Frustration effects in magnetic molecules

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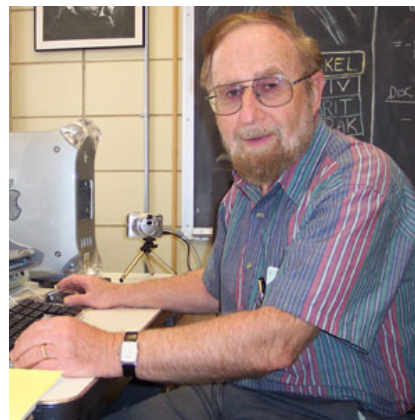# In late 20th century people coming from

transport theory　　general relativity　　nuclear physics　　Zener diodes


were triggered by a "magnetic" enthusiast.

Meanwhile a big collaboration has been established

- K. Bärwinkel, H.-J. Schmidt, J. S., M. Allalen, M. Brüger, D. Mentrup, D. Müter, M. Exler, P. Hage, F. Hesmer, K. Jahns, F. Ouchni, R. Schnalle, P. Sheche-lokovskyy, S. Torbrügge (U. Osnabrück);

- M. Luban, P. Kögerler, D. Vaknin (Ames Lab, USA);
  J. Musfeldt (U. of Tennessee, USA); N. Dalal (Florida State, USA);

- Chr. Schröder (FH Bielefeld & Ames Lab, USA);

- H. Nojiri (Tohoku University, Japan);

- R.E.P. Winpenny (Man U); L. Cronin (U. of Glasgow);

- J. Richter, J. Schulenburg, R. Schmidt (U. Magdeburg);

- S. Blügel, A. Postnikov (FZ Jülich); A. Honecker (Uni Braunschweig).

- E. Rentschler (U. Mainz); U. Kortz (IUB); A. Tennant (HMI Berlin).

. . . and various general results could be achieved

1. The suspects: magnetic molecules

2. The thumbscrew: Heisenberg model

3. Extension of Lieb, Schultz, and Mattis: k–rule for odd rings

4. Rotational bands in antiferromagnets

5. Giant magnetization jumps in frustrated antiferromagnets

6. Magnetization plateaus and susceptibility minima

7. Enhanced magnetocaloric effect

8. Hysteresis without anisotropy

9. A special triangular molecule-based spin tube

The beauty of magnetic molecules I
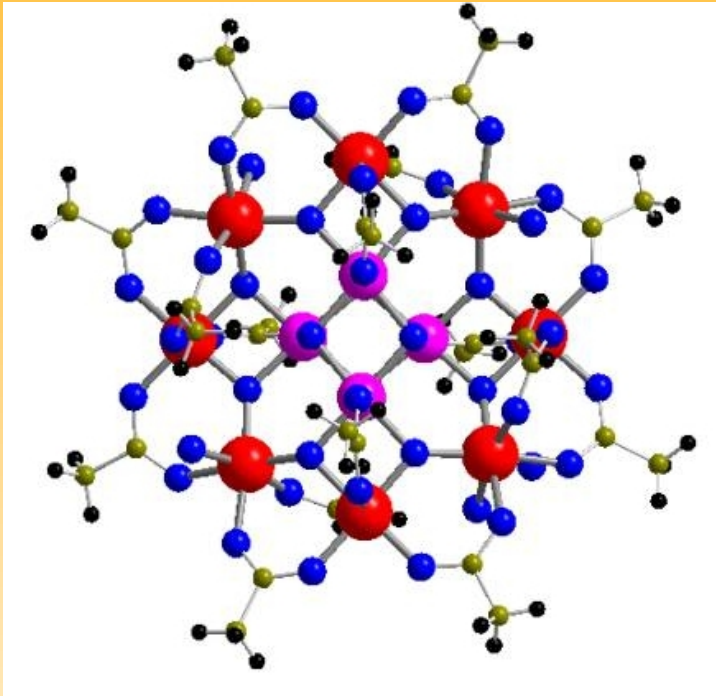
Mn$_{12}$

- Inorganic or organic macro molecules, e.g. poly-oxometalates, 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
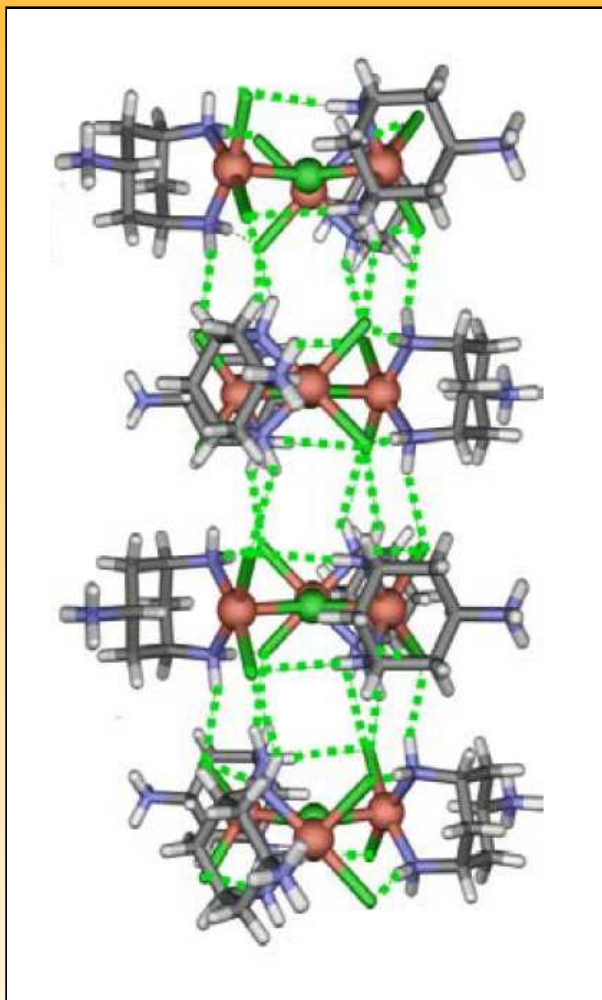
- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);

