High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality

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The Bielefeld conspiracy

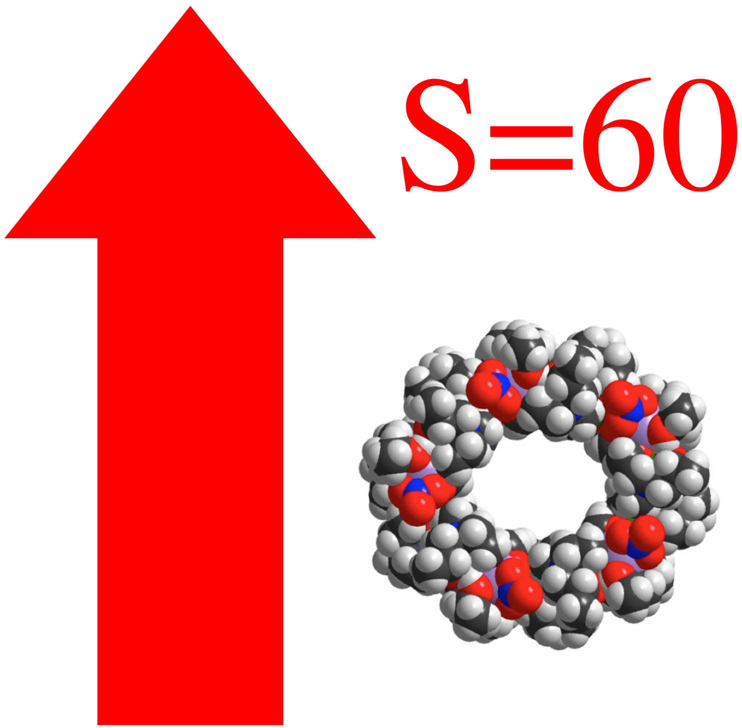
The story goes that the city of **BIELEFELD** in the German state of North Rhine-Westphalia **DOES NOT** actually **EXIST**. Rather, its existence is merely propagated by an entity known only as THEM, which has conspired with the authorities to create the illusion of the city's existence.

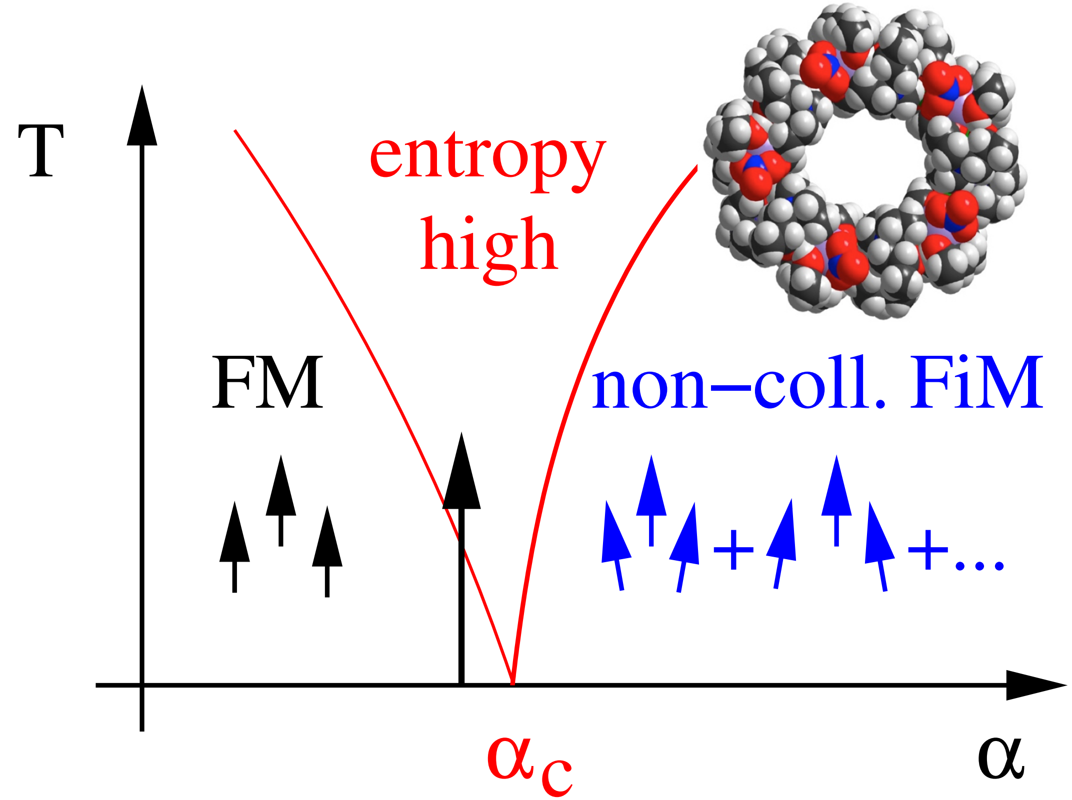
The origins of and reasons for this conspiracy are not a part of the original theory. Speculated originators jokingly include the CIA, Mossad, or aliens who use Bielefeld University as a disguise for their spaceship.

Do you know anybody from Bielefeld?

https://en.wikipedia.org/wiki/Bielefeld_Conspiracy

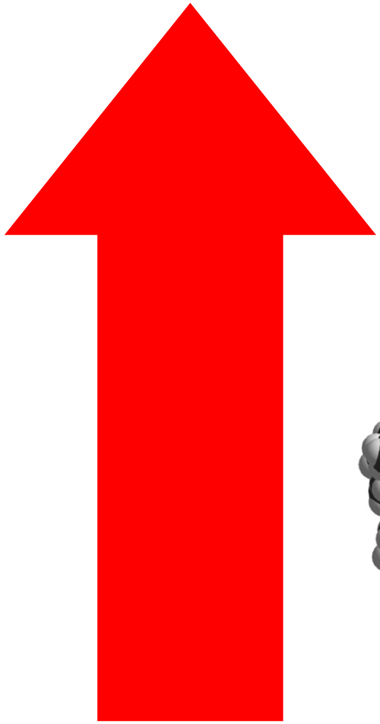
Gd$_{10}$Fe$_{10}$ – summary



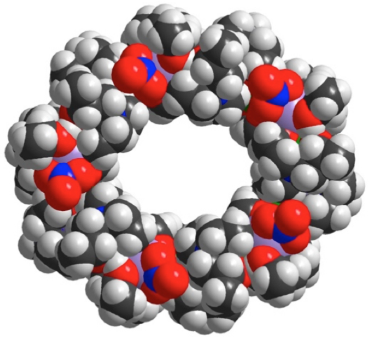


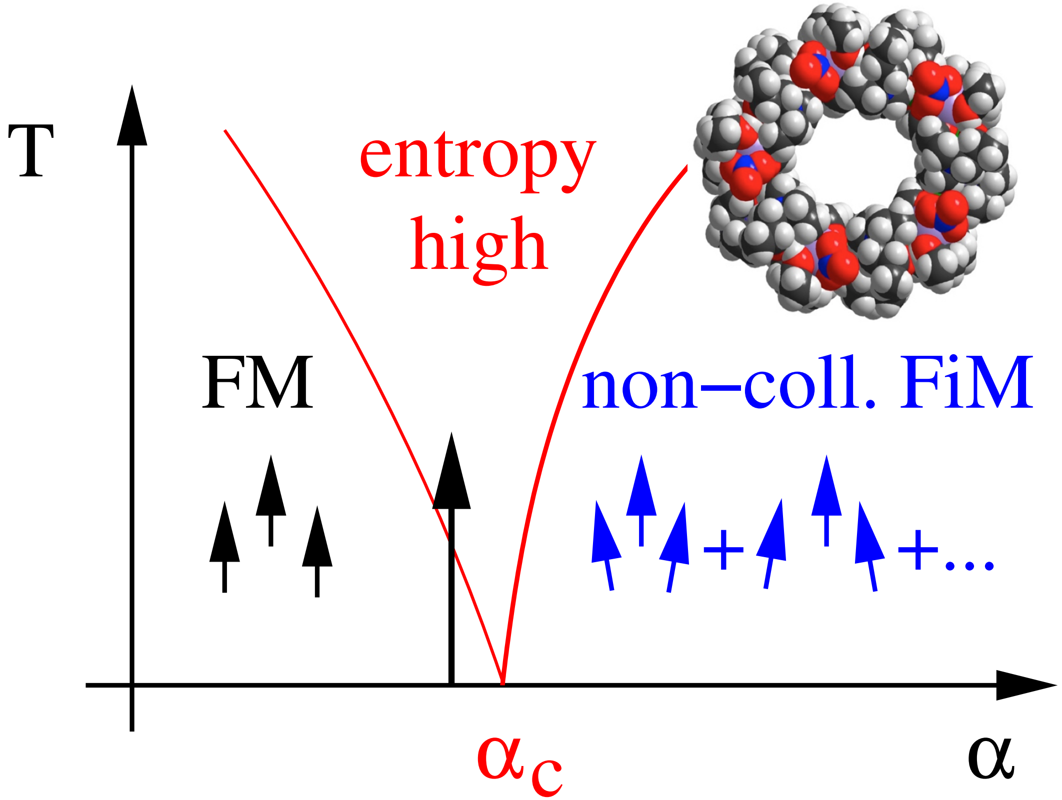
A. Baniodeh, N. Magnani, Y. Lan, G. Buth, C.E. Anson, J. Richter, M. Affronte, J. Schnack, A.K. Powell,
High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality,
npj Quantum Materials **3**, 10 (2018)

