TDPAC measurements in textured hcp samples

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Abstract. Time differential perturbed angular correlation measurements done on the 482 keV level of ^{181}Ta probe nuclei in well annealed reference foil samples of α-ZrHf, α-TiHf and α-Hf indicate that all probe nuclei are defect free, substitutional and experience quadrupole frequencies characteristic of these matrices. But mostly the ratio of the intensities of the harmonic components of the quadrupole frequency is never in $3:2:1$, which is understood to be due to the selective orientation of microcrystallites brought out by the pre thermo-mechanical treatments on the sample. This paper illustrates as to how texturing in general could cause ambiguities in the measurements of the hyperfine interaction parameters of probe nuclei particularly in hcp foil samples with or without the association of any defects and the ways to delineate the effect of texturing.

1. Introduction

The hcp samples like α-Hf, α-Ti and α-Zr are non-magnetic. The quadrupole interaction (i.e., the interaction between the quadrupole moment of probe nuclei and electric field gradient at their sites) at the isomeric state separating 133 and 482 keV γ–γ cascade of ^{181}Ta probe nuclei in these samples leads to the partial removal of degeneracy of the isomeric state into doubly degenerate states with m-values $\pm 5/2$, $\pm 3/2$ and $\pm 1/2$. Choosing the direction of the first γ ray as the quantization axis leads to the selective population of the above magnetic substates. This results in the emission of the second γ ray of the above cascade of the probe nucleus with an altered population distribution and this change is responsible for the attenuation of the angular correlation [1, 2]. The Fourier transform of the anisotropy spectra in the case of the probe nuclei occupying defect free axially symmetric charge environment in a polycrystalline hcp sample having microcrystallites oriented randomly, should have peaks at ω_1, ω_2 and ω_3 having the ratio of $1:2:3$ and the corresponding intensity ratio $\approx 3:2:1$. The symmetry of the charges that are distributed at the nearest neighbouring environment of probe nuclei is characterized by an asymmetry parameter which is roughly given as $(2 - \omega_2/\omega_1)$.

The probe nuclei occupying the defect free environment of the above matrix in a single crystal of a non-cubic and axially symmetric sample will experience the same quadrupole frequency having the similar ratio between its harmonic components as that of the polycrystalline sample. However the ratio of the intensities of the components of the

quadrupole frequency will not be $3:2:1$ and is sensitively dependent upon the orientation of the crystal with respect to detector geometry. Measurements in a single crystal indicate a drastic difference in intensities of the components of the quadrupole frequencies for different orientations of the sample with respect to detector geometry. By determining the orientation of the respective principle axes of the EFG's we can find out the geometry of the defects as trapped by probe nuclei in the measurement [3]. A textured sample is essentially composed of preferentially oriented and random microcrystallites with the former out numbering the latter. Therefore in the case of the textured sample for some fraction of the probe nuclei the principal axis of the EFG tensor will be oriented selectively and for the remaining fraction the latter will be in random. This carries the information about the orientation of microcrystallites in a sample. The formulation of angular correlation and distribution experiments in the presence of a texturized hyperfine interaction has been given by Rots *et al* [4].

The texturing effects if present *predominantly* in a hcp sample, could cause ambiguities regarding the hyperfine interaction parameters as experienced by probe nuclei viz., quadrupole frequency and asymmetry parameter. The former could be the case if the intensity of the fundamental component of the quadrupole frequency is almost zero. The latter is possible if the intensities of the second and third harmonic components of the quadrupole frequency are almost zero which in general would give an impression that the probe nuclei are occupying an axially asymmetric charge environment. These effects have to be seriously considered in textured samples in which defects are introduced by any conventional method such as light or heavy ion implantation, quenching or due to the introduction of extrinsic defects such as impurities. All TDPAC measurements in such a sample following each step of any heat treatment, in general has to be necessarily carried out in an unique position of the sample with respect to detector geometry. This is required to be done since the anisotropy spectra and hence its Fourier transform would be varying in terms of the intensities of the frequency components corresponding to probe nuclei occupying oriented microcrystallites.

Considering the case of a hcp sample, if it is well homogenized and in the form of a spherical lump it would most likely be perfectly polycrystalline with a random orientation of microcrystallites. Therefore the probe nuclei occupying the substitutional and defect free environment in it will have the ideal intensity ratio of the frequency component corresponding to the concerned matrix. Even such samples under certain conditions seem to have texturing behaviour. For example the preferred orientation of microcrystallites has been reported in In metal just below the melting point by ^{111}Cd TDPAC measurements [5]. Rasera *et al* [6] have proposed a method of rotation of the sample around an axis perpendicular to the plane of the detectors to get a polycrystalline analogue of the texturized samples.

