Perturbed-angular-correlation study of ^{111}Cd and ^{181}Ta nuclear-quadrupole relaxations in the rare-earth dihydride DyH$_{2\pm\delta}$

M. Forker and U. Hütten

Institut für Strahlen- und Kernphysik der Universität Bonn, Nussallee 14-16, D-53115 Bonn, Germany

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The static and dynamic electric quadrupole interaction (QI) of the nuclear probes ^{111}Cd and ^{181}Ta on metal sites of the rare earth (RE) dihydride DyH$_x$ has been investigated as a function of temperature ($19 \leq T \leq 900$ K) and hydrogen concentration ($1.8 \leq x \leq 2.1$) by perturbed angular correlation spectroscopy. It is shown that for non-RE nuclei with large quadrupole moments the dynamic QI caused by hopping hydrogen may strongly exceed the magnetic dipole interaction with the fluctuating $4f$ magnetic moments. Measurements of the spin relaxation of suitable non-RE nuclei may therefore provide information on the hydrogen motion in the RE hydrides in spite of the strong $4f$ paramagnetism. The nuclear-quadrupole relaxation rates, however, were found to be strongly affected by probe-impurity interactions. In DyH$_x$ the activation energy for jumps of hydrogen vacancies near the probe site, determined from the temperature dependence of the dynamic perturbation of the ^{111}Cd angular correlation, is $E_a = 0.35(2)$ and $0.45(3)$ eV for $x = 1.96$ and 1.99, respectively. The strength of the fluctuating QI of ^{111}Cd:DyH$_x$ suggests an effective hydrogen charge of $Z' \sim 0.6$.

I. INTRODUCTION

The investigation of the hydrogen diffusion in metals and intermetallic compounds is both of basic and technological interest. In many metal-hydrogen systems this dynamic process has been investigated on a microscopic scale by hyperfine spectroscopic techniques such as NMR,[1] Mössbauer,[2] and perturbed angular correlation[3] (PAC) spectroscopy by observing the nuclear spin relaxation induced by the hydrogen motion. Both magnetic and electric hyperfine interactions (HFI) may contribute. The nuclear magnetic dipole moments of the moving hydrogen (and its isotopes) and the stationary metal ions produce a fluctuating magnetic hyperfine interaction and the motion of the hydrogen charge leads to fluctuating electric-field gradients (EFG) which produce a time-dependent quadrupole interaction (QI) for nuclei with finite quadrupole moments Q. With NMR the resulting nuclear spin relaxation can be observed both for the moving and the stationary nuclei, while Mössbauer and PAC spectroscopy are restricted to the metal nuclei.

Among the hydrogen-absorbing metals the rare-earth (RE) elements La to Lu play a prominent role. All RE metals react directly with hydrogen, forming dihydrides and in most cases also trihydrides.[4–6] With the exception of LaH$_x$ (Ref. 7), CeH$_x$ (Ref. 8), and RE-like YH$_x$ (Ref. 9), this large group of hydrides, however, is practically unexplored by hyperfine spectroscopic techniques because of the strong paramagnetism of the $4f$ elements. As the inner $4f$ electrons are well shielded by the $5s^2 5p^6$ and to some extent also by the $5d$-$6s$ valence electrons, the magnetic moments of the unclosed $4f$ shell in solids are close to the free-ion moments which reach values as high as $10\mu_B$(Dy^{3+}). In the paramagnetic state these $4f$ moments produce time-dependent magnetic fields (≤ 10 kG) at neighboring lattice sites which are 3–4 orders of magnitude stronger than those caused by the nuclear magnetic moments of moving hydrogen atoms. Since for fast fluctuations the nuclear spin-relaxation rates are proportional

to $\nu^2 \tau_c$ (ν, interaction strength; τ_c, correlation or relaxation time of the fluctuation), the contribution of the moving nuclear magnetic moments to the spin relaxation is negligibly small, even though the $4f$-relaxation time might be a few orders of magnitude shorter than typical residence times between hydrogen jumps at room temperature.

It is, however, conceivable that for nuclei with large quadrupole moments Q the diffusion-related time-dependent electric quadrupole interaction exceeds the magnetic interaction with the fluctuating $4f$ fields of neighboring RE ions, in particular as the electric-field gradient produced by the negative hydrogen charge[10–12] may be strongly enhanced by the deformation of the closed electronic shells of the probe nucleus (Sternheimer correction[13]). In an EFG point-charge model the quadrupole frequency $\nu_q = eQV_{zz}/h$ produced by an effective hydrogen charge $Z'e$ at a distance r from a nucleus with quadrupole moment Q and Sternheimer correction $(1 - \gamma_\infty)$ is given $\nu_q = 2Z'e^2Q(1 - \gamma_\infty)r^{-3}h^{-1}$. For a nucleus with $Q = 1 \times 10^{-24}$ cm^2, $(1 - \gamma_\infty) = 30$ and $r = 2.5$ Å one obtains $\nu_q = Z' \times 135$ MHz. A magnetic $4f$ moment of $10\mu_B$ at the same distance r produces a magnetic field of the order of $H_{4f} \approx 10$ kG. The magnetic interaction of this field with a nuclear state of g factor $g = 1$ corresponds to a magnetic frequency of $\nu_M = g\mu_N H_{4f}/h = 7.5$ MHz.

So, for nuclei with large quadruple moments Q the nuclear spin relaxation rates could be dominated by the QI fluctuations, even if the charge transfer from the metal sites to the hydrogen[10,11] leads only to small effective hydrogen charges $Z'e$, and their measurement could then provide information on the hydrogen motion in rare-earth hydrides REH$_x$ in spite of the strong $4f$ paramagnetism.

These diffusion-related QI fluctuations in REH$_x$ compounds, however, can, if at all, only be detected by non-RE nuclei, since the unclosed $4f$ shell produces huge dynamic magnetic fields (≤ 8 MG) and EFG's ($\leq 6 \times 10^{18}$ V/cm^2) at its own nuclear site.[14] One therefore has to recur to impurity nuclei with large quadrupole moments as probes [the ^{2}H quadrupole moment is too small ($Q = 2.82 \times 10^{-27}$ cm^2) for

sufficiently large QI effects]. Among the various hyperfine spectroscopic methods, the perturbed angular correlation (PAC) technique appears to be particularly well suited for such measurements. Compared to Mössbauer spectroscopy, PAC has the advantage of an unrestricted temperature range and in contrast to NMR only very few impurity nuclei ($\leq 10^{12}$) are needed.

For an answer to the question whether the hydrogen motion in a paramagnetic RE hydride can be detected through fluctuating QI's at impurity probes, we have carried out a series of PAC measurements in dysprosium dihydride DyH$_x$ at concentrations $1.80 \leq x \leq 2.1$ with the PAC probes ^{111}Cd and ^{181}Ta which have large quadrupole moments Q [$Q = 0.83$ b and 2.53 b (Ref. 15), respectively]. In view of the impurity nature of the PAC nuclei a comparative study of the same hydride with two different probes appeared important. DyH$_x$ was chosen as a test case because (i) both ^{111}Cd and ^{181}Ta are known to occupy substitutional sites in Dy metal[16,17] and (ii) Dy has one of the largest $4f$ magnetic moments.

