

# Hyperfine Interactions at $^{181}\text{Ta}$ in $\text{Hf}_2\text{Ni}_7$ and $\text{Zr}_2\text{Ni}_7$

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We report on a time differential perturbed angular correlations (TDPAC) study of the hyperfine interactions at  $^{181}\text{Ta}$  in  $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$ . The samples were prepared by arc melting proper amounts of constituents together with a small amount of Hf containing radioactive  $^{181}\text{Hf}$  atoms. A further heat treatment was necessary to obtain samples of the required crystal structure (monoclinic symmetry in the C2/m space group). As known, two non-equivalent lattice sites of Hf/Zr metal exist in this structure.

The PAC measurements were performed at 20 - 1123 K. Two quadrupole interactions were observed, corresponding to two possible crystallographic positions of the probe atom in the studied structure. The electric quadrupole interaction parameters at  $^{181}\text{Ta}$  in  $\text{Hf}_2\text{Ni}_7$  are  $\nu_{Q1}(300\text{K}) = 586.7(65)$  MHz with  $\eta_1 = 0.79(4)$  and  $\nu_{Q2}(300\text{K}) = 466.8(41)$  MHz with  $\eta_2 = 0.20(3)$ , and in  $\text{Zr}_2\text{Ni}_7$  they are  $\nu_{Q1}(300\text{K}) = 498.4(22)$  MHz with  $\eta_1 = 1.0$  and  $\nu_{Q2}(300\text{K}) = 418.0(50)$  MHz with  $\eta_2 = 0.35(3)$ . The presence of a magnetic interaction, reported in the literature, was not confirmed.

**Key words:** Nuclear Quadrupole Interactions; Time Differential Perturbed Angular Correlations (TDPAC); Intermetallic Compounds; Hf-Ni System; Zr-Ni System.

## Introduction

Generally, the study of intermetallic compounds is aimed at understanding possible relationships between their structural and other properties, and at finding systematics enabling the prediction of the stability of new compounds.

The electronic structure of A-B compounds, where A is Zr, Hf, or V and B is Cu, Fe, Co, or Ni, has attracted great attention in the last years due to their surprising properties. Depending on their composition and stoichiometry, they show unusual magnetic properties together with superconductivity [1], they can be easily produced in the amorphous state [2], and they demonstrate numerous anomalies of physical properties (the thermal expansion of these alloys is anomalously low, the elasticity softens with lowering temperature, the high field susceptibility shows giant values, the magnetic transition temperature decreases anomalously with pressure) which are caused by mag-

netovolume effects [3]. All the above-mentioned aspects make these A-B systems particularly interesting for possible applications.

We report here a TDPAC study of  $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$ , compounds with the same type of crystallographic structure. The aim of our study was to investigate the relationship between magnetism and the presence of 3d metals in these compounds from the microscopic point of view with a local probe method.

## Experimental

The samples of  $\text{Zr}_2\text{Ni}_7$  and  $\text{Hf}_2\text{Ni}_7$  were melted together from the respective elements in an argon arc furnace. Each sample was melted several times to ensure its homogeneity. In the case of  $\text{Zr}_2\text{Ni}_7$  small amounts (less than 2 at. %) of neutron-irradiated natural hafnium containing the  $^{181}\text{Hf}$  isotope were added. Then the samples were annealed at 1100 K for 48 hours in evacuated and sealed quartz tubes. X-ray

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powder diffraction of the samples, taken with  $\text{Cu K}_\alpha$  radiation, confirmed a single phase composition of the  $\text{Zr}_2\text{Ni}_7$  and  $\text{Hf}_2\text{Ni}_7$  samples. No quenching procedure was applied after the annealing treatment.

The TDPAC measurements were carried out using the 133 - 482 keV  $\gamma$ - $\gamma$  cascade of  $^{181}\text{Ta}$  with its intermediate half-life of 10.8 ns, populated in the beta decay of  $^{181}\text{Hf}$  (42 days). Both gamma rays were detected by  $\text{BaF}_2$  scintillator detectors. The time resolution (FWHM) for this energy cascade was about 1 ns. The time differential PAC spectra were taken with the standard four-detector setup. The measurements were performed at 18 - 1100 K. For low temperatures a closed-cycle cryostat was used, and for higher temperatures a resistive oven with temperature controller. For all measurements at  $T > 300$  K the samples were sealed in evacuated quartz tubes.

