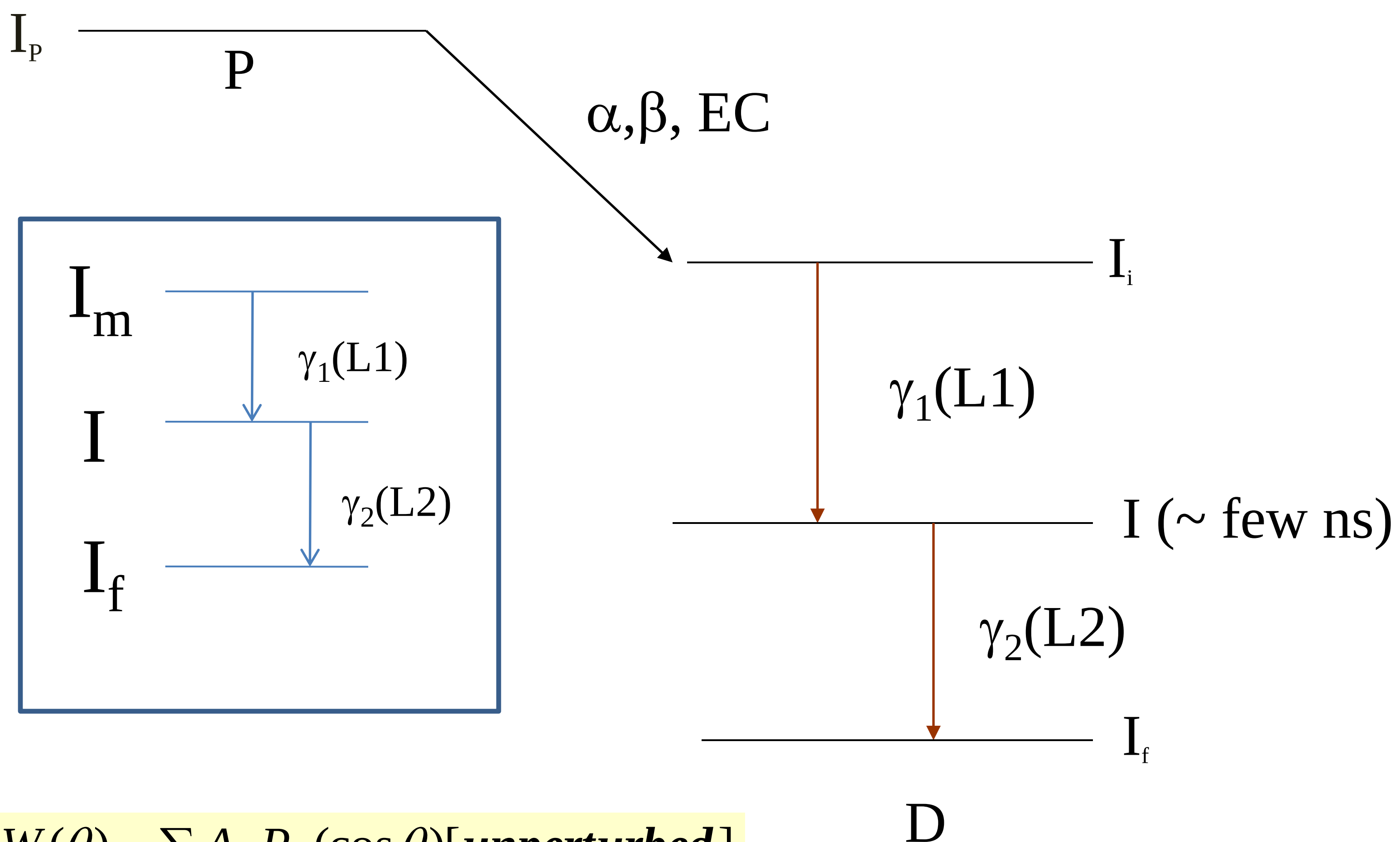
Hyperfine Interaction studies using RIB

S.K. Das
Radiochemistry Division(BARC)
VECC

Plan

- Hyperfine technique : TDPAC – An Introduction
- Studies of materials, chemical problems: Thin film, nanoparticles, Hf-compounds, Endofullerene
- Nuclear spectroscopy
- Summary and outlook

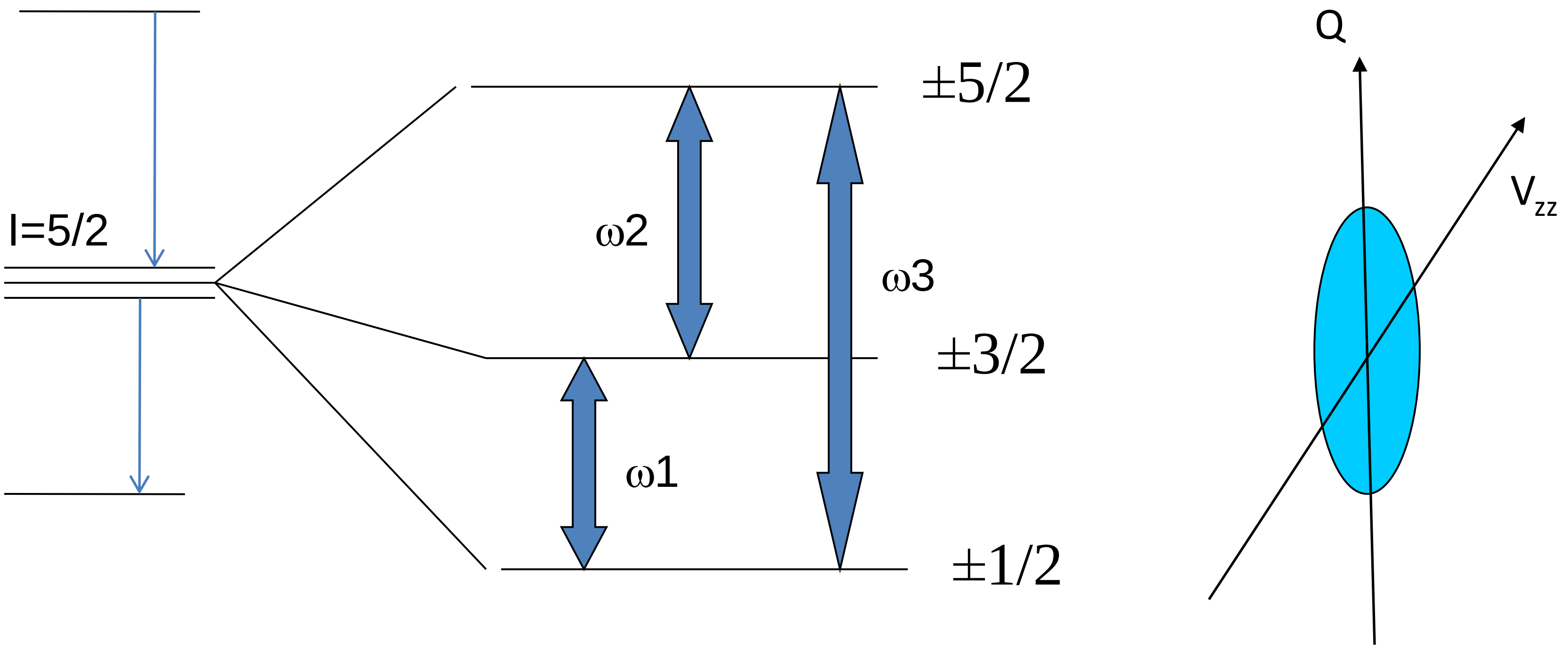
Hyperfine Interaction technique: PAC



$$W(\theta) = \sum_k A_k P_k(\cos\theta)[\textbf{\textit{unperturbed}}]$$

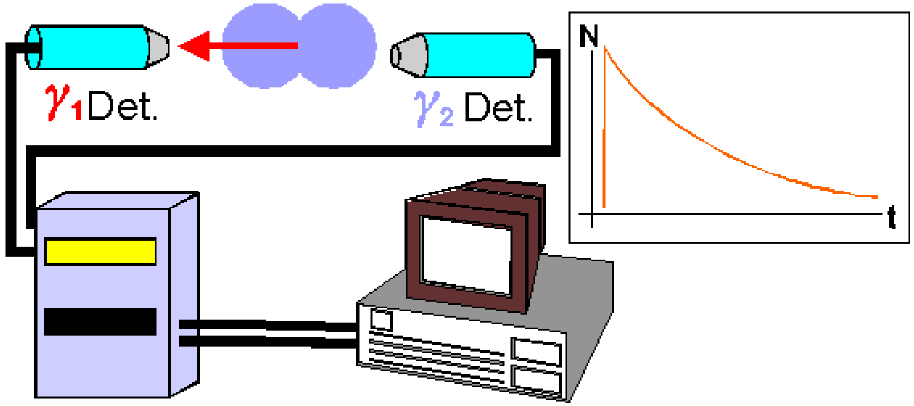
$$W(\theta) = \sum_k A_k G_k P_k(\cos\theta)[\textbf{\textit{perturbed}}]$$

