# Magnetic properties of Heterometallic {$Cr_7M$} Wheels

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## Introduction

Since experimental studies have show the relaxation of magnetization at low temperatures in the molecule $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O_4]$[a], single molecule magnets have become the subject of intense scientific investigations in both simulations and experimental works in physics and chemistry. These molecules are promising new materials for hight density magnetic storage media, quantum information and computation theory.

In this work we study magnetic rings closely related to the heterometallic {$Cr_7M$} wheels, in which one of the $Cr^{III}$ ions has been replaced by a Fe, Ni or Zn ion with spin s=2, s=1 and s=0 respectively. This extra-spin acts as local probe for spin dynamics. Such system have been synthesized recently [b]. The system is well described using the Heisenberg spin Hamiltonian with Zeeman term of applied magnetic field along the z-axis

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

where N=8, $S_1$=$S_{N+1}$ and the total spin operator $S = \sum_i^N S_i$. The symmetry operation used to study the {$Cr_7M$} wheels is represented in Figure (1)

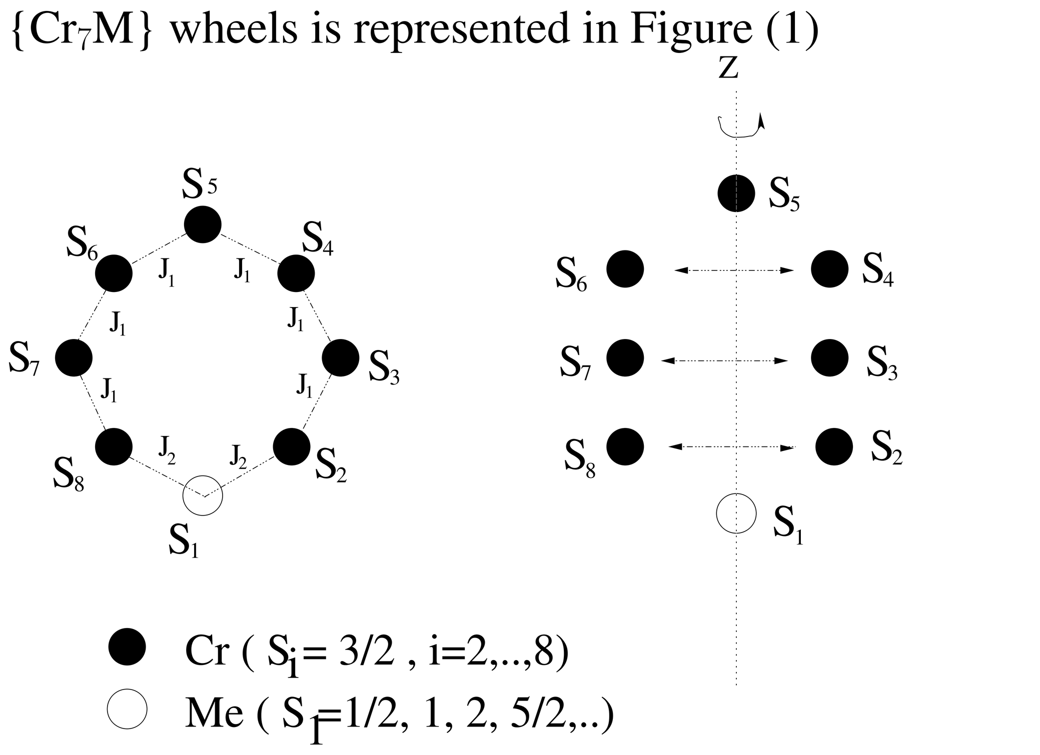


**Figure 1** Schematic representation of symmetry operation used in our calculation to study the molecular magnetic rings of heterometallic {$Cr_7M$} wheels.

[a] D. Gatteschi, *et al.* Science 265, 1054-1058 (1994)
[b] Finn K. Larsen, *et al.* Angew. Chem. Int. Ed. 2003, 42, No 1

## Energy spectrum of $FeCr_7$

The complete Hilbert space contains $4^7 * 5 = 81920$ states. The low-energy part of spectrum for the physical system Fe-$Cr_7$ is represented in Figure (2).

