A Study of the Combined Hyperfine Interactions in Bismuth Ferrite using the Time Differential Perturbed Angular Correlation (TDPAC) Spectroscopy

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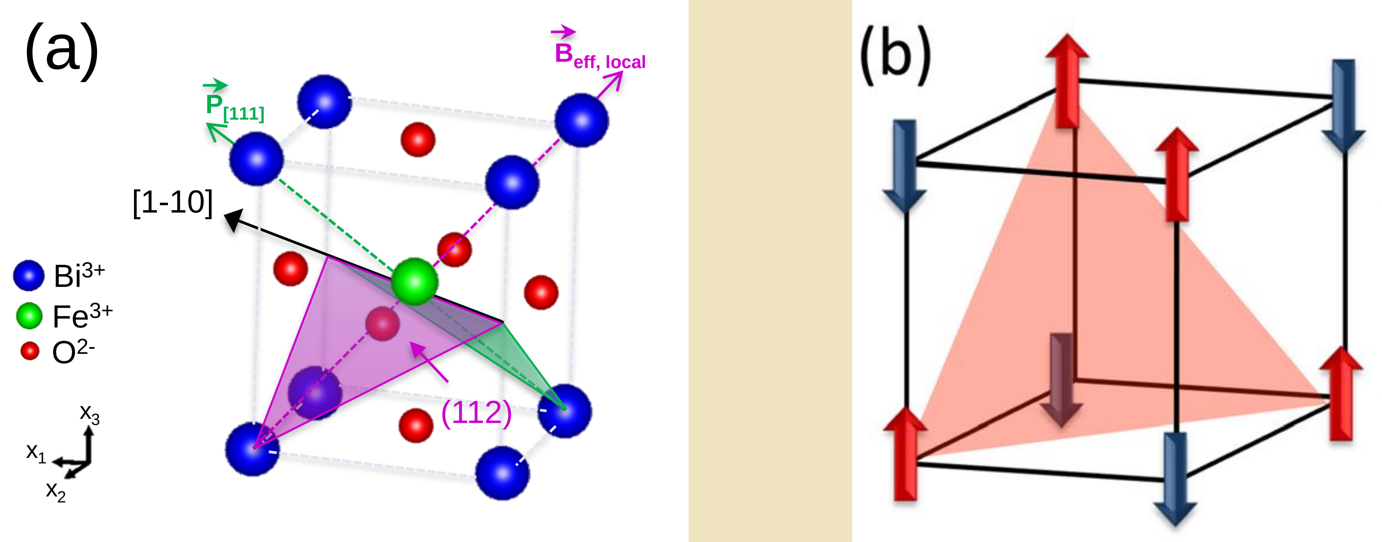
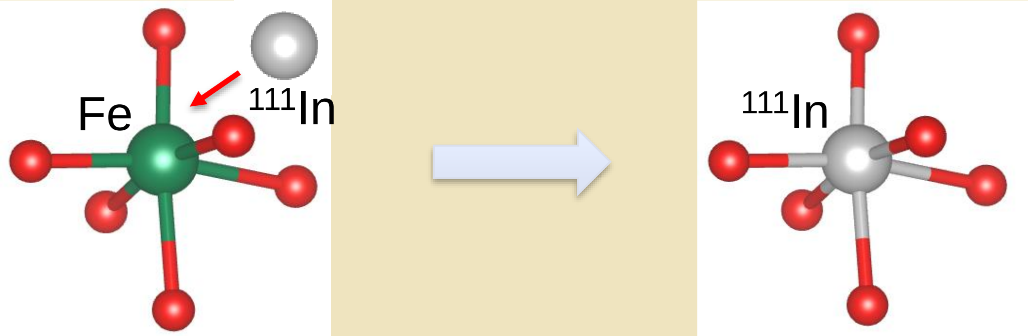
Contents

1. Ferroic orders and lattice sites of bismuth ferrite



(a) Configuration for polarization direction and effective magnetic field direction in BFO pseudocubic unit cell. This figure was made based on the source [Lebeugle 2008]. (b) Schematic of a G-type antiferromagnet highlighting the ferromagnetic order within the (111) plane. [Heron 2014]



