ELSEVIER

Journal of Alloys and Compounds 224 (1995) 127–129

Journal of
ALLOYS
AND COMPOUNDS

Pulsed-field-gradient NMR study of hydrogen diffusion in the hydrogen-stabilized Laves phase C15–$ZrTi_2H_{3.7}$

W. Renz [a], G. Majer [a,*], A.V. Skripov [b]

[a] Max-Planck-Institut für Metallforschung, Institut für Physik, D-70569 Stuttgart, Germany
[b] Universität des Saarlandes, Institut für Physikalische Chemie, D-66041 Saarbrücken, Germany

Received 19 September 1994; in final form 12 January 1995

Abstract

Hydrogen diffusion in C15–$ZrTi_2H_{3.7}$ has been measured in the temperature range 230 K to 450 K by means of pulsed-field-gradient nuclear magnetic resonance. The temperature dependence of the diffusivity shows an Arrhenius behavior, $D=D_0\cdot\exp(-H_a/k_BT)$, with an activation enthalpy $H_a=0.22$ eV and a pre-exponential factor $D_0=1.8\cdot10^{-8}$ m^2 s^{-1}. These results are in good agreement with the values derived from the proton spin–lattice relaxation rate Γ_1 measured on the same sample. Comparison of the results on D and Γ_1 yields additional information on the mechanisms of hydrogen diffusion. This permits distinction between long-range diffusion and localized motion.

Keywords: Hydrogen diffusion; Laves phase; Zirconium; Titanium; Pulsed-field-gradient NMR; NMR

1. Introduction

The pulsed-field-gradient nuclear magnetic resonance (PFG–NMR) technique permits model-independent measurements of hydrogen diffusion in metals (cf., e.g. [1]). Recent work on C14–$ZrCr_2H_{0.4}$ and C15–$ZrCr_2H_x$ ($0.2\leqslant x\leqslant0.5$) [2] has provided the first application of PFG–NMR to Laves-phase hydrides. Model-independent determinations of the hydrogen diffusivities in this class of materials are of special interest, since the data on the proton spin-lattice relaxation rate Γ_1 indicate complex diffusion mechanisms [3–6]. In some of the Laves-phase hydrides the proton Γ_1 results have been interpreted in terms of a double-peak distribution of activation enthalpies for hydrogen motion [3,5].

The hexagonal close-packed (hcp) metals Zr and Ti form *disordered* hcp alloys. The absorption of hydrogen by $ZrTi_2$ results in the formation of the cubic $ZrTi_2H_x$ Laves phase hydride ($3.1\leqslant x\leqslant4$) with the ordered C15 structure of the host atoms [7]. Neutron diffraction experiments on C15–$ZrTi_{1.86}D_{3.51}$ [7] indicate that, in contrast to other Laves-phase hydrides, in hydrogen-stabilized $ZrTi_2H_x$ hydrogen atoms occupy exclusively the tetrahedral e-sites surrounded by one Zr and three Ti atoms. The e-sites form a face-centered cubic (fcc) sublattice with lattice parameter $a_0/2$, where a_0 is the lattice parameter of the C15 host structure. Complete occupancy of these sites corresponds to $x=4$. Thus the $ZrTi_2H_{3.7}$ system provides an interesting opportunity to study hydrogen motion on a nearly filled fcc sublattice. In the present work we report on PFG–NMR investigations of hydrogen diffusivity in a $ZrTi_2H_{3.7}$ sample that has previously been studied by Γ_1 measurements at three different NMR frequencies as well as by $\Gamma_{1,\rho}$ (rotating frame) measurements with an r.f. field of $H_1=10.3$ G [3].

2. Experimental details

The preparation of the $ZrTi_2H_{3.7}$ sample has been described in [3]. According to the X-ray diffraction analysis, this sample is a single phase compound with C15 host lattice and a lattice parameter $a_0=8.167$ Å.

The hydrogen diffusivity was measured between 230 K and 450 K with a home-built PFG–NMR spectrometer at a resonance frequency of 37.2 MHz using the echo sequence introduced by Stejskal and Tanner [8]. Typical operating parameters were field-gradient pulse lengths of 1 ms and diffusion times of 2.5 ms. The diffusivities D were determined from the dependence of the echo attenuation on the amplitude of the field-gradient pulses, which were varied between 0 and 25 T m^{-1}.

