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# **$^{181}\text{Ta}$ perturbed-angular-correlation study of electric quadrupole interactions in yttrium metal and yttrium–hydrogen solid solutions**

M Forker<sup>†</sup>, U Hütten<sup>†</sup> and M Müller<sup>‡</sup>

<sup>†</sup> Institut für Strahlen-und Kernphysik der Universität Bonn, Nussallee 14–16, D-53115 Bonn, Germany

<sup>‡</sup> Facultad de Ciencias, Universidad Autonoma del Estado de Morelos, Cuernavaca 62210, Morelos, Mexico

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**Abstract.** The perturbed-angular-correlation (PAC) technique has been used to study the electric quadrupole interaction (QI) of the nuclear probe  $^{181}\text{Ta}$  in yttrium metal and yttrium–hydrogen solid solutions  $\alpha\text{-YH}_x$  with  $0 \leq x \leq 0.2$ . The temperature dependence of the quadrupole frequency  $\nu_q$  of  $^{181}\text{Ta}$  in yttrium metal, measured in the range  $290 \text{ K} \leq T \leq 1700 \text{ K}$ , follows the linear relation  $\nu_q(T) = \nu_q(0)(1 - AT)$  with  $\nu_q(0) = 423(3) \text{ MHz}$  and  $A = 4.74(4) \times 10^{-4} \text{ K}^{-1}$ . The absorption of hydrogen enhances the temperature dependence of the QI: the parameters  $\nu_q(0)$  and  $A$  of the linear temperature variation of the  $^{181}\text{Ta}$  QI in  $\alpha\text{-YH}_x$  measured between 25 K and 1000 K for  $0 \leq x \leq 0.2$  both increase with increasing concentration  $x$ . These trends are consistent with the anionic model of the electronic state of hydrogen in rare earth metals. At  $T \geq 500 \text{ K}$  a dynamic QI caused by diffusing hydrogen has been observed. The activation energy for hydrogen jumps in  $\alpha\text{-YH}_{0.10}$  deduced from the temperature dependence of the quadrupole relaxation rate is  $E_a = 0.49(15) \text{ eV}$ .

## **1. Introduction**

Measurements of nuclear electric quadrupole interactions (QI) by NQR [1], Mössbauer spectroscopy [2] and perturbed angular correlations (PACs) [3–5] are an important tool for the investigation of metal–hydrogen systems. The interaction between the quadrupole moment of a nuclear state and the tensor of electric-field gradient (EFG) reflects the charge distribution at the nuclear site and therefore carries information on structure and electronic properties of these systems. Hydrogen diffusion produces time-dependent EFGs and can therefore be studied by observing the resulting nuclear quadrupole relaxation.

In this paper we report a PAC investigation of the QI in yttrium–hydrogen solid solutions. Similar to the rare earth (R) metals and Sc, the Y–H phase diagram shows three different phases [6]: the metallic  $\alpha$ -phase  $\alpha\text{-YH}_x$ ,  $x \leq 0.2$  consists of an H–Y solid solution with the H atoms occupying the tetrahedral interstices of the hcp Y lattice, the  $\beta$ -phase  $\text{YH}_x$  (concentration range  $0.2 \leq x \leq 2$ ) crystallizes in the fcc fluorite structure and the insulating trihydride  $\text{YH}_3$  possesses  $P\bar{3}c1$  ( $D_{3d}^4$ ) symmetry [7].

The metallic  $\alpha$ -phase  $\text{RH}_x$  of the heavy R Ho to Lu, Y and Sc exhibits an interesting property: between 300 to 400 K and the lowest temperatures the phase boundary to the cubic  $\beta$ -phase is located at the same hydrogen concentration  $c_{max}$ , independent of temperature. In contrast to most other metals, the heavy R Ho to Lu, Y and Sc ( $c_{max} = 0.03\text{--}0.35$ ) can therefore

absorb considerable quantities of hydrogen even below room temperature without undergoing a change of the lattice structure.

This particular property of  $\alpha$ -RH<sub>x</sub> (R = Ho, . . . , Lu, Y, Sc), which is related to the ordering of the H sublattice into pairs and chains along the *c*-axis, offers the possibility of studying the effect of hydrogen absorption on the EFG—both static and dynamic—in an hcp metal lattice over a relatively large range of concentrations and temperatures. We have carried out such an investigation in  $\alpha$ -YH<sub>x</sub> for concentrations  $0 \leq x \leq 0.2$  and temperatures  $24 \text{ K} \leq T \leq 1000 \text{ K}$  by <sup>181</sup>Ta PAC spectroscopy. The PAC probe nucleus <sup>181</sup>Ta is known to occupy substitutional lattice sites in hcp Y metal. For a basis of comparison the <sup>181</sup>Ta QI of uncharged Y metal was determined up to  $T = 1700 \text{ K}$ .

## 2. Experimental details

### 2.1. Sample preparation and equipment

The PAC measurements were carried out with the 133–482 keV cascade of <sup>181</sup>Ta populated by the  $\beta$ -decay of the 42d isotope <sup>181</sup>Hf, which is produced by thermal neutron irradiation of natural Hf (<sup>180</sup>Hf(*n*,  $\gamma$ )<sup>181</sup>Hf). Dilute alloys of Y with radioactive Hf were prepared by electron gun melting of the metallic components. Samples prepared by melting of Y with a purity of 99.9 at.% in a vacuum of  $10^{-6}$  mbar turned out to be unsuitable because after melting a large fraction of the <sup>181</sup>Hf/Ta probes had trapped light impurities, presumably O, N and C (see below). The fraction of impurity-free <sup>181</sup>Hf probes could be increased considerably by using Y with a purity of 99.99 at.% and melting the components in an ultrahigh vacuum (UHV) of  $10^{-9}$  mbar. The highest fraction of impurity-free <sup>181</sup>Hf was obtained when the Y metal was further purified by melting several times in UHV prior to the alloying with radioactive Hf metal. This procedure was therefore used to produce the radioactive samples <sup>181</sup>Hf:Y for all hydrogenations. Typically the total Hf concentration of <sup>181</sup>Hf:Y was of the order of 0.5 at.%.

