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

Jürgen Schnack

Department of Physics – University of Bielefeld – Germany

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

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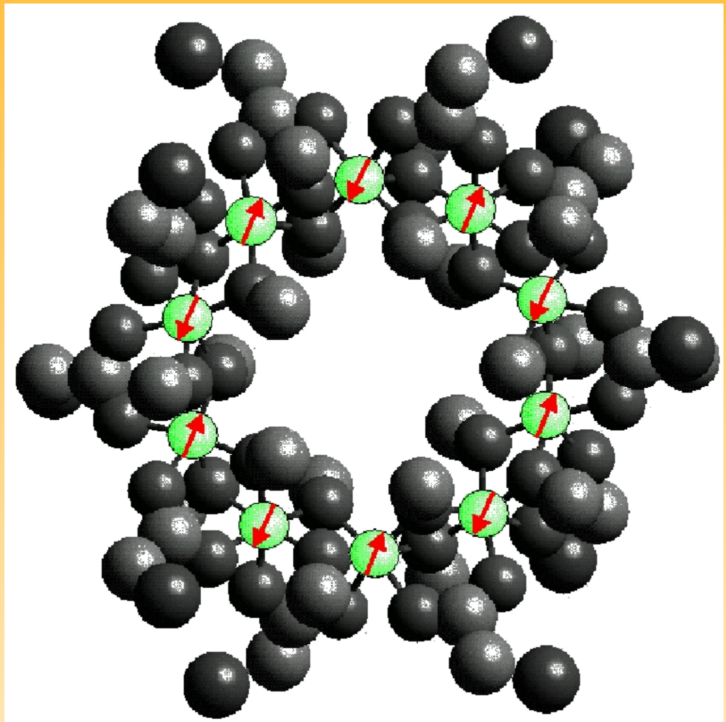
Contents for you today

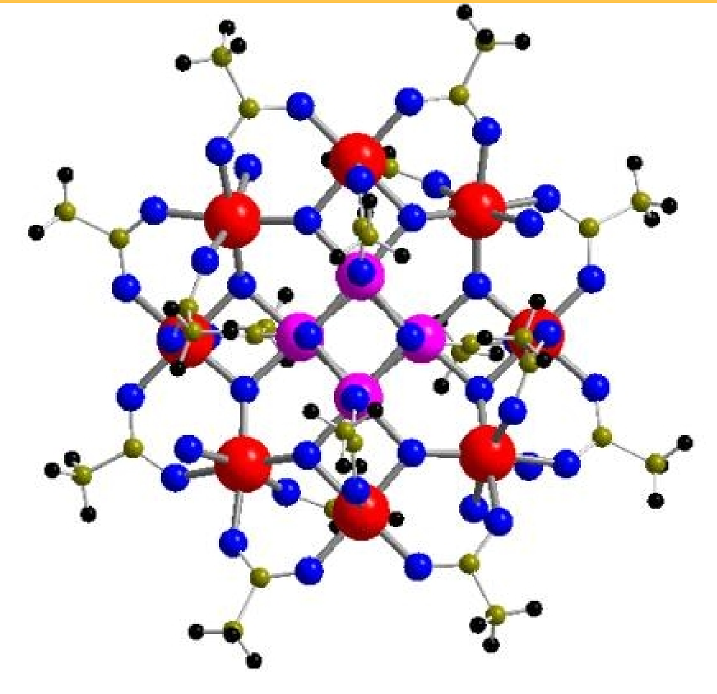


Fe_{10}

1. The suspects: magnetic molecules
2. Our research philosophy
3. Fe_{30} and friends
4. Metamagnetic phase transitions
5. Magnetostriction on the molecular level?

Magnetic Molecules

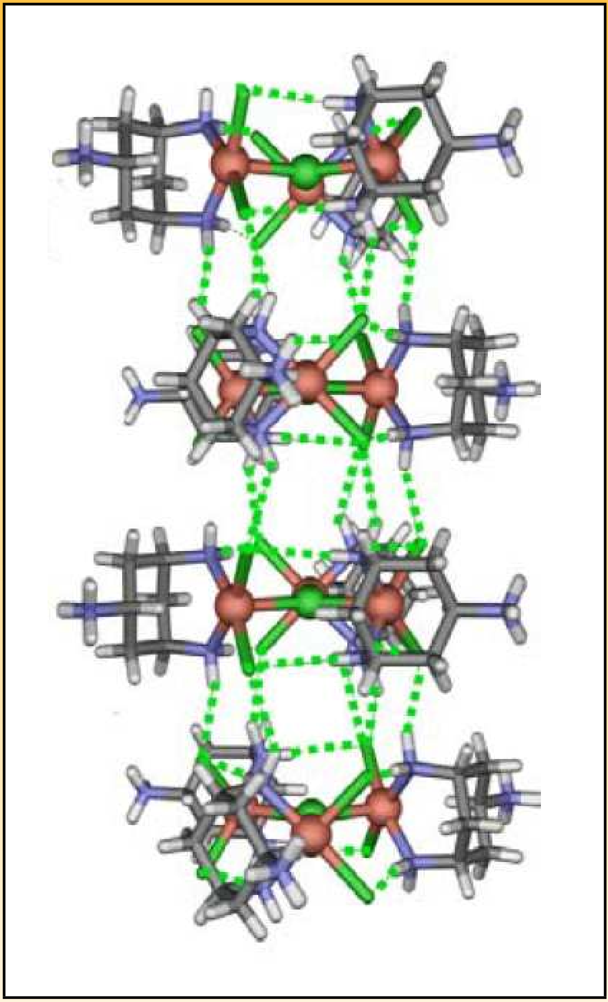
The beauty of magnetic molecules I



Mn_{12}

- Inorganic or organic macro molecules, 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);
- Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, transparent magnets, qubits for quantum computers.

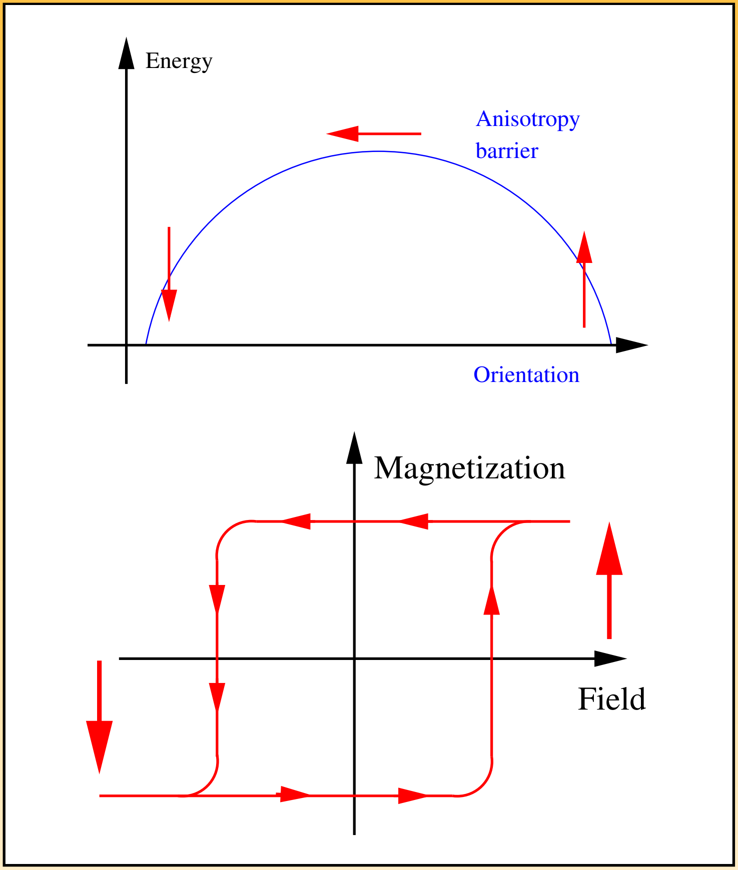
The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron and chromium rings
- 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:

