Electron Paramagnetic Resonance Studies of Ions in Metals

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Abstract. After recalling that the interaction between the diluted paramagnetic ions in a metal and the conduction electrons is described by an effective exchange parameter J, which can be measured by the shift of the resonance line of these ions, a molecular field picture is developed and a susceptibility function which gives the complete response of the ions coupled to the conduction electrons is obtained. The physical origin of the ion-conduction electron coupling (Heisenberg exchange and interband exchange) is discussed. The difficulties in comparing EPR results to other static and transport properties, which arise from the fact that an isotropic, momentum independent exchange parameter represents an insufficient model, are indicated.

A review of experimental results is established for the ions observed until now by EPR, as well an evaluation of their effective exchange parameter in some highly polarizable host matrices.

A. Introduction

The electronic paramagnetic resonance (EPR) of magnetic impurities in metals is similar to the nuclear paramagnetic resonance (NMR) in metals in many aspects. There are however some important differences and the interpretation of results is more difficult for EPR. In fact the first EPR experiments [1, 2] have been performed about ten years later than the NMR experiments. The main difficulties which are met in EPR can be enumerated as follows:

1) The ionic spin is a large local perturbation, and any conclusion for EPR experiments as regarding the electronic structure of the host metal must be analysed carefully.

2) The effective interaction Hamiltonian between the localized spins and the conduction electrons is very difficult to derive generally, especially for non S-state ions. It is usually assumed that for S-state ions an exchange type Hamiltonian is valid (similar to the contact Hamiltonian of nuclear resonance), where however the interaction parameter is not a true exchange interaction but includes also mixing effects.

3) The resonance frequency of the localized ions is very close to the resonance frequency of the conduction electrons, so dynamic effects might be important if the relaxation rate of the electrons is not very large compared to the resonance frequency.

In spite of these difficulties EPR contains extremely valuable information about parameters which cannot be obtained by NMR, in particular the effective interaction parameter whose sign and magnitude play an essential role in a number of metallic phenomena such as magnetism and transport properties.

B. Theory of EPR in metals

1) *Simple derivation of ionic g shift*

In many cases, a magnetic ion (e.g. Mn^{++} or Gd^{+++}) retains its magnetic properties nearly unchanged in a metallic matrix.

In the presence of an external magnetic field H in the z direction, the Zeeman energies are given by

$$E = - g_s \beta \, H \cdot S$$

where S is the ionic spin; β is the Bohr magneton. g_s, the ionic g value, is usually negative, but in our discussion we will assume that g_s and g_e (electronic g value) are positive. The results will be the same. A transverse field of "frequency" ω_s can introduce transitions if we satisfy

$$\omega_s = g_s \beta \, H_z$$

(with $\hbar = 1$, ω is an energy).

The main effect to be studied in EPR in metals is a coupling between a magnetic ion at site R_n and the conduction electron at site x which varies like the scalar product between their respective spins, S and σ, and which can be phenomenologically described by an exchange interaction density:

$$\mathcal{H}_{ex} = - \sum_n (1/n_0) \, J \, S \cdot \sigma(x) \, \delta(R_n - x)$$

$\sigma(x)$ is the electronic spin density. J is a parameter with the dimension of an energy, usually some fraction of an electron Volt; in the literature, the parameter $2J$ is often used instead of the parameter J. R_n are the lattice sites occupied by the magnetic ions. n_0 is the number of lattice sites per unit volume. The justification of this energy term will be discussed later.

In EPR, the allowed energy levels are now:

$$E = - S_z \left(g_s \beta \, H_z + \frac{J}{n_0} \langle \sigma_z \rangle \right)$$

where $\langle \sigma_z \rangle$ is the expectation value of the electronic spin density at site R_n.

Remembering that $\chi_z H_z = \langle \sigma_z \rangle g_e \beta$ with χ_z the conduction electron volume susceptibility, and n_0 the number of lattice sites per unit volume we obtain:

$$E = - S_z \beta \, H_z \left(g_s + \chi_z \frac{J}{n_0 \, g_e \, \beta^2} \right)$$

Hence we find a g shift

$$\Delta g_s = \frac{J \, \chi_z}{n_0 \, g_e \, \beta^2}$$

If the metallic electrons can be represented by a free electron gas, we get

$$\chi_z = \frac{1}{2} g_e^2 \, \beta^2 N(E_f)$$

and $N(E_f) = 3 \, n/4 \, E_f$ (n number of conduction electrons per unit volume)
Hence

$$\chi_z = \frac{3 \, n \beta^2}{2 \, E_f} \quad \text{and} \quad \Delta g_s = \frac{3 \, J \, n}{4 \, E_f \, n_0}$$

Hence we can measure J by determining Δg_s and χ_z, or by setting, in the simple metal,

$$J = \frac{4 \, n_0}{3 \, n} \, E_f \, \Delta g_s$$

2) Molecular field picture

The equation of motion in an external field f of a system of magnetic ions of g value g_s and magnetization M, in a metal with conduction electrons of g value g_e

and magnetization m can be described by a system of coupled Bloch equations and a molecular field constant λ describing the coupling between the ions and the electronic system. The justification of such a description is given by an exact quantum statistical analysis to be discussed below.

The molecular field acting on the ions, H, is given by $H = f + \lambda m$, the field acting on the electrons by $h = f + \lambda M$. The Bloch equations then read[1]:

$$\overset{\circ}{M} = g_s \beta (M \times H) - \Delta (M - \beta_0 H)$$

$$\overset{\circ}{m} = g_e \beta (m \times h) - \delta (m - \alpha_0 h)$$

Here α_0 is given by the equilibrium condition $m_z = \alpha_0 h_z$ and is the static susceptibility of the electron system. δ is the relaxation rate of the conduction electrons. β_0 and Δ are the analogous quantities for the ions. In order to solve the equations, we remember the cross product in the system $z, -, +$ with $p \times q = r$, and $p_{\pm} = 1/\sqrt{2} \ (p_x \pm i \, p_y)$, etc, then

$$r_+ = i \, (q_+ p_z - p_+ q_z)$$
$$r_- = i \, (p_- q_z - q_- p_z)$$
$$r_z = i \, (p_+ q_- - p_- q_+)$$

setting now $f_{\pm}$, $M_{\pm}$, $m_{\pm}$ proportional to $e^{\pm i \omega t}$ (stationary solution), $f_z = $ constant and retaining only the terms linear in $f_{\pm}$, $M_{\pm}$ and $m_{\pm}$ (small deviations from equilibrium) we obtain the equations:

$$- \omega M_+ = g_s \beta (H_+ M_z - M_+ H_z) + i \Delta (M_+ - \beta_0 H_+)$$

$$- \omega m_+ = g_e \beta (h_+ m_z - m_+ h_z) + i \delta (m_+ - \alpha_0 h_+)$$

From there the transverse susceptibilities:

$$\chi_+^e = \frac{m_+}{h_+} = \frac{g_e \beta \, m_z - i \, \delta \, \alpha_0}{g_e \beta \, h_z - \omega - i \delta} \qquad \chi_+^s = \frac{M_+}{H_+} = \frac{g_s \beta \, M_z - i \Delta \, \beta_0}{g_s \beta \, H_z - \omega - i\Delta}$$

or, remembering $m_z = \alpha_0 h_z$ and $M_z = \beta_0 H_z$ and introducing

$$\omega_e = g_e \beta f_z \qquad a = g_s \beta \lambda m_z$$
$$\omega_s = g_s \beta f_z \qquad b = g_e \beta \lambda M_z$$

$$\chi_+^e = \alpha_0 \frac{\omega_e + b - i\delta}{\omega_e + b - i\delta - \omega} = \alpha_0 \frac{\omega_e'}{\omega_e' - \omega} \qquad \chi_s^+ = \beta_0 \frac{\omega_s + a - i\Delta}{\omega_s + a - i\Delta - \omega} = \beta_0 \frac{\omega_s'}{\omega_s' - \omega}$$

By substituting these susceptibilities we find:

$$M_+ (\omega_s' - \omega) = \beta_0 \, \omega_s' \left[f_+ + \lambda \, \alpha_0 \frac{\omega_e'}{\omega_e' - \omega} (f_+ + \lambda \, M_+) \right]$$

$$m_+ (\omega_e' - \omega) = \alpha_0 \, \omega_e' \left[f_+ + \lambda \, \beta_0 \frac{\omega_s'}{\omega_s' - \omega} (f_+ + \lambda \, m_+) \right] \quad \text{and}$$

$$\boxed{\chi_+ = \frac{M_+ + m_+}{f_+} = \frac{\omega_s' \, \omega_e' \, [\alpha_0 + \beta_0 + 2 \lambda \, \alpha_0 \, \beta_0] - \omega \, (\alpha_0 \, \omega_e' + \beta_0 \, \omega_s')}{(\omega_s' - \omega) \, (\omega_e' - \omega) - \lambda^2 \, \alpha_0 \, \beta_0 \, \omega_s' \, \omega_e'}}$$.

