

Quantum Sensing for Particle Physics Using Single Molecule Magnets



Giuseppe Latino

(Firenze University & INFN)

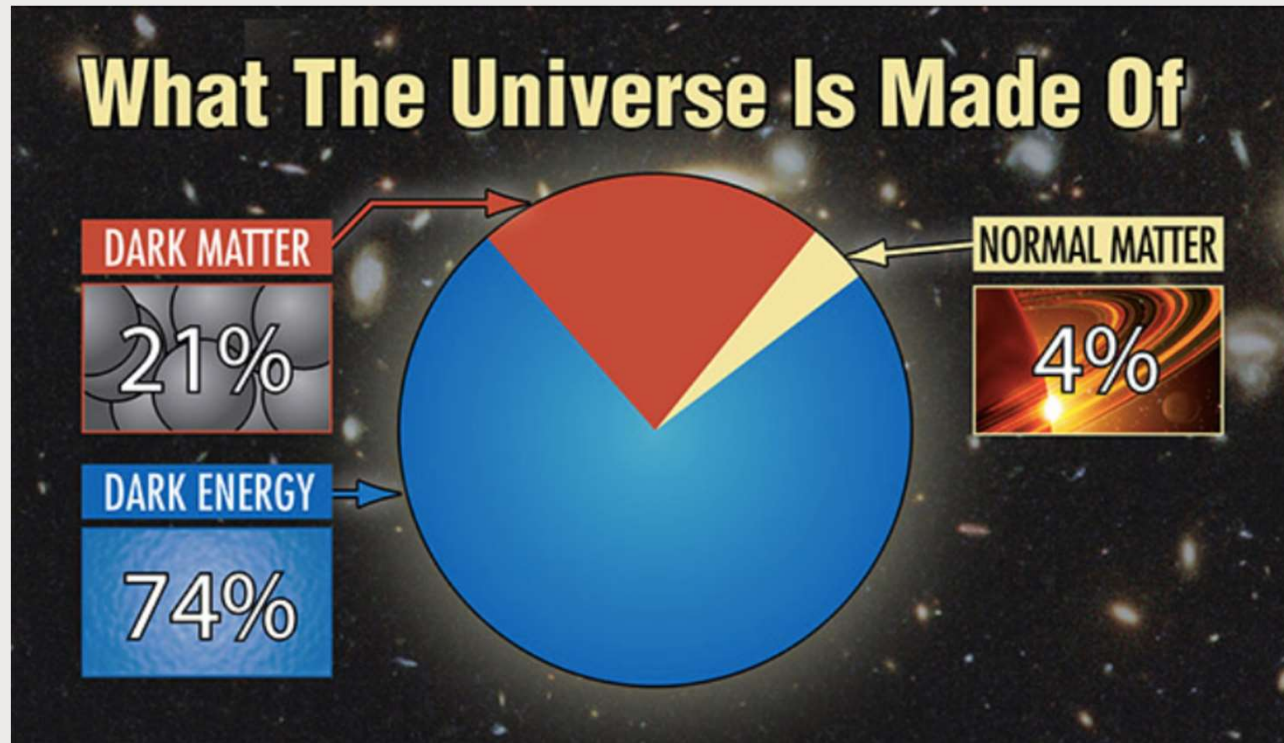
(on behalf of the NAMASSTE Group)

***35th Rencontres de Blois
Blois – October 23th, 2024***

The “Dark Side” of the Universe

Cosmological and astronomical observations:

→ indirect evidence for Dark Matter and Energy



- In short: indirect evidence for physics BSM, with new particles which (as far as we currently know) interact only through gravitational force.
- There are several candidates theoretically +/- well motivated: WIMPs, Axion, Dark Photon, ...
- Probably, several types of new particles constitute the “Dark Sector” world....
- **Need of new detection approaches allowing to go beyond current experimental limits.**

What “Quantum Sensing” Means?

“Quantum sensing” describes the use of a quantum system, quantum properties or quantum phenomena to perform a measurement of a physical quantity [1].

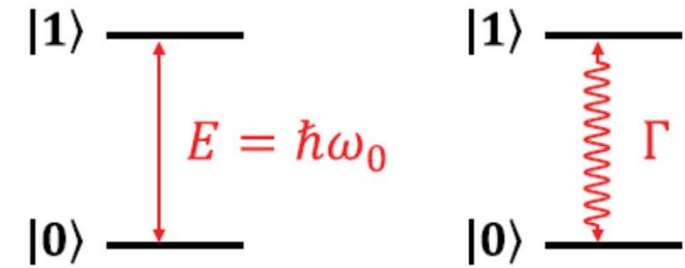


FIG. 1. Basic features of a two-state quantum system. $|0\rangle$ is the lower energy state and $|1\rangle$ is the higher energy state. Quantum sensing exploits changes in the transition frequency ω_0 or the transition rate Γ in response to an external signal V . [1]

Quantum sensors (Qs) register a change of quantum state caused by the interaction with an external system: a QS is a device whose sensing capabilities are enabled by our ability to manipulate and/or read out its quantum states [2].

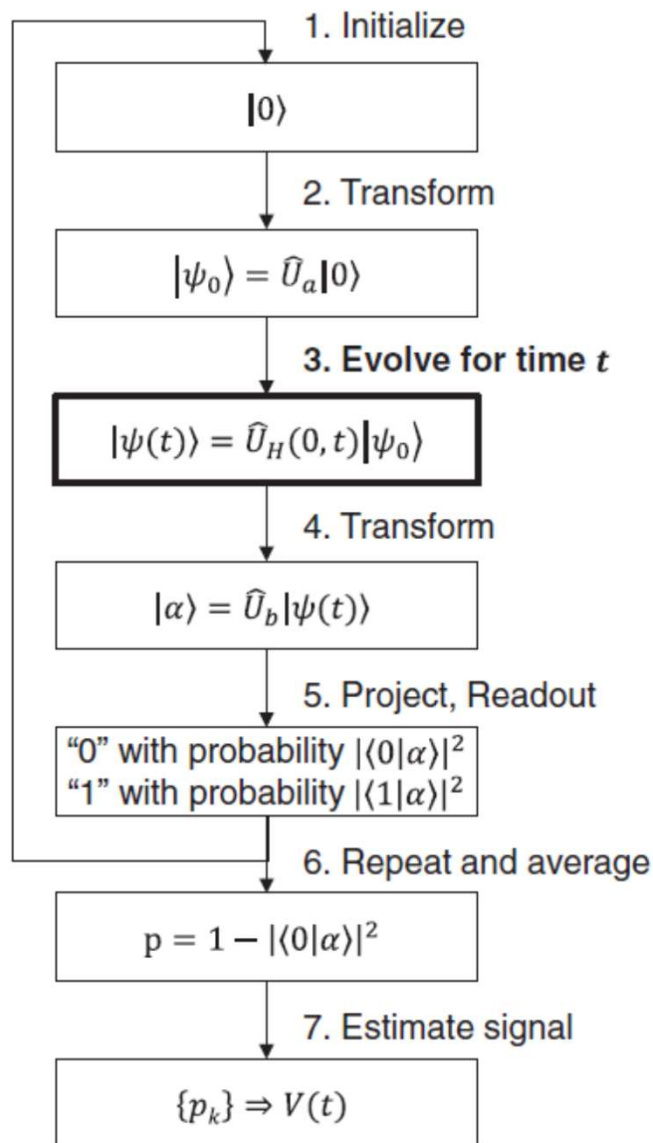
Involved energies very low, so QS very sensitive to external perturbations:

- 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] Rev. Mod. Phys. 89, 035002 (2017);

[2] arXiv:2305.11518v1 (2023)

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)

Growing Interest in Quantum Technologies @ PP Facilities

Development of quantum sensing devices for fundamental physics research represents of course one the mainstream R&D activity

CERN: Quantum Technology Initiative



<https://quantum.cern/>

FNAL: Superconducting Quantum Materials and Systems Center



<https://sqmscenter.fnal.gov/>



[1] DOI: 10.17181/CERN.XDPL.W2EX

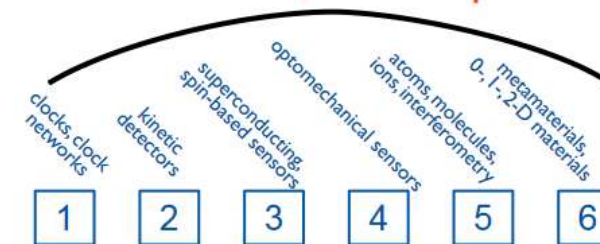
DRD5/RDq:

new CERN Collaboration recently established to implement ECFA detector R&D roadmap for QS for PP
<https://drd5.web.cern.ch/>

Other CERN ongoing activity: 2021 ECFA Report [1]



DRD5, aka "RDq"



6 families identified in ECFA roadmap

An Example: Expected Improvements in DM Search

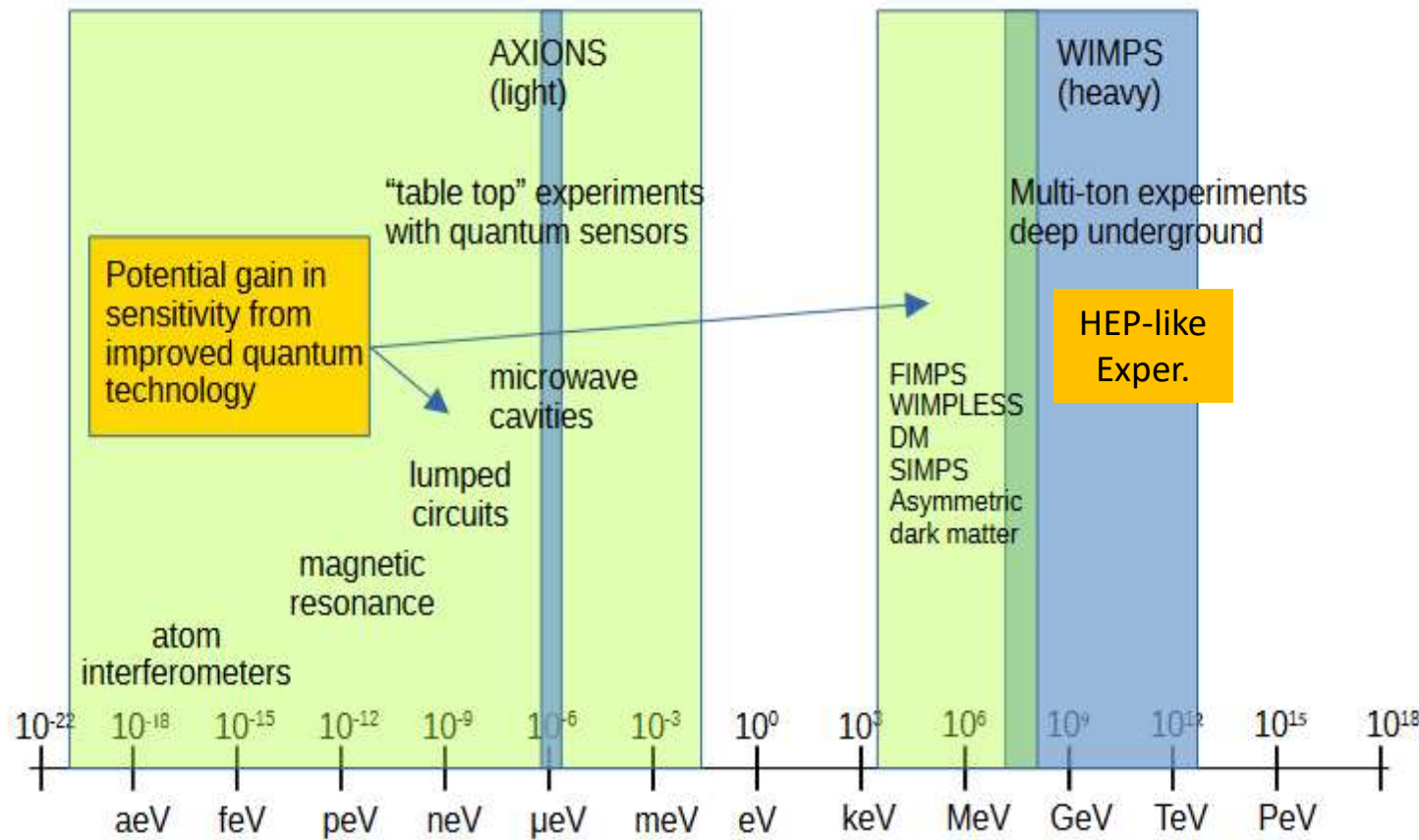
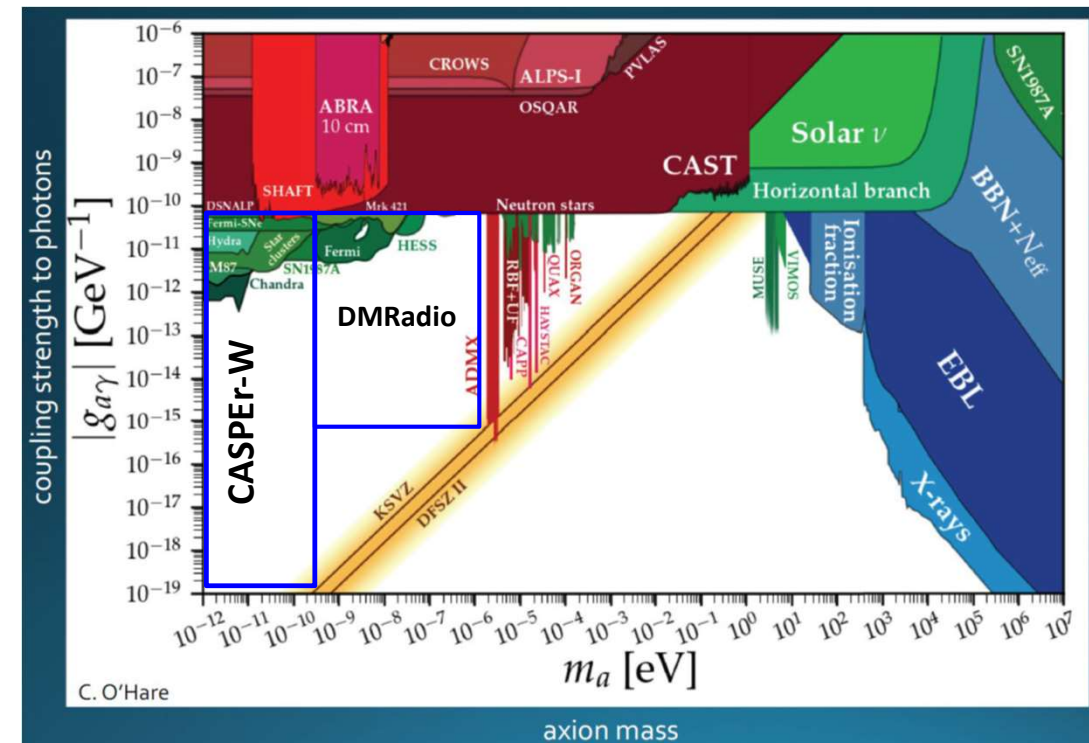