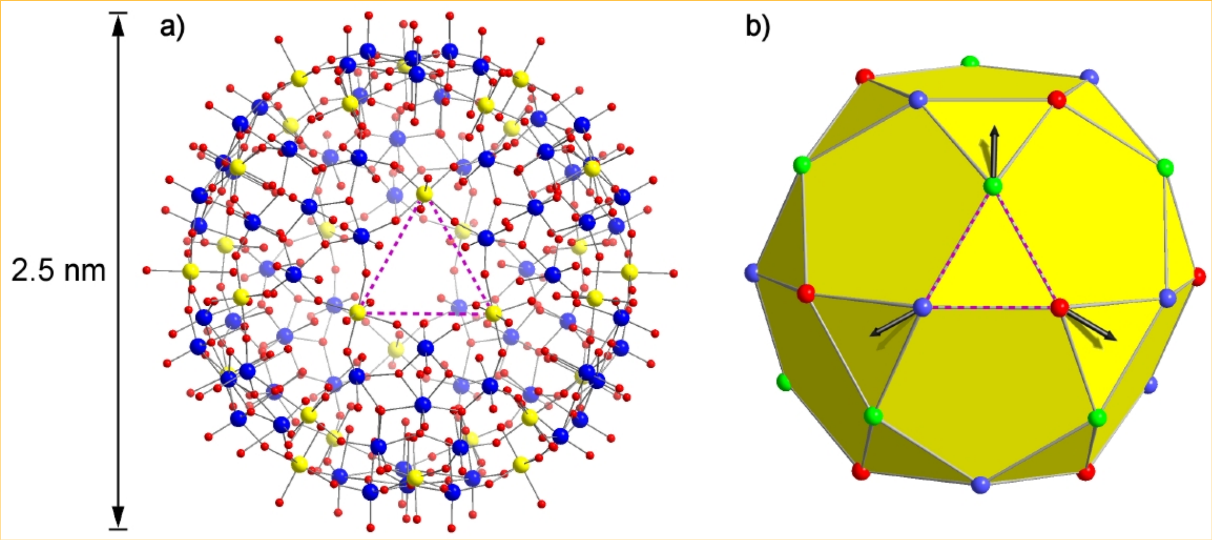
  J. Schnack, H. Nojiri, P. Kögerler, G. J. T. Cooper, L. Cronin, Phys. Rev. B 70, 174420 (2004); Sato, Sakai, Läuchli, Mila, . . .

The beauty of magnetic molecules III



- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment; e.g. $S = 10$ for Mn_{12} or Fe_8
- Anisotropy barrier dominates behavior (as in your hard drive);
- Single molecule is a magnet and shows metastable magnetization and hysteresis; but also magnetization tunneling.
- Today's major efforts: improve stability of magnetization; investigate on surfaces.

The beauty of magnetic molecules IV
$\{$Mo$_{72}$Fe$_{30}\}$ – a giant magnetic Keplerate molecule



- Structure: Fe - yellow, Mo - blue, O - red;
- Exciting magnetic properties (1).
- Quantum treatment very complicated, dimension of Hilbert space $(2s+1)^N \approx 10^{23}$ (2).

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

Our research philosophy

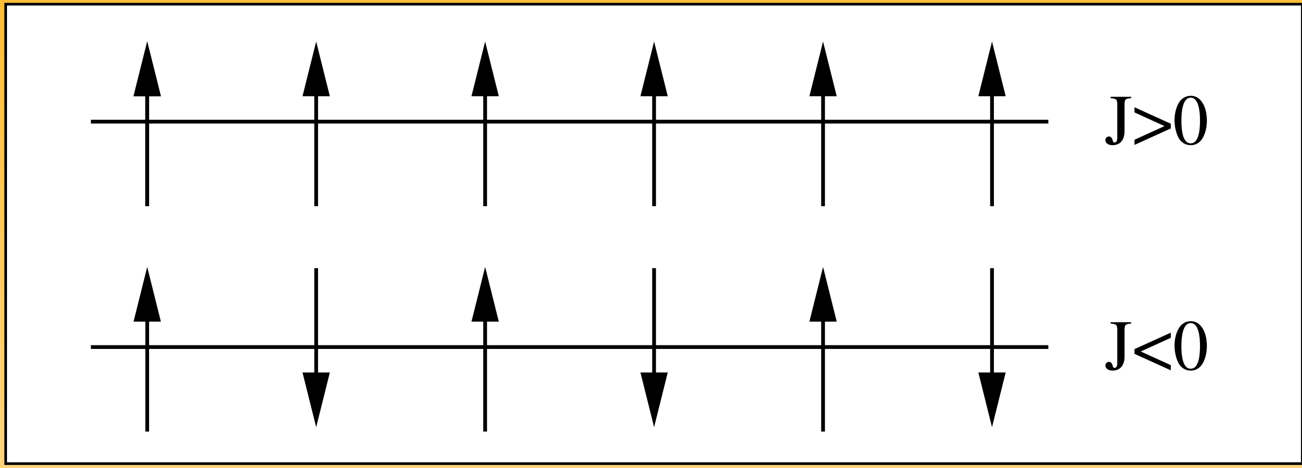
Philosophy of our research

- There are known knowns.
- There are known unknowns.
- And there are unknown unknowns.

Donald Rumsfeld

Let's start with the known knowns.

Basic magnetism



- **Heisenberg model:** $\underset{\sim}{H} = -J \sum_{<i,j>} \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j)$
- **paramagnet:** single moment, can align in a magnetic field;
- **ferromagnet:** parallel moments, $J > 0$;
- **antiferromagnet:** antiparallel moments, $J < 0$.;
- **diamagnet:** no permanent moment; moment can be induced by an applied magnetic field.

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

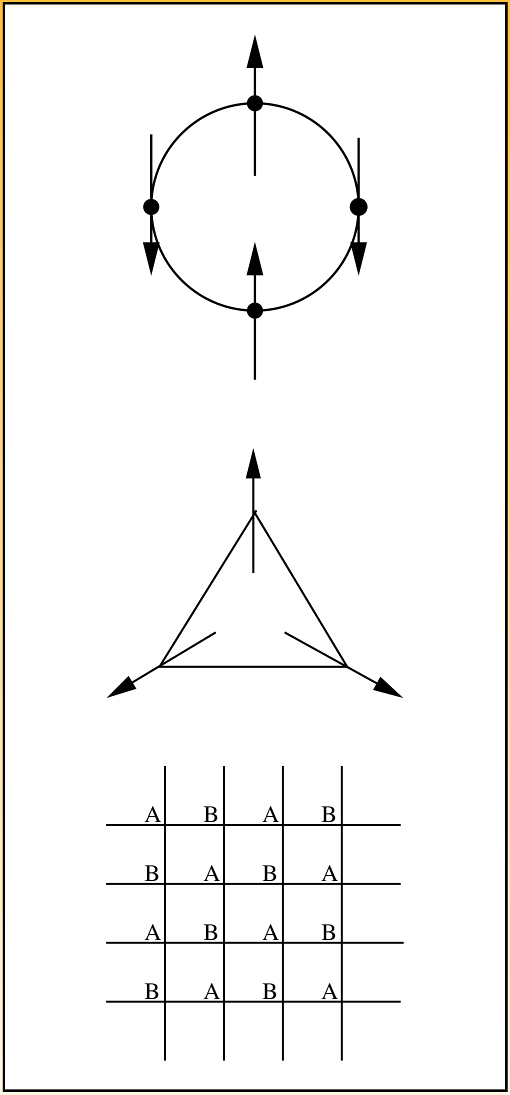
Very often anisotropic terms are utterly negligible, then . . .

