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

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Workshop on New perspectives for low-temperature refrigeration
Université de Cergy-Pontoise, France, 2 May 2018

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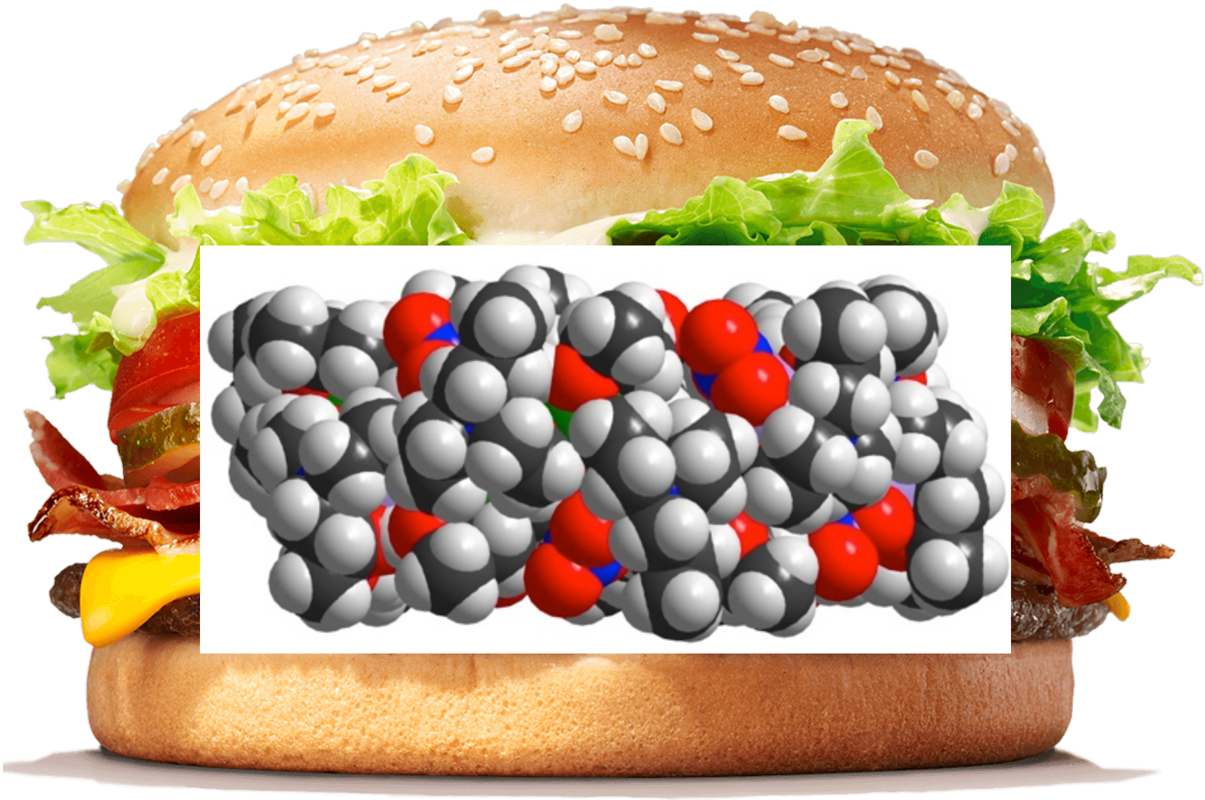
Modern didactics teaches us

All information goes to the Crocodile Brain first.

The CrocBrain is able to ask only two questions:

Is it dangerous?

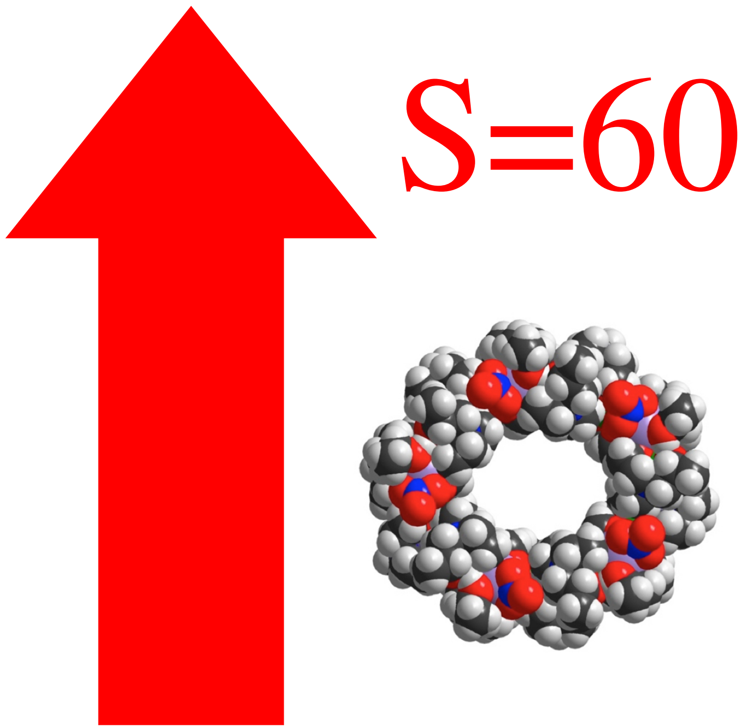
Can one eat it?

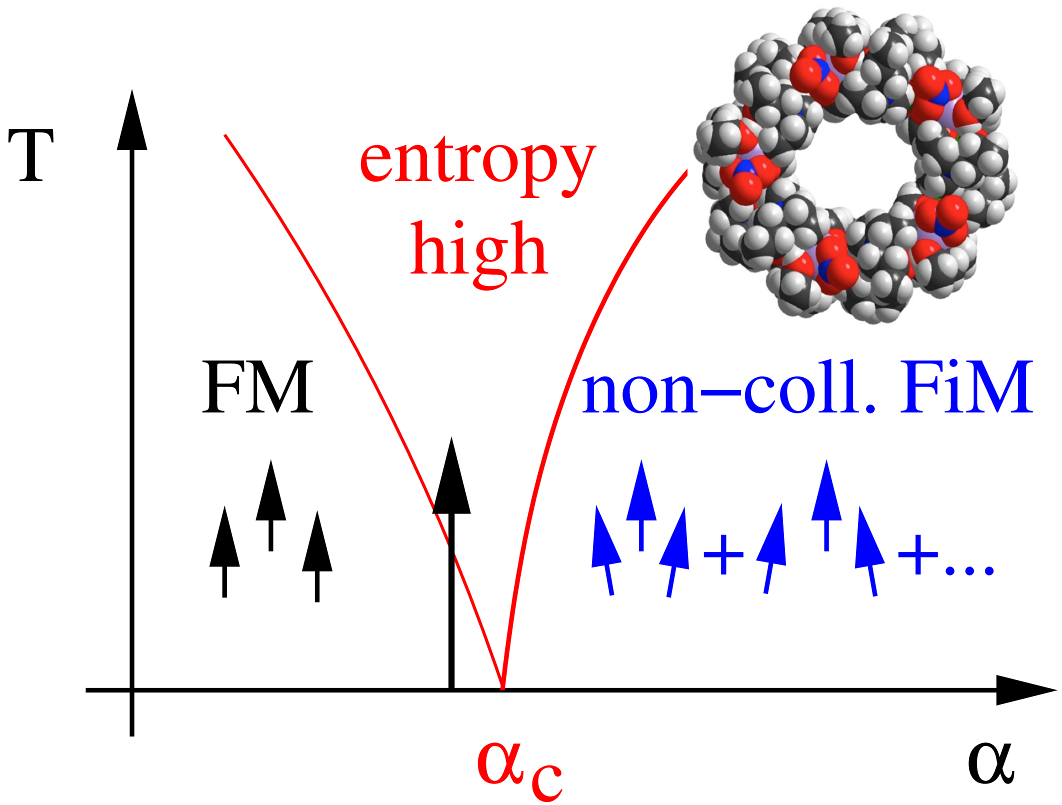


The mouth-watering $Gd_{10}Fe_{10}$!

(It’s not dangerous.)

$Gd_{10}Fe_{10}$ is yummy





A. Baniodeh, N. Magnani, Y. Lan, G. Buth, C.E. Anson, J. Richter, M. Affronte, J. Schnack, A.K. Powell,
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npj Quantum Materials **3**, 10 (2018)

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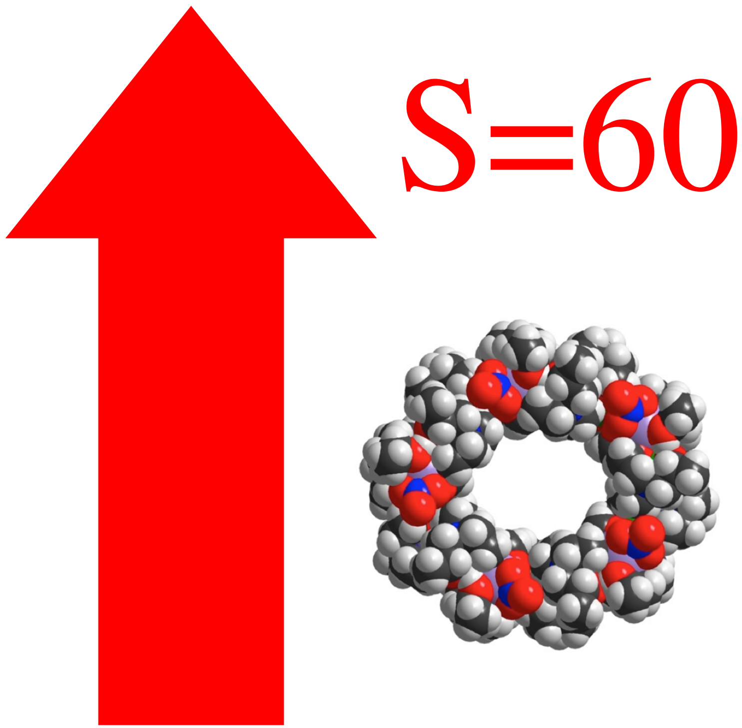

