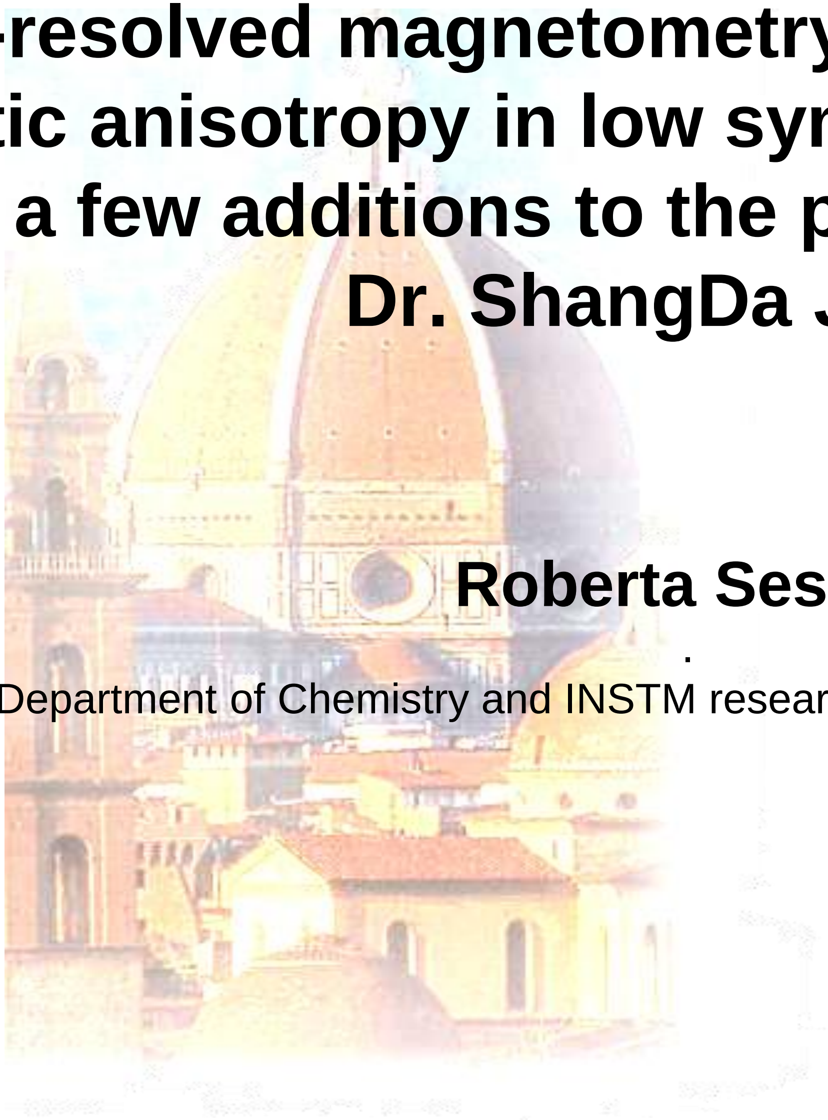
Angle-resolved magnetometry for determination of magnetic anisotropy in low symmetry environments: a few additions to the presentation of Dr. ShangDa Jiang



Roberta Sessoli

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Techniques for the determination of the magnetic anisotropy

Anisotropy parameters

•(HF-)EPR on powder

• Inelastic Neutron Scattering

•Magnetometry on powder

•Specific heat on powder

Anisotropy axes orientation

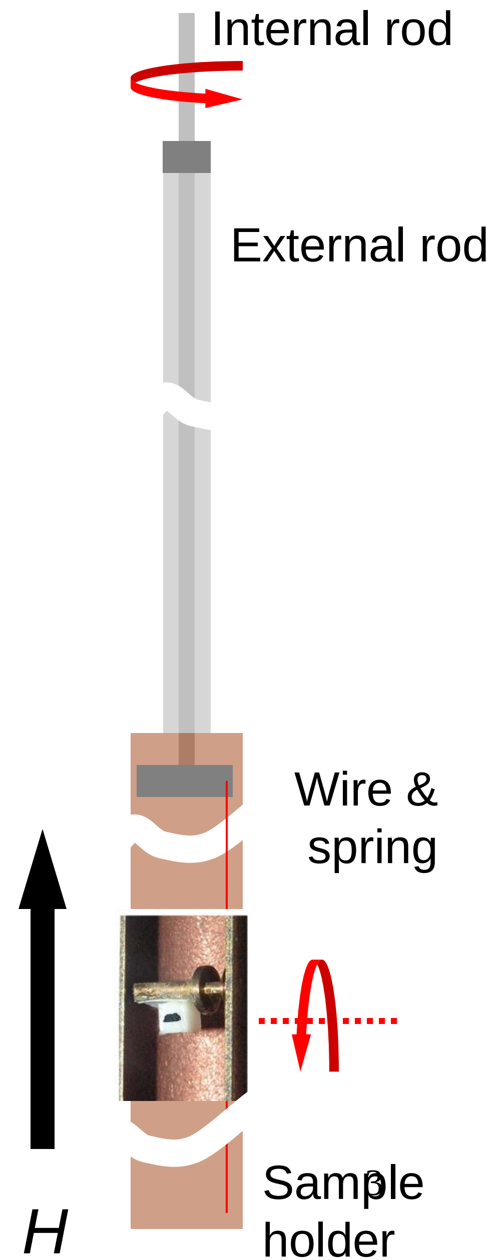
•(HF-)EPR on single crystal

•Torque Magnetometry

•Angle resolved magnetometry

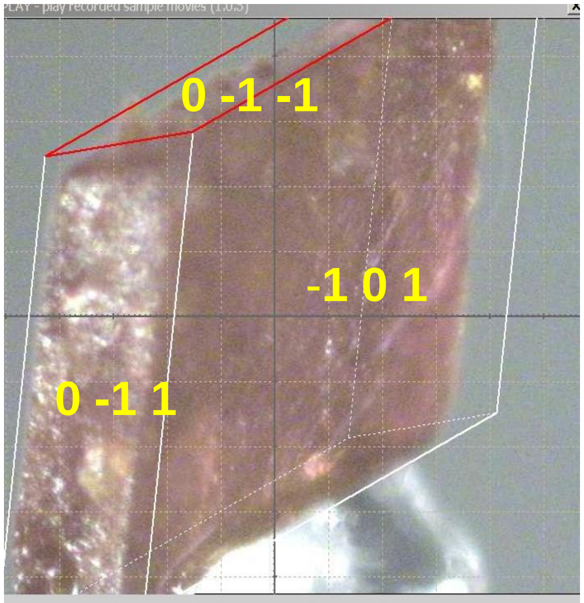
Angular resolved magnetometry: the rotator

An old technique revisited thanks to the automation & precision of horizontal sample rotator combined high sensitivity of modern SQUID magnetometers



Angular resolved magnetometry: the crystal

- 1st step: Accurate indexing of the faces

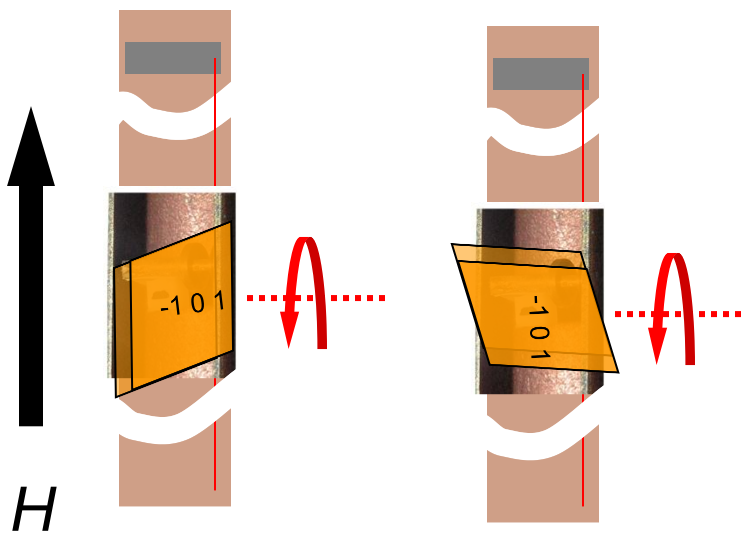


2nd step: Three rotations along orthogonal axes allow a full characterization of the magnetic anisotropy without *a priori* information

