

Magnetocalorics of magnetic molecules

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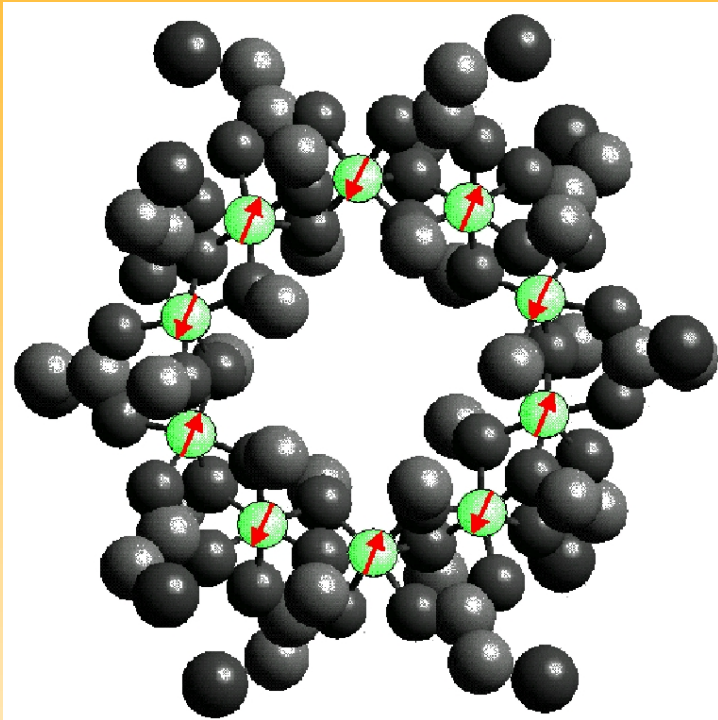


文部科学省

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Contents for you today

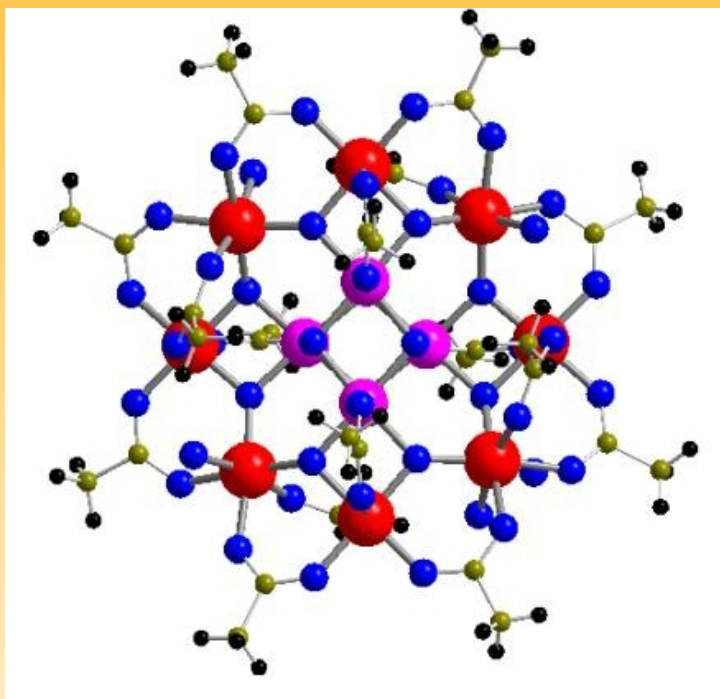


Fe₁₀

1. The suspects: magnetic molecules
2. Our research philosophy
3. The thumbscrew: Heisenberg model
4. Magnetocalorics in frustrated antiferromagnets

