Magnetism and proton-spin lattice relaxation rate T_1^{-1} in AFM molecular rings

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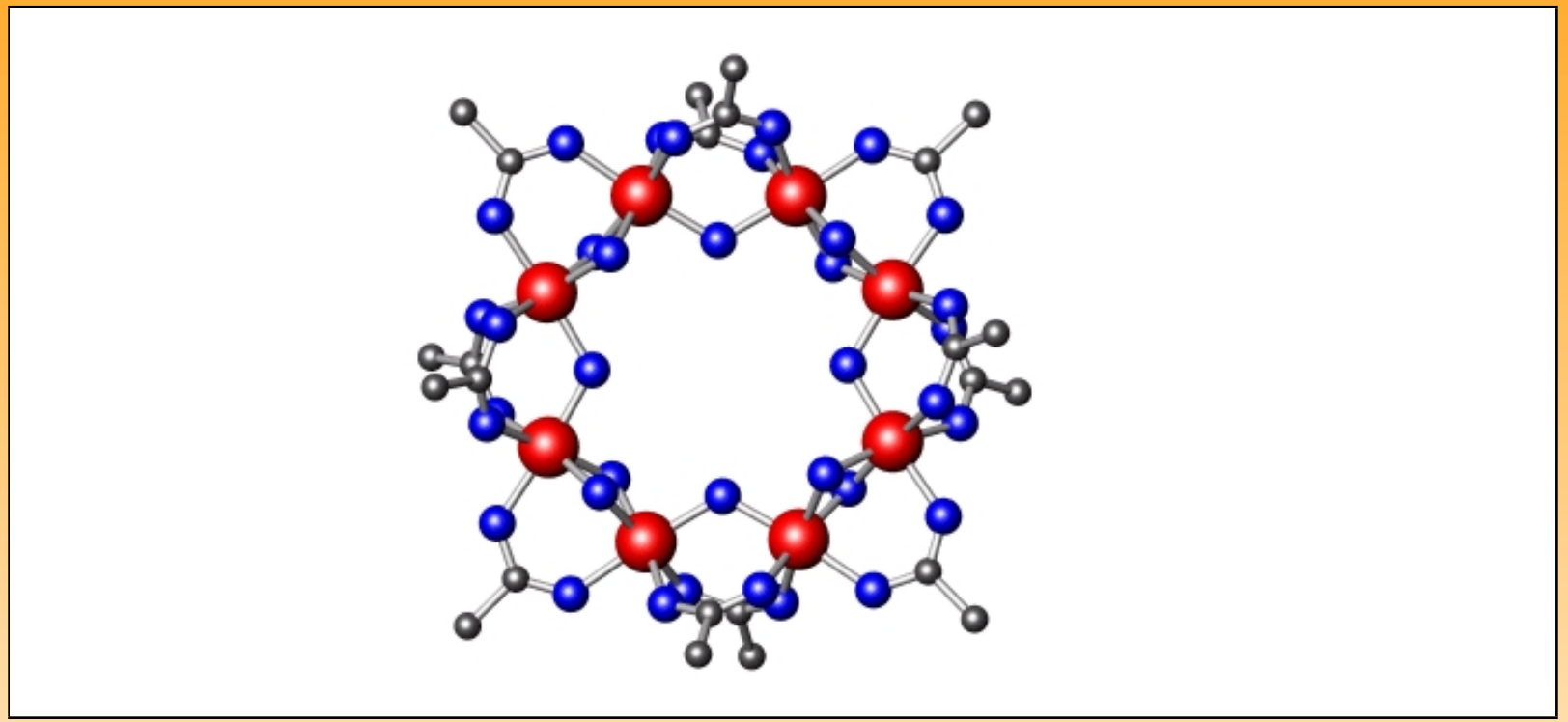
Contents

- Introduction to Molecular magnets;
- Spin Hamiltonian model;
- Energy spectrum of heterometallic $\{Cr_7M\}$ wheels;
- Low-field susceptibility;
- Quantum level crossing effects
- Proton spin-lattice relaxation time T_1;
- Prospects.

Structure of Cr_8 and MCr_7 molecular ring



- Chemical formula $[Cr_8\ F_8\ (O_2\ CCMe_3)_{16}]$;
- Cr_8 F_8 Piv_{16} (1) (HPiv= pivalic acid, trimethyl acetic acid);
- The average distances and angles are: Cr-Cr 3.389 $\pm$ 0.007 Å, Cr-F 1.916 $\pm$ 0.006 Å, Cr-O 1.947 $\pm$ 0.007 Å, Cr-F-Cr 124.4 $\pm$ 0.2°;

