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The existence of more than one jump process of hydrogen in palladium–silver alloys — an NMR study

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Abstract

The hydrogen dynamics in the α-phase of $Pd_{1-x}Ag_xH_y$ has been studied by proton nuclear magnetic resonance (NMR) measurements. Jump frequencies of the hydrogen atoms in the metal lattice have been deduced from the dipolar spin-lattice relaxation rates Γ_{1d} by applying the BPP model. In PdH_y, the temperature dependence of Γ_{1d} is well described by a single jump process for all hydrogen atoms. In contrast, in the palladium–silver alloys $Pd_{1-x}Ag_xH_y$, the Γ_{1d} data indicate more than one jump process with different activation energies. Two and three processes could be separated for $x=0.1$ and $x=0.3$, respectively. In both alloys, the diffusion process with the lowest activation energy ($E_a=226$ meV) is comparable to that in pure palladium. The jump processes with higher activation energies occur more frequently in $Pd_{0.7}Ag_{0.3}$ than in $Pd_{0.9}Ag_{0.1}$. This indicates higher energy-barriers for jumps between O-sites in silver-rich environments. Direct measurements of the long-range diffusion coefficients D were performed by pulsed-field-gradient (PFG)-NMR at temperatures up to 450 K. For both $Pd_{1-x}Ag_xH_y$ samples, $D(T)$ is well represented by a single Arrhenius law with the diffusion parameters $D_0=3.0\times10^{-7}$ m^2 s^{-1} and $E_a=230$ meV for $x=0.1$ and $D_0=2.1\times10^{-7}$ m^2 s^{-1} and $E_a=260$ meV for $x=0.3$. The diffusivities calculated from the jump frequencies of the hydrogen atoms are in good agreement with these PFG results and also with measurements using the time-lag technique.

Keywords: Hydrogen diffusion; Palladium–silver alloys; Spin lattice relaxation; Pulsed field gradient nuclear magnetic resonance

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1. Introduction

The diffusivity of hydrogen in palladium has been the topic of numerous investigations over a period of several decades (see, for example, Refs. [1,2] and references therein), and interest in this system has not subsided, in part because it is one of the very few in which hydrogen occupies the octahedral sites (O-sites). One of the earliest applications of nuclear magnetic resonance (NMR) was, for example, the study of hydrogen dynamics in palladium wires [3]. NMR offers unique capabilities to measure the diffusion of hydrogen on both macroscopic and microscopic scales [4]. The jump frequencies of hydrogen atoms can be deduced from the dipolar contribution to the proton spin-lattice relaxation rate Γ_{1d} or from the NMR linewidth, while the pulsed-field-gradient (PFG)-NMR permits direct measurements of the long-range diffusion coefficient *D*. Early NMR studies of hydrogen in the α′-phase of palladium–silver alloys, $Pd_{1-x}Ag_xH_y$ ($0.45<y<0.70$), showed a decrease in the diffusivity with increasing hydrogen content, and the activation energy was found to increase from 0.23 eV for pure palladium to 0.28 eV at 17 at.% silver [5]. The diffusivity of hydrogen in the dilute α-phase of $Pd_{1-x}Ag_xH_y$ has been measured recently by applying the electrochemical pulse time-lag technique [6,7]. These measurements have been performed on a series of $Pd_{1-x}Ag_x$ alloys ($0<x<1$), including the silver-rich side, where the hydrogen solubility is extremely low. The data reveal a nearly constant diffusivity up to a silver content of ~20 at.%, but with further increasing silver content a drastic reduction in *D* was found [6,7]. On the silver-rich side the diffusivity is, on the other hand, only slightly smaller than in pure palladium. These experimental results could be explained by a simple microscopic diffusion model [6,7]. A basic assumption of this model is that O-sites are less likely to be occupied if two or more of the Pd atoms per octahedron are substituted by Ag atoms since the site-energy of an O-site increases with the number of Ag atoms surrounding this site. It is expected that the energy-barrier for jumps between two O-sites also depends strongly on the types of atoms forming these sites.

