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Autor(en): Fischer, P. / Furrer, A. / Busch, G.

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Neutron scattering investigations of the LaNi₅ hydrogen storage system

by P. Fischer and A. Furrer

Institut für Reaktortechnik ETHZ, 5303 Würenlingen

G. Busch and L. Schlapbach

Laboratorium für Festkörperphysik ETHZ, 8093 Zürich

(5. V. 77)

Abstract. Static and dynamic properties of hydrogen in $LaNi_5H_x$ ($0 \le x \le 6$) compounds were determined by neutron scattering. Deuterium positions as well as distribution have been determined by neutron diffraction. The neutron inelastic scattering technique has been used to study the hydrogen diffusion process from the dependence of the quasielastic line width upon momentum transfer. The results are in qualitative agreement with the predictions of a jump diffusion model, and the diffusion parameters are qualitatively discussed in terms of the structure information.

1. Introduction

Metal hydrides and in particular $LaNi_5H_x$ [1] are important with respect to technical applications such as use for hydrogen storage, thermal compression, in electrochemical cells, for catalysis or hydrogen purification.

By means of neutron diffraction investigations hydrogen may be located on an atomic scale (crystal structure) and inelastic neutron scattering experiments provide primary information about the dynamics of hydrogen and in particular concerning hydrogen diffusion. Thus neutron scattering contributes essentially to the understanding of physical properties of metal hydrides.

Preliminary neutron diffraction results are published for LaNi_5D_6 [2] and LaNi_5D_7 [3]. In the former study only hexagonal lattice constants (cf. Table 1) were derived, although the presence of pseudohexagonal twinning due to an orthorhombic structure similar to PrCo_5D_x is assumed. Bowman et al. [3] proposed a structure based on the trigonal space group P31m, which corresponds to two sets of hydrogen sites. Thus hydrogen storage is associated with symmetry reduction compared to the P6/mmm space group symmetry of LaNi_5 . Because of experimental difficulties such as dominant peaks due to the steel sample container the derived structure appears to be rather uncertain.

Various structure models based on space group P6/mmm were tested in a proton nuclear magnetic resonance (NMR) study of LaNi_5H_6 [4], where moreover hydrogen diffusion (cf. also [5]) was investigated. It is concluded that a PrCo_5H_4 like structure has to be rejected for LaNi_5H_6 . Later NMR measurements of LaNi_5H_x and LaNi_5D_x [6] confirm the structure proposed by Bowman et al. [3].

In order to obtain more precise information concerning hydrogen distribution and diffusion neutron scattering experiments were made on deuterated or hydrogenated powder samples of LaNi₅, which do not show magnetic order (Pauli paramagnetism) [2,7]. In the subsequent sections of this paper we describe after discussion of experimental details the structures. In the last part measurements concerning diffusion are presented and discussed with respect to structure. (Concerning preliminary results cf. [8].)

2. Experimental details

LaNi₅ was prepared from 99.9% pure La (Research Chemicals) and 99.998% pure Ni (Koch Light) by induction melting in a water cooled copper boat in high vacuum (2×10^{-6} Torr) and subsequent quenching. X-ray analysis yields hexagonal CaCu₅ type structure for LaNi₅ (concerning lattice constants cf. Table 1).

Pauli paramagnetism of LaNi₅ was verified by measurements of magnetic susceptibility. In order to obtain samples with temperature ($70 \div 300$ K) and field ($0 \div 4$ kOe) independent magnetic susceptibility it was necessary to compensate for small evaporation losses and possible impurity effects of the starting materials by reducing the initial Ni content corresponding to LaNi_{4.97} (susceptibility 4.6 × 10⁻⁶ emu/g).

The samples were hydrogenated or deuterated in stainless steel containers at pressure of 50 bars. Hydrogenation took place within a few minutes and yielded the composition $LaNi_5H_6$ ($LaNi_5D_6$).

For the elastic (inelastic) neutron scattering experiments the samples were enclosed in cylindrical vanadium (aluminium) containers of 1 cm diameter at room temperature under constant deuterium (hydrogen) pressure up to 5 bars. The deuterium (hydrogen) content of LaNi₅ samples was measured by desorption after the neutron experiments. As hydrogenation generally results in very fine powders, LaNi₅ was measured after hydrogenation and subsequent desorption.

The neutron diffraction experiments were performed on two-axis spectrometers at reactor Diorit, Würenlingen with neutrons of wavelength $\lambda = 2.312$ and 1.192 Å, using graphite 002 and Ge 311 as monochromators respectively. The observed intensities were corrected for absorption and incoherent scattering according to the measured transmission of the samples.

