Magnetism of heterometallic wheels

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Seminar Theoretische Physik
Osnabrück University

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Outline

1. **Molecular magnetic rings**
   - Heterometallic $\{Cr_7M\}$ rings
   - Theoretical model
   - Energy spectrum
   - Low-field susceptibility
2. **Quantum level crossing effects**
   - Level crossing in heterometallic $\{Cr_7M\}$ ring
   - Spin-lattice relaxation rates T_1^{-1}
   - Electron-nucleus interactions
   - T_1^{-1} in Cr_8 and heterometallic $\{Cr_7M\}$ ring
3. **Summary**

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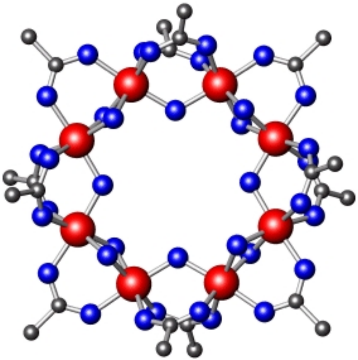
Even member AFM molecular rings



Cr_8

Quite common for transition metal ions, like Fe_6, Cu_{10}, Cr_8 and Mn_{12}.
Attracting interest $==>$ Provide good opportunities for observing quantum tunneling.

1. $[Cr_8F_8(O_2CCMe_3)_{16}]$

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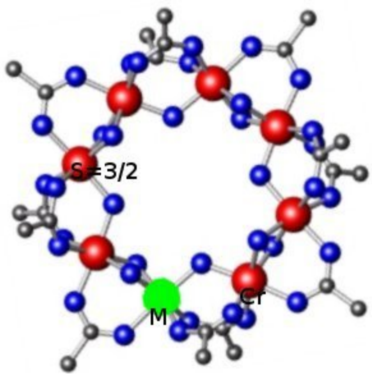
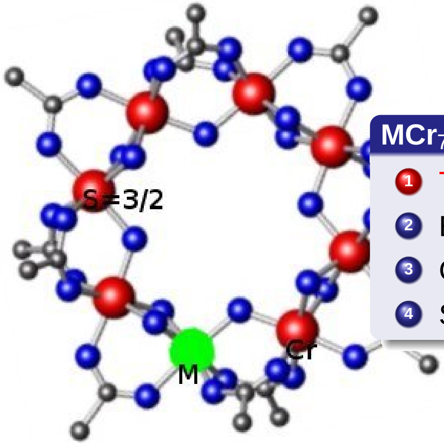


MCr_7

Quite common for transition metal ions, like Fe_6, Cu_{10}, Cr_8 and Mn_{12}.
Attracting interest ==> Provide good opportunities for observing quantum tunneling.

1. $[\{nBu_2NH_2\}\{\mathbf{Cr_7Fe}\}F_8Piv_{16}\}]$
2. $(Et_2NH_2)[\mathbf{Cr_7Cu}F_8Piv_{16}]$
3. $(R_2NH_2)[\mathbf{Cr_7Ni}F_8Piv_{16}]$
4. with $Piv_{16} = (O_2CCMe_3)_{16}$

Why substituted by metal ion ?



MCr_7

1. To create an excess spin;
2. Engineer its level structure;
3. Ground state degeneracy;
4. Spin frustration.

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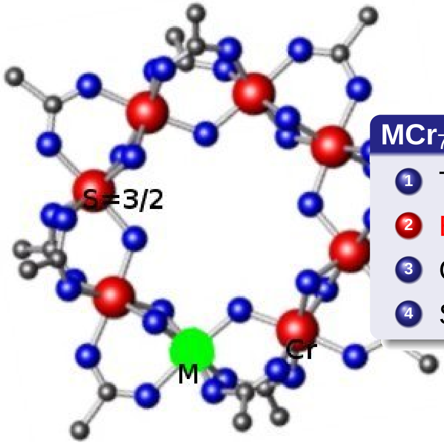

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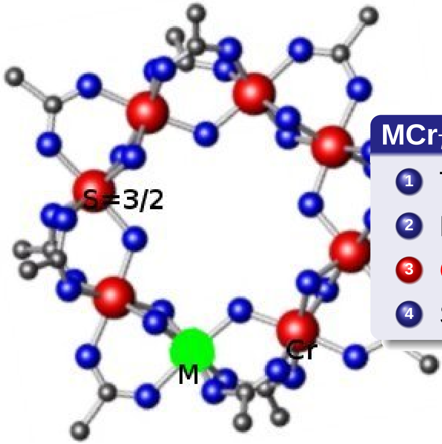