$Gd_{10}Fe_{10}$ – summary



S=60

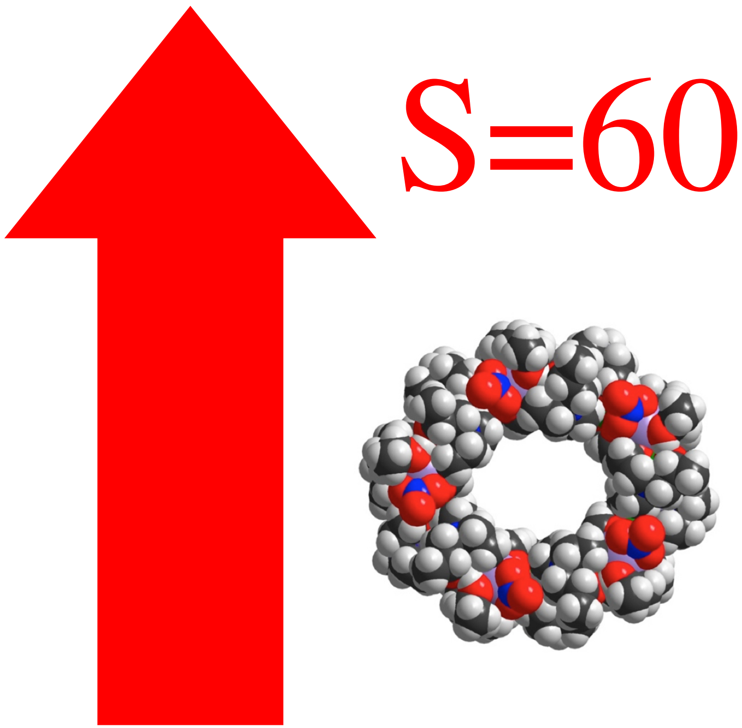


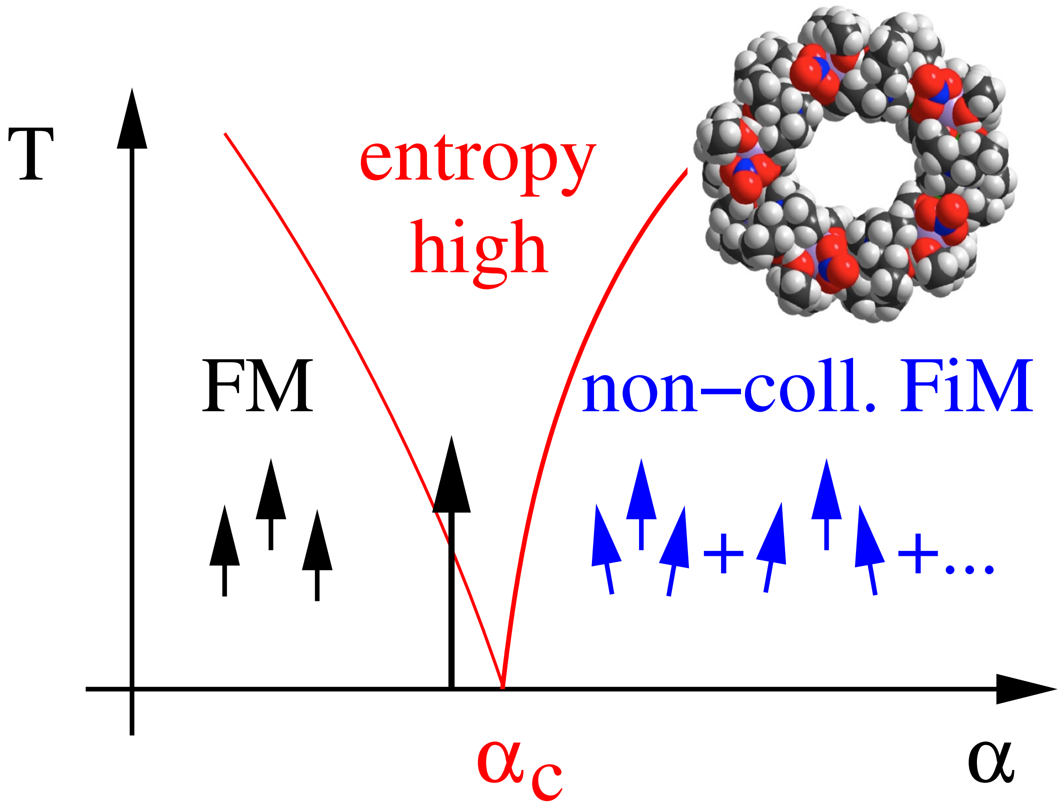


How do we know?

A. Baniodeh *et al., npj Quantum Materials* ***3****, 10 (2018)*

$Gd_{10}Fe_{10}$ – summary

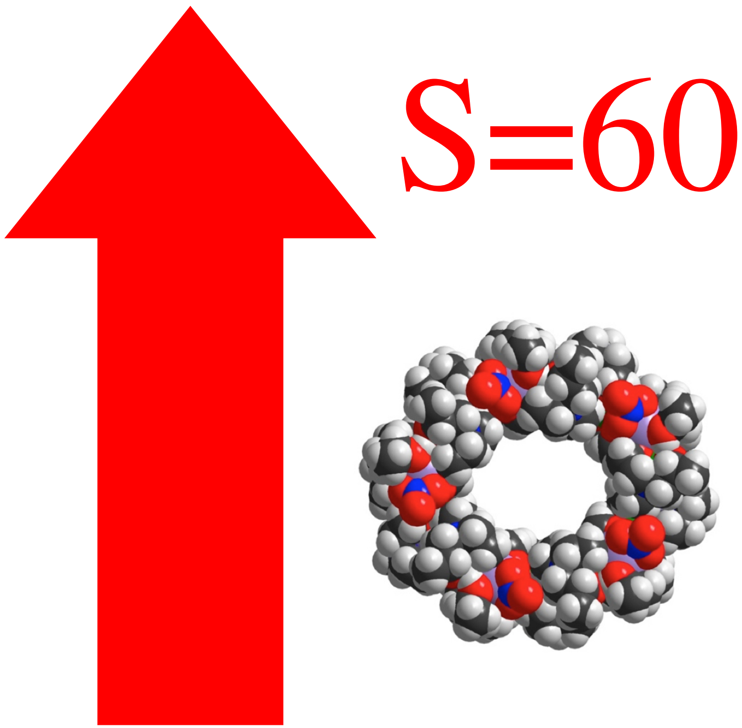


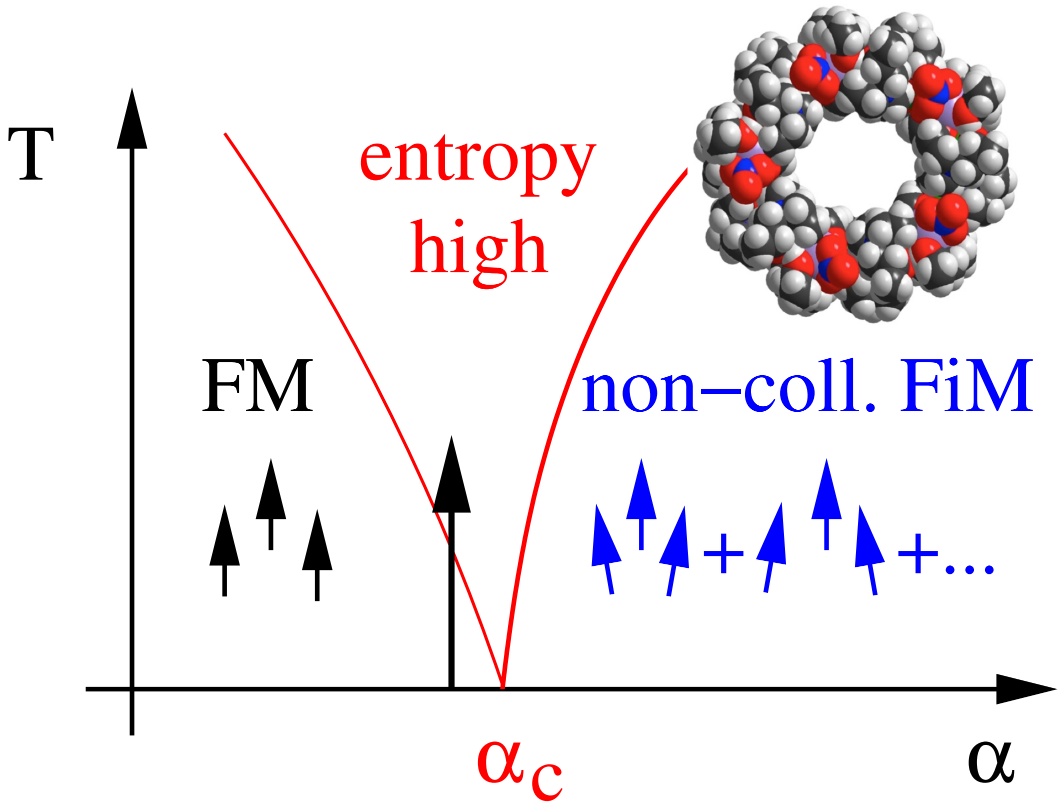


How do we know? What is a QPT?

A. Baniodeh *et al.*, *npj Quantum Materials* ***3****, 10 (2018)*

$Gd_{10}Fe_{10}$ – summary





How do we know?