In this paper we are aimed at the following: (1) the illustration of *texturing* effects in hcp foil samples and the possible ambiguities that arise in resolving and/or interpreting the intrinsic or extrinsic defects in such samples, (2) to experiment the ways to get the quadrupole interaction parameters analogue of the polycrystalline sample with random microcrystallites and hence resolve the hyperfine interaction parameters of probe nuclei associated with defects if any occur in the sample. Herewith we have proposed a method to obtain the polycrystalline analogue of the textured sample.

2. Experimental details

The TDPAC of the 133–482 keV γ–γ cascade of ^{181}Ta was measured in the samples of Hf, ZrHf and TiHf samples respectively by a three detector twin fast-slow coincidence setup [7] having NaI(Tl) detectors. One of the detectors was gated for the START (133 keV) γ-ray while the other two detectors were located at 90° and 180° respectively with respect to the START detector to detect the STOP (482 keV) γ-ray. The delayed time resolution spectra were obtained in the form of the count rate as a function of the time elapsed after the emission of the first γ-ray. The two time spectra W (90°, t) and $W(180°, t)$ were recorded simultaneously. The prompt time resolution of the setup measured with a ^{60}Co source was 2.2 ns FWHM when gated for the above cascade of ^{181}Ta [7].

From the delayed time resolution spectra $W(90°, t)$ and $W(180°, t)$, the normalized anisotropy function $R(t)$ was calculated as

$$R(t) = A_2 G_2(t) = 2 \times \frac{[W(180°, t) - W(90°, t)]}{[W(180°, t) + 2W(90°, t)]}, \tag{1}$$

where A_2 is the effective anisotropy coefficient and $G_2(t)$ is the perturbation factor. $W(90°, t)$ and $W(180°, t)$ are the coincidence count rates at 90° and 180° respectively between the START and STOP detectors. In general during the data acquisition using a three detector PAC system the START detector is moved at periodic intervals between 90° and 180° positions with respect to either of the STOP detector and the delayed time resolution spectra are obtained in the form of the count rate as a function of the time elapsed after the emission of the first γ-ray [8]. Hence for each position of the START detector two time spectra $W(90°, t)$ and $W(180°, t)$ are recorded simultaneously. This is done essentially to cancel out the term representing the efficiency of the detectors that appears in eq. (1), so that one gets the normalized anisotropy coefficient independent of any detector parameter. In this work some experiments are done as prescribed above and the remaining with a single geometry of the detecting system i.e. by keeping the START detector fixed. The latter method is justified because of the reasoning that two STOP detectors are identical and their detection efficiencies remain almost the same.

The $R(t)$ spectra were least squares fitted to the function [2]

$$R(t) = A_2 \sum_{i=1}^{r} G_2^i(t), \tag{2}$$

$$A_2 G_2^i(t) = A_2 \sum_{m=0}^{3} a_m^i \exp[-\delta_i k_m^i(\eta_i)\omega_{Q_i} t] \cos[k_m^i(\eta_i)\omega_{Q_i} t], \tag{3}$$

where $k_0^i = 0$, $k_1^i(\eta_i) + k_2^i(\eta_i) = k_3^i(\eta_i)$ and $\sum_{m=0}^{3} a_m^i(\eta_i) = 1$.

If the probe nuclei occupy axially symmetric aand non-cubic sites in a sample in which microcrystallites are randomly oriented the values of the amplitudes a_m^i are given as [2]

$$a_m = \sum_{m,m_1}' \begin{pmatrix} I & I & 2 \\ m_1 & -m & m - m_1 \end{pmatrix}, \tag{4}$$

where $2|m^2 - m_1^2| = n$ for half-integer I. The values of a_m are tabulated for the isomeric state of different spin as given in [2]. In the case of a textured sample these a_m^i have to be taken as free parameters while doing the data analysis.

The spin value of the isomeric state of ^{181}Ta being $5/2$, we have

$$\langle \nu_Q \rangle = eQV_{zz}/h = 10\omega_Q/3\pi, \tag{5}$$

where V_{zz} is the principal component of the electric field gradient (EFG) tensor. When the EFG is not axially symmetric, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ is extracted from the fit of $R(t)$ data to equation (2). The value of r which occurs in (2) is dependent upon the number of frequency components that appear in the Fourier transform of the anisotropy spectra.

