Enhanced magnetocaloric effect in strongly frustrated magnetic molecules

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JEMS, Dresden, September 2004

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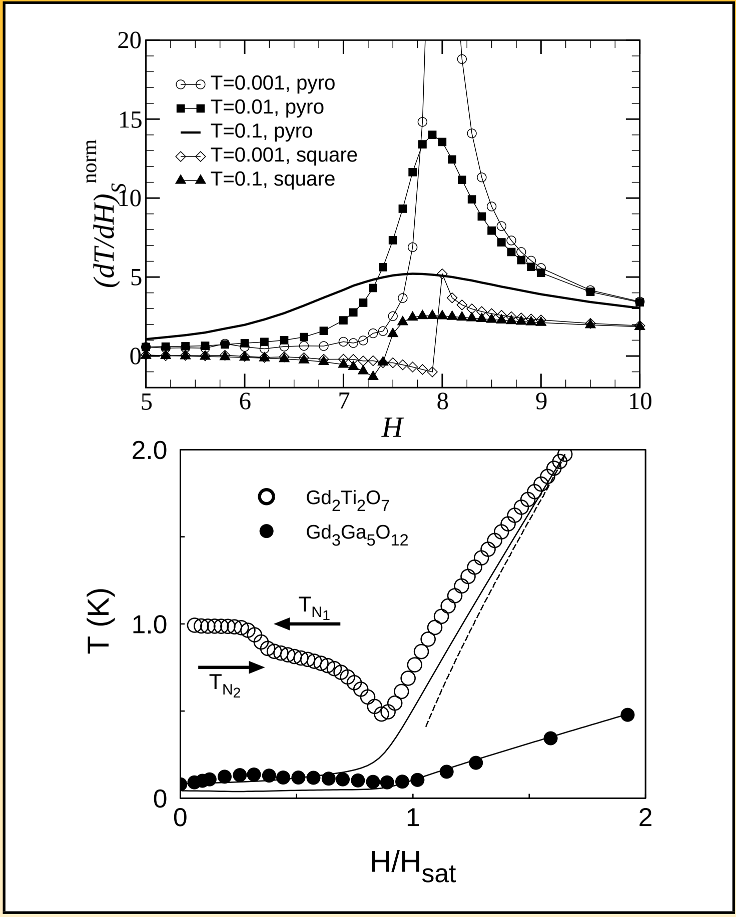
The Magnetocaloric Effect

- 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 e.g. in $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leq 0.5$).
- 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 [Karl A. Gschneidner, Jr., Ames Lab].

YES!

We investigate the magnetocaloric effect in antiferromagnets!