The hydrogenation was carried out in a quartz tube connected to a UHV system. After reaching  $10^{-10}$  mbar, the <sup>181</sup>Hf:Y samples were first out-gassed for 2 hours at 900 K and then exposed to a precisely known quantity of H<sub>2</sub> gas (percentage purity 99.9999) determined by capacitance measurements of the H<sub>2</sub> pressure in a calibrated volume, kept for 3–5 hours at 750 K and then slowly ( $5 \text{ K min}^{-1}$ ) cooled to room temperature. By varying the quantity of H<sub>2</sub> gas samples of <sup>181</sup>Hf : YH<sub>x</sub> with the H concentrations  $x = 0.05, 0.1, 0.15$  and  $0.20$  were produced. After preparation the radioactive hydrides were sealed under vacuum into small quartz tubes and heated to temperatures  $T > 290 \text{ K}$  in a furnace designed for high temperature PAC measurements [8]. The QI of <sup>181</sup>Ta in Y metal was studied to  $T \leq 1700 \text{ K}$  with the sample sealed in a quartz tube under high vacuum. Temperatures were measured with a W-3% Re/W-25% Re thermocouple and a pyrometer aimed at the sample through a quartz window of the furnace. We estimate the accuracy of the temperature measurement to be about 20 K in the high temperature limit. The PAC measurements were performed with a standard four-detector setup equipped with fast BaF<sub>2</sub> scintillators.

### 2.2. Data analysis

The angular correlation of the two successive  $\gamma$ -rays of a  $\gamma$ - $\gamma$  cascade, expressed by angular correlation coefficients  $A_{kk}$  ( $k = 2, 4$ ), may be modulated in time by hyperfine interactions in the intermediate state of the cascade. For polycrystalline samples this time modulation 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 (for details see e.g. Frauenfelder and Steffen [9]).

In this paper we are dealing with perturbations by electric quadrupole interactions (QIs) between the electric quadrupole moment  $Q$  of the intermediate state of the cascade and electric-field gradients (EFGs) acting on the PAC nucleus which is usually expressed in terms of the quadrupole frequency  $\nu_q = eQV_{zz}/h$  and the asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$ , where  $V_{ii}$  are the principal-axis components of the EFG tensor with  $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$ . In a non-cubic metal hydrogen system such as  $\text{YH}_x$  with  $x \leq 0.2$  the EFG at the probe site is produced by the H charges, the metal ions and the distribution of the valence and conduction electrons. In substoichiometric hydrides where only a fraction of the available interstices is occupied we expect both static and time dependent QIs.

At low temperatures the H atoms are ‘frozen’ and each PAC probe will see a different configuration of hydrogen atoms and thus experience a different EFG. The ensemble of the PAC probes is therefore subject to a static EFG distribution. For this case the perturbation factor is given by

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

The frequencies  $\omega_n$  are the transition frequencies between the hyperfine levels into which a nuclear state is split by the QI. They depend on the quadrupole frequency  $\nu_q$  and on the asymmetry parameter  $\eta$ . In polycrystalline samples with a statistical distribution of the EFG orientations the amplitudes  $s_{kn}$  are functions of the asymmetry parameter only. The number  $N$  of terms in equation (1) depends on the spin  $I$  of the intermediate state of the cascade. For the case of <sup>181</sup>Ta with  $I = 5/2$  one has  $N = 3$ . The exponential factor accounts for the effect of a Gaussian frequency distribution with relative width  $\delta$ . Frequently, several fractions of nuclei with different QI parameters are found in the same sample. The effective perturbation factor is then given by:

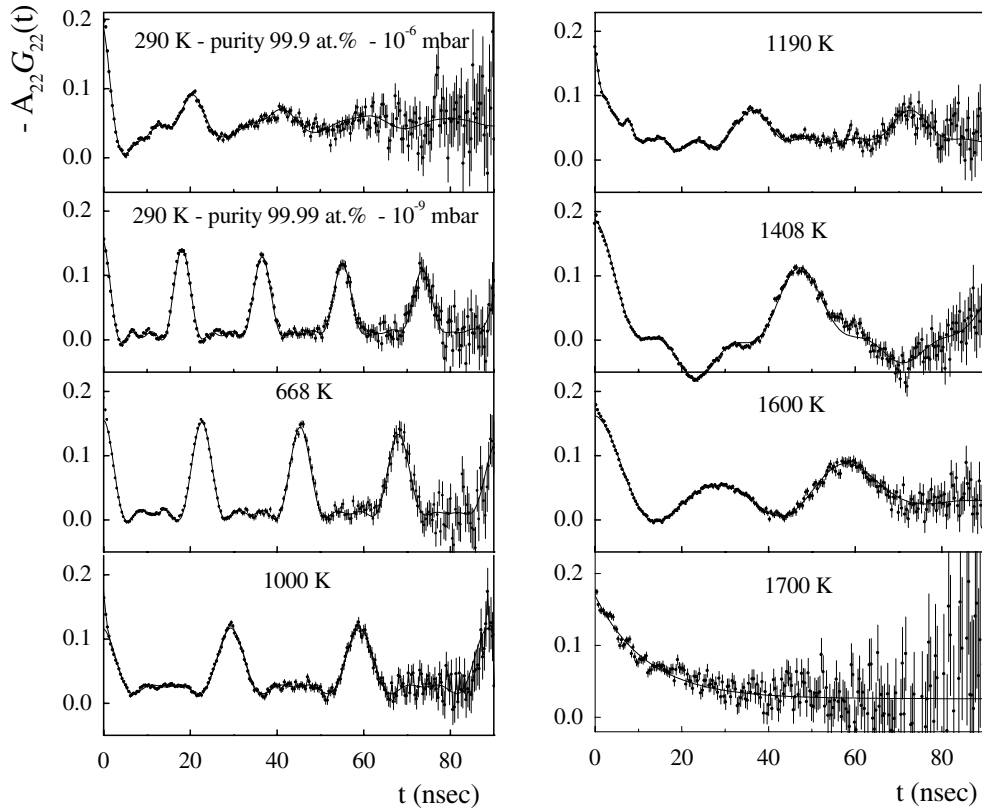
$$G_{kk}(t) = \sum_i f_i G_{kk}(t; \nu_{qi}, \eta_i, \delta_i) \quad (2)$$

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

When hydrogen diffusion sets in at higher temperatures, the moving H charges produce fluctuations of the QI. The effect of the resulting nuclear spin relaxation on the angular correlation is most appropriately described by Blume’s stochastic theory [10, 11]. For the analysis of experimental data for the complex situation of a substoichiometric hydride where the hydrogen motion leads to fluctuations of orientation, strength and symmetry of the interaction, one usually has to resort to an approximation of the Blume theory with a single relaxation parameter  $\lambda_k$ :

$$G_{kk}(t) = \Gamma_{kk}(t) \exp(-\lambda_k t). \quad (3)$$

The validity range of this approximation is discussed in [12] and [13]. For slow fluctuations ( $w \ll \nu_q^0$ ;  $w =$  jump rate,  $\nu_q^0 =$  centre frequency of the static QI distribution) the function  $\Gamma_{kk}(t)$  is given by the perturbation factor for a static QI distribution (equation (1)) and the relaxation parameter  $\lambda_k$  is proportional to the jump rate  $w$ . Fast fluctuations are adequately described by equation (3) if several jumps occur within one spin precession period ( $w > 5\nu_q^0$ ). In the fast fluctuation regime the function  $\Gamma_{kk}(t)$  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 (equation (1) with  $\delta = 0$ ). The relaxation parameter in the fast fluctuation region depends on the strength of the fluctuating QI, described by  $\nu_q^f$ , and