The EFG tensor is completely determined by the frequency ν_Q and the asymmetry parameter η. In the case of probe nuclei being present in a non-cubic and axially charge symmetric environment in a polycrystalline sample the value of the asymmetry parameter will be zero which will result in $k_m(\eta = 0) = m$. The probe nuclei present in an asymmetric charge environment are characterized by an asymmetry parameter which is given as $\eta \approx 2 - (k_2/k_1)$. The exponential factor in the sum accounts for the possible existence of a quadrupole frequency distribution which is assumed to be correctly described by a Lorentzian shape with a relative width δ. A non-vanishing value of δ implies either a significant concentration of defects and/or impurities in the material under study, or with a disordered arrangement of atoms in the probe surroundings [8, 9].

The ratio of $a_1 : a_2 : a_3$ will be approximately $3 : 2 : 1$ in the case of the probe nuclei present in an axially charge symmetric non-cubic sample in which the microcrystallites are randomly oriented. The probe nuclei present in a single crystal of the above sample will experience the same quadrupole frequency as that of the polycrystalline sample. But the difference between these two cases is shown up in the values of $a_m(\eta)$ which are dependent upon the orientation of the crystal and hence the direction of the principal axis of the EFG tensor with respect to detector geometry [10]. The theoretical expression for the time dependent anisotropy spectra $R(t)$ in a textured sample can in principle be written as a sum of fractions of probe nuclei experiencing an EFG whose principal component is oriented preferentially along some direction and the remaining fraction with the latter oriented randomly [11]. A detailed XRD measurement has to be done to get any quantitative information on texturing of the sample. But selective orientation of impurity precipitates if any in a sample could be found out by TDPAC, where XRD cannot be used if the concentration of impurity is less than the detectable limit.

3. Results and discussion

We shall first consider the results of the TDPAC measurements carried out on helium implanated α-Zr sample [12]. The homogeneous helium implanation of the sample of dimension $1\,\text{cm} \times 0.1\,\text{cm} \times 380\,\mu\text{m}$ has been carried out with a $40\,\text{MeV}$ alpha beam to a dose of $100\,\text{appm}$ at VEC, Calcutta. Measurement on α-ZrHf reference sample has shown that all probe nuclei experience a Lorentzian distribution of quadrupole frequencies having a value of $\langle \nu_{Q_0} \rangle = 310 \pm 4\,\text{MHz}$ and an asymmetry parameter $\eta_0 = 0.08$. This is
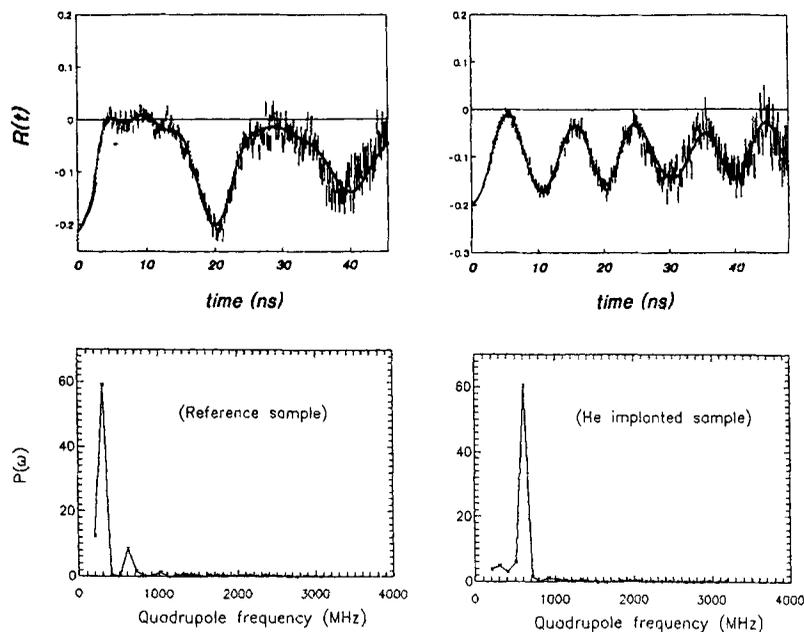
Figure 1. The experimental $R(t)$ vs t spectra and its Fourier transformed spectra at room temperature in the reference and He implanted α-ZrHf sample. The continuous curve in $R(t)$ is the one calculated using the fitted values of the parameters.

