Quantum Sensing with Single Molecule Magnets: the NAMASSTE R&D Project

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(on behalf of the NAMASSTE Group)

DRD5/DRq WorkShop
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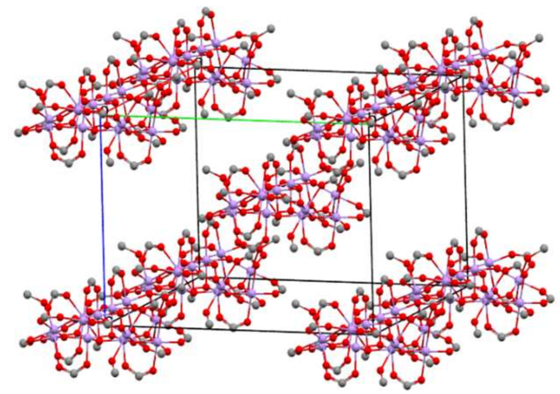
Single Molecule Magnets (SMMs)

SMMs are crystalline materials characterized by [1]:

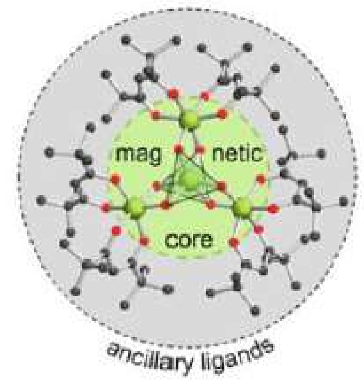
1. Regular crystalline structure, made by identical molecules with a magnetic core of a finite number (n≥1) of paramagnetic centers, with strong intramolecular exchange interactions.
2. Molecules shielded by organic ligands → weak intermolecular interactions.

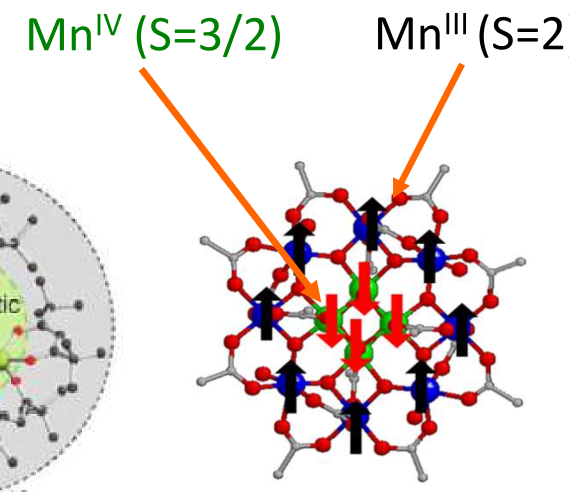
→

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



Mn_{12} crystal

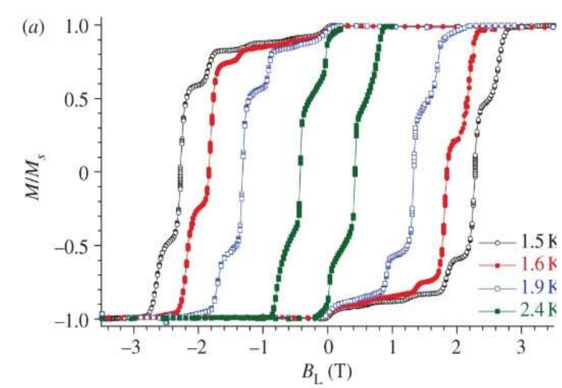


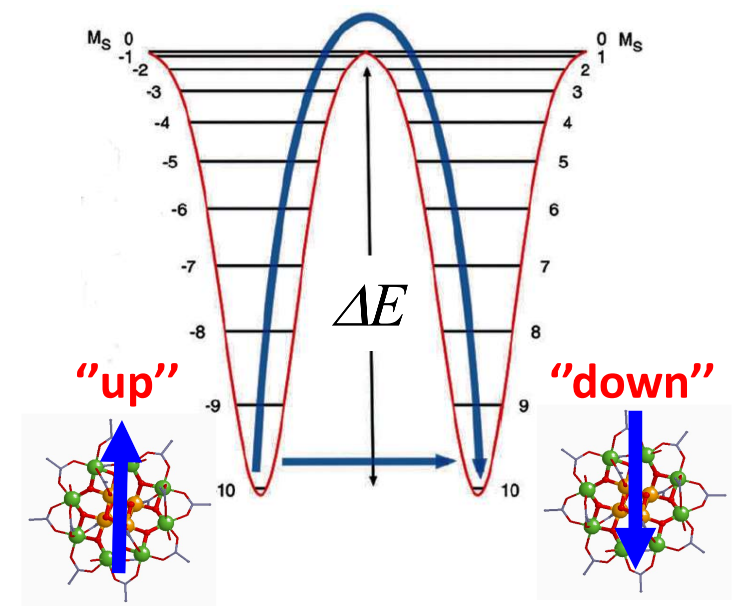


Mn_{12} core

"Reference" (the most studied) SMM, Mn_{12}:

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



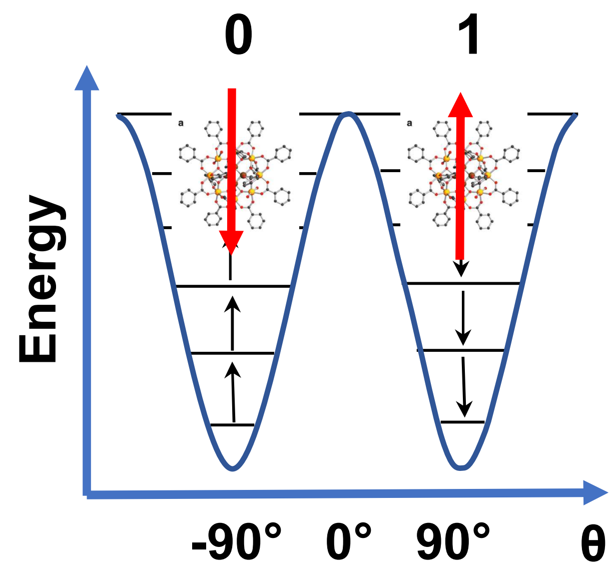


Relatively new materials with interesting potential applications …..

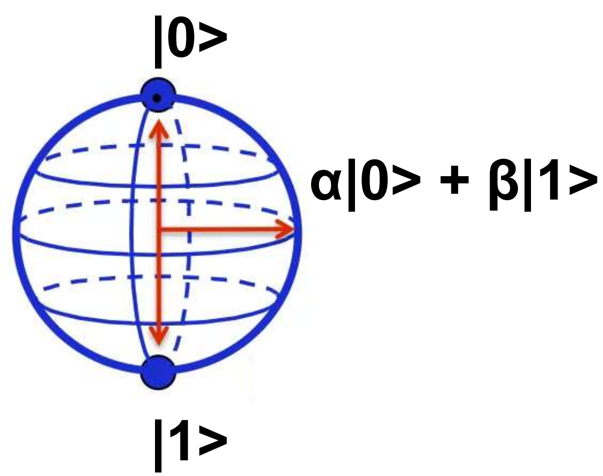
[1] Gatteschi, Sessoli, *Angew. Chem. Int. Ed.* 42 (2003)

Potential Applications of SMMs

High-density memory storage



Quantum computing [1]

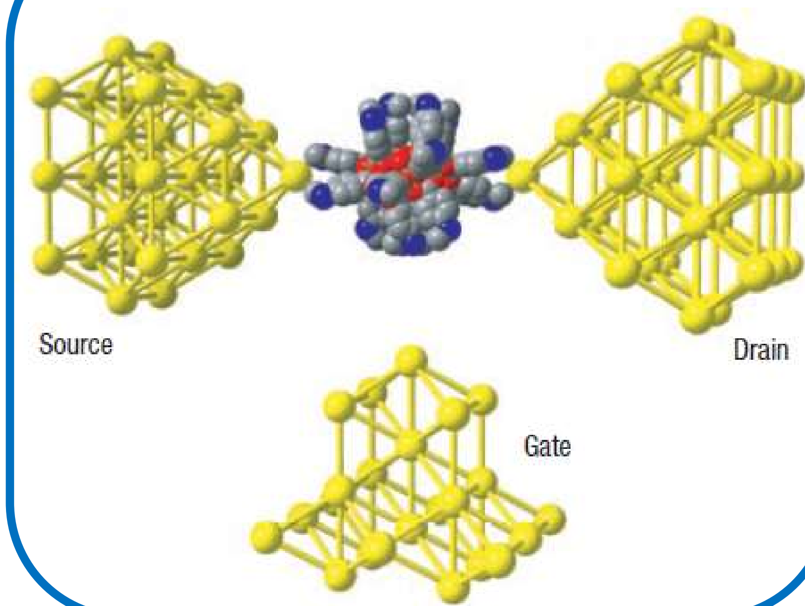


Qubit

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

Molecular spintronics

Molecular spin-transistor [2]



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

New potential application

Quantum sensors for particle detection

Are SMMs of Interest for Particle Physics ?

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

→ **SMMs as sensors can be competitive for the detection of Dark Photons at low masses**

