A short introduction into magnetic molecules

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Seminar

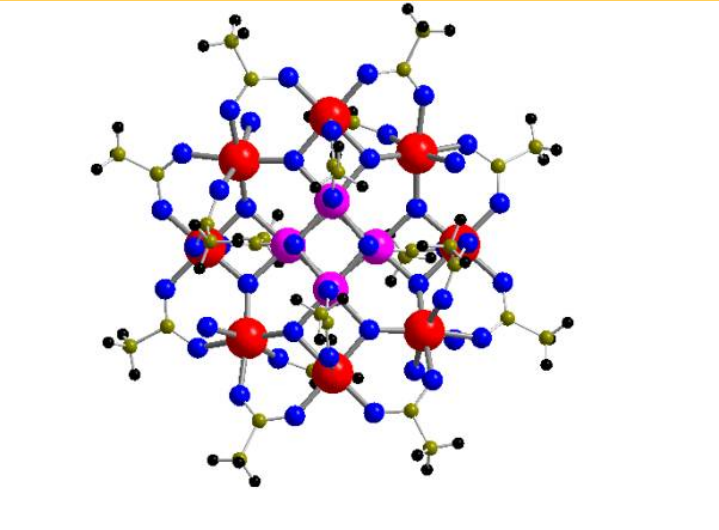
IFW Dresden, January 9th 2004

unilogo-m-rot.jpg

Contents

- The beauty of magnetic molecules
- Interesting phenomena: LIESST, magnetization tunneling
- Model Hamiltonian: Heisenberg Hamiltonian & effective Hamiltonians
- Theoretical tools
- General results: rings, bounds, rotational bands, magnetization jumps
- Outlook

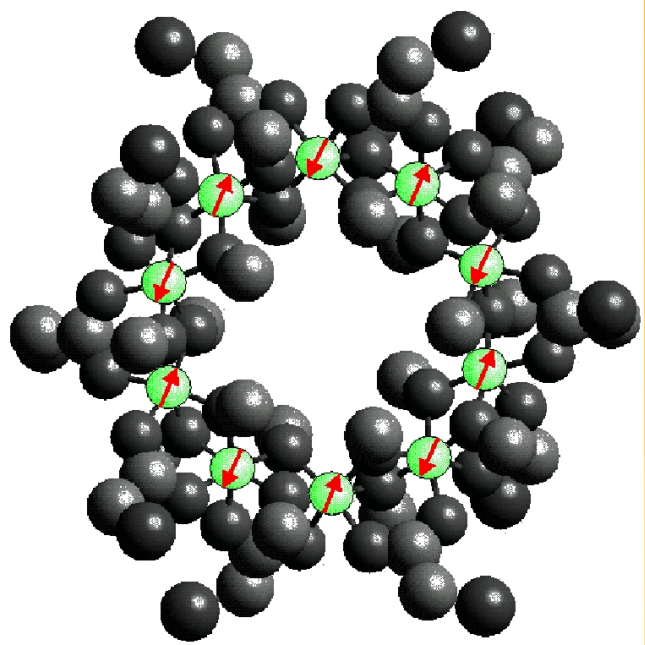
What are magnetic molecules?



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) 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.

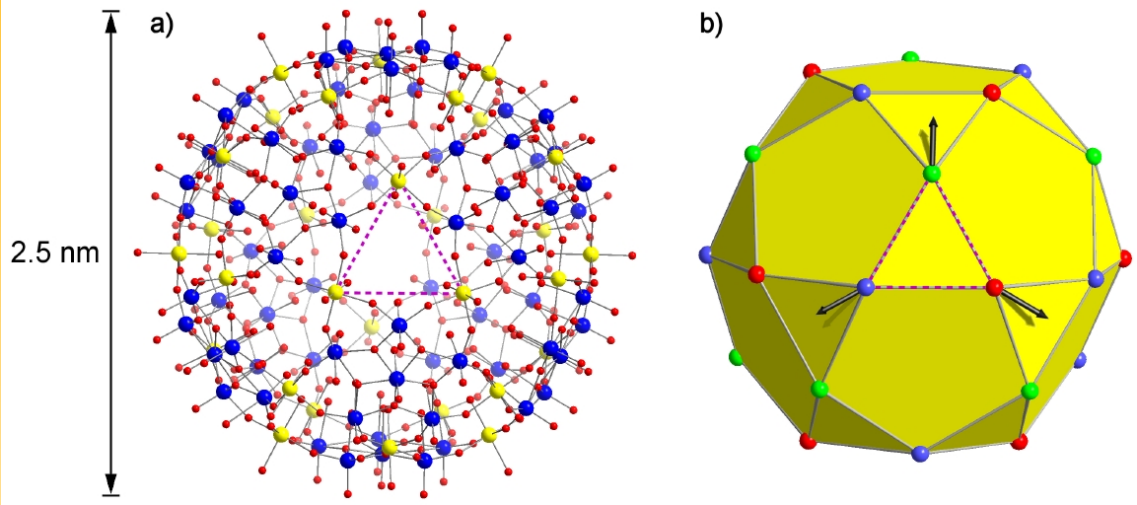
Structure of magnetic molecules



Fe_{10}

- 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.

