Frustration effects in magnetic molecules

Jürgen Schnack

Fachbereich Physik - Universität Osnabrück

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

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Mainz, September 21st 2005

Deutsche Forschungsgemeinschaft DFG

DAAD

文部科学省

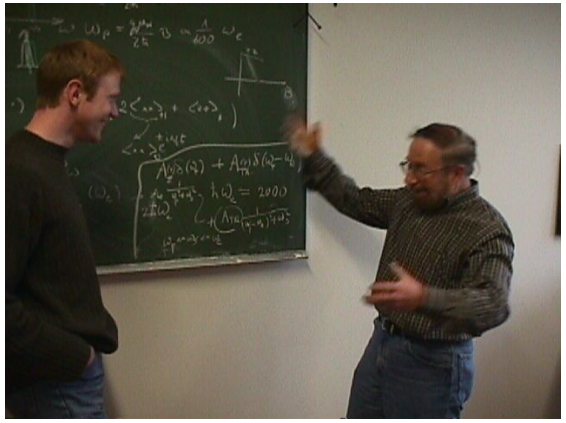
In late 20th century people coming from

transport theory

general relativity

nuclear physics

Zener diodes



were triggered by a “magnetic” enthusiast.

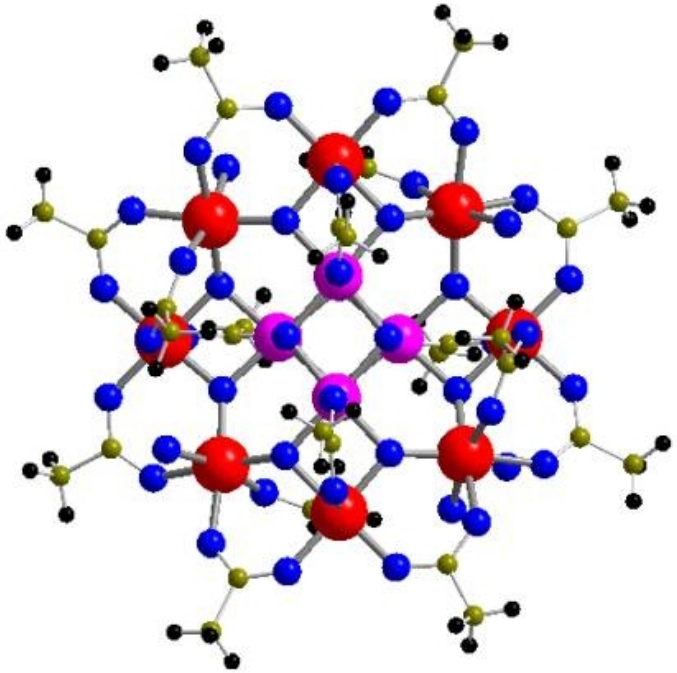
Meanwhile a big collaboration has been established

- 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 (U. Osnabrück);
- M. Luban, P. Kögerler, D. Vaknin (Ames Lab, USA);
  J. Musfeldt (U. of Tennessee, USA); N. Dalal (Florida State, USA);
- Chr. Schröder (FH Bielefeld & Ames Lab, USA);
- H. Nojiri (Tohoku University, Japan);
- R.E.P. Winpenny (Man U); L. Cronin (U. of Glasgow);
- J. Richter, J. Schulenburg, R. Schmidt (U. Magdeburg);
- S. Blügel, A. Postnikov (FZ Jülich); A. Honecker (Uni Braunschweig).
- E. Rentschler (U. Mainz); U. Kortz (IUB); A. Tennant (HMI Berlin).

. . . and various general results could be achieved

1. Extension of Lieb, Schultz, and Mattis: k–rule for odd rings
2. Rotational bands in antiferromagnets
3. Giant magnetization jumps in frustrated antiferromagnets
4. Magnetization plateaus and susceptibility minima
5. Enhanced magnetocaloric effect
6. Hysteresis without anisotropy
7. A special triangular molecule-based spin tube

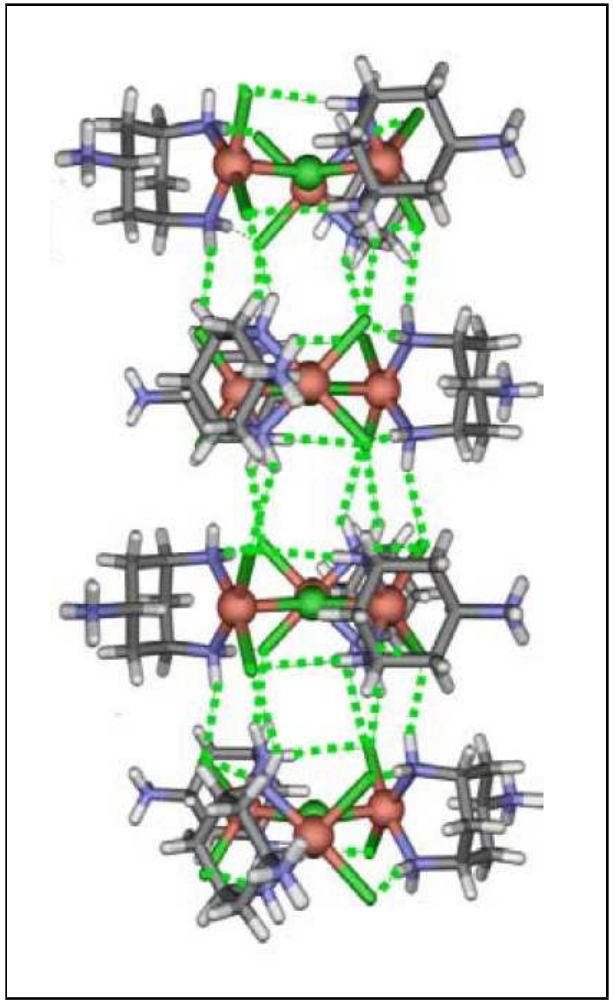
The beauty of magnetic molecules I



Mn_{12}

- Macro molecules (polyoxometalates etc.): consist of constituents like Hydrogen (H), Carbon (C), Oxygen (O), and diamagnetic ions (e.g. Mo) as well as paramagnetic ions like Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V) or Manganese (Mn);
- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- Single spin quantum number $1/2 \leq s \leq 7/2$;
- Intermolecular interaction relatively small, therefore measurements reflect the thermal behaviour of a single molecule.