Quadrupole Interaction

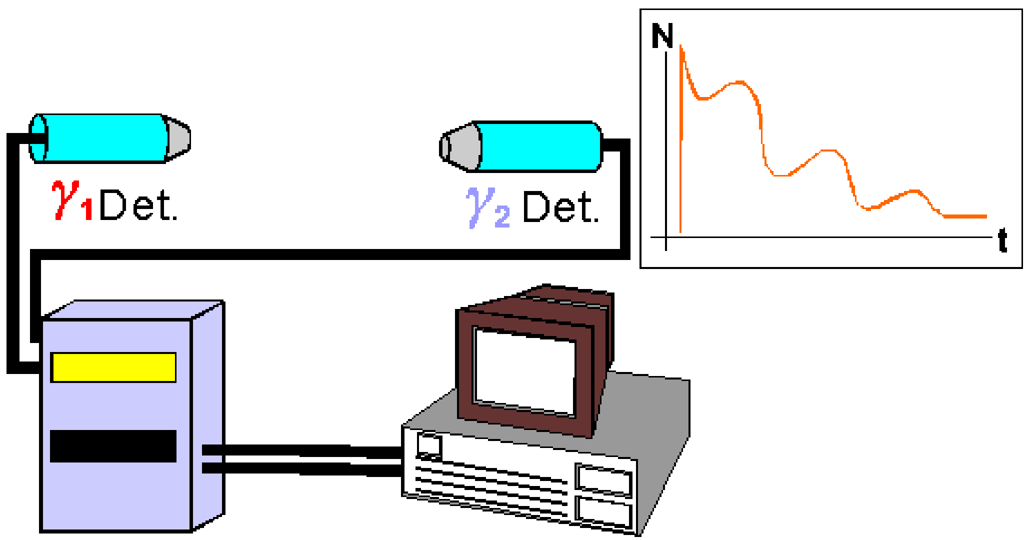


$$E(m) = eQV_{zz}[3m^2 - I(I+1)]/4I(2I-1)$$

$$= h\omega_Q[3m^2 - I(I+1)]$$



Unperturbed



Perturbed

Quadrupole interaction frequency

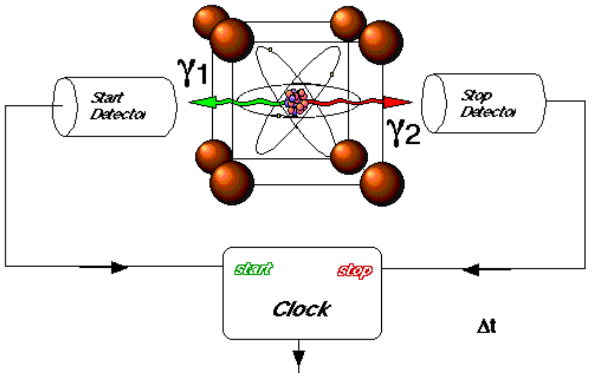
↓

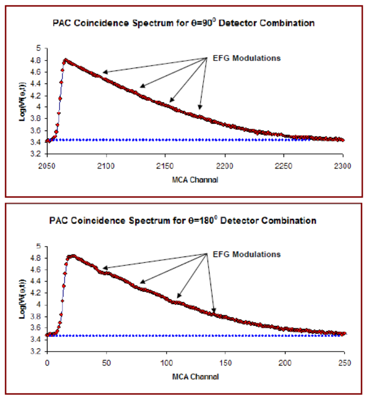
Nuclear ⊗ electronic

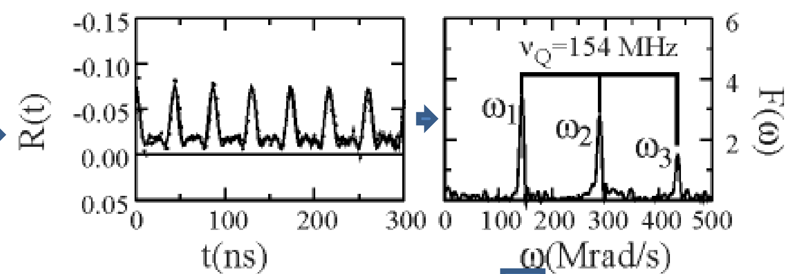
Nuclear → eQ ; Electronic → V_{zz}

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

Methodology of TDPAC technique







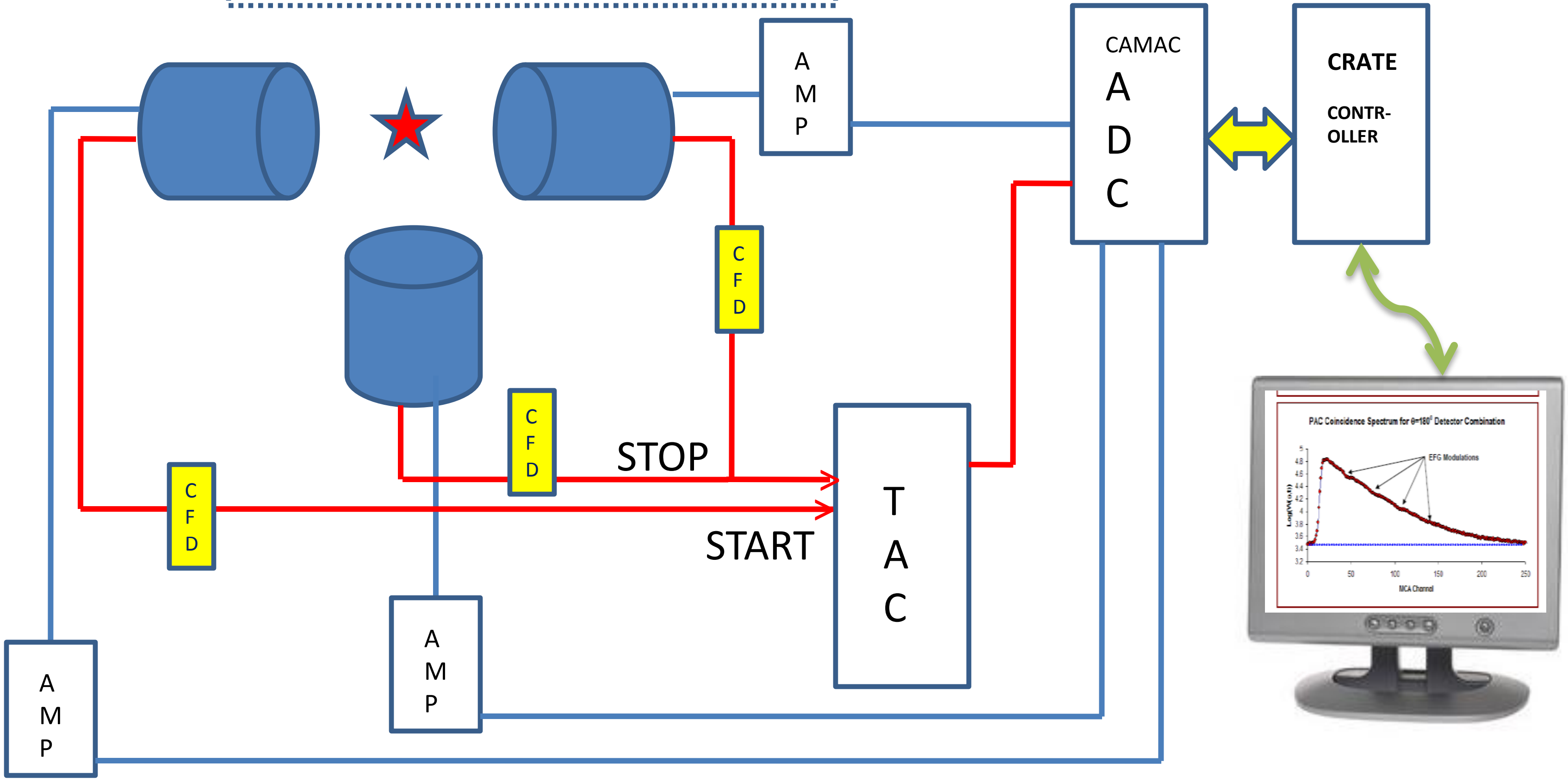
Frequency - ω_Q

Frequency Distribution - δ

Asymmetry of EFG - η

Important parameters
To understand the
Structure of a material

COINCIDENCE CIRCUIT: CAMAC

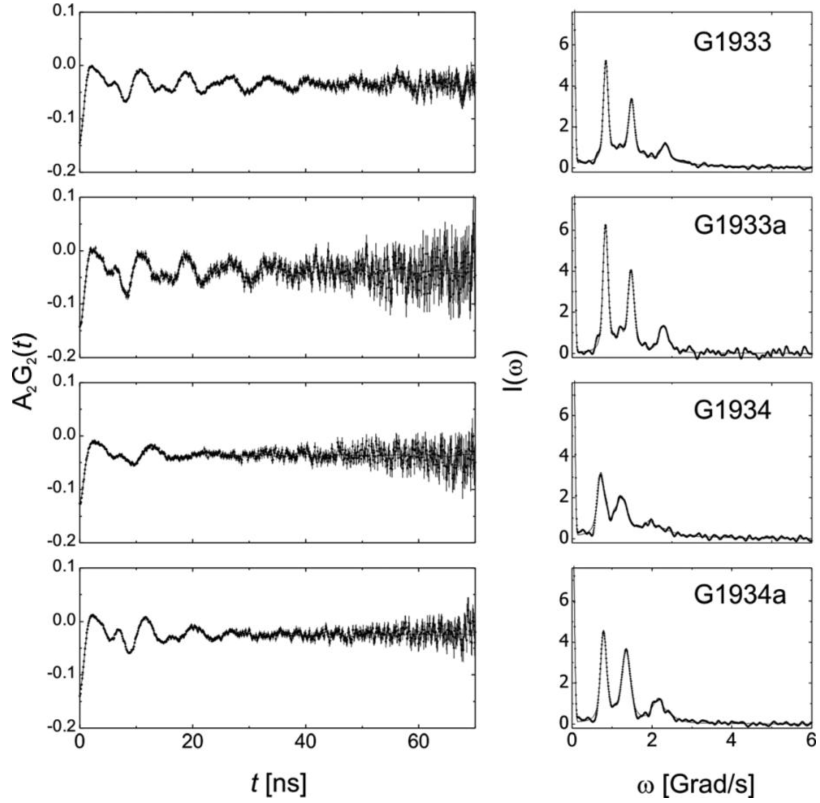


Methodology of labeling the matrix with the nuclear probe

- Neutron irradiation to make the probe in situ.
- Nuclear reaction Implantation of the probe.
- The probe can be chemically separated in the carrier free form and this can be incorporated during synthesis of the matrix.
- The nuclear probe can be accelerated (10-100 keV or so) to implant into the desired matrix.

HfO_2 thin film
on sapphire by PLD method

$^{180}Hf(n,\gamma)^{181}Hf\ (\beta^-)\ ^{181}Ta$



- Film thickness : 85-350 nm
- pO2 : 0.0003-0.3 mbar
- Annealing temp: 1073 & 1273 K

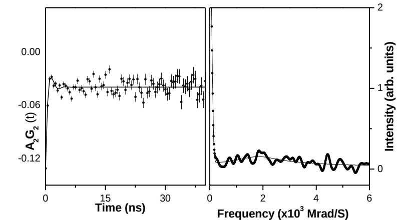
Results:

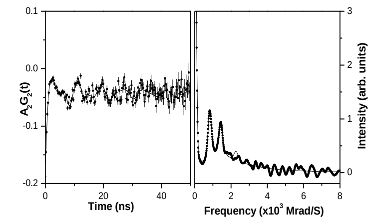
- 88% bulk monoclinic phase
- Rest are O-vacancies (?)

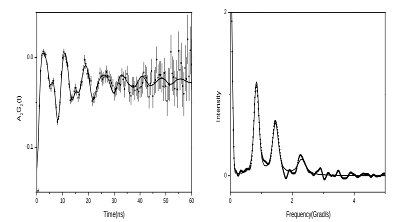
Hafnium oxide thin films studied by time differential perturbed angular correlations, C. C. Dey, S. Dey, S.C. Bedi, S. K. Das, M. Lorenz, M. Grundmann, J. Vogt and T. Butz, JOURNAL OF APPLIED PHYSICS 109, 113918 (2011)

