Frustration effects in magnetic molecules probed in high fields

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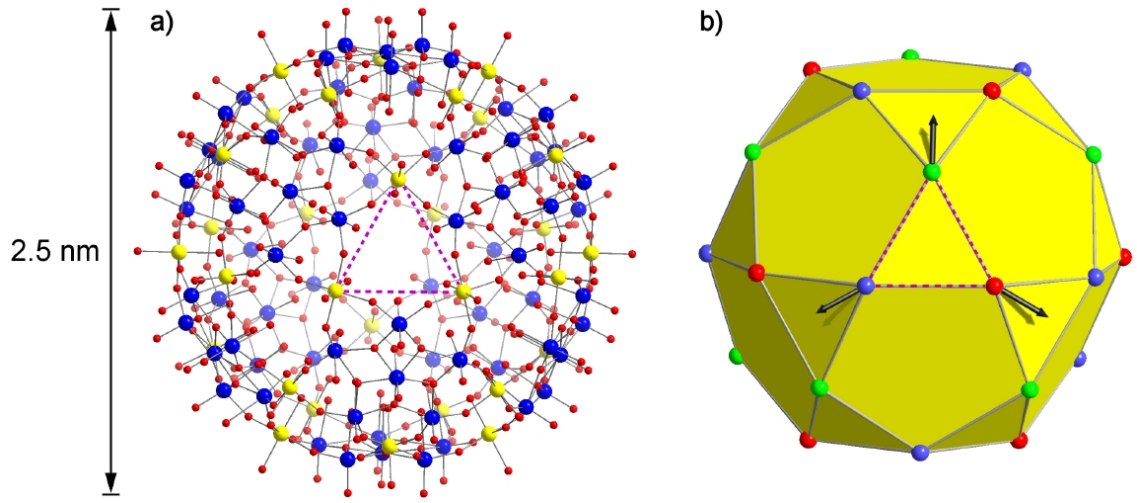
. . . who helped to obtain various general results

1. Extension of Lieb, Schultz, and Mattis: k–rule for odd spin rings
2. Rotational bands in antiferromagnets
3. Giant magnetization jumps in frustrated antiferromagnets
4. Enhanced magnetocaloric effect
5. Magnetization plateaus and susceptibility minima
6. Hysteresis without anisotropy
7. Magnetostriction on the molecular level
8. Spin tubes, molecular chains and lattices

My favorite starting point

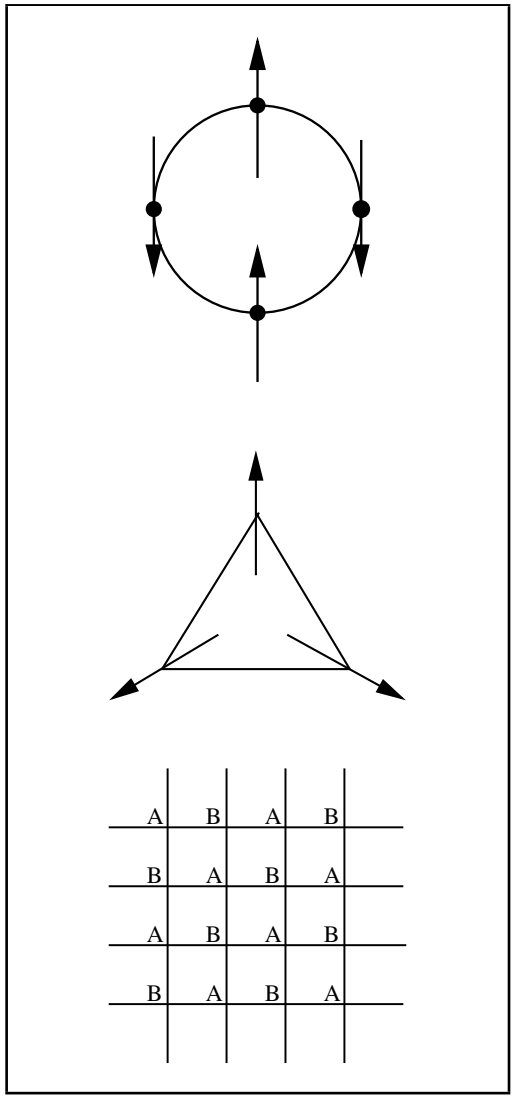
$\{Mo_{72}Fe_{30}\}$ – a molecular brother of the kagome lattice and an archetype of geometric frustration



- 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)

Definition of frustration



- You talk and everybody sleeps already at slide 3!
- Simple: An antiferromagnet is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.
- Advanced: A non-bipartite antiferromagnet is frustrated. 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).

(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)

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 . . .

