

PERTURBED ANGULAR CORRELATION INVESTIGATION OF THE ELECTRIC FIELD GRADIENT AT ^{181}Ta PROBE IN THE Hf_2Ni_7 COMPOUND

by

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The perturbed angular correlation method was employed to study the temperature dependence of electric field gradients at the ^{181}Ta probe in the polycrystalline Hf_2Ni_7 compound. The temperature evolution of the sample content was measured using high-temperature X-ray diffraction. To check the magnetic order of the sample, magnetization measurements and additional perturbed angular correlation measurements with externally applied magnetic field were performed. All obtained spectra showed no evidence of magnetic order of the Hf_2Ni_7 phase. Within the experimental resolution of the apparatus, the measured electric field gradients at ^{181}Ta probe for the two inequivalent $^{181}\text{Hf}/^{181}\text{Ta}$ sites in the Hf_2Ni_7 compound appeared as one in the range of 78-944 K. A single quadrupole interaction implies that the electric field gradients at the two Hf sites must be quite similar. At 293 K, the measured quadrupole interaction parameters are $\nu_Q = 433(1)$ MHz and $\eta = 0.300(4)$. An increase of the quadrupole frequency and a gradual rising of the asymmetry parameter were observed with increasing temperature. The high-temperature X-ray diffraction indicated a build up of HfO_2 above 693 K.

Key words: intermetallics, hyperfine interactions, perturbed angular correlation, magnetization, X-ray diffraction

INTRODUCTION

The perturbed angular correlation method is based on the interactions of an excited intermediate nuclear state of a γ - γ cascade with the external hyperfine fields present at the probe site. The measured electric field gradients (EFG) and/or magnetic hyperfine fields (MHF) at the probe site can also be determined as a function of the various macroscopic parameters and previous thermal, pressure or other sample treatments. The perturbed angular correlation (PAC) method is proven to give an abundance of information on various properties and the arrangement of the system under investigation. For example, as the EFG depends on the charge distribution of the probe-nucleus environment, applying the PAC technique in a wide temperature range, the temperature evolution of the lattice properties such as crystallographic structure, imperfections or defects can be monitored. A detailed description of the PAC method is given in ref. [1].

The hyperfine interactions of ^{181}Ta in Hf_2Ni_7 were previously investigated by several groups [2-4]. The collected data and assignments are not consistent. There are discrepancies regarding the possibility of magnetism and the number, strength and temperature behavior of quadrupole interaction frequencies for ^{181}Ta probe in this compound. Gerda *et al.* [2] found a dominant hyperfine magnetic field of $H_{\text{hf}} = 6.81(6)$ T combined with the electric hyperfine field of the strength $\omega_Q = 14.4(2)$ MHz and of the axial symmetry ($\eta = 0$) at room temperature. Also, the authors suggested existence of several other hyperfine interactions of unknown origin, possibly partly from interstitials. Marszalek *et al.* [3] measured two electric quadrupole interactions: $\nu_{Q1}(300\text{ K}) = 586.7(65)$ MHz with $\eta_1 = 0.79(4)$ and $\nu_{Q2}(300\text{ K}) = 466.8(41)$ MHz with $\eta_2 = 0.20(3)$. The descending temperature behavior of the quadrupole frequencies and almost constant asymmetry parameters with increasing temperature were found. Very recently, Silva *et al.* [4] described one dominant quadrupole interaction concluding that the EFG at the two inequivalent ^{181}Ta -sites in the Hf_2Ni_7 are quite similar. At room temperature, the dominant component deduced was characterized with $\nu_Q = 419(2)$ MHz and $\eta = 0.19(1)$.

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The Hf_2Ni_7 compound was studied using perturbed angular correlation method and high-temperature X-ray diffraction (HT-XRD). The aim was to remove the present ambiguities and provide reliable experimental results for comparison in forthcoming ab-initio calculations. Two separate series of PAC measurements without applying an external field were made in the temperature range of 78-897 K and 293-944 K. The PAC measurements with the polarizing external field at room temperature and additional magnetization measurements (1.8-350 K) were performed in order to investigate possible magnetic properties of the Hf_2Ni_7 compound. The obtained PAC spectra showed no evidence of magnetic ordering in Hf_2Ni_7 . The PAC data were finally fitted with one electric quadrupole interaction. The obtained hyperfine interaction parameters for ^{181}Ta in the Hf_2Ni_7 are consistent with the presumption of very similar EFG at the two inequivalent Ta probe sites.

