

# Frustration effects in magnetic molecules

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DPG Frühjahrstagung  
Berlin, March 5th 2005

# What happens if people coming from



transport theory



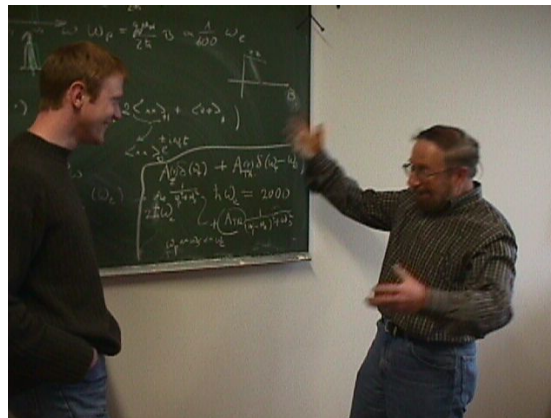
general relativity



nuclear physics



Zener diodes



are triggered by a “magnetic” enthusiast?

# Group explosion ...



# ... Invitations to fancy conferences: “Are tomorrow’s bits synthetic?” ...

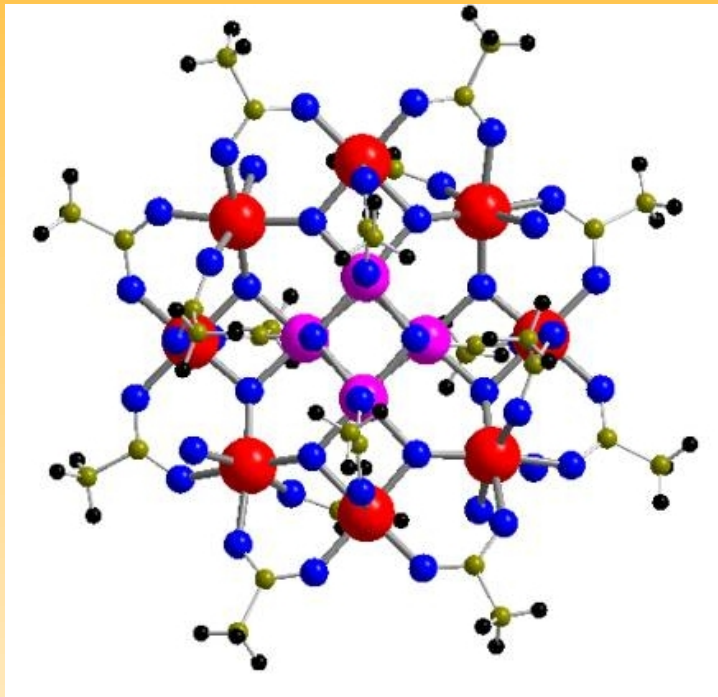


Conference by Fujitsu Siemens: *Storage in Town, Future trends in storage technology*, Hamburg, 2002

## ... and various general results

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. Metamagnetic phase transition
6. Enhanced magnetocaloric effect