in agreement with the results reported in the literature [13]. The $R(t)$ spectra and its Fourier transform of the helium implanted sample in principle could lead to a misleading inference that a large fraction (≈ 0.89) of probe nuclei are associated with a unique helium implantation induced defect experiencing a quadrupole frequency of 620 MHz and the remaining are defect free and substitutional. As this frequency coincides with the second harmonic component of the quadrupole frequency corresponding to the substitutional fraction of probe nuclei we have to find out whether the observed effect is due to texturing or due to any defect trapping by a major fraction of probe nuclei. This can be found out by carrying out the measurements in different orientations of the sample with respect to detector geometry. The variation of the intensities of the quadrupole frequency components with different orientations of the sample confirms that the result is due to the texturing effects of the sample and not due to probe nuclei trapping any defects.

In the present case the selective orientation of the microcrystallites has resulted in a larger intensity of the second harmonic component of the quadrupole frequency as observed by the probe nuclei shown in figure 1. Data analysis of the $R(t)$ spectra on the helium implanted sample taking into consideration the texturing effects of the sample has shown that the probe nuclei experience the following hyperfine interaction parameters viz., $\langle \nu_{Q_1} \rangle = 310 \pm 4$ and $\eta_1 = 0.10$. Above results indicate that all probe nuclei occupy substitutional sites in hcp Zr matrix as reported in the literature [13]. A low value of the asymmetry parameter η in the above cases implies an almost axially charge symmetric environment of probe nuclei.
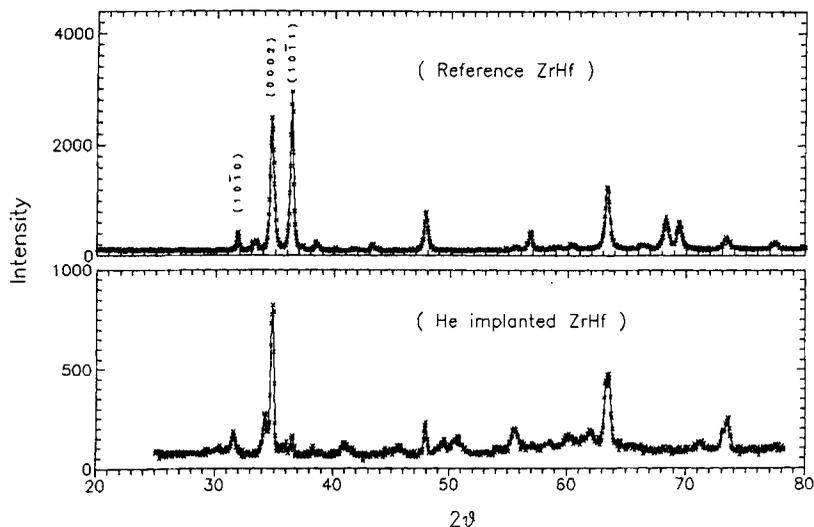
Figure 2. XRD pattern of reference and He implanted α-ZrHf sample.

The time dependent anisotropy spectra in the case of well annealed reference α-ZrHf and the helium implanted α-ZrHf samples are shown in figure 1. The XRD patterns of the reference and helium implanted samples are shown in figure 2. The helium implanted α-ZrHf sample has been observed to be texturized along (0002) direction. The significant texturing effect as has been observed in the helium implanted sample is understood to be due to the pre-thermo mechanical treatments of the sample. This measurement in helium implanted α-Zr-Hf sample illustrates as to how texturing effects of the sample, in which defects (intrinsic or extrinsic) are likely to be occuring, could lead to a possible misinterpretation about determining the hyperfine parameters of defect free and defect(s) associated fraction(s) of probe nuclei.

