

Physics of metals of high paramagnetic susceptibility

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Physics of Metals of High Paramagnetic Susceptibility

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This article will not give a general survey on the topic of paramagnetism in metals. Instead we will try to illustrate in a few examples the reasons why this field, although very old, is nevertheless at present a subject of interest to many research groups.

Group												
	III b	IV b	V b	VI b	VII b	VIII b	VIII b	VIII b	I b	II b		
Period												
4	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn		
5	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd		
6	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg		
7	Ac	Th	Pa	U	Np	Pu	Am	rare earths				

Figure 1
Periodic system

In Figure 1 we show the part of the periodic system where most metals of high susceptibility occur. The elements to be mentioned mostly in this article are shaded. Let us turn in particular to the alloys of Rh, Pd and Ag.

In Figure 2 we give the susceptibility and specific heat for the two alloy series. Also shown is what we now believe to be the bare electronic density of states. We see that the susceptibility has a relatively sharp peak at the composition Pd 95% + Rh 5%. It is as if the alloy at this composition would try very hard to become ferro-magnetic like the corresponding alloys of the 3rd period. The corresponding alloys in the 5th period show also a maximum in the paramagnetic susceptibility.

The bare density of states was recently proposed by BERK and SCHRIEFER [1] and represents somewhat of a surprise. In the old independent electronic theory, both susceptibility χ_0 and specific heat c were proportional to the density of states and given by the expression

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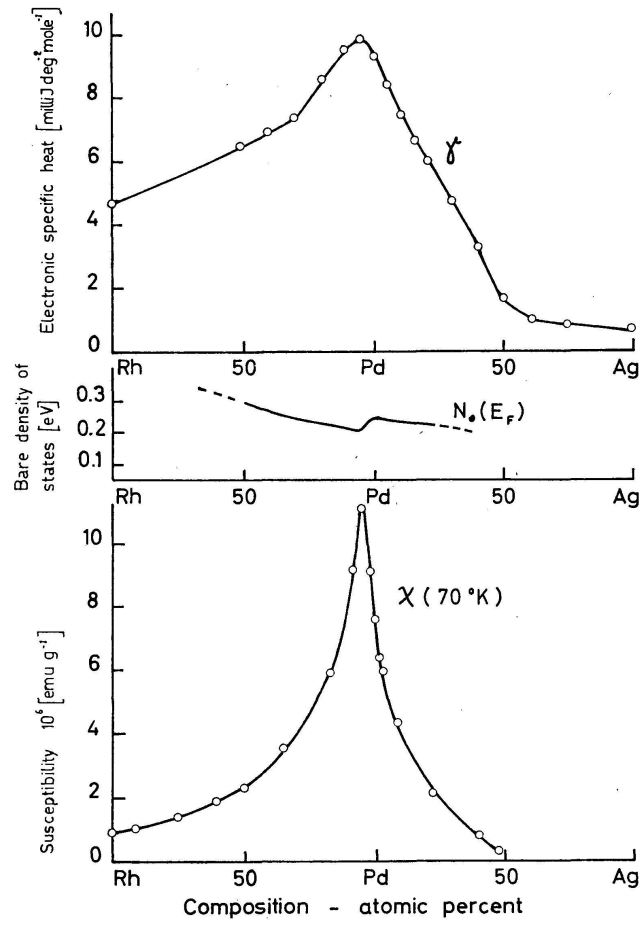


Figure 2

Susceptibility, electronic specific heat and bare density of states in Rh-Pd-Ag series

$$\chi_0 = \frac{(g\beta)^2}{2} N_0(E_f)$$

$$c = \gamma_0 T = \frac{2\pi^2}{3} k^2 N_0(E_f) T$$

It was known that the susceptibility can be enhanced by electronic exchanges in the following way:

$$\chi = \frac{\chi_0}{1 - N_0(E)\bar{v}}$$

if for simplicity one assumes a momentum independent exchange interaction \bar{v} between the conduction electrons.

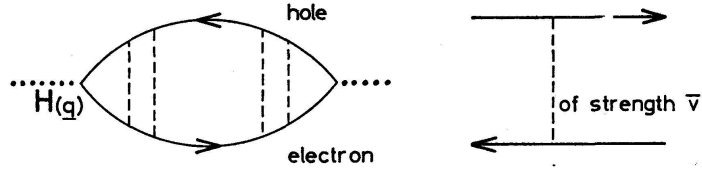


Figure 3a

Diagrammatic representation of $\chi(\vec{q})$

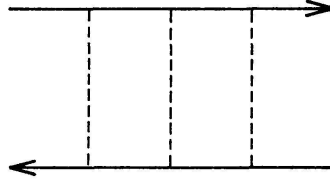


Figure 3b

Diagrammatic representation of $t(\vec{q})$

The concept of χ can be generalized to give the response not only to a uniform field but also to a magnetic plane wave characterized by $\vec{q}(\vec{q}, q_0)$. The time dependent perturbation calculation [2] leading to $\chi(\vec{q})$ can be symbolized by the Diagram 3a. In this diagram, the dotted line represents the magnetic field of vector \vec{q} to be measured. The solid arrows form an electron-hole bubble and the broken lines represent “exchange interactions” of strength \bar{v} . This exchange interaction is to be associated with the energy difference between an electron-hole pair of the same spin and an electron-hole pair of opposite spin and favours pairs of parallel spin.

