THE UNIVERSITY OF MANITOBA

THE ELECTRICAL RESISTIVITY OF SOME EXCHANGE ENHANCED SYSTEMS: (PdRh)Fe AND (PdRh)Co

by

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ABSTRACT

The electrical resistivity of two giant moment systems -- (Pd₉₅Rh₅)Fe containing between 0.8 and 1.85 at. % Fe and (Pd₉₅Rh₅)Co containing between 1.0 and 2.6 at.% Co-has been measured from 1.4 to 300K. The incremental resistivity in (PdRh)Fe alloys containing more than 1.25 at.% Fe and (PdRh)Co alloys containing more than 1.4 at. % Co is found to exhibit a T^2 limiting low temperature However for the 0.8 and 1.1 at % Fe alloys and the form. 1.0 at.% Co alloy, such a T^2 form is not clearly discernable, with $\Delta
ho$ (T) exhibiting a temperature dependence intermediate between T^2 and $T^{3/2}$. The former result is predicted from conduction electron-magnon scattering for which wave vector conservation holds, from which it is inferred that the criterion for wave vector conservation in this type of alloy is not determined by mean free path effects. Estimates of the acoustic spinwave stiffness D are derived from the measured T^2 coefficients.

These resistivity data also enable the magnetic ordering temperature, T_c , and the exchange coupling parameters, $J_{s-local}$ and $J_{d-local}$, to be evaluated.

In the disordered phase, the measured incremental resistivity of the (PdRh)Fe system is found to contain a term which decreases approximately linearly with increasing

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temperature, at a rate of $-(1.1 \pm 0.45) \times 10^{-3} \mu \Omega \text{ cm/K}$ at.% Fe. Using existing pressure data on both Pd and PdRh based alloys, it is shown that both the sign and magnitude of this term can be accounted for in terms of the volume dependence of the potential and exchange terms, in conjunction with a large coefficient of thermal expansion.

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CHAPTER ONE

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THEORETICAL CONCEPTS

1.1 Localized Magnetic Moments in Metals

If a dilute alloy is made by dissolving a first row (3d) transition atom impurity (like Fe) in a simple metal, it is often found that the impurity atom possesses a net magnetic moment. Some time ago, Friedel was able to explain the formation of these local moments in terms of the concept of the virtual bound state (VBS).^{1,2}

In metals, the bandwidths of the free electron states are so broad that the energy levels of the impurity lie, in general, within the conduction band. So. let's begin by considering a localized level (representing a d-state of the impurity atom) immersed in a sea of mobile electrons (representing the conduction band of the host). The mixing between the conduction s-electrons and the localized d-electrons shifts and broadens the energy of the localized d-state -- making it into a virtual level i.e., one which is spread out in energy because of s-d interactions (see Fig. 1-1). The virtual state can accommodate the same number of d-electrons as the original localized However, the d-electrons (or, more rigorously, the state. magnetic electrons) are partially itinerant because of the possibility that they will transfer to s-states having similar energies. As a result, the virtual bound state describes something intermediate between a localized and an itinerant situation.

To explain the presence of a net magnetic moment on the impurity, Friedel pointed out that, since the electrons in a virtual state are well localized, exchange and

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correlation forces will be very effective, especially for a narrow level, with a tendency to favouring spin alignment. When these forces prevail, the virtual bound d-state splits into two localized substates, one for spin-up (+) electrons and one for spin-down (-) electrons, having different energies. When these two states accommodate unequal numbers of electrons up to the Fermi level, a magnetic moment results, localized on the impurity site.

1.2 The Anderson Model

To put these ideas on a more quantitative basis, Anderson³ solved the following simple model. Let us assume that the impurity atom is <u>magnetic</u> (possesses a magnetic moment). This means that a d-state of, say, spin up on the impurity atom is occupied, while one of spin down is empty. Now, a spin-down electron within the d-shell will see the repulsion of the spin-up electron in the filled d-state (another spin-up electron will not, since parallel spin electrons can have no exchange energy). Thus, if the energy of the spin-up state lies a distance E_d below the Fermi surface, the energy of the spin-down localized state will be $E_d + U$, where U is the repulsive d-d interaction. This must lie above the Fermi level, because we assume this state to be empty.

As before, the mixing between the s and d electrons shifts and broadens the energy of the filled spin-up d-state (and the empty spin-down state above the Fermi level),

making it into a virtual state. However, the broadening pushes a portion of the spin-up virtual state above the Fermi level reducing the number of localized spin-up d-electrons. In the same way, a portion of the spin-down virtual state is pulled below the Fermi level thus increasing the number of localized spin-down d-electrons (see Fig. 1-2). These changes in the number of electrons are such as to decrease the difference U between the spin-up and spin-down energies- $-E_d$ moves up and $E_d + U$ moves down. The larger the s-d admixture, the smaller the energy difference between the spin-up and spin-down states. Eventually, the configuration collapses into two degenerate levels and it is no longer possible to maintain a magnetic moment.

The Anderson Hamiltonian may be expressed in the following way:

$$H = H_{s} + H_{d} + H_{corr} + H_{kd}$$
(1)

The first term, H_S , is the unperturbed energy of the free conduction s-electrons. In second-quantized notation

$$H_{s} = \sum_{\underline{k}, \sigma} E_{\underline{k}} C_{k\sigma} C_{k\sigma}$$
(2)

where $C_{k\sigma}^{+}$ and $C_{k\sigma}^{-}$ are the creation and annihilation operators, respectively, for a conduction electron of wave vector <u>k</u>, energy E_k and spin σ (σ can be + or -).

The second term, H_{d} , is the unperturbed energy of the d-states on the impurity atom. In our discussion, we will assume the physically unrealistic case of a single



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2. 1-2. Density of states in the magnetic case. The "humps" are the virtual d states of width 2Δ for up and down spins. The numbers of electrons occupying them are computed from the area of the unshaded portion, below the Fermi surface.

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1993년 1997년 1997년 전 1997년 1998년 1997년 - 1997년 nondegenerate level, because the principle of the method is easily extended to the more complicated many-level d shell. This term in the Hamiltonian is written

 $H_{d} = E_{d} (n_{d+} + n_{d-})$ (3)

where n_{d+} and n_{d-} are the numbers of spin-up (+) and spin-down (-) d electrons, respectively.

The third term, H_{corr}, is the repulsive energy among the d electrons. For electrons of the same spin, the Coulomb integral cancels the Exchange integral. This leaves us with only the antiparallel part of the Coulomb integral:

 $H_{corr} = Un_{d+} n_{d-}$ (4) H_{corr} is responsible for splitting a virtual state into two substates, one for each spin direction.

The fourth essential part of the Anderson Hamiltonian is the s-d interaction term, H_{kd} . It allows for the mixing of the conduction electron state <u>k</u> with an electron in one of the virtual d-states. Usually, H_{kd} takes the form

$$H_{kd} = \sum_{\underline{k},\sigma} \left\{ V_{kd} C_{k\sigma}^{+} C_{d\sigma} + V_{kd}^{*} C_{d\sigma}^{+} C_{k\sigma}^{\cdot} \right\}$$
(5)

where V_{kd} describes the strength of the s-d mixing (V_{kd}^{*} is the conjugate of V_{kd}). $C_{d\sigma}^{+}$ and $C_{d\sigma}^{-}$ are the creation and annihilation operators, respectively, for a d-electron of spin σ . It is the mixing term, H_{kd} , which broadens the localized d-state, making it into a virtual state.

If we solve the Anderson Hamiltonian, we arrive at the following expression for the density of states $ho_{\rm d}$ (E) of the spin-up (+) and spin-down (-) virtual d-states:³

$$\rho_{d\pm}(E) = \frac{1}{\pi} \frac{\Delta}{(E - E\pm)^2 + \Delta^2}$$
(6)

where

$$E_{\pm} = E_{d} + p.p. \int \frac{N(E_{k}) |v_{kd}|^{2}}{E - E_{k}} dE_{k} + U \langle n_{d\mp} \rangle$$

$$= \mathbf{E}_{\mathbf{d}} + \mathbf{\Gamma} + \mathbf{U} \left\langle \mathbf{n}_{\mathbf{d}} \right\rangle$$
 (7)

and

 $\Delta = \pi |v_{kd}|^2 \quad N(E) .$ (8)

E+ are the energies around which the spin-up and spin-down virtual states are centered, and 2 Δ is the width of a virtual state. N(E) is the density of states in the conduction band.

We can now determine the number of electrons, $\left< n_{d\pm} \right>$, occupying the two virtual d-states, merely by integrating $\rho_{d\pm}(E)$ up to the Fermi energy E_f (since all the states below E_f are full, at least at absolute zero). Thus

$$\left\langle n_{d\pm} \right\rangle = \frac{1}{\pi} \int_{-\infty}^{E_{f}} \frac{\Delta}{(E - E_{\pm})^{2} + \Delta^{2}} dE$$
$$= \frac{1}{\pi} \cot^{-1} \left\{ \frac{E_{\pm} - E_{f}}{\Delta} \right\} . \tag{9}$$

the expression for E_{\pm} in (7) with $E_{d} + \int$ replaced by E_d^1 , we obtain

$$\langle n_{d+} \rangle = \frac{1}{\pi} \operatorname{cot}^{-1} \left\{ \frac{E_{d}^{1} + U \langle n_{d-} \rangle - E_{f}}{\Delta} \right\}$$

$$\langle n_{d-} \rangle = \frac{1}{\pi} \operatorname{cot}^{-1} \left\{ \frac{E_{d}^{1} + U \langle n_{d+} \rangle - E_{f}}{\Delta} \right\}$$

$$(10)$$

The solutions of these two coupled equations are the intersections of the two curves obtained when $\langle n_{d+} \rangle$ is plotted as a function of $\langle n_{d-} \rangle$. Those solutions for which $\langle n_{d+} \rangle \neq \langle n_{d-} \rangle$ are at a minimum of the energy and represent the magnetic impurity states.

1.3 The s-d Model

Suppose we characterize a magnetic impurity atom by simply assigning it a spin <u>S</u>. This spin will interact with the itinerant conduction electrons, of spin <u>s</u>, through an exchange coupling of the form $-2J\underline{S}\cdot\underline{s}$, where J is the strength of the exchange interaction. This is the <u>s</u>-d model, so called because it really describes a coupling between two kinds of electrons.-the d electrons (which give rise to the impurity spin <u>S</u>) localized at the impurity sites, and the <u>s</u> electrons in the conduction band.

