

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

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Quantum Magnetism, University of Minnesota

Minneapolis, May 2nd, 2008

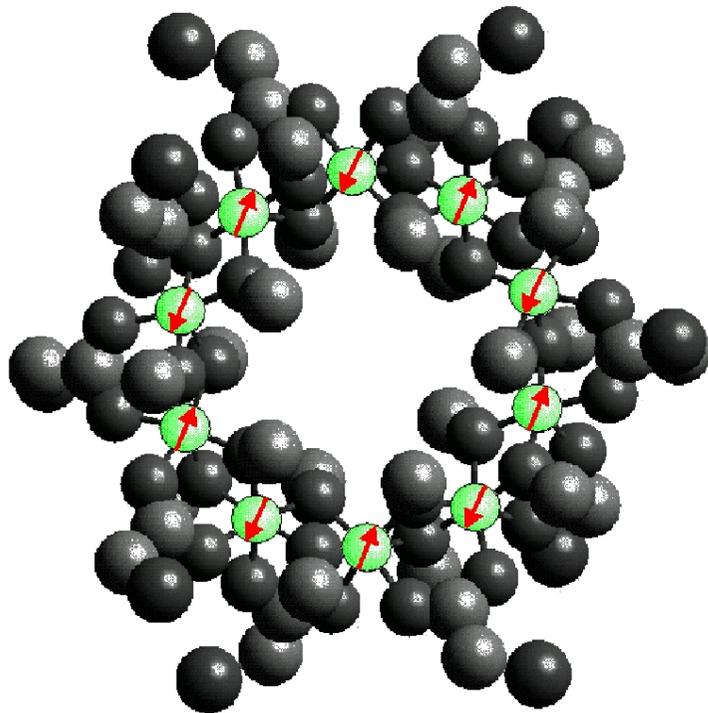


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Many thanks to my collaborators worldwide

- T. Englisch, T. Glaser, M. Höck, S. Leiding, A. Müller, Chr. Schröder, B. Soleymanzadeh (Bielefeld)
- K. Bärwinkel, H.-J. Schmidt, 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 (Osnabrück);
- M. Luban, D. Vaknin (Ames Lab, USA); P. Kögerler (RWTH, Jülich, Ames) 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. Postnikov (U. Metz)
- J. Richter, J. Schulenburg, R. Schmidt (U. Magdeburg); S. Blügel (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, H.-H. Klauß (Dresden)

