Susceptibility and proton spin-lattice relaxation rates T_1 of heterometallic spin rings

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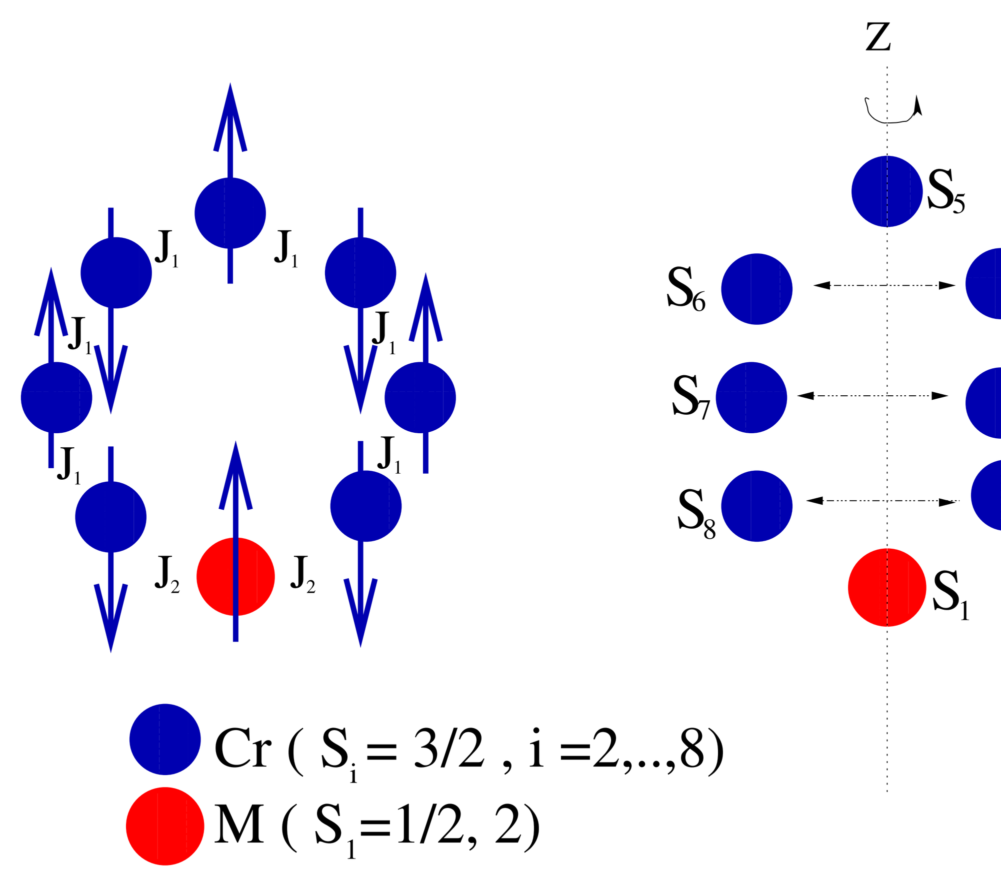
Introduction

In this work we study magnetic rings closely related to the heterometallic $\{Cr_7M\}$ wheels, in which one of the Cr^{III} ions of Cr_8 has been replaced by a Fe or Cu ion with spin s=2 and s=1/2, respectively. This extra-spin acts as local probe for the spin dynamics. Such systems have been synthesized recently [a]. The system is well described using the Heisenberg spin Hamiltonian with a Zeeman term of an applied magnetic field along the z-axis

$$\underset{\sim}{H} = 2J_1 \sum_{i=2}^{N} \vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_{i+1} + 2J_2(\vec{\underset{\sim}{s}}_1 \cdot \vec{\underset{\sim}{s}}_2 + \vec{\underset{\sim}{s}}_1 \cdot \vec{\underset{\sim}{s}}_N)$$

$$+ g\mu_B B \sum_{u}^{N} \underset{\sim}{s}_z(u), \qquad (1)$$



We use the calculated energy levels and the eigenvectors for the different rings and the values of J_1 and J_2 obtained from the fit of the magnetic susceptibility to describe semiquantitatively the behavior of the proton spin-lattice relaxation rate T_1^{-1} versus applied magnetic field (B) [b].