Figure 5.2: Axion mass range accessible via novel advanced quantum sensing techniques compared to current experiments. [1] (Blue bands: range of traditional experiments).

[1] DOI: 10.17181/CERN.XDPL.W2EX (ECFA Report)

Several proposals and ongoing experiments already on the table:

- ADMX
- CASPER
- QUAX
- DMRadio-50L/m³
- Dark SRF
-



Single Molecule Magnets (SMMs)

SMMs are crystalline materials characterized by [1]:

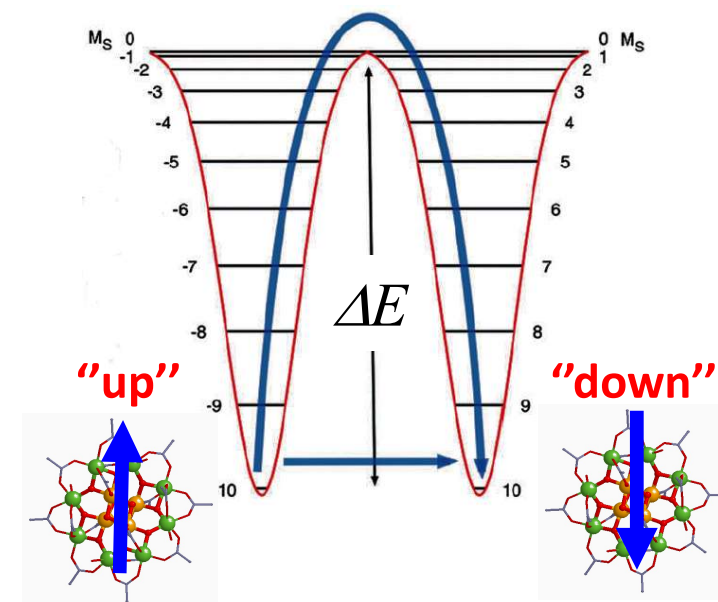
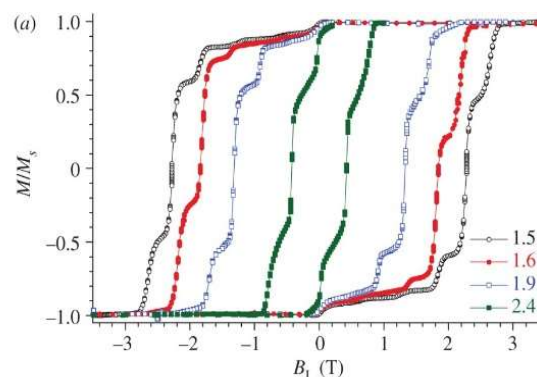
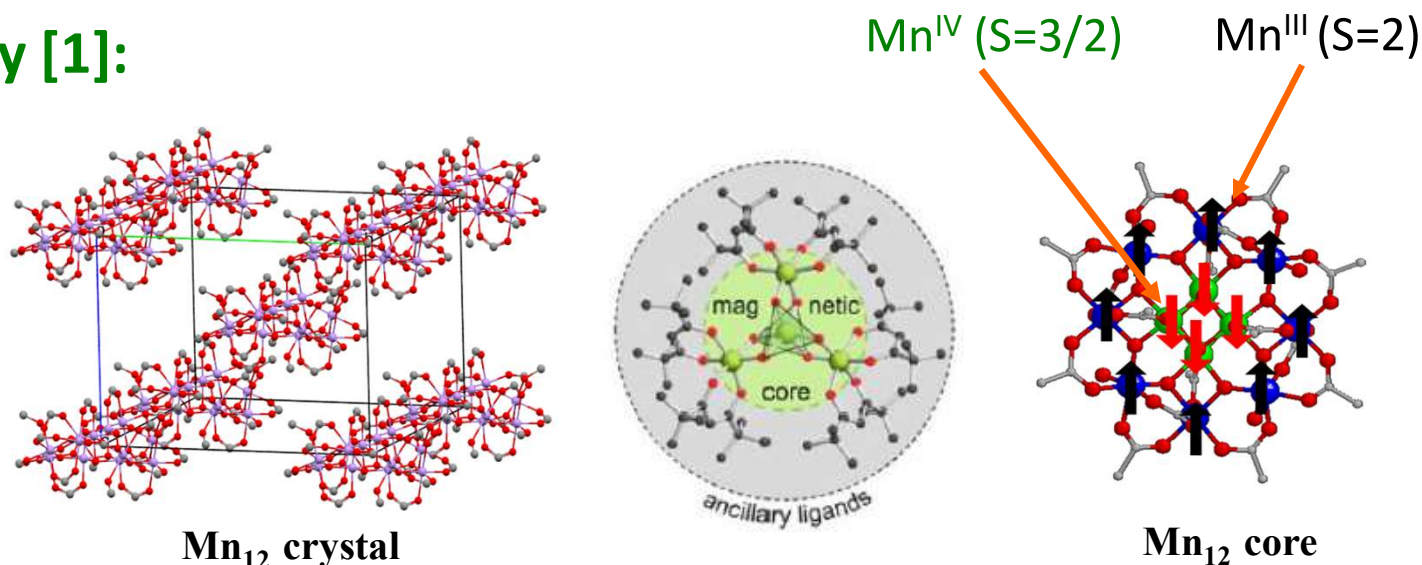
1. Regular crystalline structure, made by identical molecules with a magnetic core of a finite number ($n > 1$) of paramagnetic centers, with strong intramolecular exchange interactions.
2. Molecules shielded by organic ligands → weak intermolecular interactions.

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

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

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

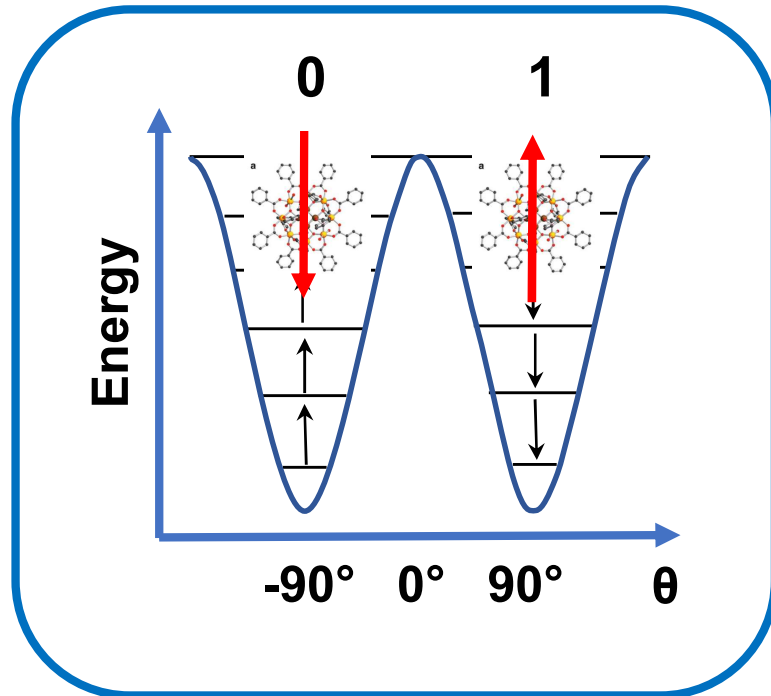
Relatively new materials with interesting potential applications



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

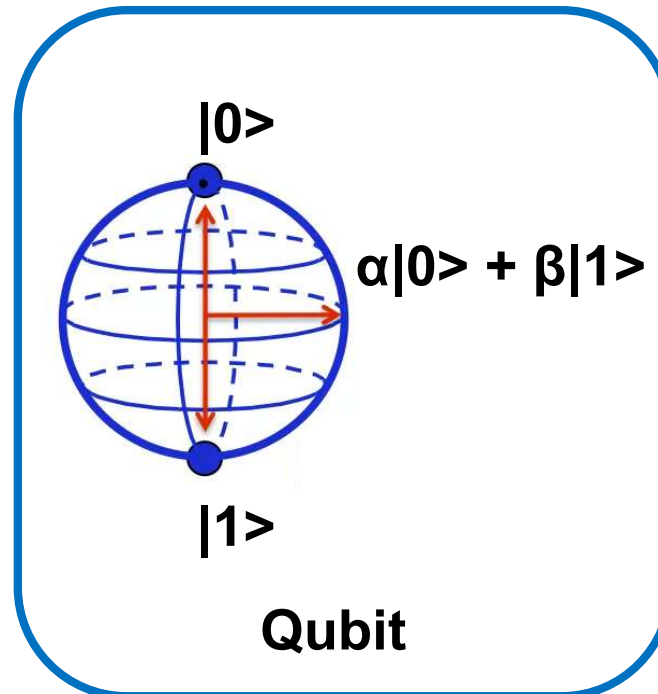
Potential Applications of SMMs

High-density memory storage [1]



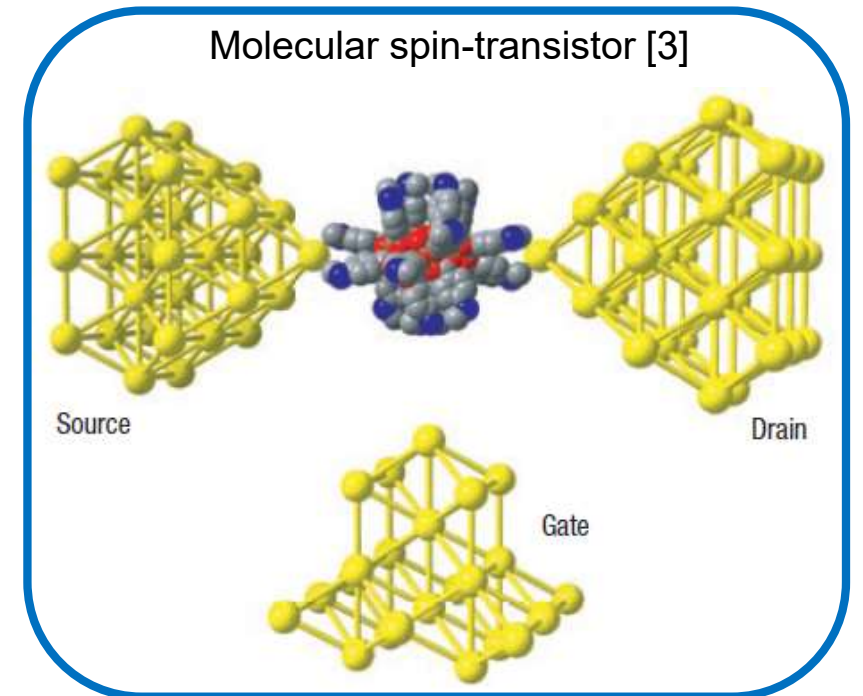
[1] Mannini *et al. Nat. Mater.* **8**, 194 (2009)

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

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, also covering a region not yet experimentally explored