The influence of the quadrupole interaction on the gamma-gamma angular correlation in polycrystalline samples is described by the perturbation factor  $G_{kk}(t)$  [4] which depends on the multipole order of the radiation, on the symmetry and time dependence of the interaction and on the nuclear spin of the relevant state ( $I = 5/2$  for  $^{181}\text{Ta}$ ). In this case the perturbation factor is given by

$$G_{22} = \sum_{n=0}^3 s_{2n}(\eta) \cos(g_n(\eta)\nu_Q t) \exp[-g_n(\eta)\delta t]. \quad (1)$$

Here the quadrupole frequencies  $\nu_Q$  correspond to the strength of the electric quadrupole interaction between the nuclear quadrupole moment of the probe nucleus and the electric field gradient (EFG). The transition frequencies  $g_n(\eta)\nu_Q$  depend on the asymmetry parameter, defined as  $\eta = |V_{xx} - V_{yy}|/V_{zz}$ . The parameters  $S_{kn}$  depend only on  $\eta$ . Lattice imperfections give rise to an electric field gradient distribution which can be approximated by a Lorentzian distribution with width  $\delta$ .

If a magnetic hyperfine interaction between the nuclear magnetic dipole moment and the magnetic hyperfine field exists, it is characterized by the Larmor frequency  $\nu_M$ . In noncubic magnetic crystals one observes the superposition of electric and magnetic hyperfine interactions. In this case the perturbation factor cannot be given in an analytical form but has to be calculated by numerical diagonalization of the Hamiltonian of the hyperfine interactions [5]. Then the interaction is characterized not only by quadrupole and Larmor frequencies  $\nu_Q$  and  $\nu_M$  but also by the angle

$\theta$  between the symmetry axis of the EFG and the direction of the magnetic hyperfine field.

Four to twelve different coincidence counting rates of pairs of detectors at different angles to each other were recorded with our equipment, and then, after being corrected for accidental background, combined in a standard  $R(t)$  ratio:

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

$$= A_{22} \sum_{i=1}^N f_i G_{22}^i(t),$$

where  $f_i$  denotes the relative fractions of different EFGs contributing to the PAC spectrum, and  $G_{22}^i(t)$  the corresponding perturbation factors. In the data analysis the least-squares procedure was applied to fit measured PAC spectra to the expression  $A_{22}G_{22}(t)$  in order to obtain the hyperfine parameters for each compound.

## Results and Conclusion

The  $\text{Zr}_2\text{Ni}_7$  structure is efficiently packed, the volume contraction that accompanies the phase formation from the constituent elements being calculated to be 4.7%. The atomic array is pseudohexagonal normal to the  $a$  and  $b$  axes, and the layering along this pseudohexagonal axis is related to other structures, particularly the cubic  $\text{MgCu}_2$  and  $\text{UNi}_5$  structures. Two non-equivalent zirconium sites of the same symmetry with sixteen-fold coordination and occupation 4(i) exist in a unit cell. Each zirconium atom in the  $\text{Zr}_2\text{Ni}_7$  structure is coordinated to 2 other zirconium atoms and to 14 nickel atoms, leading to a total coordination of 16. The coordination spheres for the two

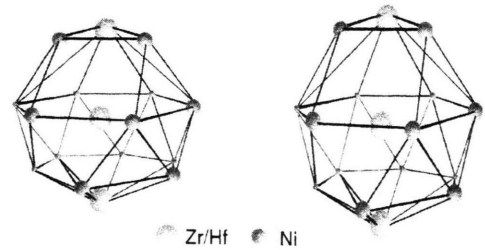


Fig. 1. The nearest neighborhood of zirconium atoms in compounds of  $\text{Zr}_2\text{Ni}_7$  type.

