Perturbed angular correlation studies at SINP

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Perturbed Angular Correlation (PAC)

a nuclear technique applied in different areas of Physics, Chemistry and Biology

Started with the application in Nuclear Physics

It has been used mostly in Condensed Matter

Application in Biology is growing

Some application of PAC in condensed matter –

- Structural and magnetic phase transitions of solids
- point defects
- Surfaces, interfaces and grain boundaries, thin films, nanocrystals
- Dynamical interactions due to fluctuation of atoms and molecules through nuclear relaxation

Advantages of PAC technique:

- Very small activity of the sample (10-100 μC) is required
- No limitation to the choice of sample environment. PAC experiments can be carried out with samples in any aggregate state, in a wide range of pressures, temperatures, and external electromagnetic fields.
- No need for applied magnetic fields or RF fields like in NMR/NQR
- Small interactions are more easily resolved than in MS

- Principal of TDPAC technique
- Experimental facility at SINP
- Experimental results in Hf/Zr based materials using ^{181}Hf probe

  Rb_2HfF_6 and Cs_2HfF_6 (synthesized chemically)

  K3HfF7 and Na3HfF7 (synthesized chemically)

  Intermetallic compounds of Zr_2Ni and ZrNi5

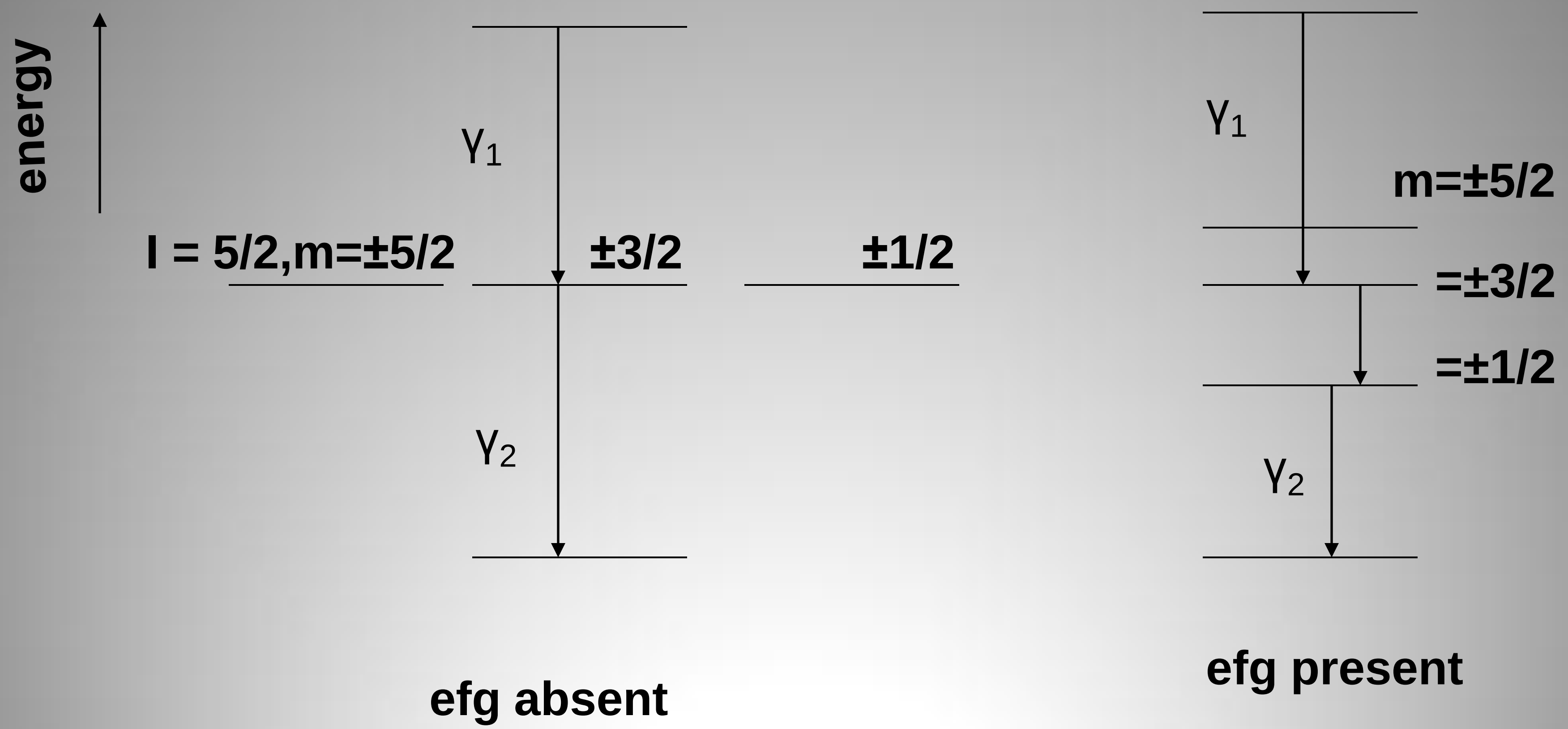
  (prepared in argon arc furnace)

γ-γ Angular correlation is perturbed due to:

- **Electric quqdrupole interaction (NQI)**
  Nuclear electric quadrupole moment interacts with the electric field gradient (efg) of the surrounding medium.

- **Magnetic interaction**
  Nuclear magnetic dipole moment interacts with the internal magnetic field or with the magnetic field applied externally.

Electric quadrupole interaction (I = 5/2)



There is m-to-m/ transitions before the 2nd γ-ray is emitted which modulates W(θ)

For static interactions of a spin I = 5/2 intermediate level in a polycrystalline solid, the perturbation function G_2 (t) due to electric quadrupole interaction

$$G_2(t) = S_0 + \sum_{k=1}^{3} S_k \cos(\omega_k t)$$

The interaction frequencies ω_1, ω_2 and ω_3 correspond to transitions between m-states of the intermediate quantum level.

The zz-component of the efg tensor Vzz in the principal-axis system (in which the off-diogonal elements vanish) is given in terms of the quadrupole frequency ω_Q by:

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

The other two diagonal elements are given in terms of the asymmetry parameter η given by

$$\eta = (V_{xx} - V_{yy}) / V_{zz}$$

In which $0 \leq \eta \leq 1$ (when V_{zz} is the largest component in Magnitude). Poisson's equation requires that

$$V_{xx} + V_{yy} + V_{zz} = 0,$$

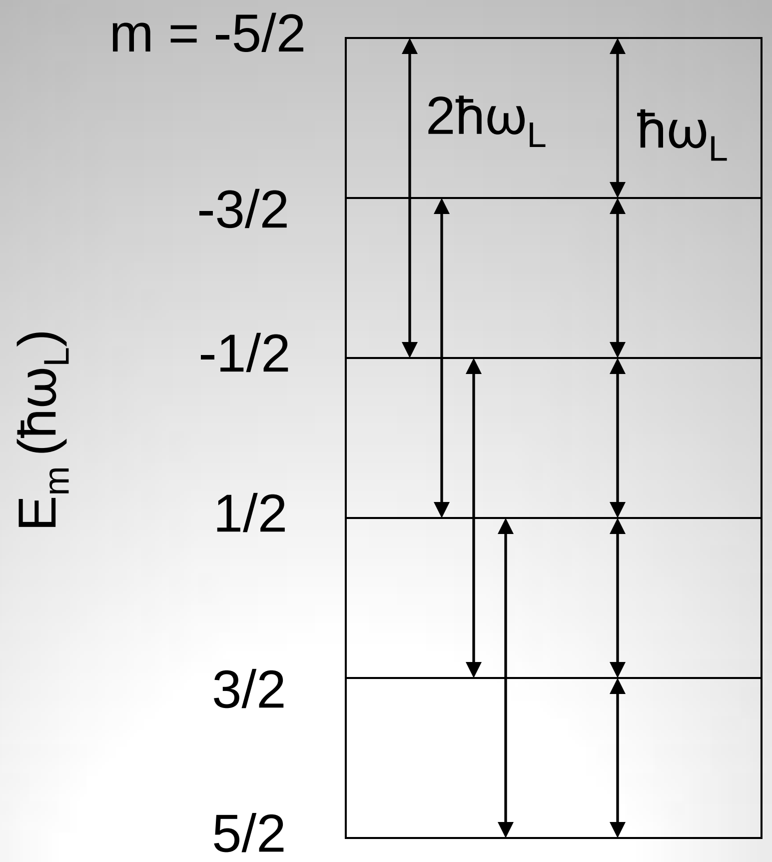
and energy conservation requires that

$$\omega_1 + \omega_2 = \omega_3$$

In the case of a static quadrupole interaction, the primary experimental task is to measure the efg i.e. V_{zz} and η

Magnetic Interaction:

I = 5/2



$\omega_L = g\mu_N H/\hbar$

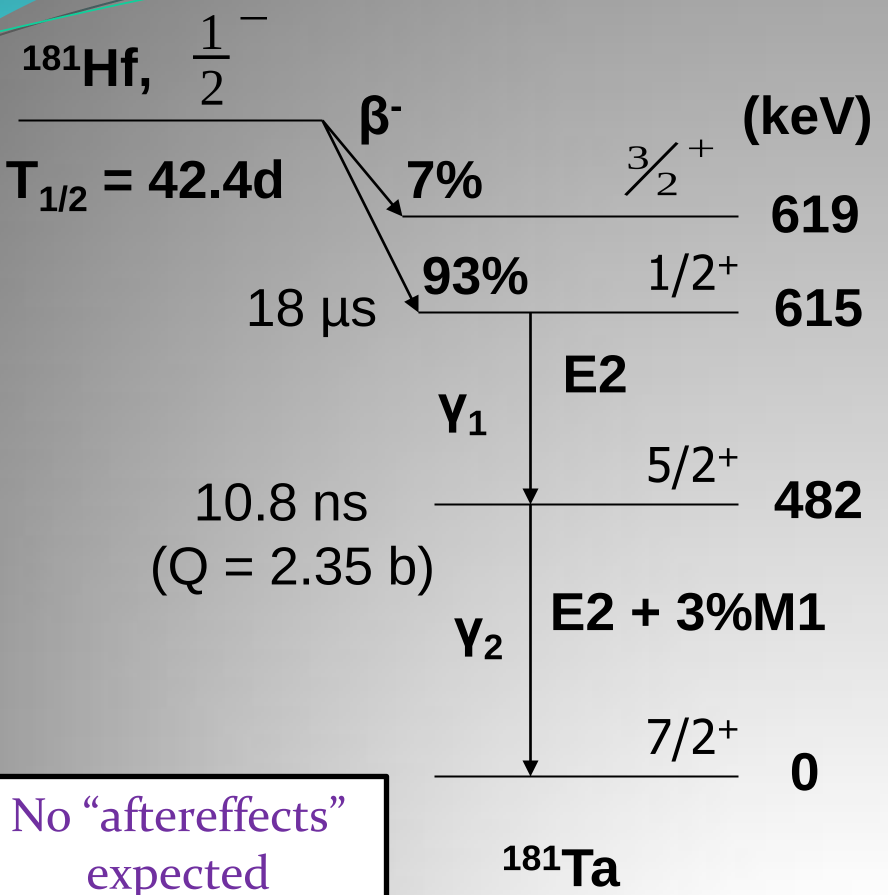
$\mu = g\mu_N I$

Ideal PAC probes:

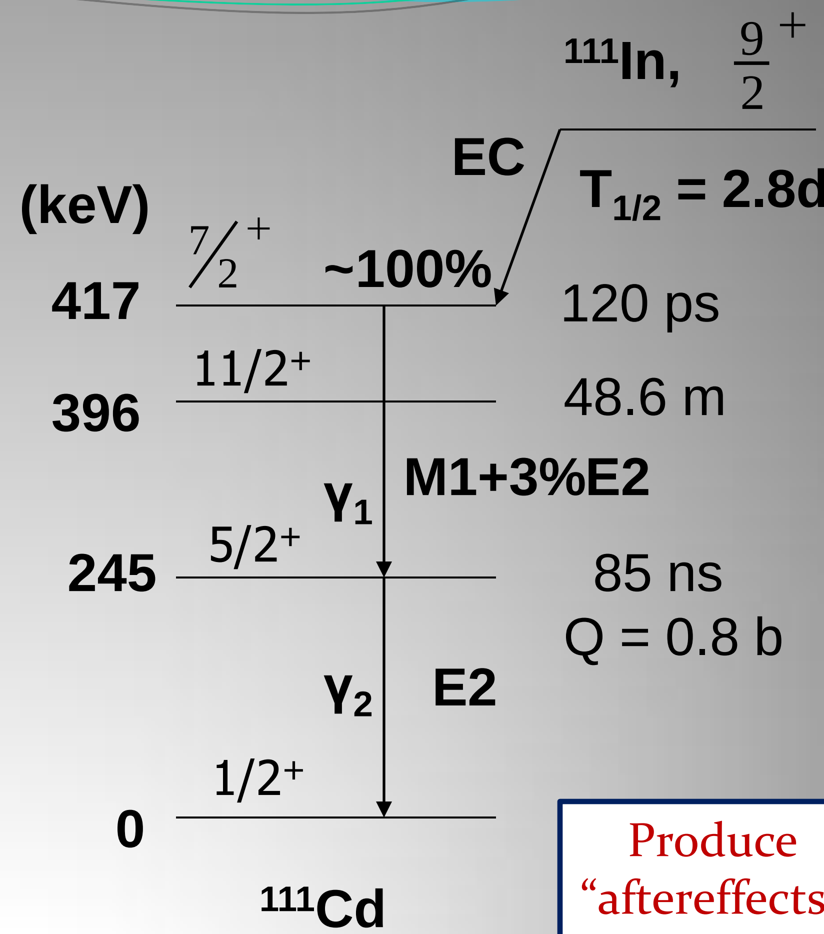
- Strong γ-γ cascade
- High angular anisotropy
- Large electric quadrupole moment and magnetic dipole moment of the intermediate level
- Longer life time of the level depopulating the preceding γ-ray in the cascade