METHODS AND PROCEDURES

The Hf_2Ni_7 polycrystalline compound was prepared by multiple arc melting of metallic Hf (98.5% Hf and 1.5% Zr) with high purity metallic Ni (99.999%), in an argon atmosphere. Buttons were turned several times to ensure homogeneity. Afterwards, three pieces were cut from the sample and prepared for the PAC, HT-XRD and magnetization measurements. Dattagupta *et al.* [5] have shown that the Hf_2Ni_7 compound is isotopic to the Zr_2Ni_7 , with a monoclinic crystal structure with C2/m space group symmetry. The atomic array is pseudo-hexagonal normal to the a- and b-axes. There are two different crystallographic positions of Hf with the same symmetry (4i) in the compound. Each Hf atom in the Hf_2Ni_7 structure is surrounded with 2 other Hf atoms and with 14 other Ni atoms (fig. 1), making total co-ordination spheres of 16 nearest neighbors with remarkably similar interatomic distances.

To check the crystallographic structure of Hf_2Ni_7 sample, X-ray diffraction measurement at 300 K was made using a Rigaku Miniflex with Cu K_α

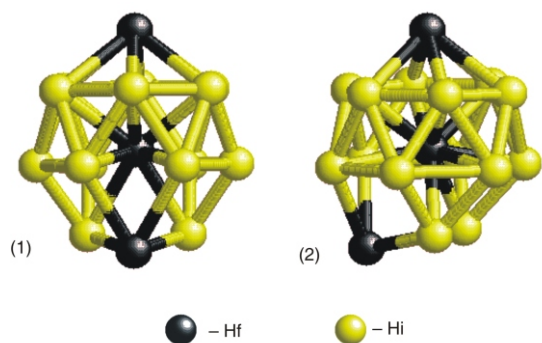


Figure 1. Nearest neighbors of the two inequivalent Hf sites in the Hf_2Ni_7

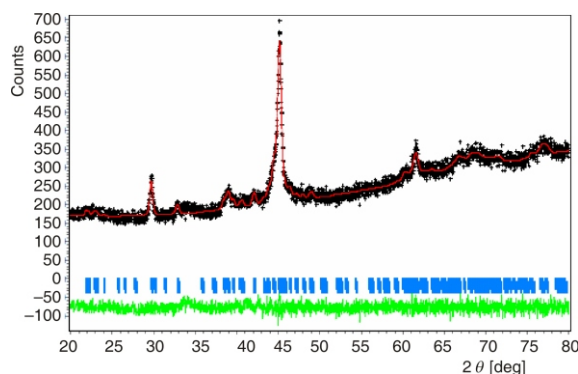


Figure 2. XRD (Cu K_α) pattern of the as-prepared Hf_2Ni_7 at 300 K. The peaks are indexed for the monoclinic structure (C2/m)

radiation ($\lambda = 1.5418 \cdot 10^{-10}$ m). It was difficult to obtain fine powder for XRD measurement, since the alloy has shown rather tough behavior. An attempt was made to determine the main peaks belonging to the Hf_2Ni_7 structure, in spite of lesser quality of collected XRD data and complexity of its crystal structure. The lattice parameters were obtained by fitting the XRD pattern of the Hf_2Ni_7 (fig. 2) with the Rietica software [6].

The XRD analysis of the Hf_2Ni_7 sample spectra taken at 300 K confirmed the Zr_2Ni_7 type (C2/m) monoclinic structure with the unit cell parameters: $a = 4.664(2)$, $b = 8.187(3)$, and $c = 12.149(5) \cdot 10^{-10}$ m, in fair agreement with previously published results [5]. It was estimated that there are less than 5% of impurity phases present in the investigated sample. The temperature evolution of the Hf_2Ni_7 sample crystal structure was monitored by high-temperature X-ray diffraction on a PANalytical X'Pert Pro MPD device (Co K_α). An Anton Paar HTK-6 oven with a Pt heating stripe was employed for HT-XRD measurements from 298 to 873 K, in steps of 25 K. The HT-XRD analysis was done with X'Pert High Score Plus software using commercial databases [7]. Magnetization measurements of magnetic susceptibility of Hf_2Ni_7 were performed using Quantum Design MPMS-XL 5 (1.8-350 K). Magnetization measurements showed that the magnetic susceptibility of Hf_2Ni_7 (fig. 3) is paramagnetic down to about 10 K, where it shows a broad antiferromagnetic peak.

The excited states of ^{181}Ta probe, used in the PAC method, are populated in the β decay of the 42 d ^{181}Hf isotope, produced in the reactor by exposing Hf to a thermal neutron flux higher than 10^{14} n/($\text{cm}^2 \cdot \text{s}$). Before the irradiation, the sample was sealed in high vacuum in a quartz ampoule. The radiation damage in the sample was minimized with the annealing for 8 days at 1223 K. The PAC measurements of the polycrystalline Hf_2Ni_7 were performed with the 133-482 keV γ - γ cascade of ^{181}Ta ion probe. The spectra were collected with three BaF_2 detectors in a fast-slow coincidence set up. The time resolution (τ_R)