Thin film of HfO_2

Evolution of thin HfO_2 film on Si (111) plane







Motivation:

- ➢Replacement of SiO_2 as gate dielectric in the semiconductor devices
- ➢Surface structure of HfO_2 thin film on Si substrate

Experiment & Resuts:

- ➢Hf metal deposited onto Si(111) substrate by Ion beam sputtering method
- ➢n-irradiated at BARC and annealed at 873, 1073 and 1273K for 4h.
- ➢Counted for TDPAC at rt

Comments:

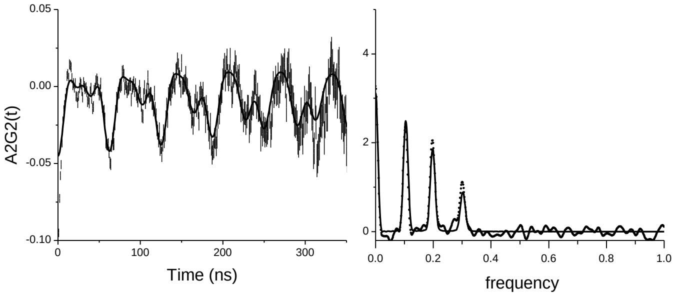
- ✓Crystalline monoclinic phase of HfO_2 attained only to a small extent (25%) even after annealing at 1273K for 4h.
- ✓Attainment of monoclinic phase is at 1273K for 10 hrs

Samples	ω_Q (Mrad/s)	η	δ (%)
Unannealed	288.0(0)	0.2(0)	23.5(1)
Annealed at 873K	288.0(0)	0.2(0)	49.3(1)
Annealed at 1073K	288.0(0)	0.2(0)	43.8(2)
Annealed at 1273K	212.1(9) 123.0(7)	0.1(0) 0.34(1)	50.8(4) 3.8(7)

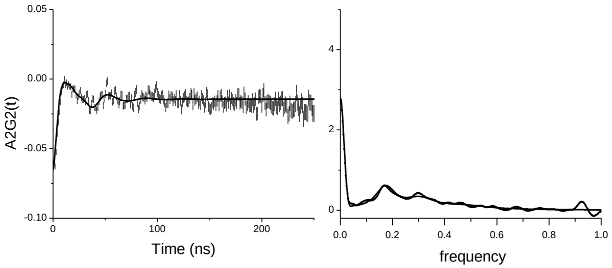
Gr IVB oxides with different probes

- Annealed at 1273K
- ^{111}In does not go into HfO_2 and ZrO_2
- ^{111}In goes into TiO_2 matrix
- Theory shows the solubility of ^{111}In Is less in Hf/ZrO_2

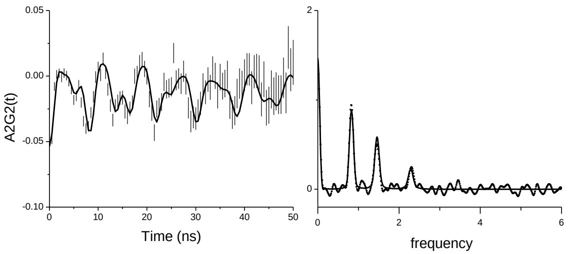
Rutile TiO_2 (^{111}In)



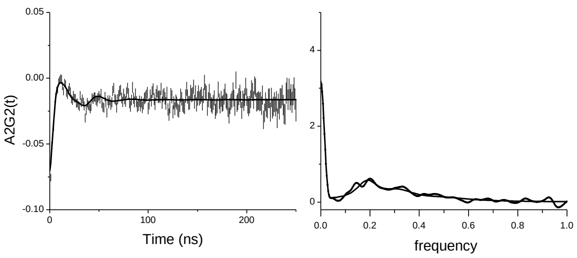
ZiO_2 (^{111}In)



HfO_2 (^{181}Hf)



HfO_2 (^{111}In)



Theory

WIEN2k calculation of EFG in HfO_2 and ZrO_2

Sample	Parameter	Neutral state	Charged state	Experimental result
HfO_2	EFG ($X10^{21} V/m^2$)	18.78	14.62	13.7[a]
	η	0.18	0.44	0.34[a]
ZrO_2	EFG ($X10^{21} V/m^2$)	14.65	14.33	13.3[b]
	η	0.40	0.45	0.32[b]

✓Experimental TDPAC parameters match closely with theoretical results when cation is in charged state.