  (to avoid "after effects")

Nuclear isotopes mostly used for PAC measurements:



No "aftereffects" expected



Produce "aftereffects"

Produced from neutron capture of ^{180}Hf

Cascade: 133-482 keV

A_2 = -0.288; A_4 = -0.076

Produced from $^{109}Ag(\alpha,2n)^{111}In$

Cascade:172-245 keV

A_2 = -0.18; A_4 = -0.0015

Some other useful probes

- ^{111m}Cd (49 min)
- ^{117}Cd (2.5 h)
- ^{199m}Hg (43 min)
- ^{204m}Pb (67 min)
- ^{111}Ag (7.5 d)
- ^{99}Mo (67 h)

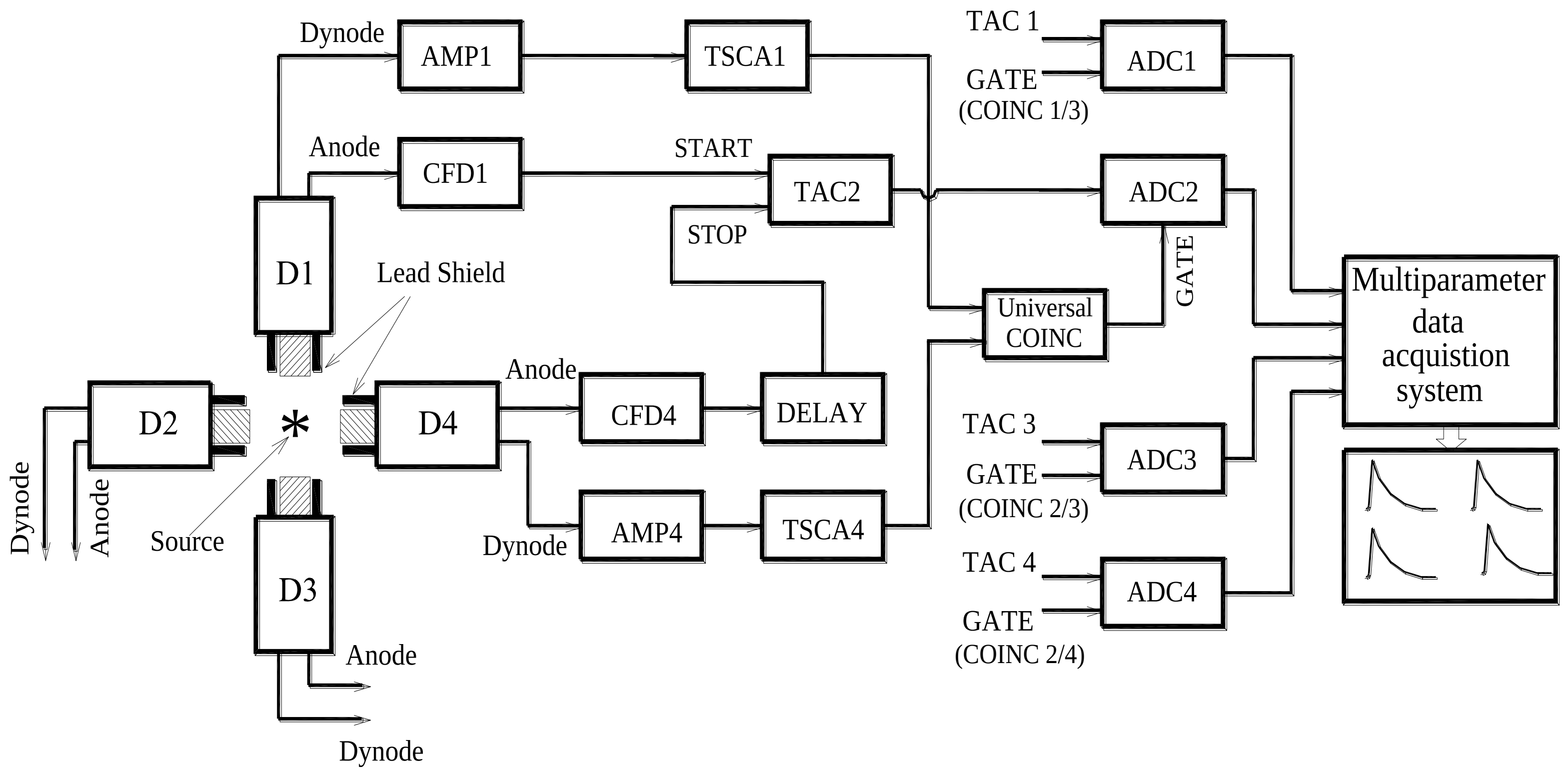
- Useful for studies in biological samples
- Can be produced using the RIB facility

PAC studies in solid state materials and in biological samples (e.g. protein macromolecules) using these probes remain mostly unexplored.

