

# The power of typicality applied to magnetic molecules and low-dimensional quantum spin systems

Jürgen Schnack

Department of Physics – University of Bielefeld – Germany

<http://obelix.physik.uni-bielefeld.de/~schnack/>

APS March Meeting 2020 Seminar, Chemistry, Colorado State University  
Fort Collins, Colorado, 3 March 2020

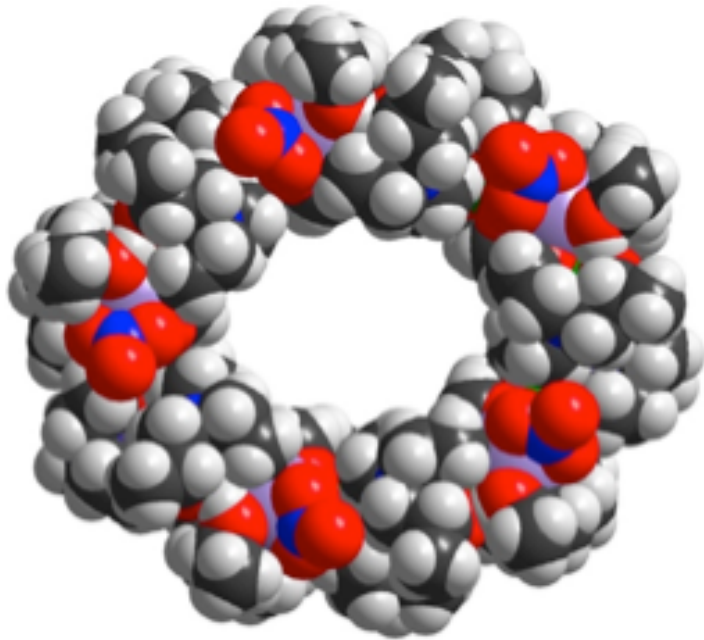
# My new office: 500 15th Street, Denver, CO 80202



# We investigate magnetic molecules

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

# You have got a molecule!



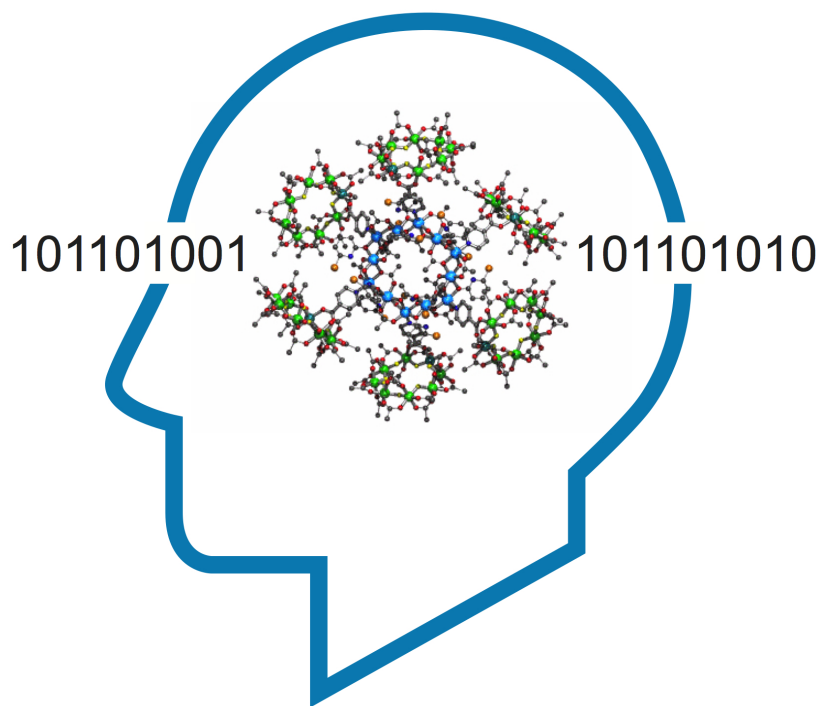
$$S = 60!$$

Congratulations!

Powell group: npj Quantum Materials **3**, 10 (2018)



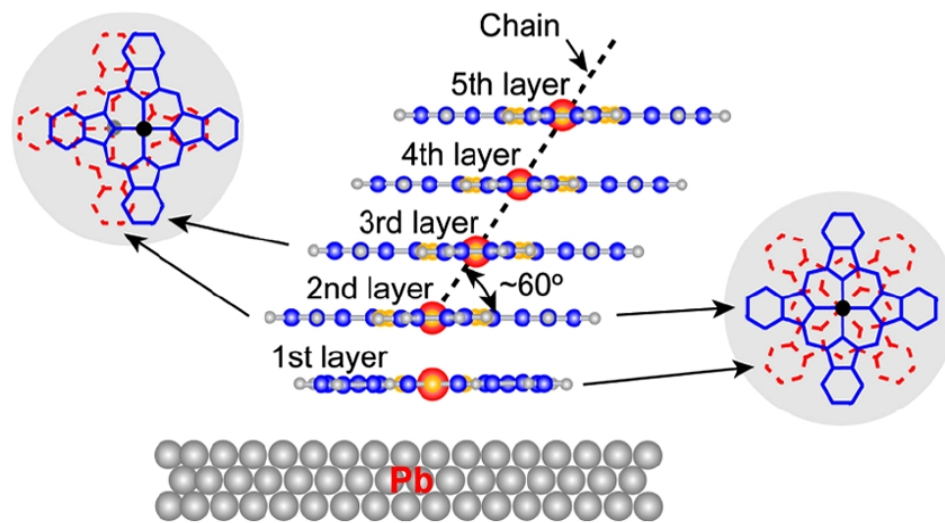
# You want to build a quantum computer!



Very smart!

Wernsdorfer group: Phys. Rev. Lett. **119**, 187702 (2017)

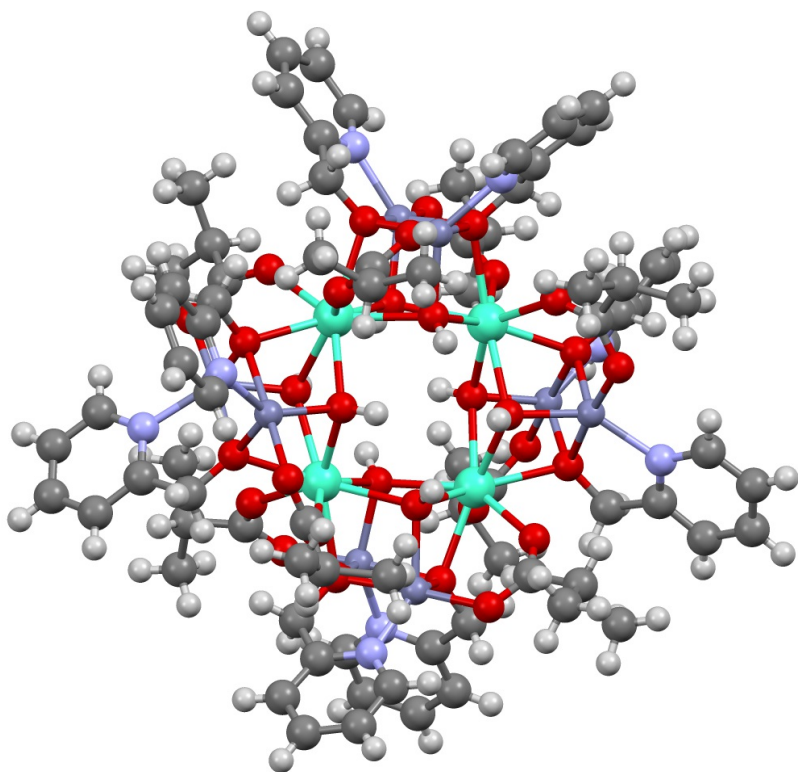
# You want to deposit your molecule!



Next generation magnetic storage!

Xue group: Phys. Rev. Lett. **101**, 197208 (2008)

# You want molecular magnetocalorics!



Brilliant!

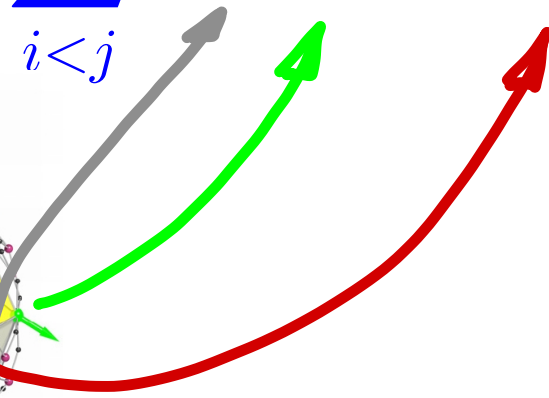
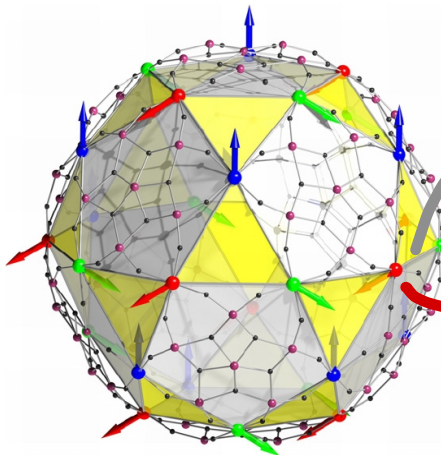
Brechin group: *Angew. Chem. Int. Ed.* **51**, 4633 (2012)

You have got an idea about the modeling!

Heisenberg

Zeeman

$$\underline{H} = -2 \sum_{i < j} J_{ij} \underline{\tilde{s}}(i) \cdot \underline{\tilde{s}}(j) + g \mu_B B \sum_i^N s_z(i)$$



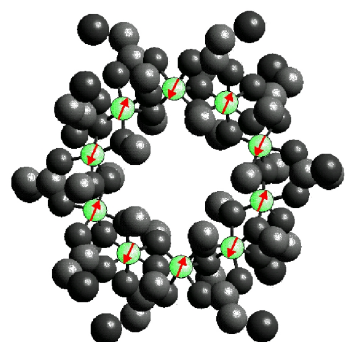
# You have to solve the Schrödinger equation!

$$\underline{\tilde{H}} |\phi_n\rangle = E_n |\phi_n\rangle$$

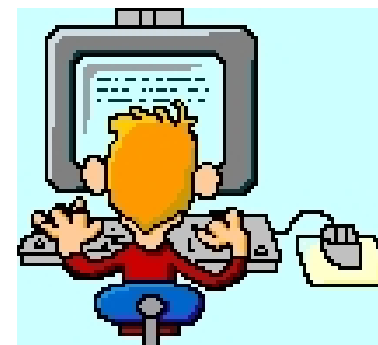
Eigenvalues  $E_n$  and eigenvectors  $|\phi_n\rangle$

- 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!