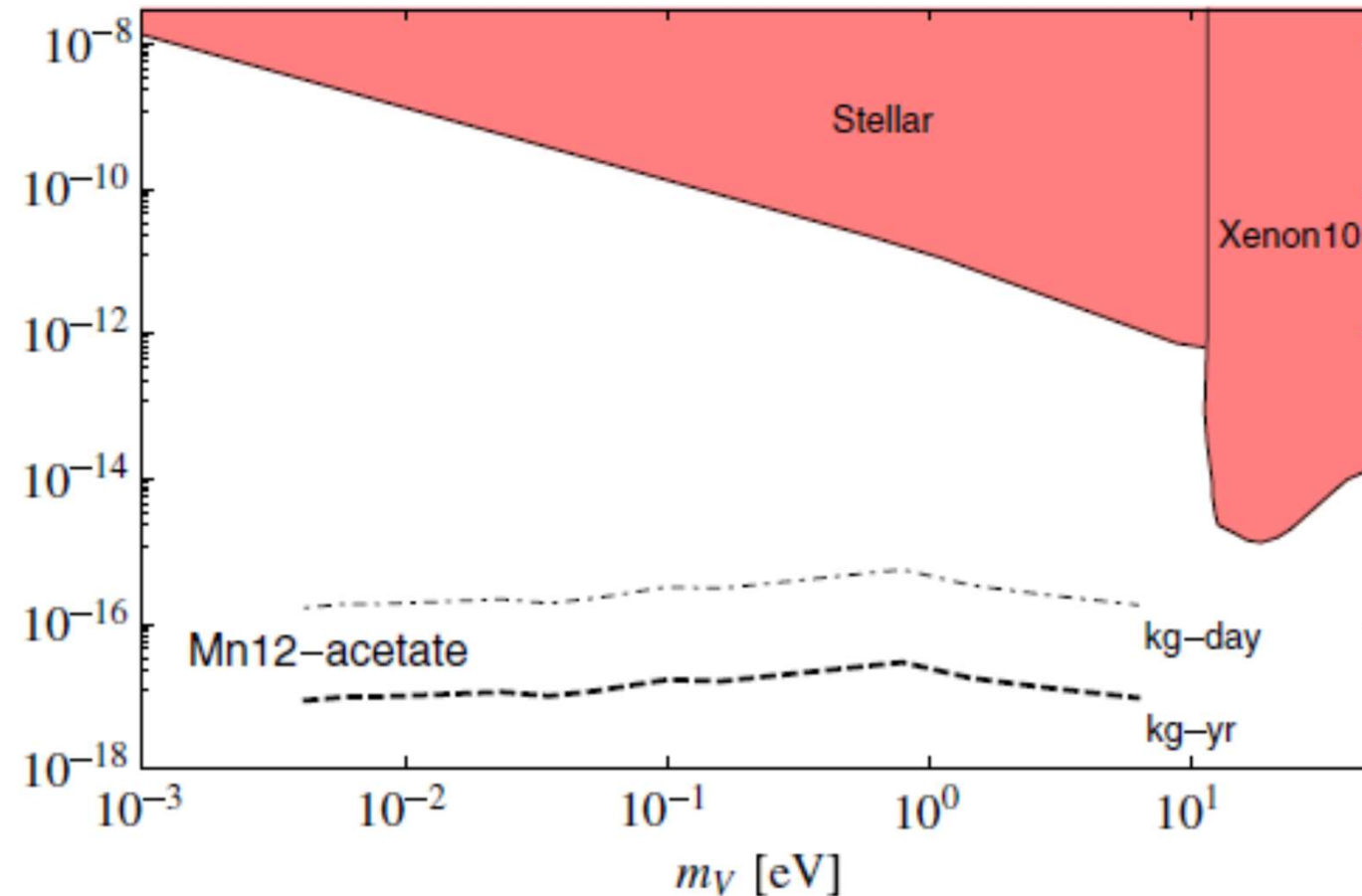


FIG. 6. Estimated sensitivity to absorption of dark vector DM in Mn_{12} -acetate, assuming an aggressive sensitivity of 1 event/kg year (dashed), and a sensitivity of 1 event/kg day (dot-dashed). The absorption data from Refs. [62,65] (described in the appendix) has been smoothed, an interpolation used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

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

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

The INFN R&D NAMASSTE Project

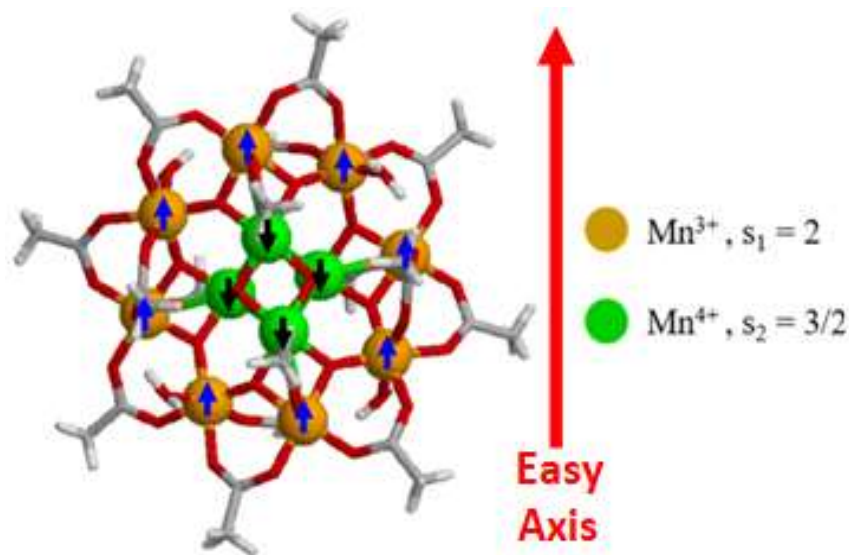
NAMASSTE: NanoMagnets for quantum Sensing and Data Storage

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

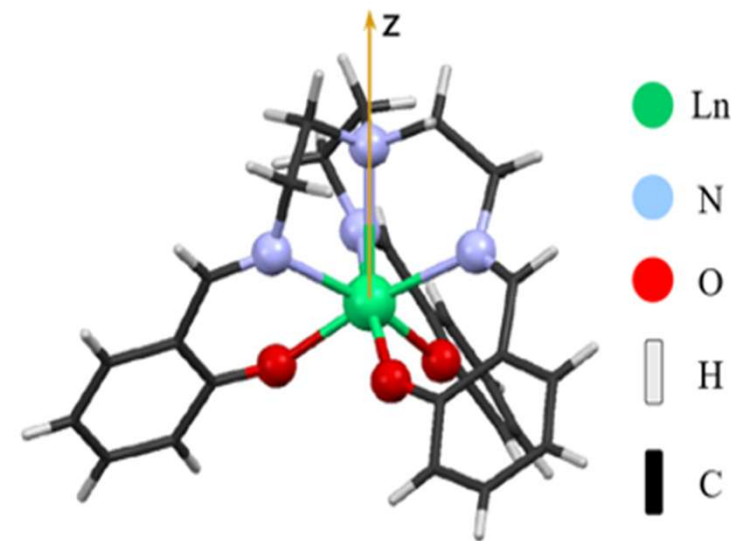
- **single molecule magnets (SMMs)**, for **high-sensitivity** sensors, potentially suited for revealing dark matter hidden photon [1],
- **single ion magnets (SIM)**, for **high-density** memory storage systems.

} Focus of this talk

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



Mn₁₂ SMM

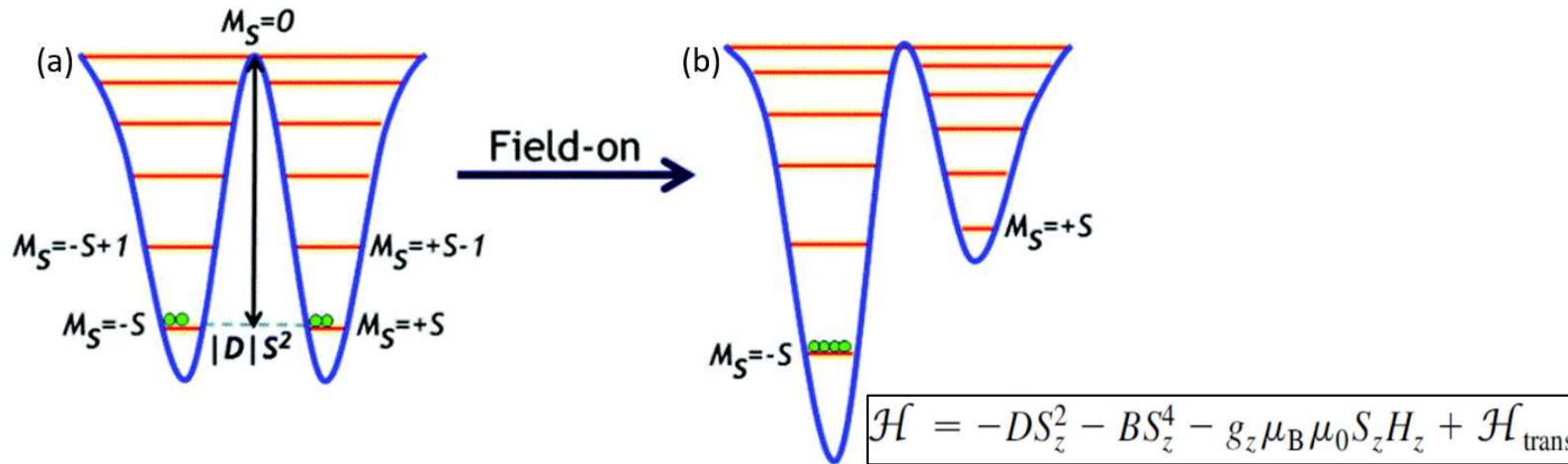


Ln-based SIM

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

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 \rightarrow first evidence of Mn12 as a sensor

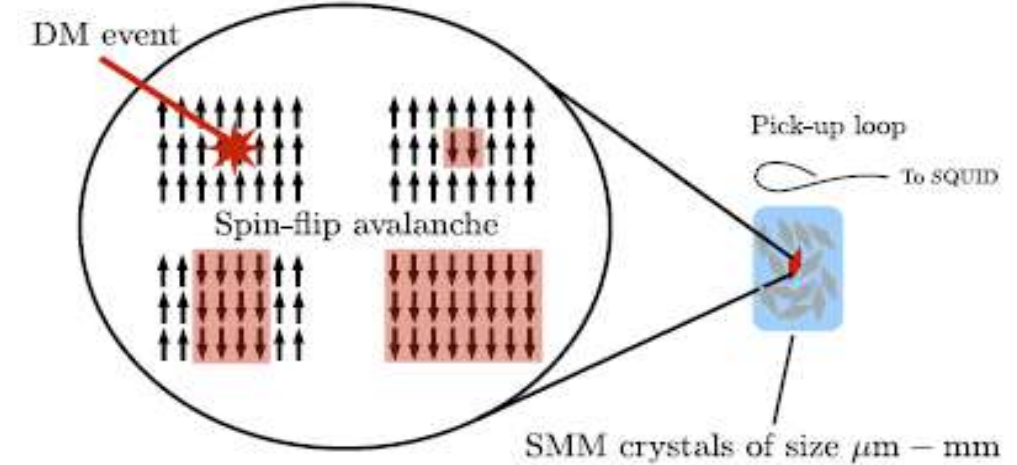
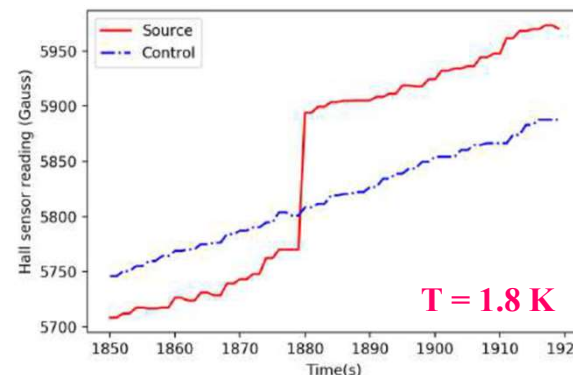
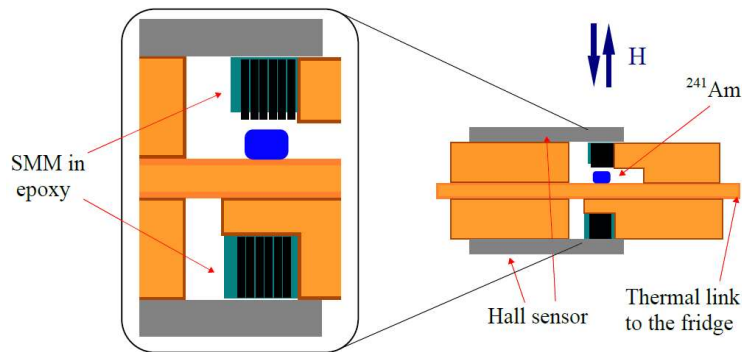


FIG. 1. DM detector concept based on magnetic deflagration in molecular nanomagnet crystals. A DM event that deposits energy in the form of heat ignites a spin-flip avalanche in the crystal which is detected by the change in magnetic flux through a pick-up loop.