This expression gives the complete response for a system of paramagnetic ions in presence of conduction electrons.

We shall now discuss certain simple cases. At first we shall neglect the damping terms. This leads to reasonable results where the frequencies ω_s and ω_e are very different.

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[1] For the discussion of a more general damping term, see ref. [6].

a) Case of NMR, ω_s is the nuclear resonance frequency, and $\omega_s \ll \omega_e$:
Neglect of the damping leads to real roots of the denominator of χ_+, these roots give the resonance frequencies. With $\varDelta = \delta = 0$, we have

$$\omega_s' = \omega_s + a, \qquad \omega_e' = \omega_e + b, \qquad \lambda^2 \alpha_0 \beta_0 \omega_s' \omega_e' = ab$$

and the resonance condition becomes

$$[a - (\omega - \omega_s)][b - (\omega - \omega_e)] - ab = 0$$

$$\omega_R = a + \omega_s - \frac{ab}{\omega_e + b - \omega_R} \simeq \omega_s + a - \frac{ab}{\omega_e} \quad \text{for small } \lambda$$

$$\simeq \omega_s + \alpha_0 g_s \beta \lambda (f_z + \lambda M_z)\left(1 - \frac{\lambda M_z}{f_z}\right)$$

$$\simeq \omega_s + \alpha_0 g_s \beta \lambda f_z + \cdots \quad \text{(the next term is of order } \lambda^3).$$

We find the simple Knight shift which is of order λ, and no term in λ^2. The reason is that the induced field h_3 (see Fig. 1) is parallel to M (see Bloch equations). This is only the case if m is obvious below its resonance frequency ω_e, and then h_3 exerts no torque on M.

b) In the case of EPR with $\omega_s \gg \omega_e$ (as might be the case of Er[3]) with $g_s = 6.7$) we obtain:

$$\omega_R = a + \omega_s - \frac{ab}{\omega_e + b - \omega_R} \simeq a + \omega_s + \frac{ab}{\omega_s} \quad \text{(for small } \lambda)$$

$$\simeq \omega_s + \alpha_0 g_s \beta \lambda (f_z + \lambda M_z)\left(1 + \frac{\lambda M_z g_e}{f_z g_s}\right).$$

In this case m is no longer parallel to M, m_+ is in fact out of phase with M_+ (excitation above resonance) and hence h_3 contributes $\alpha_0 \lambda M_z (1 + g_e/g_s)$ to the resonance frequency (see Figure 1).

c) $\omega_e = 0$ and $\omega_s = 0$ (or $f_z = 0$), a and b finite (both systems are ferromagnetic, because a and b are proportional to m_z and M_z).

The solutions of the secular equation $\omega = a - a b/(b - \omega)$ are:

$$\omega_{R1} = 0 \quad \text{and} \quad \omega_{R2} = a + b$$
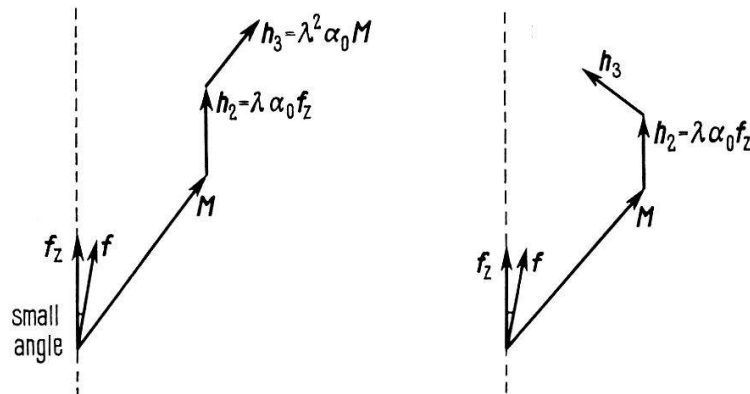

Figure 1

Molecular field model – Addition of fields

a) $\omega_s \ll \omega_e$ (case of NMR, if the magnetic impurities are the nuclei) field acting on the nuclei

$$H = f + \lambda m \simeq f + \lambda \alpha_0 h = f + \lambda \alpha_0 (f_0 + \lambda M)$$

b) $\omega_s \ll \omega_e$ (case of EPR with high g_0 values) in this case h_3 is no longer parallel to M.

At a + b we find an antiferromagnetic resonance (by developing we can see than m_+ and M_+ have opposite signs), which is however optically inactive if $g_e = g_s$, as can be seen from the expression for χ_+. The resonance at a + b was first pointed out by DONIACH [4].

d) If we apply a weak magnetic field to the ferromagnetic lattices of the former case in *c*) the frequencies will be:

$$\omega_{R1} \cong \frac{a}{a+b}\,\omega_e + \frac{b}{a+b}\,\omega_s \qquad \omega_{R2} \cong a + b + \frac{b}{a+b}\,\omega_e + \frac{a}{a+b}\,\omega_s$$

e) $\omega_e = \omega_s$, damping.

In cases c) and d) we learned that there will be no *g* shift if $\omega_e = \omega_s$ (the shifted mode being inactive). In the case of EPR with *S*-state ions, we will often find $\omega_e \cong \omega_s$ but appreciable damping of the conduction electrons. χ_+ may have to be plotted explicitly to give the resonance lines, but the position of the poles of χ_+ gives an indication on line position and width.

Taking $\varDelta \ll \omega_e = \omega_s$ and $\lambda^2\,\alpha_0\,\beta_0 \ll 1$ we find:

$$\omega_R = \omega_s' - \frac{\lambda^2\,\alpha_0\,\beta_0\,\omega_s'\,\omega_e'}{\omega_e' - \omega_R} \cong \omega_s + a - i\,\varDelta - i\,\lambda^2\,\alpha_0\,\beta_0\,\omega_s'\,\omega_e'\,\frac{1}{\delta}.$$

This means that we get the Knight shift without second order contribution in λ but with a damping proportional to ab/δ.

Note that $b \sim M_z \sim 1/T$; at low temperature we may have *b* of the order of δ and an additional broadening of the order of the Knight shift. Figure 2 and Figure 3 show cases where a broadening $1/T$ was observed for EPR of Gd respectively in Pd [5] and Pd_3U [6].

