - \sum_{n=0} \left(\frac{1}{n + 1 \; z} - \frac{1}{n + 1} \right)$$

where γ is the Euler's constant, we obtain for B

$$B = \pm \frac{1}{2} \frac{\psi\left(\frac{1}{2} + \frac{\Delta - iE_d}{2\pi}\beta\right) - \psi\left(\frac{1}{2} + \frac{M \mp iz}{2\pi}\beta\right)}{E_d - z + i\Delta \mp iM} \pm$$

$$\pm \frac{1}{2} \frac{\psi\left(\frac{1}{2} + \frac{\Delta + iE_d}{2\pi}\beta\right) - \psi\left(\frac{1}{2} + \frac{M \mp iz}{2\pi}\beta\right)}{E_d - z - i\Delta \mp iM}$$

and in exactly the same way

$$C = \frac{z - E_d \pm i\Delta}{\left[z - E_d \pm i(\Delta + M)\right]\left[z - E_d \pm i(\Delta - M)\right]}\left[\psi\left(1 + \frac{\Delta \mp iE_d}{2\pi}\beta\right) - \psi\left(1 + \frac{M\beta}{2\pi}\right)\right]$$

Summing A, B and C we obtain equation (5c) in the text.

CHAPTER 2

TEMPERATURE DEPENDENCE OF THE RESISTIVITY DUE TO THE LOCALISED SPIN FLUCTUATIONS IN SIMPLE-METAL TRANSITION-METAL ALLOYS

2.1 Introduction

In this chapter we want to discuss the effect of localised spin fluctuations on the resistivity of simple-metal transition-metal alloys. We start with some experimental considerations. It was observed by Caplin and Rizzuto (1968) that systems like Al Mn exhibit a small minimum in the total resistivity. The initial decrease of the resistivity is quadratic in temperature up to about 50K and after about 80K it becomes linear (Babić et al., 1971). Similar temperature variation (but with the characteristic temperature ranging between 1K and 1000K) was later found in several different systems in which the transition-metal or rare earth impurity is dissolved in a simple-metal host. Compiling the data on a great number of such alloys Rizzuto, Babić and Stewart (1973) have shown that the resistivity can be described by the "universal" curve which has T^2, T and ln(T) functional dependence and eventually reaches the high temperature plateau. In particular, they produced the evidence that in quite a few systems the extension of the log(T) term over several decades in temperature was due to interactions between impurity atoms.

Theoretically, the T^2 decrease in the resistivity was explained by Rivier and Zuckermann (1968) on the basis of the RPA approximation of the Anderson Hamiltonian. The main points in their derivation were:

(i) the temperature variation of the resistivity is due to the scattering of local electrons on the spin fluctuations;

(ii) the LSF propagator is defined by the expression (1), Ch. 1.

In what follows we extend their calculations to higher temperatures and show that the resistivity obtained in such a way has all the features mentioned in connection with experiment (Rivier and Zlatić, 1972).

However, as explained in the previous chapter, we do not calculate the LSF lifetime directly from the Anderson Hamiltonian but consider it as a phenomenological parameter which determines the characteristic temperature of the system. We notice that for a given temperature range one goes smoothly from "magnetic" to "non-magnetic" behaviour as τ is varied.

In the next section we first set up the Boltzmann equation for the conduction electrons in the presence of N_i impurities and derive an expression for the relaxation time in terms of d-electrons' Green function. Using the expression for $G_d(\omega)$ derived in the Chapter 1, we discuss the temperature dependence of the resistivity as a function of the LSF lifetime and parameters E_d and Δ of the Anderson model. Eventually, we compare our results with the experimental data.

2.2 The Relaxation Time

In the presence of electrical field the electrical current is given by the expression

$$j = 2e \int \frac{d^3\underset{\sim}{p}\underset{\sim}{v}\ f(\underset{\sim}{p})}{(2\pi\hbar)^2}$$

where $f(\underset{\sim}{p}, \underset{\sim}{r})$ is the non-equilibrium distribution function, $\underset{\sim}{v}$ is the velocity of the conduction electrons and the integration is performed over all momentum space.

Due to the collisions with the impurity atoms (this is assumed to be the only process through which the electrons can relax) the distribution function $f(\underset{\sim}{p})$ is changing in time. Its rate of change is given by the kinetic equation

$$\frac{df}{dt} = I(f) \qquad (2)$$

where $I(f)$ is the collision integral which has to be calculated.

If $V(\underset{\sim}{r})$ is the perturbation potential acting on the conduction electron due to the presence of all the impurities, with local potential $v(\underset{\sim}{r})$

$$V(\underset{\sim}{r}) = \Sigma_i\, v(\underset{\sim}{r} - \underset{\sim}{R}_i),$$

and $V_{\underset{\sim}{p}\underset{\sim}{p}'}$ is its matrix element (in the unit volume), the collision integral can be written as

$$I(f) = \frac{2\pi}{\hbar} \int |V_{\underset{\sim}{p}\underset{\sim}{p}'}|^2 \{f(\underset{\sim}{p})(1-f(\underset{\sim}{p}')) - f(\underset{\sim}{p}')(1-f(\underset{\sim}{p}))\} \times$$

$$\times \ (\varepsilon_{\underset{\sim}{p}} - \varepsilon_{\underset{\sim}{p}'})\ \frac{d^3p'}{(2\pi\hbar)^3} \qquad (3)$$

The first term describes the process in which the electron is scattered from the state $\mathbf{p}$ into $\mathbf{p}'$ while the second describes the transition from $\mathbf{p}'$ into $\mathbf{p}$.

In the dilute alloy, with N_i impurities placed at random, we can replace $|V_{pp'}|^2$ by the square of the average local potential $|v_{pp'}|^2$; thus, we can deal formally with the one impurity problem (Edwards, 1958; Abrikosov et al., 1964). We see how it happens in the following.

If the matrix element of the conduction electron Bloch function is given by

$$\phi_{\mathbf{p}} = e^{i\mathbf{p}\mathbf{r}}\, u_{\mathbf{p}}(\mathbf{r})$$

where $u_{\mathbf{p}}(\mathbf{r})$ is a periodic function, the matrix element $V_{\mathbf{p}\mathbf{p}'}$ can be written as

$$V_{\mathbf{p}\mathbf{p}'} = \int dV\; e^{-i(\mathbf{p}-\mathbf{p})} u_{\mathbf{p}}(\mathbf{r})\; u_{p}(\mathbf{r}) \sum_i v(\mathbf{r}-\mathbf{R}_i)$$

$$= |v_{pp'}|^2 \sum e^{-i(\mathbf{p}-\mathbf{p}')\mathbf{R}_i}$$

where the sum goes over all the impurity atoms (placed at $\mathbf{R}_i$) in the unit volume.

The average potential $|\bar{V}_{pp'}|^2$ is given by

$$|V_{\mathbf{p}\mathbf{p}'}|^2 = N_i\; |v_{\mathbf{p}\mathbf{p}}|^2$$

since we have the relation

$$\overline{\sum e^{-\,i(\mathbf{p}-\mathbf{p}')(\mathbf{R}_i-\mathbf{R}_j)}} = N_i\, \delta_{ij}$$

The momentum integration in equation (3) can be written in a standard way as $\int \ldots .\, d^3\mathbf{p} = \int \ldots .\, d\varepsilon\, \frac{dS}{v}$

and we notice that

$$\frac{2}{(2\pi\hbar)^3}\int\frac{dS}{v} = \rho(\varepsilon)$$

where the integration goes over the surfaces of constant energy, $\varepsilon(p)$ = const and $\rho(\varepsilon)$ is the density of states of the conduction electrons. In such a way the collision integral becomes

$$I(f) = \frac{2\pi}{\hbar} N_i \int \frac{dS}{v(\underset{\sim}{p}')} |v_{pp'}|^2 \{f(\underset{\sim}{p}') - f(\underset{\sim}{p})\} \qquad (4)$$

Next, we introduce the function $f_1(p)$

$$f_1 = f - f_o$$

which measures the deviations of the distribution function from its equilibrium value, and the quantity $W_{pp'}$,

$$W_{pp'} = \frac{\pi}{\hbar} N_i |v_{pp'}|^2 \rho(\varepsilon)$$

which is related to the conduction electrons' scattering cross section $\frac{d\sigma}{d\Omega}$,

$$\frac{d\sigma}{d\Omega} = \frac{2\pi}{\hbar v}|v_{pp'}|^2 \rho(\varepsilon)$$

One has

$$W_{pp'} = \frac{v\,Ni}{2}\frac{d\sigma}{d\Omega} \qquad (5)$$

For the isotropic scattering process the integration over dS in equation (4) can be transformed to an integration over solid angle and we obtain for I(f) the usual result

$$I(f) = \int \frac{d\Omega}{4\pi} W(\theta) \{f(p') - f(p)\} \tag{6}$$

When the applied electrical field E is small, and this is the case in any experimental situation, the deviations of the distribution function from its equilibrium value should be linear in $\underset{\sim}{E}$. At the same time one knows that $f(\underset{\sim}{p})$ should be a scalar so that the obvious ansatz for the form of f_1 is

$$f_1(\underset{\sim}{p}) = \underset{\sim}{p}\underset{\sim}{E}\ \eta(\varepsilon) = pE\ \eta(\varepsilon)\ \cos(\underset{\sim}{p}, \underset{\sim}{E})$$

where $\eta(\varepsilon)$ is a function of energy.

Substituting this in equation (6) and performing the integration over Ω, we obtain for the collision integral (Mott and Jones, 1936, Ch. VII, §8)

$$I(p) = - f_1(\underset{\sim}{p}) \int W(\theta)(1-\cos\theta) \frac{d\Omega}{\eta\pi}$$

Defining the relaxation time as

$$\frac{1}{\tau} = \int W(\theta)(1 - \cos\theta) \frac{d\Omega}{4\pi}$$

or

$$\frac{1}{\tau} = \frac{N_i\ v}{2} \int \frac{d\sigma}{d\Omega} (1 - \cos) \frac{d\Omega}{4\pi}$$

one can write the kinetic equation as

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \underset{\sim}{v}.\nabla_r f + e\underset{\sim}{E}.\nabla_{\underset{\sim}{p}} f = - \frac{f-f_o}{\tau} \tag{8}$$

Thus, the knowledge of the scattering amplitude of the conduction electrons enables us to find the relaxation time τ (equation (7)) and solve, in principle, the kinetic equation. Since in the resistivity (conductivity) experiments the applied electrical field is usually small the current is in a stationary state and the transport equation reads

$$e\underset{\sim}{E}\,\frac{\partial f}{\partial \underset{\sim}{p}} = -\,\frac{f-f_o}{\tau}$$

or

$$f_1 = -\,e\underset{\sim}{E}\,\underset{\sim}{v}\,\frac{\partial f_o}{\partial\,\varepsilon}\,\tau$$

The total current, given by equation (1), can now be expressed through the relaxation time as

$$\underset{\sim}{j} = 2e^2\int \underset{\sim}{v}\ (\underset{\sim}{v}\underset{\sim}{E})\ \tau\ (-\,\frac{\partial f}{\partial \varepsilon})\ \rho\ (\varepsilon)\ d\varepsilon\ \frac{d\Omega}{4\pi}$$

Integrating over the angle and assuming that the field is parallel to the z - axis, we obtain for the conductivity

$$\sigma = \frac{2e^2}{3}\ v_F^2\ \rho(\varepsilon_F)\int d\varepsilon(-\,\frac{\partial f}{\partial \varepsilon})\,\tau(\varepsilon) \tag{9}$$

Using the optical theorem we can relate the conduction electrons transport relaxation time to their scattering matrix (T-matrix). From the optical theorem we have

$$\sigma^x_{total} = -\,\frac{2}{\hbar v_F}\ \mathrm{Im}\ T_{pp}$$

where $T_{pp'}$ is the matrix element of the T-matrix which can be written as

$$T_{pp'} = 4\pi\Sigma_{\ell}(2\ell+1)T_{\ell}P_{\ell}(\cos\ \theta).$$

In the Friedel Anderson model, only the $\ell=2$ spherical component is different from zero and it can be obtained from the d-electrons' Green function as

$$T_2 = VG_dV. \tag{10}$$

Thus, the relaxation time can be written as

$$\frac{1}{\tau} = -\frac{2(2\ell+1)N_i}{\hbar} V^2 \text{ Im } G_d(\varepsilon) \tag{11}$$

G_d was calculated in the previous section and we shall use those results to discuss the resistivity of some simple-metal transition-metal alloys.

2.3 Residual Resistivity

We first look at the increase in the residual resistivity of a dilute alloy due to the presence of c-atomic % of impurities. At T=0 we have for $\Delta\rho(0)$, from equations (9) and (11),

$$\Delta\ \rho(0) = \frac{10mV^2}{e^2\ \hbar} \text{ Im } G_d(\varepsilon_F) \times \frac{c}{100} \tag{12}$$

Defining the resonant ($\ell=2$) phase shift of the conduction electrons (due to their scattering on the 3-d impurity) as

$$\text{tg}\ \delta_2 = \frac{\text{Im } T_2}{\text{Re } T_2}$$

where T_2 is the scattering matrix given by equation (10), we can rewrite the expression (12) in a well known form (Friedel and Daniel, 1964)

$$\Delta\rho(0) = c\,\rho_\mu \sin^2 \delta_2 \tag{13}$$

In eq. (10) c is the concentration of the impurities and ρ_μ is a constant which in real metals depends on the dnesity of states and the band structure of the host. (In the free electron model $\rho_\mu = (m/5\,e^2\hbar\pi\rho) = (\pi\hbar/5\,e^2 k_F)$.

This result for $\Delta\rho$ is in systematic agreement with the experimental data, as can be seen in figure (1), Ch. 3 and in the discussion thereafter. (See also Rizzuto, 1973). The maximum value of $\Delta\rho/c$ is obtained in the case when the virtual bound state is symmetrical with respect to the Fermi level ($E_d = 0$) and the corresponding phase shift is $\delta_2 = \pi/2$. This value, which defines the upper limit in the scattering power of the impurity for a given channel ($\ell = 2$, in our case), is called the unitarity limit.

