Frustration effects in magnetic molecules

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Deutsche Forschungsgemeinschaft DFG

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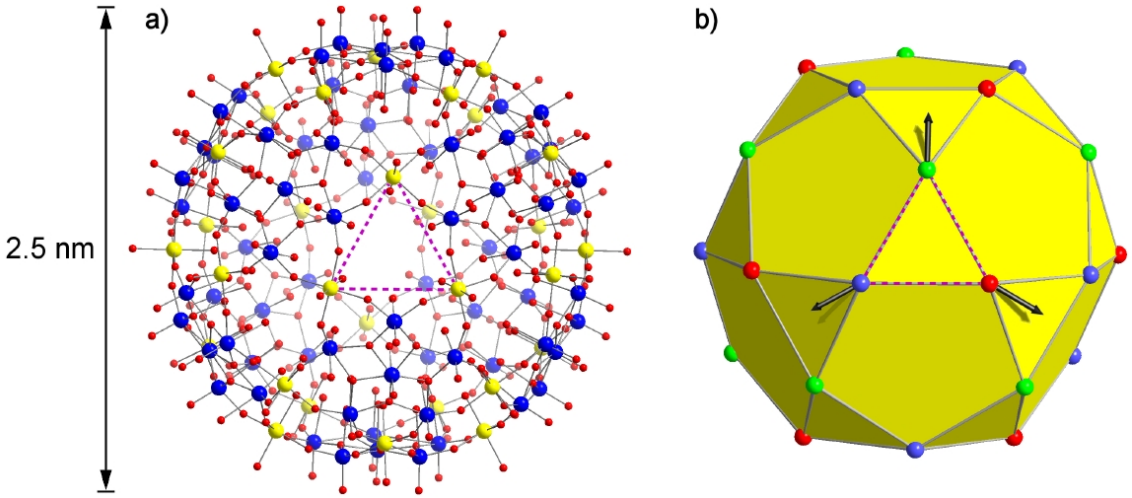
“The worldwide Ames group”

- K. Bärwinkel, H.-J. Schmidt, J. S., M. Allalen, M. Brüger, D. Mentrup, M. Exler, P. Hage, F. Hesmer, K. Jahns, F. Ouchni, R. Schnalle, P. Shechelokovskyy, S. Torbrügge (Uni Osnabrück);
- M. Luban, P. Kögerler, D. Vaknin, . . . (Ames Lab, Iowa, USA);
- Chr. Schröder (FH Bielefeld & Ames Lab, Iowa, USA);
- R.E.P. Winpenny (Man U); L. Cronin (University of Glasgow);
- H. Nojiri (Tohoku University, Japan); N. Dalal (Florida State, USA);
- J. Richter, J. Schulenburg, R. Schmidt (Uni Magdeburg);
- S. Blügel, A. Postnikov (FZ Jülich); A. Honecker (Uni Braunschweig).
- E. Rentschler (Uni Mainz); U. Kortz (IUB); A. Tennant (HMI Berlin).

General results on frustrated magnetic molecules

1. Extension of Lieb, Schultz, and Mattis: k–rule for odd rings
2. Rotational bands in antiferromagnets
3. Giant magnetization jumps
4. Enhanced magnetocaloric effect
5. Magnetization plateaus and susceptibility minima
6. Hysteresis without anisotropy

$\{Mo_{72}Fe_{30}\}$ – 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 $(2s+1)^N \approx 10^{23}$.

(1) A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001) , (2) M. Axenovich and M. Luban, Phys. Rev. B **63**, 100407 (2001)

Model Hamiltonian – Heisenberg-Model

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

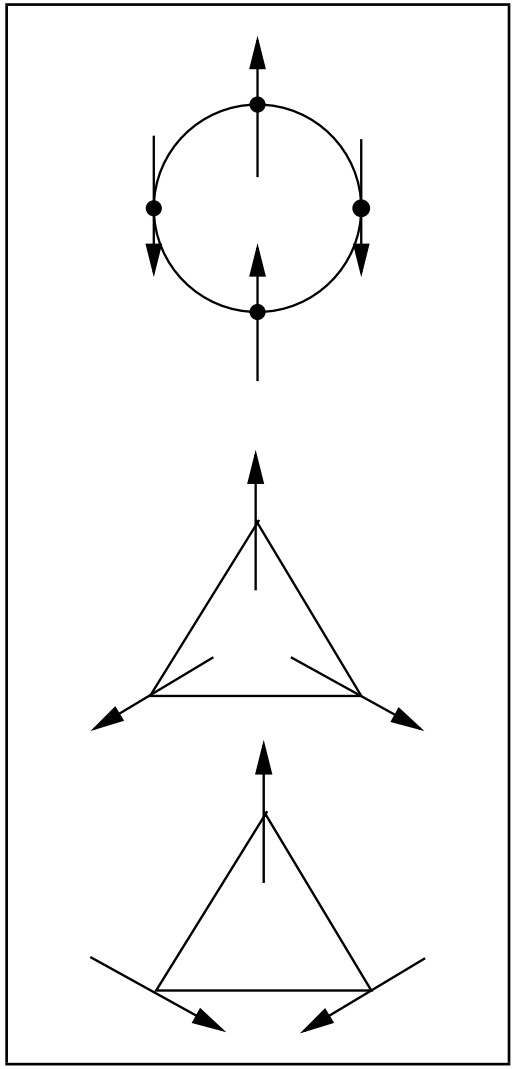
Heisenberg Zeeman

The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations.

$J < 0$: antiferromagnetic coupling.