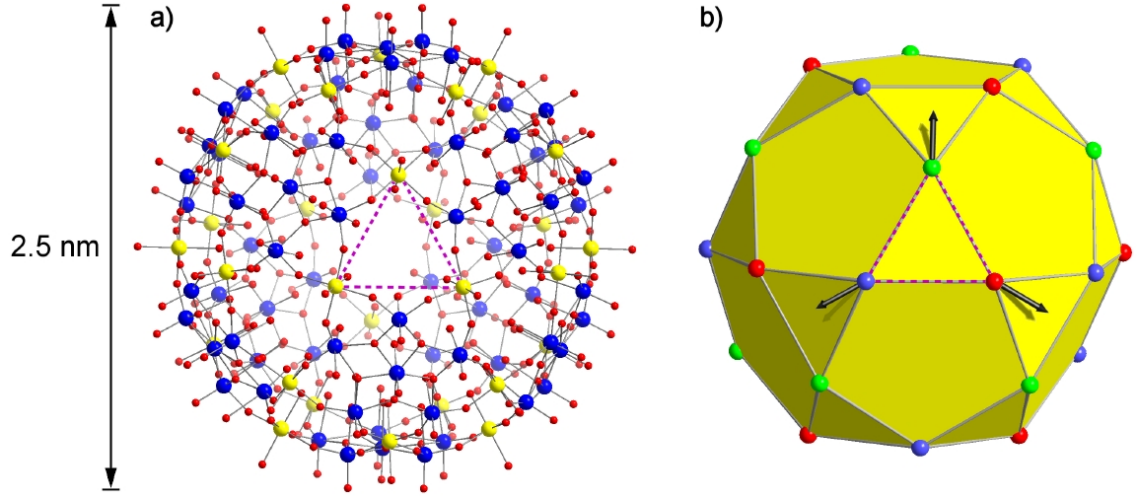
The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron rings (Fe_6, Fe_8, Fe_{10}, ...);
- 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)

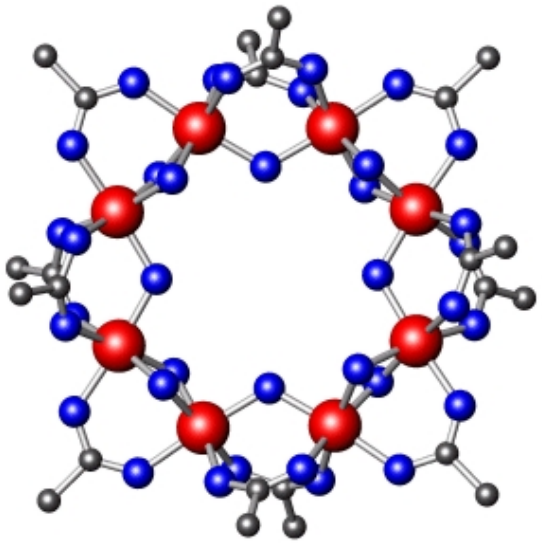
$\{Mo_{72}Fe_{30}\}$ – a molecular brother of the kagome lattice and an archetype of geometric frustration



- 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)

The beauty of magnetic molecules IV
Why magnetic molecules?



Cr_8

- Interacting spin system largely decoupled from remaining degrees of freedom;
- Transition few-spin system $\Rightarrow$ many-spin system, contribution to understanding of bulk magnetism;
- Transition quantum spin system ($s = 1/2$) $\Rightarrow$ classical spin system ($s_{\text{Fe}} = 5/2$, $s_{\text{Gd}} = 7/2$);
- Easy to produce, single crystals with $> 10^{17}$ identical molecules can be synthesized and practically completely characterized;
- Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, qubits for quantum computers.

Model Hamiltonian – Heisenberg-Model

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

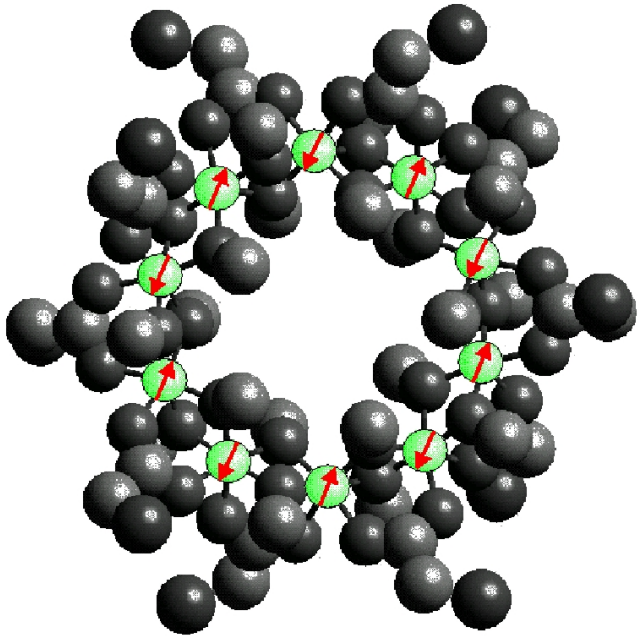
Heisenberg Zeeman

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

$J < 0$: antiferromagnetic coupling.

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

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

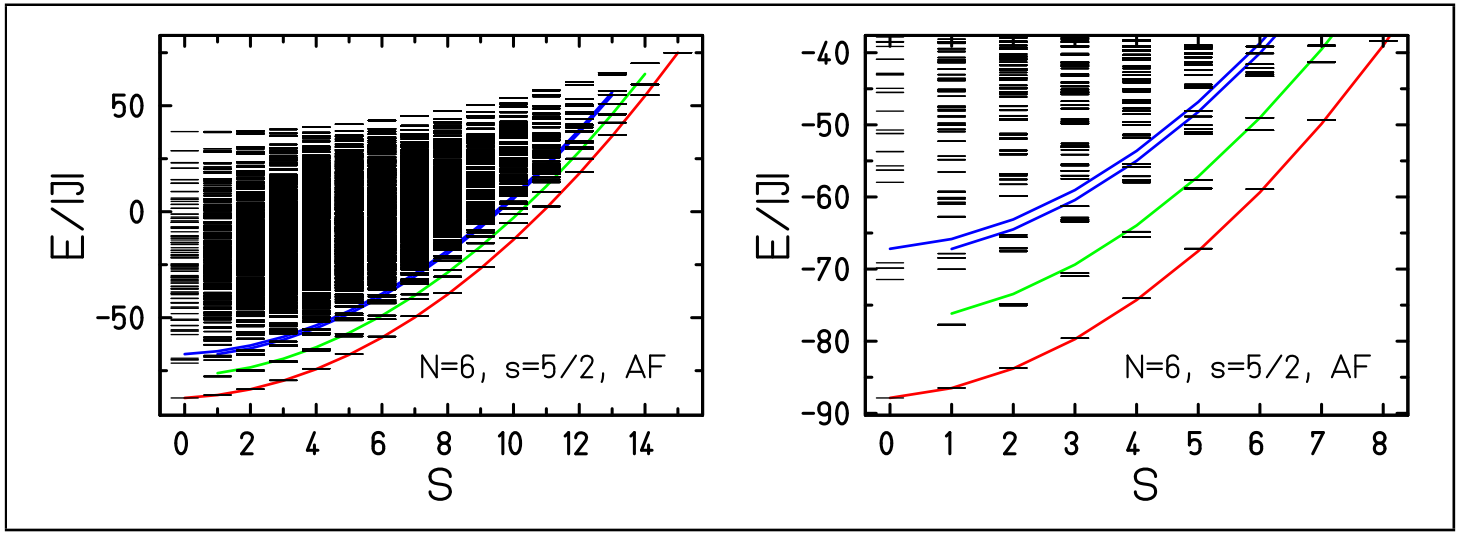
- An extended k-rule can be inferred from numerical investigations which yields the k quantum number for relative ground states of subspaces $\mathcal{H}(M)$ for even as well as odd spin rings

