Recoil Induced Room Temperature Stable Frenkel Pairs in α-Hafnium Upon Thermal Neutron Capture

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Ultrapure hafnium metal (110 ppm zirconium) was neutron activated with a thermal neutron flux of $6.6 \cdot 10^{12}$ cm^{-2}s^{-1} in order to obtain ^{181}Hf for subsequent time differential perturbed angular correlation (TDPAC) experiments using the nuclear probe ^{181}Hf(β^-) ^{181}Ta. Apart from the expected nuclear quadrupole interaction (NQI) signal for a hexagonal close-packed (hcp) metal, three further discrete NQIs were observed with a few percent fraction each. The TDPAC spectra were recorded for up to 11 half lives with extreme statistical accuracy. The fitted parameters vary slightly within the temperature range between 248 K and 373 K. The signals corresponding to the three additional sites completely disappear after ‘annealing’ at 453 K for one minute. Based on the symmetry of the additional NQIs and their temperature dependencies, they are tentatively attributed to Frenkel pairs produced by recoil due to the emission of a prompt 5.694 MeV γ-ray following thermal neutron capture and reported by the nuclear probe in three different positions. These Frenkel pairs are stable up to at least 373 K.

Key words: α-Hf; Frenkel Pairs; Nuclear Quadrupole Interaction.
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1. Introduction

Radiation damage in metals has been studied in the past by various methods, e. g. high energy electrons, heavy ions, or neutrons [1]. For the latter, applications in fusion reactors and nuclear power reactors were one of the driving forces. In this respect it is somewhat surprising that radiation damage in materials like zirconium or hafnium which play an important role in nuclear power reactors as cladding material for fuel elements and as control rods [2] did not receive the same attention as, e. g. copper. Interestingly enough, ultrahigh purity hafnium became available when hafnium-free zirconium was required for cladding.

Electron radiation damage in metals is usually carried out at temperatures as low as 4.2 K followed by the measurement of resistivity recovery upon isochronal annealing [3]. The recovery curves exhibit several stages labelled I–V with further subdivisions, e. g. I_A to I_E. The damage consists of Frenkel pairs and at higher damage concentrations more complicated structures such as clusters are formed. Stages I–III have been suggested to be associated with interstitial mobility [3]. At the end of stage I, at a temperature I_D, first correlated recombination, i. e. recombination of an interstitial with its own vacancy, occurs followed by uncorrelated recombination, i. e. recombination of an interstitial with another vacancy, at a temperature I_E. Typical values for I_D for face centered cubic (fcc) metals are in the range of a few tens of Kelvin [3]. The hexagonal close-packed (hcp) metals, and in particular the group IVb metals, have received little attention. I_D goes up to 102 K for zirconium and 120 K for titanium [3]. Unfortunately, to our knowledge there are no data for I_D for hafnium but values well below room temperature are expected. This is in sharp contrast to an interesting computer simulation carried out on hcp magnesium by Monti and Savino [4] which shows that vacancies at the third and fourth neighbour sites around an interstitial are repelled from it. There are positive interaction energies up to 79 meV. In other words, this study proposes room temperature stable Frenkel pairs. Whether this also holds true for other hcp metals like hafnium is an open question.

The inherent problem with particle induced damage studied by resistivity recovery is related to the fact that defect concentrations have to be high enough to produce measurable effects. This inevitably leads to complex damage scenarios. A very elegant way to produce single Frenkel pairs at extremely low concentrations and yet to be able to detect them was the use of neutrino recoil in the decay of ^{111}In to an excited state of ^{111}Cd via electron capture with the detection via the measurement of the nuclear quadrupole interaction (NQI) by time differential perturbed angular correlation (TDPAC) [5, 6]. Yet, there is another way of producing isolated Frenkel pairs which is only briefly mentioned in [1], namely the displacement damage resulting from the recoil which occurs when a nucleus absorbs a thermal neutron followed by the emission of a prompt high energy γ, i. e. a (n_{th},γ)-process. To our knowledge this production of defects has never been exploited before.

Here, we report on the production of room temperature stable isolated Frenkel pairs by the (n_{th},γ)-process in α-hafnium with the detection of the NQI via TDPAC. Hafnium is particularly well suited for this study because upon thermal neutron capture of ^{180}Hf there is, apart from a prompt shower of γ-rays with various energies but relatively low intensities, a very intense γ-transition from the 5.694 MeV excited level to the ground state of ^{181}Hf [7, p. 395] which leads to a recoil energy of about 90 eV. This is likely to be more than required for Frenkel pair production irrespective of anisotropy [8], although no data for hafnium seem to be available. Furthermore, the nuclear probe ^{181}Hf$(\beta^-)\,^{181}$Ta is ideally suited for TDPAC studies. The recoil due to the β-decay to ^{181}Ta and the γ-transitions in ^{181}Ta is much too low to produce Frenkel pairs. Thus the TDPAC measurement merely acts as a reporter of the previously produced defect. Finally, room temperature – and above – stable Frenkel pairs in hafnium metal might have implications for its use as control rods in nuclear power plants.

