Probing the local structure in multiferroic $SmCrO_3$

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[1]**IFIMUP and IN**- Institute of Nanoscience and Nanotechnology and Department of Physics, University of Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

[2]Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Germany

[3]**C2TN**, Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Estrada Nacional 10, 2695-066 Bobadela LRS, Portugal

G.N.P. Oliveira [1]
R. Teixeira [1]
J. Schell[2]
J.G. Correia[3]
J.P. Araújo [1]
A.M.L. Lopes [1]

Outline

- Outline
- Motivation
- $RCrO_3$ – Properties
- Macroscopic characterization
- Local probe studies (PAC)
- Conclusions

Technology & Materials

Last 70 Years

Printers — Pixel to voxel

Phones — Dial-up to smartphones

Computers — Desktops to Laptops

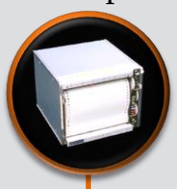
Storage — MB to TB

1946 ENIAC 1st electronic digital computer

1953 Remington-Rand high-speed printer

1963 Bell touch tone phone

1964 HP Moseley 680 strip



1971 Xerox EARS

1977 Xerographic laser print

1979 IBM HDD 250MB

1980 IBM 3380 2.2GB

1984 Comercial phones

1984 1st Maccintosh

1994 1st smartphone (IBM's Simon)

2003 Motorola Razr

2003 Blackberry color screen

2010 iPad

2016 SEAGATE SSD 60TB

1950's

1960's

1970's

1980's

1990's

2000 - 2016

1950s Typewritters in offices

1956 IBM 350 5MB

1957 IBM dot matrix printer market

1969 Bell 1st Video Phone

1976 IBM high-speed laser print

1983 Gavian 1st Laptop

1988 Consumer Ink-Jet printers

1997 HP Photosmart

2007 iPhone

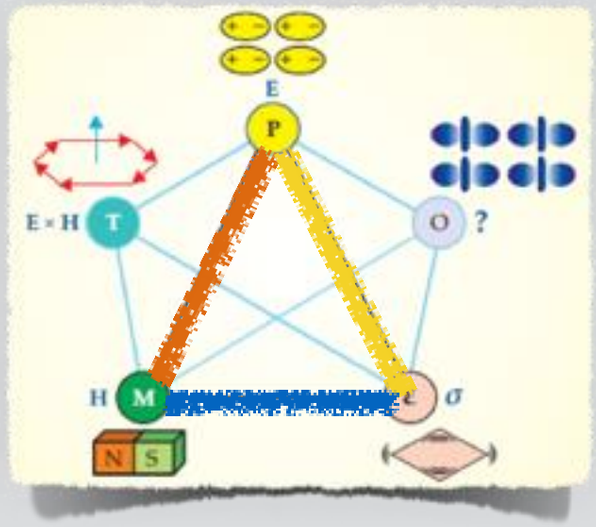
2007 Wireless printer

2008 Macbook Air

2016 Multijet Fusion 3D

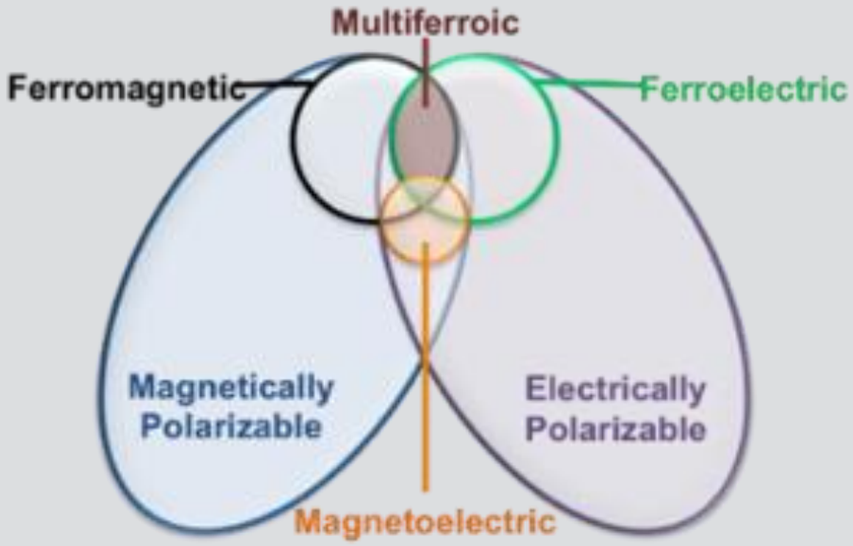
Magnetoelectric materials

Multiferroics



Ferroic Orders:

- **ferromagnetism (M)**
- **ferroeletricity (P)**
- **ferroelasticity (ε), ...**



Solid state systems exhibiting simultaneous (anti) ferroelectric ((A)FE) and (anti) ferromagnetic ((A)FM) orders - Multiferroics;

Maximization of the (A)FE-(A)FM coupling

Ability to manipulate the magnetic degrees of freedom electrically or vice-versa;

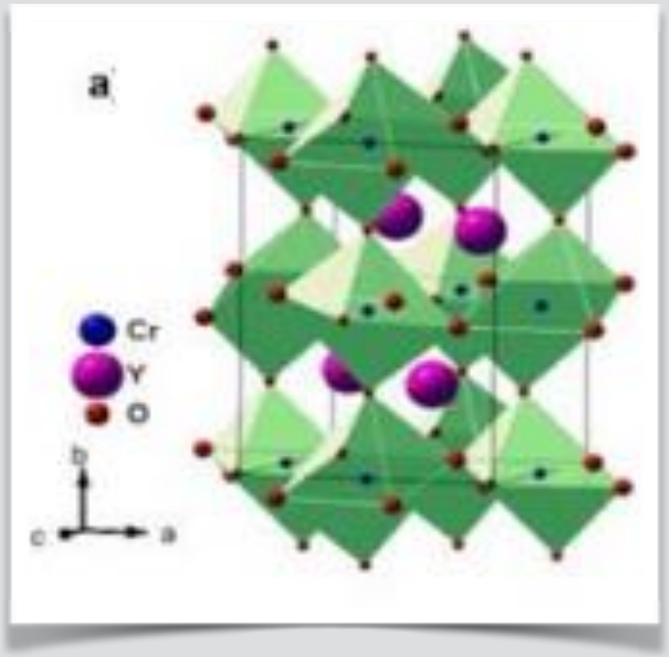
Magnetoelectric

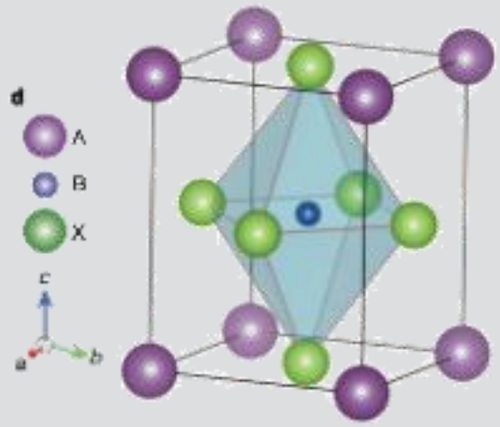
Multifunctional Materials:
Open pathways to different applications

Why Perovskites?
Why Oxides?

- Easy to synthesize large quantities
- Cheap reagents
- Oxides are usually stable
- Multiferroic properties

$RCrO_3$ - General Aspects





R=Yb, Er, Y ,Sm

B=Cr

X=O

Orthorhombically distorted perovskite-like structure

2 "independent" magnetic lattices

Magnetic Properties

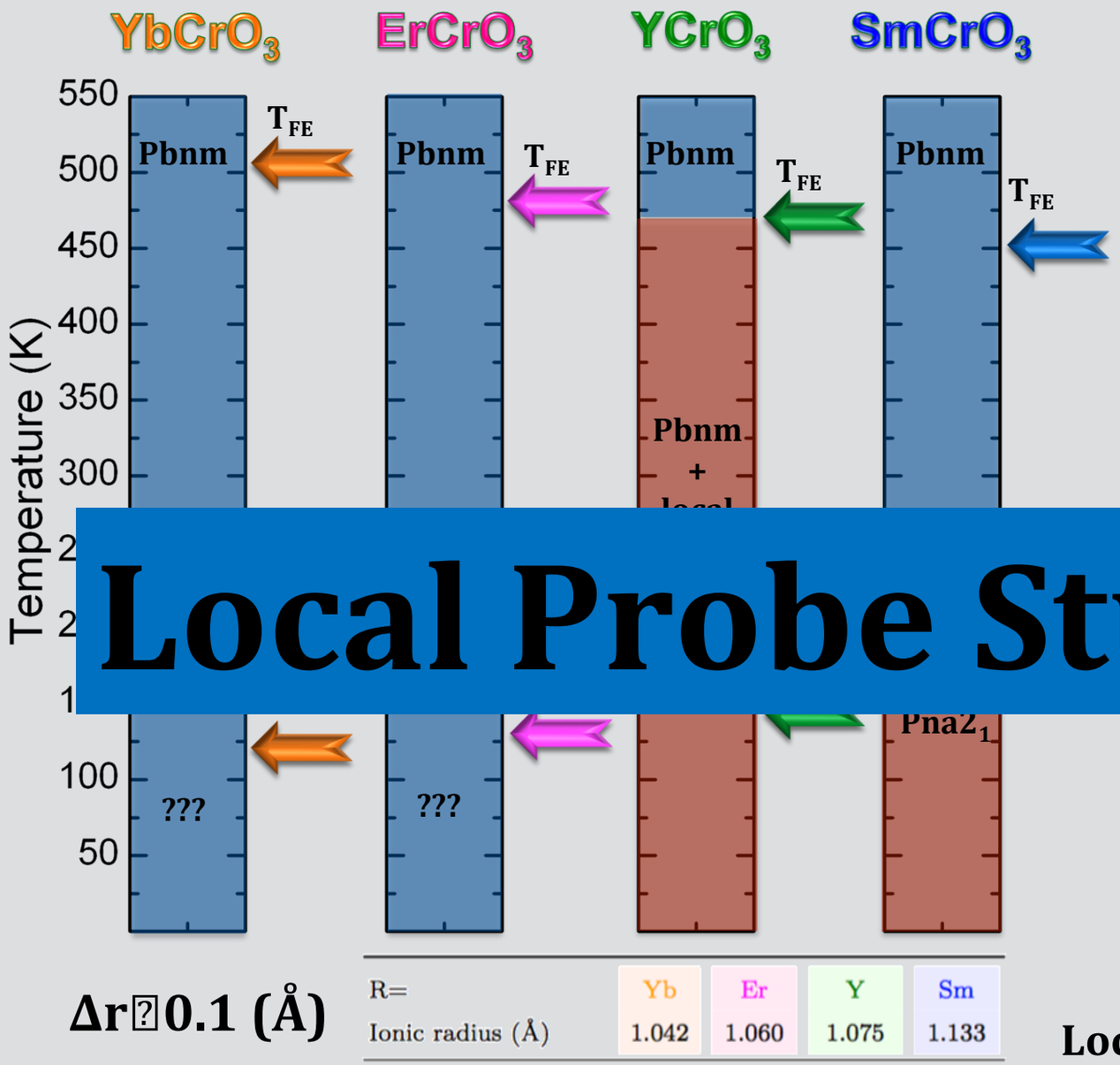
- Cr^{3+} -Cr^{3+} Isotropic
- Cr^{3+} -R^{3+} Symmetric Anisotropic
- R^{3+} -R^{3+} Antisymmetric Anisotropic
- D-M (Dzialoshinski-Moriya) interaction between Cr^{3+} spin

3 Magnetic Transitions

- $T_N Cr^{3+}$ — Antiferromagnetic Neél temperature for Cr^{3+} -Cr^{3+} ordering
- T_{SR} — Spin Reorientation
- $T_N R^{3+}$ — Antiferromagnetic Neél temperature for R^{3+} -R^{3+} ordering

For most systems!

$RCrO_3$ - General Aspects



R=	Yb	Er	Y	Sm
Ionic radius (Å)	1.042	1.060	1.075	1.133

$\Delta r \approx 0.1$ (Å)

Are they magnetoelectric?

Or even ferroelectric?

Local Probe Studies ????

Where is the T_{FE}?

Local or macroscopic symmetry changes?

But First:

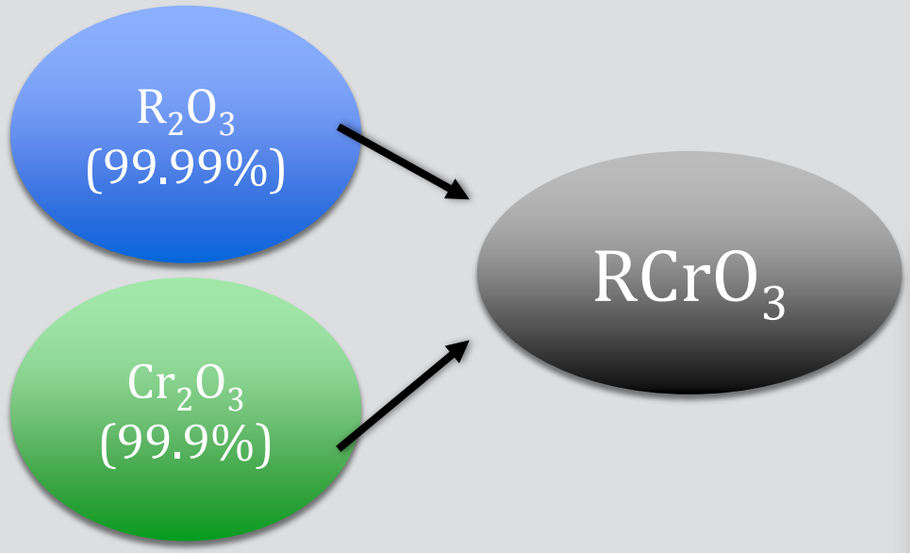
(1) Produce polycrystalline $RCrO_3$ samples by solid state reaction method with high crystallinity with R=Yb, Er, Y and Sm.