1°rot

2°rot

3°rot



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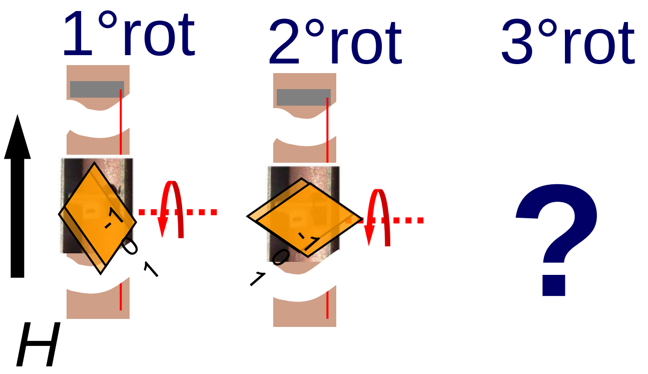
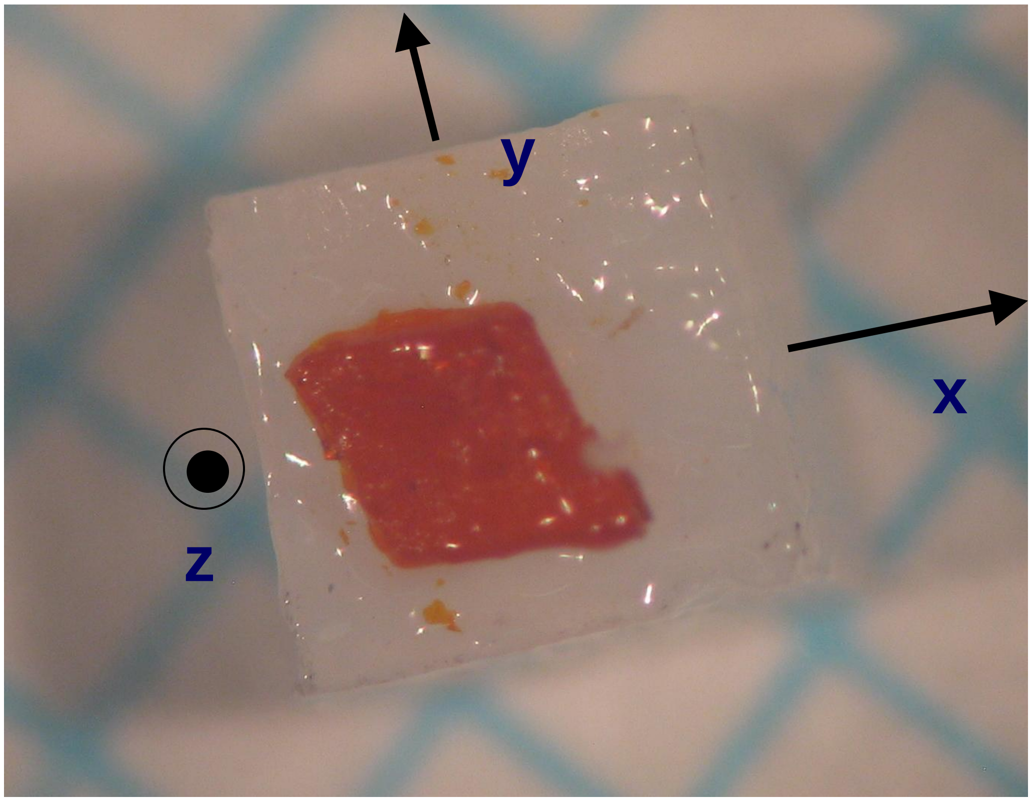
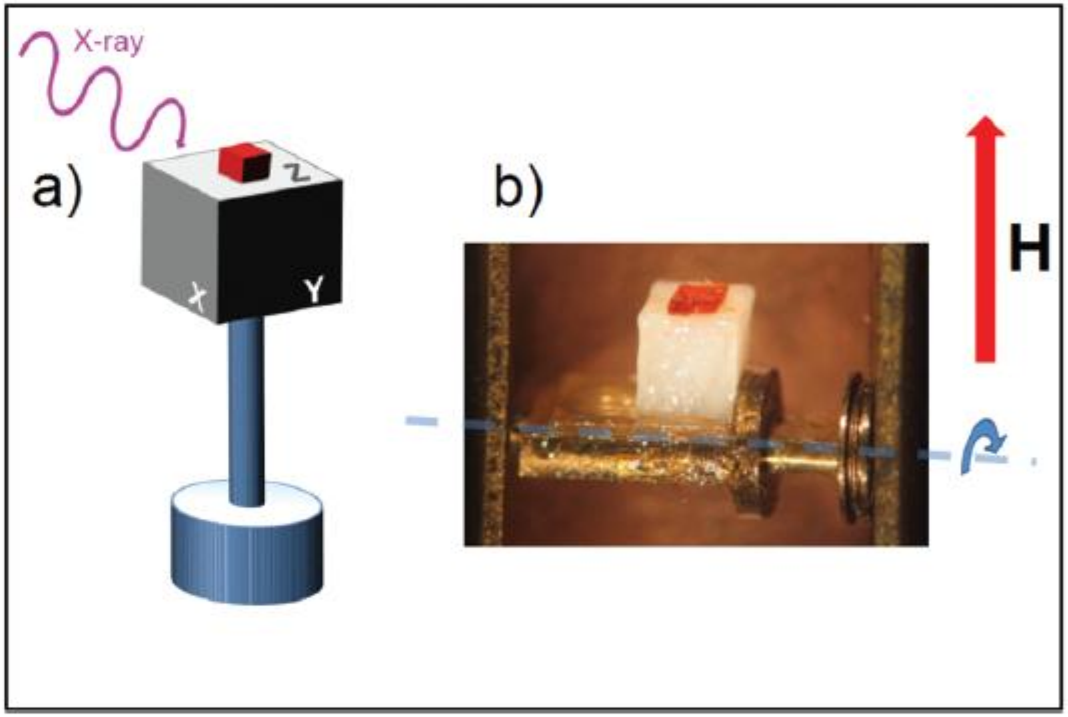
Angular resolved magnetometry: the support



A teflon cube

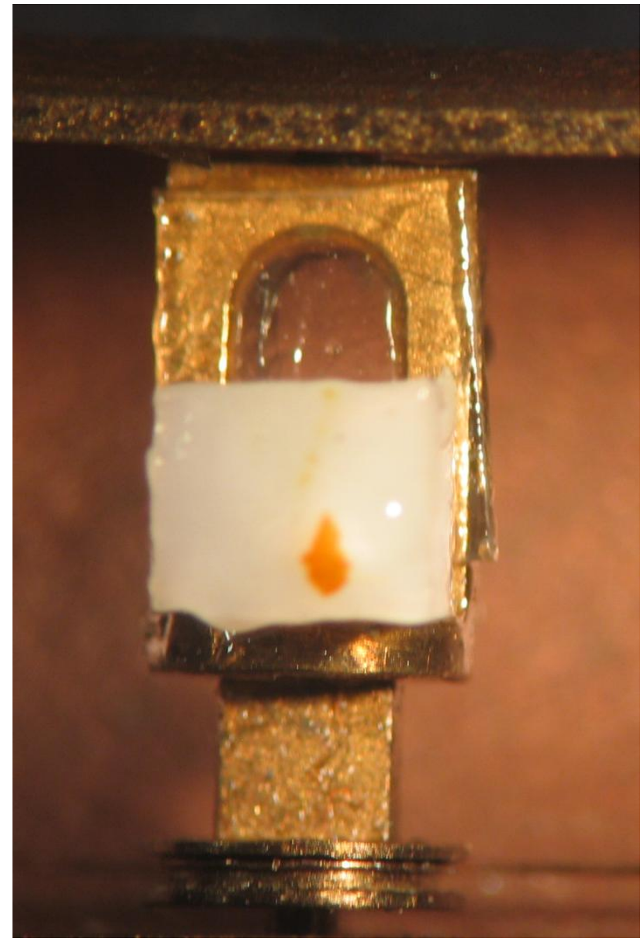


The laboratory reference frame



By indexing with a single crystal X-ray diffractometer the faces of the amorphous cube on which the crystal is glued, the laboratory reference frame is defined in the crystal lattice frame

