# Frustration-induced exotic properties of magnetic molecules and low-dimensional antiferromagnets

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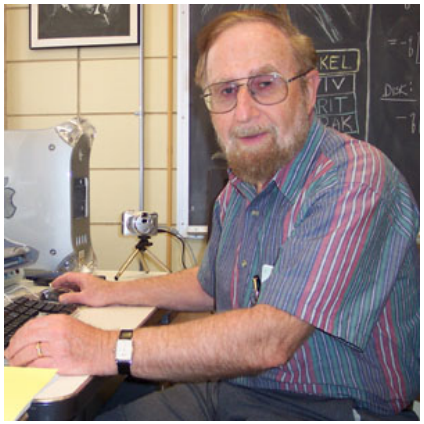
# In late 20th century people coming from

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. Shchelokovskyy, S. Torbrügge & M. Neumann, K. Küpper, M. Prinz (UOS);

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

- R.E.P. Winpenny (Man U, UK); L. Cronin (U. of Glasgow, UK);
  H. Nojiri (Tohoku University, Japan);

- A. Müller (U. Bielefeld) & Chr. Schröder (FH Bielefeld);
  J. Richter, J. Schulenburg, R. Schmidt (U. Magdeburg);
  S. Blügel, A. Postnikov (FZ Jülich); A. Honecker (U. Göttingen);
  E. Rentschler (U. Mainz); U. Kortz (IUB); A. Tennant, B. Lake (HMI Berlin);

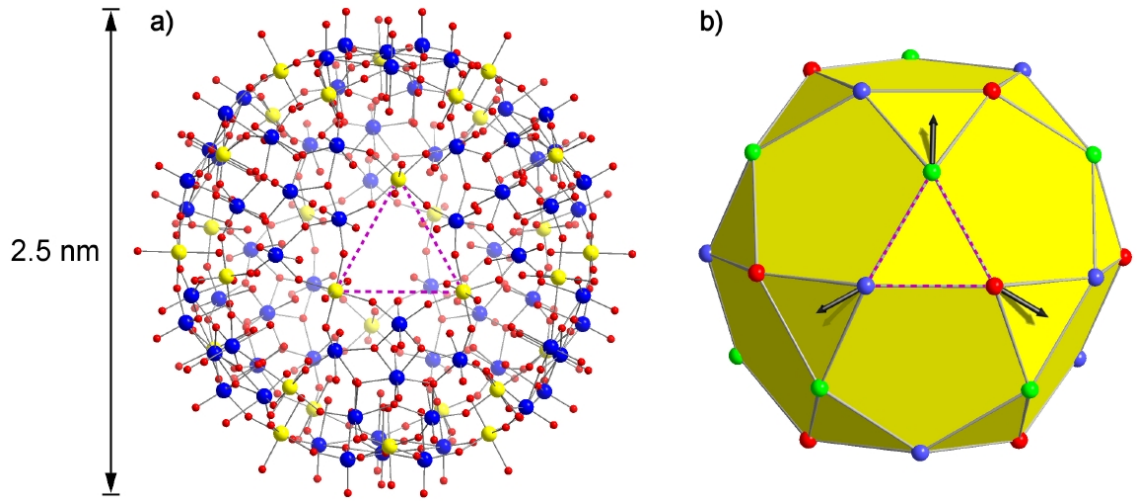
- B. Büchner, V. Kataev, R. Klingeler (IFW Dresden)

# . . . and various general results could be achieved

1. The suspects: magnetic molecules, esp. $\{\mathrm{Mo}_{72}\mathrm{Fe}_{30}\}$
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