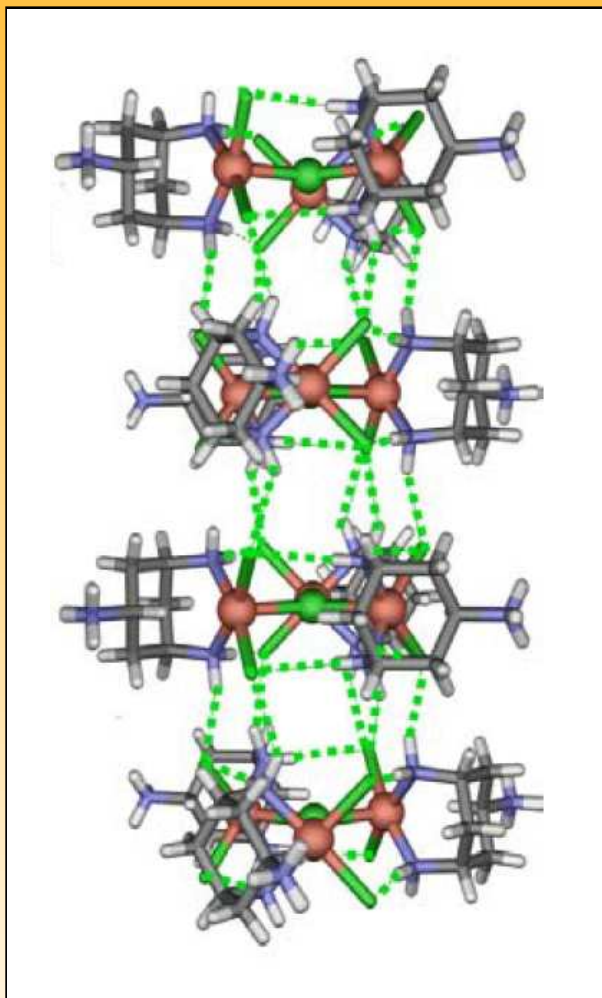
# The beauty of magnetic molecules I



Mn<sub>12</sub>

- 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

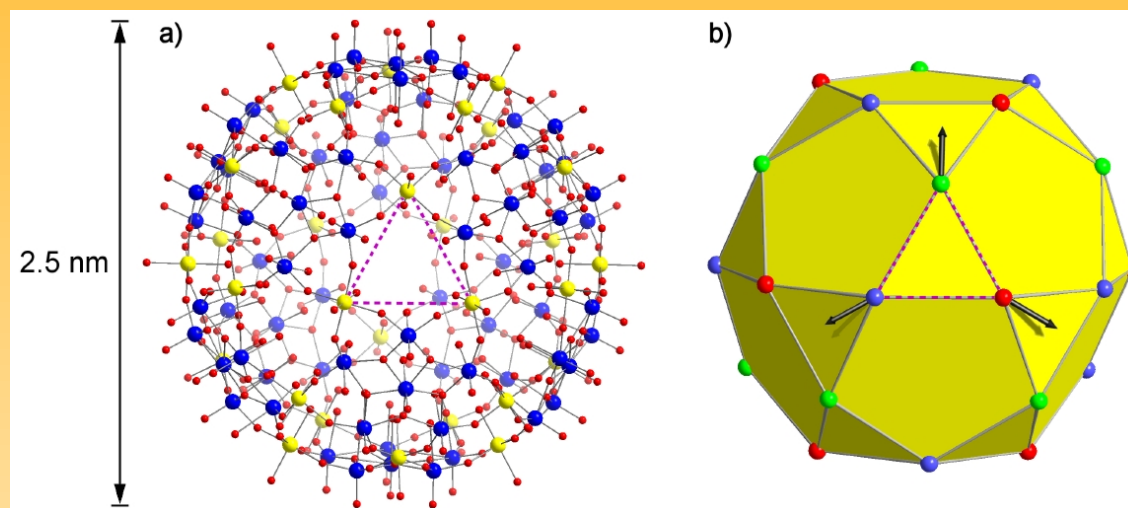


- Dimers ( $\text{Fe}_2$ ), tetrahedra ( $\text{Cr}_4$ ), cubes ( $\text{Cr}_8$ );
- Rings, especially iron rings ( $\text{Fe}_6$ ,  $\text{Fe}_8$ ,  $\text{Fe}_{10}$ , ...);
- Complex structures ( $\text{Mn}_{12}$ ) – drosophila of molecular magnetism;
- “Soccer balls”, more precisely icosidodecahedra ( $\text{Fe}_{30}$ ) 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)

# The beauty of magnetic molecules III

## {Mo<sub>72</sub>Fe<sub>30</sub>} – our favorite molecule



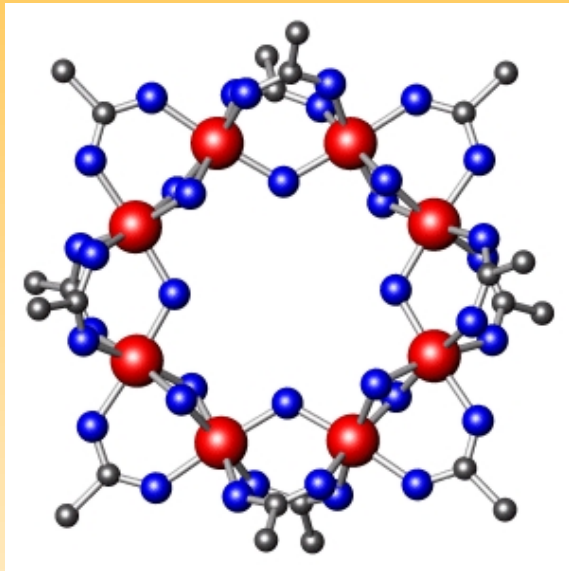
- Giant magnetic Keplerate molecule;
- Structure: Fe - yellow, Mo - blue, O - red;
- Antiferromagnetic interaction mediated by O-Mo-O bridges (1).
- Classical ground state of {Mo<sub>72</sub>Fe<sub>30</sub>}: three sublattice structure, coplanar spins (2);
- Quantum mechanical ground state  $S = 0$  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<sub>8</sub>

- 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

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

Heisenberg
Zeeman

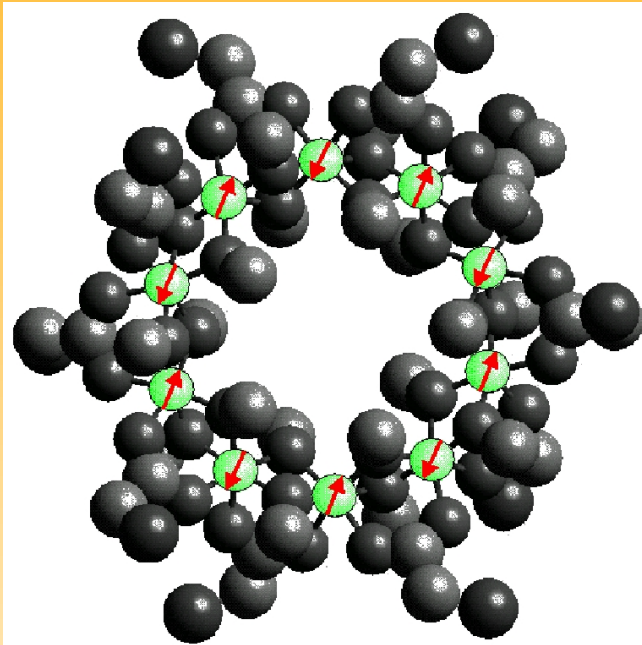
The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations.

$J < 0$ : antiferromagnetic coupling.