---

* Corresponding author.

SSDI 0925-8388(95)01543-4

3. Results and discussion

Fig. 1 shows the temperature dependence of the hydrogen diffusivity D in $ZrTi_2H_{3.7}$ measured by PFG–NMR in the temperature range 230 K to 450 K. The experimental uncertainties of the D values are about 5%, corresponding to error bars that are smaller than the size of the symbols. The solid line in Fig. 1 shows that the D values are well represented by a single Arrhenius law $D=D_0 \cdot \exp(-H_a/k_BT)$. This indicates that there are no changes in the mechanism of long-range diffusion between 230 K and 450 K. The pre-exponential factor for hydrogen diffusion in $ZrTi_2H_{3.7}$, $D_0=(1.8 \pm 0.2) \cdot 10^{-8}$ m^2 s^{-1}, is close to those values of the related Laves-phase system $ZrCr_2H_x$ investigated previously by PFG–NMR [2]. The activation enthalpy $H_a=(0.22 \pm 0.01)$ eV is significantly higher than the values $H_a \approx 0.14$ eV observed for C15–$ZrCr_2H_x$ in the same temperature range.

The relationship between D, the jump length d of hydrogen atoms, and the mean dwell time τ_d of H atoms at an interstitial site is given by

$$D=\frac{f^T d^2}{6\tau_d} \qquad (1)$$

where f^T is the tracer correlation factor. Monte Carlo calculations of the dipolar contribution to the proton spin–lattice relaxation rate for random hydrogen hopping between nearest-neighbor sites on an fcc lattice [9,10] taking into account the blocking of occupied sites (the occupation probability of an e-site in $ZrTi_2H_{3.7}$ is $c_e=0.925$) enabled us to deduce τ_d at $T_{\max}$, the temperatures of the Γ_1 and $\Gamma_{1,\rho}$ maxima. The diffusivities calculated from Eq. (1) for jumps between nearest-neighbor e-sites at a distance of $l=a_0/\sqrt{8}=2.89$ Å, using the tracer correlation factor $f^T=0.79$ [11], are included in Fig. 1. They are slightly but systematically higher than the values measured directly by PFG–NMR. The dashed line through the data points derived from Γ_1 and $\Gamma_{1,\rho}$ corresponds to the activation enthalpy $H_a=(0.22 \pm 0.02)$ eV, which is in very good agreement with the model-independent PFG result $H_a=(0.22 \pm 0.01)$ eV. This agreement suggests that the long-range diffusion in $ZrTi_2H_{3.7}$ is determined by a single diffusion mechanism, at least down to 160 K, in contrast to hydrogen diffusivity in $ZrCr_2H_x$ below 200 K, where strong deviations from Arrhenius behavior have been found [2].

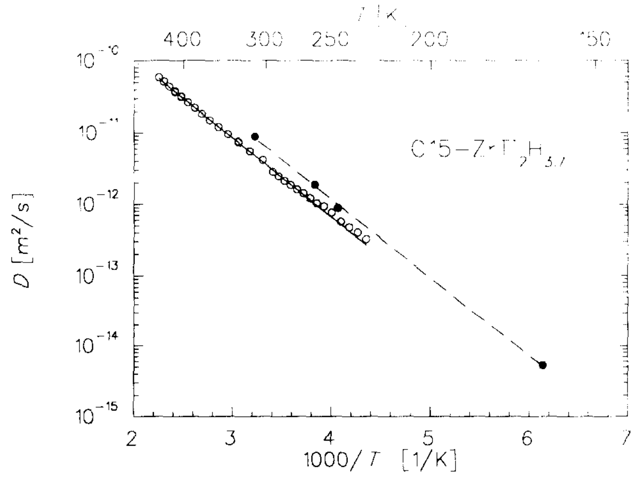

Fig. 1. Temperature dependence of hydrogen diffusivity D in $ZrTi_2H_{3.7}$. Open circles: values of D measured by PFG–NMR. Solid line: Arrhenius fit to the PFG–NMR data. Full circles: values of D calculated at the Γ_1 and $\Gamma_{1,\rho}$ maxima [3] for jumps between nearest-neighbor e-sites. Dashed line: Arrhenius fit to the relaxation rate data.

