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Hyperfine spectroscopic study of Hf_2Fe hydrides and their thermal stability

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Abstract

Perturbed angular correlation (PAC) spectroscopy has been used to investigate the hydrides of the intermetallic compound Hf_2Fe. Aiming at information on the hydrogen diffusion, measurements of the electric quadrupole interaction of ^{181}Ta on Hf sites of Hf_2FeH_x have been carried out in the concentration range $0.8 \leq x \leq 4.8$.

PAC measurements as a function of temperature show that for hydrogen concentrations $x > 1.5$ these hydrides are thermally unstable and decompose at $T \approx 650$ K. The time constant of the decomposition at 1100 K was determined by PAC spectroscopy to be $\tau = 1.0(2)$ h for $x = 3.75$. The cubic Hf hydride δ-HfH_x with $x \approx 1.6$ and the intermetallic compound $HfFe_2$ were identified as well crystallized segregation products by X-ray diffraction and ^{57}Fe Moessbauer spectroscopy. The activation energy for hydrogen jumps in the decomposition product δ-HfH_x was determined to be $E_a = 0.50(3)$ eV. The thermal stability increases towards lower hydrogen concentrations. For $x \leq 1$ the PAC spectra of Hf_2FeH_x were found to be fully reversible between 290 K and 1100 K.

Hf_2FeH_x has been reported to show magnetic order at large hydrogen concentrations and low temperatures. PAC measurements for large x values and temperatures between 290 K and 9 K, however, gave no evidence for a magnetic hyperfine field at the Hf sites. Moessbauer measurements suggest that the magnetic order temperature of $Hf_2FeH_{3.9}$ is less than 50 K.

Keywords: Hf_2Fe; Hydrogen absorbtion; PAC spectroscopy; Hydride stability

1. Introduction

Hf_2Fe belongs to the group of intermetallic compounds which may absorb large quantities of hydrogen without changing their lattice structure. This hydrogen storage capacity is both of basic and technological interest and the hydrides Hf_2FeH_x have therefore received considerable experimental attention in the past [1–7]. Most of theses experiments exploit the fact that the isotopes ^{57}Fe and ^{181}Ta which is populated in the β-decay of ^{181}Hf are excellent probes for Moessbauer and Perturbed Angular Correlation (PAC) spectroscopy, respectively, and deduce information on the changes of the Hf_2Fe properties upon hydrogenation from measurements of magnetic and electric hyperfine interactions.

Hf_2Fe crystallizes in the cubic Ti_2Ni structure (space group *Fd3m*) with 96 atoms per unit cell [8]. The 32 Fe atoms are in positions *32e*, the 64 Hf atoms are distributed on the two positions *16c* and *48f*. Hf_2Fe may absorb up to 5 H atoms per formula unit into interstitial sites. Neutron diffraction studies of Hf_2FeD_x (Ref. [5]) have established that the D(H) atoms are distributed on one triangular (T_1,*32e*) and on three of the six tetrahedral (D_{1-6}, Westlake notation [9]) interstices of Hf_2Fe, while the two sites $O_{1,2}$ with octahedral coordination remain unoccupied. The occupation of these sites varies with the hydrogen concentration which can be attributed to geometrical and chemical factors [5,9].

The H occupation of the interstices leads to a considerable lattice expansion. From $x = 0$ to $x = 5$ the cell volume increases by about 20%. The lattice expansion is, however, not a monotonous function of the hydrogen concentration. Aubertin et al. [6] report the existence of at least two distinct hydrid phases with the same cubic Ti_2Ni structure, but different lattice parameters. Hydrogenation also affects the magnetic properties [1,3,4]. While Hf_2Fe is a Pauli paramagnet, magnetic order is observed in Hf_2FeH_x at high hydrogen concentrations and low temperatures.

In recent years, the PAC technique is increasingly used for the investigation of metal–hydrogen systems (for a review see Ref. [10]). In particular, the hydrogen diffusion

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has been successfully studied in a number of pure metals [11] and intermetallic compounds [12,13]. Similar to NMR, PAC spectroscopy allows the observation of the nuclear spin relaxation caused by time-dependent hyperfine interactions from which information on the diffusion such as e.g. the activation energy may be derived. In most PAC experiments of this kind, the relevant interaction is the dynamic electric quadrupole interaction (QI) between the nuclear quadrupole moment of the PAC nucleus and the fluctuating electric-field gradient (EFG) produced by the moving H charge.

As ^{181}Hf is the mother isotope of ^{181}Ta, one of the best suited PAC probes, PAC spectroscopy appears as an ideal tool for the investigation of the hydrogen diffusion in Hf_2FeH_x on which no information is available up to now. We have started such an investigation with the intention to determine the activation energy for different hydrogen concentrations and eventually correlate the concentration dependence of the site occupation and of the activation energy.

In the course of this study we have found that for hydrogen concentrations $x>1.5$ Hf_2FeH_x decomposes into δ-HfH_x with $x\approx1.6$ and $HfFe_2$ already at moderate temperatures of $T\approx650$ K. This thermal instability was studied in some detail at different hydrogen concentrations by the PAC technique. X-ray diffraction and Moessbauer spectroscopy were used to identify the decomposition products. These experiments will be described in the following sections. First, the basic results of PAC theory relevant to this investigation shall be briefly reviewed.

2. Some elements of the theory of perturbed angular correlations for the case of substoichiometric hydrides

The angular correlation of the two successive γ rays of a γγ 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 [14]).