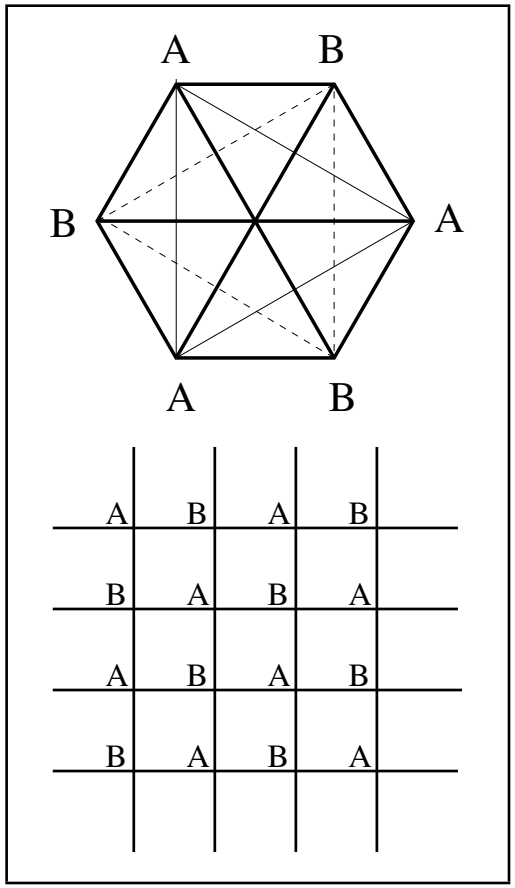
Very often additional terms – dipolar, anisotropic – are utterly negligible. If needed they can be cast in the form $\sum_{i,j} \vec{\underset{\sim}{s}}(i) \cdot \mathbf{D}_{ij} \cdot \vec{\underset{\sim}{s}}(j)$.

Classical definition of frustration



- Definition: A quantum spin system is frustrated if the corresponding classical system is frustrated, i. e. if neighboring classical spins are not aligned antiparallel.
- Problem: Need to know the corresponding classical system.

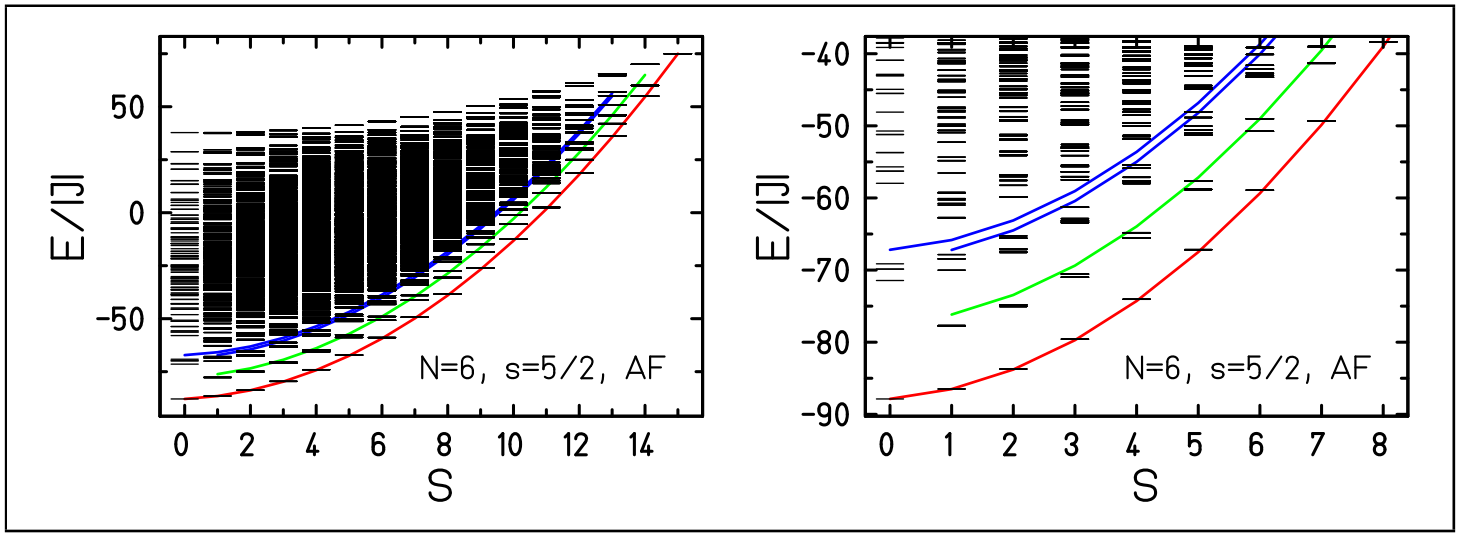
Advanced definition of frustration



- Definition: A non-bipartite system is called frustrated.
- Bipartite: If the system can be decomposed into subsystems A and B such that the coupling constants fulfil $J(x_A, y_B) \leq g^2$, $J(x_A, y_A) \geq g^2$, $J(x_B, y_B) \geq g^2$, the system is called bipartite (1,2).
- Simple bipartite cases: there are only antiferromagnetic interactions between spins of different sublattices.

(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)