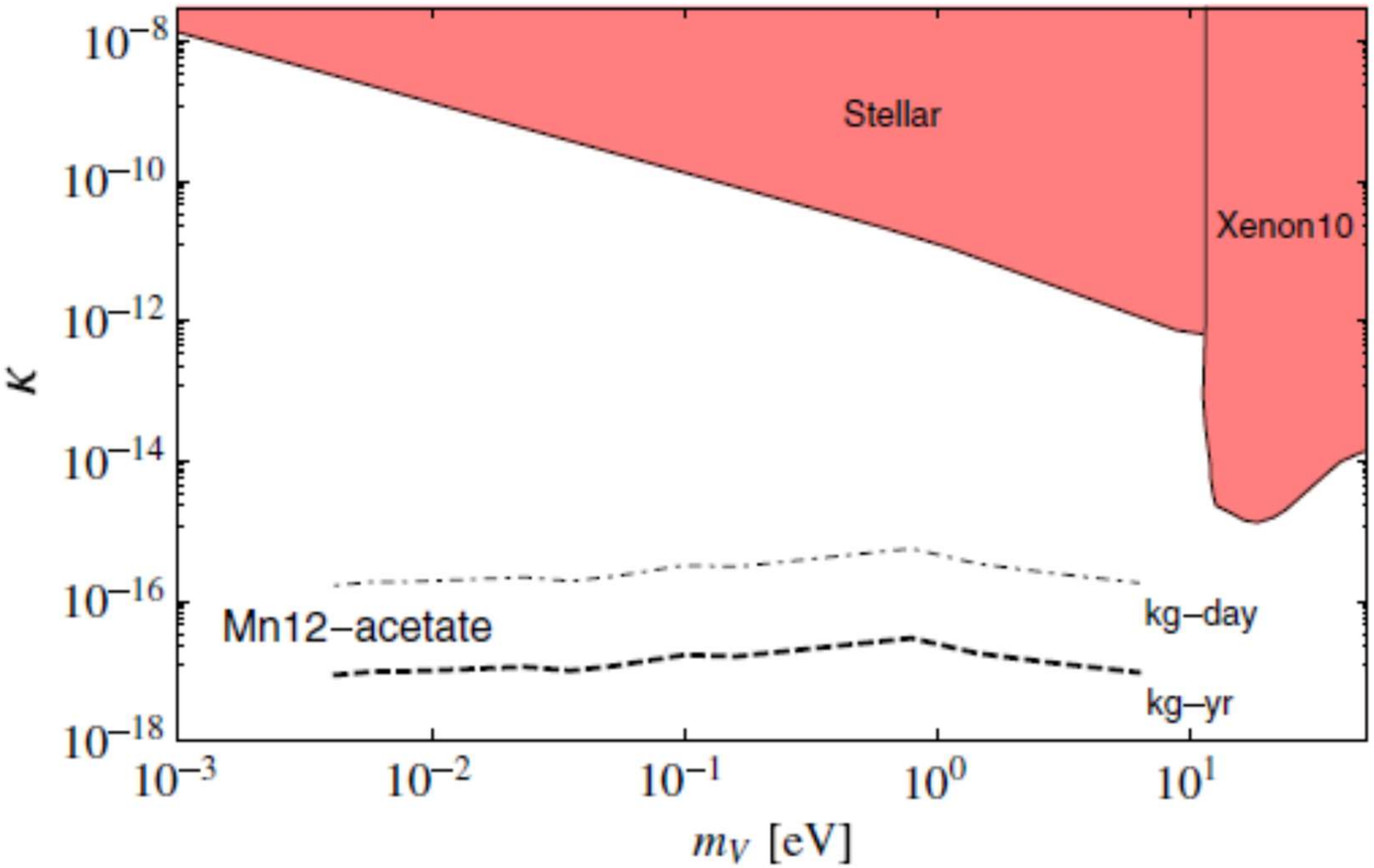


FIG. 6. Estimated sensitivity to absorption of dark vector DM in Mn_{12}-acetate, assuming an aggressive sensitivity of 1 event/kg year (dashed), and a sensitivity of 1 event/kg day (dot-dashed). The absorption data from Refs. [62,65] (described in the appendix) has been smoothed, an interpolation used in the region $m_V \sim 0.2$–0.5 eV, for which no data was available, and we use the approximation $\kappa \simeq \kappa_{\mathrm{eff}}$ (see text).

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

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

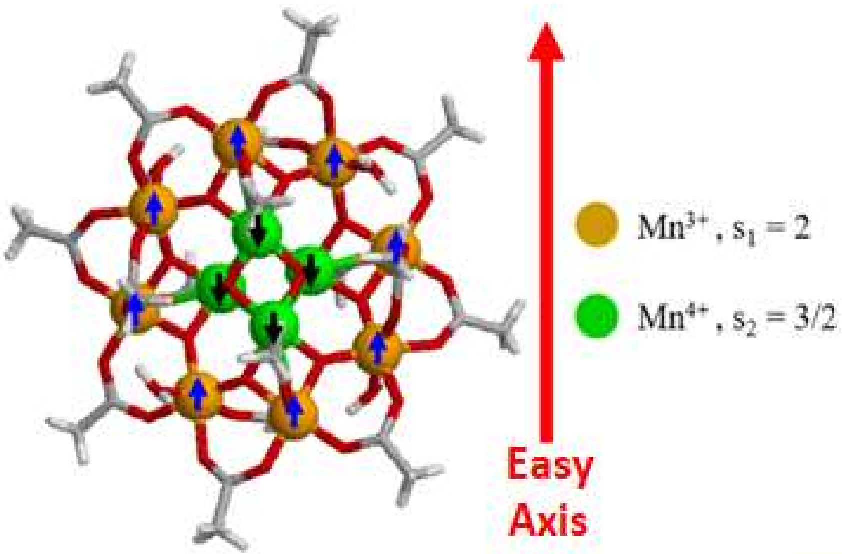
The INFN R&D NAMASSTE Project

NAMASSTE: NanoMagnets for quantum Sensing and Data Storage

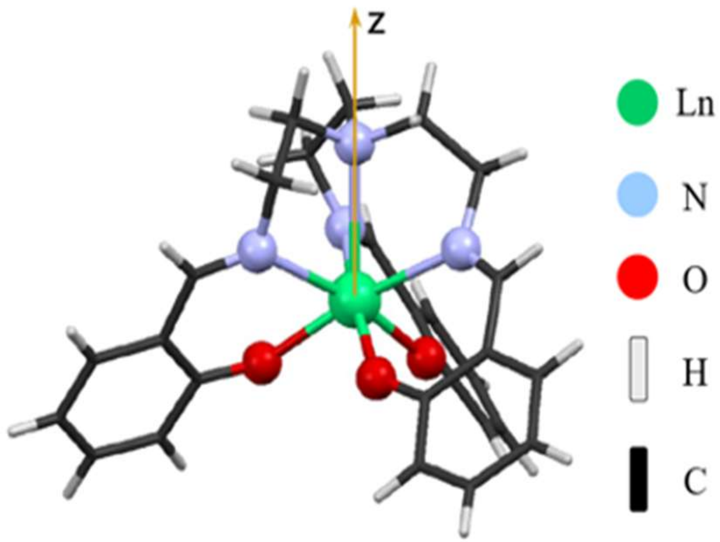
The project (financed by INFN, GrV) aims to design, synthesize, and characterize new molecular nanomagnets for two different applications:

- **single molecule magnets (SMMs)**, for **high-sensitivity** sensors, potentially suited for revealing dark matter (energy sensitivity down to ~ 10^{-3} eV): hidden photon [1], …..; } **Focus of this talk**
- **single ion magnets (SIM)**, for **high-density** memory storage systems.

Novel combination of experimental techniques (in synergy with theoretical investigation) to achieve these goals: **Magnetometry (SQUID), NMR, EPR, μ-SR**.



Mn_{12} SMM

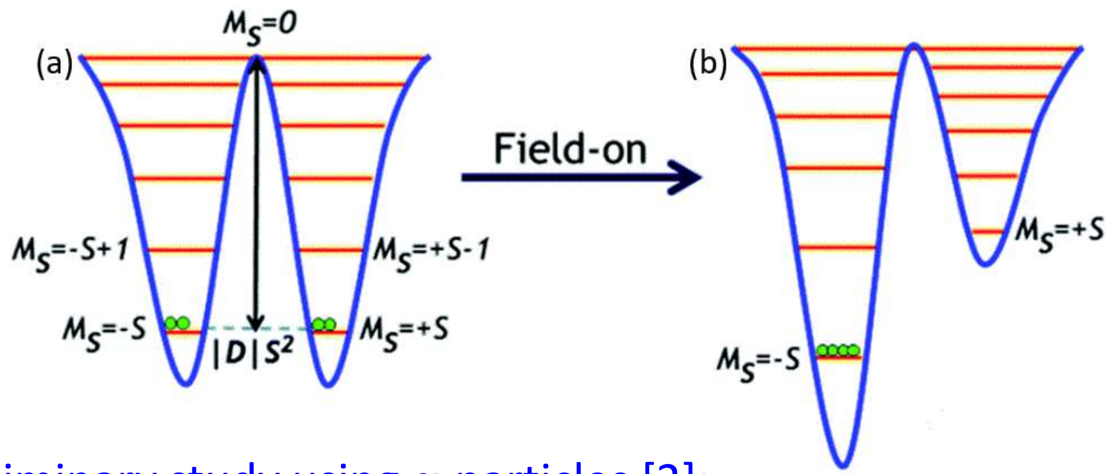


Ln-based SIM

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

SMMs as Sensors

The current detection approach [1] is based on the idea that 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.



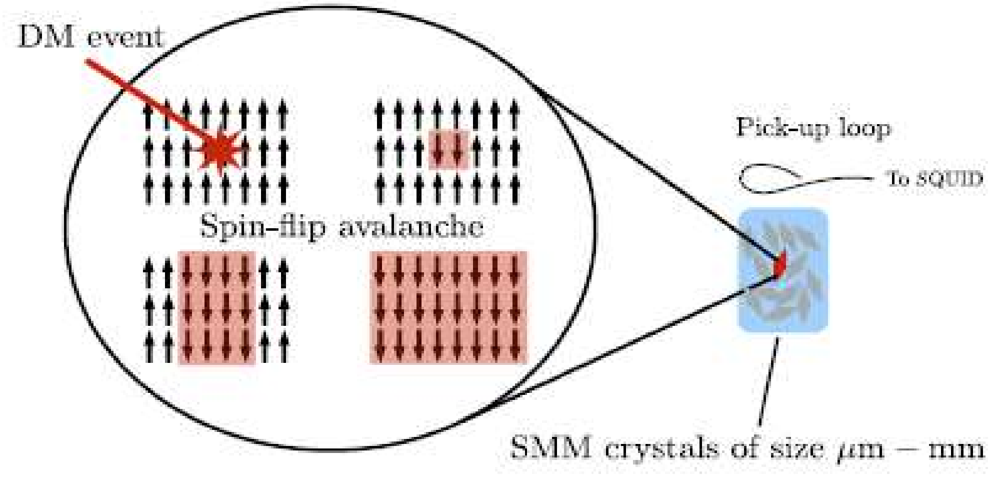
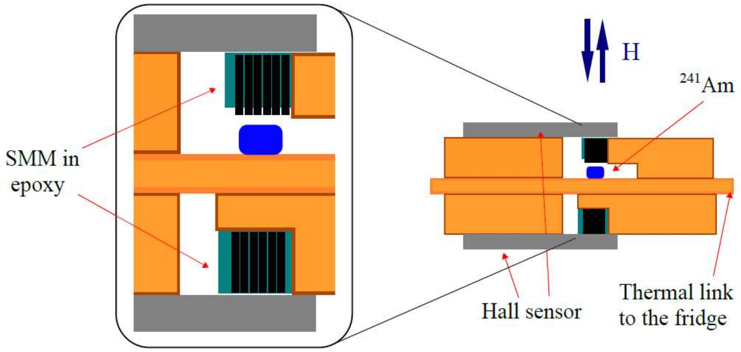
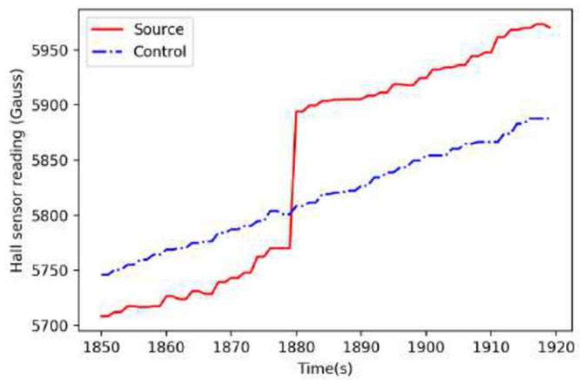


FIG. 1. DM detector concept based on magnetic deflagration in molecular nanomagnet crystals. A DM event that deposits energy in the form of heat ignites a spin-flip avalanche in the crystal which is detected by the change in magnetic flux through a pick-up loop.

