

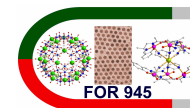
Isentropes design: advanced many-body methods for magnetic cooling

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Magdeburg, 14. 04. 2015



How can we cool things?

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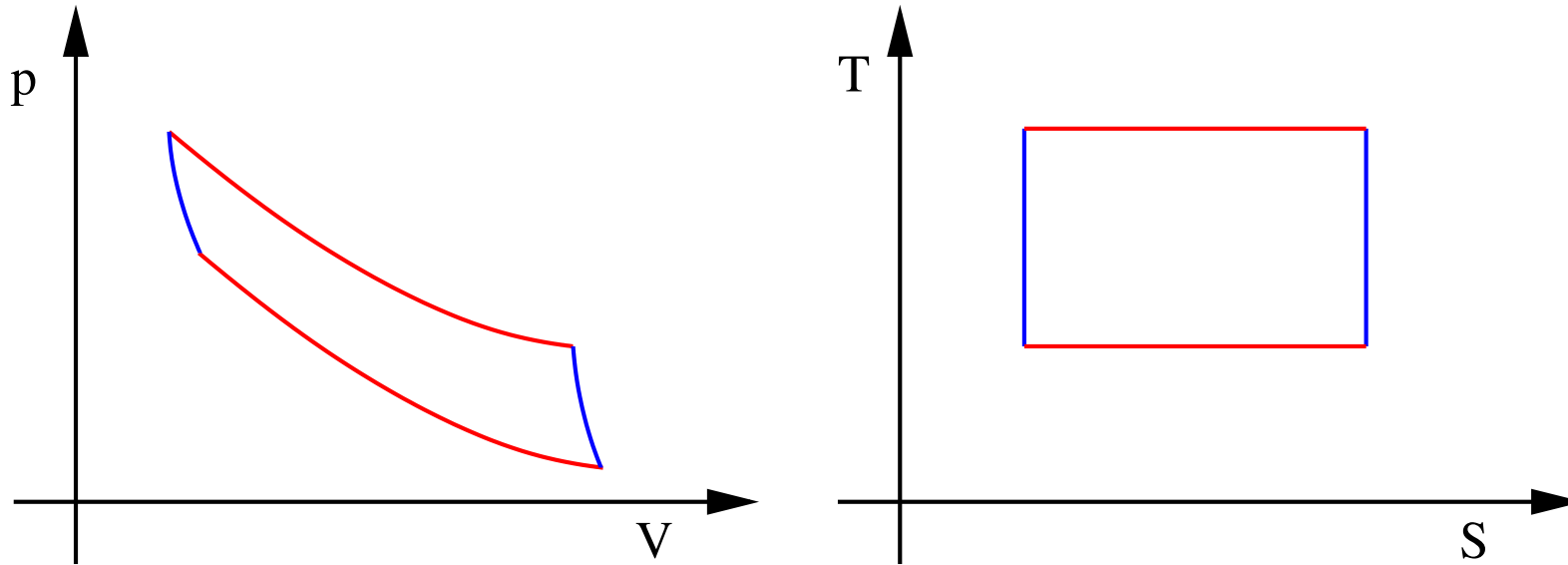
How can we cool things?

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

$C = C_p$: heat capacity at constant pressure

$\left(\frac{\partial T}{\partial p}\right)_S$ adiabatic cooling rate

How can we cool things? – Carnot process



needs work to cool one colder substance by Q_2 and releases heat Q_1 to another hotter substance

Should also work with
magnetic substances!

Contents 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. **The magnetocaloric effect**
2. Magnetocalorics of molecules
3. **Finite-Temperature Lanczos**

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 . . . 2 K/T.
- Giant magnetocaloric effect: 3 . . . 4 K/T e.g. in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ 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

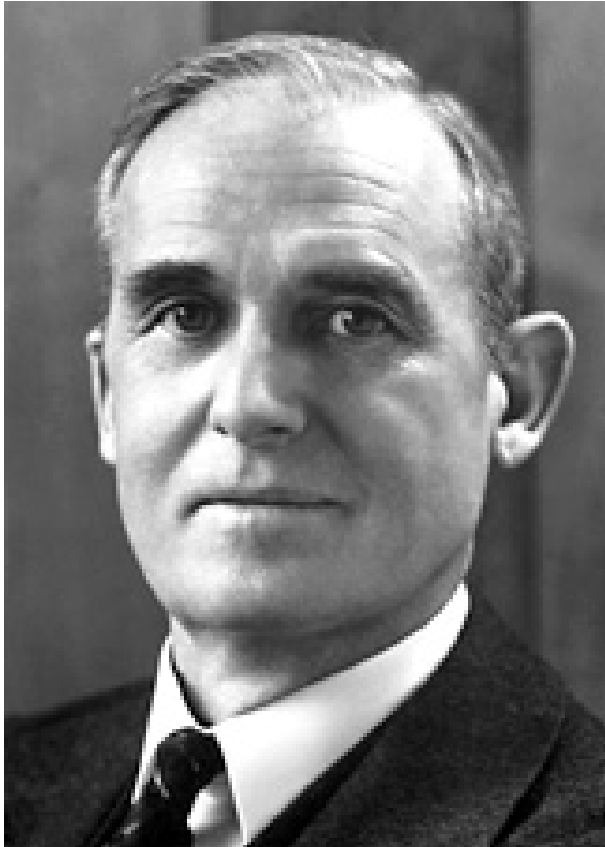
$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C} \left(\frac{\partial S}{\partial B}\right)_T$$

$C = C_B = T \left(\frac{\partial S}{\partial T}\right)_B$: 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).

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

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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.

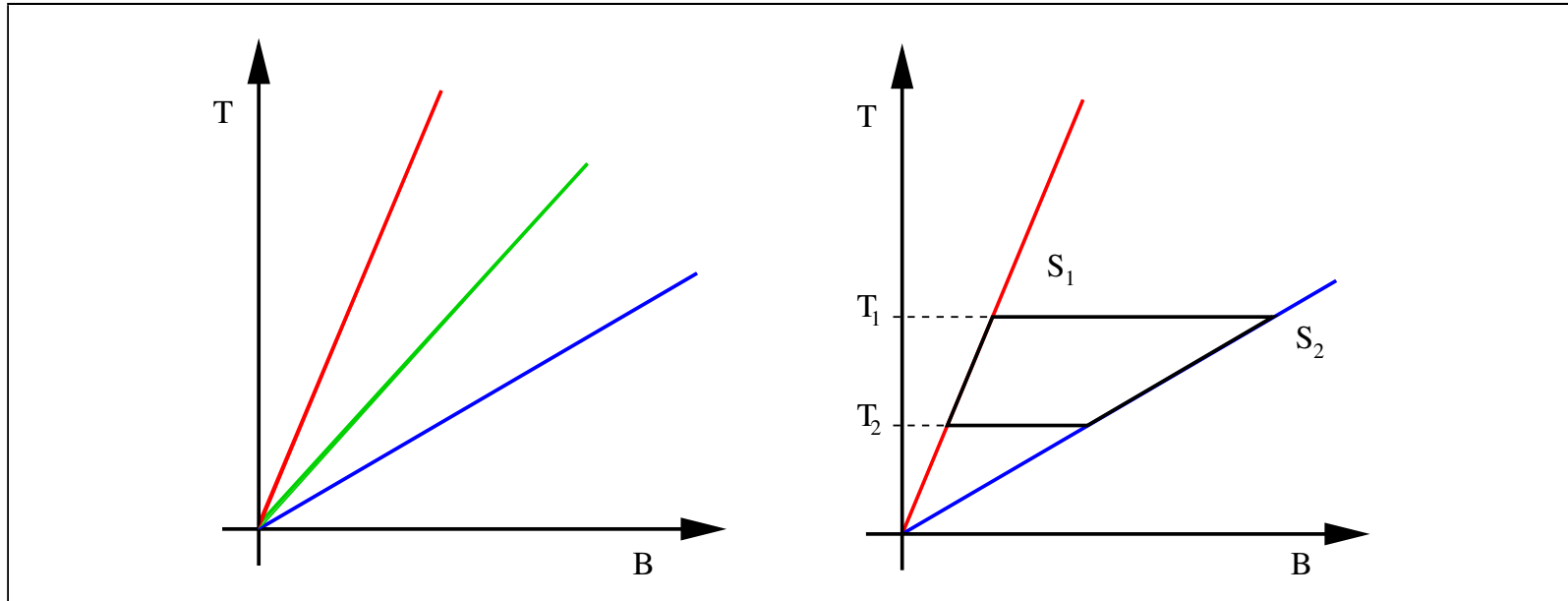
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. GIAUQUE
D. P. MACDOUGALL

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

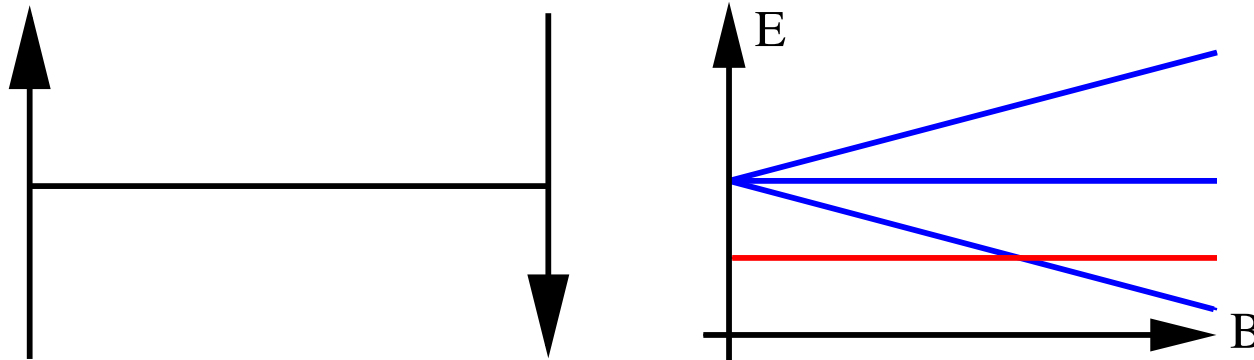
W. F. Giauque and D. MacDougall, *Phys. Rev.* **43**, 768 (1933).