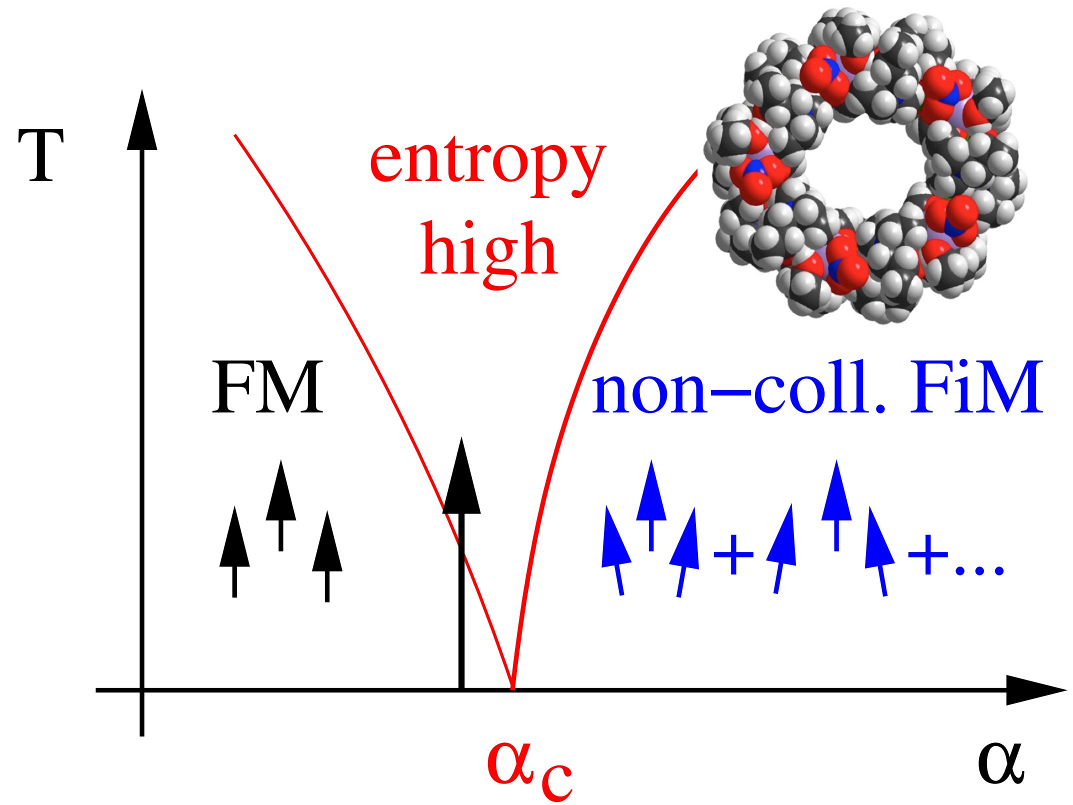

How do we know?

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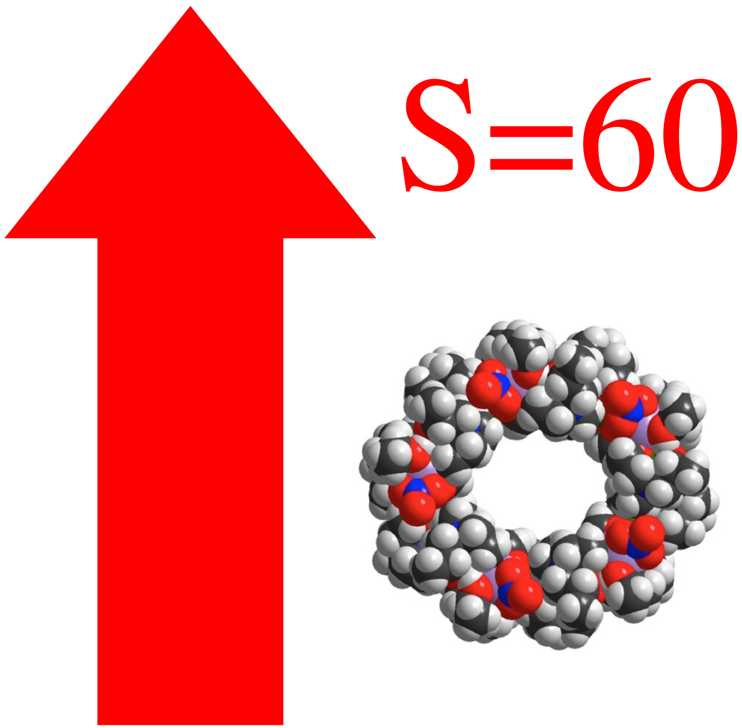
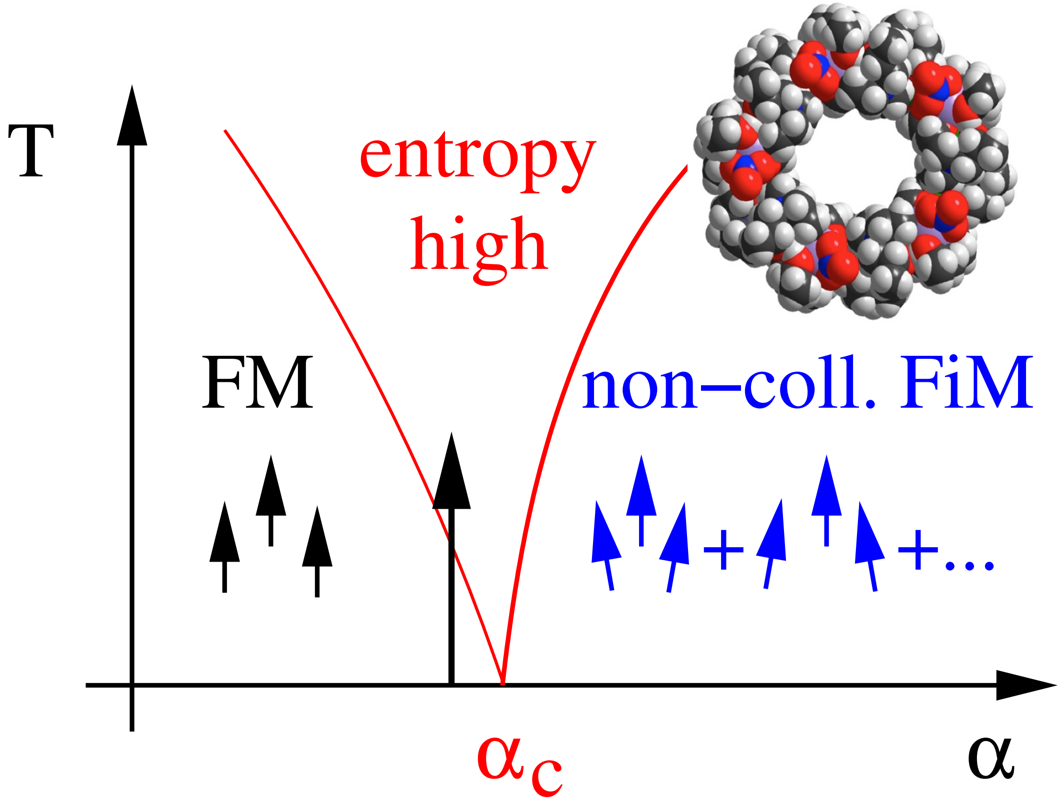
$Gd_{10}Fe_{10}$ is yummy





How do we know?

What is a QPT?

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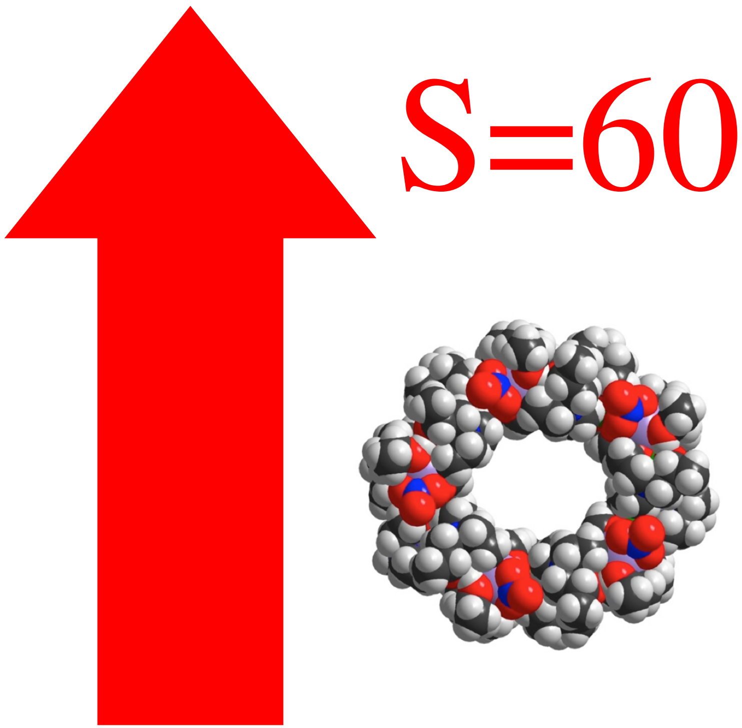