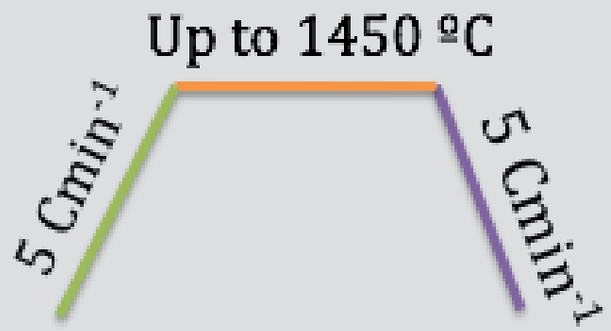
(2) Structural characterization & DC magnetization measurements.

Experimental Procedure

$SmCrO_3$ synthesis optimization

Solid State Reaction Method



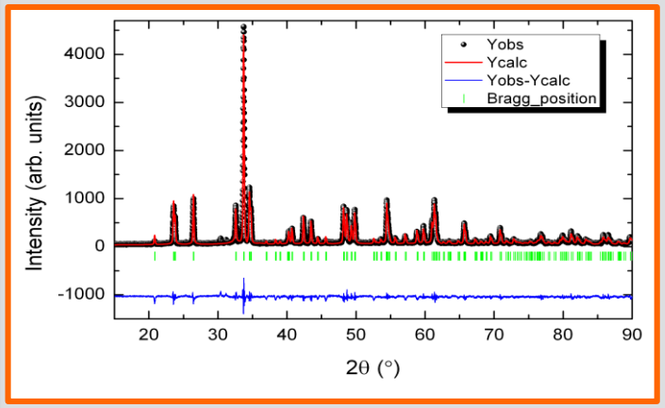


Grinded
Mix
Pellets
Fired @ high T

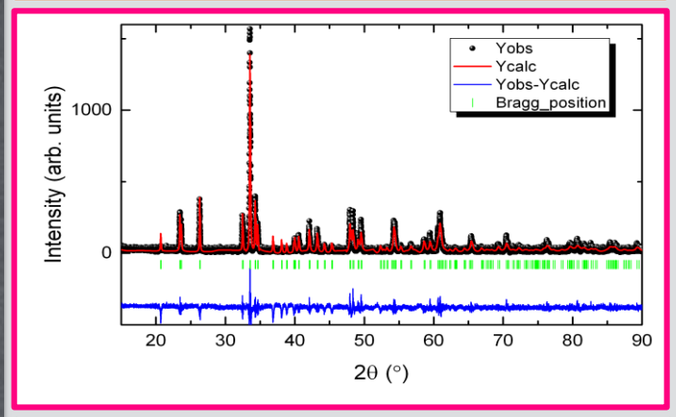
Polycrystalline Samples

Synthesis → XRD → SQUID → PAC

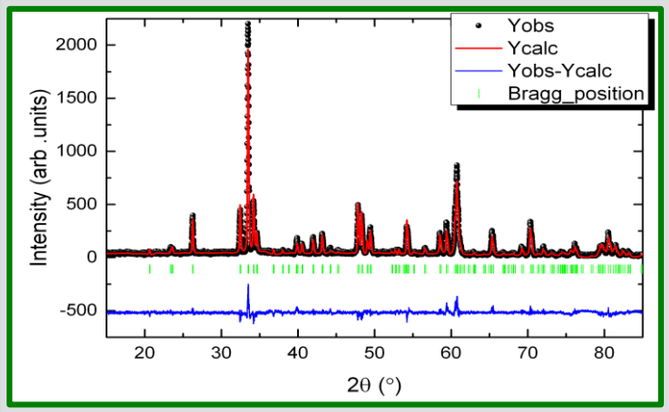
XRD Characterization



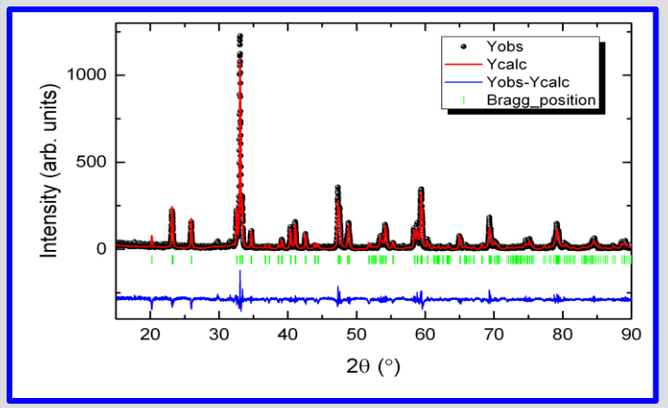
$YbCrO_3$



$ErCrO_3$



$YCrO_3$



$SmCrO_3$

Increasing Radius

Orthorhombic

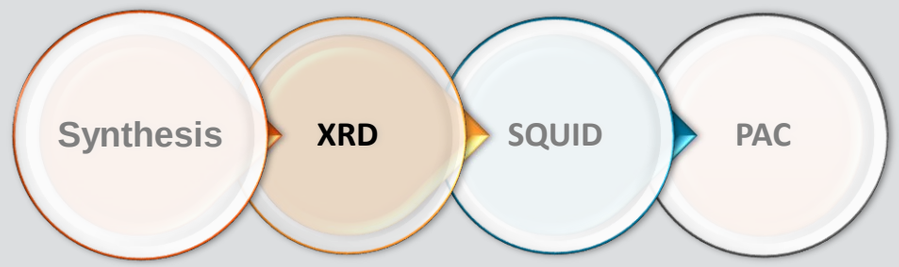
Space Group: Pbnm

Single phase

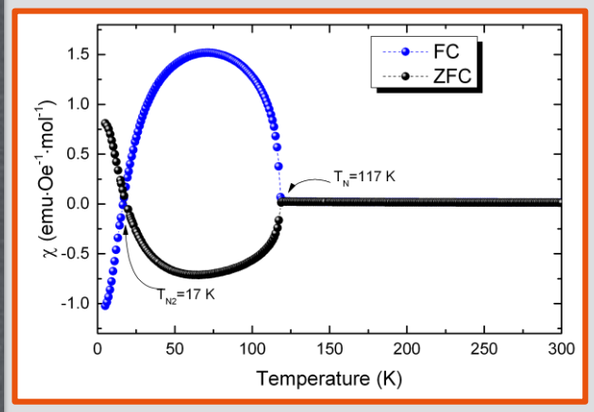
R=	Yb	Er	Y	Sm
Ionic radius (Å)	1.042	1.060	1.075	1.133
a (Å)	5.4991	5.5091	5.5157	5.4970
b (Å)	7.4847	7.5212	7.5309	7.6436
c (Å)	5.1918	5.2275	5.2419	5.3670
V (Å^3)	213.7	216.6	217.7	225.5
ρ (g/cm^3)	8.190	9.316	5.902	8.166
Cr-O1-Cr	143.27	146.60	146.89	153.14

Atomic positions: R: 4c (x, ¼, z); Cr: 4b (0, 0, ½); O (1): 4c (x, ¼, z) and O (2): 8d (x, y, z)

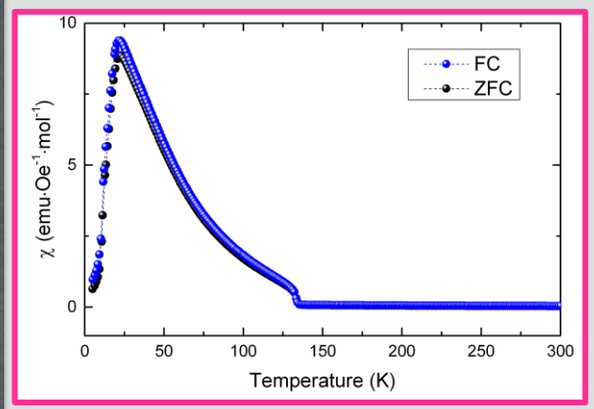
XRD Rietveld refinement output at room temperature. Experimental pattern (•), Fit curve (_), Residual difference (_) and Bragg reflections (|).



