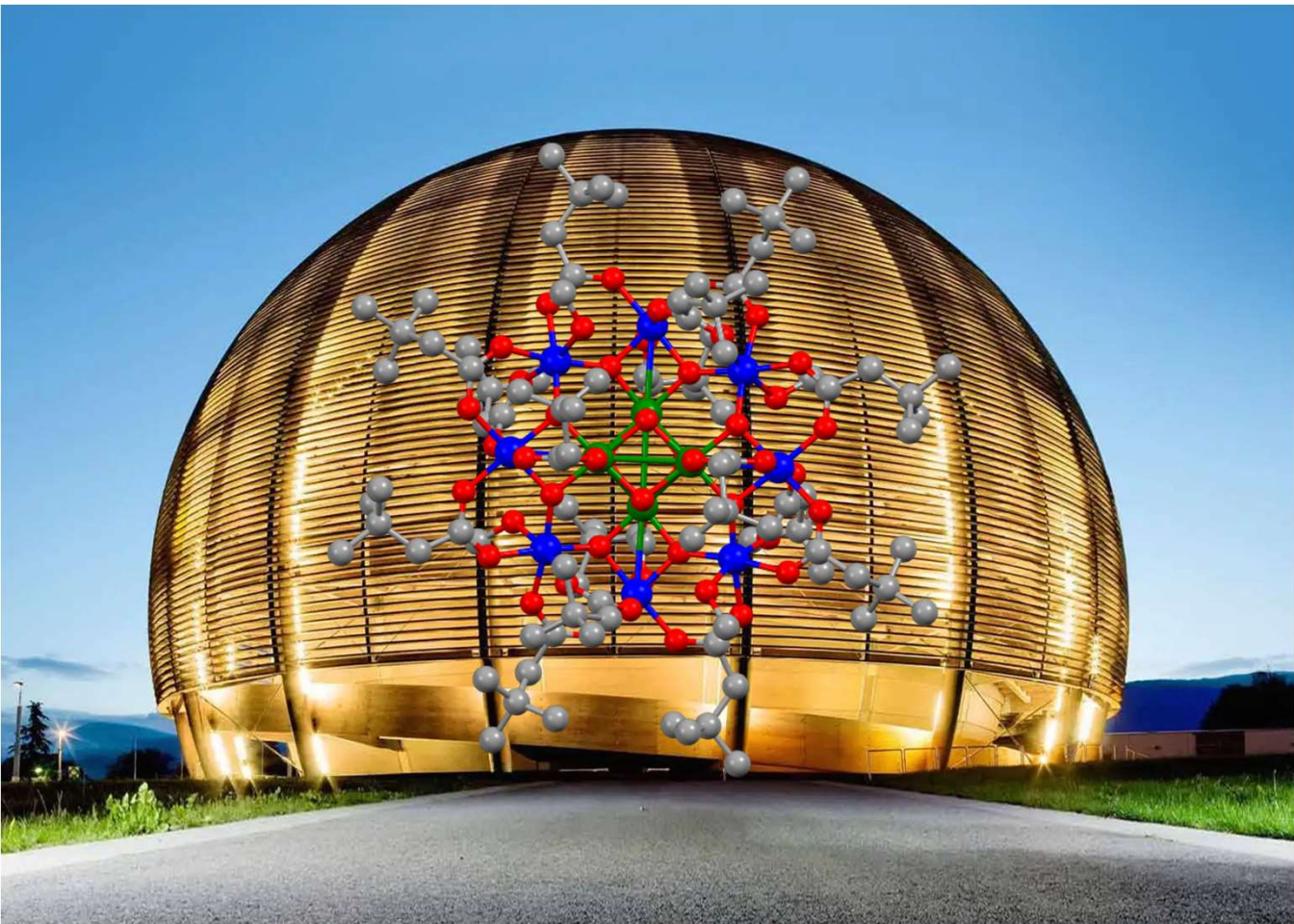


Magnetic Techniques for Quantum Sensing Using Single Molecule Magnets in the NAMASSTE Experiment



Giuseppe Latino

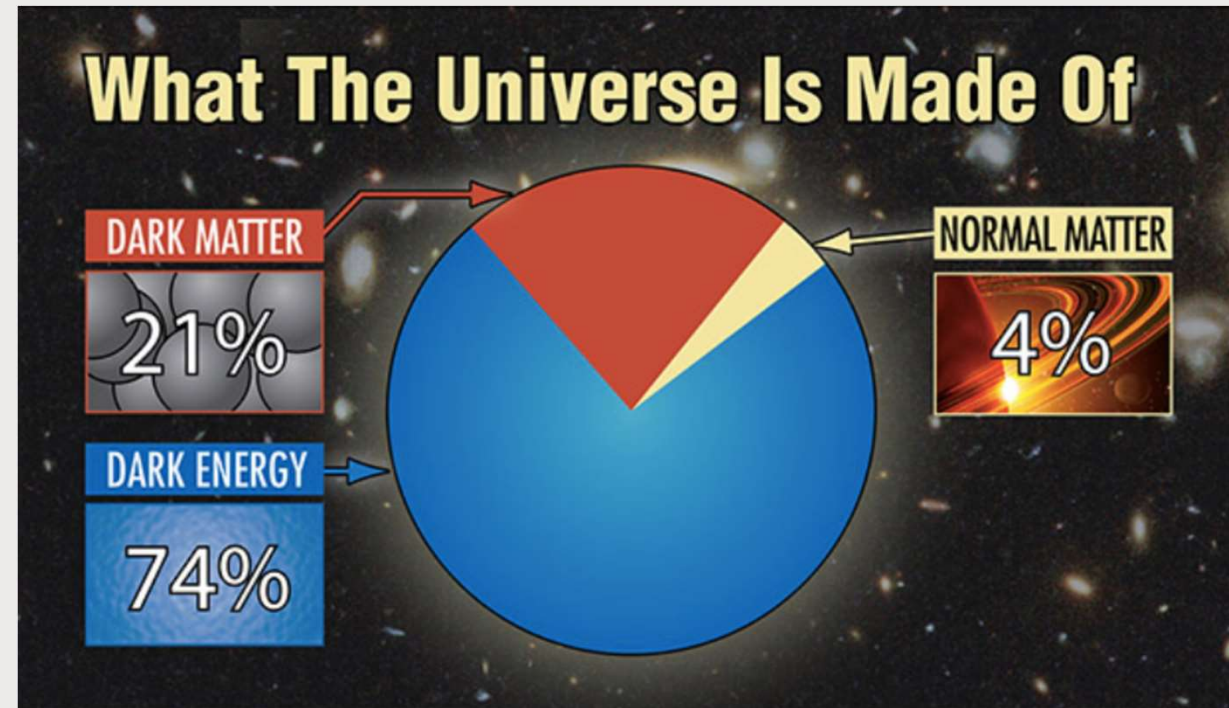
(Firenze University & INFN)

(on behalf of the NAMASSTE Group)

QT4HEP 2025
CERN – January 22th, 2025

The “Dark Side” of the Universe

Cosmological and astronomical observations:
indirect evidence for BSM Physics



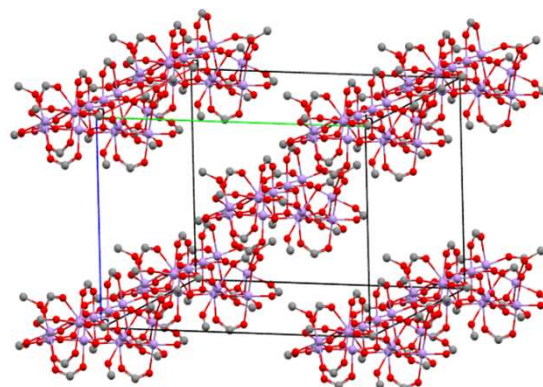
- No direct observation so far: M. Proust can be of inspiration for us
“The real voyage of discovery consists not in seeking new landscapes,
but in having new eyes” (M. Proust, ‘In Search of Lost Time’ - Vol. 5)
- **Need of new detection approaches allowing to go beyond current experimental limits
→ development of new techniques based on Quantum Sensing is a key example**



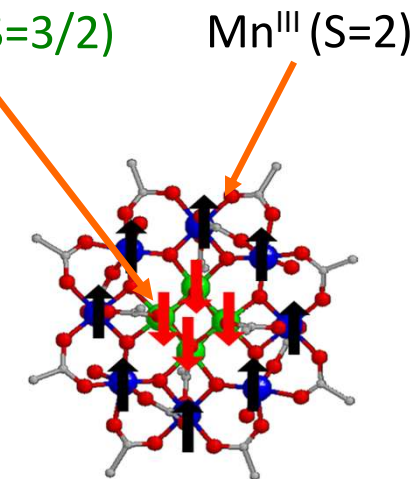
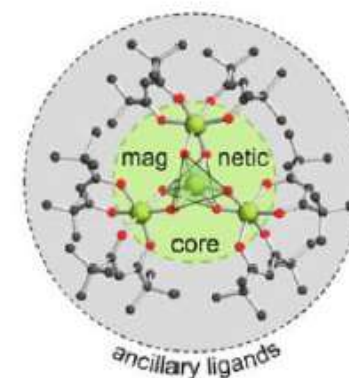
Single Molecule Magnets (SMMs)

SMMs are crystalline materials characterized by [1]:

1. Regular crystalline structure, made by identical molecules with a magnetic core of a finite number ($n > 1$) of paramagnetic centers, with strong intramolecular exchange interactions.
2. Molecules shielded by organic ligands → weak intermolecular interactions.



Mn₁₂ crystal



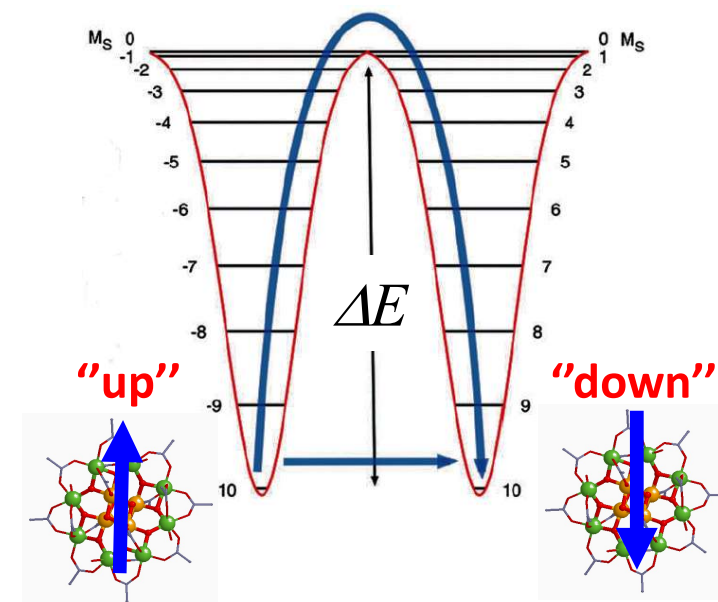
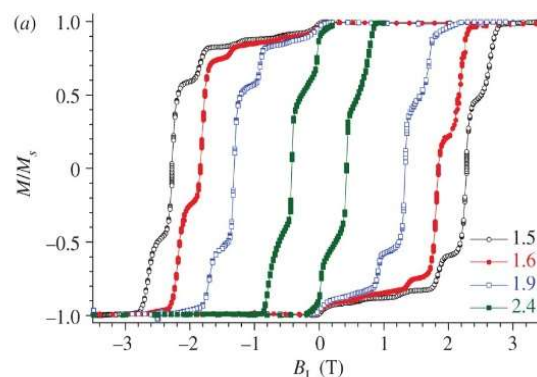
Mn₁₂ core

- Magnetically isolated molecules
- • High spin S value
- Strong uniaxial anisotropy → magnetic bi-stability at low T
- Quantum tunnelling of magnetization

“Reference” (the most studied) SMM, Mn₁₂:

$$S_{tot} = 10; \Delta E \approx 65 \text{ K}; \tau = \tau_0 \exp(-\Delta E/k_B T), \tau_0 \approx 10^{-7} \text{ s}$$

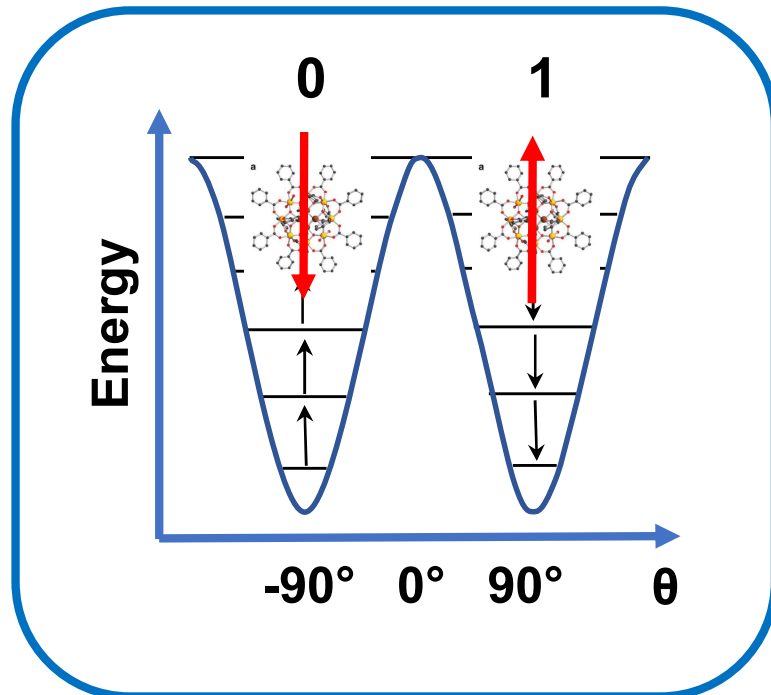
Relatively new materials with interesting potential applications