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

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

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)

Rotational bands in antiferromagnets I

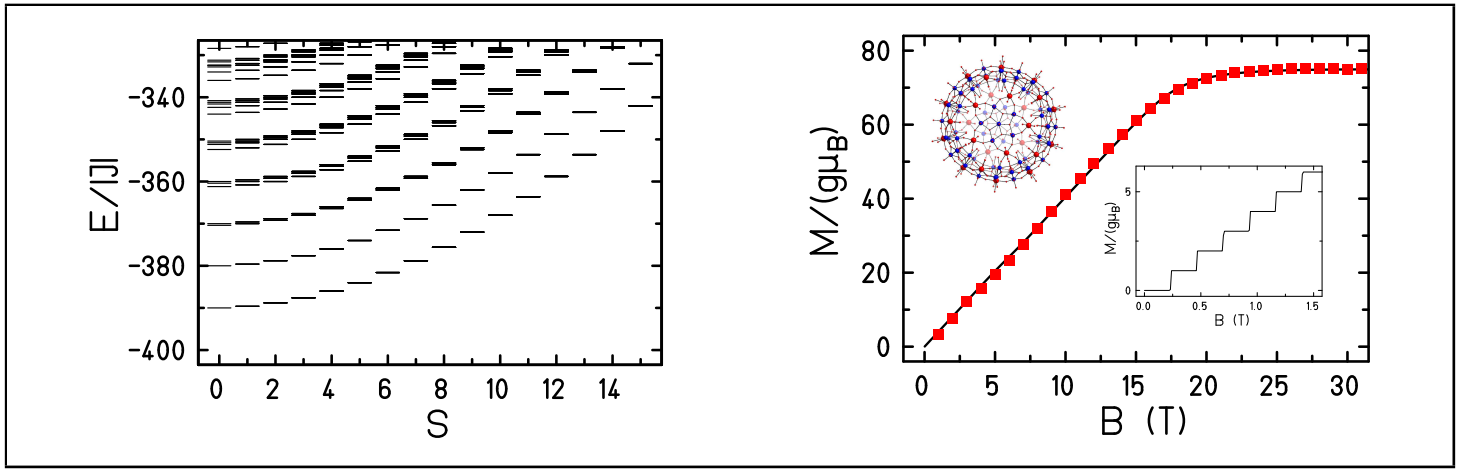


- Often minimal energies $E_{min}(S)$ form a rotational band: Landé interval rule (1);
- Most pronounced for bipartite systems (2,3), good approximation for more general systems;
- Lowest band – rotation of Néel vector, second band – spin wave excitations (4).

(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 $\{\mathrm{Mo}_{72}\mathrm{Fe}_{30}\}$

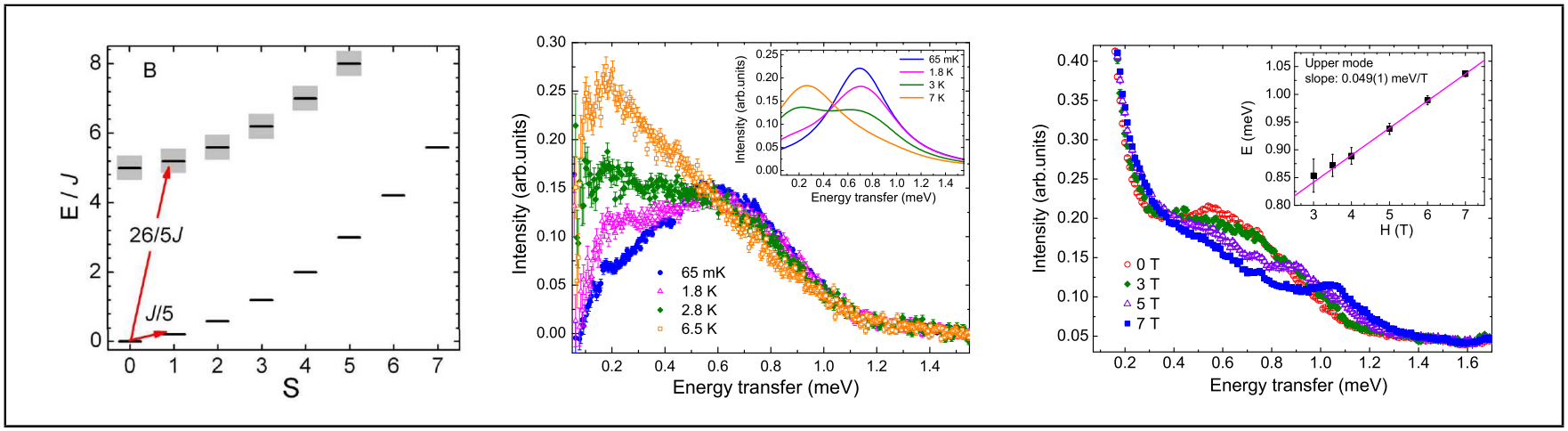
$$\underset{\sim}{H} = -2\,J \sum_{(u<v)} \underset{\sim}{\vec{s}}(u)\cdot\underset{\sim}{\vec{s}}(v) \approx -\frac{D\,J}{N}\left[\underset{\sim}{\vec{S}}^2 - \sum_{j=1}^{N_{SL}} \underset{\sim}{\vec{S}}_j^2\right] = \underset{\sim}{H}^{\mathrm{eff}}$$



