

Model-Independent Measurements of Hydrogen Diffusivity in the Lanthanum Dihydride-Trihydride System

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First model-independent measurements of the hydrogen diffusivity D in lanthanum trihydrides LaH_x ($2.00 \leq x \leq 3.0$) have been performed by PFG-NMR. At a fixed concentration $x \leq 2.92$, $D(T)$ shows single Arrhenius behavior over wide temperature ranges. The activation enthalpy decreases with increasing x from 0.55 eV ($x = 2.00$) to 0.17 eV ($x = 2.92$), resulting in a strong increase in D . The formation of a hydrogen superstructure associated with the semiconductor-to-metal transition results in a strong reduction in D . It was also observed for the first time that in the stoichiometric limit D depends on the thermal history of the sample.

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Recent experiments demonstrating the switchable optical properties of yttrium, lanthanum, and other rare-earth hydride films have again focused interest on these unusual systems [1–3]. An important factor underlying the switching speed is the diffusivity of hydrogen in the hydride. But in spite of intensive investigations over the years [4], the mechanisms of hydrogen diffusion in these systems are not yet understood.

Lanthanum forms nonstoichiometric homogeneous hydrides LaH_x with the fluorite structure in the concentration range from $x \approx 1.9$ to $x = 3.0$. The hydrogen atoms occupy predominantly the tetrahedral (T) interstitial sites at low concentrations, and with increasing concentration, the octahedral (O) sites are also filled.

Nuclear magnetic resonance (NMR) offers unique capabilities to measure the diffusion on both macroscopic and microscopic scales [5,6]. The pulsed-field-gradient technique (PFG-NMR) permits model-independent measurement of the long-range diffusivity D . We report here the first PFG measurements of hydrogen diffusivity in lanthanum hydrides, LaH_x ($2.0 \leq x \leq 3.0$), over a wide range of temperatures, $235 \leq T \leq 800$ K, as well as the discovery of unusual hysteresis effects accompanying an order-disorder transition in stoichiometric LaH_3 .

The six samples of the present work with $2.0 \leq x \leq 2.92$ are those used in previous NMR studies [7–9]. They were prepared from the highest-purity Ames Laboratory lanthanum available, having a total magnetic rare-earth impurity content, determined by mass spectroscopy, below 4.5 ppm. The LaH_3 sample has a higher magnetic rare-earth impurity content of 25 ppm. The uncertainties in the hydrogen concentrations x are about 1% of the quoted values.

The PFG measurements were performed by using the stimulated-echo sequence [10]. Typical operating parameters were gradient pulse length $\delta = 1$ ms and diffusion

time $\Delta = 10$ ms. Within Δ the hydrogen atoms diffuse over a distance of the order of $1 \mu\text{m}$. The diffusivities were determined from the variation of the echo attenuation with the amplitude of the gradient pulses up to 25 Tm^{-1} .

Figure 1 shows an Arrhenius plot of the diffusivities D measured on six LaH_x samples ($x = 2.00$ – 2.92). At a given temperature, D increases strongly with increasing x in this concentration range. At 500 K the diffusivity for $x = 2.92$ is greater by a factor of 830 than that for $x = 2.0$. Quasielastic neutron scattering (QNS) on YH_x ($1.8 \leq x \leq 2.1$) at 450 K also revealed a significant increase in the hydrogen jump rate with increasing x [11]. By contrast, in the dihydrides of zirconium [12,13] and titanium [14] the hydrogen diffusivity at a given temperature decreases with increasing hydrogen content.

