

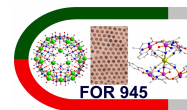
Magnetic molecules meet flat bands

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

Flatband Networks in Condensed Matter and Photonics
Center for Theoretical Physics of Complex Systems, Daejeon, South Korea



The Bielefeld conspiracy



The story goes that the city of **BIELEFELD** in the German state of North Rhine-Westphalia **DOES NOT** actually **EXIST**. Rather, its existence is merely propagated by an entity known only as **THEM**, which has conspired with the authorities to create the illusion of the city's existence.

The origins of and reasons for this conspiracy are not a part of the original theory. Speculated originators jokingly include the CIA, Mossad, or aliens who use Bielefeld University as a disguise for their spaceship.

Do you know anybody from Bielefeld?

https://en.wikipedia.org/wiki/Bielefeld_Conspiracy

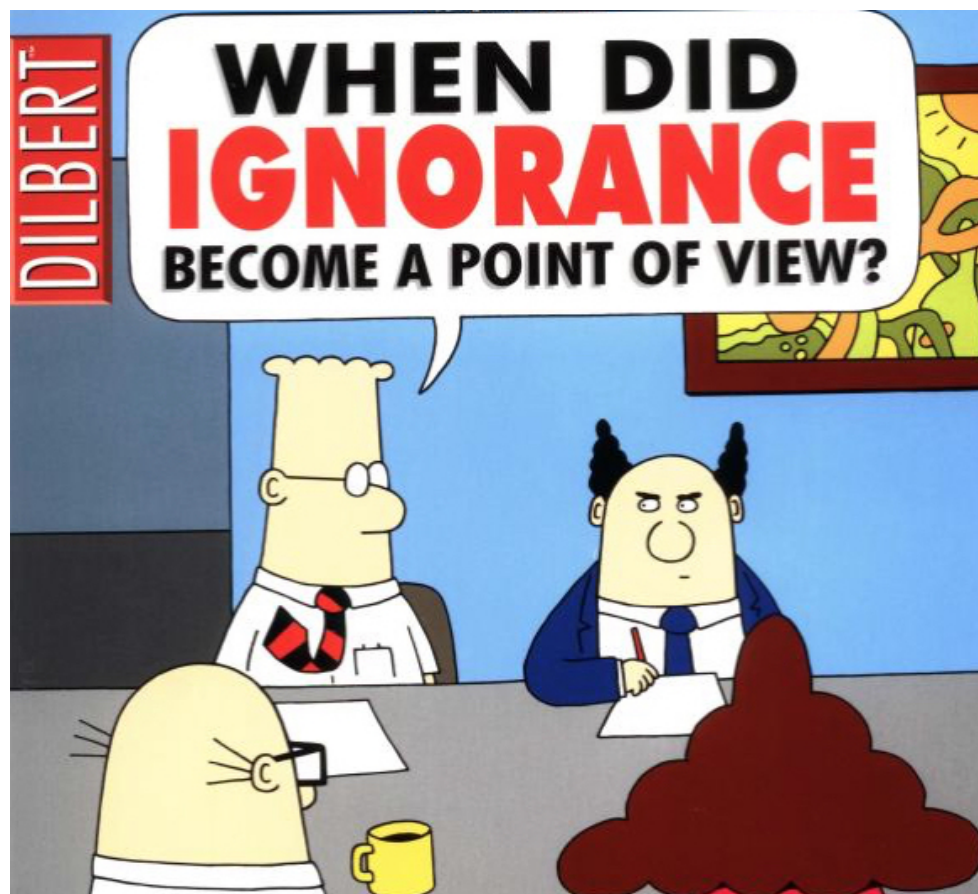
Flat Bands, How It All Began

– Andreas Mielke –

Flat Bands, How It All Began 2.0

– Jürgen Schnack –

Ignorance and bias sometimes lead to interesting (re-) discoveries



Contents for you today



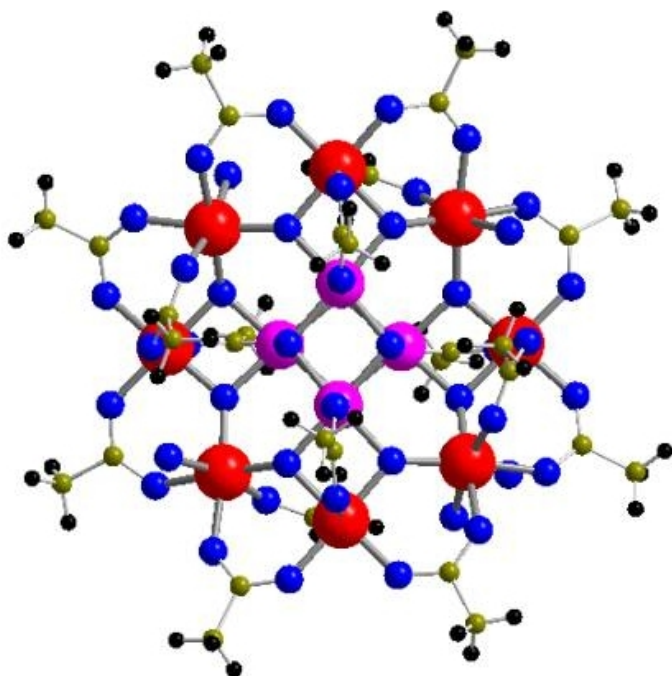
$$\begin{pmatrix} 3 & 42 & 4711 \\ 42 & 0 & 3.14 \\ 4711 & 3.14 & 8 \\ -17 & 007 & 13 \\ 1.8 & 15 & 081 \end{pmatrix}$$

1. Beauty of magnetic molecules
2. Rotational bands
3. The icosidodecahedron
4. Localized magnons
5. Flat bands
6. Magnetocalorics

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

Beauty of Magnetic Molecules

The beauty of magnetic molecules I

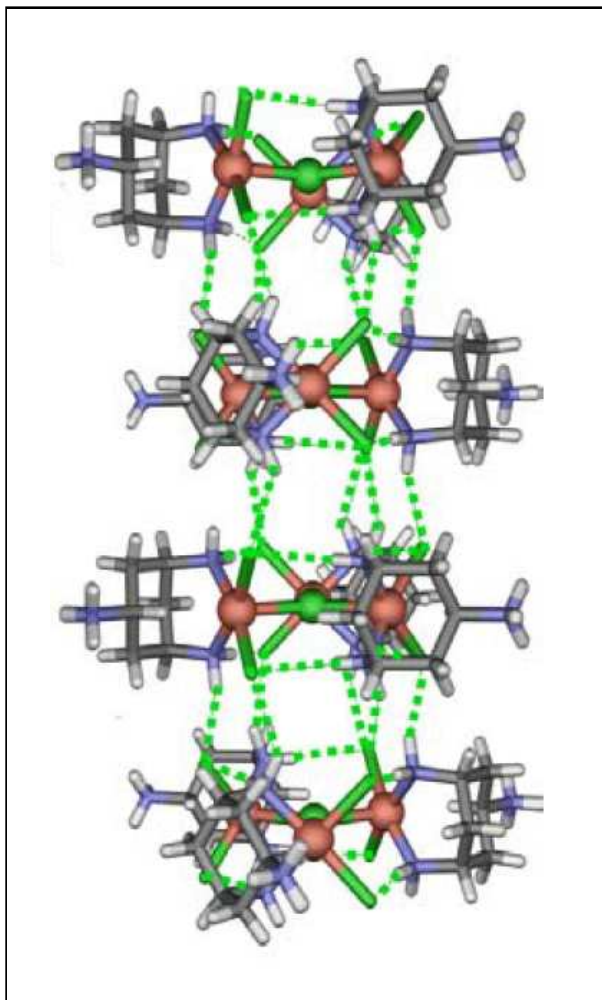


Mn₁₂

- 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

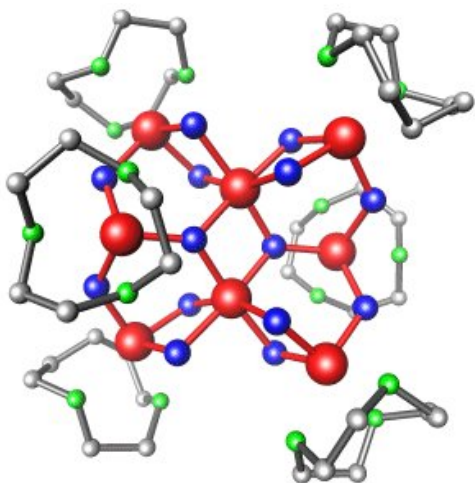
The beauty of magnetic molecules II



- 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:

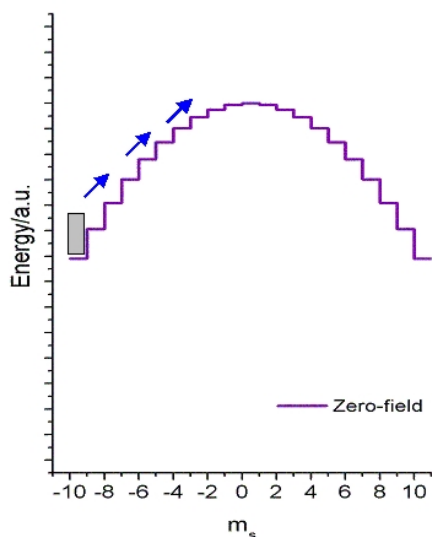
J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

The beauty of magnetic molecules III



- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;
- Example: $S = 10$ for Mn_{12} or Fe_8 ;
- Anisotropy dominates approximate single-spin Hamiltonian:

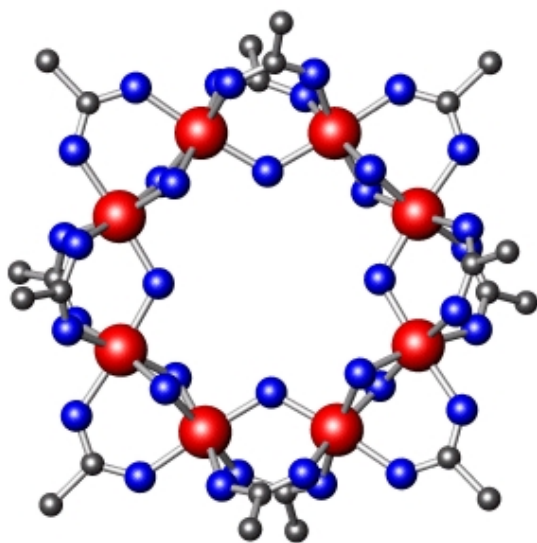
$$\tilde{H} = -D\tilde{S}_z^2 + \tilde{H}', \quad [\tilde{S}_z, \tilde{H}'] \neq 0$$



- Single molecule shows: metastable magnetization, hysteresis, ground state magnetization tunneling, thermally and phonon assisted tunneling.
- **Today's major efforts: improve stability of magnetization; investigate on surfaces.**

The beauty of magnetic molecules IV

Why magnetic molecules?



Cr₈

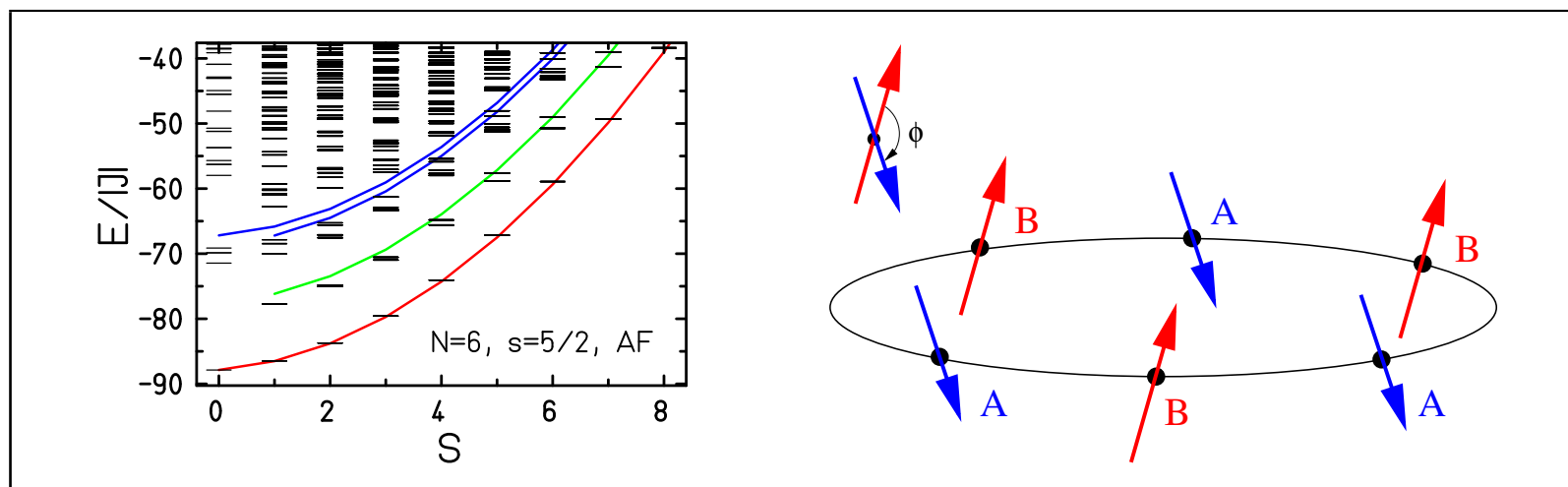
- Interacting spin system largely decoupled from remaining degrees of freedom;
- Transition few-spin system $\Rightarrow$ many-spin system, contribution to understanding of bulk magnetism; investigation of frustration effects;
- Transition quantum spin system ($s = 1/2$) $\Rightarrow$ classical spin system ($s_{\text{Fe}} = 5/2$, $s_{\text{Gd}} = 7/2$);
- Easy to produce, single crystals with $> 10^{17}$ identical molecules can be synthesized and practically completely characterized;
- **Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, qubits for quantum computers.**

Model Hamiltonian for this talk

$$H_{\sim} = \underbrace{-2 \sum_{i < j} J_{ij} \vec{s}_{\sim i} \cdot \vec{s}_{\sim j}}_{\text{Heisenberg}} + \underbrace{g \mu_B B \sum_i^N s_{\sim i}^z}_{\text{Zeeman}}$$

Rotational bands in antiferromagnets

Rotational bands in antiferromagnets I



- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- For bipartite systems (2,3): $\tilde{H}^{\text{eff}} = -2 J_{\text{eff}} \tilde{\mathbf{S}}_A \cdot \tilde{\mathbf{S}}_B$;
- 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)

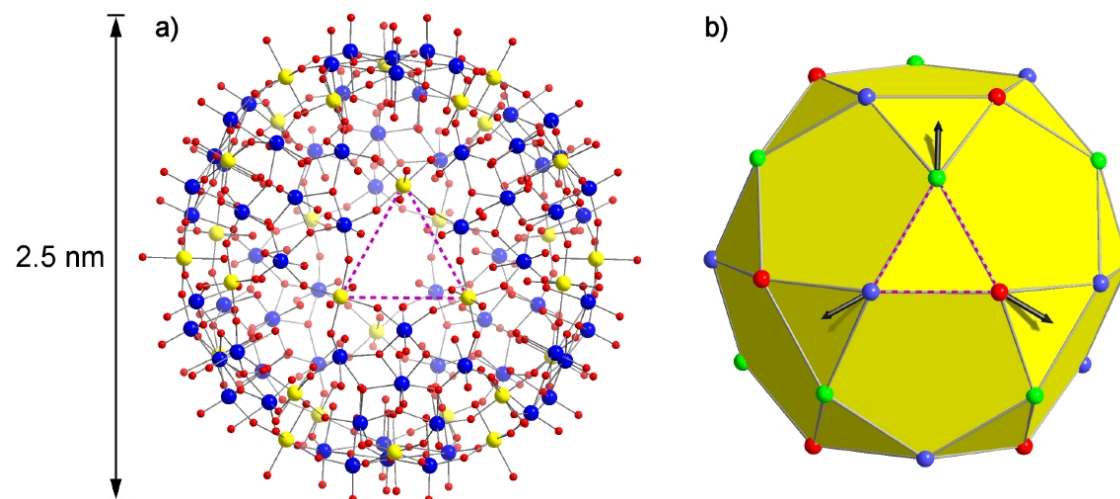
(2) J. Schnack and M. Luban, Phys. Rev. B **63**, 014418 (2001)

(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).

