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

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Quantum Magnetism, University of Minnesota

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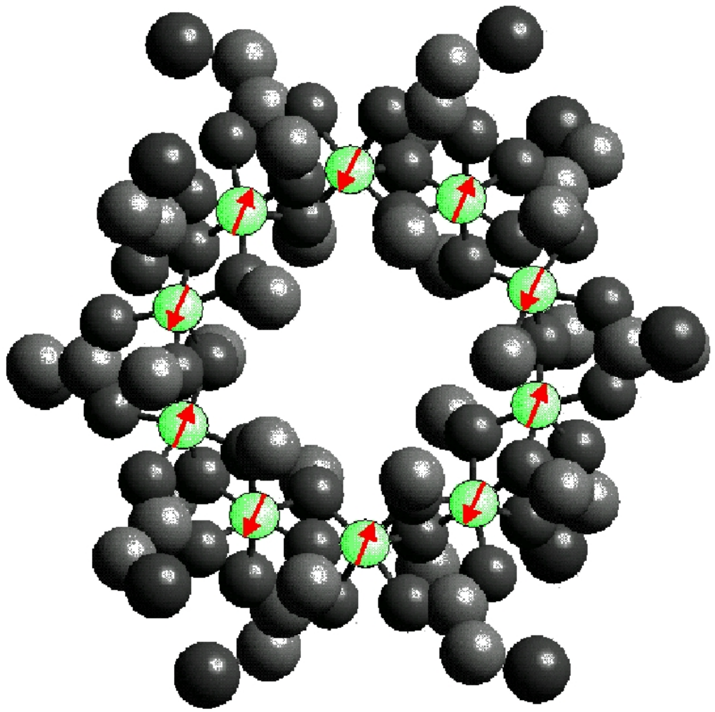
Contents for you today

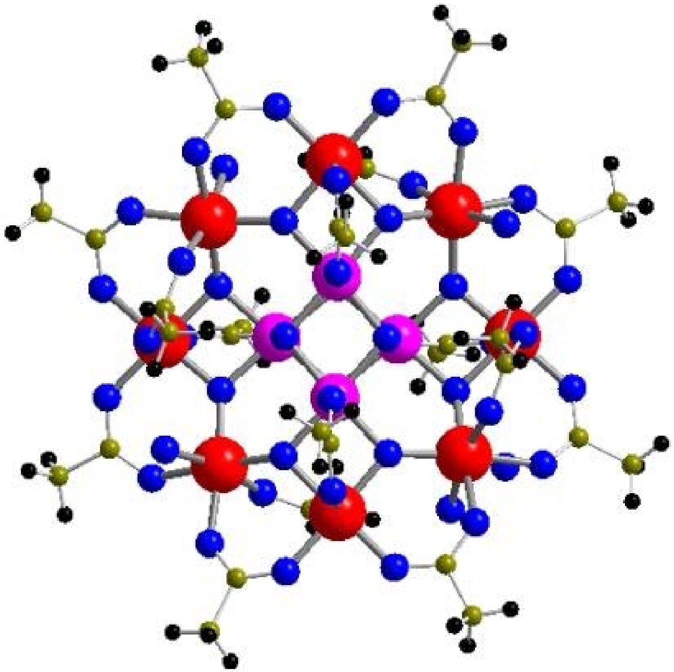


Fe_{10}

1. The suspects: magnetic molecules
2. Frustrated ring molecules
3. Corner-sharing triangles: Fe_{30} and friends
4. Edge-sharing triangles: Metamagnetic phase transitions

Magnetic Molecules

The beauty of magnetic molecules I

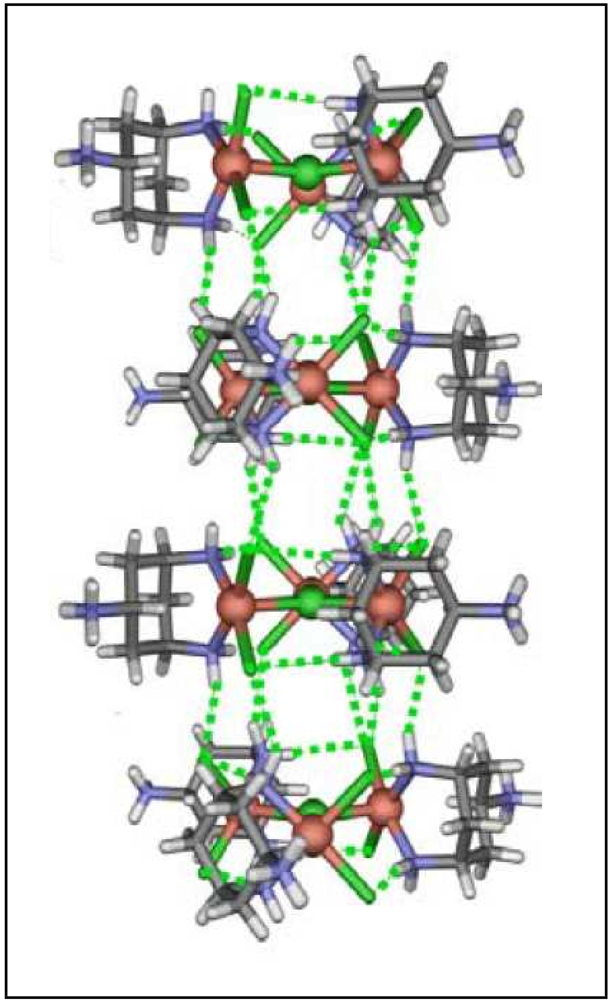


Mn_{12}

Molecular materials:

