

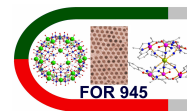
Extreme magnetocaloric properties of $\text{Gd}_{10}\text{Fe}_{10}$ sawtooth spin rings: a case study using the finite-temperature Lanczos method

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3MET workshop CB@K 2017
KIT, Karlsruhe, 5. 10. 2017



New Power Point trends: no title page!

04.10.2017 So bekommen Sie Ihr Publikum in den Griff

Diese Fehler sind tödlich für Ihre Power-Point-Präsentation

Von Severin von Hoensbroech | 37.905

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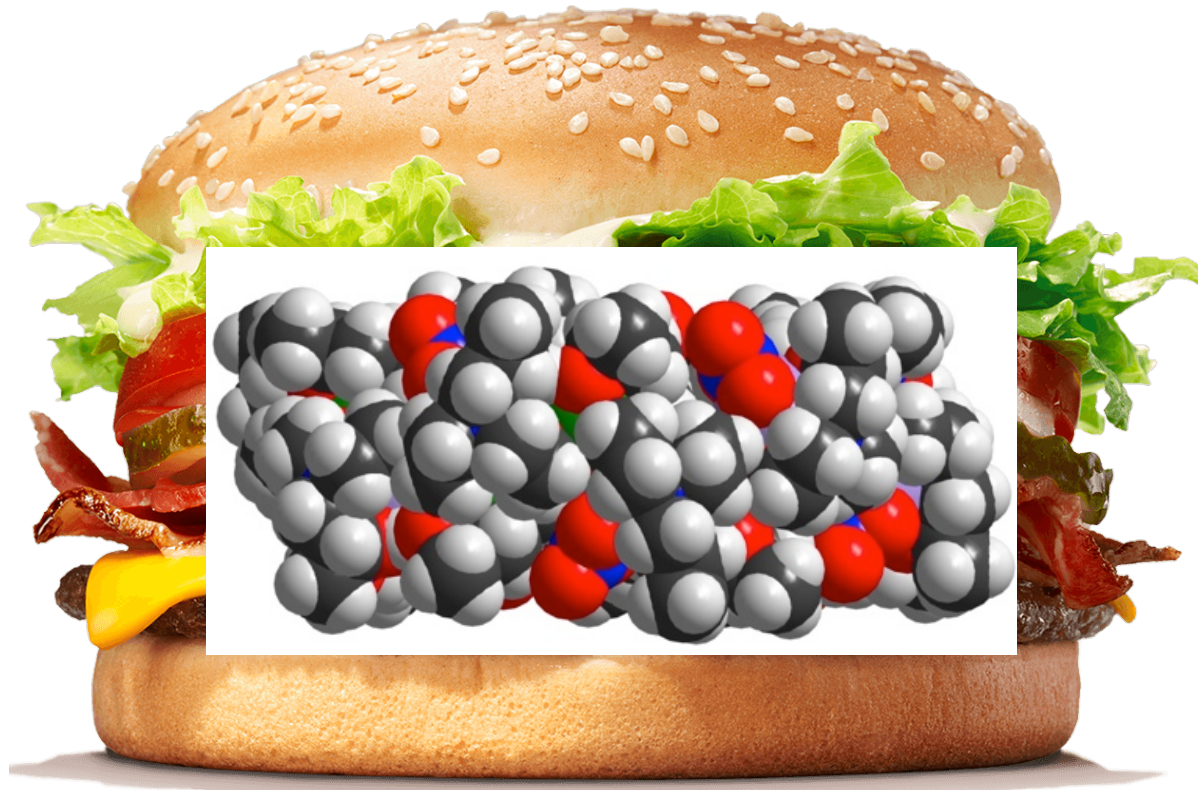


All information goes to the Crocodile Brain (Hirnstamm)
first.

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.)

Menu for you today



$$\begin{pmatrix} 3 & 42 & 4711 \\ 42 & 0 & 3.14 \\ 4711 & 3.14 & 8 \\ -17 & 007 & 13 \\ 1.8 & 15 & 081 \end{pmatrix}$$

1. Finite-Temperature Lanczos Method
2. Magnetocaloric Effect
3. Gd_7
4. $Gd_{10}Fe_{10}$

We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

Model Hamiltonian for this talk

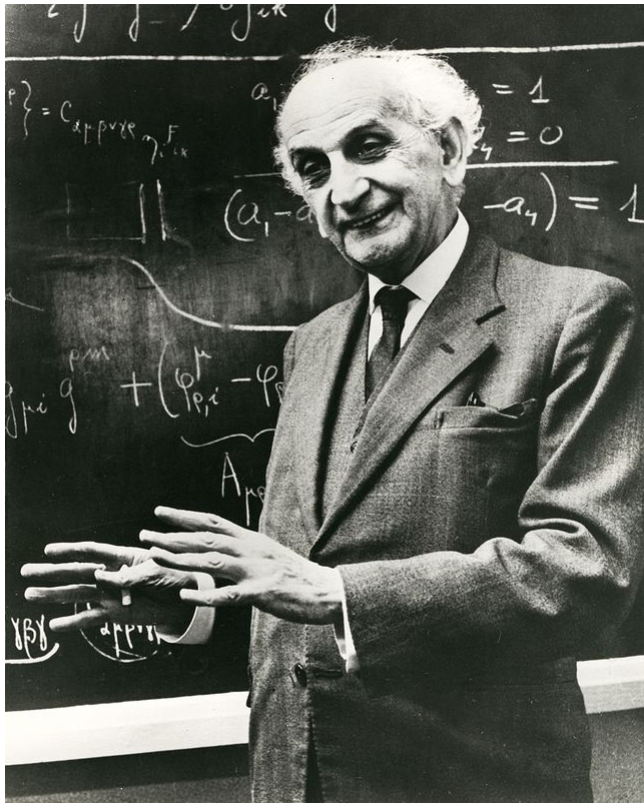
$$\tilde{H} = -2 \sum_{i < j} J_{ij} \vec{\tilde{S}}_i \cdot \vec{\tilde{S}}_j + g \mu_B B \sum_i^N \tilde{S}_i^z$$

Heisenberg
Zeeman

Finite-temperature Lanczos Method

(Yummy!)