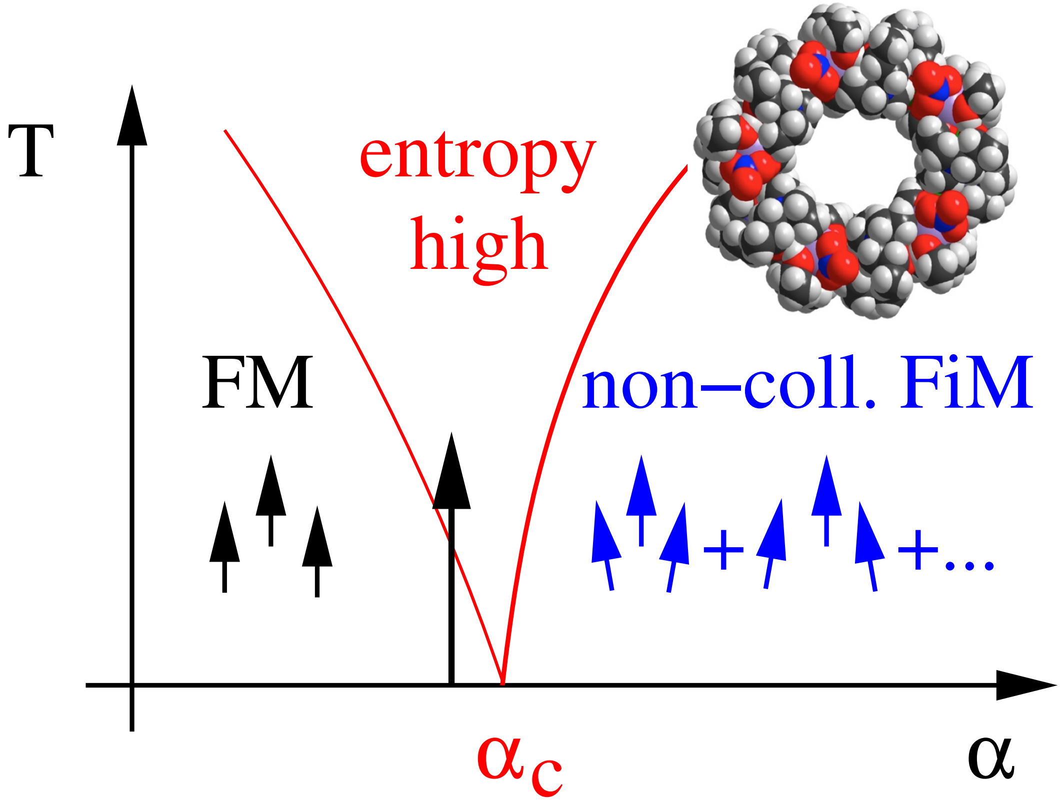

How do we know?

What is a QPT?

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

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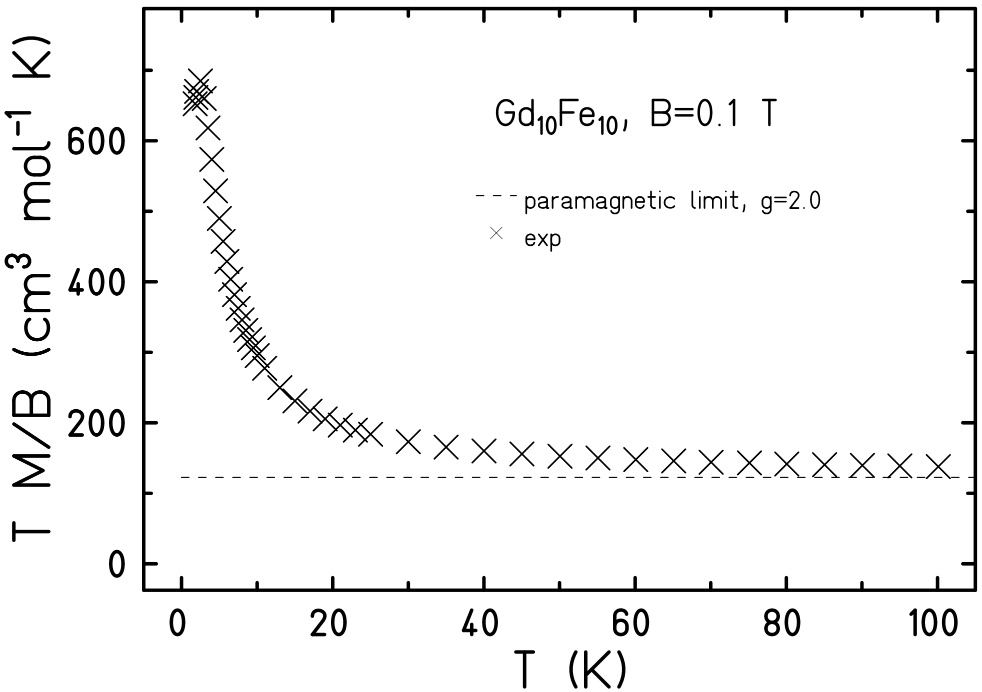
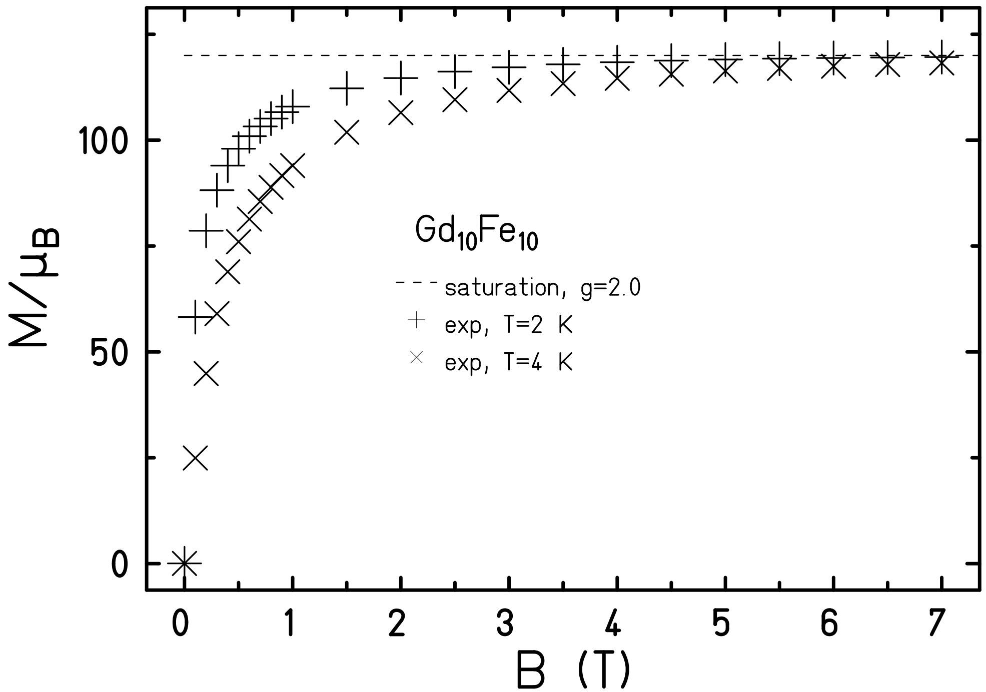
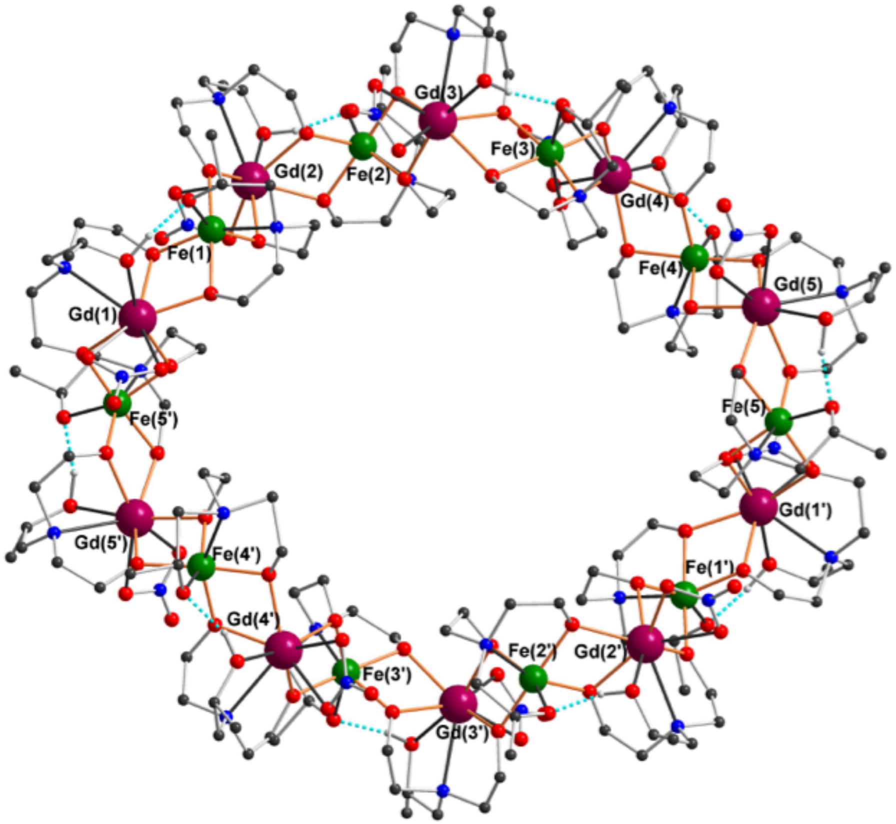
Start: experimental data

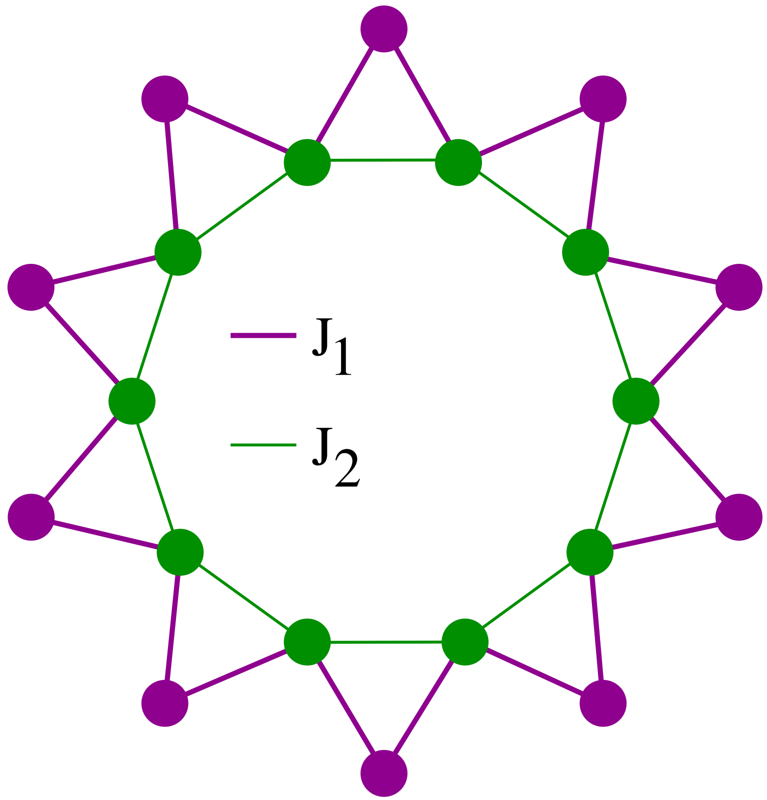
$Gd_{10}Fe_{10}$ – How to rationalize the experimental data?