The present paper reports on NMR studies of hydrogen diffusion in the dilute α-phase of $Pd_{1-x}Ag_xH_y$. The main

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aims are to obtain diffusion parameters on a microscopic scale and to investigate whether the jump processes of the hydrogen atoms are well described by a continuous distribution of activation energies around a mean value or whether more than one discrete mean activation energy exists. The jump frequencies deduced from the dipolar contribution Γ_{1d} to the spin-lattice relaxation rate Γ_1 are compared with the long-range diffusion coefficients D, which have been measured on the same samples by PFG-NMR.

2. Experimental

The samples consist of stacks of ~40 foils of size 6 mm×14 mm×30 μm, isolated by thin sheets of PTFE. This package was put into a quartz tube with an inner diameter of 7.6 mm. For hydrogen loading, the sample package inside the quartz tube was heated under vacuum up to 400 K, and then gradually cooled to room temperature in the presence of hydrogen gas. The loading procedure was completed when the equilibrium was established at room temperature, and the final hydrogen content was determined volumetrically. After hydrogen loading the quartz tube was flame-sealed taking special precautions to prevent hydrogen loss of the sample by temperature increase. Three different samples have been prepared this way for the NMR measurements, $PdH_{0.005}$, $Pd_{0.9}Ag_{0.1}H_{0.015}$ and $Pd_{0.7}Ag_{0.3}H_{0.005}$.

The NMR measurements were performed with computer-controlled Fourier-transform spectrometers using phase-alternating pulse schemes and quadrature detection. The spin-lattice relaxation rates Γ_1 were measured with an inversion-recovery pulse sequence at resonance frequencies of 36.6 and 67.6 MHz between ~200 and 500 K. For the diffusion measurements by PFG-NMR, the two-pulse spin-echo sequence [8] was applied with a typical time between the two rf pulses of $\tau_{rf}=2$ ms and magnetic field gradient pulses up to $G=25$ T m^{-1} of a typical length in the range $\Delta=0.5$–0.7 ms. The diffusion coefficients D were determined from the variation of the echo amplitude with the applied field gradient G at constant Δ and τ_{rf}. Details of the PFG spectrometer are given in Ref. [9].

3. Results and discussion

3.1. Spin-lattice relaxation rates Γ_1 and diffusion on a microscopic scale

Fig. 1 shows the temperature dependence of the proton Γ_1 in $PdH_{0.005}$ measured at 67.6 MHz.

In a metal–hydrogen system, the relaxation rate may be decomposed according to

$$\Gamma_1 = \Gamma_{1d} + \Gamma_{1e}. \tag{1}$$

The electronic contribution Γ_{1e}, resulting from the interaction between the magnetic moments of protons and conduction electrons, is characterized by the relationship

