Proton spin-lattice relaxation time T_1 in Heterometallic $\{Cr_7M\}$ Wheels

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Introduction

At low temperatures molecular magnets act as individual quantum nanomagnets and can display superparamagnetic phenomena like bistability and macroscopic quantum tunneling. The coupling between magnetic molecular levels and the environment such as phonons or nuclear spins is a crucial issue to understand these phenomena. The measurement of the proton spin-lattice relaxation rate, T_1^{-1}, is a powerful tool to investigate the spin dynamics, the degeneracy and level crossing effects, since T_1^{-1} of the protons is a sensitive probe of the ion spin dynamics.

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magnetic rings closely related to the heterometallic $\{Cr_7M\}$ wheels, in which one of the Cr^{III} ions of Cr_8 has been replaced by a Fe or Cu ion with spin s=2 and s=1/2, respectively.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

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

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

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].

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

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

where

$$\tilde{F}^{\pm} = \sum_i (D_0(i)\tilde{S}^{\pm}(i) + D_{\mp 1}(i)\tilde{S}^{z}(i) + D_{\mp 2}(i)\tilde{S}^{\mp}(i))$$

[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.

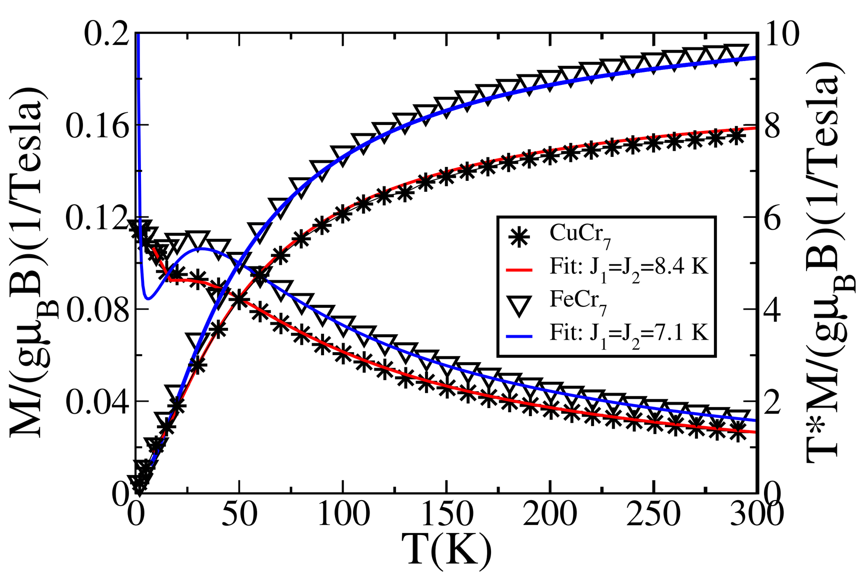

Figure 1 Variation of T*M/B and M/B versus temperature T for the anti-ferromagnetic ring system of $FeCr_7$ and $CuCr_7$: The experimental data given by black squares are determined using a Quantum Design MPMS SQUID magnetometer. The theoretical fit assuming an isotropic Heisenberg model is given by a blue and red solid line for $J1(Cr-Cr) = J2(Fe-Cr) = 7.1$ K and $J1(Cr-Cr) = J2(Cu-Cr) = 8.4$ K, for the systems $FeCr_7$ and $CuCr_7$, respectively. $B = 1$ Tesla and $g = 2$.

The complete chemical formulae of $FeCr_7$ and $CuCr_7$ are $[\{nBu_2NH_2\}\{\mathbf{Cr_7FeF_8}(O_2CCMe_3)_{16}\}]$ and $(Et_2NH_2)[Cr_7CuF_8Piv_16]$, respectively. Mössbauer spectroscopy indicates that only Fe^{II} species are present in the first compound[a]. The spectrum of Cr_8 is represented in Figure 2. The plot of T*M/B shows a value close to zero at low temperatures and a maximum in the plot of M/B vs. T at 30 K (Figure 1). This means that there is a weak anti-ferromagnetic interaction between the metal ions of the two systems. 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 $J2(Cr-Cr) = J1(Cu-Cr) = 8.4$ K, respectively, for the low magnetic field $B = 1$ Tesla and the value of $g = 2$ (estimated by means of EPR spectra and vector coupling approach)[a b]. It should be mentioned that the value of the exchange interaction in these compounds 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].