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

Heisenberg Zeeman

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

Definition of frustration



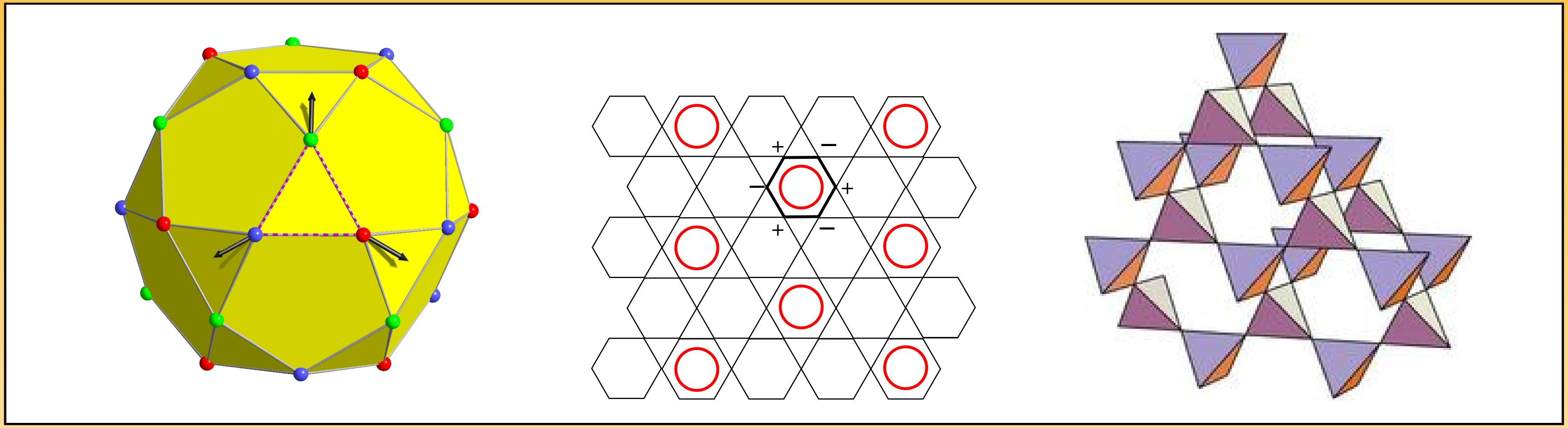
- Simple: An antiferromagnet is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.

- 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)

Fe_{30} and friends

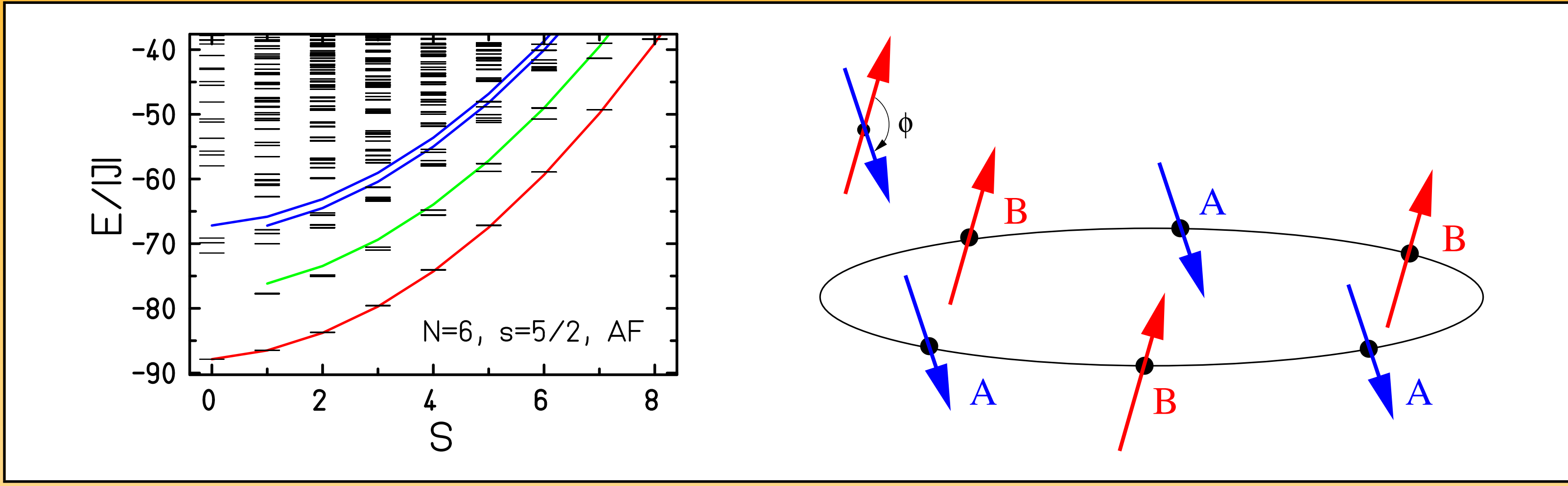
Fe_{30} and friends
Corner sharing triangles and tetrahedra



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

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

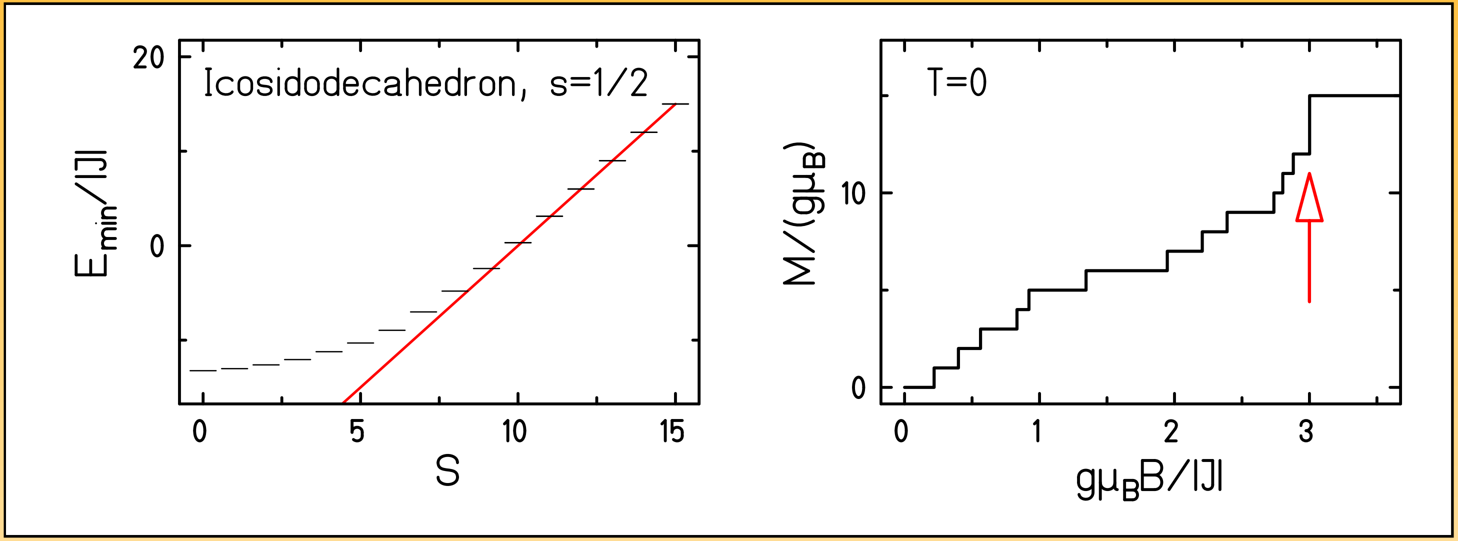
Rotational bands in non-frustrated antiferromagnets



- 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).

