Frustration effects in magnetic molecules

Jürgen Schnack

Department of Physics - University of Osnabrück

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

PhD program, Osnabrück, April 16, 2004

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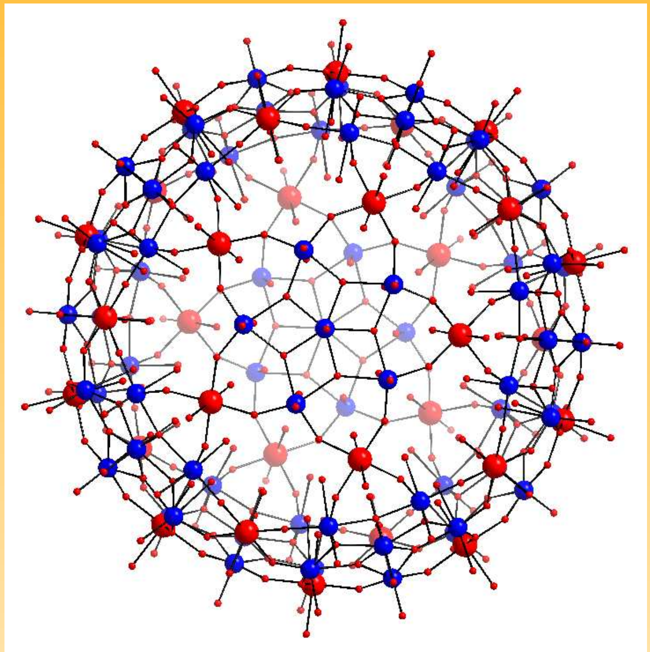
Gossip about frustration



Fe_{30}

- Typical statement: It is known that frustrated spin systems exhibit spectacular phenomena: high ground state degeneracy, re-entrance, partial disorder, controversial nature of the phase transition, order by the disorder, etc.
- What is frustration?
- New consequences of frustration?

Interaction and frustration

Heisenberg Hamiltonian

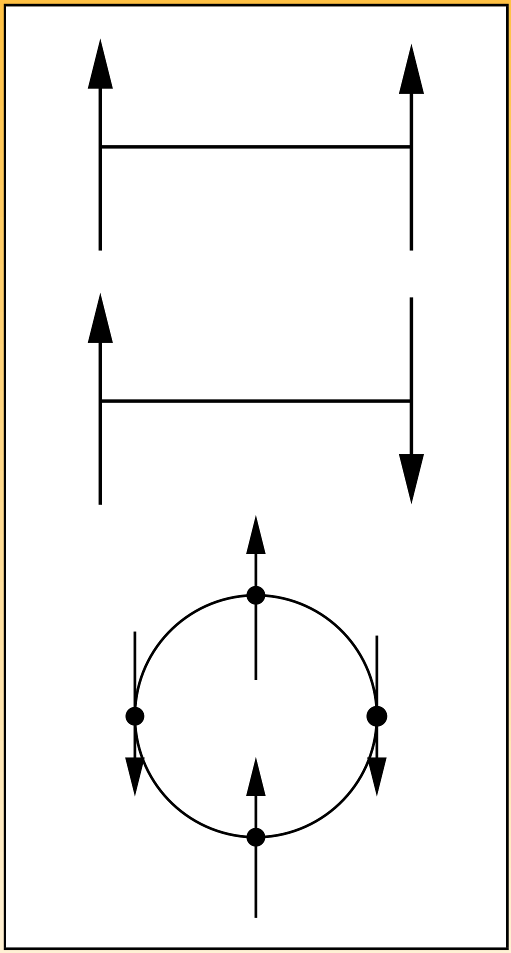
$$\underset{\sim}{H} = -\sum_{i,j} J_{ij}\,\underset{\sim}{\vec{s}}(i)\cdot\underset{\sim}{\vec{s}}(j) + g\,\mu_B\,B\sum_{i}^{N}\underset{\sim}{s}_z(i)$$

Heisenberg Zeeman

The Heisenberg 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.