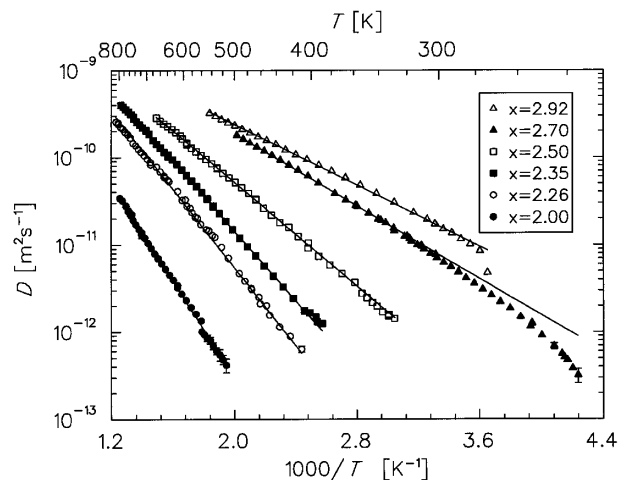


FIG. 1. Temperature dependence of the hydrogen diffusivity D in LaH_x ($2.00 \leq x \leq 2.92$) measured by PFG-NMR. The solid lines represent Arrhenius laws with the diffusion parameters given in Table I.

The solid lines in Fig. 1 represent fits of an Arrhenius law to the D values within the temperature ranges indicated in Table I. The corresponding fitting parameters are also given in Table I together with the diffusivities at 500 K. It is evident that the increase in D with increasing x is due to the decrease in the effective activation enthalpy H_a . The preexponential factors D_0 which are of the same magnitude as those found in TiH_x [14], for example, are generally the smaller the higher x . Except near $x \approx 2.3$, D_0 decreases as a linear function of $(3 - x)$, indicating that the blocking factor is determined primarily by the O -site occupancy.

For $x \leq 2.50$ the temperature dependence of D at a fixed concentration x is well represented by an Arrhenius law over the entire temperature range, and, except for the deviations at low temperatures, $D(T)$ for $x = 2.70$ and 2.92 shows also Arrhenius behavior. This result is quite remarkable considering that one expects multiple jump possibilities for hydrogen in LaH_x . Obviously, the diffusion process is always dominated by a single energy barrier, regardless of whether hydrogen occupies O or T sites. This is in accordance with the diffusion model proposed by Schreiber and Cotts [15]. In this model, the energy barrier H_a is that required to excite a hydrogen atom from a T site into an O site. The resulting vacancy in the T -site sublattice can then be filled by a hydrogen atom from another O site. As more hydrogen atoms are added and, thus, as more O sites are occupied, the electronic structure of the system is evidently modified in such a way that the H_a value of this diffusion process is substantially reduced. This behavior is comparable to that found in several fast ionic conductors where an increasing defect concentration lowers the barrier for diffusion, which may indicate collective diffusion mechanisms [16].

Measurements of the proton spin-lattice relaxation rate Γ_1 have been performed previously on the same samples at a resonance frequency of 40 MHz [9]. The activation enthalpies H_a , deduced from the dipolar contribution $\Gamma_{1,\text{dip}}$ by applying the phenomenological Bloembergen-Purcell-Pound (BPP) model [17], show the same trend as the present results. The absolute values, however, are

TABLE I. Diffusion parameters of hydrogen in LaH_x obtained by fitting Arrhenius expressions to the diffusivities D within the indicated temperature ranges. Estimated uncertainties are $\pm 3\%$ in activation enthalpies H_a and $\pm 20\%$ in preexponential factors D_0 . The diffusivities at 500 K, $D(500 \text{ K})$, have been calculated from the fitting parameters.

x	D_0 ($10^{-8} \text{ m}^2 \text{ s}^{-1}$)	H_a (eV)	T (K)	$D(500 \text{ K})$ ($10^{-12} \text{ m}^2 \text{ s}^{-1}$)
2.00	11	0.55	500–800	0.3
2.26	16	0.44	410–800	5.9
2.35	14	0.40	390–800	13
2.50	4.7	0.29	330–680	56
2.70	2.3	0.21	330–500	176
2.92	1.3	0.17	280–550	250