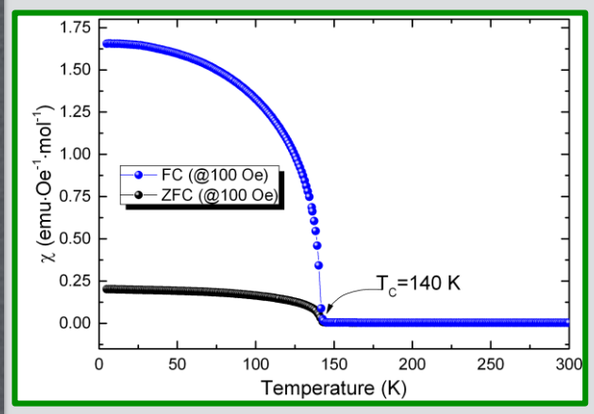
M(T) Characterization



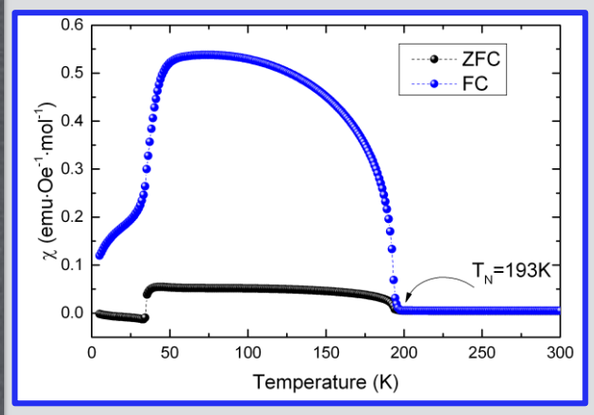
$YbCrO_3$



$ErCrO_3$



$YCrO_3$



$SmCrO_3$

Increasing Radius

Increase of $T_N Cr^{3+}$

Increase of $T_N R^{3+}$

Canted Antiferromagnetism

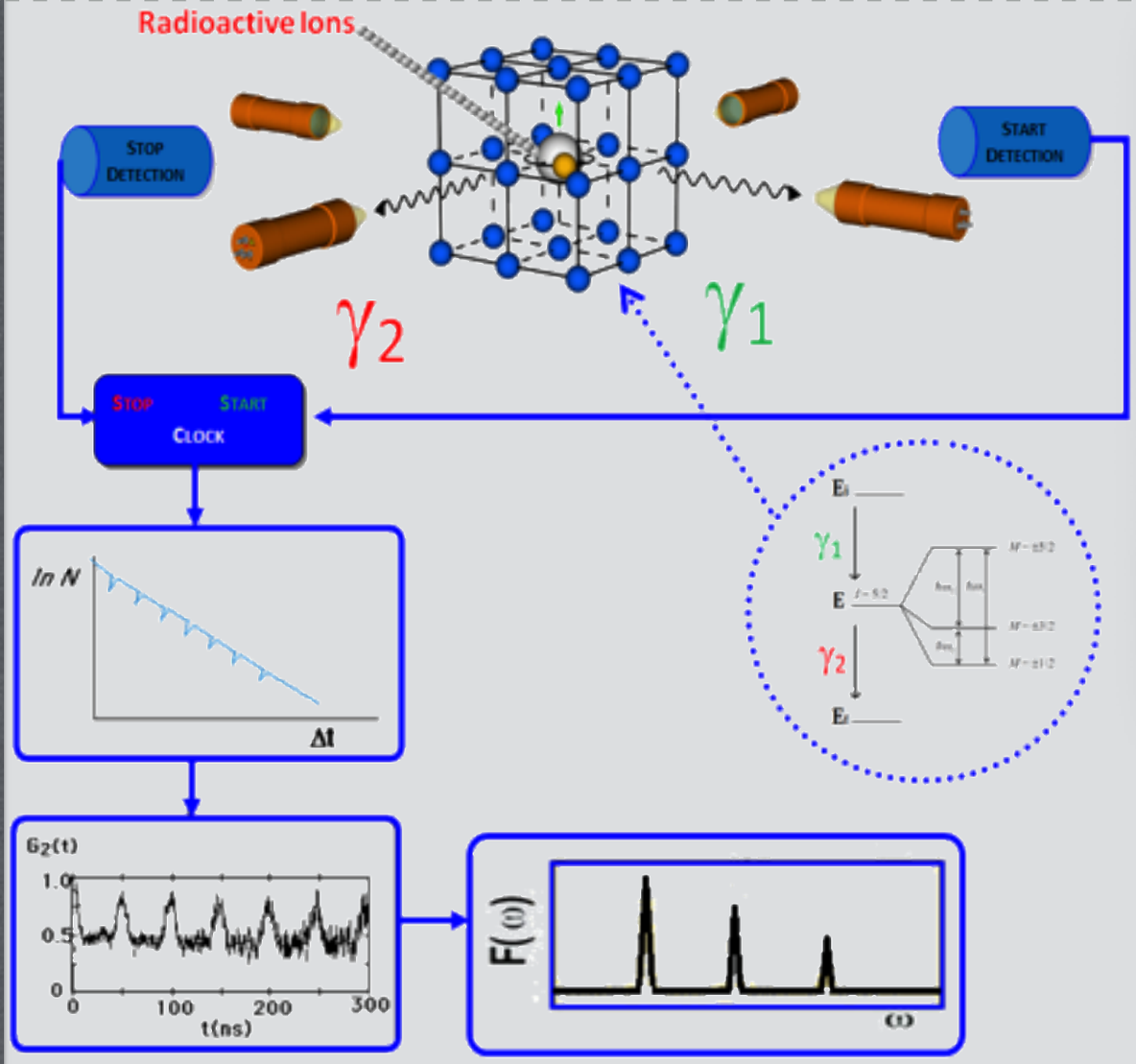
Two magnetic sublattices

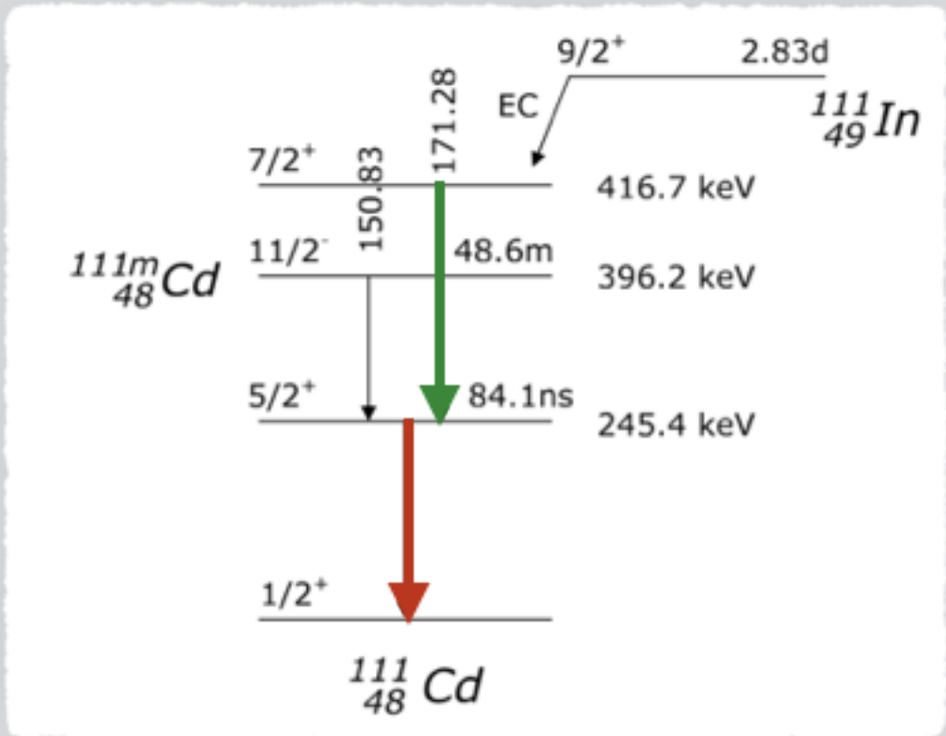
Cr^{3+} and R^{3+}

$T_N^{Cr^{3+}}$ (K)	118	134	141	193
T_{SR} (K)	12	22	–	34
$T_N^{R^{3+}}$ (K)	3[8]	6.5	–	20

Synthesis → XRD → SQUID → PAC

Local Probing (PAC)





Ion implantation @ISOLDE
Ion Diffusion @ISOLDE/LISBON

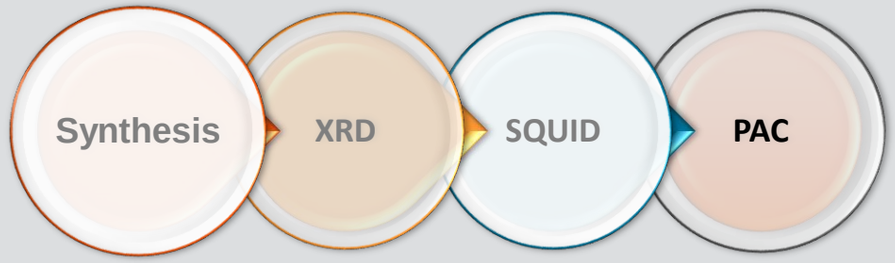
After implantation/Diffusion:
^{111m}Cd – 20 minutes @973K
^{111}In – 48 Hours @1273K

Vzz - EFG Main component
η - Asymmetry parameter

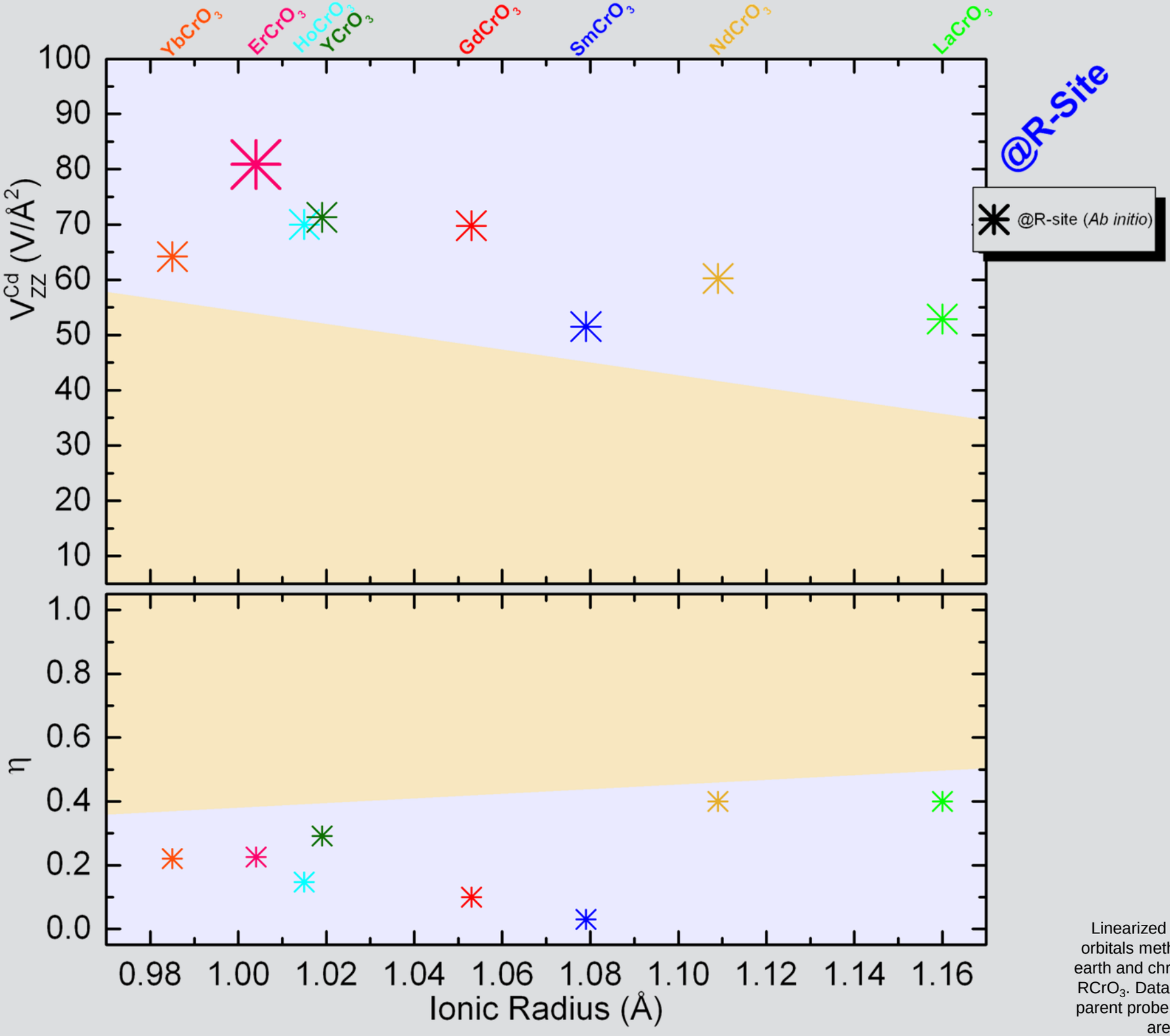
Quadrupolar Frequency $\nu_Q = \frac{(eQV_{zz})}{h}$

Asymmetry Parameter $h = \frac{V_{yy} - V_{xx}}{V_{zz}}$

EFG



Lattice probe location



Linearized augmented plane wave + local orbitals method EFG parameters in the rare-earth and chromium sites for the orthorhombic $RCrO_3$. Data on (Gd, Nd, La)CrO_3 using ^{181}Hf parent probe from literature. The dashed lines are guidelines to the eyes.

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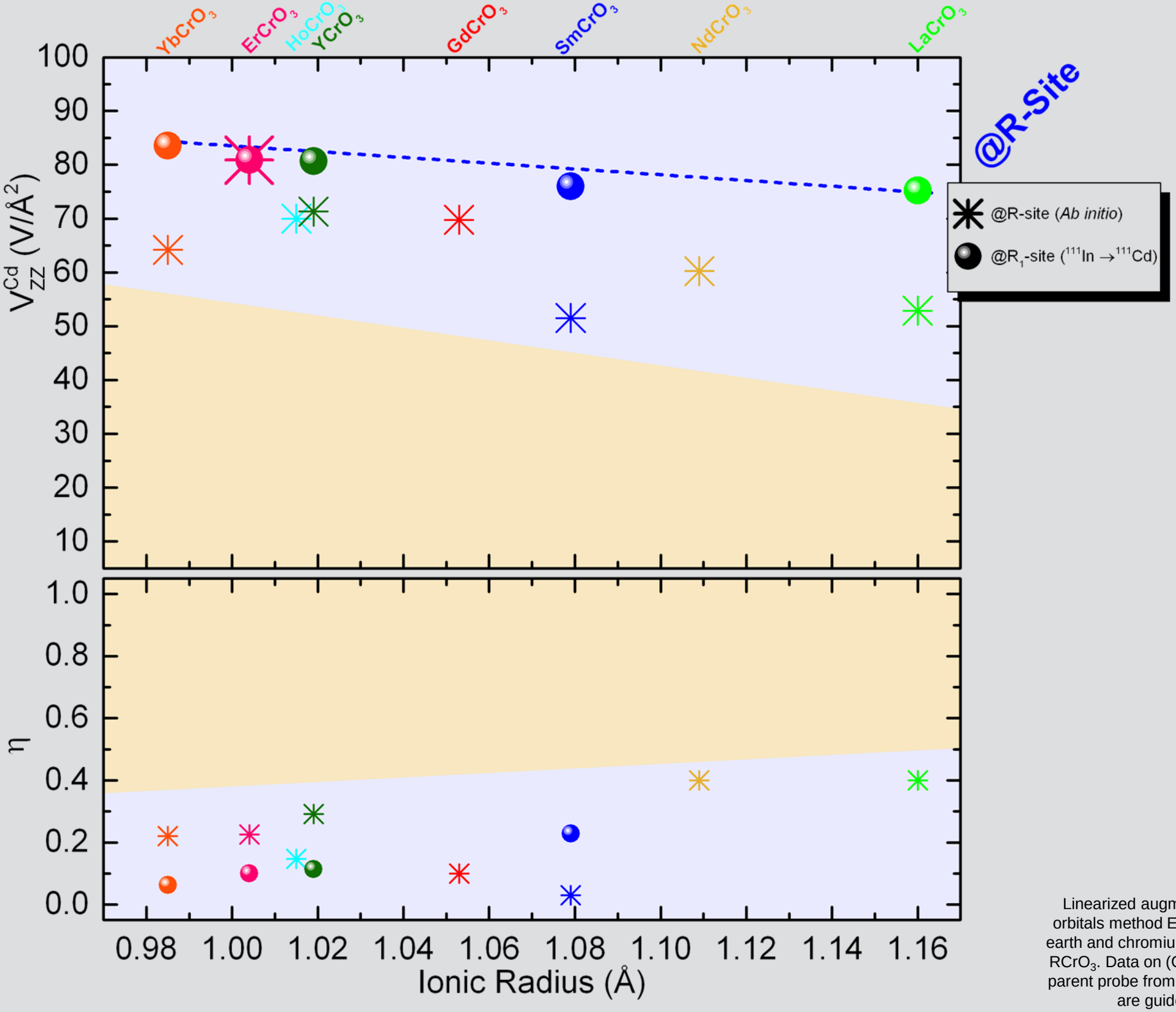

