Preformed magnetic clusters in the paramagnetic phase of a high-temperature ferromagnetic metal-organic framework

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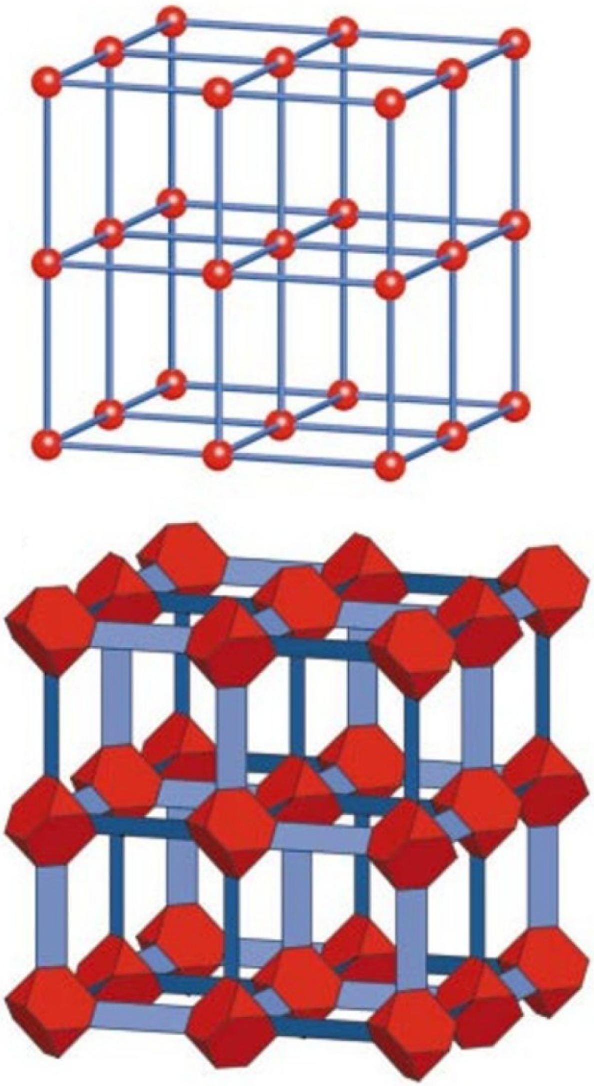
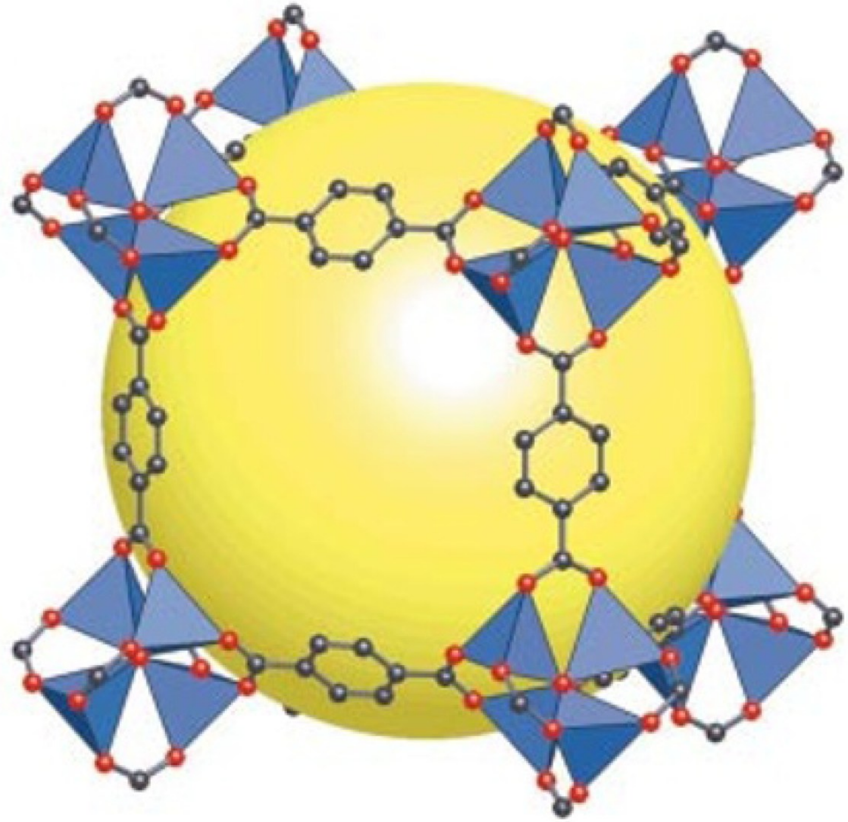
25.07.2025

MuSR 2025, Saint John’s

Metal-organic frameworks (MOFs)



Coordination solids / coordination polymers.



“MOF-5”

- Inorganic ZnO_4 tetrahedra (vertices).
- Organic benzene dicarboxylate (“bonds”).
- Yellow sphere: 12 Å diameter.

Yaghi *et al.*, *Nature* **423** 705 (2003)

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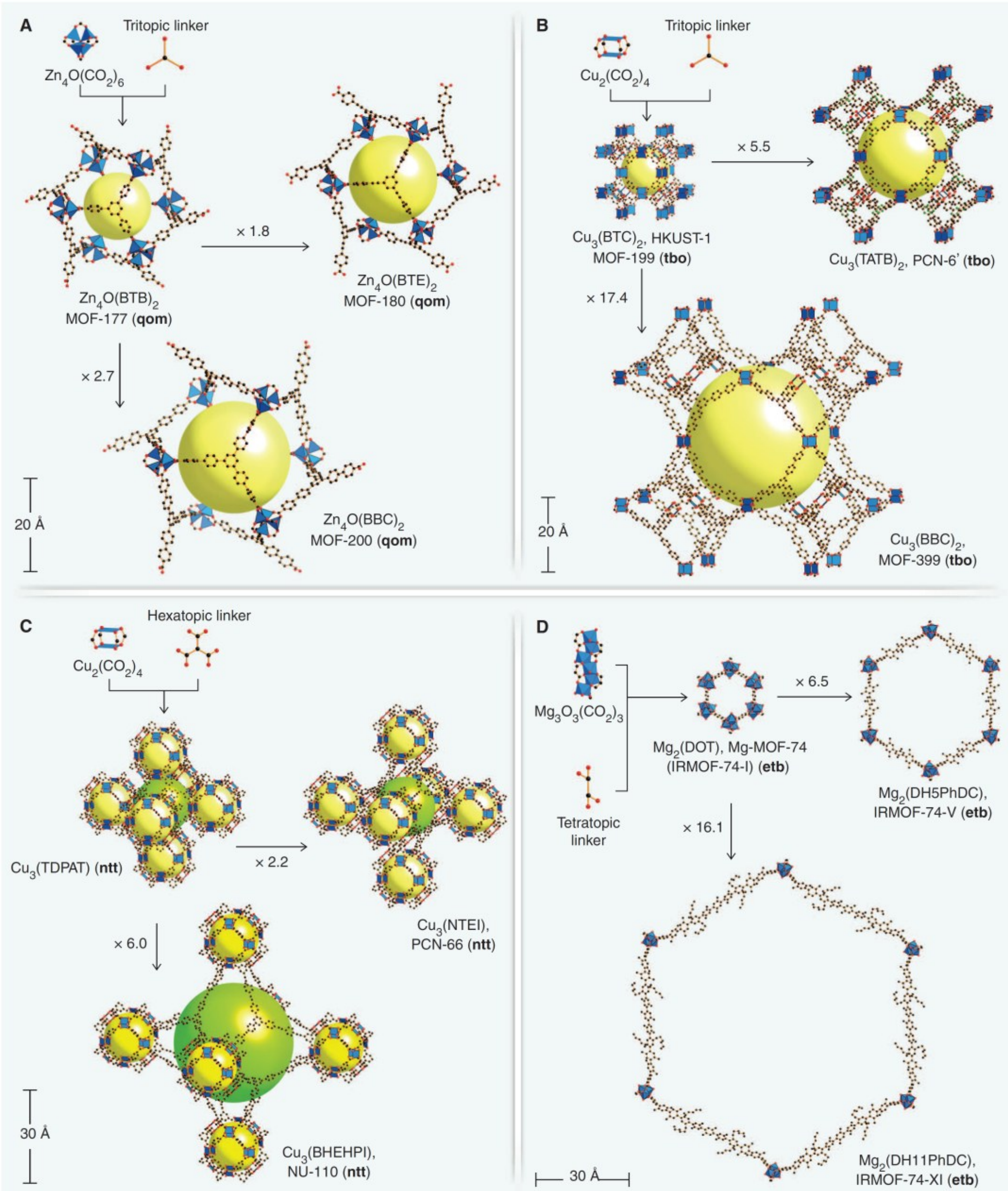


Exceptional tunability of the chemical/structural properties.

Very high porosity and surface/volume ratios. Relevant for:

- catalysis;

- gas adsorption, storage and separation.

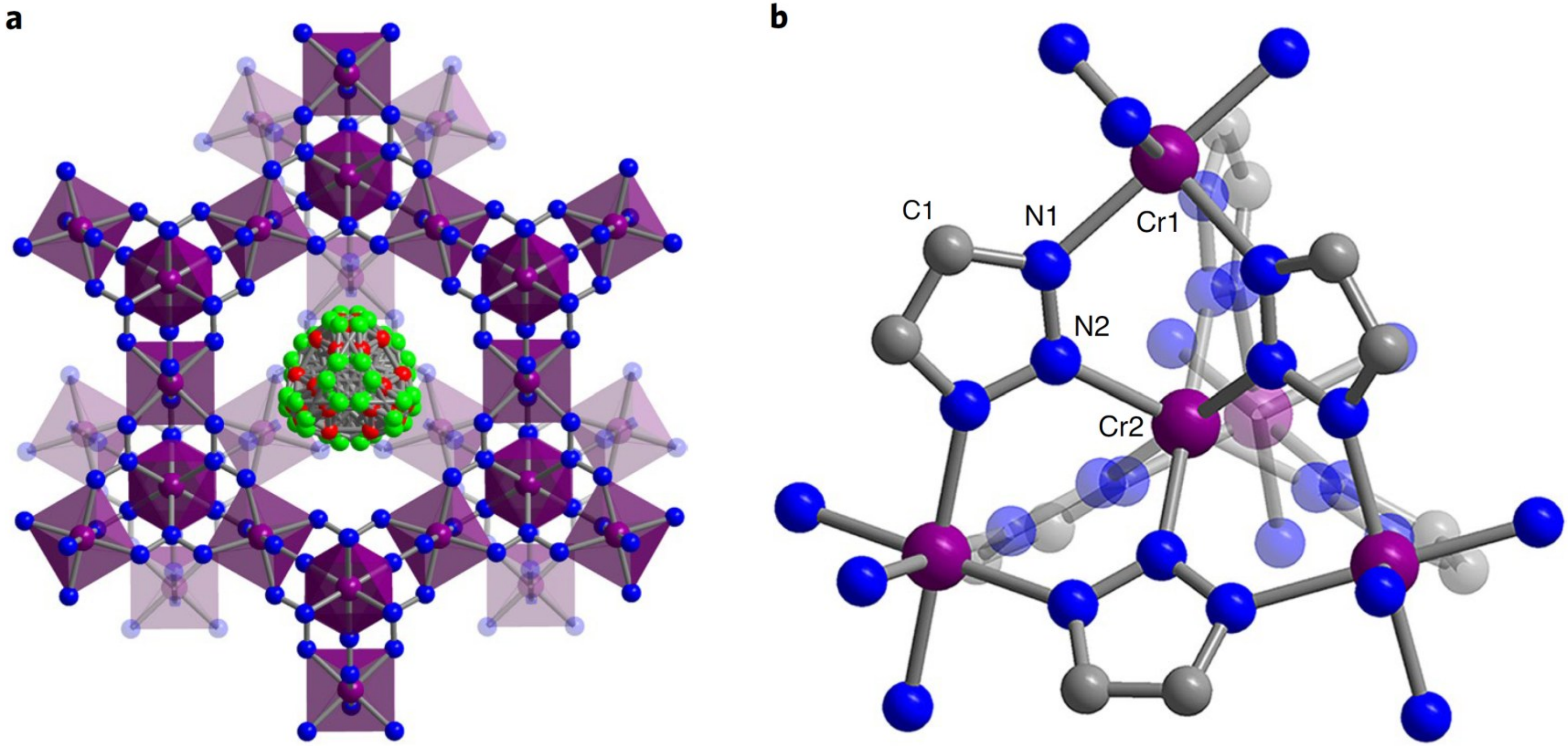
Chemical flexibility: tailored, “ad-hoc” electronic properties.

Magnetic/multiferroic MOFs: low T_C (weak exchange couplings).

Furukawa *et al.*, *Science* **341** 1230444 (2013); Thorarinsdottir, Harris, *Chem. Rev.* **120** 8716 (2020)

High-temperature ferromagnetism

$Cr(tri)_2(CF_3SO_3)_{0.33}$ (Htri, 1*H*-1,2,3-triazole)



Triflate $(CF_3SO_3)^-$ anion: mixed valence Cr^{2+}/Cr^{3+}.