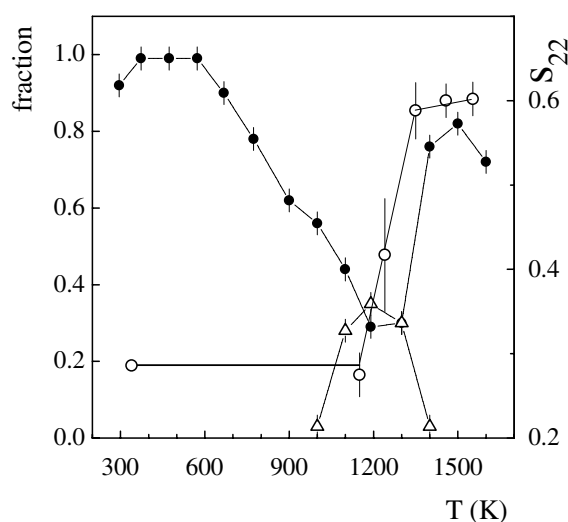
**Figure 1.** PAC spectra of  $^{181}\text{Ta}$  in Y metal at temperatures  $290\text{ K} \leq T \leq 1700\text{ K}$ . Two room temperature spectra are shown: the top-most left-hand spectrum was obtained with a sample prepared by melting radioactive Hf with Y metal of 99.9 at.% purity in a vacuum of  $10^{-6}$  mbar, for the other one Y metal with a purity of 99.99 at.% further purified by melting in UHV ( $10^{-9}$  mbar) was used.

decreases with increasing jump rate  $w$ :  $\lambda_k \propto (v_q^f)^2/w$ . In the case of over-barrier diffusion with activation energy  $E_a$  the relaxation parameter in the fast fluctuation regime follows the Arrhenius relation  $\lambda \propto \exp(E_a/kT)$ .

### 3. Measurements and results

#### 3.1. PAC measurements of $^{181}\text{Ta}$ in Y metal at temperatures $290\text{ K} \leq T \leq 1700\text{ K}$

To assess the effect of the hydrogenation on the EFG in metallic systems, precise data on the QI of the uncharged metal are of importance. The QI of  $^{181}\text{Ta}$  in Y metal has been previously investigated by Butz and Kalvius [14] for temperatures  $T \leq 450\text{ K}$ . To complement these data, we have determined the QI of  $^{181}\text{Ta}$  in Y in the temperature range  $290\text{ K} \leq T \leq 1700\text{ K}$  (see figure 1). For  $^{181}\text{Hf}/\text{Ta}$  on substitutional sites of hcp Y one expects the PAC spectrum to show the periodic modulation of the anisotropy typical for an axially symmetric QI. With samples prepared by melting of Y (99.9 at.%) in a vacuum of  $10^{-6}$  mbar we observed, however, strongly attenuated oscillations (see top-most PAC spectrum in figure 1), which reflect a broad distribution rather than a unique value of the QI. Metallic Hf is known to be an excellent getter

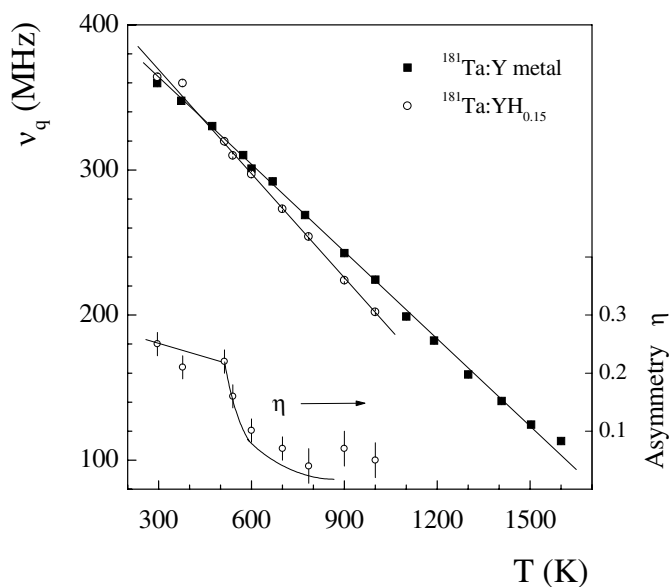


**Figure 2.** The relative intensities of two of the three fractions of  $^{181}\text{Ta}$  probes with different QI parameters detected in the PAC spectra of  $^{181}\text{Ta}:\text{Y}$ . The full circles show the fraction  $f_1$  of  $^{181}\text{Ta}$  on substitutional Y sites, the open triangles correspond to the fraction  $f_3$  of probes with  $\nu_q = 828(5)$  MHz,  $\eta = 0$ ,  $\delta = 0.07(1)$ . The intensity of the fast, unresolved component  $f_2$  with  $\nu_q \sim 2000$  MHz can be deduced from the normalization condition  $\sum_{i=1,3} f_i = 1$ . The figure also shows the amplitude  $s_{22}$  for fraction  $f_1$  (right-hand scale, open circles) obtained by adjusting the theoretical perturbation function (equation (1)) to the measured spectra with the amplitudes  $s_{2n}$  treated as free parameters. The solid line between 290 K and 1150 K corresponds to the theoretical value of  $s_{22} = 0.2857$  for polycrystalline samples.

which readily traps O and other light impurities such as C and N, and Y metal, even of very high purity, may contain such non-metallic elements up to concentrations of several hundred ppm [15]. As the trapping of an impurity strongly affects the QI seen by the PAC probe, the QI distribution can be attributed to the formation of different probe–impurity complexes by trapping of O, C etc. This interpretation is supported by the pronounced increase of the PAC oscillation amplitudes when purified Y and UHV are used for the sample preparation (see the second PAC spectrum from the top in the left-hand column of figure 1).

