ELSEVIER

Journal of Alloys and Compounds 356–357 (2003) 274–278

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

NMR studies of hydrogen diffusion in the dihydrides of hafnium

J. Gottwald[a,b], G. Majer[b,*], D.T. Peterson[c], R.G. Barnes[c]

[a]*Faculty of Integrated Arts and Sciences, Hiroshima University, 1-7-1 Kagamiyama, Higashi-Hiroshima 739-8521, Japan*
[b]*Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany*
[c]*Ames Laboratory, USDOE, Department of Physics and Department of Materials Science and Engineering, Iowa State University, Ames, IA 50011, USA*

Received 10 June 2002; accepted 25 October 2002

Abstract

The macroscopic diffusivity D and the spin-lattice relaxation rate Γ_1 of hydrogen in hafnium dihydrides, HfH_x ($1.71 \leq x \leq 1.94$), were measured at temperatures up to 770 K. The activation enthalpy for hydrogen diffusion, obtained by fitting an Arrhenius expression to the diffusivities measured by PFG-NMR, increases slightly with increasing hydrogen concentration from $H_a = 0.63$ eV ($x = 1.71$) to $H_a = 0.71$ eV ($x = 1.94$). These H_a values agree satisfactorily with those deduced from the dipolar spin-lattice relaxation $\Gamma_{1,\mathrm{dip}}$. A combined analysis of both Γ_1 and PFG measurements shows that hydrogen atoms jump predominantly from occupied tetrahedral sites (T sites) to nearest-neighbour vacant T sites. The results for HfH_x are compared with those for TiH_x and ZrH_x, the dihydrides of the other Group IVb transition metals.

Keywords: Hydrogen diffusion; Hafnium dihydrides; Nuclear magnetic resonance

PACS: 66.30.-h; 76.60.Lz

1. Introduction

In the non-stoichiometric dihydrides of the Group IVb transition metals, TiH_x, ZrH_x and HfH_x ($1.5 \leq x \leq 2.0$), hydrogen atoms occupy tetrahedral interstitial sites (T sites), which form a simple cubic (s.c.) lattice in the face-centered cubic (f.c.c.) dihydrides and a simple tetragonal (s.t.) lattice in the face-centered tetragonal (f.c.t.) dihydrides. For HfH_x the transition from the f.c.c. phase, denominated the δ phase, to the nearly stoichiometric ϵ phase (f.c.t.) occurs at $x \approx 1.86$ [1].

Nuclear magnetic resonance (NMR) has proven to be an effective technique for measuring the diffusivity of hydrogen in metals on both the macroscopic and microscopic scales [2]. The dipolar contribution to the spin-lattice relaxation rate Γ_1 depends on the mean dwell time of the nuclei at an interstitial site. Thus, diffusion data on an atomistic scale may be deduced from the relaxation rate by applying an appropriate relaxation model. Pulsed-field-gradient (PFG) spin-echo NMR, on the other hand, permits direct measurement of the macroscopic diffusivity D. Furthermore, a comparison of the PFG results with the Γ_1 data yields the mean jump distance of the migrating hydrogen atoms and thus provides information on the underlying diffusion mechanism.

The hydrogen diffusivities in the dihydrides of the Group IVb transition metals were studied in the past by several Γ_1 measurements on TiH_x [3–8] and ZrH_x [9–13] as well as by direct PFG-NMR measurements of the D values for hydrogen in ZrH_x [15,16] and in TiH_x [14,17]. It could be shown conclusively that, up to $x \approx 1.9$, hydrogen atoms in TiH_x and ZrH_x jump predominantly between nearest-neighbour T sites [14–17]. In the case of HfH_x, however, only a few NMR studies of the dipolar [6,8,18,19] and the electronic [20,21] contribution to Γ_1 exist. Many of these Γ_1 measurements were performed on two-phase samples, and the data yielded somewhat differing parameters for hydrogen diffusion [6,8,18,19]. Direct diffusion studies by PFG-NMR have not been performed thus far.

The present paper reports on NMR studies of hydrogen diffusion in well-characterized non-stoichiometric hafnium

---

*Corresponding author. Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany. Fax: +49-711-689-1932.
E-mail address: majer@nmr.mpi-stuttgart.mpg.de (G. Majer).