- 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

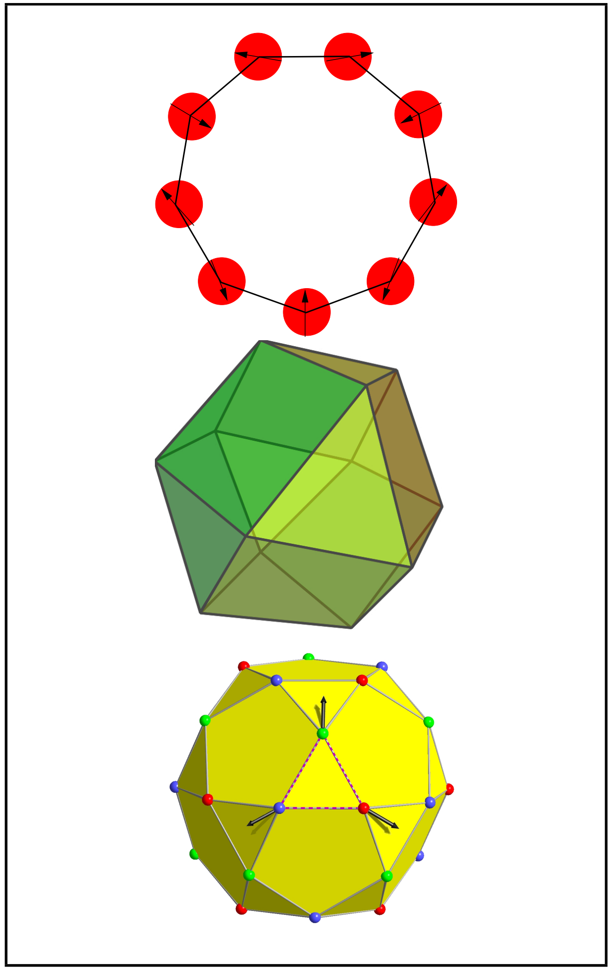


Molecular structures:

- 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



Frustrated AF molecular structures:

- Odd-membered rings (1);
- Cuboctahedra (corner-sharing triangles, 2);
- Icosidodecahedra (corner-sharing triangles, 3);
- Tetrahedra (edge-sharing triangles, 3);
- Icosahedra (edge-sharing triangles, 4).

(1) By G. Timco & R. Winpenny (Manchester) and H.C. Yao (Nanjing).
(2) By R. Winpenny (Manchester) and A. Powell (Karlsruhe).
(3) By A. Müller (Bielefeld) and P. Kögerler (Aachen & Ames).
(4) Almost (!) by R. Winpenny (Manchester).

Model Hamiltonian – Heisenberg-Model

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

Heisenberg   Zeeman

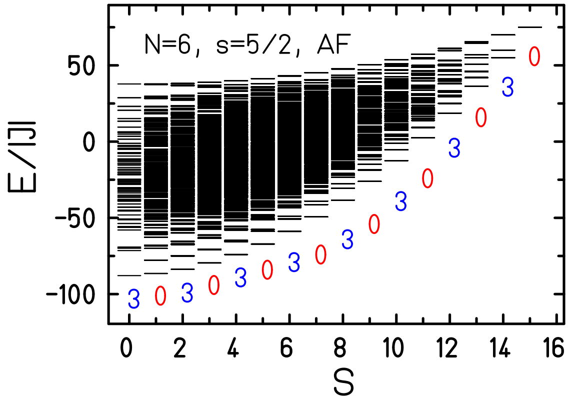
The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations; $J < 0$: antiferromagnetic coupling.

$$\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0 \qquad \& \qquad \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0$$

$$\underset{\sim}{H}\,|\,\nu\,\rangle = E_\nu\,|\,\nu\,\rangle \quad \& \quad \underset{\sim}{\vec{S}}^2\,|\,\nu\,\rangle \;=\; S_\nu(S_\nu+1)\,|\,\nu\,\rangle \quad \& \quad \underset{\sim}{S}_z\,|\,\nu\,\rangle = M_\nu\,|\,\nu\,\rangle$$

Frustrated ring molecules
(a warm-up)

Marshall-Peierls sign rule for even rings



- Expanding the ground state in $\mathcal{H}(M)$ in the product basis yields a sign rule for the coefficients

$$|\,\Psi_0\,\rangle = \sum_{\vec{m}} c(\vec{m})\ |\,\vec{m}\,\rangle \qquad \text{with} \sum_{i=1}^{N} m_i = M$$

$$c(\vec{m}) = (-1)^{\left(\frac{Ns}{2} - \sum_{i=1}^{N/2} m_{2i}\right)} a(\vec{m})$$

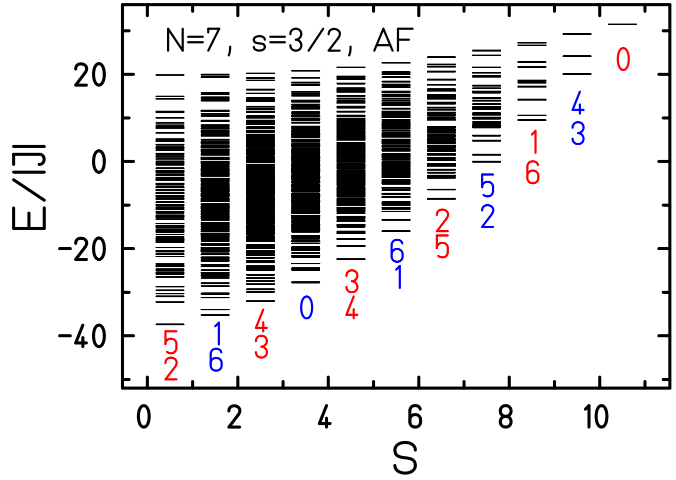
All $a(\mathbf{m})$ are non-zero, real, and of equal sign.

- Yields eigenvalues for the shift operator $\underset{\sim}{T}$:

$\exp\left\{-i\frac{2\pi k}{N}\right\}$ with $k \equiv a\,\frac{N}{2} \mod N\ , \quad a = Ns - M$

(1) W. Marshall, Proc. Royal. Soc. A (London) **232**, 48 (1955)

Numerical findings for odd rings



- For odd N and half integer s, i.e. $s = 1/2, 3/2, 5/2, \ldots$ we find that (1)
  - the ground state has total spin $S = 1/2$;
  - the ground state energy is **fourfold** degenerate.

- Reason: In addition to the (trivial) degeneracy due to $M = \pm 1/2$, a degeneracy with respect to k appears (2):
  $k = \lfloor \frac{N+1}{4} \rfloor$ and $k = N - \lfloor \frac{N+1}{4} \rfloor$

- For the first excited state similar rules could be numerically established (3).