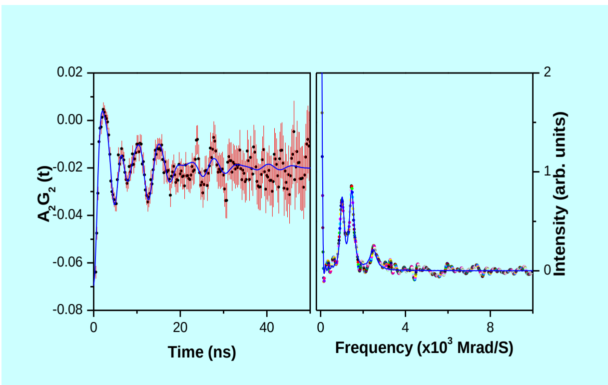
✓Probe is present in charged state inside the matrix.

Zr-doped TiO_2

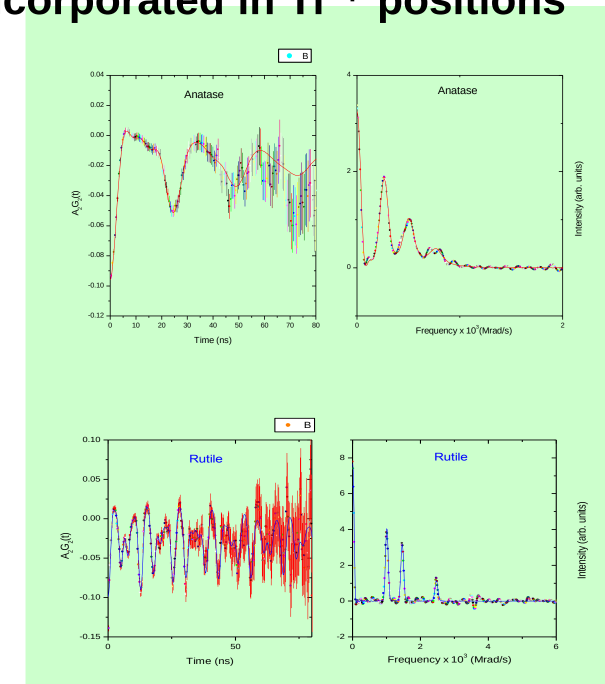
Mn-doped TiO_2

Mn-doped TiO_2: Mn^{+4} gets incorporated in Ti^{+4} positions

- **Doped TiO_2: photocatalyst, DMS, solar cell etc.**
- **Zr-doped TiO_2: cation-cation interaction between the probe and the Zr atom**



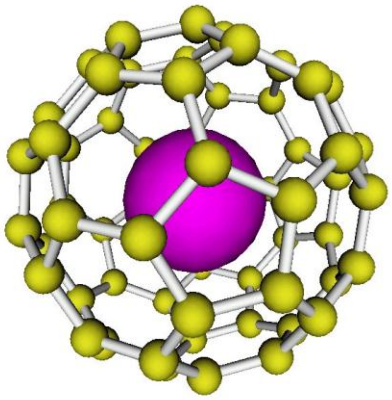
Samples	ω_Q (Mrad/S)	η	δ (%)
Pure rutile[a]	130.07(9)	0.56(1)	0.0
1% Zr/rutile	127.04(4)	0.55(1)	0.0
5% Zr/rutile	126.2(3)	0.58(1)	8.3(9)
10% Zr/rutile	127.44(7)	0.55(3)	12.8(5)



Sample	Anatase V_{zz}x10^{17}Vcm^{-2}	η	Rutile V_{zz}x10^{17}Vcm^{-2}	η
Pure TiO_2	4.62	0.22	13.65	0.56
5%Mn doped TiO_2	4.42	0.18	13.48	0.57

Zr-doped rutile TiO2: a nuclear quadrupole interaction study, D. Banerjee, **S.K. Das**, P. Das, S.V. Thakare and T. Butz, Hyperfine Interaction 198(1-3)(2011) p.193-198.

Endofullerene research



*Implantation of different radioisotopes inside the cage

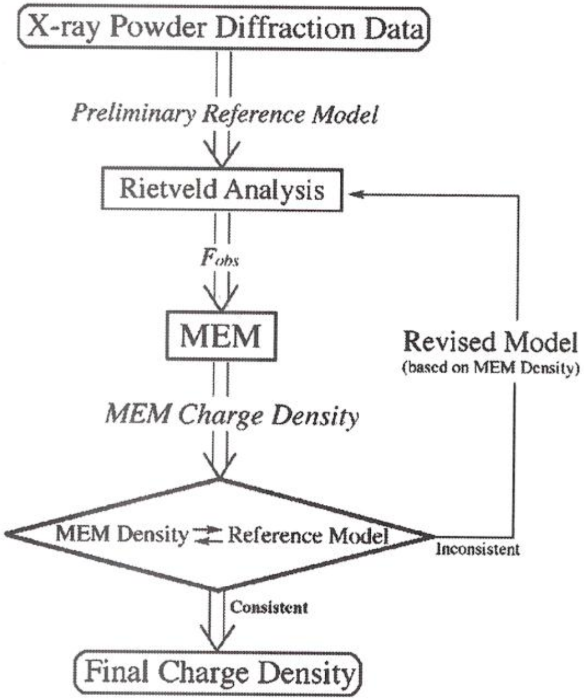
*Radiochemical separation between exo and endo fullerene

*Physicochemical studies

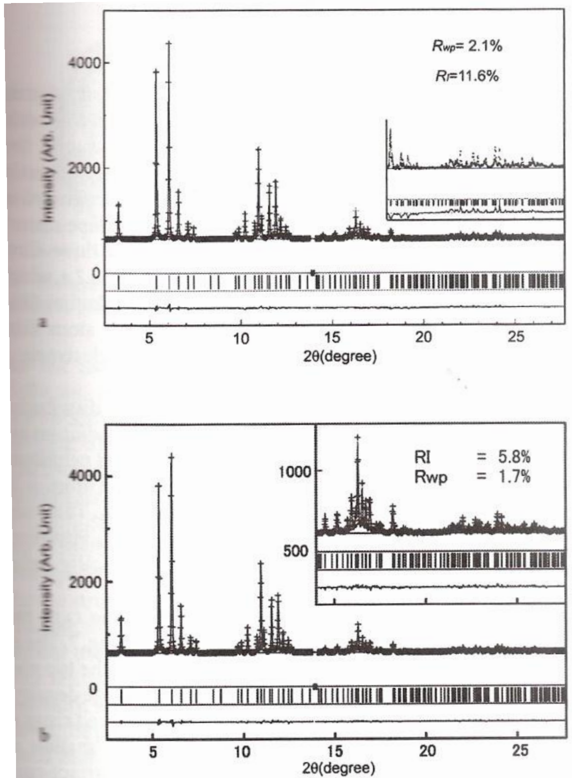
*Dynamical behavior of nuclear probes through TDPAC measurement

Charge density level structures by the MEM/Rietveld method

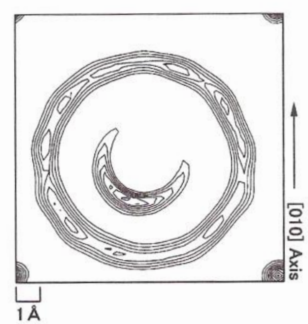
"Imaging of diffraction data"



Flow chart of the MEM/Rietveld method



...tting results of **a** the pre-Rietveld analysis and **b** the final Rietveld analysis for La@C_{82}