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

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





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

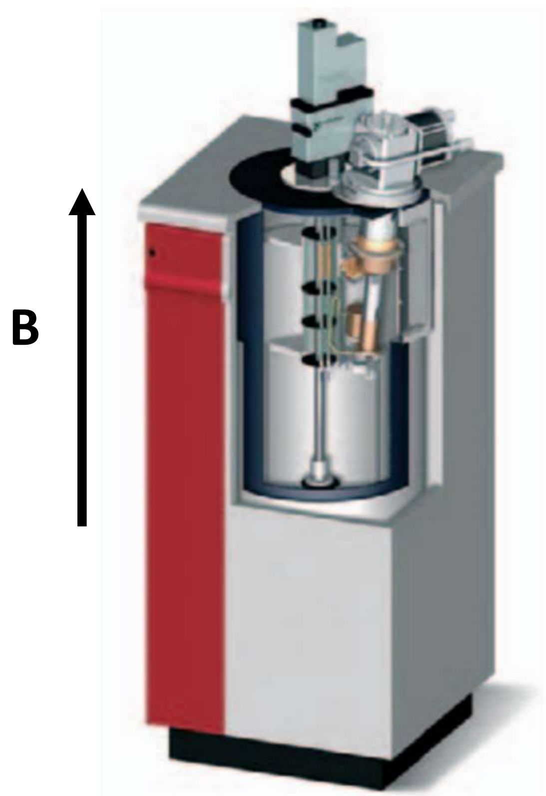
AIM OF THE NAMASSTE PROJECT:

- reproduce results with α, trying to optimize the conditions for magnetic avalanches (very promising effect for potential up-scaling in sensing volume ….);
- possibly extend to β and γ;
- investigate SMMs as sensors with other experimental techniques (EPR, NMR) characterized by an enhanced sensitivity

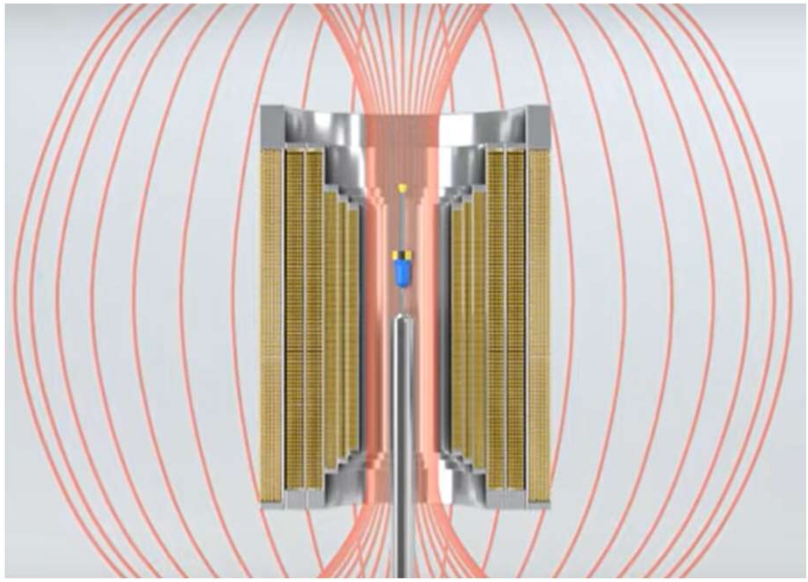
NAMASSTE: Ongoing Studies Related to Sensing

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

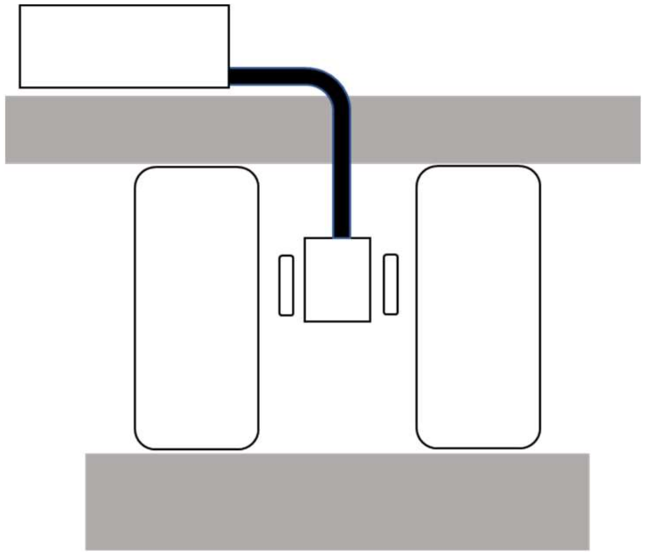
SQUID magnetometer



Nuclear Magnetic Resonance (NMR)



X-band Electron Paramagnetic Resonance (EPR)



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

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

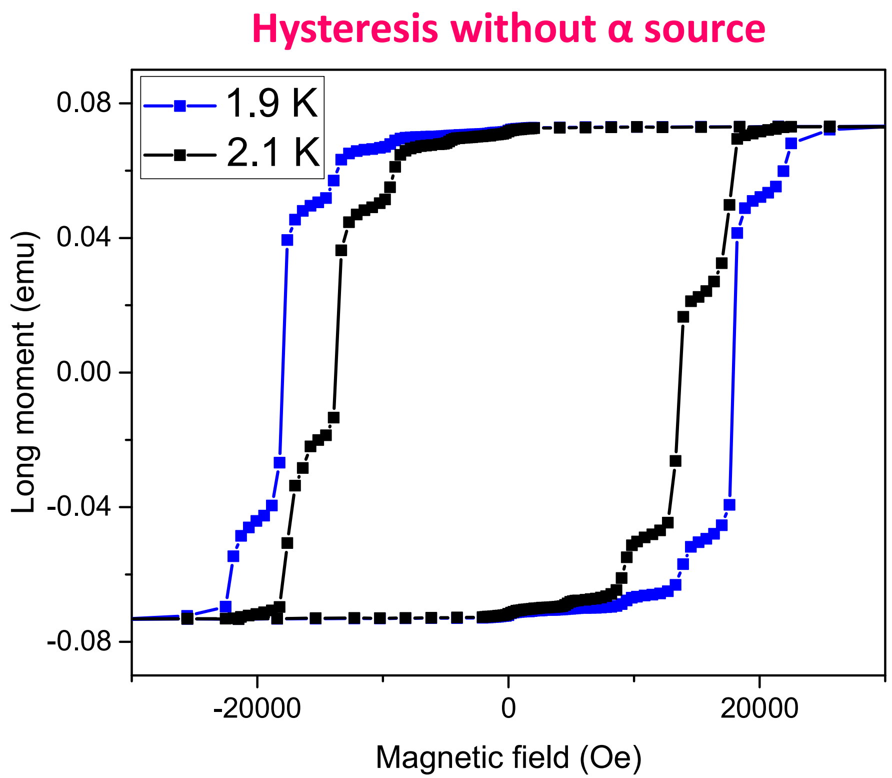
Local probe techniques: these approaches (based on the study of relaxation times) are expected to be **more sensitive** than the ones based on magnetometry.

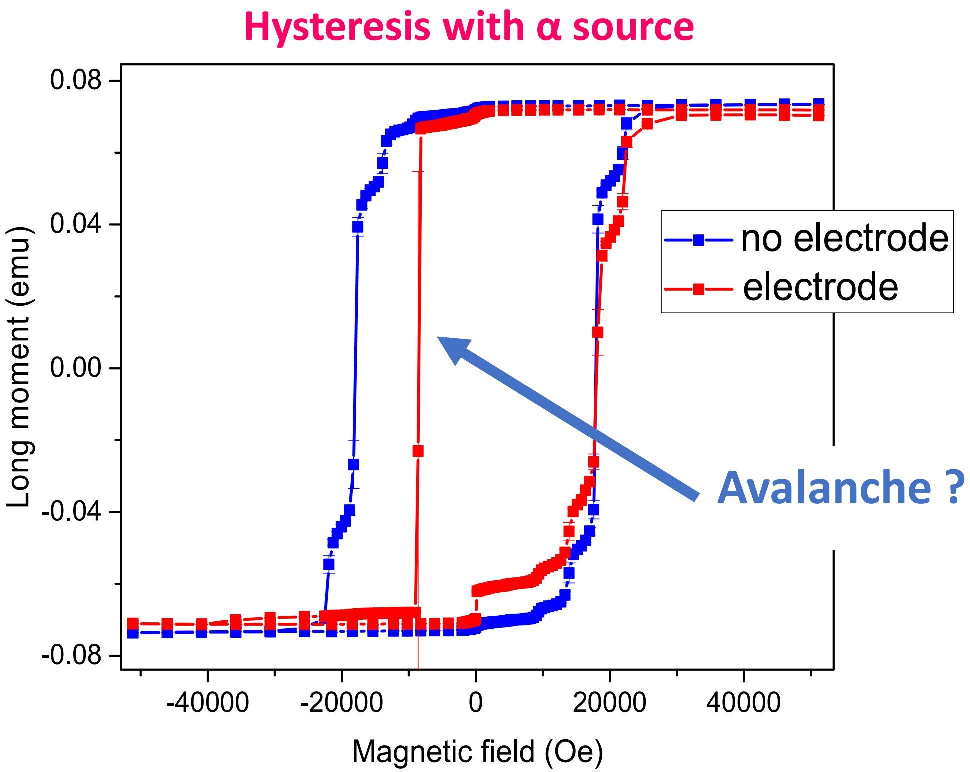
SQUID Magnetometry Studies on Mn12 (I)

Performed @ Florence Unit

Goal: reproduce the results reported in literature and identify the optimal setup conditions to obtain them

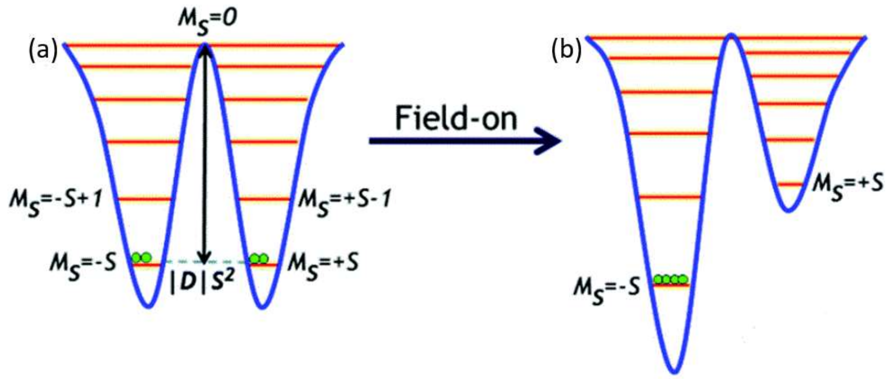
Crystals of Mn12 with the easy axis // to the external magnetic field