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

# Extension of Lieb, Schultz, and Mattis I

## $k$ -rule for even rings



Fe<sub>10</sub>

- 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 subspaces  $\mathcal{H}(M)$ .

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

# 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

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

$N$	$s$	$a$									
		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	0	5	$10 \equiv 1$	$15 \equiv 6$	$20 \equiv 2$	$25 \equiv 7$	$30 \equiv 3$	$35 \equiv 8$	$40 \equiv 4$	$45 \equiv 0$

K. Fabricius, U. Löw, K.-H. Mütter, and P. Ueberholz, Phys. Rev. B **44**, 7476 (1991)

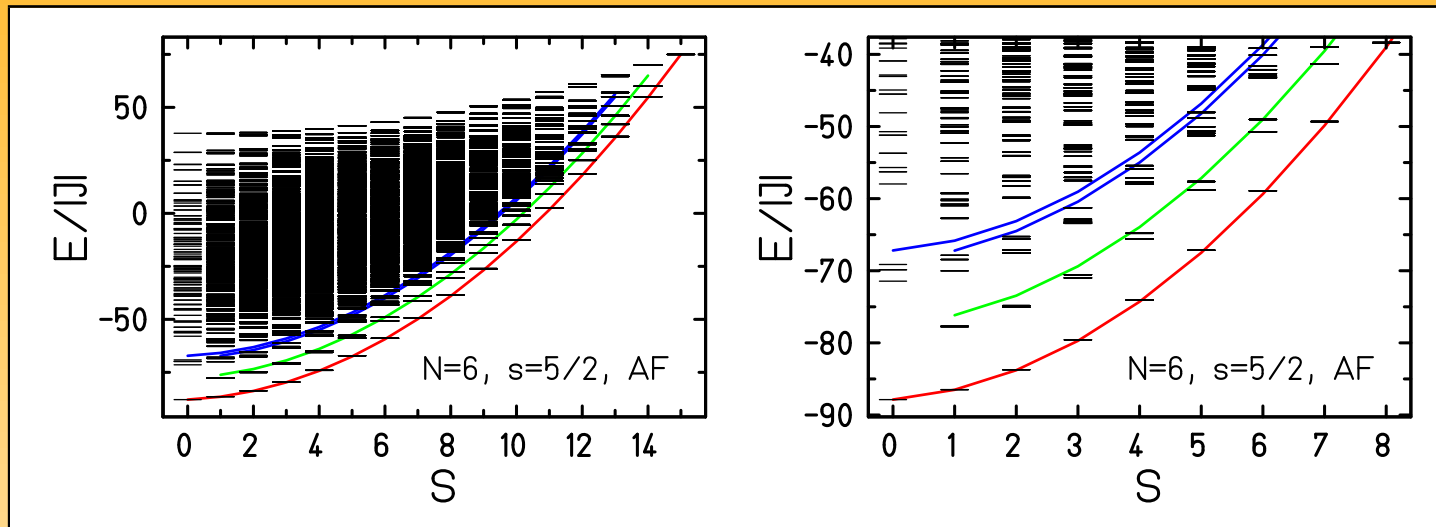
M. Karbach, Ph. D. thesis, Universität Wuppertal (1994)

K. Bärwinkel, H.-J. Schmidt, and J. Schnack, J. Magn. 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), good approximation for more general systems;
- Sometimes low-lying spectrum is a sequence of rotational bands (3).

(1) A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996), G. L. Abbati *et al.*, Inorg. Chim. Acta **297**, 291 (2000)

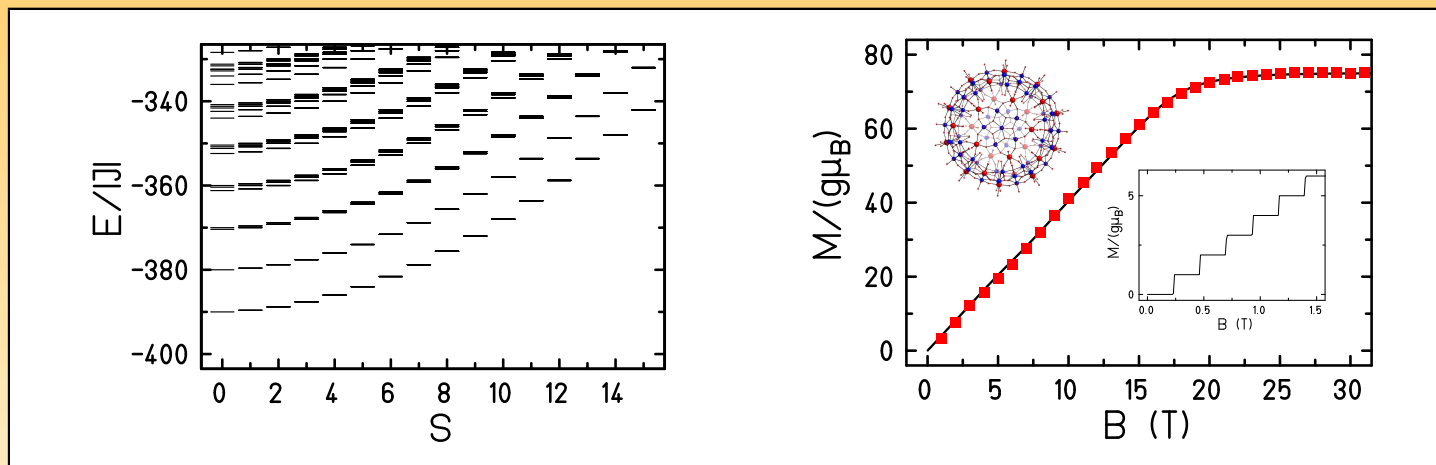
(2) J. Schnack and M. Luban, Phys. Rev. B **63**, 014418 (2001)

