TDPAC and XRPD measurements of the polycrystalline Hf$_2$Ni phase

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The high-resolution time-differential perturbed angular correlation technique (TDPAC) has been used to study the electric field gradient at ^{181}Ta impurities in the polycrystalline intermetallic compound Hf$_2$Ni in the wide temeperature range 78-1314 K. The single-phase BCT CuAl$_2$ (C16)-type structure of the compound was confirmed by X-ray diffractogram, with lattice constants found to be a = 6.479(3) Å and c = 5.271(3) Å at room temperature. The coincidence measurements between gamma rays in the cascade were recorded with a time resolution better than 0.75 ns for the 133-482 keV γ-γ cascade of ^{181}Ta nuclei. The results of measurements reveal the presence of a single nuclear quadrupole interaction (NQI) ω_Q and its linear dependence with temperature in the range 78-1134 K. In the high temperature region (1134-1314 K) the significant appearance of disordering in the lattice structure of Hf$_2$Ni was revealed, in the vicinity of the melting point of 1473 K. The XRPD measurements in the high temperature range can help in better interpretation and understanding of this complex structural and microdinamic behavior of the Hf$_2$Ni phase.

1. Introduction

The amorphous metallic alloys of early (Ti, Zr, Hf) and late (Fe, Co, Ni) transition metals are attractive from scientific point of view because they are stable over a wide composition range. Among them, Hf-based systems are very similar in their properties to systems based on Zr and Ti. Hf-Ni alloys are not an exception [1] and their hydrogen absorption and desorption properties are very pronounced [2].

With the aim of contributing to the understanding of the structural transformations and microdynamic changes taking place in these systems we studied Hf$_2$Ni polycrystalline phase with use of time differential perturbed angular correlations (TDPAC) technique [3,4]. The high-resolution TDPAC technique has proven to be a powerfool tool for this kind of investigations by measuring hyperfine interactions with the important advantage of its unrestricted temperature range and one important disadvantage in the upper frequency limit imposed by the time resolution of the scintillation detectors. The frequency limit was dramatically improved with BaF$_2$ crystals and in favorable cases the upper frequency limit of TDPAC could be extended by almost one order of magnitude to about 10 GHz. The next improvements in attaining better coincidence resolving time of the coincidence set-up, are expected to be made with BrilLanCe 380 crystals!

In this paper we present a high precision TDPAC measurements of the NQI of ^{181}Ta in Hf$_2$Ni in wide temperature range 78-1314 K in order to obtain microscopic information about the thermal changes occurring in Hf$_2$Ni through progressive lattice disordering approaching to the melting point of 1473 K. We will

continue research in this very interesting region, as well as in the low temperature region which is also not very well explored. The *ab-initio* calculations with all-electron full potential linearized augmented plane wave (FP-LAPW) formalism or a detailed theoretical study of the structure, electronic properties and the electric field gradient (EFG) at the ^{181}Ta ion probe site of the Hf$_2$Ni polycrystalline phase, complete and confirm the quality of experimental data, given in our previous paper [5].

2. Experimental

The intermetallic phase Hf$_2$Ni was prepared from high purity Ni (5N) and Hf (2N) in a RF induction furnace under a very pure argon stream and remelted several times. The phase formed peritectically with reaction: L + NiHf $\leftrightarrow$ NiHf$_2$ at 1473 K [5]. The single-phase BCT CuAl$_2$ (C16)-type structure of the compound was confirmed by X-ray diffractogram (Fig. 1), obtained on a Philips PW-1710 automated diffractometer, using a Cu tube operated at 40 kV and 35 mA, with lattice constants found to be a = 6.479(3) Å and c = 5.271(3) Å [6]. The single-phase BCT CuAl$_2$ (C16)-type structure is characterized by two sets of mutual orthogonal planes with a dense packing of hexagons (honeycomb structure) with Hf atoms, parallel to the $(1,1,0)$ and $(1,\bar{1},0)$ planes respectively. The hexagons of the different sets are fully interlocking. The Ni atoms are suited in the channels parallel to the c-axis, which are formed by this interlocking honeycomb structure. The polycrystalline sample Hf$_2$Ni was then irradiated with thermal neutrons in high neutron flux of $1.8 \cdot 10^{14}$ n cm^{-2} s^{-1} in order to produce the desired activity of ^{181}Hf. Then, the sample was annealed for 10 days at 1000 °C to remove

radiation damage. The 133-482 keV gamma cascade of [181]Ta, populated by the β decay of the parent [181]Hf nucleus was well suited for TDPAC experiments with a conventional two BaF₂ detectors coincidence set-up in wide temperature range 78-1314 K. The coincidence measurements between gamma rays in the cascade were recorded with a time resolution better than 0.75 ns [7]. Low temperature measurements were made with liquid nitrogen cryostat while at high temperature measurements a low-scattering electric furnace was used.
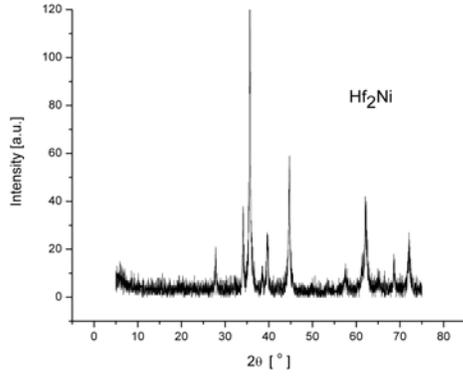

Fig. 1. XRPD pattern of Hf₂Ni at room temperature.

