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Theoretical estimates for proton-NMR spin-lattice relaxation rates of heterometallic spin rings

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Abstract

Heterometallic molecular chromium wheels are fascinating new magnetic materials. We reexamine the available experimental susceptibility data on MCr_7 wheels in terms of a simple isotropic Heisenberg Hamiltonian for M=Fe, Ni, Cu, and Zn and find in that $FeCr_7$ needs to be described with an iron-chromium exchange that is different from all other cases. In a second step we model the behavior of the proton spin lattice relaxation rate as a function of applied magnetic field for low temperatures as it is measured in Nuclear Magnetic Resonance (NMR) experiments. It appears that $CuCr_7$ and $NiCr_7$ show an unexpectedly reduced relaxation rate at certain level crossings.
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1. Introduction

Among magnetic molecules spin rings constitute a rich subgroup of highly symmetric species of various sizes which are comprising a large variety of paramagnetic ions [1,2,3,4]. The investigation of these regular structures led to a deeper understanding especially of antiferromagnetically coupled spin systems. One of the findings is the discovery and confirmation of rotational bands, see e.g. [5,6,7].

In accord with these investigations it was anticipated that spin rings, which host an odd number of spins or spins of different size, would show complementary quantum effects that would be interesting on their own. Odd membered rings for instance would violate the presuppositions for the theorems of Lieb, Schultz, and Mattis [8,9,6] and thus possess non-trivial ground states as well as low-lying excited states [10] with quantum numbers and degeneracies that differ from those of their bipartite, i.e. even-membered counterparts. The Néel-like local magnetization which in even-membered rings results from a superposition of the singlet ground state and the $(M = 0)$-component of the first excited triplet state [11,12] would in odd-membered rings assume the form of a topological soliton [13] that equally well could be pictured as a Möbius strip [14]. Although it is rather difficult to synthesize homometallic odd-membered rings, the prospects of interesting features due to frustration nevertheless fuel future efforts to synthesize odd rings.

In the case of spin ring systems comprising ions of different chemical elements the breakthrough was already achieved with the synthesis of heterometallic MCr_7 wheels [15], where one of the chromium ions of the original Cr_8 ring [4,16,17,18] is replaced by another element M=Mn, Fe, Co, Ni, Cu, Zn, and Cd. The possibility of a systematic study has initiated first investigations on these compounds as there are susceptibility measurements [15] as well as neutron scattering on $MnCr_7$, $ZnCr_7$, and $NiCr_7$ wheels [19].

In this article we reexamine earlier susceptibility measurements [15] by means of complete diagonalization (Sec. 2) in the framework of an isotropic Heisenberg model. Our results agree with first estimates given in Ref. [15] with the noticeable difference that we find that the exchange parameters of the iron ion to its neighboring chromium ions in the $FeCr_7$ wheel is

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rather different from the original chromium-chromium exchange whereas it remains practically unchanged for the other paramagnetic ions [15].

In a second step (Sec. 3) we investigate the principle structure of the proton spin-lattice relaxation rate T_1^{-1} as a function of the applied magnetic field strength at low temperatures. This quantity can be probed by Nuclear Magnetic Resonance (NMR). NMR has shown to be a powerful tool to investigate the local spin dynamics in magnetic molecules especially in the vicinity of level crossings [20,21,22]. The relaxation rate T_1^{-1} is expected to increase drastically whenever two levels approach each other due to possible resonant energy exchange with the surrounding protons. In contrast to this expectation it appears that $CuCr_7$ and $NiCr_7$ show an unexpectedly reduced relaxation rate at certain level crossings which should experimentally be observable.

The article closes with a summary and an outlook in Sec. 5.

2. Heisenberg Hamiltonian

The Hamilton operator of the isotropic Heisenberg model for heterometallic MCr_7 wheels is given by

$$\underset{\sim}{H} = 2\,J_1 \sum_{i=1}^{6} \underset{\sim}{s}(i)\cdot\underset{\sim}{s}(i+1) \qquad (1)$$
$$+2\,J_2\,\left(\underset{\sim}{s}(7)\cdot\underset{\sim}{s}(8)+\underset{\sim}{s}(8)\cdot\underset{\sim}{s}(1)\right)\ .$$

J_1 denotes the exchange parameter between nearest neighbor chromium ions whereas J_2 denotes the exchange parameters between the dopant and the two neighboring chromium ions. We chose $J > 0$ for antiferromagnetic interaction in this article.