$$\frac{1}{T_1} = (1 + exp(-\hbar\omega_N/k_B T))\frac{2\pi}{Z}\sum_{\mu,\nu} e^{-\beta E_\mu} < \psi_\mu|\tilde{F}^+|\psi_\nu >$$

$$* < \psi_\nu|\tilde{F}^-|\psi_\mu > \delta_\varepsilon(\omega_N - \frac{E_\mu - E_\nu}{\hbar}) \qquad (2)$$

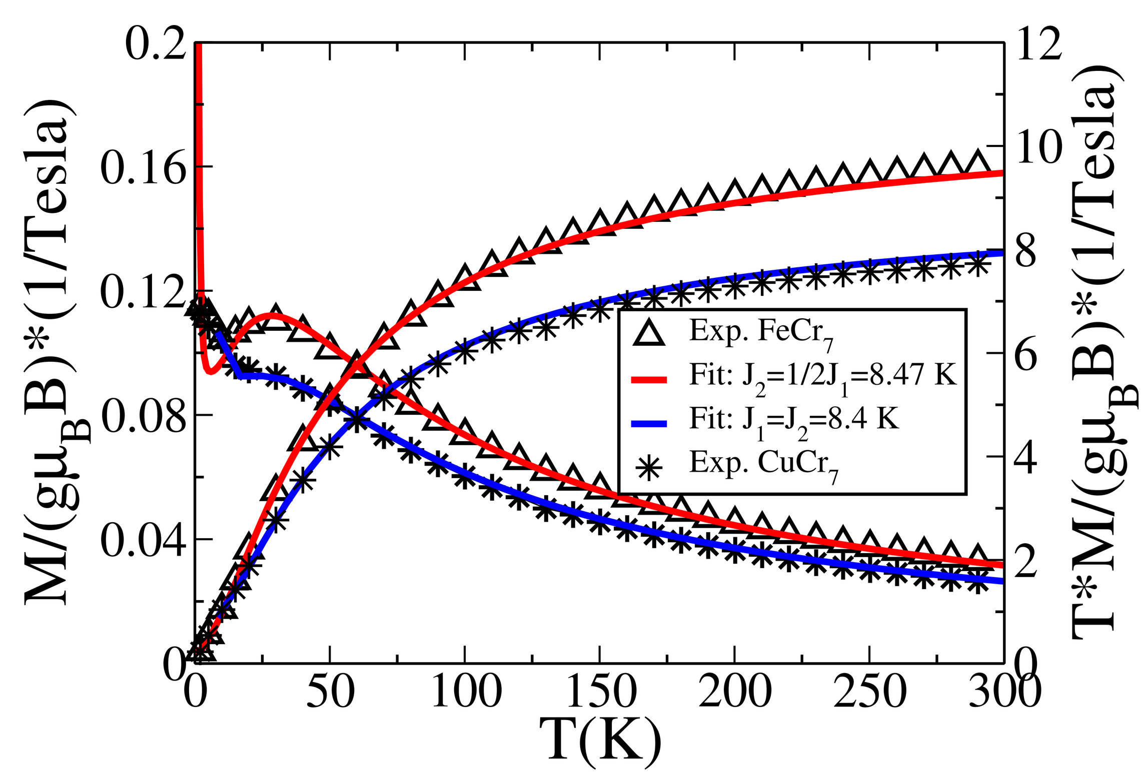
where

$$\tilde{F}^\pm = \sum_i (D_0(i)\tilde{S}^\pm(i) + D_{\mp1}(i)\tilde{S}^z(i) + D_{\mp2}(i)\tilde{S}^\mp(i))$$

[a] Finn K. Larsen, *et al.* Angew. Chem. Int. Ed. 2003, 42, No 1
[b] T. Moriya, Prog. Theor. Phys. **28**, 371 (1962)