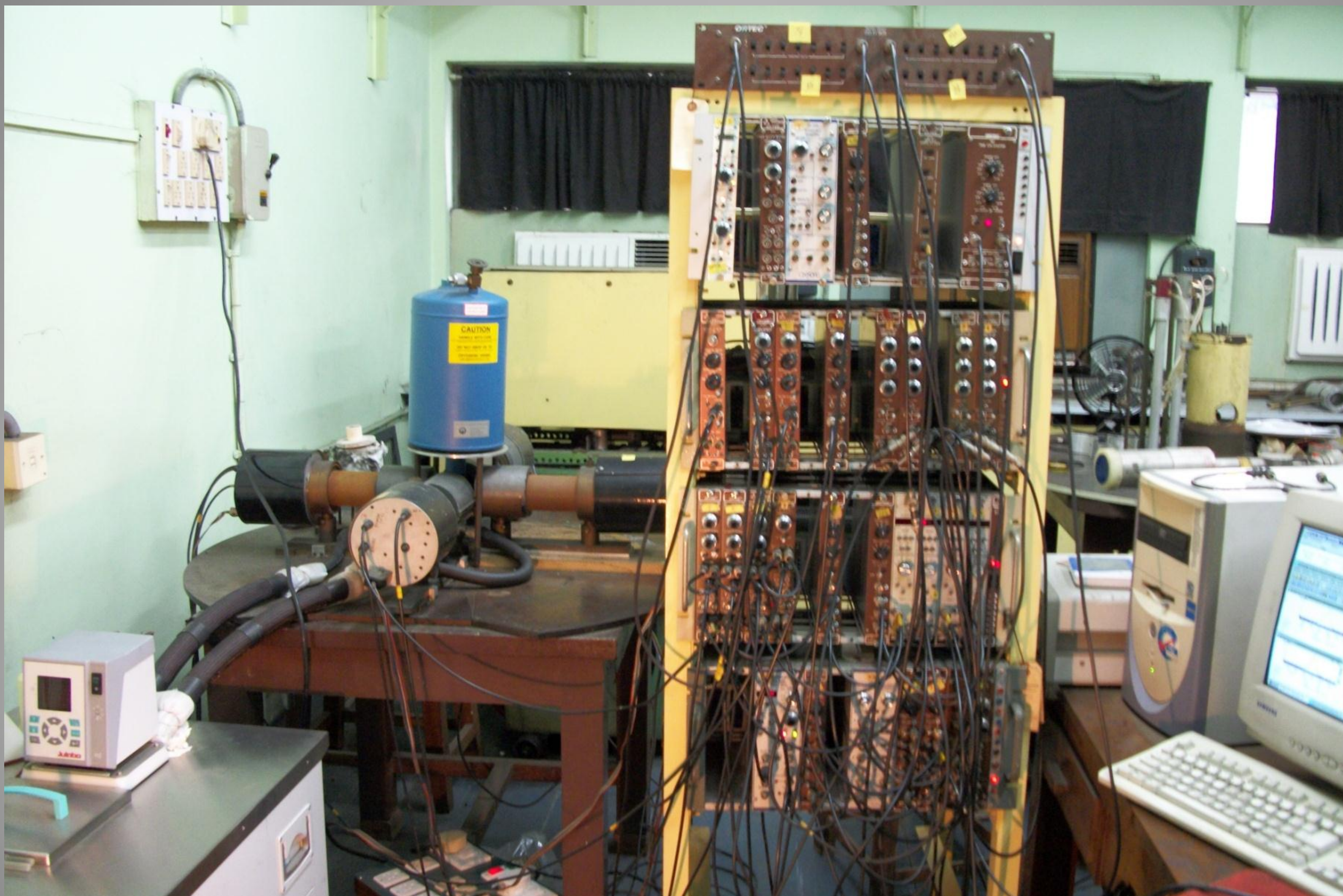
Experimental facility at SINP

- A Four detector TDPAC spectrometer with BaF_2 detectors (50.8x50.8 mm) (acquire four coincidence spectra simultaneously); time resolution ~ 350 ps for 511-511 keV γ-rays.
- A close cycle refrigerator for sample cooling (-80˚C to 90˚C)
- A NN_2 dewar for measurement at LN_2 temperature
- A resistive furnace for measurement at higher temperature (600˚C)
- An argon arc furnace for preparation of intermetallic compound

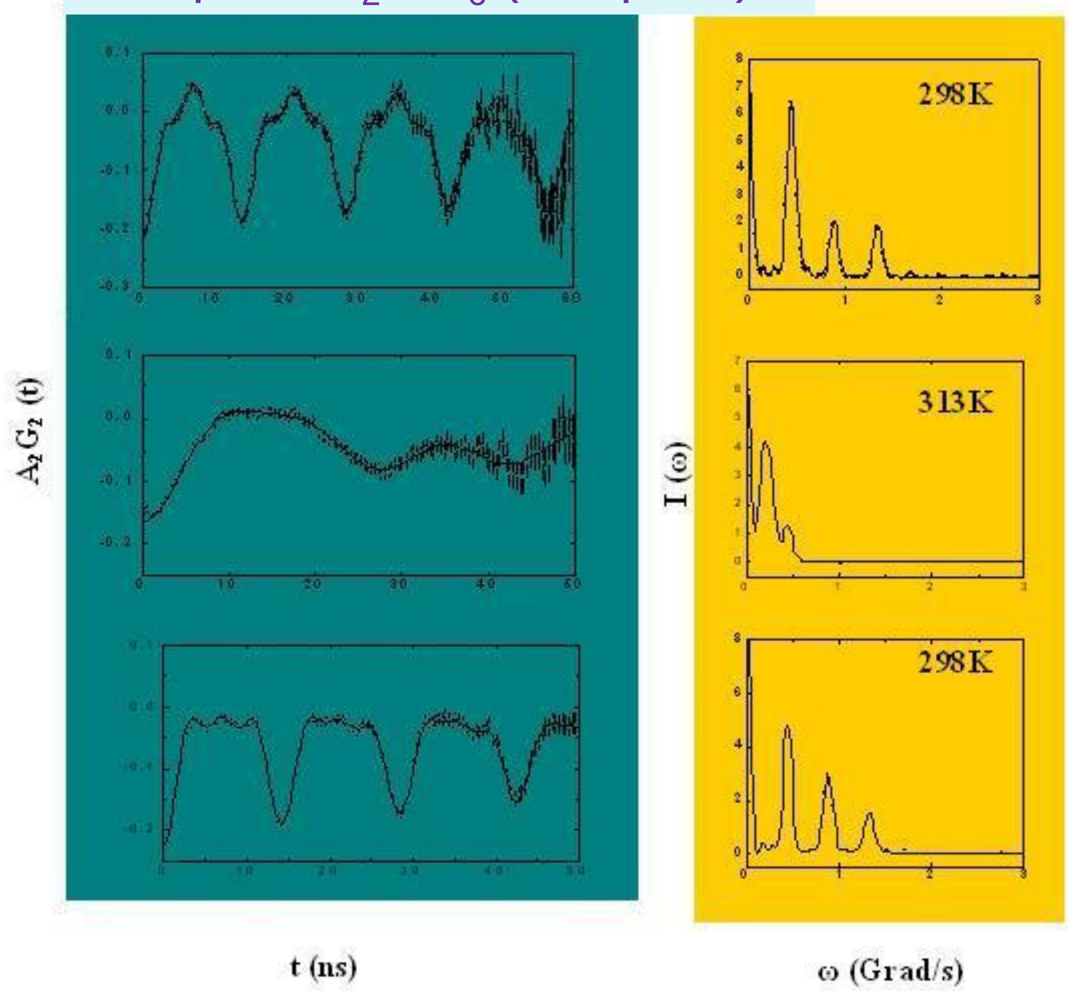
Experimental arrangement



Four slow-fast coincidences with BaF_2 detectors


CAUTION

Sample: Rb_2HfF_6 (sample 1)



ω_Q = 74.1(1) Mrad/s
η= 0.09(1); δ = 0

- Pure crystalline configuration
- In good agreement with previous result

ω_Q = 24.7(2) Mrad/s
η= 0.53(1); δ= 4(2)%

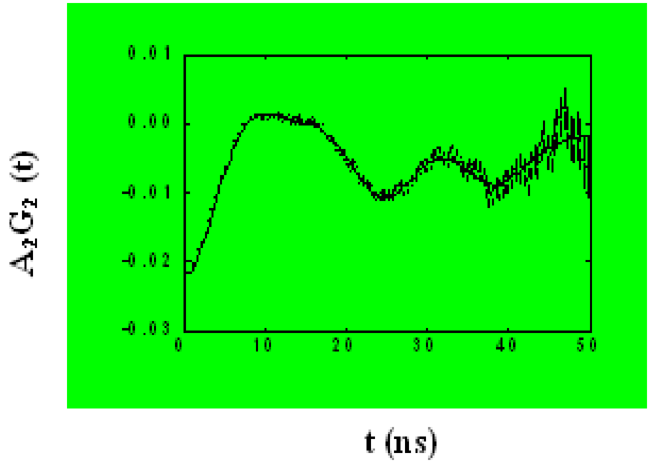
- Pure defect configuration (point defect)