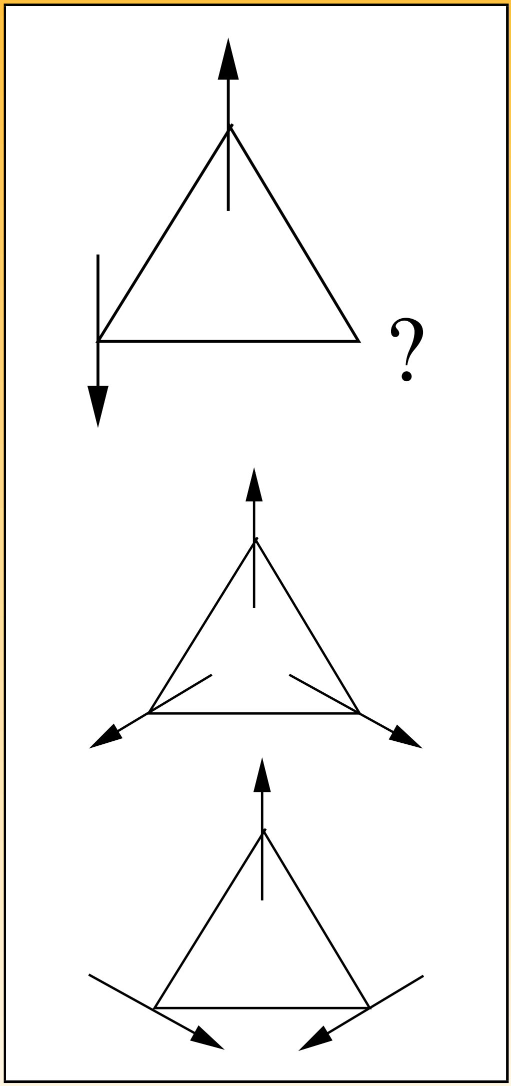
$\underset{\sim}{\vec{s}}(i)$ are the spin operators at sites i, J_{ij} is the strength of the mutual interaction, B is the applied magnetic field.

Ferromagnets and Antiferromagnets



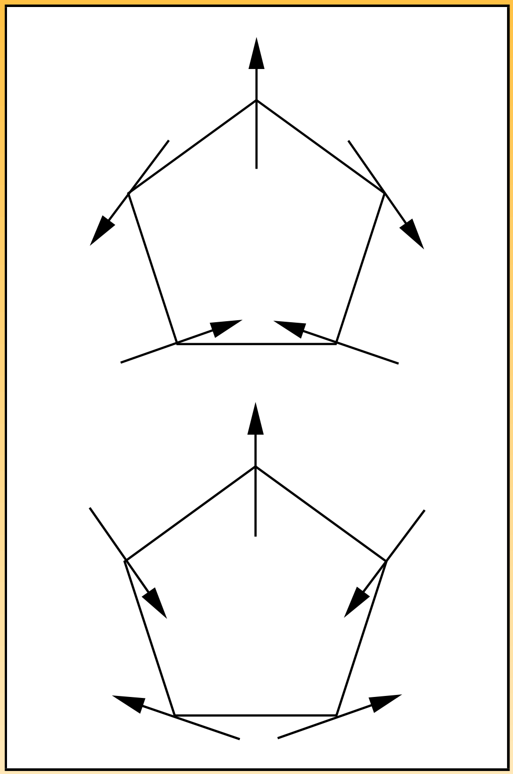
- Dimer: $\underset{\sim}{H} = -2J\, \underset{\sim}{\vec{s}}(1) \cdot \underset{\sim}{\vec{s}}(2)$
- Feromagnetic coupling: $J > 0$, classical spin vectors align parallel; $E_0 = -2Js^2$.
- Antiferomagnetic coupling: $J < 0$, classical spin vectors align antiparallel; $E_0 = 2Js^2$.
- Antiferomagnetic ring with even N: classical spin vectors align antiparallel; $E_0 = 2JNs^2$.

Simple definition of frustration



- Triangle: $\underset{\sim}{H} = -2J \left(\underset{\sim}{\vec{s}}(1) \cdot \underset{\sim}{\vec{s}}(2) \underset{\sim}{\vec{s}}(2) \cdot \underset{\sim}{\vec{s}}(3) \underset{\sim}{\vec{s}}(3) \cdot \underset{\sim}{\vec{s}}(1) \right)$
- Very simple definition of frustration: The last spin is frustrated because it does not know how to align.
- True clasical ground state in the antiferromagnetic triangle is given by relative angles of 120° between neighboring spins it is degenerate.
- But the quantum ground state is non-degenerate for integer s and fourfold degenerate for half-integer s.

