HYDROGEN DIFFUSION IN $LaNi_5H_6$ STUDIED BY QUASI-ELASTIC NEUTRON SCATTERING*

D. RICHTER and R. HEMPELMANN

Institut für Festkörperforschung, Kernforschungsanlage Jülich, Jülich (F.R.G.)

L. A. VINHAS

Instituto de Pesquisas Energéticas e Nucleares, São Paulo (Brazil)

(Received January 1982)

Summary

We present the results of new high resolution quasi-elastic neutron scattering measurements of the hydrogen diffusion coefficient in $LaNi_5H_6$ between 280 and 400 K. The crucial importance of multiple-scattering corrections in the evaluation of data at small momentum transfers is demonstrated. The diffusion coefficient follows the equation

$$D = (2.1 \pm 0.7) \times 10^{-3} \exp\{-(275 \pm 15)\ \text{meV}/kT\}\ \text{cm}^2\ \text{s}^{-1}$$

and decreases with decreasing hydrogen concentration. The anomalous concentration dependence and the existence of composite spectra at large momentum transfers is explained by hydrogen diffusion in the presence of structural traps.

1. Introduction

The intermetallic hydride $LaNi_5H_6$ is considered to be a prototype material for hydrogen storage. In addition to its desirable properties for practical applications, the $LaNi_5H_x$ system offers challenging opportunities for fundamental research. A topic of considerable interest is the mobility of hydrogen in intermetallic compounds where some unusual diffusional behaviour may occur which in general does not take place in dilute solutions of hydrogen in monatomic solids: (i) the more complicated structures provide different energetically non-equivalent hydrogen sites, some of which may act as structural traps [1]; (ii) owing to the high hydrogen concentration blocking effects, which may induce hydrogen back jump effects and hence alter the "local" hydrogen mobility on an atomic length scale [2], are important.

*Paper presented at the International Symposium on the Properties and Applications of Metal Hydrides, Toba, Japan, May 30 - June 4, 1982.

0022-5088/82/0000-0000/$02.75

Although the system $LaNi_5H_x$ has been studied a number of times using nuclear magnetic resonance (NMR) [3 - 8] and quasi-elastic neutron scattering (QNS) [9 - 12], the hydrogen diffusion coefficient and the activation energy for hydrogen diffusion in this material are not accurately known. The NMR results for the activation energy range from 230 meV [5] to 410 meV [8] while the diffusion coefficients at room temperature range from 0.7×10^{-8} cm^2 s^{-1} [7] to 11×10^{-8} cm^2 s^{-1} [5]. The neutron scattering results do not appear to be more reliable and are distributed between 110 meV [12] and 240 meV [11] and between 0.8×10^{-8} cm^2 s^{-1} [11] and 250×10^{-8} cm^2 s^{-1} [10] respectively. With the exception of the work reported in ref. 11, the neutron scattering measurements suffered from insufficient resolution and were mainly performed at large momentum transfers Q where the complicated structure of the scattering function for hydrogen diffusion in an intermetallic did not allow the self-diffusion coefficient to be determined. Our previous measurement [11] was restricted to small Q in order to obtain the macroscopic diffusion coefficient and the microscopic details of the jump process which are obtained at large Q were not investigated. Unfortunately this restriction had a further drawback since it prohibited multiple-scattering corrections which require knowledge of the scattering function over a large range of Q. Although multiple-scattering corrections have not generally been used in research on diffusion in concentrated metal hydrides, they turn out to be essential for an accurate determination of the diffusion coefficient.

In this paper we report the first results of a reinvestigation of hydrogen diffusion in $LaNi_5H_x$ which was undertaken in order to clarify the discrepancies found in the literature and to obtain information on the microscopic behaviour of the hydrogen jump process.