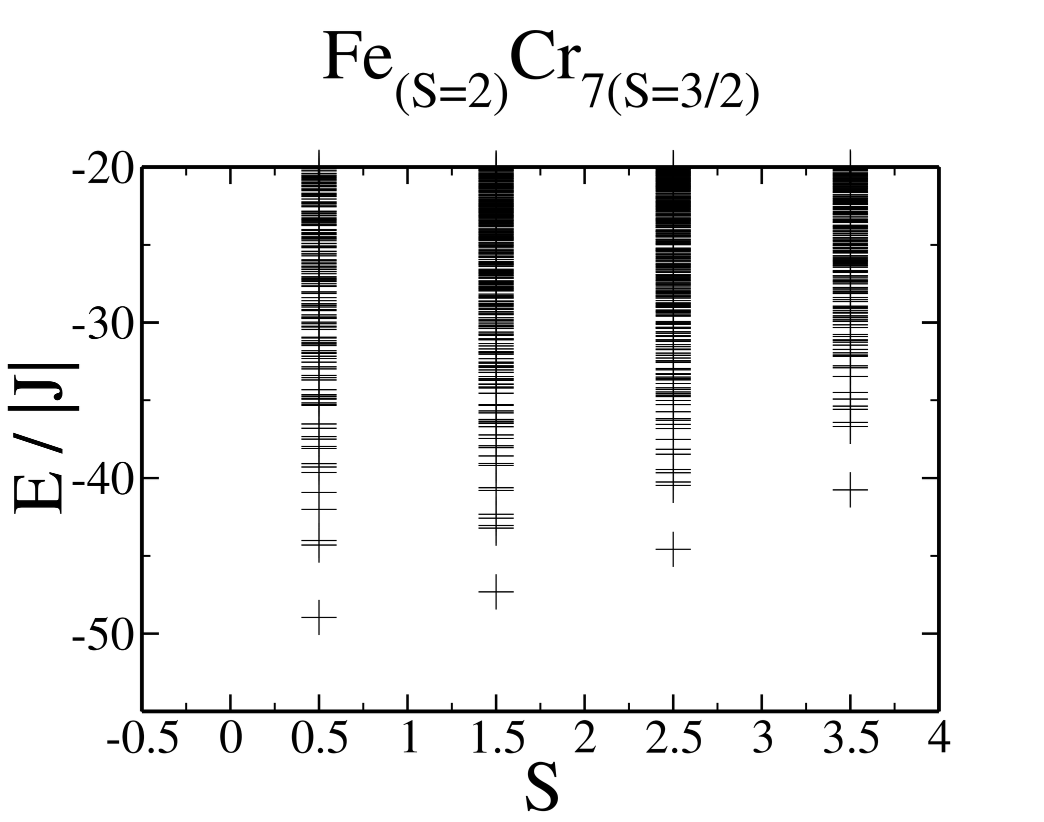


**Figure 2** Low-energy eigenvalues as a function of total spin quantum number S for a Fe-$Cr_7$ ring described by the Heisenberg spin Hamiltonian. The spectrum shows that the ground state is in $S = 1/2$.

Our calculations show that the ground state has a total spin $S = 1/2$, therefore this ground state is degenerate with M= $\pm 1/2$.