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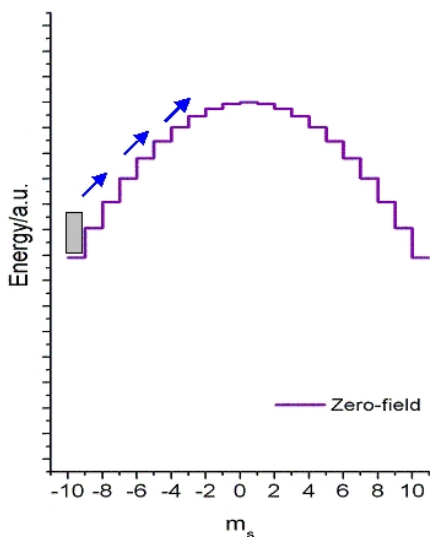
  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004)

The beauty of magnetic molecules III
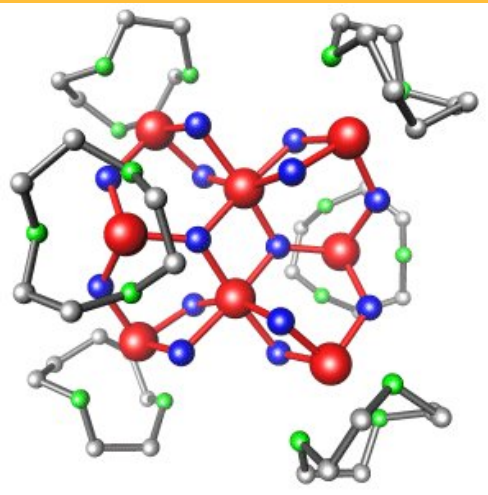
- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment;

- Example: $S = 10$ for Mn$_{12}$ or Fe$_8$;

- Anisotropy dominates approximate single-spin Hamiltonian:

$$\underset{\sim}{H} = -D\underset{\sim}{S_z^2} + \underset{\sim}{H}', \qquad \left[\underset{\sim}{S_z}, \underset{\sim}{H}'\right] \neq 0$$

- Single molecule shows: metastable magnetization, hysteresis, ground state magnetization tunneling, thermally and phonon assisted tunneling.

- Today's major efforts: improve stability of magneti- zation; investigate on surfaces.

The beauty of magnetic molecules IV
Why magnetic molecules?
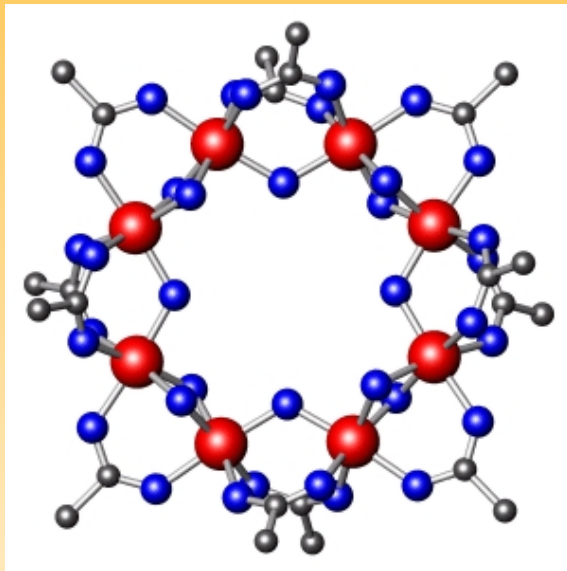
Cr$_8$

- Interacting spin system largely decoupled from remaining degrees of freedom;

- Transition few-spin system $\Rightarrow$ many-spin system, contribution to understanding of bulk magnetism;

- Transition quantum spin system ($s = 1/2$) $\Rightarrow$ classical spin system ($s_{\mathsf{Fe}} = 5/2$, $s_{\mathsf{Gd}} = 7/2$);

- 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.

unilogo-m-rot.jpg

$\{Mo_{72}Fe_{30}\}$ – a molecular brother of the kagome lattice and an archetype of geometric frustration
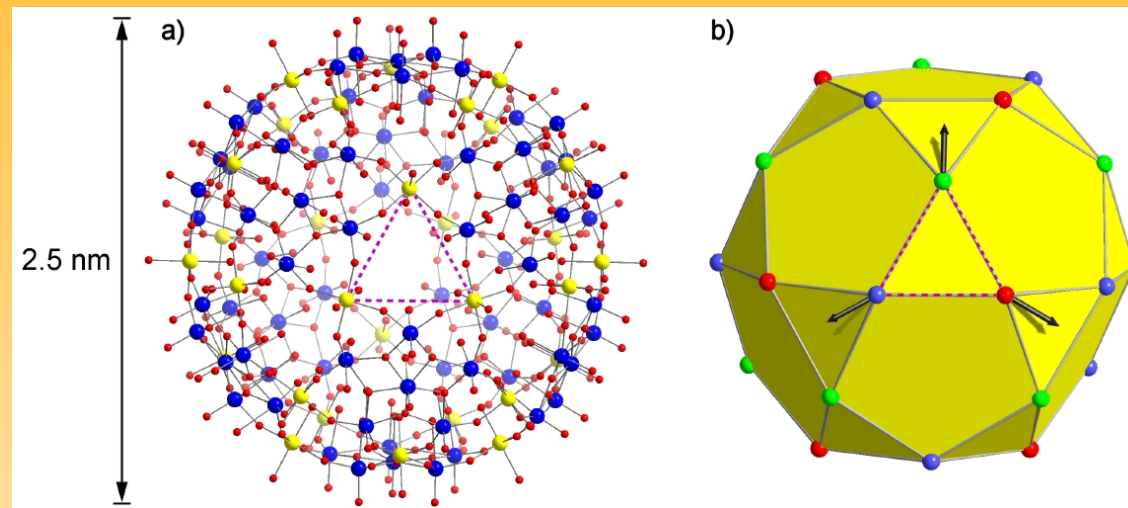
- Giant magnetic Keplerate molecule;
- Structure: Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (1).

