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Nuclear relaxation in the dideuterides of hafnium and titanium

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The deuteron spin-lattice relaxation in the substoichiometric dideuterides $HfD_x(1.68\leqslant x\leqslant 1.90)$ and $TiD_x(x=1.91)$ has been measured at temperatures between 300 and 830 K. The results are compared with previous proton NMR measurements on dihydrides of similar hydrogen contents. The deuteron relaxation rate Γ_1, which consists of quadrupolar ($\Gamma_{1,\mathrm{quad}}$), dipolar ($\Gamma_{1,\mathrm{dip}}$), and electronic ($\Gamma_{1,\mathrm{e}}$) contributions, is dominated by $\Gamma_{1,\mathrm{quad}}$. The deuterium atoms jump predominantly from occupied tetrahedral sites (T sites) to nearest-neighbor vacant T sites. The fluctuations in the electric field gradients are related to the jumps of the vacancies on the deuterium sublattice. The $\Gamma_{1,\mathrm{quad}}$ maximum occurs at a lower temperature than the $\Gamma_{1,\mathrm{dip}}$ maximum, reflecting the higher jump frequency of the vacancies compared to that of the deuterium atoms. The temperature dependence of $\Gamma_{1,\mathrm{quad}}$ yields the activation enthalpy H_a of the deuterium vacancies and thus that of the deuterium atoms in the dideuterides. These H_a values are in good agreement with the activation enthalpies of hydrogen atoms in corresponding dihydrides.

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I. INTRODUCTION

The group IVb transition metals titanium, zirconium, and hafnium absorb large quantities of hydrogen to form metallic dihydrides MeH_x with similar physical properties. These dihydrides are generally non stoichiometric with hydrogen concentrations between $x\approx 1.5$ and 2. In the lower part of this concentration range the metal atoms form a face-centered-cubic (fcc) structure, while at higher hydrogen concentrations tetragonal distortions occur. The hydrogen atoms occupy the tetrahedral interstitial sites (T sites), forming a simple cubic (or simple tetragonal) sublattice within the fcc (or fct) metal matrix.

Nuclear magnetic resonance (NMR) has been used for many years to study hydrogen diffusion in metal-hydrogen systems.[1] The jump frequency of hydrogen atoms in the dihydrides TiH_x,[2–7] ZrH_x,[8–12] and HfH_x (Ref. 13) has been deduced from the dipolar contribution to the proton spin-lattice relaxation rate Γ_1. Additionally, the long-range diffusivity of hydrogen atoms in TiH_x,[14,15] ZrH_x,[16,17] and HfH_x (Ref. 13) has been measured by pulsed-field-gradient (PFG) spin-echo NMR. The underlying diffusion mechanism in these dideuterides could be determined by a combined analysis of the Γ_1 and the PFG data.[13–17]

The same diffusion mechanism has been found for all dihydrides of the group IVb transition metals: Up to $x\approx 1.9$ the hydrogen atoms jump predominantly between nearest-neighbor T sites, and the activation enthalpy of $H_\mathrm{a}\approx 0.55$ eV for TiH_x,[15] $H_\mathrm{a}\approx 0.65$ eV for ZrH_x,[16,17] and $H_\mathrm{a}\approx 0.67$ eV for HfH_x (Ref. 13) depends only weakly on the hydrogen concentration. The decrease in the diffusivity with increasing x is due to blocking of occupied T sites. For jumps between nearest-neighbor sites on a sc lattice with blocking of occupied sites Monte Carlo calculations of the spectral density functions for the dipolar spin-lattice relaxation $\Gamma_{1,\mathrm{dip}}$ are available.[14,18,19] The results of these calculations depend slightly on $x/2$, the occupation probability of a site in the sc lattice. Sholl has introduced an analytic form for the spectral densities[19] which adequately represents the numerical data. For $x\leqslant 1.9$, the relaxation rates are well represented by the Monte Carlo calculations and a fit of Ref. 19 to the experimental data yields diffusion coefficients which are in very good agreement with the PFG results.[13–17] This confirms that the hydrogen diffusion indeed occurs by jumps from occupied to nearest-neighbor unoccupied T sites.

So far, only very few studies of deuterium diffusion in dideuterides MeD_x have been performed. The PFG-NMR measurements on TiD_x (Ref. 15) suggest a semiclassical picture of hydrogen/deuterium diffusion. The attempt frequency of hydrogen/deuterium diffusion is proportional to the vibrational frequency of the atoms at an interstitial site, which is smaller by a factor of $\sqrt{2}$ for deuterium than for hydrogen. The effective activation enthalpy in a deuteride is only slightly higher than that in a hydride with the same hydrogen/deuterium content. This difference is of the order of 0.01 eV and it is due to different zero-point motion energies of hydrogen and deuterium.