## Low-field susceptibility

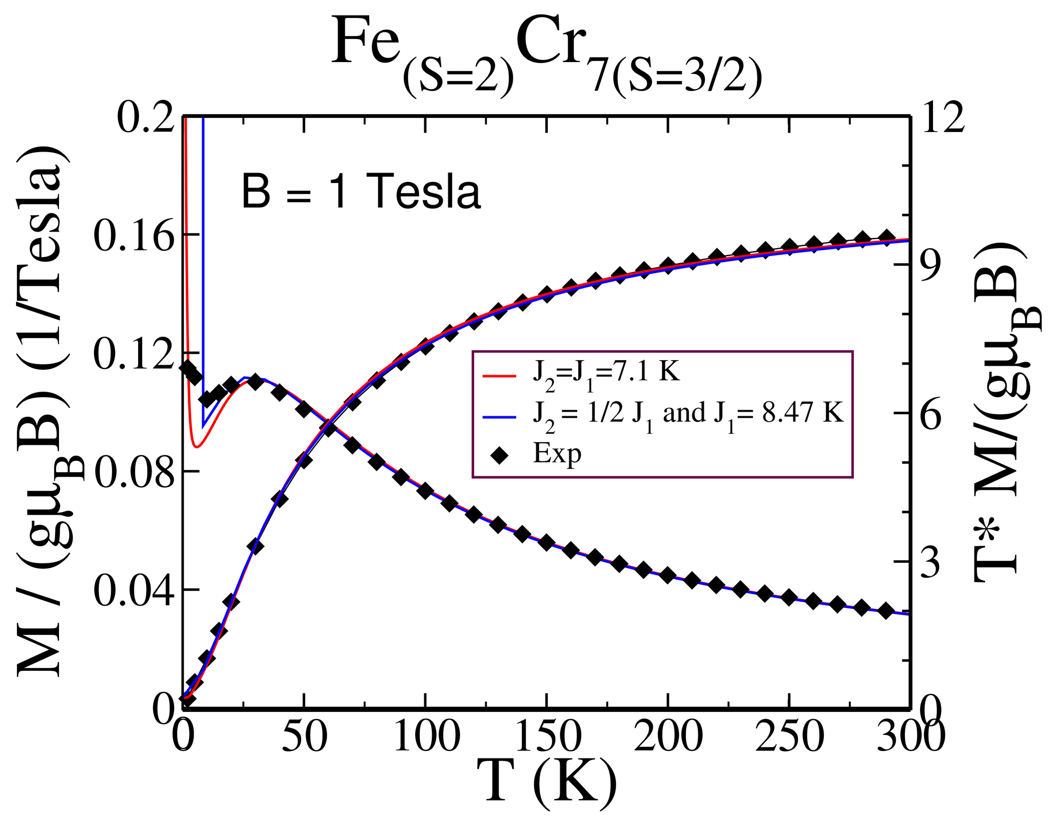


**Figure 3** Variation of T*M/B and M/B versus temperature T for the antiferromagnetic ring system of $FeCr_7$: The experimental data given by black squares are determined using a Quantum Design MPMS SQUID magnetometer. The theoretical fit assuming an isotropic Heisenberg model is given by a blue and red solid line for $J1(Cr-Cr) = J2(Fe-Cr) = 7.1$ K and $J2(Fe-Cr) = 1/2J1(Cr-Cr)$ with $J1 = 8.47$ K respectvly. $B = 1$ Tesla and $g = 2$.