At  $T > 600$  K a second component appeared in the spectra causing a very fast decrease of the anisotropy in the first few nanoseconds from which one estimates a frequency of the order of  $\nu_q \geq 2000$  MHz. As this value is at the limit of the time resolution of our equipment, the analysis provides no further details on the parameters of this ‘fast’ component. The relative intensity of the ‘fast’ component increases with temperature at the expense of the ‘metal’ component, as shown by the reduced oscillation amplitudes of the 1000 K spectrum in figure 1. The metal fraction reaches a minimum of  $f_1 \sim 0.3$  at  $T = 1200\text{--}1300$  K (see figure 2). Starting at  $T \sim 1000$  K a third component corresponding to a narrow QI distribution with the parameters  $\nu_q = 828(5)$  MHz,  $\eta = 0$ ,  $\delta = 0.07(1)$  is observed (clearly visible in figure 1 as a fast oscillation at 1190 K). This component reaches a maximum intensity  $f_3 \sim 0.3$  at 1200 K and disappears again at  $T > 1300$  K. Simultaneously the intensity of the ‘metal’ fraction grows again and reaches  $f_1 \sim 0.8$  at  $T = 1500$  K.

It is interesting to note that up to 1000 K the ‘metal’ component of the spectra could be well reproduced with the amplitudes  $s_{kn}$  of the perturbation function fixed to the theoretical values of polycrystalline samples (equation (1)). At  $T > 1000$  K, however, where the

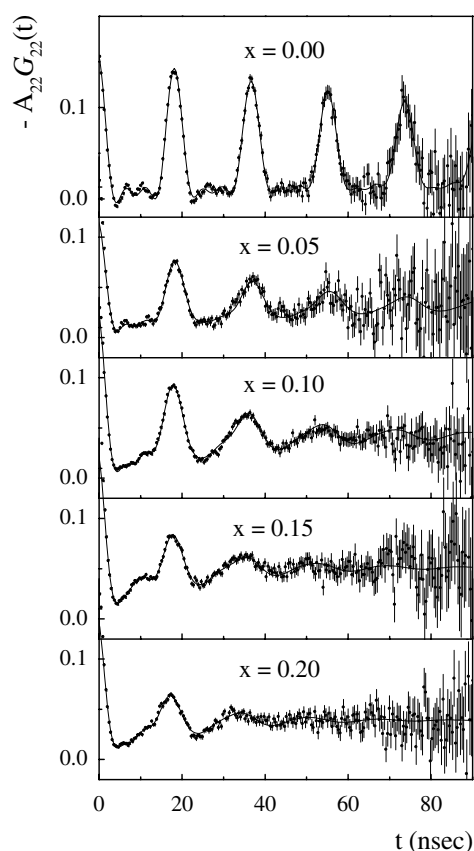


**Figure 3.** The temperature dependence of the quadrupole frequency  $\nu_q$  of  $^{181}\text{Ta}$  on substitutional sites of Y metal (full squares) and  $\alpha\text{-YH}_{0.15}$  (open points). Furthermore, the figure shows the temperature variation of the asymmetry parameter  $\eta$  of  $^{181}\text{Ta}$  in  $\alpha\text{-YH}_{0.15}$  (right-hand scale, open points).

intensity of the ‘metal’ fraction starts to recover, the amplitudes  $s_{kn}$  were found to deviate considerably from those of polycrystalline samples, indicating the onset of crystallite growth towards mono-crystalline samples. In the analysis the amplitudes had then to be treated as free parameters. As an illustration we have included in figure 2 the temperature dependence of the amplitude  $s_{22}$ . (Note: the  $s_{22}$  value at 1600 K is not shown in figure 2, because for technical reasons the measurement at this temperature was carried out with a different sample position so that the  $s_{2n}$ -values are no longer comparable to the previous measurements. This change in sample orientation is reflected by the changes in the PAC pattern between 1408 and 1600 K, respectively, in figure 1).

The relative intensities  $f_i$  of the different fractions present in high-purity samples and their QI parameters [ $\nu_{qi}$ ,  $\eta_i$ ,  $\delta_i$ ] were determined by fitting the theoretical perturbation function for static QIs (equations (1), (2)) to the measured spectra. At room temperature the spectrum could be well described by a single (‘metal’) fraction ( $f_1 \geq 0.95$ ) with the parameters  $\nu_q = 359.8(3)$  MHz,  $\eta \geq 0.05$ ,  $\delta = 0.013(1)$ . At about 1700 K the periodic modulation of the anisotropy corresponding to the hcp ‘metal’ component disappears completely and instead of a well defined frequency the spectrum now reflects a broad frequency distribution ( $\delta \sim 0.5$ ) with a small centre frequency ( $\nu_q \sim 50$  MHz).

The decrease of the quadrupole frequency of the  $^{181}\text{Ta}$  on substitutional Y sites (‘metal’ component) with increasing temperature (see figure 3) is well described by the linear relation  $\nu_q(T) = \nu_q(0)(1 - AT)$  with  $\nu_q(0) = 423(3)$  MHz and  $A = 4.74(7) \times 10^{-4} \text{ K}^{-1}$ . While the asymmetry parameter of this component is temperature independent ( $\eta \leq 0.05$  for  $290 \text{ K} \leq T \leq 1600 \text{ K}$ ) the relative width of the frequency distribution showed a slight irreversible decrease from  $\delta = 0.013(1)$  at  $T = 290 \text{ K}$  to  $\delta = 0.001(1)$  at  $T > 1000 \text{ K}$ .



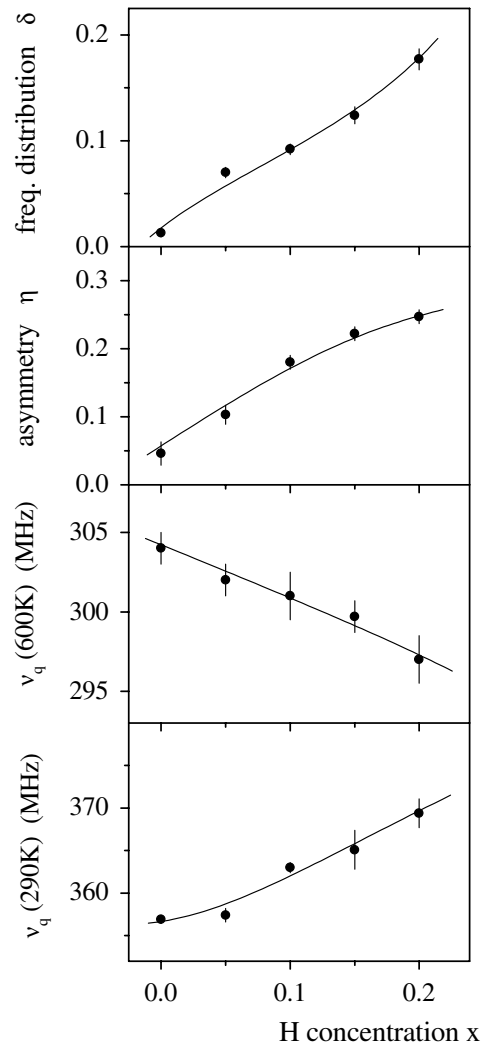
**Figure 4.** Room temperature PAC spectra of  $^{181}\text{Ta}$  in  $\alpha\text{-YH}_x$  at different hydrogen concentrations  $x$ .