Contents for you today

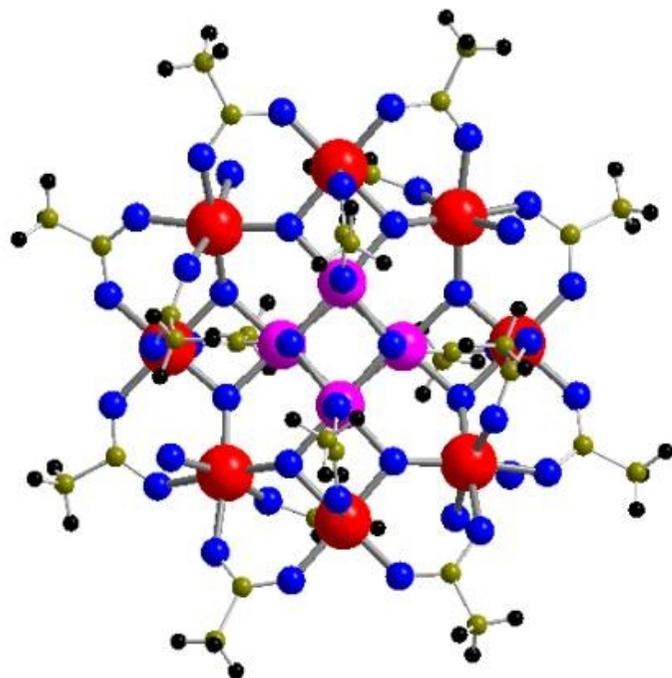


Fe_{10}

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

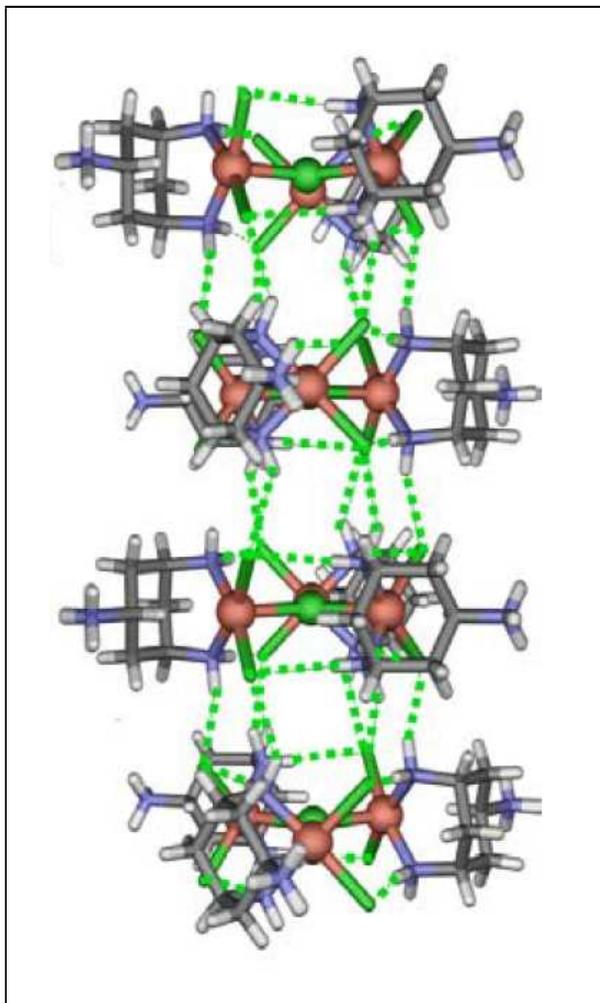


Mn_{12}

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

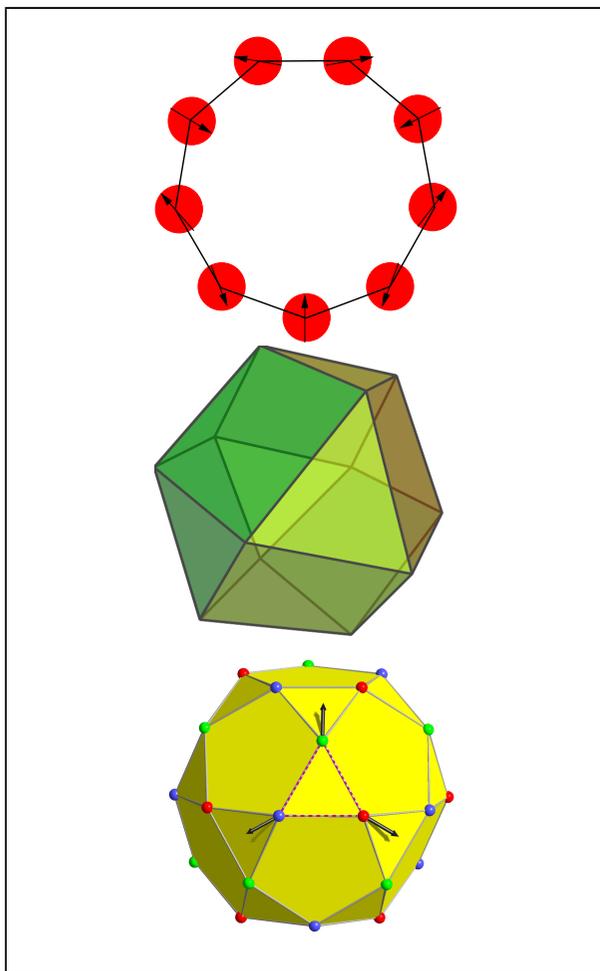


Molecular structures:

- 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

$$\underline{H} = - \sum_{i,j} J_{ij} \underline{\vec{S}}(i) \cdot \underline{\vec{S}}(j) \quad + \quad g \mu_B B \sum_i^N \underline{S}_z(i)$$

Heisenberg Zeeman

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

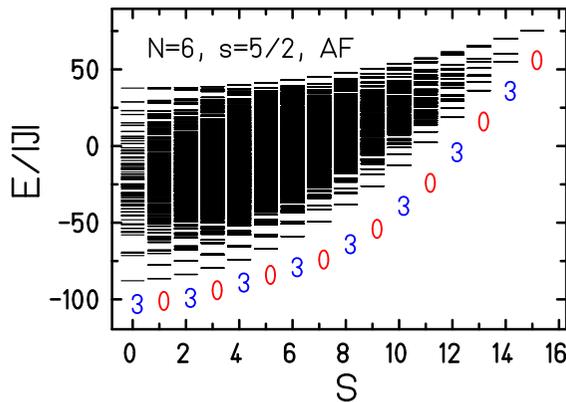
$$\left[\underline{H}, \underline{\vec{S}}^2 \right] = 0 \quad \& \quad \left[\underline{H}, \underline{S}_z \right] = 0$$

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

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



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

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

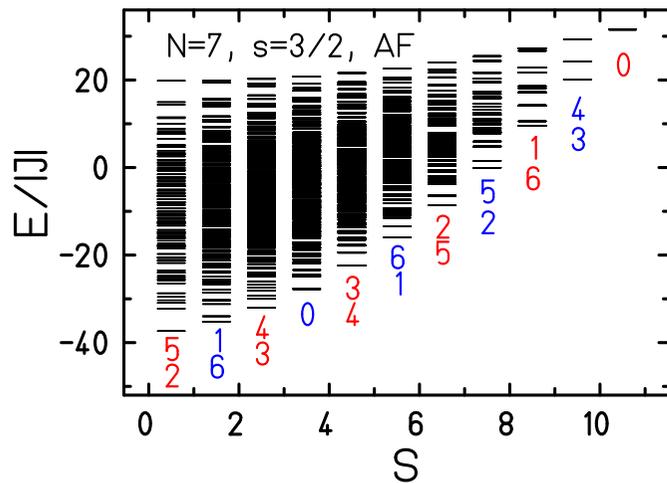
All $a(\mathbf{m})$ are non-zero, real, and of equal sign.

- Yields eigenvalues for the shift operator \tilde{T} :

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

(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. $s = 1/2, 3/2, 5/2, \dots$ 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):

$$k = \lfloor \frac{N+1}{4} \rfloor \text{ and } k = N - \lfloor \frac{N+1}{4} \rfloor$$

- 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)

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

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	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	$30 \equiv 3$	$35 \equiv 1$	$40 \equiv 4$	$45 \equiv 0$

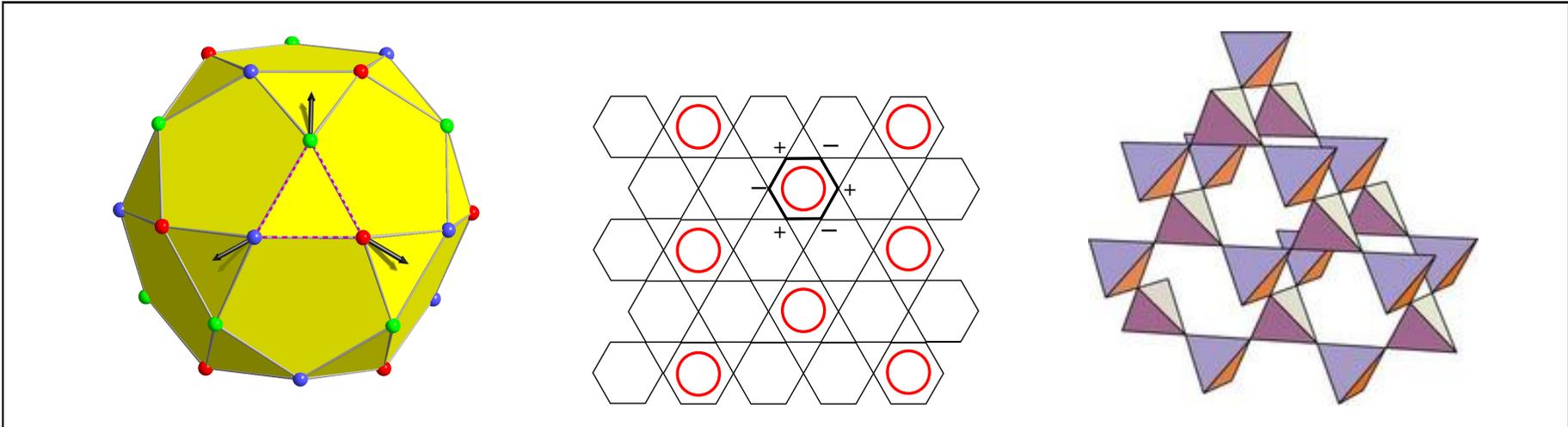
No general proof yet.