[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.**

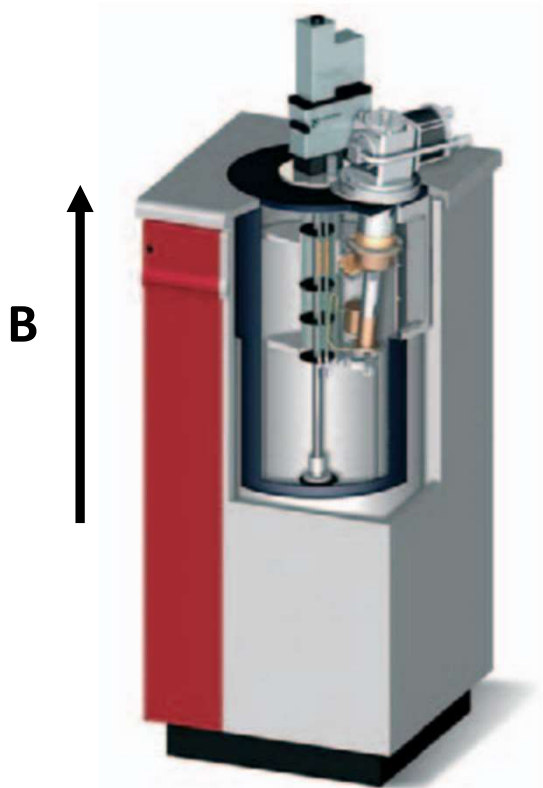
[2] Chen *et al.* arXiv:2002.09409v2

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NAMASSTE: Studies Related to Quantum Sensing

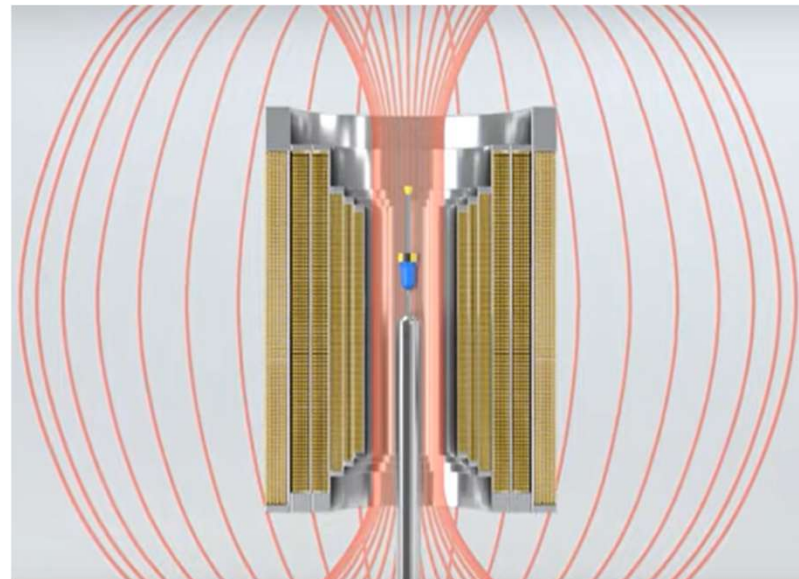
In NAMASSTE different techniques are used to study Mn_{12} in presence of **low activity** ionizing radiation sources

SQUID magnetometer



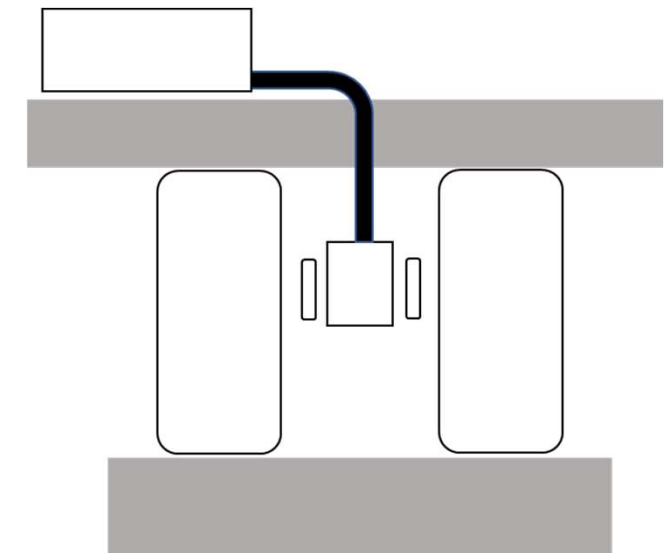
Measurement of the variation of the magnetization over the **entire volume** of the sensor: similar approach to the one reported in literature.

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)



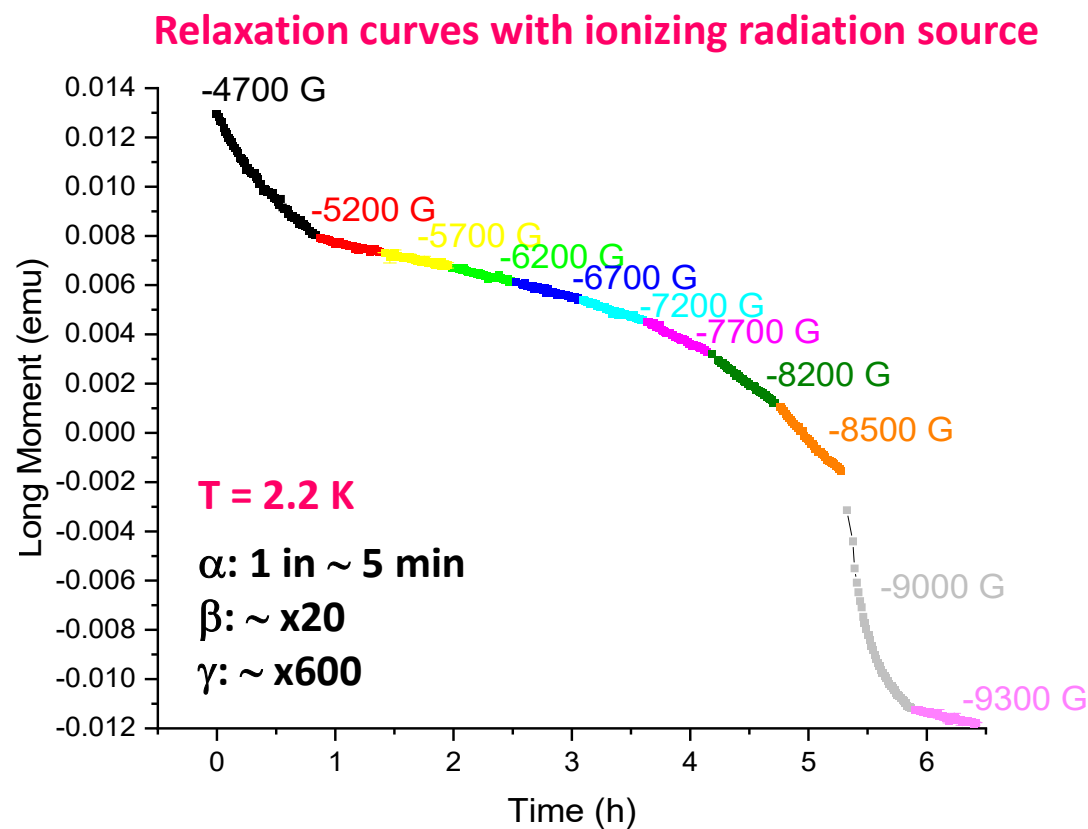
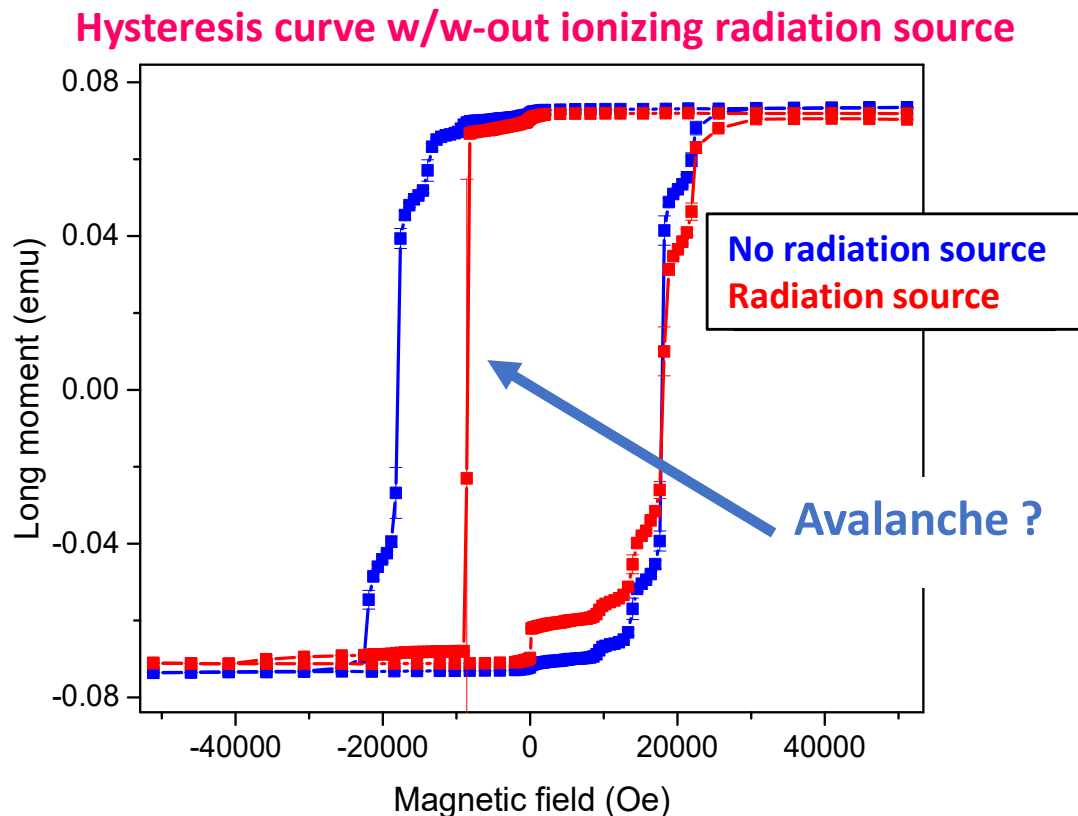
But Mn_{12} has $S = 10$
→ no intrinsic EPR signal ...

SQUID Magnetometry Studies on Mn12

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

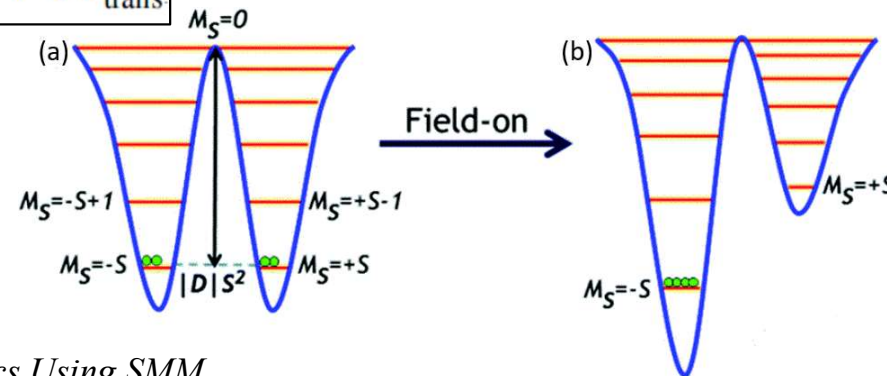


Crystals of Mn12 with the easy axis // to the external magnetic field



$$\mathcal{H} = -DS_z^2 - BS_z^4 - g_z \mu_B \mu_0 S_z H_z + \mathcal{H}_{\text{trans}}$$

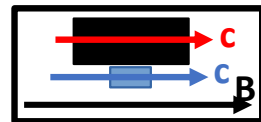
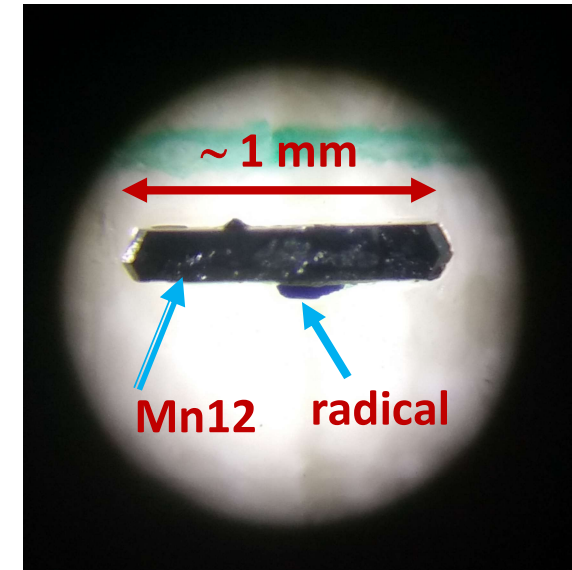
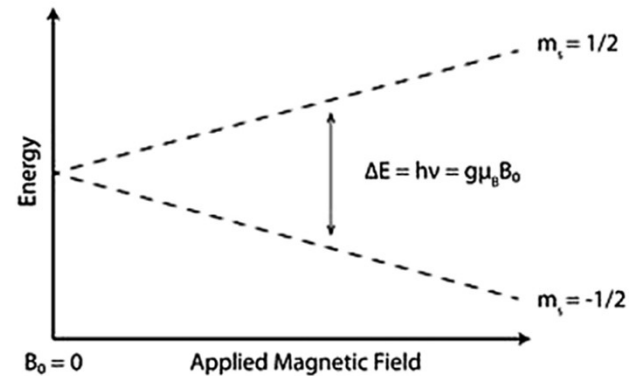
- As expected, the hysteresis loops show 'jumps' at suitable B values due to quantum tunnelling effects.
- Abrupt reversal of magnetization, compatible with 'avalanche' effects, observed only in one case during hysteresis loops.
- Further extensive relaxation studies did not show induced avalanches.