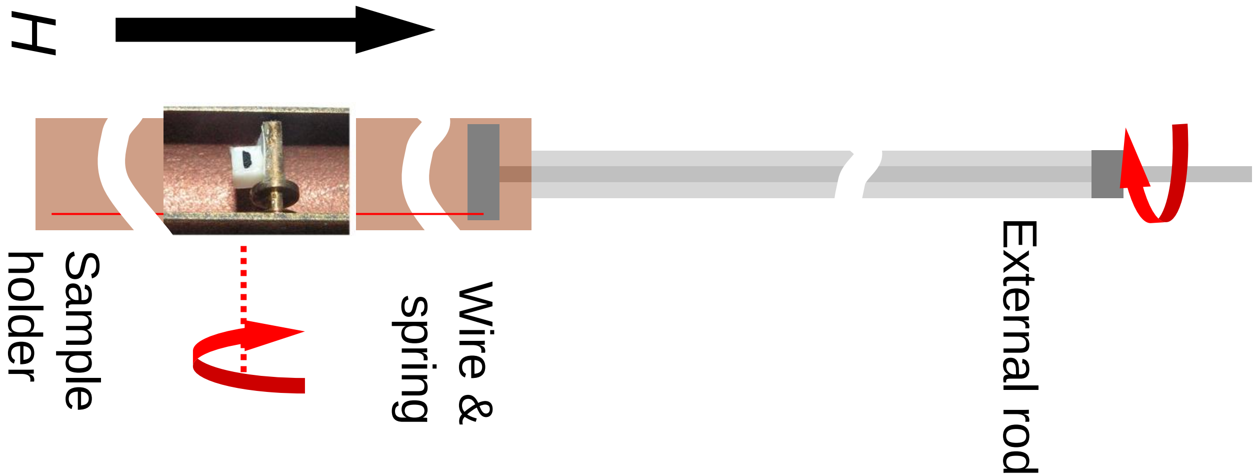
Angular resolved magnetometry: the support



© On-cube indexing of poorly defined or solvent loosing crystals

Procedures to avoid mistakes

The sign of each rotation has to be carefully checked

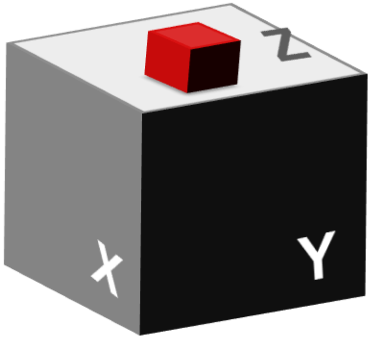


Rotation clockwise

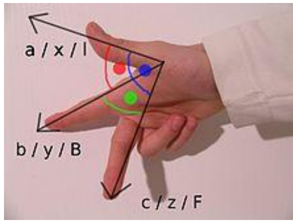
Rotation clockwise from the top = Increasing angles for QD machines

Suggested sequences of rotations

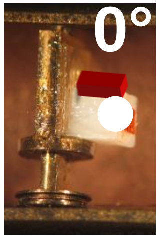
	0°	90°	180°	270°
Rot x	z	y	-z	-y
Rot y	z	-x	-z	x
Rot z	y	x	-y	-x



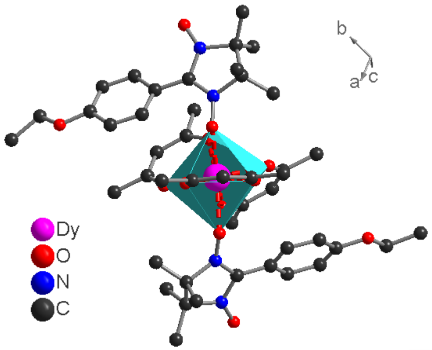
Choose a right reference frame for the cube and place the crystal on +z

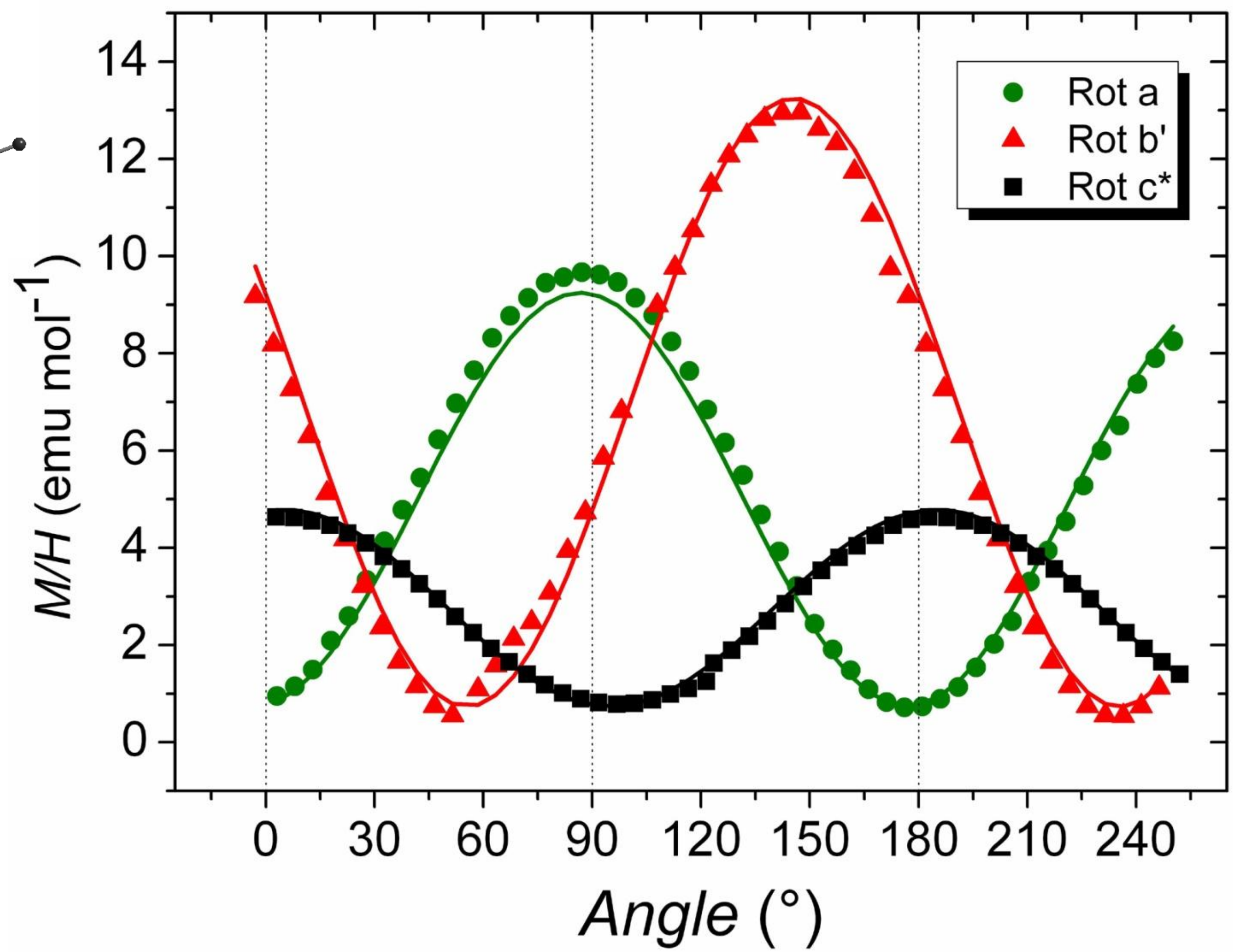


	0°	90°	180°	270°
X rot –z cube's face on the support	H//z	H//y	H//-zx	H//-yx
Y rot –z cube's face on the support	H//z	H//-x y	H//-zy	H//x y
Z rot –y cube's face on the support	H//y	H//x	H//-yz	H//-xz