Magnetic Molecules

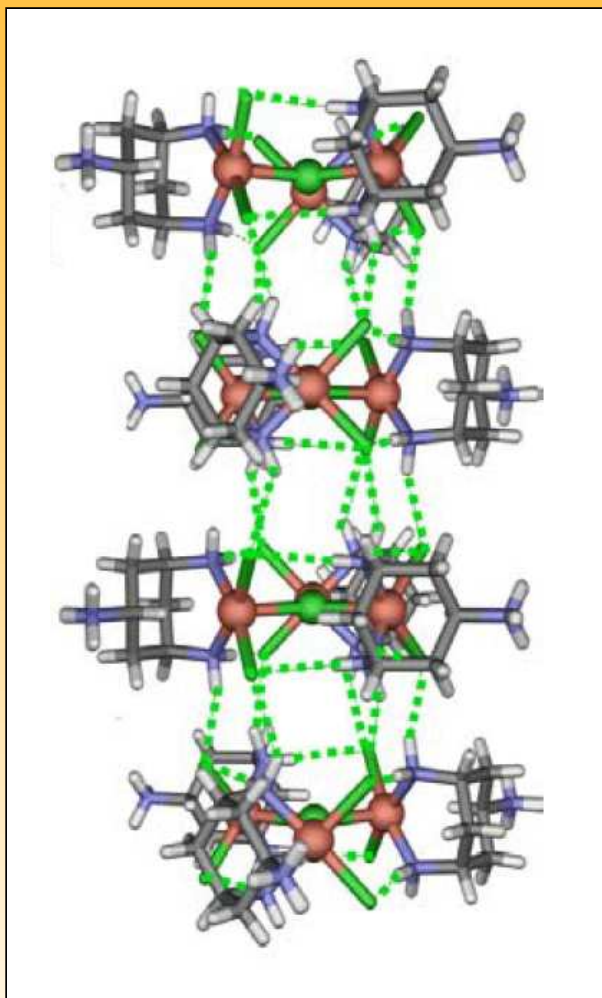
The beauty of magnetic molecules I



Mn₁₂

- Inorganic or organic macro molecules, where paramagnetic ions such as Iron (Fe), Chromium (Cr), Copper (Cu), Nickel (Ni), Vanadium (V), Manganese (Mn), or rare earth ions are embedded in a host matrix;
- Pure organic magnetic molecules: magnetic coupling between high spin units (e.g. free radicals);
- **Spin = magnetic moment (“compass needle”):** Molecule has magnetic properties.
- Speculative applications: **magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, transparent magnets, qubits for quantum computers.**

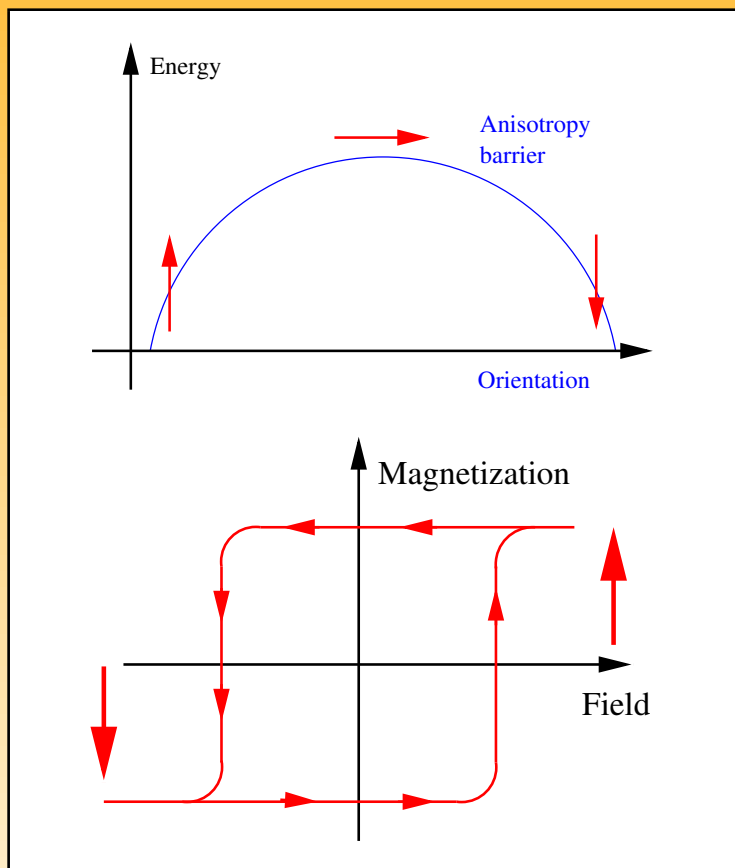
The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron and chromium rings
(order from The Manchester Magic Ring Factory,
Brunswick Street, Manchester, M13 9PL, UK);
- 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)

