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Neutron study of Al or Mn substituted $LaNi_5$ hydrogen sponges

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Résumé. — La diffraction des neutrons montre que les substitutions de Al et Mn occupent principalement le site 3g dans $LaNi_5$. La largeur anormale des raies de diffraction du composé $LaNi_5$ *activé* montre que les grains sont subdivisés en filaments. Cette anomalie disparaît pour les composés substitués.

Abstract. — Neutron diffraction measurements show that substituted Al and Mn atoms occupy mainly the 3g site in $LaNi_5$. The anomalous width of *activated* $LaNi_5$ diffraction lines shows that the grains are subdivided into filaments. These anomalies disappear for substituted compounds.

1. **Introduction.** — Partial substitution of La or Ni changes the equilibrium pressure of the related reversible hydride [1] proportionally to the primary intermetallic cell volume change [2, 3]. Little evidence has been obtained to date about the action of such substitution on the hydrogen content. Following already published neutron diffraction [4, 5] and NMR [6, 7] results for the non substituted $LaNi_5H_6$, the aim of our work is to determine the position of the substitutions and the hydrogen sites in substituted compounds.

2. **Sample characterization.** — Intermetallic compounds were prepared as described in ref. [8]. Upper limits for substitutions correspond to $LaNi_{3.8}Al_{1.2}$ and $LaNi_{2.7}Mn_{2.25}$. Homogeneous *activated* powder (5-15 μ particle size) was obtained after several absorption-desorption hydrogen cycles (40 bar at 40 °C). Shown on figure 1 are typical composition isotherms determined as explained in ref. [9]. The replacement of hydrogen by deuterium does not change the capacity of the β phase.

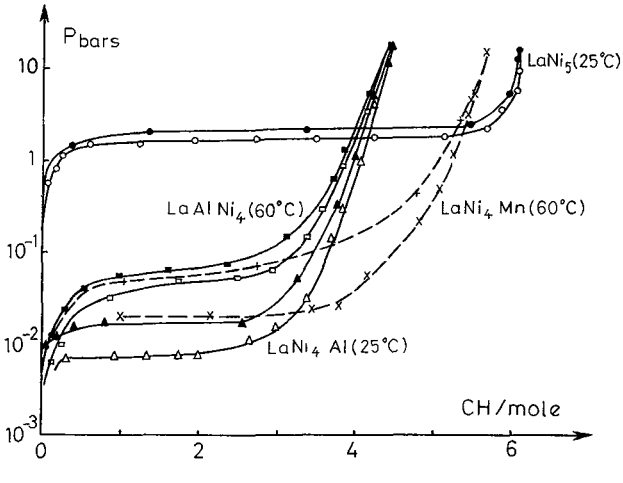

Fig. 1. — Comparison of absorption-desorption isotherms for $LaNi_5$, $LaNi_4Al$ at 25 °C and $LaNi_4Mn$, $LaNi_4Al$ at 60 °C.

3. **Crystal structure and grain size of intermetallic compounds.** — 3.1 EXPERIMENTAL. — D1A and D1B multidetector powder diffractometer of the Institut Laüe Langevin were used for neutron measurements. Scattering by the 1 mm thick quartz container was easy to correct for. The deuterium pressure (0-10 bar) applied to the sample was continuously monitored.

3.2 $LaNi_5$ ALLOY. — An obvious broadening of *hk*0 lines relative to the instrument resolution of the D1A diffractometer was detected. This indicates a lack of long range coherence in the (a, b) crystalline plane. On the contrary the narrower width of 00*l* diffraction lines shows that there is coherence along the *C* axis leading to a very anisotropic, filament like, metallic sponge model for these *activated* grains. Complementary high resolution X-ray measurements are being made on this interesting phenomenon. Intensities of individual reflections were determined by fitting gaussian peak shapes and from these the structure was refined. The $P6/_m$ mm space group with La atoms on 1a site and Ni atoms on 2c and 3g sites leads to an *R*-factor of 2.9 %, the stoichiometric effect being reflected in the replacement of 2 % La by pairs of Ni in 2e positions [table I], [10].