- Classical ground state of $\{Mo_{72}Fe_{30}\}$: 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)

Hamiltonian and Tools

Model Hamiltonian − Heisenberg-Model

$$\underset{\sim}{H} \;=\; \sum_{i,j} \vec{\underset{\sim}{s}}(i) \cdot \mathbf{J}_{ij} \cdot \vec{\underset{\sim}{s}}(j) \;\;+\;\; \sum_{i,j} \vec{D}_{ij} \cdot \left[\vec{\underset{\sim}{s}}(i) \times \vec{\underset{\sim}{s}}(j) \right] \;\;+\;\; \mu_B B \sum_i^N g_i \, \underset{\sim}{s}_z(i)$$

Exchange/Anisotropy   Dzyaloshinskii-Moriya   Zeeman

Very often anisotropic terms are utterly negligible, then . . .

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

Heisenberg   Zeeman

The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations; $J < 0$: antiferromagnetic coupling.

Our toolbox

- Analytical or numerically exact and complete diagonalization of the Hamiltonian: always superior, the complete thermodynamics is available;

- Lanczos diagonalization: some low-lying eigenstates in orthogonal subspaces;

- Density Matrix Renormalization Group technique (DMRG): often only the ground state for a given orthogonal subspace;

- Approximate Hamiltonians: good insight for certain systems;

- Classical spin dynamics: illuminating and "dangerous";

- Spin coherent states: no real improvement compared to classical spin dynamics.

unilogo-mitof.jpg

General Results
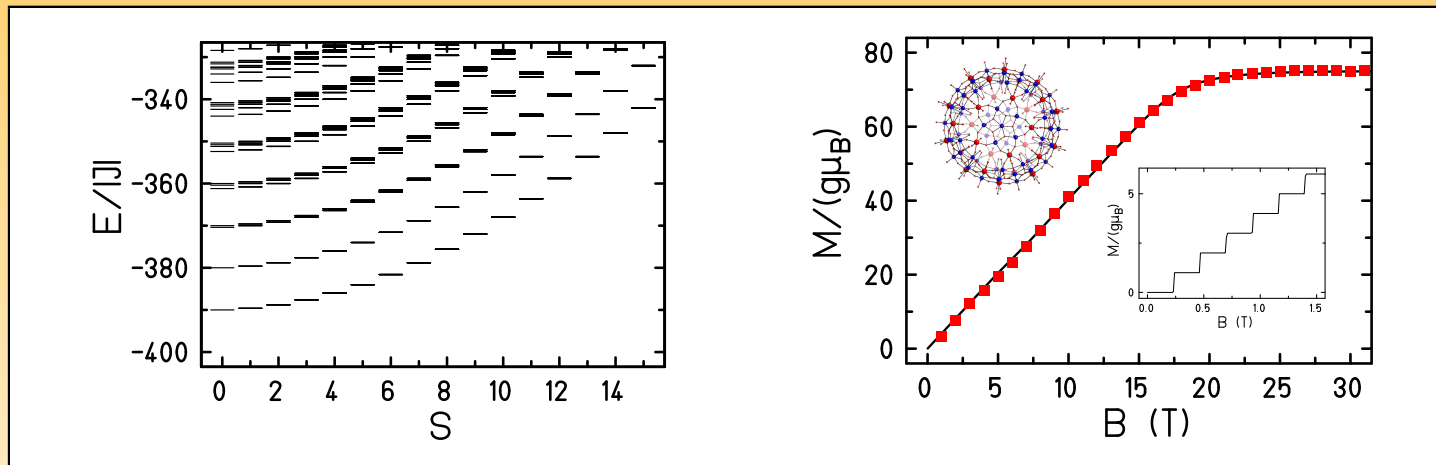
Rotational bands in antiferromagnets I
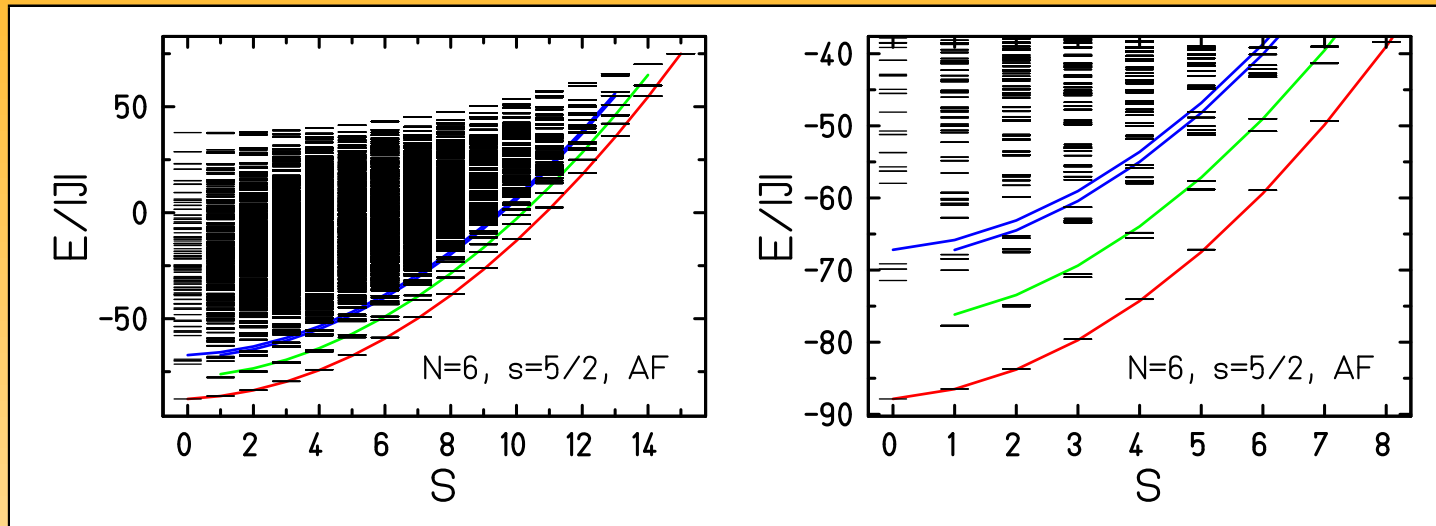
- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);

- Most pronounced for bipartite systems (2,3),
  good approximation for more general systems;

- 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).