# My favorite starting point

# $\{Mo_{72}Fe_{30}\}$ – 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)

# Model Hamiltonian – Heisenberg-Model

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

Exchange/Anisotropy Dzyaloshinskii-Moriya Zeeman

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

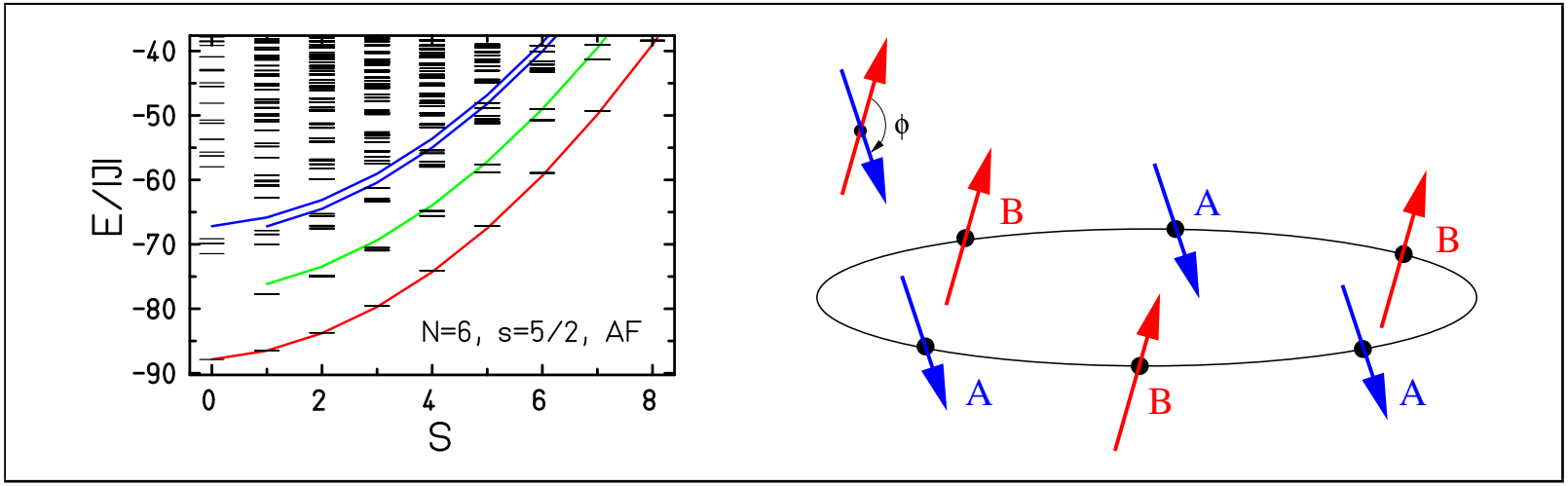
$$\underset{\sim}{H} = -\sum_{i,j} J_{ij} \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) + g \mu_B B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg Zeeman

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

# From rotational bands to giant magnetization jumps

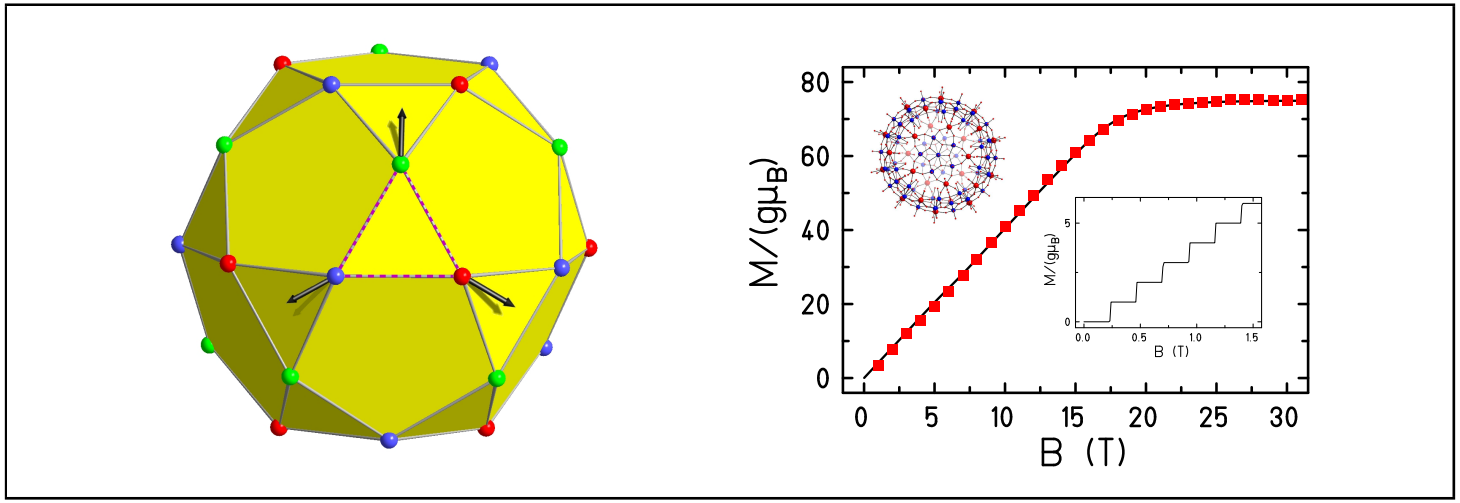
# Rotational bands in antiferromagnets I