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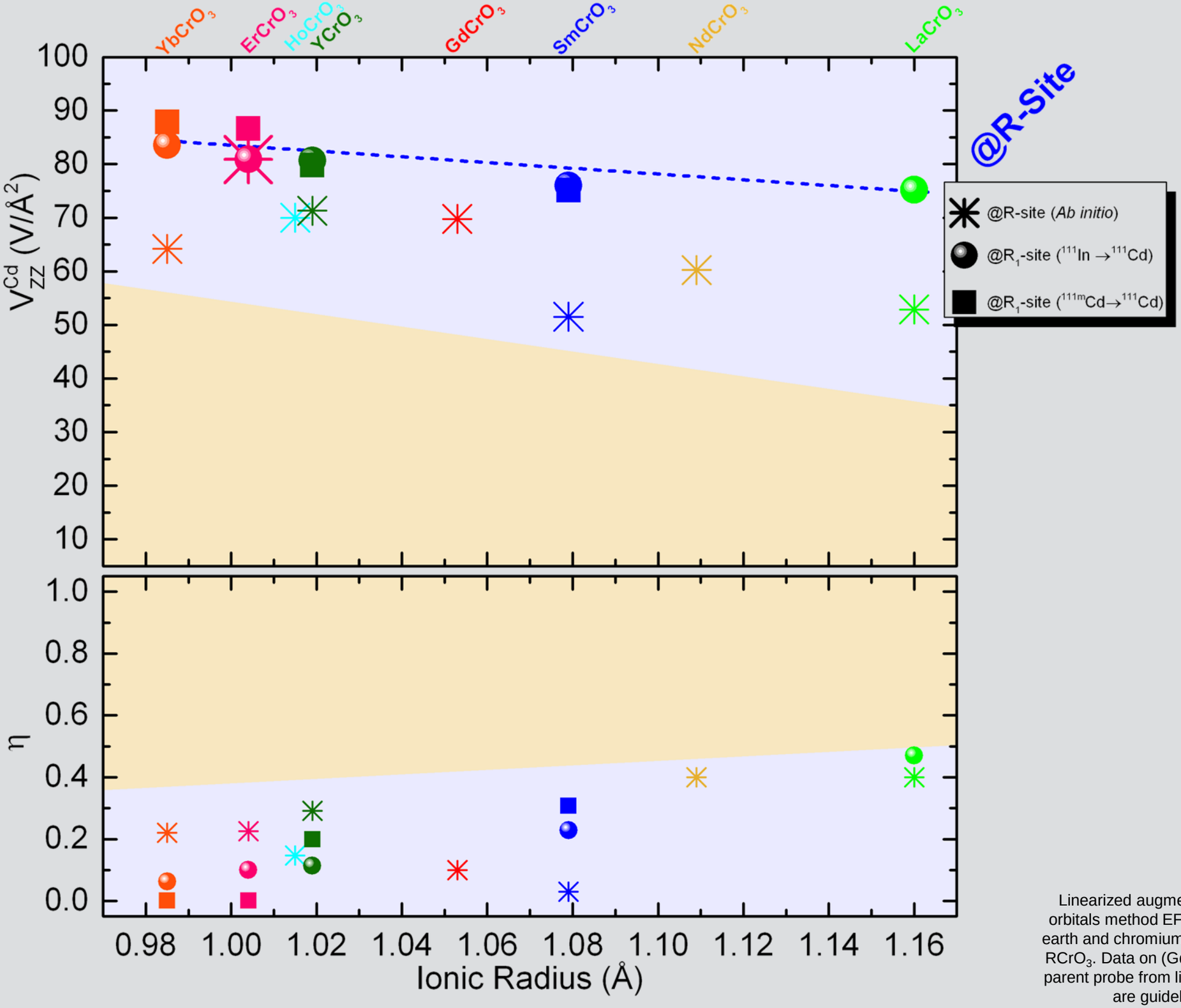

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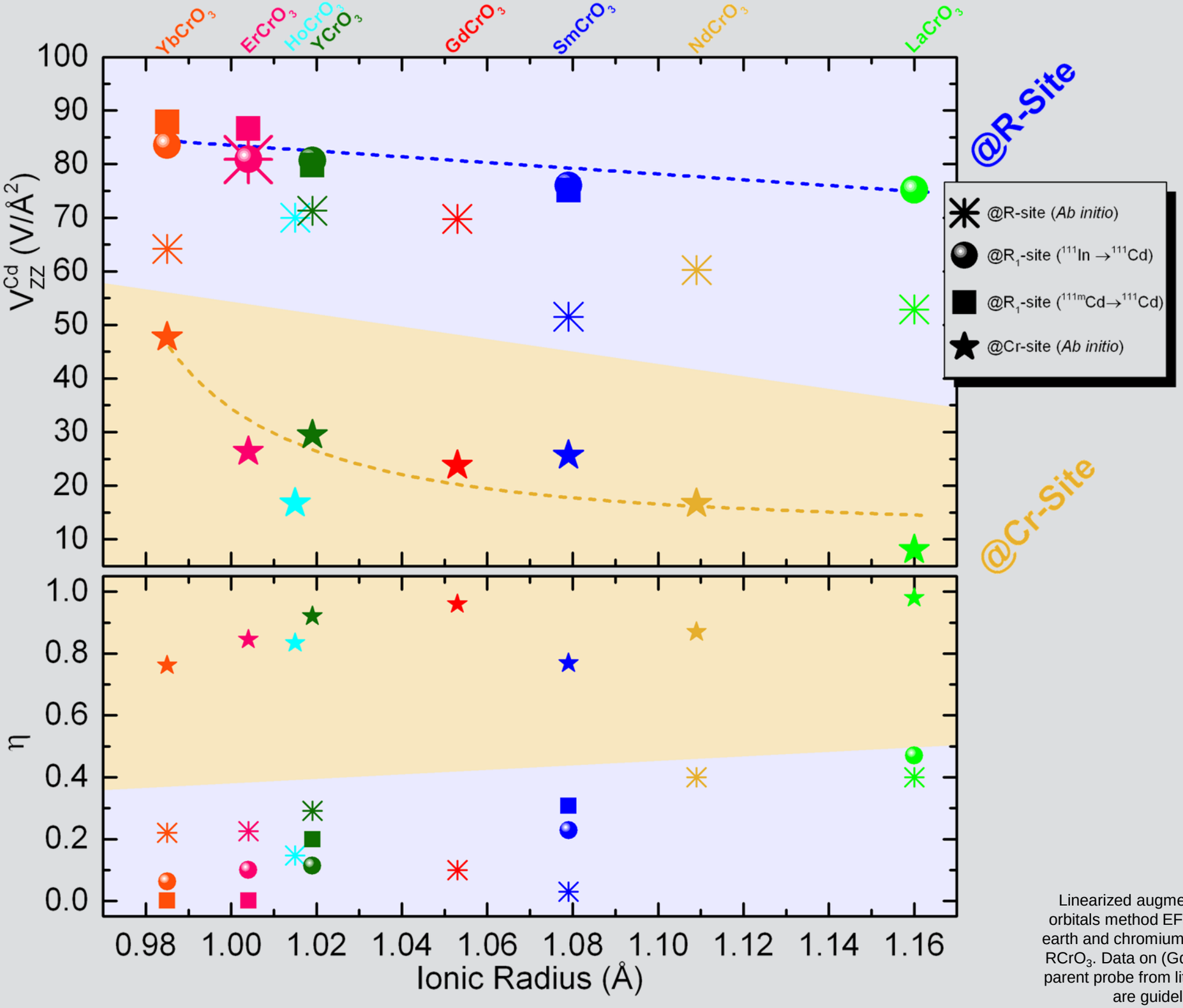

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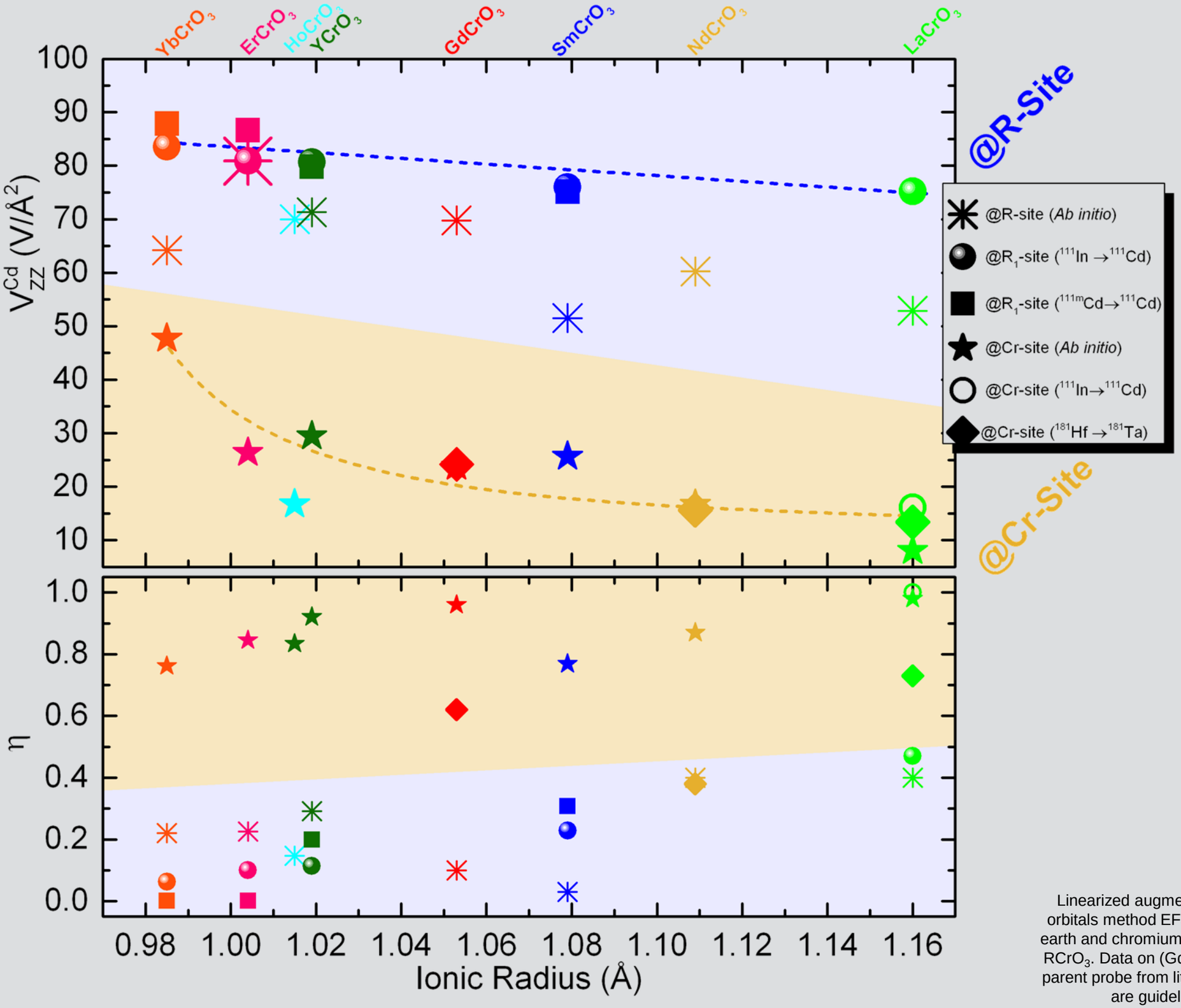