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).



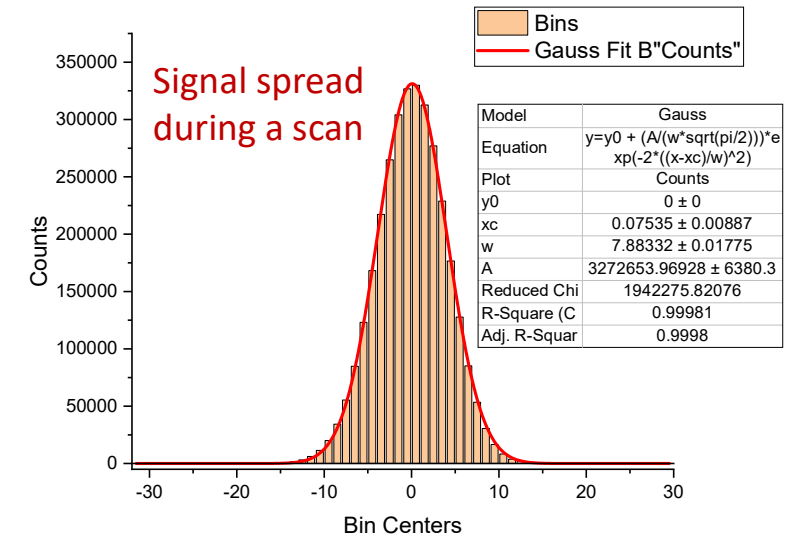
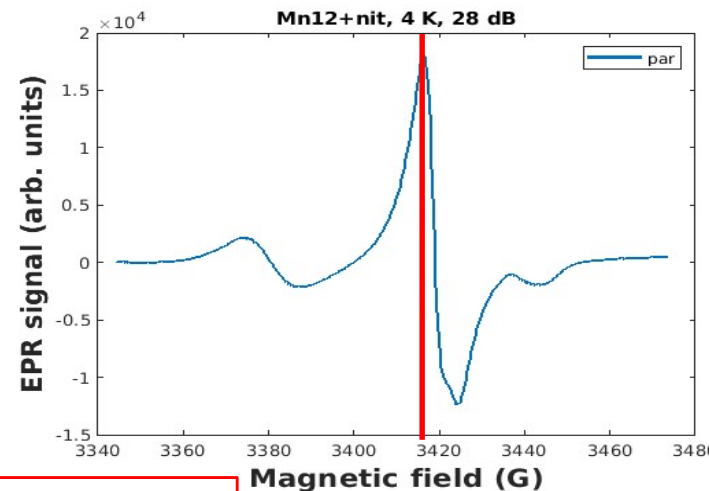
Adopted technique [1]:

- 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

NMR Studies on Mn12

Goal: introduce a new detection approach, using NMR-based techniques, by studying the relaxation 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 relaxation time τ of the magnetization from the related fit.

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

Chosen protocol:

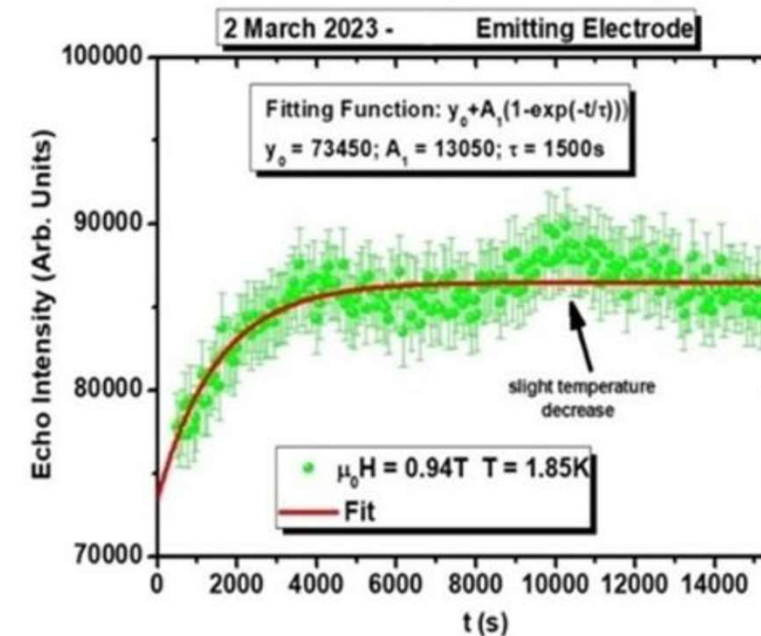
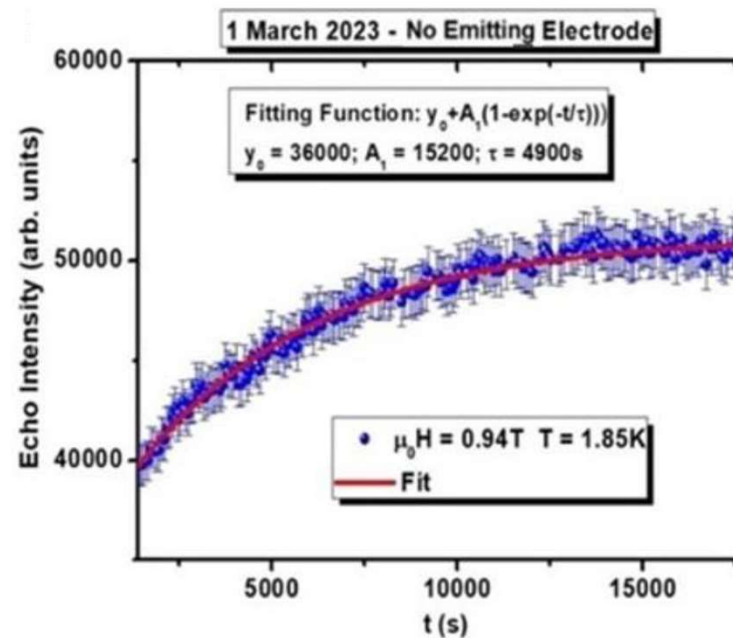
- Mn12 crystal cooled down to 1.85 K at $B = 0$ T,
- then put at fixed $B = 0.94$ T (3rd jump);
- start the measurements to follow the M recovery.

Noticeable reduction in relaxation 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.

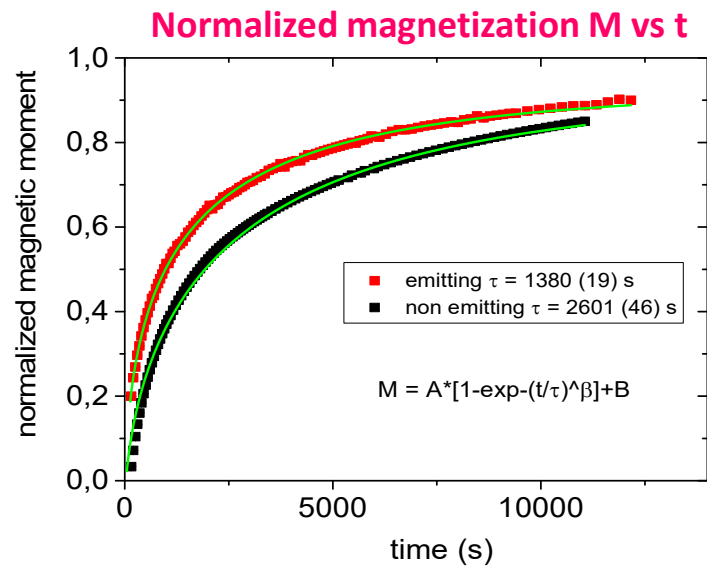
¹H NMR echo height h vs time



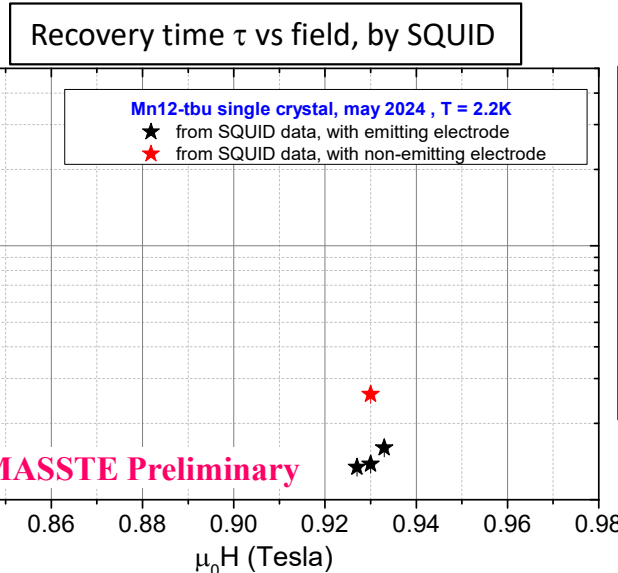
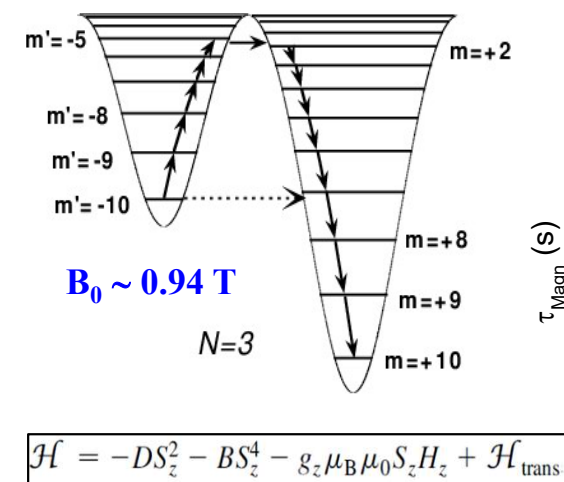
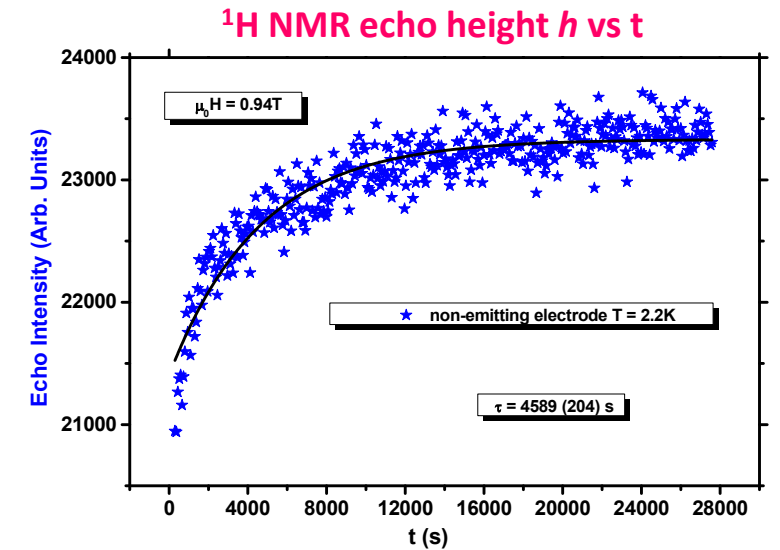
Run	No radiation source	Radiation source
September 2022	10400	3500
March 2023	4900	1500

