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Abstract: The hyperfine interaction experienced by ¹⁸¹Ta nuclei in the intermetallic compounds ZrNi₅, HfNi₅ and Hf₂Ni₇ has been investigated by perturbed angular correlation (PAC) measurements, in a temperature range $15 \text{ K} \geq T \geq 1,200 \text{ K}$. The temperature dependence of the electric quadrupole interaction of ¹⁸¹Ta in Hf₂Ni₇ suggests the existence of a reversible phase transformation at $T \geq 500 \text{ K}$.

Key Words: hyperfine interaction, magnetism, angular correlation

Introduction: Previous studies of the intermetallic compound ZrNi₅ have lead to diverging conclusions concerning their magnetic properties^(1,2,3,4). Nuclei in ferromagnetic solids experience a magnetic hyperfine field (MHF) $B_{\text{hf}}^{(1)}$. Ferromagnetic order can therefore be detected by observing the resulting Larmor precession of nuclear magnetic moments with frequency $\omega_m = 2\pi\nu_m = g\mu_N B_{\text{hf}} / \hbar$, (g denotes the nuclear g factor). In this NF we report a search for spontaneous magnetic order of ZrNi₅ and HfNi₅ by looking for the existence of a (MHF) at the Zr(Hf) site.

The search was carried out with the perturbed angular correlation (PAC) technique⁽⁵⁾. The angular correlation (AC) of two successive γ -rays of a $\gamma\gamma$ -cascade in nuclear decay may be modulated in time by hyperfine interactions (HI) in the intermediate state of the cascade. The observation of the time-dependence of an AC therefore provides information on magnetic and electric HI in condensed matter. In the present study, the isotope ¹⁸¹Ta [¹⁸⁰Hf(n, γ)¹⁸¹Hf \rightarrow ¹⁸¹Ta] was used as nuclear probe, a very convenient one for measuring HI in (Hf,Zr)-compounds which also stimulated, beside the innerent problems related to these compounds, several previous contributions in this research area, part of it here refered^(6,7,8). As far as the Zr(Hf) site has cubic symmetry, a nuclear quadrupole interaction for ¹⁸¹Ta on these sites can thus be excluded. In case the host compound Zr(Hf)Ni₅ presents spontaneous magnetic order, one therefore expects a perturbation by a pure magnetic HI; in the absence of magnetic order the AC will be unperturbed, i.e. constant in time.

At the Ni-rich end the phase diagrams of the binary Zr-Ni and Hf-Ni systems⁽⁹⁾ are rather similar with both showing the phases Zr(Hf)Ni₅ and Zr(Hf)₂Ni₇, eventually difficult to separate with strong dependence on cooling speed from the melt. For the identification of eventual Zr(Hf)₂Ni₇ contributions to the PAC spectra of ¹⁸¹Ta:Zr(Hf)Ni₅, we have also studied the HI of ¹⁸¹Ta in the isotopic compound of Zr₂Ni₇⁽¹⁰⁾, Hf₂Ni₇, as a function of temperature.

1) Experimental -

1.1 - Sample Preparation: PAC samples of ZrNi₅, HfNi₅ and Hf₂Ni₇ were produced by melting stoichiometric amounts of the metallic components -together with about 0.1 at. % of radioactive ¹⁸¹Hf metal- in an arc furnace under argon atmosphere. Inactive samples for XRD studies were prepared in the same way. In the as-prepared state, at RT, the samples of ZrNi₅ and HfNi₅ were found to be ferromagnetic. The spontaneous magnetization, an observations already reported⁽¹¹⁾, disappeared after annealing for 100 h at 1,500 K. No spontaneous magnetization was found for Hf₂Ni₇.

1.2 - Characterization by XRD: because its formation through a peritectic reaction, homogenisation of a sample of Zr(Hf)Ni₅ rapidly cooled from the melt requires annealing at high temperatures. We have studied the effect of a high-temperature treatment of rapidly cooled Zr(Hf)Ni₅ both with XRD and PAC: Fig. 1 shows the XRD pattern of HfNi₅ in the as-prepared state and after annealing at 1500 K for 100 h . The pattern of annealed ZrNi₅ was identical to that of HfNi₅. The spectra – taken at RT with K_{α} radiation – mainly consist of the pattern of a AuBe₅-type compound and agree in the main features with the ZrNi₅ spectra already reported^(4,12,13). The lattice parameter derived from the spectra in Fig. 1 [$a = 0.6686(10) \text{ nm}$ and $0.6706(10) \text{ nm}$, for HfNi₅ and ZrNi₅, respectively] also agree with the values previously reported^(4,12,13) for ZrNi₅.

