Low-frequency Spin Dynamics of Thioether-bridged Cobalt-Dioxolene Complexes

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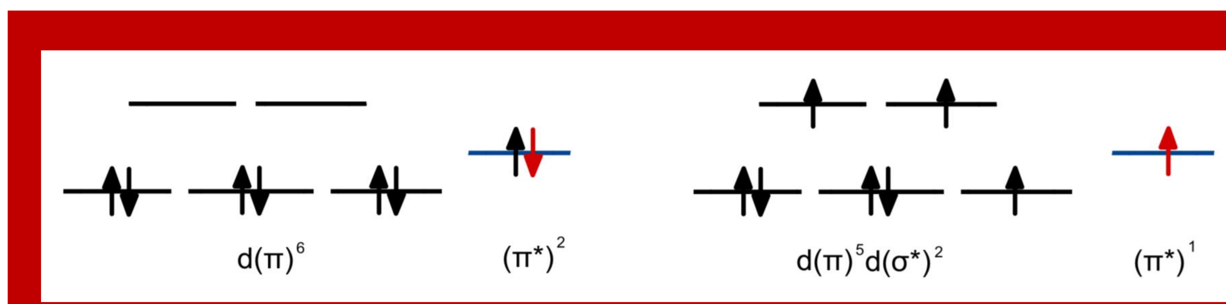
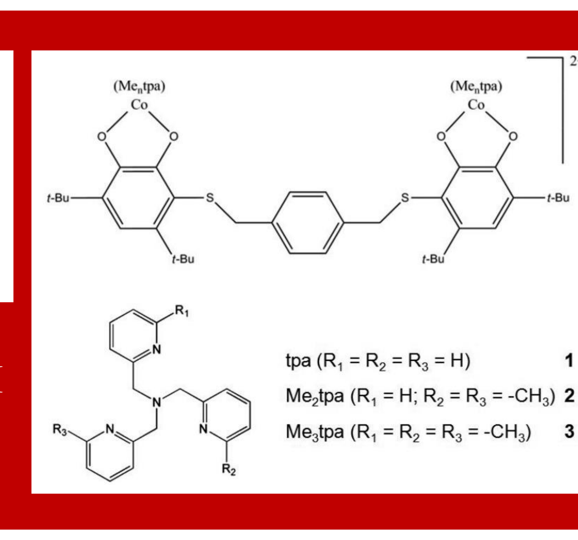
SUMMARY

- **In response to external stimuli (e.g. temperature), Spin Crossover systems (SCO) undergo a transition between two different magnetic states.**
- **In Valence Tautomers (VT), the transition is driven by an intramolecular electron transfer between a redox-active ligand and the metal ions of the molecule.**
- **We studied the static and dynamic magnetic properties of a cobalt-based valence-tautomeric complex with SQUID magnetometry and pulsed NMR.**
- **We compared the data acquired with those of two other samples, where a slightly different chemical composition results in a fixed low- or high-spin state (LS and HS, respectively).**