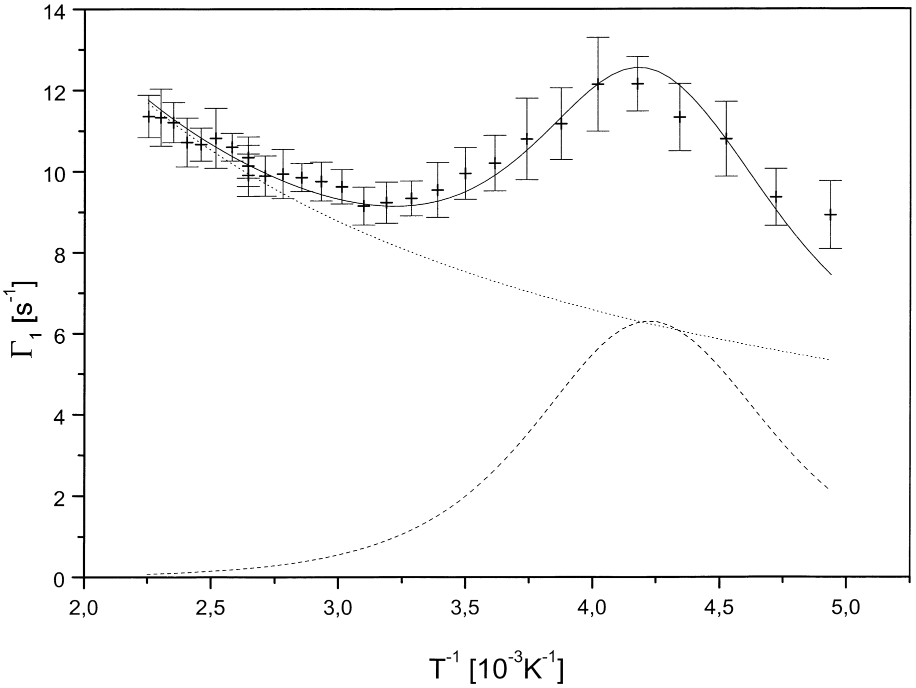

Fig. 1. Temperature dependence of the proton spin-lattice relaxation rate in $PdH_{0.005}$ measured at 67.6 MHz (—— fit curve; · · · electronic contribution; - - - dipolar contribution).

$$\Gamma_{1\mathrm{e}} = K_{\mathrm{e}} T, \tag{2}$$

with the temperature-independent Korringa constant K_{e} [10]. In order avoid the formation of β-phase clusters, the relaxation studies could not been extended to temperatures below 200 K, where the measured Γ_1 should directly reveal $\Gamma_{1\mathrm{e}}$. The dipolar spin-lattice relaxation rate $\Gamma_{1\mathrm{d}}$ is due to the magnetic dipole–dipole interaction of a given proton with neighboring protons and with the host nuclei. The simplest approximation in order to deduce information on the hydrogen jump frequencies is to analyse $\Gamma_{1\mathrm{d}}$ by using the model proposed by Bloembergen, Purcell and Pound (BPP) [11]. If one neglects the interaction of the protons with the host nuclei, the BPP-model may be written as

$$\Gamma_{1\mathrm{d}} = \frac{2}{3}\frac{M_2}{\omega}\left[\frac{y}{1+y^2} + \frac{4y}{1+4y^2}\right], \tag{3}$$

with $y = \omega\tau_{\mathrm{c}}$. $\omega/2\pi$ denotes the NMR frequency and τ_{c} is the correlation time for the diffusional process modulating the dipole–dipole interaction. The second moment M_2 is a measure of the relaxation strength. If each proton remains at an interstitial site for a mean residence time τ before it jumps to a neighboring site in an infinitely short time, the correlation time is given by

$$\tau_{\mathrm{c}} = \frac{1}{2}\tau \tag{4}$$

with

$$\tau = \tau_0 \exp\left(\frac{E_{\mathrm{a}}}{k_{\mathrm{B}} T}\right), \tag{5}$$

for a single thermally activated jump process with an activation energy E_{a} and a preexponential factor τ_0. The solid line in Fig. 1 represents a fit of Eqs. (1)–(5) to the experimental data with the parameters given in Table 1.

The obtained activation energy for hydrogen diffusion in $PdH_{0.005}$ ($E_{\mathrm{a}} = 226$ meV) is in excellent agreement with the value of 230 meV, deduced by Völkl and Alefeld from the data of 25 studies [2], and the electrochemical time-lag method [12] yielded exactly the same value. Under the assumption of a simple random walk process, a preexponential factor $D_0 = 2.8\times10^{-7}$ m^2 s^{-1} can be calculated from τ_0. This value also agrees quite well with the preexponential factor given in the review of Völkl and Alefeld ($D_0 = 2.9\times10^{-7}$ m^2 s^{-1}) [2], and with the value deduced from the time-lag measurements ($D_0 = 2.6\times10^{-7}$ m^2 s^{-1}) [12]. The E_{a} and D_0 values extracted from the relaxation data, yield a diffusion coefficient at room temperature of $D(294\ \mathrm{K}) = 3.7\times10^{-11}$ m^2 s^{-1}.