Lanczos – a Krylov space method



- Idea: exact diagonalization in reduced basis sets.
- But which set to choose???
- Idea: generate the basis set with the operator you want to diagonalize:
 $\{ |\phi\rangle, \tilde{H} |\phi\rangle, \tilde{H}^2 |\phi\rangle, \tilde{H}^3 |\phi\rangle, \dots \}$
- But which starting vector to choose???
- Idea: almost any will do!
- Cornelius Lanczos (Lánczos Kornél, 1893-1974)

(1) C. Lanczos, J. Res. Nat. Bur. Stand. **45**, 255 (1950).

Finite-temperature Lanczos Method (not dangerous)

$$Z(T, B) = \sum_{\nu} \langle \nu | \exp \left\{ -\beta \underline{H} \right\} | \nu \rangle$$

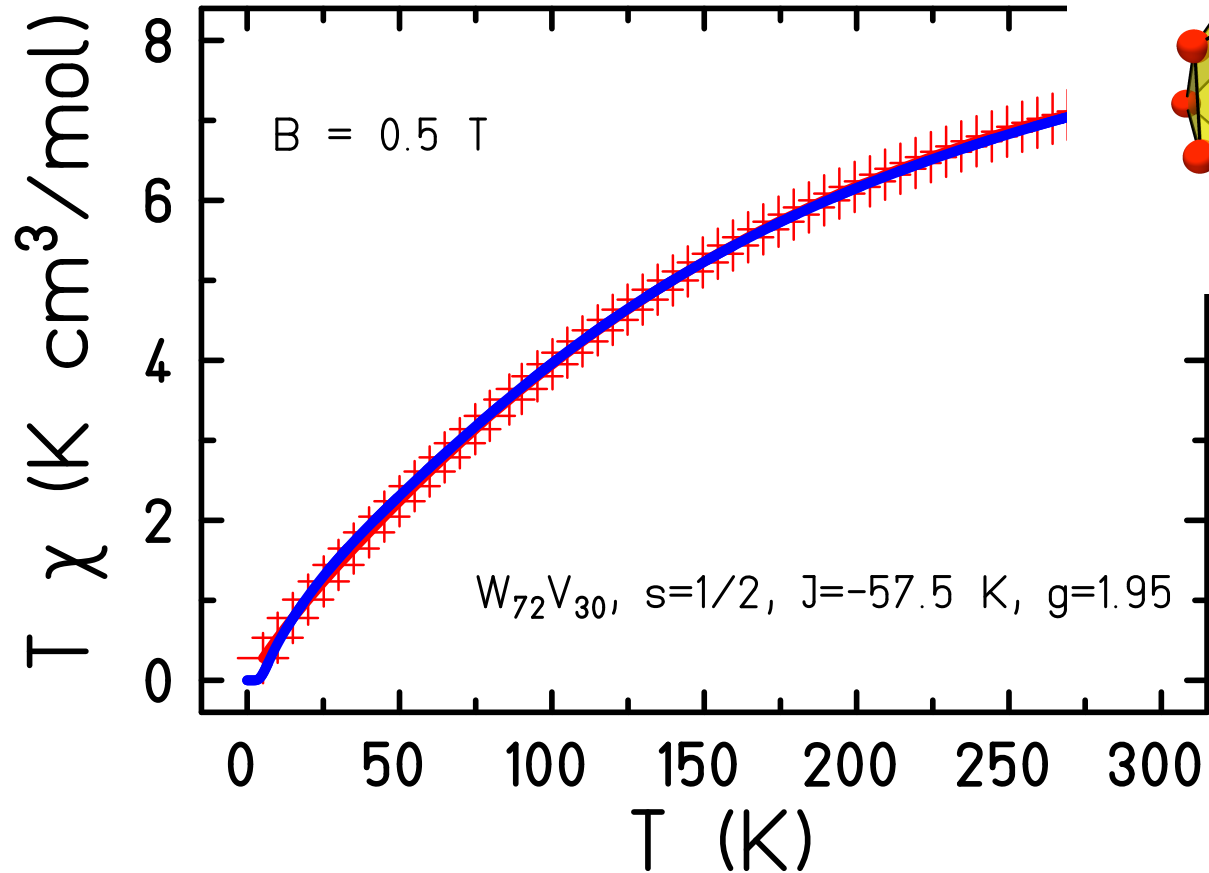
$$\langle \nu | \exp \left\{ -\beta \underline{H} \right\} | \nu \rangle \approx \sum_n \langle \nu | n(\nu) \rangle \exp \left\{ -\beta \epsilon_n \right\} \langle n(\nu) | \nu \rangle$$

$$Z(T, B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^R \sum_{n=1}^{N_L} \exp \left\{ -\beta \epsilon_n \right\} |\langle n(\nu) | \nu \rangle|^2$$

- $|n(\nu)\rangle$ n-th Lanczos eigenvector starting from $|\nu\rangle$
- Partition function replaced by a small sum: $R = 1 \dots 10, N_L \approx 100$.

