AN IMPORTANT ROLE OF TDPAC TECHNIQUE IN THE MEASUREMENTS OF HYPERFINE PARAMETERS IN PHASES OF Hf-Fe PHASE SYSTEM*

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There are numerous experimental techniques available to study solids. Among them, an outline of the basic principles of hyperfine interactions, the Time Differential Perturbed Angular (TDPAC) coincidence technique is described and particular attention is paid to information that can be obtained from a TDPAC experiment. This time the research goal was to study intermetallic compounds, present in Hf-Fe phase system. In the course of studying the hyperfine interactions of $^{181}$Ta in paramagnetic Hf$_2$Fe and ferromagnetic HfFe$_2$ sample-materials, the time differential PAC spectra were recorded with a two-detector arrangement at characteristic temperatures. These measurements provide information on the chemical environment of observed ion probe.

Electronic structure calculations were performed with WIEN 97-FLAPW program package in order to relate measured hyperfine fields at sites of $^{181}$Ta ion probes in both compounds to particular chemical and physical properties of the neighbourhood and even of the material as a whole. In comparison experimental and calculated data, there is a pretty good agreement.

1. INTRODUCTION

The Time Differential Perturbed Angular Correlations (TDPAC) is one of the most attractive and productive experimental technique for the microscopic studies of solid-state properties. Using this sensitive and very powerful tool, information on interacting internal fields (which are local quantity) via hyperfine interactions with nuclear moments of the observed ion probes inside the given sample-material can be obtained.

TDPAC method has been known for more than forty five years and has been applied to a broad range of compounds and to a large number of highly sophisticated measurements in biophysics, condensed matter and material physics [1, 2, 3]. The complementary methods are NMR and NQR in nuclear resonance experiments, Mossbauer Spectroscopy (MS), Muon Spin Rotation ($\mu$SR) and Nuclear Orientation (NO) measurements.


The essential point of TDPAC coincidence experiment is detection of spatially anisotropic gamma rays emitted from radioactive ion probe atoms, constituents of the sample-material. Ion probe atoms are usually incorporated in the sample material under study using co-melting, diffusion, deposition and implantation [4, 5].

The alloys and compounds in the Hf-Fe phase system (Fig. 1) have been a subject of numerous investigations using various techniques and calculations, both because they can be obtained in the amorphous state and are candidates to absorb hydrogen readily without changing their lattice structure. This hydrogen storage capacity is both of fundamental and technological interest with considerable attention in the past and present time [6].

The main phase compositions in the named phase system are Hf$_2$Fe and HfFe$_2$, which are Pauli paramagnet and ferromagnet respectively.

![Fig. 1. – Hf-Fe phase system [7].](image)

2. EXPERIMENTAL

Investigated polycrystalline samples Hf$_2$Fe and HfFe$_2$ were obtained in a radio-frequency induction furnace, under pure argon atmosphere, and remelted
many times in order to minimize the evaporation losses. The starting component materials were of high purity, m5n for Fe and m4n for Hf. The quality of samples was verified by X-ray powder diffractogram.

The compound Hf$_2$Fe crystallizes in a complex face centered structure of the Ti$_2$Ni type. The unit cell is face centered cubic E9, with 96 atoms and unit cell parameter $a = 12.0333(3) \text{ Å}$. The space group is Fd3m. Thirty two atoms of Fe are in 32e position, while 64 atoms of Hf are in the 16c (HfI) and 48f (HfII) position. Each atom of Hf (I) is surrounded by six atoms of Hf (II) and six atoms of Fe. Each atom of Hf (II) is surrounded by eight atoms of Hf (II), two atoms of Hf (I), and two atoms of Fe. The coordination polyhedron surrounding Hf (I) atoms is formed by two regular octahedra of Hf (II) and Fe atoms. The polyhedron of the Hf (II) site is more complex [8].

Ferromagnetic HfFe$_2$ is intermetallic compound pertaining to the Laves phase group, composed of three related crystal structures: cubic MgCu$_2$(C15), hexagonal MgZn$_2$(C14) and MgNi$_2$(C36) structure with 24, 12 and 24 atoms per unit cell, respectively. A unifying feature of the structures is the Kasper polyhedron, the coordination shell of nearest neighbours around an atom. The Kasper polyhedron around Hf atom in the HfFe$_2$ is surrounded by four other Hf atoms and twelve Fe atoms. The cubic structure has lattice constant $a = 7.034(2) \text{ Å}$, while the lattice constants for hexagonal MgZn$_2$ structure are $a = 4.974(2) \text{ Å}$ and $c = 8.114(3) \text{ Å}$ [9].