Rotational bands in antiferromagnets I

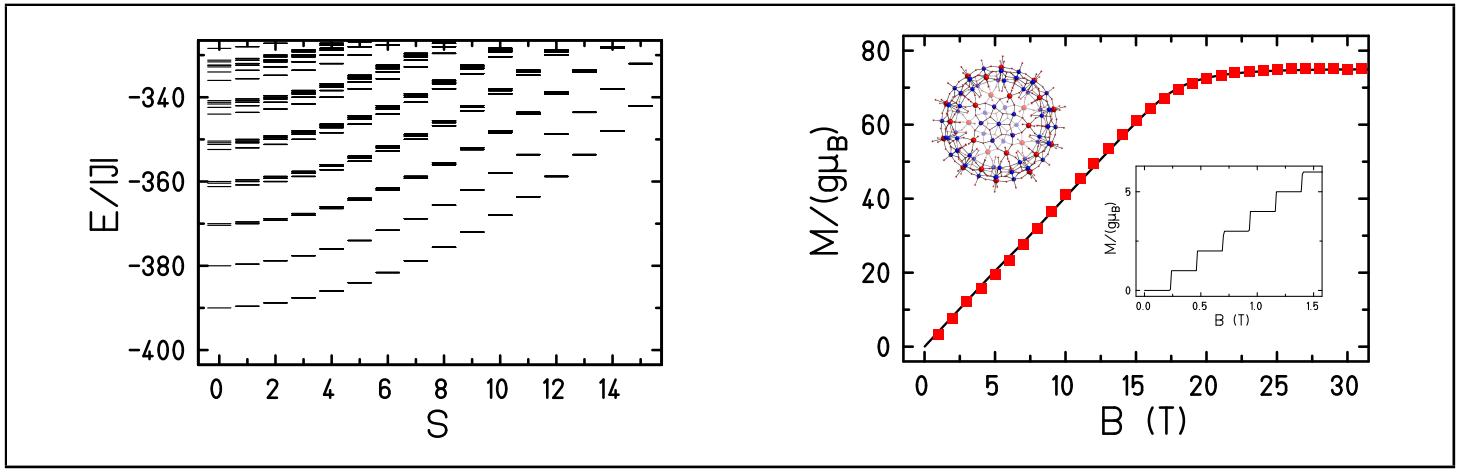


- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- Most pronounced for bipartite systems (2,3),
  might be a good approximation for more general systems;
- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(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 $\{Mo_{72}Fe_{30}\}$

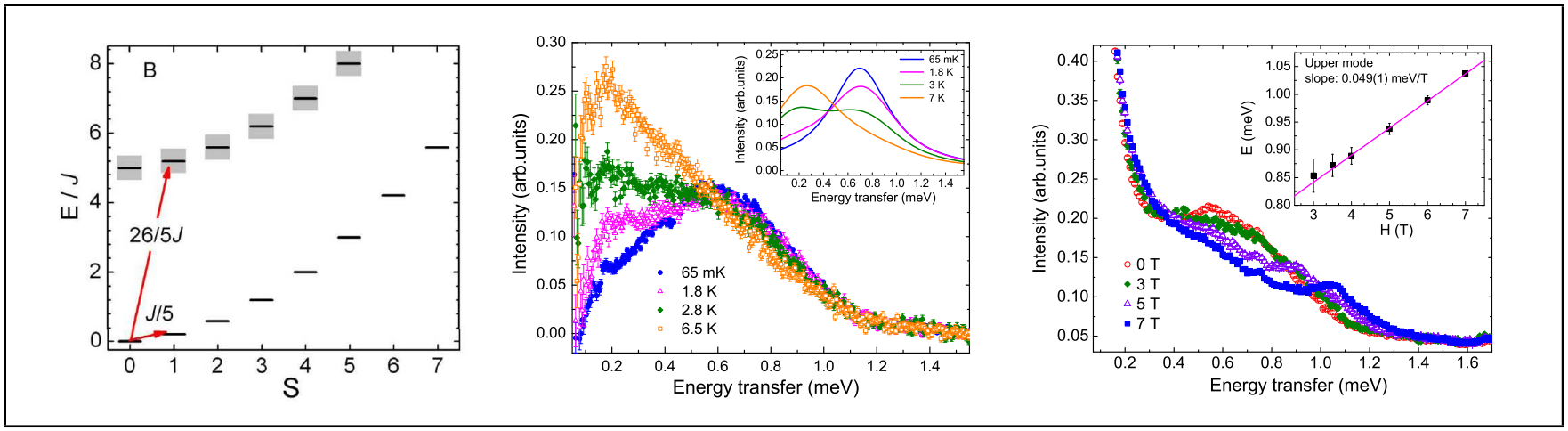
$$\underset{\sim}{H} = -2\,J \sum_{(u<v)} \vec{\underset{\sim}{s}}(u) \cdot \vec{\underset{\sim}{s}}(v) \quad \approx \quad -\frac{D\,J}{N}\left[\vec{\underset{\sim}{S}}^2 - \sum_{j=1}^{N_{SL}} \vec{\underset{\sim}{S}}_j^2\right] = \underset{\sim}{H}^{\text{eff}}$$



$\vec{\underset{\sim}{S}}_j$ sublattice spins; $D = 6$; good description of magnetization.

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

Rotational bands in antiferromagnets III
Neutron scattering at $\{Mo_{72}Fe_{30}\}$



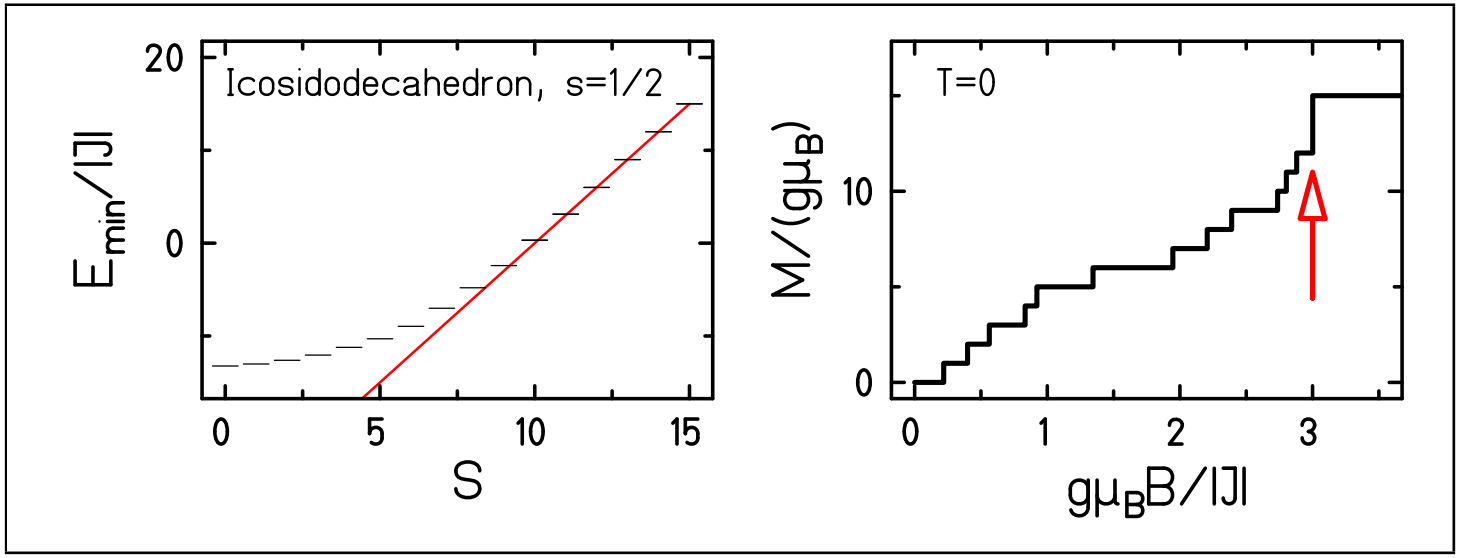
- INS shows broad peak at band separation; broad width is a sign of frustration, i.e. of the reduced significance of rotational bands.