(1) K. Bärwinkel, H.-J. Schmidt, J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
(2) $\lfloor \cdot \rfloor$ largest integer, smaller or equal
(3) J. Schnack, Phys. Rev. B **62**, 14855 (2000)

k-rule for odd rings

- An extended k-rule can be inferred from our numerical investigations which yields the k quantum number for relative ground states of subspaces $\mathcal{H}(M)$ for even as well as odd spin rings, i.e. for all rings (1)

$$k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \mod N \ , \quad a = Ns - M$$

k is independent of s for a given N and a. The degeneracy is minimal ($N \neq 3$).

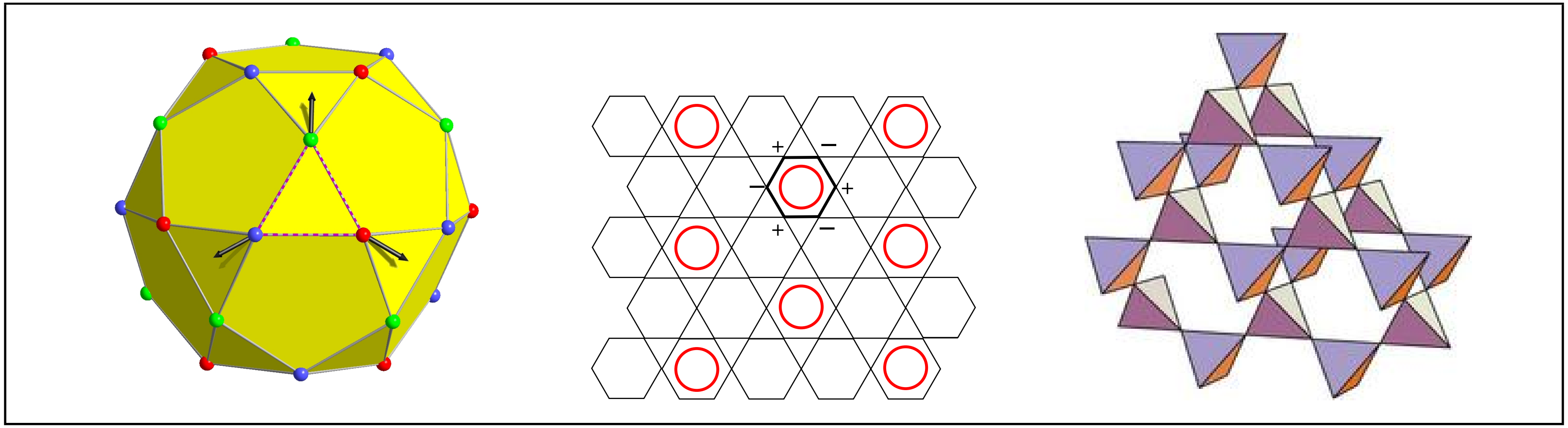
N	s	a: 0	1	2	3	4	5	6	7	8	9
8	1/2	0	4	$8 \equiv 0$	$12 \equiv 4$	$16 \equiv 0$	-	-	-	-	-
9	1/2	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	-	-	-	-	-
9	1	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	$30 \equiv 3$	$35 \equiv 1$	$40 \equiv 4$	$45 \equiv 0$

No general proof yet.

(1) K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B **68**, 054422 (2003)

Fe_{30} and friends (corner-sharing triangles)

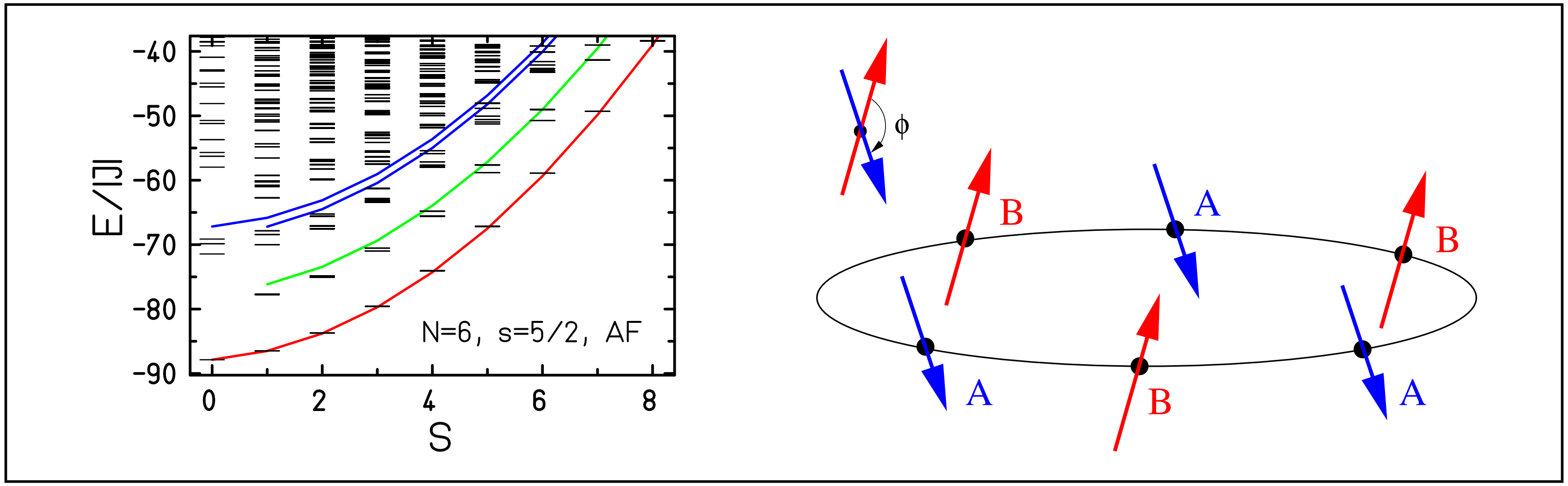
Fe$_{30}$ and friends
Corner sharing triangles and tetrahedra