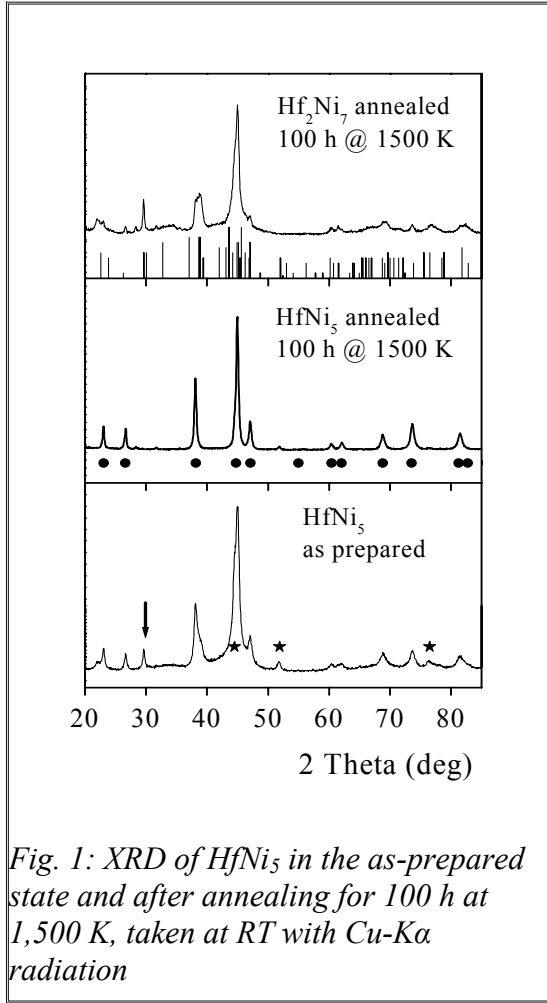


Fig. 1: XRD of HfNi_5 in the as-prepared state and after annealing for 100 h at 1,500 K, taken at RT with $\text{Cu-K}\alpha$ radiation

In addition to the peaks of a AuBe_5 -type compound, the spectrum of as-prepared HfNi_5 shows the main reflections of elemental fcc Ni (marked by the full stars in lower section of Fig. 1) and lines characteristic for Hf_2Ni_7 [see the peak at $2\theta \sim 30$ deg both in the bottom (HfNi_5) and top-most (Hf_2Ni_7) section of Fig.1]. After annealing at 1500 K, the peaks of Hf_2Ni_7 and those of fcc Ni have disappeared from the spectrum of HfNi_5 . The presence of Ni-reflections and their disappearance upon annealing indicate that the magnetization observed for as-prepared $\text{Hf}(\text{Zr})\text{Ni}_5$ can be attributed to Ni precipitates.

1.3) ^{181}Ta PAC Measurements -

1.3.1) Equipment and data analysis: the PAC spectra were recorded with a standard 4-detector set-up equipped with fast BaF_2 scintillators. Temperatures were varied between 290 K and 1400 K with a PAC furnace⁽¹⁴⁾; for temperatures $290 \text{ K} > T \geq 15 \text{ K}$ it was used a closed-cycle He refrigerator: Fig. 2 shows the RT PAC spectra of HfNi_5 and ZrNi_5 in the as-prepared state and of ZrNi_5 after annealing for 10 d at 900 K (conditions used by Drulis et al.⁽⁴⁾). Spectra of HfNi_5 recorded in the temperature range $15 \text{ K} \leq T \leq 1200 \text{ K}$ are collected in Fig. 3.