2.4 Resistivity at Finite Temperatures

Discussing the finite temperature resistivity, we start from the systems for which the LSF life time is of the order of Δ^{-1}, i.e. with the "truly" non-magnetic systems. The local Green function has a simple Hartree-Fock form and Im G_d is equal to

$$-\operatorname{Im} G_d = \frac{\Delta}{\varepsilon^2 + \Delta^2}$$

From equation (9) we obtain for the resistance

$$\rho(T) = \Delta\,\rho(0) \quad 1 - \frac{\pi^2}{3}\left(\frac{k_B T}{\Delta}\right)^2$$

which is a constant for any physical temperature ($T_\Delta \approx 10^5$K).

Examples of systems which behave in this way are Al V, Al Co or Al Ni (Krsnik et al., 1973).

Increasing the LSF lifetime (so that it becomes much longer than the characteristic time defined by the width of the virtual bound state) we expect the effect of the local spin fluctuations to show up. The contribution of the LSF to the d-electron self-energy, Σ_d, was calculated in the previous chapter. Neglecting everywhere M with respect to Δ, we write for Σ_d

$$\Sigma_d = \Delta^2 \left\{ \frac{1}{\varepsilon - E_d \pm i\Delta} \left[\frac{\pi}{M\beta} + \psi\left(1 + \frac{\Delta \mp i(\varepsilon - E_d)}{2\pi}\beta\right) - \psi\left(1 + \frac{M\beta}{2\pi}\right)\right] - \right.$$

$$\left. - \frac{\pm i\Delta}{(\varepsilon - E_d)^2 + \Delta^2}\, \psi\left(\frac{1}{2} + \frac{M \pm i\varepsilon}{2\pi}\right) \mp \frac{1}{2}\left[\frac{1}{\varepsilon - E_d \pm i\Delta}\, \psi\left(\frac{1}{2} + \frac{\Delta + i E_d}{2\pi}\beta\right) - cc\right]\right\} \tag{14}$$

We recall that $\psi(\varepsilon)$ is digamma function, M the inverse of the LSF lifetime and that the transport relaxation time is proportional to

$$\frac{1}{\tau(\varepsilon)} \sim \frac{\left(1 - \dfrac{\mathrm{Im}\,\Sigma_d}{\Delta}\right)}{\left(1 - \dfrac{\mathrm{Im}\,\Sigma_d}{\Delta}\right)^2 + \dfrac{E_d^2}{2}\left(1 + \dfrac{\mathrm{Re}\,\Sigma_d}{E_d}\right)^2} \tag{14a}$$

Equation (9), (11) and (14a) determine the LSF part of the resistivity of a dilute alloy.

Before discussing the concrete form of this resistivity, we notice (for $k_B T/\Delta \ll 1$)

(i) The structure of equation (14) enables one to define the reduced temperature and energy

$$\tilde{T} = 2\pi \frac{T}{T_k}$$

and

$$\tilde{\varepsilon} = 2\pi \frac{\varepsilon}{k_B T_k}$$

so that the LSF resistivity becomes a universal function of T/T_K.

(ii) In the case of a system for which the resonant phase shift is $\delta_2 = \pi/2$ at zero temperature, the effect of the LSF is to decrease the scattering cross section, i.e. to give rise to a minimum in the total resistivity.

We now proceed with the evaluation of the resistivity. Neglecting the Fermi window integration we replace $(-\partial f/\partial\varepsilon)$ by a delta function. The fact that all the dynamics of the scattering has been expressed in the equation (14), justifies this commonplace approximation in our case. The error made at low temperatures will be evaluated below and it will be shown that the main effect of the energy integration is to reduce the characteristic temperature, when it is defined as coefficient of the T^2 term in the resistivity.

With these assumptions we obtain for the resistivity (in the case of the virtual bound state which is symmetrical with respect to the Fermi level)

$$\Delta\rho(T) = \Delta\rho(0) \frac{1}{1-2\ell n 2 + \tilde{T}/2 + 2\,\psi(2\,\tilde{T}) - 2\,\psi(\tilde{T})} \qquad (15)$$

This "universal" curve is plotted in figure (1) as a function of the reduced temperature $\tilde{T}$ and is normalized to one at T = 0.

Three main temperature behaviours can be distinguished:

(i) Below 0.4 $\tilde{T}$ the resistivity is a parabola

$$\Delta\rho(\tilde{T}) = \Delta\rho(0) \left[1 - \left(\frac{T}{\theta_1}\right)^2 \right] \qquad (16)$$

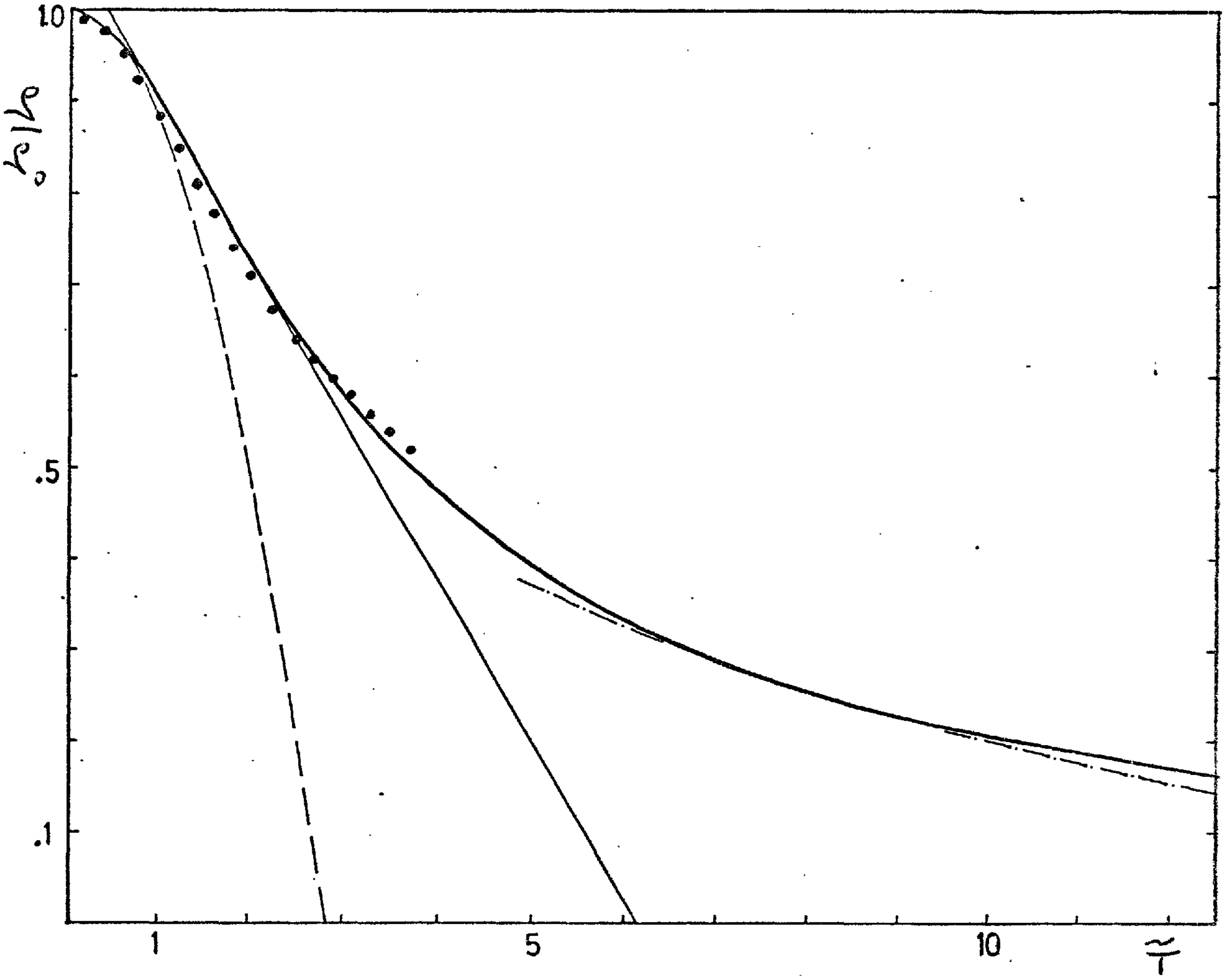
with the characteristic temperature $\theta_1^2 = (2/\pi^2)\, T_K^2$. Quadratic temperature dependence of the resistivity is a typical low temperature behaviour of a normal Fermi liquid when the electron-electron interaction gives a dominant contribution to the scattering amplitude of conduction electrons. (See e.g. Abrikosov, 1972).

To estimate the effect of the Fermi window integration we make use of the approximate expression for the relaxation time $\tau(\varepsilon, T)$, which is valid at low temperatures. From equation (11)(and equation (11), Ch. 1) we have

$$\tau^{-1} = c\, V^2\, \frac{M}{\Delta}\, \frac{\Gamma(T)}{\varepsilon^2 + \Gamma(T)^2} \qquad (17)$$

where $\Gamma(T)$ is the effective width introduced in the previous chapter. Making the Sommerfeld expansion we obtain for the resistivity the same expression as given by equation (16), but with θ_1 replaced by

Figure 1



The resistivity as a function of reduced temperature $\tilde{T} = 2\pi\ T/T_K$. Thin lines represent the three regions discussed in the text: parabolic, linear and logarithmic. Dots are the experimental points for Al Mn (Rizzuto, 1974).

θ_ρ, $\theta_\rho = \theta_1/\sqrt{2}$. Measurements of the low temperature resistivity determine the phenomenological pharameter T_k, one has $T_k = \pi\ \theta_\rho$.

(ii) In a second region, $\tilde{T} \varepsilon (0.9, 2.1)$ the resistivity is linear

$$\Delta\rho(T) = \alpha(1 - \frac{T}{\theta_2}) \qquad (18)$$

with $\alpha = 1.07\Delta\rho(0)$ and $\theta_2 = 2.83\ \theta_\rho$ (or $\theta_2 = 2.1\ \theta_1$). Linear temperature dependence is indeed expected when the conduction electrons are scattered by the Bose-like particles. Similarly to the scattering of conduction electrons on phonons, where the resistivity becomes linear at $T \simeq \theta_D/2\pi$, in the case of the LSF the linearity sets in at about $T \simeq T_K/2\pi$.
This follows from the fact that both Debye and LSF temperatures can be associated with an effective cutoff in the spectrum of the quasi-particles (Doniach, 1967).*

(iii) At temperatures above $T_K (6 < \tilde{T} < 10)$, the resistivity exhibits the logarithmic dependence characteristic of magnetic impurities

$$\Delta\rho(T) = A - B\ \ell n\ \tilde{T} \qquad (19)$$

where A = 0.757 and B = 0.565. Such a temperature dependence is relatively simple to understand in

---

* In the case of the localised spin fluctautions the lifetime of the quasi-particles coincides with the cutoff in the LSF spectrum, while in the case of phonons, τ_{ph} and θ_D are not simply related (Abrikosov et al., 1964).

the framework of the LSF theory, using a reasoning suggested by Rivier and Zuckermann (1968) as a possible explanation of the Kondo resistivity: when the temperature is higher then T_K the lifetime of conduction electrons becomes shorter than the lifetime of the spin fluctuations; the conduction electron does not have time to see that the magnetization on the impurity is ephemeral before losing the memory of its own spin. Hence, the logarithmic resistivity is characteristic of the scattering by targets having an internal structure (spin up and down) (Anderson, 1968).

Before making any comparison with the experimental data we want to look at the dependence of the resistivity on the position of the virtual bound state with respect to the Fermi level, i.e. we want to look at $\rho(T)$ as a function of E_d. To simplify the calculations, we assume first that $M \ll \Delta$ and $k_B T \ll M$. Real and imaginary part of the self-energy Σ_d (equation 14), which enter expression (14a) for the relaxation time τ, can be written (at $\varepsilon = \varepsilon_F$) as

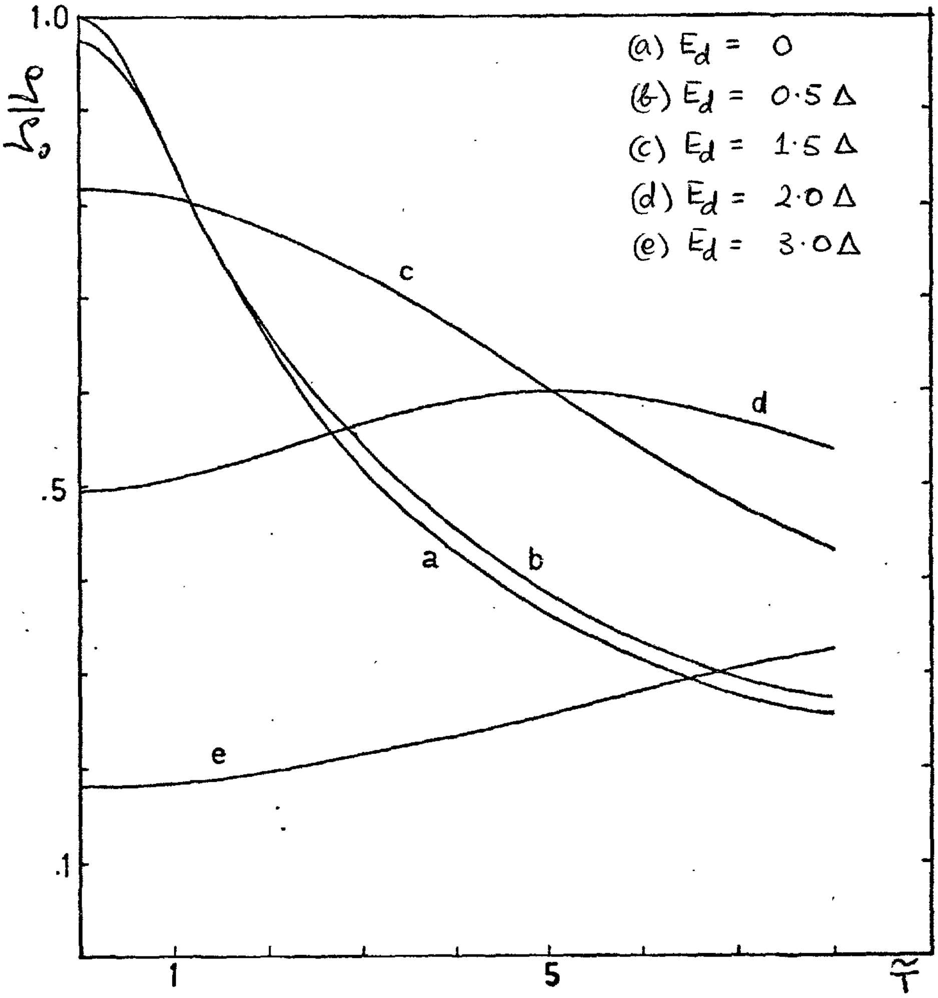
$$\frac{\mathrm{Re}\,\Sigma_d}{\Delta^2} \simeq -\frac{E_d}{E_d^2+\Delta^2}\left\{\frac{\tilde{\pi}}{M\Lambda} + \ln\frac{\Lambda}{2\tilde{\pi}}\sqrt{E_d^2+\Delta^2} - \psi\left(1+\frac{M\Lambda}{2\tilde{\pi}}\right)\right\} + $$

$$+ \frac{\Delta}{E_d^2+\Delta^2}\,\mathrm{tg}^{-1}\frac{E_d}{\Delta}$$

and

$$\frac{\mathrm{Im}\,\Sigma_d}{\Delta^2} \simeq -\frac{\Delta}{E_d^2+\Delta^2}\left\{\frac{\tilde{\pi}}{M\Lambda} + \psi\left(\frac{1}{2}+\frac{M\Lambda}{2\tilde{\pi}}\right) - \psi\left(1+\frac{M\Lambda}{2\tilde{\pi}}\right)\right\} \qquad (20)$$

Figure 2



The resistivity as a function of the position of the virtual bound state (E_d) plotted versus reduced temperature $\tilde{T}$.

