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Hydrogen diffusion in the storage compound $Ti_{0.8}Zr_{0.2}CrMnH_3$

R Hempelmann, D Richter, R Pugliesi† and L A Vinhas†

Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

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Abstract. High-resolution quasi-elastic neutron scattering has been used to study the hydrogen diffusion in the multi-component Laves phase hydride $Ti_{0.8}Zr_{0.2}CrMnH_3$, one of the most promising hydrogen storage materials for technical applications. The data analysis is complicated by multiple scattering which, even with only moderately scattering samples, leads to a fictitious line broadening at small momentum transfers and considerably hinders the determination of diffusion coefficients. An evaluation procedure is presented which allows for the necessary multiple scattering corrections independent of details of the single diffusive steps. In the temperature range of our study, 230–360 K, the hydrogen self-diffusion coefficient in $Ti_{0.8}Zr_{0.2}CrMnH_3$ obeys the Arrhenius law:

$$D=(3\pm 1)\times 10^{-4}\ \mathrm{cm^2\ s^{-1}}\exp[-(220\pm 20)\ \mathrm{meV}/k_BT].$$

This comparatively fast hydrogen diffusion is not the rate determining step in the absorption and desorption kinetics.

1. Introduction

Intermetallic hydrides have potential importance as hydrogen storage materials. For the technical application one distinguishes between so-called 'high-temperature hydrides' (with dissociation pressures above 1 bar only at temperatures above 100 °C) and 'low-temperature hydrides' (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 $LaNi_5H_6$ (Kuijpers 1973) and $TiFeH_2$ (Reilly and Wiswall 1974) are the best known representatives and have been thoroughly investigated in the literature. However, for the actual technical application hexagonal Laves phase hydrides consisting mainly of Ti, Cr and Mn were found to have the following more favourable properties.

(i) The production of the parent intermetallic compounds is comparatively cheap (as starting materials appropriate pre-alloys are used, not pure metals).

(ii) The pressure composition isotherms of the corresponding intermetallic–hydrogen systems exhibit only one plateau which extends over almost the whole composition range (in contrast to the $TiFe–H_2$ system with the intermediate hydride β TiFeH).

(iii) The kinetics of hydrogen absorption are excellent; this holds in an especially astonishing degree for the first absorption: even below 0 °C these Laves phases pick up

† On leave from Instituto de Pesquisas Energéticas e Nucleares, Sao Paulo, SP, Brazil.

hydrogen immediately without any laborious (and on a technical scale expensive) activation procedure as necessary for TiFe.

The thermodynamic properties of binary Laves phase hydrides are only suitable for hydrogen storage purposes in the case of $TiMn_{1.5} = Ti_{1.2}Mn_{1.8}H_3$ (Yamashita *et al* 1977); the dissociation pressure of $TiCr_{1.8}H_{3.5}$ is too high in the cubic and hexagonal modifications (Johnson and Reilly 1978, Johnson 1980) whereas $ZrCr_2H_{3.3}$ (Pebler and Gulbransen 1967) and $ZrMn_2H_4$ (Shaltiel *et al* 1977, van Essen and Buschow 1980) exhibit dissociation pressures far below 1 bar at room temperature. However, by appropriate combination of these binary Laves phases to multi-component pseudo-binary systems of the same structure, the thermodynamic properties can be adapted to the actual requirements. For hydrogen storage purposes the following hydrides were suggested: $Ti_{0.8}Zr_{0.2}Cr_{0.8}Mn_{1.2}H_3$ (Machida *et al* 1977); $Ti_{0.9}Zr_{0.1}V_{0.2}Cr_{0.4}Mn_{1.4}H_3$ (Gamo *et al* 1979); and $Ti_{0.8}Zr_{0.2}CrMnH_3$ (Buchner 1979, Bernauer and Buchner 1981). The latter hydride is especially suited to applications in vehicles: 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 (Töpler *et al* 1980)); the comparatively low heat of formation of the hydride (28 kJ per mol H_2) helps to overcome the heat transfer problems in the tank, and the high α–β hydrogen plateau pressure of about 2 bar at −20 °C enables the cold start of a hydrogen powered engine in a central European winter.