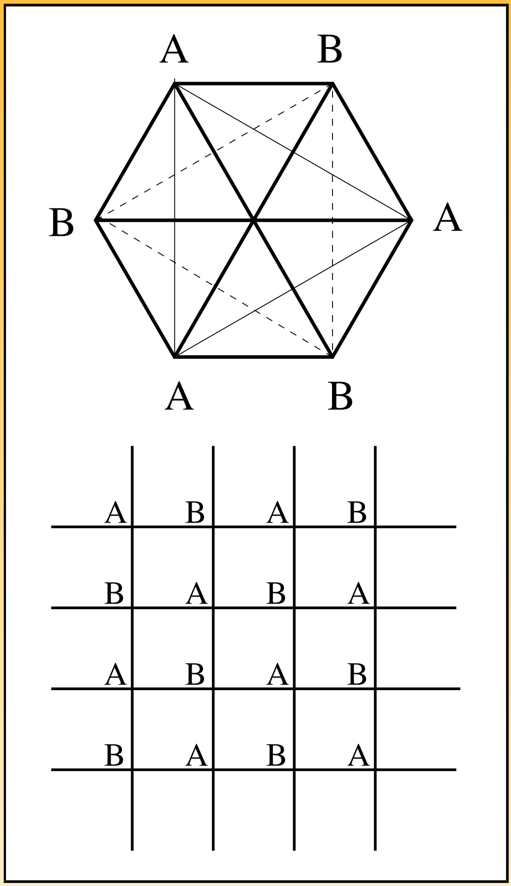
Classical definition of frustration



- 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.

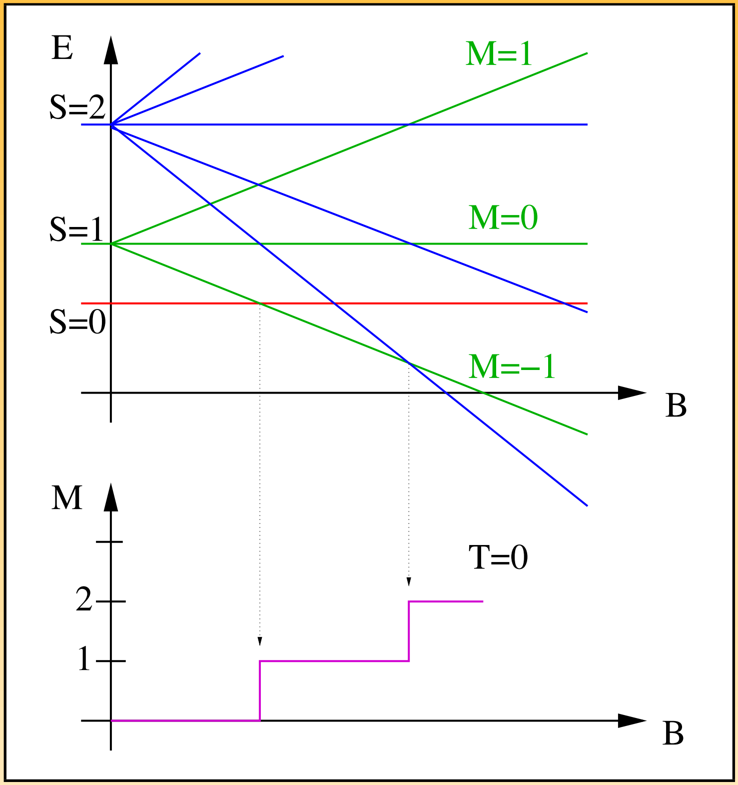
Advanced definition of frustration



- 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.
- Definition uses topological properties of the graph of interactions.