Icosidodecahedron

$\{\text{Mo}_{72}\text{Fe}_{30}\}$ – a molecular brother of the kagome lattice and an archetype of geometric frustration

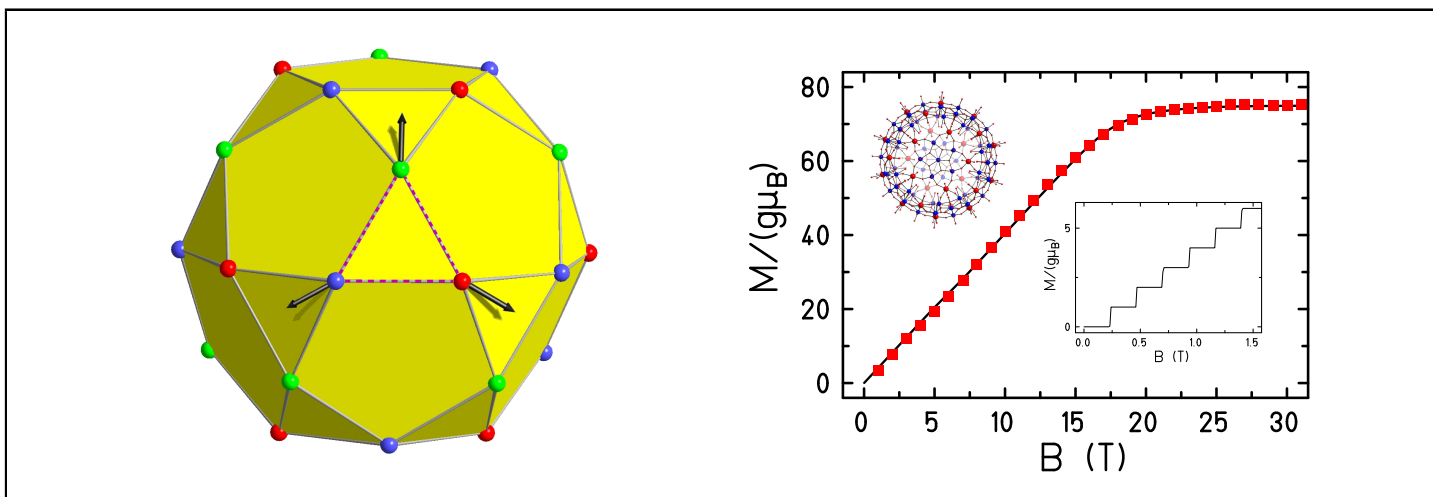


- Giant magnetic Keplerate molecule;
- Structure: Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (1).
- Classical ground state of $\{\text{Mo}_{72}\text{Fe}_{30}\}$: three sublattice structure, coplanar spins (2);
- Quantum mechanical ground state $S = 0$ can only be approximated, dimension of Hilbert space $(2s + 1)^N \approx 10^{23}$ (3).

(1) A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001) , (2) M. Axenovich and M. Luban, Phys. Rev. B **63**, 100407 (2001) , (3) M. Exler and J. Schnack, Phys. Rev. B **67**, 094440 (2003)

Rotational bands in antiferromagnets II

Approximate Hamiltonian for $\{\text{Mo}_{72}\text{Fe}_{30}\}$



$$\tilde{H} = -2J \sum_{(u < v)} \vec{\tilde{s}}(u) \cdot \vec{\tilde{s}}(v) \approx -2J_{\text{eff}} \left[\vec{\tilde{S}}_A \cdot \vec{\tilde{S}}_B + \vec{\tilde{S}}_B \cdot \vec{\tilde{S}}_C + \vec{\tilde{S}}_C \cdot \vec{\tilde{S}}_A \right] = \tilde{H}^{\text{eff}}$$

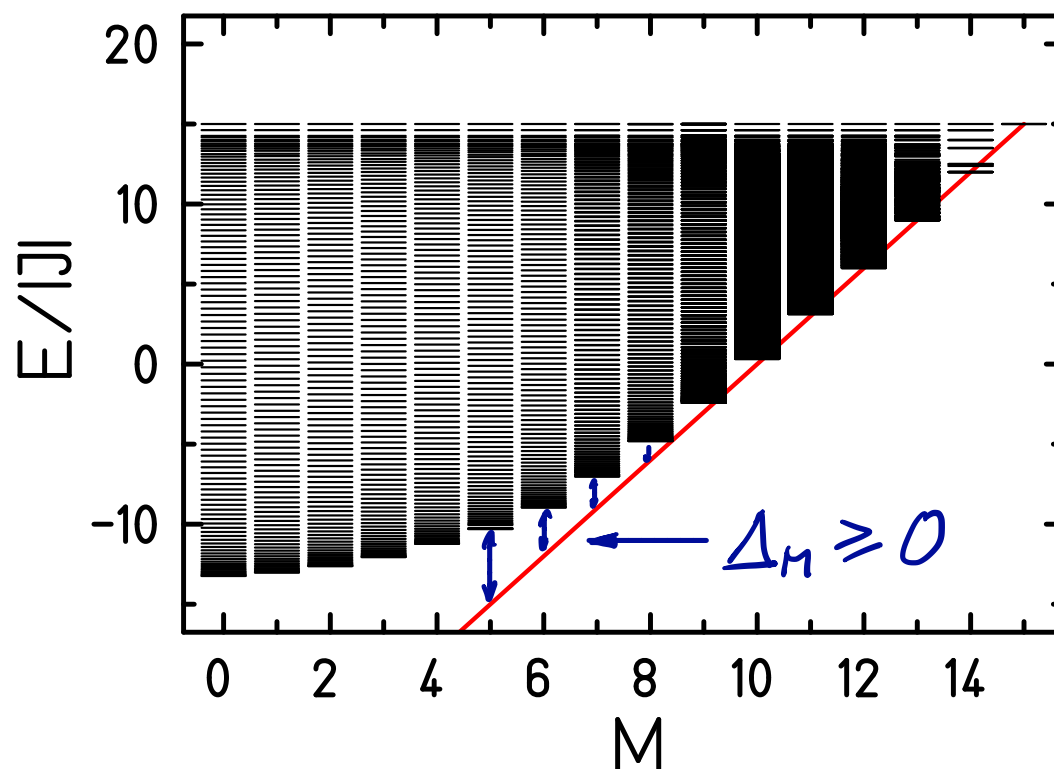
Three sublattice system, classical 120° -ground state;

Good description of low-temperature magnetization ... but
let's have a closer look at the spectrum.

