Modeling of isotropic and anisotropic magnetic molecules

Jürgen Schnack

Department of Physics – University of Bielefeld – Germany

http://obelix.physik.uni-bielefeld.de/∼schnack/

Seminar

Aachen, October 30th, 2009

Universität Bielefeld

Deutsche Forschungsgemeinschaft DFG

FOR 945

The Leverhulme Trust

Many thanks to my collaborators worldwide

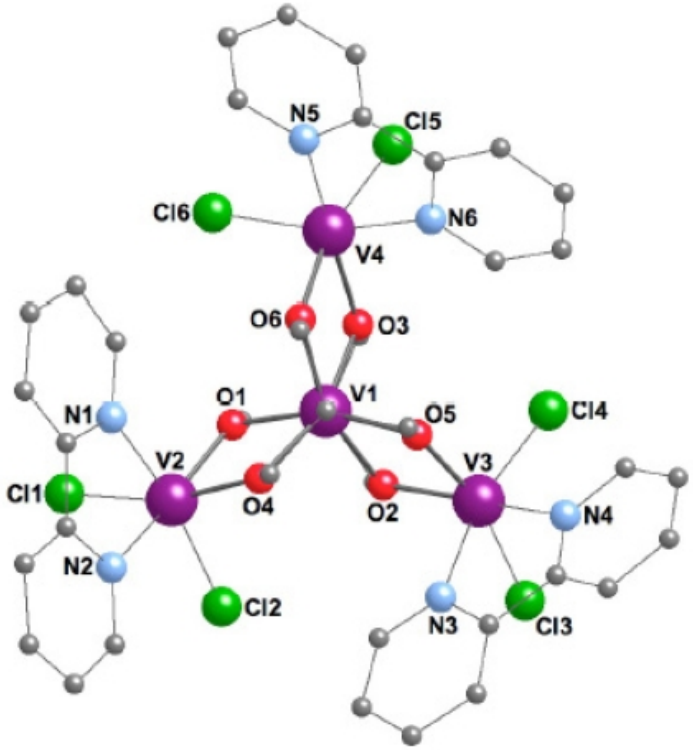
- T. Englisch, T. Glaser, M. Höck, S. Leiding, A. Müller, R. Schnalle, Chr. Schröder, J. Ummethum (Bielefeld)

- K. Bärwinkel, H.-J. Schmidt, M. Neumann (Osnabrück);

- M. Luban, D. Vaknin (Ames Lab, USA); P. Kögerler (Aachen, Jülich, Ames)
  J. Musfeld (U. of Tennessee, USA); N. Dalal (Florida State, USA);
  R.E.P. Winpenny, E.J.L. McInnes (Man U, UK); L. Cronin (Glasgow, UK);
  J. van Slageren (Nottingham);
  H. Nojiri (Sendai, Japan); A. Postnikov (Metz, France)

- J. Richter, J. Schulenburg (Magdeburg); S. Blügel (FZ Jülich); A. Honecker (Göttingen); U. Kortz (Bremen); A. Tennant, B. Lake (HMI Berlin); B. Büchner, V. Kataev, R. Klingeler, H.-H. Klauß (Dresden); P. Chaudhuri (Mühlheim); J. Wosnitza (Dresden-Rossendorf)

Contents for you today

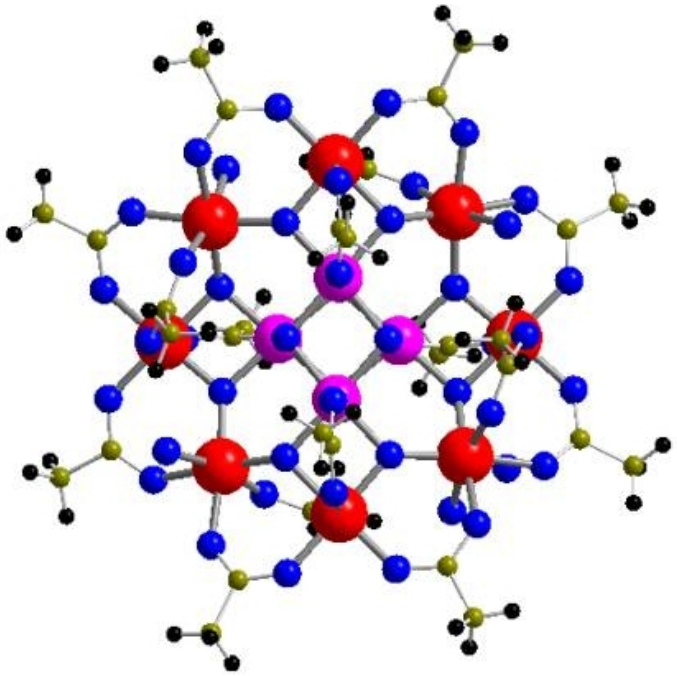


V_4

1. Introduction
2. Isotropic molecules: ITO & point group
3. Anisotropic molecules

Introduction

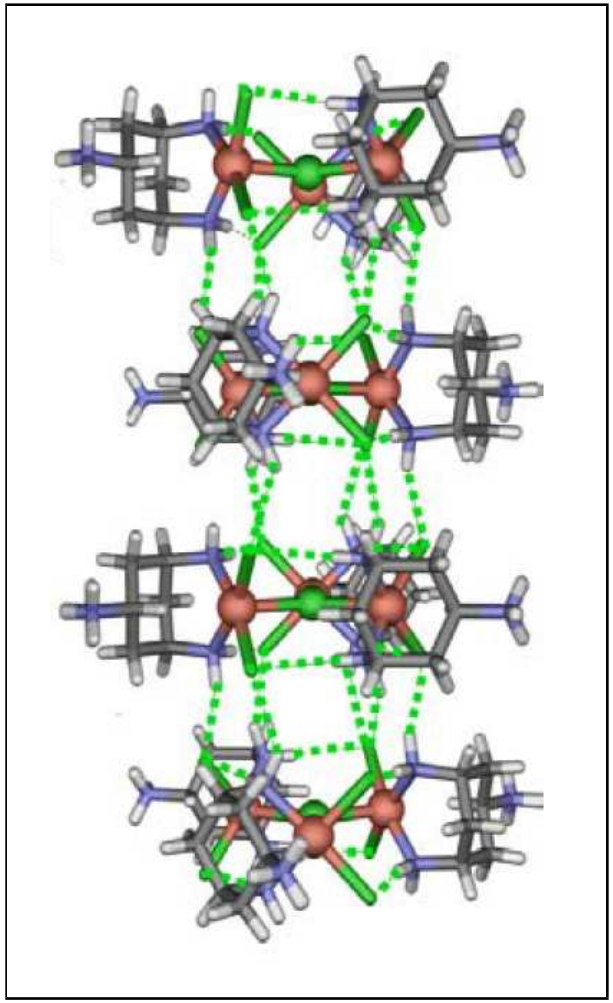
The beauty of magnetic molecules I



Mn_{12}

- 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);
- Speculative applications: magnetic storage devices, magnets in biological systems, light-induced nano switches, displays, catalysts, transparent magnets, qubits for quantum computers.