Magnetic dipolar relaxation is relatively less effective for deuterons than for protons because of the deuteron's small gyromagnetic ratio. In metal-deuterium systems, deuteron relaxation is usually dominated by quadrupolar fluctuations. Although a deuteron at a T site in a fcc lattice experiences no electric field gradient (EFG) due to the symmetry of the metal lattice, fluctuating EFGs arise from transient occupation of some neighboring interstitial sites by other deuterons. In the case of a nearly filled deuterium sublattice in substoichiometric dideuterides, the deuterium vacancies on these sublattice are the sources of fluctuating EFGs. If the metal lattice becomes tetragonal at high x values, static EFGs may also exist on the deuteron sites. However, as in the dipolar case, only the time dependent interactions result in a spin-lattice relaxation. The relaxation rate is a linear combination of spectral density functions which are the Fourier transforms of the correlation functions of the EFG fluctuations. An important difference between magnetic dipole and electric quadrupole relaxation is that in the former the nuclear dipole moment interacts separately with each of the surrounding dipoles, whereas the quadrupole moment interacts with the total EFG due to all surrounding charges taken together.[1] Hence, three-particle as well as two-particle correlation functions are needed to adequately describe quadrupolar relaxation, whereas only two-particle functions are necessary for the dipolar relaxation.

The present paper reports on deuteron Γ_1 measurements on well-characterized dideuterides of hafnium and titanium. The data are analyzed together with information available from previous NMR studies of hydrogen diffusion in fcc dihydrides. A special emphasis is put on the quadrupolar relaxation analysis in view of recent developments in the theory of quadrupolar relaxation.[20,21] It has been shown that, for an arbitrary concentration c of sources of fluctuating EFGs, the spectral density functions may simply be related to the case for a low concentration. The relaxation rates for different c only scale as $c(1-c)$ and the maxima in the rates as a function of temperature are expected to occur at the same temperature for all c.[20,21] The quadrupolar relaxation of ^{45}Sc in ScH(D)$_x$ is, for example, reasonable consistent with the maximum relaxation rate being proportional to $c(1-c)$ and with the maximum rate occurring at the same temperature for all c.[20] In the present work, the quadrupolar relaxation rates of deuterons in the substoichiometric dideuterides of hafnium and titanium have been considered. These studies enable us to test the consistency and validity of the theory of quadrupolar relaxation for relaxation of the diffusing species. A further aim of our work is to obtain comprehensive data on hydrogen and deuterium diffusion in the group IVb transition metal dihydrides/dideuterides.

II. EXPERIMENTAL DETAILS

The samples were prepared from high-purity metals at the Ames Laboratory. The metal was heated up to 1100 K under vacuum and subsequently exposed to deuterium gas in a modified Sieverts apparatus. The system was maintained at this temperature for 24 h to assure equilibrium and then gradually cooled to room temperature in the presence of the deuterium gas. The brittle deuteride was ground in a helium-filled glove box to a powder of typical grain size 50 μm. One TiD$_x$ sample ($x=1.91$) and three HfD$_x$ samples ($x=1.68$, 1.76, and 1.90) were prepared. The concentrations were first estimated from the pressure change in the calibrated volume of the system and were then precisely determined by hot-vacuum-extraction analysis. The uncertainties in the deuterium concentrations x are about 2% of the quoted values. All samples were sealed in quartz tubes of an inner diameter of 7 mm and a length of 12 mm under a pressure of about 0.1 bar of He.

Measurements of the deuteron Γ_1 were performed over the temperature range 300–830 K at resonance frequencies of 10.4 and 34.3 MHz. The NMR signals were observed with a home-built Fourier transform spectrometer using phase-alternating pulse schemes and quadrature detection. The Γ_1 values followed from fitting recovery curves to the signal amplitudes that were monitored after the 90° pulse of a $180°-\tau-90°$ pulse sequence. The sample temperature was maintained by means of a digital PID controller combined with ohmic heating and was determined by two calibrated platinum resistors to about ± 0.1 K.

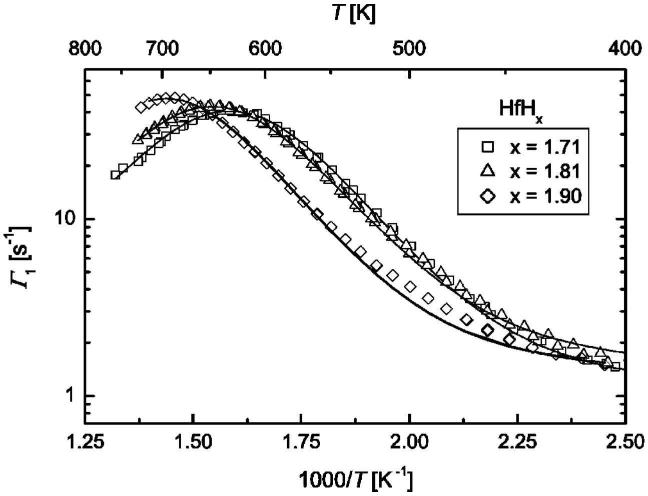

FIG. 1. Proton spin-lattice relaxation rate Γ_1 measured on HfH$_x$($x=1.71$, 1.81, 1.90) at 37.3 MHz. The solid lines represent the sum of the electronic relaxation $\Gamma_{1,e}$ [Eq. (2)] and the dipolar relaxation $\Gamma_{1,dip}$ [Sholls's model for nearest-neighbor jumps on a sc lattice (Ref. 19)]. The fitting parameters are given in Ref. 13.