In this paper we are dealing with perturbations by electric quadrupole interactions (QI) between the electric quadrupole moment Q of the intermediate state of the cascade and electric-field gradients (EFG) acting on the PAC nucleus. In substoichiometric hydrides such as Hf_2FeH_x where only a part of the available interstices is occupied we expect both static and time-dependent QI's. The EFG at the probe site is produced by the H charges and the non-cubic metal sublattice.

At low temperatures the H atoms are 'frozen' on the interstitial sites. Because of the statistical site occupation, 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 $G_{kk}(t)$ is given by:

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

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} are functions of the asymmetry parameter only. The number N of terms in Eq. (1) depends on the spin I of the intermediate state of the cascade. For the case of ^{181}Ta with $I=5/2$ one has $N=3$. The exponential factor accounts for the effect of a Gaussian frequency distribution with 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:

$$G_{kk}(t)=\sum\nolimits_i f_i\,G_{kk}(t;\,\nu_{qi},\eta_i,\delta_i) \tag{2}$$

f_i (with $\Sigma_I\ f_i=1$) is the relative intensity of the ith fraction with the QI parameters [ν_{qi}, η_i, δ_i].

When hydrogen diffusion sets in at higher temperatures, the moving H charges produce fluctuations of the QI. The resulting nuclear spin relaxation becomes observable as an attenuation of the angular correlation when the jump rate w has increased to the point that the residence time between jumps τ_R is of the same order as the PAC time window (about $10\tau_N$, with τ_N = the lifetime of the intermediate state of the cascade). With increasing jump rate w the spin relaxation rate and the resulting attenuation of the angular correlation first increase towards a maximum at $w\approx\nu_q^0$, where $\nu_q{}^0$ is the center frequency of the static QI distribution, and then decrease, analogous to the motional narrowing of a NMR signal [13].

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 [15,16]. For the analysis of the complex situation in a substoichiometric hydride where the hydrogen motion leads to fluctuations of orientation, strength and symmetry of the interaction, this general theory is impracticable and one has to resort to an approximation with a single relaxation parameter λ_k:

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

The validity range of this approximation is discussed in ref. [17]. For slow fluctuations ($w\ll\nu_q^0$) the function $\Gamma_{kk}(t)$ is given by the perturbation factor for a static QI distribution (Eq. (1)) and the relaxation parameter λ_k is proportional to the jump rate w. Fast fluctuations are adequately described by Eq. (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 (Eq. (1) with $\delta = 0$). The relaxation parameter in the fast fluctuation region depends on the strength of the fluctuating QI, described by ν_q^f, and decreases with increasing jump rate w: $\lambda_k \propto (\nu_q^f)^2/w$.

3. Experimental details

The PAC measurements were carried out with the 133–482 keV cascade of ^{181}Ta populated by the β-decay of the 42d isotope ^{181}Hf which can be produced by thermal neutron irradiation of natural Hf [^{180}Hf(n,γ)^{181}Hf]. The intermetallic compound Hf_2Fe was synthesized by melting the metallic constituents with an arc furnace in an argon atmosphere or with an electron gun in high vacuum. Both procedures lead to the X-ray diffraction pattern of Hf_2Fe without contaminations of other phases. For the PAC measurements radioactive Hf metal was used for the Hf_2Fe synthesis.

Radioactive and inactive Hf_2FeH_x were produced following the procedure used by Vulliet et al. [3]: First the intermetallic compounds were outgased at 1300 K for 1–2 h in a quartz tube connected to a vacuum of 10^{-7} mbar. A known quantity of hydrogen gas with a purity of 99.99999 at. % was then admitted at 1300 K into the calibrated volume. After 10–30 min, the furnace was switched off and the samples were allowed to cool to room temperature which typically took about 1 h. The absorbed quantity of hydrogen was determined from the pressure decrease in the calibrated volume. By variation of the initial hydrogen pressure between 100 and 900 mbar hydrides Hf_2FeH_x with H concentrations $0.8 \leq x \leq 4.8$ were obtained. The structure of the inactive hydrides was studied by X-ray diffraction (see below). For the PAC measurements at $T > 290$ K the radioactive hydrides were sealed under vacuum into small quartz tubes. For PAC measurements at $T < 290$ K the hydrides were transferred to a closed-cycle He refrigerator. The PAC measurements were performed with a standard four-detector setup equipped with fast BaF_2 scintillators. The Moessbauer measurements were carried out with a ^{57}Co:Rh source at room temperature.

4. Measurement and results

4.1. PAC and X-ray diffraction measurements

Fig. 1 shows in the top-most section the PAC spectrum of ^{181}Ta:Hf_2Fe at 290 K which is in fair agreement with the spectra previously reported in the literature [18,19]. Because the lattice structure Hf_2Fe contains two nonequivalent Hf sites (positions *48f* and *16c*, respectively) the description of the spectrum requires two fractions with different QI's. The fast, non-periodic oscillations reflect the exceptionally strong, axially asymmetric QI on site *48f*. The values of ν_q, η, δ derived by a least-squares fit analysis on the basis of Eqs. (1,2) are: site *48f*: $\nu_q =$ 1361(6) MHz, $\eta = 0.463(3)$, $\delta = 0.035(5)$, site *16c*: $\nu_q =$ 130(10) MHz, $\eta = 0$, $\delta = 0.05(1)$