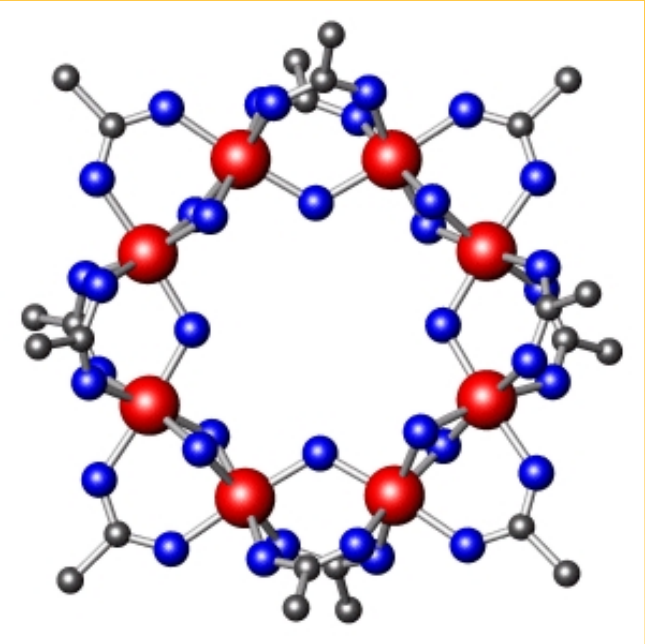
Example of magnetic macro molecules $\{Mo_{72}Fe_{30}\}$



- structure of $\{Mo_{72}Fe_{30}\}$: 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)

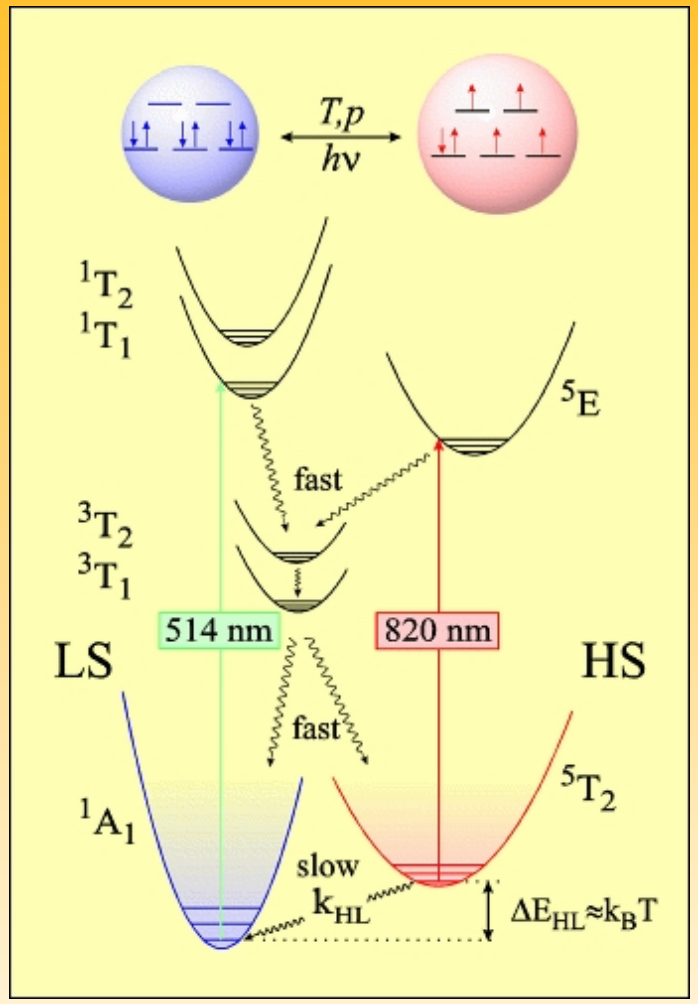
Why study magnetic molecules?



Cr_8

- 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 ($s_{\mathrm{Fe}} = 5/2$, $s_{\mathrm{Gd}} = 7/2$);
- 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.

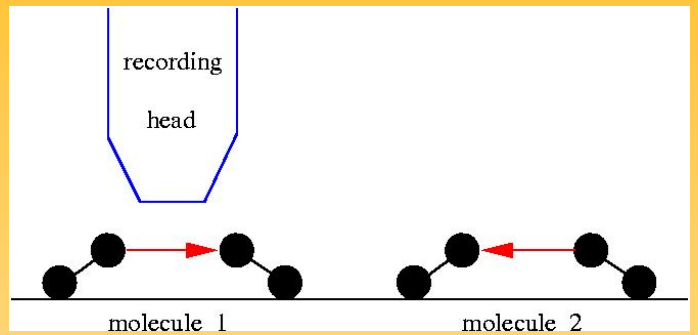
Light Induced Excited Spin State Trapping (LIESST)

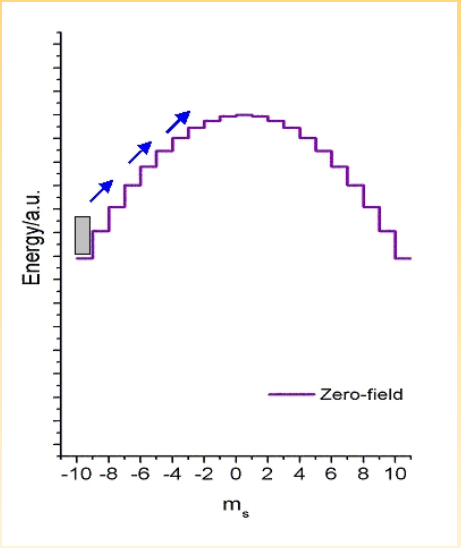


- magnetic molecules may serve as optical switches or displays;
- materials: spin crossover substances which show the LIESST effect;
- example: sixfold coordinated iron, spin-dependent radial harmonic potential;
- principle: reversible change in colour (and structure) when irradiated with laser light or when heated as well as cooled.