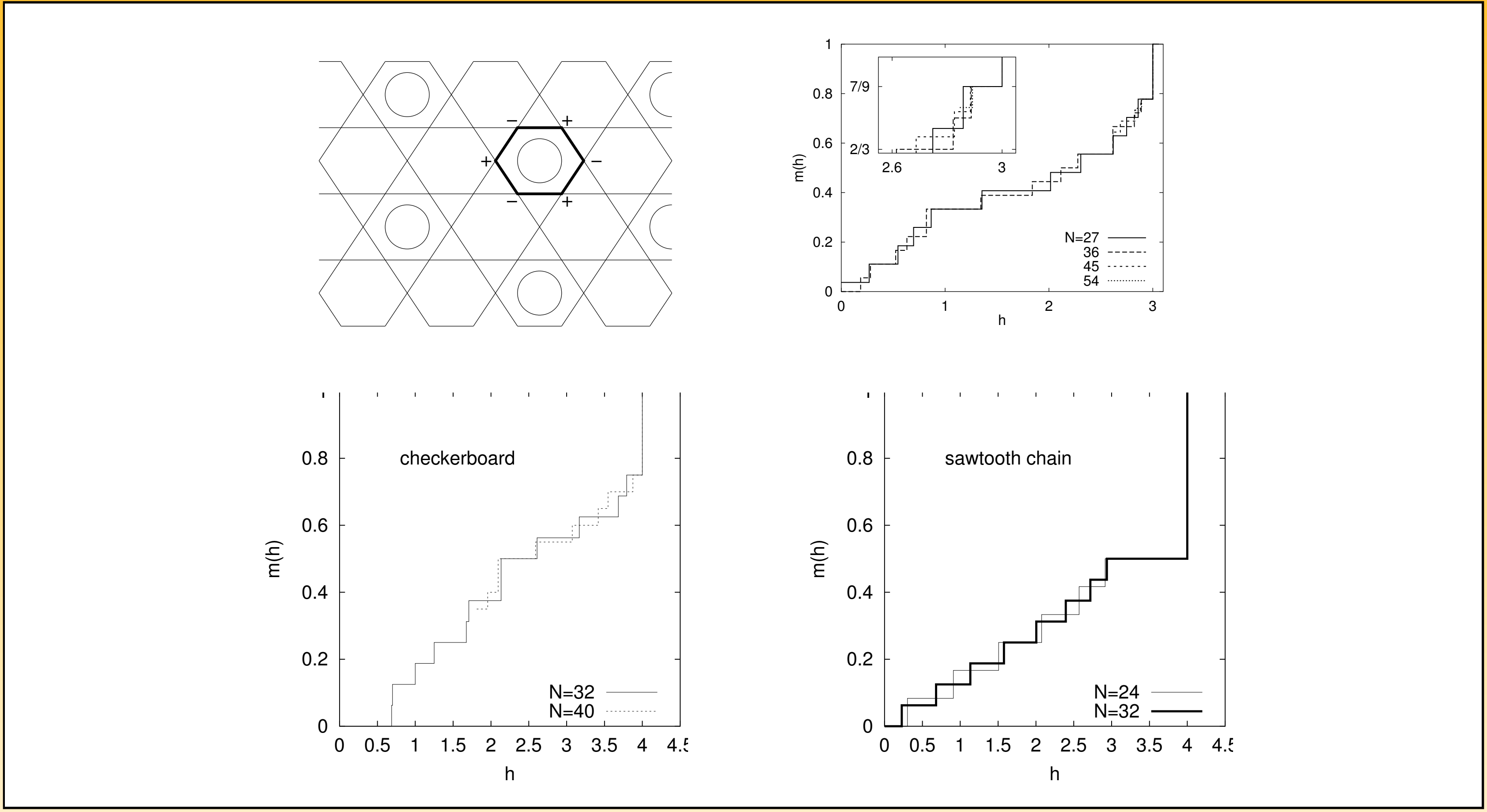
Enhanced magnetocaloric effect in frustrated magnets



- Magnetocaloric effect especially effective in frustrated classical spin systems like kagome, garnet, and pyrochlore (1);
- Upper figure: normalized cooling rate of pyrochlore and square lattice (1);
- Lower figure: enhanced magnetocaloric effect in pyrochlore antiferromagnet $Gd_2Ti_2O_7$ compared to $Gd_3Ga_5O_{12}$ (Gd-Ga-ganet), a standard material for low temperature magnetic cooling (2).

(1) M. E. Zhitomirsky, *Enhanced magnetocaloric effect in frustrated magnets*, Phys. Rev. B **67**, 104421 (2003)
(2) S. S. Sosin, L. A. Prozorova, A. I. Smirnov, A. I. Golov, I. B. Berkutov, O. A. Petrenko, G. Balakrishnan, M. E. Zhitomirsky, *Magnetocaloric effect in pyrochlore antiferromagnet $Gd_2Ti_2O_7$*, cond-mat/0404529

Independend magnons and magnetization jump



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

MCE especially large

- because of condensation of a macroscopic number of soft modes (1)
- because of condensation of independent magnons (2)
- close to quantum critical point (3)
- close to Zeeman ground state level crossings (QPT),
  well accessible in magnetic molecules (Schnack, 2)

⇒ Simple af $s = 1/2$ dimer explains effect sufficiently well.

(1) M. E. Zhitomirsky, Phys. Rev. B **67**, 104421 (2003)
(2) O. Derzhko, J. Richter, cond-mat/0404204;
M. Zhitomirsky, A. Honecker, J. Stat. Mech.: Theor. Exp. (2004) P07012;
J. Schulenburg, A. Honecker, J. Schnack, J. Richter, H.-J. Schmidt, Phys. Rev. Lett. **88** (2002) 167207
(3) L. Zhu, M. Garst, A. Rosch, Q. Si, Phys. Rev. Lett. **91**, 066404 (2003)