Magnetocaloric effect – Paramagnets



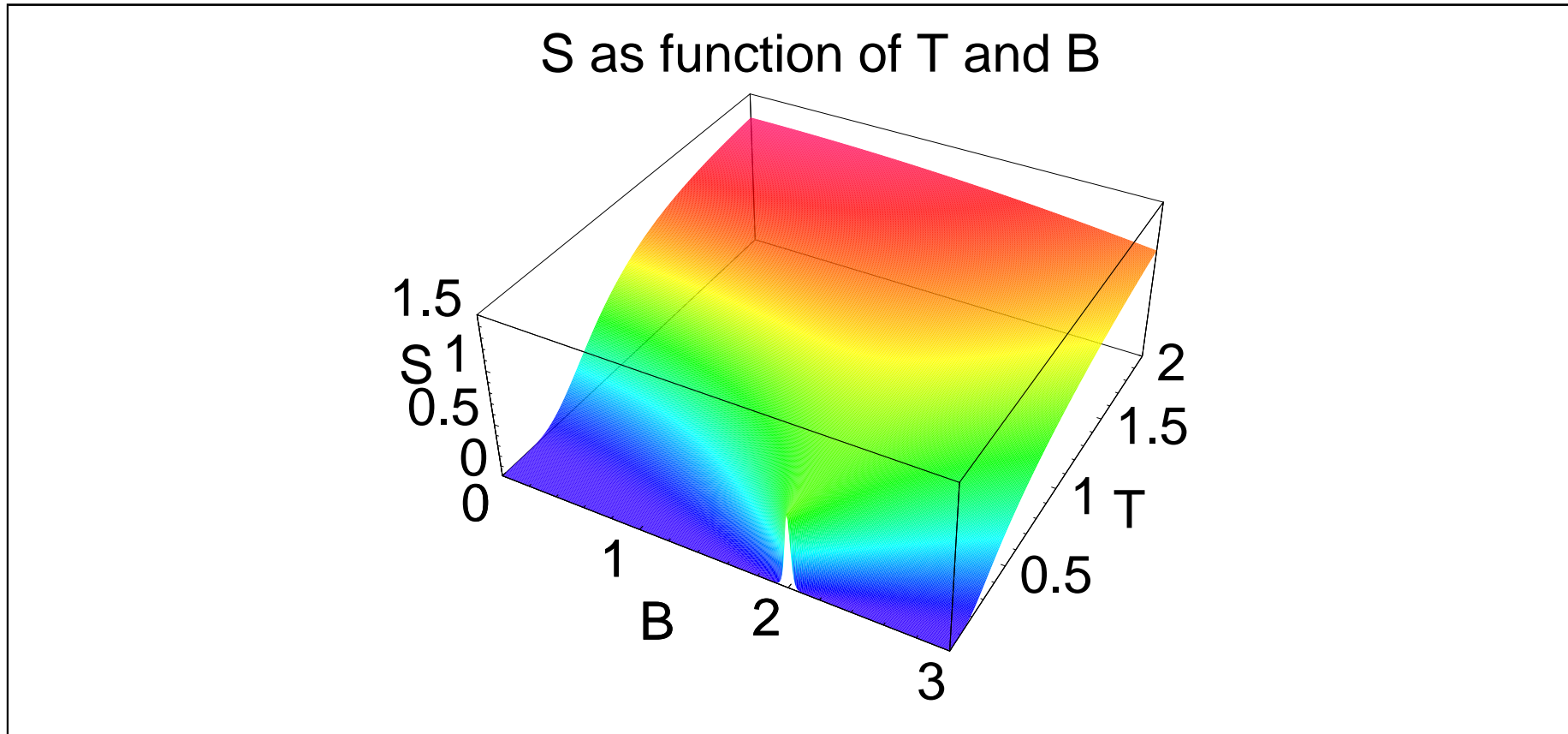
- Ideal paramagnet: $S(T, B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

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

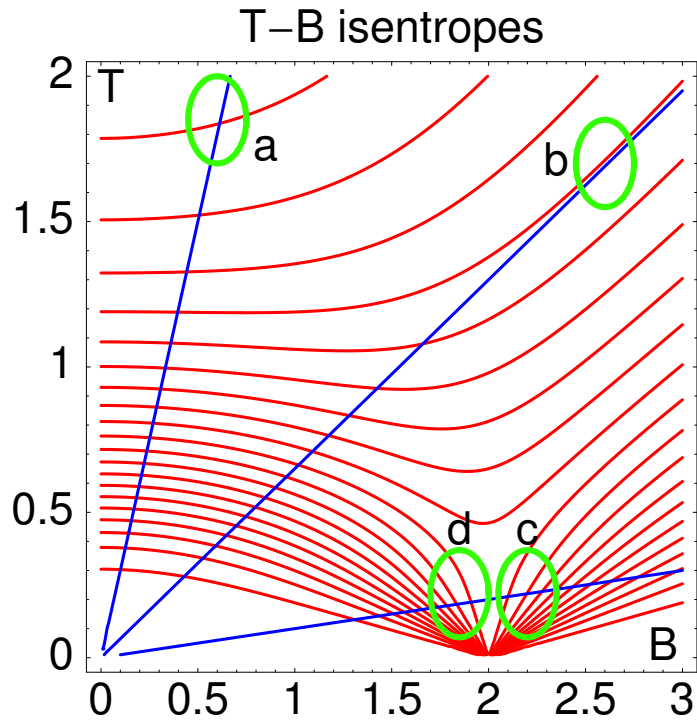
Magnetocaloric effect – at $s = 1/2$ dimer



$S(T = 0, B) \neq 0$ 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

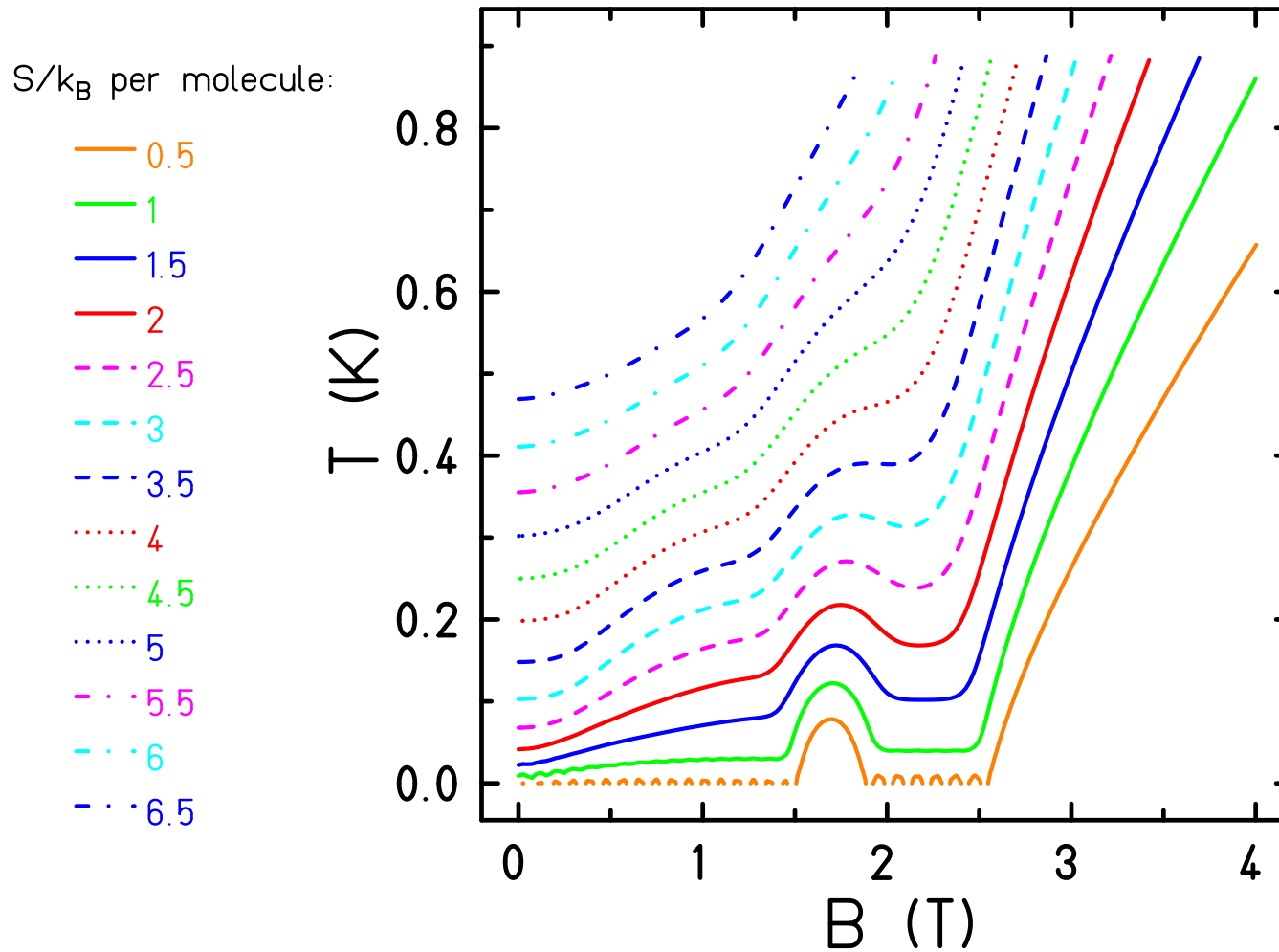
Magnetocaloric effect:

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

when compared to an ideal paramagnet.

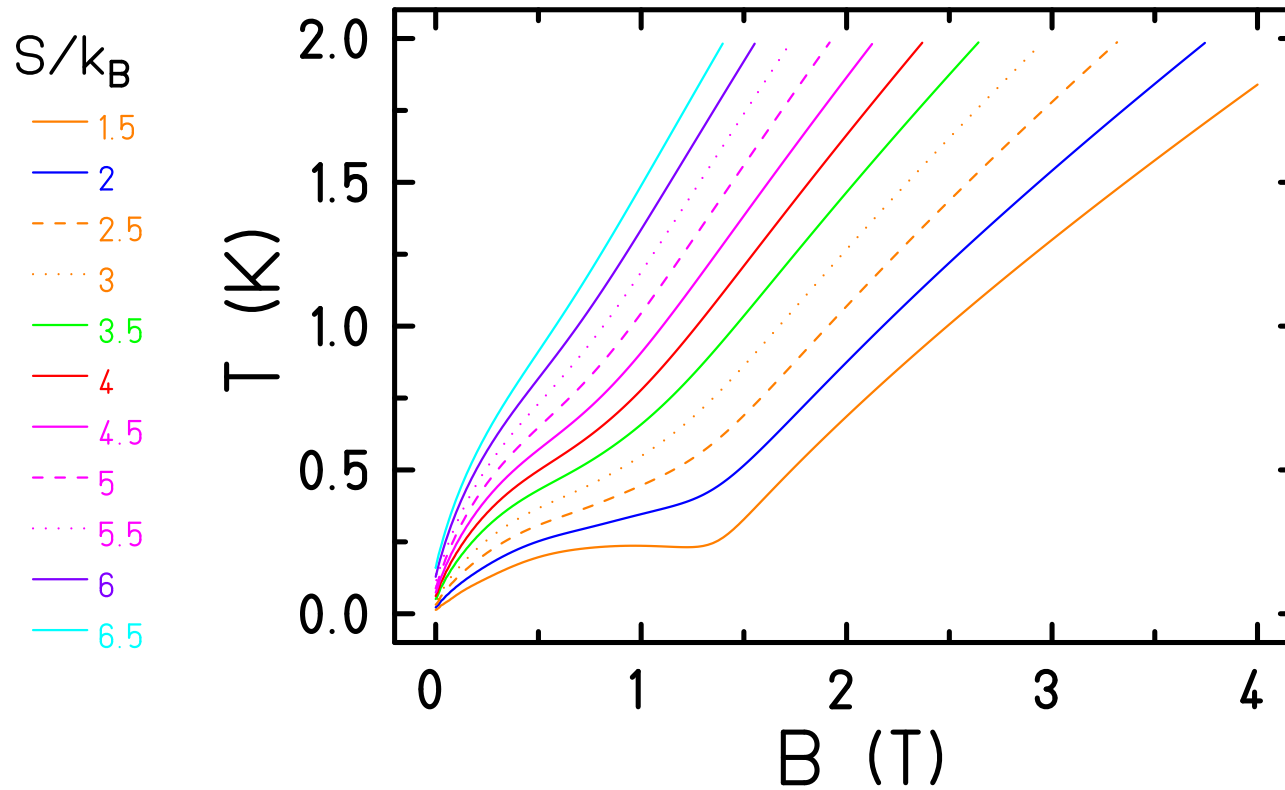
Case (d) does not occur for a paramagnet.

Typical isentropes for af spin system



Level crossings signal antiferromagnetic interactions.

