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Autor: Drulis, H.
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ELECTRON SPIN RESONANCE OF Gd^{3+} IONS IN LANTHANUM AND YTTRIUM HYDRIDES

BY

H. DRULIS

Institute for Low Temperature and Structure Research Polish Academy of Sciences

INTRODUCTION

Measurements of electron spin resonance of Gd^{3+} ions in metallic substances have received considerable attention in studying the electronic structure and the exchange interactions of the localized moments with the conduction electrons. In the present work the electron spin resonance g -shifts and linewidths have been determined for Gd^{3+} ions in the metallic and nonmagnetic lanthanum and yttrium hydrides hosts: $La/Gd/H_x$ with $1.91 < x < 2.90$ and the two samples $Y/Gd/D_{1.85}$ and $Y/Gd/H_{1.83}$.

EXPERIMENTAL

The hydrides samples were prepared by direct reaction $La-Gd$ and $Y-Gd$ alloys containing ca. 3% at. of Gd with high purity gaseous hydrogen. The ESR investigation at 9.3 $kMHz$ have been performed on polycrystalline samples of $La/Gd/H_x$ and $Y/Gd/H_{1.83}$ by using the standard transmission X-band spectrometer. The procedure outlined by Peter [1] was applied for estimating the g -shifts and the linewidths for these lines.

RESULTS AND DISCUSSION

A. g -shifts

The g -factor for Gd^{3+} doped yttrium dihydride and lanthanum hydrides have been measured in the temperature range between 77 and 300 K , and no change has been observed. At figure 1 showed the dependence of the g -shift on the H/Me atom ratio. The shift of center of the resonance line the direction of higher magnetic fields, indicates that the g values are negative in lanthanum hydride and in contrary to this, positive values have been found in yttrium dihydrides.

The effective exchange interaction integrals calculated from the relation [2]:

$$J_{sf} = \frac{\Delta g n_0 g_e \beta^2}{\chi_e} \quad (1)$$

where χ_e is the volume magnetic susceptibility of conduction electrons, n_0 — the number of the lattice sites per unit volume. The g -values, g -shifts and exchange integrals J_{sf} for Gd^{3+} are indicated in Table I.

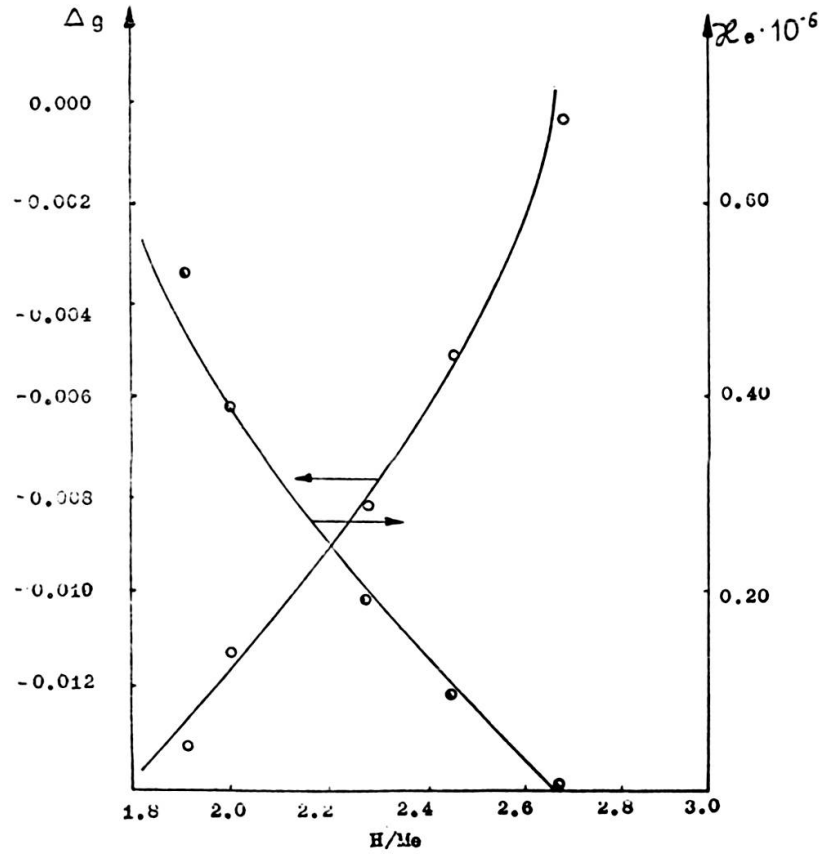


FIG. 1. — g -shifts for Gd ions and magnetic susceptibility of the host lanthanum hydride vs. H/Me atom ratio.