Adiabatic temperature change

Model Hamiltonian

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

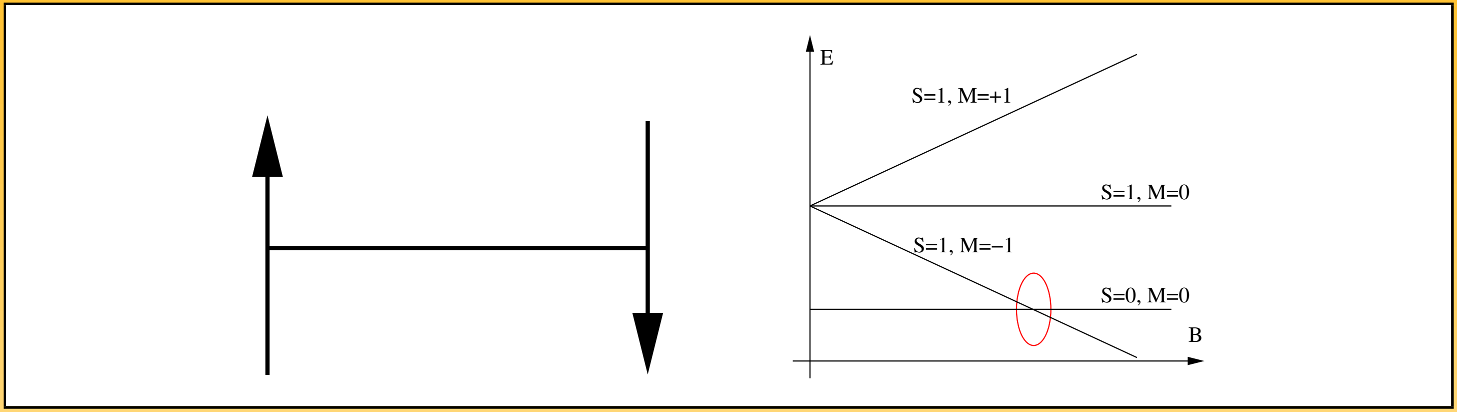
Heisenberg Zeeman

Adiabatic temperature change (absolute & relative to ideal paramagnet)

$$\left(\frac{\partial T}{\partial B}\right)_S = -T\frac{\left(\frac{\partial S}{\partial