Theoretical modelling of large magnetic molecules for magnetocalorics

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University of Cambridge, UK, 19 May 2025

UNIVERSITÄT BIELEFELD
Fakultät für Physik

Imagine . . .

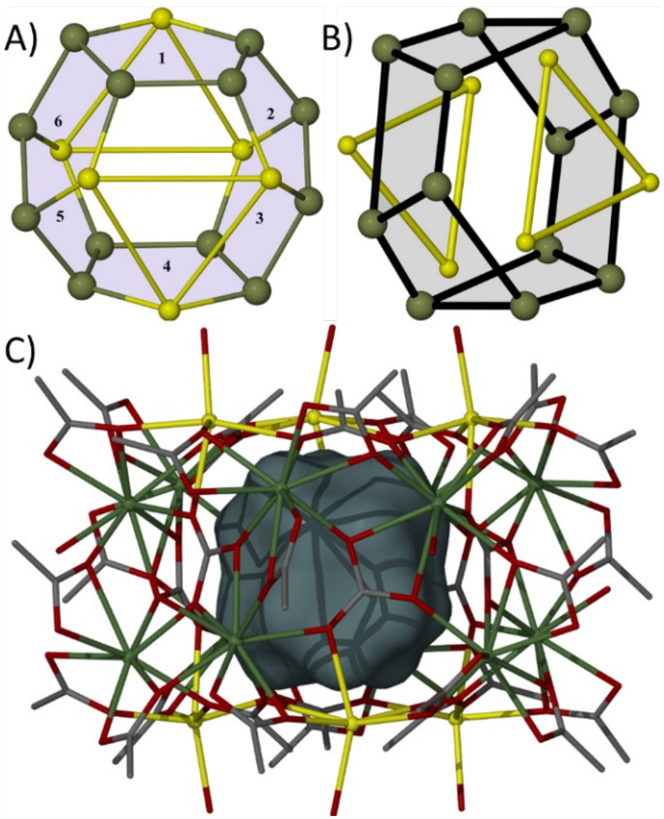
Imagine, your friendly colleague

from chemistry asks you whether

you can model their large magnetic molecules

as for instance . . .

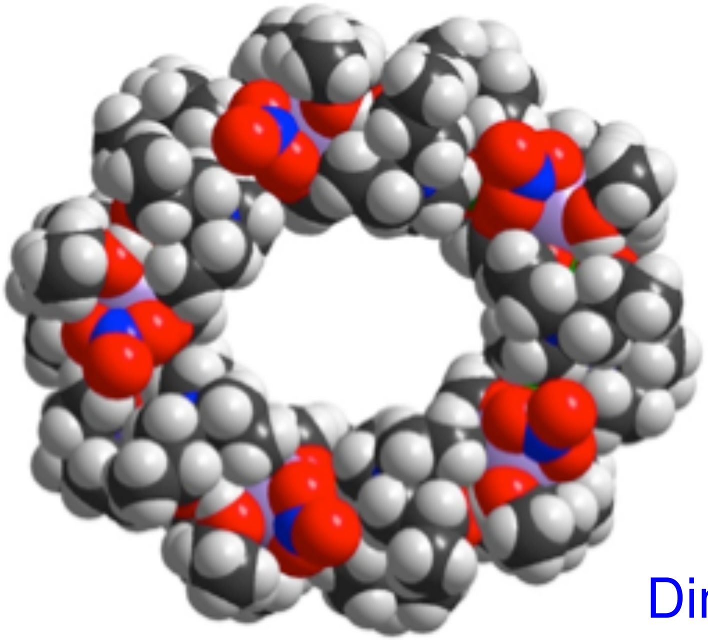
Gd_{12} for molecular magnetocalorics!



Dimension of Hilbert space 68,719,476,736!

JACS **145**, 7743-7747 (2023)

$Fe_{10}Gd_{10}$ with $S = 60$ and close to a quantum phase transition!



Dimension of Hilbert space 64,925,062,108,545,024!

npj Quantum Materials **3**, 10 (2018)

Which software could deal with such a problem?

~~MAGPACK~~

~~EasySpin~~

~~PHI~~

$\Rightarrow$ What to do? $\Leftarrow$

J. Schnack, Contemporary Physics **60**, 127-144 (2019)

Yes, we can!

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

1. Introduction to MCE
2. The numerical problem
3. Random vector machinery
4. Calorics close to a QPT
5. Anisotropic molecules

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

The magnetocaloric effect

Magnetocaloric effect – Basics

- Heating or cooling in a varying magnetic field. Predicted, discussed, discovered by Thomson, Warburg, Weiss, and Piccard (1).
- Typical rates: $0.5 \ldots 2$ K/T.
- Giant magnetocaloric effect: $3 \ldots 4$ K/T e.g. in $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leq 0.5$).
- Scientific goal I: room temperature applications.
- Scientific goal II: sub-Kelvin cooling.

(1) A. Smith, Eur. Phys. J. H **38**, 507 (2013).

Magnetocaloric effect – cooling rate

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

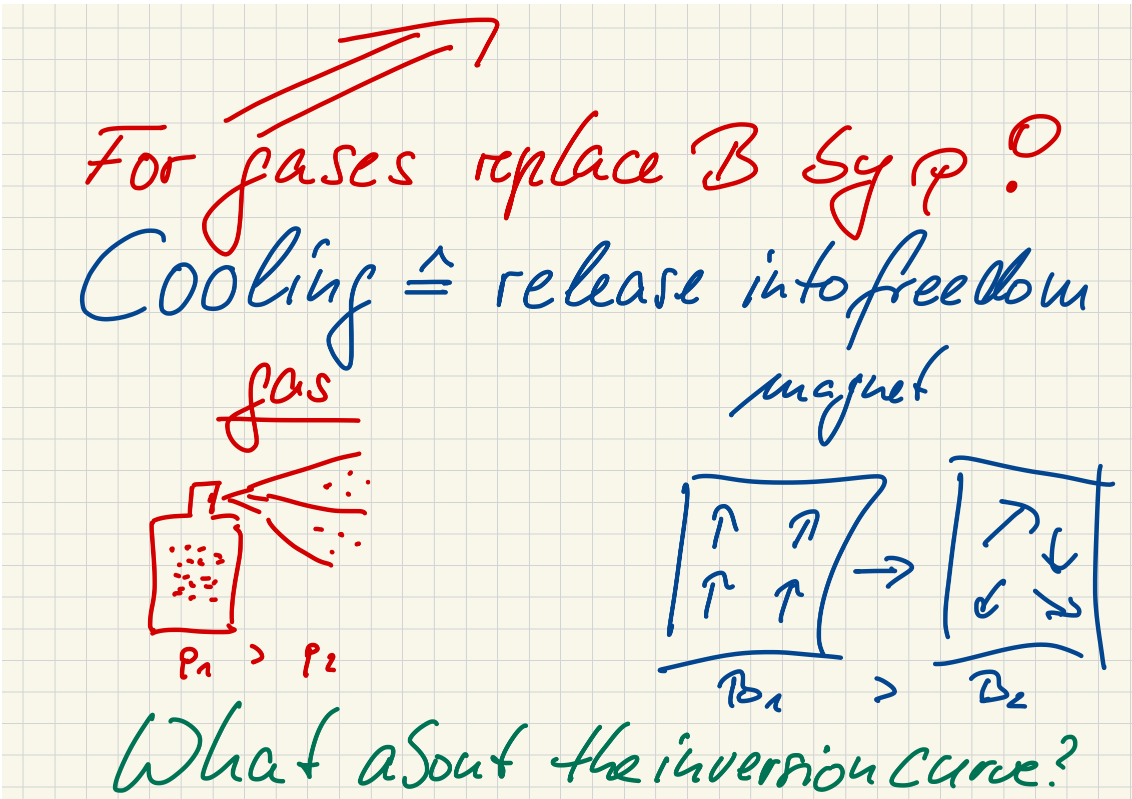
$C = C_B = T\left(\frac{\partial S}{\partial T}\right)_B$: heat capacity at constant field

MCE especially large at large isothermal entropy changes, i.e. at phase transitions (1), close to quantum critical points (2), or due to the condensation of independent magnons (3), if C smooth.

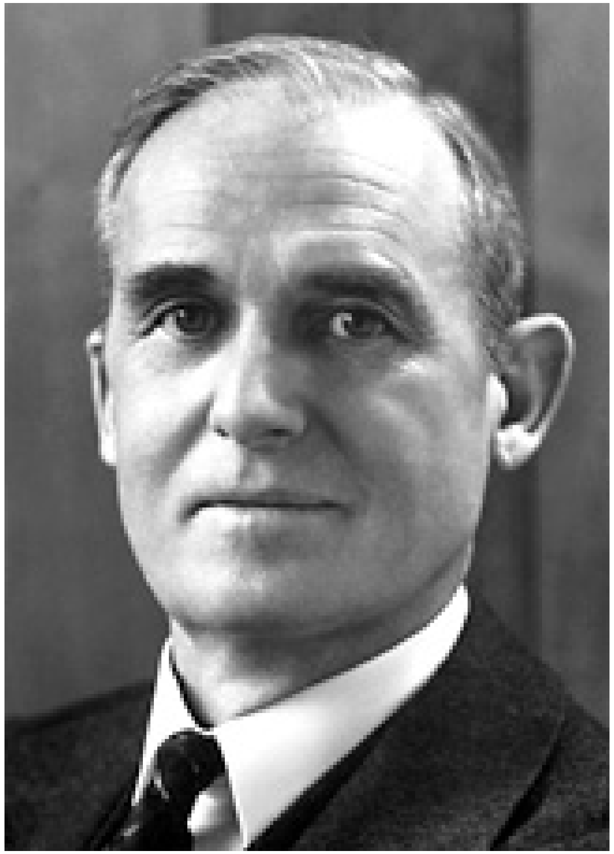
(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001).
(2) Lijun Zhu, M. Garst, A. Rosch, and Qimiao Si, Phys. Rev. Lett. **91**, 066404 (2003).
B. Wolf, Y. Tsui, D. Jaiswal-Nagar, U. Tutsch, A. Honecker, K. Removic-Langer, G. Hofmann, A. Prokofiev, W. Assmus, G. Donath, M. Lang, Proceedings of the National Academy of Sciences **108**, 6862 (2011).
(3) M.E. Zhitomirsky, A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004).

Magnetocaloric effect – cooling rate

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$



Sub-Kelvin cooling: Nobel prize 1949



The Nobel Prize in Chemistry 1949 was awarded to William F. Giauque *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

768 LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ 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 $Gd_2(SO_4)_3 \cdot 8H_2O$ 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.