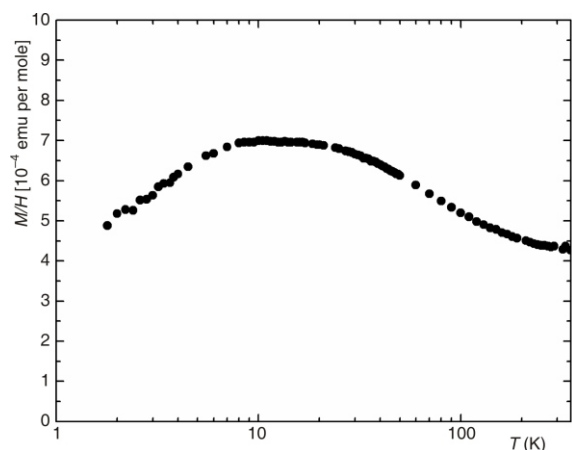


Figure 3. Magnetic susceptibility of the Hf_2Ni_7 sample in the range of 1.8-350 K, $H = 79577.5$ A/m

for the mentioned γ - γ cascade was around 1 ns. For PAC measurements above ambient temperature the quartz ampoule was mounted in a furnace, for 78 K-measurement a liquid nitrogen cryostat was used. It should be pointed out that the irradiated Hf_2Ni_7 sample was actually heated three times: (1) 1st – heating, *i. e.* annealed for 8 days at 1223 K, (2) 2nd – heating up from 78 to 897 K, and (3) 3rd – heating up from 293 to 944 K. The PAC measurements without applied external magnetic field were made during the 2nd- and 3rd-heating (the first and second PAC runs).

The PAC measurements with applied field and different geometries could provide additional information concerning the nature of the investigated hyperfine interactions. At room temperature, in the two PAC arrangements with the applied field $H_{\text{ext}} = 1.5$ kG, the field was maintained perpendicular to the plane of the BaF_2 detectors. In the first arrangement, the detectors were positioned at fixed angles $\theta = 90^\circ$ and 180° with external field applied up ($+H_{\text{ext}}$). For the second arrangement, the detectors were at fixed angles $\theta = 225^\circ$ and the field was applied up ($+H_{\text{ext}}$) and down ($-H_{\text{ext}}$).

For unpolarized sample, the coincidence spectra $N(t, \theta)$ were measured at the angles $\theta = 180^\circ$ and $\theta = 90^\circ$ between the detectors. After a linear background was subtracted, an experimentally anisotropy function $R(t)$ was formed

$$R(t) = 2 \frac{N(t, 180^\circ) - N(t, 90^\circ)}{N(t, 180^\circ) + 2N(t, 90^\circ)} \quad (1)$$

In the cases of the two detectors arrangements with the applied external magnetic field perpendicular to the detector plane, the experimental anisotropy ratio to form for polarized source is

$$E(t) = 2 \frac{N(t, 180^\circ) - N(t, 90^\circ)}{N(t, 180^\circ) + N(t, 90^\circ)} \quad (2)$$

and

$$E(t) = 2 \frac{N(t, 225^\circ) - N(t, 225^\circ)}{N(t, 225^\circ) + N(t, 225^\circ)} \quad (3)$$

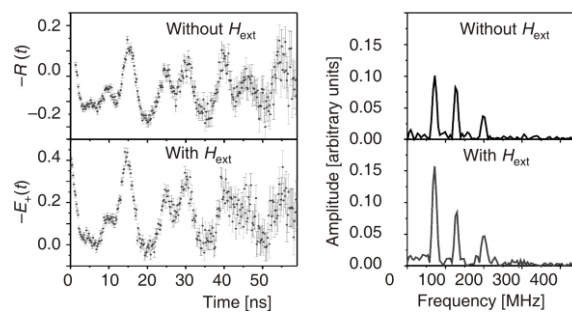


Figure 4. The ambient PAC spectra of ^{181}Ta in the Hf_2Ni_7 : without and with the applied external magnetic field in $90^\circ/180^\circ$ detectors geometry – eqs. (1), (2). The corresponding Fourier transforms are in the right section of the figure

where θ stands for the direction of the external magnetic field.

The Fourier transforms of the experimental PAC spectra from all above mentioned arrangements were compared. The PAC spectra with and without the applied external magnetic field – in the $90^\circ/180^\circ$ detectors arrangements, eqs. (1), (2) – are shown in fig. 4. The corresponding Fourier transforms are essentially the same, revealing the three dominant interaction frequencies which are slightly shifted and broadened in case of the applied field. This kind of frequency spectrum is commonly found in case of presence of the pure electric quadrupole perturbation, therefore indicating that no apparent magnetic hyperfine interaction involving Ta probe in the Hf_2Ni_7 is observed. This result is complementary to the paramagnetic nature of the Hf_2Ni_7 sample found by the macroscopic magnetization measurements and provided the PAC data to be analyzed considering only electric quadrupole interactions.