[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. B**67**094405 (2003)

Level crossing in Cr_8 rings

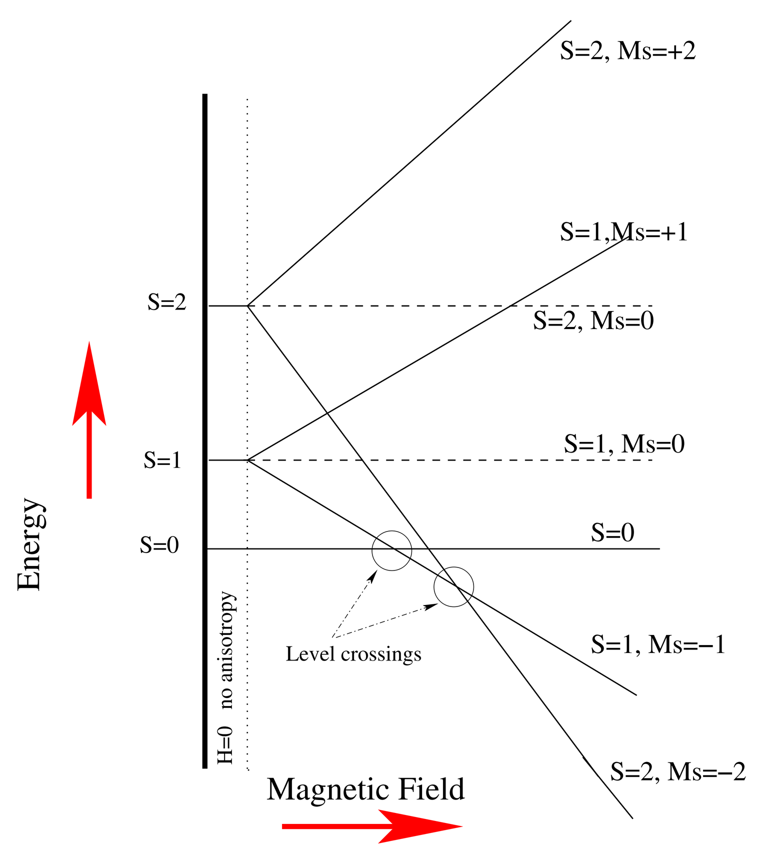

Figure 2 Energy levels vs. magnetic field for the lower energy eigenvalues for the lower three values of total spin S (0,1,2), for the AFM ring system of Cr_8. The spectrum shows the two level crossings which we try to describe in this work through proton spin-lattice relaxation rate.

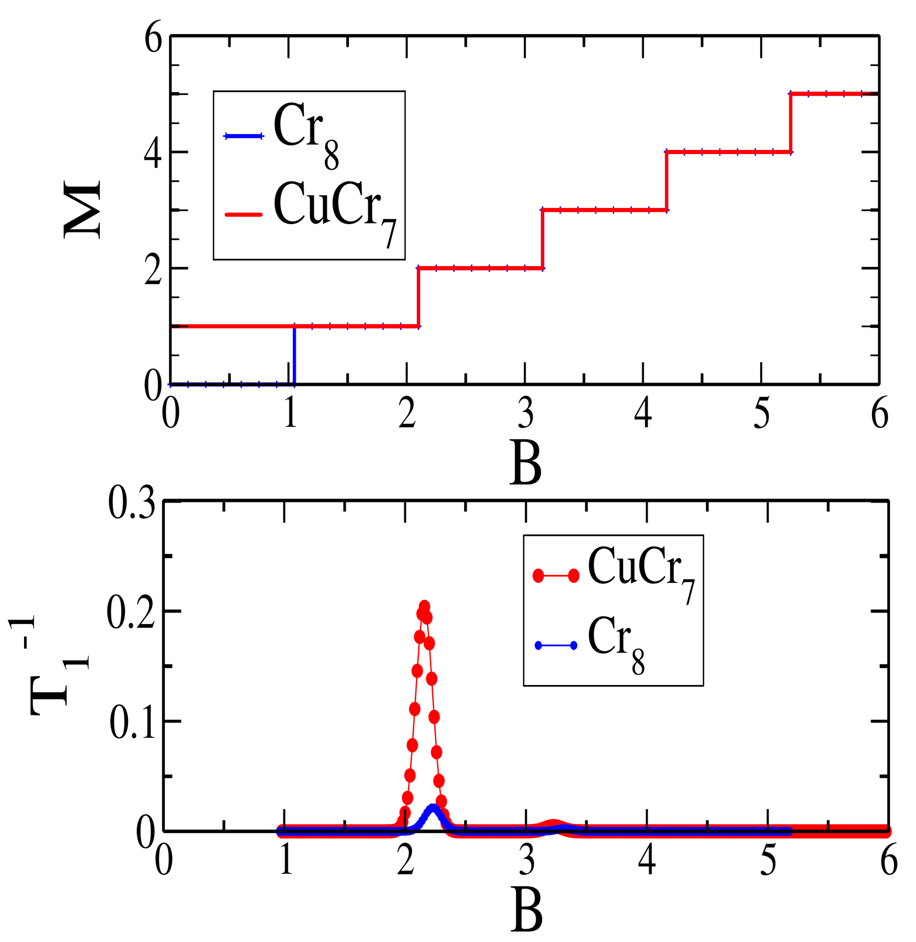

Figure 3 Magnetic field dependence of T_1^{-1} in $CuCr_7$ and Cr_8 single molecule at $T = 1.5$ K, for ($\theta = \pi/4$ and $\varphi = 0$) polar coordinates between the z-axis parallel to the applied field (B) and the nuclear spin [a].

