Magnetism of free and deposited magnetic molecules

Jürgen Schnack

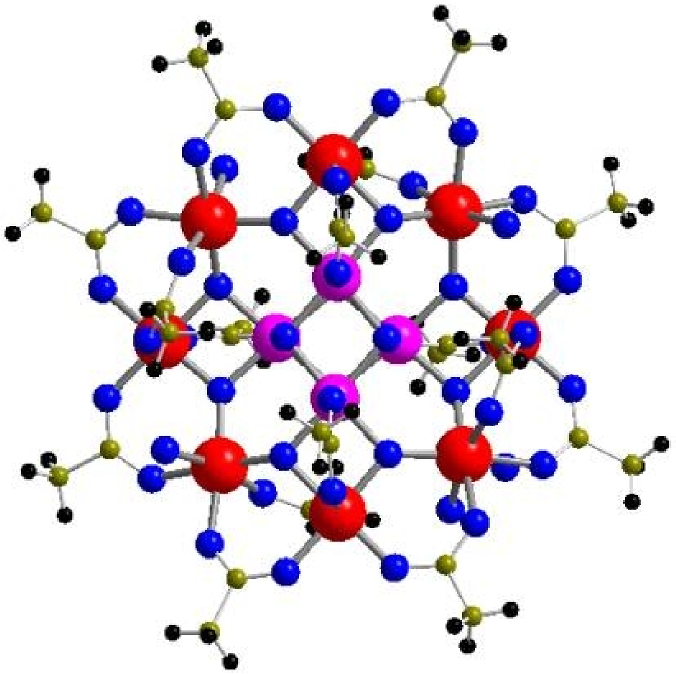
Department of Physics – University of Bielefeld – Germany

http://obelix.physik.uni-bielefeld.de/∼schnack/

Physikalisches Kolloquium,
Technische Universität Braunschweig, 18. 06. 2019

Beauty of Magnetic Molecules

The beauty of magnetic molecules I

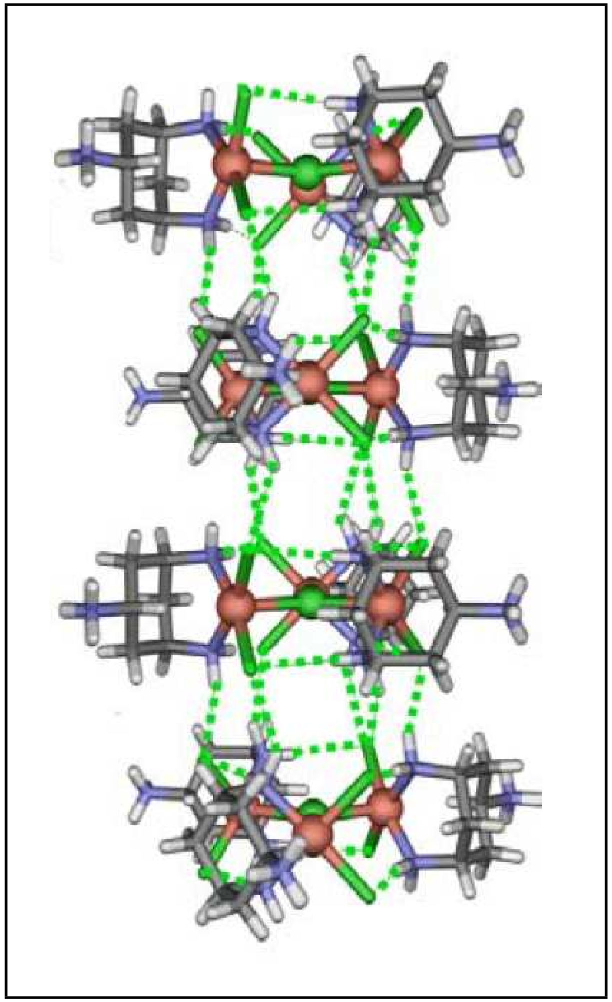


Mn_{12}

- 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

The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, . . .);
- Complex structures (Mn_{12}) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra (Fe_{30}) and other macro molecules;
- Chain like and planar structures of interlinked magnetic molecules, e.g. triangular Cu chain:

  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

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. Frustration effects in rings and lattices
2. The magnetocaloric effect
3. A quantum phase transition
4. Deposited molecules
5. Finite-Temperature Lanczos for anisotropic systems

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

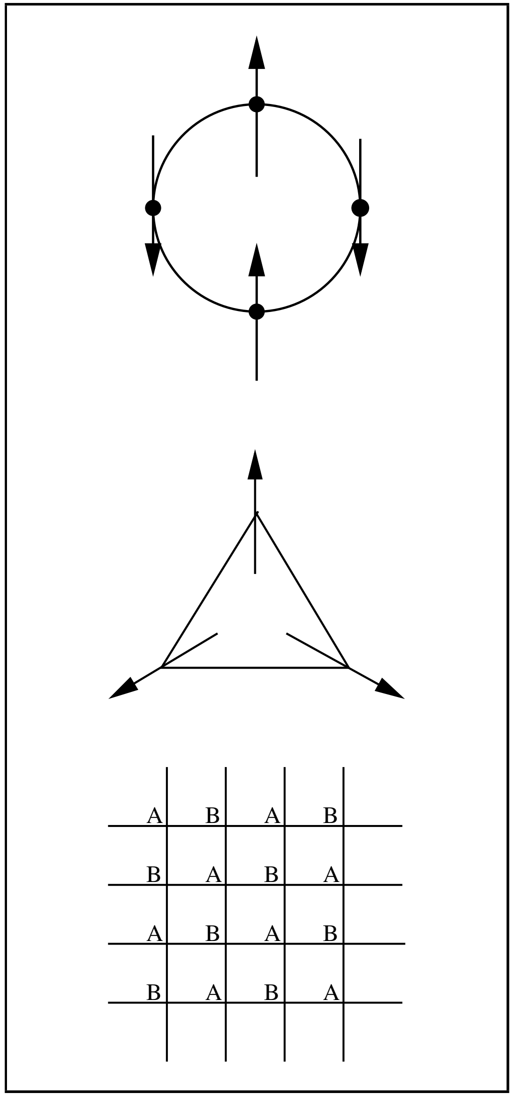
Frustration effects

Model Hamiltonian

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

Heisenberg   Zeeman

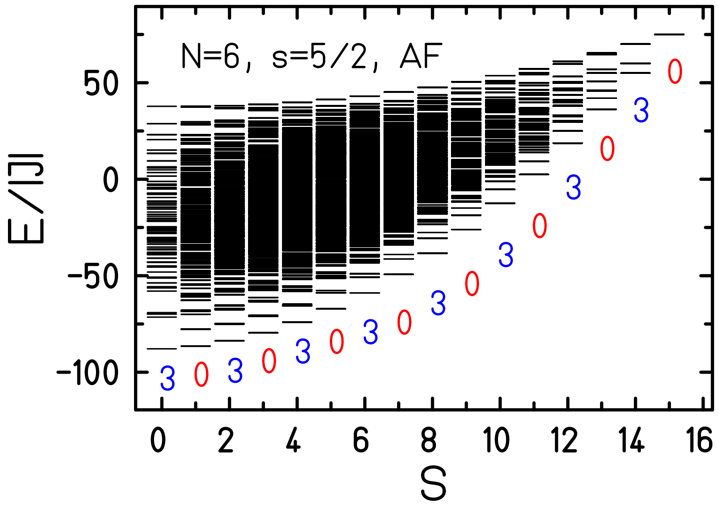
Definitions of frustration



1. You talk and everybody sleeps already at slide 3!
2. Simple: A spin system is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.
3. Advanced: A non-bipartite antiferromagnet is frustrated (exeptions, 3). A bipartite spin system can be decomposed into two sublattices A and B such that for all exchange couplings: $J(x_A, y_B) \leq g^2$, $J(x_A, y_A) \geq g^2$, $J(x_B, y_B) \geq g^2$, cmp. (1,2).
4. Competing interactions.

(1) E.H. Lieb, T.D. Schultz, and D.C. Mattis, Ann. Phys. (N.Y.) **16**, 407 (1961)
(2) E.H. Lieb and D.C. Mattis, J. Math. Phys. **3**, 749 (1962)
(3) G. Kamieniarz, W. Florek, M. Antkowiak, Phys. Rev. B 92, 140411(R) (2015)

Marshall-Peierls sign rule for even rings



- Expanding the ground state in $\mathcal{H}(M)$ in the product basis yields a sign rule for the coefficients

$$\mid \Psi_0 \,\rangle = \sum_{\vec{m}} c(\vec{m}) \mid \vec{m} \,\rangle \qquad \text{with} \; \sum_{i=1}^{N} m_i = M$$

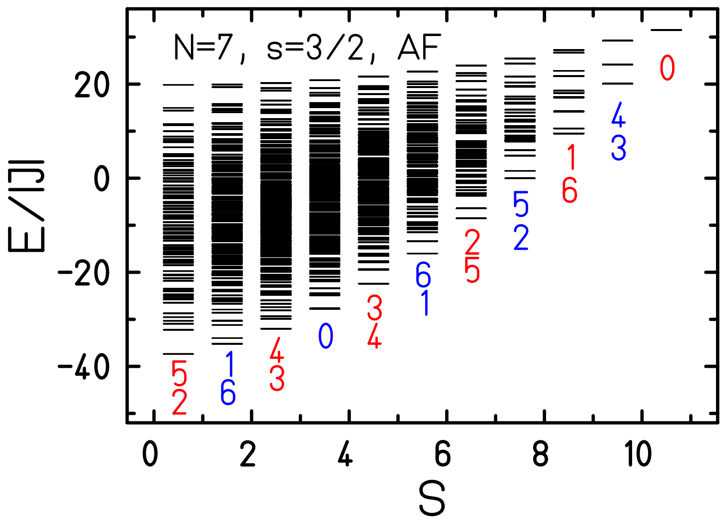
$$c(\vec{m}) = (-1)^{\left(\frac{Ns}{2} - \sum_{i=1}^{N/2} m_{2i}\right)} a(\vec{m})$$

All $a(\mathbf{m})$ are non-zero, real, and of equal sign.

- Yields eigenvalues for the shift operator $\underset{\sim}{T}$:
$\exp\left\{-i\frac{2\pi k}{N}\right\}$ with $k \equiv a\,\frac{N}{2} \mod N\;, \quad a = Ns - M$

(1) W. Marshall, Proc. Royal. Soc. A (London) **232**, 48 (1955)

Numerical findings for odd rings



- For odd N and half integer s, i.e. $s = 1/2, 3/2, 5/2, \ldots$ we find that (1)
  - the ground state has total spin $S = 1/2$;
  - the ground state energy is **fourfold** degenerate.

- Reason: In addition to the (trivial) degeneracy due to $M = \pm 1/2$, a degeneracy with respect to k appears (2):
  $k = \lfloor \frac{N+1}{4} \rfloor$ and $k = N - \lfloor \frac{N+1}{4} \rfloor$

- For the first excited state similar rules could be numerically established (3).

(1) K. Bärwinkel, H.-J. Schmidt, J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
(2) $\lfloor \cdot \rfloor$ largest integer, smaller or equal
(3) J. Schnack, Phys. Rev. B **62**, 14855 (2000)

k-rule for ~~odd~~ all(!) rings

- An extended k-rule can be inferred from our numerical investigations which yields the k quantum number for relative ground states of subspaces $\mathcal{H}(M)$ for even as well as odd spin rings, i.e. for all rings (1)

$$k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \mod N \; , \quad a = Ns - M$$

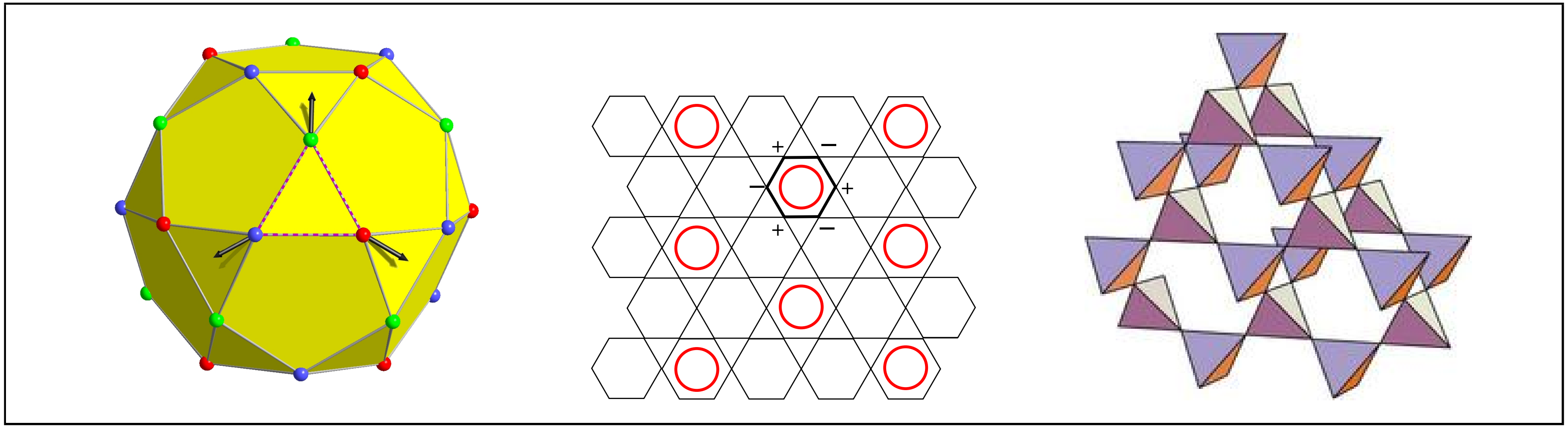
k is independent of s for a given N and a. The degeneracy is minimal ($N \neq 3$).

		a									
N	s	0	1	2	3	4	5	6	7	8	9
8	1/2	0	4	$8 \equiv 0$	$12 \equiv 4$	$16 \equiv 0$	-	-	-	-	-
9	1/2	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	-	-	-	-	-
9	1	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	$30 \equiv 3$	$35 \equiv 1$	$40 \equiv 4$	$45 \equiv 0$

No general, but partial proof yet.

(1) K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B **68**, 054422 (2003)

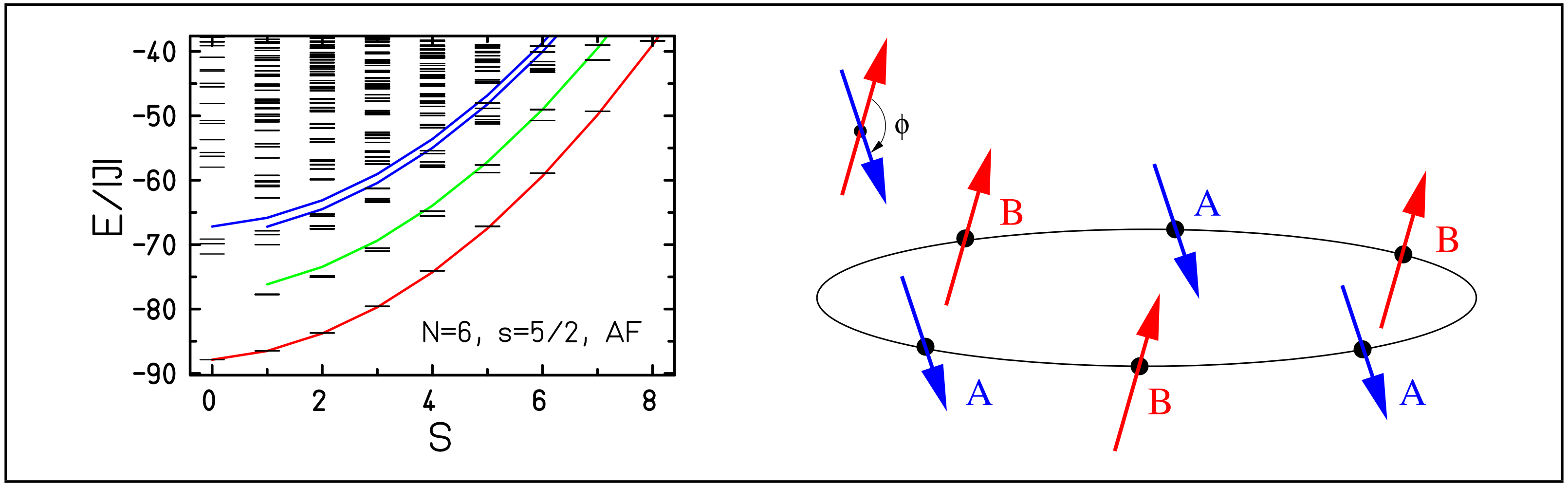
Fe_{30} and friends
Corner sharing triangles and tetrahedra



- Several frustrated antiferromagnets show an unusual magnetization behavior, e.g. plateaus and jumps.

- Example systems: icosidodecahedron, kagome lattice, pyrochlore lattice.

Rotational bands in non-frustrated antiferromagnets



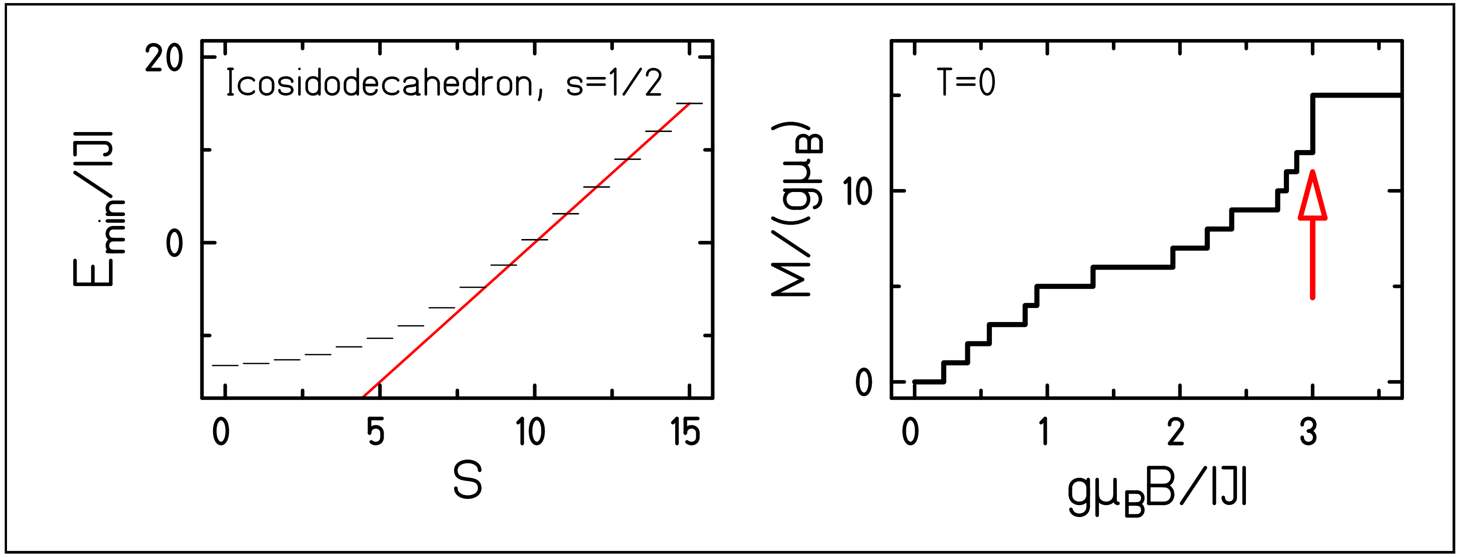
- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);

- For bipartite systems (2,3): $\underset{\sim}{H}^{\text{eff}} = -2\, J_{\text{eff}}\, \underset{\sim}{\vec{S}}_A \cdot \underset{\sim}{\vec{S}}_B$;

- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(1) A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996), G. L. Abbati *et al.*, Inorg. Chim. Acta **297**, 291 (2000)
(2) J. Schnack and M. Luban, Phys. Rev. B **63**, 014418 (2001)
(3) O. Waldmann, Phys. Rev. B **65**, 024424 (2002)
(4) P.W. Anderson, Phys. Rev. B **86**, 694 (1952), O. Waldmann *et al.*, Phys. Rev. Lett. **91**, 237202 (2003).

Giant magnetization jumps in frustrated antiferromagnets I the icosidodecahedron



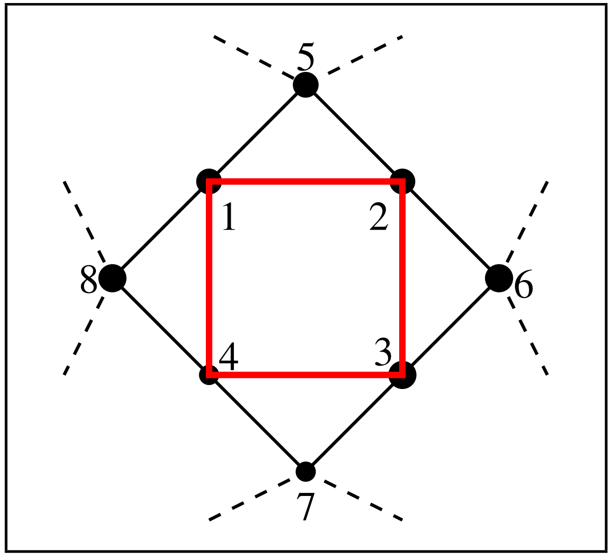
- Close look: $E_{\text{min}}(S)$ linear in S for high S instead of being quadratic (1);

- Heisenberg model: property depends only on the structure but not on s (2);

- Alternative formulation: independent localized magnons (3);

(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)
(2) H.-J. Schmidt, J. Phys. A: Math. Gen. **35**, 6545 (2002)
(3) J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)

Giant magnetization jumps in frustrated antiferromagnets II
Localized Magnons

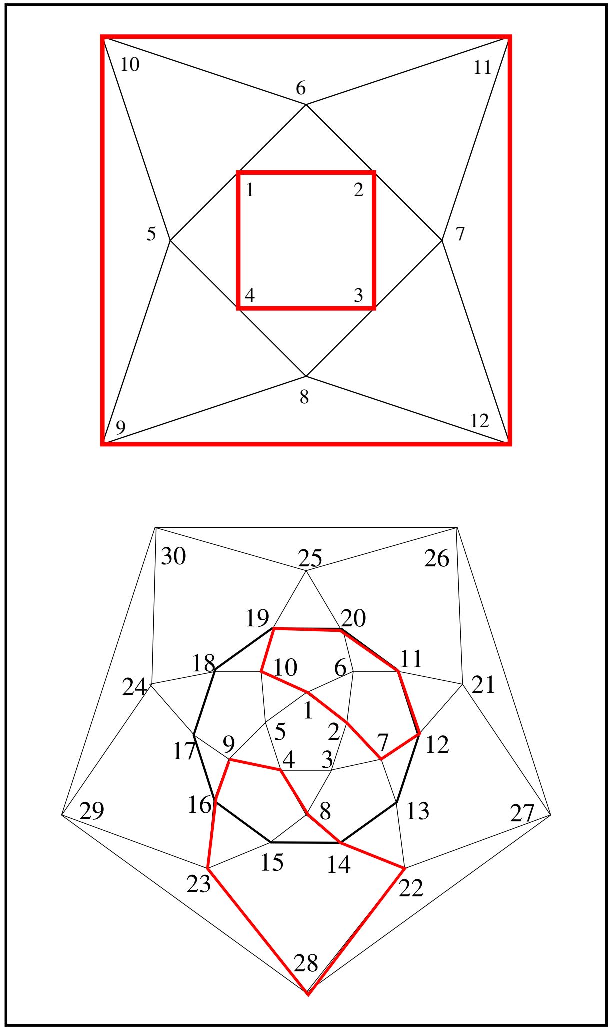


- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}\left(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle\right)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\ \dots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$
- Localized magnon is state of lowest energy (1,2).

