

MOBILITY OF HYDROGEN IN THE STORAGE COMPOUNDS $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3$ AND LaNi_5H_6 STUDIED BY QUASI-ELASTIC NEUTRON SCATTERING

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Abstract

Intermetallic hydrides have potencial importance as hydrogen storage materials. A topic of considerable interest for technical applications is the mobility of hydrogen in the intermetallic compounds, particularly the diffusion process. High resolution quasi-elastic neutron scattering technique was used to study the hydrogen diffusion in the storage materials $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3$ and LaNi_5H_6 . Quasi-elastic spectra were obtained at seven temperatures between 230 and 400K for up to 10 momentum transfers in the range 0.15 to 1.9 \AA^{-1} . From the diffusion coefficients determined at different temperatures, the following Arrhenius equation were obtained:

$$\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3: D(T) = (3 \pm 1) \times 10^{-8} \exp \{-(220 \pm 20) \text{ meV/kT}\} \text{ m}^2 \text{ s}^{-1}$$

$$\text{LaNi}_5\text{H}_6: D(T) = (2.1 \pm 0.7) \times 10^{-7} \exp \{-(275 \pm 15) \text{ meV/kT}\} \text{ m}^2 \text{ s}^{-1}.$$

The results at large momentum transfers showed evidences for the existence of more complex diffusion processes. These were explained considering the diffusion governed by the existence of energetically different interstitial sites and by blocking effects due to the high hydrogen concentration. By their properties concerning hydrogen storage capacity, hydrogen diffusion and kinetics of hydrogen absorption and desorption, $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3$ and LaNi_5H_6 can be considered the most promising storage materials for technical applications.

1. Introduction

Intermetallic hydrides have potential importance as hydrogen storage materials. For technical applications one distinguishes between so-called "high-temperature hydrides", with dissociation pressures above 1 bar only at temperatures above 100°C and "low-temperature hydrides", with dissociation pressures above 1 bar even below 0°C. The former, mostly intermetallic hydrides based on Mg, have the advantage of low weight, whereas the latter can be applied more universally. In this group the Laves phase hydrides $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3$ and LaNi_5H_6 offer many advantages for technical applications in motor vehicles and for stationary use owing to their high hydrogen contents and their suitable thermodynamic properties for hydrogen storage purposes^(1,2). A topic of considerable for practical applications and for fundamental research is the diffusion of hydrogen in the intermetallic compounds. The diffusion is one of the elementary steps of the kinetics of hydrogen absorption and desorption. One of the most suitable methods for determining hydrogen diffusion constant is the quasi-elastic neutron scattering technique, by which the hydrogen diffusion coefficient can be determined independently of the inner and outer surfaces⁽³⁾. This technique allows also to obtain information on the microscopic behaviour of the hydrogen diffusion process.

The aim of the present investigation is to determine, by quasi-elastic neutron scattering technique, the hydrogen diffusion coefficient in $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3$ and LaNi_5H_6 and to understand details of the hydrogen diffusion process in these intermetallic hydrides.

2. Quasi-elastic neutron scattering (QNS) of hydrogen in metals

If slow neutrons are scattered by a metal-hydrogen system, the intensity of scattered neutrons is mainly determined by the large incoherent scattering cross section of hydrogen, whereas other contributions can be neglected. The double differential scattering cross section $\partial^2\sigma/\partial\omega\partial\Omega$ is proportional to the incoherent scattering function $S_{\text{inc}}(Q, \omega)$ where $\hbar Q$ and $\hbar\omega$ are respectively the

momentum transfer and energy transfer during the scattering process.

At sufficiently small Q the incoherent scattering function is independent of any model concerning the single diffusive steps and is given by a single Lorentzian

$$\frac{\partial^2 \sigma}{\partial \omega \partial \Omega} \approx \frac{1}{\pi} \frac{\Gamma}{\Gamma^2 + (\hbar \omega)^2} \quad (1)$$

The width of the quasi-elastic spectrum is then proportional to the hydrogen diffusion coefficient D :

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

where T is the temperature.