Thus, the thermodynamics of the $Ti_{0.8}Zr_{0.2}CrMn$–H_2 system are well known. For practical application, however, an understanding of the kinetics of hydrogen absorption and desorption is equally desirable. This heterogeneous chemical reaction is composed of several elementary steps (Flanagan 1977): mass transport of H_2; dissociative chemisorption; surface migration; transition from the chemisorbed to the absorbed state; diffusion in the dilute α phase; phase transition and diffusion in the hydride. Since each of these steps can be rate determining, an understanding of the overall kinetics is out of the question, unless at least some of the elementary steps have been studied separately in advance. The aim of the present investigation is to understand the last step, the bulk diffusion in the hydride. The appropriate measuring technique is the quasi-elastic neutron scattering (QNS) (Springer 1972) by which the hydrogen diffusion coefficient can be determined independently of the inner and outer surfaces.

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

In a neutron scattering experiment on a metal hydride the protons—due to their exorbitantly large incoherent scattering cross section $\sigma_{\rm inc}^{\rm H}$—practically generate the complete scattering intensity of the sample. The double differential scattering cross section is then given by

$$\frac{\partial^2\sigma}{\partial\omega\,\partial\Omega}=\frac{k_{\rm f}}{k_{\rm i}}\frac{\sigma_{\rm inc}^{\rm H}}{4\pi}\exp(-2W(Q,T))S_{\rm inc}^{\rm D}(\boldsymbol{Q},\omega,T) \qquad (1)$$

($\hbar\boldsymbol{Q}$ and $\hbar\omega$ are the momentum and energy transfers of the neutrons, respectively, T is the temperature of the sample and $\exp(-2W(Q,T))$ its Debye–Waller factor). The incoherent diffusive scattering function $S_{\rm inc}^{\rm D}(\boldsymbol{Q},\omega,T)$ is obtained from Fourier transformation of the self-correlation function $G(\boldsymbol{r},t,T)$ which, in the classical limit, is the conditional probability of finding a proton at time t in position $\boldsymbol{r}$ if it has been at $\boldsymbol{r}=0$ for $t=0$. At sufficiently large $\boldsymbol{r}$, $G(\boldsymbol{r},t,T)$ no longer reflects the microscopic details of the hydrogen diffusion but the effective self-diffusion coefficient; correspondingly at sufficiently small Q the incoherent scattering function is independent of any model concerning the single diffusive steps and given by a single Lorentzian

$$S_{\mathrm{inc}}^{\mathrm{D}}(Q, \omega, T) = \frac{1}{\pi} \frac{\Gamma(Q, t)}{\Gamma(Q, t)^2 + (\hbar\omega)^2} \tag{2}$$

with line width HWHM

$$\Gamma(Q, T) = \hbar D(T) Q^2. \tag{3}$$

This was first shown by Blaesser and Perretti (1970) for the case of non-Bravais lattices. The temperature dependence of the macroscopic hydrogen self-diffusion coefficient D is expected to obey an Arrhenius law near room temperature

$$D(T) = D_0 \exp(-u/k_{\mathrm{B}} T). \tag{4}$$

It is noteworthy that a QNS experiment measures the hydrogen diffusion over microscopic distances. The typical volume probed in a scattering process at small Q is $(2\pi/Q)^3 \simeq (30\ \text{Å})^3$. Thus QNS is a bulk method where inner or outer surfaces do not play any role in the determination of the diffusion coefficient.