- Triangles trap the localized magnon, amplitudes cancel at outer vertices.

(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)
(2) H.-J. Schmidt, J. Phys. A: Math. Gen. **35**, 6545 (2002)

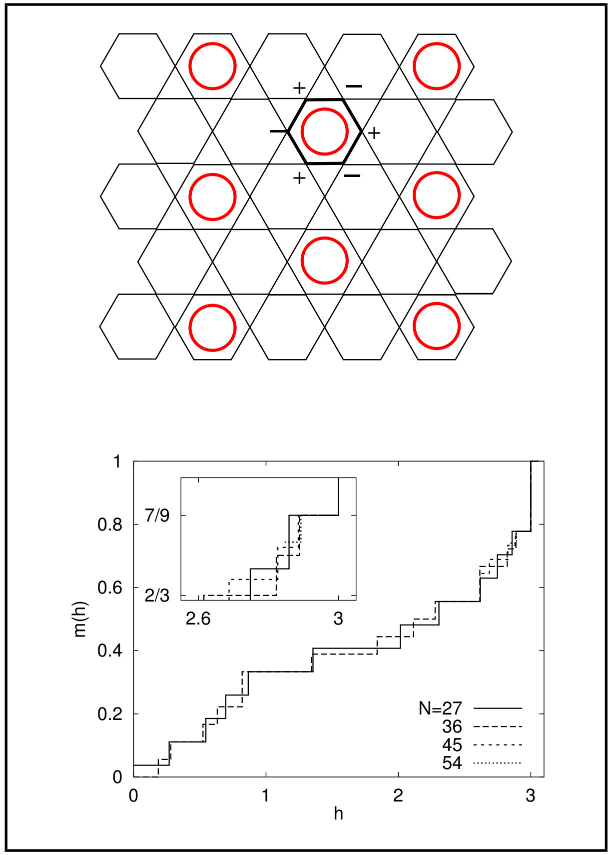
Giant magnetization jumps in frustrated antiferromagnets III



- Non-interacting one-magnon states can be placed on various molecules, e. g. 2 on the cuboctahedron and 3 on the icosidodecahedron (3rd delocalized);
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$;
- Linear dependence of E_{min} on M $\Rightarrow$ $(T = 0)$ magnetization jump;
- A rare example of analytically known many-body states!

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

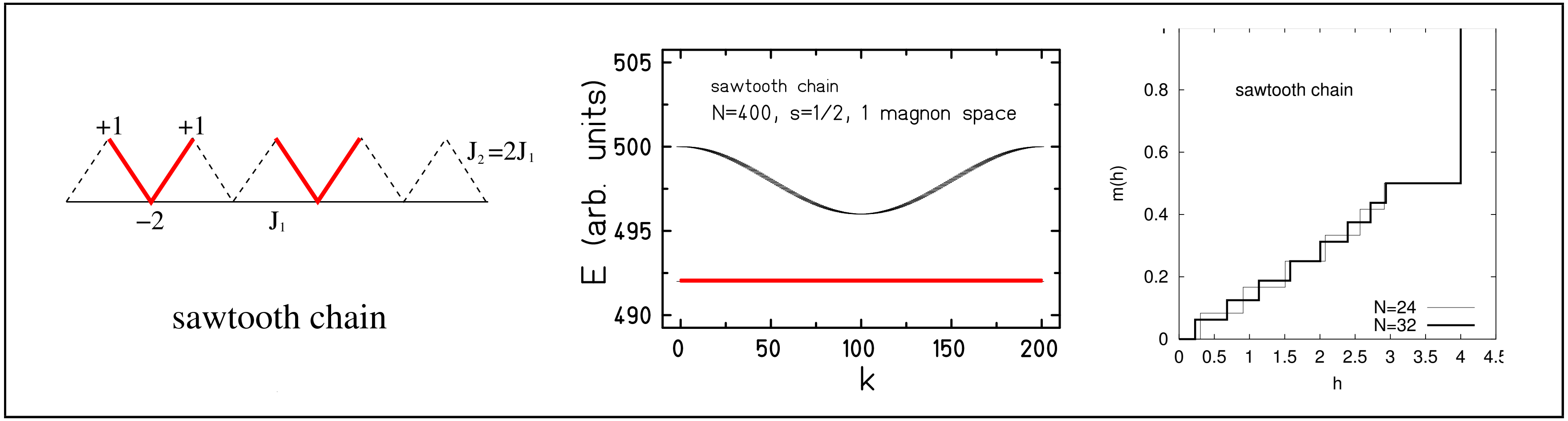
Giant magnetization jumps in frustrated antiferromagnets IV Kagome Lattice



- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore;
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$; Kagome: max. number of indep. magnons is N/9;
- Linear dependence of E_{min} on M $\Rightarrow \quad (T = 0)$ magnetization jump;
- Jump is a macroscopic quantum effect!
- A rare example of analytically known many-body states!

J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)
J. Richter, J. Schulenburg, A. Honecker, J. Schnack, H.-J. Schmidt, J. Phys.: Condens. Matter **16**, S779 (2004)

Condensed matter physics point of view: Flat band



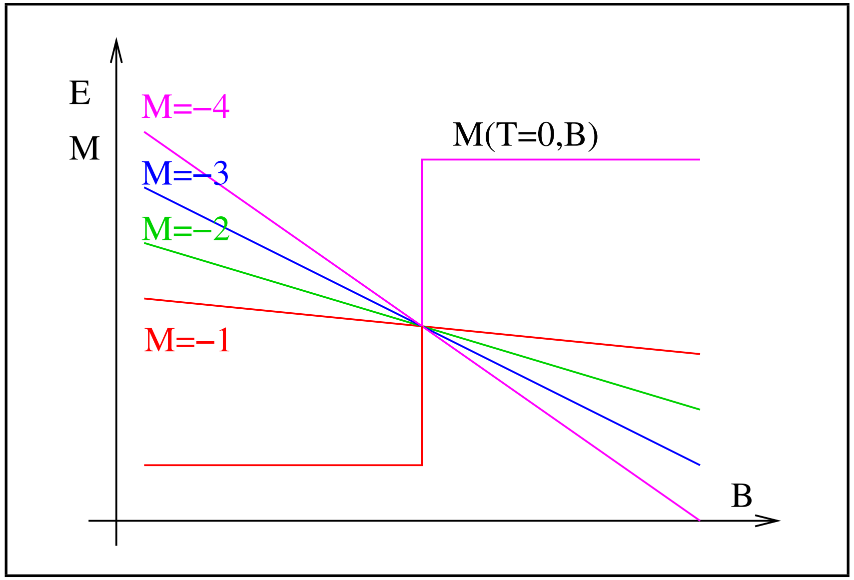
- Flat band of minimal energy in one-magnon space; localized magnons can be built from delocalized states in the flat band.

- Entropy can be evaluated using hard-object models (1); universal low-temperature behavior.

- Same behavior for Hubbard model; flat band ferromagnetism (Tasaki & Mielke), jump of N with μ (2).

(1) H.-J. Schmidt, J. Richter, R. Moessner, J. Phys. A: Math. Gen. **39**, 10673 (2006)
(2) A. Honecker, J. Richter, Condens. Matter Phys. **8**, 813 (2005)

Magnetocaloric effect I
Giant jumps to saturation



- Many Zeeman levels cross at one and the same magnetic field.
- You know this for a giant spin at $B = 0$.
- High degeneracy of ground state levels $\Rightarrow$ large residual entropy at $T = 0$.
- $$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

M. Evangelisti *et al.*, Appl. Phys. Lett. **87**, 072504 (2005).
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)
M. E. Zhitomirsky, Phys. Rev. B **67**, 104421 (2003).
M. E. Zhitomirsky and A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004).

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

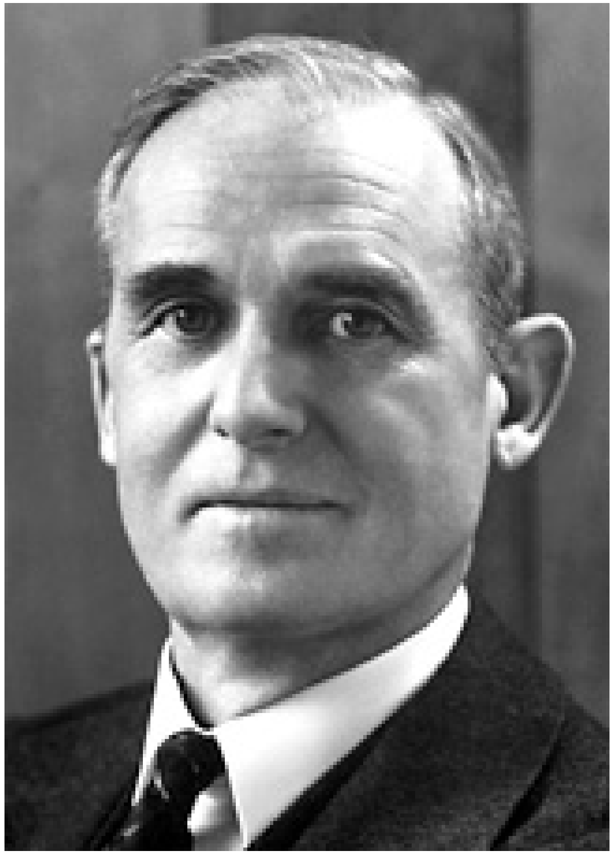
$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

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

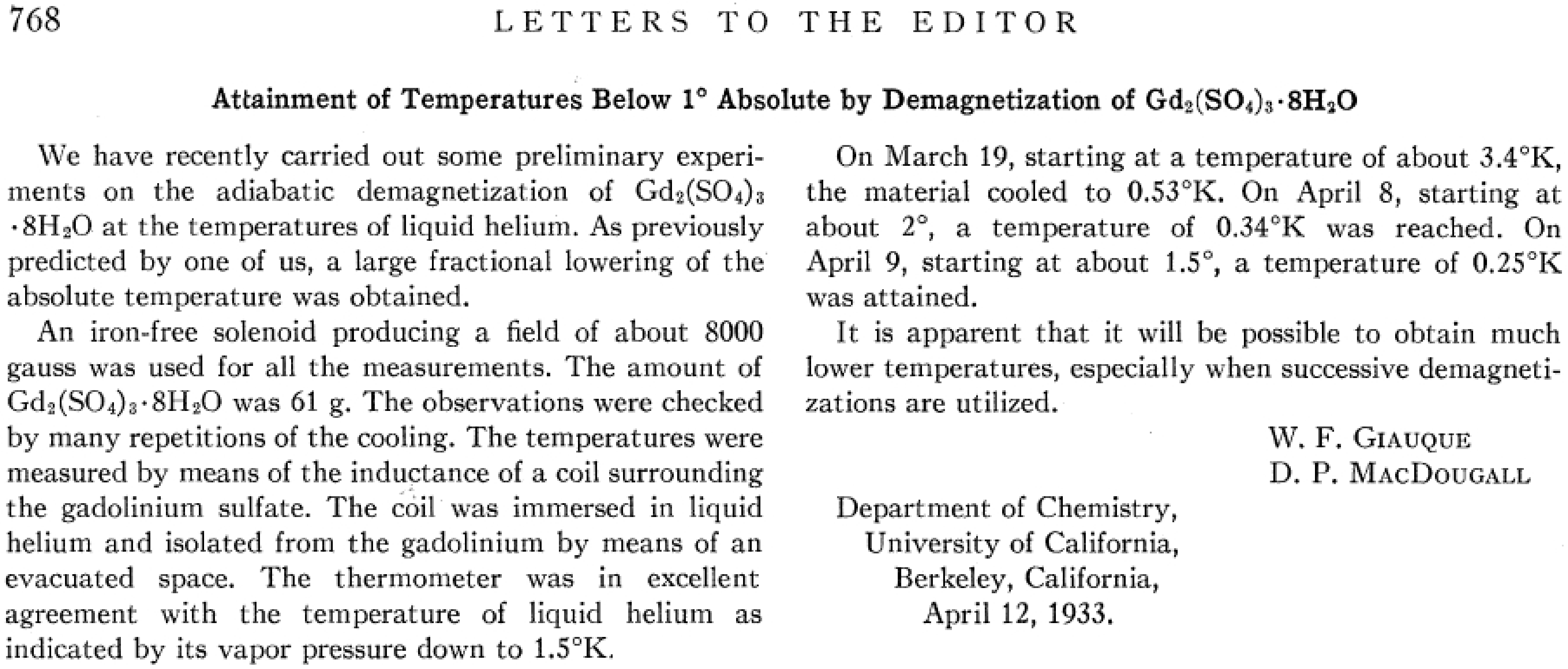
(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001).
(2) Lijun Zhu, M. Garst, A. Rosch, and Qimiao Si, Phys. Rev. Lett. **91**, 066404 (2003).
B. Wolf, Y. Tsui, D. Jaiswal-Nagar, U. Tutsch, A. Honecker, K. Removic-Langer, G. Hofmann, A. Prokofiev, 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).

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.

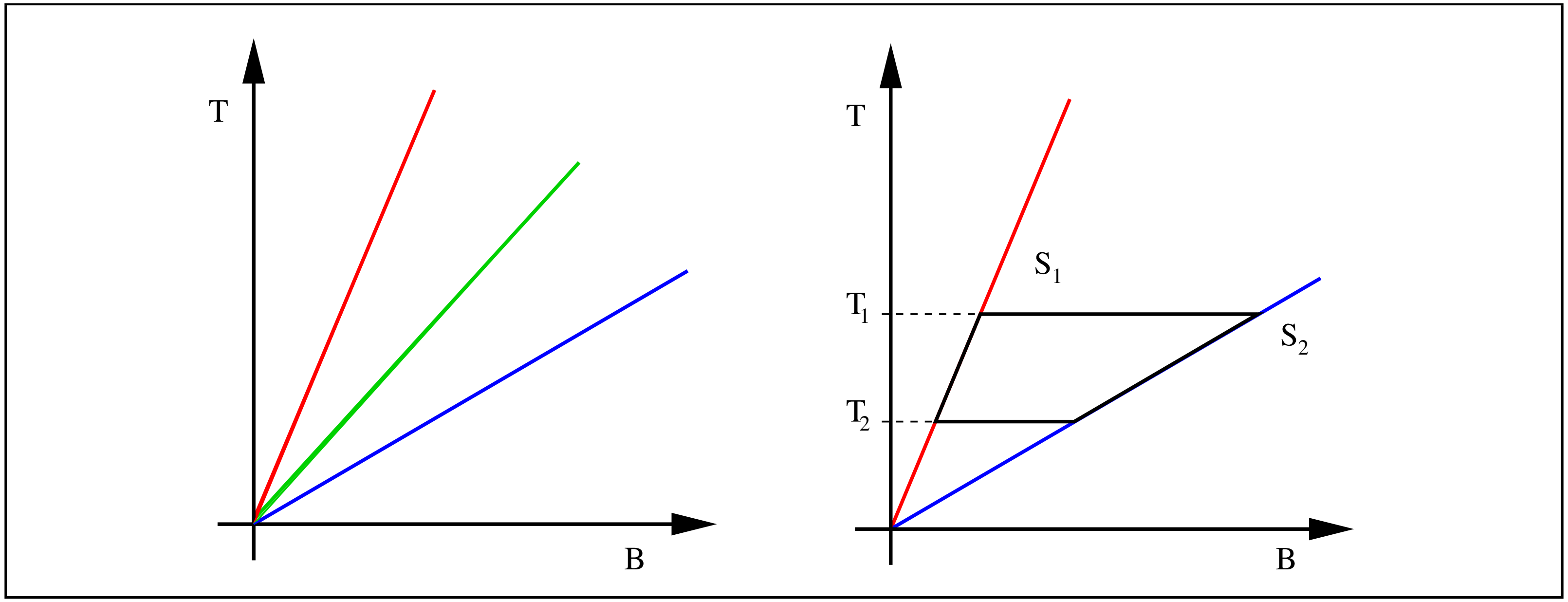
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. GIAUQUE
D. P. MACDOUGALL

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

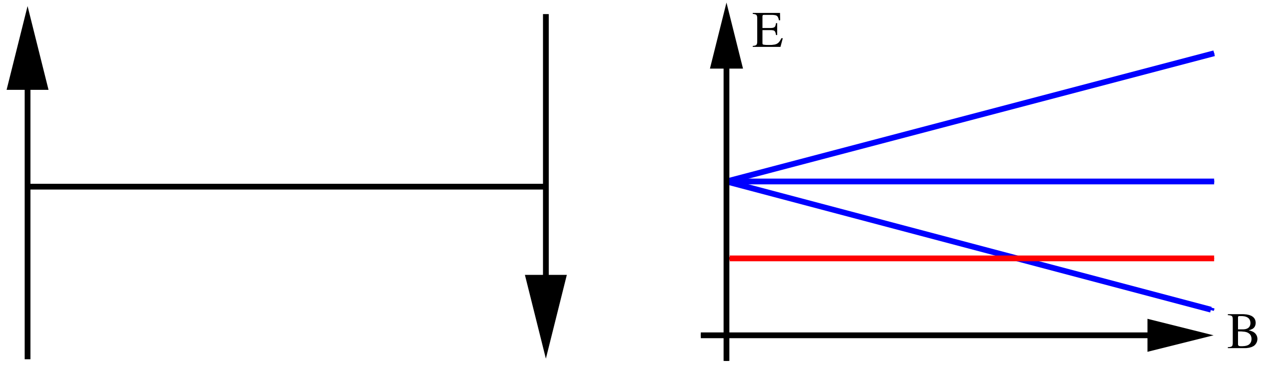
W. F. Giauque and D. MacDougall, Phys. Rev. **43**, 768 (1933).

Magnetocaloric effect – Paramagnets



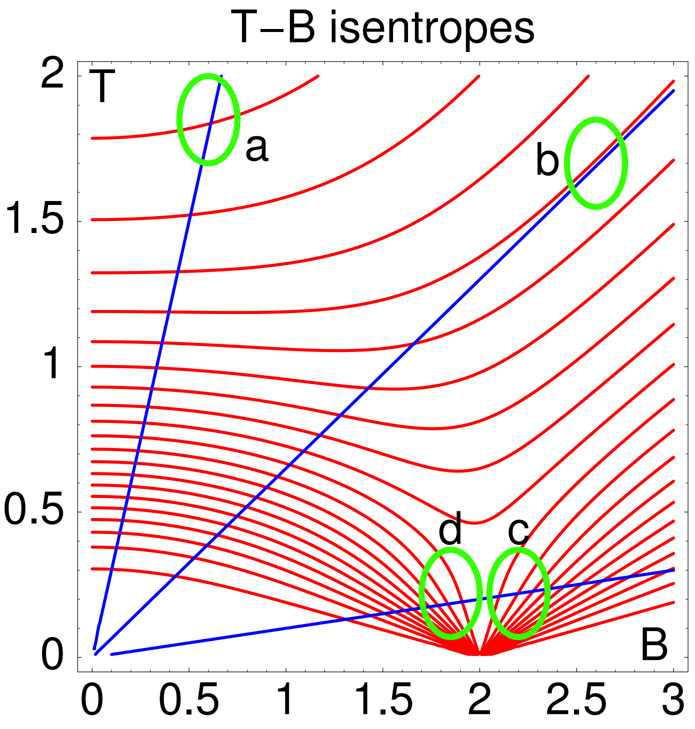
- Ideal paramagnet: $S(T,B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

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

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



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

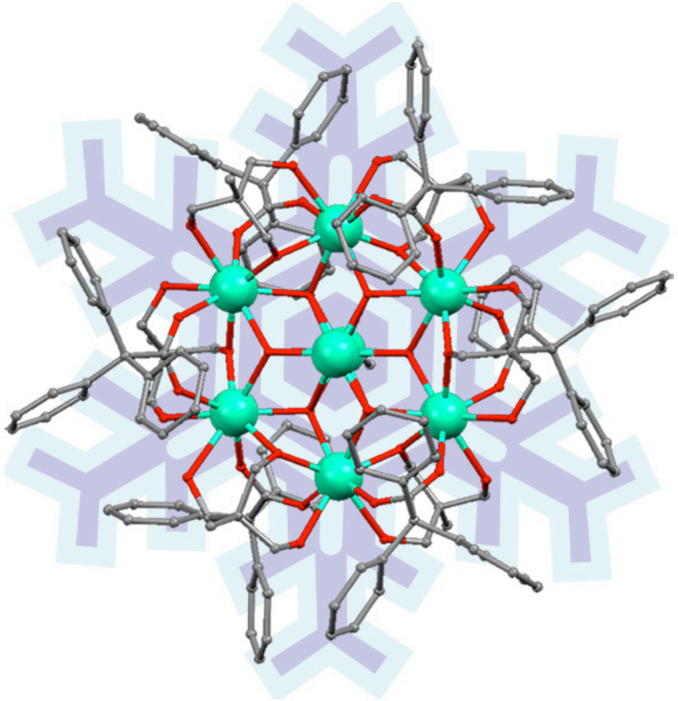
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