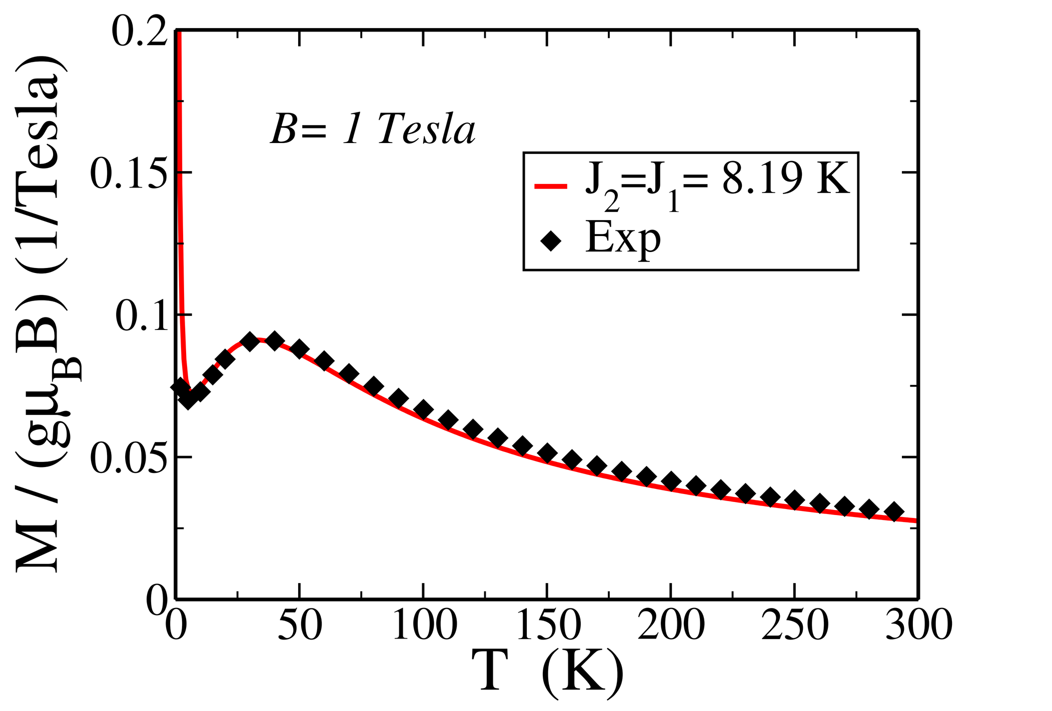


**Figure 4** Low-field (B=1 Tesla) susceptibility as a function of temperature T for a $NiCr_7$ ring: The experimentally measured data are given by black squares whereas the red solid curve shows the result of the fit with $J = 8.19$ K using an isotropic Heisenberg model and $g = 2$.

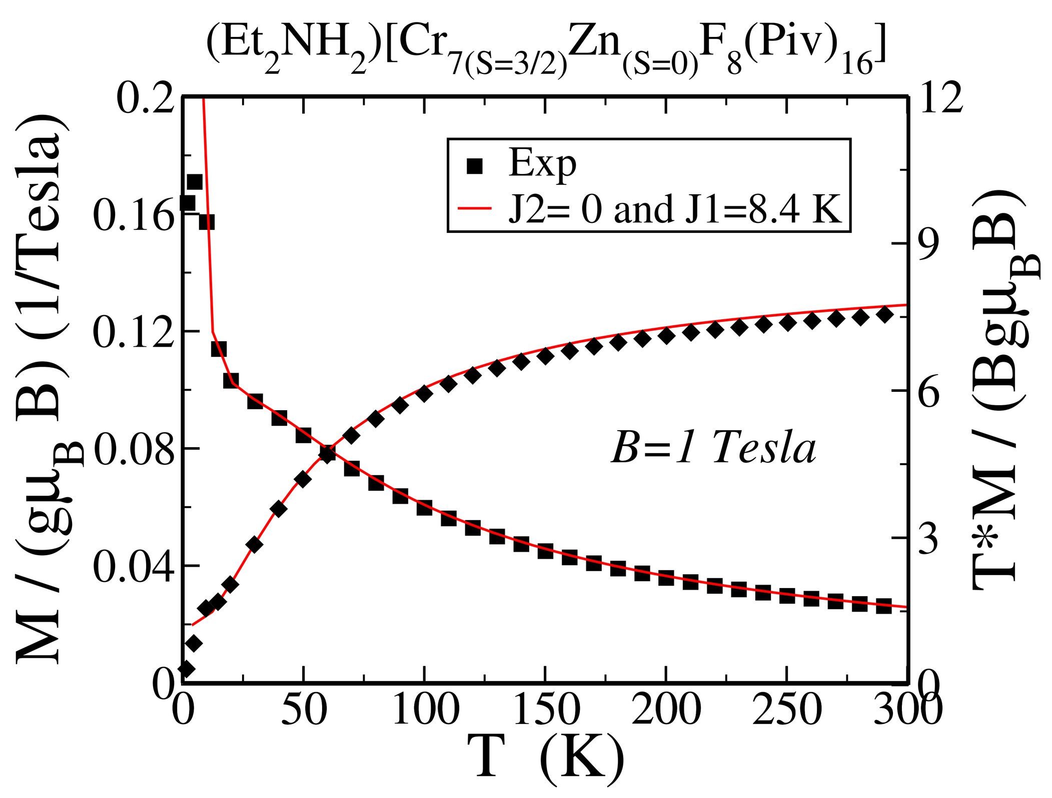


**Figure 5** Plot of T*M/B and M/B versus T for the antiferromagnetic ring system of $ZnCr_7$: The experimental data are given by black squares. The theoretical fit by an isotropic Heisenberg model is given by a solid line for $J = 8.4$ K and $g = 2$ with the applied magnetic field $B = 1$ Tesla.