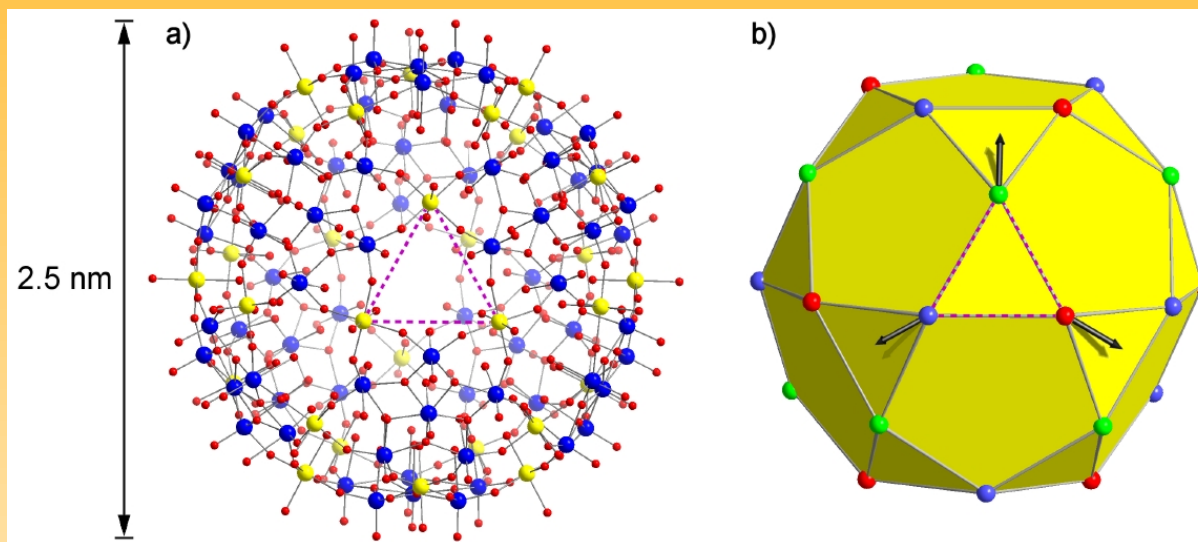
The beauty of magnetic molecules III



- Single Molecule Magnets (SMM): magnetic molecules with large ground state moment; e.g. $S = 10$ for Mn_{12} or Fe_8
- Anisotropy barrier dominates behavior (as in your hard drive);
- Single molecule is a magnet and shows metastable magnetization and hysteresis; but also magnetization tunneling.
- Today's major efforts: improve stability of magnetization; investigate on surfaces.

The beauty of magnetic molecules IV

{Mo₇₂Fe₃₀} – a giant magnetic Keplerate molecule

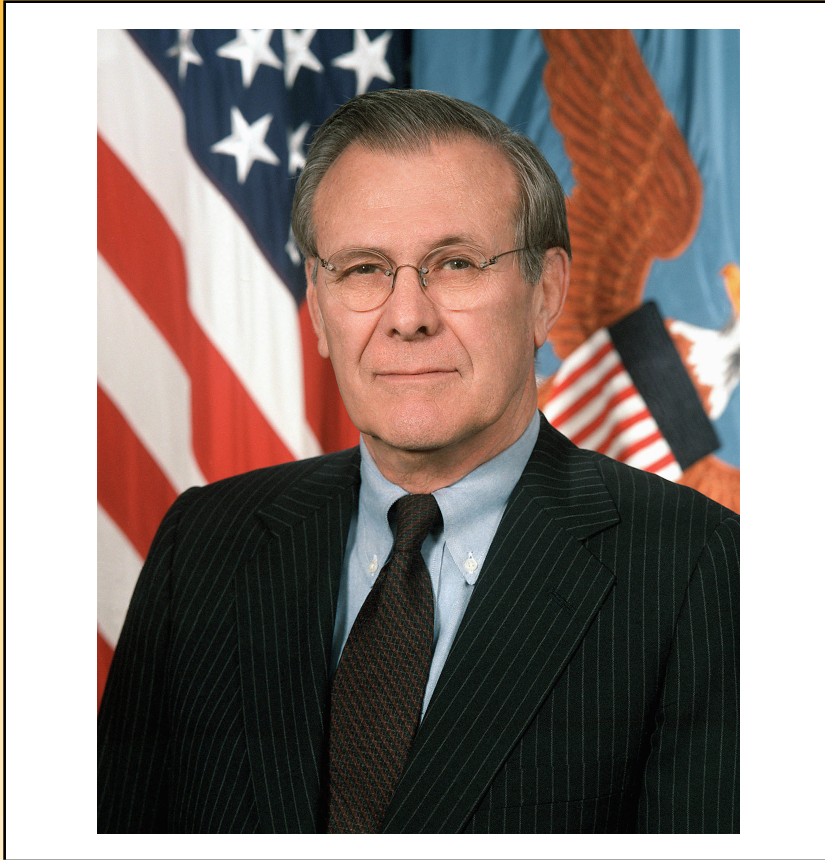


- Structure: Fe - yellow, Mo - blue, O - red;
- Exciting magnetic properties (1).
- Quantum treatment very complicated, dimension of Hilbert space $(2s + 1)^N \approx 10^{23}$ (2).

