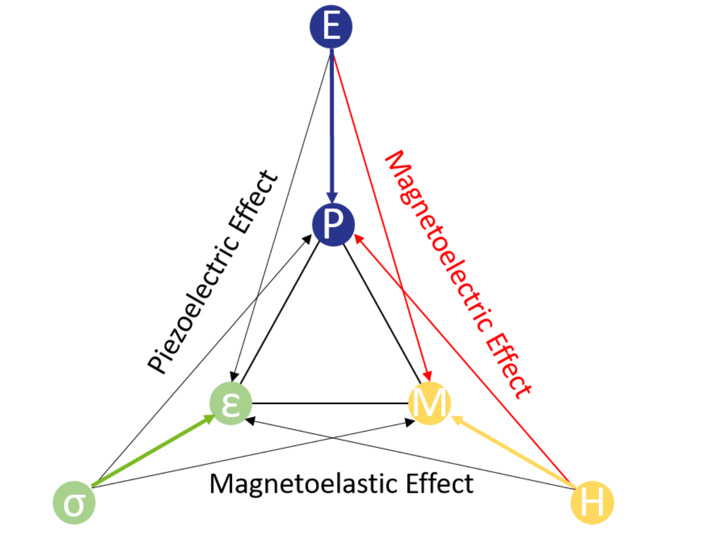
Perturbed angular correlation and x-ray diffraction studies on the **α-β** phase transition in multiferroic bismuth ferrite

DI Georg Marschick

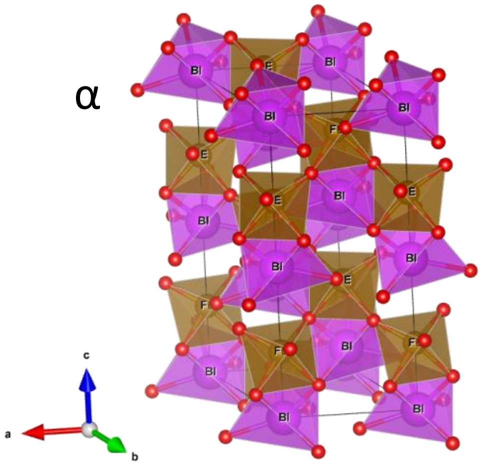
Bismuth Ferrite – $BiFeO_3$

- Quasi-cubic canted perovskite of $LiNbO_3$ type
- Curie Temperature: 820°C
- Néel Temperature: 370°C
  - Thus magnetoelectric at room temperature
- Rhombohedral α-phase
- Orthorhombic β-phase

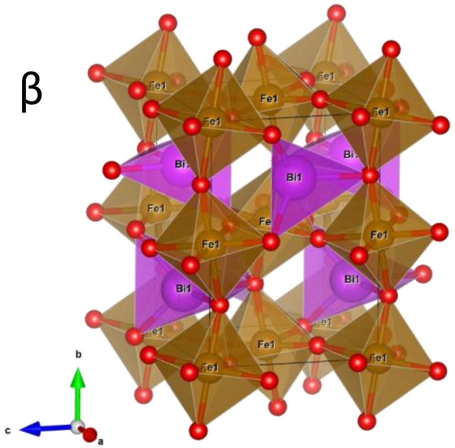


	RT	α T_N	T_C β
[1] Raman	R3c AFM	R3c PM	Pm-3m
[2] DTA, XRD, Raman	R3c AFM	R3c PM	P2mm
[3] XRD	R3c AFM	R3c PM	$P2_1/m$
[4] Ab initio calc.	R3c AFM	R3c PM	I4/mcm
[5] PND	R3c AFM	R3c PM	Pbnm
[6] XRD	R3c AFM	R3c PM	R3c
[7] XRD	R3c AFM	R3c PM	Pbnm
This work	R3c AFM	R3c PM	Pbnm

α



β



Structural studies – lattice and local properties

- Perturbed angular correlation (local properties)
  - Asymmetry and strength of Electric field gradient
  - How are local properties influenced by the phase transition?
  - Is the phase transition visible?

- X-ray diffraction (lattice properties)
  - Description of unit cell, lattice parameters and space group
  - Atomic positions, bond lengths and angles
  - Well known and understood method

Perturbed Angular Correlation (PAC)

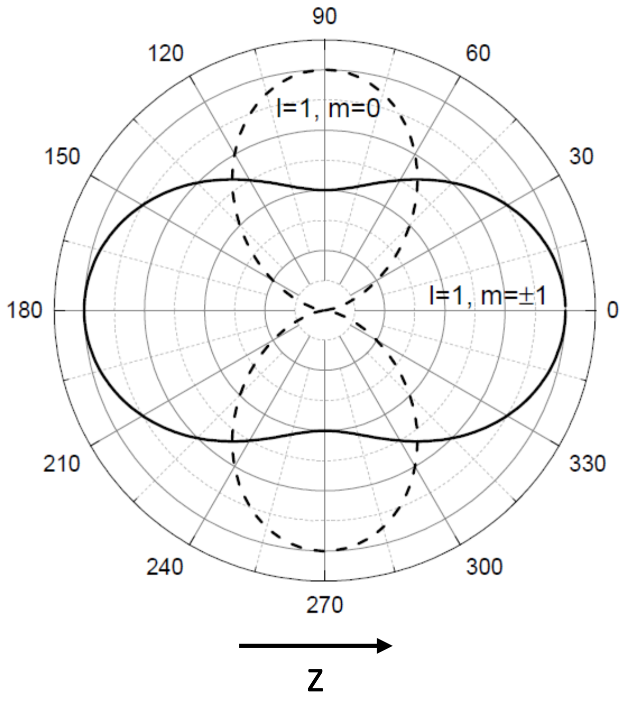
Naive theory

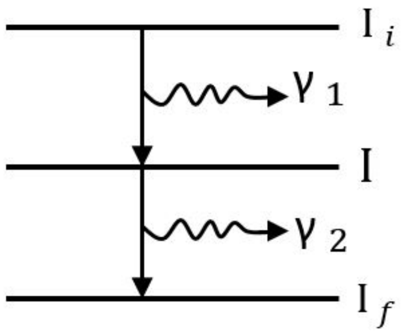
Observable	Actor / Consequence	Reason
We measure a frequency ω of angular γ-γ coincidences…	…due to force acting on the nucleus and thus „turning“ it…	…caused by electric or magnetic fields in the nucleus´ vicinity.