http://ak-guetlich.chemie.uni-mainz.de/toss/liesst.shtml

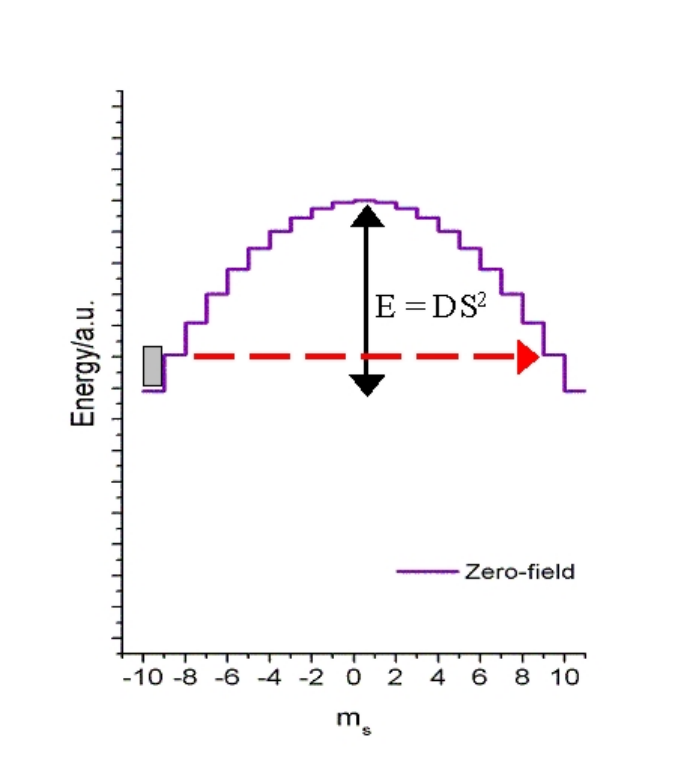
Magnetic molecules as storage media?





- Single Molecule Magnet (SMM): magnetic molecule with high ground state spin and hysteresis (usually due to large anisotropy);
- every molecule is a domain of its own; very weak intermolecular interactions; high density and nevertheless good separation of magnetic moments;
- high ground state spin possible, e.g. $S = 10$ for Mn_{12};
- theoretically possible storage density: **40 Tbits per square inch**, today: 20 Gbits per square inch (IBM), 300GB per square inch (Fujitsu 05/2002)

Magnetic molecules as storage media?

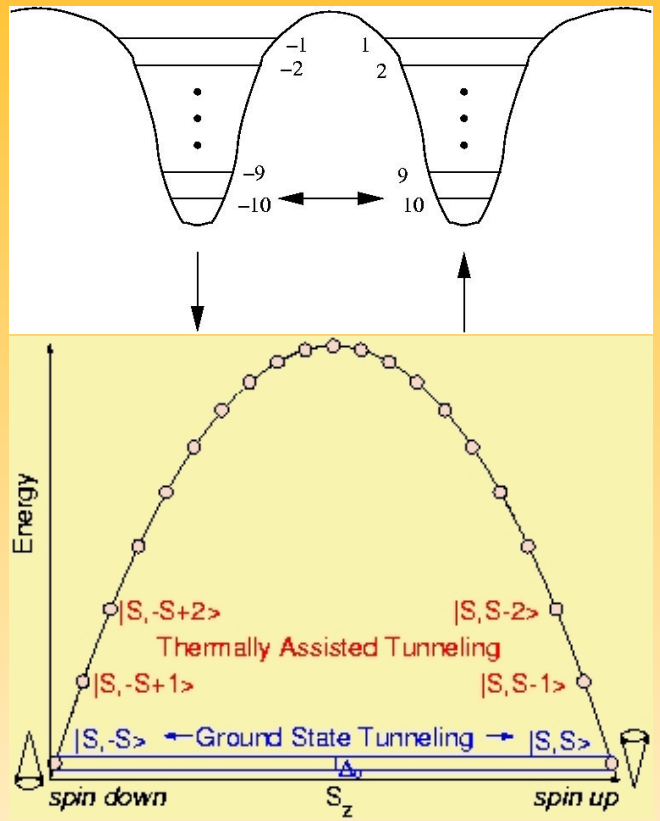


Disadvantages:

- magnetization tunneling – stabilisation by appropriate substrate?
  Prof. Blügel, Osnabrück/Jülich,
  http://www.flapw.de
- often very small coupling ($J \approx 10$ K), i.e. thermally unstable at room temperature;
- recording head must be very small and needs precise guide.

http://www.people.man.ac.uk/∼mbdssrew/winpeny_intro3.html

Magnetization tunneling



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- for SMM like Mn_{12} (l.h.s.) an effective one-spin Hamiltonian can be used:

$$\underset{\sim}{H} = -D\underset{\sim}{S}_z^2 - D_4\underset{\sim}{S}_z^4 + \underset{\sim}{H}'$$

$$\underset{\sim}{H}' = g\mu_B H_x \underset{\sim}{S}_x$$

- tunneling rate depends on initial M:

$M = 10 \Rightarrow \omega \approx 10^{-45}$Hz ($H_x = 100$ G)

$M = 2 \Rightarrow \omega \approx 10^{5}$Hz ($H_x = 100$ G)

- macroscopic magnetization tunneling possible;
- thermally activated tunneling observed.

Model Hamiltonian – Heisenberg-Model

$$\underset{\sim}{H} = -\sum_{i,j} J_{ij}\,\underset{\sim}{\vec{s}}(i)\cdot\underset{\sim}{\vec{s}}(j) - D\sum_{i}\left(\vec{e}(i)\cdot\underset{\sim}{\vec{s}}(i)\right)^2 + g\,\mu_B\,B\sum_{i}^{N}\underset{\sim}{s}_z(i)$$

Heisenberg Anisotropy Zeeman

The Heisenberg model including anisotropy, and dipol-dipol interaction if necessary, as well as a Zeeman term describes the magnetic spectrum of many molecules with high accuracy.

Reason: ions of the iron group, Russel-Saunders coupling in the free ion, $\langle\, \underset{\sim}{l}\,\rangle \approx 0$ due to chemical binding, remaining spin-orbit coupling treated perturbatively with the help of anisotropy terms.

Since the dimension of Hilbert space equals $(2s+1)^N$ the Hamiltonian can be diagonalized completely for small molecules. For larger ones approximate methods are used.

Dimension of the problem

Product basis, total dimension: $\dim(\mathcal{H}) = (2s+1)^N$

$$\underset{\sim}{s}_z(u) \,|\, m_1, \ldots, m_u, \ldots, m_N \,\rangle = m_u \,|\, m_1, \ldots, m_u, \ldots, m_N \,\rangle$$

These states span the Hilbert space and are used to construct symmetry-related basis states.

Symmetries of the Heisenberg model without anisotropy

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

Additional (point group) symmetries are possible, e.g. shifts on a ring molecule.