[1] Gatteschi, Sessoli, *Angew. Chem. Int. Ed.* 42 (2003)

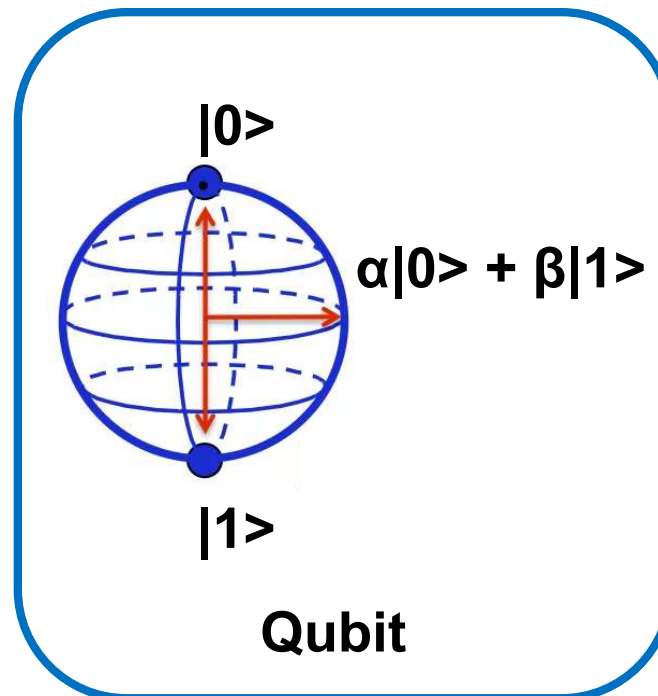
Potential Applications of SMMs

High-density memory storage [1]



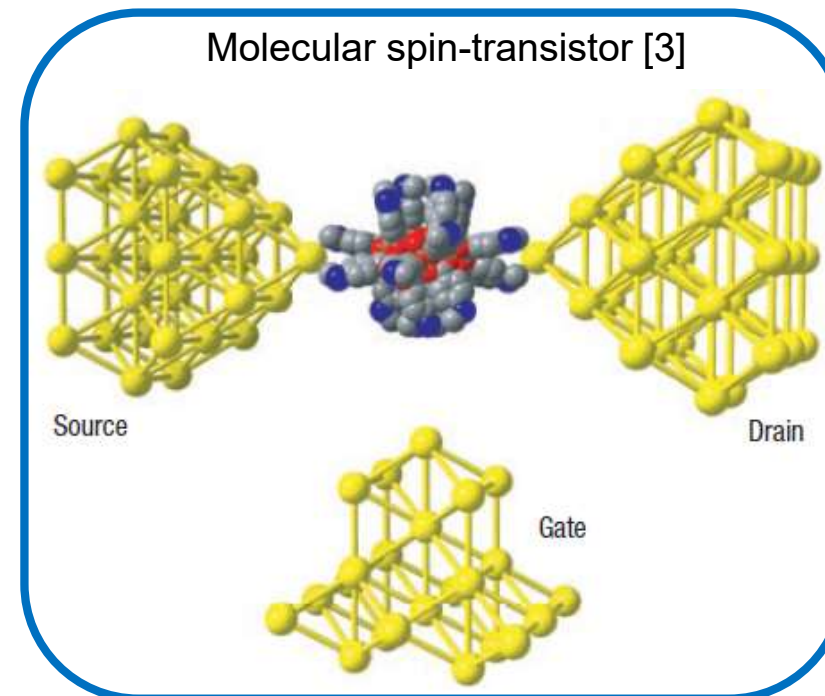
[1] Mannini *et al. Nat. Mater.* **8**, 194 (2009)

Quantum computing [2]



[2] Leunberger *et al. Nature* **410**, 789-793 (2001)

Molecular spintronics [3]



[3] Bogani *et al. Nat. Mater.* **7**, 179-186 (2008)

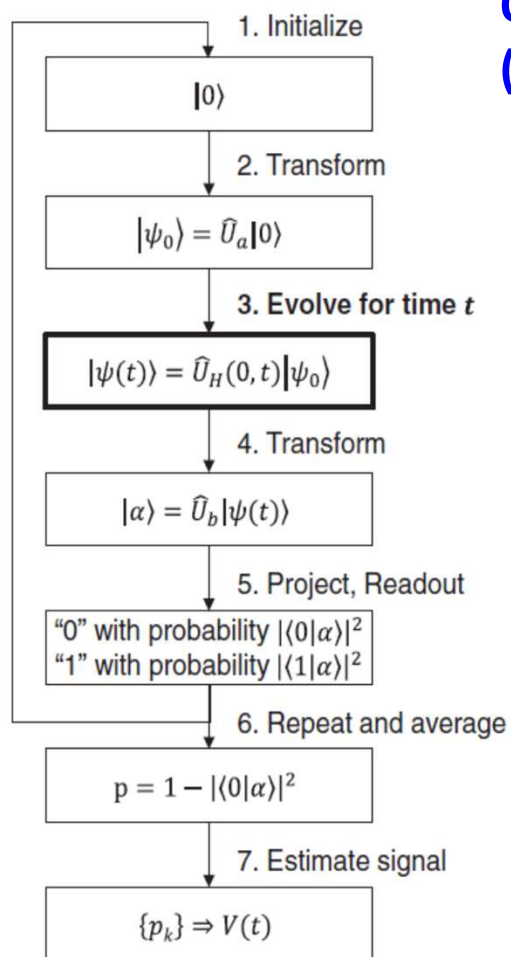


Quantum sensors for particle detection

→ Dedicated R&D activity required

Mn₁₂ SMM as Quantum Sensor

Quantum sensing experiments are typically performed following a basic methodology (“protocol”), which requires to manipulate and/or read out the quantum states of a system.



Quantum Sensor Hamiltonian: $H(t) = H_0 + H_s(t) + H_c(t)$

\nearrow “Internal” H \uparrow “Signal” H

← “Control” H (required to manipulate the sensor either before, during or after the sensing process)

Mn₁₂ Spin Hamiltonian if “no signal”: $H = H_0 + H_c$

$$H_0 \approx -DS_z^2 - AS_z^4 + H'$$

H': contains non axial (tunnelling) terms

$$H_c = -g_z \mu_B S_z B_z$$

Zeeman term obtained with a field B along the main crystal c-axis (easy axis)

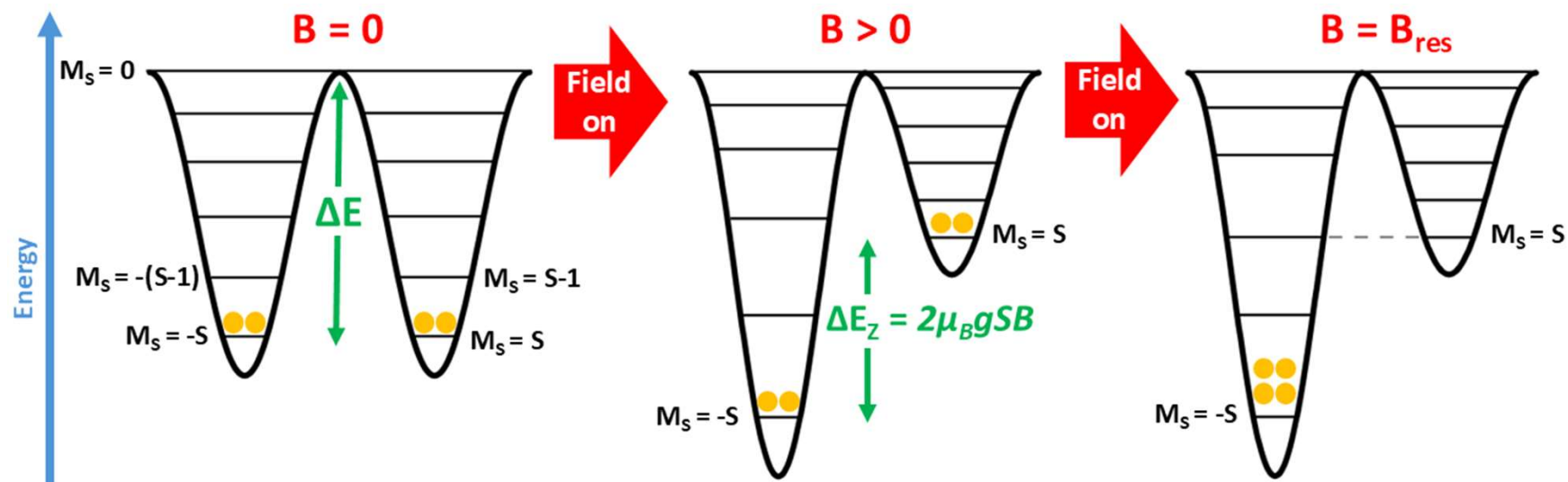


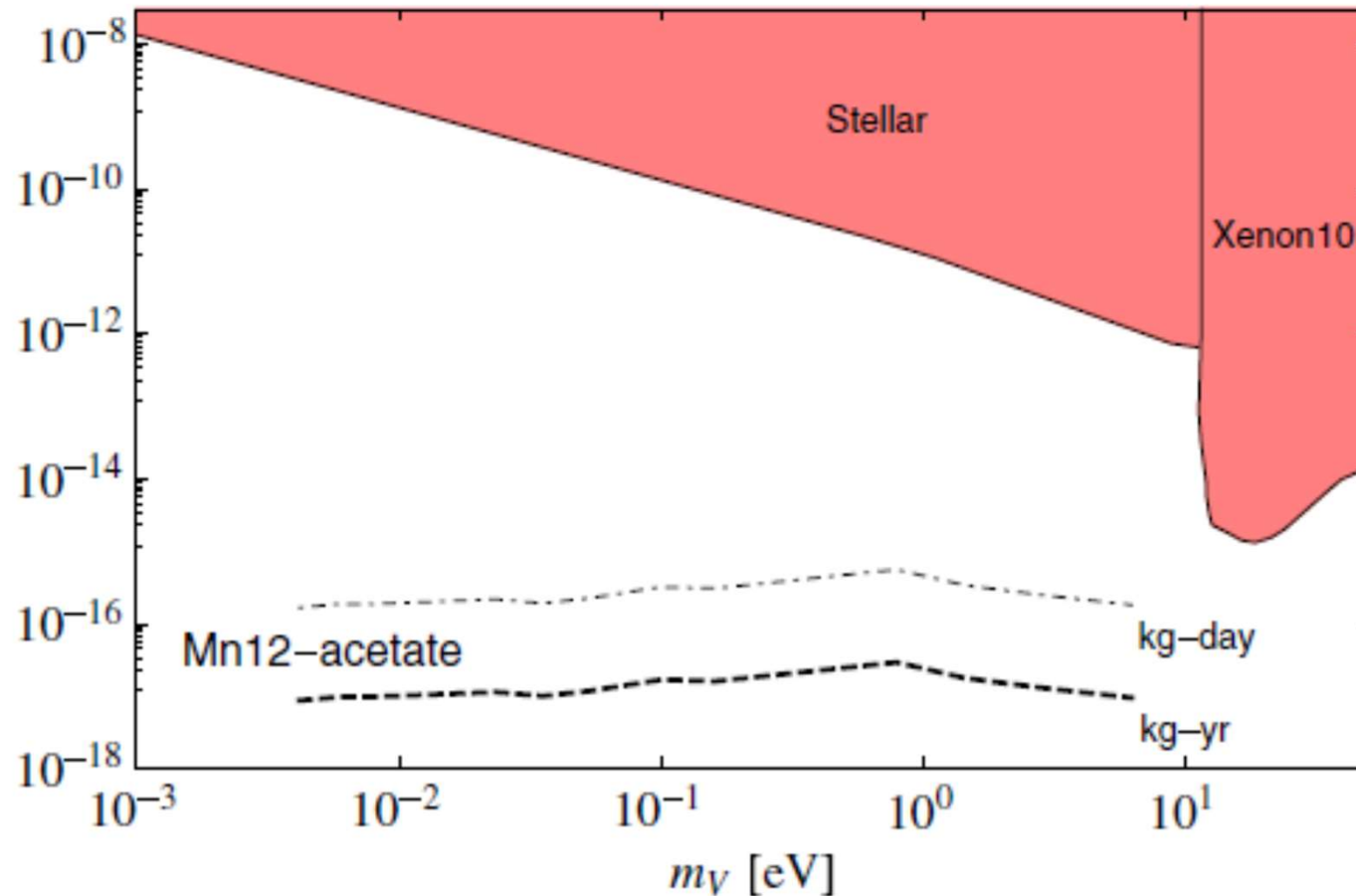
FIG. 2. Basic steps of the quantum sensing process. [1]

[1] Rev. Mod. Phys. 89, 035002 (2017)

Is Mn₁₂ SMM of Interest for Particle Physics ?