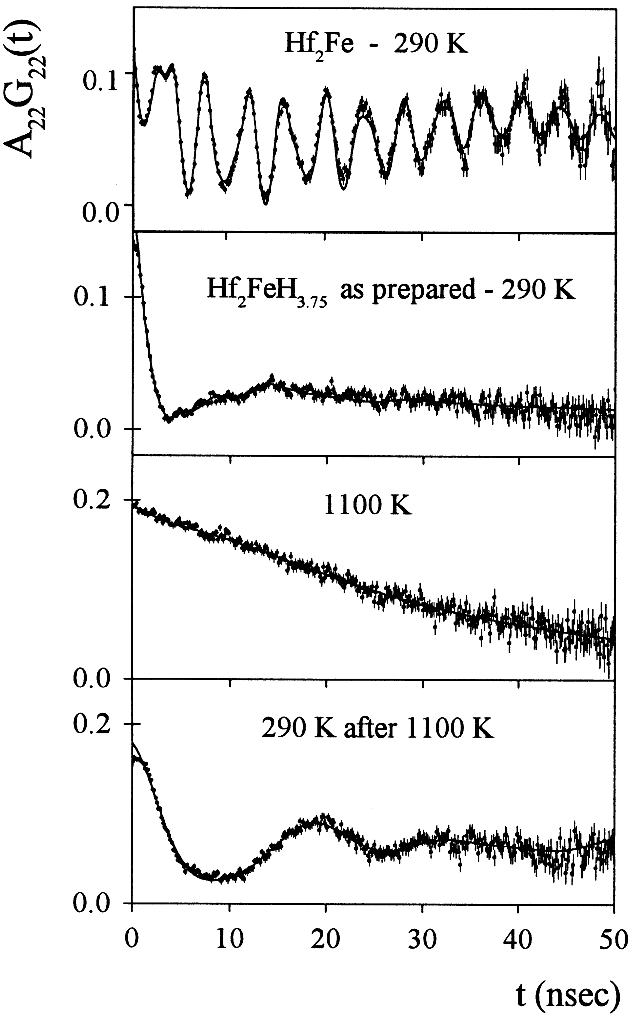

Fig. 1. PAC spectra of 181Ta in Hf_2Fe at 290 K (top most section) and in the hydride $Hf_2FeH_{3.75}$ at 290 K, 1100 K and 290 K after 1100 K.

The frequency of the minority site *16c* corresponds to a precession period of the order of the time range investigated (50 ns). Consequently, only the initial decrease of the anisotropy is measured with high precision. In the data analysis this leads to strong correlations between the fraction of this site and the relative width of the frequency distribution and also introduces a considerable uncertainty with respect to the asymmetry parameter. The values given above for the minority site were obtained with the ratio of the relative intensities of the two fractions fixed to that of the crystallographic sites, and the asymmetry parameter fixed to $\eta = 0$. The main difference to the values reported by Koicki et al [19] for site *48f* ($\nu_q = 1350(6)$ MHz, $\eta = 0.475(1)$, $\delta = 0.011(1)$ at 295 K) is the broader frequency distribution of our spectra which reflects the fact that the sample of Koicki et al. was annealed for 5 d at 900°C, while our sample was not annealed.

Hydrogenation of Hf_2Fe to H concentrations $x > 1.5$ completely alters the form of the PAC spectrum. As illustrated by the spectra of $Hf_2FeH_{3.75}$ in Fig. 1, the well-defined oscillations of the uncharged compound are wiped out and the room temperature spectra now show the typical features of a broad frequency distribution: From the time-zero point the anisotropy passes through a minimum towards a more or less constant value (‘hard core’) at large delay times. At 1100 K only a weak attenuation is observed which suggests a time dependent interaction and when returning to room temperature (RT) there are indications of weak oscillations.

As discussed in section V, the form of the 1100 K spectrum in Fig. 1 is incompatible with the Ti_2Ni structure of the Hf_2FeH_x hydrides suggesting that – although synthesized at 1300 K – Hf_2FeH_x might be thermally unstable at lower temperatures on the time scale of a typical PAC measurement of the order of 10 h and that at 1100 K we actually measured the PAC spectrum of some other Hf compound.

This hypothesis of a decomposition of Hf_2FeH_x could be confirmed by comparing the RT X-ray diffraction patterns of the same hydride in the as-prepared state and after a prolonged heat treatment in a small evacuated quartz tube at 1000 K. Fig. 2 shows as an example the X-ray spectra of $Hf_2FeH_{4.28}$ as prepared and after 24 h at 1000 K, respectively. In the as-prepared state, all observed reflection lines are consistent with the Ti_2Ni structure. After the heat treatment, however, the diffraction pattern is completely changed and all major reflections can now be attributed to the cubic δ-phase of the Hf hydrogen phase diagram with a H concentration $x \approx 1.6$. So, prolonged heating at 1000 K causes the decomposition $Hf_2FeH_{4.28} \rightarrow \delta\text{-}HfH_{1.6} + \ldots..$ The weak lines at $\vartheta = 21°$, 26° and 46° which do not belong to the $\delta\text{-}HfH_{1.6}$ pattern coincide with some of the lines of $HfFe_2$, the other intermetallic compound of the Hf-Fe phase diagram, suggesting $HfFe_2$ as another decomposition product.

For $Hf_2FeH_{3.75}$ we have determined the decomposition rate at 1100 K by rapidly heating the sample from 290 K to 1100 K and then recording PAC spectra for consecutive fixed time intervals. The changes of the PAC spectra with time allowed to determine the growth of the $\delta\text{-}HfH_{1.6}$ fraction at the expense of $Hf_2FeH_{3.75}$ (see Fig. 3) which we found to follow the relation $(1-\exp(t/\tau))$ with a growth time constant of $\tau = 1.0(2)$ h.