The s-d Hamiltonian consists of two terms--a spinindependent term and a spin-dependent term--and is usually written in the form⁴

$$H_{sd} = \sum_{i} \sum_{n} V(\underline{r}_{i} - \underline{R}_{n}) - 2 \sum_{i} \sum_{n} J(\underline{r}_{i} - \underline{R}_{n}) (\underline{s}_{i} \cdot \underline{S}_{n})$$
(11)

where $\underline{r_i}$ and $\underline{R_n}$ represent the position vectors of the ith conduction electron and the nth impurity atom, and $\underline{s_i}$ and $\underline{S_n}$ are their respective spin operators.

In the first (spin-independent) term, $V(\underline{r}_i - \underline{R}_n)$ is the deviation of the potential from perfect periodicity, due to the impurity atoms, and in the second (spin-dependent) term, $J(\underline{r}_i - \underline{R}_n)$ is the effective exchange integral between the conduction electron and the impurity atom.

In second-quantization notation, the Hamiltonian in (11) becomes⁵

$$H_{sd} = N^{-1} \sum_{k=1}^{d} \sum_{k=1}^{d} V(\underline{k}, \underline{k}^{1}) e^{i(\underline{k}-\underline{k}^{1}) \cdot \underline{R}_{n}} (a_{k}^{*}1_{+} a_{k+} + a_{k}^{*}1_{-} a_{k-})$$

$$-N^{-1} \sum_{k=1}^{d} \sum_{k=1}^{d} J(\underline{k}, \underline{k}^{1}) e^{i(\underline{k}-\underline{k}^{1}) \cdot \underline{R}_{n}} [(a_{k}^{*}1_{+} a_{k+} - a_{k}^{*}1_{-} a_{k-}) S_{n}^{z}]$$

$$+ a_{k}^{*}1_{-} a_{k+} S_{n}^{+} + a_{k}^{*}1_{+} a_{k-} S_{n}^{-}] . \qquad (12)$$

In this expression, the z axis is the spin quantization axis and S_n^{\pm} represents $S_n^{\times} \pm i S_n^{\vee}$. The quantities $a_{k\pm}^{*}$ and $a_{k\pm}$ are the creation and annihilation operators for a conduction electron with wave vector <u>k</u> and with spin parallel (+) or antiparallel (-) to the z axis. N is the total number of lattice points. $V(\underline{k}, \underline{k}^{1})$ and $J(\underline{k}, \underline{k}^{1})$ are related to the matrix elements of $V(\underline{r}_{i} - \underline{R}_{n})$ and $J(\underline{r}_{i} - \underline{R}_{n})$ between two states with wave vectors <u>k</u> and <u>k^{1}</u> as follows: $V(\underline{k}, \underline{k}^{1}) = Ne^{-i}(\underline{k}-\underline{k}^{1}) \cdot \underline{R}_{n} \int \phi_{\underline{k}}^{*}1(\underline{r}) V(\underline{r} - \underline{R}_{n}) \phi_{\underline{k}}(\underline{r}) d\tau$ $J(\underline{k}, \underline{k}^{1}) = Ne^{-i}(\underline{k}-\underline{k}^{1}) \cdot \underline{R}_{n} \int \phi_{\underline{k}}^{*}1(\underline{r}) J(\underline{r} - \underline{R}_{n}) \phi_{\underline{k}}(\underline{r}) d\tau$, (13)

where $\phi_{\underline{k}}$ represents the wave function of the conduction electron with wave vector \underline{k} . In general, $V(\underline{k},\underline{k}^1)$ and $J(\underline{k},\underline{k}^1)$ depend only on $\left|\underline{k} - \underline{k}^1\right|$.

A close relationship exists between the s-d model and the Anderson model. Schrieffer and Wolff⁶ have shown in the limit of small s-d mixing ($|V_{kd}| \ll 1$), which is the most favourable case for the occurrence of a localized moment, that the two models are in fact equivalent, and the Anderson Hamiltonian can be transformed into a form similar to (11). Moreover, the energy-dependent exchange interaction $J(\underline{k}, \underline{k}^1)$, for \underline{k} and $\underline{k}^1 \simeq \underline{k}_f$, is given by the following expression

$$V(0) = 2 \left| V_{kd} \right|^2 \frac{U}{E_d(E_d + U)} \approx \text{constant.}$$
 (14)

Now since E_d is measured relative to the Fermi energy E_f , it will be negative when a local moment exists. Consequently, J will be negative. This means that the coupling between the impurity spin and the conduction electron spins is antiferromagnetic.

1.4 The Polarization of the Conduction Electrons

How do the free electrons in the conduction band respond to the localized s-d exchange interaction? Suppose we consider only the second (spin-dependent) term in the s-d Hamiltonian given by (12). This term has the following diagonal ($k = k^1$) element.⁷

$$-N^{-1} J(0) (n_{+} - n_{-}) \sum_{n}^{I} S_{n}^{Z}$$
 (15)

where n_{+} and n_{-} represent the number of conduction electrons of up (+) and down (-) spin, respectively. This diagonal energy becomes lower and lower as $(n_{+} - n_{-})$ increases, and consequently the conduction electron spins are polarized by the spin on the impurity.

In order to obtain the spacial distribution of the conduction electron polarization $\mathcal{T}(\mathbf{r})$ around a magnetic impurity, we will replace the effect of the impurity spin with an effective magnetic field $h(\mathbf{r})$.⁸ In this way, we can simplify our calculations without losing any of the essential features. If we assume that the s-d exchange interaction is of the δ -function type (in reality, the s-d interaction has a finite range), the effective field $h(\mathbf{r})$ may be written

$$h(\mathbf{r}) = \frac{JS_Z}{g\mu_B} \delta(\mathbf{r})$$
(16)

where we have taken the site of the impurity to be at the coordinate origin (r = 0). S_z is the z-component of the localized impurity spin, and J is a constant representing the s-d coupling.

The conduction electron spin polarization $\sigma(r)$ around the impurity (at r = 0) is given by ⁸

$$\sigma(\mathbf{r}) = n_{+}(\mathbf{r}) - n_{-}(\mathbf{r})$$

= $(1/g\mu_{B}) \sum_{q}^{\prime} h(q) \chi(q) \exp(i\underline{q} \cdot \mathbf{r})$ (17)

where g is the electronic g-factor and μ_B is the Bohr magneton. h(q) is the Fourier transform of the effective field h(r):

$$h(q) = JS_{z}/g \mu_{B}$$
(18)

and $\chi(q)$ is the wave-number-dependent susceptibility of the

host metal. For a free electron gas $\chi(q)$ may be written

$$\chi(q) = -2\mu_{\rm B}^2 \sum_{k} \frac{f_{k+q} - f_k}{E_{k+q} - E_k} = 2\mu_{\rm B}^2 N(E_{\rm f}) U(q/2k_{\rm f}).$$
(19)

 E_k is the one-particle energy of a conduction electron with momentum $\hbar k$, f_k is the Fermi distribution function, and $N(E_f)$ is the density of states at the Fermi surface per spin orientation of the host metal. U(x) is the Lindhard function given by:

$$U(x) = \frac{1}{2} \left[1 + \frac{1 - x^2}{2x} \ln \left| \frac{1 + x}{1 - x} \right| \right]$$
(20)

with $x = q/2k_f$.

Using (18) for h(q) and (19) for χ (q), the expression for σ (r) becomes

$$\sigma(\mathbf{r}) = \frac{2JS_{Z}N(E_{f})}{g^{2}} \sum_{q'}^{\prime} U(q/2k_{f}) \exp(i\underline{q}\cdot\underline{r})$$
(21)

If we perform the integration over q in (21) as follows 7

$$\sum_{q} U(q/2k_{f}) \exp (i\underline{q} \cdot \underline{r}) = a \text{ constant } x F(2k_{f}r) \qquad (22)$$

where $F(x) = \frac{x \cos x - \sin x}{x^4}$ (23)

we finally obtain

$$\sigma(\mathbf{r}) = a \text{ constant } \mathbf{x} F(2\mathbf{k}_{f}\mathbf{r}).$$
(24)

The spin polarization given by (24) and shown in Fig. 1-3, oscillates and rapidly vanishes as r tends to infinity. Consequently, the polarization of the conduction electrons is concentrated in the neighbourhood of the impurity site. The oscillations in $\mathcal{O}(r)$ are known as the RKKY (Ruderman - Kittel - Kasuya - Yosida) oscillations.^{5,7,9}

$$\sigma(\mathbf{r}) = \mathbf{n}_{+}(\mathbf{r}) - \mathbf{n}_{-}(\mathbf{r})$$

$$\int_{0}^{1} \int_{0}^{1} \int_{0}^{1}$$

1.5 Exchange Enhancement and Giant Moments

So far in our discussion, we have not taken into account Coulomb interactions between conduction electrons. When we include these exchange forces, we find that the spin susceptibility has increased when compared to that of a non-interacting free electron gas. This effect is known as exchange enhancement.

For simplicity, we will replace the actual Coulomb interaction by a δ -function interaction of strength V, localized on the lattice sites. The host metal exchange enhanced spin susceptibility $\chi(q)$ is then given by¹⁰

$$\chi(q) = \frac{\chi^{0}(q)}{1 - VN(E_{f}) U(q/2k_{f})}$$
(25)

where $\chi^{0}(q) = 2 \mu_{B}^{2} N(E_{f}) \mathcal{U}(q/2k_{f})$ is the susceptibility of a non-interacting free electron gas. As a result of the enhancement factor $\gamma = \left[1 - N(E_{f}) V U(q/2k_{f})\right]^{-1}$, $\chi(q)$ is larger than $\chi^{0}(q)$ for all values of q. However, the enhancement is much greater for low q (see Fig. 1-4), and when q = 0 and $VN(E_{f}) U(0) = 1$, $\chi(0)$ becomes infinite, implying the existence of ferromagnetic ordering among the conduction electrons. (This is the Stoner condition for ferromagnetism).¹¹

Exchange enhancement is essentially a property of transition metal hosts (like Pd) in which there are d electrons in the conduction band. These d electrons belong to a narrow band, where exchange interaction effects are of prime importance, so that the Coulomb repulsion, V, is strong. This, coupled with a high density of states at the

Fermi level (due to the narrow d band), gives a large value for $VN(E_f)$, and hence for the susceptibility.