Bunting *et al.*, *Phys. Rev. D* 95, 095001 (2017):

Mn₁₂ SMM as sensor can detect Dark Photons at low masses, covering a region not yet experimentally explored with sensitivities exceeding current bounds



The tiny energy released by DM in the **meV-eV** energy range could match the fine structure of the SMMs energy levels, so exciting its intramolecular vibrational modes.

$$\mathcal{L} = -\frac{1}{4}F_{\mu\nu}^2 - \frac{1}{4}V_{\mu\nu}^2 - \frac{\kappa}{2}F_{\mu\nu}V^{\mu\nu} + \frac{m_V^2}{2}V_\mu V^\mu + eJ_{\text{em}}^\mu A_\mu$$

FIG. 6. Estimated sensitivity to absorption of dark vector DM in Mn₁₂-acetate, assuming an aggressive sensitivity of 1 event/kg year (dashed), and a sensitivity of 1 event/kg day (dot-dashed). The absorption data from Refs. [62,65] (described in the appendix) has been smoothed, an interpolation used in the region $m_V \sim 0.2\text{--}0.5$ eV, for which no data was available, and we use the approximation $\kappa \simeq \kappa_{\text{eff}}$ (see text).

But the potential for other applications in PP has yet to be fully investigated

The INFN R&D NAMASSTE Project

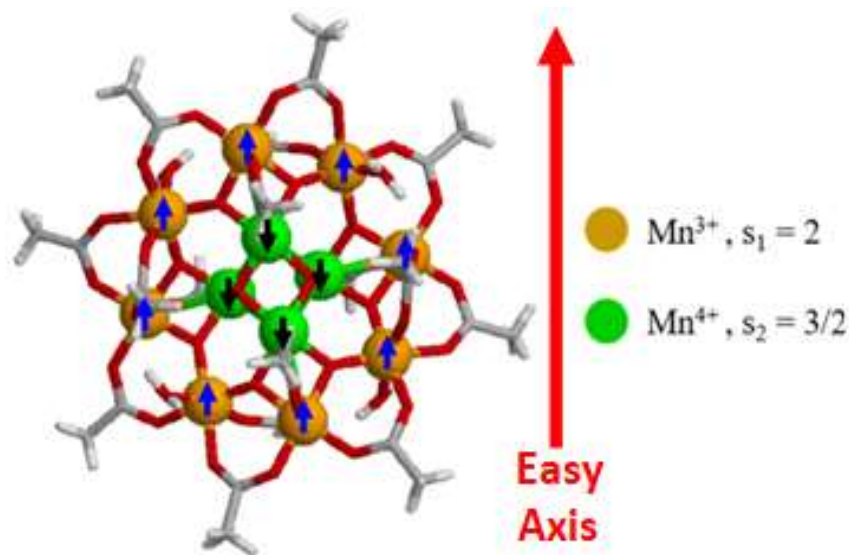
NAMASSTE: NanoMagnets for quantum Sensing and Data Storage

The project (financed by INFN, CSNV) aims to design, synthesize, and characterize new molecular nanomagnets for two different applications:

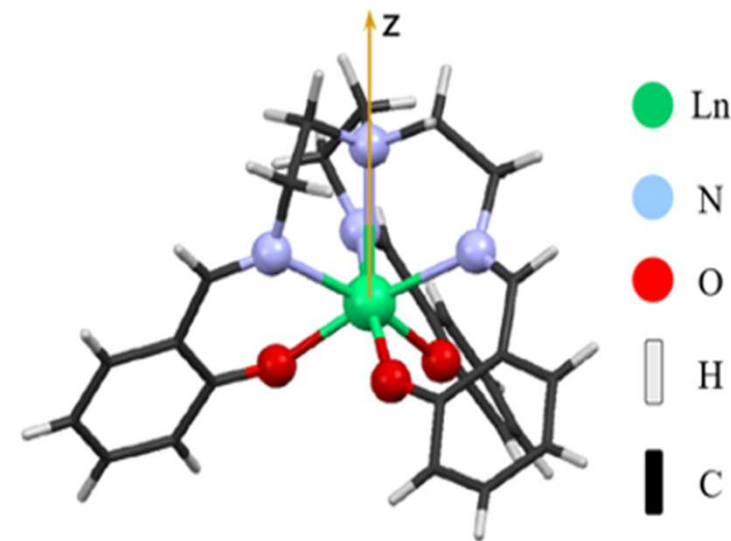
- **single molecule magnets (SMMs)**, for **high-sensitivity** sensors, potentially suited for revealing dark matter hidden photon [1],
- **single ion magnets (SIM)**, for **high-density** memory storage systems.

} Focus of this talk

Novel combination of experimental techniques: **Magnetometry (SQUID), NMR, EPR, μ -SR.**



Mn₁₂ SMM

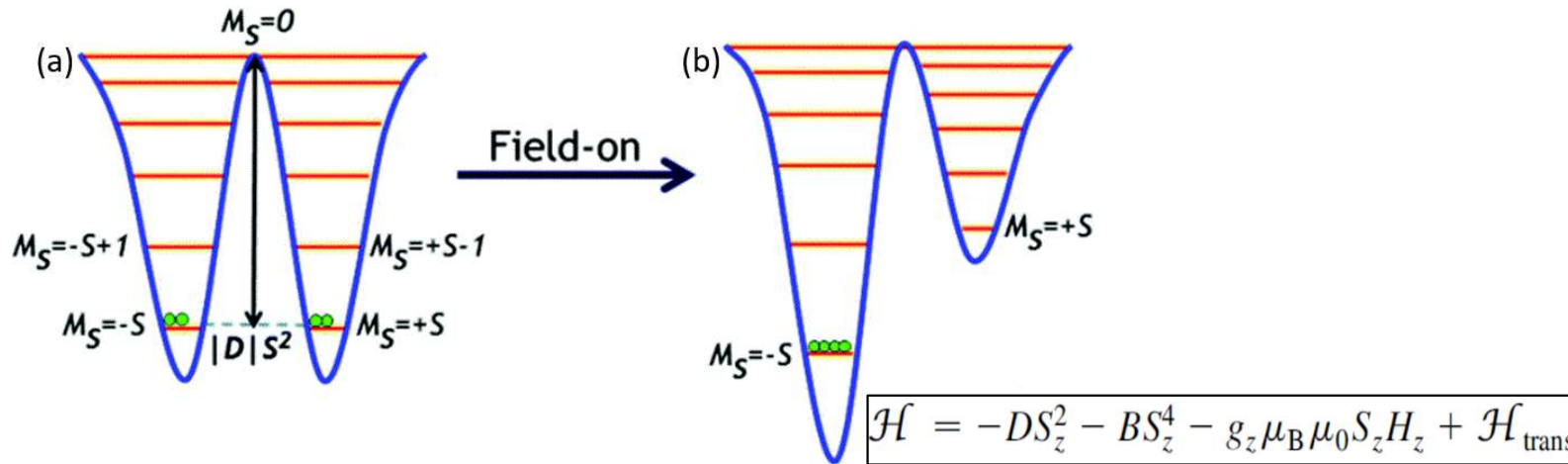


Ln-based SIM

[1] Bunting *et al. Phys. Rev. D* **95**, 095001 (2017)

Mn₁₂ SMMs as Sensors

Current detection approach [1]: an impinging particle may induce a "**magnetic avalanche**" in SMM crystals immersed in a magnetic field. This effect is triggered by the release of the Zeeman energy stored in the metastable states of the SMM in presence of an external magnetic field.



Preliminary study using α particles [2]: induced avalanches → **first evidence of Mn12 SMM as a sensor**

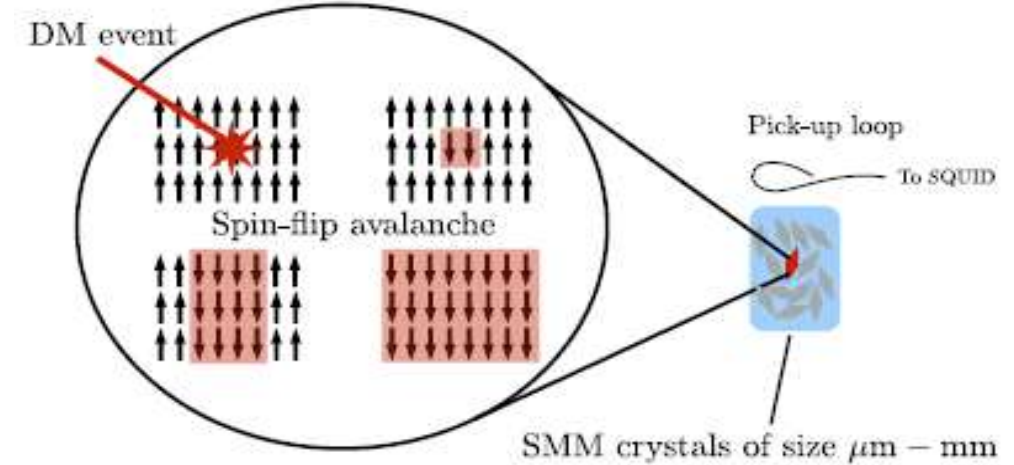
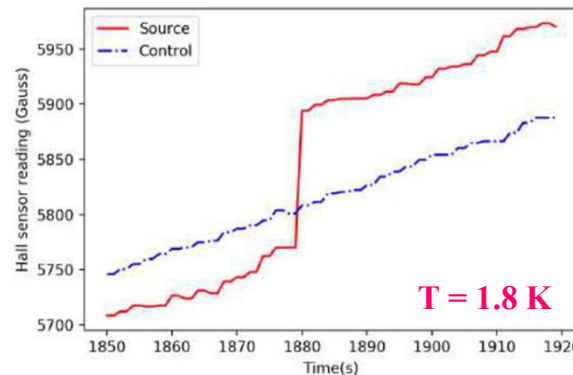
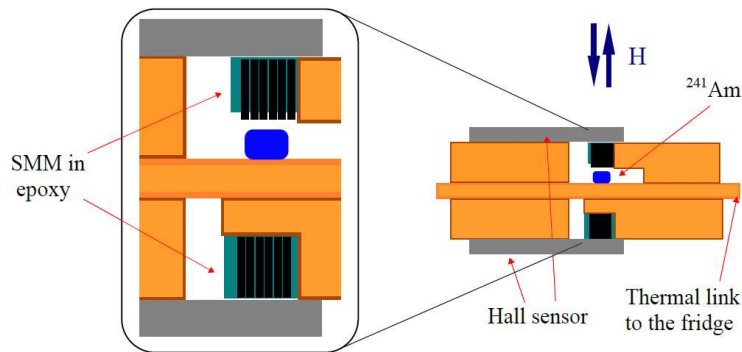


FIG. 1. DM detector concept based on magnetic deflagration in molecular nanomagnet crystals. A DM event that deposits energy in the form of heat ignites a spin-flip avalanche in the crystal which is detected by the change in magnetic flux through a pick-up loop.