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

Fe₃₀ and friends (corner-sharing triangles)

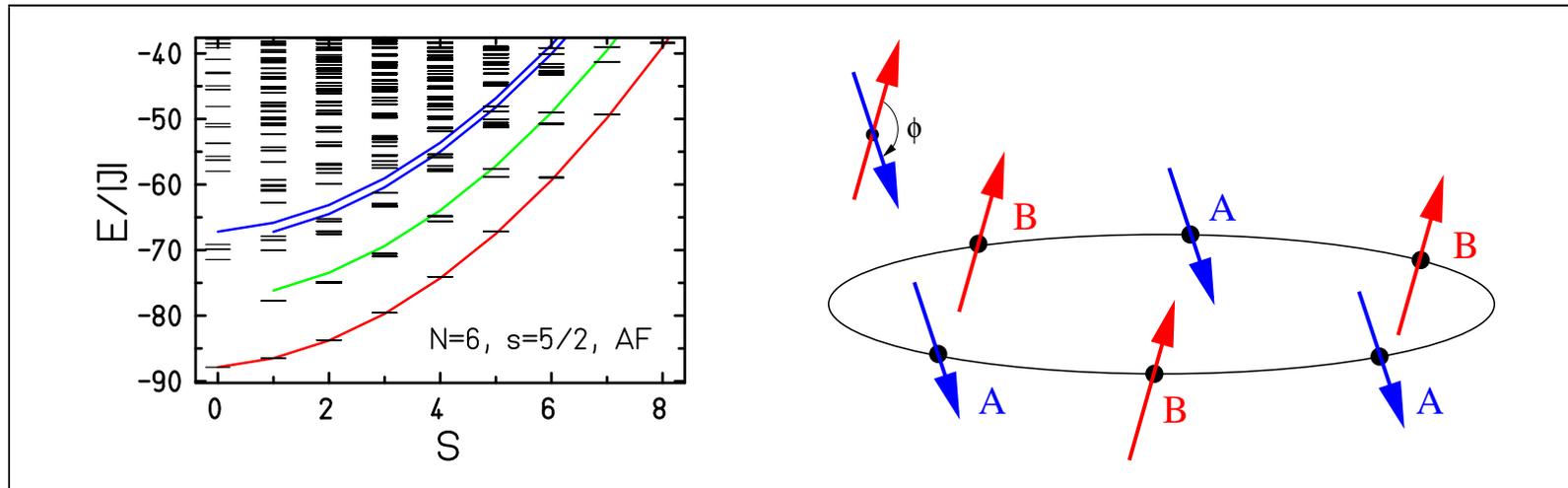
Fe₃₀ and friends

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

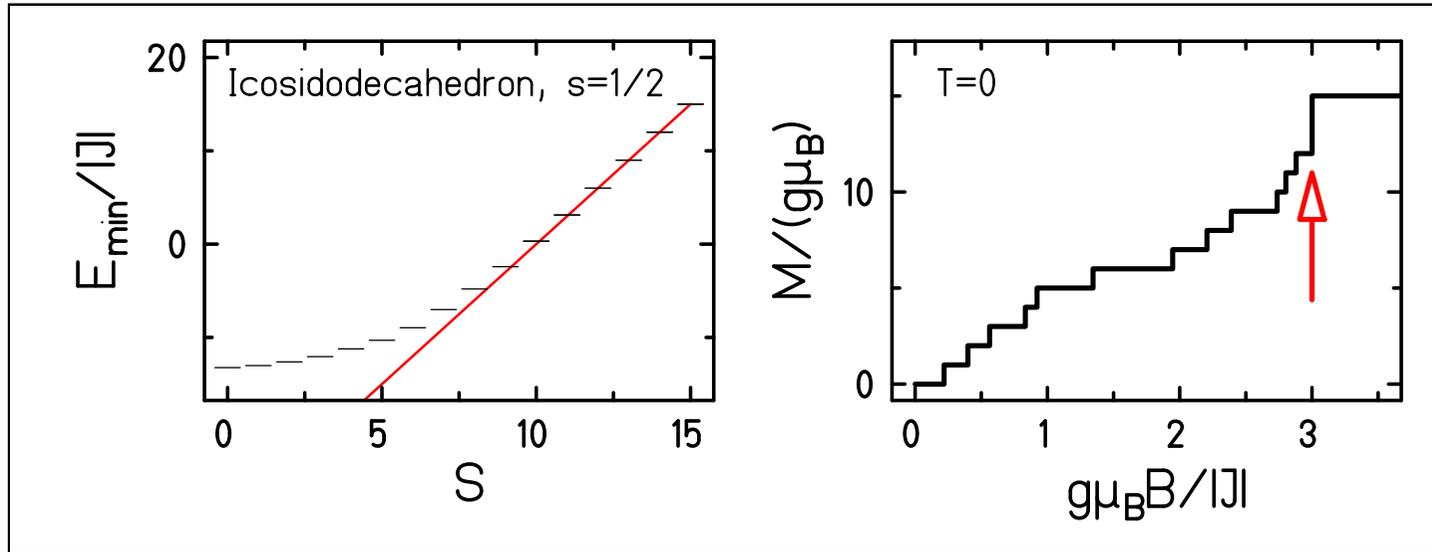


- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- For bipartite systems (2,3): $\tilde{H}^{eff} = -2 J_{eff} \tilde{S}_A \cdot \tilde{S}_B$;
- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(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