### 3.2. PAC measurements of the $^{181}\text{Ta}$ quadrupole interaction in $\alpha\text{-YH}_x$ at hydrogen concentrations $0 \leq x \leq 0.24$

The PAC of  $^{181}\text{Ta}$  in  $\alpha\text{-YH}_x$  has been investigated as a function of temperature for the H concentrations  $x = 0.10$  ( $24 \text{ K} \leq T \leq 710 \text{ K}$ ),  $x = 0.15$  ( $290 \text{ K} \leq T \leq 1000 \text{ K}$ ) and  $x = 0.20$  ( $290 \text{ K} \leq T \leq 800 \text{ K}$ ). For  $x = 0.05$  only a room temperature (RT) spectrum was taken.

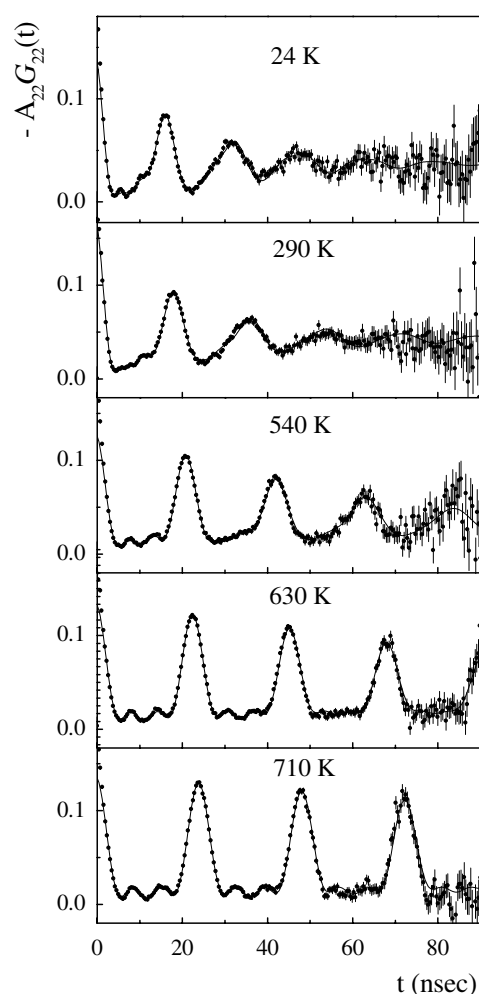
Figure 4 shows the RT spectra at different concentrations. The comparison with the spectrum of uncharged high-purity Y metal (topmost section of figure 4) shows that for  $T = 290 \text{ K}$  the absorption of H leads to a damping of the oscillation amplitudes of the perturbation factor which increases with increasing H concentration reflecting the transition from a unique QI at  $x = 0$  towards a broad QI distribution at large  $x$  values. As shown by the evolution of the spectra with temperature (see below) at  $290 \text{ K}$  the interaction can still be considered as static within the  $^{181}\text{Ta}$  PAC time window. The RT QI parameters were therefore extracted by fits of the static perturbation functions equations (1), (2) to the measured spectra. For some concentrations the fits suggested the existence of a small second component (relative intensity 10–15%) subject to a broad frequency distribution ( $\delta \sim 0.4$ ) centred at  $\nu_q \sim 600 \text{ MHz}$ , which is possibly due to the trapping of residual impurities during the hydrogenation. The QI parameters [ $\nu_q, \eta, \delta$ ] of the dominant fraction for  $T = 290 \text{ K}$  are collected in figure 5.





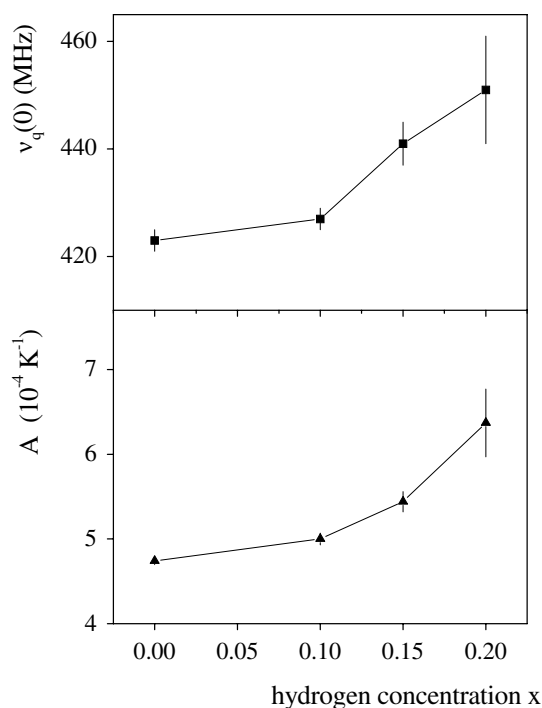
**Figure 5.** The static QI parameters  $\nu_q$ ,  $\eta$  and  $\delta$  of  $^{181}\text{Ta}$  in  $\alpha\text{-YH}_x$  at room temperature as a function of the hydrogen concentration  $x$ . The figure also shows the  $x$ -dependence of the quadrupole frequency at 600 K.

The evolution of the PAC pattern with temperature is illustrated in figure 6 for  $\text{YH}_{0.1}$  between 24 K and 710 K. For this concentration we have accumulated the highest statistical accuracy. At low temperatures the oscillations are attenuated and the anisotropy tends towards a nonzero value at large delay times. Such a ‘hard core’ value (see [9]) is only observed if the probability of hydrogen jumps within the  $^{181}\text{Ta}$  PAC time window of about 100 nanoseconds is very small. In the low temperature limit the attenuation of the oscillation amplitudes can therefore be attributed to a static QI distribution caused by the differences in the ‘frozen’ H environments seen by different PAC probes. The parameters of the static QI distribution  $[\nu_q, \eta, \delta]$  of  $\text{YH}_{0.1}$  at 24 K, obtained by a least-squares fit of equation (1) to the experimental spectrum, are  $\nu_q = 407(19)$  MHz,  $\eta = 0.22(1)$ ,  $\delta = 0.08(1)$ .