- Thermal behavior understood; dependence on external field currently investigated.

V. O. Garlea, S. E. Nagler, J. L. Zarestky, C. Stassis, D. Vaknin, P. Kögerler, D. F. McMorrow, C. Niedermayer, D. A. Tennant, B. Lake, Y. Qiu, M. Exler, J. Schnack, M. Luban, submitted; cond-mat/0505066

Giant magnetization jumps in frustrated antiferromagnets I

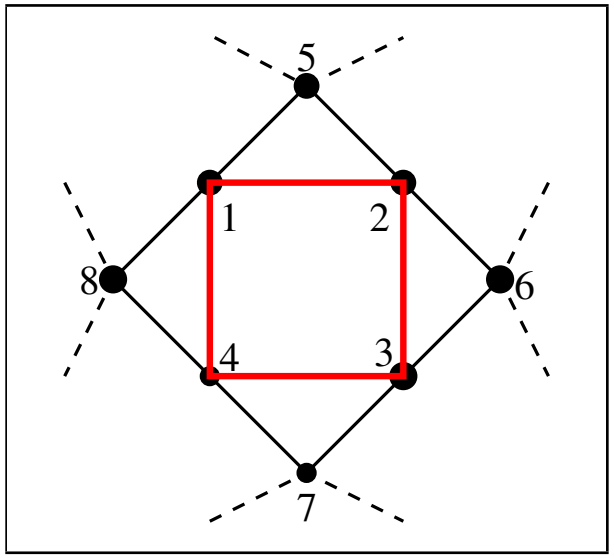
$\{\mathbf{Mo_{72}Fe_{30}}\}$



- Close look: $E_{\mathrm{min}}(S)$ 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)

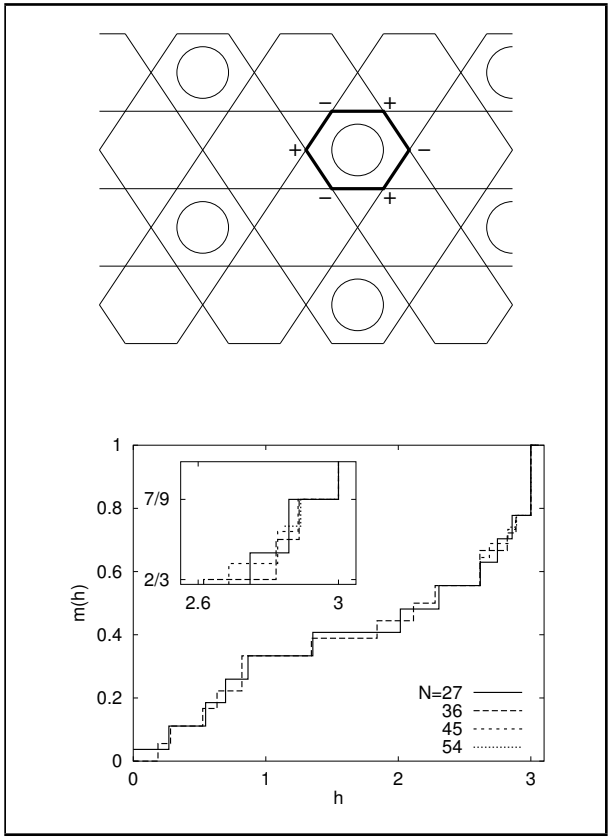
Giant magnetization jumps in frustrated antiferromagnets II
Localized Magnons



- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle)$
- $|\,1\,\rangle = \underset{\sim}{s}^{-}(1)\,|\uparrow\uparrow\uparrow\ldots\rangle$ etc.
- $$\begin{aligned}
\underset{\sim}{H}\,|\,1\,\rangle &= J\{\,|\,1\,\rangle + 1/2(\,|\,2\,\rangle + |\,4\,\rangle + |\,5\,\rangle + |\,8\,\rangle)\} \\
\underset{\sim}{H}\,|\,2\,\rangle &= J\{\,|\,2\,\rangle + 1/2(\,|\,1\,\rangle + |\,3\,\rangle + |\,5\,\rangle + |\,6\,\rangle)\} \\
\underset{\sim}{H}\,|\,3\,\rangle &= J\{\,|\,3\,\rangle + 1/2(\,|\,2\,\rangle + |\,4\,\rangle + |\,7\,\rangle + |\,6\,\rangle)\} \\
\underset{\sim}{H}\,|\,4\,\rangle &= J\{\,|\,4\,\rangle + 1/2(\,|\,1\,\rangle + |\,3\,\rangle + |\,7\,\rangle + |\,8\,\rangle)\}
\end{aligned}$$
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$

- Triangles trap the localized magnon, amplitudes cancel at outer vertices.