The effect of texturing is further illustrated by the results of the present TDPAC measurements on Hf foil. The anisotropy spectra $R(t)$ corresponding to the measurements in the Hf foil sample of area 1 cm×0.1 cm and 25 μm thickness with two different positions of the sample viz., the flat surface of the sample lies parallel to the axis connecting START and STOP detectors which are collinear, and the flat surface of the sample lying perpendicular to the latter are shown in figure 3. In the following text this will be referred to as geometry I and II respectively. The $R(t)$ spectra and their Fourier transform (figure 3) are found to be different showing the dependence of these on the position of the sample with respect to detector geometry. The Fourier spectra of the above show that the ratio of the components of the frequency is $1:2:3$, but their intensity ratio is not in $3:2:1$. This would in principle imply the selective orientation of the principal axis of the electric field gradient tensor and hence the orientation of microcrystallites of the sample. The XRD pattern of the Hf foil sample as shown in figure 4 indicates that the microcrystallites of the sample have got textured along (0002) direction as the intensity of this peak is much higher than the peak at $(10\bar{1}1)$. This is due to the reasoning that in a sample with random orientation of microcrystallites the maximum intense peak is expected to occur at $(10\bar{1}1)$ as given by ICDD (International Centre for Diffraction
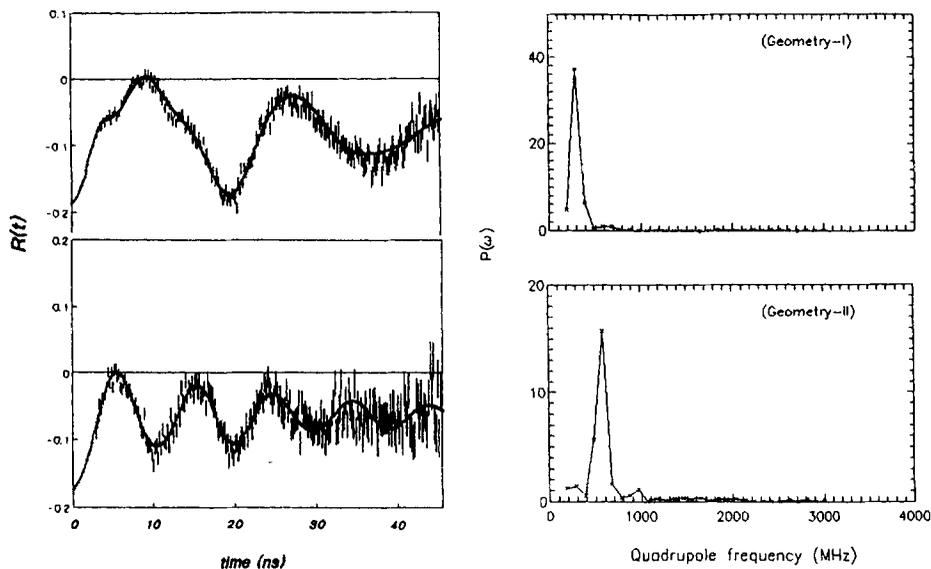
Figure 3. The fitted $R(t)$ vs t spectra and their Fourier transformed spectra at room temperature in Hf foil at two geometries of the sample as explained in the text.
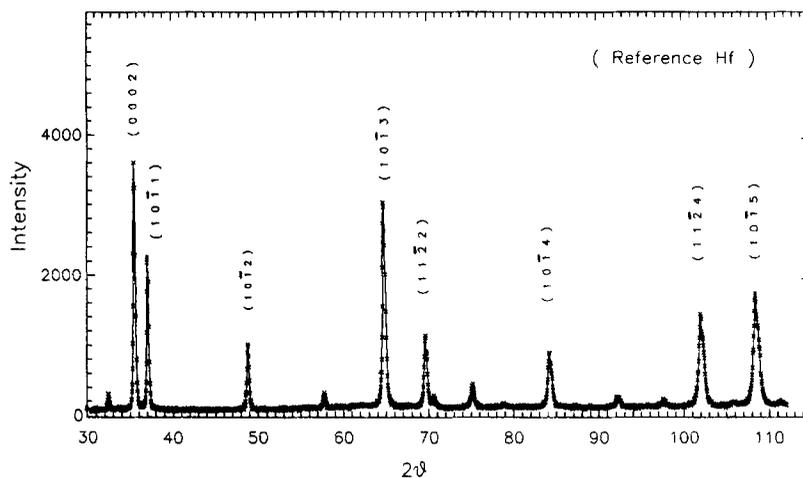

Figure 4. XRD pattern of reference α-Hf sample.

Data). These studies imply that the microcrystallites in α-Zr and α-Hf get preferentially oriented along (0002) direction due to thermo-mechanical treatments of the samples.