3.3 $LaNi_{5-x}M_x$ ALLOYS (M = Al, Mn ; $0.5 < x < 2$). — The breadth of diffraction lines found is normal so that the standard profile refinement technique [11] can be used. The same $P6/_m$ mm space group leads to the results of table I. The M atoms exhibit a strong

Table I. — *Intermetallic compounds* $LaNi_{5-x}M_x$

Comp.	$La_{1-s}Ni_{5+2s}$	$LaNi_{4.5}Al_{0.5}$	$LaNi_4Al$	$LaNi_{4.5}Mn_{0.5}$	$LaNi_4Mn$	$LaNi_3Mn_2$
a (Å)	5.017(1)	5.031(1)	5.063(1)	5.042(1)	5.096(1)	5.162(1)
c (Å)	3.993(2)	4.019(1)	4.063(1)	4.014(1)	4.075(1)	4.135(1)
s_{La}	0.020(3)	0.036(7)	0.024(8)	0.027(7)	0.021(6)	0.016(6)
s_1 ($z = 0$)		0.08(6)	0.12(8)	0.06(2)	0.23(5)	0.28(3)
s_2 ($z = \frac{1}{2}$)		0.42(9)	0.94(10)	0.40(3)	0.90(5)	1.62(2)
B_{La}	1.0(2)	0.75(20)	0.87(25)	0.70(14)	1.35(25)	0.6(2)
B_{Ni}	0.8(1)	0.6(1)	0.5(1)	0.6(1)	0.66(7)	0.90(15)
B_M		0.6(1)	0.5(1)	0.6(1)	0.66(7)	0.90(15)
Final Comp.	La Ni 0.98 5.04	La Ni Al 0.96 4.58 0.5	La Ni Al 0.98 3.98 1.06	La Ni Mn 0.97 4.6 0.46	La Ni Mn 0.98 3.9 1.13	La Ni Mn 0.98 3.14 1.9
Residu	2.9 %	5.6 %	8.6 %	6.0 %	8.4 %	8.9 %

Table II. — *Hydrides of intermetallic compounds*

$LaNi_4MnD_6$	a (Å) = 5.437(2)	c (Å) = 4.332(2)			
	Final composition : $La_{0.98}Ni_{3.9}Mn_{1.13}D_{5.97}$ Residu : 8.1 %				
	Thermal B (Å^2) La : 2.1(2) Ni, Mn : 1.3(1) D : 4.0(4)				
D site :	3f	4h	6m	12n	12o
x	0.5	0.33	0.133(1)	0.452(6)	0.227(3)
y	0.0	0.66	0.266(2)	0.0	0.454(6)
z	0.0	0.38(1)	0.5	0.117(9)	0.38(1)
n	0.59(5)	0.33(3)	1.92(9)	2.11(9)	1.02(8)

$LaNi_4AlD_4$	a (Å) = 5.310(2)	c (Å) = 4.249(2)		
	Final composition : $La_{0.98}Ni_{3.98}Al_{1.06}D_{4.8}$ Residu : 2.5 %			
	Thermal B (Å^2) La : 2.0 Ni, Mn : 1.2 D : 2.9			
D site :	3f	6m	12n	12o
x	0.5	0.132(2)	0.438(6)	0.233
y	0.0	0.264(4)	0.0	0.466
z	0.0	0.5	0.112(5)	0.34
n	0.13	1.88	2.64	0.46

preference for the 3g site (amount S_2) relative to the 2c site (amount S_1). There is no obvious difference in the behaviour of Al and Mn atoms.

4. Crystal structure of substituted $LaNi_{5-x}M_xD_y$ hydrides. — Deuterides were used to reduce neutron incoherent scattering. Using the Rietveld technique we have found possible structures for $LaNi_4MnD_6$

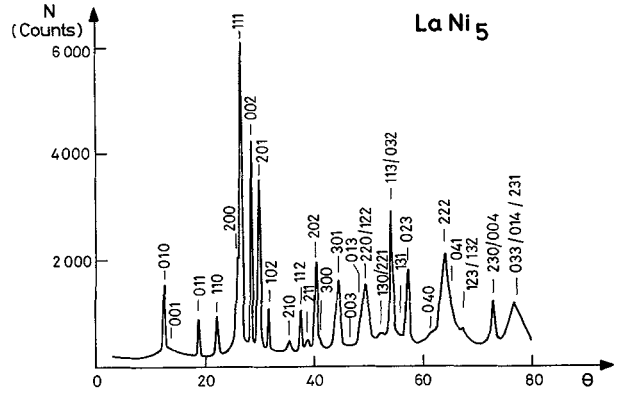

Fig. 2. — Neutron diffractogram of $LaNi_5$ (D1A : $\lambda = 1.909$ Å).

and $LaNi_4AlD_4$ [table II]. Although deuterium atoms are widely distributed on possible sites in qualitative agreement with NMR results [8, 9], some preference exists for the 6m site.

5. **Conclusion.** — We have determined the crystal structure of $LaNi_5$ and substituted Al and Mn alloys. An interesting difference appears to be the existence of subgrains in activated $LaNi_5$ which could be of some importance in rapid hydrogen uptake. We found no obvious correlation between changes of crystal structure and hydrogen content. Complementary X-ray and neutron diffraction measurements are now being made and should help for a better understanding of this interesting class of substituted compounds.

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