Neglecting anisotropy the Hamiltonian commutes with the square $\underset{\sim}{\boldsymbol{S}}^2$ and the z-component $\underset{\sim}{S}_z$ of the total spin. In addition point group symmetries can usually be exploited. In the following cases of heterometallic MCr_7 wheels only the mirror symmetry about the dopant is used. Then for not too large subspaces all energy eigenvalues and eigenvectors can be computed.

3. Low-field susceptibility

Reexamining the available experimental susceptibility data [15] in terms of complete numerical diagonalization of Hamiltonian (1) we find the same qualitative behavior as in Ref. [15]. Depending on the spin of the dopant the resulting ground state spin S assumes the following values: $S = 1/2$ for M=Fe, $S = 1$ for M=Cu, $S = 1/2$ for M=Ni, and $S = 3/2$ for M=Zn, compare also [19].

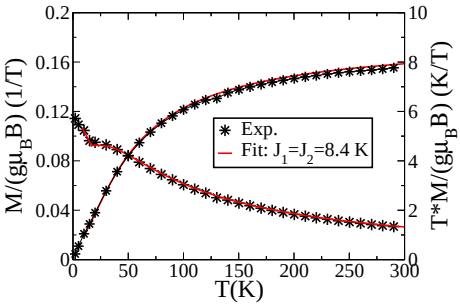

Fig. 1. Variation of $\mathcal{M}/B$ and $T\mathcal{M}/B$ as a function of temperature T for $CuCr_7$: The experimental data are given by black stars. The theoretical fit is depicted by a solid curve for $J_1 = J_2 = 8.4$ K; $B = 1$ T and $g = 2$.

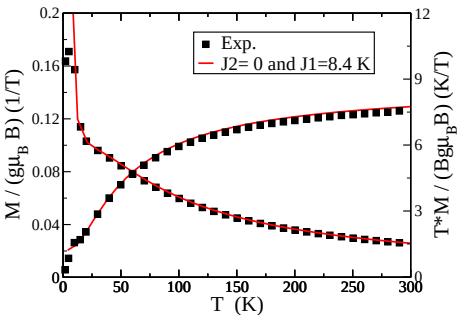

Fig. 2. Variation of $\mathcal{M}/B$ and $T\mathcal{M}/B$ as a function of temperature T for $ZnCr_7$: The experimental data are given by black squares. The theoretical fit is depicted by a solid curve for$J_1 = 8.4$ K and $J_2 = 0$ K; $B = 1$ T and $g = 2$.

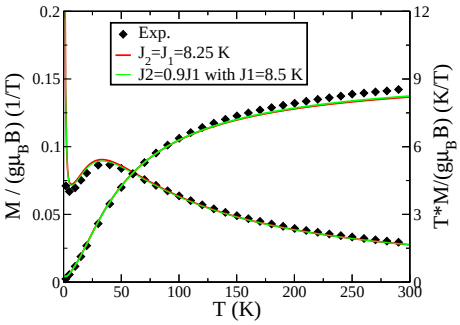

Fig. 3. Variation of $\mathcal{M}/B$ and $T\mathcal{M}/B$ as a function of temperature T for $NiCr_7$: The experimental data are presented as black diamonds. The theoretical fit for $J_1 = J_2 = 8.25$ K is given by a solid curve and for $J_1 = 8.5$ K and $J_2 = 7.425$ K by a dashed curve. $B = 1$ T and $g = 2.1$.

The susceptibility $\mathcal{M}/B$ as well as $T\mathcal{M}/B$ of $CuCr_7$, $ZnCr_7$, $NiCr_7$, and $FeCr_7$ are shown in Figures 1 - 4. For the theoretical fits a g-value of $g = 2.1$ has been used for $NiCr_7$, in all other cases $g = 2$ has been assumed.