At larger Q the neutrons sample smaller volumes and microscopic details of the single diffusive steps appear in the scattering function $S_{\mathrm{inc}}^{\mathrm{D}}(\boldsymbol{Q}, \omega, T)$. This was first considered by Chudley and Elliott (1961) who calculated $S_{\mathrm{inc}}^{\mathrm{D}}$ for a classical jump diffusion. Then for Bravais lattices $S_{\mathrm{inc}}^{\mathrm{D}}(\boldsymbol{Q}, \omega, T)$ is still a single Lorentzian (equation (2)) but with the width

$$\Gamma(\boldsymbol{Q}, T) = \frac{\hbar}{n\tau(T)} \sum_{i=1}^{n} (1 - \exp(-\mathrm{i}\boldsymbol{Q} \cdot \boldsymbol{l}_i)) \tag{5}$$

where $\boldsymbol{l}_i$ are the jump vectors to the n adjacent sites and τ is the mean residence time. For a powder of an intermetallic hydride with such a complex structure as the Laves phase hydride structure—which reveals about fifty accessible interstitial sites per unit cell and thus a large number of jump directions even in the single crystal state (Didisheim *et al* 1979)—a liquid-like isotropic arrangement of the interstitial sites is a reasonable approximation; orientational averaging of equation (5) yields

$$\Gamma(Q, T) = (6\hbar D(T)/l^2)[1 - (\sin(Ql)/Ql)] \tag{6}$$

where additionally the well-known relation $l^2 = 6D\tau$ has been inserted. By applying equation (6) one must also keep in mind that the shape of the Brillouin zone affects the Q dependence of the quasi-elastic line widths; therefore the jump length l should not be considered as the real geometric hopping distance but rather as an effective length parameter.

3. Experimental procedure

$Ti_{0.8}Zr_{0.2}CrMn$ has been prepared in bulk†. The main impurities of the starting materials were: 0.5 wt% Al, 0.1 wt% C and 0.02 wt% Si in titanium; 0.02 wt% Fe and 0.003 wt% Si in manganese; and 0.3 wt% Al, 0.25 wt% Fe and 0.1 wt% Si in chromium. Zirconium was of about the same purity. After the induction melting procedure under an Ar atmosphere and subsequent quenching the resulting $Ti_{0.8}Zr_{0.2}CrMn$ contained less than 0.05 wt% O

† By the Gesellschaft für Electrometallurgie, Nürnberg by order of the Daimler-Benz AG, Stuttgart.

and less than 0.05 wt% N. For the preparation of the hydride we evacuated the granulated intermetallic compound to $p < 10^{-5}$ mbar and then exposed it to 50 bar of H_2 gas (99.9996% commercial grade). Hydrogen absorption took place immediately at room temperature without any activation procedure. In order to obtain an overall homogeneous hydrogen concentration the sample was subjected to several hydriding–dehydriding cycles. After this procedure it disintegrated into a very fine powder with particle dimensions around 1 μm, as shown in the scanning electron micrograph of figure 1. Fresh $Ti_{0.8}Zr_{0.2}CrMn$ hydride immediately ignites when exposed to air; however, deactivation is possible. The powdered sample must be cooled to 77 K in the reactor vessel in the pressurised hydrogen; then, as the hydrogen within the specimen is completely immobile, it is withdrawn and the reactor vessel is filled with oxygen gas and kept at 77 K for some hours. This procedure seals the sample in a thin oxide layer. Afterwards it can be handled in air without any problems. The oxide layer prevents hydrogen desorption up to 200 °C as confirmed by means of differential thermal analysis (DTA). The hydrogen content was determined gas volumetrically by hot extraction; it corresponded to the composition $Ti_{0.8}Zr_{0.2}CrMnH_{3.1}$ before and $Ti_{0.8}Zr_{0.2}CrMnH_{3.0}$ after the QNS experiment. In the x-ray diffractograms of the parent intermetallic and its hydride, peaks other than those characteristic of the hexagonal Laves phase structure (C14) have not been found. The lattice constants are $a_0 = 4.911(2)$ Å and $c_0 = 8.059(5)$ Å for the uncharged compound and $a_0 = 5.311(2)$ Å and $c_0 = 8.660(5)$ Å for the hydride. Thus hydrogenation expands the lattice by 26 vol%, but the host lattice does not change its structure.