For polycrystalline samples the modulation of an AC by HI can be described by a perturbation factor $G_{kk}(t)$ which depends on the multipole order, the symmetry and time dependence of the interaction, and on the spin of the intermediate state (for details see, e.g., Frauenfelder and Steffen⁽⁵⁾). For a

pure static magnetic interaction, the perturbation factor is a function of only the Larmor frequency $\omega_m = 2\pi\nu_m = g\mu_N B_{hf} / \hbar$, in case of a static electric quadrupole interaction between the nuclear quadrupole moment Q and an electric field gradient (EFG) at the nuclear site, $G_{kk}(t)$ depends – apart from the nuclear spin I – on two parameters: the quadrupole frequency $\nu_q = eQV_{zz}/h$ and the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ where $V_{ii} = d^2V/di^2$ ($i = x, y, z$) are the principal-axes components of the EFG tensor. When several fractions of nuclei subject to different HI are found in the same sample, the effective perturbation factor is given by:

$$G_{kk}(t) = f_i \sum_i G_{kk}^i(t) \quad \text{with} \quad \sum_i f_i = 1 \quad \text{and} \quad f_i \text{ is the relative}$$

intensity of the i -th fraction. The absence of a perturbing HI is evidenced by $G_{kk}(t) = 1$.

1.3.2) Results - The PAC results include: RT spectra of HfNi_5 , and ZrNi_5 in the as-prepared state and of ZrNi_5 after annealing for 10 d at 900 K (Fig. 2/Table I) are characterized by a non-periodic oscillatory modulation of the anisotropy with time: the spectra consist of a superposition of three components $-I$ (red lines) showing a slowly decaying anisotropy which can in principle be reproduced by both a

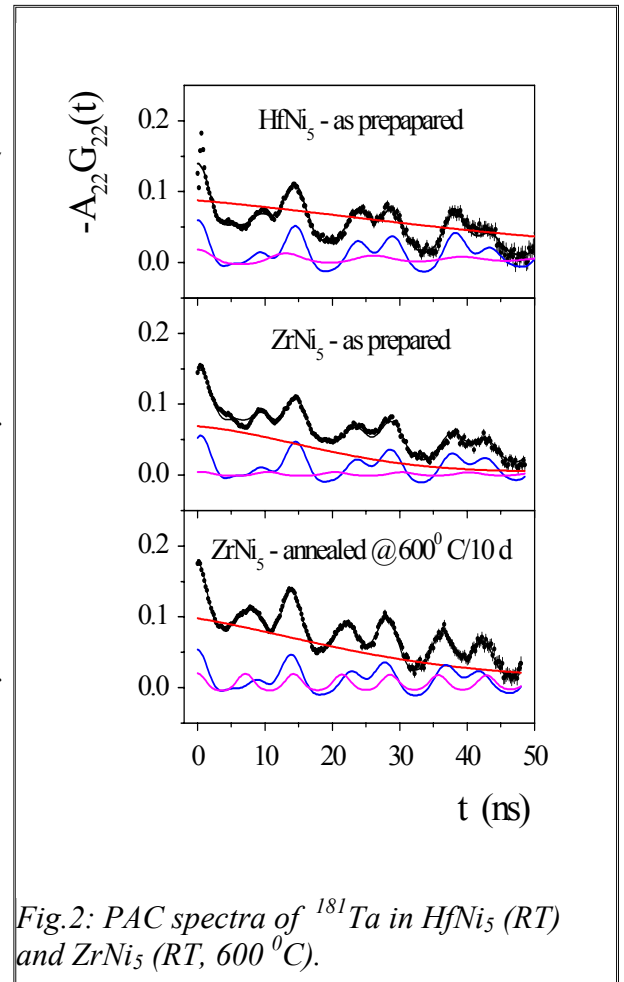


Fig.2: PAC spectra of ^{181}Ta in HfNi_5 (RT) and ZrNi_5 (RT, 600 °C).

very weak magnetic dipole or electric quadrupole interaction; II, III (blue and magenta lines) presenting an oscillatory behaviour, due to perturbations by axially asymmetric quadrupole interactions-. All the three components safely exclude the possibility of a magnetic perturbation. Also, according to these PAC spectra, if existing, as-prepared Hf(Zr)Ni₅ remains below the limit of detection ($\leq 5\%$). Furthermore (see Table I) there is little –if any– difference in the parameters ν_q and η of ZrNi₅ and HfNi₅.