2. Quasi-elastic neutron scattering on hydrogen in metals

The double-differential incoherent neutron cross section $\partial^2\sigma/\partial\omega\,\partial\Omega$ for diffusive hydrogen motion at small Q is given by [13]

$$\frac{\partial^2\sigma}{\partial\omega\,\partial\Omega} = \frac{\sigma^{\mathrm{H}}_{\mathrm{inc}}}{4\pi}\exp\{-2W(Q)\}\,\frac{1}{\pi}\,\frac{\hbar DQ^2}{(\hbar DQ^2)^2 + (\hbar\omega)^2} \tag{1}$$

where $\sigma^{\mathrm{H}}_{\mathrm{inc}}$ is the incoherent hydrogen cross section, $\exp\{-2W(Q)\}$ is the Debye–Waller factor and D is the hydrogen diffusion coefficient. It should be noted that a QNS experiment measures hydrogen diffusion over distances proportional to $2\pi/Q \approx 30$ - 40 Å. Thus QNS is a typical bulk method where the inner and outer surfaces do not play a role in the determination of the diffusion coefficient.

At larger values of Q the neutron samples smaller volumes in space and microscopic details of the single diffusion step appear in the spectrum. For powder samples where the scattering function has to be averaged over all orientations the linewidth for jump diffusion in the entire Q regime is often approximated by

$$\Gamma(Q) = \frac{6D\hbar}{l^2}\left\{1 - \frac{\sin(Ql)}{Ql}\right\} \tag{2}$$

where l is an "effective" jump length which coincides with the geometrical hopping distance only for cubic Bravais lattices.

3. Experimental details

The $LaNi_5H_x$ sample was produced by arc melting under argon. Annealing at 1400 K and subsequent X-ray investigations ensured that a single-phase compound was produced. Hydrogenation was performed using a novel aluminium container which was able to support pressures up to 150 bar and which allowed measurements to be made at temperatures up to 400 K with a low container background. In order to achieve a homogeneous hydrogen concentration the powder sample was charged and discharged several times. Finally we established an equilibrium pressure of 3 bar at room temperature. According to the pressure–concentration–temperature data of van Mal [14] this corresponds to the composition $LaNi_5H_6$. The sample transmission was 78% for 6.2 Å neutrons.

The QNS experiments were carried out using the backscattering spectrometer IN10 of the high flux reactor at the Institut Max von Laue–Paul Langevin. Quasi-elastic spectra were obtained at six temperatures between 280 and 400 K for up to 10 momentum transfers Q ($0.15\ \text{Å}^{-1} \leqslant Q \leqslant 1.9\ \text{Å}^{-1}$). Measurements were also performed at a hydrogen concentration corresponding to the minimum hydrogen concentration in the β phase β_{min} which decreases with increasing temperature.

The quasi-elastic spectra were first corrected for resolution and the resulting halfwidths at half-maximum (HWHM) obtained at 303 K are shown in Fig. 1 as a function of Q. The broken line was obtained by fitting eqn. (2) to the data. While the linewidth pattern follows the functional form of eqn. (2) at large Q, severe deviations from the Q^2 dependence are evident at small Q where $\Gamma \approx Q^2$ should hold regardless of any model assumptions. This is demonstrated even more clearly in Fig. 2 where the linewidth data obtained at small Q for two different temperatures are plotted against Q^2. Again strong deviations from the expected Q^2 law appear.

The marked distortions of the linewidth results originate from multiple-scattering processes which have a particularly strong effect on the observed linewidths at small Q. This can be understood by simple reasoning. At small momentum transfers most of the doubly scattered neutrons, which make the largest contribution to multiple scattering, have been scattered twice at large Q where the scattering function yields large linewidths. Thus they tend to cause a marked false broadening in the small Q range. At large Q, however, multiple scattering is only of minor importance: most of the doubly scattered neutrons are scattered twice at medium Q or once at a large and once at a small Q. In both cases the resulting width does not differ much from the width of the scattering function of the singly scattered neutrons.

