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Neutron diffraction investigations and magnetic properties of $RNi_{3.5}Al_{1.5}$ compounds and their hydrides (deuterides)

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Abstract

When annealed, the $RNi_{3.5}Al_{1.5}$ (R = Y, Tb, Dy, and Ho) compounds were found to crystallise with the hexagonal $CaCu_5$-type structure ($P6/mmm$). Hydrogenation under 1.5 MPa gas pressure, shows that the maximum hydrogen capacity varies with the rare earth atom from 3.8, 2.8, 3.9 to 2.42 for Tb, Dy, Ho and Y, respectively. Analysis of neutron diffraction patterns shows that Al atoms occupy only the 3 g sites. The lattice parameter expansion can be correlated both to the size of the R atom and to the amount of aluminium. Magnetisation measurements show strong ferromagnetic contribution supported by magnetic R elements, e.g. R = terbium. But the exchange couplings remain rather weak, corresponding to a Curie temperature T_c comprised from 10 to 15 K. The $TbNi_{3.5}Al_{1.5}$ hydride reveals a reinforcement of the magnetic couplings with $T_c = 105$ K. This leads to assume that nickel is magnetically polarised but reverse to terbium, owing to the $J(4f) = |L + S|$ with M(d) coupling.

Keywords: RNi_5 compounds and their hydrides; Neutron diffraction; Magnetic properties

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1. Introduction

Over the last 30 years, the RNi_5 based compounds have received great attention as hydrogen storage materials, mainly as electrodes for NiMH batteries [1]. Substitution of either the R metal or nickel by various elements was found to have considerable impact on the structure and hydrogen absorption properties reference to the prototype $LaNi_5$ compound. Hydrogen atoms are known to occupy different types of interstitial sites, thus this element can markedly influence the magnetic interaction if any, via the local co-ordination or any change in the metal bonds [2]. So, the crystal structure and the hydrogen absorption properties of parent series such as the $RNi_{3.5}Al_{1.5}$ compounds with R = Tb, Dy, Ho and Y were investigated in detail [3–6]. However, systematic studies of the structural and magnetic properties of the hydrides comparison made with the compounds have not been performed yet, as reported here after.

2. Experimental

$RNi_{3.5}Al_{1.5}$ (R = Y, Tb, Dy, and Ho) compounds were synthesized from commercial R, Ni and Al metals (purity better than 3N5) by arc melting under an argon atmosphere and then the ingots were annealed at 1123 K for at least 1 week. The compounds were hydrogenated under 1.5 MPa hydrogen gas pressure at 473 K. To get the maximum hydrogen charge, the samples were thermally cycled several times, and then they were maintained under a 1.5 MPa hydrogen gas pressure for 1 day. Neutron diffraction experiments were carried out at room temperature using the D1A diffractometer setting at the Institute Laue Langevin (Grenoble) on both the starting

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compounds and their deuterides. A profile type refinement (Rietveld analysis) of the crystal structure was carried out for all the samples in order to determine the lattice parameters, to refine the metal site occupancy (Ni/Al), to locate hydrogen atoms and to determine the total hydrogen content. Besides magnetisation measurements were performed using the extraction method on both the compounds and the hydrides, in the temperature range 4–300 K and under magnetic fields up to 10 T.

3. Results

3.1. Synthesis and hydrogen uptake

The annealed $RNi_{3.5}Al_{1.5}$ (R = Y, Tb, Dy, and Ho) compounds were found to crystallise within the hexagonal structure $CaCu_5$-type (space group $P6/mmm$) as single phase, with additional peaks well corresponding to a few traces of rare earth oxides.

After hydrogenation, all the hydrides were found stable at room temperature. Table 1 reports the hydrogen uptakes after full hydrogenation, determined by weight measurements performed before and after hydrogenation. The maximum hydrogen absorption capacity appears to depend on the rare earth atoms.

3.2. Neutron diffraction analysis

Fig. 1 displays the neutron diffraction patterns of the annealed $RNi_{3.5}Al_{1.5}$ (R = Y, Tb, Dy, and Ho) compounds. Rietveld type refinements (RIETAN code) have been carried out and the results are reported in Table 2. It is found that the Al atoms are located in the 3g metal sites only. The a and c cell parameters vary quite linearly with the radius of the 4f elements (R = Tb, Dy and Ho), except for R = Y(4d) which exhibits a slight deviation to the fits. Fig. 2 shows the neutron diffraction pattern analysis of the $TbNi_{3.5}Al_{1.5}$ compound as analysed by profile type refinement. The final full profile agreement factor is $R_P = 3.63$ and the Bragg one is $R_B = 5.07$.