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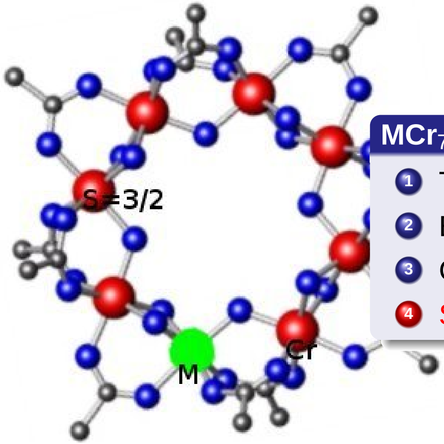

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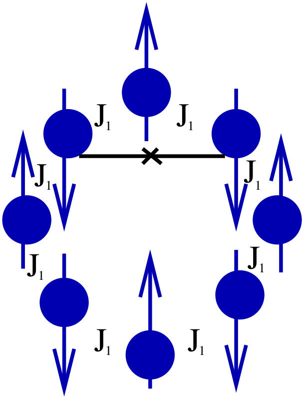
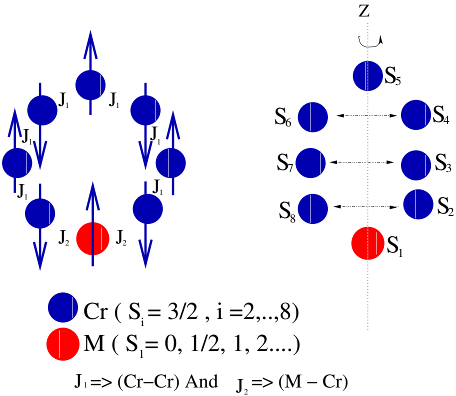
Schematic representation of Cr_8 and Cr_7M





Hamiltonian and Observables

1. Hamiltonian of the Heisenberg-Model
$\hat{H} = 2J_1 \sum_{i=2}^{N} \hat{\vec{s}}_i \cdot \hat{\vec{s}}_{i+1} + 2J_2(\hat{\vec{s}}_1 \cdot \hat{\vec{s}}_2 + \hat{\vec{s}}_1 \cdot \hat{\vec{s}}_N) + g\mu_B B \sum_{u}^{N} \hat{s}_z(u),$
2. $\mathrm{Dim}\,(\mathcal{H}) = [2s\,(1)+1] * [2s\,(2)+1] * \cdots * [2s\,(N)+1]$
3. $\underset{\sim}{s}_z(u)\,|\,m_1,\ldots,m_u,\ldots,m_N\,\rangle = m_u\,|\,m_1,\ldots,m_u,\ldots,m_N\,\rangle$

Decomposition into mutually orthogonal subspaces

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

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Observable and operator

1. Use mirror symmetry around the doping ion:
$\underset{\sim}{T_M} \, | m_1, m_2, m_3, m_4, m_5, m_6, m_7, m_8 \rangle = | m_1, m_8, m_7, m_6, m_5, m_4, m_3, m_2 \rangle$
2. The eigenvalues of $\underset{\sim}{T_M}$ are $\pm$ 1.

Decomposition of subspaces H(S,M)

$$\left\{ \begin{array}{ll} \left[\underset{\sim}{T_M}, \underset{\sim}{H} \right] & = 0 \\ \left[\underset{\sim}{H}, \underset{\sim}{S_z} \right] & = 0 \end{array} \right. \quad --- > \quad \mathcal{H}(S,M) --- > \mathcal{H}(S,M,k)$$

