Magnetocaloric properties of gadolinium based magnetic molecules studied by the Finite Temperature Lanczos Method

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The magnetocaloric effect

Magnetocaloric effect – Basics

- Heating or cooling in a varying magnetic field. Discovered in pure iron by Emil Warburg in 1881.
- Typical rates: $0.5 \ldots 2$ K/T.
- Giant magnetocaloric effect: $3 \ldots 4$ K/T e.g. in $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leq 0.5$).
- Scientific goal I: room temperature applications.
- Scientific goal II: sub-Kelvin cooling.

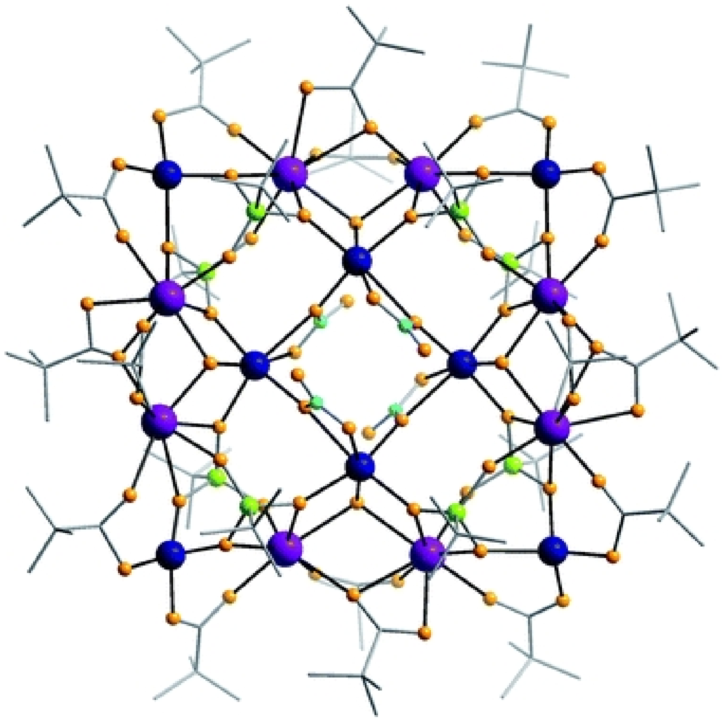
Magnetocaloric effect – cooling rate

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C}\left(\frac{\partial S}{\partial B}\right)_T$$

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)

Contents for you today

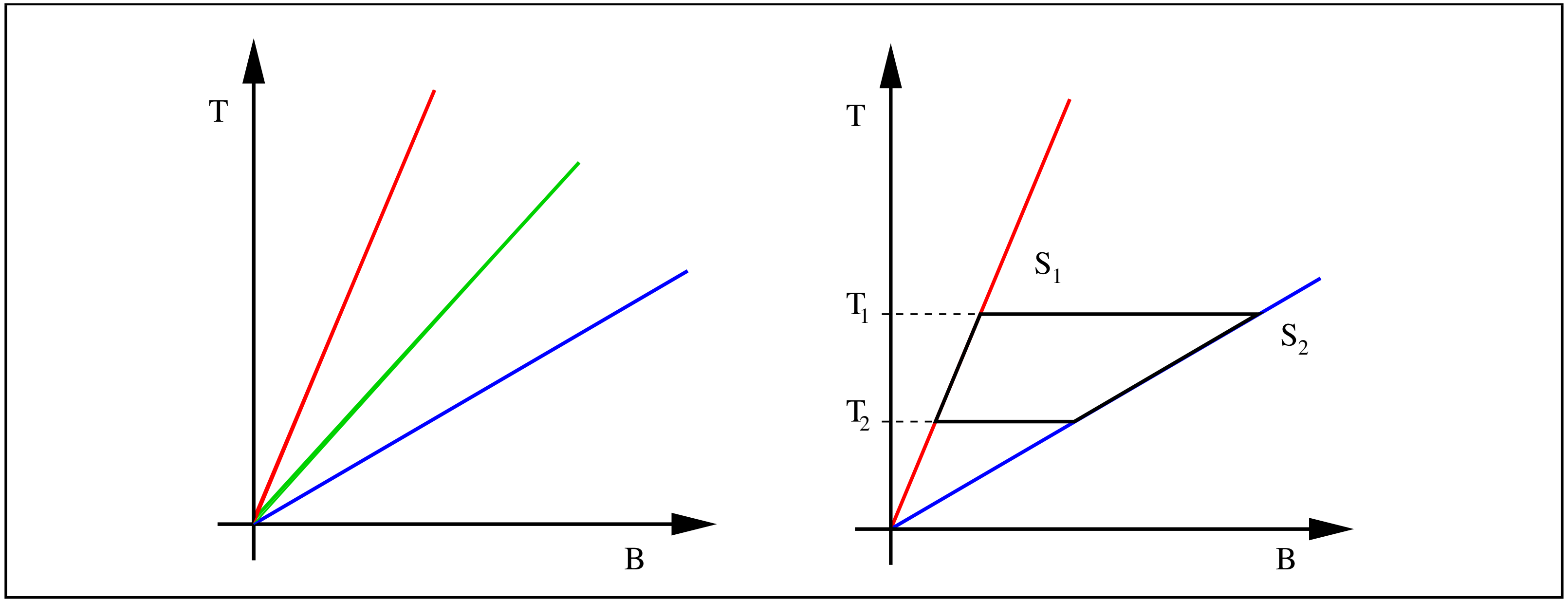


Gd_8Co_8

1. Introduction $\surd$
2. Warmup I: paramagnets
3. Warmup II: AF dimer
4. Modelling of Gd containing molecules
5. Finite-temperature Lanczos
6. Example: Gd_4M8
7. Weird ideas about dipolar interactions