J. Schnack, M. Luban, R. Modler, Europhys. Lett. **56**, 863 (2001)

The icosidodecahedron

How a bias led to a discovery



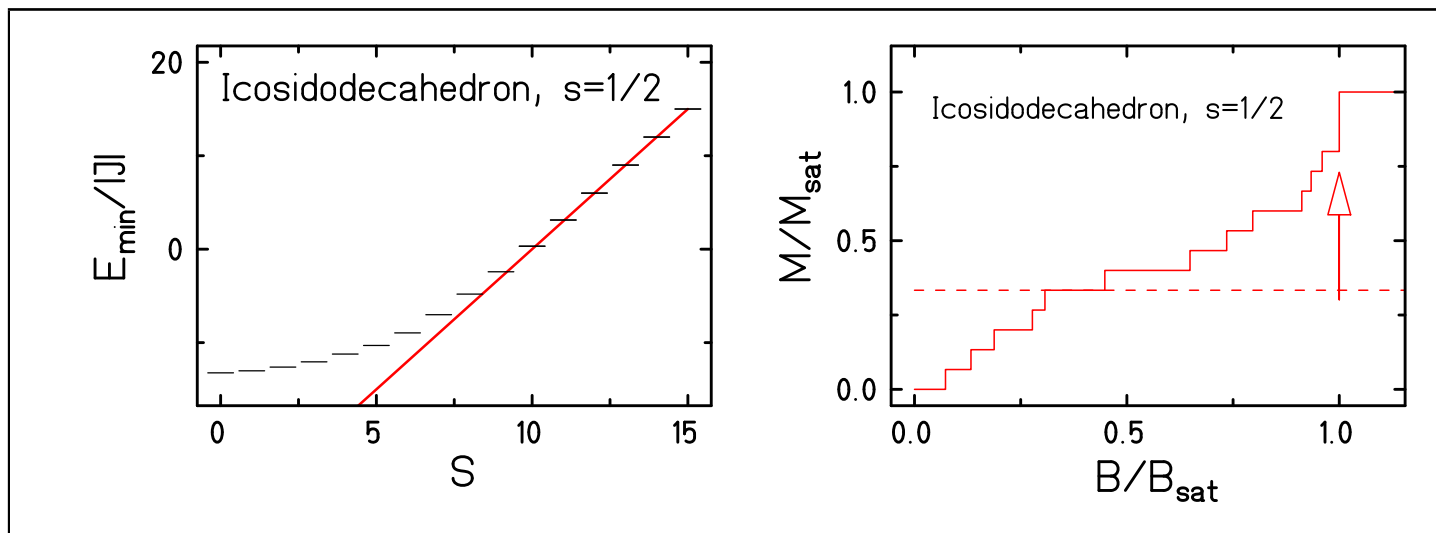
For certain AF Heisenberg spin systems, e.g. with equivalent spins only, one can show, that all energy eigenvalue lie above the line connecting the ground states for $M = Ns$ and $M = Ns - 1$.

(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)

The icosidodecahedron

How a bias led to a discovery



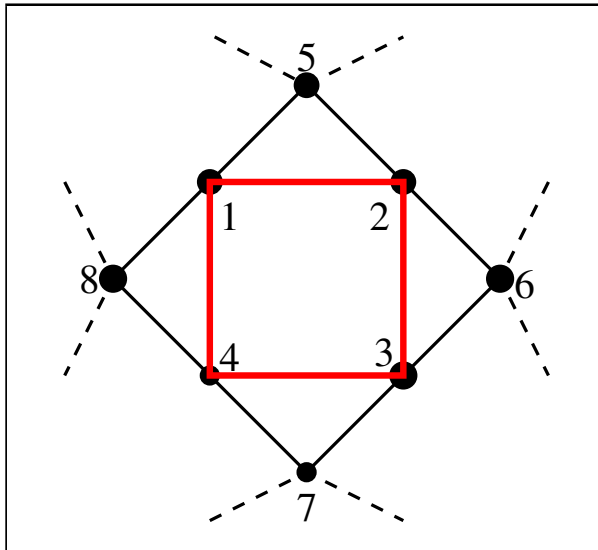
- Surprise: $E_{\min}(S)$ linear in S for high S instead of being quadratic (1);
- Heisenberg model: property depends only on the structure but not on s (2);
- Alternative formulation: independent localized magnons (3);

(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)

Localized Magnons



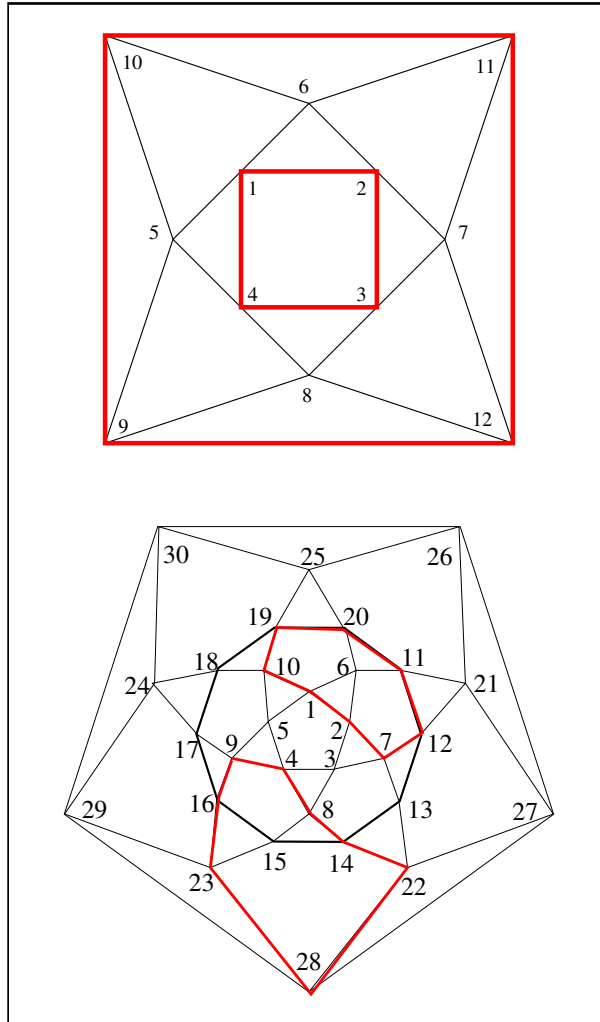
- $|\text{localized magnon}\rangle = \frac{1}{2}(|1\rangle - |2\rangle + |3\rangle - |4\rangle)$
- $|1\rangle = s_1^- |\uparrow\uparrow\uparrow \dots\rangle$ etc.
- $\tilde{H} |\text{localized magnon}\rangle \propto |\text{localized magnon}\rangle$
- Localized magnon is state of lowest energy (1,2).

- 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

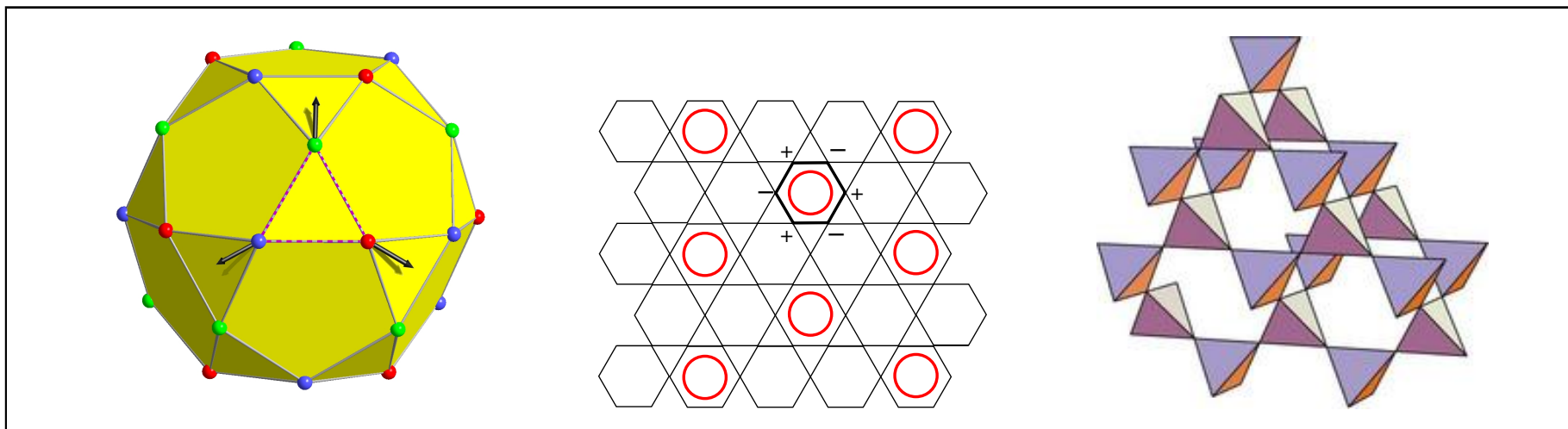


- Non-interacting one-magnon states can be placed on various molecules, e. g. 2 on the cuboctahedron and 3 on the icosidodecahedron (3rd delocalized);
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = N_S - n$;
- Linear dependence of $E_{\min}$ on M
 $\Rightarrow$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