Perturbed Angular Correlation (PAC)

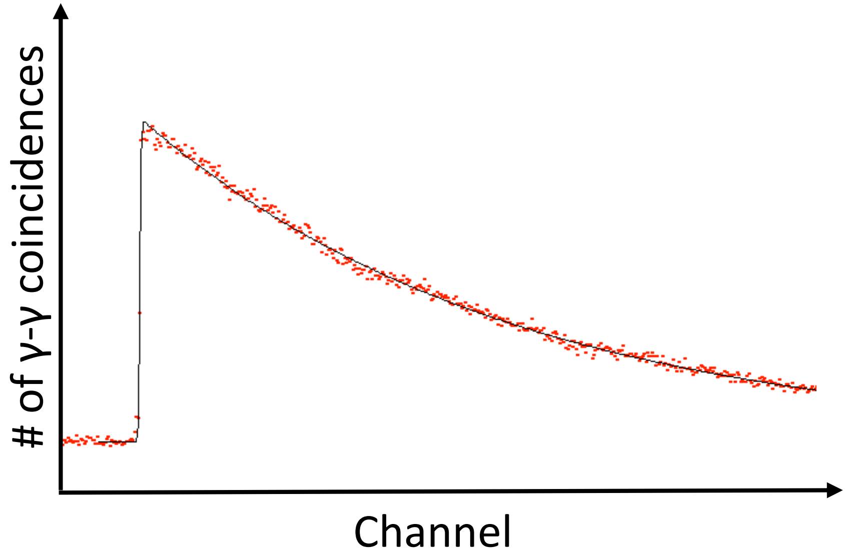
Naive theory

Emission characteristic of γ-radiation – orientation of nuclei + Conservation of angular momentum and selection rules = Anisotropic emission of a γ- γ cascade



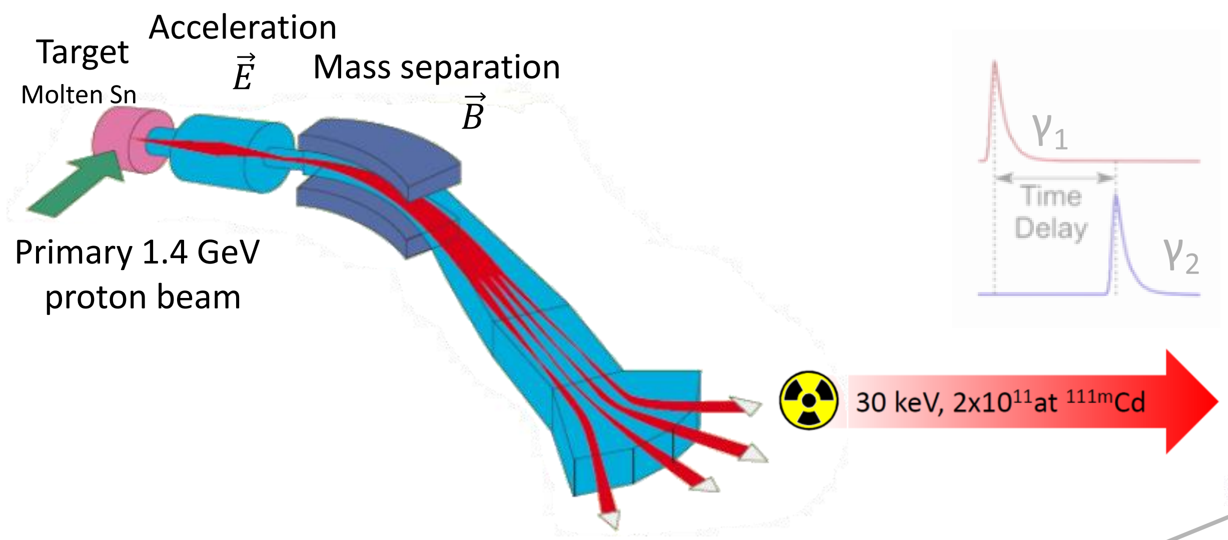


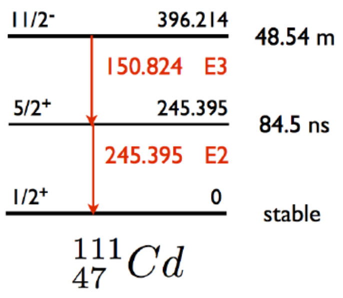
$$|I_i - I| \leq l \leq I_i + I \text{ and } M_i - M = m$$

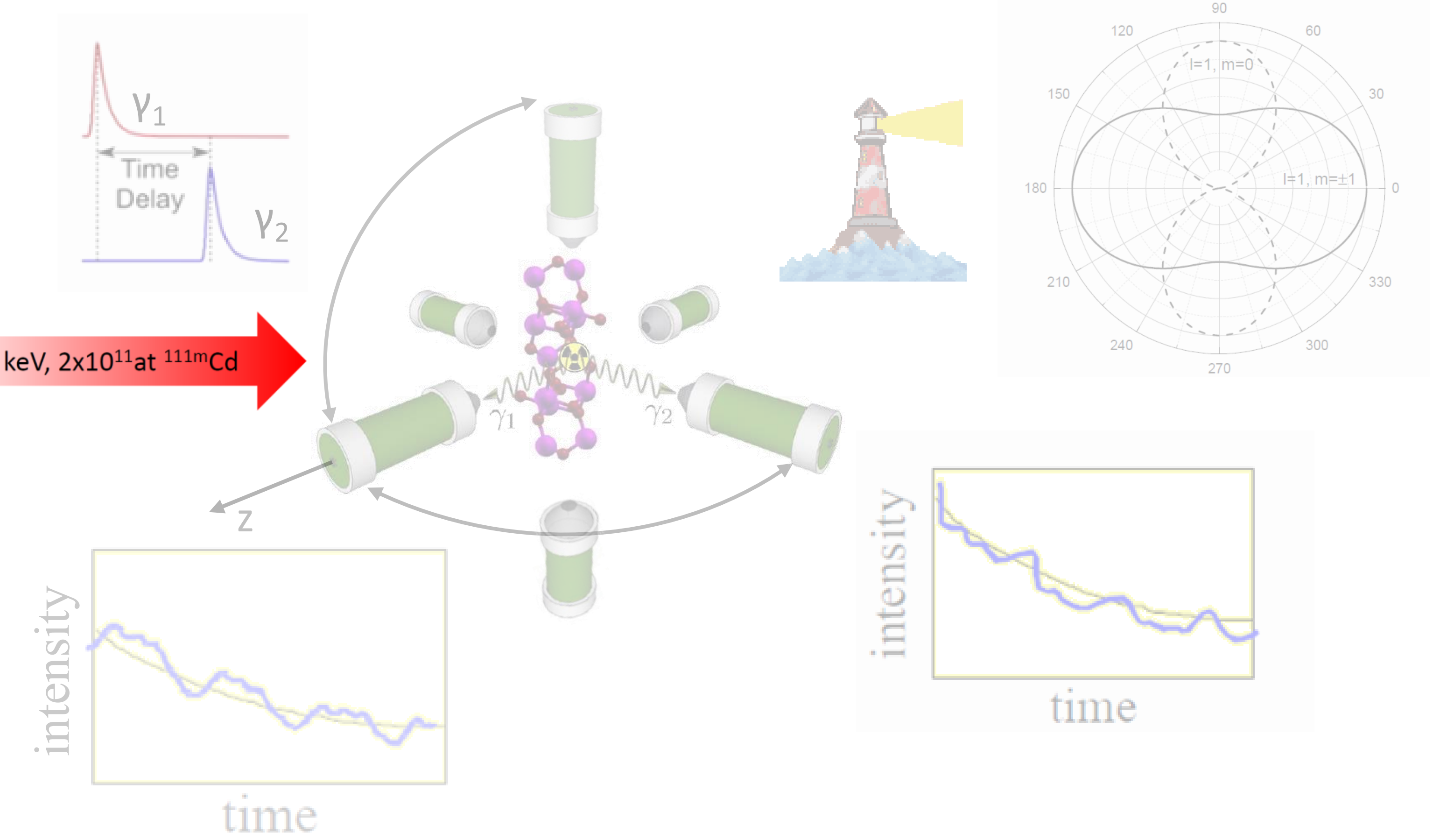


Perturbed Angular Correlation (PAC)