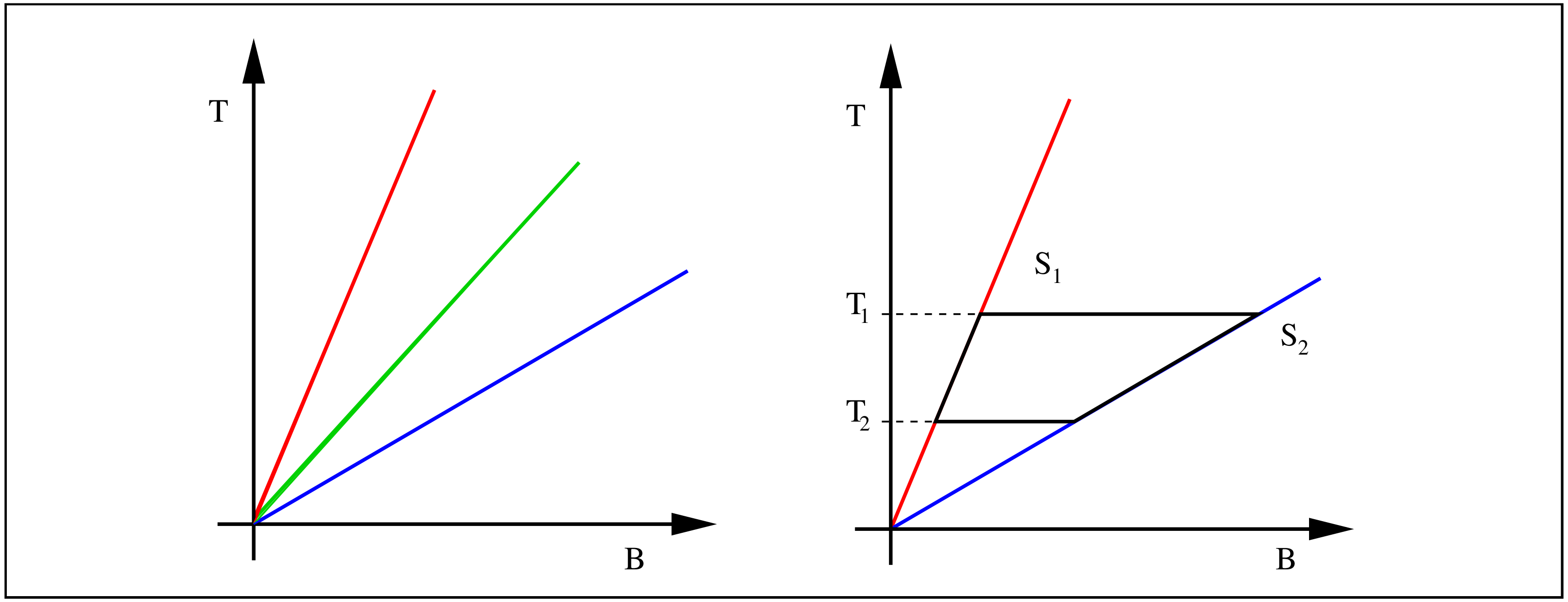
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. Giauque
D. P. MacDougall

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

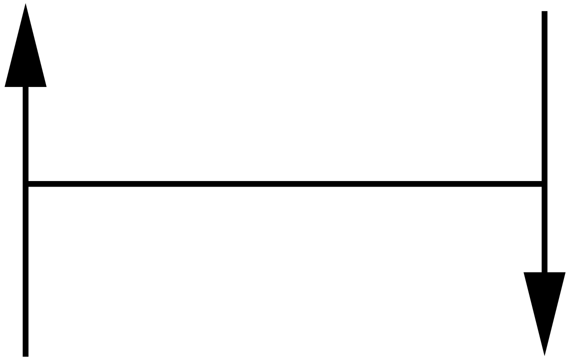
W. F. Giauque and D. MacDougall, Phys. Rev. **43**, 768 (1933).

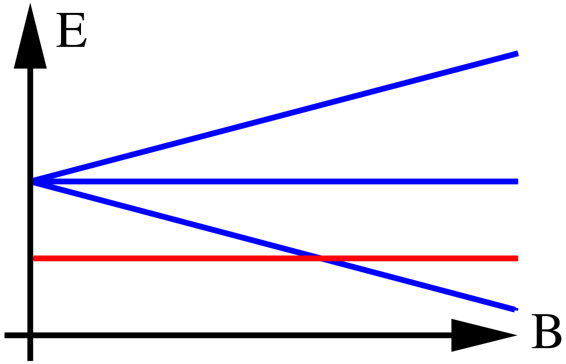
Magnetocaloric effect – Paramagnets



- Ideal paramagnet: $S(T,B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

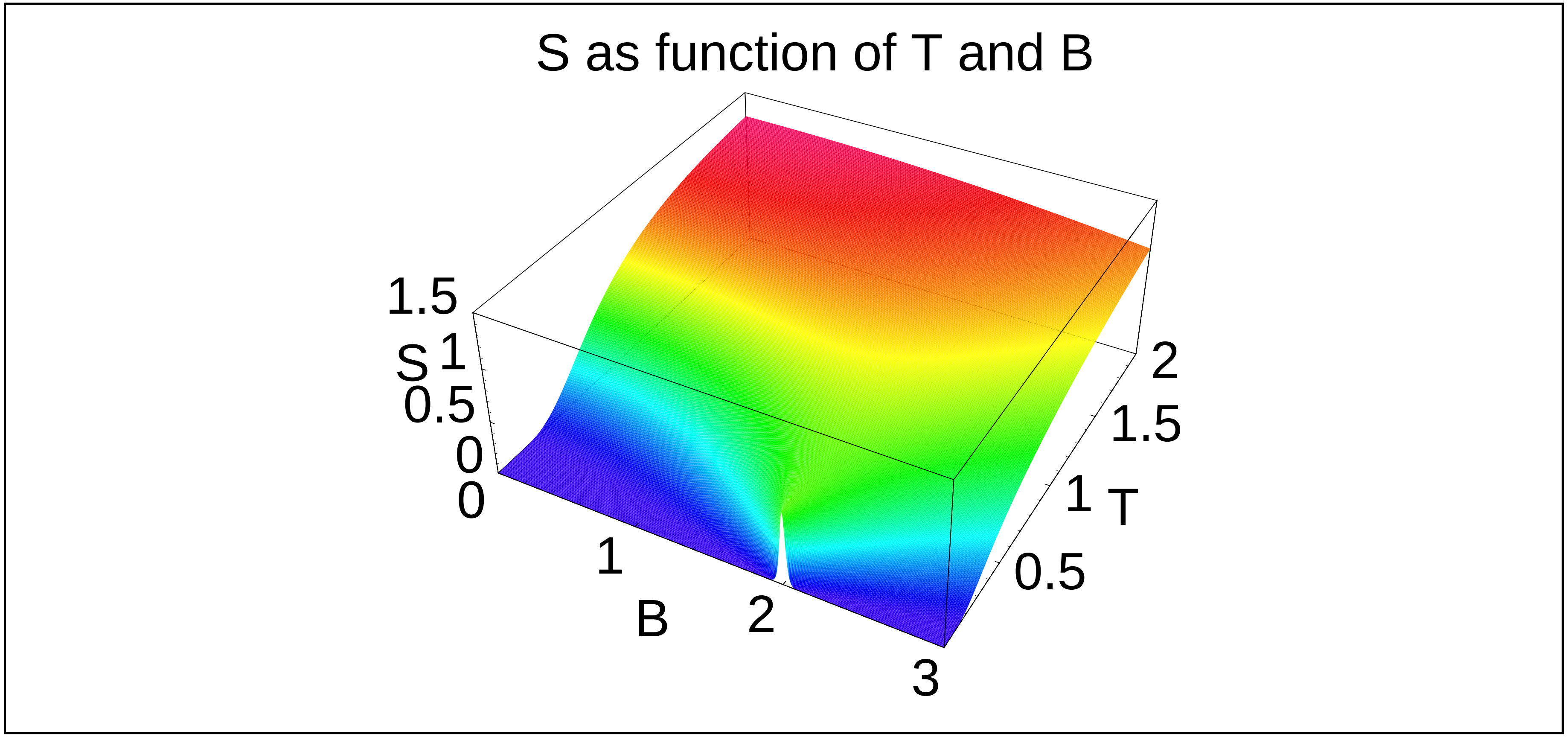
Magnetocaloric effect – af $s = 1/2$ dimer





- 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; $\quad S(T=0,B_c) = k_B \ln 2$, otherwise zero.

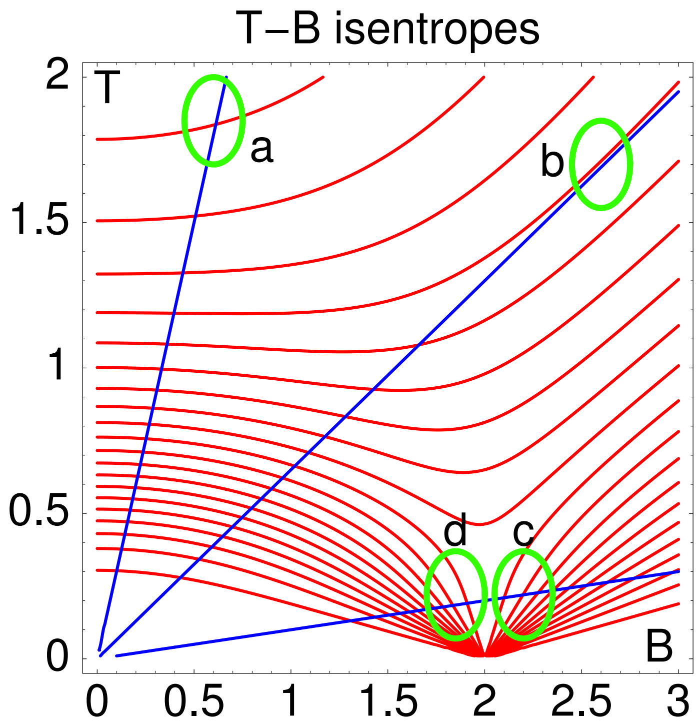
Magnetocaloric effect – af $s = 1/2$ dimer



$S(T = 0, B) \neq 0$ at level crossing due to degeneracy

O. Derzhko, J. Richter, Phys. Rev. B **70**, 104415 (2004)

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.

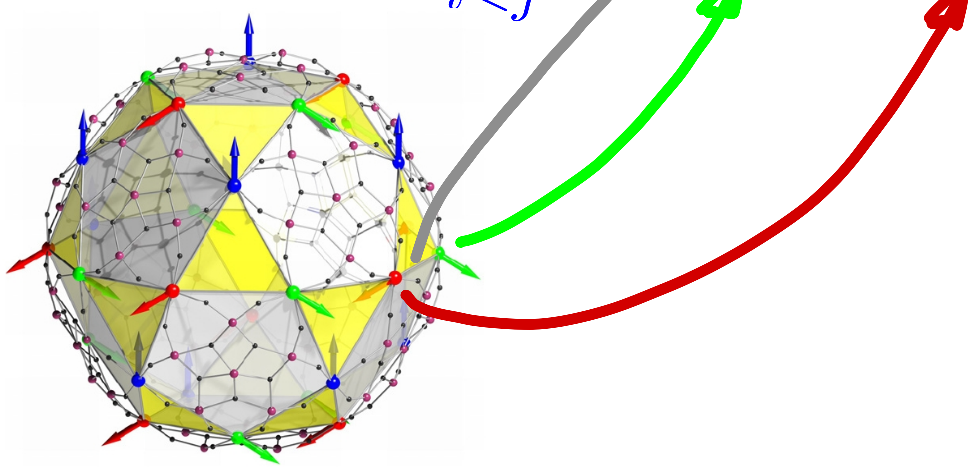
Case (d) does not occur for a paramagnet.

Let’s calculate something!

You have got an idea about the modeling!

Heisenberg Zeeman

$$\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) + g\, \mu_B\, B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$



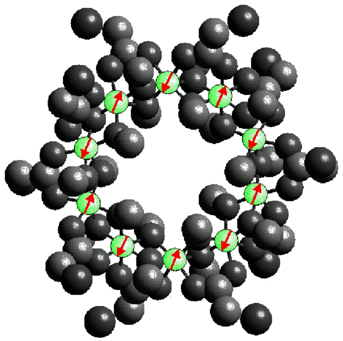
You have to solve the Schrödinger equation!

$$\underset{\sim}{H} \mid \phi_n \rangle = E_n \mid \phi_n \rangle$$

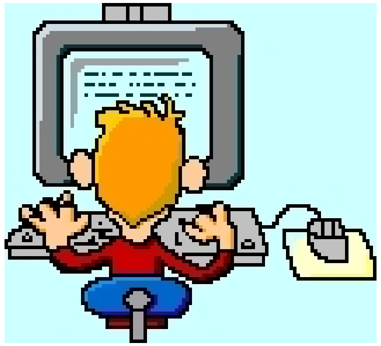
Eigenvalues E_n and eigenvectors $\mid \phi_n \rangle$

- needed for spectroscopy (EPR, INS, NMR);
- needed for thermodynamic functions (magnetization, susceptibility, heat capacity);
- needed for time evolution (pulsed EPR, simulate quantum computing, thermalization).