2. PAC Spectroscopy- Radioactive probe

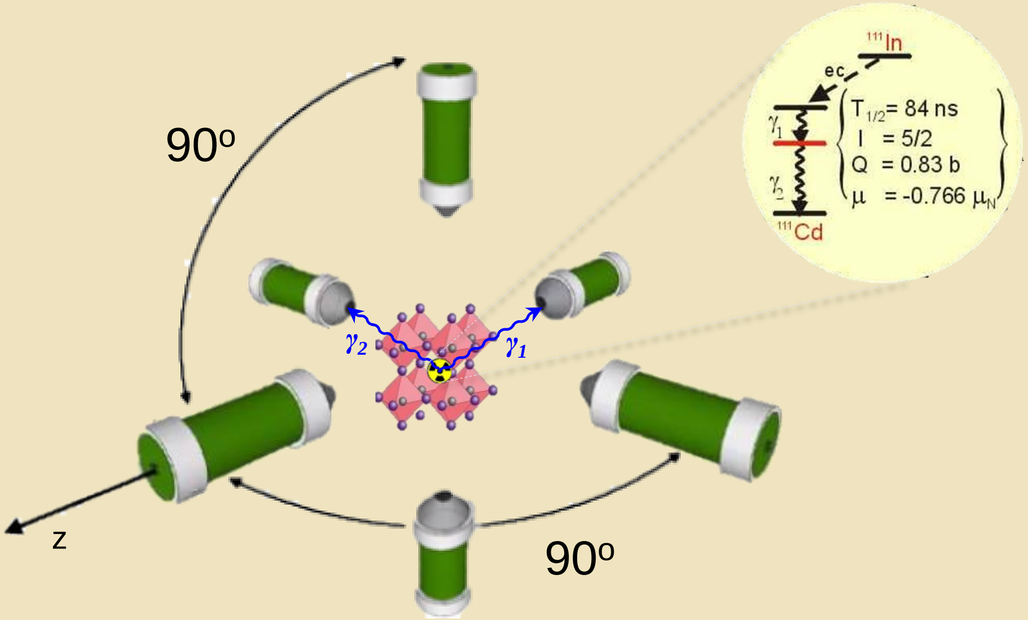
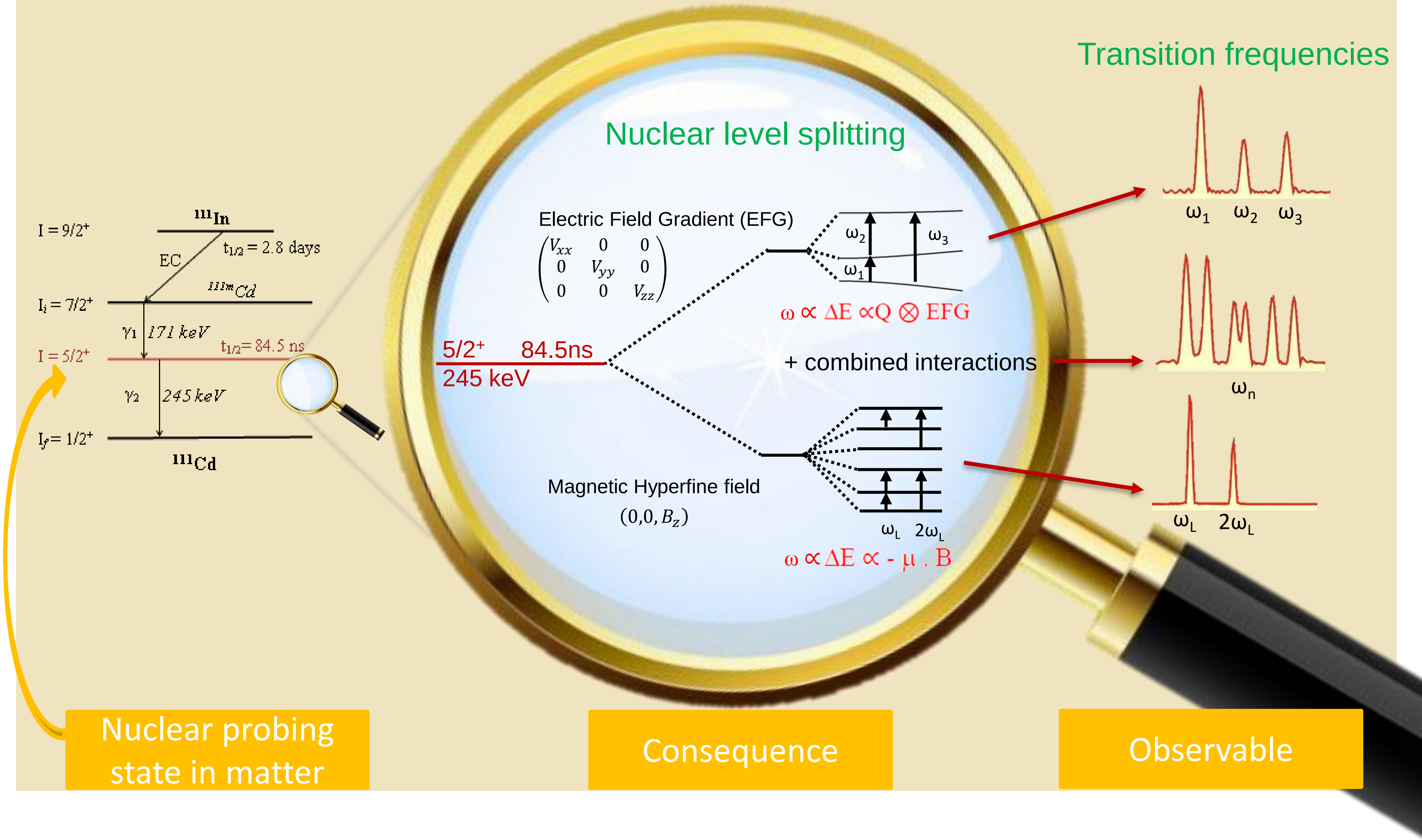