A method to probe **hyperfine interactions** in matter







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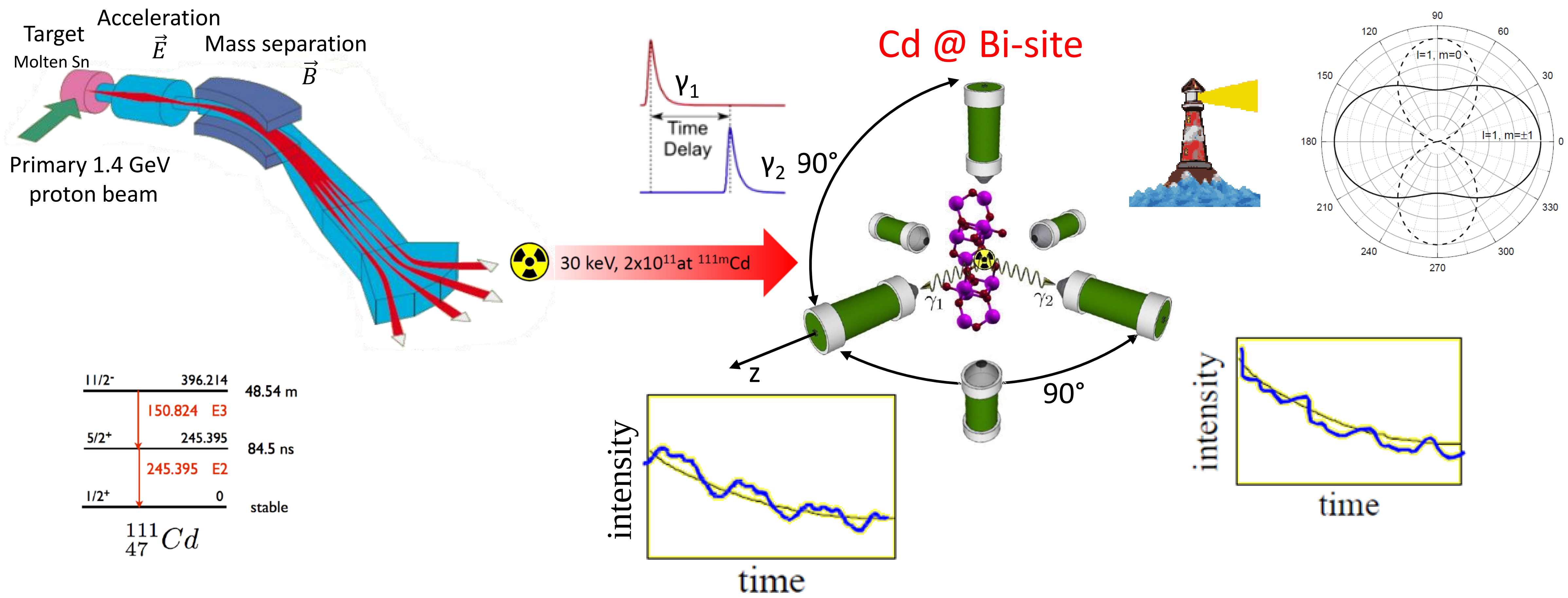

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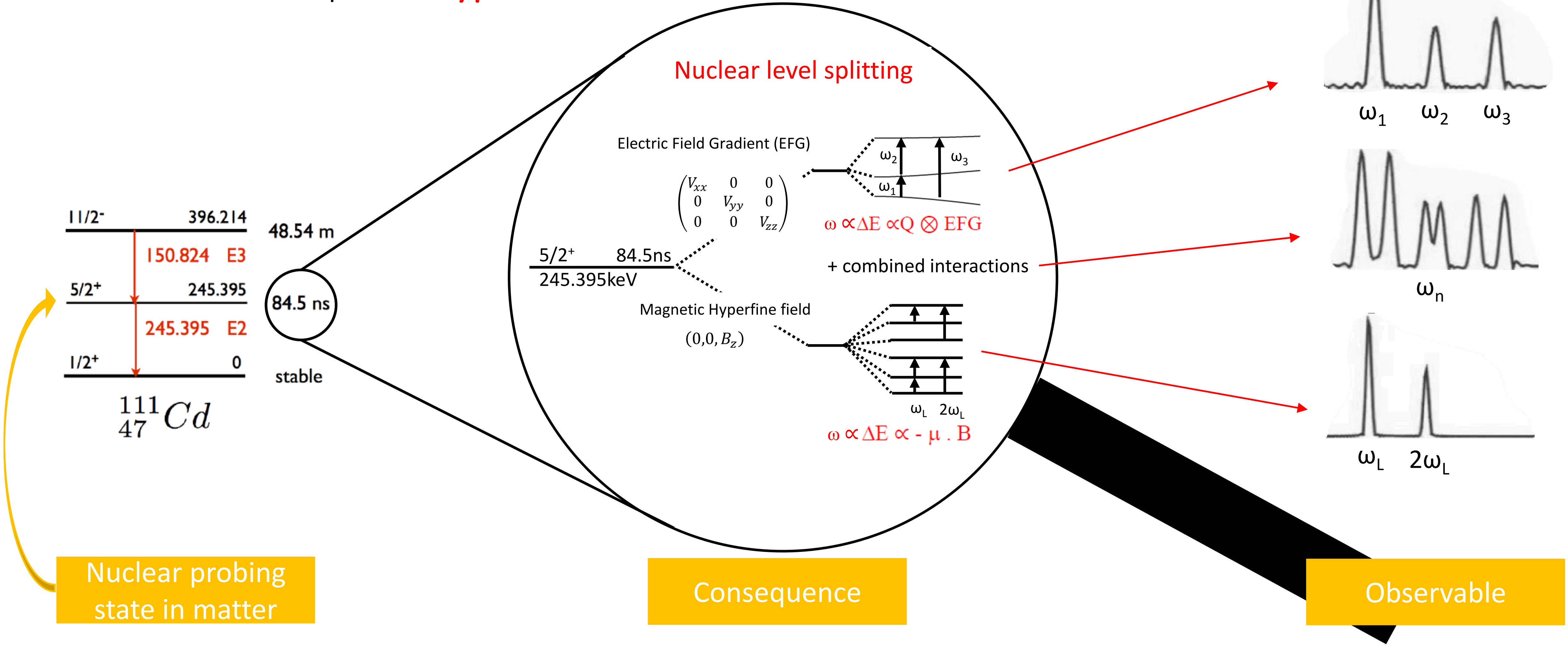