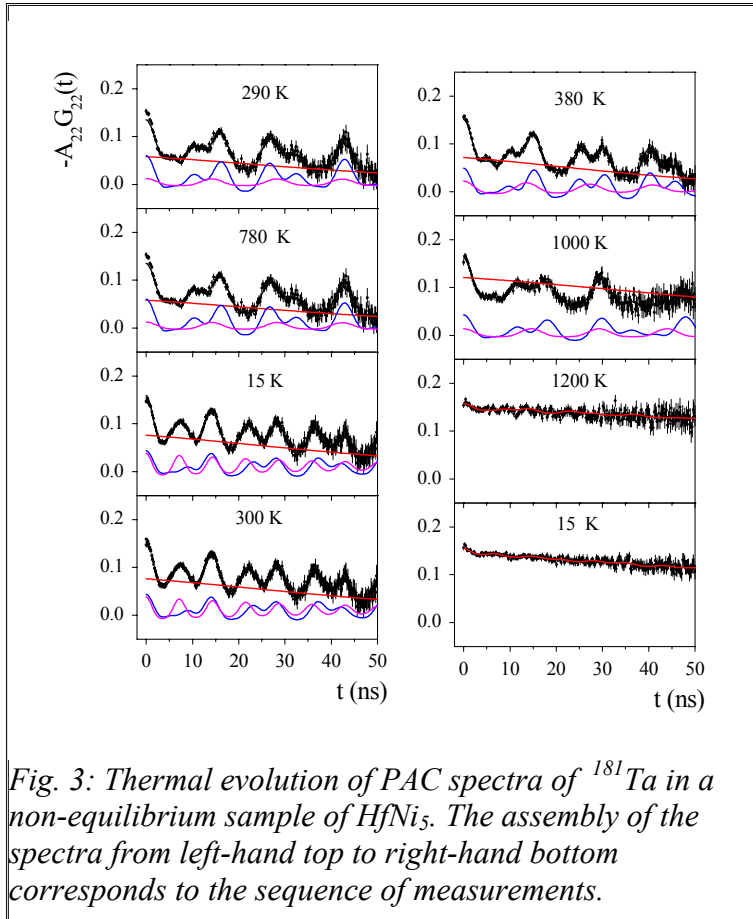


Fig. 3: Thermal evolution of PAC spectra of ¹⁸¹Ta in a non-equilibrium sample of HfNi₅. The assembly of the spectra from left-hand top to right-hand bottom corresponds to the sequence of measurements.

fractions (see Fig. 5) therefore clearly identifies component-I as Hf(Zr)Ni₅ and relates components II, III to Hf₂Ni₇. The observation that the AC of properly annealed Hf(Zr)Ni₅ is unperturbed constitutes unambiguous evidence for the absence of spontaneous magnetic order in Hf(Zr)Ni₅ at $T \geq 15$ K.

1.3.2.3 – In order to better characterize the eventual presence of Hf₂Ni₇, identified by components-II,III (bottom line in Table I) and which differ substantially from those announced for the same compound⁽¹³⁾, we have taken PAC spectra ¹⁸¹Ta/Hf₂Ni₇ in the temperature range $15 \text{ K} \leq T \leq 1200 \text{ K}$ (Fig. 4): from the two adjusted components the dominant one (rel. intensity ≥ 0.9) with a well defined oscillatory structure is superimposed on a slowly decreasing baseline, whose decay can be reproduced by a broad QI distribution centred at $\nu_q \sim 25$ MHz. The similarity of this value with that of the component-I in Hf(Zr)Ni₅ (Table I) suggests that our sample of Hf₂Ni₇ contains a slight HfNi₅ contamination. The perturbation factor of the majority component of the Hf₂Ni₇ spectra depends on the thermal history of the compound: at

Also, annealing up to 900 K leaves the relative intensities unchanged; the frequency of component-III, however, undergoes a drastic change from $\nu_q \sim 280$ MHz to $\nu_q \sim 500$ MHz.