(1) A. Müller *et al.*, Chem. Phys. Chem. **2**, 517 (2001) , (2) M. Exler and J. Schnack, Phys. Rev. B **67**, 094440 (2003)

Our research philosophy

Philosophy of our research

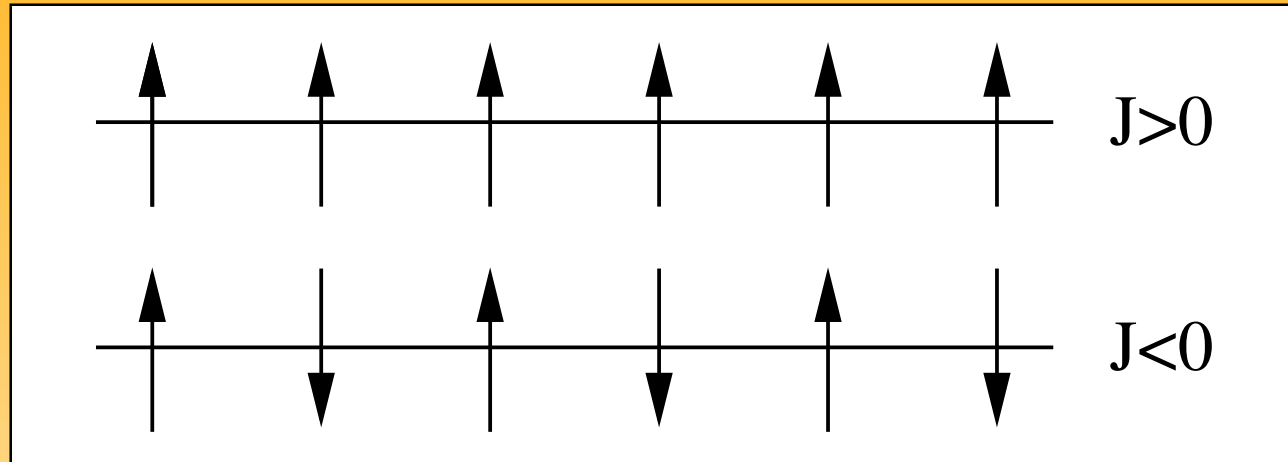


- There are known knowns.
- There are known unknowns.
- And there are unknown unknowns.

Donald Rumsfeld

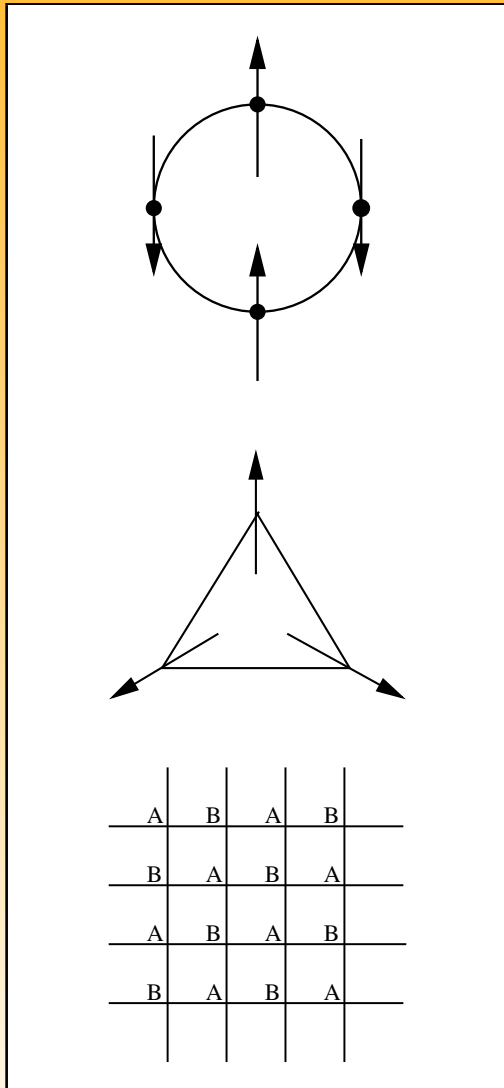
Theoretical concepts and tools (The known knowns)

Basic magnetism



- **Heisenberg model:** $\underline{H} = -J \sum_{\langle i,j \rangle} \vec{s}(i) \cdot \vec{s}(j)$
- **paramagnet:** single moment, can align in a magnetic field;
- **ferromagnet:** parallel moments, $J > 0$;
- **antiferromagnet:** antiparallel moments, $J < 0$;
- **diamagnet:** no permanent moment; moment can be induced by an applied magnetic field.

Definition of frustration



- You talk and everybody sleeps already at slide 3!
- Simple: An antiferromagnet is frustrated if in the ground state of the corresponding classical spin system not all interactions can be minimized simultaneously.
- Advanced: A non-bipartite antiferromagnet is frustrated. A bipartite spin system can be decomposed into two sublattices A and B such that for all exchange couplings:

$$J(x_A, y_B) \leq g^2, J(x_A, y_A) \geq g^2, J(x_B, y_B) \geq g^2,$$
 cmp. (1,2).

