Neutron scattering investigations of the LaNi$_5$ 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$_5$H$_x$ ($0 \leqslant x \leqslant 6$) 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$_5$H$_x$ [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$_5$D$_6$ [2] and LaNi$_5$D$_7$ [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$_5$D$_x$ 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$_5$H$_6$ [4], where moreover hydrogen diffusion (cf. also [5]) was investigated. It is concluded that a PrCo$_5$H$_4$ like structure has to be rejected for LaNi$_5$H$_6$. Later NMR measurements of LaNi$_5$H$_x$ and LaNi$_5$D$_x$ [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 $LaNi_{4.97}$ (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 $b_{La} = 8.3$ F, $b_{Ni} = 10.3$ F and $b_D = 6.67$ F.

Neutron diffraction measurements were made at room temperature on powder samples of $LaNi_5$, $LaNi_5D_{0.15}$ (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$_5$D$_x$. Standard deviations are given within parentheses and refer to the last digit. N denotes neutron diffraction. For $x = 0$, 0.2: space group P6/mmm (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					
		(a)	(b)	(c)	(a)	(b)	(c)	(d)	(e) [2]	'7' [3]
λ [Å]	2.312	2.312	2.312	1.192	2.312	2.312	2.312	2.312	2.57	1.142
a_N [Å]	5.017(5)	5.025(5)	5.025(5)	5.025(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)	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		0
z_{Ni1}	1	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	0.5	0.480(2)	0.480(2)	0.481(3)	0.476(3)		0.50
z_{Ni2}	0.5	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) }6*	2.84(4) }6*	3.6(6)		3.0
D2					3.4(1)	3.14	3.16	4.2(6)		3.8
$B(B_{La, Ni})$ [Å²]	1.1(1)	1.3(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	0.058	0.067	0.054	0.054	0.054	0.054		
RW_p	0.145	0.135	0.138	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) LaNi$_5$D$_{0.2}$ (a) and 3) LaNi$_5$D$_{0.2}$ (c, cf. Table 1).

h k l	(1) I_{obs}	±	ΔI_{obs}	I_{calc}	(2) I_{obs}	±	ΔI_{obs}	I_{calc}	(3) I_{obs}	±	ΔI_{obs}	I_{calc}
1 0 0	16408	±	199	17275	42648	±	285	46406	7903	±	133	7575
0 0 1	314		149	128	0		190	6	0		83	2
1 0 1	7511		180	7286	15539		241	15356	2835		107	2507
1 1 0	12897		202	13505	29849		283	30780	4889		121	4894
2 0 0	27127		208	24908	71893		321	67597	10944		129	10290
1 1 1	88227		331	87883	205352		494	205791	31810		197	31591
0 0 2	30348		252	30431	82744		384	77403	13053		153	11574
2 0 1	54563		298	51205	120328		432	110327	17436		167	16538
1 0 2	6674		212	6561	17144		307	17200	2413		118	2475
2 1 0	4571		218	5640	11413		314	14713	1606		114	2009
1 1 2	11790		221	12050	25199		316	26803	3313		113	3569
2 1 1	5002		162	4649	12156		238	9520	1665		88	1247
2 0 2	29514		239	27267	77180		370	72217	9433		129	8873
3 0 0	5088		175	5583	10229		246	12349	1272		85	1518
3 0 1	47970		353	48309	105778		514	109737	10669		161	12109
0 0 3	0		193	21	0		298	1	25		91	0
1 0 3									517		37	419
2 1 2									2532		69	2266
2 2 0									11554		146	12692
3 1 0									700		106	1012
2 2 1									1		1	1
1 1 3									9408		126	8667

h k l	(3) I_{obs}	±	ΔI_{obs}	I_{calc}
3 0 2	2032	±	27	1887
3 1 1	631		37	675
2 0 3	6411		144	5251
4 0 0	2517		119	2255
2 2 2	17657		161	17347
4 0 1	4231		73	4395
2 1 3	510		26	523
3 1 2	1321		79	1417
3 2 0	625		28	656
0 0 4	2492		91	2494
3 0 3	6196		114	5717
1 0 4	671		17	616
3 2 1	487		14	450
4 0 2	3653		95	3342
4 1 0	1293		42	1162
1 1 4	1109		19	1098
4 1 1	10004		142	9984
2 2 3	1		1	1
2 0 4	3744		95	2964
3 1 3	399		26	374
3 2 2	1088		78	1014
5 0 0	159		133	240