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



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

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

Can we evaluate the partition function

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

without diagonalizing the Hamiltonian?



# 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. Typicality-based estimates
2. Gd<sub>7</sub> and the magnetocaloric effect
3. Fe<sub>10</sub>Gd<sub>10</sub> and a quantum critical behavior
4. FTLM for anisotropic spin models
5. Bonus: Kagome lattice antiferromagnet – Is 42 the final answer?

We are the sledgehammer team of matrix diagonalization.  
Please send inquiries to [jschnack@uni-bielefeld.de](mailto:jschnack@uni-bielefeld.de)!

## Solution I: trace estimators

$$\text{tr}(\tilde{Q}) \approx \langle r | \tilde{Q} | r \rangle$$

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

- $|\nu\rangle$  some orthonormal basis of your choice; not the eigenbasis of  $\tilde{Q}$ , 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

$$\exp \left[ -\beta \underline{H} \right] \approx \underline{1} - \beta \underline{H} + \frac{\beta^2}{2!} \underline{H}^2 - \dots - \frac{\beta^{N_L-1}}{(N_L-1)!} \underline{H}^{N_L-1}$$

applied to a state  $|r\rangle$  yields a superposition of

$$\underline{1}|r\rangle, \quad \underline{H}|r\rangle, \quad \underline{H}^2|r\rangle, \quad \dots \underline{H}^{N_L-1}|r\rangle.$$

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

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

## Partition function I: simple approximation

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

$$O^r(T, B) \approx \frac{\langle r | Q_{\tilde{H}} e^{-\beta \tilde{H}} | r \rangle}{\langle r | e^{-\beta \tilde{H}} | r \rangle}$$

- 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???

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

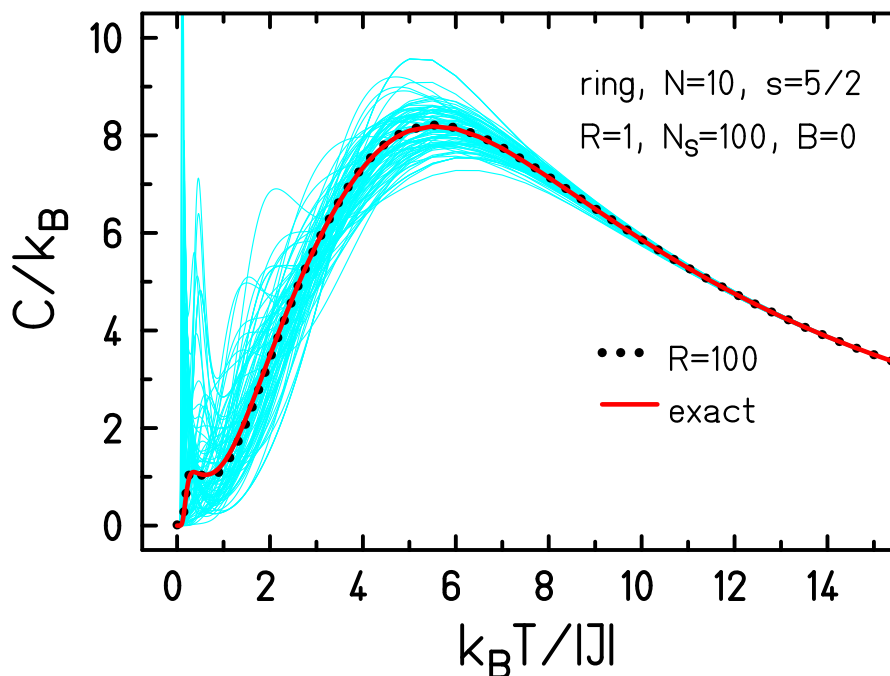
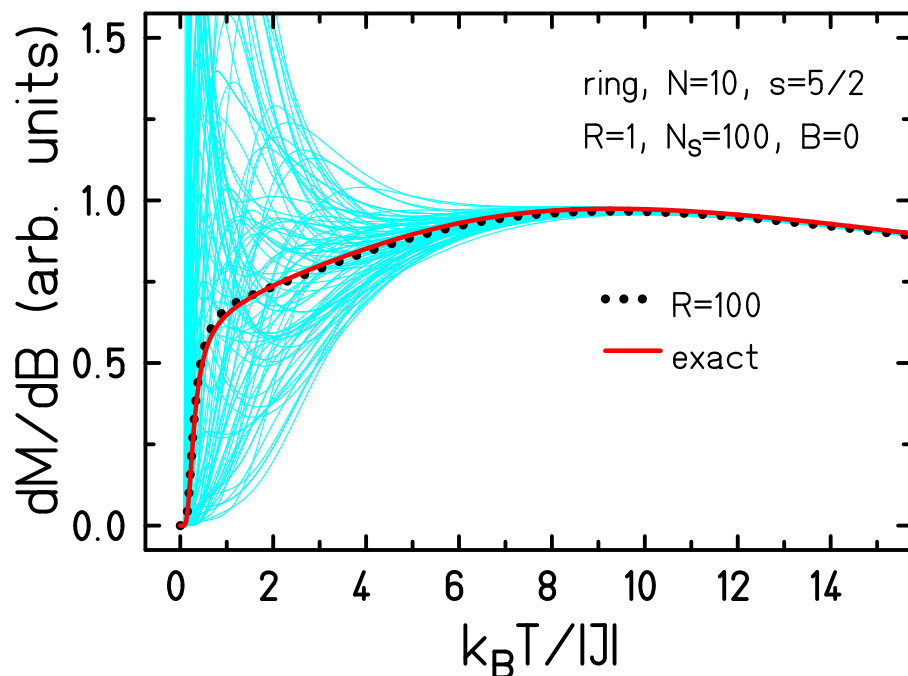
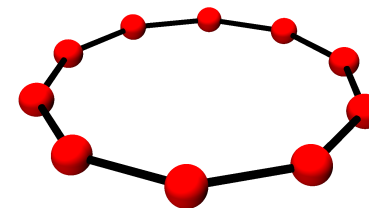
## Partition function II: Finite-temperature Lanczos Method

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

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

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

# FTLM 1: ferric wheel

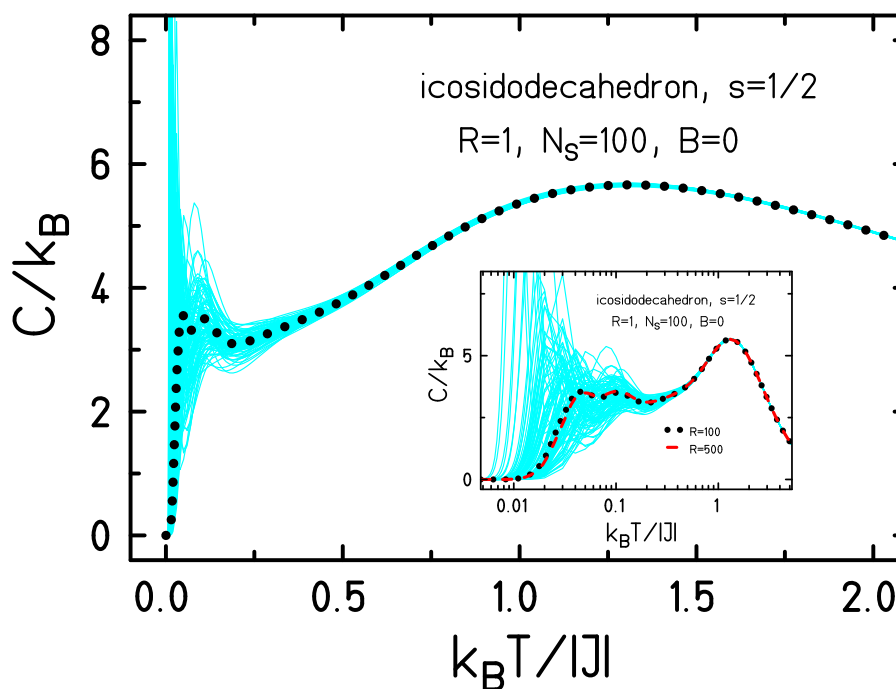
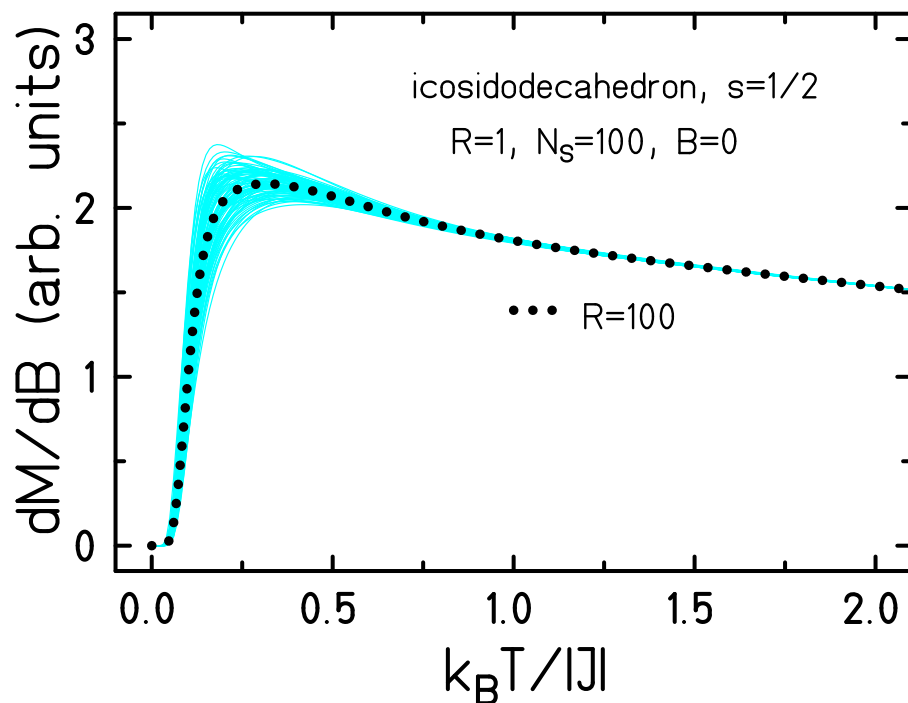
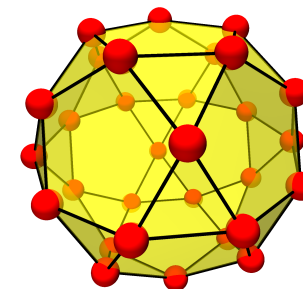


(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

(2) SU(2) & D<sub>2</sub>: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403 (2010).