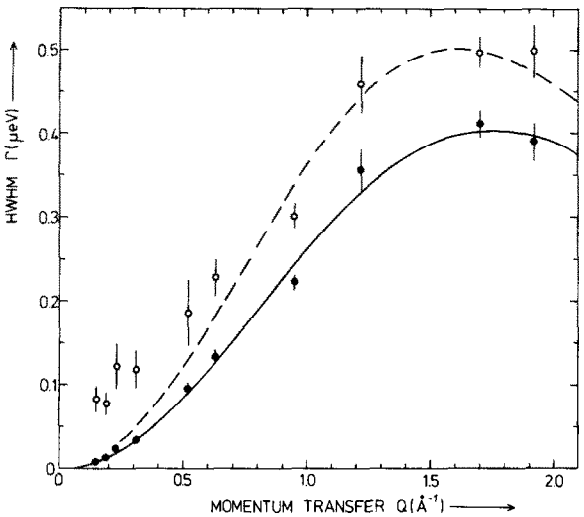

Fig. 1. Quasi-elastic linewidths obtained from $LaNi_5H_6$ at 303 K as a function of momentum transfer Q before (— — —) and after (——) performing multiple-scattering corrections. The curves were obtained by fitting the data to eqn. (2) (○, without multiple-scattering corrections; ●, with multiple-scattering corrections).

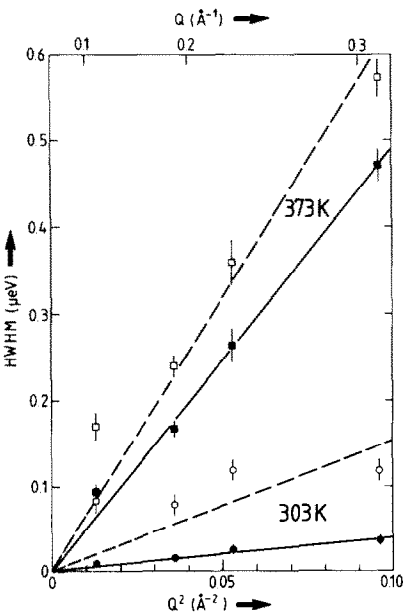

Fig. 2. Quasi-elastic linewidths obtained from $LaNi_5H_6$ at small momentum transfers Q as a function of Q^2 before (○, □) and after (●, ■) multiple-scattering corrections.

Therefore multiple-scattering corrections are essential for a reliable determination of the hydrogen diffusion coefficient at small Q. For this purpose we adapted the program Discus [15] which simulates the scattering process by a Monte Carlo method and allows for a correction of the multiple-

scattering contribution. From the discussion above it is clear that in order to correct at small Q knowledge of the scattering function at large Q is necessary. We proceeded in the following way: (i) an overall Q dependence of the observed linewidth was obtained from a fit of eqn. (2) to the linewidths corrected for resolution; (ii) multiple-scattering corrections were calculated for this linewidth pattern; (iii) the spectra were corrected and new linewidths were evaluated. The whole procedure was repeated until self-consistency was achieved which normally occurred after three cycles. The linewidths corrected in this way are included in Figs. 1 and 2. At small Q they follow the expected Q^2 behaviour and allow a reliable determination of the hydrogen diffusion coefficient. In the overall Q range their Q dependence obeys eqn. (2) (full curve in Fig. 1) where the effective jump length l is equal to 2.6 Å.

Figure 3 shows an Arrhenius representation of the diffusion coefficients. Two features should be noted: (i) as well as producing changes in the magnitude of D, multiple-scattering processes also tend to decrease the apparent activation energy for diffusion since their impact is largest at low T where the intrinsic widths at low Q are smallest; (ii) measurement along the boundary of the β phase yields the surprising result that the hydrogen diffusion coefficient decreases with decreasing hydrogen concentration and at higher temperatures the phase boundary shifts to lower hydrogen concentrations. The hydrogen self-diffusion coefficient in $LaNi_5H_6$ between 280 and 400 K is

$$D = (2.1 \pm 0.7) \times 10^{-3} \exp\{-(275 \pm 15)\ \text{meV}/kT\}\ \text{cm}^2\ \text{s}^{-1} \qquad (3)$$

At room temperature eqn. (3) yields $D = 5 \times 10^{-8}\ \text{cm}^2\ \text{s}^{-1}$.

Finally we report the following observations at large Q which will be evaluated and discussed in detail in a forthcoming publication [16].