With the exception of Eu and Yb, all RE dihydrides are cubic with the CaF$_2$-type structure. The hydrogen resides on the tetrahedral (T) sites of the fcc metal matrix. In heavy dihydrides such as DyH$_x$ the ideal CaF$_2$ structure, however, does not exist since the H atoms start to occupy the octahedral (O) interstices before the tetrahedral sites are completely filled. Changes in the magnetic behavior observed by Aarons et al.[18] indicate that in GdH$_x$ and TbH$_x$ the O-site occupation sets in at $x = 1.95$. Anderson et al.[19] derive an O-site occupation of 10 and 15 % for RE-like YH$_{1.92}$ and YH$_{1.98}$, respectively, from the ^{1}H NMR rigid-lattice second moments. Goldstone et al.[20,21] report about 8% occupied O sites for YH$_2$ from inelastic neutron scattering. In the case of DyH$_x$ the CaF$_2$-type structure extends over the concentration range $1.94 < x < 2.15$ (Ref. 6).

II. EXPERIMENTAL DETAILS

A. Sample preparation and equipment

The PAC measurements were carried out with the 133–482 keV $\gamma\gamma$ cascade of ^{181}Ta and the 172–247 keV cascade of ^{111}Cd which are populated in the β decay of ^{181}Hf and the EC decay of ^{111}In, respectively. In the first step of the sample preparation metallic Dy was therefore doped with small quantities of radioactive ^{181}Hf and ^{111}In.

The $42d$ isotope ^{181}Hf is produced by thermal neutron irradiation of natural Hf metal [^{180}Hf $(n,\gamma)^{181}$Hf]. Dilute alloys of ^{181}Hf and Dy were prepared by electron gun melting of the metallic components in ultrahigh vacuum (10^{-9} mbar). Typically the samples had a weight of the order of 100 mg with a total Hf concentration of about 0.5 at. %.

For the first ^{181}Hf:Dy samples we used sublimed metallic Dy with a purity of 99.99 at. % (based on the total metallic impurities) provided by Johnson Matthey. The PAC spectra of these samples (see Sec. III A) indicated that after melting a large fraction of the ^{181}Hf nuclei had trapped impurities, presumably light elements such as O, C,... and that his fraction increased drastically upon heating. This observation is not surprising, as it is well known that Hf is an excellent getter, in particular for oxygen and that the RE metals, even of very high metal purity, may contain nonmetallic elements up to concentrations of several hundred ppm.[22]

As PAC probes decorated with other impurities cannot be expected to provide any useful information on the hydrogen motion in a metal hydride, it appeared essential for the intended experiments to increase the fraction of impurity-free ^{181}Hf nuclei. This was achieved by an additional sublimation of the purchased Dy metal. Following the procedure described by Beaudry and Gschneider,[22] the metal was heated to 1300 °C (Dy melting point, 1407 °C) and collected on a Ta foil ($T \sim 700$ °C) on top of the crucible. Starting with charges of 500 mg, we typically obtained about 350 mg after 2 h. The sublimation product in form of a stalactite was cut 2 mm above the Ta foil in order to minimize an eventual Ta contamination.

This procedure was found to be quite effective in removing the nonmetallic impurities from the host metal. The fraction of impurity-free ^{181}Hf nuclei increased from about 65% before to $\geq 90\%$ after the sublimation. Only metal purified in this way was therefore used in the preparation of the ^{181}Hf/^{181}Ta:Dy hydrides investigated here.

For the preparation of the ^{111}In/^{111}Cd:Dy samples ^{111}In was solute extracted with ethyl ether from a commercially available solution of carrier-free ^{111}In Cl$_3$ and deposited on a Dy foil which was then melted with the UHV electron gun. The ^{111}In/^{111}Cd:Dy samples had a ^{111}In concentration of the order of 1 ppm. Although ^{111}In in metallic Dy was not found to attract impurities (see Sec. III A), the metal used for ^{111}In/^{111}Cd:Dy hydride samples was also purified by an additional sublimation.

The hydrogenation was carried out in a quartz tube connected to a UHV system. After reaching 10^{-10} mbar, in a first step the doped metal samples were slowly heated (1–2 °C/min) to 700 K and outgassed for 5 h. As the annealing study of ^{181}Hf:Dy (Sec. III A) had shown that impurity trapping by ^{181}Hf increases drastically at $T \sim 750$ K, the maximum temperature reached in the hydrogenation process was limited to 700 K. In the second step the samples were exposed to a precisely known quantity of H$_2$ gas (percent purity 99.9999), determined by capacitance measurements of the H$_2$ pressure in a calibrated volume, kept for a few hours at 620 K for homogenization and then slowly cooled to room temperature. The accuracy of the hydrogen concentration, as calculated from the metal weight and the quantity of absorbed H$_2$ gas, was of the order of $\Delta x/x \approx 0.01$. The hydrogenated samples were ground to a powder in an argon atmosphere and for measurements at $T \geq 290$ K sealed into evacuated quartz tubes. For measurements at $T < 290$ K the hydrides were transferred to a closed-cycle He refrigerator. The PAC spectra were recorded with a four-detector setup, equipped with fast BaF$_2$ scintillators.

B. Data analysis

The time modulation of the angular correlation coefficients A_{kk} ($k = 2,4$) of a $\gamma\gamma$ cascade by hyperfine interactions in polycrystalline samples can be described by a perturbation factor $G_{kk}(t)$ which depends on the multipole order, the symmetry, and the time dependence of the interaction and on the spin of the intermediate state of the cascade (for details see, e.g., Frauenfelder and Steffen[23]).

In this paper we are dealing with perturbations by static and dynamic electric quadrupole interactions (QI). The electric-field gradient (EFG) acting on a PAC probe on a

regular metal site in a fcc dihydride is produced by the vacant tetrahedral and occupied octahedral sites of the hydrogen sublattice. A contribution of the metal sublattice is expected only if its cubic symmetry is distorted by structural defects or impurities. In the case of a statistical distribution of the tetrahedral vacancies and the occupied octahedral sites each PAC probe will see a different configuration of vacancies and hydrogen atoms and thus experience a different EFG.

At low temperatures, these configurations are "frozen" (at least in the PAC time window of the order of $10\tau_N$, with τ_N=the lifetime of the intermediate state of the cascade) and the ensemble of PAC probes is therefore subject to a static EFG distribution. For a distribution of static QI's in polycrystalline samples the perturbation factor is given by

$$G_{kk}(t;\nu_q,\eta,\delta)=s_{k0}+\sum_{n=1}^{N}s_{kn}\cos(\omega_n t)\exp[-1/2(\delta\omega_n t)^2].$$

$$(1)$$

The frequencies ω_n are the transition frequencies between the hyperfine levels into which a nuclear state is split by the QI. They depend on the quadrupole frequency $\nu_q=eQV_{zz}/h$ and on the asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$ where V_{ii} are the principal-axes components of the EFG tensor. The amplitudes s_{kn} depend on η only. For the spin $I=5/2$ of ^{181}Ta and ^{111}Cd the number N of terms in Eq. (1) is $N=3$. The exponential factor accounts for the effect of a Gaussian EFG distribution of relative width δ. Frequently, several fractions of nuclei with different QI parameters are found in the same sample. The effective perturbation factor is then given by

$$G_{kk}(t)=\sum_i f_i G_{kk}(t;\nu_{qi},\eta_i,\delta_i),$$

$$(2)$$

f_i (with $\Sigma_i f_i=1$) is the relative intensity of the ith fraction with the QI parameters $[\nu_{qi},\eta_i,\delta_i]$.

At higher temperatures hydrogen diffusion sets in and gives rise to fluctuations of the QI distribution. The resulting nuclear spin relaxation becomes observable as an attenuation of the angular correlation when the fluctuation rate w has increased to the point that the residence time between hydrogen jumps τ_R is of the same order of magnitude as the PAC time window. With increasing fluctuation rate w the spin-relaxation rate and the corresponding attenuation of the angular correlation first increase towards a maximum at $w\approx\nu_q^0$, where ν_q^0 is the center frequency of the static distribution and then decrease, analogous to the motional narrowing of a NMR signal.