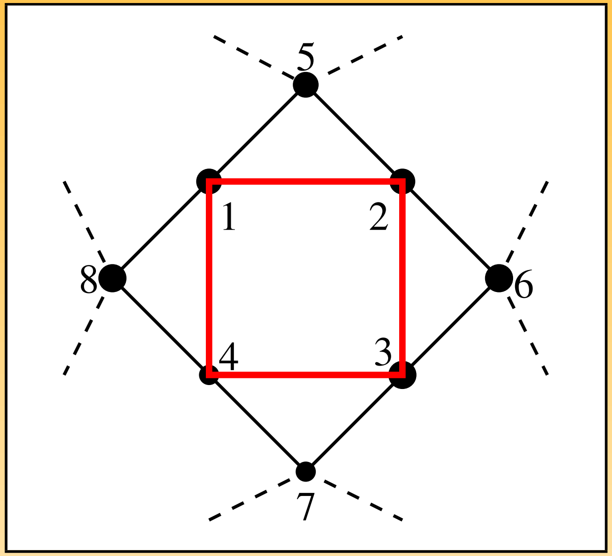
Giant magnetization jumps in frustrated antiferromagnets I $\{Mo_{72}Fe_{30}\}$



- 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

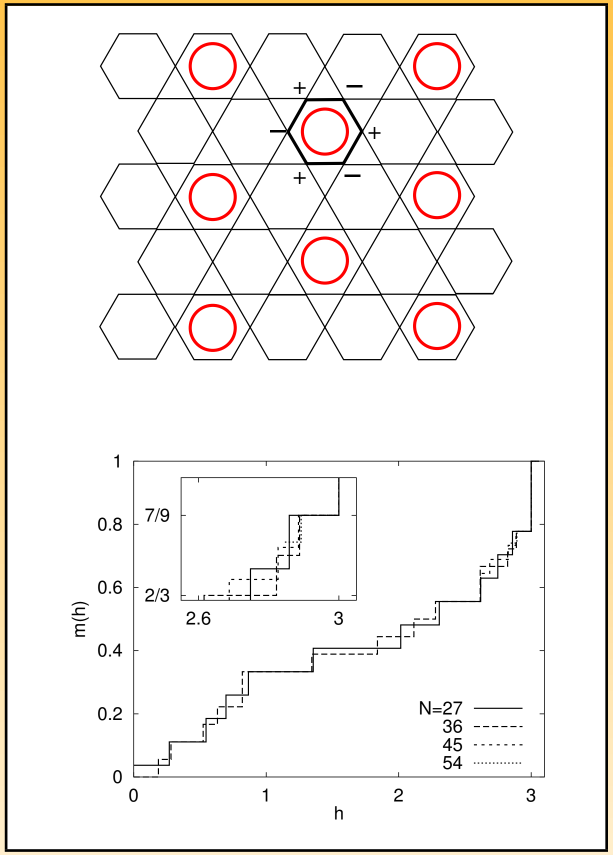


- $|\text{localized magnon}\rangle = \frac{1}{2}(|1\rangle - |2\rangle + |3\rangle - |4\rangle)$
- $|1\rangle = \underset{\sim}{s}^{-}(1)|\uparrow\uparrow\uparrow\ \ldots\rangle$ etc.
- $\underset{\sim}{H}\,|\text{localized magnon}\rangle \propto |\text{localized magnon}\rangle$
- Localized magnon is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

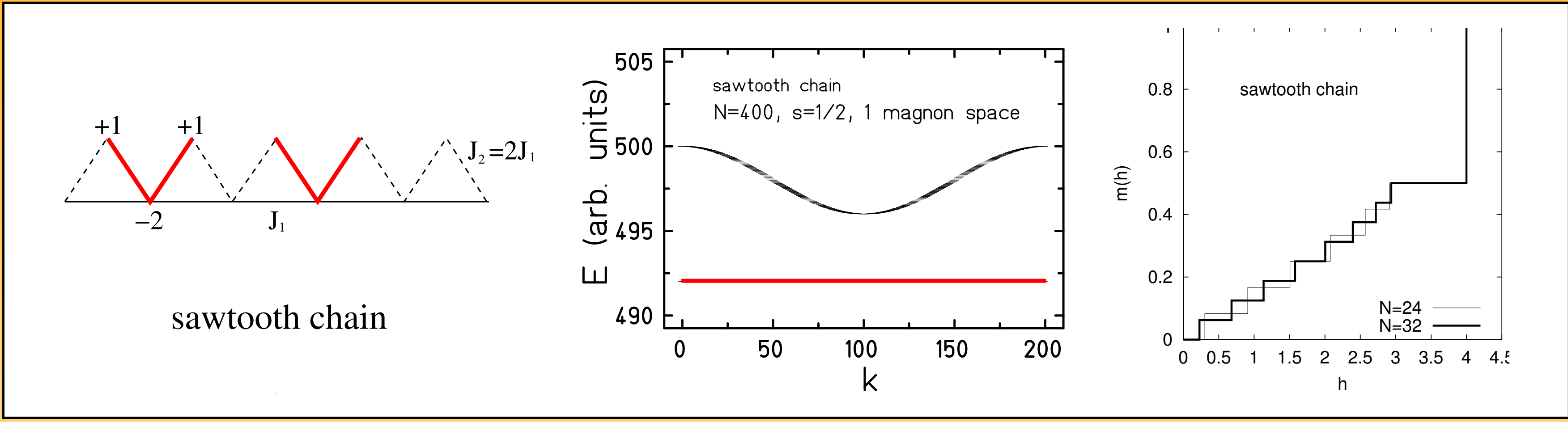
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- 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 $\Rightarrow \quad (T = 0)$ 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)

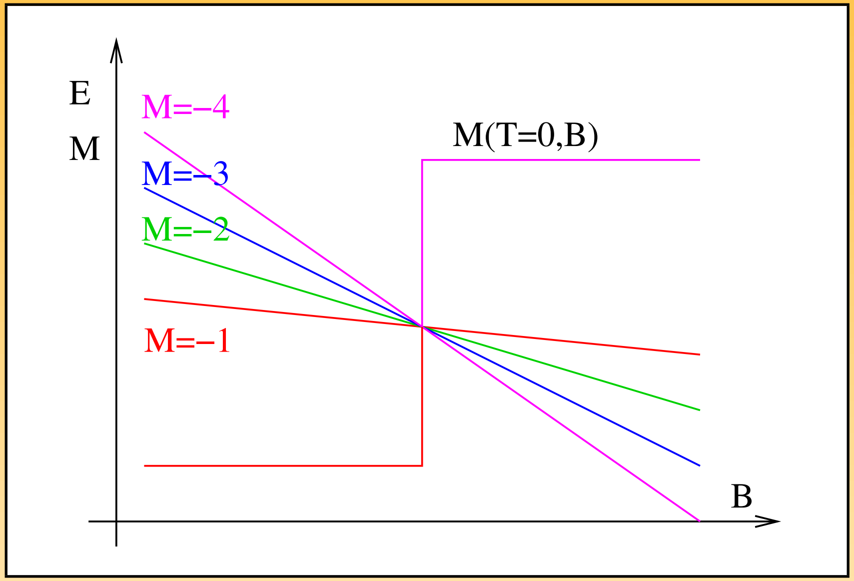
Condensed matter physics point of view: Flat band