Park *et al.*, *Nature Chemistry* **13** 594 (2021)

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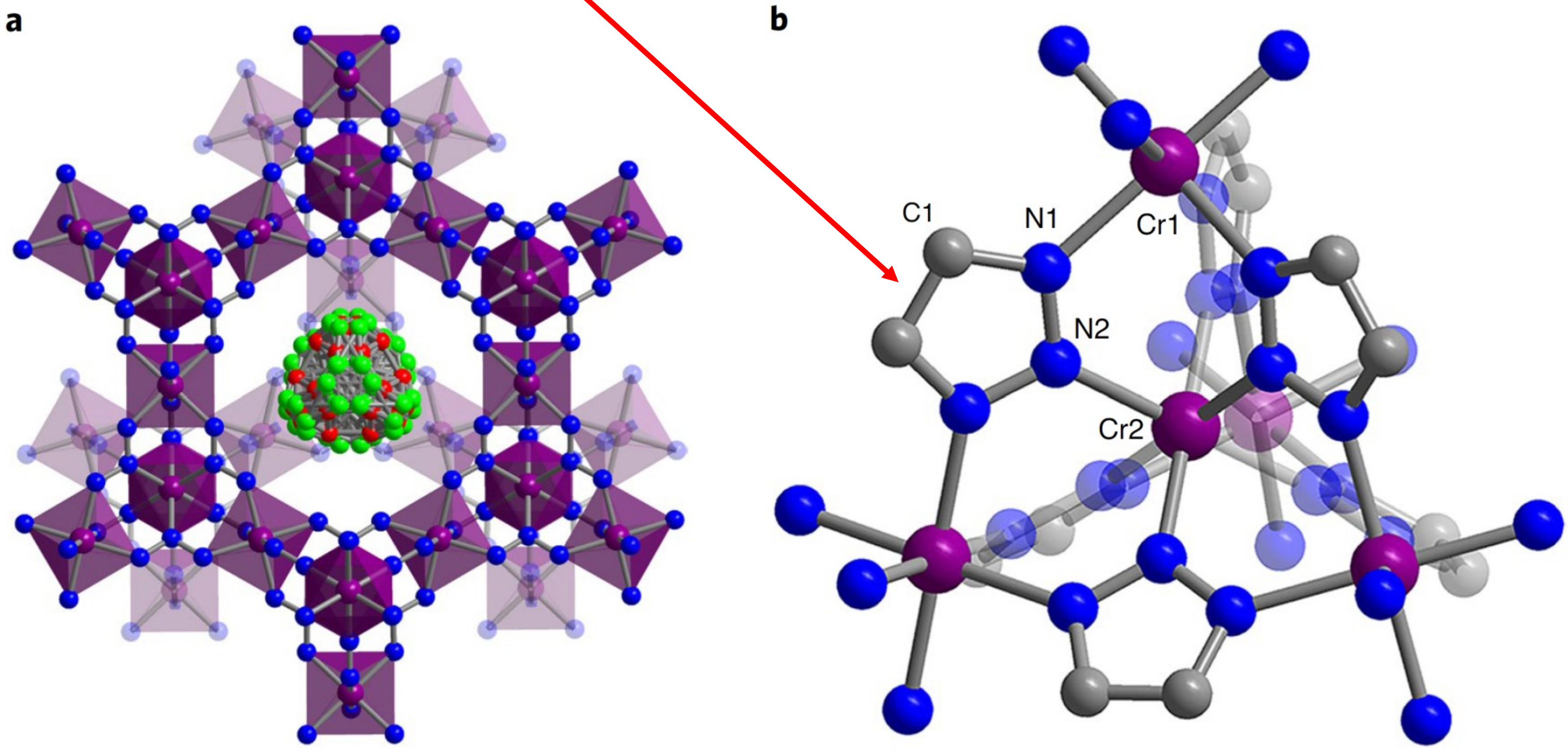

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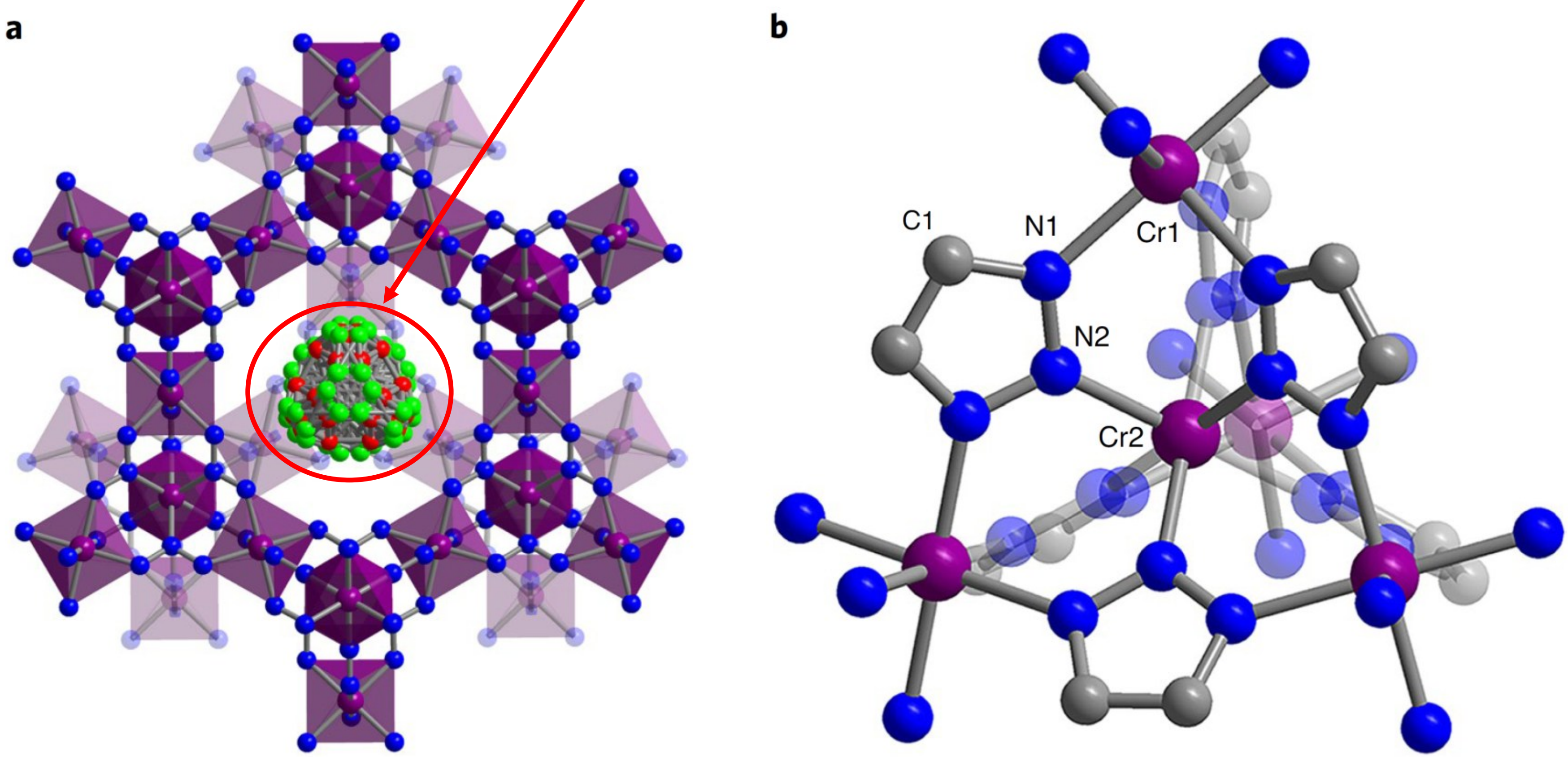

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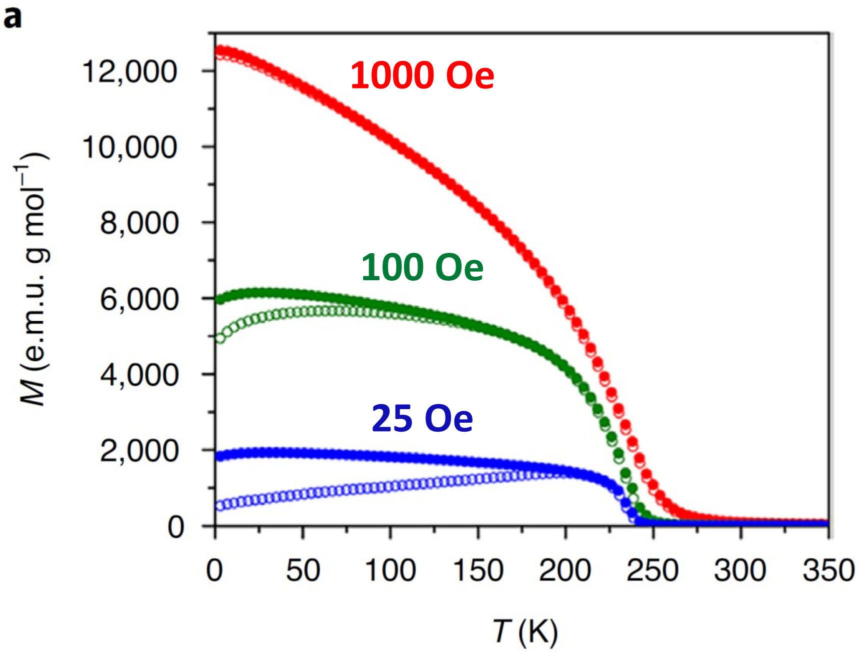
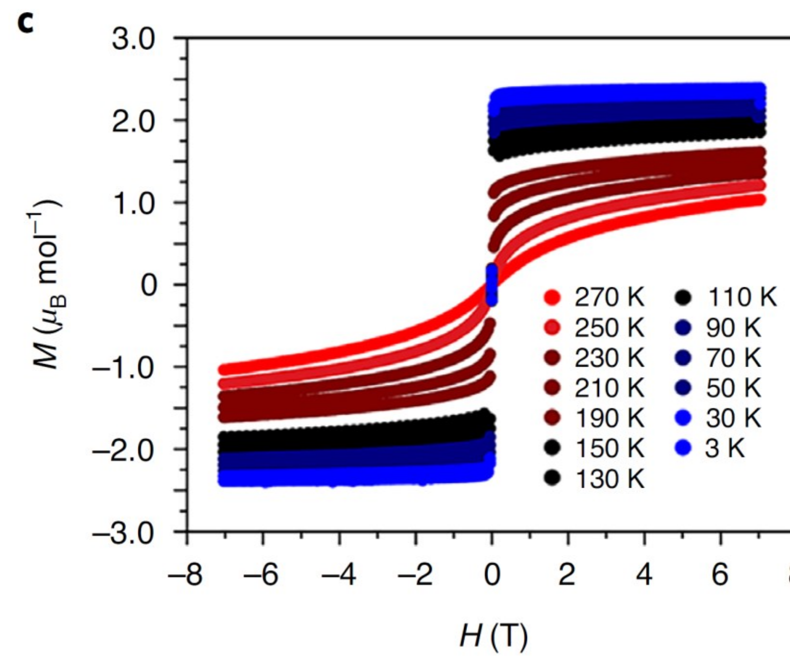
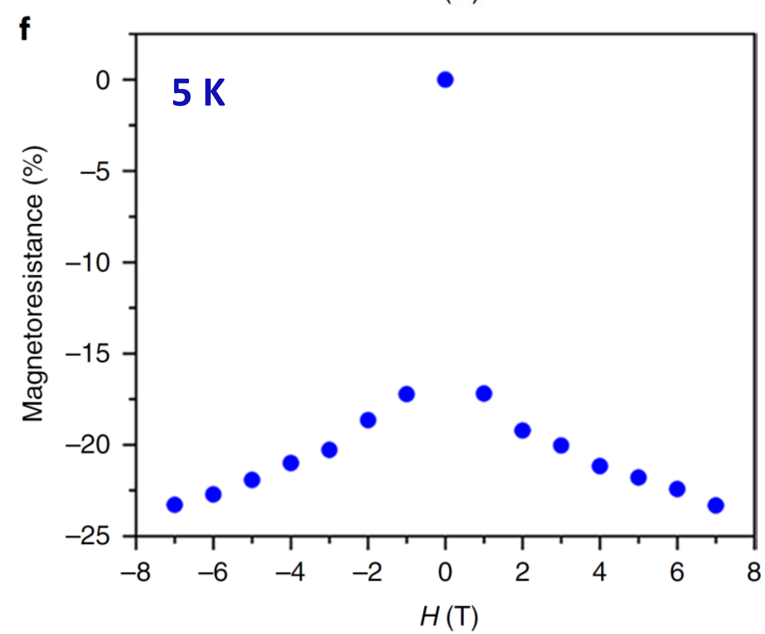




Highest critical temperature for MOFs (around 225 K).

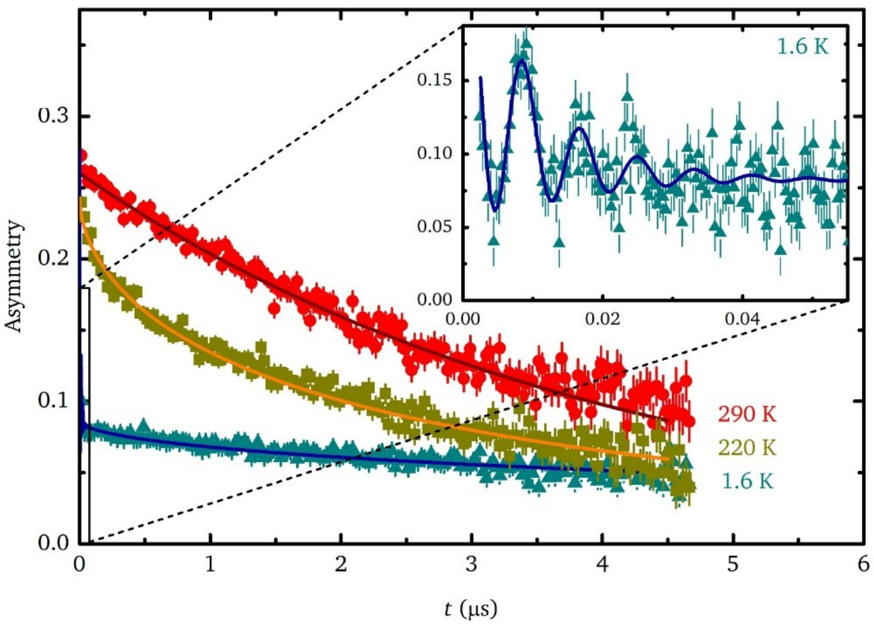
Among highest values of magnetoresistance for MOFs.

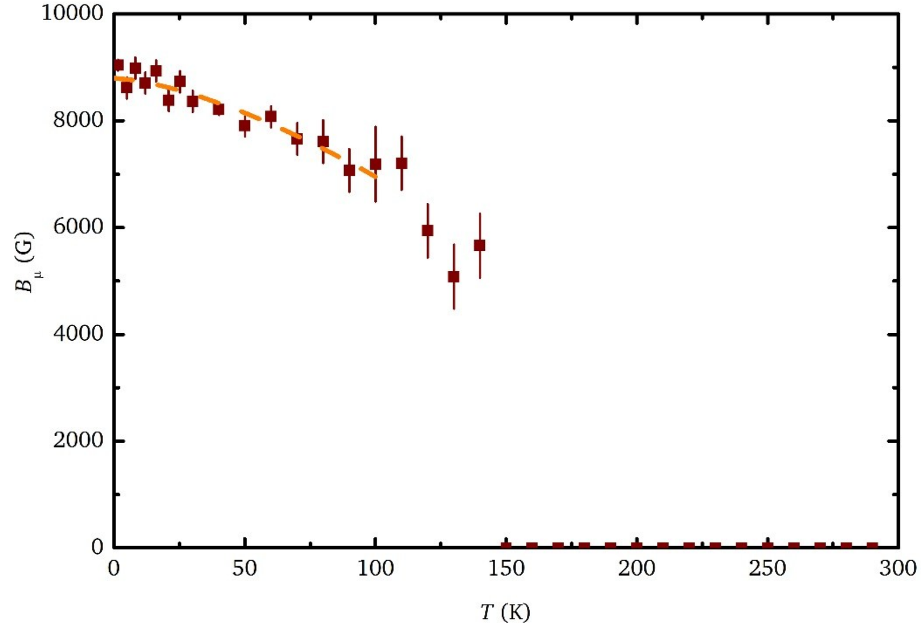
Itinerant ferromagnetism arising from double-exchange (Cr mixed valence).



Park *et al.*, *Nature Chemistry* **13** 594 (2021)

Muon-spin rotation





$$\frac{A(t)}{A(0)} = a_{T_1} \cos\left(\gamma_\mu B_\mu t + \phi\right) \exp\left(-\lambda_{T_1} t\right) + a_{T_2} \exp\left(-\lambda_{T_2} t\right) + a_L \exp\left(-\lambda_L t\right)$$

Likely implantation site close to Cr ions.

Low-temperatures Bloch-like $T^{3/2}$ law (FM).