Rotational bands in antiferromagnets II
Approximate Hamiltonian for $\{Mo_{72}Fe_{30}\}$

$$\underset{\sim}{H} = -2\,J \sum_{(u<v)} \underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v) \approx -\frac{D\,J}{N}\left[\underset{\sim}{\vec{S}^2} - \sum_{j=1}^{N_{SL}} \underset{\sim}{\vec{S}_j^2}\right] = \underset{\sim}{H}^{\text{eff}}$$
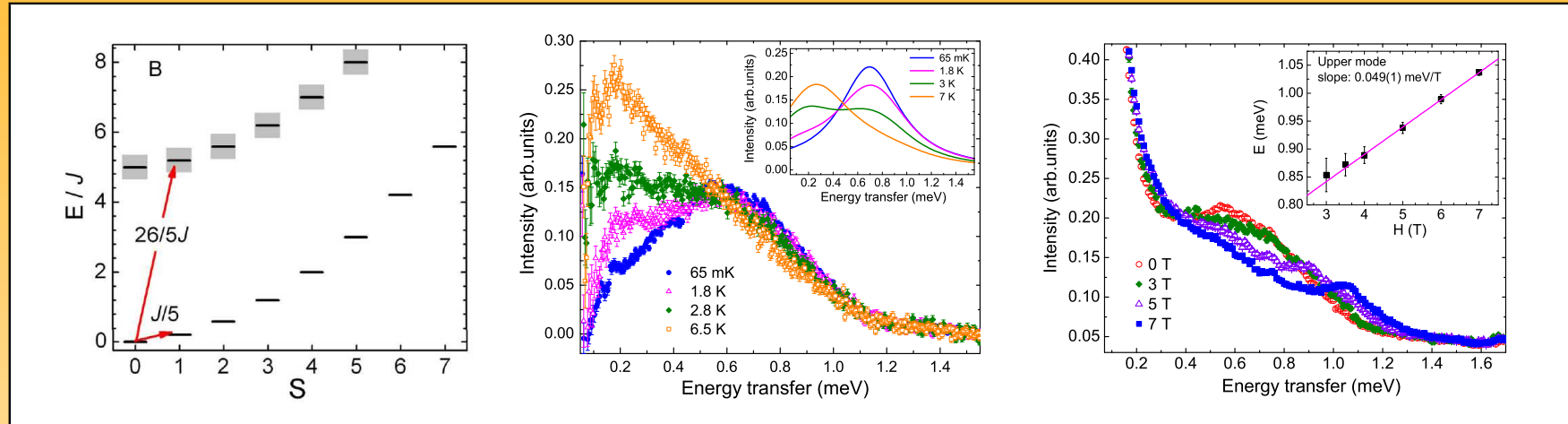

$\underset{\sim}{\vec{S}}_j$ sublattice spins; $D = 6$; good description of magnetization.

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

Rotational bands in antiferromagnets III
## Neutron scattering at $\{Mo_{72}Fe_{30}\}$

- INS shows broad peak at band separation, broad width is a sign of frustration, i.e. of the reduced significance of rotational bands.

- Thermal behavior understood; dependence on external field currently investigated.

V. O. Garlea, S. E. Nagler, J. L. Zarestky, C. Stassis, D. Vaknin, P. Kögerler, D. F. McMorrow, C. Niedermayer, D. A. Tennant, B. Lake, Y. Qiu, M. Exler, J. Schnack, M. Luban, Phys. Rev. B **73**, 024414 (2006)

Giant magnetization jumps in frustrated antiferromagnets I
$\{\mathbf{Mo}_{72}\mathbf{Fe}_{30}\}$
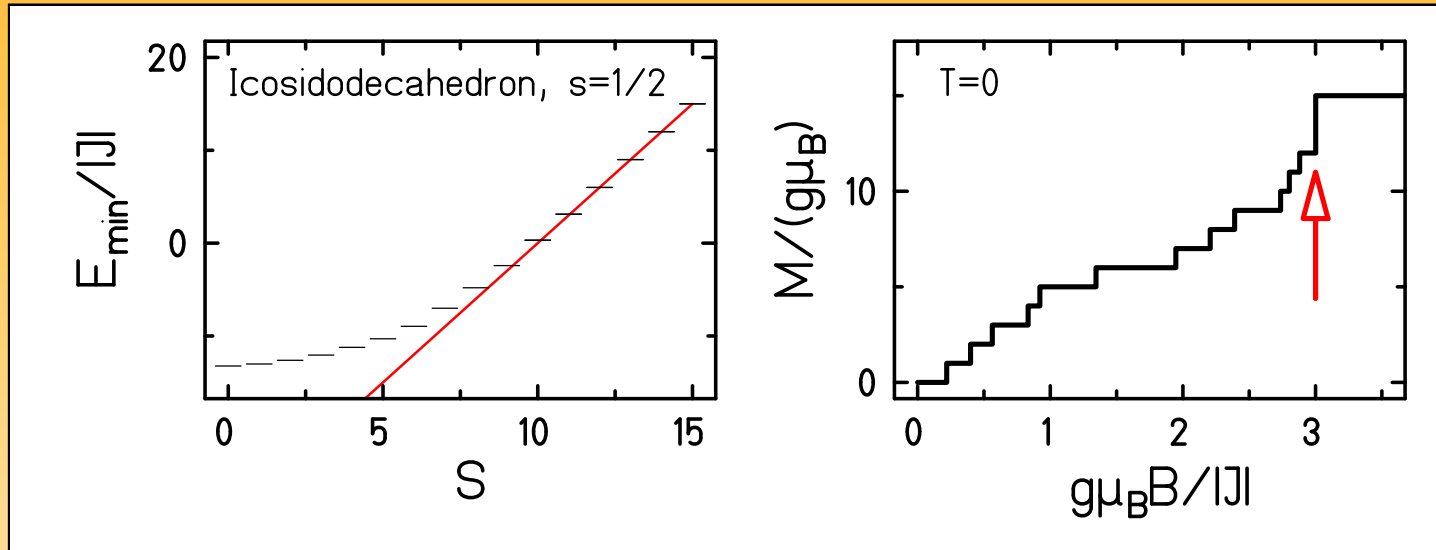
- Close look: $E_{\min}(S)$ linear in S for high S instead of being quadratic (1);