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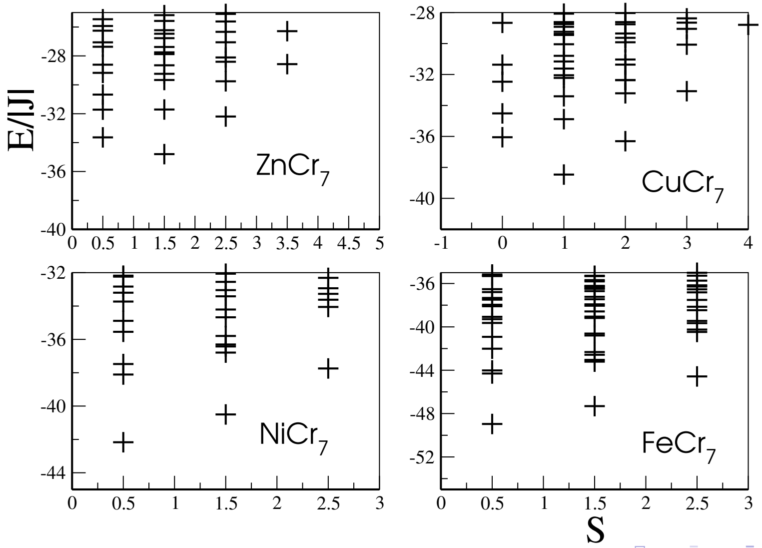
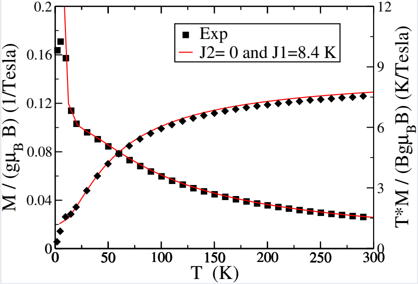
Spectrum of Heterometallic Cr_7M weel

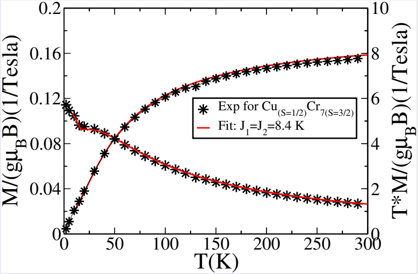


Susceptibility

$ZnCr_7$



$CuCr_7$

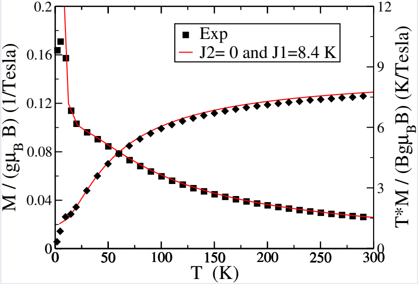


Exchange interaction

1. $ZnCr_7$: $J_1 = 8.4$ K and $J_2 = 0$ K
2. $CuCr_7$: $J_2 = J_1 = 8.4$ K

Susceptibility

$ZnCr_7$



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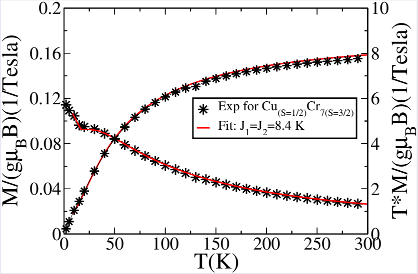

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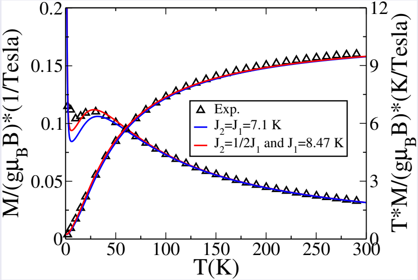
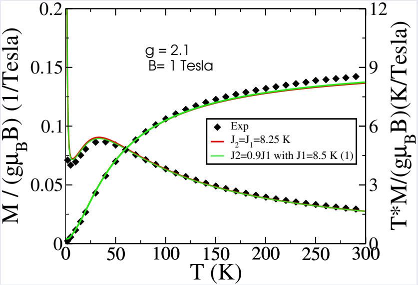


$NiCr_7$



Exchange interaction

1. $FeCr_7$: red solid line $J_2 = J_1/2$ and $J_1 = 8.47$ K
2. $NiCr_7$: $J_2 = J_1 = 8.25$ K

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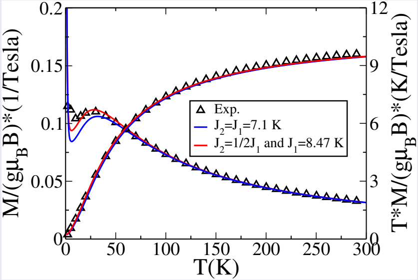

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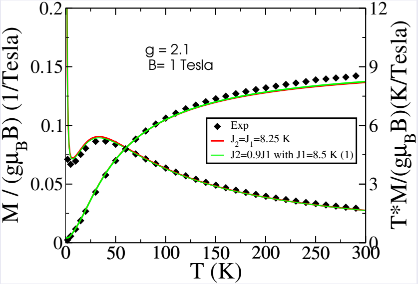