Gd$_7$ – Basics

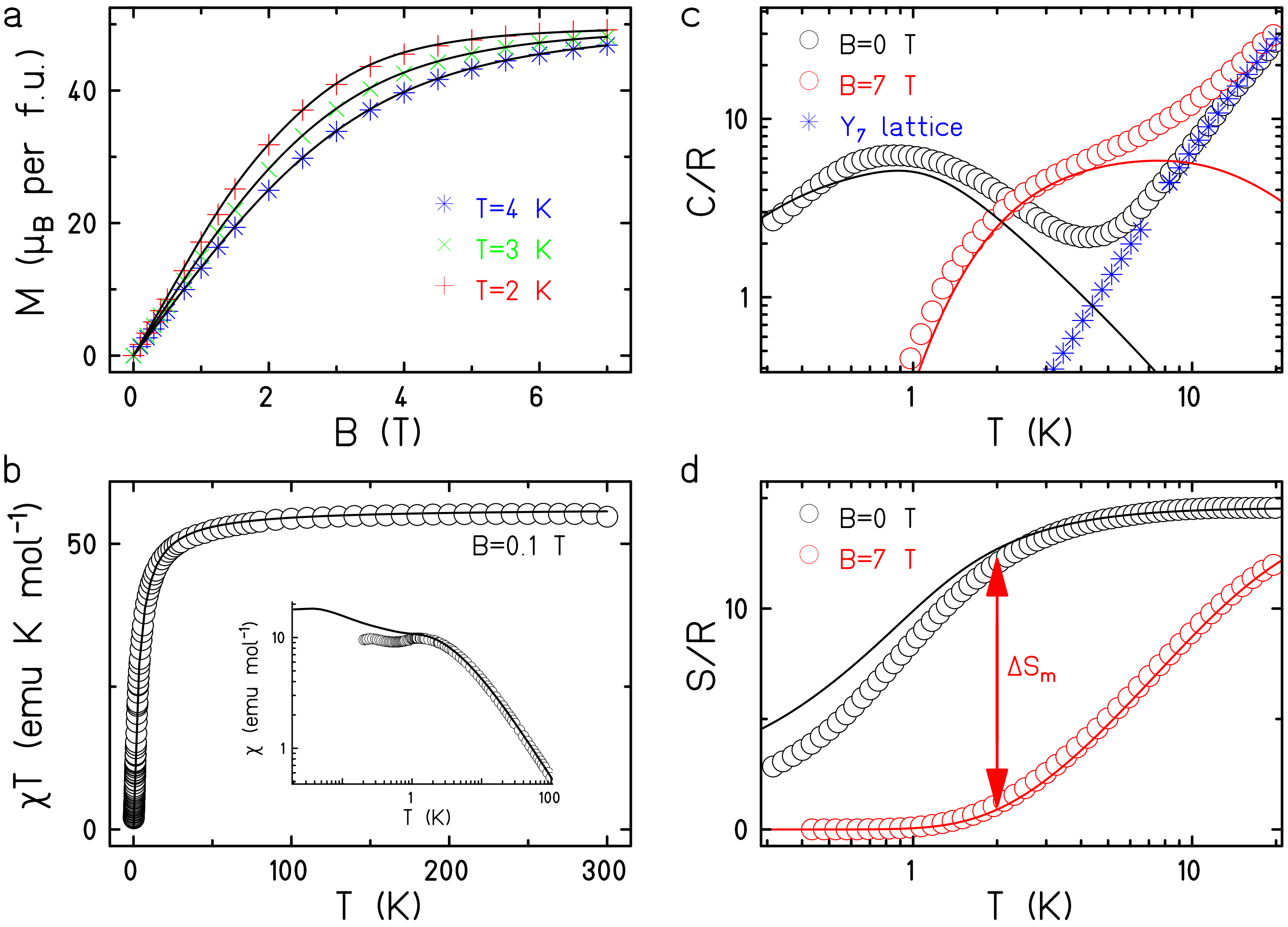


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_j + g\, \mu_B\, B \sum_i^N \underset{\sim}{s}_i^z$

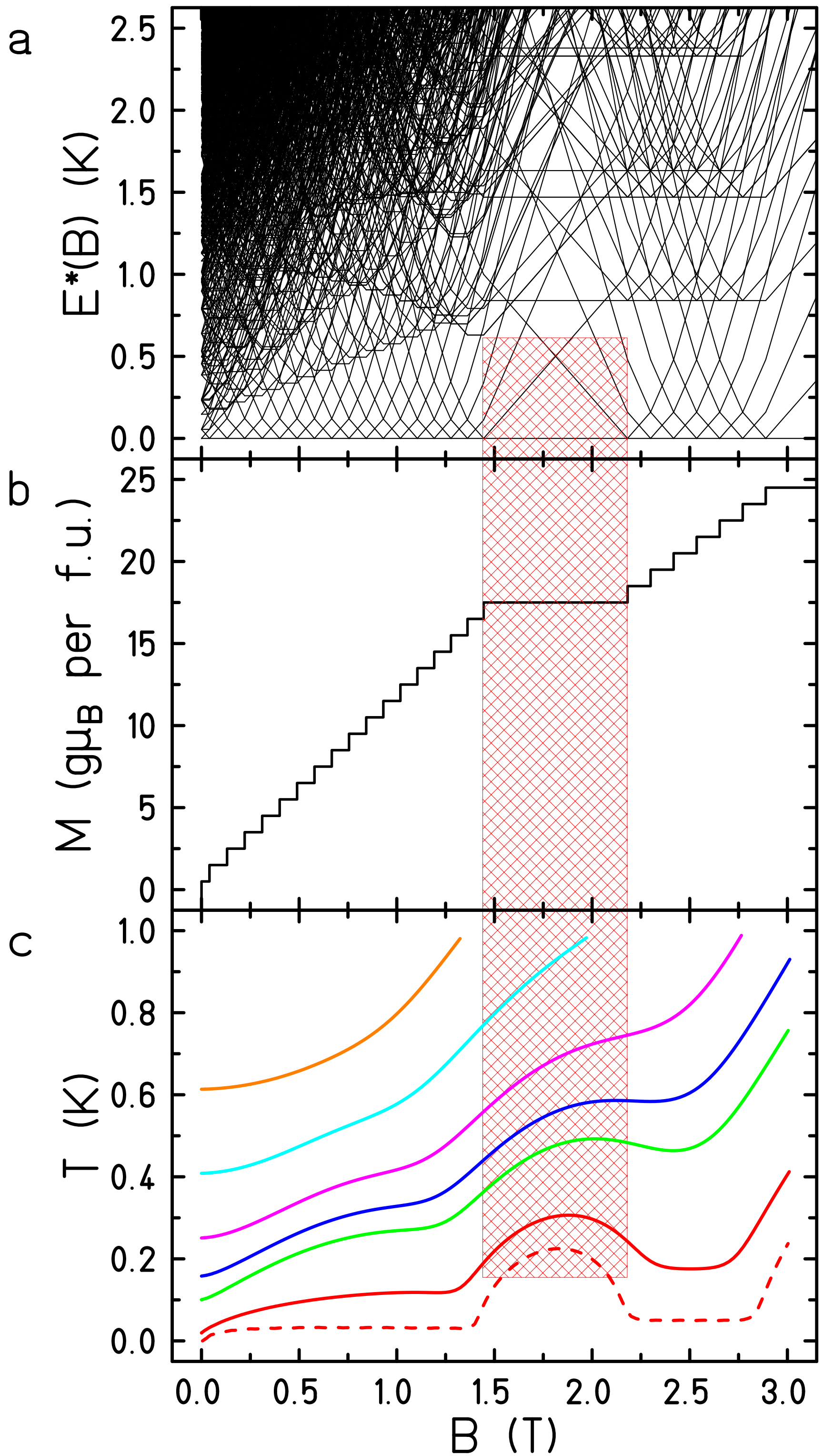
  $J_1 = -0.090(5)$ K, $J_2 = -0.080(5)$ K and $g = 2.02$.
- Very good agreement down to the lowest temperatures.

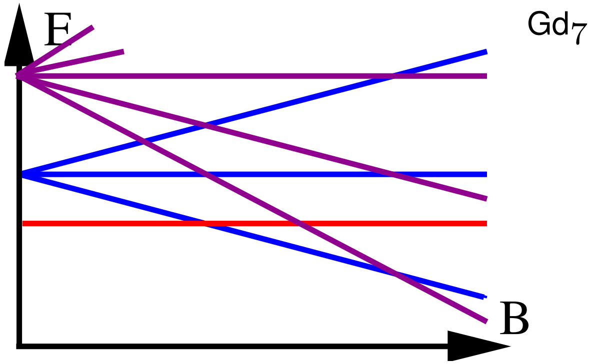
J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

Gd_7 – experiment & theory

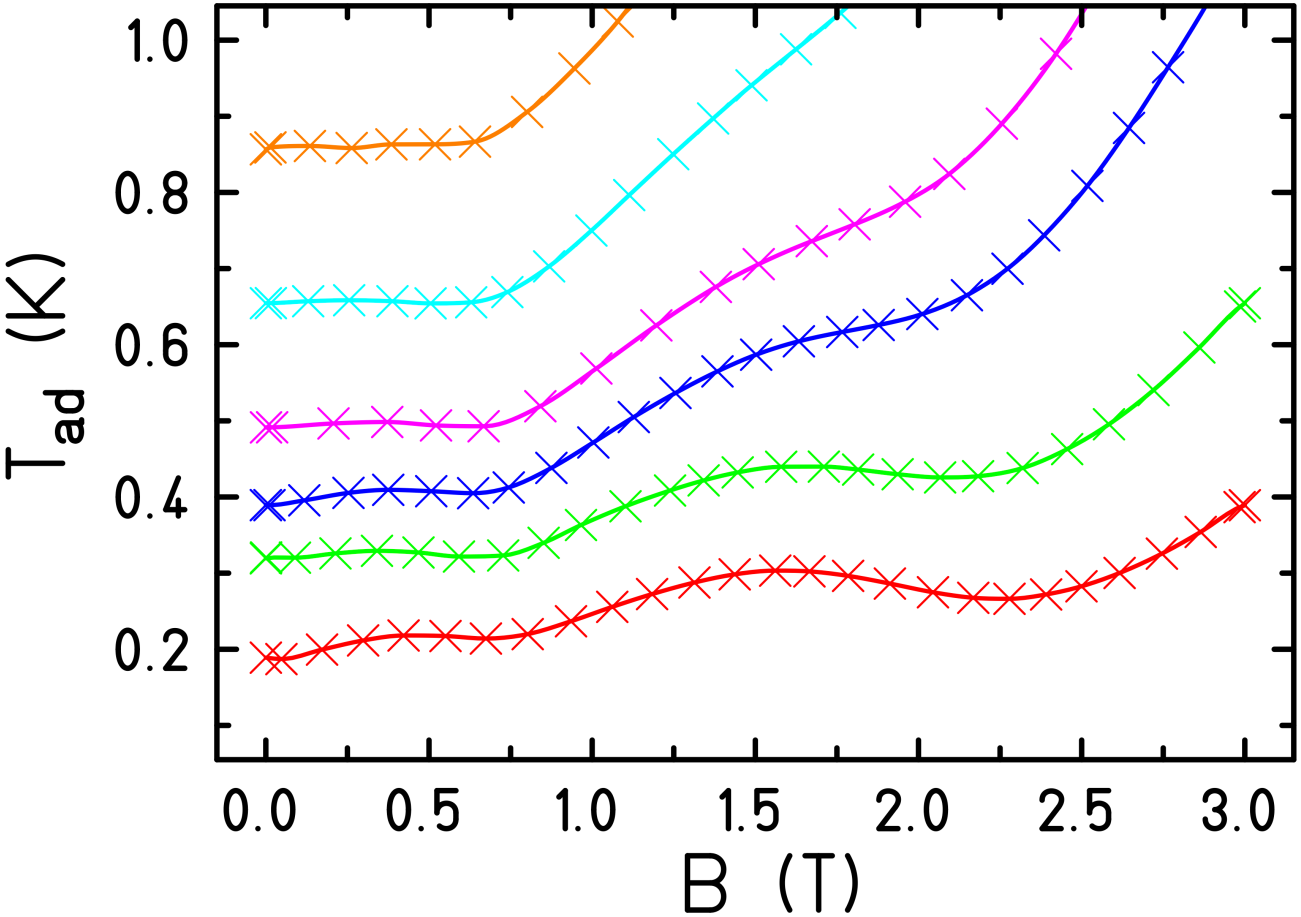


J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).


a
E*(B) (K)
2.5
2.0
1.5
1.0
0.5
0.0
b
M (gμ_B per f.u.)
25
20
15
10
5
0
c
T (K)
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
B (T)


E
Gd$_7$
B

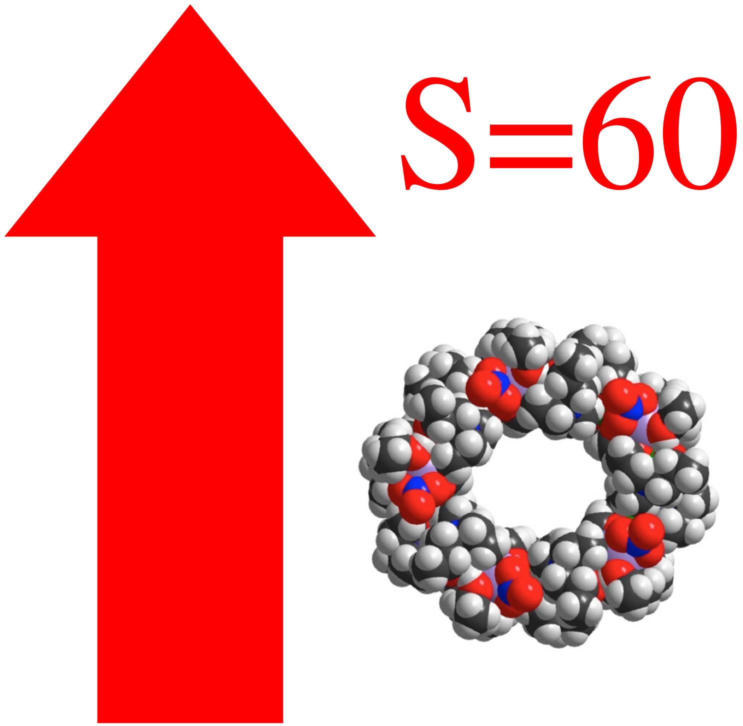
Gd$_7$ – Experimental cooling

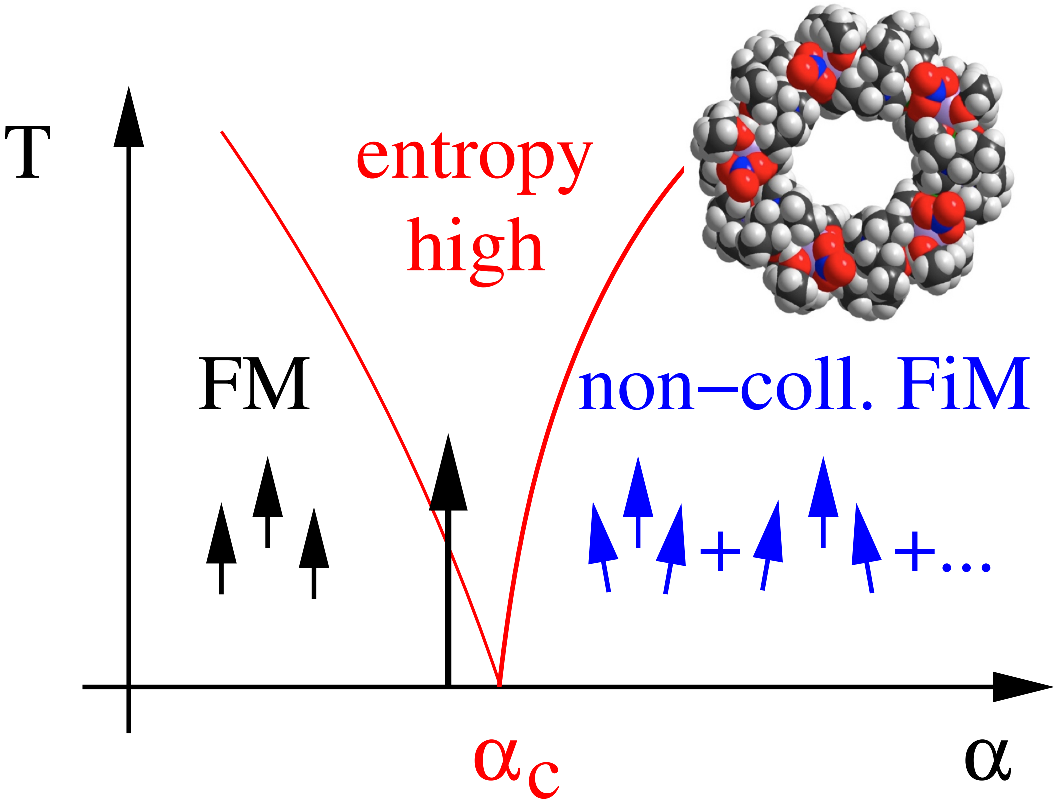


J. W. Sharples, D. Collison, E. J. L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nat. Commun. **5**, 5321 (2014).

A quantum phase transition

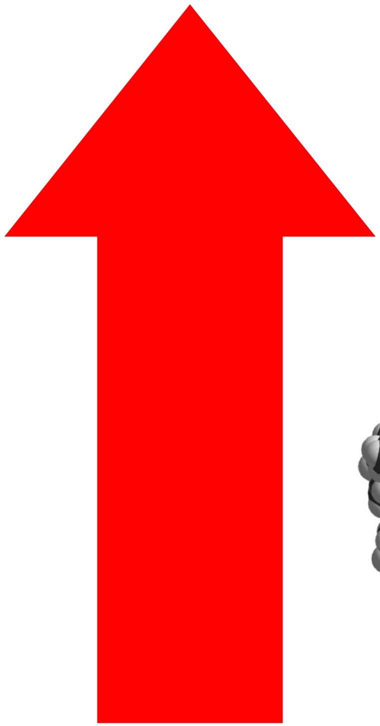
$\mathrm{Gd}_{10}\mathrm{Fe}_{10}$ – summary



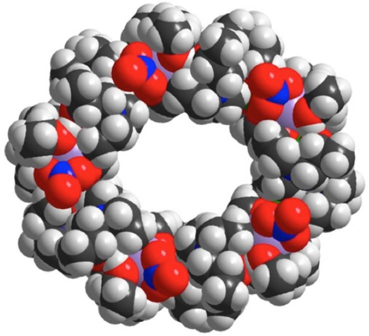


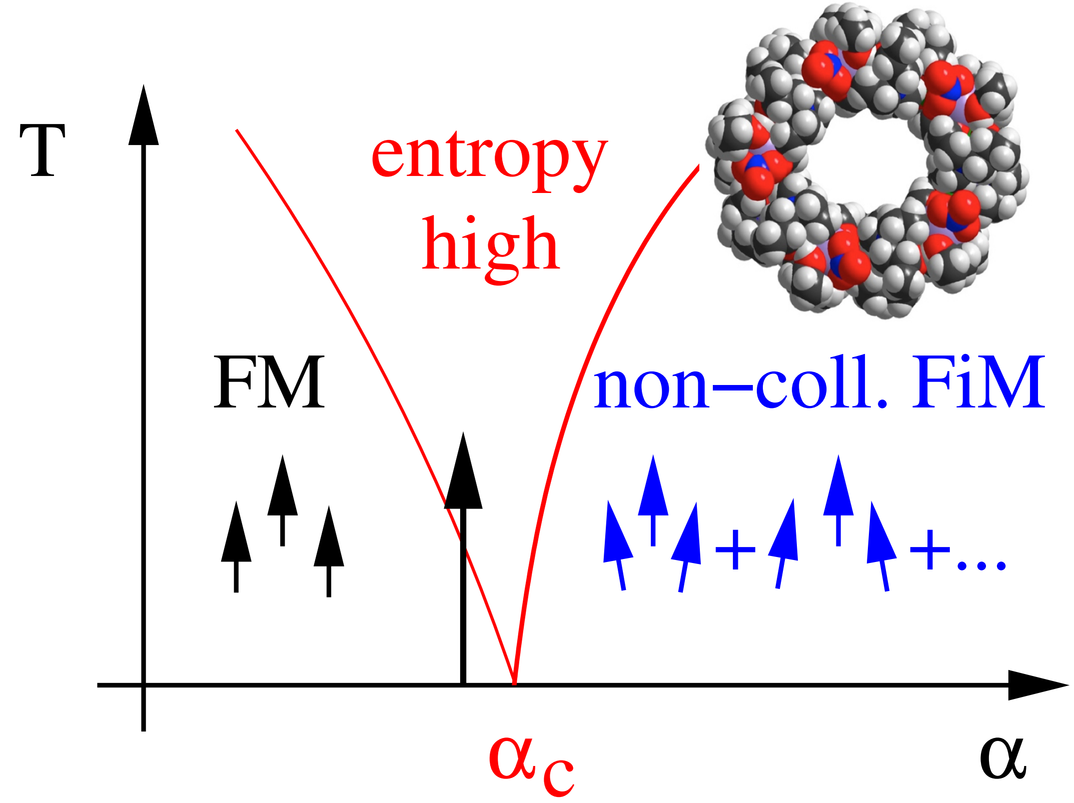
A. Baniodeh, N. Magnani, Y. Lan, G. Buth, C.E. Anson, J. Richter, M. Affronte, J. Schnack, A.K. Powell,
High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality,
npj Quantum Materials **3**, 10 (2018)

$Gd_{10}Fe_{10}$ – summary



S=60

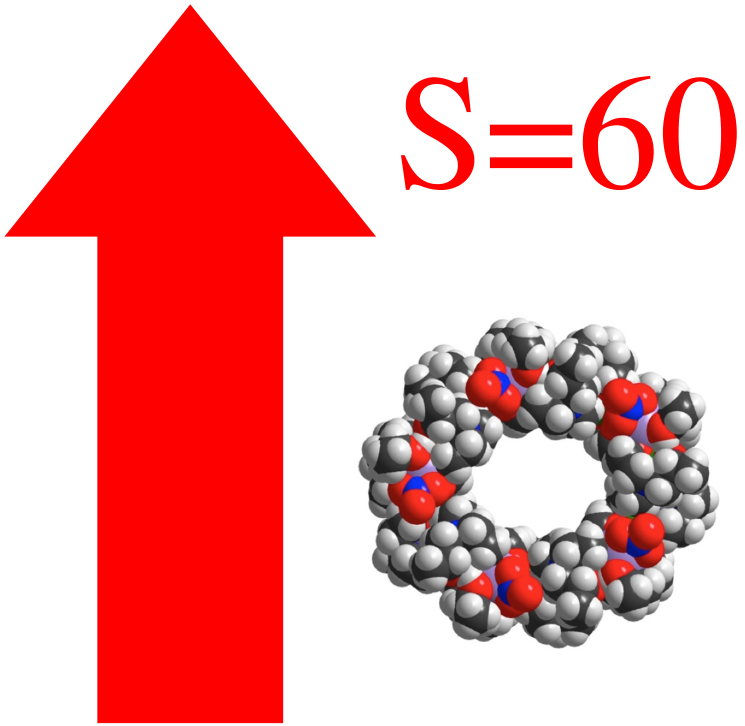


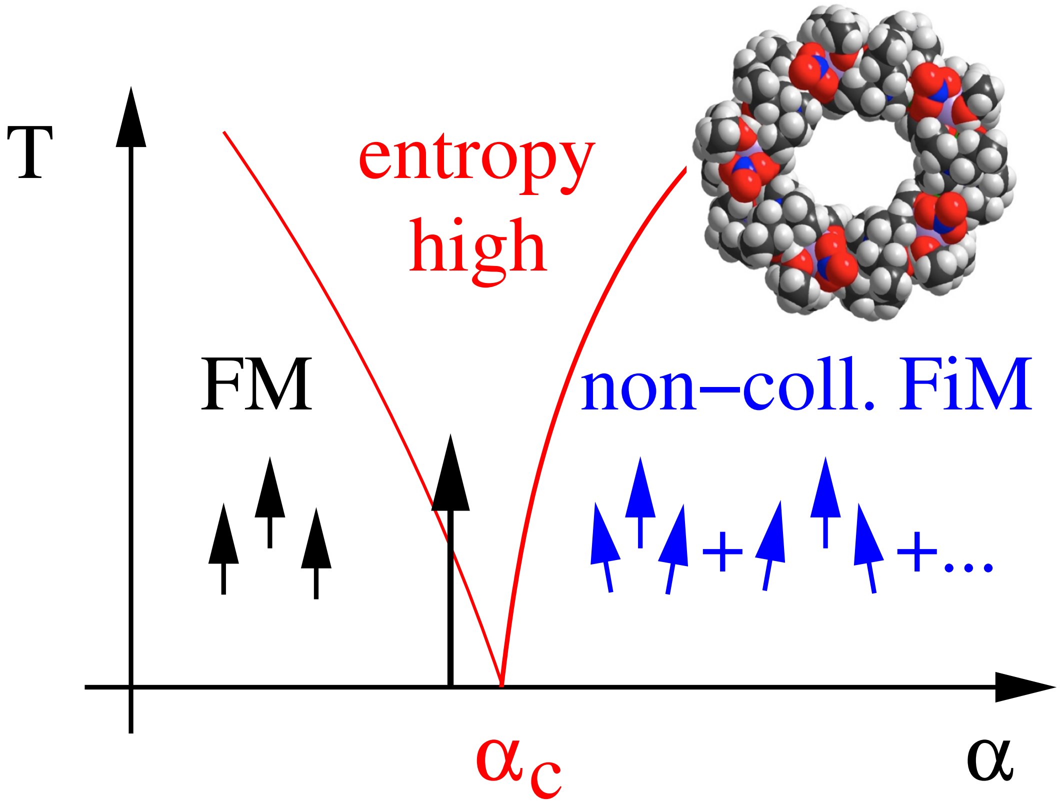


How do we know?