0925-8388/02/$ – see front matter © 2002 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(02)01271-9

dihydrides HfH_x ($1.71 \leq x \leq 1.94$), which were prepared from high-purity metal. The main aims of the study were to obtain model-independent values of the hydrogen diffusivity by PFG-NMR and to determine the diffusion mechanism by a combined analysis of the PFG data and the Γ_1 data measured on the same samples. The results are compared with the diffusivities measured previously in the dihydrides of zirconium [15,16] and titanium [17].

2. Experimental

The samples were prepared from high-purity hafnium at the Ames Laboratory. The metal was heated to 1100 K under vacuum and subsequently exposed to hydrogen gas at a pressure appropriate to obtain the desired hydrogen concentration. The system was maintained at this temperature for 24 h to ensure equilibrium was attained and then gradually cooled over several days to room temperature in the presence of hydrogen gas. Four HfH_x samples (x = 1.71, 1.81, 1.90, 1.94) were prepared with powder sizes of about 50 μm. The concentrations were determined by hot-vacuum-extraction analysis to an accuracy of about 1% of the quoted values. All samples were sealed in quartz tubes under a pressure of about 0.1 bar of He. The pressure–temperature–composition diagrams of TiH_x [22], ZrH_x [23] and HfH_x [24] indicate that the same equilibrium pressure is already reached in HfH_x at a temperature which is about 100 and 200 K lower than for TiH_x and ZrH_x, respectively. To ensure that reversible outgassing of the samples during high-temperature measurements reduces the hydrogen content in the samples at most by 1%, and to avoid too high hydrogen pressures inside the quartz tubes, a temperature of 770 K was not exceeded in any of our NMR measurements on HfH_x. The proton Γ_1 was measured by an inversion-recovery pulse sequence between 350 and 770 K at resonance frequencies of 37.3, 49.8 and 67.7 MHz. After having completed the Γ_1 measurements of $HfH_{1.90}$, a small crack in the sample tube was observed. It could not be excluded that this sample had lost some hydrogen and therefore it was not used for subsequent PFG measurements.

The diffusion measurements were carried out at 37.3 MHz using a laboratory-built PFG-NMR spectrometer with homogeneous field-gradient pulses up to 25 T/m [25]. The two-pulse spin-echo sequence introduced by Stejskal and Tanner [26] and, predominantly in the range of smaller diffusivities, the stimulated spin-echo sequence proposed by Tanner [27] were used for the PFG experiments. The diffusion coefficients D were calculated from the variation of the echo amplitude with applied field gradient. The accuracy of a PFG experiment may, in principle, be affected by the presence of magnetic field gradients due to a random variation of the magnetization in powdered metal hydride samples [14]. As a general trend, this effect becomes more severe as the diffusion time increases. Since we found that the stimulated-echo sequence with its inherent long diffusion times and the two-pulse spin-echo method yield the same results within statistical uncertainties, we conclude that the upper limit for the systematic error in D is well below 5%.

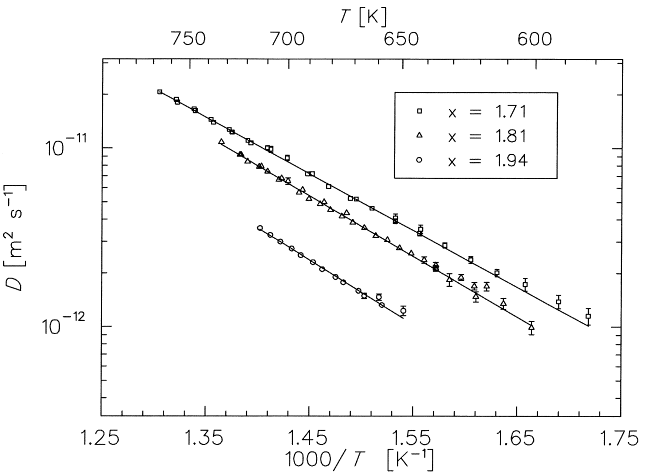

Fig. 1. Temperature dependence of the hydrogen diffusivity in HfH_x ($x = 1.71$, 1.81, 1.94) measured by PFG-NMR. The solid lines were obtained by fitting Arrhenius expressions $D = D_0 \exp(-H_a/k_B T)$ to the diffusion coefficients. The diffusion parameters are summarized in Table 1.