(1) Finn K. Larsen, *et al.*, Angew. Chem. Int. Ed. 2003, 42, No.1

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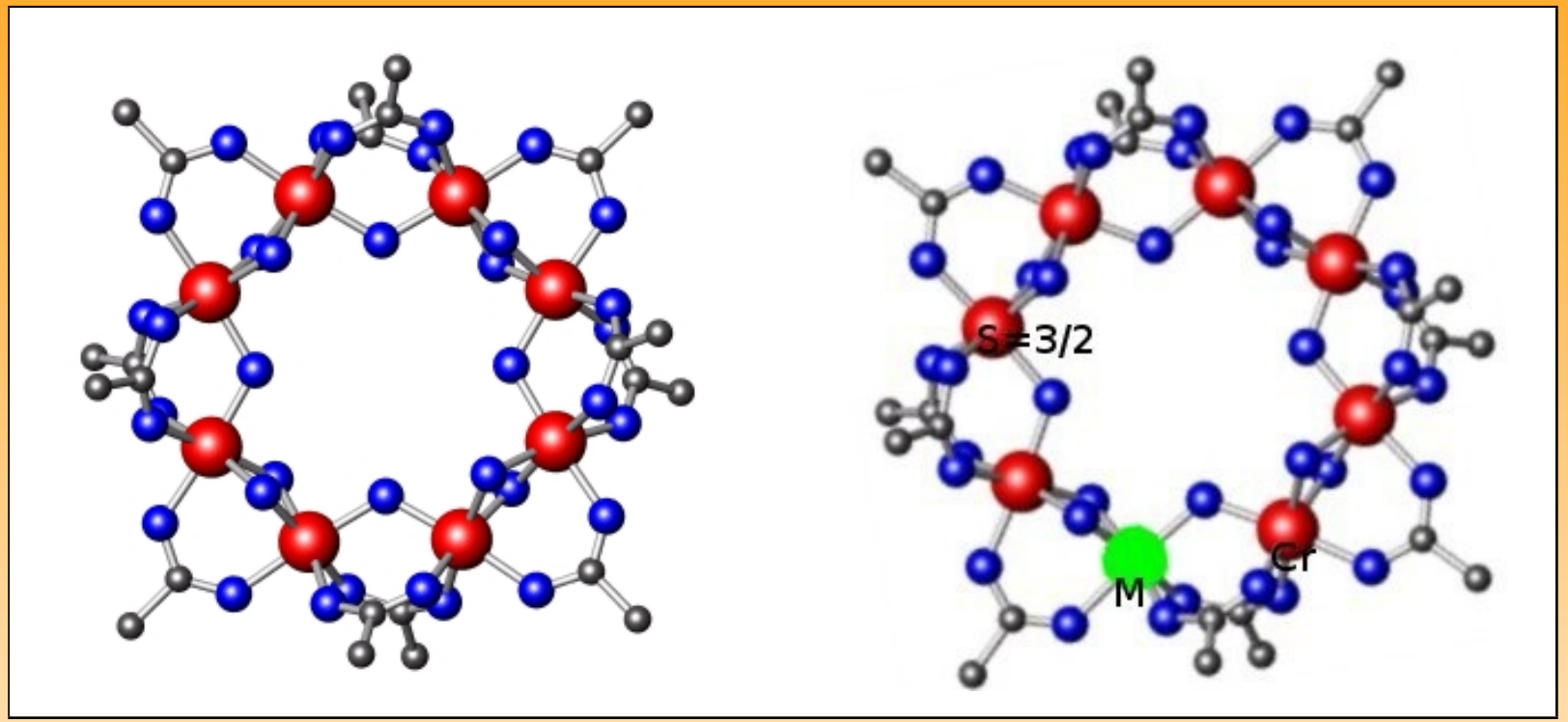

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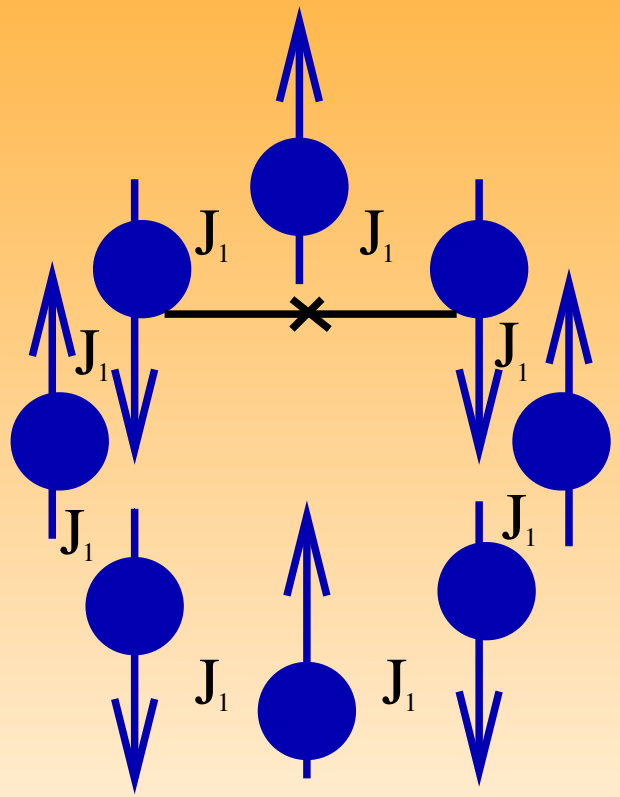
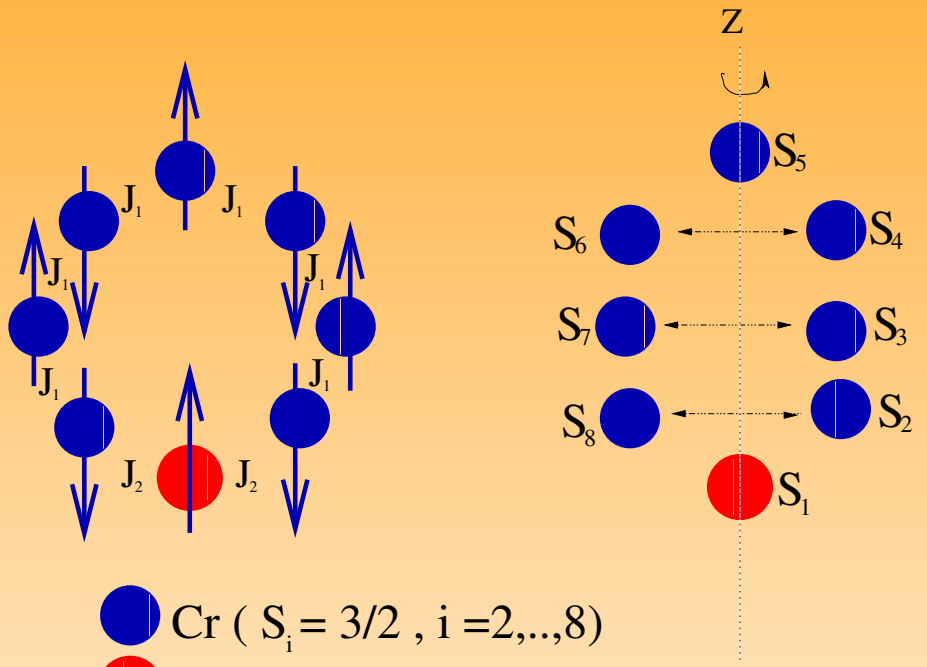
Schematic representation of Cr_8 and Cr_7M

AFM ring systems Cr_8 and Cr_7M in which one of the Cr^{III} ions replaced by a dopant ion to create an excess spin.