Decomposition into mutually orthogonal subspaces

Hilbert space $\mathcal{H}$ can be decomposed into mutually orthogonal subspaces $\mathcal{H}(M)$ with $M = \sum_u m_u$ (M is the quantum number belonging to $\underset{\sim}{S}_z$)

$$\left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0 \quad : \quad \mathcal{H} = \bigoplus_{M=-S_{\text{max}}}^{+S_{\text{max}}} \mathcal{H}(M) \,, \quad S_{\text{max}} = Ns$$

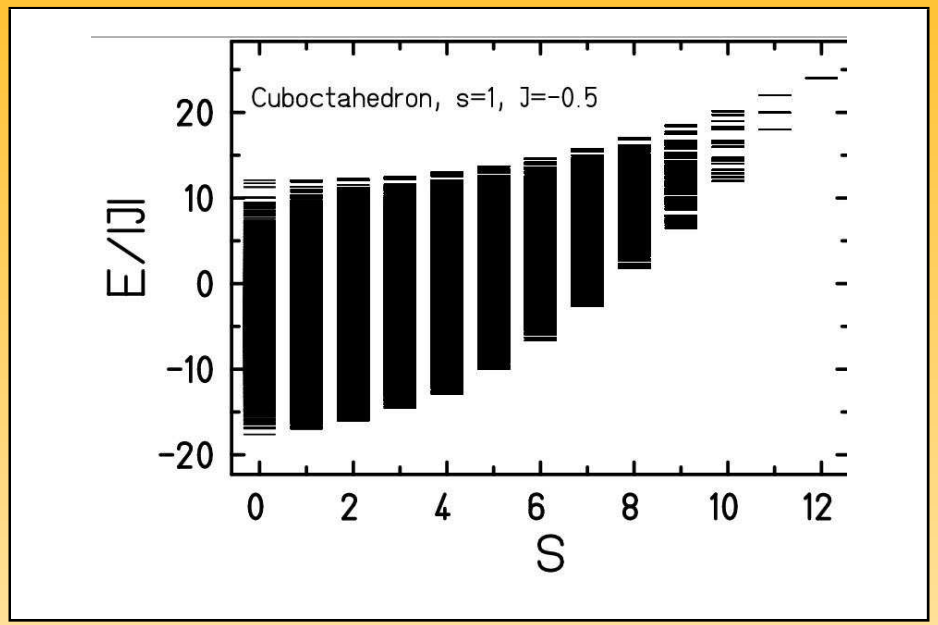
dimension of $\mathcal{H}(M)$ (de Moivre)

$$\dim\left(\mathcal{H}(M)\right) \quad = \quad f(N, 2s+1, S_{\text{max}} - M)$$

$$\text{with} \quad f(N,\mu,\nu) = \sum_{n=0}^{\lfloor \nu/\mu \rfloor} (-1)^n \binom{N}{n} \binom{N-1+\nu-n\mu}{N-1}$$

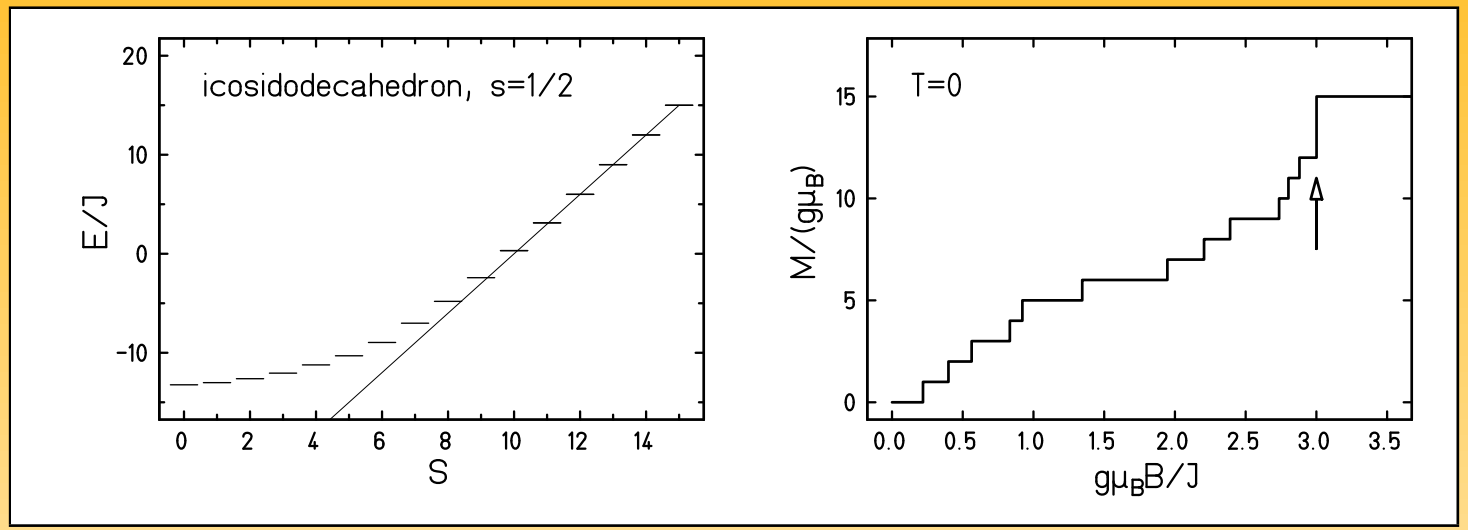
The dimension of the largest subspace is relevant. If more symmetries apply this dimension will be further reduced.