- 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).

# Rotational bands in antiferromagnets II
# Approximate Hamiltonian for $\{\mathrm{Mo}_{72}\mathrm{Fe}_{30}\}$




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

Three sublattice system, classical $120^\circ$-ground state;
Good description of low-temperature magnetization.

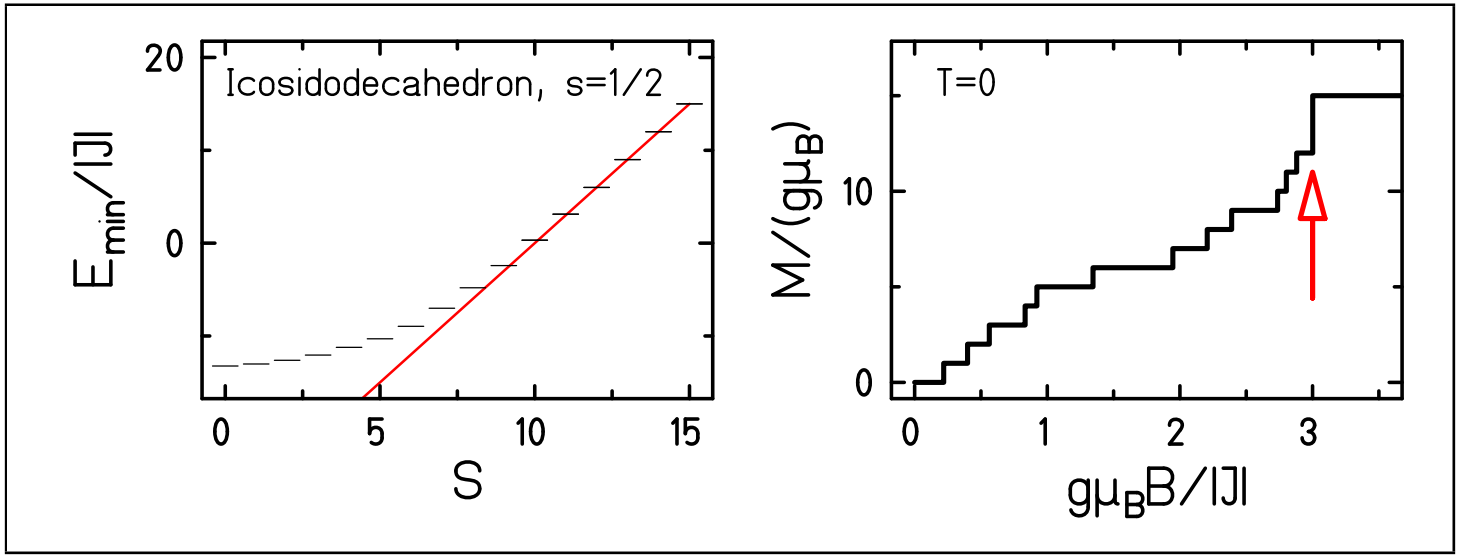
J. Schnack, M. Luban, R. Modler, Europhys. Lett. **56**, 863 (2001)

# Surprise!

The parabola is straight . . .

. . . at least at the top end!

