Magnetic molecules for magnetocalorics

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MolCal

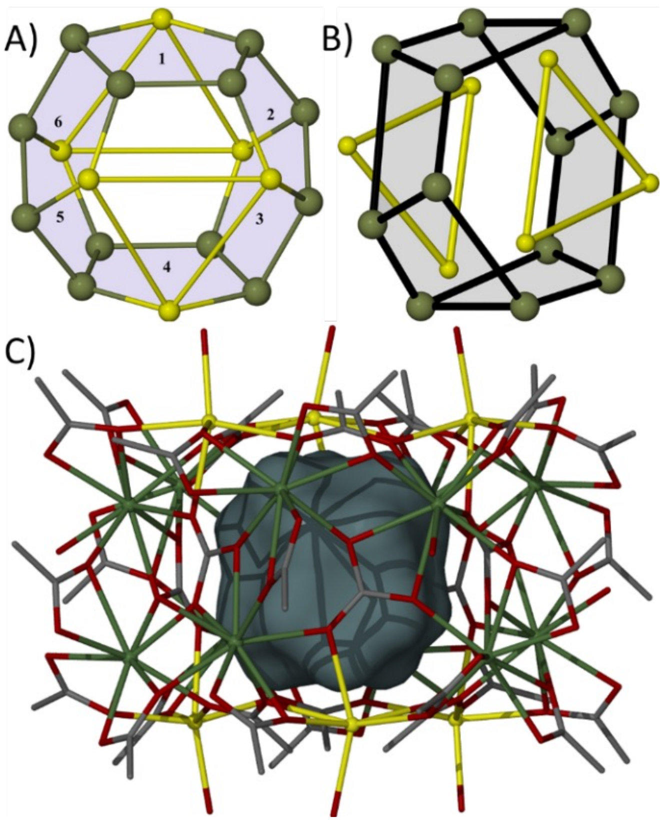
You can cool with molecules!

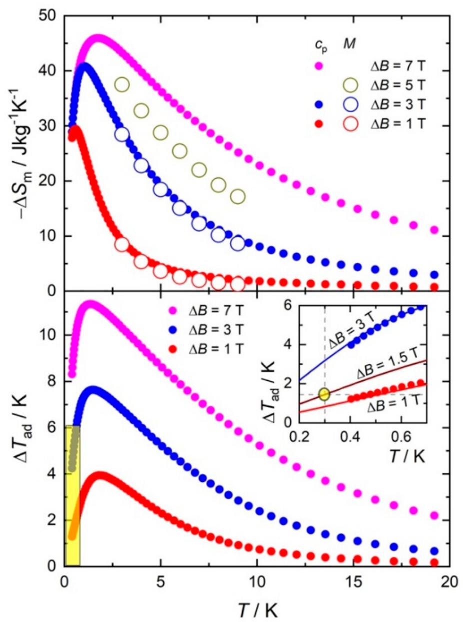
Entropy $S = S(T, \vec{B})$

Entropy $S = S(T, \vec{B})$

. . . you can cool with everything!

Gd$_{12}$ for molecular magnetocalorics!

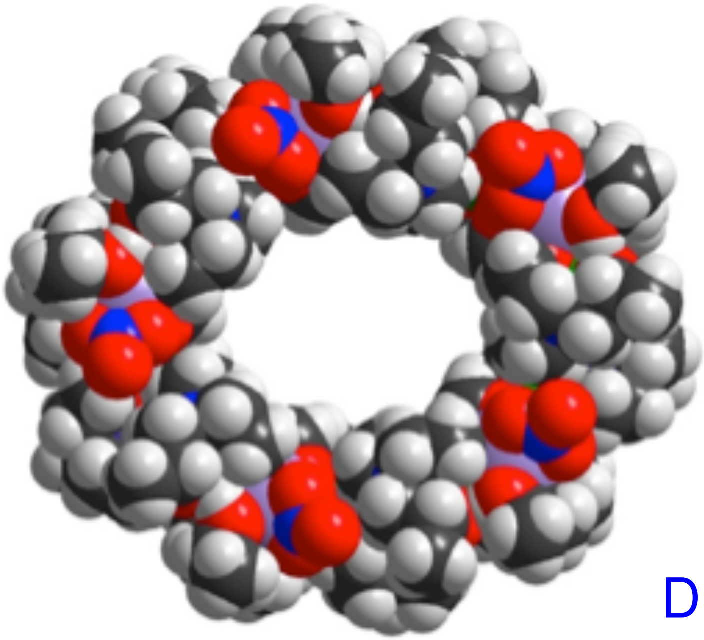


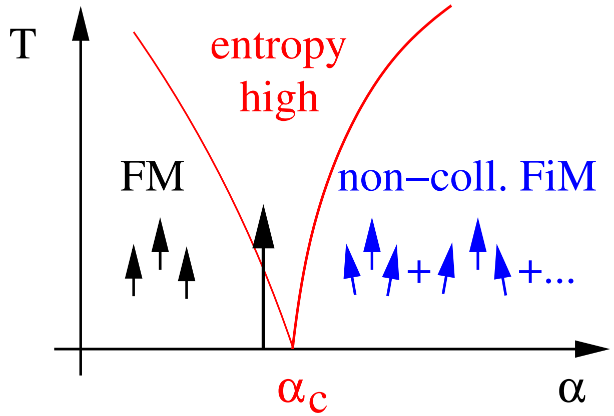


JACS **145**, 7743-7747 (2023)

Dimension of Hilbert space 68,719,476,736

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

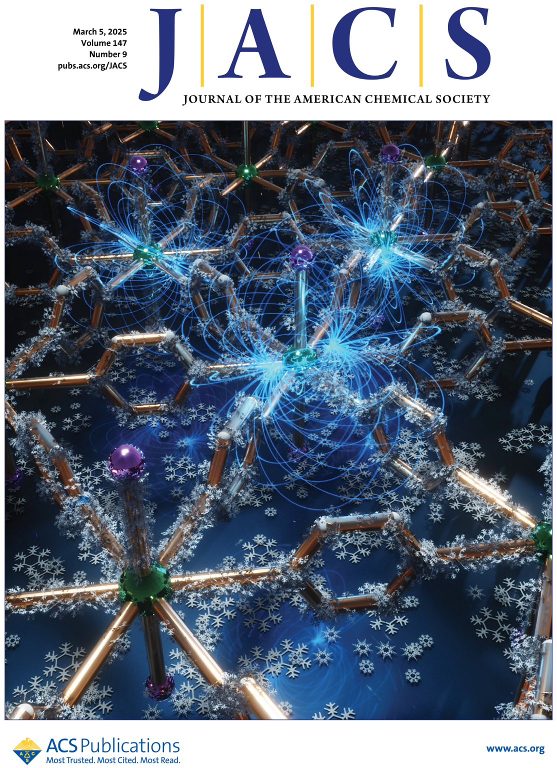


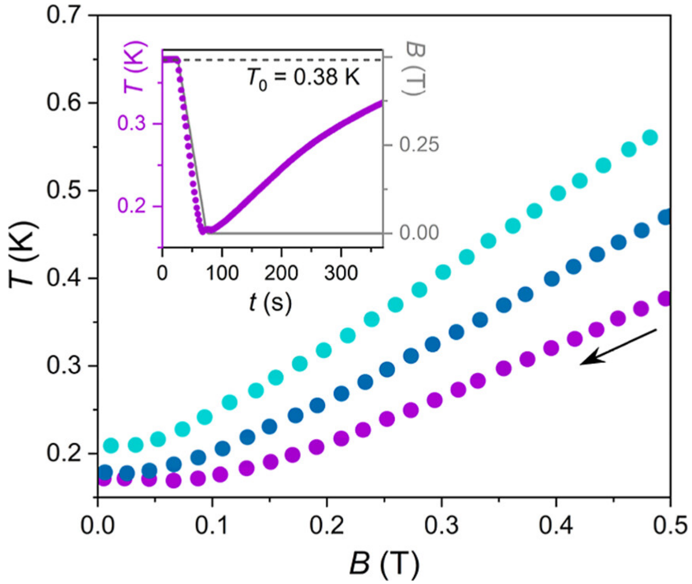


Dimension of Hilbert space 64,925,062,108,545,024

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

Eu triangular lattice

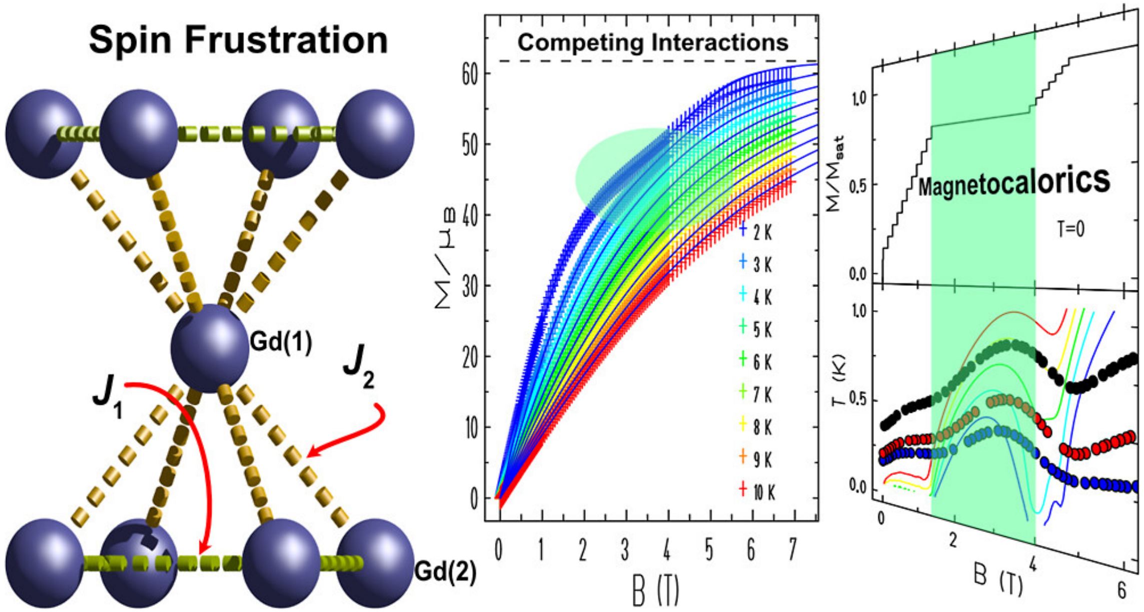




infinite triangular lattice

JACS **147**, 7597-7603 (2025)

Strong quantum effects for Gd_9



competing interactions

JACS **147**, 43578-43583 (2025)

Yes, we can!