Since the enhanced susceptibility χ (q) can be related to an exchange interaction between d electrons in the conduction band, we are now led to consider how this exchange interaction affects the RKKY oscillations in the conduction electron spin polarization. The polarization σ (r) is again given by

 $\sigma(\mathbf{r}) = (1/g\mu_B) \sum_{q'}^{l} h(q) \chi(q) \exp(i\underline{q} \cdot \underline{\mathbf{r}})$ (26) but $\chi(q)$ is now the exchange enhanced susceptibility in (25). If, as before, we assume a δ -function coupling between the magnetic impurity spin and the conduction electron spins, then h(q) is again given by

$$h(q) = \frac{JS_Z}{g\mu_B} , \qquad (27)$$

and the spin polarization (26) becomes

 $\sigma(\mathbf{r}) = a \text{ constant } x \sum_{q'} \chi(q) \exp(i\underline{q} \cdot \underline{r})$

= (a constant) \times (Fourier transform of $\chi'(q)$) (28) Thus $\sigma(r)$ is proportional to the Fourier transform of $\chi'(q)$. But in Fig. 1-4 we see that the effect of exchange enhancement is to build up the low q region so that $\chi'(q)$ looks more and more peaked (for small values of q) as $VN(E_f)$ increases. This results in a longer and longer range for $\sigma(r)$ as the ferromagnetic instability $[VN(E_f) \cup (0) = 1]$ is approached. The exchange enhancement thus pushes out the first zero of the RKKY oscillations (we say that the RKKY oscillations have been suppressed) and increases their



Fig. 1-4. The q-dependent susceptibility of an electron gas. The solid curve $\chi^{O}(q)$ is drawn for no electronelectron interactions; the dashed curve is the exchange enhanced susceptibility $\chi(q)$ for the case $N(E_F)V = 0.9$. Note that the enhancement is q dependent, being largest at low q.

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amplitude (see Fig. 1-5). However, at sufficiently large distances from the impurity the polarization is again oscillatory.

Had we considered the finite range of the Coulomb interaction, the V appearing in the expression (25) for

 χ (q) would have become effectively q-dependent. This causes an even more rapid increase in χ (q) with decreasing q, and accordingly contributes to make the range of the magnetic disturbance even longer.

A direct consequence of the enhancement of the range of the induced spin polarization in transition metal hosts, is the formation of giant magnetic moments associated with the impurity atoms. The giant moment consists of the on-site impurity moment plus the attendant spin polarization in the host's d band. Moments as large as $12\mu_{\rm B}$ have been observed per Fe impurity in Pd.¹²

1.6 The Ordered Ground State of the Alloy

We have seen that when a localized moment (in the form of a magnetic impurity atom of spin \underline{S}_1) is introduced into a metal, the conduction electron spins develop an oscillating polarization in the vicinity of this moment. If there is another localized spin \underline{S}_2 present, it will interact with this induced spin polarization, resulting in an indirect coupling between the two localized impurity spins, so that \underline{S}_2 tends to line up parallel or antiparallel to \underline{S}_1 . In this way, impurity-impurity interactions eventually



lead to magnetic ordering of the impurity system.

In the low-concentration limit (< 1- at.% impurity), the nature of the ordered ground state of the alloy is determined essentially by the spacial variation of the conduction band polarization. The relatively rapid RKKY oscillations induced in the host's conduction band lead to a "disordered" antiferromagnetic ground state.¹³ In transition metal hosts (like Pd), where the effect of exchange enhancement suppresses the RKKY oscillations out to relatively large distances from the impurity, 14,15 the ordered ground state is of predominantly ferromagnetic character, being determined by a ferromagnetic coupling between giant However, there are still some impurities (at least moments. in the less concentrated alloys) which reside in regions of oscillating spin polarization and these remain frozen in an antiferromagnetic configuration.

In alloys containing several atomic percent impurity, complications arise due to the effect of direct interimpurity coupling (operative virtually only when impurities are nearest neighbours). Alexander and Anderson,¹⁶ and Moriya¹⁷ have investigated the effects due to a direct interaction between two nearest-neighbour magnetic impurities. The relevant conclusions reached on the basis of their approach are that impurities with nearly halffilled d shells tend to couple antiferromagnetically; ferromagnetic coupling is increasingly favoured as the number of d electrons increases.

We will now proceed to investigate the dynamic properties of the ordered phase of dilute alloys, in particular those alloys which form a well defined ferromagnetic ground state, even at very low concentrations of dissolved impurity. A typical such alloy is <u>PdFe</u>. Let's begin by considering a model in which the impurity (Fe) spins <u>S</u> are coupled to the itinerant d electrons (of spin $\underline{\sigma}_d$) in a single Pd d band via an exchange interaction of the form $-2J_{d-local} \underline{S} \cdot \underline{\sigma}_d$.^{18,19} The dynamical spin states that we are studying, arise from a coupling between the Fe spins <u>S</u>, which results from the polarization they induce in the itinerant Pd d band--in other words, a Heisenberg coupling between Fe spins via an exchange enhanced, frequency dependent RKKY interaction.

In order to discuss the dynamic properties of the combined system of the localized Fe spins coupled to the itinerant Pd spins, it is convenient to consider a generalized space and time dependent susceptibility function for the whole system:¹⁸

 $K(\underline{R}_{i} - \underline{R}_{j}, t - t^{1}) = -\theta(t - t^{1}) \left\langle \left[\overline{\sigma}(\underline{R}_{i}, t), \sigma'(\underline{R}_{j}, t^{1}) \right] \right\rangle (29)$ In this equation, $\theta(t)$ is the unit step function and \underline{R}_{i} and \underline{R}_{j} label the lattice sites. $\sigma'(\underline{R}, t)$ and $\sigma'(\underline{R}, t)$ are the <u>+</u> components of the spin density of the d-band electrons.

The total Hamiltonian H for the coupled system of d-band electrons plus the impurities is given by

$$H = H_{Pd} + H_{int}$$
(30)

 H_{Pd} is the Hamiltonian for the Pd d electrons

$$H_{pd} = \sum_{k,\sigma} E_k C_{k\sigma}^+ C_{k\sigma} + I \sum_{i} n_{i+} n_{i-}$$
(31)

where the E_k are the single-particle d-band electron energies, I is the strength of the repulsion between d electrons of opposite spin on the same atomic site, and n_{i+} and n_{i-} are the numbers of spin up (+) and spin down (-) d electrons on the ith lattice site. $C_{k\sigma}^+$ and $C_{k\sigma}^$ are the creation and annihilation operators for the d-band electrons.

 H_{int} is the Hamiltonian for the interaction between the set of localized iron spins \underline{S}_i on the impurity sites \underline{R}_i^{Fe} and the spin density $\mathcal{O}_d(\underline{R}_j)$ of the itinerant Pd d electrons at lattice site j:

$$H_{int} = -J_{d-local} \sum_{i} \frac{S_{i}}{I} \cdot \underline{\sigma}_{d}(\underline{R}_{i}^{Fe})$$
(32)

where J_{d-local} is an energy parameter measuring the effective exchange coupling.

If we calculate the Fourier transform $K(\underline{q},\omega)$ of the generalized susceptibility function in (29) we find

$$K(\underline{q},\omega) = \frac{\chi_0(\underline{q},\omega)}{1 - \left\{ I + 2J^2 R^1 / (JR-\omega) \right\} \chi_0(\underline{q},\omega)}$$
(33)

 $\chi_{o(q,w)}$ is the unenhanced susceptibility function for the magnetized (polarized) Pd d band,

$$\chi_{0}(\underline{q}, w) = \frac{1}{N} \sum_{k}^{\prime} \frac{n_{k, +} - n_{k+q, -}}{\omega - (E_{k} - E_{k+q}) - IR - 2JR^{1}}$$
(34)

where n_{k+} is the number of d electrons with wave vector k and spin up and N is the total number of lattice sites.

 $\mathbf{22}$

R and R^1 are the reduced magnetizations of the Pd and Fe spin systems, respectively, and are defined by

$$R = \frac{1}{N} \sum_{k}^{+} (n_{k+} - n_{k-}); R^{1} = -\frac{N_{Fe}}{N} \langle S^{Z} \rangle .$$
(35)

Note that, in (33), we may regard $\left\{ I + 2J^2 R^1 / (JR - \omega) \right\}$ as an effective frequency dependent interaction constant $I_{eff}(\omega)$.

Now (33) may be rewritten in an alternative form. For this purpose we introduce the exchange enhanced susceptibility function

$$\chi(\underline{q},\omega) = \frac{\chi_{0}(\underline{q},\omega)}{1 - I \chi_{0}(\underline{q},\omega)}$$
(36)

where $\chi_{0}(\underline{q},\omega)$ is given by (34). The function $K(\underline{q},\omega)$ then becomes

$$K(\underline{q},\omega) = \frac{(JR - \omega) \chi(\underline{q},\omega)}{JR - 2J^2R^1 \chi(\underline{q},\omega) - \omega}$$
(37)

Also, from (34) and (36), if $q \rightarrow o$ and $\omega \rightarrow o$

$$\chi(0,0) = R/2JR^{1}, \qquad (38)$$

so that (37) may be written in the form

$$K(\underline{q},\omega) = \frac{(JR - \omega) \chi(\underline{q},\omega)}{2J^2R^1 \left[\chi(0,0) - \chi(\underline{q},\omega)\right] - \omega}$$
(39)

The energies of the dynamical spin states of the system are given by the position of the poles of (39), that is, by

$$\omega = 2J^2 R^1 \left[\chi(o, o) - \chi(\underline{q}, \omega) \right] .$$
(40)

This relation is precisely of the form appropriate to spin waves in a Heisenberg spin system in which the spins are coupled by an interaction analogous to the RKKY interaction.²⁰ In the present case, the form of the RKKY

 $\mathbf{23}$

interaction is modified by exchange enhancement, see (36), and contains an essential frequency dependence resulting from the magnetization of the Pd d band. This strong frequency dependence leads to a new dynamical consequence: the appearance of an "optical" mode (finite frequency at q = 0) branch of the magnon spectrum. This mode would not be obtained if the usual, frequency independent form of the RKKY interaction were used.

If we evaluate (40), in the limit $q \rightarrow 0$, we find that it takes the form

 $\omega(JR + 2JR^{1} - \omega) = 0 \text{ as } q \rightarrow 0$ (41) Hence there are two spin wave models at $q \rightarrow 0$, namely, an acoustic mode

$$\omega_{\rm ac} = 0 \tag{42}$$

an an optical mode

$$\omega_{\rm op} = \rm{JR} + 2\rm{JR}^{1} \tag{43}$$

The presence of two branches in the spin wave spectrum (see Fig. 1-6) is natural for a material in which two nonequivalent spin systems (local moments and itinerant d electrons) contribute to the magnetization process.

So, in summary, we can say that

 At temperatures well below the magnetic ordering temperature, T_c, the coupled motion of the localized Fe spins and d electrons can be described by spin waves. These spin waves result from a Heisenberg model in which the impurity spins interact with one another via



an exchange enhanced, frequency dependent RKKY coupling; this coupling results from the magnetization of the itinerant d electrons which can be associated with the occurrence of giant moments.

2. As a result of the coupling between the two spin systems (local moments and itinerant d electrons), the spin wave spectrum is shown to have two branches, only one of which has zero frequency in the long wavelength limit (the acoustic mode).

