Complete diagonalization studies of anisotropic magnetic molecules

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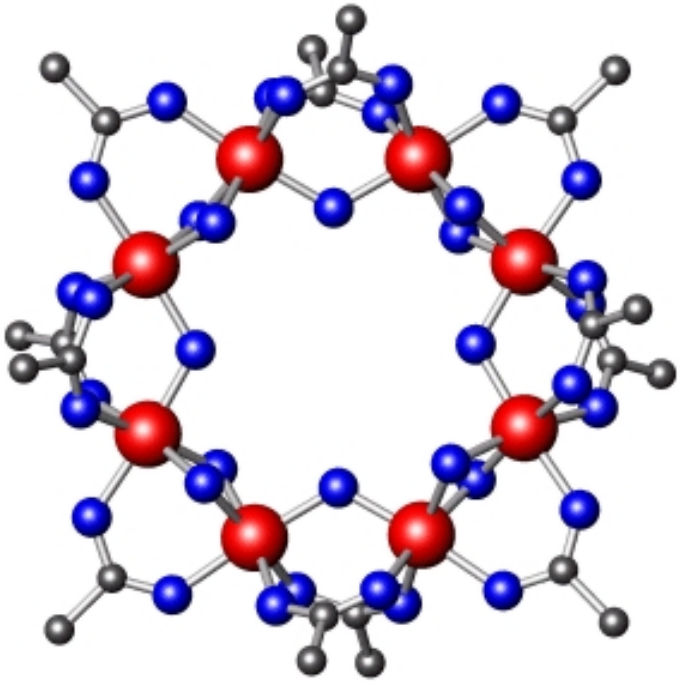
Contents for you today