Using the approximative expression for ψ-functions (Abramovitz and Stegun, 1965) valid at low temperatures ($M\beta >> 1$)

$$\psi(1 + \frac{M\beta}{2\pi}) \simeq \frac{\pi}{M\beta} + \ln\frac{M\beta}{2\pi} - \frac{1}{12}(\frac{2\pi}{M\beta})^2 + \theta(\frac{k_BT}{M})^4$$

we obtain, up to logarithmic accuracy i.e. $\ln(M/\Delta) << 1$,

$$1 - \frac{\operatorname{Im}\Sigma_d}{\Delta} \simeq 1 + \frac{\Delta^2}{E_d^2 + \Delta^2}\,\frac{\pi^2}{2}\cdot(\frac{k_BT}{M})^2$$

and

$$1 + \frac{\operatorname{Re}\Sigma_d}{E_d} \simeq C_d\left[C_d - \frac{\Delta}{E_d^2 + \Delta^2}\,\frac{2\pi^2}{3}\,(\frac{k_BT}{M})^2\right] \qquad (21)$$

where

$$C_d = 1 - \frac{\Delta^2}{E_d^2 + \Delta^2}\ln\frac{\sqrt{E_d^2 + \Delta^2}}{M}$$

Let us discuss two limiting cases:

If $E_d << \Delta$ we see from equations (14a) and (21) that the main effect of increasing E_d is to decrease residual resistivity and to slow down the temperature variations of $\rho(T)$. But all the features of $\rho(T)$ mentioned previously, in connection with eq. (15), remain basically unchanged.

In the opposite limit, $E_d >> \Delta$, we can neglect the first term in the denominator of eq. (14a), which results in a drastic change of the resistivity as a function of temperature. We have

$$\rho(T) \simeq \frac{\Delta - \operatorname{Im}\Sigma_d}{(E_d + \operatorname{Re}\Sigma_d)^2} \qquad (22)$$

which is, in the low temperature limit, a quadratic function of temperature with a positive coefficient of T^2.

In Figure (2) we have shown some of the results for the temperature dependence of the resistivity as a function of E_d, obtained by the computer analysis of equations (9) and (14a).

We notice, however, that in the situation in which $E_d >> \Delta$ the present treatment which completely neglects the electron-electron and hole-hole correlation, is susceptible to the criticism of Schrieffer and Mattis (1965). It is unlikely, in the case when the virtual bound state is either completely full or completely empty, that the electron-hole correlation gives the most dominant contribution to the self-energy Σ_d. For this reason we compare our results with the experimental data only for the systems in which the virtual bound state is nearly half-full, i.e. E_d close to zero.

2.5 Comparison with Experiment and Conclusion

Recently, there have been a lot of experimental efforts to determine accurately the single impurity contribution to the resistivity of dilute alloys, eliminating spurious effects like those due to phonon scattering or interactions between the impurities. Systematic presentation of experimental data, for a number of bulk properties, on alloys where the "isolated" transirion metal atom is dissolved in a simple metal host is given in the review paper by C. Rizzuto (1974). Typical temperature dependence of the systems we are concerned with is shown in Figures (3) and (4) (Rizzuto, 1974), and it can be summarized as follows.

At lowest temepratures a T^2 temperature variations is observed of the form

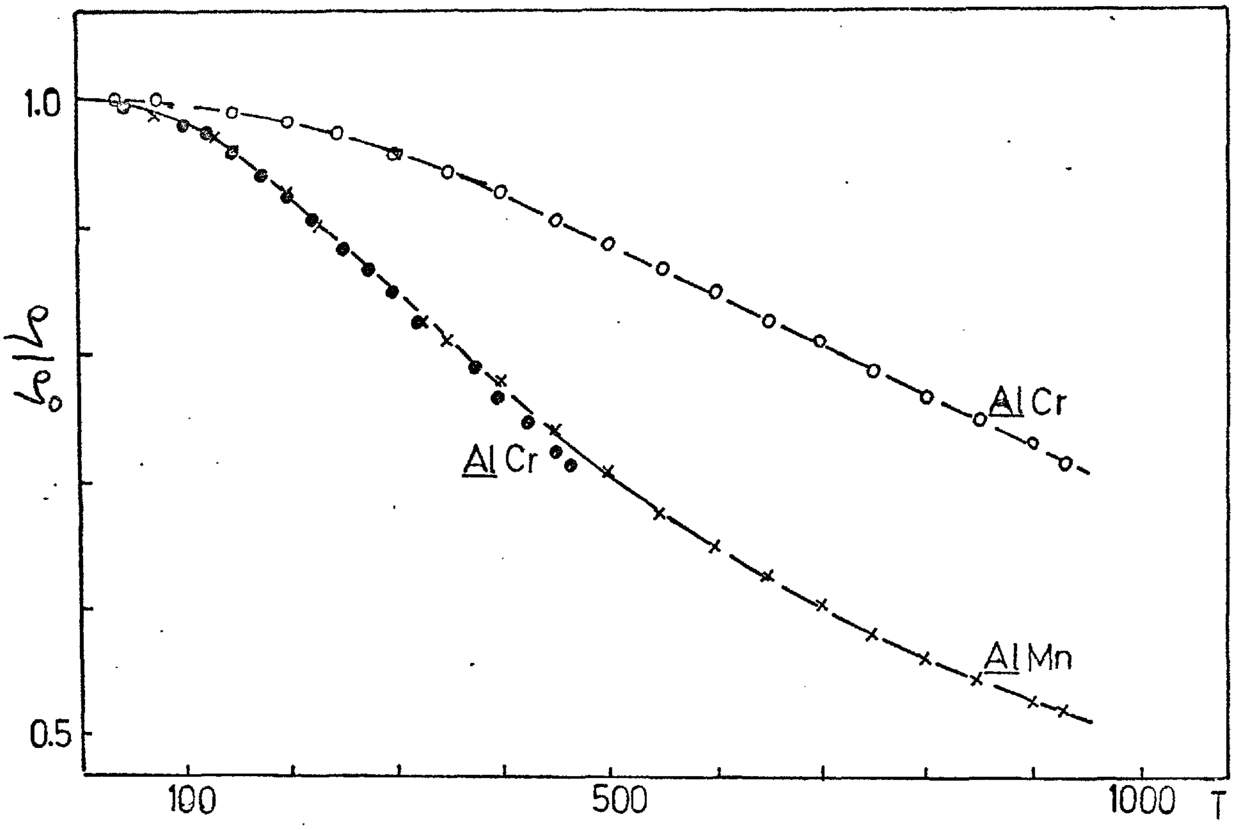
$$\rho(T) = \Delta\rho_o \left[1 - \left(\frac{T}{\theta_\rho}\right)^2\right]$$

which defines the experimental "scaling" temperature θ_ρ. As shown by Rizzuto (1974), θ_ρ agrees very well with the characteristic temperature $\theta_\times$ obtained from the Curie-Weiss plot of the susceptibility. Resistivity varies as T^2 up to about 0.1 θ_ρ, then has an extended linear region between about 0.1 to 0.8 θ_ρ and then varies as ln(T) between about θ_ρ and 6 θ_ρ.

Recalling that theoretically θ_ρ is defined as T_K/π we see, from the discussion following equation (15) in the preceding section, that the agreement between theory and experiment is excellent in the parabolic and linear resistivity regions. In Figure (1), the experimental data for Al Mn and Al Cr are fitted to the calculated curve (eq. 15), by choosing $k_B T_K$ = 0.13 eV for Al Mn and $k_B T_K$ = 0.26 eV for Al Cr.

Above θ_ρ the agreement between theory and experiment is less good: theoretically we would expect from eq. (15) logarithmic temperature dependence between about 3 θ_ρ and 6 θ_ρ, while experimentally it is observed between θ_ρ and 6 θ_ρ. However, we notice that "most systems where T^2.

Figure 3



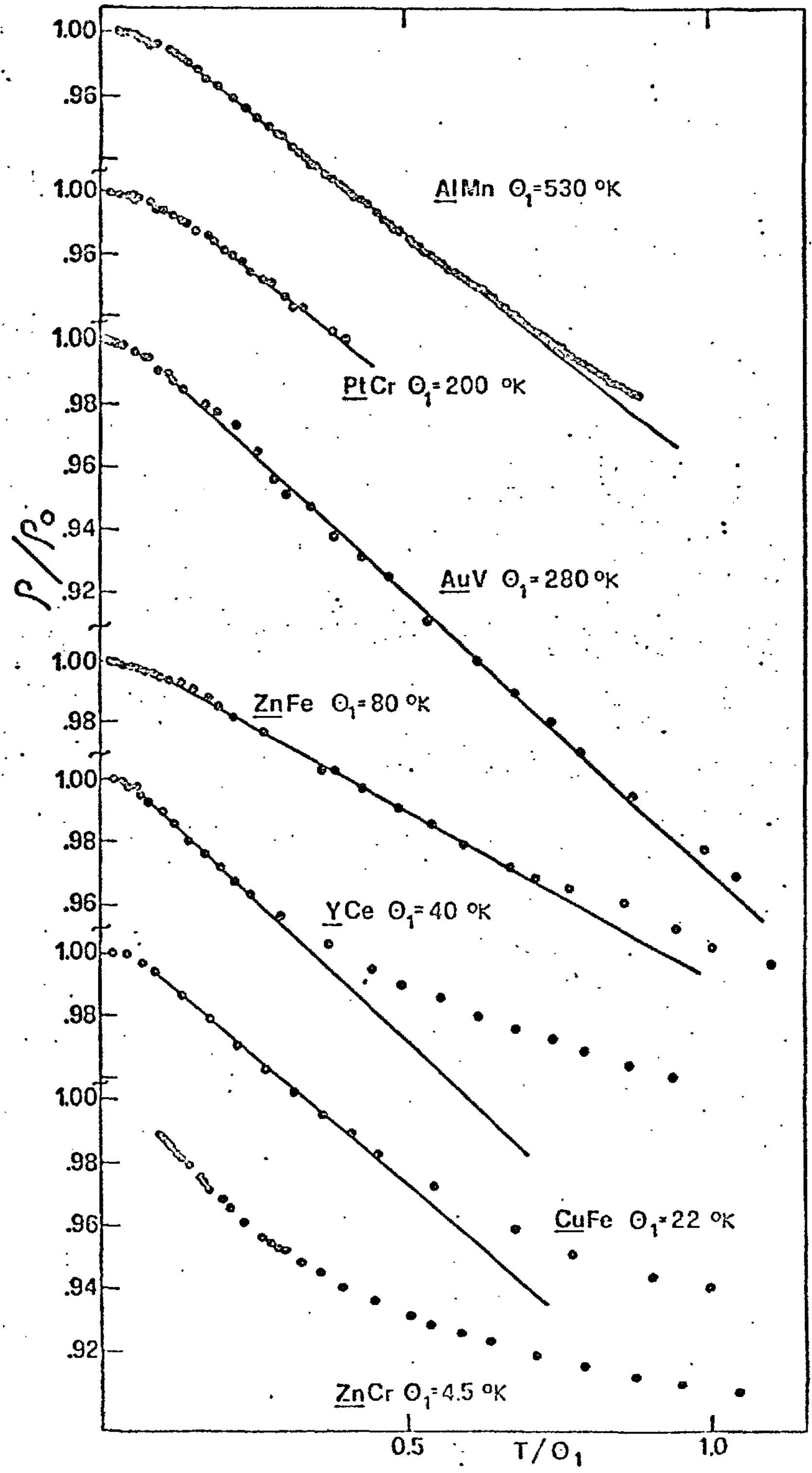
The values of the impurity resistivity normalised to the zero-temperature value against temperature for Al Mn (x) and Al Cr (o) alloys. The data on Al Cr can be scaled to those on Al Mn by using the temperature scale divided by two (•).

variations has been observed also have θ_ρ values in the temperature region where the phonon contribution is difficult to subtract accurately so that a detailed knowledge of the resistivity behaviour at and across θ_ρ is still limited" (Rizzuto, 1974). Theoretically, discrepancies at higher temperatures might be due to the fact that we are completely neglecting all the potential scattering from the impurity atoms and also that we are using the unrenormalised theory.

With respect to Figure (2), we mention that the Fermi window integration increase largely the temperature interval in which the resistivity behaves logarithmically, pushing it at the same time to lower temperatures.