As hydrogen diffusion is a thermally induced process, the temperature dependence of the macroscopic hydrogen diffusion coefficient D is expected to obey an Arrhenius law

$$D(T) = D_0 \exp(-E_A/kT) \quad (3)$$

where D_0 is a constant and E_A is the activation energy for hydrogen diffusion process.

It should be noted that QNS experiment measures hydrogen diffusion over microscopic distances. The typical volume probed in a scattering process at small Q is $(2\pi/Q)^3 \approx (30\text{\AA})^3$. Thus QNS is a bulk method where inner or outer surfaces do not play any role in the determination of the diffusion coefficient. At large values of Q the neutron samples smaller volumes in space and microscopic details of the single diffuse steps appear in the QNS spectrum. For powder samples where the scattering function has to be averaged over all orientations the linewidth for jump diffusion in the entire Q range is often approximated by

$$\Gamma(Q) = \frac{6 D \hbar}{\ell^2} \left| 1 - \frac{\sin(Q\ell)}{Q\ell} \right| \quad (4)$$

where ℓ is an "effective" jump length.

3. Experimental procedure

The $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}$ and LaNi_5 alloys were produced by arc melting under

argon. X-ray investigations ensured that a single-phase compound was produced. For the preparation of the hydrides, the granulated intermetallic compounds were evacuated to 10^{-7} mmHg and then exposed to 80 bar of H_2 gas. After the hydrogen absorption, the samples were charged and discharged several times in order to achieve an overall homogeneous hydrogen concentration. Finally equilibrium pressures corresponding to the composition $Ti_{0.8}Zr_{0.2}CrMnH_3$ and $LaNi_5H_6$ were established, according to the pressure-concentration-temperature data for these compounds (2,4).

The QNS experiments for $Ti_{0.8}Zr_{0.2}CrMnH_3$ and $LaNi_5H_6$ were carried out using the high resolution backscattering spectrometers⁽⁵⁾ installed at the reactors of KFA-Jülich, Germany, and Institut Laue-Langevin, France, respectively. For $Ti_{0.8}Zr_{0.2}CrMnH_3$, quasi-elastic spectra have been recorded at seven temperatures between 230 and 360 K with seven momentum transfers Q between 0.24 and 1.85 \AA^{-1} for each temperature, while for $LaNi_5H_6$ quasi-elastic spectra were obtained at six temperatures between 280 and 400 K for up to 10 momentum transfers Q in the range $0.15 - 1.9 \text{ \AA}^{-1}$. For $LaNi_5$ measurements were also performed at a hydrogen concentration corresponding to the minimum hydrogen concentration of the β phase β_{min} , which decreases with increasing temperature.

In order to obtain the linewidth Γ , the QNS spectra, corrected for multiple scattering effects^(4,6), were fitted, independently for each temperature and momentum transfer, with Lorentzian functions (equation (1)) convoluted with the corresponding resolution functions. The obtained linewidths are shown in Figure 1 as a function of Q ; the lines in Figure 1 were obtained by fitting equation (4) to the data. The Q^2 dependence of the resulting linewidths (Figure 2) were fitted with equation (2) in order to obtain the hydrogen diffusion coefficient in the intermetallic compound for each temperature.

4. Results and discussion

The hydrogen diffusion coefficients in $Ti_{0.8}Zr_{0.2}CrMnH_3$ and $LaNi_5H_6$, obtained following the procedures described in the previous section, are shown in

Figure 3 where the hydrogen diffusion coefficients are plotted as a function of temperature. More exactly, Figure 3 is a plot of $\ln D(T)$ vs $1000/T$. By fitting equation (3) to be the hydrogen diffusion coefficients shown in Figure 3, the activation energy E_A for the diffusion process and the pre-exponential factor D_0 were determined. Thus, the following Arrhenius equations were obtained:

$$\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3: D(T) = (3 \pm 1) \times 10^{-8} \exp(-(220 \pm 20) \text{ meV}/kT) \text{ m}^2 \text{ s}^{-1} \quad (5)$$

$$\text{LaNi}_5\text{H}_6: D(T) = (2.1 \pm 0.7) \times 10^{-7} \exp(-(275 \pm 15) \text{ meV}/kT) \text{ m}^2 \text{ s}^{-1} \quad (6)$$

yielding for the diffusion coefficients at room temperatures $6.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $5.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ respectively.