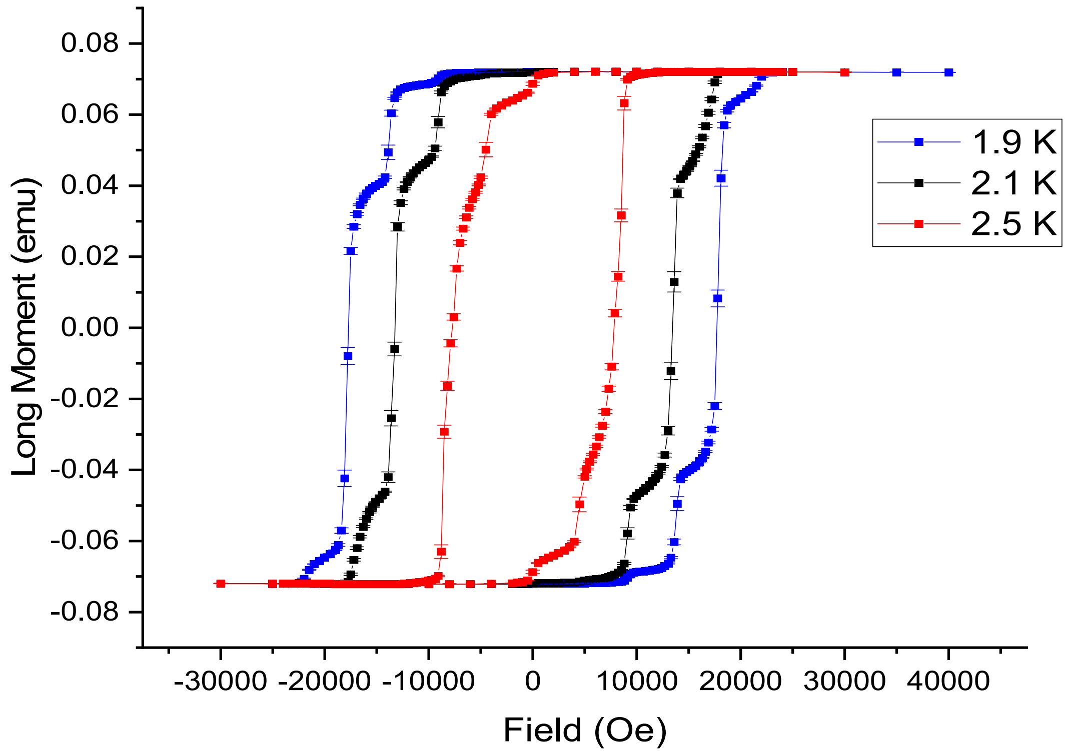
- **As expected, the hysteresis loops show 'jumps' at suitable B values due to quantum tunnelling effects.**
- **Abrupt reversal of magnetization, compatible with an 'avalanche' effect, observed only in one case.**

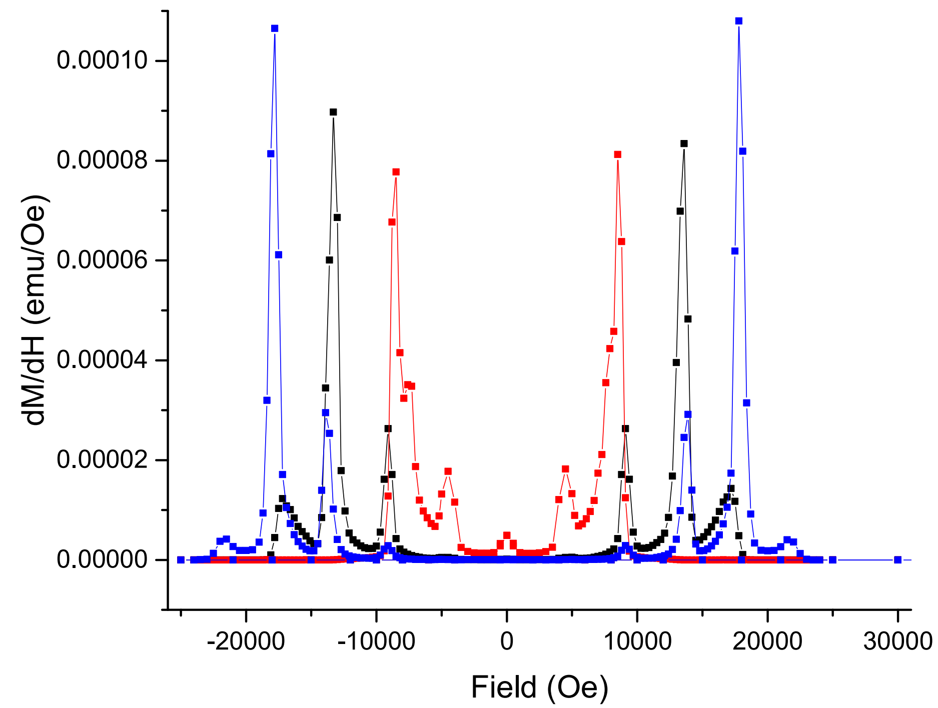
Need to carry out further studies.

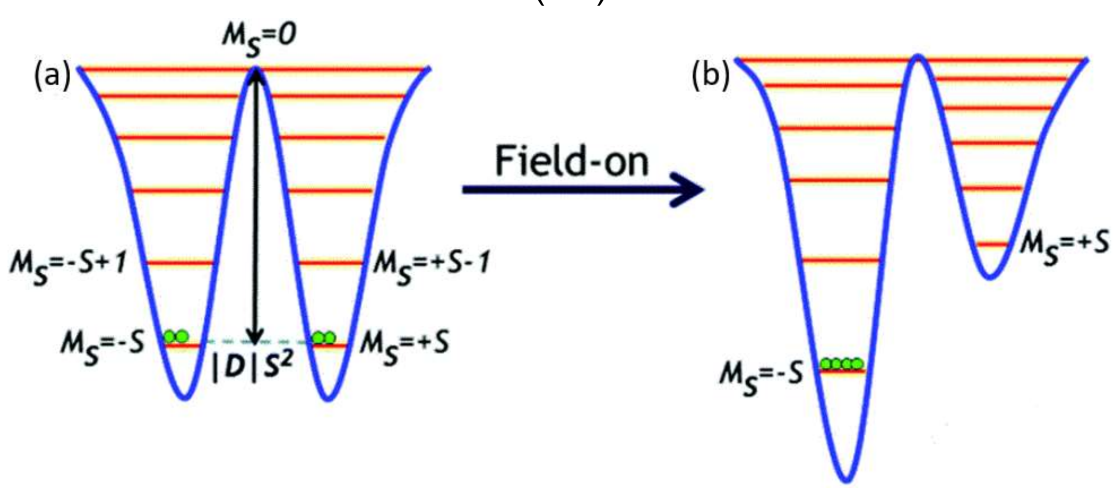


Macroscopic Quantum Effects in Hysteresis Loops

Hysteresis loops on Mn12 (no α) at various 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

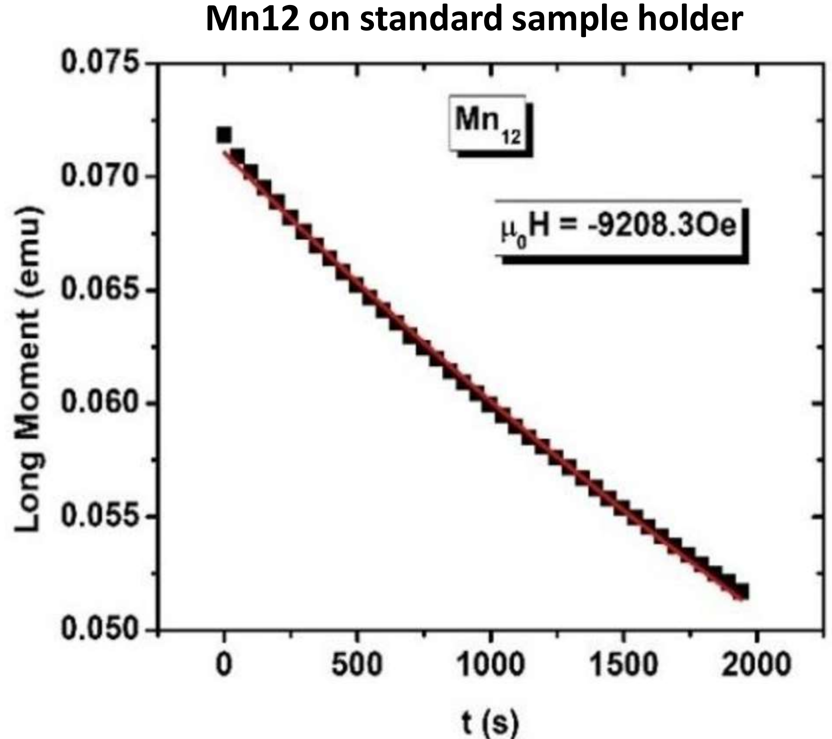
SQUID Magnetometry Studies on Mn12 (II)

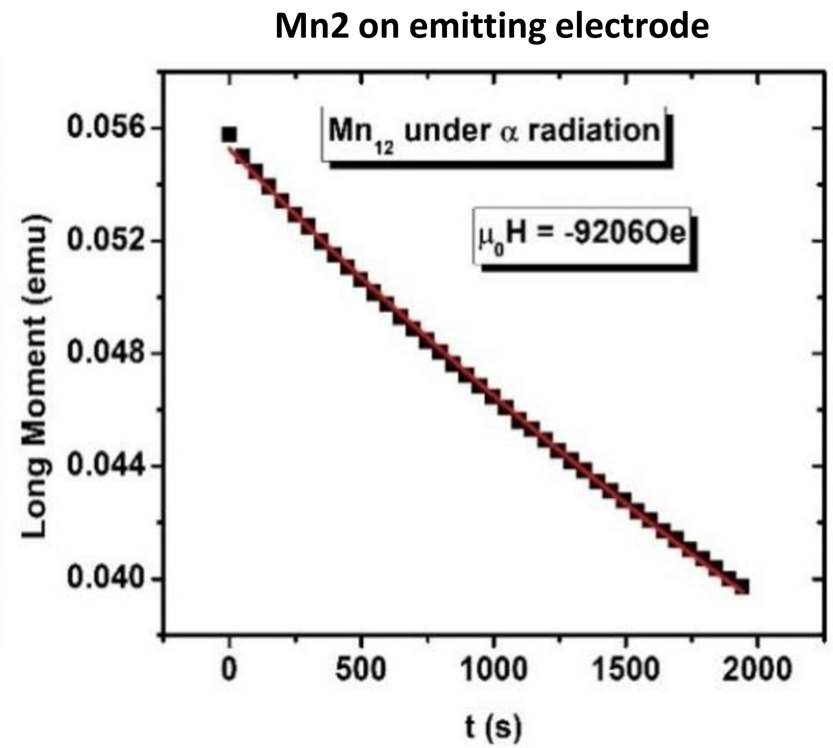
Round - II of SQUID measurements: preliminary studies of relaxation times for the magnetization M

Study of relaxation times at B values around the 3rd "jump" at B ~ -9100 Oe
(T = 1.9 K; before each measurement B is set at 3T, then inverted).