3) *Validity of molecular field picture*

The secular equation for EPR in metals can be written in the form

$$\omega_R = \omega_s + g_s\,\beta\,\lambda\,\chi_z^e\,(\omega = 0)\,f_z + \lambda^2\,g_s\,\beta\,M_z\{\chi_z^e\,(\omega = 0) - \chi_+^e(\omega)\}\,.$$
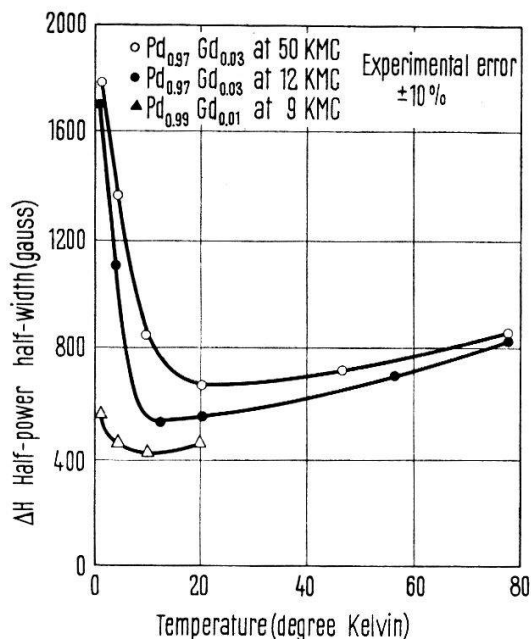
Figure 2

Dependence of linewidth on temperature for different fields and concentrations of Gd in Pd.
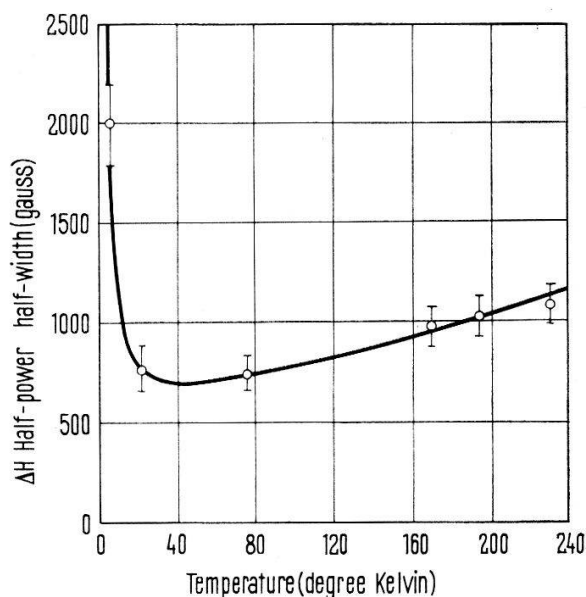
Figure 3

Dependence of linewidth on temperature for 2% atl Gd in U Pd_3

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A similar form was previously obtained from a quantum statistical analysis [7] of this problem without use of the molecular field approximation. The term in the parenthesis is given in this calculation by

$$\sum_{R_n \neq 0}' \{\overline{\chi}^e_+ (\omega, R_n) - \overline{\chi}^e_z (\omega = 0, R_n)\}$$

where the functions $\overline{\chi}^e_+ (\omega, R)$ and $\overline{\chi}^e_z (\omega, R)$ are the space dependent non local susceptibilities, and the R_n are the lattice sites occupied by the magnetic ions.

It turns out [7] that $Re\ \chi^e_+(\omega, R_n)$ and $Re\ \chi^e_z(\omega, R_n)$ differ appreciably only at large distances ($|q|$ small), so that in summing over their differences, the sum can be replaced by an integral over space. Then real part of the bracket is proportional to

$$Re\ [\chi^e_+ (\omega, q = 0) - \chi^e_z (\omega = 0, q = 0)]$$

where $\chi^e_+(\omega, q)$ and $\chi^e_z(\omega, q)$ are the susceptibilities in function of the wave vector q. But the values of these functions for $q = 0$ are exactly the uniform susceptibilities considered in the molecular field model.

We conclude that this model is successful since the dynamical behaviour of the conduction electrons manifests itself only at large values of R_n, or small values of q. This is also the justification of the recent RPA calculations by DONIACH [4] on this problem.

4) *Interelectronic exchange enhancement*

a) Enhanced g shift

The quantity $E_f \Delta g_s$ is a measure of the exchange parameter J only in the case of a free electron gas. In certain cases, χ_z is severely enhanced by interelectronic exchange. If this exchange interaction is taken to be strongly localized and hence constant in k space, it can be characterized by a parameter $\overline{v}$ and the enhanced susceptibility is given by [8] [9]:

$$\chi_z = \chi_{z,0}\ \frac{1}{1 - N(E_f)\ \overline{v}}.$$

Here $\chi_{z,0}$ is the free band susceptibility: $\chi_{z,0} = (1/2)\ g_e^2\ \beta^2\ N(E_f)$.

Recent work by BERK and SCHRIEFFER [10] shows that in the alloy series Rh-Pd-Ag the density of states is small and varies relatively little with alloy composition or temperature, and that χ_z is large because of exchange enhancement. The density of states $N(E_f)$ can in these cases not be inferred from the electronic specific heat as this quantity is also enhanced by the interelectronic exchange, although the enhancement factor is generally smaller than the one applicable to χ_z.

The characteristic maximum in g shifts for EPR in the Rh-Pd-Ag series [5] is then mostly due to the exchange enhancement of the susceptibility, more precisely of the contribution χ_z due to the d-holes.

b) Enhanced range of $\overline{\chi}^e(\omega, R)$

The enhanced susceptibility of a standard band is given by

$$\chi_z(\omega,\ q) = \frac{1}{2}\ g_e^2\ \beta^2\ \frac{N(E_f)\ U\ (\omega, q)}{1 - \overline{v}N(E_f)\ U\ (\omega, q)}$$

where $2\ N(E_f)\ U\ (\omega, q)$ is given by the well known function $P^{RPA}(\omega, q)$ in the RPA approximation.

By developing $P^{RPA}(\omega, q)$ for small values of $|q|$ one finds that the range of $\overline{\chi}_z(\omega, R)$ is enhanced proportionally to $[1 - \overline{v}N(E_f)]^{-1/2}$. Thus in Pd, with an enhancement of χ_z of ~ 50 [10], the range should be enhanced by about $\sqrt{50} \simeq 7$.

c) Anomalous Korringa relation

The exchange of an ionic spin to an electronic spin makes possible a relaxation mechanism known as Korringa broadening Δ_K. Between this broadening and the g-shift Δg_s there holds, in the absence of interelectronic exchange, the well known Korringa relation [11].

$$\Delta_K = \pi\,(\Delta g_s)^2\,kT$$

(this broadening is given in units of ω, the usual angular frequency multiplied by $\bar{h}$)

$$\Delta_K = \frac{g_s^2\,J^2 kT}{2\,n_0^2\,g_e^2\,\beta\,\omega_s}\,Im\,\chi_{+,0}^e\,(\omega_s,\,\boldsymbol{R}=0)\quad\text{(Ref. [7])}.$$

In the presence of exchange enhancement, the Korringa relation no longer applies in its simple form. Δg_s is enhanced by

$$[1 - \bar{v}\,N(E_f)]^{-1}$$

$$\chi_+^e\,(\omega,\,\boldsymbol{q}) = \frac{1}{2}\,g_e^2\,\beta^2\,\frac{N(E_f)\,U_+(\omega,\,\boldsymbol{q})}{1 - \bar{v}N(E_f)\,U_+(\omega,\,\boldsymbol{q})}$$

setting $U_+(\omega,\,\boldsymbol{q}) = U'(\omega,\,\boldsymbol{q}) + i\,U''(\omega,\,\boldsymbol{q})$ since, as we have seen in B.3, $U_+(\omega,\,\boldsymbol{q})$ is nearly equal to $U(\omega,\,\boldsymbol{q})$ for most values of $\boldsymbol{q}$, we find

$$Im\,\{\chi_+^e(\omega,\,\boldsymbol{q})\} = \frac{1}{2}\,g_e^2\,\beta^2\,\frac{N(E_f)\,U''(\omega,\,\boldsymbol{q})}{[1 - \bar{v}N(E_f)\,U'\,(\omega,\,\boldsymbol{q})]^2 + [\bar{v}N(E_f)\,U''(\omega,\,\boldsymbol{q})]^2}.$$

$Im\{\bar{\chi}_+^e\,(\omega_s,\,\boldsymbol{R}=0)\}$ then becomes a sum over all values of $\boldsymbol{q}$. As $U(\omega_s,\,\boldsymbol{q})$ is generally a decreasing function of $|\,\boldsymbol{q}\,|$, we see that Δ_K is less enhanced than predicted by the simple Korringa relation.

In both Figures 2 and 3 we find that there is a broadening $\sim T$ at higher temperature and that this broadening is less than predicted by the simple Korringa relation.