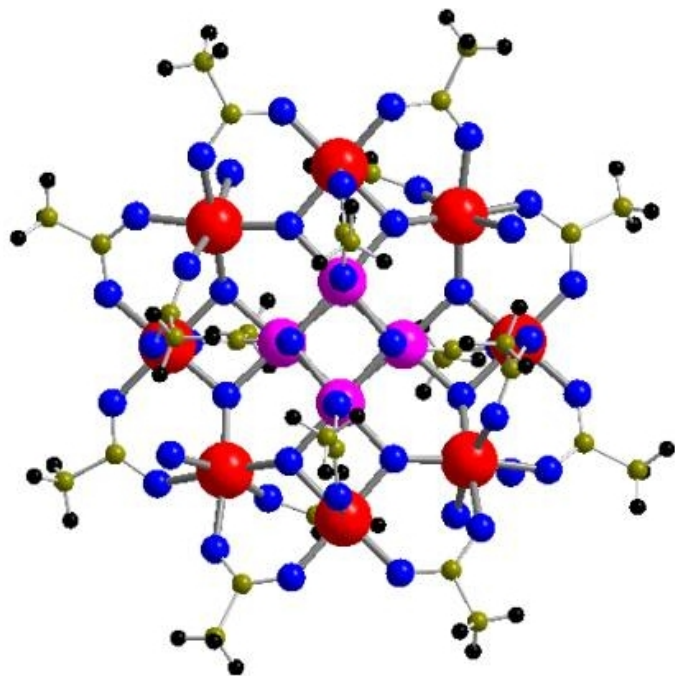
Typical isentropes for high-spin system



Typical for high-spin ground state.

Nice ideas,
but can one measure it?
With magnetic molecules?

The beauty of magnetic molecules I

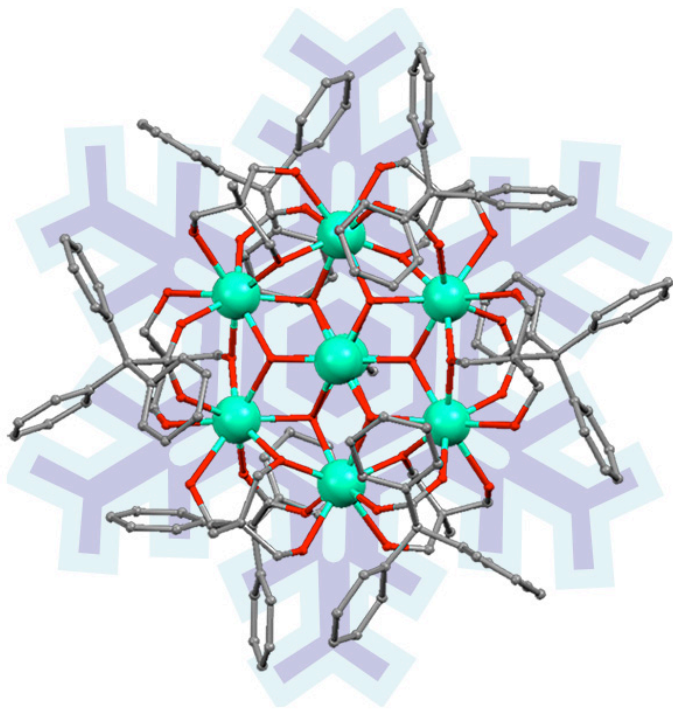


Mn₁₂

- Inorganic or organic macro molecules, e.g. polyoxometalates, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;
- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- Single spin quantum number $1/2 \leq s \leq 7/2$;
- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

Magnetism goes Nano, Ed. Stefan Blügel, Thomas Brückel, and Claus M. Schneider, FZ Jülich, Institute of Solid State Research, Lecture Notes **36** Jülich 2005

Gd₇ – Basics

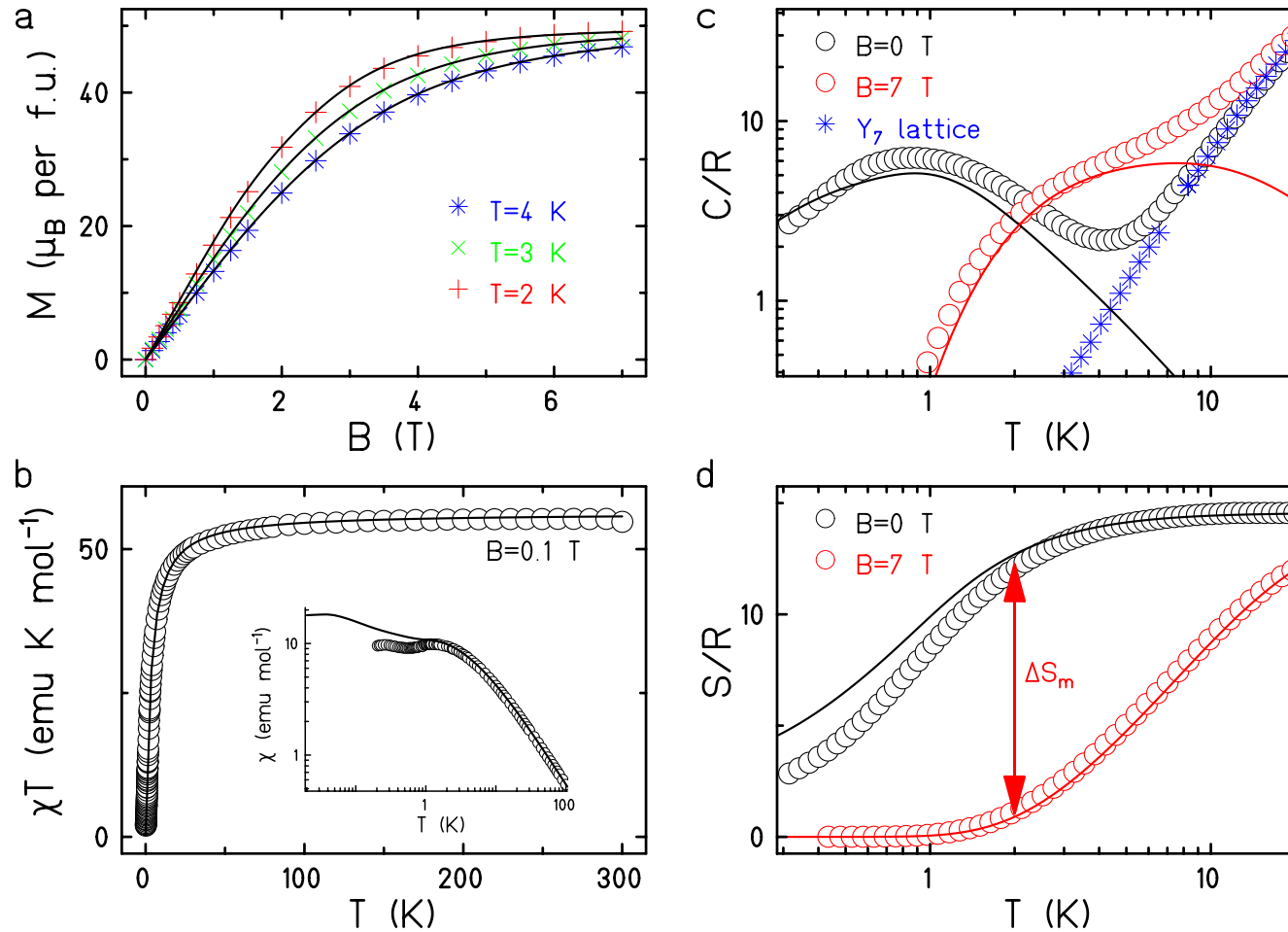


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $$\underline{H} = -2 \sum_{i < j} J_{ij} \underline{\tilde{S}}_i \cdot \underline{\tilde{S}}_j + g \mu_B B \sum_i^N \tilde{S}_i^z$$

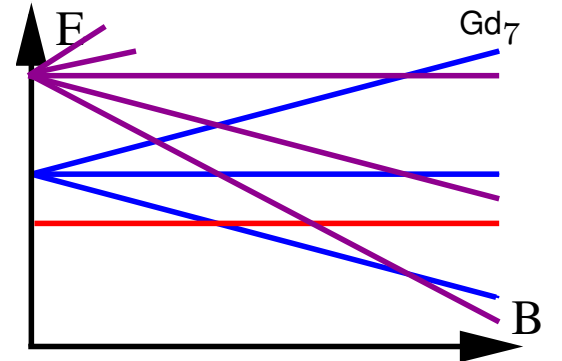
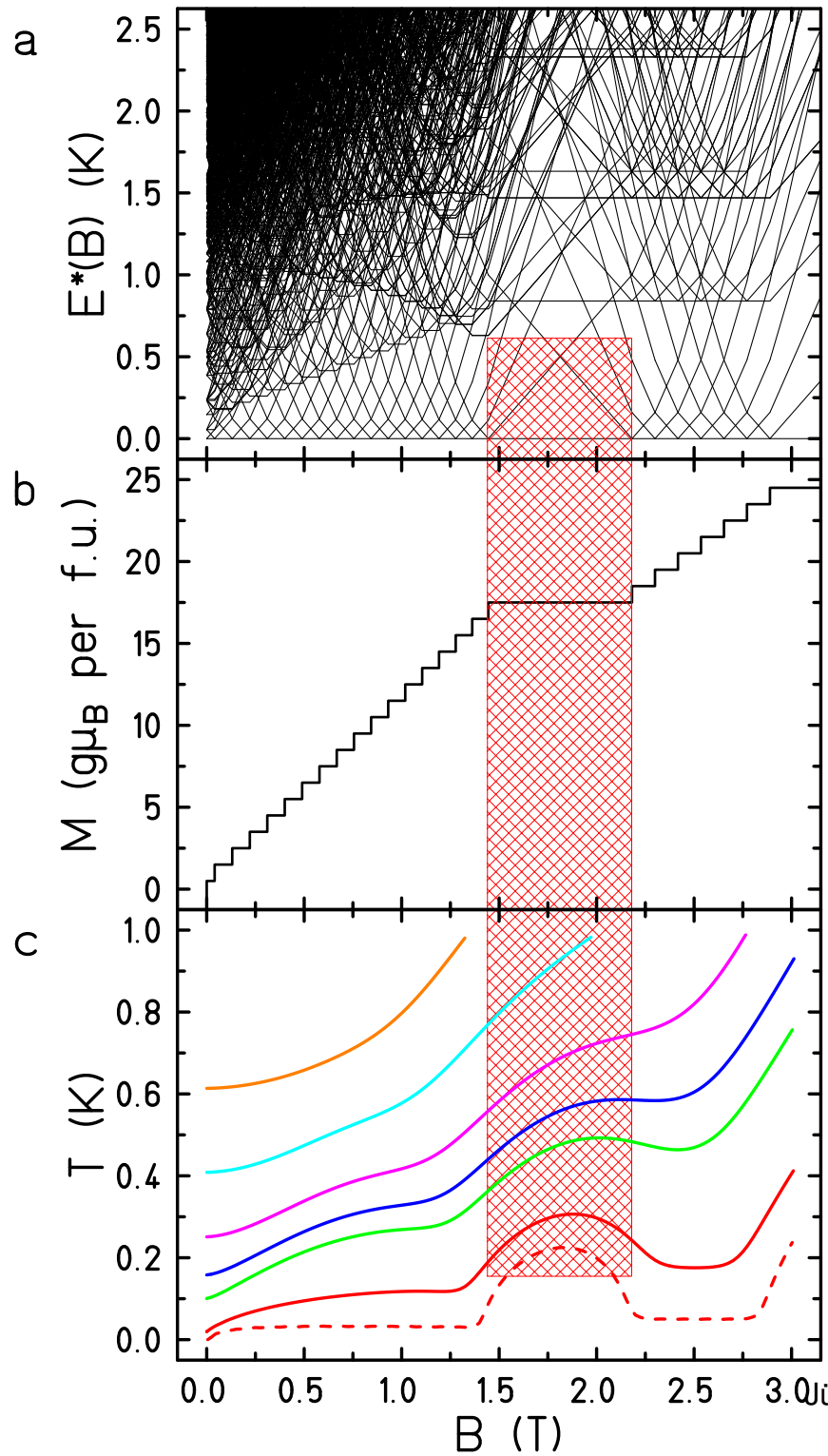
 $J_1 = -0.090(5) \text{ K}, J_2 = -0.080(5) \text{ K}$
 and $g = 2.02$.
- **Very good agreement down to the lowest temperatures.**