Prando *et al.*, *to be submitted* (2025)

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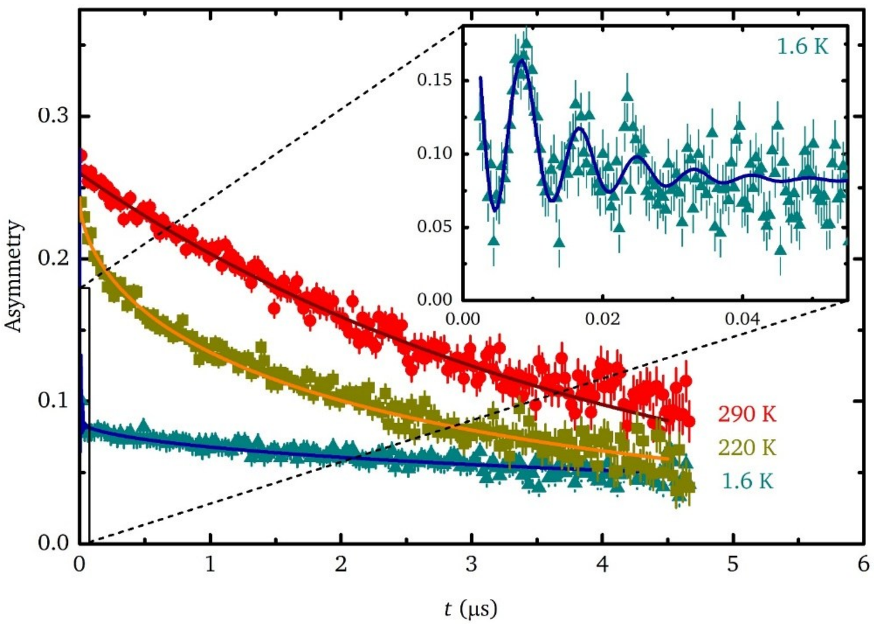

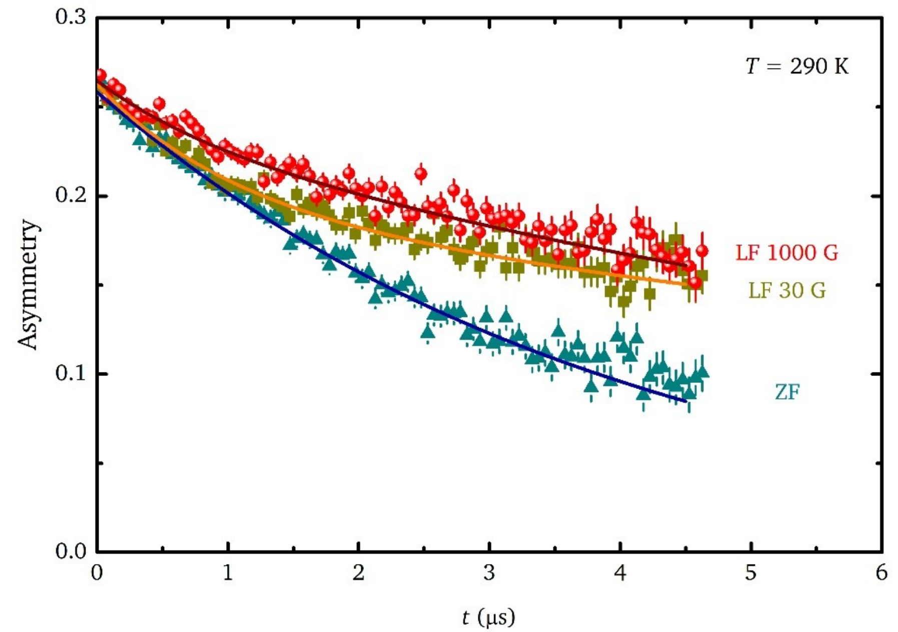

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Unusual survival of dynamics well-above the critical temperature.

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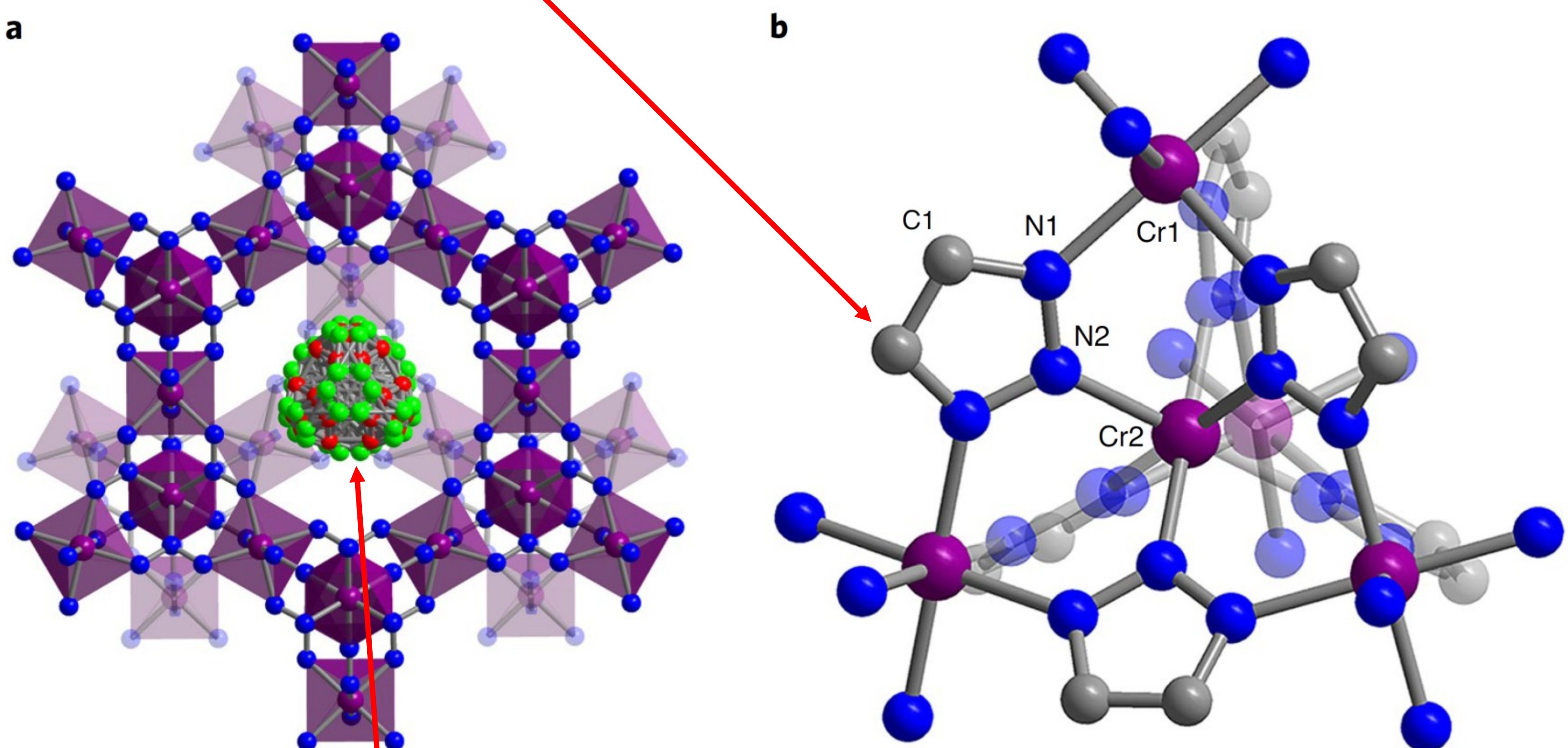
Nuclear magnetic resonance

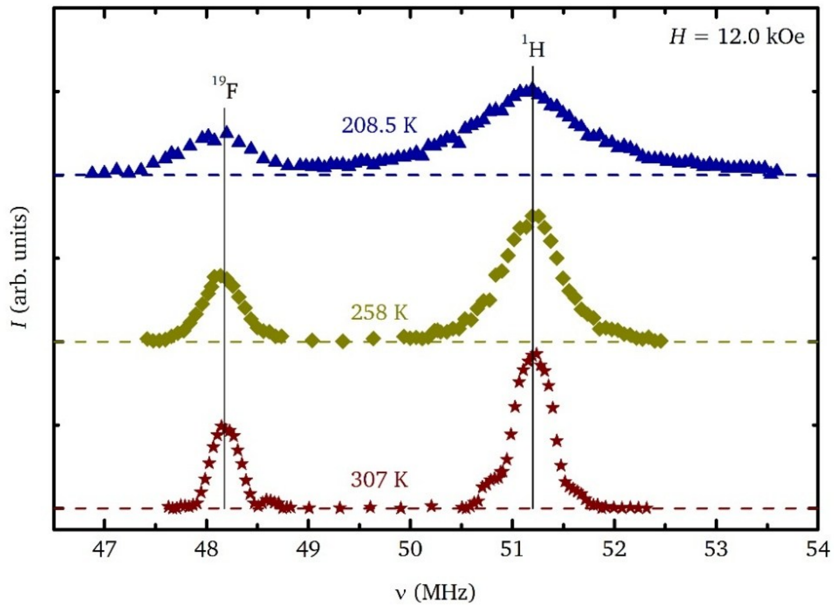
^{1}H nuclei in the metal-organic framework.

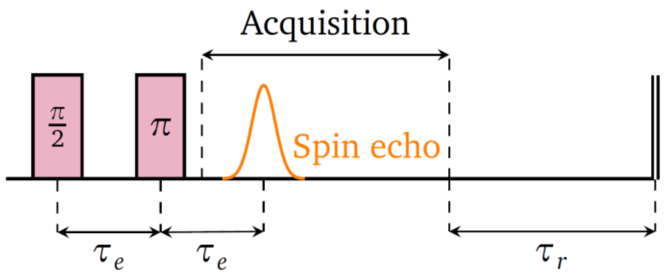


^{19}F nuclei in the charge-balancing triflate anion.

Park *et al.*, *Nature Chemistry* **13** 594 (2021)

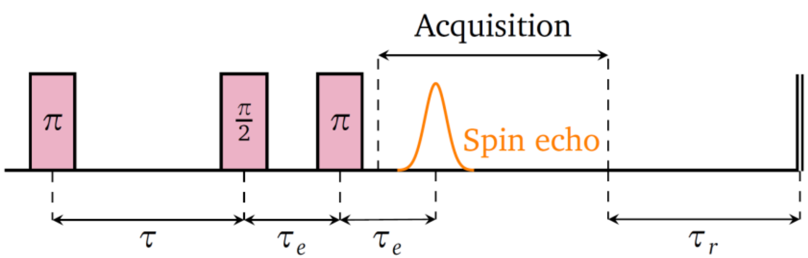
Nuclear magnetic resonance



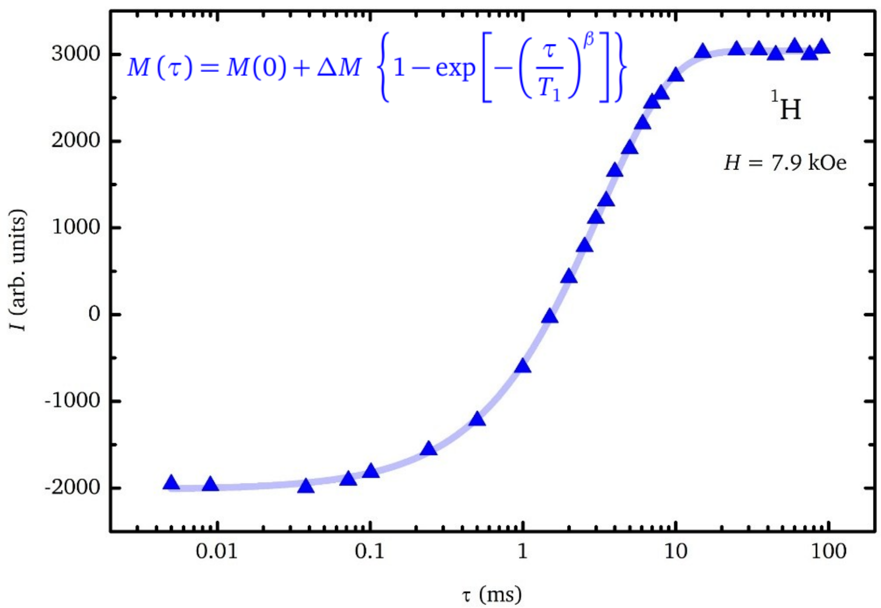


Signal clearly resolved for both nuclei.

Progressive inhomogeneous broadening induced by ferromagnetic phase.

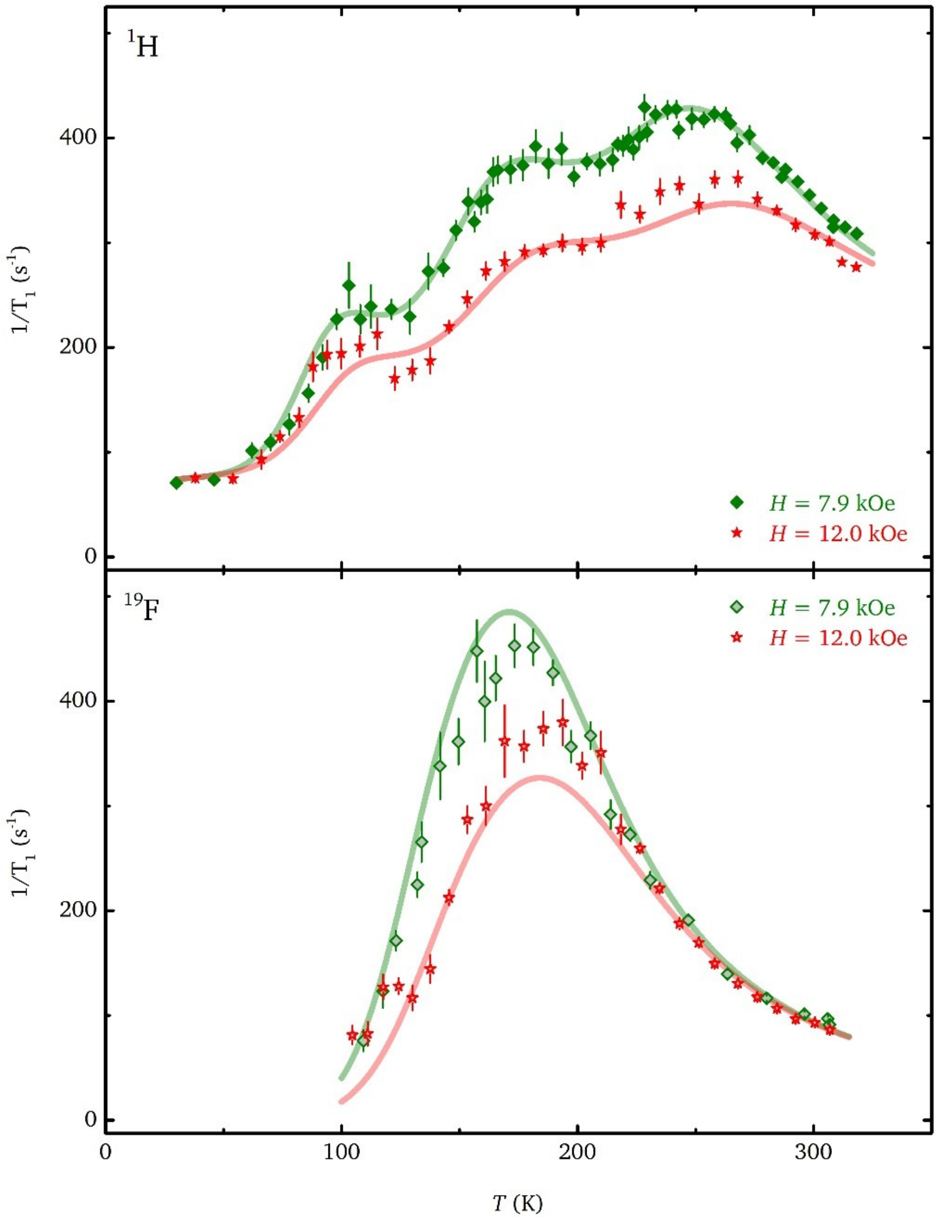


$$\frac{1}{T_1} \propto \underbrace{\int_{-\infty}^{+\infty} d\tau \, \langle h_\perp(\tau)\, h_\perp(0) \rangle \exp(\imath \omega_L \tau)}_{J(\omega_L)}$$



Prando *et al.*, *to be submitted* (2025)

Spin-lattice relaxation rate



Weak bump at around 100 K (^{1}H only).