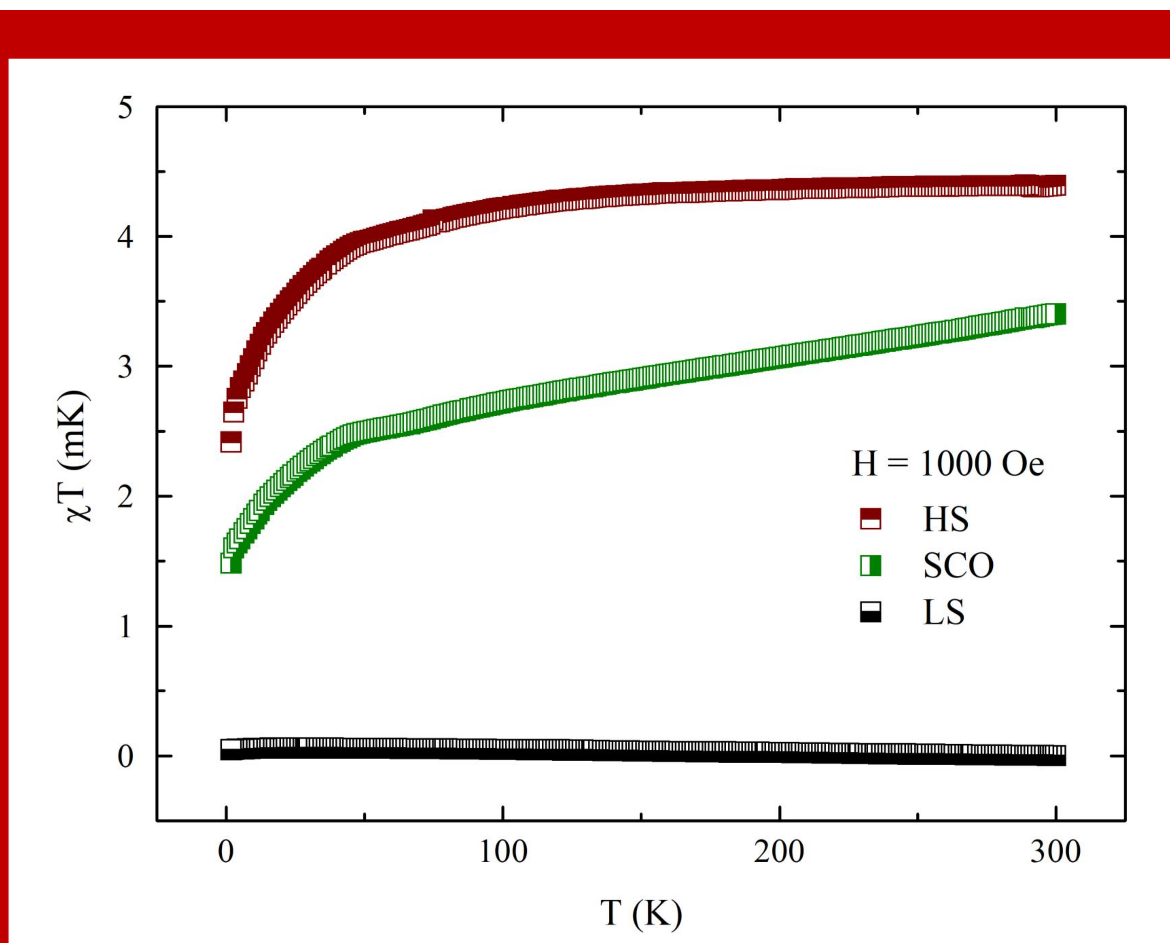


Example of a VT-SCO transition. Reprinted from [1]