(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)

Model Hamiltonian – Heisenberg-Model

$$\tilde{H} = \sum_{i,j} \vec{\tilde{s}}(i) \cdot \mathbf{J}_{ij} \cdot \vec{\tilde{s}}(j) + \sum_{i,j} \vec{D}_{ij} \cdot [\vec{\tilde{s}}(i) \times \vec{\tilde{s}}(j)] + \mu_B B \sum_i^N g_i \tilde{s}_z(i)$$

Exchange/Anisotropy
Dzyaloshinskii-Moriya
Zeeman

Very often anisotropic terms are utterly negligible, then ...

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

Heisenberg
Zeeman

The Heisenberg Hamilton operator together with a Zeeman term are used for the following considerations; $J < 0$: antiferromagnetic coupling.

Magnetocalorics

(Known and unknown knowns)

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 ... 2 K/T.
- 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 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).

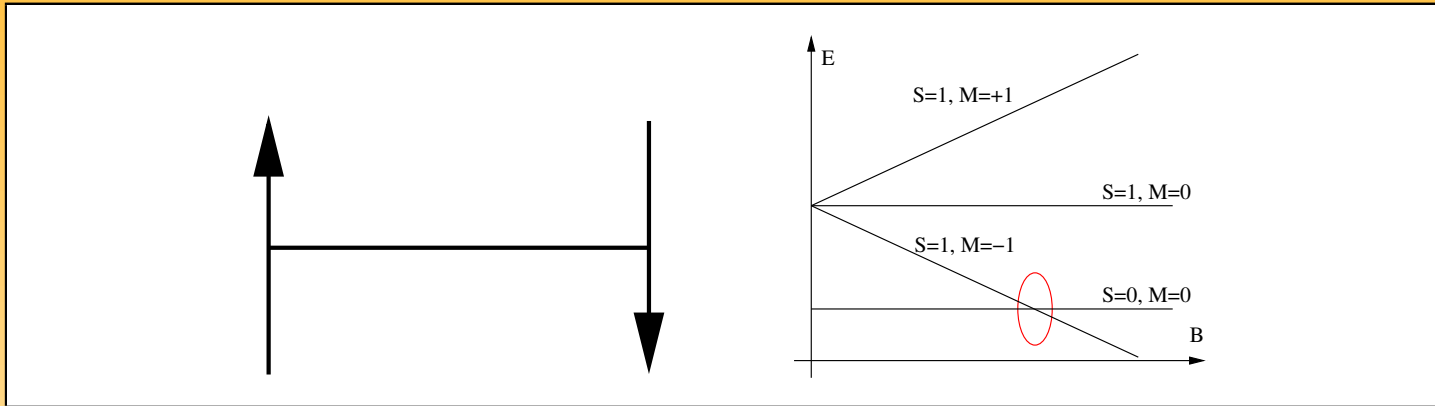
(1) V.K. Pecharsky, K.A. Gschneidner, Jr., A. O. Pecharsky, and A. M. Tishin, Phys. Rev. B **64**, 144406 (2001)

(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)