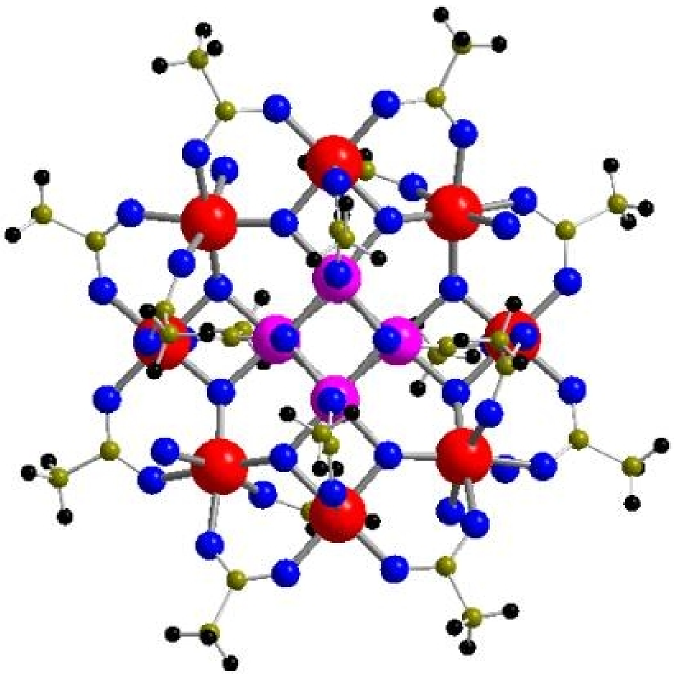
What is a QPT?

In $Gd_{10}Fe_{10}$?

A. Baniodeh *et al.*, *npj Quantum Materials* ***3****, 10 (2018)*

Short Introduction:
Beauty of Magnetic Molecules

The beauty of magnetic molecules I

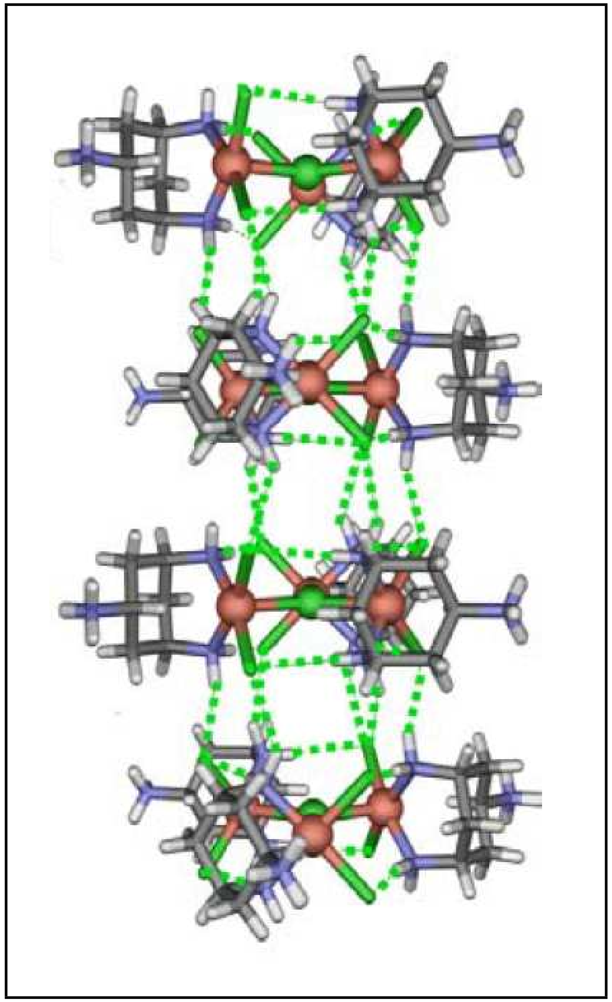


Mn_{12}

- Inorganic or organic macro molecules, e.g. polyoxometalates, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;
- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- Single spin quantum number $1/2 \leq s \leq 7/2$;
- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

Magnetism goes Nano, Ed. Stefan Blügel, Thomas Brückel, and Claus M. Schneider, FZ Jülich, Institute of Solid State Research, Lecture Notes **36** Jülich 2005

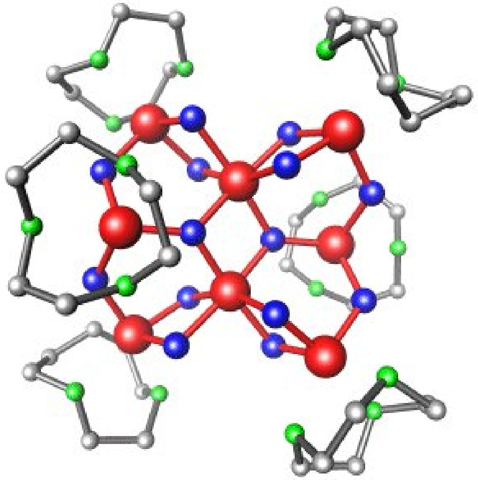
The beauty of magnetic molecules II

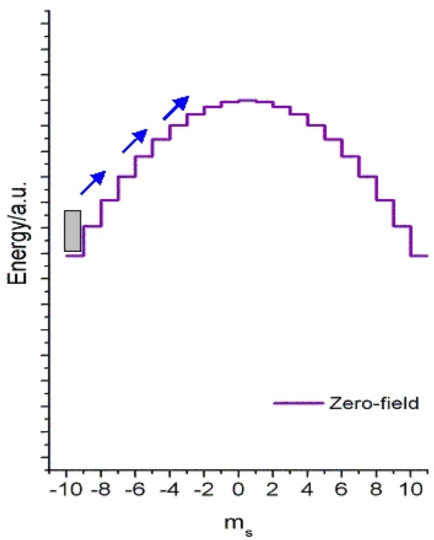


- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, ...);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures of interlinked magnetic molecules, e.g. triangular Cu chain:

  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

The beauty of magnetic molecules III





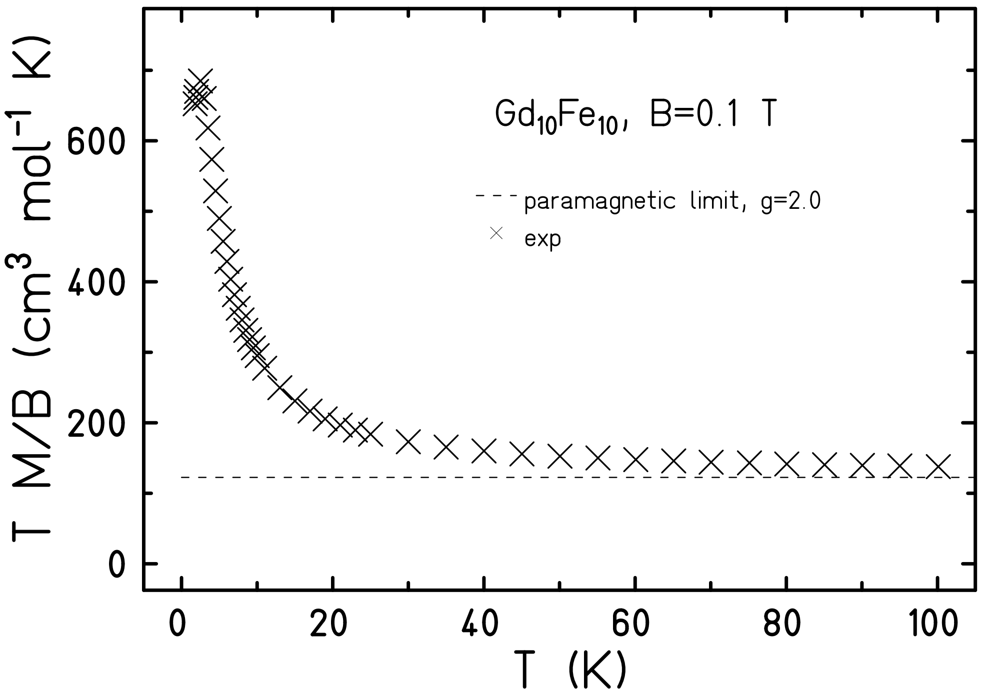
- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;
- Example: $S = 10$ for Mn_{12} or Fe_8;
- Anisotropy dominates approximate single-spin Hamiltonian:

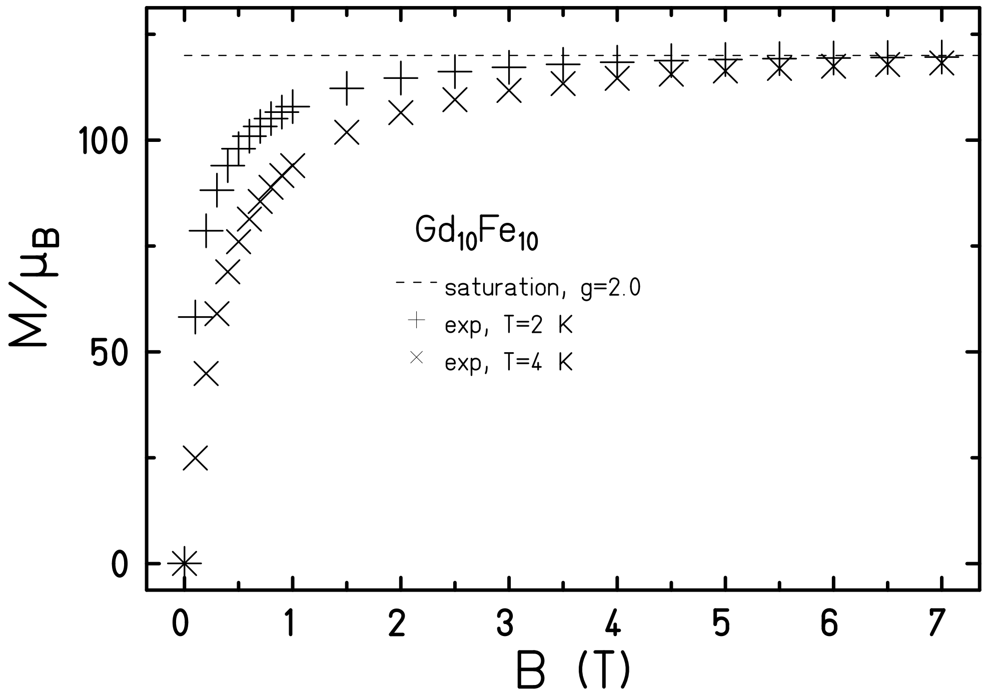
$$\underset{\sim}{H} = -D\underset{\sim}{S}_z^2 + \underset{\sim}{H}', \qquad \left[\underset{\sim}{S}_z, \underset{\sim}{H}'\right] \neq 0$$

- Single molecule shows: metastable magnetization, hysteresis, ground state magnetization tunneling, thermally and phonon assisted tunneling.
- Today's major efforts: improve stability of magnetization; investigate on surfaces.