The perturbation of an angular correlation by discrete jumps which may involve strong changes of the interaction is most appropriately described by Blume's stochastic theory.[24,25] For the analysis of the complex situation in a substoichiometric hydride where hydrogen motion leads to fluctuations of orientation, strength, and symmetry of the interaction, this general theory is, however, impracticable and one has to resort to an approximation with a single relaxation parameter λ_k:

$$G_{kk}(t)=\Gamma_{kk}(t)\exp(-\lambda_k t).$$

$$(3)$$

The validity range of the approximation has been discussed in detail in Ref. 26. For slow fluctuations ($w\ll\nu_q^0$) the function $\Gamma_{kk}(t)$ is given by the perturbation factor in the absence of fluctuations and λ_k is proportional to the fluctuation rate w. In Ref. 26 it has been shown that in the case of a slowly fluctuating QI distribution the separation of the effect of the static and the dynamic components of the distribution on the angular correlation is problematic and an analysis based on Eq. (3) may lead to incorrect conclusions with respect to the hydrogen motion. The conclusions presented in this paper are therefore mainly based on data from the fast-fluctuation region.

Fast processes are adequately described by Eq. (3) if several jumps occur within one spin precession period ($w\geq 5\nu_q^0$). The function $\Gamma_{kk}(t)$ then depends on the time average of the interaction. For a vanishing time average one has $\Gamma_{kk}(t)=1$, for a nonzero average $\Gamma_{kk}(t)$ has the form of a static perturbation function for the time averaged QI. λ_k is proportional to the Abragam and Pound spin-relaxation constant[27] λ_k^{AP} which depends on the strength of the fluctuating QI, described by the frequency ν_q^f, and the fluctuation rate w: $\lambda_k\propto(\nu_q^f)^2/w$. As the proportionality constant is not precisely known, the analysis of fast dynamic processes based on Eq. (3) provides no absolute values of the quantity $(\nu_q^f)^2/w$. However, the approximation maintains the linearity between the derived relaxation parameter and the inverse jump rate: $\lambda_k\propto 1/w$. For Arrhenius processes with $w=w_0\exp(-E_a/kT)$ one then has $\ln\lambda_k\propto E_a/kT$, so that the activation energy of the jump process can be correctly deduced from the temperature dependence of the single relaxation parameter λ_k, provided ν_q^f does not change much with temperature.

When comparing activation energies determined by PAC with those of other techniques, e.g., ^{1}H-NMR, one must keep in mind that the PAC probe is an impurity in most of the investigated systems which because of the r^{-3} dependence of the QI detects only charges jumping in its neighborhood. As the potential in the vicinity of an impurity site may differ from that of the regular lattice sites, it can *a priori* not be excluded that the barrier height measured by PAC is affected by the impurity itself. PAC therefore provides the activation energies for hydrogen and vacancy jumps near the probe site which may differ from the activation energy in the undoped compound. Experimental information on this aspect is presently not available.

III. MEASUREMENTS AND RESULTS

A. ^{181}Ta and ^{111}Cd PAC study of the quadrupole interaction in Dy metal

For a PAC experiment aiming at the observation of the hydrogen motion in a rare-earth hydride a large fraction of probe nuclei on substitutional sites of an otherwise unperturbed metal lattice is of central importance. Prior to the hydrogenation we have therefore studied this regular site fraction in Dy samples of different purity and have also determined its temperature dependence in order to establish the maximum temperature which may be reached in the hydrogenation procedure without losses in the regular site fraction by impurity trapping.
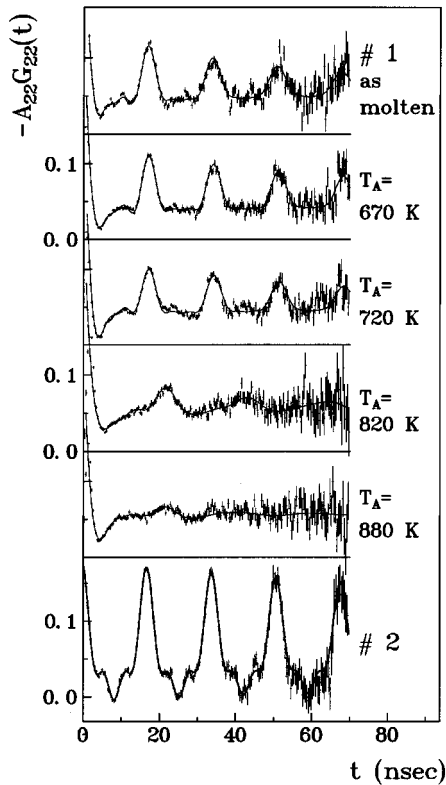
FIG. 1. PAC spectra of ^{181}Ta in metallic Dy of different purity, measured at room temperature after annealing at T_A for 12 h in a vacuum of 10^{-10} mbar. Sample no. 1 was prepared with Dy metal (purity 99.99 at. %) purchased from Johnson Matthey, sample no. 2 after purification by an additional sublimation.

Figure 1 shows the PAC spectra $A_{22}G_{22}(t)$ of ^{181}Ta:Dy taken at room temperature after annealing at a temperature T_A for 12 h in a vacuum of 10^{-10} mbar. The coefficient A_{22} reflects the experimental anisotropy at the time zero point and has not been corrected for the finite solid angle extended by the detectors. Sample no. 1 was prepared with Dy as purchased from Johnson Matthey, sample no. 2 (bottommost spectrum in Fig. 1) after purification by the additional sublimation described in Sec. II A.

The as-molten spectrum of sample no. 1 shows the typical periodic PAC pattern of an axially symmetric QI, as it is expected for ^{181}Ta on substitutional sites of hexagonal Dy. The amplitude of this component is a measure of the fraction f_1 of probes on substitutional sites. A numerical analysis by a least-squares fit of Eqs. (1) and (2) to the data gives $f_1 \approx 0.6$ and the QI parameters $\nu_{q1} = 395(3)$ MHz, $\eta_1 = 0.11(2)$, and $\delta_1 = 0.04(1)$ which agree well with previously reported values.[17]

The second component in the spectrum with amplitude $f_2 = 1 - f_1 \approx 0.4$ is characterized by a large frequency distribution ($\delta_2 = 0.30$) centered at $\nu_{q2} = 680(30)$ MHz, $\eta_2 = 0.23(7)$ and reflects the ^{181}Ta nuclei with a defect environment where nearby impurities, structural defects, grain boundaries, etc., produce a broad distribution of the EFG values.

When sample no. 1 was heated in an evacuated quartz tube the regular site fraction was found to decrease with increasing temperature, as can be clearly seen from Fig. 1, and had almost completely vanished after 12 h at 880 K. The
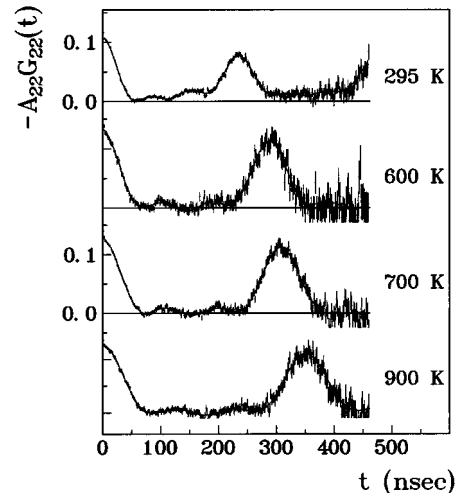

FIG. 2. PAC spectra of ^{111}Cd in Dy metal (purity 99.99 at. %, purchased from Johnson Matthey) at different temperatures.

obvious explanation of this observation is the formation of ^{181}Hf-impurity complexes, when impurities dissolved in the host metal become mobile at higher temperatures. As mentioned above, the most probable elements involved are O and C. Samples with such a large fraction of probe-defect complexes are clearly unsuited as starting material for the hydride preparation.