5. *Indirect g-shifts*

In the previous section we have learned that interelectronic exchange can appreciably increase the range of the non local susceptibility $\bar{\chi}_z(\boldsymbol{x})$. Correspondingly, the range of the exchange field $h(\boldsymbol{x})$, which is set up around a magnetic ion because this ion polarizes the conduction electrons, is also increased [12]. Such a magnetic field $h(\boldsymbol{x})$ may oscillate as a function of $|\,\boldsymbol{x}\,|$, and has in general also a mean value. In section B.3) we showed that, if only one species of magnetic ions is present in a metallic host, only the mean value of $h(\boldsymbol{x})$, there called the molecular field, is of importance, and that the fluctuations, are rather remarkably, not observable, and furthermore that there are no shifts due to $h(\boldsymbol{x})$ if $\omega_s \ll \omega_e$ or $\omega_s = \omega_e$. The reason for this behaviour was that the field $h(\boldsymbol{x})$ processes in phase with the total magnetization.

If we introduce magnetic impurities of a second kind, having different g values, then a different situation obtains. The magnetization and electronic polarization of these second impurities process no longer in phase with the magnetization of the electrons under observation, and therefore the z component of $h(\boldsymbol{x})$ due to the second impurities is fully effective in producing a line shift and also a line broadening due to the fluctuations in $h(\boldsymbol{x})$.

The broadening can be calculated by just considering the z component of $h(\boldsymbol{x})$ in the case of *extreme dilution* of both ionic species, and more exactly by just calculating the second moment of $h(\boldsymbol{x})$ around its mean value as will be shown below. In

moderate dilutions, the higher moments will become important and lead to exchange narrowing effects which are to be calculated in a more elaborate analysis.

To get the result for extreme dilutions, consider first the case of a resonating ion, say Mn^{++}, at the origin, and of one other magnetic ion, say Tb^{+++}, at $\boldsymbol{R}_i$. It will shift the resonance of the Mn^{++} by $h\,(\boldsymbol{R}_i)$.

If we now consider that every site $\boldsymbol{R}_i \neq 0$ of the lattice can be occupied with equal probability by the Tb^{+++}, we obtain a probability $n(h)$ for having a resonance shift by h. The mean shift will be:

$$p_1 = \int\limits_{-\infty}^{+\infty} h\, n(h)\, dh = \frac{1}{N} \sum_{\boldsymbol{R}_i \neq 0} h\,(\boldsymbol{R}_i)$$

where N is the number of lattice sites.

The kth moment p_k of this distribution is given by:

$$p_k = \int\limits_{-\infty}^{+\infty} h^k n(h)\, dh = \frac{1}{N} \sum_{\boldsymbol{R}_i \neq 0} h^k(\boldsymbol{R}_i)$$

If two Tb ions are present, the probability is

$$n^{(2)}\,(h) = \int\limits_{-\infty}^{+\infty} n(h - h')\, n(h')\, dh'$$

If the Fourier transform of $n(h)$ is $\overline{n}(l)$, then $\overline{n}^{(2)}(l) = [\overline{n}(l)]^2$ and for M Tb ions, $\overline{n}^{(M)}(l) = [\overline{n}(l)]^M$. The kth moment in presence of M ions is given by:

$$P_k = \int\limits_{-\infty}^{+\infty} h^k n(h)^{(M)}\, dh = \left\{ \frac{\partial^k}{\partial l^k}\, [\overline{n}(l)]^M \right\}_{l=0}$$

For instance we have now the mean shift in the case of M ions:

$$P_1 = \left\{ M\,[\overline{n}(l)]^{M-1}\, \frac{\partial \overline{n}(l)}{\partial l} \right\}_{l=0}$$

Or, with $n(0) = 1$ [$n(h)$ normalized] and $\{\partial \overline{n}(l)/\partial l\}_{l=0} = p_1$

$$P_1 = M p_1 = \frac{M}{N} \sum_{\boldsymbol{R}_i \neq 0} h(\boldsymbol{R}_i) = c \sum_{\boldsymbol{R}_i \neq 0} h(\boldsymbol{R}_i)$$

P_1 gives the line shift, it is proportional to the ionic concentration c.

The mean square deviation or second moment with respect to the center of the shifted line is:

$$B = \int\limits_{-\infty}^{+\infty} (h - P_1)^2\, n^{(M)}\,(h)\, dh = P_2 - 2\,P_1^2 + P_1^2.$$

But

$$P_2 = \left\{ \frac{\partial^2}{\partial l^2}\, [\overline{n}(l)]^M \right\}_{l=0} = M \left\{ \frac{\partial}{\partial l} \left\{ ([\overline{n}(l)]^{M-1}\, \frac{\partial \overline{n}(l)}{\partial l} \right\} \right\}_{l=0}$$

$$P_2 = M\,(M-1) \left\{ [\overline{n}(l)]^{M-2} \left[\frac{\partial \overline{n}(l)}{\partial l} \right]^2 \right\}_{l=0} + M \left\{ [\overline{n}(l)]^{M-1}\, \frac{\partial^2 \overline{n}(l)}{\partial l^2} \right\}_{l=0}$$

$$P_2 = M^2\, p_1^2 - M\, p_1^2 + M\, p_2 \quad \text{and} \quad \text{with} \quad P_1 = M\, p_1$$

$$B = P_2 - P_1^2 = M\,(p_2 - p_1^2) = c \left[\sum_{\boldsymbol{R}_i \neq 0} h^2(\boldsymbol{R}_i) - \frac{1}{N} \left(\sum_{\boldsymbol{R}_i \neq 0} h(\boldsymbol{R}_i) \right)^2 \right].$$

$$B = \frac{c}{N} \sum_{\boldsymbol{R}_i = 0} \sum_{\boldsymbol{R}_j = 0} [h(\boldsymbol{R}_i) - h(\boldsymbol{R}_j)]^2\, .$$

If $h(\boldsymbol{R}_j)$ has the simple form $h(\boldsymbol{R}_j) = \text{constant for } |\,\boldsymbol{R}_j\,| \leqslant R_0$, $h(\boldsymbol{R}_j) = 0$ otherwise, we find that the ratio $z = p_1^2/B$ is given by the number z of Tb^{+++} within the radius R_0 around each Mn^{++} ($\sqrt{z} \simeq$ ratio of frequency shift to linewidth). The range R_0 of an arbitrary field $h(\boldsymbol{R}_i)$ may be defined by calculating z for this field and a given c, and finding R_0 which gives the same z for the same c and the above simple function.

The values B and z are rather easily determined by EPR experiments. The evaluation of these experiments is relatively easy if $\chi_z^e(\boldsymbol{R})$ is greatly enhanced by inter-electronic exchange and therefore of long range since at reasonable distances we may expect $h(R)$ to vary like $\chi_z^e(\boldsymbol{R})$, and to be given by:

$$h(\boldsymbol{R}_j) = \frac{J_1 J_2}{2\,n_0\,g_e\,\beta} \langle S_z \rangle\, \chi_z^e\,(\boldsymbol{R}_j) \qquad \text{Ref. [6]}$$

Here, J_1 and J_2 are the exchange coupling constants of the two ionic species.

In case of a non S-state ion, we have $\langle S_z \rangle = (g_L - 1)\, \langle J_z \rangle$, where g_L is the ionic Landé factor and $\langle J_z \rangle$ the mean z component of the total ionic angular momentum.

As z becomes quite large in the case of long range, we can measure P_1 and therefore J_2 if we know J_1 and $\chi_z^e(\boldsymbol{R}_j)$. This makes possible the determination of the exchange parameter for magnetic impurities, which EPR cannot determine directly.

The method of indirect g shifts was used for instance to determine the J_2 constants for the rare earth ions in Pd by observing P_1 induced on the resonance of either Gd^{+++} [5] or Mn^{++} [13]. These latter ions are in an S-state and have reasonable relaxation times even above the magnetic ordering temperatures. The rare earth ions which orbital moments could not be observed directly because of short relaxation times and anisotropy of paramagnetic spectrum. It is however possible that work at high dilution in monocrystalline hosts should bring to light the EPR spectra of rare earths in non S-states.

In normal metals, where $\chi_z^e(\boldsymbol{R}_j)$ is of short range and oscillatory, we observe broadenings which are so large that the shifts can hardly be identified. This is to be expected if one assumes that at short range $h(\boldsymbol{R}_j)$ is also proportional to $\chi_z^e(\boldsymbol{R}_j)$. This assumption is however not well founded as will be discussed in the next section.