The decomposition product $\delta\text{-}HfH_x$ presents clear evidence for dynamic perturbations. Fig. 4 shows the PAC spectra of $Hf_2FeH_{2.5}$ heated for 10 h to 1000 K and then

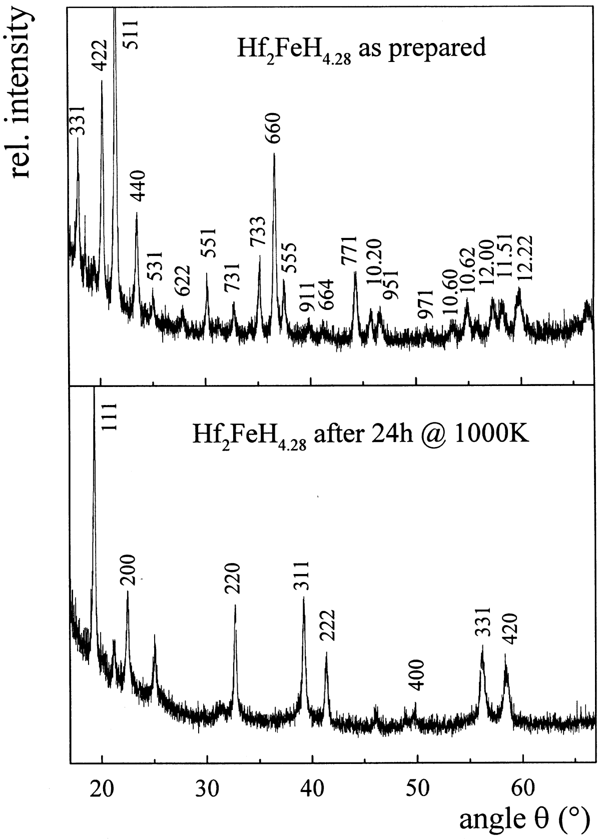

Fig. 2. X-ray diffraction pattern of $Hf_2FeH_{4.28}$ after preparation (upper section) and after annealing at 1000 K for 24 h in an evacuated quartz tube. The Miller indices in the upper section are those of the Ti_2Ni structure, the indices given in the lower section are those of $\delta\text{-}HfH_{1.6}$.

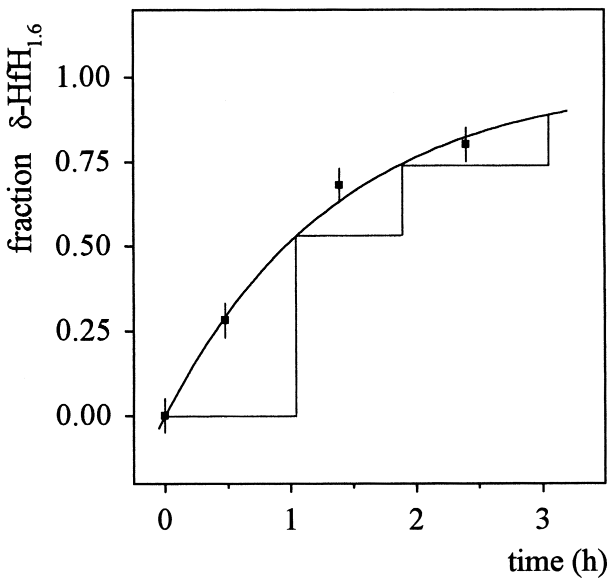

Fig. 3. The growth of $\delta\text{-}HfH_{1.6}$ at the expense of $Hf_2FeH_{3.75}$ at 1100 K as a function of time, determined by recording PAC spectra for consecutive fixed time intervals. The lengths of these intervals are given by the horizontal lines.

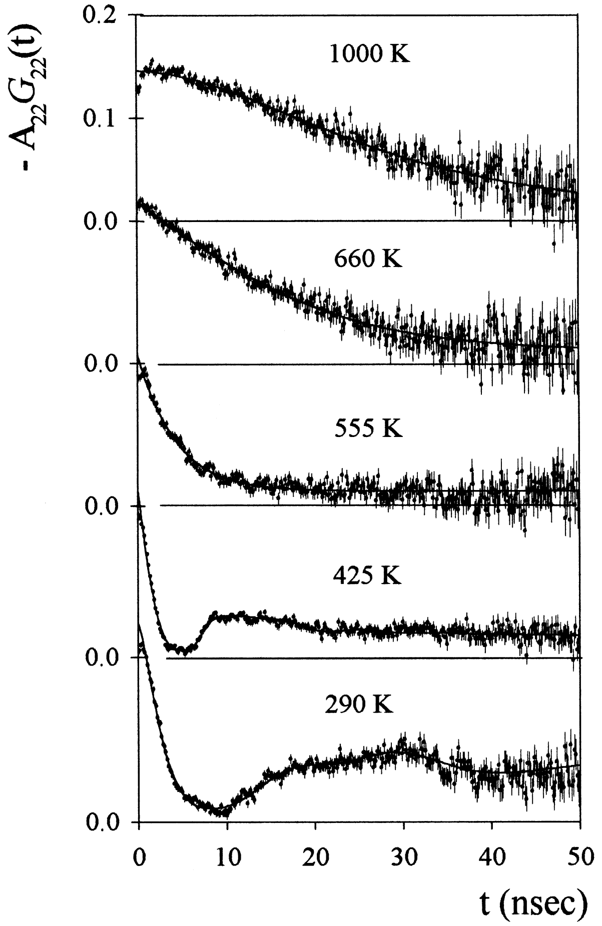

Fig. 4. ^{181}Ta: PAC spectra of δHfH$_{1.6}$ produced by decomposition of Hf$_2$FeH$_{2.5}$ at 1000 K.