Since the neutron activation was carried out at temperatures around 330 K, any observed defect must be stable up to at least this temperature. An advantage of the defect production at such 'high' temperatures is that all defects anneal but the most stable ones. We report on three different defect NQIs and try to associate them to three different nuclear probe environments based on the asymmetry parameter for the NQI and their temperature dependencies measured in the temperature range between 248 K and 373 K. Such a wide temperature range is normally inaccessible for materials with a much lower annihilation temperature. Furthermore, we show that all three defect signals disappear upon 'annealing' at 453 K for one minute.

2. Experimental Details

Ultrapure hafnium metal containing only 110 wt/ppm zirconium was purchased from Teledyne Wah Chang [9]. Samples of $1\,\text{mm}\times 1\,\text{mm}\times 0.3\,\text{mm}$ were spark-cut and electro-polished, thereby carefully avoiding any mechanical forces which could lead to plastic deformations. The first sample was neutron activated with a thermal neutron flux of $6.6\cdot 10^{12}\,\text{cm}^{-2}\text{s}^{-1}$ for 20 minutes in the research reactor BER II at the Hahn–Meitner Institute, Berlin, in order to obtain ^{181}Hf for subsequent TDPAC experiments using the nuclear probe ^{181}Hf$(\beta^-)\,^{181}$Ta. The concentration of ^{181}Hf is estimated to be about 10^{-7}. We used an efficient 6-detector camera with conventional nuclear electronics with conically capped BaF_2 scintillators [10]. The time resolution of the spectrometer was about 700 ps full width at half maximum and is not critical because all observed frequencies are rather low. The activity was chosen low enough in order to record delayed coincidences up to 120 ns, i. e. 11 half lives of the $I = 5/2$ intermediate state in the $133-482$ keV γ–γ-cascade in ^{181}Ta. Conventionally, about 60 ns are observed only. Due to the texture of the samples, we cannot make a hard statement that we observe the full expected anisotropy A_{22}. However, the observed anisotropies are close to our value of -0.17 for our scintillators and our rather short source–detector distances as checked with a liquid sample of ^{181}Hf in concentrated hydrofluoric acid. Between 1 and 8 billion coincidences were recorded at each temperature point. The temperature was adjusted with a heated/cooled flow of silicone oil through a small glass tube containing the encapsulated sample. The thermocouple was directly underneath the sample ampoule. After the sample activity had decayed, the neutron activation and data taking was repeated with identical parameters.

In addition, a further sample was neutron activated to a 10-fold higher activity (approx. 200 min) and stored until the activity level was appropriate for the TDPAC measurement, i. e. 4 – 5 months. After completion of the TDPAC experiments and after the sample activity had decayed, the neutron activation and data taking was repeated, too. All four samples gave identical results and will therefore not be treated separately.

3. Results

In Figure 1a, the data taken at room temperature (298 K) are shown as time spectrum (left) and its cosine-transform (right) together with the fit results. The accuracy of the measurement and the quality of the fits are so high that the data points and the solid line of the fit are barely distinguishable at early times. It is immediately clear that there are deviations from a strictly periodic perturbation function, as would be expected for an axially symmetric electric field gradient (EFG) in an hcp metal. The theoretical functions consisted of three frequencies for each site, as expected for a nuclear spin $I = 5/2$, with the highest frequency being the sum of the lower two [11]:

$$G_{22}(t) = S_{20} + \sum_{n=1}^{3} S_{2n} \exp\left(-\frac{1}{2}\omega_n^2 \tau_R^2\right) \cdot \exp\left(-\delta\omega_n t\right) \cos \omega_n t \,. \qquad (1)$$

Here, the amplitudes S_{2n} depend on the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ with V_{zz} denoting the largest component in magnitude of the EFG tensor, and have fixed values for powder samples. The frequencies ω_n depend on $\omega_Q = eQV_{zz}/40\hbar$ and η [11]. Here, Q denotes the nuclear quadrupole moment of the $I = 5/2$ state in ^{181}Ta. τ_R denotes the experimental time resolution and δ the Lorentzian frequency distribution. In case of a Gaussian frequency distribution, the factor $\exp(-\delta\omega_n t)$ is replaced by $\exp(-\frac{1}{2}\delta^2\omega_n^2 t^2)$.

We actually required three additional sites apart from the main component, as will be illustrated below. We allowed for a finite damping (corresponds to line broadening of the peaks in the cosine-transformed data), either assuming a Lorentzian or a Gaussian distribution function, for the prominent fraction. There was very little difference between both assumptions concerning the χ^2-values because all lines were rather sharp. The residual very small line broadening is probably due to distant defects and will not be considered further. Since all samples exhibited some texture, we allowed for freely adjustable amplitudes for the three frequencies of the prominent contribution. The deviation from powder amplitudes, however, was small, partly because the 6-detector cube arrangement with 30 subgroups and corresponding averaging tends to reduce texture effects anyway.

For the minority sites, we used the powder amplitudes because the deviation from the powder values for the prominent site were already small and would be far below the statistical accuracy for the minority sites.

