Identification of phase components in Zr-Ni and Hf-Ni intermetallic compounds; Investigations by perturbed angular correlation spectroscopy and first principles calculations

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Abstract

Time-differential perturbed angular correlation (TDPAC) measurements have been carried out in stoichiometric ZrNi\textsubscript{3} and HfNi\textsubscript{3} intermetallic compounds using \textsuperscript{181}Ta probe in the temperature range 77-1073 K considering the immense technological applications of Zr-Ni and Hf-Ni intermetallic compounds. In ZrNi\textsubscript{3}, four components due to the production of Zr\textsubscript{2}Ni\textsubscript{7}, Zr\textsubscript{8}Ni\textsubscript{21}, Zr\textsubscript{7}Ni\textsubscript{10} and ZrNi\textsubscript{3} have been found at room temperature. The HfNi\textsubscript{3} sample produces five electric quadrupole interaction frequencies at room temperature. The phase HfNi\textsubscript{3} is strongly produced in stoichiometric sample of HfNi\textsubscript{3} where two non-equivalent Hf sites are found to be present. Besides this phase, two other phases due to Hf\textsubscript{2}Ni\textsubscript{7} and Hf\textsubscript{8}Ni\textsubscript{21} have been found but, we do not observe any phase due to Hf\textsubscript{7}Ni\textsubscript{10}. X-ray diffraction and TEM/energy dispersive X-ray spectroscopy (EDX) measurements were used to further characterize the investigated materials and it was found that these results agree with the TDPAC results. In order to confirm findings from TDPAC measurements, density functional theory (DFT) based calculations of electric field gradients (EFG) and asymmetry parameters at the sites of \textsuperscript{181}Ta probe nucleus were performed. Our calculated results are found to be in excellent agreement with the experimental results.

Keywords: A. hydrogen absorbing materials; A. intermetallics; B. mechanical alloying; C. hyperfine interactions; D. perturbed angular correlations, PAC; D. X-ray diffraction;

1. Introduction

The elements zirconium and hafnium are alloyed with cobalt, nickel, titanium, palladium etc. to form many intermetallic compounds which have technological applications. Zirconium-nickel alloys are found to have useful hydrogen storage properties. It was shown that the compounds Zr\textsubscript{8}Ni\textsubscript{21}, Zr\textsubscript{9}Ni\textsubscript{11}, Zr\textsubscript{7}Ni\textsubscript{10}, Zr\textsubscript{2}Ni\textsubscript{7}, ZrNi are good hydrogen absorbing materials to form interstitial metal

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hydrides (MH) which have important application in nickel metal hydride (NiMH) batteries as negative electrode material. The electrochemical properties of several Zr-Ni intermetallic compounds were studied earlier [1–6] by different workers. In ZrNi$_3$, catalytic hydrogen activity was reported by Wright et al. [7]. The hafnium alloyed with nickel, niobium, and tantalum are also useful and can withstand high temperature and pressure. Hafnium alloys are useful in medical implants and devices due to their bio-compatibility and corrosion resistance [8]. The alloys of Ni-Ti-Hf exhibit shape memory behavior [9]. Intermetallic compounds of Hf and transition metals (Fe, Co, Pd, Pt) have also hydrogen storage properties [10], with high H/M ratio at room temperature.

Time differential perturbed angular correlation (TDPAC) or simply PAC is an important nuclear technique to study the structural properties of compounds that contain hafnium and zirconium. Effects of a $\gamma-\gamma$ angular correlation in a crystalline environment are measured by this technique through hyperfine interaction (electric quadrupole and/or magnetic dipole). In electric quadrupole interaction, the quadrupole moment of the probe nucleus interacts with the electric field gradient (EFG) that arises in a crystalline material with noncubic symmetry due to charge distribution of the probe environment. In magnetic interaction, the magnetic dipole moment of the probe nucleus interacts with the internal/external magnetic field. Using this technique, several studies in Hf/Zr-Ni systems were carried out earlier to investigate their EFGs and magnetic properties [11–17]. Recently we have studied the structural properties of (Zr/Hf)$_8$Ni$_{21}$, (Zr/Hf)$_7$Ni$_{10}$ using the PAC technique [18, 19]. However, we do not find any previous PAC studies in (Zr/Hf)Ni$_3$. In the present report, attempts have been made to produce the intermetallic compounds (Zr/Hf)Ni$_3$ by arc melting of the constituent elements taken in stoichiometric ratios and characterize them by PAC spectroscopy. According to Becle et al. [20], the ZrNi$_3$ was formed from Zr$_2$Ni$_5$ and Zr$_2$Ni$_7$ at 940 $^\circ$C or below by a peritectoid reaction. The stable phase of ZrNi$_3$ was obtained at room temperature by annealing the sample at $\sim$860 $^\circ$C. They found that the phase ZrNi$_3$ was not stable and decayed at 940 $^\circ$C following $4\text{ZrNi}_3 \rightarrow \text{Zr}_2\text{Ni}_7 + \text{Zr}_2\text{Ni}_5$. The phase ZrNi$_3$, however, was not found by other workers [21–23]. J. H. N. Van Vucht [24] also failed to produce ZrNi$_3$ by replacing Ti with Zr in TiNi$_3$. In order to help identifying the different phases produced in the investigated samples, the electric field gradients were calculated by density functional theory (DFT) and compared with the measured EFGs. The temperature dependent PAC measurements enabled us to find any structural changes in the material and give information on the structural stability of the compound.

The ZrNi$_3$ is known to be a hexagonal close-packed compound of the SnNi$_3$ type with space group $P6_3/mmc$. The lattice parameters were reported to be $a=5.309$ Å and $c=4.303$ Å [20]. Crystal structure of HfNi$_3$ was also reported by L. Bsenko [25]. It was found [25] that HfNi$_3$ exists in two modifications. A high temperature $\alpha$-HfNi$_3$ phase and a low temperature $\beta$-HfNi$_3$ phase. The crystal parameters for the two phases were reported to be $a=5.27$ Å, $c=19.2324$ Å and $a=5.2822$ Å, $c=21.3916$ Å for the $\alpha$ and $\beta$ phases, respectively.