All susceptibility curves are compatible with antiferromagnetic exchange. In the first example of $CuCr_7$, Fig. 1, a common exchange interaction explains the ex-

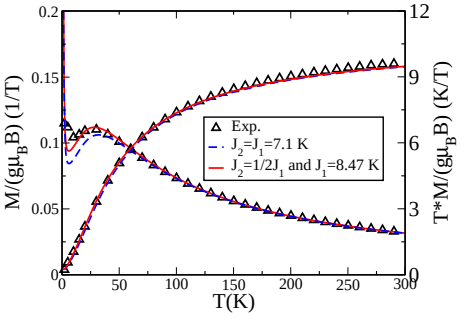

Fig. 4. Variation of $\mathcal{M}/B$ and $T\mathcal{M}/B$ as a function of temperature T for $FeCr_7$: The experimental data are depicted by black triangles. The theoretical fit for $J_1 = J_2 = 7.1$ K is given by a dashed curve and for $J_1 = 8.47$ K and $J_2 = J_1/2$ by a solid curve. $B = 1$ T and $g = 2$.

perimental data. This exchange is practically the same as in Cr_8 [4], thus unchanged in the heterometallic compound. The second example of $ZnCr_7$, Fig. 2, constitutes a spin chain since the Zn ion is diamagnetic. The original Cr-Cr interaction is not altered whereas the coupling to the Zn ion is $J_2 = 0$. The third example deals with $NiCr_7$, Fig. 3. Here we find that the experimental data can either be described by a common but slightly reduced exchange interaction or by an almost unchanged Cr-Cr interaction and a 10 % smaller Cr-Ni exchange. This has also been reported in Ref. [23], whereas Ref. [19] favors a 15 % bigger J_2. The last example of $FeCr_7$, Fig. 4, shows the biggest deviation from the assumption of a common and almost unchanged exchange parameter. Although a single exchange constant provides a reasonable fit to the experimental data [15], a better approximation – especially at low temperatures – is given if one assumes that the Cr-Cr exchange is not much altered whereas the Cr-Fe exchange is reduced to half the size of the Cr-Cr exchange.

4. Spin-lattice relaxation rates

Having determined the Heisenberg exchange parameters of several heterometallic MCr_7 wheels we investigate how the rather different structures of low-lying levels of the various rings expresses itself in proton spin-lattice relaxation rates as would be measured by Nuclear Magnetic Resonance (NMR).

Following the general theory of nuclear relaxation [24] we determine the inverse relaxation time T_1^{-1} from spin-spin correlation functions as

$$\frac{1}{T_1} = \left(1 + e^{-\frac{\hbar\omega_N}{k_B T}}\right) \frac{2\pi}{Z(T,B)} \sum_{\mu,\nu} e^{-\beta E_\mu} \langle\, \psi_\mu \,|\, \underset{\sim}{F}^{+} \,|\, \psi_\nu \,\rangle \times \langle\, \psi_\nu \,|\, \underset{\sim}{F}^{-} \,|\, \psi_\mu \,\rangle \delta_\varepsilon(\omega_N - \frac{E_\mu - E_\nu}{\hbar}) \,. \quad (2)$$

Here ω_N denotes the nuclear Lamor frequency, E_μ and E_ν are energy eigenvalues of Hamiltonian (1) augmented by a Zeeman term. The operators $\underset{\sim}{F}^{\pm}$ are given by

$$\underset{\sim}{F}^{\pm} = \sum_{i=1}^{N} \Big(D_0(i)\underset{\sim}{s}^{\pm}(i) + D_{\mp 1}(i)\underset{\sim}{s}^{z}(i) + D_{\mp 2}(i)\underset{\sim}{s}^{\mp}(i) \Big) \,, \quad (3)$$

where $D_0(i) = \alpha_i(3\cos\theta_i - 1)$, $D_{\pm 1}(i) = \alpha_i \sin\theta_i \cos\theta_i \exp(\mp i\varphi_i)$, $D_{\mp 2} = 1/2\alpha_i \sin^2\alpha_i \exp(\mp 2i\varphi_i)$ are the usual geometrical factors of the dipolar interaction, $\alpha_i = 3\gamma_N\gamma_S/(2r_i^3)$. θ_i and φ_i are the polar coordinates of the vector $\boldsymbol{r}$ describing the relative positions of the two spins. In the following we assume an isotropic case with φ=0 and α_i=1. γ_S and γ_N are the gyromagnetic ratios of the electronic and nuclear spins, respectively.