Marked maximum at around 170 K (both ^{1}H and ^{19}F).

Marked maximum at around 250 K (^{1}H only).

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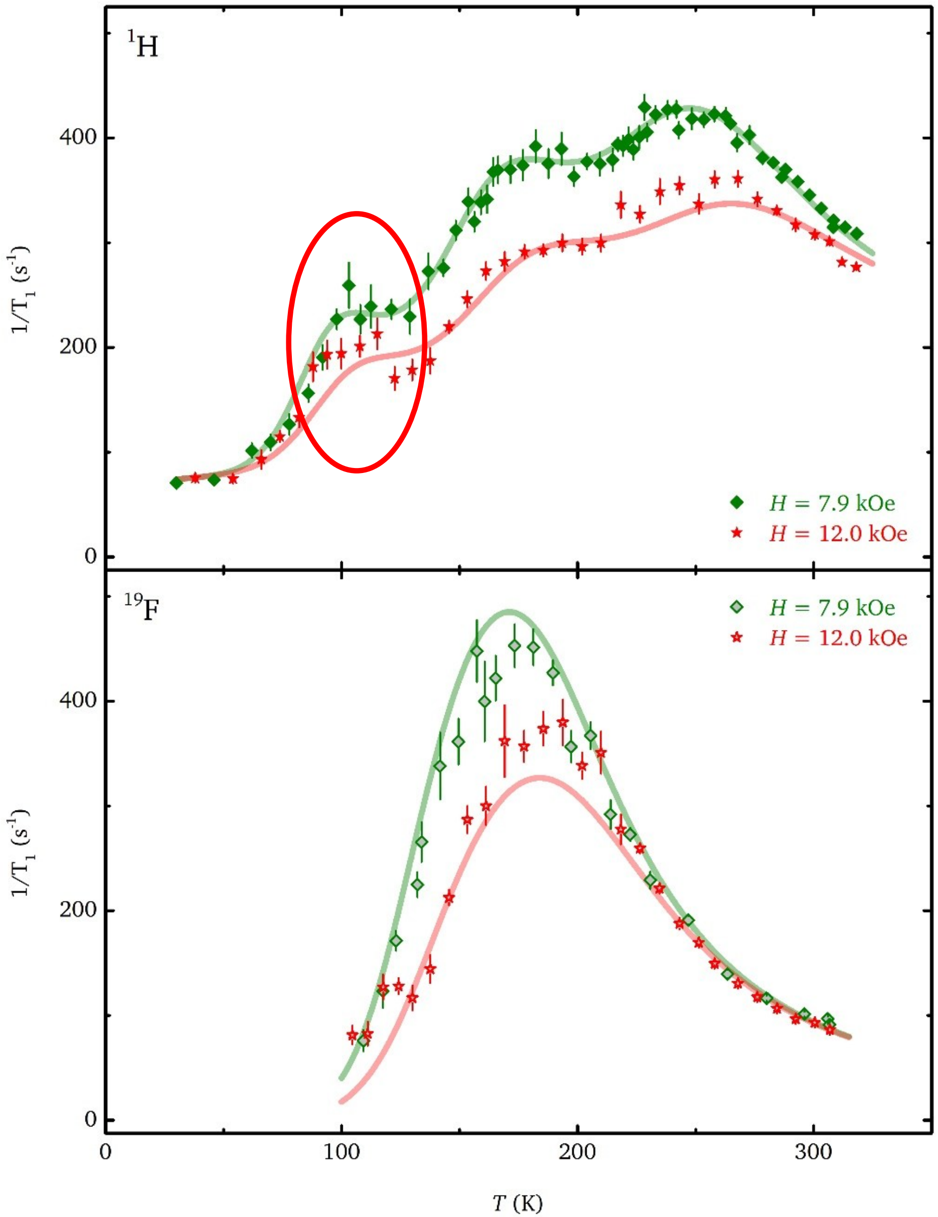

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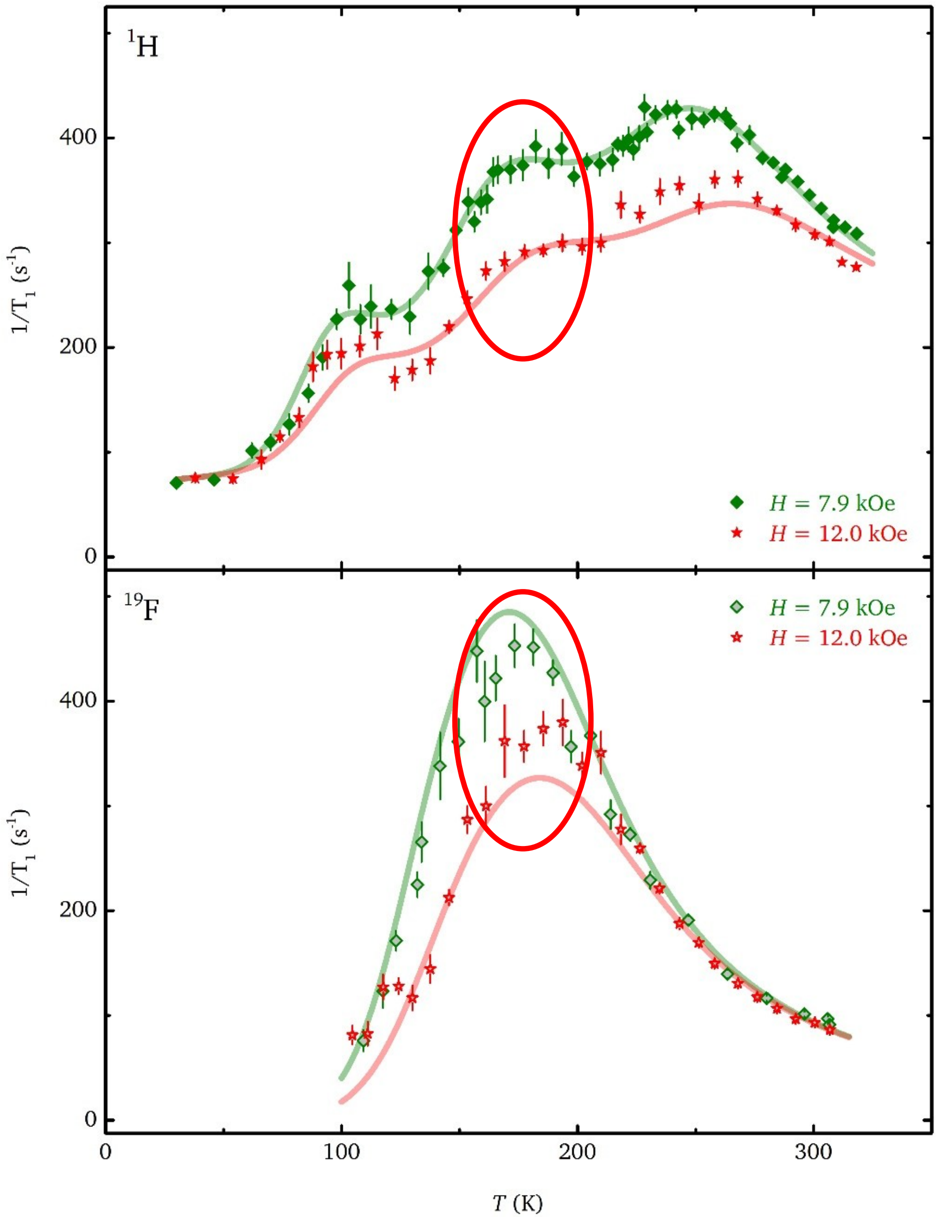

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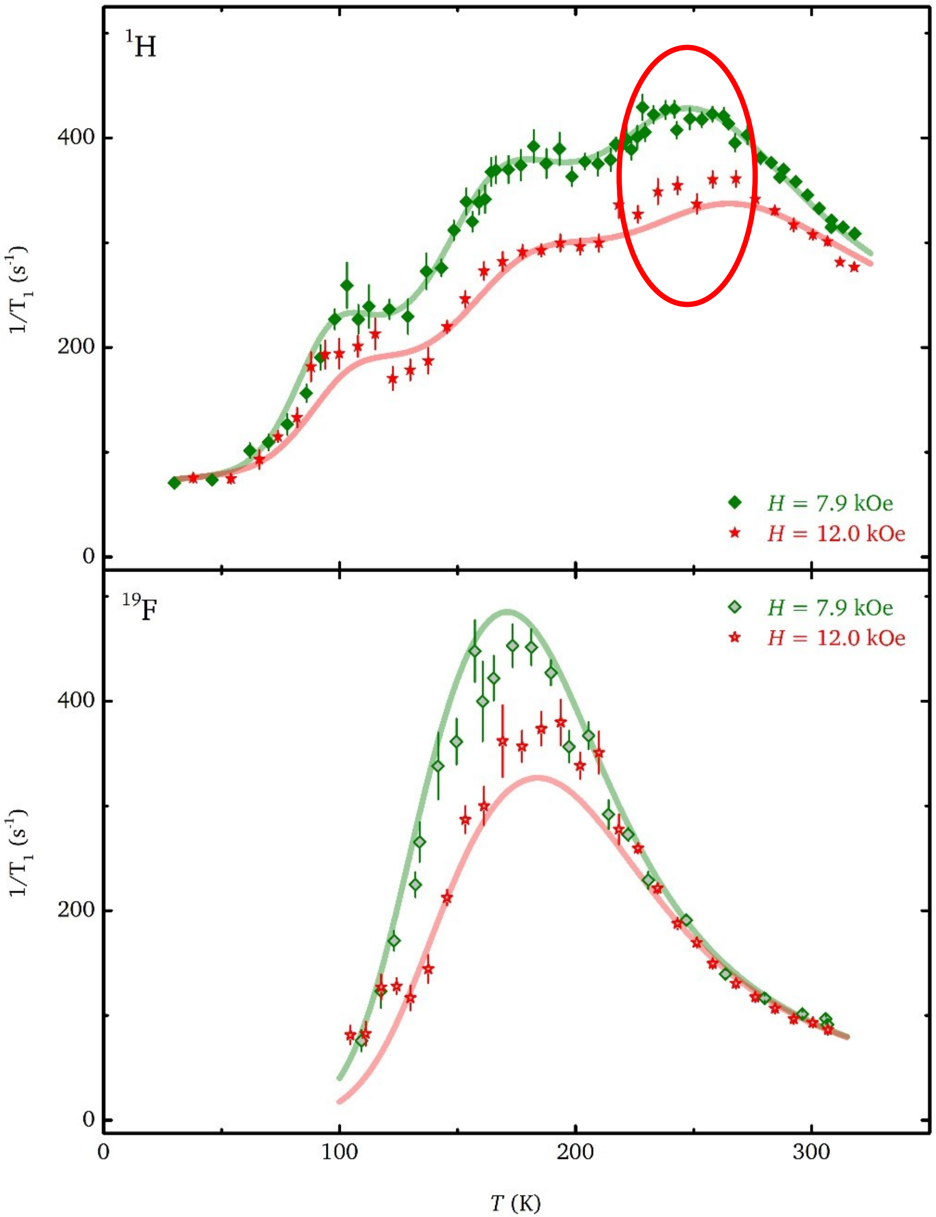

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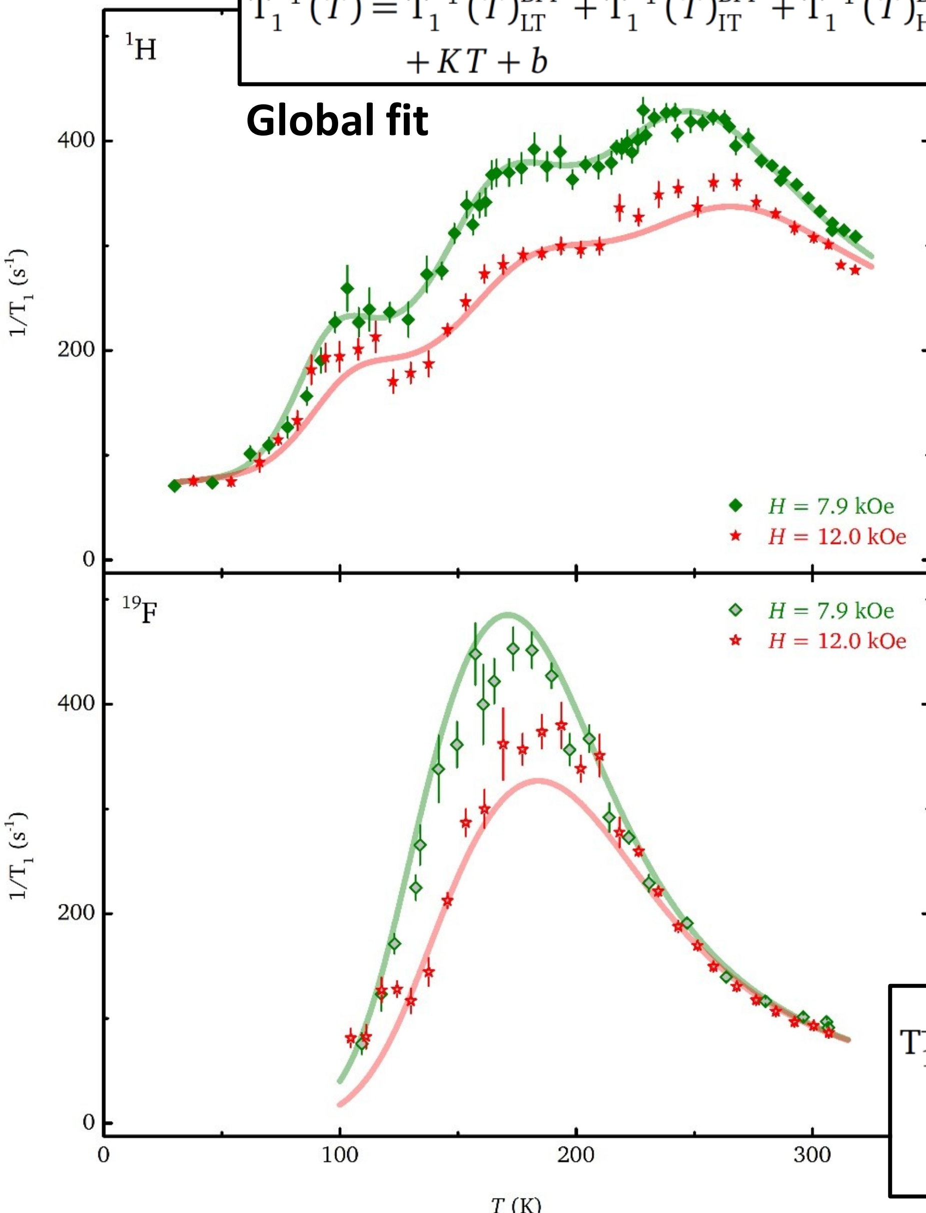
Spin-lattice relaxation rate

$$T_1^{-1}(T) = T_1^{-1}(T)^{BPP}_{LT} + T_1^{-1}(T)^{BPP}_{IT} + T_1^{-1}(T)^{BPP}_{HT} + KT + b$$

Global fit



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$$T_1^{-1}(T)^{BPP} = CJ(\omega_L)$$

$$J(\omega) = \frac{\tau_c}{1+\omega^2\tau_c^2} \qquad C \sim \gamma^2 \langle \Delta B^2 \rangle$$