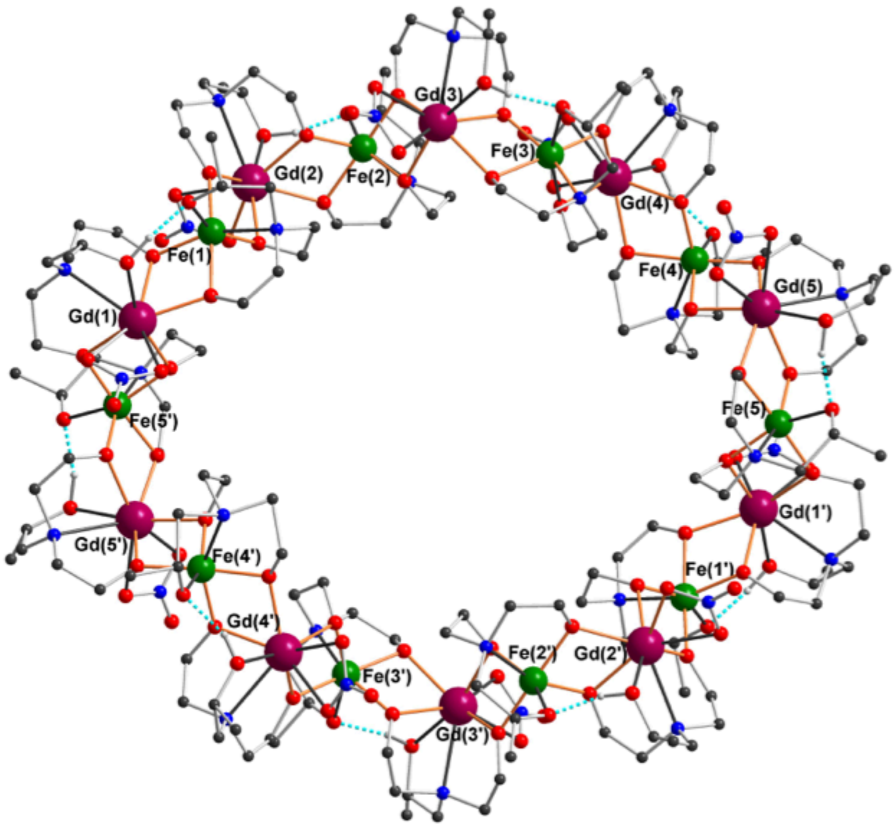
Start: experimental data

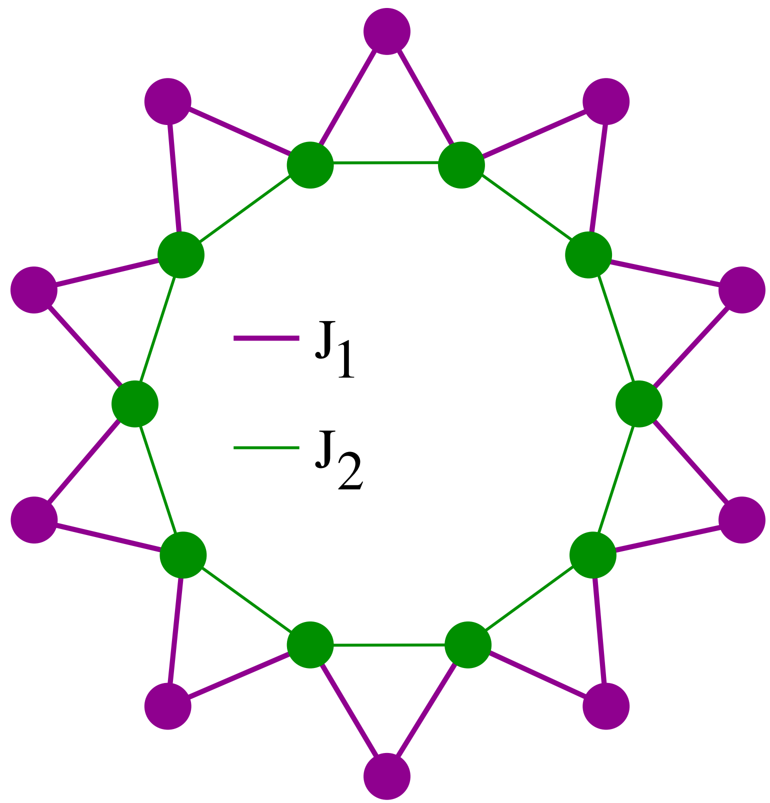
$Gd_{10}Fe_{10}$ – How to rationalize the experimental data?





$Gd_{10}Fe_{10}$ – structure = delta chain





green: Fe ($s = 5/2$), purple: Gd ($s = 7/2$)