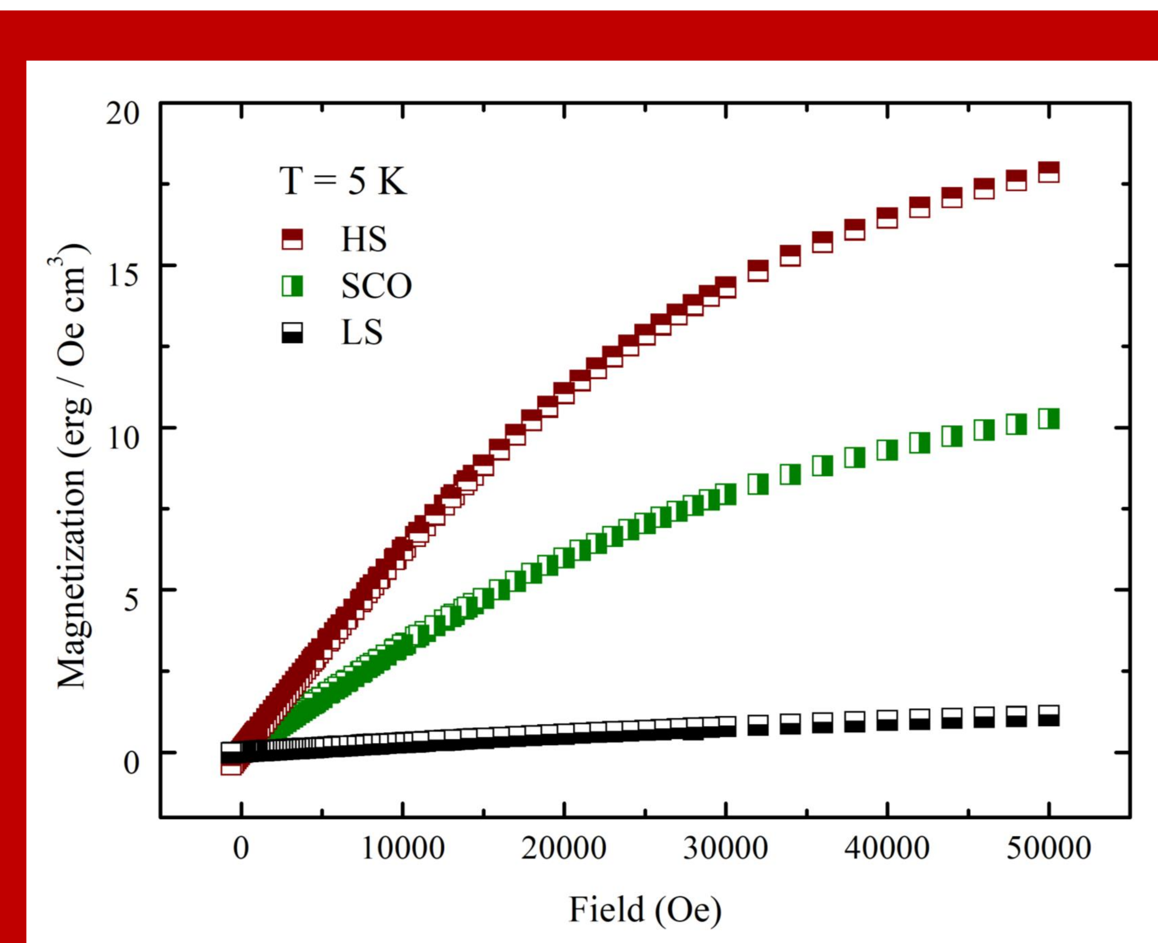


$Co_2(Me_ntpa)_2$diox-S-diox $(PF_6)_2\cdot$MeOH
n = 0, 2, 3. Reprinted from [2]