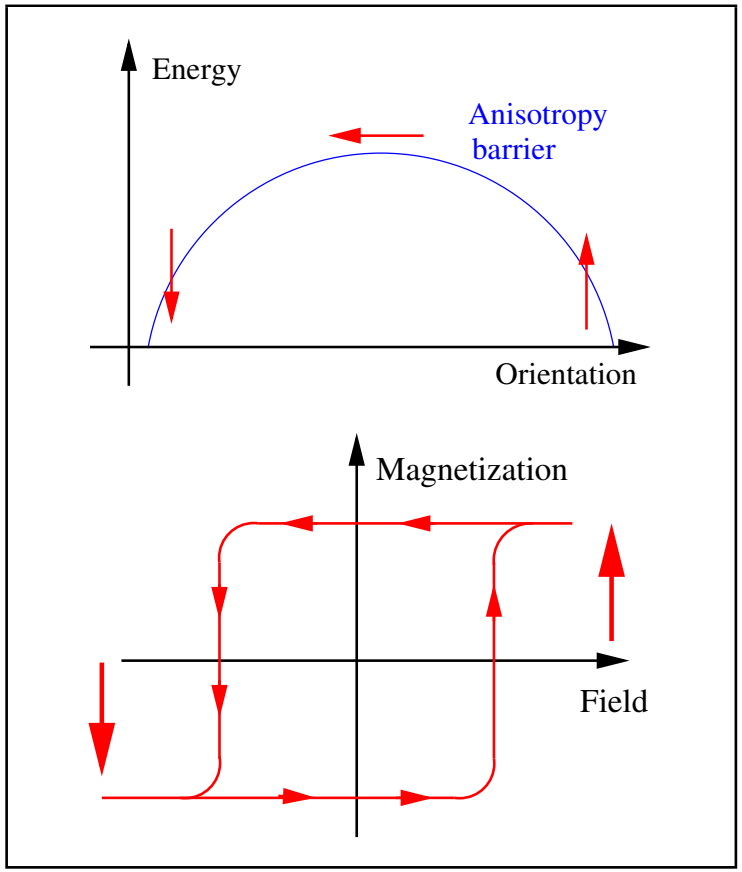
The beauty of magnetic molecules II



- Dimers (Fe_2), tetrahedra (Cr_4), cubes (Cr_8);
- Rings, especially iron and chromium rings
- 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); Sato, Sakai, Läuchli, Mila, . . .

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; rational design; investigate on surfaces.

Model Hamiltonian (spin only)

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

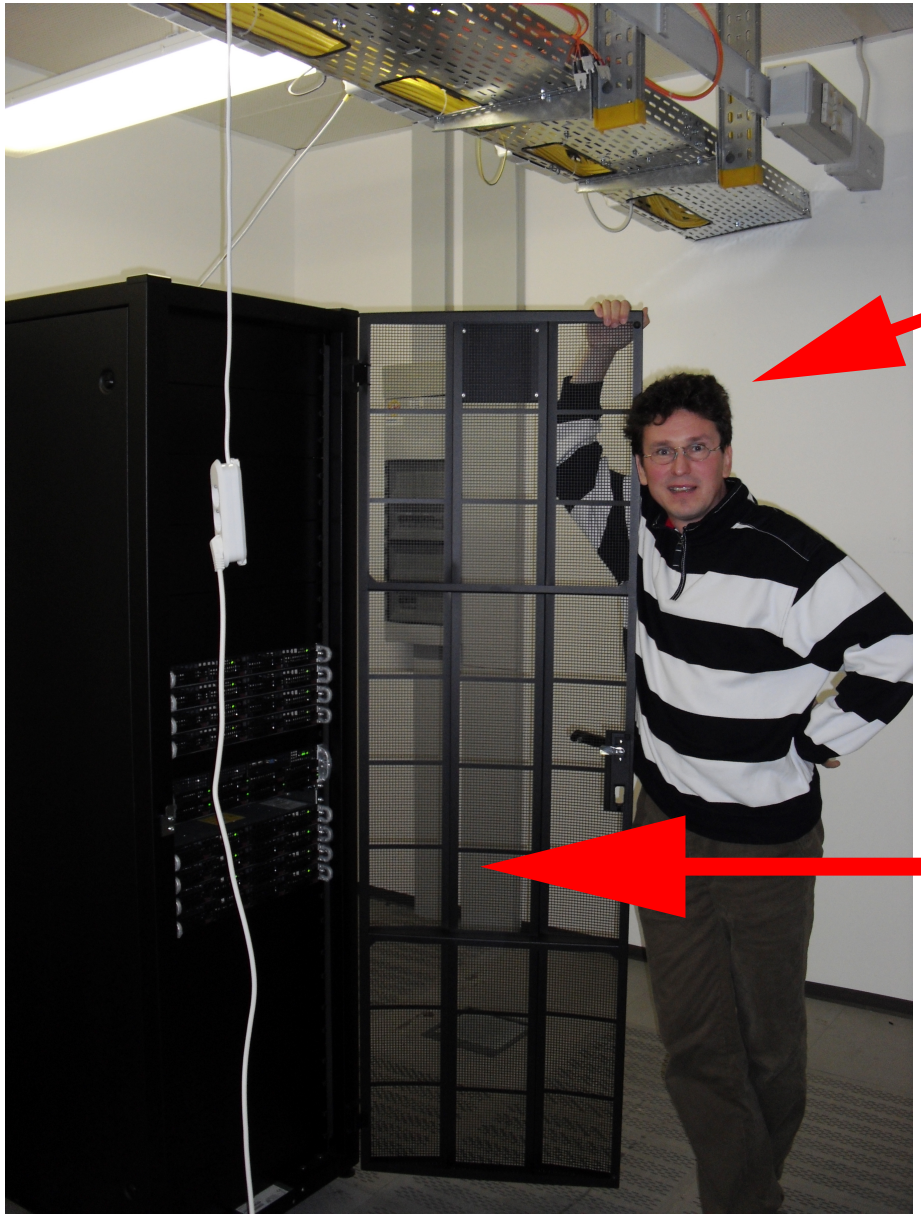
Exchange/Anisotropy Dzyaloshinskii-Moriya Zeeman

Isotropic Hamiltonian

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

Heisenberg Zeeman

Thank God, we have computers



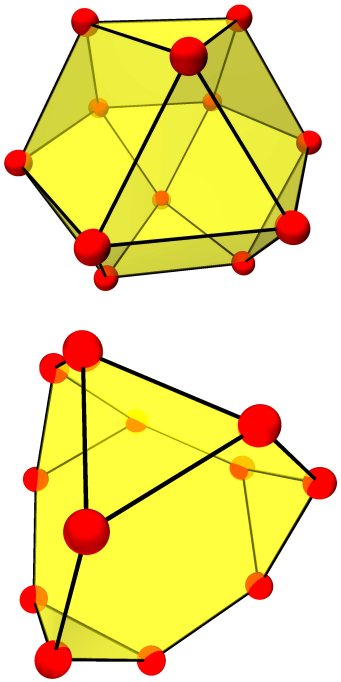
“cell professor”

128 cores, 384 GB RAM

. . . but that’s not enough!