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

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

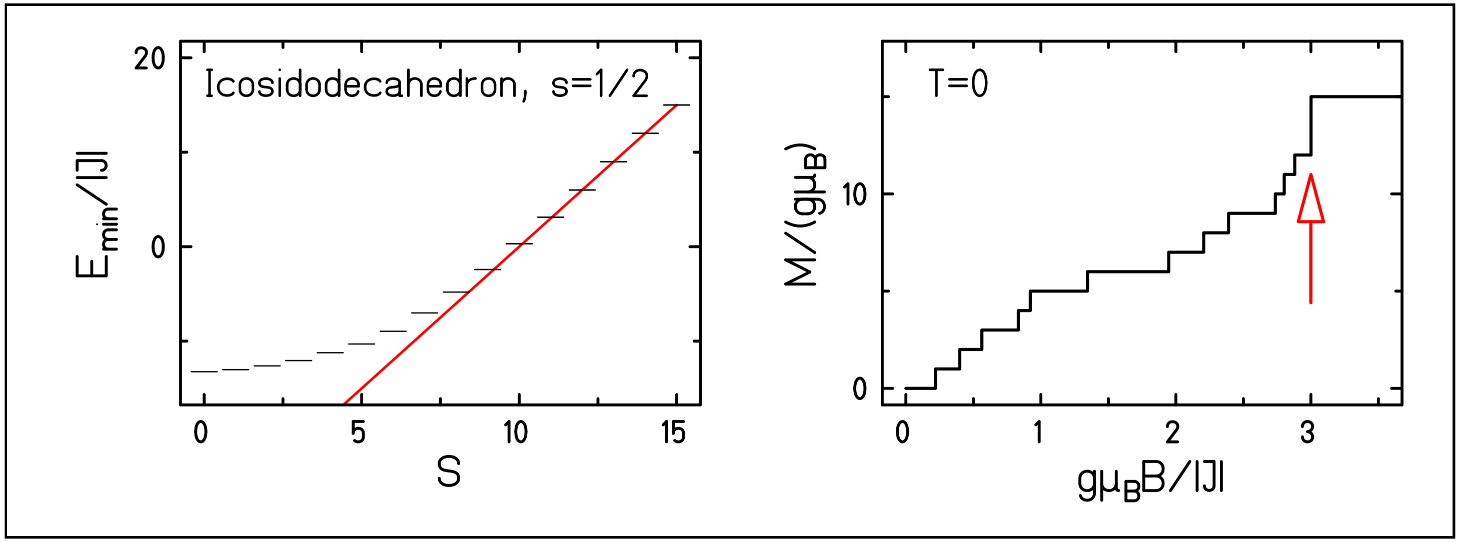
Rotational bands in non-frustrated antiferromagnets



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

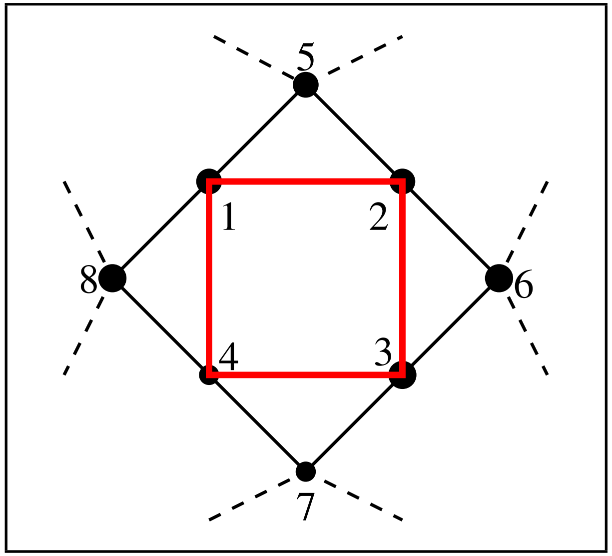
Giant magnetization jumps in frustrated antiferromagnets I
$\{$Mo$_{72}$Fe$_{30}\}$



- 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

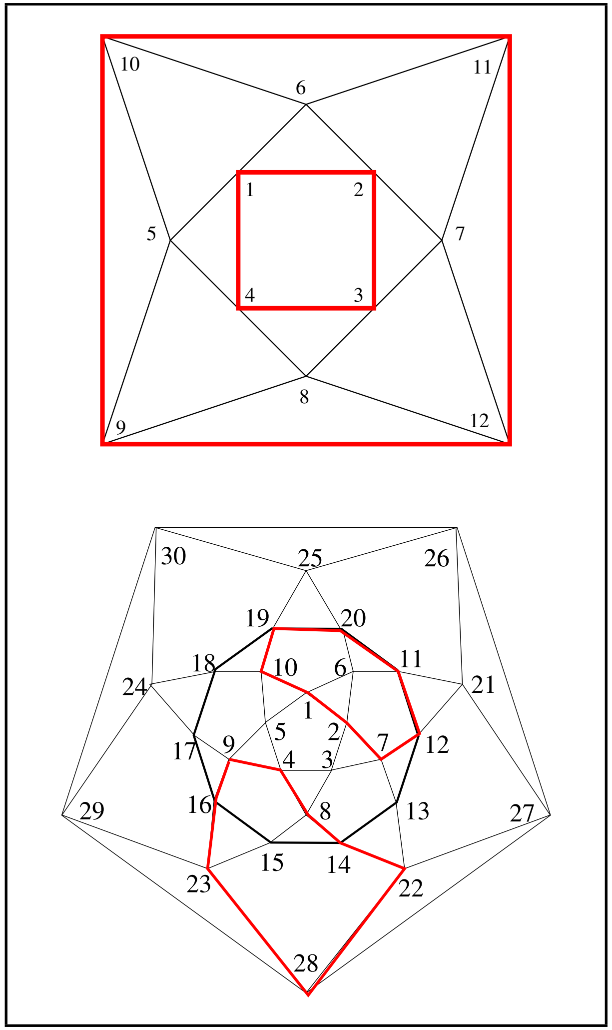


- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}\left(|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle\right)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\ \ldots\rangle$ etc.
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized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



- 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 $M = Ns - n$;
- Linear dependence of E_{min} on M $\Rightarrow$ $(T = 0)$ magnetization jump;
- A rare example of analytically known many-body states!