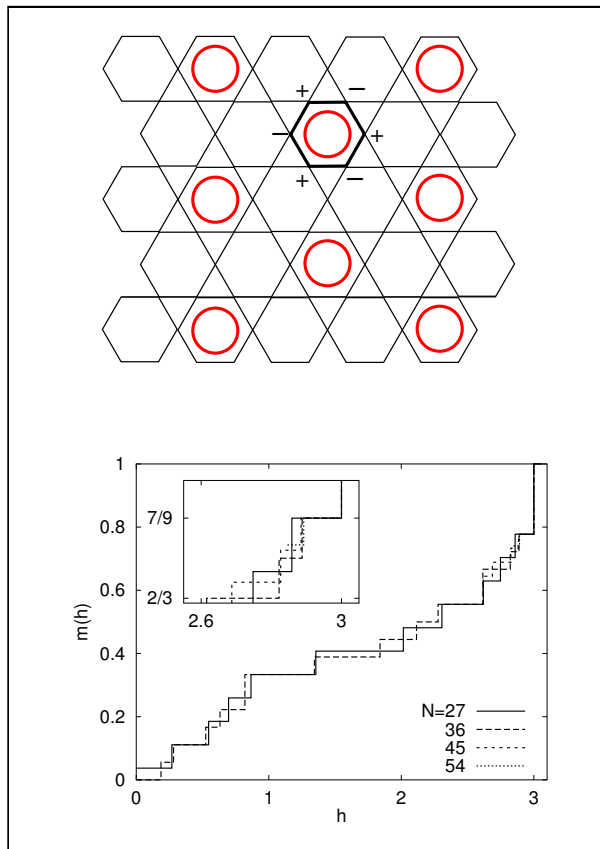
Fe₃₀ and friends

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.

Giant magnetization jumps in frustrated antiferromagnets III Kagome Lattice

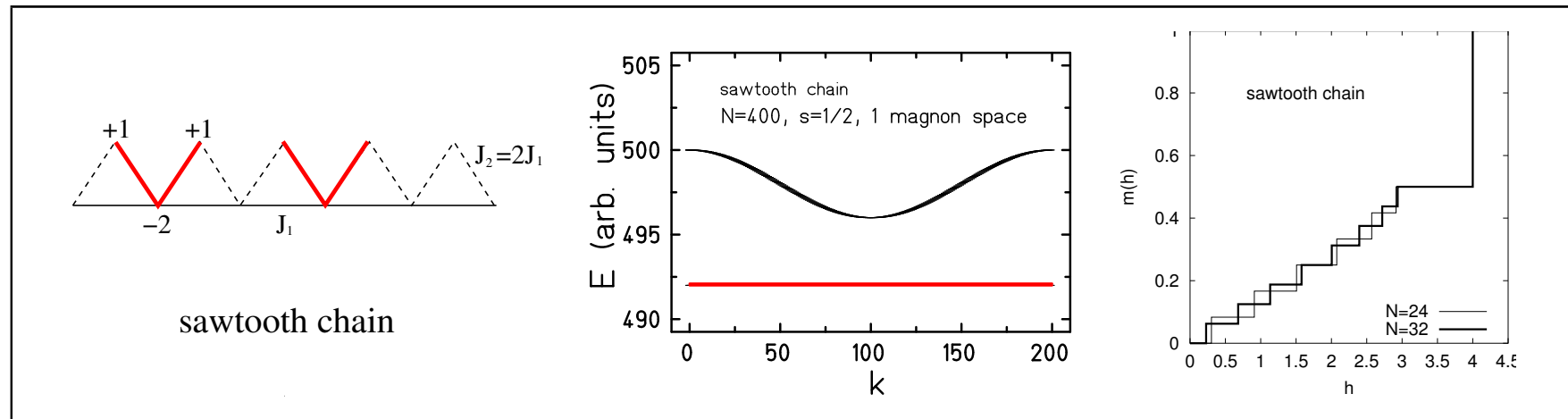


- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore;
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = N_s - n$;
Kagome: max. number of indep. magnons is $N/9$;
- Linear dependence of $E_{\min}$ on M
 $\Rightarrow (T = 0)$ 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)

The magnetocaloric effect

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.

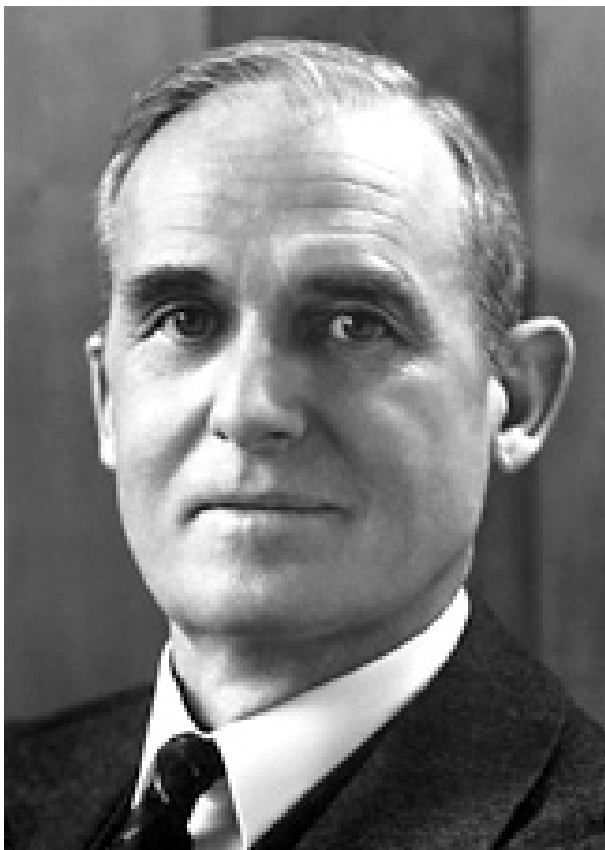
(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001).

(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. Giaque *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.