Mn12 SMM as Sensors: Main NAMASSTE Results

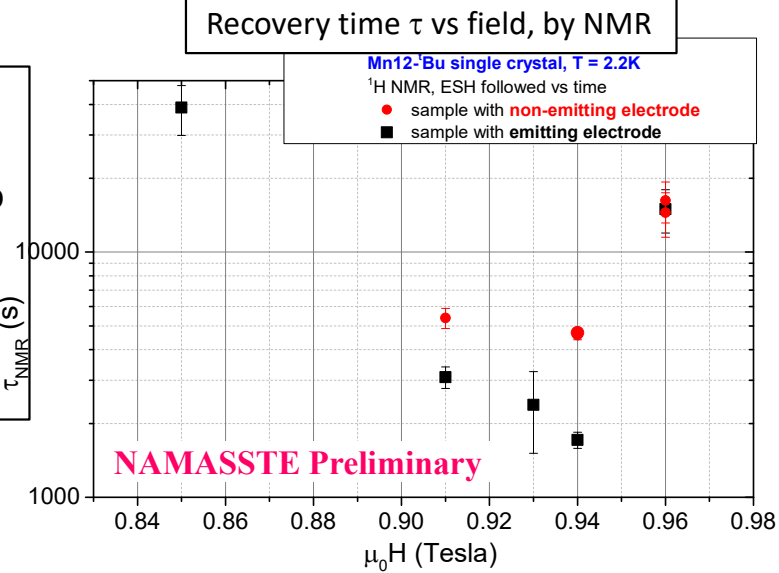
Quantum sensing based on NMR and SQUID measurements: studies on relaxation times



M recovery:
SQUID
NMR



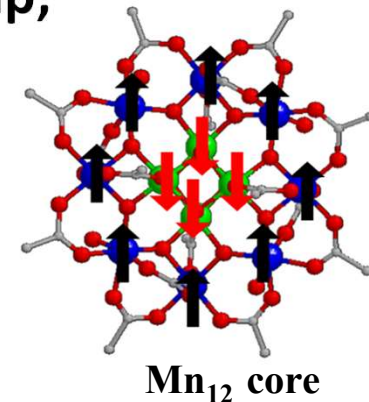
In SQUID and NMR experiments, a reduction in magnetization recovery time is observed due to impinging radiation (α , β , γ):
ionizing radiation induces perturbations in the Mn12 spin dynamics



Magnetic Techniques for Quantum Sensing Using Single Molecule Magnets (PRL, to be submitted)

Summary & Conclusions

- In the search for New Physics (ex. DM) 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 developments of Quantum Sensing for Particle Physics go in this direction.
- The NAMASSTE R&D project investigated the possibility to use SMMs as QS by studying Mn₁₂ with SQUID-, NMR- and EPR-based techniques under the incidence of ionizing radiation:
 - SQUID magnetometry studies did not show induced “avalanche” effects with our setup;
 - EPR-based measurements did not show changes in the absorption spectrum;
 - **NMR- and SQUID-based studies showed a clear reduction in relaxation 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

The Dark Matter

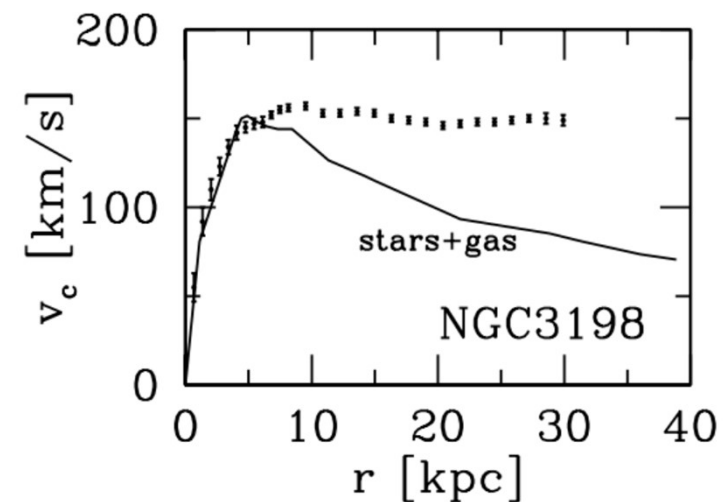
Cosmological and astronomical observations:

→ we are missing something

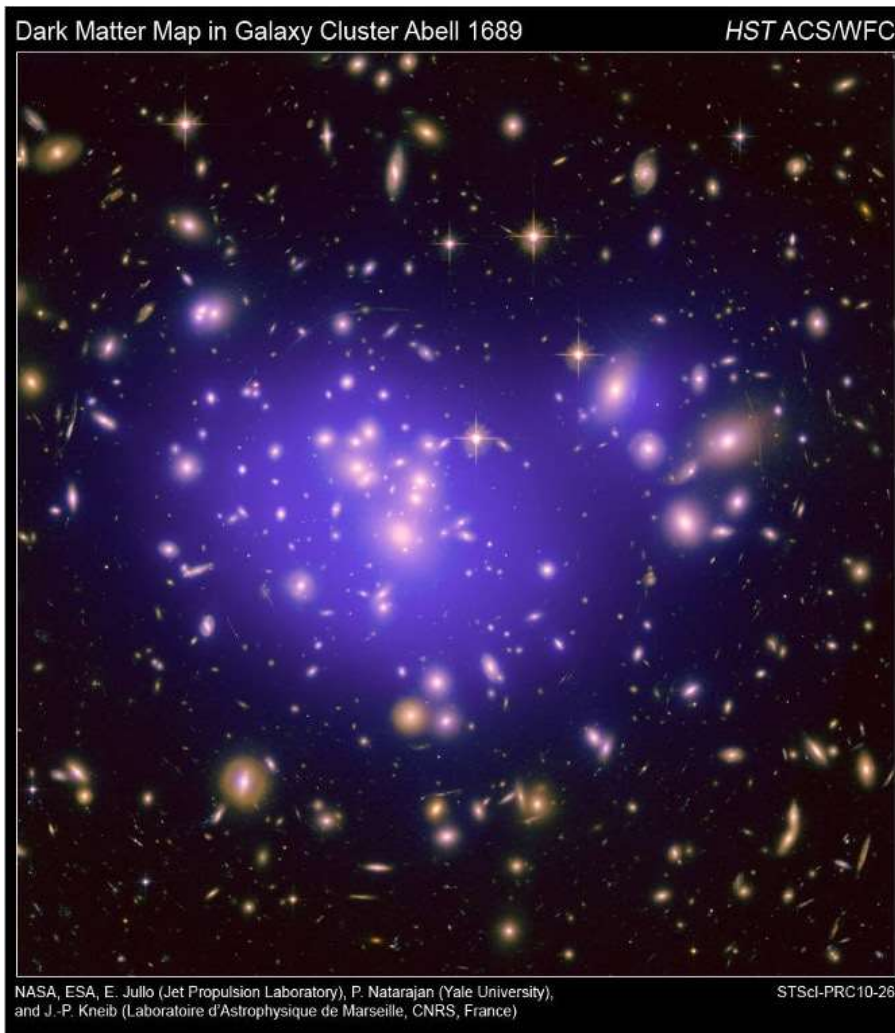
- **1933**: F. Zwicky observed that galaxies in the Coma cluster orbit much faster than their combined mass can explain; he postulated the existence of a new form of invisible matter, which he named "**Dark Matter**".

- **1970**: V. Rubin and W.K. Ford discovered that the rotational curves of galaxies are flat

$$\frac{GMm}{r^2} = m \frac{v^2}{r} \Rightarrow v = \sqrt{\frac{GM(r)}{r}}$$
$$v = \text{const.} \Rightarrow M(r) \sim r$$



→ If modifications on General Relativity are excluded, the Dark Matter overcomes the ordinary matter in galaxies, even outside their core



NASA's Hubble Space Telescope shows an immense cluster of galaxies located 2.2 billion light-years away. The cluster's gravitation warps light. Dark matter cannot be photographed, but its model distribution is shown in the blue overlay.

What “Quantum Sensing” Means?

“Quantum sensing” (QS) describes the use of a quantum system, quantum properties or quantum phenomena to perform a measurement of a physical quantity [1].

Quantum sensors (q-S) register a change of quantum state caused by the interaction with an “external” system. Then, a q-S is a device whose measurement (sensing) capabilities are enabled by our ability to manipulate and/or read out its quantum states [2].

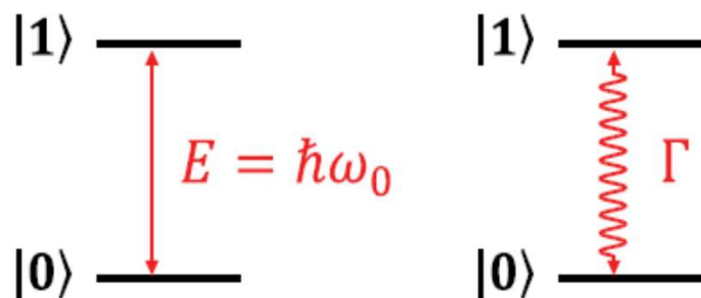


FIG. 1. Basic features of a two-state quantum system. $|0\rangle$ is the lower energy state and $|1\rangle$ is the higher energy state. Quantum sensing exploits changes in the transition frequency ω_0 or the transition rate Γ in response to an external signal V . [1]

Typically, QS describes one of the following [1] (which can be seen as sensor type definitions):

- (I) Use of a quantum object to measure a physical quantity (classical or quantum). The quantum object is characterized by quantized energy levels. Specific examples include electronic, magnetic or vibrational states of superconducting or spin qubits, neutral atoms, or trapped ions.
- (II) Use of quantum coherence (i.e., wavelike spatial or temporal superposition states) to measure a physical quantity.
- (III) Use of quantum entanglement to improve the sensitivity or precision of a measurement, beyond what is possible classically.

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

[2] S. D. Bass, M. Doser, arXiv:2305.11518v1 (2023)

Quantum Sensing Definitions

Typically, a q-system can be considered a q-S if:

- 1) it has discrete energy levels, usually 2 levels with gap E ;
note: many properties of more complex QS can be modelled via such a “q-bit like” sensor;
- 2) it can be initialized in a given known state; its state can be read;
- 3) it can be coherently manipulated, typically via t-dependent fields (indeed, not mandatory for all protocols);
- 4) it is possible to quantify its interaction with an “external perturbation” $V(t)$ via a transduction (or coupling) parameter γ defined as:

$$\gamma = \partial^q E / \partial V^q$$

note: the interaction with V induces changes in the transition energy E and/or in the transition rate Γ

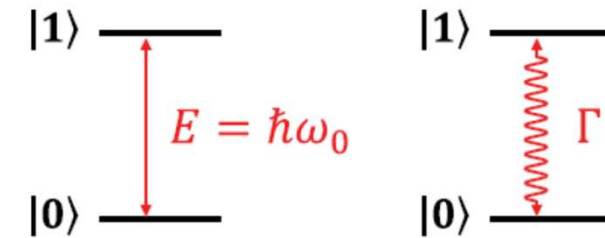


FIG. 1. Basic features of a two-state quantum system. $|0\rangle$ is the lower energy state and $|1\rangle$ is the higher energy state. Quantum sensing exploits changes in the transition frequency ω_0 or the transition rate Γ in response to an external signal V . [1]

A q-S is characterized by:

- 1) type of “external perturbation” to which it is sensitive;
- 2) intrinsic sensitivity (minimum detectable signal per unit of time), scaling as:

$$\text{sensitivity} \propto \frac{1}{\gamma \sqrt{T_\chi}}$$

γ : transduction parameter

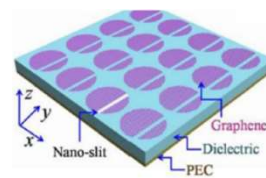
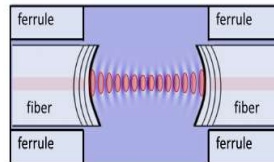
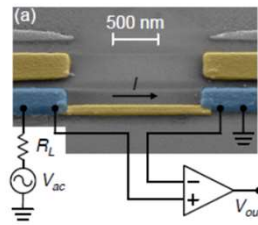
T_χ : decoherence (or relaxation) time

Quantum Sensors for Low Energy PP Applications

QS for low energy particle physics: the energy scale being probed is related to the one of the energy levels of the sensor itself (single interaction, typically at \leq eV scale).

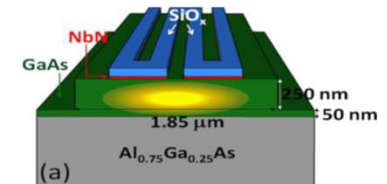
Physics Goals

- Search for NP/BSM (ex. α_{em} variations)
- Axions, ALP's, DM & non-DM UL-particle searches
- ν physics (masses)
- Tests of QM (ex. wavefunction collapse, decoherence)
- EDM searches, tests of fundamental symmetries

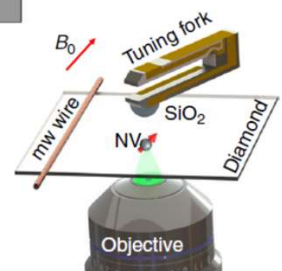


Quantum Technologies (as identified in ECFA roadmap [1])

Clocks and clocks networks

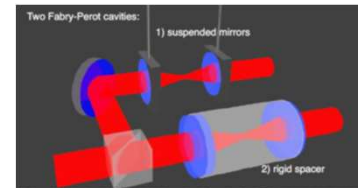


Kinetics detectors



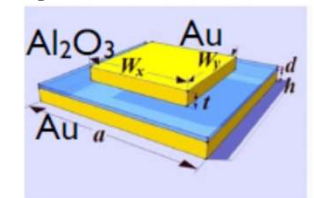
Superconducting (TES, SNSPD, ...) and spin-based devices (NV-diamonds, SMMs,)

Optomechanical sensors



Atoms, molecules, ions, interferometry

Metamaterials, 0/1/2-D materials



[1] DOI: 10.17181/CERN.XDPL.W2EX

Quantum Sensors for High Energy PP Applications

QS for high energy particle physics: quantum systems form part of a larger system, in which their specific properties enhance existing methods or enable novel types of detectors optimized for high energy particle physics (multiple interaction, typically at $> \text{KeV}$ scale).