III. RESULTS AND DISCUSSION

For a comparison with the present results on deuterated samples, the proton spin-lattice relaxation rates Γ_1 measured previously on HfH$_x$ ($x=1.71$, 1.81, and 1.90) (Ref. 13) are shown in Fig. 1. The shift in the position of the relaxation maximum to higher temperatures indicates a decrease in the diffusivity with increasing x, which is in agreement with PFG measurements.[13] In metallic systems the total spin-lattice relaxation rate may generally be written as

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

In the case of spin $\frac{1}{2}$ nuclei such as protons no electric quadrupole relaxation $\Gamma_{1,quad}$ occurs. The electronic relaxation $\Gamma_{1,e}$ results from the interaction between the magnetic moments of protons and conduction electrons, and it is usually expressed by the Korringa relation[22]

$$\Gamma_{1,e} = T \cdot C_K^{-1}. \tag{2}$$

The dipolar spin-lattice relaxation rate $\Gamma_{1,dip}$ is due to the magnetic dipole-dipole interaction of a given proton with neighboring protons and, in general, also with the host nuclei. In the case of HfH$_x$, the dipolar interaction between the protons and the host metal nuclei can be neglected due to the low natural abundance and small nuclear moments of the two Hf isotopes ^{177}Hf and ^{179}Hf. Thus, $\Gamma_{1,dip}$ results only from

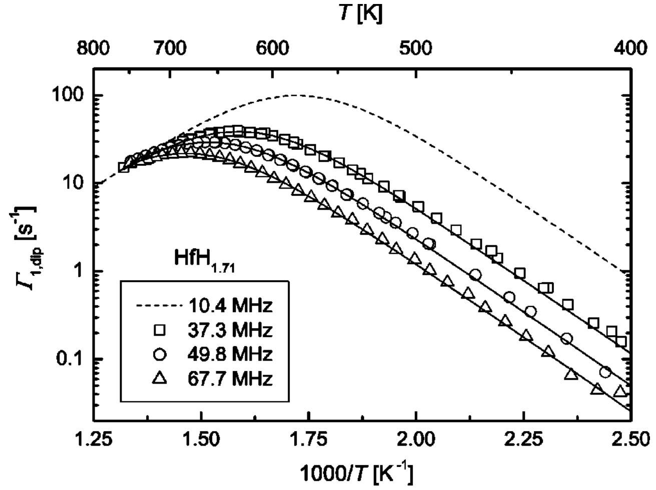

FIG. 2. Dipolar spin-lattice relaxation rate $\Gamma_{1,\mathrm{dip}}$ of hydrogen in $\mathrm{HfH}_{1.71}$ measured at 37.3, 49.8, and 67.7 MHz (from Ref. 13). The solid lines represent Sholl's model (Ref. 19) for $\Gamma_{1,\mathrm{dip}}$ at these frequencies and the dashed line is the corresponding curve at 10.4 MHz.

the diffusion-modulated dipole-dipole interaction between the protons. Figure 2 shows $\Gamma_{1,\mathrm{dip}}$ obtained by subtracting Eq. (2) with $C_{\mathrm{K}}=310$ Ks from Γ_1 measured on $\mathrm{HfH}_{1.71}$.[13]

These data are well described by the Monte Carlo calculations[19] for nearest-neighbor jumps on a sc lattice. The thin solid lines in Figs. 1 and 2 are obtained by fitting[19] to the $\Gamma_{1,\mathrm{dip}}$ data under the assumption of a single thermally activated process of hydrogen motion according to the mean dwell time

$$\tau=\tau_0\cdot\exp(H_{\mathrm{a}}/k_{\mathrm{B}}T). \tag{3}$$

The $\Gamma_{1,\mathrm{dip}}$ curve for $\mathrm{HfH}_{1.71}$ expected at 10.4 MHz is also included in Fig. 2. This curve has been calculated by using the prefactor $\tau_0=1.2\times10^{-14}$ s and the activation enthalpy $H_{\mathrm{a}}=0.67$ eV, which have been obtained by the simultaneous fit to the $\Gamma_{1,\mathrm{dip}}$ data measured at 37.3, 49.8, and 67.7 MHz.