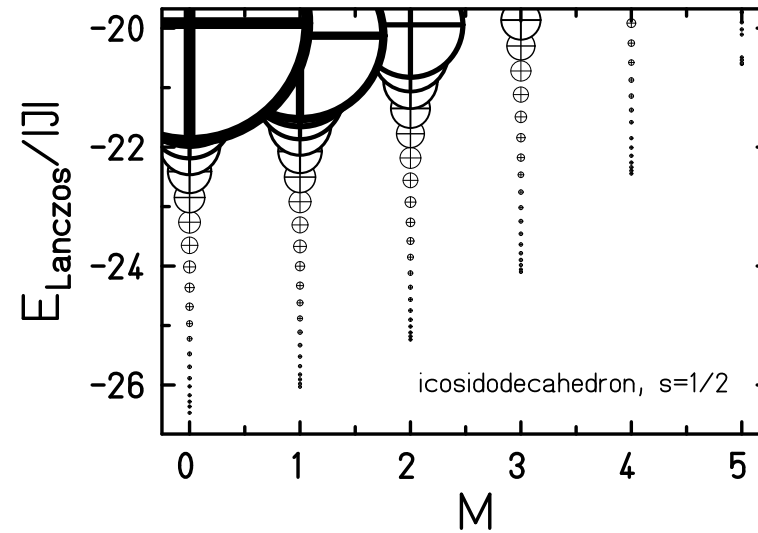
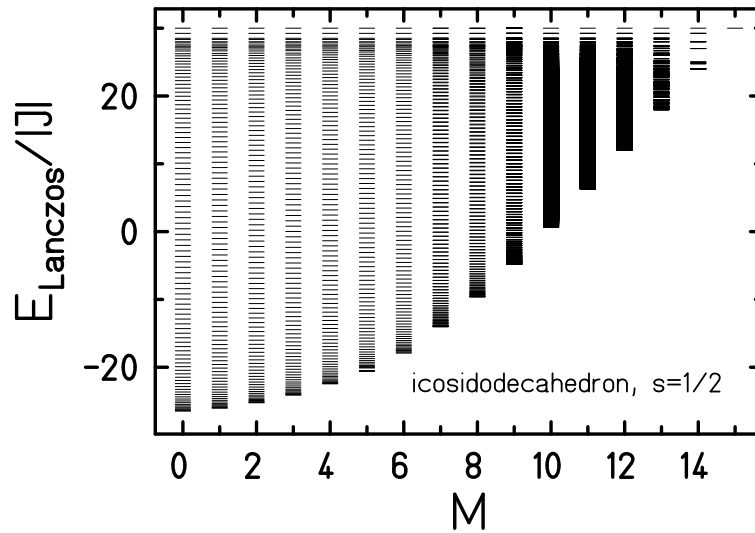
J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

Icosidodecahedron $s = 1/2$



Exp. data: A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, Chem. Commun., 3351 (2009).

Icosidodecahedron $s = 1/2$



The true spectrum will be much denser. This is miraculously compensated for by the weights.

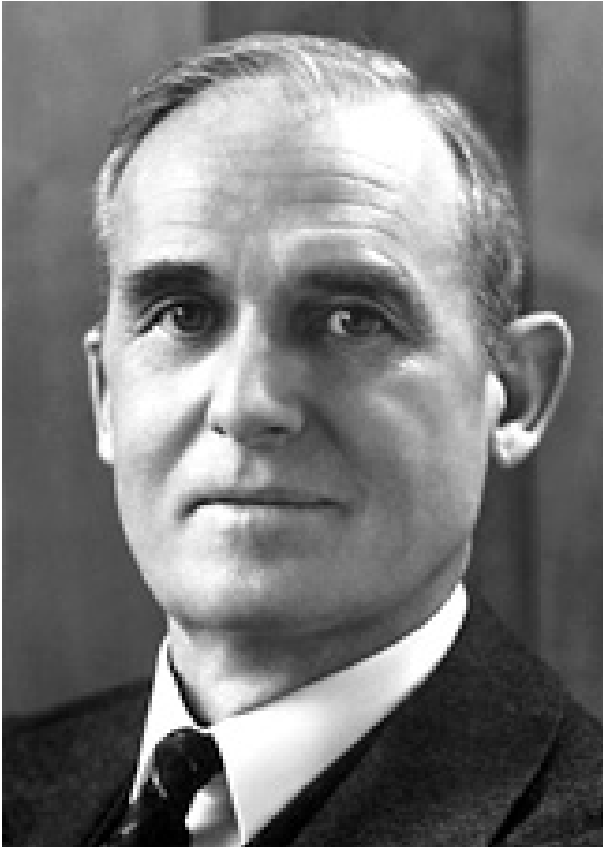
$$Z(T, B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{\nu=1}^R \sum_{n=1}^{N_L} \exp\{-\beta \epsilon_n\} |\langle n(\nu, \Gamma) | \nu, \Gamma \rangle|^2$$

J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535 (2010).

The magnetocaloric effect

(You'll love it!)

Sub-Kelvin cooling: Nobel prize 1949



The Nobel Prize in Chemistry 1949 was awarded to William F. Giaouque *for his contributions in the field of chemical thermodynamics, particularly concerning the behaviour of substances at extremely low temperatures.*

Sub-Kelvin cooling: Nobel prize 1949

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LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to 1.5°K.

On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at about 1.5°, a temperature of 0.25°K was attained.

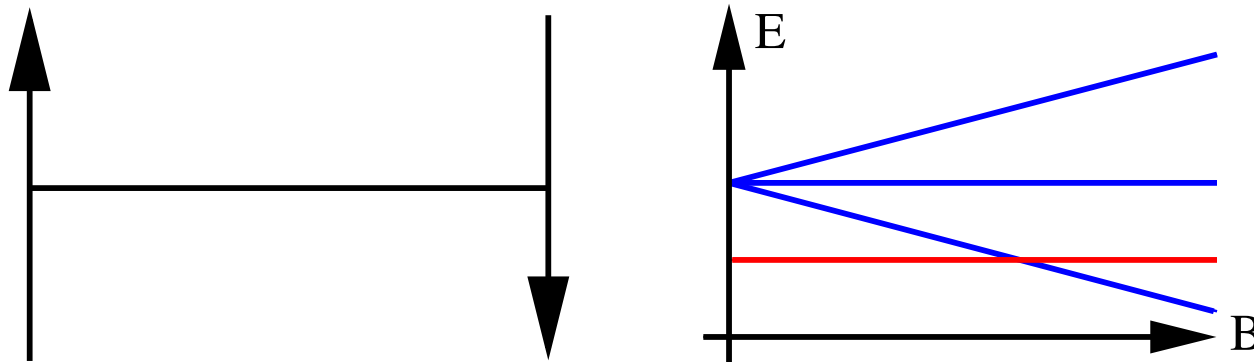
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. GIAUQUE
D. P. MACDOUGALL

Department of Chemistry,
University of California,
Berkeley, California,
April 12, 1933.