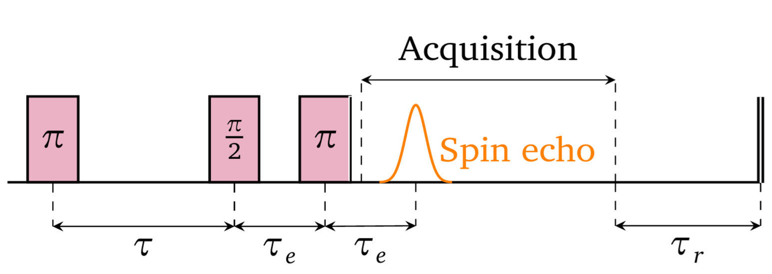
DC SQUID MAGNETOMETRY

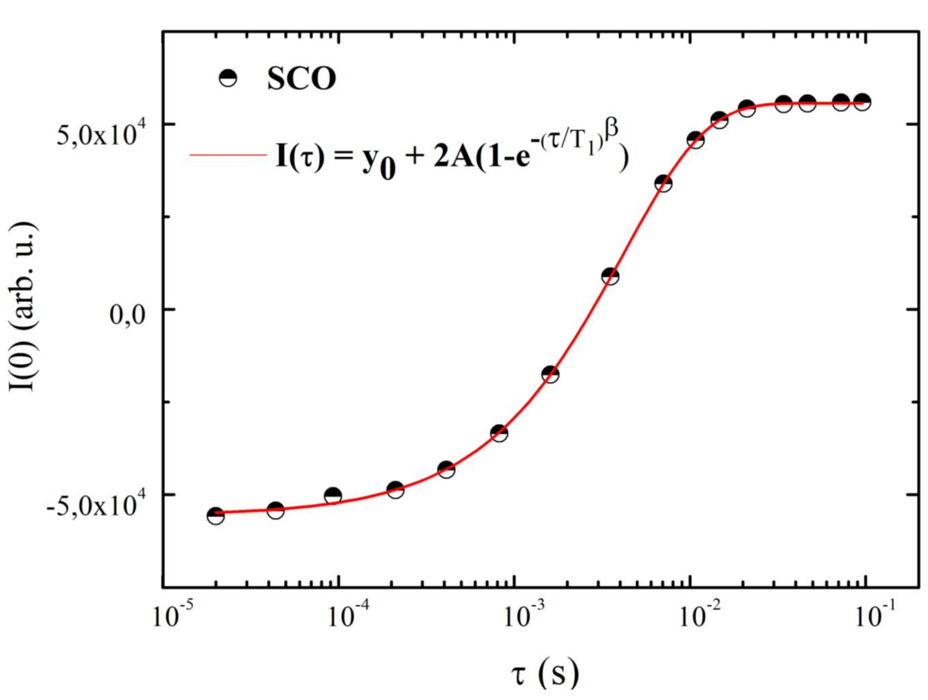


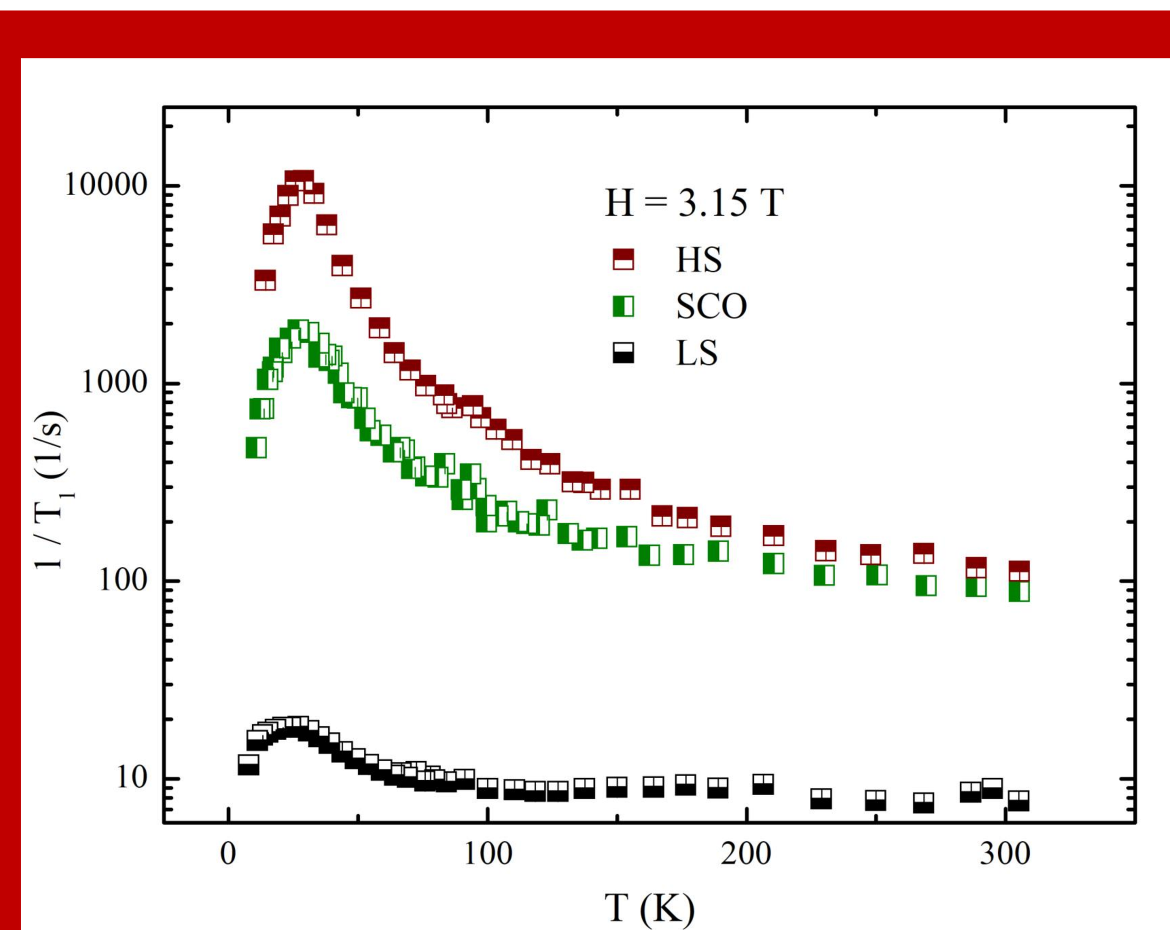
1. **HS and LS display paramagnetic behavior as $\chi T \simeq const.$**
2. **SCO undergoes a gradual spin-crossover transition with:** $\%_{HS} = 57$ ***at*** $T = 50$ ***K***, $\%_{HS} = 77$ ***at*** $T = 300$ ***K***
3. **The reached states do not coincide with those of the reference samples.**
4. **At $T \simeq 25$ *K*, SQUID and NMR measurements indicate the onset of population on the energy levels [1,2].**