- Flat band of minimal energy in one-magnon space, 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)

Magnetocaloric effect I
Giant jumps to saturation



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

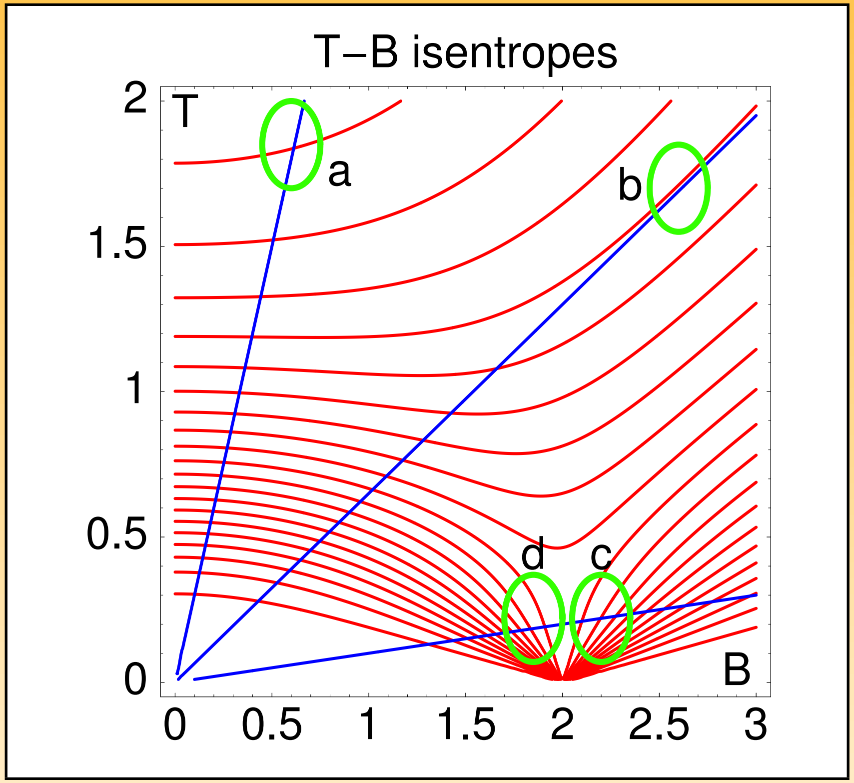
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)

A. Honecker, J. Richter, Condensed Matter Physics **8**, 813 (2005)

H.-J. Schmidt, J. Richter, R. Moessner, J. Phys. A: Math. Gen. **39**, 10673 (2006)

O. Derzhko, J. Richter, A. Honecker, H.-J. Schmidt, Low Temp. Phys. **33**, 745 (2007)

Magnetocaloric effect II
Isentrops of af $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

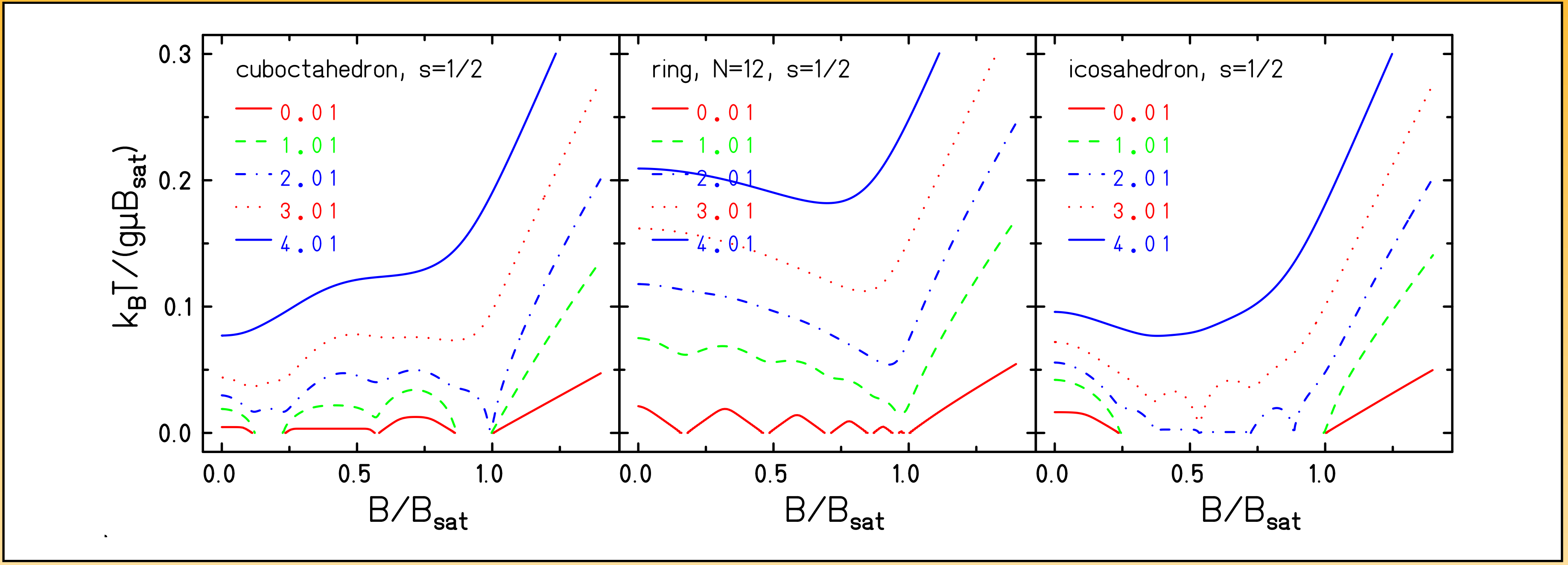
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

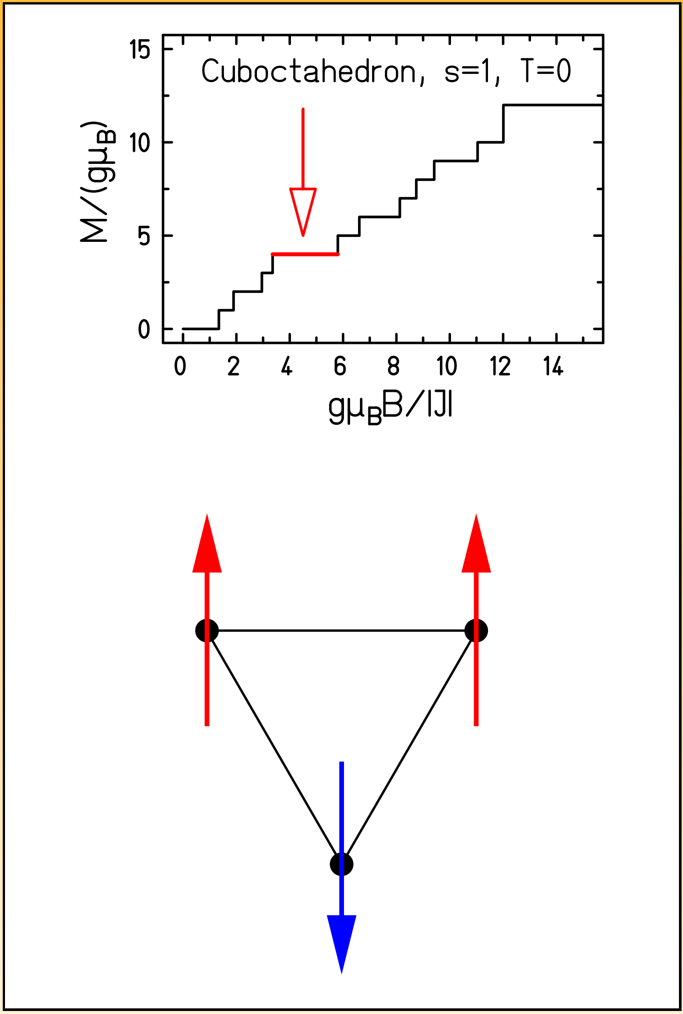
Magnetocaloric effect III – Molecular systems