Figure made based on the source [Barbosa 2019]

KATAME (digital 6-detectors setup) at **ISOLDE** [Nagl 2010]

Comment: New electric quadrupole moment value: $Q(^{111}Cd, 5/2^{+}) = +0.664(7)b$. „Free molecule studies by perturbed gamma-gamma angular correlation: A new path to accurate nuclear quadrupole moments" H. Haas et al, PRB, 2021. [Haas 2021]

2. PAC Spectroscopy
A method to probe hyperfine interactions in matter



Nuclear level splitting

Electric Field Gradient (EFG)

$$\begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}$$

$\omega \propto \Delta E \propto Q \otimes \text{EFG}$

+ combined interactions

Magnetic Hyperfine field

$(0, 0, B_z)$

$\omega \propto \Delta E \propto - \mu \cdot B$

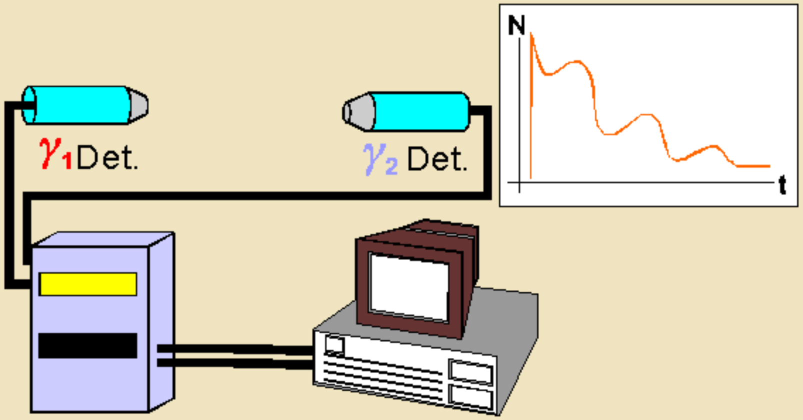
Transition frequencies

Nuclear probing state in matter

Consequence

Observable

2. PAC Spectroscopy-Perturbation functions



$$N_{ij}(\theta,t) = N_0\epsilon_i\epsilon_j\Omega_i\Omega_j.\,exp\left(-\frac{t}{\tau}\right).\,W(\theta,t) + U$$

$$W(\theta) \sim \sum_{k=even}^{k_{max}} A_{kk}\boldsymbol{G_{kk}(t)}P_k(cos\theta)$$

$$G_{22}(t) = \sum_{i=1}^{m} f_i\left[a_{0i} + \sum_{n=1}^{30} a_{ni}\cos(\omega_{ni}t) \times \exp\left(-0.5\left((\delta_i\omega_{ni}t)^p + (\omega_{ni}\tau_R)^2\right)\right)\right] \times \exp(-\lambda_i t)$$

[Catchen 1994, Matthew 2011, Dogra 2009, Forker 2013]