Isotropic magnetic molecules

Advanced ITO & Point Groups I



Group theory for highly symmetric molecules:

- $\underset{\sim}{H} = -\sum_{i,j} J_{ij}\ \underset{\sim}{\vec{s}}_i \cdot \underset{\sim}{\vec{s}}_j + g\mu_B \underset{\sim}{\vec{S}} \cdot \vec{B}$;
- $\left[\underset{\sim}{H}, \underset{\sim}{\vec{S}}^2\right] = 0, \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] = 0;$
- Irreducible Tensor Operator (ITO) approach, MAGPACK (1);
- Additional point group symmetries (2).

(1) D. Gatteschi and L. Pardi, Gazz. Chim. Ital. **123**, 231 (1993); J. J. Borras-Almenar, J. M. Clemente-Juan, E. Coronado, and B. S. Tsukerblat, Inorg. Chem. **38**, 6081 (1999).
(2) O. Waldmann, Phys. Rev. B **61**, 6138 (2000); V. E. Sinitsyn, I. G. Bostrem, and A. S. Ovchinnikov, J. Phys. A-Math. Theor. **40**, 645 (2007); R. Schnalle and J. Schnack, Phys. Rev. B **79**, 104419 (2009).

Reminder ITO

$$\underset{\sim}{H}_{\text{Heisenberg}} = \sqrt{3} \sum_{i,j} J_{ij} \, \underset{\sim}{T}^{(0)}(\{k_i\}, \{\overline{k}_i\} | k_i = k_j = 1)$$

Irreducible Tensor Operator approach

- Express spin operators and functions thereof as ITOs;
- Use vector coupling basis $|\, \alpha \; S \; M \,\rangle$ and recursive recoupling;
- Numerical implementation e.g. MAGPACK.

(1) Gatteschi, Tsukerblat, Coronado, Waldmann, ...
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Advanced ITO & Point Groups II

$$\mathcal{P}^{(n)} \mid \alpha\, S\, M \,\rangle = \left(\frac{l_n}{h} \sum_R \left(\chi^{(n)}(R) \right)^* \underset{\sim}{G}(R) \right) \mid \alpha\, S\, M \,\rangle$$

Point Group Symmetry

- Projection on irreducible representations (Wigner);
- *Basis function generating machine*;
- Orthonormalization necessary.

(1) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Advanced ITO & Point Groups III

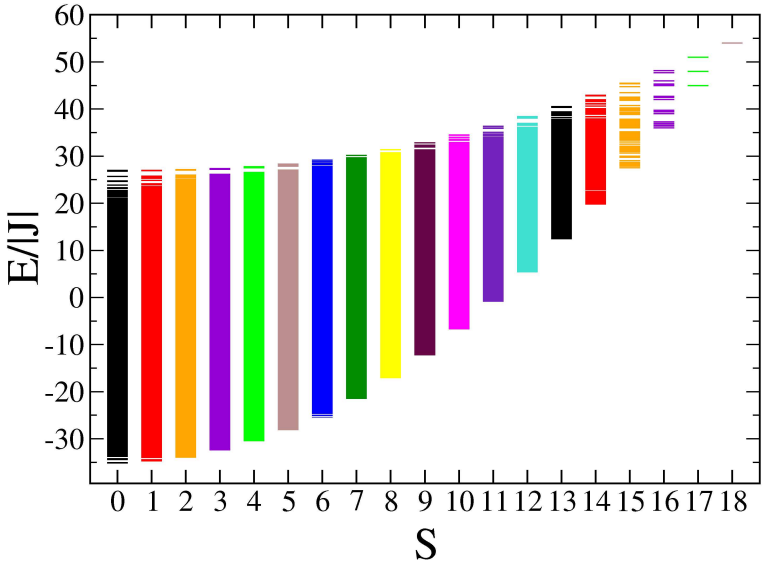
$$\underset{\sim}{G}(R)\,|\,\alpha\,S\,M\,\rangle_a = \sum_{\alpha'} |\,\alpha'\,S\,M\,\rangle_a\;{}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$$

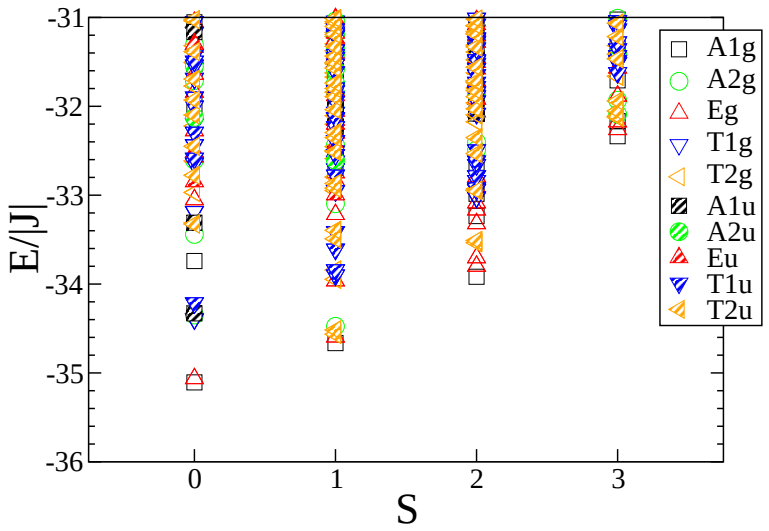
Serious problem: Recoupling

- So far: only point groups that are compatible with the coupling scheme are used (1);
- Problem: otherwise complicated basis transformation between different coupling schemes;
- Solution: implementation of graph-theoretical results to evaluate recoupling coefficients ${}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$ (2).

