Magnetization and electron spin resonance studies of GdRh2 - GdFe 2 alloys

A. Tari, C. Larica

▶ **To cite this version:**

Magnetization and electron spin resonance studies of GdRh$_2$-GdFe$_2$ alloys

A. Tari (*)

School of Physical and Molecular Sciences, University College of North Wales, Bangor, Gwynedd LL57 2UW, U.K.

and

C. Larica

The Blackett Laboratory, Physics Department, Imperial College of Science and Technology,
Prince Consort Road, London SW7 2BZ, U.K.

Résumé. — On a étudié les composés intermétalliques Gd(Rh$_{1-x}$Fe$_x$)$_2$ pour $x \leqslant 0,15$, au moyen de mesures d'aimantation et de RPE. Dans le composé sans fer on trouve une valeur 2,01 ± 0,007 pour le facteur g et on observe l'effet *bottleneck* pour le gadolinium. On montre que ces observations sont en accord avec le résultat obtenu par NMR avec le gadolinium dans le même composé. La substitution du fer par le rhodium ouvre le *bottleneck* et résulte en un changement du caractère des électrons de conduction. Les mesures magnétiques indiquent que le fer est non magnétique, à la limite diluée et que le gadolinium a un moment de $\sim 7~\mu_B$ dans le composé GdRh$_2$. La structure des composés change de C15 à C14 quand on arrive à 15 at % Fe.

Abstract. — Magnetization and ESR studies of the intermetallic compounds Gd(Rh$_{1-x}$Fe$_x$)$_2$, in the region $x \leqslant 0.15$, are reported. In the iron-free compound a resonance bottleneck is observed and a g-value of 2.01 ± 0.007 is measured for gadolinium. These are shown to be in accordance with the NMR study of the same compound. The substitution of iron for rhodium leads to the opening of the bottleneck and a change in the band character of the compound. The magnetization measurements reveal a moment of $\sim 7~\mu_B$ for gadolinium in GdRh$_2$ and the absence of moment on iron in dilute limit. The crystal structure of the series changes from cubic laves to hexagonal laves of MgZn$_2$ type on reaching 15 at % Fe substitution.

1. **Introduction.** — A recent investigation by spin echo NMR of ^{165}Ho in Ho$_{0.01}$Gd$_{0.99}$(Rh$_{1-x}$Fe$_x$)$_2$, for $x \leqslant 0.06$, revealed a number of interesting features [1]. In the iron-free compound the intraionic magnetic dipole parameter a_1 and hence the bare moment for holmium was found to be about 11 % less than the free ion value. This and the ~ 21 % reduction in the quadrupole parameter p were the largest observed for holmium in any system with comparable exchange strength, taken to be represented by the Curie temperature. The reductions in a_1 and p were attributed to the presence of a strong crystal field in this series. Particularly interesting was the persistent fall in the quadrupole parameter with increasing iron content which was ascribed to the change in the band structure due to iron substitution. It was concluded that in dilute limit iron is nonmagnetic in this series.

Reported here is a further study of the same alloys and two further samples containing 2 and 15 at % Fe, by means of Electron Spin Resonance (ESR) and magnetic measurements. The ESR provides, among others, information about the band structure through the sign and form of coupling between conduction electrons and 4f-moments and about the onset of magnetic ordering. The sign and magnitude of coupling constant is obtained, in the Korringa regime, from the g-shift, Δg of the resonating probe ion (here gadolinium) and the onset of magnetic ordering is reflected in the minimum of the temperature variation of the line width ΔH. The g-shift and the excess or deficiency in the saturation moment over the free ion value is related to the $q = 0$ component of the exchange integral $J(q = 0)$ of the local moment and conduction electrons wave functions. The exchange coupling between a rare earth spin **S** and conduction electrons **s**.

$$H = - J(0)\, \mathbf{S}.\mathbf{s} \qquad (1)$$

results in an indirect interaction between rare earth moments. This is usually assumed to be of Ruder-

(*) Now at the University of Petroleum and Minerals, Dhahran, Saudi Arabia.