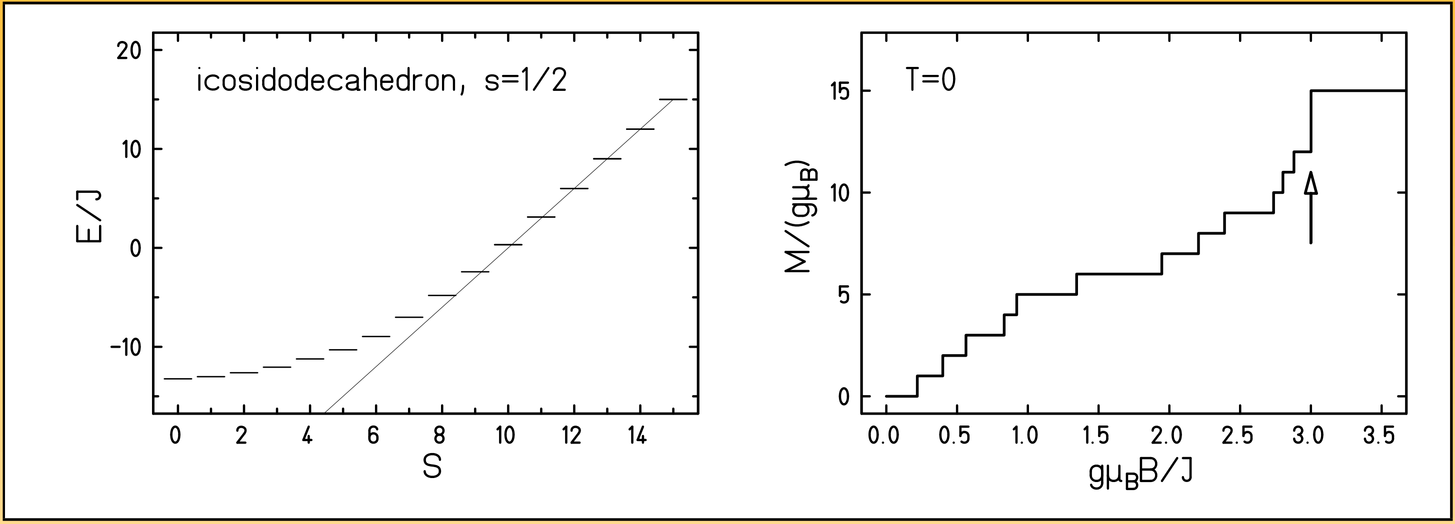
Consequences of frustration

Zeeman level splitting



- $\underset{\sim}{H}_{\text{Zeeman}} = g\,\mu_B\,B\,\sum_i^N\,\underset{\sim}{s}_z(i)$
- $E_\nu(B) = E\nu(B=0) + g\,\mu_B\,B\,M_\nu$
- The lowest level for a given magnetic field B is the new ground state. This state defines the magnetization at $T=0$.
- If $E_{\text{min}}(S)$ quadratic in S (Landé interval rule) then the magnetization steps are equidistant.