Exact diagonalization



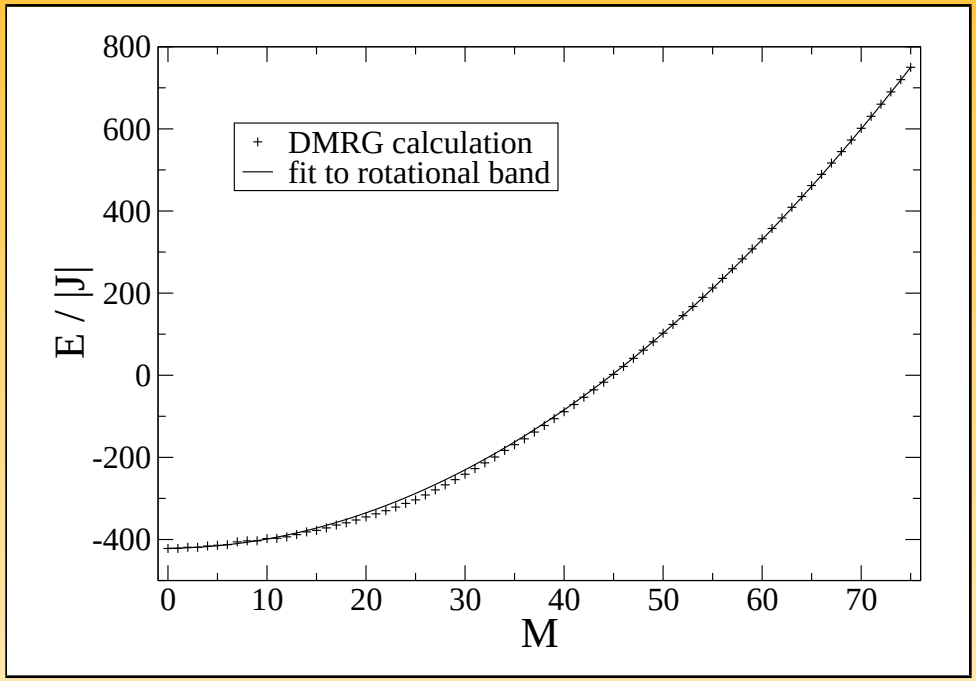
- Numerically exact diagonalization feasible up to RAM size;
- Example: 10,000x10,000 complex*16, 1.6 GB RAM needed;
- Not much we can do at this point, wait for more RAM

The best we can do: Low-lying states



- Low-lying states sufficient for low-temperature physics;
- Low-lying states important for quantum phase transitions, e.g. magnetization jumps.
- Several methods available to obtain extreme eigenvalues: projection, Lánczos, DMRG.

$\{Mo_{72}Fe_{30}\}$ - lowest rotational band with DMRG



- first DMRG calculation for a magnetic macro-molecule (1);
- difficult to calculate since quasi two-dimensional and finite;
- convergence with $1/m$ instead of $\exp(-m)$;
- relative ground state energies form an almost quadratic band (rotational band hypothesis).

(1) M. Exler, J. Schnack, Phys. Rev. B **67** (2003) 094440

Theoretical findings

- Improvement of the theorem of Lieb, Schultz, and Mattis for spin rings;
- Construction of general bounds for the minimal energies of antiferromagnetic spin systems;
- Approximation of the low-lying spectrum by rotational bands;
- Discovery of giant magnetization jumps on certain frustrated spin lattices;
- Example of daily work: new molecule-based triangular copper chain.

Spin rings

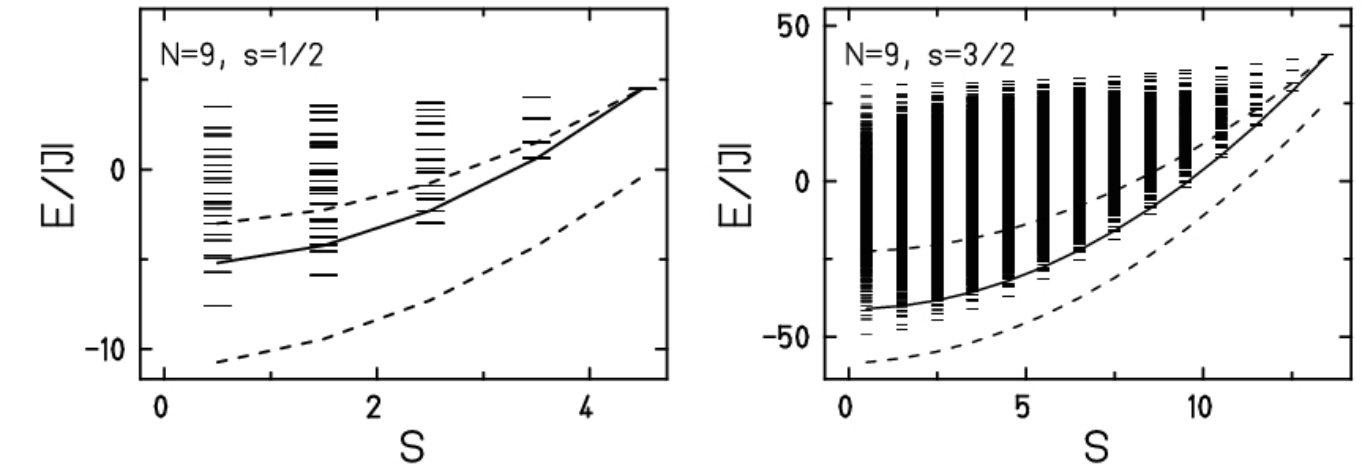
Extended k-rule for relative ground states in subspaces $\mathcal{H}(M)$

$$\text{If } N \neq 3 \quad \text{then} \quad k \equiv \pm a\lceil\frac{N}{2}\rceil \mod N \ .$$

- Moreover the degeneracy of the relative ground state is minimal, i.e. twofold degenerate if there are two different shift quantum numbers $(k, N-k)$ and non-degenerate if $k = 0$ mod N or $k = N/2$ mod N, the latter for even N;
- $a = Ns - M$; shift quantum numbers do not depend on s;
- $\lceil N/2 \rceil$ denotes the smallest integer greater than or equal to $N/2$;
- for $N = 3$ extraordinary shift quantum numbers exist due to an additional degeneracy.