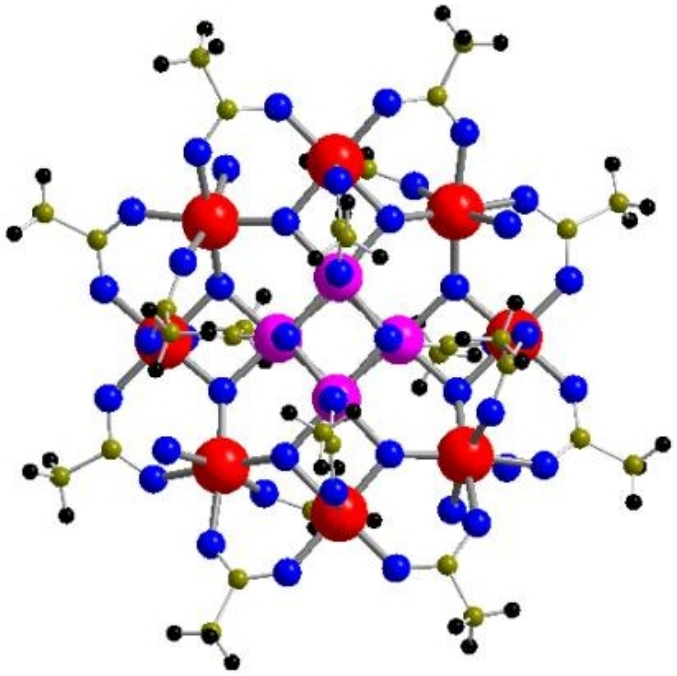


Cr_8

1. Some recent anisotropic magnetic molecules
2. Hamiltonian and evaluation
3. Examples and results

Some recent anisotropic magnetic molecules

Some recent anisotropic magnetic molecules I

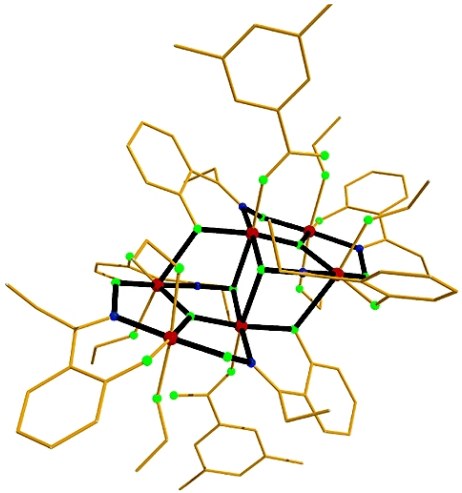


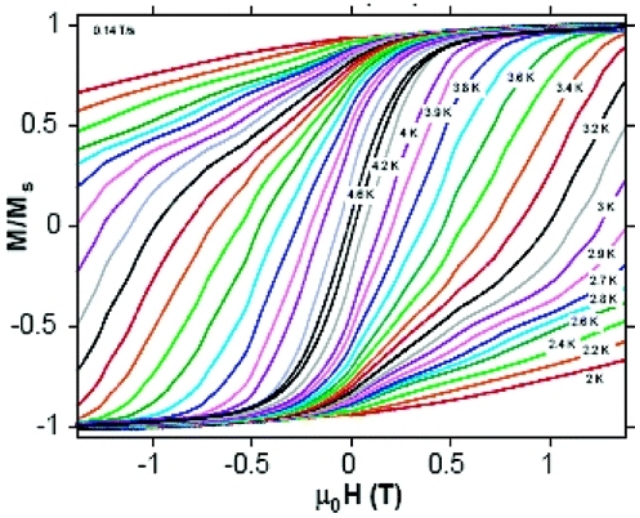
Mn_{12}

Mn_{12}-acetate:

- O.k., not really recent (1980);
- Still one of the most impressive anisotropies among single molecule magnets.

Some recent anisotropic magnetic molecules II



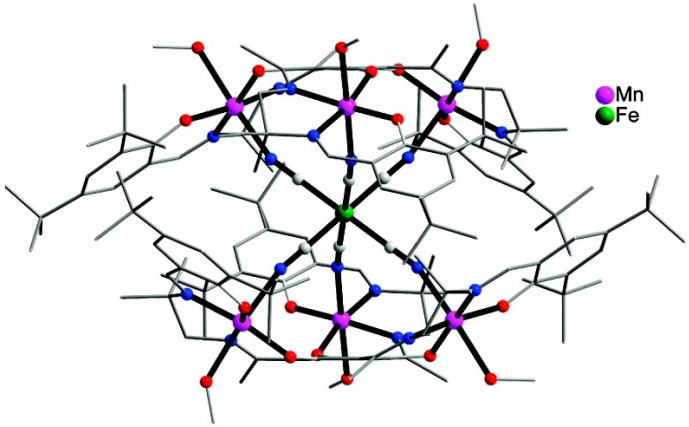


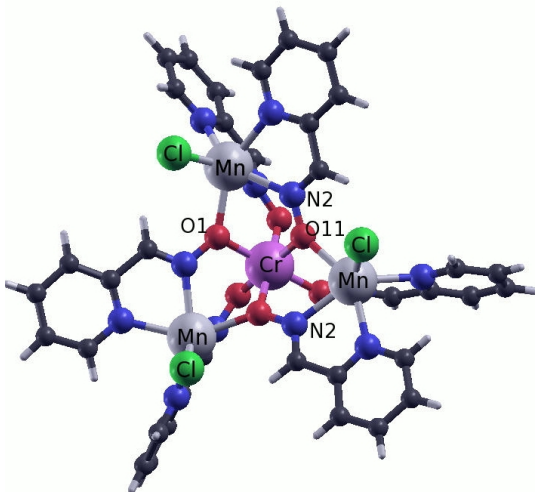
$[Mn^{III}_6O_2$(Et-sao)$_6$(O_2CPh(Me_2))$_2$(EtOH)$_6]$:

- $S = 12$ ground state with $D = -0.43$ cm^{-1};
- $U_{\text{eff}} = 86.4$ K and a blocking temperature of about 4.5 K.

C. J. Milios *et al.*, J. Am. Chem. Soc. **129**, 2754 (2007)
S. Carretta *et al.*, Phys. Rev. Lett. **100**, 157203 (2008)

Some recent anisotropic magnetic molecules III





Molecules by Thorsten Glaser and Phalguni Chaudhuri:

- Mn_6M', e.g. M′=Cr, Fe (1);
- Mn_3Cr (2).