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

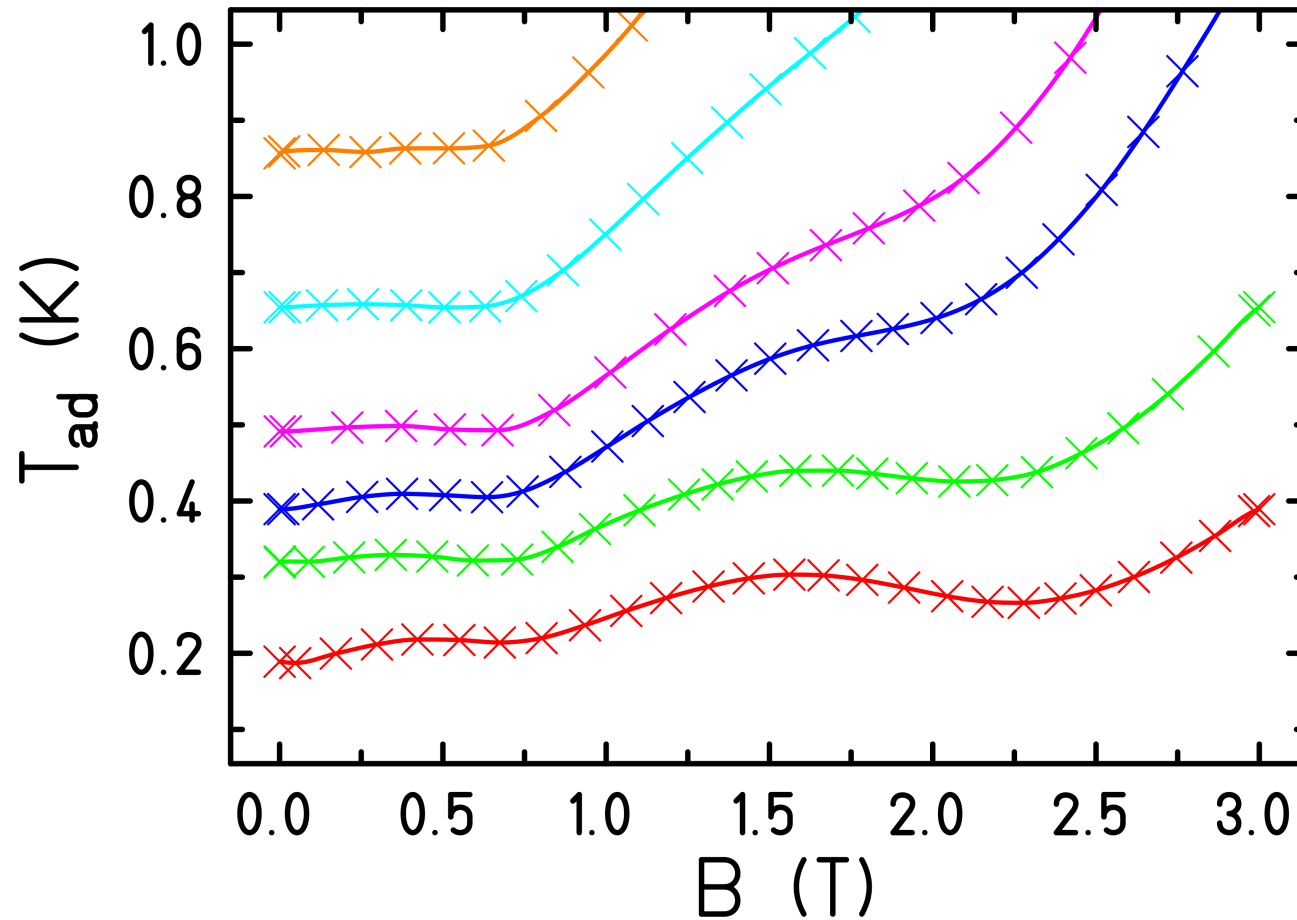
Gd₇ – experiment & theory



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



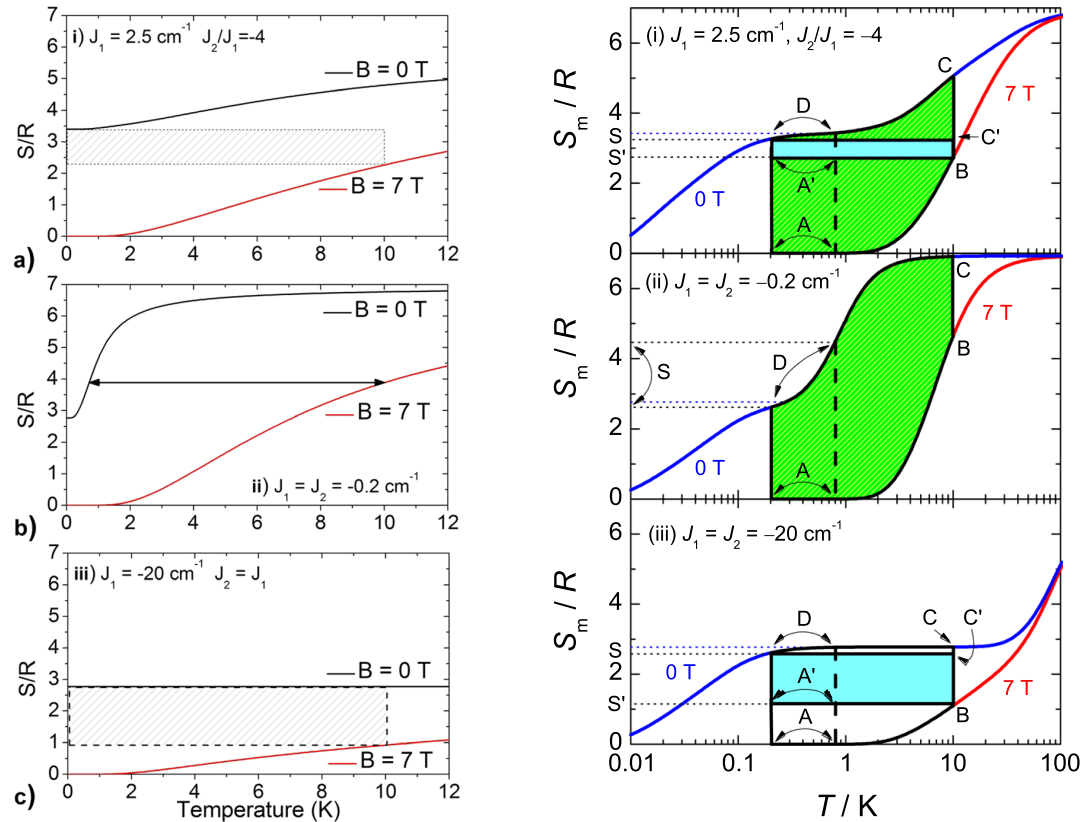
Gd₇ – Experimental cooling



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

Outlook: Design of applications

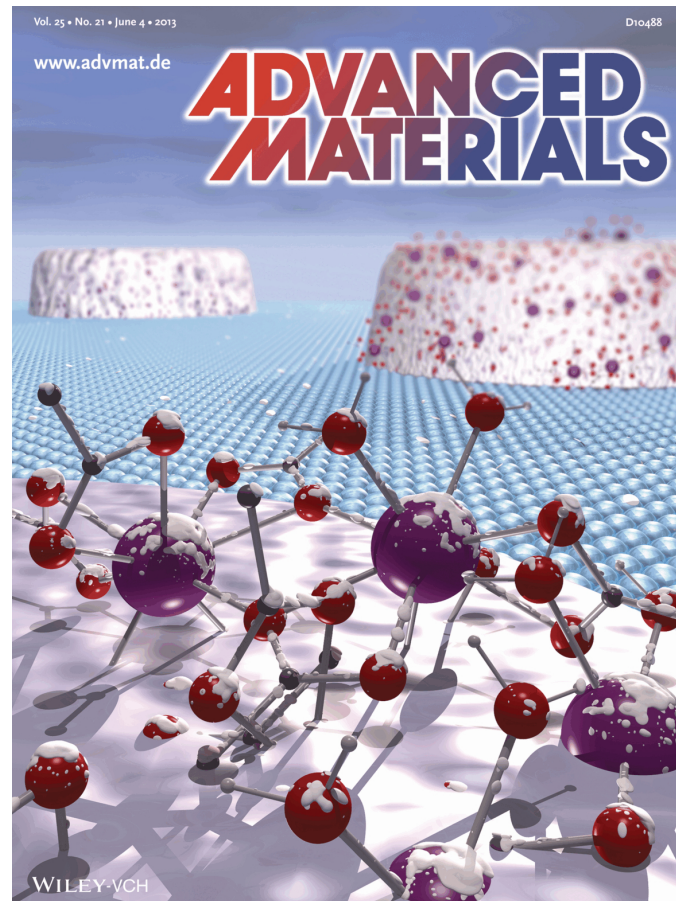
Cycles: Carnot or Ericsson?



Applicable temperature range? Maximum entropy difference at cold temperature?

E. Garlatti, S. Carretta, J. Schnack, G. Amoretti, P. Santini, Appl. Phys. Lett. **103**, (2013); M. Evangelisti, G. Lorusso, and E. Palacios, Applied Physics Letters **105**, (2014); E. Garlatti *et al.*, Applied Physics Letters **105**, 046102 (2014).

MCE surface cooler



G. Lorusso, M. Jenkins, P. Gonzalez-Monje, A. Arauzo, J. Sese, D. Ruiz-Molina, O. Roubeau, M. Evangelisti, Marco, Adv. Mater. **25**, 2984 (2013); V. Corradini, A. Ghirri, A. Candini, R. Biagi, U. del Pennino, G. Dotti, E. Otero, F. Choueikani, R. J. Blagg, E. J. L. McInnes, M. Affronte, Adv. Mater. **25**, 2816 (2013).

How can one calculate such things?

(Partition function, observables in the canonical ensemble)

Complete diagonalization: The easy version

Most physicists do this!

Model Hamiltonian – Heisenberg and more

$$\underline{H} = -2 \sum_{i < j} J_{ij} \vec{s}_i \cdot \vec{s}_j + \sum_{i,j} \vec{s}_i \cdot \mathbf{D}_{ij} \cdot \vec{s}_j + \mu_B B \sum_i^N g_i s_i^z$$

Heisenberg
Anisotropy, ...
Zeeman

The Heisenberg model including anisotropy, and dipol-dipol interaction if necessary, as well as a Zeeman term describes the magnetic spectrum of many molecules with high accuracy.

Reason: Ions of the iron group have quenched angular momentum $\langle \underline{l} \rangle \approx 0$ due to chemical binding, remaining spin-orbit coupling treated perturbatively with the help of anisotropy terms. This is different for rare earth ions!

Since the dimension of Hilbert space equals $(2s + 1)^N$ the Hamiltonian can be diagonalized completely for small molecules. For larger ones approximate methods are used.

Product basis and symmetries

Product basis, total dimension: $\dim(\mathcal{H}) = (2s + 1)^N$

$$\underline{S}_u^z |m_1, \dots, m_u, \dots, m_N\rangle = m_u |m_1, \dots, m_u, \dots, m_N\rangle$$

These states span the Hilbert space and are used to construct symmetry-related basis states. Use $a_u = s_u - m_u$ for computation (integer).

Symmetries of the Heisenberg model without anisotropy

$$\left[\underline{H}, \underline{\vec{S}}^2 \right] = 0 \quad , \quad \left[\underline{H}, \underline{S}_z \right] = 0$$

Additional (point group) symmetries are possible, e.g. shifts on a ring molecule.