mann-Kittel-Kasuya-Yosida (RKKY) type. When treated in the molecular field approximation this interaction leads to

$$\theta \approx \frac{\Gamma}{3 \, k_{\mathrm{B}}} (g_i - 1)^2 \, J(J + 1) \qquad (2)$$

for the paramagnetic Curie temperature which, in this model, is equal to the ferromagnetic Curie temperature T_c. In (2) Γ is the constant of couplings between rare earth spins, g_i is the ionic g-value and J is the total angular momentum. The expression relating g-shift Δg, to the diagonal part of the exchange integral $J(q = 0)$ is :

$$\Delta g = g - g_i = \frac{J(q = 0) \chi_e}{g_e \, \mu_{\mathrm{B}}^2} \qquad (3)$$

where χ_e and g_e are the susceptibility and g-value respectively of the conduction electrons. Although the exchange integral $J(q = 0)$ is positive in sign and therefore should lead to a positive g-shift, one frequently observes a negative g-shift ; particularly in the alloys with conduction electrons of d-character. In the situation that the conduction electrons cannot discharge to the lattice the energy they receive from the relaxing probe ion, the so-called resonance bottle-necking occurs. In such a case the measured g-value is, in the limit of strong exchange coupling, a susceptibility weighed mean of g_e and g_i [2, 3]. Although the ESR bottleneck is thought to be rare in the alloys and compounds involving transition metals, recently both in alloys [3] and compounds [4] a resonance bottleneck has been reported. The series $Gd(Rh_{1-x}Fe_x)_2$ reported here is a further example of the ESR bottlenecking in rare earth transition metal compounds.

2. Samples and experimental techniques. —

Seven samples containing c = 0, 0.4, 1, 2, 3, 6 and 15 at % Fe have been investigated. The samples, other than the two containing 2 and 15 at % Fe, contain 1 at % Ho and were those previously studied by NMR. The details of their preparation is given by Tari [1]. The 2 and 15 at % Fe samples do not contain holmium. All the compounds are cubic Laves (C15 structure) except the iron rich compound which is hexagonal Laves phase of $MgZn_2$ type (C14 structure).

The ESR measurements were made on powder samples, with an X band spectrometer in the temperature range 77-300 K, and magnetic measurements with a vibrating sample magnetometer in the temperature interval 4.2-300 K. The temperature sensors were Au + 0.3 % Fe against chrommel thermocouples.

Saturation magnetizations were obtained at 4.2 K from the plot of magnetisation I against the inverse of the applied field extrapolated to $H \to \infty$. The highest field attained was 9 kG. The ordering temperatures were obtained from $I^2 - (H/I)$ isotherms.

3. Results and discussion. —

The temperature dependence of the linewidth ΔH and g-values of the samples containing c = 0, 0.4, 2 and 6 at % Fe are shown in figures 1-4. In the paramagnetic region the g-values are temperature independent. The line-widths are linear in temperature and may conveniently be expressed as $\Delta H = r + bT$. The g-value of (2.01 ± 0.007) and slope of the line-width with temperature b, for the iron-free compound is in agreement with those previously reported by Taylor and Coles [5]. The agreement shows that the presence of 1 at % Ho does not affect the ESR parameters. The g-value of 2.01 $\pm$ 0.007 and that of Taylor and Coles (2.005 ± 0.010) are considerably higher than the value 1.967 reported by Davidov and Shaltiel [6]. These authors observed a temperature dependent g-value which is revealed neither in our measurements nor in that of Taylor and Coles [5]. In the next section we shall return to the discrepancy between the g-values measured for Gd in $GdRh_2$ in this laboratory and that by Davidov and Shaltiel.