(1) O. Waldmann, Phys. Rev. B **61**, 6138 (2000).
(2) R. Schnalle, Ph.D. thesis, Osnabrück University (2009)

Advanced ITO & Point Groups IV

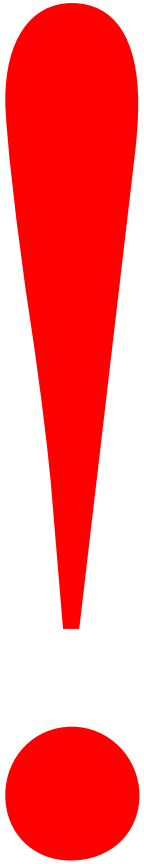




Cuboctahedron, $s = 3/2$, Hilbert space dimension 16,777,216; symmetry O_h (1).
Evaluation of recoupling coefficients very time consuming. (1,2)

(1) J. Schnack and R. Schnalle, Polyhedron **28**, 1620 (2009);
(2) R. Schnalle and J. Schnack, Phys. Rev. B **79**, 104419 (2009).

Summary – Isotropic molecules



- Combined use of SU(2) and point group symmetries possible.
- Numerical effort for recoupling coefficients enormous.
- Representation with smaller matrices.
- Further insight: spectroscopic labeling, selection rules for transitions.
- Works also for frustrated molecules, where QMC does not converge.

Anisotropic magnetic molecules

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!

(1) J. Schnack, Condens. Matter Phys. **12**, 323 (2009);

How to obtain the magnetization?

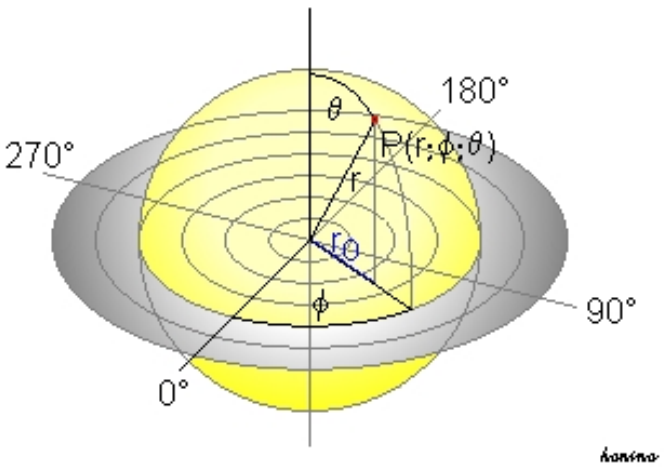
Numerical differentiation

- 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!).

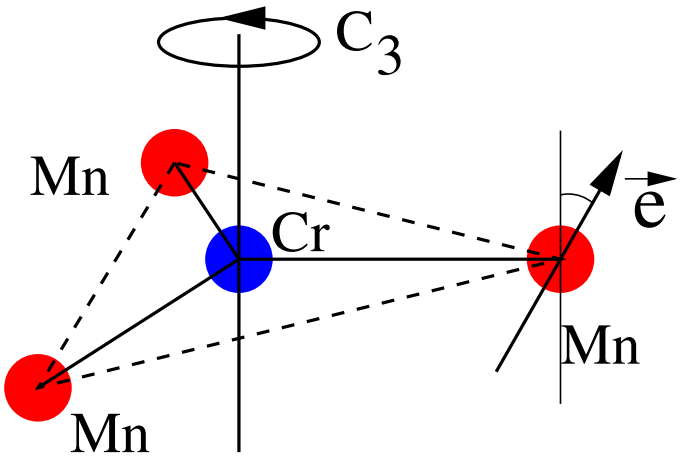
Orientational average for powder samples



- 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`

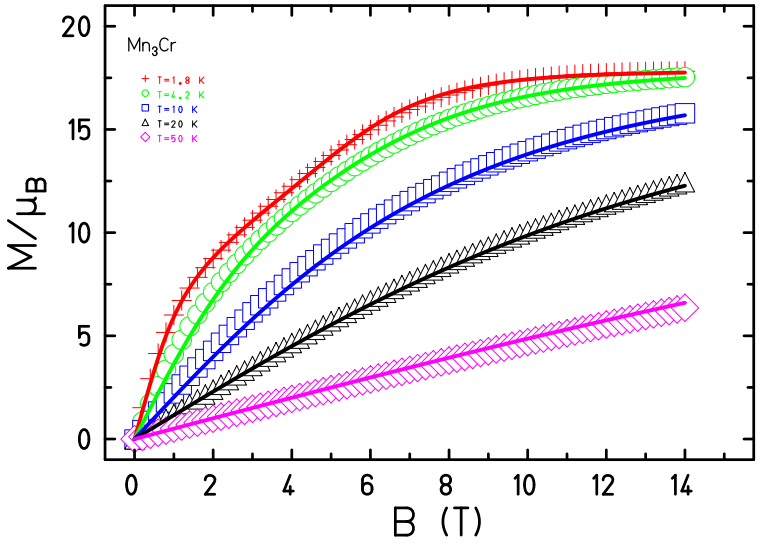
Mn$_3$Cr I

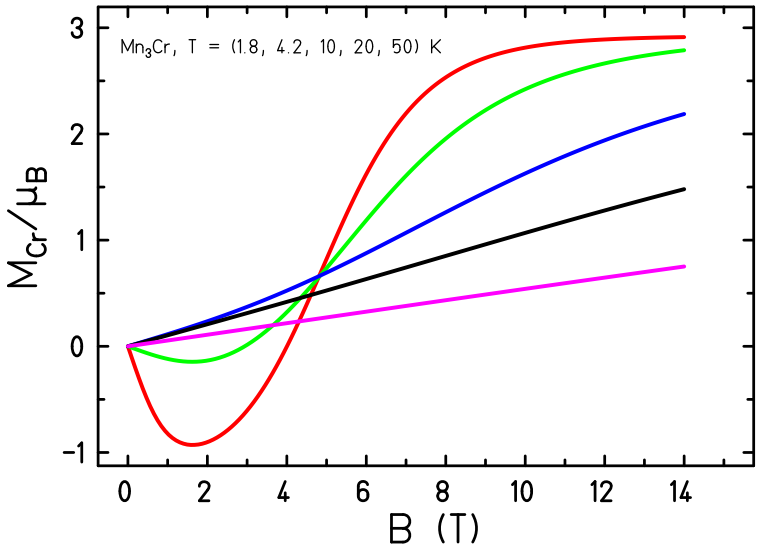


Mn$_3$Cr:

- 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

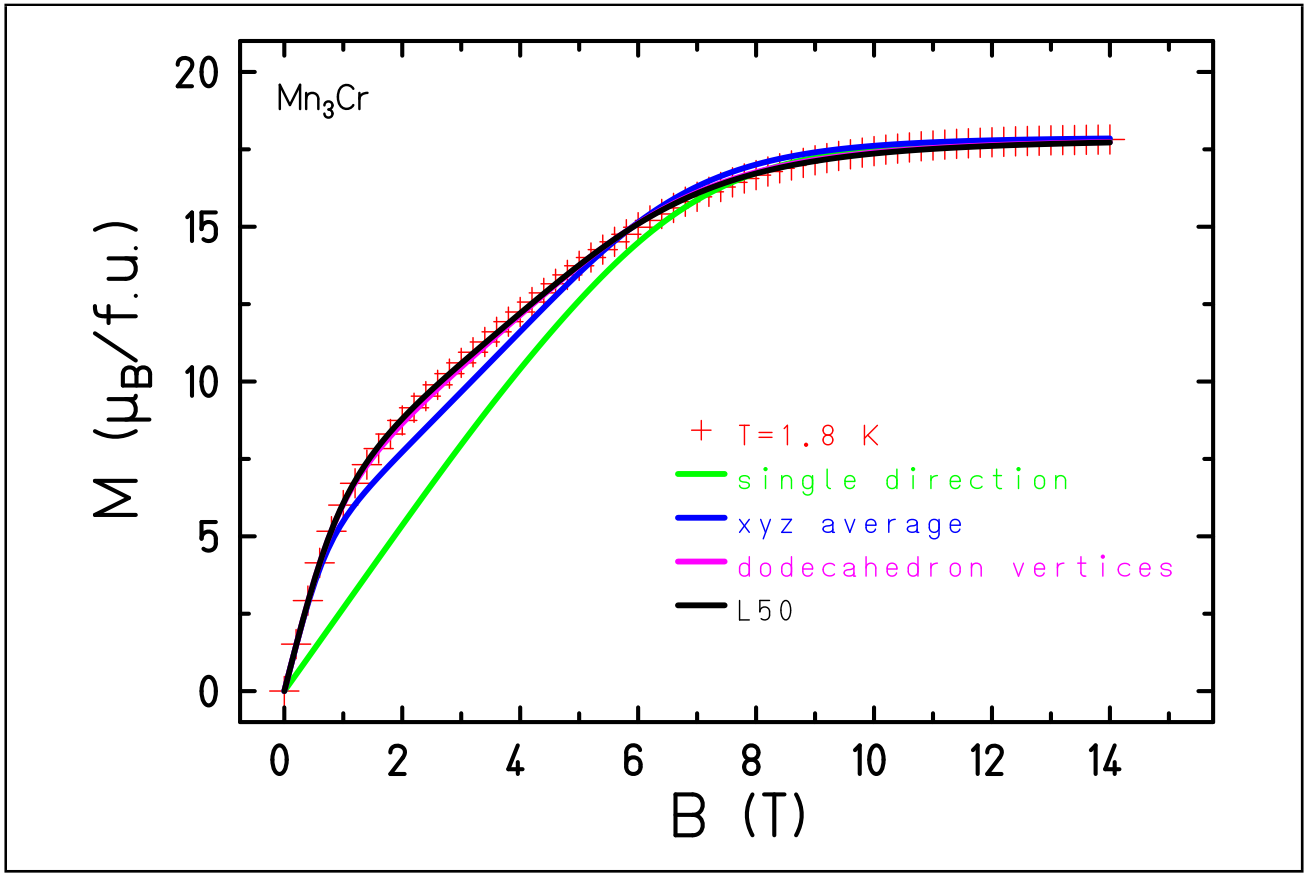




Result: $J_1 = -0.29$ cm^{-1}, $J_2 = -0.07$ cm^{-1},
$d_{\mathrm{Mn}} = -1.05$ cm^{-1}, $\vartheta_{\mathrm{Mn}} = 15°$, $d_{\mathrm{Cr}} = +0.40$ cm^{-1}.

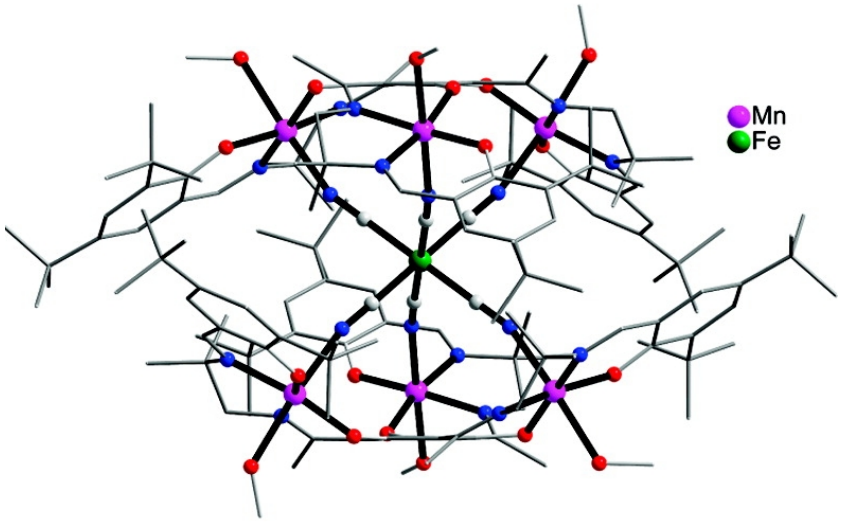
M. Prinz, K. Kuepper, C. Taubitz, M. Raekers, B. Biswas, T. Weyhermüller, M. Uhlarz, J. Wosnitza, J. Schnack, A. V. Postnikov, C. Schröder, S. J. George, M. Neumann, P. Chaudhuri, Inorg. Chem., still struggling with the referees.

