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Neutron scattering investigations of the LaNi_5 hydrogen storage system

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(5. V. 77)

Abstract. Static and dynamic properties of hydrogen in LaNi_5H_x ($0 \leq x \leq 6$) 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 pseudo-hexagonal 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 LaNi_5 , 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

LaNi_5 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 CaCu_5 type structure for LaNi_5 (concerning lattice constants cf. Table 1).

Pauli paramagnetism of LaNi_5 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 $\text{LaNi}_{4.97}$ (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 LaNi_5 samples was measured by desorption after the neutron experiments. As hydrogenation generally results in very fine powders, LaNi_5 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 $b_{\text{La}} = 8.3$ F, $b_{\text{Ni}} = 10.3$ F and $b_{\text{D}} = 6.67$ F.

Neutron diffraction measurements were made at room temperature on powder samples of LaNi_5 , $\text{LaNi}_5\text{D}_{0.15}$ (α -phase) and LaNi_5D_6 (β -phase). The composition x corresponds to desorption measurements. Results are summarized in Tables 1 to 3.

Table 1

Structure parameters of LaNi_5D_x . Standard deviations are given within parentheses and refer to the last digit. N denotes neutron diffraction. For $x = 0, 0.2$: space group $\text{P6}/\text{mm}$ (atom positions: La: 1a, Ni1: 2c, Ni2: 3g, D: 3f); for $x = 6$: space group P31m (atom positions: La: 1a, Ni1: 2b, Ni2: 3c, D1: 3c, D2: 6d). B = Debye-Waller parameter (intensity $\sim e^{-2W}$, $W = B(\sin \theta/\lambda)^2$). R , RW_p = agreement values concerning integrated and profile intensities, respectively [9].

x	0	0.2	6						γ [3]
	(a)	(b)	(c)	(a)	(b)	(c)	(d)	(e) [2]	
λ [Å]	2.312	2.312	2.312	2.312	2.312	2.312	2.312	2.57	1.142
a_N [Å]	5.017(5)	5.025(5)	5.025(5)	5.410(5)	5.410(5)	5.410(5)	5.410(5)	5.393	5.387
c_N [Å]	3.986(5)	3.988(5)	3.988(5)	4.293(5)	4.293(5)	4.293(5)	4.293(5)	4.285	4.273
positional parameters									
z_{La}	0	0	0	0	0	0	0		0
z_{Ni1}	1	1	1	0.94(1)	0.93(1)	0.93(1)	0.94(1)		0.95
x_{Ni2}	0.5	0.5	0.5	0.480(2)	0.480(2)	0.481(3)	0.476(3)		0.50
z_{Ni2}	0.5	0.5	0.5	0.482(8)	0.479(8)	0.481(7)	0.483(7)		0.48
x_{D1}	0.5	0.5	0.5	0.470(3)	0.471(3)	0.469(3)	0.477(5)		0.50
z_{D1}	0	0	0	0.077(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}				0.832(4)	0.828(4)	0.831(4)	0.832(4)		0.86
z_{D2}				0.56(2)	0.55(2)	0.56(2)	0.56(1)		0.58
deuterium distribution									
D1	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	3.16	4.2(6)		3.8
$B(B_{\text{La, Ni}})$ [Å ²]	1.1(1)	1.3(1)	0.86(4)	2.0(2)	2.0(2)	2.2(3)	1.0(7)		
B_D						1.6(3)	4(1)		
R	0.037	0.053	0.067	0.054	0.054	0.054	0.054		
RW_p	0.145	0.135	0.179	0.173	0.173	0.173	0.172		

*) Values corresponding to desorption measurements.

Table 2
Observed, absorption corrected and calculated integrated intensities of 1) LaNi_5 , 2) $\text{LaNi}_5\text{D}_{0.2}$ (a) and 3) $\text{LaNi}_5\text{D}_{0.2}$ (c, cf. Table 1).