1.3.2.2 - $15 \text{ K} \leq T \leq 1200 \text{ K}$ spectra of HfNi₅, and ZrNi₅ (Fig. 3), show for the first compound two interesting aspects: (i) the frequency of component-III, when cooled from 780 K, increases drastically by almost a factor of 2; this change which can also be seen in Fig.2 for ZrNi₅ is fully reversible by heating to $T > 350$ K. (ii) At $T \sim 1000$ K the relative intensity of the component-I starts to increase at the expense of the oscillatory components and at $T = 1200$ K the oscillations have irreversibly disappeared, and with its anisotropy practically constant in time, *i.e.* unperturbed and this behaviour persists when the sample is cooled to 15 K, a behaviour also found for ZrNi₅. From the XRD pattern of Hf(Zr)Ni₅ we know that high temperature annealing eliminates Hf₂Ni₇ and Ni precipitates and produces a single-phase Hf(Zr)Ni₅ compound. The temperature dependence of the

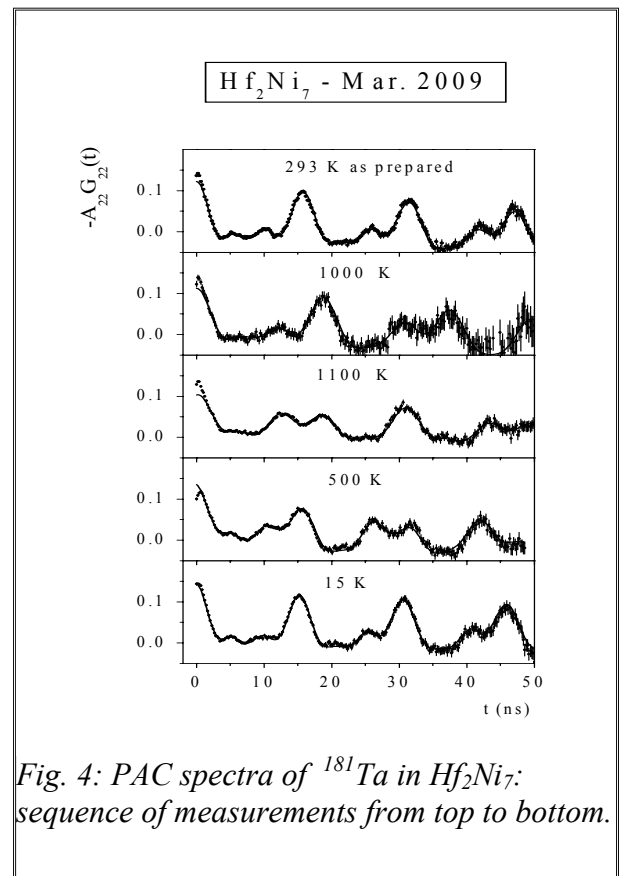


Fig. 4: PAC spectra of ¹⁸¹Ta in Hf₂Ni₇: sequence of measurements from top to bottom.

RT one observes an almost periodic, practically non-damped oscillation pattern which reflects⁽⁵⁾ a perturbation by a unique, almost axially symmetric EFG. At $T \sim 1050$ K, however, the asymmetry parameter increases abruptly from $\eta = 0.23$ to $\eta = 0.53$, producing a non-periodic pattern. This increase is reversible with a hysteresis of about 550 K: at $T \sim 470$ K, the pattern returns to near-periodicity.

The main results of the least-squares fit analysis of the HfNi_5 and Hf_2Ni_7 spectra are collected in Fig. 5 which shows fractions and QI parameters ν_q and η as a function of temperature.

2) Discussion - As the main result of the present investigation, spontaneous magnetic order of $\text{Hf}(\text{Zr})\text{Ni}_5$ can be definitely ruled out for temperatures $T \geq 15$ K. After appropriate annealing, all oscillatory components in the PAC spectra have disappeared and the angular correlation is unperturbed at $T \geq 15$ K which is unambiguous evidence for the absence of a magnetic hyperfine field.

As a by-product, the study established some new features of the ^{181}Ta QI and the structure of Hf_2Ni_7 . First, there is the observation that - in contrast to the previous PAC study⁽¹³⁾ of Hf_2Ni_7 - the PAC spectra in Fig. 4 are well described by a single, rather sharp QI (apart from the minority component attributed to HfNi_5). Since the $C2/m$ structure of $\text{Hf}(\text{Zr})_2\text{Ni}_7$ contains two non-equivalent Zr(Hf) sites with fourteen Ni and two Hf(Zr) nearest neighbours each, a single QI implies that the EFG's at the two Hf(Zr) sites must be quite similar. Inspection of the structure shows that the differences of the nearest-neighbour Ni and Hf(Zr) environments of the Hf(Zr) sites are in fact only very slight and in a point-charge estimate the EFG's at the two Hf(Zr) sites produced by the Ni- and the Zr-sublattice, respectively, differ by less than 10 percent. A confirmation by an ab-initio calculation of the EFG would be valuable.