Further we have carried out [181]Ta TDPAC measurements in α–Ti-Hf in the cold worked condition and following each isochronal annealing treatment of the sample from 323 to 973 K in steps of 50 K and for a duration of 30 minutes [14]. The measurements done on the 482 keV level of [181]Ta probe nuclei in well annealed α-TiHf sample of 300 μm thickness indicate that all probe nuclei experience a Lorentzian distribution of
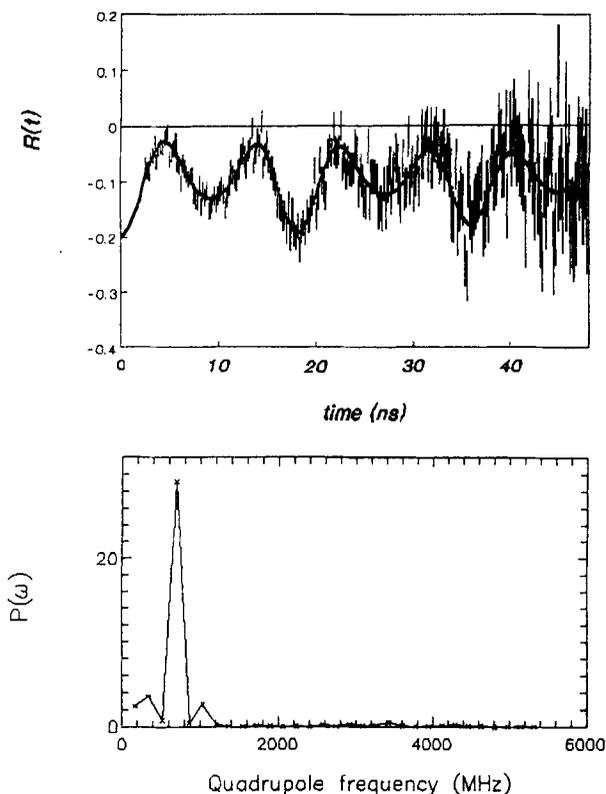
Figure 5. The fitted $R(t)$ vs t spectra and their Fourier transformed spectra at room temperature in TiHf cold worked sample following the annealing treatment at 873 K.

frequencies with a relative width $\delta = 0.042$ having a mean value $\langle \nu_Q \rangle = 340 \pm 2\,\text{MHz}$ and an asymmetry parameter $\eta = 0.04$. This agrees with the reported results for the probe nuclei occupying defect free substitutional sites in hcp Ti matrix. The TDPAC spectra and its Fourier transform following isochronal annealing treatment of the sample at 873 K, which is nearly the re-crystallization temperature of Ti, implies the existence of *texturing* of the sample as shown in figure 5. A predominant texturing of the cold worked sample is confirmed by a comparison of the XRD spectra of the reference and cold worked sample as shown in figure 6. It can be seen that $(10\bar{1}1)$, $(10\bar{1}2)$ and $(10\bar{1}3)$ peaks are predominant in intensities in the cold worked sample. Further based on their intensities it can be deduced that the microcrystallites have got predominantly oriented in $(10\bar{1}3)$ direction.

From the XRD pattern it can be seen that all the above peaks are observed to have shifted to lower 2θ values in the cold worked and subsequently heat treated sample compared to reference one. A shift of (0002) peak towards a lower 2θ by $0.17°$ in the cold worked sample following the final step of annealing treatment implies the growth of unit cells in the c direction by 0.3853%. The growth of the preferentially oriented microcrystallites could be shown up in a TDPAC measurement as a continued increase in the intensity of fundamental or any harmonic component of the quadrupole frequency of substitutional fraction of probe nuclei with annealing treatment of the sample. Care has
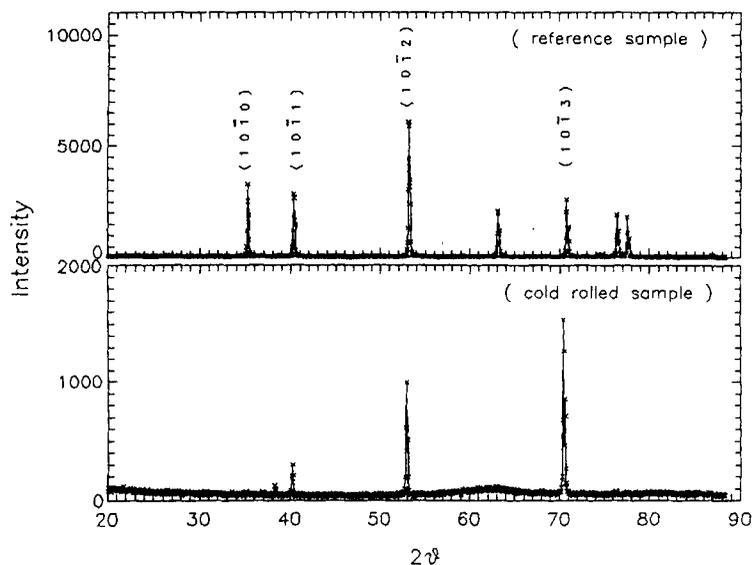
Figure 6. XRD pattern for reference, cold worked and isochronal annealed α-TiHf sample.