Table 3
Observed, absorption corrected and calculated integrated intensities of LaNi$_5$D$_6$ (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$_5$D$_x$ 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$_7$Ni$_3$ 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 Å [1]; c_X = 3.98*, 3.987 Å [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$_5$D$_6$) 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 (LaNi$_5$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 P6/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 $\lambda = 2.312$ Å, neglecting deuterium). Therefore it is intended to perform also measurements on a LaNi$_5$D$_x$ 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 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',
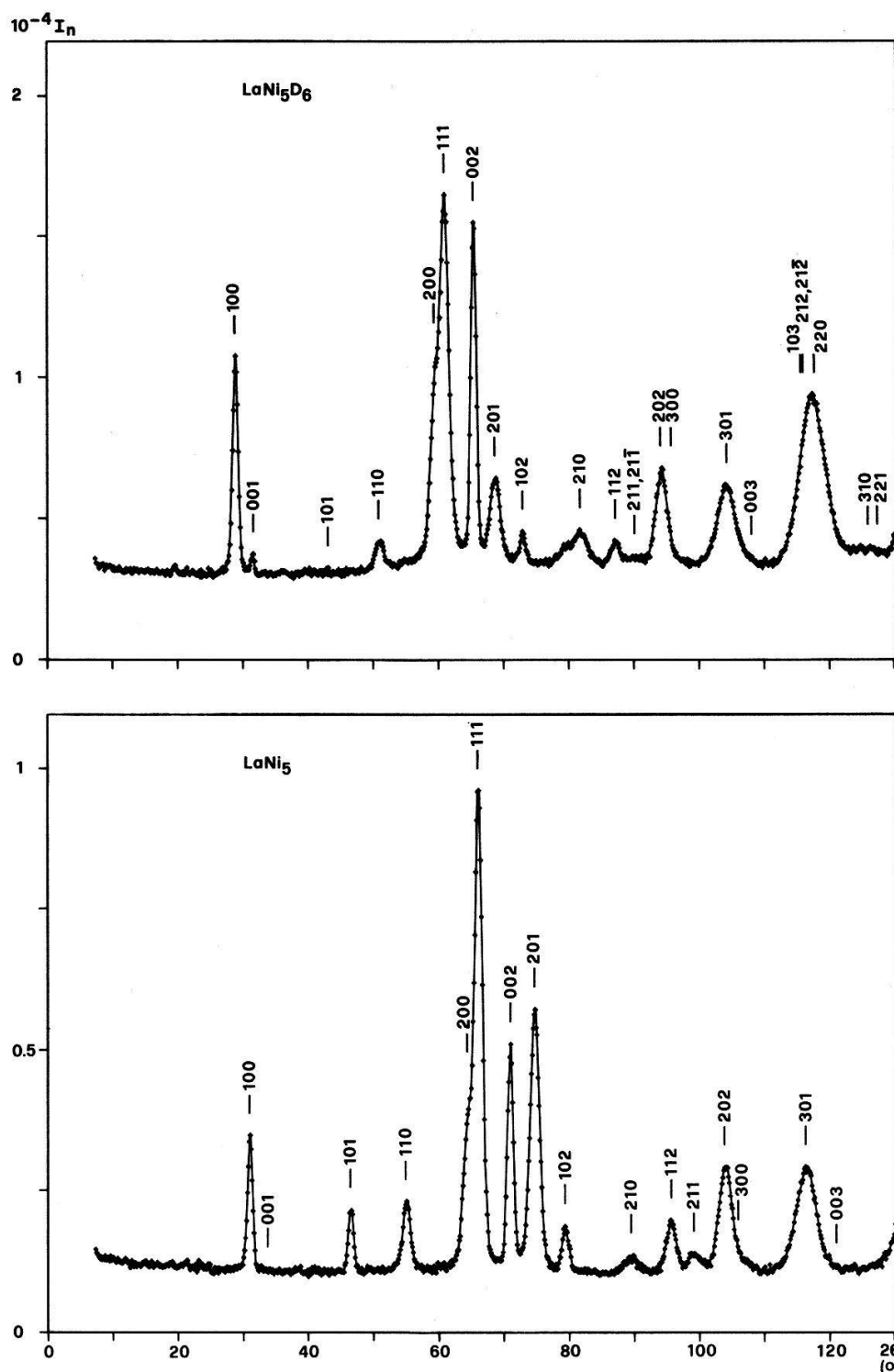
Figure 1
Neutron diffraction patterns (absorption corrected) of LaNi$_5$ and LaNi$_5$D$_6$. 2θ = scattering angle, I_n = neutron intensity.