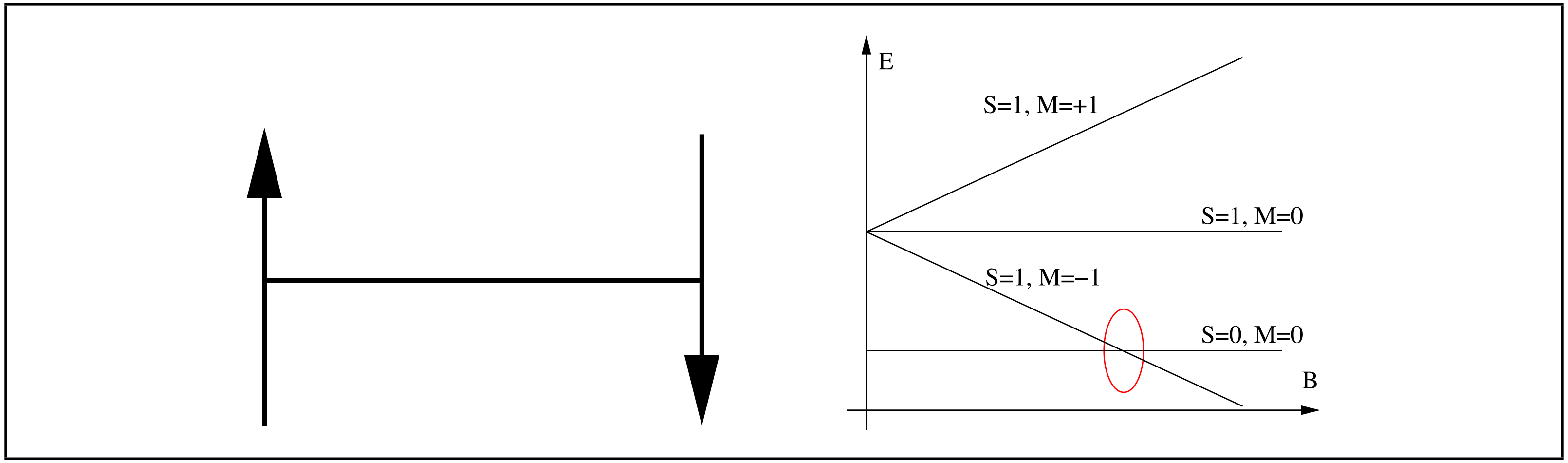
Warmup

Magnetocaloric effect – Paramagnets



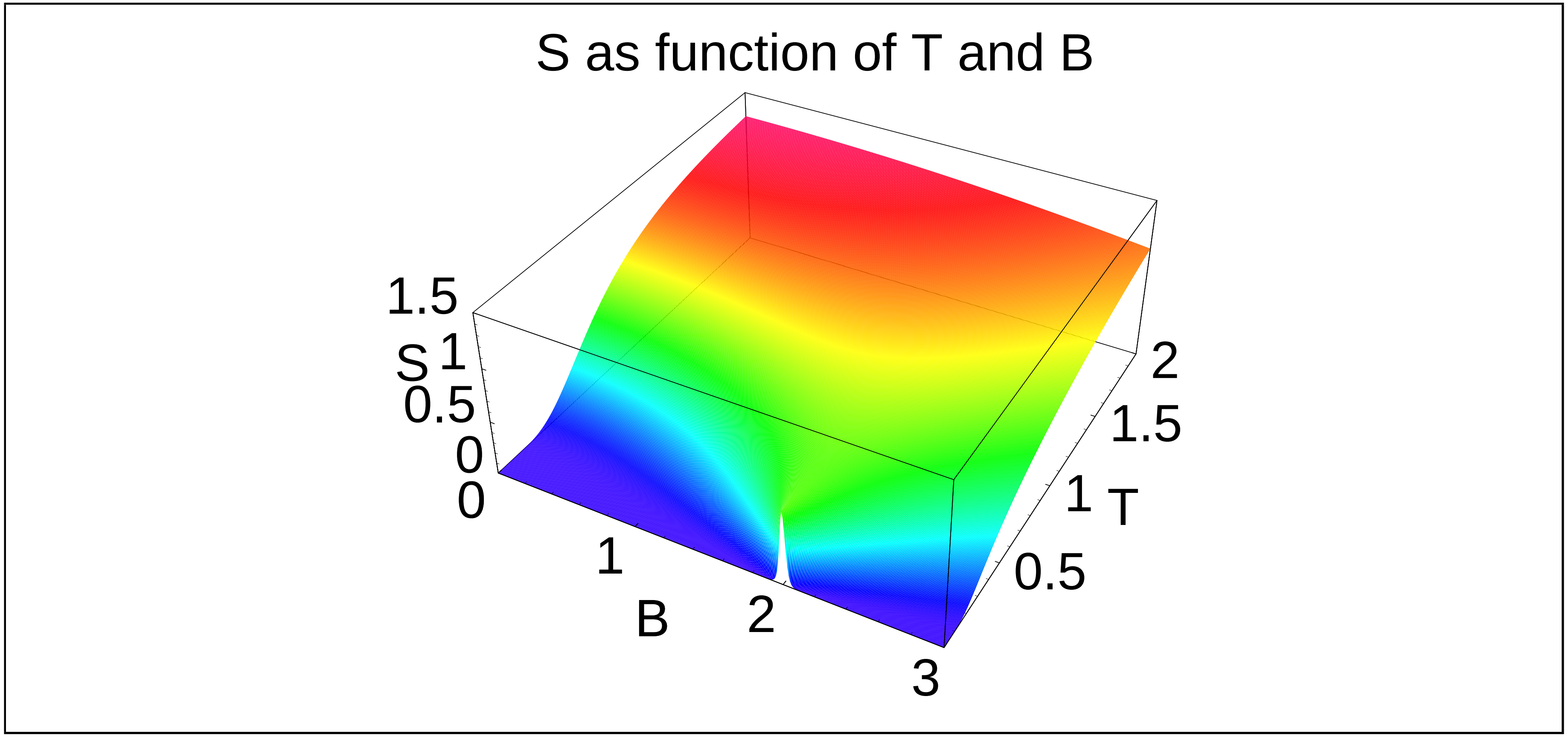
- Ideal paramagnet: $S(T, B) = f(B/T)$, i.e. $S = const \Rightarrow T \propto B$.
- At low T pronounced effects of dipolar interaction prevent further effective cooling.

Magnetocaloric effect – af $s = 1/2$ dimer



- Singlet-triplet level crossing causes a peak of S at $T \approx 0$ as 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; $\quad S(T = 0, B_c) = k_B \ln 2$, otherwise zero.

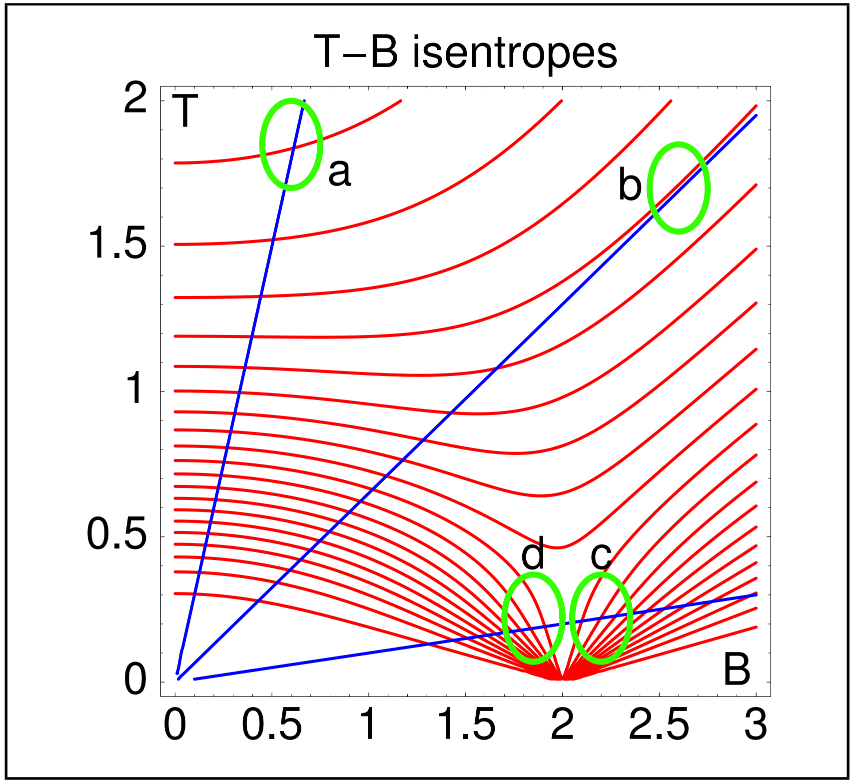
Magnetocaloric effect – af $s = 1/2$ dimer



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

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

Magnetocaloric effect – af $s = 1/2$ dimer



blue lines: ideal paramagnet, red curves: af dimer

Magnetocaloric effect:

(a) reduced,

(b) the same,

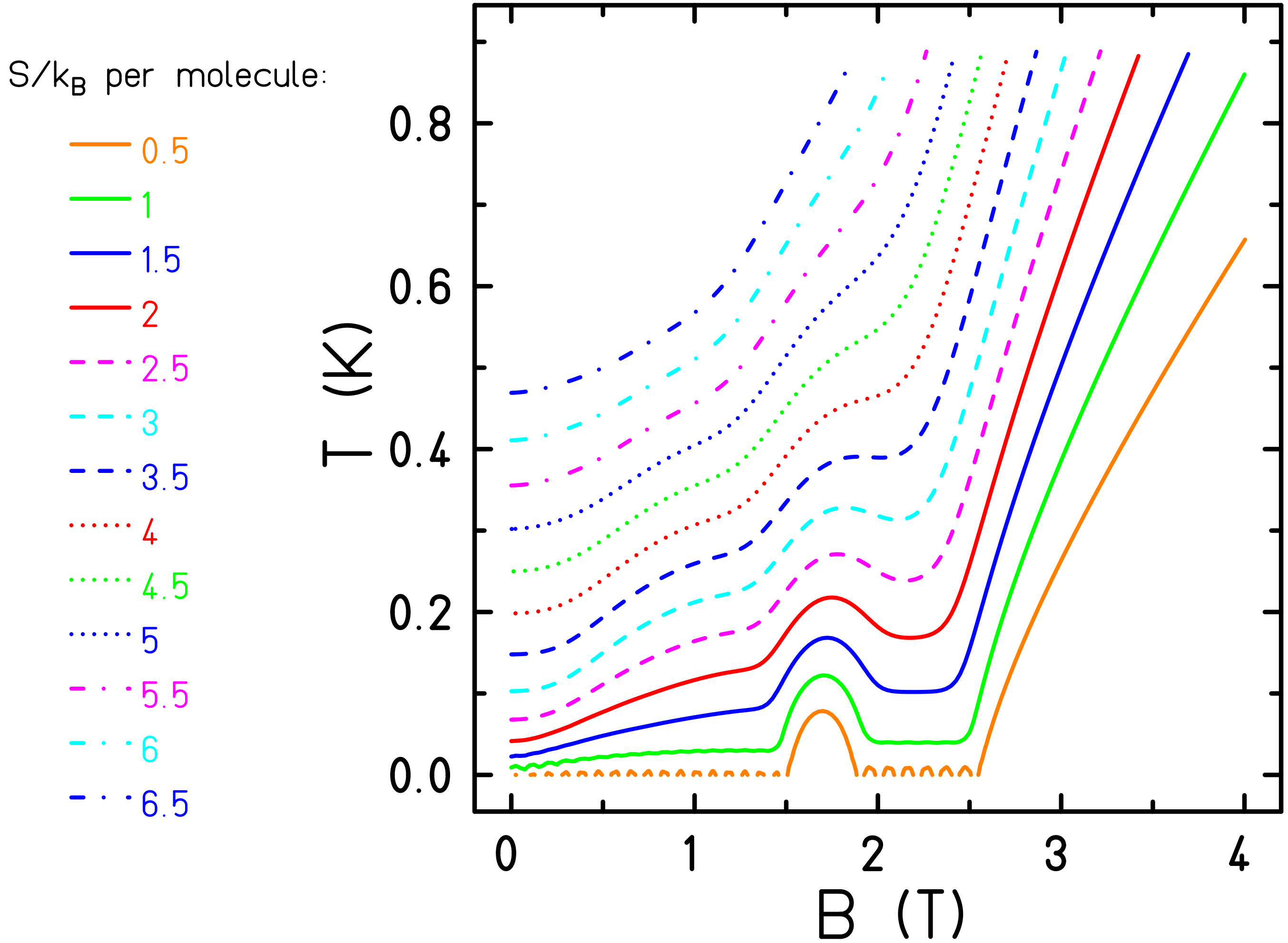
(c) enhanced,

(d) opposite

when compared to an ideal paramagnet.

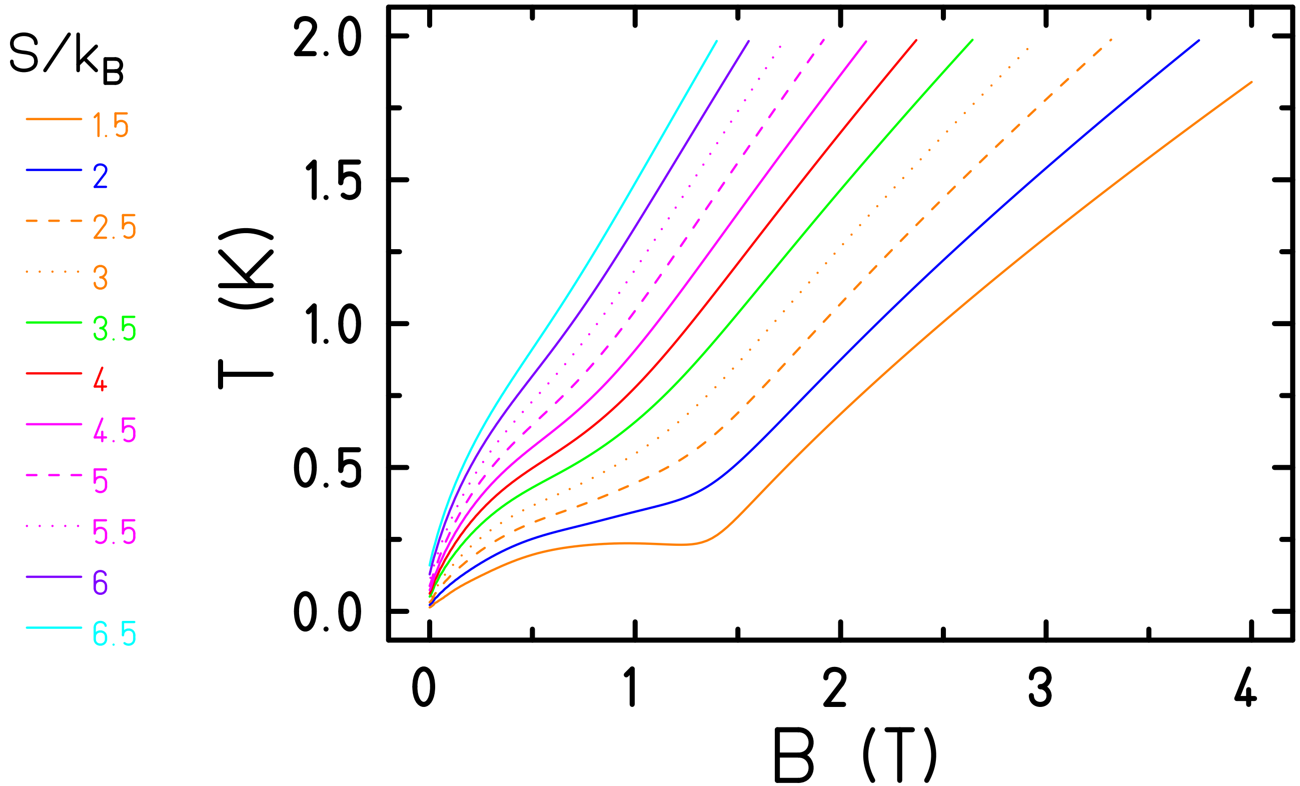
Case (d) does not occur for a paramagnet.

Typical isentropes for af spin system



Level crossings signal antiferromagnetic interactions.

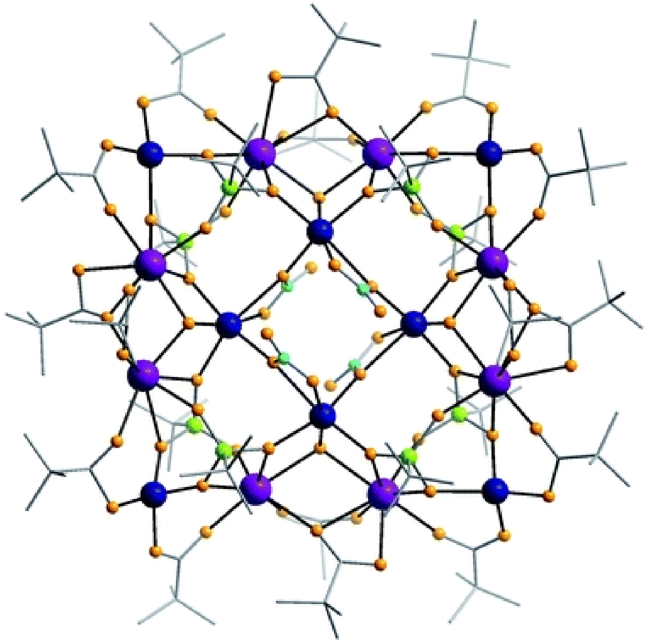
Typical isentropes for high-spin system



Typical for high-spin ground state. Cooling rate depends on T and B.

Modelling of Gd containing molecules

Magnetocaloric effect – Why Gd compounds?



- High spin of $s = 7/2$;
- Weak exchange $\Rightarrow$ high density of states;
- Can vary the entropy with moderate fields.
- But large Hilbert spaces!
  Complete diagonalization impossible.