The bottommost spectrum in Fig. 1 (sample no. 2 at room temperature) illustrates that the impurity concentration could be strongly reduced by additional sublimation of the purchased metal. The spectrum shows practically no damping and the regular site fraction is visibly much larger than in the as-molten state of sample no. 1. The analysis gives $f_1 \gtrsim 0.9$, so that now less than 10% of the probes are involved in some kind of probe-defect complex. As a consequence of some texture in sample no. 2, the amplitudes s_{kn} [see Eq. (1)] of this spectrum differ from the values for a polycrystalline compound. We have studied the annealing behavior of the sublimated samples up to 720 K and observed no changes in the room-temperature spectra, in contrast to the pronounced deterioration of the unpurified samples.

The absence of an attenuation in the spectrum of sample no. 2 reflects not only a highly regular probe environment, but also indicates that the PAC relaxation caused by the fluctuating $4f$ moments of neighboring Dy^{3+} ions and by interactions with the conduction electrons is very weak. The upper limit of the corresponding relaxation parameter λ_{4f} compatible with the spectrum is $\lambda_{4f} \lesssim 1$ MHz.

With the probe ^{111}In/^{111}Cd we found no evidence for an attractive probe-impurity interaction. Figure 2 shows the PAC spectra of ^{111}Cd:Dy measured at different temperatures for a sample prepared with as-purchased Dy. Here we observed an increase of the regular site fraction from $f_1 = 0.65$ at 295 K to $f_1 \approx 1$ at 600 K and above which probably reflects the relaxation of stresses produced by the rapid cooling of the sample in the water-cooled electron gun. The additional sublimation of the host metal had no effect on the PAC spectrum. The upper limit of the $4f$-relaxation parameter $\lambda_{4f} \lesssim 1$ MHz compatible with the loss of amplitude in the ^{111}Cd:Dy spectrum is of the same order as for ^{181}Ta:Dy.

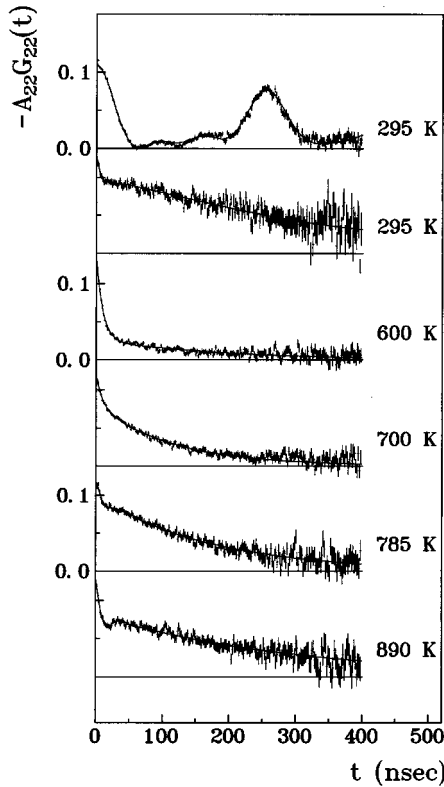FIG. 3. PAC spectra of ^{111}Cd in DyH$_{1.96}$ at different temperatures. The topmost spectrum is that of ^{111}Cd in Dy metal.

The room-temperature quadrupole frequency ν_q (^{111}Cd:Dy; 295 K)=26.3(3) MHz agrees within the experimental precision with the results of previous measurements.[28] Between 295 and 900 K, ν_q (^{111}Cd:Dy) follows the relation $\nu_q(T)=\nu_q(0)(1-AT)$ with $\nu_q(0)=29.9(4)$ MHz and $A=4.7(2)\times10^{-4}$ K^{-1}. Such a linear temperature dependence has been observed in all previous investigations of impurity EFG's in RE metal hosts, in contrast to the $T^{3/2}$ behavior of sp metals. The present result for the strength parameter A fits well into the ^{111}Cd:RE systematics which shows a linear decrease of the relative temperature derivative $\delta\ln\nu_q/\delta T$ across the RE series.[29]

B. ^{111}Cd PAC study of dysprosium dihydride DyH$_x$ at the hydrogen concentration $x=1.96$ and $x=1.99$

The QI of ^{111}Cd in DyH$_x$ was studied at the stoichiometries $x=1.96$ and 1.99. At both concentrations we found clear evidence for dynamic perturbations related to the hydrogen diffusion. Figure 3 shows the PAC spectra of ^{111}Cd:DyH$_{1.96}$ at different temperatures. For comparison we have included the spectrum of ^{111}Cd in metallic Dy (topmost in Fig. 3). At $T=295$ K the spectrum of ^{111}Cd:DyH$_{1.96}$ consists mainly of a slow decrease of the anisotropy with time which reflects the deviations from cubic symmetry caused by vacant tetrahedral and occupied octahedral hydrogen sites. Structural defects probably also contribute to the resulting frequency distribution which contains slowly fluctuating components associated with the hydrogen motion and static components from the structural defects. Fitting a static QI distribution to the spectrum, one obtains a center frequency
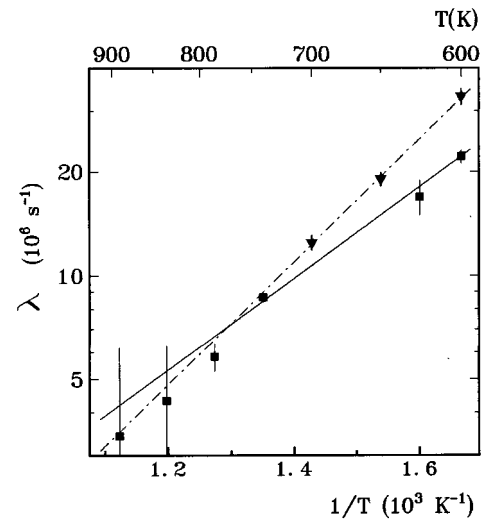

FIG. 4. The temperature dependence of the relaxation parameter λ of ^{111}Cd:DyH$_{1.96}$ for $T\geq600$ K. The triangles and squares refer to the thermal history. The sample was first heated to 700 K (triangles), then cooled back to 600 K, and subsequently heated to 900 K (squares).

$\nu_{q1}=2.5(2)$ MHz and a relative width $\delta_1=0.5(1)$. The smaller, rapidly decaying component in the spectrum [$\nu_{q2}=115(15)$ MHz, $\delta_2=0.7(2)$, $f_2\approx0.3$] which do not change with temperature can be associated with the fraction of probes in stable probe-defect complexes produced during the sample preparation and carries no information on the hydride properties. At higher temperatures the spectra present the typical features of a dynamic perturbation. Between 295 and 600 K the relaxation of the angular correlation increases with temperature to a complete destruction of the anisotropy within a few nanoseconds which is followed by a "motional narrowing" recovery in direction of the constant anisotropy expected for the time-averaged cubic symmetry of fcc DyH$_{1.96}$. Because of the difficulties of separating the effect of the static and the dynamic components of a slowly fluctuating frequency distribution on the angular correlation (see Sec. II B), only the fast-fluctuation region at $T\geq600$ K was studied in detail.

The data for $T\geq600$ K were analyzed with a two-fraction model, with f_1 describing the fraction of probes subject to a time-dependent QI and f_2 accounting for nuclei in the stable probe-defect complexes detected in the room-temperature spectrum. The relaxation effects seen by fraction f_1 were described by a single relaxation parameter λ [Eq. (3)] assuming a cubic ensemble average [$\Gamma_{22}(t)=1$]. The amplitude f_2 and the interaction parameters of the fraction subject to the static QI distribution [Eq. (1)] were found to change very little with temperature.