3. Results and discussion

3.1. Pulsed-field-gradient NMR studies on HfH_x

Fig. 1 shows the temperature dependence of the hydrogen diffusivities in HfH_x measured by PFG-NMR. At a given temperature the diffusivities decrease with increasing x. The solid lines in Fig. 1 were obtained by fitting an Arrhenius law to the diffusion coefficients. The corresponding activation enthalpies H_a and pre-exponential factors D_0 are given in Table 1, together with the diffusivities at 700 K, calculated from the fitting parameters. In this concentration range, the change in H_a with x is not very large [$H_a = 0.63$ eV ($x = 1.71$) to $H_a = 0.71$ eV ($x = 1.94$)], similar to what has been reported for $x \leq 1.9$ in the substoichiometric dihydrides of zirconium [15,16] and titanium [17].

It is evident from Fig. 1 that, for each sample, the

Table 1
Diffusion parameters of hydrogen in HfH_x obtained by fitting Arrhenius expressions to the diffusivities measured by PFG-NMR. The diffusivities at 700 K, D(700 K), were calculated from the fitting parameters

x	D_0 (10^{-7} m^2 s^{-1})	H_a (eV)	D(700 K) (10^{-12} m^2 s^{-1})
1.71	2.8±0.5	0.63±0.01	8.4
1.81	4.3±0.3	0.67±0.01	6.4
1.94	3.9±0.5	0.71±0.02	2.8

temperature dependence of D is well represented by a single Arrhenius term over the entire temperature range. In the case of $ZrH_{1.93}$ [16] and $TiH_{1.94}$ [17], very small but distinct deviations from the Arrhenius behaviour of $D(T)$ were found, indicating the onset of a second diffusion mechanism. For $HfH_{1.94}$, however, the temperature range covered by the PFG data is too small to reveal any non-Arrhenius behaviour.

The diffusivities found for HfH_x are higher than those in the ZrH_x and TiH_x systems with a similar x. A comparison of the present results for $HfH_{1.94}$ with the diffusivities measured previously in $ZrH_{1.93}$ [16] and $TiH_{1.94}$ [17] is given in Fig. 2.

3.2. Measurements of the spin-lattice relaxation rate of HfH_x

In order to analyse the diffusion mechanism, Γ_1 was measured on the same samples. Fig. 3 shows the Γ_1 data measured on HfH_x ($x = 1.71$, 1.81, 1.90 and 1.94) between 350 and 770 K at a resonance frequency of 37.3 MHz. The shift in the position of the relaxation maxima to higher temperatures indicates a decrease in the diffusivity with increasing x, which is in agreement with the PFG results. A typical example of the frequency dependence of the Γ_1 data, as measured on $HfH_{1.71}$, is given in Fig. 4. The Γ_1 data show no contributions of paramagnetic impurities, indicating the high purity of the starting metal. Furthermore, cross-relaxation processes between hydrogen and the host metal nuclei are also negligible due to the low natural abundance and the small nuclear moments of the two Hf isotopes, ^{177}Hf and ^{179}Hf.

Thus, only two contributions to the spin-lattice relaxation rate may be considered according to

$$\Gamma_1 = \Gamma_{1,\mathrm{e}} + \Gamma_{1,\mathrm{dip}} \tag{1}$$

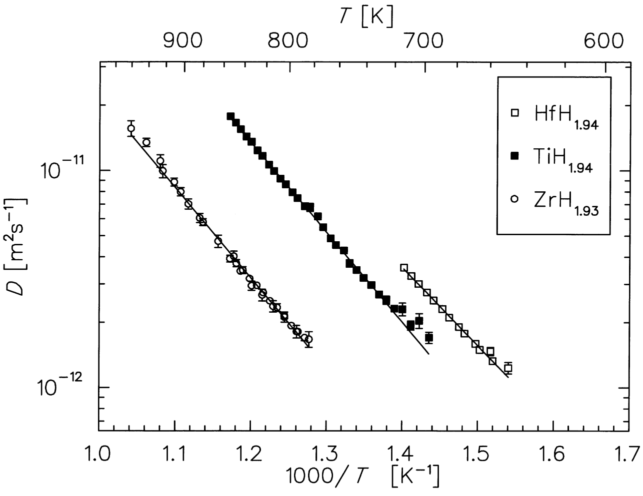

Fig. 2. Comparison of the hydrogen diffusivities in $ZrH_{1.93}$ [16], $TiH_{1.94}$ [17] and $HfH_{1.94}$.