The data analysis for the most accurate spectrum taken at 298 K was performed in the following way. It is immediately clear from the cosine-transform that apart from the prominent fraction there have to be additional sites showing up as little shoulders in the flank of the peaks or intensity in between two prominent peaks. The latter one around a frequency of about 0.45 to $0.50 \cdot 10^3$ Mrad/s could in principle correspond to one broad peak. However, there is no corresponding broad harmonic and, hence, it is more likely associated with a site having an η close to unity. Therefore, the prominent site and the well-resolved large-η site were fitted first which resulted in a high χ^2. Nevertheless, these two fractions were subtracted from the data in order to reveal the additional sites. The remaining peaks could unambiguously be attributed to two further sites. Then a fit with all four sites was performed and a χ^2 of 2.51 was achieved, a value which is quite acceptable considering the extreme statistical accuracy of the data. Then the prominent fraction was again subtracted (see Fig.1b) and the subsequent decomposition into the three remaining fractions shows that this is a consistent way to analyze the data (see Figs. 1c–e). As can be seen from Figure 1c–e, there is very little damping, and we therefore kept the damping parameter δ fixed at 0 for the minority sites for the sake of consistency. In some cases we also had to fix η of site 4 to 0. It is small anyway and affects the eigenvalues of the quadrupole Hamiltonian quadratically only for small values of the asymmetry parameter. There is a very small dispersive-type distortion around $1.1 \cdot 10^3$ Mrad/s which is a result of small oscillations around 35 ns which are due to problems in electronics, likely related to a blocking signal of the constant fraction discriminator; it has no effect on the true physical signals and would have required months

Table 1. Fitted hyperfine parameters for NQI of ^{181}Ta in ultrapure hafnium metal after thermal neutron capture and 'annealed' at 453 K and subsequently quenched: Temperature T, site number, quadrupole frequency ω_Q, asymmetry parameter η, Lorentzian distribution δ, site fraction f for all observed sites, and χ^2.

T (K)	Site number	ω_Q (Mrad/s)	η	δ (%)	f (%)	χ^2
248	1	49.55(6)	0.076(7)	0.9(1)	91 (1)	0.958
	2	47.0(5)	0.89(2)	0	3.8(4)	
	3	82 (1)	0.50(5)	0	1.5(8)	
	4	57.2(5)	0.23(4)	0	3.4(5)	
260.5	1	49.35(2)	0.06(0)	0.48(7)	87 (1)	0.807
	2	46.7(5)	0.92(3)	0	3.0(3)	
	3	81.1(3)	0.54(1)	0	5.1(7)	
	4	58.2(2)	0	0	5.1(4)	
273	1	49.30(2)	0.057(5)	0.96(5)	89 (1)	1.04
	2	46.4(3)	0.90(1)	0	3.5(2)	
	3	79.1(4)	0.54(1)	0	3.3(6)	
	4	57.7(2)	0	0	4.3(3)	
285.5	1	49.02(3)	0.045(0)	0.74(8)	83 (2)	0.77
	2	45.8(4)	0.89(2)	0	3.8(4)	
	3	78.5(3)	0.549(7)	0	8(1)	
	4	56.7(3)	0	0	5.3(5)	
298	1	49.00(1)	0.048(2)	0.67(1)	86.6(3)	2.51
	2	45.77(8)	0.909(4)	0	3.7(1)	
	3	79.12(8)	0.520(3)	0	4.4(2)	
	4	56.28(5)	0.168(6)	0	5.3(1)	
310.5	1	48.86(2)	0.058(9)	0.37(9)	85 (2)	0.683
	2	47.2(4)	0.89(2)	0	5.3(5)	
	3	78.8(4)	0.45(2)	0	5(1)	
	4	56.4(3)	0.20(3)	0	5(1)	
323	1	48.71(2)	0.072(5)	0.59(6)	90 (1)	1.384
	2	45.2(5)	0.94(4)	0	3.1(3)	
	3	75.7(5)	0.67(2)	0	3.2(5)	
	4	56.9(4)	0.13(5)	0	4.1(5)	
335.5	1	48.50(2)	0.056(6)	0.53(6)	92 (1)	0.639
	2	44.9(7)	0.89(4)	0	2.3(3)	
	3	75.7(7)	0.64(3)	0	2.7(7)	
	4	57.3(5)	0	0	2.9(4)	
348	1	48.32(2)	0.03(1)	0.43(9)	90 (2)	0.711
	2	44.9(9)	0.89(5)	0	2.4(5)	
	3	73.6(5)	0.67(2)	0	4.7(8)	
	4	58.9(8)	0	0	2.5(5)	
360.5	1	48.19(3)	0	0.68(5)	91 (1)	1.01
	2	44 (1)	1	0	0.6(2)	
	3	76.2(3)	0.53(1)	0	5.7(9)	
	4	57.2(6)	0	0	2.3(4)	
373	1	48.10(3)	0.04(1)	0.2(1)	90 (2)	0.611
	2	47 (1)	0.80(5)	0	2.6(8)	
	3	74.5(7)	0.69(2)	0	4(1)	
	4	58 (1)	0	0	2.6(7)	
298[a]	1	49.02(2)	0.03(1)	0.50(4)	98.6(3)	0.733
	2	42.3(9)	0.76(4)	0	1.4(3)	

[a] Quenched after annealing.

to eliminate. In this respect, fully digital spectrometers are definitely superior [12].