Mn$_3$Cr III – Angular averaging



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

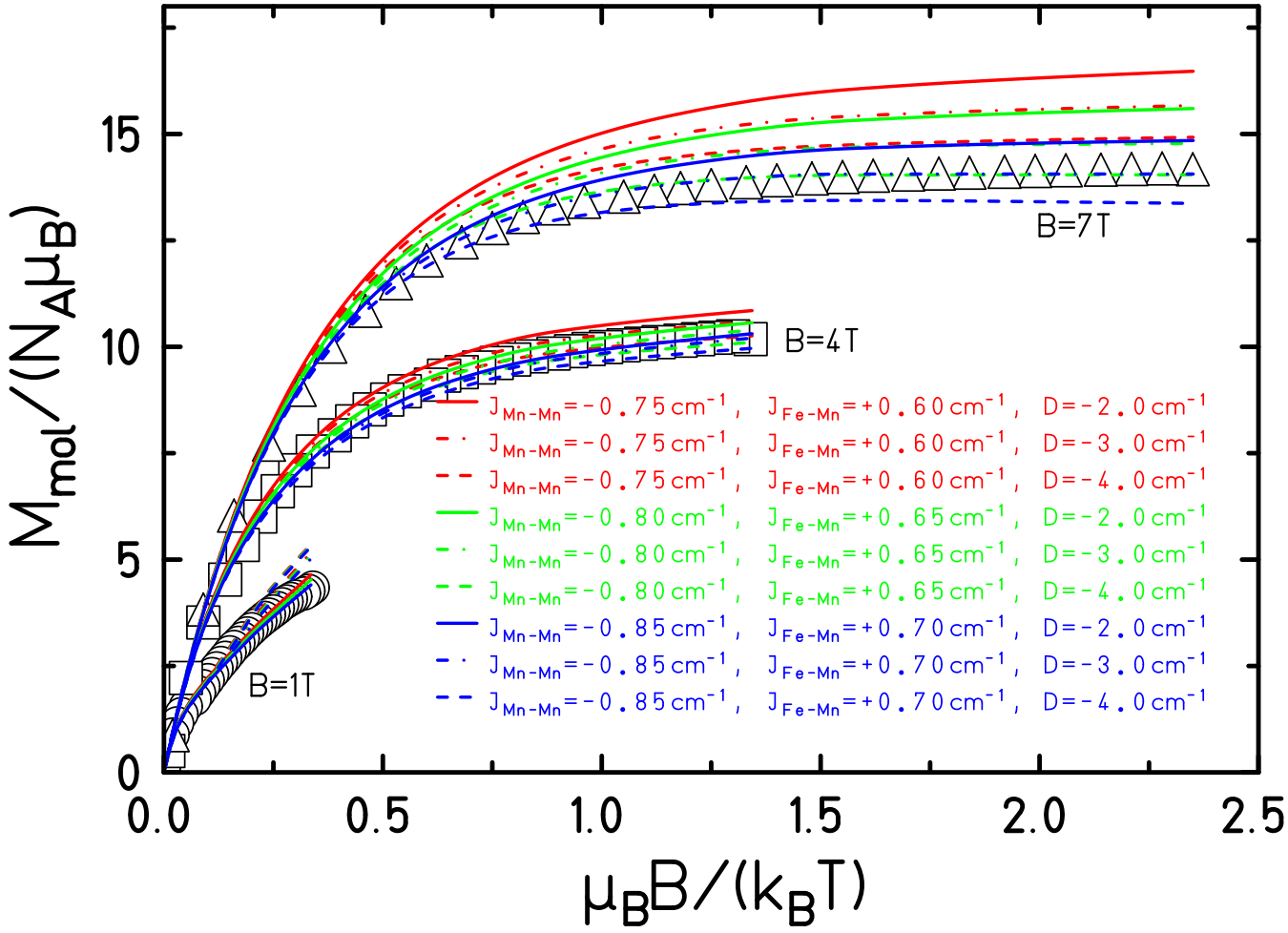
Mn$_6$Fe I



- 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.

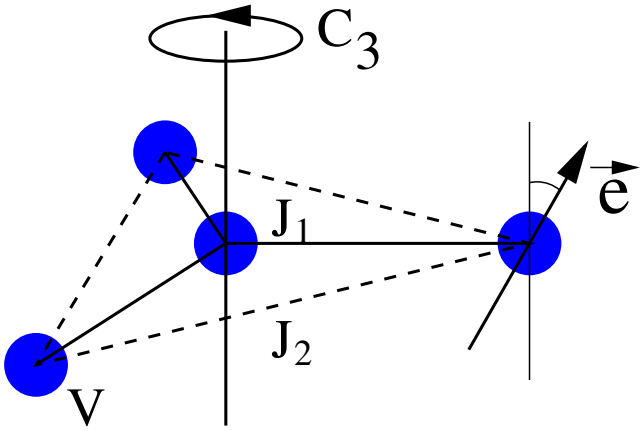
(1) T. Glaser, M. Heidemeier, T. Weyhermüller, R. D. Hoffmann, H. Rupp, P. Müller, Angew. Chem.-Int. Edit. **45**, 6033 (2006).
(2) T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, Inorg. Chem. **48**, 607 (2009).

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).

V_4 I

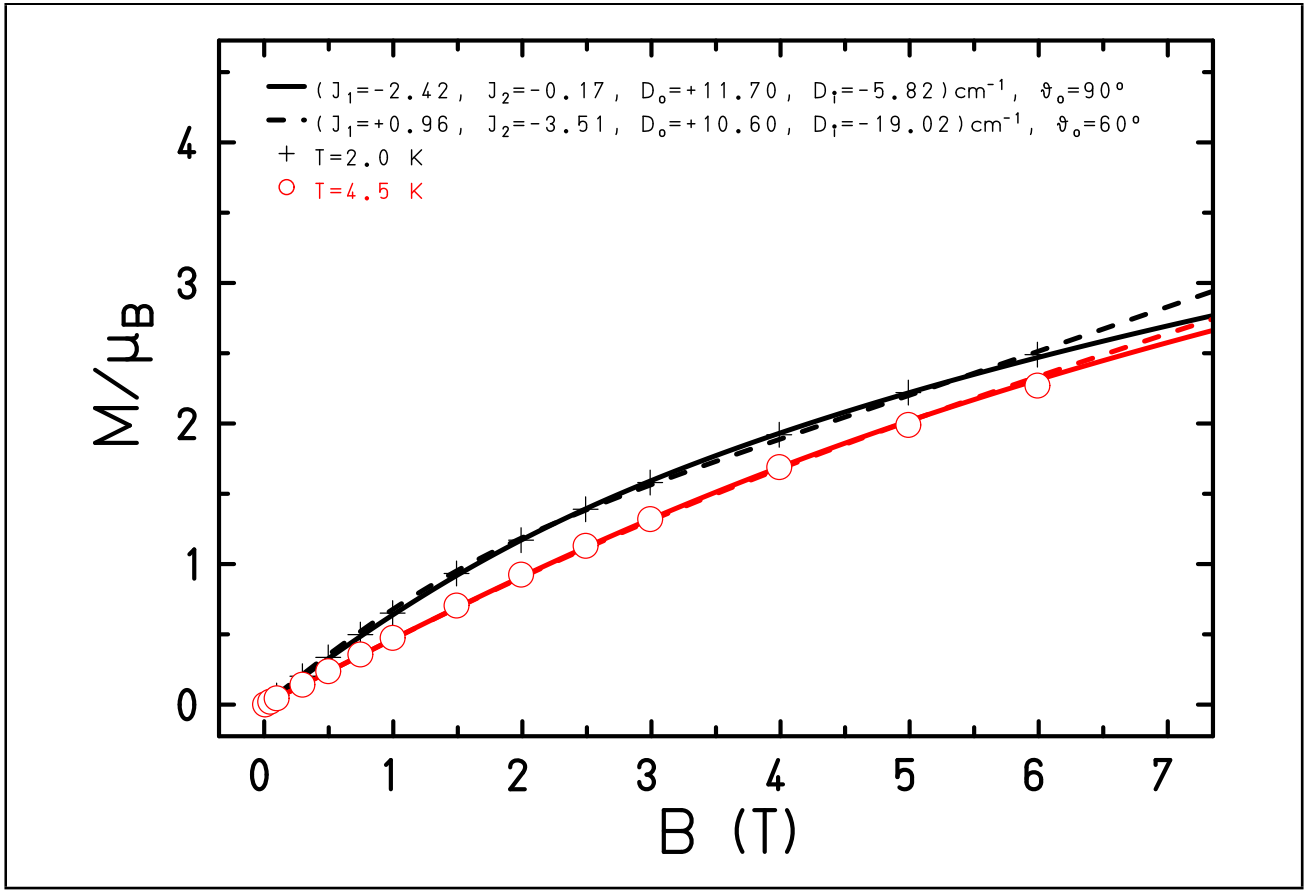


$[V^{III}_4Cl_6(thme)_2(bipy)_3]$

- 4 V^{III}_4 ions with $s = 1$; approximate C_3 symmetry;
- 2 exchange interactions;
- Central V: axial anisotropy;
- Outer Vs: local anisotropy axis with azimuthal angle ϑ.
- Powder average.