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





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

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Model Hamiltonian

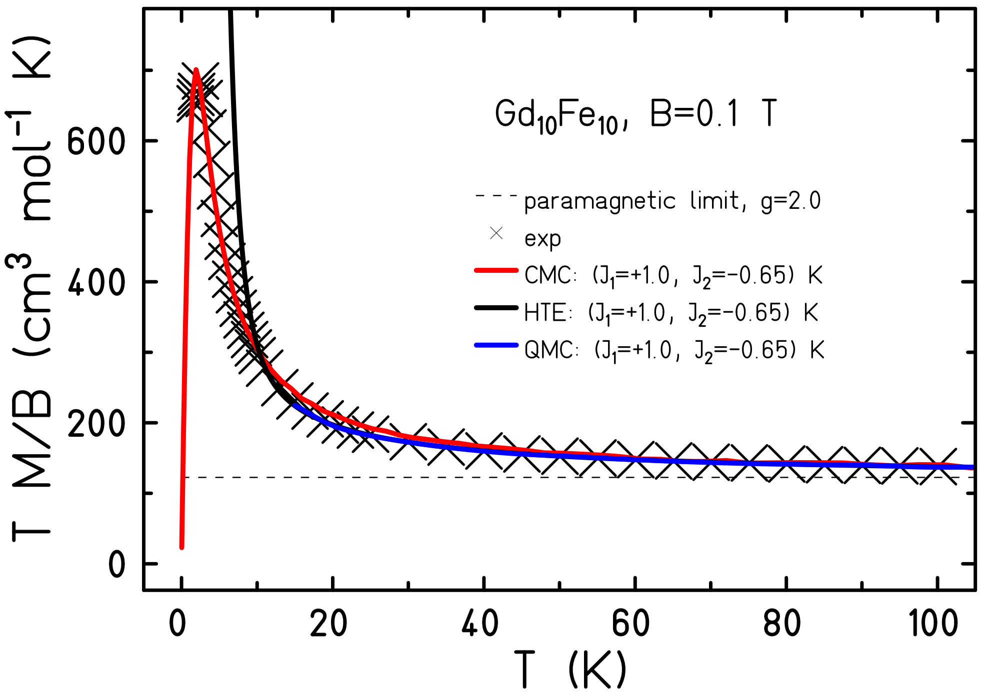
$$\underset{\sim}{H} = -2J_1 \sum_i \underset{\sim}{\vec{s}}_{\text{Gd},i} \cdot \left(\underset{\sim}{\vec{s}}_{\text{Fe},i} + \underset{\sim}{\vec{s}}_{\text{Fe},i+1} \right)$$

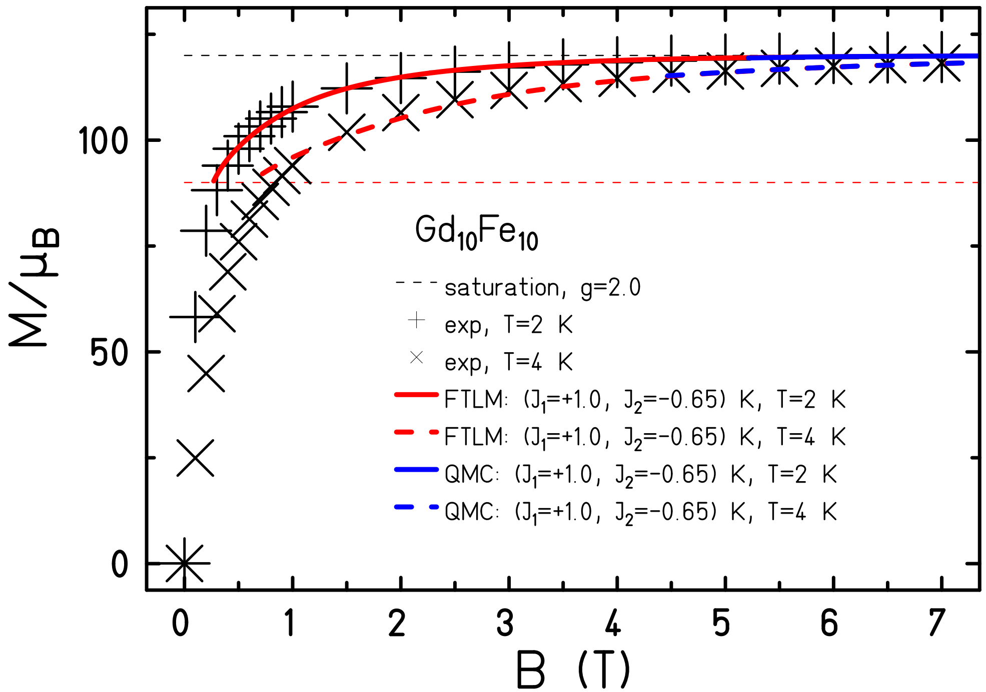
$$-2J_2 \sum_i \underset{\sim}{\vec{s}}_{\text{Fe},i} \cdot \underset{\sim}{\vec{s}}_{\text{Fe},i+1} + g\,\mu_B\,B \sum_i \left(\underset{\sim}{s}^z_{\text{Gd},i} + \underset{\sim}{s}^z_{\text{Fe},i} \right)$$

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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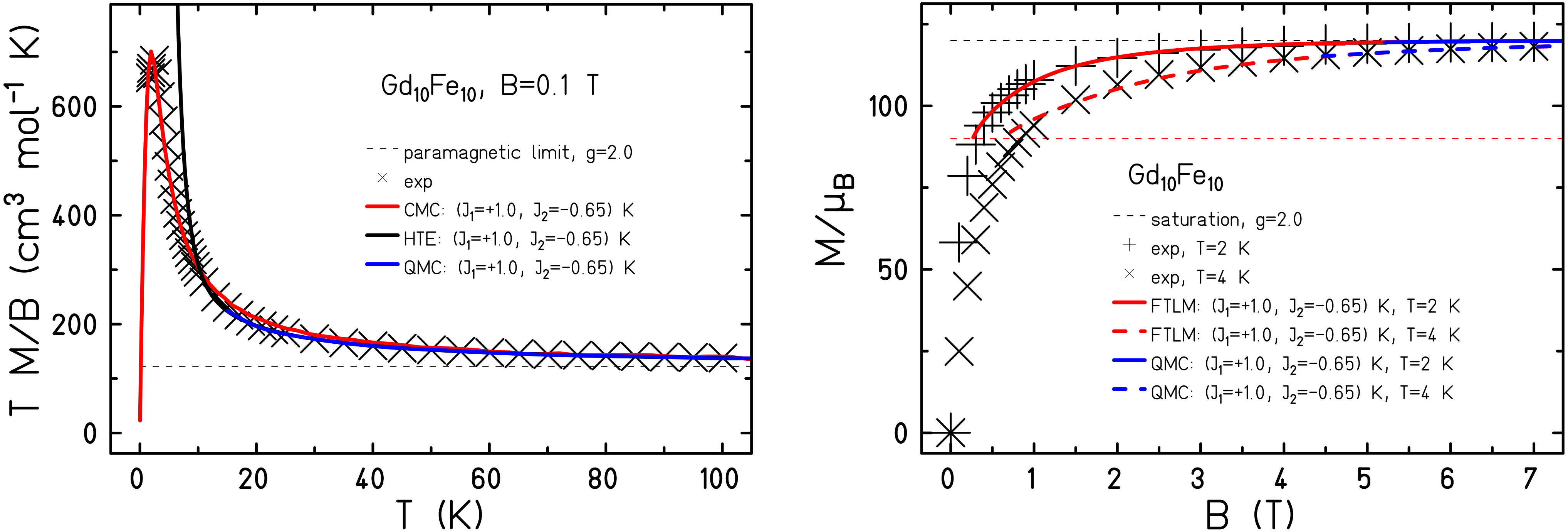
Summary: theory methods

- Complete diagonalization: exact; Dimension of largest Hilbert space $< 10^5$.
- High-temperature series expansion: $\mathcal{O} \approx \sum_{\mu=0}^{\mu_{\text{max}}} o_\mu \, T^{-\mu}$, o_μ known up to $\mu_{\text{max}} = 6$ for mixed spin systems; $\mu_{\text{max}} = 11$ otherwise [1].
- Finite Temperature Lanczos Method (FTLM): pseudo-spectrum, low-lying levels good, approximation of partition function, time-evolution; DoH $< 10^{10}$ [2].
- Quantum Monte Carlo (QMC): approximation of partition function, observables; bad/no convergence for competing interactions (frustration) due to negative sign problem; otherwise HUGE systems possible [ALPS].
- Classical Monte Carlo (CMC): spins are classical vectors; reasonable approximation for large spins such as $s = 5/2$ and $s = 7/2$.