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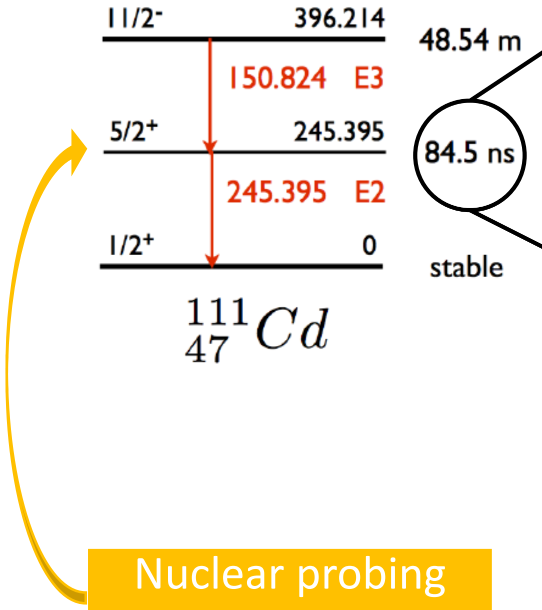
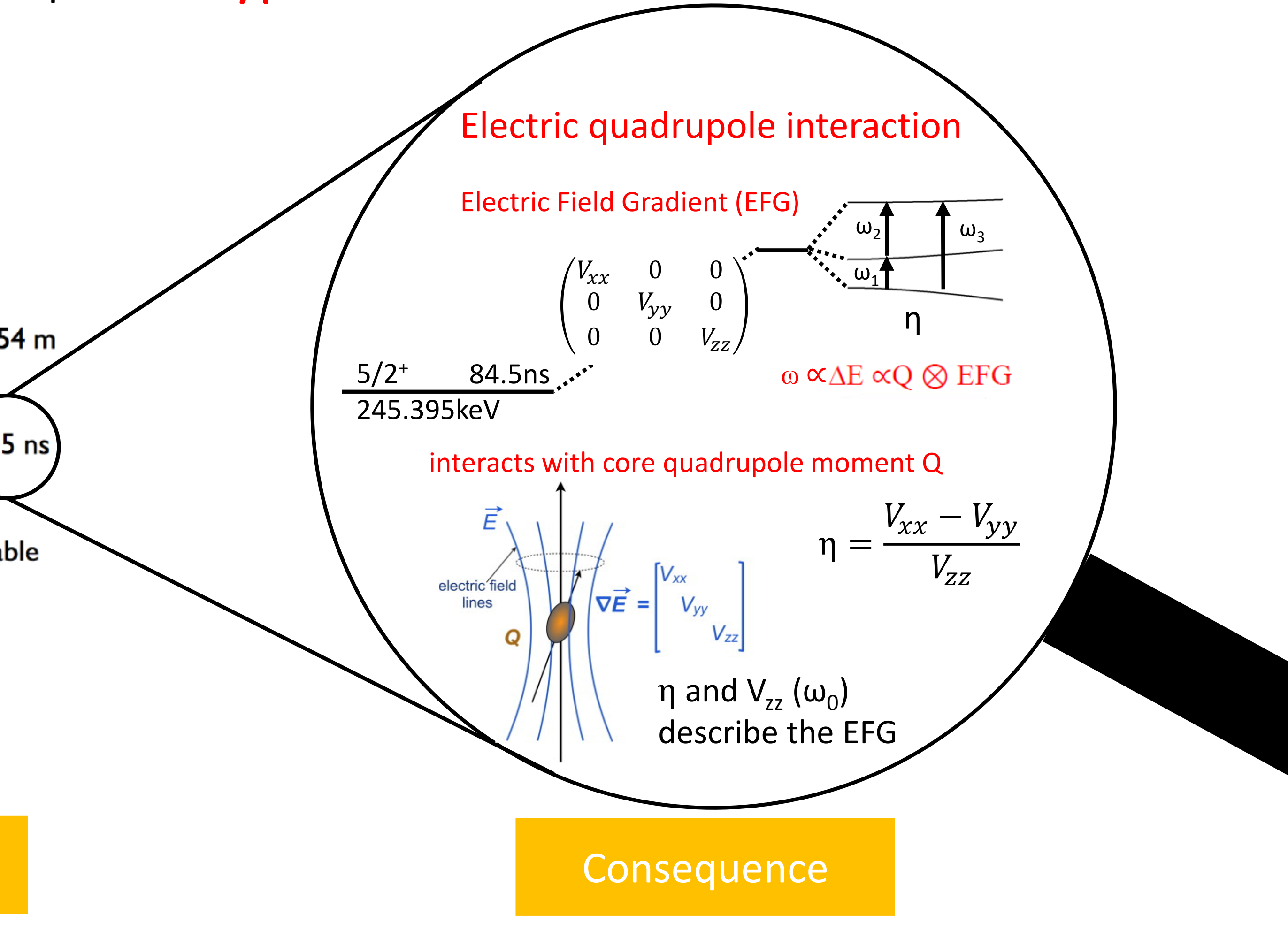
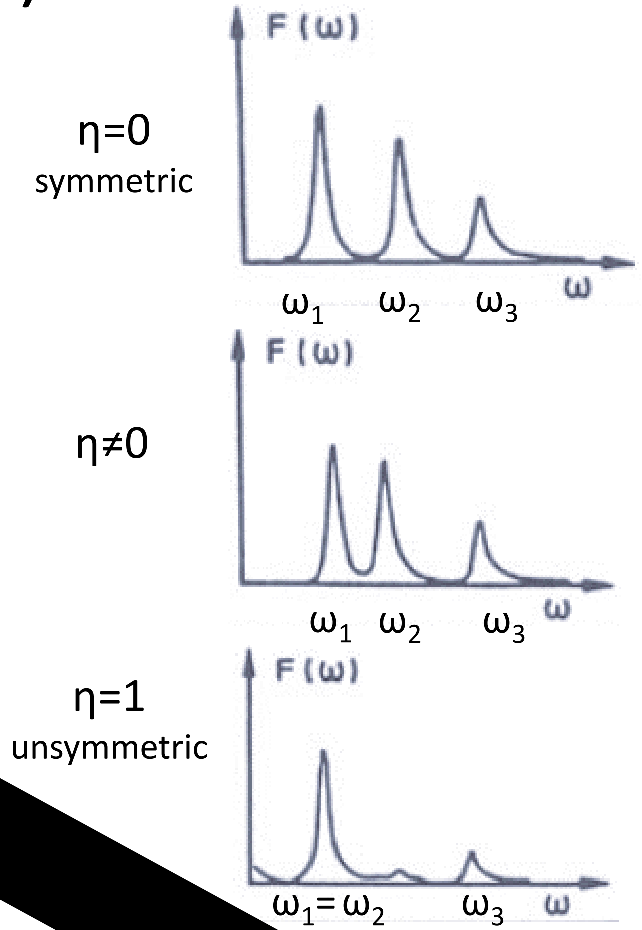