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

$Gd_{10}Fe_{10}$ – summary



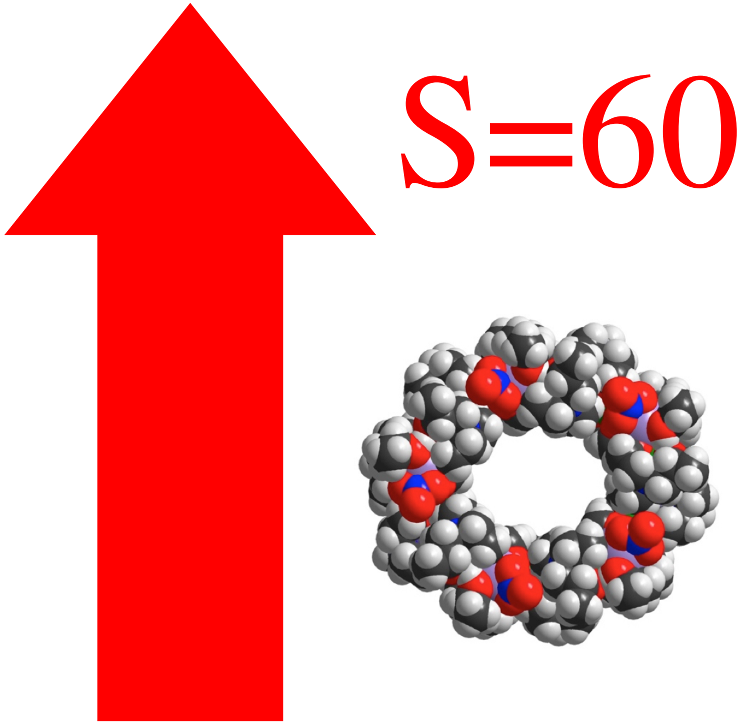


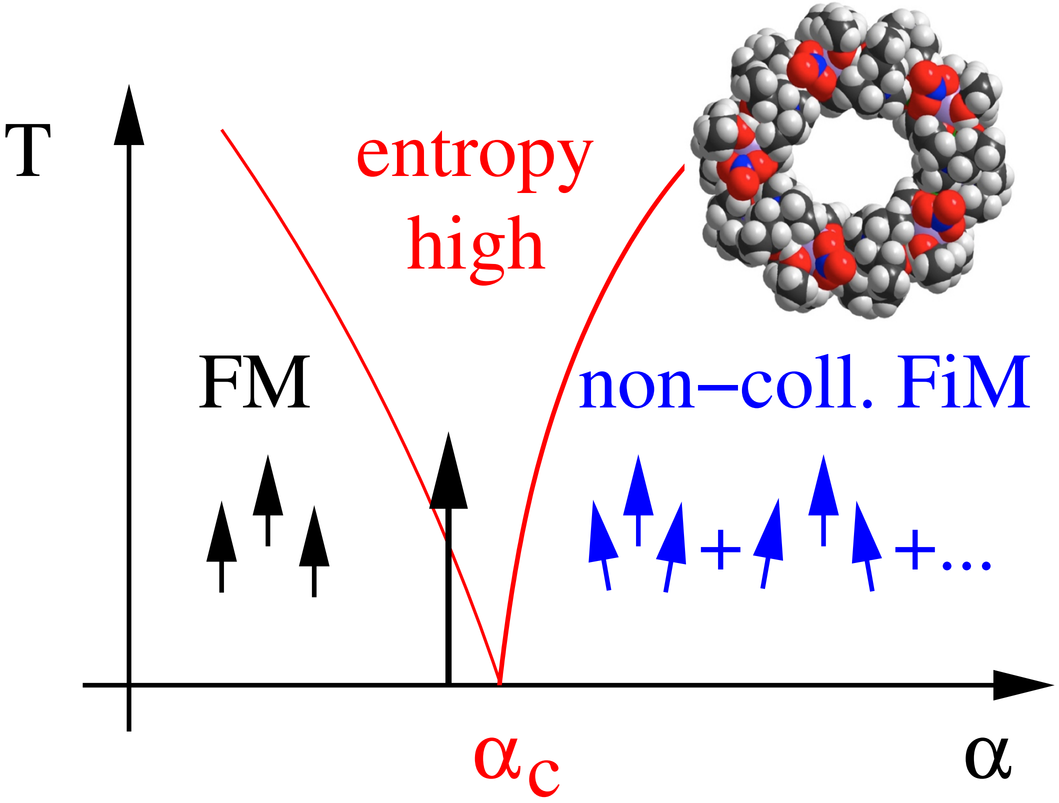
How do we know?

What is a QPT?

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

$\mathrm{Gd}_{10}\mathrm{Fe}_{10}$ – summary





How do we know?

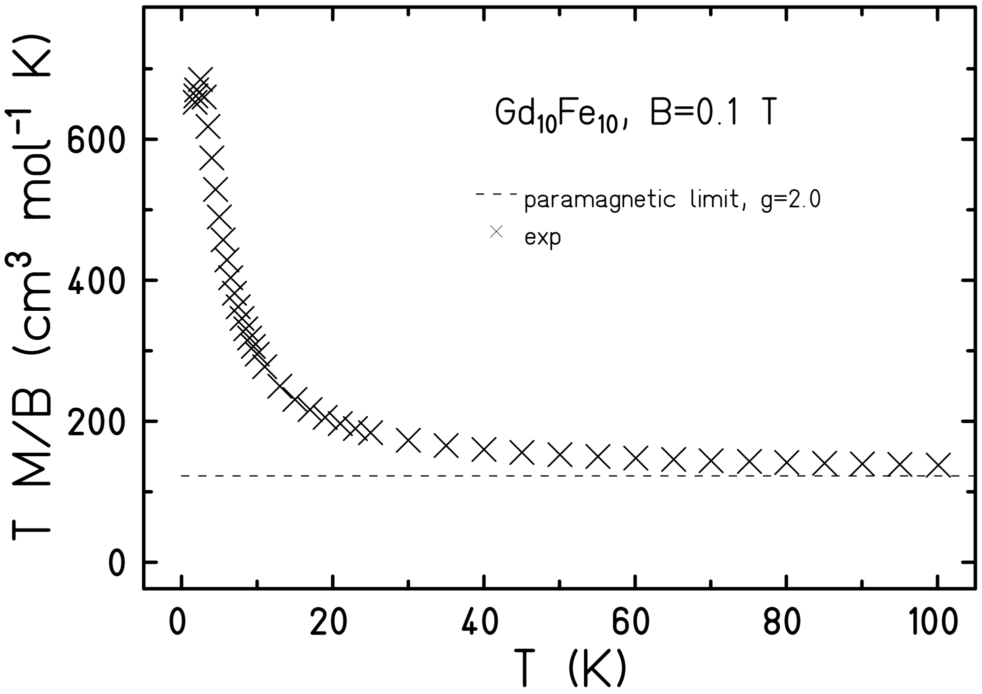
What is a QPT?

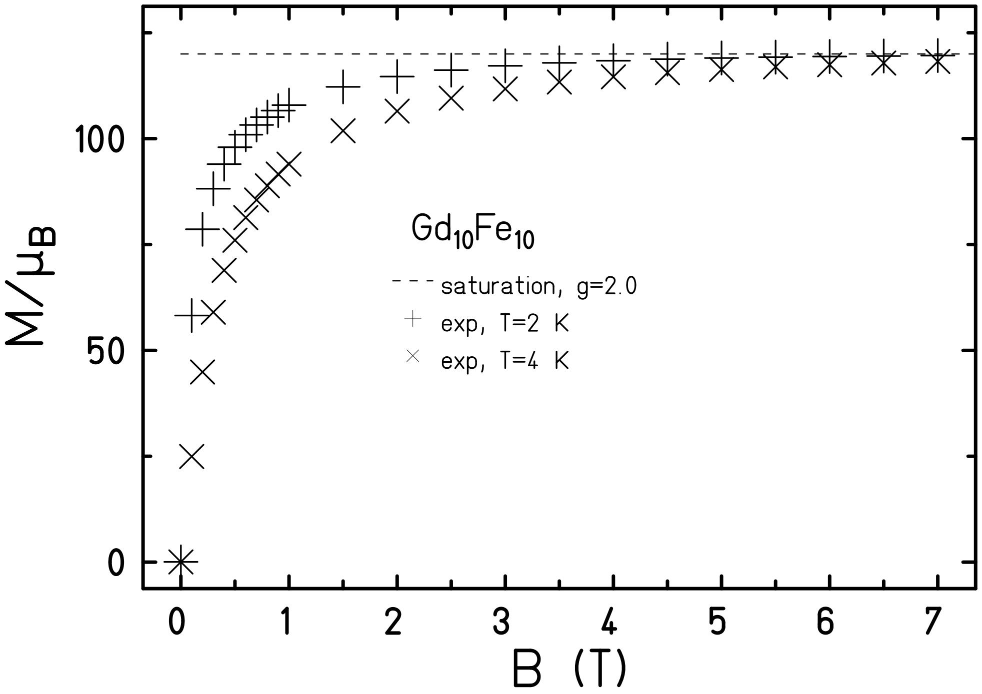
In $\mathrm{Gd}_{10}\mathrm{Fe}_{10}$?

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

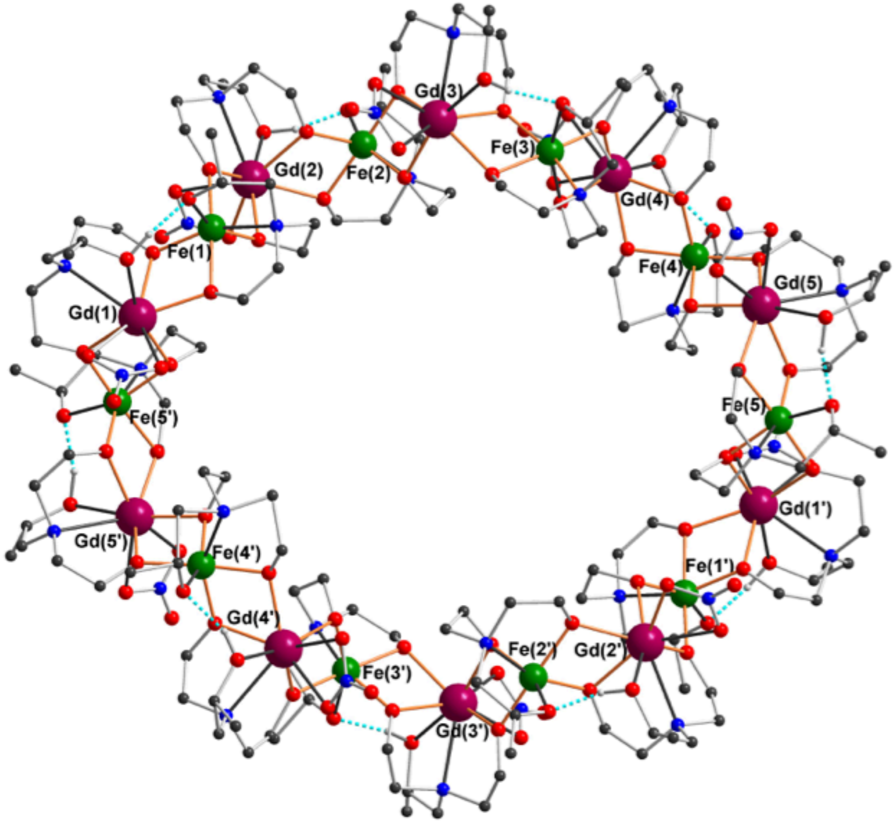
Start: experimental data

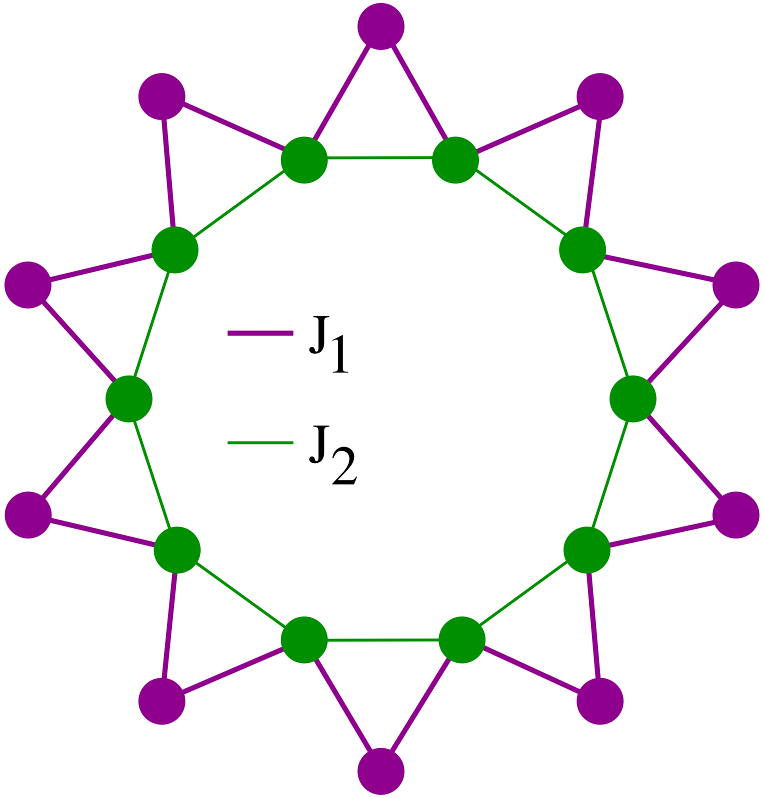
$Gd_{10}Fe_{10}$ – How to rationalize the experimental data?





$\mathrm{Gd}_{10}\mathrm{Fe}_{10}$ – structure = delta chain





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

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Model Hamiltonian

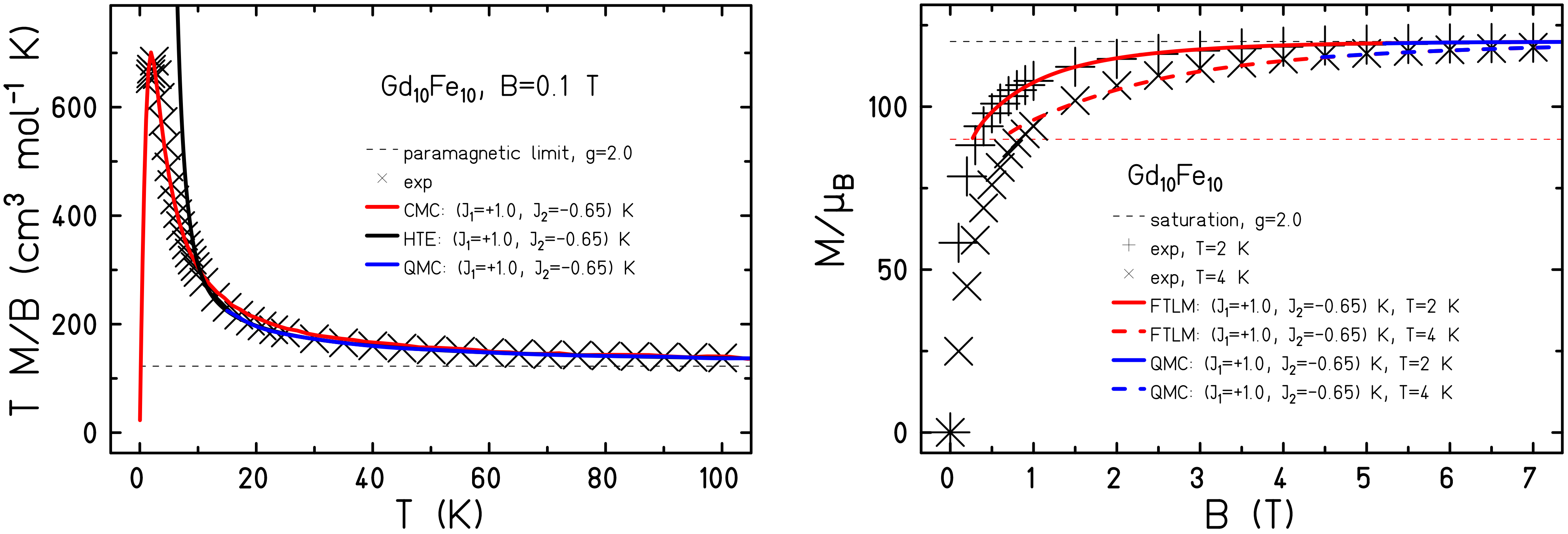
$$\underset{\sim}{H} = -2J_1 \sum_i \underset{\sim}{\vec{s}}_{\text{Gd},i} \cdot \left(\underset{\sim}{\vec{s}}_{\text{Fe},i} + \underset{\sim}{\vec{s}}_{\text{Fe},i+1} \right)$$

$$-2J_2 \sum_i \underset{\sim}{\vec{s}}_{\text{Fe},i} \cdot \underset{\sim}{\vec{s}}_{\text{Fe},i+1} + g\,\mu_B\,B \sum_i \left(\underset{\sim}{s}^z_{\text{Gd},i} + \underset{\sim}{s}^z_{\text{Fe},i} \right)$$

Dimension of Hilbert space
$(2s_{\text{Gd}} + 1)^{10}(2s_{\text{Fe}} + 1)^{10} \approx 6.5 \cdot 10^{16}$

What would you do?

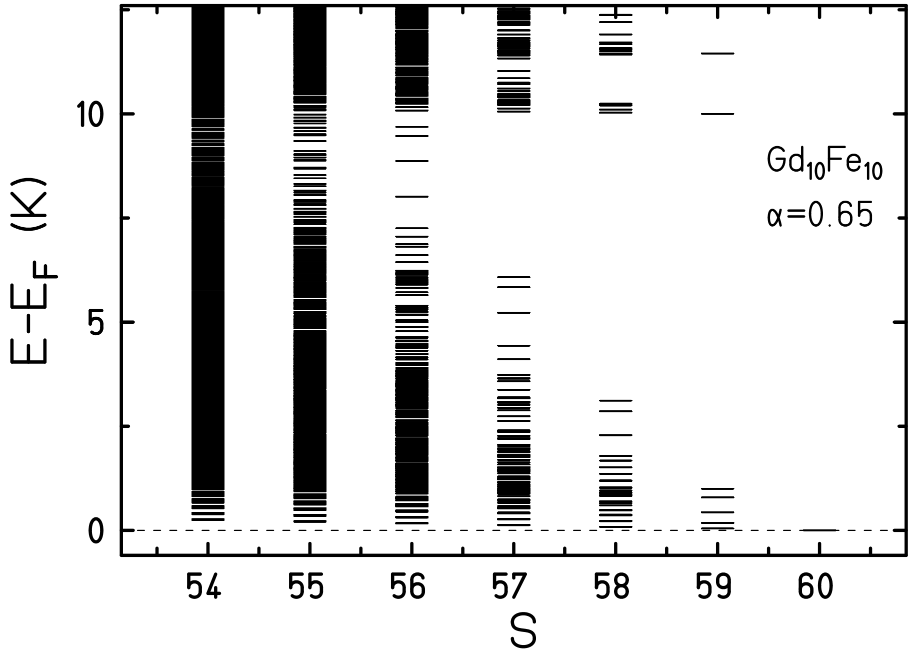
$Gd_{10}Fe_{10}$ – Methods

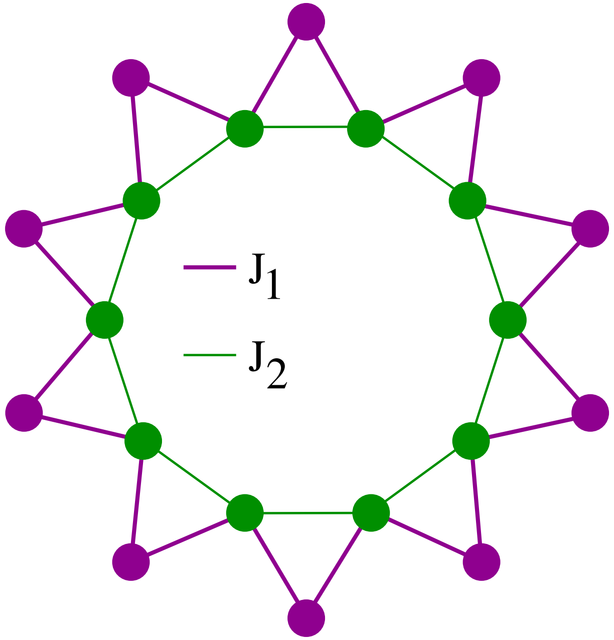


Methods: HTE, QMC, CMC, FTLM $\Rightarrow J_1 = 1.0$ K, $J_2 = -0.65$ K

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

$\mathrm{Gd}_{10}\mathrm{Fe}_{10}$ – $S = 60$



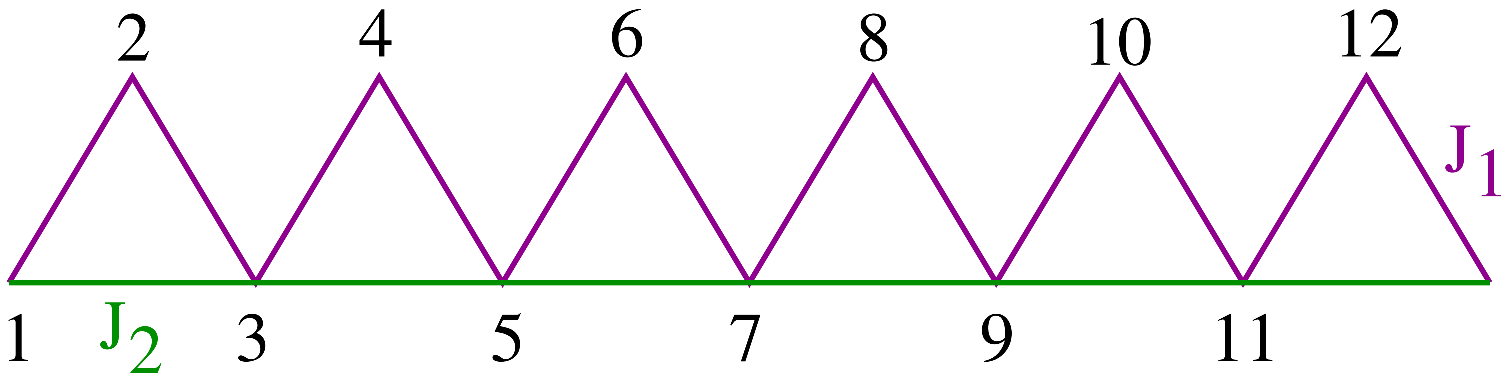


⇒ $S = 60$, largest ground state spin of a molecule to date

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

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

Excursus: sawtooth (delta) chain



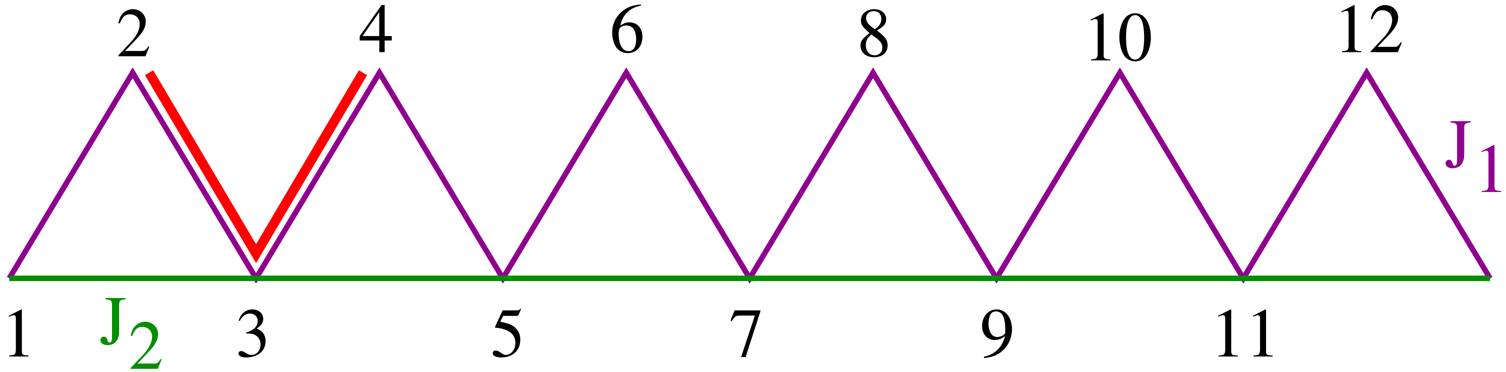
⇒ special properties for $J_1 > 0$ (ferro) and $J_2 < 0$ (af) at certain α_c