Molecular magnetic rings Cr_8



Schematic representation of Cr_7M rings

The Hamiltonian of the Heisenberg-Model

The isotropic Heisenberg model with Zeeman term of an external magnetic field can be written as:

$$\hat{H} = 2J_1 \sum_{i=2}^{N} \hat{\vec{s}}_i \cdot \hat{\vec{s}}_{i+1} + 2J_2(\hat{\vec{s}}_1 \cdot \hat{\vec{s}}_2 + \hat{\vec{s}}_1 \cdot \hat{\vec{s}}_N) + g\mu_B B \sum_{u}^{N} \hat{s}_z(u),$$

Dimension of the problem: $\text{Dim}\,(\mathcal{H}) = [2s\,(1)+1] * [2s\,(2)+1] * \cdots * [2s\,(N)+1]$

$$\underset{\sim}{s}_z(u)\;|\,m_1,\ldots,m_u,\ldots,m_N\,\rangle = m_u\;|\,m_1,\ldots,m_u,\ldots,m_N\,\rangle$$

Decomposition into mutually orthogonal subspaces

$$\begin{cases} \left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0 \\ \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0 \end{cases} \quad \Longrightarrow \quad \mathcal{H} = \bigoplus\nolimits_{M=-S_{\text{max}}}^{+S_{\text{max}}} \mathcal{H}(S,M)$$

Cyclic shift operator $T_{\underset{\sim}{M}}$

$T_{\underset{\sim}{M}}$ is defined by:

$$T_{\underset{\sim}{M}} \,|\, m_1, m_2, m_3, m_4, m_5, m_6, m_7, m_8 \,\rangle = |\, m_1, m_8, m_7, m_6, m_5, m_4, m_3, m_2 \,\rangle$$

The eigenvalues of $T_{\underset{\sim}{M}}$ are the N-th roots of unity $\quad z_k = exp(-i\frac{2\pi k_m}{N_c})$

The shift quantum number k_m=0,1, and N_c number of cycle;

$$\begin{cases} \left[T_{\underset{\sim}{M}}, \vec{\underset{\sim}{H}}\right] = 0 \\ \left[T_{\underset{\sim}{M}}, \underset{\sim}{S}^2\right] = 0 \end{cases} \Longrightarrow \quad \mathcal{H}(S,M) \longrightarrow \mathcal{H}(S,M,k) \quad eigenspaces$$

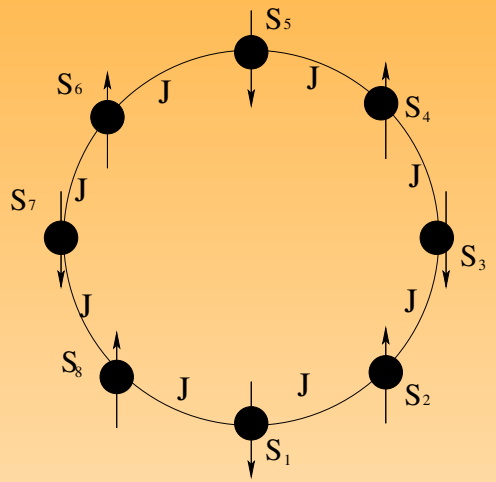
$$|\, \psi_k \,\rangle = 1/\sqrt{N} \sum_{\nu=0}^{N-1} (exp(i\frac{2\pi k_m}{N_c}) T_{\underset{\sim}{M}})^{\nu} \,|\, \psi_1 \,\rangle \;\; With: \;\; |\, \psi_1 \,\rangle = |\, m_1, m_2, \ldots, m_N \,\rangle$$

Cr_8 Anti-ferromagnetic ring

Single molecule magnets are cluster formed by a finite number of exchange-coupled transition metal-ions.