The high resolution backscattering spectrometer at the FRJ-2 Dido reactor in Jülich was used for the neutron scattering experiment over the energy range $-4 \leqslant \hbar\omega \leqslant +4$ μeV. 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 Å^{-1} for each temperature. Additional spectra at $T = 50$ K—where all the hydrogen is immobile and scatters elastically—were used as resolution functions for the deconvolution. Since the deactivated $Ti_{0.8}Zr_{0.2}CrMnH_3$ does not lose hydrogen below 200 °C in spite of the high hydrogen equilibrium pressure, a simple thin-walled aluminium container could be used with negligible container background. The thickness of the sample was 0.7 mm and the transmission 0.76. The background was determined with an uncharged $Ti_{0.8}Zr_{0.2}CrMn$ sample in an identical container.

4. Data evaluation with multiple scattering correction

Since the detected neutron flux contains contributions from neutrons scattered twice or more in the sample, the relationship between the measured scattered intensity and the scattering function is not a straightforward convolution of equation (1) with the corresponding resolution function. The scattering function for multiply scattered neutrons is the multiple self-convolution (over Q and ω) of the scattering function for once scattered neutrons. Thus, multiple scattering always results in a fictitious additional line broadening which can actually be disastrous for the narrow line widths at small Q: here most of the twice scattered neutrons, which are the largest multiple scattering contribution, occur at large Q, where the scattering function already yields broad line widths without self-convolution. At large Q, on the other hand, multiple scattering is only of minor importance: most of the twice scattered neutrons occur at medium Q or else once at large and once at small Q, respectively. In both cases the resulting width is not significantly different from the width of the scattering function of once scattered neutrons.

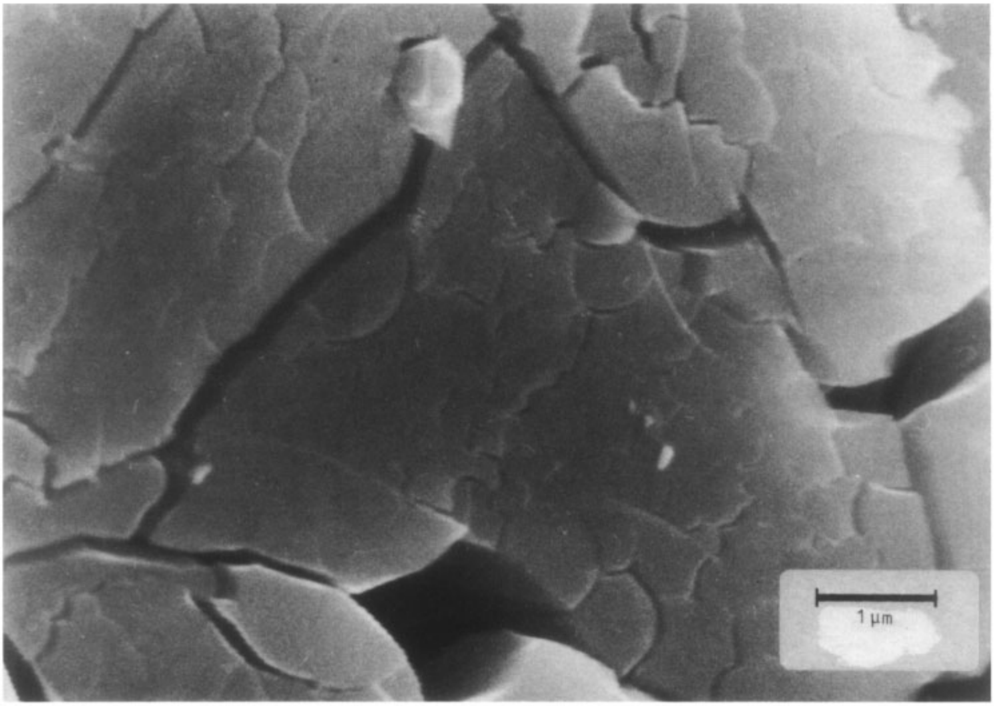

Figure 1. Scanning electron micrograph of the surface of $Ti_{0.8}Zr_{0.2}CrMnH_3$ after several hydriding–dehydriding cycles (acceleration voltage 32 kV).