Decomposition into mutually orthogonal subspaces

If $\left[\underline{H}, \underline{S}_z \right] = 0$, the Hilbert space \mathcal{H} can be decomposed into mutually orthogonal subspaces $\mathcal{H}(M)$ (M is the quantum number belonging to \underline{S}_z)

$$\left[\underline{H}, \underline{S}_z \right] = 0 \quad : \quad \mathcal{H} = \bigoplus_{M=-S_{\max}}^{+S_{\max}} \mathcal{H}(M), \quad S_{\max} = Ns$$

$\mathcal{H}(M)$ contains all states $|m_1, \dots, m_u, \dots, m_N\rangle$ with $\sum_i m_i = M$.

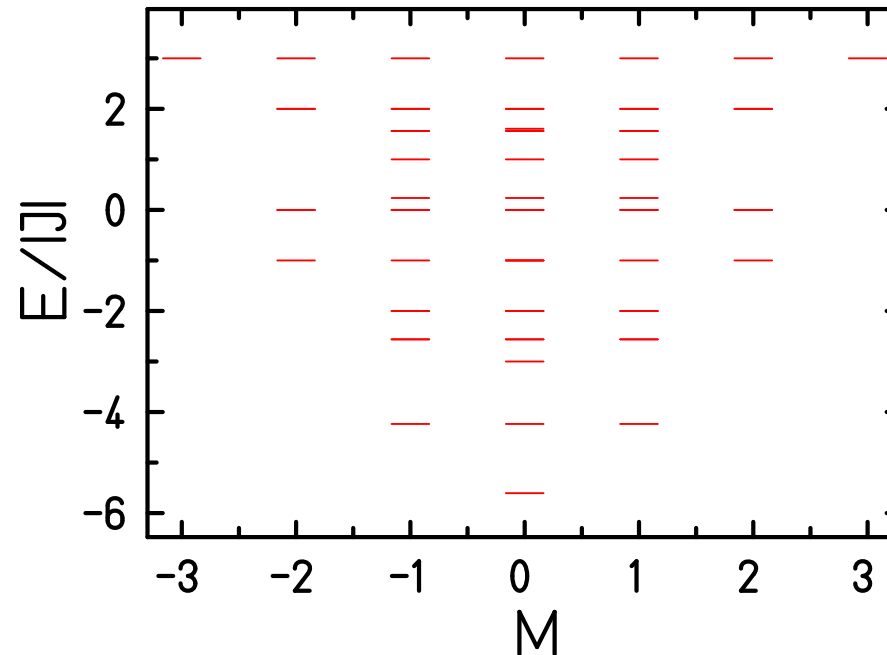
The Hamiltonian is diagonalized in all subspaces separately. The dimension of the largest subspace determines whether a Hamiltonian can diagonalized completely. If further symmetries apply this dimension will be further reduced.

For practical purposes $\vec{s}_i \cdot \vec{s}_j = s_i^z s_j^z + \frac{1}{2} \left[s_i^+ s_j^- + s_i^- s_j^+ \right]$.

Example: spin ring with $N = 6, s = 1/2$

- Total dimension of \mathcal{H} : $Dim(\mathcal{H}) = (2 \times 1/2 + 1)^6 = 64$;
- $M = 3$: $|\Omega\rangle = |+++++\rangle$; $Dim(\mathcal{H}(M)) = 1$;
- $M = 2$: $| - + + + + \rangle$ and cyclic shifts; $Dim(\mathcal{H}(M)) = 6$;
- $M = 1$: $| - - + + + \rangle, | - + - + + \rangle, | - + + - + \rangle$ and cyclic shifts;
 $Dim(\mathcal{H}(M)) = 15$;
- $M = 0$: $| - - - + + \rangle, | - - + - + \rangle, | - + - - + \rangle, | - + - + - \rangle$
and cyclic shifts; $Dim(\mathcal{H}(M)) = 20$;
- Dimensional check: $64 = 1 + 6 + 15 + 20 + 15 + 6 + 1 \checkmark$
- Inclusion of translational symmetry leads to orthogonal subspaces $\mathcal{H}(M, k)$ with $k = 0, \dots, 5$. Then the largest dimension is 4.

Exact diagonalization



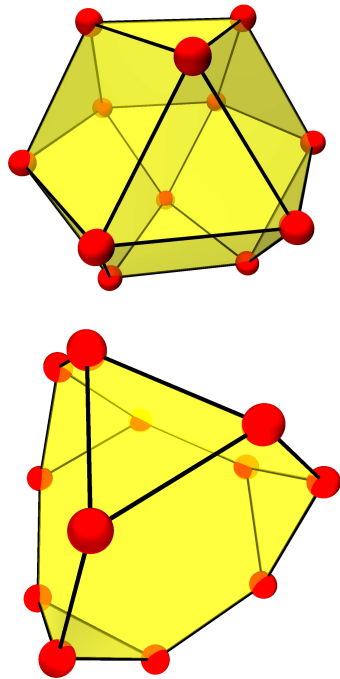
- Numerically exact diagonalization feasible up to RAM size;
- Example: 10,000x10,000 complex*16, 1.6 GB RAM needed;
- Not much we can do at this point, wait for more RAM 😊

Complete diagonalization: SU(2) & point group symmetry

Quantum chemists need to be much smarter since they have smaller computers!

- (1) D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.* **123**, 231 (1993).
- (2) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, *Inorg. Chem.* **38**, 6081 (1999).
- (3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Irreducible Tensor Operator approach



Spin rotational symmetry SU(2):

- $\underline{H} = -2 \sum_{i < j} J_{ij} \underline{\vec{S}}_i \cdot \underline{\vec{S}}_j + g\mu_B \underline{\vec{S}} \cdot \underline{\vec{B}} ;$
- Physicists employ: $[\underline{H}, \underline{S}_z] = 0;$
- Chemists employ: $[\underline{H}, \underline{\vec{S}}^2] = 0, [\underline{H}, \underline{S}_z] = 0;$

Irreducible Tensor Operator (ITO) approach;
Free program MAGPACK (2) available.

- (1) D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.* **123**, 231 (1993).
 (2) J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, *Inorg. Chem.* **38**, 6081 (1999).
 (3) B. S. Tsukerblat, *Group theory in chemistry and spectroscopy: a simple guide to advanced usage*, 2nd ed. (Dover Publications, Mineola, New York, 2006).

Idea of ITO

$$\begin{aligned}
 \underline{H}_{\text{Heisenberg}} &= -2 \sum_{i < j} J_{ij} \vec{s}_i \cdot \vec{s}_j \\
 &= 2\sqrt{3} \sum_{i < j} J_{ij} \underline{T}^{(0)}(\{k_i\}, \{\bar{k}_i\} | k_i = k_j = 1)
 \end{aligned}$$

Irreducible Tensor Operator approach

- Express spin operators and functions thereof as ITOs;
- Use vector coupling basis $|\alpha S M\rangle$ and recursive recoupling.

(1) Gatteschi, Tsukerblat, Coronado, Waldmann, ...
 (2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Point Group Symmetry

$$|\alpha' S M \Gamma\rangle = \mathcal{P}^{(\Gamma)} |\alpha S M\rangle = \left(\frac{l_{\Gamma}}{h} \sum_R \left(\chi^{(\Gamma)}(R) \right)^* \mathcal{G}(R) \right) |\alpha S M\rangle$$

Method:

- Projection onto irreducible representations Γ of the point group (1,2);
- No free program, things are a bit complicated (3,4).

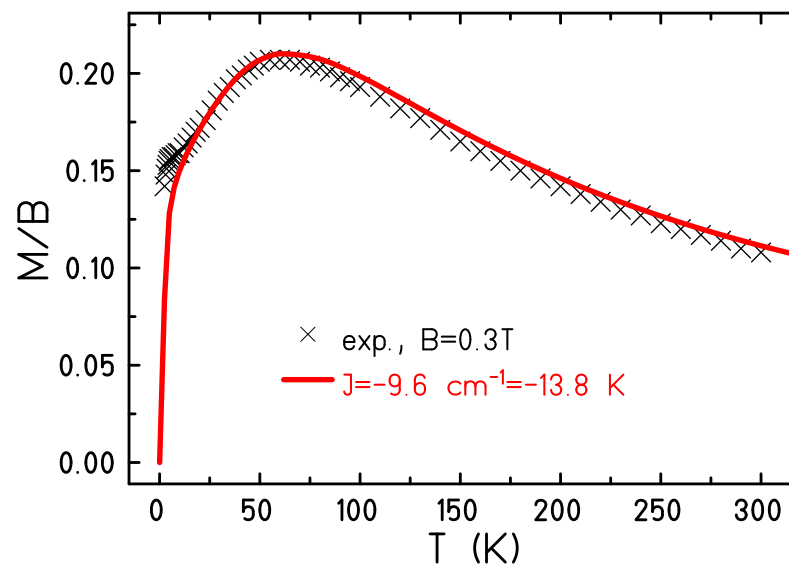
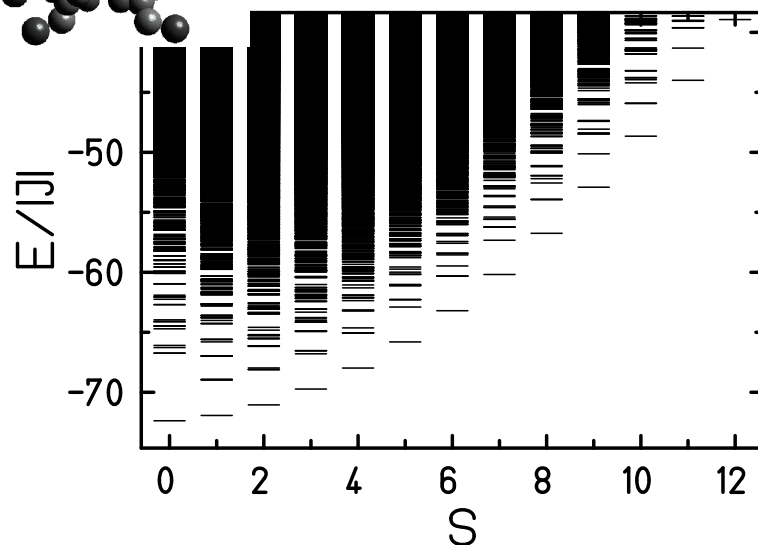
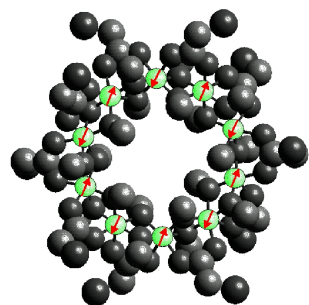
(1) M. Tinkham, *Group Theory and Quantum Mechanics*, Dover.

(2) D. Gatteschi and L. Pardi, *Gazz. Chim. Ital.* **123**, 231 (1993).

(3) O. Waldmann, *Phys. Rev. B* **61**, 6138 (2000).

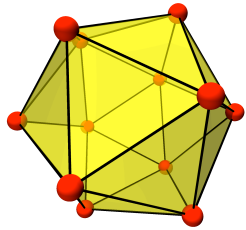
(4) R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010) \Leftarrow contains EVERYTHING.