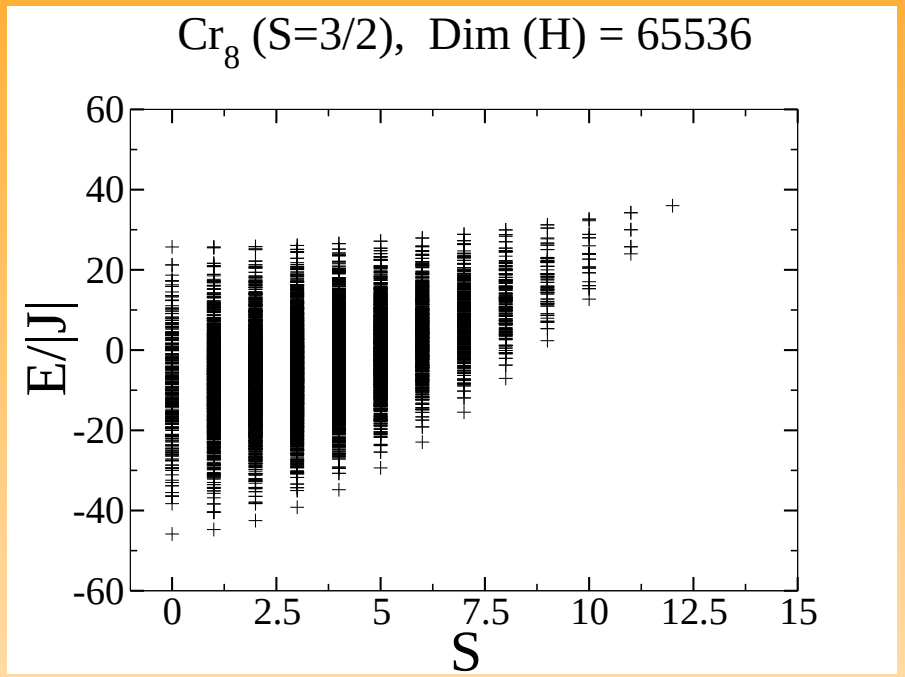
● Cr

S(i)=3/2, i=1,..,8



Molecular magnetic rings

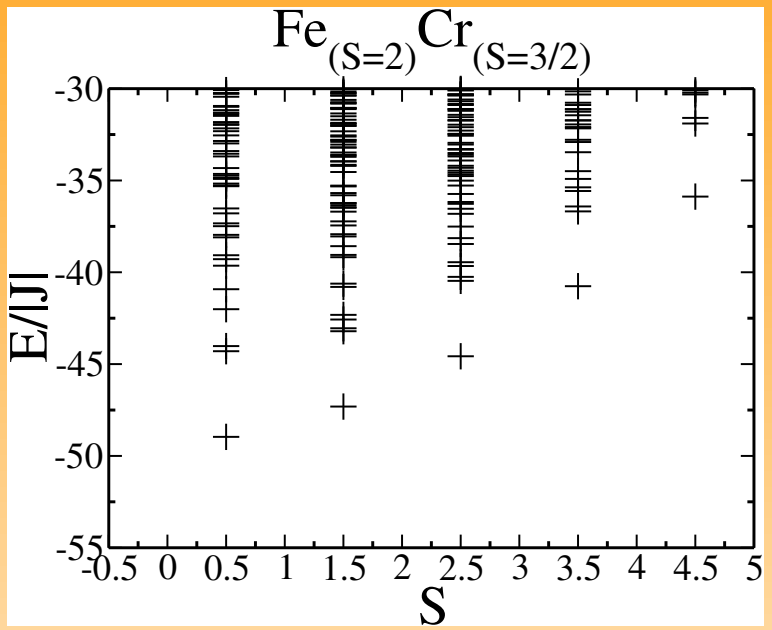
Cr_8 (S=3/2)



Exact diagonalisation

Cr_8

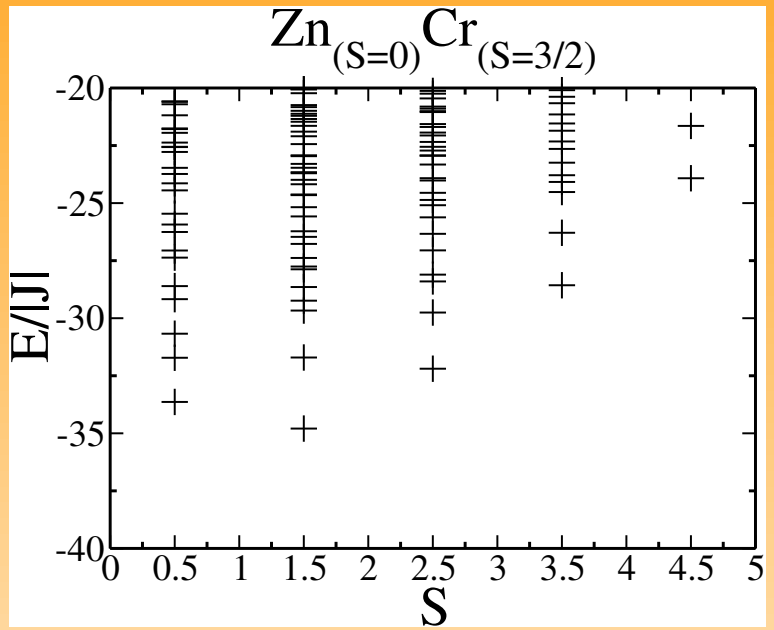
Exact diagonalisation of $FeCr_7$ and $ZnCr_7$ antiferromagnetic ring



$Fe_{(S=2)}Cr_{7(S=3/2)}$

Ground state S=1/2

- 7 Cr with spin S=3/2 and 1 Fe with spin 2;
- Dimension of Hilbert space H= 81920;

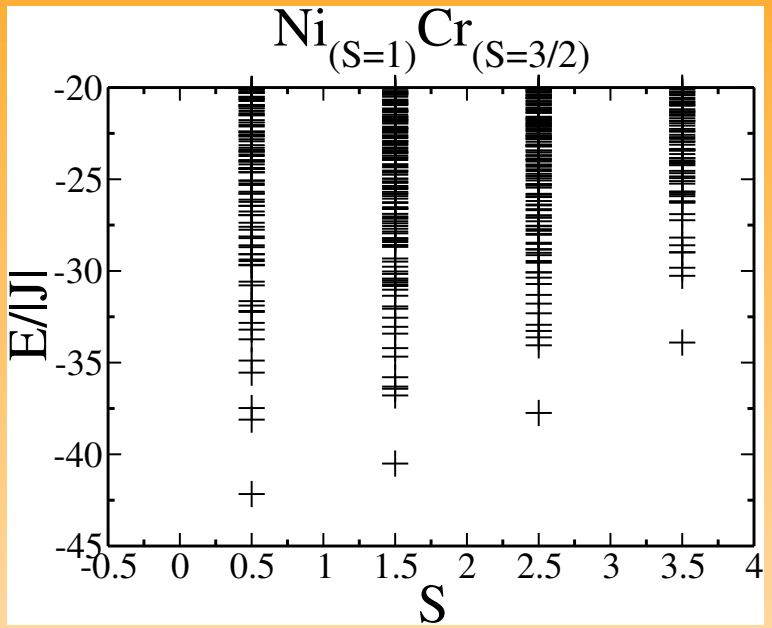


$Zn_{(S=0)}Cr_{7(S=3/2)}$

Ground state S=3/2

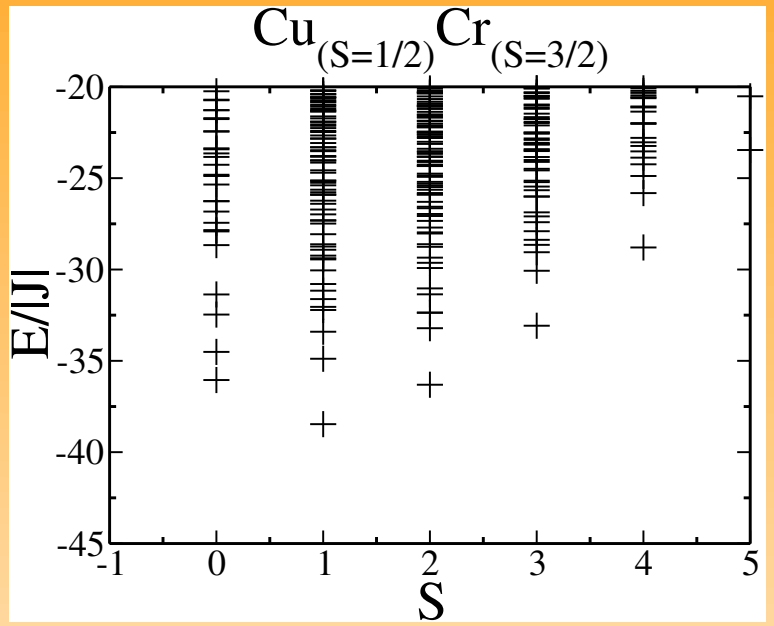
- 7 Cr with spin S=3/2 and 1 Zn with spin 0;
- Dimension of Hilbert space H= 16384;