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)

Excursus: sawtooth (delta) chain



$\Rightarrow \mid F\,\rangle = \mid S = S_{\text{max}}, M = S_{\text{max}}\,\rangle$ fully polarized ferromagnetic state

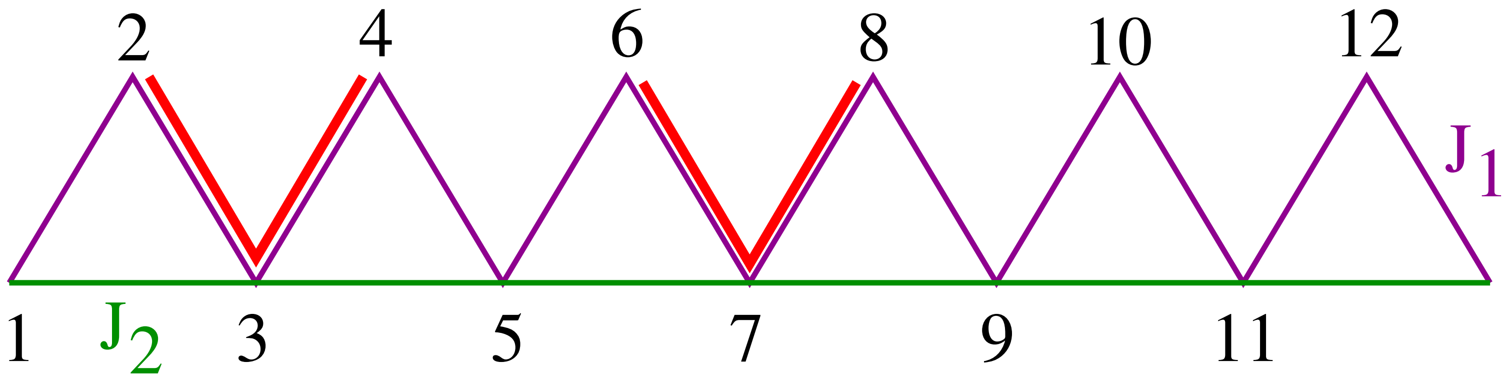
$\Rightarrow$ | 1 localized magnon at (2,3,4) $\rangle = (\underset{\sim}{s}_2^- + \underset{\sim}{s}_4^- + 2\underset{\sim}{s}_3^-) \mid F\,\rangle$;

$E = E_F, M = S_{\text{max}} - 1$

$\Rightarrow$ Can be everywhere. Flat band in one-magnon space. Degenerate with $\mid F\,\rangle$.

(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)

Excursus: sawtooth (delta) chain

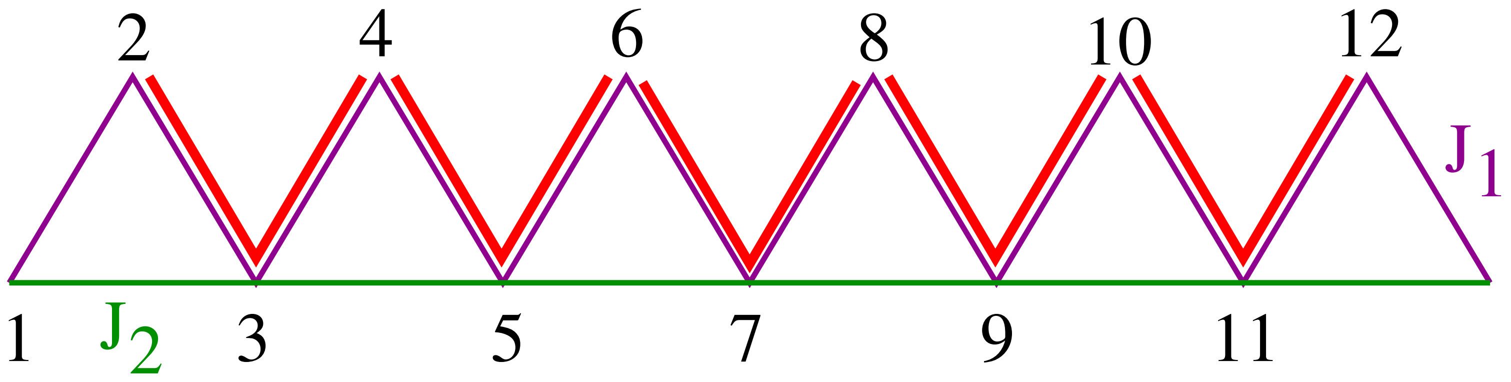


$\Rightarrow$ $|$ 2 localized magnons $\rangle$; $E = E_F, M = S_{\text{max}} - 2$

$\Rightarrow$ Can be everywhere. Flat band in two-magnon space. Degenerate with $|\, F \,\rangle$.

(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)

Excursus: sawtooth (delta) chain



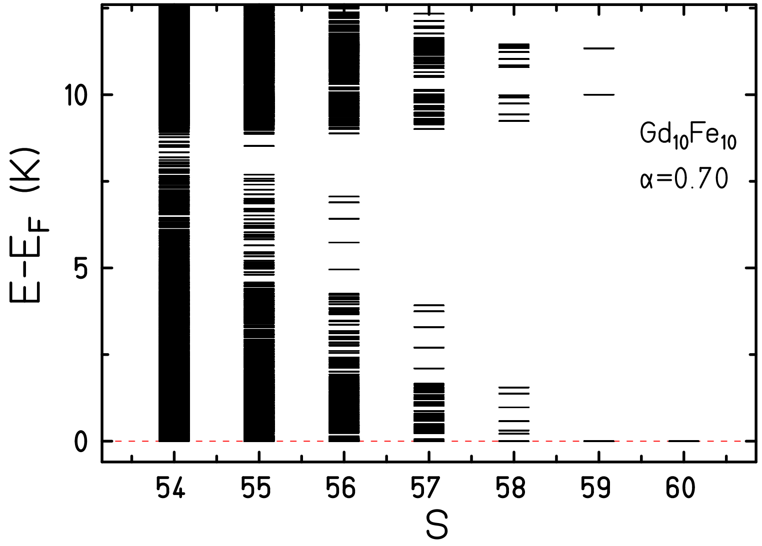
$\Rightarrow$ $|$ max. number of localized magnons $\rangle$; $E = E_F, M = S_{\text{max}} - N/2$

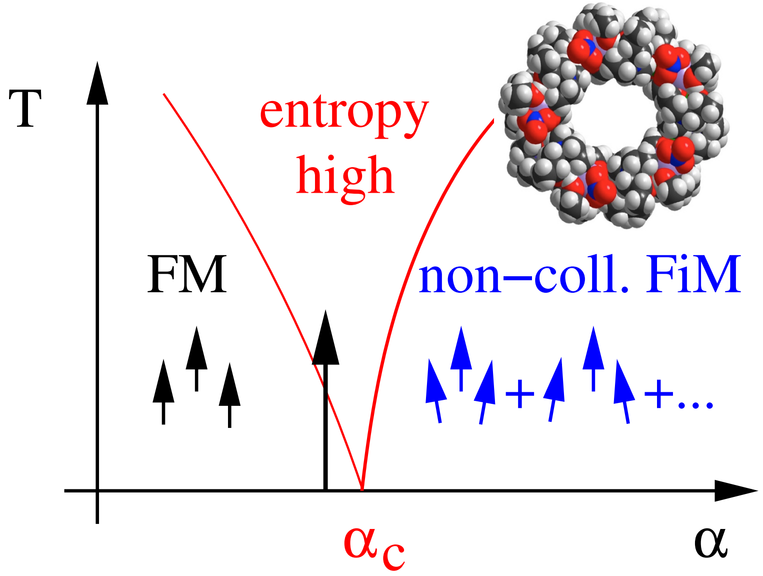
$\Rightarrow$ Macroscopic number of localized magnons. Degenerate with $|\, F \,\rangle$.

$\Rightarrow$ Extensive entropy.

(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)

$Gd_{10}Fe_{10}$ – QCP





⇒ for $s_1 = 5/2$ and $s_2 = 7/2$: $\alpha_\mathrm{c} = 0.70$

⇒ as function of α Quantum Phase Transition at α_c

from $S = 60$ ground state to ground state with $S = 54$.

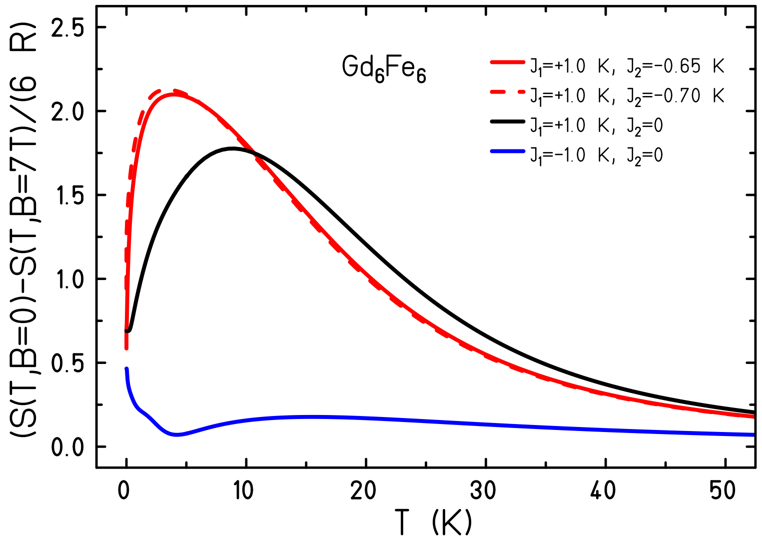
($\Delta S = N/4 + 1$ in general)

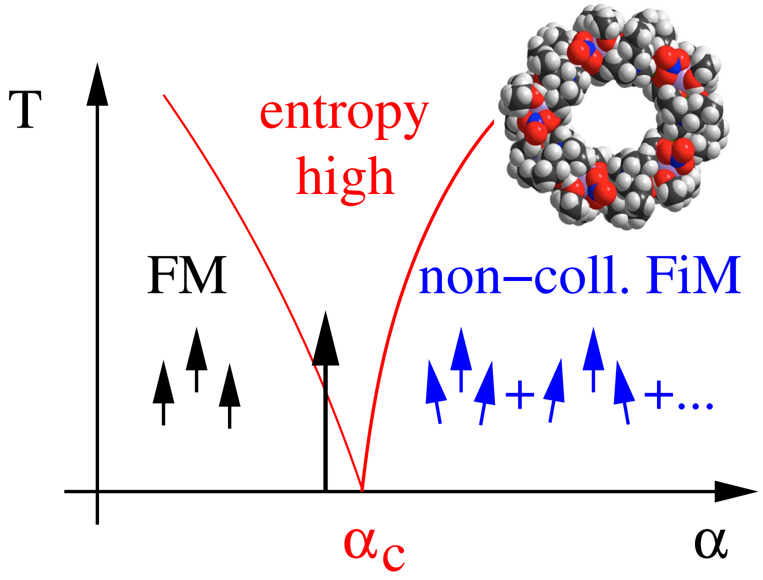
A. Baniodeh *et al.*, *npj Quantum Materials* ***3****, 10 (2018)*

Quantum Phase Transition

Non-analytic behavior of thermodynamic functions at $T = 0$ for variation of another external parameter, e.g. field, pressure; here α – maybe varied by pressure.

$\mathbf{Gd_{10}Fe_{10}}$ – $T > 0$





⇒ although QPT and QCP at $T = 0$,

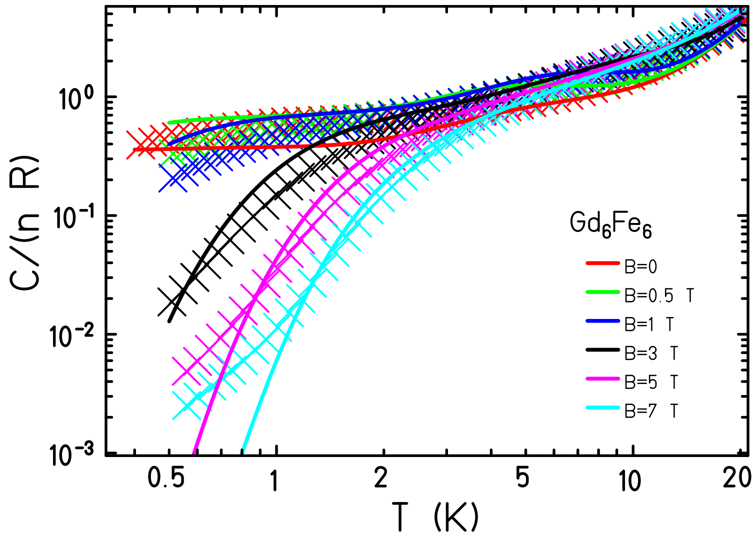
noticeable at elevated temperatures (arrow);

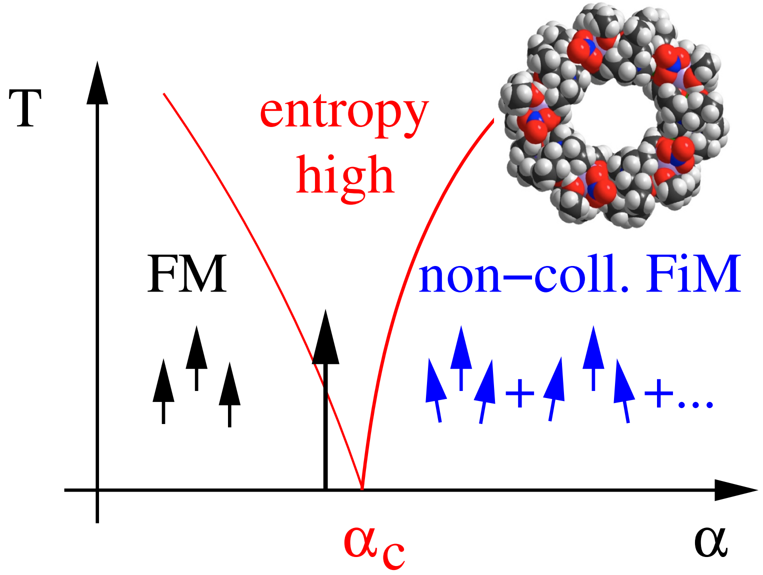
⇒ example isothermal entropy change:

little difference between $\alpha = 0.70$ and $\alpha = 0.65$.

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

$Gd_{10}Fe_{10}$ – heat capacity





⇒ heat capacity assumes very large values even down to lowest temperatures;

⇒ evaluated by means of FTLM for a smaller (hypothetical) system Gd_6Fe_6;

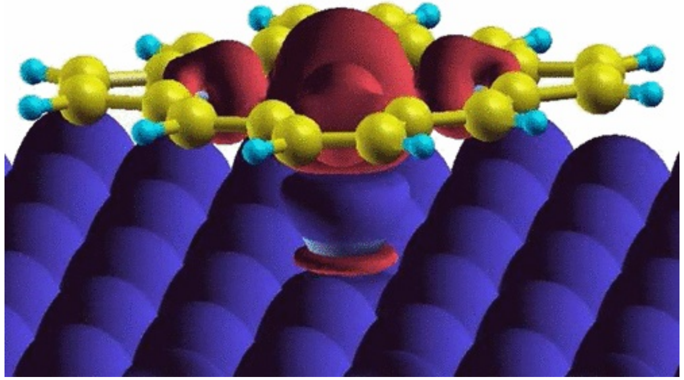
⇒ magnetic field separates $S = 60$ ground state, C drops.

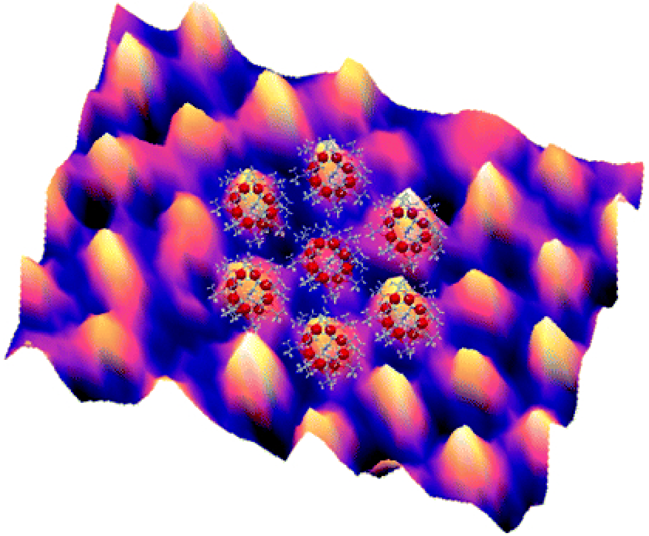
A. Baniodeh *et al., npj Quantum Materials* ***3****, 10 (2018)*

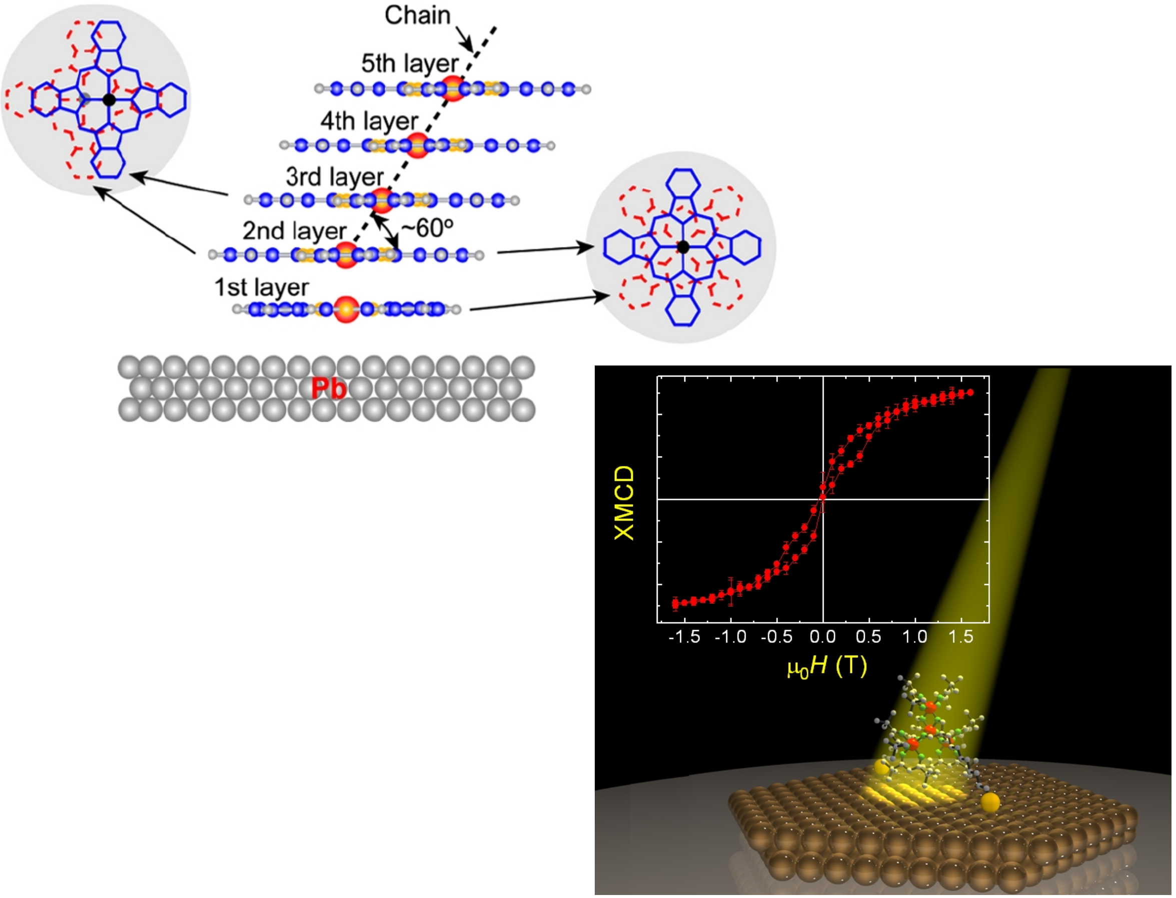
Numerical Renormalization Group calculations

(Good for deposited molecules.)