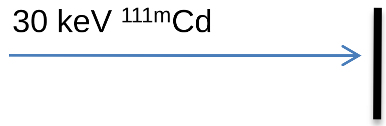


La@C_{82}

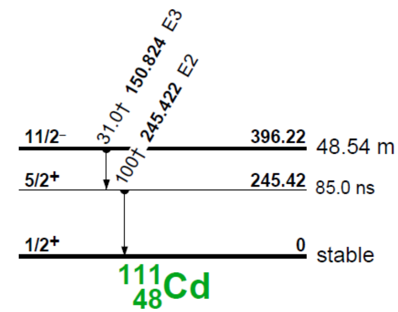
...(100) section of the MEM charge density of La@C_{82} based on pre-Rietveld analysis. ...es are drawn from 0.0 to 4.5 $e/Å^3$ with 0.3 $e/Å^3$ intervals

Masaki Takata etal. ***Structure and Bonding, vol. 109, (2004) 59-84***

$^{111m}Cd@C_{60}$ ISOLDE experiment



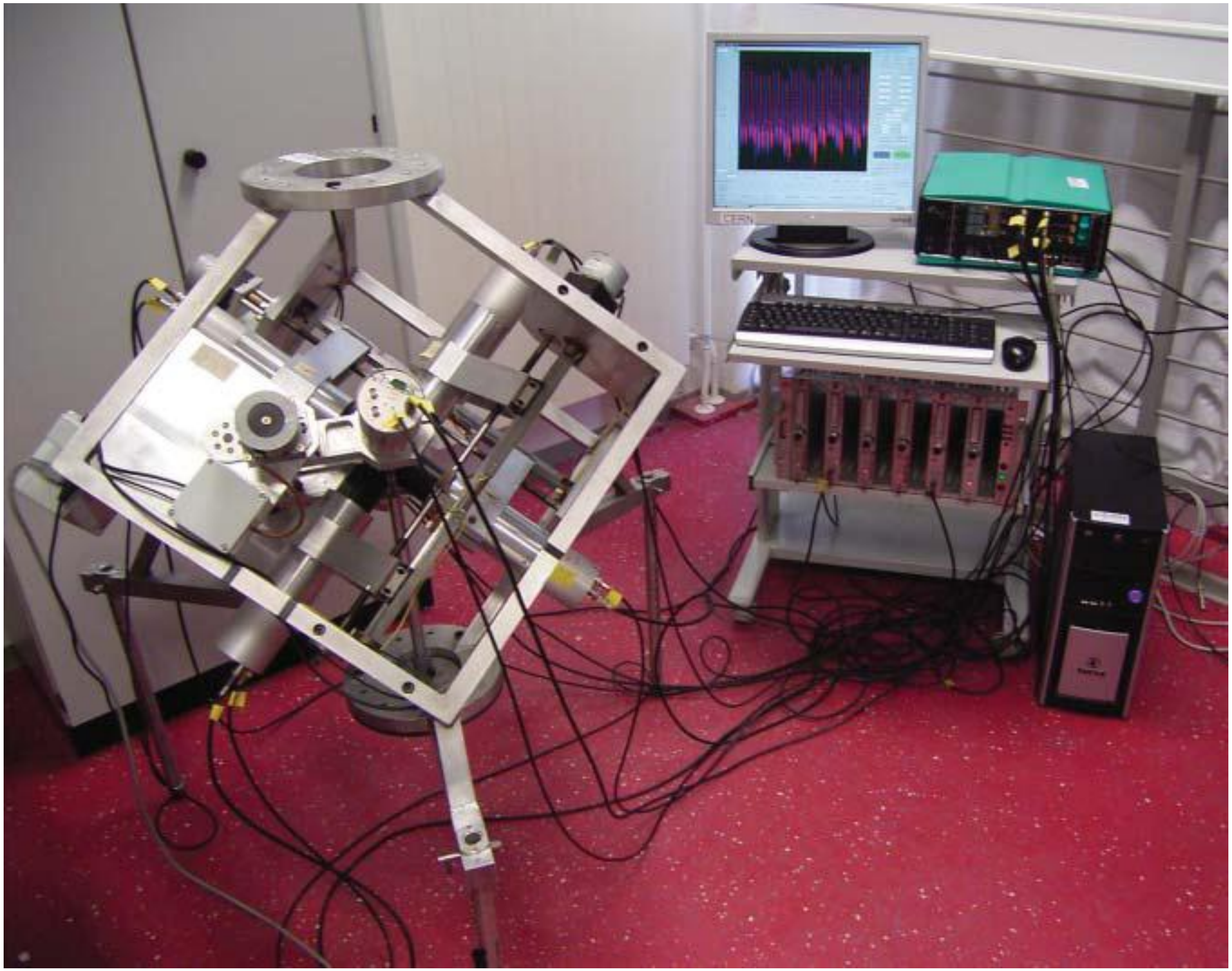
$^{Nat}Sn(p_{1.0\ GeV},2pxn)^{111m}Cd$



- Total no. of ^{111m}Cd ~ $3x10^{11}$ in 45 min
- Chemical separation of the irradiated C_{60}
- TDPAC counting on 6- $LaBr_3$ detector system

PAC study of the static and dynamic aspects of an atom inside a fullerene cage

S.K. Das [1], R. Guin [1], D. Banerjee [1], P. Das [1], T. Butz [2], V. S. Amaral [3], J.G. Correia [4], M. B. Barbosa [4]
1 Radiochemistry Laboratory, Variable Energy Cyclotron Centre, Bhabha Atomic Research Centre,
1/AF Bidhan nagar, Kolkata 700064, India
Variable Energy Cyclotron Centre, Kolkata 700064, India
2 Fakultät für Physik und Geowissenschaften, Universität Leipzig, Linnéstr.5, 04103 Leipzig, Germany
3 Departamento de Física e CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal
4 ITN, Sacavém, Portugal and ISOLDE-CERN



$^{111m}Cd@C_{60}$ ISOLDE experiment: results

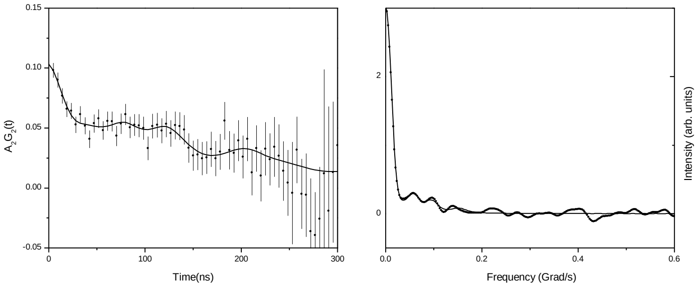


Fig 1. TDPAC spectrum for the $^{111m}Cd@C_{60}$ endofullerene (left) and the corresponding Fourier spectrum (right).

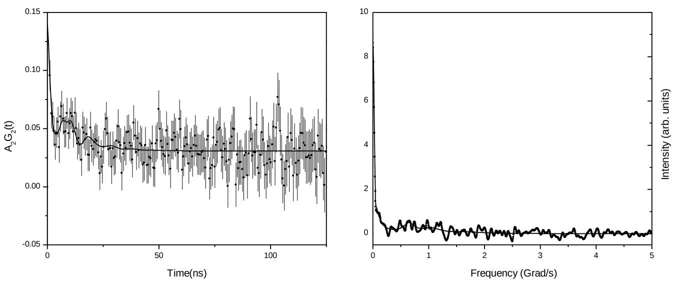
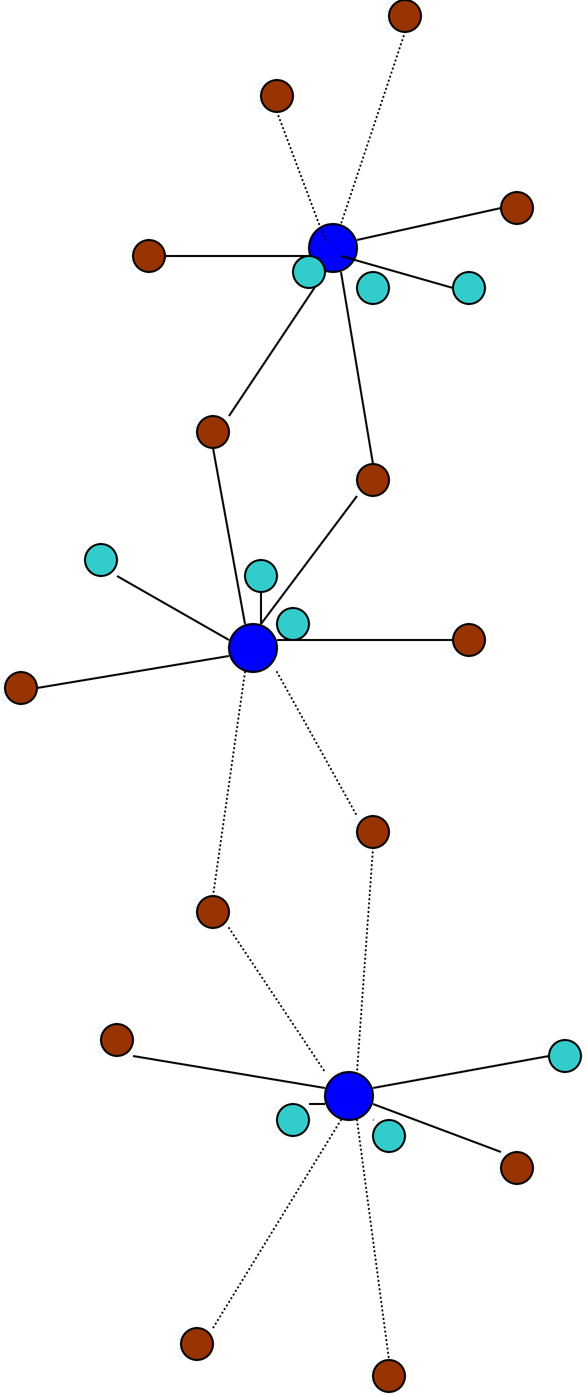