(3) SU(2) & C<sub>N</sub>: T. Heitmann, J. Schnack, Phys. Rev. B **99**, 134405 (2019)

# FTLM 2: icosidodecahedron

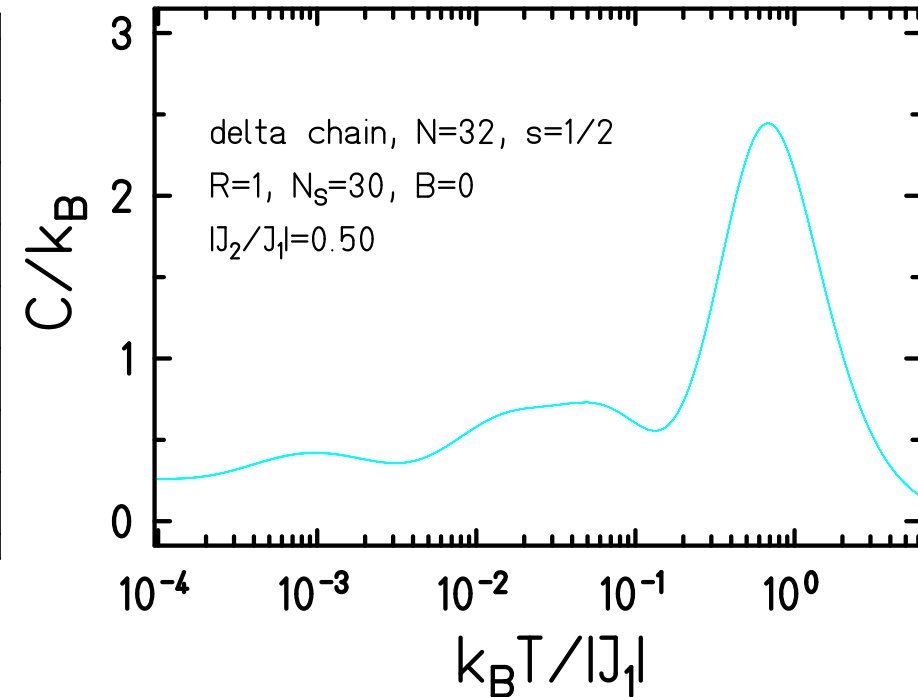
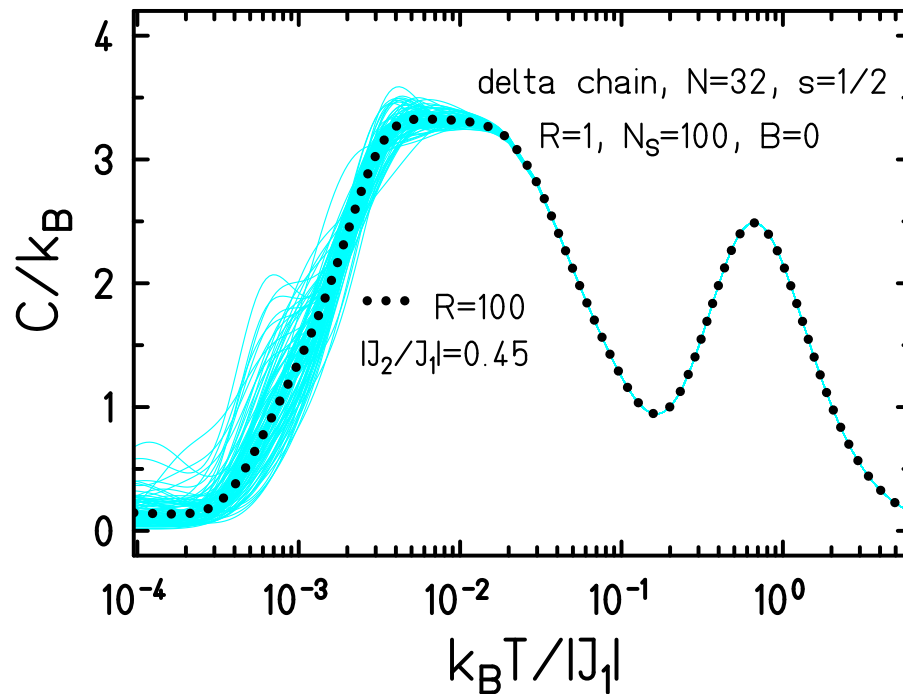
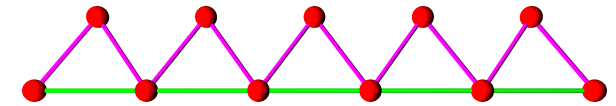


(1) J. Schnack, J. Richter, R. Steinigeweg, Phys. Rev. Research **2**, 013186 (2020).

(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.

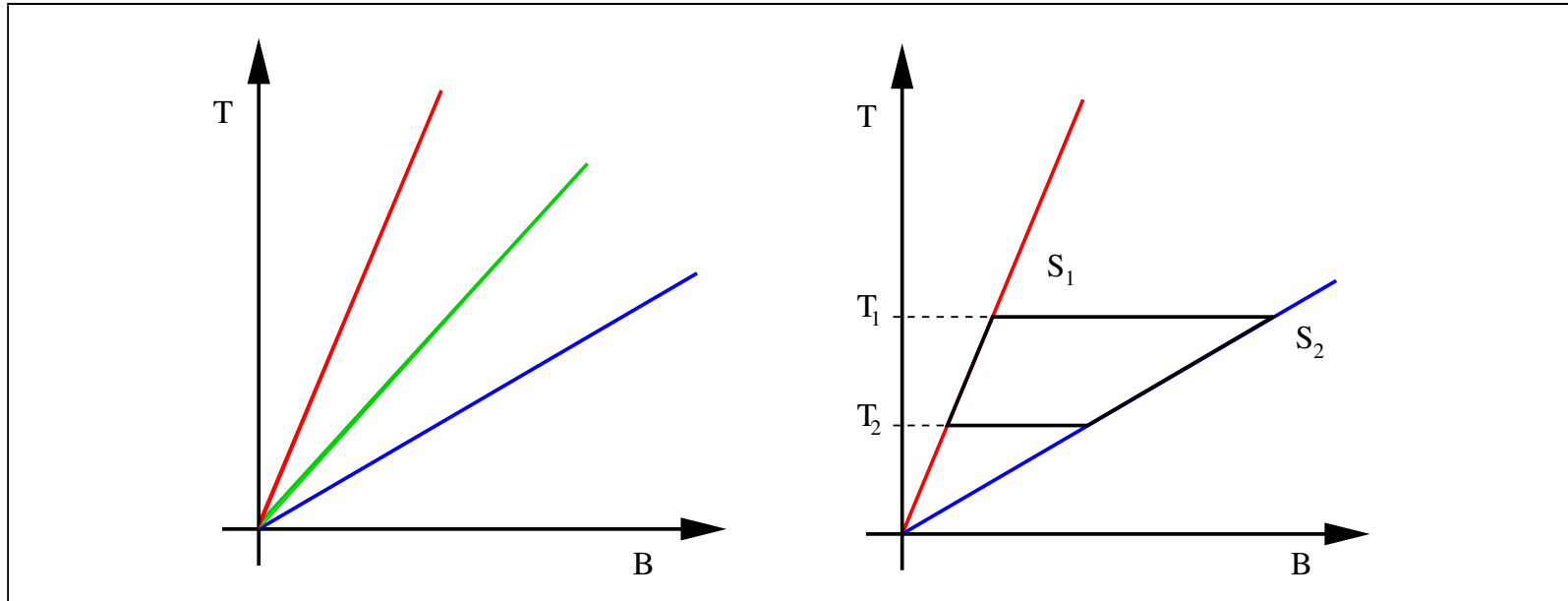
Frustration, technically speaking, works in your favour.