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

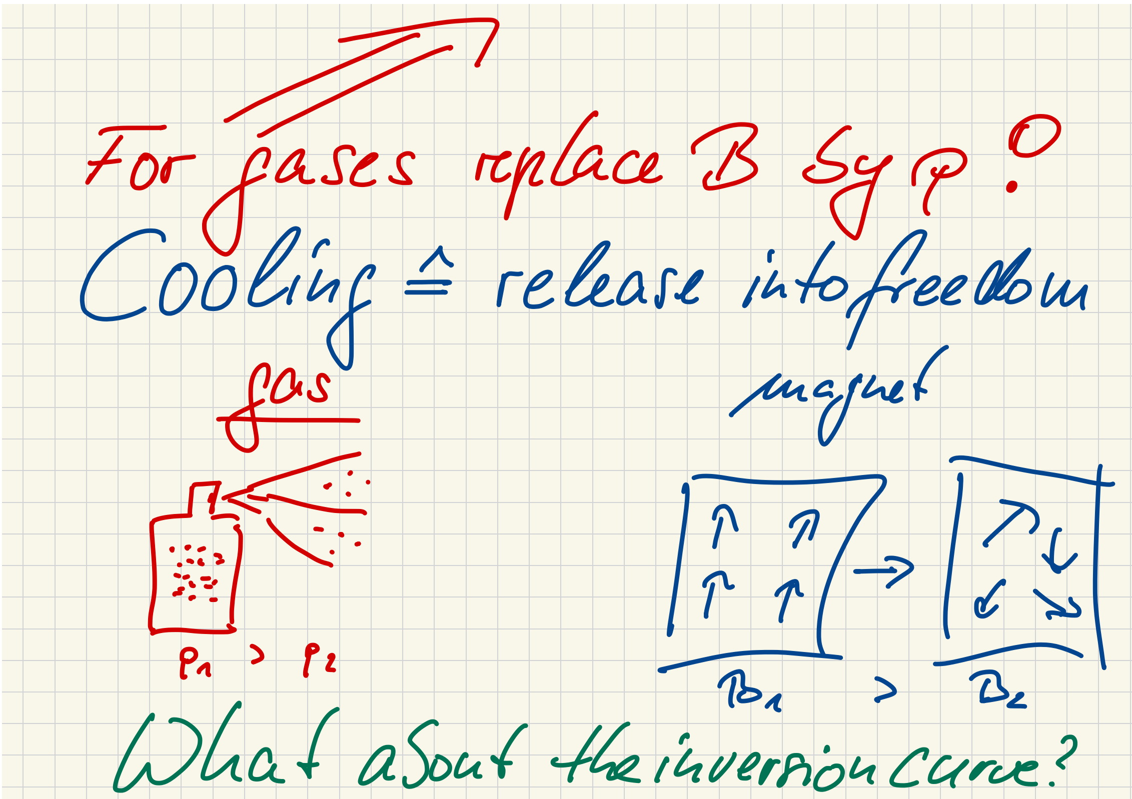
We are the sledgehammer team of matrix diagonalization.
Please send inquiries to jschnack@uni-bielefeld.de!

The magnetocaloric effect

Entropy $S = S(T, \vec{B})$

Magnetocaloric effect – cooling rate

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



Magnetocaloric effect – cooling rate

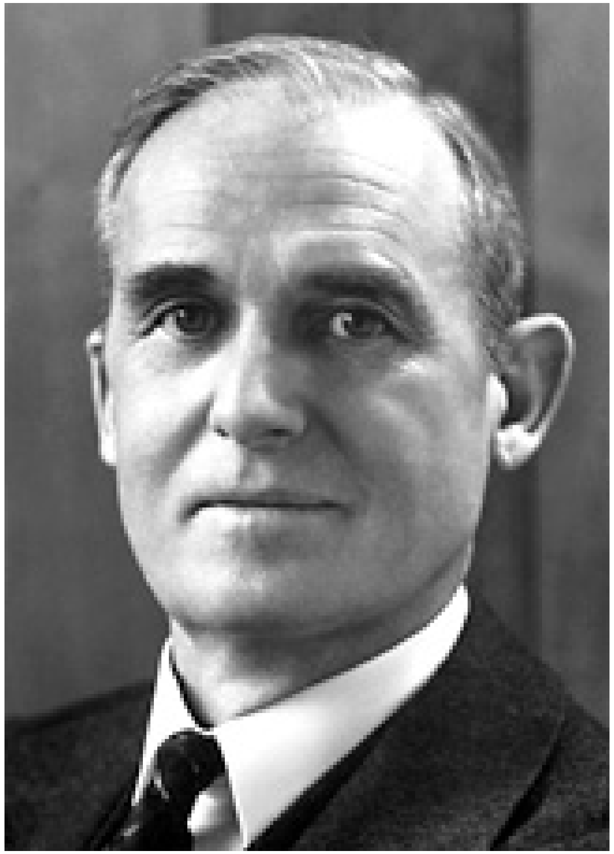
$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

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.

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

(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).
(4) A. Smith, Eur. Phys. J. H **38**, 507 (2013). $\Leftarrow$ History

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

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.

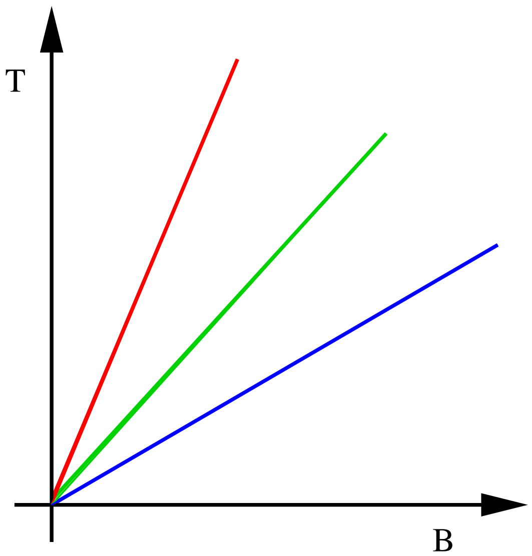
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