You want to deposite a molecule

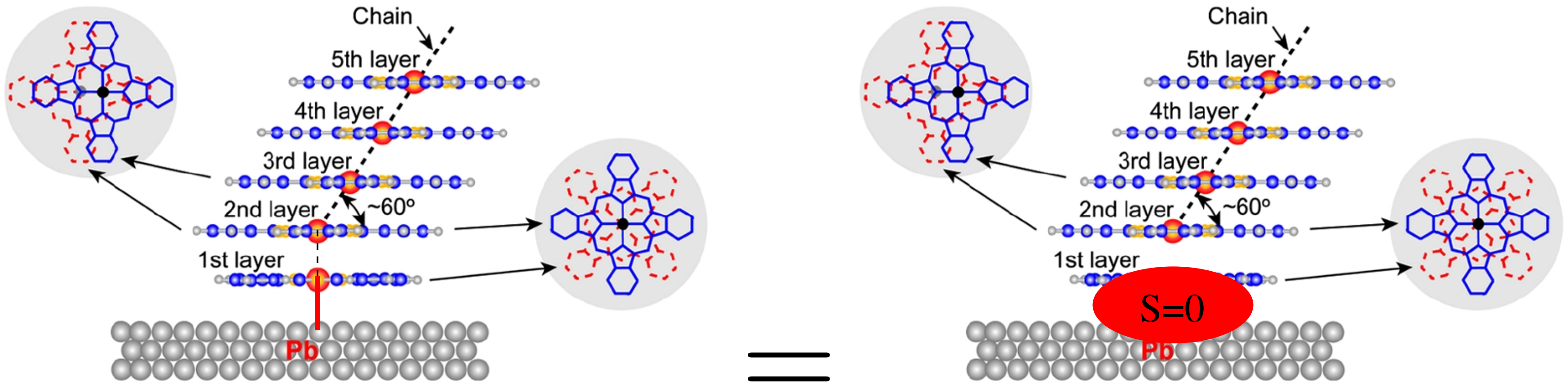






M. Bernien *et al.*, Phys. Rev. Lett. **102**, 047202 (2009); A. Ghirri*et al.*, ACS Nano, **5**, 7090-7099 (2011); X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008); M. Mannini *et al.*, Nature Materials **8**, 194 - 197 (2009).

Physical example (ICMM 2010)

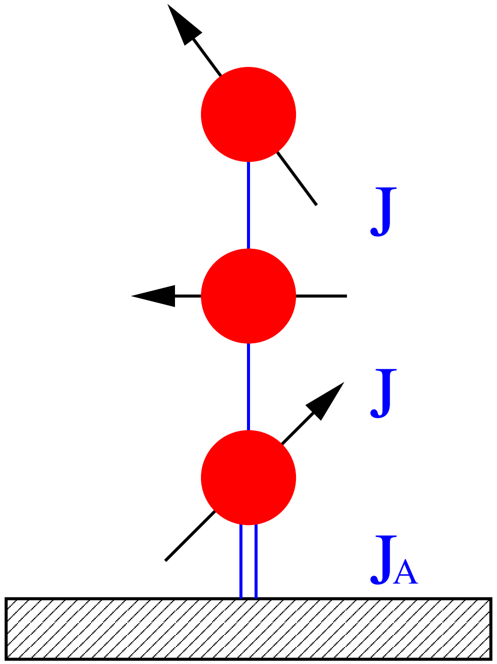


Stack of deposited Cobalt phthalocyanine (CoPc) molecules;
Co^{2+} with spin $s = 1/2$.

Under which circumstances is the picture of total screening correct?

X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

NRG – minimal model (already an approximation!)



- $\underset{\sim}{H} = \underset{\sim}{H}_{\text{electrons}} + \underset{\sim}{H}_{\text{coupling}} + \underset{\sim}{H}_{\text{impurity}}$

  $\underset{\sim}{H}_{\text{electrons}} = \sum_{i\neq j,\,\sigma} t_{ij} \underset{\sim}{d}^{\dagger}_{i\sigma} \underset{\sim}{d}_{j\sigma} + g_e \mu_B B \underset{\sim}{S}^z$

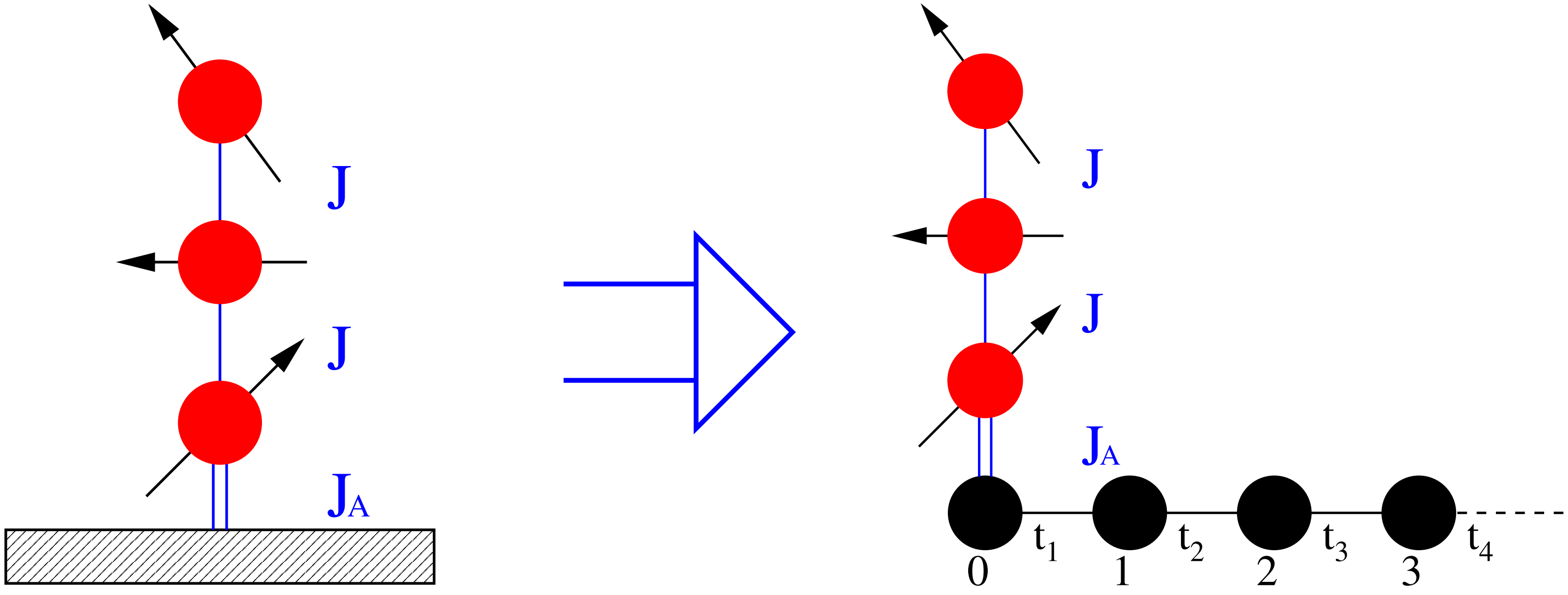
  $\underset{\sim}{H}_{\text{coupling}} = -2 J_A \underset{\sim}{\boldsymbol{S}} \cdot \underset{\sim}{\boldsymbol{s}}_0$, $\underset{\sim}{\boldsymbol{s}}_0$ – spin density at contact

- $\underset{\sim}{H}_{\text{impurity}} =$ Hamiltonian of your molecule!

- NRG $\equiv$ construction of a small (!) effective model in order to evaluate properties of the deposited cluster, the impurity (3).

(1) K. G. Wilson, Rev. Mod. Phys. **47**, 773 (1975)
(2) M. Höck, J. Schnack, Phys. Rev. B **87**, 184408 (2013)
(3) *Impurity* is a technical term in this context and not an insult to chemists.

NRG in a cartoon



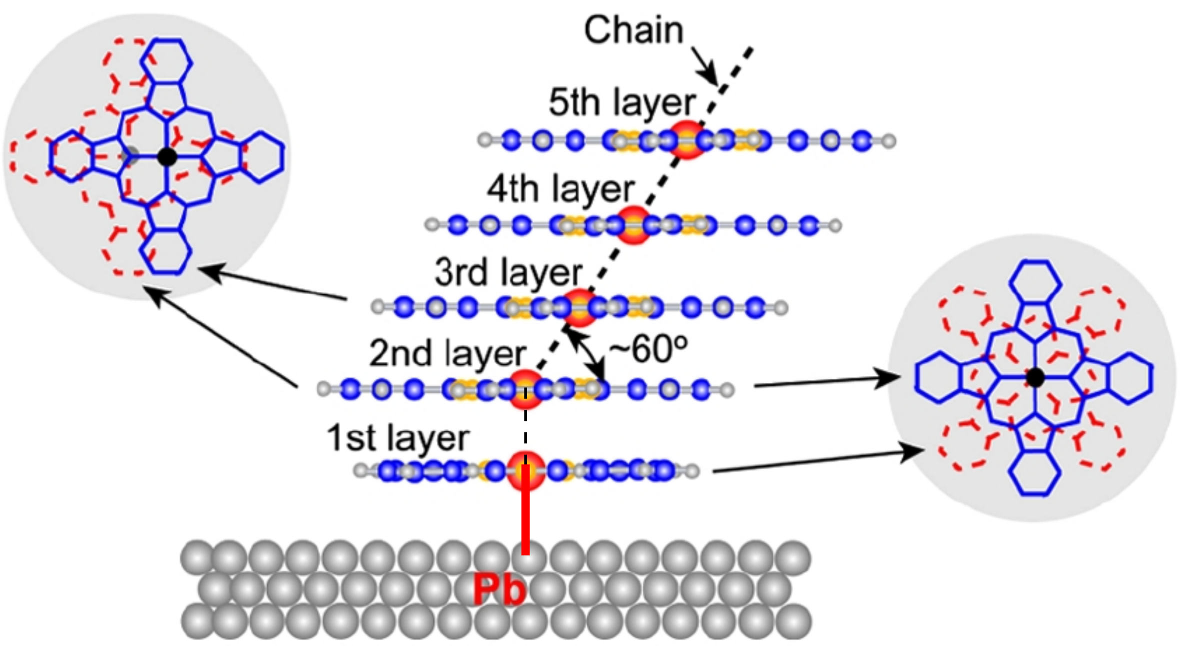
Metallic surface is replaced by semi-infinite Hubbard chain;

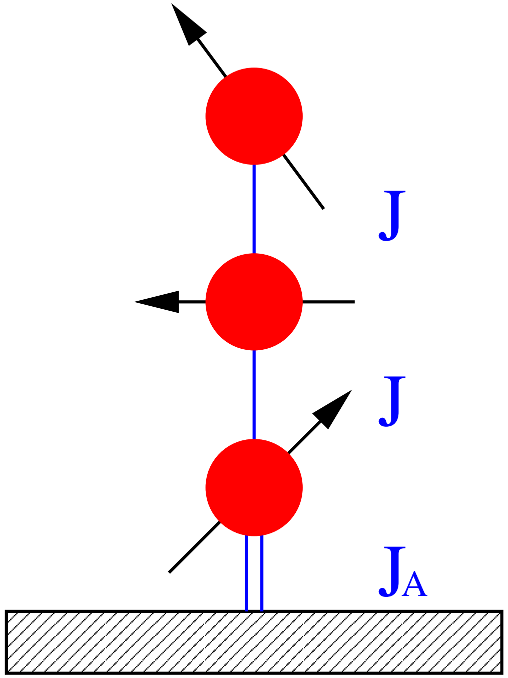
Parameters of the chain: hopping matrix elements and on-site energies;

Stepwise enlargement of the chain $(t_1 > t_2 > t_3 \dots)$;

Truncation of basis set when matrices grow too big.

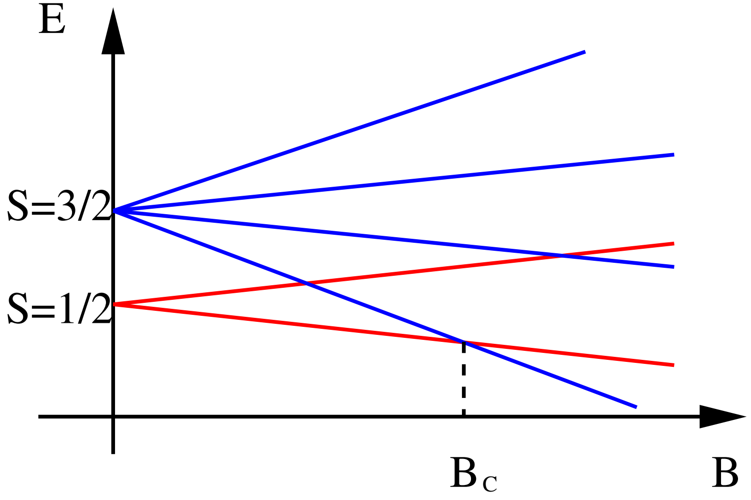
Once more: deposited chain



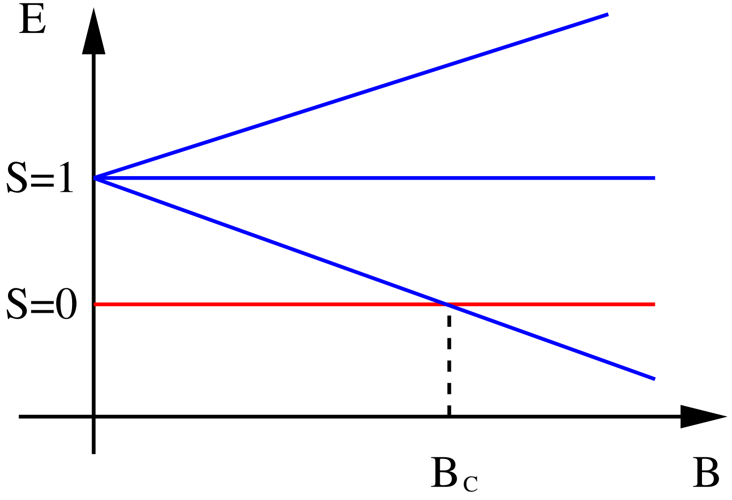


X. Chen *et al.*, Phys. Rev. Lett. **101**, 197208 (2008).

Energy levels of limiting cases for deposited trimer



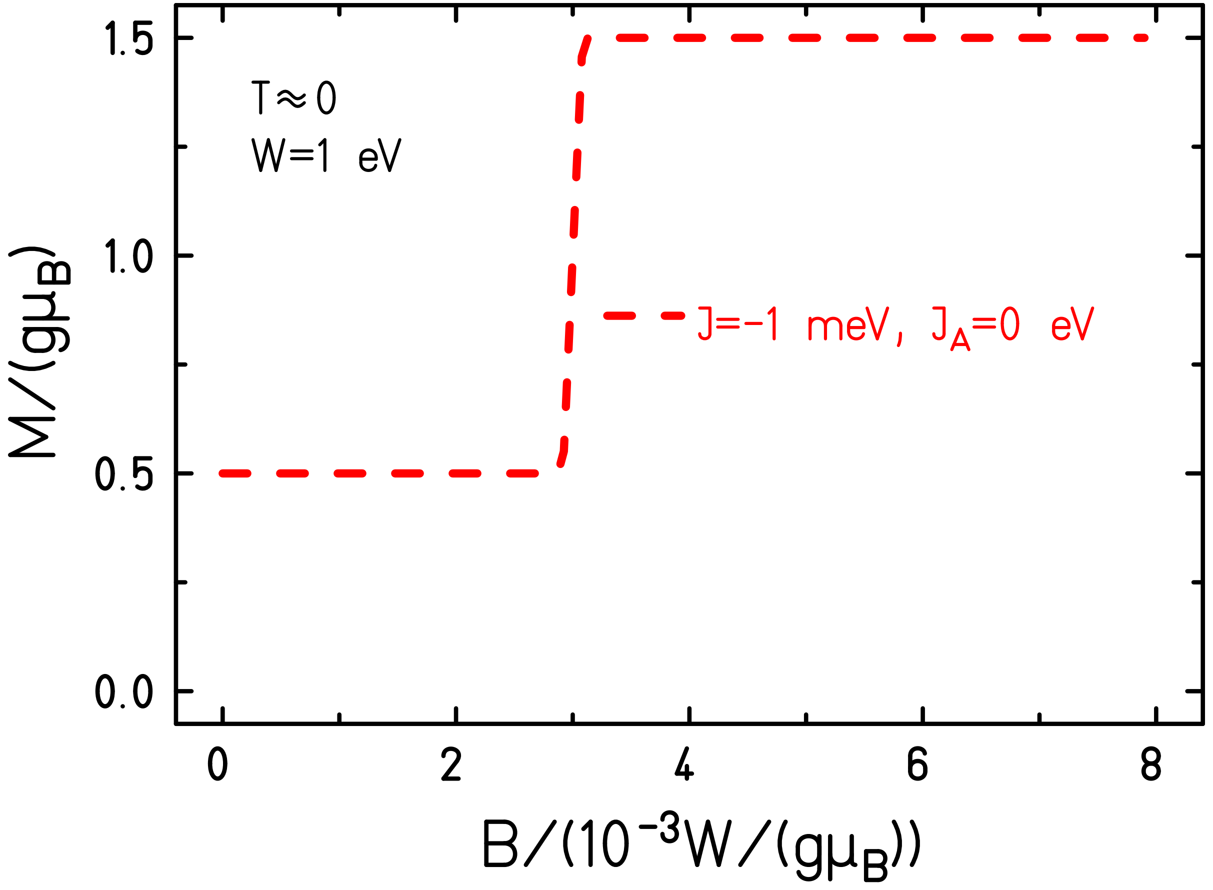
- energy levels of a trimer

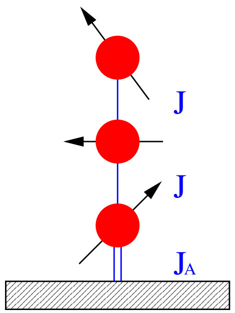


- energy levels of a dimer

Magnetization curves different; could be seen in XMCD.
NRG calculates observables also between limiting cases
and can thus tell under which circumstances a limiting case applies.

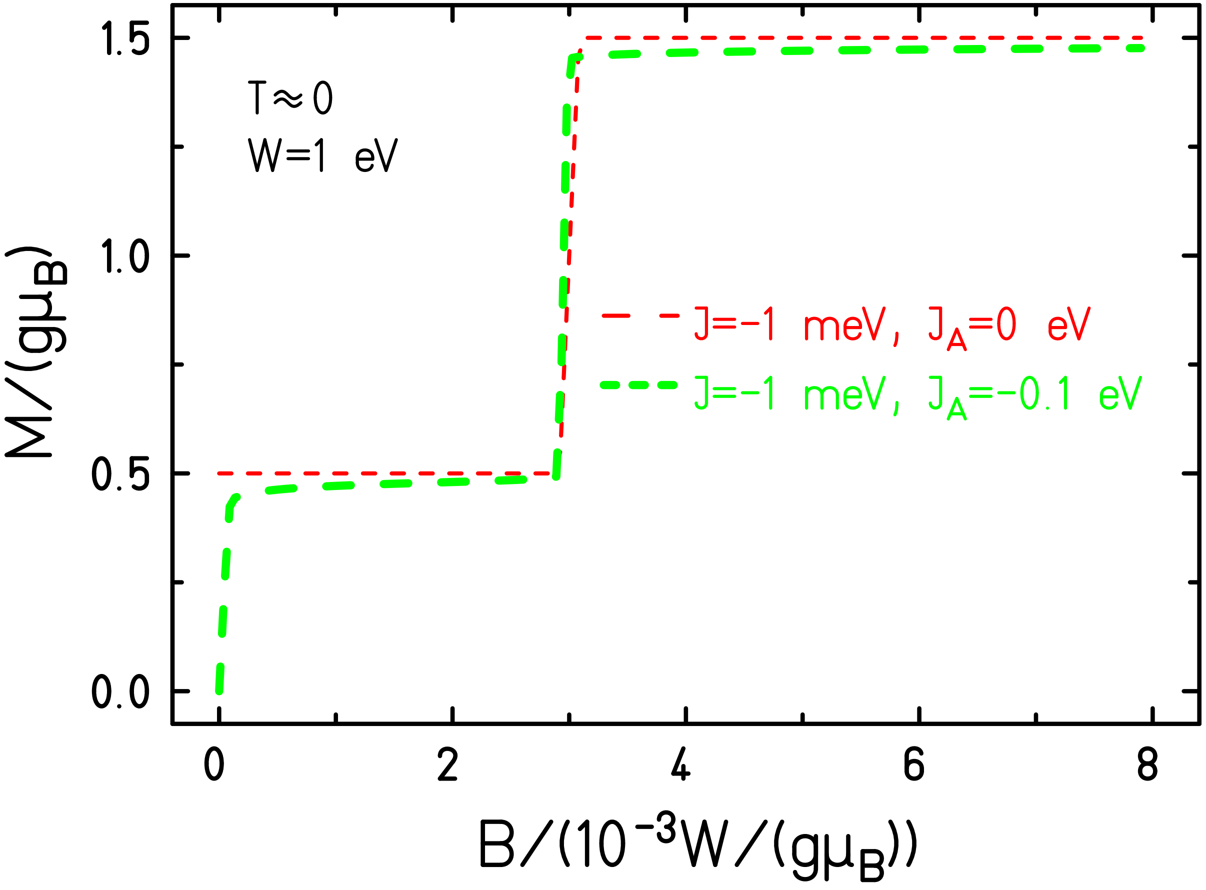
Increasing coupling to the substrate

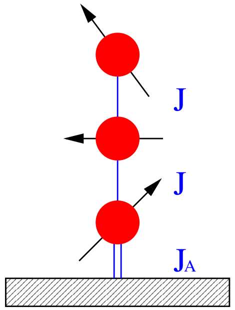




H.-T. Langwald, J. Schnack, Eur. Phys. J. B **92**, 56 (2019)