In conclusion, we have shown in this chapter that the resistivity of a dilute alloy due to scattering of conduction electrons on localised spin fluctuations is given by a universal function of temperature. The resistivity is at the unitarity limit at T=0 and decreases with increasing temperature, successively as T^2, T, ln(T) and 1/T. Theoretical results agree rather well with the experimental data and, in particular, they enable one to explain in the unified picture behaviour of systems as different as <u>Cu</u> Fe and <u>Al</u> Mn: the scaling temperature being defined by the life-time of the spin fluctuations.

Figure 4



The values of the impurity resistivity, normalised to the zero-temperature value, against the temperature normalised to θ_ρ. The low temperature T^2 dependence gives way gradually to a temperature dependence slower than T, through an extended linear region (Rizzuto, 1974).

CHAPTER 3

LOW TEMPERATURE THERMOELECTRIC POWER OF DILUTE Al-3d ALLOYS

3.1 Introduction

In this chapter we shall use the results obtained so far to calculate the low temperature thermoelectric power of aluminium-based transition-metal alloys.

These alloys have been measured at low concentrations by Boato and Vig (1967) and more recently, at higher concentrations, by Vucić, Cooper and Babić (1973). It is observed that at low temperatures (T → 0) the thermopower (TEP) has the usual T^3 term due to the phonon-drag in the host, which is the same for all the aluminium alloys. In addition, there is a linear term which varies significantly as one moves through the 3d-series and which is experimentally determined (Boato and Vig, 1967) from the plot of the TEP divided by temperature against T^2; i.e. plotting S/T vs. T^2.

Looking at the absolute value of the zero-temperature slope $|dS/dT|$ of the TEP (i.e. at the coefficient of the linear part) as a function of the atomic number one observes:

(i) $|dS/dT|$ of Al Ti and Al V is an order of magnitude smaller than of any other 3d-alloy;

(ii) $|dS/dT|$ is at its maximum for Al Mn;

(iii) a change in sign of dS/dT takes place between Ti and V. The corresponding behaviour of the residual resistivities is given by the function which has its maximum at Cr and then decreases slowly (and asymmetrically) as one goes towards the ends of the 3d-series.

The aluminium based transition metal alloys are thought to be a classical example of a system which should be analysed in terms of the Friedel-Anderson virtual bound state (v.b.s.) (Friedel, 1958; Anderson, 1961). Indeed, the change in the residual resistivity fits nicely with the concept of the v.b.s. moving across the Fermi level, i.e. with the resonant scattering of conduction electrons on the d-like extra orbital, due to the impurity. Reasoning along the same lines one would expect the slope of the TEP to be proportional to the derivative of the residual resistivity as a function of the atomic number, i.e. changing sign between <u>Al</u> Cr and <u>Al</u> Mn, and reaching the maximum (minimum) at <u>Al</u> V (<u>Al</u> Fe). The observed behaviour however, is rather different (see Figure 1 or Table 1).

Here we present a simple explanation of these low temperature TEP data, on the basis of the localised spin fluctuations (LSF) or "single pole dominance" approximation of the Anderson model (Suhl, 1967; Rivier and Zuckermann, 1968). The virtual bound state is still a useful concept to start with but one has to go beyond the Hartree-Fock approximation.

We show that the asymmetry in the zero-temperature slope of the TEP is due, on the one hand to simple potential scattering (this gives rise to non-resonant phase-shifts different from zero), and on the other hand to the presence of the long-lived local magnetic fluctuations which take place in certain simple metal-transition metal alloys. These fluctuations, when present, give rise to a "giant" slope in the TEP. A measure of their relative importance is given by the quantity $\tau\Delta$ where τ is the life-time of the LSF and Δ is the width of the v.b.s. in the usual Friedel-Anderson sense. When $\tau \approx \Delta^{-1}$ the LSF approximation, as we shall see later, is identical to the Hartree-Fock approximation, whereas if $\tau >> \Delta^{-1}$ the dynamics of localised spin fluctuations has to be taken explicitly into account.

Simple potential scattering will be included in our treatment in a standard way. We express the conduction electron cross section as a function of the phase shifts, and keep the non-resonant ($\ell \neq 2$) terms in addition to the resonant ones throughout the calculations. (Usually, the non-resonant phase shifts are neglected in the discussions of the Anderson model).

That the potential scattering is of the considerable importance for Al 3d-alloys can be shown in several ways. Comparing the relevant parts of the electronic configuration of the host and the impurity one sees that for the metallic aluminium this configuration reads $3s^2 3p^1$, whereas for the 3d-impurity (with the exception of Cr) we have $3d^n 4s^2$. (n equals 2 to 8 as one goes from Ti to Ni. This indicates that part of the screening is due to p-electrons.

The Knight shift measurements on the series of liquid aluminium-3d dilute alloys (Flynn et al., 1967) interpreted on the basis of the Friedel-Blandin theory, indicates that the p-phase shift is between $\eta_1 = -\pi/3$ and $\eta_1 = -\pi/6$ and its absolute value increases as one goes from Ni to Ti.

Eventually, the asymmetry in the residual resistivity, ρ_0, can be simply explained assuming non-resonant phase shifts different from zero (G. Grüner, private communication) and using the expression (Friedel, 1958)*

$$\Delta\rho_0 = C \, \Sigma_\ell \sin^2 (\eta_{\ell-1} - \eta_\ell) \qquad (1)$$

In calculating the TEP (and residual resistivity) we have assumed the following choice of phase shifts, consistent with the facts mentioned above and with the Friedel sum rule. The p-phase shift is equal to $\eta_1 = -\pi/6$ for Cr, Mn, Fe, Co and Ni and $\eta_1 = -\pi/3$ for V and Ti. The s-phase shift (ℓ=0) is assumed to be zero for all the impurities except Cr, which alone in the 3d-transition series has an incomplete s-shell ($3d^5 4s^1$) and for which we put $\eta_0 = -\pi/2$.

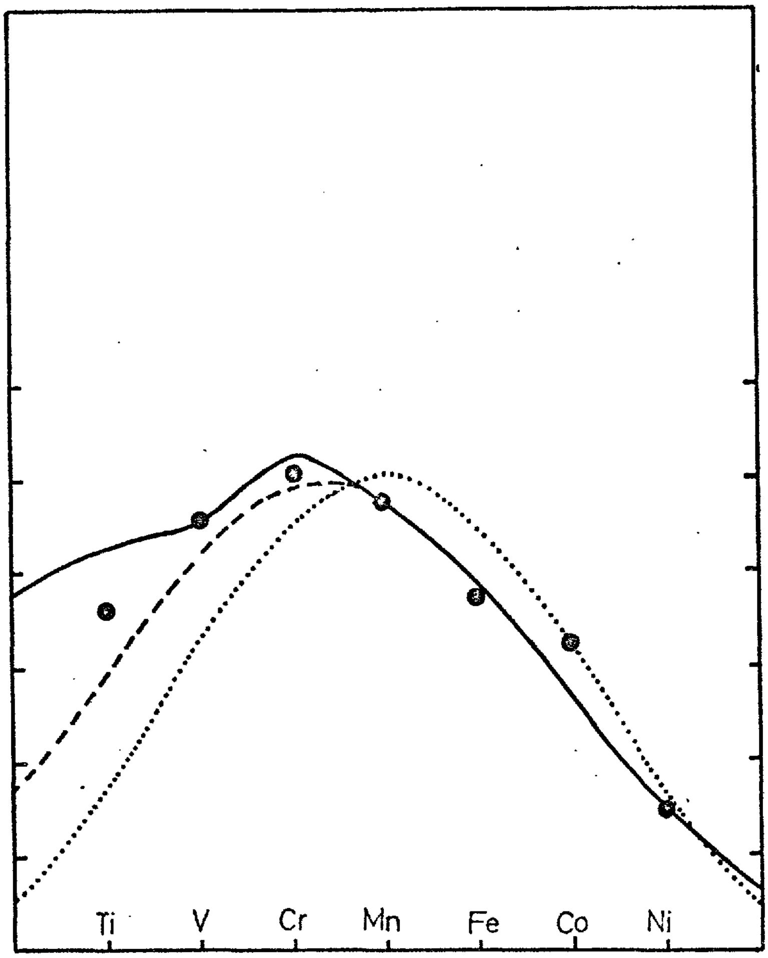
The residual resistivity, calculated with this choice of phase shifts, is shown in Figure (1).

The plan of the chapter is as follows: in the next section we rederive the Friedel expression for the TEP in

---

* The phase shift analysis and the Friedel sum rule, which we are using together with eq. (1), have been demonstrated to be valid in the case of many-body interactions by Langer and Ambegaokar, 1961.

Figure 1



The residual resistivity of Al -3d alloys normalised to Al Mn value.

● experimental data; —— calculated values;

.... as due to virtual bound state;

---- effect of the non-resonant phase shift ($\delta_1 = -\pi/6$ throughout the series).

terms of phase shifts; in the following section the resonant ($\ell = 2$) phase shift is calculated using the LSF approximation of the Anderson model; eventually, the results of the calculation are compared with the experimental data.

3.2 Expression for TEP in Terms of Phase Shifts

As in the case of the resistivity (Chapter 2), we calculate the thermoelectric power, expressing it as a function of the relaxation time $\tau(\varepsilon)$, and then relate $\tau(\varepsilon)$ to the scattering cross section $\partial\sigma/\partial\Omega$ (or T-matrix). At low temperatures the TEP can be written as (Mott and Jones, 1936)

$$S = -\frac{2}{3}\frac{k_B T}{|e|}\left[\frac{\partial}{\partial\varepsilon}\ \ell n\ \tau(\varepsilon)\right]_{\varepsilon = \varepsilon_F}$$

and, from the Boltzmann equation, we have for the relaxation time

$$\frac{1}{\tau(\varepsilon)} = \frac{N_i\, v}{2}\int \frac{\partial\sigma}{\partial\Omega}\,(1 - \cos\theta)\,\frac{d\Omega}{4\pi}$$

where, as before N_i is the number of impurities per unit volume and $\underset{\sim}{v}$ is the velocity of the conduction electrons. Expressing $\partial\sigma/\partial\Omega$ in terms of conduction electrons phase shifts (Messiah, 1958; Ch. X)

$$\frac{\partial\sigma}{\partial\Omega} = \frac{1}{k_B^2}\left|\ \Sigma_\ell\ (2\ell + 1)\ e^{i\eta_\ell}\ \sin\eta_\ell\ P_\ell(\cos\theta)\ \right|^2$$

and integrating over Ω we obtain

$$S = -\frac{\pi^2}{3}\frac{k^2 T}{|e|}\frac{3\sin(2\eta_2) - 2\sin^2(\eta_1-\eta_2)}{\sin^2(\eta_o-\eta_1) + 2\sin^2(\eta_1-\eta_2) + 3\sin^2(\eta_2)}\frac{\partial\eta_2}{\partial\varepsilon}\bigg|_{\varepsilon=\varepsilon_F} \tag{2}$$

which relates TEP to the phase shifts (Daniel and Friedel, 1964) and which is completely analogous to the Friedel expression for the residual resistivity given by eq. (1).

In eq. (2), it is assumed that only $\ell = 0$, $\ell = 1$ and $\ell = 2$ phase shifts are different from zero, and the whole expression is evaluated at the Fermi level. The resonant (η_2) phase shift can be obtained from the T-matrix for the scattering of the conduction electrons on the 3d impurity in aluminium, as by definition

$$\eta_\ell = tg^{-1}\frac{\mathrm{Im}\,T_\ell}{\mathrm{Re}\,T_\ell} \tag{3}$$

where T_ℓ is the matrix element of the scattering matrix in the angular momentum representation.

3.3 Calculation of the Resonant Part of the T-Matrix

As before, we assume that as far as the transport properties and the formation of local moments is concerned, the aluminium based-transition metal alloys are well described by the orthogonal Anderson Hamiltonian. The conduction electron's T-matrix is then given by

$$T_2(\varepsilon) = V^2 G_d(\varepsilon) \tag{4}$$

where V is the matrix element for the mixing of the conduction electrons with the localised d-states, and $G_d(\varepsilon)$ is the d-electrons Green function.

We calculate $G_d(\varepsilon)$ in the LSF approximation by assuming first that the scattering of an electron-hole pair of opposite spin is the only many-body contribution to the self-energy $\Sigma_d(\varepsilon)$. (Among others, we are neglecting the electron-electron correlation as discussed by Schrieffer and Mattis, (1965), mainly on the ground that in the low-density, low temperature limit, where this type of correlation is important to obtain the correct magnetic behaviour, most of the alloys we are concerned with (i.e. Al Ti, Al V, etc.) are non-magnetic already, even in the Hartree-Fock approximation).

Secondly, in calculating the d-electron self-energy

$$-i\ \Sigma_d(\varepsilon) = k_B T\ \Sigma_n\ \tilde{\Gamma}(i\varepsilon_n)\ G_d^o(i\ \varepsilon_n + \varepsilon) \tag{5}$$

we assume that the electron-hole T-matrix is well approximated by the expression $\tilde{\Gamma}(\varepsilon) = -i\pi\Delta^2/(M-i\varepsilon)$ where $M = k_B T_K$ is the inverse of the LSF life-time τ^* (Rivier, 1968; Lederer and Mills, 1967) and $G_d(\varepsilon) = (\varepsilon - E_d \pm i\Delta)^{-1}$ is the bare d-electron Green's function. However, in contradistinction to the earlier LSF theories where τ had been calculated in the RPA approximation, M is here taken to be a phenomenological parameter.

---

[*] The transverse susceptibility has clearly the same analytical properties as those of $\tilde{\Gamma}(\varepsilon)$.

Within these approximations it is straightforward to evaluate first Σ_d (ε) (Rivier, 1968) and then the Green's function G_d which is determined by the Dyson equation $G_d = (\varepsilon - E_d + i\Delta - \Sigma_d)^{-1}$. This approximation was discussed in Chapter 1 and here we recall only some of the results for the spectral density $A(\varepsilon)$ relevant for the calculations ($A(\varepsilon) = -\mathrm{Im}\, G_d \sim |T|^2$).