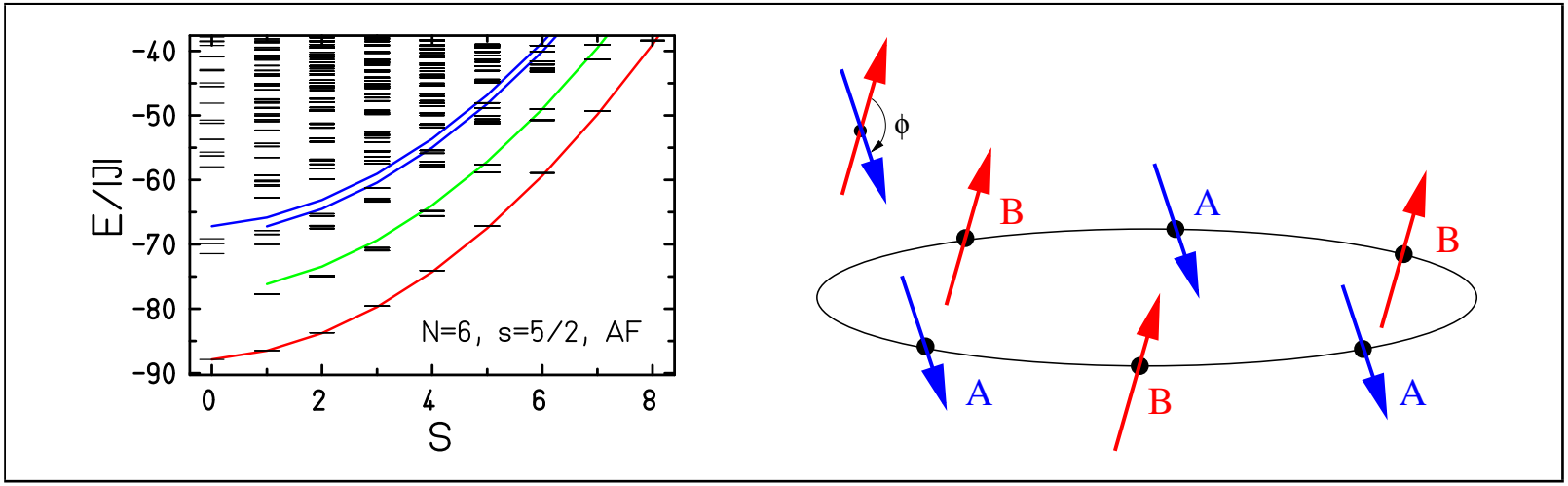
$$\underset{\sim}{H} = -\sum_{i,j} J_{ij} \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) + g \mu_B B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg Zeeman

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

Rotational bands in antiferromagnets

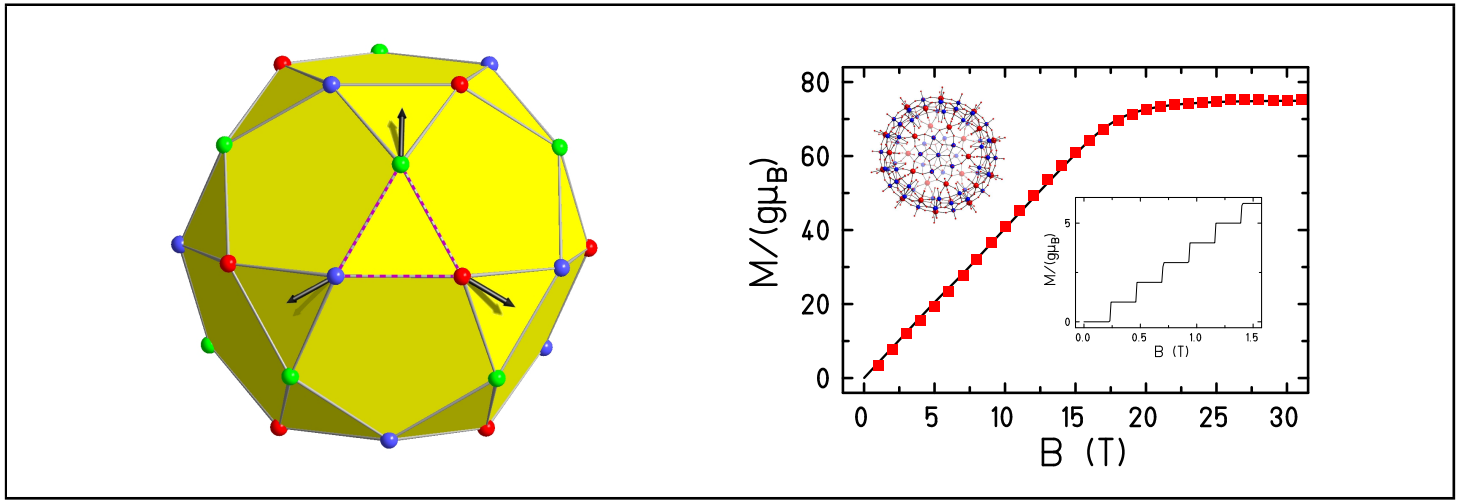
Rotational bands in antiferromagnets I



- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- For bipartite systems (2,3): $\underset{\sim}{H}^{\text{eff}} = -2\, J_{\text{eff}}\, \underset{\sim}{\vec{S}}_A \cdot \underset{\sim}{\vec{S}}_B$;
- 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 $\{\mathrm{Mo}_{72}\mathrm{Fe}_{30}\}$