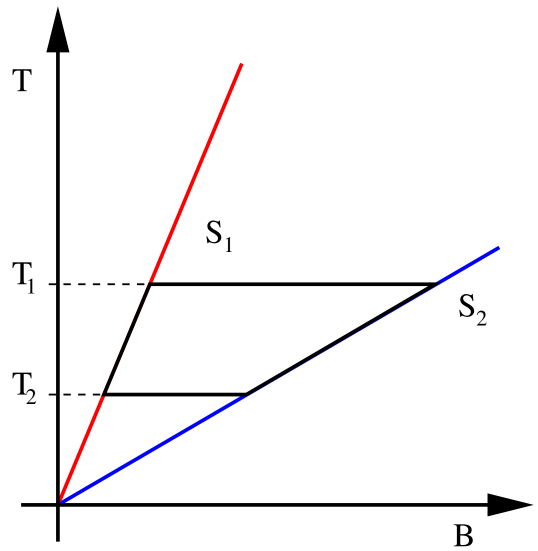
W. F. GIAUQUE
D. P. MACDOUGALL

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

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

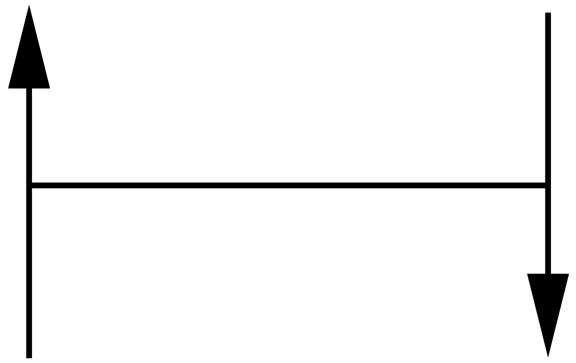
Magnetocaloric effect – Paramagnets

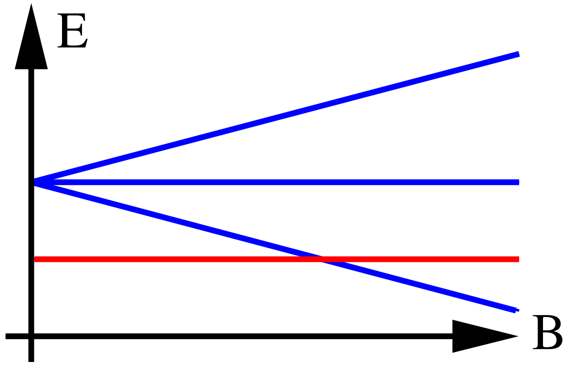




- Ideal paramagnet: $S(T, B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

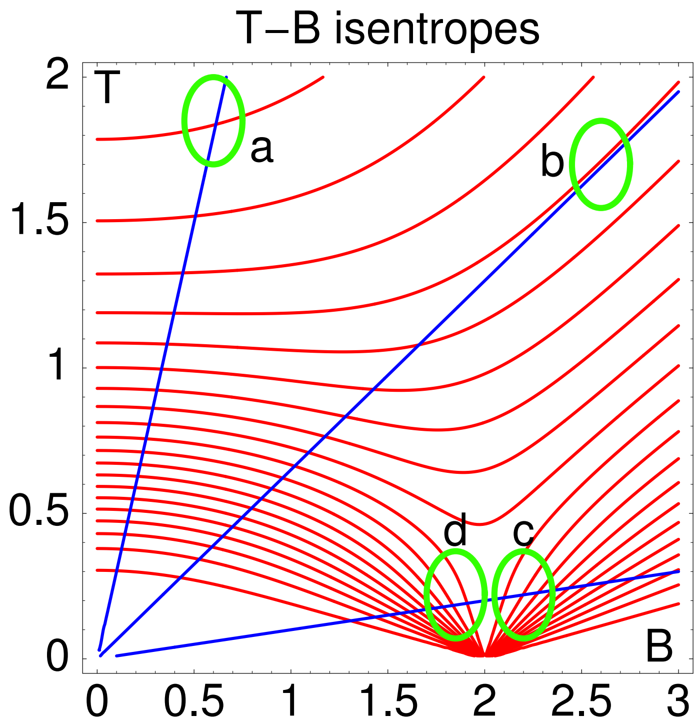
Magnetocaloric effect – af $s = 1/2$ dimer





- 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



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

(c) enhanced,

(d) opposite

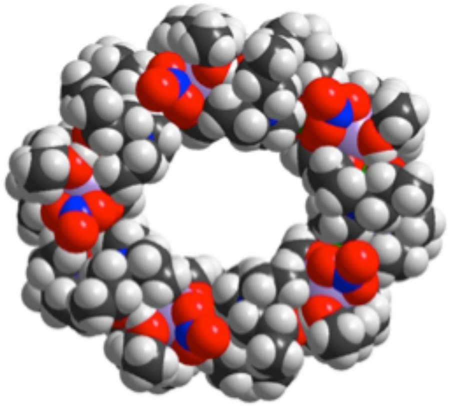
when compared to an ideal paramagnet.

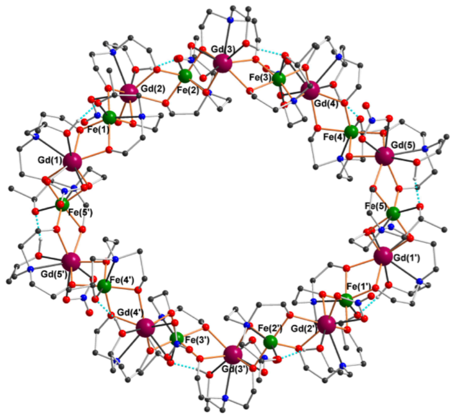
Case (d) does not occur for a paramagnet.

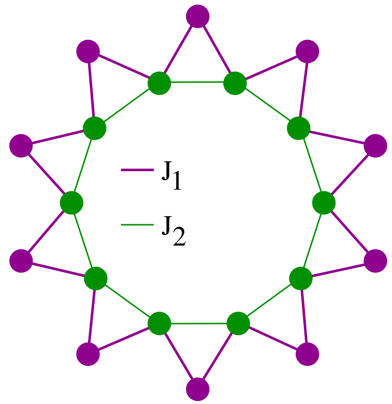
Theory calculations

$Gd_{10}Fe_{10}$ – one example for quantum magnetism

Reduction + modelling.







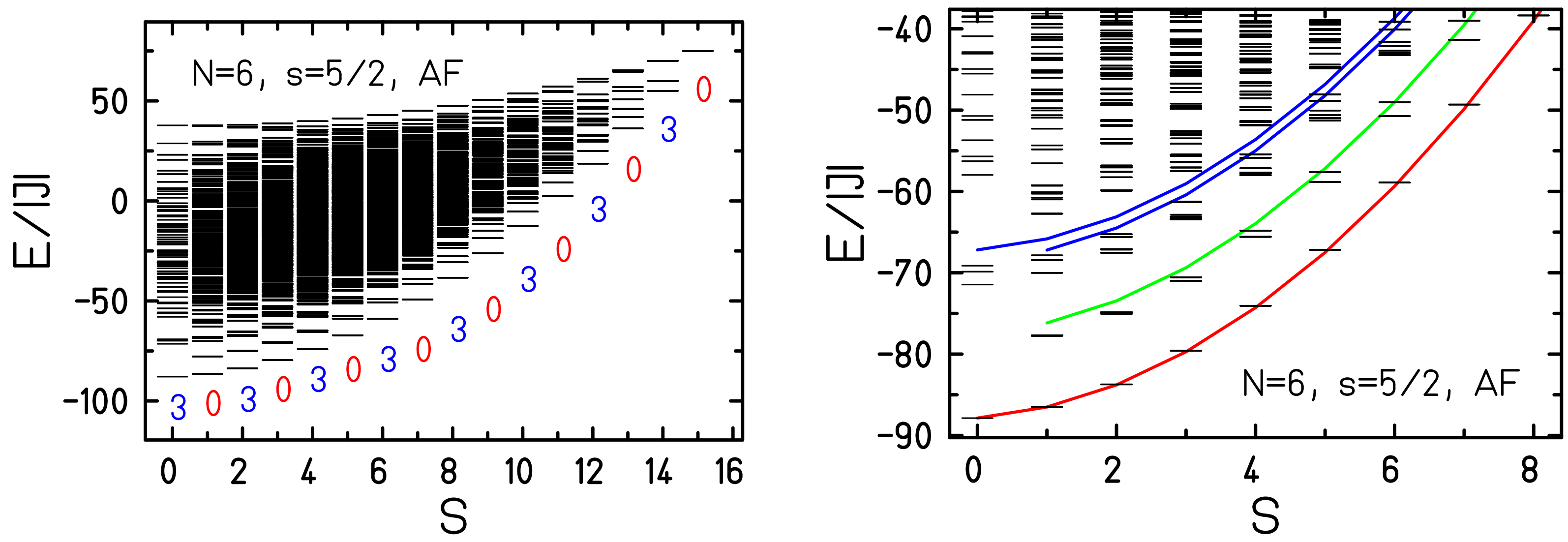
green: Fe ($s = 5/2$), purple: Gd ($s = 7/2$)

$$\underset{\sim}{H} = \sum_{i \leq j} \underset{\sim}{\vec{s}}_i \cdot \mathbf{J}_{ij} \cdot \underset{\sim}{\vec{s}}_j + \mu_B \vec{B} \cdot \sum_{i}^{N} \mathbf{g} \cdot \underset{\sim}{\vec{s}}_i$$

The effective model also depends on what you measure!

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

Example: Heisenberg model for spin rings



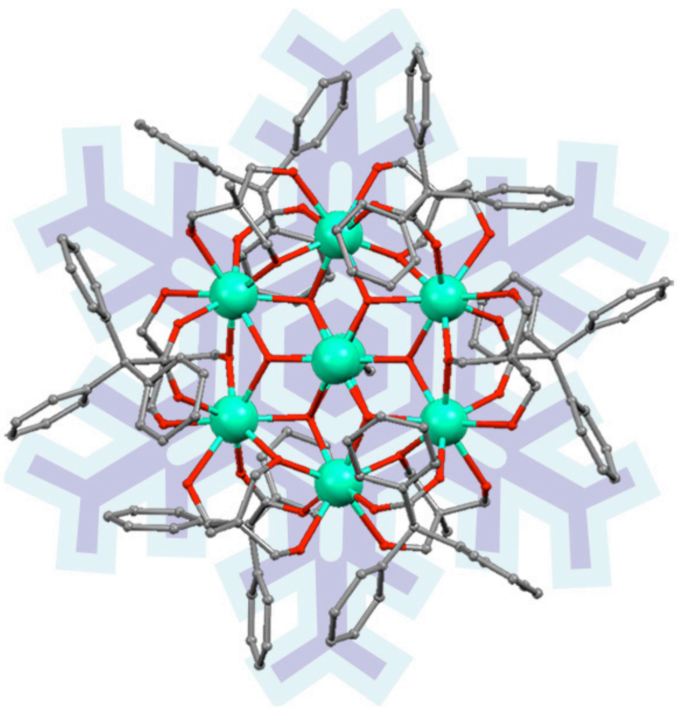
1. finite-dimensional Hilbert space, product basis;
2. Hamiltonian matrix, symmetries, e.g., $SU(2)$ and point groups;
3. exact diagonalization, canonical ensemble, equilibrium thermodynamics;
4. time-dependent problems.

