Enhanced magnetocaloric effect in strongly frustrated magnetic molecules

Jürgen Schnack, (University of Osnabrück)
Johannes Richter (University of Magdeburg)

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

JEMS, Dresden, September 2004
Contents

• The magnetocaloric effect (MCE)
• The enhanced magnetocaloric effect
• Independent magnons and magnetization jump
• Simple antiferromagnetic spin-$\frac{1}{2}$ dimer
• MCE in connection with magnetization tunneling
• Outlook
The Magnetocaloric Effect

- Discovered in pure iron by E. Warburg in 1881.
- Heating or cooling in a varying magnetic field.
- Typical rates: \(0.5 \ldots 2 \text{ K/T} \) (adiabatic temperature change).
- Giant magnetocaloric effect: \(3 \ldots 4 \text{ K/T} \) e.g. in \(\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4\) 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 $\text{Gd}_2\text{Ti}_2\text{O}_7$ compared to $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (Gd-Ga-ganet), a standard material for low temperature magnetic cooling (2).

Independend magnons and magnetization jump

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.

(2) O. Derzhko, J. Richter, cond-mat/0404204;
Adiabatic temperature change

Model Hamiltonian

\[
\hat{H} = - \sum_{i,j} J_{ij} \vec{s}(i) \cdot \vec{s}(j) + g \mu_B B \sum_{i} \vec{s}_z(i)
\]

Heisenberg  
Zeeman

Adiabatic temperature change (absolute & relative to ideal paramagnet)

\[
\left( \frac{\partial T}{\partial B} \right)_S = -T \frac{\partial S}{\partial B} \frac{T}{C}, \quad \left( \frac{\partial T}{\partial B} \right)_{\text{para}} S = -B \frac{\partial S}{\partial B} \frac{T}{C}
\]

All thermodynamic functions depend on \(T\) and \(B\) in the following, i. e.

\(S(T, B), C(T, B), M(T, B)\).
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 as function of T and B

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

C as function of T and B
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.

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).


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);
**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

Mikeska, Kolezhuk, *One-dimensional magnetism*
Richter, Schulenburg, Honecker, *Q. Mag. in 2-D*
Schnack, *Molecular Magnetism*
Ivanov, Sen, *Spin Wave Analysis*
Laflorencie, 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*