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

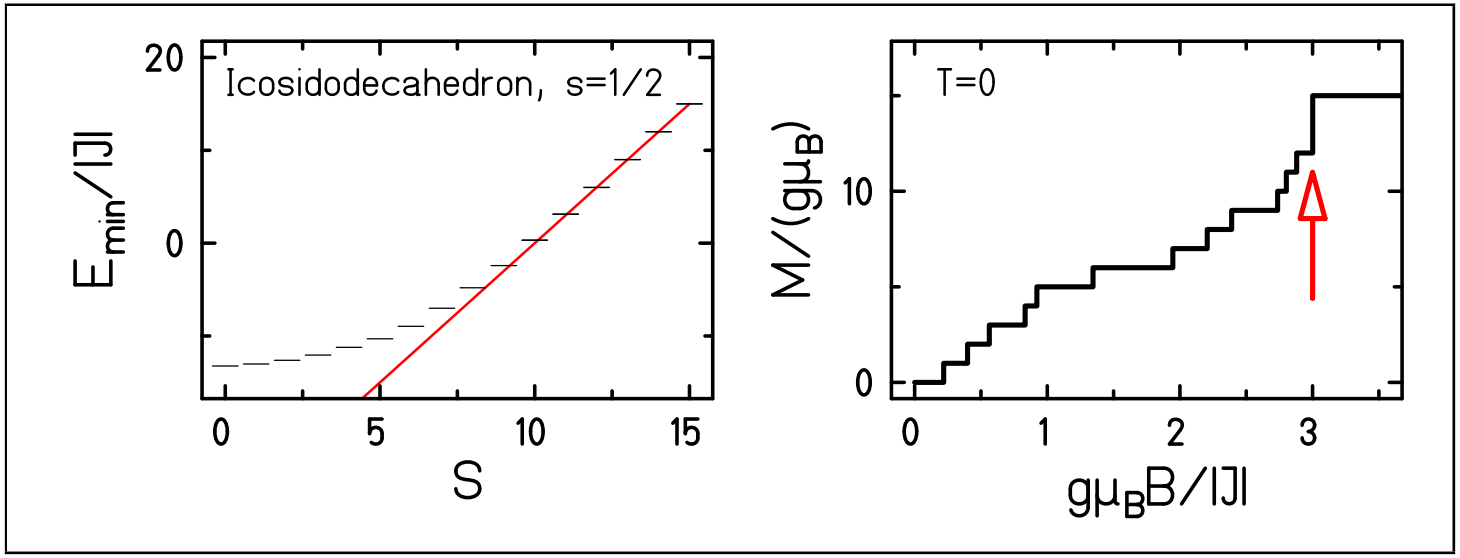
Three sublattice system, classical $120°$-ground state;

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)

Giant magnetization jumps

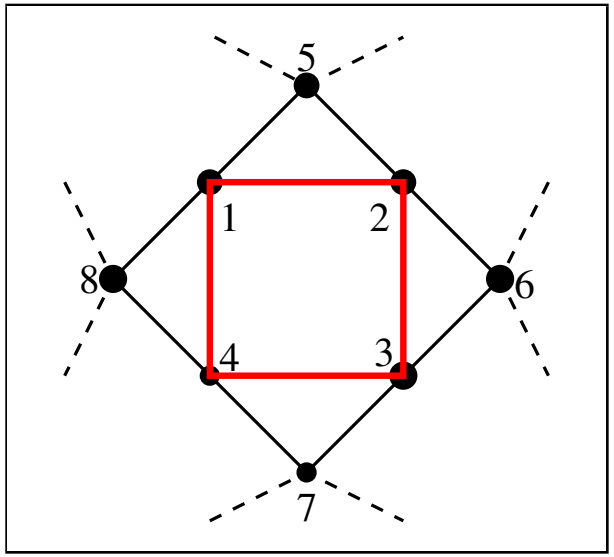
Giant magnetization jumps in frustrated antiferromagnets I $\{\mathbf{Mo}_{72}\mathbf{Fe}_{30}\}$



- 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

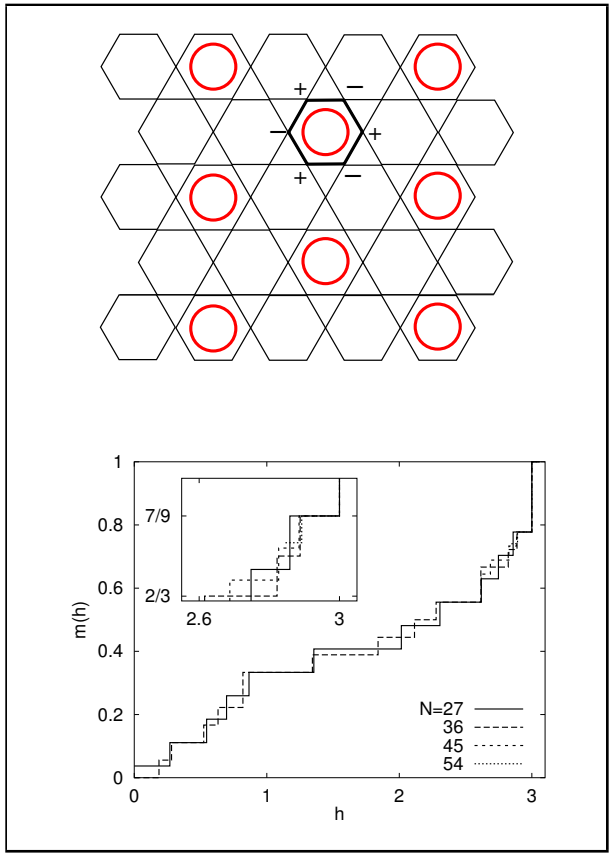


- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\,\ldots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$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

