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Interaction of hydrogen with magnetism in Y–Gd alloys

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Abstract

When introduced into the h.c.p. rare earths, hydrogen either precipitates, at low enough temperatures, into the β-phase dihydride or forms the peculiar α*-phase composed of H–R–H pairs occupying second-neighbour tetrahedral sites along the *c*-axis. In order to understand the origin of these structures, we have investigated the interaction of H with the magnetic configurations present in some Y–R systems by electrical resistivity measurements. Recent experiments on $Y_yTb_{1-y}H_x$ have shown a correlation between the (*y*-dependent) existence of the α*-phase and eventual modulated magnetism, via the Fermi surface topology. The present results obtained on the $(Y–Gd)H_x$ system seem to confirm the idea regarding the analogy between magnetic and structural modulations (spin–density vs. charge–density waves).

Keywords: Hydrogen interaction; Magnetism; Y–Gd alloys

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1. Introduction

It is by now a well established experimental fact that some of the heavy h.c.p. lanthanides (Ho, Er, Tm, and Lu) as well as their analogues Sc and Y form with hydrogen a low-temperature solid solution phase, α*-RH_x, consisting of second-neighbour pairs on tetrahedral sites along the *c*-axis surrounding a metal atom, H–R–H; these pairs organise themselves, below 150–170 K into short-range-ordered quasi-unidimensional chains zig-zagging around the *c*-axis, with a periodicity of 3.75 c (or 7.5 interlayer planes) as determined by neutron scattering (for a detailed review, see Ref. [1]). First attempts to reproduce the orientational ordering in α*-phase systems through statistical thermodynamics using lattice statics methods were made by Tatarenko and Tsynman [2], who assumed an empirical 'electrochemical' repulsive potential, taking into account H–H correlation (blocking) and strain-induced distortion effects. It remained unclear, however, what was responsible for the solubility limit in the α*-phase ($x_{\max}^{\alpha^*}$ varying between 0.03 and 0.35 for R=Ho through Sc) and, in particular, why it did not form at all in the other h.c.p. lanthanides but precipitated as dihydride at once.

On the other hand, we noted earlier, when studying the interaction of H with magnetic structures in the magnetically ordering rare earths, that there seemed to exist a correlation between the turning (or interplane) angle ω_i (itself de Gennes-factor dependent) of the various *c*-axis modulated magnetic configurations and the possible presence of the α*-phase solid solution via the Fermi-surface topology of the rare earths or their intermetallics (see Ref. [3] for a discussion). In particular, we observed [4] that, in the alloy system $Y_yTb_{1-y}H_x$, hydrogen entered into solution for $y=0.9$, where the helical turning angle ω_i was 48–50°, but not for $y=0.2$, with an $\omega_i=32°$, the former value corresponding to a modulation of $(7–7.5)c/2$, which is just the above mentioned periodicity of the α*-chains. Pursuing this direction, we confirmed the absence of the solid solution in the $Y_{0.4}Gd_{0.6}$ alloy [5] and the appearance of GdH_2 precipitates instead. It thus appears more and more probable that the topology of the Fermi surface is the driving mechanism for both the magnetic modulations and the charge (or concentration) density waves in alloys.

The present paper describes the influence of hydrogen upon the resistivity of the Y_yGd_{1-y} system for $y=0.3$, which is in the vicinity of a multicritical region [6]. In fact, the competition between the FM order of pure Gd and the helical AF of Y-rich alloys leads, in this interval, to an additional transition: after the PM–FM(I) transition at $T_C=219$ K to a *c*-axis aligned FM and, before entering the low-*T* canted FM(II) region, the system turns helical AF at $T_N=203$ K. Since hydrogen acts upon the structural

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parameters and the crystal field of the alloy it was interesting to investigate its eventual magneto-elastic effect in the multicritical region and compare with the previously obtained data [5] in the simpler system with $y=0.4$, where the transition is directly PM–AF. A discussion of the literature on Y–Gd alloys without H had been given in Ref. [5].

2. Experimental

First, 20×1 mm^2 specimens of $\approx$200-μm thickness were prepared from cold-worked and electropolished $Y_{0.3}Gd_{0.7}$ foils furnished by the Ames Laboratories (Ames, Iowa). The starting material was 99.99% Y and 99.97% Gd. The foils were provided with four spot-welded Pt wires for the electrical contacts and then outgassed in a quartz furnace at 700–750°C in a vacuum of $<10^{-6}$ Torr before H loading. The loading conditions were the same as in Ref. [5]: 500°C in a tungsten crucible, homogenizing for 8 h. The used concentrations were 0.05, 0.10, 0.20 H (to ±0.015) and one unannealed H-free alloy as reference.