Repeated exchange interactions give rise to a so-called t -matrix indicated symbolically in Figure 3b, which, in case of momentum independent \bar{v} is given by the simple expression

$$t(\vec{q}) = \frac{\bar{v}}{1 - P(\vec{q})\bar{v}}$$

and leads to the expression for the susceptibility:

$$\chi(\vec{q}) = \frac{2\beta^2 P(\vec{q})}{1 - P(\vec{q})\bar{v}}$$

We see that $P(\vec{q})$ is except for factors $\chi(\vec{q})$ in absence of exchange ($\bar{v} = 0$). A lucky accident wants it that $P(\vec{q})$ can be obtained in closed form in the case of a parabolic band.

In the case of the special alloy Pd 95% + Rh 5% the enhancement factor $\alpha = 1/[1 - N_0(E)\bar{v}]$ has the large value of about 50, and hence the multiple exchanges are very important.

Up to now it was believed that even if the susceptibility is strongly exchange enhanced, the specific heat was nevertheless unaffected by this exchange [3].

Under these conditions, one would say that the bare density of states should show the same peak as the one of the specific heat in Figure 2a. The new work of BERK and SCHRIEFFER shows that the larger exchange found in the alloy series in question gives rise to a strongly frequency-dependent interaction between electrons with the result that a specific heat γ is now enhanced. The exact enhancement is given by an integral equation, but approximately, for large exchange, it can be given as

$$\gamma \cong 2 \gamma_0 (1 + \log \alpha)$$

where γ_0 is the unenhanced specific heat constant.

This result is not restricted just to the alloy series mentioned. It will for instance also apply for the Pt alloys. Furthermore, we have found that there exists quite a number of alloy series made up of inter-metallic compounds where a similar situation must prevail.

The work of BERK and SCHRIEFFER is based on the model of a momentum independent exchange which is supposed to be responsible for the observed high paramagnetic susceptibility. Once one believes in this model, it becomes possible also to discuss a number of other properties of high susceptibility metals. It becomes for instance apparent that an exchange interaction which favours strongly parallel electrons will at the same time be an obstacle to the formation of the superconducting state (theory of BARDEEN, COOPER and SCHRIEFFER) which depends on the formation of anti-parallel spins. At least, this is so as long as we consider metals with only one band.

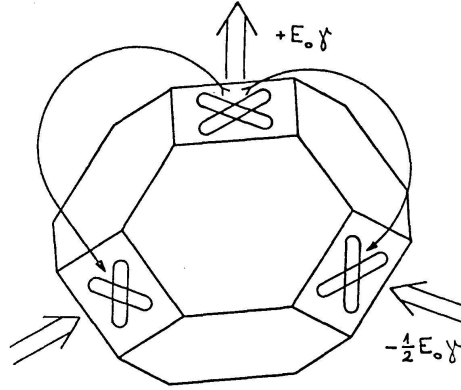
In the case of transition metals, it is quite possible that one band is strongly exchange enhanced and gives therefore rise to a large susceptibility (this will often be a d -band), while another conduction band with little exchange could become superconducting, and we believe to have observed examples of this.

Another property related to the susceptibility is the shear modulus [4]. In Figure 4 we show the Brillouin zone for the f.c.c. structure, as found for instance in the Rh-Pd-Ag alloys. The band structure of our alloys is not understood in detail, but for simplicity we may assume that on the square faces of the Brillouin zone pockets of holes are located. When a shear deformation is applied, it will raise one pair of pockets by an energy γE_0 (E_0 is the deformation potential) and the two other pairs are lowered correspondingly. After this has happened, the holes on top will transfer into the two pockets whose energy is lowered.

This transfer will lower the shear energy, hence the shear modulus. If we assume that the exchange interaction \bar{v} takes place only between the holes in each pocket, the change in the shear modulus, ΔG is found to be given by:

$$\Delta G = - \frac{2 E_0^2}{g_e^2 \beta^2} \chi$$

where E_0 is the deformation potential, usually of order of an electron volt, and β is the Bohr magneton.



$$\Delta G \gamma_{\frac{1}{2}}^2 = -\Delta \chi_d E_o^2 \gamma_{\frac{1}{2}}^2 / g_e^2 \beta^2$$

Figure 4
Brillouin zone of the f.c.c. structure of Pd

The correlation between G and χ as function of the mean atomic mass \overline{M} is difficult to see, as we are not yet master of the impurity and dislocation effects. The correlation between the respective temperature coefficients however should be less sensitive to these effects, since the variation of χ between 70 °K and 300 °K is quite large.

In Figure 5 we show this correlation as it was recently observed by the Geneva group.