(1) T. Glaser *et al.*, Angew. Chem.-Int. Edit. **45**, 6033 (2006)
(2) S. Khanra *et al.*, Dalton Trans. 481 (2007)

Hamiltonian and evaluation

General Model Hamiltonian

$$\underset{\sim}{H} = \sum_{i,j} \vec{\underset{\sim}{s}}(i) \cdot \mathbf{J}_{ij} \cdot \vec{\underset{\sim}{s}}(j) + \sum_{i,j} \vec{D}_{ij} \cdot \left[\vec{\underset{\sim}{s}}(i) \times \vec{\underset{\sim}{s}}(j) \right] + \mu_B \vec{B} \cdot \sum_i \mathbf{g}_i \cdot \vec{\underset{\sim}{s}}(i)$$

Exchange/Anisotropy Dzyaloshinskii-Moriya Zeeman

$$+ \sum_{k,l,m,n} J'_{klmn} \left(\vec{\underset{\sim}{s}}(k) \cdot \vec{\underset{\sim}{s}}(l) \right) \left(\vec{\underset{\sim}{s}}(m) \cdot \vec{\underset{\sim}{s}}(n) \right) + \ldots$$

generalized biquadratic

Let's stick to on-site anisotropy

$$\underset{\sim}{H}_{\mathsf{a}} = \sum_i \vec{\underset{\sim}{s}}(i) \cdot \mathbf{D}_i \cdot \vec{\underset{\sim}{s}}(i) \;, \qquad \mathbf{D}_i \equiv \text{local anisotropy tensor}$$

$$= \sum_i d_i \, \underset{\sim}{s}_z^2(i) + \sum_i e_i \left(\underset{\sim}{s}_x^2(i) - \underset{\sim}{s}_y^2(i) \right)$$

- $\mathbf{D}_i$ has three principal axes;
- d_i & e_i are eigenvalues of $\mathbf{D}_i$;
- $|d_i| > |e_i|$ defines the local z-direction;
- $d_i < 0$ easy axis, $d_i > 0$ hard axis;

Getting eigenvalues

$$\underset{\sim}{H}(\vec{B}) \;=\; -\sum_{i,j} J_{ij}\,\vec{\underset{\sim}{s}}(i)\cdot\vec{\underset{\sim}{s}}(j) \;+\sum_{i} d_i\left(\vec{e}_i\cdot\vec{\underset{\sim}{s}}(i)\right)^2+ \;\mu_B\,\vec{B}\cdot\sum_i \mathbf{g}_i\cdot\vec{\underset{\sim}{s}}(i)$$

- $\left[\underset{\sim}{H},\vec{\underset{\sim}{S}}^2\right]\neq 0,\ \left[\underset{\sim}{H},\underset{\sim}{S}_z\right]\neq 0$; $\Rightarrow$ MAGPACK does not work!
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ for every field (direction and strength)!
- If you are lucky, point group symmetries still exist. Use them!

How to obtain the magnetization?

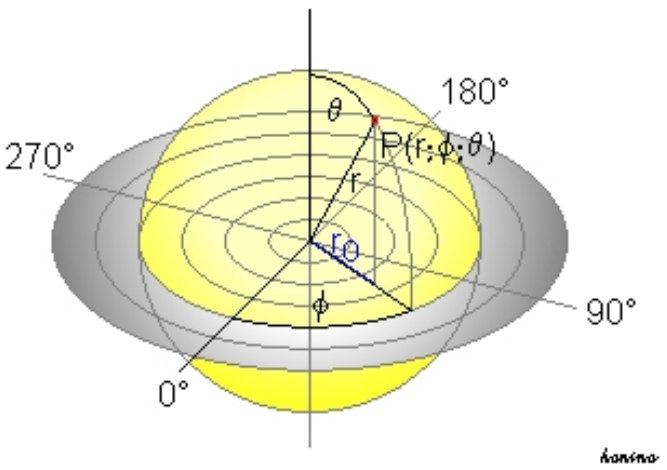
Numerical differentiation

- For each field $\vec{B}$ you evaluate the energy eigenvalues TWICE:
  $M_\nu(\vec{B}) = -\Big(E_\nu(\vec{B}(1+\varepsilon)) - E_\nu(\vec{B})\Big)/(\varepsilon B)$
- Numerical differentiation is a serious mathematical subject – good accuracy requires fine-tuning.