[1] H.-J. Schmidt, A. Lohmann, J. Richter, Phys. Rev. B 84, 104443 (2011); Phys. Rev. B 89, 014415 (2014). [2] J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994); J. Schnack and O. Wendland, Eur. Phys. J. B **78** (2010) 535-541.

$Gd_{10}Fe_{10}$ – Methods



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

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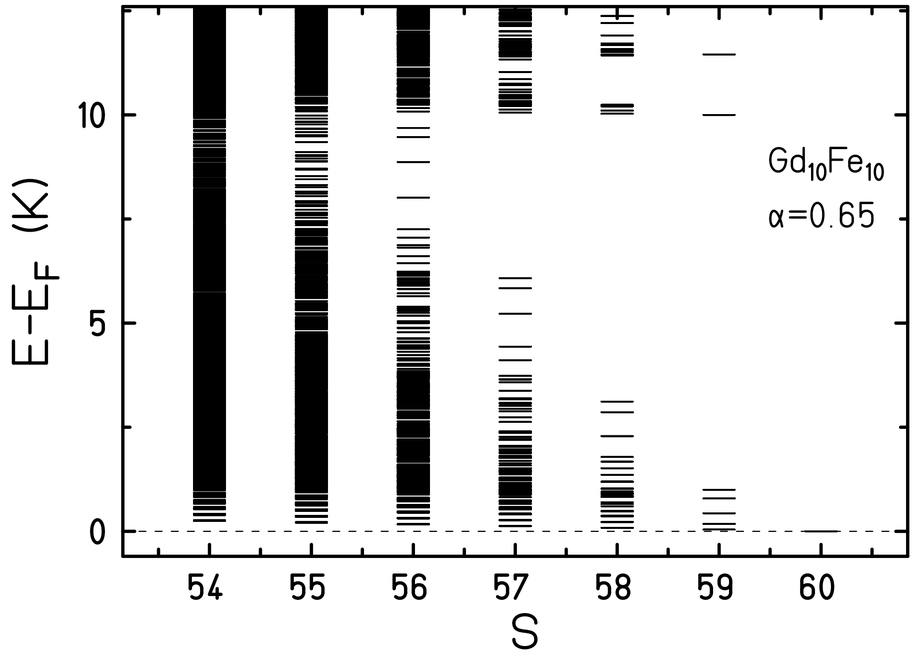
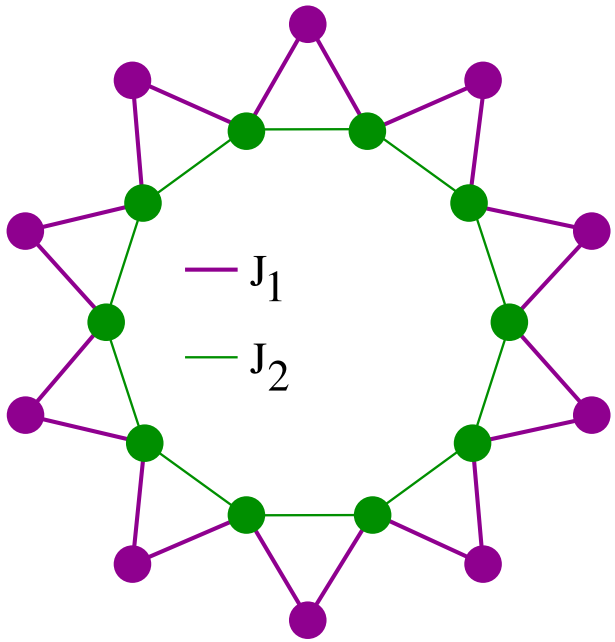
$Gd_{10}Fe_{10}$ – $S = 60$





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

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

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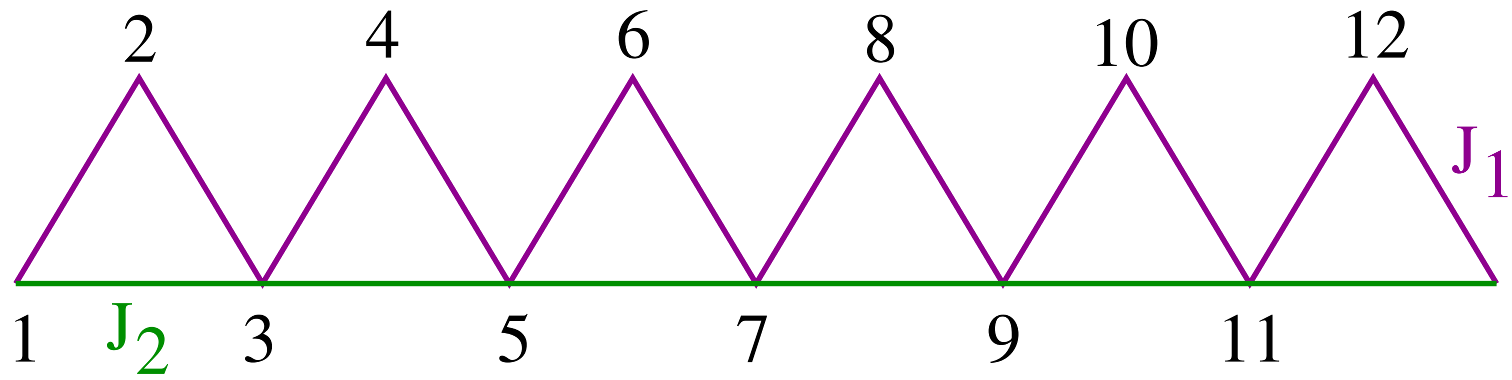
Excursus: sawtooth (delta) chain



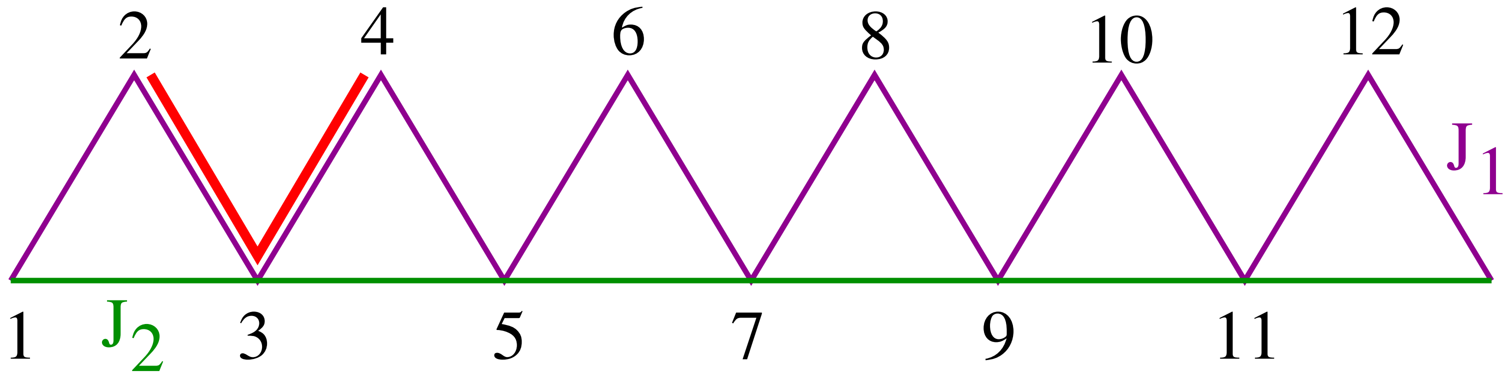
$\Rightarrow$ special properties for $J_1 > 0$ (ferro) and $J_2 < 0$ (af) at certain α_c

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).

Excursus: sawtooth (delta) chain



$\Rightarrow \mid F\,\rangle = \mid S = S_{\text{max}}, M = S_{\text{max}}\,\rangle$ 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).
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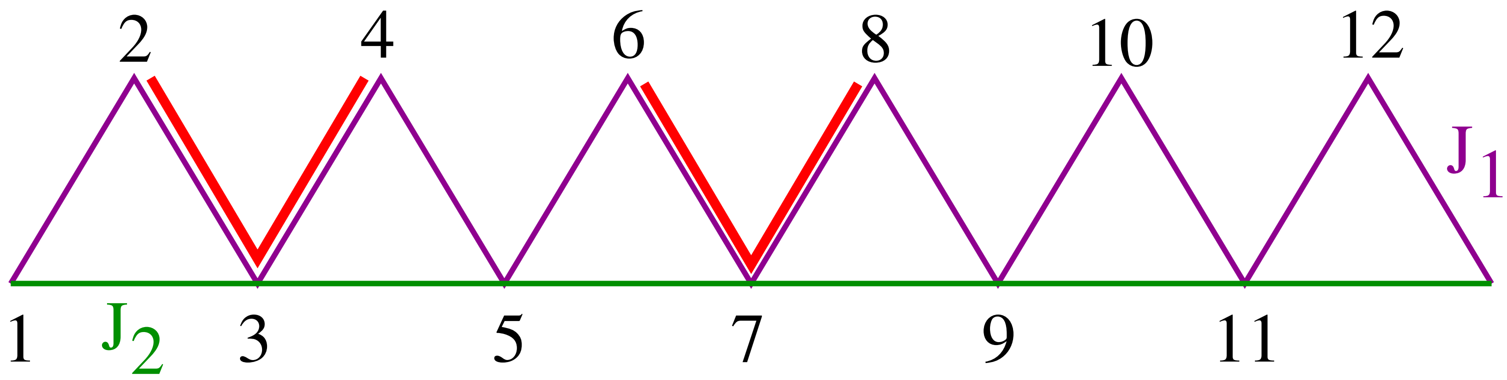
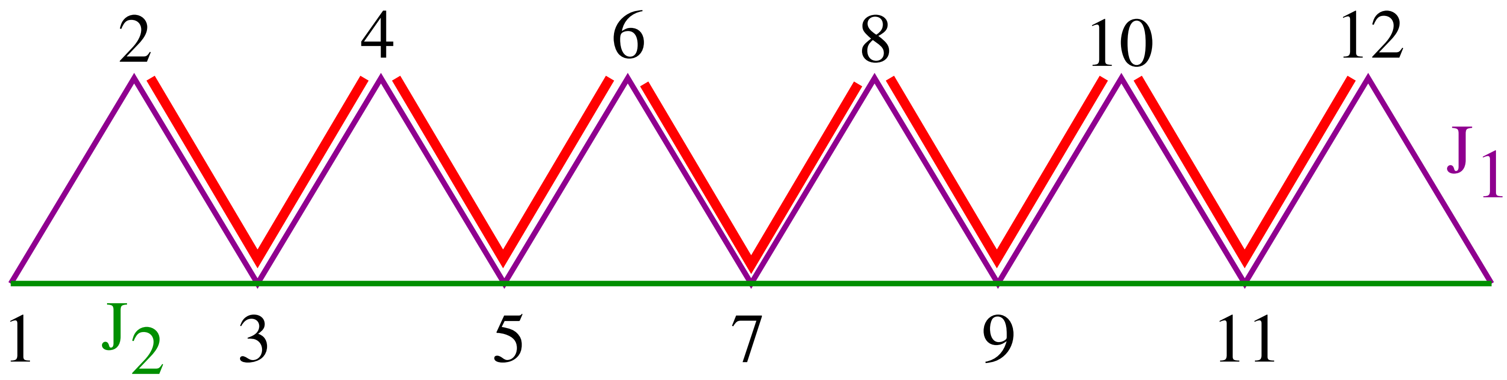