The fact remains that the exchange interaction can be estimated from the broadening of EPR due to magnetic ions of a second kind, however the analysis of such results is more delicate than in the case of long range polarization and will not give the sign of the exchange interaction of the ions of second kind.

6. *Nature of exchange interaction*

So far we have assumed that the ionic spin $\boldsymbol{S}_n$ on lattice site $\boldsymbol{R}_n$ is coupled to the electron of spin $\boldsymbol{\sigma}(x)$ at site x *by* a model interaction $(1/n_0)\, J\, \boldsymbol{S}_n \cdot \boldsymbol{\sigma}(x)\, \delta(x - \boldsymbol{R}_n)$. Such a model interaction has been fruitful for obtaining insight into the behaviour of magnetic ions in metallic solutions but it represents a rather inadmissible simplification of the microscopic problem. The correct treatment of the ion-electron exchange interaction and its different physical main features is a topic of interest to current solid state theory: in what follows we indicate certain results obtained by simple perturbation theory. At reasonably high temperature, such an approach may be justified. The interaction leading to the polarization effects to be considered here is the Coulomb repulsion between the electrons in the metallic band and on the magnetic ions.

We distinguish between matrix elements containing two itinerant and two localized functions to be called "Heisenberg exchange" and between contributions due to matrix elements containing only one itinerant wave function, to be called "Interband exchange".

a) Heisenberg exchange

The contribution is of the form

$$\mathcal{H}_{ex}^{H} = -\frac{1}{n_0} \sum_{k,q,n} e^{iq \cdot R_n} J_k^H(q) \cdot \sigma_k(-q) \cdot S_n$$

with

$$\sigma_k(-q) \cdot S_n = \sigma_k^z(-q) S_n^z + \sigma_k^+(-q) S_n^- + \sigma_k^-(-q) S_n^+$$

$$\sigma_k^z = a_{k+}^x a_{(k-q)+} - a_{k-}^x a_{(k-q)-}$$

$$\sigma_k^+ = a_{k+}^x a_{(k-q)-}$$

$$\sigma_k^- = a_{(k-q)-}^x a_{k+}$$

where we have used the well known second quantization operator:

$$J_k^H(q) = n_0 \iint dx_1\, dx_2\, \psi_{fn}^*(x_1)\, \psi_k^*(x_2)\, \frac{1}{|x_1 - x_2|}\, \psi_{fn}(x_2)\, \psi_{k-q}(x_1)\, e^{-iq \cdot R_n}$$

ψ_{fn} is the localized wave function of an electron bound to a magnetic ion n and ψ_k is the wave function of an itinerant electron.

$J_k^H(q)$ has the dimension and the order of magnitude of an atomic exchange energy, and is independent of R_n. From our previous discussion we see that the g shift in EPR in the absence of dynamical effects is given by the parameter $J = J_k^H(q = 0)$. The simple treatment of the Korringa effect and of the indirect g shift given previously was based on the assumption that $J_k(q)$ was equal to J for all k and q.

In their recent work WATSON and FREEMAN [14] have shown that this assumption is in general not justified. However in the case of the rare earths, at least the dependence on k can be neglected and it is permissible to consider the dependence only on the magnitude of the vector q. ($|q| = q$).

In that case $\mathcal{H}_{ex}$ can be written as

$$\mathcal{H}_{ex} = -\sum_n S_n \cdot \int \sigma(x)\, J^H(x - R_n)\, dx$$

where

$$J^H(x) = \frac{1}{n_0} \sum_q J^H(q)\, e^{iq \cdot x}$$

and

$$\sigma(x) = \frac{1}{\sqrt{n_0}} \sum_q e^{-iq \cdot x}\, \sigma(q).$$

If we neglect the q dependence of $J_k^H(q)$ we find back our simplified model Hamiltonian which leads to the spin spin coupling given by KASUYA [15] and the simple expression for $h(x)$ given in the previous section.

b) Interband exchange

If we had only the Heisenberg exchange we would find for the difference of the energies of a metal with one impurity spin $S_z = S$ and a particular conduction

electron spin $\sigma_z = -1/2$ and the same metal with the given electron in the state $\sigma_z = +1/2$

$$\Delta E^H = + S\, J_k^H\, (\boldsymbol{q} = 0)$$

ΔE^H describes however not the full energy difference.

Interband exchange makes a comparable or even greater contribution ΔE^I. We obtain, then, an effective exchange constant

$$J = \frac{\Delta E^H + \Delta E^I}{S} = J^H + J^I$$

Interband exchange is due to virtual ionization processes of the magnetic ions. The processes can be illustrated by means of an energy density diagram (Figure 4). The vertical axis gives the energy, the abscissa the density of the conduction electrons. E_f is the Fermi level and E_1 is a level below E_f which contains p bound electrons. In our example we give three bound f electrons corresponding to Nd in the $S = 3/2$ state. To the right are given the $+$ spin states, to the left the $-$ spin states. The virtual processes of interest are:

1) the ion absorbs an electron with spin $-$ ($\sim k_F \rightarrow f$)

2) the ion absorbs an electron with spin $+$ ($\sim k_F \rightarrow f$)

In both cases the energy needed is E_{abs}.

3) the ion emits an electron to the Fermi surface ($f \rightarrow \sim k_F$), the energy needed is E_{em}.

Strictly speaking E_{em} and E_{abs} depend on the quantum numbers L^*, S^*, J^* of the intermediate ionic states, but these effects are neglected here. All absorption processes are characterized by the same energy E_{abs} and the same matrix element V, all emission processes by the same energy E_{em} and the same matrix element U.

Each process of type 1) lowers the energy of the $-$ electron by V^2/E_{abs}. The energy contribution is by our convention to be counted negatively in ΔE^I. As there are seven orbital states with $-$ spin that can be reached by our electron, the total contribution of type 1) processes is $-7\, V^2/E_{abs}$. The processes of type 2) make the contribution $(7 - p)V^2/E_{abs}$.
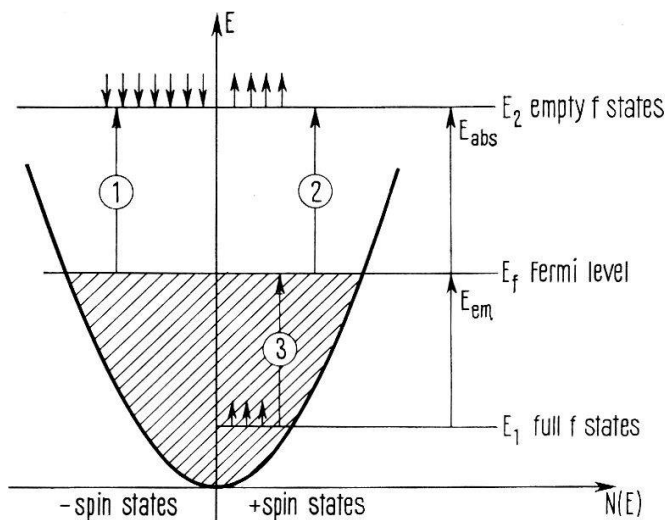

Figure 4

Interband exchange — Virtual ionization processes of the magnetic ion

The processes of type 3), which raise the energy of a + electron, make the contribution $p\ U^2/E_{em}$. Since $2\ S = p$ we find

$$J^I = -2\left(\frac{V^2}{E_{abs}} + \frac{U^2}{E_{em}}\right) = \frac{\Delta E^I}{S}.$$

There remains the question of the nature of the off diagonal elements U and V. These elements connect states which differ only by one electronic state. If we had calculated our one electron functions by an unrestricted Hartree-Fock procedure, these elements would be zero, and there would be no interband exchange. This exchange is therefore connected with the choice of the unperturbed wave functions. The reason why we cannot suppose to have started with correct H-F functions is, that in this case our starting configuration would already contain the conduction electron polarization which we would like to put in evidence.

To simplify this discussion let us consider a case where the ground state (magnetic ion + unpolarized conduction electrons) is given by a single determinantal function ψ_0 (streched case). Hence we are looking for the matrix element between ψ_0 and $a^*_{k,\sigma} a_{4f,m,\sigma}\ \psi_0$ in second quantized notation.