The value of τ_0 obtained in this way may be compared with that based on inelastic neutron scattering measurements of optical vibration frequencies. For metal hydrides, the attempt frequency for single particle hopping on an empty lattice, $\nu_0=\tau_0^{-1}$, is related to the optic mode frequency ν_0^0 by[23]

$$\nu_0=z\cdot\nu_0^0, \tag{4}$$

where $z=6$ is the number of neighbor sites on the simple cubic T-site sublattice of hydrogen in the fcc (or fct) hydrides. Ross *et al.*[24] summarized the measurements of ν_0^0 for many metal hydrides, including ZrH_2, for which $h\nu_0^0=141$ meV. Taking account of the difference in atomic radius between Hf and Zr yields $h\nu_0^0=144$ meV for HfH_2. With this value of $h\nu_0^0$, Eq. (4) yields $\nu_0=2.1\times10^{14}\ \mathrm{s}^{-1}$, and therefore $\tau_0=0.48\times10^{-14}$ s, which is very close to that above based on the proton Γ_1 measurements. This excellent agreement, in contrast to earlier examples, is largely attributable to the present use of spectral density functions based on Monte Carlo calculations.[19]

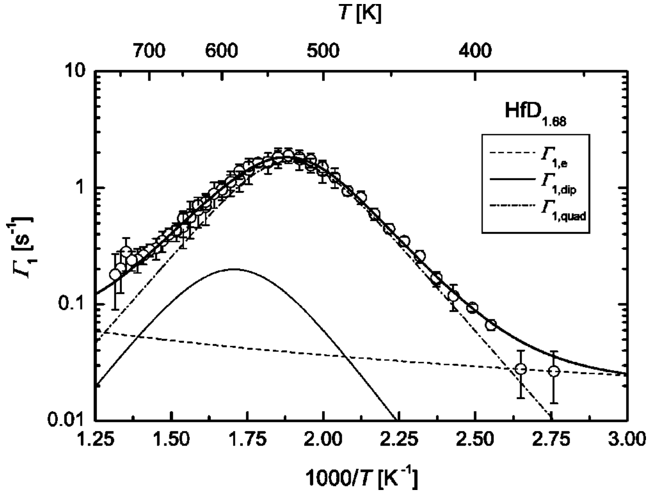

FIG. 3. Deuteron spin-lattice relaxation rate Γ_1 measured on $\mathrm{HfD}_{1.68}$ at 10.4 MHz. The electronic and dipolar contribution is represented by the dashed and solid lines, respectively. The quadrupolar relaxation $\Gamma_{1,\mathrm{quad}}$ is shown by the dash-dotted line, and the sum of the three contributions is given by the bold solid line.

Figure 3 shows the deuteron spin-lattice relaxation Γ_1 measured on $\mathrm{HfD}_{1.68}$ at 10.4 MHz. These data reveal only one relaxation maximum at about 530 K, although magnetic dipole and electric quadrupole interactions are expected to contribute to Γ_1 [see Eq. (1)]. In order to separate the contributions, we have to take into account that in dihydrides the isotope effect of hydrogen diffusion is rather small[15] and H_{a} is almost concentration independent for $x\leqslant1.9$. Thus, the $\Gamma_{1,\mathrm{dip}}$ maximum in a dideuteride occurs at about the same temperature as in a dihydride of comparable hydrogen content. The 10.4-MHz curve for $\mathrm{HfH}_{1.71}$ (cf. Fig. 2) indicates that the $\Gamma_{1,\mathrm{dip}}$ maximum of $\mathrm{HfD}_{1.68}$ is expected at about 580 K, and the observed maximum at 530 K must be mainly due to $\Gamma_{1,\mathrm{quad}}$.

The dipolar relaxation of deuterons $\Gamma_{1,\mathrm{dip}}^{\mathrm{d}}$ is related to that of protons $\Gamma_{1,\mathrm{dip}}^{\mathrm{p}}$ at the same resonance frequency according to

$$\frac{\Gamma_{1,\mathrm{dip}}^{\mathrm{d}}}{\Gamma_{1,\mathrm{dip}}^{\mathrm{p}}}=\frac{\gamma_{\mathrm{d}}^4}{\gamma_{\mathrm{p}}^4}\,\frac{I_{\mathrm{d}}(I_{\mathrm{d}}+1)}{I_{\mathrm{p}}(I_{\mathrm{p}}+1)}. \tag{5}$$