2. Experimental details

To produce the intermetallic compounds ZrNi$_3$ and HfNi$_3$, stoichiometric amounts of constituent elements procured from M/S Alfa Aesar were taken. The purity of the metals used were: Zr-99.2% (excluding Hf), Hf-99.95% (excluding Zr) and Ni-99.98%. To introduce the $^{181}$Hf probe, each sample was remelted by adding an active piece of Hf wire ($\sim$1 mg). Shiny globule samples were formed after melting in the arc furnace. Natural Hf ($\sim$ 30% $^{180}$Hf) was pre-activated to $^{181}$Hf
Figure 1: The background subtracted XRD powder pattern in the stoichiometric sample of ZrNi$_3$. The line represents the fit to the measured data. The vertical bars A, B, C and D denote the Bragg angles corresponding to Zr$_2$Ni$_7$, ZrNi$_3$, Zr$_8$Ni$_{21}$ and Zr$_7$Ni$_{10}$, respectively. The bottom line shows the difference between the observed and the fitted pattern.

Figure 2: EDX spectrum and TEM image of ZrNi$_3$ in Dhruba reactor, Mumbai by thermal neutron capture with a flux $\sim 10^{13}/\text{cm}^2/\text{s}$ for 7 days. Samples were then sealed in evacuated quartz tubes to carry out measurements at high temperatures. Separate inactive stoichiometric samples of ZrNi$_3$ and HfNi$_3$ were also prepared in similar manners for X-ray diffraction and TEM/energy dispersive X-ray spectroscopy (EDX) measurements. XRD measurements were carried out using the Rigaku X-ray diffractometer TTRAX-III and Cu $K_\alpha$ radiation. Transmission electron microscopy (TEM) measurements were carried out using FEI, Tecnai G2 F30, S-Twin microscope equipped with a high angle annular dark-field (HAADF) de-
Figure 3: TDPAC spectra in the stoichiometric sample of ZrNi$_3$ at different temperatures. Left panel shows the time spectra and the right panel shows the corresponding Fourier cosine transforms. The PAC spectrum at room temperature designated by 298$^\circ$ K is taken after the measurement at 1073 K. A set of three arrows indicates the three transition frequencies of a particular component.

The perturbed angular correlation is a nuclear technique to measure the hyperfine interactions between the nuclear moments of the probe nucleus and the hyperfine fields present in the investigated sample. The probe $^{181}$Hf emits two successive $\gamma$-rays, 133 and 482 keV, passing through...
Figure 4: Variations of quadrupole frequency ($\omega_Q$), asymmetry parameter ($\eta$) and site fraction $f(\%)$ with temperature for the components of Zr$_2$Ni$_7$, ZrNi$_3$, Zr$_8$Ni$_{21}$ and Zr$_7$Ni$_{10}$.

the 482 keV intermediate level ($T_{1/2}=10.8$ ns) with a spin angular momentum $I=5/2^+ \hbar$ [26]. The extra-nuclear electric field gradients present in the sample interact with the nuclear quadrupole moment of the intermediate level ($Q=2.35$ b [26]). Due to this interaction, the angular correlation of the 133-482 keV $\gamma$-$\gamma$ cascade is perturbed. The perturbation function is given by [27],

$$G_2(t) = \left[S_{20}(\eta) + \sum_{i=1}^{3} S_{2i}(\eta) \cos(\omega_i t) \exp(-\delta \omega_i t) \exp\left[-\frac{(\omega_i \tau_R)^2}{2}\right]\right].$$

(1)

The above expression of perturbation function is valid for a polycrystalline sample and for $I=5/2^+$ of intermediate state of the probe nucleus. The frequencies $\omega_i$ are the transition frequencies between different $m$-sublevels arising due to hyperfine splitting. A damping of perturbation function (Lorentzian) was considered through the first exponential which can arise due to structural defects in the sample. Here, $\delta$ is the frequency distribution width. The finite time resolution ($\tau_R$) of the coincidence set up was considered through the second exponential. If more than one quadrupole interaction is present in the sample due to the presence of different component phases or due to two or more non-equivalent sites of a particular phase, the perturbation function can be written as

$$G_2(t) = \sum_i f_i G_2^i(t)$$

(2)
Figure 5: The background subtracted XRD powder pattern in HfNi$_3$. The line represents the fit to the measured data. The vertical bars A, B and C denote the Bragg angles corresponding to HfNi$_3$, Hf$_2$Ni$_7$ and Hf$_8$Ni$_{21}$, respectively. The bottom line shows the difference between the observed and the fitted pattern.

where, $f_i$ is the fraction of the $i$-th component and $G_2^i(t)$ is the corresponding perturbation function. A fitting to expression (1) determines the quadrupole frequency $\omega_Q$ through the measured values of $\omega_1$, $\omega_2$ and $\omega_3$. The quadrupole frequency is directly related to the electric field gradient ($V_{zz}$) through the relation

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}$$  \hfill (3)$$

For an axially symmetric EFG ($\eta=0$), $\omega_Q$ is related to $\omega_1$, $\omega_2$ and $\omega_3$ by $\omega_Q=\omega_1/6=\omega_2/12=\omega_3/18$. The asymmetry parameter is defined as the ratio

$$\eta = \frac{(V_{xx} - V_{yy})}{V_{zz}}$$  \hfill (4)$$

and its value lies between 0 and 1. For $\eta \neq 0$, this simple relation between $\omega_Q$ and $\omega_i$’s does not hold but, produces a more complex relation [28].

A four detector LaBr$_3$(Ce)-BaF$_2$ set up was used for present TDPAC measurements. The crystal sizes were $38 \times 25$ mm$^2$ and $51 \times 51$ mm$^2$ for LaBr$_3$(Ce) and BaF$_2$, respectively. The 133 keV $\gamma$-rays were detected in the LaBr$_3$(Ce) detector and the 482 keV $\gamma$-rays were detected in the BaF$_2$ detector. Standard slow-fast coincidence assemblies were employed to acquire four coincidence spectra at 180$^\circ$ and 90$^\circ$ [29]. A typical prompt time resolution (FWHM) of $\sim$800 ps has been obtained for the energy window settings of $^{181}$Ta $\gamma$-rays. The perturbation function $G_2(t)$ was obtained from the ratio of coincidence counts at 180$^\circ$ and 90$^\circ$. Details on the experimental set up and data acquisition can be found in our earlier report [29].