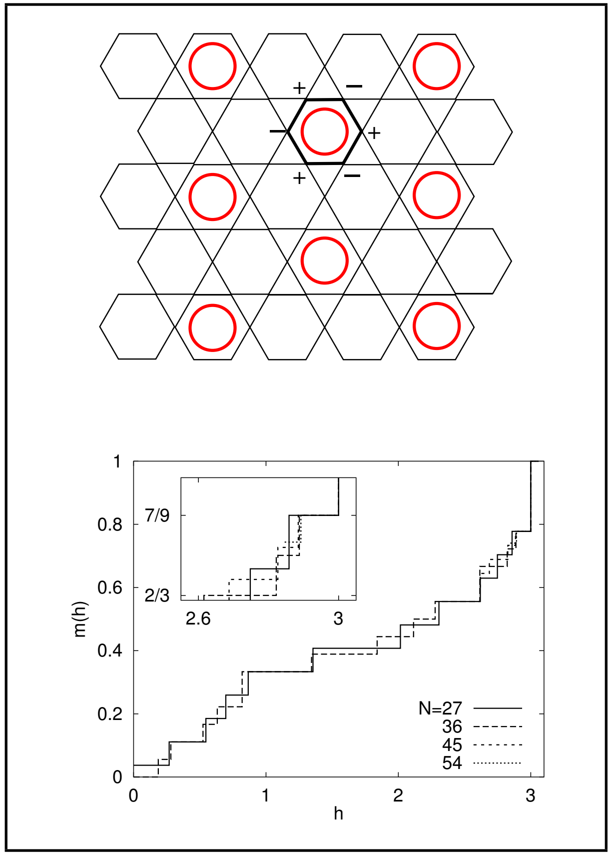
J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

Extended lattices and flat bands

More in Johannes Richter's talk
(next on this program)

CANCELED

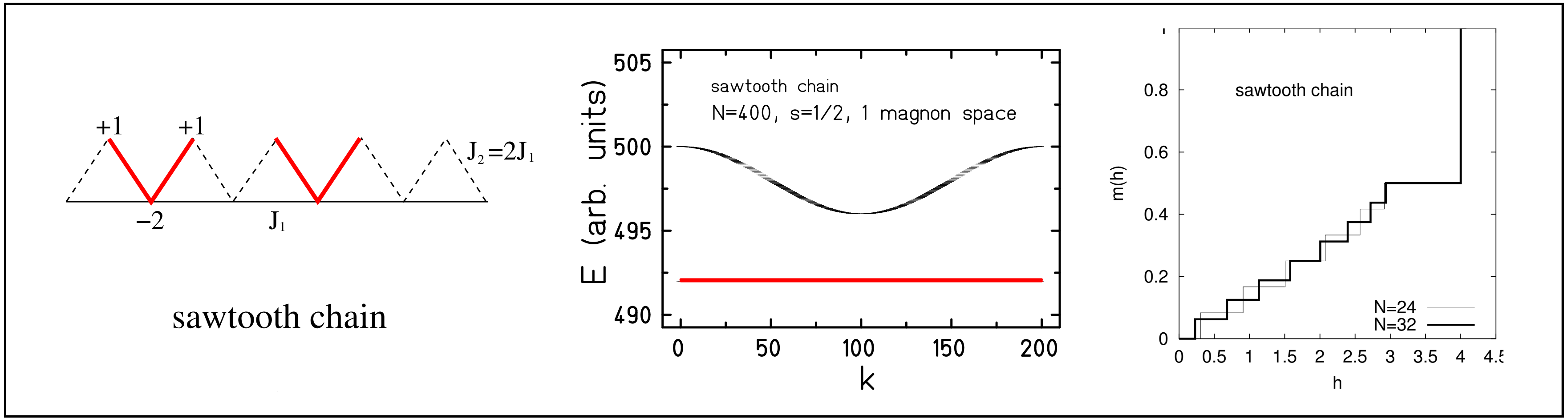
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



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

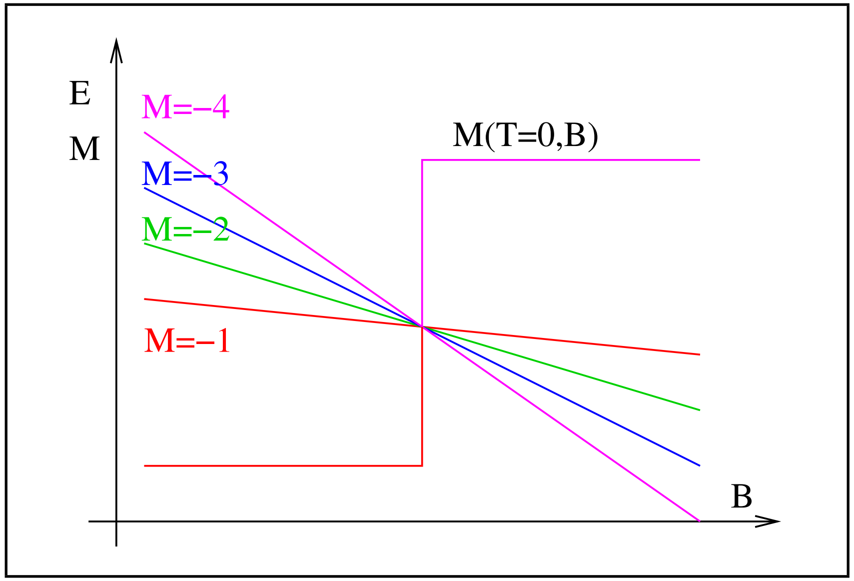
Condensed matter physics point of view: Flat band



- 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; universal low-temperature behavior.
- Same behavior for Hubbard model; flat band ferromagnetism (Tasaki & Mielke), jump of N with μ (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 $T = 0$.
- $$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