The validity of the Arrhenius law for these intermetallic compounds in the investigated temperature range is demonstrated by the excellent fit of equation (3) to the experimental results shown in Figure 3. Another feature should be noted at this figure: measurements along the boundary of the LaNi_5H_x β phase yield the surprising result that the hydrogen diffusion coefficient decreases with decreasing hydrogen concentration, considering that at higher temperatures the phase boundary shifts to lower hydrogen concentrations. 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.

The understanding of the kinetics of hydrogen absorption and desorption by intermetallic compounds is quite important for practical application. This heterogeneous chemical reaction is composed of several elementary steps: mass transport of H_2 ; dissociation chemisorption; surface migration; transition from the chemisorbed to the absorbed state; diffusion in the dilute phase; phase transition and diffusion in the hydride. The slowest of these elementary steps regulates the overall kinetics of hydrogen absorption and desorption in the intermetallic compound^(7,8). From the values of diffusion coefficient determined experimental

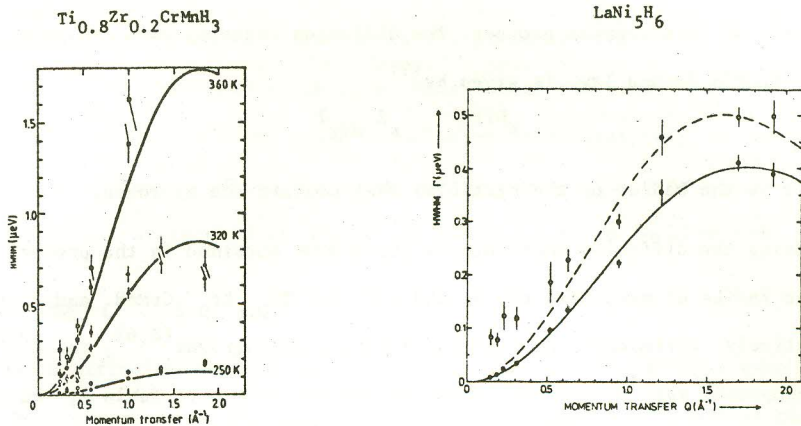


Figure 1. Q and T dependence of QNS line widths before (open symbols) and after (full symbols) multiple scattering correction (MSC).

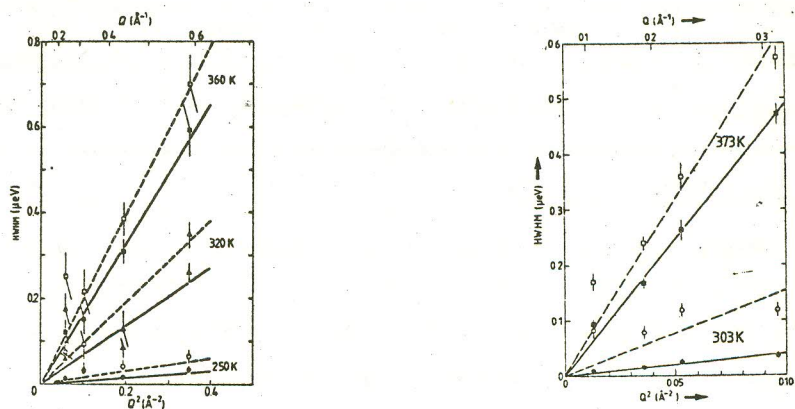


Figure 2. Quasi-elastic line widths obtained at small momentum transfers Q as a function of Q^2 before and after MSC.