In the case when $M \simeq \Delta$, (i.e. for all the alloys except Al Mn and Al Cr), $A(\varepsilon)$ is a simple Lorenzian of width Δ and therefore the LSF approximation is here equivalent to the non-magnetic Hartree-Fock approximation of the Anderson model. All the physical properties are easily obtained using Friedel's analysis, i.e. assuming that the conduction electrons are scattered on a simple v.b.s. of the width Δ (Δ = 1.2 eV).

On the other hand, when $\Delta >> M >> kT$, $A(\varepsilon)$ is a triply peaked function symmetrical around the Fermi level, with two broad side-peaks of the width Δ, and a very narrow, temperature dependent peak of width $\Gamma(T) << \Delta$, at the Fermi level. ($\Gamma(T) \to M$ as $T \to 0$)

To obtain η_2, in the situations in which the LSF contributions are important, we write from (3) and (4)

$$\eta_2 = tg^{-1} \frac{\Delta - \mathrm{Im}\, \Sigma d}{Ed - \varepsilon - \mathrm{Re}\, \Sigma d} \qquad (6)$$

where the full expression for $\Sigma_d(\varepsilon)$ is given in Chapter 1 (eq. 5).

For the symmetrical Anderson Hamiltonian ($E_d = 0$), at low temperatures and for $M << \Delta$, this is equal to (up to logarithmic accuracy, i.e. $\Delta/M >> \ell n\, \Delta/M >> 1$)

$$\eta_2 = tg^{-1} \frac{M}{\varepsilon}$$

In the same way we get for $\partial\eta_2/\partial\varepsilon$

$$\frac{\partial\eta_2}{\partial\varepsilon}\bigg|_{\varepsilon \simeq \varepsilon_F} = \frac{1}{M}$$

taking the zero of energy at the Fermi level.

We see that for Al Mn and Al Cr (for which $E_d = 0$), η_2 goes through the resonance at the Fermi level; i.e. it is equal to $\frac{\pi}{2}$ at $\varepsilon = \varepsilon_F$. However, $\partial\eta_2/\partial\varepsilon$ instead of being equal to $1/\Delta$ at $\varepsilon = \varepsilon_F$, as in the Friedel theory, is here enhanced to $1/M$. The residual resistivity is unaffected by LSF.

Before turning to the evaluation of the TEP, from eq. (2), we remark that same results can be obtained from a very simple physical picture. As already mentioned, at low temperatures and for energies close to ε_F, $A(\varepsilon)$ is a very narrow Lorentzian of width $\Gamma(T)$. In fact for $T << T_k$ and $\varepsilon << M << \Delta$, the Green's function has an approximate form, $G_d(\varepsilon) \simeq G_d^{eff}(\varepsilon)$,

$$G_d^{eff}(\varepsilon) = \frac{M}{\Delta} \frac{1}{\varepsilon + i\Gamma(T)} \qquad (7)$$

and the scattering matrix can be approximated by an effective T-matrix, $T_{eff} = V^2 G_d^{eff}(\varepsilon)$. Because at low temperatures, the only contribution to the transport properties comes from the conduction electrons with energies close to the

Fermi level, we see that it is possible to replace the resonant scattering on a d-orbital in the presence of the many-body effects (i.e. scattering from a v.b.s. with an internal structure: spin up or down) by equivalent scattering on a single but temperature dependant v.b.s. of an effective width $\Gamma(T)$. Repeating the standard Friedel procedure and replacing everywhere Δ by $\Gamma(T)$, all our results are easily obtained.

3.4 Comparison with Experiment and Conclusion

We are in the position now to evaluate the linear part of the TEP of the Al-3d alloys. Resonant phase shifts are calculated along the lines indicated in the previous section, with the numerical values of the enhancement factor M/Δ determined from the low temperature (parabolic) part of the resistivity.*

Using eq. (2), which gives the TEP in terms of phase shifts, we calculate S/T which is plotted in Fig. (2) together with the existing experimental data. Dotted line represents the Hartree-Fock result, with only the resonant ($\ell = 2$) phase shift different from zero. Addition of one single non-resonant phase shift, equal for all the impurities, gives rise to an asymmetry in the TEP curve (broken line in fig. (2)). The final Hartree-Fock result for S/T of the Al-3d alloys is shown by the full line in Fig. (2).

---

* We have chosen the parabolic part of the resistivity to evaluate the parameter M ($M = k_B T_K$) because the low temperature resistivity measurements seem to determine most accurately the single impurity effects in aluminium based alloys (Rizzuto, 1974; Grüner, 1973).

The effect of the localised spin fluctuations, when present, is indicated with crosses below the H-F line. Values of the parameters used in this paper to calculate the TEP are shown in Table 1. We have taken $\Delta = 1.2$ eV.

The residual resistivity, calculated from eq. (1) with the phase shifts chosen as above, is shown in Figure 1. The overall agreement between the experimental and the theoretical data is rather satisfactory, both for the low temperature thermopower and the residual resistivity. The discrepancy in Al Fe can probably be ascribed to a LSF contribution $\tau^{-1}/\Delta = 0.45$ first noticed by Grüner (1972). (The ordinate scale in this paper should be shifted by one order of magnitude.) It is clear, however, that this enhancement is far too small to be seen in the resistivity measurements. We notice:

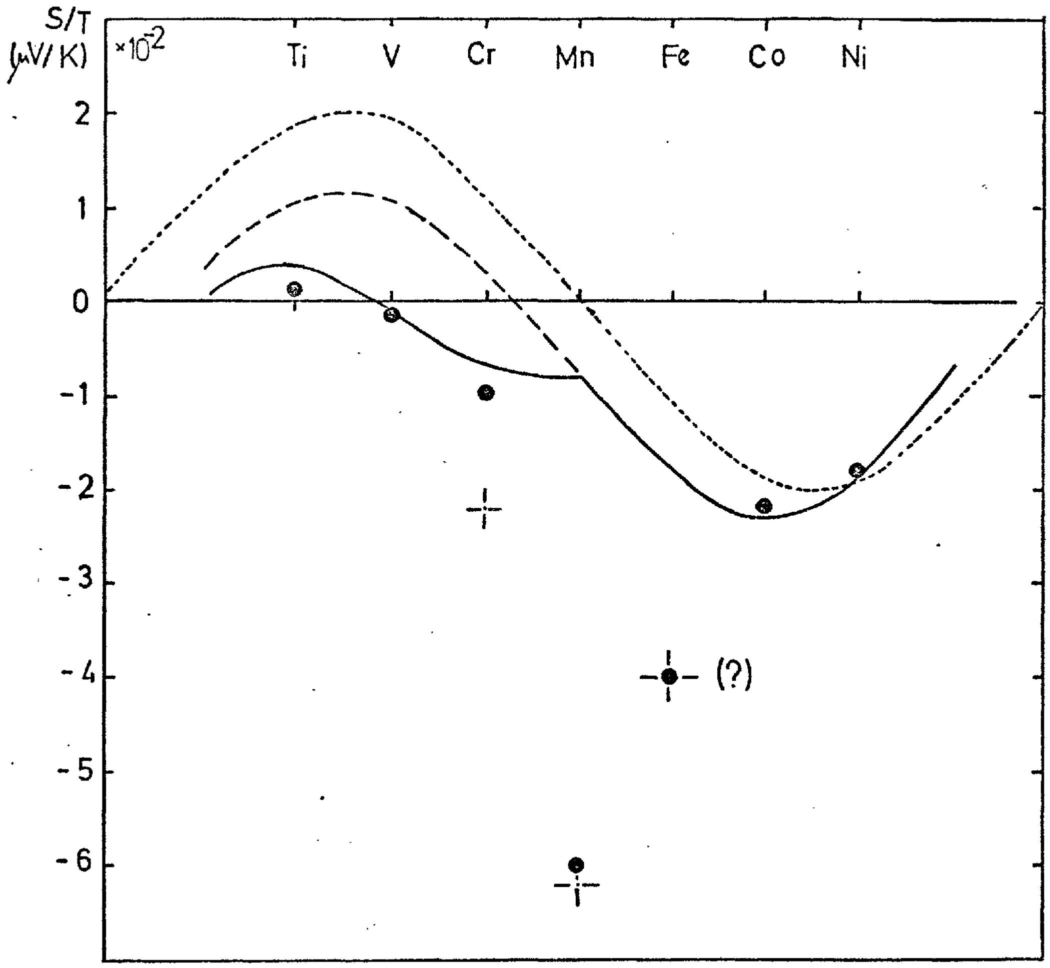
(i) S/T values of Al Mn and Al Cr are largely enhanced due to the LSF and S/T is at its maximum for Al Mn.

(ii) Even in the case when there are no LSF effects, the curve of S/T is asymmetric due to the potential scattering of conduction electrons on impurity atoms.

(iii) The change in sign of S/T as a function of the atomic number takes place between Ti and V.

At this point we would like to emphasise again that the choice of the particular values of the non-resonant phase shifts is non-essential for the understanding of the

Figure 2



Zero-temperature slope, S/T, of the thermopower plotted as a function of the atomic number of the impurity for Al-3d alloys.

●	experimental data;
———	theory, when LSF effects are not included;
+	effect of LSF;
.....	as due to a virtual bound state alone;
-----	effect of the non-resonant phase shift ($\delta_1 = -\pi/6$ throughout the series).

Table 1

	Ti	V	Cr	Mn	Fe	Co	Ni
Electronic structure of the impurity	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$
Number of electrons screened by $\ell = 2$ phase shifts	3	4	5	5	6	7	8
Values of the non-resonant ($\ell = 1$) phase shift	$-\pi/3$	$-\pi/3$	$-\pi/6$	$-\pi/6$	$-\pi/6$	$-\pi/6$	$-\pi/6$
ρ_o experimental values (≠) ($\mu\Omega$ cm/at %)	6.5	7.5	8.5	7.8	6.0	3.5	2.0
ρ_o computed values normalised to Al Mn ($\mu\Omega$ cm/at %)	7.1	7.5	8.6	7.8	6.3	4.2	2.1
τ_{sf}^{-1}/Δ determined from the T^2 term in the resist.	1	1	0.30	0.12	(0.45)** 1	1	1
S/T experimental low temperature values (μ V/K^2)	x +0.001	x -0.001	x -0.01	x -0.06	x -0.04	+ -0.022	+ -0.018
S/T calculated low temperature values (μ V/K^2)	+0.004	-0.001	-0.022	-0.062	(-0.04)** -0.018	-0.023	-0.018

x Boato and Vig, 1967

\+ Vučić, Cooper and Babić, 1973

≠ Grüner, 1973

** possible enhancement (see text)

general features of the TEP of al-3d alloys. The only important thing is that the non-resonant phase shifts are different from zero, i.e. that there is a simple potential scattering in addition to the resonant scattering. (This resembles once again, the situation one has in the Kondo effect; exchange scattering alone is not sufficient to explain the anomalous TEP of the Kondo alloys. (Suhl and Wong, 1967; Kondo, 1969).

However, in order to have an asymmetrical residual resistivity, the correct sign for the thermopower and obey the NMR result (that the potential scattering increases as one goes from Ni to Ti), we have associated different values of the non-resonant phase shifts with the left-hand side and the right-hand side of the 3d series, within the constraint imposed by the Friedel sum rule.

In conclusion, we have calculated the low temperature thermoelectric power of aluminium-based transition-metal alloys and shown that the experimental data can be understood on the basis of the LSF approximation of the Anderson model. There are two essential points in our calculations:

(i) the self-energy of local d-electron can be modified due to presence of the long-lived local magnetic fluctuations. Hence, the effective width of the virtual bound state can become much smaller than in the Hartree-Fock approximation of the Friedel-Anderson theory.

(ii) in addition to the resonant scattering, the conduction electrons also undergo potential scattering, which means that the non-resonant phase shifts are going to be different from zero.

Both of these points have been well known to the experimentalists: Boato and Vig (1967) came to the conclusion that the width of the v.b.s. in aluminium is much smaller for the impurities in the middle of the 3d-series than at the end of the series, while the importance of the non-resonant phase shifts for the understanding of TEP in Al-3d alloys was stressed by G. Grüner and J. Cooper (private communications).

CHAPTER 4

TEMPERATURE DEPENDENCE OF THE RESISTIVITY DUE TO THE LOCALISED SPIN FLUCTUATIONS IN TRANSITION-METAL TRANSITION-METAL ALLOYS

4.1 Introduction

In this chapter we shall apply the concept of the localised spin fluctuations to alloys in which both solvent and solute are transition metals. Since the work of Matthias et al. (1960) and Clogston et al. (1962) on the formation of local moments, transition-metal transition-metal alloys have often been the subject of interest in metal physics and have stimulated a lot of experimental and theoretical investigations. Here, our attention will be confined to the resistivity properties, since they provide clearest evidence and need for the LSF approach. Experimental data (Coles, 1963; Coles et al., 1964) showed a variety of behaviours including deep resistivity minima for Mo Fe, constant impurity resistivities for Nb Fe or Ru Fe and anomalous low temperature decreases in resistivity of Rh Fe. More detailed investigations of ternary alloys of $(\underline{Nb}_x \underline{Mb}_{1-x})$ Fe (Sarachik et al., 1964) revealed that the resistivity minima are strongly correlated with the appearance of a local moment on the iron atoms, detected from the susceptibility measurements, and could be nicely explained in the frame of the s-d model.

Resistance anomalies with positive temperature coefficients were subsequently found in Ir Fe (Sarachik, 1968), Pd Ni (Schindler and Rice, 1967), Rh Mn, Rh Co (Coles et al., 1971), Pt Co, Pt Fe (Loram et al., 1972) and several alloys and compounds of actinides (Brodsky, 1971; 1974). It emerged that in all these systems the resistivity behaves in a more or less similar fashion; it increases rapidly with increasing temperature up to a certain characteristic temperature T_K, above which it starts to flatten out, eventually reaching the high temperature plateau. At the same time the impurity susceptibility changes from temperature independent to Curie-Weiss behaviour with a negative θ_{C-W} of the order of T_K (Knapp, 1967; Loram et al., 1972).

In an early attempt to explain the resistivity data of these alloys they were considered as Kondo systems in which the conduction electrons are coupled ferromagnetically to the impurity moment ($J > 0$), so that the coefficient of the logarithmic term in the Kondo expression for the resistivity becomes positive (Kondo, 1964). However, the application of the Kondo model to these alloys is hard to reconcile with the already mentioned susceptibility behaviour which indicates a decrease of the effective impurity moment as $T \to 0$.