Nuclear probing state in matter



Consequence

Transition frequencies



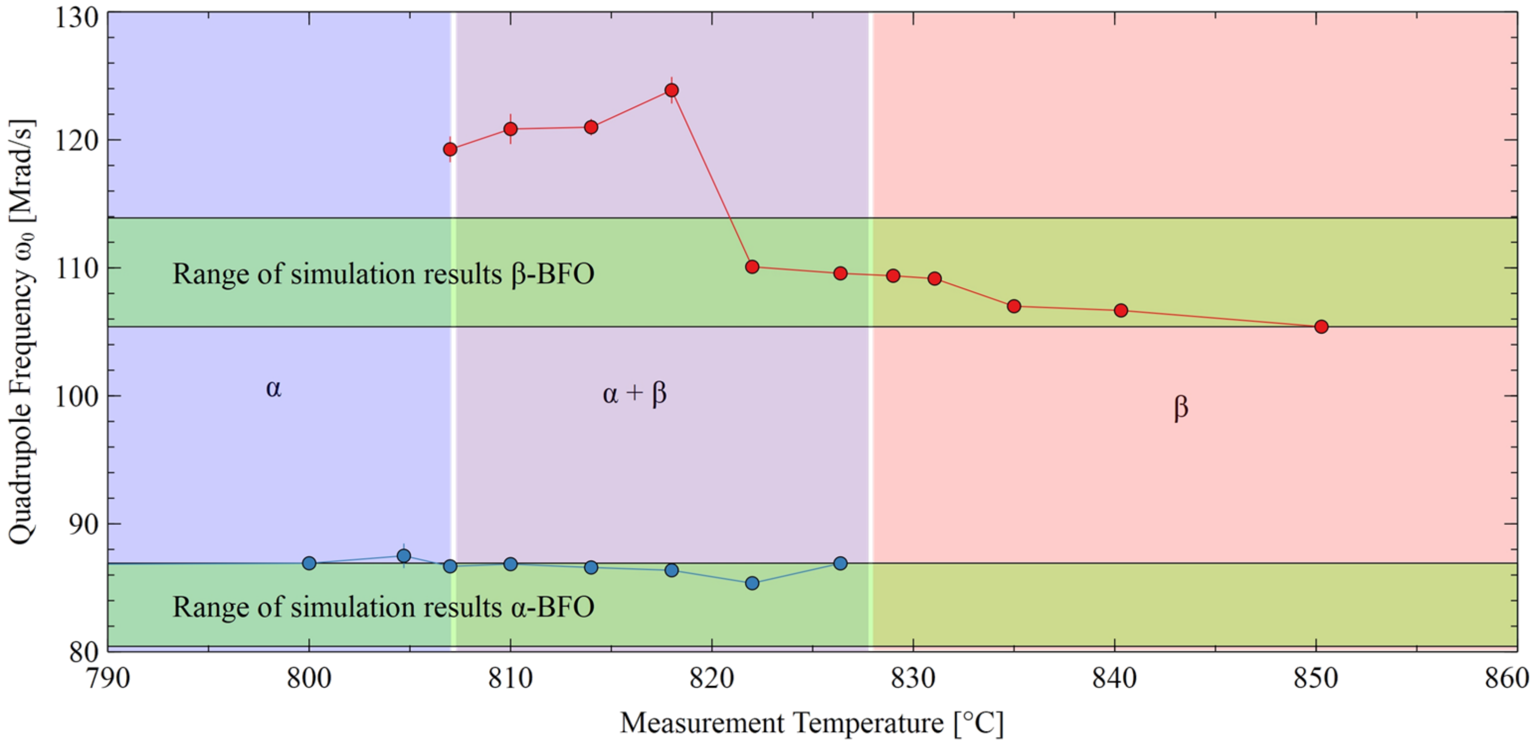
Observable

DFT Simulations at University of Aveiro (PT)

Density functional theory simulations to calculate Vzz and η done for Cd @ Bi

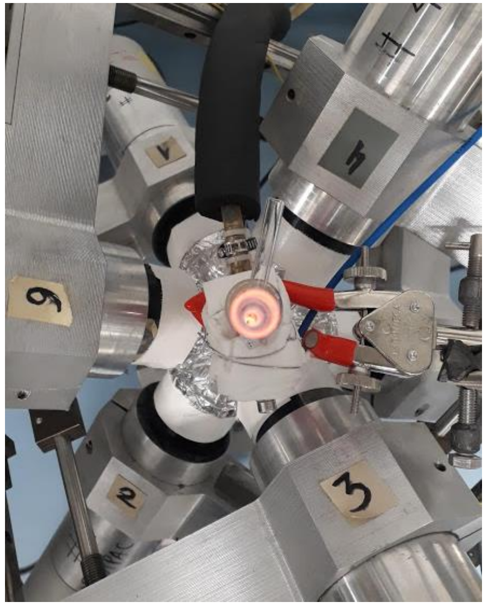
Range of values follows the error
of the Q values of Cd of Q=0.641(25) b

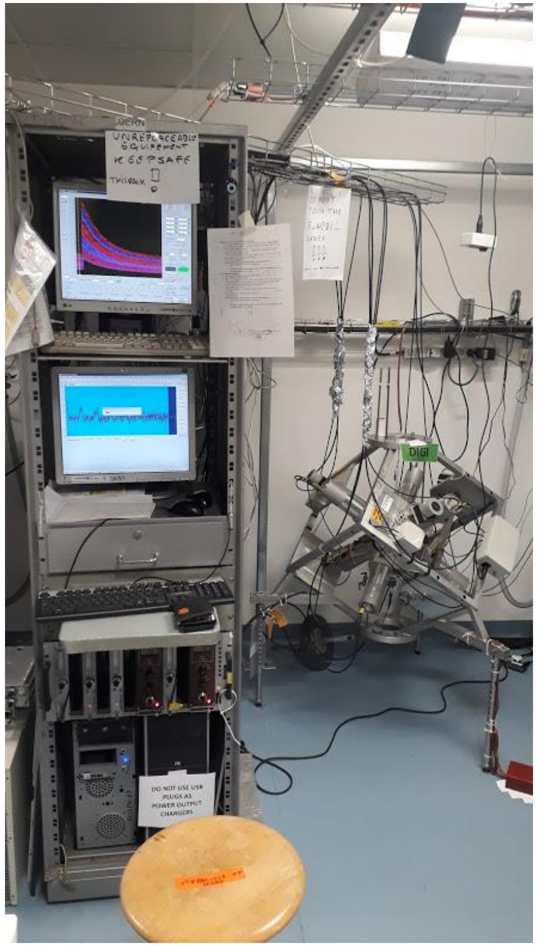
$$\omega_0(V_{ZZ}) = \frac{6 * e * Q * V_{ZZ}}{4I(2I-1) * \hbar}$$