For polycrystalline sample, a possible modulation in time of the angular correlation of the two successive γ -rays in the cascade can be described by a perturbation factor $G_{kk}(t)$. The angular correlation of the measured ^{181}Ta γ - γ cascade is expressed by angular correlation coefficient A_{22} ($A_{22} \gg A_{44}$). The perturbation factor $G_{22}(t)$ in the case of static electric quadrupole interaction of the ^{181}Ta intermediate level $I = 5/2$ is given by

$$G_{22}(t) = a_{20} \sum_{n=1}^3 a_{2n} \exp\left(\frac{\omega_n \tau_R}{2}\right) \exp(-\delta \omega_n t) \cos(\omega_n t) \quad (4)$$

where ω_n depend on the electric quadrupole frequency ω_Q and the asymmetry parameter η , and a_{2n} are functions of η . The EFG at the ^{181}Ta site is completely described only by two parameters, ω_Q and η

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar} \quad (5)$$

$$\eta = \frac{|V_{xx} - V_{yy}|}{V_{zz}} \quad (6)$$

when the reference axes are chosen in such a way that the diagonal components of the EFG satisfy the condition $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, *i. e.* $0 \leq \eta < 1$. Small lattice imperfections are accounted for with the electric quadrupole frequency distribution width δ . $Q = 2.36(5) \cdot 10^{-28} \text{ m}^2$ is the quadrupole moment for the ^{181}Ta intermediate level of the measured γ - γ cascade [8].

Instead of ω_Q obtained from fitting procedure eq. (5), for comparison with previously published results, we used the spin-independent quadrupole frequency ν_Q

$$\nu_Q = \frac{20}{\pi} \omega_Q = \frac{eQV_{zz}}{h} \quad (7)$$

In general case, when several fractions of probe nuclei with different hyperfine interactions are found in the sample, the anisotropy function is given by the sum

$$R(t) = \sum_i A_{22}^{eff} f_i G_{22}^i(t) \quad (8)$$

A_{22}^{eff} is the experimental anisotropy factor and the sum runs over all sites i having different hyperfine fields and the perturbation factor $G_{22}^i(t)$ is containing information on the i -th hyperfine interaction present in the sample. The data analysis of the experimental PAC spectra was performed with the least-square fitting procedure using the DEPACK program [9].

RESULTS AND DISCUSSION

The objective of the conducted PAC research was to resolve the presence and investigate the temperature dependence of the electric and/or magnetic hyperfine interactions of ^{181}Ta probe in the Hf_2Ni_7 phase. The magnetization and high-temperature X-ray diffraction measurements were used to elucidate the possible phase transformation and to clear up the temperature evolution picture of the Hf_2Ni_7 sample.

The XRD phase analysis of the as-prepared Hf_2Ni_7 sample (fig. 2) indicated the presence of less than 5% of impurity phases. In accordance with the Hf-Ni phase diagram, the traces of the neighboring HfNi_5 and HfNi_3 (low temp.) phases in the Hf_2Ni_7 sample were taken into account, but the peak at $34^\circ 2\theta$ could originate from the Hf_2Ni phase.

Some typical high-temperature X-ray diffraction scans ($\text{Co K}\alpha$) of the Hf_2Ni_7 sample are presented in fig. 5. As seen in the fig. 5, the XRD pattern of the sample at 873 K shows a distinct form from the one taken in the as-prepared state at 298 K. Silva *et al.* [4] suggested that there should be a reversible phase transformation of Hf_2Ni_7 starting at 500 K. During the HT-XRD measurements of the Hf_2Ni_7 sample no change at 500 K was observed, but there is a strong change in XRD patterns beginning at 673 K. The new

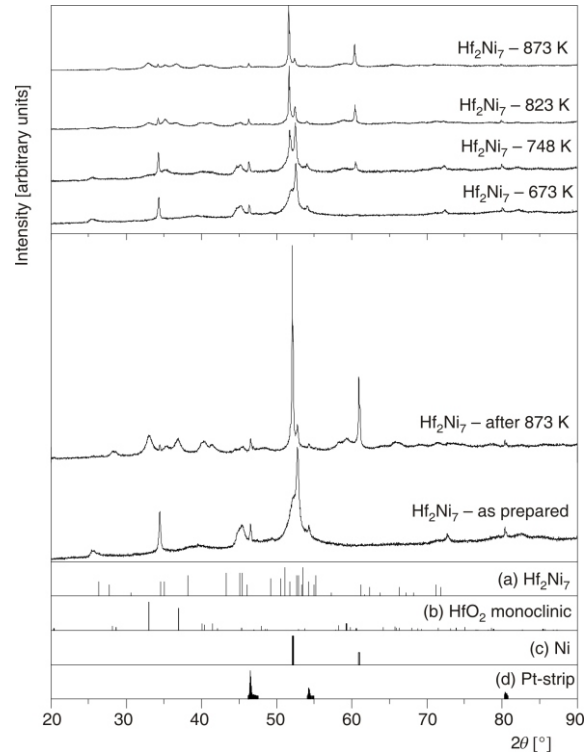


Figure 5. High-temperature XRD ($\text{Co K}\alpha$) patterns of the Hf_2Ni_7 in the as-prepared state and at different temperatures. The XRD fingerprints of: (a) the monoclinic Zr_2Ni_7 type structure; (b) HfO_2 monoclinic; (c) Ni and (d) Pt are presented at the bottom