Another attempt to obtain a resistivity which would decrease with decreasing temperature in the framework of the s-d model was due to Fisher (1967), Kondo (1968) and

Nagaoka (1968). In calculations valid above T_K they find that the presence of non-magnetic potential scattering from the magnetic impurity gives rise to an extra factor in the coefficient of the logarithmic term which is proportional to $\sin 2\eta_2(\varepsilon_F)$. Then if the potential scattering is strong enough, i.e. the phase shift $\eta_2(\varepsilon_F)$ is larger than $\pi/4$, the sign of the Kondo resistivity effect will be reversed. However, a rather fundamental objection to the application of this mechanism to explain the behaviour of above mentioned alloys arises from the small magnitude of their residual resistivities. If the phase shift $\eta_2(\varepsilon_F)$ is large, the residual resistivity which is proportional to $\sin^2\eta(\varepsilon_F)$ should be large as well. In fact, just the opposite is found: residual resistivities of <u>Rh</u> Fe or <u>Ir</u> Fe, for example, are one order of magnitude smaller than in normal Kondo systems (Nagasawa, 1970). The reason for such a small amount of potential scattering is that in all these alloys the electronic structure of solute and solvent is rather similar. As a rule, in all the systems in which the <u>Rh</u> Fe -like anomaly is observed, both the impurity (3d-metal) and the host (4d or 5d-metal) belong to the same or neighbouring columns of the periodic table. This situation is exactly the opposite of what one has in normal-metal transition-metal alloys. There, the relevant part of the impurity electronic structure has a d-like character while the band electrons are s- or p- like. As shown by Rivier and Zitkova (1971), in the former case the localised state can be expressed as a linear combination of the host electronic states, while in the latter case they are orthogonal to each other. If a dilute alloy is described by the non-orthogonal Anderson Hamiltonian, we could, in principle, deal with the intermediate situations. However, because of the similarity between the impurity and the host, we shall assume that the Wolff Hamiltonian with zero potential scattering is a sufficiently good representation of these particular transition-metal transition-metal alloys.

4.2 Lederer and Mills Two Band Model

The first explanation of the properties of the above mentioned alloys in terms of localised spin fluctuations was given by Lederer and Mills (1968) in their discussion of the low temperature resistivity of dilute Pd Ni. They start from the observation that although an isolated Ni ion is non-magnetic in Pd, if the Ni concentration exceeds 2%, the Ni sites acquire a moment and the spins order ferromagnetically. Thus, one should expect to find the low-frequency fluctuations in the spin density to be enhanced in the vicinity of the impurity cell, compared to their amplitude far from the impurity.

To calculate the transport properties of such a system they assumed that the electrical current is carried by the s-electrons of Pd, while the principal low temperature contribution to the transport relaxation rate comes from the scattering of the s-electrons by the already described spin density fluctuations in the d-band. The Hamiltonian which corresponds to this process is given by

$$H_{s-d} = - J_{s-d} \sum_{kk'} a^{+}_{k\sigma} \sigma_{\sigma\nu} a_{k'\nu} d^{+}_{o\alpha} \sigma_{\alpha\gamma} d_{\gamma o} \qquad (1)$$

where $a^{+}_{k\alpha}$ is the conduction electron creation operator, $d^{+}_{o\alpha} = (1/N) \sum_{k} d^{+}_{k\alpha}$ is the d-electron Wannier creation operator at the impurity site and J_{s-d} is an effective electron-LSF coupling constant.

The electrical resistivity produced by inelastic collisions of s-electrons with spin fluctuations can be obtained by applying the standard variational procedure to the Boltzmann equation (Ziman, 1960). Kaiser and Doniach (1970) showed that $\rho(T)$ can be written as

$$\rho(T) \sim \frac{1}{T} \sum_{k,k'} f_{k}(1-f_{k'}) W_{k\to k'}(\varepsilon_{k}-\varepsilon_{k'}) \qquad (2)$$

where f_{k} is the Fermi distribution function and $W_{k\to k'}$ is the scattering rate from filled conduction state of energy ε_{k} into empty state ε_{k}'. If the coupling constant J_{s-d} is small the transition probability $W_{k\to k'}$ in the Born approximation is

$$W_{k\to k'} \sim J^{2}_{s-d} S_{kk'}(\varepsilon) \qquad (3)$$

where $S_{k,k'}(\varepsilon)$ is the d-spin density correlation function so that applying the fluctuation-dissipation theorem we can write

$$W_{k\to k'} \sim J^{2}_{s-d} n(\varepsilon) \operatorname{Im} \chi^{+-}_{k,k'}(\varepsilon) \qquad (4)$$

Here, $\chi^{+-}_{k,\,k'}(\varepsilon)$ is the local response function of the d-electron spin density operator (Kittel, 1964) which was calculated by Lederer and Mills (1968) in the RPA. The essential point in the theory is that in the case of an alloy where the 3d-impurity is dissolved in the exchange enhanced host, average of $\chi^{+-}_{k,\,k'}$ over all the k-states may be reasonably well approximated by a Lorentzian response (Kaiser and Doniach, 1970; Lederer, 1970)

$$\operatorname{Im}\chi(\varepsilon) = \frac{\varepsilon}{T_K^2 + \varepsilon^2} \tag{5}$$

From equations (2) and (5) it follows that one can define the reduced temperature and energy variables, $\tilde{T} = T/T_K$ and $\tilde{\varepsilon} = \varepsilon/T_K$, such that the resistivity becomes a universal function of T (Kaiser and Doniach, 1970; Kaiser, 1971). Performing the calculations one finally obtains

$$\rho(T) \sim \frac{1}{T}\int d\varepsilon \, \frac{\varepsilon}{(e^{\beta\varepsilon} - 1)(1 - e^{\beta\varepsilon})} \, \frac{\varepsilon}{1 + \varepsilon^2} \tag{6}$$

The low temperature limit of this expression is given by (Lederer and Mills, 1968)

$$\rho(T) = \rho_o \, \frac{\pi}{3} \, (\frac{T}{T_K})^2 \tag{7}$$

and it is in agreement with experiments. At higher temperatures, $\rho(T)$ becomes linear in T but for the enhancement factor T_K independent of T the resistivity never saturates, nor even decreases below the linear law. In order to obtain the saturation one has to assume that T_K is extremely large, on one hand, and that it is temperature dependent, on the other hand. Yet, it is not at all clear that the assumptions which were made to arrive at expression (6) will hold in this situation. The temperature dependence of T_K is an ad'hoc assumption which can be justified if one assumes the temperature dependent band susceptibility (which would involve another parameter, the paramagnon lifetime). Moreover, numerical results of Jullien, Beal-Monod and Coqblin (1973) show that in the Kaiser and Doniach theory the saturation limit is practically never reached unless the local degeneracy temperature is of the order of the conduction electron degeneracy temperature (paramagnon temperature). This would mean that the saturation effect would not be observable in practice, in contradiction with the experimental data on Rh Fe (Rusby, 1974) which saturate at about 30K.

4.3 Spin Fluctuations in One Band Model

We propose here a different model to describe the transport properties of a system in which both solute and solvent are transition metals. First, we assume that in an alloy like Rh Fe or Ir Fe the hybridisation between s- and d-electrons is sufficiently strong to allow the transport properties to be discussed in terms of one electron band only*. Second, we suppose that the appropriate Hamiltonian to deal with the above mentioned systems is the Wolff Hamiltonian (Wolf, 1969), which reads

$$H = H_o + H_i \tag{8}$$

where H_o describes the condustion band and H_i is the interaction part due to the presence of the impurity. Explicitly, we write H_i as

$$H_i = W \sum_\sigma a^+_{o\sigma} a_{o\sigma} + U n_{o\uparrow} n_{o\downarrow} \tag{9}$$

where $n_{o\sigma} = a^+_{o\sigma} a_{o\sigma}$, $a^+_{o\sigma} = (1/\sqrt{N}) \Sigma_k a^+_k$ is the creation operator for the localised electron and a^+_k is the creation operator for the conduction band. As before, N is the number of atoms in unit volume, W is the one-body scattering potential and U is the extra Coulomb repulsion between electrons of the opposite spin which takes place in the impurity cell.

---

* Similar assumption was made by Larkin and Melnikov (1971) in their paper on the properties of magnetic impurities in nearly magnetic hosts. They assumed that the effect of alloying is to introduce a well defined spin in the exchange enhanced conduction band of the host and then studied such a system using the modified s-d model. They demonstrate that the effective s-d coupling is greatly modified due to the interactions between the impurity spin and the spin fluctuations (paramagnons, as defined by Doniach and Engelsberg, 1966). In these circumstances the Kondo effect may qualitatively differ from that in normal metals. In particular, for $T > T_K$ in this model the impurity resistivity and the effective magnetic moment decrease with the decreasing temperature for any value of J_{s-d}. However, for $T < T_K$ the resistivity does not approach zero in a simple power fashion as is observed experimentally (Abrikosov and Migdal, 1970).

Following Lederer and Mills (1967) we argue that the effect of adding the 3d-impurity to the 4d or 5d host results in an increase of the amplitude of the local spin fluctuations at the impurity site. This is a fairly physical assumption because one should expect the large long-lived spin fluctuations to occur in order to smooth out the magnetic transition, i.e. to prevent a second order phase transition from taking place in a local system.

In this sense we assume, as in the case of the Anderson model discussed in the previous chapters, that the dominant contribution to the conduction electron self-energy comes from the scattering on the LSF which takes place at the impurity site. Defining the LSF propagator χ_o as before, we assume that the electron-hole resonance (repeated scattering of an electron-hole pair of opposite spin) forms the most important Bose-like excitations in the system (Suhl, 1967; Rivier and Zuckermann, 1968; Hamann, 1969). Thus we write the self-energy as

$$-i\Sigma_o =$$

(10)

where 〰 is the LSF propagator and —>— is the conduction electron Green function in the presence of the perturbation.

Here, we would like to point out that in contrast to Lederer and Mills (1968) and Kaiser and Doniach (1970), who calculated the resistivity by applying the variational procedure to the Boltzmann equation, we calculate the conductivity, i.e. we calculate the self-energy of a local electron and relate it to the transport relaxation time $\tau(\varepsilon)$. (Abrikosov, et al., 1964). As discussed in Ch. 3, in the multiple scattering approximation we can write for $\tau(\varepsilon)$

$$\frac{1}{\tau} = n_i \, T_1 \tag{11}$$

where T_1 is the scattering matrix for the single impurity and which, in the case of the Wolff Hamiltonian, can be written in terms of the self-energy Σ_o as

$$T_1 = \frac{W + \Sigma_o}{1 - G_o(W + \Sigma_o)} \tag{12}$$

In equation (12), $G_o(\varepsilon)$ is the bare (U = 0) local Green function defined by

$$G_0(\varepsilon) = \sum_k \frac{1}{\varepsilon - \varepsilon_k + i_\delta} \tag{13}$$

and W the simple potential scattering defined above.

To calculate Σ_o we define first the Green function $G_1(\varepsilon)$ which enables one to get rid of the one-body potential W (Messiah, 1958; Ch. XIX):

$$G_1(\varepsilon) = \frac{1}{1 - WG_o(\varepsilon)} \tag{14}$$

and which we assume is Lorentzian in form:

$$G_1(\varepsilon) = \frac{1}{\varepsilon - E_o + i\,\Gamma} \tag{15}$$

For simplicity, we shall put W = 0, so that E_o represents the centre of the host band of width Γ and the density of states ρ(ε)

$$\rho(\varepsilon) = \frac{1}{\pi} \frac{1}{(\varepsilon - E_o)^2 + \Gamma^2} \tag{16}$$

Although this assumption is strictly valid only for equivalent alloys, we believe that the extremely low residual resistivity of all the systems we are concerned with indicates that this will be a reasonably good approximation in the general case. The full Green function ($U \neq 0$) is determined by the Dyson equation

$$G(\varepsilon) = \frac{1}{G_1^{-1} - \Sigma_o(\varepsilon)} \tag{17}$$

and with the above assumptions we can write for the self-energy Σ_o

$$- i \, \Sigma_o(\varepsilon) = k_B T \sum_n \chi_o(i\varepsilon_n) \, G(i\varepsilon_n + \varepsilon) \tag{18}$$

To evaluate expression (18) for Σ_o we assume the following:

(i) the LSF propagator is sufficiently well approximated by a function with only one simple pole close to the the real axis, i.e.

$$\chi_o(\varepsilon) = \frac{c}{M + i \varepsilon} \tag{19}$$

(ii) we restrict the calculations to the unrenormalised theory and replace G(ε) in expression (18) by $G_o(\varepsilon)$.

Clearly, (i) and (ii) represents the same approximation as that made by Lederer and Mills (1967) and Rivier and Zuckermann (1968) and which we discussed at some length in Ch. 2. The LSF temperature is defined as $k_B T_K = M$. Making the analytical continuation we replace the summation over the imaginary frequencies with an integral over the real axes noticing that the expression (18) is formally the same as expression (3') for Σ_d in Ch. 2, if E_o is replaced by E_d and Γ by Δ.