10%–15% lower than the results obtained in the model-independent PFG measurements. This is consistent with previous reports [14,18] that the BPP model tends to yield H_a values that are too small. Early measurements of the temperature dependence of the proton NMR linewidth in several LaH_x samples ($x \leq 2.85$) [15] yielded H_a values which are in good agreement with the present PFG results. From recent QNS experiments on LaH_x the value $H_a \approx 0.17 \text{ eV}$ was deduced for $x = 2.75$ and for $x = 2.96$, while $H_a \approx 0.20 \text{ eV}$ was reported for $x = 2.50$ [19]. The increase in H_a with decreasing x is in accordance with the present and with previous NMR studies but, as pointed out by the authors [19], the QNS result for $x = 2.50$ can only be considered as a gross approximation as the corresponding linewidth broadening is almost 2 orders of magnitude smaller than the instrument resolution.

Another significant result of the PFG studies is the deviation from Arrhenius behavior of D at lower temperatures in $\text{LaH}_{2.70}$ and $\text{LaH}_{2.92}$. In $\text{LaH}_{2.70}$ this deviation starts at about 300 K, but hydrogen atoms retain a rather high mobility, even down to 235 K. In contrast to that, in $\text{LaH}_{2.92}$ the diffusivity drops down within the temperature range from 275 to 270 K so strongly that the spin-spin-relaxation time is reduced from $T_2 \approx 10 \text{ ms}$ to values well below 1 ms, which are much too short for PFG measurements. This drastic decrease of the hydrogen diffusivity can be explained most easily by hydrogen ordering. The formation of a hydrogen superstructure reduces the number of sites available for hydrogen occupation and, thus, the hydrogen diffusivity.

Shinar and co-workers [4] studied the temperature dependence of the bulk resistivity in LaH_x ($2.70 \leq x \leq 2.93$) and found transitions from semiconducting behavior at high temperatures to metallic behavior at low temperatures. The transitions occur at roughly the same temperatures, where D starts to deviate from Arrhenius behavior. The O -site hydrogen vacancies in LaH_x possess donor-like electron states, and the formation of a superstructure of these vacancies may yield a donor band around the Fermi energy [4]. The present diffusion data clearly support this idea that hydrogen ordering is related to the semiconductor-to-metal transition.

Neutron diffraction studies revealed ordering of ^2H in La^2H_x on the O -site sublattice in the concentration range $2.2 \leq x \leq 2.6$ [20,21], accompanied by a tetragonal distortion of the host lattice. Tetragonal distortions of La^2H_x samples were also observed in the concentration range $2.65 \leq x \leq 2.85$ [4,22], but for $x = 2.70$ only below 240 K. On the other hand, in the sample $\text{La}^1\text{H}_{2.70}$ the semiconductor-to-metal transition and the deviation from Arrhenius behavior of $D(T)$ occurs at about 300 K. This difference in the transition temperature may be ascribed to a pronounced isotope effect. Furthermore, neutron diffraction indicates that for $x = 2.50$ ordering of ^2H starts at 385 K and is fully developed in the vicinity of 200 to 230 K [21], whereas the hydrogen diffusivity in $\text{La}^1\text{H}_{2.50}$ shows no deviation from Arrhenius behavior in

the entire temperature range from 330 to 680 K. This may indicate that the effect of hydrogen ordering on the diffusivity is less severe for lower hydrogen concentrations.

At the composition limit LaH_3 both the T and the O sites are ideally fully occupied, but it has been found that the hydrogens are displaced off-center from the ideal O -site positions along the $\langle 111 \rangle$ directions [23]. There are eight possibilities for such off-center displacements from each O site. The diffusivities D of hydrogen in LaH_3 measured by PFG-NMR between 250 and 500 K are shown in Fig. 2. The fit curves for $x = 2.70$ and 2.92 of Fig. 1 are included for comparison. Several features of these data are noteworthy.

First, it is remarkable that in the stoichiometric limit, where essentially all T and O sites are occupied, hydrogen continues to retain a high diffusivity. Clearly, $D(T)$ does not follow an Arrhenius law over an extended temperature range in the trihydride.