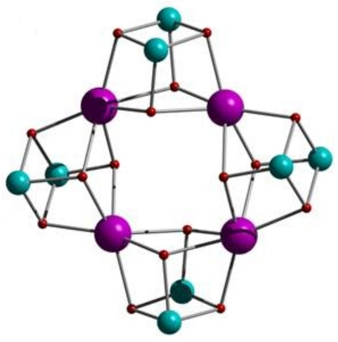
Yan-Zhen Zheng, Marco Evangelisti, Richard E. P. Winpenny, Chem. Sci. **2**, 99-102 (2011)

Model Hamiltonian

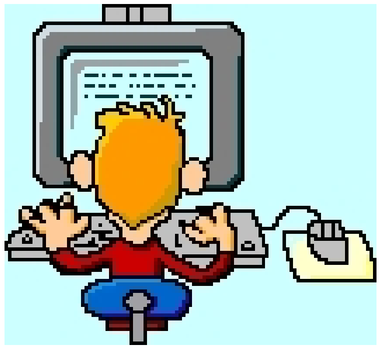
$$\underset{\sim}{H} = -2 \sum_{i<j} J_{ij}\, \underset{\sim}{\vec{s}}(i) \cdot \underset{\sim}{\vec{s}}(j) \quad + \quad g\, \mu_B\, B \sum_{i}^{N} \underset{\sim}{s}_z(i)$$

Heisenberg   Zeeman

In the end it's always a big matrix!



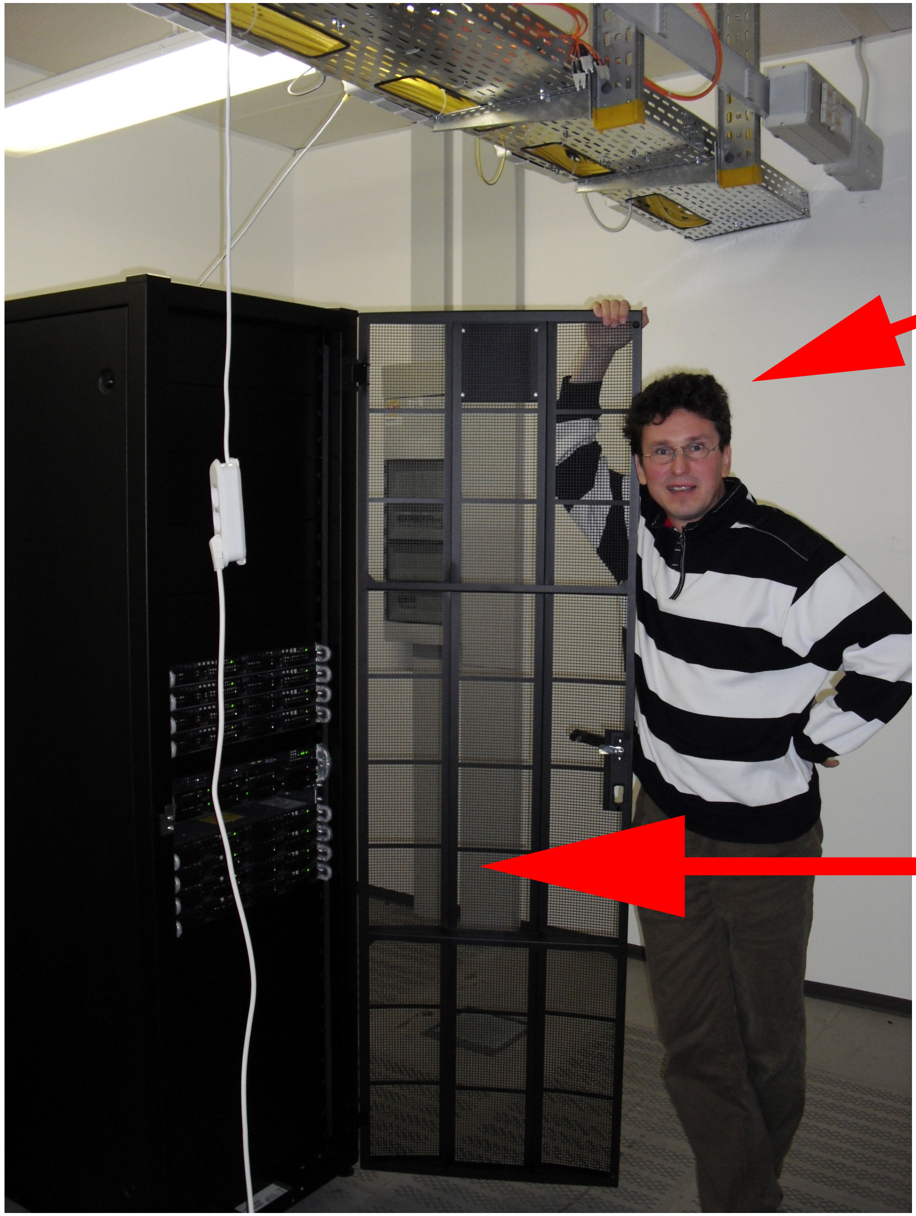
$$\Rightarrow \begin{pmatrix} -27.8 & 3.46 & 0.18 & \cdots \\ 3.46 & -2.35 & -1.7 & \cdots \\ 0.18 & -1.7 & 5.64 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \Rightarrow$$



Gd_4Ni_8: $4 \times s = 7/2$, $8 \times s = 1$

Dimension=26,873,856. Maybe too big?

Thank God, we have computers



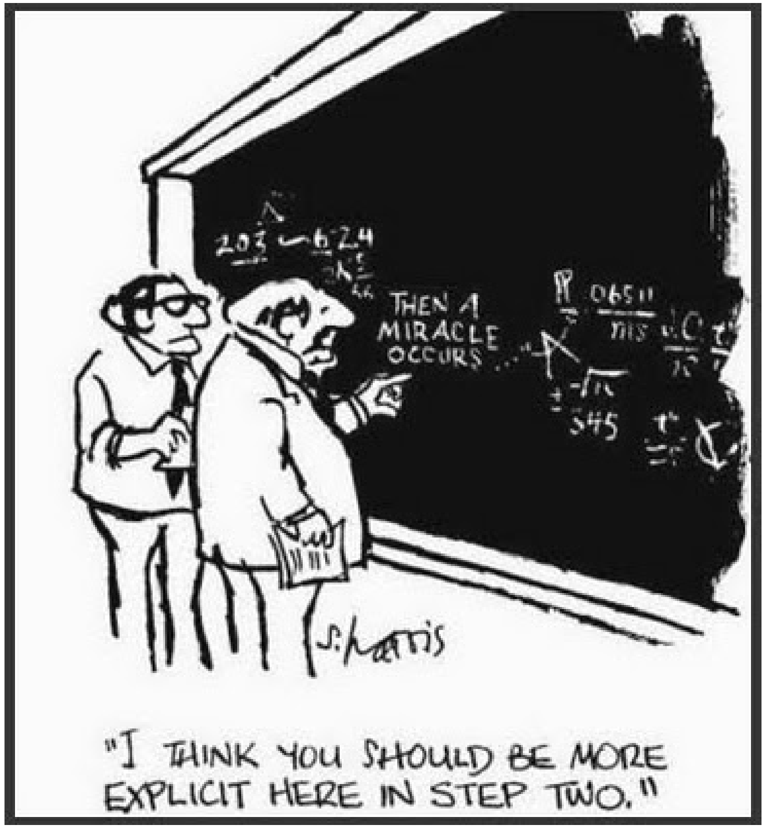
"Espresso-doped multi-core"

128 cores, 384 GB RAM

. . . but that's not enough!

Finite-temperature Lanczos Method

Finite-temperature Lanczos Method



Finite-temperature Lanczos Method I

$$Z(T,B) = \sum_\nu \langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} |\, \nu \,\rangle$$

$$\langle\, \nu \,|\, \exp\left\{-\beta \underset{\sim}{H}\right\} |\, \nu \,\rangle \approx \sum_n \langle\, \nu \,|\, n(\nu) \,\rangle \exp\left\{-\beta\epsilon_n\right\} \langle\, n(\nu) \,|\, \nu \,\rangle \qquad \text{(Step 2)}$$

$$Z(T,B) \approx \frac{\text{dim}(\mathcal{H})}{R} \sum_{\nu=1}^{R} \sum_{n=1}^{N_L} \exp\left\{-\beta\epsilon_n\right\} |\langle\, n(\nu) \,|\, \nu \,\rangle|^2$$

- $|\, n(\nu) \,\rangle$ n-th Lanczos eigenvector starting from $|\, \nu \,\rangle$
- Partition function replaced by a small sum: $R = 1 \ldots 10, N_L \approx 100$.