*The experimental data was supplied by Prof. E. Rentschler from University of Mainz (Germany).*

## Discussion

The magnetic behavior (susceptibility measurements) of each wheels is broadly similar and suggest an antiferromagnetic exchange interaction between the metal ions, and the energy spectrum shows that the ground state is degenerate.

- **Fe-$Cr_7$**: The complete compound is $[\{nBu_2NH_2\}\{\mathbf{Cr_7Fe}F_8(O_2CCMe_3)_{16}\}]$. Mössbauer spectroscopy indicates that only $Fe^{II}$ specis are present[a]. The spectrum of this system is represented in Figure 2. The plot of T*M/B shows a value close to a zero at low temperatures and a maximum in plot M/B versus T at 30 K (Figure 3). This means that there is a weak antiferromagnetic interaction between the metal ions of this system. The theoretical fit curve using an isotropic Heisenberg model is given by a red and blue solid line for $J1(Cr-Cr) = J2(Fe-Cr) = 7.1$ K and $J2(Fe-Cr) = 1/2J1(Cr-Cr)$ with $J1 = 8.47$ K, respectvly, for the low magnetic field $B = 1$ Tesla and the value of $g = 2$ (estimated by means EPR spectra and vector coupling approach)[a b]. Furthermore the fit with $J1 = J2$ seems to be better than with $J2 = 1/2J1$, therefore substituting chromium ($Cr^{III}$) by iron ($Fe^{II}$) has not much effect on the compound. It should be mentioned that the value of the exchange interaction in this compound is close to the value obtained in tetragonal crystal form of $[Cr_8F_8Piv_{16}]$, $(J = 1.5\, meV = 17.4\, K) * 1/2 = 8.7$ K [cd].

- **Ni-$Cr_7$**: The original compounds is $[\{Me_2NH_2\}\{\mathbf{Cr_7Ni}F_8(O_2CCMe_3)_{16}\}]$. In fact, the M/B versus T curves (Figure 4), indicates a dominating antiferromagnetic interaction between the $Cr-Cr$ and $Cr-Ni$ ions and $S = 1/2$ ground state. The theoretical fit curve for $g = 2$ gives $J2 = J1 = 8.19$ K.

- **Zn-$Cr_7$**: The Zn ion in this system is not magnetic, therefore the ring simulated in this case contains seven spins and there is no interaction between $Cr-Zn$, $J2 = 0$. The experimental data is fitted with the theoretical curve for $J1 = 8.4$ K (Figure 5). The plot of T*M/B versus T curves shows a value close to a zero at low temperatures.

[a] Finn K. Larsen, *et al.* Angew. Chem. Int. Ed. 2003, 42, No 1
[b] A. Bencini and D. Gatteschi *EPR of exchange Coupled Systems, Springer*, Berlin (1989)
[c] Joris van Slageren, *et al.* Chem. Eur. J **2002**, 8 No.1
[d] S. Carretta, *et al.* Phy. Rev. **B67**094405 (2003)

## Summary

In conclusion we have presented the exchange parameters of molecular magnetic rings of heterometallic {$Cr_7M$} wheels where M=Fe, Ni and Zn with spin $S = 2$, 1 and 0 respectivly. In order to study these different systems we have used a mirror symmetry operation around the doping ion, we have evaluated the different energy spectra and used these energy eigenvalues to adjust the curves of T*M/B and M/B versus T with the experiment ally measured data. We will further develop the work to evaluate the spin correlation function to study the dynamics of excess spin and we compare our results with NMR spectra mesurement.