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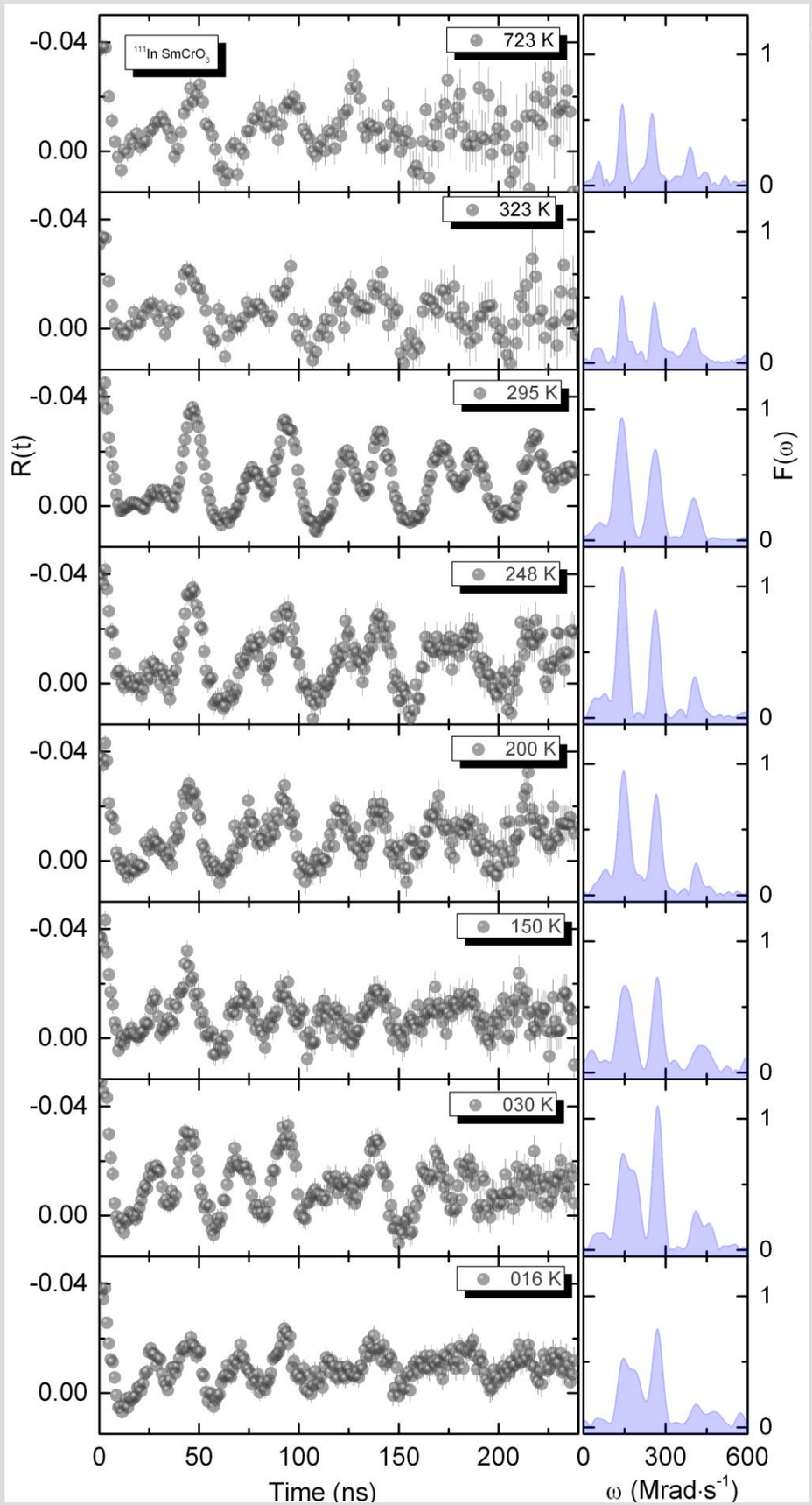
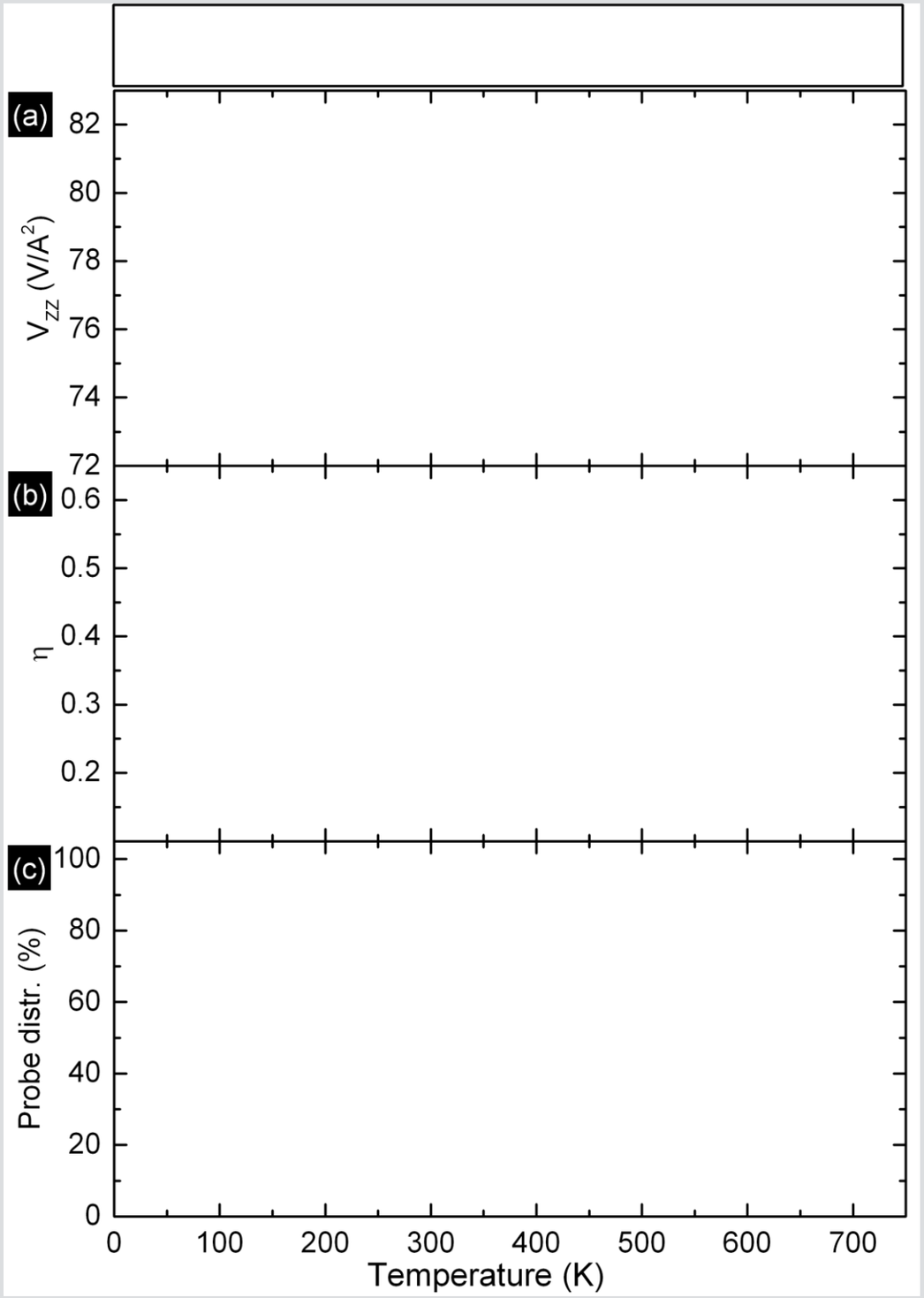
Local Probing in $SmCrO_3$



(a) Experimental electric field gradient principal component with ^{111}In for the $SmCrO_3$ sample. **(b)** Asymmetry parameter. **(c)** Probe distribution.



Representative R(t) functions, corresponding fits and respective Fourier transform taken at different temperatures for the ^{111}In probe in $SmCrO_3$.

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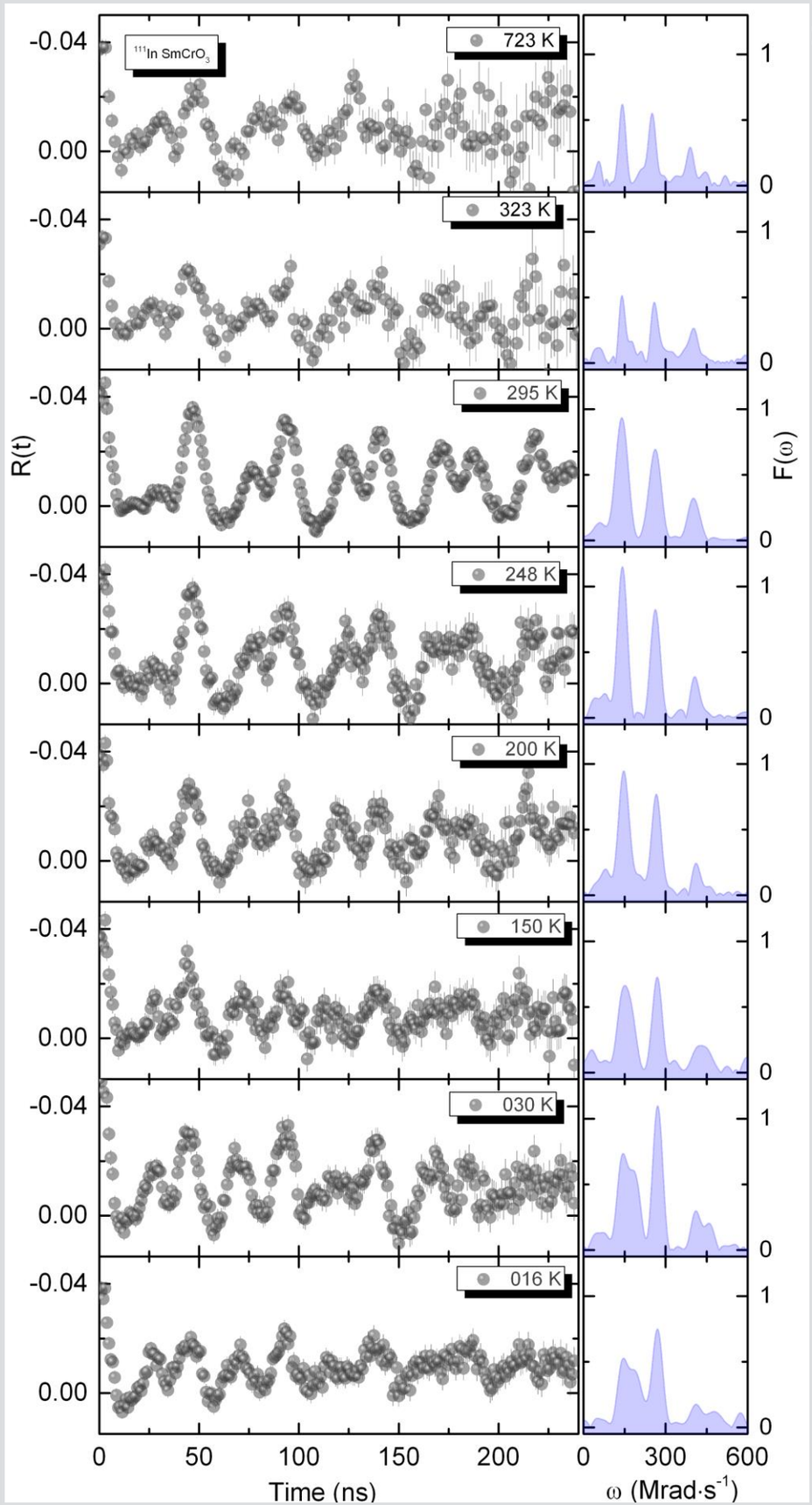

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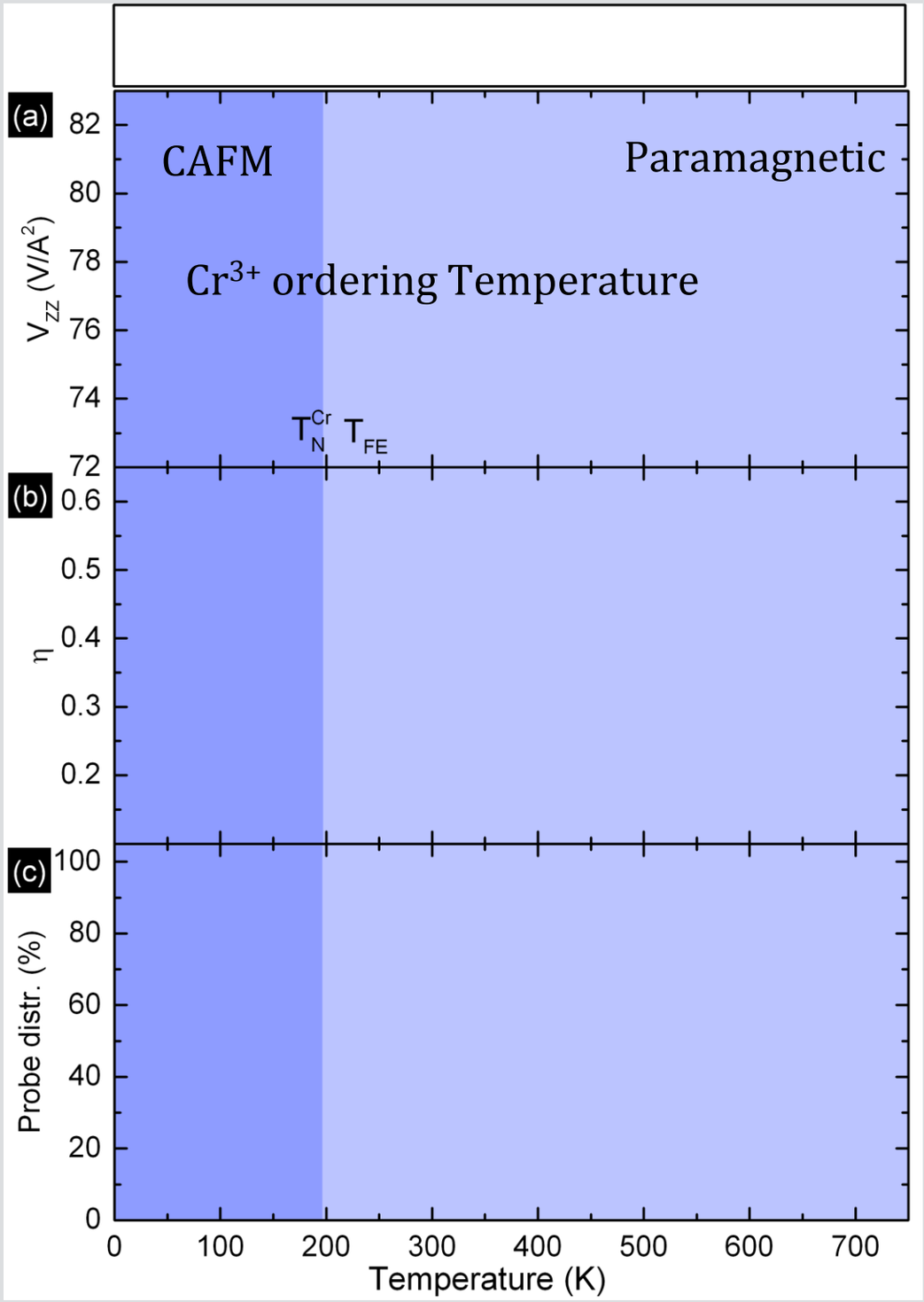