{Mo₇₂Fe₃₀}



- 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);

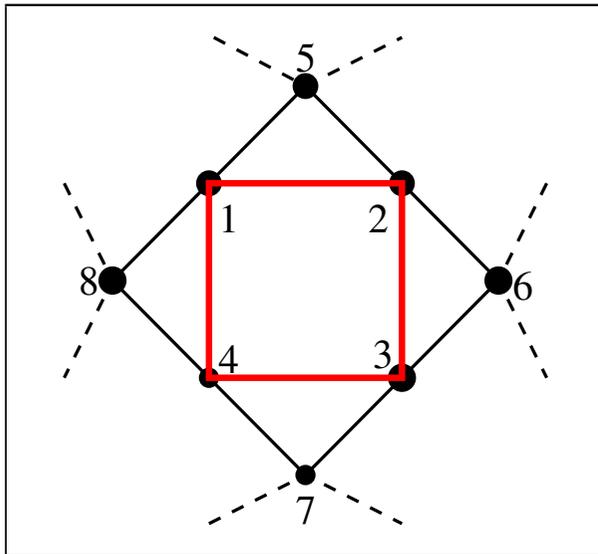
(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

(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



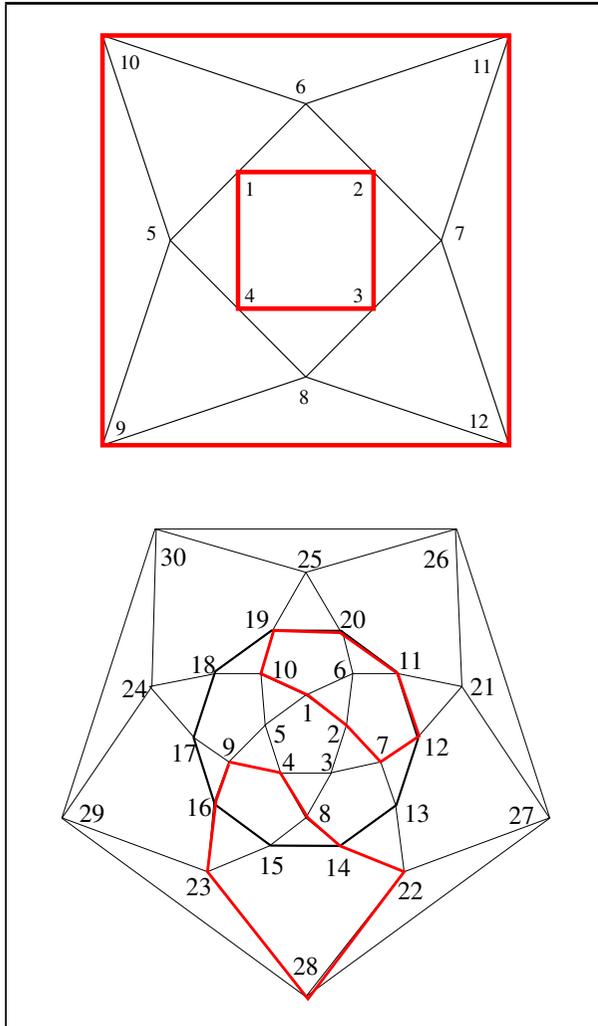
- $|\text{localized magnon}\rangle = \frac{1}{2} (|1\rangle - |2\rangle + |3\rangle - |4\rangle)$
- $|1\rangle = \tilde{s}^-(1) |\uparrow\uparrow\uparrow \dots\rangle$ etc.
- $\tilde{H} |\text{localized magnon}\rangle \propto |\text{localized magnon}\rangle$
- Localized magnon is state of lowest energy (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 $M = N_s - n$;
- Linear dependence of E_{\min} on M
 \Rightarrow ($T = 0$) magnetization jump;
- A rare example of analytically known many-body states!

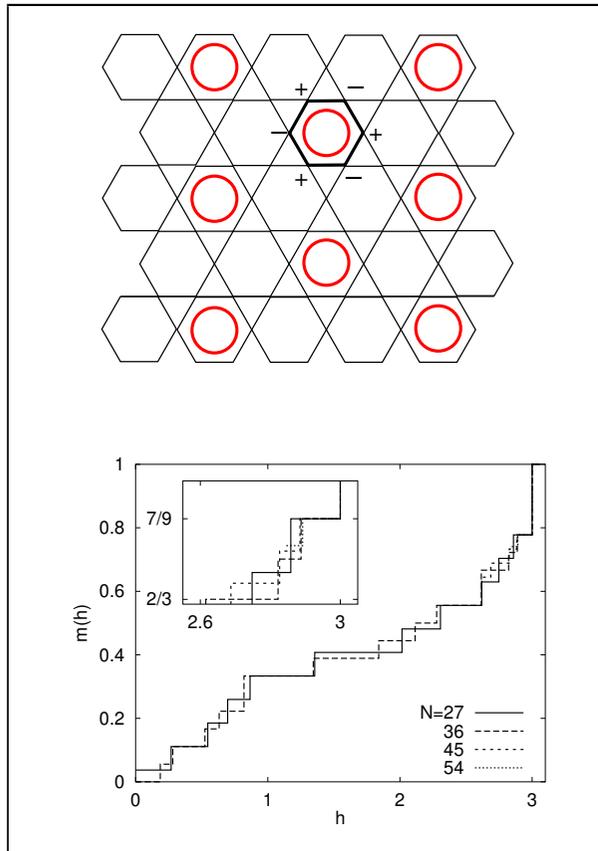
J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