$\Rightarrow$ $|$ 2 localized magnons $\rangle$; $E = E_F, M = S_{\text{max}} - 2$

$\Rightarrow$ 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



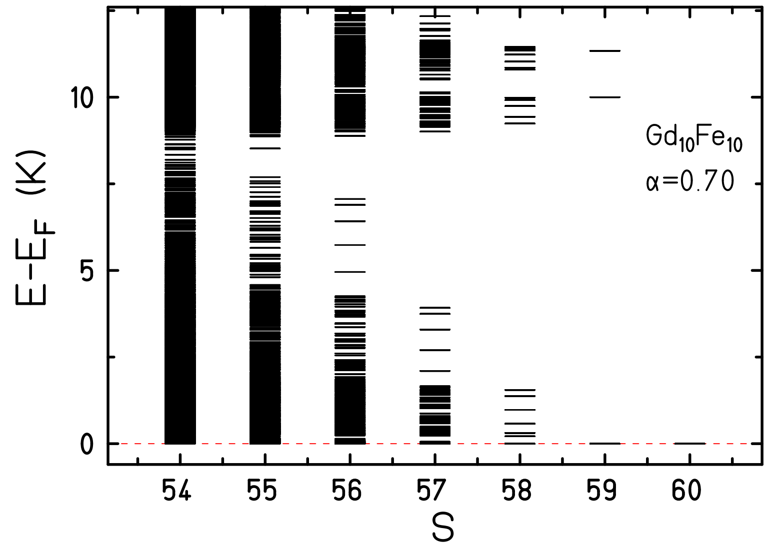
$\Rightarrow$ $|$ max. number of localized magnons $\rangle$; $E = E_F, M = S_{\text{max}} - N/2$

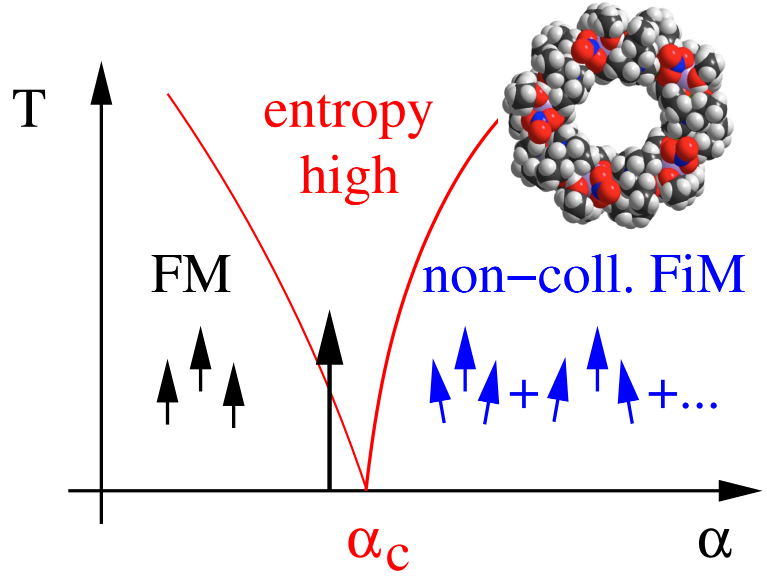
$\Rightarrow$ Macroscopic number of localized magnons. Degenerate with $|\,F\,\rangle$.

$\Rightarrow$ 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 $s_2 = 7/2$: $\alpha_{\text{c}} = 0.70$

⇒ 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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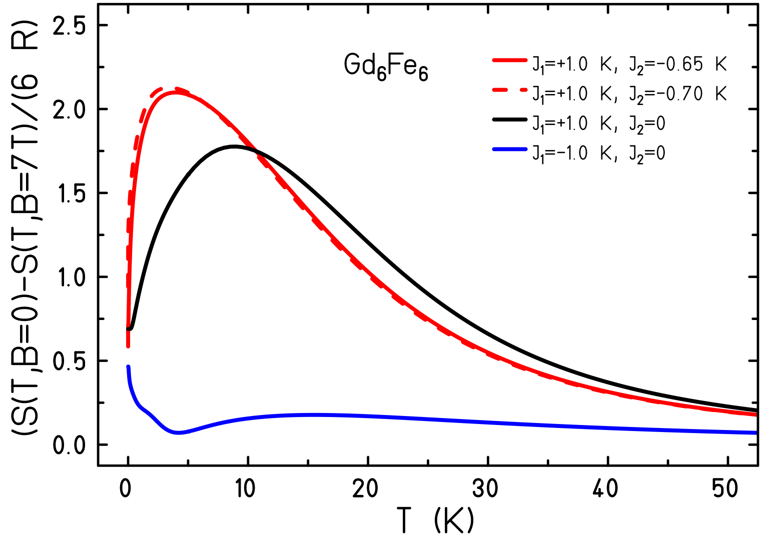
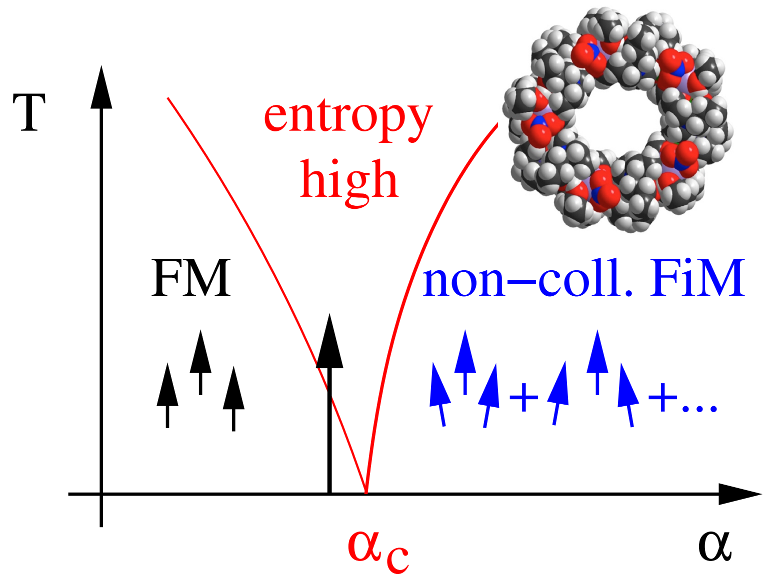
Quantum Phase Transition

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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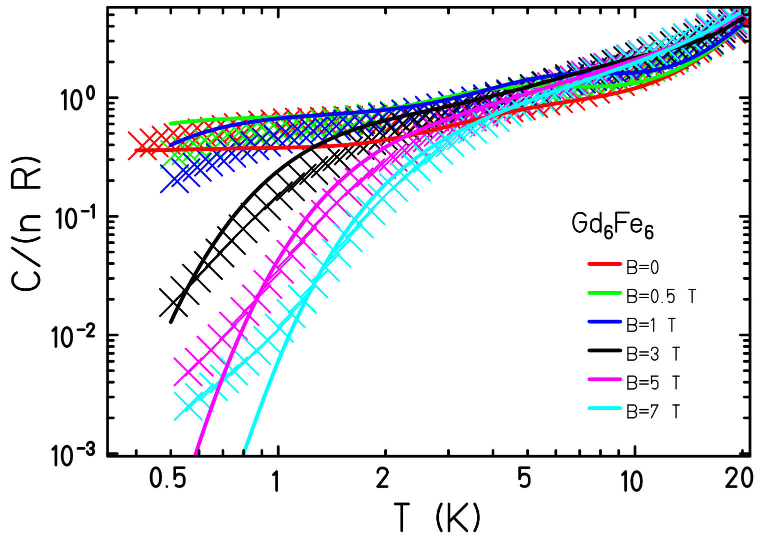
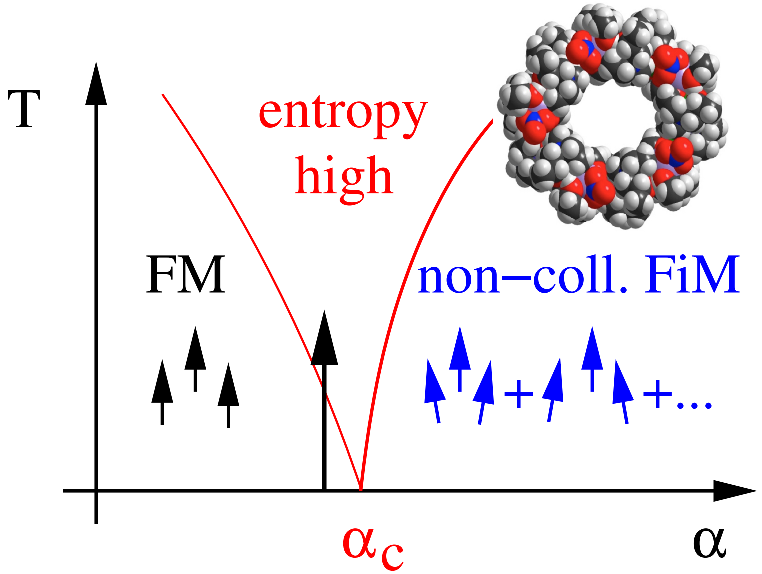
$Gd_{10}Fe_{10}$ – heat capacity