The inelastic neutron experiments were carried out on a triple-axis spectrometer at the reactor Diorit. The incoming neutrons filtered by cooled beryllium had an energy of 5 meV. Since the observed line widths due to hydrogen diffusion were rather small, the experiments have been repeated on a MARC spectrometer with improved energy resolution (incoming neutron energy: 4.6 meV) and larger intensity. The agreement between the resulting line widths obtained from the two measurements was satisfactory.

3. Localization of Deuterium

The final diffraction patterns were analyzed by means of the profile method [9], using the neutron scattering lengths $b_{\text{La}} = 8.3 \text{ F}$, $b_{\text{Ni}} = 10.3 \text{ F}$ and $b_{\text{D}} = 6.67 \text{ F}$.

Neutron diffraction measurements were made at room temperature on powder samples of LaNi₅, LaNi₅D_{0.15} (α -phase) and LaNi₅D₆ (β -phase). The composition x corresponds to desorption measurements. Results are summarized in Tables 1 to 3.

Structure paramete space group P6/mm B = Debye-Waller	rs of LaNi ₅ D _x . m (atom positi parameter (int	Standard dev ons: La: 1a, N ensity $\sim e^{-2w}$	iations are g i1:2c, Ni2:3; , $W = B(\sin \theta)$	iven within par g, D: 3f); for $x = \theta(\lambda)^2$). R, RW_p	rentheses and = 6: space g = agreemen	refer to the la roup P31m (a it values conce	tst digit. N de tom position trning integra	notes neutr s: La: la, Ni ted and pro	on diffraction. 1: 2b, Ni2: 3c, file intensities,	For $x = 0, 0.2$: D1: 3c, D2: 6d). respectively [9].
x	0	0.2	t		9		3			.[2] ,2,
		(a)	(q)	(c)	(a)	(9)	(c)	(p)	(e) [2]	
λ [Å] a _N [Å] c _N [Å]	2.312 5.017(5) 3.986(5)	2.312 5.025(5) 3.988(5)	2.312 5.025(5) 3.988(5)	1.192 5.025(5) 3.988(5)	2.312 5.410(5) 4.293(5)	2.312 5.410(5) 4.293(5)	2.312 5.410(5) 4.293(5)	2.312 5.410(5) 4.293(5)	2.57 5.393 4.285	1.142 5.387 4.273
positional										
	0	0	0	0	0	0	0	0		0
$z_{\rm Ni1}$	-	-	-		0.94(1)	0.93(1)	0.93(1)	0.94(1)		0.95
$x_{\rm Ni2}$	0.5	0.5	0.5	0.5	0.480(2)	0.480(2)	0.481(3)	0.476(3)		0.50
$z_{\rm Ni2}$	C.U	0.5	0.5	0.5	0.470(3)	0.471(3)	0.461(7) 0.469(3)	(1)(2)(1)(1)(1)(1)(1)(1)(1)(1)(1)(1)(1)(1)(1)		0.50
10 2 ¹¹		0	0	0	(7)7(7)	0.076(7)	0.076(8)	0.081(7)		0.08
X _{D2}					0.180(4)	0.176(4)	0.179(4)	0.182(4)		0.25
y_{D2} z_{D2}					0.832(4) 0.56(2)	0.828(4) 0.55(2)	0.831(4) 0.56(2)	0.832(4) 0.56(1)		0.86 0.58
deuterium										
DI		0.26(2)	0.15*	0.24(2)	3.0(1)	2.86(4)	2.84(4))	3.6(6)		3.0
D2					3.4(1)	3.14 $\int_{0^{-1}}^{0^{-1}}$	3.16 ⁰⁷	4.2(6)		3.8
$B(B_{\text{La, Ni}}) \left[\overset{\circ}{A}^2 \right]$	1.1(1)	1.3(1)	1.3(1)	0.86(4)	2.0(2)	2.0(2)	2.2(3)	1.0(7)		
R RW	0.037 0.145	0.053 0.135	0.058 0.138	0.067 0.179	0.054 0.173	0.054 0.173	0.054	0.054		

*) Values corresponding to desorption measurements.