Extended lattices and flat bands

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

CANCELLED

Giant magnetization jumps in frustrated antiferromagnets III Kagome Lattice

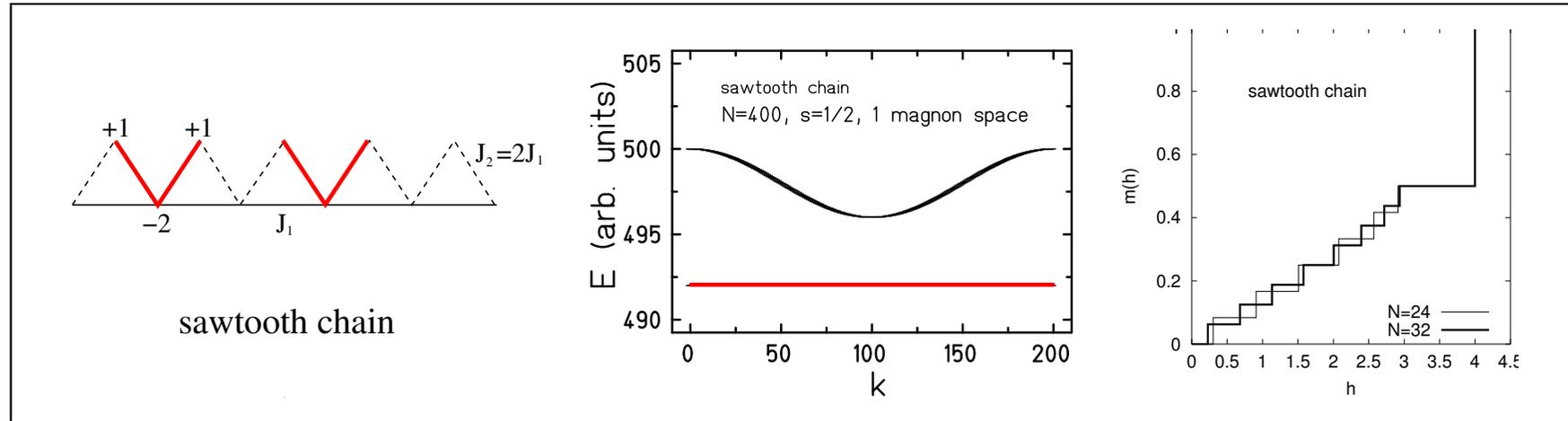


- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore;
- Each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$;
Kagome: max. number of indep. magnons is $N/9$;
- Linear dependence of E_{\min} on M
 \Rightarrow ($T = 0$) 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

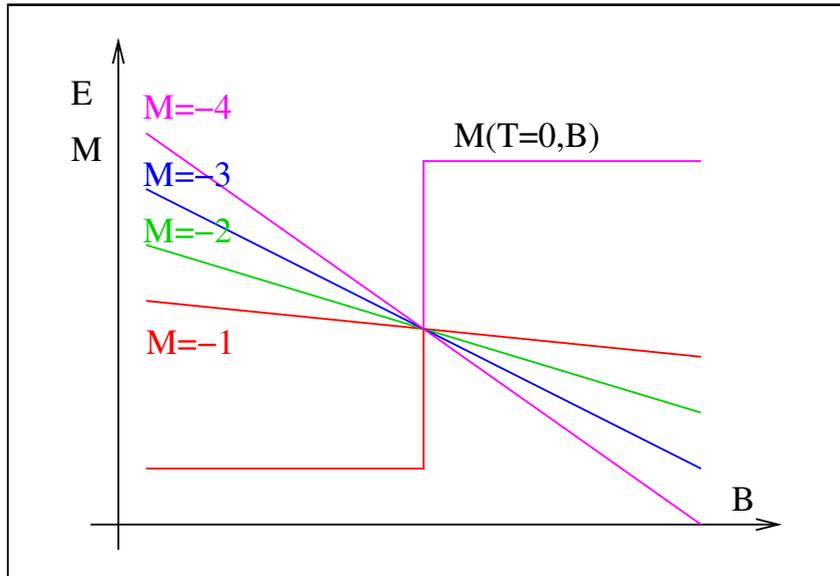


- Flat band of minimal energy in one-magnon space; localized magnons can be built from delocalized states in the flat band.
- Entropy can be evaluated using hard-object models; universal low-temperature behavior.
- Same behavior for Hubbard model; flat band ferromagnetism (Tasaki & Mielke), jump of N 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)

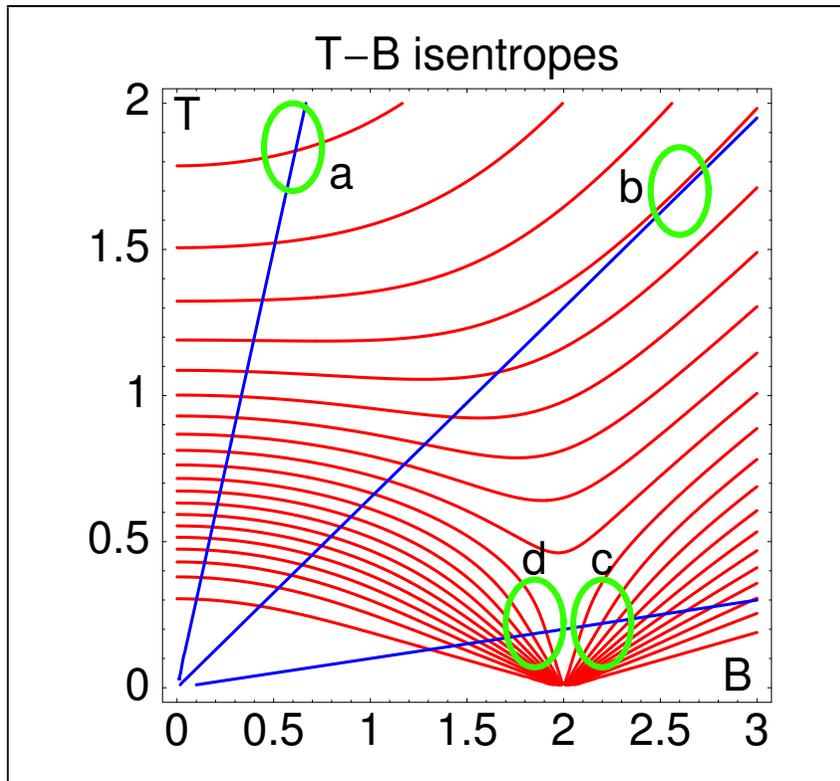
A. Honecker, J. Richter, Condensed Matter Physics **8**, 813 (2005)