⇒ 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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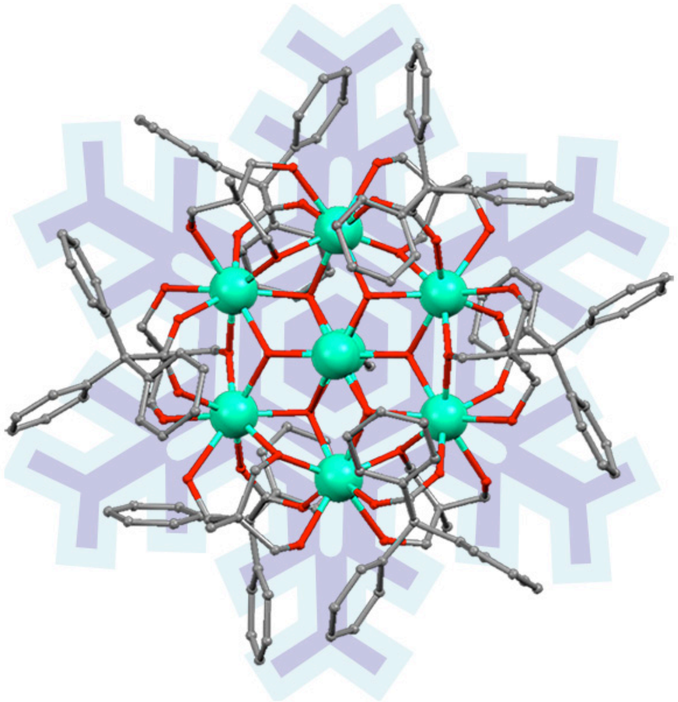
If time permits . . .

. . . a bit on Gd_7

Gd$_7$ – Magnetocalorics

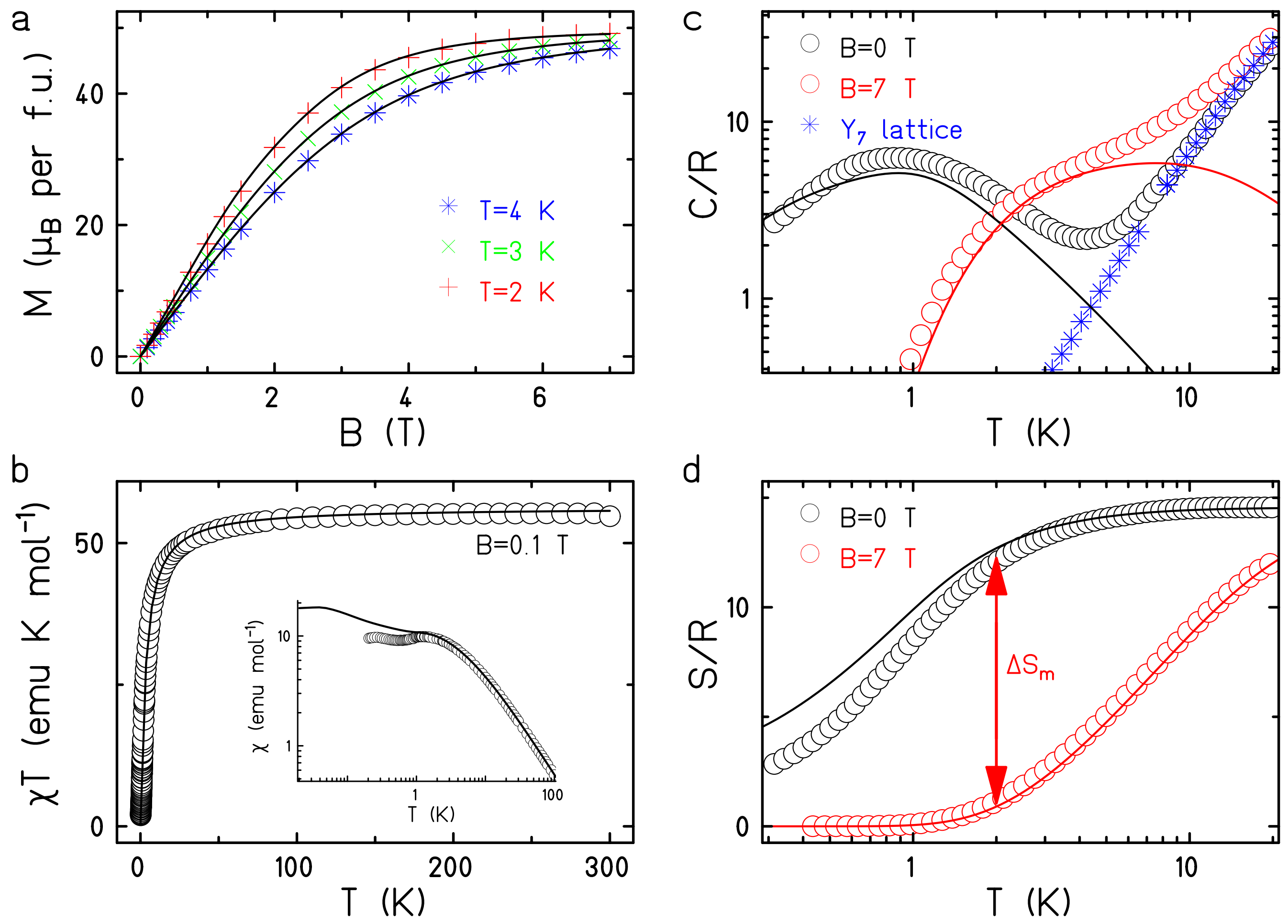


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2\sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\,\mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

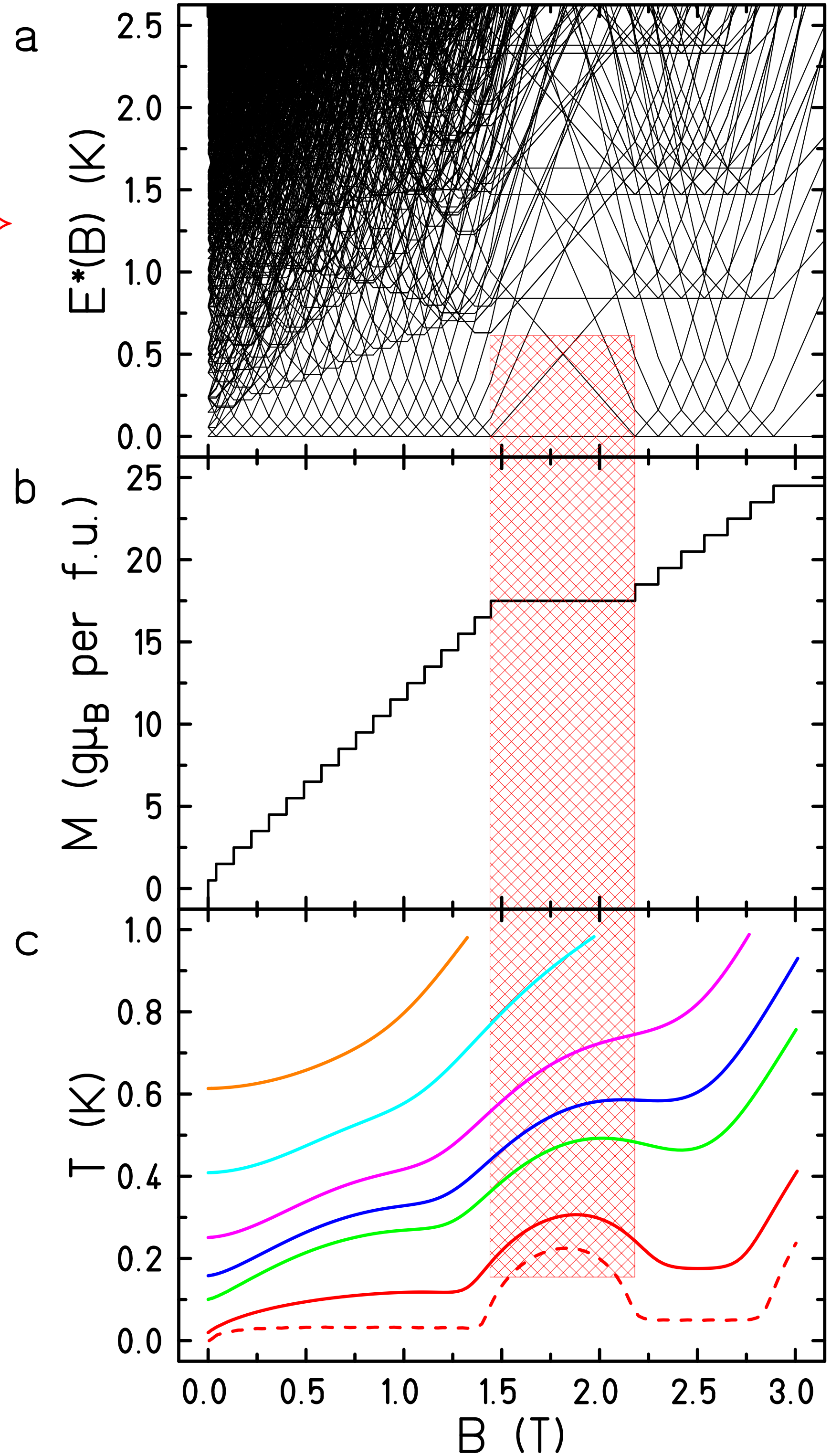
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