The dipolar relaxation is proportional to the hydrogen/deuterium concentration, and the relation given above holds for identical concentrations. With the spin quantum numbers $I_{\mathrm{p}}=\frac{1}{2}$ and $I_{\mathrm{d}}=1$ and the gyromagnetic ratios $\gamma_{\mathrm{p}}=2.6752\times10^8\ \mathrm{rad\,s^{-1}\,T^{-1}}$ and $\gamma_{\mathrm{d}}=0.4106\times10^8\ \mathrm{rad\,s^{-1}\,T^{-1}}$ the right side of Eq. (5) is given by 1/675. The solid line in Fig. 3 represents $\Gamma_{1,\mathrm{dip}}^{\mathrm{d}}$ of deuterons in $\mathrm{HfD}_{1.68}$, which has been calculated from $\Gamma_{1,\mathrm{dip}}^{\mathrm{p}}$ of the protons in $\mathrm{HfH}_{1.71}$ by using Eq. (5) and by taking into account that τ_0 is larger by a factor of $\sqrt{2}$ for deuterium than for hydrogen. The slight difference in the concentrations has also been taken into account by scaling $\Gamma_{1,\mathrm{dip}}^{\mathrm{d}}$ with a factor 1.68/1.71.

The electronic relaxation in a deuteride is also smaller than that in a hydride by a factor

$$\frac{\Gamma_{1,e}^{d}}{\Gamma_{1,e}^{p}}=\frac{\gamma_{d}^{2}}{\gamma_{p}^{2}}, \tag{6}$$

which is given by 1/42.3. The electronic relaxation thus obtained is included as a dashed line in Fig. 3.

The comparison of the dipolar and the electronic relaxation of the deuterons in $\mathrm{HfD}_{1.68}$ with the experimental data shows that the relaxation rate is indeed dominated by the quadrupolar contribution $\Gamma_{1,\mathrm{quad}}$. This is in agreement with previous studies of the deuteron spin-lattice relaxation in $\mathrm{HfD}_{1.7}$ by Weaver,[25] which also indicate that the quadrupole interactions are the dominant relaxation mechanism. The correlation functions for quadrupolar relaxation are different from those for dipolar relaxation. The dipolar interaction is a coupling between pairs of spins, and so the relevant correlation function describes the time evolution of the separation of a particular pair of spins. The characteristic time constant of the dipolar interaction is the correlation time $\tau_c=\tau/2$, if τ is the mean dwell time after which one of the two interacting nuclei jumps. The quadrupolar interaction, however, is a coupling between a particular nucleus and the total EFG due to the collective effect of all other diffusing nuclei. For low concentrations of deuterium vacancies on the deuterium sublattice in the fcc dideuterides, these vacancies are the only sources of the EFGs. In this case, the characteristic time constant of the quadrupolar interaction is the correlation time $\tau_c=\tau_v$, the mean time between two jumps of a deuterium vacancy. As has been shown recently,[20,21] the quadrupolar correlation function is $c(1-c)$ times the dipolar correlation function for a single atom undergoing a random walk on the structure. The spectral density functions and nuclear spin relaxation rates may therefore be simply expressed in terms of the corresponding theory for the low spin concentration limit.

The dash-dotted line in Fig. 3 is obtained by fitting Sholl's calculations[19] for $c\to 0$ to the Γ_1 data of $\mathrm{HfD}_{1.68}$ after subtracting $\Gamma_{1,e}$ and $\Gamma_{1,\mathrm{dip}}$. This fit yields an activation enthalpy for the motion of the deuterium vacancies and thus of the deuterium atoms of $H_a=0.67$ eV, which is in excellent agreement with the value found for hydrogen diffusion in $\mathrm{HfH}_{1.71}$.[13] This confirms that the isotope effect of diffusion is very weak in the dihydrides/dideuterides. The sum of $\Gamma_{1,e}$, $\Gamma_{1,\mathrm{dip}}$ and $\Gamma_{1,\mathrm{quad}}$ thus obtained (bold solid line in Fig. 3) describes the experimental Γ_1 data very well.

The fact that the $\Gamma_{1,\mathrm{quad}}$ maximum occurs at a lower temperature than the $\Gamma_{1,\mathrm{dip}}$ maximum reflects the higher jump frequency of the vacancies compared to that of the deuterium atoms. The jump frequency of the deuterium atoms τ^{-1} is related to that of the deuterium vacancies τ_v^{-1} according to

$$(1-c)\cdot\tau^{-1}=c\cdot\tau_v^{-1} \tag{7}$$

if $c=1-x/2$ denotes the deuterium vacancy concentration. The ratio τ/τ_v at a given fixed temperature increases from 5.25 at $c=0.16$ $(x=1.68)$ to 19.0 at $c=0.05$ $(x=1.90)$. In this concentration range the hopping frequency of the deuterium vacancies is in a good approximation concentration independent. The position of the $\Gamma_{1,\mathrm{quad}}$ maximum, which is determined by the hopping frequency of the deuterium vacancies, is therefore also expected to be nearly concentration independent. The hopping of the deuterium atoms, however, decreases with increasing x due to blocking of occupied sites, which results in a decrease of the diffusivities and in a shift of the position of the $\Gamma_{1,\mathrm{dip}}$ maximum to higher temperatures (cf. Fig. 1).