In the end it’s always a big matrix!



$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



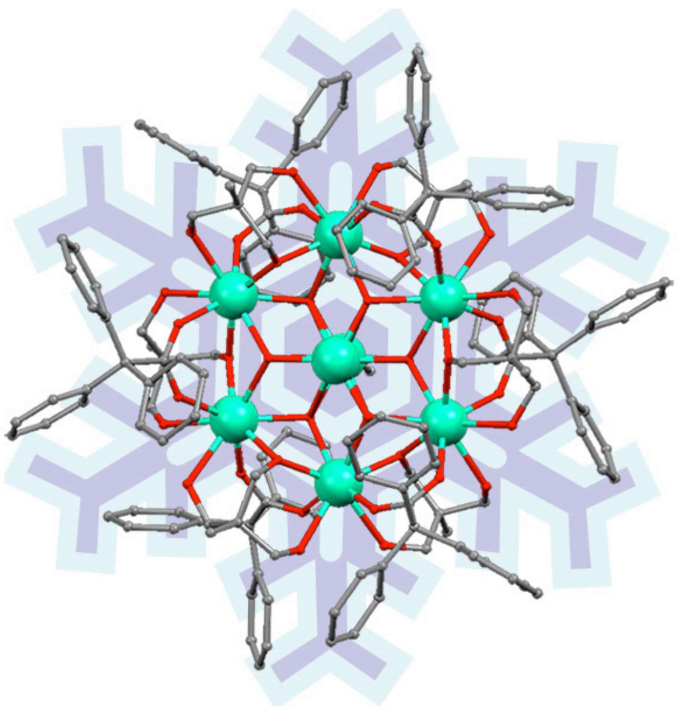
$\mathrm{Fe}_{10}^{\mathrm{III}}$: $N = 10$, $s = 5/2$, $\dim(\mathcal{H}) = (2s+1)^N$

Dimension=**60,466,176**. Maybe too big?

Let’s start with something small:

Gd_7

Gd$_7$ – Basics

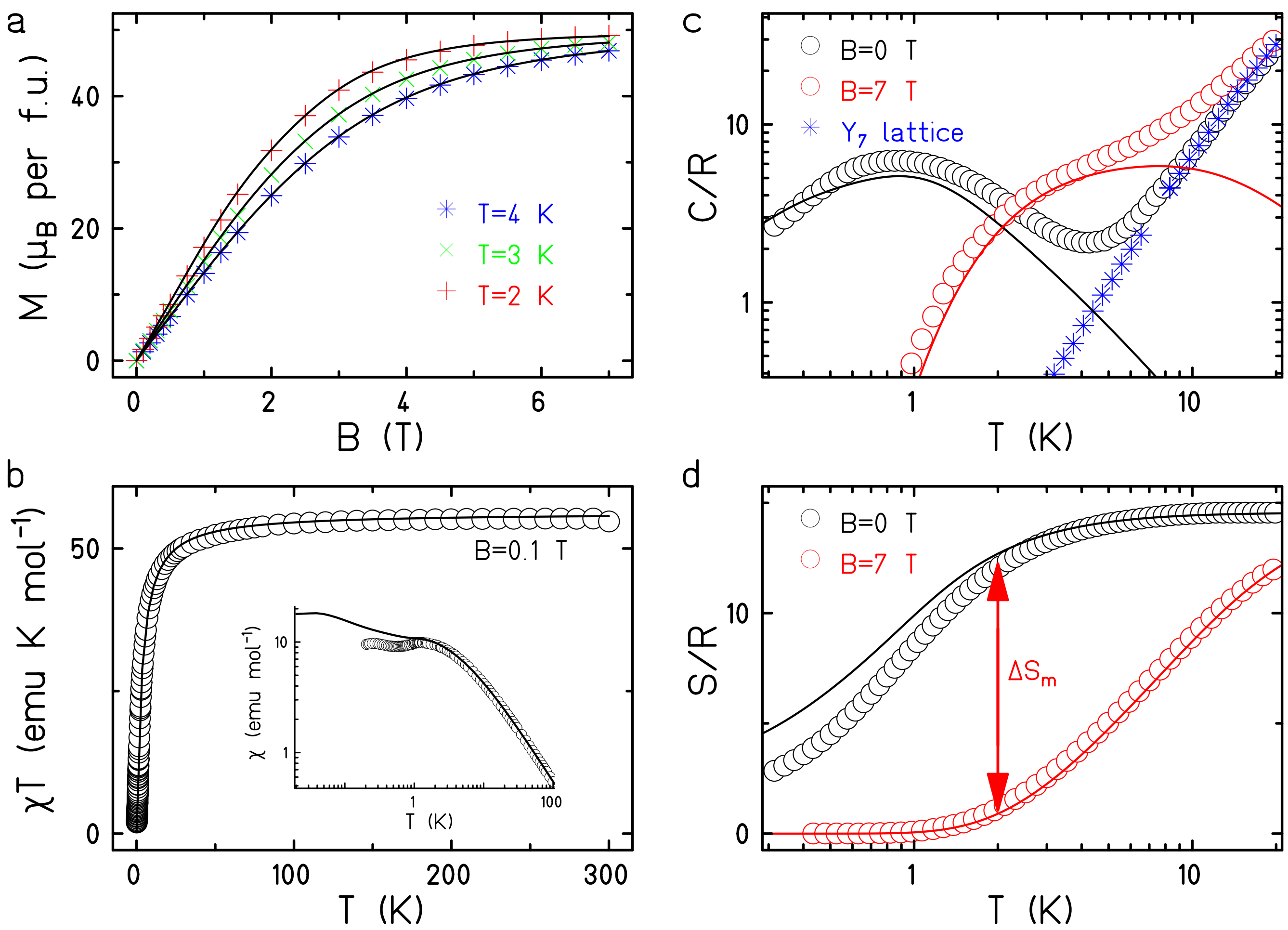


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij} \, \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g \, \mu_B \, B \sum_i^N \, \underset{\sim}{s}_i^z$

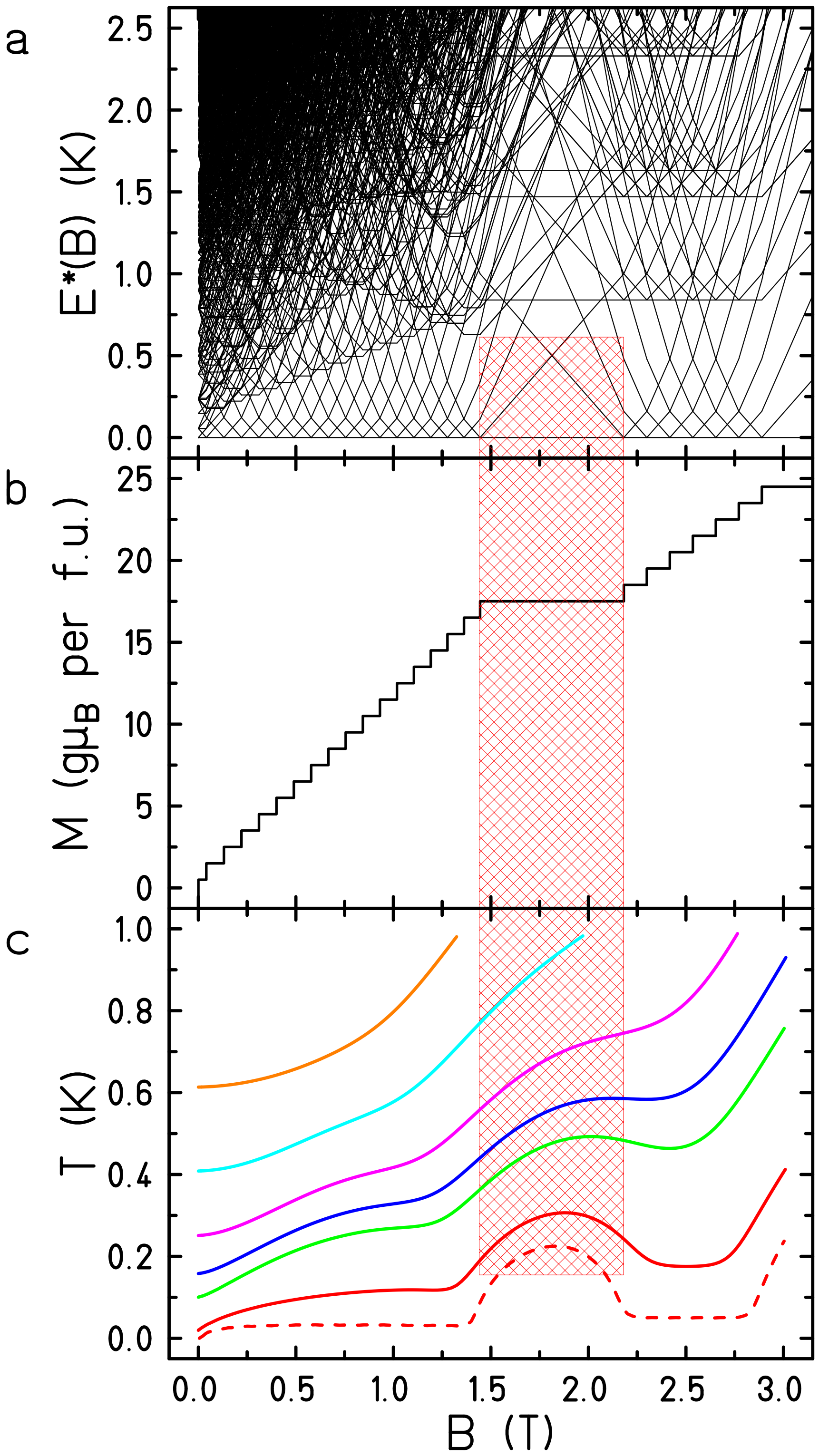
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