crystalline phase(s) started to grow at 673 K. Although the HT-XRD patterns were obtained in vacuum of 10^{-3} mbar, the assumption was that the sample started to oxidize internally: $\text{Hf}_2\text{Ni}_7 + 2\text{O}_2 \rightarrow 2\text{HfO}_2 + 7\text{Ni}$. The process of internal oxidation is commonly found for many intermetallic compounds at elevated temperatures [10]. There were no detectable monoclinic HfO_2 peaks present at 673 K. The process of internal oxidation begins around 693 K: a small peak at $59^\circ 2\theta$ (HfO_2 monoclinic) is observed at 698 K together with a small peak at $52^\circ 2\theta$ and $61^\circ 2\theta$ (both belong to fcc Ni). At the same time the main diffraction peaks of Hf_2Ni_7 phase at $34^\circ 2\theta$, $46^\circ 2\theta$, and $53^\circ 2\theta$ started to decrease. Peaks at $46.5^\circ 2\theta$ and $54^\circ 2\theta$ belong to Pt heating stripe. From the pattern at 298 K, taken after HT-XRD measurements up to 873 K, it was estimated that the sample contains over 70 wt% monoclinic HfO_2 and 20 wt% fcc Ni. The rest is Hf_2Ni_7 and probably cubic HfO_2 with defects.

As mentioned before, the Fourier transforms of the PAC spectra of unpolarized and polarized sample spectra exhibited essentially the same three major interaction frequencies. The frequencies were minimally shifted and broadened when an external magnetic field was applied, which indicate that the applied field is only a small perturbation compared to the splitting of ^{181}Ta intermediate level due to the electric quadrupole inter-

action. At the same time, the presence of the three clearly distinguished peaks in the frequency spectra obtained during the 2nd- and 3rd-heating but without applied field, was consistent at all temperatures. These facts coupled with the paramagnetic nature of the sample were used to simplify the interpretation of the measured spectra. The best fit with one quadrupole interaction meant that both electric field gradients have very similar magnitude so the two different sites are observable as one.

Several other assumptions regarding the crystallographic structure of the Hf₂Ni₇ and the existence of impurity phases were also considered but consequently rejected during the fitting procedure. Since the magnetic hyperfine interaction was excluded at the beginning from consideration, the two inequivalent crystallographic positions of Hf atoms of lower symmetry in the structure of Hf₂Ni₇ compound imposed at least two electric quadrupole interactions with non-zero asymmetry parameters for preliminary fitting procedure of the PAC spectra. Also, in the course of the fitting process, it was carefully looked for well known PAC fingerprints of the impurity phases observed by XRD in the sample and for HfO₂ presence because of the risk of internal oxidation. The PAC components with the hyperfine parameters of ¹⁸¹Ta probes in Hf₂Ni [11,12], HfNi₅ [4, 13, 14], and HfO₂ [15, 16] were checked and remained below the limit of detection (1%). There is no PAC study of the HfNi₃ (low temperature) phase known to the authors. Considering the HfNi₃ structure (hexagonal (P63/mmc) Pd₂RhTa type structure [17]), the electric quadrupole interactions should be associated with this structure. Throughout the fitting procedure when only one electric quadrupole interaction emerged as dominant, it was concluded that the HfNi₃ phase was also below the detection limit of all undertaken PAC measurements.

The experimental PAC spectra were preliminarily fitted with two sets of different but comparable quadrupole interaction parameters. It turned out during the fitting process of the second PAC run that the two quadrupole frequencies merged into one. The final refinement resulted in excellent fit for the second set and moderately fit for the first set of PAC measurements under assumption of unique electric quadrupole interaction. Within the experimental resolution of the apparatus, the measured electric field gradients at ¹⁸¹Ta probe for the two inequivalent ¹⁸¹Hf/¹⁸¹Ta sites in the Hf₂Ni₇ compound appeared as one in the range of 78-944 K. The selected ¹⁸¹Ta-PAC spectra of the Hf₂Ni₇ sample together with the fitted curves are presented in fig. 6. The temperature evolution of the quadrupole frequency ν_Q and asymmetry parameter η of ¹⁸¹Ta probe in the Hf₂Ni₇ sample during the 2nd-heating and 3rd-heating are shown in figs. 7 and 8.