Exact diagonalisation of $NiCr_7$ and $CuCr_7$ antiferromagnetic ring



$Ni_{(S=1)}Cr_{7(S=3/2)}$

Ground state S=1/2



$Cu_{(S=1/2)}Cr_{7(S=3/2)}$

Ground state S=1

- 7 Cr with spin S=3/2 and 1 Ni with spin 1;
- Dimension of Hilbert space H= 49152;

- 7 Cr with spin S=3/2 and 1 Cu with spin 1/2;
- Dimension of Hilbert space H= 32768;

Magnetic susceptibility

- The zero-field magnetic susceptibility of the antiferromagnetic Heisenberg model is given by:

$$\chi_B = \frac{\partial M}{\partial B} = \beta(g\mu_B)^2\{<< \underset{\sim}{S_z}^2 >> - << \underset{\sim}{S_z} >>^2\}$$

Magnetic susceptibility

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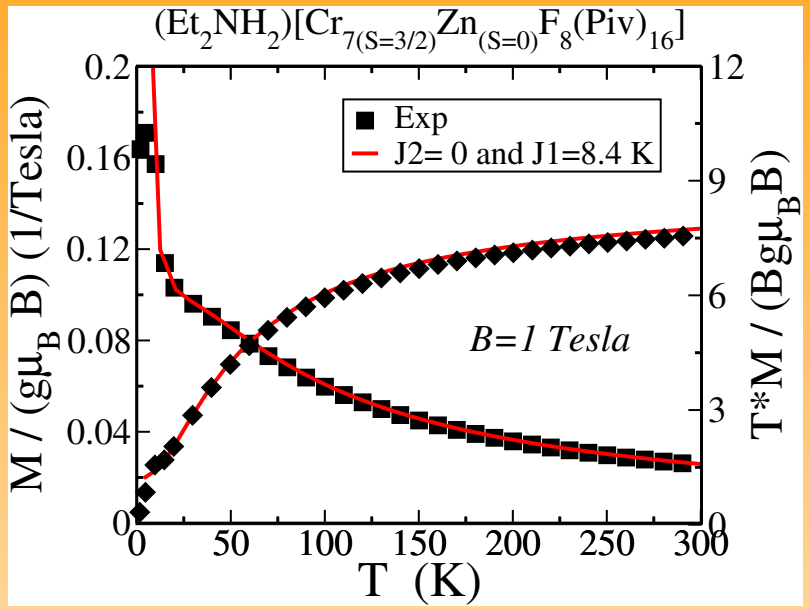
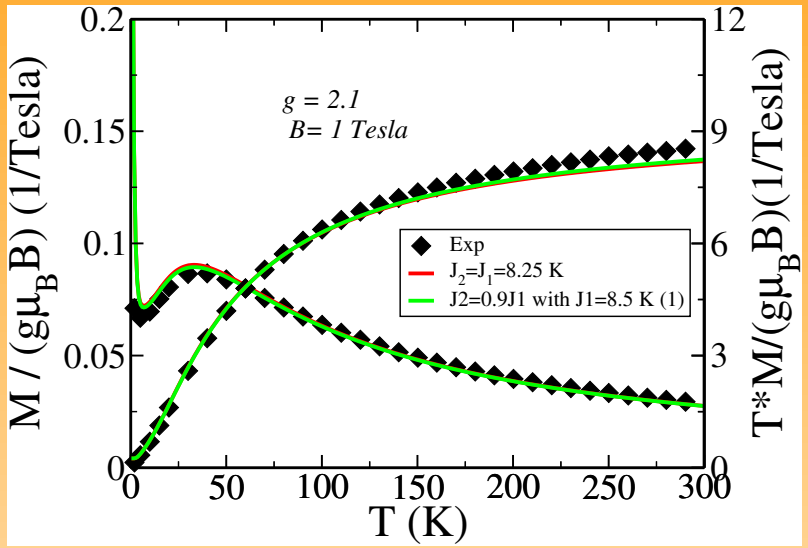
$$= \beta(g\mu_B)^2 \left\{ \frac{\sum_\nu M_\nu^2 e^{-\beta E_\nu}}{\sum_\nu e^{-\beta E_\nu}} - (\frac{\sum_\nu M_\nu e^{-\beta E_\nu}}{\sum_\nu e^{-\beta E_\nu}})^2 \right\}$$

Low-field magnetic susceptibility of $ZnCr_7$ and $NiCr_7$



$Zn_{(S=0)}Cr_{7(S=3/2)}$



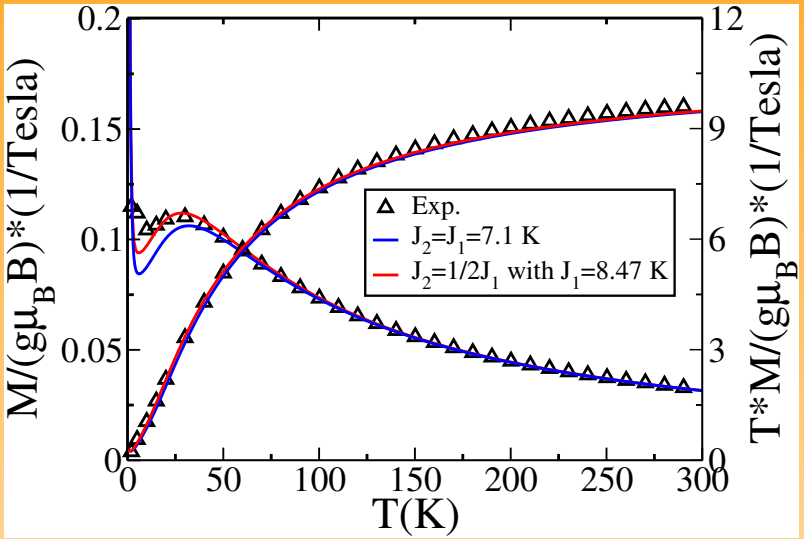
$Ni_{(S=1)}Cr_{7(S=3/2)}$

- The red solid line for $J2(Zn-Cr) = 0$ K and $J1(Cr-Cr) = 8.4$ K, and g=2;