The temperature dependences of the proton Γ_1 measured in $Pd_{0.9}Ag_{0.1}H_{0.015}$ at 67.6 MHz and in $Pd_{0.7}Ag_{0.3}H_{0.005}$ at 36.6 MHz are shown in Figs. 2 and 3. It is evident that the total relaxation rate Γ_1 decreases with increasing silver content due to the decrease of the electronic contribution $\Gamma_{1\mathrm{e}}$. A similar decrease in Γ_{e} with increasing silver content has also been observed at higher hydrogen concentrations in the α′-phase of $Pd_{1-x}Ag_xH_y$ [5].

The main difference to the behavior in $PdH_{0.005}$ is that the temperature dependence of $\Gamma_{1\mathrm{d}}$ is no longer well represented by a single BPP curve for the silver-containing alloys. This must be related to the barrier- and site-energy distribution that is expected due to the partial substitution of Pd atoms by Ag atoms. The distribution in the τ values, which results from the distribution in the activation energies, is usually taken into account by calculating the dipolar spin-lattice relaxation rate as [4]

$$\Gamma_{1\mathrm{d}} = \int \Gamma_{1\mathrm{d}}(E_{\mathrm{a}}) G(E_{\mathrm{a}})\, \mathrm{d}E_{\mathrm{a}} \tag{6}$$

where $G(E_{\mathrm{a}})$ is a normalized distribution function of the E_{a} values, and $\Gamma_{1\mathrm{d}}(E_{\mathrm{a}})$ is defined by Eqs. (3)–(5). A continuous distribution of the E_{a} values results in a reduced maximum relaxation rate, and the $\Gamma_{1\mathrm{d}}$ curve becomes asymmetric and broadened. An excellent example of the applicability of this approach is given by hydrogen in amorphous $Zr_3RhH_{3.5}$ [13]. In the present case, however, the relaxation curves are much better described by two or more discrete activation energies than by a distribution around a mean value. Thus, we replaced the integral in Eq. (6) by a summation according to

$$\Gamma_{1\mathrm{d}} = \sum_i \Gamma_{1\mathrm{d}}(M_{2,i}, E_{\mathrm{a},i}) \tag{7}$$

with different values for $E_{\mathrm{a},i}$ and $M_{2,i}$ in Eqs. (3)–(5). In order to reduce the number of adjustable parameters, we assumed for all jump processes the same prefactor τ_0. For the $Pd_{0.9}Ag_{0.1}H_{0.015}$ sample a fit with two activation energies was found to be adequate (Fig. 2), while for $Pd_{0.7}Ag_{0.3}H_{0.005}$ an appropriate fit requires the assumption of three activation energies (Fig. 3). The obtained fit parameters are summarized in Table 1. Within certain limits one could certainly assume different prefactors τ_0,

Table 1
Fit parameters of the spin-lattice relaxation rate curves in Figs. 1–3

Alloy	K_{e} (K^{-1} s^{-1})	$M_{2,i}$ (10^8 s^{-2})			τ_0 (s)	$E_{\mathrm{a},i}$ (meV)			E_{a} (meV)
		$M_{2,1}$	$M_{2,2}$	$M_{2,3}$		$E_{\mathrm{a},1}$	$E_{\mathrm{a},2}$	$E_{\mathrm{a},3}$	
$PdH_{0.005}$	0.0263	28			4.5×10^{-14}	226			226
$Pd_{0.9}Ag_{0.1}H_{0.015}$	0.0212	7.7	4.4		4.5×10^{-14}	226	283		247
$Pd_{0.7}Ag_{0.3}H_{0.005}$	0.0118	4.0	4.0	1.5	4.5×10^{-14}	226	269	324	260

E_{a} are mean values weighted by the second moments $M_{2,i}$.