(3) O. Waldmann, Phys. Rev. B **65**, 024424 (2002)

# Rotational bands in antiferromagnets II

## Approximate Hamiltonian for $\{\text{Mo}_{72}\text{Fe}_{30}\}$

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

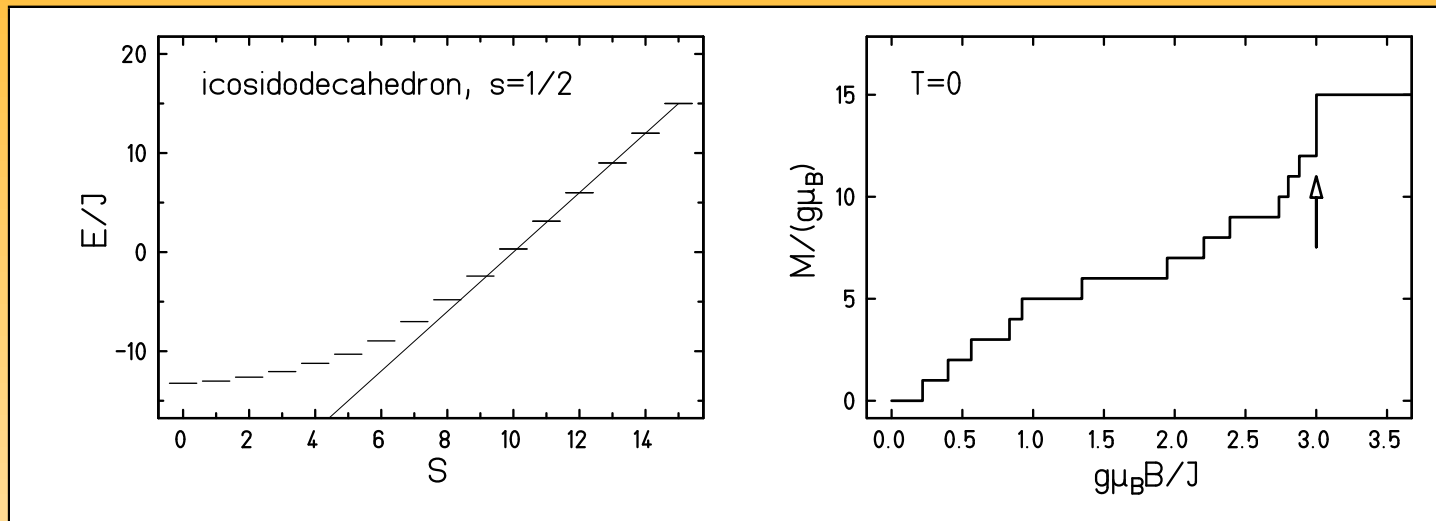


$\tilde{S}_j$  sublattice spins;  $D = 6$ ; INS shows broad peak at band separation.

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

# Giant magnetization jumps in frustrated antiferromagnets I

## {Mo<sub>72</sub>Fe<sub>30</sub>}



- $E_{\min}(S)$  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);

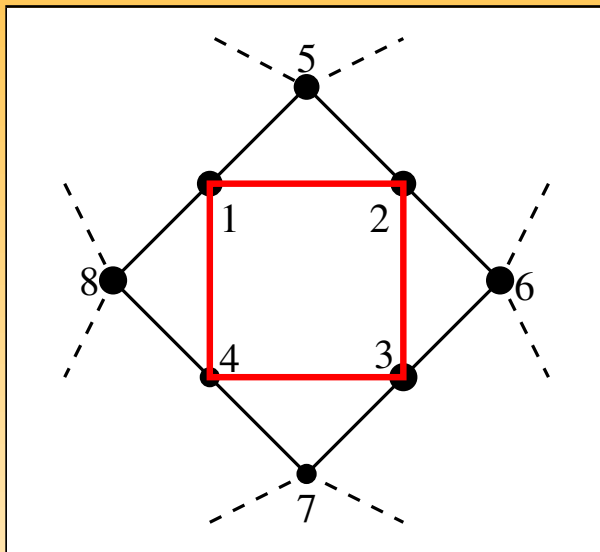
(1) J. Schnack, H.-J. Schmidt, J. Richter, J. Schulenburg, Eur. Phys. J. B **24**, 475 (2001)