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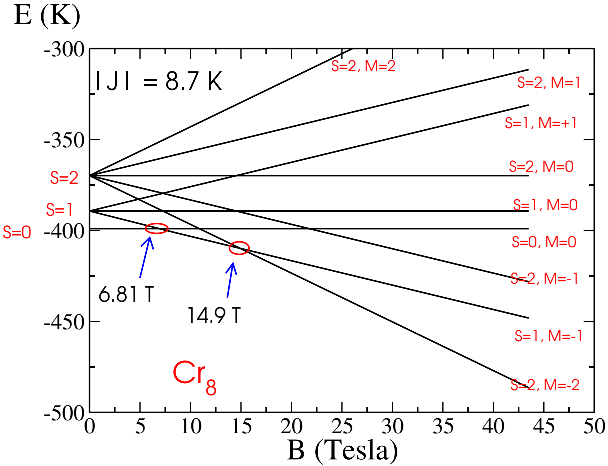
3. Summary

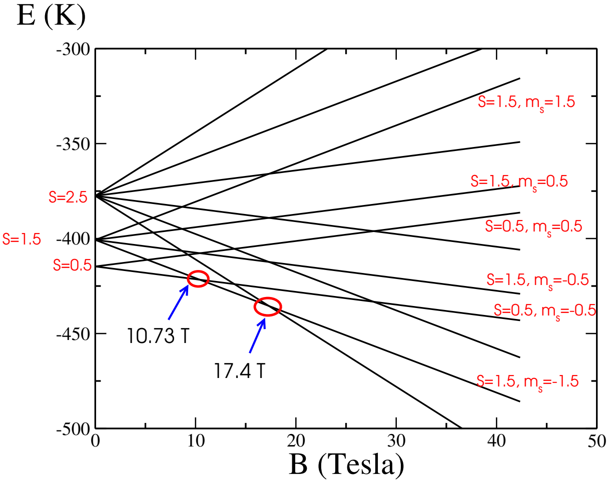
Energies levels vs B in Cr_8

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

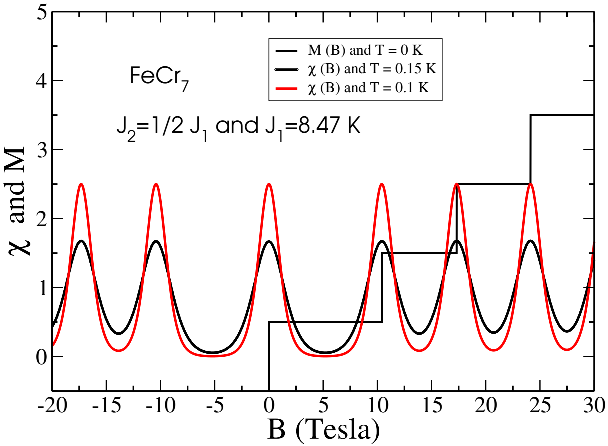


Energies levels vs B in $FeCr_7$

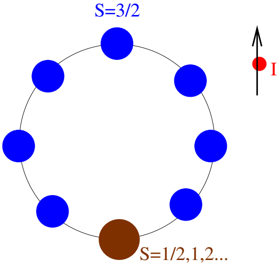
Energies levels vs magnetic field for the lower three spins values (S=1/2, 3/2 and 5/2) in $FeCr_7$ molecular ring;



Magnetic susceptibility as a function of B for $FeCr_7$



Spin-lattice relaxation rates T_1^{-1}



Definition

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.

1. 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);
2. T_1^{-1} can be measured by various techniques: Inversion Recovery Fourier Transform (PSFT), Progressive Saturation (PSFT).