As seen in fig. 7, the measured Ta site frequency reduces gradually from 444 MHz at 78 K to 365 MHz

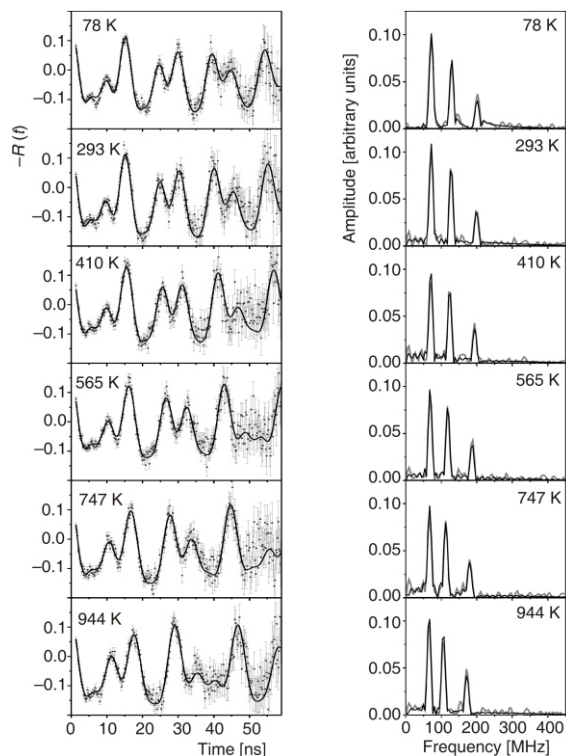


Figure 6. Selected ¹⁸¹Ta-PAC spectra with corresponding Fourier transforms obtained at 78 K, and during 3rd-heating of the Hf₂Ni₇ sample up to 944 K

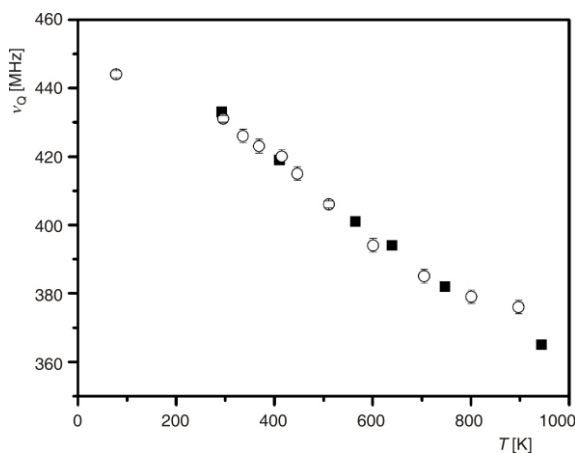


Figure 7. Temperature variation of the quadrupole frequency ν_Q of ¹⁸¹Ta probe in the Hf₂Ni₇ sample: the temperature evolution of the quadrupole coupling parameters during the 2nd-heating is marked with open circle symbol and during the 3rd-heating with full square symbol

at 944 K. The T^k dependencies with $k=1$ and 1.5, could not reproduce the temperature dependence of the quadrupole frequency in the whole measured temperature range. Nevertheless, the quantity of data was sufficient to permit recognition of empirical trend. The overall inspection of data indicates an almost linear T -dependence of the quadrupole frequency starting at room temperature, particularly prominent for the second run. There is an apparent deviation visible at

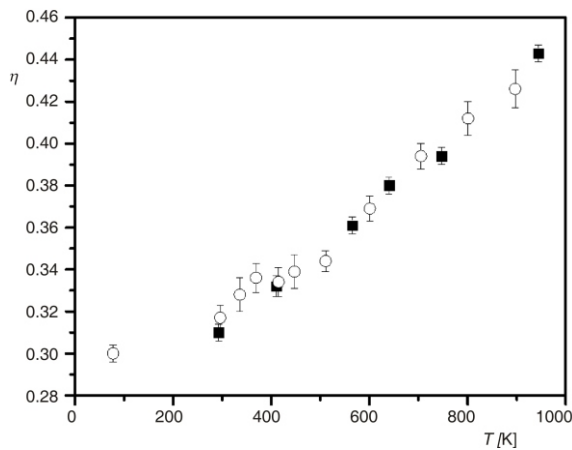


Figure 8. Temperature dependence of the asymmetry parameter η of ^{181}Ta probe in the Hf_2Ni_7 sample: the temperature evolution of the quadrupole coupling parameters during the 2nd-heating is marked with open circle symbol and during the 3rd-heating with full square symbol

900 K for the first run. The asymmetry parameter (fig. 8) is continuously ascending from 0.30 at 78 K to 0.44 at 944 K: a small jump (296-370 K) followed by short plateau (370-500 K) was observed in the first run. The frequency distribution parameter for the second run was very small ($\delta \sim 1\text{-}2\%$). The observed narrow frequency distribution confirmed that the Ta probe atoms occupy mostly substitutional positions in the Hf_2Ni_7 structure and are rather free from defects. For the first run, relatively larger variations of the gradients from nucleus to nucleus (δ less than 5%) and Ta site fraction not far from unity were obtained from the fit under the assumption of unique quadrupole interaction taken over from the second run fit.