J. Jaklic and P. Prelovsek, Phys. Rev. B **49**, 5065 (1994).

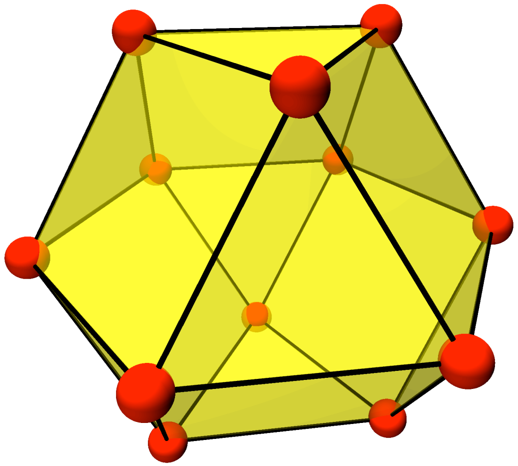
Finite-temperature Lanczos Method II

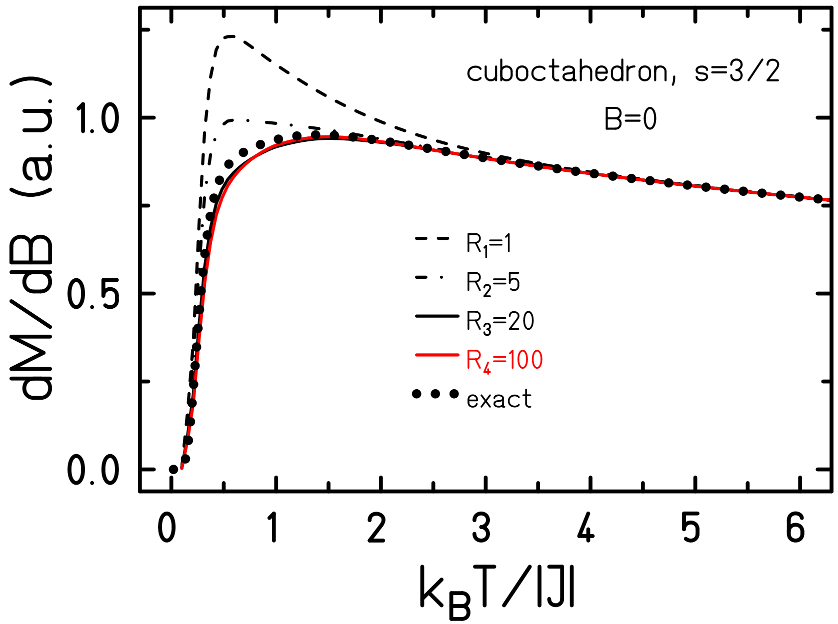
$$Z(T,B) \approx \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} \exp\{-\beta\epsilon_n\} \, |\langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma\,\rangle|^2$$

- Approximation better if symmetries taken into account.
- Γ denotes the used irreducible representations.

J. Schnack and O. Wendland, Eur. Phys. J. B **78** (2010) 535-541

How good is finite-temperature Lanczos?

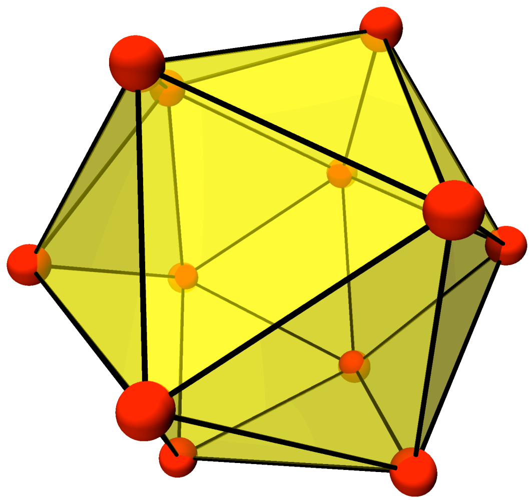


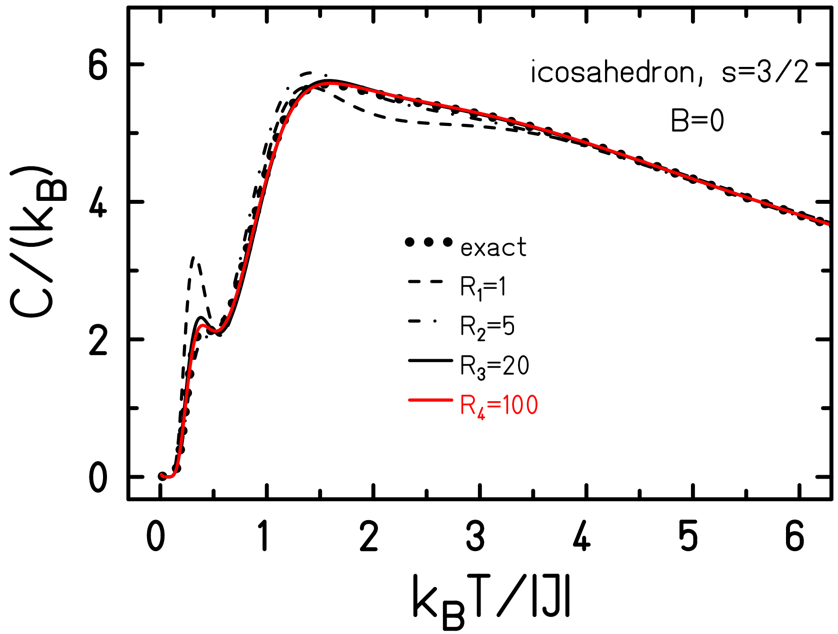


- Works very well: compare frustrated cuboctahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

How good is finite-temperature Lanczos?