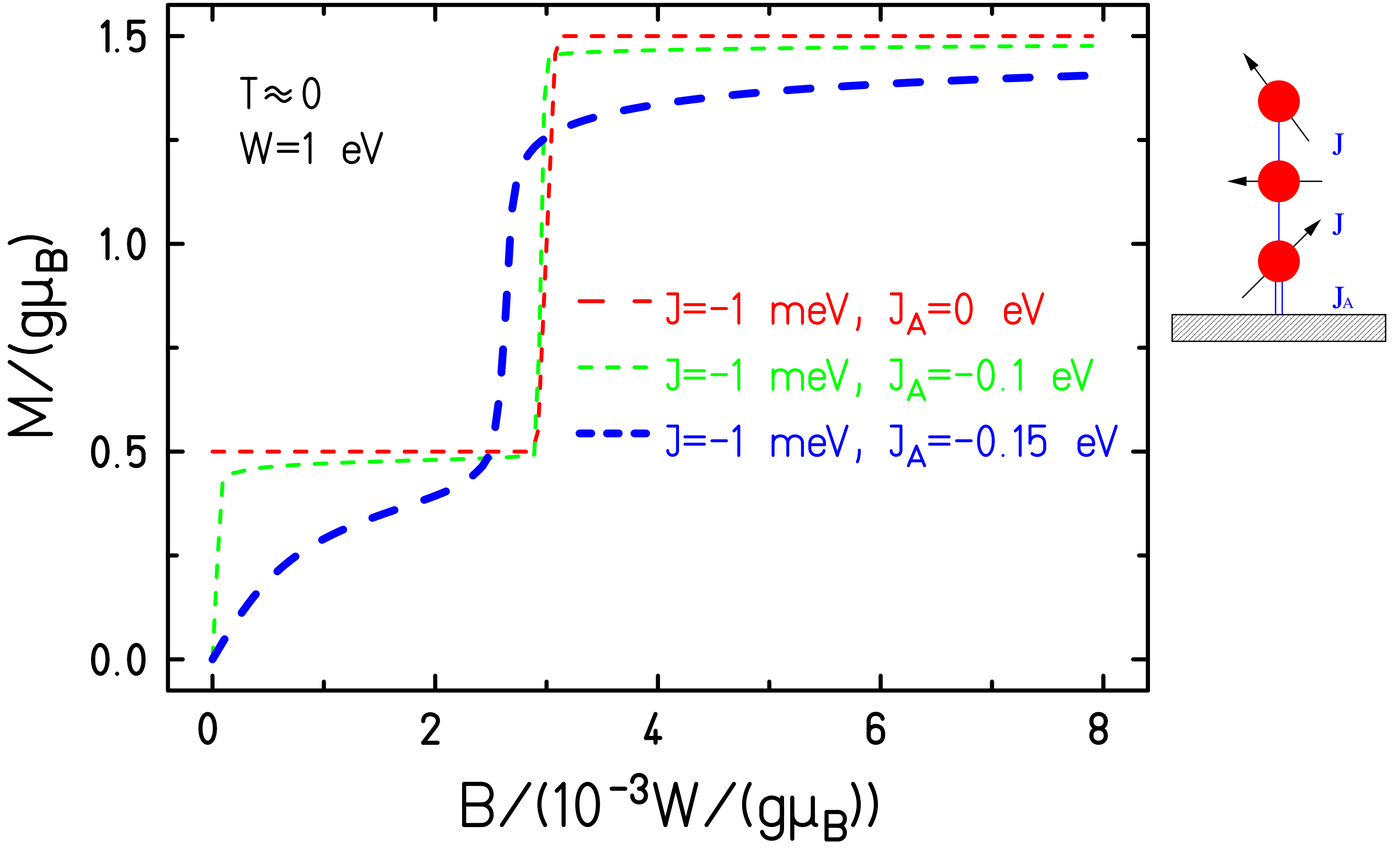
Increasing coupling to the substrate





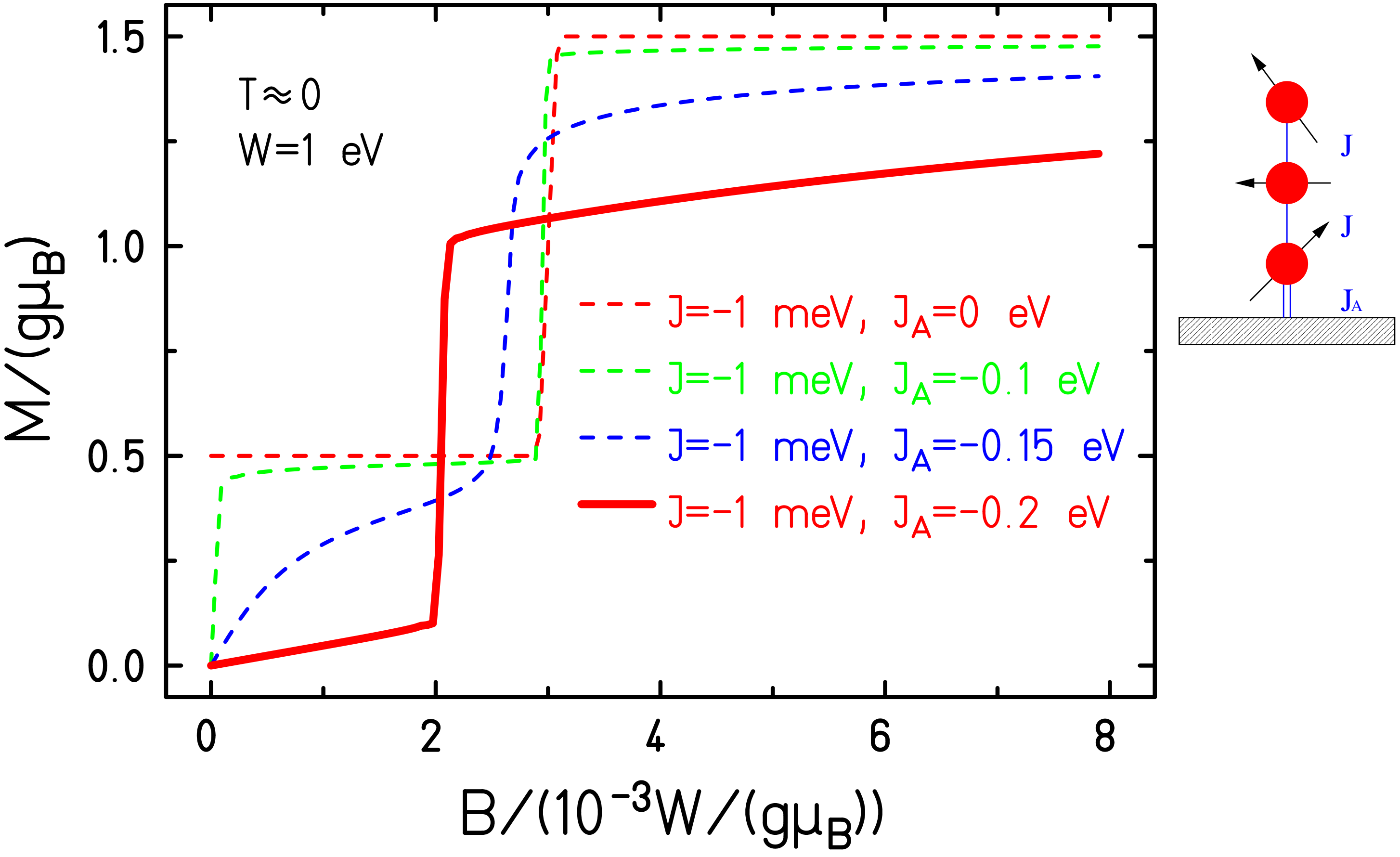
H.-T. Langwald, J. Schnack, Eur. Phys. J. B **92**, 56 (2019)

Increasing coupling to the substrate



H.-T. Langwald, J. Schnack, Eur. Phys. J. B **92**, 56 (2019)

Increasing coupling to the substrate



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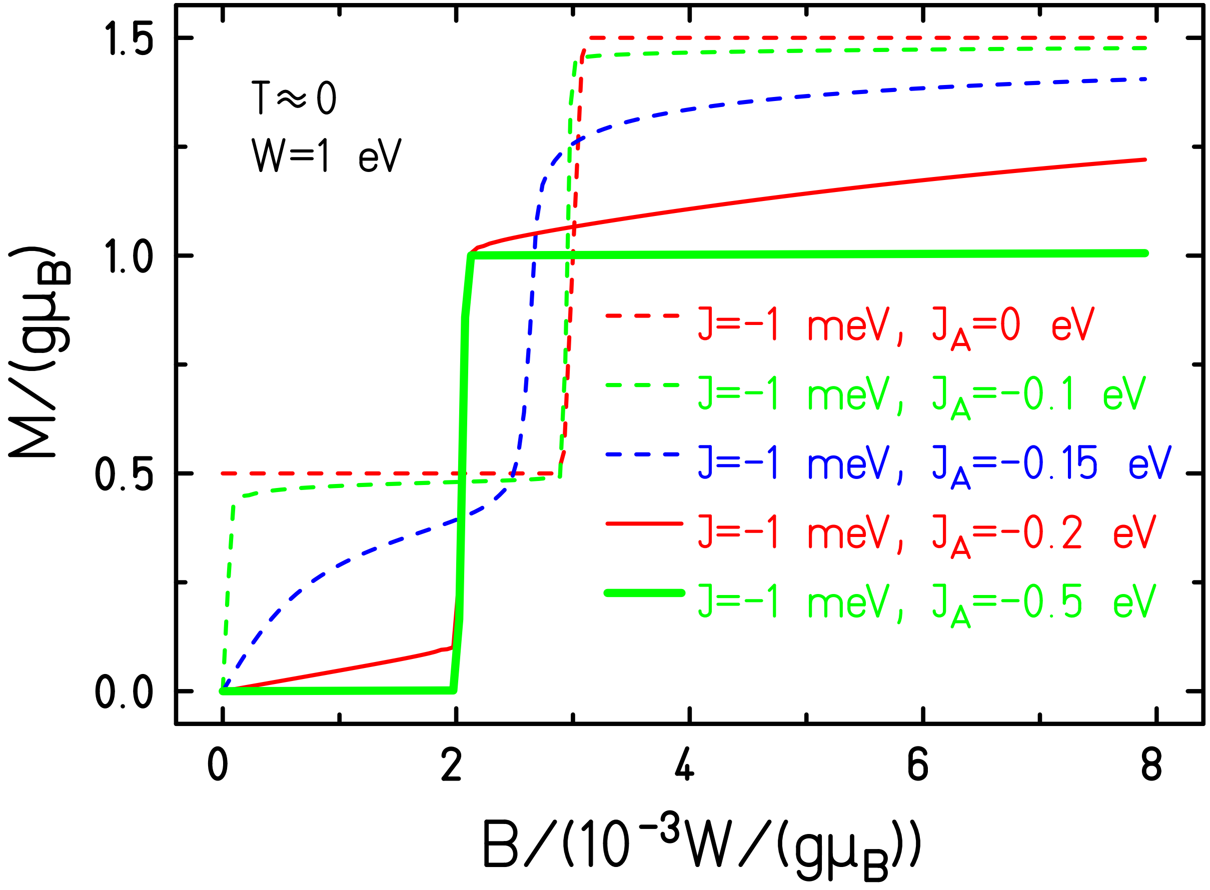
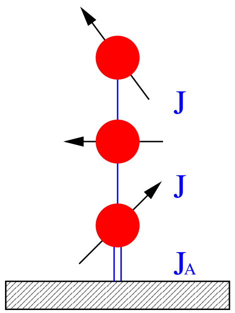
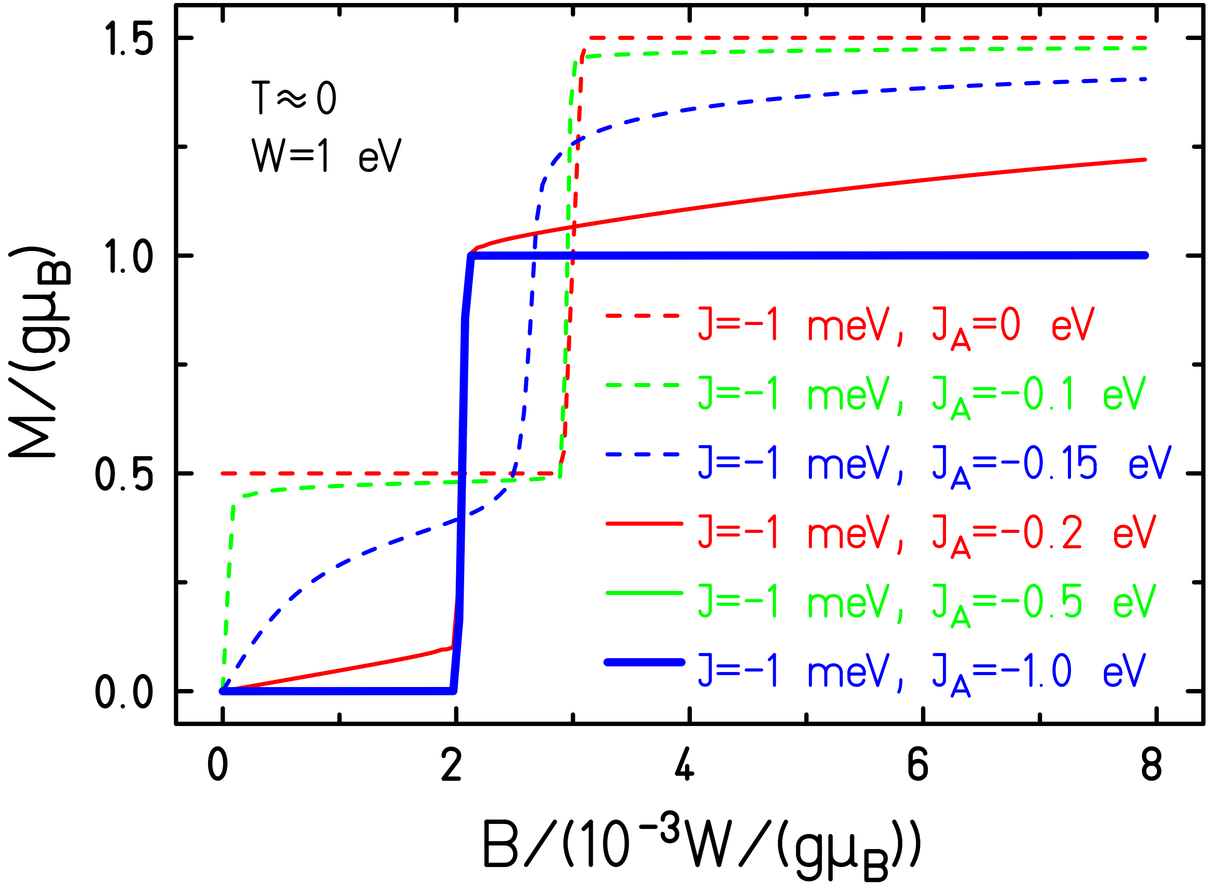
Increasing coupling to the substrate

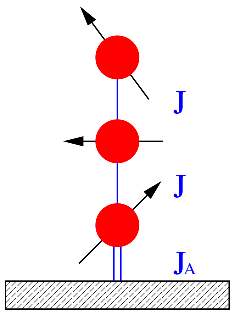




H.-T. Langwald, J. Schnack, Eur. Phys. J. B **92**, 56 (2019)

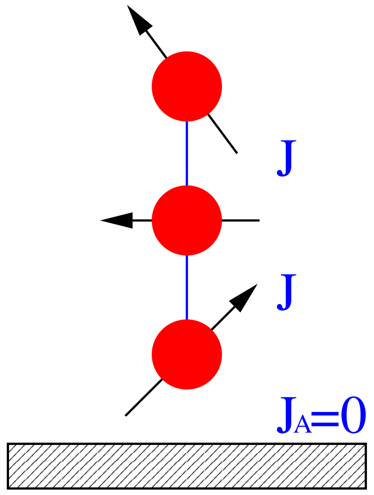
Increasing coupling to the substrate

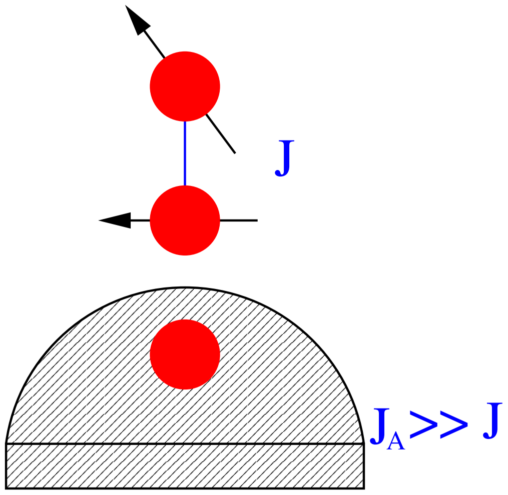




H.-T. Langwald, J. Schnack, Eur. Phys. J. B **92**, 56 (2019)

Weak vs. strong coupling





- weak coupling limit:
  unperturbed molecule (trimer)
- strong coupling limit:
  effective remainder (dimer)

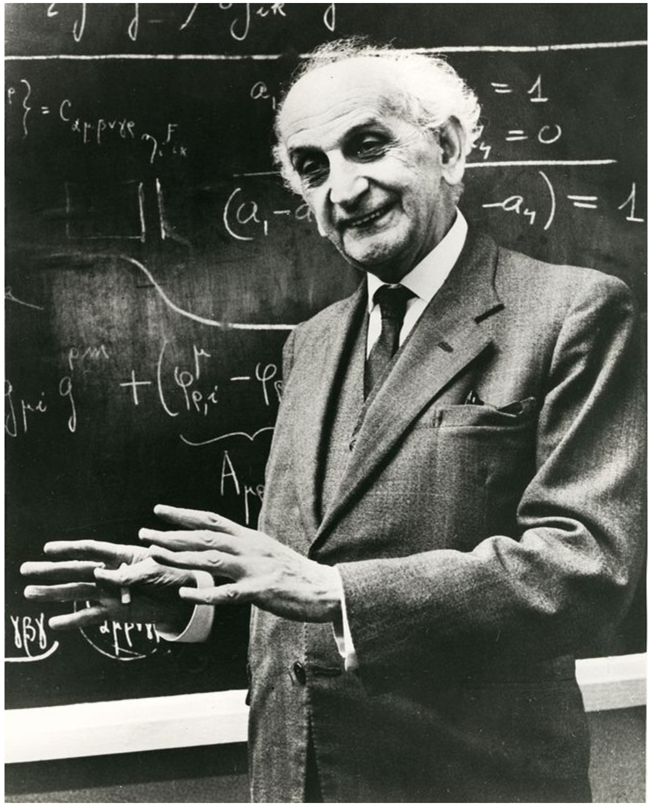
- $|J_A| \lessapprox 0.1W$
- $|J_A| \gtrapprox 0.5W$

Inbetween: no simple characterization $+$ further sequential screening possible

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: $\{\,|\,\phi\,\rangle, \underset{\sim}{H}\,|\,\phi\,\rangle, \underset{\sim}{H}^2\,|\,\phi\,\rangle, \underset{\sim}{H}^3\,|\,\phi\,\rangle, \dots\,\}$
- 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

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

$$\langle\,\nu\,|\,\exp\left\{-\beta \underset{\sim}{H}\right\}\,|\,\nu\,\rangle \approx \sum_n \langle\,\nu\,|\,n(\nu)\,\rangle \exp\left\{-\beta\epsilon_n\right\} \langle\,n(\nu)\,|\,\nu\,\rangle \qquad \text{(Step 2)}$$

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

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

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

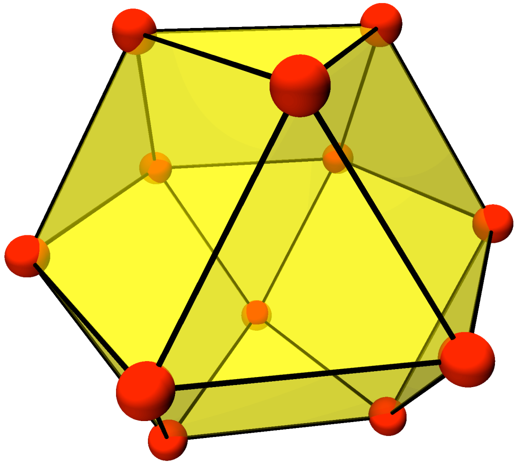
Finite-temperature Lanczos Method II

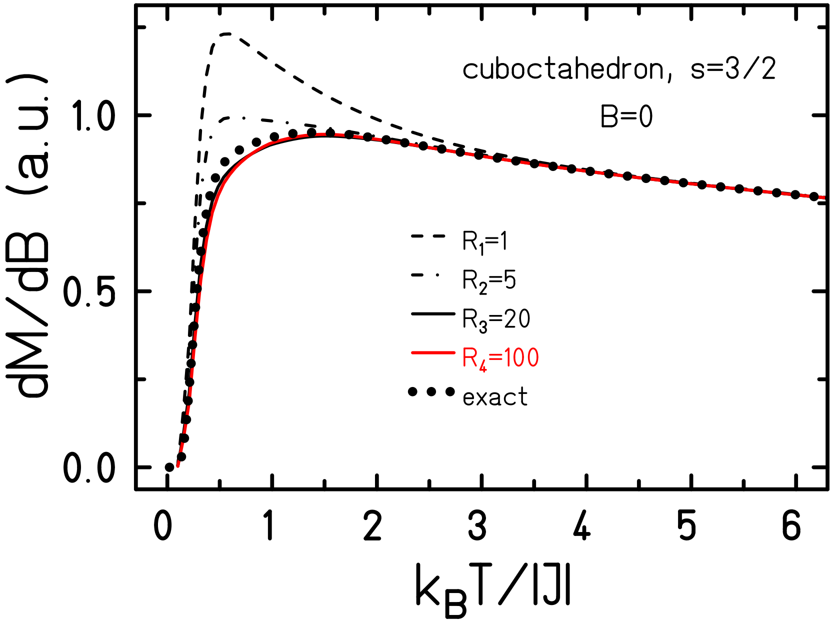
$$Z(T,B) \approx \sum_{\Gamma} \frac{\text{dim}(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} \exp\left\{-\beta\epsilon_n\right\} |\langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma\,\rangle|^2$$

- Approximation better if symmetries taken into account.
- Γ denotes the used irreducible representations;
  often this is just the $\underset{\sim}{S}^z$ symmetry, i.e. $\Gamma \equiv M$

J. Schnack and O. Wendland, Eur. Phys. J. B **78** (2010) 535-541

How good is finite-temperature Lanczos?