The radiation damage is expected to be annealed by a thermal treatment 1223 K/8 days in vacuum, so one possible source of discrepancies of the first and second run is an influence of impurity phases that were subsequently annealed out during progressively heating throughout the first run. In principle, another possible source of such discrepancies may be the three detectors assemblies not being optimal because one has also to take into account the different detector efficiencies and energy window adjustments in practice. Due to this kind of asymmetry of the three detector $90^\circ/180^\circ$ arrangement these influences are not fully cancelled by forming the ratio $R(t)$.

There is partial agreement of the results from this work with the results obtained by Silva *et al.* [4] for the pure Hf_2Ni_7 phase. The deduced ν_Q - and η -values from the fitting procedure are somewhat higher and there is no sharp η jump around 500 K, but the data support the assumption [4] that the two EFG at ^{181}Ta inequivalent sites are quite similar. As the mother isotope of the probe atom is a constituent of the investigated compound, a preferential occupation of one of the Hf sites can be excluded. In the work of Silva *et al.*

[4], along with the PAC study of Hf_2Ni_7 , the HfNi_5 compound was investigated. The three PAC components were found in the PAC spectrum of the unannealed HfNi_5 sample [4] – the two of them were linked to the Hf_2Ni_7 phase. The obtained results in this work, however, resemble much more to the ones of the component II of the unannealed HfNi_5 sample (at room temperature, $\nu_Q = 443$ MHz and $\eta = 0.31$ [4]). Silva *et al.* [4] related this component to the Hf_2Ni_7 phase and to the “cooling behavior” of Hf_2Ni_7 and described it as hexagonal high-temperature Hf_2Ni_7 phase. The two different high-temperature and room temperature phases of Hf_2Ni_7 have been suggested previously by Dattagupta *et al.* [5]. It may seem that the high-temperature Hf_2Ni_7 phase was observed in the course of the present PAC investigations. This is unlikely, since the sample was not quenched from high temperature and its crystal structure was consistent with the monoclinic one. The most probable reason of these divergences may be the sample, which is difficult to produce. The high-temperature XRD data of the Hf_2Ni_7 sample could resolve this situation, but the data were damaged from the internal oxidation of the sample. Nevertheless, there is an overall conclusion that the values and T -dependencies of the quadrupole parameters for Hf_2Ni_7 phase strongly depend on the heat treatment of the compound. An ab-initio calculation of the EFG at the Ta sites of Hf_2Ni_7 that may clarify the presented as well as previously published results will not be available in the close future. The computational efforts to calculate the EFG at the Hf sites of Hf_2Ni_7 that are in progress may be, to a certain degree, very helpful.

CONCLUSIONS AND RECOMMENDATIONS

The nature and temperature variations of the ^{181}Ta hyperfine interactions were investigated by the perturbed angular correlation measurements of the polycrystalline Hf_2Ni_7 sample. The PAC arrangements with the applied external magnetic field complemented with the magnetization measurements were carried out in order to analyze the magnetic ordering of the sample. No evidence of magnetic hyperfine interactions was found by PAC in the Hf_2Ni_7 sample and magnetization measurements showed that the magnetic susceptibility of Hf_2Ni_7 is paramagnetic down to about 10 K, where it shows a broad antiferromagnetic peak. The high-temperature X-ray diffraction measurements of the Hf_2Ni_7 sample showed that there is no change in the sample structure and composition up to 693 K, where the onset of internal oxidation is observed.

The electric field gradients at ^{181}Ta probe for the two inequivalent $^{181}\text{Hf}/^{181}\text{Ta}$ sites in the Hf_2Ni_7 compound have very similar magnitude and are observable

as unique one in the temperature range of 78-944 K. The measured Ta site frequency reduces gradually with rising temperature, with an almost linear T -dependence starting at room temperature. The asymmetry parameter is continuously ascending with increasing temperature. The obtained results are in partial agreement with the previously reported ones, indicating that the values and T -dependencies of the nuclear quadrupole interaction parameters of the ^{181}Ta probe depend strongly on the heat treatment of the Hf_2Ni_7 compound. The clarification of the presented as well as previously published experimental results is expected from the *ab-initio* calculation of the EFG at the Ta sites of Hf_2Ni_7 (not available at the moment). Certain clues may be obtained from the calculations of the EFG at the Hf sites of Hf_2Ni_7 that are in progress.