4.4 Temperature Dependence of the Resistivity in One Band Model

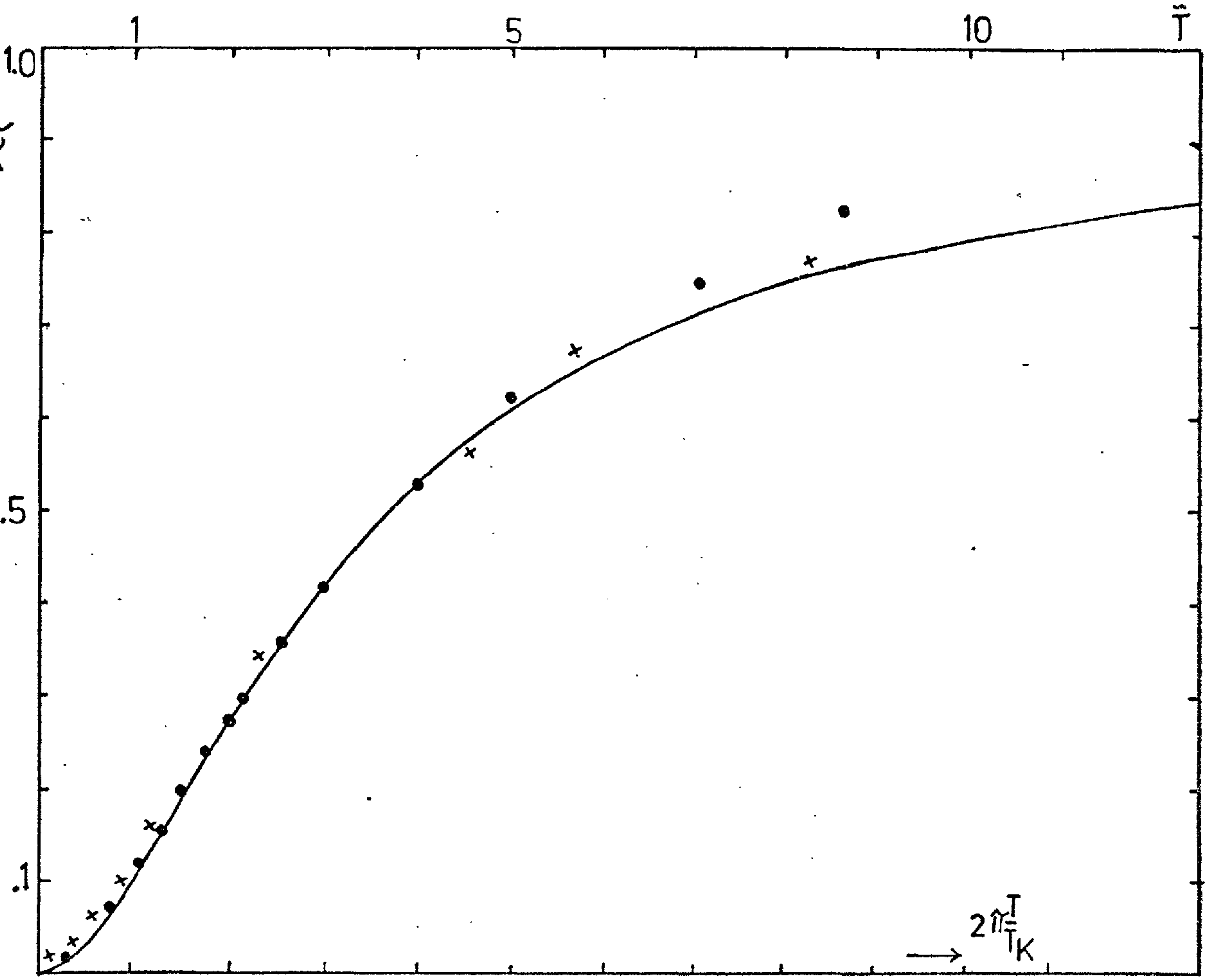
In such a way, and with all the integrals being evaluated in Ch. 2 (Appendix I), we obtain an explicit expression for $\Sigma_o(\varepsilon)$ (hence for T_1 and $\tau(\varepsilon)$) in terms of parameters M, E_o, Γ and as a function of temperature and energy. As before, the conductivity is obtained from (eq. 9 , Ch. 2)

$$\sigma = 2\frac{e^2 v_F\ \rho_F}{3} \int d\varepsilon\ (-\frac{\partial f}{\partial \varepsilon})\ \tau\ (\varepsilon) \tag{20}$$

where v_F is the Fermi velocity, ρ_F is the density of conduction electrons at the Fermi level and $f(\varepsilon)$ is the Fermi function.. Evaluating this expression we put $E_o = 0$ and neglect the Fermi window integration putting $(-\partial f/\partial\varepsilon) = \delta(\varepsilon)$. Finally, we can write the resistivity as

$$\rho(T) = \rho_o \left\{ 1 - \frac{1}{1 + \frac{\pi}{M\beta} + \psi(\frac{1}{2} + \frac{M\beta}{2\pi}) - \psi(1 + \frac{M\beta}{2\pi})} \right\} \tag{21}$$

Figure 1



The normalised resistivity as a function of the reduced temperature $\tilde{T} = 2\pi\ T/T_K$. The curve is a plot of equation (21).

o measurements of Rusby (1974) for Rh Fe (T_K = 15 K);

x measurements of Sarachik (1968) for Ir Fe (T_K = 225 K).

where $\psi(\varepsilon)$ is the digamma function. If we denote by R(T) the resistivity which was obtained in the Anderson model assuming that the spin fluctuations take place just in the impurity d-orbital and define reduced resistivity $\tilde{\rho} = \rho/\rho_o$, we have the simple relation

$$\tilde{\rho}(T) = 1 - R(T) \tag{22}$$

The essential difference between the present problem and that treated in Ch. 2 lies in the coupling between the conduction electrons and the LSF. Here the conduction electron is dragged into the LSF by its own kinetic energy; the scattering mechanisms at the impurity, potential W and LSF Σ_o add up in series. In Ch. 2 the conduction electron had to scatter into the extra d orbital before seeing the LSF (represented by the self-energy Σ_d) which modulates the resonant scattering pseudopotential from

$$\frac{V^2}{\varepsilon - E_d}$$

to (Rivier, 1968)

$$\frac{V^2}{\varepsilon - E_d - \Sigma_d}$$

to yield the familiar expression for the scattering matrix (Anderson, 1961)

$$T(\varepsilon) = \frac{V^2}{\varepsilon - E_d - \Sigma_d - V^2 G_o}$$

instead of eq. (12). Since the effective scattering potential due to the LSF, Σ_d or Σ_o, increases with increasing temperature following the thermal increase in the number of LSF, the scattering cross section and hence the resistivity, increases with temperature towards the unitarity limit (corresponding to $T(\varepsilon) = - G_o(\varepsilon)^{-1}$ or a phase shift $\delta = \pi/2$ at the Fermi level). In the case treated in Ch. 2, the resonant phase shift is already $\pi/2$ at $T = 0$, so that the additional scattering by the LSF cannot but decrease the resistivity.

Next we notice that, as in Ch. 2, the resistivity (eq. 21) is a universal function of T/T_K. As long as the dominant contribution to the resistivity of a dilute alloy comes from the scattering by the localised spin fluctuations, the temperature dependence of the resistivity will have the same functional form, no matter how different the systems might appear. The illustration of this universality is given by the resistivities of Rh Fe and Ir Fe which scale to the same curve (Figure 1) if we plot them as a function of the reduced temperature $\tilde{T} = 2\pi(T/T_K)$ and chose $T_K = 15K$ for Rh Fe and $T_K = 225K$ for Ir Fe.

The characteristic temperature separates two different regimes. Below T_K, the impurity appears to be non-magnetic, while above T_K one cannot distinguish between the LSF and the permanent moment at the impurity site, because the lifetime of thermal fluctuations becomes shorter than the characteristic time of the magnetic fluctuations on the impurity site.

Let us now discuss the temperature dependence of the resistivity given by the equation (21). We distinguish the following temperature regimes:

(i) Below 0.4 $\tilde{T}$ the resistivity is parabolic

$$\tilde{\rho}(T) = \frac{\pi^2}{2}\left(\frac{T}{T_K}\right)^2 \tag{23}$$

which is the characteristic behaviour of a normal Fermi liquid when the dominant contribution to the scattering matrix comes from the electron-electron interactions.

(ii) At temperatures of the order of $\tilde{T} \simeq 0.9 \frac{T_K}{2\pi}$, the resistivity becomes linear in T. We have

$$\tilde{\rho}(T) = \gamma(T - \theta) \tag{24}$$

with $\gamma = (1.12/T_K)$ and $\theta = (0.2\ T_K/\pi)$. Again linear temperature dependence is expected when the conduction electrons are scattered on Bose like particles.

(iii) Above the spin fluctuation temperature, the resistivity becomes logarithmic

$$\tilde{\rho}(T) = c + B\ \ln\left(\frac{T}{T_K}\right) \tag{25}$$

where c = 0.68 and B = 0.24. As discussed in the previous chapter, such temperature dependence is indicative of a target with an internal structure (spin up and down, Anderson, 1968). Above T_K the LSF-impurity behaves like a well defined spin, although the effective coupling constant J between the impurity "spin" and the conduction electron spin (if it is possible to define J at all by a Schrieffer-Wolff (1966) transformation) is enormous in an alloy described by the Wolff Hamiltonian (the Wannier orbital of the impurity is right at the Fermi surface).

(iv) Finally, for $T \to \infty$ resistivity approaches a constant value as 1/T

$$\tilde{\rho}(T) \simeq \frac{1}{\Gamma}\left[1 - 2\pi \frac{T_K}{T}\right] \tag{26}$$

We recognise this constant as a maximum in the scattering power of the target on which the conduction electron is scattered and by analogy with the LSF in the Al Mn we say that the resistivity is at the unitarity limit. For Coles alloys we can show that this limit is the same as the Yosida limit (Kasuya, 1956; Yosida, 1957; Friedel and de Gennes, 1958) by the following argument.

Yosida limit is defined as the high temperature constant part of the resistivity which is due to the scattering of conduction electrons on an assembly of random spins. In the two band model and for the conduction electrons only weakly coupled to the local spin (small J), it is obtained as a result of the lowest order perturbation theory (Born approximation). For large coupling constant, this approximation ceases to be valid and the scattering matrix has to be calculated by more sophisticated methods (Abrikosov, 1965; Suhl, 1965; Nagaoka, 1967; Bloomfield and Hamann, 1967). One obtains that for high temperatures the resistivity approaches the unitarity limit, rather than the value given by the simple perturbation theory. (See e.g. Kondo 1969, equations (19.1), (19.2), and (22.8). Since the present single band model could be regarded as containing the impurity spins and conduction electrons with an extremely large coupling constant J, the Yosida limit is the same as the unitarity limit.

The presence of a high temperature plateau in addition to the logarithmic dependence of the resistivity is a further indication that, above T_K, the LSF describe a true spin in the sea of the conduction electrons. The fact that $\tilde{\rho}$ is not far from the unitarity limit in Rh Fe was first emphasised by Anderson (1968), summarizing a paper by Geballe et al. (1966).

Although in Coles alloys we can explain the replacement of the Yosida limit by a unique, spin independent, high temperature limit (unitarity limit), this remains a puzzle in general; in the case of the Anderson model we have seen that the resistivity tends to zero as $T \to \infty$, regardless of E_d (see Fig. (2)). In the case of the Wolff model it is easy to show that $\tilde{\rho} \to 1/\Gamma$ as $T \to \infty$, regardless of W. This clearly does not correspond to the experimental data for the Kondo alloys. We should recall here that this theory includes s-wave scattering only and is non-renormalised; therefore it is weak in the $\Sigma \to \infty$ limit, which is just the situation we encounter when $T \to \infty$.

Before comparing our results with the experimental data we want to make a comment on the specific heat of Coles alloys. We are concerned with the low temperature contribution to the electronic specific heat due to the localised spin fluctuations. As in Ch. 2, we calculate the entropy of the local interacting Fermi gas from which the impurity part of the specific heat is simply obtained as

$$C_V = T\left(\frac{dS}{dT}\right) \tag{27}$$

Carrying out the same procedure as in Ch. 2, we obtain for C_V

$$C_V = \frac{\pi^2 k_B^2 T}{3} \Sigma_\sigma \frac{1}{\pi} \text{Im} \quad G_o^{R^{-1}} \frac{dG_o^R}{\partial \varepsilon} \tag{28}$$

where $G_o^R(\varepsilon)$ is the Fourier transform of the local Green function evaluated at zero temperature. Using for $G_o^R(\varepsilon)$ expression (17) we obtain

$$C_V = \frac{2\pi \ k_B T}{3T_K} \tag{29}$$

The dependence of C_V on the inverse of the spin fluctuation temperature is a characteristic feature of the local enhancement and it is in sharp contrast with the uniform enhancement theory (Berk and Schrieffer, 1966; Doniach and Engelsberg, 1966).

4.5 Comparison with Experiment and Conclusion

In analysing experimental data, we assume that the impurity part of the resistivity is simply given by