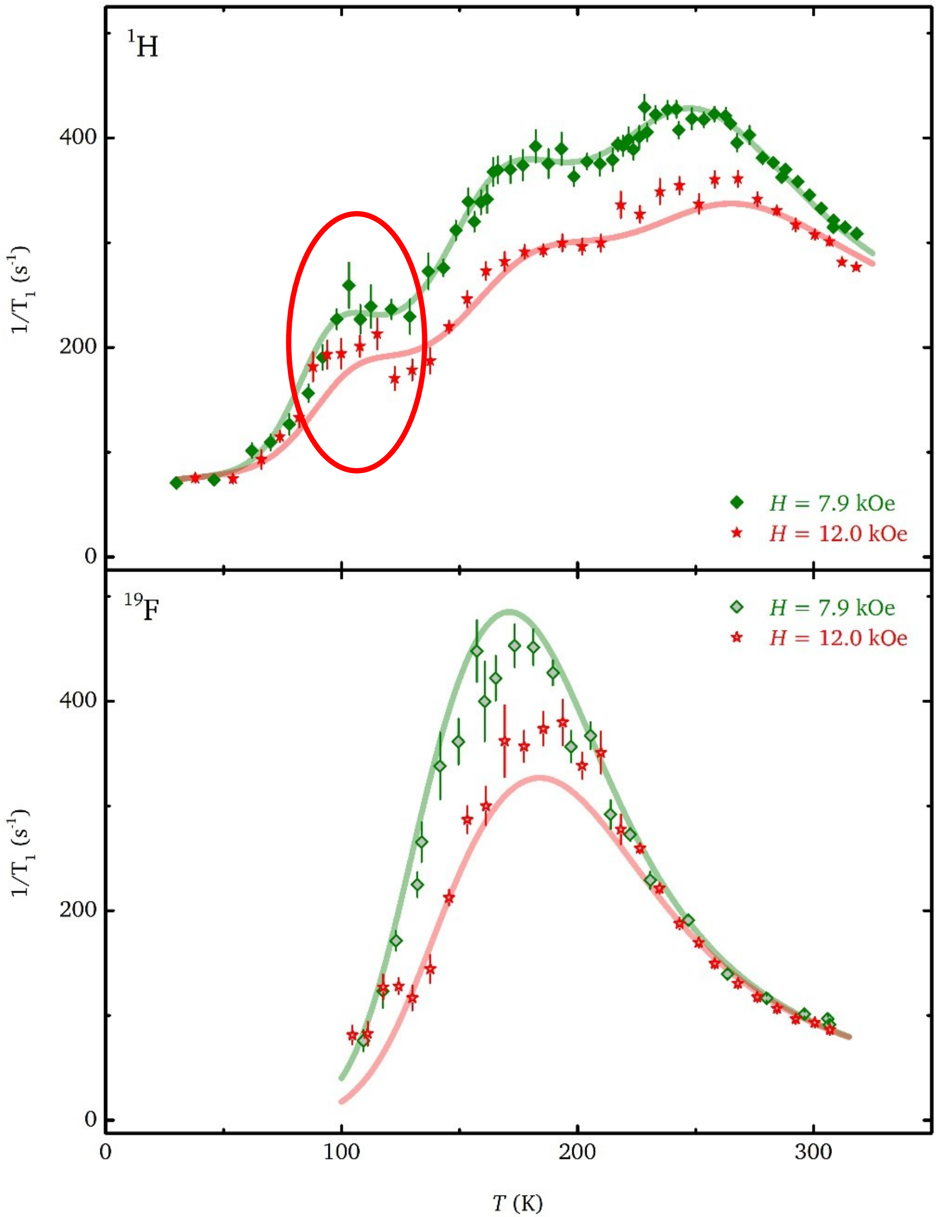
$$\tau_c = \tau_0 \exp(\vartheta/T)$$

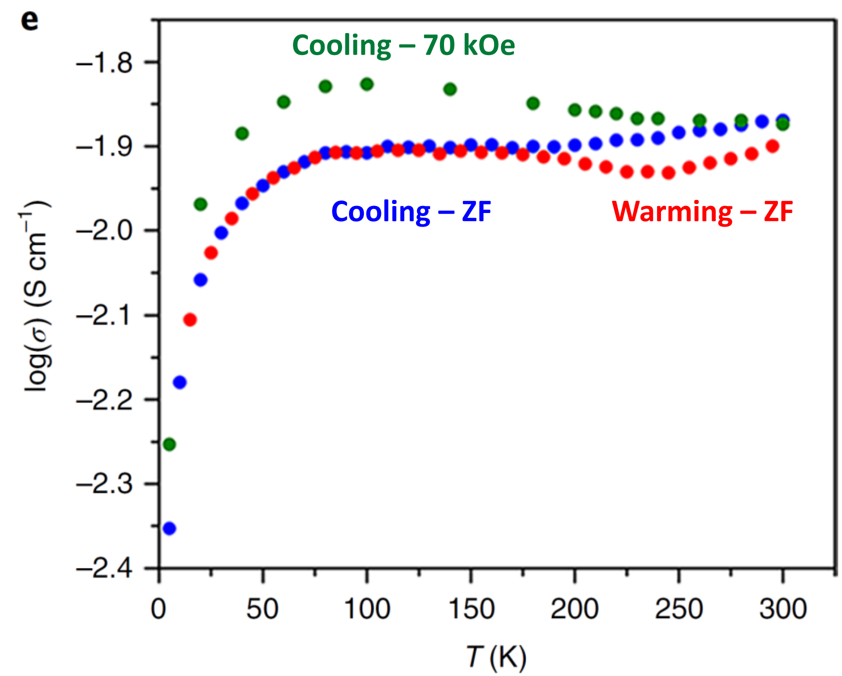
$$T_1^{-1}(T) = \frac{C\ T}{4\omega_L \delta\vartheta} \left\{ \arctan\left[\sinh\left(\frac{\vartheta+\delta\vartheta}{T} + \ln(\omega_L\tau_0)\right)\right] - \arctan\left[\sinh\left(\frac{\vartheta-\delta\vartheta}{T} + \ln(\omega_L\tau_0)\right)\right]\right\}$$

Global fit

Prando *et al., to be submitted* (2025)

Low temperatures





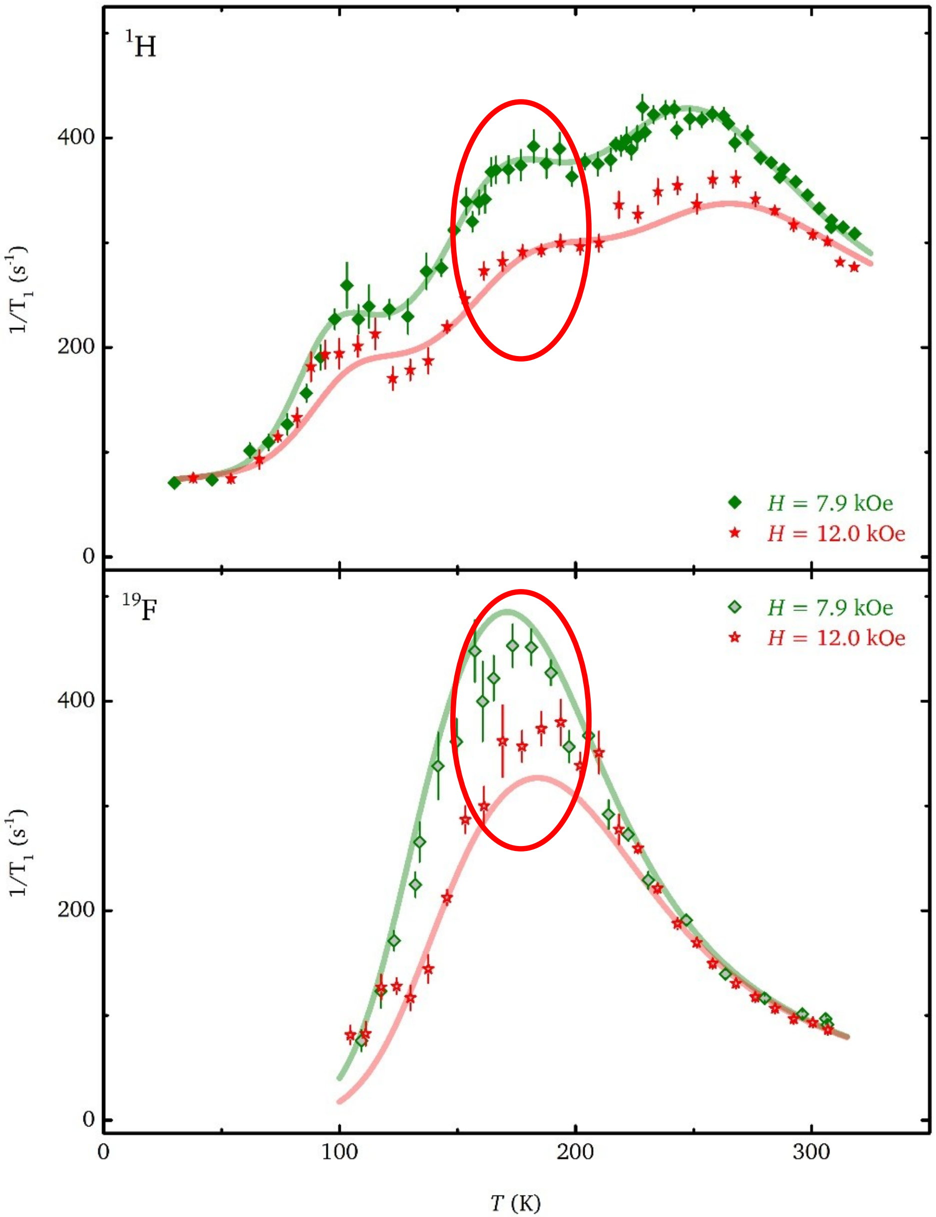
Correlation with sudden decrease of electrical conductivity.

Likely impact of charge localization probed by ^{1}H nuclei in the MOF structure.

Weak signal amplitude hampers further investigation of this region.

Prando *et al.*, *to be submitted* (2025); Park *et al.*, *Nature Chemistry* **13** 594 (2021)

Intermediate temperatures



$$T_1^{-1}(T) = T_1^{-1}(T)^{\mathrm{BPP}}_{\mathrm{LT}} + T_1^{-1}(T)^{\mathrm{BPP}}_{\mathrm{IT}} + T_1^{-1}(T)^{\mathrm{BPP}}_{\mathrm{HT}} + KT + b$$

	C (10^{10} s^{-2})	τ_0 (10^{-11} s)	ϑ (K)
LT	5.65 ± 0.25	3.4 ± 1.7	500 ± 50
IT	9.0 ± 0.5	1.8 ± 0.6	960 ± 60
HT	9.4 ± 0.4	1.20 ± 0.15	1525 ± 35

$$T_1^{-1}(T) = \frac{C\,T}{4\omega_L \delta\vartheta}\left\{\arctan\left[\sinh\left(\frac{\vartheta+\delta\vartheta}{T} + \ln(\omega_L\tau_0)\right)\right] - \arctan\left[\sinh\left(\frac{\vartheta-\delta\vartheta}{T} + \ln(\omega_L\tau_0)\right)\right]\right\}$$

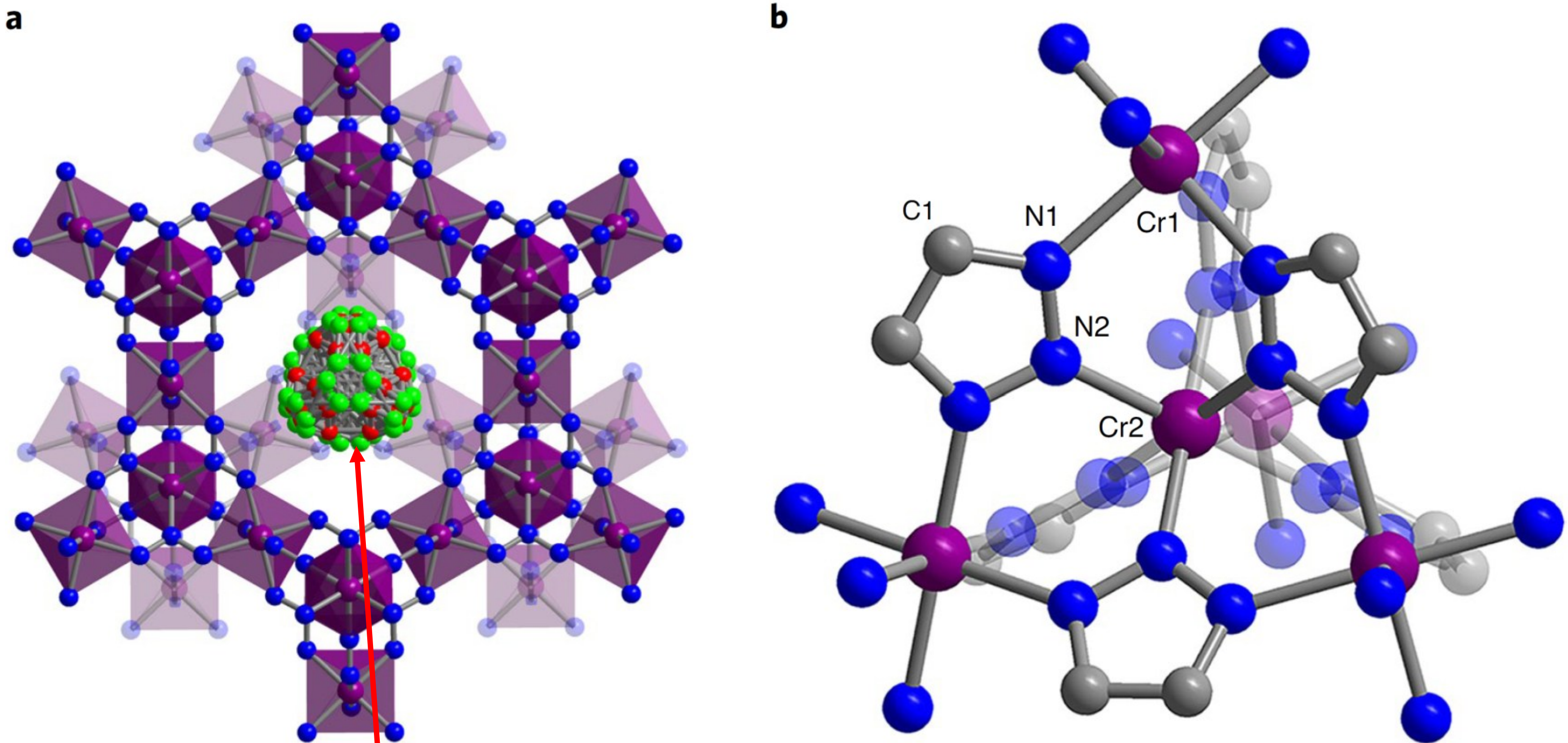
C (10^{11} s^{-2})	τ_0 (10^{-11} s)	ϑ (K)	$\delta\vartheta$ (K)
2.35 ± 0.05	1.4 ± 0.1	990 ± 15	205 ± 15

Both nuclei probe the same dynamics.