A. Baniodeh *et al., npj Quantum Materials* ***3****, 10 (2018)*

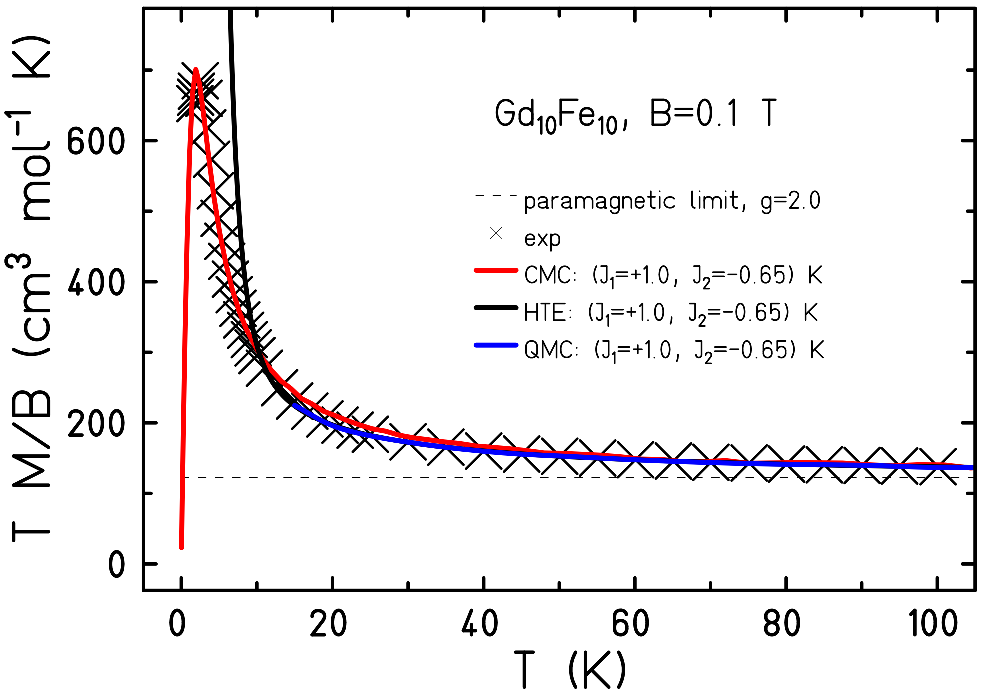
Model Hamiltonian

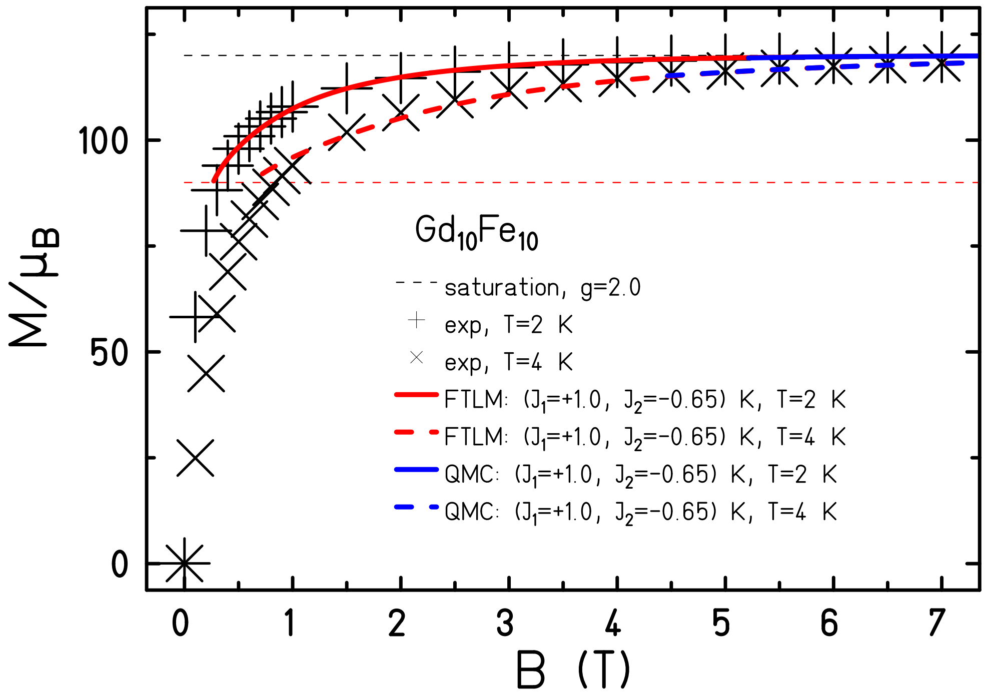
$$\underset{\sim}{H} = -2J_1 \sum_i \vec{\underset{\sim}{s}}_{\text{Gd},i} \cdot \left(\vec{\underset{\sim}{s}}_{\text{Fe},i} + \vec{\underset{\sim}{s}}_{\text{Fe},i+1} \right) -2J_2 \sum_i \vec{\underset{\sim}{s}}_{\text{Fe},i} \cdot \vec{\underset{\sim}{s}}_{\text{Fe},i+1} + g\,\mu_B\,B \sum_i \left(\underset{\sim}{s}^z_{\text{Gd},i} + \underset{\sim}{s}^z_{\text{Fe},i} \right)$$

Dimension of Hilbert space
$(2s_{\text{Gd}} + 1)^{10}(2s_{\text{Fe}} + 1)^{10} \approx 6.5 \cdot 10^{16}$

What would you do?

$Gd_{10}Fe_{10}$ – Methods





Methods: HTE, QMC, CMC, FTLM $\Rightarrow J_1 = 1.0$ K, $J_2 = -0.65$ K

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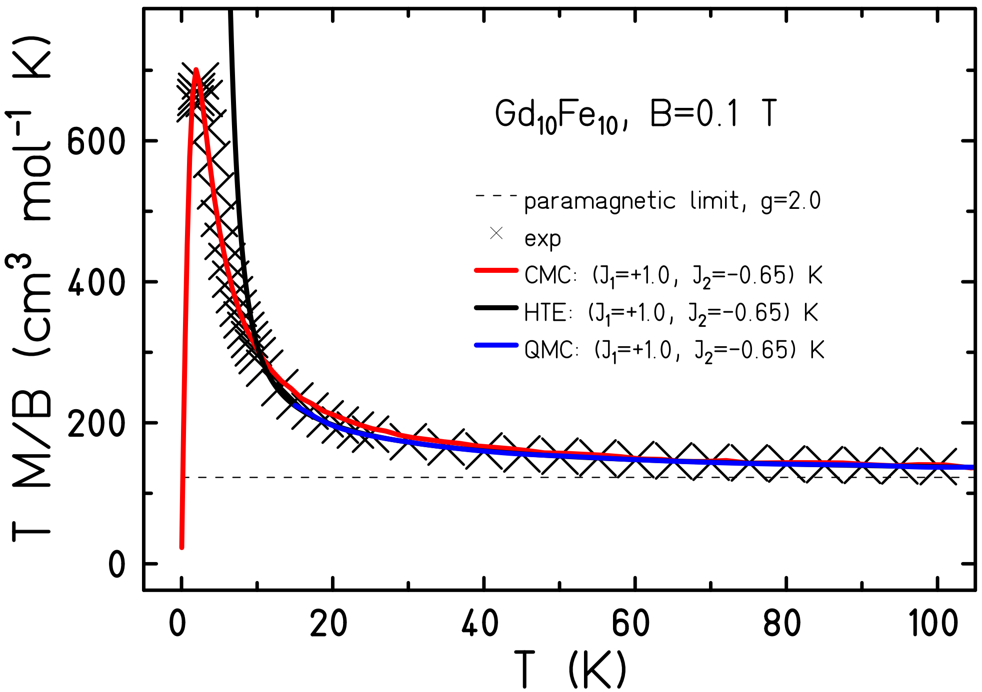
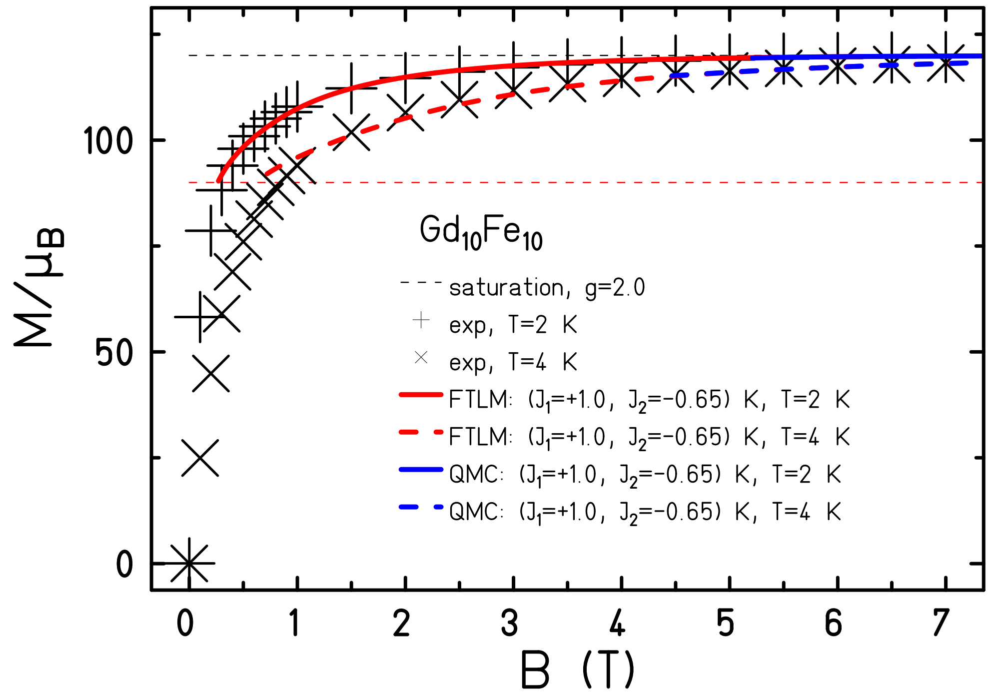
Summary: theory methods

- Complete diagonalization: exact; spectra, transitions, observables, time-evolution; Dimension of largest Hilbert space $< 10^5$.
- High Temperature Series Expansion (HTE): write thermodynamic functions as a Taylor series in β, evaluate coefficients according to your model; powers of order 10 possible.
- Finite Temperature Lanczos Method (FTLM): pseudo-spectrum, low-lying levels good, transitions, observables, time-evolution; DoH $< 10^{10}$.
- Quantum Monte Carlo (QMC): observables; bad/no convergence for competing interactions (frustration) due to negative sign problem; otherwise HUGE systems possible.
- Density Matrix Renormalization Group (DMRG): low-lying target states, correlation functions, short time evolution, maybe thermodynamics; best for 1-d; HUGE systems possible.

$Gd_{10}Fe_{10}$ – Methods





Methods: HTE, QMC, CMC, FTLM $\Rightarrow J_1 = 1.0$ K, $J_2 = -0.65$ K

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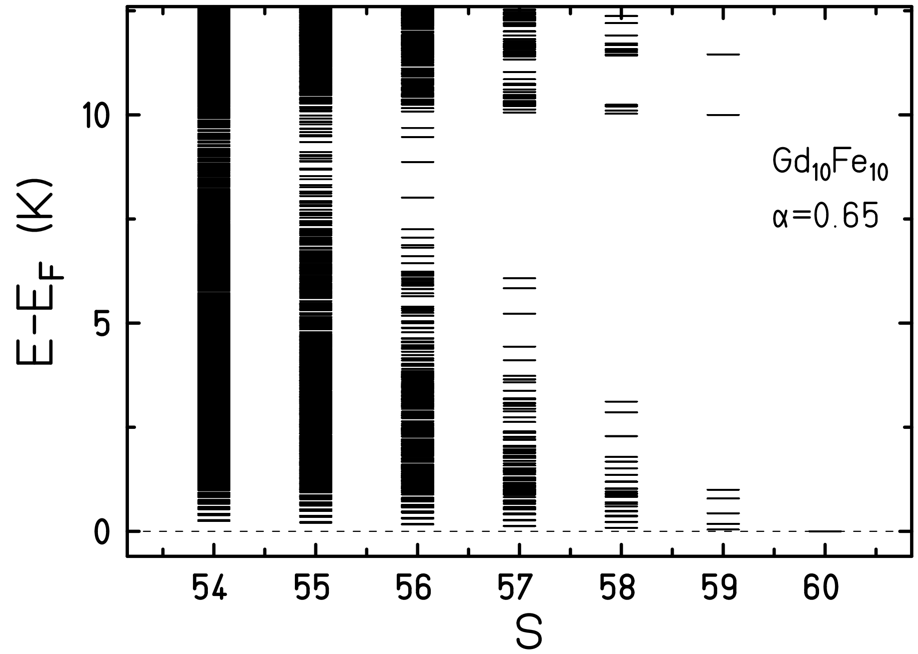
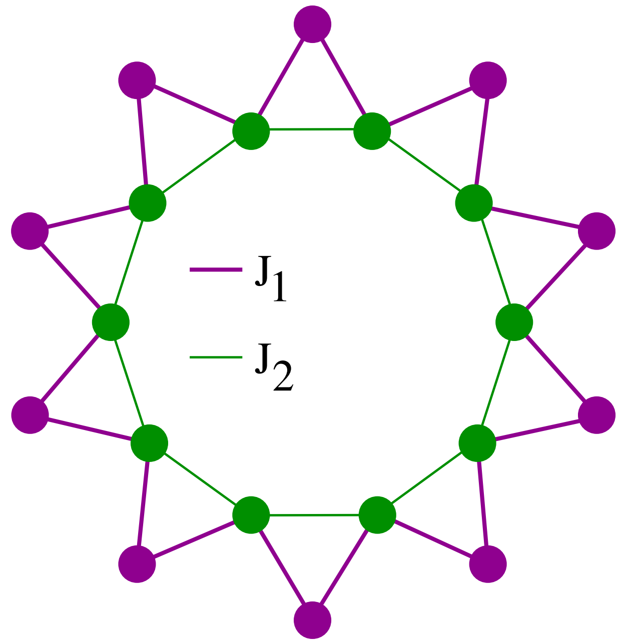
$Gd_{10}Fe_{10}$ – $S = 60$