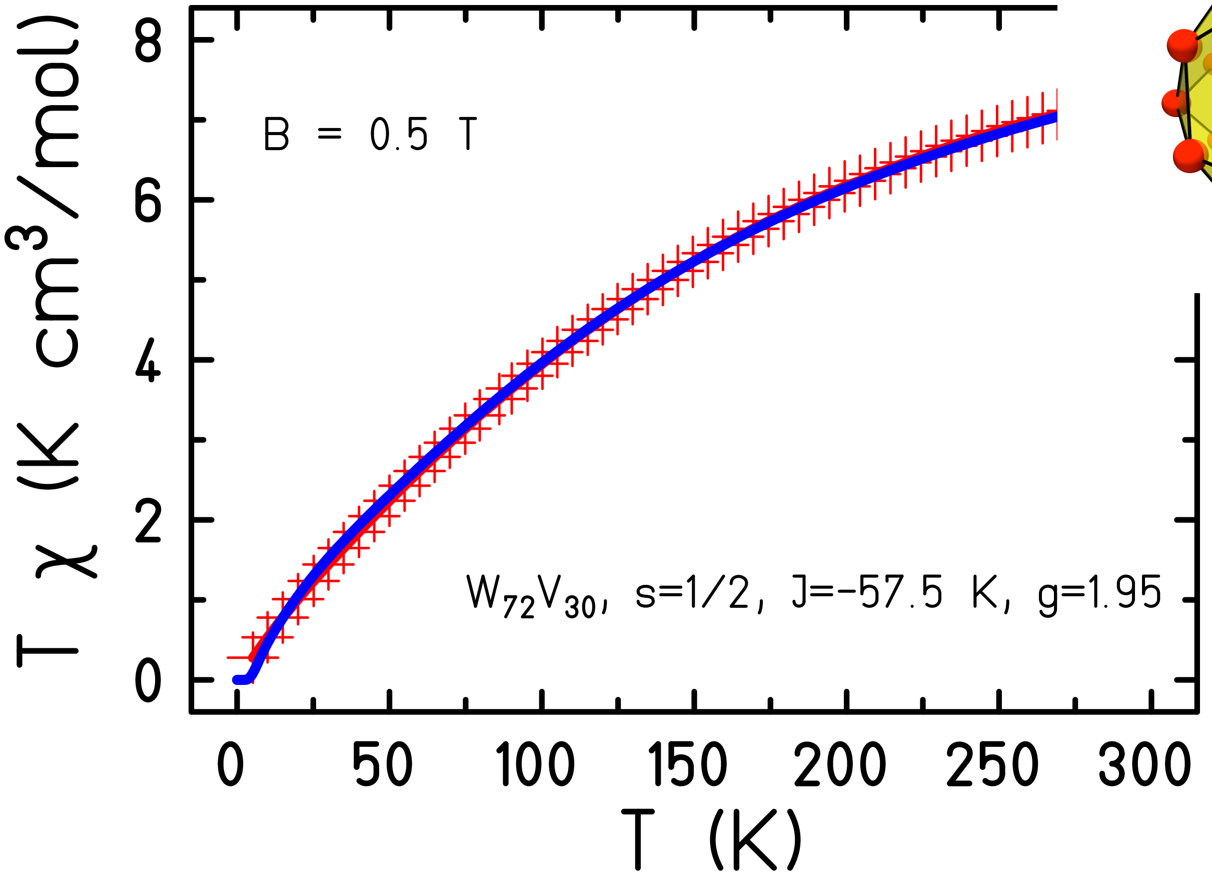


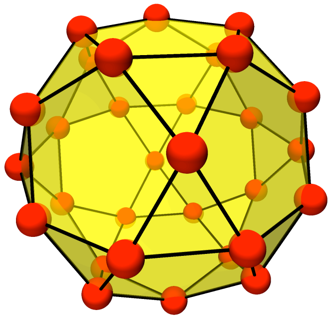


- Works very well: compare frustrated icosahedron.
- $N = 12, s = 3/2$: Considered $< 100,000$ states instead of 16,777,216.

Exact results: R. Schnalle and J. Schnack, Int. Rev. Phys. Chem. **29**, 403-452 (2010).
FTLM: J. Schnack and O. Wendland, Eur. Phys. J. B **78**, 535-541 (2010).

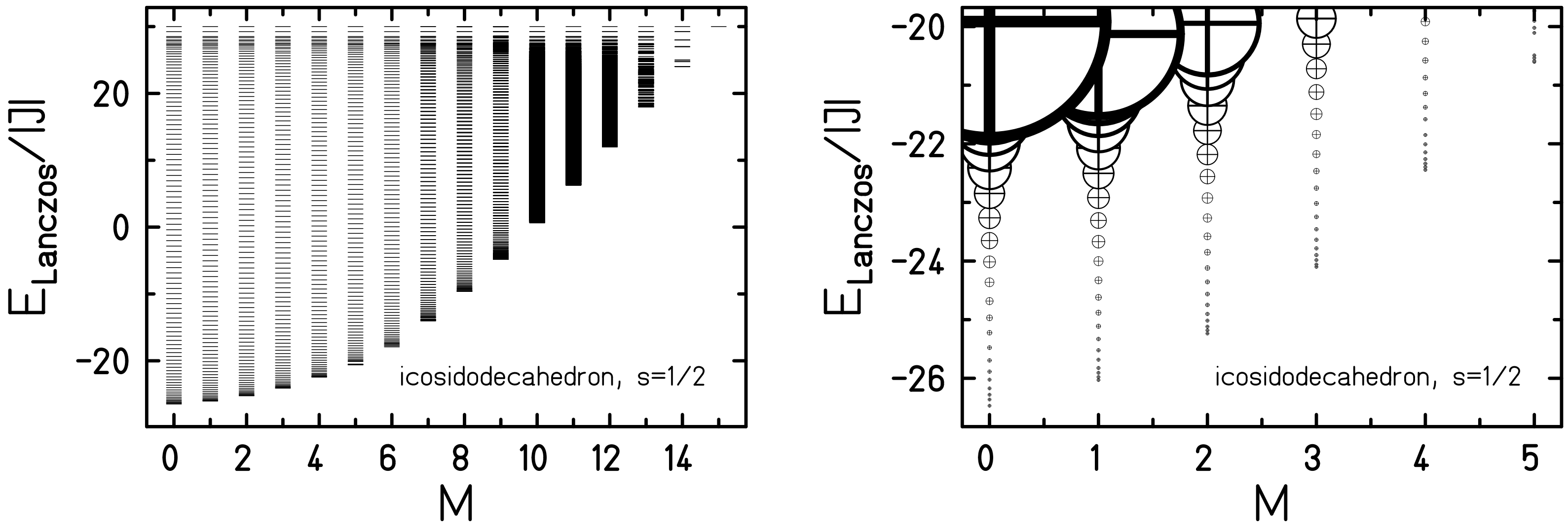
Icosidodecahedron $s = 1/2$





Exp. data: A. M. Todea, A. Merca, H. Bögge, T. Glaser, L. Engelhardt, R. Prozorov, M. Luban, A. Müller, Chem. Commun., 3351 (2009).

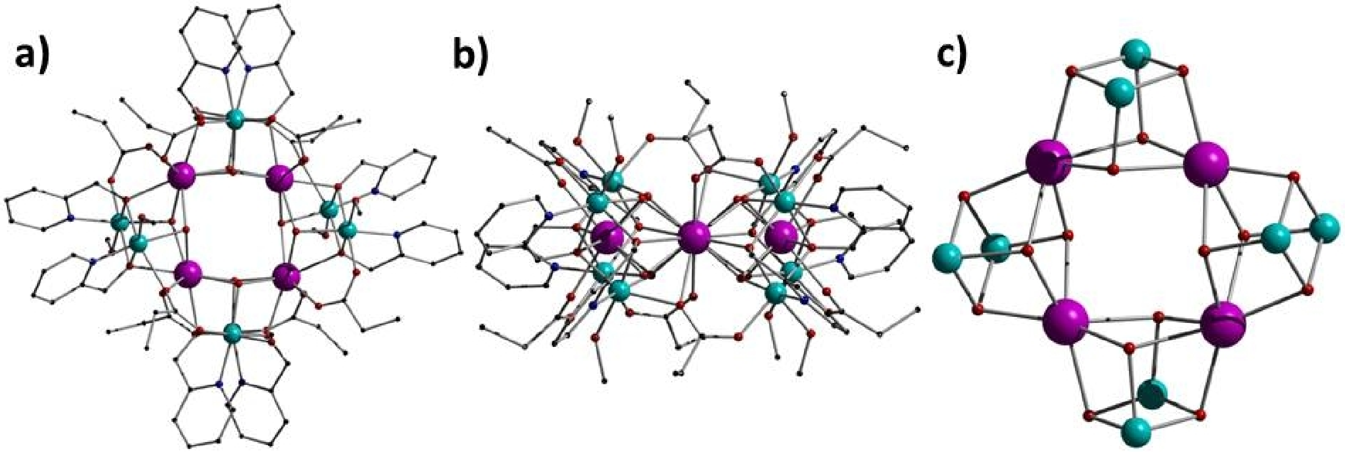
Icosidodecahedron $s = 1/2$



- The true spectrum will be much denser. This is miraculously compensated for by the weights.