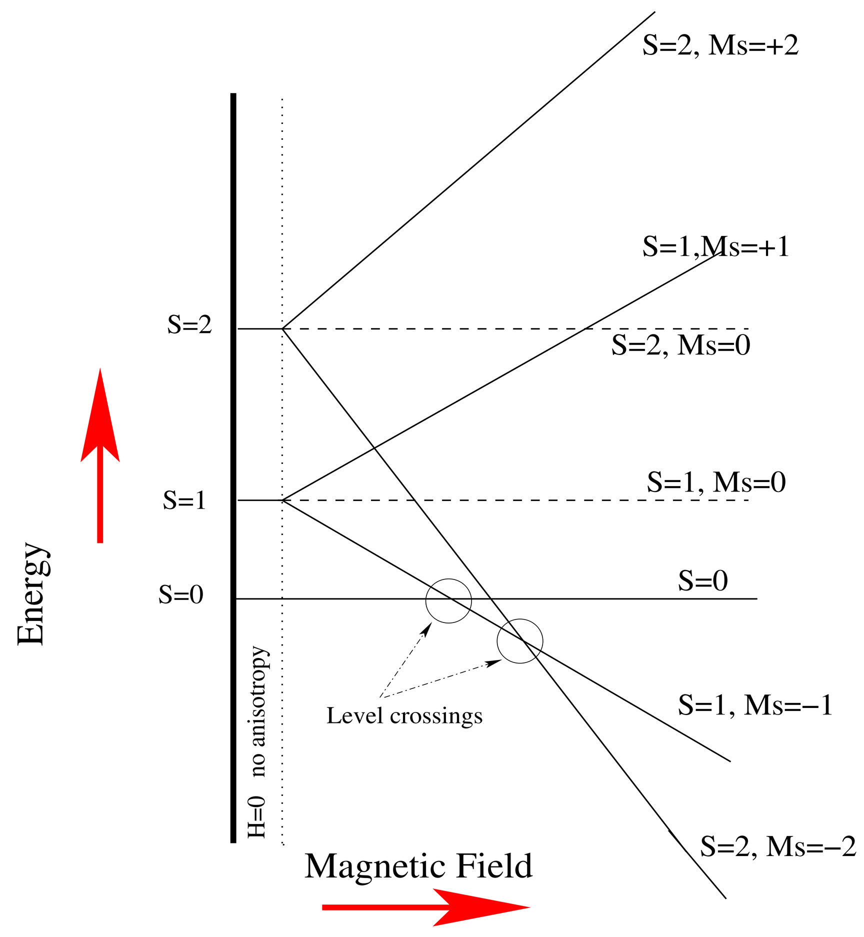
Low-field susceptibility

The energy spectra of our calculations show that the ground state has a total spin $S = 1/2$ in $FeCr_7$ and $S = 1$ in $CuCr_7$, therefore this ground state is degenerate in both compounds.