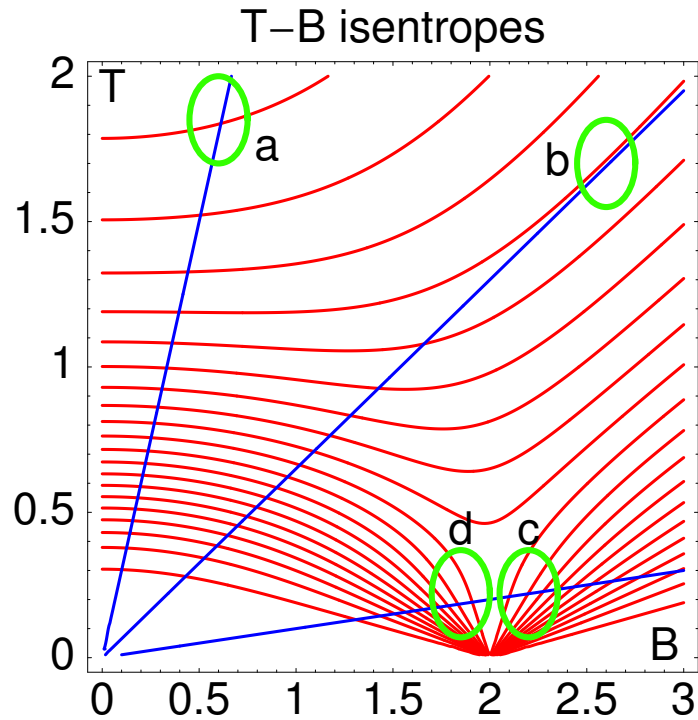
W. F. Giauque and D. MacDougall, *Phys. Rev.* **43**, 768 (1933).

Magnetocaloric effect – af $s = 1/2$ dimer



- Singlet-triplet level crossing causes a peak of S at $T \approx 0$ as function of B .
- $M(T = 0, B)$ and $S(T = 0, B)$ not analytic as function of B .
- $M(T = 0, B)$ jumps at B_c ; $S(T = 0, B_c) = k_B \ln 2$, otherwise zero.

Magnetocaloric effect – af $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

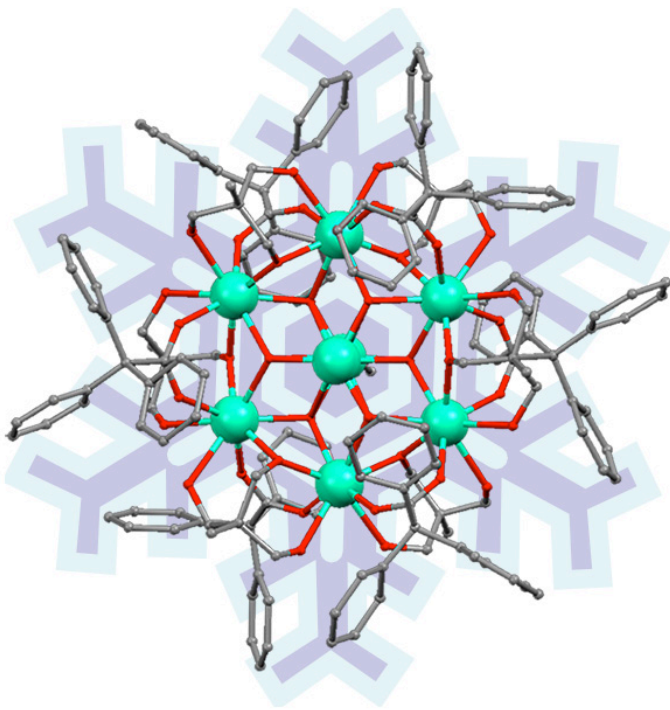
Magnetocaloric effect:

- (a) reduced,
- (b) the same,
- (c) enhanced,
- (d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

Gd₇ – Magnetocalorics



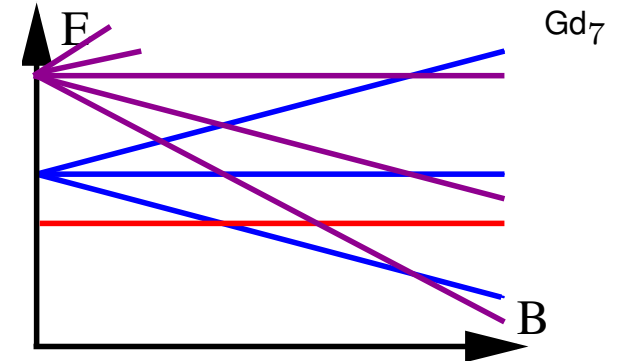
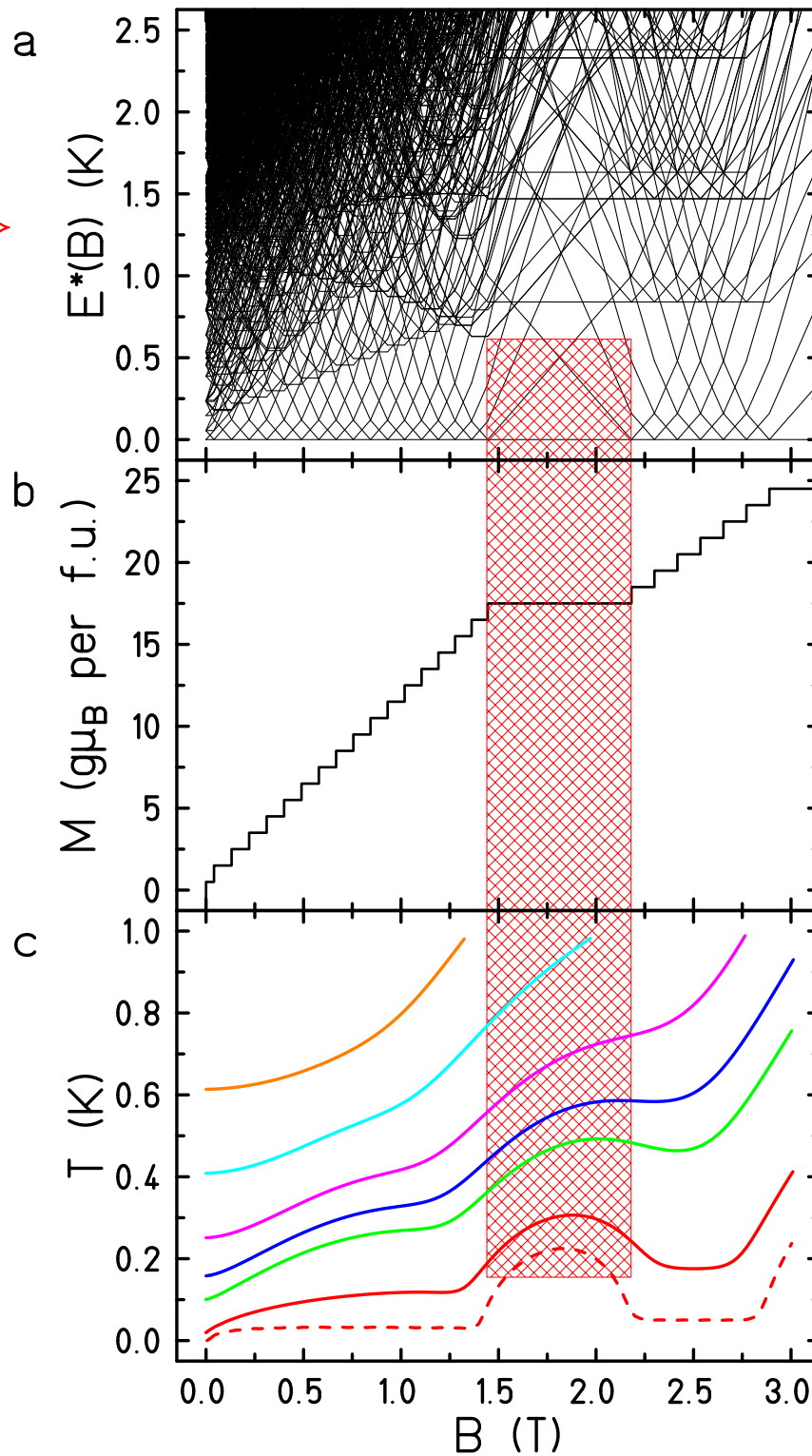
- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $$\underline{H} = -2 \sum_{i < j} J_{ij} \vec{s}_i \cdot \vec{s}_j + g \mu_B B \sum_i^N s_i^z$$