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

Let's start with something small:

Gd_7

Gd$_7$ – Basics

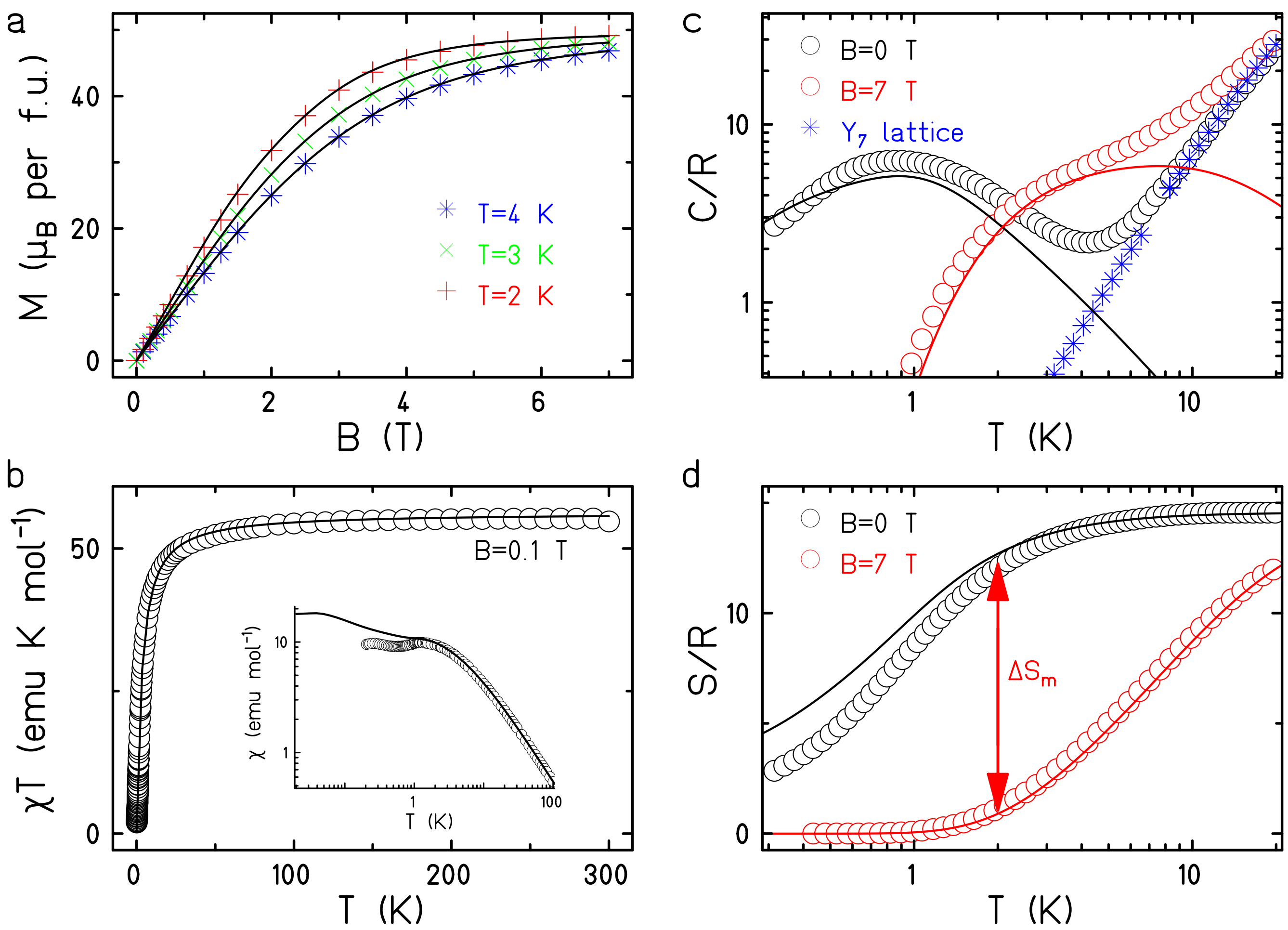


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij} \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\, \mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

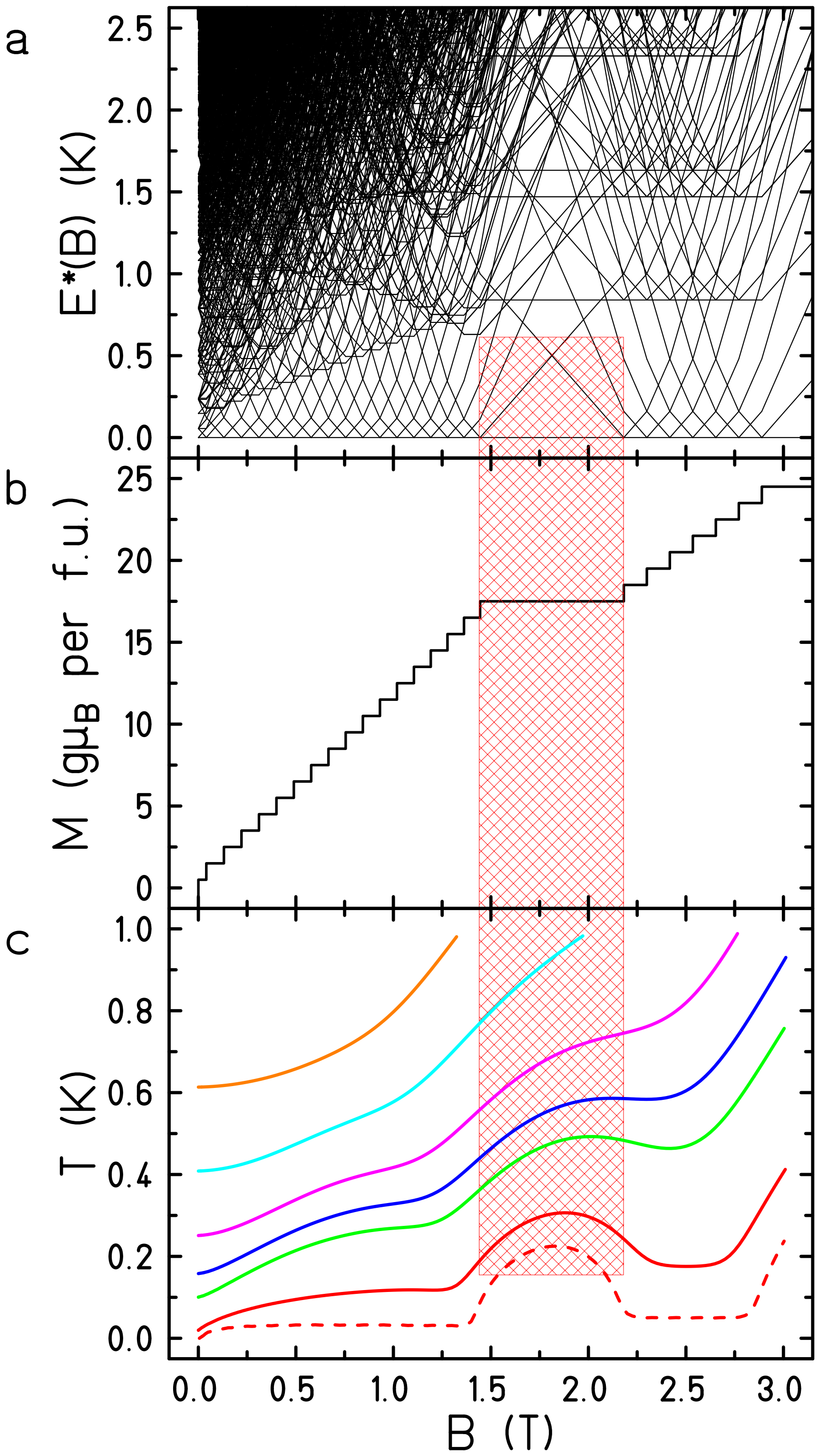
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

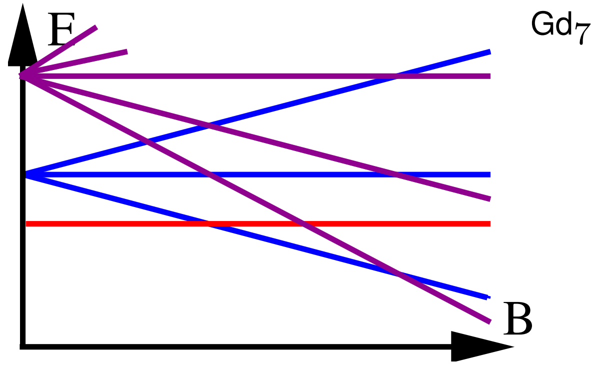
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