As an alternative, we may use Eq. (1) to estimate from Γ_1 and D a mean jump length $\bar{d}$ for hydrogen diffusion. At the temperature of the Γ_1 maximum at 9 MHz, $T_{\max}=(246 \pm 5)$ K, this gives us $\bar{d}=(2.5 \pm 0.2)$ Å. The deviation from the value expected for jumps between nearest-neighbor e-sites in $ZrTi_2H_x$, $\bar{d}=2.89$ Å, may indicate the importance of correlation effects in the hydrogen motion that have not been taken into account in the relaxation model [9,10]. However, $\bar{d} \approx 2.5$ Å is close to those values found for other Laves-phase hydrides with similar lattice parameters: $ZrCr_2H_{0.5}$ ($\bar{d} \approx 2.1$ Å) [2], $ZrV_2H_{2.9}$ ($\bar{d} \approx 2.4$ Å) [12] and $HfV_2H_{3.3}$ ($\bar{d}=2.0$–2.5 Å) [13].

In an earlier work [3] the temperature and frequency dependences of the proton spin–lattice relaxation rates in $ZrTi_2H_x$ (x = 3.7 and 3.9) were described in the framework of the Bloembergen–Purcell–Pound model [14] with a double-peak distribution of the activation enthalpy H_a. This approach implies a coexistence of two types of hydrogen motion on different frequency scales, as has been observed in a number of intermetallic hydrides [15]. The major Γ_1 and $\Gamma_{1,\rho}$ peaks for C15–$ZrTi_2H_{3.7}$ yielded an activation enthalpy, $H_{a1}=0.22$ eV, which is in excellent agreement with the PFG–NMR result and can thus be ascribed to long-range diffusion.

The additional process with an average activation enthalpy $\bar{H}_{a2}=0.16$ eV, as deduced from the Γ_1 and $\Gamma_{1,\rho}$ curves [3], does not manifest itself in the PFG–NMR data, at least not above 230 K. One may think of an additional hydride phase giving rise to the $\bar{H}_{a2}$ peak in the Γ_1 and $\Gamma_{1,\rho}$ spectra, but this would result in a non-exponential spin–lattice relaxation and a two-component ^{1}H free-induction decay in a certain temperature range, neither of which have been observed [3]. We propose therefore that the hydrogen diffusion in $ZrTi_2H_x$ should be discussed in the frame of a coexistence of long-range diffusion *and* localized motion.

Fig. 2 shows the spatial arrangement of different interstitial sites in the C15-type lattice [16]. It can be seen that transitions between e-sites are likely to occur via intermediate g-sites formed by two Zr and two Ti atoms. In this case, in addition to e-g-g-e transitions leading to the long-range diffusion, back-and-forth jumps

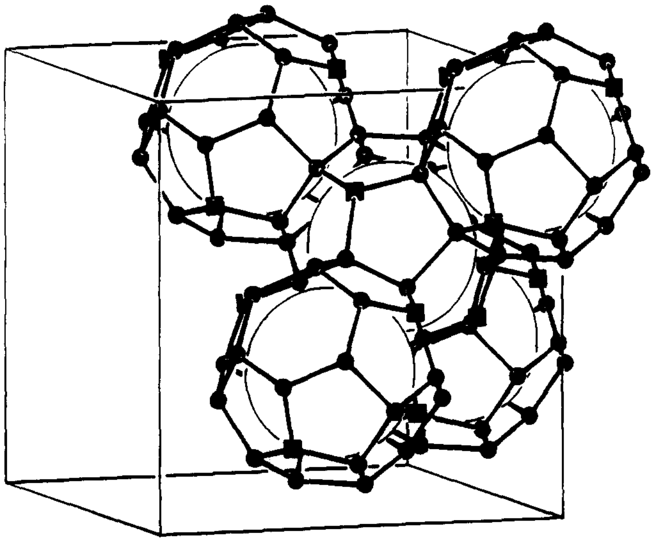

Fig. 2. Spatial arrangement of different interstitial sites in $ZrTi_2H_x$ (from [16]). Full squares: e-sites. Full circles: g-sites. Large open circles represent Zr atoms.

within an e-g pair are possible, too. These jumps do not contribute to the long-range diffusion but introduce an additional time scale determined by the mean residence time of an H atom at a g-site.