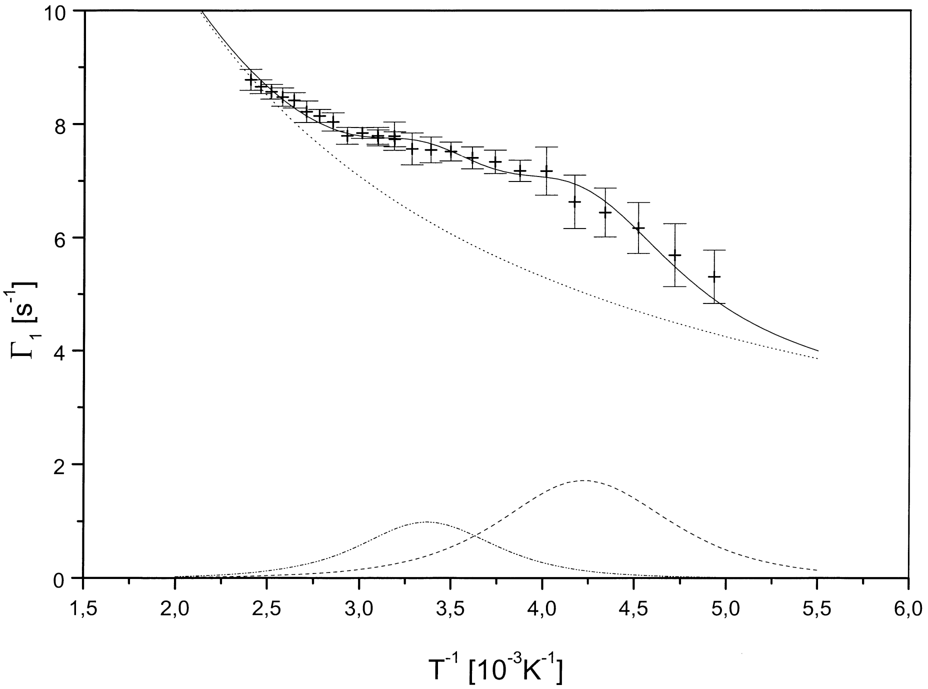

Fig. 2. Temperature dependence of the spin-lattice relaxation rate in $Pd_{0.9}Ag_{0.1}H_{0.015}$: + experimental data at 67.6 MHz; —— BPP fit; · · · electronic contribution; - - - dipolar contribution (process 1); · · - · · - dipolar contribution (process 2).

resulting in somewhat different values for $E_{a,i}$. In any case, a main result of the present work is that the microscopic diffusion behavior of hydrogen in palladium–silver alloys must be described by two (in $Pd_{0.9}Ag_{0.1}$) or even three (in $Pd_{0.7}Ag_{0.3}$) superimposed diffusion processes with different activation energies.

The slower a diffusion process the higher the temperature at which the corresponding Γ_{1d} maximum occurs at a