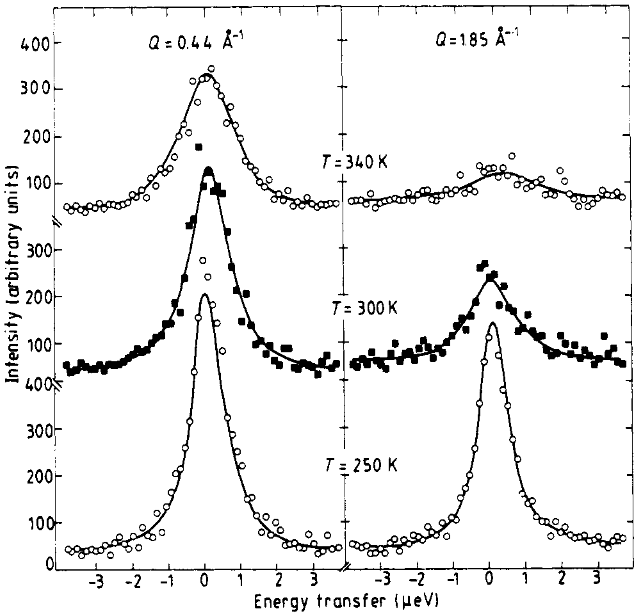

Figure 2. Typical QNS spectra of $Ti_{0.8}Zr_{0.2}CrMnH_3$: the curves represent fits of convoluted Lorentzians to the experimental intensities.

A correction for multiple scattering has been developed by Johnson (1974). His Monte Carlo program DISCUS simulates the scattering process and calculates the correction factor $R = J_1/(J_1 + J_2 + J_3)$ as a function of the energy transfer for given Q and T values, where

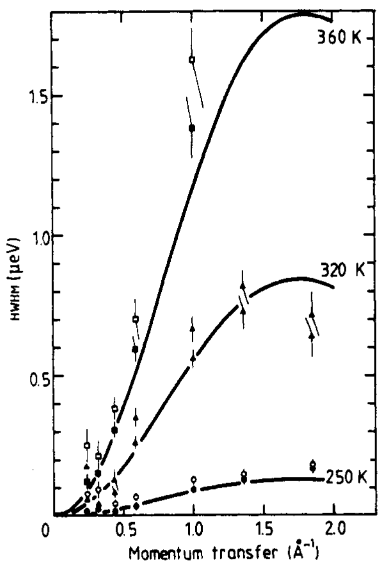

Figure 3. Q and T dependence of the resolution corrected line widths before (open symbols) and after (full symbols) multiple scattering correction: the curves correspond to one simultaneous fit of equations (6) and (4) to the final line widths.

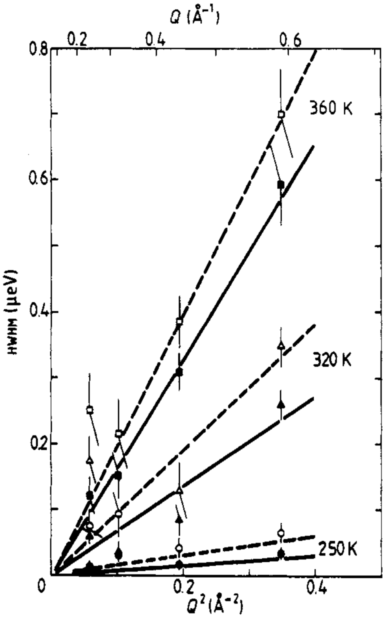

Figure 4. Q^2 and T dependence of the resolution corrected line widths at small Q before (open symbols) and after (full symbols) multiple scattering correction; the lines correspond to one simultaneous fit of equations (3) and (4) to the uncorrected line widths (broken lines) and to the final line widths (full lines) at small Q.