 $J_1 = -0.090(5) \text{ K}, J_2 = -0.080(5) \text{ K}$
 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).

← ← → → □ ? *

not dangerous ⇒

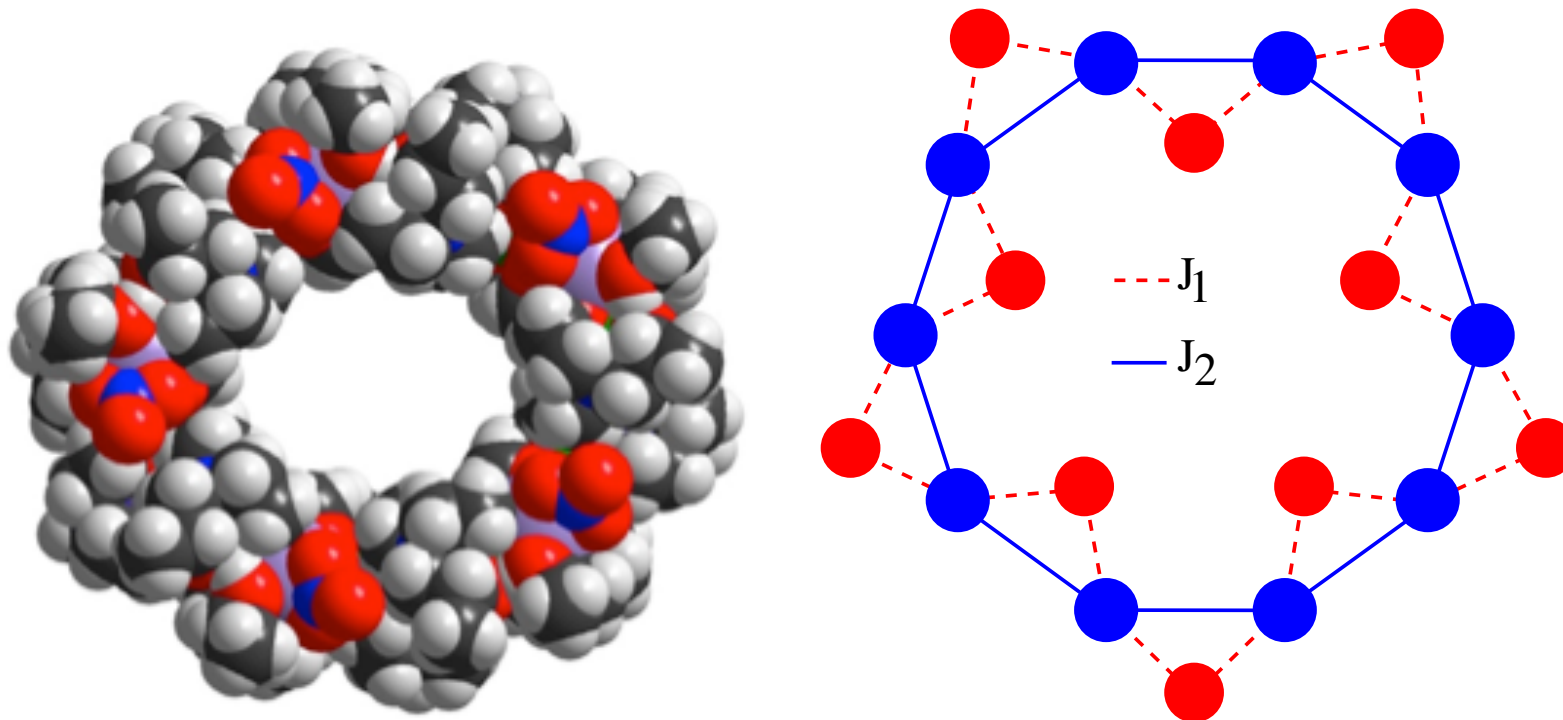


The molecular barbecue:
isentropic broiling!

$Gd_{10}Fe_{10}$

(Main course is near!)