slowly cooled to RT. At high temperatures the anisotropy decreases only very slowly with time which constitutes evidence for the complete decomposition of the initial hydride (see Section 5). As temperature is decreased, the attenuation of the angular correlation becomes stronger and at $T = 555$ K the anisotropy is completely destroyed within a few nanoseconds. The fact that the anisotropy drops below the 'hard core' of $G_{22}(\infty) = 0.2$ constitutes clear evidence for the dynamical character of the perturbation [14]. At still lower temperatures, the anisotropy starts to recover and at 290 K the spectrum has the typical form for a perturbation by a relatively broad distribution of static QI's. By adjusting the approximation (Eq. (3)) of the perturbation factor for dynamic interactions, the relaxation parameter λ was determined for the different temperatures. The results are collected in Fig. 5 in the form of an Arrhenius plot.

This decomposition of Hf$_2$FeH$_x$ was studied in more detail by X-ray diffraction and PAC spectroscopy for different hydrogen concentrations. X-ray spectra of the same hydride annealed for prolonged periods at different temperatures were measured at room temperature. After synthesis, the X-ray pattern of most of the inactive hydrides showed only reflections corresponding to the Ti$_2$Ni structure. Occasionally, however, we also observed slight contaminations (<20%) by δ-HfH$_x$. The effect of the heat treatment was found to be different for low ($x \leq 1.5$) and high concentration hydrides ($x > 1.5$). Systematically, for high concentrations the diffraction peaks started to broaden after annealing at 600 K, after 800 K frequently only few broad peaks remained and after 1000 K the diffraction pattern of δ-HfH$_{1.6}$ emerged. For H concentrations $x < 1.5$ occasionally a small fraction of δ-HfH$_x$ developed after prolonged heating at 1000 K, but in most cases the Ti$_2$Ni structure was found to survive annealing up to at least $T = 1000$ K. From the X-ray diffraction of the unannealed samples we determined the Hf$_2$FeH$_x$ lattice parameter a as a function of the hydrogen concentration x. The results were in excellent agreement with those of Aubertin et al. [6], also with respect to the observation of a phase separation at intermediate concentrations $x \approx 2$–3.

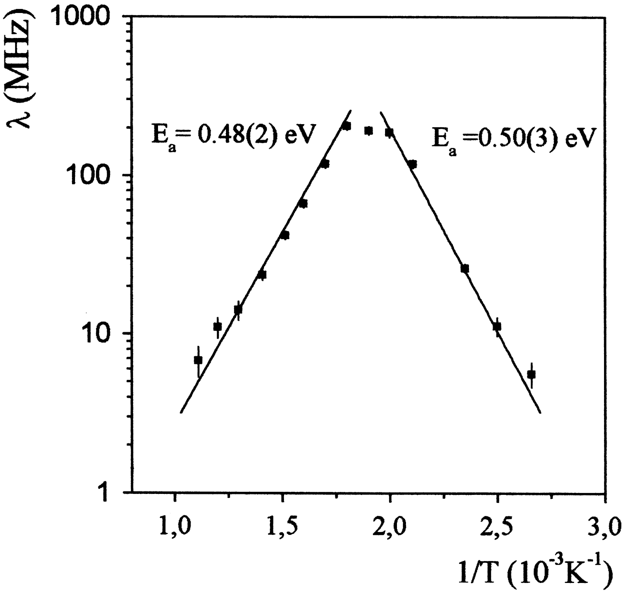

Fig. 5. Arrhenius plot of the relaxation parameter λ of δ-HfH$_{1.6}$, derived by a least-squares fit of Eq. (3) to the spectra shown in Fig. 4.

^{181}Ta PAC measurements of the same hydride were carried out at increasing temperatures and a RT spectrum was taken after each temperature increase of 100 K. Fig. 6 illustrates such a series of measurements for the hydride Hf$_2$FeH$_{4.1}$. Clear changes of both the RT spectra and those measured at temperatures T occur around $T \approx 650$ K. In the RT spectra the minimum of the perturbation function shifts from ≈ 3 ns before annealing at 650 K to ≈ 6–7 ns, reflecting a strong drop of the center frequency of the frequency distribution. The spectra at T remain unchanged up to 650 K and then start to evolve towards the slowly decaying anisotropy typical for δ-HfH$_x$ at high temperatures. The spectra for $T \leq 600$ K could be well reproduced

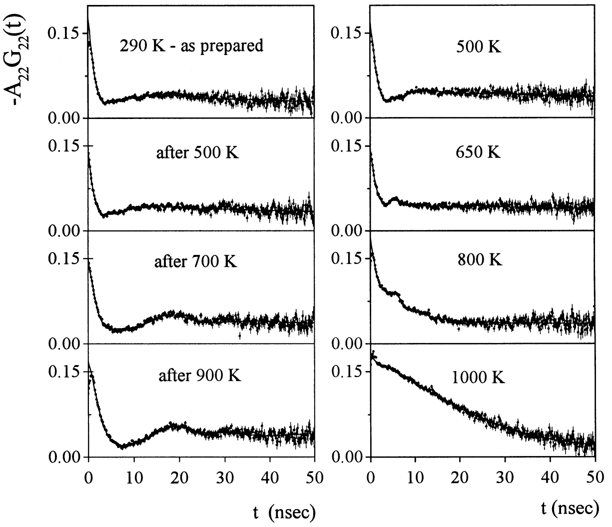

Fig. 6. PAC spectra of ^{181}Ta in $Hf_2FeH_{4.1}$. The right-hand column shows spectra measured at the indicated temperatures, the left-hand column shows the spectra recorded at RT after the measurement at the indicated temperature.