[1] Bunting *et al.* *Phys. Rev. D* **95**, 095001 (2017)

AIM OF THE NAMASSTE PROJECT:

- reproduce and optimize the conditions for α -induced magnetic avalanches (of potential interest for **up-scaling** in sensing volume ...);
- possibly extend to β and γ ;
- **investigate other detection approaches.**

[2] Chen *et al.* arXiv:2002.09409v2

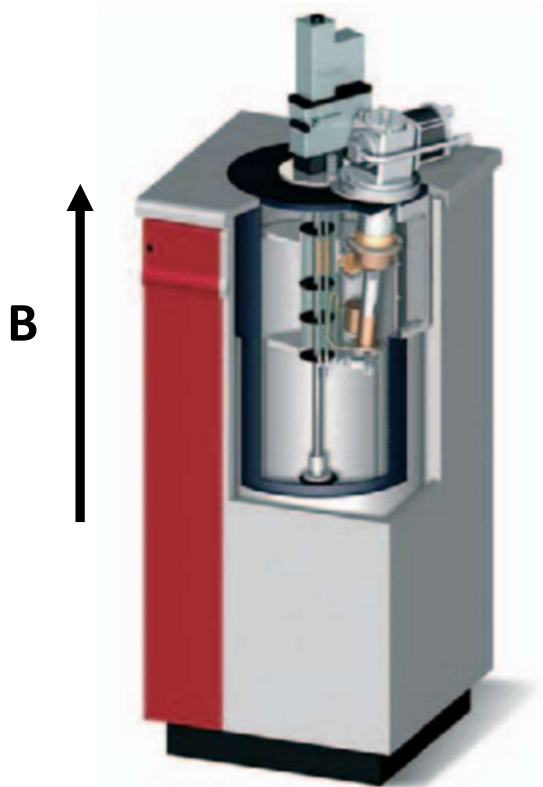
QT4HEP 25 – Jan. 22, 2025

G. Latino – Magnetic Techniques for Quantum Sensing Using SMM

NAMASSTE: Studies Related to Quantum Sensing

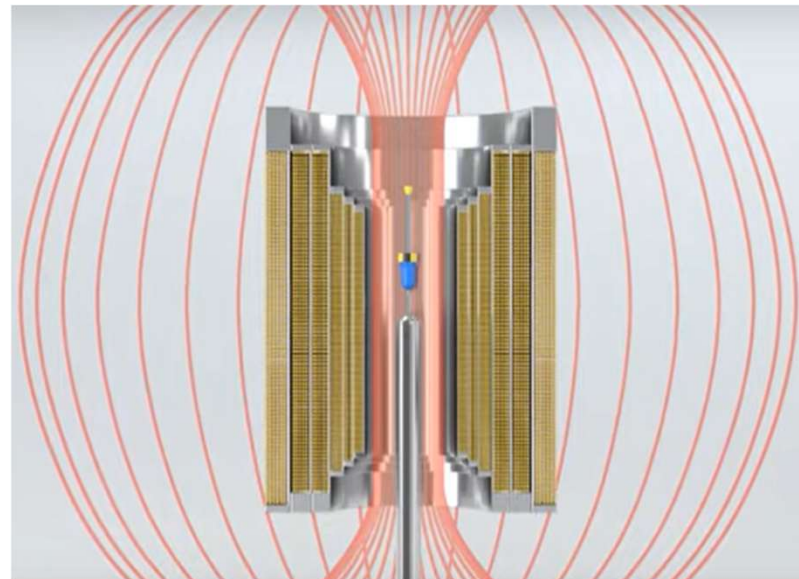
In NAMASSTE different techniques are used to study Mn_{12} in presence of **low activity** ionizing radiation sources

SQUID magnetometer



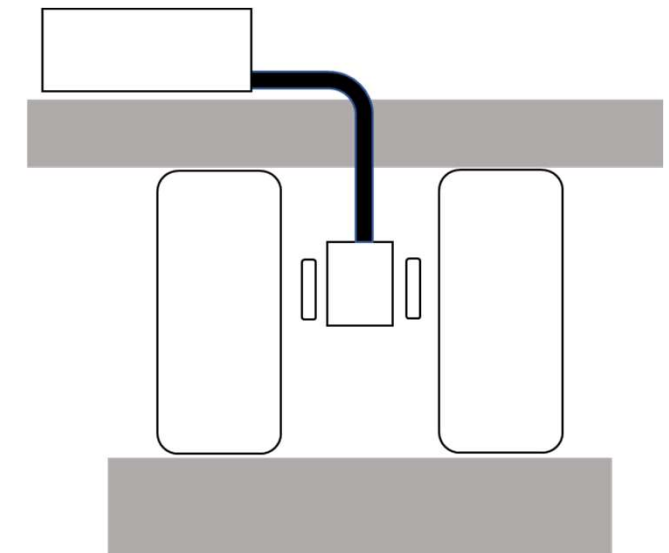
Measurement of the variation of the magnetization over the **entire volume** of the sensor: similar approach to the one reported in literature.

Nuclear Magnetic Resonance (NMR)



Local probe techniques: these approaches (based on the study of relaxation times) are expected to be **more sensitive** than the ones based on magnetometry.

X-band Electron Paramagnetic Resonance (EPR)



But Mn_{12} has $S = 10$
→ no intrinsic EPR signal ...

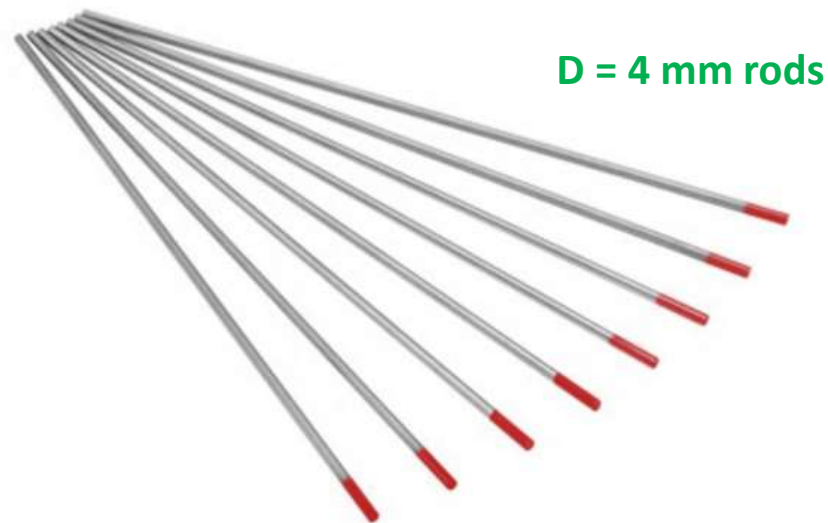
Radiation Sources for the NAMASSTE Experiment

Requirements: very low activity α sources to be adapted to the small dimensions of the involved instruments

Made from electrodes used for special welding (tungsten with **2% Th**), by precision machined cut to fit specific technical needs of the devices.

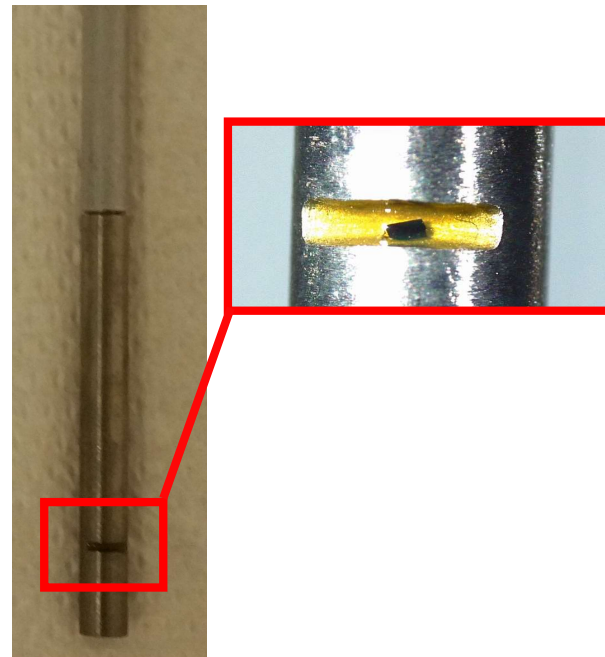
Measured surface activity:

- α (from prim./sec. decays) $\sim 0.2 \alpha /(\text{mm}^2 \text{ min})$
- β (from sec. decays) ~ 20 times α activity
- γ (from sec. decays) ~ 600 times α activity



Availability of similar non-radioactive electrodes (pure W), to be used for “reference” measurements without particle radiation in the same experimental configuration.

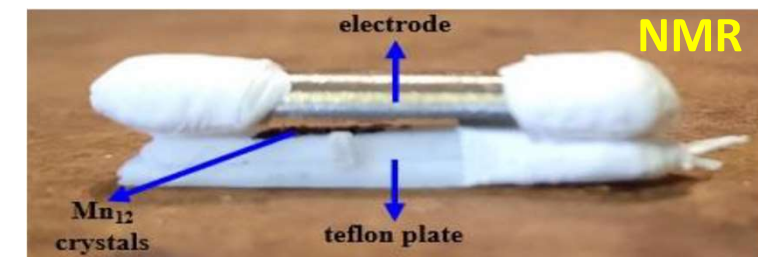
EPR-I: cylindrical geometry with small transversal cut



First approach, but:

- EPR signal very sensitive to position in cavity
- ~ 35 times reduction in EPR signal intensity w.r.t. using standard crystal sample holder

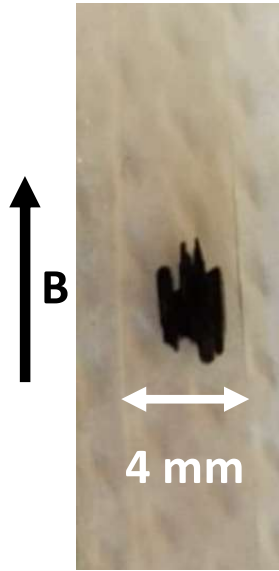
SQUID, NMR, EPR-II: semi-cylindrical geometry



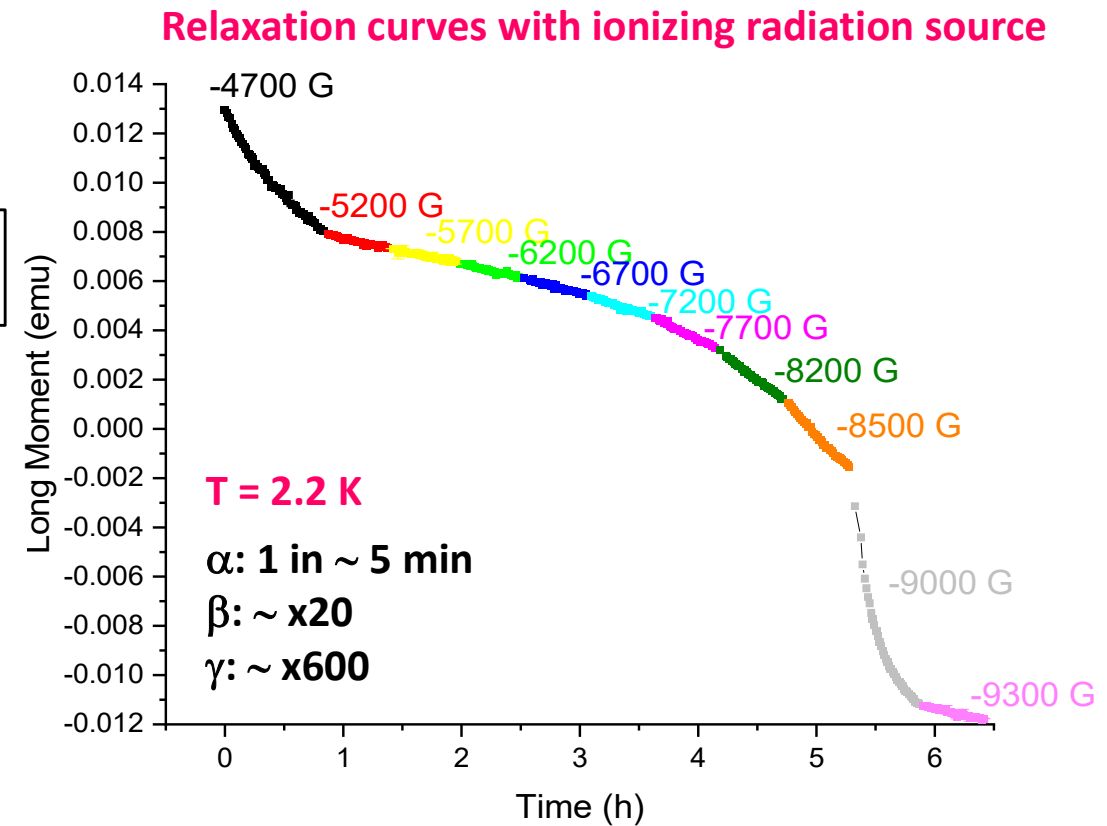
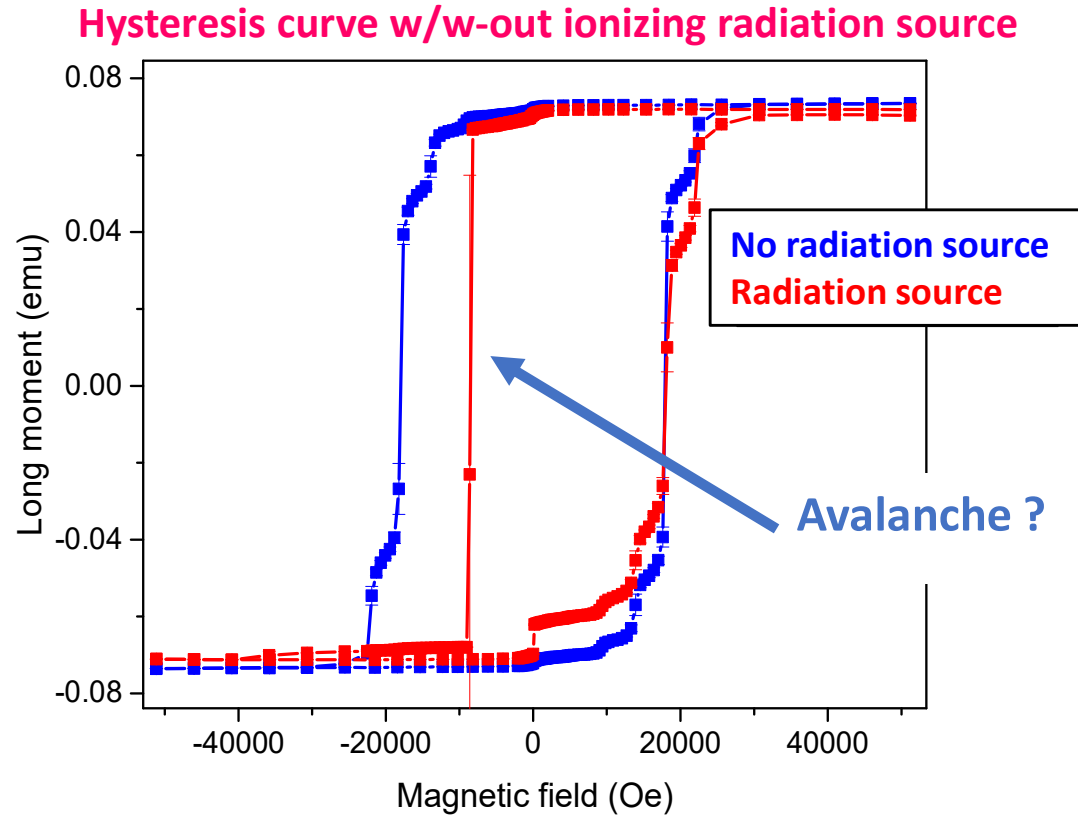
- Good signals w.r.t. standard crystal sample holders
- Only ~ 5 times reduction in EPR signal intensity