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Table 1 Inture para

	I _{calc}	1887	675	5251	2255	17347	4395	523	1417	656	2494	5717	616	450	3342	1162	1098	9984	-	2964	374	1014	240
	$\Delta I_{\rm obs}$	27	37	144	119	161	73	26	62	28	16	114	17	14	95	42	19	142	_	95	26	78	133
(3)	$I_{obs} \pm$	2032	631	6411	2517	17657	4231	510	1321	625	2492	6196	671	487	3653	1293	1109	10004	T	3744	399	1088	159
	h k l	302	3 1 1	203	400	222	401	213	312	320	004	303	104	321	402	4 1 0	114	4 1 1	223	204	313	322	500
	I_{calc}	7575	2	2507	4894	10290	31591	11574	16538	2475	2009	3569	1247	8873	1518	12109	0	419	2266	12692	1012	-	8667
	$\Delta I_{ m obs}$	133	83	107	121	129	197	153	167	118	114	113	88	129	85	161	16	37	69	146	106	-	126
(3)	$I_{obs} \pm$	7903	0	2835	4889	10944	31810	13053	17436	2413	1606	3313	1665	9433	1272	10669	25	517	2532	11554	700	Ι	9408
	$I_{ m calc}$	46406	9	15356	30780	67597	205791	77403	110327	17200	14713	26803	9520	72217	12349	109737	-						
	$\Delta I_{ m obs}$	285	190	241	283	321	494	384	432	307	314	316	238	370	246	514	298						
(2)	$I_{obs} \pm$	42648	0	15539	29849	71893	205352	82744	120328	17144	11413	25199	12156	77180	10229	105778	0						
	$I_{ m calc}$	17275	128	7286	13505	24908	87883	30431	51205	6561	5640	12050	4649	27267	5583	48309	21						
	$\Delta I_{ m obs}$	199	149	180	202	208	331	252	298	212	218	221	162	239	175	353	193						
(1)	$I_{obs} \pm$	16408	314	7511	12897	27127	88227	30348	54563	6674	4571	11790	5002	29514	5088	47970	0						
	h k l	100	001	101	1 1 0	200	111	002	201	1.02	210	1 1 2	2 1 1	202	300	301	003	103	212	220	310	221	113

Table 2 Observed, absorption corrected and calculated integrated intensities of 1) LaNi₅, 2) LaNi₅D_{0.2} (a) and 3) LaNi₅D_{0.2} (c, cf. Table 1).

Table 3

$I_{\rm obs}$ ±	$\Delta I_{\rm obs}$	$I_{\rm calc}$	h k l	I_{obs} ±	$\Delta I_{\rm obs}$	Icalc
53178	347	51064	2 1 1	149	12	115
3065	250	2948	211	2208	181	1705
0	256	292	202	50868	422	52740
10764	294	9174	300	1679	206	1336
64608	339	63173	301	64168	492	62918
136887	446	129343	003	2278	262	3559
84921	435	87889	103	6298	64	5896
32242	354	31736	212	916	7	863
5580	344	9596	$2 \ 1 \ \overline{2}$	13932	104	13127
18244	392	12446	2 2 0	176757	573	173186
8617	337	10451	3 1 0	21770	411	24070
			2 2 1	1995	50	2174
	$\begin{array}{c} I_{obs} & \pm \\ 53178 \\ 3065 \\ 0 \\ 10764 \\ 64608 \\ 136887 \\ 84921 \\ 32242 \\ 5580 \\ 18244 \\ 8617 \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Observed	abaamstian	anneaded on	المغرا بيدا مم			-CLANE	n	(of a	Table 1	1
Observeu,	ausorption	corrected an	a calculated	integrated	intensities	OI Lainis	$\boldsymbol{\nu}_6$	(ci. a,	, radie i	J.

Illustrative diffraction patterns are shown in Fig. 1. Apparently hydrogen storage in LaNi₅ is associated with essential, reversible modifications of the hexagonal CaCu₅ type structure of LaNi₅ (cf. also Tables 2 and 3), yielding ternary compounds. Considerable line broadening due to small grain size of the LaNi₅D_x powders as a consequence of hydrogen absorption and desorption raised difficulties in least squares fitting of the profile intensities. (Despite similar instrumental conditions the peak halfwidths of e.g. La₇Ni₃ were found to be roughly 50% smaller.)

Positions and intensities of the measured* LaNi₅ sample confirm the lattice constants ($a_x = 5.01^*$, 5.017 Å [1]; $c_x = 3.98^*$, 3.987 Å [1]) and the CaCu₅-type structure (cf. Table 1).

At low deuterium concentrations (α -phase) the lattice expands slightly in the basal plane ($\Delta a/a \sim 0.16\%$), whereas c remains almost constant ($\Delta c/c \sim 0.05\%$). Similar X-ray results are mentioned in [2]. In the β -phase (LaNi₅D₆) the unit cell is expanded 8% and 25% with respect to lattice constants and volume respectively – almost without change of the c/a ratio – compared to LaNi₅.