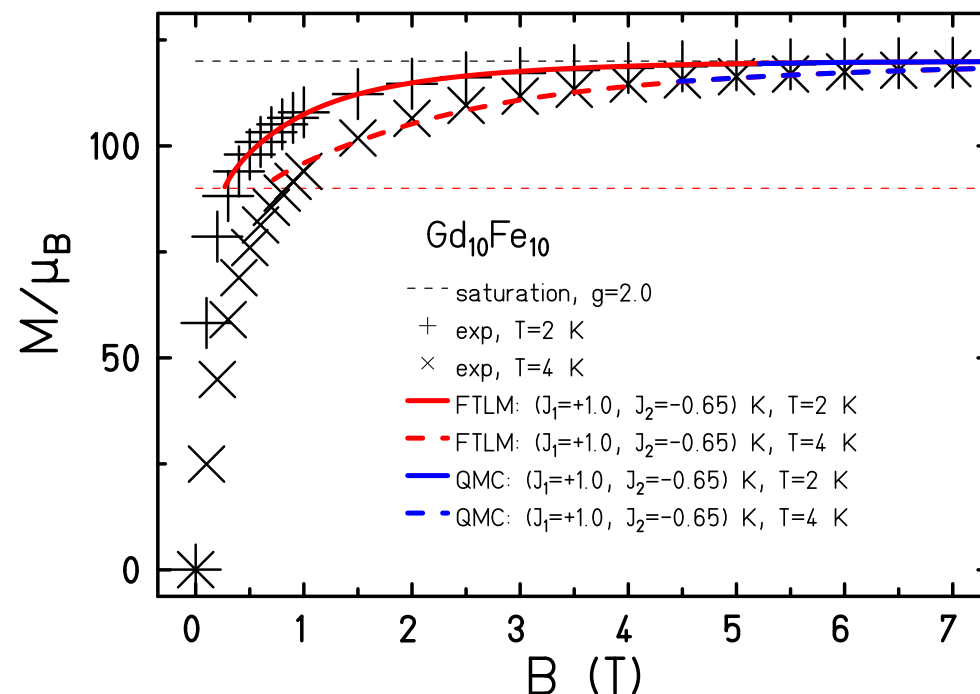
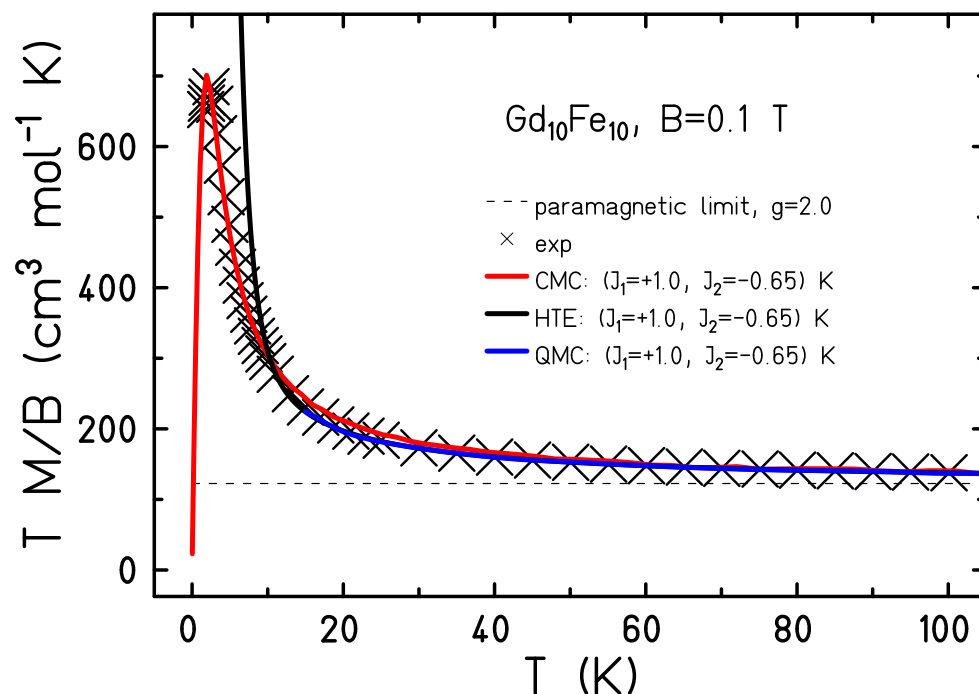
Gd₁₀Fe₁₀ – structure



blue: Fe ($s = 5/2$), red: Gd ($s = 7/2$)

Amer Baniodeh, Nicola Magnani, Yanhua Lan, Gernot Buth, Christopher E. Anson, Johannes Richter, Marco Affronte, Jürgen Schnack, Annie K. Powell, *High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality*, submitted

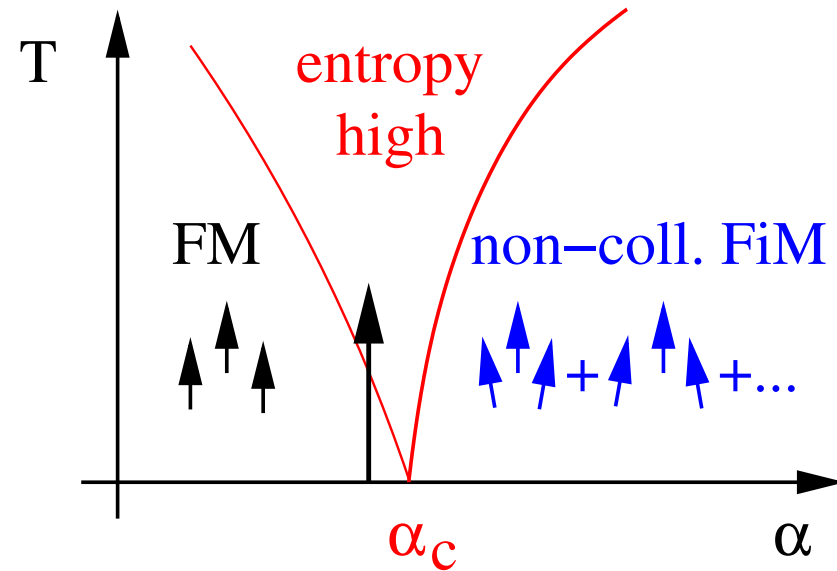
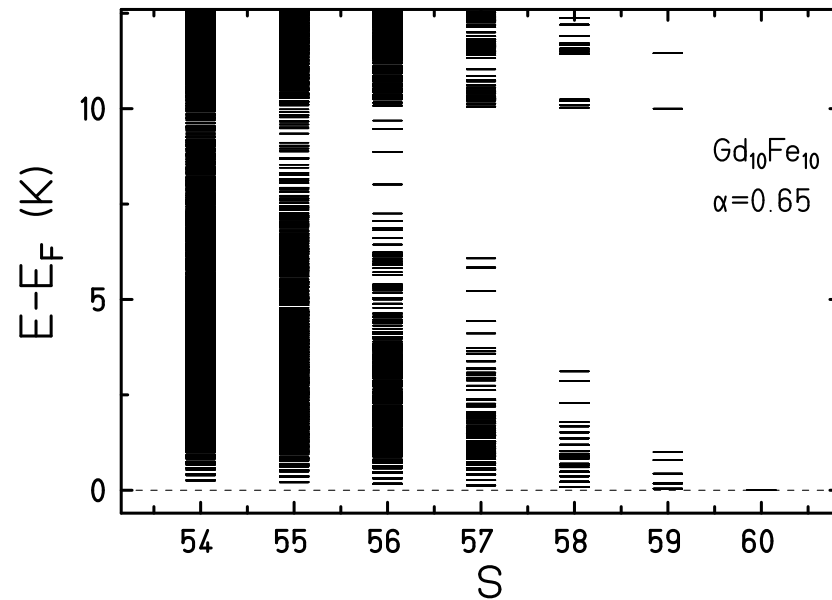
Gd₁₀Fe₁₀ – How to find the parameters?