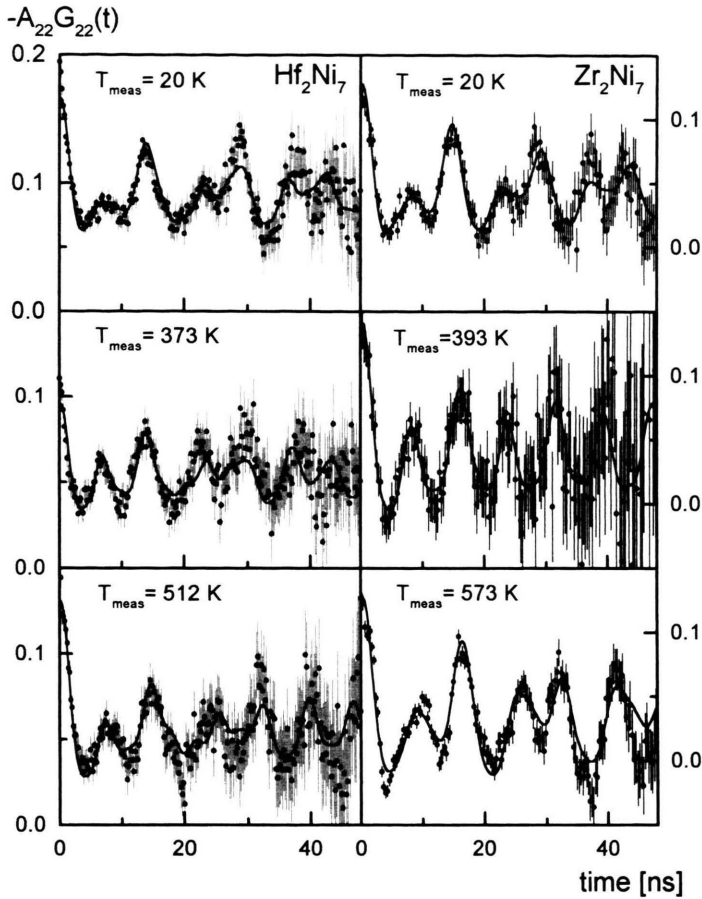


Fig. 2. TDPAC spectra of  $^{181}\text{Ta}$  in  $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$  compounds at various temperatures.

independent zirconium atoms are remarkably similar, as evident in Figure 1.

Figure 2 shows the temperature evolution of the measured PAC spectra in  $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$  together with the results of fitting.

The main question addressed in this paper is about the influence of 3d atoms (Ni) on the magnetism in  $\text{A}_2\text{B}_7$  compounds. Three members of this family are found, but their magnetic properties are scarcely known, and only a few studies are available in the literature. For example Amamou [6] showed that all compounds of the Zr-Ni system with exception of  $\text{ZrNi}_5$  present a usual temperature-independent Pauli paramagnetism. According to this paper, the critical concentration for the appearance of magnetism in Zr-Ni compounds is around 83.3at.% Ni and, therefore only  $\text{ZrNi}_5$  has been found to be a weak ferromagnet ( $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$  are assumed to be line compounds at 77.8 at% Ni). Magnetic properties of the Hf-Ni system were not studied except for hyperfine

field measurements [7], which showed a magnetic interaction in  $\text{Hf}_2\text{Ni}_7$  compound. The third member of the  $\text{A}_2\text{B}_7$  family,  $\text{Hf}_2\text{Co}_7$ , is reported in [8] as being ferromagnetic with a Curie point of around 150 °C. Taking all this information into account, we tried to fit our data with combined interactions, magnetic and electric quadrupole. We also considered the situation that the probe atoms occupy either one or both lattice sites suggested by the crystal structure.

However, the least-squares-fit analysis of the experimental PAC spectra of  $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$  samples gave the most consistent results in the whole temperature range for only two quadrupole interactions, corresponding to two possible crystallographic positions of the probe atom. Zirconium atoms occupy sites of low symmetry in the structure, which is reflected in a non-zero asymmetry parameter for both sites. Point charge model calculations of the ionic contribution to the electric field gradient, based on the lattice parameters of  $\text{Zr}_2\text{Ni}_7$  [9] and with the assumption of