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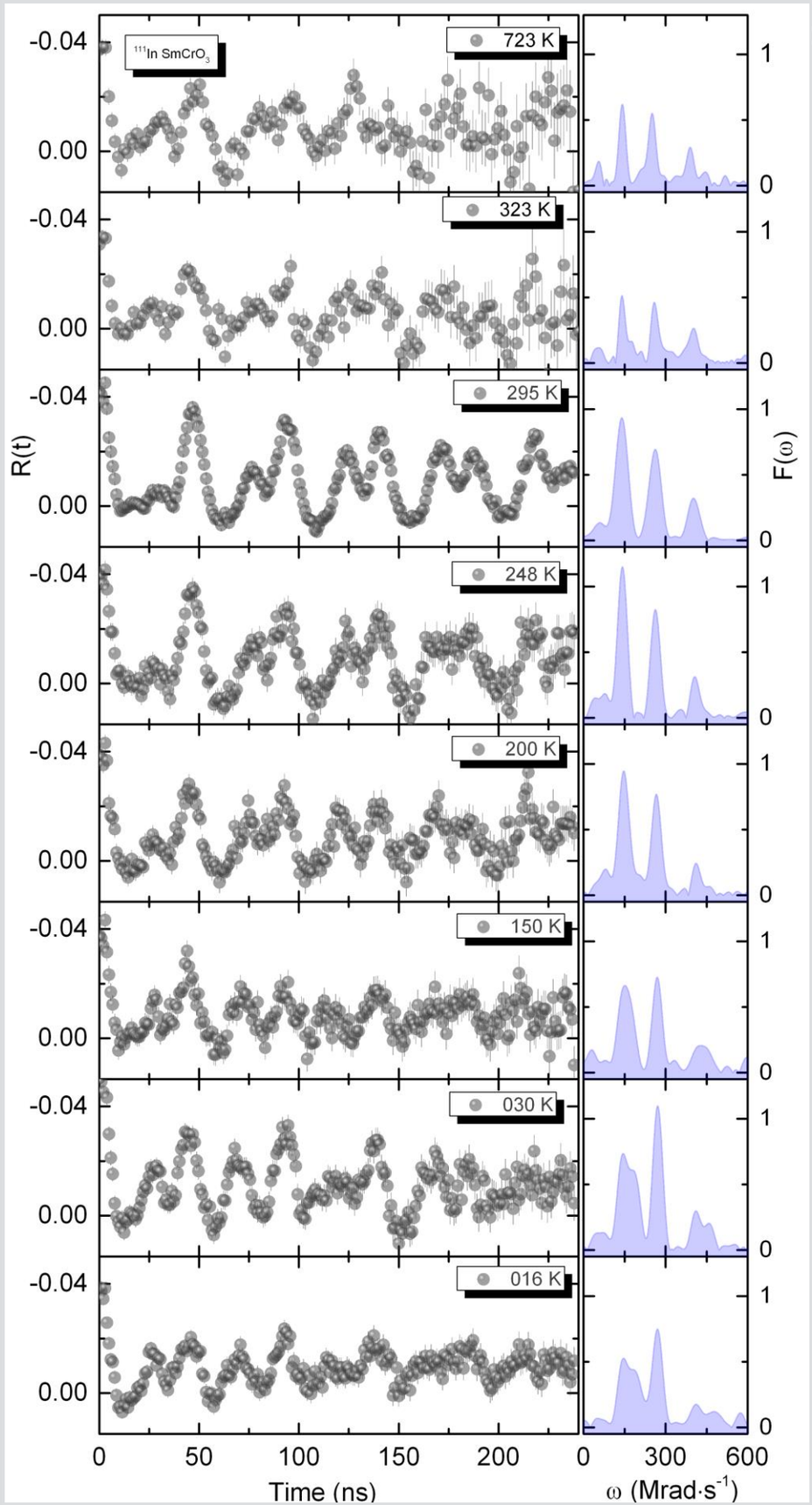

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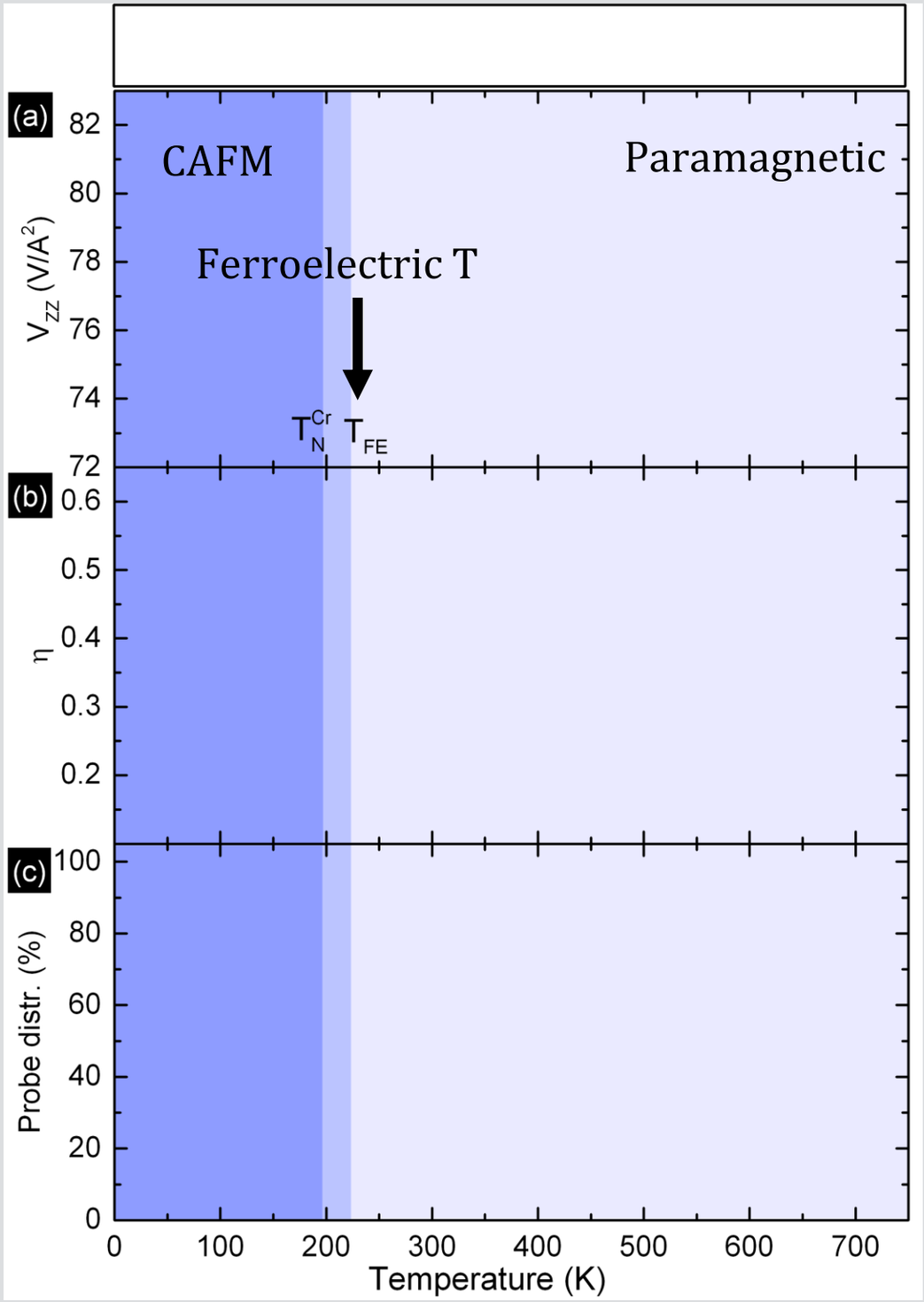

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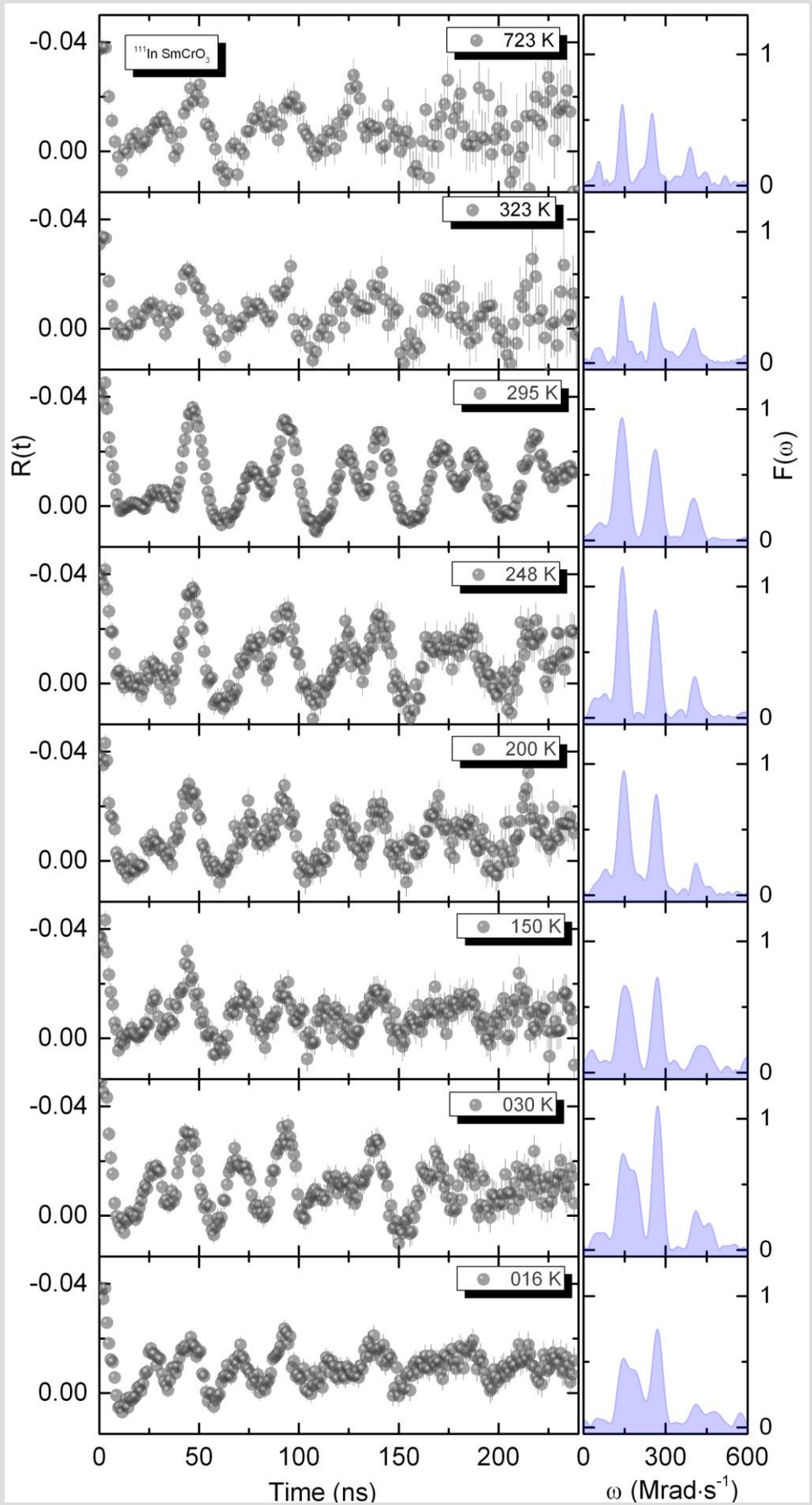

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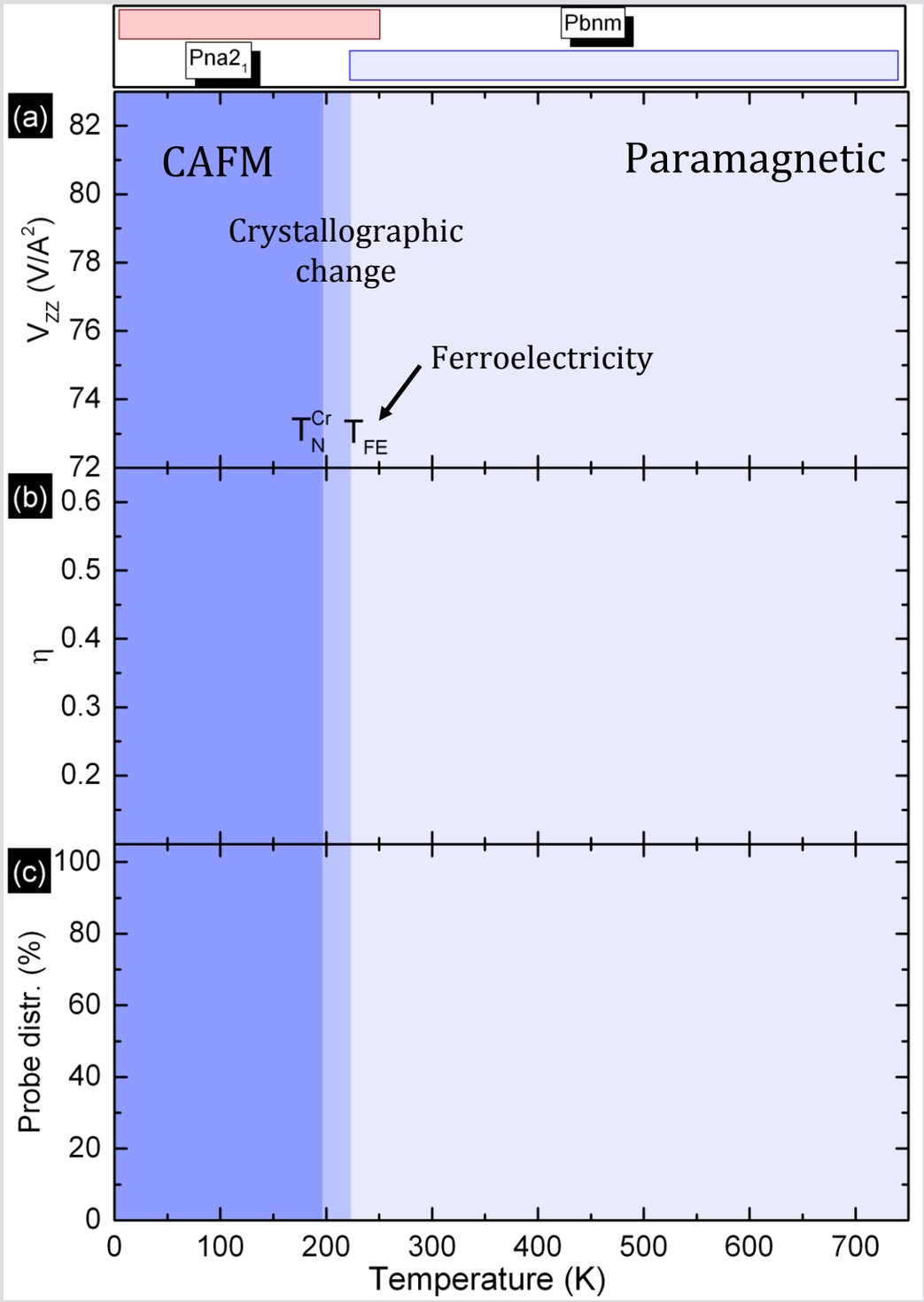