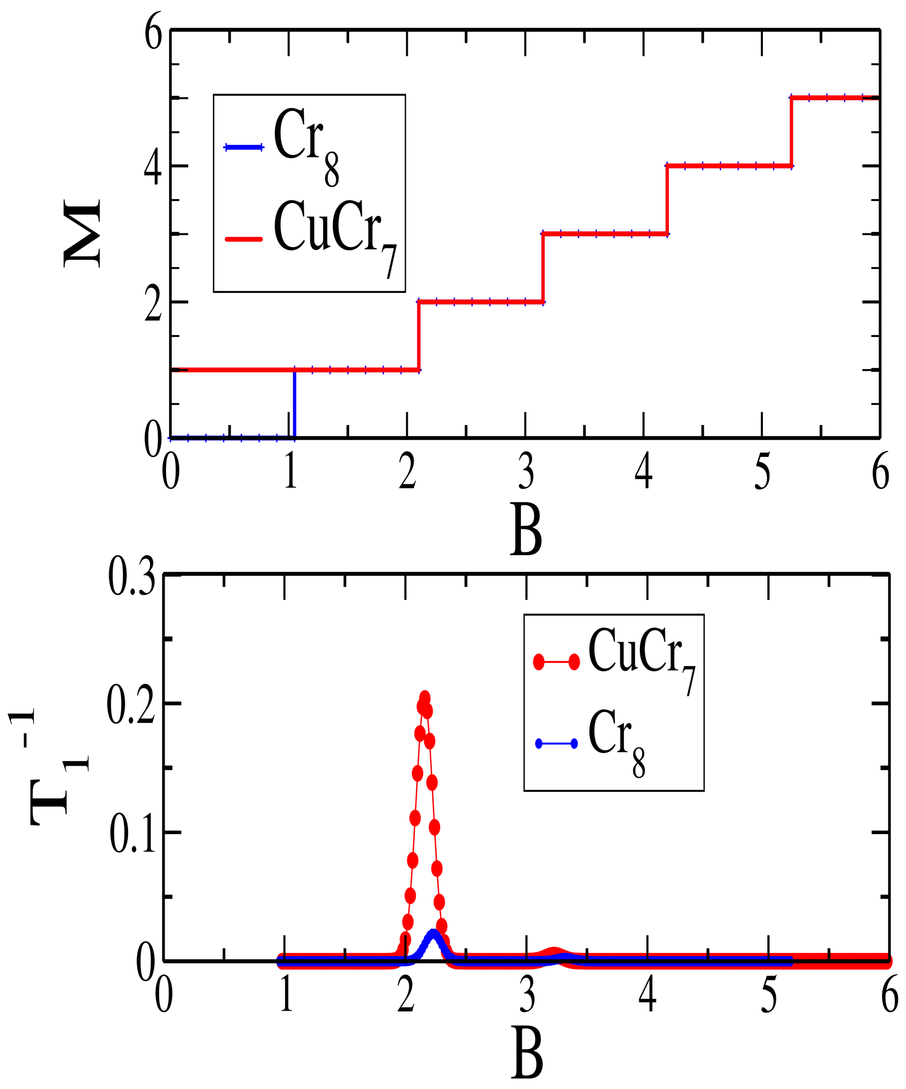


Variation of T*M/B and M/B versus temperature T for the anti-ferromagnetic ring system of $FeCr_7$ and $CuCr_7$: The experimental data given by black squares are determined using a Quantum Design MPMS SQUID magnetometer. The theoretical fit assuming an isotropic Heisenberg model is given by a red and blue solid line for $J2(Fe-Cr) = 1/2J1(Cr-Cr)$ with $J1 = 8.47$ K and $J1(Cr-Cr) = J2(Cu-Cr) = 8.4$ K, for the systems $FeCr_7$ and $CuCr_7$, respectively. $B = 1$ Tesla and $g = 2$.

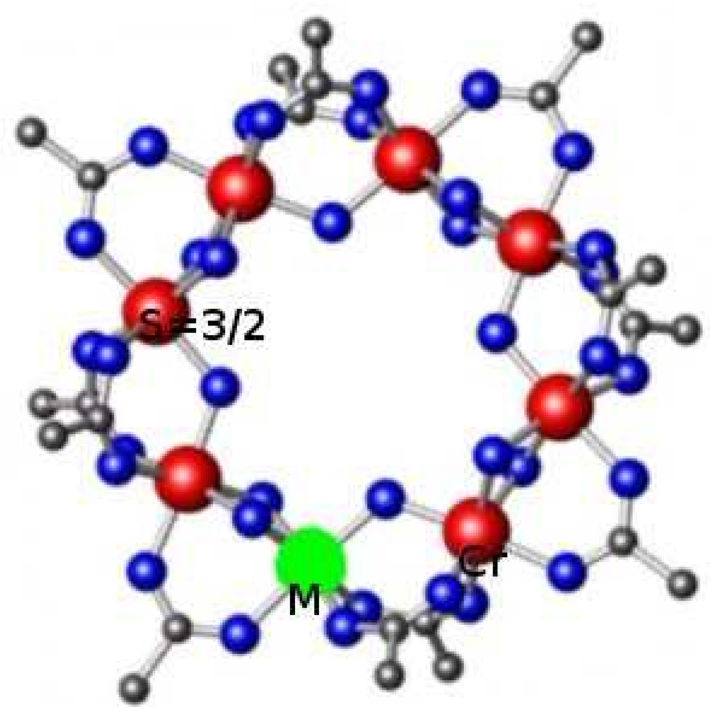
Level crossing and proton spin-lattice relaxation rates