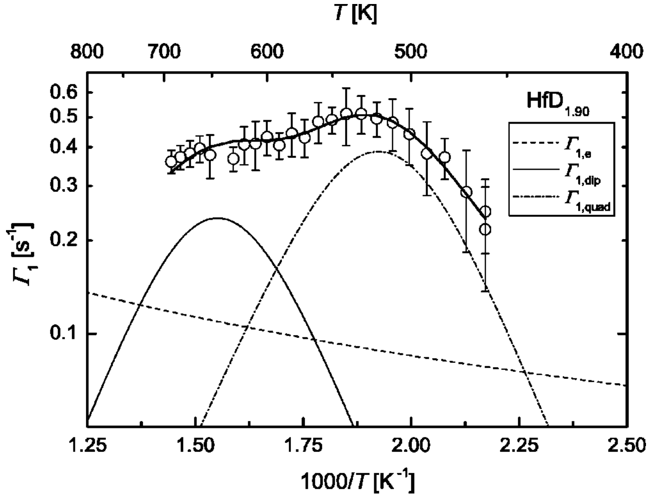

FIG. 4. Deuteron spin-lattice relaxation rate Γ_1 measured on $\mathrm{HfD}_{1.90}$ at 10.4 MHz. $\Gamma_{1,e}$ and $\Gamma_{1,\mathrm{dip}}$ are given by the dashed and solid lines, respectively. The quadrupolar relaxation $\Gamma_{1,\mathrm{quad}}$ is represented by the dash-dotted line, and the sum of $\Gamma_{1,e}$, $\Gamma_{1,\mathrm{dip}}$ and $\Gamma_{1,\mathrm{quad}}$ is given by the bold solid line.

Figure 4 shows the deuteron Γ_1 data of $\mathrm{HfD}_{1.90}$. The different contributions to Γ_1 according to Eq. (1) have been determined as outlined above for $\mathrm{HfD}_{1.68}$. In the case of $\mathrm{HfD}_{1.90}$ the temperatures of the dipolar and quadrupolar relaxation maxima differ more than in $\mathrm{HfD}_{1.68}$ reflecting the greater difference in the jump frequencies of deuterium atoms and deuterium vacancies. Furthermore, the quadrupolar relaxation is substantially smaller than in the sample with the lower concentration of deuterium vacancies, which are the sources of the EFGs.

A comparison of the relaxation data measured on three HfD_x samples with different x is given in Fig. 5. The electronic contributions are already subtracted and the quadrupolar contributions are indicated by the dash-dotted lines. The sum of the $\Gamma_{1,\mathrm{quad}}$ and $\Gamma_{1,\mathrm{dip}}$ curves obtained by fitting Sholl's calculation[19] is shown by the solid lines. In all three samples the relaxation rate is dominated by the quadrupolar contribution. The position of the $\Gamma_{1,\mathrm{quad}}$ maximum is, indeed, nearly concentration independent, and it is observed at $T_{\mathrm{quad}}\approx 525$ K. While in this concentration range the hopping frequency of the deuterium vacancies varies only slightly with c, the quadrupolar relaxation strength changes significantly with the concentration of fluctuating EFGs. The maximum quadrupolar relaxation rate increases by more than a factor of 3 from $\Gamma_{1,\mathrm{quad}}^{\max}=0.39\ \mathrm{s}^{-1}$ for $c=0.05$ $(x=1.90)$ to $\Gamma_{1,\mathrm{quad}}^{\max}=1.34\ \mathrm{s}^{-1}$ for $c=0.16$ $(x=1.68)$. For an arbitrary concentration c of diffusing vacancies (or atoms), the spectral density functions and consequent relaxation rates are expected to scale with concentration as $c(1-c)$.[20,21] Within the experimental uncertainty, this prediction is in agreement