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

Amer Baniodeh, Nicola Magnani, Yanhua Lan, Gernot Buth, Christopher E. Anson, Johannes Richter, Marco Affronte, Jürgen Schnack, Annie K. Powell, *High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality*, submitted

Gd₁₀Fe₁₀ – Why is it interesting?



⇒ $\alpha_{\text{Gd}_{10}\text{Fe}_{10}} = |J_2|/J_1 = 0.65$ (1) ⇒ $\alpha_c = s_{\text{Gd}}/(2s_{\text{Fe}}) = 0.7$ (2,3)

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

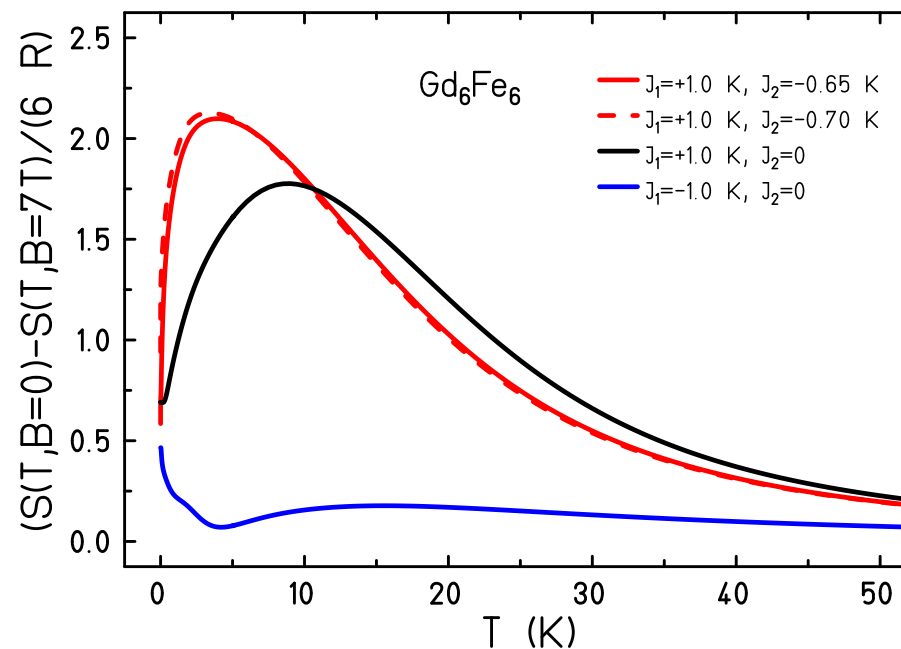
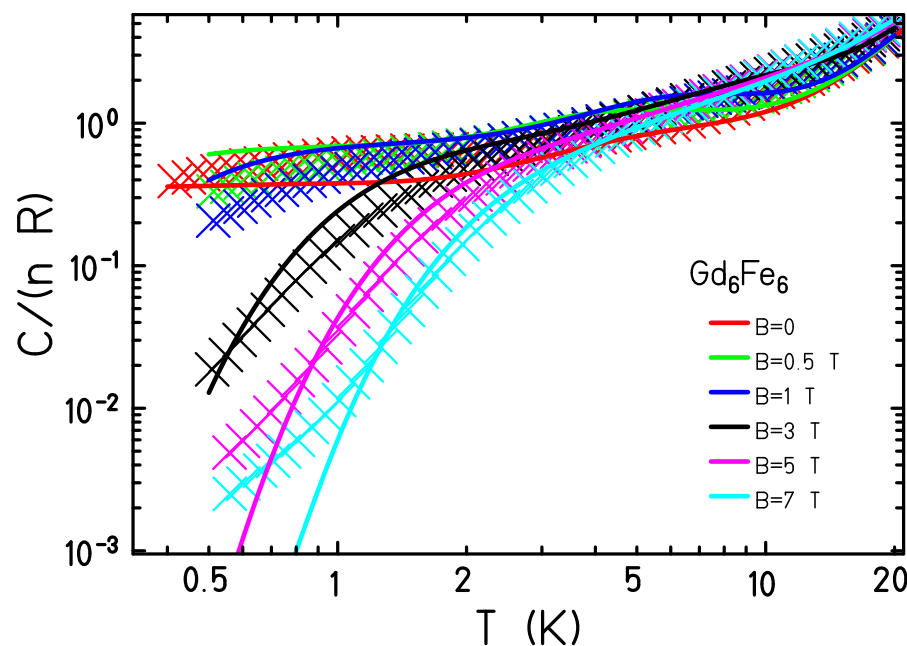
⇒ at α_c flat band, extensive entropy (2,3)

(1) our submitted manuscript

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

(3) D. V. Dmitriev and V. Y. Krivnov, Phys. Rev. B **92**, 184422 (2015).