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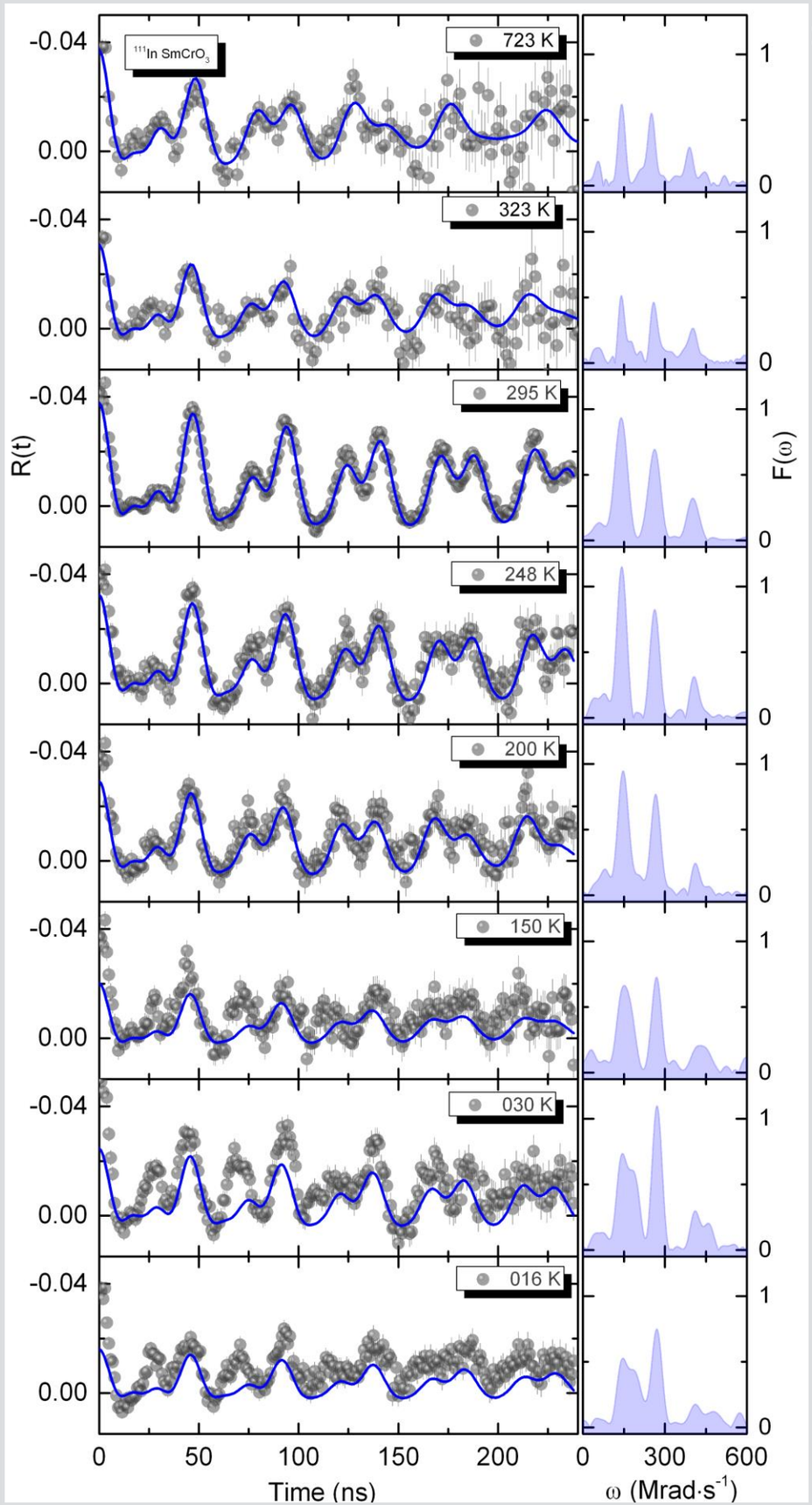

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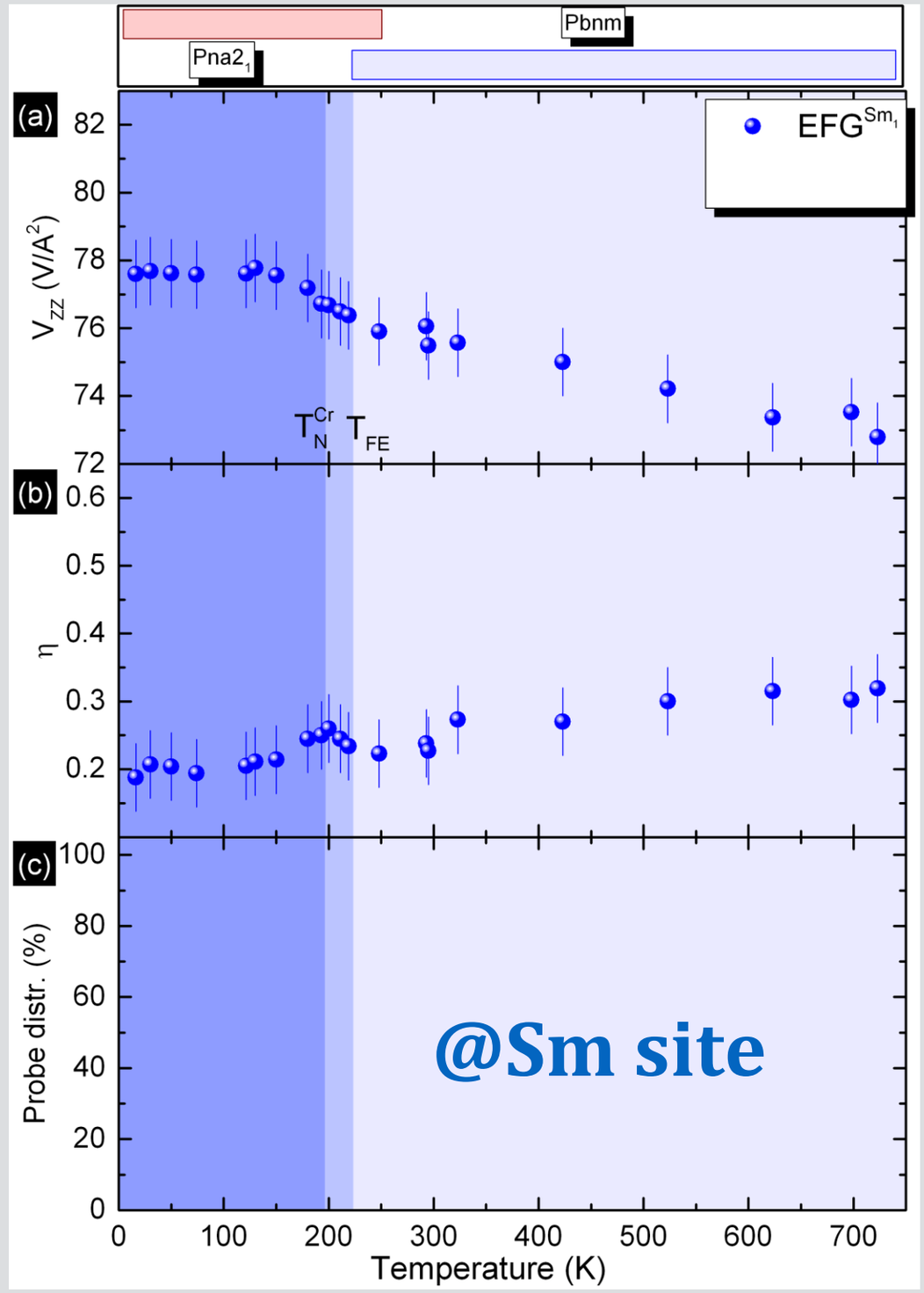

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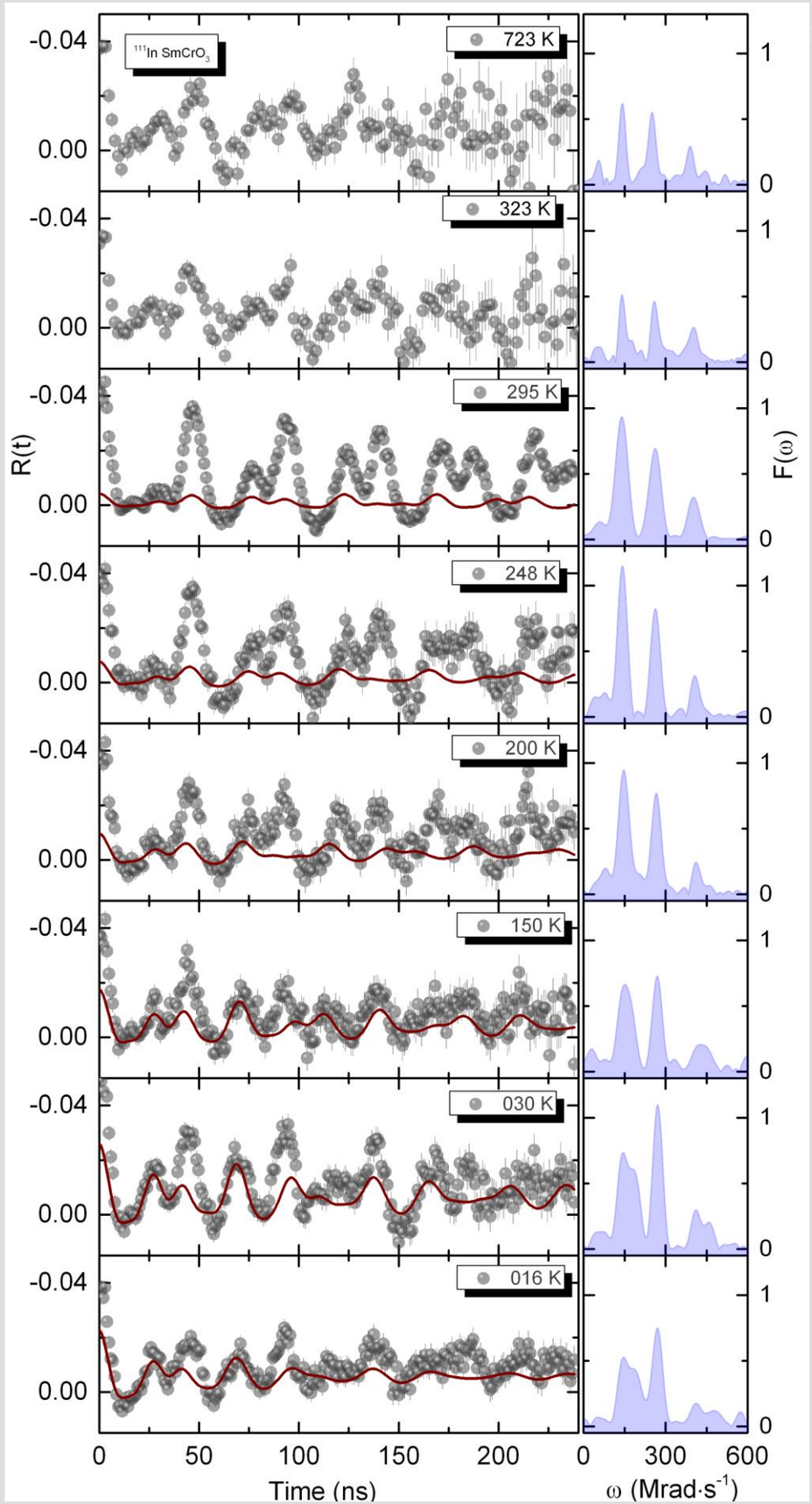

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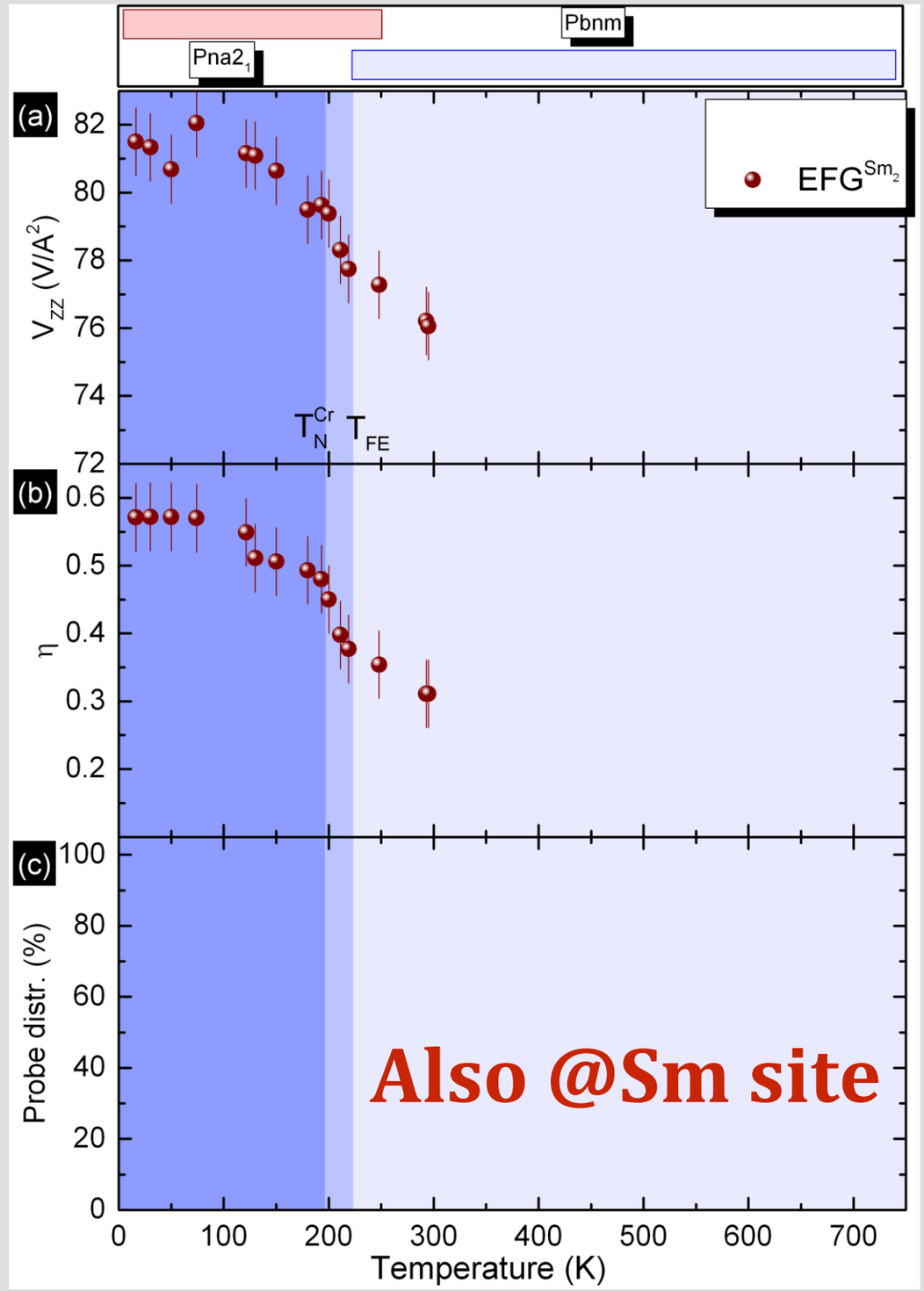