J_i is the flux of i fold scattered neutrons. Johnson has already pointed out the importance of multiple scattering corrections for accurate determinations of diffusion coefficients. His procedure has been applied iteratively to hydrogen diffusion in metals by Anderson *et al*

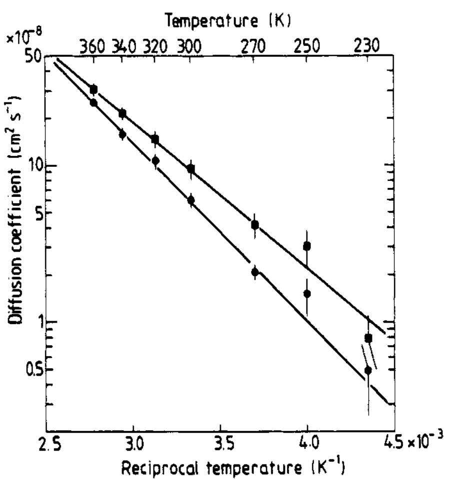

Figure 5. Arrhenius plot of the hydrogen self-diffusion coefficient in $Ti_{0.8}Zr_{0.2}CrMnH_3$ determined without (■) and with (●) multiple scattering corrections; the 'experimental diffusion coefficients' have been obtained from fits of the Q^2 law to the resolution corrected line widths at small Q (equation (3)), the straight lines represent fits of the Arrhenius law to the 'experimental diffusion coefficients' (equation (4)).

(1977) and later by the present authors (Hempelmann *et al* 1982, Richter *et al* 1982) and will be summarised only briefly here.

(A1) All QNS spectra are independently fitted with equations (1) and (2), which were convoluted with the corresponding resolution functions; some spectra are displayed in figure 2.

(B) The Q and T dependences of the resulting line widths are simultaneously fitted with equations (6) and (4) (figure 3) in order to determine intermediate values of D_0, l and u.

(C) With these values as input, DISCUS calculates the multiple scattering correction functions R. Typical examples are displayed in the description of DISCUS (Johnson 1974).

(A2) As (A1), but in the fitting routine the theoretical scattering function $S^D(Q, \omega, T)$ describing single scattering processes (equations (6) and (4)) is divided by $R(Q, \omega, T)$ to give the corresponding scattering function for multiple scattering.

Steps (A), (B) and (C) are repeated until self-consistency of the line widths is achieved. It was reached normally after three cycles. Then in a final step

(D) the Q and T dependences of the self-consistent line widths at small Q only are simultaneously fitted with equations (3) and (4) in order to determine the final values of D_0 and u for the hydrogen diffusion coefficient. Figure 4 demonstrates that the corrected line widths in fact obey the Q^2 law of equation (3); with decreasing Q the uncorrected line widths are increasingly too large.

5. Results

The data evaluation of the previous section yields

$$D = (3 \pm 1) \times 10^{-4}\ \mathrm{cm^2\ s^{-1}} \exp(-(220 \pm 20)\ \mathrm{meV}/k_B T) \tag{7}$$

for the hydrogen self-diffusion coefficient in the technical hydrogen storage compound $Ti_{0.8}Zr_{0.2}CrMnH_3$. The validity of the Arrhenius law in the investigated temperature range is demonstrated in figure 5; the diffusion coefficients $D(T)$ result from separate fits of equation (3) to the resolution corrected line widths for each temperature. For comparison this figure also contains the diffusion coefficients obtained from equation (3) without multiple scattering corrections. The activation energy would amount to (185 ± 10) meV, the diffusion coefficient at 300 K would be $9.2 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$ whereas equation (7) yields the correct value $6.0 \times 10^{-8}\ \mathrm{cm^2\ s^{-1}}$ at 300 K.

The differences between corrected and uncorrected values increase with decreasing temperature. Thus multiple scattering yields too small an activation energy of the diffusion coefficient. Changes of the same order of magnitude from 240 to 275 meV have recently been obtained in a QNS study on $LaNi_5H_6$ (Richter *et al* 1982).