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

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

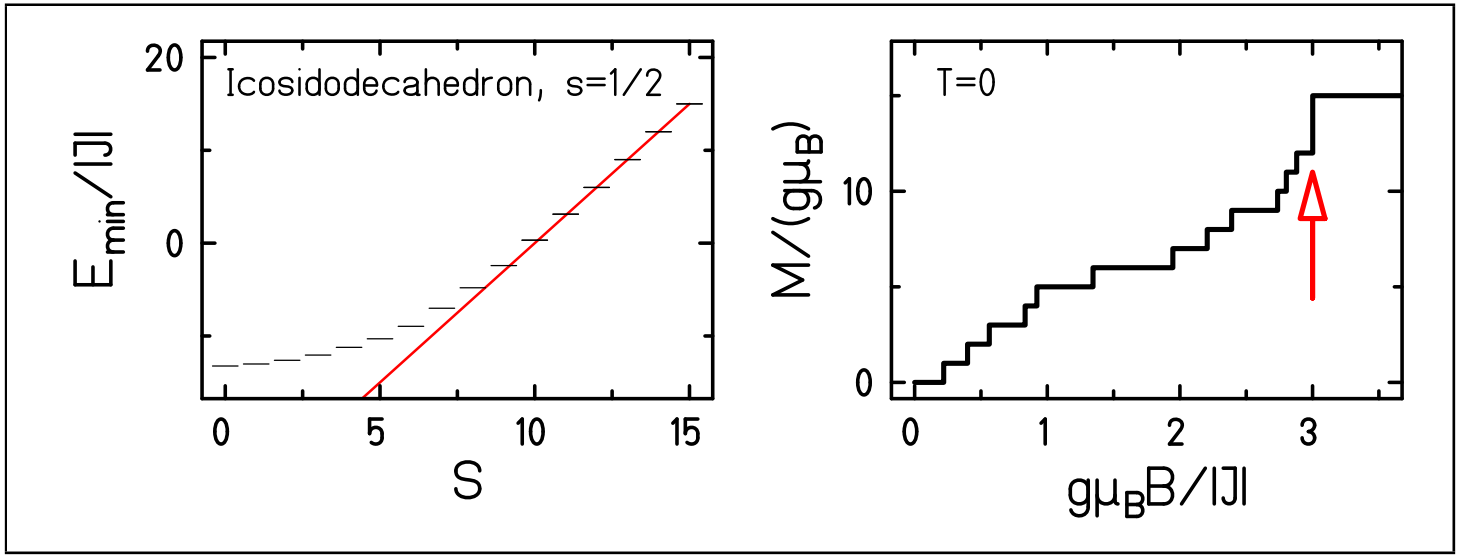
Rotational bands in antiferromagnets III
Neutron scattering at $\{Mo_{72}Fe_{30}\}$



- 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

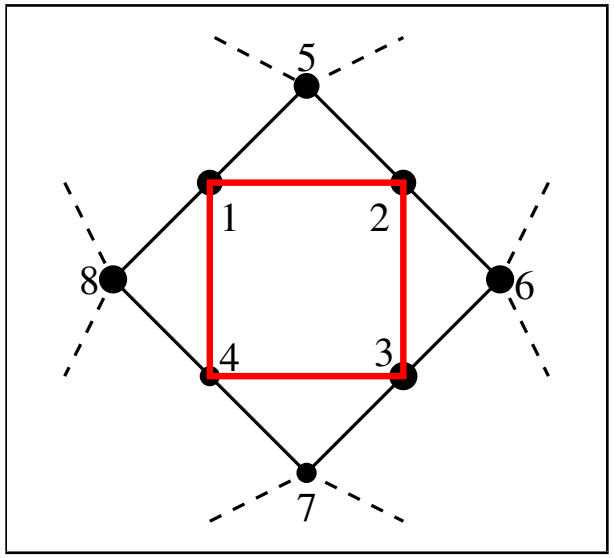
Giant magnetization jumps in frustrated antiferromagnets I $\{\mathbf{Mo}_{72}\mathbf{Fe}_{30}\}$



- 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)

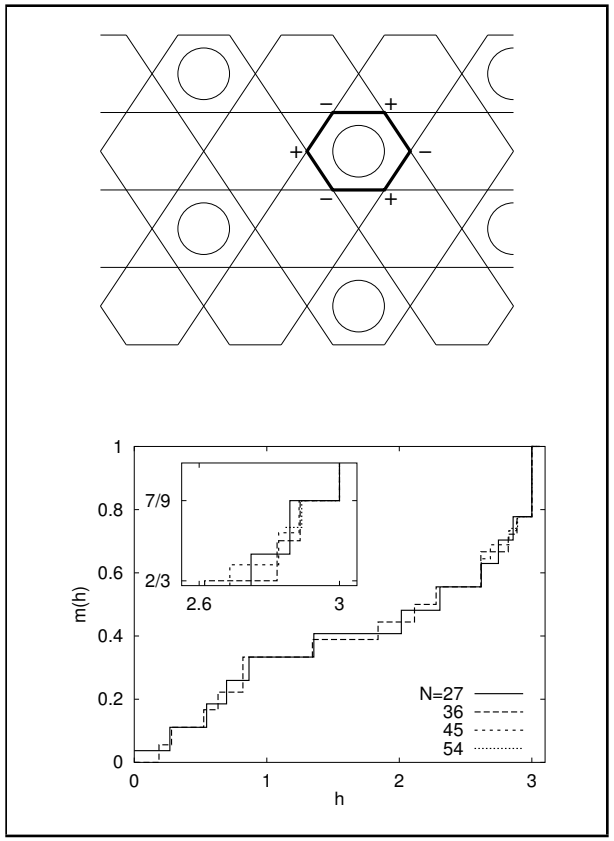
Giant magnetization jumps in frustrated antiferromagnets II
Localized Magnons



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

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

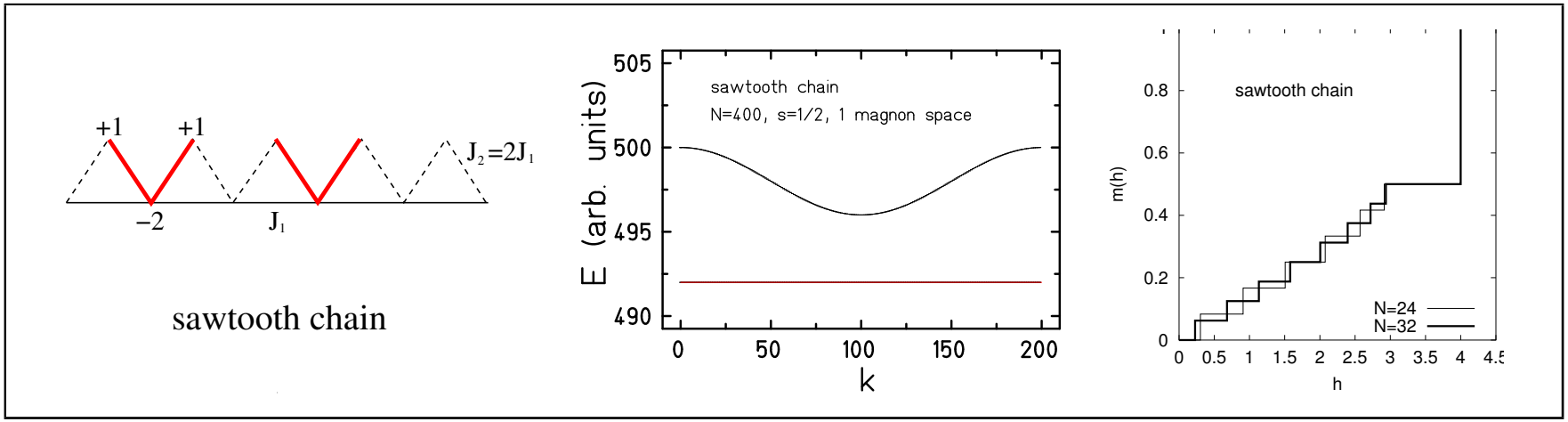
Giant magnetization jumps in frustrated antiferromagnets III
Kagome Lattice



- Non-interacting one-magnon states can be placed on various lattices, e. g. the kagome 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

