μSR evidence of a marked exchange-interaction effect on the local spin dynamics of Tb-based molecular nanomagnets

Manuel Mariani[1,2], Muhammad Maikudi Isah[3], Paolo Arosio[2,4], Zaher Salman[5], Lorenzo Sorace[6], Giordano Poneti[7], Samuele Sanna[3] and Alessandro Lascialfari[1,8]

(1) Department of Physics, University of Pavia, Italy,
(2) INFN Sezione di Milano, Italy,
(3) Department of Physics and Astronomy "A. Righi", University of Bologna and INFN Sezione di Bologna, Italy,
(4) Department of Physics, Univ. degli Studi di Milano and INFN Sezione di Milano, Italy,
(5) Laboratory for Muon spin Spectroscopy, Paul Scherrer Institut, Villigen, Switzerland,
(6) Department of Chemistry, University of Firenze and INFN Sezione di Firenze, Italy,
(7) Dipartimento di Scienze Ecologiche e Biologiche, Univ. degli Studi della Tuscia, Italy,
(8) INFN Sezione di Pavia, Italy.

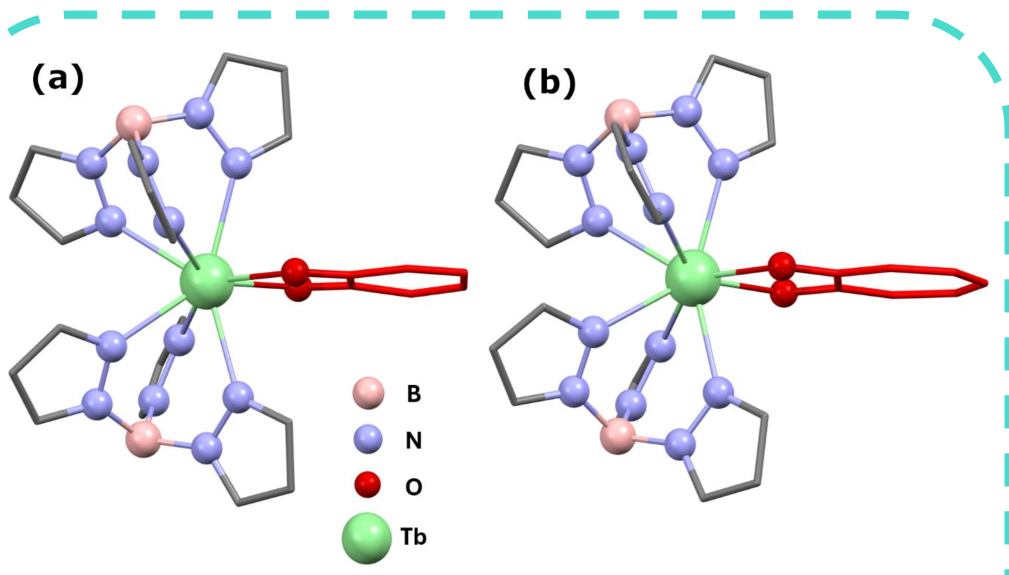
INTRODUCTION

Molecular nanomagnets offer many accessible spin states: they are actively studied as data storage devices at the single-molecule level and are promising for various applications in quantum technologies [1, 2]. Their use requires a detailed comprehension of the factors affecting their spin dynamics, like e.g. spin orbit, crystal-field, hyperfine and/or exchange interactions, and spin-phonon coupling. Here, we present a longitudinal field muon spin relaxation (LF-μSR) study of two Terbium (Tb) single ion magnets (SIM) in applied longitudinal fields, B_L = 50, 150 and 300 mT, one including a paramagnetic ligand group and the other a diamagnetic one. The comparison among the two complexes allowed to single out the role of the exchange coupling among the Tb(III) ion and the SQ paramagnetic radical.