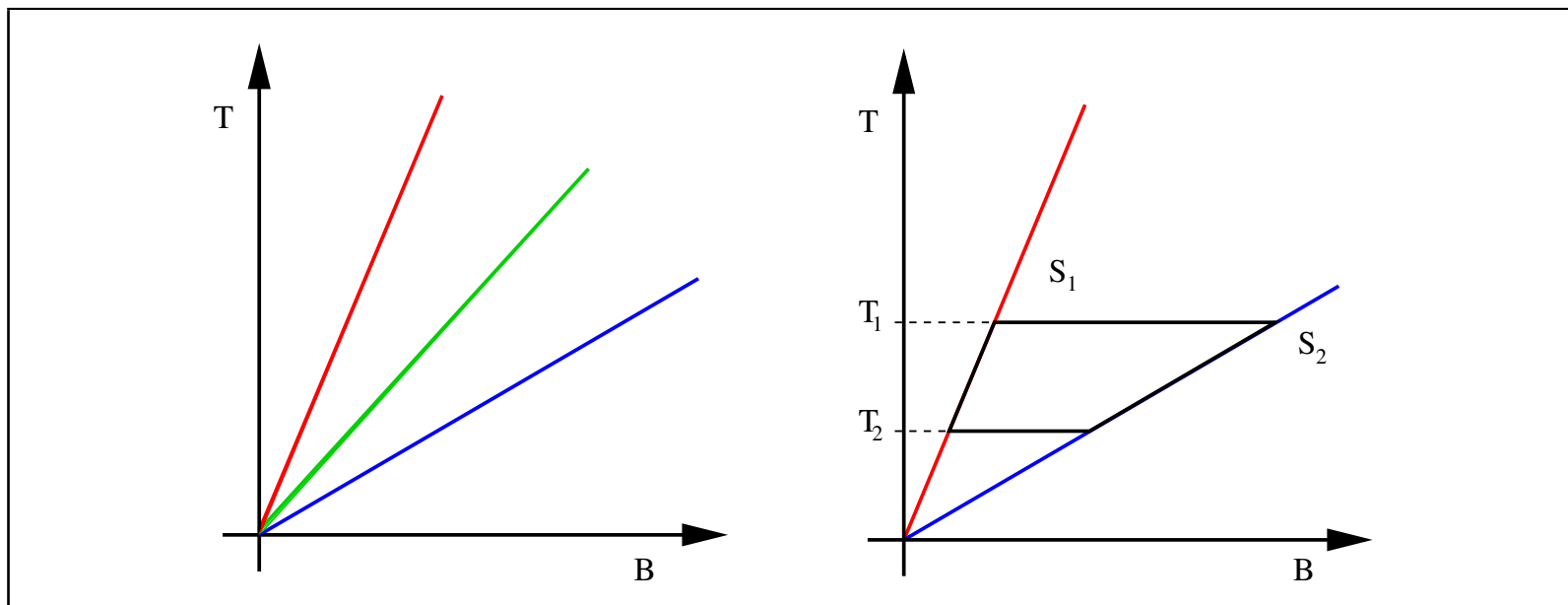
It is apparent that it will be possible to obtain much lower temperatures, especially when successive demagnetizations are utilized.

W. F. GIAUQUE
D. P. MACDOUGALL

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

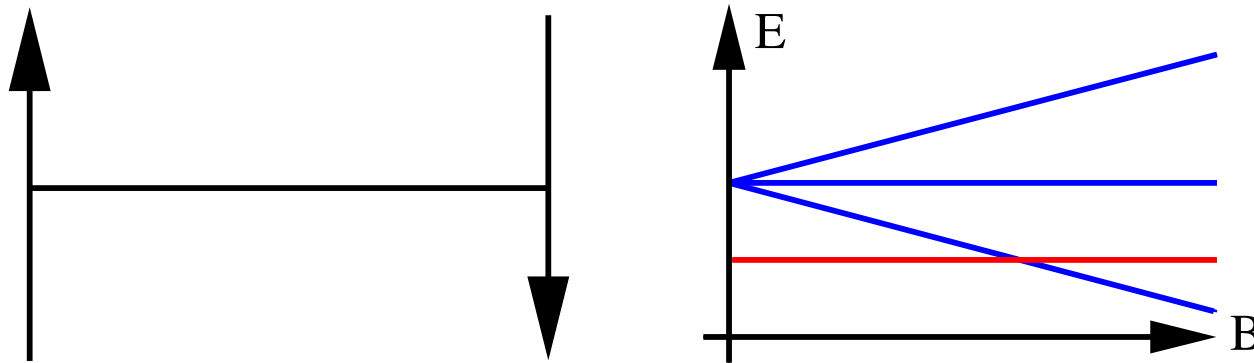
W. F. Giauque and D. MacDougall, *Phys. Rev.* **43**, 768 (1933).

Magnetocaloric effect – Paramagnets



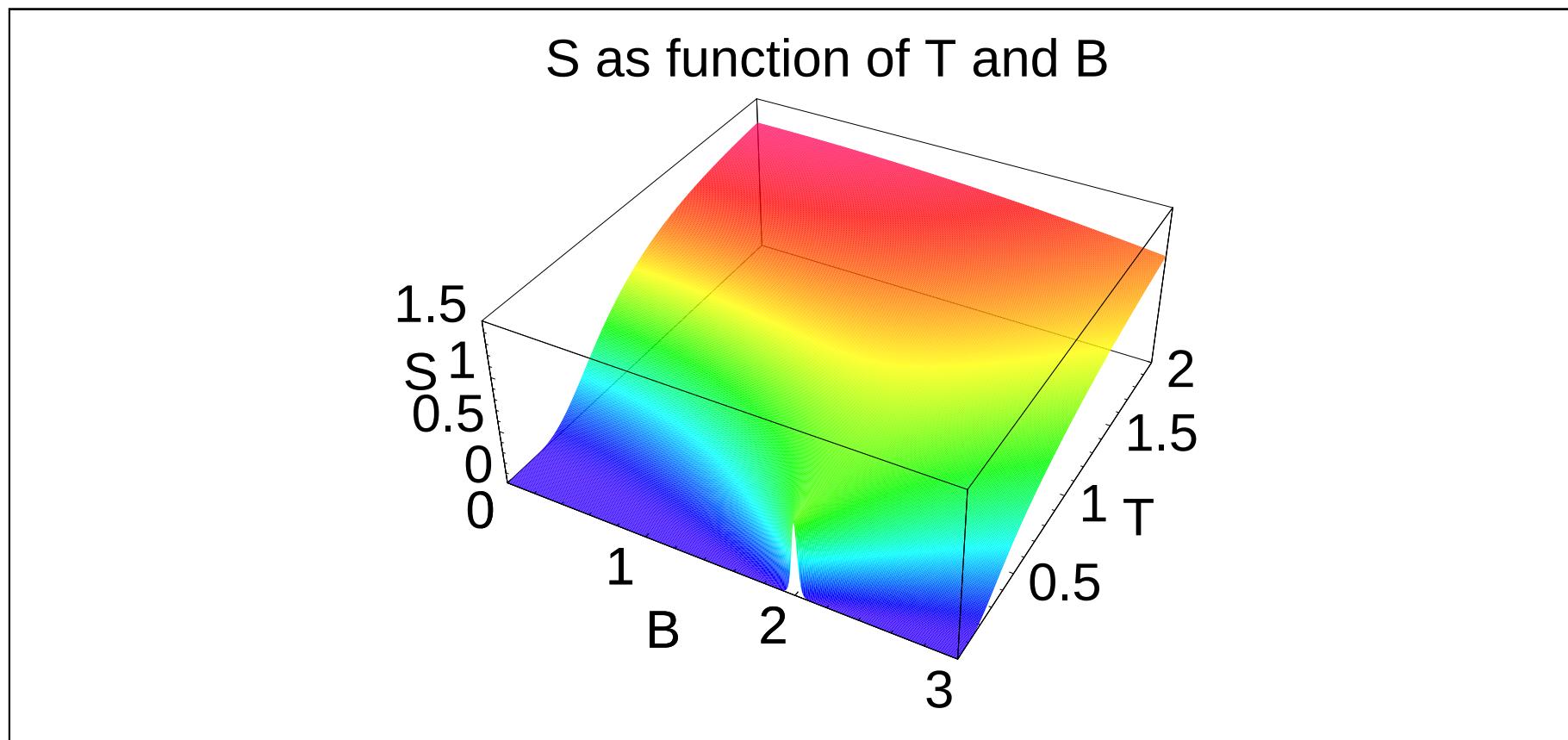
- Ideal paramagnet: $S(T, B) = f(B/T)$, i.e. $S = \text{const} \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

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.