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

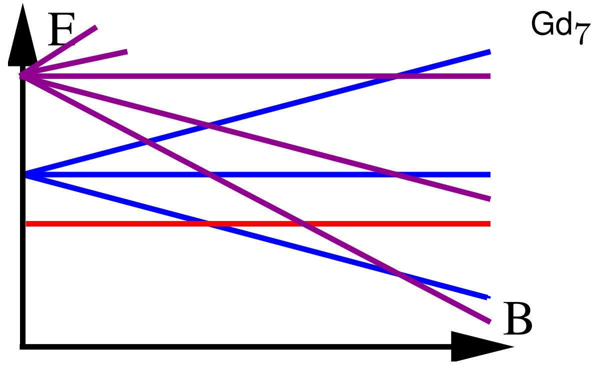
Gd$_7$ – experiment & theory



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

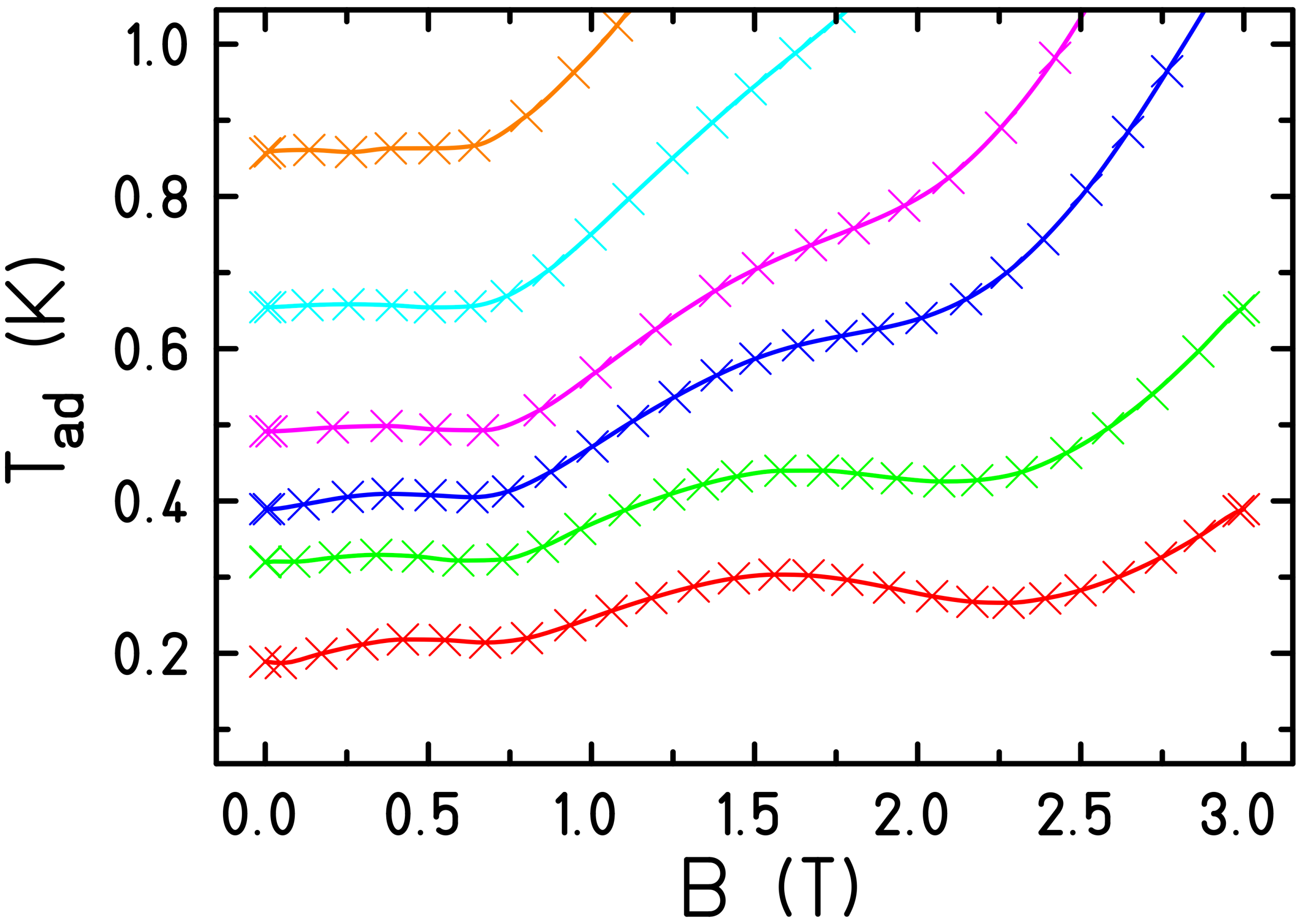


a
b
c
E*(B) (K)
M (gμB per f.u.)
T (K)
B (T)
0.0
0.5
1.0
1.5
2.0
2.5
3.0



E
Gd7
B

Gd$_7$ – Experimental cooling



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

Typicality approach to molecular magnetism

Can we evaluate the partition function

$$Z(T,B) = \text{tr}\left(\exp\left[-\beta \underset{\sim}{H}\right]\right)$$

without diagonalizing the Hamiltonian?

Yes, with magic!

Solution I: trace estimators

$$\text{tr}\left(\underset{\sim}{Q}\right) \approx \langle\, r \,|\, \underset{\sim}{Q} \,|\, r \,\rangle = \sum_{\nu} \langle\, \nu \,|\, \underset{\sim}{Q} \,|\, \nu \,\rangle + \sum_{\nu \neq \mu} r_\nu r_\mu \langle\, \nu \,|\, \underset{\sim}{Q} \,|\, \mu \,\rangle$$

$$|\, r \,\rangle = \sum_{\nu} r_\nu \,|\, \nu \,\rangle \,, \quad r_\nu = \pm 1$$

- $|\, \nu \,\rangle$ some orthonormal basis of your choice; not the eigenbasis of $\underset{\sim}{Q}$, since we don't know it.
- $r_\nu = \pm 1$ random, equally distributed. Rademacher vectors.
- Amazingly accurate, bigger (Hilbert space dimension) is better.

M. Hutchinson, Communications in Statistics - Simulation and Computation **18**, 1059 (1989).

Solution II: Krylov space representation

$$\exp\left[-\beta \underset{\sim}{H}\right] \;\approx\; \underset{\sim}{1} - \beta \underset{\sim}{H} + \frac{\beta^2}{2!}\underset{\sim}{H}^2 - \cdots \frac{\beta^{N_L-1}}{(N_L-1)!}\underset{\sim}{H}^{N_L-1}$$

applied to a state $\mid r \,\rangle$ yields a superposition of

$$\underset{\sim}{1} \mid r \,\rangle, \quad \underset{\sim}{H} \mid r \,\rangle, \quad \underset{\sim}{H}^2 \mid r \,\rangle, \quad \ldots \underset{\sim}{H}^{N_L-1} \mid r \,\rangle \;.$$

These (linearly independent) vectors span a small space of dimension N_L;
it is called Krylov space.

Let's diagonalize $\underset{\sim}{H}$ in this space!

Partition function I: simple approximation

$$Z(T,B) \quad \approx \quad \langle\, r\,|\, e^{-\beta \underset{\sim}{H}}\,|\, r\,\rangle \approx \sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}} |\langle\, n(r)\,|\, r\,\rangle|^2$$

$$O^{\mathrm{r}}(T,B) \quad \approx \quad \frac{\langle\, r\,|\, \underset{\sim}{O} e^{-\beta \underset{\sim}{H}}\,|\, r\,\rangle}{\langle\, r\,|\, e^{-\beta \underset{\sim}{H}}\,|\, r\,\rangle} = \frac{\langle\, r\,|\, e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{O} e^{-\beta \underset{\sim}{H}/2}\,|\, r\,\rangle}{\langle\, r\,|\, e^{-\beta \underset{\sim}{H}/2} e^{-\beta \underset{\sim}{H}/2}\,|\, r\,\rangle}$$

- Wow!!!
- One can replace a trace involving an intractable operator by an expectation value with respect to just ONE random vector evaluated by means of a Krylov space representation???
- Typicality = any random vector will do: $|\, r\,\rangle \equiv (T = \infty)$

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

Partition function II: Finite-temperature Lanczos Method

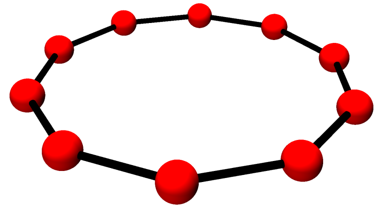
$$Z^{\text{FTLM}}(T,B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{r=1}^{R} \sum_{n=1}^{N_L} e^{-\beta \epsilon_n^{(r)}} |\langle\, n(r) \,|\, r \,\rangle|^2$$

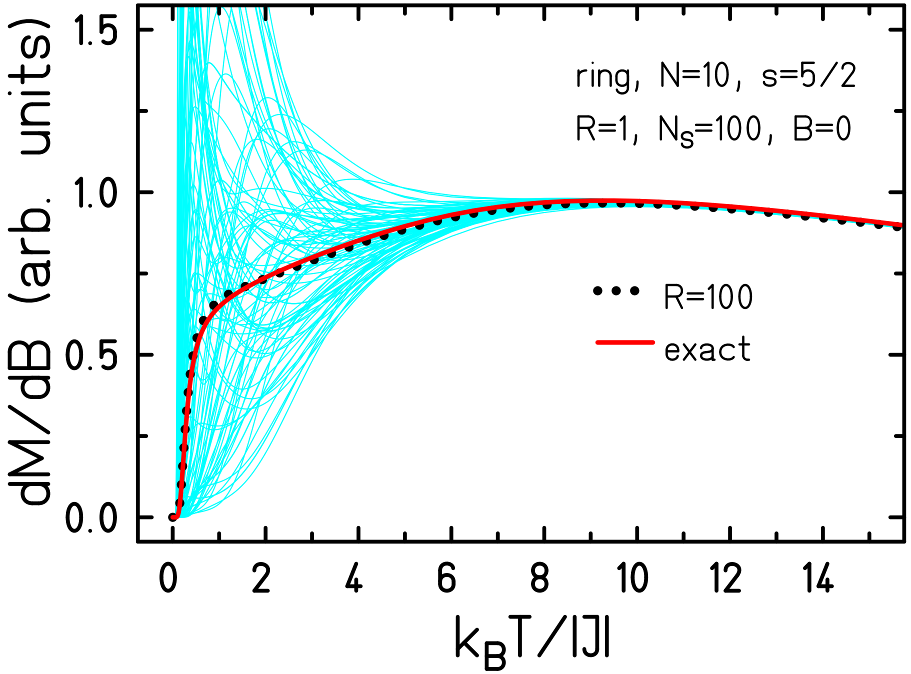
- Averaging over R random vectors is better.
- $|\, n(r) \,\rangle$ n-th Lanczos eigenvector starting from $|\, r \,\rangle$ (now normalized).
- Partition function replaced by a small sum: $R = 1 \dots 100$, $N_L \approx 100$.
- Use symmetries! Copy Hilbert subspaces!

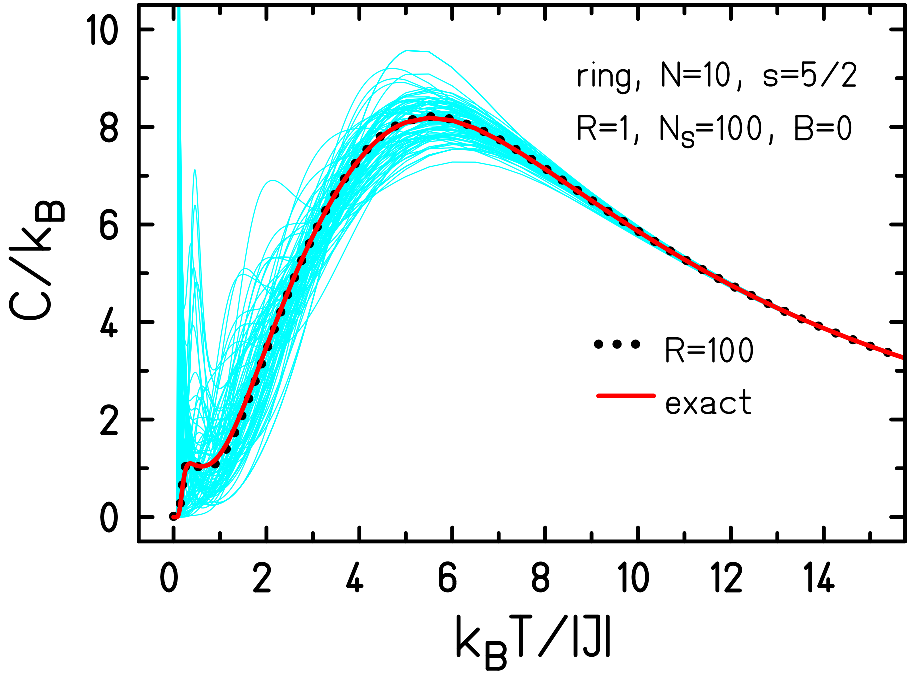
$$\text{Tr}\left(\underset{\sim}{S}^z e^{-\beta \underset{\sim}{H}} \right) \approx \sum_{M=M_{\text{min}}}^{M_{\text{max}}} \frac{\dim(\mathcal{H}(M))}{R} \sum_{r=1}^{R} \sum_{n=1}^{N_L} M e^{-\beta \epsilon_n^{(M,r)}} |\langle\, n(M,r) \,|\, M,r \,\rangle|^2$$