$$\rho_{imp}(T) = \rho(T) + \rho_{potential}$$
$$= \rho_{alloy} - \rho_{host}$$

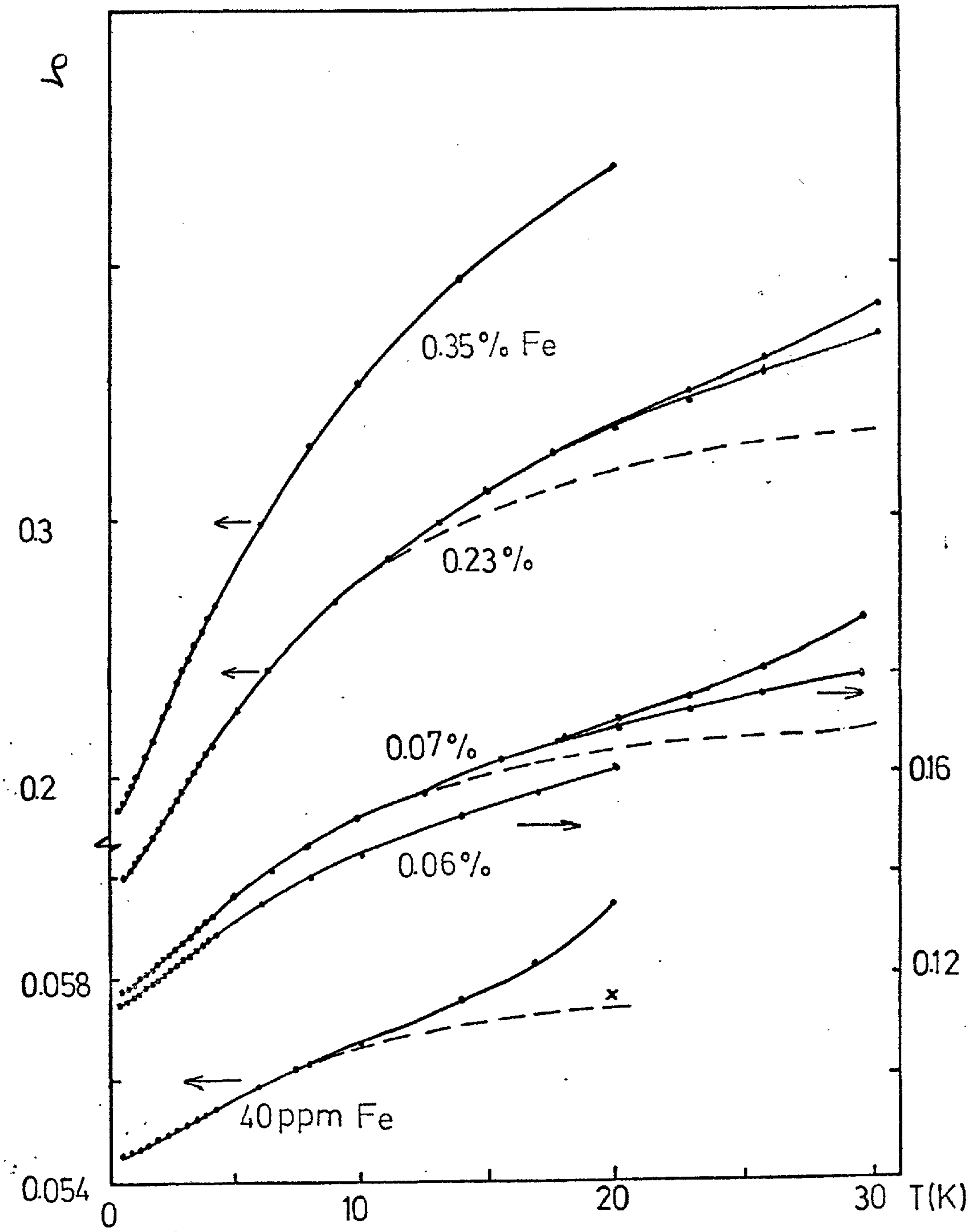
and that the small potential scattering which is due to impurity atoms does not contribute to the temperature dependence of the resistivity, i.e. that $\rho_{potential} = \rho_{imp}(0)$. Linear variations of $\rho_{imp}(T)$ with concentration support our assumption that for dilute alloys the addition of impurities does not significantly change the electron-phonon resistivity.

In Figure (1) the low concentration resistivity data on Rh Fe and Ir Fe are compared with the theoretical curve (eq. 21). The LSF temperature T_K is chosen to be T_K = 15K for Rh Fe and T_K = 225K for Ir Fe. These values are about eight times those extracted from the low temperature regimes by Kaiser and Doniach (1970) but agree with those derived from the susceptibility measurements of Waszink (1965) and of Knapp and Sarachik (1969).

Apart from Rh Fe and Ir Fe the logarithmic behaviour of the resistivity has been suggested as the best possible fit to the Pt Fe measurements of Loram et al. (1972), with $T_K \simeq$ 2K or higher.

Parabolic and linear low temperature regimes have been seen in various systems: Rh Co (Coles et al., 1971), Rh Mn (Coles et al., 1971), Pd Ni (Schindler and Rice, 1967), but in most of these cases the resistivity was measured

Figure 2



Resistivity data on various Rh Fe alloys against temperature (Rusby, 1974). The concentration effects tend to decrease the LSF temperature and push the onset of the logarithmic part of the resistivity towards lower temperatures. Dashed lines are the theoretical curves (equation 21).

only over limited temperature range so that it is difficult to determine the characteristic temperature accurately.

Also, in analysing the experimental data one has to be sure that they correspond to the single impurity limit. We notice that the interaction effects tend to decrease the LSF temperature, as can be seen in Rusby's data on the resistivity of several Rh Fe alloys (Figure 2). As the iron concentration increases, the coefficient of the T^2 term also increases and the onset of the linear region is depressed towards lower temperatures, until at about 0.6% iron the magnetic order sets in.

In conclusion, we have shown in this chapter that the resistivity of "Coles" alloys can be described by a model involving a single band of host electrons scattered by localised spin fluctuations. A single band is probably a good representation of the electronic states in Rh and Ir (Loram and Grassie, 1972).

The resistivity is given by the universal function of temperature which is zero at T = 0 and increases with increasing temperature, successively as T^2, T, ln(T) and 1/T towards the unitarity limit.

The nature of the spin fluctuations is the same for "Kondo" alloys (Chapter 2) and "Coles" alloys. The resistivity is initially an increasing or decreasing function of temperature depending on the affinity between impurity and host. A given alloy lies between the orthogonal and overcomplete limit of the representation {host conduction states, impurity localised states}, the two limits being described by the Anderson and Wolff Hamiltonian, respectively.

REFERENCES

Abramowitz, M. and Stegun, I.A., 1965, Handbook of Mathematical Functions (Dover, New York).

Abrikosov, A.A., 1972, Vedenye v Teoriyu Normalnih Metalov (Nauka, Moscow).

Abrikosov, A.A., Gorkov, L.P. and Dzyaloshinskii, I. Ye., 1965, Quantum Field Theoretical Metohds in Statistical Physics, 2nd ed. (Pergamon, Oxford).

Abrikosov, A.A. and Migdal, A.A., 1970, J. Low. Temp. Phys. 3, 519.

Aoki, R. and Ohtsuka, T., 1969, J. Phys. Soc. Japan 26, 651.

Anderson, P.W., 1961, Phys. Rev. 124, 41.

Anderson, P.W., 1968, in Many Body Problem, ed. C. de Witt and R. Balian (Gordon and Breach, New York).

Anderson, P.W., 1973, Comments Solid St. Phys. 5, 73; 3, 153; 1, 190; 1, 31.

Babić, E. et al., 1971, Phys. Rev. Lett. 27, 805.

Beaglehole, D. and Wihl, M., 1972, J. Phys. F: Metal Phys. 2, 43.

Beal-Monod, M.T. and Mills, D.L., 1970, Phys. Rev. Lett. 24, 225.

Berk, N.F. and Schrieffer, J.R., 1966, Phys. Rev. Lett. 17, 433.

Bloomfield, P.E. and Hamann, D.R., 1967, Phys. Rev. 164, 856.

Boato, G. and Vig, J., 1967, Solid St. Commun. 5, 649.

Brodsky, M.B., 1971, in Magnetism and Magnetic Materials, ed. C.D. Graham, Jr. and J.J. Rhyne (AIP, New York).

Brodsky, M.B., 1974, Phys. Rev., to be published.

Callender, A.B. and Schnatterly, S.E., 1973, Phys. Rev. B7, 4385.

Caplin, A.D. and Rizzuto, C., 1968, Phys. Rev. Lett. 21, 746.

Caroli, B., Lederer, P. and Saint James, D., 1969, Phys. Rev. Lett. 23, 700.

Clogston, A.M. et al., 1962, Phys. Rev. 125, 541.

Coles, B.R., 1963, Phil. Mag. 8, 335.

Coles, B.R., Waszink, J.H. and Loram, J.W., 1964, Proc. Int. Conf. on Magnetism, Nottingham.

Coles, B.R., Mozumder, S. and Rusby, R., 1971, Proc. 12th Int. Conf. Low Temp. Phys., Kyoto, 1970, ed. Kanda, (Academic Press, Japan).

Daniel, E. and Friedel, J., 1964, Proc. 9th Int. Conf. Low Temp. Phys., Part B, eds. J.G. Daunt, D.O. Edwards, F.J. Milford, M. Yaqub (Plenum Press, New York).

de Gennes, P.G. and Friedel, J. 1958, J. Phys. Chem. Solids 4, 71.

Doniach, S., 1967, Proc. Phys. Soc. 91, 86.

Doniach, S. and Engelsberg, S., 1966, Phys. Rev. Lett. 17, 750.

Edwards, S.F., 1958, Phil. Mag. 3, 1020.

Fisher, K., 1967, Phys. Rev. 158, 613.

Flynn, C.P., Rigney, D.A. and Gardner, J.A., 1967, Phil.

Mag. 15, 1255.

Friedel, J., 1958, Nuovo Cim. Suppl. 7, 287.

Friedel, J. and Blandin, A., 1959, Phil. Mag. 4, 180.

Geballe, T.H. et al., 1966, J. Appl. Phys. 37, 1181.

Grüner, G., 1972, Solid State Commun. 10, 1039.

Grüner, G., 1973, Adv. Phys., to be published.

Grüner, G. and Zawadowski, A., 1972, Solid State Commun. 11, 663.

Hamann, D.R., 1969, Phys. Rev. 186, 549.

Hamann, D.R., 1969a, Phys. Rev. Lett. 23, 95.

Hargita, C. and Corradi, G., 1969, Solid State Commun. 7, 1535.

Hassing, R.F. and Esterling, D.M., 1973, Phys. Rev. B7, 432.

Hubbard, J., 1959, Phys. Rev. Lett. 3, 77.

Jullien, R., Beal-Monod, M.T. and Coqblin, B., 1973, Phys. Rev. Lett. 30, 1057.

Kaiser, B.A., 1971, Ph.D. Thesis, University of London (unpublished).

Kaiser, B.A. and Doniach, S., 1970, Int. J. Magnetism, 1, 11.

Kasuya, J., 1956, Prog. Theor. Phys., Kyoto, 16, 58.

Kittel, C., 1966, Introduction to Solid State Physics, 3rd ed. (Wiley, New York).

Kjöllerström, B., 1969, Phil. Mag. 19, 1207.

Kjöllerström, B., Scalapino, D.J. and Schrieffer, J.R., 1966, Phys. Rev. 148, 665.

Klein, A.P. and Heeger, A.J., 1966, Phys. Rev. 144, 458.

Kondo, J., 1964, Prog. Theor. Phys. 169, 437.

Kondo, J., 1969, Solid State Physics, vol. 23, eds. F. Seitz, D. Turnbull and H. Ehrenreich (Academic Press, New York).

Knapp, G.S., 1967, Phys. Lett. 25A, 114.

Knapp, G.S., and Sarachik, M.P., 1969, J. Appl. Phys. 40, 1474.

Krsnik, R., Babić, E. and Rizzuto, C., 1973, Solid State Commun., 12, 861.

Landau, L. and Lifshitz, E.M., 1963, Statistical Physics, 3rd ed. (Pergamon, Oxford).

Langer, J.S. and Ambegaokar, 1961, Phys. Rev. 121, 1091.

Larkin, A.I. and Melnikov, V.I., 1971, Zh. Exp. Teor. Fiz. 61, 1232.

Larsen, J., 1973, to be published.

Lavrentiev, M. and Chabat, B., 1972, Méthodes de la théorie des fonctions d'une variable complexe, (Mir, Moscow).

Lederer, P., 1970, Proc. Nato Advanced Study Institute "Magnetism-Current Topics", La Colle sur Loup, 1970, to be published.

Lederer, P. and Mills, D.L., 1967, Solid State Commun. 5, 131.

Lederer, P. and Mills, D.L., 1968, Phys. Rev. 165, 837.

Levine, M. and Suhl, H., 1968, Phys. Rev. 171, 567.

Loram, J.W., White, R.J. and Grassie, A.D.C., 1972, Phys. Rev. B5, 3659.

Loram, J.W. and Grassie, A.D.C., 1973, to be published.

Matthias, B.T. et al., 1960, Phys. Rev. Lett. 5, 542.

Messiah, A., 1958, *Quantum Mechanics*, (North-Holland, Amsterdam).

Mott, N.F. and Jones, H., 1936, *The Theory of the Properties of Metals and Alloys*, (Oxford University Press, London).

Morandi, G. and Ratto, C.F., 1974, preprint.

Myers, H., Wallden, L. and Karlsson, A., 1968, Phil. Mag. *18*, 725.

Nagaoka, Y., 1968, Prog. Theor. Phys. (Kyoto), *39*, 533.

Nagasawa, H., 1970, Phys. Lett. *32A*, 271.

Narath, A., 1972, Crit. Rev. Solid State Phys. *3*, 1.

Narath, A., and Weaver, H.T., 1969, Phys. Rev. Lett. *23*, 233.

Rivier, N., 1968, Ph.D. Thesis, University of Cambridge (unpublished).

Rivier, N. and Zuckermann, M.J., 1968, Phys. Rev. Lett. *21*, 904.

Rivier, N. and Zitkova, J., 1971, Adv. Phys. *20*, 143.

Rizzuto, C., 1974, Rep. Prog. Phys., in press.

Rizzuto, C., Babić, E. and Stewart, A.M., 1973, J. Phys. F: Metal Phys. *3*, 825.

Rusby, R.L., 1974, J. Phys. F: Metal Phys. *4*, in press.

Sarachik, M.P., 1968, Phys. Rev. *170*, 679.

Sarachik, M.P., Corenzwit, E. and Longinotti, L.D., 1964, Phys. Rev. *135*. A1041.

Schindler, A.I. and Rice, M.J., 1967, Phys. Rev. 164, 759.

Schrieffer, J.R., 1970, CAP Summer School Lectures, Banff.

Schrieffer, J.R. and Mattis, D.C., 1965, Phys. Rev. 140, A1412.

Schrieffer, J.R. and Wolff, P.A., 1966, Phys. Rev. 149, 491.

Schrieffer, J.R., Evenson, W.E. and Wang, S.Q., 1971, J. Physique Colloque C1, C1.

Schrieffer, J.R. et al., 1969, Phys. Rev. Lett. 23, 92.

Sherrington, D., 1971, J. Phys. C: Solid State Phys. 4, 401.

Schweitzer, J.W., Abito, G.F. and Delinger, W.G., 1972, Phys. Rev. B6, 4238.

Star, W.M., 1971, Ph.D. Thesis, University of Leiden (unpublished).

Stratonovich, R.L., 1957, Dok. Akad. Nauk SSSR, 1097.

Suhl, H., 1967, Phys. Rev. Lett. 19, 442.

Suhl, H. and Wong, D., 1967, Physics 3, 17.

Vučić, Z., Cooper, J. and Babić, E., 1973, to be published.

Waszink, J.H., 1965, Ph.D. Thesis, University of London (unpublished).

Wolff, P.A., 1961, Phys. Rev. 124, 1030.

Yosida, K., 1957, Phys. Rev. 107, 396.

Ziman, J.M., 1960, Electrons and Phonons, (Oxford University Press, London).