The substitution of iron for rhodium leads to a reduction in the g-value and increase in the slope of linewidth $b = \mathrm{d}(\Delta H)/\mathrm{d}T$ as shown in figure 5 and figure 6 respectively. Also shown in these figures are the variation, with iron concentration, of the saturation moments μ_s per formula unit, the temperature of line-width minimae T_m and the ordering temperature
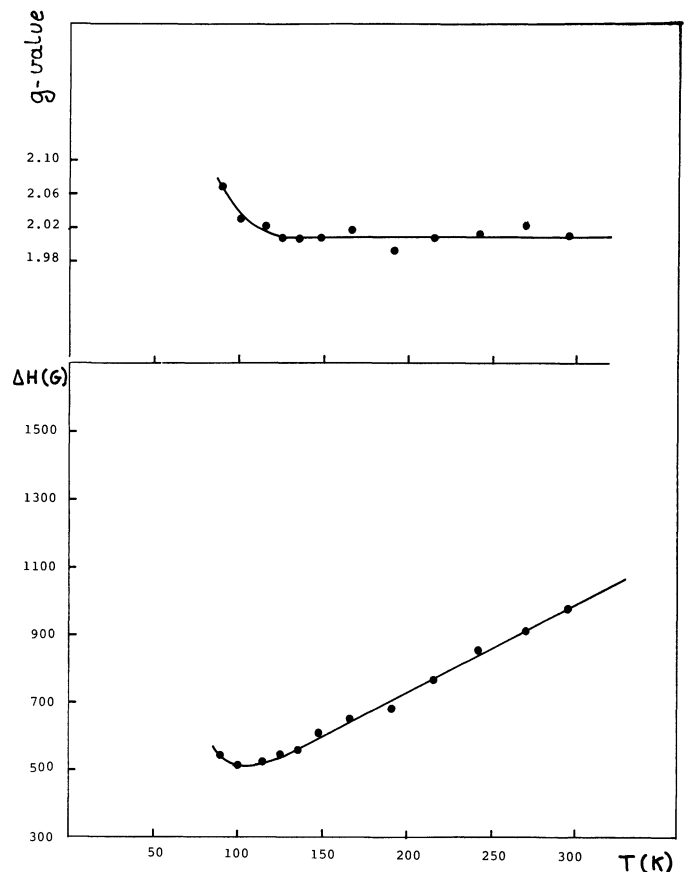

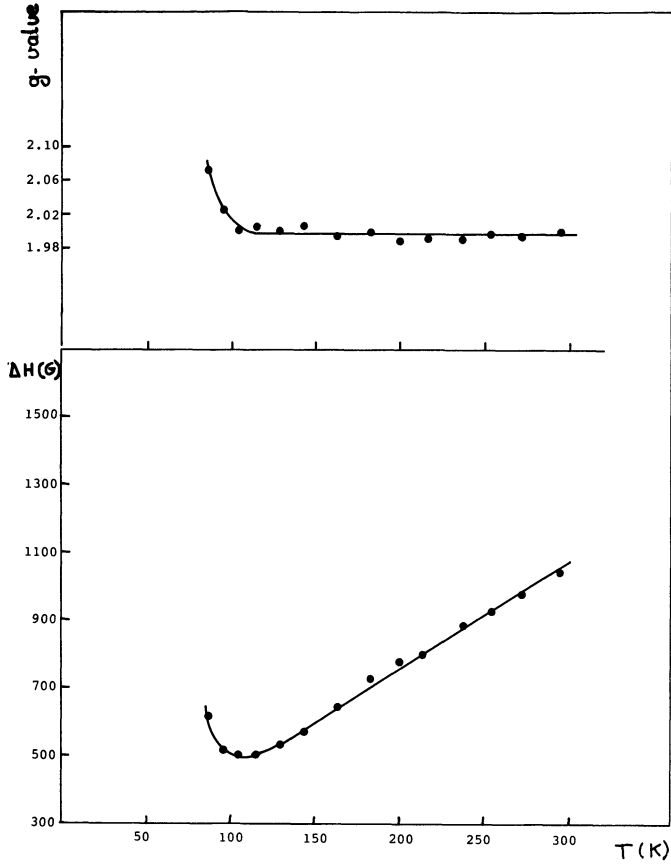Fig. 1. — Temperature dependence of g value and linewidth of $GdRh_2$.