6. Discussion

The measurement of hydrogen self-diffusion coefficients in metals is rapidly becoming a standard task for QNS, particularly for cases where the specimen disintegrates into a powder upon hydrogenation or where inconvenient conditions exist such as high temperatures or pressures (Springer 1979). In principle the method is straightforward: the resolution corrected line widths of QNS spectra at small momentum transfers have merely to be fitted to the Q^2 law of equation (3), which is considered to be generally valid for any degree of complexity of the metal–hydrogen system to be investigated. In practice, however, problems do arise. It is not *a priori* clear up to which limit a Q value is 'small', so at each temperature several spectra at different small Q values should be measured and the Q dependence of the line widths checked. Thereby, in the majority of cases, the Q^2 law will be found to be invalid due to multiple scattering. The Q dependence of the directly obtained line widths in figure 4 is no exception: a 20% scattering probability, as approximately exhibited by our $Ti_{0.8}Zr_{0.2}CrMnH_3$ sample is generally considered as a reasonable compromise in order to obtain enough scattering intensity without too much multiple scattering. However, the latter preferably falsifies the line widths at small momentum transfers. Therefore the determination of the hydrogen diffusion coefficient can no longer be based on the general validity of the Q^2 law. In order to correct for multiple scattering at small Q, as outlined in § 4, knowledge of the scattering function at large Q is necessary. This is often hopelessly complicated for multi-component systems due to complex structures with energetically different interstitial sites and also due to possible correlation effects in the case of high hydrogen concentrations (Kehr *et al* 1981). However, for the purpose of multiple scattering corrections at small Q, it is not necessary to know all the details of the scattering function at large Q, since the self-convolution over Q and ω in DISCUS smooths them out. Therefore, it is justified that equation (6) is combined with equation (4) as an approximation of the scattering function. The success of the evaluation procedure in the removal of multiple scattering distortions is apparent from the Q^2 dependence of the corrected line widths in figure 4 up to $Q = 0.59$ Å^{-1}.

A comparison with other metal–hydrogen systems in table 1 shows that the hydrogen diffusion in $Ti_{0.8}Zr_{0.2}CrMnH_3$ is slower than in Pd with a similar activation energy, considerably slower than in the Vb metals with much lower activation energies, but faster than in most of the intermetallic hydrides studied up to now. In TiFeH (with large quantitative discrepancies in the diffusion coefficients outlined in the literature) and in Ti_2NiH_2 the protons are rather immobile, whereas $LaNi_5H_6$ exhibits a comparative hydrogen diffusion coefficient at room temperature but has a higher activation energy similar to $TiCr_{1.8}H_{2.6}$.

The hydrogen mobility in the related compound $Ti_{1.2}Mn_{1.8}H_3$ has been studied in detail (Hempelmann *et al* 1982). On a microscopic scale it is governed by the existence of energetically different interstitial sites and by blocking effects due to the high hydrogen concentration. The hydrogen diffusion could be described quantitatively in terms of three motional states where the hydrogen atoms: (i) propagate over the energetically higher sites:

Table 1. Comparison of hydrogen self-diffusion coefficients in different metal–hydrogen systems.

Specimen	D_0 ($cm^2 s^{-1}$)	u (meV)	$D_{300 K}$ ($cm^2 s^{-1}$)	Reference
α $PdH_{x\to 0}$	5.3×10^{-3}	236	4.9×10^{-7}	Wicke *et al* (1978)
α $NbH_{x\to 0}$, $T > 250$ K	3.6×10^{-4}	108	5.5×10^{-6}	Völkl and Alefeld (1978)
β Ti_2NiH_2	2.0×10^{-4}	345	3.2×10^{-10}	Töpler *et al* (1978)
β TiFeH	7.2×10^{-4}	500	2.9×10^{-12}	Lebsanft *et al* (1979)
β TiFeH	4.2×10^{-7}	330	1.2×10^{-12}	Bowman and Tadlock (1979)
β $LaNi_5H_6$	3.2×10^{-4}	250	2.1×10^{-8}	Halstead *et al* (1976)
β $LaNi_5H_6$	2.1×10^{-3}	275	5.0×10^{-8}	Richter *et al* (1982)
β $TiCr_{1.8}H_{2.6}$	—	270	—	Bowman and Johnson (1980)
β $Ti_{1.2}Mn_{1.8}H_3$	5.9×10^{-4}	225	9.8×10^{-8}	Hempelmann *et al* (1982)
β $Ti_{0.8}Zr_{0.2}CrMnH_3$	3.1×10^{-4}	220	6.0×10^{-8}	Present work
α $Mg_2NiH_{0.3}$	6.7×10^{-5}	280	1.3×10^{-9}	Töpler *et al* (1982)