- 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)

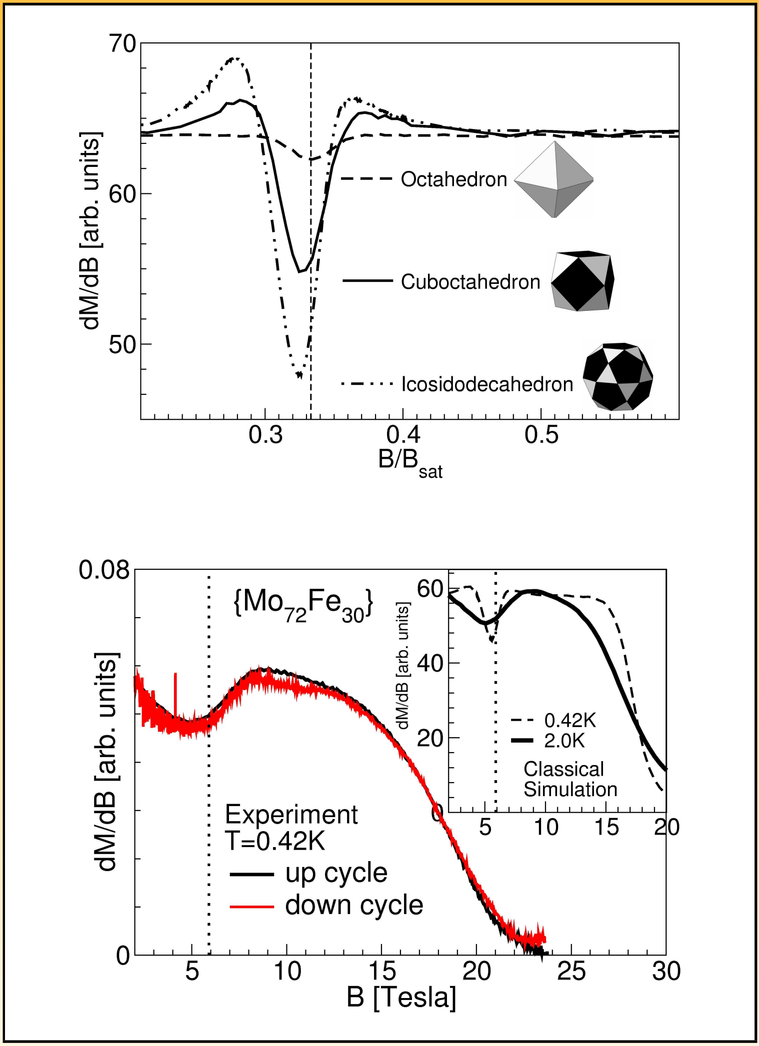
Magnetization plateaus and susceptibility minima



- 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.

Recent comprehensive review by I. Rousochatzakis, A.M. Läuchli, F. Mila, arXiv:0711.3231v1

Magnetization plateaus and susceptibility minima

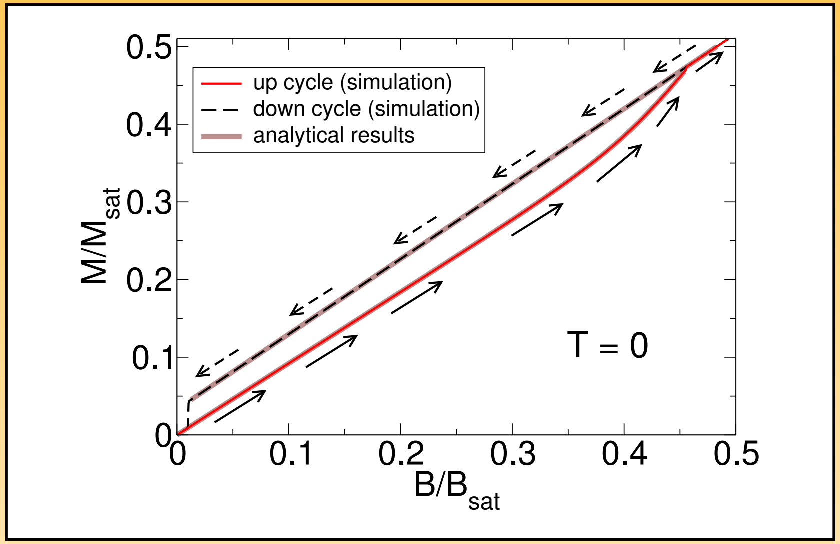


- Susceptibility shows a pronounced dip at $B_{\text{sat}}/3$ (classical calculations and quantum calculations for the cuboctahedron).
- Obvious in case of plateau at $\mathcal{M}_{\text{sat}}/3$, more subtle for other frustrated systems.
- Experimentally verified for $\{\text{Mo}_{72}\text{Fe}_{30}\}$.

  C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, P. Kögerler, Phys. Rev. Lett. **94**, 017205 (2005)
- Measurement reveals that couplings in Fe_{30} might be randomly distributed (unexpected unknown unknown!)

Metamagnetic phase transitions

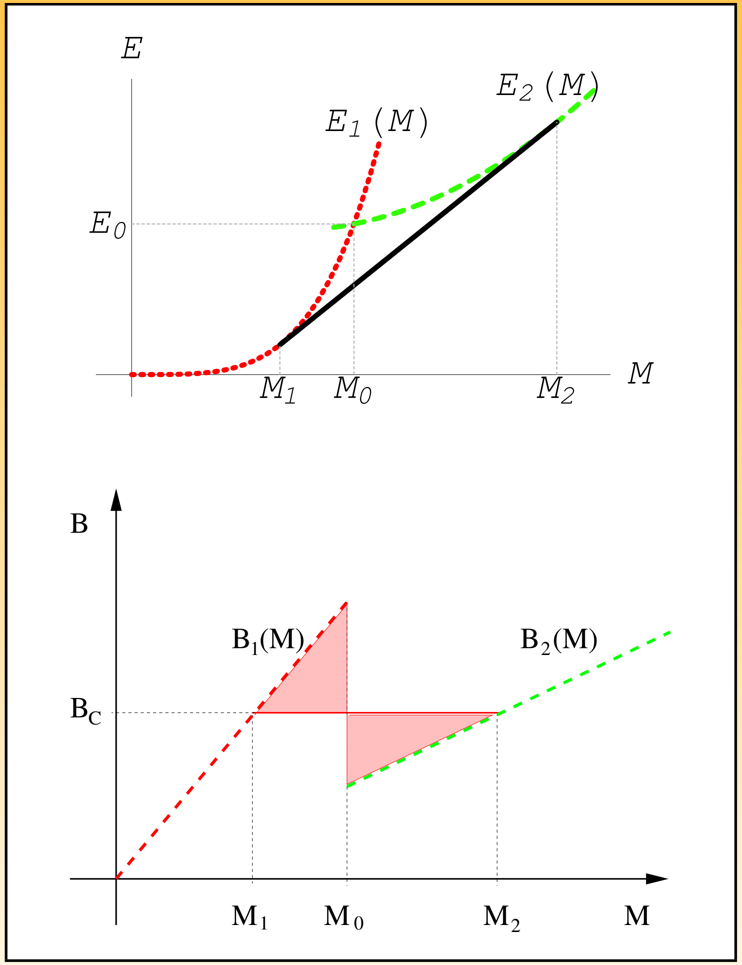
Metamagnetic phase transition I Hysteresis without anisotropy