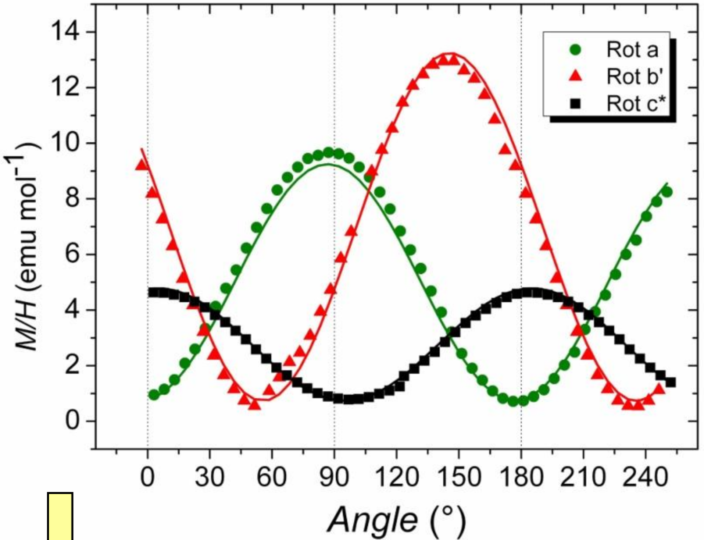


Characterization of the magnetic anisotropy of $Dy(hfac)_3(NITR)_2$





Characterization of the magnetic anisotropy of $Dy(hfac)_3(NITR)_2$



Experimental data are simulated assuming a simple tensorial relation

$$\vec{M} = \chi \cdot \vec{H}$$

and taking into account that only the component of M along H is measured

For each rotation :

$$M(\theta) = H(\chi_{\alpha\alpha}\cos^2(\theta) + 2\chi_{\alpha\beta}\cos(\theta)\sin(\theta) + \chi_{\beta\beta}\sin^2(\theta))$$

Where α, β are the cyclic permutation of the reference frame axes

$$\chi = \begin{pmatrix} 4.7599 & 0.3578 & -5.8439 \\ 0.3578 & 0.7758 & 0.4681 \\ -5.8439 & 0.4681 & 9.2236 \end{pmatrix}$$

Characterization of the magnetic anisotropy of $Dy(hfac)_3(NITR)_2$

Diagonalization of the susceptibility matrix

$$\chi' = \mathbf{R}^{-1} \cdot \chi \cdot \mathbf{R}$$

Provides us with the principal values of the susceptibility:

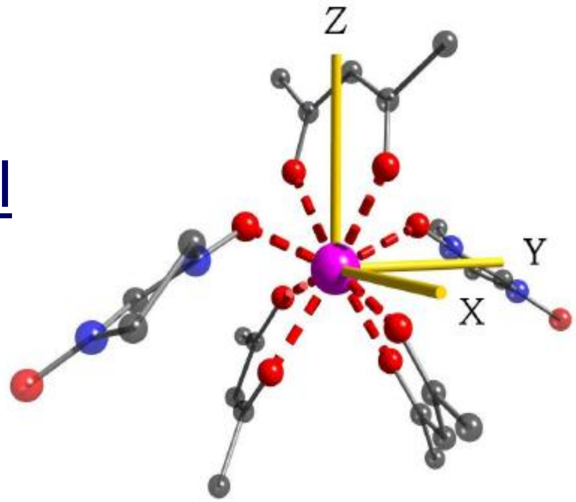
$$\chi = \begin{pmatrix} 4.7599 & 0.3578 & -5.8439 \\ 0.3578 & 0.7758 & 0.4681 \\ -5.8439 & 0.4681 & 9.2236 \end{pmatrix}$$

$\chi_x = 0.2 \pm 0.1\ \mathrm{emu \cdot K \cdot mol^{-1}}$

$\chi_y = 1.3 \pm 0.1\ \mathrm{emu \cdot K \cdot mol^{-1}}$

$\chi_z = 13.2 \pm 0.2\ \mathrm{emu \cdot K \cdot mol^{-1}}$

The eigenvector matrix R provides us with the principal directions of the magnetic anisotropy



Characterization of the magnetic anisotropy of $Dy(hfac)_3(NITR)_2$

Diagonalization of the susceptibility matrix

$$\chi' = \mathbf{R}^{-1} \cdot \chi \cdot \mathbf{R}$$

Provides us with the <u>principal values</u> of the susceptibility:

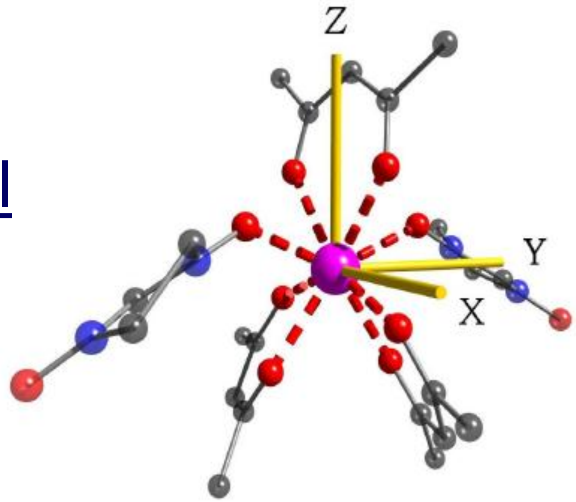
$$\chi = \begin{pmatrix} 4.7599 & 0.3578 & -5.8439 \\ 0.3578 & 0.7758 & 0.4681 \\ -5.8439 & 0.4681 & 9.2236 \end{pmatrix} \Rightarrow$$

$\chi_x = 0.2 \pm 0.1$ emu·K·mol^{-1}

$\chi_y = 1.3 \pm 0.1$ emu·K·mol^{-1}

$\chi_z = 13.2 \pm 0.2$ emu·K·mol^{-1}

The eigenvector matrix R provides us with the <u>principal directions</u> of the magnetic anisotropy



The non-linear case

The previous treatment to extract the susceptibility tensor assumes that it is of second rank and that the susceptibility does not depend on H

The last assumption is often not valid because of:

- **saturation**
- **antiferromagnetic interactions overcome by the magnetic field**

A more complex analysis, no more model-free, is necessary

A case study: a spin-canted Dy(III) Single Chain Magnet

Characterization of the magnetic anisotropy of $Dy(hfac)_3(NITR)_2$

- **Magnetometry is NOT a LOCAL probe**

- **It averages over all the species in the crystal**

- **Triclinic crystals have one magnetically independent site and are ideal candidates for this technique**

- **In monoclinic system <u>b</u> is a principal axis**

- **In orthorombic system <u>a</u>, <u>b</u>, and <u>c</u> are principal axes**

A noon triclinic case: the Cp*ErCOT SMM

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An Organometallic Single-Ion Magnet