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

FTLM 1: ferric wheel





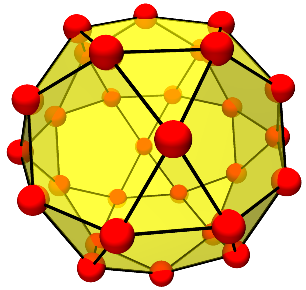


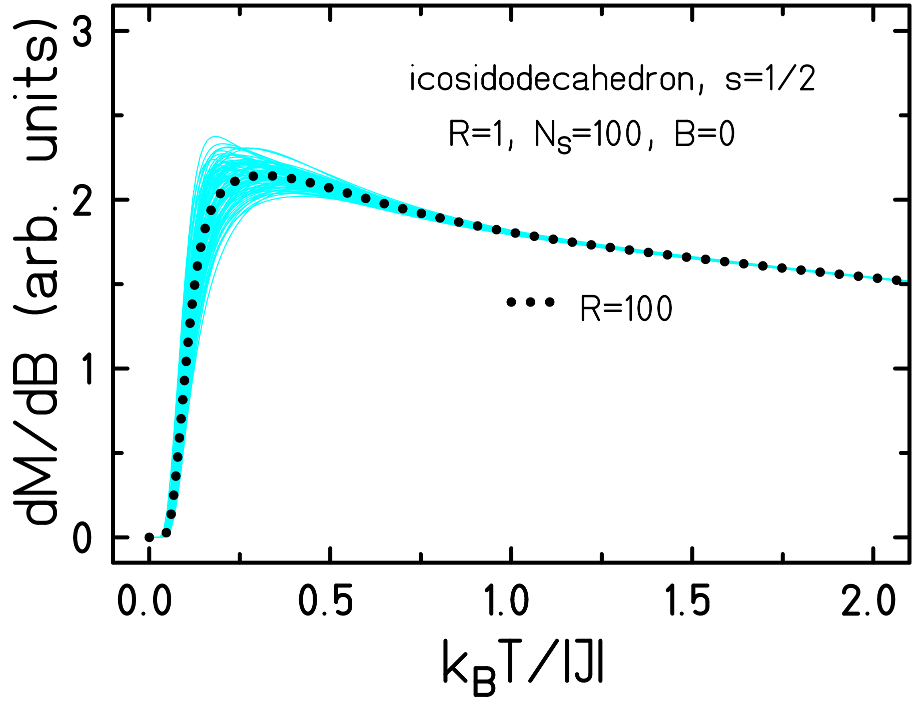
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

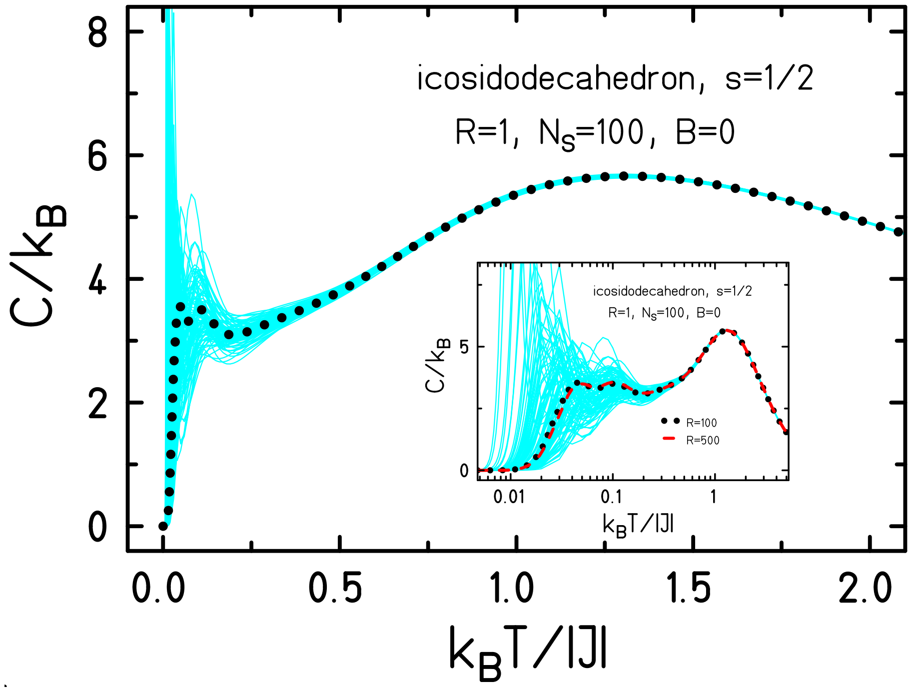
(2) SU(2) & D_2: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

(3) SU(2) & C_N: T. Heitmann, J. Schnack, Phys. Rev. B **99**, 134405 (2019)

FTLM 2: icosidodecahedron



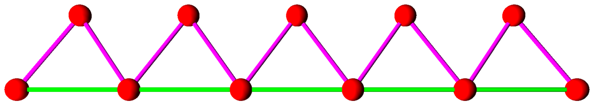


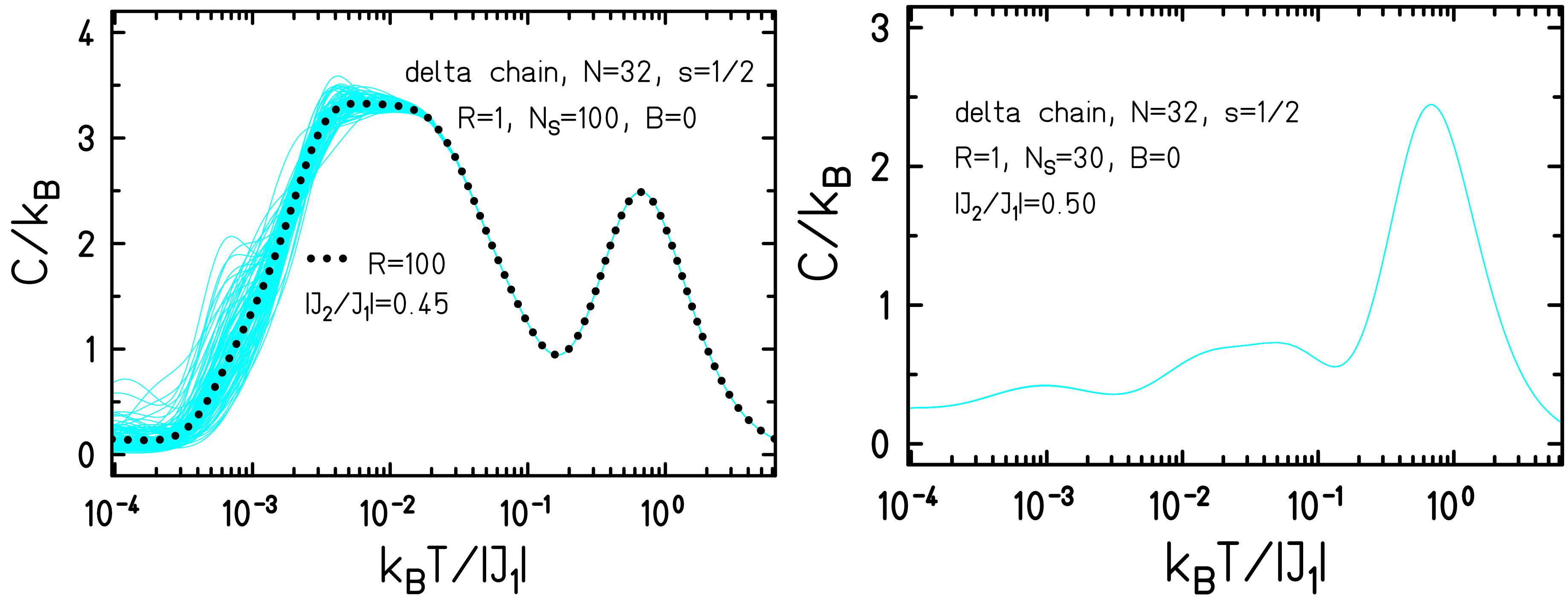


(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

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

FTLM 3: sawtooth chain





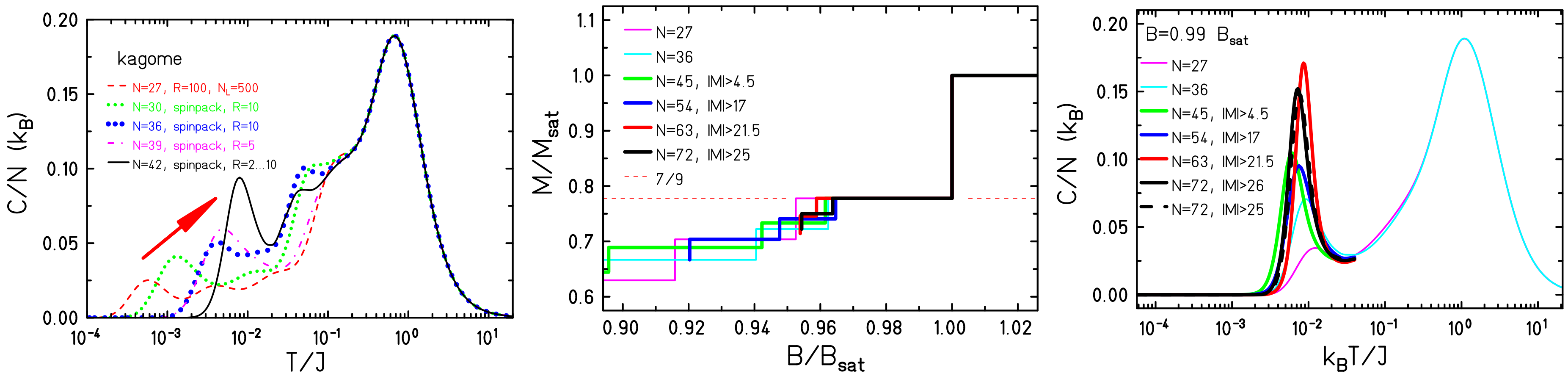
$|J_2/J_1| = 0.45$ – near critical, $|J_2/J_1| = 0.50$ – critical.

Frustration, technically speaking, works in your favour.

(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020)

(2) J. Schnack, J. Richter, T. Heitmann, J. Richter, R. Steinigeweg, Z. Naturforsch. A 75, 465 (2020)

FTLM 4: kagome (using spinpack)



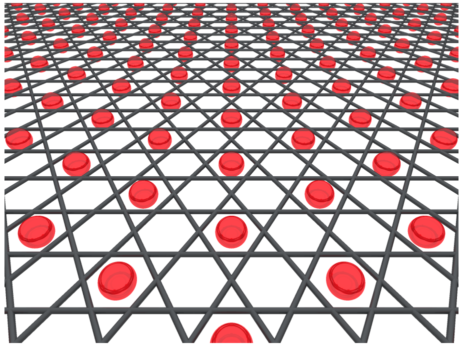
Specific heat of kagome with $N = 42$ – role of low-lying singlets

(1) J. Schnack, J. Schulenburg, J. Richter, Phys. Rev. B **98**, 094423 (2018)

Magnon crystalization at high field.