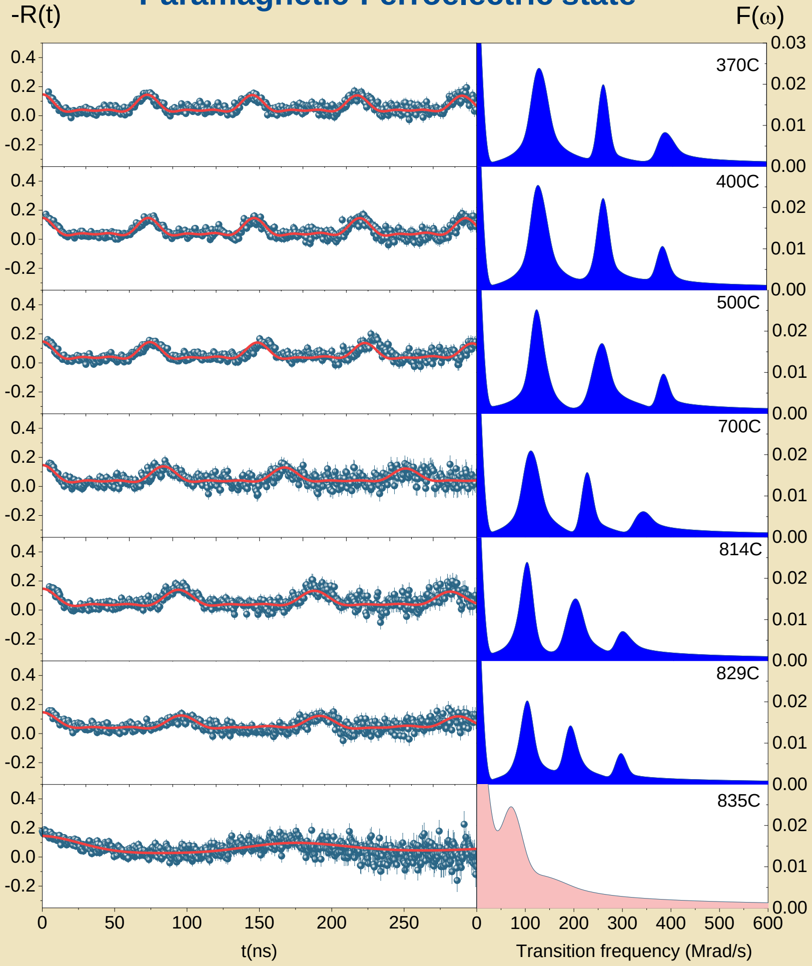
$$R(t) = 2.\frac{\bar{N}(180^0,t) - \bar{N}(90^0,t)}{\bar{N}(180^0,t) + 2.\bar{N}(90^0,t)} = 2\frac{W(180,t) - W(90,t)}{W(180,t) + 2W(90,t)} \approx A_{22}^{eff}G_{22}(t)$$

Picture source: PD Dr Reiner Vianden, faculty for mathematics and sciences of the Rheinische Friedrich-Wilhelms University Bonn, Germany. Available at https://tdpac.hiskp.uni-bonn.de/pac/