TABLE I

H/Me atom ratio	$\chi_g 10^6$ emu/g	$\chi_{corr} 10^6$ emu/g	$\chi_e 10^6$ emu/cc	g	Δg	J_{sf} eV
$La/Gd/H_{1.91}$	0.42	0.74	3.77	1.979	-0.013	-0.009
$La/Gd/H_{2.03}$	0.40	0.72	3.69	1.980	-0.012	-0.007
$La/Gd/H_{2.29}$	0.24	0.59	3.07	1.984	-0.007	-0.006
$La/Gd/H_{2.46}$	0.13	0.49	2.56	1.987	-0.005	-0.005
$La/Gd/H_{2.69}$	0.0	—	—	1.991	—	—
$Y/Gd/H_{1.83}$	1.60	2.00	—	2.003	+0.011	+0.004
$Y/Gd/D_{1.85}$	1.60	2.00	—	1.998	+0.007	+0.002

According to the theory of Kondo [3] the experimental measurements effective exchange interaction integrals J_{sf} are the sum of two terms $J_{sf} = J_1 + J_2$ which:

1. the "ferromagnetic" exchange term ($J_1 > 0$) and
2. the "antiferromagnetic" s - f mixing term ($J_2 < 0$).

According to the above ideas it is possible to explain the observed negative values of the g -shifts in many metallic systems [2] as well as in the case of Gd^{3+} doped lanthanum hydride. Contrary to this, positive values of J_{sf} have been found in lanthanum-gadolinium alloys [4]. The change of the sign on passing from the La - Gd to La - Gd - H alloys indicates predominant contribution of covalent mixing to J_{sf} in the latter case. Following Kondo J_2 is given by:

$$J_2 = -\frac{V_0^2}{2S} \left[\frac{1}{E_{abs}} + \frac{1}{E_{em}} \right] \quad (2)$$

Here V_0 —a perturbing potential, and the energy parameters E_{abs} and E_{em} representing the energy required to take on electron near the Fermi level and place it in an empty $4f$ state (E_{abs}) and energy necessary to put an f electron at the Fermi level (E_{em}) respectively. According to Herbst [5], the sum $E_{abs} + E_{em}$ for metallic gadolinium equals $12 eV$ and ratio $E_{abs}/E_{em} = 0.41$. The positive J_{sf} values for La - Gd and Y - Gd alloys can be explained by relatively high values of both E_{abs} and E_{em} . The situation changes on passing to the La - Gd - H alloys, where, probably, the relative displacement of the empty and full $4f$ state against the Fermi level causes the contribution of the covalent mixing to be remarkable, due to a marked diminution of either E_{abs} or E_{em} as compared with La - Gd alloys. Hence, the observed changes of J_{sf} (Table I) with increasing hydrogen content may be explained on the basis of more widely accepted anionic model of the electronic structure of rare-earth hydrides on assuming E_{abs} to be markedly smaller than E_{em} . Only in this case the depopulation of the conduction band with rising hydrogen concentration, and a resulting increase of the E_{abs} value, are followed by the observed diminution of the absolute value of J_{sf} .

The exchange interaction integral J_{sf} of Gd^{3+} ions in the yttrium dihydride and Y - Gd alloys has positive values indications predominant contribution "ferromagnetic" type interaction magnetic ions with conduction electrons. It is possibly connected with more s -band character conduction electrons near Fermi level in both phases of the yttrium.