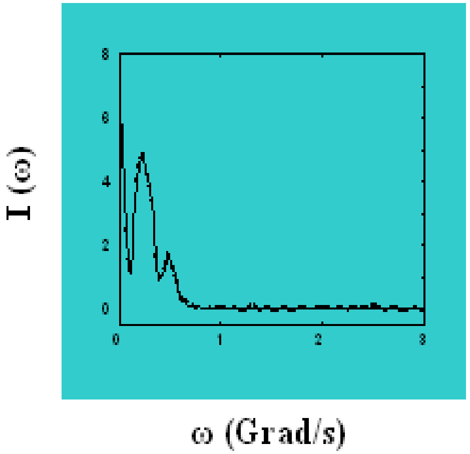
After measurement at 353K

- reversible

- Defect-probe interaction was not observed from previous measurements (Martínez et al. Phys. Rev B 35 (1987) 5244

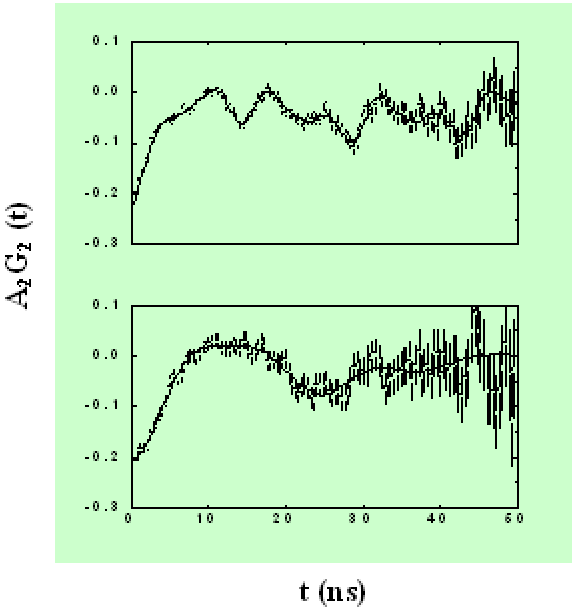
Sample: Rb_2HfF_6 (sample 2)

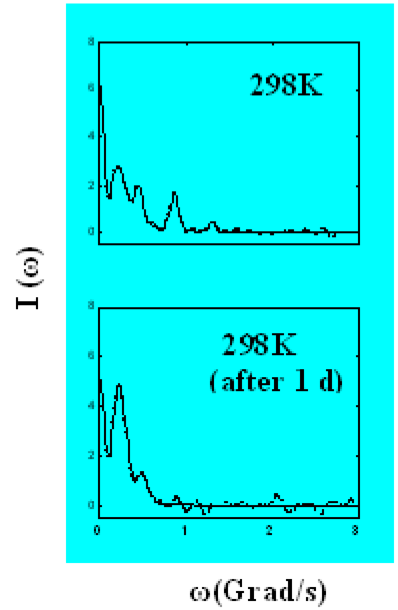




- At RT
- Pure defect configuration

Rb_2HfF_6 (sample 3)