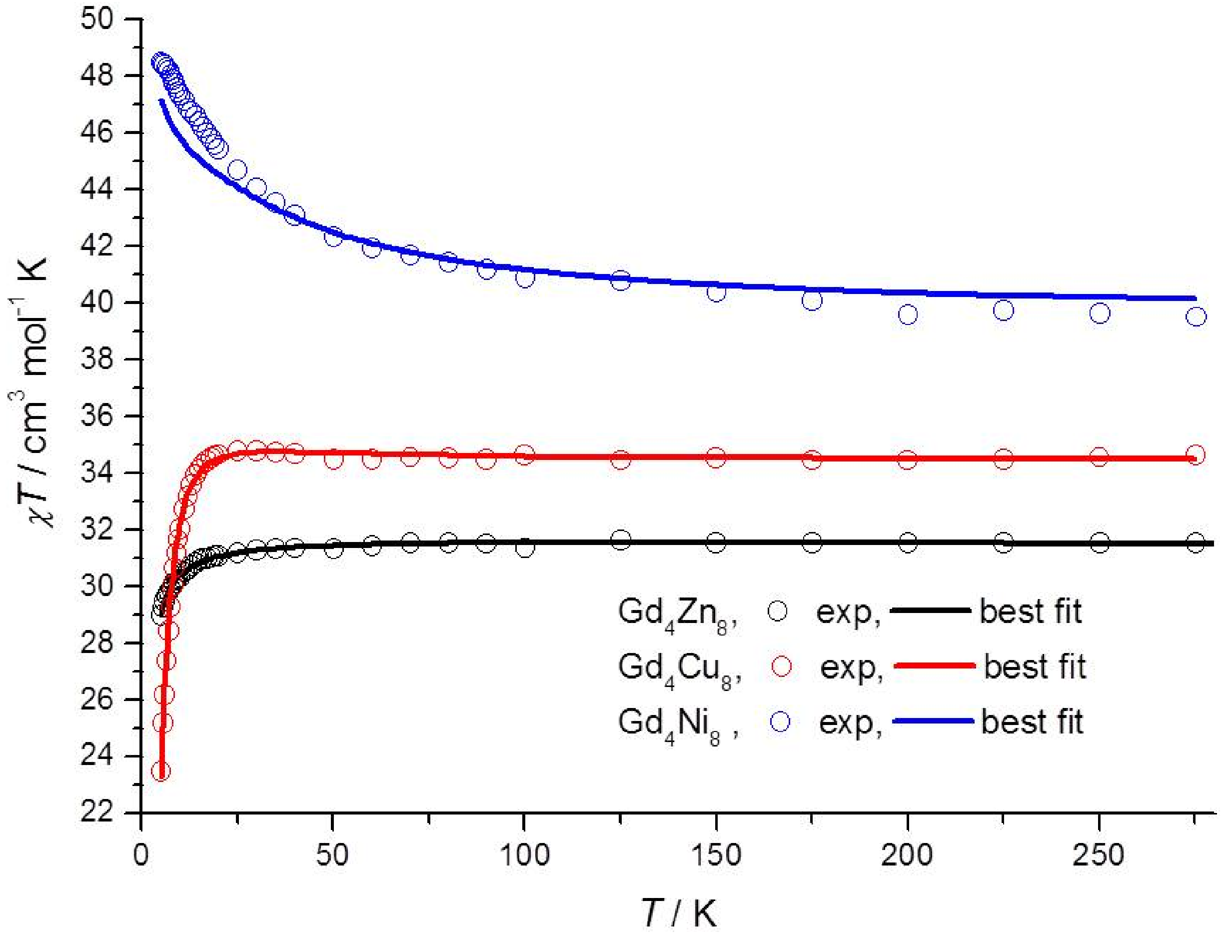
$$Z(T,B) \approx \sum_{\Gamma} \frac{\dim(\mathcal{H}(\Gamma))}{R_\Gamma} \sum_{\nu=1}^{R_\Gamma} \sum_{n=1}^{N_L} \exp\left\{-\beta\epsilon_n\right\} \left|\langle\, n(\nu,\Gamma) \,|\, \nu,\Gamma \,\rangle\right|^2$$

Example Gd_4M_8



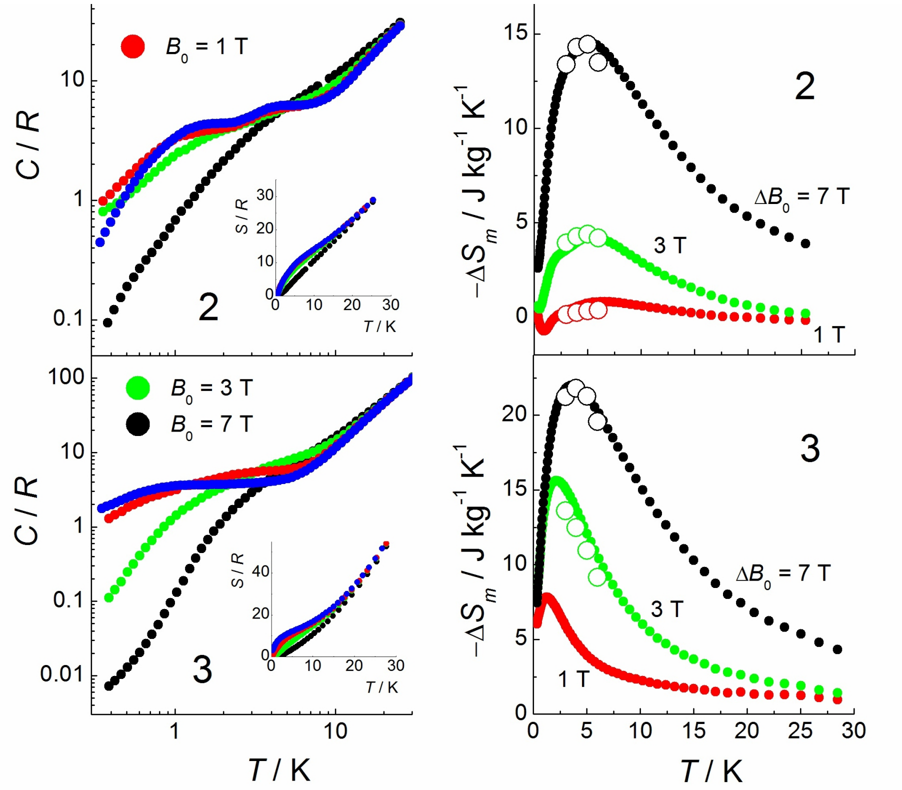
T. N. Hooper, J. Schnack, St. Piligkos, M. Evangelisti, E. K. Brechin, Angew. Chem. Int. Ed. **51** (2012) 4633-4636.

Gd_4M_8 – Susceptibility



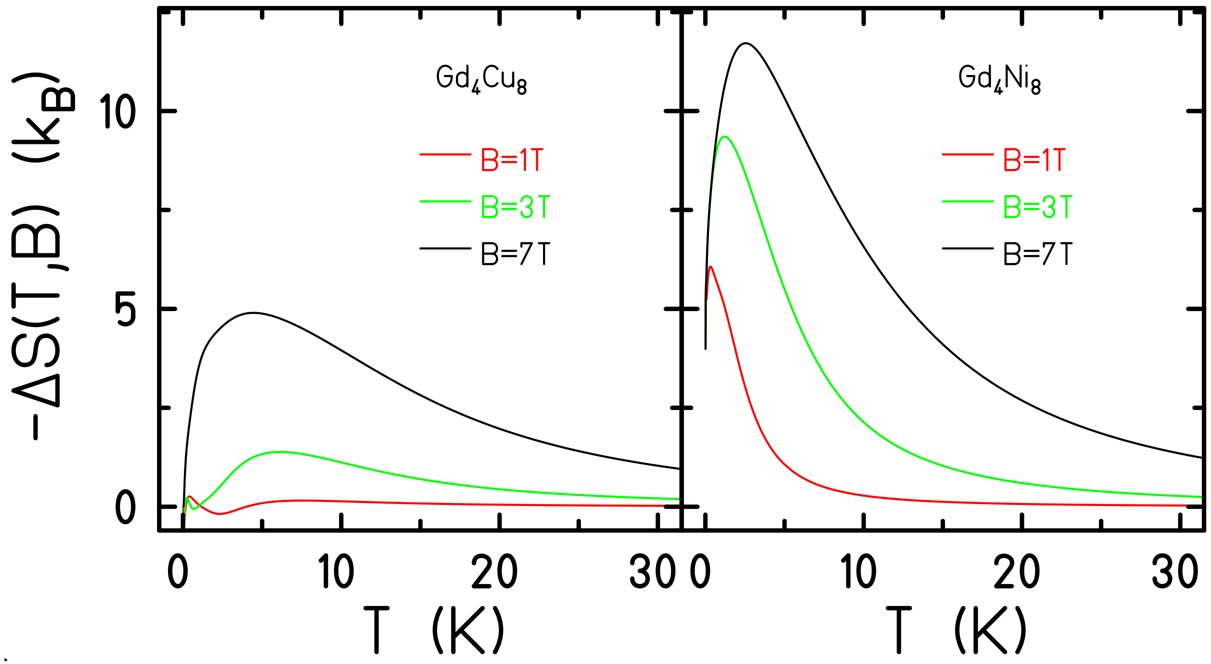
T. N. Hooper, J. Schnack, St. Piligkos, M. Evangelisti, E. K. Brechin, Angew. Chem. Int. Ed. **51** (2012) 4633-4636.