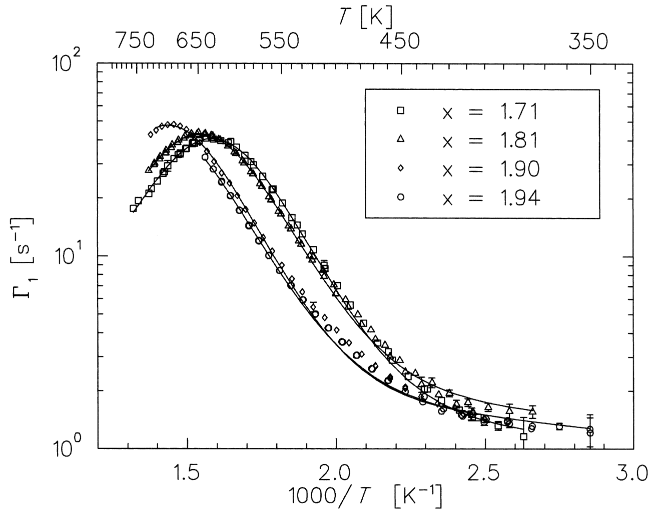

Fig. 3. Spin-lattice relaxation rate Γ_1 of hydrogen in HfH_x ($x = 1.71$, 1.81, 1.90, 1.94) measured at 37.3 MHz. The solid lines were obtained by fitting Eq. (1) to the experimental data. The fitting parameters for C_K, τ_0 and H_a are given in Table 2.

The interaction between the magnetic moments of protons and conduction electrons leads to the electronic relaxation $\Gamma_{1,\mathrm{e}}$, which is described by the Korringa relation [28]:

$$\Gamma_{1,\mathrm{e}} = T \cdot C_{\mathrm{K}}^{-1} \tag{2}$$

The dipolar spin-lattice relaxation rate $\Gamma_{1,\mathrm{dip}}$ results from the diffusion modulated magnetic dipole–dipole interaction between the hydrogen nuclei. For the dihydrides of zirconium [15,16] and titanium [17] it was shown previously that hydrogen jumps predominantly between adjacent T sites (direct T–T jumps), at least up to $x \approx 1.9$. For such a diffusion process, analytic representations of Monte Carlo

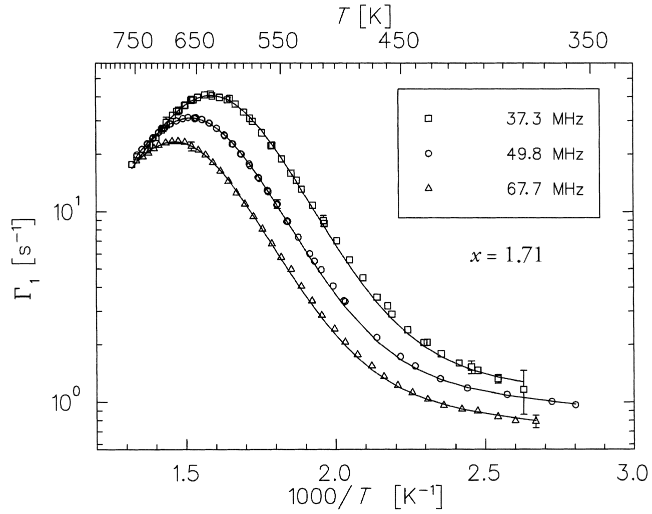

Fig. 4. Γ_1 data for hydrogen in $HfH_{1.71}$ measured at 37.3, 49.8 and 67.7 MHz. The solid lines represent the sum of the electronic relaxation $\Gamma_{1,\mathrm{e}}$ [Eq. (2) with $C_K = 310$ K s] and the dipolar relaxation $\Gamma_{1,\mathrm{dip}}$ (Sholl model [29] with $\tau_0 = 1.2 \times 10^{-14}$ s^{-1} and $H_a = 0.67$ eV).