1.7 Conduction Electron-Magnon Scattering

We are now in a position to calculate the additional resistivity $\Delta \rho(T)$ of the alloy (PdFe) over that of the pure host (Pd) by considering the scattering of s conduction electrons from acoustic mode spin wave excitations (the s electrons dominate the conductivity in view of their relatively low effective mass). The s band electrons couple, at the impurity sites, to these excitations via an isotropic coupling $-2JS \cdot \sigma_s$, with the effective exchange constant J having two contributions. The first comes from "direct" coupling of the s electrons to the localized (Fe) spins, the second from an "indirect" coupling via the excitation of an electron-hole pair in the coupled d band, which then scatters from a localized spin.²¹

The Hamiltonian which describes the s electronmagnon scattering is the s-d Hamiltonian given by (12).

We will denote it by $H_{s-local}$ and write it in the following way:

$$H_{s-local} = N^{-1} \sum_{k=k}^{l} \sum_{n}^{l} \exp \left\{ i (\underline{k} - \underline{k}^{1}) \cdot \underline{R}_{n} \right\} X$$

$$\left\{ \begin{bmatrix} V(\underline{k}, \underline{k}^{1}) - S_{n}^{z} J(\underline{k}, \underline{k}^{1}) \end{bmatrix} a_{k}^{*} a_{k+} + \begin{bmatrix} V(\underline{k}, \underline{k}^{1}) + S_{n}^{z} J(\underline{k}, \underline{k}^{1}) \end{bmatrix} a_{k}^{*} a_{k-} - J(\underline{k}, \underline{k}^{1}) (a_{k}^{*} a_{k-} S_{n}^{-} + a_{k}^{*} a_{k-} A_{k+} S_{n}^{+}) \right\} . \quad (44)$$

The probabilities $P(\underline{k}_{\pm}, \underline{k}^{1}_{\pm})$ for scattering from conduction electron state k_{\pm} (with spin parallel (+) or antiparallel (-) to the z axis and energy $E_{\underline{k}_{\pm}}$) to state $\underline{k}^{1\pm}$, can be obtained from (44) using the Golden rule:

$$P(\underline{k} \rightarrow \underline{k}^{1}) = \frac{2\pi}{\hbar} \left| \left\langle k^{1} \right| H_{s-local} \left| k \right\rangle \right|^{2} N_{f}(E_{k}), \quad (45)$$

where $N_f(E_k 1)$ is the final density of states with energy $E_k 1$.

(a) With Wave-vector Conservation

Suppose that we conserve both energy and wavevector for scattering of an s electron from state k to k^{1} . Then

1. for
$$k_{\pm} \rightarrow k^{\perp}_{\pm}$$
; $E_{k1} = E_{k}$ and $k^{\perp} = k$
2. for $k_{-} \rightarrow k^{\perp}_{+}$; $E_{k1} = E_{k} - E_{q}$
and $k^{\perp} = k - q$ (46)
3. for $k_{+} \rightarrow k^{\perp}_{-}$; $E_{k1} = E_{k} + E_{q}$
and $k^{\perp} = k + q$

where E_q is the energy of a spin wave of wave-vector \underline{q} .

Remember that at temperatures $T \ll T_c$, the dynamic behaviour of the coupled impurity spin system can be described by spin waves. Hence, the local spin operators S_n^z and S_n^{\pm} in (44) can be transformed into spin wave variables. Neglecting 3- and 4- operator terms at low temperatures, we obtain²²

$$P(\underline{k}_{\pm}, \underline{k}^{1}_{\pm}) = \frac{2\pi c}{\hbar N} \left[\left| V(\underline{k}, \underline{k}^{1}) \right|^{2} + 2(S - \frac{1}{N} \sum_{q}^{\prime} n_{q}) \\ \times \left| V(\underline{k}, \underline{k}^{1}) \right| \left| J(\underline{k}, \underline{k}^{1}) \right| + (S^{2} - \frac{2S}{N} \sum_{q}^{\prime} n_{q}) \left| J(\underline{k}, \underline{k}^{1}) \right|^{2} \right] \\ \times f(\underline{k}) \left[1 - f(\underline{k}^{1}) \right] \delta(E_{k} - E_{k}^{1}) \delta(\underline{k} - \underline{k}^{1}) .$$
(47)

$$P(\underline{k}-, \underline{k}^{1}+) = \frac{4 \pi \operatorname{Sc}}{\hbar N} \left| J(\underline{k}, \underline{k}^{1}) \right|^{2} \operatorname{n}_{q} f(\underline{k}) \left[1 - f(\underline{k}^{1}) \right]$$
$$\times \delta (E_{k} - E_{q} - E_{k}^{1}) \delta (\underline{k} - \underline{q} - \underline{k}^{1}) .$$
(48)

$$P(\underline{k}+, \underline{k}^{1}) = \frac{4\pi \text{ sc}}{\hbar N} \left| J(\underline{k}, \underline{k}^{1}) \right|^{2} (n_{q} + 1) f(\underline{k}) \left[1 - f(\underline{k}^{1}) \right]$$
$$\times \delta(E_{k} + E_{q} - E_{k} 1) \delta(\underline{k} + \underline{q} - \underline{k}^{1}).$$
(49)

 n_q is the number operator for spin waves of wave vector <u>q</u>. The factor c, representing the concentration, is the result of performing an ensemble average over impurity spin positions. The f's are the Fermi factors.

With the above scattering probabilities, we can proceed to solve the steady state Boltzmann equation.^{23,24} Note, however, that as far as scattering from spin wave excitations is concerned, elastic scattering events (as in (44) where the electron scatters without flipping its spin) induce no change in k and hence do not contribute to $\Delta \rho$ (t). If we use the fact that for acoustic mode spin wave excitations $E_q = Dq^2$ for low temperatures (where D is the acoustic spin wave stiffness constant) and if we assume that $V(\underline{k}, \underline{k}^1)$ and $J(\underline{k}, \underline{k}^1)$ in (44) are independent of k and \underline{k}^1 , we finally obtain²²

$$\Delta \rho (T \ll T_{c}) = \frac{3 \pi m * c}{2 e^{2} \hbar N E_{f}} \left[|V|^{2} + \frac{\pi^{2} |J_{s-10cal}|^{2} s}{12} \left(\frac{k_{B}T}{D k_{F}^{2}} \right)^{2} \right], (50)$$

after including a contribution to $\Delta\rho(T)$ from straight forward potential scattering. Here m* is the effective mass of the s band electrons, E_F is the Fermi energy, k_B is Boltzmann's constant and k_F is the Fermi wave vector. Thus a T^2 limiting form for $\Delta\rho(T)$ is predicted for electronmagnon scattering in which wave-vector conservation does hold.

(b) Without k-vector Conservation

However, the absence of translational invariance in the impurity spin system (assumed randomly distributed in the dilute alloy) implies a lack of translational symmetry in the s-d Hamiltonian for the alloy and suggests that wave-vector conservation need not hold for electronmagnon scattering in such systems. If we now calculate the scattering probabilities conserving energy but not the k-vector, we find²⁵

$$P(\underline{k}\pm, \underline{k}^{1}\pm) = \alpha_{1} \left[\left| V(\underline{k}, \underline{k}^{1}) \right|^{2} \pm 2 \left(S_{1} - \frac{1}{N} \sum_{q'}^{l} n_{q} \right) \right.$$

$$x \left| V(\underline{k}, \underline{k}^{1}) \right| \left| J(\underline{k}, \underline{k}^{1}) \right| + \left(S_{1}^{2} - \frac{2S_{1}}{N} \sum_{q'}^{l} n_{q} \right) \left| J(\underline{k}, \underline{k}^{1}) \right|^{2} \right]$$

$$x \left. \delta \left(E_{k\pm} - E_{k} \underline{1}\pm \right) \right]$$

$$P(\underline{k}-, \underline{k}^{1}+) = \alpha_{1} N^{-1} \sum_{q'}^{l} \left| J(\underline{k}, \underline{k}^{1}) \right|^{2} 2S_{1} \left(n_{q} + 1 \right)$$

$$x \left. \delta \left(E_{k-} - E_{k} \underline{1}+ - E_{q} \right) \right]$$

$$(52)$$

$$P(\underline{k}+,\underline{k}^{1}-) = \alpha_{1} N^{-1} \sum_{q} |J(\underline{k},\underline{k}^{1})|^{2} 2S_{i}n_{q}$$

$$x \delta(E_{k+} + E_{q} - E_{k}1_{-}), \qquad (53)$$
where $\alpha_{1} = 2\pi c_{1} (f_{1}N)^{-1}$

where $\alpha_1 = 2 \pi c (\hbar N)^{-1}$.

Solving the Boltzmann equation once again, enables us to derive the following expression for the temperature dependent resistivity²⁶

$$\Delta \rho \left(\mathbf{T} \ll \mathbf{T}_{c} \right) = \frac{3\pi \, \mathbf{m} \ast \, \mathbf{f}_{l} \, \mathbf{c}}{2 \, \mathbf{e}^{2} \, \mathbf{E}_{f} \, \mathbf{N} \, \mathbf{f}_{c}} \left[\mathbf{v}^{2} - 3 \mathbf{J}^{2} \mathbf{S}^{2} + \frac{\mathbf{J}^{2} \mathbf{S} \, \mathbf{f}_{l}}{2 \, \pi^{2} \mathbf{N}} \left(\frac{\mathbf{k}_{B} \mathbf{T}}{\mathbf{D}} \right)^{3/2} \\ \times \left\{ 4 \, \Gamma \left(\frac{3}{2} \right) \, \mathbf{G} \left(\frac{3}{2} \right) + \mathbf{F}_{\frac{1}{2}} \left(\mathbf{0} \right) \right\} \right] \,. \tag{54}$$

 $\int (x)$, G(x) and F_k (x) are the appropriate gamma, Riemann-Zeta and Fermi-Dirac functions, and Ω is the atomic volume. Thus a T^{3/2} limiting low temperature form is predicted for the resistivity $\Delta \rho(T)$ in the absence of k-vector conservation.
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CHAPTER TWO

EXPERIMENTAL METHODS

2.1 Apparatus

The resistance of the various alloys was measured using the standard four probe technique (refer to Fig. 2-1). A Guildline constant current source (model 9770B, stable to 1 part in 10^6) was used to supply a highly stable current to the series connected samples. A Guildline low thermal selector switch (model 9145 Al0) applied the voltage drop from across a particular sample to a Tinsley Diesselhorst thermoelectric free potentiometer (type 3589 R). The potentiometer, in combination with a Tinsley photocell galvanometer amplifier (type M.S.2 45E), was used to measure both the sample voltage and current. (The potentiometer-galvanometer combination was capable of reproducible measurements to 10^{-8} volts). The current through the samples was determined by measuring the voltage that it produced across an 0.10 Ω Guildline standard resistor (model 9200) connected in series with the specimens. A Tinsley thermoelectric free reversing switch (type 4092) allowed both direct and reverse readings to be taken, so that thermal voltage effects would be cancelled out.