Example: Fe₁₀

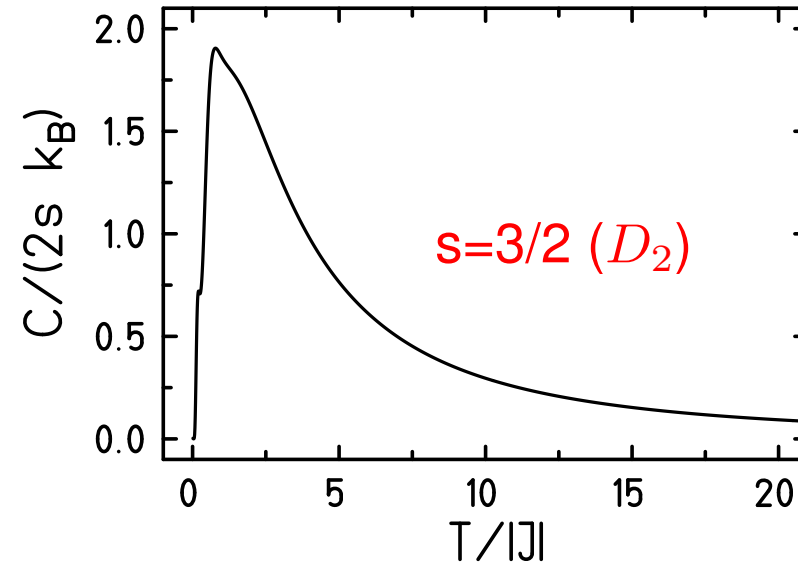
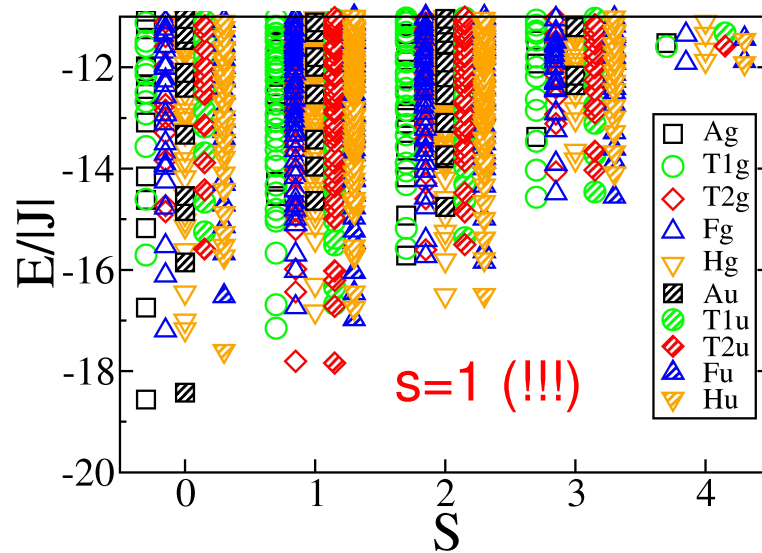


Spin ring, $N = 10$, $s = 5/2$, Hilbert space dimension 60,466,176; symmetry D_2 (1).

- (1) R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010).
 (2) C. Delfs *et al.*, *Inorg. Chem.* **32**, 3099 (1993).



Example: Icosahedron



Icosahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry I_h ; Evaluation of recoupling coefficients for $s = 3/2$ in I_h **practically impossible** (1).

(1) R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).

World-leading, but ...

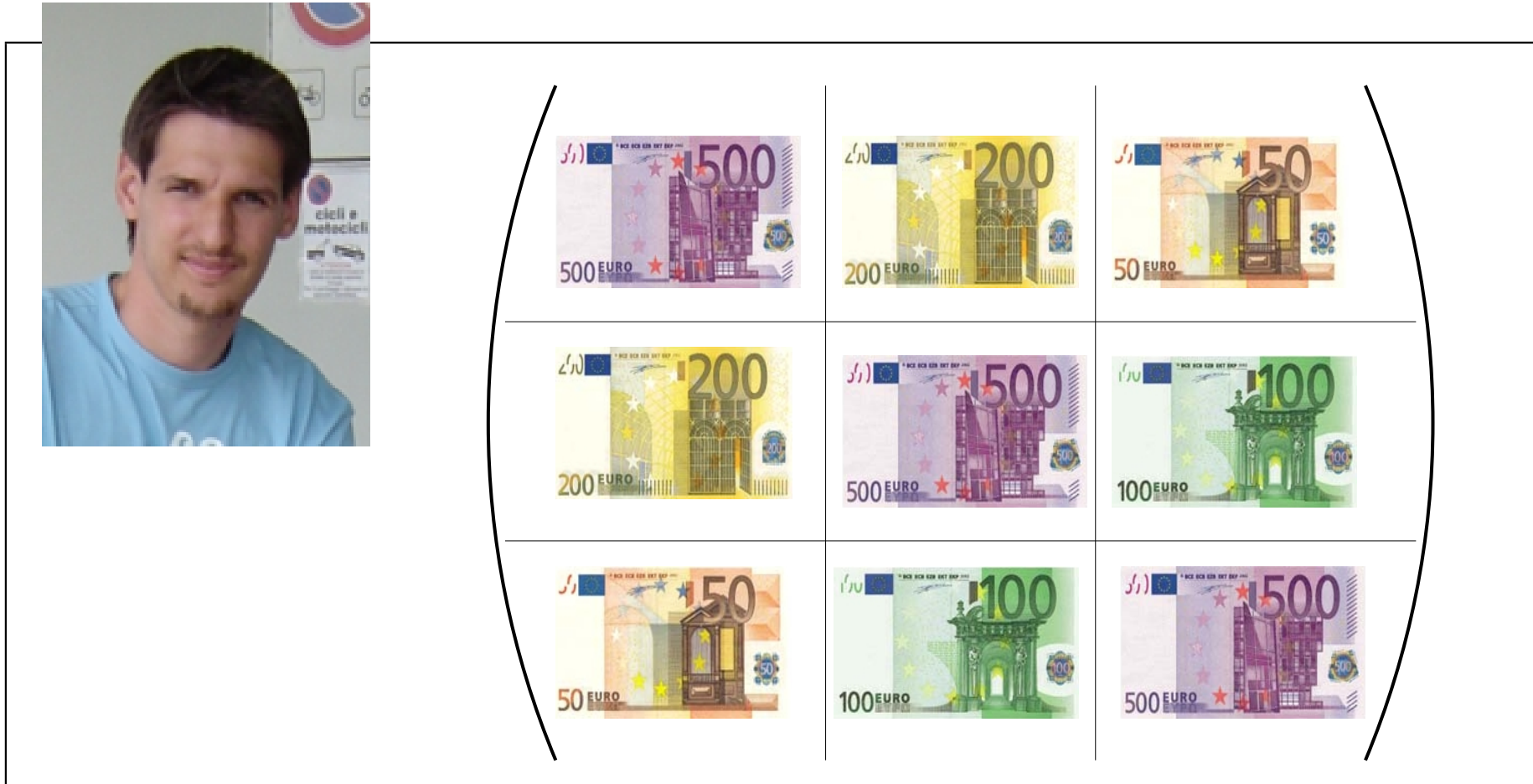
This world-leading method
was developed in Osnabrück,
unfortunately ...

World-leading, but ...

... too late!

**There are more powerful and
easy to program methods.**

Nevertheless, matrix theory goes on ...

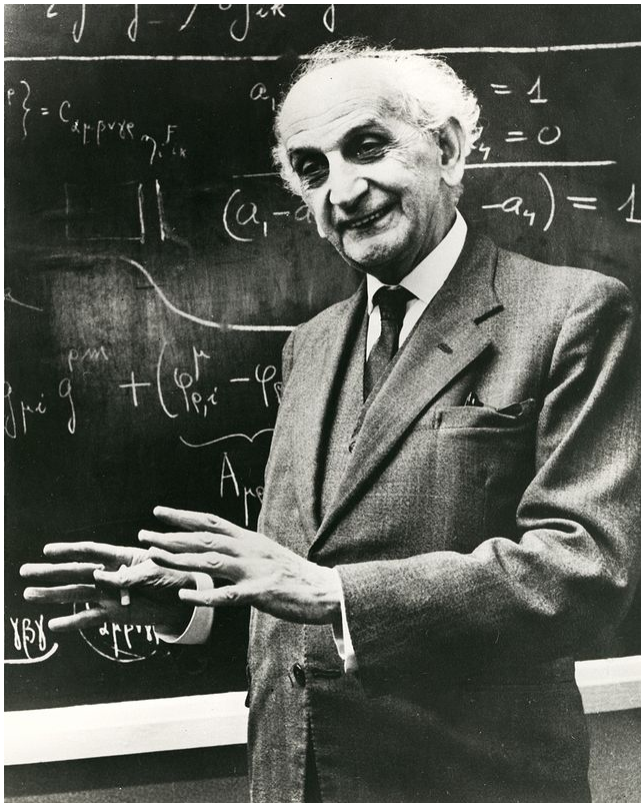


... at the Hessische Landesbank!

Finite-temperature Lanczos Method

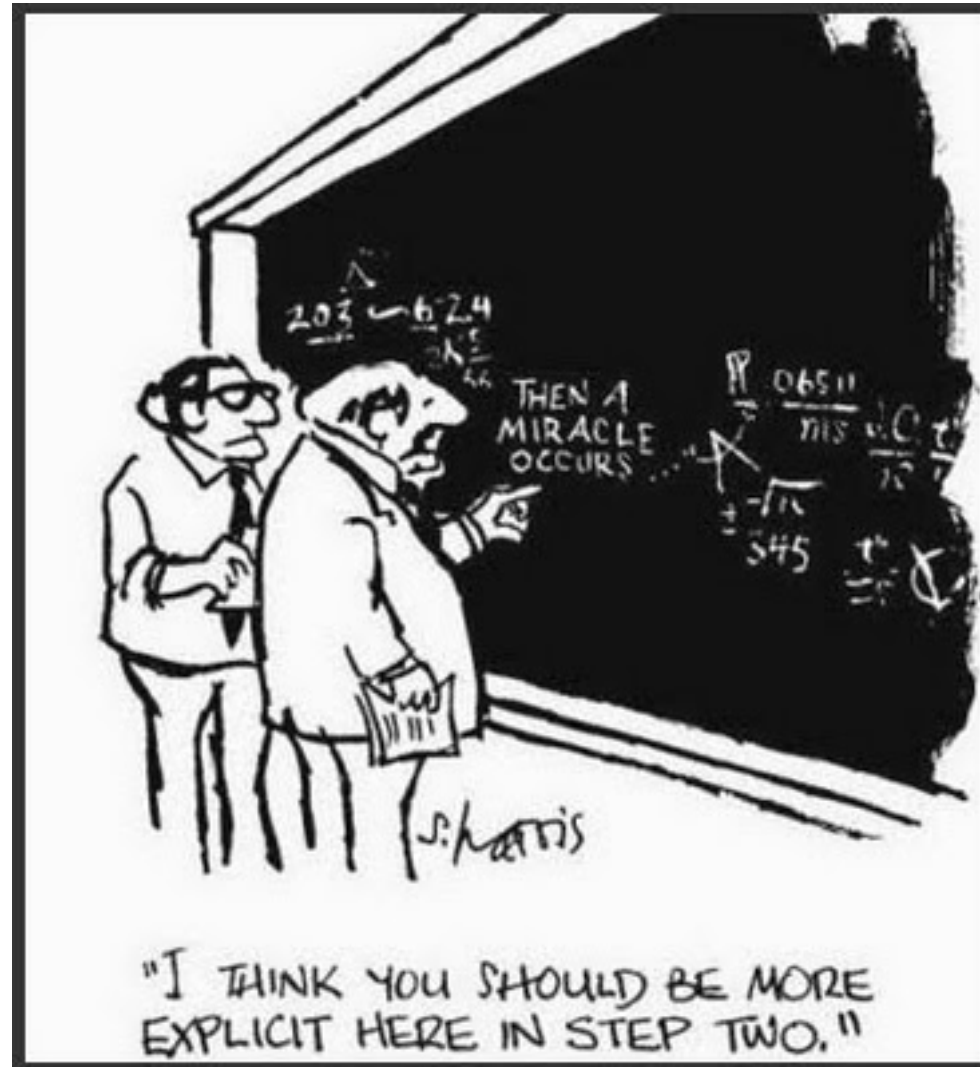
(Good for dimensions up to 10^{10} .)