(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



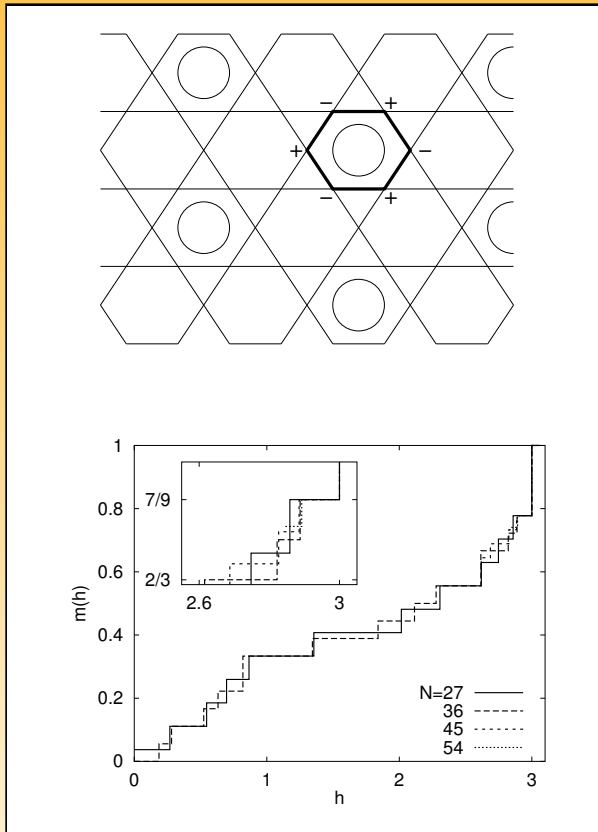
- $|\text{localized magnon}\rangle = \frac{1}{2}(|1\rangle - |2\rangle + |3\rangle - |4\rangle)$
- $|1\rangle = \underline{s}^-(1) |\uparrow\uparrow\uparrow \dots\rangle$  etc.
- $\underline{H} |1\rangle = J\{|1\rangle + 1/2(|2\rangle + |4\rangle + |5\rangle + |8\rangle)\}$   
 $\underline{H} |2\rangle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

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



# Giant magnetization jumps in frustrated antiferromagnets III

## Kagome Lattice

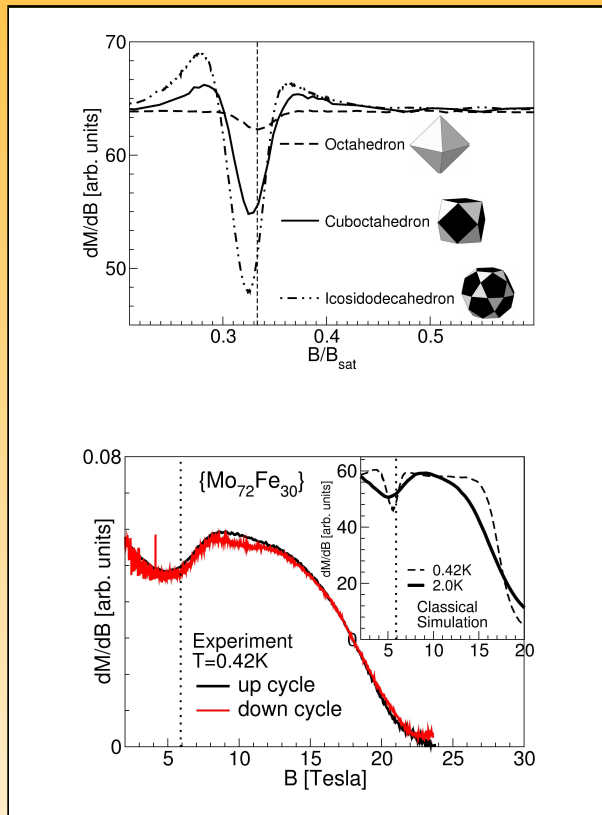


- Non-interacting one-magnon states can be placed on various lattices, e. g. the kagome lattice;
- Each state of  $n$  independent magnons is the ground state in the Hilbert subspace with  $M = Ns - n$ ;
- Linear dependence of  $E_{\min}$  on  $M$   
 $\Rightarrow$  magnetization jump;
- Maximal number 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)

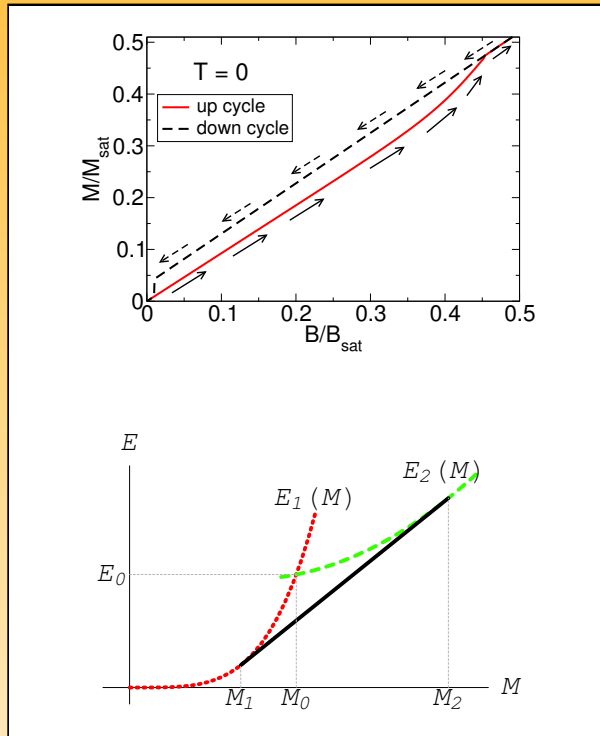
# Magnetization plateaus and susceptibility minima



- Octahedron, Cubooctahedron, Icosidodecahedron – little (polytope) brothers of the kagome lattice with increasing frustration.
- Cubooctahedron & Icosidodecahedron realized as magnetic molecules.
- Cubooctahedron & Icosidodecahedron feature plateaus, e.g. at  $\mathcal{M}_{sat}/3$  and independent magnons.
- Susceptibility shows a pronounced dip at  $B_{sat}/3$  (classical calculations and quantum calculations for the cubooctahedron).
- Experimentally verified with  $\{Mo_{72}Fe_{30}\}$ .