Fit of M vrs t according to:

$$M(t) = M(0)e^{-\frac{t}{\tau}}$$





Field (Oe)	Mn_{12} τ(s)	α-irradiated Mn_{12} τ(s)
3	1.16×10^9	0.93×10^9
-8400	9.73×10^4	9.83×10^4
-8800	4.21×10^4	5.21×10^4
-9200	5.97×10^3	5.80×10^3
-9600	2.87×10^4	2.12×10^4
-10000	7.06×10^4	5.31×10^4

- No substantial differences observed, as instead found in preliminary NMR measurements (see next slide).
- No abrupt changes of M observed under α radiation. as reported in literature (but around 2nd jump) [1].

Need to carry out further studies.

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

NMR Studies on Mn12

Performed @ Pavia Unit

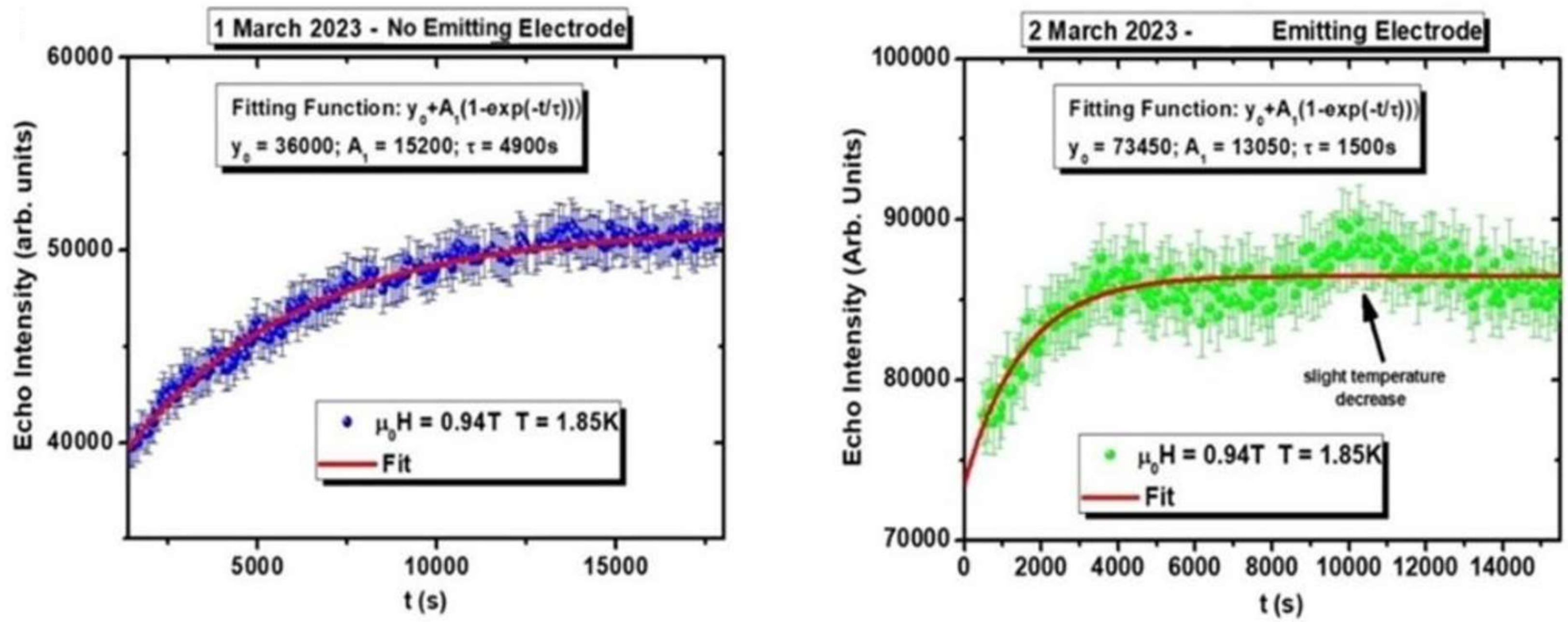
Goal: use NMR-based techniques to study relaxation times of Mn12 crystals with/without irradiation.

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 relaxation time τ of the magnetization from the related fit.

Chosen protocol:

- Mn12 crystal cooled down to 1.85 K at B = 0 T.
- Then put at fixed B = 0.94 T (3rd jump).
- Start the measurements.



Noticeable reduction in relaxation time of magnetization τ in presence of particle radiation

Run	No Emitting Electrode τ (s)	Alpha Emitting Electrode τ (s)
September 2022	10400	3500
March 2023	4900	1500

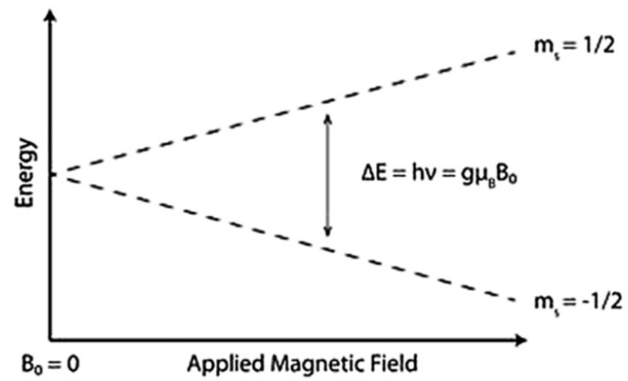
[1] Jang *et al.*, PRL 84 2977 (2000)

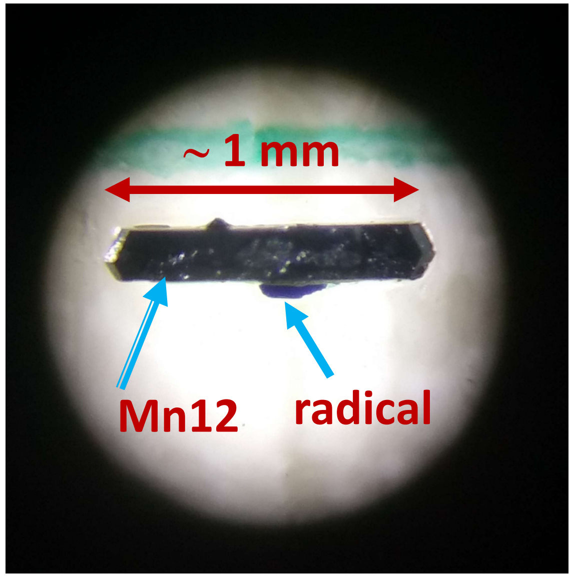
EPR Studies on Mn12

Performed @ Firenze Unit

Goal: use EPR-based techniques to study behaviour of Mn12 crystals with/without irradiation.

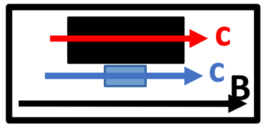
EPR: absorption spectroscopy technique used to study chemical species with unpaired electrons; the details of EPR spectra depend on the electron interaction with the nearby environment.





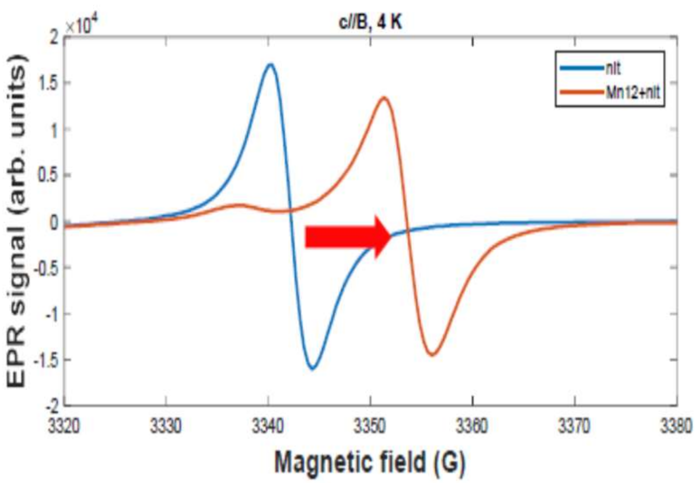
Adopted technique [1]:

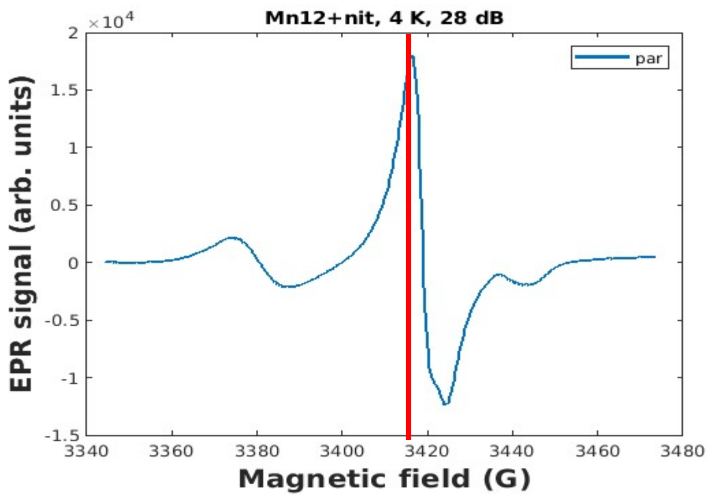
- Mn12 does not show an intrinsic EPR signal at the frequencies of the available device (X band).
- Then couple the Mn12 crystal to a radical crystal (specifically: NitPBAh, an organic radical), so to have an EPR signal sensitive to variations in Mn12 magnetization.



