

Magnetic Techniques for Quantum Sensing Using Single Molecule Magnets

Alberto Cini^{1,2}, Lorenzo Sorace^{3,2}, Fabio Santanni^{3,2}, Setareh Fatemi⁴, Francesca Brero^{5,4}, Elio Giroletti⁴,
Mauro Merlo⁶, Maria Fittipaldi^{1,2}, Giuseppe Latino^{1,2}, Alessandro Lascialfari^{5,4}, Paolo Santini^{7,8}, Manuel Mariani^{5,9}

¹ Department of Physics and Astronomy, University of Florence, Via Sansone 1, Sesto F.no, 50019, Italy.

² National Institute for Nuclear Physics (INFN) - Florence Unit, Via B. Rossi 1, Sesto F.no, 50019, Italy.

³ Department of Chemistry "U. Schiff", University of Florence, Via della Lastruccia 3, Sesto F.no, 50019, Italy.

⁴ National Institute for Nuclear Physics (INFN) - Pavia Unit, Via A. Bassi 6, Pavia 27100, Italy.

⁵ Department of Physics, University of Pavia, Via A. Bassi 6, Pavia 27100, Italy.

⁶ Nucleco, at JRC NDWMD, Site Laboratory for Radioactivity Measurement (LMR), Via E. Fermi 2749 Ispra 20027, Italy.

⁷ Department of Mathematical, Physical and Computer Sciences, University of Parma, Parco Area delle Scienze 7/A, Parma 43124, Italy.

⁸ National Institute for Nuclear Physics (INFN) - Milano-Bicocca Unit, Parma group, Parco Area delle Scienze 77A, Parma 43124, Italy.

⁹ National Institute for Nuclear Physics (INFN) - Milan Unit, Via Celoria 16, Milan 20133, Italy.

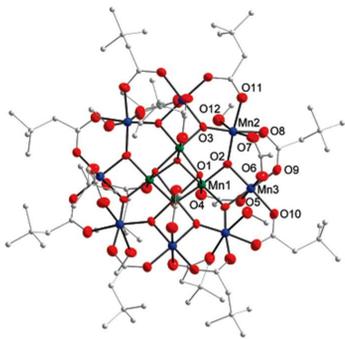


INTRODUCTION

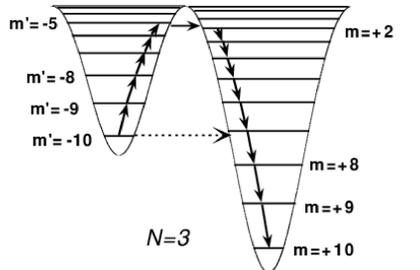
An investigation of the effects on $[\text{Mn}_{12}\text{O}_{12}(\text{Bu-CH}_2\text{CO}_2)_{16}(\text{CH}_3\text{OH})_4] \cdot \text{CH}_3\text{OH}$ ($\text{Mn}_{12}\text{BuAc}$) [1] single molecule magnet (SMM) magnetic properties due to impinging of ionizing particles, is presented. Single crystals of $\text{Mn}_{12}\text{BuAc}$ [1] have been studied by means of ^1H Nuclear Magnetic Resonance (NMR) and SQUID magnetometry, looking for differences in the experimental parameters when the sample is hit or not by α and β particles, and γ radiations.

SAMPLE

Single crystals of $\text{Mn}_{12}\text{BuAc}$



Energy levels and M relaxation



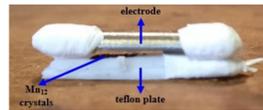
$$\mathcal{H} = -DS_z^2 - BS_z^4 - g_z \mu_B \mu_0 S_z H_z + \mathcal{H}_{\text{trans}}$$

$$\text{Thermal activation: } \tau = \tau_0 \exp[-\Delta/(k_B T)]$$

$$\text{Quantum tunneling: } \tau_T$$

EXPERIMENTAL METHODS

The system was prepared in the form of one or few aligned SMM single crystals and the measurements performed at $T \sim 2.2\text{K}$ for NMR and SQUID magnetometry, with the external magnetic field applied parallel to the c easy axis. In NMR experiments, the echo signal height (ESH) was followed as a function of time at different fields, while in SQUID measurements the recovery of the equilibrium value of the Magnetization was monitored; the possible difference in spin dynamics among the sample not hit by particles (SNP) and the one with particles impinging (SWPI), is in principle expected to be higher [2,3].