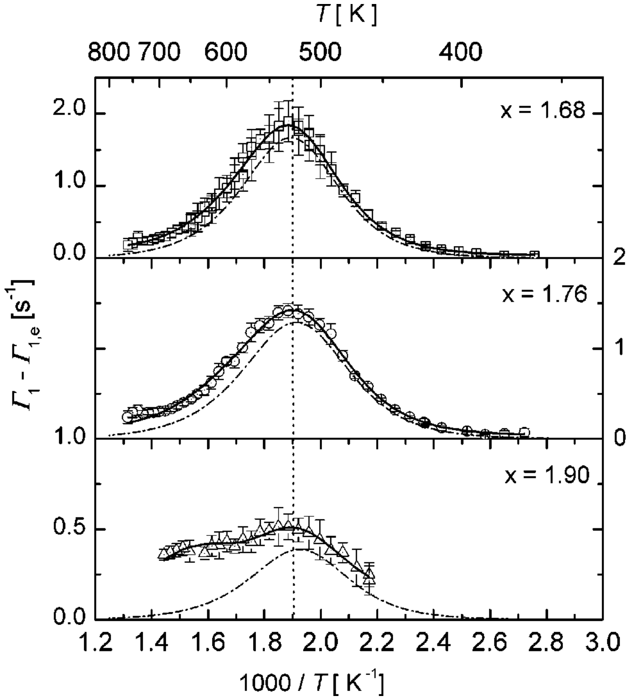

FIG. 5. Spin-lattice relaxation rate of deuterons in $\mathrm{HfD}_x(1.68 \leqslant x \leqslant 1.90)$ at 10.4 MHz. The electronic contribution has been subtracted from the experimental data. The quadrupolar contribution $\Gamma_{1,\mathrm{quad}}$ is represented by the dash-dotted lines, and the sum of $\Gamma_{1,\mathrm{dip}}$ and $\Gamma_{1,\mathrm{quad}}$ is given by the bold solid lines.

with the present results. $\Gamma_{1,\mathrm{quad}}^{\max}/c(1-c)$ is plotted in Fig. 6 as a function of the deuterium vacancy concentration $c=(1-x/2)$ in HfD_x. The error bars in Fig. 6 correspond to experimental uncertainties of $\pm 2\%$ in $\Gamma_{1,\mathrm{quad}}^{\max}$ and $\pm 2\%$ in x.

The quadrupolar relaxation has also been studied in a titanium dideuteride. Fig. 7 shows the deuteron Γ_1 measured on $\mathrm{TiD}_{1.91}$ at the resonance frequency $\omega/2\pi = 34.3$ MHz. In this case, the dipolar and quadrupolar contributions to Γ_1 are well separated. The dashed line indicates $\Gamma_{1,\mathrm{e}}$ and the thin solid curve is the dipolar contribution that has been deduced from proton Γ_1 data of TiH_x.[15] The quadrupolar relaxation, indicated by the dash-dotted line, has been fitted by Sholl's calculations for $c \to 0$ and it yields an activation enthalpy of $H_\mathrm{a} = 0.66$ eV. About the same H_a value has been deduced from the proton $\Gamma_{1,\mathrm{dip}}$ in TiH_x with a comparable hydrogen content of $x = 1.94$.[15]

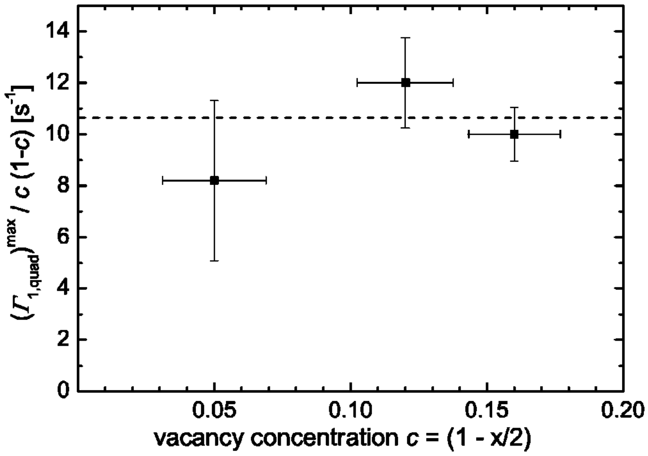

FIG. 6. Maximum quadrupolar relaxation $\Gamma_{1,\mathrm{quad}}^{\max}$ of deuterons in HfD_x divided by $c(1-c)$ for the deuterium vacancy concentrations $c = 0.05$, 0.12, and 0.16. The dashed line is a guide to the eyes.

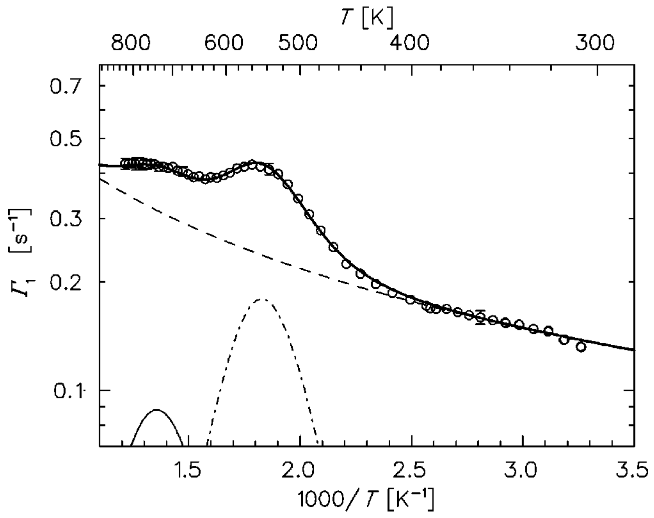

FIG. 7. Deuteron spin-lattice relaxation rate Γ_1 measured on $\mathrm{TiD}_{1.91}$ at 34.3 MHz. The electronic (dashed line), dipolar (solid curve), and quadrupolar contributions (dash-dotted curve) are indicated. The sum of these contributions is given by the bold solid line.