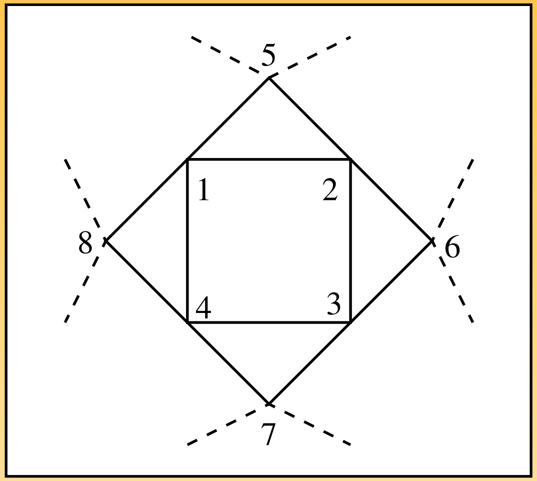
{$Mo_{72}Fe_{30}$} - magnetization jump



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

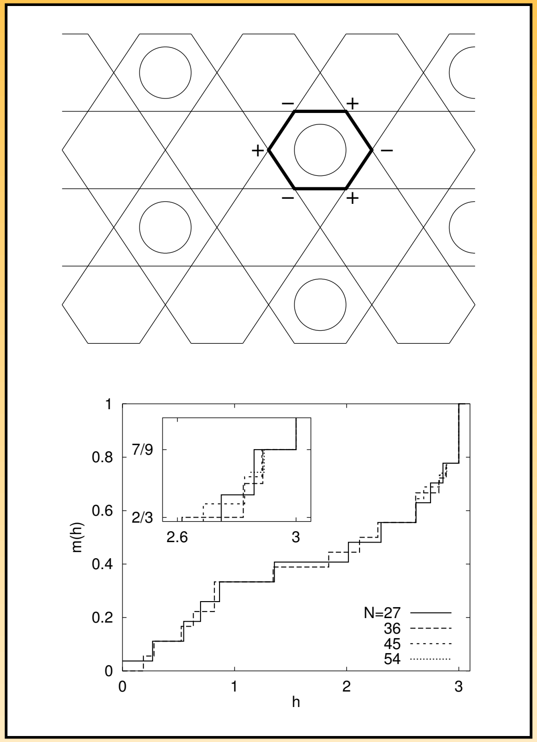
Localized Magnons



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

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

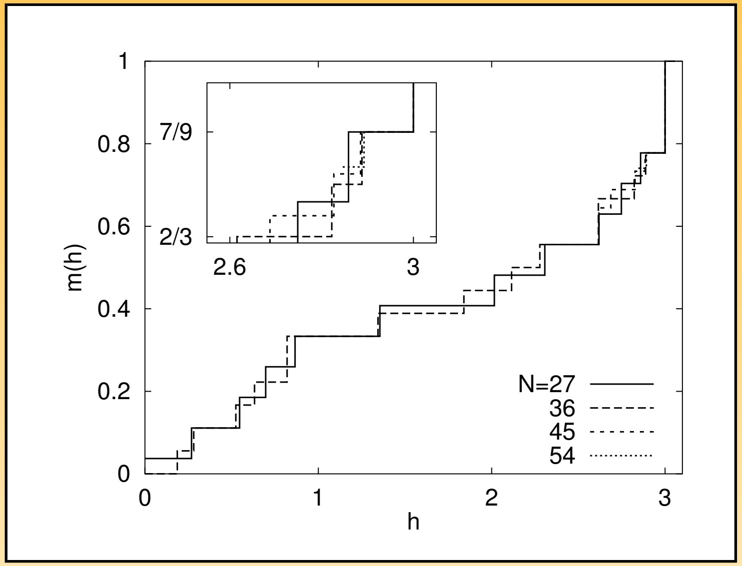
Kagomé Lattice



- 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!

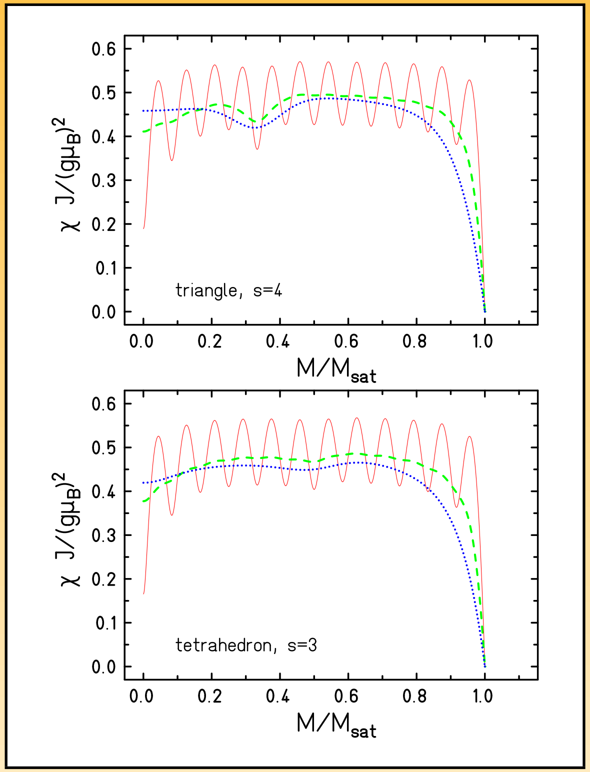
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002)

Plateaus



- Plateaus of the magnetization curve are a very popular subjects nowadays.
- Especially structures built of corner sharing triangles often show a plateau at $M_{\text{sat}}/3$.
- Lattices like the Kagomé lattice are examples for such a behavior.
- The properties of such frustrated lattices are supposed to be related to high temperature superconductivity.