Magnetocaloric effect II

Simple af $s = 1/2$ dimer

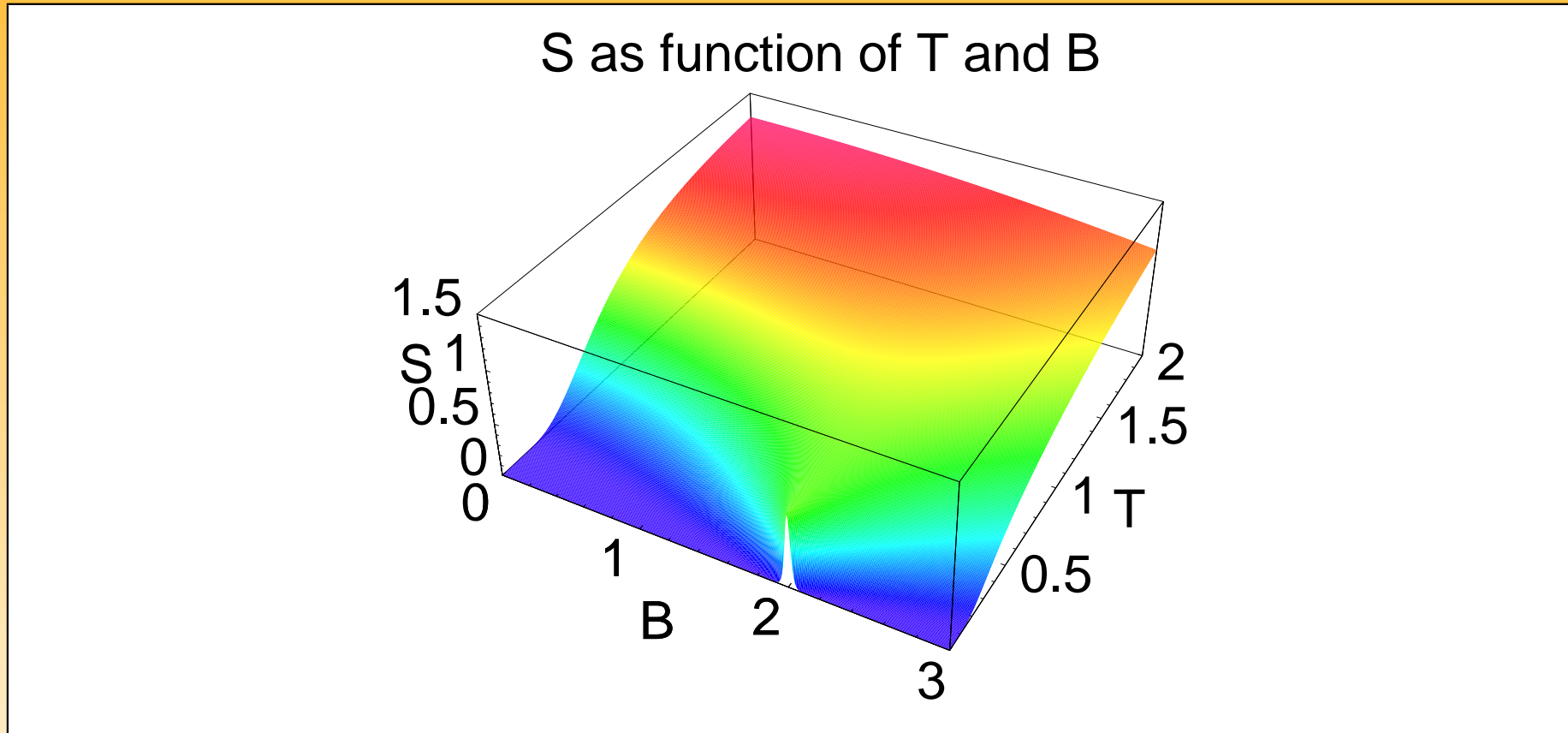


- Singlet-triplet level crossing causes a “quantum phase transition” (1) at $T = 0$ as a function of B .
- $M(T = 0, B)$ and $S(T = 0, B)$ not analytic as function of B .
- $M(T = 0, B)$ jumps at B_c ; $S(T = 0, B_c) = k_B \ln 2$, otherwise zero.

(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.