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 I

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

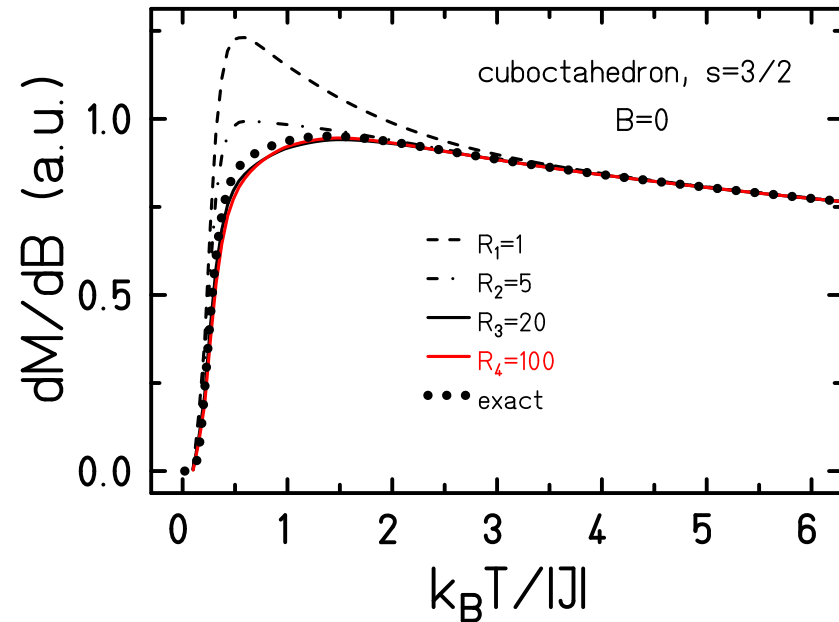
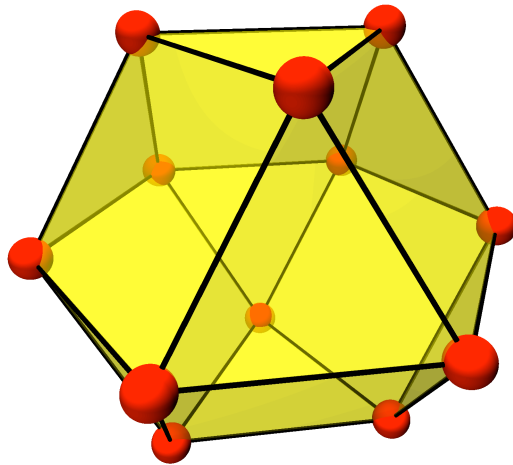
$$\langle \nu | \exp \{ -\beta \tilde{H} \} | \nu \rangle \approx \sum_n \langle \nu | n(\nu) \rangle \exp \{ -\beta \epsilon_n \} \langle n(\nu) | \nu \rangle \quad (\text{Step 2})$$

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

- $|n(\nu)\rangle$ 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).

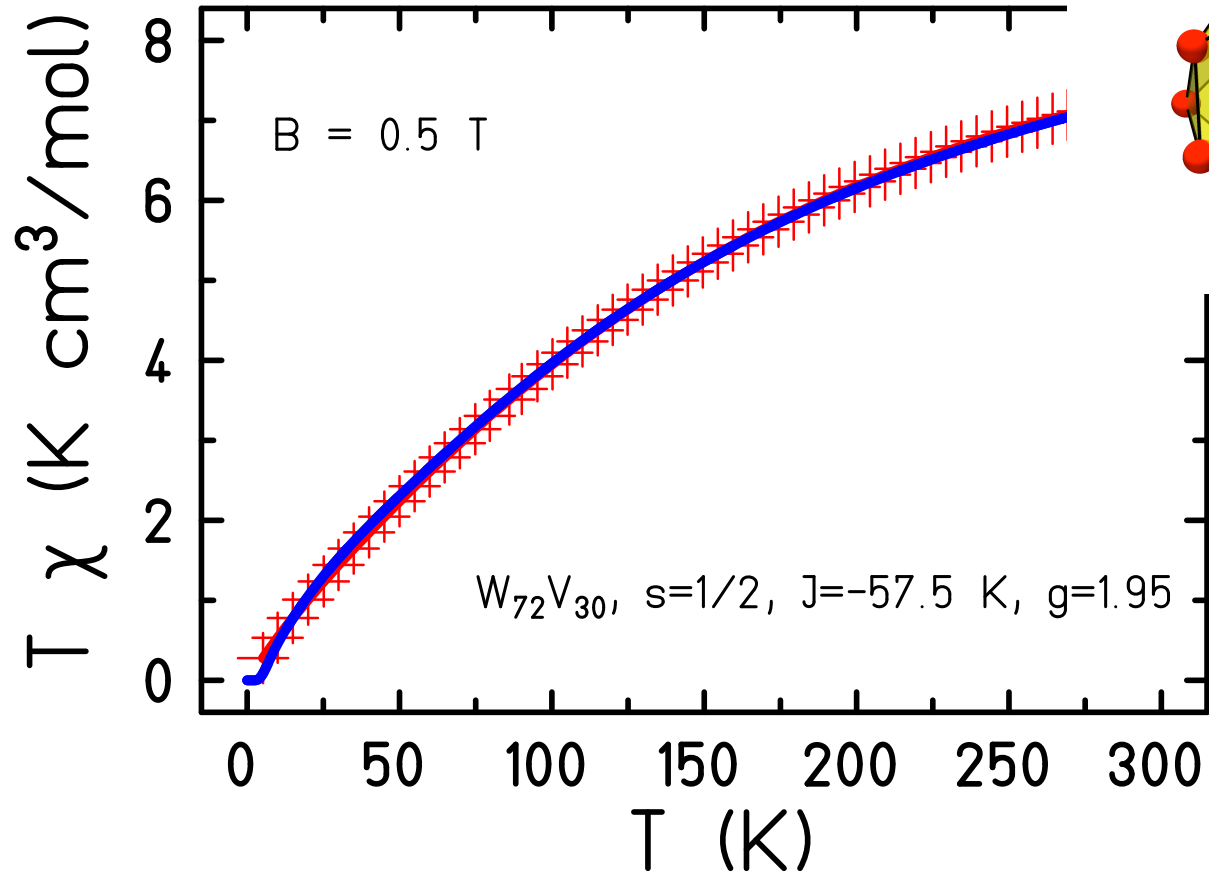
How good is finite-temperature Lanczos?



- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

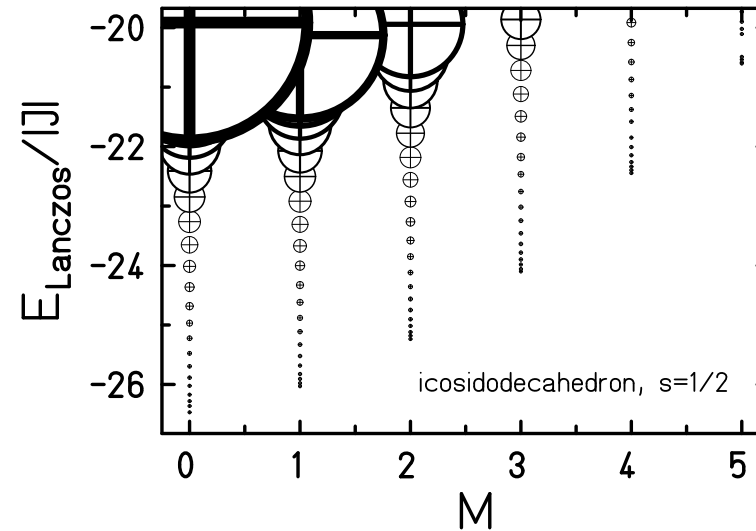
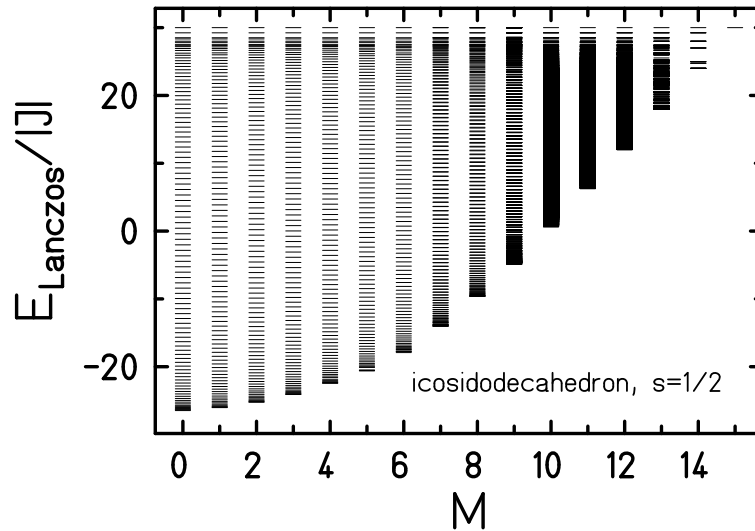
Exact results: R. Schnalle and J. Schnack, *Int. Rev. Phys. Chem.* **29**, 403-452 (2010).
 FTLM: J. Schnack and O. Wendland, *Eur. Phys. J. B* **78**, 535-541 (2010).

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).

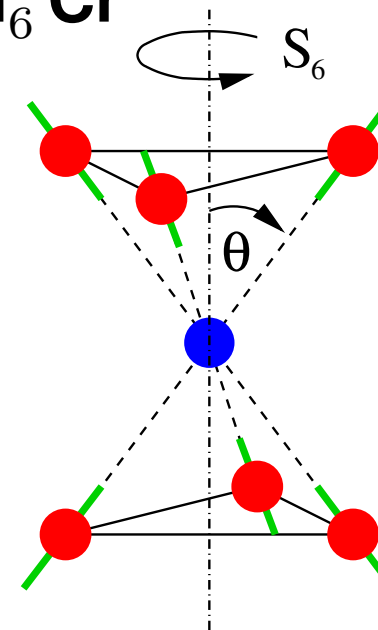
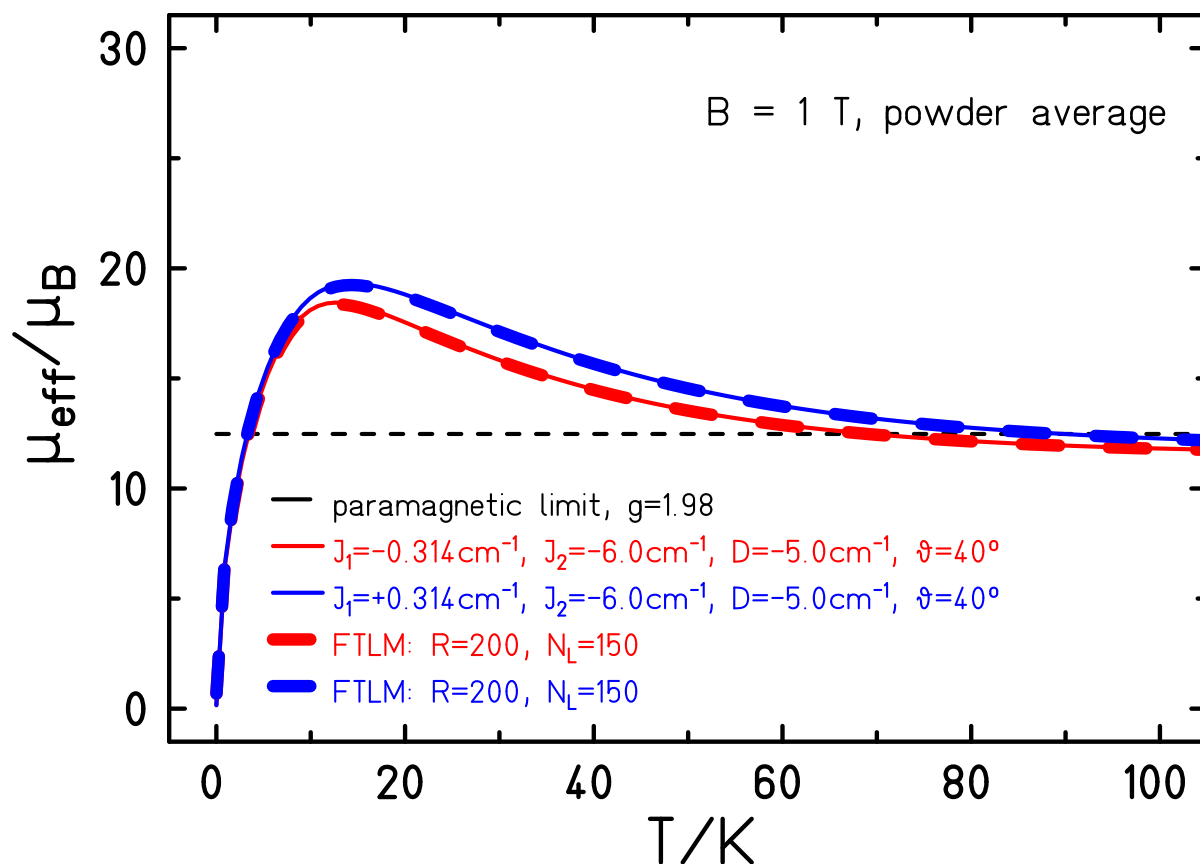
Icosidodecahedron $s = 1/2$