In order to prove whether the separation of the maxima in $\Gamma_{1,\mathrm{quad}}$ and $\Gamma_{1,\mathrm{dip}}$ is as expected for a vacancy mechanism on the deuterium sublattice we have to take into account that the dipolar relaxation maximum occurs in $\mathrm{TiD}_{1.91}$ $(x/2 = 0.955)$ at the temperature T_dip, at which the condition $\omega\tau/2 = 0.24$ is fulfilled.[19] At the temperature T_quad of the quadrupolar relaxation maximum, the hopping frequency of the deuterium vacancies is related to the NMR frequency according to $\omega\tau_\mathrm{v} = 0.39$, as obtained from Ref. 19 for $c \to 0$. Together with Eq. (7) this relation yields the hopping frequency of the deuterium atoms at the quadrupolar relaxation maximum, $\tau^{-1}(T_\mathrm{quad}) = c/(1-c)\cdot\omega/0.39$. At the temperature of the dipolar relaxation maximum, the hopping frequency of the deuterium atoms is given by $\tau^{-1}(T_\mathrm{dip}) = \omega/(2\cdot 0.24)$. With Eq. (3) the ratio of the deuterium hopping frequencies at T_dip and T_quad can be calculated according to

$$\exp\left[\frac{H_\mathrm{a}}{k_\mathrm{B}}\left(T_\mathrm{quad}^{-1} - T_\mathrm{dip}^{-1}\right)\right] = \frac{(1-c)}{c}\cdot\frac{0.39}{2\cdot 0.24}, \tag{8}$$

which allows one to calculate the temperature

$$T_\mathrm{quad} = \left[\frac{1}{T_\mathrm{dip}} + \frac{k_\mathrm{B}}{H_\mathrm{a}}\cdot\ln\left(\frac{(1-c)}{c}\cdot\frac{0.39}{0.48}\right)\right]^{-1} \tag{9}$$

at which the quadrupolar relaxation maximum is expected if the dipolar relaxation maximum occurs at T_dip. With the dipolar relaxation maximum at $T_\mathrm{dip} = 740$ K (cf. Fig. 7), the quadrupolar relaxation maximum in $\mathrm{TiD}_{1.91}$ $(c = 0.045)$ is expected to occur at $T_\mathrm{quad} = 580$ K. Experimentally the quadrupolar relaxation maximum has been observed at about

550 K, which is in reasonable agreement with the expected value if we take into account the uncertainties of ±3% in H_a, ±2% in x, and ±1.0% in T_{dip}.

IV. SUMMARY

Over wide temperature ranges the deuterium spin-lattice relaxation rate in the substoichiometric dideuterides of hafnium and titanium is dominated by the quadrupolar relaxation $\Gamma_{1,\mathrm{quad}}$. An important feature of the quadrupolar relaxation is that the quadrupole moment interacts with the total electric field gradient (EFG) due to all surrounding charges taken together. In nearly stoichiometric dideuterides, however, the vacancies in the deuterium sublattice are the only sources of EFGs. In this case the $\Gamma_{1,\mathrm{quad}}$ maximum occurs at a lower temperature than the $\Gamma_{1,\mathrm{dip}}$ maximum, reflecting the higher jump frequency of the deuterium vacancies compared to that of the deuterium atoms. The activation enthalpy of deuterium vacancy motion and thus of deuterium atom motion in HfD_x and TiD_x is deduced from the temperature dependence of $\Gamma_{1,\mathrm{quad}}$. The obtained values are given in Table I. Within the experimental uncertainty, these values agree well with the activation enthalpies of hydrogen motion in dihydrides of the same hydrogen content, indicating the classical mechanism of hydrogen/deuterium diffusion. While the position of the $\Gamma_{1,\mathrm{quad}}$ maximum is concentration independent in the dideuterides, the amplitude scales as $c(1-c)$ with the deuterium vacancy concentration c. These results are consistent with the recently developed theoretical picture that the correlation functions for quadrupolar relaxation at a given concentration c are the same as the dipolar correlation functions for $c \rightarrow 0$.

TABLE I. Activation enthalpy of deuterium motion in HfD_x ($x=1.68$, 1.76, and 1.90) and $\mathrm{TiD}_x (x=1.91)$. The values correspond to the fits shown in Figs. 3–5 and in Fig. 7. Estimated uncertainties are ±3%.

Sample	x	H_a (eV)
HfD_x	1.68	0.67
	1.76	0.61
	1.90	0.66
TiD_x	1.91	0.66

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