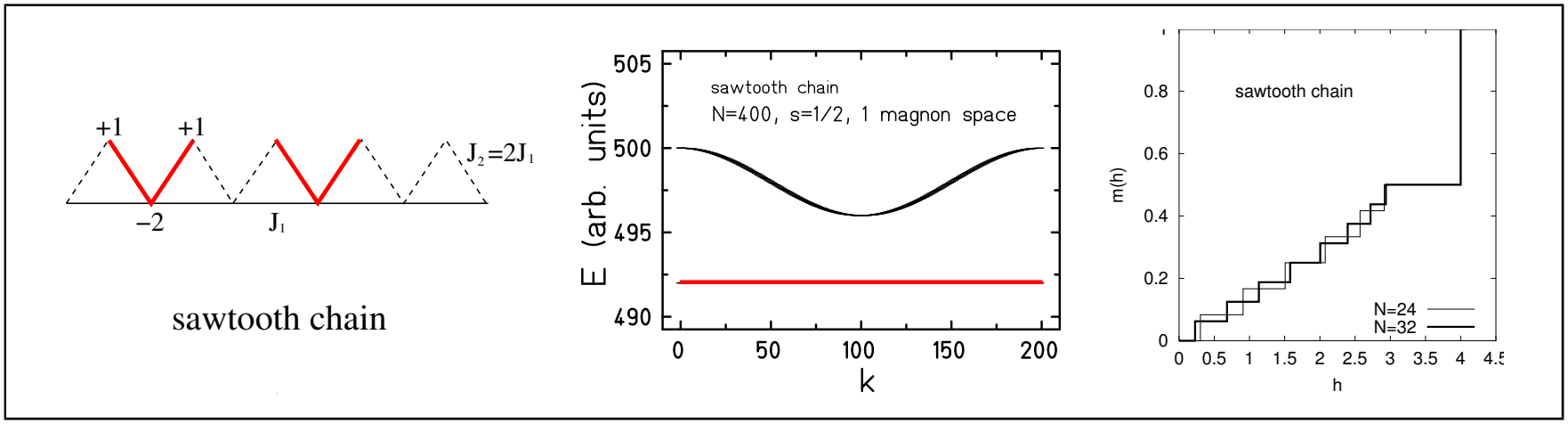
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- 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_{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

Enhanced magnetocaloric effect I
Basics

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

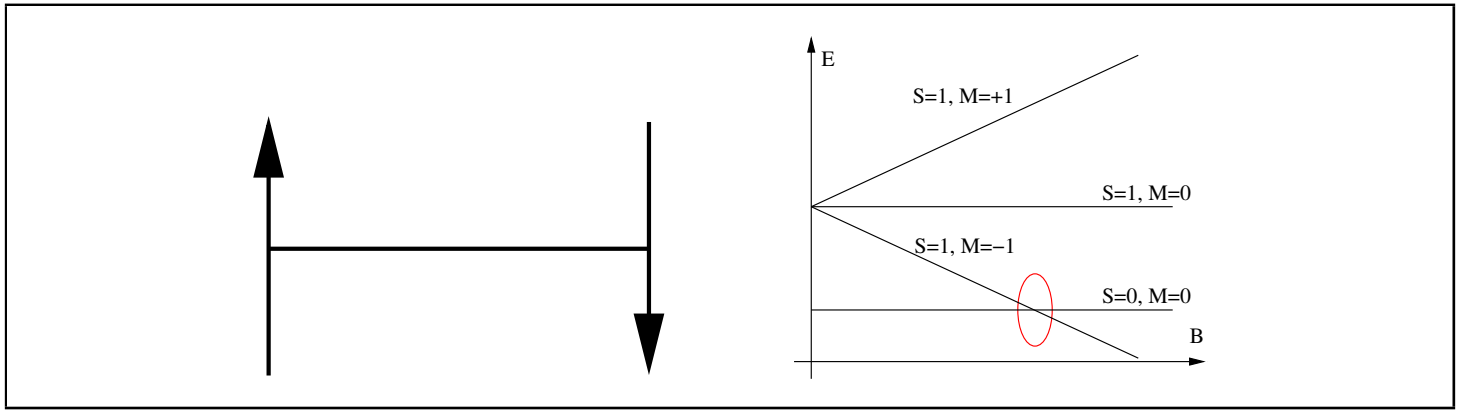
(adiabatic temperature change)

- 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)