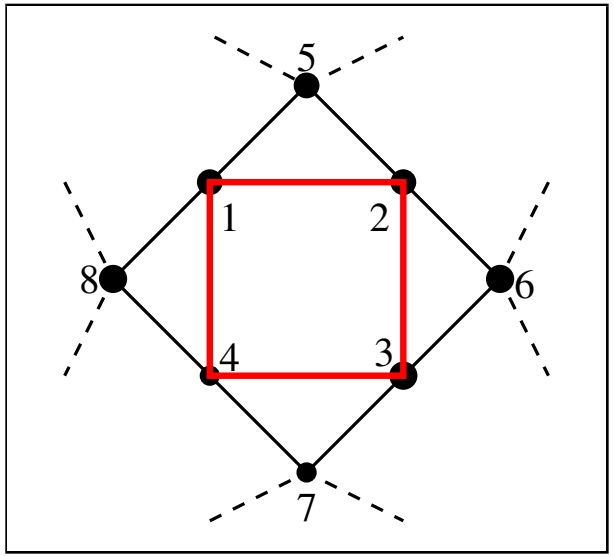
# Giant magnetization jumps in frustrated antiferromagnets I $\{\mathbf{Mo}_{72}\mathbf{Fe}_{30}\}$




- 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

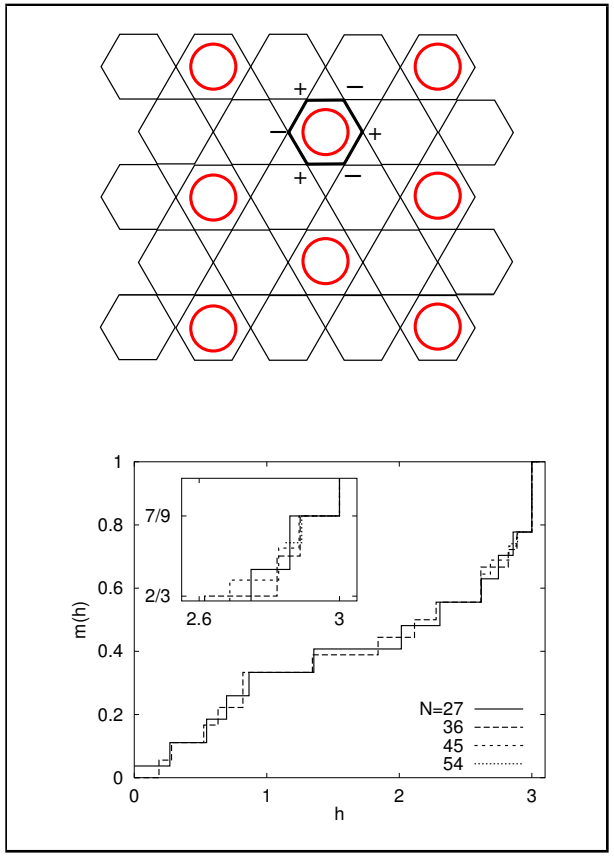



- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\,\ldots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$
- 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)