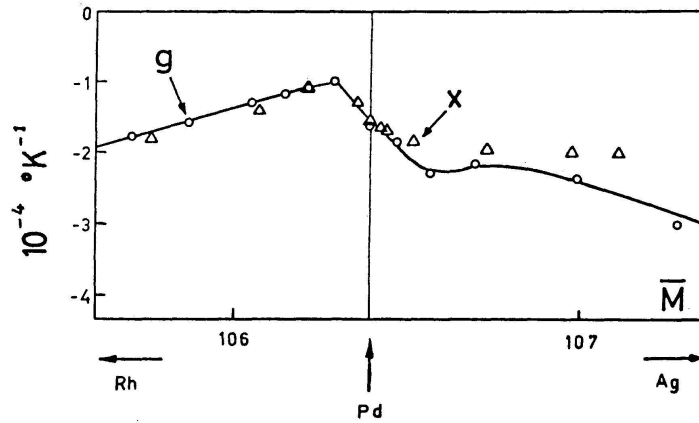


Figure 5
Temperature coefficients of the shear moduli, measured and calculated

Let us now turn briefly to the problem of magnetic impurities in metals of high magnetic susceptibility. The characteristic properties of such a system are due to an exchange interaction between the spin of the mag-

netic ions \vec{S} and the spin of the conduction electrons $\vec{\sigma}$. This interaction is often described by the very simplified form $J \cdot \vec{S} \cdot \vec{\sigma}$. The dynamic susceptibility of such a system was studied by GIOVANNINI in his thesis. In order to use the diagram techniques also for spins larger than $\frac{1}{2}$ (as is the case for instance for Gd ions), he produced together with KOIDÉ a generalisation of WICK's theorem for spins [5]. This procedure works quite well in perturbation expansions, but it is somewhat cumbersome at finite temperatures and will have to compete with ABRIKOSOV's new method [6] and the scattering theoretical methods now becoming available.

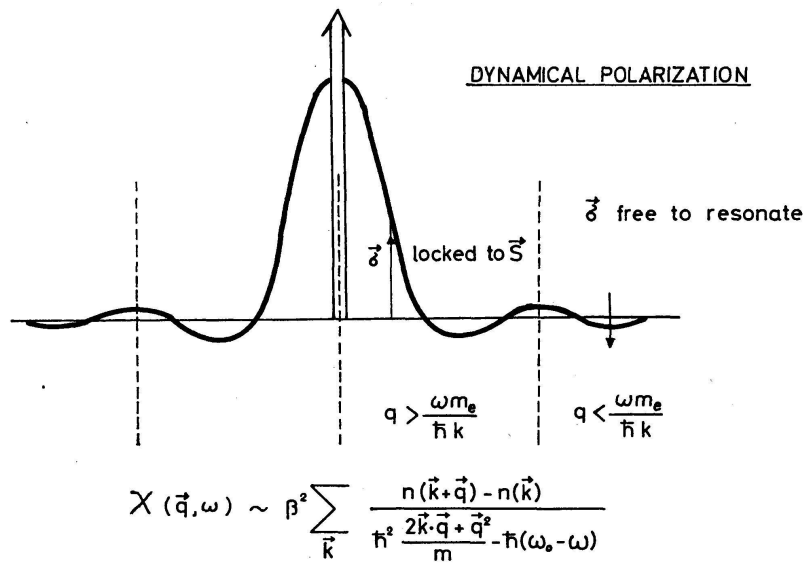


Figure 6

Dynamical polarization

The main results of GIOVANNINI concerning the *paramagnetic resonance behaviour* of the system of ions and free electrons can also be reproduced by a molecular field calculation. This is not obvious if one looks at the field distribution such as is created around a well localized ion. This distribution is shown in Figure 6, it is essentially the spatial FOURIER transform of the function $\chi(\vec{q}, \omega)$ and it is found to be itself strongly localized. However, if we look at the expression for $\chi(\vec{q}, \omega)$ we find that it shows resonant behaviour only for small q , where $\omega_0 - \omega$ is no longer negligible ($q = |\vec{q}|$). It is then essentially only the $q = 0$, or uniform component of the electron magnetization which participates in the resonance phenomenon, and herein lies the justification of the molecular field model. The model leads to an equation for coupled oscillators:

$$(\omega - \omega_s - a)(\omega - \omega_e - b) = ab$$

where ω_s ionic resonance frequency

ω_e electronic resonance frequency

a Knight shift (displacement of the ionic resonance by the electronic magnetism)

b "Day" shift (displacement of the ionic resonance by the ionic magnetism)

In Figure 7, we see the magnetization \vec{M} precessing essentially in the applied field \vec{f} . The Knight shift is given by the molecular field due to the electron polarization due to \vec{h}_2 , proportional to the molecular field constant λ .