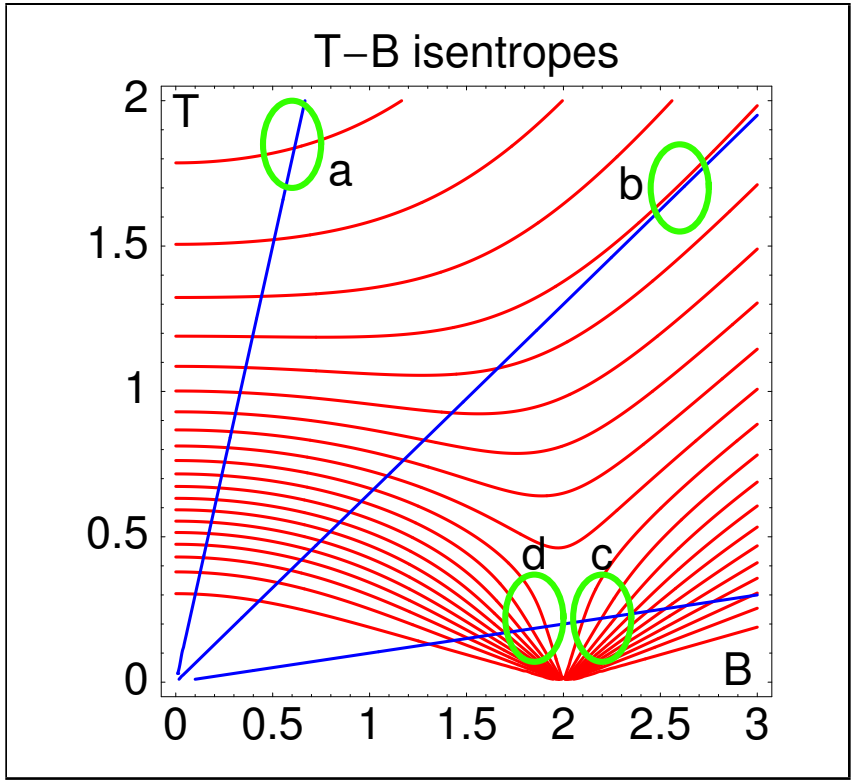
Enhanced magnetocaloric effect II
Simple af $s = 1/2$ dimer



- 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 IV
Isentrops of af $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

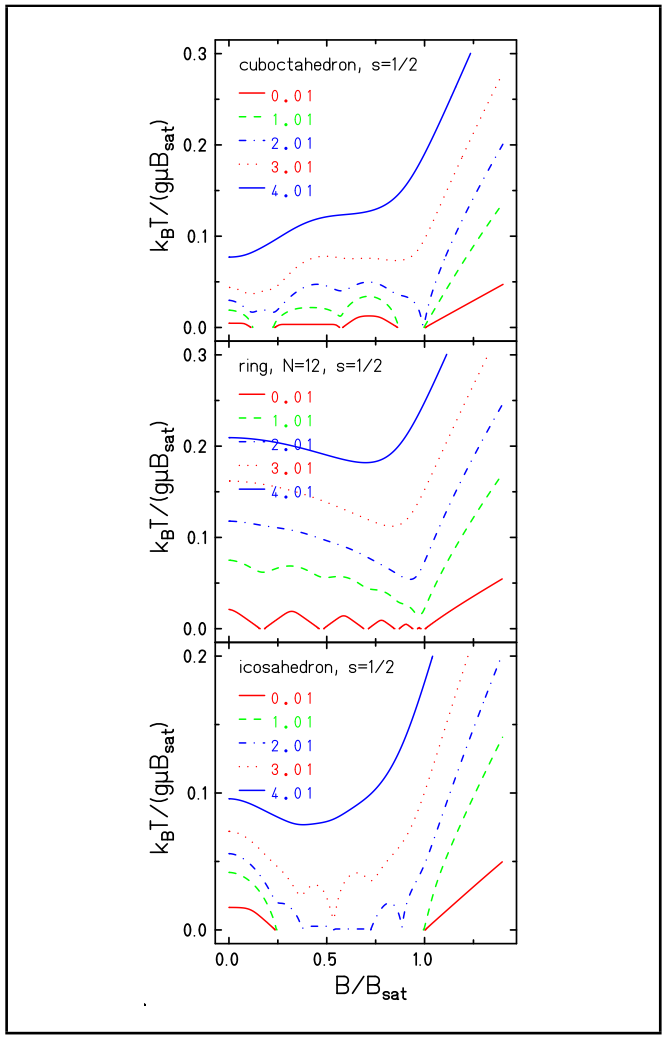
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