The electrical measurements were made simultaneously on all samples using the classical four-point dc method in a pumped liquid-helium cryostat between 1.3 and 300 K, with a relative sensitivity of better than 10^{-8} Ω cm. The absolute precision, due mainly to the geometrical shape factor determination, is of the order of a few %.

3. Results and discussion

An overall view of the thermal resistivity variation for the different H concentrations is given in Fig. 1. The two principal observations are the break at $T_C\approx220$ K (comparing favourably with the early measurements on the H-free alloy [7]) and the decrease of the resistivity upon the addition of H. However, neither the value of T_C nor that of the residual resistivity, $\rho_r\approx38$–40 μΩ cm, seem to vary much with x. These are immediate indications that hydrogen does not enter in solution in the alloy but precipitates at once into the (lower resistivity) dihydride. At the same time, the magnetic spin-disorder resistivity — responsible for the variation below T_C — decreases due to increasing loss of Gd ions to the dihydride. This is shown in the inset of Fig. 1 where we have plotted $\rho_m^0=\rho_{ext}(0)-\rho_r$, i.e. subtracting the phonon and the impurity contributions. The decrease of ρ_m^0 with increasing x is due to weakening exchange interaction caused by pumping off conduction electrons to the dihydride. Table 1 summarizes the relevant experimental data for the various H concentrations.

Let us investigate the region around T_C a bit closer and compare it with the behaviour of the corresponding specimens in the $Y_{0.4}Gd_{0.6}H_x$ alloy [5]. This is done through the derivative plot in Fig. 2. At a first glance, the two sets of curves look very similar, just shifted by 30 K as concerns the transition towards paramagnetism. A careful look, however, does show some changes. Though the qualitative T-dependence for the pure alloys ($x=0$) in the two cases remains comparable, the addition of H acts differently: instead of the smooth decrease towards T_N seen for $y=0.4$, one notes now a kind of plateau, even peaking slightly around 205 K before the drop at T_C, in the case $y=0.3$. Interestingly, two transitions were also signalled but not characterised in specific-heat measurements on single crystals of $Y_{0.3}Gd_{0.7}$ by Legvold et al. [8]. It looks as if the magneto-elastic effect introduced by hydrogen revealed the FM(I)–AF transition at $T_N=203$ K as determined by Bates et al. [6] on single crystals but not observed on the pure polycrystalline alloy. No such effect takes place for $y=0.4$, which is far from the sensitive multicritical area of the phase diagram.

Finally, a further H-dependent phenomenon can be remarked at low temperatures, which is exhibited in Fig. 3. A hump grows upon the introduction of H, which is

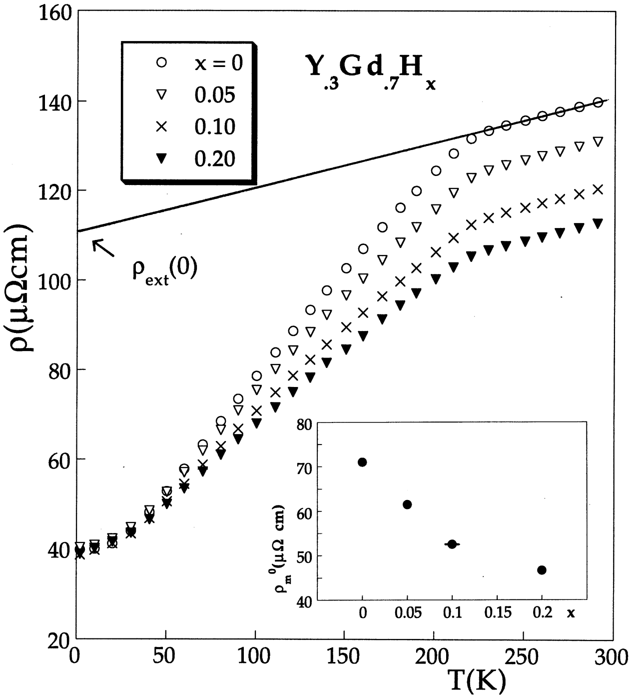

Fig. 1. Thermal variation of the resistivity of $Y_{0.3}Gd_{0.7}H_x$ for various x-values, indicating the extrapolated $\rho_{ext}(0)$ after subtraction of the phonon contribution, for $x=0$. The inset gives the x-dependence of the spin-disorder resistivity, $\rho_m^0=\rho_{ext}(0)-\rho_r$.