$\Rightarrow$ $S = 60$, largest ground state spin of a molecule to date

$\Rightarrow$ $\alpha_{Gd_{10}Fe_{10}} = |J_2|/J_1 = 0.65$ What if J_2 stronger?

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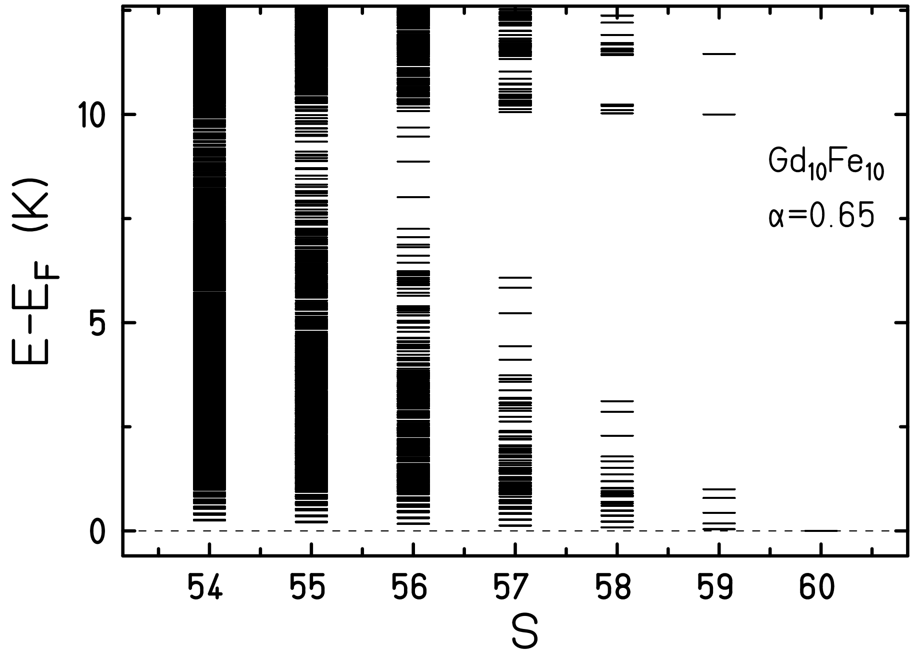
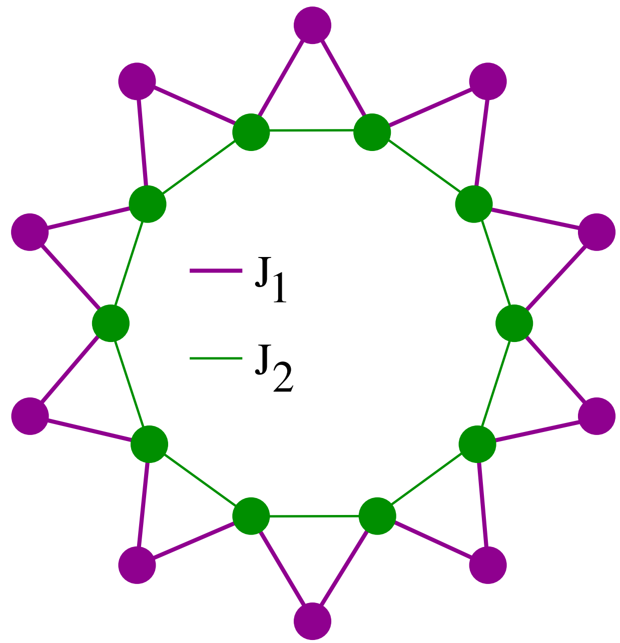
$Gd_{10}Fe_{10}$ – $S = 60$



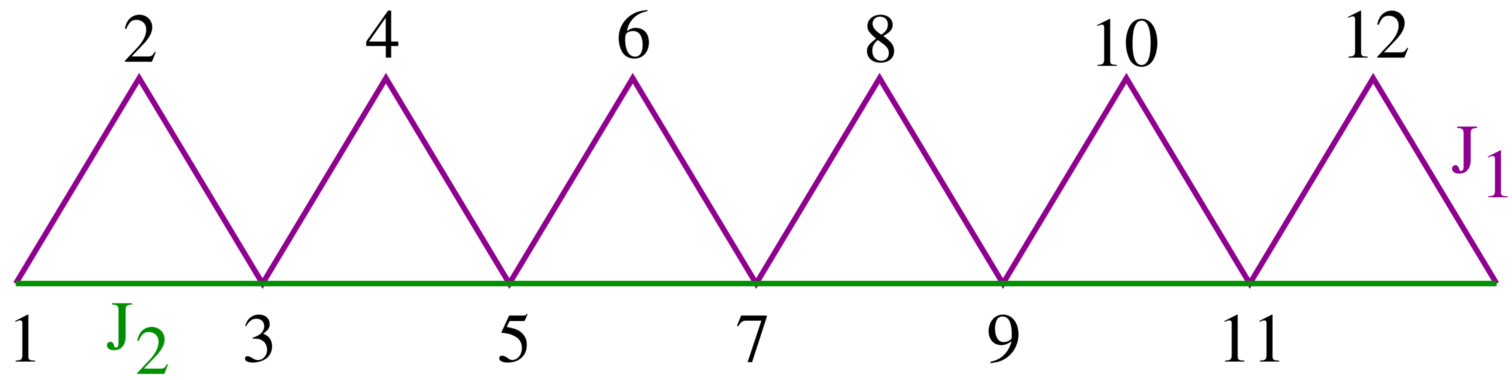


$\Rightarrow$ $S = 60$, largest ground state spin of a molecule ~~to date~~ for about one month

$\Rightarrow$ $\alpha_{Gd_{10}Fe_{10}} = |J_2|/J_1 = 0.65$ What if J_2 stronger?

Wei-Peng Chen, Jared Singleton, Lei Qin, Agustin Camon, Larry Engelhardt, Fernando Luis, Richard E. P. Winpenny, Yan-Zhen Zheng, Quantum Monte Carlo simulations of a giant $\{Ni_{21}Gd_{20}\}$ cage with a $S = 91$ spin ground state, Nature Communications **9**, 2107 (2018)

Excursus: sawtooth (delta) chain



$\Rightarrow$ special properties for $J_1 > 0$ (ferro) and $J_2 < 0$ (af) at certain α_c

e.g. $\alpha_c = |J_2|/J_1 = 0.5$ if $s_i = 1/2\ \forall i$

$\Rightarrow$ flat band of (multi-) magnon states; huge ground state degeneracy (1,2)

(1) V. Y. Krivnov, D. V. Dmitriev, S. Nishimoto, S.-L. Drechsler, and J. Richter, Phys. Rev. B **90**, 014441 (2014).
(2) D. V. Dmitriev and V. Y. Krivnov, Phys. Rev. B **92**, 184422 (2015).