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

# Metamagnetic phase transition I

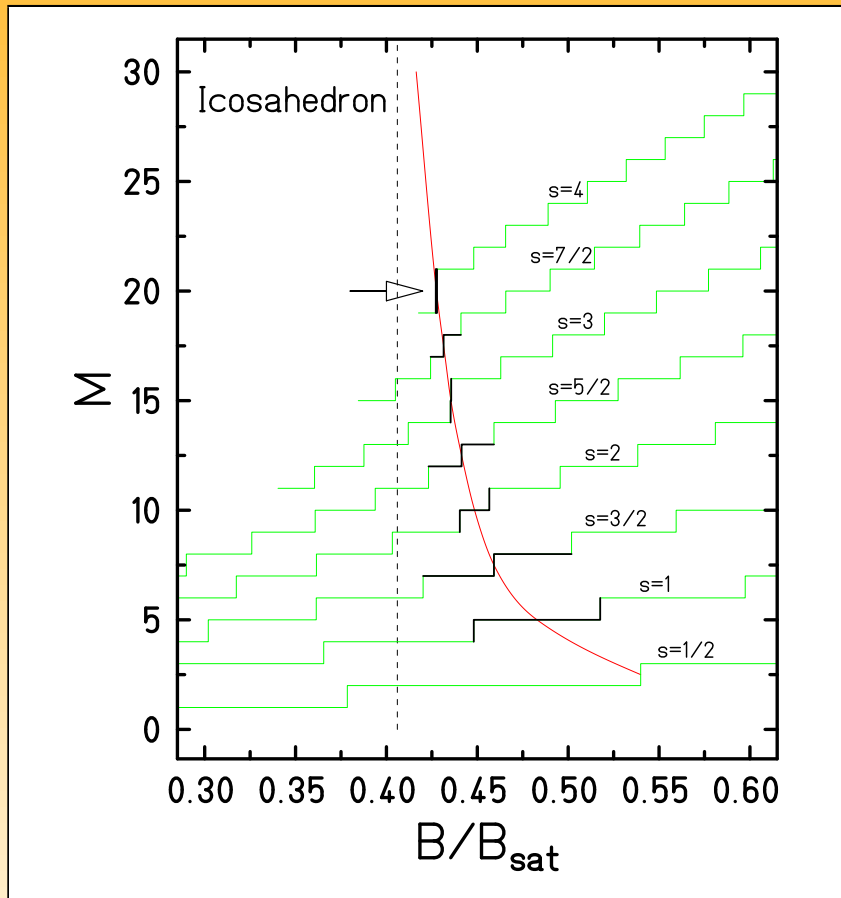


- Normally hysteretic behavior of SMM is an outcome of magnetic anisotropy.
- The classical AF Heisenberg Icosahedron exhibits a pronounced hysteresis loop.
- It shows a first order phase transition at  $T = 0$  as function of  $B$ .
- The minimal energies are realized by two families of spin configurations.
- The overall minimal energy curve is not convex  $\Rightarrow$  magnetization jump.

$\Rightarrow$  Christian Schröder, MA 14.6, 15.00 Uhr, TU H1012 (with movies).

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett., submitted, cond-mat/0501558

# Metamagnetic phase transition II



- Quantum analog:  
Non-convex minimal energy levels  
⇒ 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., submitted, cond-mat/0501558

no more time option

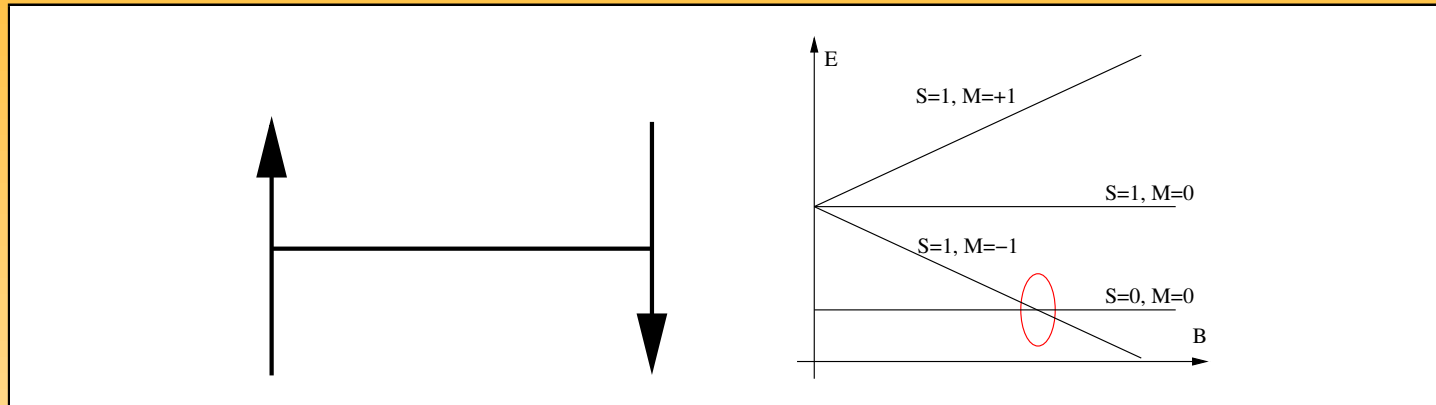
# Enhanced magnetocaloric effect I

## Basics



- Discovered in pure iron by E. Warburg in 1881.
- Heating or cooling in a varying magnetic field.
- Typical rates: 0.5 ... 2 K/T (adiabatic temperature change).
- Giant magnetocaloric effect: 3 ... 4 K/T e.g. in  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  alloys ( $x \leq 0.5$ ).
- MCE especially large: due to condensation of a macroscopic number of soft modes (Zhitomirsky), due to condensation of independent magnons (Zhitomirsky, Honecker, Richter), close to quantum critical points (Rosch).