In the α -phase (LaNi₅D_{0.25±0.02} according to neutron diffraction, in reasonable agreement with the composition x = 0.15 determined by desorption, cf. Table 1) best agreement of observed and calculated intensities was obtained for space group P6/mmm (LaNi₅), assuming a statistical distribution of deuterium on or at least "centered" on positions $3f(\frac{1}{2}00, 0\frac{1}{2}0, \frac{1}{2}\frac{1}{2}0)$. The small deuterium concentration renders a precise localization of deuterium difficult, because the contribution to the structure factor is correspondingly small (R = 0.069 at $\lambda = 2.312$ Å, neglecting deuterium). Therefore it is intended to perform also measurements on a LaNi₅D_x sample with maximum deuterium content in the α -phase ($x \sim 0.5$ [1]). Considering the structure model, a main lattice expansion within the basal plane is expected. Presumably the local distortions around deuterium atoms are larger than the average distortions reflected in the lattice constants.

Concerning the β -phase (x = 6) the interpretation of the measurements does not appear to be possible within the context of the P6/mmm space group of LaNi₅, in agreement with previous investigations [3, 6]. Reasonable fits of the measured integrated intensities were obtained for space group P31m ($R \sim 0.05$, cf. Table 1) and less satisfactory agreement results for space groups P3 (deuterium D on sites 3d and 3d',





 $R \sim 0.08$) and P3m1 (D on 3d and 3d', $R \sim 0.10$). Results of calculations based on different numbers of parameters are compared in Table 1 (a ÷ d), which yield the same R value. The neutron intensities indicate a deuterium content $x = 6.4 \pm 0.2$, in reasonable agreement with the value 6.0 determined by desorption. Positional parameters and deuterium distribution do not depend essentially on the assumptions made concerning thermal motion, except for d, Table 1, where the too large x value is caused by correlations with the temperature factor of deuterium. Insertion of large amounts of deuterium in LaNi₅ leads to a marked distortion of the Ni configuration (cf. Table 1). The crystal structure (space group P31m) of LaNi₅D₆ is shown in Fig. 2. It corresponds to the model proposed by Bowman et al. [3], which implies a statistical distribution of approximately 3 deuterium atoms on tetrahedral sites 6d (D2) and completely occupied (3D) tetrahedral sites 3c (D1). The corresponding smallest Ni–D distances of 1.45 to 1.74 Å are remarkably short. Of reasonable magnitude appear the smallest La–D distances of 2.50 to 2.91 Å. Concerning hydrogen diffusion the shortest D–D distances of 1.57 and 1.69 Å (D2–D2), 2.48 Å (D1–D2), 2.59 Å (D2–D2), 2.61 Å and 2.68 Å (D1–D2), 2.72 Å (D1–D1), 2.79 Å (D1–D2) as well as 2.83 Å and 3.06 Å (D2–D2) are presumably of importance. Seemingly sites 3c (corresponding approximately to positions 3f with respect to space group P6/mmm) are first filled during hydrogen storage. Finally interstices 3c are 100% and positions 6d 57% occupied in LaNi₅D₆.



Figure 2

Projection of the crystal structure of LaNi_5D_6 (space group P31m) on the basal plane perpendicular to [001] (basic translations *a*, *b*). Four units cells are shown. Atomic radii of La (\cdots : z = 0) and Ni (--: z = -0.06, ---: z = 0.482) are estimated on the basis of the LaNi₅ structure ($r_{\text{La}} \sim 1.99$ Å, $r_{\text{Ni}} \sim 1.25$ Å). Open (z = 0.077) and filled circles (z = 0.56) indicate approximately 100 and 50% occupied deuterium positions respectively.

4. Hydrogen diffusion in LaNi₅H_x

The neutron inelastic scattering technique has been used to study the dynamics of hydrogen in LaNi₅H_x (x = 0, 0.2, 6) at room temperature. Such measurements can provide information about the diffusion constant, diffusion rates and activation energies. Furthermore, in some cases hydrogen jump distances and directions and thus site occupations can be determined from the dependence of the quasielastic line width Γ upon momentum transfer $\hbar Q$.

In the data analysis the scattering contributions of LaNi_5 have been subtracted from the observed energy spectra of LaNi_5H_x by taking account of the different transmission factors due to hydrogenation. Then the resulting quasielastic peaks have been fitted to a single Lorentzian folded over the incident neutron spectrum, with the width and height as fitting parameters. The measured widths Γ for x = 6 are shown in Fig. 3 which displays a broad maximum at $Q = 1.6 \text{ Å}^{-1}$. The experiments for x = 0.2 are not yet completed, but the results obtained so far indicate a similar maximum shifted to $Q = 2.3 \text{ Å}^{-1}$.