3. Experimental Results-PAC spectra

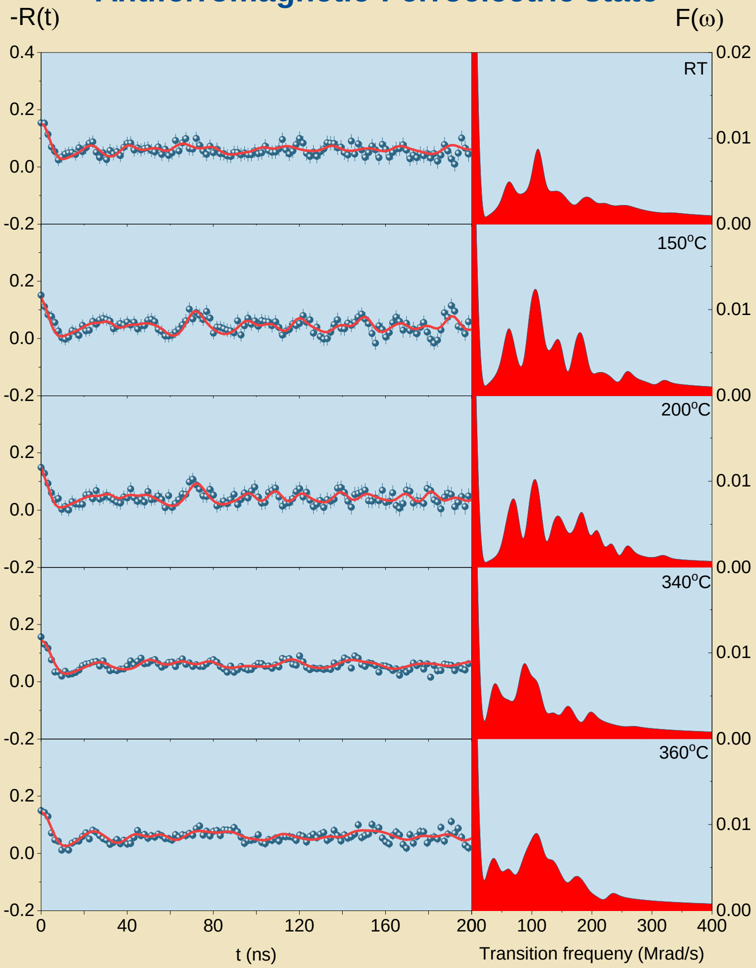
Open-Minded

Paramagnetic-Ferroelectric state



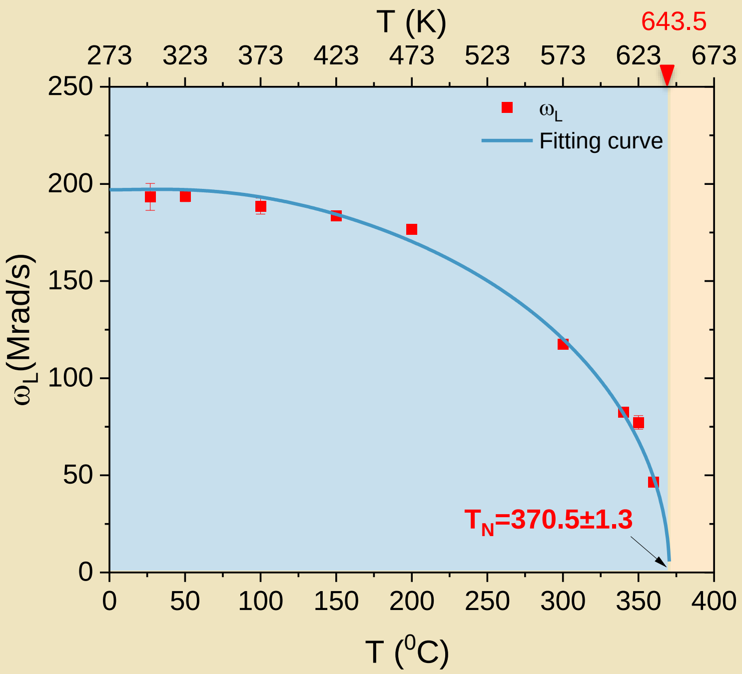
Left: PAC spectra at different measuring temperatures (370 °C – 835°C. Right: The corresponding FFTs.

Antiferromagnetic-Ferroelectric state

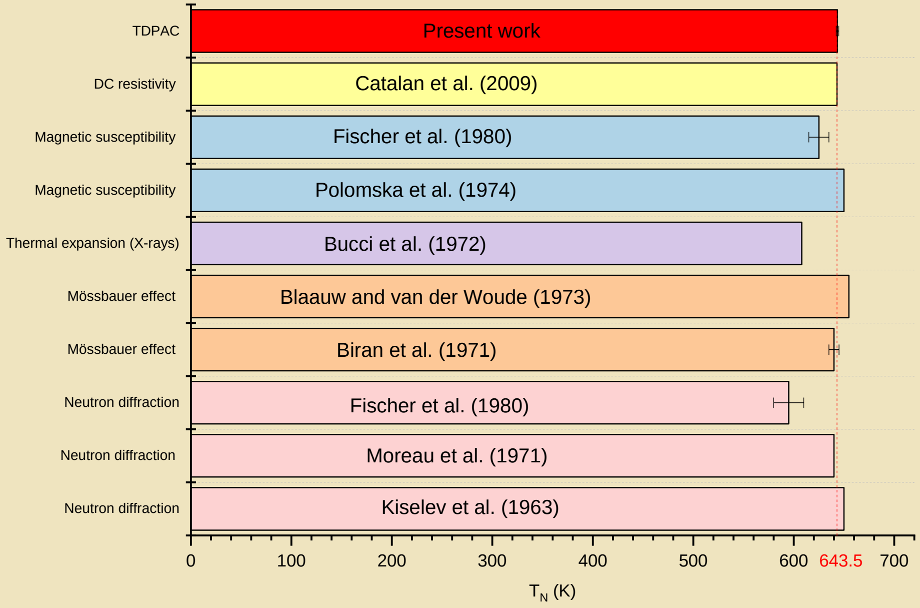


Left: PAC spectra at different measuring temperatures (RT – 360°C). Right: The corresponding FFTs.