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

Bounds

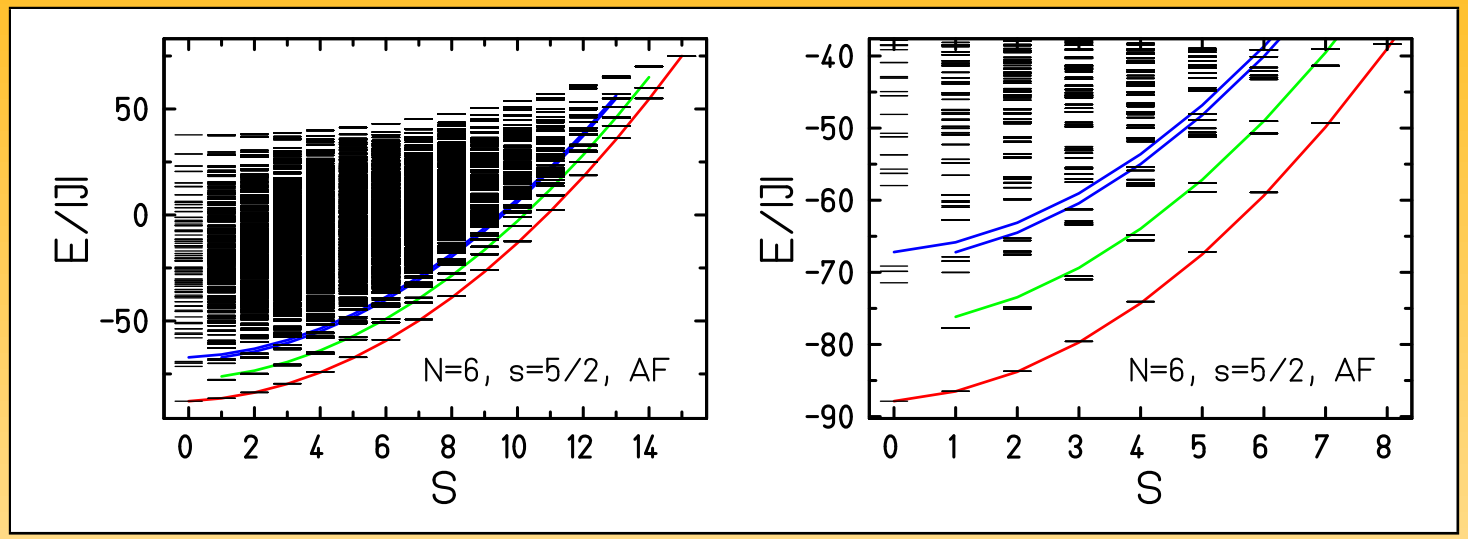


- confine minimal energies as function of M or S (1),
  improve bounds by Berezin and Lieb (2) and our first try (3);

- bounds must be obeyed by approximations like DMRG;
  (parabolic) bounds may serve as approximation of lowest (rotational) band.

(1) K. Bärwinkel, H.-J. Schmidt, and J. Schnack, Eur. Phys. J. B **33** (2003) 285
(2) E. H. Lieb, Commun. Math. Phys. **31**, 327 (1973)
F. Berezin, Commun. Math. Phys. **40**, 153 (1975)
(3) H.-J. Schmidt, J. Schnack, and M. Luban, Europhys. Lett. **55**, 105 (2001)

Rotational bands



- 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)

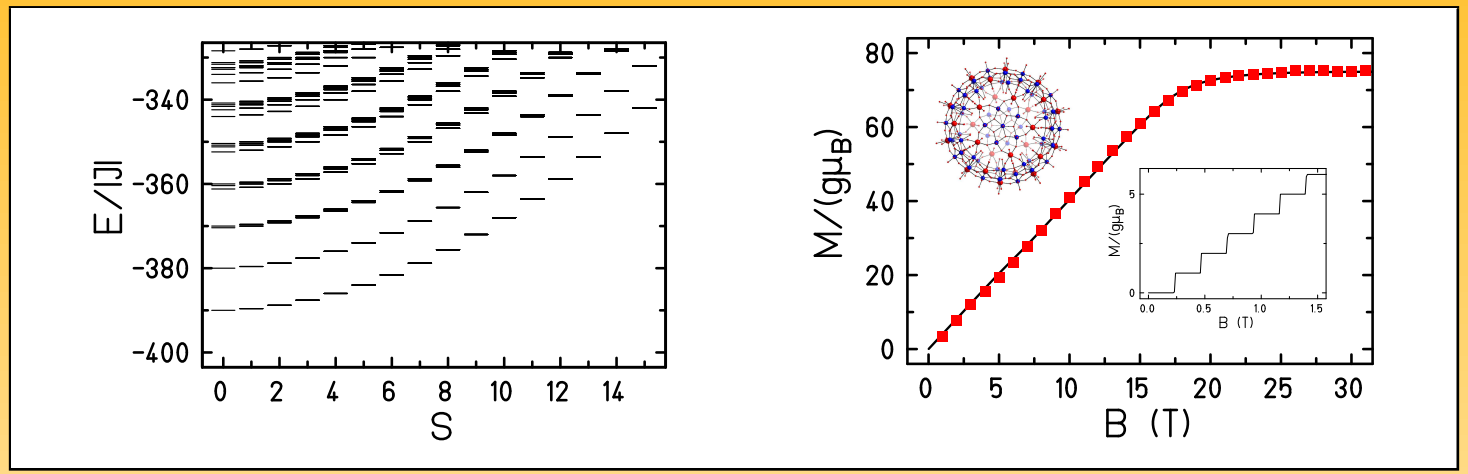
$\{Mo_{72}Fe_{30}\}$ - rotational band hypothesis

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

- Aim: approximate low-lying spectrum by rotational bands;
- Fe_{30}: $N_{SL} = 3; \quad S_A, S_B, S_C = 0, 1, \ldots, 25; \quad S = 0, 1, \ldots, 75;$
- $D = 6$ either from classical counterpart or symmetry considerations or properties of coupling matrix;

J. Schnack, M. Luban, R. Modler, Europhys. Lett. **56** 863 (2001)
H.-J. Schmidt, J. Schnack, and M. Luban, Europhys. Lett. **55**, 105 (2001)