The results for the relaxation parameter λ are plotted in Fig. 4 on a logarithmic scale versus the inverse temperature $1/T$. These data show that the relaxation parameter at a given temperature depends on the thermal history of the hydride: The sample was first heated to 700 K (triangles), then cooled back to 600 K and subsequently heated to 900 K (squares). Cycling the sample through 700 K results in a decrease of the relaxation parameter at 600 K by about 35%. Both sets of data (triangles and squares, respectively) satisfy the relation
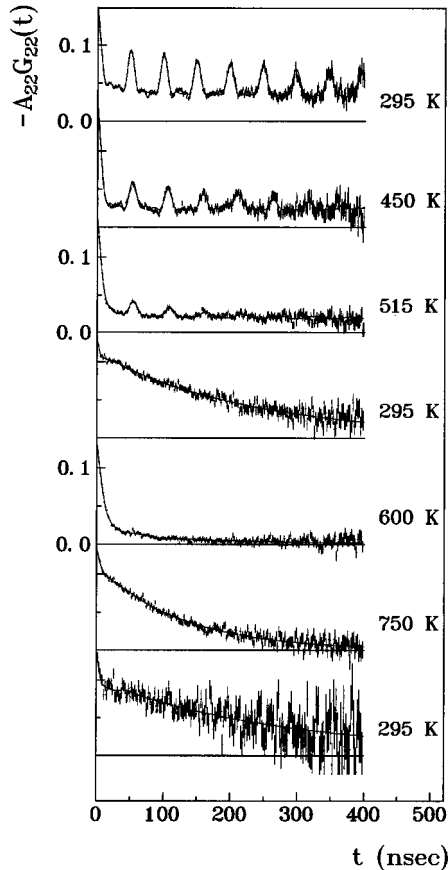
FIG. 5. PAC spectra of ^{111}Cd in DyH$_{1.99}$ (first sample) at different temperatures. From top to bottom, the spectra are arranged in the chronological order of the measurements.

$\ln \lambda \propto E_a / kT$ for fast overbarrier diffusion. The slope, however, decreases from $E_a = 0.35(2)$ eV to $E_a = 0.26(2)$ eV after cycling through 700 K.

Figure 5 shows ^{111}Cd PAC spectra at the hydrogen concentration $x = 1.99$. Two samples were studied at this concentration. In both cases the first room-temperature spectrum of ^{111}Cd:DyH$_{1.99}$ measured after the hydrogenation (as an example, see the topmost spectrum in Fig. 5) showed a periodic, almost undamped oscillation [$\nu_q = 135(1)$ MHz, $\eta = 0.08(2)$ at 295 K] of considerable amplitude ($f_2 \approx 0.15$–0.4) superimposed on a slowly decreasing anisotropy (f_1). This oscillation was found to persist with decreasing amplitude up to temperatures of about 550 K. At $T > 550$ K the oscillation had completely disappeared from the spectra and no longer reappeared when returning to room temperature. The continuously decreasing background (f_1) decays visibly faster with increasing temperature and at 600 K the anisotropy is completely wiped out within 50 nsec. At still higher temperatures one observes the recovery characteristic for the fast-fluctuation regime. Figure 6 shows the temperature dependence of the relaxation parameter λ for $T \geq 600$ K, obtained with Eq. (3) and $\Gamma_{22}(t) = 1$ for fraction f_1. The data are well described by the relation $\ln \lambda \propto E_a / kT$ with an activation energy of $E_a = 0.45(3)$ eV.

Once the first sample had been heated above 550 K, its room-temperature spectrum was fully reversible up to 800 K. In the second sample, however, the relaxation parameter at a
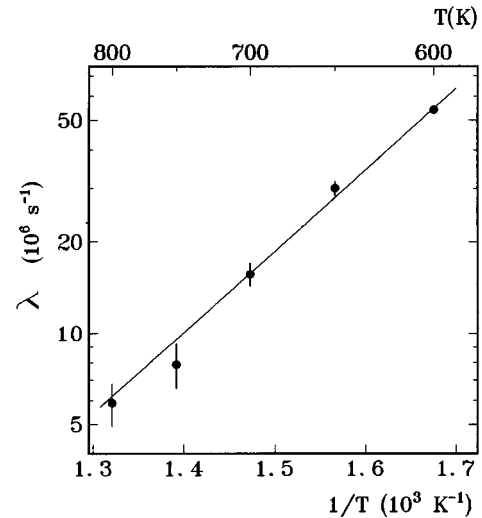

FIG. 6. The relaxation parameter λ of ^{111}Cd:DyH$_{1.99}$ (first sample) for $T \geq 600$ K versus $1/T$.

given temperature was found to depend sensitively on time and on the thermal history. Figure 7 shows the spectra of the second $x = 1.99$ sample at 655 K after 2 and 17 h of data collection, respectively, and at 655 K after heating to 690 K (bottommost in Fig. 7). The dotted line in Fig. 7 represents the 655 K spectrum after 2 h. Clearly, in this sample the relaxation parameter decreases irreversibly with time and the underlying process can be accelerated by cycling through slightly higher temperatures.

C. ^{181}Ta PAC study of dysprosium dihydrides DyH$_x$ in the concentration range $1.8 \leq x \leq 2.1$

The QI of ^{181}Ta in DyH$_x$ was studied as a function of temperature ($19 \leq T \leq 900$ K) at hydrogen concentrations

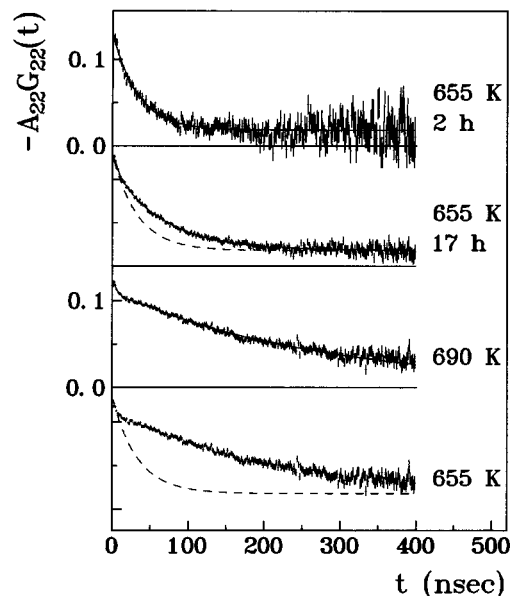FIG. 7. PAC spectra of ^{111}Cd in DyH$_{1.99}$ (second sample) at 655 K after 2 and 17 h of data collection, respectively, at 690 K and at 655 K after 690 K. The dotted line represents the 655 K spectrum after 2 h.
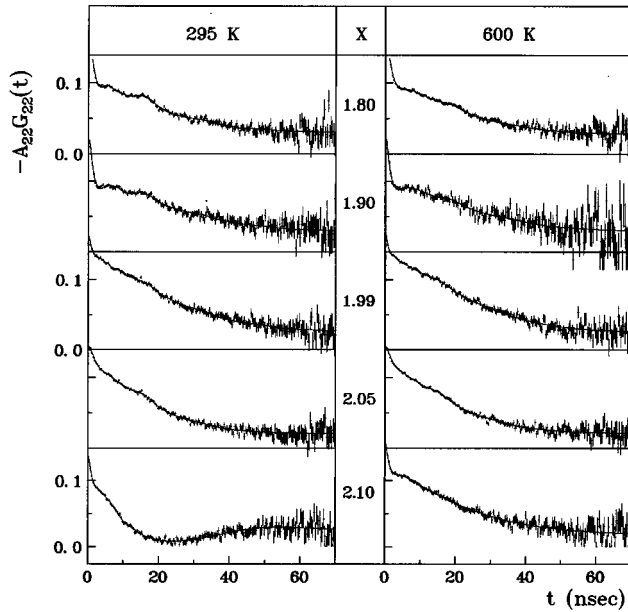
FIG. 8. PAC spectra of ^{181}Ta in dysprosium dihydrides DyH$_x$ in the concentration range $1.8 \leq x \leq 2.1$ at 295 K and 600 K.

ranging from $x=1.8$ to 2.1. The effect of hydrogen concentration and temperature is illustrated in Fig. 8 where the PAC spectra measured at $T=295$ and 600 K are compared for various concentrations x. Even without numerical analysis it is evident that for $x \leq 2.05$ the spectra do practically not react to changes in temperature and vary, if at all, only little with the hydrogen concentration. Only at $x=2.1$ the shape of the spectrum changes considerably between 295 and 600 K.