- 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)

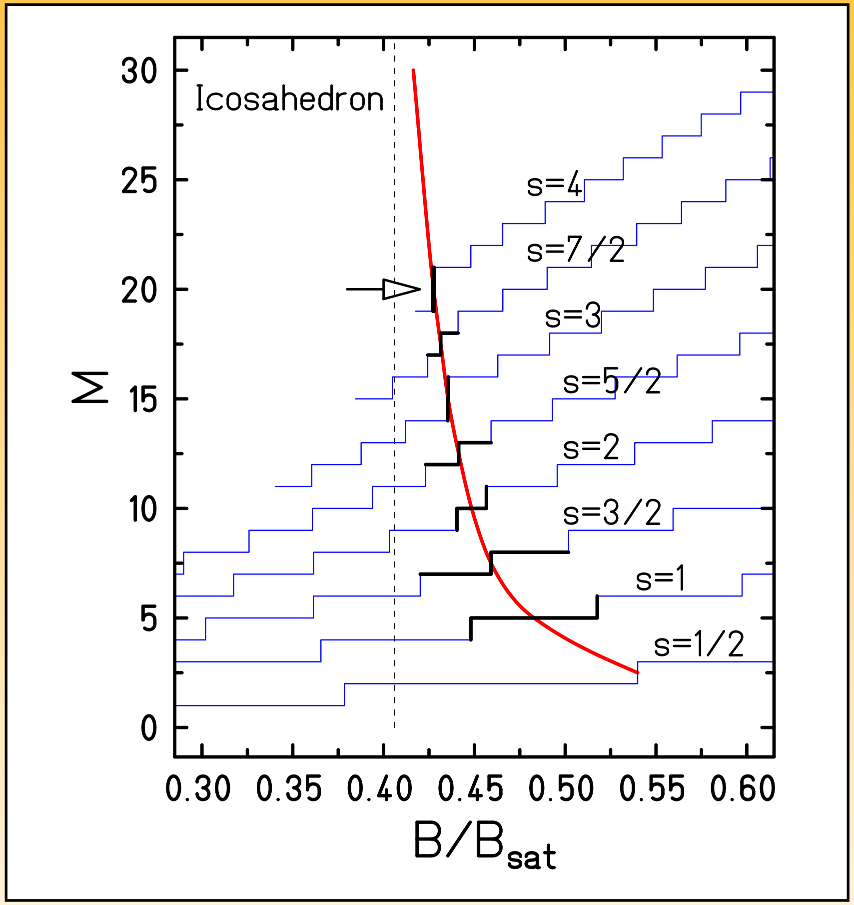
Metamagnetic phase transition II
Non-convex minimal energy



- 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 $\Delta M > 1$.

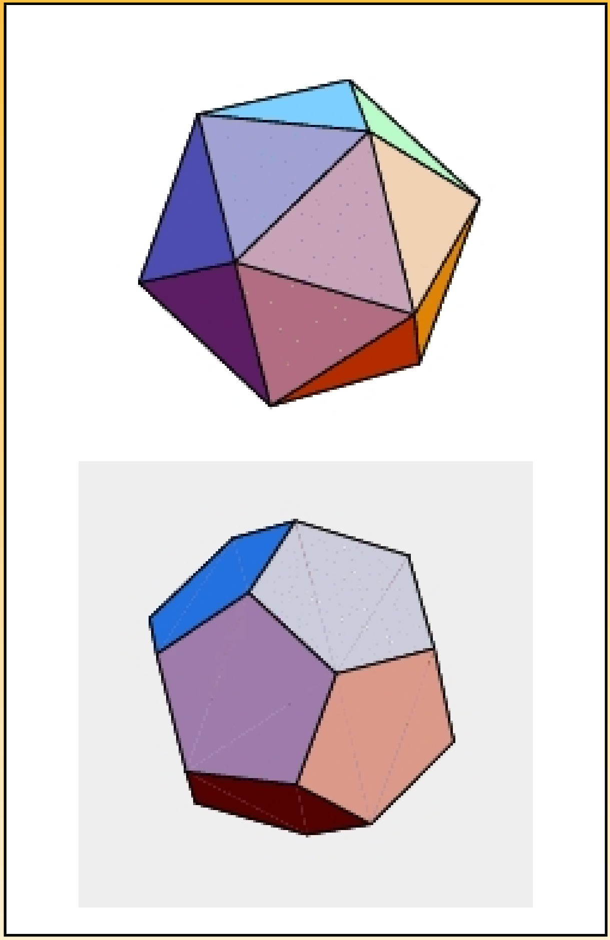
- Lanczos diagonalization for various s
  Theory achievement: work with vectors with 10^9 entries.

- 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

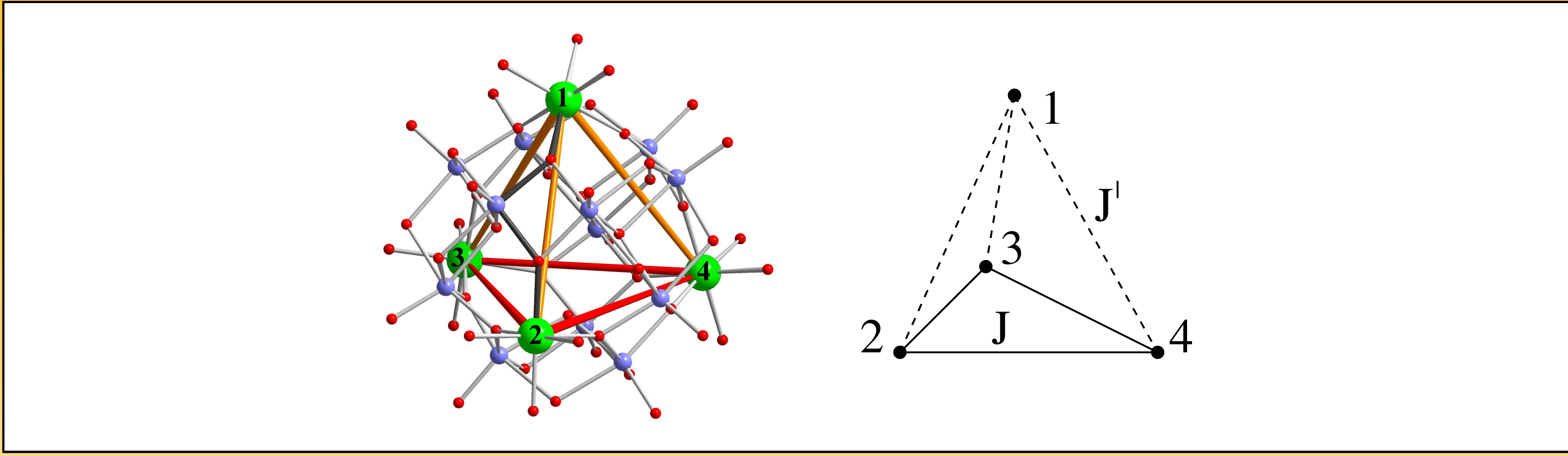


- First noticed in the context of the Buckminster fullerenes C_{20} and C_{60} (1).
- It seems to be important that the ground state is not coplanar and spins do not fold umbrella-like in field. The symmetry of low-field and high-field ground states needs to be different;
  Counter examples: $\{Mo_{72}Fe_{30}\}$, 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, Phys. Rev. B **76**, 104434 (2007)

Magnetostriction on the molecular level?