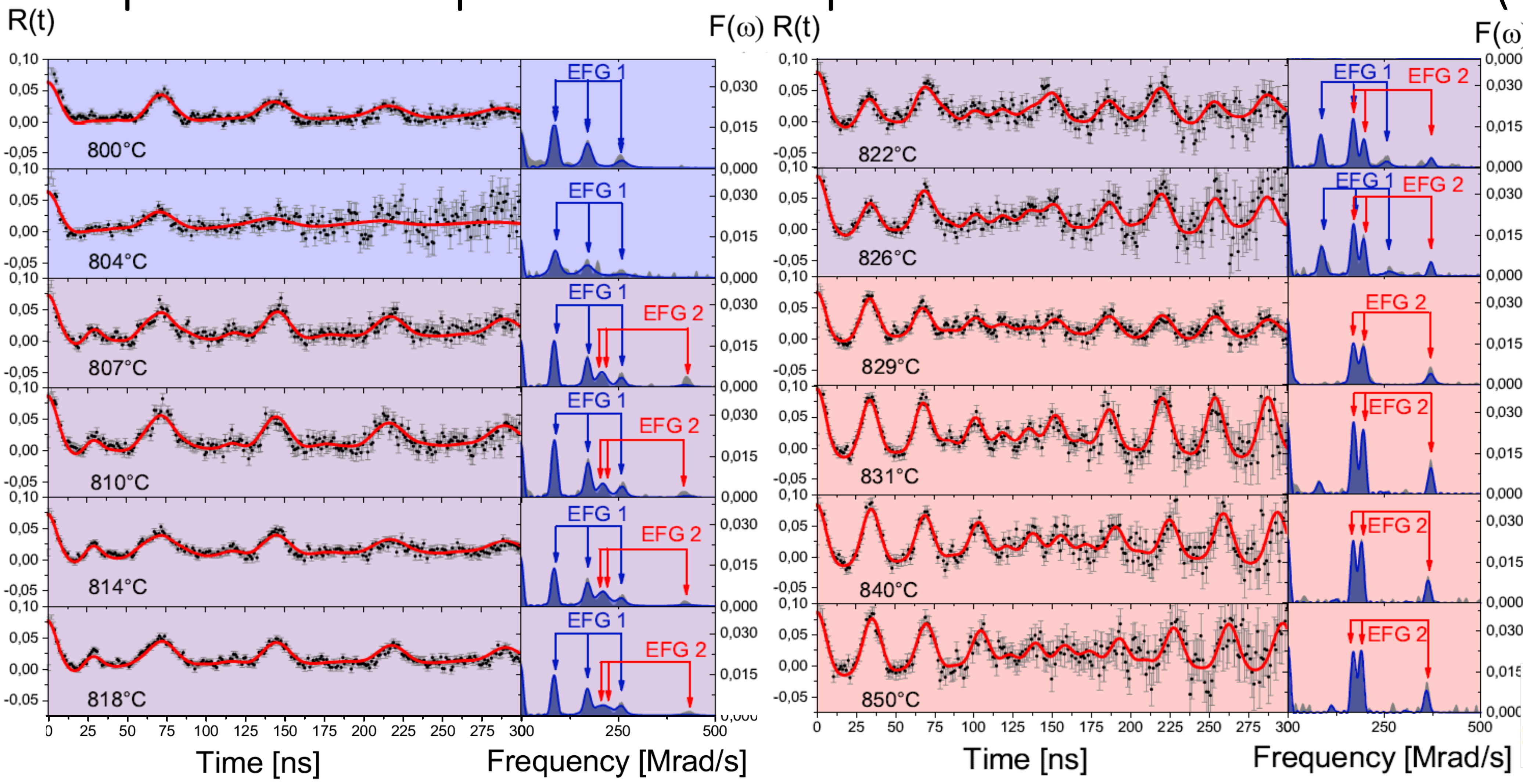
PAC Studies at CERN - ISOLDE (CH)

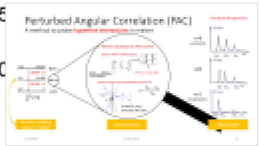
- $BiFeO_3$ samples were cut and ^{111m}Cd implanted at GLM beamline at 30keV
- 6 detector fully digital spectrometer
- High temperature measurements directly after implanting
- One temperature per sample



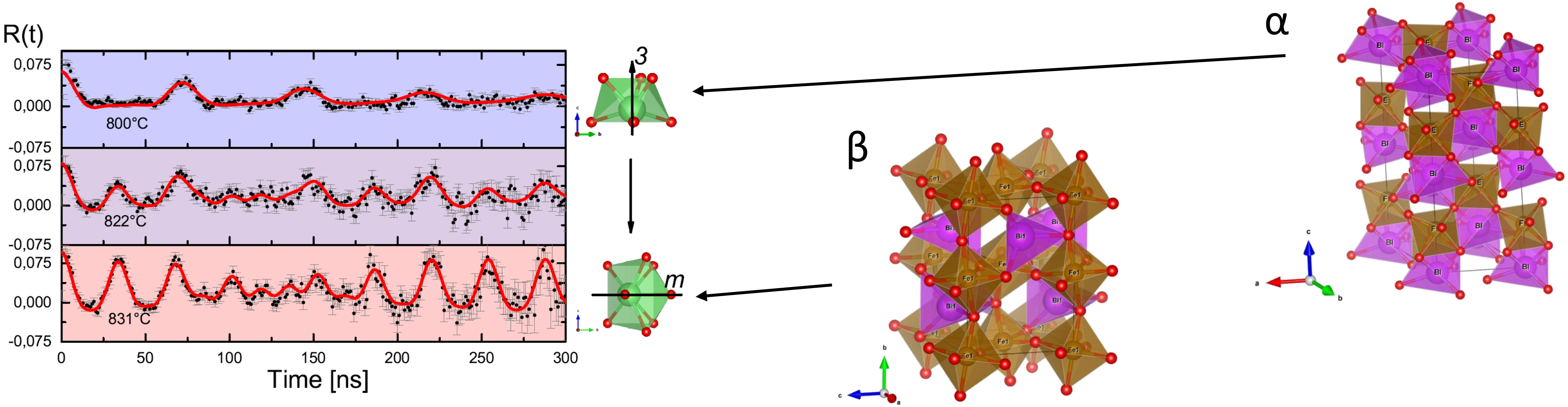


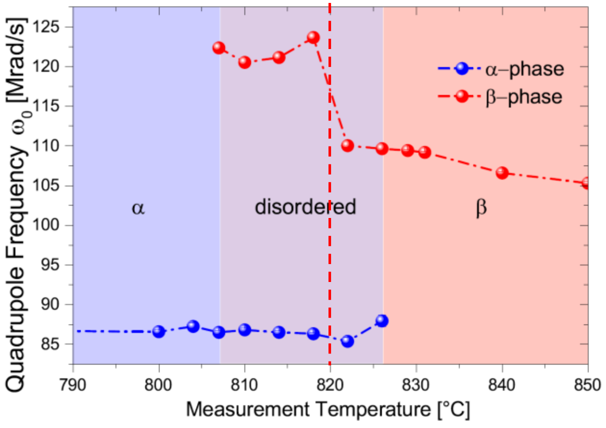
Temperature dependence of perturbation function R(t)