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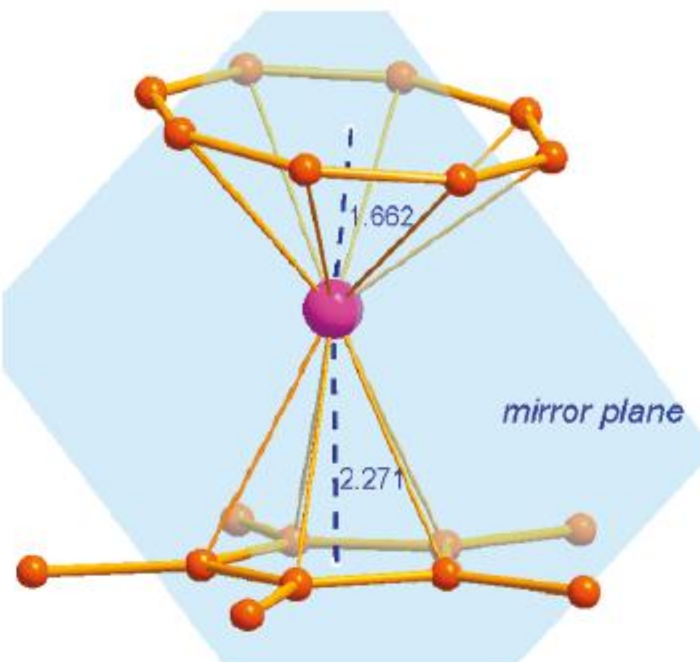
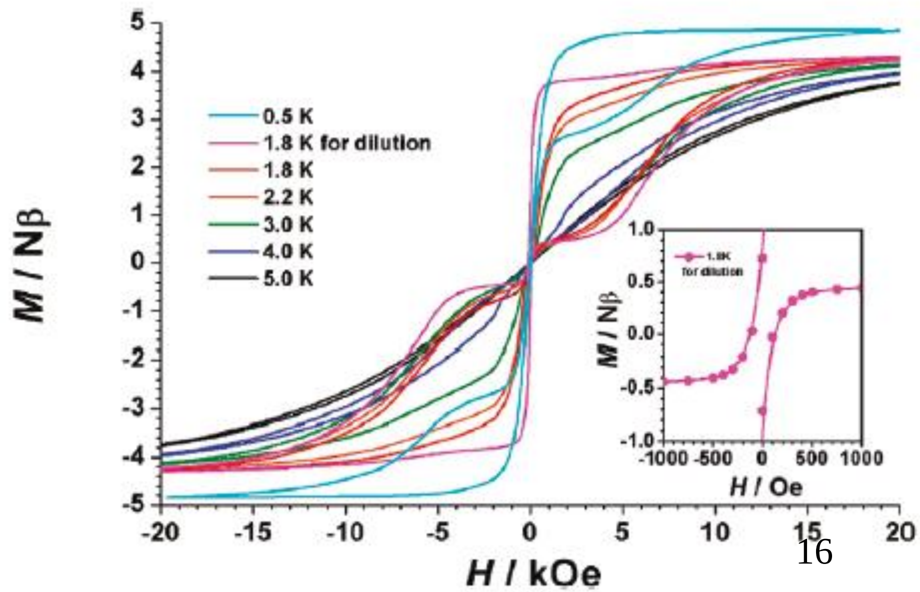
S Supporting Information

Very air sensitive !!





The Cp*ErCOT case

CHEMISTRY
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FULL PAPER

DOI: 10.1002/chem.201302600

Angular-Resolved Magnetometry Beyond Triclinic Crystals: Out-of-Equilibrium Studies of Cp*ErCOT Single-Molecule Magnet**

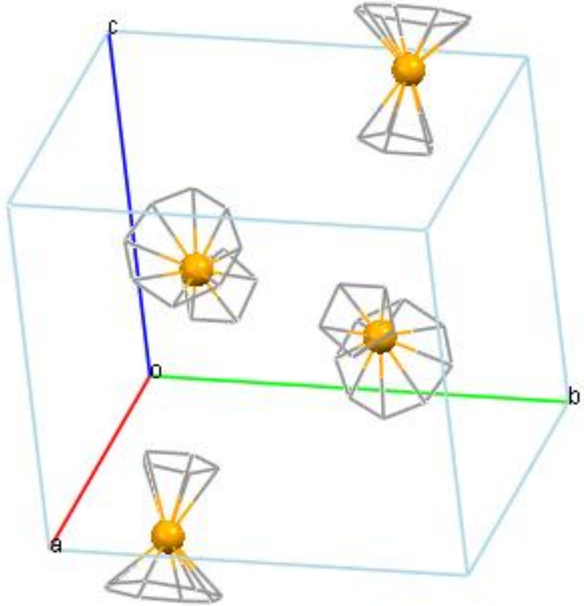
Marie-Emmanuelle Boulon,[a] Giuseppe Cucinotta,[a] Shan-Shan Liu,[b] Shang-Da Jiang,[b] Liviu Ungur,[c] Liviu F. Chibotaru,[c] Song Gao,[b] and Roberta Sessoli*[a]

The Cp*ErCOT case: an orthorombic crystal

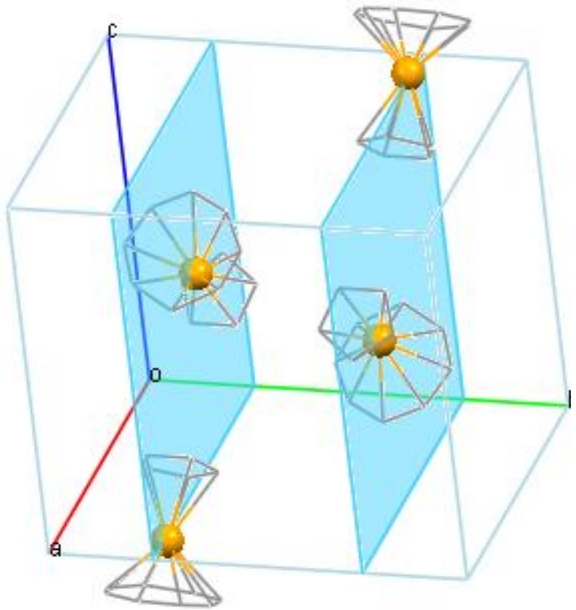
$C_{18}H_{23}Er$ *Pnma*	a = 10.2662(8)Å
	b = 13.3052(13)Å
	c = 11.8298(11)Å