Gd$_7$ – experiment & theory

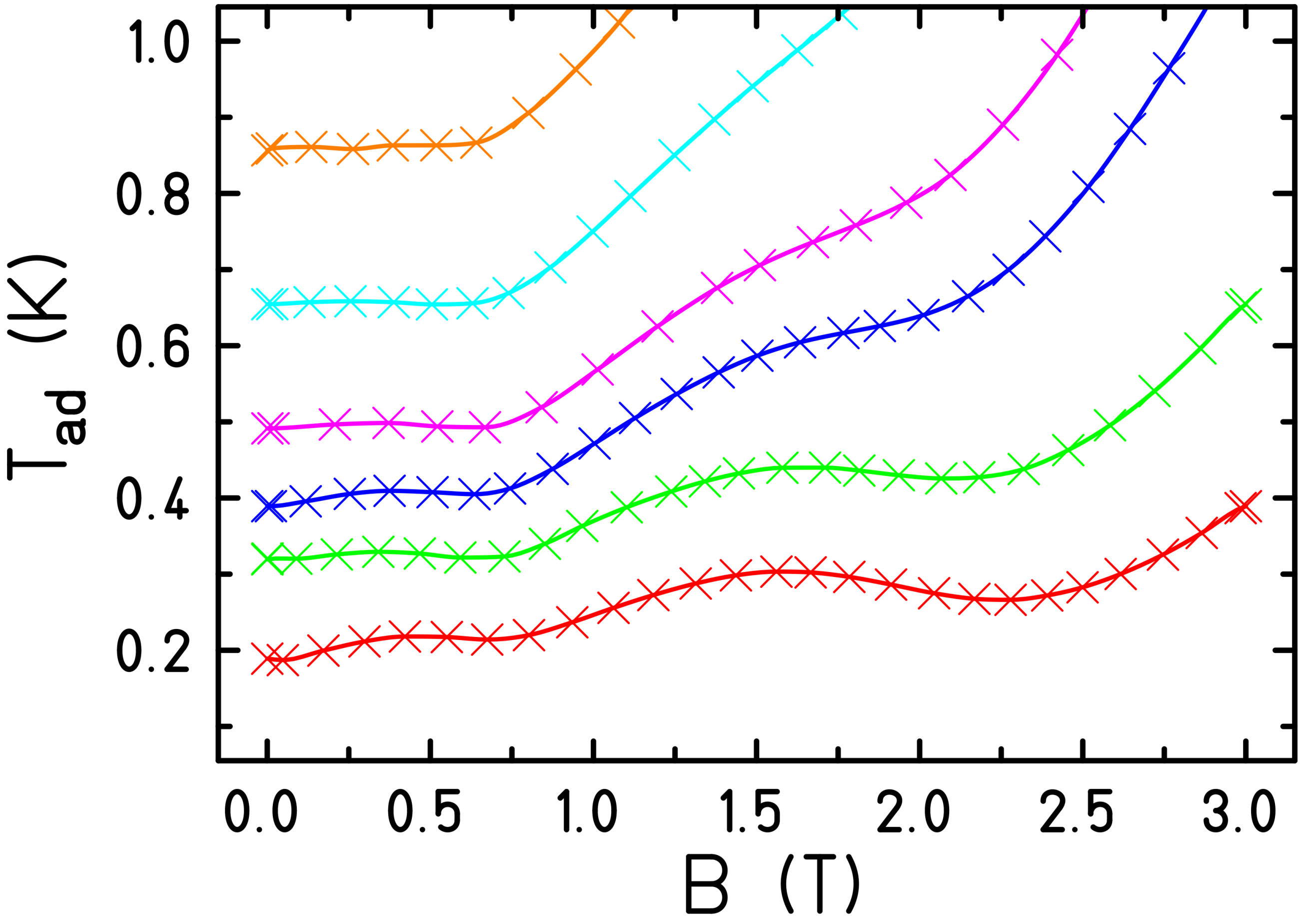


J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).


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
0
5
10
15
20
25
0.2
0.4
0.6
0.8


E
B
Gd7

Gd$_7$ – Experimental cooling



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

How to model big molecules?

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

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

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

- $|\, \nu \,\rangle$ some orthonormal basis of your choice; not the eigenbasis of $\underset{\sim}{O}$, 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 $|\, r\,\rangle$ yields a superposition of

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

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

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

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

- 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

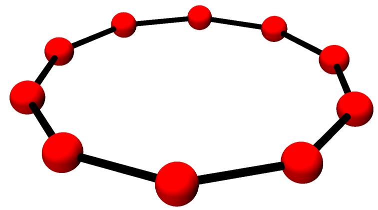
$$Z^{\text{FTLM}}(T,B) \approx \frac{\dim(\mathcal{H})}{R} \sum_{r=1}^{R} \sum_{n=1}^{N_L} e^{-\beta\epsilon_n^{(r)}} |\langle\, n(r) \,|\, r \,\rangle|^2$$

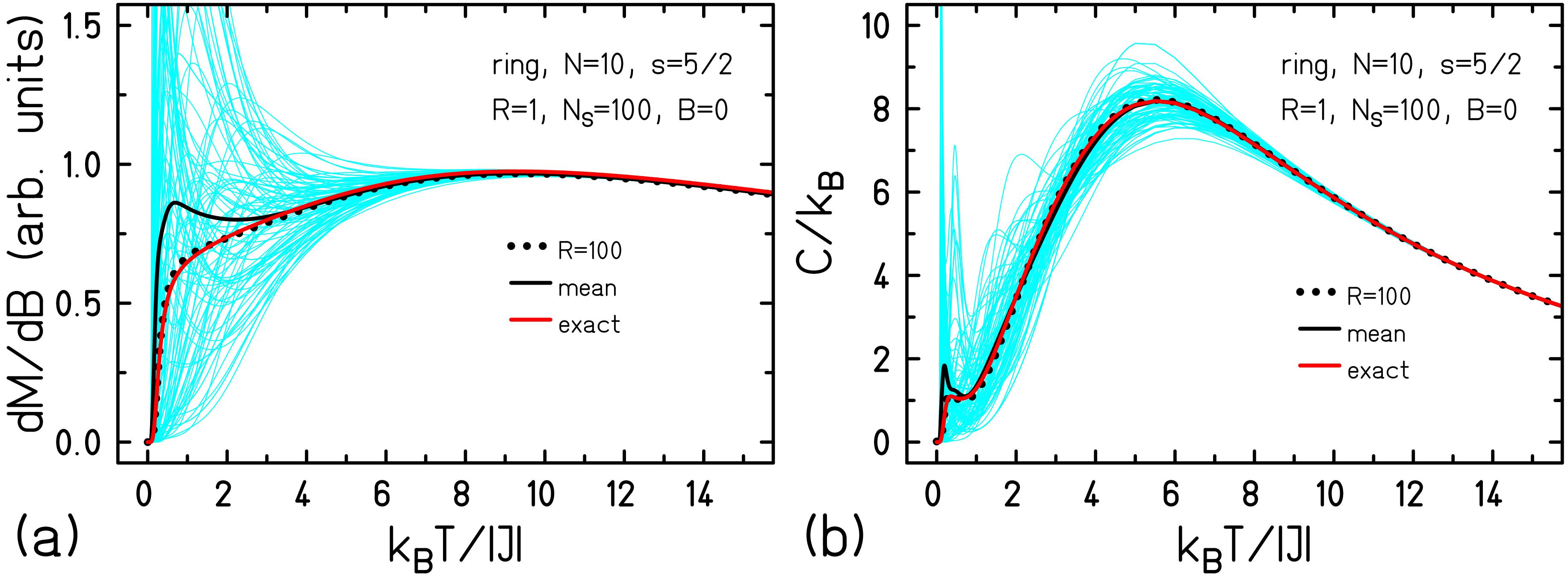
- Averaging over R random vectors is better.
- $|\, n(r) \,\rangle$ n-th Lanczos eigenvector starting from $|\, r \,\rangle$ (now normalized).
- Partition function replaced by a small sum: $R = 1 \dots 100, N_L \approx 100$.
- Use symmetries! Copy Hilbert subspaces!

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

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

FTLM 1: ferric wheel



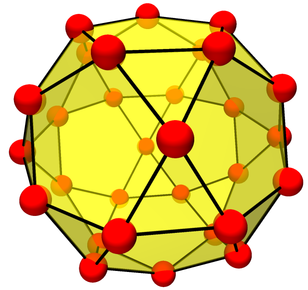


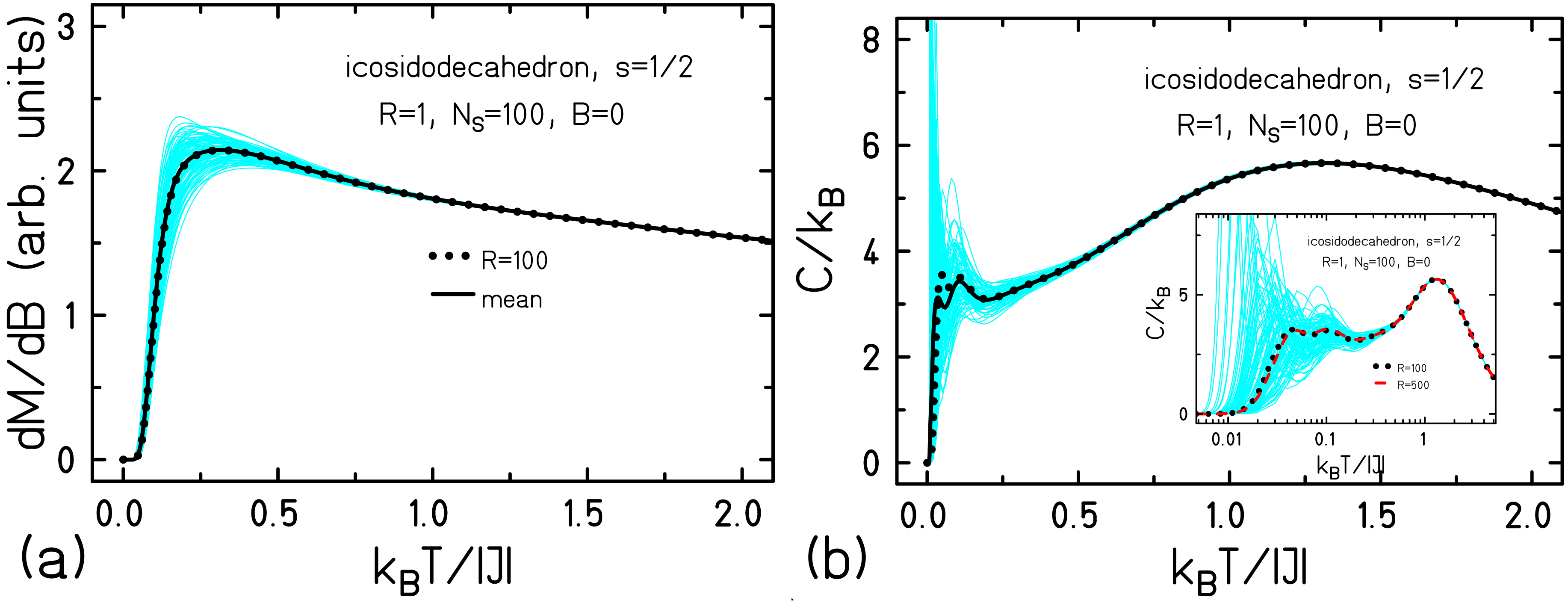
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