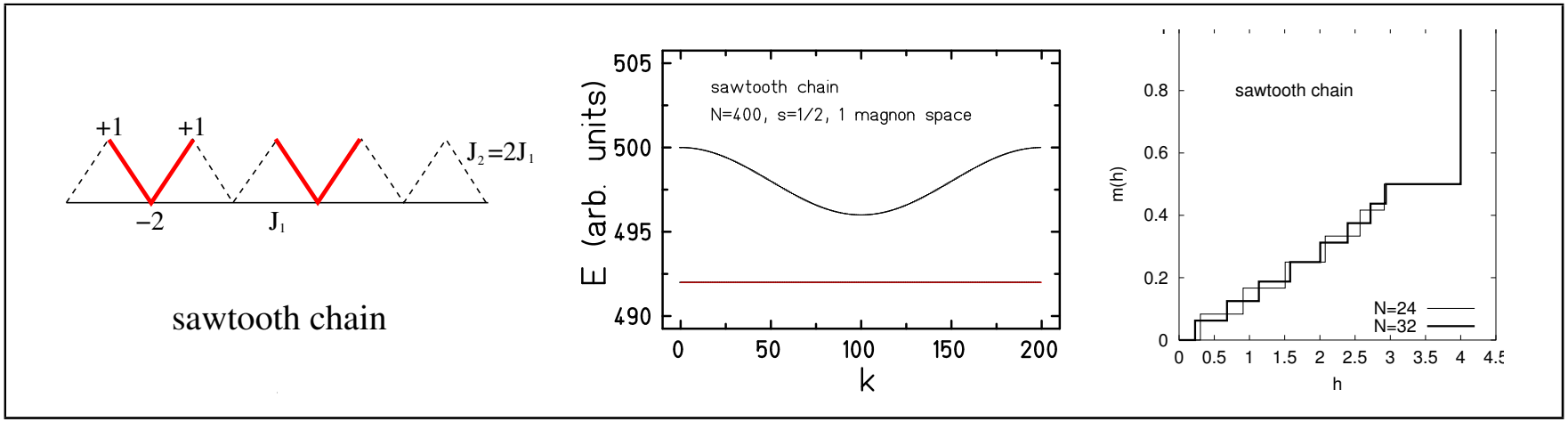
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- Non-interacting one-magnon states can be placed on various lattices, e. g. kagome or pyrochlore lattice;
- 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
  $\Rightarrow$ magnetization jump;
- Maximal number of independent magnons: N/9;
- Jump is a macroscopic quantum effect!

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;
- Sawtooth chain exceptional since degeneracy is $N/2$ (very high).

J. Richter, J. Schulenburg, A. Honecker, J. Schnack, H.-J. Schmidt, J. Phys.: Condens. Matter **16**, S779 (2004)

Enhanced magnetocaloric effect I
Basics

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

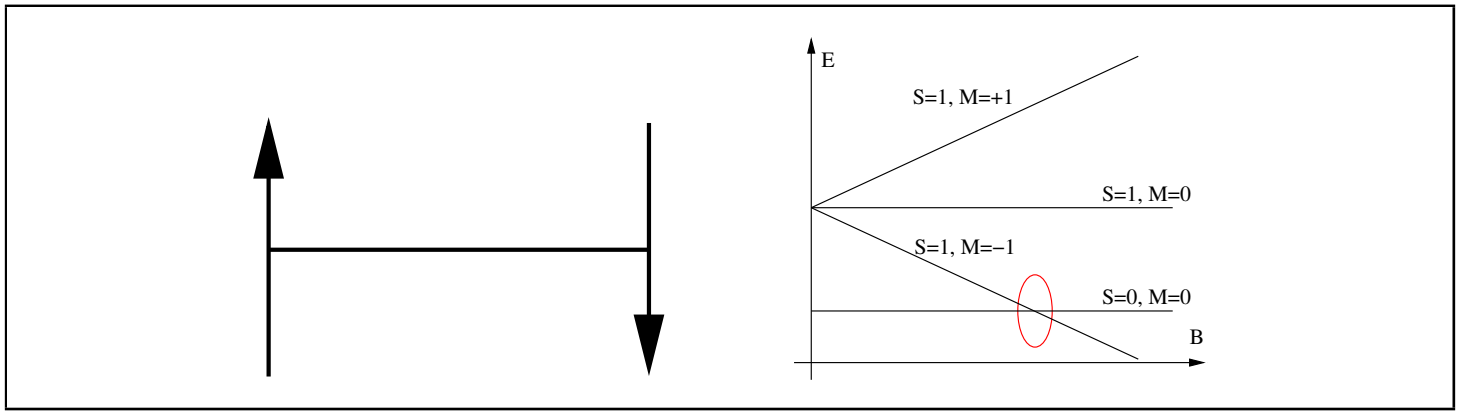
(adiabatic temperature change)

- 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)