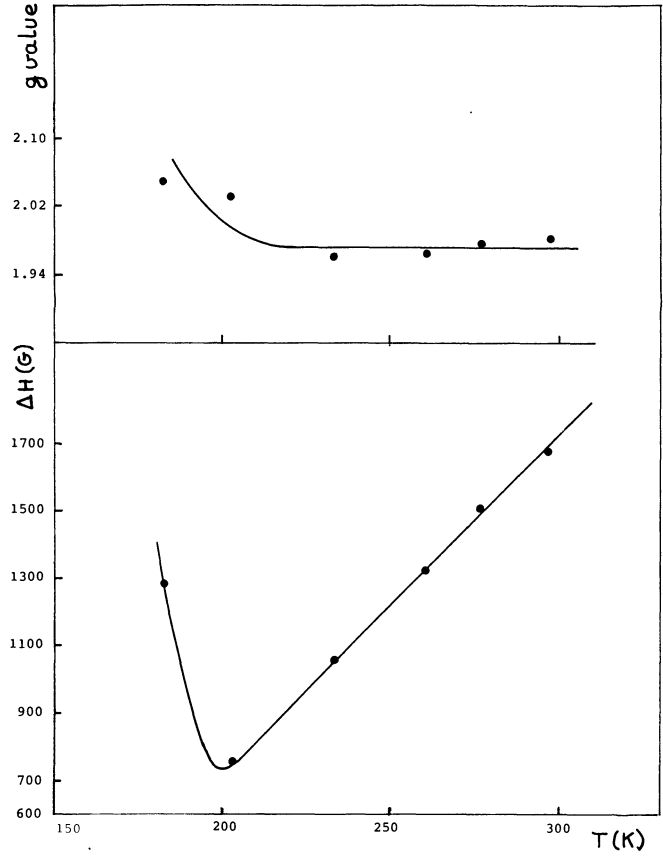Fig. 2. — Temperature dependence of g value and linewidth of $Gd(Rh_{0.996} Fe_{0.004})_2$.

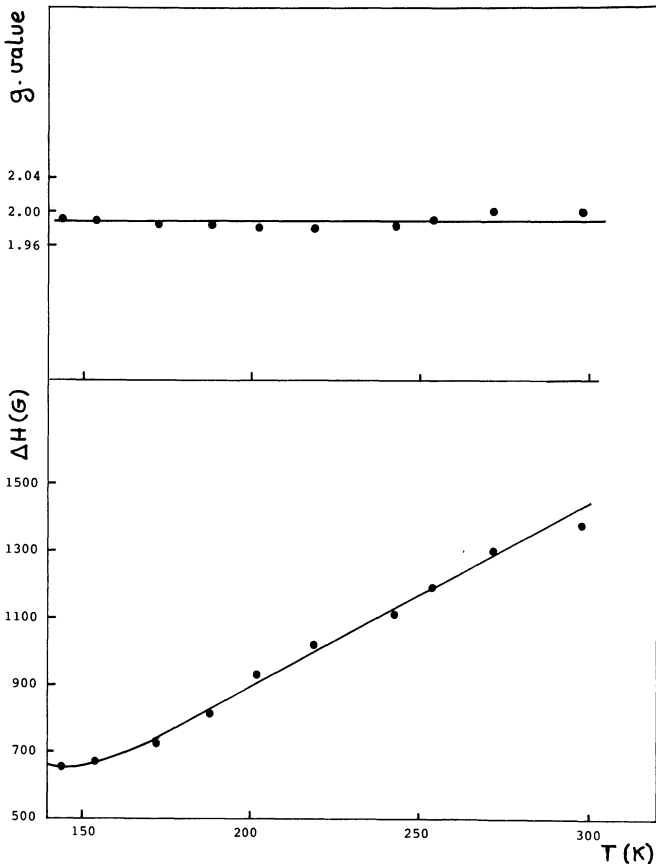Fig. 4. — Temperature dependence of g value and linewidth of $Gd(Rh_{0.94}Fe_{0.06})_2$.

Fig. 3. — Temperature dependence of g value and linewidth of $Gd(Rh_{0.98} Fe_{0.02})_2$.

T^* of the compounds. The similarity of behaviour of T_m, b and T^* is sufficiently evident from figure 6. The change of T_m, b and T^* with iron concentration is rapid around 3 at % Fe.

The increase of $b = d(\Delta H)/dT$ with iron concentration indicates that the gadolinium ESR in $GdRh_2$ is bottlenecked. The substitution of iron gradually opens the bottleneck and above 3 at % Fe the opening appears to be complete, figure 6.

The g-values, T_m, b and μ_s are listed in Table I. As this table shows the same moment is measured for both the end compound and that containing 1 at % Fe.

Using the lattice parameter and $\frac{4}{3} \pi M_s = 5.1$ kG given for $GdRh_2$ [8] a value of 6.96 μ_B is calculated for gadolinium which is in excellent agreement with the value we have measured. A similar value has also been reported by Hrubec and Steiner [9]. If, therefore, one takes the gadolinium moment to be 6.96 μ_B in $GdRh_2$ then the moment on iron in $Gd(Rh_{0.97}Fe_{0.03})_2$ is only $\sim 0.05 \mu_B$.