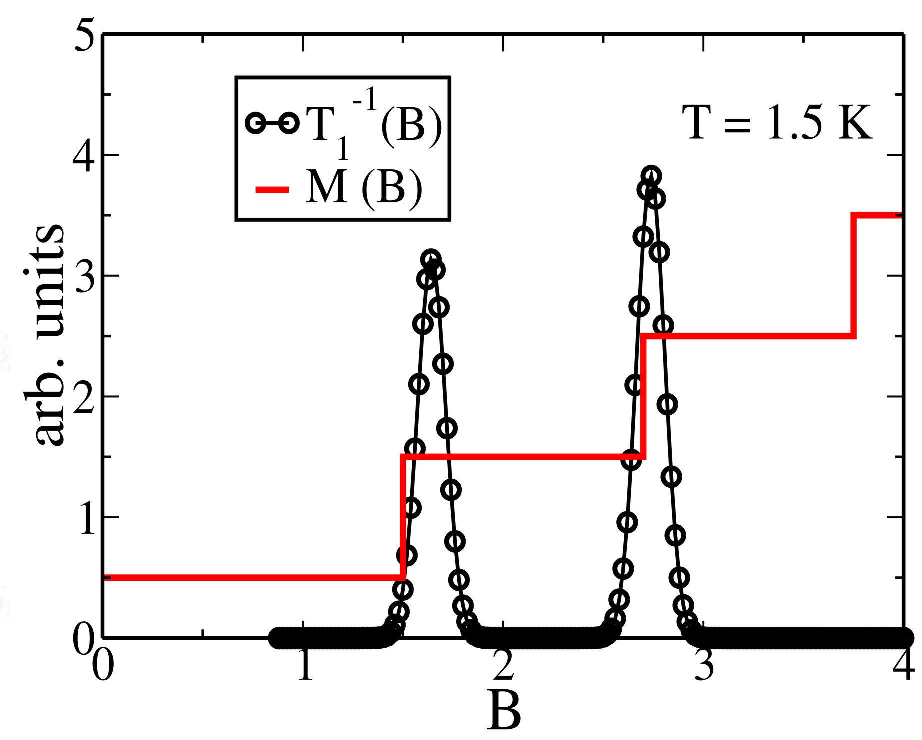


Energy levels vs. magnetic field for the lower energy eigenvalues for the lower three values of total spin S (0,1,2), for the AFM ring system of Cr_8. The spectrum shows the two level crossings which we try to describe in this work through proton spin-lattice relaxation rate.



Magnetic field dependence of T_1^{-1} in $CuCr_7$ and Cr_8 single molecule at $T = 1.5$ K, for ($\theta = \pi/4$ and $\varphi = 0$) polar coordinates between the z-axis parallel to the applied field (B) and the nuclear spin [a].





The proton spin-lattice relaxation rate T_1^{-1} as function of the applied magnetic field B, (according to Eq.(2)), for the anti-ferromagnetic ring system of $FeCr_7$ with Temperature $T = 1.5$ K.

[a] A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961)

Summary

In conclusion we have presented an investigation of the proton spin-lattice relaxation rate T_1^{-1} at low temperature in molecular heterometallic $\{Cr_7M\}$ wheels where M=Fe and Cu with spin $s = 2$ and $1/2$, respectivly. In all rings the curves of T_1^{-1} vs the applied magnetic field B are peaked at values close to the fields where the steps were observed in the magnetization. This means that the level crossing and the nearly degenerate molecular levels of different rings are strongly coupled to the movement of nuclear spins. We will further develop the work to invistigate the spin dynamics of the excess spin of the heterometallic $\{Cr_7M\}$ wheels.

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