B. Linewidths

The linewidths of the ESR spectra have been determined in the temperature range between 120 - $470 K$. It has been found that temperature dependence of the

linewidths is different for the samples of composition close to MeH_2 and for samples with higher hydrogen content. Thus for the samples $La/Gd/H_{1.91;2.03}$ and both samples yttrium dihydride the linewidths DH changes linearly with temperature (fig. 2) which is thought to originate mostly from the spin lattice relaxation due mainly to a Korringa type relaxation via conduction electrons [6]:

$$\frac{\partial DH}{\partial T} = \frac{\pi (\Delta g)^2 k}{g \beta} \quad (3)$$

In the Table II are given the experimental values of the g -shifts and the g -values calculated from the slope of straight lines of figure 2 by using the relation 3.

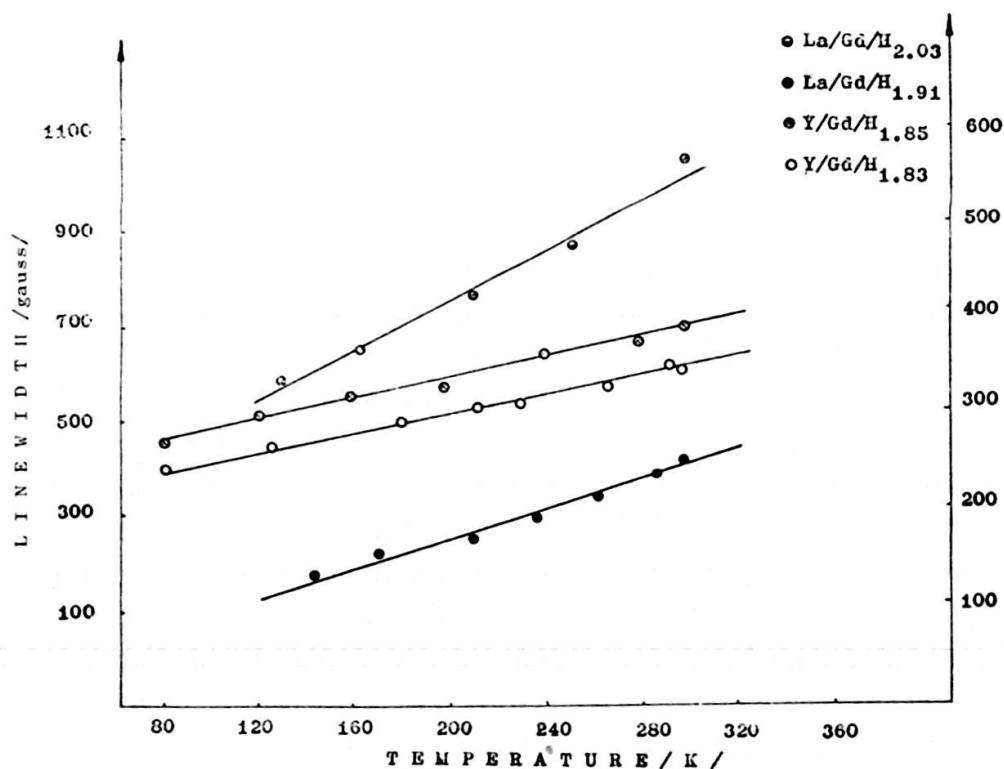


FIG. 2. — ESR linewidth against temperature for dihydrides

TABLE II

Samples	$\frac{\partial DH}{\partial T}$ Gs/K	$ \Delta g $ Korr calc.	Δg exp.
<i>LaH</i> _{1.91}	1.63 ± 0.3	0.008	-0.013
<i>LaH</i> _{2.03}	2.69 ± 0.3	0.011	-0.012
<i>YH</i> _{1.83}	0.57 ± 0.1	0.002	+0.007
<i>YD</i> _{1.85}	0.57 ± 0.1	0.002	+0.007