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

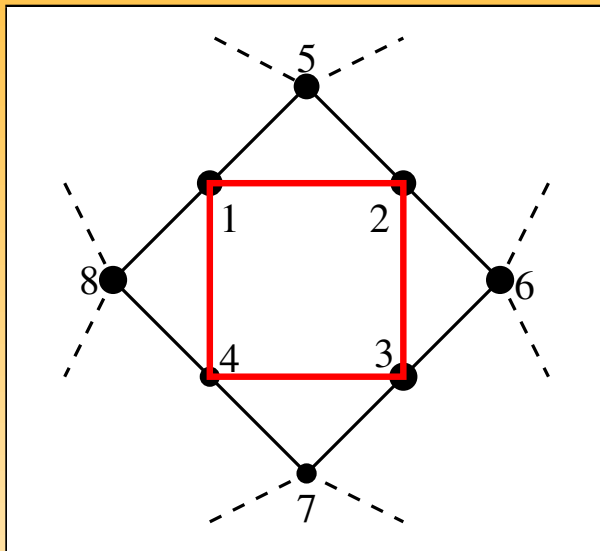- Alternative formulation: independent localized magnons (3);

(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)

Giant magnetization jumps in frustrated antiferromagnets II
Localized Magnons

- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}\left(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle\right)$

- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\ \ldots\rangle$ etc.

- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$
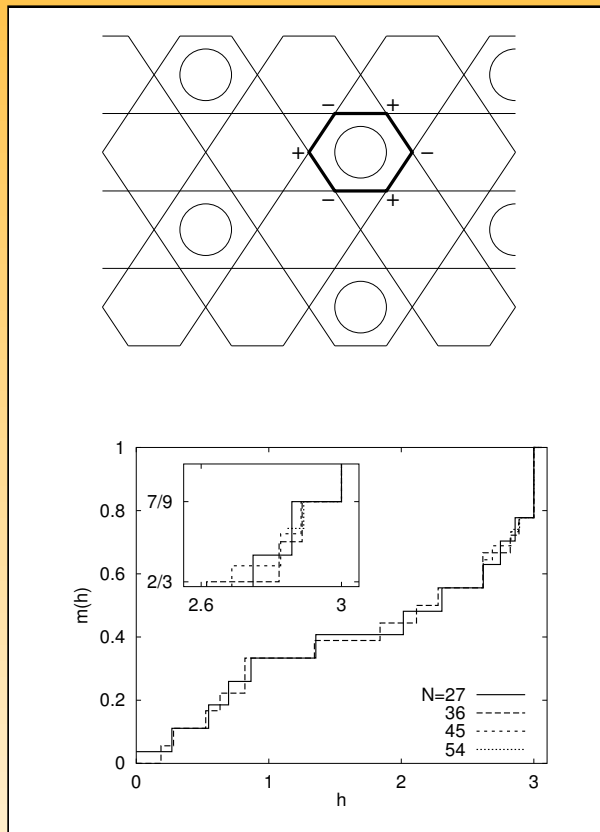
- Localized magnon is state of lowest energy (1,2).

- 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
# 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 $M = Ns - n$;

- Linear dependence of $E_{\min}$ on M
⇒   magnetization jump;

- Maximal number of independent magnons: N/9;

- Jump is a macroscopic quantum effect!

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
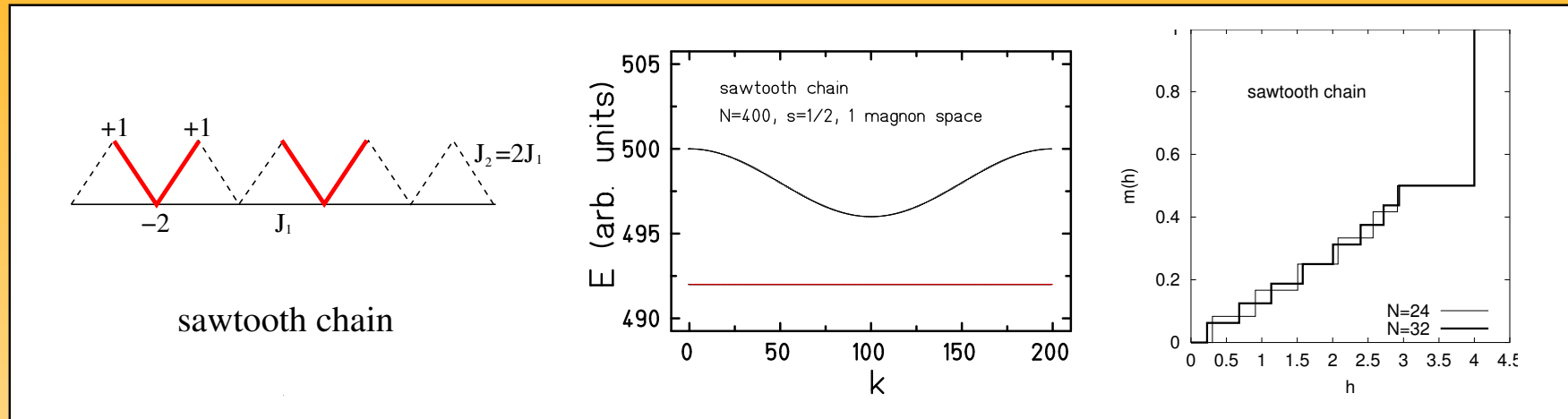
- Flat band of minimal energy in one-magnon space, i. e. high degeneracy of ground state energy in $\mathcal{H}(M = Ns - 1)$;