Second, a smooth change (crossover) in the diffusion mechanism occurs roughly between 300 and 400 K. As long as only one diffusion process with a unique jump distance L exists, the diffusion coefficient may be written as

$$D = f^T L^2 / 6\tau_d, \quad (1)$$

where f^T denotes the tracer correlation factor and τ_d the mean dwell time of the migrating hydrogen atoms. A temperature dependence of D as shown in Fig. 2 is expected if the jump distance L (and/or f^T) is smaller at high temperatures than at low temperatures, assuming that the activation enthalpy H_a is the same in both regimes. The Γ_1 data give no evidence of a change in H_a related to

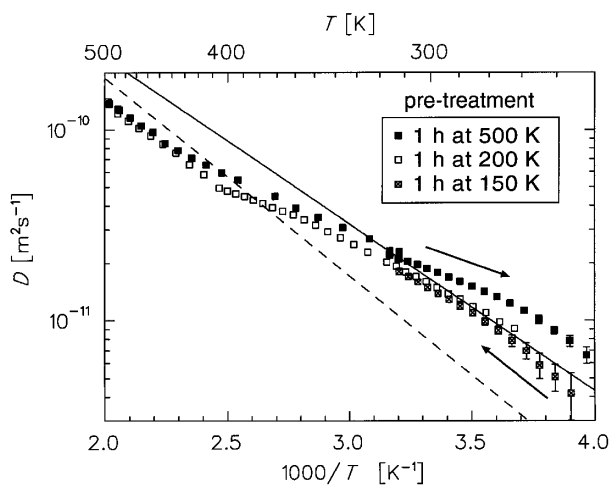


FIG. 2. Hydrogen diffusivities D measured by PFG-NMR after different pretreatments of LaH_3 . Data were taken from high to low temperatures after keeping the sample for 1 h at 500 K (solid squares), and from low to high temperatures after keeping it for 1 h at 200 K (open squares) or at 150 K (open squares with crosses). Whether the data are taken on warming or on cooling the sample is also indicated by the arrows. The solid line shows, for comparison, the fit from Fig. 1 to $D(T)$ of $\text{LaH}_{2.92}$. The dashed line shows the corresponding curve of $\text{LaH}_{2.70}$.

the crossover in $D(T)$ [9]. A transition from occupancy of off-centered T sites at lower temperatures to centered T sites at higher temperatures has been postulated [24]. From an off-center position some neighboring sites are more and some are less distant than from the center of the same site, regardless of whether it is a T site or an O site. Thus, although the diffusion mechanism in the stoichiometric limit is not yet understood, one may speculate that such a phase transition is accompanied by a change in the effective value of L .

Third, superimposed on this general temperature dependence, the measured values of D depend on the thermal history of the LaH_3 sample. A run from low to high temperatures yields smaller diffusivities than one from high to low temperatures. The full squares in Fig. 2 are data points of a measurement started at high temperatures after having maintained the sample temperature at 500 K for 1 h. The open squares represent two series of measurements started at low temperatures. Before these measurements were started, the sample was kept for 1 h at 200 and 150 K (open squares with crosses), respectively.

In thermal equilibrium, a hydrogen superstructure on off-centered O sites exists at low temperatures [4]. It is reasonable to assume that the hysteresis in the diffusivity is related to a hysteresis in the phase transition from the disordered to the ordered occupancy of off-centered O sites. The different D values can then be attributed to the difference in site-blocking factors between the ordered and disordered phases. Previous NMR measurements of resonance line shapes and $\Gamma_1(T)$ showed the coexistence of ordered and disordered phases in the high x -value samples over the temperature range 180–280 K, with hydrogen hopping frequencies that differ by about a factor of 2 [8]. This factor of 2 correlates well with the differences between the D values measured by PFG-NMR at about 250 K after different pretreatments of the sample (cf. Fig. 2). The occurrence of a hysteresis provides a strong indication that the host metal lattice itself undergoes a structural change, although such a change has never been demonstrated for $x > 2.80$ despite the appearance of extra lines in the x-ray powder diffraction pattern of $\text{LaH}_{2.99}$ [22].