(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 (2020) accepted, arXiv:2002.00411

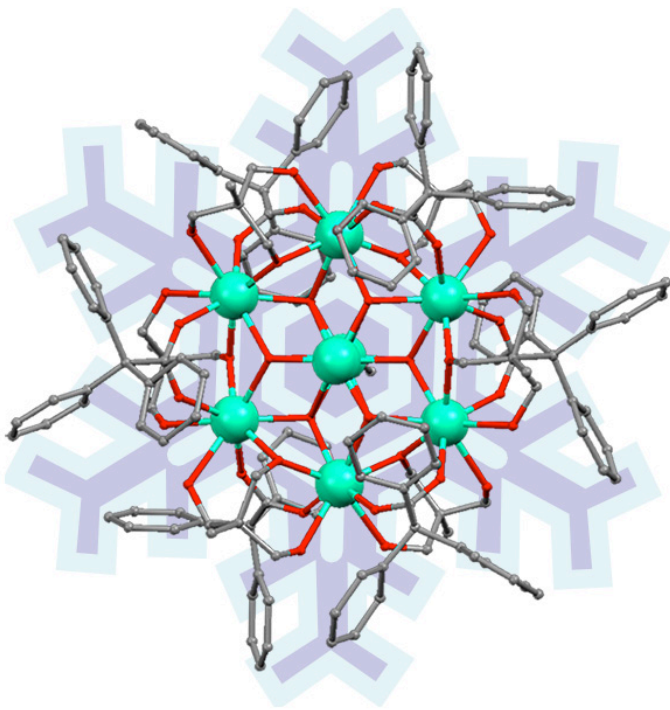
# Gd<sub>7</sub> and the magnetocaloric effect

# 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.

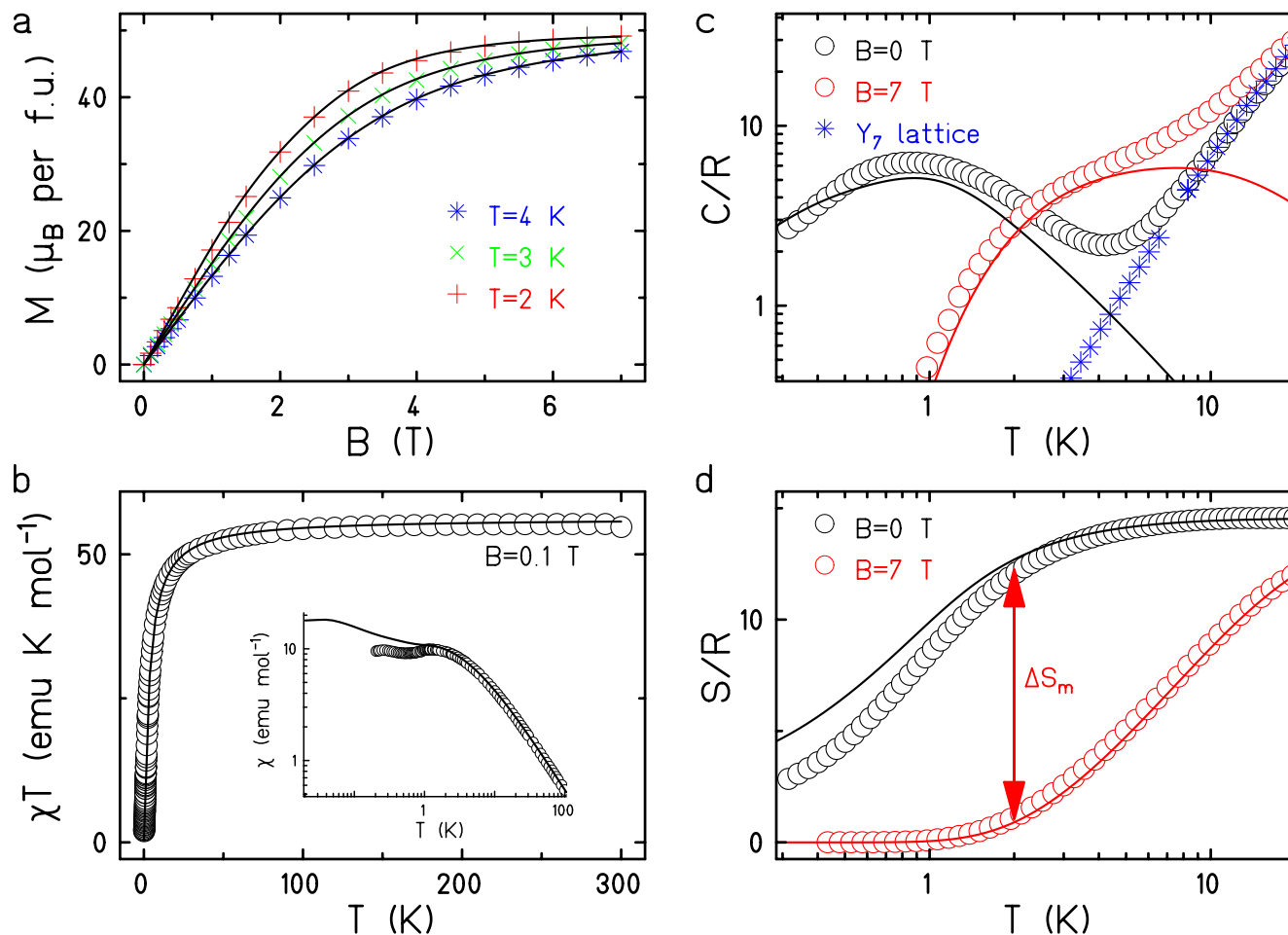
## Gd<sub>7</sub> – Basics



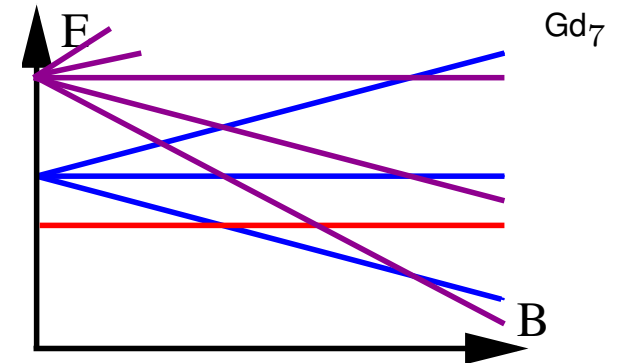
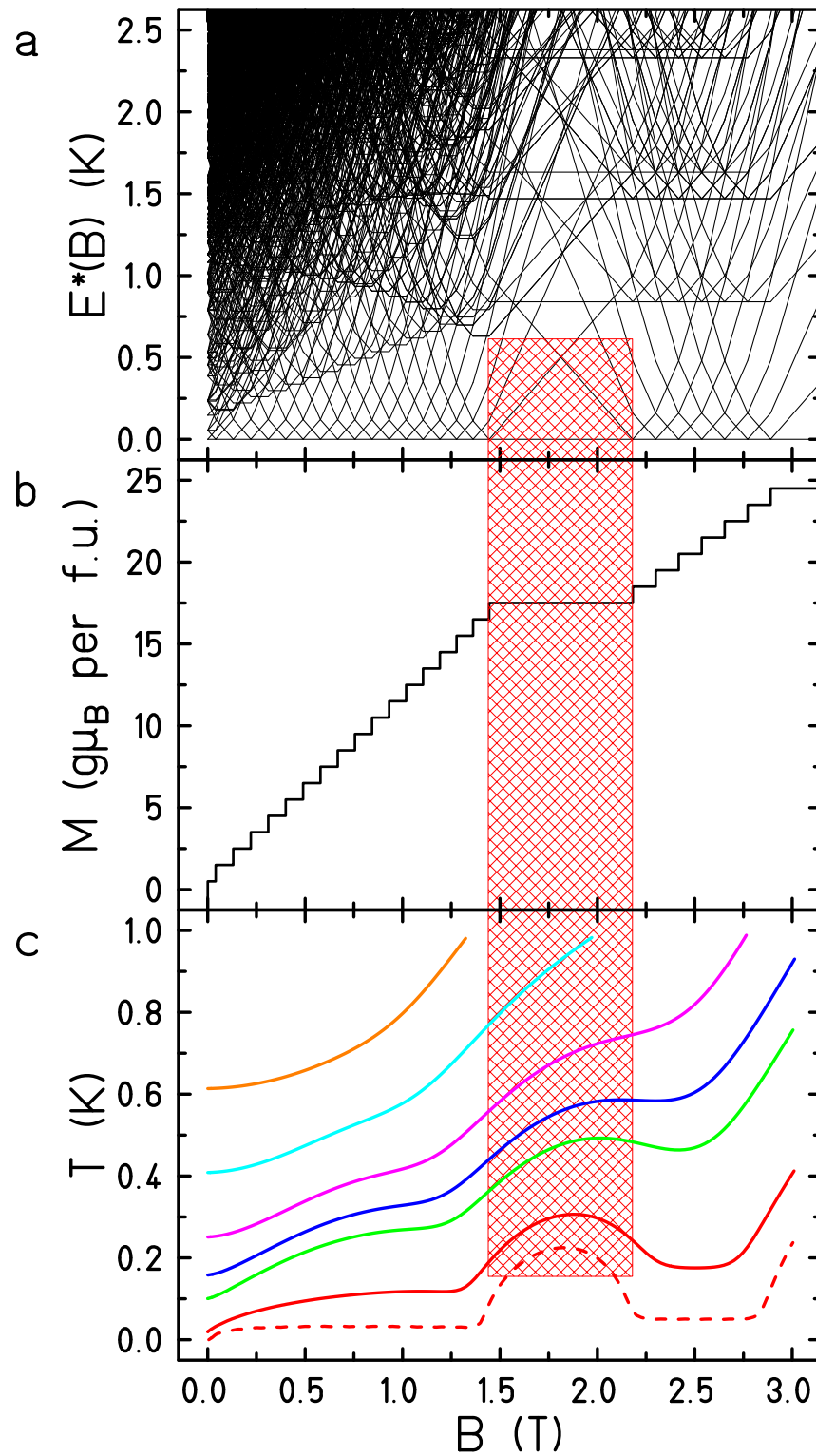
- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $$\underline{H} = -2 \sum_{i < j} J_{ij} \vec{\zeta}_i \cdot \vec{\zeta}_j + g \mu_B B \sum_i^N \zeta_i^z$$
  
 $J_1 = -0.090(5) \text{ K}, J_2 = -0.080(5) \text{ K}$   
 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).