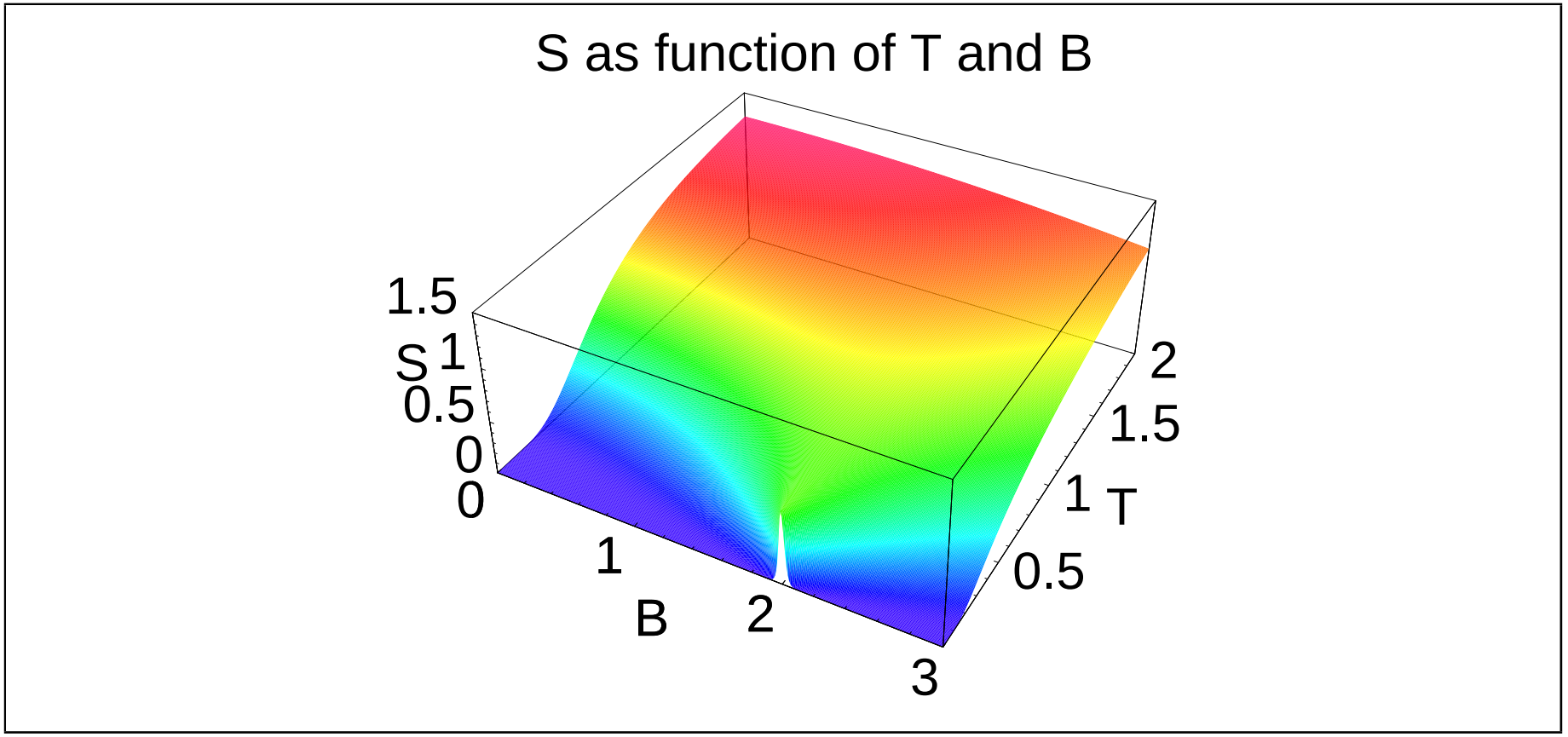
Enhanced magnetocaloric effect II
Simple af $s = 1/2$ dimer



- 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.

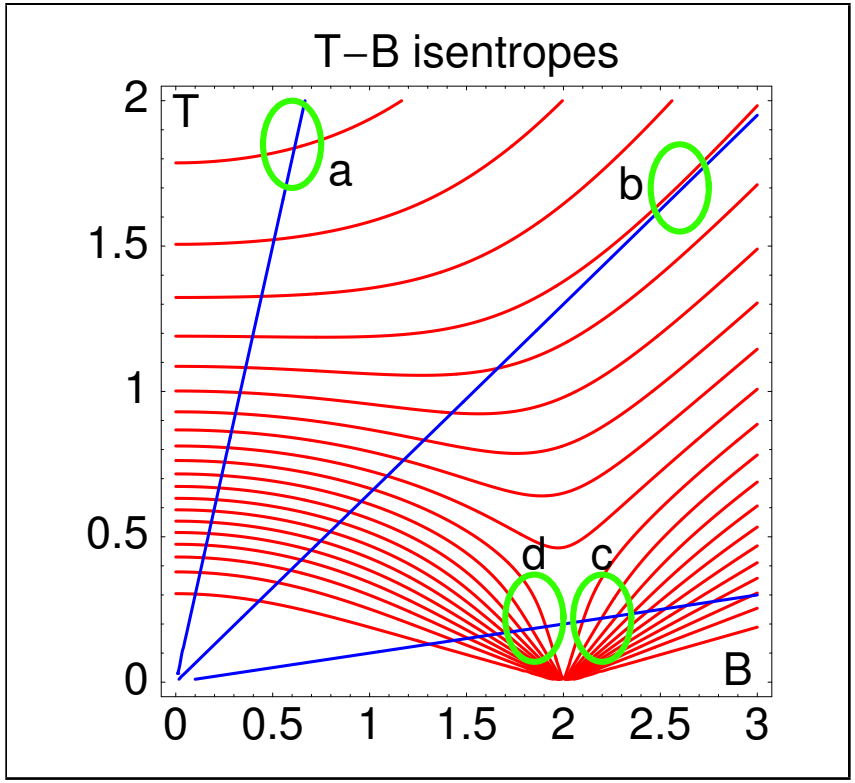
Enhanced magnetocaloric effect III
Entropy of af $s = 1/2$ dimer



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

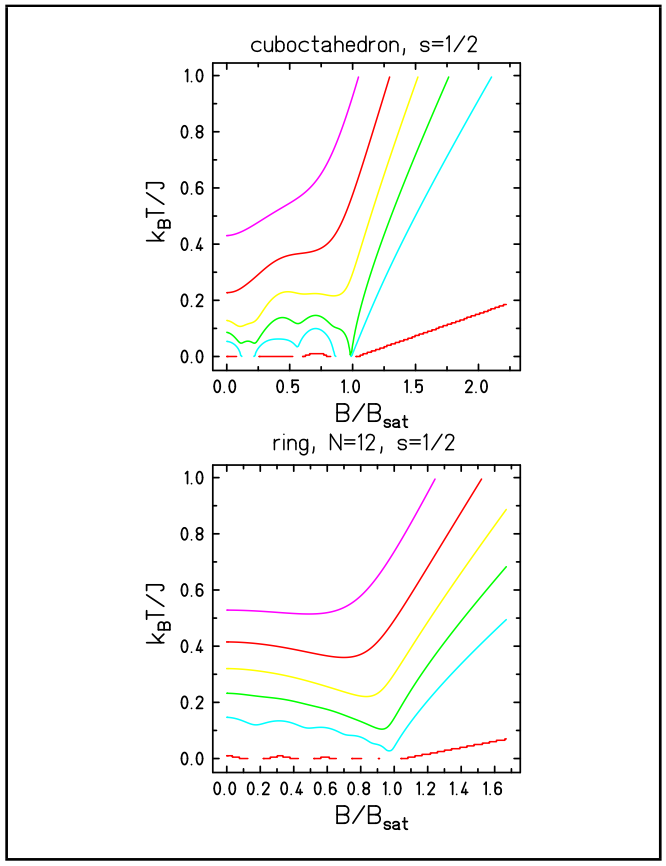
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