Electron-Nucleus Interactions

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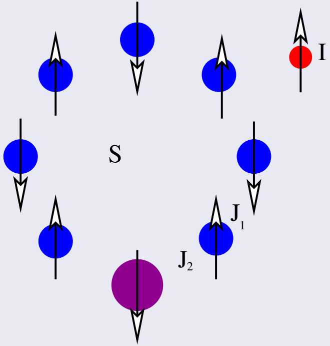

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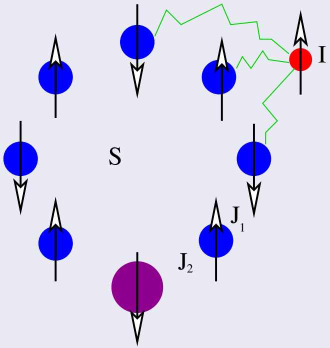

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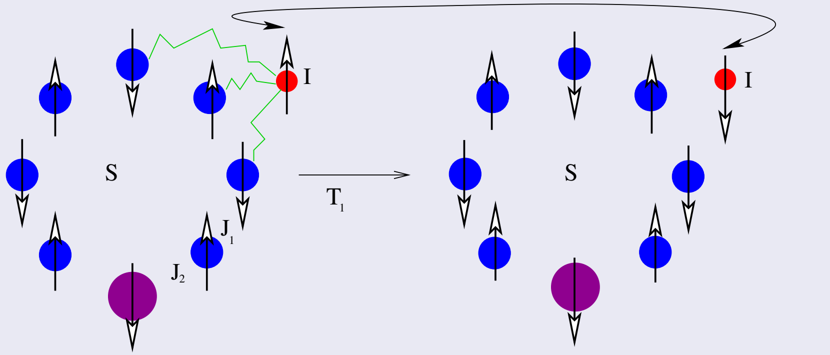

Electron-Nucleus Interactions

Dipolar coupling between nuclear spin I and electron spin S_i:

$$\hat{H} = \underset{\sim}{F}^z \underset{\sim}{I}^z + \underset{\sim}{F}^+ \underset{\sim}{I}^- + \underset{\sim}{F}^- \underset{\sim}{I}^+$$

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

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

Where

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Where

$D_0(i) = \alpha_i (3\cos\theta_i - 1)$,
$D_{\pm 1}(i) = \alpha_i \sin\theta_i cos\theta_i \exp(\mp i\varphi_i)$,
$D_{\mp 2} = 1/2\alpha_i \sin^2\theta_i \exp(\mp 2i\varphi_i)$
$\alpha_i = \frac{3\gamma_N\gamma_S}{2r_i^3}$ are the geometrical factors of the dipolar interaction,

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Where

- 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 factor φ=0 and α_i=1;
- γ_S and γ_N the gyromagnetic rations.

Spin-lattice relaxation rates T_1^{-1}

NMR: Correlation of the individual spin S_i:

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

$$< F^+(t)F^-(o) >= \frac{1}{Z} \sum_{\mu} < \psi_\mu | e^{i\frac{E_\mu t}{\hbar}} \tilde{F}^+ e^{-i\frac{\tilde{H}t}{\hbar}} \tilde{F}^- | \psi_\mu > e^{-\beta E_\mu}$$

$$= \frac{1}{Z} \sum_{\mu,\nu} e^{i\frac{(E_\mu - E_\nu)t}{\hbar}} e^{-\beta E_\mu} < \psi_\mu | \tilde{F}^+ | \psi_\nu >< \psi_\nu | \tilde{F}^- | \psi_\mu >$$

With Fourier transform:

$$\ldots.\frac{1}{Z} \sum_{\mu,\nu} e^{-\beta E_\mu} < \psi_\mu | \tilde{F}^+ | \psi_\nu >< \psi_\nu | \tilde{F}^- | \psi_\mu > \int_{-\infty}^{+\infty} e^{-i\frac{(E_\nu - E_\mu)t}{\hbar} + i\omega_N t} dt$$

Spin-lattice relaxation rates T_1^{-1}

$$\frac{1}{T1} = (1 + exp(-\hbar\omega_N/k_B T))\frac{2\pi}{Z}\sum_{\mu,\nu} e^{-\beta E_\mu} < \psi_\mu|\tilde{F}^+|\psi_\nu >$$

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

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Where

$\omega_N = \gamma_N B$, γ_N = g_N $\frac{\mu_N}{\hbar}$
γ_N: gyromagnetic ratio of the necleus;
δ_ε = smeared-function, i.e Gaussian or Lorentzian, $\varepsilon \backsimeq$ decay width.
g_N: Lande factor of nuclear $\backsimeq$ 5.5854;
μ_N: nuclear magneton = 5.0508 10^{-27} A m^2;
$\frac{\mu_N}{k_B} = 0.0003658$ K/T