All $\Delta g_{Korringa}$ values exceed Δg_{exp} ones except those for sample of the $LaH_{2.03}$. It seems to be connected with the neglecting of the interelectronic correlation and exchange effects [7]. Quite different behaviour is revealed by the samples with higher hydrogen content. Here the linewidth is constant in low temperature region, markedly increases above ca. 200 K, and then becomes again temperature independent at higher temperatures (fig. 3). Apparently these changes cannot be directly explained by self-diffusion of hydrogen which is too slow [8] in the investigated temperature range. It is believed that the observed changes of the linewidth may correspond to a specific phase transition in lanthanum hydride similar to those recently found in some other *IIIB* group hydrides. The same behaviour of the *ESR* linewidth has been found for frozen lithium-ammonia solutions [9] and ascribed to a phase transition occurring in lithium. Neutron diffraction studies revealed [10] that nonstoichiometric cerium deuteride shows an order-disorder phase transition below room temperature. On the other side, a precise *X-ray* diffractometry of $CeD_{2.75}$ disclosed the cubic to tetragonal deformation below ca. 230 K [11]. Furthermore, acoustic velocity measurements on cubic polycrystalline hydrides of scandium, yttrium and erbium [12] suggest that previously not observed phase transition may occur in all these hydrides in the region 230-250 K, i.e. in nearly the same temperature region.

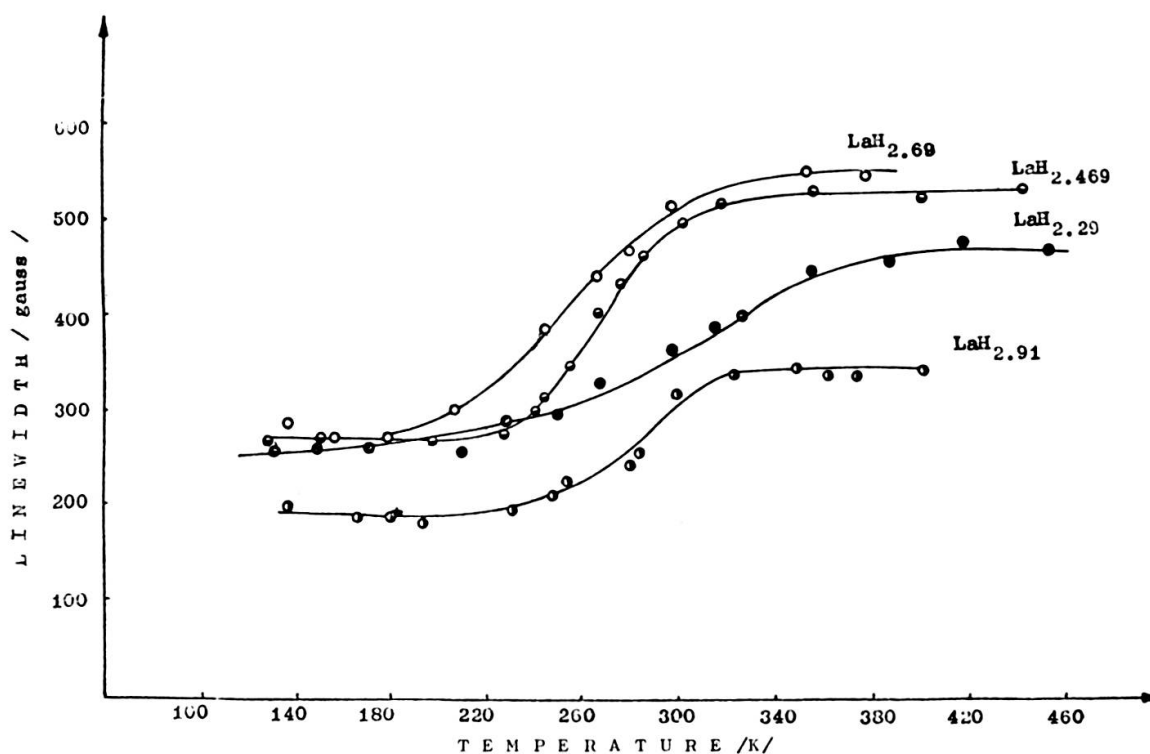


FIG. 3. — The linewidth against temperature for $La/Gd/H_x$
 $2.29 \leq x < 2.91$

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