3. Results and discussion

TDPAC spectra were measured at the angles 90° and 180° at the thirteen temperatures 78, 295, 346, 420, 589, 729, 876, 967, 1076, 1134, 1191, 1237, 1314 K and presented according to the experimental perturbation function:

$$R(t) = 2\frac{N(180^0,t) - N(90^0,t)}{N(180^0,t) + 2N(90^0,t)} = A_{22}Q_2G_2(t) \qquad (1)$$

These delayed coincidence spectra with the fitted curves $A_{22}G_2(t)$ and their corresponding Fourier transforms are shown in Fig. 2. Here A_{22} is the unperturbed correlation coefficient, Q_2 is the solid angle correction and $G_2(t)$ is the perturbation coefficient containing information on NQI in a sample. The NQI of the quadrupole moment Q of the intermediate level $I = 5/2$ in [181]Ta with an EFG V_{zz} results in hyperfine splitting of the level into three sublevels so that the perturbation factor has the form:

$$G_2(t) = a_{20} + \sum_{n=1}^{3} a_{2n} exp(-\frac{(\omega_n\tau_R)^2}{2})\exp(-\delta\omega_n t)\cos(\omega_n t) \quad (2)$$

where ω_n depend on ω_Q and η, and $a's$ are functions of η and:

$$\omega_Q = \frac{eQV_{ZZ}}{4I(2I-1)\hbar} \quad , \quad \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad , \qquad (3)$$

where δ is the Lorentzian distribution width to describe small lattice imperfections. The first exponential term in the sum of the equation (2) accounts for the finite time resolution (τ_R) of the coincidence system.

The values of the quadrupole coupling parameters extracted from the fitting procedure are reported in table 1. From presented figures is evidently that the polycrystalline sample Hf₂Ni exhibits a single NQI with little damping (δ) and a large asymmetry parameter η. The quadrupole frequency ω_Q varies lineary with temperature in temperature range 78-1134 K with the slope $1.8(1)\cdot10^4$ rad s⁻¹ K⁻¹. In the temperature region 1134-1314 K, close to the melting point (1473 K) of the sample, the appearance of disordering of the lattice structure (Fig. 3) reflects on the values of NQI (ω_Q). The EFG's are calculated according to relation (3), with the known value of the quadrupole moment $Q = +2.36(5)\times10^{-24}$ cm² for the $I = 5/2$ state of [181]Ta ion probe.

Table 1. The NQI parameters for [181]Ta impurities in the intermetallic compund Hf₂Ni.

T (K)	ω_Q (Mrad s⁻¹)	η	δ	V_{ZZ} (10^{17} V cm⁻²)
78	94.2(3)	0.745(4)	0.034(2)	10.5(3)
293	92.6(3)	0.759(4)	0.018(2)	10.3(3)
346	92.8(3)	0.777(5)	0.023(3)	10.3(3)
420	88.5(3)	0.806(5)	0.015(3)	9.9(2)
589	85.3(3)	0.846(5)	0.007(3)	9.5(2)
729	83.5(3)	0.865(5)	0.009(3)	9.3(2)
876	80.1(3)	0.889(7)	0.012(4)	8.9(2)
967	79.7(3)	0.907(10)	0.020(4)	8.9(2)
1076	78.1(3)	0.902(9)	0.016(4)	8.7(2)
1134	76.8(3)	0.902(8)	0.013(4)	8.6(2)
1191	76.5(4)	0.897(10)	0.014(4)	8.5(2)
1237	76.4(5)	0.899(4)	0.023(6)	8.5(2)
1314	77.0(9)	0.918(32)	0.035(9)	8.6(3)

This high-resolution and high-statistics systematic TDPAC analysis allowed the study of the temperature dependence of the NQI at [181]Ta site ion probe in Hf₂Ni sample in the temperature range 78-1134 K where the temperature dependence is linear. The observation of progressive disordering of crystal structure in the range 1134-1314 K is evident looking at the behavior of ω_Q which exhibits nearly constant values with very little oscillations.

An examination of the spin rotation patterns presented in Fig. 2, showed that the [181]Ta ion probe occupies a unique site in the Hf₂Ni lattice where a large asymmetric parameter η shows a considerable temperature variation. The temperature dependence of the frequency distribution width δ is evident also.