3. PAC Results

3.1 Stoichiometric ZrNi$_3$ sample

The X-ray powder diffraction pattern found in the stoichiometric sample of ZrNi$_3$ is shown in the Figure 1. The present X-ray pattern was best fitted by known crystallographic parameters of Zr$_2$Ni$_7$
The contributions of ZrNi$_3$ and Zr$_7$Ni$_{10}$ were found to be very small compared to Zr$_2$Ni$_7$ and Zr$_8$Ni$_{21}$. It can be pointed out that the two stoichiometric samples of ZrNi$_3$ for XRD and PAC measurements are not same. The presence of ZrNi$_3$ phase in this stoichiometric sample of ZrNi$_3$ has been confirmed from TEM/EDX measurement (Figure 2) also. The atomic percentages for Zr and Ni at the indicated spot have been found to be 24.4(3) and 75.6(2), respectively.

The PAC spectrum in the stoichiometric sample of ZrNi$_3$ at room temperature is shown in Figure 3. The spectrum was best fitted by considering four electric quadrupole interactions. The sample produced was found to have non-random orientation of microcrystals and the spectrum was fitted by considering free $S_{2n}$ coefficients. The results of different components found are shown in Table 1. The main frequency component (∼48%) produces values of $\omega_Q=70.9(2)$ Mrad/s, $\eta=0.25(2)$. This component can be assigned to Zr$_2$Ni$_7$ by comparing the values of $\omega_Q$ and $\eta$ with the earlier reported results in Zr$_2$Ni$_7$ [12, 17]. From previous PAC measurements in ZrNi$_5$ also, a similar component to this was obtained and attributed to Zr$_2$Ni$_7$ [11, 34]. The ZrNi$_5$ has a cubic crystal structure and no EFG at the probe site is expected due to ZrNi$_5$. The component 2 with a symmetric EFG ($\eta∼0$) can be attributed to ZrNi$_3$ by comparing with our calculated results from density functional theory (discussed later). The crystal structure of ZrNi$_3$ is hexagonal close-packed and, therefore, a value of $\eta=0$ is expected for this compound. However, this is found to be a minor phase compared to other phases produced in this sample. The results of component 3 can be compared with our recent results in Zr$_8$Ni$_{21}$ [18]. This component is found to be similar to one component of Zr$_8$Ni$_{21}$ found from our previous measurements [18] and can, therefore, be attributed to Zr$_8$Ni$_{21}$. The component 4 can be attributed to Zr$_7$Ni$_{10}$ by comparing with the results found in Zr$_7$Ni$_{10}$ [19]. A similar component to this was found in Zr$_8$Ni$_{21}$ also where it was attributed to Zr$_7$Ni$_{10}$ [18].

The results of temperature dependent PAC measurements in the stoichiometric ZrNi$_3$ are given in the Table 1. The corresponding TDPAC spectra are shown in Figure 3. It is found that the component fraction due to ZrNi$_3$ is present in the temperature range (77-973 K). At 77 K, the site fraction of ZrNi$_3$ was found to be maximum (∼30%). In the temperature range 77-873 K,
four component fractions are found to be present with no appreciable change in parameters. The fractional variations of different components are shown in Figure 4. At 973 K, a distinct change in PAC spectrum has been observed. At this temperature, the component due to Zr$_7$Ni$_{10}$ disappears. On the other hand, a new frequency component with values of $\omega = 53.0(4)$ Mrad/s, $\eta = 0$ appears. This component is similar to that found in Zr$_8$Ni$_{21}$ at 1073 K \cite{18}. The site percentage of this

Figure 7: TDPAC spectra in the stoichiometric sample of HfNi$_3$ at different temperature. Left panel shows the time spectra and the right panel shows the corresponding Fourier cosine transforms. The PAC spectrum at room temperature designated by 298° K is taken after the measurement at 1073 K. A set of three arrows indicates the three transition frequencies of a particular component.
new component is found to be $\sim 39\%$ at this temperature and it enhances abruptly at 1073 K ($\sim 90\%$). At 1073 K, only two components are found to be present. The minor component found at this temperature is due to Zr$_2$Ni$_7$. We have repeated the measurement at room temperature after the measurement at 1073 K. The remeasured spectrum at room temperature produces a strong electric quadrupole interaction ($\sim 81\%$) with values of $\omega_Q=56.5(1)$ Mrad/s, $\eta=0$. This component can be recognized as the same component that appeared at 973 and 1073 K. Besides this, two other components are found here. The component due to Zr$_8$Ni$_{21}$ reappears with a small fraction ($\sim 8\%$) and the component due to Zr$_2$Ni$_7$ is also found to be present.

In the present Zr-Ni sample, the predominant component found at 1073 K and subsequently at room temperature can probably be assigned to Hf. At temperatures below 973 K, the probe atoms which were settled at various lattice sites come out from the lattice positions after gaining sufficient energy at high temperature. It seems that at 1073 K, only a small fraction of the probe nucleus ($\sim 10\%$) is attached with the Zr-Ni compounds. A similar phenomenon was observed from our recent PAC investigation in Zr$_8$Ni$_{21}$[18].

The evolution of quadrupole frequency, asymmetry parameter and site fraction with temperature for different components observed are shown in Figure 8. It is found that quadrupole frequencies for the components Zr$_2$Ni$_7$, ZrNi$_3$ and Zr$_8$Ni$_{21}$ vary with temperature following $T^{3/2}$ relationship. For the Zr$_8$Ni$_{21}$ component, a similar temperature dependent behavior was observed.
Figure 9: Models of cells used in the study of HfNi$_3$

Figure 10: Model of cell used in the study of ZrNi$_3$

from our previous PAC investigation in Zr$_8$Ni$_{21}$\cite{18}. For these three components, values of $\omega_Q$ have been fitted using the relation

$$\omega_Q(T) = \omega_Q(0)[1 - \beta T^{3/2}]$$

where, $\omega_Q(0)$ is the extrapolated value at 0 K. The results of $\eta$ and site fraction for different components are also plotted (Figure 11). These results do not show large variations except the site fraction of Zr$_2$Ni$_7$ which decreases drastically at 1073 K ($\sim$10%) compared to the fraction found at 973 K ($\sim$41%). The fitted results are listed in Table 2. Contrary to these, $\omega_Q$ for the component Zr$_7$Ni$_{10}$ is found to obey a linear temperature dependent behavior. In this case, we have fitted the results of $\omega_Q(T)$ using the relation

$$\omega_Q(T) = \omega_Q(0)[1 - \alpha T].$$

Both $T^{3/2}$ and $T$ variations of EFG (proportional to $\omega_Q$) for metallic and intermetallic systems are found in literature \cite{35}.