(1)			(2)			(3)			(3)				
<i>h k l</i>	<i>I</i> _{obs}	Δ <i>I</i> _{obs} ±	<i>I</i> _{calc}	<i>I</i> _{obs}	Δ <i>I</i> _{obs} ±	<i>I</i> _{calc}	<i>I</i> _{obs}	Δ <i>I</i> _{obs} ±	<i>I</i> _{calc}	<i>h k l</i>	<i>I</i> _{obs}	Δ <i>I</i> _{obs} ±	<i>I</i> _{calc}
1 0 0	16408	199	17275	42648	285	46406	7903	133	7575	3 0 2	2032	27	1887
0 0 1	314	149	128	0	190	6	0	83	2	3 1 1	631	37	675
1 0 1	7511	180	7286	15539	241	15356	2835	107	2507	2 0 3	6411	144	5251
1 1 0	12897	202	13505	29849	283	30780	4889	121	4894	4 0 0	2517	119	2255
2 0 0	27127	208	24908	71893	321	67597	10944	129	10290	2 2 2	17657	161	17347
1 1 1	88227	331	87883	205352	494	205791	31810	197	31591	4 0 1	4231	73	4395
0 0 2	30348	252	30431	82744	384	77403	13053	153	11574	2 1 3	510	26	523
2 0 1	54563	298	51205	120328	432	110327	17436	167	16538	3 1 2	1321	79	1417
1 0 2	6674	212	6561	17144	307	17200	2413	118	2475	3 2 0	625	28	656
2 1 0	4571	218	5640	11413	314	14713	1606	114	2009	0 0 4	2492	91	2494
1 1 2	11790	221	12050	25199	316	26803	3313	113	3569	3 0 3	6196	114	5717
2 1 1	5002	162	4649	12156	238	9520	1665	88	1247	1 0 4	671	17	616
2 0 2	29514	239	27267	77180	370	72217	9433	129	8873	3 2 1	487	14	450
3 0 0	5088	175	5583	10229	246	12349	1272	85	1518	4 0 2	3653	95	3342
3 0 1	47970	353	48309	105778	514	109737	10669	161	12109	4 1 0	1293	42	1162
0 0 3	0	193	21	0	298	1	25	91	0	1 1 4	1109	19	1098
1 0 3							517	37	419	4 1 1	10004	142	9984
2 1 2							2532	69	2266	2 2 3	1	1	1
2 2 0							11554	146	12692	2 0 4	3744	95	2964
3 1 0							700	106	1012	3 1 3	399	26	374
2 2 1							1	1	1	3 2 2	1088	78	1014
1 1 3							9408	126	8667	5 0 0	159	133	240

Table 3
Observed, absorption corrected and calculated integrated intensities of LaNi_5D_6 (cf. a, Table 1).

$h\ k\ l$	I_{obs}	\pm	ΔI_{obs}	I_{calc}	$h\ k\ l$	I_{obs}	\pm	ΔI_{obs}	I_{calc}
1 0 0	53178		347	51064	2 1 1	149		12	115
0 0 1	3065		250	2948	2 1 $\bar{1}$	2208		181	1705
1 0 1	0		256	292	2 0 2	50868		422	52740
1 1 0	10764		294	9174	3 0 0	1679		206	1336
2 0 0	64608		339	63173	3 0 1	64168		492	62918
1 1 1	136887		446	129343	0 0 3	2278		262	3559
0 0 2	84921		435	87889	1 0 3	6298		64	5896
2 0 1	32242		354	31736	2 1 2	916		7	863
1 0 2	5580		344	9596	2 1 $\bar{2}$	13932		104	13127
2 1 0	18244		392	12446	2 2 0	176757		573	173186
1 1 2	8617		337	10451	3 1 0	21770		411	24070
					2 2 1	1995		50	2174

Illustrative diffraction patterns are shown in Fig. 1. Apparently hydrogen storage in LaNi_5 is associated with essential, reversible modifications of the hexagonal CaCu_5 type structure of LaNi_5 (cf. also Tables 2 and 3), yielding ternary compounds. Considerable line broadening due to small grain size of the LaNi_5D_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. La_7Ni_3 were found to be roughly 50% smaller.)

Positions and intensities of the measured* LaNi_5 sample confirm the lattice constants ($a_x = 5.01^*$, 5.017 \AA [1]; $c_x = 3.98^*$, 3.987 \AA [1]) and the CaCu_5 -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 (LaNi_5D_6) 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 LaNi_5 .