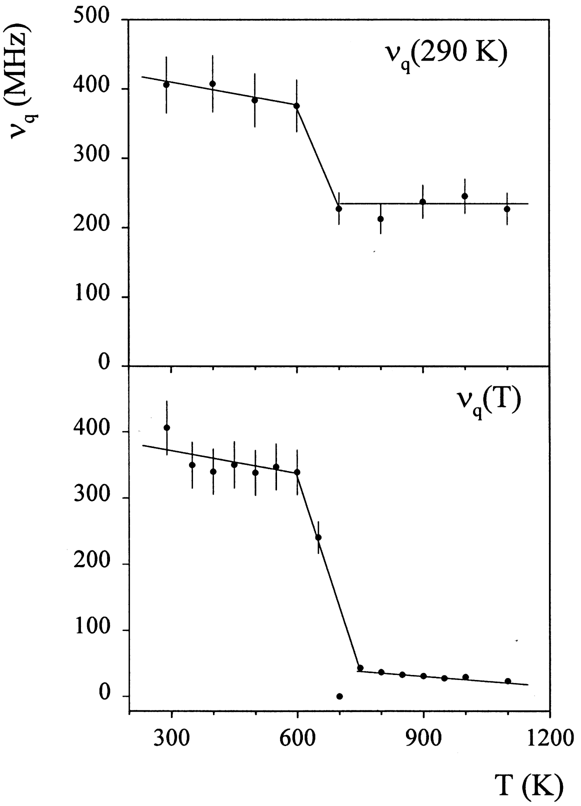

Fig. 7. The center frequency of the QI distribution, determined by a least-squares fit of Eqs. (1,3) to the spectra shown in Fig. 6. The upper section shows the center frequency at 290 K after a 10-h PAC measurement at temperature *T*, the lower section the center frequency at temperature *T*.

by a static frequency distribution (Eq. (1)). Fits with the dynamic perturbation function of (Eq. (3) gave an upper limit for the relaxation parameter of $\lambda < 10$ MHz.. For $T > 600$ K the spectra were best described by the dynamic perturbation function Eq. (3) with $\Gamma_{22}(t)$ having the form of Eq. (1).

The main result of this analysis is given by Fig. 7. The lower section shows the center frequency $\nu_q(T)$ of the frequency distribution as a function of temperature, the upper section the value of ν_q(290 K) observed at RT after the measurement at temperature *T*. Between 600 K and 700 K ν_q(290 K) changes abruptly by almost a factor of two. In the same temperature interval the center frequency $\nu_q(T)$ drops from about 350 MHz to almost zero. As discussed in Section 5, the simultaneous abrupt decrease of both ν_q(290 K) and $\nu_q(T)$ is clear evidence for the decomposition of $Hf_2FeH_{4.1}$ at $T \approx 650$ K.

By measuring ν_q(290 K) and $\nu_q(T)$ in several hydrides, we have studied the decomposition as a function of the hydrogen concentration *x*. These PAC results confirm the X-ray diffraction measurements: For all concentrations $x > 1.5$, the decomposition occurs at $T \approx 650$ K. For concentrations $x < 1$ the PAC spectra still showed some oscillations similar to those of the Hf_2Fe, in agreement with the previous observation of Vulliet et al. [3] and were found to be fully reversible between 290 K and 1000 K, indicating thermal stability up to at least 1000 K. Surprisingly, however, these spectra showed – if at all – only very weak indications for dynamic interactions on sites *48f* or *16c*. The upper limit of the relaxation parameter compatible with the spectra is $\lambda \leq 15$ MHz. A full understanding of the PAC spectra of the low concentration hydrides requires further studies. In view of the limited stability of the hydrides, PAC measurements aiming at information on the hydrogen motion must be accompanied by X-ray measurements of the radioactive PAC samples.

The hydrides Hf_2FeH_x have been reported to show magnetic order at high concentrations and low temperatures. PAC measurements in Hf_2FeH_x ($x = 0.87$, 3.75 and 4.1, unannealed) between 290 K and 9 K, however, gave no evidence for a magnetic hyperfine field at the Hf/Ta sites.

4.2. Moessbauer measurements

The X-ray diffraction pattern of $Hf_2FeH_{4.28}$ kept at 1000 K for 24 h (Fig. 2) suggests $HfFe_2$ as another decomposition product. $HfFe_2$ is easily identified by Moessbauer spectroscopy, because $HfFe_2$ is magnetically ordered at RT with magnetic hyperfine fields at the Fe sites of the order of 18 T, which give rise to well resolved Moessbauer sextets [20]. For further evidence that $HfFe_2$ is formed in the decomposition of Hf_2FeH_x we therefore measured the RT Moessbauer spectra of $HfFe_2$, of $Hf_2FeH_{4.3}$ as prepared and after heating for 24 h to 1000 K in an evacuated quartz tube, and of $HfFe_2$ produced by arc melting of the