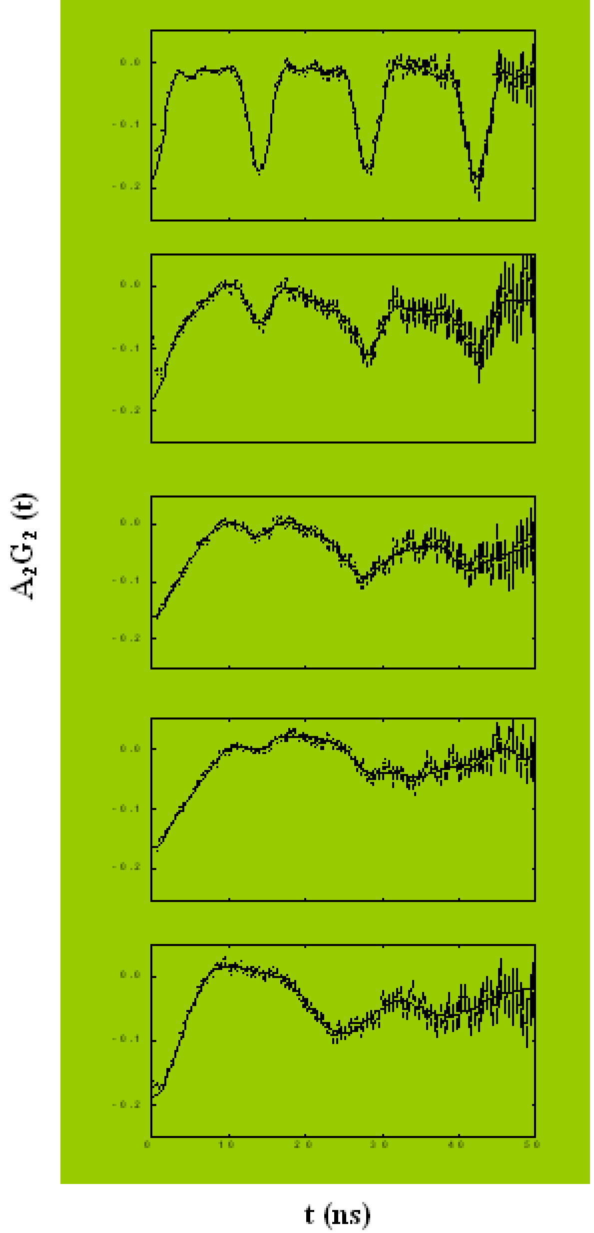


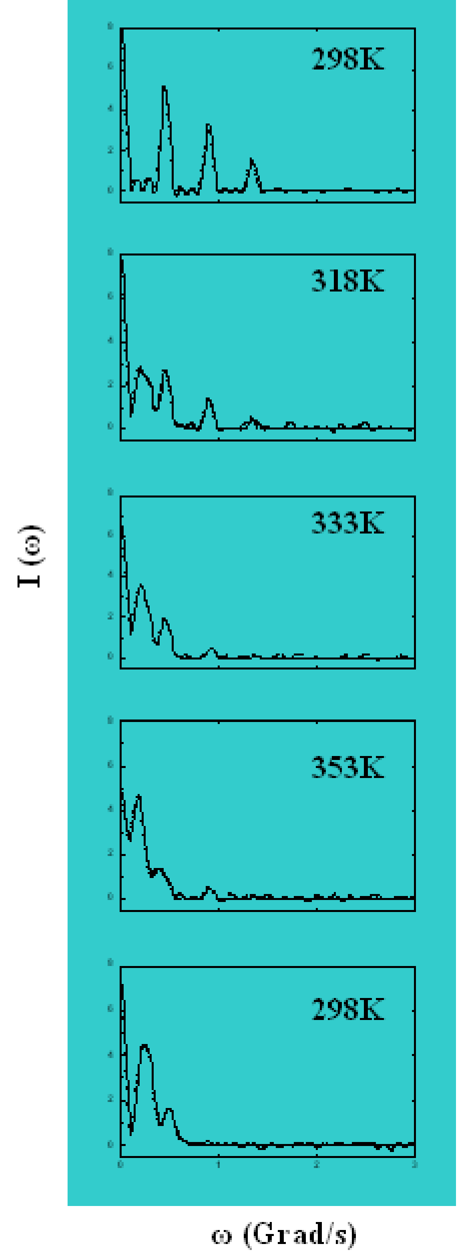


Both crystalline and defect configuration

Pure defect configuration

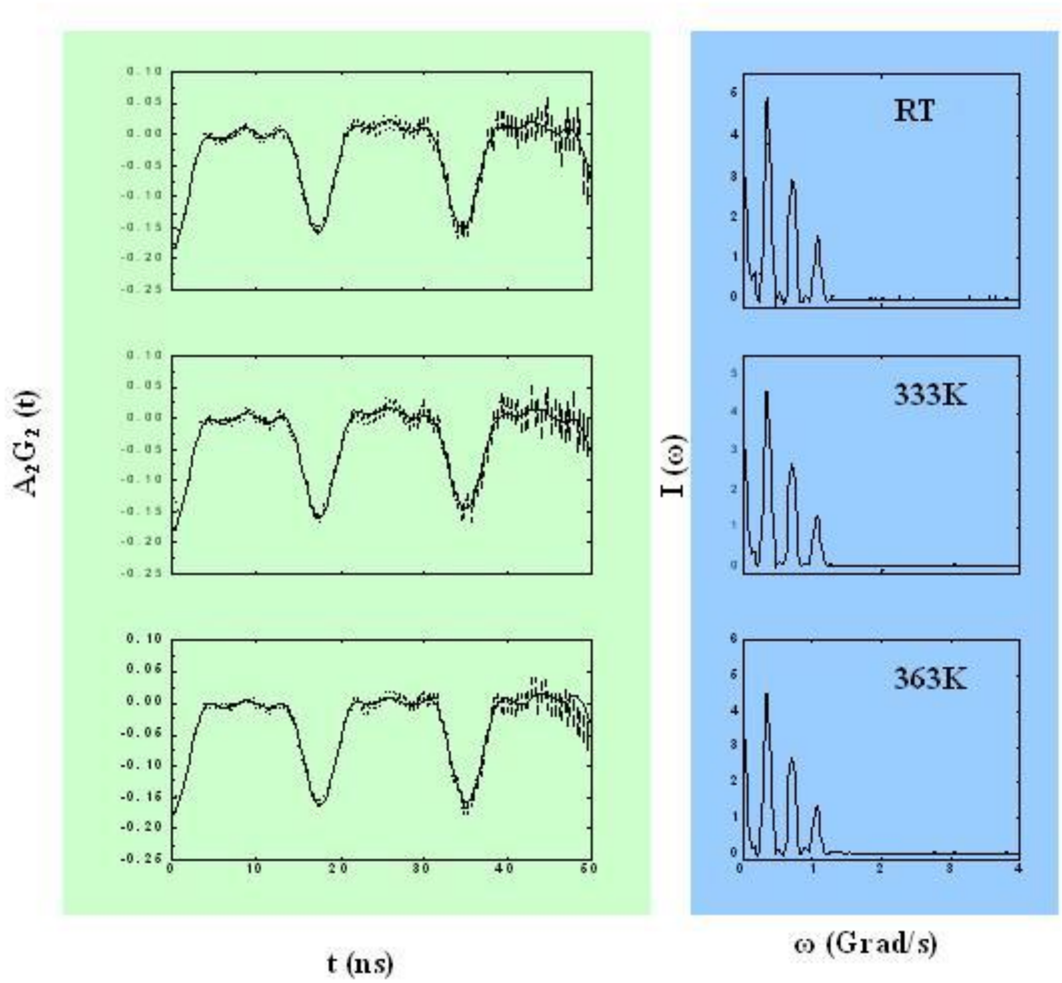
Sample: Rb_2HfF_6 (sample 4)





- Defect configuration increases with temperature

- Defect is fully trapped when heated at 353K and cooled subsequently at RT



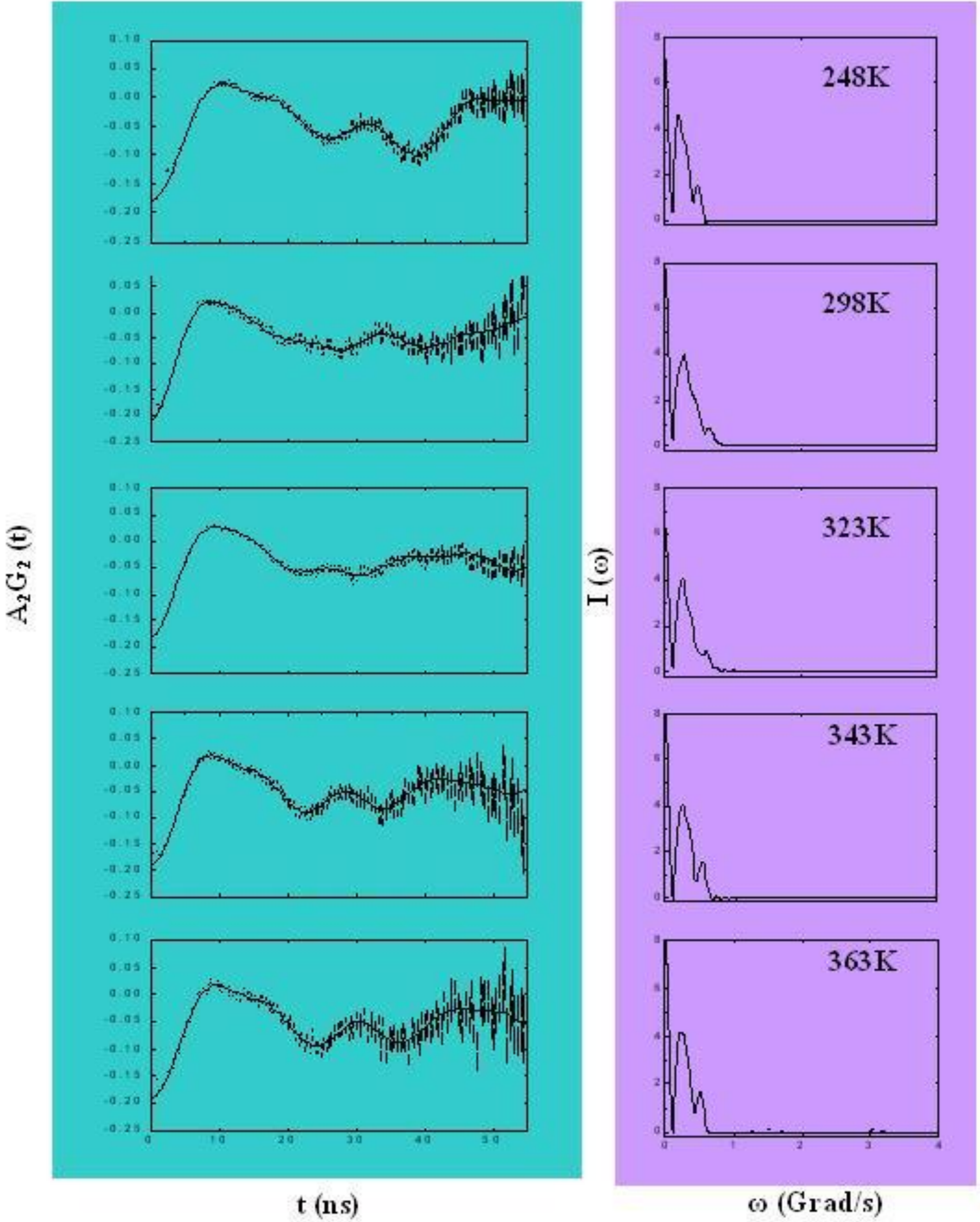
- Spectra similar to that in Rb_2HfF_6 indicate Rb_2HfF_6 and Cs_2HfF_6 have same crystal structure (isomorphic)