NUCLEAR MAGNETIC RESONANCE – T_1

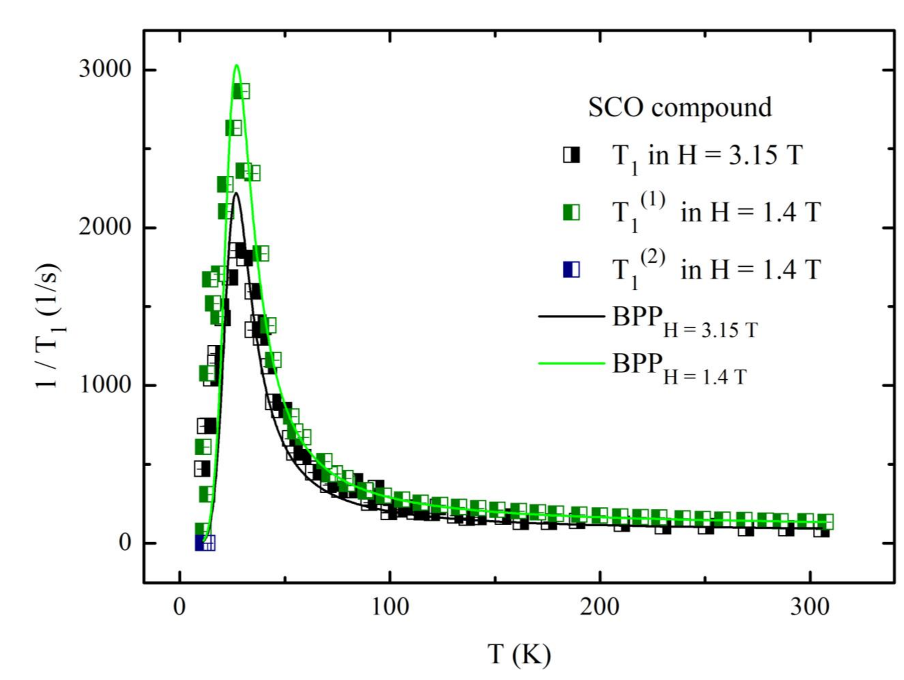




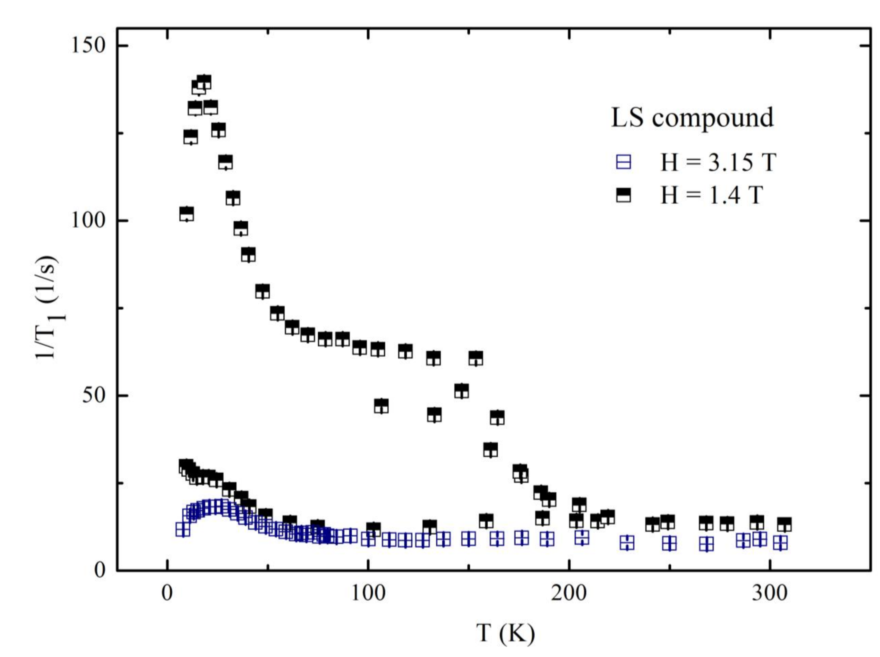


- **BPP peak attributable to population of multiplets.**