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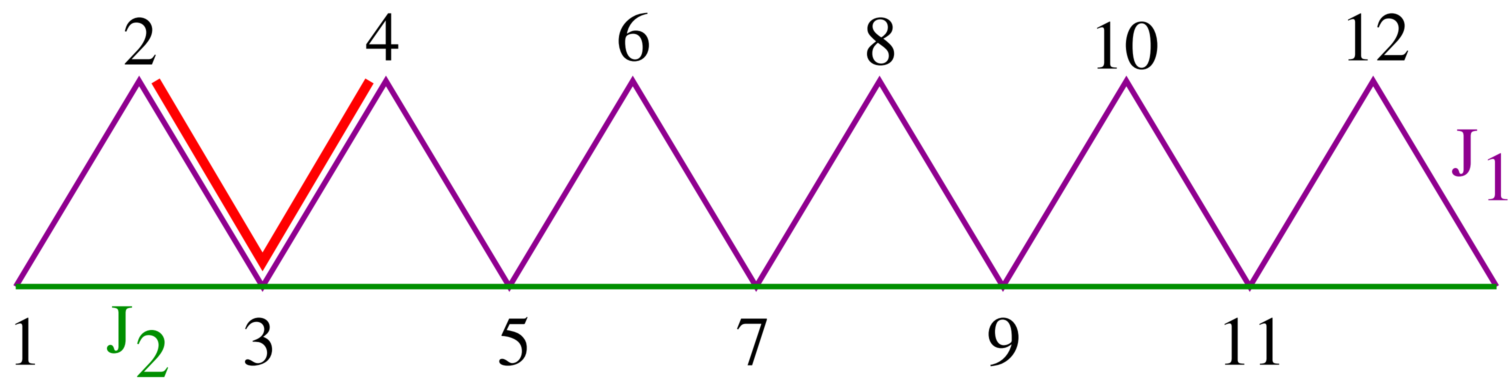


$\Rightarrow \mid F \,\rangle = \mid S = S_{\text{max}}, M = S_{\text{max}} \,\rangle$ fully polarized ferromagnetic state

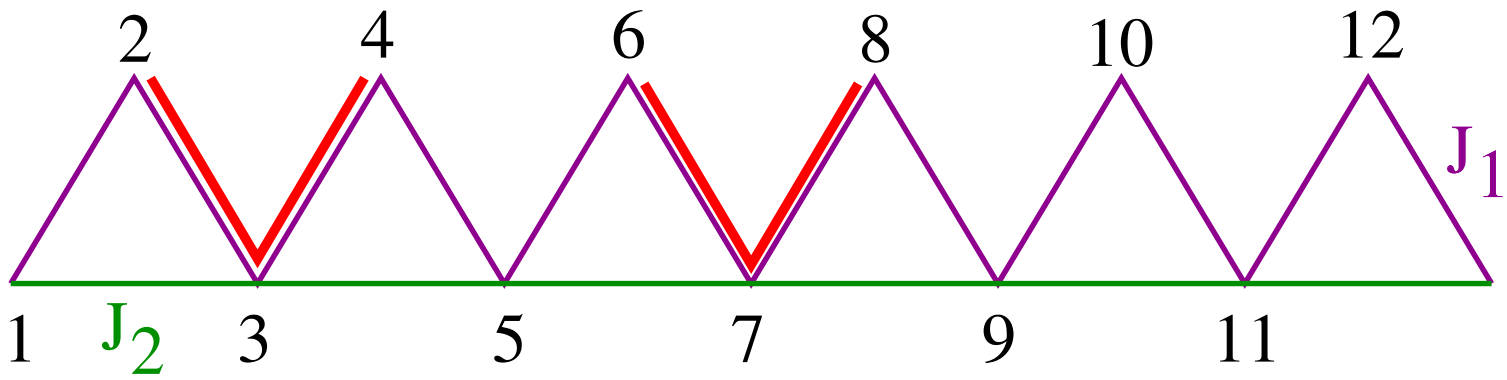
$\Rightarrow$ | 1 localized magnon at (2,3,4) $\rangle = (\underset{\sim}{s}_2^- + \underset{\sim}{s}_4^- + 2\underset{\sim}{s}_3^-) \mid F \,\rangle$;

$E = E_F, M = S_{\text{max}} - 1$

$\Rightarrow$ Can be everywhere. Flat band in one-magnon space. Degenerate with $\mid F \,\rangle$.

(1) V. Y. Krivnov, D. V. Dmitriev, S. Nishimoto, S.-L. Drechsler, and J. Richter, Phys. Rev. B **90**, 014441 (2014).
(2) D. V. Dmitriev and V. Y. Krivnov, Phys. Rev. B **92**, 184422 (2015).
(3) J. Schnack, Contemporary Physics (2019), doi:10.1080/00107514.2019.1615716

Excursus: sawtooth (delta) chain

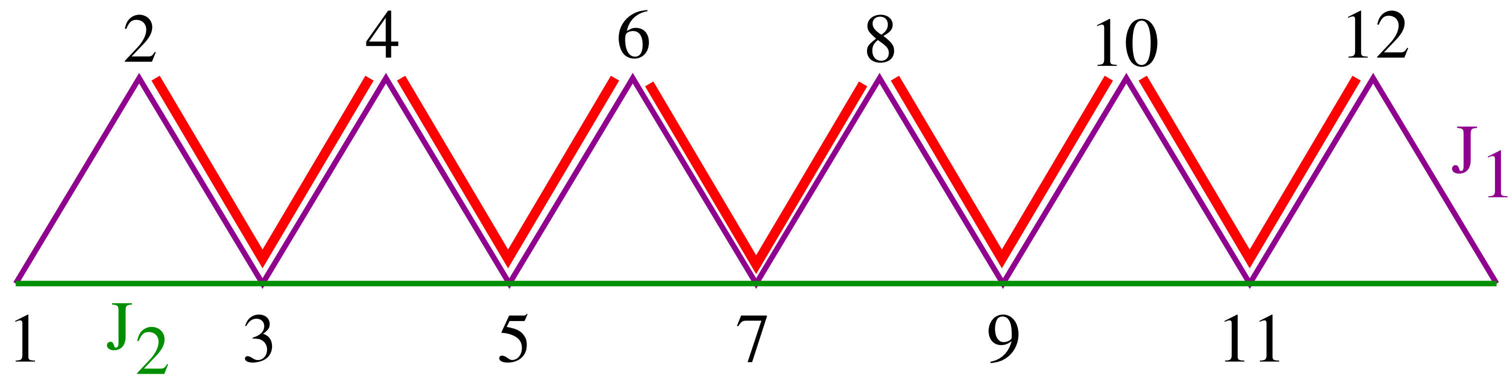


⇒ $|\,$2 localized magnons$\,\rangle$; $E = E_F$, $M = S_{\text{max}} - 2$

⇒ Can be everywhere. Flat band in two-magnon space. Degenerate with $|\,F\,\rangle$.

(1) V. Y. Krivnov, D. V. Dmitriev, S. Nishimoto, S.-L. Drechsler, and J. Richter, Phys. Rev. B **90**, 014441 (2014).
(2) D. V. Dmitriev and V. Y. Krivnov, Phys. Rev. B **92**, 184422 (2015).

Excursus: sawtooth (delta) chain



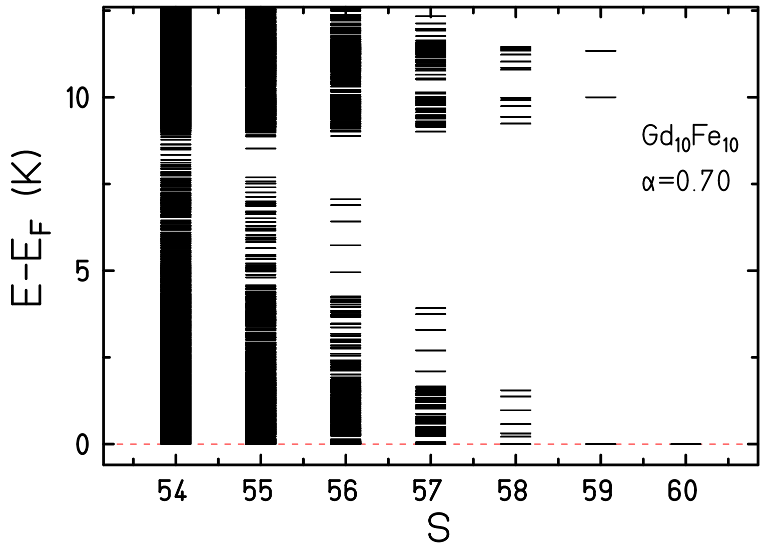
$\Rightarrow$ $\mid$ max. number of localized magnons $\rangle$; $E = E_F, M = S_{\text{max}} - N/2$

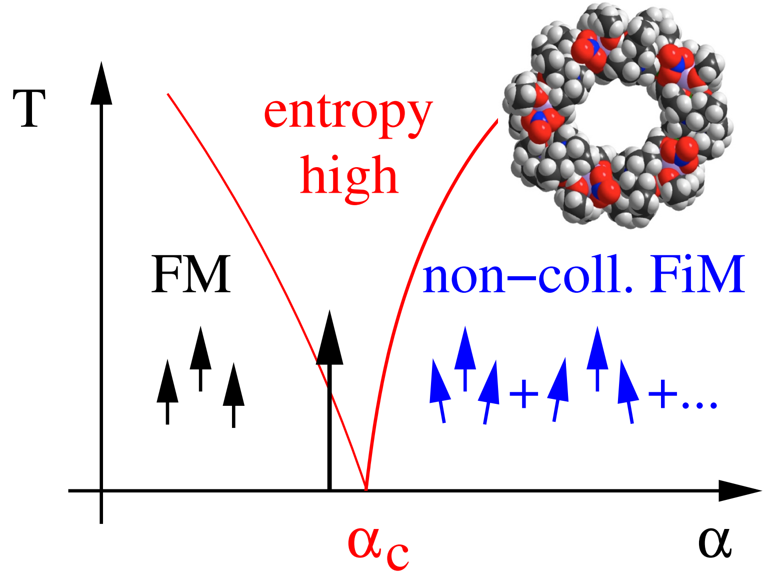
$\Rightarrow$ Macroscopic number of localized magnons. Degenerate with $\mid F \rangle$.

$\Rightarrow$ Extensive entropy.

(1) V. Y. Krivnov, D. V. Dmitriev, S. Nishimoto, S.-L. Drechsler, and J. Richter, Phys. Rev. B **90**, 014441 (2014).
(2) D. V. Dmitriev and V. Y. Krivnov, Phys. Rev. B **92**, 184422 (2015).