Gd$_4$M$_8$ – experimental $C(T,B)$ and $S(T,B)$



T. N. Hooper, J. Schnack, St. Piligkos, M. Evangelisti, E. K. Brechin, Angew. Chem. Int. Ed. **51** (2012) 4633-4636.

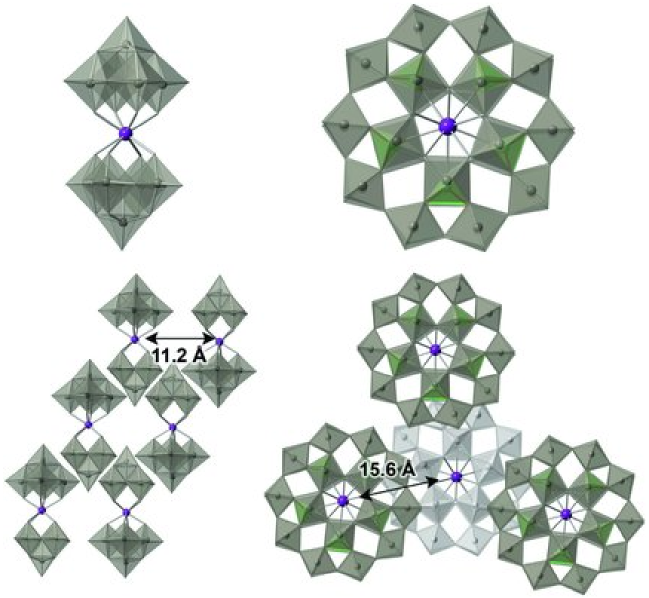
Gd_4Ni_8 – theoretical $S(T, B)$



Problem: Experimental values somewhat smaller, probably due to dipolar interactions.

Weird ideas about dipolar interactions

Dipolar Interactions

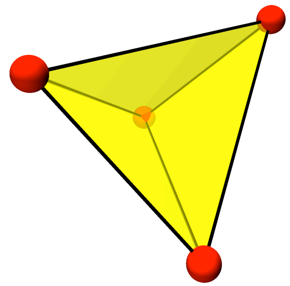


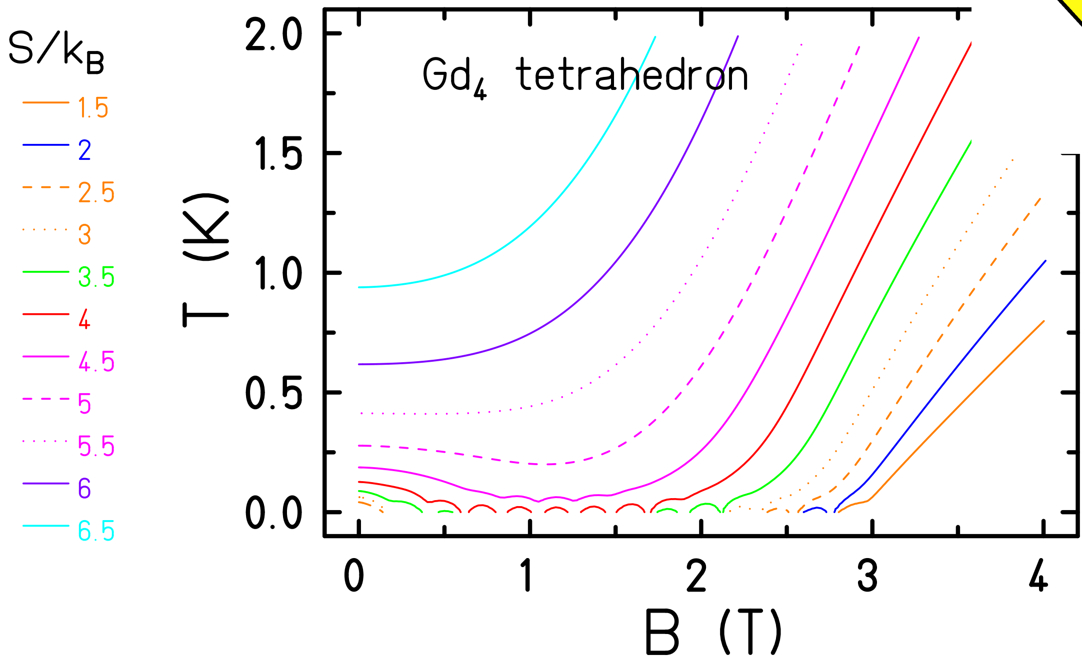
- Dipole-dipole interactions disturb/prevent sub-Kelvin cooling.
- Experimental solution: dilution of magnetic centers (1).
- Theoretical solution: Create low-energy entropy without magnetic moment (2)!

(1) M.-J. Martinez-Perez, O. Montero, M. Evangelisti, F. Luis, J. Sese, S. Cardona-Serra, E. Coronado, Adv. Mater. **24** (2012) 4301-4305.

(2) J. Schnack, C. Heesing, Eur. Phys. J., submitted, arXiv:1207.0299

A fictitious Gd_4 tetrahedron

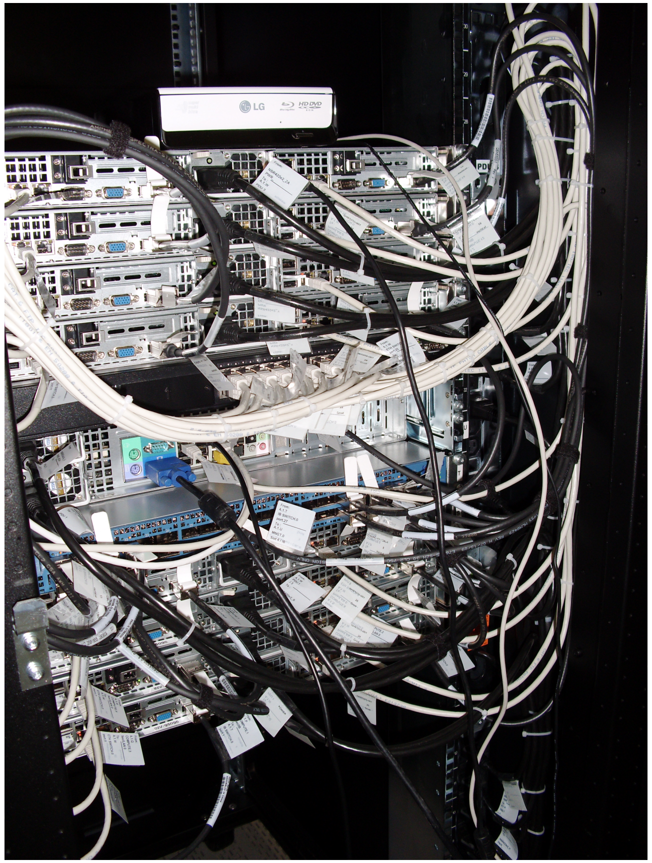




Ground state 8-fold degenerate!

All isentropes with $S \leq k_B \log(8) = 2.08 k_B$ head for absolute zero.

Summary



- Finite-temperature Lanczos is a good approximate method for Hilbert space dimensions smaller than 10^{10}.
- I believe that this is the future.
- Gd-containing magnetic molecules useful for sub-Kelvin cooling and *design of isentropes* in the $T-B$–plane.
- Euan, Eric and Marco are ingenious.
  It is a pleasure to work with them.

Many thanks to my collaborators worldwide

- T. Glaser, Chr. Heesing, M. Höck, N.B. Ivanov, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum, O. Wendland (Bielefeld)

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- M. Luban (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames); R.E.P. Winpenny, E.J.L. McInnes (Man U, UK); L. Cronin, M. Murrie (Glasgow, UK); E. Brechin (Edinburgh, UK); H. Nojiri (Sendai, Japan); A. Postnikov (Metz, France); M. Evangelisti (Zaragosa, Spain)

- J. Richter, J. Schulenburg (Magdeburg); A. Honecker (Göttingen); U. Kortz (Bremen); A. Tennant, B. Lake (HMI Berlin); B. Büchner, V. Kataev, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); J. Wosnitza (Dresden-Rossendorf); J. van Slageren (Stuttgart); R. Klingeler (Heidelberg); O. Waldmann (Freiburg)

Thank you very much for your attention.

The end.

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