SQUID Magnetometry Studies on Mn₁₂

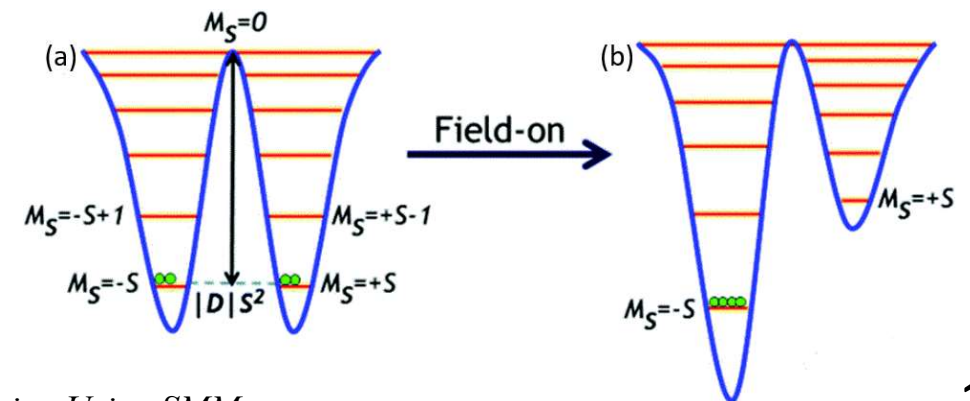
Goal: reproduce the results reported in literature (induced avalanches) and identify the optimal conditions to obtain them.



Crystals of Mn₁₂ with the easy-axis // to the external magnetic field



- As expected, the hysteresis loops show 'jumps' at suitable B values due to quantum tunnelling effects.
- Abrupt reversal of magnetization, compatible with 'avalanche' effects, observed only in one case during hysteresis loops.
- Further extensive relaxation studies did not show induced avalanches.



NMR Studies on Mn₁₂

Goal: introduce a new detection approach, using NMR-based techniques, by studying the recovery time of Mn12 crystals with/without irradiation.

Adopted technique [1]:

- acquisition of the echo signal intensity height (related to the magnetization of the crystal) as a function of time;
- measurement of the recovery time τ of the magnetization from the related fit.

[1] Jang *et al.*, PRL 84 2977 (2000)

Chosen protocol:

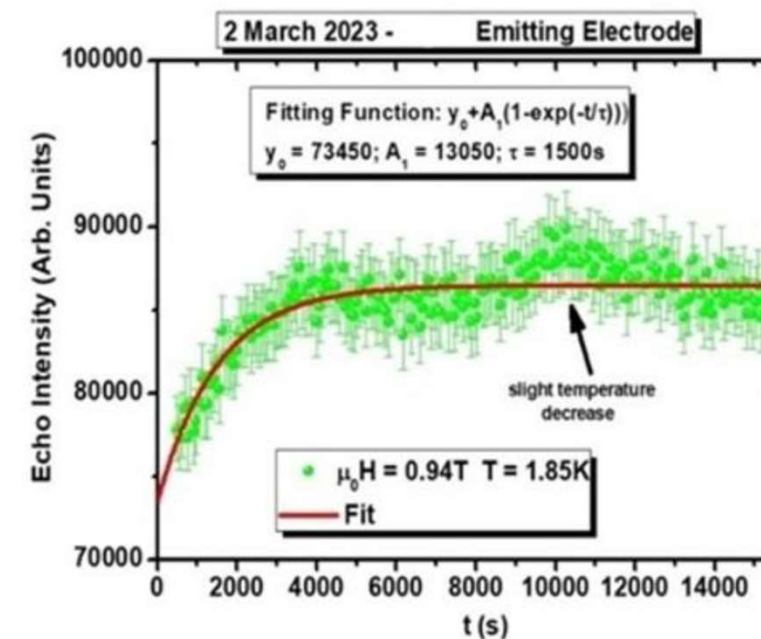
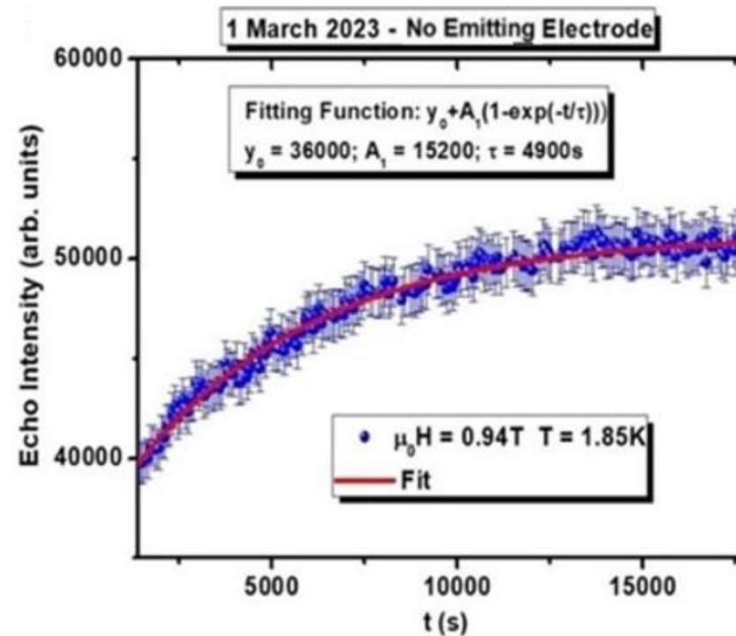
- Mn12 crystal cooled down to 1.85 K at B = 0 T,
- then put at fixed B = 0.94 T (2rd crossing);
- start the measurements to follow the M recovery.

Noticeable reduction in recovery time τ of M in presence of ionizing radiation

In order to establish a new detection method, based on studying perturbations on τ , further measurements and checks were performed to consolidate these results:

- at different B fields;
- similar studies with SQUID magnetometry.

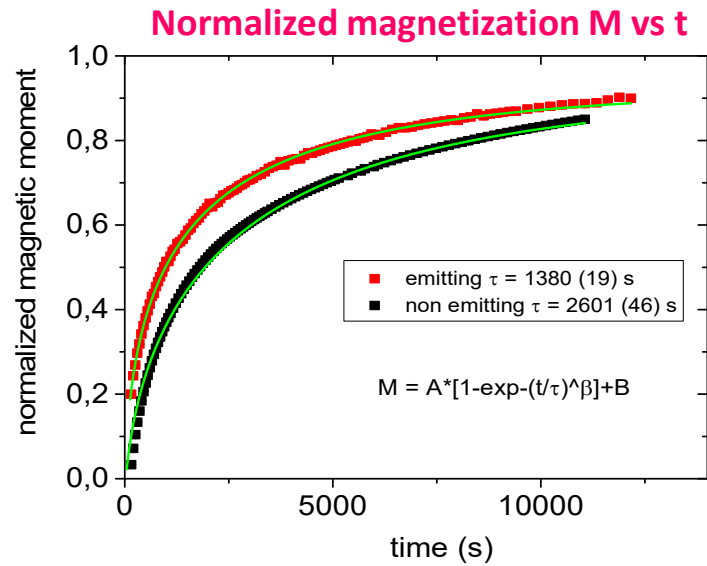
¹H NMR echo height *h* vs time



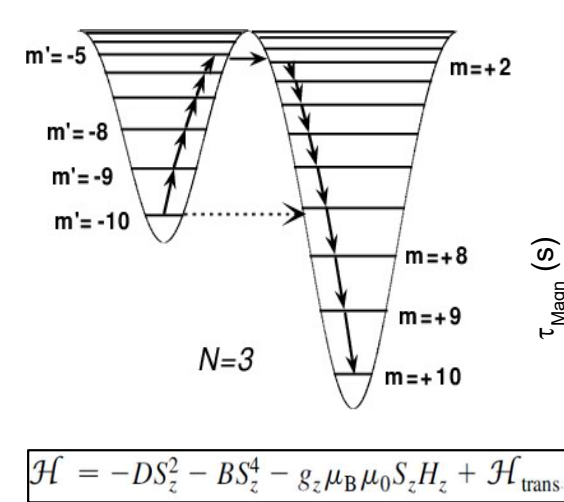
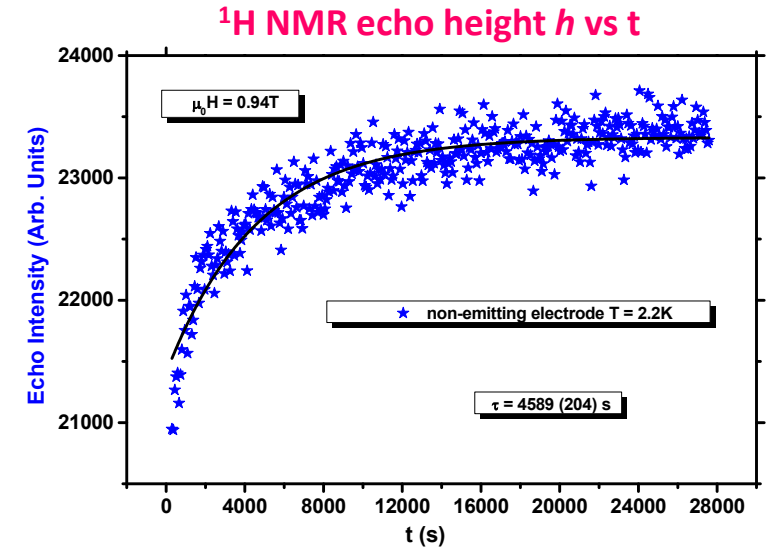
Run	No radiation source	Radiation source
September 2022	10400	3500
March 2023	4900	1500

Mn₁₂ SMMs as Sensors: Main NAMASSTE Results

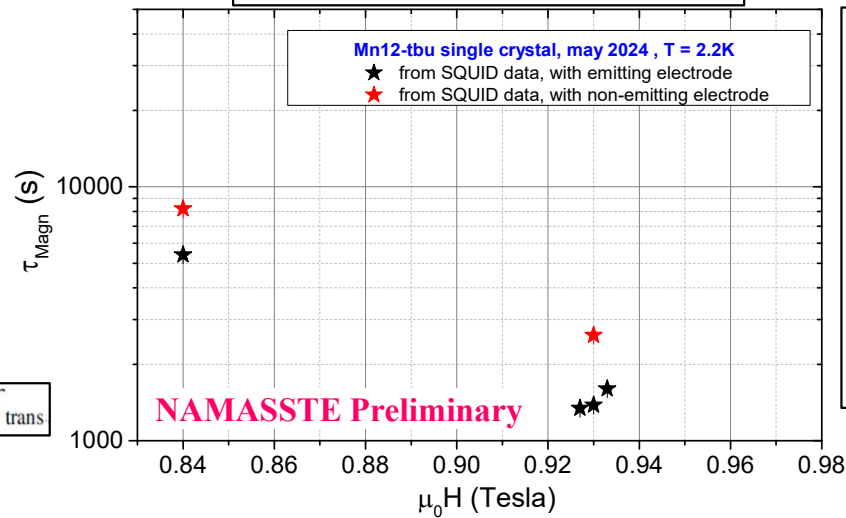
Quantum sensing based on NMR and SQUID measurements: studies on recovery times