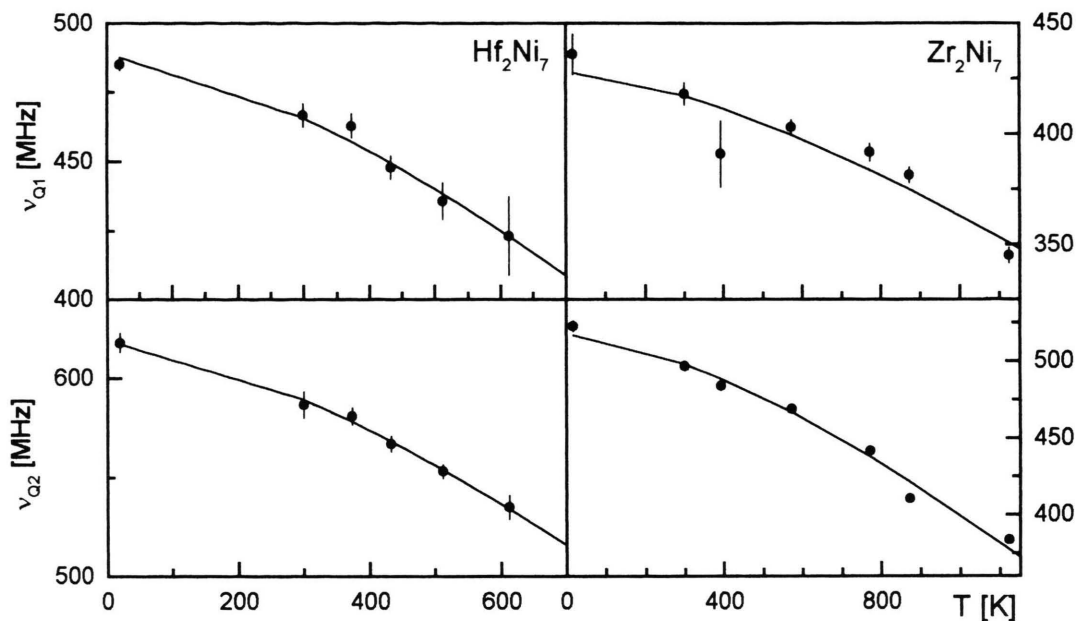


Fig. 3. Temperature dependences of quadrupole frequencies for  $\text{Zr}_2\text{Ni}_7$ -type compounds.

Table I. The experimental quadrupole interaction parameters of  $^{181}\text{Ta}$  in compounds of the  $\text{Zr}_2\text{Ni}_7$  type.

Compound	$\nu_Q(300\text{ K})$ [MHz]	$\eta$	$\nu_Q(0)$ [MHz]	$b$ [ $10^{-5}\text{ K}^{-3/2}$ ]
$\text{Hf}_2\text{Ni}_7$	586.7(65)	0.79(4)	617.8(17)	0.892(29)
	466.8(41)	0.20(3)	488.0(28)	0.877(61)
$\text{Zr}_2\text{Ni}_7$	498.4(22)	1.0*	517.2(43)	0.717(40)
	418.0(50)	0.35(3)	427.7(71)	0.477(84)

zero charge on Ni atoms and +4 charge on Zr atoms, yielded values of  $\eta$  equal to 0.03 and 0.48 for the two non-equivalent sites of Zr.

Since the  $^{181}\text{Ta}$  nucleus originates from the decay of  $^{181}\text{Hf}$  which is a component of the host  $\text{Hf}_2\text{Ni}_7$ , only hafnium lattice sites are substituted by the isotope probes. Direct evidence as to which site is occupied by Hf atoms in the  $\text{Zr}_2\text{Ni}_7$  compound is not available, but the measured quadrupole interaction parameters are very close to those found in the  $\text{Hf}_2\text{Ni}_7$  compound. Hf and Zr belong to the same IIIA-group of transition metal elements and exhibit great chemical and physical similarities. This implies that in both compounds the  $^{181}\text{Ta}$  probe has the same atomic environment and resides on the same site.

The fitted quadrupole interaction parameters are shown in Table I. For both compounds two probe fractions were observed with site occupations of about

50% in accordance with the crystallographic data. The measured asymmetry parameter showed very small changes with temperature. In one case (marked in Table I with \*) better fits were obtained if the asymmetry parameter was kept constant during fitting. The frequency distribution  $\delta$  was very narrow for both compounds. It did not exceed 2.5(1)% indicating a well-defined environment of probe atoms in the systems that were studied.

In the simplest approach, the temperature dependence of the electric quadrupole interaction is attributed to thermal lattice expansion. However, this approach is not sufficient, because the dependence of the electric hyperfine interaction on temperature is usually stronger and in some cases in the opposite direction to that predicted from thermal lattice expansion. An additional factor has to be taken into account, and this is the effect of lattice vibrations, which leads to the well-known formula [10] describing the temperature dependence of the electric quadrupole interaction

$$\nu_Q(T) = \nu_Q(0)(1 - bT^{3/2}). \quad (3)$$

Here the parameter  $b$  represents the strength of the temperature variation of the quadrupole interaction.

The measured temperature dependences of the quadrupole frequencies in  $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$  are

shown in Fig. 3, and the parameters, fitted with (3), are collected in Table I.

To conclude, two electric quadrupole interactions were observed, reflecting the crystalline structure of the studied compounds. The temperature dependence of the electric quadrupole interaction follows the  $T^{3/2}$  law, and the strength of the observed dependence is slightly larger than for other compounds belonging to the Hf-Ni and Zr-Ni systems [11]. We were not able to observe a magnetic hyperfine interaction in  $\text{Hf}_2\text{Ni}_7$  and  $\text{Zr}_2\text{Ni}_7$ . A possible reason might be that this interaction is weak in comparison to the electric quadrupole interaction. In such a case it is difficult

to distinguish the two interactions in the PAC spectrum. Measurements of susceptibility and magnetization and also theoretical band structure calculations of the hyperfine fields could help to clear up this problem.

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