Figure 3

Widths Γ of the quasielastic line for neutron scattering from hydrogen in LaNi₅H₆ as a function of Q^2 ($\hbar Q$ = momentum transfer) at room temperature.

Our results are in qualitative agreement with the predictions of a jump diffusion model, supposing that the diffusion process consists of thermally activated steps which are statistically independent. This assumption is likely to be justified if the hydrogen atom performs many oscillations between successive steps. Furthermore, we neglect the time needed for a jump from site to site compared to the mean time of stay τ ($1/\tau$ = mean jump rate). Finally we assume that correlation effects do not affect the jump probability. This may hold even for the high hydrogen concentration

in $LaNi_5H_6$, since there are many unoccupied interstitial positions available (see Fig. 2). The jump diffusion model yields [10]

$$\Gamma = \frac{2\hbar}{n\tau} \sum_{j=1}^{n} (1 - \exp\{-i\mathbf{Q} \cdot \mathbf{R}_j\}), \qquad (1)$$

where \mathbf{R}_{j} is the jump vector. From the maximum in Fig. 3 we obtain for LaNi₅H₆ jump lengths of the order of 4 Å which are considerably larger than the shortest H–H distances. On the other hand the preliminary results for LaNi₅H_{0.2} suggest jump distances of 2.5 ÷ 3 Å in agreement with the shortest H–H distances given in Section 3.

For $Q \rightarrow 0$ equation (1) approaches

$$\Gamma = 2\hbar D Q^2,\tag{2}$$

i.e. the diffusion constant D can be determined from the initial slope of Γ vs. Q^2 . From Fig. 3 we obtain for LaNi₅H₆ $D = (1.2 \pm 0.5) \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ which is an order of magnitude larger than the value obtained from NMR studies [4]. Results for LaNi₅H_{0.2} are not yet available in the low Q region.

5. Conclusions

The main features of deuterium storage in hexagonal LaNi₅D_x compounds have been established with respect to crystal structure by means of neutron diffraction. Associated with the formation of ternary compounds the lattice expands, and reversible modifications of the CaCu₅-type structure of LaNi₅ occur. In the α -phase ($x \sim 0.2$) deuterium is distributed on sites 3f (space group P6/mmm as for x = 0), corresponding to primary expansion in the basal plane. In the case of large deuterium concentration (β -phase, $x \sim 6$) the unit cell is expanded 25% with respect to volume, almost with the same c/a ratio as for LaNi₅. The structure parameters of the model based on space group P31m [3] are refined. The Ni configuration is considerably distorted compared to LaNi₅. Deuterium fills tetrahedral interstices 3c and occupies 57% of tetrahedral sites 6d according to a statistical distribution.

The inelastic neutron scattering results provide information concerning the dynamics of hydrogen in the hydrogen storage system LaNi_5H_x . The data are qualitatively discussed in terms of a jump diffusion model and related to the structure. The diffusion constant $D = (1.2 \pm 0.5) \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ is an order of magnitude larger than the value obtained from NMR studies [4]. From the size of the diffusion constant we conclude that diffusion does not control the hydrogen sorption rates in LaNi₅ compounds.

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REFERENCES

- [1] H. H. VAN MAL, Philips Res. Repts Suppl. 1 (1976).
- [2] F. A. KUIJPERS, Philips Res. Repts Suppl. 2 (1973).
- [3] A. L. BOWMAN, J. L. ANDERSON and N. G. NERESON, Proc. Tenth Rare Earth Res. Conf., Carefree, Arizona (1973) p. 485.
- [4] T. K. HALSTEAD, J. Solid State Chem. 11, 114 (1974).
- [5] T. K. HALSTEAD, N. A. ABOOD and K. H. J. BUSCHOW, Solid State Commun. 19, 425 (1976).
- [6] R. G. BARNES, W. C. HARPER, S. O. NELSON, D. K. THOME and D. R. TORGESON, J. Less Common Met. 49, 483 (1976).
- [7] H. OESTERREICHER, J. CLINTON and H. BITTNER, Mat. Res. Bull. 11, 1241 (1976).
- [8] G. BUSCH, L. SCHLAPBACH, W. THOENI, TH. V. WALDKRICH, P. FISCHER, A. FURRER and W. HÄLG, Second International Congress on Hydrogen in Metals, Paris (1977).
- [9] H. M. RIETVELD, RCN-Report 104 (Petten, The Netherlands 1969).
 W. VON WARTBURG, Report AF-SSP-46 (IRT, Würenlingen 1970).
- [10] See for example T. Springer, Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids (Springer, Berlin, 1972).