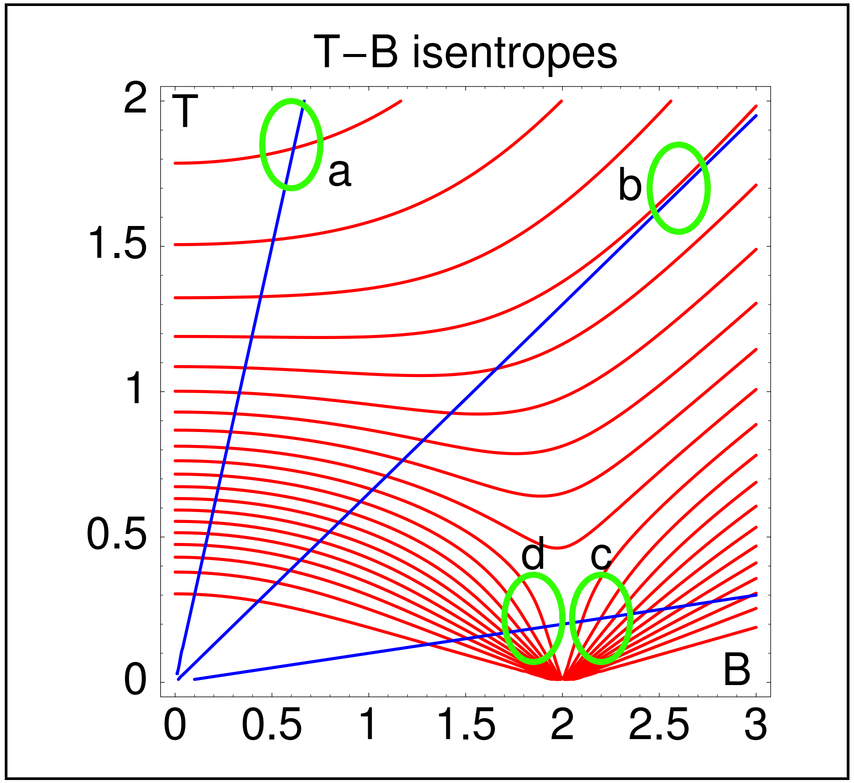
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)

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,

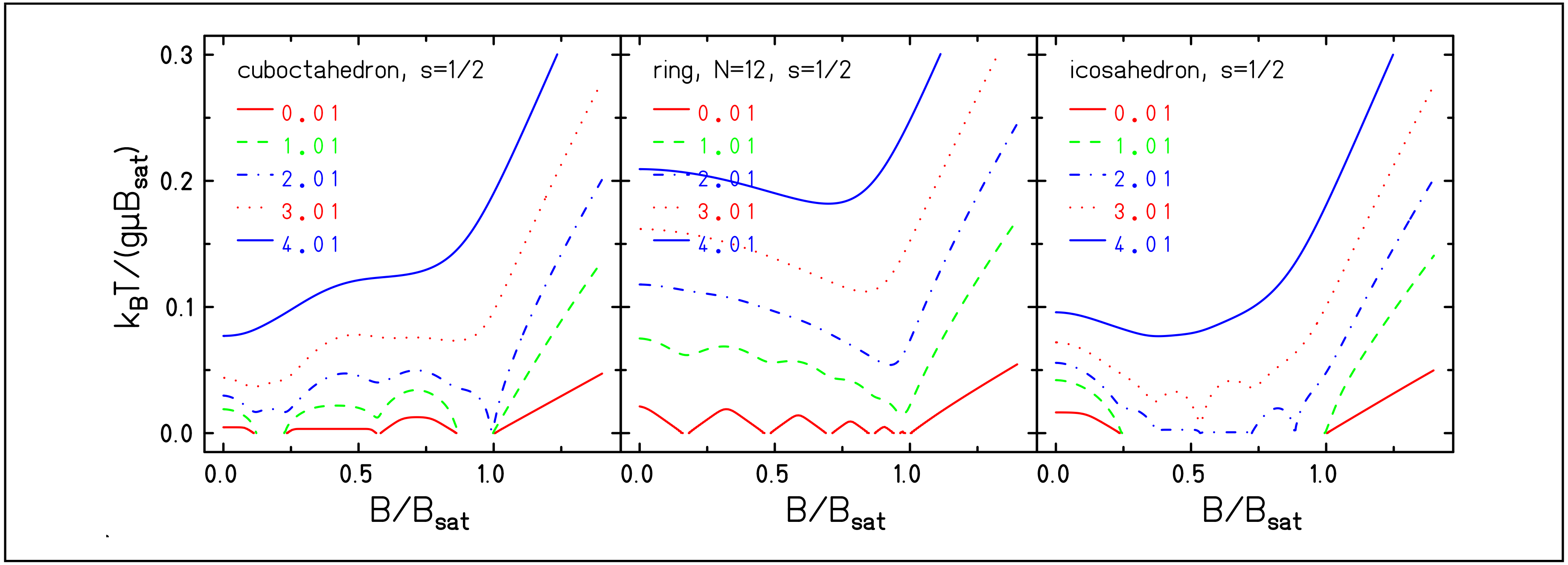
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

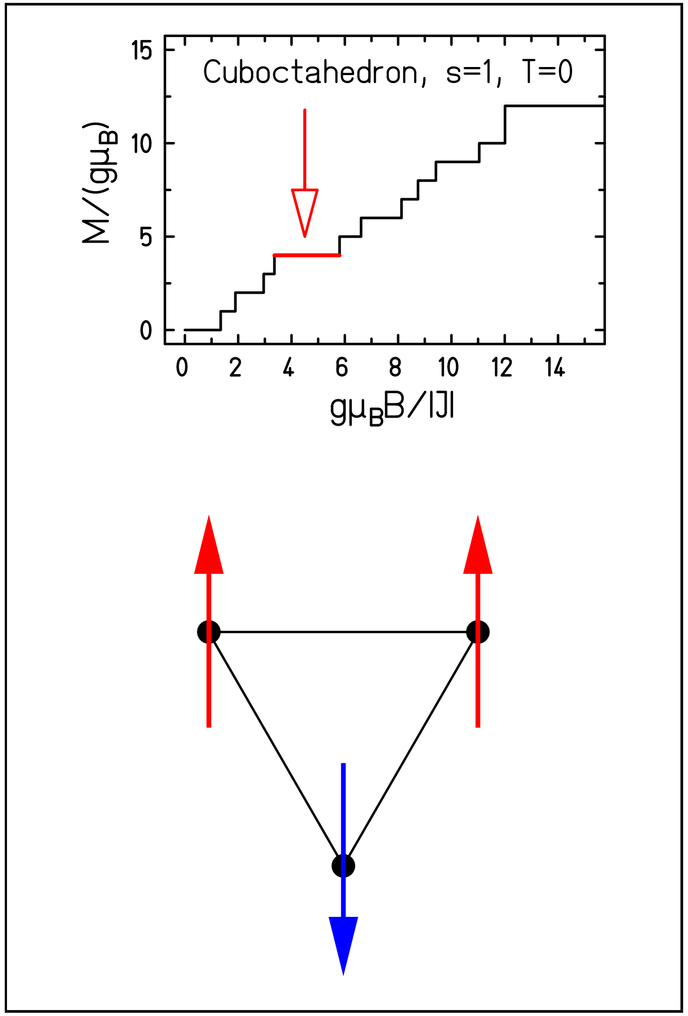
Magnetocaloric effect III – Molecular systems