In the α -phase ($\text{LaNi}_5\text{D}_{0.25 \pm 0.02}$ 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 $\text{P6}/\text{mmm}$ (LaNi_5), assuming a statistical distribution of deuterium on or at least “centered” on positions $3f$ ($\frac{1}{2} 0 0$, $0 \frac{1}{2} 0$, $\frac{1}{2} \frac{1}{2} 0$). 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 $\lambda = 2.312\text{ \AA}$, neglecting deuterium). Therefore it is intended to perform also measurements on a LaNi_5D_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 $\text{P6}/\text{mmm}$ space group of LaNi_5 , 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 $3d'$,

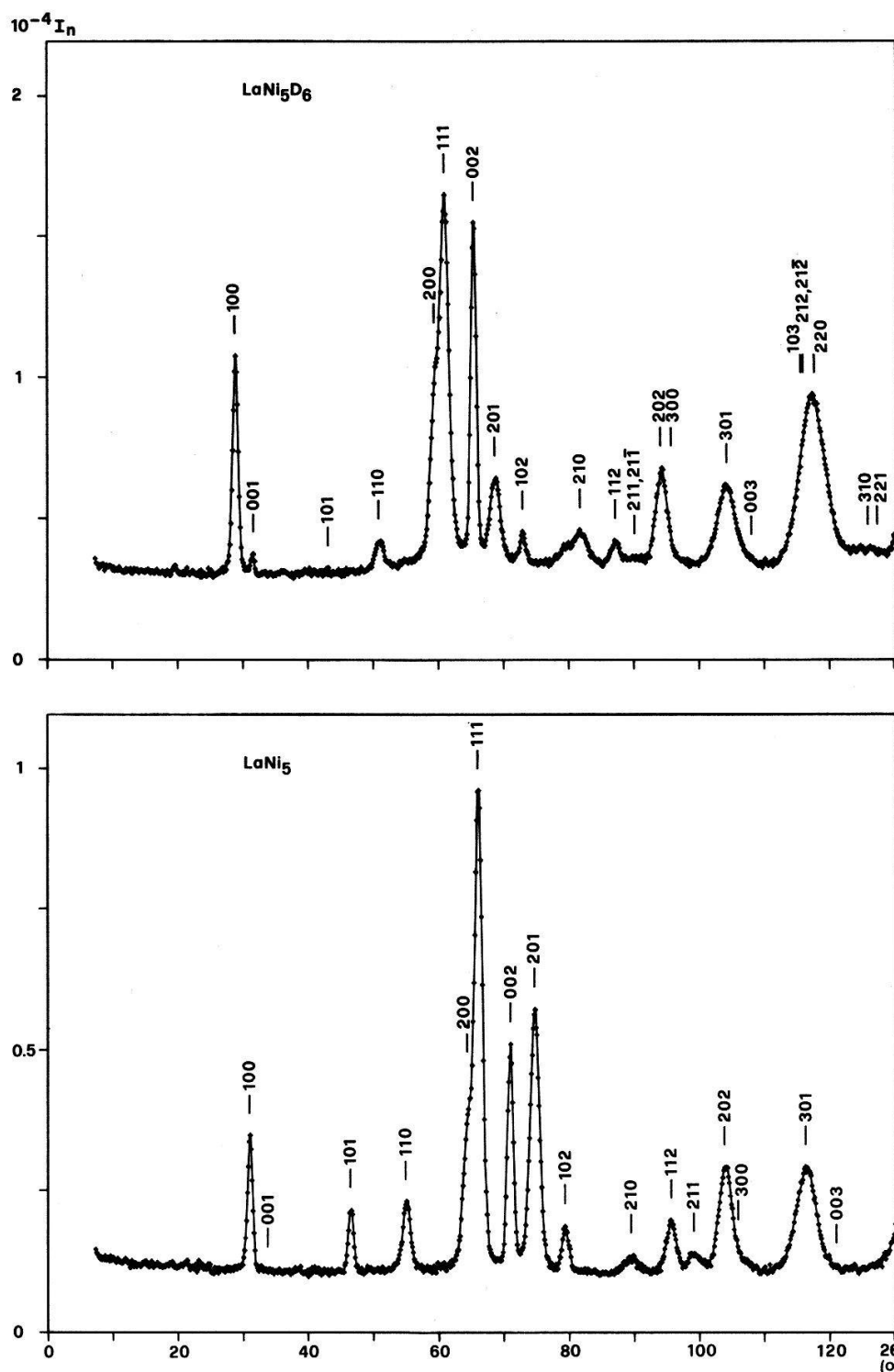


Figure 1
Neutron diffraction patterns (absorption corrected) of LaNi_5 and LaNi_5D_6 . 2θ = scattering angle, I_n = neutron intensity.