OBJECTIVES

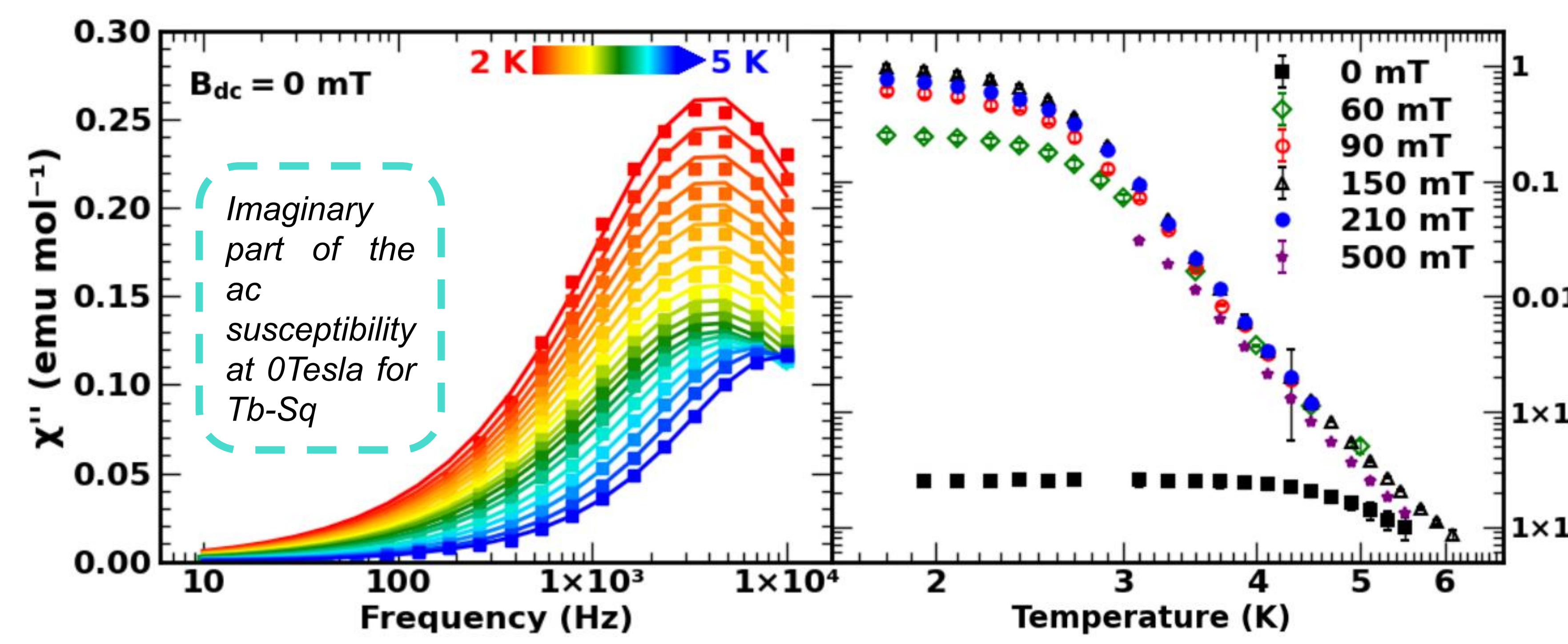
Comparative study of the spin dynamics of two Tb-based complexes isostructural in their first coordination sphere but with two different ligands: $Tb(DTBSQ)(HBPz_3)_2$ (**Tb-SQ**) and $Tb(Trp)(HBPz_3)_2$ (**Tb-Trp**) (DTBSQ=3,5-di-tert-butylsemiquinonato, Trp=tropolonate, $HBPz_3$=hydrotrispyrazolyl-borate). The semiquinonato (**SQ**) ligand is paramagnetic, with a consequent insurgence of exchange coupling, while the tropolonato (**Trp**) ligand is diamagnetic.

SAMPLES



Molecular structure of (a) TbSQ, and (b) Tbtrp complexes

ac SQUID MEASUREMENTS



Relaxation time obtained from ac susceptibility at different applied fields for Tb-Sq