- Experimental data by Quantum Design MPMS SQUID magnetometer;
- The red solid line for $J1(Cr-Cr) = J2(Ni-Cr) = 8.25$ K;

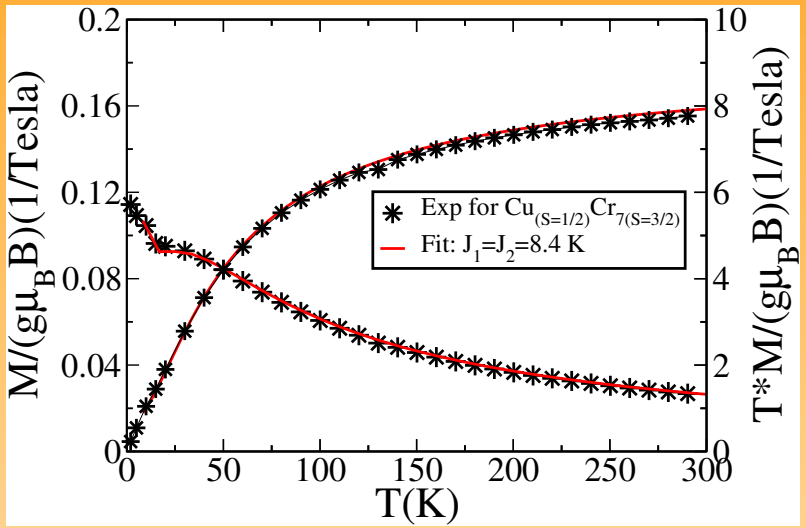
(1) A. Lascialfari *et al.*, J. Magn. Magn. Mater. 272-276, 1042-1047 (2004)

Low-field magnetic susceptibility of $FeCr_7$ and $CuCr_7$



Zero-field magnetic susceptibility

$Fe_{(S=2)}Cr_{7(S=3/2)}$



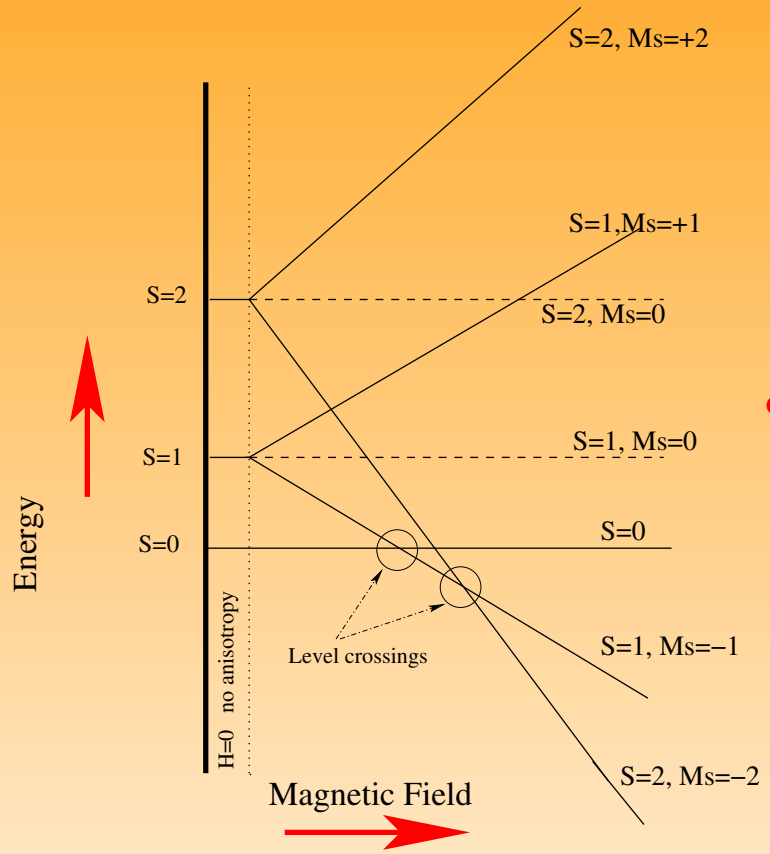
Zero-field magnetic susceptibility

$Cu_{(S=1/2)}Cr_{7(S=3/2)}$

- Blue solid line for $J1(Cr-Cr) = J2(Fe-Cr) = 7.1$ K ;
- Red solid line for $J2(Fe-Cr) = 1/2J1(Cr-Cr)$ with $J1 = 8.47$ K;

- Experimental data by Quantum Design MPMS SQUID magnetometer;
- The red solid line for $J1(Cr-Cr) = J2(Cu-Cr) = 8.4$ K;

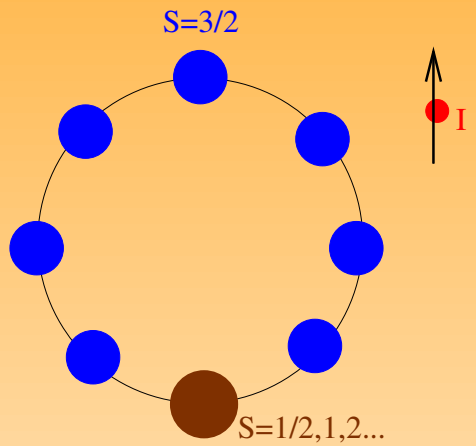
Quantum level crossing effects



- Energies levels vs magnetic field for the lower three spins values (S=0, 1 and 2) in Cr_8 molecular ring;

Spin-lattice relaxation rates T_1^{-1}

The relaxation time T_1 represents the "lifetime" of the first order rate process that returns the magnetization to the Boltzmann equilibrium along the $+Z$ axis.



- I: Nuclear spin;
- S: Electrons spin;
- T_1^{-1} depends highly on the type of nuclei (for $I = 1/2$ and low magnetogyric ratio usually yields long T_1, $I > 1/2$ have very short relaxation time);
- Depends also about physical state, on the viscosity of the solution, the temperature... etc.
- T_1^{-1} can be measured by various techniques: Inversion Recovery Fourier Transform (PSFT), Progressive Saturation(PSFT).