Enhanced magnetocaloric effect V
Two molecular spin systems

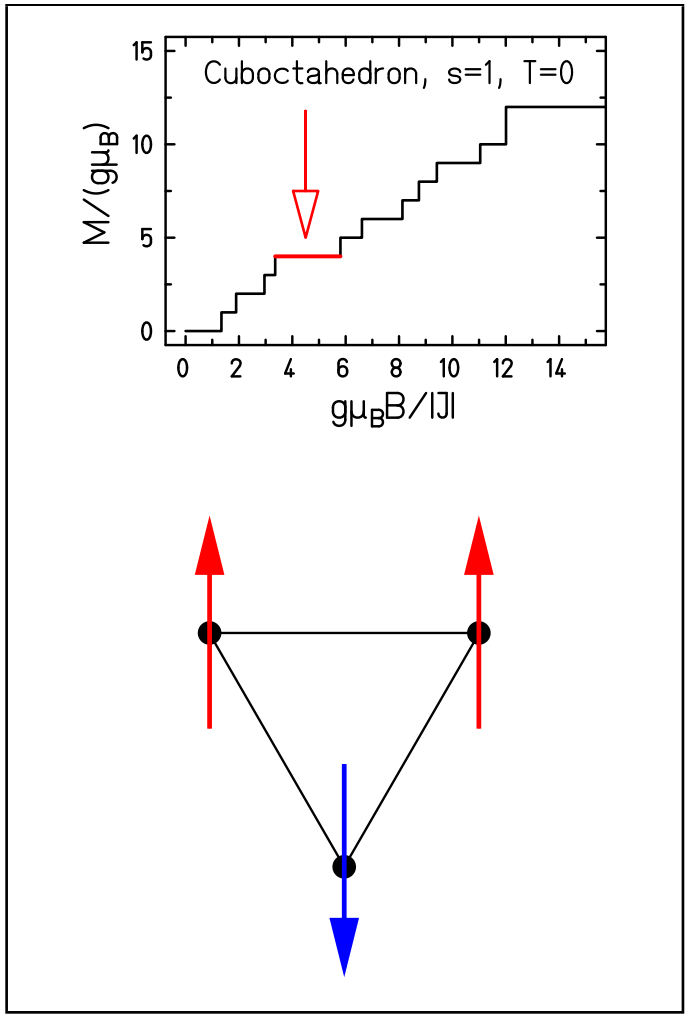


- Graphics: isentrops of the frustrated cuboctahedron, non-frustrated ring ($N = 12$), and the frustrated icosahedron;
- Cuboctahedron: independent magnons and high jump to saturation, i.e. high cooling rate;
- Ring: normal level crossing, normal jump;
- Icosahedron: unusual behavior due to edge-sharing triangles, many high degeneracies all over the spectrum; high cooling rate.

(1) J. Schnack, R. Schmidt, J. Richter, submitted, cond-mat/0703480

Magnetization plateaus

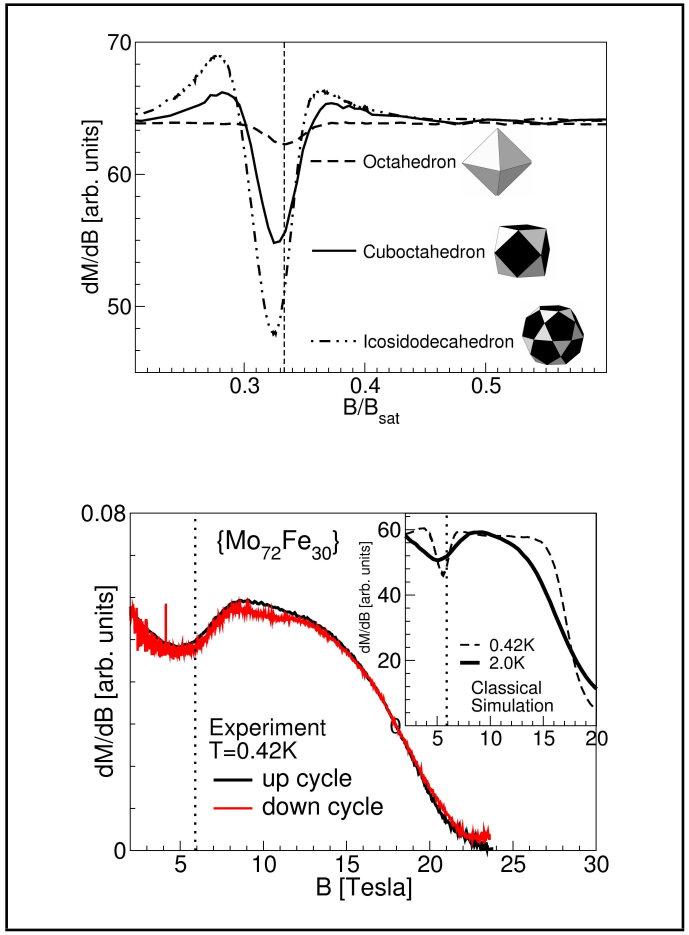
Magnetization plateaus and susceptibility minima



- Octahedron, Cubocthedron, Icosidodecahedron: little (polytope) brothers of the kagome lattice with increasing frustration.
- Cubocthedron & Icosidodecahedron realized as magnetic molecules.
- Cubocthedron, Icosidodecahedron & kagome feature plateaus, e.g. at $\mathcal{M}_{\text{sat}}/3$.
- Plateau at $\mathcal{M}_{\text{sat}}/3$ due to **uud**–configuration. This configuration contributes substantially to the classical partition function; it is stabilized by quantum fluctuations (typical quantum balder-dash).