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

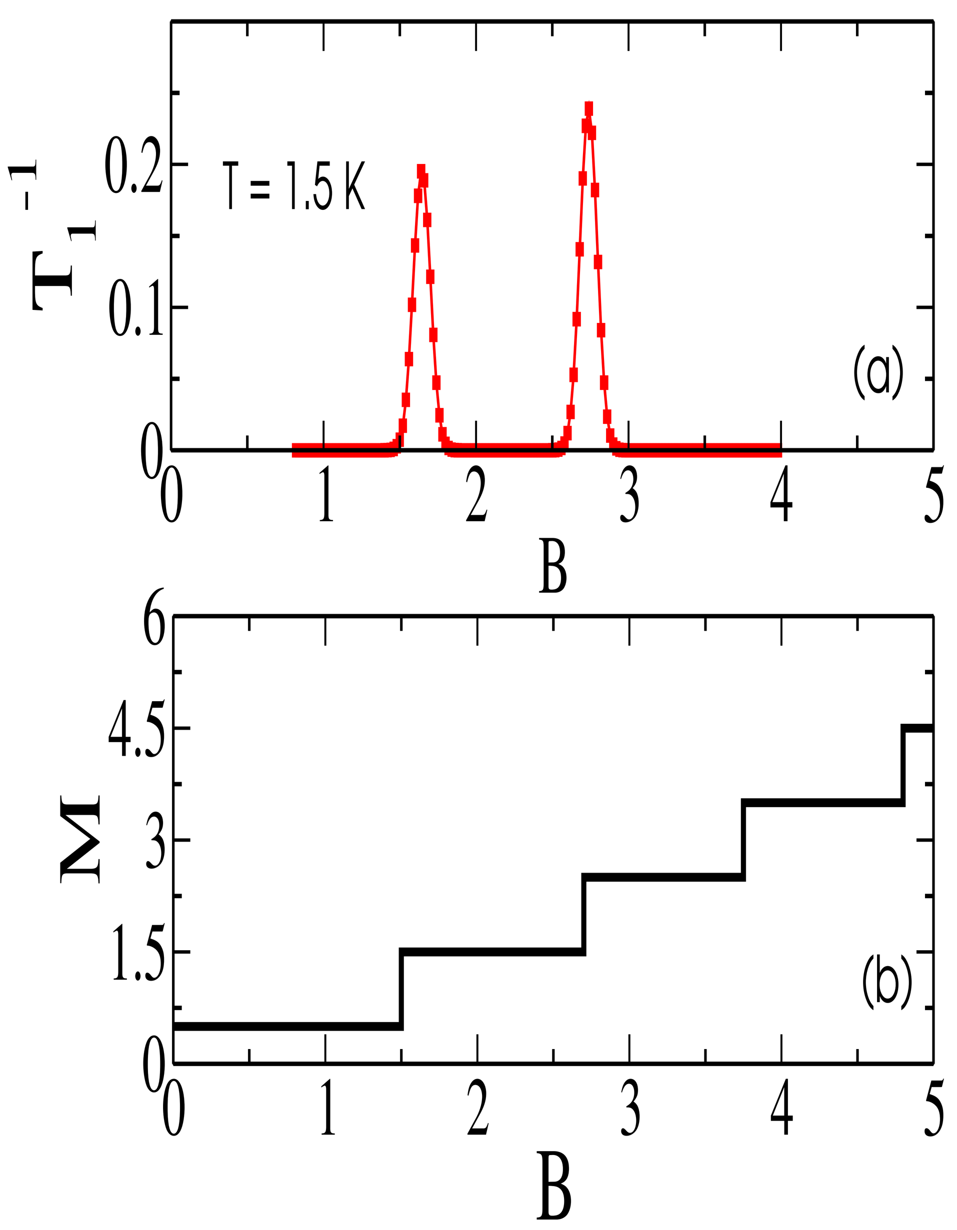

Figure 4 The proton spin-lattice relaxation rate T_1^{-1} as function of the applied magnetic field B, (according to Eq.(2)), for the anti-ferromagnetic ring system of $FeCr_7$ with Temperature $T = 1.5$ K.

Proton spin-lattice relaxation rates

The theoretical calculation of proton spin-lattice relaxation rates T_1^{-1} as a function of the magnetic field at fixed temperature T are represented in Fig. 3 and 4 for the three AFM rings Cr_8, $CuCr_7$, and $FeCr_7$, (according to Eq.(2)). In all three cases a strong enhancement of T_1^{-1} is clearly observed close to critical field values. These values correspond very closely to the fields where steps are observed in the magnetization vs B. Furthermore, the peaks observed for the compound $CuCr_7$, in which one of the Cr^{III} ions has been replaced by a Cu are heigher than the peaks of the Cr_8 ring. The calculation of T_1^{-1} was performed with the same angles $\theta = 45°$ and $\varphi = 0°$ (polar coordinates) between the the z-axis parallel to B and the nuclear spin [a]. It should be mentioned that the calculation was evaluated with the twenty low-energy levels of the three subspaces with spin quantum number S (S=0, 1 and 2) for the three anti-ferromagnetic ring systems Cr_8, $CuCr_7$ and $FeCr_7$ with (S=3/2,1/2 and 5/2 respectively).

[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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