# Gd<sub>7</sub> – experiment & theory



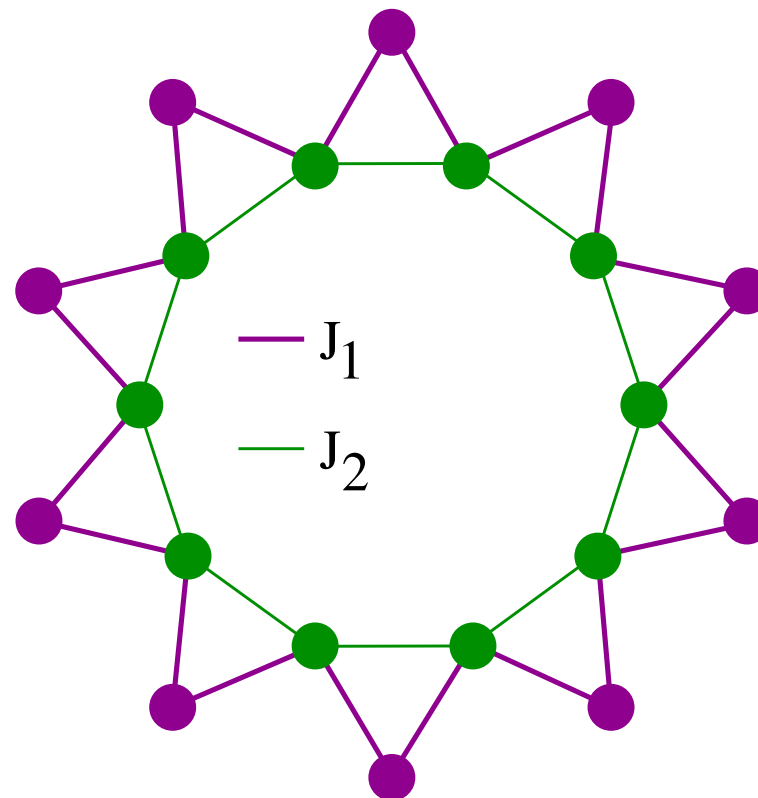
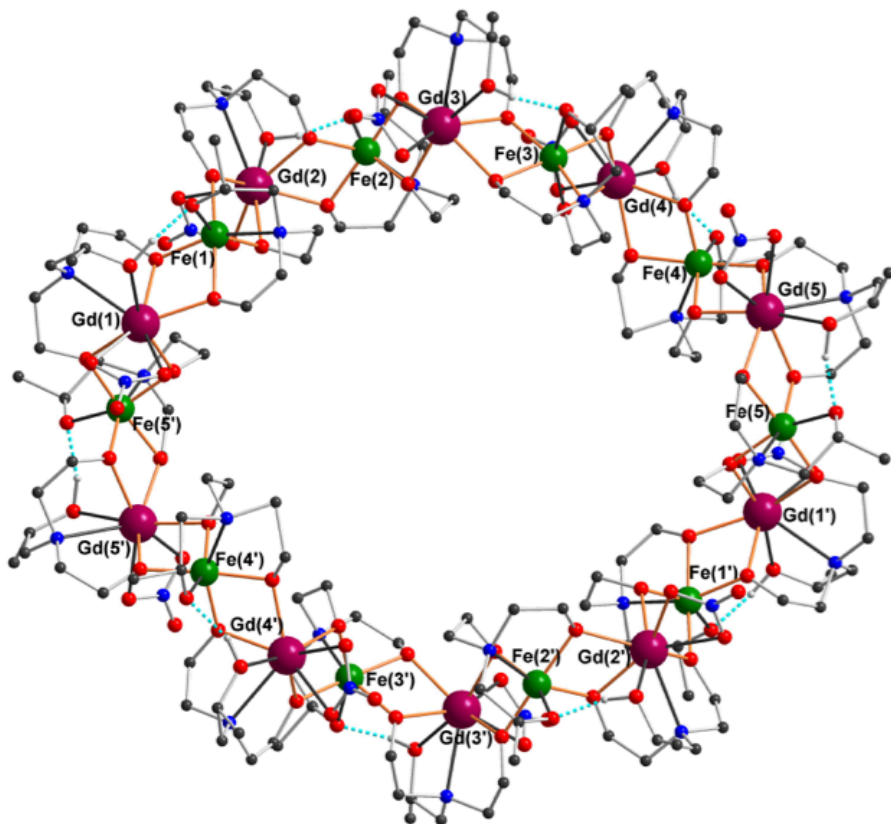
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).



# $\text{Fe}_{10}\text{Gd}_{10}$ and quantum critical behavior



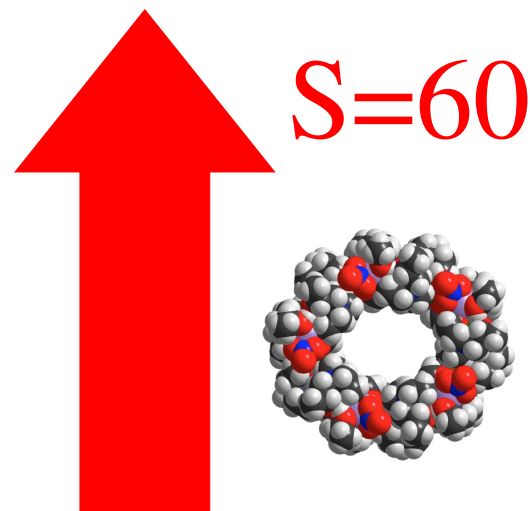
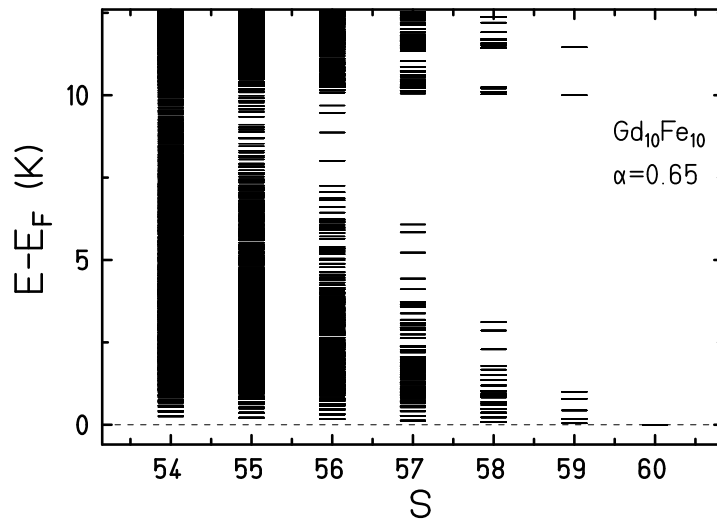
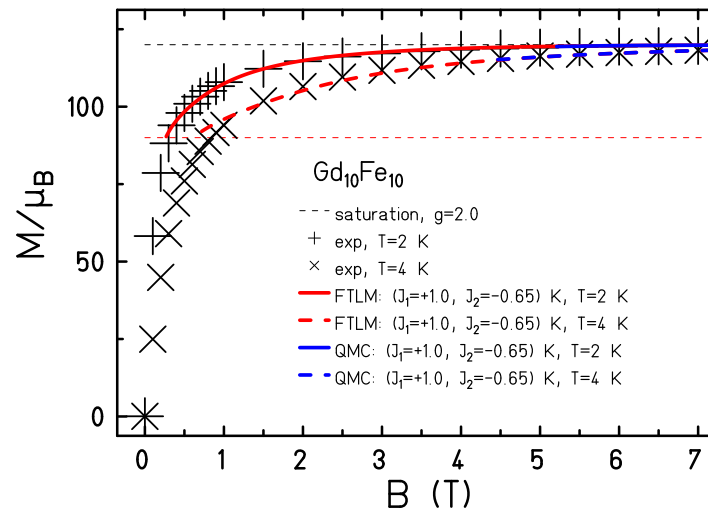
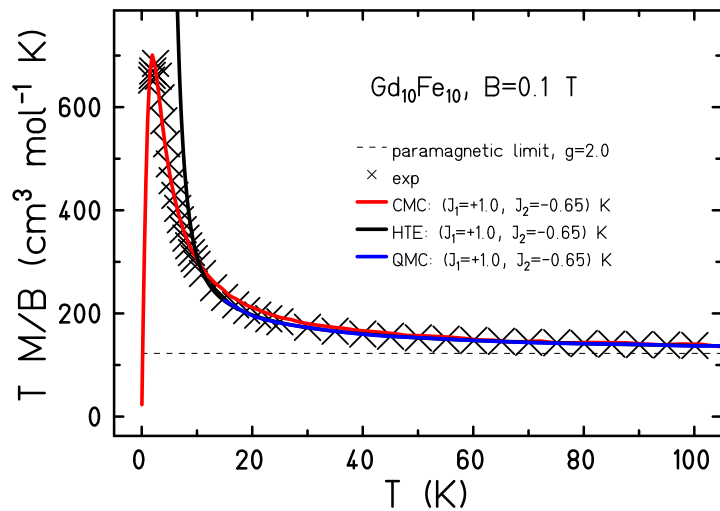
# Gd<sub>10</sub>Fe<sub>10</sub> – structure = delta chain