(ii) rest at structural traps; and (iii) exhibit a rapid local motion. The resulting hydrogen diffusion coefficient agrees well with that in $Ti_{0.8}Zr_{0.2}CrMnH_3$ which is not unexpected in view of the structural and electronic similarities of both hydrides. Accordingly we expect the exact scattering function of $Ti_{0.8}Zr_{0.2}CrMnH_3$ to be similarly complex.

Finally we estimate whether bulk hydrogen diffusion could be the rate determining step of the complex absorption and desorption kinetics of the system $Ti_{0.8}Zr_{0.2}CrMn{-}H_2$ as mentioned in the introduction. If bulk diffusion is the slow step, the hydrogen content n_t at time t of spherical particles with radius r is obtained as a solution of Fick's second law (Crank 1970):

$$\frac{n_t}{n_\infty} = 1 - \frac{6}{\pi^2} \sum_{m=1}^{\infty} \frac{1}{m^2} \exp\left(-\frac{m^2 \pi^2 D t}{r^2} \right). \tag{8}$$

When t is not too small the higher order terms can be neglected and the reaction rate constant is given by

$$K^{\text{diffusion}} = \pi^2 D / r^2. \tag{9}$$

In equations (8) and (9) the diffusion constant D is assumed to be concentration independent, and for a rough estimation these equations can be applied to $Ti_{0.8}Zr_{0.2}CrMnH_x$, since—in analogy to the system $LaNi_5H_x$ (Richter *et al* 1982)—the hydrogen diffusion coefficient in the β $Ti_{0.8}Zr_{0.2}CrMn$ hydride is expected to depend only slightly on the hydrogen concentration and since the hydrogen diffusion coefficient in the α phase is of the same order of magnitude. For $T = 300$ K, with $D = 6.0 \times 10^{-8}$ cm^2 s^{-1} (equation (8)) and $r \approx 0.5$ μm (figure 1), the diffusion controlled reaction-rate constant would amount to about 200 s^{-1}. A comparison with the experimental values $K_{300\,\mathrm{K}}^{\text{absorption}} \simeq 360$ h^{-1} = 0.10 s^{-1} and $K_{300\,\mathrm{K}}^{\text{desorption}} \simeq 200$ h^{-1} = 0.06 s^{-1} for the closely related hydride $Ti_{0.8}Zr_{0.2}Cr_{0.8}Mn_{1.2}H_x$ (Suda *et al* 1980) clearly indicates that the diffusion rate is orders of magnitude larger than the macroscopic absorption and desorption rates. Besides this the temperature dependences are different: whereas the absorption and desorption rates exhibit activation energies of approximately 80 and 110 meV, respectively, the activation energy for the hydrogen diffusion of 220 meV is about twice that value. In contrast to the well-known hydrogen storage system $TiFeH_x$ where the unusually slow hydrogen diffusion has to be considered as rate determining (Lebsanft *et al* 1979), the hydrogen atoms in the hexagonal multi-component Laves phase hydride $Ti_{0.8}Zr_{0.2}CrMnH_3$ are comparatively mobile as demonstrated in the present QNS study; evidently this fast hydrogen diffusion is not the elementary step which regulates the overall kinetics of hydrogen absorption and desorption in the new technical hydrogen storage system $Ti_{0.8}Zr_{0.2}CrMn{-}H_2$.

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