The data taken in the temperature range from 248 K and 373 K looked rather similar, apart from an obvious temperature dependence of the fitted frequencies. The asymmetry parameters were practically temperature independent. Data taken at temperatures below room temperature are from samples which were not heated before. This was important because there was an indication that the minority fractions started to fade away gradually when the sample temperature approached 373 K. This is best visible in the small increase of the

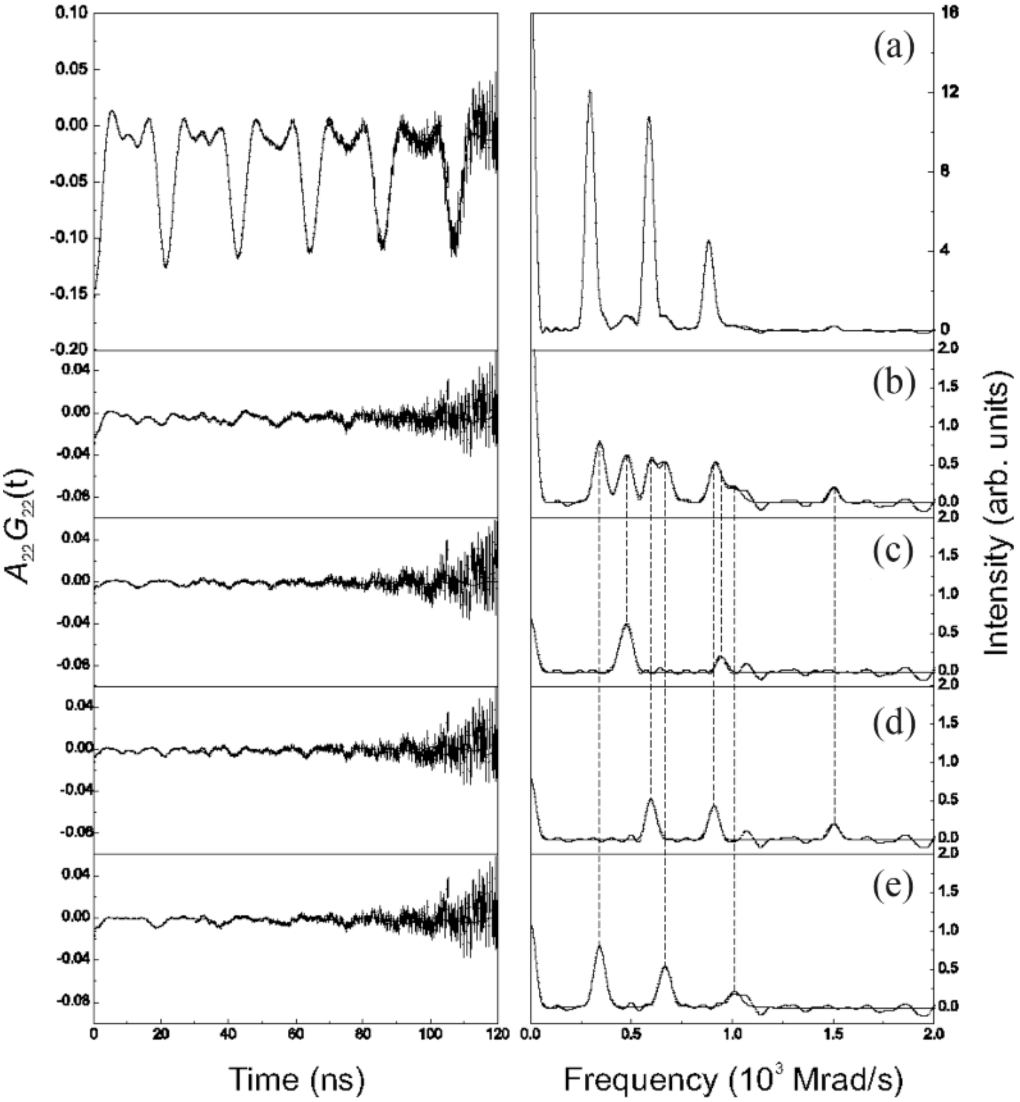

Fig. 1. (a) TDPAC spectrum (left) and its cosine-transform (right) for ^{181}Ta in ultrapure hafnium metal at 298 K after thermal neutron capture. (b) Same as (a) with the majority component subtracted. (c) – (e) Decomposition of the spectrum of (b) into three individual fractions starting with the almost antiaxial site, followed by the intermediate asymmetry site, and the small asymmetry site. Note that the ordinates in the time spectra and the cosine transforms for (b) – (e) are blown up compared to (a).

complementary fraction of the prominent site f_1. All fit results are compiled in Table 1.

The temperature dependence of the frequency of the prominent site is shown in Figure 2 whereas it is shown in Figure 3 for the three minority sites.

The linear slopes for f_1 to f_3 – in the limited temperature range linear slopes are quite adequate – are for the majority fraction and two minority fractions in units of Mrad/sK: $-0.0120(2)$, $-0.015(5)$ (large-η site, f_2), and $-0.055(3)$ (intermediate-η site, f_3), respectively. For the small-η site (f_4), a quadratic fit was found to be more appropriate. We quote no slope but note that the overall temperature dependence is very small. These temperature dependencies will help to associate certain probe-defect configurations with the hyperfine parameters obtained for the minority sites although we do not attempt to interpret these slopes quantitatively.