3. Experimental Results- Electromagnetic coupling below Néel temperature

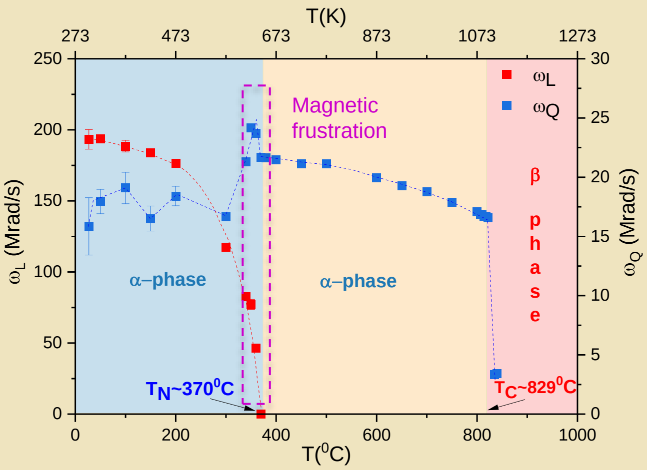


Temperature dependence of the Larmor frequencies. The fitting function is derived from the analytical solution of the Weiss equation.

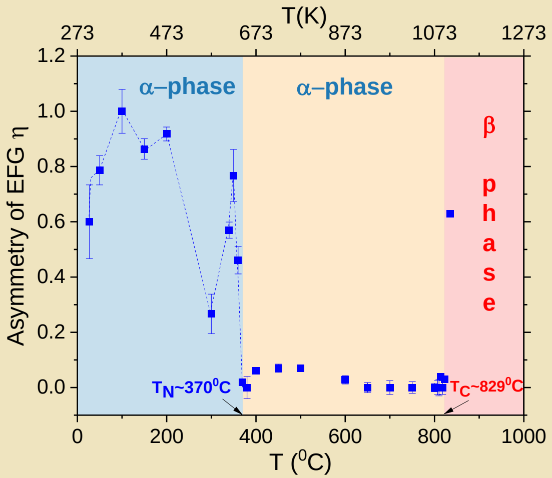


List of results for the Néel temperature of $BiFeO_3$, as determined using various experimental techniques.

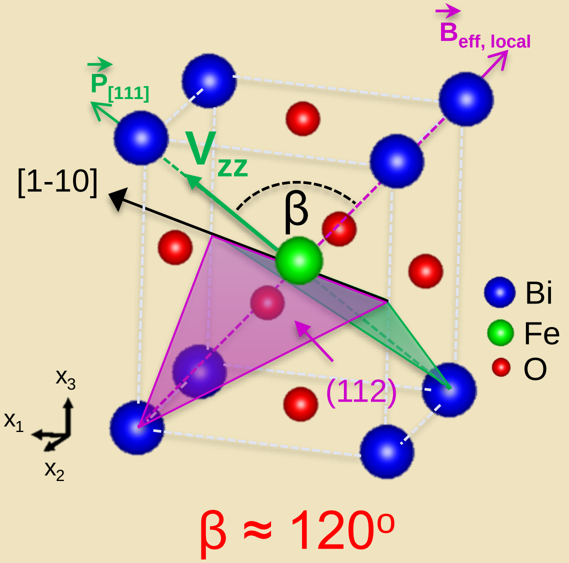
3. Experimental Results- Electromagnetic coupling below Néel temperature



Temperature dependence of the quadrupole (ω_Q) and Larmor (ω_L) frequencies.