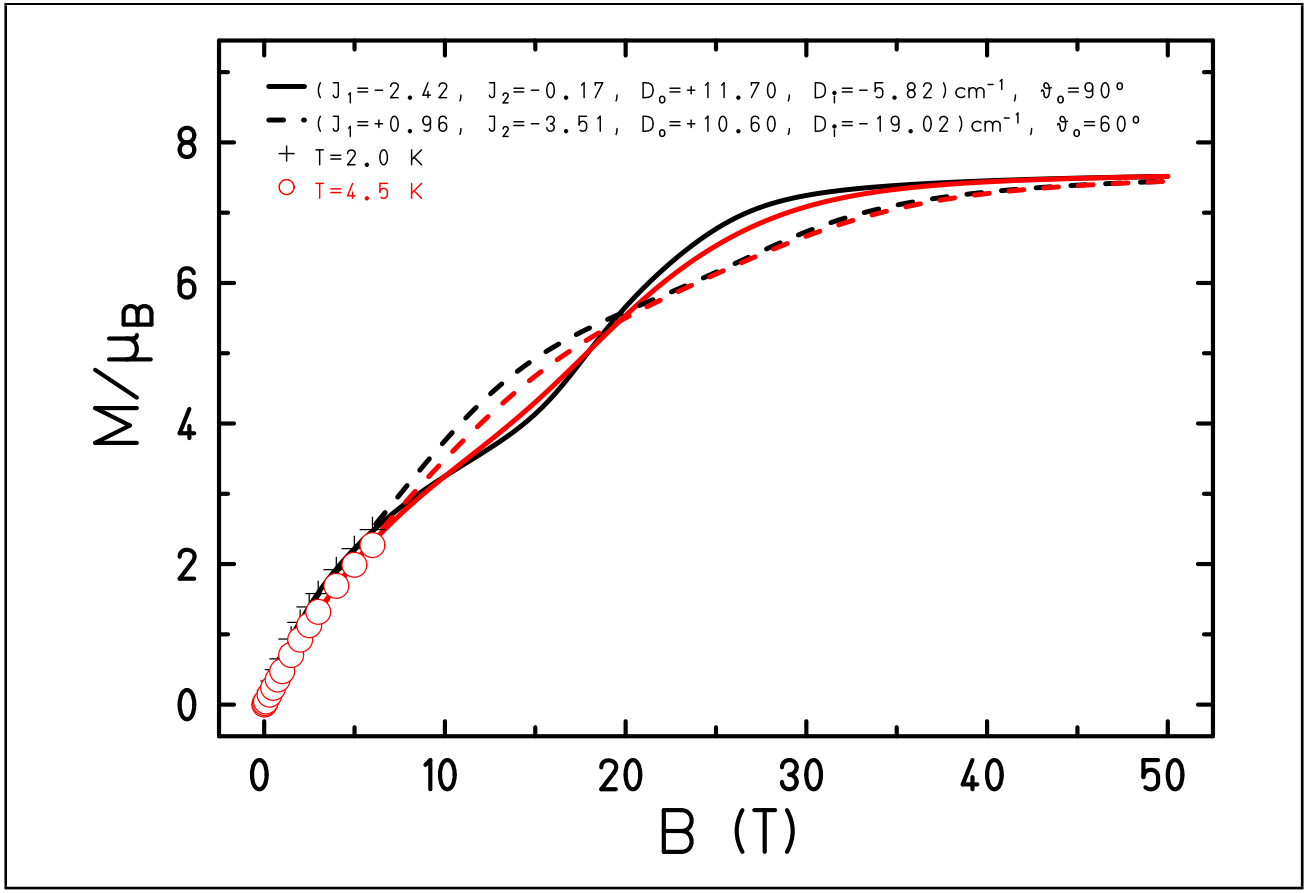
Ian S. Tidmarsh, Luke J. Batchelor, Emma Scales, Rebecca H. Laye, Lorenzo Sorace, Andrea Caneschi, Jürgen Schnack and Eric J.L. McInnes, Dalton Trans. (2009) 9402