For good temperature homogeneity, the samples were mounted in thermal contact with a high conductivity copper block. (The temperatures of the specimens never differed by more than a few millidegrees). The copper block was designed to hold up to six specimens (usually five alloys and one pure metal), each of them to be mounted



on a pair of knife-edge supports, located near opposite ends of the block. Wires, attached to the base of each of the knife-edge supports, provided the voltage tap-off connections.

Since resistivity as a function of temperature was being sought, a means of varying and controlling the temperature was necessary.

Temperatures below 4.2K were obtained by pumping on liquid He⁴ contained in a dewar vessel surrounding the samples; pressure stabilization was achieved using a manostat device (refer to Fig. 2-2 for a flow diagram of the vacuum system), while the temperature was measured to within 5 millidegrees by observing the He⁴ vapour pressure with a system of two manometers connected to the He bath.

Temperatures above 4.2K were obtained by slowly heating up the copper mounting block, and hence the samples, with a heater coil wound around the block. For temperature sensing, a carbon resistor (100 Ω Allen Bradley) was mounted close to the samples in thermal contact with the specimen block. The resistance of the carbon resistor (which varies roughly logarithmically with temperature) was monitored using an a-c phase-sensitive Wheatstone bridge, the rectified output from which was fed into the heater coil (see Fig. 2-3). The feedback current from the bridge proved sufficient to obtain regulated temperatures up to 25K. Above this point, a Heathkit power supply (model IP-27), was series connected to the bridge





output, permitting temperatures beyond room temperature. Above 4.2K, the temperature was measured using a nonlinear gas thermometer. The uncertainty in the temperature was always less than 0.5% of the temperature and over much of the range it was considerably less than this value.

2.2 Preparation of the Alloys

The starting materials used in the present investigation were 99.999% pure Pd wire, 99.999% pure Rh sponge, 99.9985% pure Fe rod (all supplied by Johnson Matthey, London) and 99.998% pure Co sheet (obtained from Metals Research, Cambridge, U.K.).

The Rh sponge was fashioned into a compacted pellet form using a hardened stainless steel dye, and metallic Rh was produced by melting several such pellets on the water cooled copper hearth of an argon arc furnace, using a tungsten electrode.

A host alloy, of approximate composition $Pd_{95}Rh_5$ was then prepared by arc melting the appropriate amounts of the two elements. The alloy was inverted and remelted several times to ensure homogeneity. Next, two master alloys of 5 at % Fe in $(Pd_{95}Rh_5)$ and 2.6 at % Co in $(Pd_{95}Rh_5)$ were prepared. (PdRh)Fe alloys containing nominally 0.8, 1.1, 1.25, 1.5 and 1.85 at % Fe, and (PdRh)Co alloys containing nominally 1.0, 1.4, 1.8 and 2.2 at % Co were produced by successively diluting each of the two master alloys. At each stage, melting losses were negligibly small (weight losses < 0.03%). Each alloy was homogenized by inverting and remelting it several times.

After melting, the button-shaped alloy s were cold rolled between Melinex sheets (to prevent the transfer of impurities from the rollers to the alloys) and long, narrow resistance specimens were cut in the form of strips of approximate dimensions 10 cms x 0.2 cms x 0.01 cms.

After etching in a warm dilute acid (consisting of 1/5 H₂O, 1/5 conc. HNO₃, and 3/5 HCl by volume plus a few drops of H₂O₂) to remove surface contamination, the samples were given a strain relieving anneal at 850° C for 30 hrs. in vacuo.

The absolute resistivity ρ of the samples was obtained from the formula

$$\rho = R\left(\frac{A}{1}\right)$$

by measuring their form factors (ratio of the cross-sectional area A to length 1) to within $\pm 0.5\%$ using a technique recently described by Loram et. al.

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CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Introduction

The occurrence of giant moments associated with small amounts of transition metal impurities dissolved in exchange enhanced matrices has been known for many years,^{1,2} yet the nature of the ordered ground state of such alloy systems, and especially the elementary excitations from it, are currently far from well understood.³⁻⁶ In particular, the interpretation of transport measurements, at low temperatures, on the ordered phase of these and related systems⁶⁻¹³ appears to indicate that wavevector (k vector) conservation may not hold for electron-local moment scattering, even when the local moment dynamics are represented by collective modes (spin waves).^{13,14,15}

For the giant moment alloys of Pd containing less than 1 at % Fe or Co, the incremental resistivity $\Delta\rho(T)$ follows a $T^{3/2}$ limiting low temperature $(T \ll T_c)$ form,^{7,9} as would be predicted on the basis of electron-spin wave scattering with non conservation of the k vector (see Chapter 1, equation (54)). For Fe or Co concentrations greater than 2 at %, it is found that $\Delta\rho(T) \propto T^2$ for $T \ll T_c$. A T^2 limiting form for $\Delta\rho(T)$ is that predicted from electron-magnon scattering in which wavevector conservation does hold^{16,17} (see Chapter 1, equation (50)). For a 1 at % Fe or Co alloy, $\Delta\rho(T)$ exhibits a limiting temperature dependence intermediate between $T^{3/2}$ and T^2 .

In the isolated (or single) impurity limit, the impurity potential clearly lacks translational symmetry,



Fig. 3-1. The measured resistivities of the (PdRh)Fe alloys plotted as a function of temperature. The lowest curve is the Pdg5Rh5 host. The other curves are arranged in order of increasing Fe content.



2. The measured resistivities of the (PdRh)Co alloys plotted as a function of temperature. The lowest curve is the Pd95Rh5 host. The other curves are arranged in order of increasing Co content. and calculations of the incremental resistivity $\Delta \rho$ (T) based on conduction electron scattering from such a potential should consequently proceed without conservation of the <u>k</u> vector. However, it is not clear at what point, or on what basis, <u>k</u> vector conservation is restored, as the impurity concentration c increases. As we have seen, in both the PdFe and PdCo systems, the transition from a $T^{3/2}$ (nonconservation) to a T^2 (conservation) form for $\Delta \rho$ (T) when T $\ll T_c$, occurs around 2 at.% impurity. Skalski et al¹¹ point out that, at and above this concentration, the induced polarization in the Pd (host) d-band displays considerable homogeneity.

3.2 (PdRh)Fe and (PdRh)Co

In this chapter, we will discuss electrical resistivity measurements on dilute alloys of Fe and Co in $(Pd_{95}Rh_5)$. In this host, the effects of exchange enhancement (for second transition series alloys) reaches a maximum.¹⁸ This implies that a homogeneous polarization should be induced in the host's d band at Fe and Co concentrations rather less than 2 at.%. However, the effect of 5 at.% Rh should substantially reduce the mean free path of the conduction electrons.

In figures 3-1 and 3-2, the general features of the data are reproduced by plotting the measured resistivities ρ as a function of temperature T up to 300K. From these two figures, we see that the zero temperature resistivities of the two PdRh (host) alloys containing nominally



Fig. 3-3. The incremental Fe resistivity at T = 0 plotted against the nominal Fe concentration.



Fig. 3-4. The incremental Co resistivity at T = 0 plotted against the nominal Co concentration.

the same concentration of Rh (5 at.%), are 9.337 μ M -cms and 9.120 μ M -cms respectively. Both of these values are in good agreement with recent measurements by Purwins et al.¹⁹ In addition, no temperature dependence in the resistivity of either Pd₉₅Rh₅ host was observed in the low temperature region. From figures 3-1 and 3-2, we can also estimate $\Delta \rho$ (T = 0) for the addition of both Fe and Co impurities to this host, and these values are plotted against the nominal Fe and Co concentrations in figures 3-3 and 3-4 respectively. The data in the figures indicate that, for Fe in PdRh

 $\Delta \rho (T = 0) = 1.90 \pm 0.05 \,\mu \, \Omega \, \text{cms/at.\% Fe}$ (1) and for Co in PdRh

 $\Delta \rho(T = 0) = 1.46 \pm 0.08 \ \mu \Omega \ cms/at. \% \ Co \qquad (2)$ very close to the values for Fe in Pd⁷ and Co in Pd.²⁰

3.2 (a) Estimates of the Magnetic Ordering Temperature and Spin Disorder Resistivities

To date, two techniques have been adopted to estimate the magnetic ordering temperature T_c in giant moment systems. The first identifies T_c with the maximum in $\Delta \rho$ (T),⁷⁻⁹ the other with the maximum in $d\rho$ /dT.^{11,21} In any event, the presence of short range order above T_c causes the resistivity to rise with increasing temperature. Such an effect should be more pronounced in the alloys examined here, compared with similar amounts of Fe or Co in Pd, due to statistically fluctuating environments present in two-component host matrices (like PdRh). Under the



Fig. 3-5. The resistivity of the 0.8 and 1.1 at. % Fe alloys plotted against temperature over restricted temperature intervals.







Fig. 3-7. The resistivity of the 1.85 at. % Fe alloy plotted against temperature over a restricted temperature interval.



Fig. 3-8. The resistivity of the 1.0 and 1.4 at. % Co alloys plotted against temperature over restricted temperature intervals.



Fig. 3-9. The resistivity of the 1.8 and 2.2 at. % Co alloys plotted against temperature over restricted temperature intervals.



Fig. 3-10. The resistivity of the 2.6 at. % Co alloy plotted against temperature over a restricted temperature interval.

circumstances, the maxima in dho/dT should represent a better estimate of T_c in these systems. However, the presence of 5 at. % Rh presents additional complications since the Rh atoms produce a very large potential scattering background which substantially reduces the fractional contribution of the spin disorder component to the total resistivity. These complications are evident in figures 3-5 to 3-10, in which an attempt is made to establish the maxima in $doldsymbol{
ho}/dT$ for both the (PdRh)Fe and (PdRh)Co alloys. These figures are "enlargements" of rather small temperature intervals of the data in figures 3-1 and 3-2, since only in this way can we pick out the spin disorder contribution. It is clear however, from these figures, that the temperature interval between successive points, in the appropriate temperature range, is too large to use a point by point technique for estimating $d\rho/dT$. It should be noted that the size of the points in figures 3-5 to 3-10 exceed the estimated error in both $\Delta
ho$ and T. Consequently, we simply draw smooth curves through the "high" and "low" temperature points, taking T_c as the temperature at which these curves intersect. The shape of the curves implies that d
ho/dT increases from the low temperature side to a maximum at the point of intersection. The uncertainty in the value for T_c estimated in this way is typically half the temperature interval between successive points at T_c. The estimated T_c's are listed in Table One.