B}\right)_T}{C} \quad , \quad \frac{\left(\frac{\partial T}{\partial B}\right)_S}{\left(\frac{\partial T}{\partial B}\right)_S^{\text{para}}} = -B\frac{\left(\frac{\partial S}{\partial B}\right)_T}{C}$$

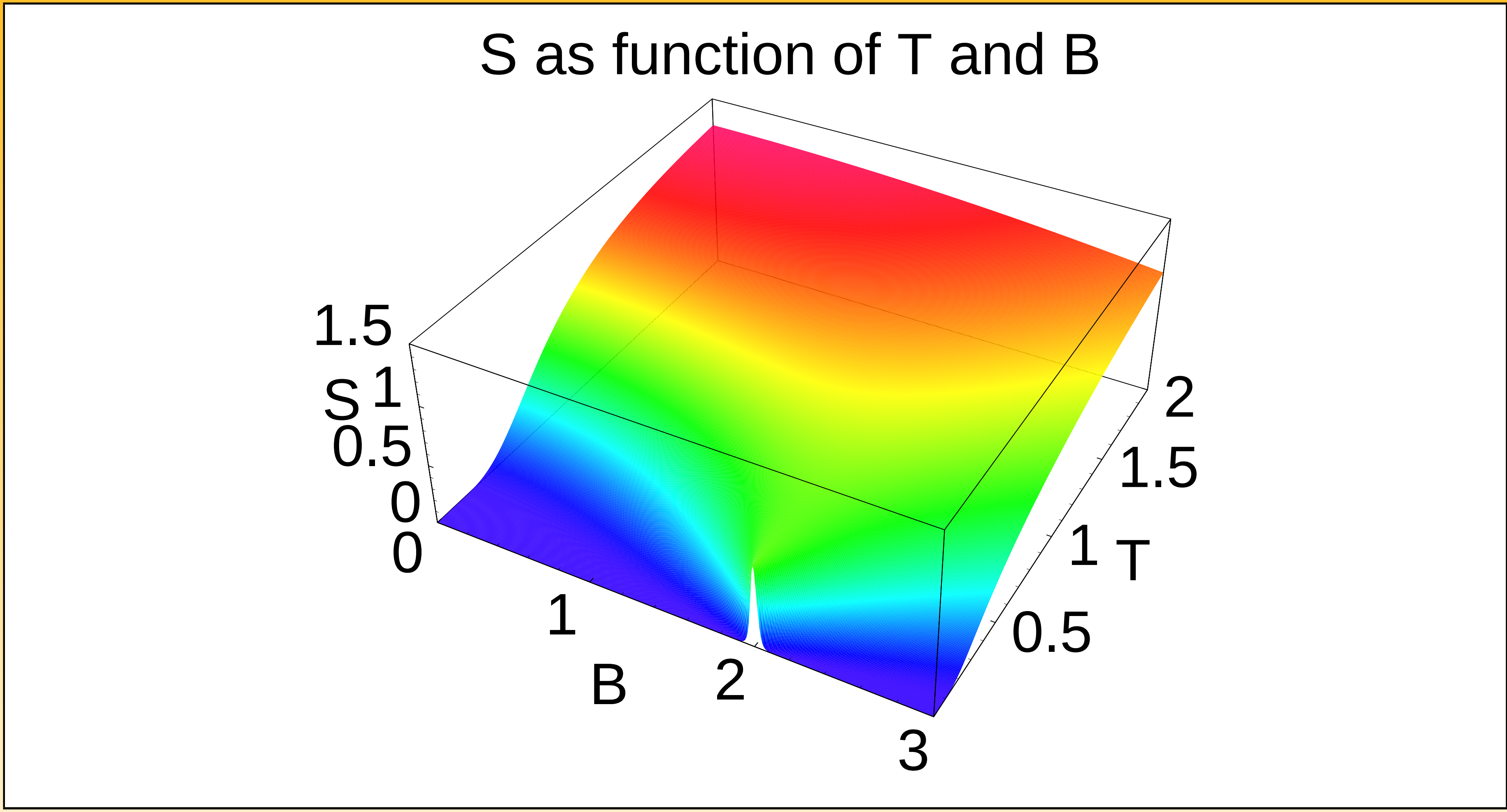
All thermodynamic functions depend on T and B in the following, i. e. $S(T, B), C(T, B), M(T, B)$.