MOLECULAR FIELD MODEL - ADDITION OF FIELDS

a) $\omega_s \ll \omega_e$ (NMR, ion = nucleus)

$$\vec{H} = \vec{f} + \lambda \vec{m} \approx \vec{f} + \lambda \alpha_e \vec{h} \approx \vec{f} + \lambda \alpha_e (\vec{f}_z + \lambda \vec{M})$$

b) $\omega_s \gg \omega_e$ (EPR, with high g_s value)

in this case \vec{h}_3 is no longer $\parallel \vec{M}$

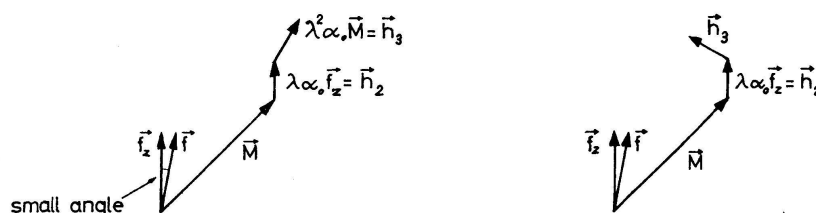


Figure 7

Molecular field model—Addition of fields

Furthermore there is a field \vec{h}_3 due to the electron polarization induced by the ionic magnetization \vec{M} .

In the NMR case (Figure 7a) \vec{h}_3 is parallel to \vec{M} and hence of no importance to resonance (no torque!). In the other case, illustrated in Figure 7b, \vec{M} precesses faster than the resonance frequency of the electrons; \vec{h}_3 has therefore a transverse component, out of phase with \vec{M} , and a contribution in addition to the simple Knight shift results. If $\omega_s \sim \omega_e$, \vec{h}_3 will show resonant behaviour, complicating further the situation. In particular, the ionic resonance will then show a damping due to the motion of \vec{h}_3 and proportional to \vec{M} , hence inversely proportional to temperature (Figure 8). Such a damping appears only for indirect coupling and is therefore characteristic for indirect couplings by conduction electrons. In the case of direct coupling between magnetic ions, no such additional damping term is expected, because this damping is due to the dissipation by the conduction electrons.

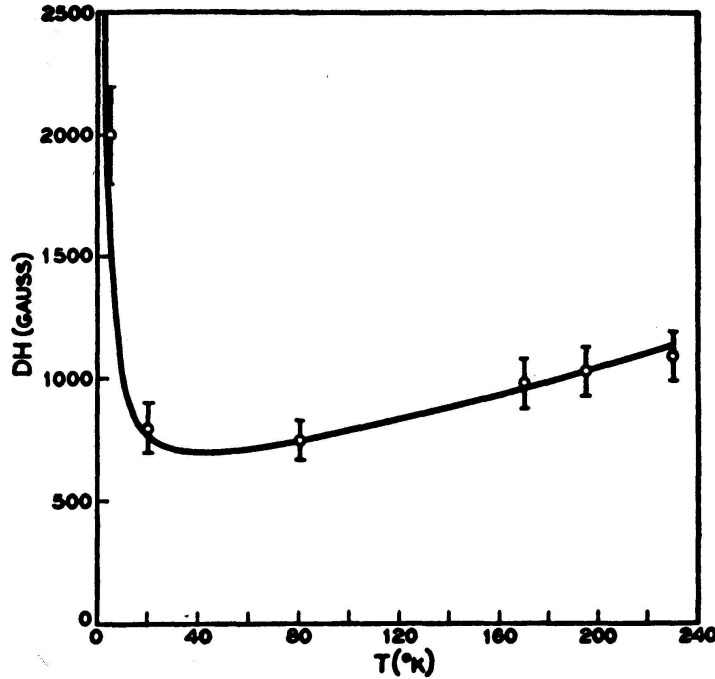


Figure 8

Half-width at half intensity of 2 at. % Gd on UPd_3 as a function of the temperature

In Figure 9, we show two series of measurements, the first being on Rh-Pd-Ag alloys. In them, Gd was introduced as magnetic impurity and its g shift measured. The shifts are negative with respect to the free ion value. They show a pronounced maximum at the composition of maximum susceptibility, as might be expected. Experimentally one finds that this maximum occurs also in other alloys where the $4d$ -band gets filled up. As a second example we give the (Ni-Cu)₅-La alloy series. If plotted against the electron concentration in the same way as the Rh-Pd-Ag alloys, they show the same maximum in the g shift.

Susceptibility measurements in the latter alloy series were not possible because of traces of metallic Ni.

Table I gives some experimental results concerning work in the domain of paramagnetic resonance of impurities on metallic hosts. We find for instance La-Ru₂ as another compound with a d -band to be filled, showing negative g shift if doped with Gd⁺⁺⁺. Pd + H₂ is interesting because it loses its g shift since the H is interstitially absorbed and its electrons fill the magnetic d -holes. In partially hydrogenated Pd, two phases are recognized from two lines at low temperature:

Mn⁺⁺ in Pd shows also a strong g shift, which however for this ion is positive, indicating a positive polarization of the conduction electrons for this case.

The magnetic moment P should be related to the g shift by $P = P_0(1 + \Delta g/g_0)$ and this relation is approximatively fulfilled for Gd and Mn in Pd.