For $x \leq 2.05$ the spectra show, apart from a fast initial decay which can be attributed to the fraction of ^{181}Ta nuclei trapped in probe-defect complexes of the unloaded metal, a slow decrease of the anisotropy with an oscillation of small amplitude superimposed. As discussed in detail in Sec. IV, the fact that the spectra do not change with temperature implies a perturbation by a static QI. The measurements were therefore analyzed with a two-site model, using static perturbation functions [Eqs. (1) and (2)]. The initial decay of the anisotropy has not been taken into account.

The slow decrease of $A_{22}G_{22}(t)$ is caused by a frequency distribution with QI parameters $\nu_{q1}=25(5)$ MHz and $\delta_1=0.50(5)$ (η_1 assumed zero) which are only slightly temperature dependent. After heating to 1200 K the room-temperature frequency of this fraction ($f_1 \sim 0.8$–0.9) decreases irreversibly by a factor of 3 to $\nu_{q1}=8(1)$ MHz, indicating that with increasing temperature the probe environment approaches cubic symmetry.

The QI parameters of the oscillation superimposed on the slow decrease of $A_{22}G_{22}(t)$ are $\nu_{q2}=405(10)$ MHz, $\eta_2=0$, and $\delta_2=0.18(3)$ at 295 K. The relative amplitude of this fraction is largest at $x=1.8$ ($f_2=0.22$) and varies between 0.1 and 0.15 at the other concentrations. The frequency of this fraction is very close to that of ^{181}Ta in Dy metal: $\nu_q(^{181}$Ta:Dy;295 K$)=392(2)$ MHz (see Sec. III A).

At $x=2.1$ the spectra show clear evidence for time-dependent perturbations by diffusing hydrogen (see Fig. 9). At $T \leq 295$ K one observes a finite anisotropy at large delay times (hard-core value) which is characteristic for a static
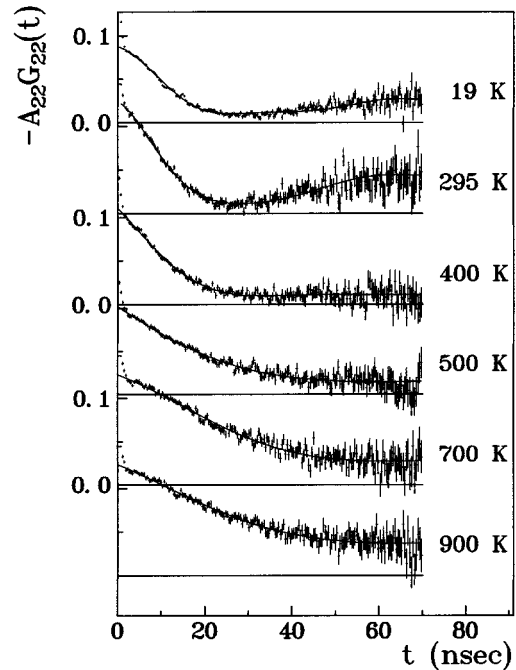

FIG. 9. PAC spectra of ^{181}Ta:DyH$_{2.1}$ at different temperatures.

frequency distribution as caused by "frozen," statistically distributed hydrogen atoms. With increasing temperature the "hard core" vanishes (see the 400 K spectrum in Fig. 9) and at still higher temperatures the anisotropy starts to recover towards the unperturbed value expected for the cubic time average of hydrogen diffusing rapidly among the tetrahedral and octahedral sites of fcc DyH$_x$. The spectra were fully reversible between 295 and 900 K.

From 800 to 900 K the spectrum does not change any more which indicates that the dynamic interaction has averaged out at these temperatures. The remaining attenuation of the anisotropy therefore reflects a static frequency distribution probably due to structural defects and probe-impurity complexes as also found for $x < 2.1$. A fit of a static distribution to the 900 K spectrum gives the QI parameters $\nu_q=10(1)$ MHz, $\delta=0.48(5)$ with the asymmetry parameter fixed to the value at 295 K ($\eta=0.8$).

For the determination of the dynamic interaction parameters at $T < 900$ K the approximation of a single relaxation parameter [Eq. (3)] was fitted to the measured spectra, using for $\Gamma_{22}(t)$ the perturbation function of a static QI distribution [Eq. (1)]. It was assumed that the static distribution width, obtained from the 900 K spectrum, does not change with temperature. In the fits the relaxation parameter λ and the quadrupole frequency ν_q were treated as free parameters while the distribution width δ was fixed to the 900 K value $\delta=0.48$ and the asymmetry parameter to the room-temperature value $\eta=0.8$. Treating η as a free parameter affects the absolute value of the frequency, but does not change its temperature dependence nor the results for the relaxation parameter.

The temperature dependence of the quadrupole frequency ν_q is shown in Fig. 10. In Fig. 11 we have plotted the relaxation parameter λ versus the inverse temperature $1/T$ for
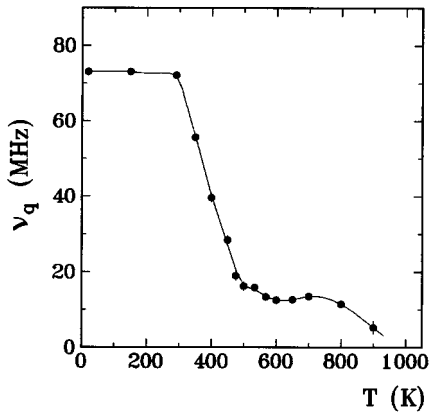
FIG. 10. The temperature dependence of the quadrupole frequency ν_q of ^{181}Ta in DyH$_{2.1}$.

$T \gtrsim 450$ K. The data follow the Arrhenius relation $\ln \lambda \propto E_a/kT$ with a slope of 0.25(2) eV.

IV. DISCUSSION

In the following we shall discuss the main observations of this ^{111}Cd and ^{181}Ta PAC study of static and dynamic QI's in DyH$_x$ and suggest possible interpretations.

(i) With ^{111}Cd as probe we have observed time-dependent perturbations in all investigated samples. A comparison of the maximum relaxation parameter $\lambda_{max} \sim 35$–55 MHZ (see Figs. 4 and 6) with $\lambda_{4f} \lesssim 1$ MHz, estimated from the metal spectra, gives a positive answer to the main question of this study. The contribution of the hydrogen motion to the spin relaxation strongly exceeds the effect of the fluctuating $4f$ moments.