$R \sim 0.08$) 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 LaNi_5 leads to a marked distortion of the Ni configuration (cf. Table 1). The crystal structure (space group $P31m$) of LaNi_5D_6 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 LaNi_5D_6 .

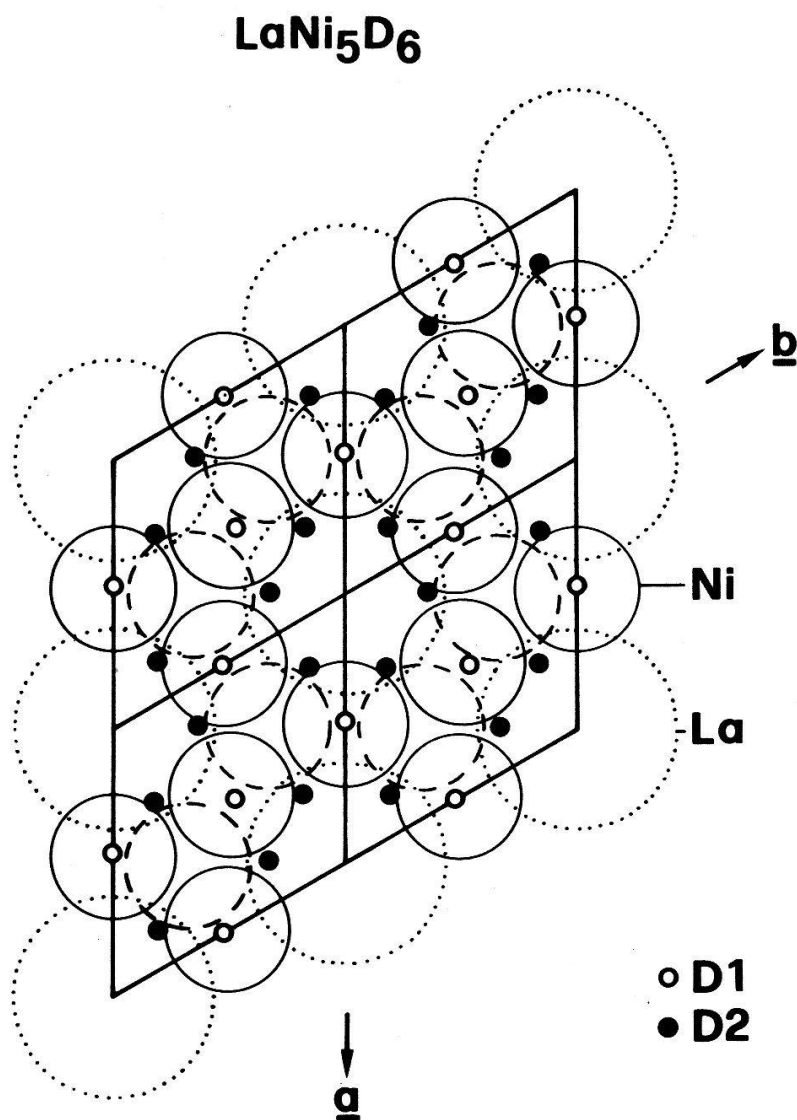


Figure 2

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 LaNi_5 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 LaNi_5H_x

The neutron inelastic scattering technique has been used to study the dynamics of hydrogen in LaNi_5H_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 $Q = 1.6 \text{ \AA}^{-1}$. The experiments for $x = 0.2$ are not yet completed, but the results obtained so far indicate a similar maximum shifted to $Q = 2.3 \text{ \AA}^{-1}$.