Orthorhombic system: 2 orientations

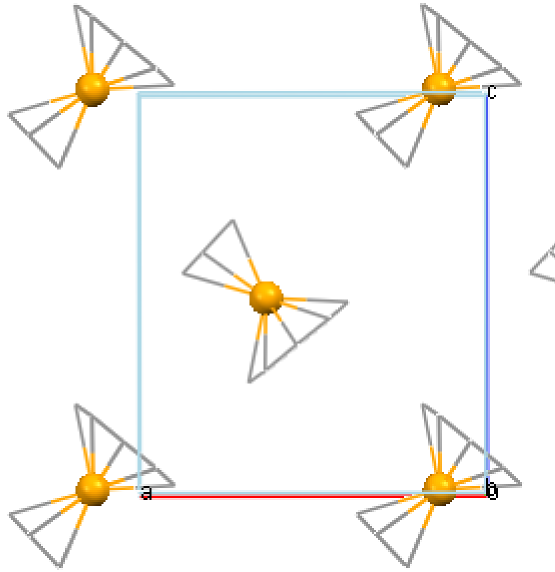
Unit cell view



Mirror planes // to (ac) plane



Along b-axis view



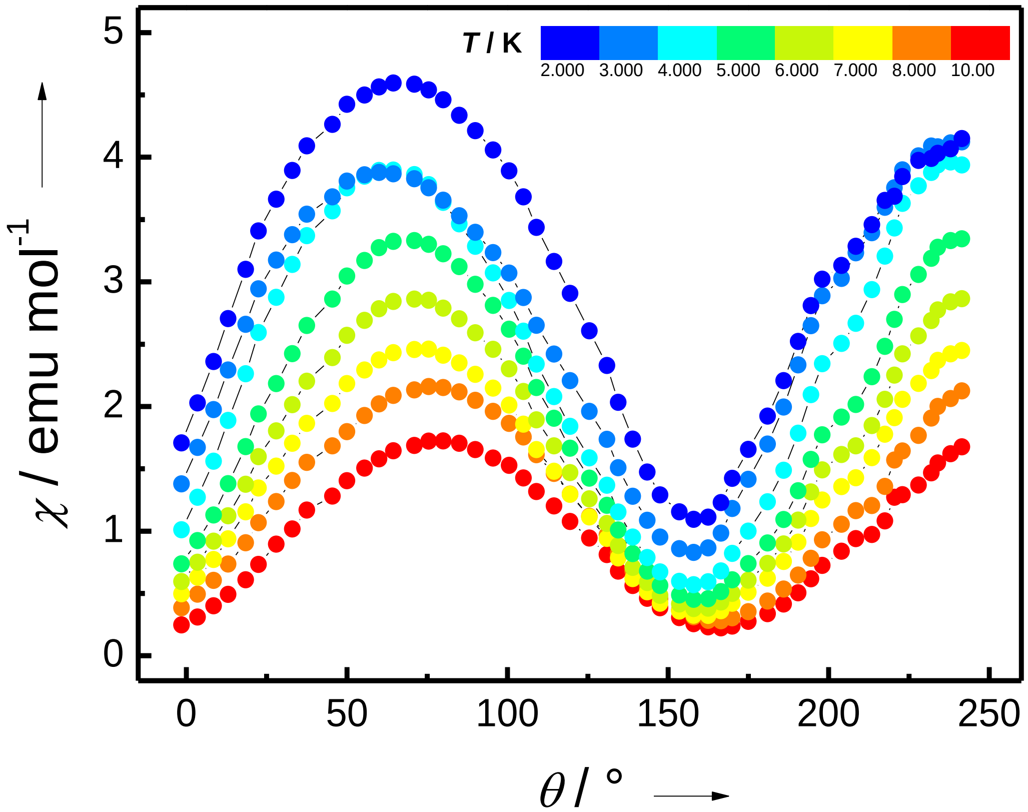
Molecules lie on mirror planes

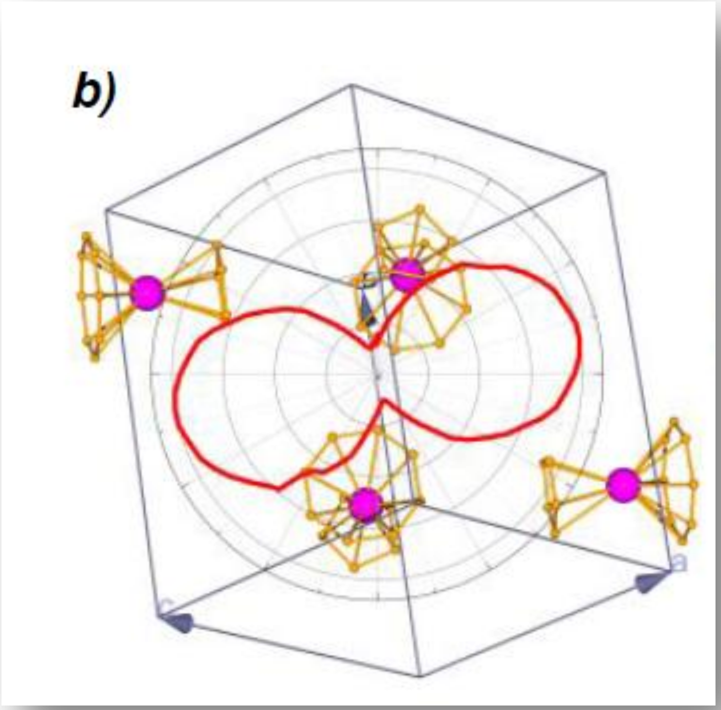
Angle between molecular pseudo-axis ~ 95°

The Cp*ErCOT case

Difficult manipulation of the crystal in the glovebox:

<u>Rotation 1</u> along $\omega_1 = 0.614004a - 0.340304b + 0.712175c$

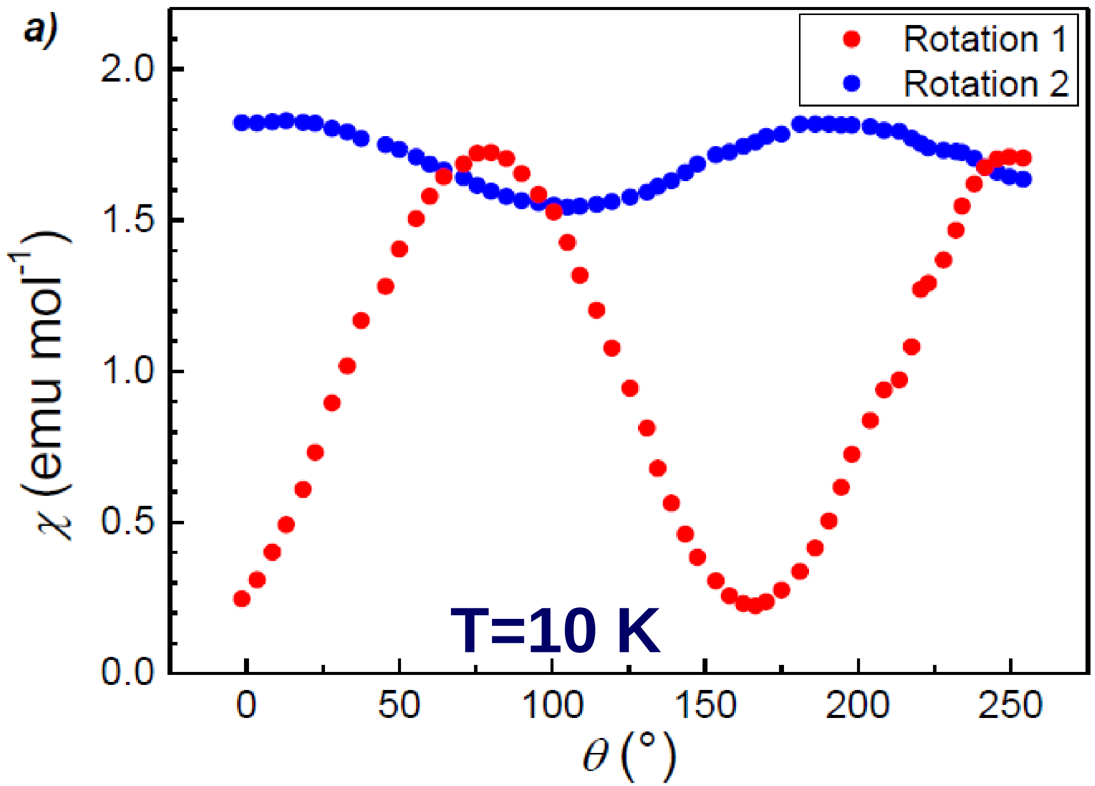


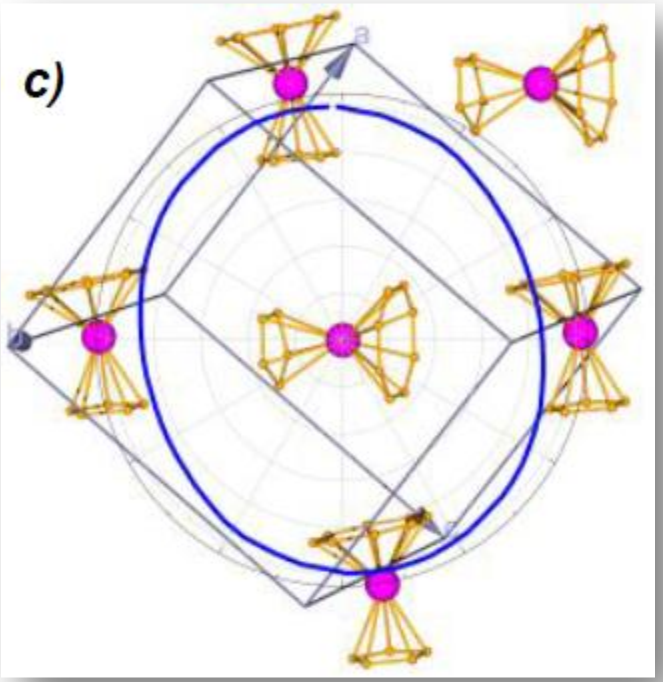


The Cp*ErCOT case

Difficult manipulation of the crystal in the glovebox:

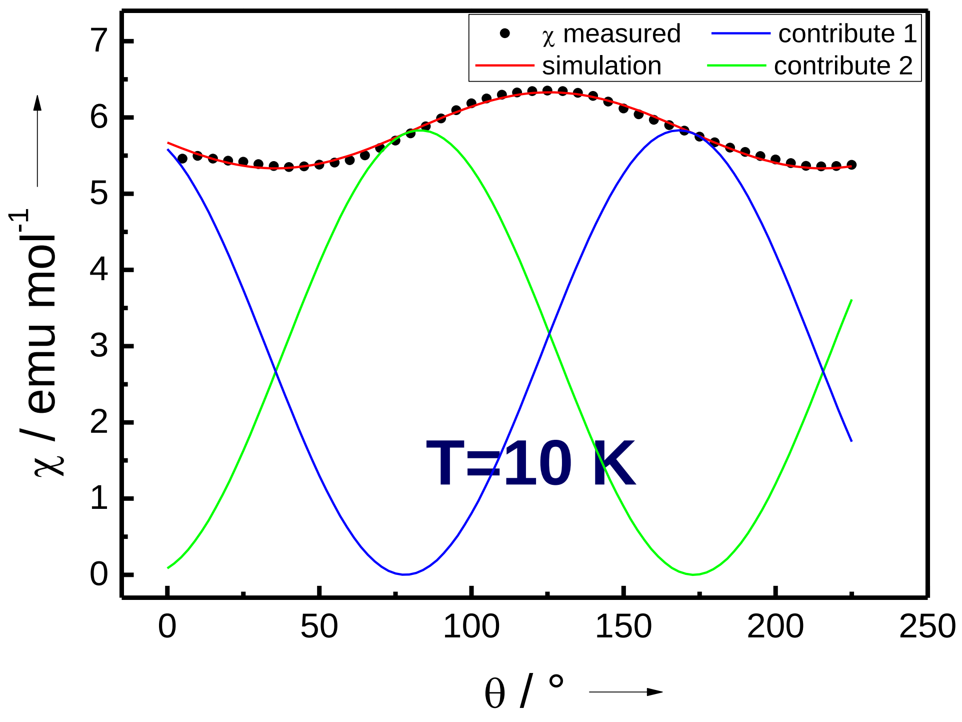
<u>Rotation</u> 2: along ω_2= 0.317728*a* + 0.931653*b* + 0.176271*c*

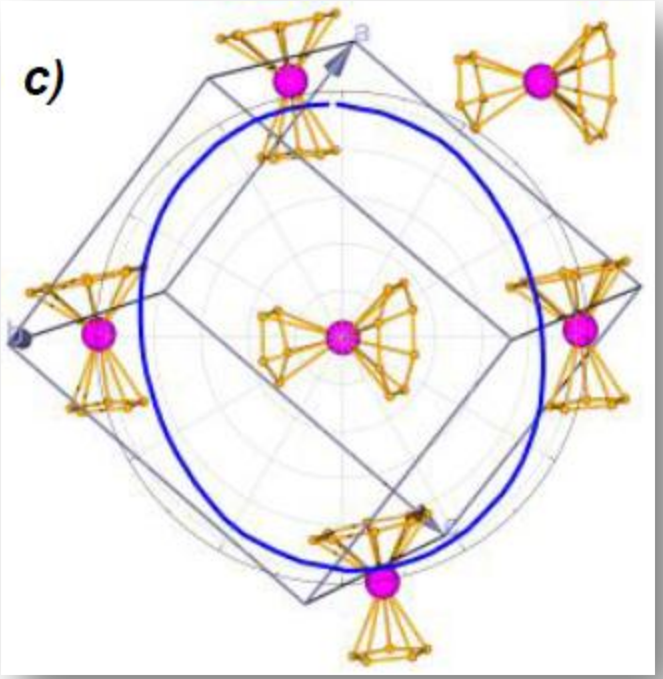




Simulation with two Ising contributions

Rotation 2: along ω_2= 0.317728a + 0.931653b + 0.176271c



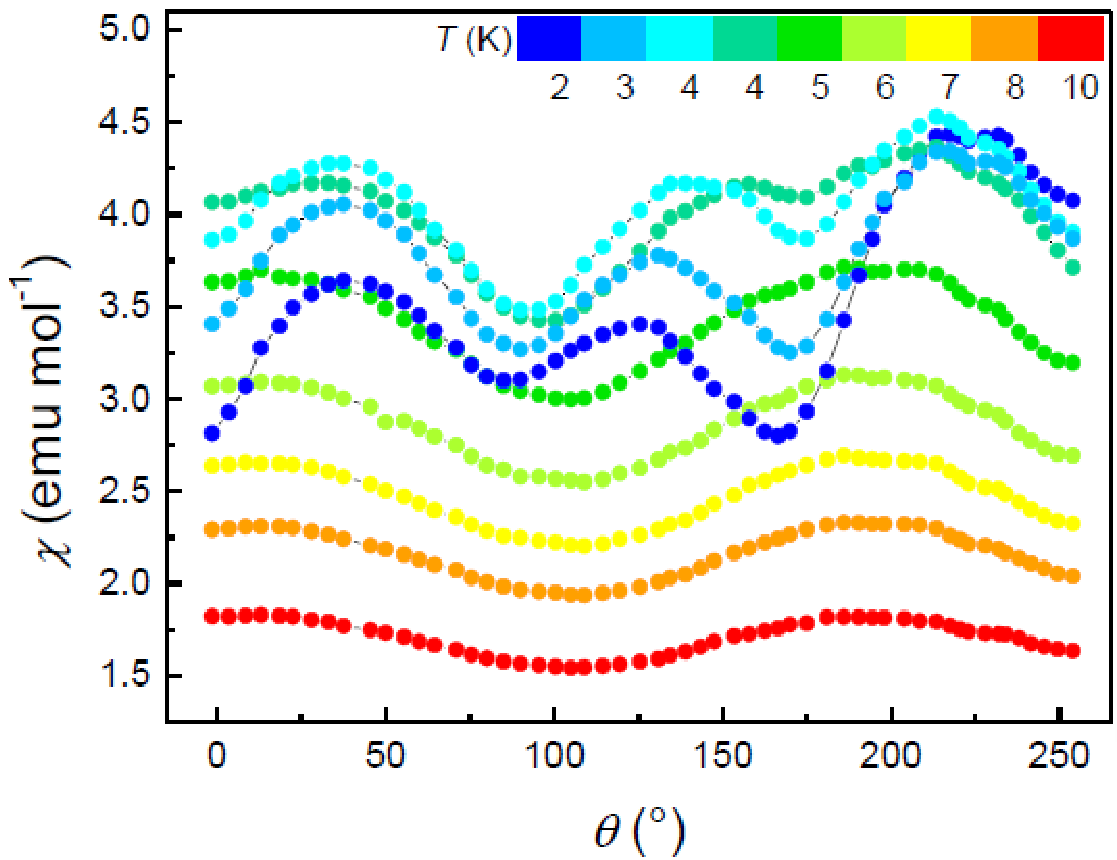


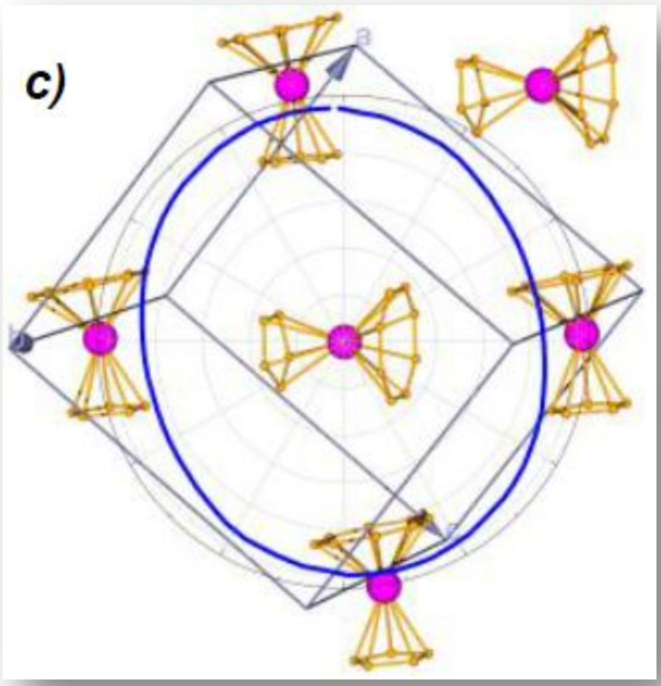
This interpretation is not unique: how to verify it?