EXPERIMENTAL METHODS

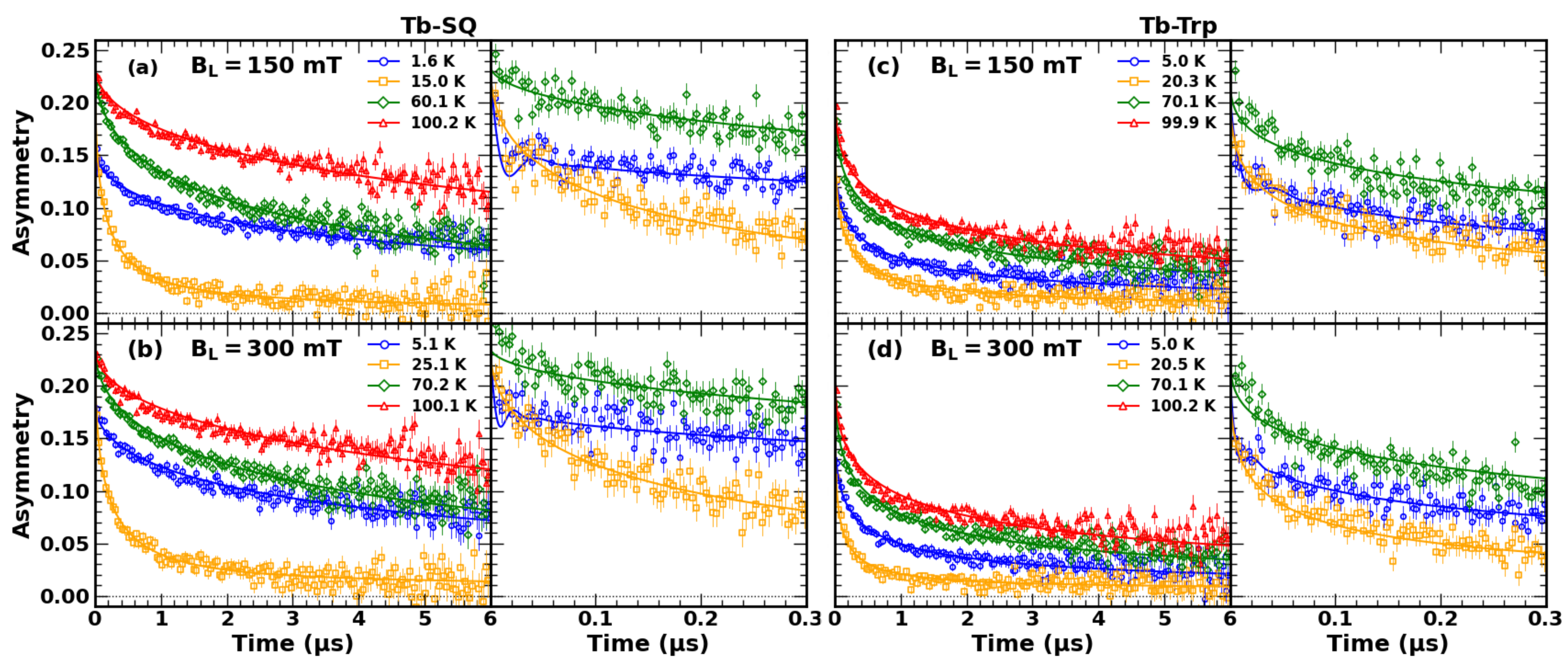
The systems were prepared in form of powders, and the measurements performed :

(i) in the range 1.5 K < T < 200 K at fixed magnetic field B_L = 50, 150, 300 mT, for the LF-μSR case;

(ii) (ii) 2 K < T < 5.5 K, 10 Hz < ν < 10 kHz , μ_0H = 0-0.5 Tesla, in the case of ac SQUID magnetometry.