In some cases, the spin relaxation of the spectra was fully reversible between room temperature and 800 K, while in others, as illustrated in Fig. 7 for a sample with concentration $x = 1.99$, irreversible changes towards a static, weakly per-
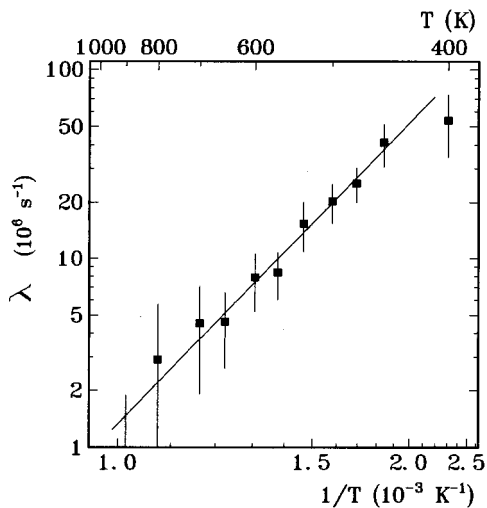

FIG. 11. The relaxation parameter λ of ^{181}Ta:DyH$_{2.1}$, derived by a fit of Eq. (3) to the spectra shown in Fig. 9, vs the inverse temperature $1/T$.

turbing QI occurred at temperatures $T > 650$ K. The observation of a static interaction in a hydride with clearly visible spin-relaxation effects at lower temperature indicates that at higher temperatures the probes no longer ''see'' the hydrogen motion and implies, since PAC probes are rather ''short-sighted'' observers due the r^{-3} dependence of the EFG, the absence of vacancy jumps in the nearest-neighbor (NN) hydrogen shell of the probe. From the weak interaction strength we may further infer that this static probe environment is close to cubic symmetry.

The time scale of the irreversible changes from a fluctuating to a static probe environment of a few hours (see Fig. 7 as an illustration) suggests that the migration of heavier atoms than H, probably of nonmetallic impurities, is involved in this process. The migration of the probes to, e.g., grain boundaries appears unlikely because the QI seen by PAC nuclei on grain boundaries is usually much stronger. The most probable explanation therefore appears to be the formation of probe-impurity complexes which shield the probes from the hydrogen motion in the sense that the hydrogen cannot come close enough to be seen by the probes. The hydrogen probably plays some role in the formation of these stable configurations since they are are not observed in the unloaded metals.

The fact that irreversible changes occurred only in some cases in an unsystematic way can be understood in this picture if samples prepared by apparently the same procedure had in fact different impurity concentrations. Although the regular site fraction of the unloaded Dy metal was very similar in all cases and the same care was taken to avoid migration of nonmetallic impurities during the hydrogenation, we have no quantitative information on the concentration of nonmetallic impurities in the different samples.

(ii) The temperature dependence of the ^{111}Cd relaxation parameter λ (see Figs. 4 and 6) gives the activation energies $E_a(x)$ for vacancy jumps in DyH$_x$ near the probe site. Using only data from the temperature range where the spectra are fully reversible, we obtain $E_a = 0.35(2)$ and 0.45(3) eV for $x = 1.96$ and 1.99, respectively. This increase of $E_a(x)$ towards $x = 2$ can be compared to the behavior of $E_a(x)$ in other transition metal hydrides: In LaH$_{2-\delta}$, YH$_{2-\delta}$, ScH$_{2-\delta}$ (Ref. 30) the activation energy decreases, in ZrH$_{2-\delta}$ (Ref. 31) it increases with increasing hydrogen concentration. Jerosch-Herold et al.[30] correlate these opposite trends to the observation that the hydrides of the first group all exhibit a finite octahedral site occupation, setting in at $x \approx 1.9$, whereas ZrH$_{2-\delta}$ does not, so that an additional energy is required to create vacancies in the hydrogen sublattice of ZrH$_{2-\delta}$ close to $x = 2$. Extending this correlation to DyH$_{2-\delta}$, one would expect, contrary to the experimental values, a decrease of $E_a(x)$ towards $x = 2$, because the existence of a dysprosium trihydride and the susceptibility and neutron diffraction results[6] for the RE neighbor hydrides GdH$_{2-\delta}$ and TbH$_{2-\delta}$ indicate a nonzero octahedral site occupation in DyH$_{2-\delta}$.

(iii) The fluctuating QI at the ^{111}Cd site in DyH$_{1.96}$ and DyH$_{1.99}$, expressed by the frequency ν_q^f, is of considerable strength, as indicated by the complete destruction of the anisotropy at 600 K in less than 50 nsec (see Figs. 3 and 5). The frequency ν_q^f can be estimated without knowledge of the residence time by using the fact that the maximum value λ_{max} of the attenuation parameter and ν_q^f are related by

$\lambda_{max} \approx 1/2 \, \nu_q^f$ (Refs. 26 and 32).

The frequency ν_q^f allows an estimate of the effective charge associated with the tetrahedral hydrogen vacancies. In view of the r^{-3} dependence of the EFG and the small vacancy concentration at $x=1.99$, it is reasonable to assume that the dominant contribution to the relaxation comes from a single vacancy jumping in the NN hydrogen shell of the probe nucleus. For $^{111}Cd^{2+}$ [$Q=0.83$ b, $(1-\gamma_\infty)=32$, Ref. 33] the quadrupole frequency produced by a single charge $Z'e$ at a distance $r=2.25$ Å (NN metal-vacancy separation) is $\nu_q = 2(Z'e)eQ(1-\gamma_\infty)r^{-3}h^{-1} \approx 160 \times Z'e$ MHz. The experimental value of $\nu_q^f \approx 110$ MHz ($\lambda_{max} \approx 55$ MHz for $x=1.99$, see Fig. 6) then corresponds to an effective vacancy charge of $Z'e \approx 0.6e$. It is interesting to note that this value is much larger than the ^{45}Sc NMR result for $ScH_{2-\delta}$ ($Z' \approx 0.1$), obtained with the same point charge model and the free-ion Sternheimer correction from the maximum of the ^{45}Sc relaxation rate.[30] Although the Sternheimer corrections in the solid may differ to some extent from the free-ion values used for the estimate of Z' and although the systematics of the crystal-field parameters of the RE dihydrides[6] suggests an increase of the effective charge at the H anions across the RE series and, this large difference raises the question of systematic differences in the QI relaxation rates measured by NMR and PAC, possibly caused by the impurity nature of the probe (see Sec. II B). A comparative PAC study of the hydrogen diffusion in ScH_2 with different PAC probes would therefore be of interest.

(iv) The observation of an unattenuated oscillation of large amplitude with frequency $\nu_q=135$ MHz appearing in the $^{111}Cd:DyH_{1.99}$ spectrum after the hydrogenation (see Fig. 5) is unexpected. The axial symmetry and the small linewidth of this QI point towards a configuration consisting of the probe and a single charge associated with either an atom or a vacancy at a well-defined distance in an otherwise cubic environment. A single H atom on an octahedral site, a tetrahedral H vacancy or a monovacancy of the fcc RE sublattice trapped by the probe would satisfy the observed symmetry. For a configuration involving a H atom or a H vacancy, however, we would expect the oscillation to reappear always upon cooling which is not the case (see Fig. 5). It therefore appears more likely that RE monovacancies are involved. The symmetry change of the RE lattice from hcp to fcc during the hydrogenation probably leads to a certain concentration of RE vacancies which may be trapped by the probes when the hydride is slowly cooled to room temperature (see Sec. II A). The resulting probe-vacancy pairs dissolve upon heating above 550 K. Support for this interpretation comes from the interaction strength of the oscillation which is in the same range ($\nu_q=100$–150 MHz) as the monovacancy frequencies at ^{111}Cd in fcc and bcc metals.[34] It remains an open question why the 135 MHz component was only observed in the $x=1.99$ samples.