The temperature variation of the inverse susceptibility χ^{-1} of the alloys containing $c = 0, 1$ and 15 at % Fe are shown in figure 7. The behaviour of the two dilute alloys are similar except when approaching their respective paramagnetic Curie temperatures. The inverse susceptibility of the $GdRh_2$ is linear
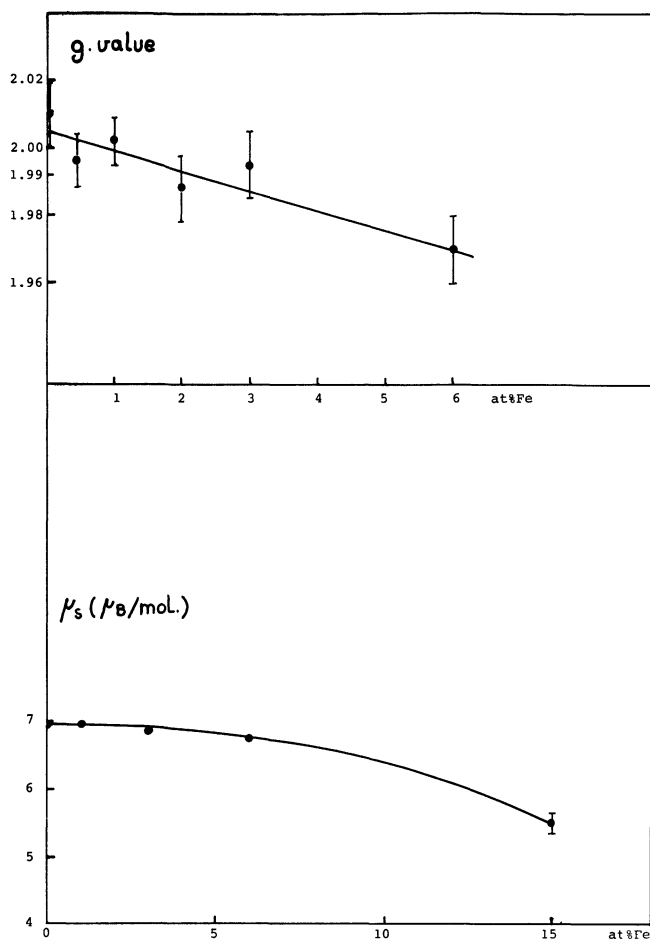
Fig. 5. — The variation of g value (upper curve) and saturation magnetization with iron concentration of $Gd(Rh_{1-x}Fe_x)_2$ compounds.

Fig. 6. — The variation with iron content of the linewidth minima (•), ordering temperatures (×) and the thermal gradient of the linewidth (O) of the $Gd(Rh_{1-x}Fe_x)_2$ compounds.

over the entire paramagnetic region while that of 1 at % Fe alloy shows a deviation from linearity in the vicinity of its paramagnetic Curie temperature. The iron-rich compound shows a behaviour distinctly different from those of the two dilute samples; its hyperbolic form is typical of ferrimagnetic substances (see e.g. Burzo [10]). Other compounds show beha-
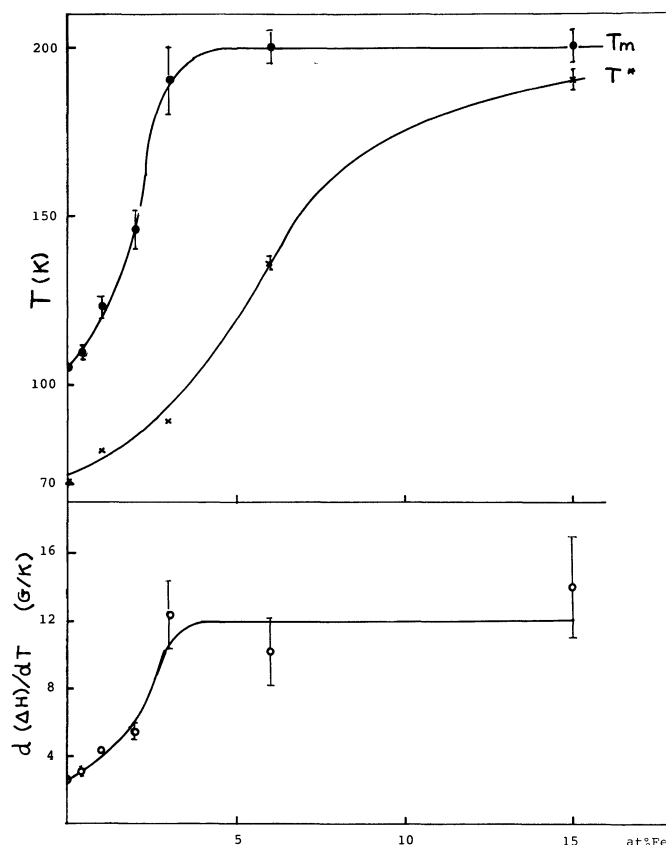
viour intermediate between that of 1 at % Fe and 15 at % Fe alloys.