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

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

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

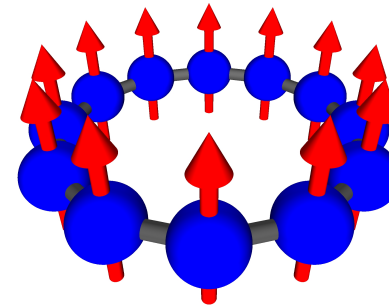
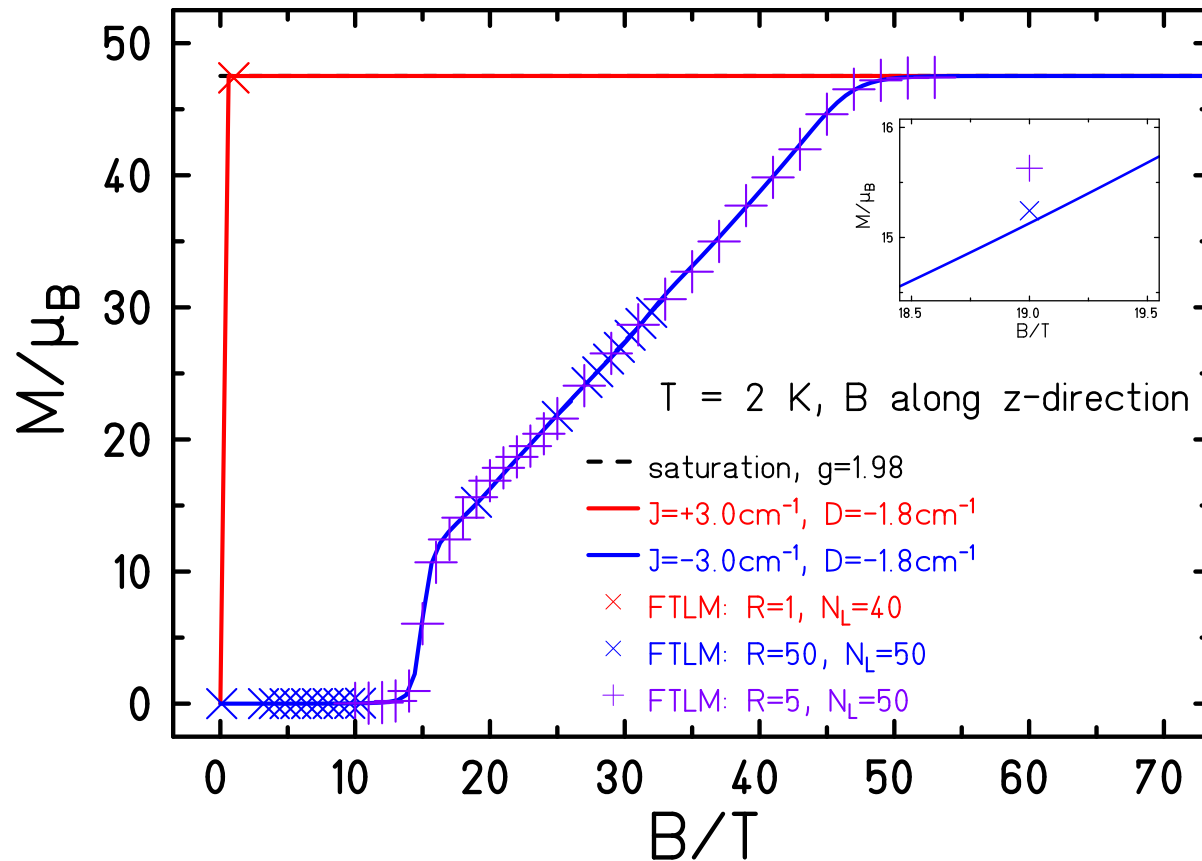


$s = 2, s = 3/2$
 $\dim(\mathcal{H}) = 62,500$
 non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

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



$s = 2$

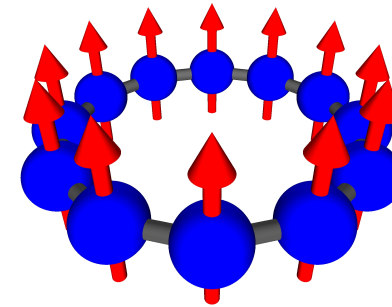
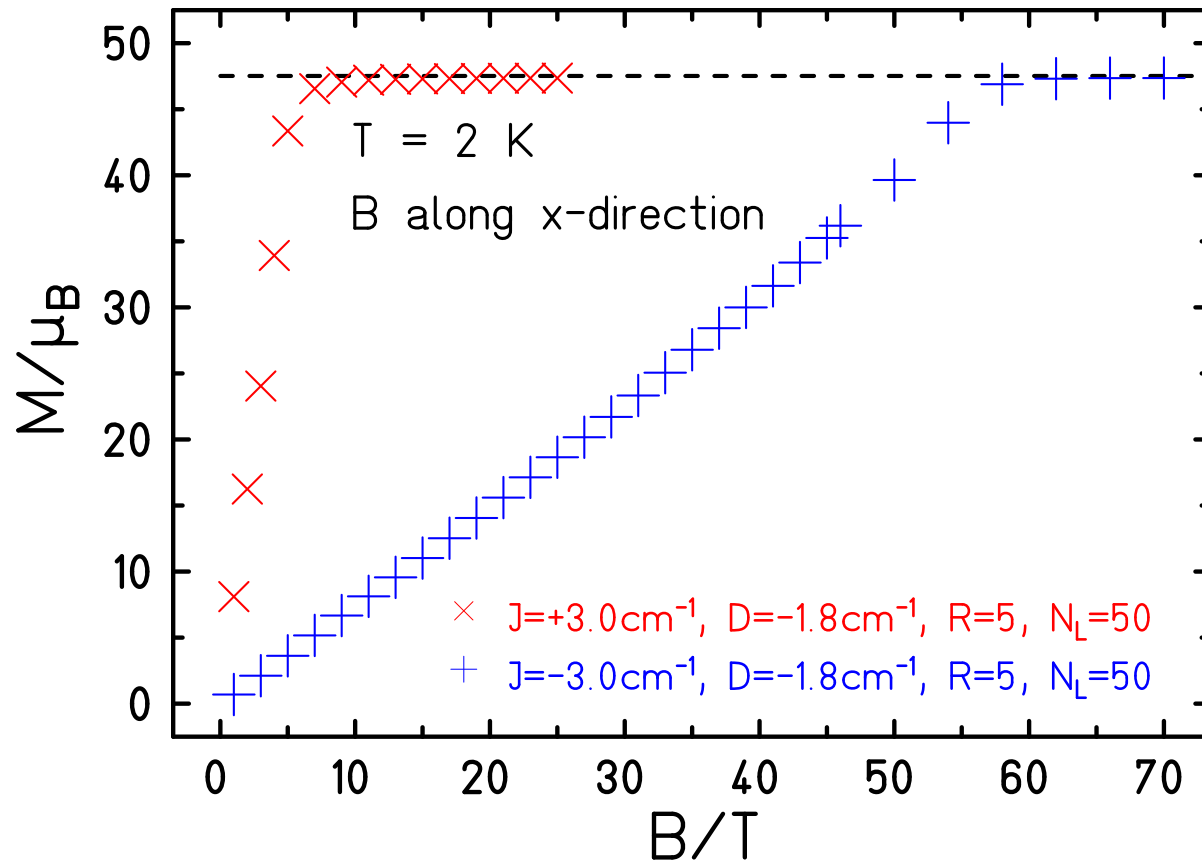
$\dim(\mathcal{H}) = 244, 140, 625$

collinear easy axes

A few days compared to *impossible!*

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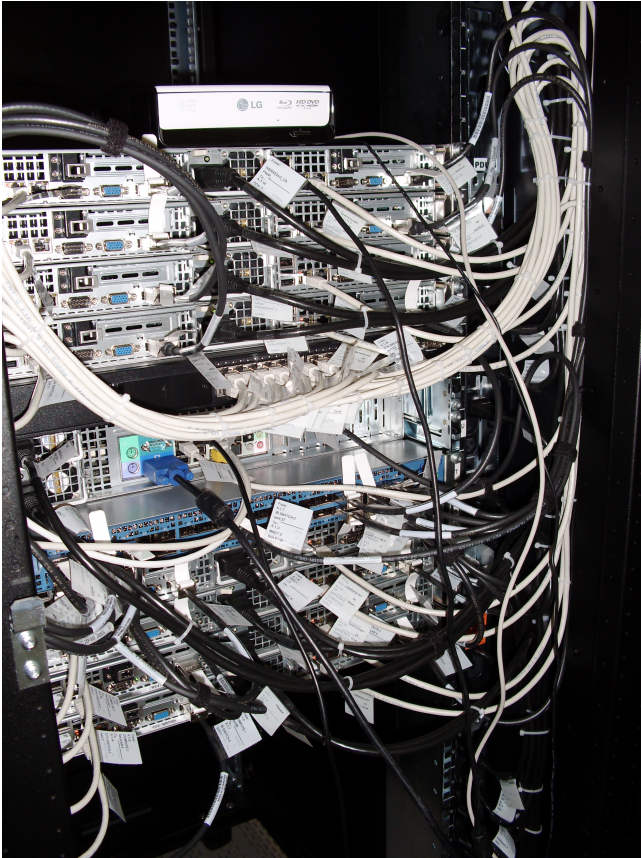
A fictitious $\text{Mn}_{12}^{\text{III}}$ – M_x vs B_x



No other method can deliver these curves!

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Summary



- Exact diagonalization is great but limited.
- Finite-temperature Lanczos is a VERY GOOD approximate method for Hilbert space dimensions smaller than 10^{10} .
- Magnetic molecules for storage, q-bits, MCE, and since they are nice.
- Isentropes for interacting systems are much richer than for paramagnets. Good for applications away from $(T = 0, B = 0)$.

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- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück)
- 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); W. Wernsdorfer (Grenoble); M. Evangelisti (Zaragosa); E. Garlatti, S. Carretta, G. Amoretti, P. Santini (Parma); Gopalan Rajaraman (Mumbai)
- J. Richter, J. Schulenburg (Magdeburg); A. Honecker (Göttingen); U. Kortz (Bremen); A. Tennant, B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); 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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