The values of H_a deduced from the proton spin–lattice relaxation measurements [3] on $ZrTi_2H_{3.7}$ and $ZrTi_2H_{3.9}$ suggest that there is no strong change in the activation enthalpy for the long-range diffusion when the hydrogen concentration in $ZrTi_2H_x$ approaches the stoichiometric limit $x=4$. This result is in accordance with Γ_1 studies performed on deuterium in C15–$ZrCr_2D_x$ over a wider concentration range ($3.1 \leqslant x \leqslant 4.0$) [17] and may serve as an additional indication that intermediate sites play an important role for hydrogen diffusion in $ZrTi_2H_x$.

4. Summary

Pulsed-field-gradient NMR measurements of the long-range hydrogen diffusivity D in hydrogen-stabilized C15–$ZrTi_2H_{3.7}$ have been performed over the temperature range 230 K to 450 K. Γ_1 measurements performed on the same sample revealed the coexistence of two types of motion on different time scales. The present PFG results allow us to identify one type of motion as long-range diffusion and the other one as localized motion, that has no effect on the PFG measurements. Comparison of the Γ_1 and the PFG data indicate that there is no change in the mechanism of long-range diffusion between 160 K and 450 K. The mean jump length of hydrogen $\bar{d}$, deduced from a combined analysis of Γ_1 and D, is found to be slightly smaller than the distance between nearest-neighbor e-sites. This deviation from the expected value might be due to correlation effects in the hydrogen motion, which have not been taken into account in the spin–lattice relaxation model.

Acknowledgments

The authors would like to thank Prof. Dr. H.C.A. Seeger and Dr. L. Schimmele for many helpful discussions. A.V. Skripov acknowledges financial support from the Alexander von Humboldt Foundation.

References

[1] R.M. Cotts, in G. Alefeld and J. Völkl (eds.), *Hydrogen in Metals I*, Springer, Berlin, 1978, p. 227.
[2] W. Renz, G. Majer, A.V. Skripov and A. Seeger, *J. Phys.: Condens. Matter, 6* (1994) 6367.
[3] A.V. Skripov, S.V. Rychkova, M.Yu. Belyaev and A.P. Stepanov, *Solid State Commun., 71* (1989) 1119.
[4] A.V. Skripov, M.Yu. Belyaev and A.P. Stepanov, *Solid State Commun., 78* (1991) 909.
[5] A.V. Skripov, M.Yu. Belyaev, S.V. Rychkova and A.P. Stepanov, *J. Phys.: Condens. Matter, 3* (1991) 6277.
[6] A.V. Skripov and M.Yu. Belyaev, *J. Phys.: Condens. Matter, 5* (1993) 4767.
[7] N.F. Miron, V.I. Shcherbak, V.N. Bykov and V.A. Levdik, *Sov. Phys. Crystallogr., 16* (1971) 266.
[8] E.O. Stejskal and J.E. Tanner, *J. Chem. Phys., 42* (1965) 288.
[9] D.A. Faux, D.K. Ross and C.A. Sholl, *J. Phys. C: Solid State Phys., 19* (1986) 4115.
[10] C.A. Sholl, *J. Phys. C: Solid State Phys., 21* (1988) 319.
[11] R.A. Tahir-Kheli and R.J. Elliott, *Phys. Rev. B, 27* (1983) 844.
[12] C. Schönfeld, R. Schätzler and R. Hempelmann, *Ber. Bunsenges. Phys. Chem., 93* (1989) 1326.
[13] R.L. Havill, J.M. Titman, M.S. Wright and M.A. Crouch, *Z. Phys. Chem. N.F., 164* (1989) 1083.
[14] N. Bloembergen, E.M. Purcell and R.M. Pound, *Phys. Rev., 73* (1948) 679.
[15] D. Richter, R. Hempelmann and R.C. Bowman, in L. Schlapbach (ed.), *Hydrogen in Intermetallic Compounds II*, Springer, Berlin, 1988, p. 97.
[16] K. Yvon and P. Fischer, in L. Schlapbach (ed.), *Hydrogen in Intermetallic Compounds I*, Springer, Berlin, 1988, p. 87.
[17] S.V. Rychkova, *Ph.D. Thesis*, Institute of Metal Physics, Ekaterinburg, 1992.