The alloys containing less than 3 at % Fe exhibit a resonance bottleneck effect, figure 6. This occurs when the conduction electrons have a predominant s-character since d-electrons are well tied to the lattice and therefore are efficient in the transfer of energy from gadolinium ion to the lattice.

Dormann *et al.* [11, 12] have carried out a detailed investigation on $Gd_{1-x}La_xT_2$ compounds (T = Rh,

Table I. — *Summary of present data on the compounds investigated.*

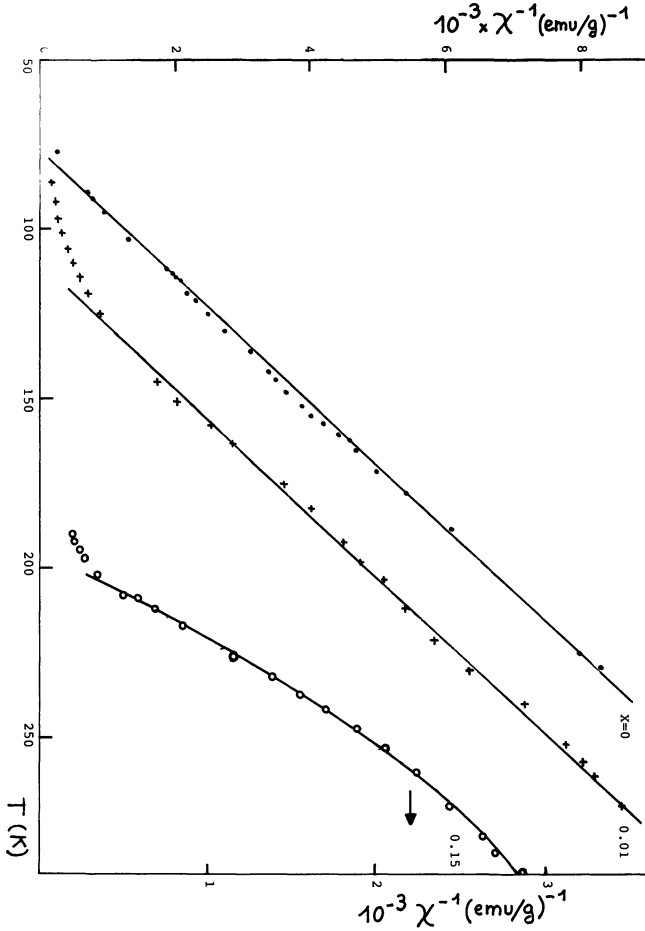| Iron concentration (at %)	g (pm)	T_m (K)	$\dfrac{d(\Delta H)}{dT}$ (Gauss/K)	Saturation moment (μ_B/Mol)
—	—	—	—	—
0	2.010 ± 0.007	105 ± 3	2.6 ± 0.2	6.96
0.42	1.997 ± 0.008	109 ± 3	3.1 ± 0.3	—
1	2.003 ± 0.006	123 ± 3	4.3 ± 0.3	6.97
2	1.988 ± 0.01	146 ± 6	5.5 ± 0.5	—
3	1.995 ± 0.015	190 ± 10	12.4 ± 2	6.84
6	1.972 ± 0.015	200 ± 5	10.2 ± 2	6.75
15	—	200 ± 5	14 ± 3	5.5
100	—	—	—	3.9 (*)

(*) Taken from Besnus *et al.* (7).