- Localized magnons can be built from those eigenstates of the translation operator, that belong to the flat band;

- There is a relation to flat band ferromagnetism (H. Tasaki & A. Mielke), compare (1).

(1) A. Honecker, J. Richter, Condens. Matter Phys. **8**, 813 (2005)

Enhanced magnetocaloric effect I
Basics

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

(adiabatic temperature change)

- Heating or cooling in a varying magnetic field. Discovered in pure iron by E. Warburg in 1881.

- 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 ($x \leq 0.5$).

- 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).

(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)
(3) M.E. Zhitomirsky, A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004)

Enhanced magnetocaloric effect II
## Simple af $s = 1/2$ dimer
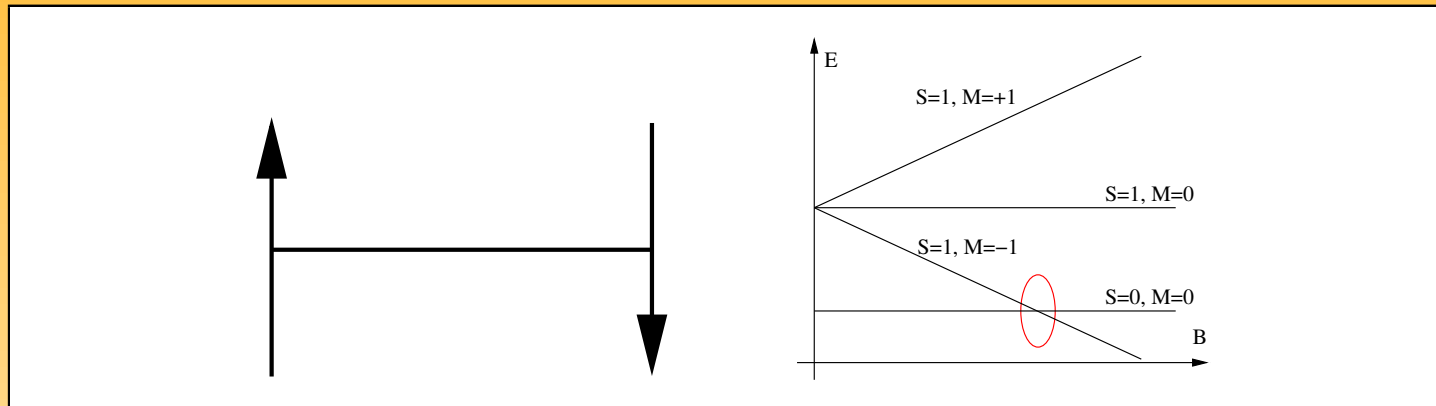
- Singlet-triplet level crossing causes a "quantum phase transition" (1) at $T = 0$ as a function of B.

- $M(T = 0, B)$ and $S(T = 0, B)$ not analytic as function of B.

- $C(T, B)$ varies strongly as function of B for low T.

(1) If you feel the urge to discuss the term "phase transition", please let's do it during the coffee break. I will bring Ehrenfest along with me.

Enhanced magnetocaloric effect III
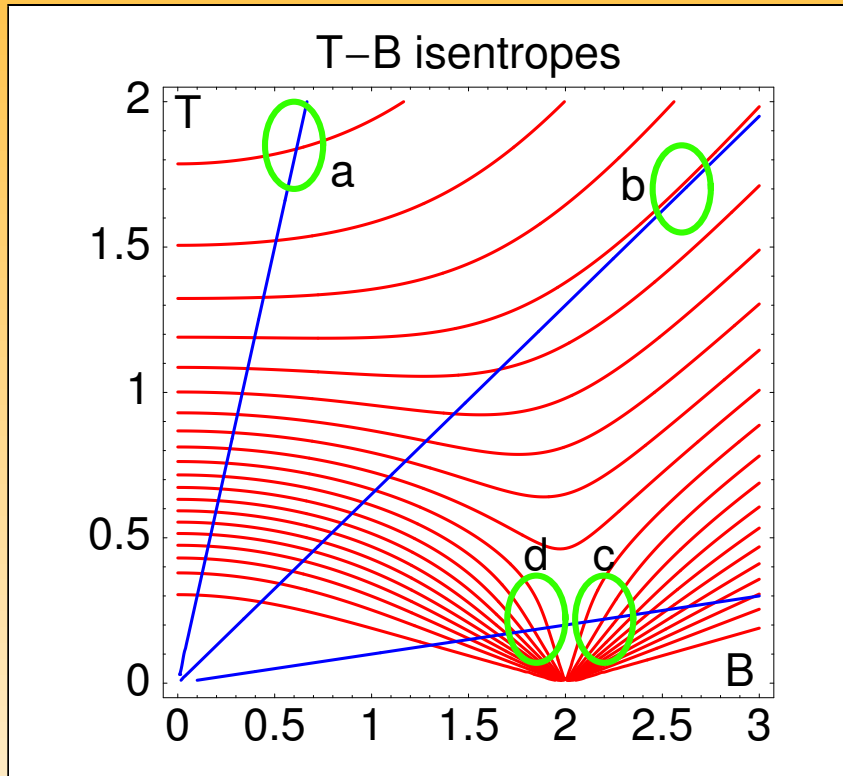## Entropy of af $s = 1/2$ dimer