Spin-lattice relaxation rates T_1^{-1}

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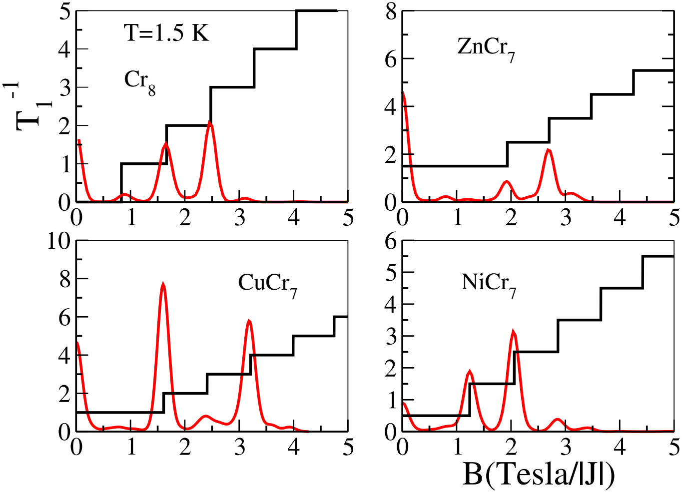
Where

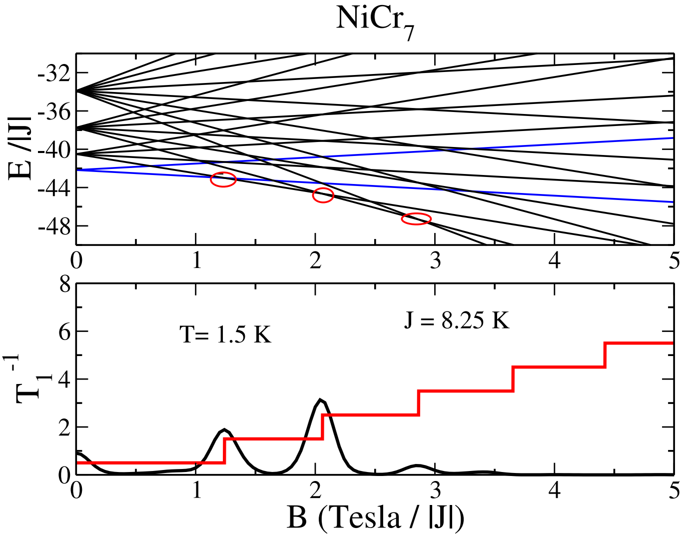
$E_\nu - E_\mu = E_\nu(B = 0) - E_\mu(B = 0) + g_e \mu_B B(M_\nu - M_\mu)$
with:
g_e: Lande factor of electron;
μ_B: electron magneton: 9,274 10^{-24} A m^2;
$\frac{\mu_B}{k_B} = 0.67$ K/T

T_1^{-1} in $\{Cr_7Fe\}$ molecular ring

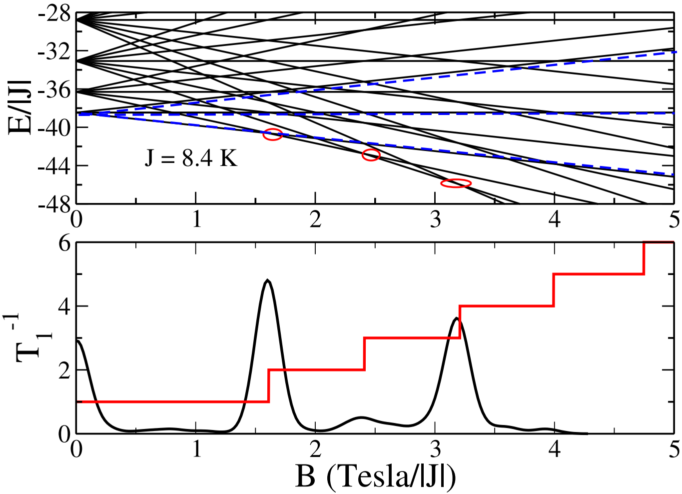
Contribution of the lowest M-subspaces with: $0 \leqslant M \leqslant 5$