At RT

- ω_Q = 60.46(7) Mrad/s η = 0.05(2); δ = 0

- Defect –probe interaction not observed in Cs_2HfF_6

Sample: Cs_2HfF_6



Sample: K_3HfF_7

- Two discrete interaction frequency observed
- Two inequivalent probe site

At RT

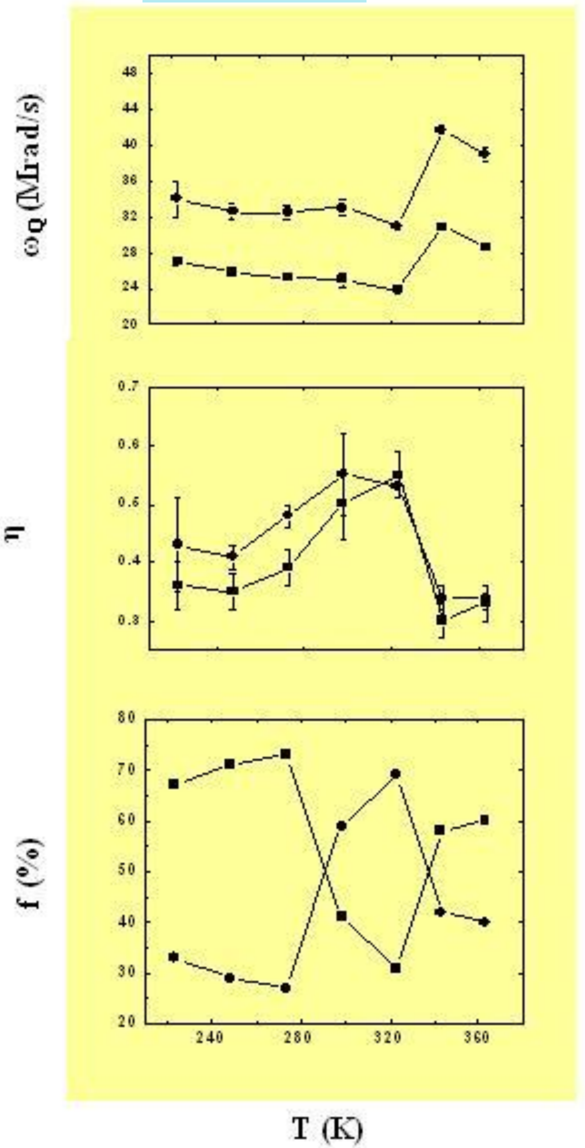
$\omega_Q(1)$ = 33.1(9) Mrad/s
η = 0.55(7); δ = 9(2)% (59%)
$\omega_Q(2)$ = 25.0(8) Mrad/s
η = 0.50(6); δ = 0 (41%)

At 343K

$\omega_Q(1)$ = 41.8(5) Mrad/s
η = 0.34(2); δ = 0 (42%)
$\omega_Q(2)$ = 30.9(2) Mrad/s
η = 0.30(3); δ = 0 (58%)

- Indicates a phase transition

K_3HfF_7

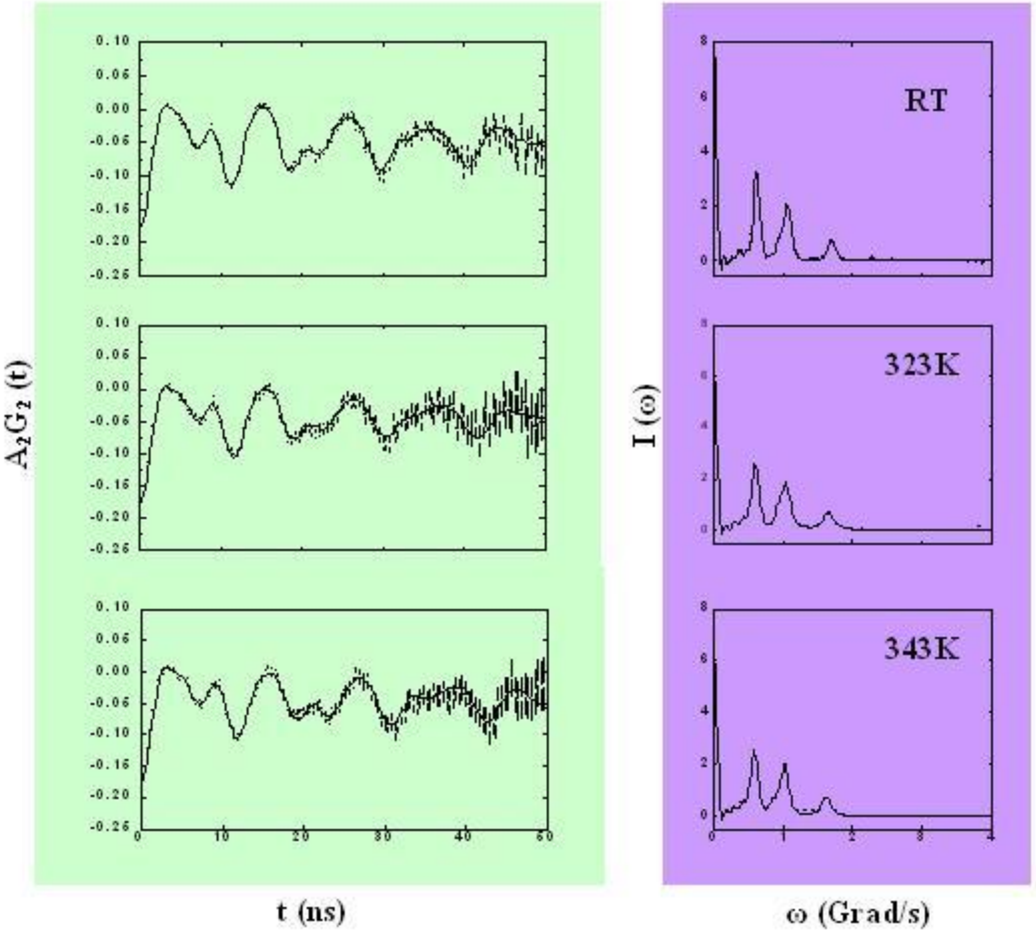


➢Temperature variations in ω_Q and η clearly indicate a structural phase transition at ~ 340K