V_4 II



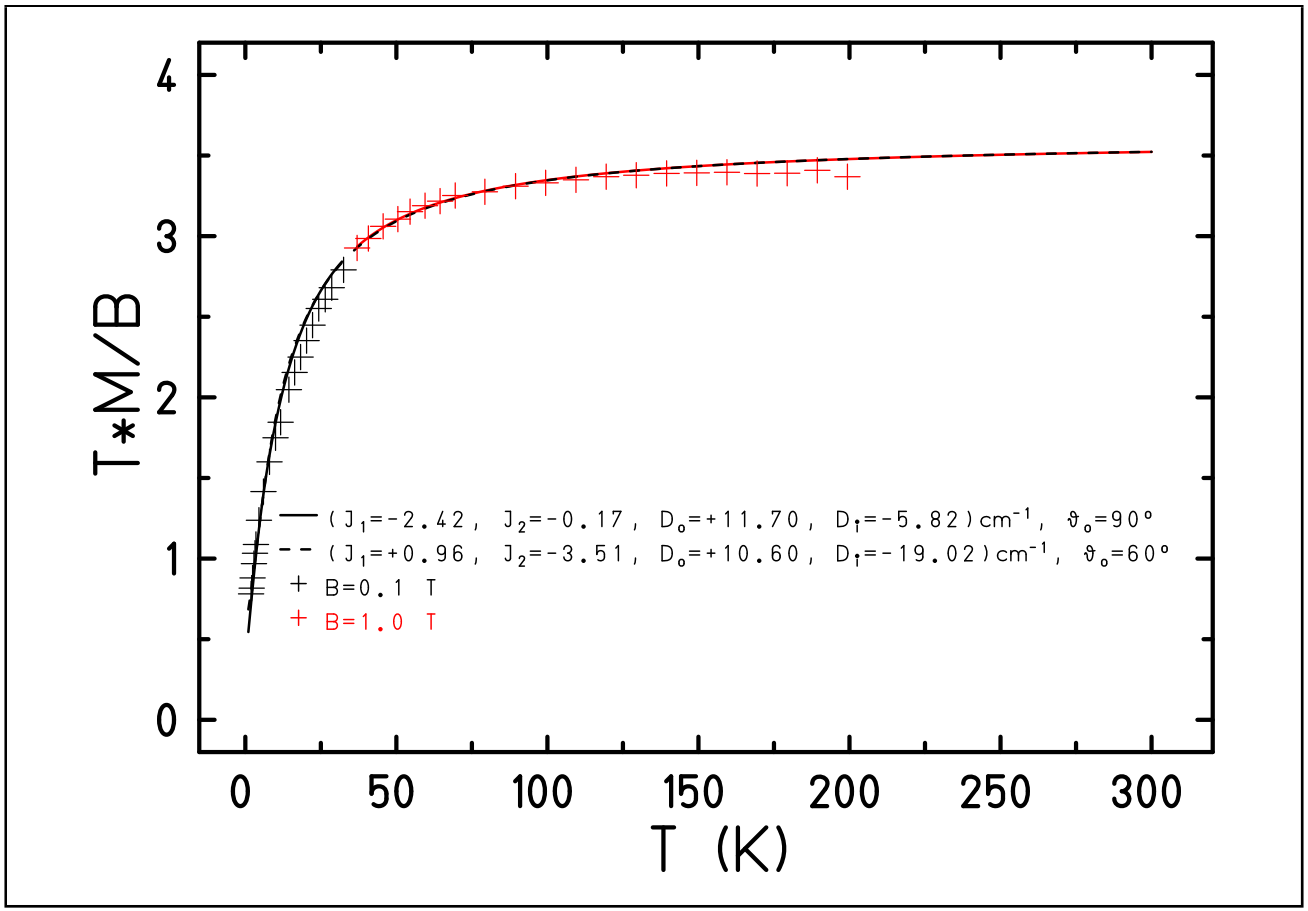
Two equally good parameter sets.

V_4 III



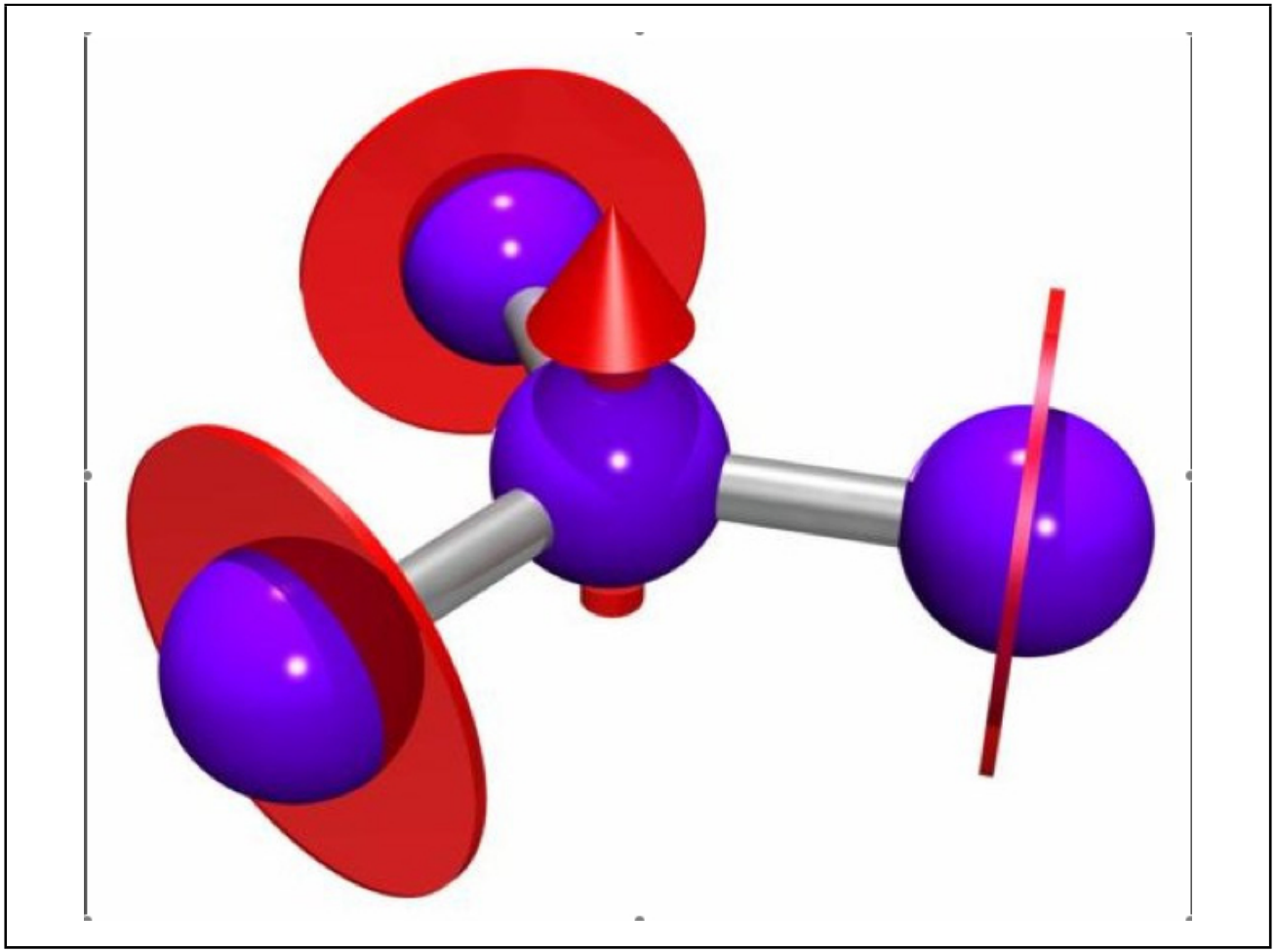
High fields could distinguish.

V$_4$ IV



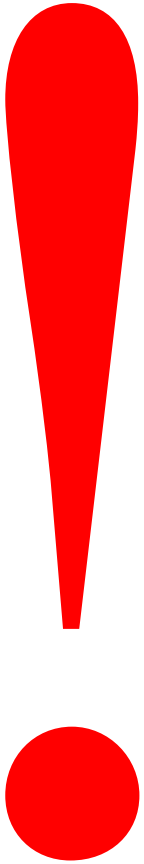
Accuracy of measurement limits modeling.

V_4 – Anisotropy tensors



Cartoon of anisotropy tensors.

Summary – Anisotropic molecules



- 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, i.e. also E–terms.
- Element-selective calculations possible.

Thank you very much for your attention.

Molecular Magnetism Web

www.molmag.de

Highlights. Tutorials. Who is who. Conferences.