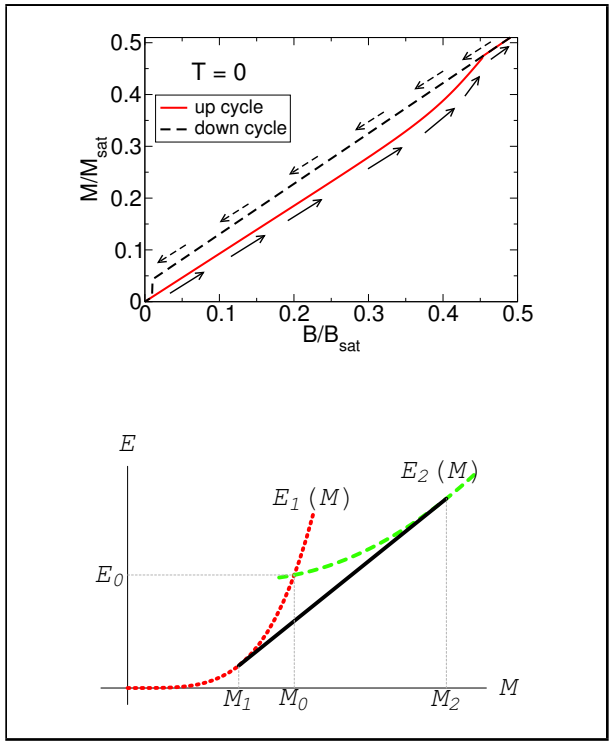
Enhanced magnetocaloric effect V
Two molecular spin systems



- 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

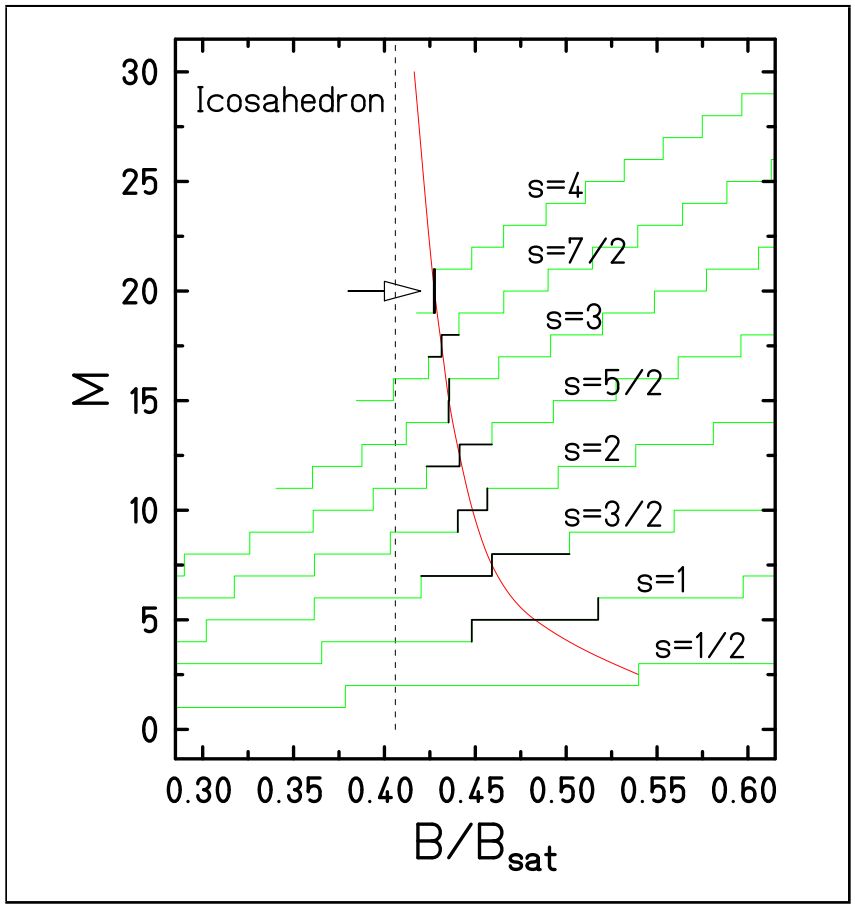
Metamagnetic phase transition I
Hyteresis without anisotropy



- 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)

no more time option

Summary

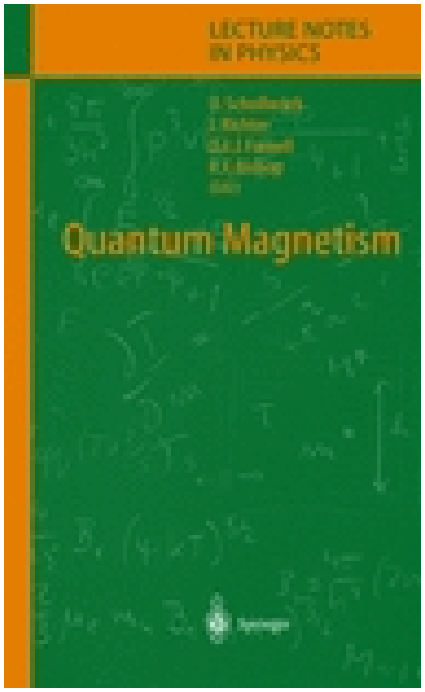
Frustration can lead to exotic behavior.

And, the end is not in sight, . . .

. . . , however, this talk is at its end!

Thank you very much for your attention.

Buy now!