Table 1
Evolution of the hydrogen absorption capacity vs. the rare earth atom R

Rare earth atom R	Y	Tb	Dy	Ho
H-uptake	2.42	3.8	2.8	3.9

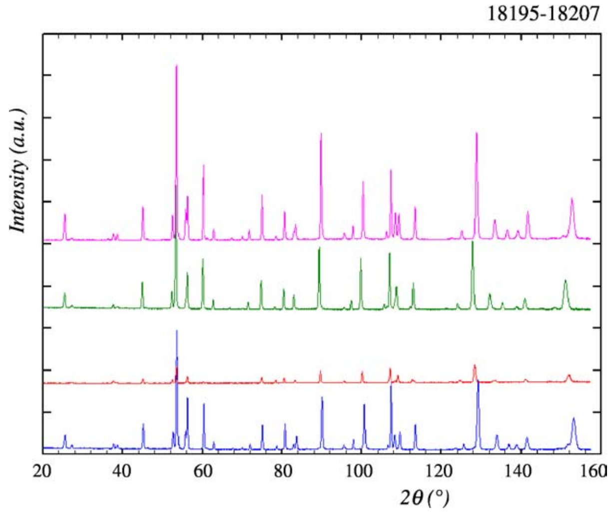

Fig. 1. Neutron diffraction patterns of the compounds $RNi_{3.5}Al_{1.5}$ with R = Y, Tb, Dy and Ho, up to down.

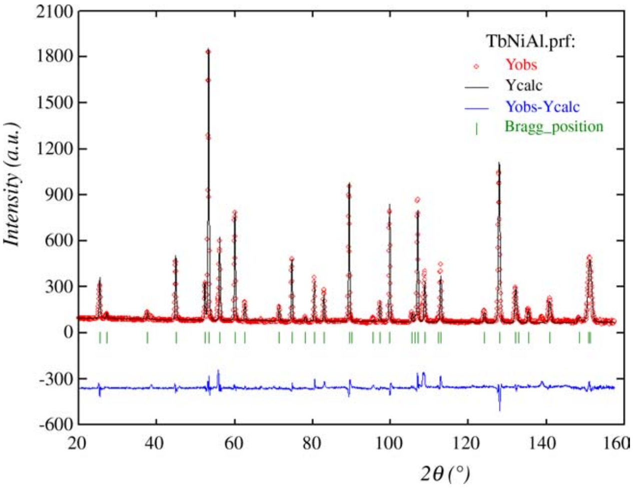

Fig. 2. Neutron diffraction pattern of $TbNi_{3.5}Al_{1.5}$ as profile Rietveld calculated (up continuous line) to the experiment (dots). The difference pattern ($I_{obs} - I_{cal}$) is represented down, intermediate are the ticks for all the possible diffraction lines.

Fig. 3 shows the neutron diffraction pattern recorded at 300 K for the parent $TbNi_{3.5}Al_{1.5}D_{3.8}$ hydride (deuteride). In Table 3 we gathered the data resulting from a profile type refinement based on the occupancy of two only of the five possible sites involved for $LaNi_5$, as the most satisfying set of sites to consider for the best agreement factor [7]. Further

Table 2
Results of the profile analysis of neutron diffraction patterns

Rare Earth Element (R)	Y	Tb	Dy	Ho
Lattice parameters				
a (Å)	4.9713(3)	4.9970(1)	4.9825(2)	4.9614(2)
c (Å)	4.0451(3)	4.0559(1)	4.0527(2)	4.0474(2)
V (Å^3)	99.97	101.27	100.61	99.63
Al(3g)				
Relative occupancy	0.034(2)	0.043(1)	0.032(2)	0.033(2)
Concentration per fu	1.088	1.376	1.024	1.056

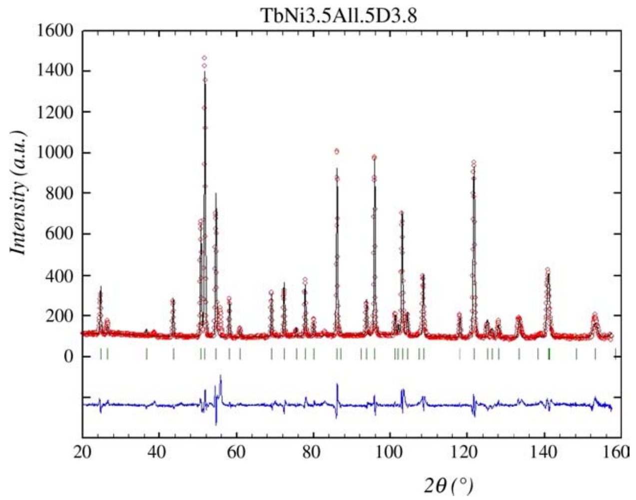

Fig. 3. Neutron diffraction pattern of $TbNi_{3.5}Al_{1.5}D_{3.65}$ as profile Rietveld calculated (up continuous line) to the experiment (dots). The difference pattern ($I_{obs} - I_{cal}$) is represented down, intermediate are the ticks for all the possible diffraction lines.

attempts involving additional or different sets of sites do not lead to a better R factor, by far.