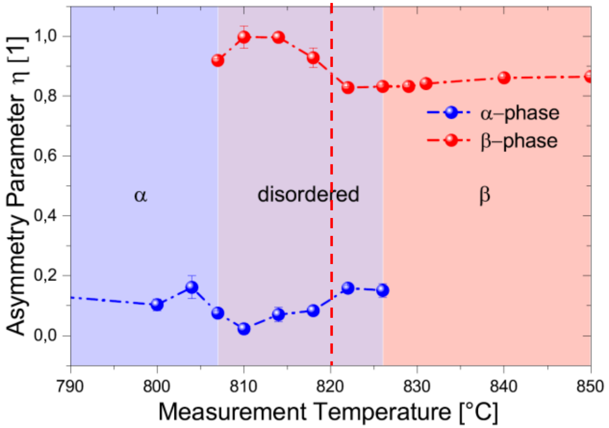


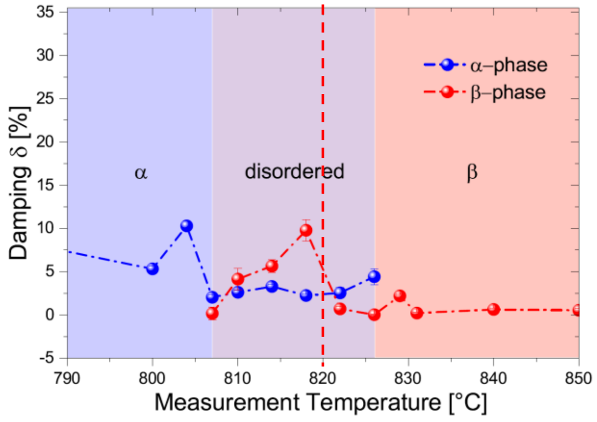


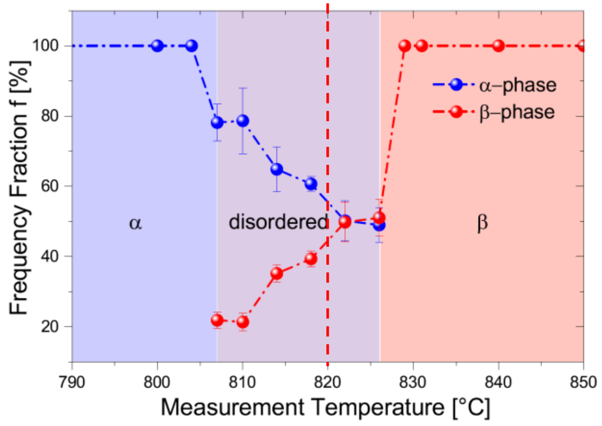
Temperature dependence of error function R(t)





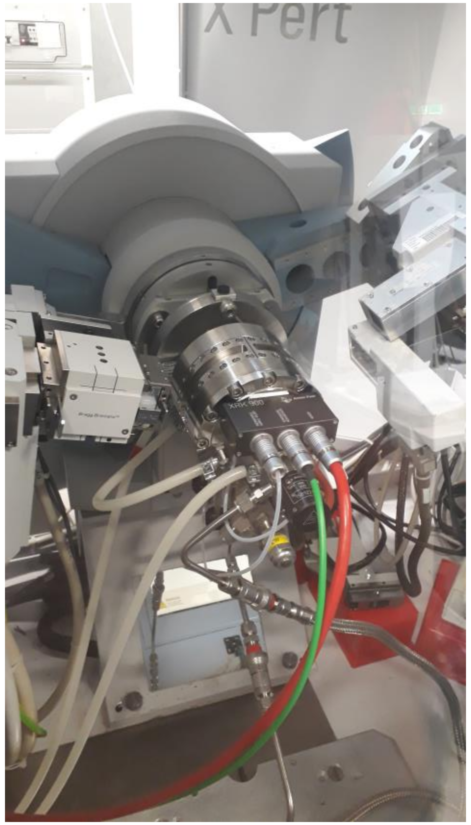






X-ray diffraction studies at TU Wien (AT)

- Samples were ground and placed on Pt-sample holder
- Single temperature Bragg Brentano measurement (20°-70°)
- Sweep measurements 30-33° (800-840-800°C)