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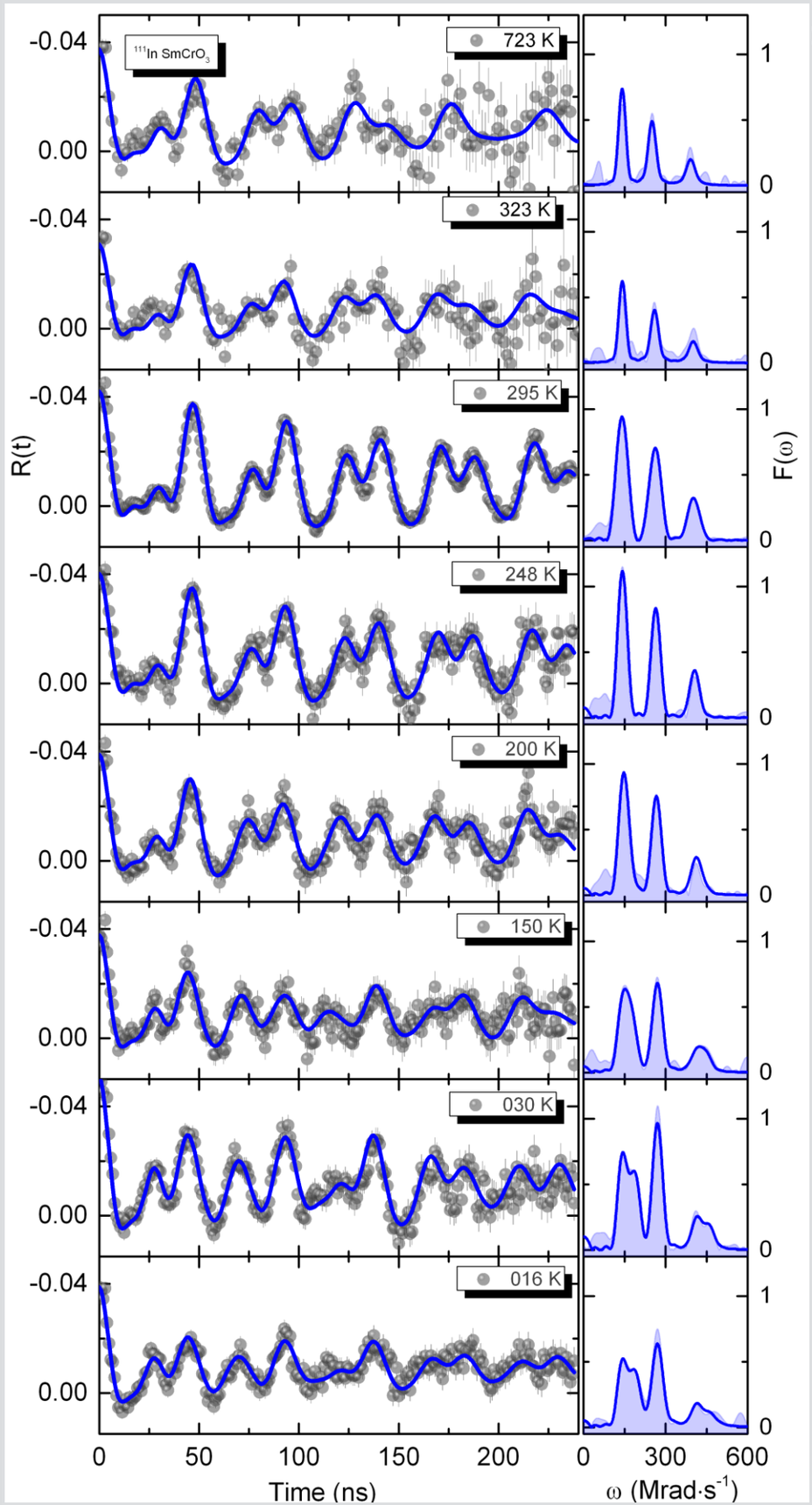

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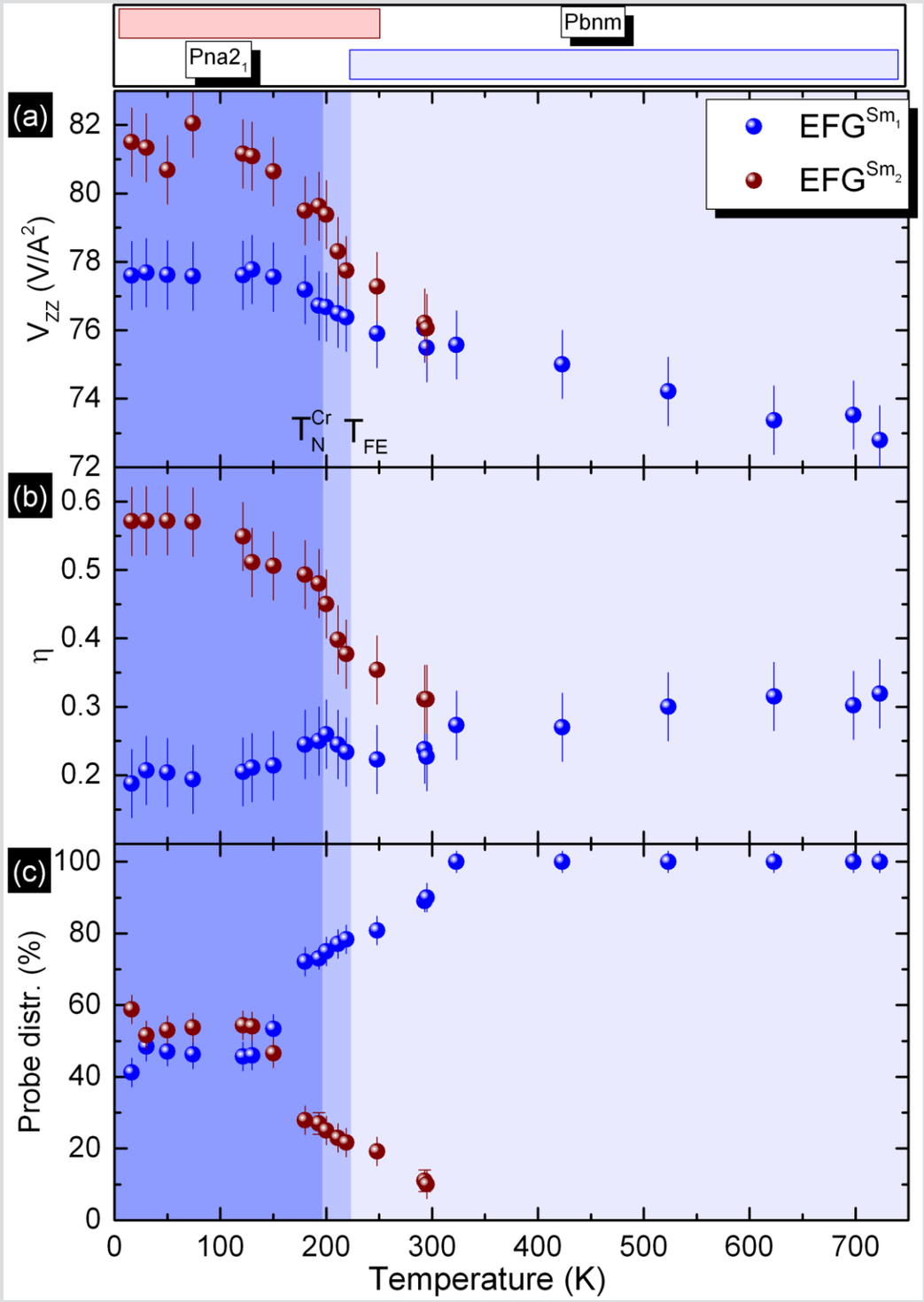

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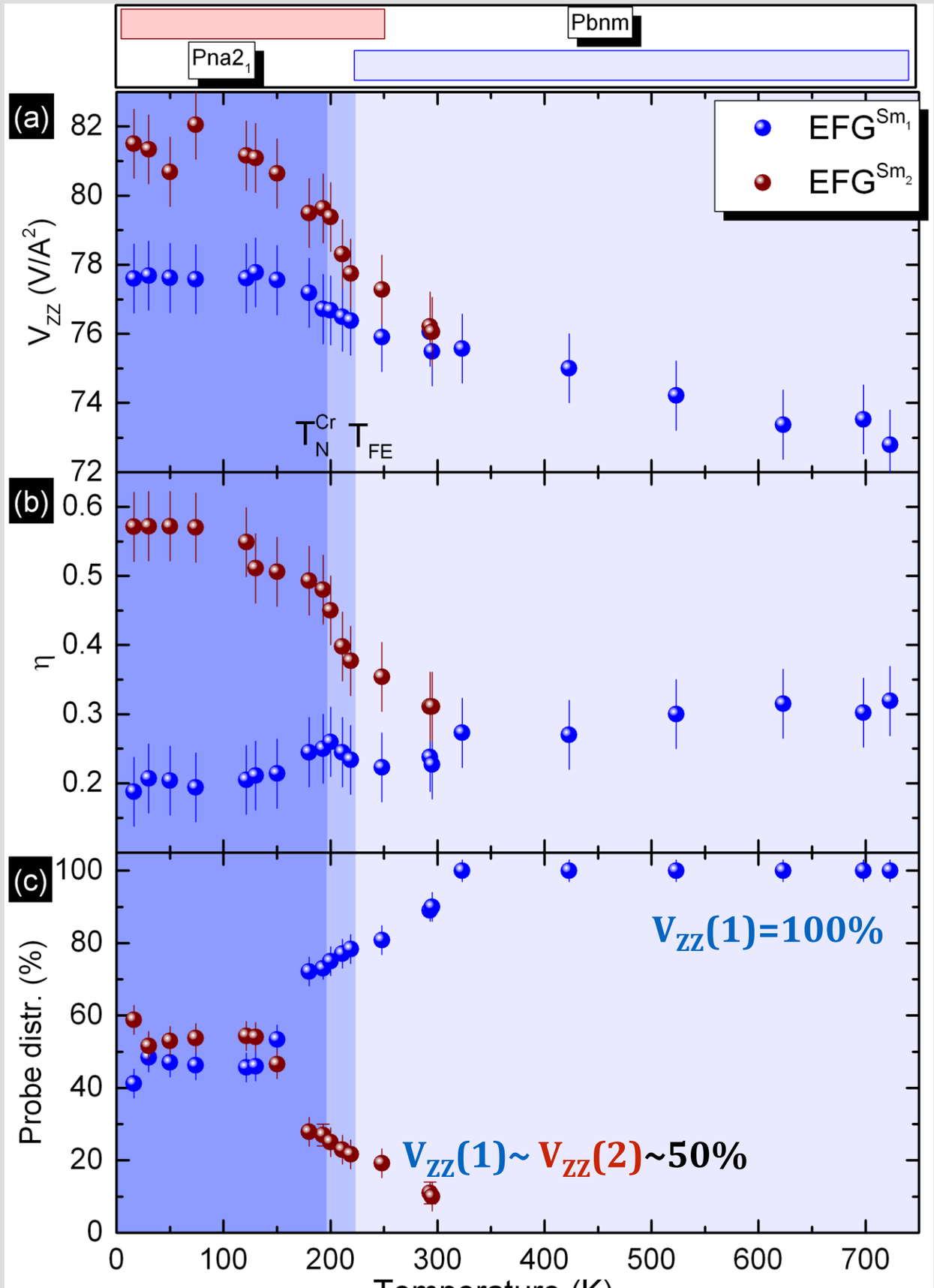

723K → 300K

1 Local Environment

Below 300K

2 Local Environments

Local inhomogeneous state emerges
Above T_{FE} and $T_N(Cr)$
Above crystallographic phase transition

$V_{ZZ}(1) \sim V_{ZZ}(2)$

$\eta(1) < \eta(2)$

regular and distorted environments (most probably polar and non polar states) coexist

Conclusions

Data compatible with the most recent reports, where polar octahedral rotations and/or cation displacements are at the origin of a polar order in the paramagnetic state

Our results point to a more subtle scenario, where locally an inhomogeneous state emerges. In this new state regular and distorted environments (most probably polar and non polar states) coexist.

Future work:

Local Probe studies in the other $RCrO_3$ systems

Use of different probes

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Thank You

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Any questions?