Chosen protocol (device driven):

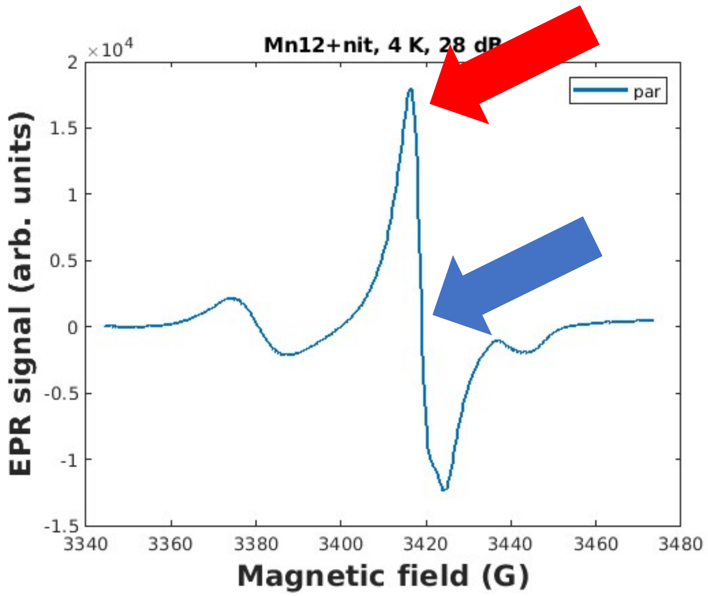
- Mn12+radical crystals cooled down to 3.9 K at B = 0 T.
- Then put B (// c-axis) around working value ~ 3400 G.
- After proper tuning, get EPR signal (derivative of absorption spectrum) with measurements on short timescales (~ 1 ms) at a fixed B value.
- Make stability studies.



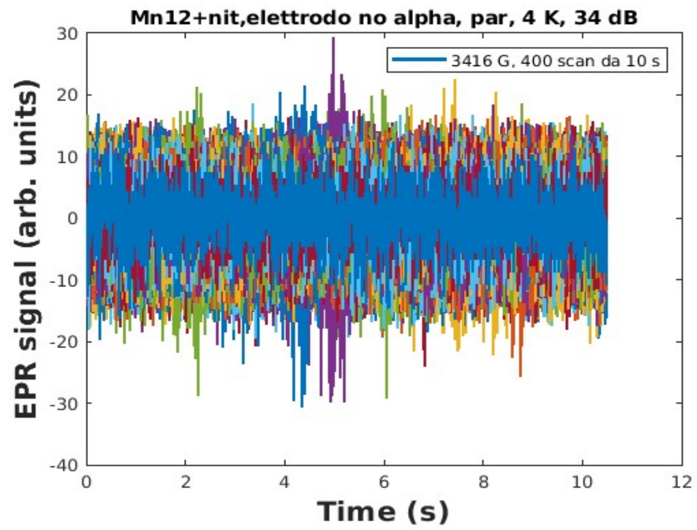


[1] Rakvin *et al.*, Jour. of Mag. Res., 165 (2003) 260-264

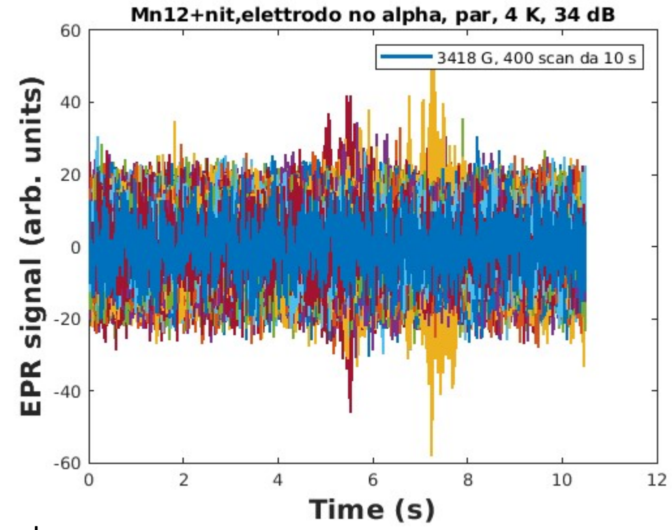
Mn12+Radical: EPR Studies without Particle Radiation



MAX

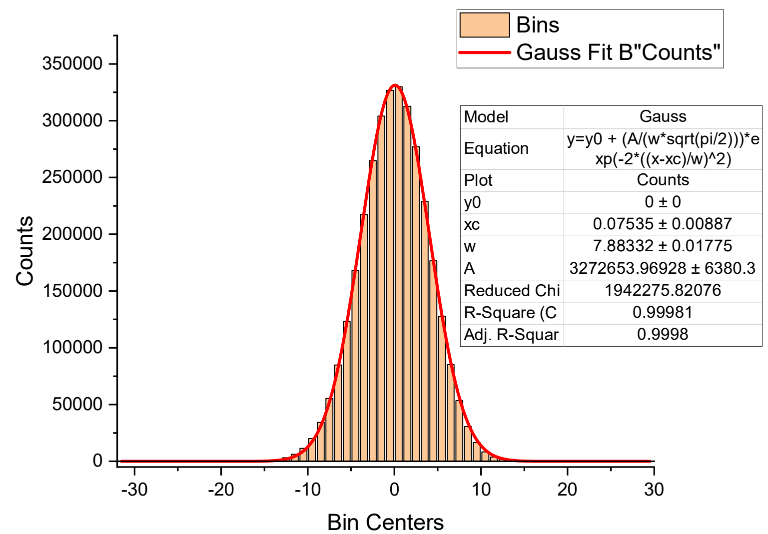


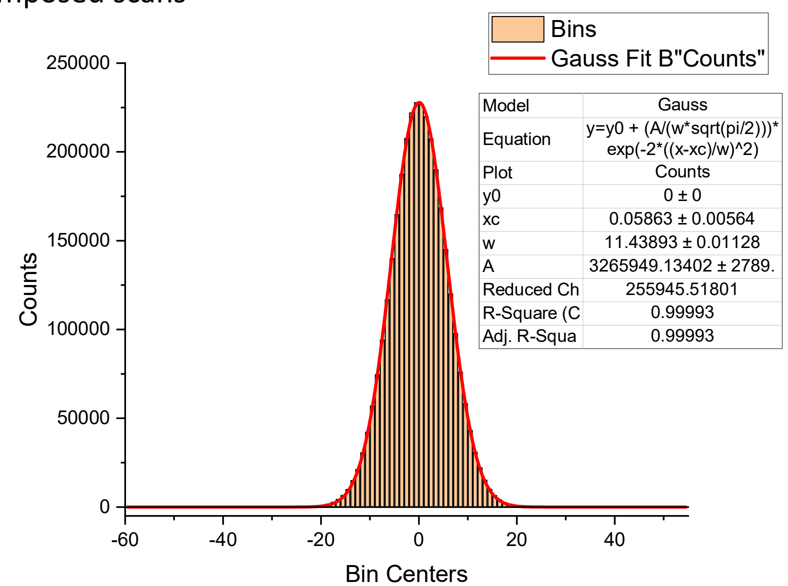
ZERO



400 superimposed scans

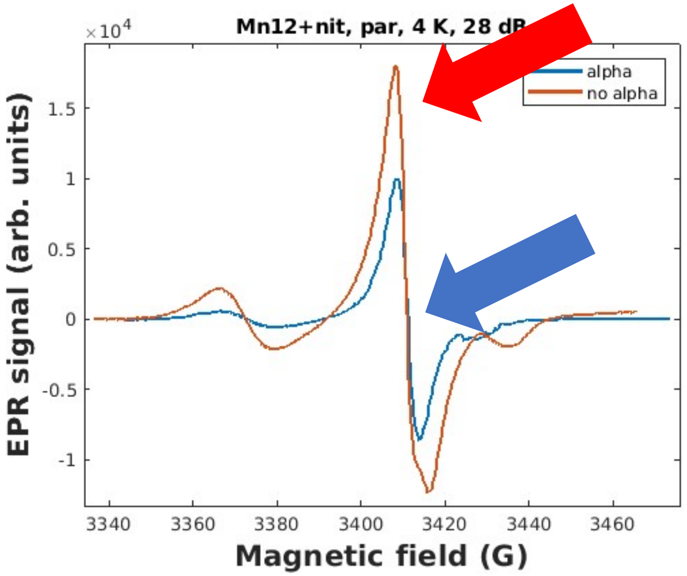
- System at T = 3.9 K, with c//B
- EPR at fixed B fields as a function of time (400 scans with sweep time = 10 s and 8192 points/scan)
- Analysis algorithm to select candidate events (values greater than 5σ w.r.t. noise fluctuations)





Very symmetric (Gaussian) distributions

Mn12+Radical: EPR Studies with Particle Radiation



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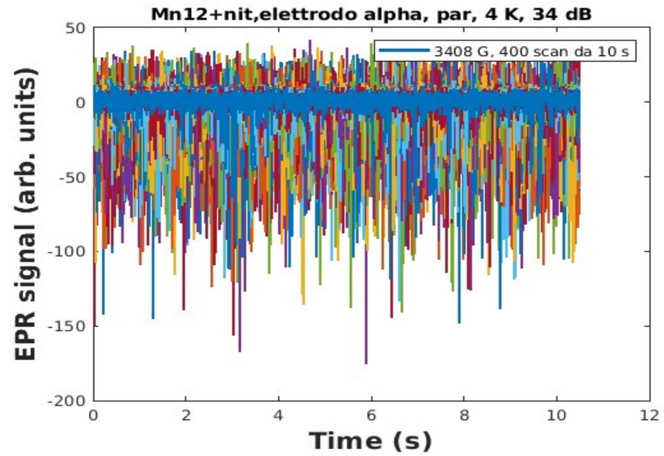