The first of the occupied site (6m) by hydrogen is for 40 at.% and the second one (12n) is for 60 at.% occupied. The refined formula is $TbNi_{3.5}Al_{1.5}D_{3.65}$ close to the nominal composition (3.8 D atoms/f.u.) for a relative volume increase of 8.8%, i.e. ∼ 2.4Å^3/H atom. The occupied sites by hydrogen are those tetrahedra making a compromise with a relatively lower coordination with the 3g sites (that contain the Al atoms for a little less than 50 at.%) and at least one lanthanum neighbour atom. Besides, this agrees to the fact that the p-element (Al) is known to form no attracting metal bond with hydrogen, quite oppositely to lanthanum.

3.3. Magnetisation measurements

Here, we report only on the magnetic characteristics of the $TbNi_{3.5}Al_{1.5}$ compound and its hydride, a more general analysis of all the materials will be presented in a forthcoming paper.

First, measurements were made versus temperature under a low magnetic field ($H = 0.5$ T). The $TbNi_{3.5}Al_{1.5}$ shows a net magnetic ordering at low temperature with a high ferromagnetic component. The reverse susceptibility fits well a Curie–Weiss law with $T_c \sim 13$ K as seen in Fig. 4a. The hydride $TbNi_{3.5}Al_{1.5}H_{3.8}$ behave similarly to the compound at low temperature with $T_{c1} \sim 15$ K. However, a change of the slope of the reverse susceptibility takes place close to 225 K, an extrapolation from the high temperatures was made to correspond to $T_{c2} \sim 105$ K as shown in Fig. 4b.

Table 3
Results of the profile analysis of the neutron diffraction pattern of $TbNi_{3.5}Al_{1.5}D_{3.8}$

Lattice parameters			
a(Å)		c(Å)	V(Å^3)
5.1464(2)		4.1594(1)	110.16
x	y	z	Relative occupancy
D atom parameters			
6m 0.119(2)	0.238(2)	0.5	0.045
12n 0.457(2)	0.0	0.111(2)	0.069(2)

Under higher magnetic field (e.g. $H = 10$ T), it is shown that both the compound and its hydride can be polarised very similarly in the 3–300 K range of temperatures range. However, extrapolation of the saturation magnetisation reveals a little higher (for T down to 0 K) for the hydride reference to the compound. For both systems, an inflection point of the magnetisation versus temperature trace is found close to 105 K (∼ T_{c2}). Extrapolation of the magnetisation to infinite fields suggests that the moment of Tb should be close to the theoretical value of 9 μ_B, but the Ni moment if any, should be no more than 0.2 μ_B.

From magnetic measurements performed at 3 K in the low field range (<2 T), magnetisation of the hydride is found slightly lower than that of the compound. It seems that the hydride exhibits a little higher magnetic anisotropy than the compound. However, the traces recorded in the lowest magnetic fields range reveal a more complex behaviour than just for a simple ferromagnetic system with a metamagnetic behaviour (?). An inflexion point sets around 0.12 T for the compound and around 0.2 T for the hydride as seen in Fig. 5a and b.

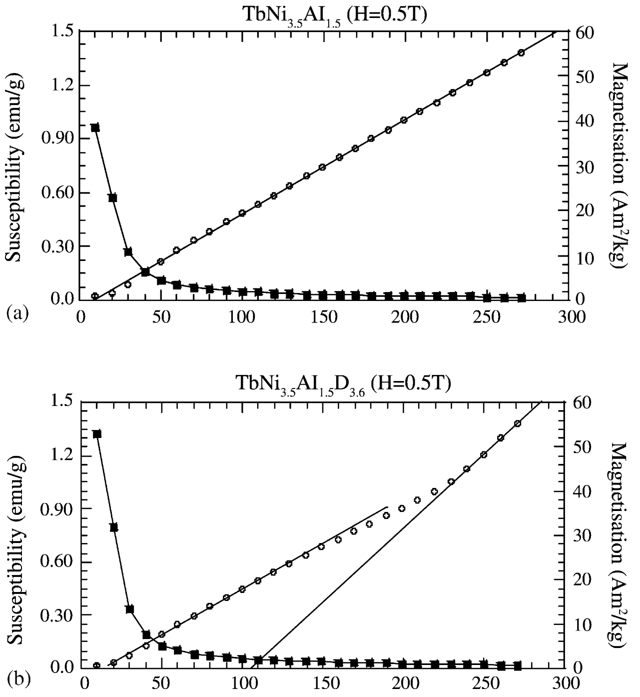

Fig. 4. (a) Direct magnetic susceptibility (left scale, black squares) and reverse (right scale, open circles) as determined vs. temperature in a field of 0.5 T for $TbNi_{3.5}Al_{1.5}$. (b) Direct magnetic susceptibility (left scale, black squares) and reverse (right scale, open circles) as determined vs. temperature in a field of 0.5 T for $TbNi_{3.5}Al_{1.5}D_{3.65}$.