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3.2 Stoichiometric HfNi₃ sample

The XRD measurement in the stoichiometric sample of HfNi₃ has been carried out at room temperature (Figure 3). Analysis of the X-ray powder pattern was done using the known crystallographic data of HfNi₃ for low temperature phase [27], Hf₂Ni₇ [20] and Hf₈Ni₁₅ [37]. The X-ray spectrum shows that major contribution comes from HfNi₃. It was reported [20] that high temperature phase of HfNi₃ was formed from the melt and Hf₂Ni₇ by peritectic reaction. Apart from HfNi₃, there are phases due to Hf₂Ni₇ and Hf₈Ni₂₁. But, no prominent peak due to Hf₇Ni₁₀ was found in the XRD spectrum. The phase HfNi₃ has been confirmed from our TEM/EDX measurement also (Figure 6). The atomic percentages for Hf and Ni at the indicated spot have been found to be 24.4(2) and 74.3(2), respectively.

The PAC spectrum observed in HfNi₃ at room temperature after preparing the sample in argon arc furnace is shown in Figure 7. It is found that five electric quadrupole frequencies are required to fit the time spectrum. Analysis was done by considering free S₂n coefficients. The major component (33%) found with values of ω₂1=32.0(3) Mrad/s, η=0 (Table 3) can be attributed to HfNi₃ by comparing with our calculated results from DFT (discussed later). From our previous studies in Hf₈Ni₁₅ [18] and Hf₇Ni₁₀ [19], a component similar to this was observed and tentatively assigned to HfNi₃. Component 2 can also be attributed to HfNi₃ because the values of EFG and asymmetry parameter for this component are found to be in good agreement with the calculated results from DFT (discussed later). The component 3 has been attributed to Hf₂Ni₇ by comparing with the earlier reported results in Hf₂Ni₇ [11, 12]. From previous PAC measurement in HfNi₃, a similar component to this was also found and attributed to Hf₂Ni₇ [11]. The component 4 (∼14%) with values of ω₃₂=94.8(6) Mrad/s and η=0.67(2) can be assigned to Hf₈Ni₂₁. From our recent investigation in Hf₈Ni₂₁ [18], similar values of quadrupole frequency and asymmetry parameter were found. In Hf₈Ni₂₁, however, two non-equivalent Hf sites were found. But, in this stoichiometric HfNi₃ sample, we have found only one site of Hf₈Ni₂₁. The other non-equivalent site of Hf₈Ni₂₁ is not observed here. Besides these, a component with symmetric EFG (component 5) was found which can be attributed to pure hcp Hf by comparing the values of ω₂₁ and η with earlier reported results [38]. Probably, this component arises due to unreacted Hf with Ni. Decrease of this component at 973 and 1073 K indicates that more Hf reacts with Ni to form compounds at high temperatures.

Temperature dependent PAC results are given in Table 3. The corresponding PAC spectra are shown in Figure 7. In the temperature range 77-873 K, there are no appreciable changes in the PAC spectra. At 973 K, the component Hf₈Ni₂₁ disappears. The component due to Hf₈Ni₂₁ does not appear at 1073 K also. But other four components are found to exist at 1073 K. However, unlike stoichiometric ZrNi₃, no additional component is observed at 1073 K. The PAC measurement was then repeated at room temperature. At this temperature, two components of HfNi₃ reappear which indicates that HfNi₃ is a stable phase. The component Hf₈Ni₂₁ does not appear when remeasured at room temperature. The components of Hf₂Ni₇ and Hf are found to be present when remeasured at room temperature.

The evolution of the quadrupole frequency, η and site fraction with temperature for the different components observed in stoichiometric HfNi₃ are shown in Figure 8. The components Hf₈Ni₂₁ and Hf₂Ni₇ follow the same T⁵/₂ temperature dependence as found for Zr₈Ni₂₁ and Zr₂Ni₇ in ZrNi₃. The EFG for the two components of HfNi₃ are found to vary different manner. The quadrupole frequency of HfNi₃(2) varies with temperature following T⁵/₂ relationship (Eqn. 5). On the other hand, a linear temperature dependent behavior (Eqn. 6) was found for the HfNi₃(1) component.
Variation of the quadrupole frequency for the hexagonal Hf was also found to be linear. The fitted results are shown in Table 2. The variations of $\eta$ and site fractions for different components do not show large changes (Figure 8).

4. DFT calculations

The first-principles density functional theory (DFT) calculations were performed with the WIEN2k simulation package [39] based on the full potential (linearized) augmented plane waves method (FP (L)APW). Electronic exchange-correlation energy was treated with generalized gradient approximation (GGA) parametrized by Perdew-Burke-Ernzerhof (PBE) [40]. In our calculations the muffin-tin radii for Hf, Ni, Zr and Ta were 2.3, 2.1, 2.3 and 2.3 a. u., respectively. The cut-off parameter $R_{mt}K_{max}$ for limiting the number of plane waves was set to 7.0, where $R_{mt}$ is the smallest value of all atomic sphere radii and $K_{max}$ is the largest reciprocal lattice vector used in the plane wave expansion.

The Brillouin zone integrations within the self-consistency cycles were performed via a tetrahedron method [41], using 6-50 $k$ points in the irreducible wedge of the Brillouin zone (4×4×2 and 8×8×8 meshes for Ta doped HfNi$_3$ and ZrNi$_3$, respectively) for the supercell calculations. The atomic positions were relaxed according to Hellmann-Feynman forces calculated at the end of each self-consistent cycle, with the force minimization criterion 2 mRy/a.u.. In our calculations the self-consistency was achieved by demanding the convergence of the integrated charge difference between last two iterations to be smaller than 10$^{-5}$ e. All the calculations refer to zero temperature.

4.1 HfNi$_3$

HfNi$_3$ at the temperatures below 1200°C, has the $\gamma$-Ta(Pd,Rh)$_3$-type structure, with a stacking of ten AB$_3$ layers in the sequence ABCBCACBCB. The space group is $P6_3/mmc$ and the unit cell dimensions are $a=5.2822(2)$, $c=21.3916(18)$ Å at room temperature [25]. This structure contains 40 atoms in the unit cell, distributed at 6 non-equivalent crystallographic positions, 3 for Hf atoms and 3 for Ni atoms (Table 5).