Prando *et al.*, *to be submitted* (2025)

Intermediate temperatures

^{1}H nuclei in the metal-organic framework.



^{19}F nuclei in the charge-balancing triflate anion.

Park *et al.*, *Nature Chemistry* **13** 594 (2021)

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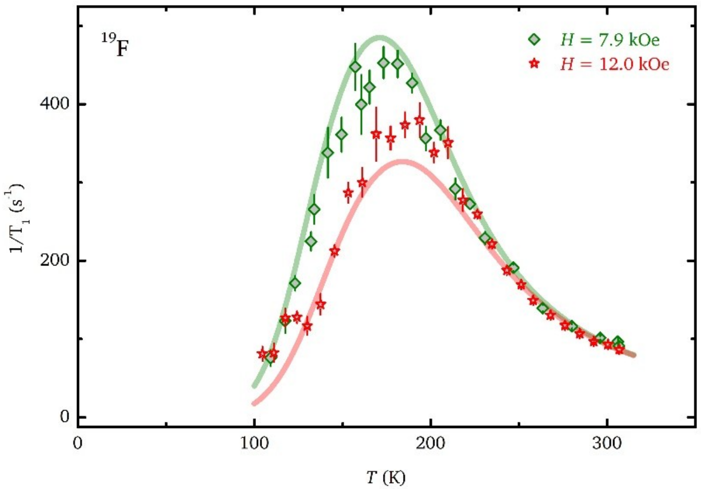
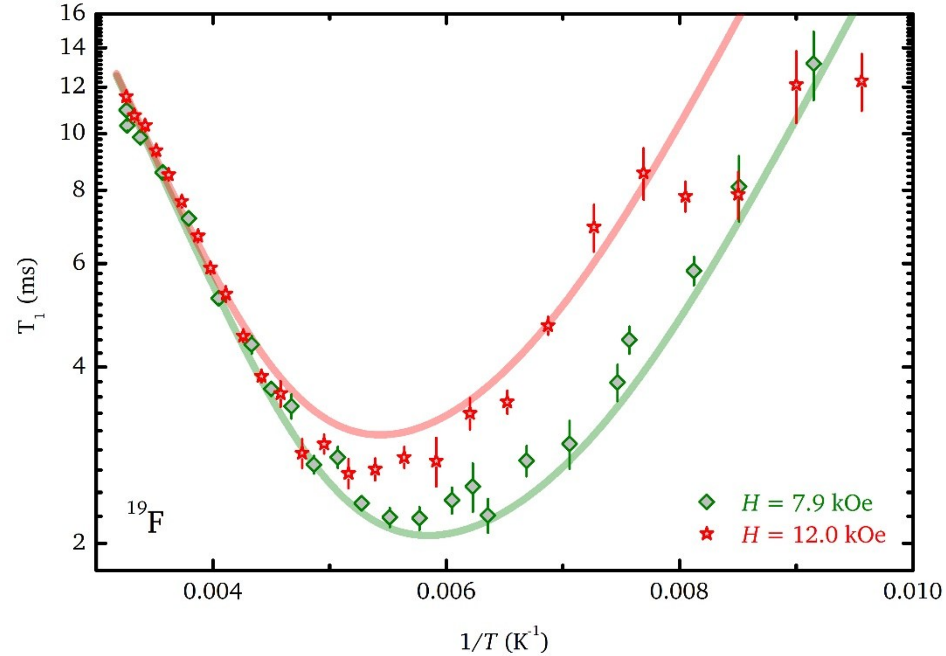
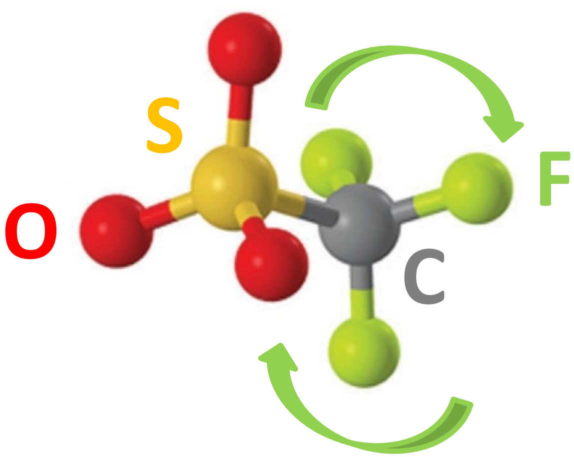


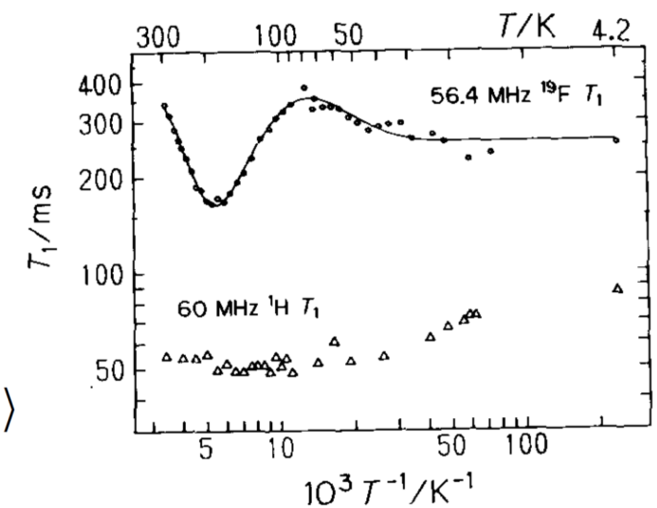


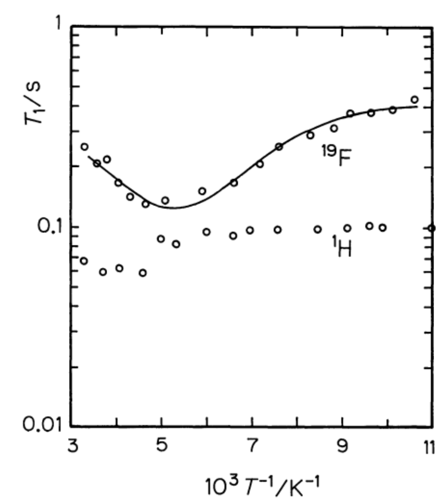


$$\vartheta = 900 \div 1300\ \mathrm{K}$$

$$\tau_0 = 10^{-12} \div 10^{-11}\ \mathrm{s}$$

$$C \sim \gamma^2 \langle \Delta B^2 \rangle$$

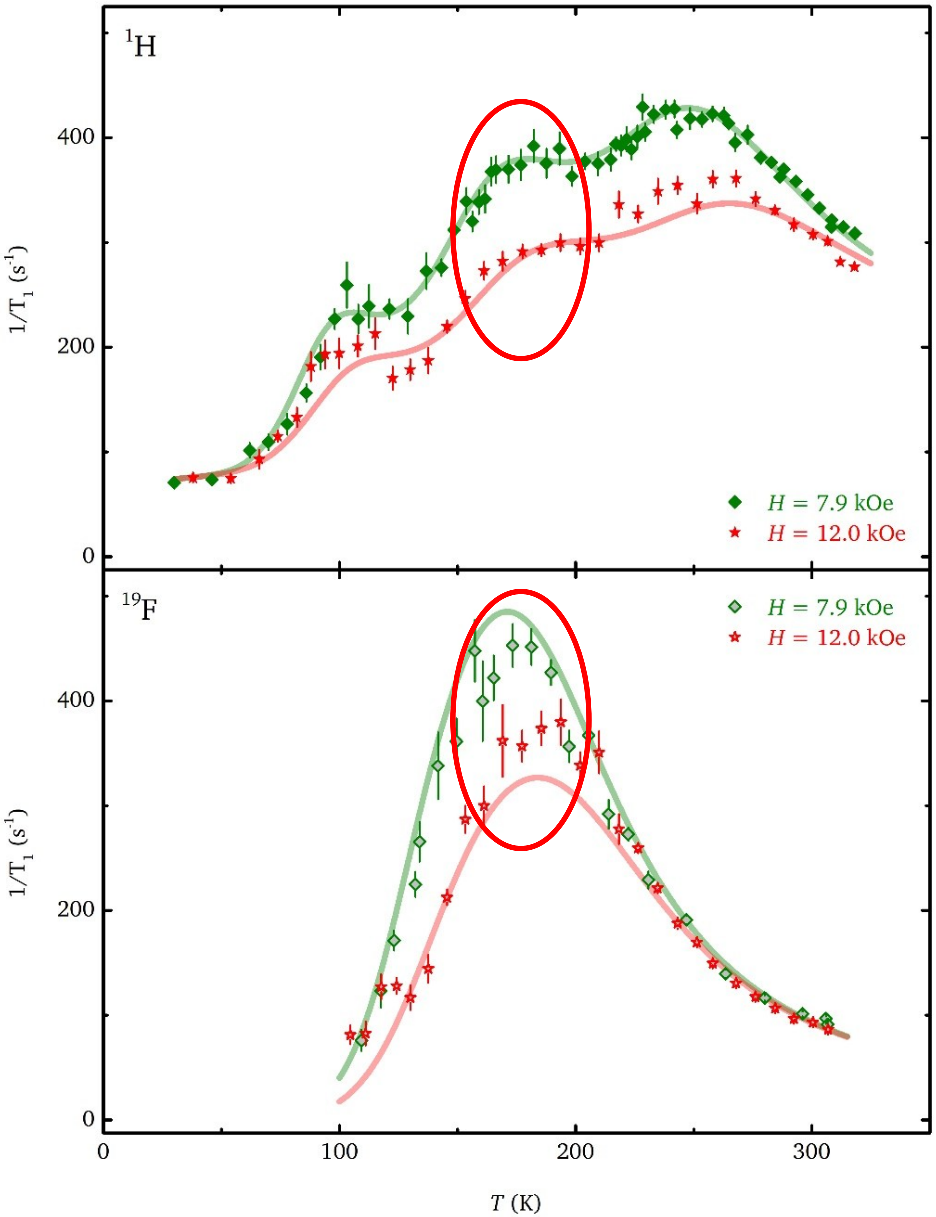




Intense fluctuating field in MOF (around 10 times). Rotary dynamics in FM background.

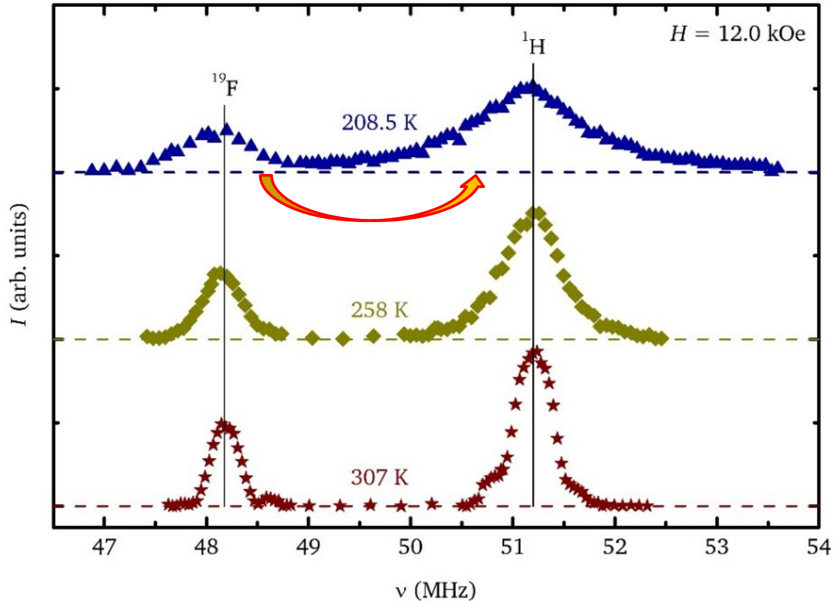
Prando *et al.*, *to be submitted* (2025); Mizuno *et al.*, *Bull. Chem. Soc. Jpn.* **63** 3323 (1990); Iida *et al.*, *Synth. Met.* **48** 1 (1992)

Intermediate temperatures



Molecular rotary dynamics induces relaxation at intermediate temperatures.

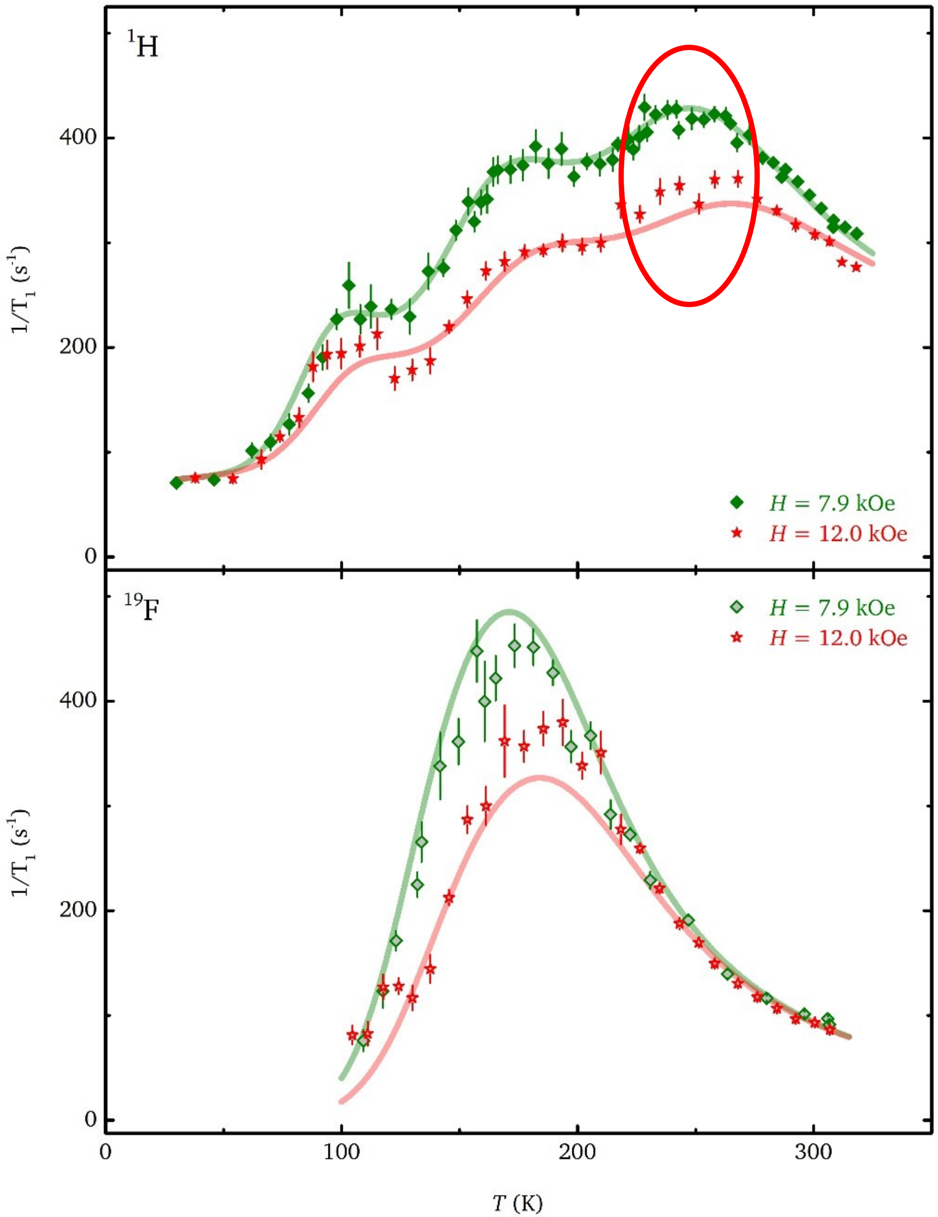
Short relaxation times on ^{19}F: intense local fluctuating magnetic fields due to the ferromagnetic background.