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

Isentropes of an $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

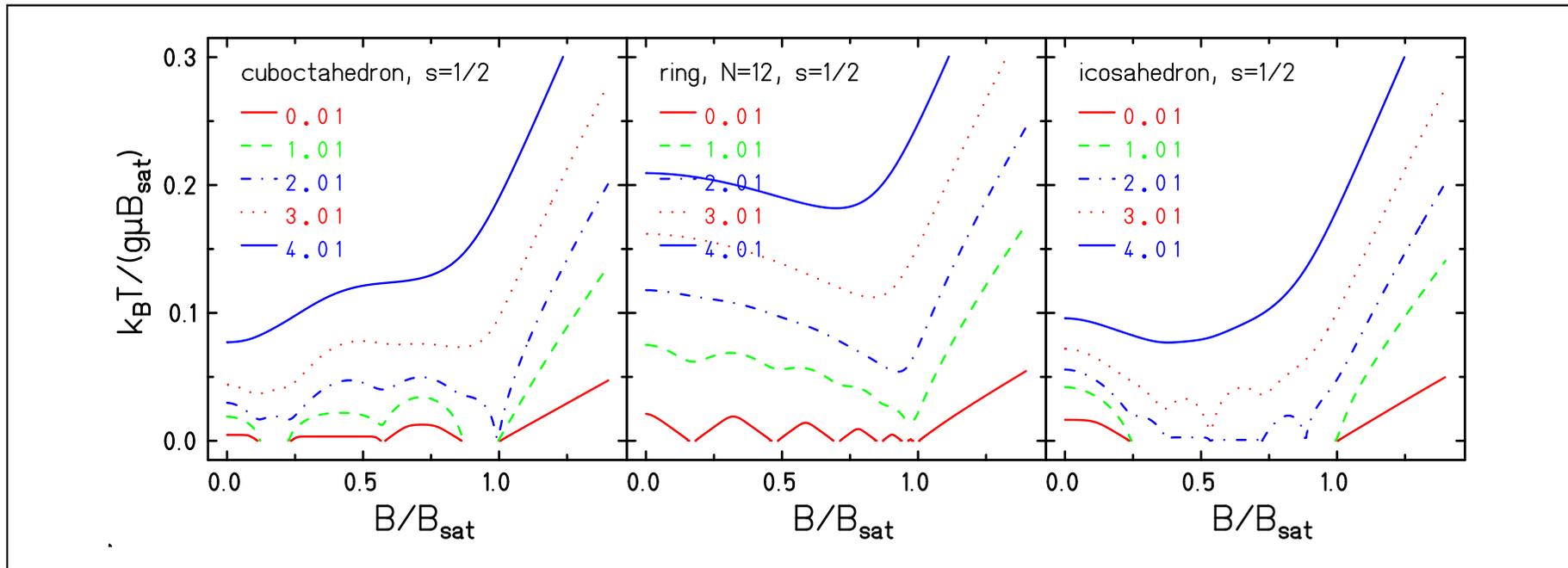
Magnetocaloric effect:

- (a) reduced,
- (b) the same,
- (c) enhanced,
- (d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

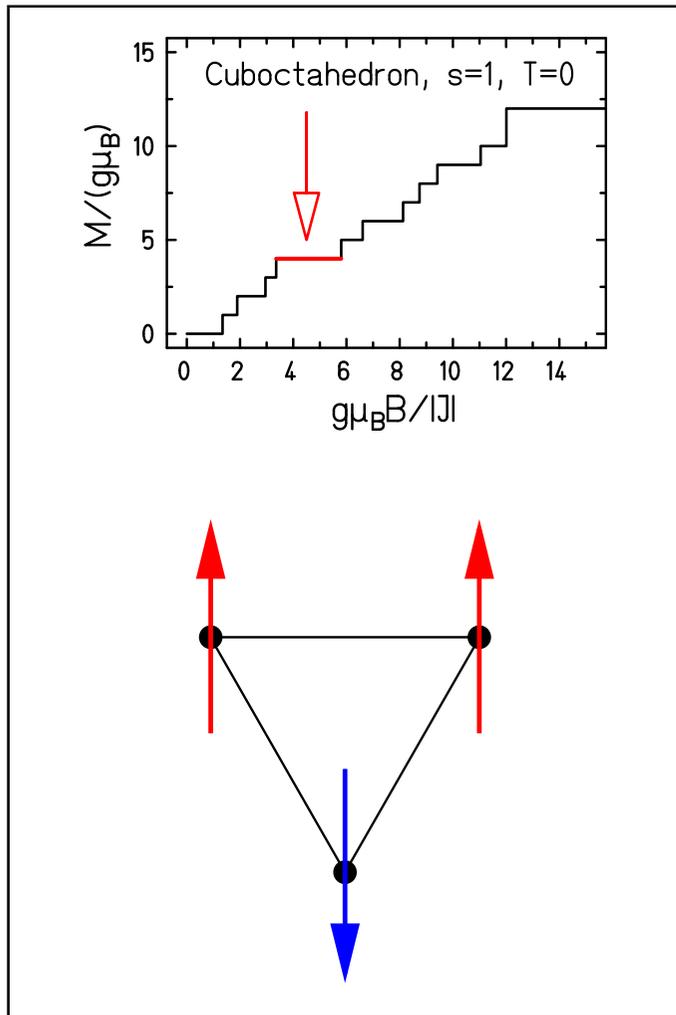
Magnetocaloric effect III – Molecular systems