Simple af $s = 1/2$ dimer I



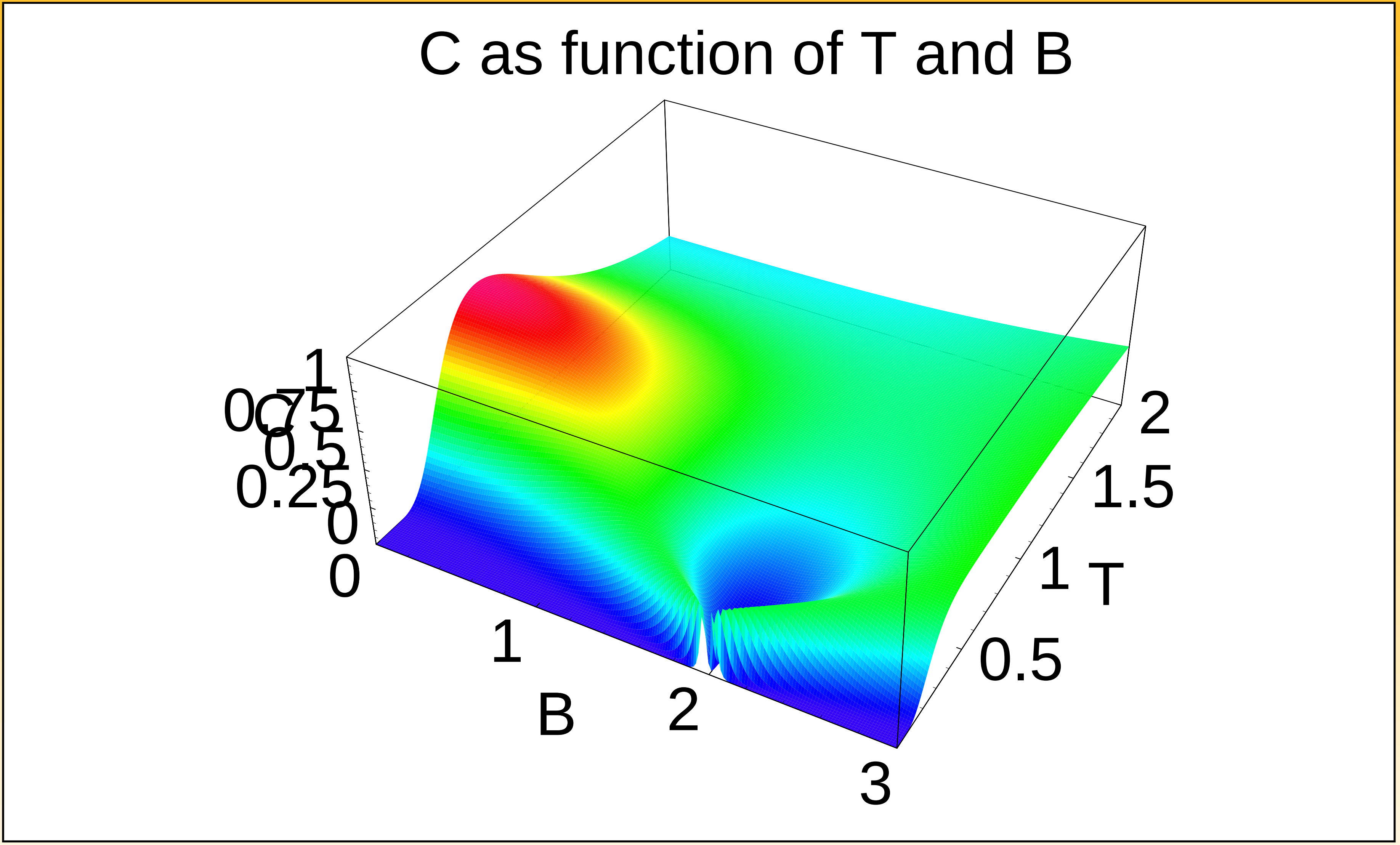
- Singlet-triplet level crossing causes a “quantum phase transition” at $T = 0$ as a function of B.
- $M(T = 0, B)$ and $S(T = 0, B)$ not analytic as function of B.
- $C(T, B)$ varies strongly as function of B for low T.