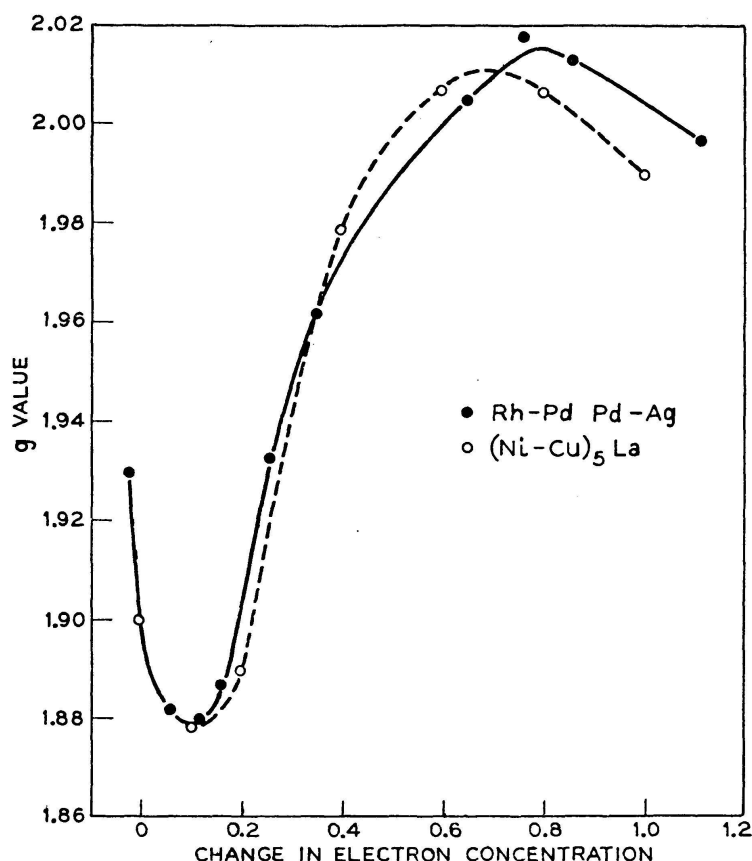


Figure 9

Comparison of the Gd g values at 20.4 °K in Rh-Pd, Pd-Ag alloys and Ni_5La , Cu_5La mixed intermetallic compounds as a function of the change in the electron concentration. The two curves were shifted horizontally so that their two minima coincide. The zero in the electron concentration is arbitrary

Eu metal shows also *EPR* due to Eu^{++} . Er is the only non S state ion so far observed; some doubts are permitted as to whether the resonance was not seen in a surface oxide sheet, as the microwaves penetrate only into a skin depth. Non S state ions must in general be studied in single crystals. However, non S state ions induce also a polarization in the conduction electrons, and this polarization can be picked up *indirectly* by observing the resonance of, for example Gd^{+++} . For this to be possible, it is however necessary that the induced polarization be not too strongly localized, and this is the case again in the metals whose susceptibility is highly exchange enhanced.

Thus it is in Pd that we have made the most extensive measurements of indirect resonance and measured in particular the exchange constants of most rare earths, as well as Co, Ni, Fe. These latter metals are particularly interesting as they induce polarizations many times the size of their own magnetic moment, so that an analysis in terms of a conduction electron polarization becomes questionable. Saturation of this polariza-

Table I
EPR g values—Direct g shift

Gd ion (in insulating crystal $g \cong 1.99$)		
Host = simple metal		
Pd + 3% Gd	$g = 1.887 \pm 0.007$	PETER, SHALTIEL (62)
Ag + 3% Gd	1.995 ± 0.007	PETER, SHALTIEL (62)
Rh + 3% Gd	1.989 ± 0.007	PETER, SHALTIEL (62)
Gd metal	1.94 ± 0.02	RODBELL, MOORE (64)
Host = alloy or intermetallic compound		
Pd ₅₀ Ag ₅₀ + 3% Gd	1.995	
Pd + 60% H	~ 2.00	SHALTIEL (63)
GdAl ₂ + 5% Gd	1.982 ± 0.003	JACCARINO, PETER (60)
LaNi ₅ + 5% Gd	1.877 ± 0.007	SHALTIEL, PETER (64)
YNi ₅ + 5% Gd	1.900 ± 0.007	SHALTIEL, PETER (64)
LaPt ₅ + 5% Gd	2.022 ± 0.007	SHALTIEL, PETER (64)
La Ru ₂	1.86	SHALTIEL, WERNICK (64)
YRu ₂	1.93	SHALTIEL, WERNICK (64)
LaPt ₂	2.00	SHALTIEL, WERNICK (64)
Mn ion (in insulating crystal $g \cong 2.00$)		
Mg + 0.7% Mn	2.02 ± 0.01	OWEN <i>et al.</i> (57)
Cu + 0.5% Mn	2.01 ± 0.01	OWEN <i>et al.</i> (57)
Ag + 2% Mn	2.010 ± 0.005	SHALTIEL, WERNICK (64)
Au + 2% Mn	2.005 ± 0.005	SHALTIEL, WERNICK (64)
Pd + 2% Mn	2.090 ± 0.005	SHALTIEL, WERNICK (64)
Eu ion (in insulating crystal $g \cong 1.99$)		
Eu metal	1.985 ± 0.015	PETER, MATTHIAS (60)
Er ion (in insulating crystal $g = 6.78$)		
Ag + 0.3 Er	6.75 ± 0.10	GRIFFITHS, COLES (66)

tion was observed for instance by studying the shear modulus of Pd doped with Fe [7].