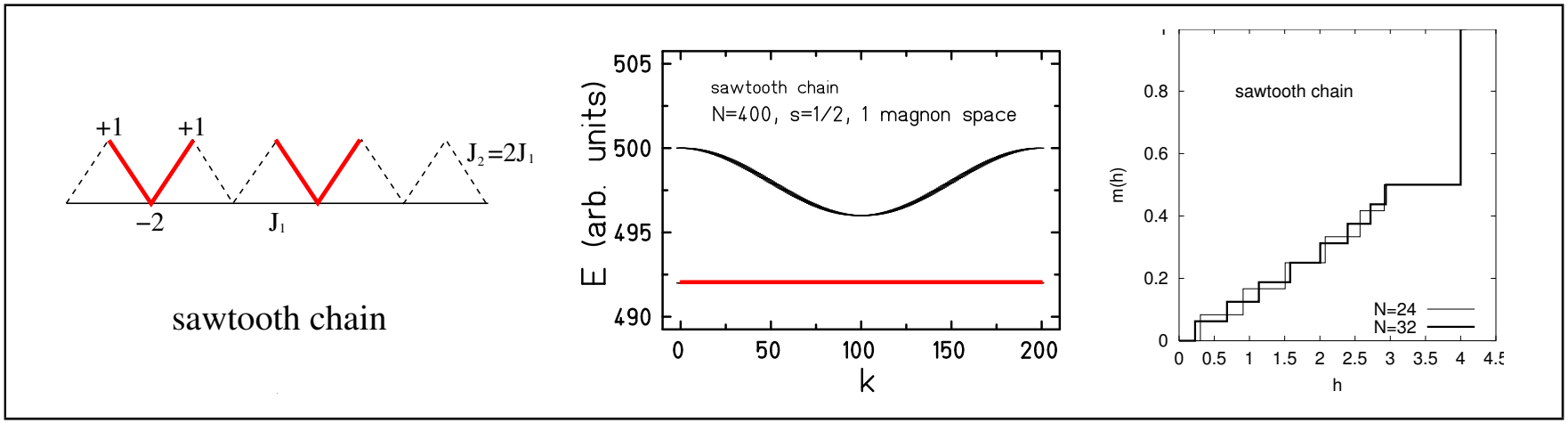
# Giant magnetization jumps in frustrated antiferromagnets III
# Kagome Lattice




- 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 $M = Ns - n$; Kagome: max. number of indep. magnons is N/9;
- Linear dependence of $E_{\text{min}}$ on $M$ $\Rightarrow$ 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, 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

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

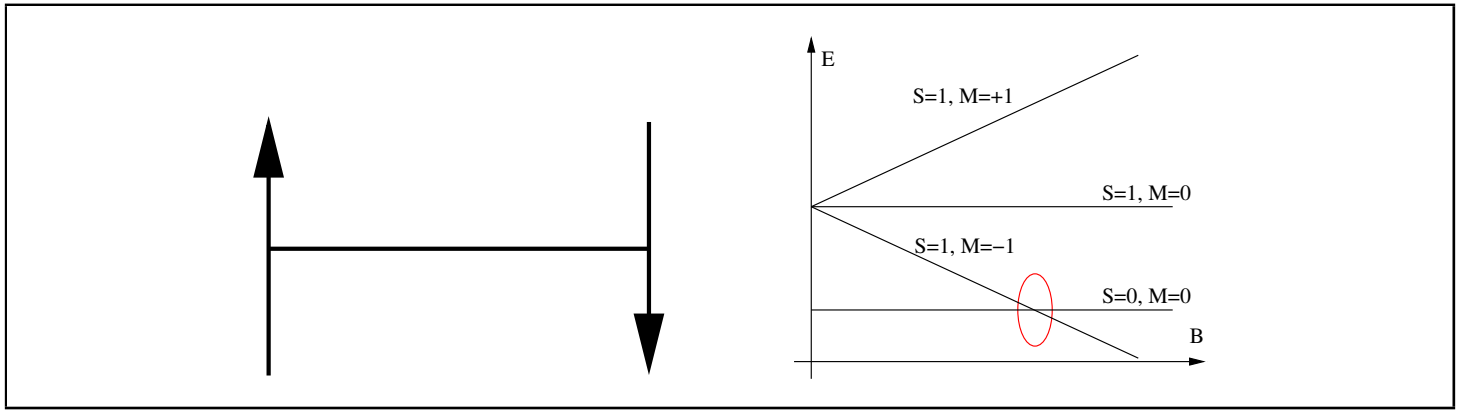
(adiabatic temperature change)

- 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)