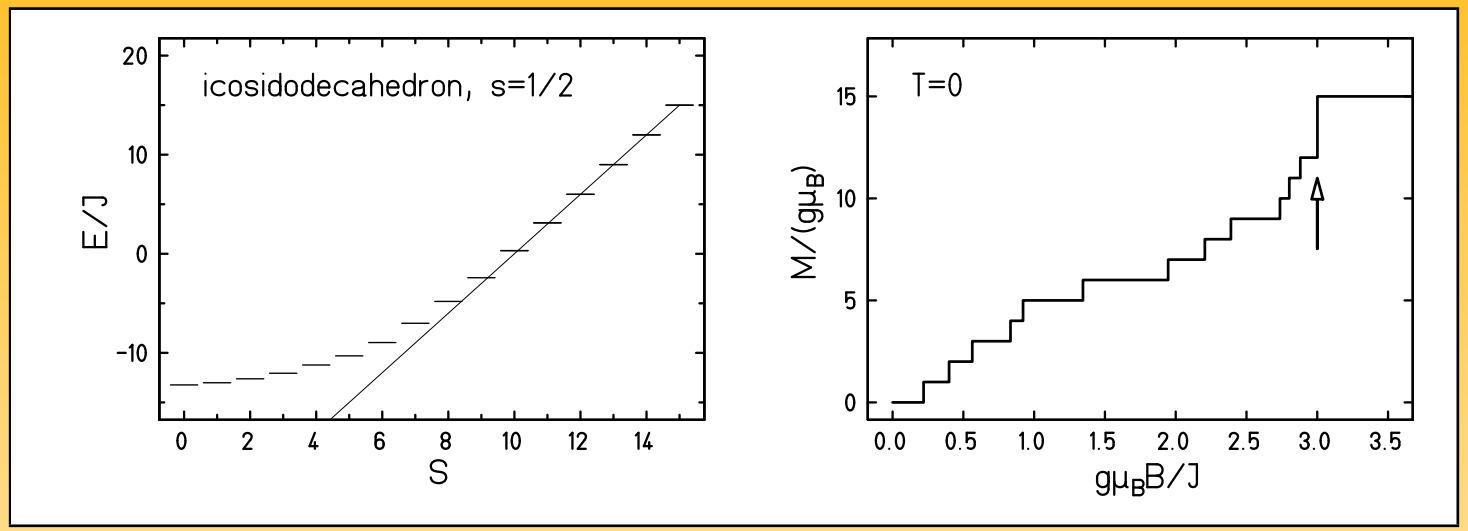
$\{Mo_{72}Fe_{30}\}$ - magnetization



- sequence of rotational bands rather unrealistic for this frustrated system;
- nevertheless magnetization at $T = 0.46$ K very well reproduced.

J. Schnack, M. Luban, R. Modler, Europhys. Lett. **56** 863 (2001) 863
A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001)

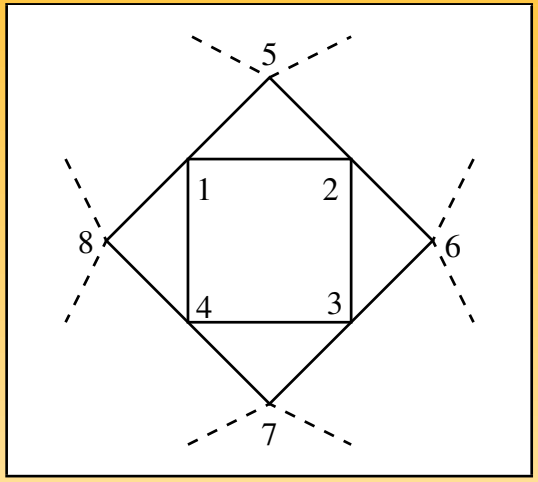
$\{Mo_{72}Fe_{30}\}$ - magnetization jump



- $E_{\text{min}}(S)$ 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** (2002) 167207

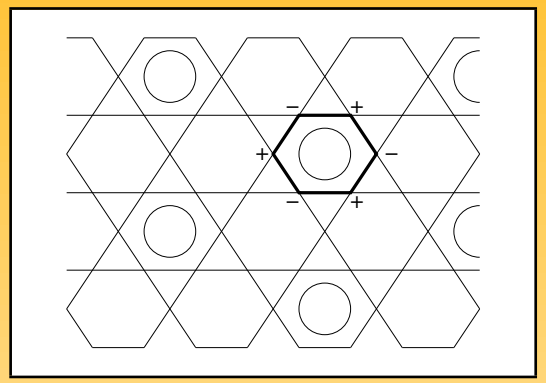
Localized Magnons



- $|\,\text{localized magnon}\,\rangle = \frac{1}{2}(\,|\,1\,\rangle - |\,2\,\rangle + |\,3\,\rangle - |\,4\,\rangle)$
- $|\,u\,\rangle = \underset{\sim}{s}^{-}(u)\,|\,\Omega\,\rangle$; $|\,\Omega\,\rangle$ – magnon vacuum; $u = 1, 2, 3, 4$
- $\underset{\sim}{H}\,|\,1\,\rangle = J\{\,|\,1\,\rangle + 1/2(\,|\,2\,\rangle + |\,4\,\rangle + |\,5\,\rangle + |\,8\,\rangle)\}$
- $\underset{\sim}{H}\,|\,\text{localized magnon}\,\rangle \propto |\,\text{localized magnon}\,\rangle$