Cross-relaxation on ^{1}H induced by spin diffusion over the broadened line.

Prando *et al., to be submitted* (2025)

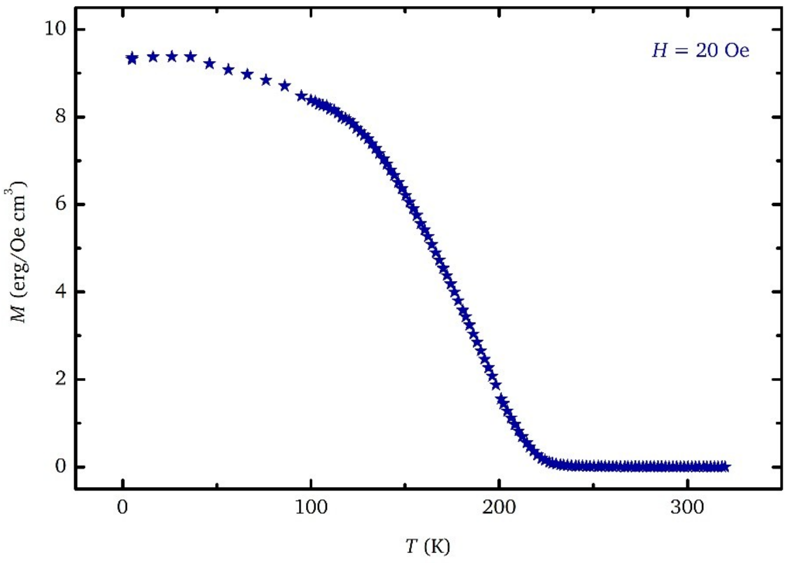
High temperatures



Lack of any sharp anomaly due to critical dynamics at the critical temperature.

Persistence of slow, activated dynamics probed by ^{1}H on the MOF.

Unconventional nature of the paramagnetic/ferromagnetic transition.



Prando *et al., to be submitted* (2025)

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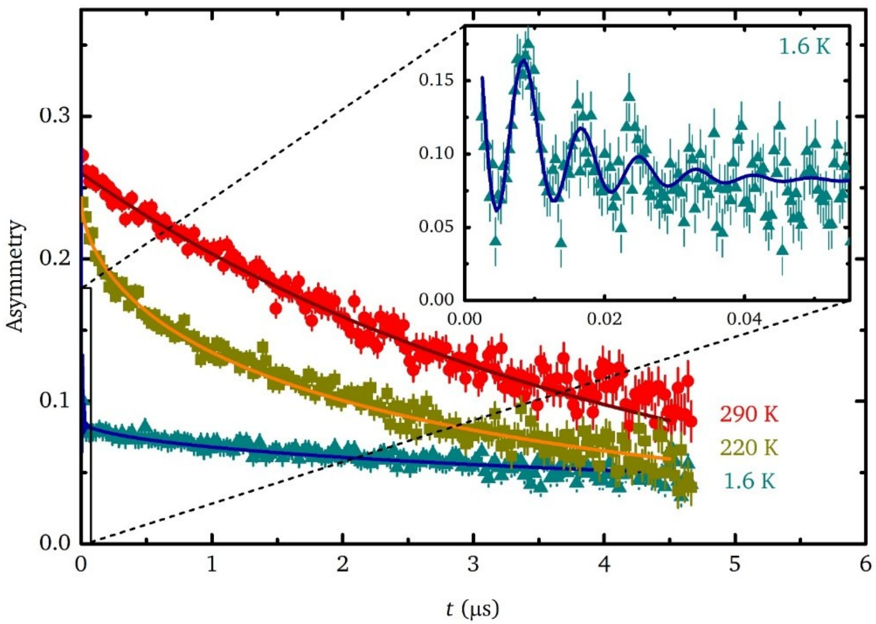

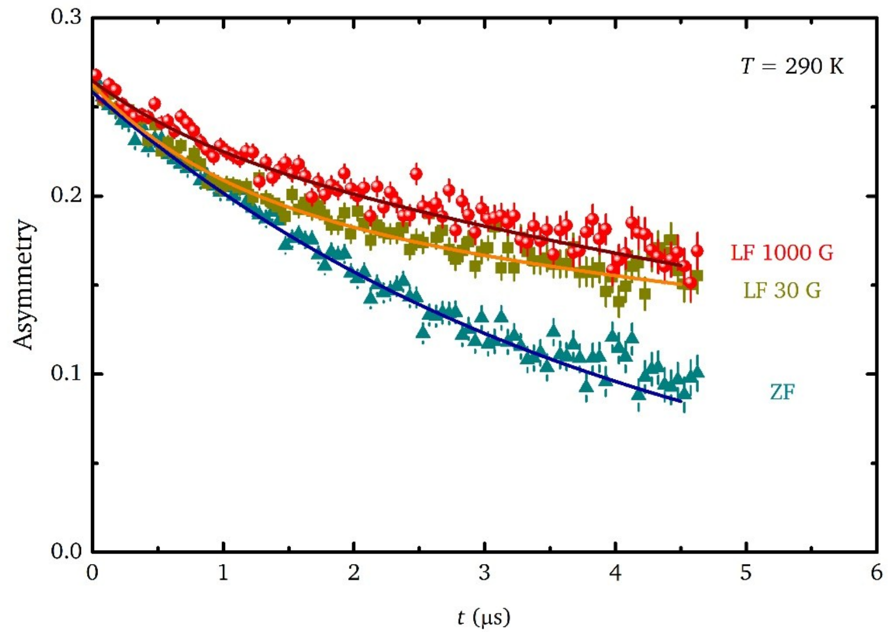

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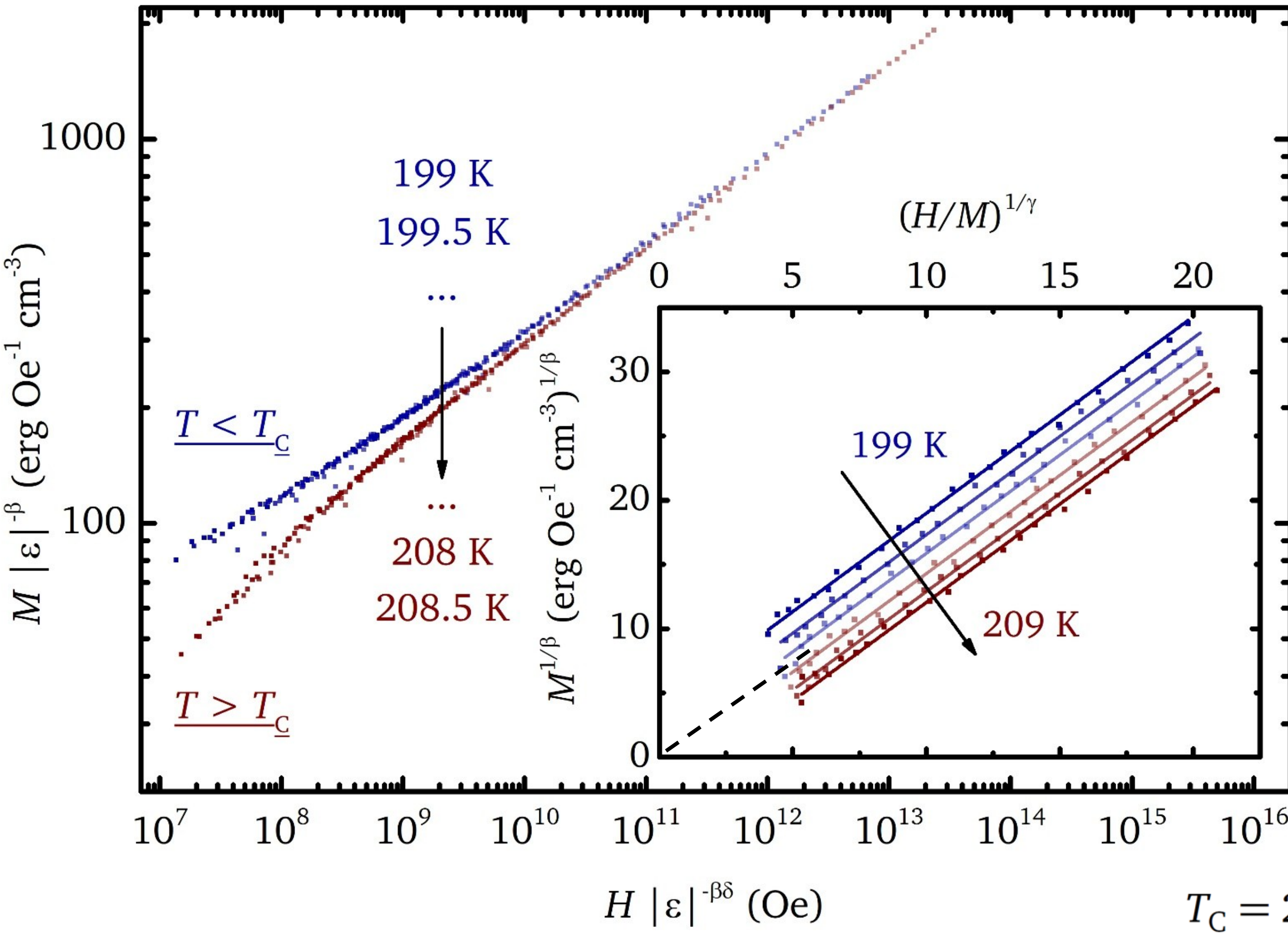


$$H = H_{ext} - 4\pi N M$$

$$\frac{M}{|\varepsilon|^{\beta}} = F_{\pm}\left(\frac{H}{|\varepsilon|^{\beta\delta}}\right)$$

$$\varepsilon = \frac{T - T_c}{T_c}$$

$T_C = 203.8$ K

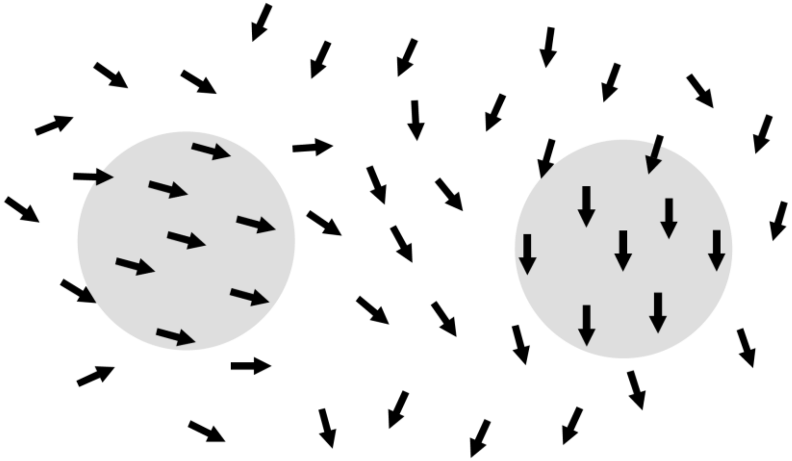
	Results	3D Heisenberg	Mean-field
β	**0.73**	0.36	0.5
δ	**4.2**	4.86	3
γ	**2.336**	1.39	1

Isothermal dc magnetometry

- Static scaling
- Arrott-Noakes approach

Prando *et al.*, *to be submitted* (2025); Chaikin, Lubensky, *Principles of condensed matter theory* (1994)

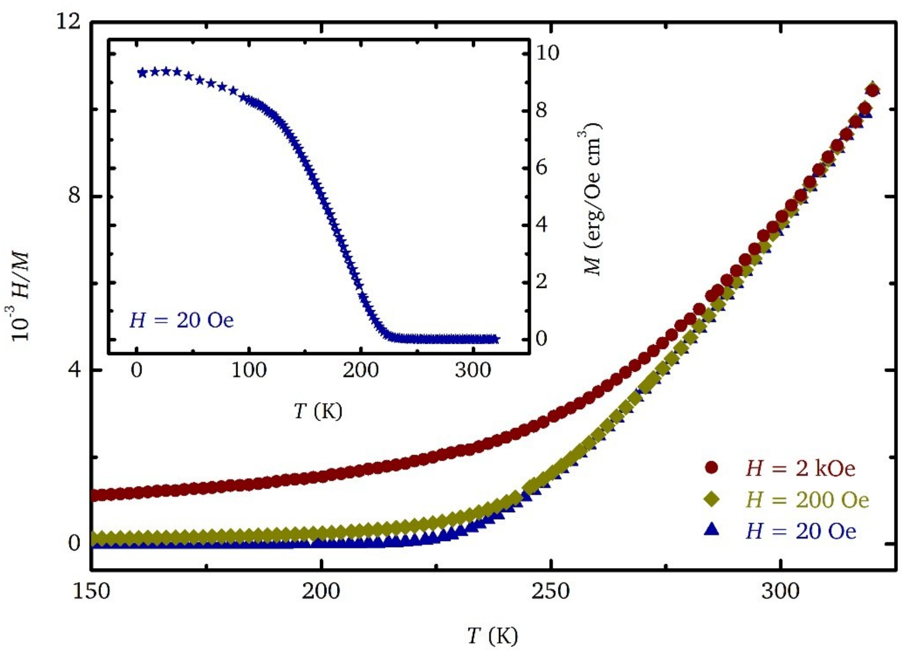
Clustered state



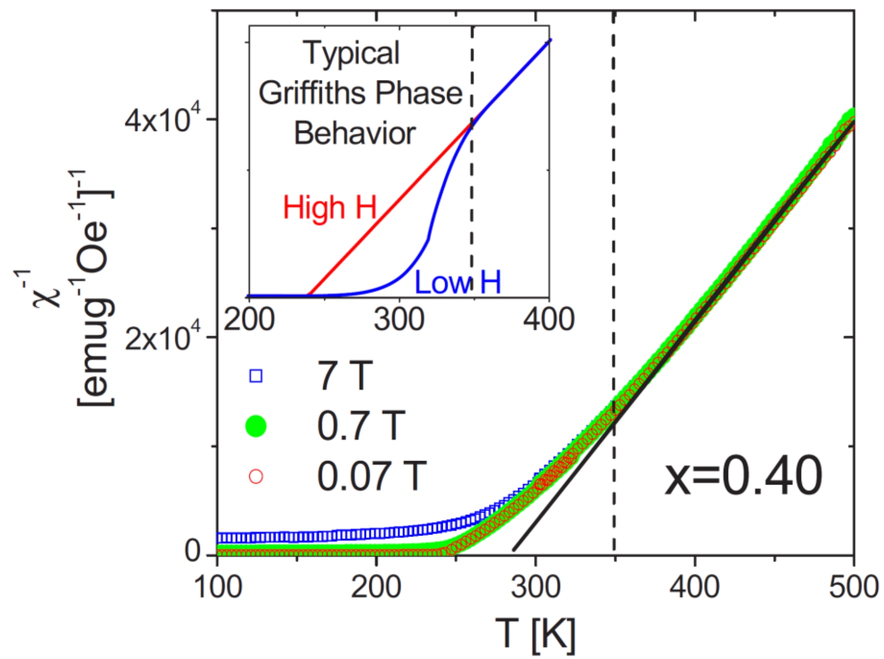
Unusual values of critical exponents compatible with magnetoelectronic phase separation above T_C (manganites, cobaltites).