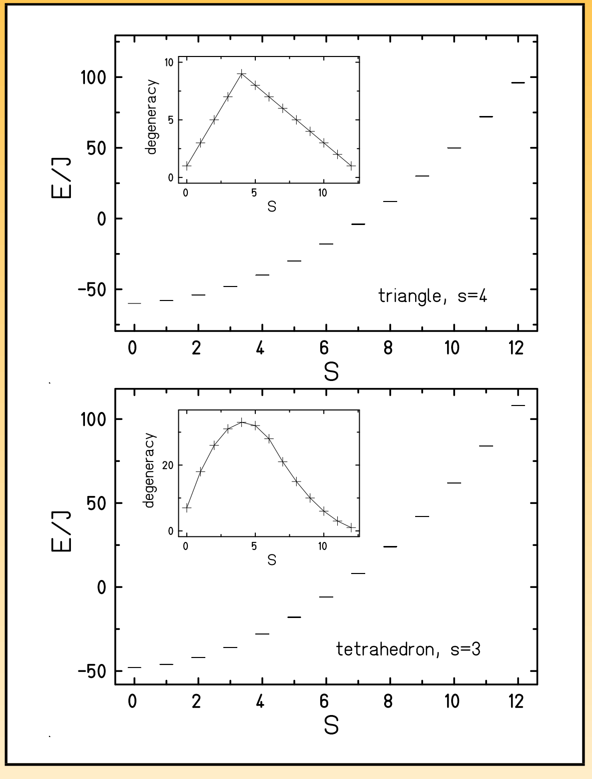
Susceptibility minima I



- Several frustrated Heisenberg spin systems feature a local minimum in the susceptibility as function of magnetic field B (1).
- Triangular, Kagomé, garnet lattice, icosidodecahedron, cuboctahedron, and triangle have a dip around $B_{\text{sat}}/3$, more precise $M_{\text{sat}}/3$.
- Pyrochlore lattice and tetrahedron feature a dip around $B_{\text{sat}}/2$, more precise $M_{\text{sat}}/2$.
- Phenomenon emerges in spin systems with sublattice structure.

(1) C. Schröder, H. Nojiri, J. Schnack, P. Hage, P. Kögerler, and M. Luban, to be submitted soon

Susceptibility minima II

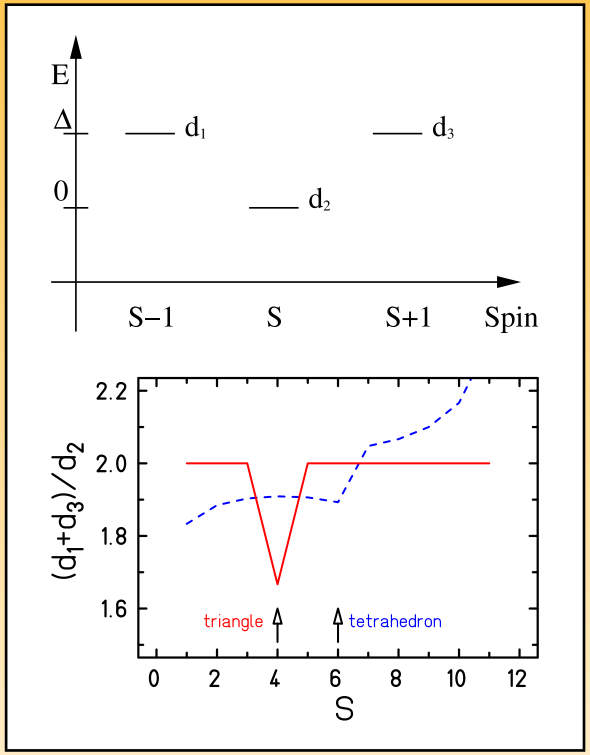


$$\underset{\sim}{H}^{\text{triangle}} = J\left[\underset{\sim}{\vec{S}}^2 - 3\,\underset{\sim}{\vec{s}}^2\right]$$

$$\underset{\sim}{H}^{\text{tetrahedron}} = J\left[\underset{\sim}{\vec{S}}^2 - 4\,\underset{\sim}{\vec{s}}^2\right] .$$

- Spectra of triangle with $s = 4$ and tetrahedron with $s = 3$ identical – rotational band, Landé rule.
- Difference in magnetization behavior stems from different degeneracies!
- The degeneracies of energy eigenvalues result from the various ways to couple 3 or 4 intrinsic spins to a given total spin S.