(v) The PAC probe ^{181}Ta appears to be less suited as an observer of the hydrogen motion in RE hydrides than ^{111}Cd. The fact that for concentrations $x \lesssim 2.05$ the $^{181}Ta:DyH_x$ spectra do not react to changes in temperature or hydrogen concentration (see Fig. 8) is incompatible with a dynamic interaction, as can be seen from a comparison with the relaxation maximum $\lambda_{max} \lesssim 55$ MHz of $^{111}Cd:DyH_{2-\delta}$. As $\lambda_{max} \approx 1/2\nu_q^f Q$ scales with $(1-\gamma_\infty)Q$, the value expected for

^{181}Ta is $\lambda_{max} \lesssim 330$ MHz, corresponding to a relaxation time $\tau_{min}=1/\lambda_{max} \gtrsim 3 \times 10^{-9}$ sec clearly within the ^{181}Ta PAC time window. The observation of slowly decaying, temperature-independent spectra therefore implies that the ^{181}Ta probes are completely shielded from the hydrogen motion and subject to a distribution of weak static [$\nu_q(295 \text{ K}) \approx 8$ MHz after 1200 K, see Sec. III C] rather than dynamic QI's. This is probably due to the same process which causes the irreversible changes from a fluctuating towards a static probe environment observed in some of the $^{111}In/^{111}Cd:DyH_x$ samples. Apparently for $^{181}Hf/^{181}Ta$ the formation of probe-defect complexes involving nonmetallic impurities occurs with a much higher rate, so that already after hydrogenation all ^{181}Hf nuclei are embedded in such defect configurations and shielded from the hydrogen motion.

Although we have no quantitative information on the concentration of the nonmetallic impurities in our samples, it is puzzling that at $x \lesssim 2.05$ practically all $^{181}Hf/^{181}Ta$ are shielded from the hydrogen motion. Since ^{181}Hf decays first to an excited 17 μsec state of ^{181}Ta migrating defects could be trapped by ^{181}Ta in the 17 μsec interval before the 133–482 keV PAC cascade is populated. In this case very few nonmetallic impurity atoms would be sufficient to shield all ^{181}Ta nuclei. The irreversible changes by heating (see Sec. III C), however, show that not ^{181}Ta but the parent isotope ^{181}Hf is affected by the impurities. As these do not distinguish between stable and radioactive Hf nuclei, the impurity concentration necessary to shield all PAC nuclei is of the order of the total Hf concentration of 0.5 at. % which is much higher than we would expect in view of the purification and the large regular site fraction of the unloaded metal samples.

The $^{181}Ta:DyH_{x \lesssim 2.05}$ spectra contain a small component (10–20 %) with the frequency of ^{181}Ta in Dy metal (see Sec. III C) which suggests an admixture of α-Dy to the dihydride phase. The x-ray diffraction pattern of the samples, however, showed no reflexes pertaining to α-Dy. Possibly, the impurity $^{181}Hf/^{181}Ta$ tends to stabilize the α structure in its vicinity.

(vi) Evidence for ^{181}Ta spin relaxation has been found only at the hydrogen concentration $x=2.1$. The presence of dynamic perturbations in this sample is indicated not only by the Arrhenius behavior of the relaxation parameter λ (Fig. 11), but also by the abrupt decrease of the quadrupole frequency ν_q at $T \sim 400$ K (Fig. 10) which marks the point where the residence time between hydrogen jumps becomes shorter than the PAC time window. Motional narrowing sets in and the measured quadrupole frequency approaches the vanishing time average of the QI in a fcc hydride. The remaining interaction at $T>400$ K is the result of structural defects and other imperfections.

The low-temperature value of ν_q reflects the ensemble average of the static QI distribution produced by the "frozen," randomly distributed vacancies and hydrogen atoms. With $Q(1-\gamma_\infty)_{181Ta}/Q(1-\gamma_\infty)_{111Cd} \approx 6$ one estimates that the corresponding ensemble average of the static EFG seen by ^{181}Ta in $DyH_{2.1}$ ($\nu_q \sim 70$ MHz; Fig. 10) is about a factor of 5 larger than that of ^{111}Cd in $DyH_{1.99}$ ($\nu_q \sim 2.5$ MHz, Sec. III B). This difference is probably due to the larger octahedral site occupation at $x=2.1$. Assuming that the O-site occupation starts at $x=1.95$, the fraction of probes with at least one octahedral nearest hydrogen neighbor and thus an O-site

EFG contribution is 62% at $x = 2.1$, but only 22% at $x = 1.99$.

On the other hand, when comparing the dynamic perturbations in ^{181}Ta:DyH$_{2.1}$ and ^{111}Cd:DyH$_{1.99}$, one notes that the relaxation is comparably strong in both cases ($\lambda_{max} \approx 55$ MHz and $\lambda_{max} \approx 55$ MHz in ^{181}Ta:DyH$_{2.1}$ and ^{111}Cd:DyH$_{1.99}$, respectively). Since $\lambda_{max} \propto \nu_q^f$, this observation implies that the average dynamic EFG acting on the probes in ^{181}Ta:DyH$_{2.1}$ is a factor of 6 smaller than in ^{111}Cd:DyH$_{1.99}$.

Close to $x = 2$, the main contributions to the fluctuating EFG should come from single vacancies jumping in the NN T shell or single hydrogen atoms in the NN O shell (with the O-site occupation starting at $x = 1.95$, the probability of a probe to have both a NN T vacancy and an NN O-hydrogen atom is 3% at $x = 2$). If one assumes that the effective vacancy and hydrogen charges do not differ, one would not expect the dynamic EFG to change much with the O-site occupation, in contrast to the experimental observation of a much smaller dynamic EFG at $x = 2.1$. If at all, the average dynamic EFG should increase as the O sites are slightly closer to the probe than the NN T sites.

The relatively weak relaxation in ^{181}Ta:DyH$_{2.1}$ therefore suggests that probe-defect complexes have also formed at $x = 2.1$, but due to a smaller impurity concentration only a fraction of the probes is affected. With part of the probes subject to a weak static QI, an analysis assuming that all nuclei are exposed to QI fluctuations would produce a reduced value of the dynamic EFG and underestimate the activation energy.

Although there is no doubt as to the presence of a dynamic perturbation in ^{181}Ta:DyH$_{2.1}$, the quantitative analysis of these measurements therefore suffers from considerable systematic uncertainties which are most probably a consequence of probe-impurity interactions. To overcome these problems for a future use of the probe ^{181}Ta a quantitative study of the ^{181}Ta relaxation rates as a function of the impurity type and concentration is required.

V. SUMMARY

The static and dynamic electric quadrupole interaction (QI) of the nuclear probes ^{111}Cd and ^{181}Ta on RE sites of the RE dihydride DyH$_x$ has been investigated as a function of temperature ($19 \leq T \leq 900$ K) and hydrogen concentration ($1.8 \leq x \leq 2.1$) by perturbed angular correlation (PAC) spectroscopy.

It is shown that for non-RE nuclei with large quadrupole moments the dynamic QI caused by hopping hydrogen may strongly exceed the magnetic dipole interaction with the fluctuating $4f$-magnetic moments. Measurements of the spin relaxation of suitable non-RE probe nuclei may therefore provide information on the hydrogen motion in the RE hydrides in spite of the strong $4f$ paramagnetism. The nuclear quadrupole relaxation rates, however, can be strongly reduced by probe-impurity interactions. PAC studies of the hydrogen diffusion in RE hydrides therefore require a quantitative control of the impurity concentration.

The temperature dependence of the dynamic perturbation of the ^{111}Cd angular correlation in DyH$_x$ gives an activation energy for jumps of hydrogen vacancies near the probe site of $E_a = 0.35(2)$ and $0.45(3)$ eV at $x = 1.96$ and 1.99, respectively. The strength of the fluctuating QI of ^{111}Cd:DyH$_x$ suggests an effective hydrogen charge of $Z' \sim 0.6$.

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