Magnetic properties and spin dynamics in molecular magnets with integer spin values

Alessandro Lascialfari[1], Federico Aimo Rusnati[1], Samuele Sanna[2], Fatemeh Adelnia[1], Alice Radaelli[1], Manuel Mariani[3], Alessandro Chiesa[4], Claudio Sangregorio[5], R. Winpenny[6], G. Timco[6], Stefano Carretta[4] Ferdinando Borsa[2]

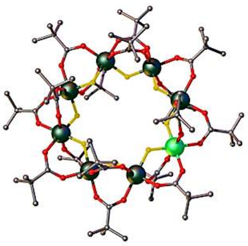
[1]Department of Physics and INSTM, Università degli studi di Milano, Milano, Italy
[2] Department of Physics and INSTM, Università degli studi di Pavia, Pavia, Italy
[3] Department of Physics and Astronomy, Università degli studi di Bologna, Bologna, Italy
[4] Department of Physics and Earth Sciences, Università degli studi di Parma, Parma, Italy
[5] ICCOM-CNR and INSTM, Sesto F.no (FI), Italy
[6] School of Chemistry, Manchester University, Manchester (UK)

Introduction

The fundamental idea underlying the here presented research project is to utilize SMMs to investigate the evolution of the ground state of a one dimensional spin integer system as the number of spins N increases until the limit of an infinite chain. For the semi-integer spin “ring” (i.e. closed periodic chain) systems the energy levels’ scheme is approximately described by the Landè formula, i.e. E(S) = (P/2)·S·(S+1) with P = 4J/N, which predicts a discrete energy levels’ structure and thus also a gap between the ground state and the first excited state, but it leads to a gapless ground state in the limit of N going to infinite. This has been verified experimentally. In the case of an integer spin chain composed by a finite number of spins there is again a discrete levels’ structure and a gap between the ground state and the first excited state, but by increasing the number of spins one should find a significant deviation from Lande’ s rule, signaling the approach to the infinite spin chain, where the Haldane gap is present. In the current work, we performed magnetization and susceptibility measurements, in addition to a ^{1}H Nuclear Magnetic Resonance (NMR) and Muon Spin Rotation (MuSR) investigation of V7Zn and V7Ni molecular systems. These heterometallic nanomagnets of recent synthesis contain seven spin s=1 vanadium ions and one s=0 (Zn^{2+}) or s=1 (Ni^{2+}) ion, arranged in the form of regular “open” or “closed” rings, respectively. The ground state has been found antiferromagnetic (AF) and the average exchange coupling constant among the magnetic ions was estimated to be of the order of few Kelvin degrees. While ^{1}H NMR nuclear spin-lattice relaxation rate data are of difficult interpretation because of the so-called wipeout effect, the MuSR longitudinal relaxation rate measured at different magnetic fields as a function of temperature in the range 1.5<T<100 K, follows a heuristic Bloembergen-Purcell-Pound model. So, for such low number of spins, our data suggest that no Haldane effect is present. Future measurements on s=1 rings with higher number of spins are thus planned.

Sample studied : V_7Zn

- AFM open ring with integer (s=1) spins
- Tetragonal structure
- V(III) : s=1 , l=0 ; Zn(II) : s=0 , l=0



Spin Hamiltonian

$$\mathcal{H} = \mathcal{H}_{ex} + \mathcal{H}_{cf} + \mathcal{H}_{dip} + \mathcal{H}_z$$

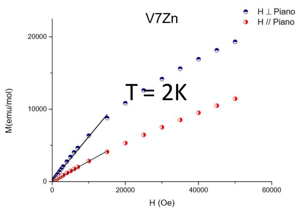
$$\mathcal{H}_{ex} = -\sum_{i=1}^{N} J_i\, \mathbf{s_i}\cdot\mathbf{s_{i+1}} \longrightarrow \boxed{/\sim -35K}$$