**Figure 6.** PAC spectra of  $^{181}\text{Ta}$  in  $\alpha\text{-YH}_{0.10}$  at different temperatures.

With increasing temperature the damped pattern observed at 24 K evolves towards almost undamped periodic oscillations at  $T > 700$  K (see figure 6). Qualitatively, the same behaviour was found at the concentrations  $x = 0.15$  and  $x = 0.20$ . This reversible recovery of the oscillation amplitudes corresponds to the motional narrowing of an NMR signal and is clear evidence for a time dependent QI caused by diffusing H ions (see section 2). In the high temperature limit, the fluctuations are fast relative to the  $^{181}\text{Ta}$  PAC time window and the PAC pattern is determined by the time average of the QI which in the present case has axial symmetry ( $\eta = 0$ ). For  $T > 24$  K, the analysis was therefore carried out with the approximation equation (3) of the Blume theory for stochastic perturbations, with  $\Gamma_{kk}(t)$  given by equation (1), adjusting the parameters  $\nu_q$ ,  $\eta$ ,  $\delta$  and  $\lambda$  to the measured spectra. The analysis provides accurate values for the QI parameters  $\nu_q$  and  $\eta$ . In figure 3 the changes in the temperature dependence of  $\nu_q$  and  $\eta$  by hydrogenation are illustrated by comparing  $\text{YH}_{0.15}$  to uncharged Y metal. For all concentrations the quadrupole frequency shows a linear temperature dependence  $\nu_q(T) = \nu_q(0)(1 - AT)$ . The variation of the parameters  $\nu_q(0)$  and  $A$  with the hydrogen concentration is shown in figure 7.



**Figure 7.** The parameters  $\nu_q(0)$  and  $A$  of the linear temperature dependence.  $\nu_q(T) = \nu_q(0)(1 - AT)$  versus the hydrogen concentration  $x$ .

The determination of the parameters  $\delta$  and  $\lambda$  is less precise, because a static frequency distribution ( $\delta$ ) and a time-dependent interaction ( $\lambda$ ) both cause a damping of the oscillation amplitudes and are difficult to separate if—as in the present case—the static QI distribution is rather narrow and the dynamic QI is weak compared to the centre frequency of the static distribution (for a detailed discussion see [13]). Up to  $T < 500$  K the spectra could be well reproduced by a static distribution alone ( $\lambda = 0$ ), with  $\delta$  having practically the same value as at 24 K. For  $T \geq 500$  K a finite relaxation parameter becomes necessary to describe the recovery of the oscillation amplitudes. At the highest temperature measured both the relaxation parameter and the width of the frequency distribution were treated as adjustable parameters. As the spectra are fully temperature reversible, annealing effects could be excluded, which justifies the assumption that the width of the static frequency distribution in the fast fluctuation range is temperature independent. At lower temperatures we therefore fixed the width of the frequency distribution to the value obtained in the high temperature limit and only adjusted the relaxation parameter. In figure 8 the values of  $\lambda$  obtained for  $^{181}\text{Ta} : \text{YH}_{0.10}$  under these conditions are plotted as a function of the inverse temperature. A fit of the Arrhenius relation  $\lambda \propto \exp(E_a/kT)$  to the values of  $\lambda$  in figure 8 gives an activation energy of  $E_a = 0.49(15)$  eV. The error is mainly due to the systematic uncertainty introduced by the assumption of a temperature independent static frequency distribution which was estimated by carrying out the analysis for different fixed values of the parameter  $\delta$ . For  $x = 0.15$  the activation energy is the same within this error interval. This value is in good agreement with previous results obtained by NMR and other techniques [16–18]. In the case of  $x = 0.20$  a meaningful determination of  $E_a$  was not possible because the fast fluctuation range investigated was too small.

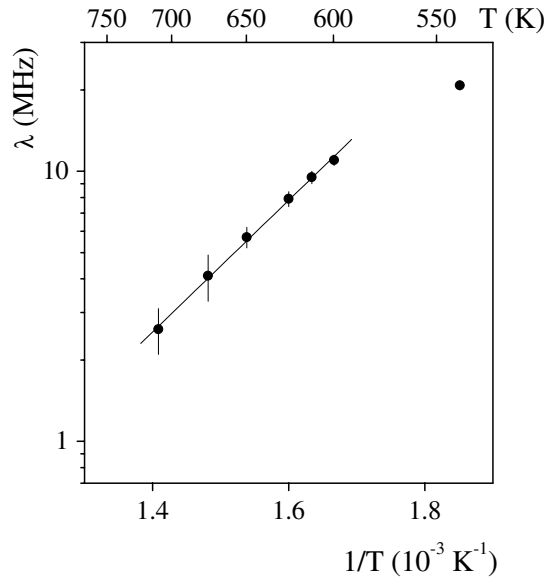


Figure 8. The relaxation parameter  $\lambda$  (equation (3)) of <sup>181</sup>Ta in  $\alpha$ -YH<sub>0.10</sub>.

#### 4. Discussion

##### 4.1. Quadrupole interactions of <sup>181</sup>Ta in Y metal

The dominant one of the three fractions of <sup>181</sup>Ta probes observed in Y metal ( $f_1$ ) is subject to a well defined QI of axial symmetry and can therefore be attributed <sup>181</sup>Ta on substitutional sites of the metal lattice ('metal' fraction). The QI parameters of <sup>181</sup>Ta on substitutional Y sites have previously been measured by Butz and Kalvius [14] from 4.2 K to 450 K. The result of these authors for the room temperature quadrupole frequency is in excellent agreement with the value  $\nu_q(290 \text{ K}) = 359.8(3) \text{ MHz}$  obtained in this study. The information provided by the corresponding electric-field gradient  $V_{zz}(\text{<sup>181</sup>Ta:Y; 290 K}) = 5.93 \times 10^{17} \text{ V cm}^{-2}$  on the host and probe dependence of EFGs in non-cubic metals is discussed in detail in [19].

The present study provides new data on the temperature dependence of the <sup>181</sup>Ta:Y quadrupole frequency up to 1600 K. Thermal vibrations of the host lattice atoms are generally considered as the main mechanism responsible for the temperature dependence of the QI in solids. In most non-cubic metals, especially in the sp metals, the decrease of the QI with increasing temperature follows a  $T^{3/2}$ -relation, which is thought to reflect the temperature variation of the mean square vibrational amplitudes of the host atoms [20,21]. This interpretation is supported by the pronounced correlation between the strength parameter of the  $T^{3/2}$ -relation and the inverse spring constant  $(M\Theta_D^2)^{-1}$  of the lattice [22], with  $\Theta_D$  the Debye temperature and  $M$  the atomic mass.