Susceptibility minima III

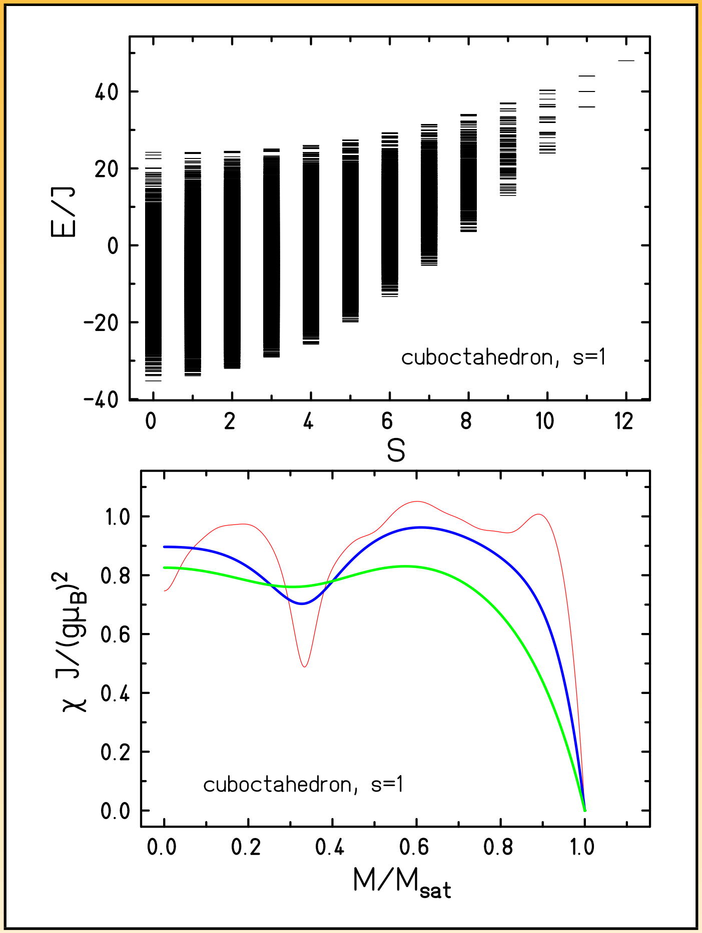


- Stability analysis with three level system

$$\mathrm{d}M \quad \approx \quad -\beta\,(g\mu_B)^2\,e^{-\beta\Delta}\,\frac{d_1+d_3}{d_2}\,\mathrm{d}B$$

- Minimum of χ whenever $(d_1+d_3)/d_2$ is minimal.
- Triangle: minimum at $S_{\text{max}}/3$, tetrahedron: minimum at $S_{\text{max}}/2$.
- Alternative: degeneracy functions consist of two branches, intersection shows up in higher derivatives of $Z(T,B)$

Susceptibility minima IV



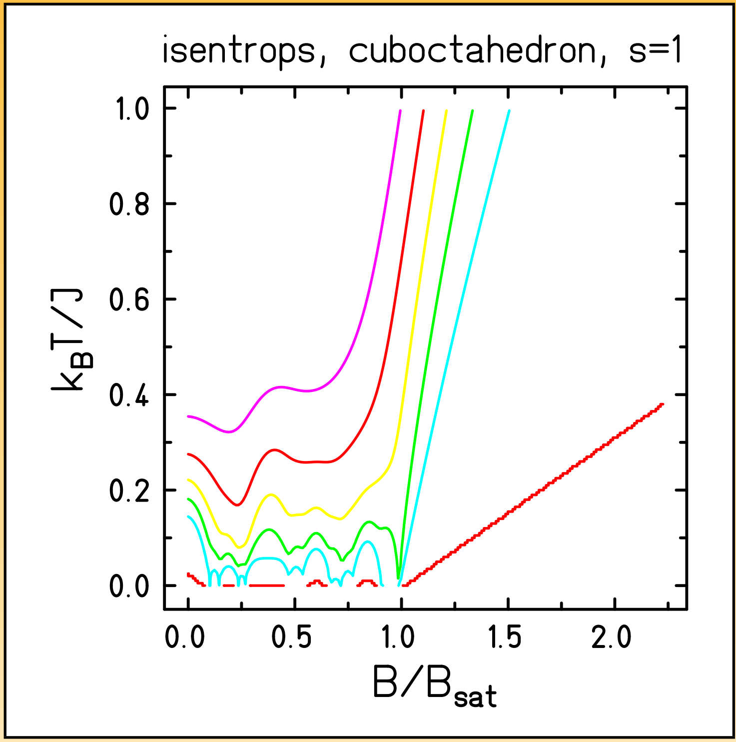
- Local minimum in χ is observed in several extended spin structures.
- Three-sublattice systems: triangle, octahedron, cuboctahedron, icosidodecahedron as well as triangular, Kagomé, and garnet lattice.
- Four-sublattice systems: tetrahedron and pyrochlore lattice.
- Explanation quantum mechanically difficult, classical explanation much clearer.