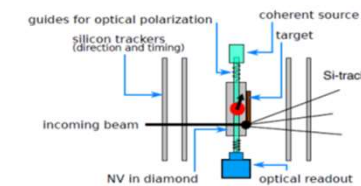
Not yet developed concepts (still speculative)

Typical Requests for Improvements in:

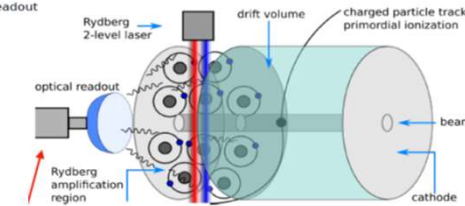
- tracking (hit positions, material budget)
- timing (TOF for PID)
- calorimetry (shower shape, timing, granularity)
- novel observables (helicity/polarization)

Applications from Quantum Technologies (as proposed in ECFA roadmap [1])

Spin-based sensors
Helicity detectors



Atoms, molecules, ions
Rydberg atom TPC's



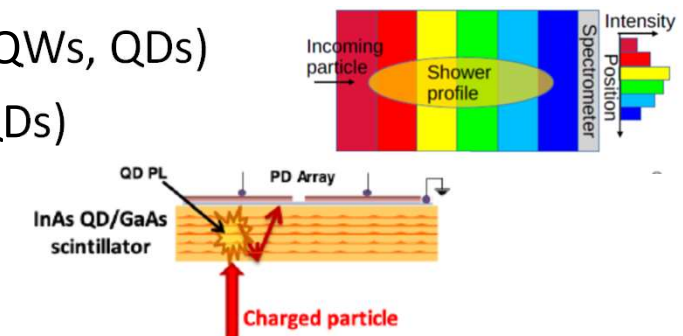
Metamaterials, 0/1/2-D materials

Ultra-fast scintillators based on perovskites

Active scintillators (QCL, QWs, QDs)

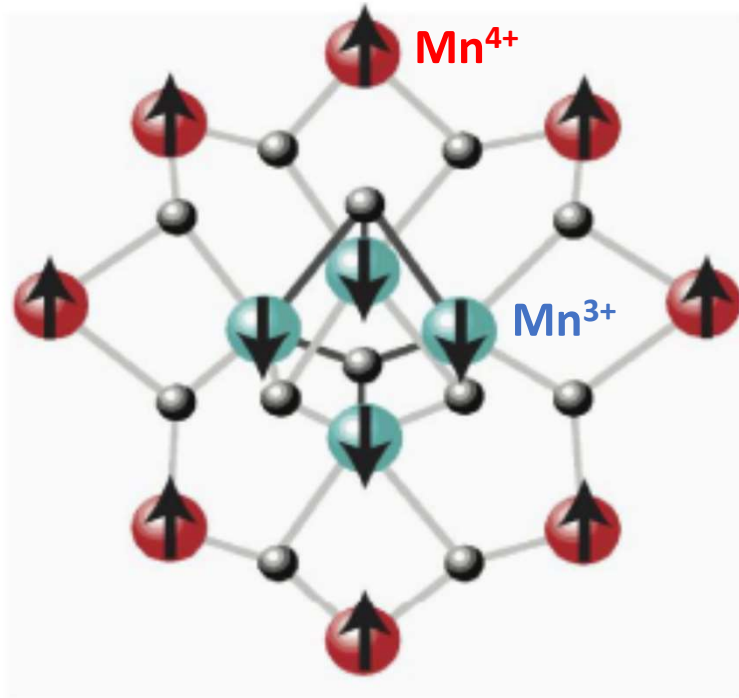
Chromatic calorimetry (QDs)

GEMs (graphene)



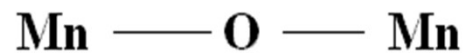
[1] DOI: 10.17181/CERN.XDPL.W2EX

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)

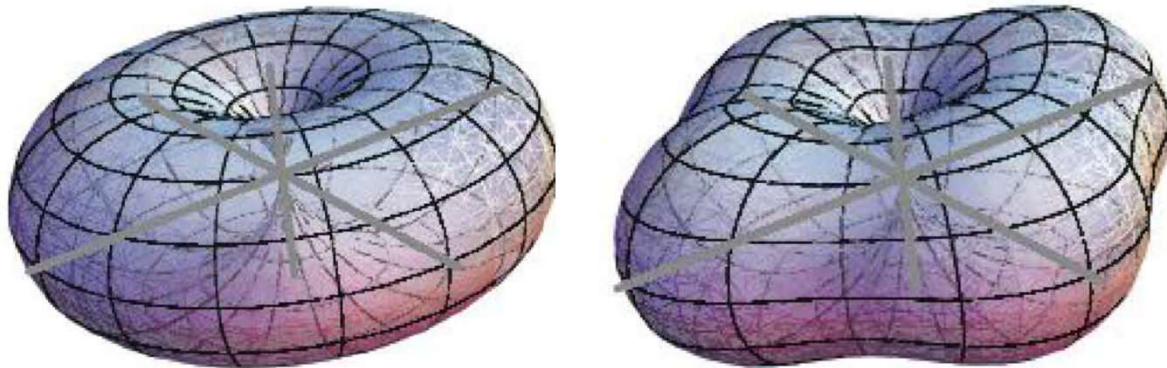
Mn₁₂ Spin Hamiltonian (in absence of an “external perturbation”)

$$H = H_0 + H_c$$

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”: $H_c = -g_z\mu_B S_z H_z$ (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



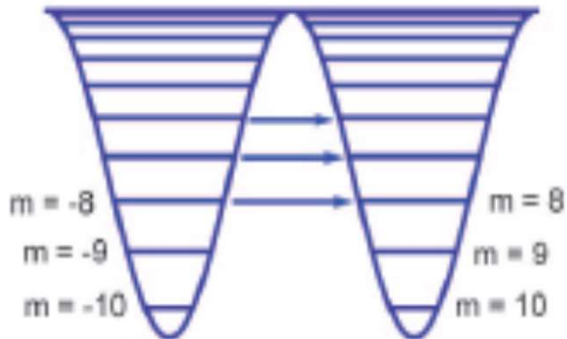
Left: spherical polar plots of energy as a function of orientation for a classical spin with uniaxial anisotropy.
Right: same as above, with additional fourth-order transverse anisotropy [1].

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

Some Details on Mn₁₂ SMM (III)

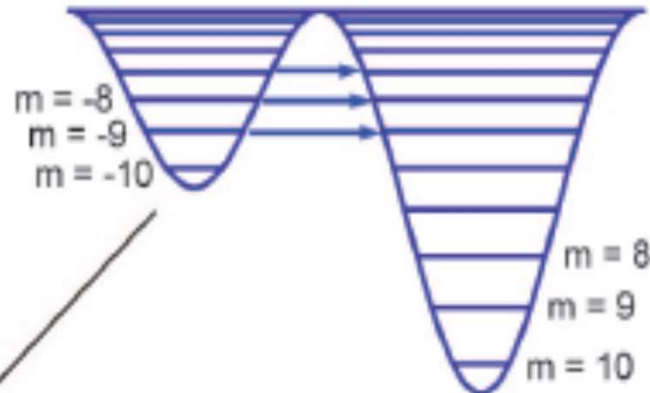
$$H = H_0 = -DS_z^2 - AS_z^4 + H'$$

N = 0



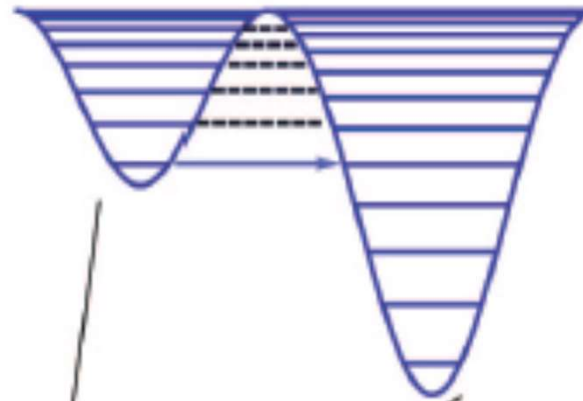
$$H \approx -DS_z^2 + H' + H_C$$

N = 4



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

N = 4

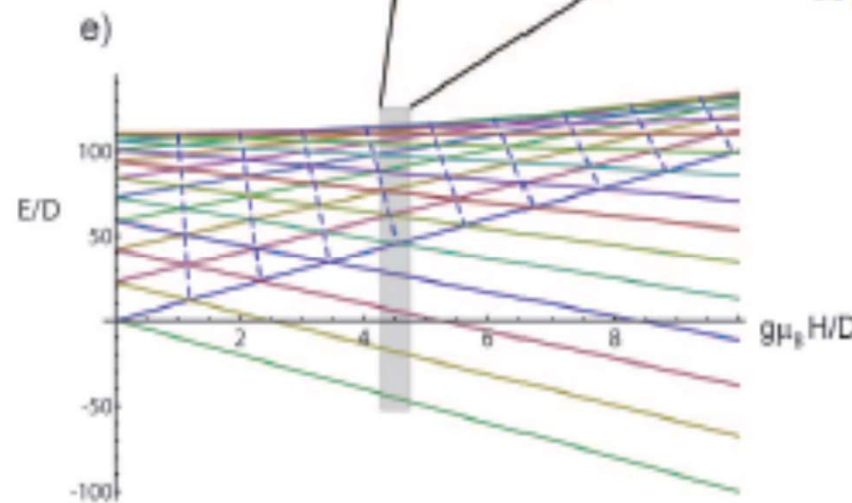
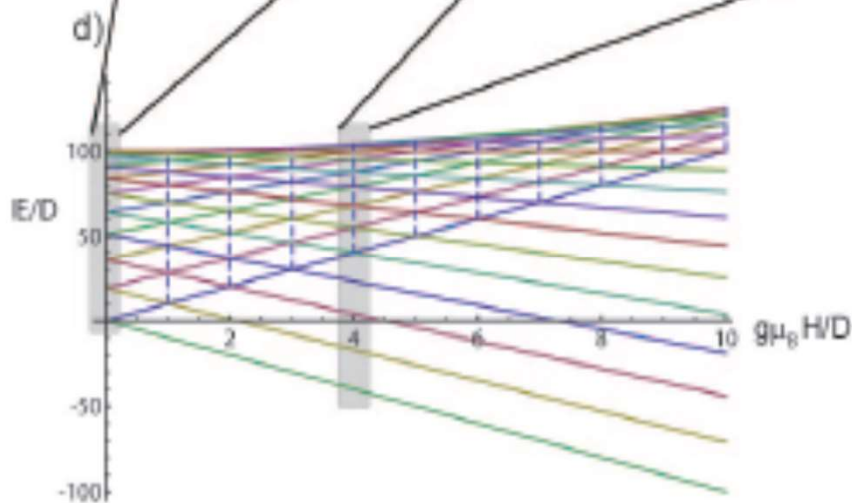


Energy levels “align” if:

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

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

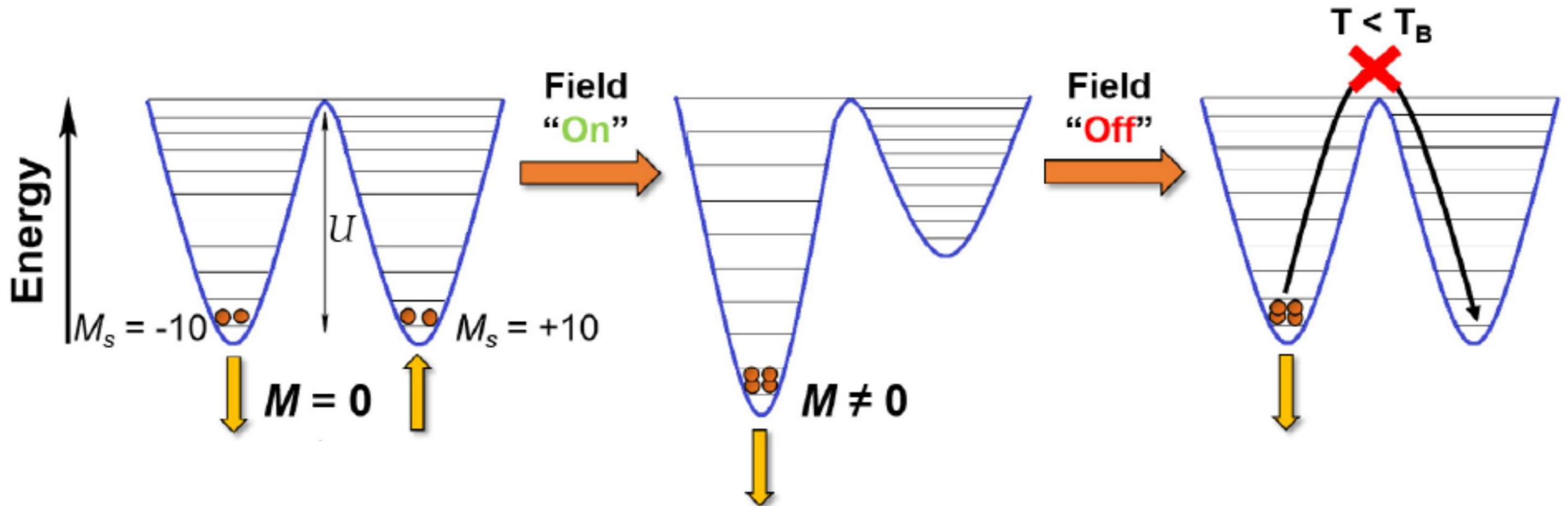
for $A \neq 0$ ($N = m' + m$)



Some Details on Mn₁₂ SMM (IV)

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)



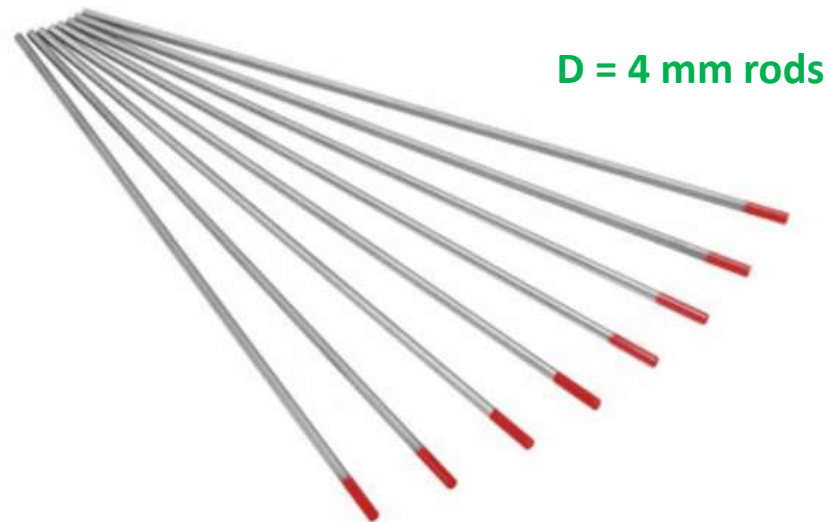
Radiation Sources for the NAMASSTE Experiment

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

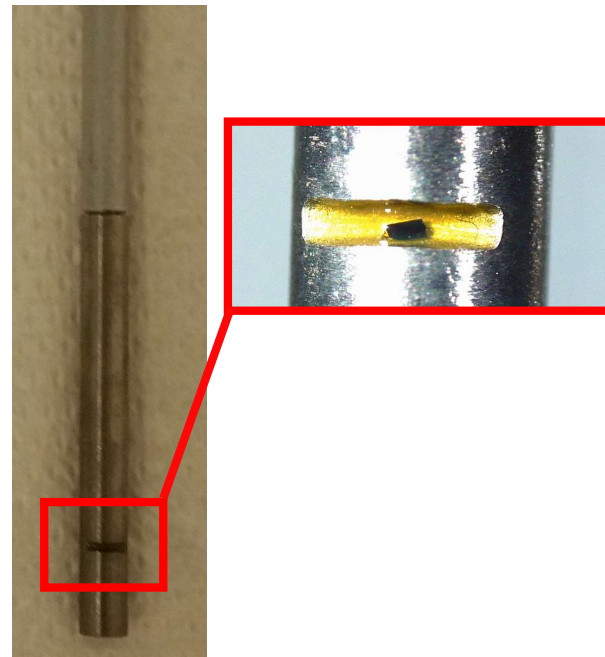
Made from electrodes used for special welding (tungsten with **2% Th**), by precision machined cut to fit specific technical needs of the devices.

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



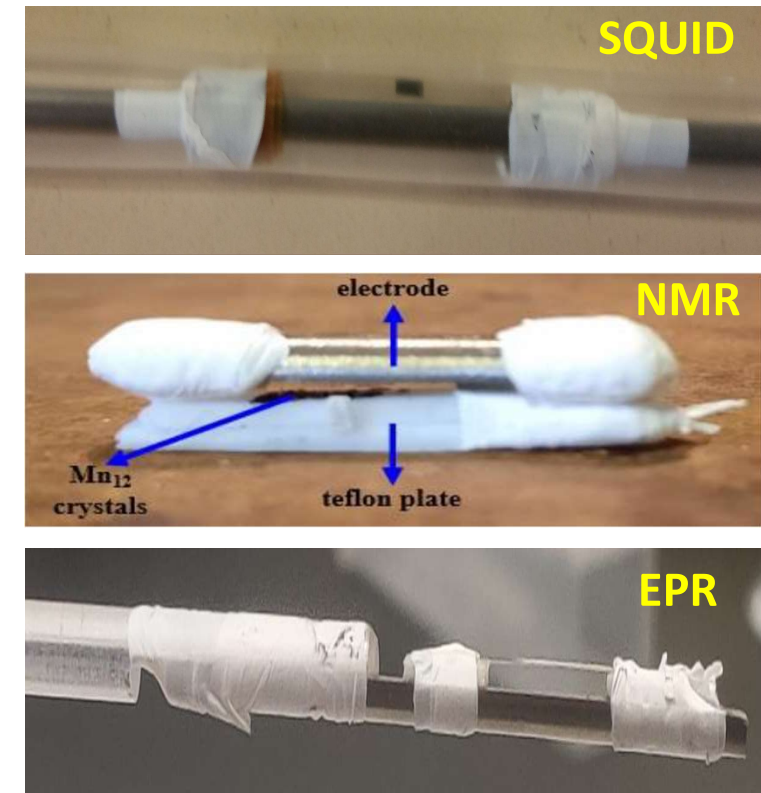
EPR-I: cylindrical geometry with small transversal cut



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

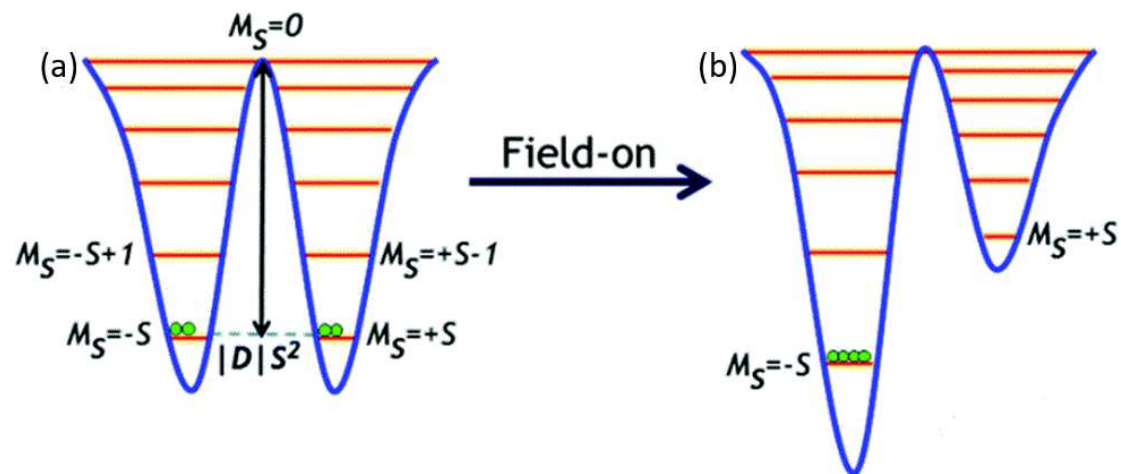
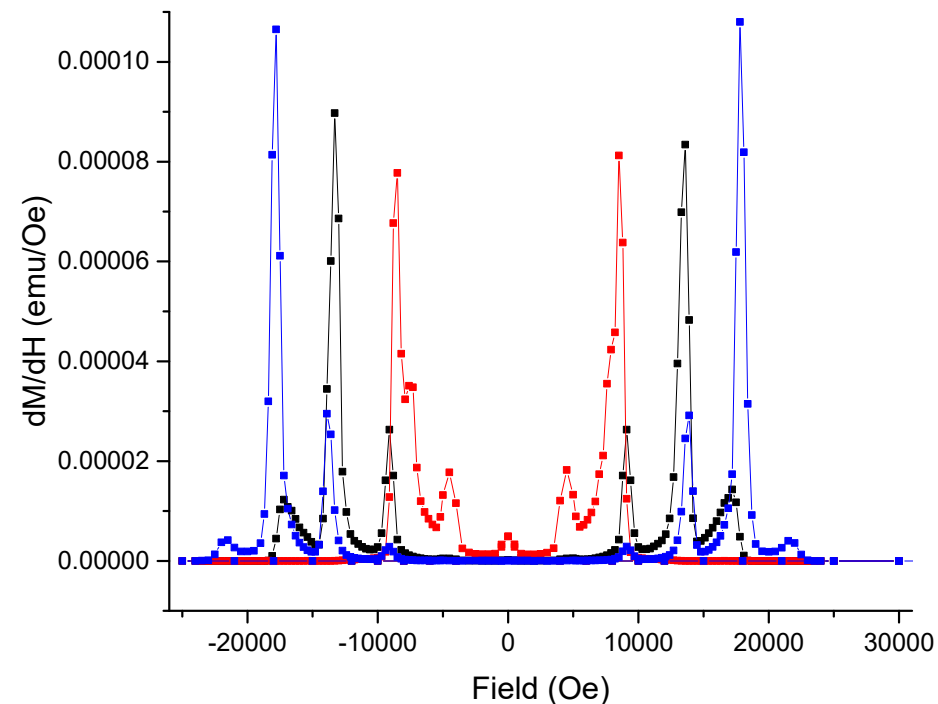
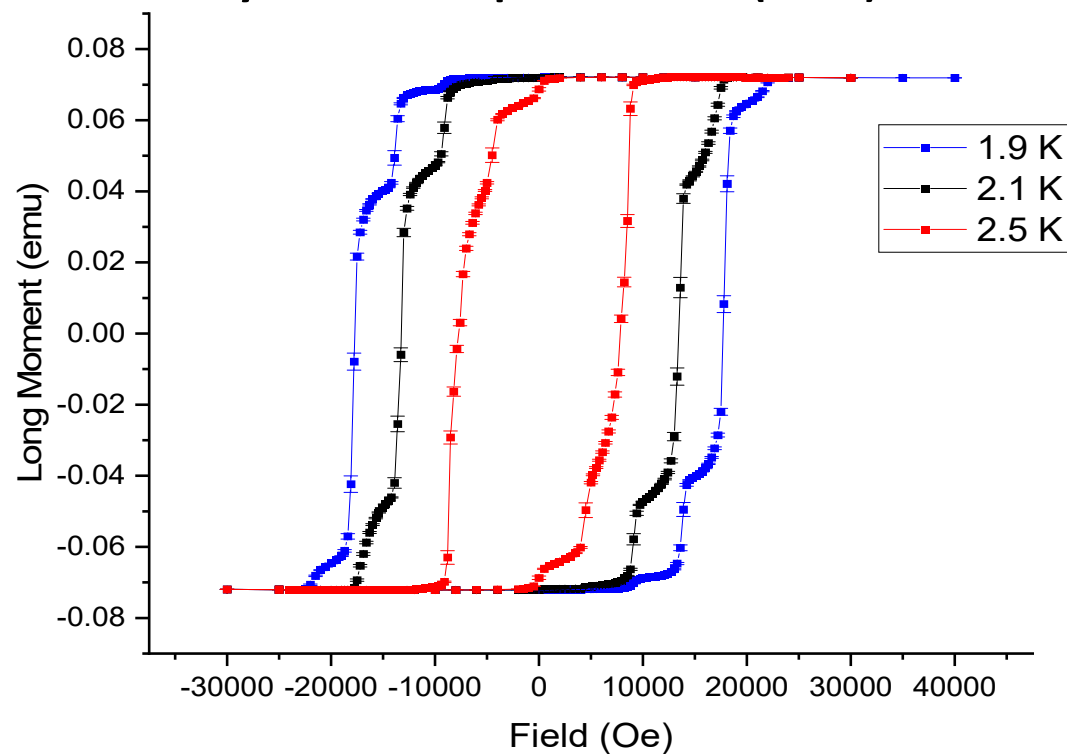


- Good signals w.r.t. standard crystal sample holders
- Only ~ 5 times reduction in EPR signal intensity

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

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