Fig 2. TDPAC spectrum for the C_{60} decomposed products on the filter paper (left) and the corresponding Fourier spectrum (right).

Samples	ω_Q (Mrad/s)	η	δ (%)	Amplitude	Fast Amplitude	Fast λ
$^{111m}Cd@C_{60}$	8.14(42)	0.42(9)	9.3(5.7)	0.038(8)	0.098(86)	0.003(3)
Filter Paper	90.7(8.4)	0.43(13)	18.1(9.0)	0.089(37)	0.046(7)	0.089(22)



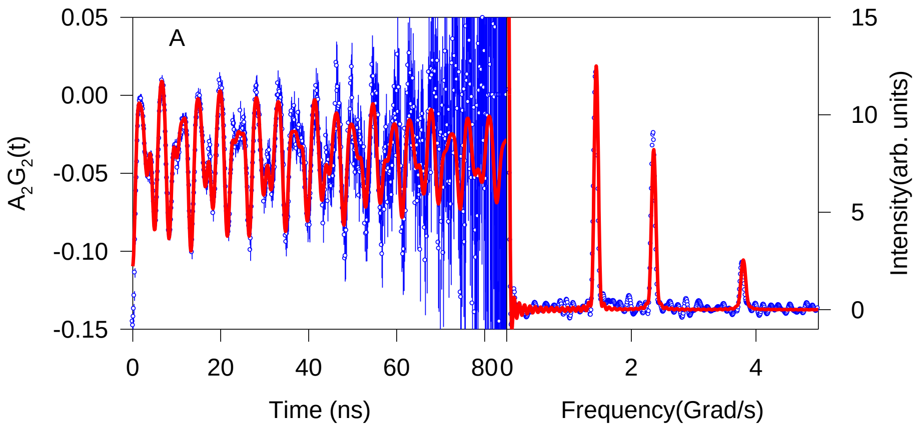
TDPAC study of Hafnium Fluoride $HfF_4,3H_2O$

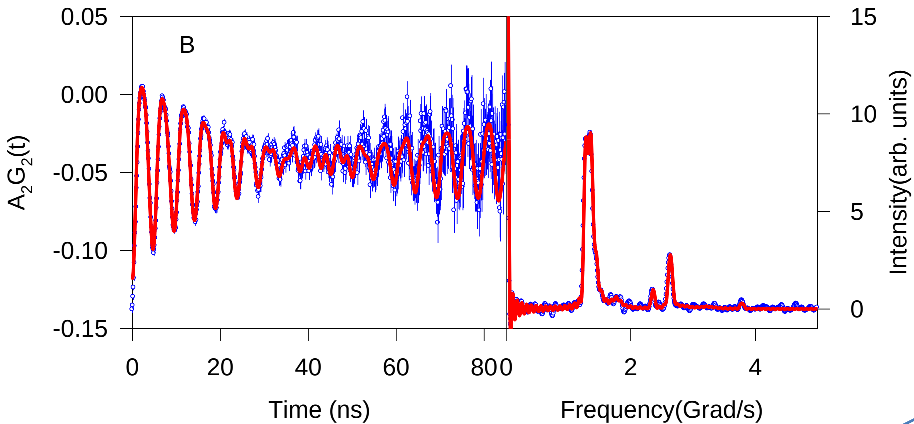
Tetra fluorides of Hf, Zr, U, Th, Pu are isostructural.

X ray data indicates the existence of two crystalline forms.

Structure and the dehydration/hydration Processes are not clearly understood.

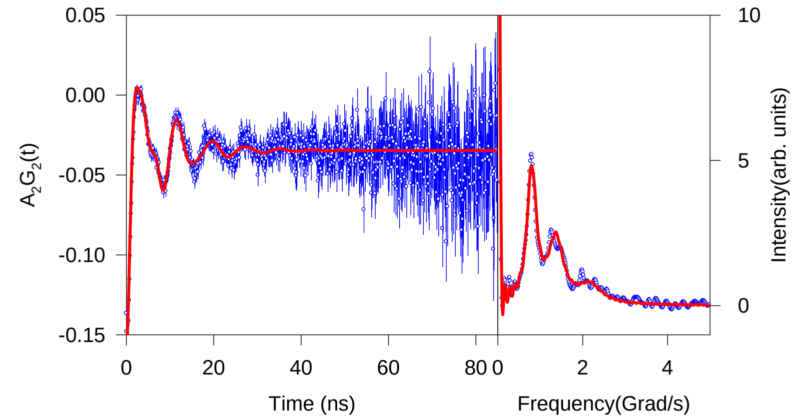
TDPAC work- for HfF_4 samples prepared by drying at RT and at 40°C under IR lamp.





A. Hf metal + HF acid dried at RT

B. Dried at 40 deg C under IR lamp



Dehydrated Hafnium fluoride (HfF_4)

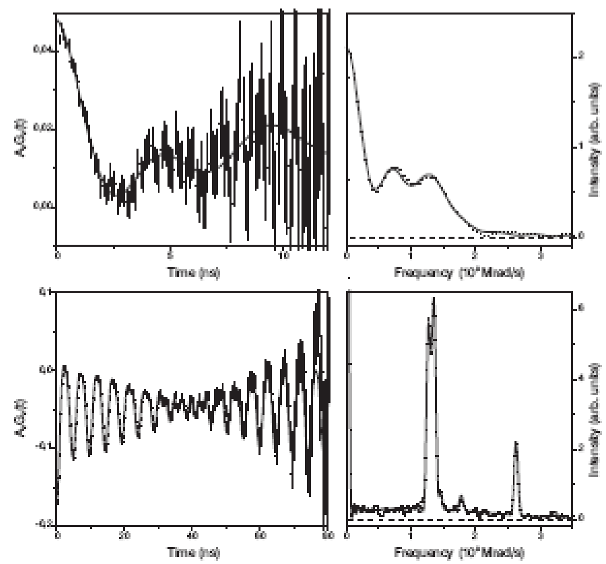
Sample (HfF_4, $3H_2O$)	ω_Q (Mrad/s)	η	δ (%)	Site %
RT	203.1(1)	0.42(1)	0.4(4)	100

40°C (IR) I	126.7(1)	0.93(1)	0.5(1)	63
II	134.2(3.6)	0.99(5)	7.1(1.5)	18
III	161.8(9)	0.76(3)	3.5(7)	11
IV	202.8(3)	0.41(4)	0.1(2)	8