Magnetocaloric effect III

Entropy of a $s = 1/2$ dimer

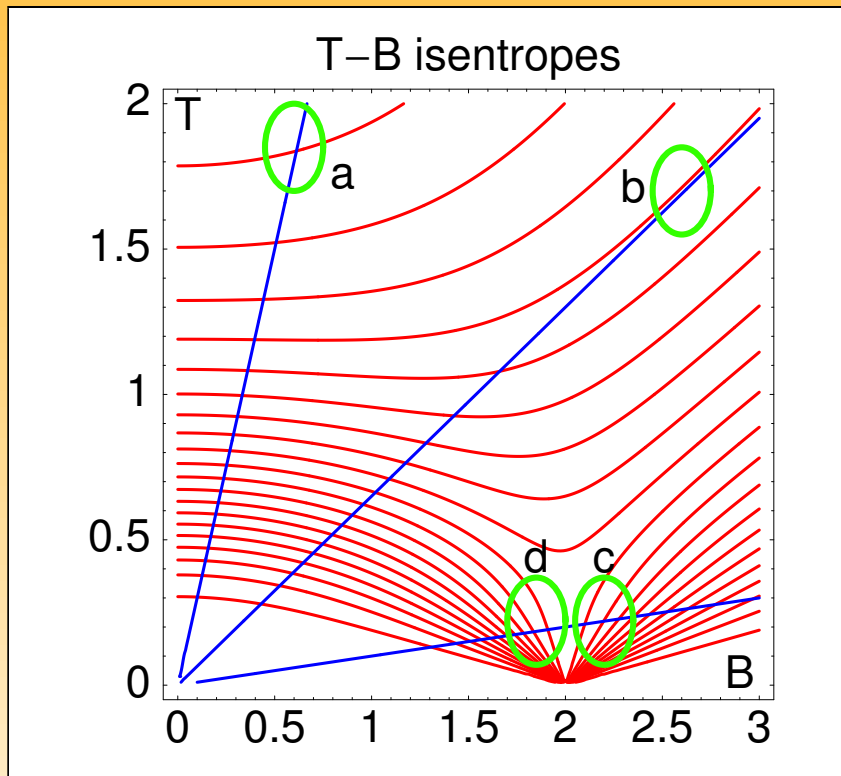


$S(T = 0, B) \neq 0$ at level crossing due to degeneracy

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

Magnetocaloric effect IV

Isentropes of an $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

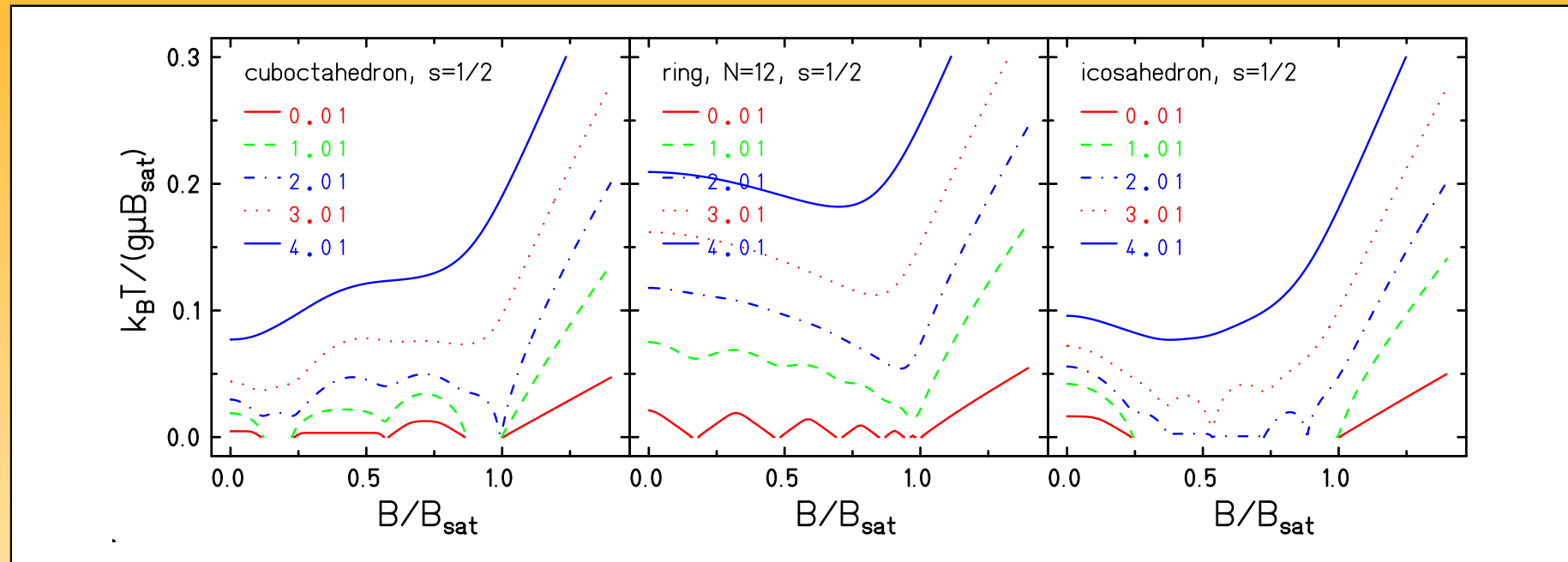
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

Case (d) does not occur for a paramagnet.