After obtaining the optimized structural parameters, we constructed 2×2×1 supercell from periodically repeating unit cells of the host crystals. To simulate PAC measurements at Hf1 position, we replaced one Hf atom in the supercell at the position (0 0 1/4) with Ta (Figure 9a [42]). In the case of Ta at the Hf2 and Hf3 positions due to the complexity of the calculations, we had to replace two Hf atoms at the corresponding position with Ta, thus obtaining the cell with 50 non-equivalent atoms (Figure 9b and c). We checked that the two Ta atoms are sufficiently far from each other (11.1 Å) to avoid significant impurity-impurity interactions. After determining the self-consistent charge density we obtain the electric field gradient (EFG) tensor $V_{ij}$ using the method developed in reference [43]. The usual convention is to designate the largest component of the EFG tensor as $V_{zz}$. The asymmetry parameter $\eta$ is then given by $\eta= (V_{xx}-V_{yy})/V_{zz}$, where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. All the calculations refer to zero temperature.

The theoretically determined cell and structure parameters for the investigated structure, along with the experimental values obtained from X-ray diffraction measurements are given in Table 3. The theoretical volume slightly overestimates the experimental one. The bulk modulus $B_0$, obtained by fitting the data to the Murnaghan’s equation of state [44] is also given in Table 4. The calculated interatomic distances, given in Table 5 are also slightly larger than the measured ones, but the overall agreement is good.
The calculated EFGs in the pure compound as well as at Ta probe position in the $\beta$-HfNi$_3$ are given in Table 6. It can be observed that EFG is smallest at Hf1 position and the largest at Hf2 position. This trend preserves also for the electric field gradients calculated at corresponding Ta positions, but the EFGs are now larger from 30% to 60%. We see that the calculated result for EFG at the Ta probe site replacing Hf3 atom ($3.5 \times 10^{21} \text{ V/m}^2$) is in excellent agreement with the measured value of $EFG = 3.68 \times 10^{21} \text{ V/m}^2$ ($\omega_Q(0) = 32.9 \text{ Mrad/s}$) for the component HfNi$_3^{(1)}$, thus confirming that the mentioned component of the measured PAC spectra originates from HfNi$_3$. Similarly, the calculated results at the Ta probe site replacing Hf2 atom ($V_{zz} = 7.1 \times 10^{21} \text{ V/m}^2$ and $\eta = 0$) are in excellent agreement with our measured values of HfNi$_3^{(2)}$ component ($V_{zz}(0) = 7.3 \times 10^{21} \text{ V/m}^2$ and $\eta = 0$) which confirms that this component also originates from HfNi$_3$.

4.2 ZrNi$_3$

ZrNi$_3$ crystallizes in the hexagonal Ni$_3$Sn type structure, which possesses two non-equivalent crystallographic positions, Zr 2c and Ni 6h [20]. The optimized lattice constants, which slightly overestimate the experimental values, are given in Table 3. The calculated EFG at Zr position is $-3.0 \times 10^{21} \text{ V/m}^2$, with zero asymmetry parameter. In order to simulate PAC measurement, we constructed $2 \times 2 \times 2$ supercell from periodically repeating unit cell and then replaced one of the Zr atoms by Ta (Figure 10 [42]). The point group symmetry around the impurity Ta atom remained the same as around the original Zr atom, but the number of non-equivalent positions increased. The calculated EFG at the Ta probe atom $-8.4 \times 10^{21} \text{ V/m}^2$ is in excellent agreement with two mutually similar EFG values from measured PAC spectra ($8.2$ and $8.48 \times 10^{21} \text{ V/m}^2$, corresponding to $\omega_Q(0) = 72.9$ and $76 \text{ Mrad/s}$, respectively). The fact that the corresponding calculated asymmetry parameter is zero, enables us to assign the $76 \text{ Mrad/s}$ component to ZrNi$_3$ and thus definitely confirm the presence of this phase in our stoichiometric sample.

5. Conclusion

From TDPAC and XRD measurements, multiple phases have been found in the stoichiometric samples of ZrNi$_3$ and HfNi$_3$. The presence of ZrNi$_3$ and HfNi$_3$ in these stoichiometric samples have been confirmed from TDPAC, XRD and TEM/EDX measurements. From PAC studies, it is found that ZrNi$_3$ is produced as a minor phase while the phase HfNi$_3$ is found to be largely produced. Also, our temperature dependent PAC studies show that HfNi$_3$ is a very stable phase. In the stoichiometric samples of ZrNi$_3$ and HfNi$_3$, secondary phases due to (Zr/Hf)$_8$Ni$_{21}$ and (Zr/Hf)$_2$Ni$_7$ are found to be produced. In ZrNi$_3$, the phase due to Zr$_7$Ni$_{10}$ is observed while no phase due to Hf$_7$Ni$_{10}$ is found in HfNi$_3$ sample. Only one and the same crystallographic site of (Zr/Hf)$_8$Ni$_{21}$ is found in present stoichiometric samples of ZrNi$_3$ and HfNi$_3$ although two non-equivalent sites were found in (Zr/Hf)$_8$Ni$_{21}$ [18]. The experimental values of EFG and $\eta$ for ZrNi$_3$ and HfNi$_3$ are found to be in excellent agreement with the theoretically calculated values of EFG and $\eta$ at $^{181}$Ta impurity sites by the first-principles density functional theory based on the FP (L)APW. From our calculation, three non-equivalent Hf sites in HfNi$_3$ have been found whereas two of these have been observed from PAC measurements. In ZrNi$_3$, on the other hand, the present DFT calculation produces one EFG corresponding to a single Zr site. From our PAC measurements in ZrNi$_3$ also, a single frequency component has been found.

The solubility of Hf in Ni is found to be less compared to Zr in Ni. The Hf solubility in Ni is found to increase with temperature and it decreases again when the temperature is lowered. In
Zr-Ni compounds, the binding energy of Hf probe to the lattice sites is not strong enough at high temperature and, probably, the probe atoms are detached from the compound at $\sim1000$ K.