to be taken to keep the sample at an unique position with respect to detector geometry during the course of the measurements. Precipitation of probe impurities if any could be observed by TDPAC measurements in any sample. In some cases these precipitates could get oriented preferentially under certain thermal treatments. We have observed selective orientation of Hf precipitates in Cu, Al matrix by [181]Ta TDPAC measurements [15].

All these measurements in α-Hf, α-ZrHf and α-TiHf illustrate the *texturing* effects of these samples.

We have proceeded in the following way the measurements in a Hf foil to average out the effects of texturing and hence get the analogue of the perfectly polycrystalline sample and also the defect(s) related hyperfine parameter(s) of probe nuclei.

(1) In this method, for getting the polycrystalline analogue of the textured sample, we have proceeded as follows. We have averaged the experimental anisotropy spectra obtained in the above mentioned two geometry I and II of the sample and analysed the resultant anisotropy spectra $R(t)$, to derive the hyperfine interaction parameters of probe nuclei in the polycrystalline analogue of the sample. The data analysed $R(t)$ spectra is shown in figure 7. The Fourier transform of the spectra indicates the occurrence of peaks at 290, 580 and 870 MHz with their intensities approximately in the ratio $3:2:1$, as indicated in figure 7. The averaged spectrum as compared to the individual spectrum obtained in each geometry of the sample as shown in figure 3, shows that the former leads to the results analogous of the perfect polycrystalline sample.

(2) Also we have done the measurements by rotating the sample along an axis perpendicular to the plane of the detectors at different speed of rotations of the sample viz., 1 and 2 rps. It has been found from the Fourier transform of the $R(t)$ spectra obtained in the above cases that the ratio of the intensity of the quadrupole frequency components tends to approach that of the polycrystalline sample. A slight dependence of the intensities
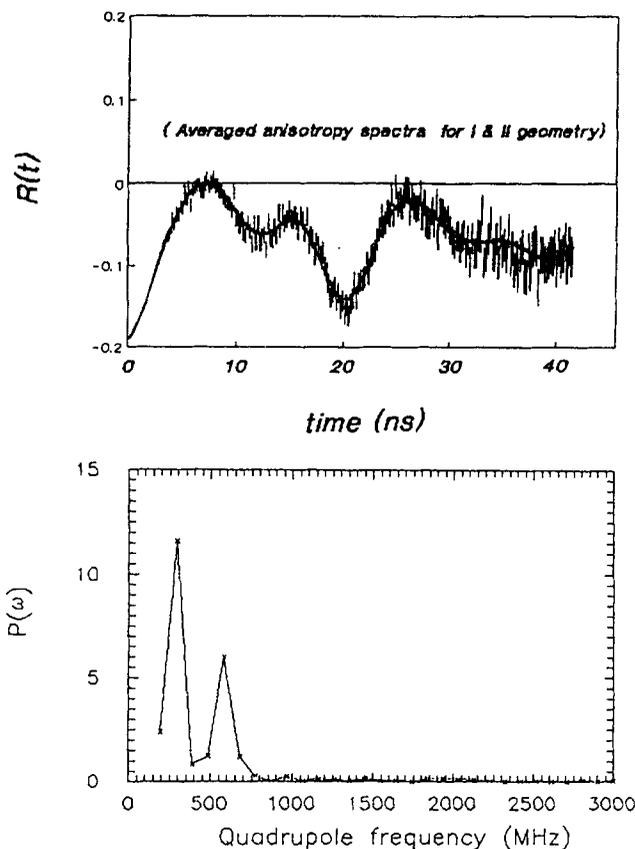
Figure 7. The fitted $R(t)$ vs t spectra and their Fourier transformed spectra at room temperature in Hf foil. The $R(t)$ is the average of the experimental spectra obtained at two geometries of the Hf sample as explained in the text.

of the quadrupole frequency components is seen with increasing speed of rotation of the sample. This has been illustrated in figure 8. The probe nuclei are found to experience a quadrupole frequency $\langle \nu_{Q_0} \rangle = 290 \pm 4\,\text{MHz}$ and an asymmetry parameter $\eta_0 = 0.08$. By rotating the sample about an axis perpendicular to the plane of the detector, we could average the selective orientations of microcrystallites of the sample. Therefore we may infer that the fraction of probe nuclei occupying the oriented microcrystallites may not contribute for the total anisotropy observed in the experiment. Hence this leads to a slight loss of anisotropy depending upon the speed of rotation. This can be seen in figure 8.