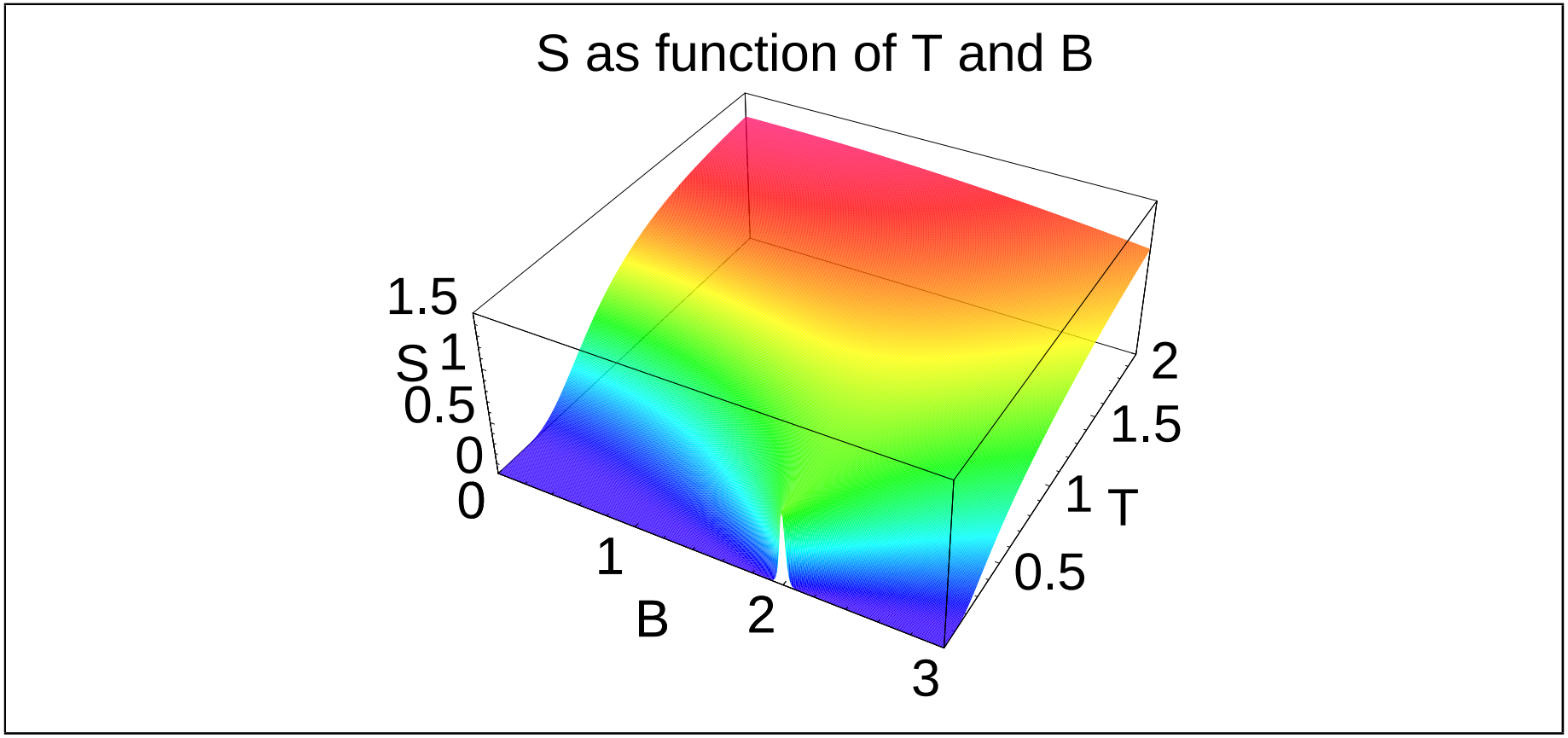
# Enhanced magnetocaloric effect II
# Simple af $s = 1/2$ dimer




- 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.