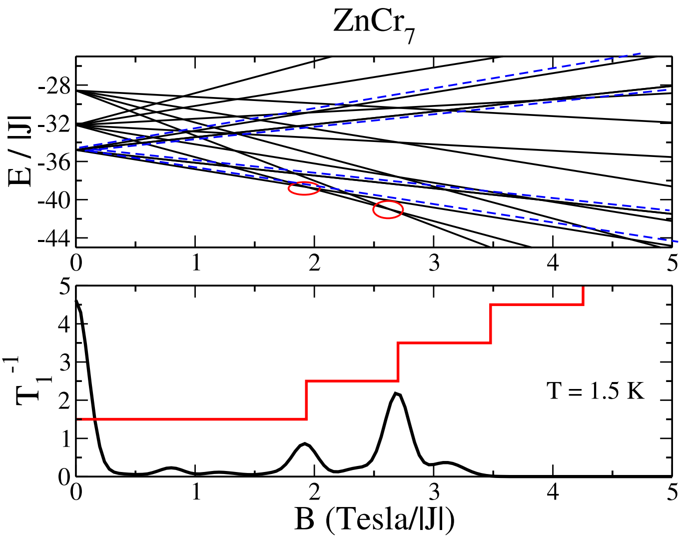
T_1^{-1} in $\{NiCr_7\}$ molecular ring



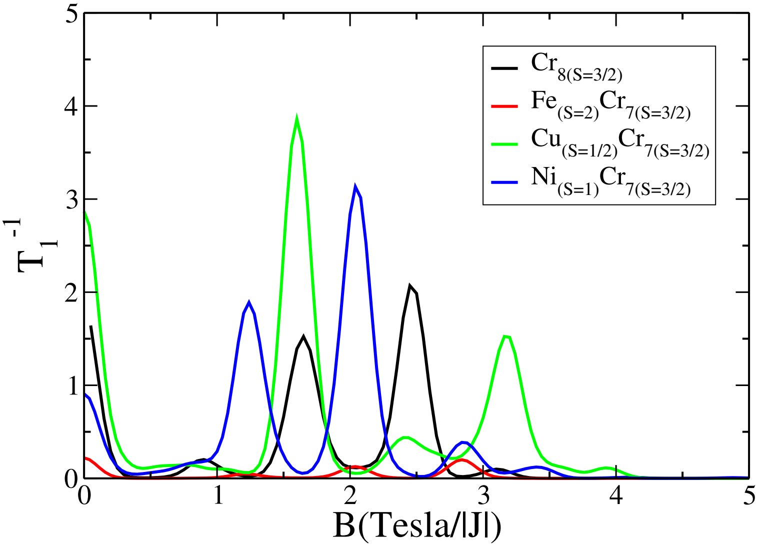
T_1^{-1} in $\{CuCr_7\}$ molecular ring



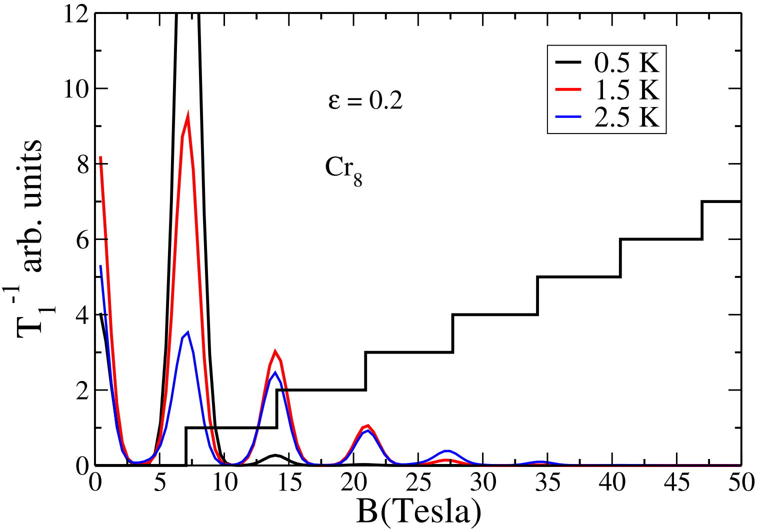
T_1^{-1} in $\{ZnCr_7\}$ molecular ring



T_1^{-1} in Cr_8 and heterometallic $\{Cr_7M\}$ ring



T_1^{-1} in $\{Cr_8\}$ molecular ring



Outline

Summary

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- 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 at low temperature: resonant relaxation.
- The peaks observed for the compounds in which one Cr^{III} ions has been replaced by a Cu, Ni ($S_i < S_{Cr}$) are higher than the peaks of the Cr_8 ring $==>$ long relaxation time.
- Short relaxation time in the case $FeCr_7$ comparing to the Cr_8 at low temperature region.