Set-up for NMR measurements: white hard teflon plate where glued Mn_{12}Bu single crystals lay and face the electrode source



Set-up for SQUID measurements: single crystal of Mn_{12}Bu glued on an acetate foil and mounted on the electrode source

SQUID MEASUREMENTS

In SQUID experiments, after a ZFC process, various magnetic fields were applied at $T = 2.2\text{K}$. Differences in the magnetization recovery times after the application of the field were observed among the SNP and SWPI conditions.

NMR MEASUREMENTS

When the field is applied at $T = 2.2\text{K}$ after a zero-field-cooling process, the ESH increased following the slow recovery of the magnetization with a characteristic recovery time τ_R [4], in both SNP and SWPI cases., displaying differences.

ECHO HEIGHT vs MAGNETIZATION

$$h(t) = a(1 - e^{-Wt}) + b$$

$$= (a + b) \left(1 - \frac{a}{a+b} e^{-Wt}\right)$$

where W is the rate of growth of the echo intensity, $a + b$ is the equilibrium intensity of echo signal, i.e., $h(\infty)$, and $a/(a + b)$ is the initial fractional reduction of the echo intensity.

$$h(t) \propto [N_p N_m - N_p^{\text{ch}}(t)]$$

where N_p is the number of protons in a single Mn_{12} molecule, N_m is total number of molecules, and $N_p^{\text{ch}}(t)$ is the number of protons which undergo a change of average local field between the time interval separating the $\pi/2$ - π pulses and the one separating the π pulse and the echo. If we define N_m^{eff} as the effective number of molecules whose protons are affected by the local field change due to a molecular spin flip and $P_m^{\text{flip}}(t)$ the fraction of total molecules which change orientation in the time interval τ [4]:

$$h(t) = h_0 \exp\left(-\frac{2\tau}{T_2}\right) [1 - N_m^{\text{eff}} P_m^{\text{flip}}(t)]$$

$$\cong h_0 \exp\left(-\frac{2\tau}{T_2}\right) [1 - N_m^{\text{eff}} W \tau e^{-Wt}]$$

From (1) and (2) one has $\tau_{\text{NMR}} = \tau_{\text{Magnetiz}}$.

^1H NMR ECHO HEIGHT vs TIME and MAGNETIZATION vs TIME

The function for fitting the return of the echo signal to its equilibrium value is:

$$h(t) = h_0 + A(1 - e^{-(t/\tau_R)^\beta})$$

h_0 is the echo amplitude at $t = 0$, $h_0 + A$ is the echo amplitude at $t \rightarrow \infty$ (equilibrium).

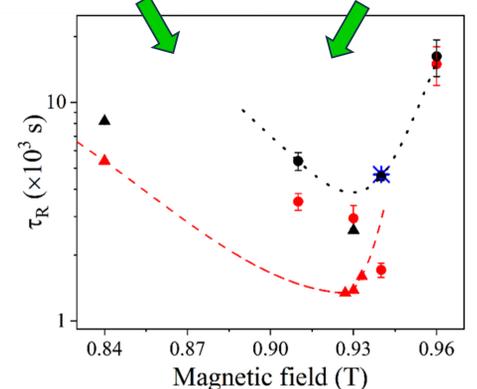
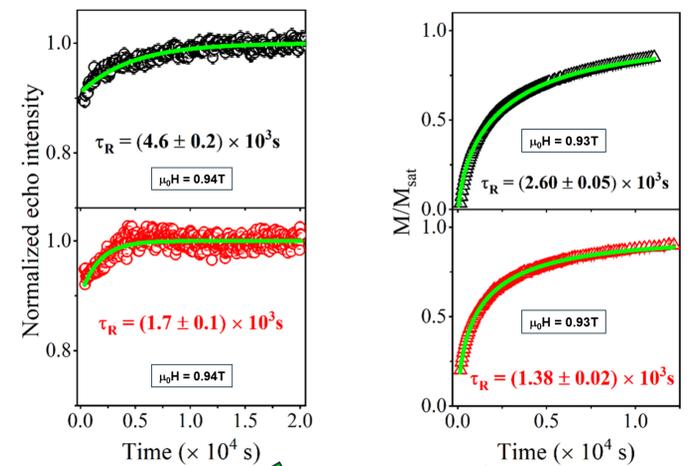
M_0 is the magnetization at $t = 0$ s (ideally zero), M_{sat} is the saturation magnetization.

β is the stretching exponent ($0.5 < \beta < 1$); τ_R an average relaxation time of the M toward the equilibrium.

$$M(t) = M_0 + M_{\text{sat}}(1 - e^{-(t/\tau_R)^\beta})$$

The investigation was performed by varying the external field applied

- with both the techniques under SWPI conditions, τ_R decreased considerably its value
- NMR data, in general, showed a more pronounced τ_R shortening compared to SQUID ones.