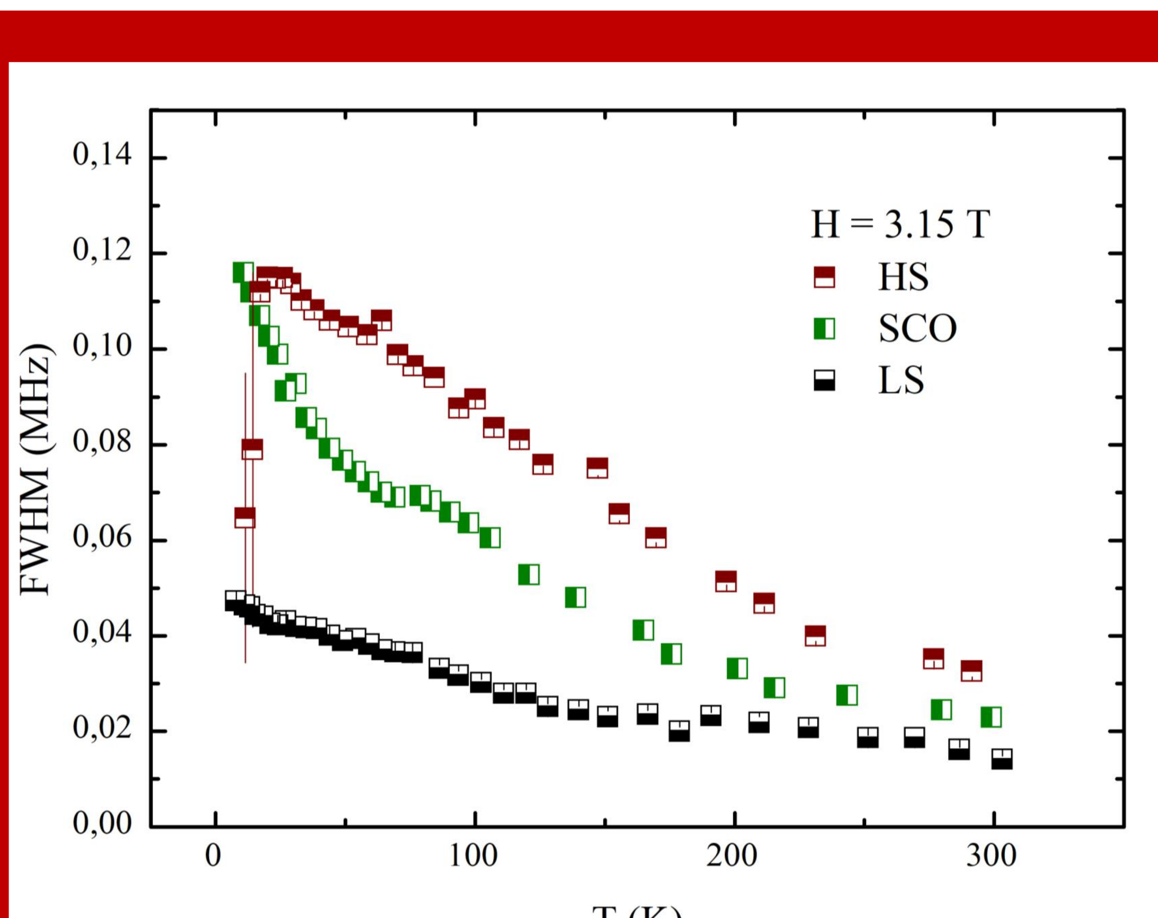
$$\frac{1}{T_1} = A' \cdot \chi T \cdot \frac{\tau_0 \exp\left(\frac{\Delta}{T}\right)}{1 + \omega_L^2 \tau_0^2 \exp^2\left(\frac{\Delta}{T}\right)}$$