In figures 3-11 and 3-12, T_c is plotted against the Fe and Co concentrations c. These figures closely resemble the corresponding situation in <u>Pd</u>Fe and PdCo



(PdRh)Fe

Fig. 3-11. The estimated magnetic ordering temperatures $T_{\rm C}$ plotted against the nominal Fe concentration.



Fig. 3-12. The estimated magnetic ordering temperatures $T_{\rm C}$ plotted against the nominal Co concentration.

alloys of comparable concentration.^{21,12} In the case of both (PdRh)Fe and (PdRh)Co, T_C increases at a rate of about 48K/ at % impurity, slightly more rapidly than in either PdFe or PdCo. This result is not unexpected in view of the increased effects of exchange enhancement.

In figures 3-13 to 3-16, the impurity (Fe and Co) resistivities $\Delta \rho(\mathbf{T}) = \rho_{alloy}(\mathbf{T}) - \rho_{host}(\mathbf{T})$ are plotted against temperature up to 300K. The vertical arrows mark the positions of the estimated magnetic ordering temperatures \mathbf{T}_c , obtained above (from $d\rho/d\mathbf{T}$). In all the alloys, there is a significant rise in $\Delta \rho(\mathbf{T})$ above \mathbf{T}_c . As previously mentioned, this rise is associated with the presence of short range order, which is rather more pronounced here than in the PdFe and PdCo systems, due presumably to statistically fluctuating environments present in two component host matrices. The presence of appreciable short range order was the reason for using $d\rho/d\mathbf{T}$ to define \mathbf{T}_c , as opposed to other methods.

In subsequent discussion, we will make use of an expression for the spin disorder contribution to the incremental resistivity. To aid in this discussion,

 $\Delta \rho$ (T = 0) and $\Delta \rho$ (peak) are also listed in Table One. The difference, $\Delta \rho$ (peak) - $\Delta \rho$ (T = 0), measures the total change in the spin disorder contribution to the incremental resistivity, with $\Delta \rho$ (peak) representing the contribution from the totally disordered state. This latter state is one in which short range order is also

(PdRh)Fe



Fig. 3-13.

The incremental Fe resistivity for the 0.8 and 1.1 at. % Fe alloys plotted against the temperature T. The vertical arrows mark the estimated T_c 's.



Fig. 3-14.

The incremental Fe resistivity for the 1.25 and 1.5 at. % Fe alloys plotted against the temperature T. The vertical arrows mark the estimated T_c 's.



Fig. 3-15. The incremental Fe resistivity for the 1.85 at. % Fe alloy plotted against the temperature T. The vertical arrow indicates the estimated T_c .



Fig. 3-16. The incremental resistivities of the five (PdRh)Co alloys plotted as a function of temperature T. The vertical arrows indicate the estimated T_c 's. The error bars represent the uncertainty due to the shape factor.

dispersed and consequently we do not use $\Delta \rho(T_c \text{ from } d\rho/dT)$.

We will also comment, in a later section, on the negative temperature coefficient in $\Delta\rho(T)$ at higher temperatures, clearly evident in the (PdRh)Fe alloys (see figures 3-13 to 3-15).

3.2 (b) The Temperature Dependence of $\Delta \rho(T)$ Well Below T_c

Figures 3-17 and 3-18 show an attempt to establish the presence of a T^2 term at low temperatures in some of the (PdRh)Fe and (PdRh)Co alloys. The technique employed¹¹ for the (PdRh)Fe system is to plot the thermal part of the incremental resistivity, i.e.,

 $\Delta(T) = \Delta\rho(T) - \Delta\rho(T = 0)$ (3) against T². For the (PdRh)Co system, the incremental resistivity $\Delta\rho(T)$ itself has been plotted against T². Figure 3-17 demonstrates the presence of a substantial T² term in the 1.25, 1.5 and 1.85 at % Fe alloys, while figure 3-18 shows a similar T² behaviour for the 1.4, 1.8, 2.2 and 2.6 at % Co alloys. The estimated magnitude of these T² terms are listed in Table Two. They are approximately concentration independent (for the range investigated here), and their magnitudes in the (PdRh)Fe system correspond closely with those observed in <u>PdFe</u> alloys containing up to 4 at % Fe. The magnitudes of the T² terms in the (PdRh)Co system are slightly higher than those observed in PdCo alloys of comparable concentration.



Fig. 3-17. The thermal part of the low temperature incremental Fe resistivity plotted against T^2 , for the five (PdRh)Fe alloys.



Fig. 3-18.

8. The low temperature incremental Co resistivity plotted against T², for the five (PdRh)CO alloys.

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For the 0.8 and 1.1 at.% Fe and the 1.0% Co samples, no clear temperature dependence is established, with Δ (T) (or $\Delta \rho$ (T)) exhibiting a behaviour intermediate between T² and T^{3/2}. We do not regard the variation in the T² coefficients listed in Table One as significant.

In very dilute <u>Pd</u>Fe and <u>Pd</u>Co alloys (C < 0.8 at. % impurity), where the induced d-band polarization is inhomogeneous (and the ordered ground state, although of predominantly ferromagnetic character, contains a significant fraction of antiferromagnetically coupled impurities, 5,22,23) a T^{3/2} limiting low temperature form for $\Delta \rho$ (T) is observed. The transition from a T^{3/2} to T² limiting form occurs at concentrations for which this d-band polarization displays considerable homogeneity (around C ~ 1 to 2 at. % impurity).²⁴ While the T² limiting form for $\Delta \rho$ (T) is restored, for both Fe and Co in Pd₉₅Rh₅, at slightly lower concentrations than for Fe and Co in Pd, the situation here mirrors the characteristics of this latter system.

Measurements have recently been performed²⁵ on the Matthiessen's Rule deviation $\Delta(T) = \rho_{alloy}(T) - \rho_{alloy}(0)$ - $\rho_{host}(T)$, in dilute, non magnetic, Al based alloys containing small amounts of transition metal impurity. The analysis of these measurements indicated that $\Delta(T)$ has a T³ limiting low temperature form. Such a temperature dependence could be reproduced within the usual Bloch-Gruneissen formulation by invoking impurity induced electronphonon scattering events for which k vector conservation

was relaxed. The rationale for this procedure lay in the impurity-limited mean free path of the conduction electrons (the alloys were considered to be in the "dirty" limit), from which it followed via the Uncertainty Principle, that momentum conservation could be relaxed.

In magnetically ordered PdFe and PdCo alloys, there must also be an impurity-limited electronic mean free path, yet a $T^{3/2}$ (non conservation) to T^2 (conservation) form for $\Delta
ho$ (T) is effected by in increasing the Fe or Co concentration. If indeed a mean free path effect were responsible here for the T $^{3/2}$ (non conservation) form for $\Delta
ho$ (T), it should follow that in $Pd_{95}Rh_5$ based alloys, this $T^{3/2}$ limiting form should persist to higher Fe and Co concentrations than in either PdFe or PdCo, since in two component hosts the mean free path is considerably shorter than in single component hosts (as evidenced by the large values for $\Delta \rho$ (T = 0)). Just the opposite effect is observed. A T² limiting form for $\Delta \rho$ (T) is established at <u>lower</u> Fe and Co concentrations. From this we can infer that the restoration (or the removal) of k vector conservation in these types of alloys is not a mean free path effect. However, the restoration does appear to be correlated with the onset of homogeneous d-band polarization.

3.2 (c) Numerical Estimates for Various Parameters

In this section we will attempt to extract from the experimental data, numerical estimates of various physical parameters (such as exchange coupling, etc.).

3.2 (c) (i) From the Magnetic Ordering Temperature

On the assumption that the onset of magnetic order is regulated by the characteristics of the alloy's d-band, Long and Turner¹⁴ derived the following expression for T_c :

$$k_{\rm B}T_{\rm c} = \frac{|J_{\rm d-local}|^2 \operatorname{CS}^1(\operatorname{S}^1 + 1) \operatorname{N}(\operatorname{E}_{\rm f})}{30 \operatorname{K}_{\rm o}^4} \left(\frac{2}{z}\right)^{2/3} .$$
(4)

Here k_B is Boltzmann's constant, $J_{d-local}$ is the effective exchange coupling between the impurity (Fe and Co) moments and the d-band electrons, c is the impurity concentration and S¹ is the "on site" impurity spin. $N(E_f)$ is the bare (unenhanced) density of states at the Fermi energy E_f , while K_0^{-2} is the exchange enhancement factor and Z is the number of d-holes per atom. For Fe in PdRh, we will take $S^1 = 1.5$ (as for Fe in Pd)²⁴ while for Co in PdRh, $S^1 = 1.0$ (as for Co in Pd)²⁶.

The static susceptibility of the $Pd_{95}Rh_5$ host may be written as:

$$\chi = \frac{g_{e}^{2} \mu_{B}^{2} N(E_{f})}{4K_{o}^{2}}$$
(5)

where g_e is the conduction electron g-factor. Assuming $g_e = 2$ and using $K_o^{-2} \simeq 9$ (from high field measurements on $Pd_{95}Rh_5$ at low temperatures)²⁷ and with $\chi = 12.73$ e.m.u./gm (Budworth),²⁸ we obtain a value for the bare density of states:

 $N(E_f) \simeq 4.6 \text{ states /eV atom}$ (6)

Using this value in equation (4), along with Z = 0.36 (as in Pd)²⁴ and the estimates of T_c listed in Table One, we obtain the values for $J_{d-local}$ shown in Table Two.

3.2 (c) (ii) From the Spin Disorder Resistivity

In Table One, values were listed for $\Delta\rho$ (peak), the estimated contribution to the incremental resistivity from the totally disordered (paramagnetic) state, and $\Delta\rho$ (T = 0), the estimated contribution from the completely ordered phase. Using the usual form for the s-d Hamiltonian (see Chapter 1, equation (12)), we can modify Yosida's calculation³⁰ for the case of ferromagnetic ordering, to yield, in the limit where potential scattering is much stronger than exchange scattering:

$$\Delta \rho(\text{peak}) - \Delta \rho(T = 0) = \frac{3\pi m_s^* \Omega_c}{2e^2 \hbar E_f N} \left[J_{s-\text{local}}^2 S(1 + 4S) \right]. (7)$$

The coefficient before the square bracket in this equation is the result of assuming that the conductivity is dominated by s-band electrons, these being treated in an effective mass (m_s^*) approximation.⁶ In the absence of detailed information, we assume that various parameters, such as the s-electron effective mass, the number of atoms per unit volume $(N\Omega^{-1})$, the Fermi Energy E_f , etc. are the same here as in Pd. The numerical value for this coefficient is then $6.56\mu\Omega$ cms/(eV)² at.%. Within the framework of an s-d model, S is identified with the giant moment spin¹⁹ (and is 4.5 for dilute Fe in Pd¹⁹ and 4.7 for dilute Co in Pd).²² Adopting these values here,²⁹ along with the estimates of $\Delta \rho$ (peak) - $\Delta \rho$ (T = 0) listed in Table One, the values of $|J_{s-local}|$ shown in Table Two are obtained from equation (7). The slight concentration dependence in $|J_{s-local}|$ for the (PdRh)Fe system, results from $\Delta \rho$ (peak) - $\Delta \rho$ (T = 0) increasing rather faster than linearly with c (actually marginally faster than c^{4/3}--this is considerably slower than the c² dependence observed in PdFe,¹¹ but this could be the result of our inclusion of the effects of short range order in $\Delta \rho$ (peak)).