Using eigenvectors of $\underset{\sim}{H}(\vec{B})$

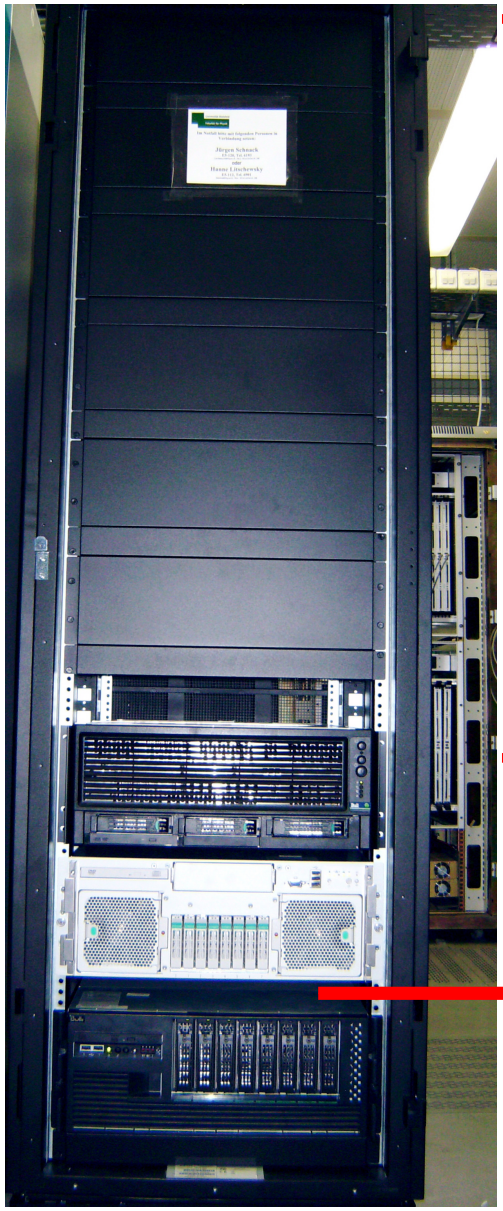
- Evaluate the energy eigenvectors: greater numerical effort, for INS anyway necessary;
- For each $\vec{B}$, evaluate and store E_ν and $\vec{M}_\nu(\vec{B}) = \mu_B \langle\, \nu \,|\, \sum_i^N \mathbf{g}_i \cdot \underset{\sim}{\vec{s}}(i) \,|\, \nu \,\rangle$.
- Accurate, but time consuming (eigenvectors!).

Orientational average for powder samples



- If you have a single crystal, doze off for the rest of my talk.
- Average over x-, y-, and z-direction: poor;
- Average over random directions: large fluctuations;
- Use Lebedev-Laikov grids: The parameters ensure that angular integration of polynomials $x^k \cdot y^l \cdot z^m$, where $k + l + m \leq 131$ can be performed with a relative accuracy of $2 \cdot 10^{-14}$.
- I am using LLG with 50 (25) orientations.

V. I. Lebedev and D. N. Laikov, Dokl. Akad. Nauk **366**, 741 (1999); and link to program on `www.molmag.de`



- Thank God we have computers!