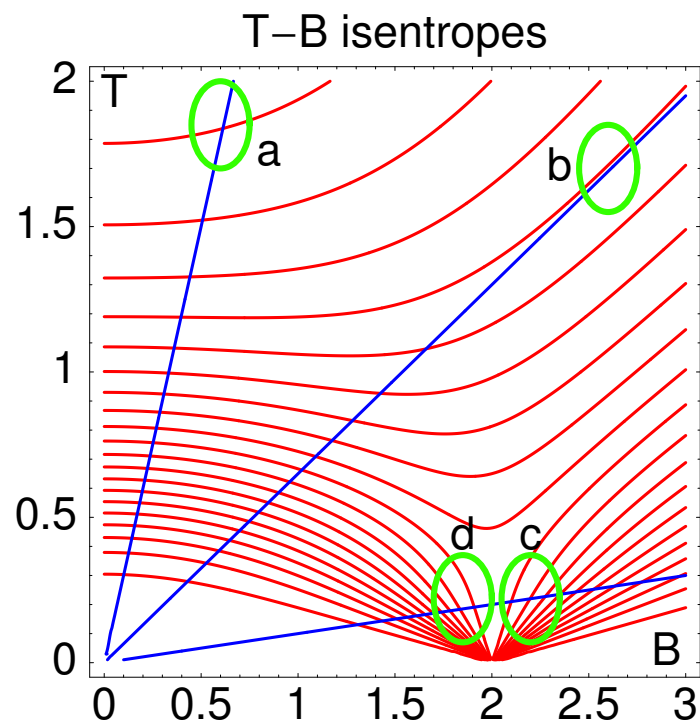
Magnetocaloric effect – af $s = 1/2$ dimer



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

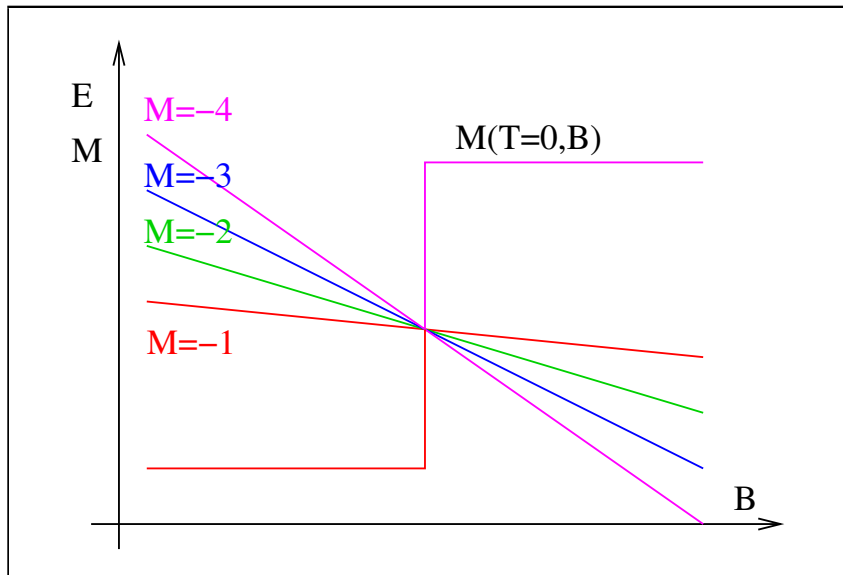
(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

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 $T = 0$.

•

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

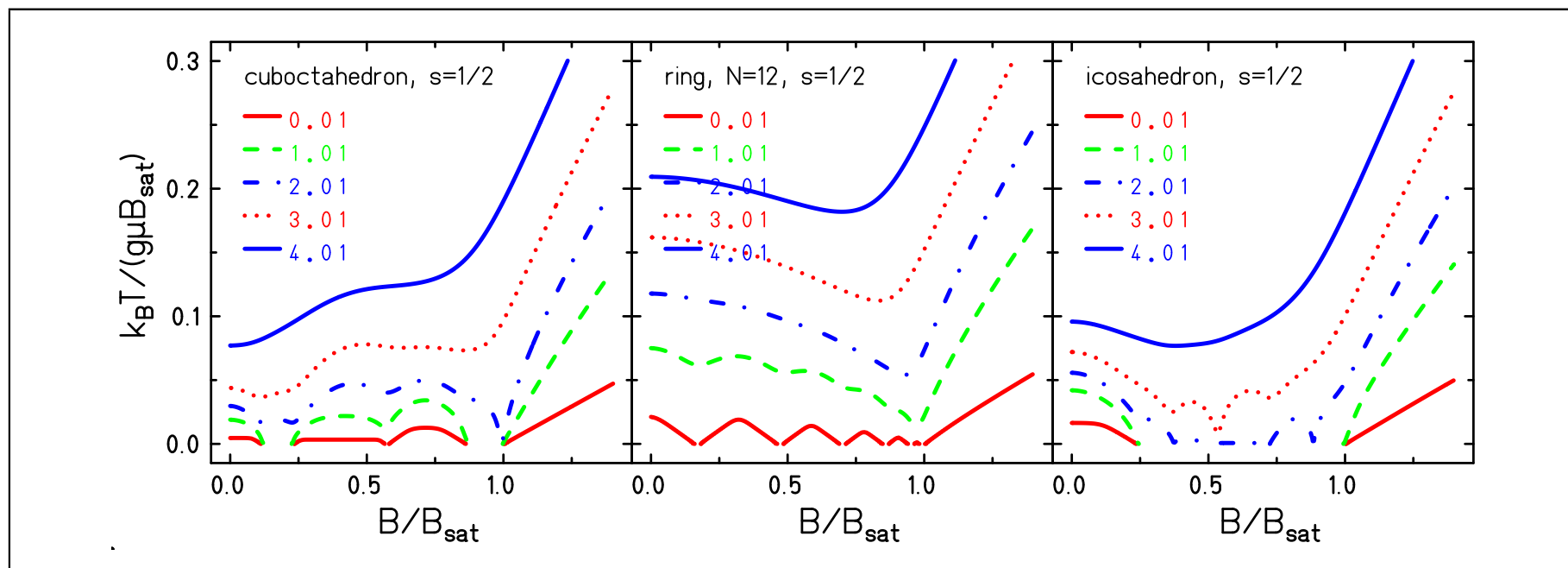
M. Evangelisti *et al.*, Appl. Phys. Lett. **87**, 072504 (2005).

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).

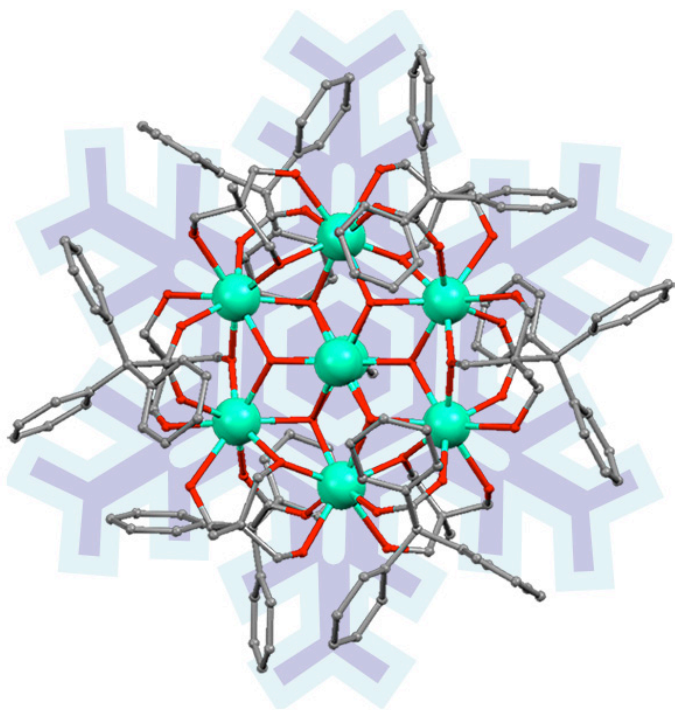
Magnetocaloric effect – Molecular systems



- Cuboctahedron: high cooling rate due to independent magnons;
- Ring: normal level crossing, normal jump;
- Icosahedron: unusual behavior due to edge-sharing triangles, high degeneracies all over the spectrum; high cooling rate.