$[Mo^V_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}(H_2O)_3\}_4] = \{Ni_4Mo_{12}\}$



- $[Mo^V_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}(H_2O)_3\}_4] = \{Ni_4Mo_{12}\}$ (1)
- Ni-Ni distances: $d_{12} = 6.700(5)$ Å, $d_{13} = d_{14} = 6.689(1)$ Å, $d_{23} = d_{24} = 6.616(1)$ Å, $d_{34} = 6.604(1)$ Å.
- Superexchange interactions J' and J represented by dashed and solid lines.

(1) A. Müller, C. Beugholt, P. Kögerler, H. Bögge, S. Bud'ko, and M. Luban, Inorg. Chem. **39**, 5176 (2000)

$\{Ni_4Mo_{12}\}$: naive expectations

Hamiltonian for almost perfectly tetrahedral symmetry and $s = 1$ (1)

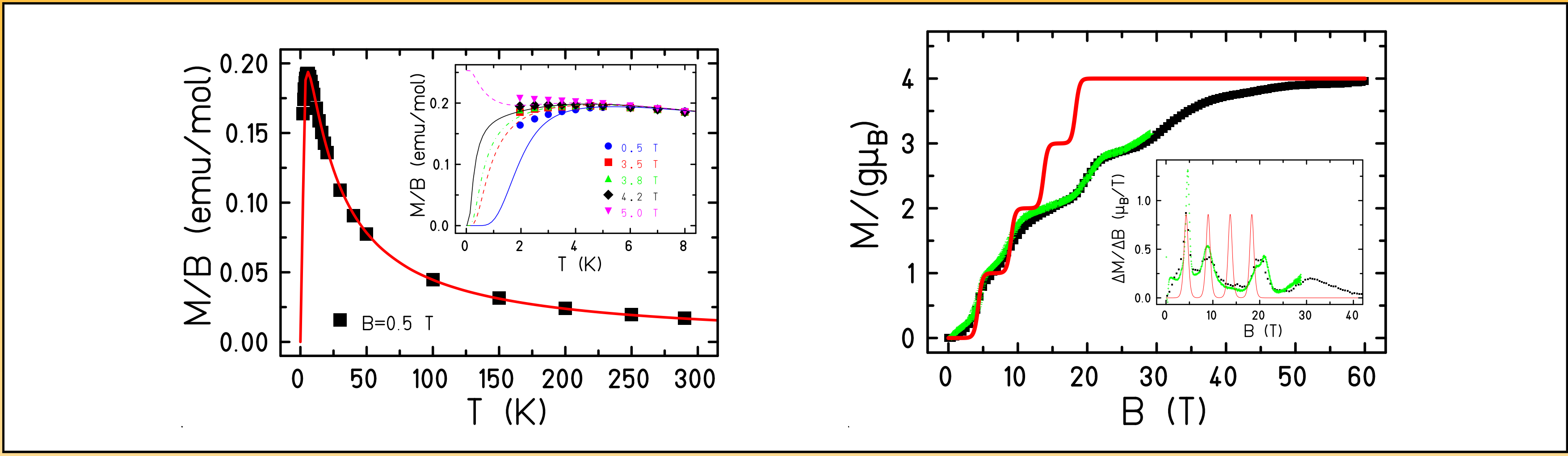
$$\underset{\sim}{H} = -2J \sum_{u<v} \underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v) + g\mu_B \vec{B} \cdot \sum_u \underset{\sim}{\vec{s}}(u) = -J \left[\underset{\sim}{\vec{S}}^2 - 4s(s+1) \right] + g\mu_B B \, \underset{\sim}{S}_z$$

Low-temperature magnetization curve $\mathcal{M}(B)$ should display four steps at

$$B_{S\rightarrow(S+1)} = -\frac{2J}{g\mu_B}(S+1)$$

(1) A. Müller, C. Beugholt, P. Kögerler, H. Bögge, S. Bud'ko, and M. Luban, Inorg. Chem. **39**, 5176 (2000)

{Ni_4Mo_{12}}: the reality



- Susceptibility reasonably well reproduced, finer details wrong.
- Magnetization deviates substantially: steps at 4.5, 8.9, 20.1, and 32 T.
- Use of two different exchange constants cannot account for the behavior.

Hamiltonian v.2007 (service pack II)

$$\underset{\sim}{H} = \underset{\sim}{H}_{\text{H}} + \underset{\sim}{H}_{\text{ani}} + \underset{\sim}{H}_{\text{biq-v.2007}} + \underset{\sim}{H}_{\text{Z}}$$

Generalized biquadratic terms:

$$\underset{\sim}{H}_{\text{biq-v.2007}} = - \sum_{t,u,v,w} j_{tuvw} \left(\underset{\sim}{\vec{s}}(t) \cdot \underset{\sim}{\vec{s}}(u) \right) \left(\underset{\sim}{\vec{s}}(v) \cdot \underset{\sim}{\vec{s}}(w) \right)$$

Original biquadratic terms: indices pairwise the same, i.e. $t = v$ & $u = w$.

(1) Norikiyo Uryû, S.A. Friedberg, Phys. Rev. **140**, A1803 (1965)
(2) V.V. Kostyuchenko, I.M. Markevtsev, A.V. Philippov, V.V. Platonov, V.D. Selemir, O.M. Tatsenko, A.K. Zvezdin, A. Caneschi, Phys. Rev. B **67**, 184412 (2003)
(3) V.V. Kostyuchenko, Phys. Rev. B (2007) accepted; M. Brüger, Ph.D. thesis, 2007

Interpretation

Interpretation of the generalized fourth-order terms:

- Higher order terms in the derivation of a spin Hamiltonian from the Hubbard model (1);
- Higher order terms in the derivation of a spin Hamiltonian from a spin-phonon Hamiltonian (2);
- Which scenario is valid? Maybe both!
- In the spin-phonon scenario the appearance of these terms means that the prefactors are not small. Since the prefactors are given by matrix elements of the Hesse matrix, this is equivalent to soft bonds! MAGNETOSTRICTION!
- These terms naturally lead to non-equidistant steps in the magnetization.

(1) V.V. Kostyuchenko *et al.*, Phys. Rev. B **67**, 184412 (2003)
(2) C. Kittel, Phys. Rev. **120**, 335 (1960); M. Brüger, Ph.D. thesis, 2007

I hope I could show you, that

There are interesting known knowns!

Models, Frustration, Magnetocalorics,

. . .

I hope I could show you, that

There are interesting known unknowns!

edge-sharing triangle-systems,

molecular magnetostriction, . . .

And I hope, that

There are many more

unknown unknowns

to be discovered.

The end is not in sight,

however, this talk is at its end!

Thank you very much for your attention.

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