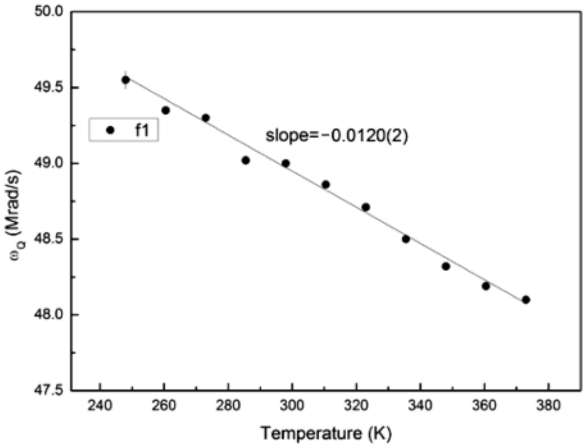

Fig. 2. Temperature dependence of the quadrupole frequency of the majority site. The slope is in units of Mrad/sK.

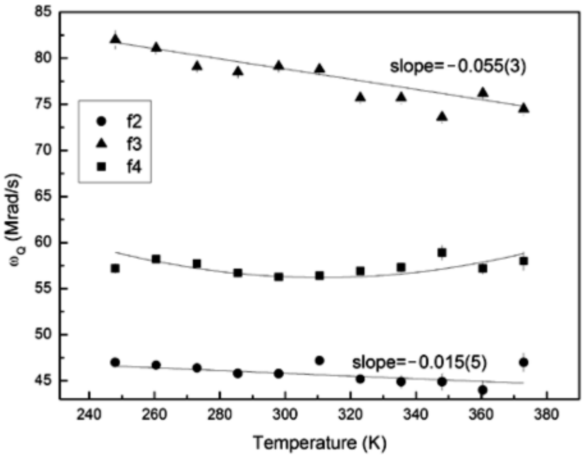

Fig. 3. Temperature dependence of the quadrupole frequency of the three minority sites. Different symbols denote the fractions labelled f_2 to f_4. The slopes are in units of Mrad/sK.

In order to get an idea under what annealing conditions the minority fractions would disappear, we wrapped the sample into an aluminium foil, immersed it for 1 minute into an oil bath heated at 453 K, and then dipped it into liquid nitrogen chilled iso-pentane for a very rapid quench. The rapid quench should guarantee that there is no further annealing during slow cooldown. Our expectation was that under these mild conditions either nothing happens or only one or maybe two defect signals disappear. To our surprise, all three defect signals vanished. The corresponding spectrum is shown in Figure 4 and clearly demonstrates that there is only a single site with a rather small deviation from axial symmetry and very small damping plus a very small fraction of 1.4(3)% of a site with hyperfine parameters distinctly different from the previous ones.

4. Discussion

First, we want to comment on the sample. Incidentally, it was purchased from the same company [9] as that used for self-diffusion studies by Herzig et al. [13] who quote a zirconium concentration of 129 wt/ppm and further impurities at much lower levels. Although our sample is very likely from a different batch, we believe that rather similar impurity levels also apply to our sample. More importantly, the sample was characterized as a very coarse-grained hafnium ingot. Therefore, we want to exclude grain-boundary effects from our discussion. Needless to say that the rather small admixture of zirconium of 110 ppm is not responsible for our observations. The average Zr–Zr distance is about 10 lattice constants and there is no reason to believe that zirconium atoms would be attracted by the tantalum impurity and diffuse over such large distances at room temperature within the 17.8 µs half life of the start level of the 133 – 482 keV γ–γ-cascade.

Hafnium metal crystallizes in the hcp structure with room temperature lattice constants $a = 320.0$ pm and $c = 506.2$ pm. The value for $c/a = 1.582$ is low compared to the ideal packing ratio 1.633. However, to start with, we shall neglect this deviation from the ideal packing ratio and consider hafnium atoms to have twelve nearest neighbours. This simplification will be relaxed later.

Next we discuss the role of the (n_{th}, γ)-process. An important information comes from the fact that the samples which differed by a factor of 10 in neutron activation gave identical results. The defects are therefore related to the thermal neutron capture and are not produced by fast neutrons. Clearly, the 10-fold higher activation produces 10 times more defects, but after the decay of 90% of the activity only the remaining 10% of ^{181}Hf atoms (‘hot atoms’) report the defects. Uncorrelated defects may exist but are not detectable with the present technique. Moreover, the defects are stable at room temperature for more than four months. The relevant nuclear reaction as far as the TDPAC-observation is concerned is ^{180}Hf(n_{th}, γ) ^{181}Hf. The other Hf-isotopes play no role. The symbol γ actually stands for a prompt shower of γ-emissions with various energies and low intensities plus a rather intense γ-transition from the 5.694 MeV excited ½$^+$ level to