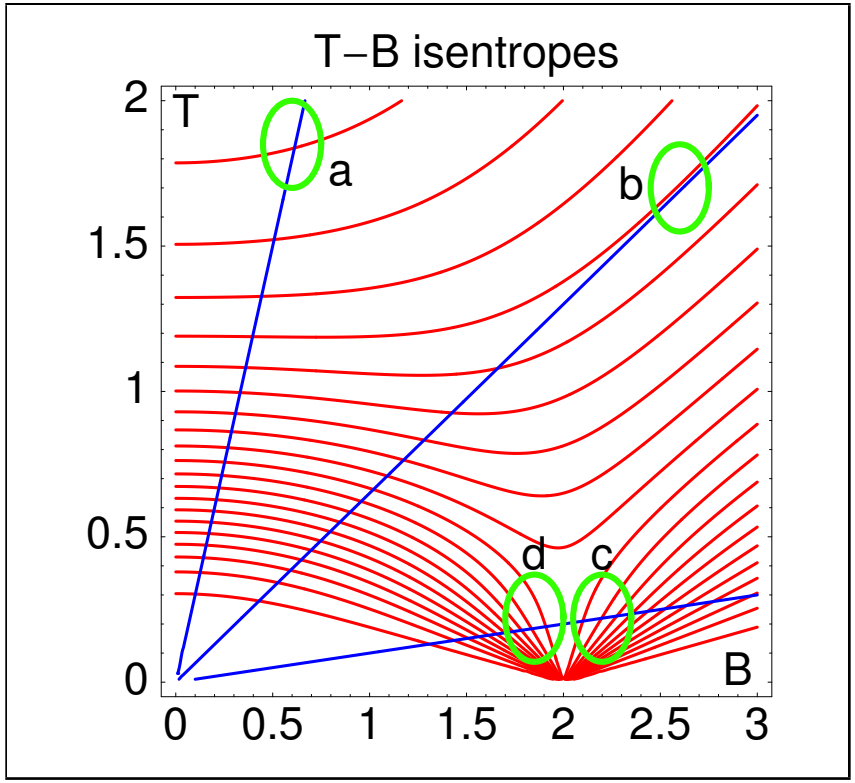
# Enhanced magnetocaloric effect III
# Entropy of af $s = 1/2$ dimer




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




blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

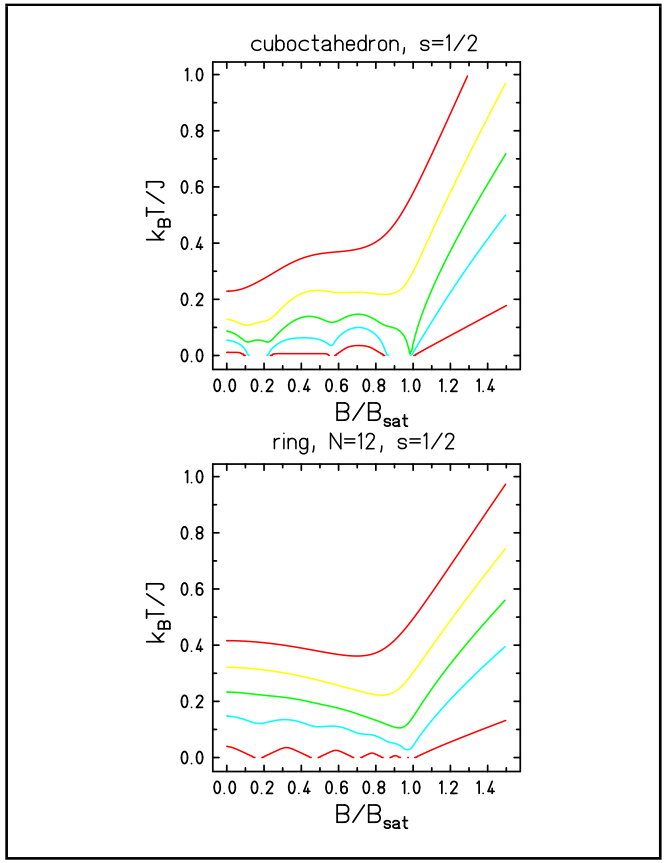
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