The Magnetocaloric Effect

- Discovered in pure iron by E. Warburg in 1881.
- Heating or cooling in a varying magnetic field.
- Typical rates: $0.5 \ldots 2$ K/T (adiabatic temperature change).
- Giant magnetocaloric effect: $3 \ldots 4$ K/T in $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leq 0.5$).
- Also interesting: refrigerant capacity, which is the measure of how much heat can be transferred from a cold to a hot reservoir in one ideal thermodynamic cycle.
- Magnetocaloric effect especially effective in frustrated classical spin systems (1).

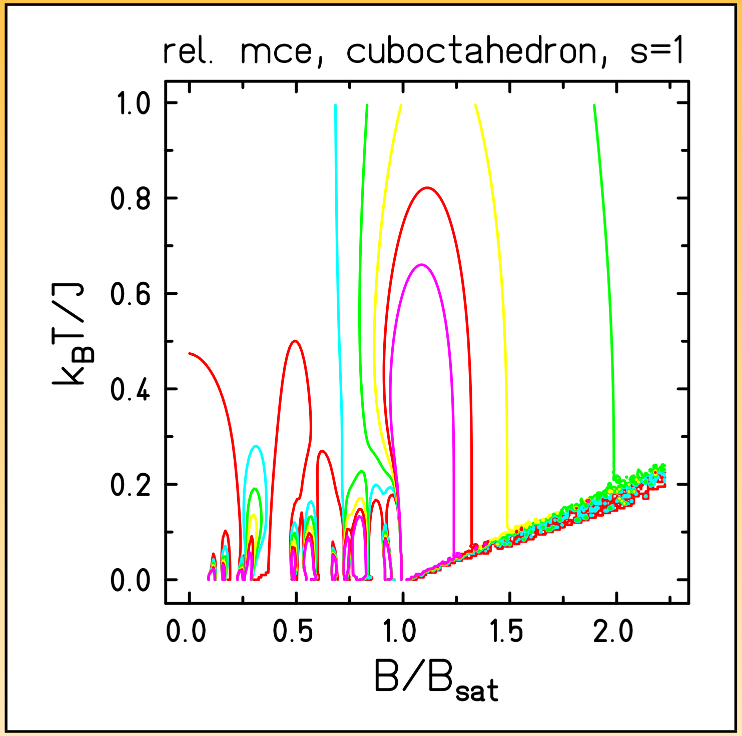
(1) M. E. Zhitomirsky, *Enhanced magnetocaloric effect in frustrated magnets*, Phys. Rev. B **67**, 104421 (2003)

Adiabatic temperature change



- Adiabatic process: no heat transfer to the environment, i.e. constant entropy d$S = 0$.
- Effect strong around jumps of the magnetization curve.
- Adiabatic temperature change especially strong at the large jump to saturation.

Relative magnetocaloric effect



- In paramagnets, i. e. uncoupled magnetic moments (spins), we find $(\partial T/\partial B)_S^{\text{para}} = T/B$.

- Interacting spin systems can exceed the paramagnetic limit.

- Figure shows $(\partial T/\partial B)_S/(\partial T/\partial B)_S^{\text{para}}$

- Again in the vicinity of the large jump to saturation the effect is much stronger than in a paramagnet.

Application of the magnetocaloric effect

- Application for magnetization cooling: at room temperature for everyday applications, at very low-temperature for extreme cooling.

- Magnetic refrigeration: cost effective, save considerable energy (20 to 30%) over conventional gas compression technology; environmentally friendly, since eliminating ozone depleting chemicals (CFCs), green house gases (HCFCs and HFCs), and hazardous chemicals (NH_3) [Karl A. Gschneidner, Jr., Ames Lab].

Thank you very much for your attention.

The end.