Dimer II – entropy

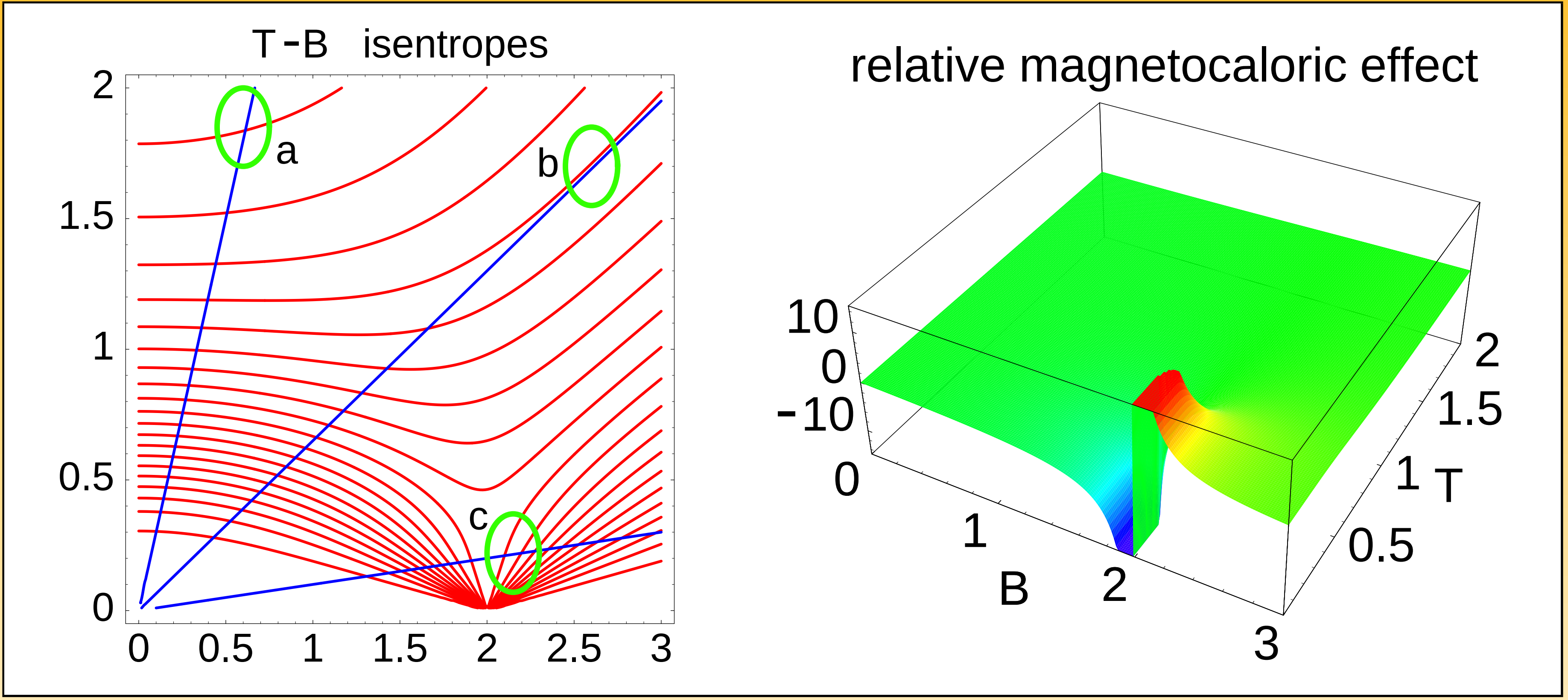


$S(T=0,B) \neq 0$ at level crossing due to degeneracy, see also
O. Derzhko, J. Richter, Phys. Rev. B accepted, cond-mat/0404204

Dimer III – heat capacity

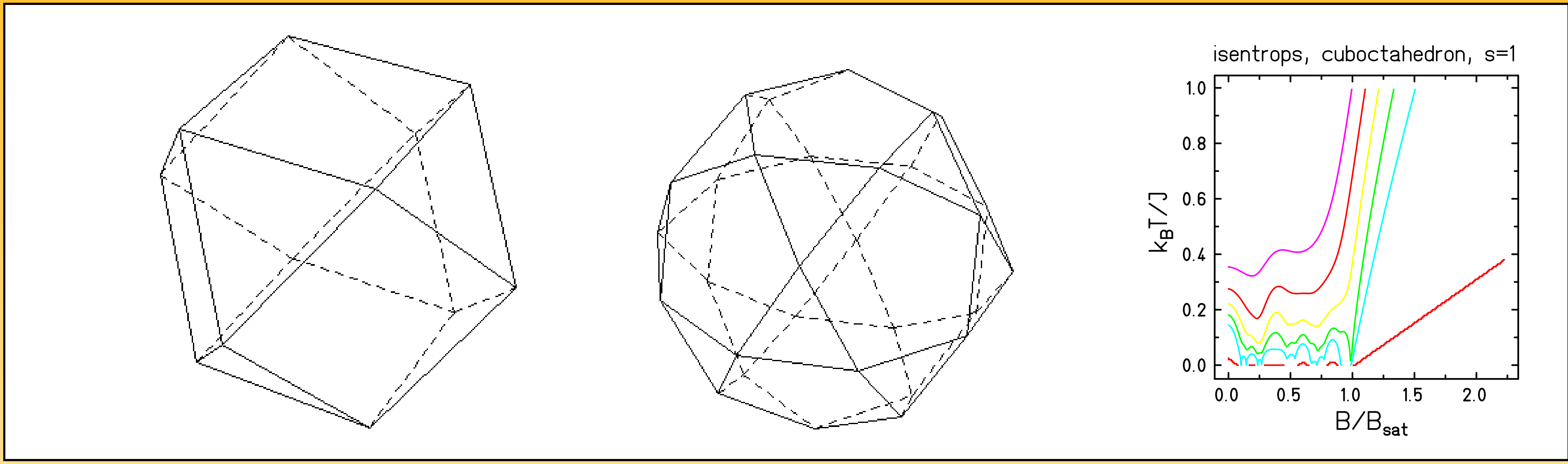


Simple af $s = 1/2$ dimer IV



Magnetocaloric effect: reduced (a), the same (b), enhanced (c) when compared to an ideal paramagnet.