calculations exist [29], which yield slightly c-dependent values of $\Gamma_{1,\mathrm{dip}}$ as a function of the mean dwell time τ_d of the hydrogen atoms. $c = x/2$ denotes the occupation probability of a T site. (The slight tetragonal distortion in ϵ-HfH$_x$ is not considered in this model.) The solid lines in Figs. 3 and 4 are obtained by fitting Eqs. (1) and (2) to the Γ_1 data, under the assumption of a single thermally activated diffusion process. Sholl's calculations [29] for $c = 0.90$ and $c = 0.99$ were used to analyse the $\Gamma_{1,\mathrm{dip}}$ data of HfH$_x$ with $x \leq 1.81$ and $x \geq 1.90$, respectively. The Korringa products and diffusion parameters thus obtained are given in Table 2. The H_a values of Table 2 are generally in good agreement with the activation enthalpies measured by PFG-NMR. The quality of the Γ_1 fits is excellent for $x = 1.71$ and 1.81, whereas for $x \geq 1.90$ the data reveal slight deviations from the fitting curves (cf. Fig. 3). This may indicate that also in HfH$_x$, as observed previously in ZrH$_x$ and in TiH$_x$, at intermediate hydrogen concentrations ($x \approx 1.9$) a second thermally activated process starts contributing to the diffusion. Moreover, for $x = 1.94$ the analysis of Γ_1 yields an activation enthalpy of 0.66 eV, which is significantly smaller than $H_a = 0.71$ eV measured by PFG-NMR. This difference may be due to the different temperature ranges covered by the Γ_1 ($T \leq 640$ K) and the PFG ($T \geq 650$ K) data and it is consistent with the observations on other dihydrides [16,17] that, in this concentration range, an additional diffusion process with a higher activation enthalpy exists.

As in the case of the titanium dihydrides [17], the Γ_1 data of HfH$_x$ can also be described reasonably well in the framework of the BPP model [2], resulting in H_a values that are about 15% lower than the results obtained with the lattice-specific calculations.

By a combined analysis of the $\Gamma_{1,\mathrm{dip}}$ and the PFG data the correctness of the T–T jump model can be assessed. If only jumps between one kind of interstitial site with a fixed jump distance L are involved, the diffusion can be described as

$$D = f^{\mathrm{T}} L^2 / 6\tau_d \tag{3}$$

The x-dependent tracer correlation factor f^{T} was calculated by Fedders and Sankey [30] and the mean dwell time τ_d at the temperature of the relaxation maximum, $T_{\max}$, follows from the calculations of Sholl [29]. Since $D(T_{\max})$ was measured by PFG-NMR model-independently, Eq. (3) may be used to calculate the mean jump distance L. The values $L = 2.30 \times 10^{-10}$ and 2.40×10^{-10} m are obtained in this way for HfH$_x$ with $x = 1.71$ and 1.81, respectively. These L values are in good agreement with $a_0/2 = 2.35 \times 10^{-10}$ m, the distance between nearest-neighbour T sites in the f.c.c. dihydride HfH$_x$ with lattice parameter $a_0 = 4.7 \times 10^{-10}$ m. This result confirms that the same diffusion mechanisms occur in all dihydrides of the Group IVb transition metals, with direct T–T jumps at least up to $x \approx 1.9$.

Table 2
Activation enthalpies H_a, prefactors τ_0 and Korringa constants C_K deduced from Γ_1 data of HfH$_x$ using lattice-specific Monte Carlo calculations [29] for $\Gamma_{1,\mathrm{dip}}$

x	H_a (eV)	τ_0 (10^{-14} s)	C_K (K s)
1.71	0.67±0.01	1.2	310
1.81	0.67±0.01	1.5	240
1.90	0.71±0.02	1.6	272
1.94	0.66±0.02	4.5	273

4. Summary

The hydrogen diffusivity D in hafnium dihydrides, HfH$_x$ ($1.71 \leq x \leq 1.94$), was measured by means of PFG-NMR and spin-lattice relaxation rates Γ_1 at temperatures up to 770 K. The activation enthalpy H_a for hydrogen diffusion increases with increasing hydrogen concentration from $H_a = 0.63$ eV ($x = 1.71$) to $H_a = 0.71$ eV ($x = 1.94$). The diffusivities in HfH$_x$ are greater than those in ZrH$_x$ and TiH$_x$ systems with a similar x value. The dipolar spin-lattice relaxation $\Gamma_{1,\mathrm{dip}}$ can be well described by Sholl's calculations for direct T–T jumps on the s.c. sublattice. A combined analysis of both Γ_1 and D data indicates that up to $x \approx 1.9$ hydrogen atoms jump predominantly between neighbouring T sites. At higher concentrations a comparison of PFG and Γ_1 data indicates a second diffusion process with a higher activation enthalpy. However, in the case of HfH$_x$, this second diffusion process could not be seen directly from the PFG data as in the case of the dihydrides of zirconium and titanium. This is a consequence of the smaller temperature range covered by the PFG measurements on HfH$_x$ because of the higher hydrogen pressure at a given temperature compared to ZrH$_x$ and TiH$_x$.