3.2 (c) (iii) From the T² Coefficient

In Chapter 1, section 7, a calculation was performed on the basis of the s-d Hamiltonian, and an expression for the resistivity obtained assuming <u>k</u> vector conservation. This yielded the following equation for the T² coefficient: Coeff. of T² term = $\frac{3\pi m_{\rm s}^* \Omega_{\rm c}}{2e^2 \ {\rm NE}_{\rm f} \hbar} \cdot \frac{\pi^2 {\rm S}}{12} \left| {\rm J}_{\rm S-10ca1} \right|^2 \left(\frac{{\rm k}_{\rm B}}{{\rm D}_{\rm k_{\rm f}} 2} \right)^2$. (8) Here D is the acoustic spin wave stiffness, and k_f is the Fermi wave vector. With the aid of equation (7): T² coeff. = $\frac{\pi}{12} \left(\frac{{\rm k}_{\rm B}}{{\rm D}_{\rm k_{\rm f}} 2} \right)^2 \frac{\left[\Delta \rho \left({\rm peak} \right) - \Delta \rho \left({\rm T} = 0 \right) \right]}{(1 + 4{\rm S})}$. (9) Using the measured T² coefficients in conjunction with equation (9) means that estimates for D can be obtained which depend only on the values assigned to S and k_f. Again, the lack of detailed information forces us to use values for S and k_f (= 0.9A^{O-1}) estimated for Pd.¹² These lead to the values for D listed in Table Two. For the (PdRh)Fe system D increases with concentration approximately as $c^{2/3}$. The corresponding approach applied to the T² coefficients in PdCo alloys¹² leads to slightly larger values for D, which is observed to increase linearly with c. These discrepancies are attributed to our using S = 4.5 for (PdRh)Fe and S = 4.7 for (PdRh)Co, obtained from magneto resistance measurements^{19,22} on Pd = 0.1 at % Fe and on Pd = 0.098 at % Co respectively. Certainly, as the impurity concentration increases, so does giant moment overlap, leading to a decreasing giant moment spin S (hence the actual concentration dependence of D will be faster than that predicted by equation (9) using a concentration independent spin).³²

3.2 (c) (iv) Temperature Dependence of
$$\Delta \rho(T)$$

For the (PdRh)Fe System in the Paramagnetic Regime

From second order perturbation theory³⁰ based on the s-d Hamiltonian, the incremental (Fe) resistivity $\Delta \rho$ (T) in the paramagnetic regime is given by: $\Delta \rho$ (T \gg T_c) = $\frac{3\pi m_s^* c}{2 \hbar e^2 E_f} \cdot \frac{\Omega}{N} \left[v^2 + J_{s-local}^2 S(s+1) \right]$ (10)

and is clearly temperature independent. An inspection of figures 3-13 to 3-15 indicates that this is not so for the (PdRh)Fe alloys examined here; experimentally $\Delta\rho(T\gg T_c)$ is observed to have a considerable <u>negative</u> temperature coefficient. Within experimental error this amounts to a linear decrease of $\Delta\rho(T\gg T_c)$ with increasing temperature. In figure 3-19, the high temperature slopes, ie,



Fig. 3-19.

The high temperature slopes of the $\Delta \rho$ (T) versus T graphs in figures 13, 14 and 15, plotted against nominal Fe concentration. The large error bars are the result of including the shape factor uncertainty in estimating these slopes.

$$\alpha = -\frac{d}{dT} \left[\Delta \rho(T \gg T_c) \right]$$

are plotted against the impurity (Fe) concentration. The large error bars in this figure result from our including the estimated $\pm 0.5\%$ shape factor uncertainty in computing these slopes. Again, within experimental error, these slopes scale linearly with impurity concentration, i.e.,

$$\frac{1}{c} \frac{d}{dT} \left[\Delta \rho(T \gg T_c) \right] = - (1.1 \pm 0.45) \times 10^{-3} \mu \Omega cm / K \text{ at } \%.$$

We now discuss possible sources for such an effect. Certainly, third order perturbation theory calculations using the s-d Hamiltonian 33 would lead to a temperature dependence in $\Delta
ho$ (T \gg T $_{
m c}$) (the Kondo effect). This source, however, may be rejected on the basis of the observed temperature dependence (linear versus logarithmic) on the temperature region in which it occurs (T > 60 K). A temperature dependent $\[\Delta
ho (T \gg T_c) \]$ could also arise from conduction electron scattering from localized spin fluctuations (lsf) at the impurity site.^{34,35,36} Recent phase shift calculations, 37, 38, 39 which phenomenologically introduce potential scattering of arbitrary strength into the 1sf model, appear to correctly reproduce the sign of the lsf-induced temperature coefficient in $\Delta
ho$ (T) for all first transition series impurities in Pd, 40 and for latter half first transition series impurities in Rh.³⁹ Such an approach predicts a positive temperature dependence in

 $\Delta \rho$ (T \gg T_c) for both Fe in Pd and Fe in Rh. Furthermore, this would only be observable at temperatures well below 1 K

in PdFe, although it has been observed above He temperatures in RhFe.⁴¹ Once again, such a mechanism may be rejected here, since it requires that the addition of 5 at % Rh to Pd not only raise its characteristic lsf temperature (T_S) by many orders of magnitude, but also produce a temperature coefficient in $\Delta \rho$ (T \gg T_c) opposite in sign to that predicted for Fe in either host.

Having rejected these two mechanisms, let us examine possible sources for this effect in "conventional" Mattheissen's Rule deviations.⁴² We begin by correcting this data for the effects of thermal expansion.⁴³ From equation (10):

$$\frac{\partial \ln \left[\Delta \rho(T \gg T_{c})\right]}{\partial \ln \Omega} = 1 + \frac{1}{\left[V^{2} + J_{S-local}^{2} S(S+1)\right]} \begin{cases} 2 |V|_{\Omega} \frac{\partial V}{\partial \Omega} \\ + J_{S-local}^{2} S\left[2(S+1) \frac{\partial \ln J_{S-local}}{\partial \ln \Omega} \\ + (2S+1) \frac{\partial \ln S}{\partial \ln \Omega} \right] \end{cases}$$
(11)
If we assume that $\partial \ln J_{S-local}$ is equal to

 $\frac{\partial \ln \Omega_{d}}{\partial \ln \Omega_{d}}, \text{ then it, and } \frac{\partial \ln \Omega_{d}}{\partial \ln \Omega_{d}}, \text{ can be taken directly}} \\ \frac{\partial \ln \Omega_{d}}{\partial \ln \Omega_{d}}, \text{ from Fawcett's work.}^{44} \text{ However, we still need to evaluate} \\ \frac{\partial V}{\partial \Omega_{d}}. \text{ This can be obtained by noting that:} \\ \frac{\partial \ln \left[\Delta \rho(T=0)\right]}{\partial \ln \Omega_{d}} = 1 + \frac{1}{\left[V^{2} - 3S^{2} J_{S-1}^{2} - 3ca 1\right]} \cdot \left\{2 \left|V\right| \Omega_{d} \frac{\partial V}{\partial \Omega_{d}} - 6J_{S-1}^{2} - 3ca 1S^{2} \left(\frac{\partial \ln J_{S-1} - 3ca 1}{\partial \ln \Omega_{d}} + \frac{\partial \ln S}{\partial \ln \Omega_{d}}\right)\right\}.$ (12)

In both equations (11) and (12), band parameters $(m_s^* \text{ and } E_f)$ are assumed to be volume independent. From pressure data⁴⁵ on PdFe, the estimated value for $\frac{1}{\Delta\rho(T=0)} \frac{d\Delta\rho(T=0)}{d\Omega_f}$ is 5 x 10⁻⁶ per bar, leading to

$$\frac{\partial \ln \left[\Delta \rho \left(T = 0 \right) \right]}{\partial \ln \Omega} = -10$$

Using the same value for Fe in $Pd_{95}Rh_5$, and noting that $(v^2 - 3s^2 J_{s-local}^2)$ and $\begin{bmatrix} v^2 + J_{s-local}^2 S(S + 1) \end{bmatrix}$ can be obtained from the measured $\Delta \rho(T = 0)$ and $\Delta \rho(T = T_c)$ respectively,^{7,8,9} leads via the assumptions following equation (11) and the use of equation (12) to:

$$2 \left| \mathbf{V} \right| \bigcap_{i} \frac{\partial \mathbf{V}}{\partial \Omega_{i}} = -3.6 \quad . \tag{13}$$

With this value in equation (11) we get:

$$\frac{\partial \ln \left[\Delta \rho(T \gg T_c) \right]}{\partial \ln \Omega} = -10.6 \qquad (14)$$

It is straight forward to show that:

$$\frac{d\left[\Delta\rho(T\ggT_{c})\right]}{dT} \simeq 3\gamma \frac{\partial \ln\left[\Delta\rho(T\ggT_{c})\right]}{\partial \ln\Omega} \left\{ \Delta\rho(T\simeq T_{c}) \right\}$$
(15)

where Υ is the linear coefficient of thermal expansion. At 4.2K, $\Upsilon(Pd_{95}Rh_5) \simeq 1.6 \ \Upsilon(Pd).^{44}$ Using this ratio at higher temperatures⁴⁶ yields

 $\Upsilon(\text{Pd}_{95}\text{Rh}_5) \simeq 19 \text{ x } 10^{-6} \text{ per K}$

in the appropriate temperature range. 47 From equation (15):

$$\frac{d \left[\Delta \rho(T \gg T_{\rm c})\right]}{dT} \simeq -1.3 \times 10^{-3} \mu \Omega_{\rm cm/K} \text{ at } \%$$

and thus appears to account⁴⁸ for the measured temperature variation in $\Delta \rho$ (T \gg T_c). (A value of 0.8 x $10^{-3}\mu \Omega$ cm/K at. % is obtained assuming γ (Pd95Rh5) = γ (Pd)). While other corrections, such as atomic volume changes on alloying, can undoubtedly contribute to $\Delta \rho$ (T \gg T_c), an evaluation of such a contribution to equation (15) requires a knowledge of the temperature variation of the volume dependence of the resistivity of the Pd₉₅Rh₅ host.⁴² Such information is currently not available.