The TDPAC is found to be an useful nuclear technique to detect weak component phases that are produced in a material. Particularly, a $\text{LaBr}_3(\text{Ce})\cdot\text{BaF}_2$ set up is found to be very useful for separating the minor component phases when multiple components are present in the sample.

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Table 1: Results of PAC measurements in stoichiometric sample of ZrNi$_3$

| Temperature (K) | Component | $\omega_Q$ (Mrad/s) | $\eta$ | $\delta$ (%) | $f$ (%) | Assignment |
|----------------|-----------|---------------------|-------|--------------|--------|------------|
| 77             | 1         | 72.2(9)             | 0.28(5) | 0 | 33(3) | Zr$_2$Ni$_7$ |
|                | 2         | 75.7(8)             | 0      | 0 | 30(3) | ZrNi$_3$  |
|                | 3         | 97.6(6)             | 0.71(2) | 0 | 29(3) | Zr$_3$Ni$_21$ |
|                | 4         | 65.5(8)             | 0.59(2) | 0 | 16(3) | Zr$_8$Ni$_{10}$ |
| 298            | 1         | 70.9(2)             | 0.25(2) | 0 | 48(3) | Zr$_2$Ni$_7$ |
|                | 2         | 74.5(9)             | 0      | 0 | 13(3) | ZrNi$_3$  |
|                | 3         | 95.2(3)             | 0.603(8) | 0 | 25(3) | Zr$_3$Ni$_21$ |
|                | 4         | 59.9(5)             | 0.62(2) | 0 | 14(3) | Zr$_8$Ni$_{10}$ |
| 373            | 1         | 69.9(3)             | 0.25(6) | 0 | 50(3) | Zr$_2$Ni$_7$ |
|                | 2         | 71(2)               | 0      | 0 | 9(3)  | ZrNi$_3$  |
|                | 3         | 92.9(6)             | 0.60(2) | 0 | 26(3) | Zr$_3$Ni$_21$ |
|                | 4         | 58(1)               | 0.72(4) | 0 | 15(3) | Zr$_8$Ni$_{10}$ |
| 473            | 1         | 68.2(4)             | 0.30(6) | 0 | 41(3) | Zr$_2$Ni$_7$ |
|                | 2         | 72(1)               | 0      | 0 | 21(3) | ZrNi$_3$  |
|                | 3         | 89.8(8)             | 0.60(2) | 0 | 20(3) | Zr$_3$Ni$_21$ |
|                | 4         | 56.8(8)             | 0.64(5) | 0 | 18(3) | Zr$_8$Ni$_{10}$ |
| 573            | 1         | 67.3(4)             | 0.24(5) | 0 | 35(3) | Zr$_2$Ni$_7$ |
|                | 2         | 72.4(8)             | 0      | 0 | 22(3) | ZrNi$_3$  |
|                | 3         | 90.5(5)             | 0.62(1) | 0 | 27(3) | Zr$_3$Ni$_21$ |
|                | 4         | 57.3(9)             | 0.68(4) | 0 | 16(3) | Zr$_8$Ni$_{10}$ |
| 673            | 1         | 64.6(4)             | 0.18(7) | 0 | 34(3) | Zr$_2$Ni$_7$ |
|                | 2         | 71.3(9)             | 0      | 0 | 20(3) | ZrNi$_3$  |
|                | 3         | 87.7(6)             | 0.62(2) | 0 | 25(3) | Zr$_3$Ni$_21$ |
|                | 4         | 55.5(8)             | 0.66(3) | 0 | 21(3) | Zr$_8$Ni$_{10}$ |
| 773            | 1         | 63.1(6)             | 0.38(8) | 0 | 34(3) | Zr$_2$Ni$_7$ |
|                | 2         | 67.6(5)             | 0      | 0 | 22(3) | ZrNi$_3$  |
|                | 3         | 84.0(5)             | 0.59(1) | 0 | 20(3) | Zr$_3$Ni$_21$ |
|                | 4         | 53.5(4)             | 0.69(2) | 0 | 24(3) | Zr$_8$Ni$_{10}$ |
| 873            | 1         | 61.1(2)             | 0.36(3) | 0 | 48(3) | Zr$_2$Ni$_7$ |
|                | 2         | 68.8(8)             | 0      | 0 | 19(3) | ZrNi$_3$  |
|                | 3         | 81.7(9)             | 0.55(4) | 0 | 18(3) | Zr$_3$Ni$_21$ |
|                | 4         | 52(1)               | 0.75(3) | 0 | 15(3) | Zr$_8$Ni$_{10}$ |
| 973            | 1         | 60.3(5)             | 0.43(3) | 0 | 41(2) | Zr$_2$Ni$_7$ |
|                | 2         | 53.0(4)             | 0      | 0 | 39(2) | Hf       |
|                | 3         | 66(2)               | 0      | 0 | 8(2)  | ZrNi$_3$  |
|                | 4         | 78(2)               | 0.55(4) | 0 | 11(2) | Zr$_3$Ni$_21$ |
| 1073           | 1         | 52.0(1)             | 0      | 0 | 90(2) | Hf       |
|                | 2         | 60(1)               | 0.31(5) | 0 | 10(2) | Zr$_2$Ni$_7$ |
| 298†           | 1         | 56.5(1)             | 0      | 0 | 81(2) | Hf       |
|                | 2         | 71.9(8)             | 0.19(5) | 0 | 11(2) | Zr$_2$Ni$_7$ |
|                | 3         | 95(1)               | 0.65(3) | 0 | 8(2)  | Zr$_3$Ni$_21$ |

† after measurement at 1073 K
Table 2: Results of temperature dependent variations of $\omega_Q$ for different components in the stoichiometric samples of ZrNi$_3$ and HfNi$_3$.