Molecules exhibiting jumps to saturation

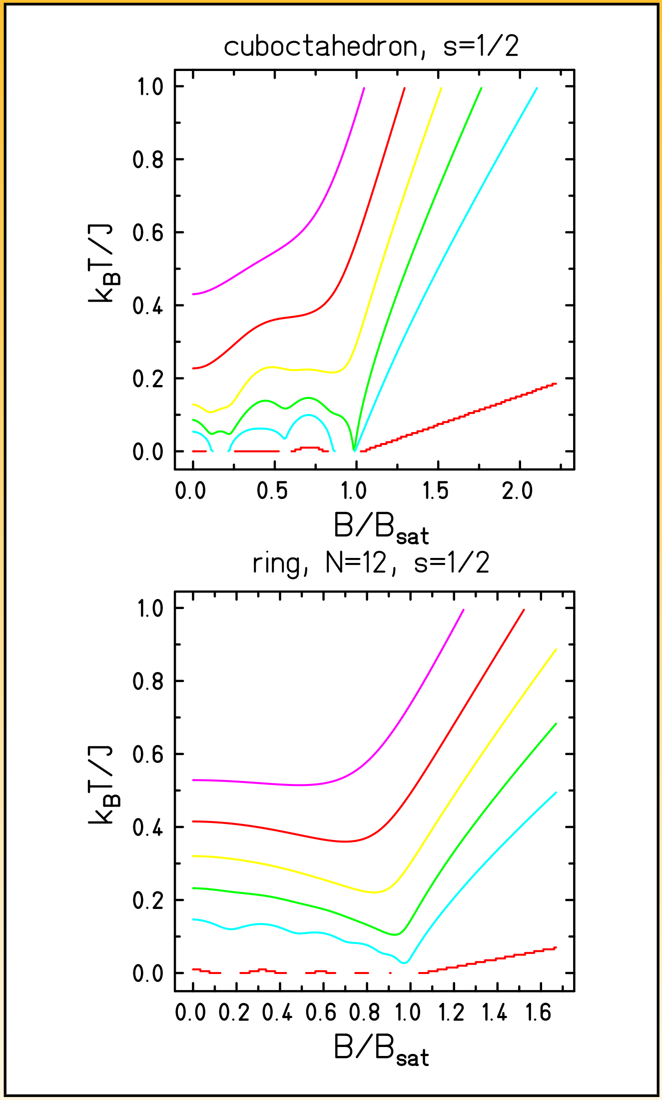


- Molecules with the structure of a cuboctahedron or icosidodecahedron exhibit magnetization jumps to saturation of $\Delta M = 2$ and $\Delta M = 3$, respectively. Chemical realization: cuboctahedron (1) and icosidodecahedron (2)

- Enhanced cooling rate at the saturation field.

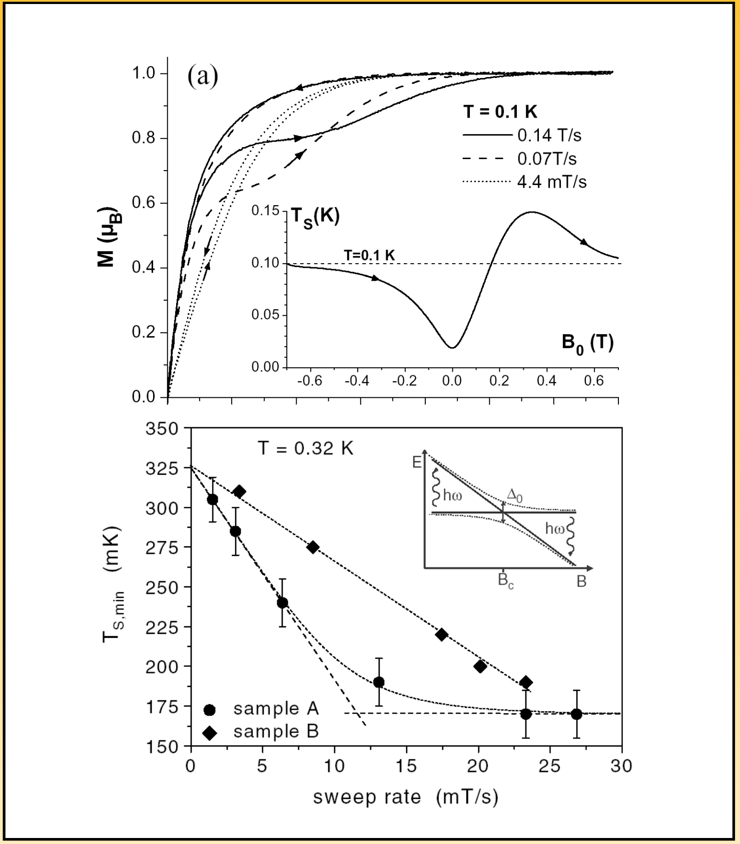
(1) A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, S. Parsons, R. E. P. Winpenny, J. Chem. Soc.-Dalton Trans. (1997) 485; (2) A. Müller *et al.*, Chem. Phys. Chem. **2** (2001) 517

Comparison of two molecules with $N = 12$ and $s = 1/2$



- 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.