- 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)

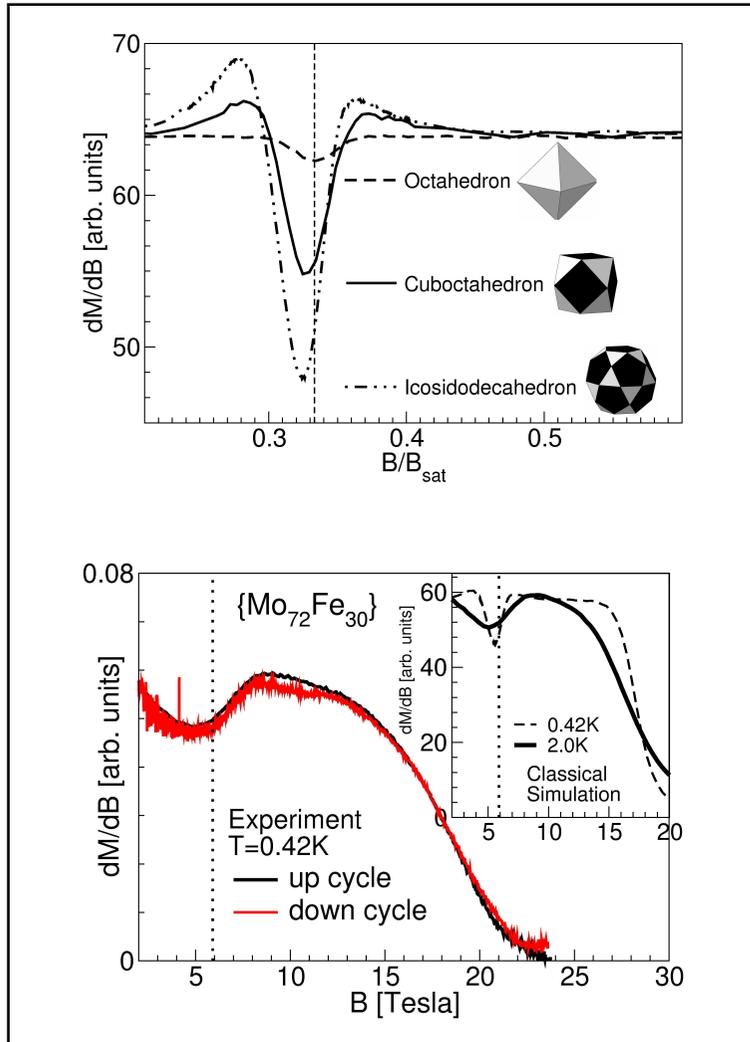
Magnetization plateaus and susceptibility minima



- 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

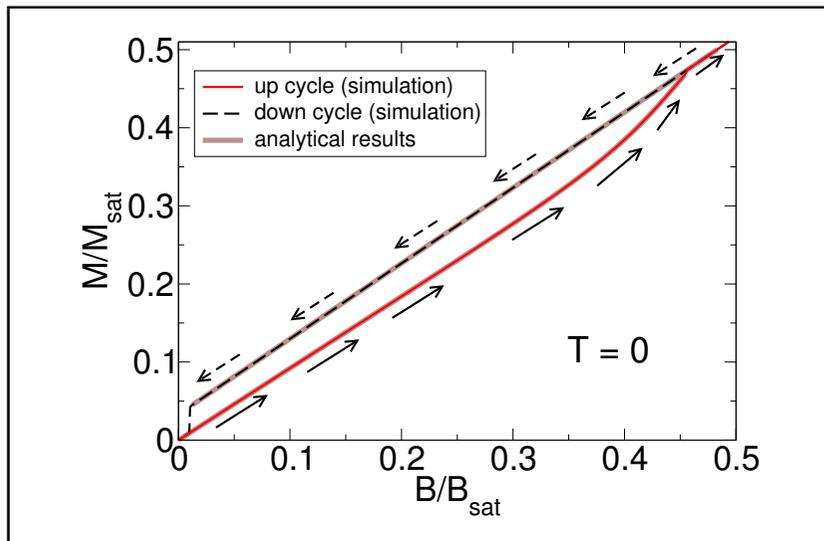


- Susceptibility shows a pronounced dip at $B_{sat}/3$ (classical calculations and quantum calculations for the cuboctahedron).
- Obvious in case of plateau at $\mathcal{M}_{sat}/3$, more subtle for other frustrated systems.
- Experimentally verified for $\{Mo_{72}Fe_{30}\}$.
C. Schröder, H. Nojiri,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