S as function of T and B
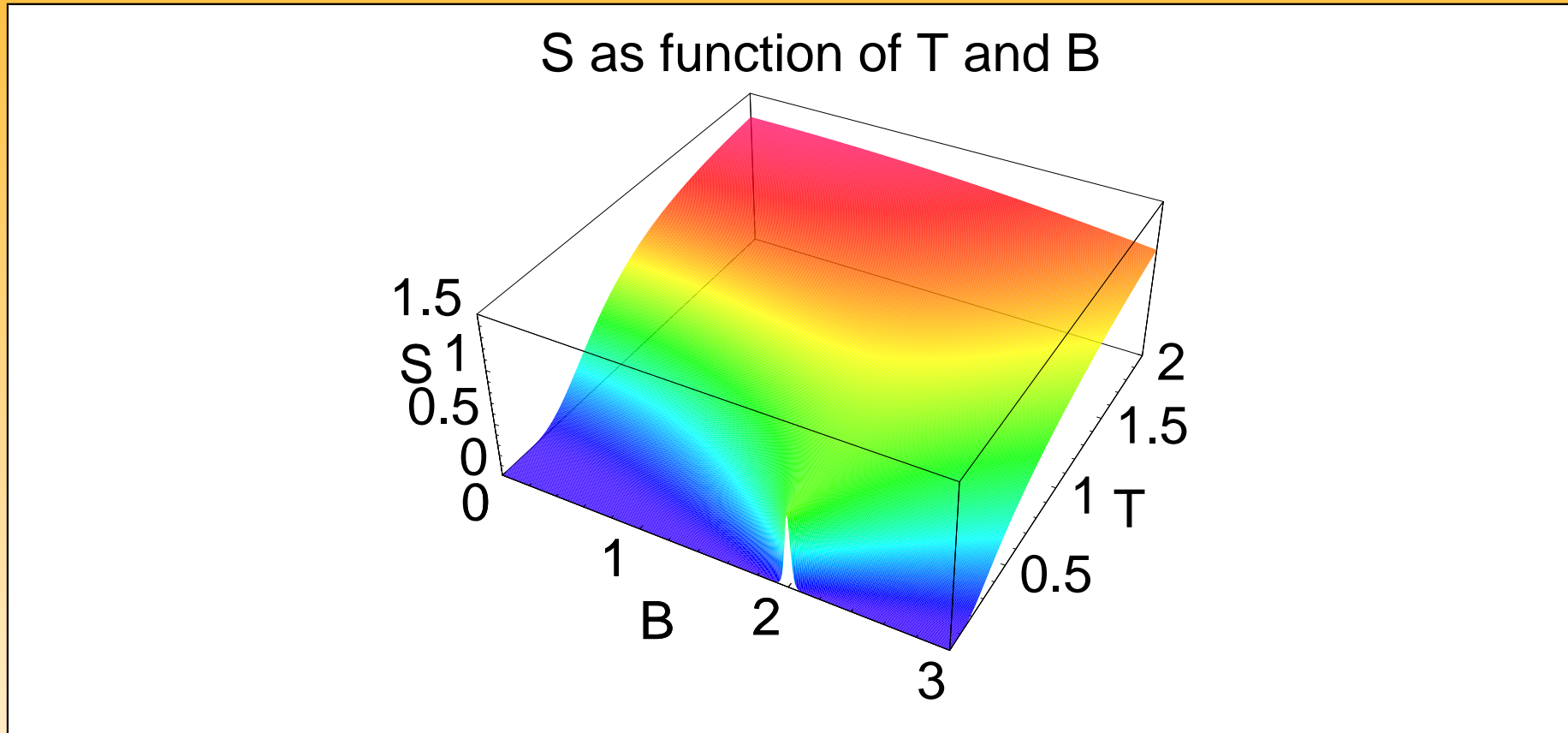
$S(T = 0, B) \neq 0$ at level crossing due to degeneracy

O. Derzhko, J. Richter, Phys. Rev. B **70**, 104415 (2004)

Enhanced magnetocaloric effect IV
Isentrops of af $s = 1/2$ dimer

T−B isentropes

blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

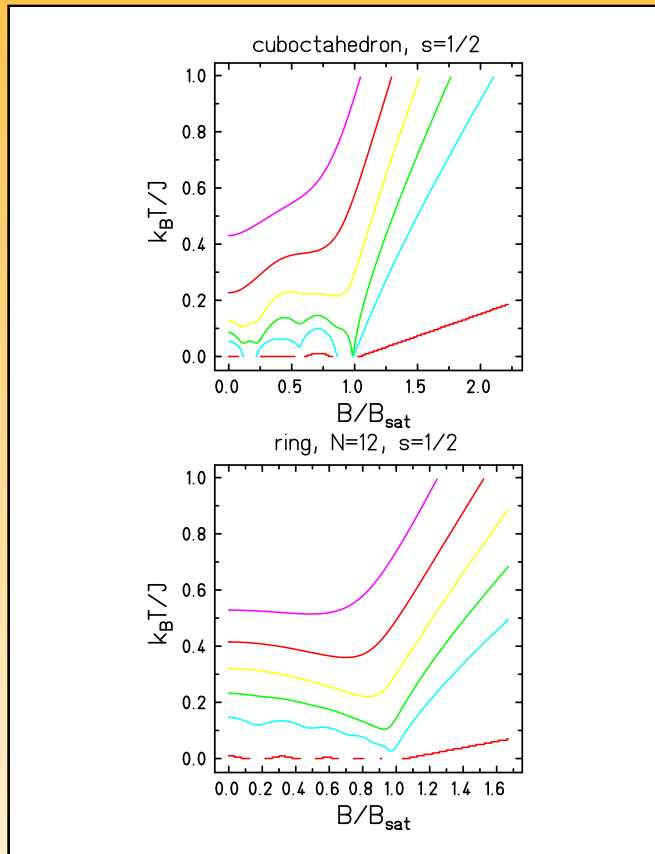(a) reduced,

(b) the same,

(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

Enhanced magnetocaloric effect V
Two molecular spin systems


cuboctahedron, s=1/2

ring, N=12, s=1/2

- Graphics: isentrops of the frustrated cubocta-hedron and a $N = 12$ ring molecule;