Electron-Nucleus Interaction

$$\hat{H} = \underset{\sim}{F}^z \underset{\sim}{I}^z + \underset{\sim}{F}^+ \underset{\sim}{I}^- + \underset{\sim}{F}^- \underset{\sim}{I}^+ \qquad (1)$$

$$With : \underset{\sim}{F}^z = \sum_{i=1}^{N} (\frac{2}{3} D_0(i) \underset{\sim}{S}^z(i) + D_{+1}(i) \underset{\sim}{S}^+(i) + D_{-1}(i) \underset{\sim}{S}^-(i))$$

$$\underset{\sim}{F}^{\pm} = \sum_{i=1}^{N} (\frac{-1}{6} D_0(i) \underset{\sim}{S}^{\pm}(i) + D_{\mp 1}(i) \underset{\sim}{S}^z(i) + D_{\mp 2}(i) \underset{\sim}{S}^{\mp}(i))$$

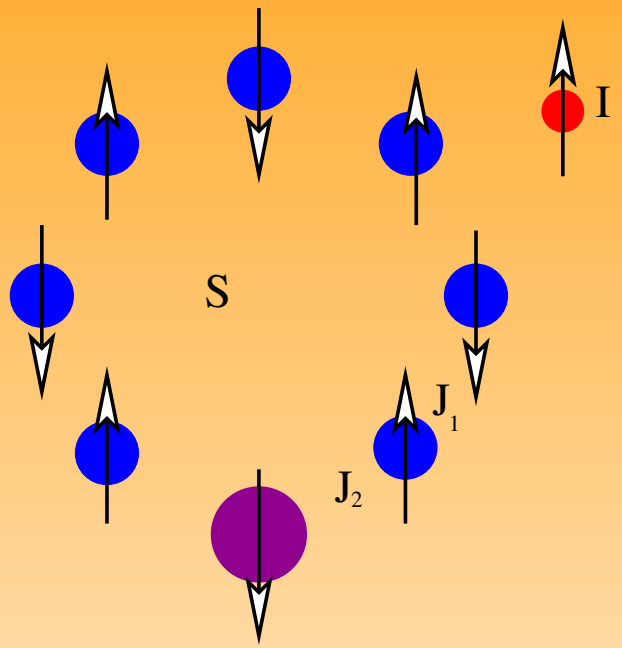
Where $D_0(i) = \alpha_i(3\cos\theta_i - 1)$,
$D_{\pm 1}(i) = \alpha_i \sin\theta_i cos\theta_i \exp(\mp i\varphi_i)$,
$D_{\mp 2} = 1/2\alpha_i \sin^2 \alpha_i \exp(\mp 2i\varphi_i)$
$\alpha_i = \frac{3\gamma_N \gamma_S}{2r_i^3}$

are the geometrical factors of the dipolar interaction,

θ_i and φ_i are the polar coordinates of the vector r_i describing the relative positions of the two spins;
In the case of an isotropic g factorφ=0 and α_i=1;
γ_S and γ_N the gyromagnetic rations-of the electronic and nuclear spins.

(1) A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961)

Spin-lattice relaxation rates T_1^{-1}



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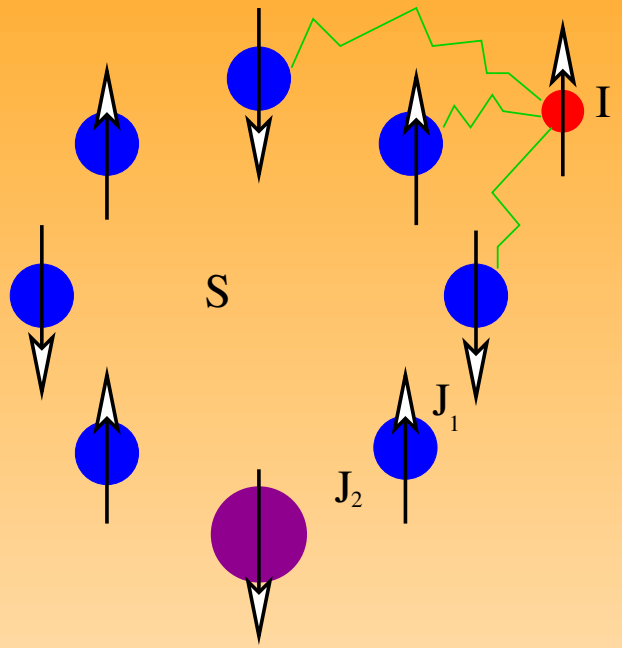
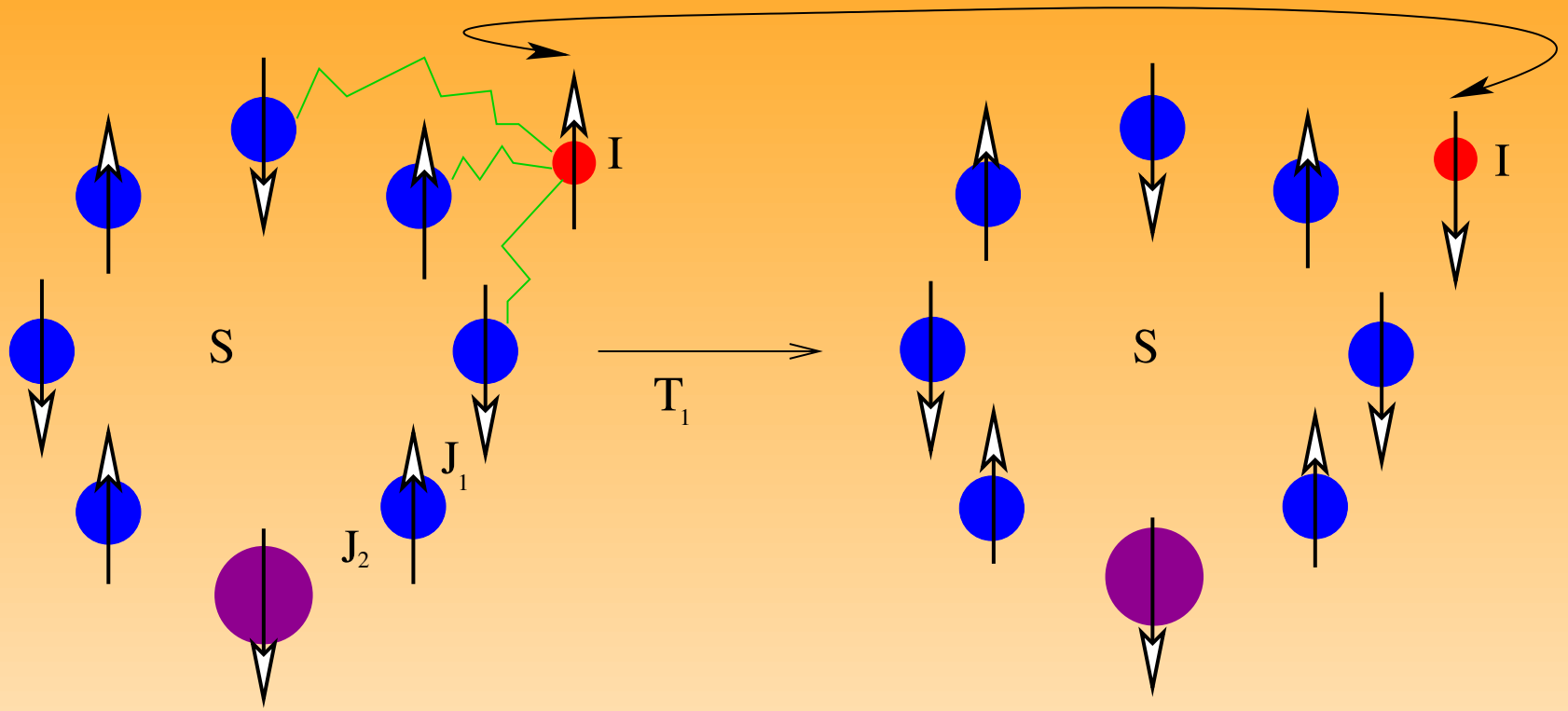