After irradiation of samples in a reactor, the additional thermal treatment at 900°C for 240 hours in a vacuum of about $10^{-3}$ Pa was made, to eliminate possible radiation defects produced in the reaction $^{180}$Hf(n,$\gamma$) $^{181}$Hf $\rightarrow$ $^{181}$Ta. The irradiated and annealed samples were crushed into small pieces (several milligrams every piece) with negligible self-absorption of gamma rays, which were used as sources for the measurements.

In the course of studying the hyperfine interactions of $^{181}$Ta in Hf$_2$Fe and in HfFe$_2$, the time differential PAC spectra were recorded with a two-detector arrangement, equipped with fast BaF$_2$ scintillators (35mm $\Phi$X40 mm and 35 mm $\Phi$X10 mm) coupled to XP2020Q photomultiplier tubes.

The first nine dynodes of the photomultiplier tubes were used to ensure good time resolution. The perturbed angular correlation of the 482–133 keV cascade of the $^{181}$Ta ion probe was measured. Since high frequency electric quadrupole interactions (EQI) are involved, a high-resolution coincidence set-up had to be used.

The time resolution of the coincidence system was obtained for the positive timing signals from the seventh dynodes of the photomultipliers, and was maintained at the level of 0.5 ns throughout the experiment. The high and low temperature TDPAC measurements were performed with a low gamma ray scattering furnace and liquid-nitrogen Dewar structure, respectively [10].
3. RESULTS AND DATA ANALYSIS

In this paper we report the results of the measurements of electric quadrupole interaction (EQI) at $^{181}$Ta ion probes (activated Hf(I) and Hf(II) ions through corresponding nuclear reaction) in Hf$_2$Fe at room temperature, as well as hyperfine magnetic field measurements in the Laves phase HfFe$_2$ by TDPAC technique.

TDPAC spectrum for Hf$_2$Fe at 295 K is presented in Fig. 2. The general feature of measured spectra at 295K is a persistent high frequency oscillating component which is superimposed on a relatively smooth amplitude attenuation component, pronounced in the first part of the spectrum [11].

The dominant EQI observed in Hf$_2$Fe is that at $\omega_Q (\text{Hf 48f}) = 212 (1)$ Mrad/s at 295 K and is experienced by about 80% of all Hf atoms in the compound. The second EQI measured is characterized with $\omega_Q (\text{Hf 16c}) = 21 (1)$ Mrad/s and is assigned to atoms at the Hf 16c site (25% of all Hf atoms in the compound). The corresponding electric field gradients at Hf sites in Hf$_2$Fe are $V_{zz} = 22.3 (1) \times 10^{17}$ V/cm$^2$ and $V_{zz} = 2.2 (1) \times 10^{17}$ V/cm$^2$ for Hf 48f and 16c position, respectively [10]. The curves registering TDPAC spectra in the Laves phase HfFe$_2$ at 293 K and 453 K are given in Fig. 3. The solid curves represent the result of the computer fit. Analysis revealed two hyperfine magnetic field (HMF) components (Table 1), one of which corresponds to the magnetic perturbation with the value 13.82 T at 293 K and sustains up to temperature of 523 K. It is due to the interaction at the regular Hf site of the cubic C15 HfFe$_2$ structure. The second component has HMF of 8.0 T at 293 K. It is not perceivable in the 453 K spectrum above the Curie point of the C14 structure (427 K). In 523 K spectrum there is no magnetic interaction, but a weak electric quadrupole interaction is visible [12].

Because of very high precision of the measurements of hyperfine interactions with TDPAC technique (errors less than 1%), and its analytic ability, it is possible to make useful application and further treating of sample material through measurements of temperature dependence, behavior of sample material in

\textit{Table 1}

<table>
<thead>
<tr>
<th>Structure type</th>
<th>Larmor frequency $\omega_L$ [Mrad/s]</th>
<th>Internal magnetic field $H_{int}$ [T]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T = 293 K)</td>
<td>(T = 453 K)</td>
</tr>
<tr>
<td>MgCu$_2$</td>
<td>860 (5)</td>
<td>440 (30)</td>
</tr>
<tr>
<td>MgZn$_2$</td>
<td>500 (20)</td>
<td>0</td>
</tr>
</tbody>
</table>
Fig. 3. – TDPAC spectra at two characteristic temperatures for HfFe$_2$.

presence of external magnetic fields, measurements with other techniques which
give results complementary to TDPAC method, etc.