The distribution of magnetization around a Fe ion in Pd has been made directly visible by low angle neutron diffraction by LOW, Figure 10. This figure gives however only the envelope of the true moment distribution. Because of the Bloch nature of the wave functions, the polarization is modulated by the lattice structure, as can be seen by the study of the magnetization on a single crystal of Pd with Fe in dilute solution Figure 11, made by neutron diffraction by WALTER C. PHILLIPS [8]. The FMR g value of this complex is ~ 2.1 and does not change much as the Pd host is hydrogenated [9].

Let us now turn to the question of the *origin of the exchange between ions and conduction electrons*. An important contribution comes undoubtedly from the contribution due to processes where an itinerant electron is exchanged against a magnetic electron on one of the magnetic ions. These simple exchange processes lead to a conduction electron

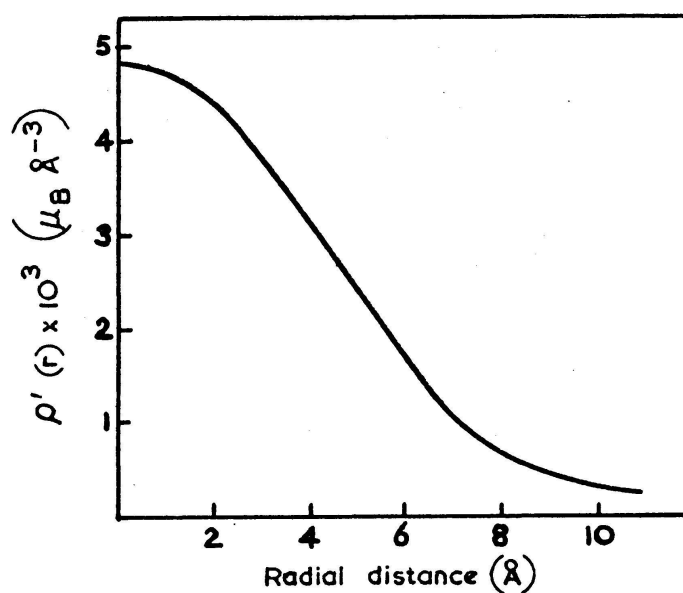


Figure 10

The distribution of magnetic moment density $p'(r)$ in the Pd matrix surrounding a Fe atom in a dilute Pd-Fe alloy. The plot is derived from a Fourier inversion of neutron scattering data for an alloy containing $\frac{1}{4}$ atomic % Fe

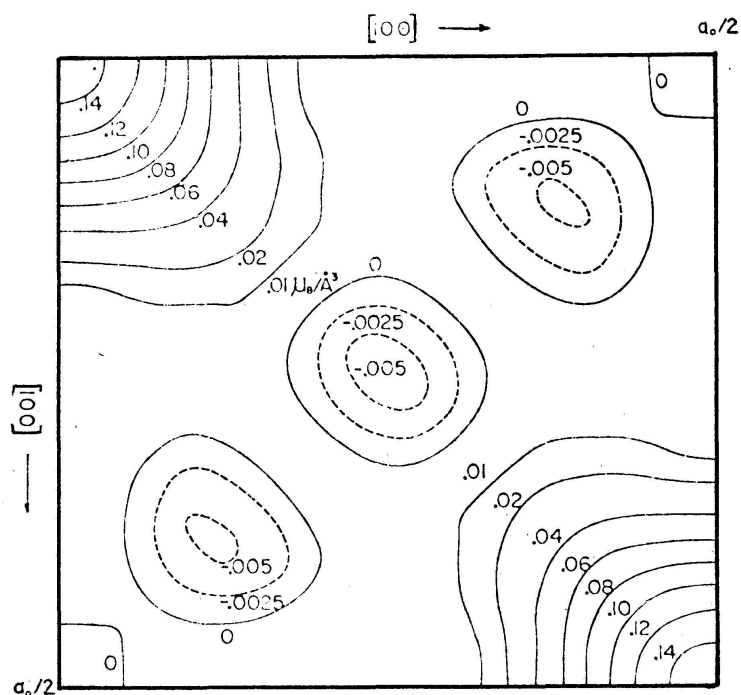


Figure 11

Magnetic-moment density in Bohr magnetons per \AA^3 on the cube face of a Pd + 1.3% Fe single crystal

polarization which on the average is parallel to the polarization of the ionic spins. Correspondingly, only positive g shifts would be expected in the *EPR* experiments. However, as seen in Table I, the g shifts are experimentally found to be of either sign. Responsible for this is an interaction which is found only in metals, not in atoms or insulating materials. The processes of interest for this interaction are virtual emissions from the occupied magnetic level into the empty part of the band, and virtual absorptions of conduction electrons into the empty $4f$ states on the ion. These emission and absorption processes will be determined by certain one-electron off-diagonal matrix elements, and the question of the magnitude of these matrix elements is a delicate one. We could for instance start with Hartree wavefunctions for the conduction electrons in the field shown by the ions if averaged over all spin states. This procedure, if carried out correctly, would give zero probability for the emission and absorption processes in question.