M recovery:
SQUID
NMR

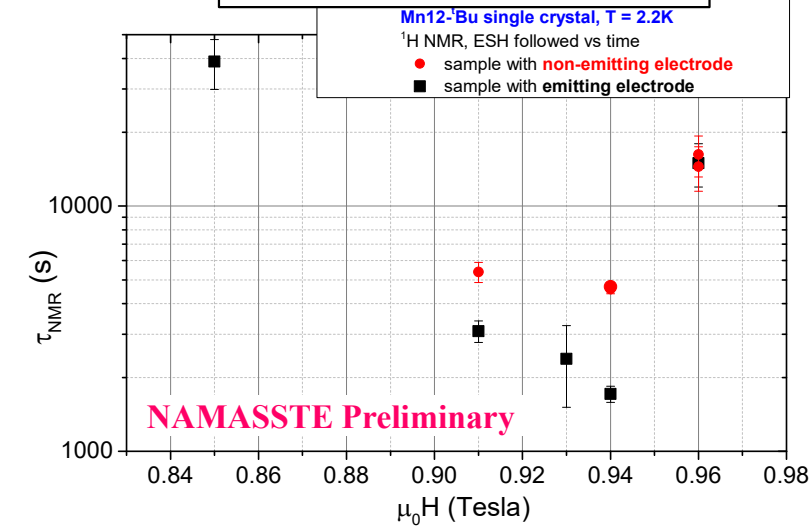


Recovery time τ vs field, by SQUID



In SQUID and NMR experiments, a reduction in magnetization recovery time is observed due to impinging radiation (α , β , γ):
ionizing radiation induces perturbations in Mn12 spin dynamics

Recovery time τ vs field, by NMR

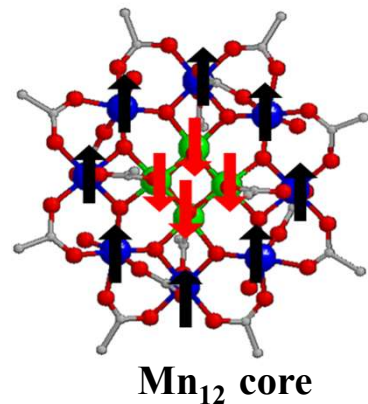


Magnetic Techniques for Quantum Sensing Using Single Molecule Magnets

(PRL, to be submitted)

Summary & Conclusions

- In the search for New Physics (ex. DM) the development of devices based on Quantum Sensing for Particle Physics can play a key role.
- The NAMASSTE R&D project investigated the possibility to use SMMs as QS by studying Mn₁₂ under the incidence of ionizing radiation with complementary techniques:
 - SQUID magnetometry studies did not show induced “avalanche” effects;
 - EPR-based measurements did not show changes in the EPR absorption spectrum;
 - NMR- and SQUID-based studies showed a clear reduction in recovery time of M (i.e. perturbation in spin dynamics) induced in Mn₁₂ by ionizing radiation:
 - introduction of a new detection technique, potentially opening to the use of SMMs as quantum sensors for particle detection.
- Further studies foreseen: to search for improvements and/or different sensing conditions and to properly understand (also via theoretical modelling) the SMM-radiation interaction
 - [Next_NAMASSTE INFN R&D Project](#)



Backup Slides

What “Quantum Sensing” Means?

“Quantum sensing” describes the use of a quantum systems, properties or phenomena to perform a measurement of a physical quantity.

Given quantum sensors (Qs) register a change of quantum state caused by the interaction with an “external system” their sensing capabilities are related to our ability to manipulate and/or read out its quantum states [1,2].

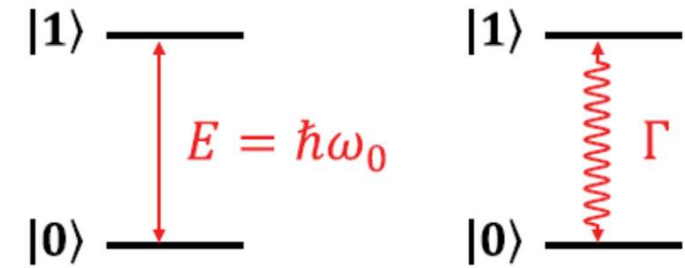


FIG. 1. Basic features of a two-state quantum system. $|0\rangle$ is the lower energy state and $|1\rangle$ is the higher energy state. Quantum sensing exploits changes in the transition frequency ω_0 or the transition rate Γ in response to an external signal V . [1]

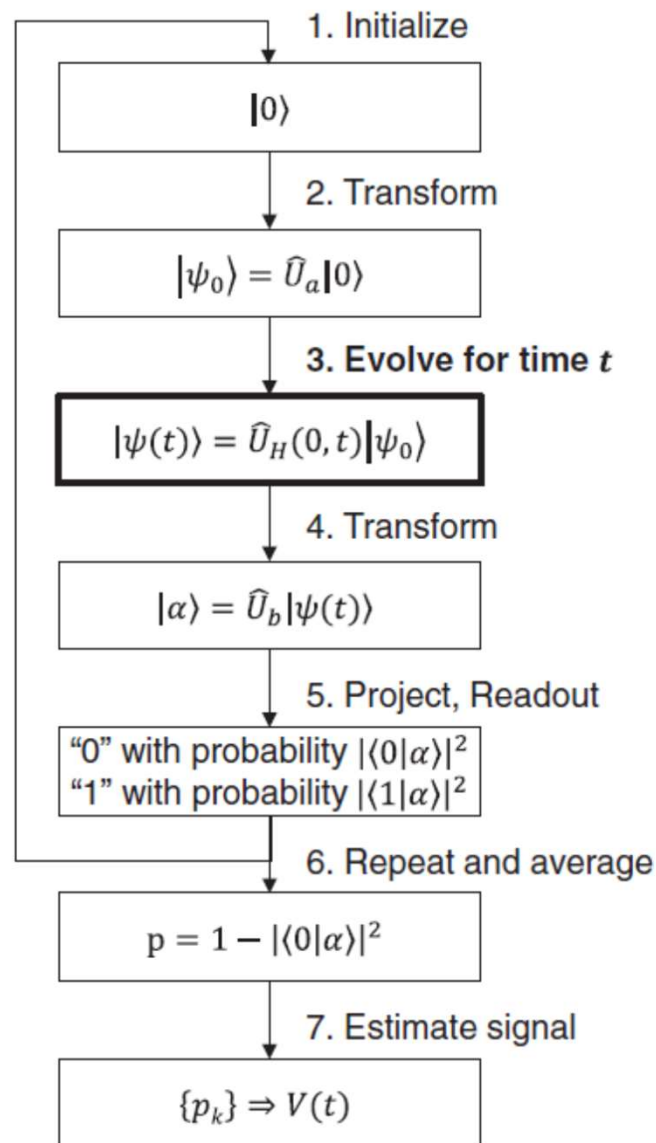
Involved energies very low, so QS very sensitive to external perturbations:

- Big potentialities as precision measuring devices: why not considering them in Particle Physics?
- Interdisciplinary (PP community, “Quantum” community, ...) R&D efforts and projects required.
- Already many quantum systems “on the market” to be characterized as quantum sensors.

[1] C. L. Degen *et al.* *Rev. Mod. Phys.* 89, 035002 (2017);

[2] S.D. Bass, M. Doser, *Nat. Rev. Phys.* 6, 329 (2024).

Quantum Sensing Basic Protocol



Quantum sensing experiments are typically performed following a basic methodology (“protocol”).

In a more generic scheme the quantum sensor:

- is initialized in a suited known state
- can be coherently manipulated
- interacts with a physical quantity (signal) for some time
- is read out (→ evaluation of transition probability)
- the physical quantity is reconstructed from the readouts (signal estimation)

The protocol can be optimized to detect weak signals or small signal changes with the highest possible sensitivity

Quantum Sensor Hamiltonian: $\hat{H}(t) = \hat{H}_0 + \hat{H}_V(t) + \hat{H}_{\text{control}}(t)$

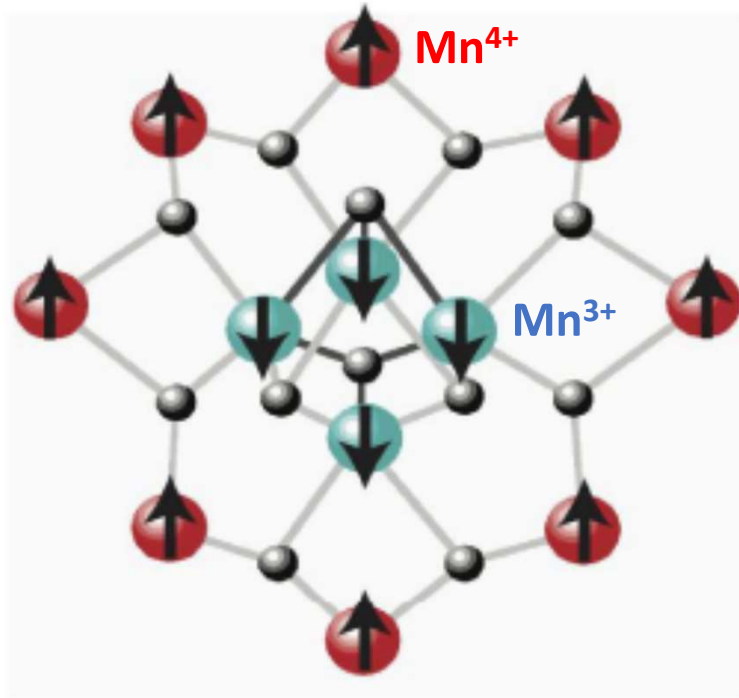
“Internal” H “Signal” H “Control” H

“Control” H required to manipulate the sensor either before, during or after the sensing process.

FIG. 2. Basic steps of the quantum sensing process. [1]

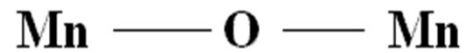
[1] Rev. Mod. Phys. 89, 035002 (2017)

Some Details on Mn₁₂ SMM (I)



[5] arXiv:1001.4194v2

The magnetic core of Mn₁₂-ac has 4 Mn³⁺ ($S = 3/2$) ions in a central tetrahedron surrounded by 8 Mn⁴⁺ ($S = 2$) ions. The ions are coupled by superexchange through oxygen bridges with the net result that the four inner and eight outer ions point in opposite directions, yielding a total **spin $S = 10$** . The magnetic core is surrounded by acetate ligands, which serve to isolate each core from its neighbors and the molecules crystallize into a body-centered tetragonal lattice. While there are very weak exchange interactions between molecules, the exchange between ions within the magnetic core is very strong, resulting in a rigid **spin 10** object that has no internal degrees of freedom at low temperatures.



Superexchange in MnO:
on each side the (O-Mn) electron couple has spin = 0 → the Mn on the 2 sides have opposite spin

Superexchange interaction through oxygen bridges →

- ferromagnetic coupling among the 4 inner Mn³⁺ and 8 outer Mn⁴⁺ ions.
- antiferromagnetic coupling among inner Mn³⁺ and outer Mn⁴⁺ ions.

Some Details on Mn₁₂ SMM (II)

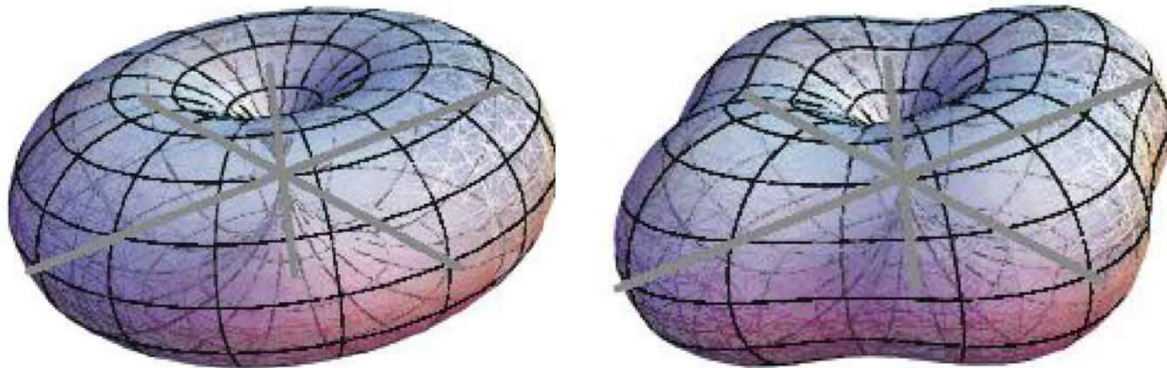
Mn₁₂ Spin Hamiltonian (in absence of an “external perturbation”)

$$H = H_0 + H_c$$

H₀ is the “internal Hamiltonian”: $H_0 \approx -DS_z^2 - AS_z^4 + H'$ (H': non axial contribution)
D = 0.548 K, A = 1.173·10⁻³ K

H_c is the “control Hamiltonian”: $H_c = -g_z\mu_B S_z B_z$ (Zeeman energy due to z-axis oriented magnetic field)
g_z = 1.94

H' contains non axial (tunnelling) terms: $H' \approx E(S_x^2 - S_y^2) + (C/2)(S_+^4 + S_-^4) - g\mu_B S_x H_x + \dots$
H_x due to any possible “internal” field