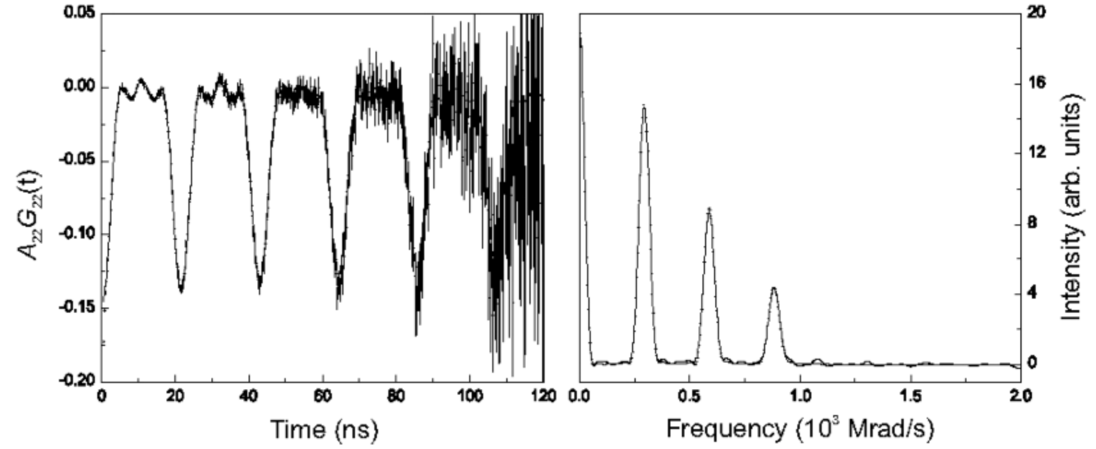

Fig. 4. TDPAC spectrum (left) and its cosine-transform (right) for ^{181}Ta in ultrapure hafnium metal recorded at 298 K after thermal neutron capture and subsequent 'annealing' at 453 K for 1 minute followed by a rapid quench in liquid nitrogen chilled iso-pentane.

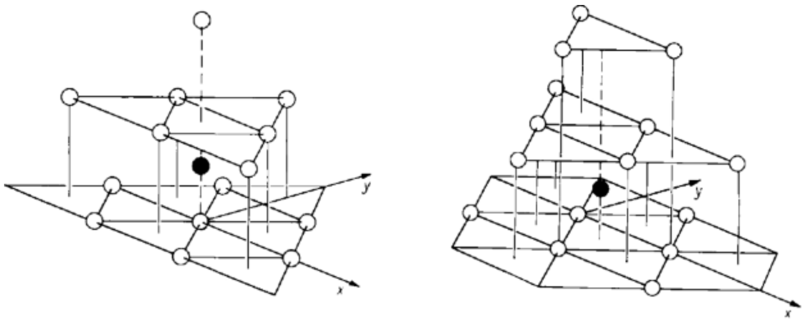

Fig. 5. Trigonal interstitial site (left); hexagonal interstitial site (right). The hexagonal planes are separated by $c/2$ (after [20]).

the ½⁻ ground state of ^{181}Hf [7, p. 395]. Whereas the isotropic 'shower' of γ-rays should have no effect on the emitting atom, the uni-directional intense 5.694 MeV γ-ray leads to a recoil energy of about 90 eV. This is high enough for a primary knock-on process on neighbouring atoms leading to collision cascades with focusing in certain directions thus producing a vacancy at the original 'hot' ^{181}Hf site with a neighbouring 'hot' atom and an inactive 'cold' interstitial several lattice constants away. In addition, the interstitial could also be the 'hot' atom itself. In principle, the high recoil energy of 90 eV could produce more defects but a single Frenkel pair. However, the fact that all three defect NQIs are rather sharp strongly suggests that we are dealing with well-defined nearest neighbour defects and the vacancy and interstitial are sufficiently far apart in order to guarantee that either the vacancy or the interstitial influences the nuclear probe but not both. The defect production at around 330 K ensures that only Frenkel pairs which are stable at this temperature survive.

In principle, the absorption of oxygen atoms has to be considered, too, because hafnium metal is a very efficient getter. This was the reason why we kept the 'annealing' temperature as low as 453 K. It is even possible that the starting material already contained enough oxygen. In order to yield a signal corresponding to an interstitial oxygen atom in the first or second nearest neighbour position to the nuclear probe the oxygen atom would have to diffuse and to be trapped at the daughter ^{181}Ta. At first glance, this seems rather unlikely at 298 K and below. However, the start level of the γ–γ-cascade in ^{181}Ta has a half life of 17.8 µs and the ^{181}Ta impurity could lead to long-range lattice distortions which could enhance the trapping efficiency. However, we want to exclude the possibility that the observed defect configurations are related to trapped oxygen because the 'defect' signals disappeared after the 'annealing' at 453 K for one minute followed by a very rapid quench (except for the appearance of a new signal with a very small fraction of 1.4(3)%), to be discussed below.

For the further discussion, we note that contrary to vacancies being nearest neighbours to probe atoms in fcc or bcc metals with lead to axially symmetric EFGs, hcp metals offer the additional advantage of yielding both the strength of the EFG and the asymmetry parameter η.