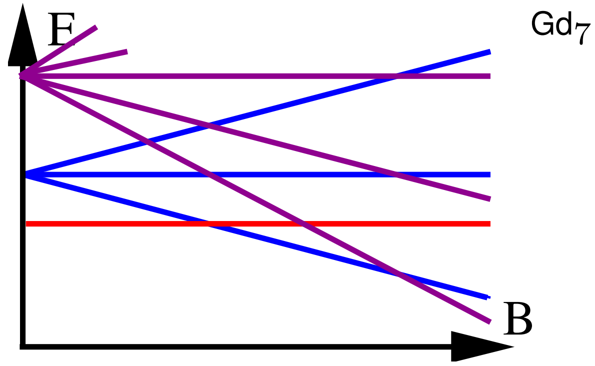
Gd$_7$ – experiment & theory



J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

not dangerous ⇒

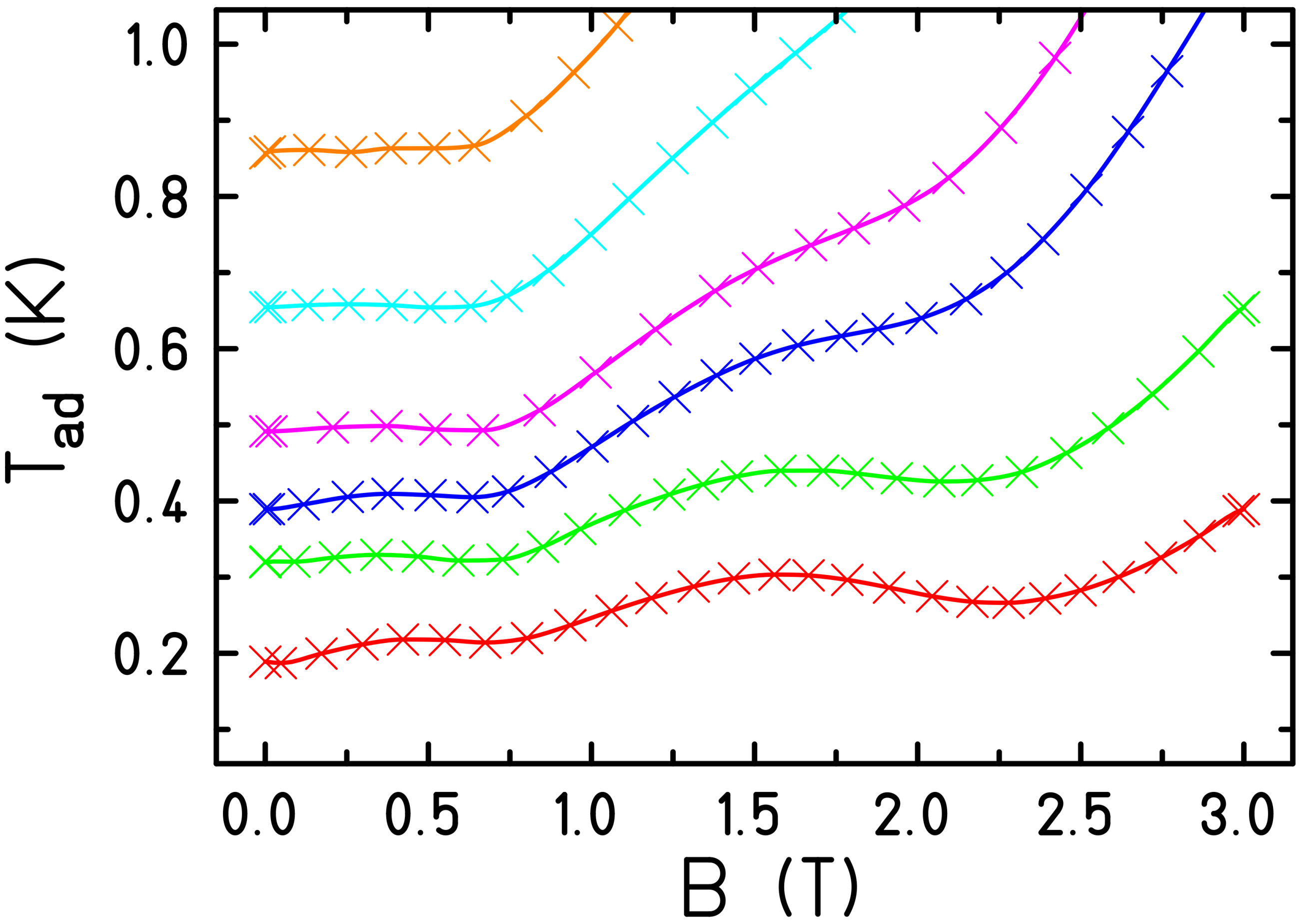




The molecular barbecue:

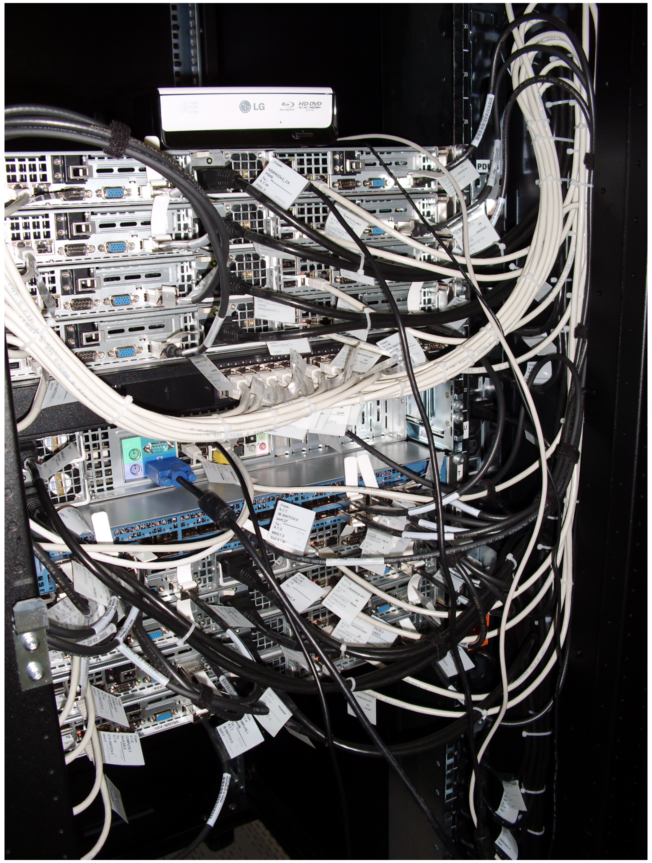
isentropic broiling!

Gd$_7$ – Experimental cooling



J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

$Gd_{10}Fe_{10}$ – 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.

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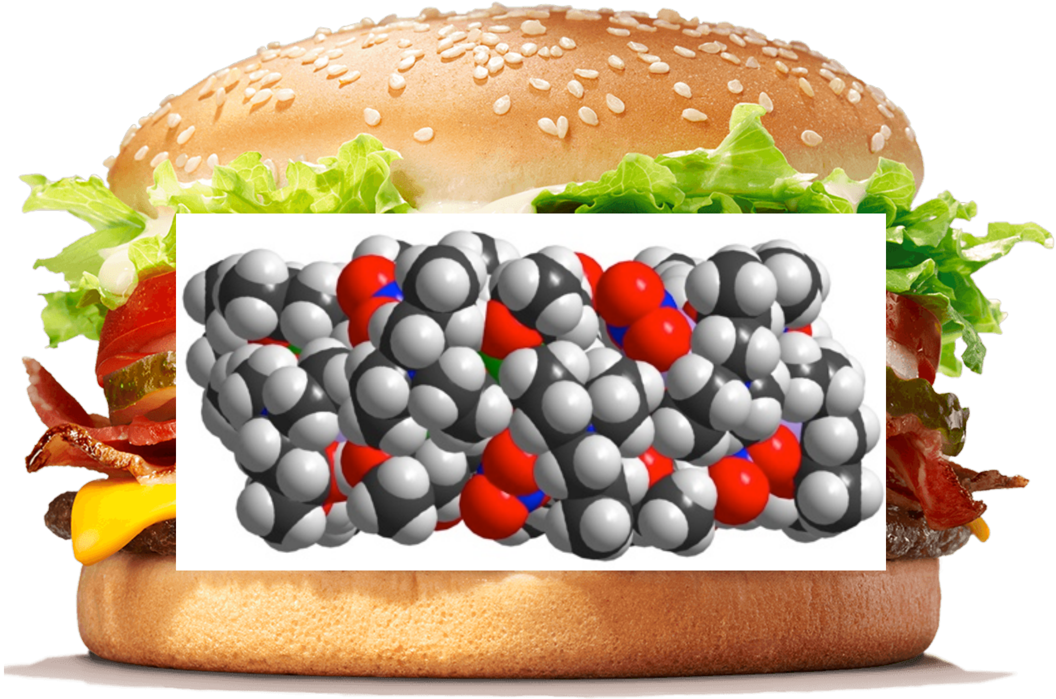

Man does not live by bread alone!

$Gd_{10}Fe_{10}$!

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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- **J. Richter**, J. Schulenburg (Magdeburg); B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); **A. Powell**, W. Wernsdorfer (Karlsruhe); E. Rentschler (Mainz); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your attention.

The end.

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