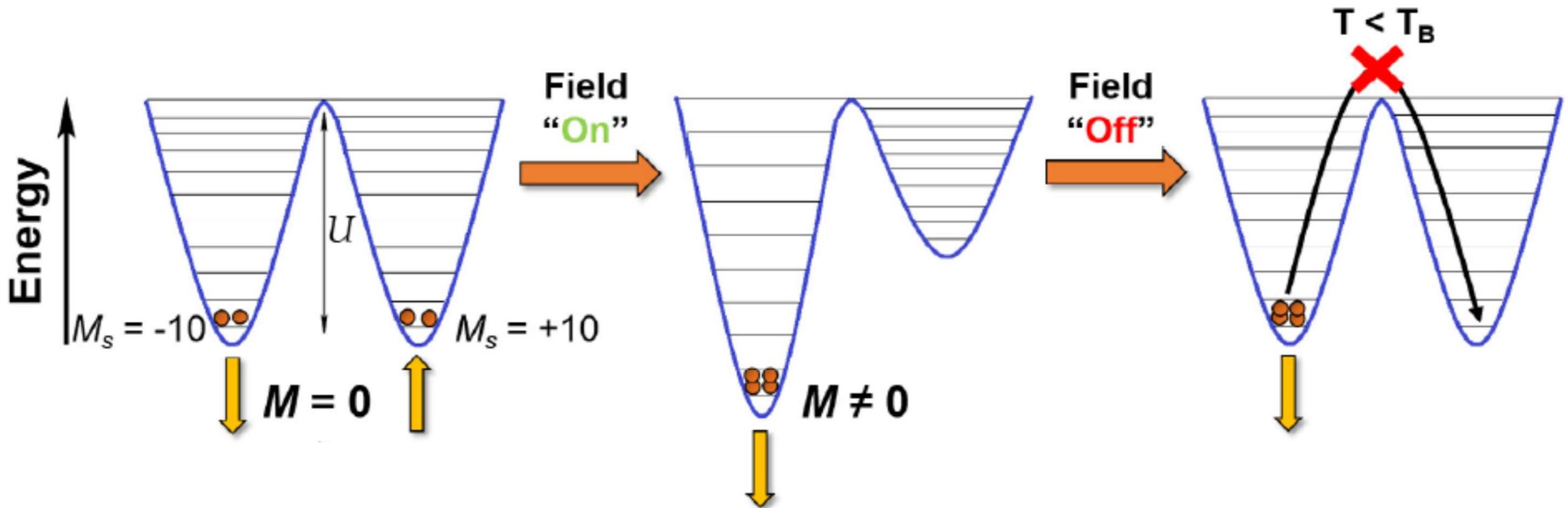
Left: spherical polar plots of energy as a function of orientation for a classical spin with uniaxial anisotropy.
Right: same as above, with additional fourth-order transverse anisotropy [1].

[1] Friedman and Sarachik, *Ann. Rev. Cond. Matt. Phys.* **1**, 109 (2010)

Some Details on Mn₁₂ SMM (III)

Control Hamiltonian $H_c = -g_z \mu_B S_z H_z$

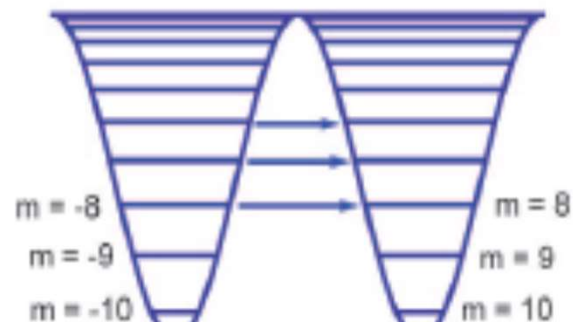
obtained with a magnetic field H oriented along the main crystal c -axis (easy axis)



Some Details on Mn₁₂ SMM (IV)

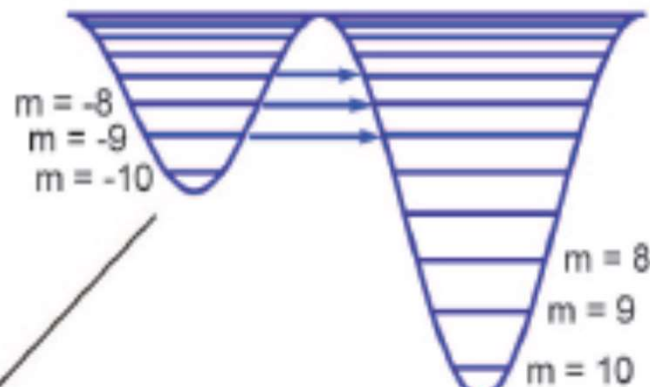
$$H = H_0 = -DS_z^2 - AS_z^4 + H'$$

N = 0



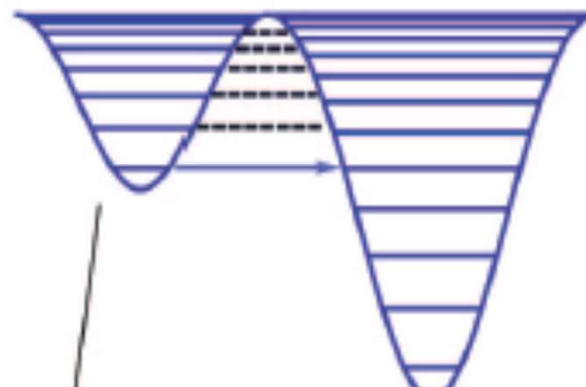
$$H \approx -DS_z^2 + H' + H_C$$

N = 4



$$H = -DS_z^2 - AS_z^4 + H' + H_C$$

N = 4

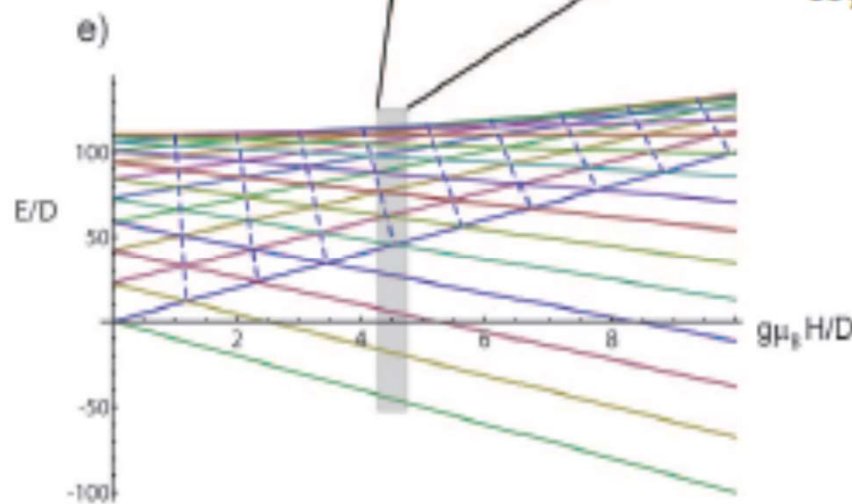
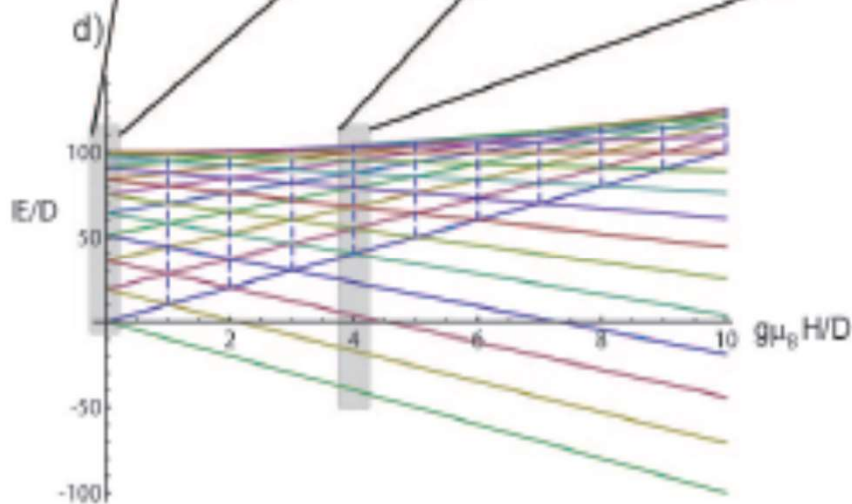


Energy levels “align” if:

$$H_N = ND/g_z\mu_B \quad \text{for } A = 0$$

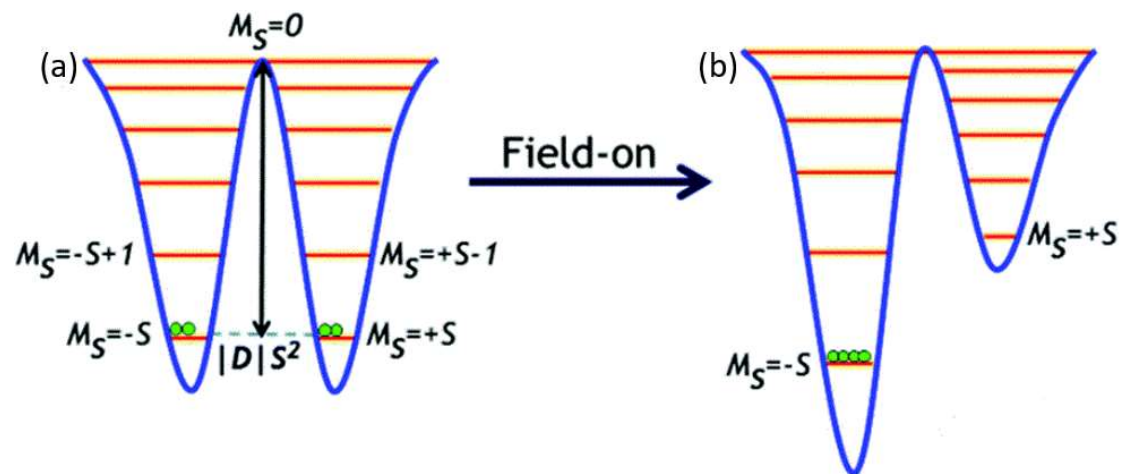
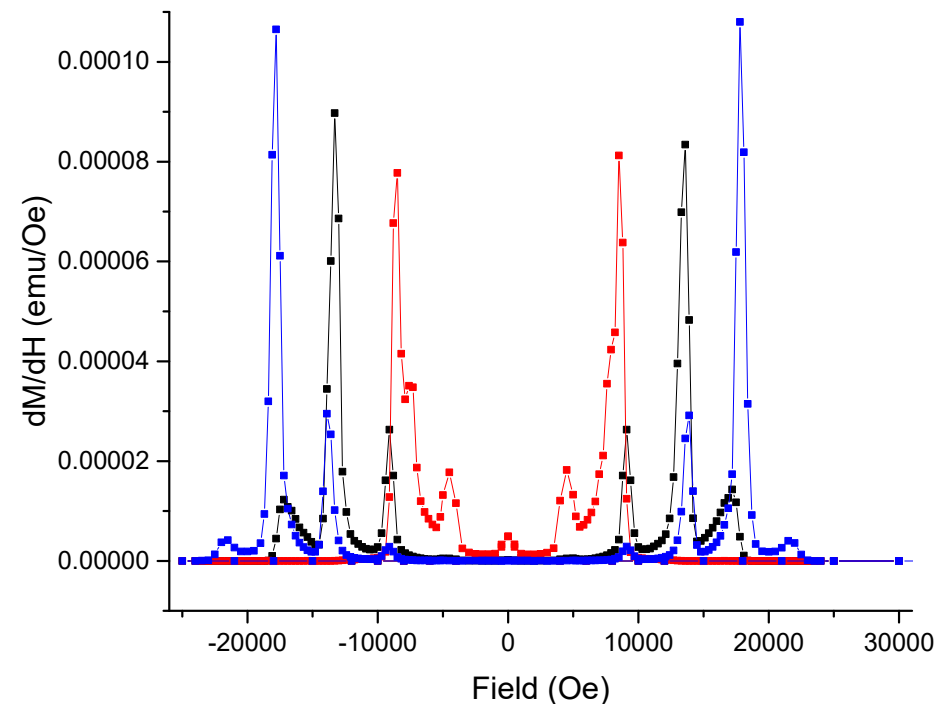
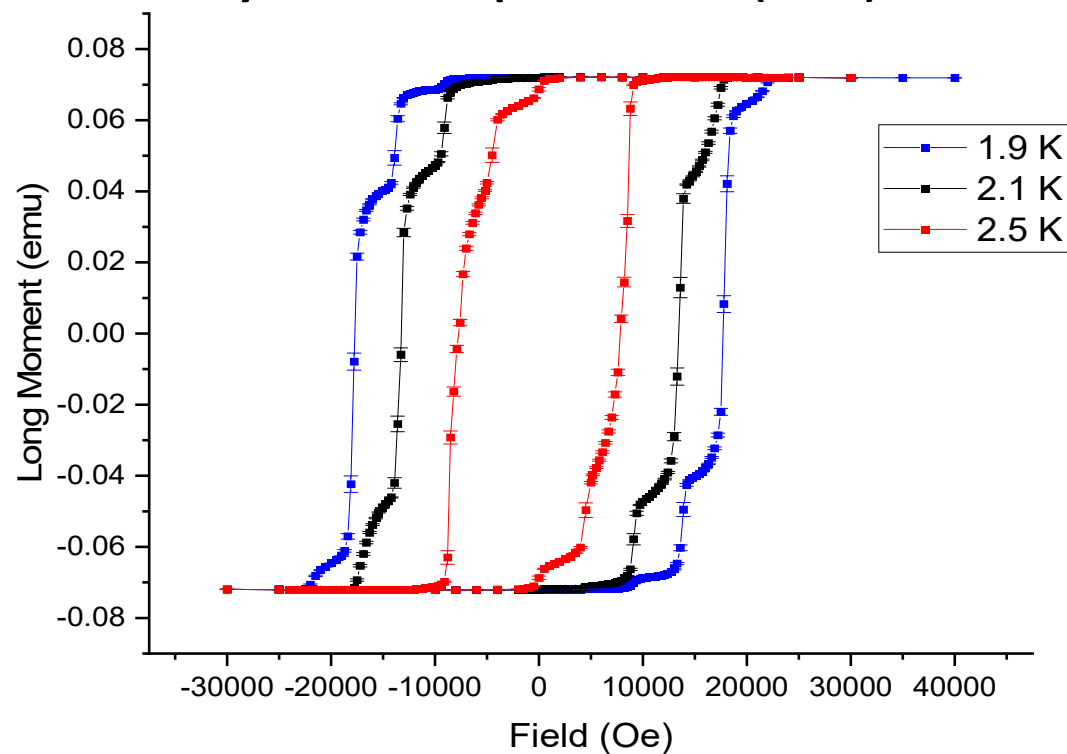
$$H_{m',m} = \frac{D(m' + m)}{g_z\mu_B} \left[1 + \frac{A}{D}(m'^2 + m^2) \right]$$