(i) While at small Q the line shape of the QNS spectra can accurately be described as a single lorentzian after the inaccuracies due to multiple

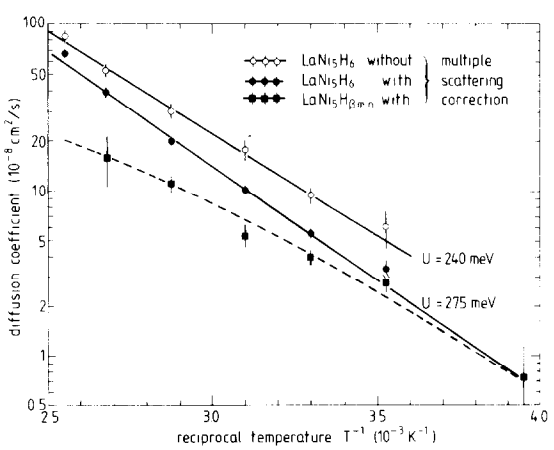

Fig. 3. Hydrogen diffusion coefficient in $LaNi_5H_6$ before and after the multiple-scattering correction. The results for the β_{min} sample are also included (see text).

scattering have been removed by appropriate corrections (see the extremely small error bars in Fig. 1), the line shape at larger momentum transfers reveals strong deviations (see the large error bars in Fig. 1 both with and without multiple-scattering corrections). The quasi-elastic spectra are composed of narrow and broad components which appear to have different temperature dependences.

(ii) The integrated intensity of the quasi-elastic spectra decreases with increasing temperature. This decrease becomes more significant at large Q and is much more pronounced than that predicted by the Debye–Waller factor.

4. Discussion

Our measurement and evaluation of the quasi-elastic neutron spectra for $LaNi_5H_6$ lead to a hydrogen diffusion coefficient which allows a consistent interpretation of more than 40 individual neutron spectra and constitutes a very careful determination of hydrogen diffusion coefficients in hydrides with high hydrogen concentrations. The room temperature value of $D(300\ \mathrm{K}) = 5 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$ falls in the middle of the range of comparable NMR results which extend from $1.4 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$ [8] to $11 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$ [5], whereas all the previous low resolution neutron scattering results [9, 10, 12] ($(80 - 250) \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$) are grossly inaccurate. The NMR studies yielded values between 230 and 300 meV for the activation energy. Karlicek and Lowe [8] reported two activation energies of 410 and 210 meV. The higher value was obtained from field gradient techniques and was assigned to long-range diffusion. Our value of 275 meV is again located within the range of the NMR results. Our original neutron scattering result of 242 meV [11] is reproduced in the data without applying the multiple-scattering corrections of Fig. 3, whereas the value of 110 meV found by Noreus *et al.* [12] is clearly out of the question.

We now comment on the concentration dependence of the hydrogen diffusion coefficient which decreases with decreasing hydrogen concentration. Such behaviour can be understood in terms of energetically non-equivalent hydrogen sites or structural traps which are saturated first. The remaining hydrogen which does not find an empty trap is able to diffuse faster. This fraction increases with increasing hydrogen concentration and can produce an increasing hydrogen diffusion coefficient despite the increased blocking. Preliminary results for α-$LaNi_5H_x$ [16] show an even smaller diffusion coefficient than our β_{min} sample in agreement with our model. The experimental observation of composite spectra at large Q further confirms the picture of hydrogen diffusion in the presence of structural traps where broad and narrow components in the spectra reflect the fractions of trapped and free hydrogen and exhibit different temperature dependences [17]. Such a process has recently been considered quantitatively by Hempelmann *et al.* [1] and has been successfully applied to the intermetallic hydride $Ti_{1.2}Mn_{1.8}H_3$.