C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, P. Kögerler, Phys. Rev. Lett. **94**, 017205 (2005)

Magnetization plateaus and susceptibility minima

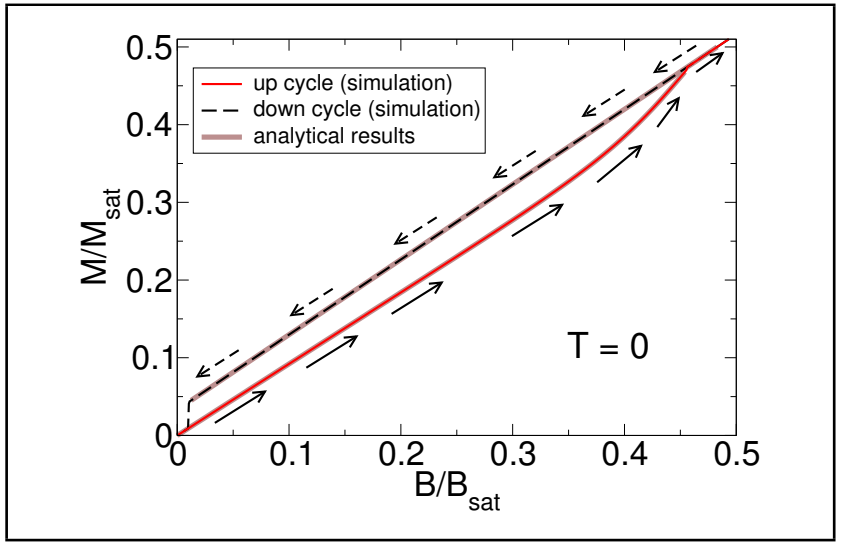


- Susceptibility shows a pronounced dip at $B_{\text{sat}}/3$ (classical calculations and quantum calculations for the cuboctahedron).
- Obvious in case of plateau at $\mathcal{M}_{\text{sat}}/3$, more subtle for other frustrated systems.
- Experimentally verified for $\{\text{Mo}_{72}\text{Fe}_{30}\}$.

C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, P. Kögerler, Phys. Rev. Lett. **94**, 017205 (2005)

Hysteresis without anisotropy

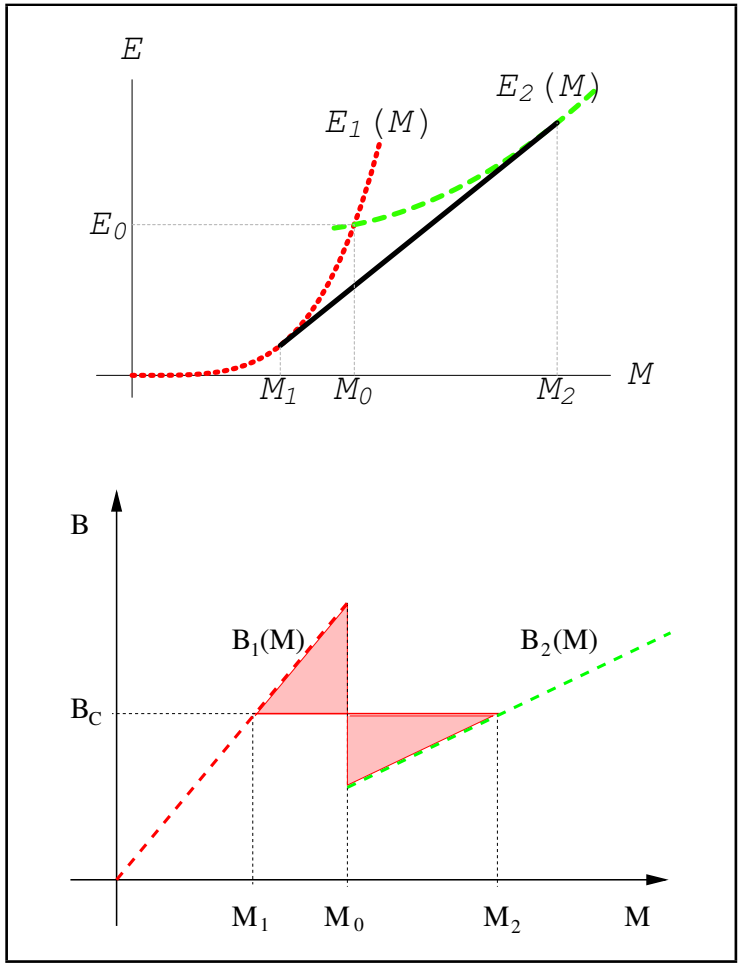
Metamagnetic phase transition I
Hysteresis without anisotropy



- Heisenberg model with isotropic nearest neighbor exchange
- Hysteresis behavior of the classical icosahedron in an applied magnetic field.
- Classical spin dynamics simulations (thick lines).
- Analytical stability analysis (grey lines).