Magnetocaloric effect V – Molecular systems

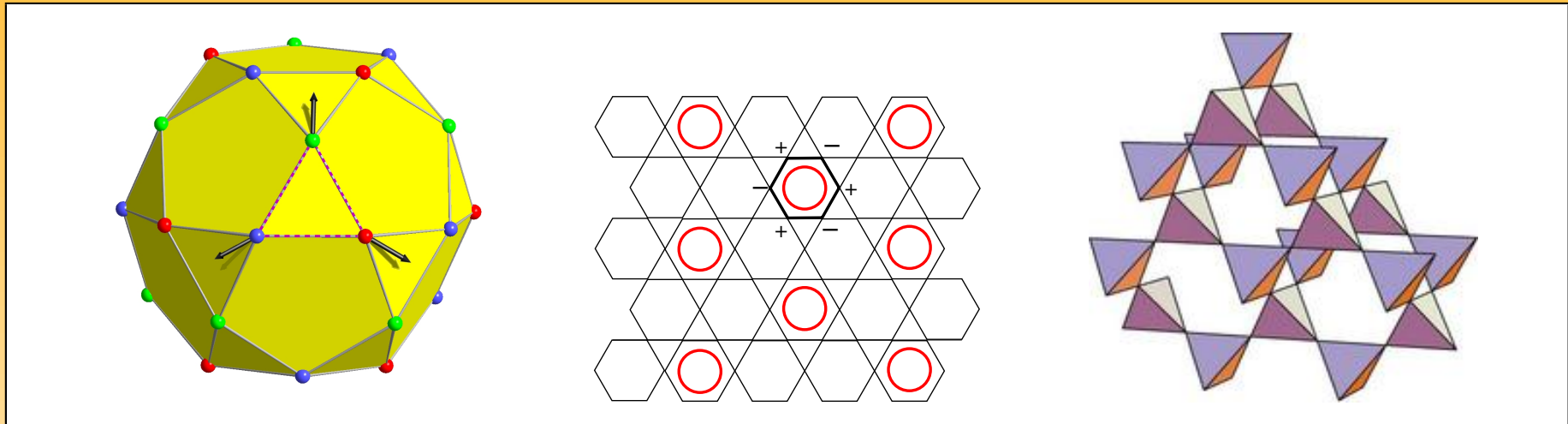


- Cuboctahedron: high cooling rate due to independent magnons;
- Ring: normal level crossing, normal jump;
- Icosahedron: unusual behavior due to edge-sharing triangles, many high degeneracies all over the spectrum; high cooling rate.

J. Schnack, R. Schmidt, J. Richter, Phys. Rev. B **76**, 054413 (2007)

Magnetocaloric effect VI

Connection to magnetization jumps



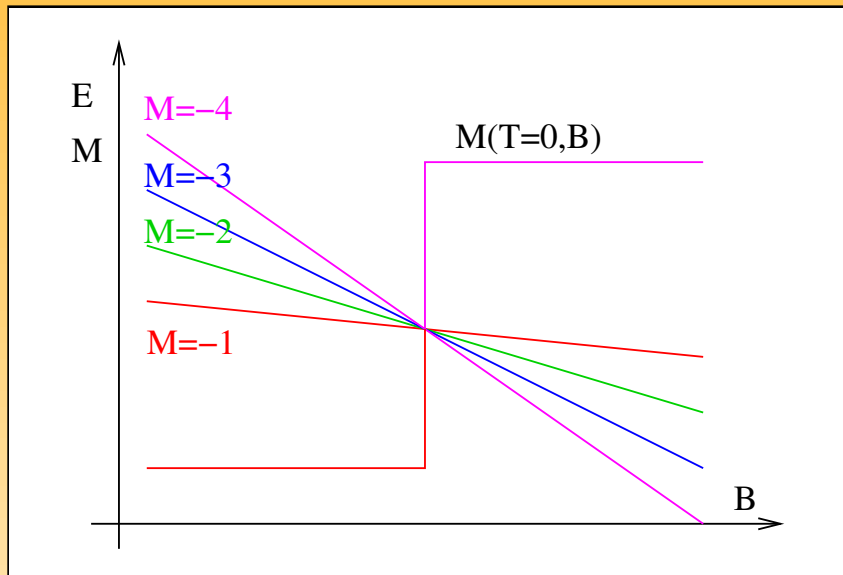
- Several frustrated antiferromagnets show an unusual behavior at the saturation field (1,2). AF = $\uparrow\downarrow$, saturation = $\uparrow\uparrow\uparrow\uparrow \dots$
- Example systems: icosidodecahedron, kagome lattice, pyrochlore lattice.

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

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

Magnetocaloric effect VII

Giant jumps to saturation



- Many Zeeman levels cross at one and the same magnetic field.
- High degeneracy of ground state levels \Rightarrow large residual entropy at $T = 0$.
- In addition giant magnetization jump to saturation.

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

A. Honecker, J. Richter, Condensed Matter Physics **8**, 813 (2005)

H.-J. Schmidt, Johannes Richter, Roderich Moessner, J. Phys. A: Math. Gen. **39**, 10673 (2006)

O. Derzhko, J. Richter, A. Honecker, H.-J. Schmidt, Low Temp. Phys. **33**, 745 (2007)

I hope I could show you, that

There are interesting known knowns!

Models, Frustration, Magnetocalorics,

...

I hope I could show you, that

There are interesting known unknowns!

edge-sharing triangle-systems, . . .

And I hope, that

**There are many more
unknown unknowns!**

The end is not in sight, . . .

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

Thank you very much for your attention.

German Molecular Magnetism Web

www.molmag.de

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