Y is one the few metals which show a distinctly different behaviour: in the temperature range  $290 \text{ K} \leq T \leq 1500 \text{ K}$  the quadrupole frequency of <sup>181</sup>Ta:Y is a linear function of temperature  $\nu_q(T) = \nu_q(0)(1 - AT)$  with the parameters  $\nu_q(0)$  and  $A$  given in section 3. (Our value for  $\nu_q$  at 450 K differs by about 7% from that of Butz and Kalvius [14]. In the latter study the sample was heated in direct contact with a hot oil bath and was thus possibly contaminated.) Evaluation of the <sup>181</sup>Ta:Y data of Butz and Kalvius [14] (for  $4 \text{ K} \leq T \leq 300 \text{ K}$ ) results in a

considerably smaller value  $A(^{181}\text{Ta:Y}) = 3.5(4) \times 10^{-4} \text{ K}^{-1}$  indicating a deviation from the linear  $\nu_q(T)$ -relation towards low temperatures.

With respect to the temperature dependence of the QI yttrium thus resembles the heavy rare earth metals (R) Gd to Lu: for these elements a linear temperature dependence of the QI has been observed with various nuclear probes with the strength parameter  $A$  decreasing linearly with increasing R atomic number [23]. The possible relation of these observations to the electronic structure of the R Metals has been discussed in [19]. The 4d metal Y resembles the 5d element Lu in the valence electron configuration and many other properties, and for most probe nuclei studied in both hosts the RT quadrupole frequencies are very similar. As the inverse spring constants of both metals are practically identical  $((M\Theta_D^2)^{-1} = 1.69$  and  $1.68$  (in units of  $10^{-7} \text{ amu}^{-1} \text{ K}^{-2}$ ) for Y and Lu, respectively, calculated with the Debye temperatures given by Scott [24], one might expect the strength parameter  $A$  to fit into the R systematics [16, 20] at the Lu position and in fact our value  $A(^{181}\text{Ta:Y}) = 4.74(4) \times 10^{-4} \text{ K}^{-1}$  for  $290 \text{ K} \leq T \leq 1600 \text{ K}$  is only slightly larger than  $A(^{181}\text{Ta:Lu}) = 4.05(14) \times 10^{-4} \text{ K}^{-1}$ , measured by Rasera *et al* [25] in the range  $4 \text{ K} \leq T \leq 655 \text{ K}$ .

The second ( $\nu_q \approx 2000 \text{ MHz}$ ) and the third ( $\nu_q = 828(5) \text{ MHz}$ ,  $\eta = 0$ ,  $\delta = 0.07(1)$ ) of the three components observed in the  $^{181}\text{Ta:Y}$  PAC spectra cannot be identified unambiguously. Up to  $T \approx 1200 \text{ K}$  both increase at the expense of the ‘metal’ fraction and both disappear when at  $T > 1200 \text{ K}$  the metal fraction grows again. This suggests that these two components reflect the trapping and de-trapping of different light impurities by the PAC probe  $^{181}\text{Hf}/^{181}\text{Ta}$ . As Hf is a strong getter for light impurities, the number of PAC probes decorated with one or more impurities can be expected to first increase with temperature because of the increasing impurity mobility. The QI of these probes will differ from that seen by the non-decorated nuclei and accordingly the ‘metal’ fraction will decrease with temperature. In the present case at least two different impurities with different diffusion coefficients in Y are involved, as indicated by the different QI parameters of the impurity fractions and the fact that they appear at different temperatures. At  $T > 1200 \text{ K}$  the probe–impurity configurations start to dissolve and the metal fraction recovers. It is remarkable that both impurity fractions start to disappear simultaneously with the onset of the crystallite growth, as indicated by the temperature of the coefficient  $s_{22}$  (see figure 2). Apparently, as the sample evolves towards a single crystal, the light impurities are expelled to the grain boundaries.

The periodic PAC pattern characteristic for an hcp metal disappears at about  $1700 \text{ K}$ , close to the transition from the hexagonal  $\alpha$ - to the cubic  $\beta$ -phase of Y at  $T_{\alpha \rightarrow \beta} \sim 1740 \text{ K}$ . In the cubic  $\beta$  phase we would expect the QI to vanish completely. Instead we observe a weak QI distribution, which possibly reflects the onset of a reaction between the sample and the quartz vessel. Such a reaction has been found in a high temperature PAC investigation of the QI of  $^{181}\text{Ta}$  in Zr [8] metal at  $T > 1600 \text{ K}$ .

#### 4.2. Quadrupole interactions of $^{181}\text{Ta}$ in $\alpha\text{-YH}_x$

The main experimental observations concerning the hydrogen induced changes of the QI parameters of  $^{181}\text{Ta}$  in  $\alpha\text{-YH}_x$  can be summarized as follows:

- (i) At temperatures  $T \leq 290 \text{ K}$  the spectra are characterized by a static distribution of axially asymmetric QIs. All QI parameters, i.e. the frequency  $\nu_q$ , the asymmetry parameter  $\eta$  and the width  $\delta$  of the QI distribution are found to increase with increasing hydrogen concentration (see figure 5).
- (ii) The decrease of the quadrupole frequency with increasing temperature is stronger for higher hydrogen concentration  $x$  so that in the high temperature limit  $T \geq 600 \text{ K}$  the quadrupole frequency at a given temperature decreases with increasing  $x$  in contrast to the

increase observed at  $T \leq 290$  K (compare the two bottom-most sections of figure 5). This is expressed by the concentration dependence of the parameters  $\nu_q(0)$  and  $A$  in figure 7, obtained by fitting the relation  $\nu_q(T) = \nu_q(0)(1 - AT)$  to the  $\nu_q$ -values for  $T \geq 290$  K.

- (iii) For all concentrations  $x$ , the asymmetry parameter decreases rather abruptly from  $\eta \approx 0.3$  at  $T \leq 500$  K to  $\eta \leq 0.05$  at  $T \geq 600$  K (see figure 3).

When trying to understand these observations, the anisotropic lattice expansion, the changes of the Debye temperature upon hydrogenation and the influence of the hydrogen charge have to be discussed.