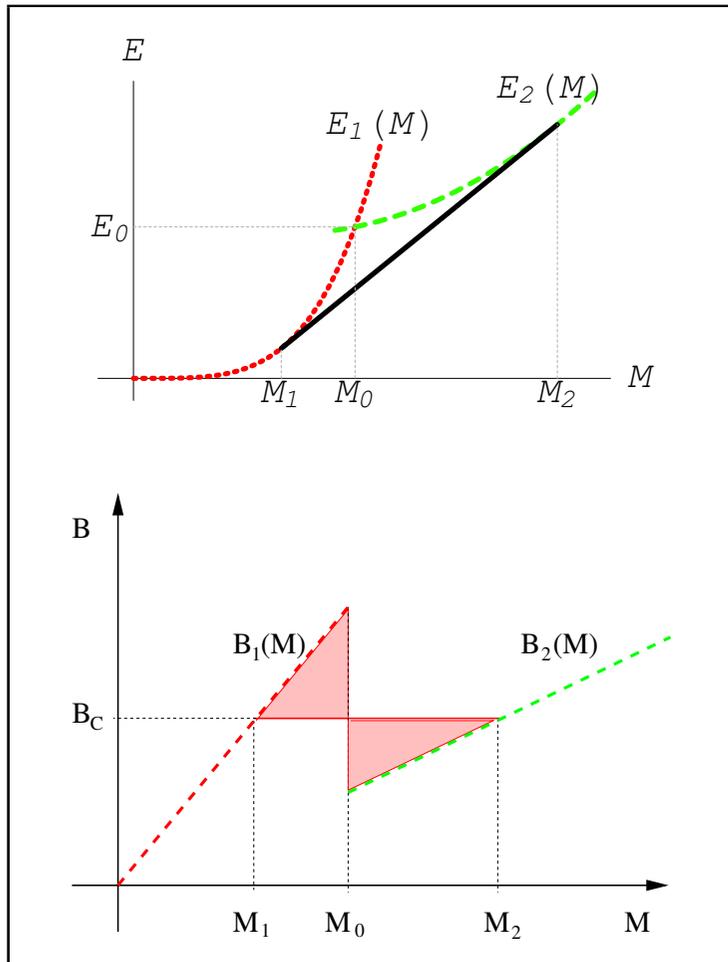


- Heisenberg model with isotropic nearest neighbor exchange
- Hysteresis behavior of the classical icosahedron in an applied magnetic field.
- Classical spin dynamics simulations (thick lines).
- Analytical stability analysis (grey lines).

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

Metamagnetic phase transition II

Non-convex minimal energy

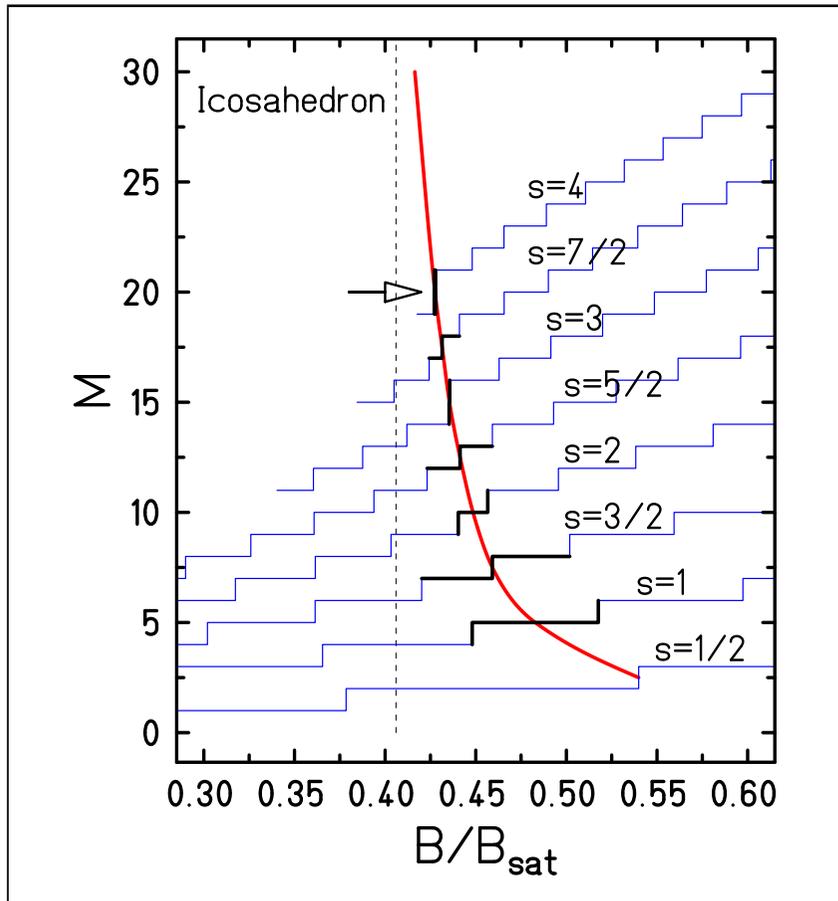


- Minimal energies realized by two families of spin configurations (1): $E_1(M)$ – “4- θ -family”, $E_2(M)$ – “decagon family”
- Overall minimal energy curve is not convex.
- Maxwell construction yields ($T = 0$) 1st order phase transition at B_c (1,2,3)
- ($T = 0$)–magnetization dynamics extends into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

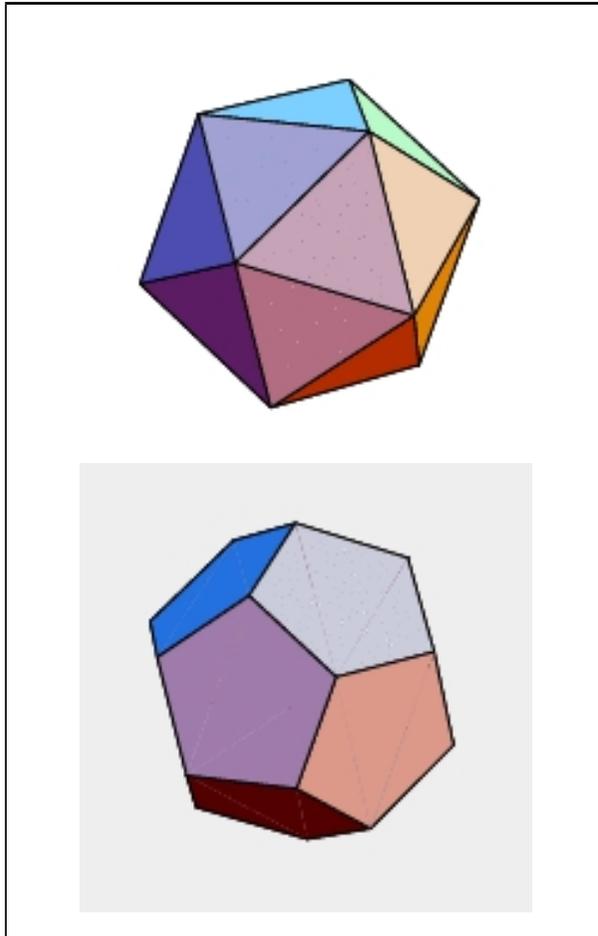
Quantum icosahedron



- Quantum analog:
Non-convex minimal energy levels
⇒ 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