Spin-lattice relaxation rates T_1^{-1}

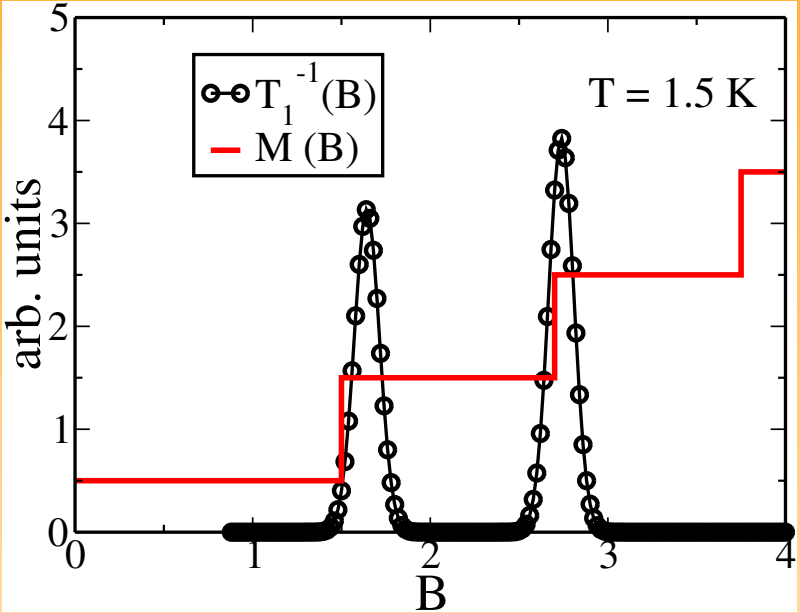


The proton-spin lattice relaxation rate T_1^{-1} is given by:

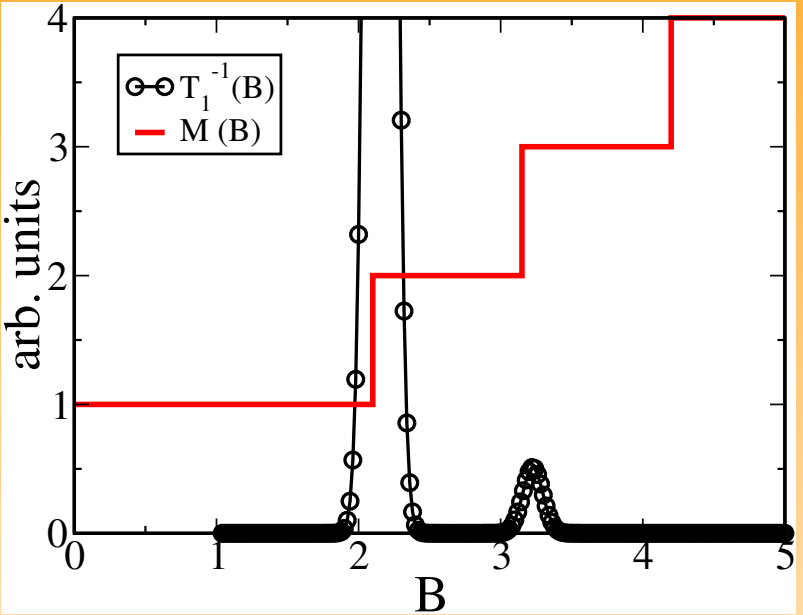
$$\frac{1}{T_1} = (1 + exp(-\hbar\omega_N/k_BT)) \int_{-\infty}^{+\infty} < F^+(t)F^-(o) > e^{(+i\omega_N t)}dt \qquad (2)$$

(2) T. Moriya, Prog. Theor. Phys. **28**, 371 (1962)

Magnetisation and proton spin-lattice relaxation rate T_1^{-1} as function of B



$Fe_{(S=2)}Cr_{7(S=3/2)}$



$Cu_{(S=1/2)}Cr_{7(S=3/2)}$

- Magnetisation versus applied magnetic field at zero-temperature for $FeCr_7$ and $CuCr_7$ molecular ring, given by a red solid line.
- The proton spin-lattice relaxation rate T_1^{-1} as function of the applied magnetic field B, for the 2 antiferromagnetics ring system $FeCr_7$ and $CuCr_7$ with Temperature $T = 1.5$ K, given by black circle;

Prospects

- There is no big influence for the exchange parameters in the case of substitution of one metals ions in the Cr_8, just in the case of Fe.
- Strong enhancement of T_1^{-1} is observed at magnetic field values where steps are observed in the magnetization: resonant relaxation.
- Spin dynamics of antiferromagnetic ring systems of Heterometallic $\{Cr_7M\}$ wheels.
- Start: 01/04/2003, scheduled end: end of 2005.