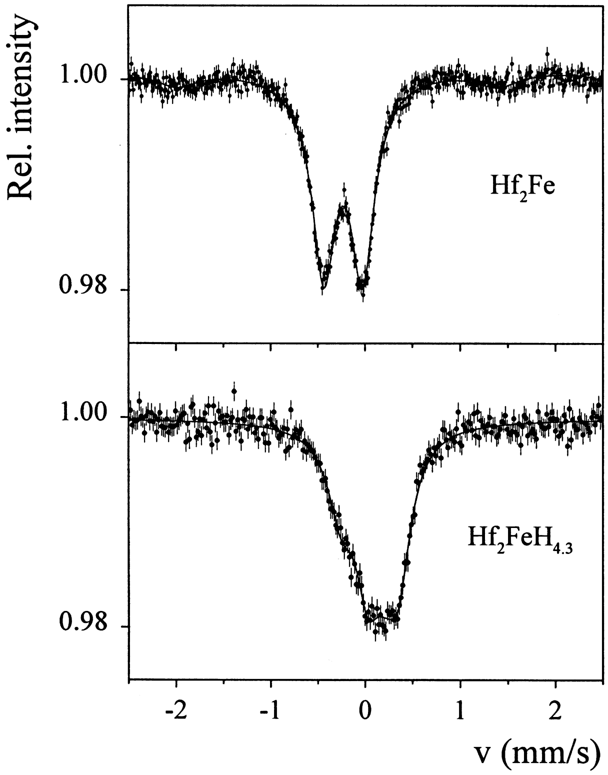

Fig. 8. Room temperature Moessbauer spectra of Hf_2Fe and $Hf_2FeH_{4.3}$ as prepared.

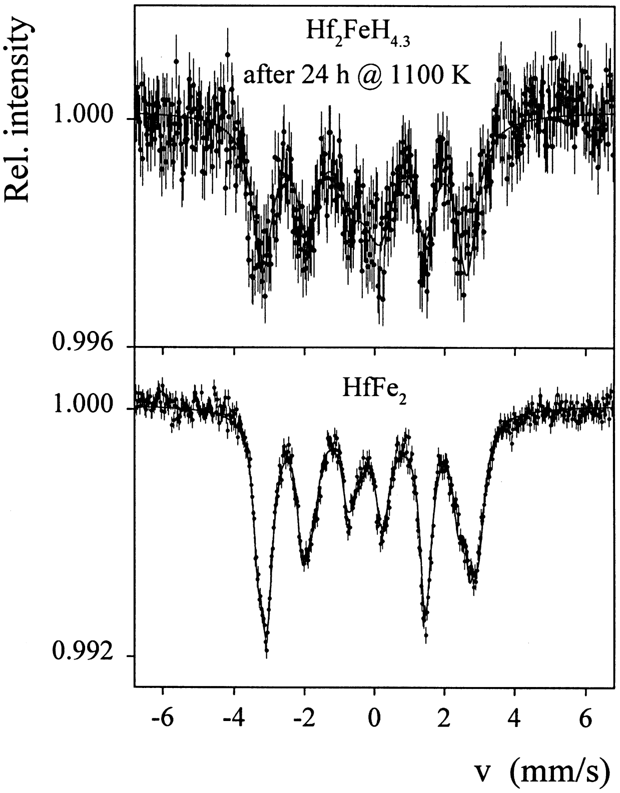

Fig. 9. Room temperature Moessbauer spectra of $Hf_2FeH_{4.3}$ heated for 24 h to 1000 K and of $HfFe_2$.

metallic constituents. These spectra are shown in Figs. 8 and 9.

In the as-prepared state, the spectrum of $Hf_2FeH_{4.3}$ agrees well with the results of previous measurements [3,6,7] of high concentration hydrides Hf_2FeH_x (for a discussion of the differences between Hf_2Fe and Hf_2FeH_x see e.g. Ref. [6]). After 24 h at 1000 K, however, the RT spectrum $Hf_2FeH_{4.3}$ consists of a sextet from which we can conclude that a magnetically ordered compound has formed during the prolonged heat treatment. The pronounced similarity of this sextet with that of $HfFe_2$ produced by melting Hf and Fe (see Fig. 9) identifies $HfFe_2$ as a second decomposition product. The description of molten intermetallic $HfFe_2$ requires two fraction of Fe nuclei subject to slightly different combined magnetic and electric hyperfine interactions, in agreement with previous results [20]. The same parameters reproduce the spectrum of the decomposition product $HfFe_2$. In this case, however, the line widths are about 50 % larger than in molten $HfFe_2$, suggesting a considerable degree of disorder in the decomposition product.

Measurements of $Hf_2FeH_{3.9}$ at RT and at 50 K gave identical spectra, indicating a magnetic order temperature smaller than the value of 73 K reported for Hf_2FeH_3 (Ref. [1]).

5. Discussion and conclusions

In summary, we have used PAC spectroscopy to investigate the hydrides of the intermetallic compound Hf_2Fe. Aiming at information on the hydrogen diffusion, measurements of the electric quadrupole interaction of ^{181}Ta on Hf sites of Hf_2FeH_x have been carried out in the concentration range $0.8 \leq x \leq 4.8$ and temperatures between 9 K and 1100 K.

The PAC spectra observed at high temperatures were found to be incompatible with the Ti_2Ni structure of the Hf_2FeH_x hydrides and gave the first indication of the thermal instability of these compounds: At 1000 K many H jumps can be expected to occur within the PAC time window and the PAC spectrum is determined by the time average of the QI. The slow decrease of the anisotropy at high temperatures (see the 1100 K spectrum in Fig. 1) implies that the time average of the QI is almost zero (corresponding to $\Gamma_{22}(t) \approx 1$ in Eq. (3)) or that the time-averaged charge distribution surrounding the PAC probes has almost cubic symmetry. This, however, is practically impossible to reconcile with the crystal structure of Hf_2FeH_x. The metal sublattice produces a very strong QI on the majority site *48f* (see Section 4.1), and to obtain an almost vanishing time average at high temperatures, the H motion would have to cancel the contribution of the metal sublattice. With point-charge calculations of the EFG we found that this requirement is impossible to satisfy, whatever one assumes for the H charge and the diffusion paths.