$HfF_4.3H_2O$

$HfF_4.HF,2H_2O$

$Hf_2OF_6.H_2O$



Probe: ^{180m}Hf

Probe: ^{181}Ta

TDPAC spectra for HfF4.HF.2H2O

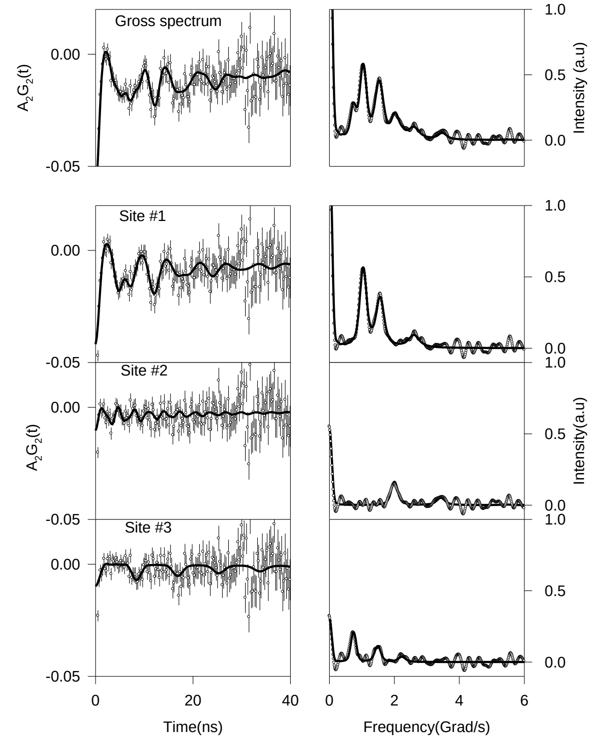
A comparative time differential perturbed angular correlation study of the nuclear quadrupole interaction in $HfF_4.HF.2H_2O$ using ^{180m}Hf and $^{181}Hf(\beta^-)^{181}Ta$ probes: Is Ta an innocent spy ? By T. Butz, **S.K. Das**, Yurij Manzhur, Z. Naturoforschung(accepted)

Mimicking Pu sorption on hydroxyapatite using $^{181}Hf/^{181}Ta$ probe

Hydroxyapatite: $[Ca_5(PO4)_3OH]$

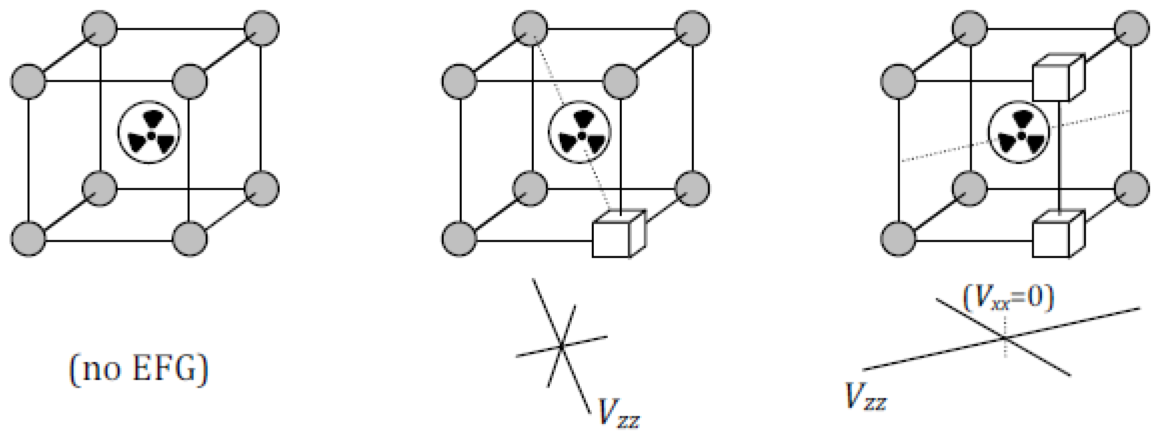
Ca(I) ions are surrounded by nine Oxygen atoms[three O(1), three O(2), and three O(3)] and Ca(II) is surrounded by six oxygen atoms[one O(1), one O(2) and four O(3)] of phosphate groups (PO_4).

Site	ω_Q(Mrad/s)	η	δ(%)	Site %
I	136.7	0.54	8.0	58
II	300.1	0.36	5.8	28
III	124.6	0.00	5.5	14



Study of cation-localization in apatite and orthophosphate structures using $^{181}Hf/^{181}Ta$ probe, D. Banerjee, S.K. Das, S.V. Thakare, J. Radioanal. Nucl. Chem. 290, 187-190 (2011).

Defect study



- ➢Defect formation energy
- ➢Association energy
- ➢Migration energy

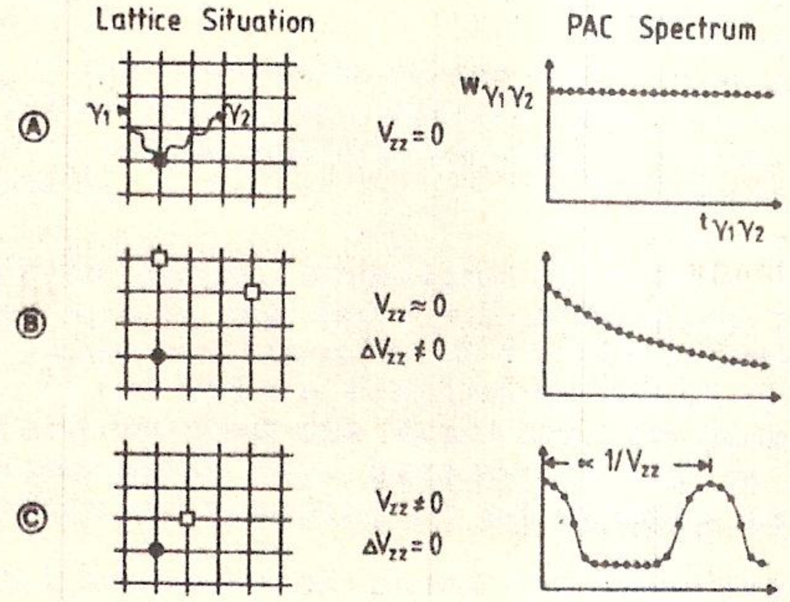
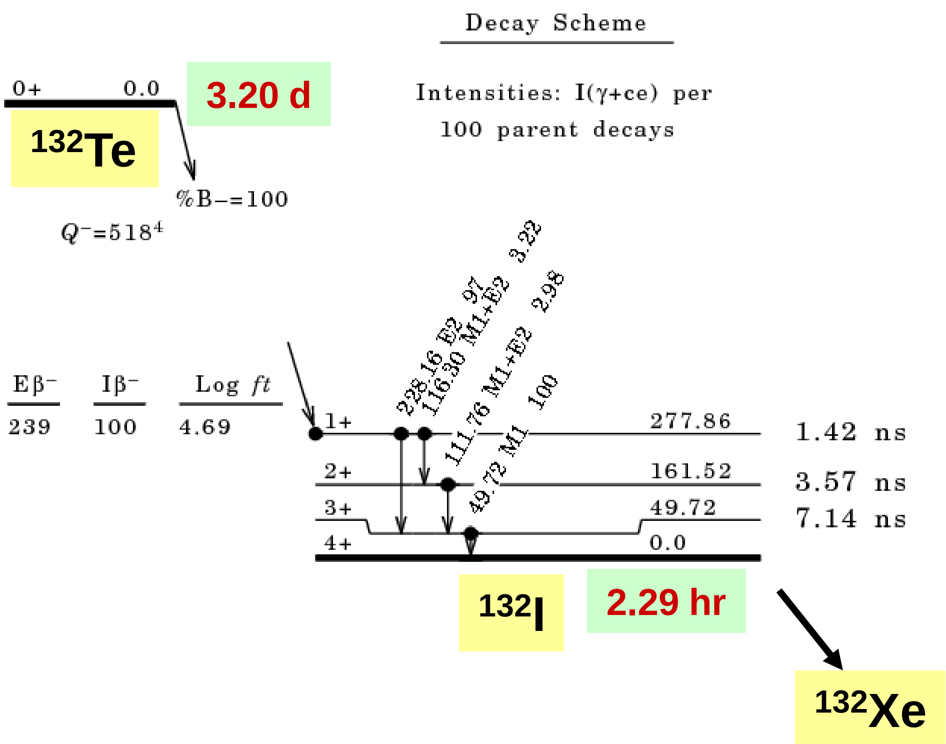


Fig.1 Microscopic display of typical arrangements of impurities (full circle) and defects (open square) in a cubic lattice, as characterized by electric field gradient V_{zz}, and the corresponding experimental spectra.