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 $\div$ 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 $LaNi_5D_6$.
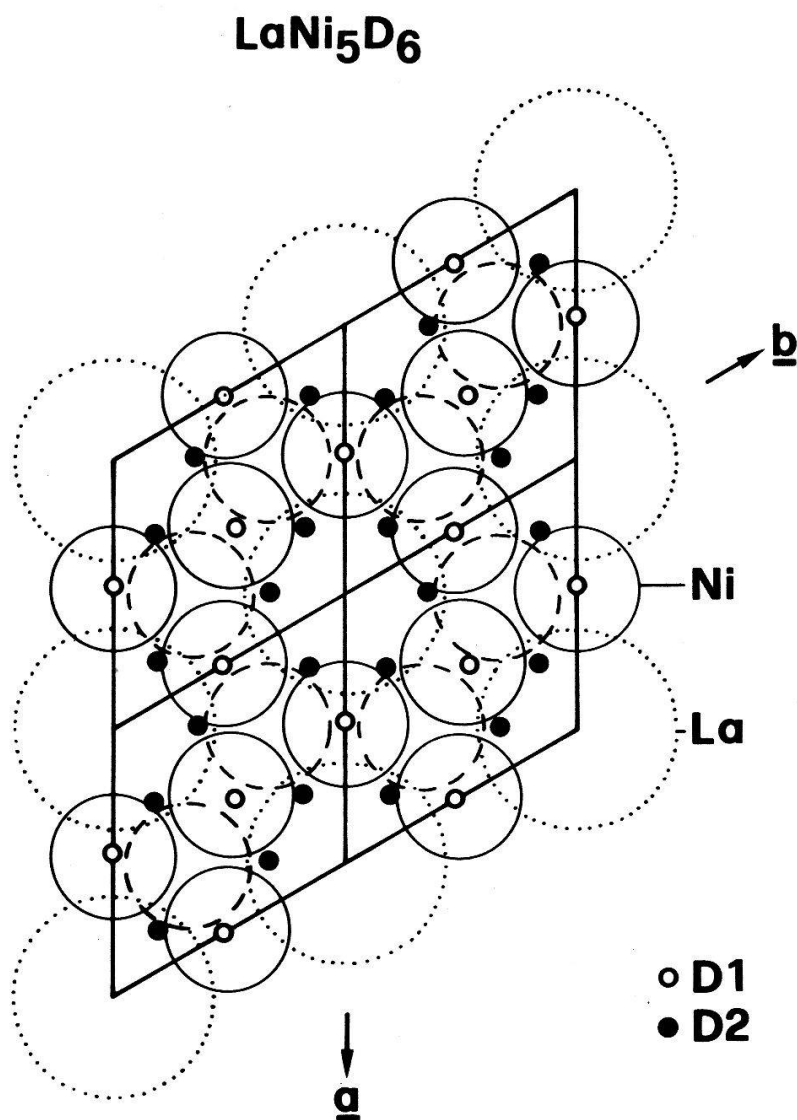