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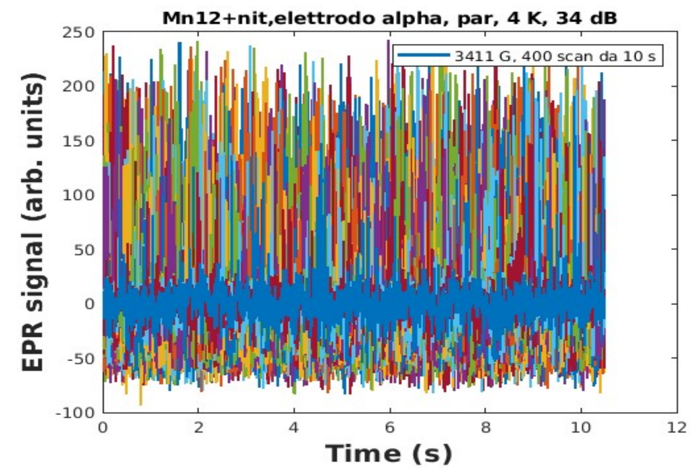
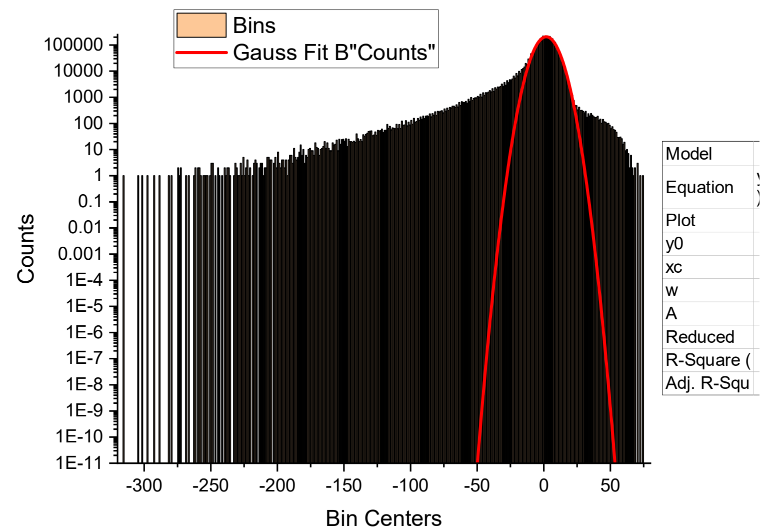
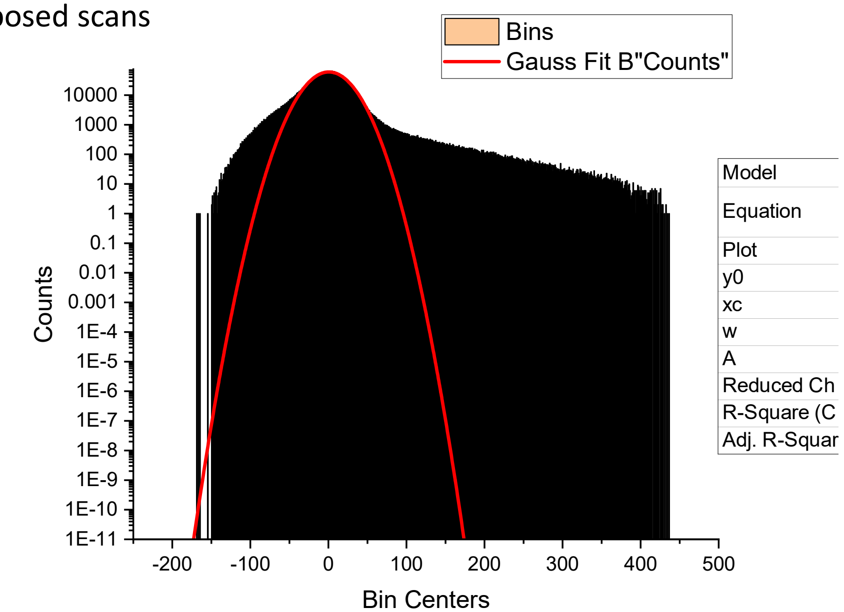


400 superimposed scans





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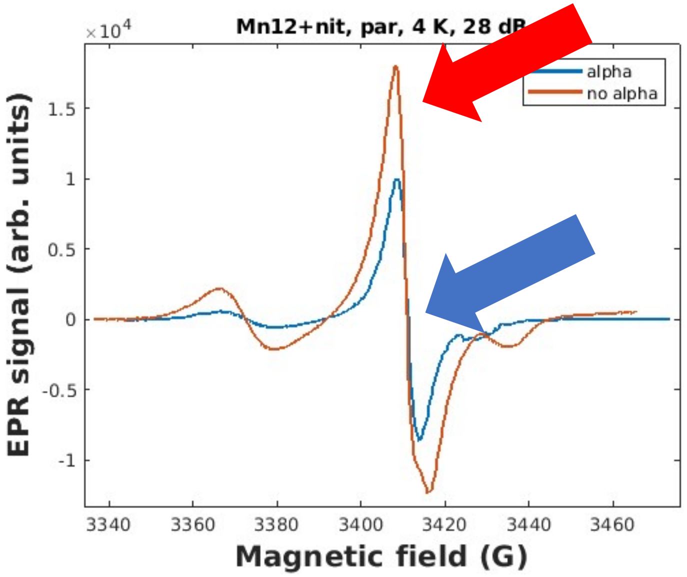
- EPR at fixed B fields as a function of time (400 scans with sweep time = 10 s and 8192 points/scan)
- Analysis algorithm to select candidate events (values greater than 5σ w.r.t. noise fluctuations)

Distributions are no more symmetric: impact of particle radiation ?

Mn12+Radical: EPR Studies with Particle Radiation



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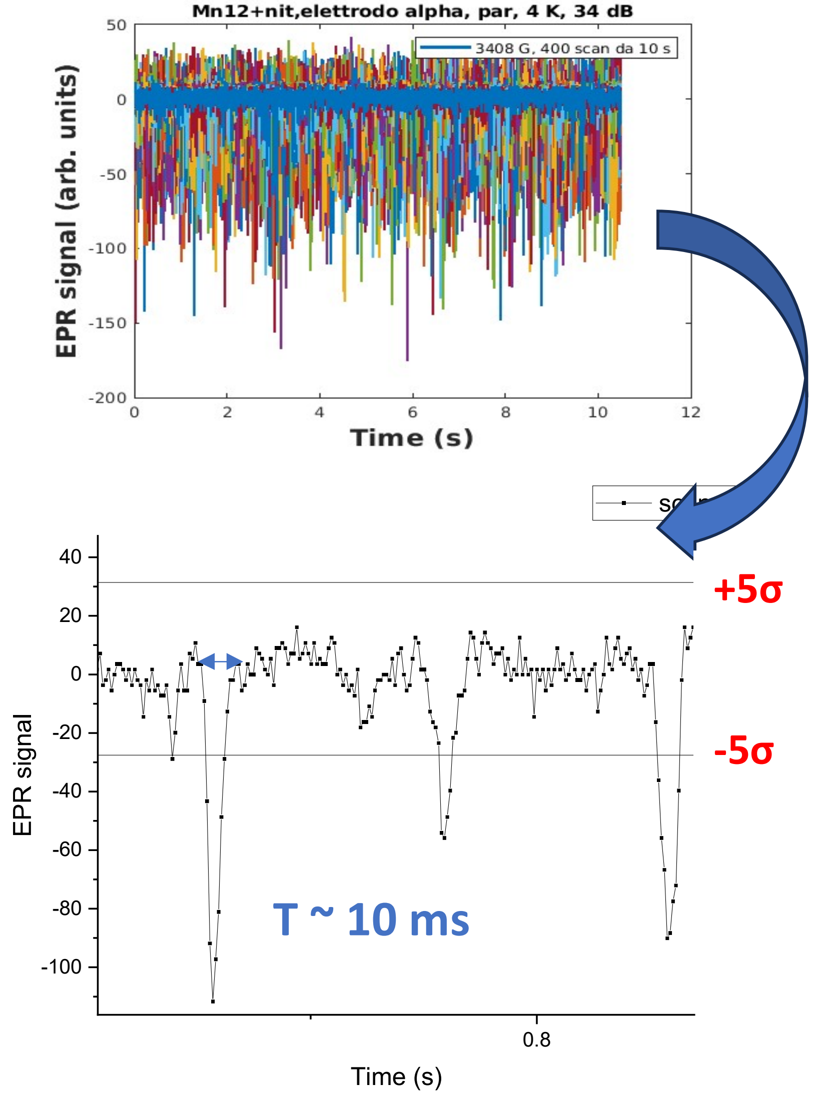
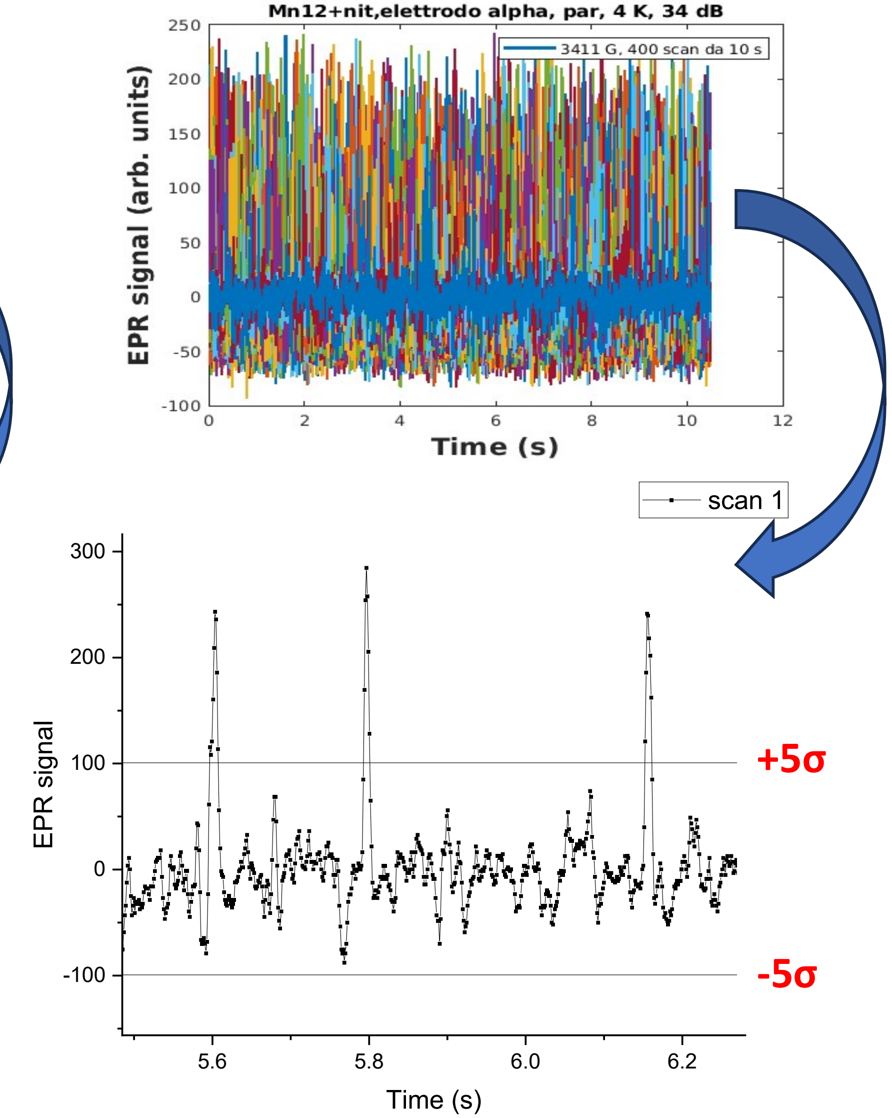
MAX



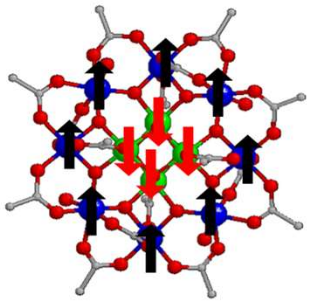
ZERO



When studying single scans we see what look clear signals …..