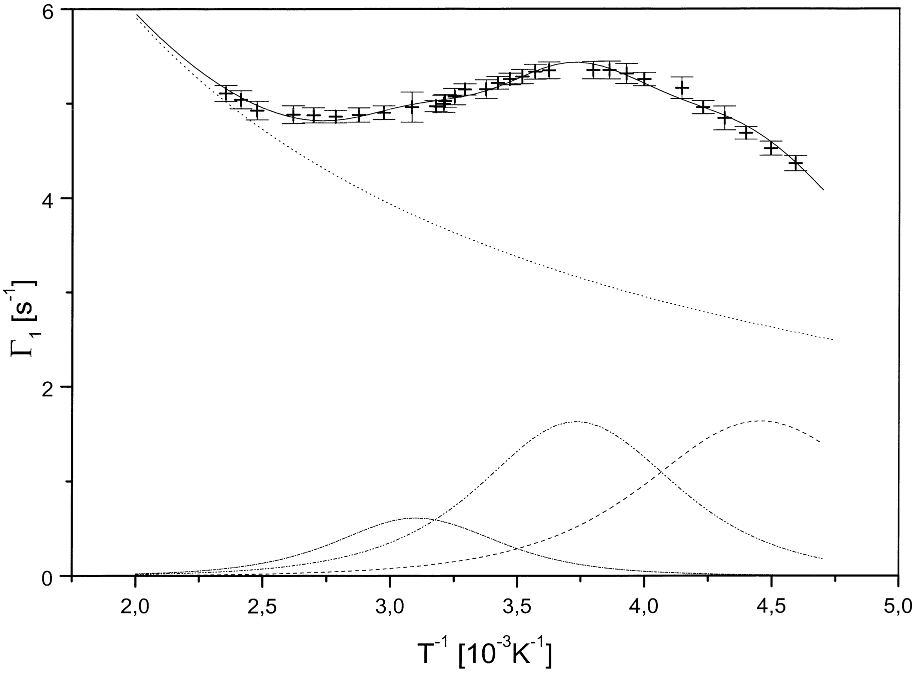

Fig. 3. Temperature dependence of the spin-lattice relaxation rate in $Pd_{0.7}Ag_{0.3}H_{0.005}$: + measuring data at 36.6 MHz; —— BPP fit; · · · electronic contribution; - - - dipolar contribution (process 1), · · - · · - dipolar contribution (process 2); · - · - · - dipolar contribution (process 3).

given NMR frequency. The relaxation data measured in $Pd_{0.9}Ag_{0.1}H_{0.015}$ at 67.7 MHz reveal a pronounced peak at ~235 K, comparable to the peak in pure palladium (Fig. 1). The second peak at ~275 K is caused by a slower diffusion process. In $Pd_{0.7}Ag_{0.3}H_{0.005}$, where the data are taken at 36.6 MHz, the peak due to the fastest diffusion process appears at ~225 K, and two slower diffusion processes give rise to relaxation peaks at higher temperatures (Fig. 3). In both $Pd_{1-x}Ag_xH_y$ samples the fastest diffusion process (with the smallest activation energy) is well described by the diffusion parameters of hydrogen in pure palladium (cf. Table 1). This result is in good agreement with the diffusion model proposed previously on the basis of time-lag measurements and computer simulations. According to that model, the hydrogen diffusion in $Pd_{1-x}Ag_x$ alloys takes place preferably by a 'roundabout way' via Pd-rich diffusion paths avoiding Ag-rich regions [6,7]. Higher activation energies are required for diffusion paths via O-sites, which are partly formed by silver atoms. One may speculate that the $E_{a,2}$ values are mainly related to hydrogen jumps over O-sites with one silver atom per octahedron, and the higher $E_{a,3}$ value is required for jumps over O-sites where more than one Pd atom is substituted by Ag atoms.

Another interesting result is that for both $Pd_{1-x}Ag_xH_y$ samples the sum of the $M_{2,i}$ values is less than M_2 for hydrogen in PdH_y, although the hydrogen content in the palladium–silver alloys is in one case equal to and in the other case even higher than that in the pure palladium (cf. Table 1). This indicates additional processes of hydrogen motion in $Pd_{1-x}Ag_xH_y$, which do not contribute to the relaxation rates in the considered temperature range. One may think of hydrogen motion via silver-rich environments with jump frequencies that are substantially lower than the NMR frequency.

3.2. Macroscopic diffusion coefficients measured by PFG-NMR

Model-independent measurements of the long-range diffusion coefficient D of hydrogen in the palladium–silver alloys have been performed by PFG-NMR. The temperature dependence of the D values is shown in Fig. 4. At a given temperature, the hydrogen diffusivity is smaller in $Pd_{0.7}Ag_{0.3}H_{0.005}$ than in $Pd_{0.9}Ag_{0.1}H_{0.015}$. A similar decrease in the diffusivity with increasing silver content has been observed previously by time-lag measurements [1] and by PFG-NMR studies of the α′-phase of palladium–silver alloys [5]. However, at a small silver content ($x=0.1$) the diffusivities of hydrogen agree very well with those in pure palladium. This is evident from the dashed line in Fig. 4, representing $D(T)$ for hydrogen in α-PdH_y [2]. A nearly constant diffusion coefficient up to a silver content of 20 at.% has also been found by time-lag measurements, indicating that hydrogen diffusion takes place preferably in Pd-rich environments [6,7].