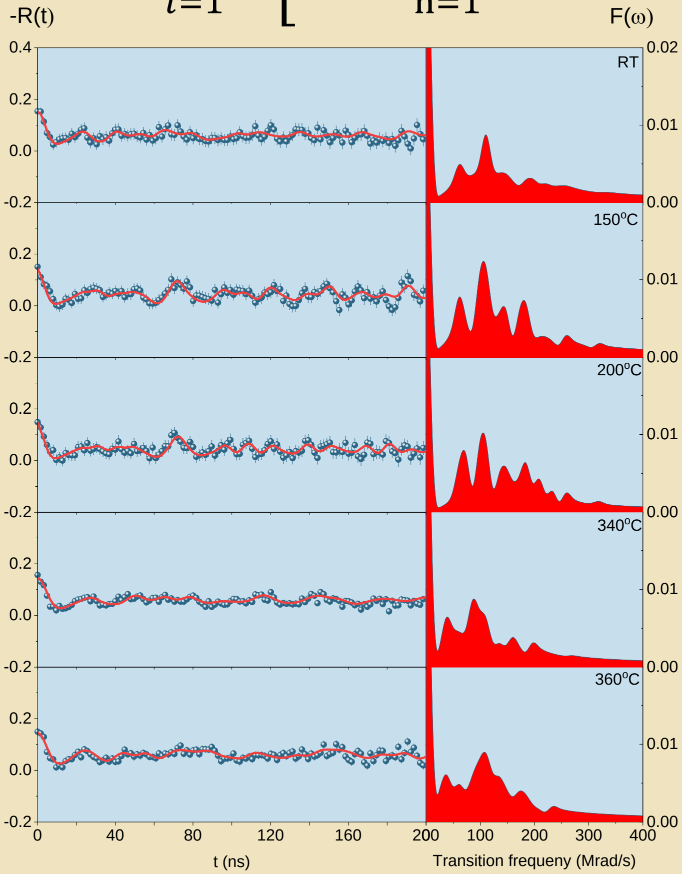


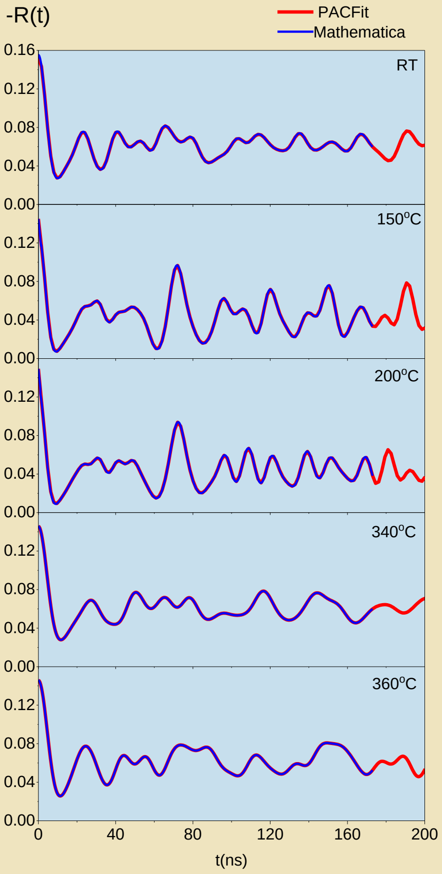
Temperature dependence of the asymmetry parameter (η).



3. Experimental Results - Mathematica Simulations

$$G_{22}(t) = \sum_{i=1}^{m} f_i \left[a_{0i} + \sum_{n=1}^{30} a_{ni} \cos(\omega_{ni} t) \times \exp\left(-0.5\left((\delta_i \omega_{ni} t)^p + (\omega_{ni} \tau_R)^2\right)\right)\right] \times \exp(-\lambda_i t)$$





[Catchen 1994, Matthew 2011, Dogra 2009, Forker 2013]

Comparison between Mathematica calculations and the fittings done by PACFit for our PAC measurements at different temperatures. The red curves were intentionally plotted up to 170 ns to note the degree of overlap between the artificial TDPAC spectra and our experimental fits.