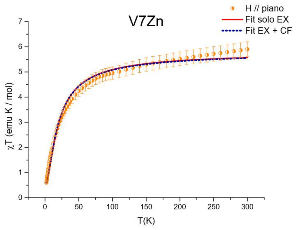
$$\mathcal{H}_{cf} = \sum_{i=1}^{N}\{d_i[s_{zi}^2 - \frac{s_i(s_i+1)}{3}] + e_i[s_{ix}^2 - s_{iy}^2]\} \longrightarrow \boxed{/\sim -10K}$$

$$\mathcal{H}_{dip} = \frac{g^2\mu^2}{2}\sum_{i>j}[\frac{(\mathbf{s_i}\cdot\mathbf{s_j})}{r_{ij}^3} - 3\frac{(\mathbf{s_i}\cdot\mathbf{r_{ij}})(\mathbf{s_j}\cdot\mathbf{r_{ij}})}{r_{ij}^5}] \longrightarrow \boxed{/< 1K}$$

$$\mathcal{H}_z = \mu_b\sum_{i=1}^{N} g\mathbf{H}s_{iz} \longrightarrow \boxed{/\sim 1.5K\ (1T)}$$

Magnetization and magnetic susceptibility: effects of quantum structure



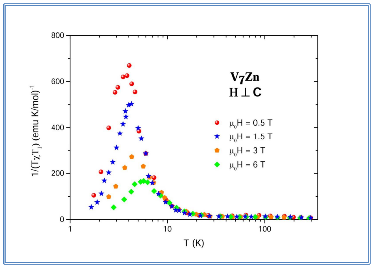


Data fitting : Hilbert space dimension is $dim = \prod_{i=1}^{7}(2s_i+1) = 3^7 = 2187$

$$\mathcal{H} = -\sum_{i=1}^{N} J_i\, \mathbf{s_i}\cdot\mathbf{s_{i+1}} + \mu_b\sum_{i=1}^{N} g\mathbf{H}s_{iz} \Longrightarrow \boxed{\begin{array}{l} g_\perp = 1.76 \quad J_\perp = -2.4K \\ g_{//} = 1.82 \quad J_{//} = -5.6K \end{array}}$$

$$\mathcal{H} = -\sum_{i=1}^{N} J_i\, \mathbf{s_i}\cdot\mathbf{s_{i+1}} + \mu_b\sum_{i=1}^{N} g\mathbf{H}s_{iz} + \sum_{i=1}^{N}\{d_i[s_{zi}^2 - \frac{\mathbf{s_i}(\mathbf{s_i}+1)}{3}] \Longrightarrow \boxed{\begin{array}{l} d_\perp = -1.7K \quad J_\perp = -2.0K \\ d_{//} = -1.1K \quad J_{//} = -5.4K \end{array}}$$

NMR Results

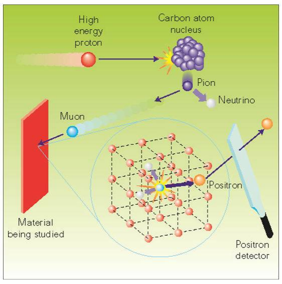


- Nuclear spin-lattice relaxation rate displays an anomaly
- **No BPP law satisfied**

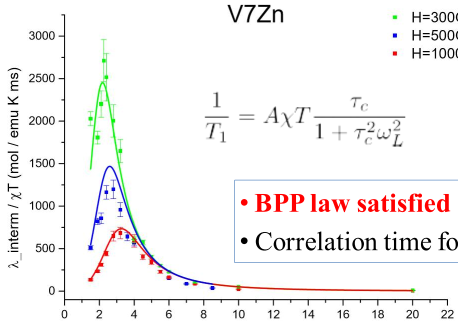
* **Problems of wipe-out effect** !!

MUSR Results

PSI facility, Villigen-Switzerland



Muon spin relaxation
Muons implant in matter



$$\frac{1}{T_1} = A\chi T\frac{\tau_c}{1+\tau_c^2\omega_L^2} \qquad \tau_c = CT^{-\alpha}$$

- **BPP law satisfied**
- Correlation time follows a power law

Conclusions

- Strong anisotropy effects from M(H) and χ(T)
- Possibily an exchange coupling intrinsically anisotropic
- The muon longitudinal relaxation rate presents a peak following a BPP law
- Results explained in terms of a single power-law correlation time

The Italian FIRB project “ New Challenges in molecular nanomagnetism: from spin dynamics to quantum-information processing ” funded this research.