for $A \neq 0$ ($N = m' + m$)



Macroscopic Quantum Effects in Hysteresis Loops

Hysteresis loops on Mn12 (no α) at different T

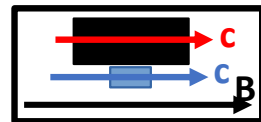
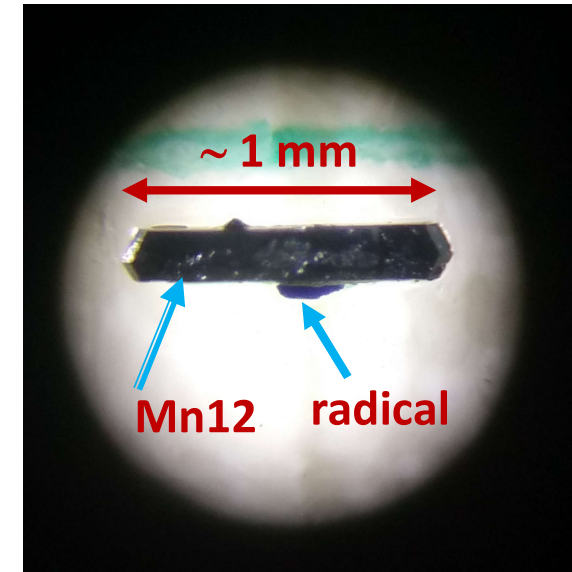
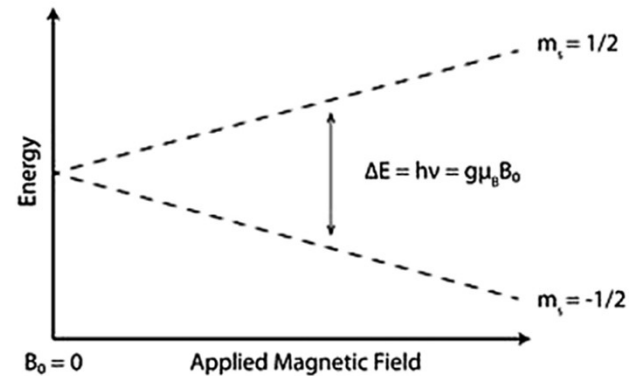


- 1° jump = 0 Oe
- 2° jump = 5000 Oe
- 3° jump = 9100 Oe
- 4° jump = 13900 Oe
- 5° jump = 17800 Oe
- 6° jump = 21500 Oe

Electron Paramagnetic Resonance (EPR) Studies on Mn12

Goal: investigate the possibility to introduce a new detection approach, based on EPR techniques, by studying the behaviour of Mn12 crystals with/without irradiation.

EPR: absorption spectroscopy technique used to study chemical species with unpaired electrons; the details of EPR spectra depend on the electron interaction with the nearby environment (in our case, with the Mn12 magnetization).



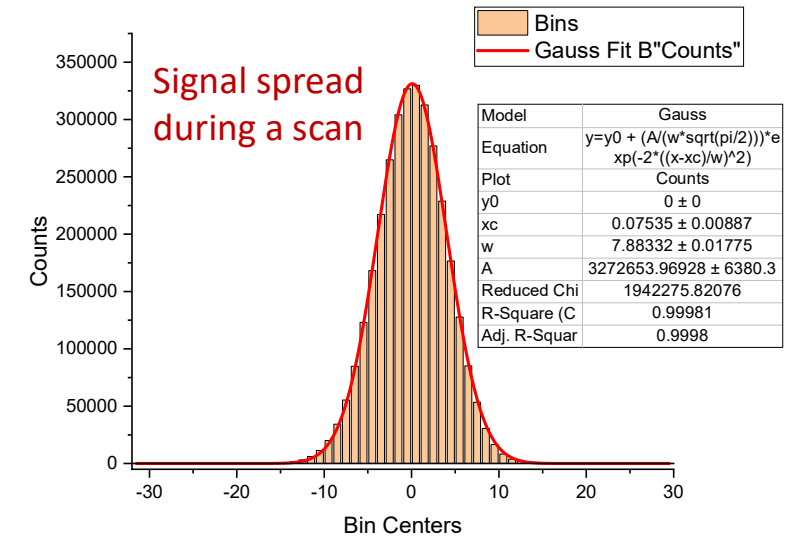
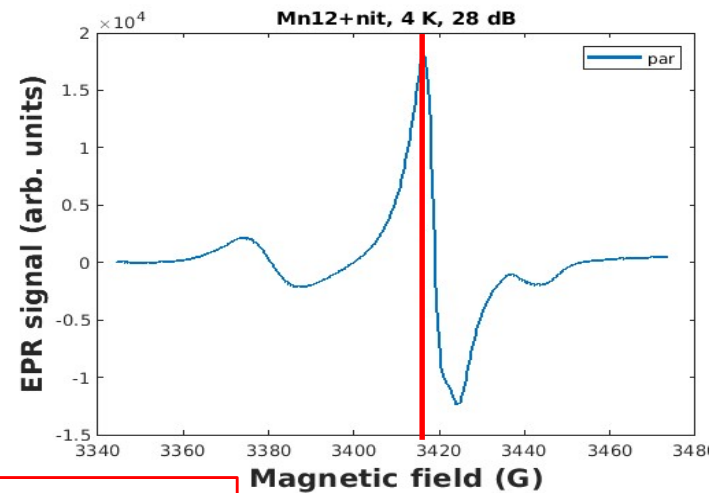
Adopted technique [1]:

- Mn12 does not show an intrinsic EPR signal at the frequencies of the available device (X band).
- Then couple the Mn12 crystal to a radical crystal (specifically: NitPBAh, an organic radical), so to have an EPR signal sensitive to variations in Mn12 crystal magnetization.

[1] Rakvin *et al.*, Jour. of Mag. Res., 165 (2003) 260-264

Chosen protocol (device driven):

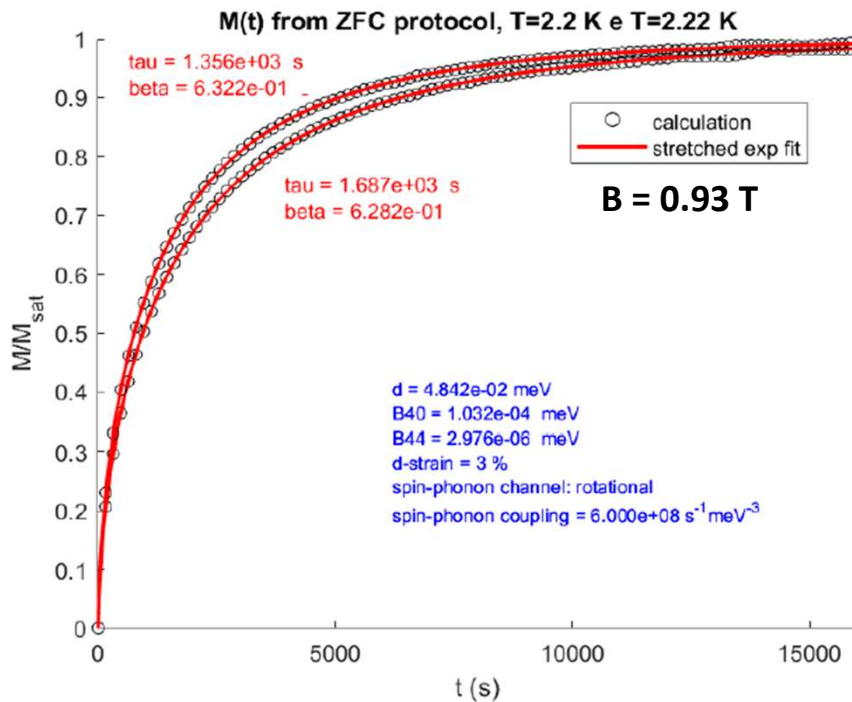
- Mn12+radical crystals cooled down to 3.9 K at $B = 0$ T.
- Then put B (// c -axis) around working value ~ 0.34 T.
- Get EPR signal (derivative of absorption spectrum) with measurements on short timescales (~ 1 ms) at a fixed B value.
- Check for induced perturbations in EPR spectra, by making stability studies in several runs of 400 10s-scans.



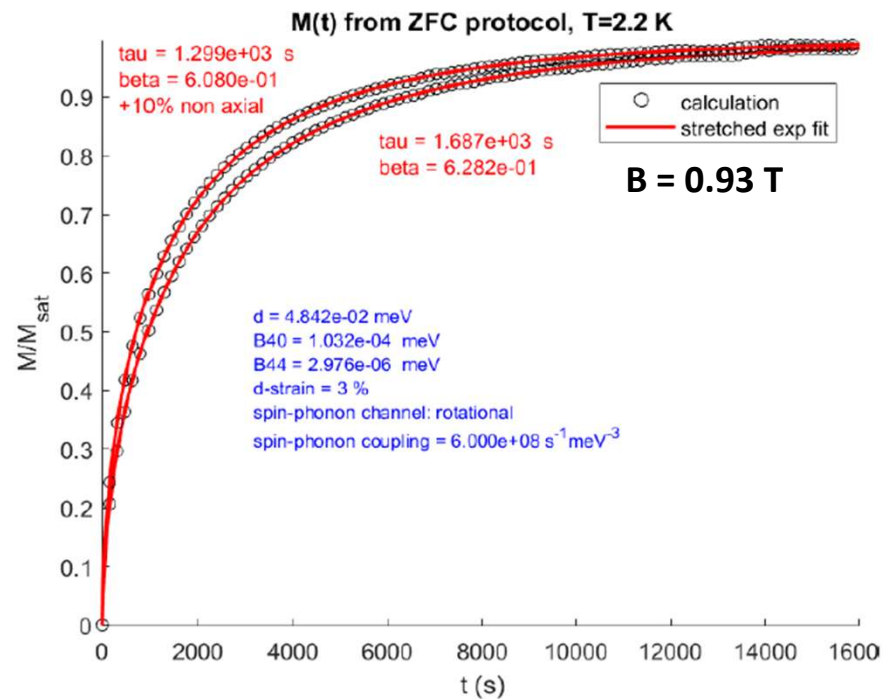
No indication of signal instability induced by ionizing radiation

Modelling of Radiation-Induced Perturbation in M Dynamics

The simulation considers: the Mn_{12} SMM spin Hamiltonian with two axial terms and one term for the tunnelling; a standard model for the spin-phonon coupling; master equation for the relaxation.



Modelling in terms of an induced (0.02K) global increase in temperature



Modelling the in terms of an induced increase in tunnelling mechanism

B (T)	Configuration	τ (s)	β
0.84	Standard	8584	0.9017
	Increase in T	6808	0.8908
	Increase in B_4^4	6544	0.8928
0.93	Standard	1687	0.6282
	Increase in T	1356	0.6322
	Increase in B_4^4	1299	0.6080