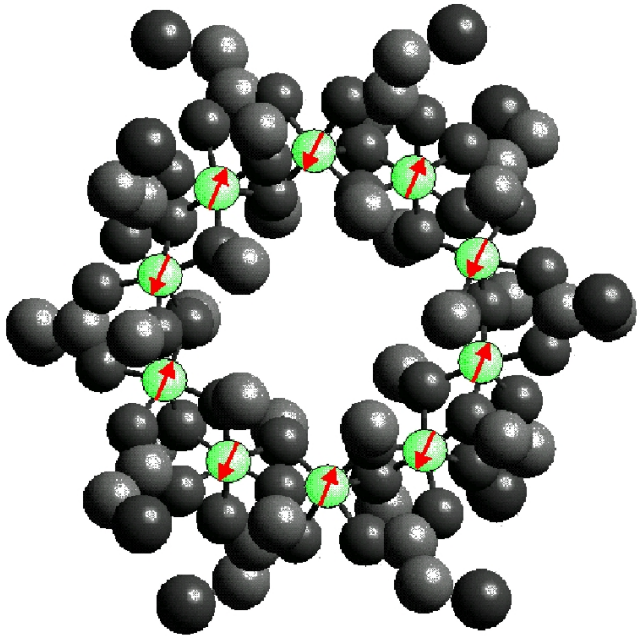
Quantum Magnetism

Lecture Notes in Physics , Vol. 645
Schollwöck, U.; Richter, J.; Farnell, D.J.J.; Bishop, R.F. (Eds.)
2004, XII, 478 p., Hardcover, 69,95 €
ISBN: 3-540-21422-4

Mikeska, Kolezhuk, *One-dimensional magnetism*
Richter, Schulenburg, Honecker, *Q. Mag. in 2-D*
Schnack, *Molecular Magnetism*
Ivanov, Sen, *Spin Wave Analysis*
Laflorencie, Poilblanc, *Low-Dim. Gapped Systems*
Cabra, Pujol, *Field-Theoretical Methods*
Farnell, Bishop, *Coupled Cluster Method*
Klümper, *Integrability of Quantum Chains*
Sachdev, *Mott Insulators*
Lemmens, Millet, *Spin Orbit Topology, a Triptych*

Appendix

Extension of Lieb, Schultz, and Mattis I
k–rule for even rings



Fe_{10}

- Goal: general properties of the magnetic spectrum depending on the structure, e.g. ground state quantum numbers.
- Properties of certain low-lying states known for bipartite spin systems (Marshall, Peierls, Lieb, Schultz, Mattis).
- For AF Heisenberg rings of even N thus the momentum quantum number k is known for relative ground states of subsapces $\mathcal{H}(M)$.

- Translational (shift) operator $\underset{\sim}{T}$ moves ring by one site: $\left[\underset{\sim}{H}, \underset{\sim}{T}\right] = 0$,
  Eigenvalues of $\underset{\sim}{T}$: $\exp\{-i2\pi k_\nu/N\}$, $k_\nu = 0, \ldots, N-1$.

Extension of Lieb, Schultz, and Mattis II
k–rule for odd rings

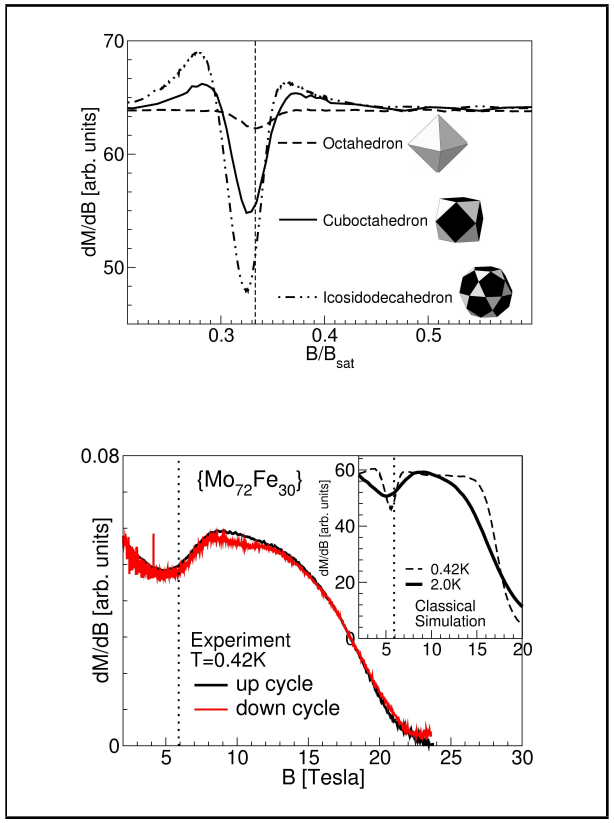
- An extended k-rule can be inferred from numerical investigations which yields the k quantum number for relative ground states of subspaces $\mathcal{H}(M)$ for even as well as odd spin rings

$$\text{If } N \neq 3 \quad \text{then} \quad k \equiv \pm a\lceil\frac{N}{2}\rceil \mod N\,, \quad a = Ns - M$$

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

K. Fabricius, U. Löw, K.-H. Mütter, and P. Ueberholz, Phys. Rev. B **44**, 7476 (1991)
M. Karbach, Ph. D. thesis, Universität Wuppertal (1994)
K. Bärwinkel, H.-J. Schmidt, and J. Schnack, J. Magn. Magn. Mater. **220**, 227 (2000)
J. Schnack, Phys. Rev. B **62**, 14855 (2000)
K. Bärwinkel, P. Hage, H.-J. Schmidt, and J. Schnack, Phys. Rev. B **68**, 054422 (2003)

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 feature plateaus, e.g. at $\mathcal{M}_{\text{sat}}/3$ and independent magnons.
- Susceptibility shows a pronounced dip at $B_{\text{sat}}/3$ (classical calculations and quantum calculations for the cuboctahedron).
- Experimentally verified with $\{\text{Mo}_{72}\text{Fe}_{30}\}$.

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