In the case of virtual emission, the coulomb interaction between the ionic 4 f electrons $\psi_{4f,m,\sigma}(x_1)$ and the itinerant electrons $\psi_{k,\sigma}(x_2)$ give rise to a matrix element

$$\langle a^*_{k,\sigma}\ a_{4f,m,\sigma}\ \psi_0 \mid a^*_{k,\sigma} \Big(\sum_{m'} a^*_{4f,m',\sigma'}\ a_{4f,m',\sigma'}\Big)\ I^0\ a_{4f,m,\sigma} \mid \psi_0\rangle$$

if we restrict ourselves to the part of the coulomb interaction which is spherical both in x_1 and x_2.

In the case of the rare earths, this turns out to be the principal contribution [16].

The coulomb integral I^0 connects then $\psi_{4f,m,\sigma}$ and the part in $\psi_{k,\sigma}$ which possesses f, m symmetry $\xi^k_{f,m}\ \langle f, m \mid k\rangle$. In calculating the average J^H on all directions of k, it is permissible to replace $\langle f, m \mid k\rangle$ by a factor N_k which depends only on $k = \mid k \mid$ and whose magnitude gives the amount of f character of the conduction electrons. The m', σ' are to be summed over the p occupied levels on the ion. Since we treat the emission case, the $4f, m, \sigma$ state is one of the occupied levels, and the matrix element becomes $(p-1)I^0$. If the 4 f, m, σ state would have been an unoccupied level, the element would have been $p\ I^0$.

It is easily seen that, if we calculate the average element for any set of p functions m', σ' we obtain $(p - p/14)\ I^0$, the average value for the matrix element. This average matrix element has already been dealt with when calculating the unperturbed wave functions in the absence of ionic magnetism. For our effective element U we retain only the difference between the actual element and the average element [16]:

$$U = \left[(p-1) - \left(p - \frac{p}{14}\right)\right]I^0 = \frac{p-14}{14}\ I^0.$$

By analogous reasoning, we obtain $V = p/14\ I^0$

$$J^I = -\frac{I^{02}}{98}\left[\frac{p^2}{E_{abs}} + \frac{(14-p)^2}{E_{em}}\right].$$

From this we expect a parabolic behaviour of J in function of p. Such a behaviour is seen in the plot of this for rare earths in palladium, determined by indirect g-shift [6], and rare earths in (R.E.)Al$_2$ [17],, determined by indirect Knight shifts.

The fact that the parabolia rises more steeply for small p indicates that $E_{em} < E_{abs}$ in the beginning of the R.E. series (e.g. Ce^{+++} easily gives up its f electron).

Note added in Proof. The quantity $(p - p/14)\, I^0$ subtracted from the matrix elements between f orbitals and conduction electron states represents the matrix element of an average potential of the unpolarised ion which is supposed to have been diagonalised out in the starting set of unpolarised conduction electron wave functions. A simpler average potential would be the coulomb potential from $(p - 1/2)\, f$ orbitals (neglecting exchange). This potential would lead to minimum off diagonal matrix elements $V = U = I^0/2$ and represents hence the potential which leads to optimum unpolarised wave functions. With it, we would get $J^I = (I^0)^2(1/2\, E_{abs} + 1/2\, E_{em})$.

It is an interesting question to what extent we are allowed to substract the average matrix element. In the case where the magnetic ion presents the same average potential as all the other lattice sites to the conduction electrons, it seems to be particularly justified. If the average potential deviates, it should give rise to interference terms in the scattering amplitude which can be observed by anomalies in the thermopower [18]. The average potential gives also rise to shielding effects which may enhance, diminish or even suppress the exchange couplings.

7. *Dependence of different physical properties on exchange parameter*

A certain number of experimental properties depend on ion-electron exchange. In particular, the effective magnetic moment of magnetic ions in dilute metallic solution should be enhanced by exchange polarization. From ref. [6] we have

$$\langle \sigma \rangle = \frac{1}{2}\left(g_e\, \beta\, H_z + \frac{1}{n_0}\, J\, \langle S \rangle \right) N(E_f)$$

the magnetic moment due to the exchange part is

$$p' = g_e\, \beta\, \langle \sigma \rangle = \frac{1}{2}\, g_e\, \beta\, \frac{1}{n_0}\, J\, \langle S \rangle\, N(E_f) \qquad p' = \frac{J\, \chi_z}{n_0\, g_e\, \beta}\, \langle S \rangle$$

since

$$\chi_z = \frac{1}{2}\, g_e^2\, \beta^2\, N(E_f).$$

The total magnetic moment is given by

$$p = p_0 + p' = g_s\, \beta\, \langle S \rangle + \frac{J\, \chi_z}{n_0\, g_e\, \beta}\, \langle S \rangle$$

$$p = p_0\left(1 + \frac{J\, \chi_z}{n_0\, g_s\, g_e\, \beta^2} \right) = p_0\left(1 + \frac{\Delta g_s}{g_s} \right)$$

furthermore

$$p(T) = p_0\left(1 + \frac{\Delta g_s(T)}{g_s} \right).$$

For Gd and Mn in Pd such a relation is approximately fulfilled. The direct or indirect g shifts should also permit to predict the conduction electron polarization measured by neutron diffraction.

In the case of Fe in Pd, there is no simple correlation between indirect g shifts and polarization indicated by neutron diffraction. The experiments mentioned so far concern the average conduction electron polarization and should stand in simple correlation with the direct EPR g shift.

Other properties, such as the magnetic order in dilute alloys, the lowering of the superconducting transition temperature by magnetic ions and the low temperature anomalies in resistance and thermopower, depend on the parameter $J_k(q)$ for all values of k and q and it is hardly permitted to compare numerically these quantities with $J_{k_F}(q = 0)$ obtained from EPR shifts. In the case of the rare earths, the couplings measured are of smaller magnitude than the couplings deduced from the measurements of Curie temperature T_c by means of the model of constant (q-independent) J. As WATSON and FREEMAN [14] show, the true polarization is probably more distributed than the one given by constant J, so that the values for J deduced from T_c are probably overestimated.

In the case of Mn in Cu, J from EPR is positive while the presence of a resistance minimum would indicate a negative J [19]. Here again, Watson's work shows that a sign change between $q = 0$ and $q = 2\ k_F$ is quite possible, which could explain the seeming discrepancy between the $J_{k_F}(q = 0)$ derived from EPR and the value of J from Kondo's analysis, which is more closely related to $J_{k_F}(q = 2\ k_F)$.

The indirect EPR measurements give insight into the spatial distribution of the polarization. They should be more closely related to the study of magnetic order. Neutron diffraction gives in favorable cases (e.g. Fe in Pd) direct information on polarization distribution. Another good tool is the study of NMR, but it has been sucessfully applied only in the case of a series of ordered intermetallic compounds such as (R.E.) Al$_2$ [17]. The spatial electronic charge density around gold in Pt has been studied by this technique [20]. Analogous studies where the polarization density is measured on different shells of neighbours, should be extremely helpful.

In metals with a complex band structure, we must be careful in comparing transport properties, as different bands may be responsible for different properties (e.g. in Pd, the s band for transport and the highly exchange coupled d band for magnetism). The present analysis needs to be extended to include the actual structure of the different conduction bands, which often does not justify the free electron approximation, as well as interelectronic exchange (see B.4), shielding effects mentioned above and the effect of crystalline fields on ions in metallic solution. These latter effects will become better understood once the anisotropic spectra of non S-state ions in solution in single crystals have been observed.

In conclusion, we repeat that the direct g shift determines a relatively simple quantity, $J_{|k|}(q = 0)$, which should be comparable to the magnetic moment and neutron diffraction measurements, after dynamic effects are properly taken into account. The indirect shifts as well as relaxation studies depend on more complicated averages of $J_k(q)$, just as do several other properties depending on ion-electron exchange, and in many cases, a more detailed study of particular cases will be necessary. This is particularly the case for transition metal ions, for which a constant J model is even less justified than for rare earths.