MCE in connection with magnetization tunneling

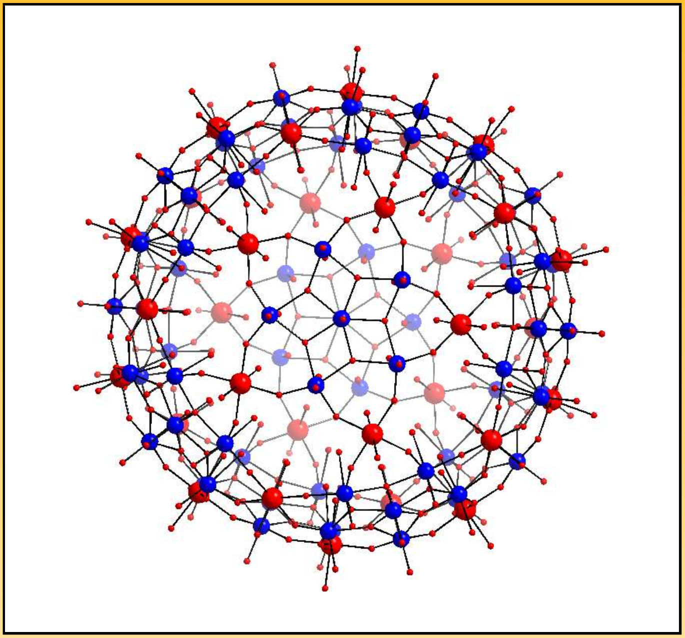


- Magnetization tunneling at (avoided) level crossings is one of the corner phenomena of molecular magnetism.
  Temperature of spin system varies with field sweep, compare e. g. upper figure and (1);

- Accessible temperature change strongly depends on available relaxation processes, i. e. phonons, phonon bottleneck etc. (1);
  Lower figure: dependence of temperature change on field sweep rate for Cr_8 molecular rings (2).

(1) I. Chiorescu, W. Wernsdorfer, A. Müller,H. Bögge, B. Barbara, *Butterfly hysteresis loop and dissipative spin reversal in the $S = 1/2$, V_{15} molecular complex*, Phys. Rev. Lett. **84** (2000) 3454
(2) O. Waldmann, R. Koch, S. Schromm, P. Müller, I. Bernt, R.W. Saalfrank, *Butterfly hysteresis loop at nonzero bias field in antiferromagnetic molecular rings: Cooling by adiabatic magnetization*, Phys. Rev. Lett. **89** (2002) 246401

Outlook



- Magnetic molecules provide a new class of materials where the magnetocaloric effect should be large and well-accessible.
- Magnetization jump in $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and similar frustrated molecules should give rise to an especially enhanced MCE.
- Even unfrustrated molecules show an enhanced MCE at ground state level crossings.

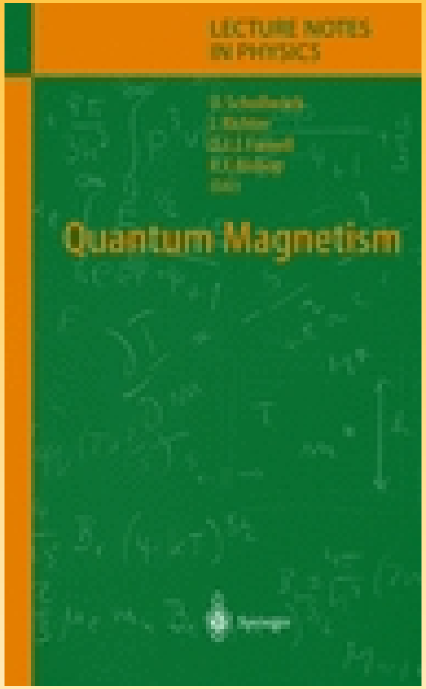
- Open problems: relaxation processes in substances built of magnetic molecules, heat conductance etc.

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);
- Prof. M. Luban, Dr. P. Kögerler, Dr. Chr. Schröder (Ames Lab, Iowa, USA);
- Prof. H. Nojiri (Tohoku University, Japan);
- Prof. R. Winpenny (Manchester), Dr. L. Cronin (Glasgow);
- Prof. B. Büchner, Dr. R. Klingeler (IFW Dresden);
- Prof. J. Richter, Dr. J. Schulenburg, R. Schmidt (Uni Magdeburg);
- Dr. A. Honecker (Uni Braunschweig); Prof. S. Blügel (FZ Jülich);

Buy now!



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

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