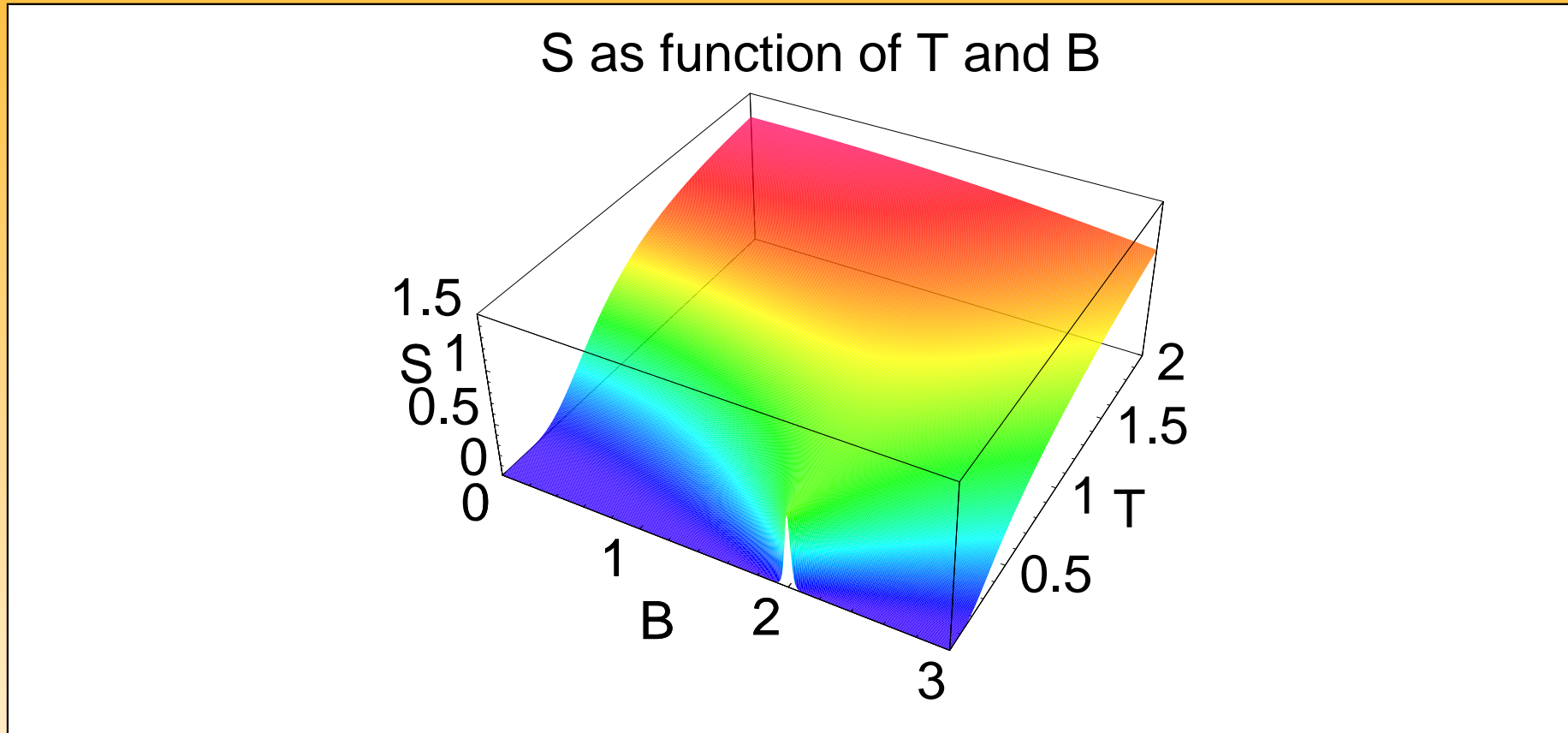
## Enhanced magnetocaloric effect II Simple af $s = 1/2$ dimer



- Singlet-triplet level crossing causes a “quantum phase transition” 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  $T$ .