The Cp*ErCOT case

Temperature dependence of the angular resolved magnetization shows additional peaks at low temperature

<u>Rotation</u> 2: along ω_2= 0.317728*a* + 0.931653*b* + 0.176271*c*

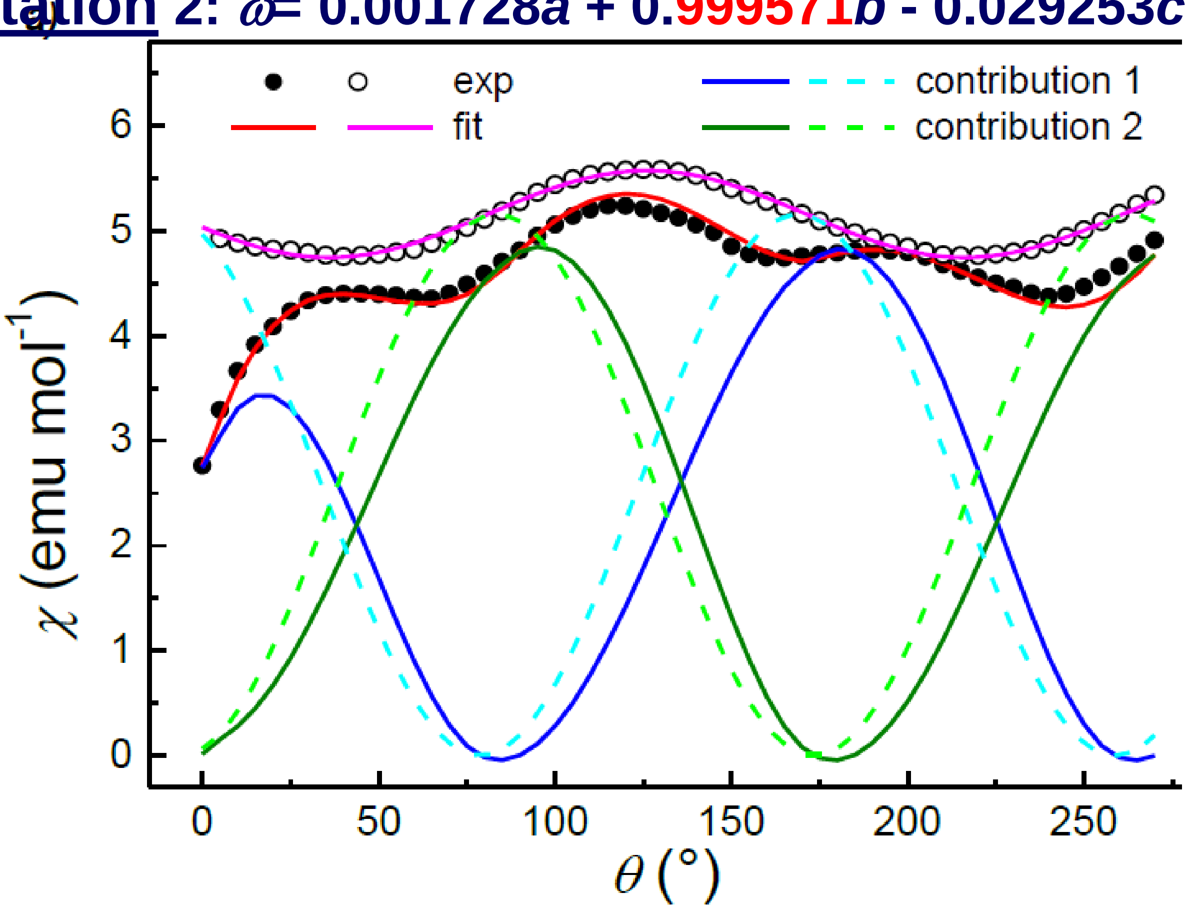




Out of equilibrium measurements

At T=4 K the butterfly hysteresis of this SMM is open and data are taken at different rotation rate of the field.
For long waiting time the sinusoidal behavior is restored

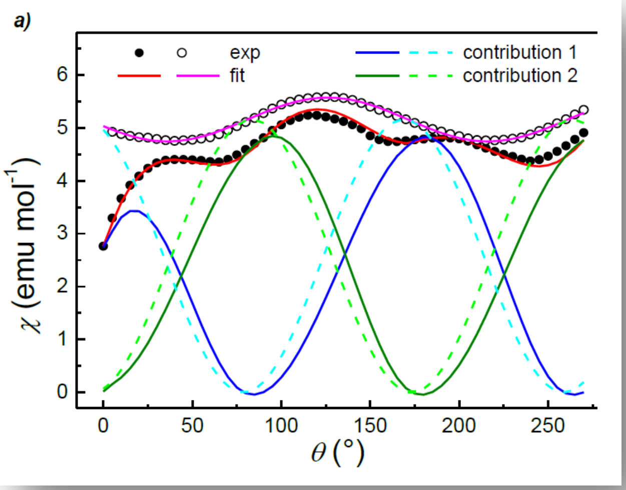
<u>Rotation</u> 2: ω= 0.001728*a* + 0.999571*b* - 0.029253*c*



2500 s ∀ angle

50 s ∀ angle

Out of equilibrium measurements



Simulation of out of equilibrium M

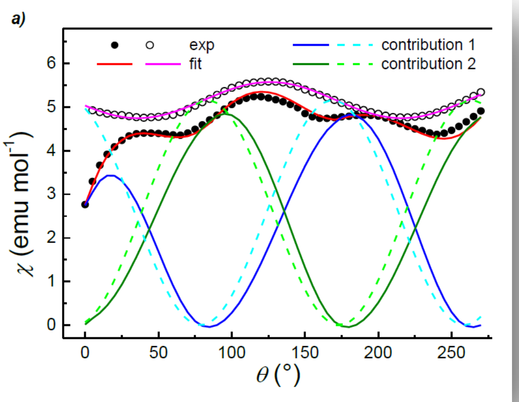
$$M(\theta, i) = M_{eq}(\theta, i) + \Delta M_i e^{-\frac{\sigma_i}{\tau_j(H)}}$$

H is constant but θ changes, thus M_{eq} changes with θ
σ Is the time elapsed between rotation and measurement

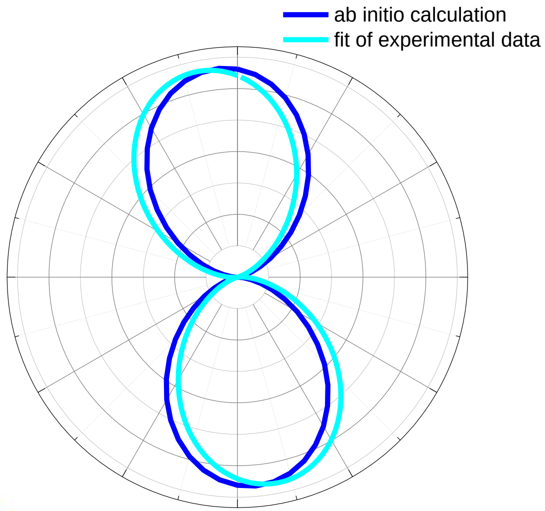
Best simulation obtained for: $\tau = \tau_0 + A\,H\,|\cos(\theta)|$

With τ_0=105(5)s, A=0.210 s Oe^{-1} increasing fields
A=0.140 s Oe^{-1} decreasing fields

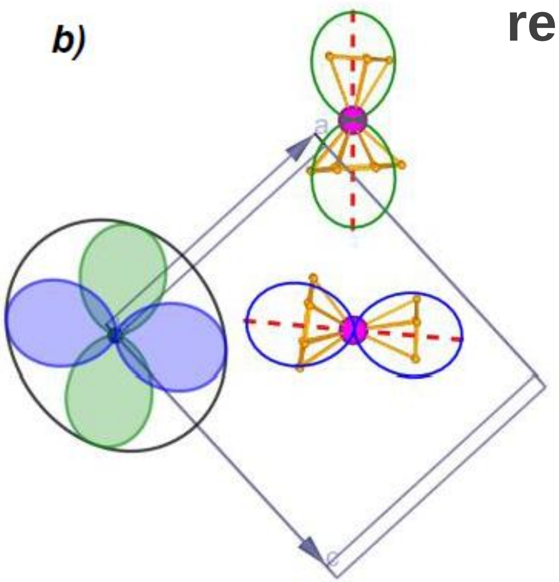
Comparison with ab-initio estimation



Ab initio Theory provides the answer



Rotation data are reproduced with two Ising contributions but a problem remains:



Who Is who ?