The spin-lattice relaxation is a resonant process [24] which ideally should only occur if the transition energy $E_\mu - E_\nu$ in the spin system matches the nuclear Lamor frequency. Nevertheless, the interaction of the whole system with its surrounding broadens levels. In addition the experimental resolution is limited. We therefore allow transitions which deviate up to ε from strict energy conservation. This is taken care of by a Gaussian distribution function $\delta_\varepsilon(\omega_N - \frac{E_\mu - E_\nu}{\hbar})$. This function could in principle depend both on temperature and on applied field [22,25]. We will neglect such possible dependencies and use the same function with $\varepsilon = 0.2$ K for all calculations. The interested reader is referred to Refs. [22,25], where possible temperature and field dependencies are discussed.

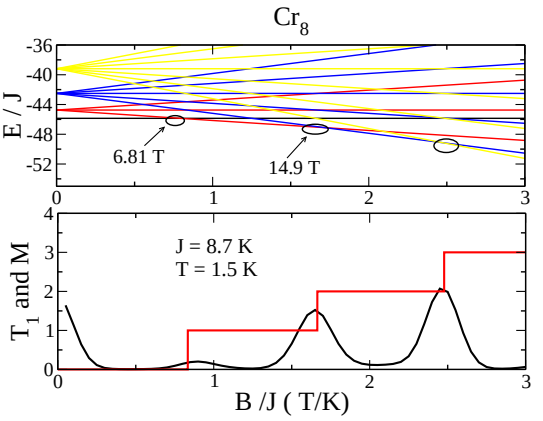

Fig. 5. Top panel: Zeeman splitting of the low-lying levels of Cr_8. The crossing fields are highlighted and the values of the two lowest fields given. Bottom panel: $(T = 0)$-magnetization (steps) and relaxation rate T_1^{-1} as function of the applied field normalized to the coupling J.

The spin-lattice relaxation of the mother substance Cr_8 has been investigated in great detail [22,25], but

predominantly as a function of temperature for certain small applied magnetic fields. In the following we discuss the behavior of the relaxation rate as a function of magnetic field for a typical small temperature of $T = 1.5$ K [21]. This function highlights the behavior of the magnetic system at low-lying (dominantly ground state) Zeeman level crossings, since there resonant cross relaxation occurs. Experimentally such data are rarely accessible due to the fact that often the level crossing fields are outside the producible field range. In the case of Cr_8 [21] and Fe_{10} [20] these data could nevertheless be measured thanks to moderate exchange constants. One important result of these measurements is that the values of the level crossing fields for even-membered Heisenberg rings follow the Landé interval rule [20], which is nowadays understood as rotational modes [5], rotation of the Néel vector [26,27] or tower of states [26,28].

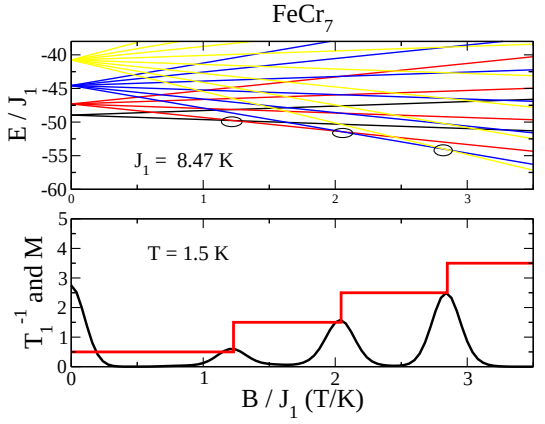

Fig. 6. Top panel: Zeeman splitting of the low-lying levels of $FeCr_7$. The crossing fields are highlighted and the values of the two lowest fields given. Bottom panel: $(T = 0)$-magnetization (steps) and relaxation rate T_1^{-1} as function of the applied field normalized to the coupling J_1.

An obvious difference between Cr_8 and the heterometallic MCr_7 wheels is given by the fact that all of the discussed wheels have ground states with non-vanishing total spin. Therefore, for $FeCr_7$ (Fig. 6), $ZnCr_7$ (Fig. 7), $CuCr_7$ (Fig. 8), and $NiCr_7$ (Fig. 9) resonant relaxation occurs already at very low magnetic fields, which expresses itself in the pronounced maximum seen around $B = 0$ in Figs. 6-9.