Second, the abrupt increase of the asymmetry parameter at $T \sim 1050$ K and its decrease at $T \sim 470$ K (Fig. 5) suggest a reversible phase transformation in Hf_2Ni_7 . Indications for the existence of two different structures of Hf_2Ni_7 have also been found⁽¹⁰⁾, with reporting that mechanical deformation possibly transforms the $C2/m$ RT structure $\text{Hf}_2\text{Ni}_{7,r}$ into a hexagonal high-temperature phase $\text{Hf}_2\text{Ni}_{7,h}$.

The chief objective of the auxiliary PAC study of Hf_2Ni_7 (Fig. 4) was the identification of the oscillatory components found in the PAC spectra of "as-prepared" $\text{Hf}(\text{Zr})\text{Ni}_5$. This goal was only partly attained. Because of the similarity in the temperature dependence of the quadrupole frequency ν_q (see Fig. 5) there can be little doubt that component-II of these spectra (Figs. 2,3,5) represents precipitates of Hf_2Ni_7 . Interestingly, the asymmetry parameter η of component-II follows the trend observed in Hf_2Ni_7 when cooling from 1200 K which suggests that Hf_2Ni_7 precipitates in the high temperature phase when HfNi_5 is quenched from the melt. The interpretation of component-III is at present not clear. The observation that with increasing temperature component-III transforms into component-II (Fig. 5) suggests a relation to Hf_2Ni_7 . An understanding of the sharp transition of the quadrupole frequency at 285 K, however, requires further studies by other techniques: XRD at different temperatures might be helpful.

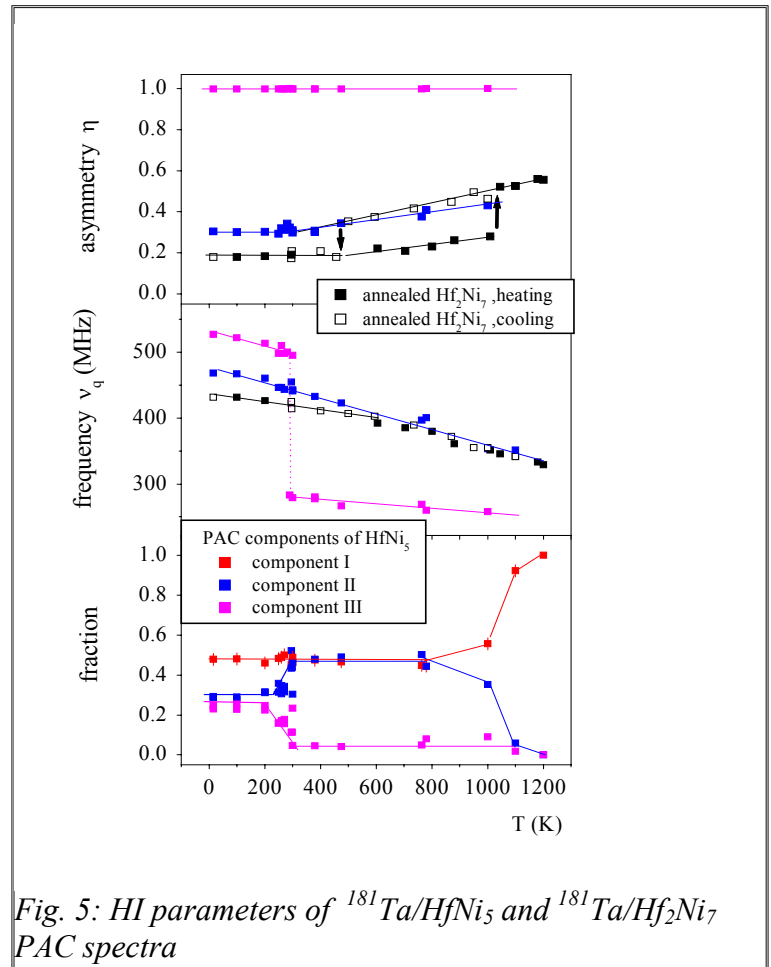


Fig. 5: HI parameters of $^{181}\text{Ta}/\text{HfNi}_5$ and $^{181}\text{Ta}/\text{Hf}_2\text{Ni}_7$ PAC spectra

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