# Enhanced magnetocaloric effect III

## Entropy of a $s = 1/2$ dimer

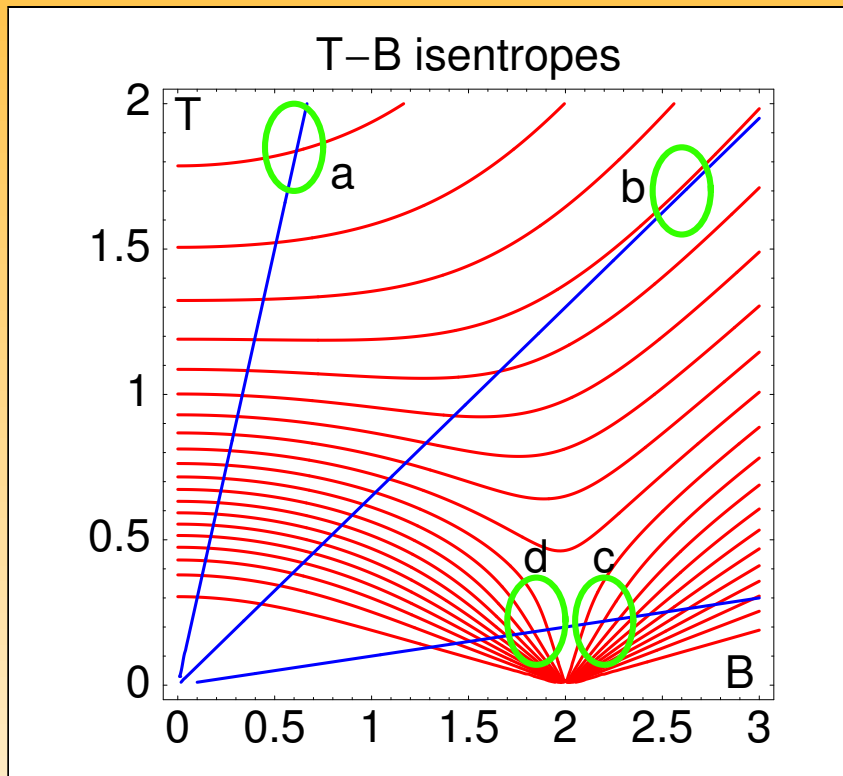


$S(T = 0, B) \neq 0$  at level crossing due to degeneracy

O. Derzhko, J. Richter, Phys. Rev. B **70**, 104415 (2004)

# Enhanced magnetocaloric effect IV

## Isentropes of af $s = 1/2$ dimer



Magnetocaloric effect:

(a) reduced,

(b) the same,

(c) enhanced,

(d) opposite

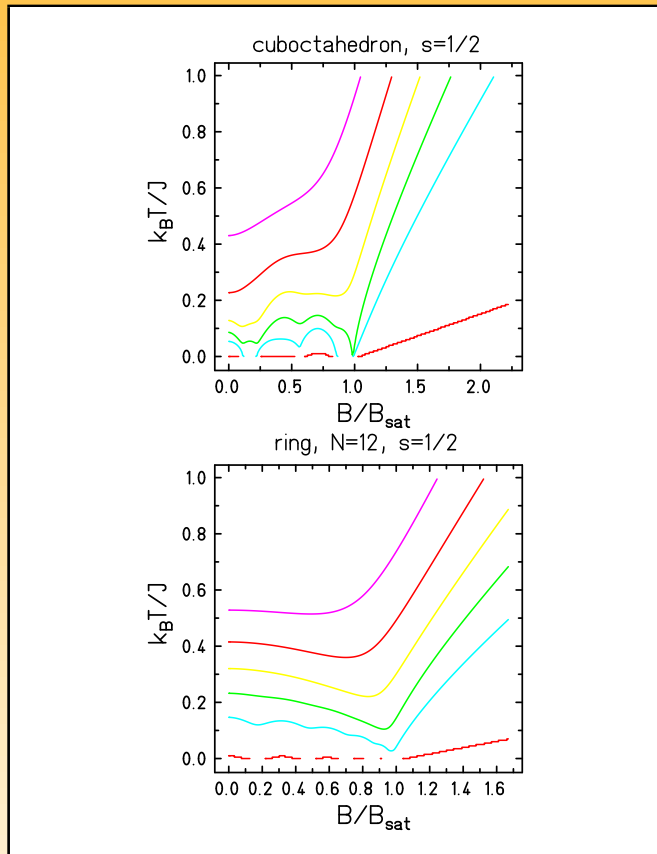
when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.



# Enhanced magnetocaloric effect V

## Two molecular spin systems



- Graphics: isentropes 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.

# Collaboration

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

Thank you very much for your attention.

## Buy now!

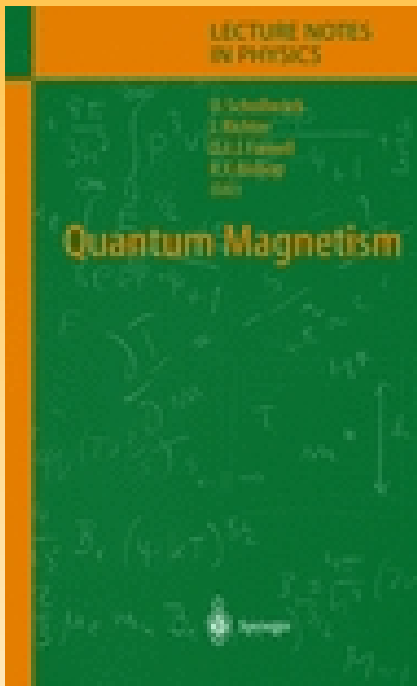
### *Quantum Magnetism*

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Mikeska, Kolezhuk, *One-dimensional magnetism*

Richter, Schulenburg, Honecker, *Q. Mag. in 2-D*

Schnack, *Molecular Magnetism*

Ivanov, Sen, *Spin Wave Analysis*

Laflorie, 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*