The second deviation from the behavior of Cr_8 consists in pronounced differences of the maximum rates at higher Zeeman level crossings in the cases of $CuCr_7$ and $NiCr_7$. Within the employed framework and the assumed approximations the relaxation at the crossing between $S = 1$ and $S = 2$ in $CuCr_7$ (Fig. 8) appears to be rather small. The same is true for the relaxation at the crossing between $S = 5/2$ and $S = 7/2$ in $NiCr_7$ (Fig. 9).

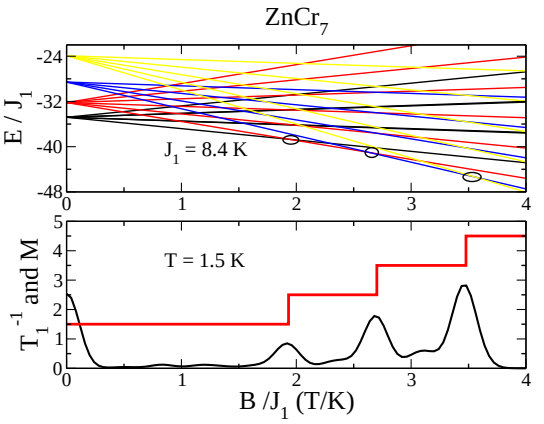

Fig. 7. Top panel: Zeeman splitting of the low-lying levels of $ZnCr_7$. The crossing fields are highlighted and the values of the two lowest fields given. Bottom panel: $(T = 0)$-magnetization (steps) and relaxation rate T_1^{-1} as function of the applied field normalized to the coupling J_1.

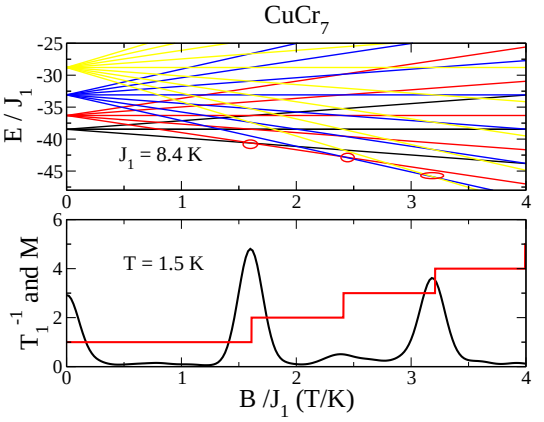

Fig. 8. Top panel: Zeeman splitting of the low-lying levels of $CuCr_7$. The crossing fields are highlighted and the values of the two lowest fields given. Bottom panel: $(T = 0)$-magnetization (steps) and relaxation rate T_1^{-1} as function of the applied field normalized to the coupling J_1.

5. Summary and outlook

In this article we have reexamined the available experimental susceptibility data [15] on heterometallic MCr_7 ring molecules in terms of a simple isotropic Heisenberg Hamiltonian for M=Fe, Ni, Cu, and Zn. Our main results are that in the case of $FeCr_7$ the iron-chromium exchange is different from the chromium-chromium exchange in contrast to the other cases and that for $CuCr_7$ and $NiCr_7$ unexpectedly reduced proton spin-lattice relaxation rates T_1^{-1} occur at certain level crossings. It would be very interesting to see whether this behavior could be experimentally verified or whether the additional anisotropic terms

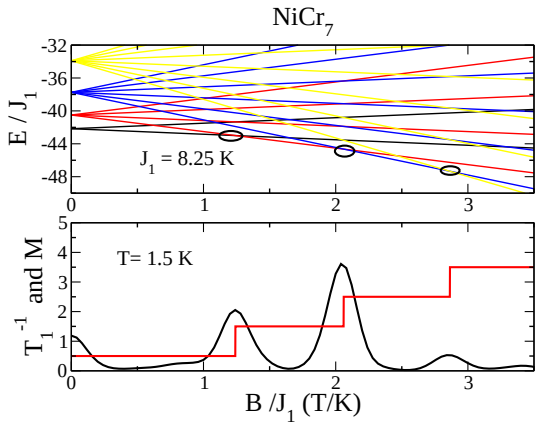

Fig. 9. Top panel: Zeeman splitting of the low-lying levels of $NiCr_7$. The crossing fields are highlighted and the values of the two lowest fields given. Bottom panel: $(T = 0)$-magnetization (steps) and relaxation rate T_1^{-1} as function of the applied field normalized to the coupling J_1.

in the Hamiltonian [4,16,17,15,19] alter the picture completely.

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