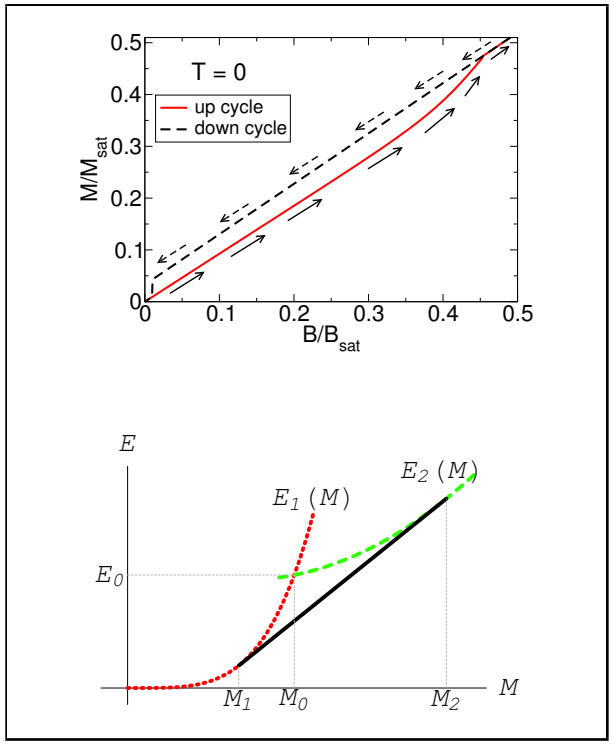
# Enhanced magnetocaloric effect V
# Two molecular spin systems




- Graphics: isentrops of the frustrated cuboctahedron and a $N = 12$ ring molecule;
- Cuboctahedron features independent magnons and extraordinarily high jump to saturation;
- Degeneracy and $(T = 0)$–entropy at saturation field higher for the cuboctahedron;
- Adiabatic (de-) magnetization more efficient for the frustrated spin system.

no more time option

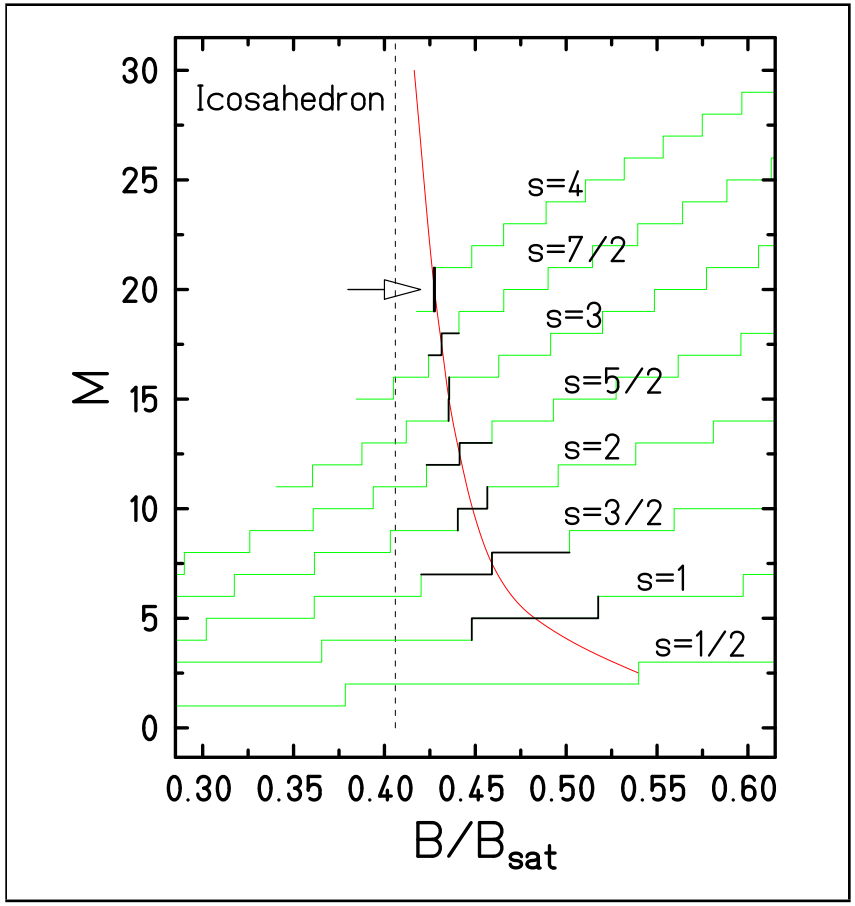
# Metamagnetic phase transition I
# Hyteresis without anisotropy




- 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)

# 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.

German Molecular Magnetism Web

# www.molmag.de

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