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

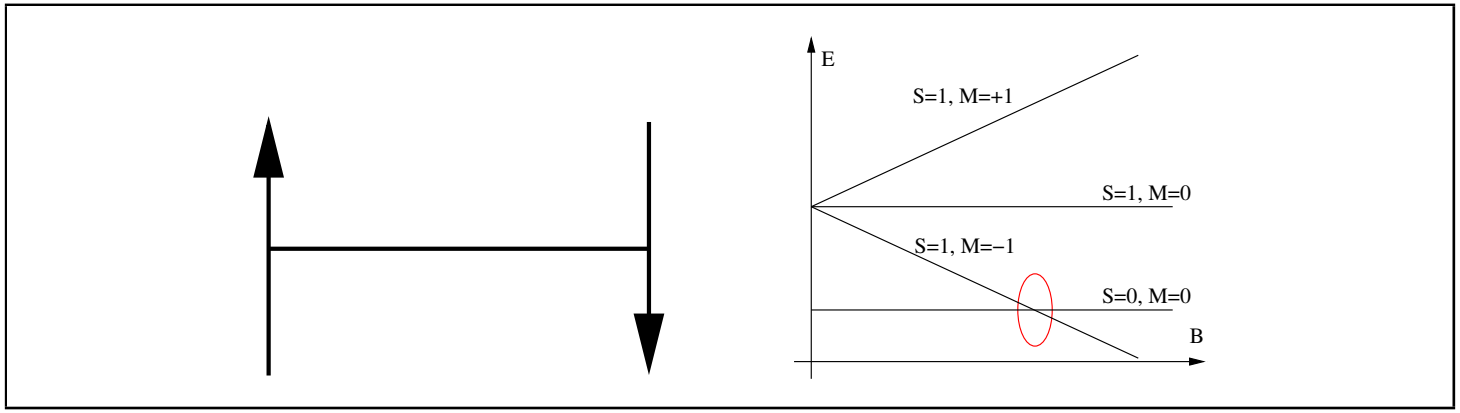
(adiabatic temperature change)

- 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)

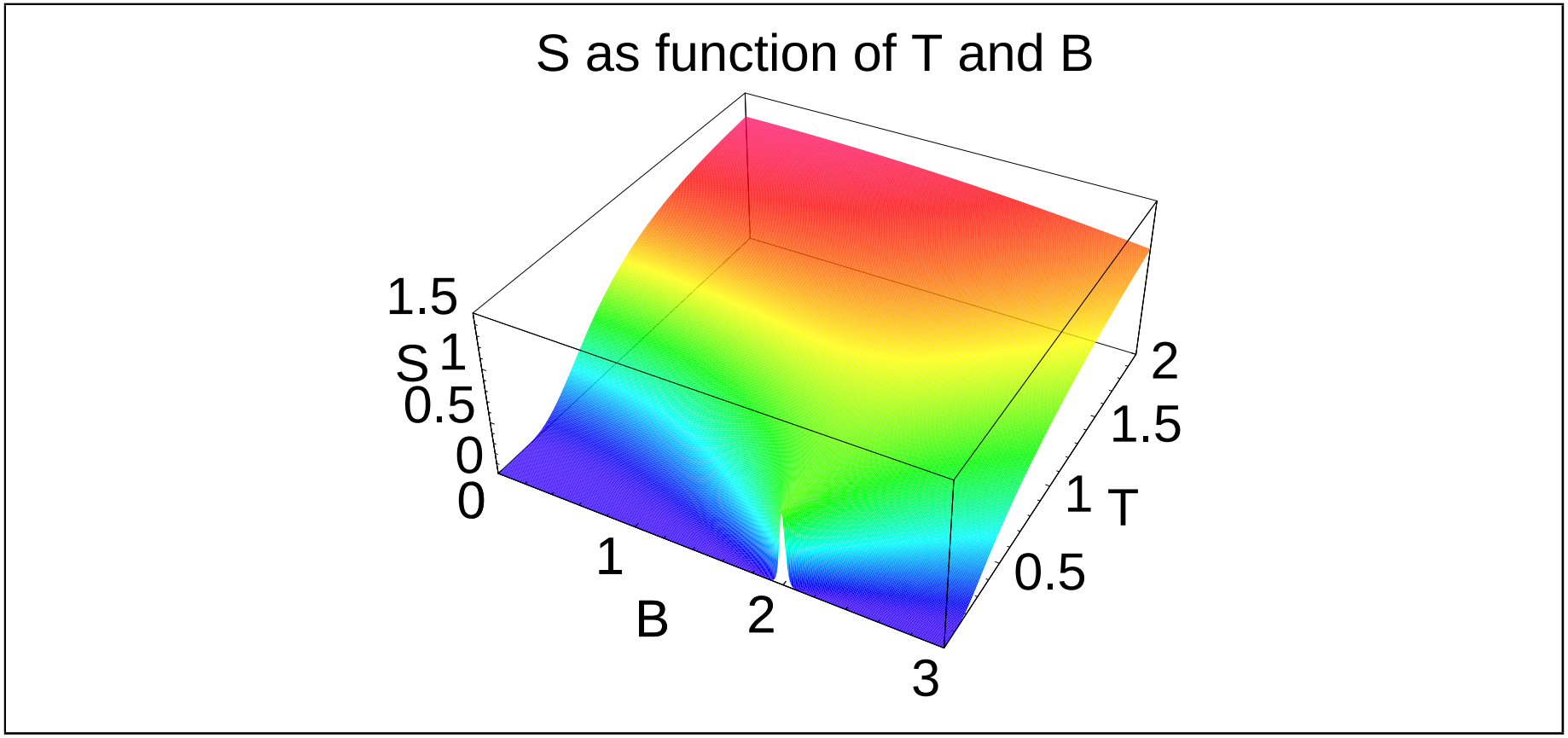
Enhanced magnetocaloric effect II
Simple af $s = 1/2$ dimer



- 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.