We now attempt to assign specific defect configurations to the observed minority signals. The signal with axial symmetry or rather small deviations thereof with fraction f_4 is most intriguing at first glance because the lattice site must have three-fold rotational symmetry. A possible candidate is an interstitial position for the 'hot' probe atom between three hafnium atoms. This assignment is strongly biased by the structure of the ω-phase where two hexagonal planes are believed to collapse [14]. Admittedly, associated with this collapse is a drastic expansion of the a-axis. However, here we are dealing with an isolated interstitial only. Yet, an interstitial position in the hexagonal plane would require quite a large lattice relaxation and, therefore, a position above or below the hexagonal plane would be much more likely. In this context it is interesting to note that the NQI of ^{181}Ta in ω-Zr at the B-site is 60.73 Mrad/s at room temperature [15, 16], close to the small or vanishing asymmetry parameter site (55.97(9) Mrad/s) in the present data for hafnium. Moreover, it is interesting to note that the NQI of ^{181}Ta in ω-Zr on the B-site *increases* with pressure about a factor of 2 stronger than for α-Zr, whereas the NQI *decreases* with pressure at the A-site [15, 16]. This could, of course, be related to very dissimilar electron charge distributions at both sites as discussed in [15, 16], it could, however, also call for an internal parameter, i. e. the two planes do not exactly collapse but rather approach each other and this approach is pressure dependent. Such ideas have been discussed in terms of a commensurate charge density wave [17]. An incomplete collapse resulting in a 'rumpled' plane has also been discussed in [18]. The problem to obtain high quality data on lattice constants and possible internal parameters of the ω-phase lies in the fact that no high quality single crystals of the metastable ω-Zr seem to exist, let alone of ω-Hf under very high pressure.

Fendrik et al. [19] – and Tomé et al. already in 1979 [20] – report on computer simulations of magnesium which revealed that the most stable interstitial configuration is exactly such a position which they call 'trigonal' (see Fig. 5 left). It is a little confusing that Tomé et al. [20] depicted the trigonal interstitial right above a vacancy in their Figure 2, presumably to introduce the nomenclature for neighbouring sites only. It does not mean that the vacancy and the trigonal interstitial are very close neighbours. The other interstitial site in the hcp structure is what Tomé et al. [20] call 'hexagonal' (see Fig. 5 right). Our argument in favour of the trigonal site is the following: the position along the c-direction is not given by symmetry for the trigonal site, as discussed in [20], contrary to the case of the hexagonal site. This is exactly what provides an internal parameter which can be pressure dependent, as discussed above for the ω-phase. In fact, instead of a complete collapse of two hexagonal planes in the ω-phase, we propose an approach of one hexagonal plane to the other occupying exclusively trigonal interstitial sites. This would immediately explain the unusual pressure dependence of the NQI at ^{181}Ta as observed for ω-Zr [15, 16]. It looks like the late A. W. Overhauser was right: the ω-phase can be described by a 1d commensurate charge density wave along the c-axis with period $3c$, accompanied by a lateral glide, while the degree of anharmonicity rules the (pressure dependent) mutual approach of two hexagonal planes (B-sites).

Another possibility for a defect with axial symmetry would be a vacancy at (0,0,0,1) with the 'hot' atom at the origin. We favour the first assignment for the following reason. All defect signals have negative slopes for the temperature dependence of the NQI, except f_4 which is nonlinear but small. For a vacancy, a distance of c above/below the probe atom this would be surprising because enhanced lattice vibrations would be expected and rather important. On the contrary, for the trigonal interstitial with large lattice relaxations, i. e. a rather tight configuration, a rather weak temperature dependence – possibly including a weakly temperature dependent internal parameter – of the NQI would be more plausible.

The other two signals with intermediate and large asymmetry parameters are more difficult to assign. In order to obtain such large asymmetry parameters in the range from 0.5 to 0.9, we require a nearest or next-nearest neighbour vacancy or a 'cold' interstitial close to the probe atom. A natural choice for a nearest vacancy would be a vacancy in the hexagonal plane leading to a large η close to unity and one in the plane at $\pm c/2$ leading to the intermediate η. The temperature dependence of the frequency of the fraction of the almost antiaxial site (see Fig. 3) resembles that of the prominent site. This seems to be at variance with a nearest neighbour vacancy in the hexagonal plane. Therefore, we prefer for the large-η site an assignment of an interstitial 'cold' atom in the close neighbourhood to the probe atom, maybe on a trigonal interstitial site, like the one discussed above for the 'hot' atom.

On the contrary, the temperature dependence of the frequency of the intermediate asymmetry site is about a factor of 5 stronger than that of the regular site (see Fig. 3) which suggests much larger local vibration amplitudes, e. g. due to a nearby vacancy, either in the hexagonal plane or in the plane at $\pm c/2$, whichever is more stable.

Unfortunately, the scatter in the fractions of the minority sites is too large to extract further hints for the possible configuration with the exception that all fractions tend to decrease with increasing temperature from about 15% in total to about 10% in total. However, judging from the most accurate data at 298 K, we note that the fractions are rather similar and lie between 3.7% and 5.3%. This gives a first hint that we are dealing with but one type of Frenkel pair.

Further support for this idea comes from the observation that all three defect signals disappear upon 'annealing' at 453 K. Although there are no data on isochronal annealing in the temperature range between 373 K and 453 K, there is little freedom left for a vastly different annealing behaviour between the three defect signals. Thus, it is plausible that we are dealing with one type of Frenkel pair only, the signatures differing in the position of the 'hot' 'reporting' atom with respect to the Frenkel pair: the site with $\eta \approx 0$ corresponds to the 'hot' interstitial with a distant vacancy; the site with $\eta \approx 0.5$ corresponds to a 'cold' interstitial as nearest neighbour to the 'hot' atom with a distant vacancy; the site with $\eta \approx 1$ corresponds to a nearest neighbour vacancy to the 'hot' atom with a distant 'cold' interstitial. The fact that only three defect configurations but no more are observed now finds an easy explanation: there is a 'hot' interstitial (there is no 'hot' vacancy), and there are a 'cold' interstitial and a 'cold' vacancy near to the 'hot' reporting atom. This means that the recoil of the prompt 5.694 MeV deexcitation γ-ray in ^{181}Hf after thermal neutron capture of ^{180}Hf produces room temperature (and above) stable Frenkel pairs in hafnium metal with a probability of 10% – 15%, i. e. the sum of the three fractions f_2 to f_4.