Summary & Conclusions

- In the search for New Physics 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).
- The efforts for the development of Quantum Sensing in Particle Physics go in this direction.
- The aim of the NAMASSTE R&D project is to investigate the possibility to use SMMs as quantum sensors.
- The well-known SMM Mn12 is studied under the effect of low activity sources.
- SQUID magnetometry studies do not show systematic effects so far.
- NMR-based studies show a clear reduction in relaxation time of the magnetization.
- EPR-based measurements show clear temporary (~ 10 ms) changes in the absorption spectrum.
- Further measurements and checks are required to consolidate the results and to search for improvements and/or different sensing conditions.



Mn_{12} core

Backup Slides

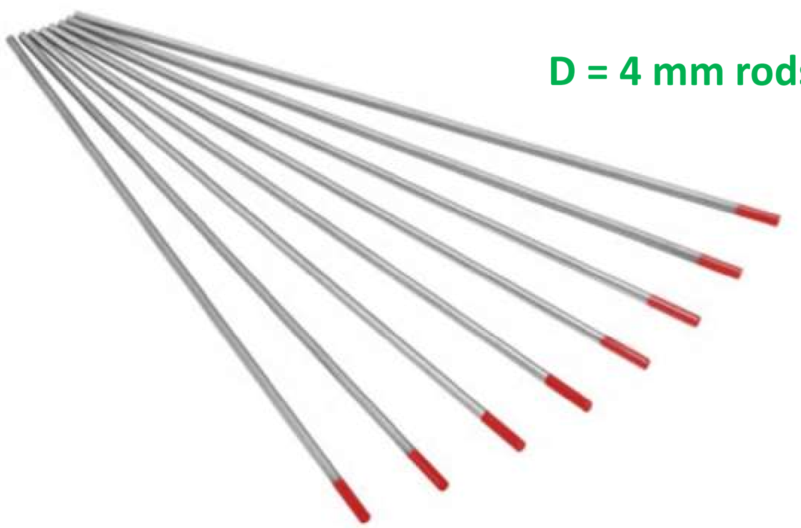
Radiation Sources

Requirements: <u>very low</u> 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.

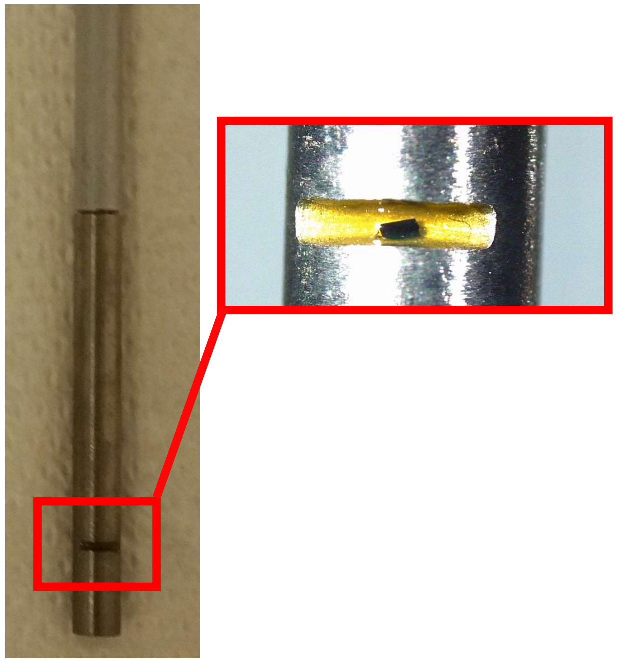
Measured surface activity:

- α (from prim./sec. decays) ~ 0.2 α /(mm^2 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 <u>same</u> experimental configuration.

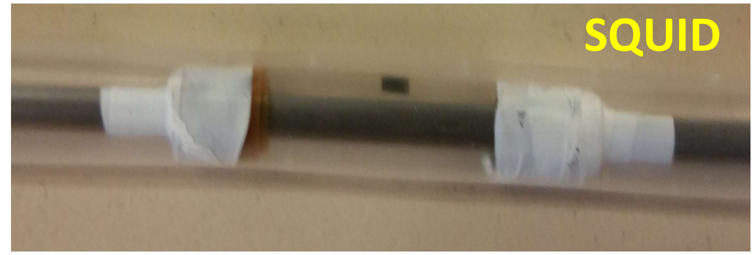
EPR-I: cylindrical geometry with small transversal cut

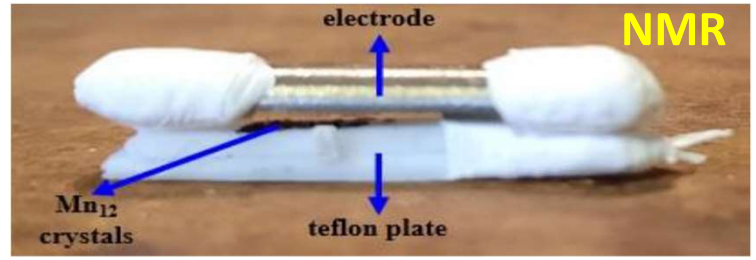


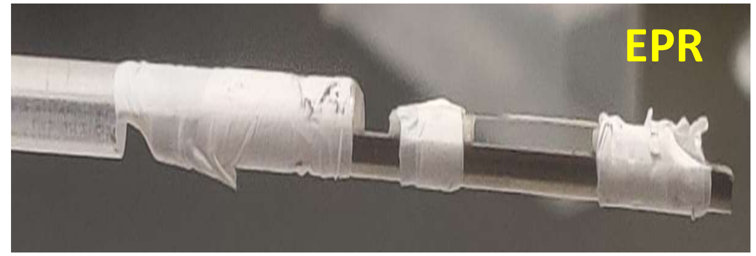
First approach, but:

- 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

Quantum Sensing Basic Protocol

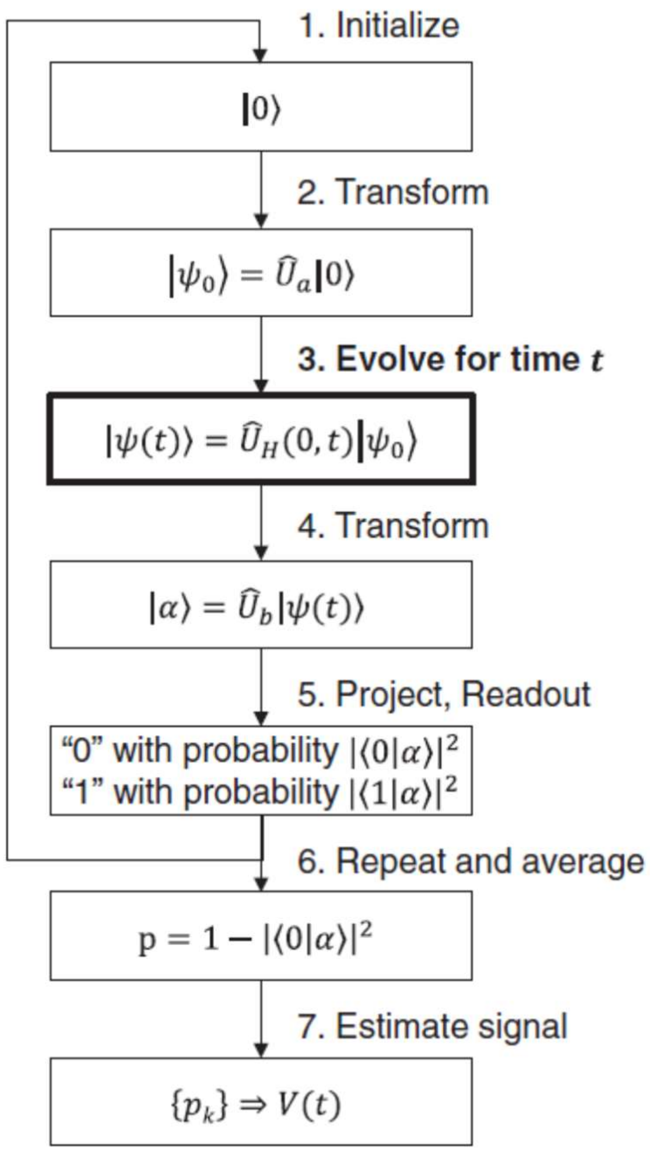


FIG. 2. Basic steps of the quantum sensing process. [1]

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**
- **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 <u>weak signals</u> or <u>small signal changes</u> 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.

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

Simulation of Radiation-SMM Interaction

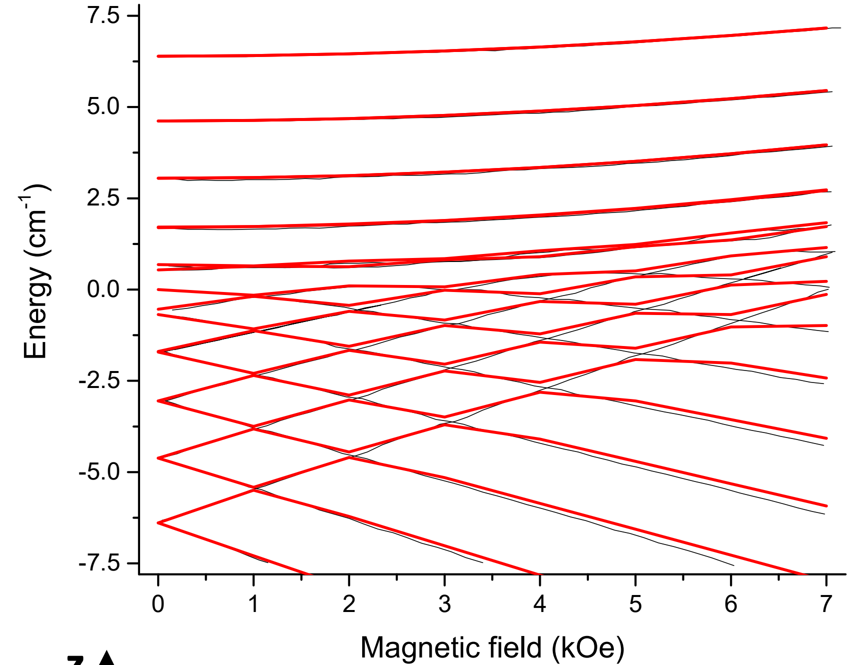
Goal: implement a model for simulating the behavior of SMM under the influence of a specific radiation; of importance for potential future applications, <u>currently absent in the literature</u>.

Development of Fortran program to calculate the energy levels of a classic Hamiltonian which describes the Mn12 SMM in a static magnetic field B.

$H = H_0 + H_1$, **with:**

"Control" H

$$H_0 = D\left[S_z^2 - \frac{S(S+1)}{3}\right] + g\mu_B \vec{B}\cdot\vec{S} \quad \text{and} \quad H_1 = E(S_x^2 - S_y^2)$$



The program has been tested by comparing its results with those reported in the literature for the same set of parameters as a function of *D*, *E* and *B*

Development in progress: preliminary approach in the simulation of the Mn12-charged particle interaction in terms of magnetic field induced by α or β particle on Mn12 molecule;
→ <u>introduction of a perturbative term in H (time-dependent) related the passage of the particle.</u>