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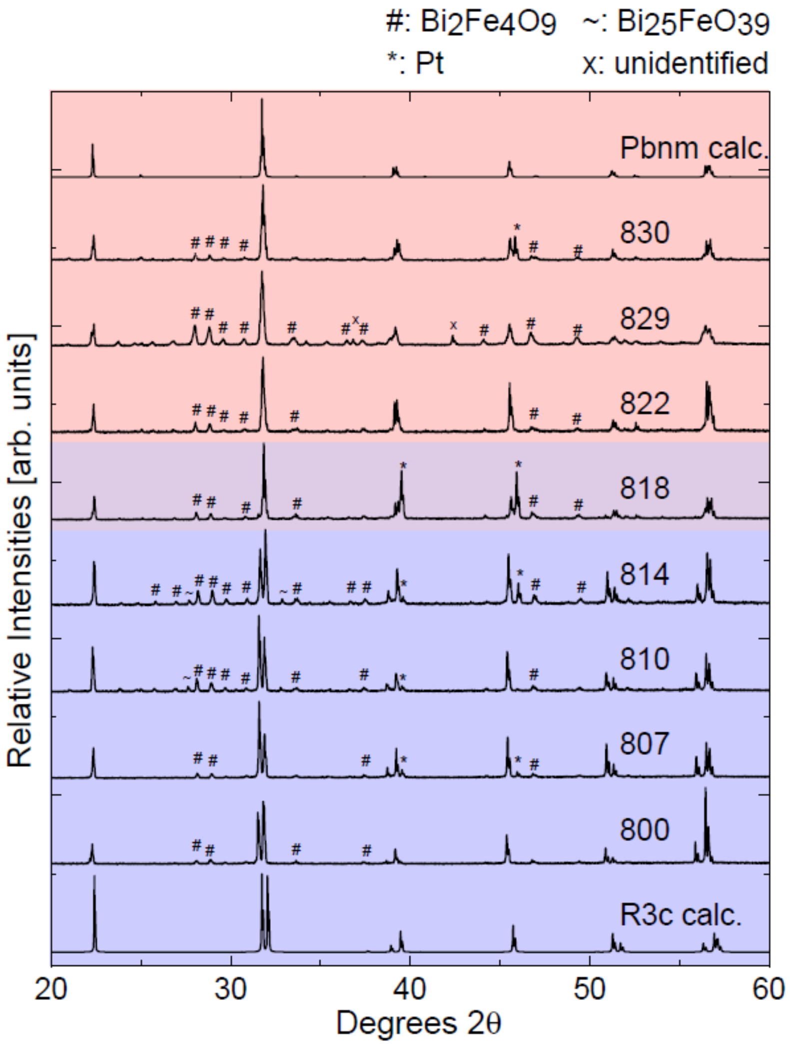
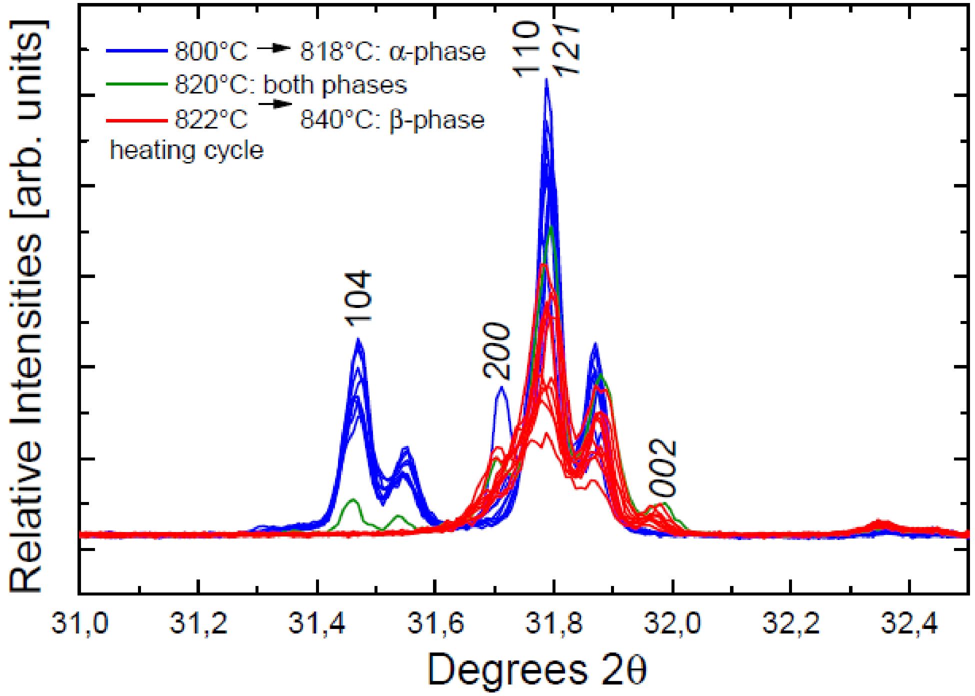


← Single temperature measurements

Both measurements show a phase transition at 818-820°C

Sweep measurement 30°-33°



Results

- The results of both experimental methods agree with a phase transition from rhombohedral α-BFO in *R3c* setting to orthorhombic β-BFO with its *Pbnm* space group at 820°C
- PAC results suggest a forecast of the first order phase transition by the Cd probe ion as it senses the preceding symmetry change of the Bi(Cd) coordination environment
- Phase transition is visible through a drop in quadrupole interaction frequency ω_0
- DFT results support the PAC results

- XRD single temperature measurements suggest a phase transition temperature of 818°C, sweep measurements indicate a transition temperature of 820°C
- The XRD results support the results gained with PAC

Thank you!

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DFT Details

- VASP Code (Vienna Ab-Initio Simulation Package)
- projector augmented wave method with a general gradient approximation
  - $5d^{10}6s^{2}6p^{3}$ for Bi
  - $2s^{2}2p^{4}$ for Fe
  - $3p^{6}3d^{6}4s^{2}$ for O
  - $4d^{10}5s^{2}$ for Cd
- Alpha phase: 2x2x1 supercell with 4x4x3 k-point grid
- Beta phase: 2x2x1 supercell with 5x5x4 k-point grid
- Bi2Fe4O9: 2x1x2 supercell with 3x2x4 k-point grid
- Energy cut-off 450eV
- Self consistent stop @ values < 10e-5 eV

DFT Results

System		V_{zz}^{DFT} $[\frac{10^{21}V}{m^2}]$	η^{DFT} [1]	ΔH^{DFT} [eV]	ω_0^{DFT} [Mrad/s]
α-BFO (FM / AFM)	Cd @ Bi	5.72 / 5.37	0/0	8.4 / 2.6	80.3-86.8 / 75.4-81.5
	Cd @ Fe	5.46 / 4.07	0/0	8.8 / 5.5	76.7-82.9 / 57.1-61.8
β-BFO (FM / AFM)	Cd @ Bi	-7.51 / -6.88	0.39 / 0.26	4.2 / 1	105.4 - 113.97 / 96.57 - 104.41
	Cd @ Fe	2.37 / 8.43	0.87 / 0.18	5.4 / 2.2	33.3 - 35.9 / 118.33 - 127.93
$Bi_2Fe_4O_9$ (FM)	Cd @ Bi	9.99	0.12	-	140.22 - 151.61
	Cd @ Fe	7.99	0.84	-	112.15 - 121.25

TABLE I. Simulated values of V_{zz} and ΔH as well as the calculated value of ω_0. The range of the results of ω_0 is caused by the uncertainity of Q.

Ion radii

CN	Ion				
	Cd^{2+}	Bi^{3+}	Fe^{3+}	In^{3+}	Mn^{3+}
IV	0.84	-	0.49	-	-
V	0.87	0.99	-	-	0.58
VI	0.95	1.02	0.55 (LS) 0.645 (HS)	0.79	0.58 (LS) 0.65 (HS)
VII	1	-	-		
VIII	1.07	1.11	-	0.923	-
XII	1.31	-	-		

TABLE III. Effective ion radii of Cd^{2+}, Bi^{3+} and Fe^{3+} ions in Å for different coordination numbers CN.[32]

PAC Results

Temp. [°C]	ω_0^{PAC} [Mrad/s]	ω_0^{PAC} [Mrad/s]
500	106(6)	
603	91(3)	
650	88.5(3)	
703	87(1)	
776	86.8(5)	
800	86.6(3)	
804	87.3(5)	
807	86.5(2)	122(0)
810	86.8(2)	120.54(0)
814	86.5(2)	121.14(0)
818	86.3(2)	123.67(0)
822	85.4(5)	110.05(0)
826	88.0(1)	109.66(0)
829		109.4(1)
831		109.2(1)
840		106.6(2)
850		105.3(3)