LaNi₅D₆

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 $LaNi_5$ structure ($r_{La} \sim 1.99$ Å, $r_{Ni} \sim 1.25$ 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 $Q = 1.6$ Å^{-1}. The experiments for $x = 0.2$ are not yet completed, but the results obtained so far indicate a similar maximum shifted to $Q = 2.3$ Å^{-1}.
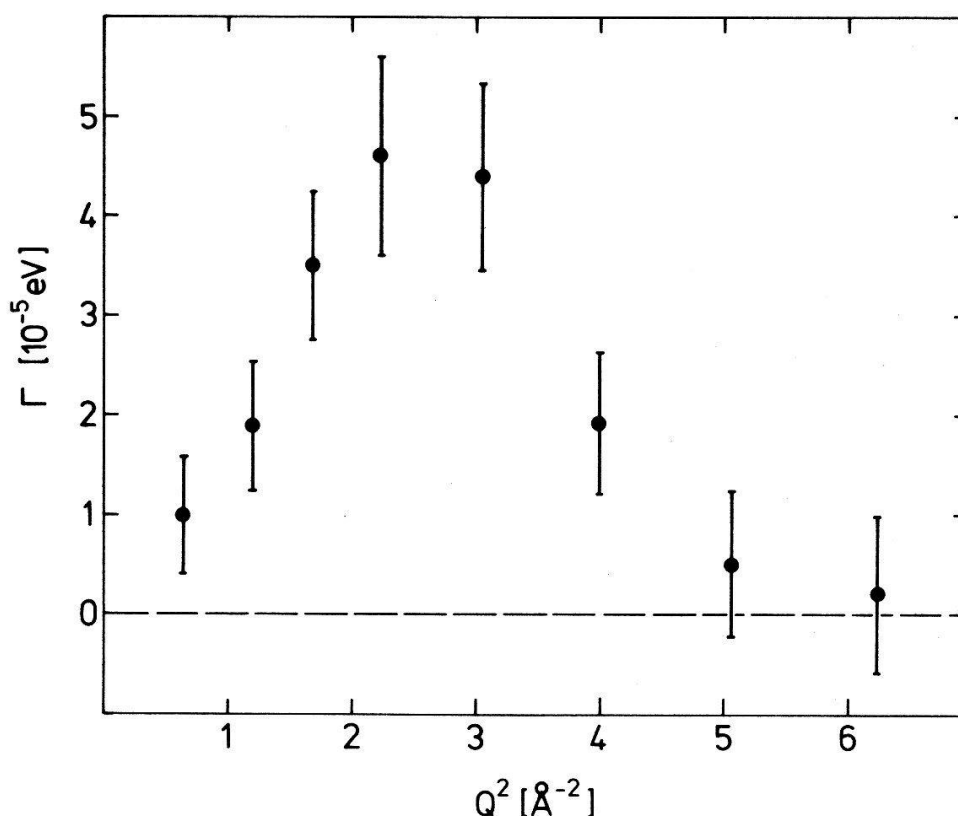

Figure 3
Widths Γ of the quasielastic line for neutron scattering from hydrogen in $LaNi_5H_6$ as a function of Q^2 ($\hbar Q$ = momentum transfer) at room temperature.

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]

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

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 $LaNi_5H_{0.2}$ 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

$$\Gamma = 2\hbar DQ^2, \tag{2}$$

i.e. the diffusion constant D can be determined from the initial slope of Γ vs. Q^2. From Fig. 3 we obtain for $LaNi_5H_6$ $D = (1.2 \pm 0.5) \times 10^{-6}$ cm²s⁻¹ which is an order of magnitude larger than the value obtained from NMR studies [4]. Results for $LaNi_5H_{0.2}$ 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 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 $LaNi_5$. 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 $D = (1.2 \pm 0.5) \times 10^{-6}$ cm²s⁻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.

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).