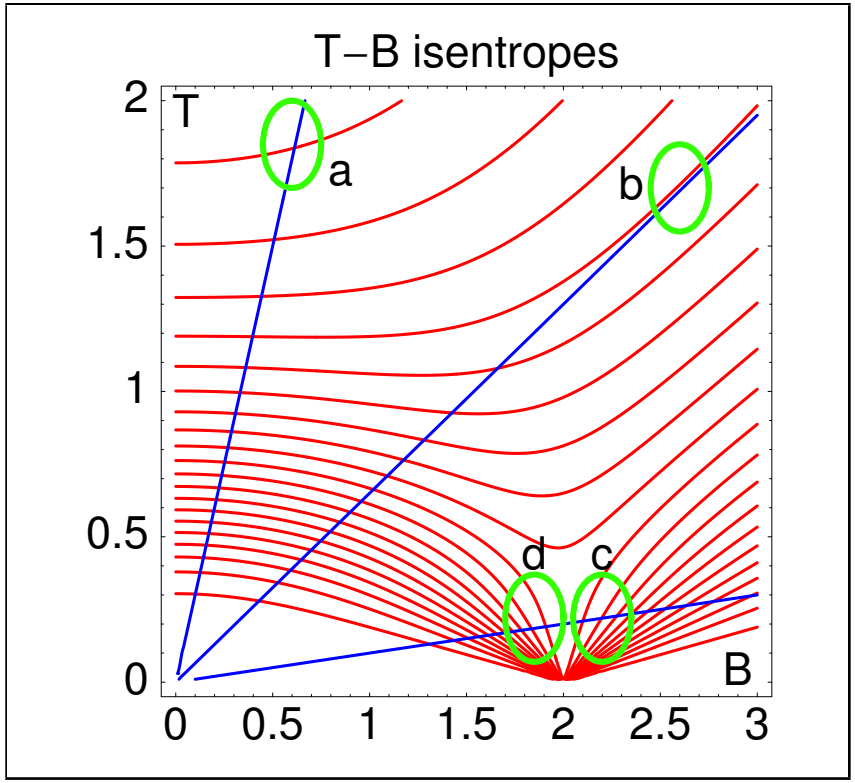
Enhanced magnetocaloric effect III
Entropy of af $s = 1/2$ dimer



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

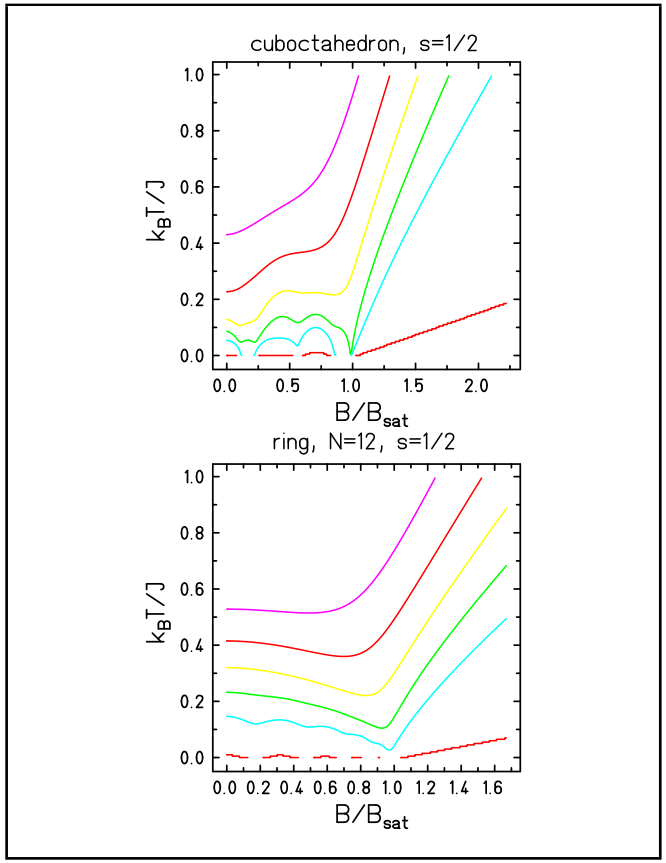
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

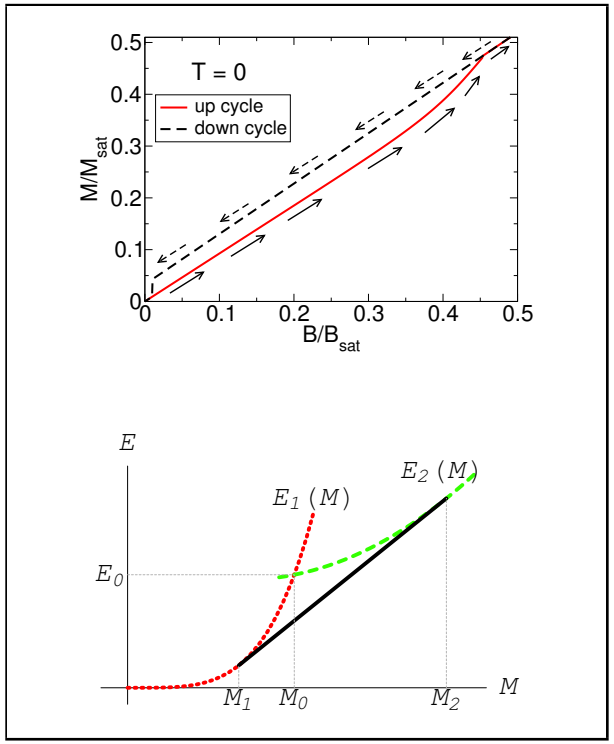
Enhanced magnetocaloric effect V
Two molecular spin systems



- 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

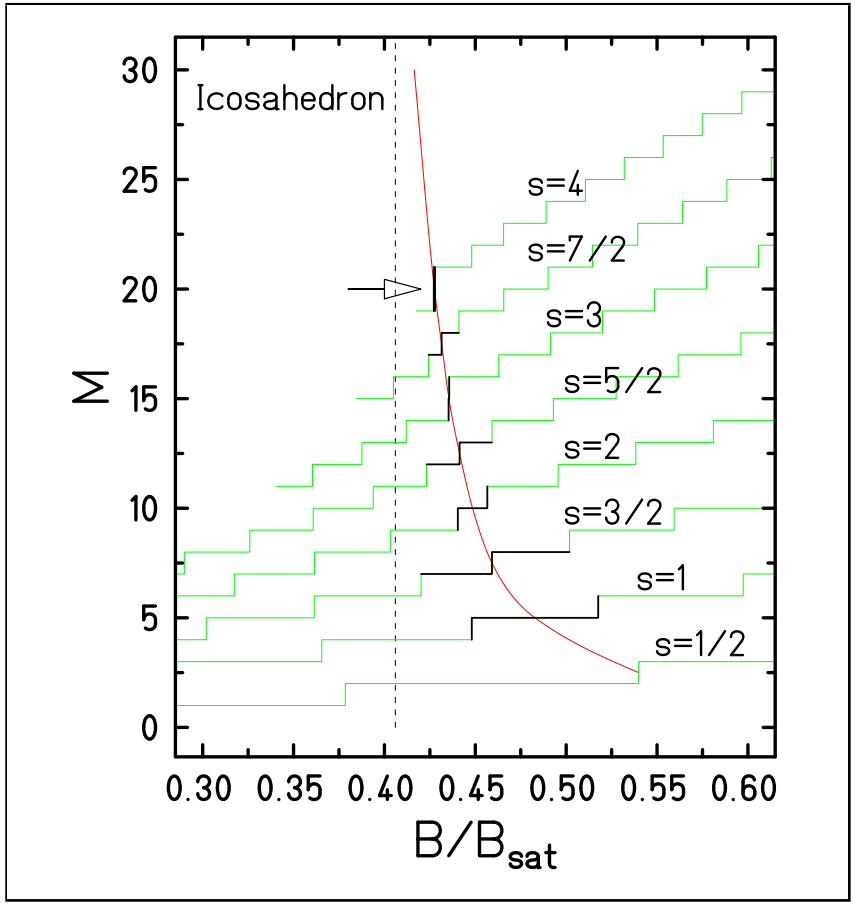
Metamagnetic phase transition I



- 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.