The effective V_{zz}'s acting on the Ta nuclei change in the range $(8.6-10.5)\times10^{17}$ V cm⁻² at the measured temperatures. The measured EFG's values strongly depend on the local environment of the probe atoms and are in

good agreement with previously reported measurements [8]. The calculations of the EFG at Ta impurity in Hf_2Ni

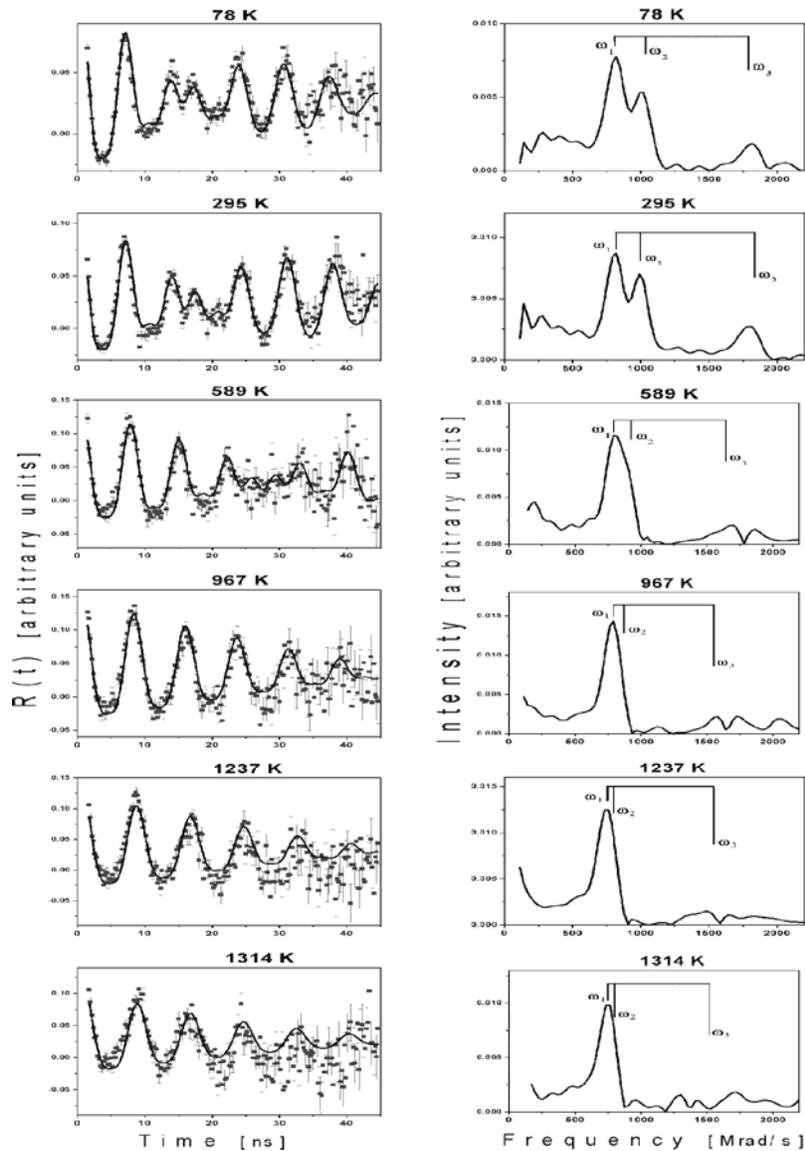intermetallic phase needed for interpreting the measured results are on the way.

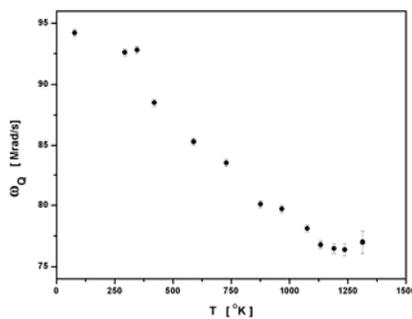Fig. 2. The fitted TDPAC spectra of ^{181}Ta in Hf_2Ni and corresponding Fourier transforms measured at different temperatures.

Fig. 3. Quadrupole frequency ω_Q for ^{181}Ta impurities in polycrystalline compound Hf_2Ni as a function of temperature.

4. Conclusions

The linear temperature dependence of the NQI at ^{181}Ta site ion probe in Hf_2Ni sample in the temperature range 78-1134 K was observed by high-resolution TDPAC measurements. The progressive disordering crystal structure in the range 1134-1314 K is evident looking at the behavior of ω_Q which exhibits nearly constant values with very little oscillations. The TDPAC experimental approach to the high temperature region 1134-1314 K opens a new possibility to observe the structural deformation of the Hf_2Ni lattice and we will try, in the close future, to study its deterioration as close as possible to the melting point, using TDPAC and XRPD methods.

Acknowledgement

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