- Cuboctahedron features independent magnons and extraordinarily high jump to saturation;

- Degeneracy and $(T = 0)$–entropy at satura-tion field higher for the cuboctahedron;

- Adiabatic (de-) magnetization more efficient for the frustrated spin system.

no more time option

Metamagnetic phase transition I
Hyteresis without anisotropy
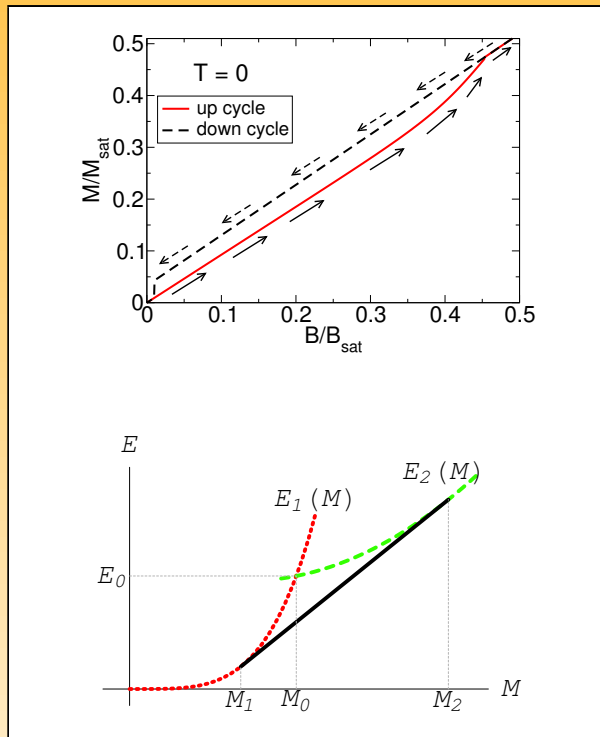
- Normally hysteretic behavior of Single Molecule Magnets is an outcome of magnetic anisotropy.

- The classical AF Heisenberg Icosahedron exhibits a pronounced hysteresis loop.

- It shows a first order phase transition at $T = 0$ as function of B.

- The minimal energies are realized by two families of spin configurations.

- The overall minimal energy curve is not convex $\Rightarrow$ magnetization jump.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)
D. Coffey and S.A. Trugman, Phys. Rev. Lett. **69**, 176 (1992).

Metamagnetic phase transition II
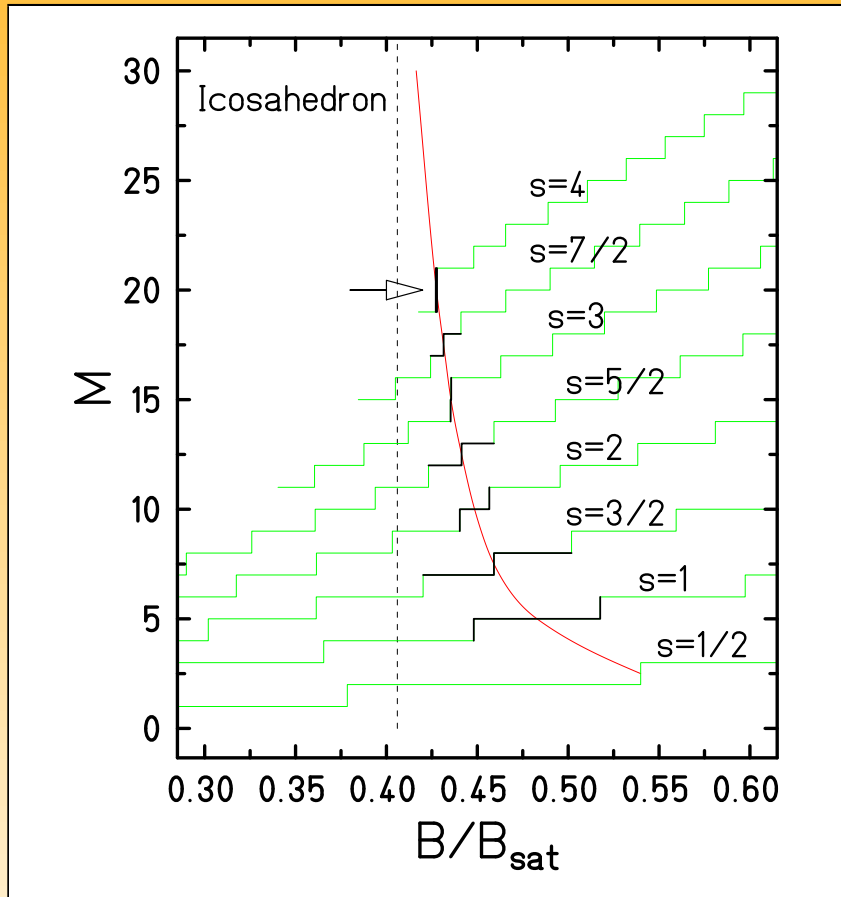
- Quantum analog:
  Non-convex minimal energy levels
  $\Rightarrow$ magnetization jump of $\Delta M > 1$.

- Lanczos diagonalization for various s.

- True jump of $\Delta M = 2$ for $s = 4$.

- Polynomial fit in $1/s$ yields the classically observed transition field.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)

no more time option

Summary

Frustration can lead to exotic behavior.

And, the end is not in sight, . . .

. . . , however, this talk is at its end!

Thank you very much for your attention.

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