Fig. 7. — Temperature variation of the inverse susceptibility for the compounds Gd(Rh$_{1-x}$Fe$_x$)$_2$; (●) $x = 0$, (+) $x = 0.01$ and (O) $x = 0.15$.

Ir and Pt) by means of spin echo NMR. Of these, they obtained the largest hyperfine field for the self polarisation term H_s(Gd) and total transferred term H_N(Gd), due to both nearest neighbours and remote gadolinium ions, for gadolinium in GdRh$_2$. Neglecting the wave vector dependence of the hyperfine coupling constants a_s and a_d for s and d electrons and the exchange integrals J_{f-s} and J_{f-d} Dormann et al. write :

$$H_N(\text{Gd}) = 2\,\mu_B[a_s \langle s \rangle_s + a_d \langle s \rangle_d] \qquad (4)$$

$$\theta_p \approx T_c \approx \frac{S(S+1)}{3\,k_B \langle S \rangle} [J_{f-s} \langle s \rangle_s + J_{f-d} \langle s \rangle_d] . \qquad (5)$$

Where S is the spin of gadolinium and, $\langle s \rangle_s$ and $\langle s \rangle_d$ are the density of s and d electrons respectively at gadolinium site. Taking $a_s = 3.9 \times 10^6$ G/μ_B [13], $J_{f-s} \approx J_{f-d} = 0.16$ eV and using

$$a_{5d} \approx - 0.1 \times a_{6s} \text{ [14] .}$$

Dormann et al. solve the above two equations for $\langle s \rangle_s$ and $\langle s \rangle_d$ and find that in GdRh$_2$ $\langle s \rangle_s$ is higher than $\langle s \rangle_d$. The large and positive H_s(Gd) (≈ 10 T) is

taken to support this conclusion since H_s(Gd) reflects mainly the s electrons density at the gadolinium nucleus due to the strong hyperfine coupling for s electrons. These authors suggest that the strong electronegativity of rhodium leads to electron transfer from gadolinium to the 4d shell of rhodium, in this the 5d electrons of gadolinium playing the prominent role.

The forgoing is in keeping with the occurrence of an ESR bottleneck for gadolinium in GdRh$_2$ and support the finding of a positive g-shift for gadolinium in this compound.

In the dilute limit, both in binary RhFe alloys [15] and, as this work shows, in Gd(Rh$_{1-x}$Fe$_x$)$_2$ compounds iron is non magnetic. However, since at quite low concentrations ($\leqslant 3$ at %) irons shows the presence of a moment, isolated iron atoms will have localised spin fluctuations. With increasing iron concentration the spin fluctuations will tend to be stabilised as good moments and the solute iron atoms will, in any case, be a source of strong scattering for conduction electrons leading to the opening of the bottleneck.

In the presence of the ESR bottleneck the linewidth and g-shift are given by

$$\Delta H = \Delta H_0 \frac{R}{1+R} \qquad (6)$$

and

$$\Delta g = \Delta g_0 \frac{R^2}{(1+R)^2} \qquad (7)$$

where ΔH_0 and Δg_0 are the line width and g-shift in the Koringa limit and where the term giving rise to the dynamical effects is neglected. The bottleneck factor R is the ratio of the relaxation rate of the conduction electrons to the lattice, to that to the localised moment : $R = \delta_{el}/\delta_{ei}$. When R is of the order of unity or less the system is bottlenecked. The bottleneck is fully open when $R \gg 1$.

The relaxation rate of the conduction electrons to the lattice δ_{el}, will have contributions from rhodium, iron and rare earth ions and may, therefore, be written as

$$\delta_{el} = \delta_{el}^0 + \frac{\partial \delta_{el}}{\partial c} c + \frac{\partial \delta_{el}}{\partial (1-c)} (1-c) + p \frac{\partial \delta_{el}}{\partial c^2} c^2$$

$$= A_0 + A_1 c + A_2 c^2 \qquad (8)$$

where

$$A_0 = \delta_{el}^0 + \frac{\partial \delta_{el}}{\partial (1-c)}, \quad A_1 = \frac{\partial \delta_{el}}{\partial c} - \frac{\partial \delta_{el}}{\partial (1-c)}$$

and

$$A_2 = P \frac{\partial \delta_{el}}{\partial c^2}, \quad P$$

being a constant ; c is the concentration of iron and $(1 - c)$ is that of rhodium. In eq. (8) the first term