Table 1
Measured sample characteristics in the system $Y_{0.3}Gd_{0.7}H_x$

x	ρ_r [a]	$\rho_{ext}(0)$	ρ_m^0	T_C (K)	T_N (K)	$T_N^{GdH_2}$ (K)
0	39.75	110.8	71.05	221	–	–
0.05	40.20	101.7	61.5	220.5	≈200	≈5
0.10	38.50	91.0	52.5	221	≈200	≈5
0.20	38.75	85.4	46.65	220	205	5.5

[a] All ρ-values are in μΩ cm.

peaking at ≈5.5 K and resembles strongly the low-T behaviour of the $y=0.4$ alloy [5]. There, the peak occurred at 3.6 K and was attributed to the magnetic transition of the dihydride, $T_N^{GdH_2}$. Its higher value in the present alloy is consistent with its higher T_C (as seen above) and is due to the larger de Gennes factor $\xi=(1-y)(g_J-1)^2 J(J+1)$.

In conclusion, the introduction of hydrogen into $Y_{0.3}Gd_{0.7}$ leads to the precipitation of GdH_2 for the smallest used H concentrations (signalled by a magnetic transition at 5.5 K), resulting in a decreasing spin-disorder resistivity, ρ_m^0, and revealing the FM(I)–AF transition at 205 K.

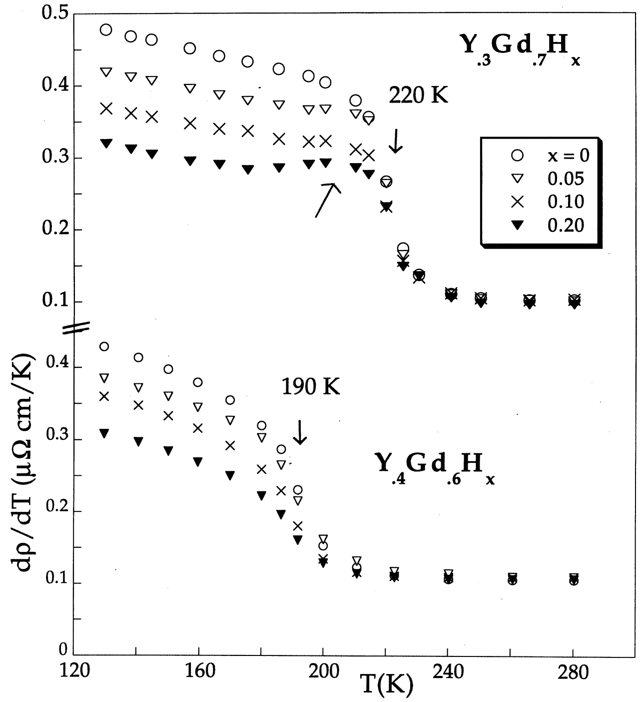

Fig. 2. Resistivity derivatives of $Y_yGd_{1-y}H_x$, with $y=0.4$ and 0.3, in the region of the respective magnetic order–disorder transitions. Note the revelation of the FM(I)–AF transition near 200 K for the H-loaded $y=0.3$ specimens.

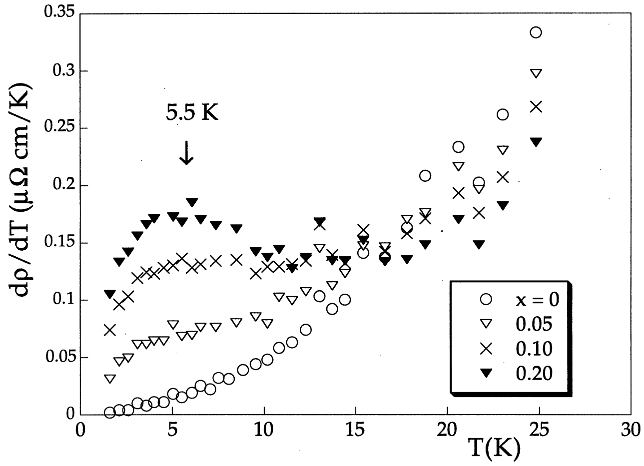

Fig. 3. Resistivity derivatives of $Y_{0.3}Gd_{0.7}H_x$ at low temperatures, with the growing peak at $T_N^{GdH_2}$.

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