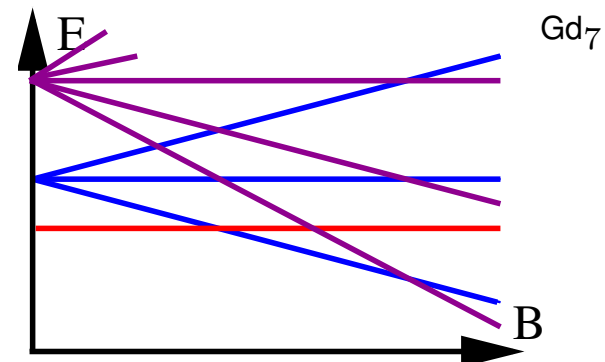
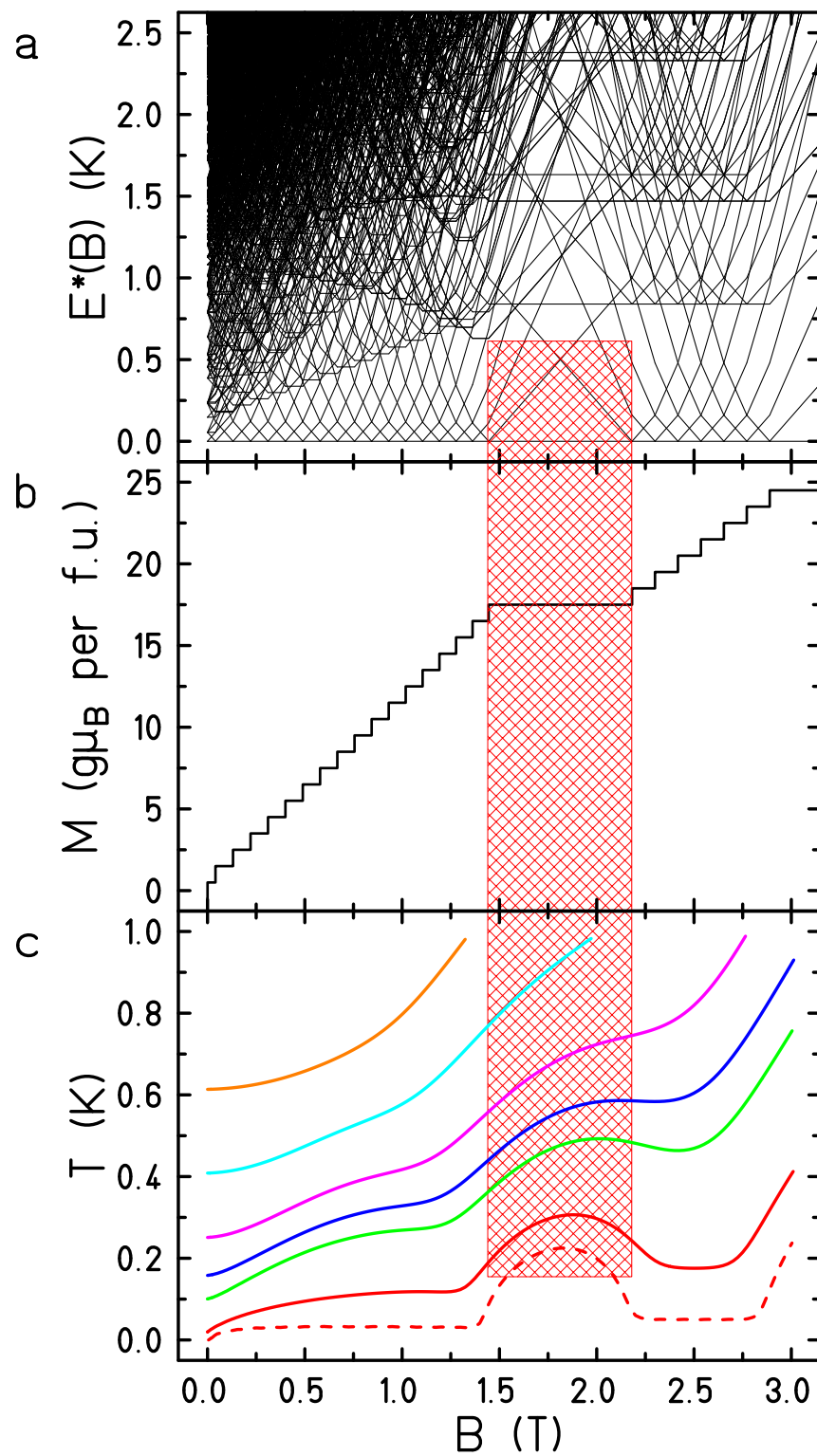
J. Schnack, R. Schmidt, J. Richter, Phys. Rev. B **76**, 054413 (2007)

Gd₇ – Magnetocalorics

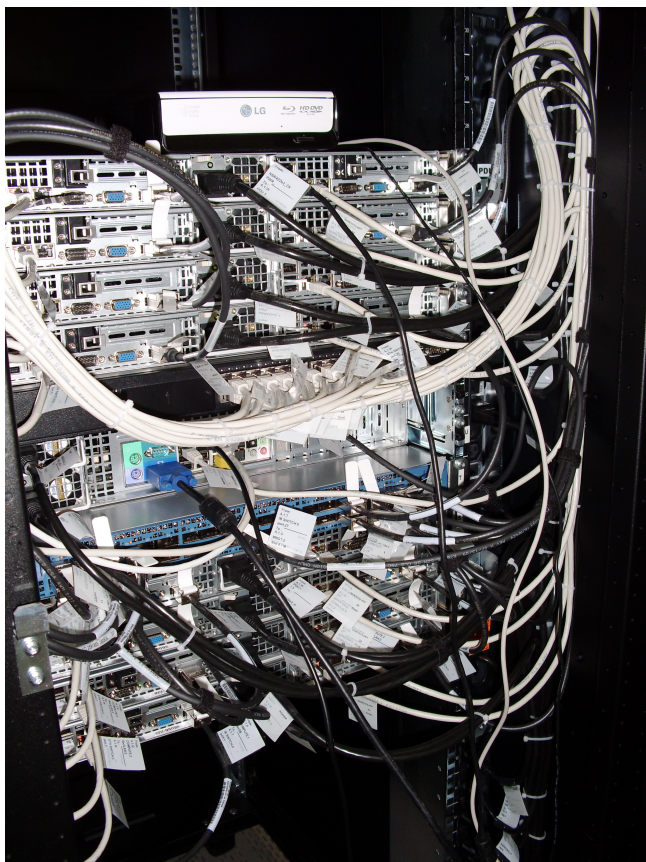


- Often magnetocaloric observables not directly measured, but inferred from Maxwell's relations.
- First real cooling experiment with a molecule.
- $$\underline{H} = -2 \sum_{i < j} J_{ij} \vec{s}_i \cdot \vec{s}_j + g \mu_B B \sum_i^N s_i^z$$
$$J_1 = -0.090(5) \text{ K}, J_2 = -0.080(5) \text{ K}$$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



Summary



- Independent magnons = powerful concept for certain frustrated magnetic molecules.
- Combination with C_N point groups leads to flat bands.
- Isentropes for interacting systems are much richer than for paramagnets. Good for applications away from $(T = 0, B = 0)$.
- Flat-band systems or molecules hosting independent magnons yield large cooling rates at the saturation field.

J. Schnack, Dalton Trans. **39**, 4677 (2010).

Many thanks to my collaborators worldwide

- M. Czopnik, T. Glaser, O. Hanebaum, Chr. Heesing, M. Höck, N.B. Ivanov, H.-T. Langwald, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum (Bielefeld)
- 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); A. Honecker (U de Cergy-Pontoise); E. Garlatti, S. Carretta, G. Amoretti, P. Santini (Parma); A. Tennant (ORNL); Gopalan Rajaraman (Mumbai)
- J. Richter, J. Schulenburg (Magdeburg); U. Kortz (Bremen); B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); E. Rentschler (Mainz); 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

Highlights. Tutorials. Who is who. Conferences.