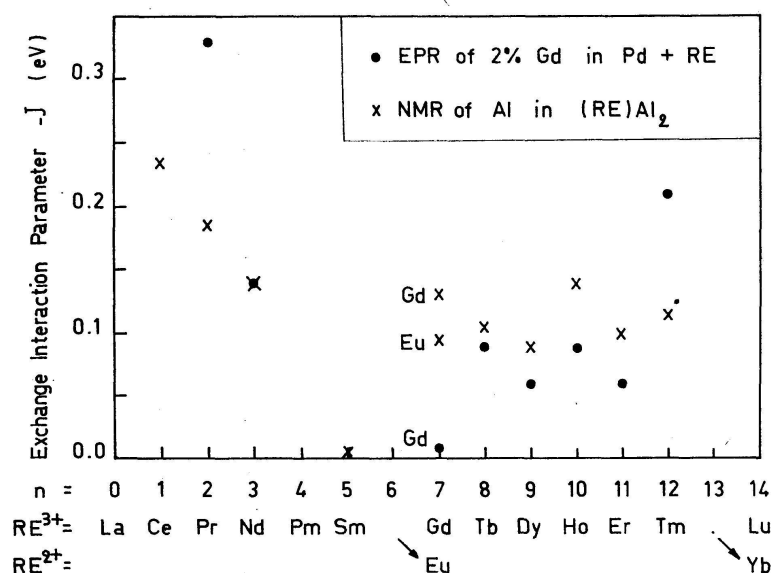


Figure 12

Interband exchange in rare earths. Experimental J value of exchange parameter

It is therefore specifically the exchange part of the ionic potential which determines these virtual processes. Based on this idea, WATSON, KOIDÉ and myself [10] were able to calculate the exchange interactions for the rare earths in metals and to reproduce essentially the systematic behaviour of the exchange parameter shown in Figure 12. In this figure, we give the exchange parameter for two series of measurements involving the rare earths in two different metals. In both cases, we find negative exchange interactions, whose magnitude is larger at the beginning and the end of the Lanthanide series than in the middle, and this behaviour would indeed be expected from the perturbation calculations cited above.

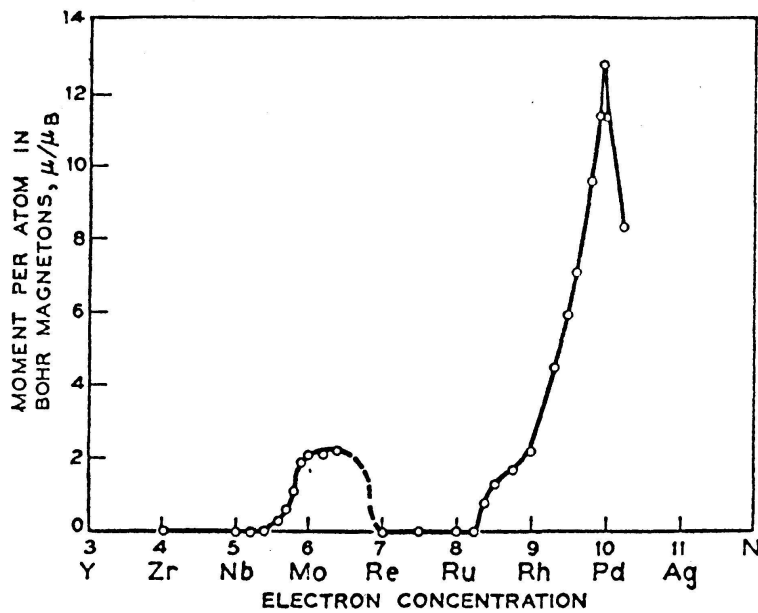


Figure 13

Magnetic moment in Bohr magnetons of an iron atom dissolved in various second row transition metals and alloys as a function of electron concentration

As we have seen, this exchange mechanism leads to essentially negative conduction polarisation. If strong enough, it will suppress entirely the ionic magnetization. That such a suppression can indeed occur, is shown in Figure 13. Fe was dissolved in part of the second transition series and we see that it has a giant moment in the now well-known Rh-Pd region, but no moment at all in the Nb-Mo region. In that region, the virtual ionisation processes apparently destroy the magnetic moments completely [11]. When the magnetic ion is so strongly perturbed as is the case in the Nb region of the periodic system, a simple perturbation calculation is certainly no longer sufficient. A more complete calculation applicable to this situation was first proposed by ANDERSON [12].