| Component phases | $\omega_Q(0)$ (Mrad/s) | $V_{zz}(0)$ ($\times 10^{21}$ V/m$^2$) | $\alpha$ ($\times 10^{-4}$) K$^{-1}$ | $\beta$ ($\times 10^{-6}$) K$^{-3/2}$ |
|------------------|------------------------|-------------------------------------|--------------------------------|----------------------------------|
| Zr$_2$Ni$_7$     | 72.9(4)                | 8.2(1)                               | 6.2(4)                          |                                  |
| ZrNi$_3$         | 76(1)                  | 8.48(9)                              | 4.3(6)                          |                                  |
| Zr$_8$Ni$_{21}$  | 98.2(5)                | 11.0(2)                              | 6.5(3)                          |                                  |
| Zr$_7$Ni$_{10}$  | 64(2)                  | 7.28(5)                              | 2.3(3)                          |                                  |
| HfNi$_3$$^1$     | 32.9(4)                | 3.68(3)                              | 1.6(2)                          |                                  |
| HfNi$_3$$^3$     | 65.7(4)                | 7.3(1)                               | 7.0(4)                          |                                  |
| Hf$_2$Ni$_7$     | 72.2(4)                | 8.1(1)                               | 5.7(2)                          |                                  |
| Hf$_7$Ni$_{21}$  | 99.3(6)                | 11.1(2)                              | 6.6(4)                          |                                  |
| Hf               | 53.3(6)                | 5.95(6)                              | 0.8(2)                          |                                  |
Table 3: Results of PAC measurements in the stoichiometric HfNi$_3$ sample

| Temperature (K) | Component | $\omega_Q$ (Mrd/s) | $\eta$ | $\delta$(%) | $f$(%) | Assignment |
|----------------|-----------|---------------------|------|----------|------|----------------|
| 77             | 1         | 32.8(7)             | 0    | 0        | 26(2) | HfNi$_3$       |
|                | 2         | 66.0(7)             | 0    | 0        | 18(2) | HfNi$_3$       |
|                | 3         | 72.1(1)             | 0.19(8) | 0        | 15(2) | Hf$_2$Ni$_7$   |
|                | 4         | 100.1(5)            | 0.68(2) | 0        | 22(2) | Hf$_2$Ni$_7$   |
|                | 5         | 54.6(8)             | 0    | 0        | 19(2) | Hf             |
| 298            | 1         | 32.0(3)             | 0    | 0        | 32(2) | HfNi$_3$       |
|                | 2         | 64.3(8)             | 0    | 0        | 16(2) | HfNi$_3$       |
|                | 3         | 70.6(6)             | 0.39(3) | 0        | 15(2) | Hf$_2$Ni$_7$   |
|                | 4         | 94.8(6)             | 0.67(2) | 0        | 14(2) | Hf$_2$Ni$_7$   |
|                | 5         | 52.6(4)             | 0    | 0        | 23(2) | Hf             |
| 373            | 1         | 31.4(5)             | 0    | 0        | 30(2) | HfNi$_3$       |
|                | 2         | 69.1(7)             | 0    | 0        | 18(2) | HfNi$_3$       |
|                | 3         | 70.1(1)             | 0.25(fixed) | 0 | 12(2) | Hf$_2$Ni$_7$   |
|                | 4         | 94.0(6)             | 0.69(2) | 0        | 22(2) | Hf$_2$Ni$_7$   |
|                | 5         | 51.1(7)             | 0    | 0        | 18(2) | Hf             |
| 473            | 1         | 29.8(4)             | 0    | 0        | 30(2) | HfNi$_3$       |
|                | 2         | 69.1(7)             | 0    | 0        | 18(2) | HfNi$_3$       |
|                | 3         | 67.9(6)             | 0.20(6) | 0        | 19(2) | Hf$_2$Ni$_7$   |
|                | 4         | 91.9(6)             | 0.65(2) | 0        | 19(2) | Hf$_2$Ni$_7$   |
|                | 5         | 51.7(7)             | 0    | 0        | 19(2) | Hf             |
| 573            | 1         | 29.1(6)             | 0    | 0        | 25(2) | HfNi$_3$       |
|                | 2         | 58.1(1)             | 0    | 0        | 17(2) | HfNi$_3$       |
|                | 3         | 65.1(1)             | 0.17(9) | 0        | 19(2) | Hf$_2$Ni$_7$   |
|                | 4         | 90.8(7)             | 0.66(2) | 0        | 21(2) | Hf$_2$Ni$_7$   |
|                | 5         | 49.9(5)             | 0    | 0        | 18(2) | Hf             |
| 673            | 1         | 29.2(6)             | 0    | 0        | 31(2) | HfNi$_3$       |
|                | 2         | 56.3(2)             | 0    | 0        | 7(2)  | HfNi$_3$       |
|                | 3         | 64.1(1)             | 0.38(6) | 0        | 17(2) | Hf$_2$Ni$_7$   |
|                | 4         | 87.5(8)             | 0.66(3) | 0        | 23(2) | Hf$_2$Ni$_7$   |
|                | 5         | 49.6(7)             | 0    | 0        | 22(2) | Hf             |
| 773            | 1         | 28.2(6)             | 0    | 0        | 32(2) | HfNi$_3$       |
|                | 2         | 56.2(9)             | 0    | 0        | 17(2) | HfNi$_3$       |
|                | 3         | 62.1(1)             | 0.31(7) | 0        | 19(2) | Hf$_2$Ni$_7$   |
|                | 4         | 87.1(1)             | 0.68(6) | 0        | 12(2) | Hf$_2$Ni$_7$   |
|                | 5         | 49.5(5)             | 0    | 0        | 19(2) | Hf             |
| 873            | 1         | 28.6(6)             | 0    | 0        | 33(2) | HfNi$_3$       |
|                | 2         | 54.2(2)             | 0    | 0        | 19(2) | HfNi$_3$       |
|                | 3         | 61.1(1)             | 0.34(6) | 0        | 17(2) | Hf$_2$Ni$_7$   |
|                | 4         | 81.1(1)             | 0.70(4) | 0        | 19(2) | Hf$_2$Ni$_7$   |
|                | 5         | 49.9(1)             | 0    | 0        | 13(2) | Hf             |
| 973            | 1         | 28.2(4)             | 0    | 0        | 31(2) | HfNi$_3$       |
|                | 2         | 52.1(7)             | 0    | 0        | 16(2) | HfNi$_3$       |
|                | 3         | 59.9(3)             | 0.31(2) | 0        | 27(2) | Hf$_2$Ni$_7$   |
|                | 4         | 49(1)               | 0    | 0        | 5(2)  | Hf             |
| 1073           | 1         | 28(1)               | 0    | 0        | 39(2) | HfNi$_3$       |
|                | 2         | 53(4)               | 0    | 0        | 25(2) | HfNi$_3$       |
|                | 3         | 58(1)               | 0.47(9) | 0        | 27(2) | Hf$_2$Ni$_7$   |
|                | 4         | 50(4)               | 0    | 0        | 9(2)  | Hf             |
| 298$^\dagger$ | 1         | 31.6(3)             | 0    | 0        | 49(2) | HfNi$_3$       |
|                | 2         | 70(2)               | 0    | 0        | 10(2) | HfNi$_3$       |
|                | 3         | 71(1)               | 0.50(5) | 0        | 17(2) | Hf$_2$Ni$_7$   |
|                | 4         | 51.9(7)             | 0    | 0        | 23(2) | Hf             |