➢Results are in large disagreement with previous reported results (Preswich et al., HFI 12(1982) 329 Lowe et al., Chem. Phys. Lett. 46 (1977) 531)

▪From earlier study, a phase transition at 250K was reported by Preswich et al. A single interaction frequency was reported above 252K (ω_Q = 47(4) Mrad/s; η = 0.19(3); δ = 15(1)%)

Sample: Na_3HfF_7



- Three interaction frequency appear

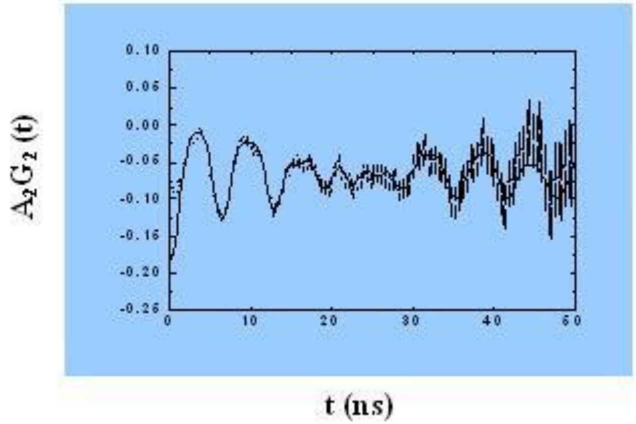
At RT

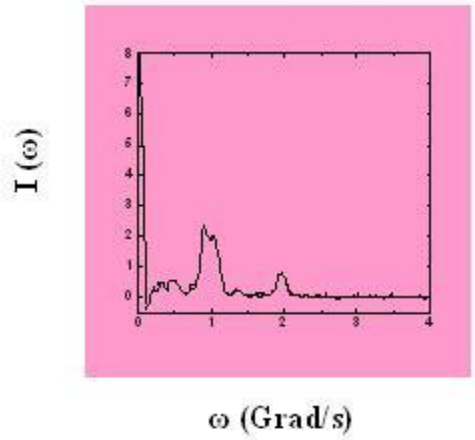
$\omega_Q(1)$ = 91.7(2) Mrad/s
η = 0.358(5); δ = 2.5(3)%
(83%)
$\omega_Q(2)$ = 50(1) Mrad/s)
η = 0.65(12); δ = 3(1)%
(13%)
$\omega_Q(3)$ = 45(2) Mrad/s
η = 0.46(8); δ = 0
(4%)

- The sole previous measurement gives RT values
$\omega_Q(1)$ = 67.6 Mrad/s; η = 0.40 (50%)
$\omega_Q(2)$ = 119.8 Mrad/s; η = 0.15 (50%)
(J. Phys. Chem. Solids, 37 (1976) 1019)

- Disagrees with earlier reported results

Zr_2Ni (prepared in Arc Furnace at SINP)





- Three interaction frequency appear
- $\omega_Q(1) = 96.5\ (3)$ Mrad/s; $\eta = 0.838(4)$; $\delta = 1.8(4)\%$ (80%)
  in good agreement with earlier reported result
- $\omega_Q(2) = 73(1)$ Mrad/s; $\eta = 0.44(4)$; $\delta = 0$ (11%)
- $\omega_Q(3) = 37(1)$ Mrad/s; $\eta = 0.57(6)$; $\delta = 0$ (9%)

- $\omega_Q(2)$ and $\omega_Q(3)$ are probably due to point defects
  - crystal structure favor the formation of point defect
  - no point defect observed earlier

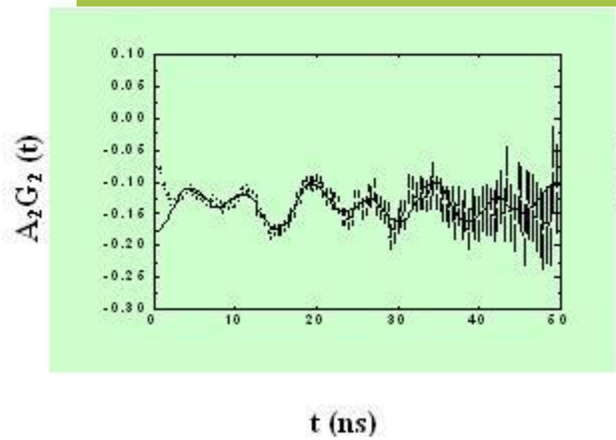
$ZrNi_5$ system

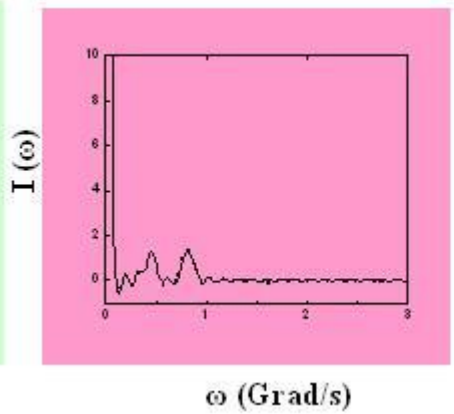
- In this system a strong ferromagnetic ordering was reported earlier (Drulis et al. JMM, 256 (2003) 139) from magnetization vs. temperature data with a Curie temperature 647 K (374˚C)

- The crystal structure of Hf(Zr)Ni5 has cubic symmetry with zero electric field gradient which means no NQI. A flat perturbation is expected.

- Magnetic ordering in Hf(Zr)Ni5 can be easily checked from PAC measurements

$ZrNi_5$ (prepared in arc furnace at SINP)





ω_Q = 41.3(3) Mrad/s;
η = 0.74(3); δ = 0

- The PAC data can be fitted with a single quadrupole interaction only. No magnetic interaction is required
- A large base line shifts indicates a significant fraction (~58%) of probe nuclei experience no efg due to sitting in a cubic environment
- Remaining 42% probe experience an efg, probably due to defect configuration (point defect)
- At RT, no magnetic ordering in $ZrNi_5$ is observed by PAC. Supports earlier result of Silva et al. (JMM, 322(2010) 1841

Thank you