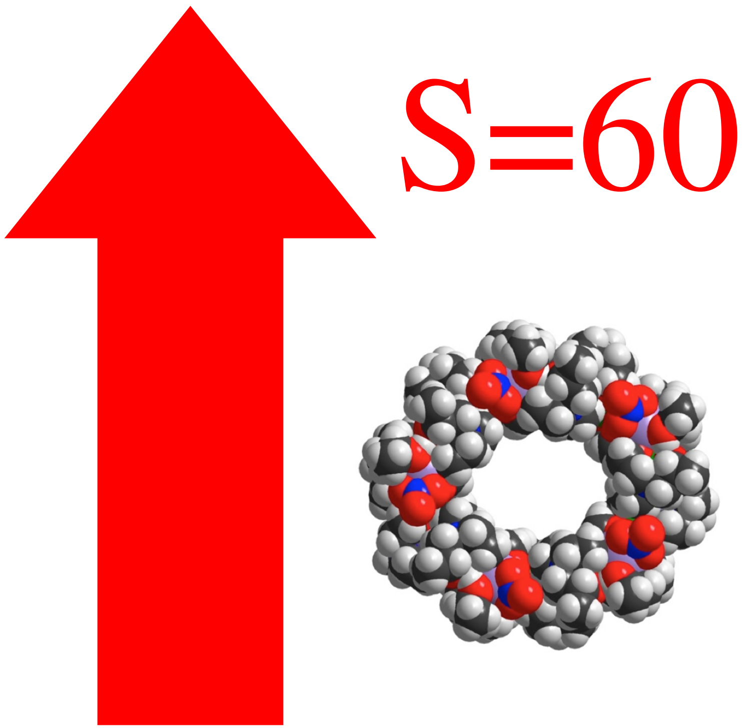
(2) J. Schnack, J. Schulenburg, A. Honecker, J. Richter,
Phys. Rev. Lett. **125**, 117207 (2020)

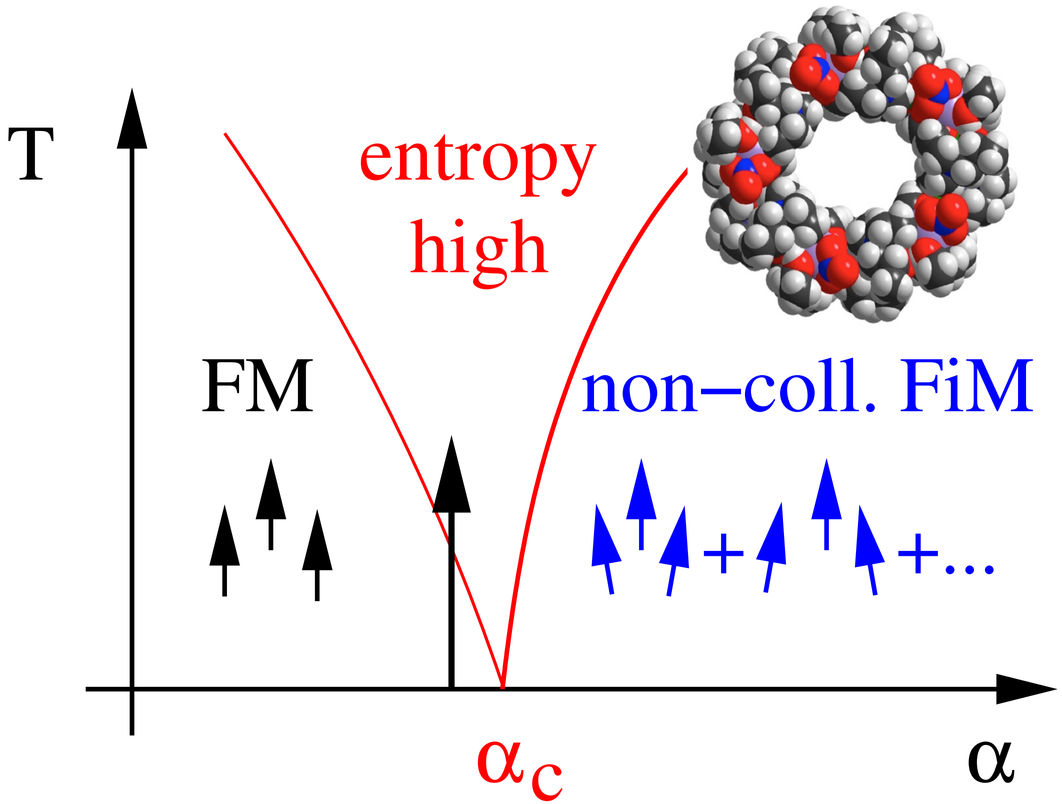
. . . and many more results with Johannes Richter.



$Fe_{10}Gd_{10}$ and quantum critical behavior

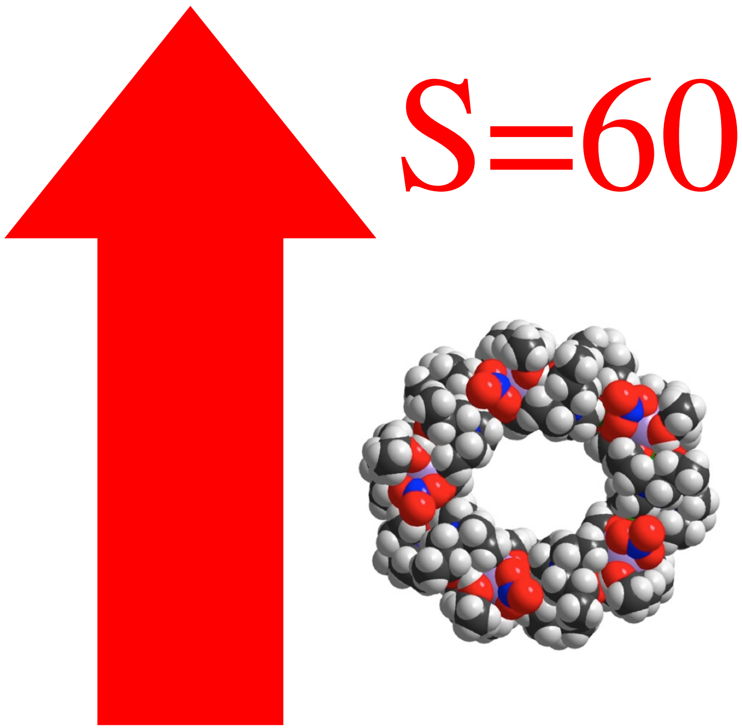
$Gd_{10}Fe_{10}$ – summary

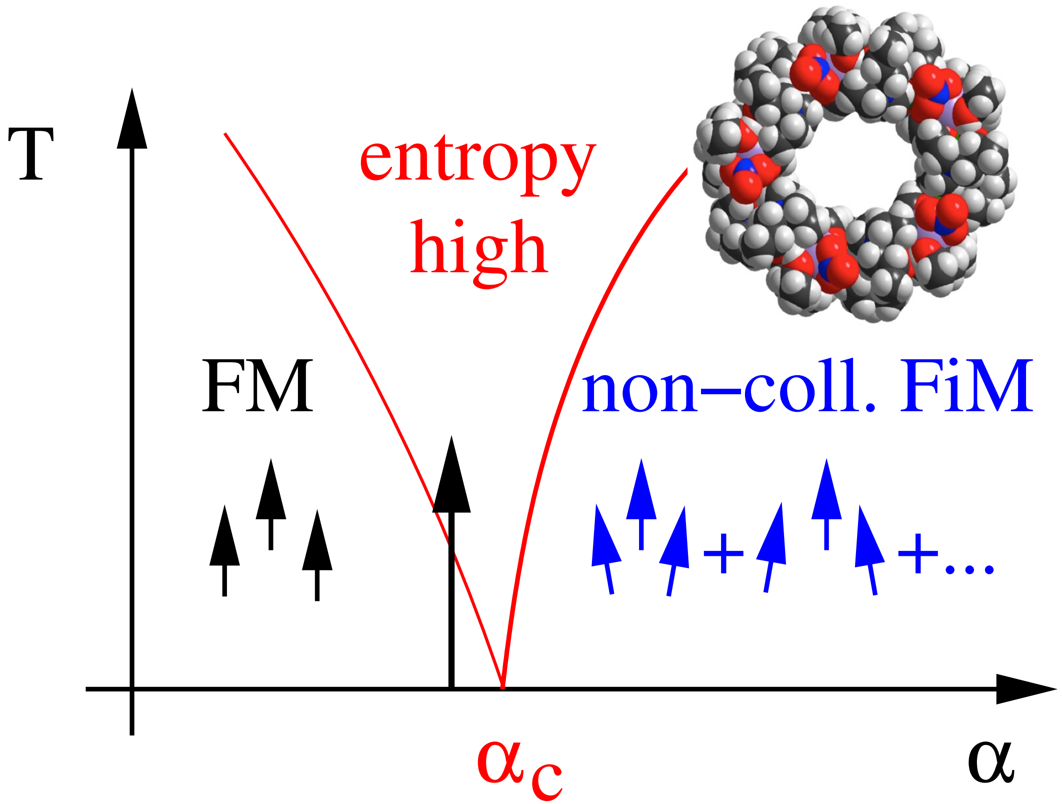




A. Baniodeh, N. Magnani, Y. Lan, G. Buth, C.E. Anson, J. Richter, M. Affronte, J. Schnack, A.K. Powell,
High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality,
npj Quantum Materials **3**, 10 (2018)

$Gd_{10}Fe_{10}$ – summary

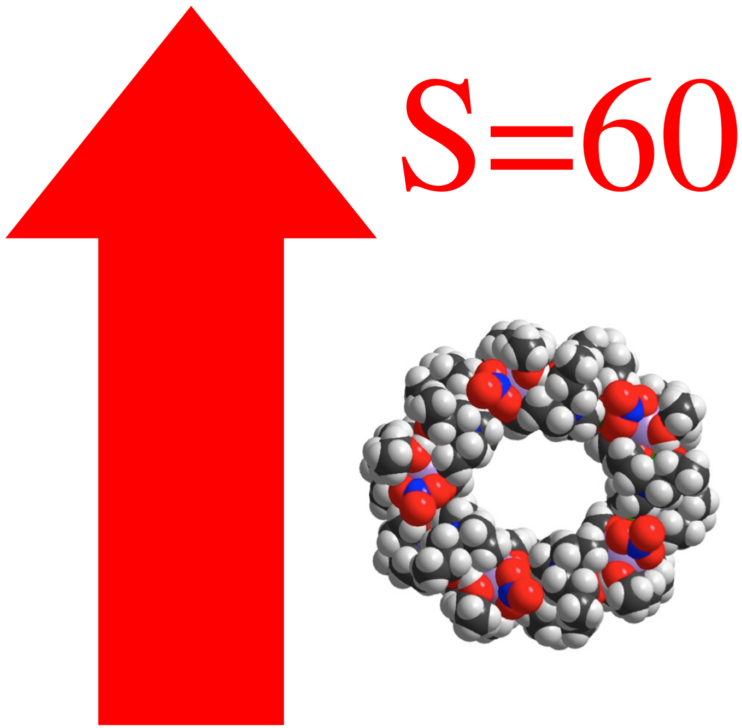


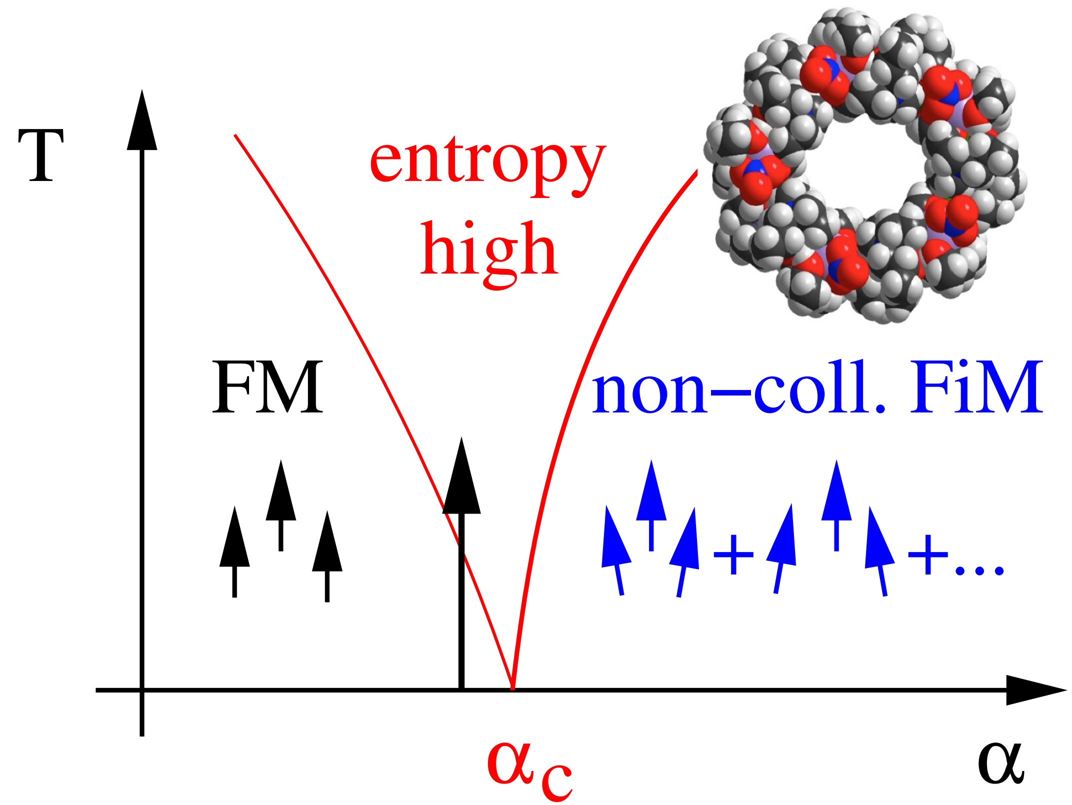


How do we know?