C. EPR measurements

1. Experimental technique

The apparatus for EPR studies on ions in metals can be relatively simple. The signal is due to the susceptibility of the magnetic impurities contained within a skin

depth. Real and imaginary part of this signal are mixed due to the metallic conductivity. If polycrystalline material is to be studied, its surface can be increased by using powdered samples until the resistive power loss becomes large. In such a case the use of a sample cavity is not justified, a straight through system can be used [21]. Real and imaginary parts will be further mixed because of standing waves in the waveguide containing the sample. A decomposition of the observed line into parts of even and odd symmetries helps to locate the line center, particularly if the line is not too wide compared with the field for resonance. As the line width is usually rather frequency independent it is advantageous to work at as high frequencies and fields as possible. The gain in precision will be important, even though the gain in signal strength is less important because of decrasing skin depth. For the study of single crystals with dilute impurities a high sensitivity spectrometer with suitable cavity will be advantageous.

The g factors measured have to be connected for demagnetizing effects. These effects are not simply related to the well known demagnetizing factors since the RF field acts only within the skin depth. Experimentally, this problem was studied by RODBELL [22]. Corrections for demagnetizing effects can be made by varying the magnetization with temperature and extrapolate to zero magnetization. In very dilute samples, demagnetization shifts, which are of the order of $2\pi M$, are negligible.

2. Results from direct g shift measurements

A considerable amount of data on EPR of magnetic ions is now available, as can be seen in Table 1. Most of this work is concerned with the S-state ions Mn^{++}, Eu^{++} and Gd^{+++}. Er^{+++} is the only example of an non S-state ion observed in dilute solution. Careful additional work will be helpful to decide whether these observations correspond truly to Er in metallic solution and whether no formation of an insulating Er compound takes place on the sample surface.

We have grouped the results into solutions in simple metals, and in metallic alloys and compounds. Finally some results of resonance of magnetic ions in magnetically ordered samples are cited since they give valuable insight in the magnetic behaviour of non S ions.

Results are most abundant for the Gd^{+++} ion. In Gd metal, the g value is 1.94 for paramagnetic resonance and 2.00 for ferromagnetic resonance, as seen from the careful work of Rodbell.

A consistent explanation of these data does not appear to be possible in terms if the constant J model. Harris, Poplewell and Tebble have made measurements of various solutions of Gd in Lu and Y and have found that the anomalously low g of Gd disappears with increasing dilution. We expect the constant J model to apply mostly in dilute magnetic alloys.

The measurements of Gd in Pd predict a negative conduction electron polarization. In these alloys, GRANGLE [23] finds a saturation magnetization less than 7 Bohr magnetons expected from $p_{sat} = gJ\beta$ with $g = 2.00$. Reasonably large g shifts are found mostly in metals with large, presumably exchange enhanced, susceptibilities. A remarkable case is the (R.E.) Ru_2 cited in Table 1. They are all superconducting and the electrons responsible for superconductivity should therefore not be exchange enhanced [24]. It is possible that in these cases the g shifts are due to the d electrons

Table I

Direct g-shifts

Host	g-value	T[°K]	a) ΔH [gauss]	b) χ host $\left[\dfrac{\text{emu}}{\text{cm}^3}\right]$	J [eV]	Ref.
				$\times 10^{-5}$		
Gd³⁺ ion (in insulating crystal $g \simeq 1.992$)						
Simple metal:						
$Ag_{97}Gd_3$	1.995 ± 0.007	20°		0.3*	–	ref. [5]
Gd metal	1.94 ± 0.02	301°		–	–	ref. [20]
$La_{87}Gd_{13}$	1.995 ± 0.010			0.9* (77°)	–	c)
$Lu_{92}Gd_8$	2.010 ± 0.010			0.1 (77°)	+ 0.07	c)
$Pd_{97}Gd_3$	1.887 ± 0.007	20°	750	9*	– 0.009	ref. [5]
$Rh_{97}Gd_3$	1.989 ± 0.010	47°	760	1*	–	ref. [5]
$Sc_{90}Gd_{10}$	1.995 ± 0.010	·		1.5* (77°)	–	c)
$Y_{96}Gd_4$	1.998 ± 0.010			0.7* (77°)	–	c)
Alloy:						
$Ag_{67}Cd_{30}Gd_3$	2.010 ± 0.007	20°			–	ref. [5]
$Pd_{49}Ag_{49}Gd_2$	1.995 ± 0.010	20°		0	–	ref. [5]
$Pd_{48}Ag_{48}Tb_2Gd_2$	1.995 ± 0.010	20°		–	–	ref. [5]
$Pd_{97}Gd_3$ with						
H/Pd = 0.6	2.00 ± 0.01			0	–	d)
Intermetallic compound						
$GdAl_2$	1.982 ± 0.003	260°	500	0.3 (est.)	– 0.03	ref. [16] ref. [5]
$LaAl_2$ +1 to 5% Gd	1.99			0.2 (300°)	–	e)
$LaIr_2$ +1 to 5% Gd	1.97			0.02 (300°)	–	e)
$LaPt_2$ +1 to 5% Gd	2.00			diamagnetic	–	e)
$LaRh_2$ +1 to 5% Gd	1.98			0.2 (300°)	–	e)
$CeRu_2$ +1 to 5% Gd	1.96			–	–	e)
$LaRu_2$ +1% Gd	1.85 ± 0.01	20°	1200	1.3	– 0.05	f)
$ThRu_2$ +1% Gd	1.96 ± 0.01	20°		–	– 0.05	f)
$ScRu_2$ +1 to 5% Gd	1.94			1.1 (300°)	– 0.03	c)
YRu_2 +1 to 5% Gd	1.93			1.3 (300°)	– 0.03	e)
$ZrRu_2$ +1 to 5% Gd	1.97				– 0.01	e)
UPd_3 +2% Gd	2.11 ± 0.01	4°	2000	48	+ 0.002	ref. [6]
UPd_3 +2% Gd	2.07 ± 0.01	40°	700	28	+ 0.002	ref. [6]
$GdCu_5$	2.009 ± 0.007	68°	875	–	–	ref. [6]
YCu_5 +5% Gd	2.000 ± 0.007	20°	350	–	–	ref. [6]
$ThIr_5$ +5% Gd	1.973 ± 0.007	20°	640	–	–	ref. [6]
$GdNi_5$	1.942 ± 0.007	78°	905	–	–	ref. [6]
$LaNi_5$ +5% Gd	1.877 ± 0.007	20°	550	–	–	ref. [6]
UNi_5 +5% Gd	1.953 ± 0.007	20°	470	–	–	ref. [6]
$ThNi_5$ +5% Gd	1.913 ± 0.007	20°	525	–	–	ref. [6]
YNi_5 +5% Gd	1.900 ± 0.007	20°	525	–	–	ref. [6]
$LaPt_5$ +5% Gd	2.022 ± 0.010	20°	860	–	–	ref. [6]
Mn²⁺ ion (in insulating crystal $g \simeq 2.00$)						
$Ag_{98}Mn_2$	2.010 ± 0.005	20°	120	0.3	–	ref. [13]
$Au_{98}Mn_2$	2.005 ± 0.005	20°	725	0.5*	–	ref. [13]
$Cu_{98.6}Mn_{1.4}$	2.01 ± 0.01	77°	310	0.3*	–	ref. [2]
$Mg_{99.3}Mn_{0.7}$	2.02 ± 0.01	4°	230	0.3*	+ 0.03	ref. [2]
$Pd_{98}Mn_2$	2.09 ± 0.01	20°	1500	9*	+ 0.007	ref. [13]

Table I (continuation)

Host	g-value	$T[^\circ K]$	a) ΔH [gauss]	b) χ host $\left[\dfrac{\text{emu}}{\text{cm}^3}\right]$	J [eV]	Ref.
				$\times 10^{-5}$		
		Eu^{2+} ion (in insulating crystal $g \cong 1.99$)				
Eu metal	1.985 ± 0.015	120° to 300°	1300	–	–	g)
EuAl$_2$	1.994 ± 0.003			–	–	ref. [16]
		Er^{3+} ion (in insulating crystal $g \cong 6.78$)				
Ag$_{97.7}$Er$_{0.3}$	6.73 ± 0.10	2.5°	70	0.3*	–	h)
		Ferromagnetic resonance				
Co metal	2.20 ± 0.03	RT		–	–	i)
Fe metal	2.094 ± 0.003	RT		–	–	j)
Gd single crystal	2.00 ± 0.02	<273°	200 min.	–	–	ref. [20]
Ni single crystal	2.22 ± 0.03	130° to 630°	50 min	–	–	k)
Pd$_{99}$Fe$_1$	~2.2	4°	700	–	–	ref. [6] m)
Pd$_{99}$Fe$_1$ with H/Pd = 0.7	~2.2	4°	700	–	–	m)
		Rare earth metal (Eu and Gd excepted)				
Ce metal	–	–	–	–	−0.06	n)
Dy, Er, Tb	–	–	–	–	–	p)

*) corrected value, see not b)

a) ΔH is the half-power half-width

b) χ_{host} is the spin susceptibility of the host matrix. In order to obtain this value the diamagnetic and orbital contributions were substracted from the total susceptibility in certain cases (noted by a*)) when these contributions could be estimated. One must be cautious with the non-corrected values, particularly if they are small.