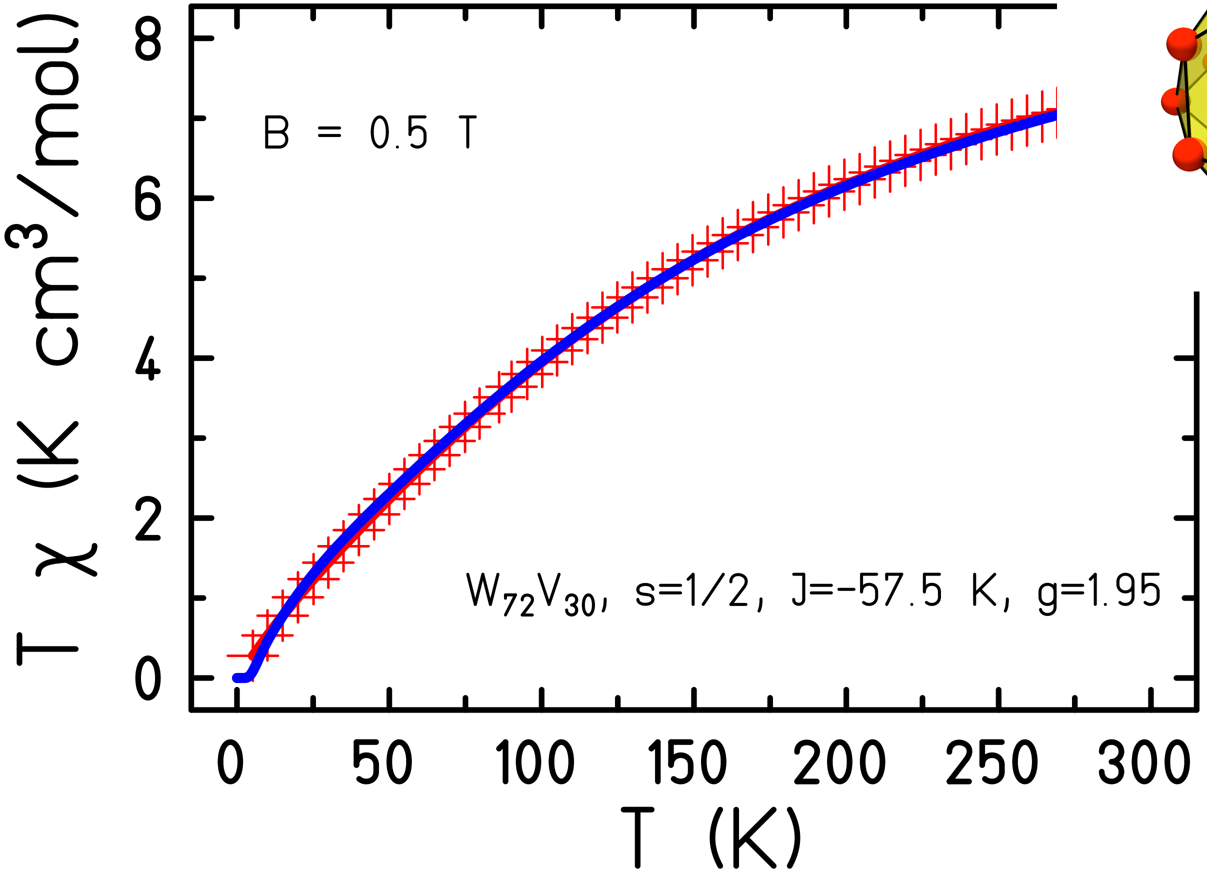


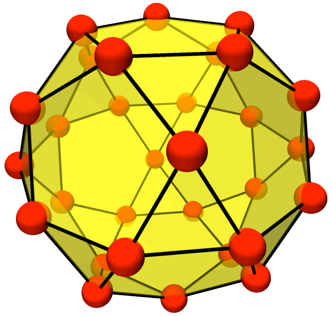


- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

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).

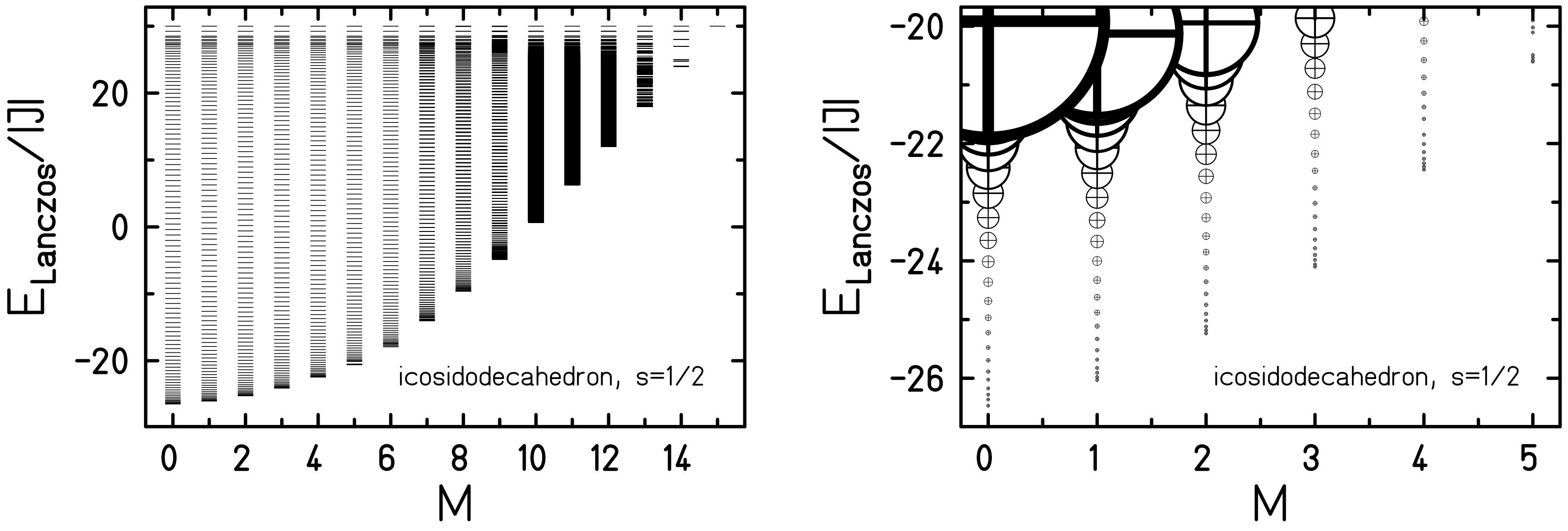
Icosidodecahedron $s = 1/2$





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.

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

Finite-temperature Lanczos Method III

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

- Problem: for anisotropic Hamiltonians no symmetry left
  → accuracy drops (esp. for high T).

- Simple traces such as Tr $\left(\underset{\sim}{S}^z\right) = 0$ 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)

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

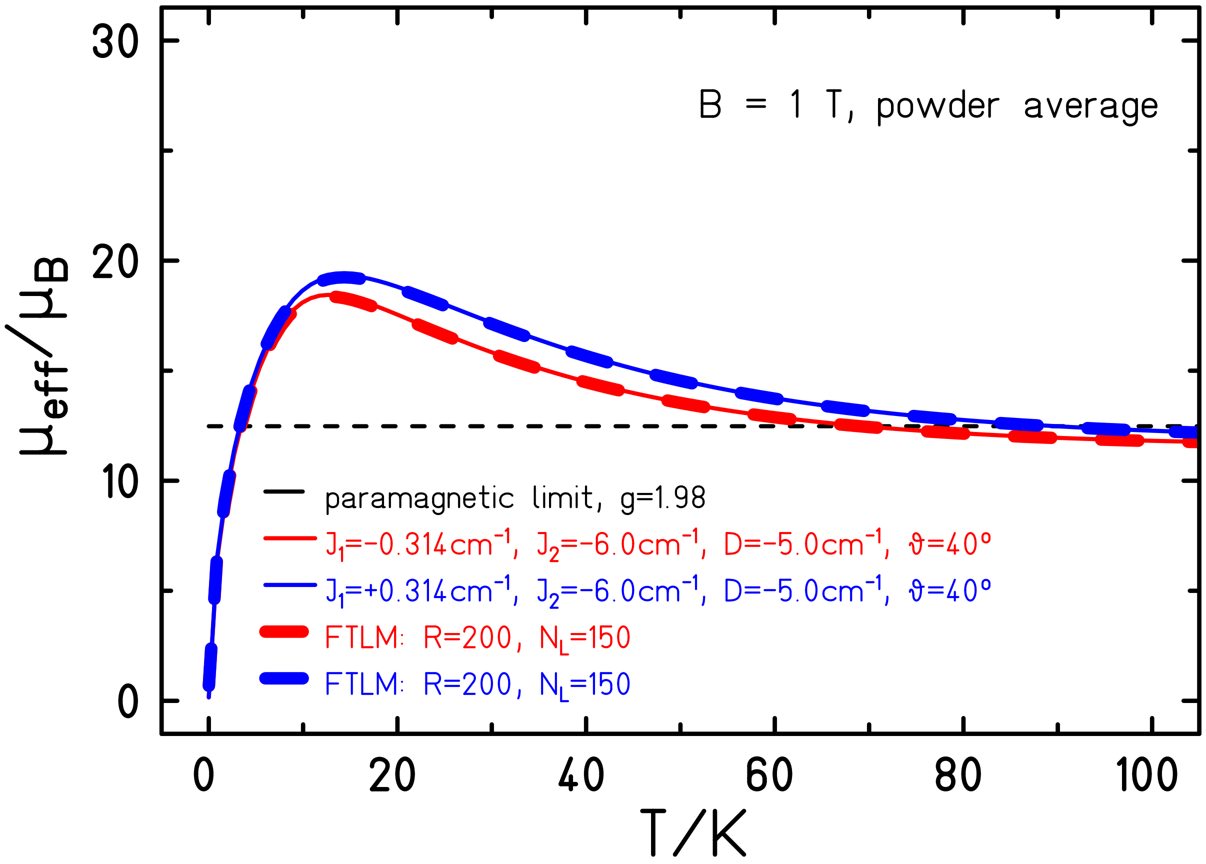
Use Lanczos energy eigenvector $\mid n(\nu)\,\rangle$ and time-reversed counterpart $\mid \tilde{n}(\nu)\,\rangle$

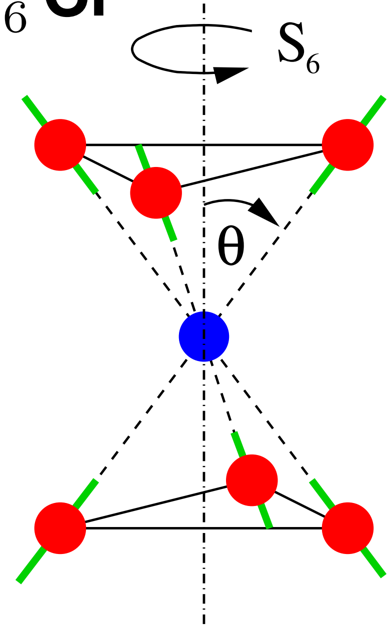
$$\mid n(\nu)\,\rangle = \sum_{\vec{m}} c_{\vec{m}} \mid \vec{m}\,\rangle \qquad , \qquad \mid \tilde{n}(\nu)\,\rangle = \sum_{\vec{m}} c^{*}_{\vec{m}} \mid -\vec{m}\,\rangle$$

- 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: Mn$_6^{III}$Cr^{III}





$s = 2$, $s = 3/2$

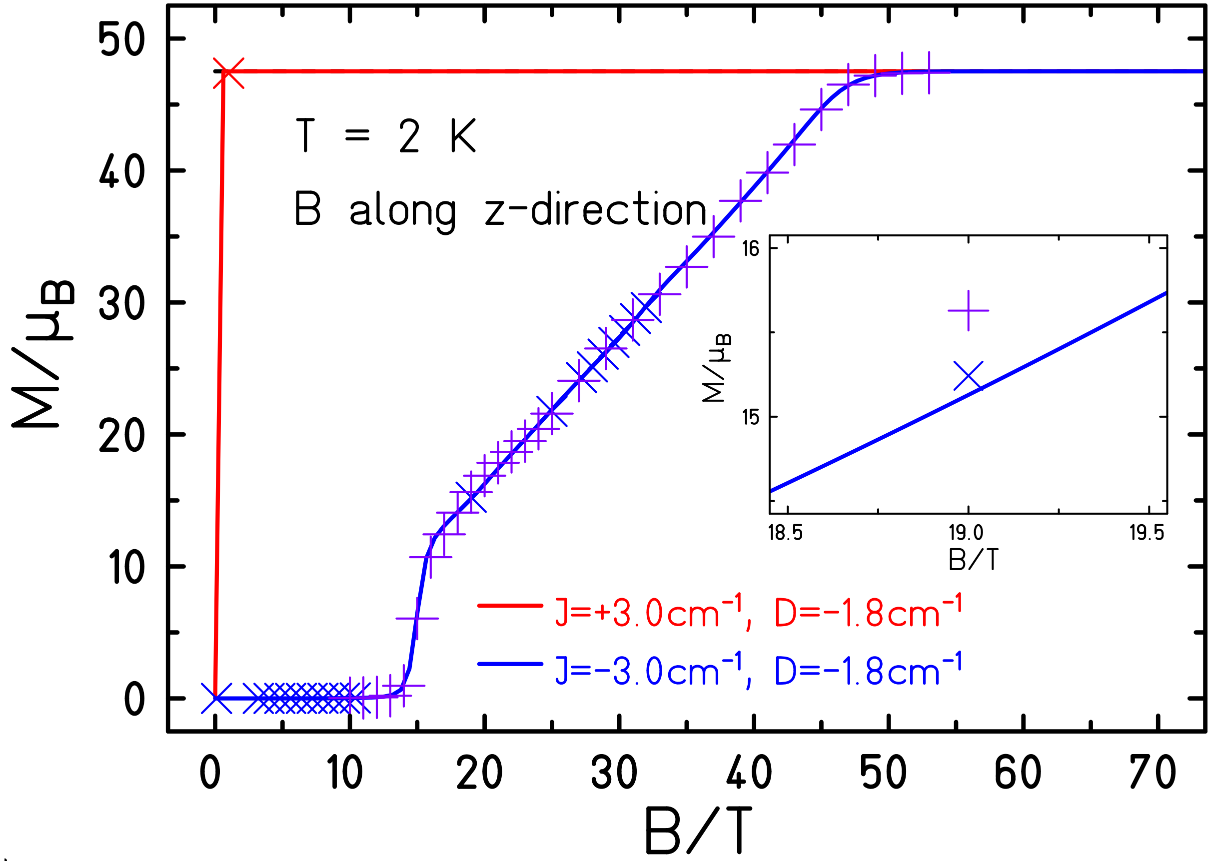
dim$(\mathcal{H}) = 62,500$

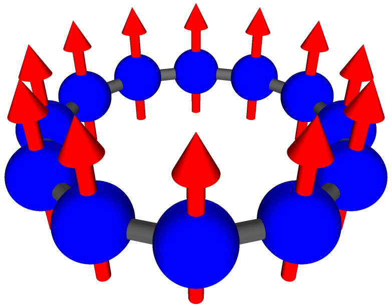
non-collinear easy axes

Hours compared to days, notebook compared to supercomputer!

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

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





$s = 2$

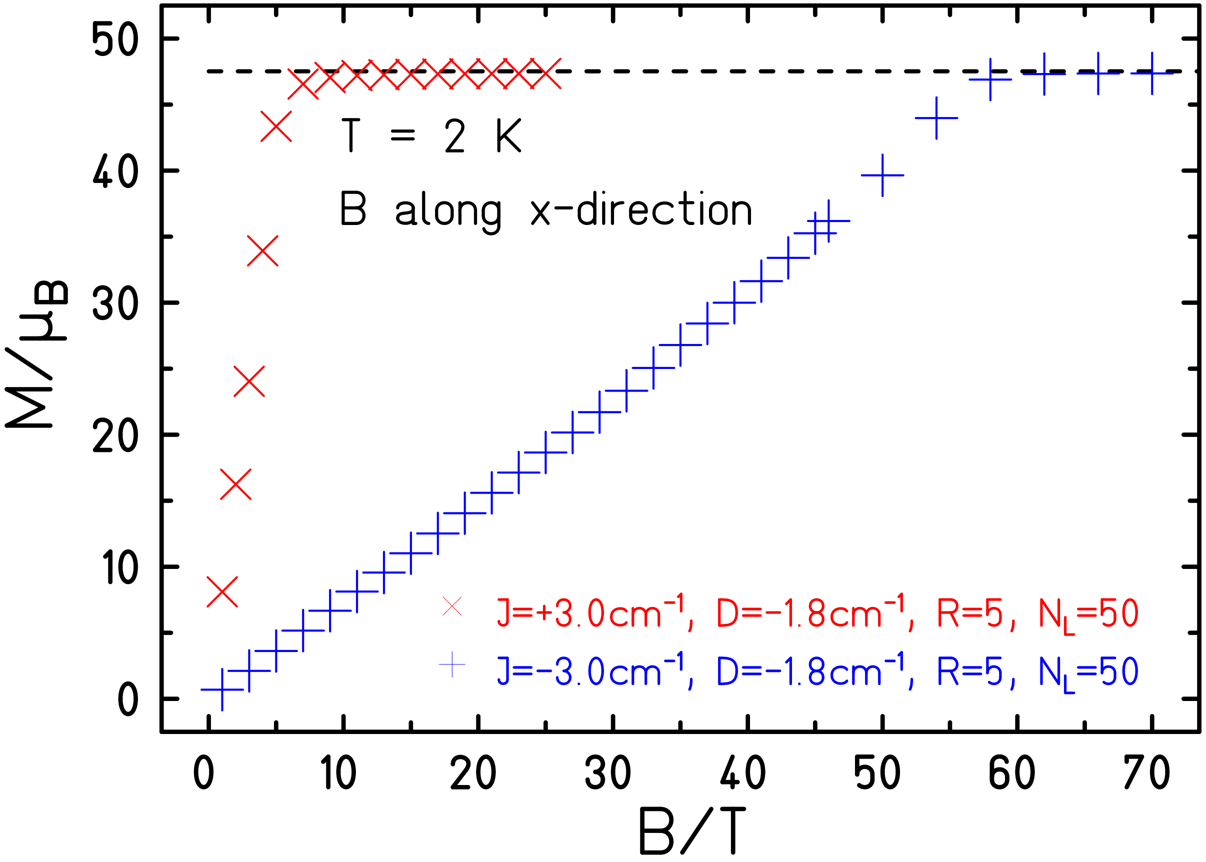
$\dim(\mathcal{H}) = 244,140,625$

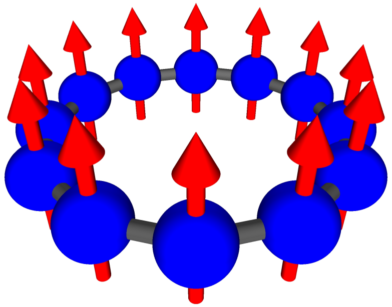
collinear easy axes

A few days compared to *impossible*!

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

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

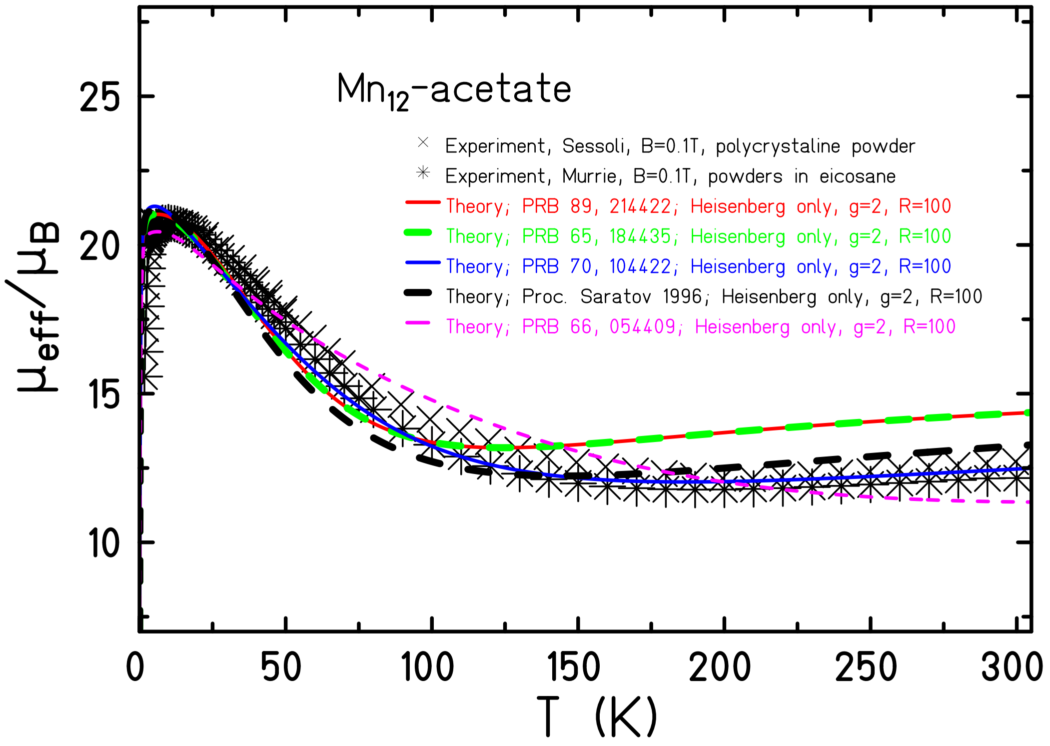




No other method can deliver these curves!

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

Effective magnetic moment of Mn_{12}-acetate

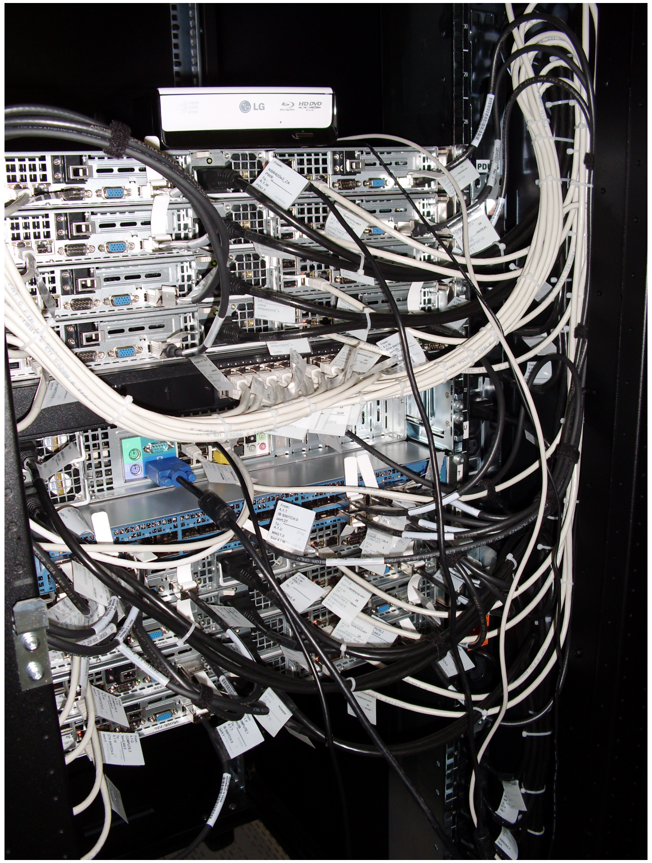


We can check DFT parameter predictions for large molecules! Normally! ☹

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).

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 $(T = 0, B = 0)$.
- Screening can lead to interesting limiting cases, which might show different (worse/better) behavior compared to the free molecule.
- ED, HTE, CMC, QMC, FTLM, DMRG, DDMRG, thDMRG for magnetic molecules.

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Thank you very much for your attention.

The end.

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