(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

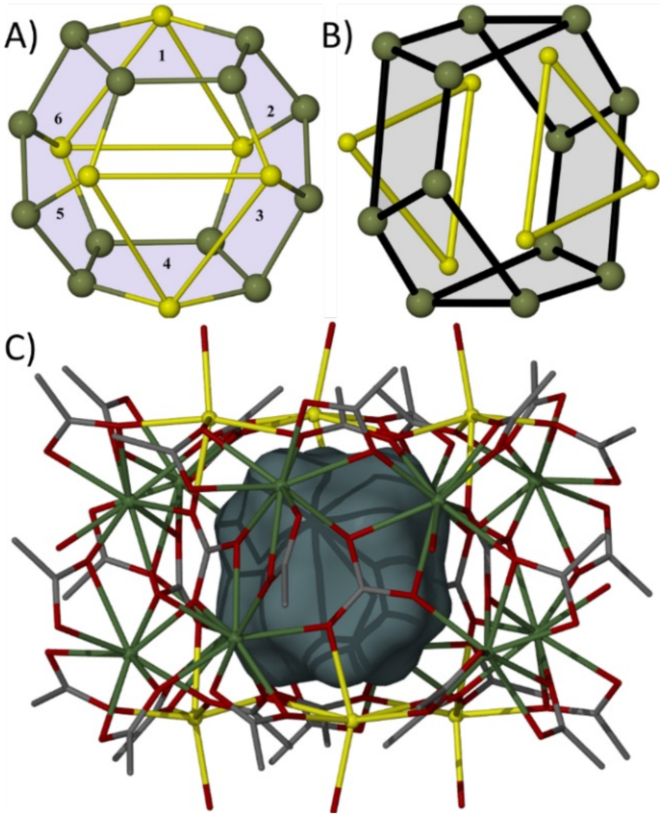


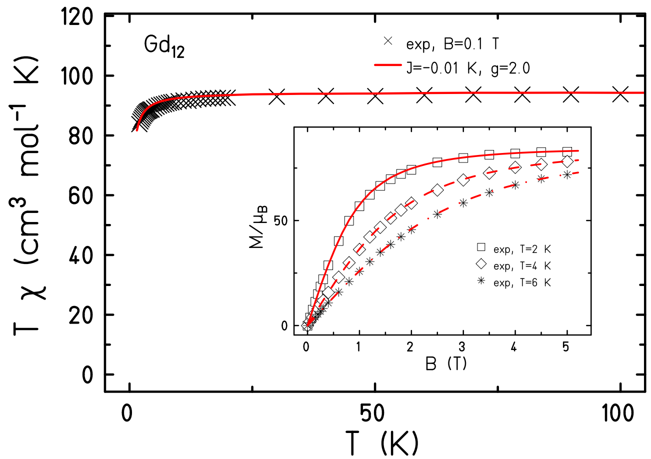


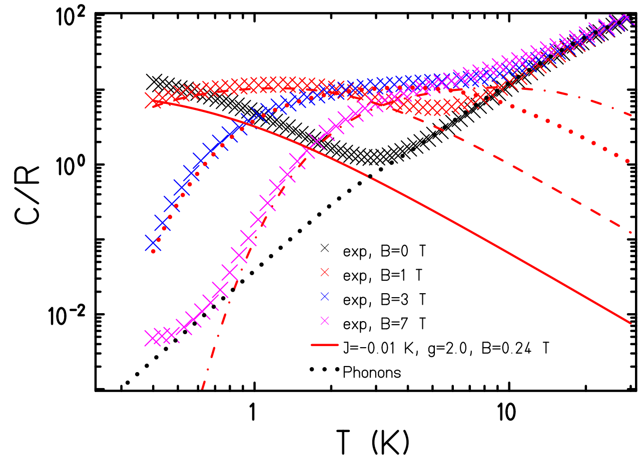
(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

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

FTLM 3: Gd$_{12}$ – dim $= 68,719,476,736$



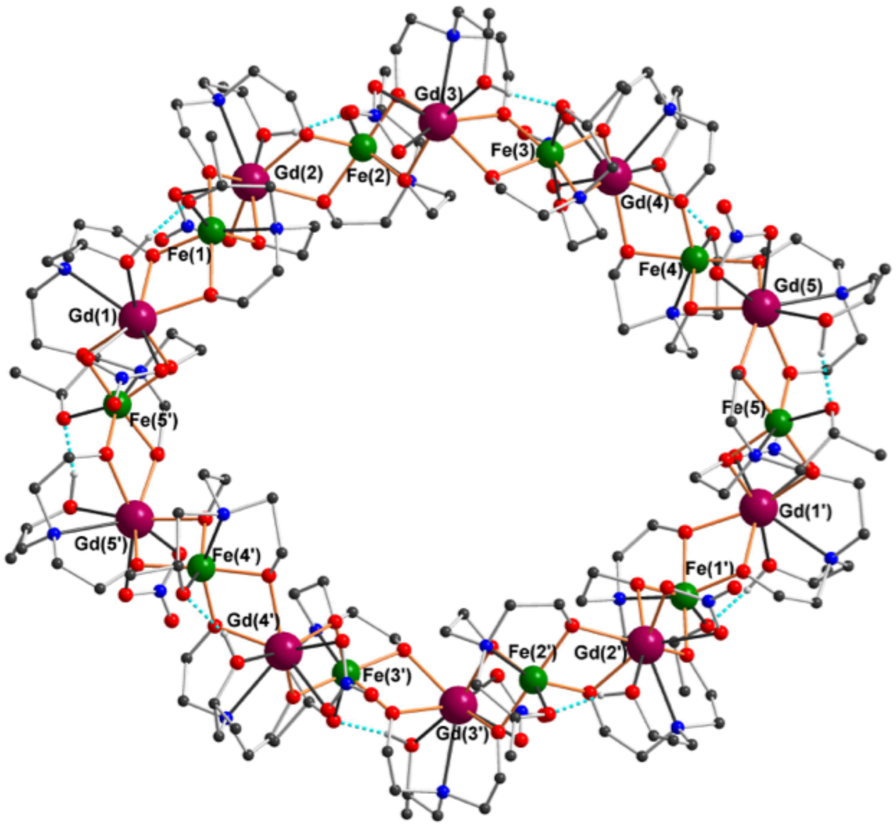


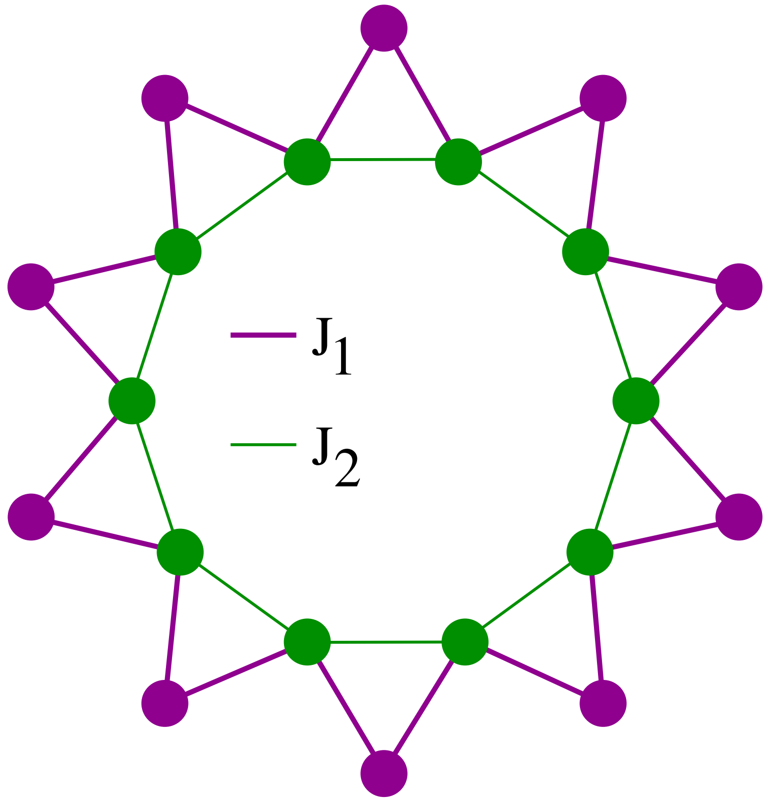


T. G. Tziotzi, D. Gracia, S. J. Dalgarno, J. Schnack, M. Evangelisti, E. K. Brechin, and C. J. Milios, J. Am. Chem. Soc. **145**, 7743 (2023).