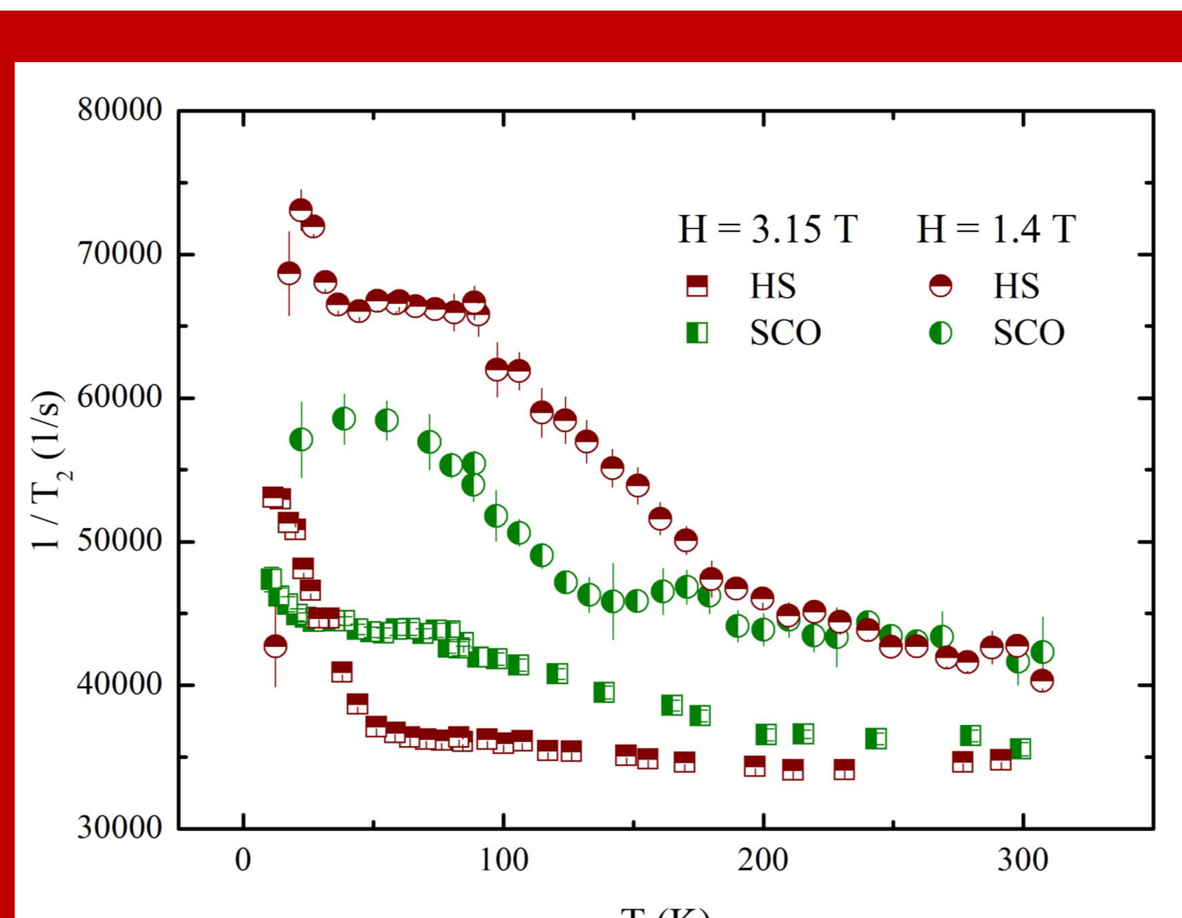


- **Seemingly thermal history of LS in $H = 1.4$ *T*.**
- **Possible spin-glassy behavior or FM impurity.**
- **Not totally reproducible.**



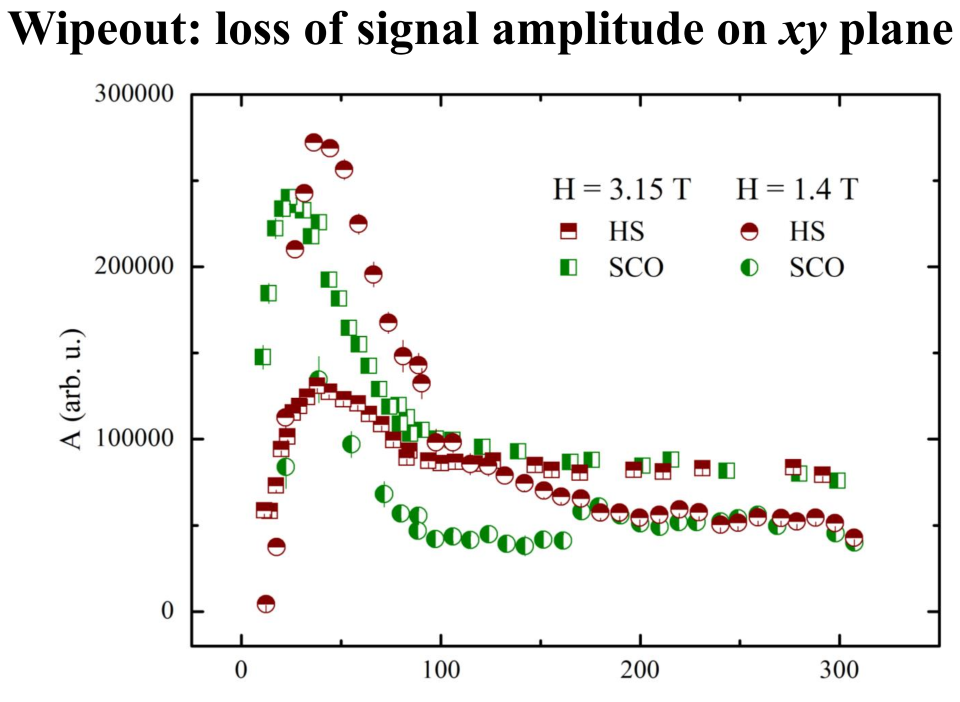
FWHM and T_2





- **Low T: quasi-static distribution of local magnetic fields (Gaussian lineshape and high $1/T_2$)**
- **High T: paramagnetism of the molecules (Lorentzian shape and low $1/T_2$)**

- **Wipeout: loss of signal amplitude on *xy* plane [3].**



[1] F. Caracciolo *et al.*, Phys. Rev. B, 98, 054416 (2018), [2] G. Poneti *et al.*, Inorg. Chem., 52, 11798-11805 (2013), [3] A. Lascialfari *et al.*, Phys. Rev. B, 72, 014440 (2005)