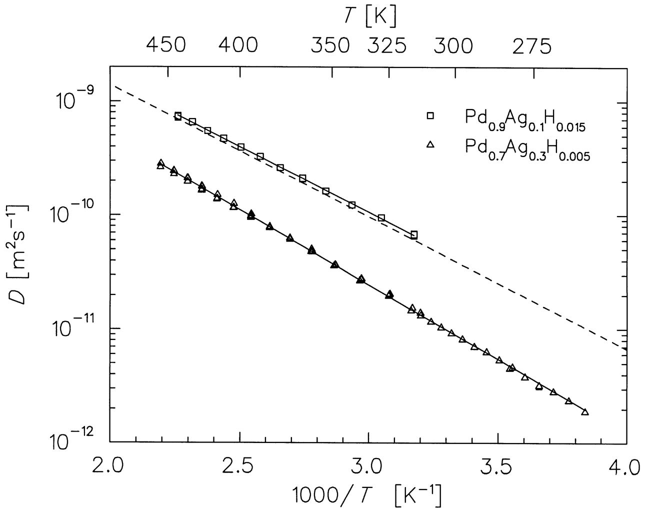

Fig. 4. Arrhenius plot of the hydrogen diffusivity D in $Pd_{0.9}Ag_{0.1}H_{0.015}$ and $Pd_{0.7}Ag_{0.3}H_{0.005}$ measured by PFG-NMR. The dashed line shows, for comparison, the diffusivity in pure palladium [2].

Over the entire temperature range the D values of both $Pd_{1-x}Ag_xH_y$ samples are well represented by single Arrhenius laws,

$$D = D_0 \exp(-E_a/k_B T) \tag{8}$$

with the diffusion parameters given in Table 2. For comparison, the D_0 and E_a values deduced from electrochemical time-lag measurements [1,14] and the diffusion coefficients at $T=294$ K are also included in Table 2. The agreement in the diffusion parameters and the values for D(294 K) is satisfactory, considering that quite different methods have been applied and that the samples may have slightly different H concentrations. Interestingly, the activation energy in $Pd_{0.9}Ag_{0.1}H_{0.015}$ is very close to $E_a=228$ meV, deduced from PFG measurements on α′-$PdH_{0.7}$ [15].

The fact that the hydrogen diffusion in $Pd_{0.9}Ag_{0.1}H_{0.015}$ occurs predominantly by jumps between O-sites formed by Pd atoms explains why the activation energy for long-range diffusion ($E_a=230$ meV) is very close to $E_{a,1}$ found in this system. On the other hand, in the case of $Pd_{0.7}Ag_{0.3}H_{0.005}$, where it is more likely that one or more of the Pd atoms per octahedron are substituted by Ag atoms, the E_a value for long-range diffusion (260 meV) is in very good agreement with the mean value deduced from the relaxation data (cf. Table 1).

4. Summary and outlook

The jump processes of hydrogen in $Pd_{1-x}Ag_xH_y$ have been studied by Γ_1 measurements and the diffusion coefficients D have been determined directly by PFG-NMR. As a main result, the data show clearly the existence of more than one jump process in the silver-containing alloys. The discrete jumps frequencies with different activation

Table 2
Comparison of diffusion data obtained by PFG-NMR (this paper) and time-lag techniques

Alloy	$D_0 \times 10^7$ (m^2 s^{-1})		E_a (meV)		D(294 K)$\times 10^{11}$ (m^2 s^{-1})	
	PFG	Time-lag [1]	PFG	Time-lag [1]	PFG	Time-lag [1]/[14]
$Pd_{0.9}Ag_{0.1}$	3.0	4.3	230	232	3.4	4.5/3.2
$Pd_{0.7}Ag_{0.3}$	2.1	2.3	260	243	0.7	1.6/1.0

energies are related to jumps between O-sites, which have different surroundings with respect to the Pd to Ag atomic ratio. As a general trend, the activation energies are higher the more palladium atoms per octahedron are substituted by silver atoms. This is consistent with the microscopic diffusion model proposed previously on the basis of time-lag measurements and computer simulations [6,7]. An unambiguous assignment of the activation energies to certain diffusion paths requires further NMR studies over extended ranges in silver content, temperature and NMR frequency. Moreover, a more rigorous extension of the BPP model, which incorporates simultaneous barrier- and site-energy distributions [16], to disordered systems may provide further insight into the microscopic mechanisms of diffusion.

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