The measurements conducted either by averaging the $R(t)$ obtained at different geometries of the sample or by rotating it at a constant speed of rotation during the measurements would result in the polycrystalline analogue of the textured samples. These measurements would help us to find out the hyperfine interaction parameters of the defect(s) related fraction(s) occurring in such hcp samples without any ambiguity as we are able to delineate the fraction of probe nuclei that are defect free in the matrix.
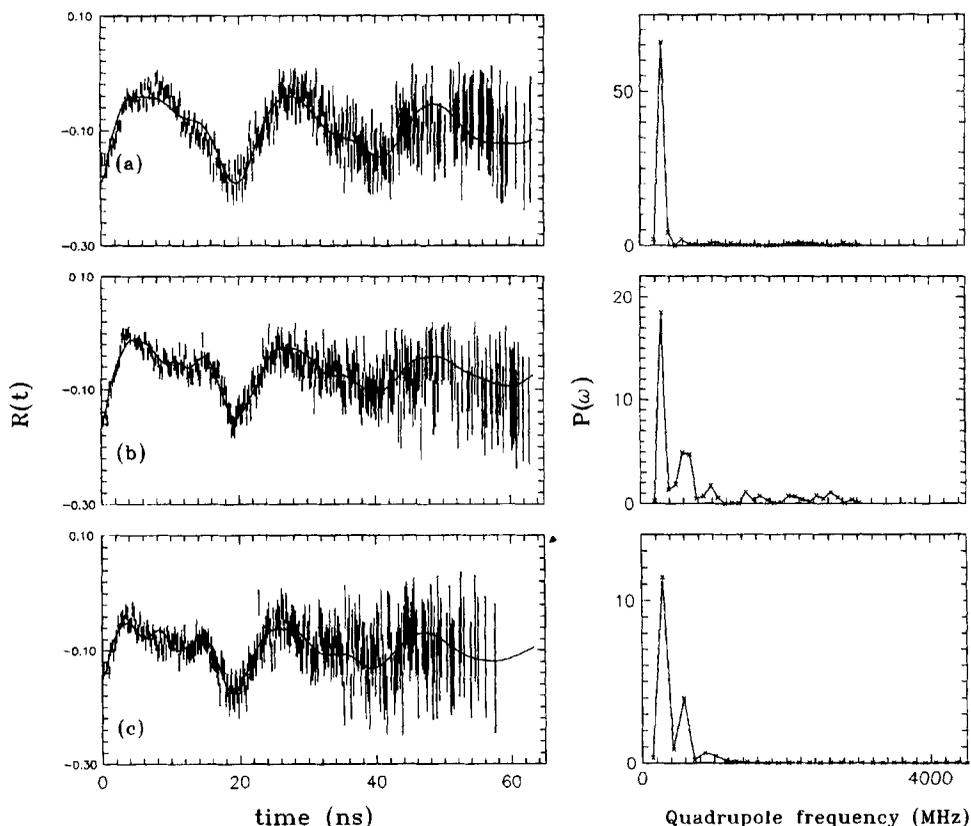
Figure 8. The fitted $R(t)$ vs t spectra and their Fourier transformed spectra at room temperature in Hf foil under the following conditions: **(a)** without rotation, **(b)** 1 rps and **(c)** 2 rps.

4. Conclusions

The orientation of microcrystallites has been observed in polycrystalline foil samples of Hf, α-ZrHf and α-TiHf by TDPAC measurements and further confirmed by XRD measurements. It is conjectured that the TDPAC measurements done at an unique positioning of the sample following each step of the annealing treatments, would give an indication about the growth of microcrystallites if any in the sample. The experimental ways of arriving at the polycrystalline analogue of the texturized samples have been discussed. A new method of averaging the $R(t)$ spectra obtained at different positions of the sample to obtain the polycrystalline analogue of the textured sample has been proposed.

Acknowledgements

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