Information

Advances and Prospects in Molecular Magnetism

362. Wilhelm und Else Heraeus-Seminar

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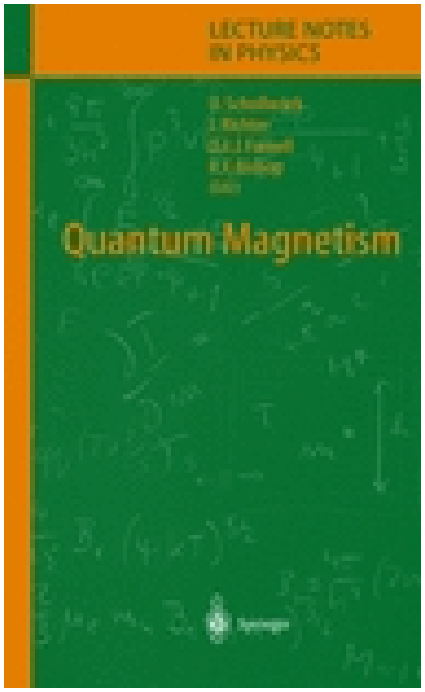
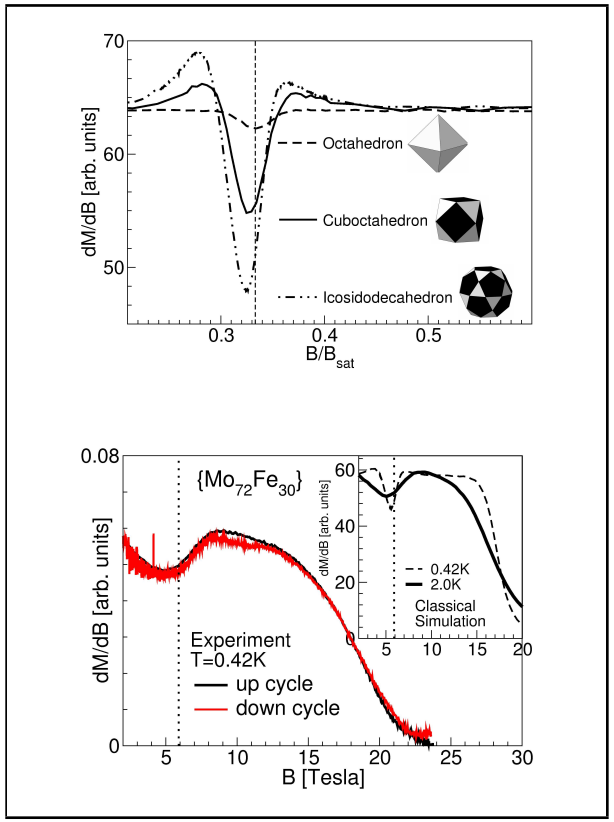


Quantum Magnetism

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*

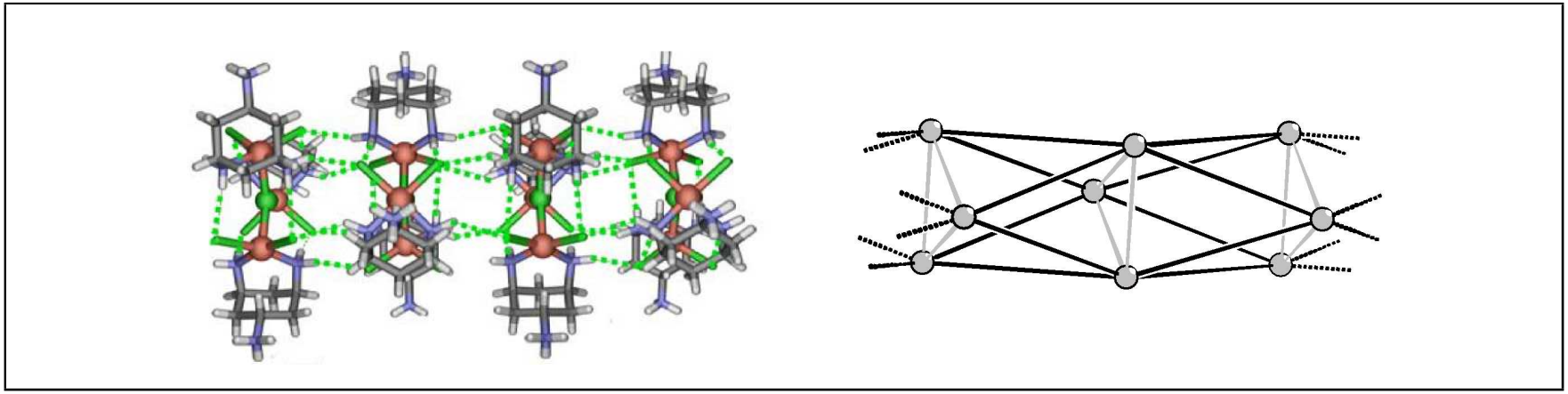
Magnetization plateaus and susceptibility minima



- 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)

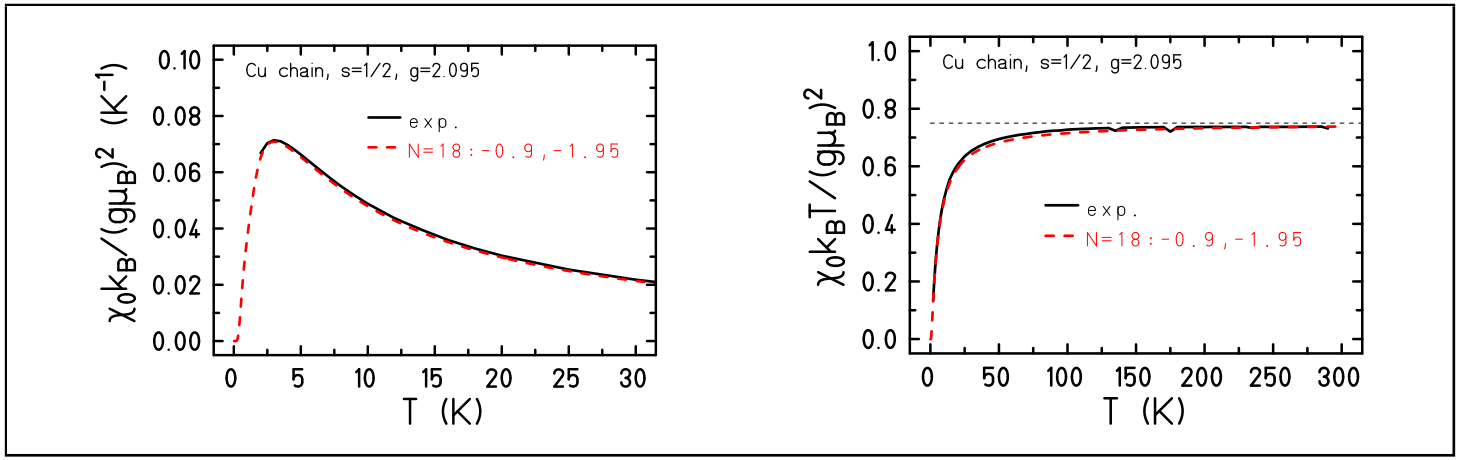
A frustrated triangular Cu chain



- $[(CuCl_2tachH)_3Cl]Cl_2$, tach $=$ *cis,trans*-1,3,5-triamino-cyclohexane (1)
- One-dimensional stack of antiprisms of af coupled equilateral copper(II) triangles: three-leg ladder with frustrated rung boundary condition.
- Intra-triangle couplings J_1 – grey lines, inter-triangle couplings J_2 – black lines.