- 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)

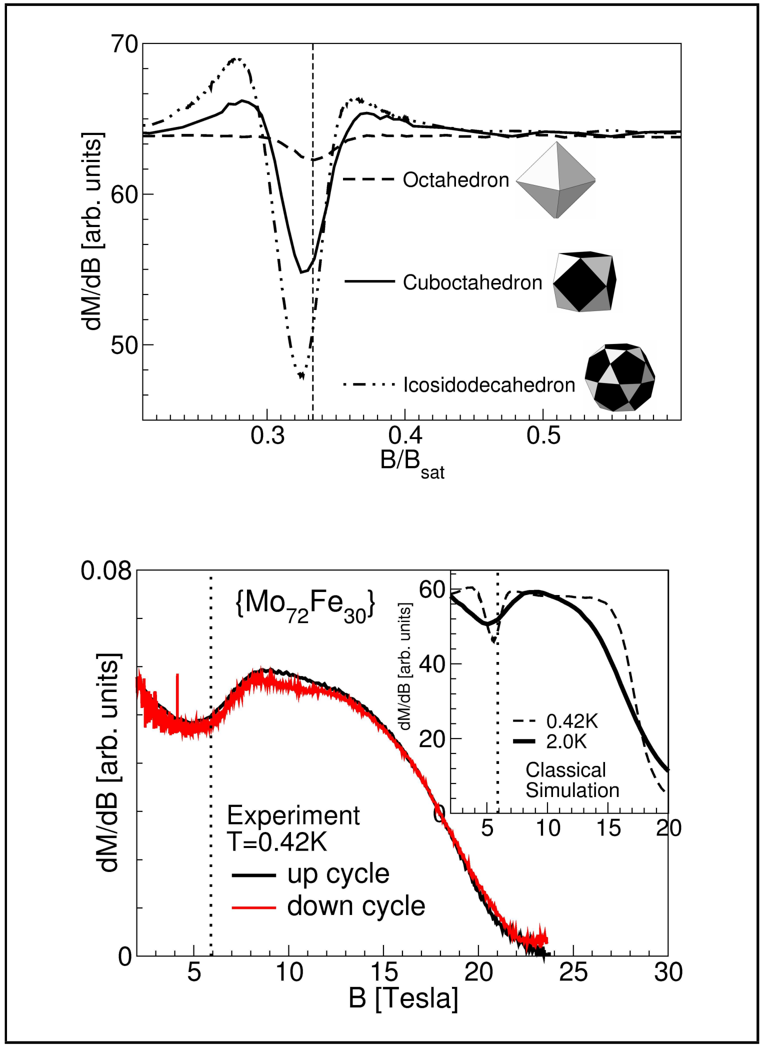
Magnetization plateaus and susceptibility minima



- 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, Phys. Rev. B **77**, 094420 (2008)

Magnetization plateaus and susceptibility minima



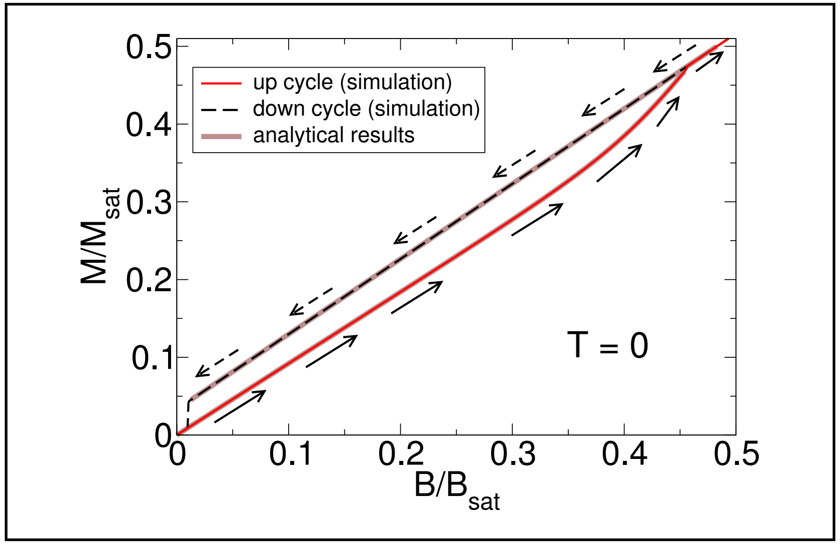
- Susceptibility shows a pronounced dip at $B_{\text{sat}}/3$ (classical calculations and quantum calculations for the cuboctahedron).
- Obvious in case of plateau at $\mathcal{M}_{\text{sat}}/3$, more subtle for other frustrated systems.
- Experimentally verified for $\{\text{Mo}_{72}\text{Fe}_{30}\}$.

  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

  Chr. Schröder *et al.*, arXiv:0801.2065v1

Metamagnetic phase transitions (edge-sharing triangles)