Finally we consider the missing intensity fraction. The observation of a quasi-elastic intensity which decreases strongly with increasing T can be understood as a consequence of additional broad quasi-elastic components in the spectrum. Most of their intensity lies outside the limited energy window of the backscattering spectrometer (± 11 μeV). Since their relative fraction increases strongly with Q, they have to be associated with a local jump mechanism which could either be a consequence of structural effects or be related to hydrogen back jumps [2]. Similar observations have also been made for $Ti_{1.2}Mn_{1.8}H_3$ and $ZrMn_2H_3$ [1] and $Ti_{0.8}Zr_{0.2}CrMnH_3$ [18], indicating that their appearance might be independent of the structure and be due to back jumps as a consequence of the high hydrogen concentration.

5. Conclusion

We have performed high resolution quasi-elastic neutron scattering measurements in order to determine the hydrogen diffusion coefficient in $LaNi_5H_6$. Extensive investigations of the influence of multiple scattering on the quasi-elastic spectra revealed its crucial importance at small momentum transfers where the diffusion coefficient can be measured independently of model assumptions. The diffusion coefficient was found to exhibit an anomalous concentration dependence which was related to the existence of composite spectra at large momentum transfers and was interpreted in terms of diffusion in the presence of structural traps.

Acknowledgments

The authors gratefully acknowledge the technical assistance of the staff of the Institut Max von Laue–Paul Langevin and valuable discussions with A. Heidemann. One of us (L.A.V.) would like to thank the Comissão Nacional de Energia Nuclear of Brazil and the Fundação de Amparo à Pesquisa do Estado de São Paulo for the financial support that allowed his participation in this research.

References

1 R. Hempelmann, D. Richter and A. Heidemann, *J. Less-Common Met.*, *88* (1982) 343.
2 K. W. Kehr, R. Kuttner and K. Binder, *Phys. Rev. B*, *23* (1981) 4931.
3 T. K. Halstead, *J. Solid State Chem.*, *11* (1974) 114.
4 T. K. Halstead, N. A. Abood and K. H. J. Buschow, *Solid State Commun.*, *19* (1976) 425.
5 E. F. Khodosov, A. I. Linnik, G. F. Kobsenko and V. G. Evanchenko, *Fiz. Met. Metalloved.*, *44* (1977) 178.
6 E. F. Khodosov, A. I. Linnik, G. Kobsenko and V. G. Evanchenko, *Proc. 2nd Int. Conf. on Hydrogen in Metals, Paris, 1977*, Pergamon, Oxford, 1977, Paper 1D10.
7 R. C. Bowman, D. M. Gruen and M. H. Mendelsohn, *Solid State Commun.*, *32* (1979) 501.

8 R. F. Karlicek and I. J. Lowe, *J. Less-Common Met., 73* (1980) 219.
9 A. Furrer, L. Schlapbach and P. Fischer, *Rep. AF-SSP-102/103*, 1977 (Eidgenössisches Institut für Reaktortechnik/Eidgenössische Technische Hochschule, Zurich).
P. Fischer, A. Furrer, G. Busch and L. Schlapbach, *Helv. Phys. Acta, 50* (1977) 421.
10 G. Busch, L. Schlapbach, W. Thoeni, Th. von Waldkirch, P. Fischer, A. Furrer and W. Haelg, *Proc. 2nd Int. Conf. on Hydrogen in Metals, Paris, 1977*, Pergamon, Oxford, 1977, Paper 1D7.
11 E. Lebsanft, D. Richter and J. Töpler, *Z. Phys. Chem. N.F., 116* (1979) 175.
12 D. Noreus, L. G. Olsson and U. Dahlborg, *Chem. Phys. Lett., 67* (1979) 432.
13 T. Springer, *Quasielastic Neutron Scattering for the Investigation of Diffusive Motions in Solids and Liquids, Springer Tracts Mod. Phys., 64* (1972).
14 H. H. van Mal, *Philips Res. Rep., Suppl., 1* (1976).
15 M. W. Johnson, *DISCUS, Rep. AERE-R7682*, 1974 (Atomic Energy Research Establishment, Harwell).
16 D. Richter and R. Hempelmann, to be published.
17 D. Richter and T. Springer, *Phys. Rev. B, 18* (1978) 126.
18 R. Hempelmann, D. Richter, R. Pugliesi and L. A. Vinhas, *J. Phys. F*, to be published.