takes into account scattering from imperfections, such as impurities present in the starting material. The second and third terms account for scattering from iron and rhodium sites respectively and the fourth term for the effect of two nearest neighbour iron atoms. In the dilute limit the probability of finding two nearest neighbour iron atoms is $\sim c^2$ and such a pair will act as a different scattering centre to that of an isolated iron atom due to its lower spin fluctuation temperature. The contribution of the rare earth ions to δ_{ei} is included into δ_{ei}^0 since their concentration is not varied. At high temperatures the relaxation rate of the conduction electrons to the localised moment δ_{ei} is given by Hasegava [16]

$$\delta_{ei} = x \frac{8\pi}{3\hbar} \rho(E_F) J_{f-e}^2 S(S + 1) \qquad (9)$$

where x is the concentration of rare earths and therefore constant in our case. The bottleneck factor may therefore be written as

$$R = A + Bc + Dc^2 \qquad (10)$$

where A, B and D may be treated as constants parameters to be determined from fitting to the experimental data.

It is a simple matter to fit the data points to the equation (6) and (7) to obtain R and hence Δg_0 and ΔH_0 if the effect of iron substitution were simply to open the bottleneck. In the series investigated here, however, iron substitution also appears to affect the band structure because if the effect of iron were only to open the bottleneck then Δg would remain positive (see eq. (7)) and possibly approaching a larger

value in the unbottlenecked limit. The steady decrease of g to negative values (fig. 5) implies that iron substitution modifies the nature of the $GdRh_2$ compound more drastically than just a scattering centre, possibly modifying the band character of the compound. The rapidity with which the C15 structure becomes unstable with respect to C14 structure supports the idea of such a change, a point which may be confirmed by the study of isomer shift in a Mössbauer effect measurement.

4. **Conclusion.** — In $GdRh_2$ gadolinium is bottlenecked. This and the g-value of (2.01 ± 0.007) found for gadolinium in this compound is in keeping with the NMR studies of Dormann et al. [11, 12], and casts doubt on the g-values of 1.967 reported by Davidov and Shaltiel [6].

In the dilute limit iron is non magnetic in the series $Gd(Rh_{1-x}Fe_x)_2$, but undergoes spin fluctuations which stabilise as good moment when iron concentrations exceed about 1 at %. In both cases iron acts as a strong scattering centre for the conduction electrons leading to the opening of the ESR bottleneck. The substitution of iron for rhodium also leads to a change in the band character of the alloys and results in structural change on reaching 15 at %.

References

[1] Tari, A., Phys. Status Solidi a 46 (1978) 173.
[2] Schultz, S., Shanabarger, M. R. and Platzmann, P. M., Phys. Rev. Lett. 19 (1967) 749.
[3] Alguie, G., Kreisler, A. and Burger, J. P., Solid State Commun. 26 (1978) 265.
[4] Chiu, L. B., Ellison, P. R., Steward, A. M. and Taylor, K. N. R., J. Phys. F : Metal Phys. 9 (1979) 373.
[5] Taylor, R. H. and Coles, B. R., J. Phys. F : Metal Phys. 5 (1975) 121.
[6] Davidov, D. and Shaltiel, D., Phys. Rev. 169 (1968) 329.
[7] Besnus, M. J., Herr, A. and Fischer, G., J. Phys. F : Metal Phys. 9 (1979) 745.
[8] Dormann, E., Huck, M. and Buschow, K. H. J., J. Magn. Magn. Mater. 4 (1977) 47.

[9] Hrubec, J. and Steiner, W., J. Physique Colloq. 40 (1979) C5-198.
[10] Burzo, E., Phys. Rev. B 17 (1978) 1414.
[11] Dormann, E., Schaefhausen, L. and Buschow, K. H. J., J. Magn. Magn. Mater. 2 (1976) 177.
[12] Dormann, E., Huck, M. and Buschow, K. H. J., Z. Phys. B 27 (1977) 141.
[13] Campbell, I. A., J. Phys. C 2 (1969) 1338.
[14] Narath, A. and Aldermann, D. W., Phys. Rev. 143 (1966) 328.
[15] Rusby, R., J. Phys. F : Metal Phys. 4 (1974) 1265.
[16] Hasegava, H., Prog. Theor. Phys. 21 (1959) 483.