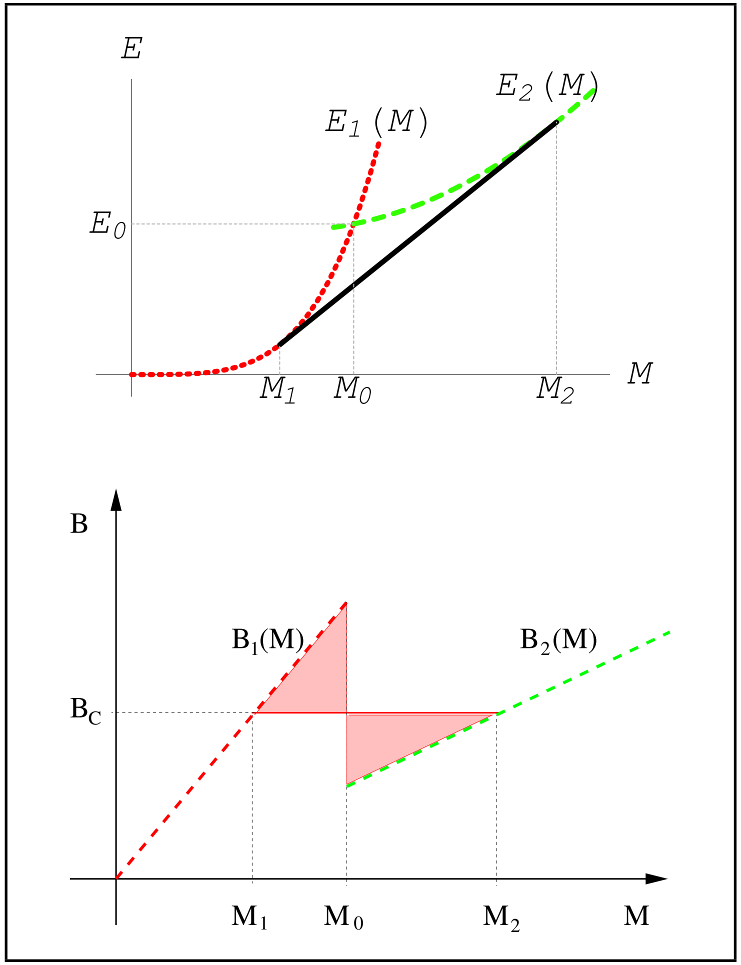
Metamagnetic phase transition I
Hysteresis without anisotropy



- 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)

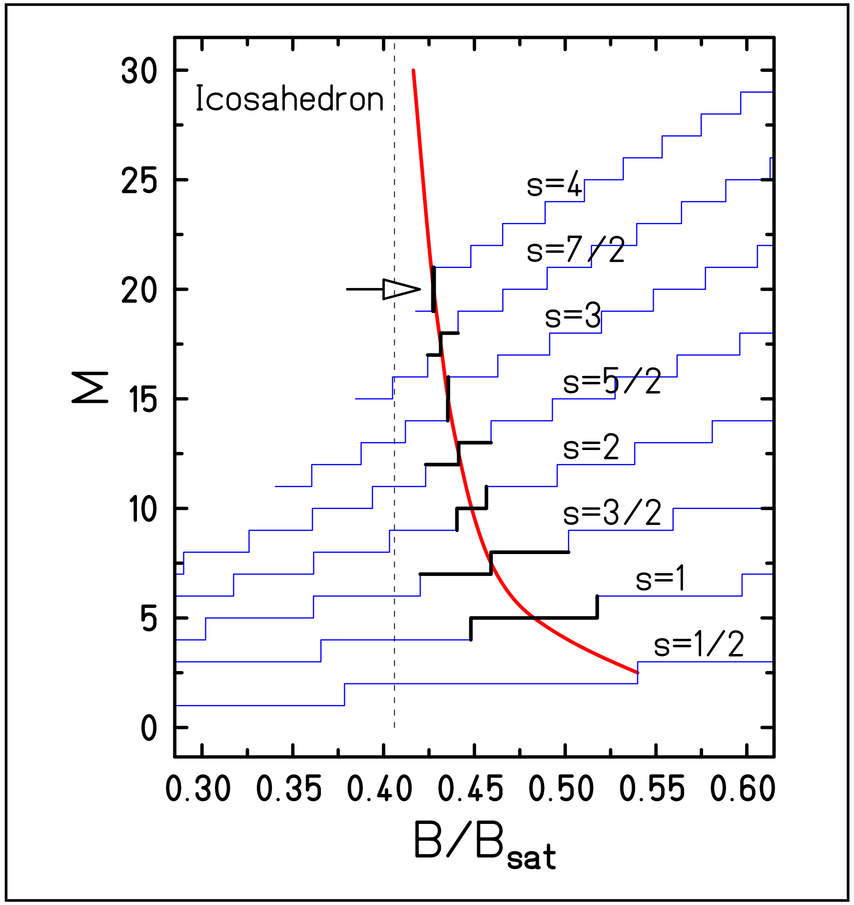
Metamagnetic phase transition II
Non-convex minimal energy



- 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

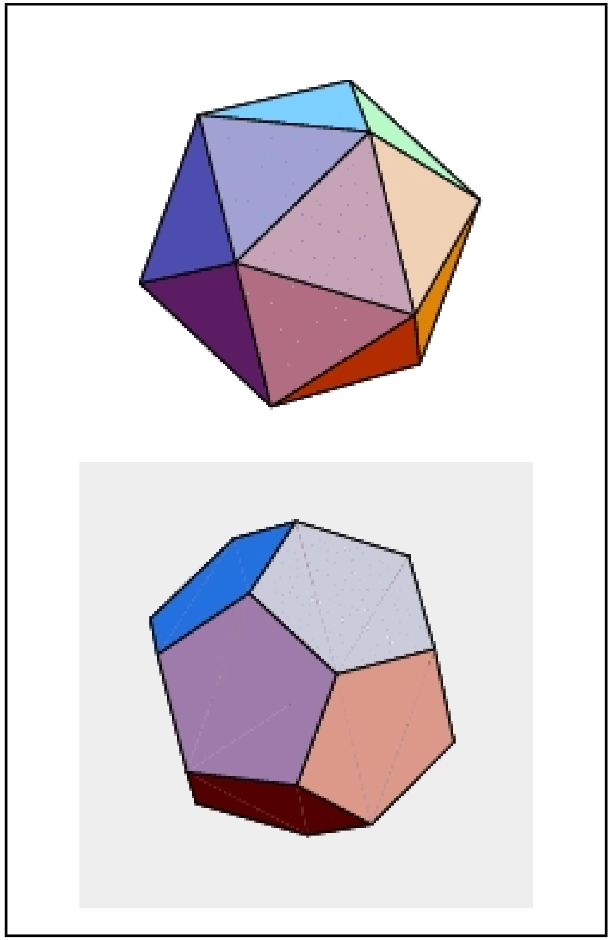
Metamagnetic phase transition III
Quantum icosahedron



- Quantum analog:
  Non-convex minimal energy levels
  $\Rightarrow$ magnetization jump of $\Delta M > 1$.
- Lanczos diagonalization for various s
  vectors with up to 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)

no more time option

Thank you very much for your attention.

German Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. DFG SPP 1137