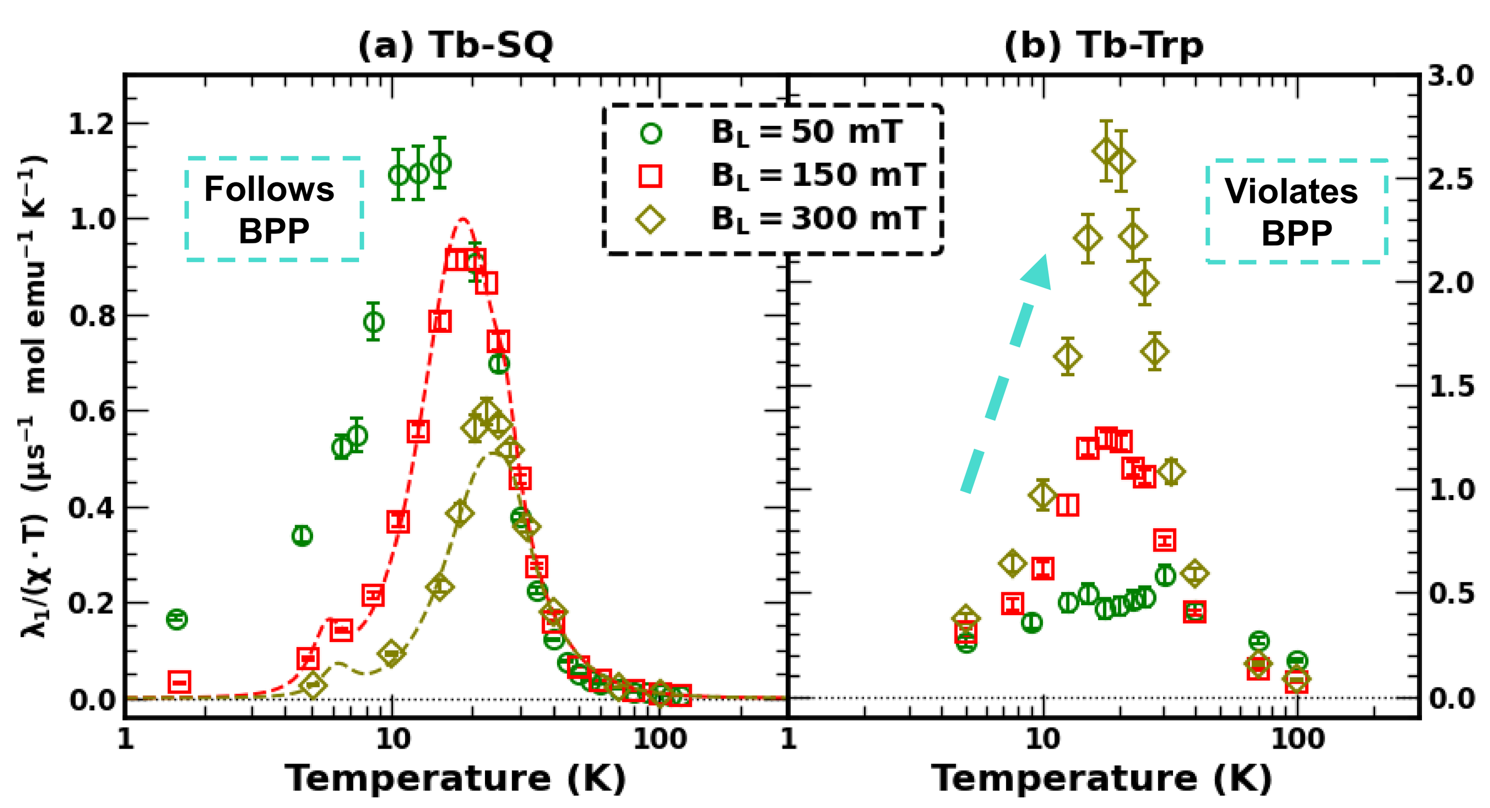
μSR MEASUREMENTS: Time evolution of muon spin polarization

$$A(t) = A_1 G_s^{\mathrm{Lor}}(\Delta, B_L, t)\exp\left[-(\lambda_1 t)^{\beta}\right] + A_2 \exp\left(-\lambda_2 t\right).$$



The LF-μSR data of both powder samples show an asymmetry behaviour which can be fitted to the sum of a phenomenological static (Δ) Lorentzian Kubo-Toyabe function in applied LF [3], $B_L = \omega_L/\gamma_\mu$ multiplied by a stretched dynamic relaxation (λ_1) and an exponential decay.

μSR MEASUREMENTS: Spin–Lattice relaxation time λ_1



BPP law : $\lambda_1(T, B_L) = C \cdot \chi T \cdot \dfrac{\tau_c}{1 + (\gamma^{\mu} B_L \tau_c)^2}$

correlation times:

$\tau_c \propto T^{-\alpha_i}$ (i = direct, Raman-like)

$\tau_c = \tau_0 \exp(\mathbf{U_{eff}}/T)$

TbSQ: fit of the peak with 3 contributions from Raman-like ($\boldsymbol{\alpha} = \mathbf{3.1}(1)$), Orbach ($\boldsymbol{\tau_0} = \mathbf{0.1}$ ps, U_{eff} = **280**(2) K), & direct ($\boldsymbol{\alpha} = \mathbf{8.5}(3)$)

Conclusions

This study allowed us to single out: (i) the possible role of a different Ln magnetic center (Tb^{3+} or Dy^{3+}) for the spin dynamics of the system; (ii) the influence of the exchange interaction on the physical properties, when the Tb magnetic ion is bound to the paramagnetic SQ (s = 1/2) ligand; here the magnetic anisotropy and crystal field → magnetic anisotropy barrier, are different with respect to the case of systems where the Tb center is bound to a diamagnetic (e.g. Trp, s = 0) radical → unusual spin dynamics [4].

References

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Acknowledgments

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