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while the superconductivity is due to the s band. The fact that at T_c the g factors and the NMR Knight shifts do not change is consistent with this hypothesis. It appears that nearly full d bands lead to negative shifts for the Gd^{+++} ion g value. The same ion has a large positive g shift in UPd$_3$ where the magnetic ions presumably belong to a $5f$ band. A positive g shift is also observed for Mn in Pd, where the g shift of Gd is negative. Mn shows also slight positive shifts in the noble metal, as well in

Mg. The alloy $Ag_{48}Pd_{48}Tb_2Gd_2$ was measured in order to show that the absence of a g shift in this alloy is not due to the equality of g factors (ref. [5], p. 1400). The study of the EPR of Gd in hydrogenated Pd confirmed the presence of two phases. With the possible exception of Er in Ag, no ion with orbital angular momentum has been observed in EPR in metallic solution. On the other hand, several measurements of magnetic ions in magnetic ordered states have been carried out. Some of them are indicated at the end of Table I.

3. *Results from indirect g shift measurements*

Table II contains first of all the indirect g shifts produced by small rare earth concentration on the EPR of Gd in Pd. It was verified that these indirect shifts are proportional to the susceptibility of the additional impurities, by varying this sus-

Table II
Indirect g-shifts

Impurity concentration	g	Temp. [°K]	ΔH [gauss]	J_{ER} [eV]	Ref.
	g-value of 2% Gd in Pd with rare earth ions impurities				
2% Ce	1.887 ± 0.007	20°	650		ref. [6]
2% Pr	1.843 ± 0.007	20°	620	-0.33	ref. [6]
2% Nd	1.860 ± 0.007	20°	840	-0.14	ref. [6]
2% Pm	1.899 ± 0.007	20°	900		ref. [6]
2% Sm	1.899 ± 0.007	20°	610		ref. [6]
2% Eu		20°	610		ref. [6]
none [Gd only]	[1.887 ref.]		675	-0.009	ref. [6]
2% Tb	1.998 ± 0.007	20°	1230	-0.09	ref. [6]
2% Dy	1.908 ± 0.007	20°	840	-0.06	ref. [6]
2% Ho	1.974 ± 0.007	20°	850	-0.09	ref. [6]
2% Er	1.913 ± 0.007	20°	790	-0.06	ref. [6]
2% Tm	1.956 ± 0.007	20°	735	-0.21	ref. [6]
2% Yb					ref. [6]
2% Ln	1.887 ± 0.007	20°	520		ref. [6]
	g-value of 2% Mn in Pd with rare-earth ions impurities				
none	2.105	4°	680		ref. [13]
1% Pr	2.195	4°	1300	-0.11	ref. [13]
0.2% Ho	2.055	4°	1200	-0.07	ref. [13]
0.5% Tb	–	4°	2500		ref.[13]
	g-value of 3% Gd in Pd with iron-group ions impurities				
none	1.888 ± 0.007	20°	650		ref. [6]
0.2% Ni	1.862 ± 0.007	20°	840		ref. [6]
1% Ni	1.860 ± 0.010	20°	1160		ref. [6]
1.5% Ni	1.830 ± 0.010	20°	1400		ref. [6]
0.1% Fe	1.890 ± 0.010	20°	1000		ref. [6]
0.2% Fe	1.906 ± 0.007	20°	950		ref. [6]
0.3% Fe	2.000 ± 0.010	20°	2800		ref. [6]
0.1% Co	1.847 ± 0.007	20°	600		ref. [6]
0.2% Co	1.890 ± 0.010	20°	810		ref. [6]
0,3% Co		20°	2000		ref. [6]

ceptibility both by changing temperature and concentration. The proportionality thus verified gives some confidence in the interpretation of the indirect g shifts by means of the constant J model in the case of the rare earths. In Table II and in Fig. 5 we see that the J values are all negative, that they show a behaviour not incomparable with the considerations of section B.6.b. As Kasuya (private communication) has pointed out, the deviation to the right of Gd from a simple parabolic behaviour could be due to crystalline field splittings of different nature for ions with even or odd numbers of f electrons (Kramers degeneracy).

Also given are in Figure 5 the results of the determination by NMR in (R.E.)Al$_2$ [17]. For the Gd Al$_2$ we give a corrected J value determined in a more recent paper [25].
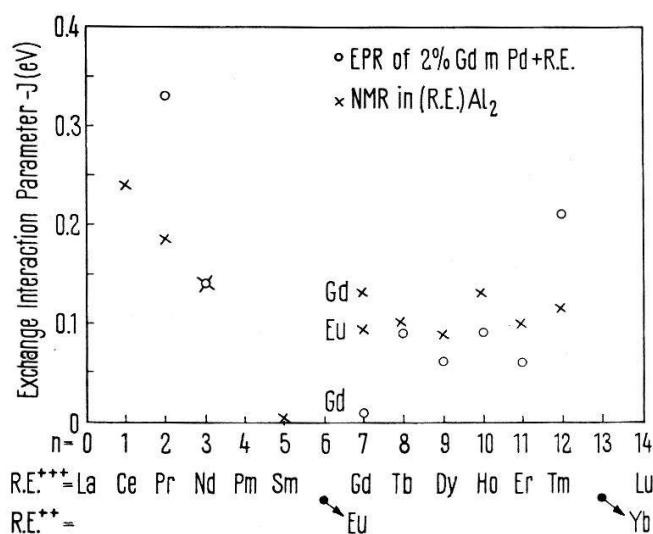

Figure 5

Effective exchange in rare earths

Experimental J values plotted as a function of number n of f electrons.

The data on the J for R.E. using Mn^{++} as a probe are in agreement with those using Gd$_{+++}$ as a probe. This indicates that a constant J model is not unreasonable also for interpreting the EPR results for Mn in Pd. Indirect g shifts were also in YNi$_4$ [6], indicated large exchange enhancement also in this alloy.

In GdAl$_2$, the broadening due to the other rare earths was observed, and values of J_2 were derived from the broadenings observed. However this analysis, based on the constant J hypothesis, will probably have to be modified, and exchange effects will have to be duly taken in account.

Indirect g shifts due to Ni, Co, Fe in Pd are considerably more difficult to interpret. Ni in concentrations below 1.5% seems to increase the band susceptibility, as suggested by the temperature dependence of this susceptibility. Correspondingly the magnitude of the g shift of the Gd^{+++} resonance is increased. Co and Fe in Pd exhibit "giant moments" in their susceptibility (both effective paramagnetic moment and saturation ferromagnetic moment) corresponding to a polarization of the Pd atoms in a region several lattice sites wide around the magnetic ions, as seen from neutron diffraction [26] [27]. Hence we would expect to find large negative indirect g shifts of the EPR of Gd, whereas, in the case of Fe, these shifts are positive (indicating negative conduction electron polarization). However, recent work by CLOGSTON et al.

[28] and KIM [29], indicates that the idea of simple conduction electron polarization is not sufficient to explain the phenomena connected with giant moment. The possibility of the formation of independent magnetic moments, on the Pd sites close to the Fe sites is suggested.

Acknowledgments

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