τ_R extracted NMR (circles) and SQUID (triangles) data vs $\mu_0 H$ at $T = 2.2\text{K}$, with crystals facing a non-emitting (black) and emitting (red) source. The blue asterisk is the NMR measure repeated after heating up to room temperature. The black-dotted (red-dashed) lines are guides for the eye, related to NMR non-emitting (SQUID emitting) data

MODEL AND DISCUSSION

- SQUID "non-emitting" measures based on H_{SPIN} :

$$H_{\text{SPIN}} = -D\hat{S}_z^2 - CS_z^4 + B_4^1 \frac{1}{2} (\hat{S}_+^4 + \hat{S}_-^4) - g\mu_B (B + B_{\text{dip}}) \hat{S}_z$$

with quadratic and quartic axial anisotropy terms, quartic non-axial term; $g = 2$; $B_{\text{dip}} = 0.025\text{M}(t)/M_{\text{sat}}$

- Magnetic relaxation due to spin-phonon coupling arising from small rotations of the molecule around its equilibrium position

- Rate for the transition from level m to level n of H_{SPIN} is:

$$W_{mn} = A\Delta^3 (e^{\frac{\Delta}{kT}} - 1)^{-1} \sum_{\alpha=x,y,z} \langle m | [H, S_\alpha] | n \rangle^2$$

- Master equations for state populations yield 20 distinct time constants; the longest one, τ_R , governs the long-term relaxation of magnetization.

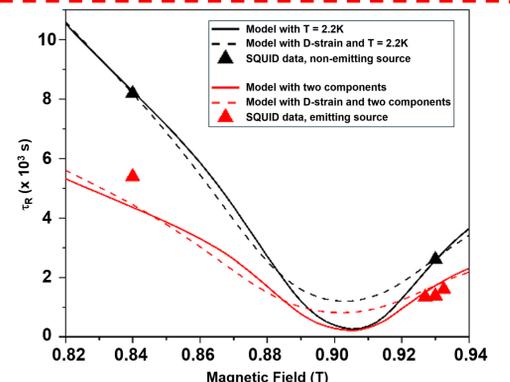
- τ_R is t -dependent: a stretched exponential curve fits $M(t)$ well, with τ_R and β comparable with the experiments.

- SQUID "emitting" measures: energy deposit due to impinging radiation in a limited region of the sample. It is supposed that:

- sample contains two components, each described by W_{mn} rates: the first at $T = 2.2\text{K}$, while the second at higher T_H
- Spins in the hot component are taken as a fixed fraction (w_H) of the non-relaxed spins
- The heat of the hot region is generated by the decay of metastable spins initially triggered by an impinging particle

- The observed reduction of τ_R is captured by assuming $T_H = 2.8\text{K}$ and $w_H = 1.4\%$,

- NMR measurements also shows a comparable acceleration of the relaxation under irradiation, but τ_R s are longer than expected (the use of multiple crystals in NMR measurements could be responsible for this difference).



Solid black line: calculation from H_{SPIN} and W_{mn} , with $T = 2.2\text{K}$, $D/k_B = 0.57\text{K}$, $C/k_B = 1.2\text{mK}^4$, $B_4^1/k_B = 6.2\mu\text{K}^4$, $A = 1.2\text{meV}^{-5}\text{s}^{-1}$ and $B_{\text{dip}} = 0.025\text{M}(t)/M_{\text{sat}}\text{T}$. Dashed black line: same calculation including gaussian D-strain with width $\sigma_D = 0.02\text{D}$, and $A = 1\text{meV}^{-5}\text{s}^{-1}$. Red lines: same parameters including a second component ($T_H = 2.8\text{K}$ and $w_H = 1.4\%$).

CONCLUSIONS

Dynamical properties of $\text{Mn}_{12}\text{BuAc}$ SMM crystals were studied by means of NMR relaxation and SQUID magnetometry under the effect, or not, of a low-activity ionizing radiation source. From the experiments a shortening of the characteristic recovery time τ_R was pointed out when the SMM is hit by the radiation. In the case of SQUID measurements, this phenomenon was also justified through a model reproducing experimental conditions. These results open the way to the use of molecular nanomagnets as quantum sensors also for elementary particles and radiation.

References: [1] Barra et al., *J. Am. Chem. Soc.* 129, 10754 (2007); [2] P.C. Bunting et al., *Phys. Rev. D* 95, 095001 (2017); [3] H. Chen et al., arXiv:2002.09409v2 (2020); [4] Z. H. Jang et al., *Phys. Rev. Lett.* 84, 2977 (2000)