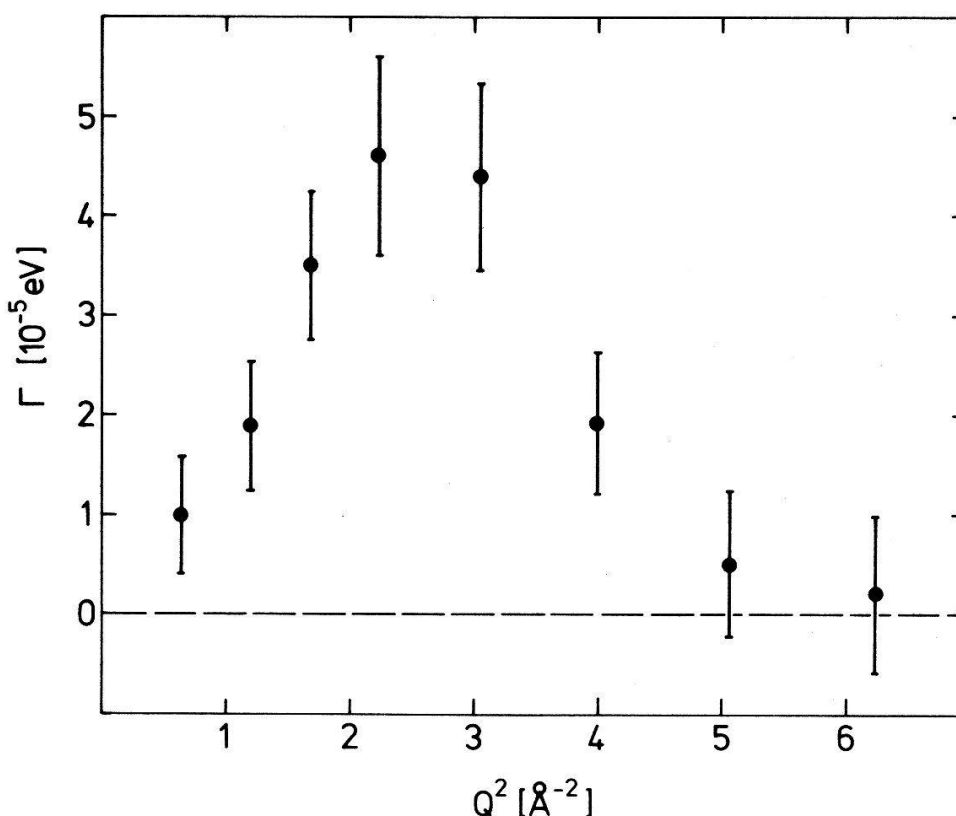


Figure 3

Widths Γ of the quasielastic line for neutron scattering from hydrogen in LaNi_5H_6 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]

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

where \mathbf{R}_j is the jump vector. From the maximum in Fig. 3 we obtain for LaNi_5H_6 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 $\text{LaNi}_5\text{H}_{0.2}$ suggest jump distances of $2.5 \div 3$ Å in agreement with the shortest H–H distances given in Section 3.

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

$$\Gamma = 2\hbar D Q^2, \quad (2)$$

i.e. the diffusion constant D can be determined from the initial slope of Γ vs. Q^2 . From Fig. 3 we obtain for LaNi_5H_6 $D = (1.2 \pm 0.5) \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ which is an order of magnitude larger than the value obtained from NMR studies [4]. Results for $\text{LaNi}_5\text{H}_{0.2}$ are not yet available in the low Q region.

5. Conclusions

The main features of deuterium storage in hexagonal LaNi_5D_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 CaCu_5 -type structure of LaNi_5 occur. In the α -phase ($x \sim 0.2$) deuterium is distributed on sites 3f (space group $\text{P6}/\text{mmm}$ 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 LaNi_5 . The structure parameters of the model based on space group P31m [3] are refined. The Ni configuration is considerably distorted compared to LaNi_5 . 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 LaNi_5 compounds.

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