$^\dagger$ after measurement at 1073 K
Table 4: The parameters of the $\beta$-HfNi$_3$ and ZrNi$_3$ structure, given in Å.

|                | Our calculated results | Experimental results (X-ray diffraction) | Earlier calculated results (WIEN 2k) |
|----------------|------------------------|------------------------------------------|-------------------------------------|
| **HfNi$_3$**  |                        |                                          |                                     |
| $a$            | 5.285                  | 5.282(3)                                 | 5.267                               |
| $c$            | 21.419                 | 21.391(18)                               | 21.411                              |
| $B$ [GPa]      | 186                    |                                          |                                     |
| Hf 2b          | 0 0 1/4                | 0 0 1/4                                  | 0 0 1/4                             |
| Hf2 4f         | 1/3 2/3 0.3488         | 1/3 2/3 0.3488                           | 1/3 2/3 0.3489                      |
| Hf3 4f         | 1/3 2/3 0.5458         | 1/3 2/3 0.5458                           | 1/3 2/3 0.5461                      |
| Ni 6h          | 0.5110 0.022 1/4       | 0.5117 0.024 1/4                        | 0.5107 0.0213 1/4                  |
| Ni2 12k        | 0.156 0.312 0.0514     | 0.156 0.312 0.0514                       | 0.1563 0.3126 0.0512               |
| Ni3 12k        | 0.8320 0.6640 0.1495   | 0.8316 0.6632 0.1495                     | 0.8322 0.6645 0.1496               |
| **ZrNi$_3$**   |                        |                                          |                                     |
| $a$            | 5.319                  | 5.309                                    | 5.267                               |
| $c$            | 4.305                  | 4.303                                    | 21.411                              |
| $B$ [GPa]      | 177                    |                                          |                                     |
| Zr 2c          | 1/3 2/3 1/4            | 1/3 2/3 1/4                              | 1/3 2/3 1/4                         |
| Ni 6h          | 0.8435 0.687 1/4       | 0.829 0.658 1/4                          | 0.844291 0.688581 1/4              |
Table 5: The interatomic distances (Å) less than 3.5 Å in β-HfNi₃.

| Number of bonds | Interatomic distances measured from X-ray diffraction [25] | Interatomic distances calculated from the WIEN2k |
|----------------|------------------------------------------------------------|--------------------------------------------------|
| Hf1            |                                                            |                                                  |
| Hf1-Ni1 6      | 2.643(4)                                                   | 2.645                                            |
| Hf1-Ni3 6      | 2.644(4)                                                   | 2.648                                            |
| Hf2            |                                                            |                                                  |
| Hf2-Ni3 6      | 2.642(3)                                                   | 2.643                                            |
| Hf2-Ni2 3      | 2.682(5)                                                   | 2.684                                            |
| Hf2-Ni1 3      | 2.670(2)                                                   | 2.673                                            |
| Hf3            |                                                            |                                                  |
| Hf3-Ni2 3      | 2.638(5)                                                   | 2.640                                            |
| Hf3-Ni2 6      | 2.646(3)                                                   | 2.647                                            |
| Hf3-Ni3 3      | 2.684(5)                                                   | 2.686                                            |
| Ni1            |                                                            |                                                  |
| Ni1-Ni1 2      | 2.455(1)                                                   | 2.457                                            |
| Ni1-Ni3 4      | 2.603(5)                                                   | 2.605                                            |
| Ni1-Hf1 2      | 2.643(4)                                                   | 2.645                                            |
| Ni1-Hf2 2      | 2.670(2)                                                   | 2.673                                            |
| Ni1-Ni1 2      | 2.827(1)                                                   | 2.828                                            |
| Ni2            |                                                            |                                                  |
| Ni2-Ni2 2      | 2.471(8)                                                   | 2.474                                            |
| Ni2-Ni3 2      | 2.571(6)                                                   | 2.575                                            |
| Ni2-Ni2 2      | 2.623(8)                                                   | 2.624                                            |
| Ni2-Hf3 1      | 2.638(5)                                                   | 2.640                                            |
| Ni2-Hf3 2      | 2.646(3)                                                   | 2.647                                            |
| Ni2-Hf2 1      | 2.682(5)                                                   | 2.684                                            |
| Ni2-Ni2 2      | 2.812(8)                                                   | 2.812                                            |
| Ni3            |                                                            |                                                  |
| Ni3-Ni2 2      | 2.571(6)                                                   | 2.575                                            |
| Ni3-Ni1 2      | 2.603(5)                                                   | 2.605                                            |
| Ni3-Ni3 2      | 2.616(8)                                                   | 2.615                                            |
| Ni3-Hf2 2      | 2.642(3)                                                   | 2.643                                            |
| Ni3-Hf1 1      | 2.644(4)                                                   | 2.648                                            |
| Ni3-Ni3 2      | 2.666(8)                                                   | 2.670                                            |
| Ni3-Hf3 1      | 2.684(5)                                                   | 2.686                                            |
Table 6: Calculated EFG values for HfNi₃ in units of $10^{21} \text{ V/m}^2$ and asymmetry parameters

| Probe         | Lattice Site | EFG          | asymmetry parameter ($\eta$) |
|---------------|--------------|--------------|-----------------------------|
| no probe      | Hf₁ 2b 0 0 1/4 | -1.3         | 0                           |
| (pure compound) | Hf₂ 4f 1/3 2/3 0.3488(2) | -5.0 | 0                           |
|               | Hf₃ 4f 1/3 2/3 0.5458(1) | -2.2 | 0                           |
| ¹⁸¹Ta         | Hf₁ 2b 0 0 1/4 | -1.7         | 0                           |
|               | Hf₂ 4f 1/3 2/3 0.3488(2) | -7.1 | 0                           |
|               | Hf₃ 4f 1/3 2/3 0.5458(1) | -3.5 | 0                           |