Magnetization not compatible with development of clustered Griffiths state.

Persisting slow dynamics due to clusters.

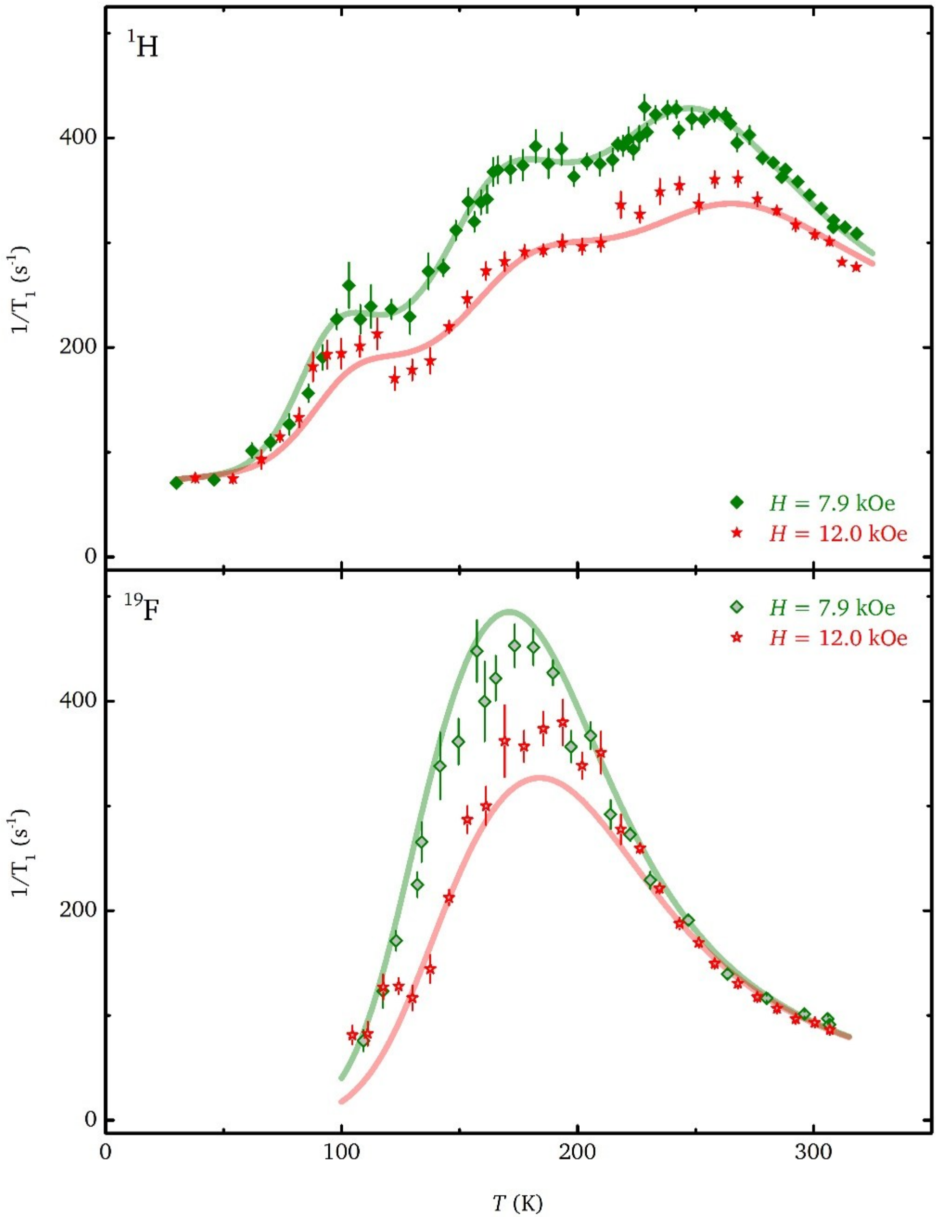


$La_{1-x}Sr_xCoO_3$



Prando *et al.*, *to be submitted* (2025); Kaminski, Das Sarma, *Phys. Rev. Lett.* **88** 247202 (2002); He *et al.*, *Phys. Rev. B* **76** 014401 (2007)

Summary



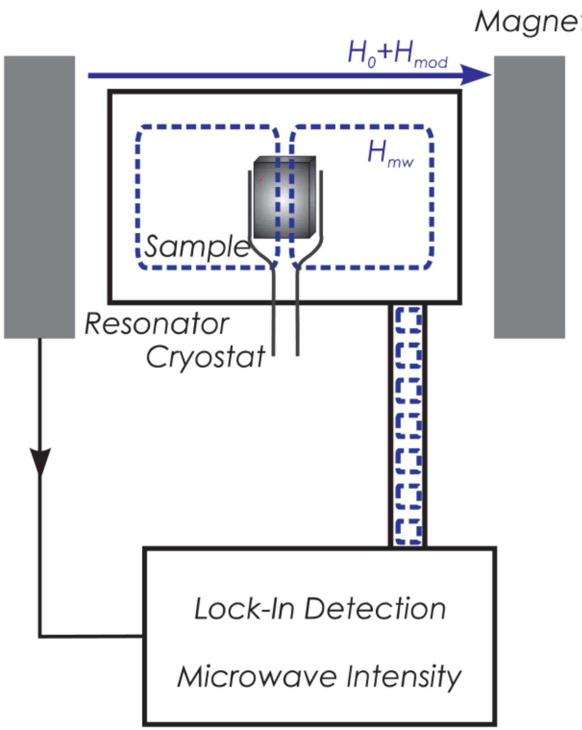
<u>Low temperatures</u>:
evidences of charge localization from electrical conductivity suggests the origin of the NMR relaxation.

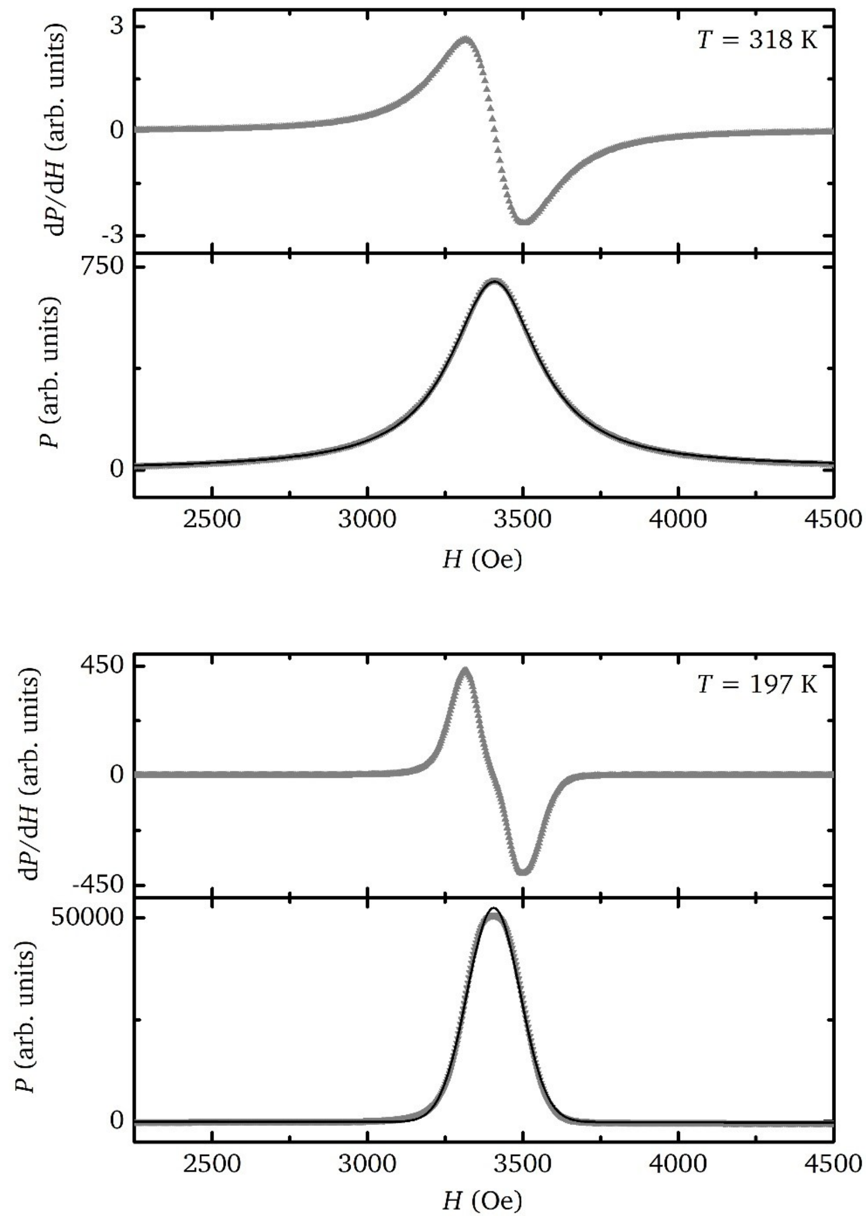
<u>Intermediate temperatures</u>:
rotary dynamics of triflate anion in a FM background drives relaxation on ^{19}F and on ^{1}H in turn.

<u>High temperatures</u>:
unusual persistence of slow dynamics tracked by NMR and muon-spin rotation. Likely origin in magnetoelectronic phase separation in the paramagnetic phase, resembling what observed in oxides.

Prando *et al.*, *to be submitted* (2025)

Ferromagnetic resonance (X-band)





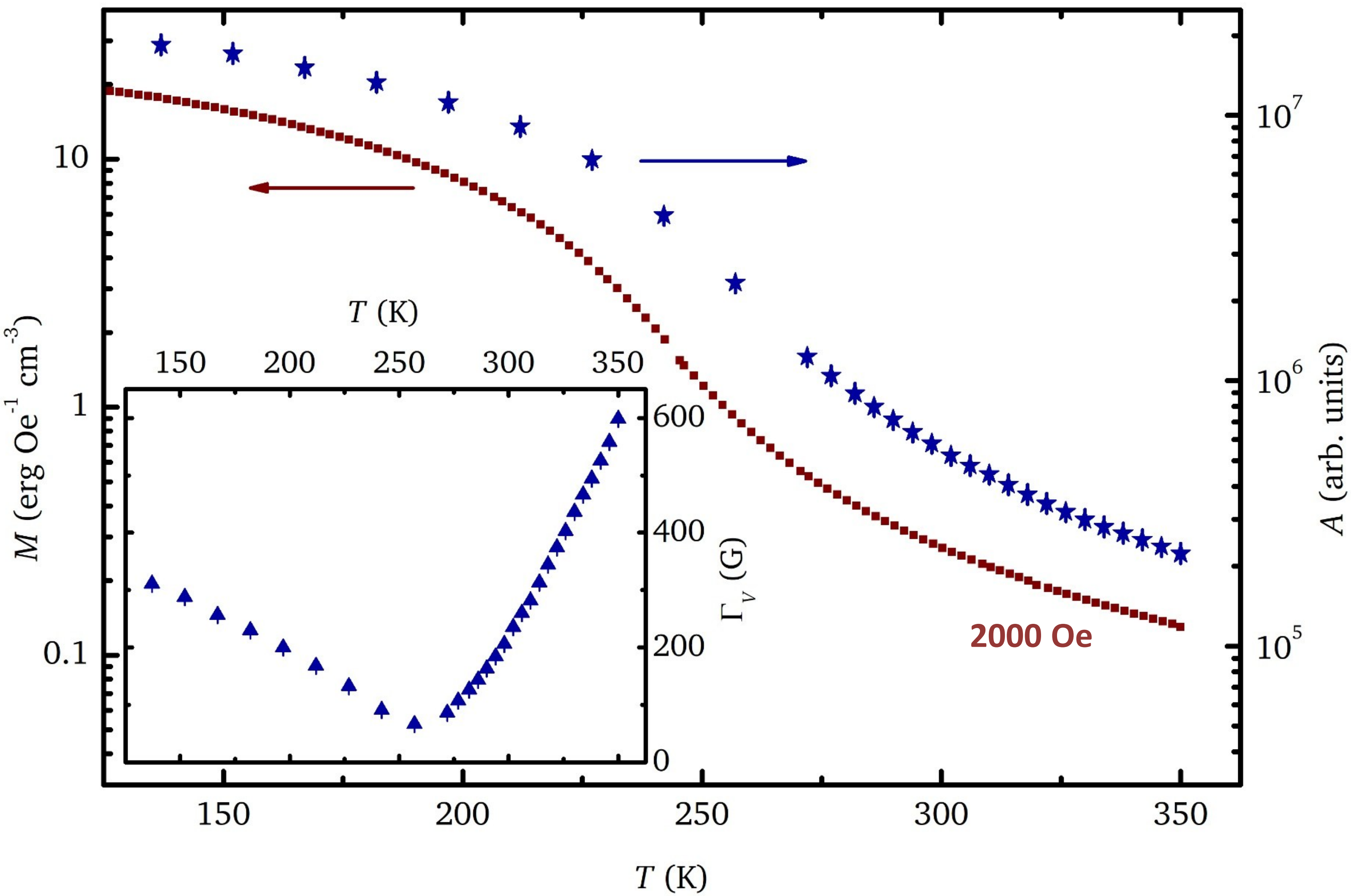
Voigt lineshape:

$$y = \frac{2A}{\Gamma_G}\left(\frac{\ln(2)}{\pi}\right)^{1/2}\frac{a}{\pi}\int_{-\infty}^{+\infty}\frac{\exp\left(-t^2\right)}{a^2+(\nu-t)^2}\,\mathrm{d}t + B\cdot H + y_0$$

$$a = \sqrt{\ln(2)}\,\frac{\Gamma_L}{\Gamma_G} \qquad \Gamma_V \simeq 0.5346\,\Gamma_L + \sqrt{0.2166\,\Gamma_L^2 + \Gamma_G^2}$$

Lipps, *Ph. D. Thesis* (2011); Prando *et al.*, *to be submitted* (2025)

Ferromagnetic resonance (X-band)



Conventional correlation between FMR amplitude and dc magnetization + conventional behaviour of lineshape.

No anomaly detected around 170 K. Nuclear relaxation not of magnetic origin at intermediate temperatures.

Prando *et al.*, *to be submitted* (2025)