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

$Gd_{10}Fe_{10}$ – summary



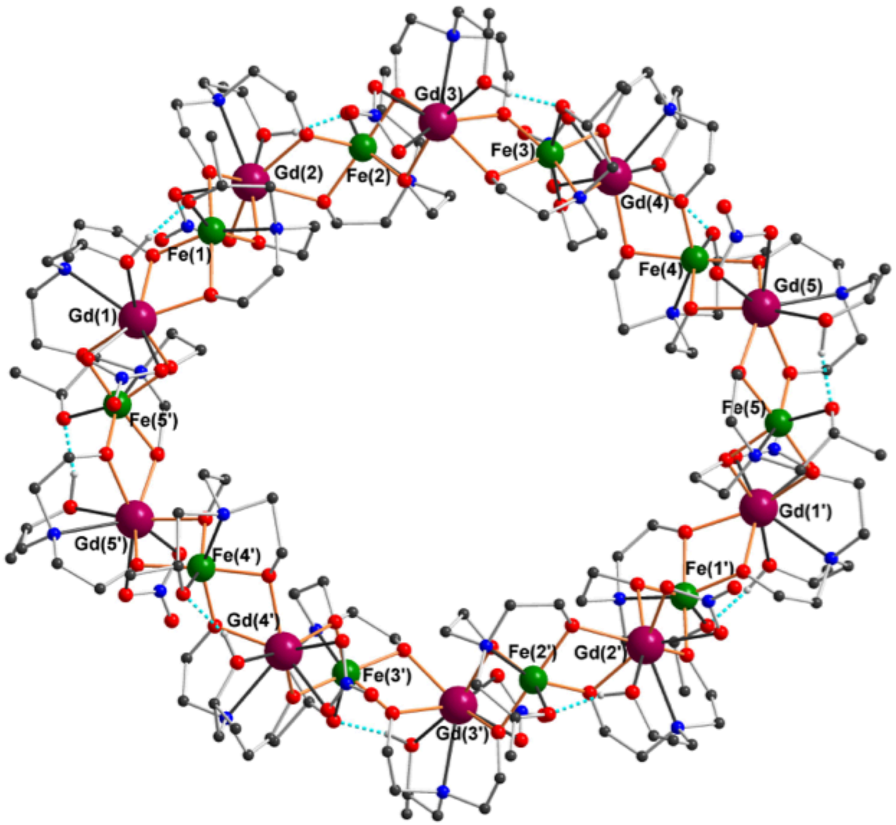


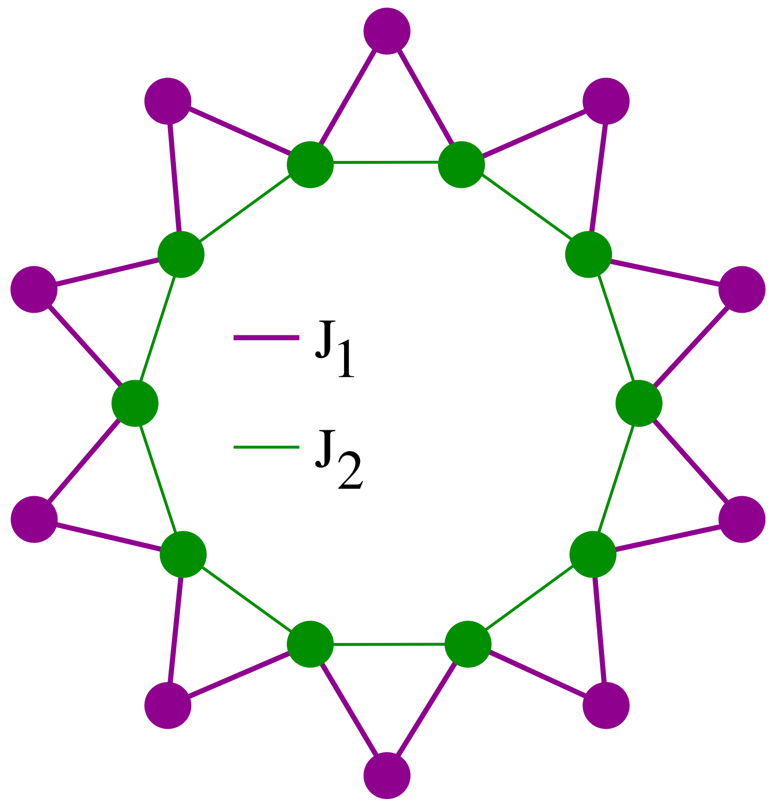
How do we know?

What is a QPT?

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

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



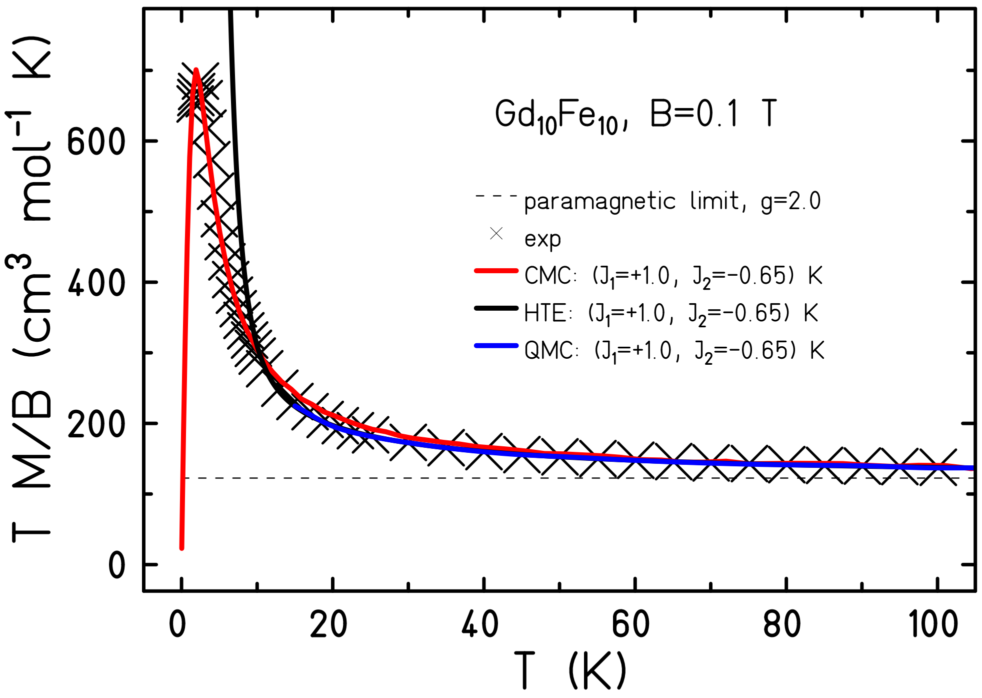


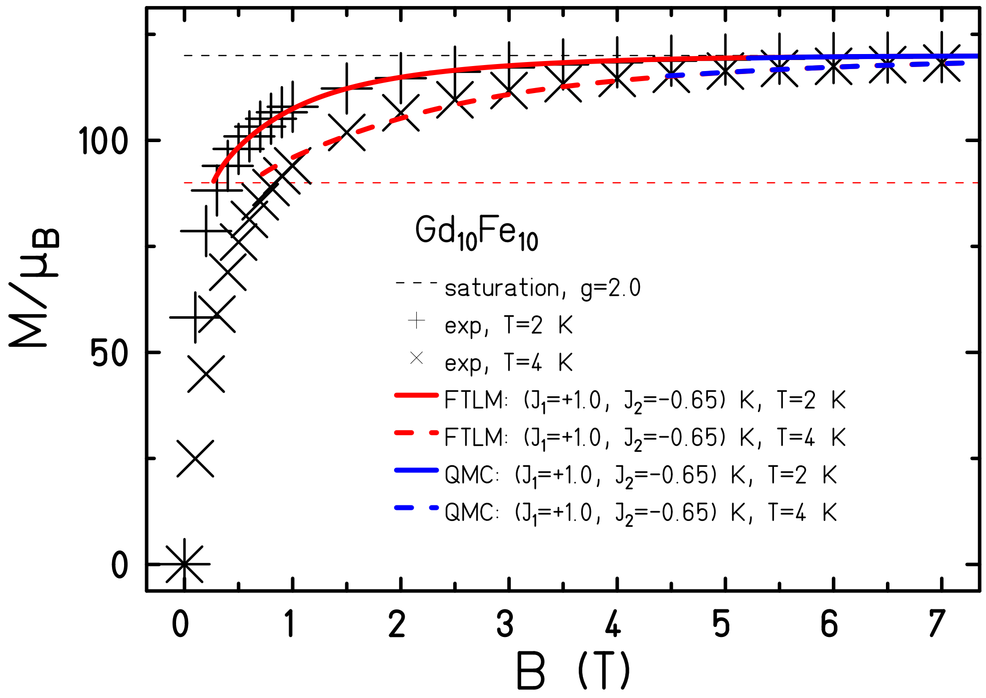
purple: Gd ($s = 7/2$), green: Fe ($s = 5/2$)