$Gd_{10}Fe_{10}$ – QCP





⇒ for $s_1 = 5/2$ and $s_2 = 7/2$: $\alpha_c = 0.70$

⇒ as function of α Quantum Phase Transition at α_c
from $S = 60$ ground state to ground state with $S = 54$.
($\Delta S = N/4 + 1$ in general)

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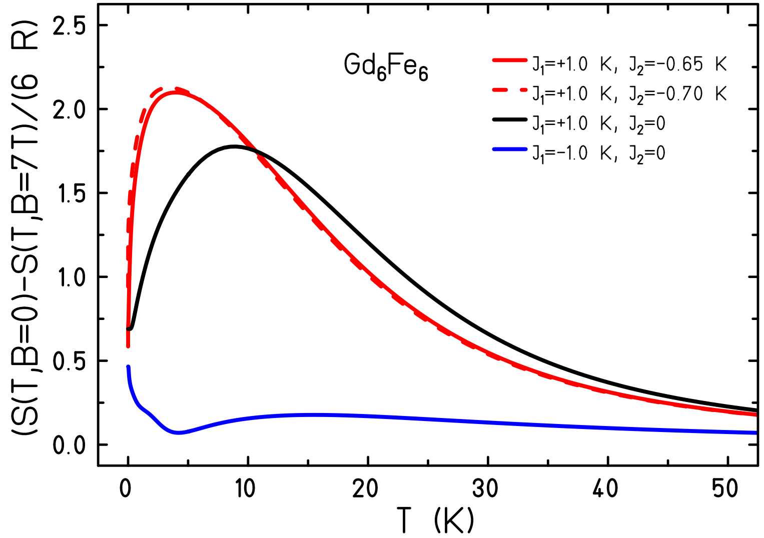
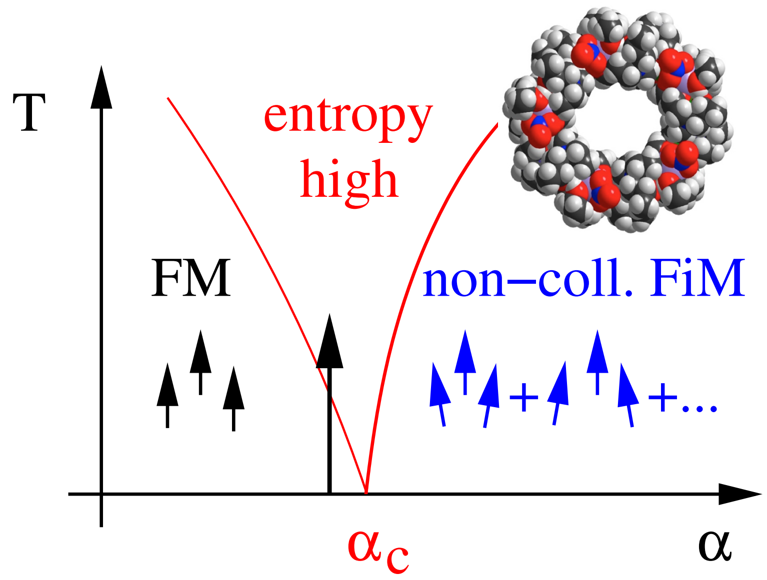
Quantum Phase Transition

Non-analytic behavior of thermodynamic functions at $T = 0$ for variation of another external parameter, e.g. field, pressure; here α – maybe varied by pressure.

$Gd_{10}Fe_{10}$ – $T > 0$





⇒ although QPT and QCP at $T = 0$,

noticeable at elevated temperatures (arrow);

⇒ example isothermal entropy change:

little difference between $\alpha = 0.70$ and $\alpha = 0.65$.

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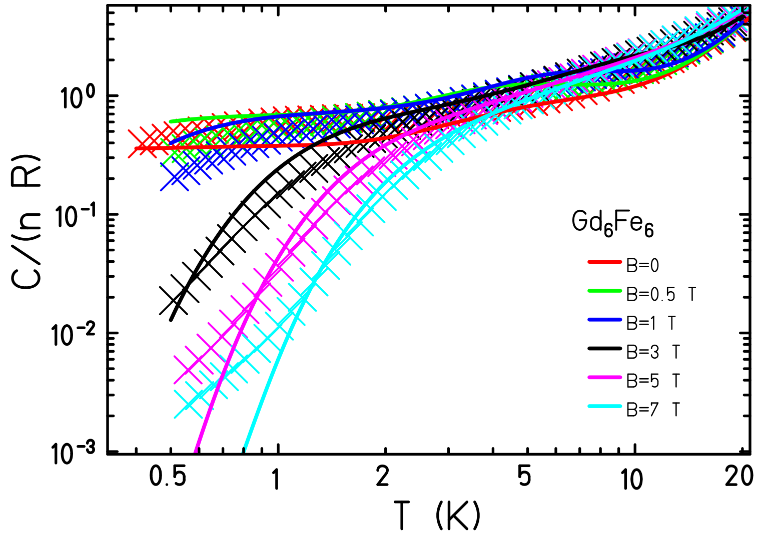
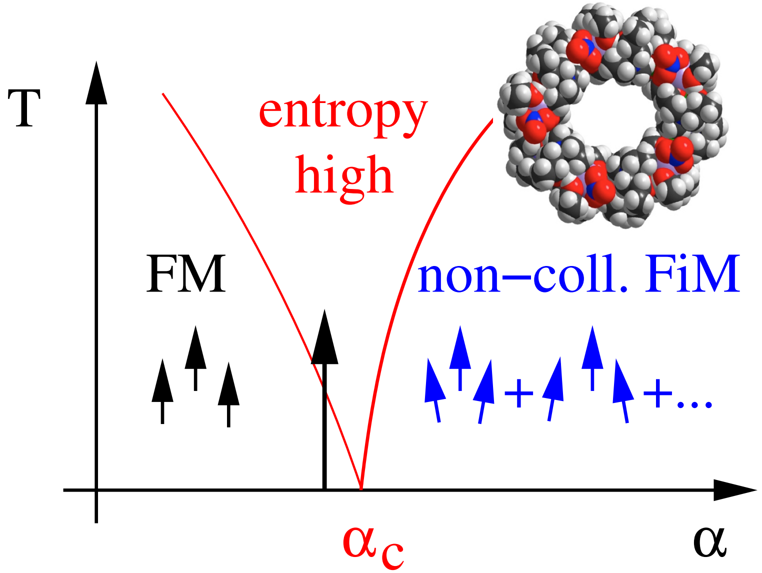
$Gd_{10}Fe_{10}$ – heat capacity





⇒ heat capacity assumes very large values

even down to lowest temperatures;

⇒ evaluated by means of FTLM for a smaller (hypothetical) system Gd_6Fe_6;

⇒ magnetic field separates $S = 60$ ground state, C drops.

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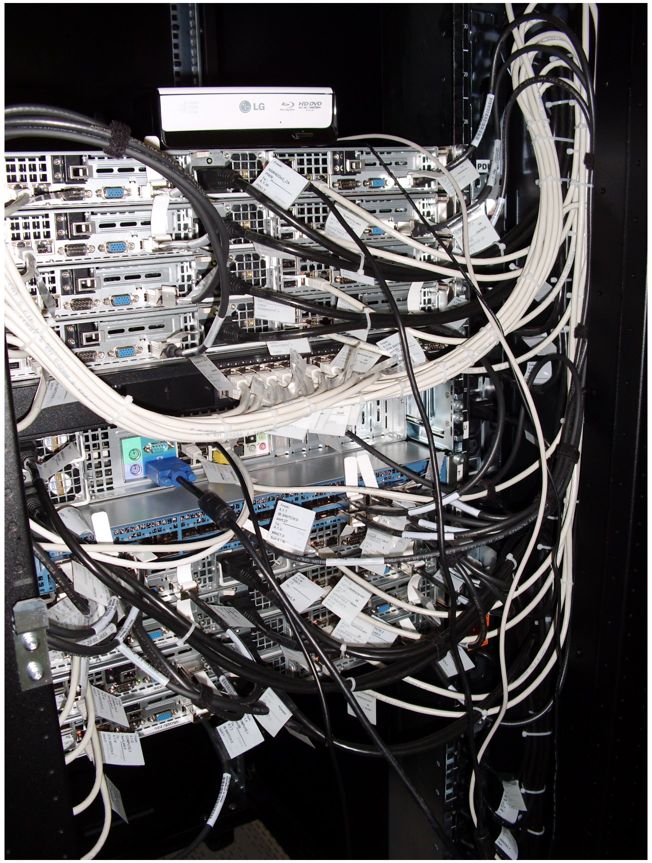
$Gd_{10}Fe_{10}$ – Summary



- Sawtooth chain has a rich phase diagram: magnetization plateaux, magnetization jumps, flat bands, quantum phase transitions.
- $Gd_{10}Fe_{10}$ is a lucky punch.
- Largest ground state spin of a single molecule to date: $S = 60$.
- Quantum Phase Transition observable in a molecule with structure of a sawtooth chain.

$\Leftarrow$ And yes, we use big computers.

A. Baniodeh, N. Magnani, Y. Lan, G. Buth, C.E. Anson, J. Richter, M. Affronte, J. Schnack, A.K. Powell, High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality, npj Quantum Materials **3**, 10 (2018)

Many thanks to my collaborators



- C. Beckmann, M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, N.B. Ivanov, H.-T. Langwald, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum (Bielefeld)
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Thank you very much for your attention.

The end.

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