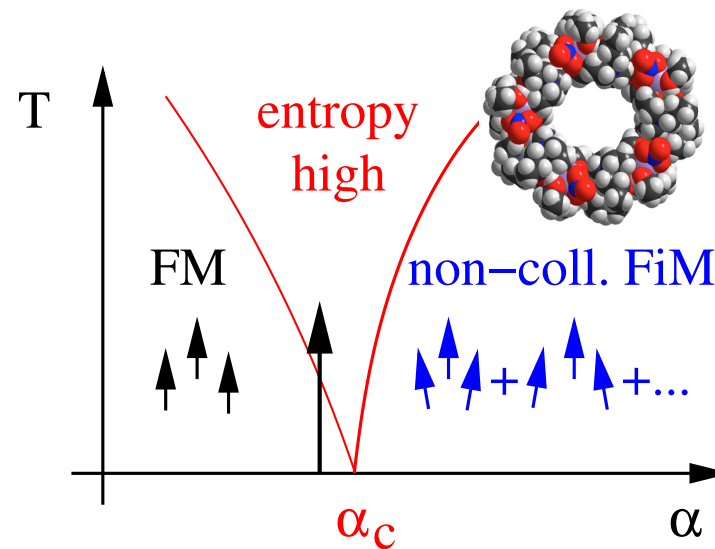
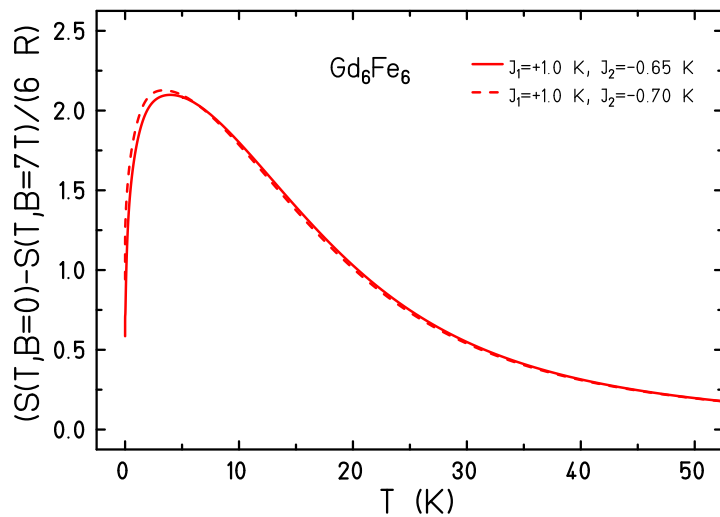
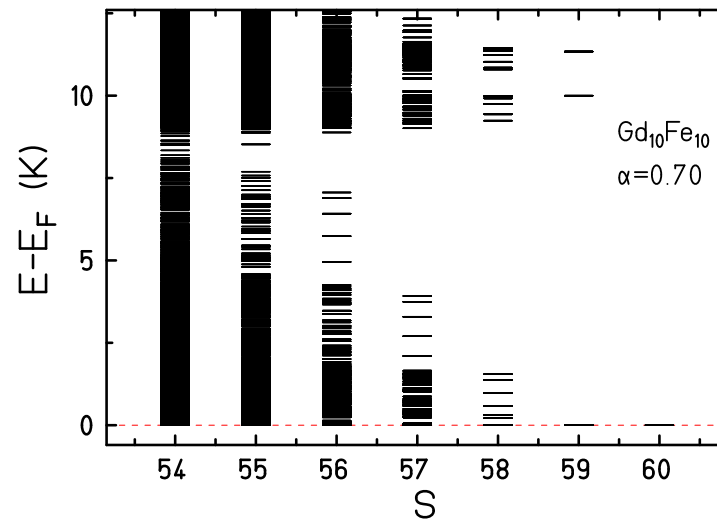
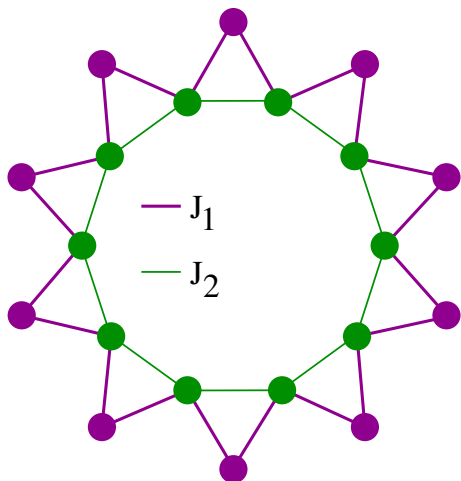
purple: Gd ( $s = 7/2$ ), green: Fe ( $s = 5/2$ )

We will see:  $J_1$  ferro,  $J_2$  antiferro

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



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



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

# Single Molecule Magnets

## Finite-temperature Lanczos Method III

$$\tilde{H} = -2 \sum_{i < j} \vec{\tilde{S}}_i \cdot \mathbf{J}_{ij} \cdot \vec{\tilde{S}}_j + \sum_i \vec{\tilde{S}}_i \cdot \mathbf{D}_i \cdot \vec{\tilde{S}}_i + \mu_B B \sum_i g_i \tilde{S}_i^z$$

- Problem: for anisotropic Hamiltonians no symmetry left  
→ accuracy drops (esp. for high  $T$ ).
- Simple traces such as  $\text{Tr} \left( \tilde{S}^z \right) = 0$  tend to be wrong for  $R$  not very big.

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

## Finite-temperature Lanczos Method IV

Employ very general symmetry (time-reversal invariance)

$$\vec{\mathcal{M}}(T, -\vec{B}) = -\vec{\mathcal{M}}(T, \vec{B})$$

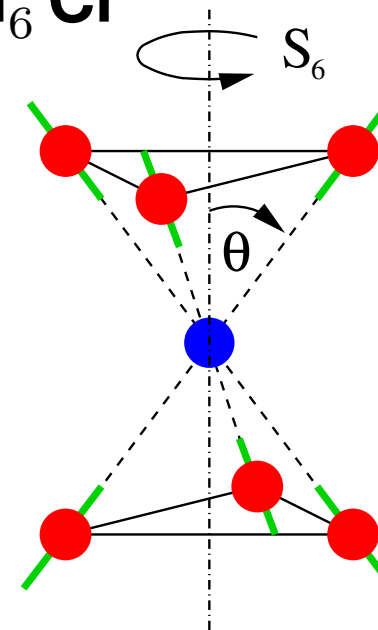
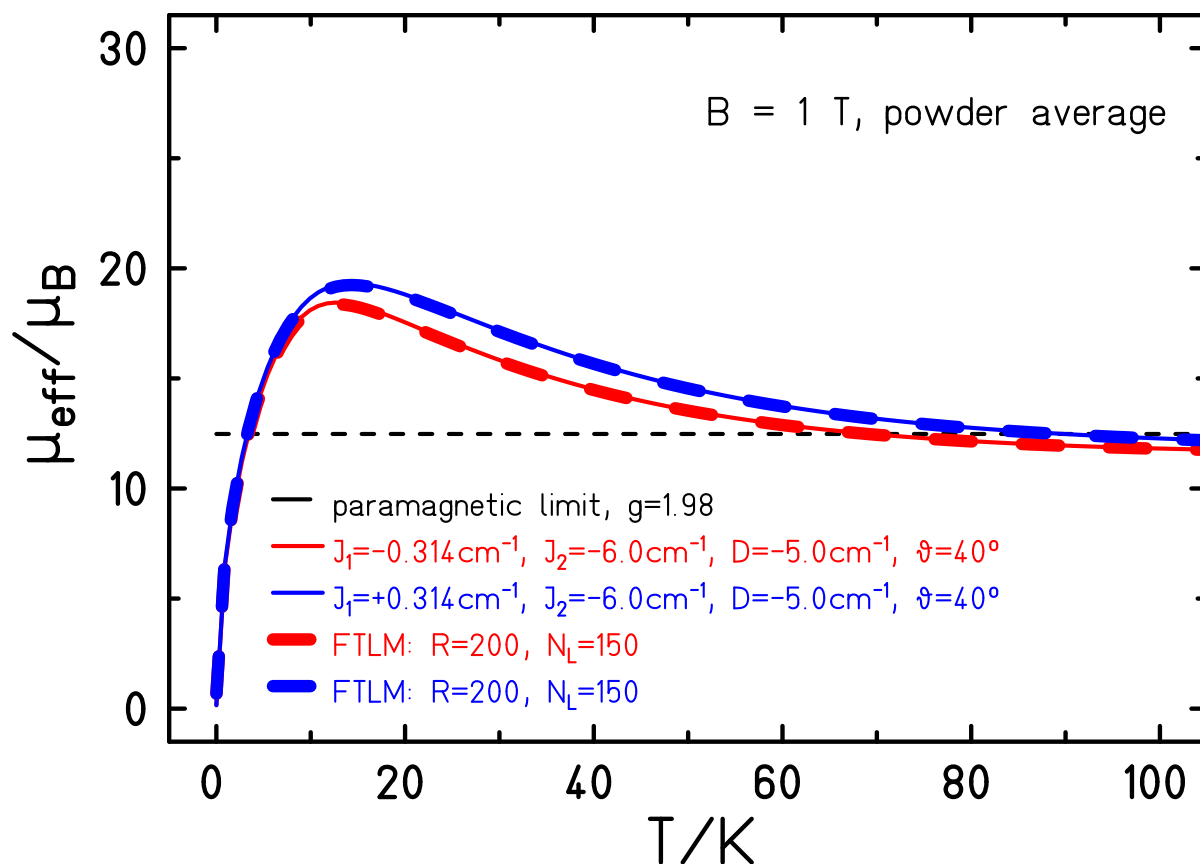
Use Lanczos energy eigenvector  $|n(\nu)\rangle$  and time-reversed counterpart  $|\tilde{n}(\nu)\rangle$

$$|n(\nu)\rangle = \sum_{\vec{m}} c_{\vec{m}} |\vec{m}\rangle \quad , \quad |\tilde{n}(\nu)\rangle = \sum_{\vec{m}} c_{\vec{m}}^* |-\vec{m}\rangle$$

- Restores  $\vec{\mathcal{M}}(T, -\vec{B}) = -\vec{\mathcal{M}}(T, \vec{B})$  and (some) traces.
- More practical: use pairs of time-reversed random vectors; still accurate.

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

# Glaser-type molecules: $\text{Mn}_6\text{Cr}^{\text{III}}$



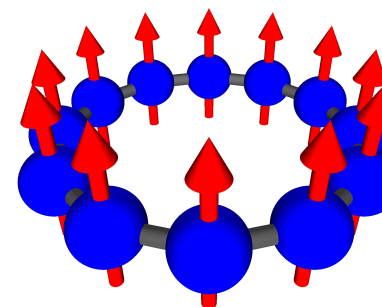
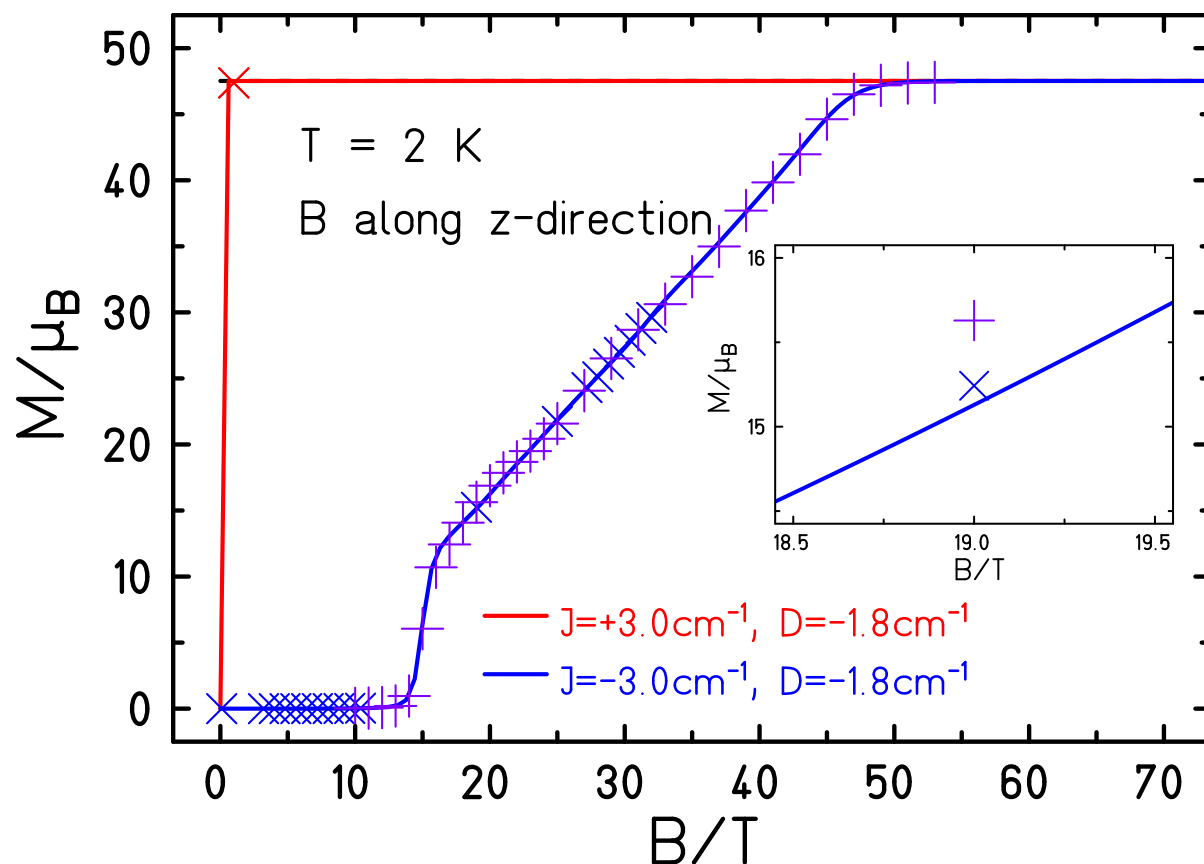
$s = 2, s = 3/2$   
 $\dim(\mathcal{H}) = 62,500$   
 non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)