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

Kagome Lattice

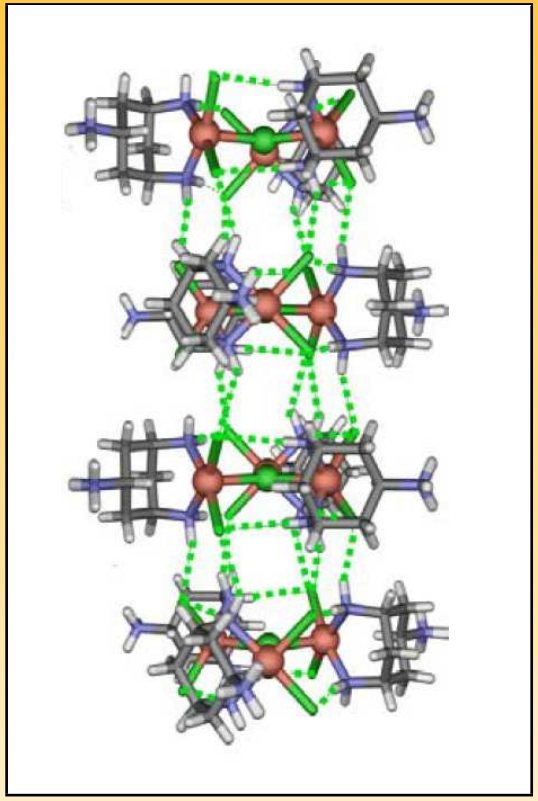


- localized one-magnon state indicated by bold lines;
- non-interacting one-magnon states can be placed on the grid; each state of n independent magnons is the ground state in the Hilbert subspace with $M = Ns - n$;

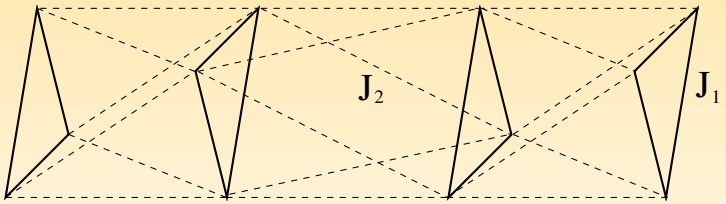
- $\Rightarrow$ linear dependence of E_{min} on M; magnetization jump;
- maximal number of independent magnons: N/9;
- magnetization jump is a macroscopic quantum effect!

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

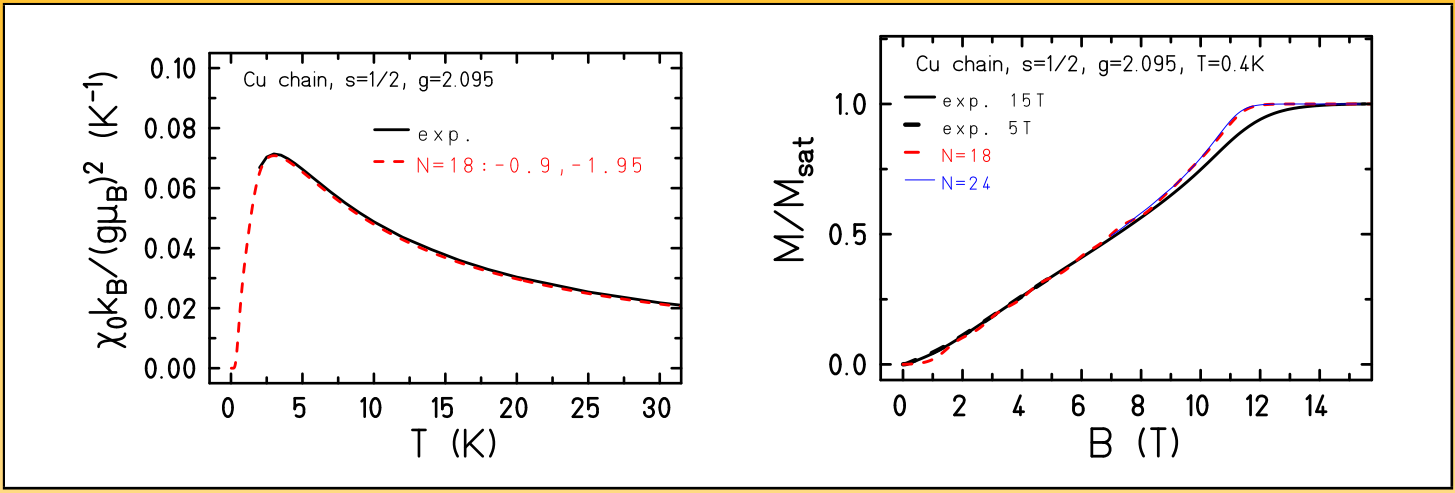
Triangular Cu-chain I



- $[Cl(CuCl_2tachH)_3]X_2$ chain;
- tach = *cis,trans*-1,3,5-triamino-cyclohexane;
- X = Cl (**1**) or Br (**2**));
- stack of Cu-triangles coupled by hydrogen-bonded Cu-Cl$\cdots$H-N-Cu super-exchange pathways (6.82 Å); intra-triangle Cu-Cu distance is 4.46 Å.
- couplings:



Triangular Cu-chain II



- Natural assumption: weakly coupled triangles, i. e. at low T effective $s = 1/2$-chain;
- Consequence: plateau at $1/3$ saturation magnetization;
- Surprise: no plateau, $J_1 = -0.9$ K and $J_2 = -1.95$ K, i. e. of similar size;
- Gap: singlet-triplet gap extrapolated to 0.4 K.

Outlook

- magnetic molecules is a booming field:
  ICMM-2000: 200 participants,
  ICMM-2002: 425 participants;
  DFG-SPP 1137
- huge advances in coordination chemistry, it seems to be possible to synthesize “every” structure;
- dynamics plays a bigger and bigger role: relaxation, hysteresis, magnetooptical switching.

- interesting molecules: complicated couplings + anisotropy,
  bigger and bigger $\Rightarrow$ huge Hilbert spaces;
- systematics which connects structure and properties of observables
  highly required;
- interlinked structures of magnetic molecules are beyond nowadays computing - what to do?

Thank you very much for your attention.

Collaboration

- Prof. K. Bärwinkel, Prof. H.-J. Schmidt, M. Allalen, M. Brüger, D. Mentrup, M. Exler, P. Hage, F. Hesmer, F. Ouchni, P. Shechelokovskyy (Uni Osnabrück);
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- Prof. H. Nojiri (Okayama University, Japan);
- Prof. S. Blügel (FZ Jülich);
- Prof. J. Richter, J. Schulenburg (Uni Magdeburg);
- Dr. A. Honecker (Uni Braunschweig).