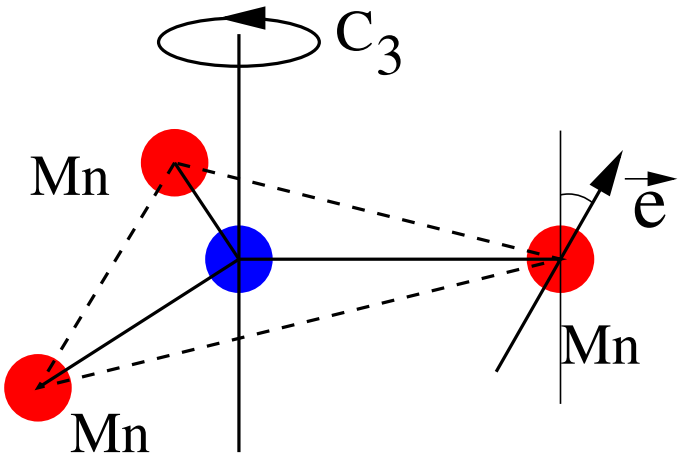
- Golden Future: 200,000 € in 2009
  64 cores (Nehalem architecture),
  512 GB RAM
  (an amazing computer power)

- 2008: BULL NovaScale R480
  4 XEON TIGERTON (a 4 cores),
  48 GB RAM

- 2007: BULL NovaScale 3045
  4 ITANIUM MONTECITO (a 2 cores),
  64 GB RAM
  (already an amazing computer power,
  but one can get used to it ;-))

Examples and results

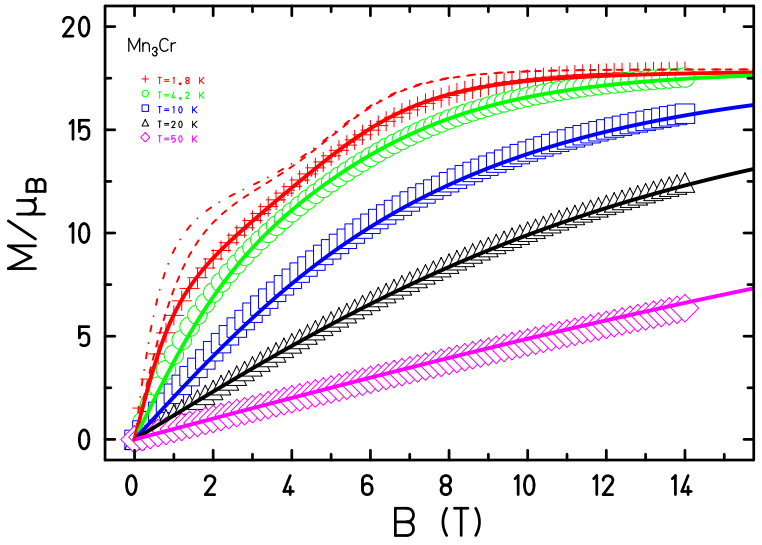
Mn$_3$Cr I

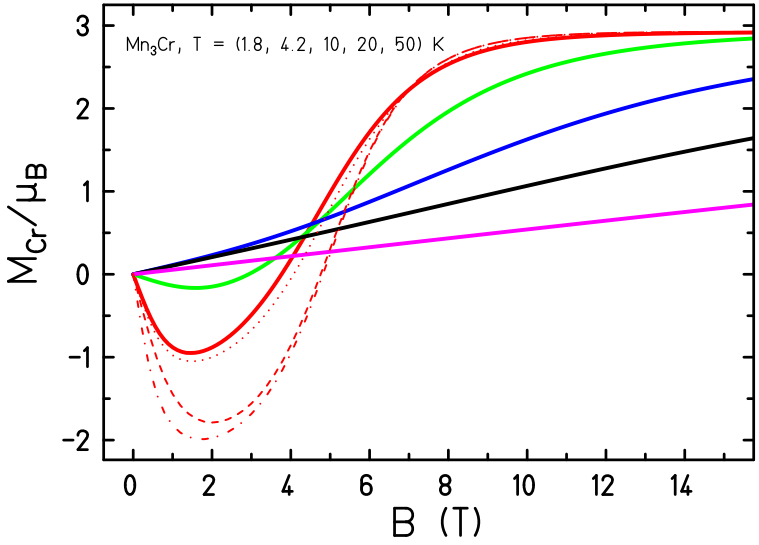


Mn$_3$Cr:

- Assume C_3 symmetry;
- Two couplings: J_1 to central Cr, J_2 between Mn;
- Model Mn anisotropy by local axis $\vec{e}(\vartheta, \phi)$.
  Due to C_3 symmetry $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}}$.
  Only relative $\phi = 120°$ determined.
- Model Cr anisotropy by local axis $\vec{e}(\vartheta, \phi)$.
  Due to C_3 symmetry $\vartheta_{\text{Cr}} = 0, \phi_{\text{Cr}} = 0$.
- Mn: s=5/2, g=2.0; Cr: s=3/2, g=1.95

Mn$_3$Cr II – Results

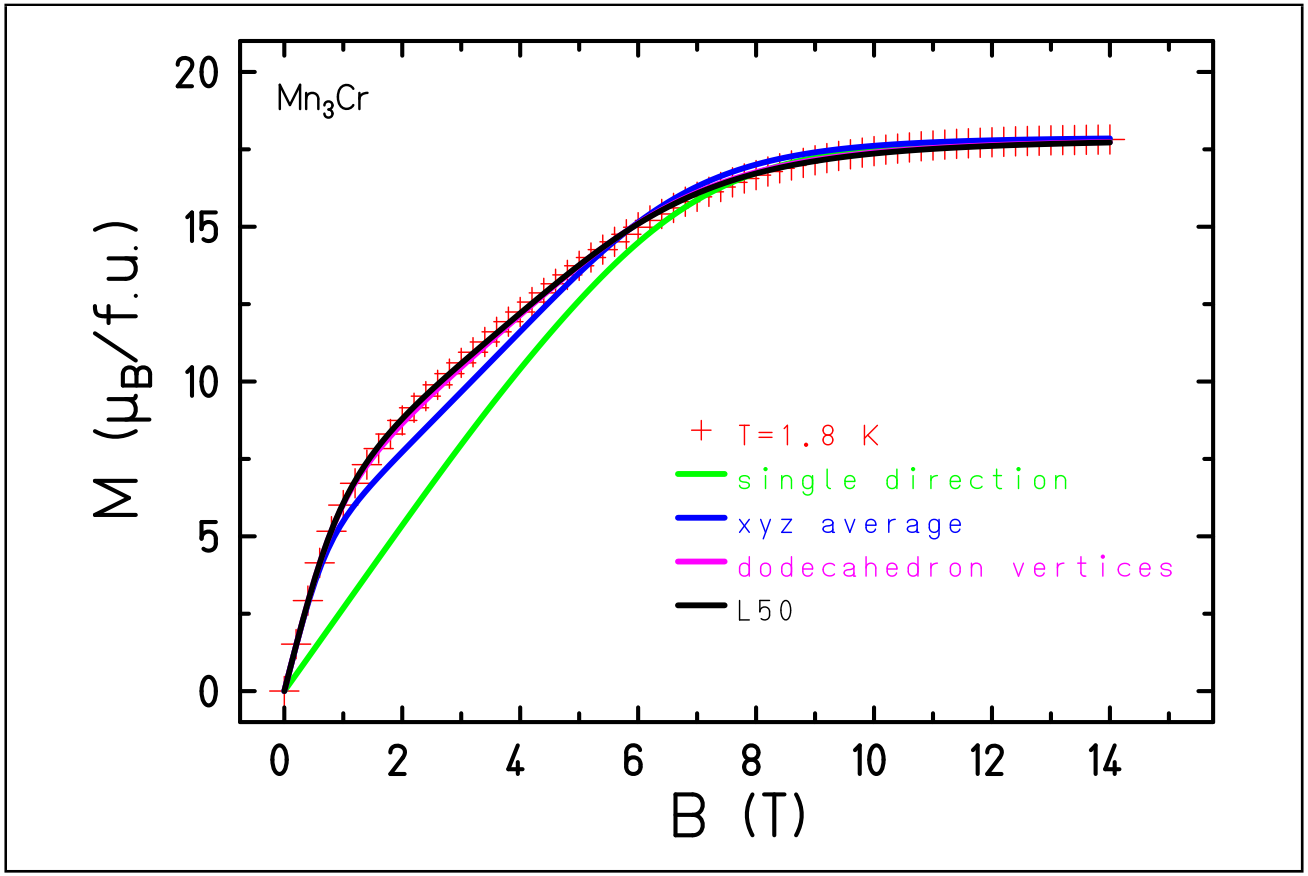




Result: $J_1 = -0.29$ cm^{-1}, $J_2 = -0.07$ cm^{-1},
$d_{\mathrm{Mn}} = -1.05$ cm^{-1}, $\vartheta_{\mathrm{Mn}} = 15°$, $d_{\mathrm{Cr}} = +0.40$ cm^{-1}.