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

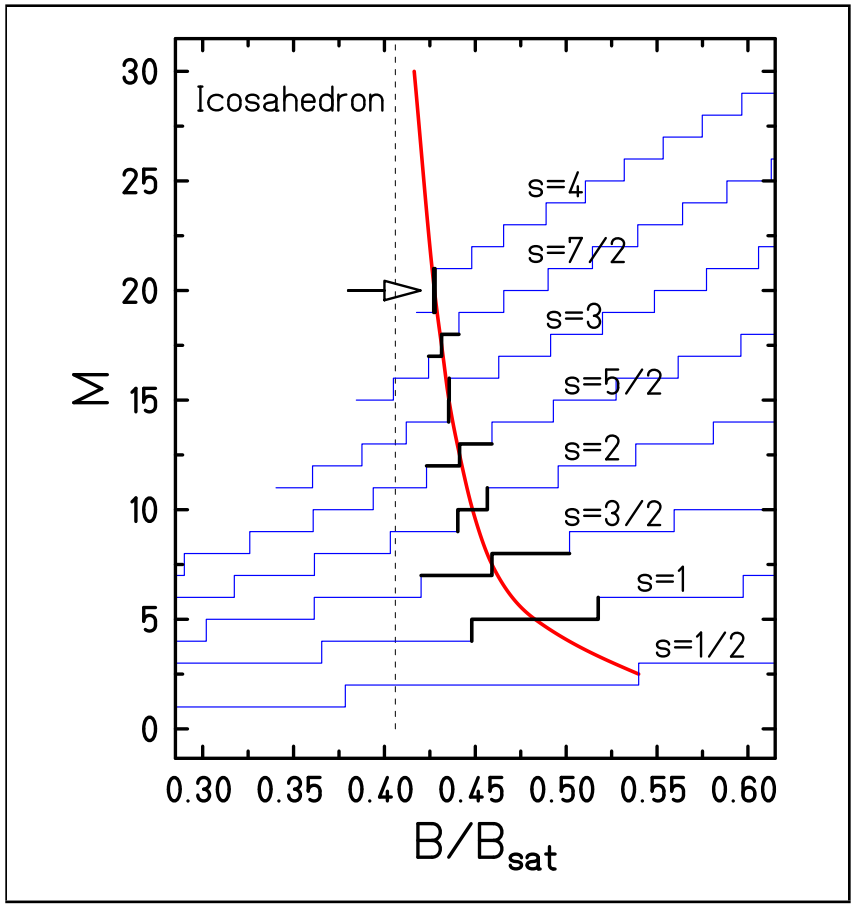
Metamagnetic phase transition II
Non-convex minimal energy



- Minimal energies realized by two families of spin configurations (1): $E_1(M)$ – "4-θ-family", $E_2(M)$ – "decagon family"
- Overall minimal energy curve is not convex.
- Maxwell construction yields ($T = 0$) 1st order phase transition at B_c (1,2,3)
- ($T = 0$)–magnetization dynamics extends into metastable region.

(1) C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)
(2) D. Coffey and S.A. Trugman, Phys. Rev. Lett. **69**, 176 (1992)
(3) C. Lhuillier and G. Misguich, in *High Magnetic Fields*, Eds. C. Berthier, L. Levy, and G. Martinez, Springer (2002) 161-190

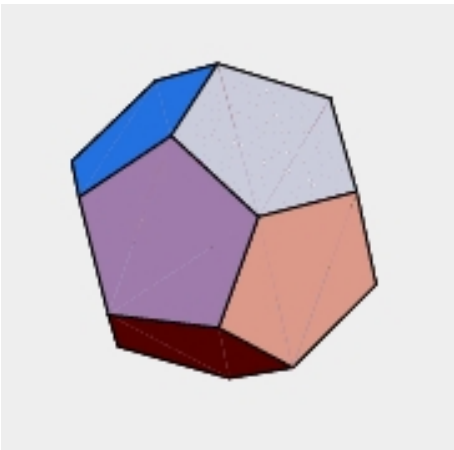
Metamagnetic phase transition III
Quantum icosahedron



- 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)

Similar transitions



- First noticed in the context of the Buckminster fullerenes C_{20} and C_{60} (1).
- It seems to be important that the ground state is not coplanar and spins do not fold umbrella-like in field. The symmetry of low-field and high-field ground states needs to be different;
  Counter examples: $\{Mo_{72}Fe_{30}\}$, kagome lattice.
- This phase transition exists for many polytopes with icosahedral symmetry: numerical investigations for $20 \leq n \leq 720$ by N.P. Konstantinidis (2).

(1) D. Coffey and S.A. Trugman, Phys. Rev. Lett. **69**, 176 (1992).
(2) N.P. Konstantinidis, unpublished.

Summary and Outlook

1. Frustrated molecules such as cuboctahedron and icosidodecahedron share many properties with the kagome lattice, i.e. besides being interesting on their own, they help to understand certain frustrated lattices.

2. Does bistability (hysteresis) exist in quantum versions of certain frustrated molecules (icosahedron, dodecahedron)?
   Any implications for buckyballs (Hubbard model)?

3. High-fields indispensable for an understanding of magnetic molecules. Many molecules are thus so far not understood!!!

4. Magnetostriction in $\{Ni_4Mo_{12}\}$ was discovered using high fields.

5. x-ray at high fields would be a valuable tool to prove magnetostriction.
   $\Rightarrow$ Hiroyuki Nojiri

I hope I could show you, that

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

Highlights. Tutorials. Who is who. DFG SPP 1137