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

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



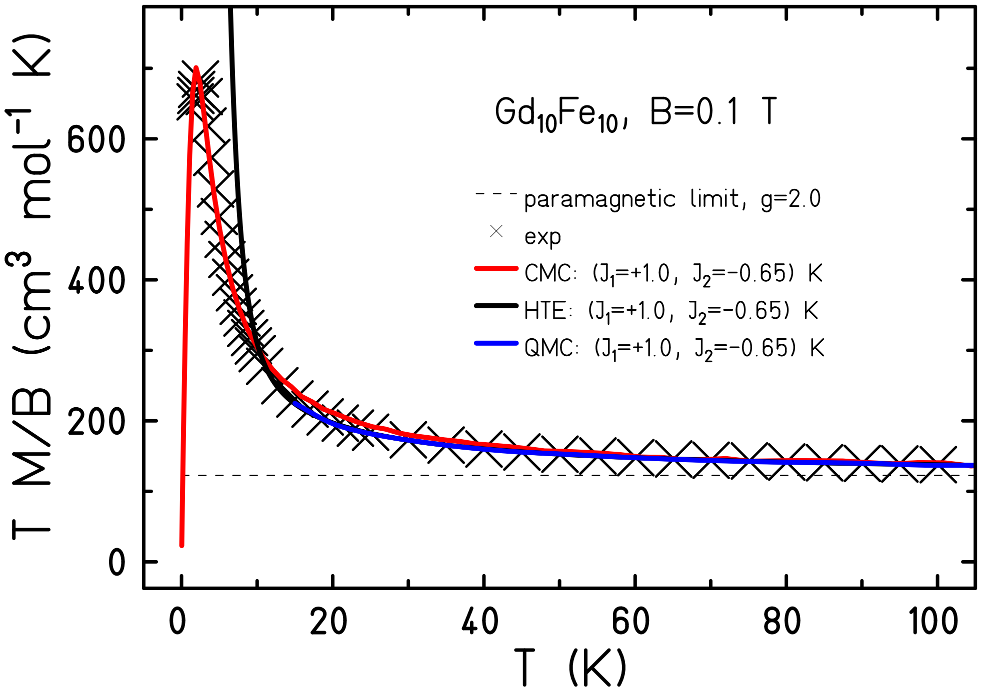


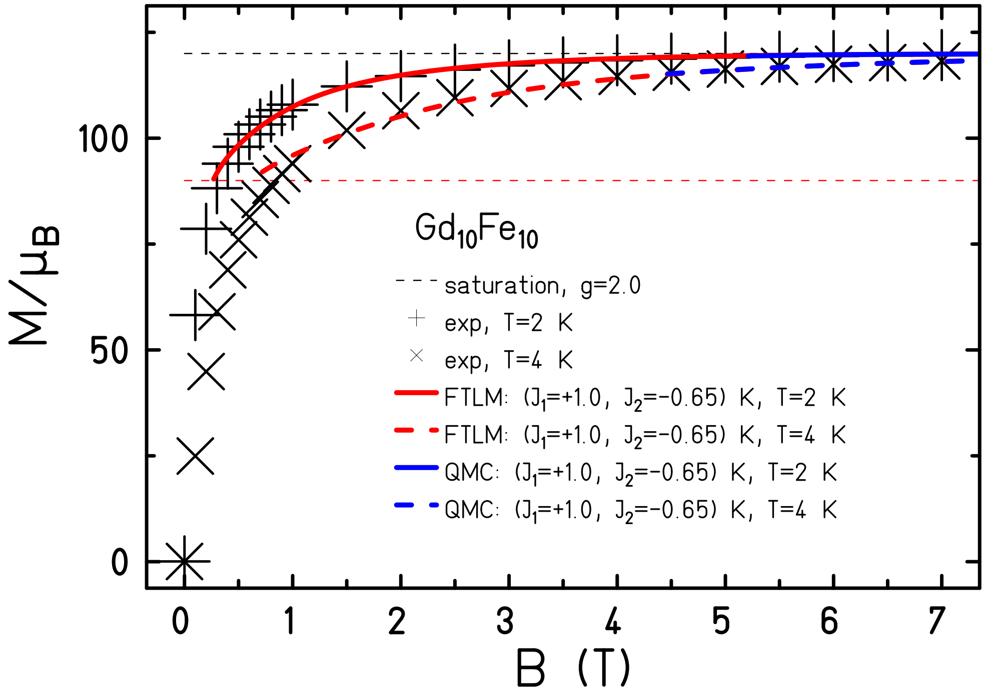
purple: Gd ($s = 7/2$), green: Fe ($s = 5/2$)

We will see: J_1 ferro, J_2 antiferro

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

Gd$_{10}$Fe$_{10}$ – Methods



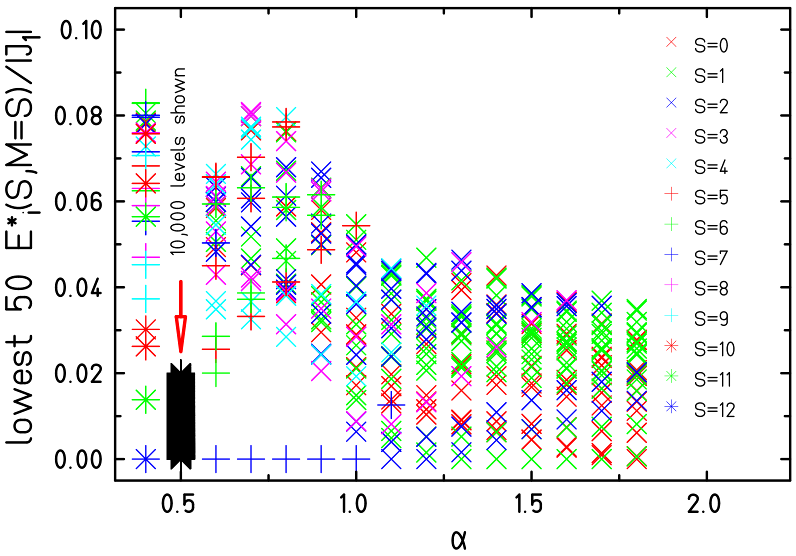


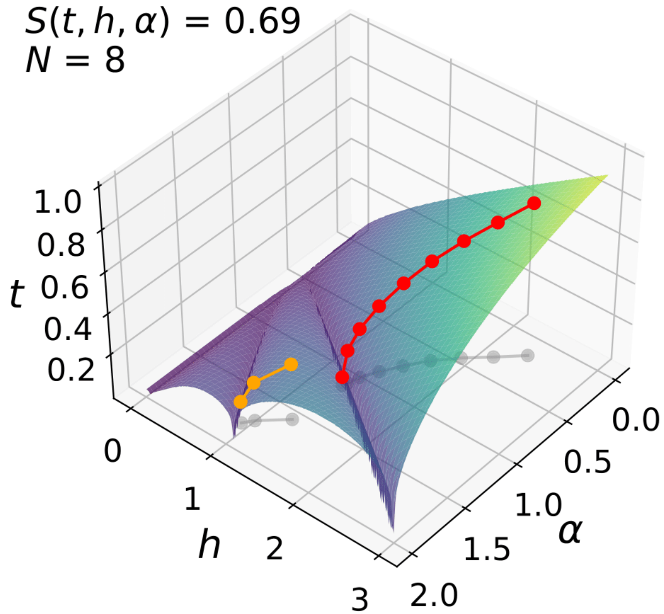
Methods: HTE, QMC, CMC, FTLM $\Rightarrow J_1 = 1.0$ K, $J_2 = -0.65$ K

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

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

$Gd_{10}Fe_{10}$ – 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. Large ground state spins deliver many low-lying levels, but also favour dipolar ordering.
- Good MCE materials need a balance of molecular and lattice optimization.

Thank you very much for your attention.

Many thanks to my collaborators














- C. Beckmann, M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, K. Irländer, N.B. Ivanov, H.-T. Langwald, A. Müller, H. Schlüter, R. Schnalle, Chr. Schröder, J. Ummethum, P. Vorndamme, J. Waltenberg, D. Westerbeck (Bielefeld)
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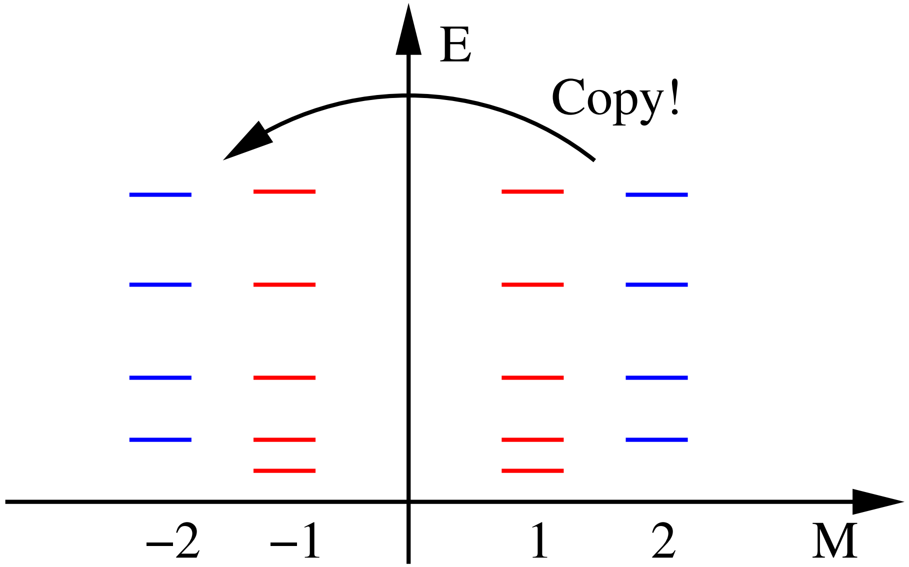
Highlights. Tutorials. Who is who. Conferences.

Why is FTLM so good?



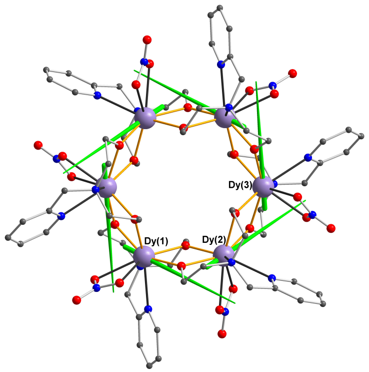
$\underset{\sim}{S}^z$–symmetry is used, spectra are generated in orthogonal subspaces $\mathcal{H}(M \geq 0)$

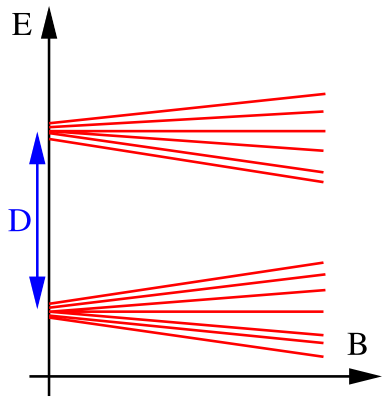
spectra for subspaces $\mathcal{H}(M < 0)$ are taken as copies

What would happen if you would generate the spectra for subspaces $\mathcal{H}(M)$ and $\mathcal{H}(-M)$ in independent random processes?