4. ELECTRONIC STRUCTURE CALCULATIONS

Electronic structure calculations were performed using WIEN 97-FLAPW
program package [13]. Exchange and correlation effects were included within
generalized gradient approximation (GGA) with the parameterization given by
[14]. Muffin-tin radii for Hf and Fe were 2.3 and 2.15 a.u., respectively. Core-
valence states separation was settled at –7.0 Ry. Core states were treated fully
relativistically, while valence states were treated within scalar relativistic
approximation. Plain-wave cut-off parameters were 8.0 and 8.5 for Hf2Fe and
HfFe2, respectively.

For the Hf2Fe the Brillouin zone integration was performed using a k-mesh
of 47 k points in the irreducible BZ wedge. After determing the self-consistent
charge density we obtain the EFG tensor Vij using the method developed in [15].
The usual convention is to designate the largest component of the EFG tensor as $V_{zz}$. The asymmetry parameter $\eta$ is then given by

$$\eta = \frac{|V_{xx} - V_{yy}|}{V_{zz}}.$$  

The calculated results for EFG are $-23.1 \cdot 10^{21}$ V/m$^2$, $4.2 \cdot 10^{21}$ V/m$^2$ and $2.7 \cdot 10^{21}$ V/m$^2$ for Hf 48f, Hf 16c and Fe 32d position, respectively. The calculations showed that the main contribution to the EFG for both Hf atoms comes from their p electrons and the main contribution to the EFG for Fe atom comes from its d electrons.

For the HfFe$_2$ C15 structure spin-polarized calculations were carried out with 56 k points in the irreducible wedge of Brillouin zone. Spin magnetic moments calculated as a difference of the number of electrons with spin up and down inside the muffin-tin sphere are $-0.32$ $\mu_B$ for Hf and $1.92$ $\mu_B$ for Fe. The main contribution to the magnetic moments comes from the spin polarization of d states. Calculated hyperfine magnetic fields are $-20.61$ T at Hf and $-16.92$ T at Fe atomic site [12].

Calculations for the hexagonal C14 HfFe$_2$ structure are in progress.

5. DISCUSSION

In order to demonstrate the feasibility of this technique, we have measured the TDPAC spectra of the intermetallic compounds, paramagnetic Hf$_2$Fe and ferromagnetic HfFe$_2$, as a function of temperature, using $^{181}$Ta source. Applications of TDPAC coincidence technique to hyperfine interactions measurements are still actual. Hence the great interest in this field will certainly stimulate more systematic and detailed investigations, regarding better time resolution and more complete software packages.

As was presented in this paper the utilization of the TDPAC method has led to a variety of interesting results. The results of TDPAC measurements at $^{181}$Ta sites in paramagnetic polycrystalline Hf$_2$Fe have demonstrated the possibility of precise measurements of electric quadrupole interactions (EQI) at the two non equivalent-crystallographic positions -the high-frequency at the 48f-site with many details and the low-frequency at the 16c-site interaction exhibiting a clear anomaly with respect to that at the 48f-site. These data reveal the rich phenomenology associated with this metallic system.

Concerning the measurements at $^{181}$Ta sites in HfFe$_2$ we have obtained data for hyperfine magnetic fields for every particular structure independently. Hyperfine magnetic field for predominant cubic structure C15-MgCu$_2$ (more
than 60%) is $H_{hf}(^{181}\text{Ta}) = 13.9 \pm 0.1$ (T) at room temperature and no pronounced temperature anomaly for $H_{hf}$ was observed, i.e. its temperature dependence is similar to that of the bulk magnetization [16]. The corresponding value for hexagonal structure C14-MgZn$_2$ (about 40%) is $7.5 \pm 0.2$ (T). These values have changed slightly for the annealed sample (13.8 ± 0.1 (T) for MgCu$_2$ and $8.0 \pm 0.2$ (T) for MgZn$_2$ structure), but the change in the ratio of different structures in the sample is significant. Namely, in the annealed sample it was observed the existence of the cubic MgCu$_2$ structure in an amount of 83% and hexagonal MgZn$_2$ type structure in an amount of 17% annealing has brought to increase of the share of MgCu$_2$ type structure for almost 20%. From this we can conclude that annealing doesn’t affect magnetic properties significantly, but it brings to change in crystal structure [17]. The presence of the third phase MgNi$_2$ (less than 5%) is not observed in the investigated sample-material.

When comparing results obtained from experiments and calculations, one should have in mind that values obtained from calculations correspond to EQI (EFG)-Hf$_2$Fe or to MDI ($H_{hf}$) – HfFe$_2$ at 0K and that both these properties decrease with temperature. The agreement of measured and calculated is quite good, except the calculated data for $H_{hf}$ at $^{181}\text{Ta}$ in MgZn$_2$ which are still in progress.

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REFERENCES