3. Experimental Results - DFT Simulations

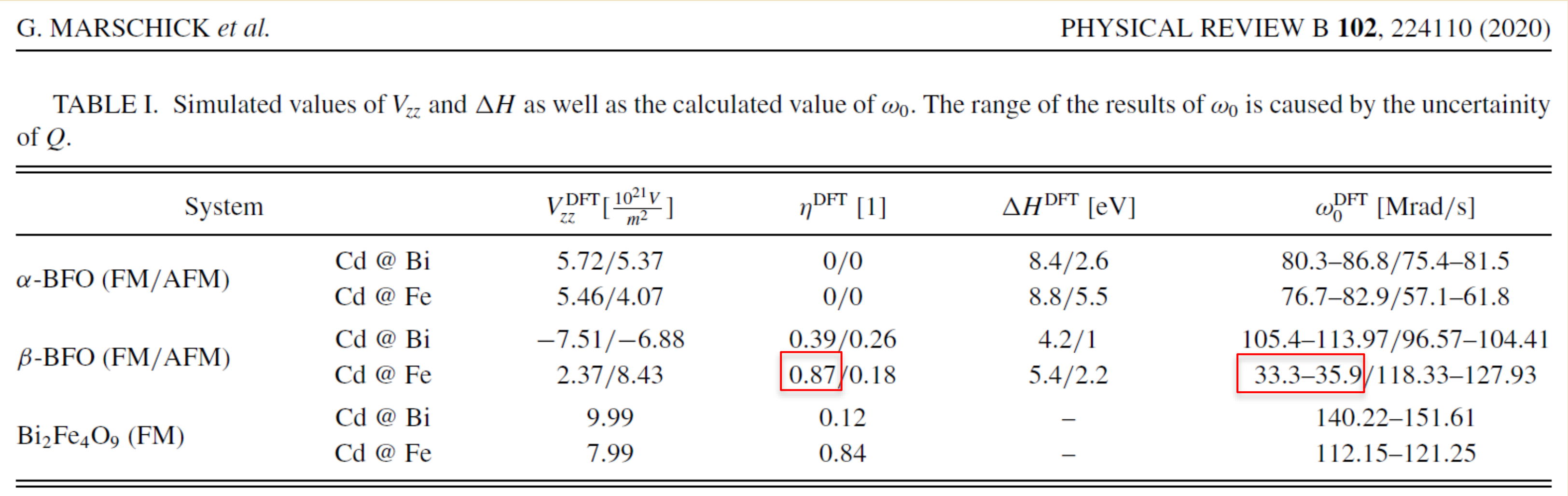


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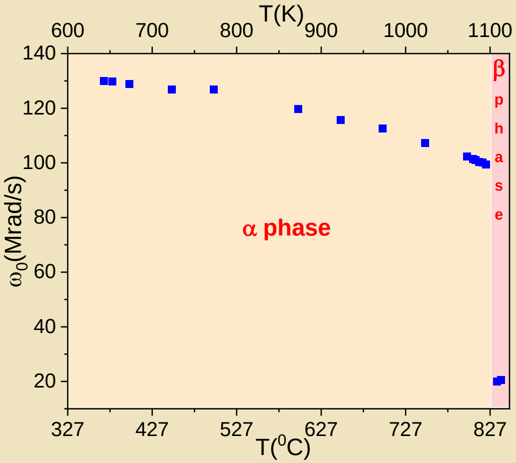
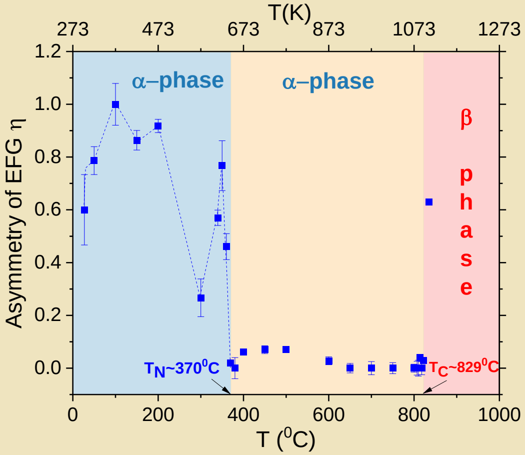
TABLE I. Simulated values of V_{zz} and ΔH as well as the calculated value of ω_0. The range of the results of ω_0 is caused by the uncertainity of Q.

System		$V_{zz}^{\mathrm{DFT}}[\frac{10^{21}V}{m^2}]$	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





CN	Ionic radius (A)		
	Bi^{3+}	Fe^{3+}	In^{3+}
IV	-	0.49	-
V	0.96	-	-
VI	1.03	0.55(LS) 0.645(HS)	0.79
VIII	1.17	-	0.92

[Shannon 1976]

4. Conclusions

- PAC spectroscopy is a potential method to study the local fields at lattice sites in materials generally and in BFO specifically.
- ^{111}In probe is located at the B-site of the BFO structure, which corresponds to substitution of iron atoms.
- Coupling between electric and magnetic interactions exists at the Fe site below the Néel temperature.

Acknowledgements

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THANK YOU ☺

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