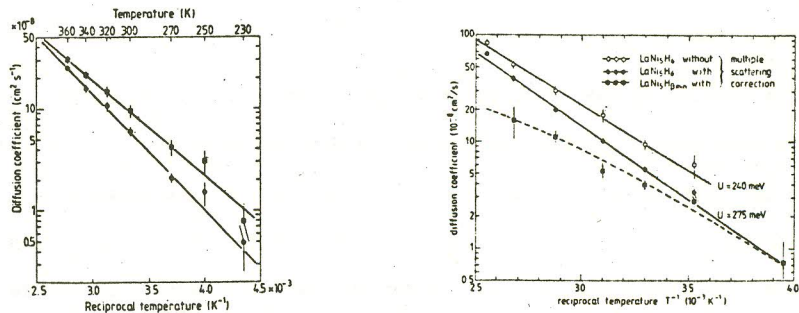


Figure 3. Arrhenius plot of the hydrogen diffusion coefficient in the studied intermetallic compounds before and after MSC.

ly, it is possible to estimate whether bulk diffusion could be the rate determining step of this complex process. The diffusion reaction-rate constant, according to Fick's second law, is given by⁽⁹⁾

$$K^{DIFF} = \pi^2 D/r^2 \quad (7)$$

where r is the radius of the particles that contain the hydrogen.

Using the diffusion coefficients for $T=300K$ obtained in the present paper and the radius of particles $r=0.5\mu$ and $r=2\mu$ for $Ti_{0.8}Zr_{0.2}CrMnH_3$ and $LaNi_5H_6$ respectively, estimated from scanning electron micrographs^(2,6), the K^{DIFF} for both compounds were determined. These values are listed in Table 1, which includes the absorption (K^{ABS}) and desorption (K^{DES}) reaction-rate constants obtained by other authors⁽⁸⁾ for a comparison.

Table 1. Reaction-rate constants

| Compound | $K^{DIFF} (s^{-1})$ | $K^{ABS} (s^{-1})$ | $K^{DES} (s^{-1})$ |
|---------------------------|---------------------|--------------------|--------------------|
| $Ti_{0.8}Zr_{0.2}CrMnH_3$ | 200 | 0.1 | 0.06 |
| $LaNi_5H_6$ | 12 | 0.02 | 0.01 |

The data of Table 1 clearly indicate that the diffusion rates are orders of magnitude larger than the macroscopic absorption and desorption rates. Evidently these fast hydrogen diffusion is not the elementary step which regulates the overall kinetics of hydrogen absorption and desorption in the systems $Ti_{0.8}Zr_{0.2}CrMn-H_2$ and $LaNi_5-H_2$.

The results of QNS obtained at large momentum transfers showed evidences for the existence of complex diffusion process. 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 scattering have been removed by appropriate corrections, the line shape at larger momentum transfers reveals strong deviations. The quasi-elastic spectra are composed of narrow and broad components which appear to have different temperature dependence.

The experimental observation of composite spectra at large Q further confirms the picture of hydrogen diffusion in the presence of energetically different interstitial sites and blocking effects due to the high hydrogen concentration. The hydrogen diffusion could be described quantitatively in terms of three motional states⁽¹⁰⁾ where the hydrogen atoms propagate over energetically higher sites; rest at structural traps; and exhibit a rapid local motion.

5. Conclusion

Hydrogen diffusion coefficient in $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3$ and LaNi_5H_6 were determined very carefully by QNS technique. It was observed that the fast hydrogen diffusion in these compounds is not the elementary step which regulates the overall kinetics of hydrogen absorption and desorption. By their properties concerning hydrogen storage capacity, hydrogen diffusion and low energy consumption hydrogenation process, LaNi_5H_6 and $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMnH}_3$ can be considered the most promising storage materials for technical applications. The latter hydride is especially suited to applications in vehicles because it is astonishingly resistant to impurities in the hydrogen refuel gas; hydrogen absorption and desorption take place even in the presence of 4 vol % CO and 5 vol % Nitrogen and Methane^(1,11).

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