The effect of the anisotropic lattice expansion can be estimated using the result of a point-charge lattice sum calculation by Das and Pommerantz [26] according to which the EFG at a substitutional site of a hcp lattice is proportional to  $[0.0065 - 4.3584(c/a - 1.633)]/a^3$ . The axial ratio of hcp Y is  $c/a = 1.571$  at 290 K [27] and increases both with increasing temperature  $T$  at a given concentration  $x$  and with increasing  $x$  at a given  $T$  [6]. The lattice parameter  $a$  also increases with temperature and concentration [6]. The anisotropic lattice expansion can therefore be expected to cause a decrease of the QI both with increasing temperature and concentration. For the room temperature lattice parameters the point-charge lattice sum of Das and Pommerantz [26] predicts a decrease of the EFG by about 20% between  $x = 0$  and  $x = 0.20$ . The room temperature measurements, however, show an increase of  $\nu_q$  with increasing  $x$  (figure 5).

In the case of  $\alpha$ -LuH<sub>x</sub> and  $\alpha$ -ScH<sub>x</sub> the Debye temperature  $\Theta_D$  of the metal host lattice increases with increasing concentration [6]. Assuming the same holds for  $\alpha$ -YH<sub>x</sub>, one would expect the strength parameter  $A \propto (M\Theta_D^2)^{-1}$  of the temperature dependence of the QI (section 3.1) to decrease with increasing  $x$ . Experimentally, however, we found an increase of  $A$  with increasing  $x$  (see figure 7).

Clearly, neither the anisotropic lattice expansion nor the changes of the Debye temperature can account for the above observations. In particular, the increase of the room temperature asymmetry parameter and width of the frequency distribution with increasing  $x$  and the abrupt change of the asymmetry at  $T \approx 500$  K cannot be explained.

The following qualitative arguments suggest that the observed hydrogen induced changes of the QI parameters are mainly related to the hydrogen charge. As the EFG decreases with the third power of the charge–probe distance, a qualitative discussion of the effect of the hydrogen charge on the QI of <sup>181</sup>Ta on a metal site can be limited to the nearest neighbour (nn) hydrogen atoms. It is well established that the hydrogen atoms in  $\alpha$ -RH<sub>x</sub> (R = Y, Sc, Lu) are localized predominantly on the tetrahedral interstices (T sites) of the hcp metal lattice [6]. Relative to a PAC probe on a metal site at position (0, 0, 0) of the hcp lattice, there are two sites  $T_0$  along the  $c$ -axis at (0, 0,  $\pm 3/8$ ) and six equivalent sites  $T_1$  at (2/3, 1/3,  $\pm 1/8$ ) etc.

At 290 K the QI is static within the PAC time window (see section 3.2) and—neglecting H–H pairing—we deal with the ensemble average of a static random distribution of the hydrogen atoms on the nn T sites. At concentrations  $x \leq 0.2$ , only two configurations with zero and one H atom in the nn shell, respectively, have to be considered (the probability of having two H atoms on eight nn T sites at  $x = 0.2$  is only 15%). In this approximation one then has three classes of PAC probes: those with no nn H atom, those with one H on  $T_1$  and those with one H on  $T_0$ , each one with a different QI. With increasing occupation of sites  $T_0$  and  $T_1$  the fraction of probes with the sharp QI of the uncharged metal decreases and new components are expected. The fact that we observe a distribution rather than several well separated frequencies implies that the QI differences between these configurations are small and suggests a small effective H charge. The increased width of the distribution with concentration  $x$  (figure 5) reflects the increasing number of slightly different configurations.

A H charge on  $T_0$  changes the magnitude of the metal EFG, but maintains its axial symmetry because  $T_0$  is situated on the  $c$ -, i.e. the symmetry, axis. A charge on site  $T_1$ , however, is located off the symmetry axis and therefore produces an axial asymmetry which depends on the relative charges of the metal and the hydrogen atoms. A point-charge lattice sum calculation of the EFG for a hcp lattice with metal charge  $+3e$  shows that a negative H charge of  $-0.03e$  on  $T_1$  is sufficient to produce an asymmetry of  $\eta \approx 0.4$ . The observed increase of the asymmetry parameter with  $x$  (figure 5) can therefore be attributed to the increase of the  $T_1$  population.

With increasing temperature relaxation effects appear in the PAC spectra and at  $T \geq 600$  K numerous H jumps occur within the PAC time window. In the high temperature limit all T sites then have equal occupation probability, i.e. we deal with the time-average of a rapidly fluctuating QI. If all rather than one  $T_1$  sites are occupied, the charge distribution around the PAC probe becomes axially symmetric. The abrupt change of the asymmetry parameter from  $\eta \approx 0.3$  to  $\eta \leq 0.05$  at  $T \approx 500$  K (figure 3) can therefore be explained by the transition from a static ensemble-averaged to a dynamic time-averaged QI.

The quadrupole frequency of the ensemble average ( $T \leq 290$  K) increases, that of the time average ( $T \geq 600$  K) decreases with the H concentration (figure 5). Changes of the quadrupole frequency are expected because at  $T \leq 290$  K the T site occupation and at  $T \geq 600$  K the time-averaged charge increases with increasing H concentration. A quantitative explanation of the observed trends is beyond of the scope of this paper. We have, however, carried out a point-charge lattice sum calculation of the EFG, assuming a metal charge of  $+3e$  and effective hydrogen charges  $Z'e \leq 0.1e$ . According to these calculations, a negative H charge on a single  $T_1$  site leads to an increase of the total (metal + H) lattice EFG, while the occupation of all equivalent  $T_1$  sites with negative charges produces a decrease of total EFG. The assumption of a positive hydrogen charge reverses the sign of these changes. Qualitatively, the observed trends therefore suggest a small, negative hydrogen charge which is consistent with the anionic model of the electronic state of hydrogen in rare earth metals.

In summary, we have investigated the electric quadrupole interaction (QI) of  $^{181}\text{Ta}$  in Y metal and Y–H solid solutions as a function of temperature and hydrogen concentration. The temperature dependence of the quadrupole frequency  $\nu_q$  of  $^{181}\text{Ta}$  in yttrium metal, measured in the range  $290 \text{ K} \leq T \leq 1700 \text{ K}$ , follows the linear relation  $\nu_q(T) = \nu_q(0)(1 - AT)$  with  $\nu_q(0) = 423(3) \text{ MHz}$  and  $A = 4.74(4) \times 10^{-4} \text{ K}^{-1}$ . Absorption of hydrogen affects the QI parameters and their temperature dependence. At  $T \leq 290$  K all QI parameters—frequency, asymmetry and linewidth—increase; at high temperatures the frequency decreases with increasing H concentration. These trends are qualitatively consistent with a small negative H charge. Quadrupole relaxation caused by diffusing hydrogen has been observed at  $T \geq 500$  K and the activation energy for hydrogen jumps has been determined for  $\alpha\text{-YH}_{0.10}$ .

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