The 'annealing' and quench experiment unambiguously demonstrates that we are dealing with a terminal annealing. From the temperatures where the additional signals disappear, we estimate around 40 meV for the stability of the observed Frenkel pairs. In addition, all arguments about trapping of residual gas atoms or other impurities are invalidated because the TDPAC spectrum is as clean as possible. The rather small asymmetry parameter and damping could be due to residual distant defects. Annealing at higher temperatures would possibly enhance oxygen-uptake and -trapping, even in good vacuum.

The 'clean' spectrum shows that ^{181}Ta is an 'innocent' spy, i. e. it does not create its own environment, contrary to the observation in $HfF_4 \cdot HF \cdot 2H_2O$ [21]. It certainly does not trap impurities, vacancies or interstitial hafnium atoms within the half life of 17.8 µs of the start level of the cascade in ^{181}Ta. This is certainly a benefit of dealing with high-purity metals.

Finally, the new and rather small fraction 1.4(3)% in the 'annealed' and quenched sample with $\omega_Q = 42.3(9)$ Mrad/s and $\eta = 0.76(4)$ will be discussed. It is intriguing that $\omega_Q = 42.10(3)$ Mrad/s and $\eta = 0.68(1)$ has been reported for 0.1% hafnium in the bcc metal niobium with a trapped interstitial oxygen atom on the second nearest neighbour octahedral position using ^{181}Hf(β^-) ^{181}Ta TDPAC [22]. Of course, a bcc metal with a hafnium impurity – a well-known getter – should not be compared with an ultrapure hafnium metal (hcp) where the oxygen trapping would have to occur during the 17.8 µs half life of the start level of the γ–γ-cascade in the daughter nucleus ^{181}Ta. We believe that the 1.4(3)% fraction of the 'annealed' and quenched sample could indicate the onset of oxygen-uptake at 453 K and trapping at 298 K. This could happen near to the surface of the sample and thus no macroscopic diffusion processes are required. In any case, there is no evidence of oxygen-uptake and -trapping in the spectra recorded in the temperature range from 248 K to 373 K because no obvious irregularities were observed in the NQI frequencies as shown in Figures 2 and 3.

At present, without detailed information about lattice relaxations around the defects, we have to refrain from speculating about the magnitudes of the NQIs. However, ab initio calculations for various Frenkel pair configurations would be rather helpful for site assignments.

Such calculations must include the foreign atom tantalum, the defect, and the lattice relaxations and therefore are rather difficult to perform. First results using the Wien2k code for tantalum in pure hafnium metal yield $V_{zz} = +6.3(5) \cdot 10^{21}$ V/cm^2 [23] which has to be compared to the present experimental value of $V_{zz} = |5.46(12)| 10^{21}$ V/cm^2 using the quadrupole moment of the $I = 5/2$ state of $Q = 2.36(5)$ b [24]. The accuracy and reliability of Q is good enough as discussed in [24] and is not responsible for the discrepancy. This shows that supercell calculations with many electrons including spin–orbit coupling and lattice relaxation are not yet completely satisfactory and, hence, the hope to obtain reliable values for complicated impurity–defect configurations is still limited at present.

5. Summary and Outlook

Isolated Frenkel pairs have been produced by the recoil of the prompt 5.694 MeV γ-emission after thermal neutron capture of ^{180}Hf as identified by their NQIs. Tentative assignments are given for all three observed defect configurations. The sample could be 'annealed' at 453 K to yield a defect-free NQI-signal. The unexpected stability of the Frenkel pairs could be related to hetero-phase fluctuations [25]. We believe that our observations could also be of importance for zirconium metal.

Our observations could have consequences for possible irregular lattice sites in hafnium/zirconium alloys, since earlier TDPAC-experiments exhibited rather complex spectra even at admixture levels in the order of 1% zirconium [26] (the same is true for zirconium containing 1% hafnium), a rather surprising observation for chemically very similar elements, both hcp structures, almost identical lattice constants, and complete miscibility. Zirconium and hafnium are, in fact, difficult to separate. The only large difference is in the atomic mass and, hence, in the local lattice vibrations. In view of the fact that the NQI data for pure zirconium and pure hafnium were almost identical (nuclear quadrupole frequency $\omega_Q = 47.86(24)$ Mrad/s and 48.84(17) Mrad/s [26]) this is difficult to understand. In fact, previous TDPAC investigations using ^{181}Hf as nuclear probe in 'nominally pure' hafnium metal all exhibited frequency distributions and/or deviations from axial symmetry, inconsistent with the hcp structure [27]. We believe that the propensity of the group IVb metals to undergo phase transitions from the hcp to the ω-structure upon pressure is associated with such local lattice vibrations, very likely including stable defect configurations. A related phenomenon is the stabilization of the ω-phase by alloying [14]. Channeling experiments with planar and axial geometry would help to clarify the lattice location of atoms in these alloys provided high quality single crystals can be grown.

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