# A fictitious $\text{Mn}_{12}^{\text{III}}$ – $M_z$ vs $B_z$

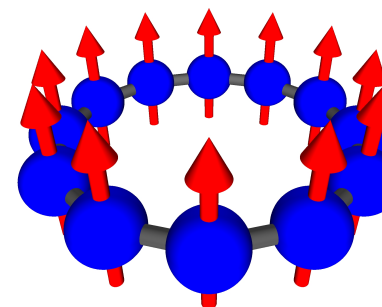
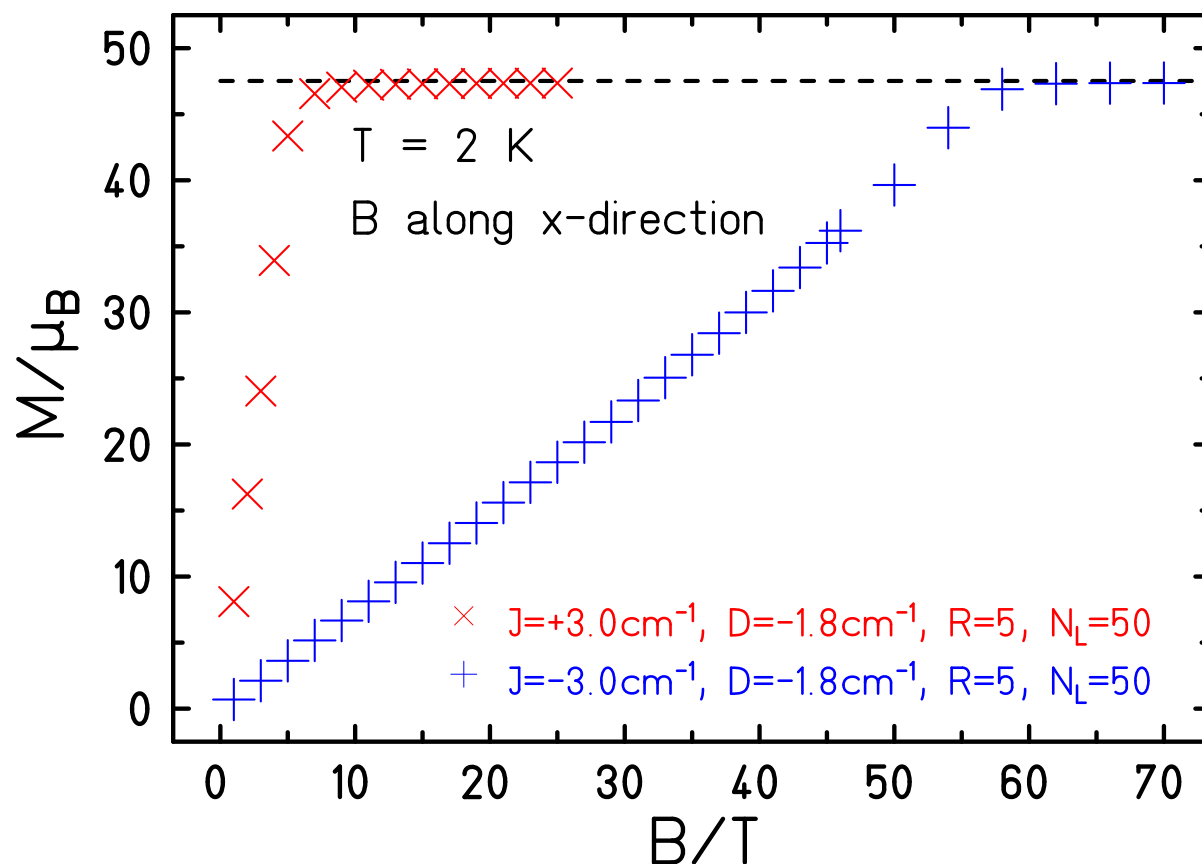


$s = 2$   
 $\dim(\mathcal{H}) = 244, 140, 625$   
 collinear easy axes

A few days compared to *impossible!*

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

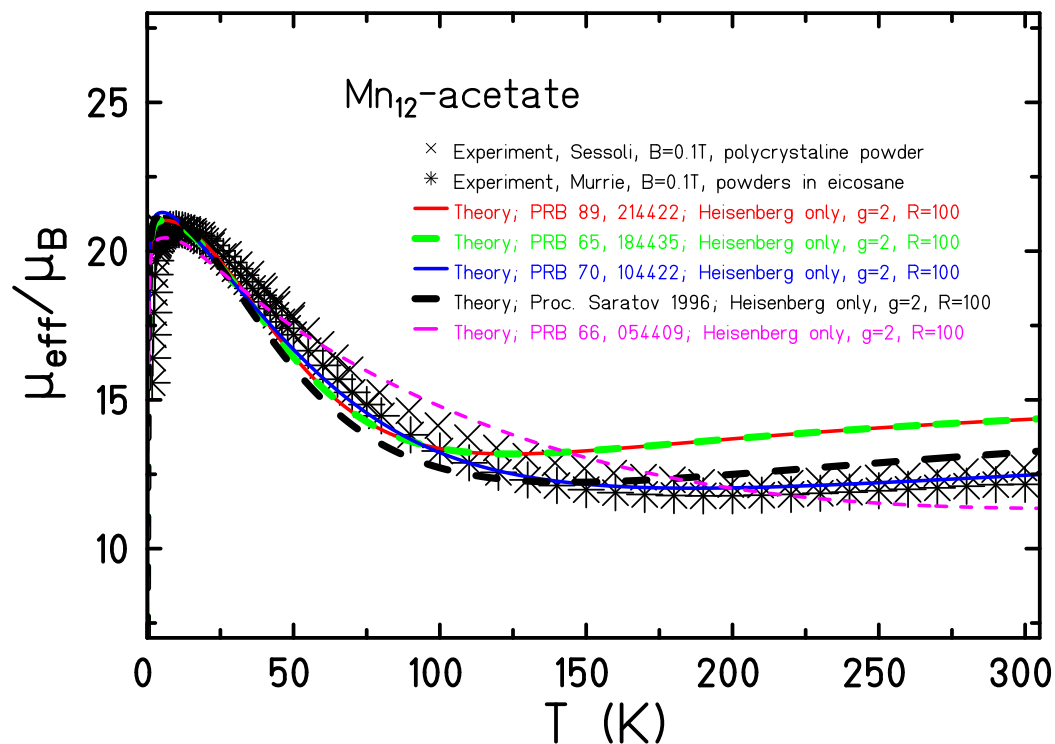
# A fictitious $\text{Mn}_{12}^{\text{III}}$ – $M_x$ vs $B_x$



No other method can deliver these curves!

O. Hanebaum, J. Schnack, Eur. Phys. J. B **87**, 194 (2014)

# Effective magnetic moment of Mn<sub>12</sub>-acetate



We can check DFT parameter predictions for large molecules! **Normally!**

O. Hanebaum, J. Schnack, Phys. Rev. B **92** (2015) 064424

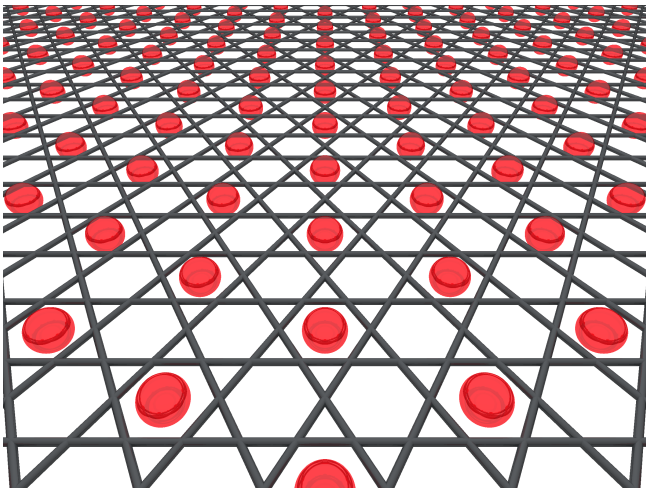
⇒ S. Ghassemi Tabrizi, A. V. Arbuznikov, and M. Kaupp, J. Phys. Chem. A **120**, 6864 (2016).



# The kagome lattice antiferromagnet

Is 42 the final answer?