Acknowledgements

The authors are very grateful to the Deutsche Forschungsgemeinschaft for financial support (Project MA 1382/1). One of the authors (J.G.) would also like to thank the Japanese Society for the Promotion of Science fellowship program for financial support. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

References

[1] Z. Berant, Y. Levitin, S. Kahane, A. Wolf, M.H. Mintz, Hyperfine Interactions 52 (1989) 383.

[2] R.G. Barnes, in: H. Wipf (Ed.), Hydrogen in Metals, Vol. III, Springer, Berlin, 1997, p. 93.

[3] C. Korn, D. Zamir, J. Phys. Chem. Solids 31 (1970) 489.

[4] C. Korn, D. Zamir, J. Phys. Chem. Solids 34 (1973) 725.

[5] C. Korn, S.D. Goren, Phys. Rev. B 22 (1980) 4727.

[6] Ye.F. Khodosov, N.A. Shepilov, Phys. Status Solidi b 47 (1971) 693.

[7] A. Schmolz, F. Noack, Ber. Bunsenges. Phys. Chem. 78 (1974) 339.

[8] J.M. Pope, P.P. Narang, K.R. Doolan, J. Phys. Chem. Solids 42 (1981) 519.

[9] K.R. Doolan, P.P. Narang, J.M. Pope, J. Phys. F 10 (1980) 2073.

[10] R.C. Bowman Jr., B.D. Craft, J. Phys. C 17 (1984) L477.

[11] C. Korn, S.D. Goren, J. Less-Common Met. 104 (1984) 113.

[12] C. Korn, S.D. Goren, Phys. Rev. B 33 (1986) 68.

[13] J.-W. Han, D.R. Torgeson, R.G. Barnes, D.T. Peterson, Phys. Rev. B 44 (1991) 12353.

[14] L.D. Bustard, R.M. Cotts, E.F.W. Seymour, Phys. Rev. B 22 (1980) 12.

[15] G. Majer, W. Renz, A. Seeger, R.G. Barnes, Z. Phys. Chem. 181 (1993) 187.

[16] G. Majer, W. Renz, R.G. Barnes, J. Phys.: Condensed Matter 5 (1994) 2935.

[17] U. Kaess, G. Majer, M. Stoll, D.T. Peterson, R.G. Barnes, J. Alloys Comp. 259 (1997) 74.

[18] Y.F. Khodosov, N.A. Shepilov, V.I. Savin, Fiz. Met. Metalloved. 32 (1971) 189.

[19] H.T. Weaver, J. Magn. Reson. 15 (1974) 84.

[20] E.F. Khodosov, N.A. Shepilov, Phys. Status Solidi b 49 (1972) K83.

[21] E.F. Khodosov, N.A. Shepilov, Sov. Phys. Solid State 14 (1972) 807.

[22] T.R.P. Gibb Jr., J.J. McSharry, R.W. Bragdon, J. Am. Chem. Soc. 73 (1951) 1751.

[23] E. Fromm, E. Gebhardt, Gase und Kohlenstoffe in Metallen, Reine und angewandte Metallkunde in Einzeldarstellungen, Vol. 26, Springer, Berlin, 1976.

[24] R.K. Edwards, E. Veleckis, J. Phys. Chem. 66 (1962) 1657.

[25] P. Galvosas, F. Stallmach, G. Seiffert, J. Kärger, U. Kaess, G. Majer, J. Magn. Reson. 151 (2001) 260.

[26] E.J. Stejskal, J.E. Tanner, J. Chem. Phys. 42 (1965) 288.

[27] J.E. Tanner, J. Chem. Phys. 52 (1970) 2523.

[28] J. Korringa, Physica 16 (1950) 601.

[29] C.A. Sholl, J. Phys. C: Solid State Phys. 21 (1988) 319.

[30] P.A. Fedders, O.F. Sankey, Phys. Rev. B 18 (1978) 5938.