In order to study this hysteresis more precisely, the following experiment has been performed: The sample was cooled to 200 K once, and this temperature was maintained for 1 h. Subsequently, the sample was repeatedly heated to a temperature T_{heating} for 0.5 h before D was measured at $T = 310$ K. T_{heating} was increased in steps of about 10 K from 325 to 480 K but the diffusion data were always taken at 310 K. Figure 3 shows that $D(310$ K) increases by about 15% in the range of T_{heating} between 420 and 450 K.

Measurements of the heat capacities also provide indications of hysteresis effects in lanthanum trihydrides [24]. The data for La^2H_3 , measured on heating from 1.2 to 300 K, revealed four peaks, indicating four phase transitions. One of these peaks, at 230.5 K, is not observed

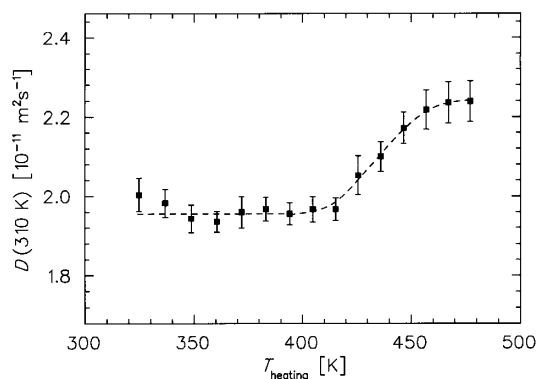


FIG. 3. Diffusivities of hydrogen in LaH_3 measured at 310 K as a function of T_{heating} , the temperature to which the sample was heated for 0.5 h before the data were taken. In order to have a well defined situation to start with, the sample temperature was maintained for 1 h at 200 K before this series of measurements was started. The line is a guide to the eyes.

if the measurement is started at 220 K. This peak was interpreted as due to the transition from random to ordered occupancy of off-centered O sites. The authors concluded from the absence of this peak that the ordered arrangement of deuterium on off-centered O sites was not formed when the sample was cooled to only 220 K [24]. This interpretation is consistent with the present diffusion studies on La^1H_3 , which suggest that the formation of a superstructure on off-centered O sites requires rather low temperatures, but, once it is formed, it may exist over extended temperature ranges. The measurements of the heat capacity of LaH_3 yielded only two peaks, at 241 and at 270 K [4,24]. The authors assumed that two of the phase transitions in La^2H_3 collapse into one transition in La^1H_3 and that a transition from occupancy of off-centered T sites to centered T sites in La^1H_3 falls outside of the temperature range of their measurements [24]. They proposed that this third transition in the case of La^1H_3 occurs at about 315 K [24]. This temperature is in fair agreement with the onset of the crossover in the diffusion mechanism (cf. Fig. 2). In contrast to the behavior in La^2H_3 , the observed peaks in the heat capacity of La^1H_3 were independent of the starting temperature of the measurements [4,24].

In summary, the diffusivity D of hydrogen in the lanthanum trihydrides LaH_x has been measured for the first time over wide ranges in concentration and temperature using PFG-NMR. For $2.00 \leq x \leq 2.92$ the activation enthalpy for hydrogen motion H_a decreases substantially with increasing x , resulting in a strong increase in D . At the transition from semiconducting behavior at high temperatures to metallic behavior at low temperatures a pronounced reduction in D is observed. This result is consistent with the model that the transition is associated with the formation of a superlattice on the O -site sublattice. In the stoichiometric limit LaH_3 the measured D values depend on the thermal history of the sample, indicating a hysteresis in the formation of an ordered structure of hydrogen on the off-centered O sites.

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