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REFERENCES

- [1] Frauenfelder, H., Steffen, R. M., in: Alpha-, Beta- and Gamma-Ray-Spectroscopy (Ed. K. Siegbahn), North Holland, Amsterdam, 1965, Chapter XIX: Angular Distribution of Nuclear Radiation, pp. 1101-1199
- [2] Gerdau, E., *et al.*, Hyperfine Interactions of ^{181}Ta in $\text{Ni}_{1-x}\text{Hf}_x$, *Hyperfine Interact.*, 1 (1976), 1, pp. 459-467
- [3] Marszalek, M., *et al.*, Hyperfine Interactions at ^{181}Ta in Hf_2Ni_7 and Zr_2Ni_7 , *Z. Naturforsch., A* 55 (2000), 1-2, pp. 49-53
- [4] Silva, P. R. J. *et al.*, Perturbed Angular Correlation Studies of ^{181}Ta Hyperfine Interactions in Hf-Ni and Zr-Ni Compounds, *J. Magn. Magn. Mater.*, 322 (2010), 13, pp. 1841-1846
- [5] Dattagupta, J. P., Schubert, K., Über die Isotypie von Zr_2Ni_7 and Hf_2Ni_7 , *Z. Metallk.*, 64 (1973), pp. 789-792
- [6] Hunter, B., RIETICA—A Visual RIETVELD Program, International Union of Crystallography Commission on Powder Diffraction Newsletter No. 20, 1998, Chester, UK, <http://www.rietica.org>
- [7] ***, X'Pert High Score Plus 2.0a, PANalytical BV, Lelyweg 1, Almelo, the Netherlands. PDF-2 2002 Database, ICDD, Newton Square, Penn., USA, ICSD Database, release 2009/1, FIZ Karlsruhe, Germany
- [8] Butz, T., Lerf, A., Comment on Mössbauer Studies of the 6.2 keV γ -Rays of ^{181}Ta -Dichalcogenides, *Phys. Lett., A* 97 (1983), 5, pp. 217-218
- [9] Lindgren, B., Depack Software, *Hyperfine Interactions, C* 1 (1996), p. 613
- [10] Bedi, S. C., Forker, M., Hyperfine Interactions at Ta Impurities in Cobalt and Cobalt-Hafnium Intermetallic Compounds, *Phys. Rev., B* 47 (1993), 22, pp. 14948-14960

- [11] Cekić, B., *et al.*, TDPAC and XRPD Measurements of the Polycrystalline Hf_2Ni Phase, *Journal of Optoelectronics and Advanced Materials*, 10 (2008), 4, pp. 794-797
- [12] Koteski, V., *et al.*, FP-LAPW Study of Hf_2Ni : Structure, Electronic Properties, and Electric Field Gradients, *Journal of the Physical Society of Japan*, 73 (2004), 8, pp. 2158-2163
- [13] Umićević, A., *et al.*, Magnetic Dipole and Electric Quadrupole Interactions of ^{181}Ta Probe in Ni-Hf Alloy, *J. Alloys Compd.*, 475 (2009), 1-2, pp. 38-41
- [14] Cekić, B., *et al.*, The Time Differential Perturbed Angular Correlation Study of the Ni-5 at.% Hf Alloy, *J. Alloys Compd.*, 480 (2009), 1, pp. 40-42
- [15] Koički, S., *et al.*, Temperature Dependence of Electric Quadrupole Interaction of ^{181}Ta in HfO_2 , *Hyperfine Interact.*, 14 (1983), 2, pp. 105-110
- [16] Ayala, A., *et al.*, Temperature Dependence of the Hyperfine Electric-Field-Gradient Tensor at ^{181}Ta in HfO_2 , *Phys. Rev., B* 50 (1994), 6, pp. 3547-3552
- [17] Bsenko, L., The Crystal Structure of Two Modifications of HfNi_3 , *Acta Crystallographica, B* 34 (1978), 11, pp. 3201-3204

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**ИСПИТИВАЊЕ ГРАДИЈЕНТА ЕЛЕКТРИЧНОГ ПОЉА ПРИСУТНОГ НА
МЕСТУ ^{181}Ta У ЈЕДИЊЕЊУ Hf_2Ni_7 МЕТОДОМ ПЕРТУРБОВАНИХ
УГАОНИХ КОРЕЛАЦИЈА**

Температурска зависност градијента електричног поља присутног на месту ^{181}Ta пробе у Hf_2Ni_7 поликристалном узорку је истраживана методом пертурбованих угаоних корелација (*PAC* метода). Еволуција састава узорка са променом температуре је проучавана методом високотемпературске рендгенске дифракције. У циљу испитивања магнетног уређења узорка извршена су мерења магнетизације узорка и допунска мерења пертурбованих угаоних корелација уз примену спољашњег магнетног поља. Магнетно уређење узорка није опажено у свим експерименталним *PAC* спектрима. У оквиру експерименталне резолуције *PAC* апаратуре, градијенти електричног поља присутни на две не-еквивалентне позиције $^{181}\text{Hf}/^{181}\text{Ta}$ пробе у Hf_2Ni_7 једињењу су измерени као један јединствени градијент у температурском опсегу од 78 од 944 К. Бележење једне квадруполне интеракције имплицира да су градијенти електричног поља на две позиције Hf веома слични. На 293 К, измерени параметри квадруполне интеракције су $\nu_Q = 433(1)$ MHz и $\eta = 0.300(4)$. Са порастом температуре, јачина квадруполне интеракције опада, а параметар асиметрије постепено расте. Високотемпературска рендгенска дифракција је показала да долази до интерне оксидације узорка изнад 693 К.

*Кључне речи: интјерметјалици, хитјерфине интјеракције, пјертјурбоване угаоне корелације,
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