(1) Georg Seeber, Paul Kögerler, Benson M. Kariuki, and Leroy Cronin, Chem. Commun. (Cambridge) **2004**, 1580 (2004).

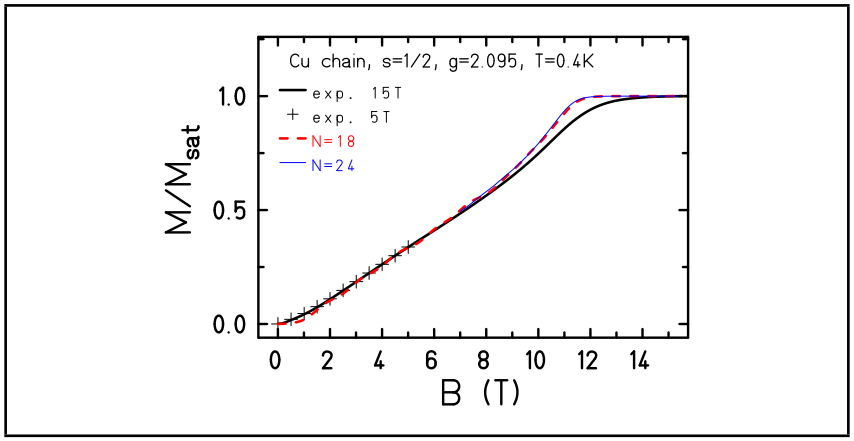
Triangular Cu chain: susceptibility



- Intra-triangle exchange J_1: bridging chloro ligand and hydrogen bonds; Cu-Cu distance is 4.46 Å.
- Inter-triangle exchange J_2: hydrogen-bonded Cu-Cl$\cdots$H-N-Cu super-exchange; Cu-Cu distance is 6.82 Å.
- Conjecture: weakly coupled triangles, i. e. $|J_2| \ll |J_1|$
  $\Rightarrow$ independent triangles at high T; effective spin-$1/2$ chain at low T: wrong!

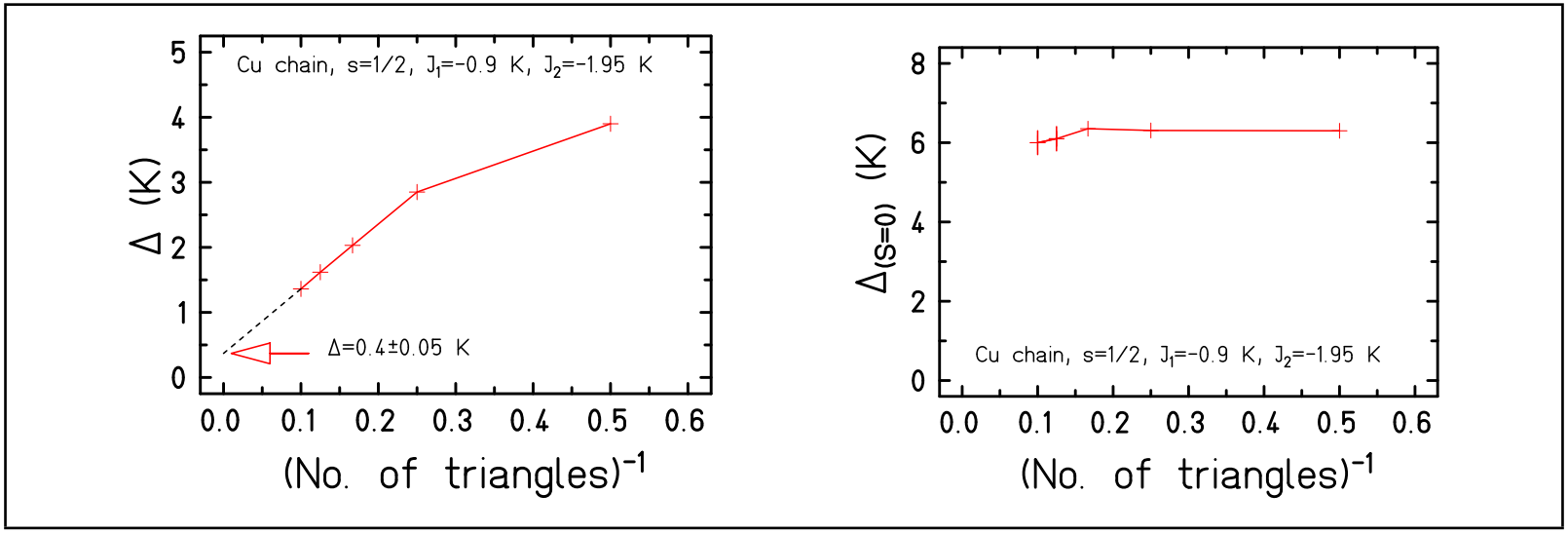
(1) Jürgen Schnack, Hiroyuki Nojiri, Paul Kögerler, Geoffrey J. T. Cooper, Leroy Cronin, Phys. Rev. B **70**, 174420 (2004)

Triangular Cu chain: magnetization



- Weakly coupled triangles would result in pronounced plateau at $1/3$ of the saturation magnetization.
- High-field magnetization measurement shows, however, no plateau.
- Solution: isotropic Heisenberg model with antiferromagnetic exchange parameters $J_1 = -0.9$ K and $J_2 = -1.95$ K and $g = 2.095$ (average of small g-anisotropy).
- Deviations at high field: g-anisotropy and staggered field; deviations at low field: singlet-triplet gap overestimated in finite systems.

Triangular Cu chain: gaps



- Singlet-triplet gap $\Delta_{0-1} \gtrapprox 0.4 \pm 0.05$ K; singlet-singlet gap $\Delta_{0-0} \approx 6$ K
- Ground state non-degenerate (1),
  whereas twofold degenerate for weakly coupled triangles (2).

(1) Jürgen Schnack, Hiroyuki Nojiri, Paul Kögerler, Geoffrey J. T. Cooper, Leroy Cronin, Phys. Rev. B **70**, 174420 (2004)
(2) A. Lüscher, R. M. Noack, G. Misguich, V. N. Kotov, and F. Mila, Phys. Rev. B **70**, 060405(R) (2004)

no more time option