Effective model for Dy$_6$

$$\underset{\sim}{H} = \sum_{k<\ell} \underset{\sim}{\vec{j}}_k \cdot \mathbf{J}_{k\ell} \cdot \underset{\sim}{\vec{j}}_\ell + \sum_k \underset{\sim}{\vec{j}}_k \cdot \mathbf{D}_k \cdot \underset{\sim}{\vec{j}}_k + \mu_B \vec{B} \cdot \sum_k g_k \underset{\sim}{\vec{j}}_k$$

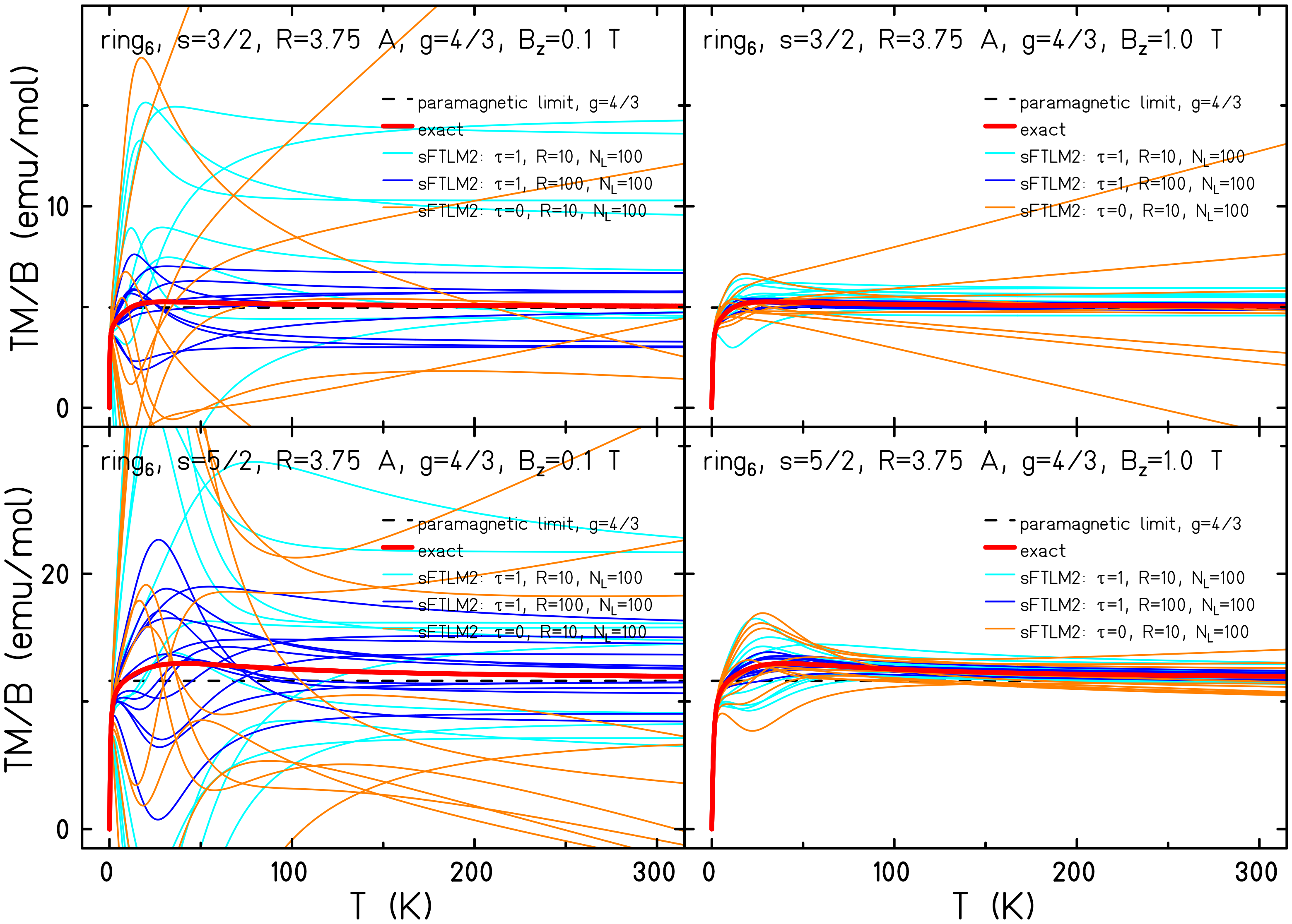




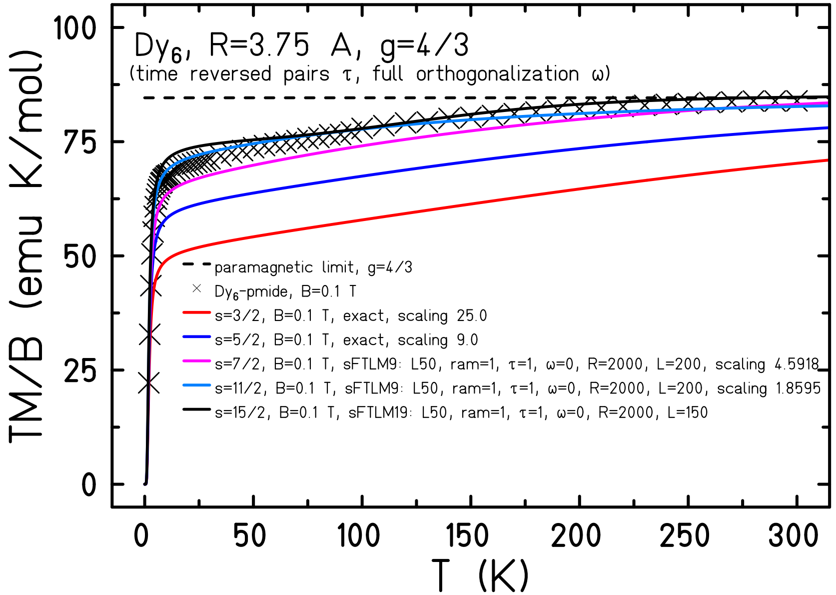
- Very strong alternating easy axes with $D \approx -20$ K. $J \approx -0.02$ K and (stronger) dipolar interaction.
- Hamiltonian has no symmetries! Anisotropy is dominant.
- dim$\mathcal{H} = 16,777,216 \quad \Rightarrow \quad$ FTLM!

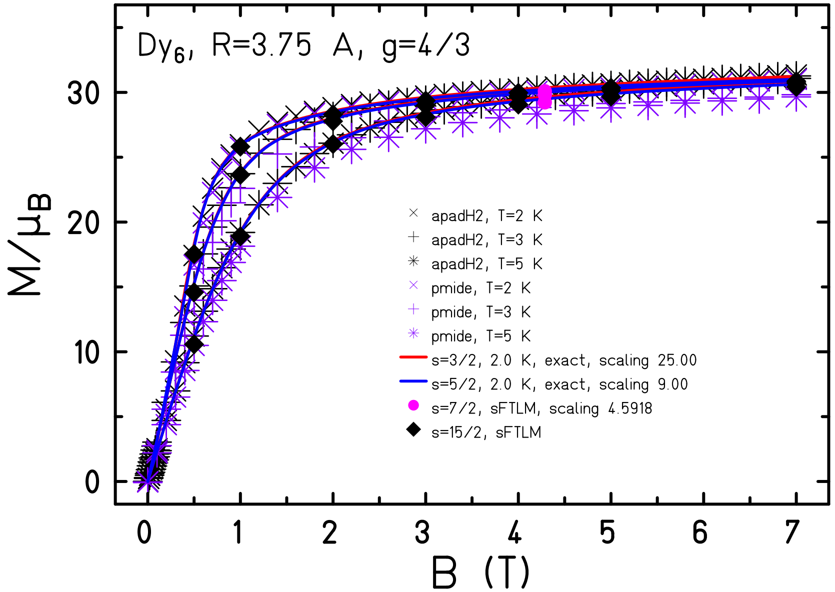
Warning! Method is approximate and holds only for small enough B since spin and orbital angular momentum have got different g_k.

Problem – FTLM converges badly for anisotropic models



Dy_6 – results





1. Use pairs of time-reversed random vectors (1)

2. Use symmetric version of FTLM (2):

$$\mathrm{Tr}\left(\underset{\sim}{Q} e^{-\beta \underset{\sim}{H}}\right) = \mathrm{Tr}\left(e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}/2}\right) \approx \langle\, r \,|\, e^{-\beta \underset{\sim}{H}/2} \underset{\sim}{Q} e^{-\beta \underset{\sim}{H}/2} \,|\, r \,\rangle \neq \langle\, r \,|\, e^{-\beta \underset{\sim}{H}} \underset{\sim}{Q} \,|\, r \,\rangle$$

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(2) M. Aichhorn, M. Daghofer, H. G. Evertz, and W. von der Linden, Phys. Rev. B **67**, 161103(R) (2003).
(3) D. Westerbeck, Ph.D. thesis, Bielefeld University (2025).