We conclude this section by noting that the large measured values for $\frac{1}{c} \frac{d\left[\Delta\rho(T\gg T_c)\right]}{dT}$ are accounted for by the large volume dependence of the potential (V) and exchange (J_{S-local}) integrals associated with Fe in

Pd95Rh5, in conjunction with a large thermal expansion coefficient.

3.2 (c) (v) The (PdRh)Co System in the Paramagnetic Regime

In contrast to the (PdRh)Fe system, which we have just examined, the decrease in the incremental resistivities of the (PdRh)Co alloys above the "peak" is very gradual. In fact, the "peaks" in the Co resistivities occur at such high temperatures and are so much broader than those in the corresponding Fe resistivities, that it is very difficult to establish any temperature dependence at high temperatures with any degree of certainty (compare figure 3-16 with figures 3-13, 3-14 and 3-15). This difference in behaviour between the two systems has a possible explanation on the basis of localized spin fluctuations (LSF).

In developing the theory in Chapter 1, we confined

our discussion to exchange enhanced systems which possess well defined local moments. However, some alloys (like RhFe) belong to the class of "nearly magnetic" alloys. This means that in these alloys (which contain 3-d transition metal impurities) the host metal, which may or may not exhibit an enhanced susceptibility, will support localized moments, but these may not be well defined due to the constant flipping of the impurity spin S. In the LSF model, we assume that there exists a characteristic time τ_{sf} , corresponding to the lifetime of these fluctuations of the localized spin S and which governs the magnetic behaviour of the impurity. When the LSF's are faster than the fluctuations induced by temperature (thermal fluctuations), one observes a non-magnetic behaviour. Consequently, the conduction electrons do not "see" a magnetic moment and no scattering occurs. However, as the temperature increases, the LSF's eventually become slower than the thermal fluctuations and, in fact. become indistinguishable from a genuine spin (in other words, a magnetic behaviour is observed). As a result. the conduction electrons will be scattered by the LSF's. The transition between the non-magnetic and magnetic regime is smooth and occurs near the spin fluctuation temperature Tsf, which is defined by the relation

$$T_{sf} = \frac{\hbar}{k\tau_{sf}}$$
 (16)

The resistivity component ρ_{sf} , due to the scattering of conduction electrons from localized spin fluctuations at the impurity sites, increases with temperature successively as T^2 , T and lnT, finally tending to the Yosida unitarity limit³⁰ ($\rho_{sf}(T) \rightarrow J^2 S(S + 1)$ as $T \rightarrow \infty$). A characteristic knee in the curve occurs at the spin fluctuation temperature T_{sf} and marks the onset of the logarithmic regime (see Figure 3-20).



Fig. 3-20. The spin fluctuation resistivity as a function of temperature.

Above T_{sf} , where the resistivity shows a logarithmic temperature dependence, there is no qualitative difference between the resistivity due to LSF's and that characteristic of the spin flip scattering of conduction electrons by a well defined localized magnetic moment.

In the following table we have listed estimates of the spin fluctuation temperatures T_{sf} for several related systems.

Alloy	Tsf
PdFe	≪ 1K
PdCo	< 1K
$RhFe^{35}$	\sim 2K
RhCo ⁴⁹	\sim 10 ² - 10 ³ K

The data in this table implies that the addition of Rh to PdFe and PdCo should increase the spin fluctuation temperature T_{sf} . Moreover, if the spin fluctuation temperature behaves in a similar manner to the Kondo temperature T_k in systems like CuAuFe^{50,51} (where Cu plays the same role as Rh), then it is not unreasonable to expect the presence of 5 at % Rh in (PdRh)Fe and (PdRh)Co to increase T_{sf} by a factor of 3 or 4 over that in PdFe and PdCo.

However, despite the presence of Rh, the spin fluctuation temperature of (PdRh)Fe undoubtedly remains considerably less than 1K. Consequently, the only observable portion of the ρ_{sf} curve in figure 3-20 which contributes to the Fe resistivity is the flat (temperature independent) region. This means that spin fluctuations will have no observable effect on the Fe resistivities in the paramagnetic region.

On the other hand, judging from the table, the effect of Rh on (PdRh)Co is probably significant enough to cause the logarithmic portion of the ρ_{sf} curve to play an important part in the Co resistivities, even in the paramagnetic region. It is because the Co resistivities contain this logarithmically increasing spin fluctuation component, that the Co resistivity curves continue to rise well above the magnetic ordering temperature T_c and also exhibit much broader maxima than do the Fe resistivities. It is probably also the reason why the Co resistivities do not fall off nearly as abruptly in the paramagnetic region as the Fe resistivities.

It is interesting to note that the same sort of behaviour can be observed in the closely related PdCo⁹ and PdFe⁷ systems. Here again, the transition from ferromagnetic to paramagnetic regions is much less clearly defined in the PdCo system than in the PdFe system due to the much higher spin fluctuation temperature of PdCo.

Summary

The electrical resistivity of two giant moment systems - (PdRh)Fe and (PdRh)Co - has been measured from 1.4 to 300K. It is found that the incremental resistivity of (PdRh)Fe alloys containing more than 1.25 at. % Fe and (PdRh)Co alloys containing more than 1.4 at. % Co exhibit a T^2 limiting low temperature form (a result predicted from conduction electron-magnon scattering for which wave vector conservation holds). The resistivity data also enabled us to evaluate the magnetic ordering temperature, T_c , and the exchange coupling parameters $J_{d-local}$ and $J_{s-local}$.

(a) (PdRh)Fe				
Alloy (at % Fe)	$T_{c} (from \frac{d\rho}{dT})$	Δρ(T=0) (μΩcm.)	$\Delta \rho$ (peak) (μ Ω cm.1)	$\frac{\Delta \rho(\text{peak}) - \Delta \rho(T=0)}{(\mu \Omega \text{cm.})}$
0.8	22.5 ± 1 K	1.618	1.803	0,185
1.1	44 ± 2.5	2.148	2.386	0.238
1.25	47 <u>+</u> 2.5	2.328	2.664	0.336
1.5	62.5 ± 2.5	2.710	3,165	0.455
1.85	70 <u>+</u> 2.5	3.413	4.011	0.598

Table One

(b) (PdRh)Co

Alloy (at % Co)	$T_c (from \frac{d\rho}{dT})$	Δρ(T=0) (μΩcm.)	Δρ(peak) (μΩcm.)	$\frac{\Delta \rho(\text{peak}) - \Delta \rho(\text{T}=0)}{(\mu \Omega \text{ cm.})}$
1.0	57.7 <u>+</u> 2.5 K	1.715	2.470	0.765
1.4	66.6 <u>+</u> 2.5	2.161	2.700	0.539
1.8	87.2 <u>+</u> 1.5	2.641	3 ,800	1.159
2.2	105.4 <u>+</u> 1.5	3.390	4,815	1.425
2.6	124.0 ± 2.5	3.582	5,239	1.657

(a)	(PdRh)Fe

Alloy (at % Fe)	T^2 coefficient (10-4 μ Ω cm/K ²)	Jd-local (eV)	J _{s-local} (eV)	D (KA ⁰²)
0.8	no clear temp.	0.041	0.020	
1.1	dependence	0.048	0.020	
1.25	2.4 <u>+</u> 0.15	0.047	0.022	9.61 <u>+</u> 0.3
1.5	2.6 ± 0.15	0.049	0.023	10.75 ± 0.3
1.85	2.4 ± 0.15	0.047	0.024	12.82 <u>+</u> 0.3

(b) (PdRh)Co

Alloy (at % Co)	T^2 coefficient (10-4 μ Ω cm/K ²)	^J d-local (eV)	$J_{s-local}$	D (KA ⁰²)
1.0	no clear temp. dep.	0.080	0,035	
1.4	3.3 <u>+</u> 0.15	0.073	0.025	10.17 <u>+</u> 0.3
1.8	3.5 <u>+</u> 0.15	0.073	0.032	14.48 ± 0.3
2.2	3.4 ± 0.15	0.073	0.033	16.29 ± 0.3
2.6	3.4 ± 0.15	0.073	0.032	17.57 ± 0.3

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29. From reference 2, the moment per Fe "atom" derived from measurements in the paramagnetic regime on l at. % Fe in $Pd_{95}Rh_5$ is $\simeq 13\mu_8$. Following Peter et al. (Helv. Phys. Acta 40, 301 (1967)) we write the g value as:

$$g = g_s + \frac{g_e J_{d-local N(E_F)}}{2K_o^2}$$

g_s and g_e are the local moment and conduction electron Lande factors respectively (both taken as equal to 2 for simplicity). Using the listed values for N(E_F), K_o⁻² and J_{d-local}, we find g \simeq 4.0; the corresponding value for S is then 2.8. If this value for S is used, the listed estimates for $|J_{s-local}|$ are increased by a factor of 1.6. The corresponding approach for Pd - 1 at. % Fe yields g \simeq 3.4, and S \simeq 2.4, so that the associated $|J_{s-local}|$ should be increased by 1.8.

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32. With S - 2.8 from ref. 31, the corresponding values for D are:

Alloy (at. % Fe)	$D (KA^2)$
1.25	10.8
1.5	12.1
1.85	14.4

in much better agreement with the Pd Co estimates. 33. J. Kondo, Prog. Theoret. Phys. Kyoto 32, 37 (1964).

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- 46. See, for example, J. G. Collins and G. K. White, <u>Progress in Low Temperature Physics</u> Vol. IV (Editor,
 - C. J. Gorter) (North-Holland, Amsterdam, 1964) p. 465. We note that this procedure works approximately for the exchange enhanced metals Pd and Pt, and hence assume (in the absence of detailed information) that it also works for PdRh.
- 47. We take Υ to be independent of temperature above about 100K; however, Pd (F. C. Nix and D. MacNair, Phys. Rev. <u>61</u>, 74 (1942)), $\left[\Upsilon(300K) - \Upsilon(100K)\right]\Upsilon(300K)^{-1} \sim$ 0.3. We do not feel that our measurements are

sufficiently accurate to employ a temperature dependent γ .

- 48. For PdFe, the required parameter can be taken directly from: $\frac{d\left[\Delta\rho(T\gg T_{c})\right]}{dT} \simeq -3\gamma K \frac{d(\Delta\rho(T_{c}))}{d\rho}$ where K is the compressibility and $\frac{d(\Delta\rho(T_{c}))}{d\rho}$ can be taken from reference 45. We find $\frac{d\Delta\rho(T\gg T_{c})}{dT} \simeq -3.5 \times 10^{-4} \mu M cms/K/at. \%$ approximately four times smaller than in $(Pd_{95}Rh_{5})Fe$, and so becomes comparable with shape factor uncertainties.
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