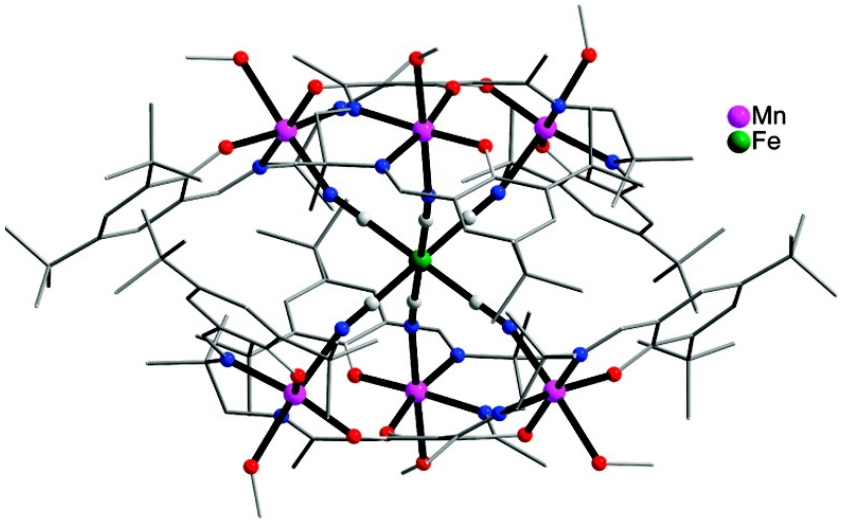
M. Prinz, K. Kuepper, C. Taubitz, M. Raekers, B. Biswas, T. Weyhermüller, M. Uhlarz, J. Wosnitza, J. Schnack, A. V. Postnikov, C. Schröder, S. J. George, M. Neumann, P. Chaudhuri, in preparation.

Mn$_3$Cr III – Angular averaging



For a good fit you need several directions, at least 10.