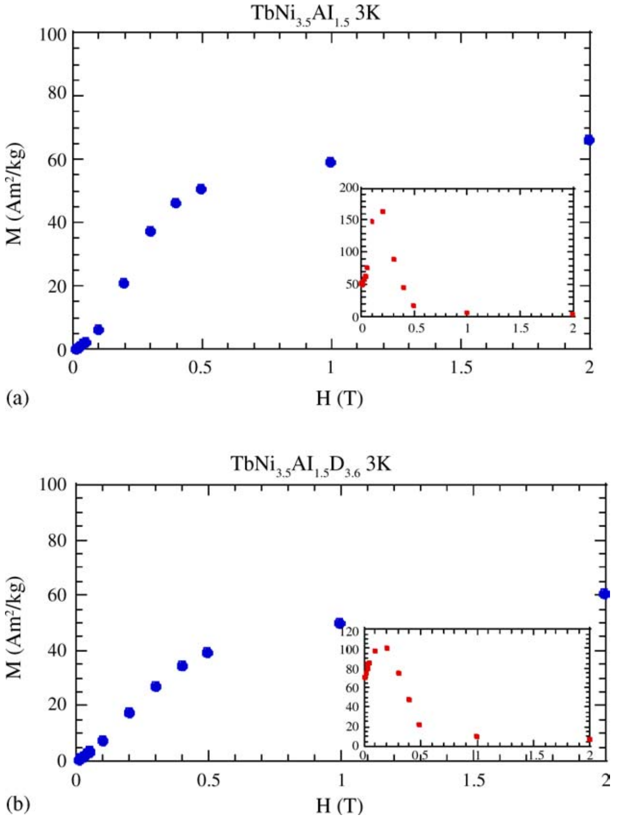

Fig. 5. (a) 3 K magnetisation measurement for $TbNi_{3.5}Al_{1.5}$ up to $H = 2$ T. (b) 3 K magnetisation measurement for $TbNi_{3.5}Al_{1.55}D_{3.65}$ up to $H = 2$ T. Inserts show the derivative traces of the magnetisation curves indicating a reinforcement of the critical field from 0.12 and 0.2 T for the compound and its hydride, respectively.

4. Discussion and conclusion

The $RNi_{3.5}Al_{1.5}$ compounds crystallise within the prototype hexagonal $CaCu_5$-type structure. Rietveld analysis of neutron diffraction data revealed that Al occupies preferentially the Ni(3g) sites. This agrees with what was earlier reported by Joubert et al. [7], so that large atoms such as Mn and Al occupy the Ni(3g) sites instead of the Ni(2a) sites. As seen in Table 2, the refined Al content was found lower than the nominal composition for R = Y, Dy and Ho. The cell parameter behaviour can be directly related to the radius of the R element, as well as for the impact of Al substitution to Ni(3g).

The magnetisation measurements performed on the $RNi_{3.5}Al_{1.5}$ compounds, reveal a strong ferromagnetic contribution from the rare earth metal e.g. Tb, which is supported by a weak Tb–Tb exchange coupling ($T_{c1} \sim 13$ K). Hence, at 3 K the curves M(H) are typically characteristics for a metamagnetic behaviour. Hence, either the magnetic structure should be not collinear or some magnetic disordering in the couplings should originate from not well polarised Ni sites, as the result of the ∼ 50%Al/50%Ni statistical occupancy of the (3g) sites. For the hydride, the Ni magnetic polarisation appears reinforced up to the ordering temperature $T_{c2} \sim 105$ K. If we consider that Ni should have a small but opposite moment to that of Tb ($J = |L + S|$ rule), the critical field able to polarise this small moment should be close to 0.25 ± 0.05 T.

Apart the magnetic frustration related to the substitution of ∼ 50% of Al to Ni, the impact of Al covalent-type bonding should as well contribute to reduce a potential Ni polarisation as observed for the pure compound. However, hydrogenation could reinforce a polarisation of Ni since H-bonds transfer electrons for the valence band to deeper energy levels. Then, anti-bonding states should be created beyond the Fermi level E_F. Hence, a net Ni moment should explain both the persistence of magnetic correlations up to 105 K and the weak magnetic “hardening” of the hydride M(H) traces as measured at 3 K. Moreover, assuming that Tb takes its theoretically saturation moment of 9 μ_B, an estimate of the Ni moment deduced from magnetisation extrapolated to infinite fields is of 0.2 μ_B. Band structure calculations will be undertaken soon to enlighten this specific aspect.

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