# Kagome lattice antiferromagnet – scientific problems

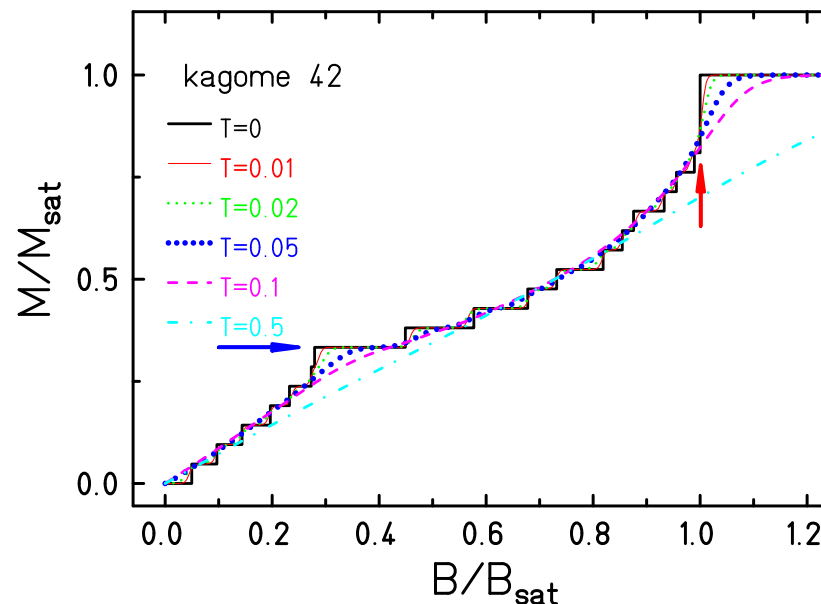
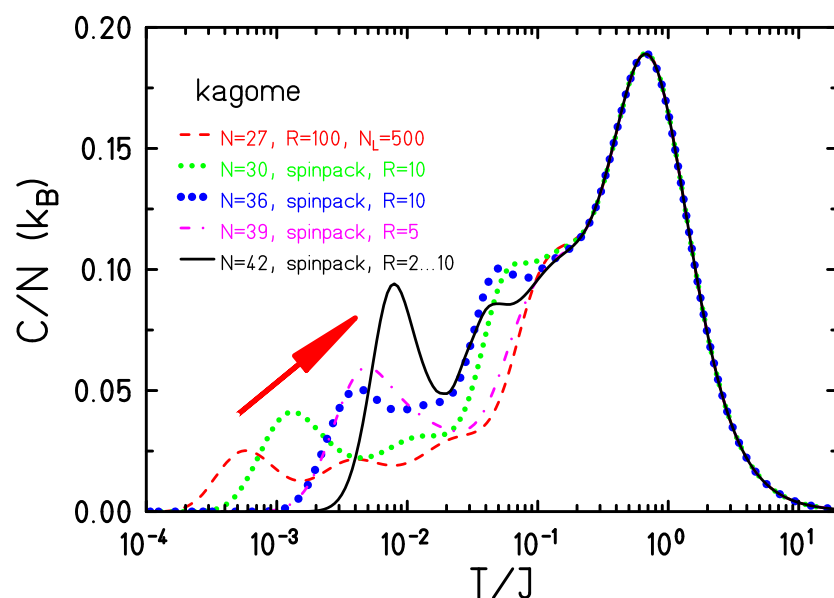


- Thermodynamic functions, in particular heat capacity and susceptibility (1)
- “Condensation” of low-lying singlets below the first triplet?
- Magnetization jump to saturation
- Thermal stability of magnetization plateaus, e.g. at  $\mathcal{M}_{\text{sat}}/3$ .
- Notoriously enigmatic (2)!

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

(2) A.M. Läuchli, J. Sudan, R. Moessner, Phys. Rev. B **100**, 155142 (2019)

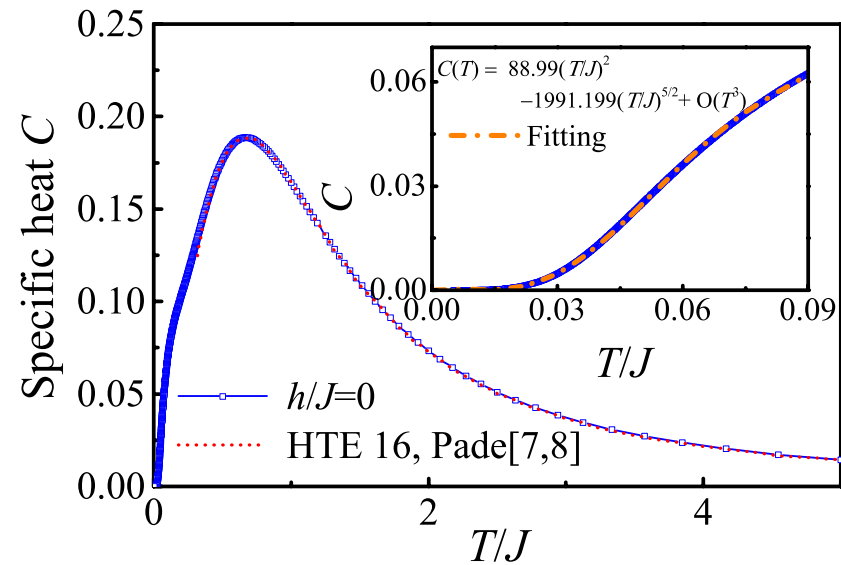
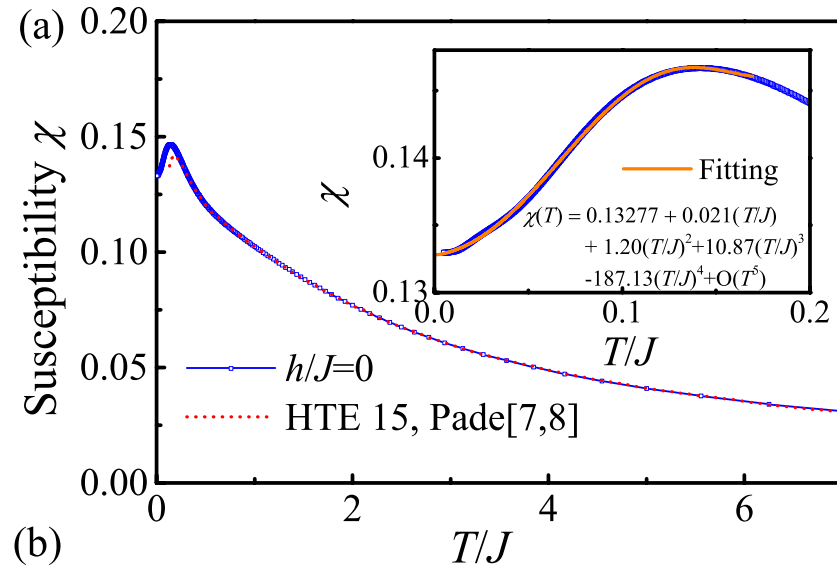
# Kagome 42 – magnetic properties



- Low- $T$  peak moves to higher  $T$  with increasing  $N$ .
- **Density of low-lying singlets seems to move to higher excitation energies!**

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

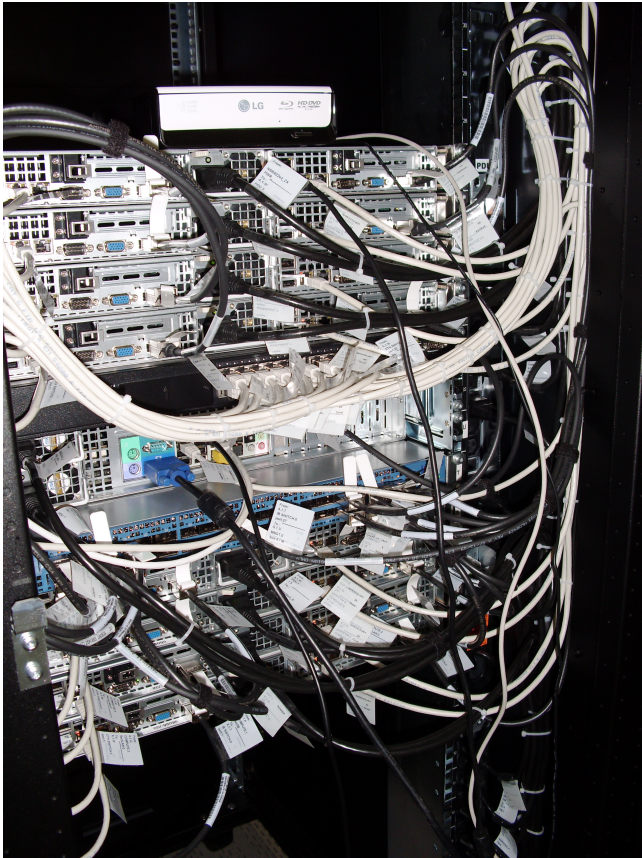
# Kagome – tensor network calculations



- Tensor network calculations for the infinite system (1).

(1) Xi Chen, Shi-Ju Ran, Tao Liu, Cheng Peng, Yi-Zhen Huang, Gang Su, Science Bulletin **63**, 1545 (2018).

# Summary



- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- Molecules taught us about frustrated systems.
- Isentropes for interacting systems are much richer than for paramagnets. Good for applications away from  $(T = 0, B = 0)$ .
- Quantum phase transitions may allow barocaloric applications.
- ED, HTE, CMC, QMC, FTLM, DMRG, DDMRG, thDMRG for magnetic molecules.



# 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, P. Vorndamme (Bielefeld)
- **K. Bärwinkel, T. Heitmann, R. Heveling, H.-J. Schmidt, R. Steinigeweg (Osnabrück)**
- M. Luban (Ames Lab); 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 (Zaragoza); A. Honecker (U Cergy-Pontoise); E. Garlatti, S. Carretta, G. Amoretti, P. Santini (Parma); A. Tennant (ORNL); Gopalan Rajaraman (Mumbai); M. Affronte (Modena)
- J. Richter, J. Schulenburg (Magdeburg); B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); A. Powell, W. Wernsdorfer (Karlsruhe); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your  
attention.

The end.

Molecular Magnetism Web

[www.molmag.de](http://www.molmag.de)

Highlights. Tutorials. Who is who. Conferences.