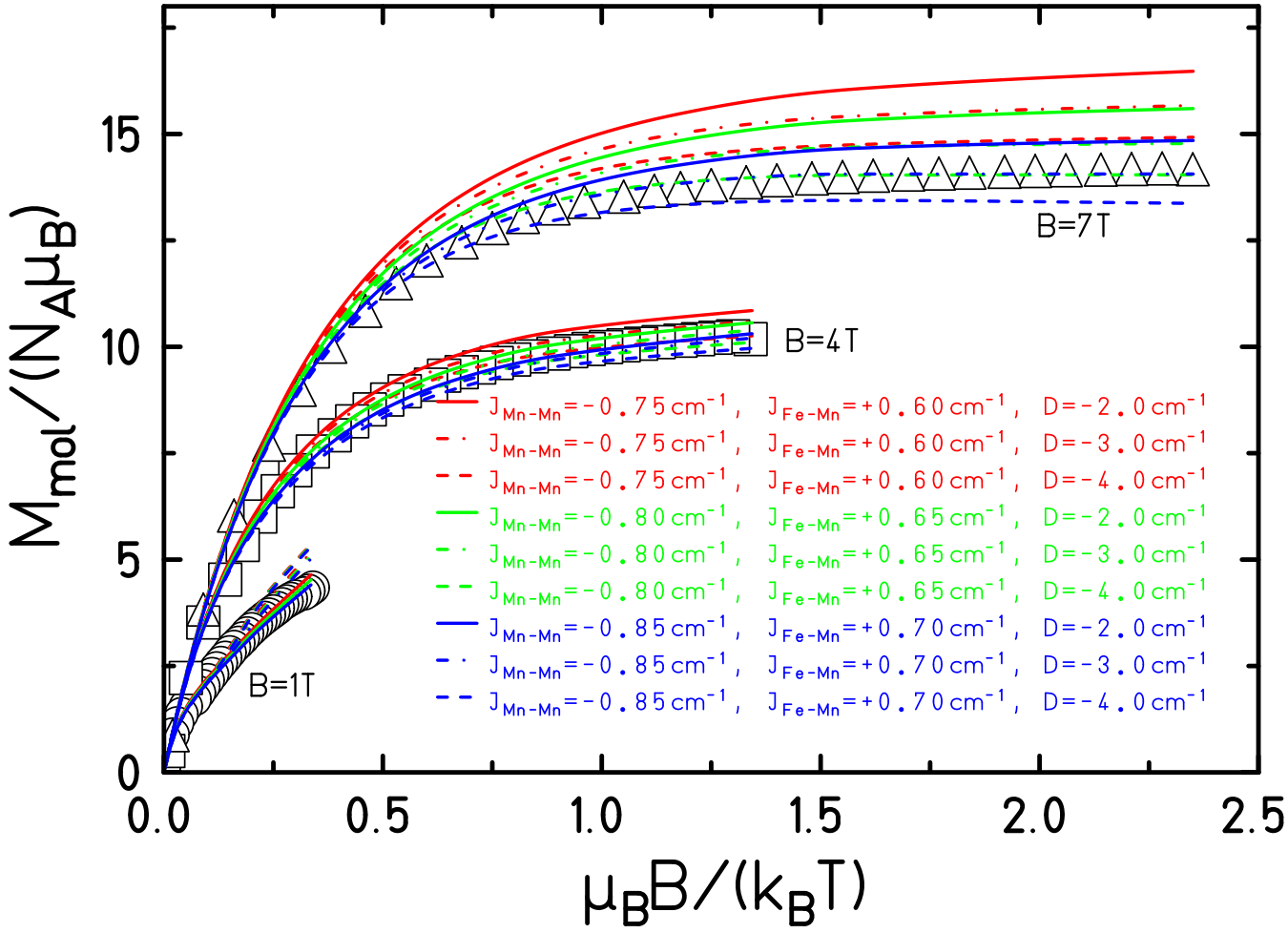
Mn$_6$Fe I



- Rational design of strict C_3 symmetry of local easy axes (Thorsten Glaser): e.g. Mn$_6$Cr (1), Mn$_6$Fe (2)
- Mn$_6$Fe: J_1 between Mn in caps, J_2 to central Fe; Mn anisotropy modeled by local axis $\vec{e}(\vartheta, \phi)$ with $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}} = 36.5°$. Only relative $\phi = 120°$ determined.
- Mn: s=2, g=1.98; Fe: s=1/2, g-tensor.

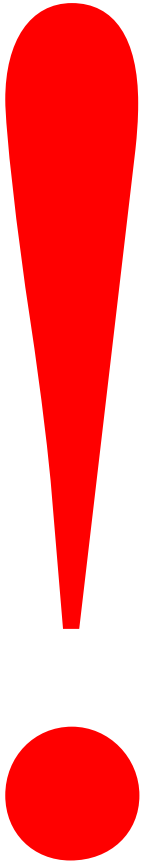
(1) T. Glaser, M. Heidemeier, T. Weyhermüller, R. D. Hoffmann, H. Rupp, P. Müller, Angew. Chem.-Int. Edit. **45**, 6033 (2006).
(2) T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, Inorg. Chem. **48**, 607 (2009).

Mn$_6$Fe II – Results



T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, Inorg. Chem. **48**, 607 (2009).

Summary



- It is possible to determine local anisotropy axes with rather high accuracy.
- Complementary *ab initio* calculations on local $\mathbf{D}$–tensors would be valuable.
- Powders have to be averaged properly.
- Single crystals would probably allow to obtain the full local $\mathbf{D}$–tensor.
- Element-selective calculations possible.

Thank you very much for your attention.

German Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. DFG SPP 1137.