X-ray diffraction measurements after prolonged heating at 1000 K confirmed the decomposition of Hf_2FeH_x. The cubic Hf hydride δ-HfH_x with $x \approx 1.6$ and the intermetallic compound $HfFe_2$ were identified as decomposition products by X-ray diffraction and ^{57}Fe Moessbauer spectroscopy. The decomposition leads predominantly to δ-$HfH_{1.6}$ which explains the form of the high temperature PAC spectra: In δ-$HfH_{1.6}$, the metal sublattice crystallizes in the fcc CaF_2 structure and the only contribution to the EFG comes from the H charges, which are on the tetrahedral interstices of the CaF_2 lattice. The static or slowly fluctuating H distribution produces a finite QI at RT. For fast H motion – relative to the ^{181}Ta PAC time window, as it occurs in Hf hydrides for $T > 500$ K [20] –, however, all interstitial sites are equally populated on the time-average, the charge distribution surrounding the PAC probes has therefore cubic symmetry and consequently the EFG at the Hf sites vanishes. The weak remaining interaction can be attributed to structural and chemical defects.

The high temperature PAC spectra showed no contribution from magnetically ordered $HfFe_2$. From the X-ray pattern after decomposition (Fig. 2) one estimates a $HfFe_2$ fraction of ≤ 10 %. To satisfy the mass balance, some further Fe compound is required. Other decomposition products could, however, not be identified by the techniques employed in this study. Possibly, Fe is in an amorphous form and therefore difficult to detect by X-ray diffraction and Moessbauer spectroscopy.

The activation energy for hydrogen jumps in the decomposition product δ-$HfH_{1.6}$ was determined by PAC measurements of $Hf_2FeH_{2.5,}$ starting at 1000 K. Fig. 5 shows the observed relaxation parameter λ, plotted on a logarithmic scale vs. $1/T$. In the slow fluctuation region one has $\lambda \propto w$ (w = jump rate), for fast fluctuations $\lambda \propto 1/w$ (see Section 2). So, for over-barrier diffusion with $w = w_0 \exp(-E_a/kT)$, where E_a is the activation energy for the hydrogen jumps, one expects $\ln \lambda \propto \pm E_a/kT$, with the positive and negative sign applying to the region of fast and slow fluctuations, respectively. This expectation is fully born out by the data in Fig. 5, both at low and high temperatures $\ln \lambda$ is a linear function of the inverse temperature. For both regions one obtains within the errors the same value of the activation energy $E_a = 0.50(3)$ eV. This value is in excellent agreement with the activation energy of Hf hydrides synthesized by H charging of Hf metal [21].

The decomposition of Hf_2FeH_x was studied for different H concentrations x by PAC and X-ray diffraction measurements. In PAC measurements as a function of temperature the decomposition was observed by abrupt changes of the center frequency ν_q of the frequency distribution for both $\nu_q(T)$ and ν_q (290 K) after heating to temperatures T (see Fig. 7). The irreversible decrease of ν_q(290 K) is a consequence of the different lattice structures of Hf_2FeH_x and δ-$HfH_{1.6}$ which produce different static charge distributions at the site of the PAC probes. The abrupt decrease of $\nu_q(T)$ from ≈ 350 MHz to almost zero at $T \approx 650$ K reflects the formation of δ-$HfH_{1.6}$ because only in a compound with cubic symmetry of the metal lattice rapid hydrogen motion at high temperatures can lead to a vanishing time average of the QI (see above).

The tendency towards decomposition increases with increasing H concentration. All hydrides with $x > 1.5$ were found to be thermally unstable and – on the time scale of a typical PAC experiment of the order 10 h – decompose at $T \approx 650$ K. The time constant of the decomposition of $Hf_2FeH_{3.75}$ at 1100 K was determined by PAC spectroscopy to be $\tau = 1.0(2)$ h. The PAC spectra of hydrides with $x \leq 1$ were fully reversible between 290 K and 1100 K.

In most Hf hydrides [21] and those of intermetallic compounds [22] the ^{181}Ta relaxation parameter reaches its maximum value of $\lambda \approx 50$–300 MHz at temperatures $T \leq$ 550 K. In a preliminary PAC study of Hf_2CoH_3, which has the same lattice structure as $Hf_2FeH_{x,}$ Baudry et al. [12] report ^{181}Ta relaxation rates of about $\lambda \approx 80$ MHz at 300 K. It is therefore surprising that practically no indications of dynamic perturbations were found in the PAC spectra of the high concentration hydrides Hf_2FeH_x before decomposition at $T \approx 650$ K ($\lambda < 10$ MHz). Possibly, the exceptionally strong static QI of the Hf_2Fe metal sublattice makes the detection of the fluctuating components of the QI difficult. For a better understanding of this difference between Hf_2FeH_x and Hf_2CoH_x, a detailed PAC study of Hf_2CoH_x is under way.

Hf_2FeH_x has been reported to show magnetic order at large hydrogen concentrations and low temperatures. PAC measurements for large x values and temperatures between 290 K and 9 K, however, gave no evidence for a magnetic hyperfine field at the Hf sites. Moessbauer measurements suggest that for $x \approx 4$ the magnetic order temperature is less than 50 K.

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