Gd₁₀Fe₁₀ – magnetocalorics

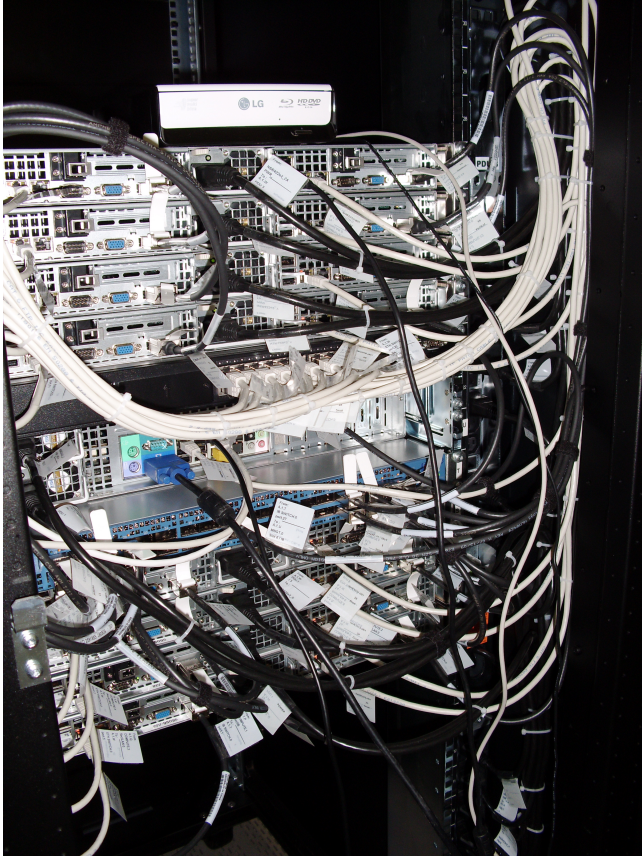


⇒ very large specific heat as well as isothermal entropy changes

⇒ entropy of Gd₁₀Fe₁₀ almost the same as for critical system

Amer Baniodeh, Nicola Magnani, Yanhua Lan, Gernot Buth, Christopher E. Anson, Johannes Richter, Marco Affronte, Jürgen Schnack, Annie K. Powell, *High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality*, submitted

Summary



- Sawtooth chain has a rich phase diagram: magnetization plateaux, magnetization jumps, flat bands, quantum phase transitions.
- Finite-temperature Lanczos is a good approximate method for Hilbert space dimensions smaller than 10^{10} .
- Isentropes for interacting systems are much richer than for paramagnets. Good for applications away from $(T = 0, B = 0)$.
- Outlook: maybe we can squeeze the molecule across the QCP.

J. Schnack, H.-J. Schmidt, J. Richter, and J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001).

J. Schulenburg, A. Honecker, J. Schnack, J. Richter, and H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002).

J. Schnack, Dalton Trans. **39**, 4677 (2010).

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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- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); D. Collison, R.E.P. Winpenny, E.J.L. McInnes, F. Tuna (Man U); L. Cronin, M. Murrie (Glasgow); E. Brechin (Edinburgh); H. Nojiri (Sendai, Japan); A. Postnikov (Metz); M. Evangelisti (Zaragosa); A. Honecker (U de Cergy-Pontoise); E. Garlatti, S. Carretta, G. Amoretti, P. Santini (Parma); A. Tennant (ORNL); Gopalan Rajaraman (Mumbai)
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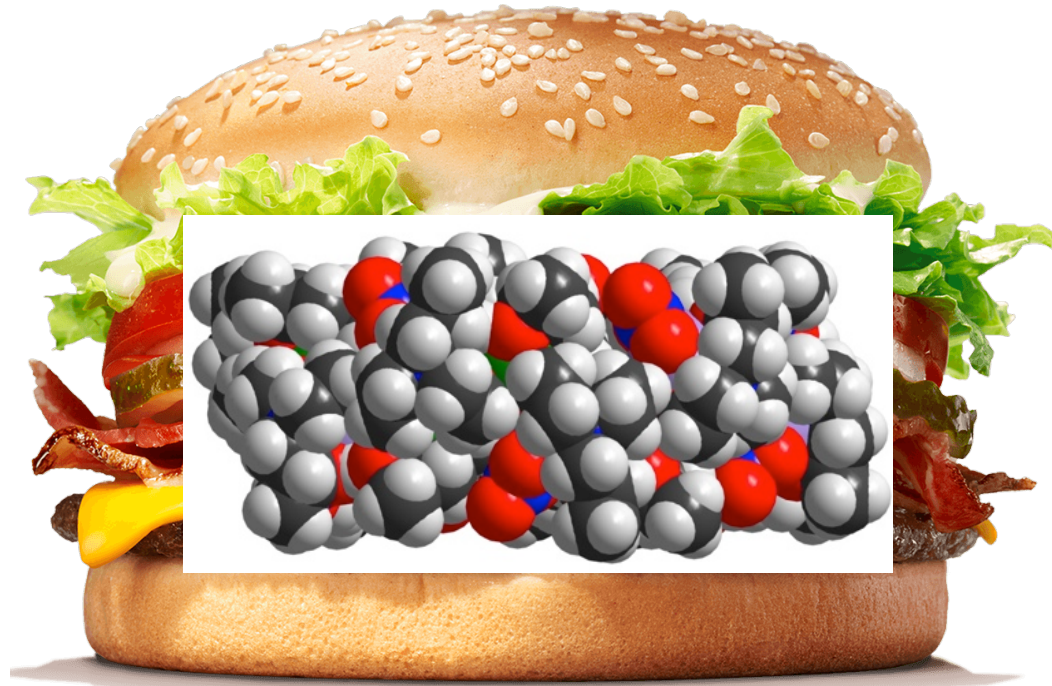
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The end.

New Power Point trends: no ThankYou page!

1. Teil: Diese Fehler sind tödlich für Ihre Power-Point-Präsentation
2. Teil: **Wieviele Bulletpoints sind gut? - Kein einziger!**
3. Teil: **Die drei großen Missverständnisse der Power-Point-Präsentation**
4. Teil: **Information alleine ist überflüssig bis schädlich**
5. Teil: **Bitte keine VielenDankfürIhreAufmerksamkeitFolien!**

Damit meine Aussagen und Botschaften in den Gehirnen meiner Zuhörer haften bleiben, muss ich dafür sorgen, dass diese Gehirne auf der "Es gibt was zu essen" Basis funktionieren. Die Psychologen nennen das "heiße Kognitionen".



Man does not live by bread alone!

Gd₁₀Fe₁₀!

Molecular Magnetism Web

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