We will see: J_1 ferro, J_2 antiferro

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

$Gd_{10}Fe_{10}$ – Methods

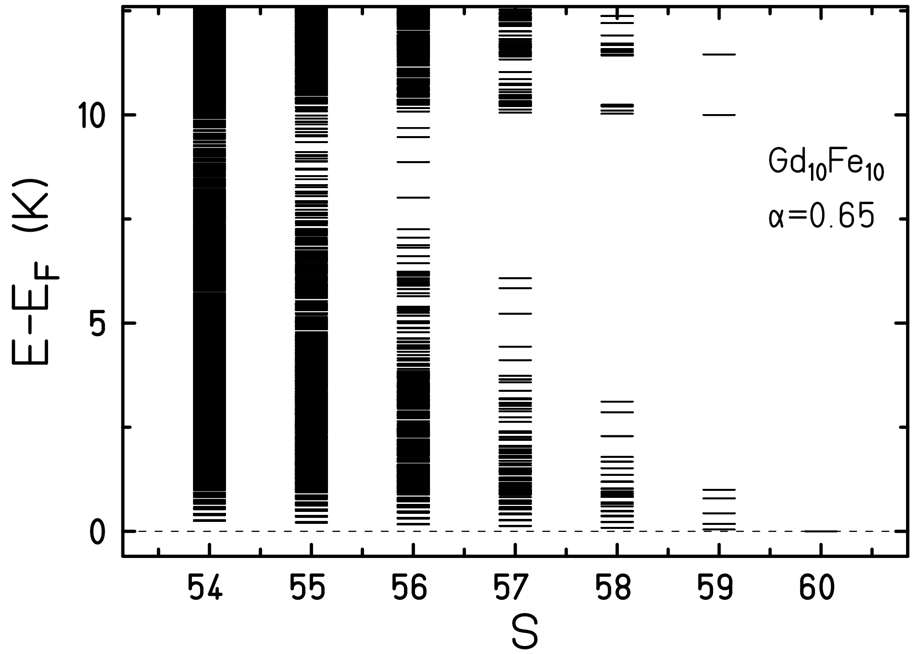


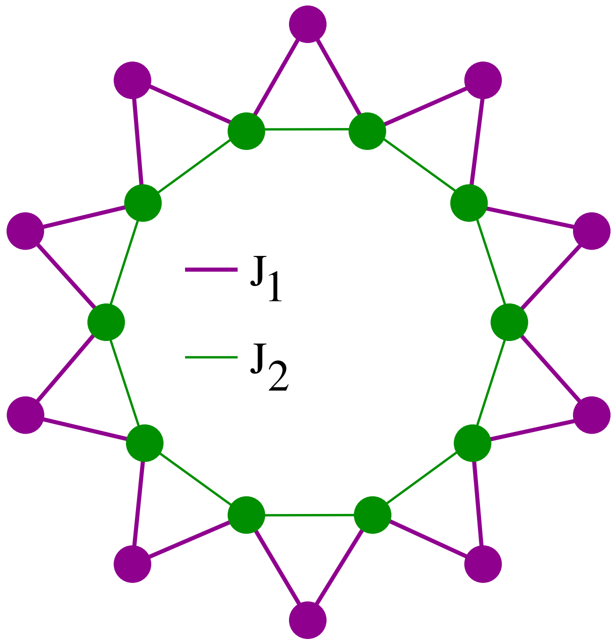


Methods: HTE, QMC, CMC, FTLM $\Rightarrow J_1 = 1.0$ K, $J_2 = -0.65$ K

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

Gd$_{10}$Fe$_{10}$ – $S = 60$



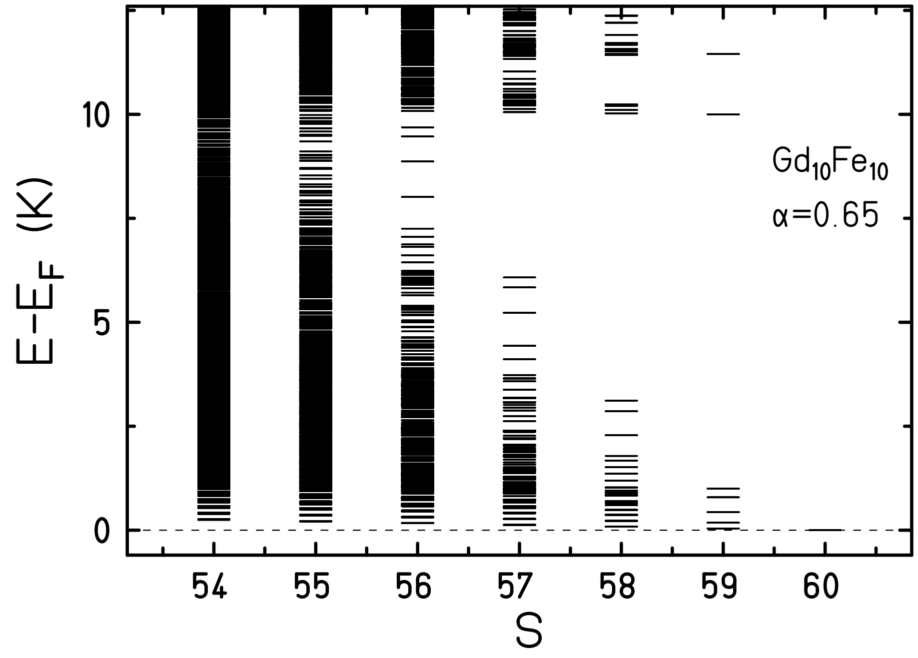


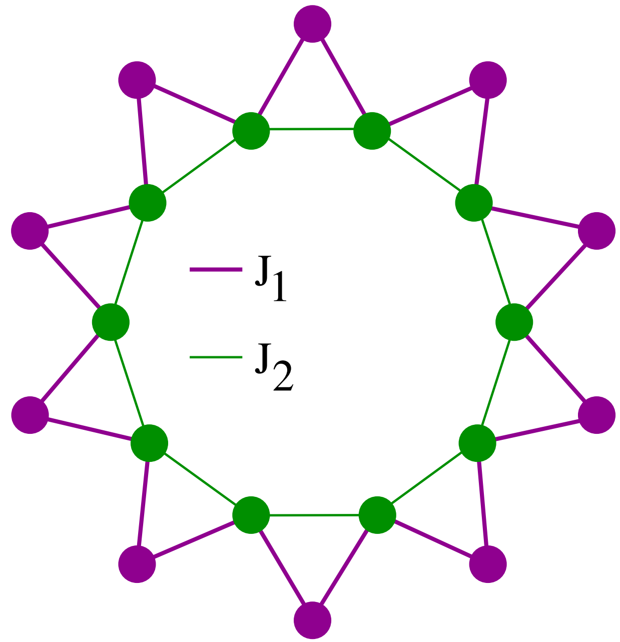
⇒ $S = 60$, largest ground state spin of a molecule to date

⇒ $\alpha_{\text{Gd}_{10}\text{Fe}_{10}} = |J_2|/J_1 = 0.65$ What if J_2 stronger?

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

$Gd_{10}Fe_{10}$ – $S = 60$



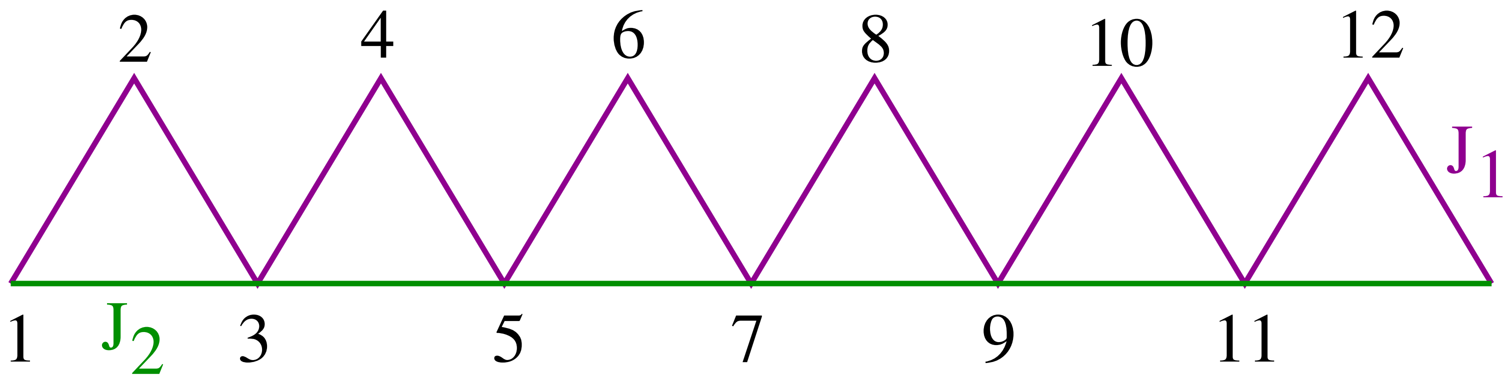


$\Rightarrow$ $S = 60$, largest ground state spin of a molecule ~~to date~~ for about one month

$\Rightarrow$ $\alpha_{Gd_{10}Fe_{10}} = |J_2|/J_1 = 0.65$ 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



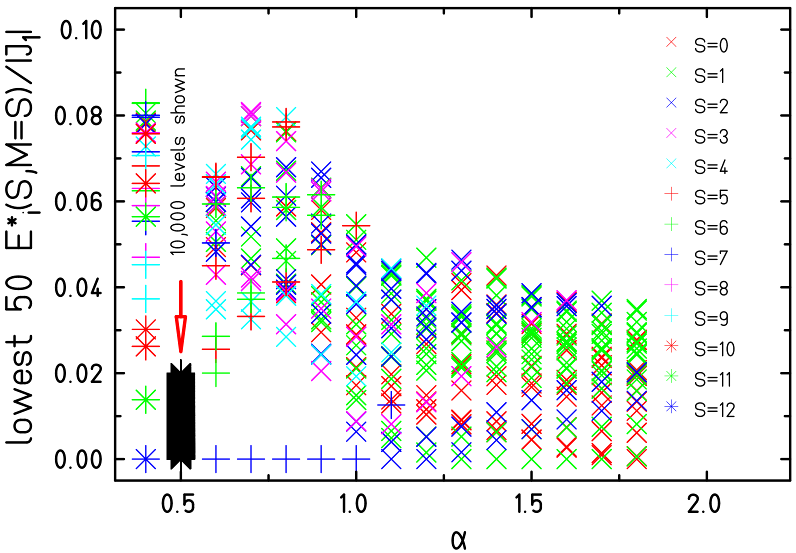
⇒ special properties for $J_1 > 0$ (ferro) and $J_2 < 0$ (af) at certain α_c

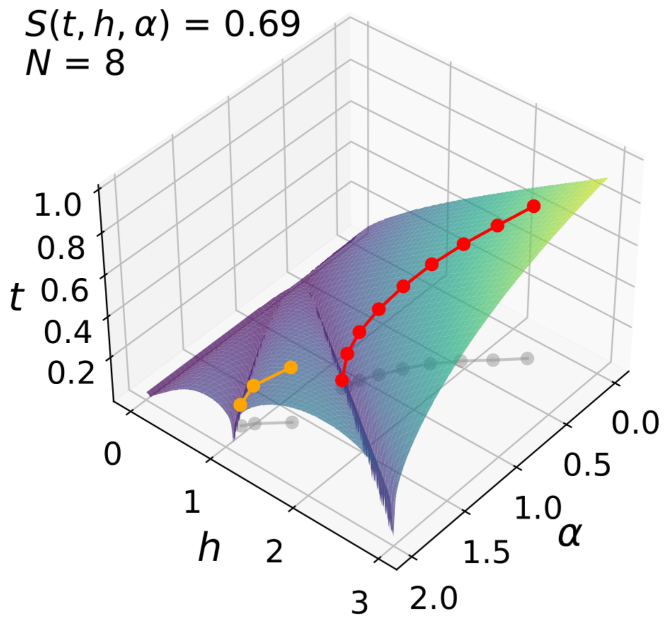
e.g. $\alpha_c = |J_2|/J_1 = 0.5$ if $s_i = 1/2\ \forall i$

⇒ 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).
(3) D. V. Dmitriev and V. Y. Krivnov, J. Richter, J. Schnack, Phys. Rev. B **99**, 094410 (2019)

$Gd_{10}Fe_{10}$ – intermezzo: delta chain $s = 1/2$





quantum phase transition

magneto- and barocaloric

$\alpha = |J_2/J_1|$

$t = k_B T/|J_1|,\ h = g\mu_B B/|J_1|$

Magneto- and barocalorics allow to heat and cool via changes of magnetic field and pressure: Entropy $S = S(T, \vec{B}, \alpha)$

N. Reichert, H. Schlüter, T. Heitmann, J. Richter, R. Rausch, and J. Schnack, Z. Naturforsch. A **79**, 283 (2024).

Summary

- FTLM is a phantastic method that delivers quasi-exact equilibrium observables for systems with Hilbert-(sub)-spaces with dimensions up to 10^{11}.
- Frustrated spin systems can show very unusual and exciting magnetocaloric properties.
- Improvement of FTLM for very anisotropic spin systems such as toroidal magnetic molecules is on its way.

Thank you very much for your attention.

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