Procedure

- ZIRLO = Zr-1Sn-1Nb-0.1Fe
- Defects: irradiation with charged particles
- Implantation of probe in ZIRLO
- Data analysis to obtain EFG at the probe site
- Theoretical calculation of EFG to understand defect nature

Lifetime & Q-moment measurement of excited states of ^{132}I



S. K. Das et al., EPJ A4, 1 (1999).
M. Diksic et al., PRC 10, 1172 (1974).
M. Tanigaki et al., PRC 80, 034304 (2009).

Various lifetimes reported :
0.96ns, 2.9ns, 1.12ns

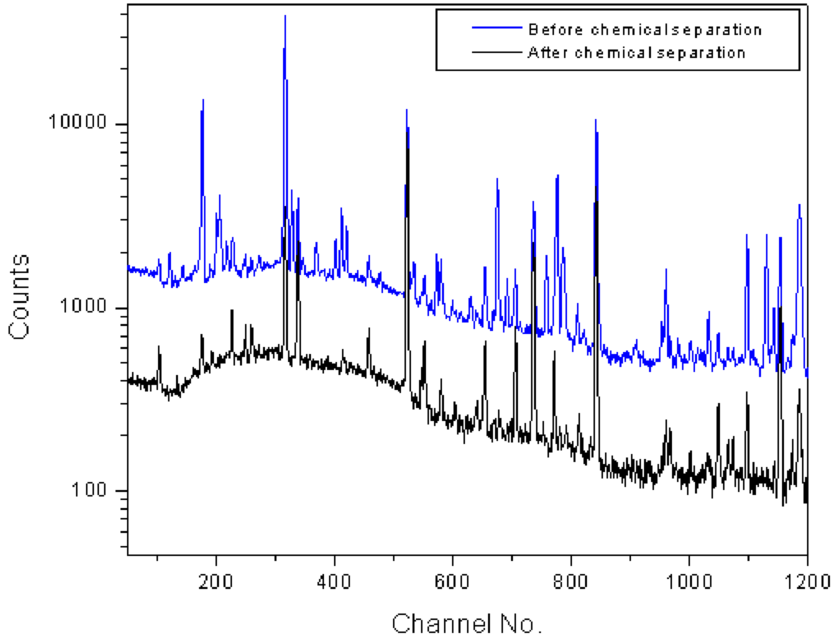
Experimental plan at VECC

- measure the lifetimes using different detector system
- Quadrupole moment by TDPAC / IPAC

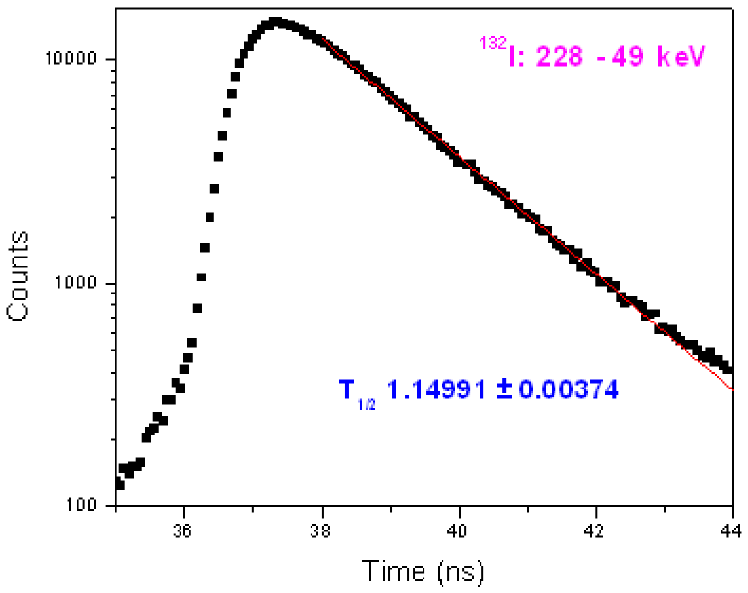
Lifetime measurement of excited states of ^{132}I with BaF2 detectors

^{235}U + p (16 MeV, 200 nA) → ^{132}Te as one of the fission products
→ chemical separation of ^{132}Te
→ counting with three BaF2 detectors

Total spectrum before and after chemical separation
Taken with a 50% HPGe detector

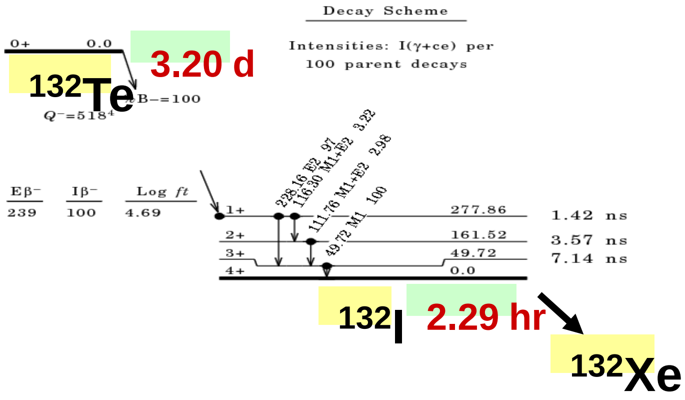


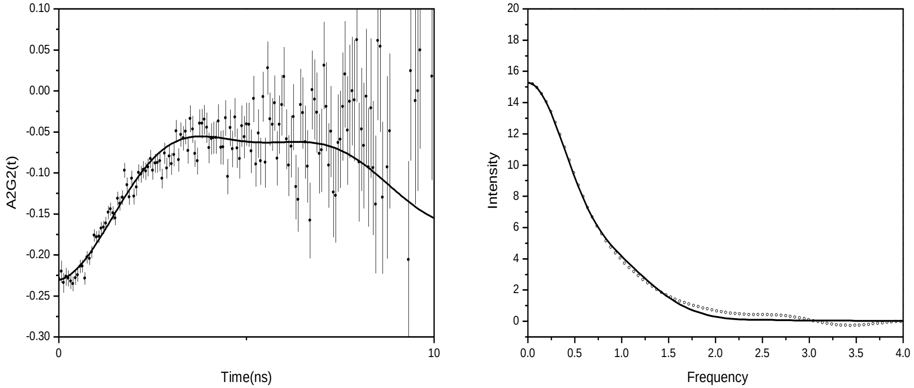
TAC spectrum for
228 – 49 keV coincidence



Quadrupole moment

228-49 keV cascade





TDPAC study 49 keV state of ^{132}I in Te metal

ω_Q = 290 Mrad/s
η = 1

Study from Decay – Off-beam study

- **Systematic Study of ($\nu h_{11/2} d_{3/2}$) 7^- isomeric states in even – even $^{126, 128}$Te**
- **Possible to be produced by decay of $^{126, 128}$(I, Sb) ($t_{1/2}$ ~ hrs-days)**

^{124}Te	^{126}Te	^{128}Te	^{130}Te	^{132}Te
2673 keV	2497 keV	2337 keV	2146 keV	1925 keV
	152 ps	2.4 ns	115 ns	28 μs

- ^{126}Te- 6+, 1776 keV level, 68 ps
  (can be measured by IPAC)

In beam Study

✓ ^{132}I has been studied from decay of ^{132}Te

✓$^{124, 126, 128, 130}$I – cannot be produced from decay

✓Possible to be produced and studied in-beam

^{130}I --------- $(6-)_1$;69 keV level , 133 ns,
$(6-)_2$ 85 keV level, 254 ns- μ known from (p,nγ)

^{128}I ---------- 2- 12.3 ns 133 keV level,
4- .845 μs 137 keV μ known
6-, 167 keV 175 ns level

^{126}I --------- 1+ 56 keV level, 15.9 ns,
(1+, 2+, 3+) 110 keV, 56 ns μ known,
(1-,2-,3-) 122 keV, 13.5 ns

^{124}I -------------- 3+, 55 keV, 52 ns,
4-, 123 keV 9.6 ns,
250 keV, 14 ns (Jp not known),
6-, 287 keV, 1.6 ns,
7- 311 keV, , 1.3 ns

Summary and outlook

- Study of Gr-IVB metal oxides (pure and doped): bulk, thin film and nano materials using ^{180m}Hf
- Mimicking Pu with ^{180m}Hf probe
- ^{199m}Hg, ^{80m}Br beam for endofullerene studies
- $^{111}In/^{111}Cd$ beam for atomic after effect studies in cubic semiconductors viz. InSb, CdTe, InP, InAs
- Nuclear spectroscopy (Q- moment) of $^{126,128}Te$; $^{124-130}I$ isotopes

Team

- D. Banerjee
- R. Guin
- Parnika Das
- Tumpa Bhattacharya
- Sarmistha Bhattacharya
- P.Y. Nabhiraj

Thank you