So far we have spoken only of the static magnetization and of the paramagnetic resonance of impurity ions. Let me conclude with some remarks on the relevance of this work to *transport phenomena*. We have parametrized the magnetic ion-conduction electron exchange by an operator $JS \cdot \sigma$. If J were a constant, it should seem simple to calculate the scattering of the conduction electrons due to this potential and thus obtain a relaxation time from which in turn transport properties such as resistivity, thermopower and superconducting transition temperature lowering can be calculated. However, if one tries to do this, two interesting accidents happen.

First, one realises that the correlation between the different experiments as far as the magnitude and even the sign of J is concerned, is not very good. As we now know thanks to a new calculation by WATSON and FREE-

In Figure 14 we give an example of the value J as a function of $\vec{k} - \vec{k}' = k - k' = \vec{Q}$ [13]. This true momentum dependence, which is much more complex than the constant value for J which we have assumed previously and which was used in much of the work concerning this problem, will have to be taken into account before a satisfactory agreement between parameters from susceptibility and resonance (low angle scattering) and transport properties (high angle scattering) is reached.

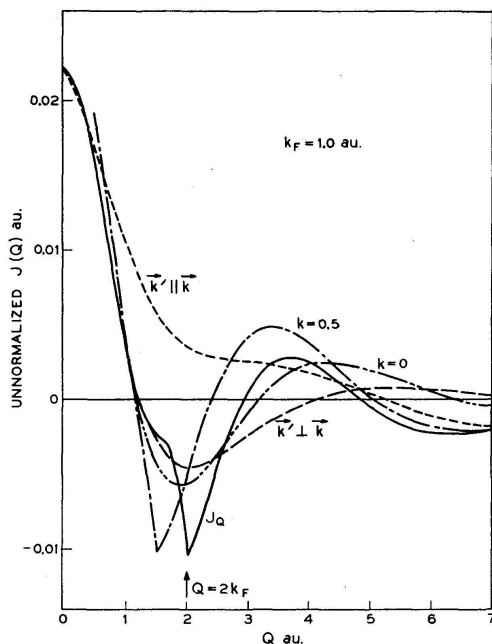


Figure 14
 J as a function of k and k'

$$\varrho \cong \varrho_m [1 + (J/E_f) \log (T/\Delta)]$$
$$\varrho_m \sim J^2 S(S+1)$$

This seems to be the explanation of the “resistance minimum” often observed at low temperatures, and expected from KONDO’s [14] expression in those cases where J is negative. Similarly, the new scattering term gives rise to a “giant thermo power” at low temperatures, a phenomenon that has long puzzled metal physicists. More elaborate calculations indi-

cate the existence of a singularity in scattering amplitude for negative J at a temperature $T_C \cong \Delta \cdot e^{-\frac{1}{|J|N(E_f)}}$. This points to the possibility of a transition to a condensed state below this temperature T_C , whose value is difficult to determine as long as the detailed k, k' dependence of J has not been taken into account properly. The nature of this transition is as yet not clear.

It is thus to be expected that there is still some excitement ahead in the physics of paramagnetic metals of high susceptibility. On one hand, much detailed experimentation and explicit calculation remains to be done. On the other hand, one has yet to find even a qualitative understanding of metals containing magnetic impurities at very low temperatures.

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REFERENCES

1. BERK N.F., and SCHRIEFFER J.R.: Influence of ferromagnetic exchange interactions on superconductivity (preprint).
2. WOLFF P.A.: Phys.Rev. 129, 84; 1963.
3. CLOGSTON A.M., JACCARINO V. and YAFET, Y: Phys.Rev. 134 A, 6-50; 1964.
4. BELMAHI O., MERCK M., PERRÉARD E., PETER M., WALKER E., SCHRIEFFER J.R.: HPA 39, 338; 1966.
5. GIOVANNINI B., PETER M., KOIDÉ S.: Phys.Rev. 149, 1, 251-256; 1966.
6. ABRIKOSOV, A.A.: Physics 2, 5; 1965.
7. WALKER E.: (Private communication, to be published).
8. PHILLIPS W.C.: Phys.Rev. 138, A 1849; 1965.
9. DUPRAZ J.: (Private communication, to be published).
10. WATSON R.E., KOIDÉ S., FREEMAN A., PETER M.: Phys.Rev. A 139, 167-178; 1965.
11. CLOGSTON A.M., MATTHIAS B.T., WILLIAMS H.J., CORENZWIT E., SHERWOOD R.C., PETER M.: Phys.Rev. 125, 541-552; 1962.
12. ANDERSON, P.W.: Phys.Rev. 124, 41; 1961.
13. WATSON R.E. and FREEMAN A.J.: Exchange coupling and conduction electron polarization in metals (preprint).
14. KONDO J.: Prog.Theor.Phys. 32, 37; 1964.