Modelling of Isotropic and Anisotropic Magnetic Molecules

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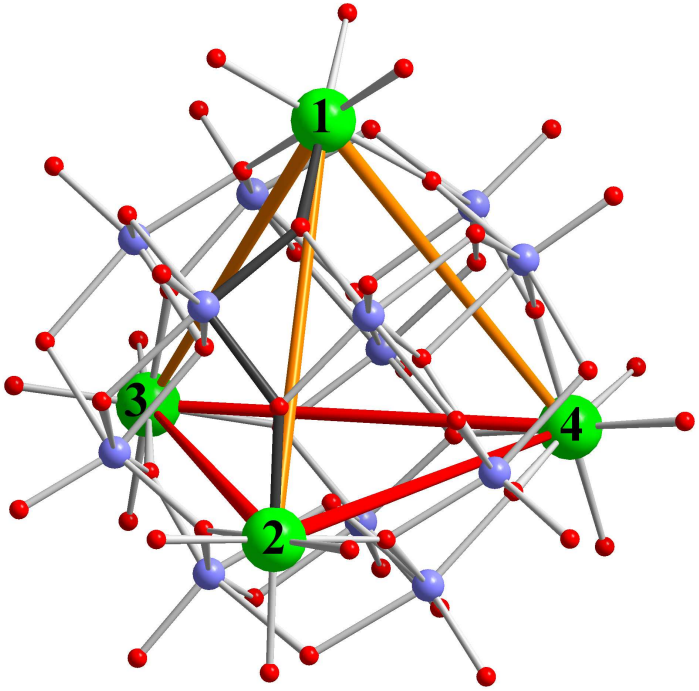
$\{Ni_4Mo_{12}\}$– summary and spin-offs

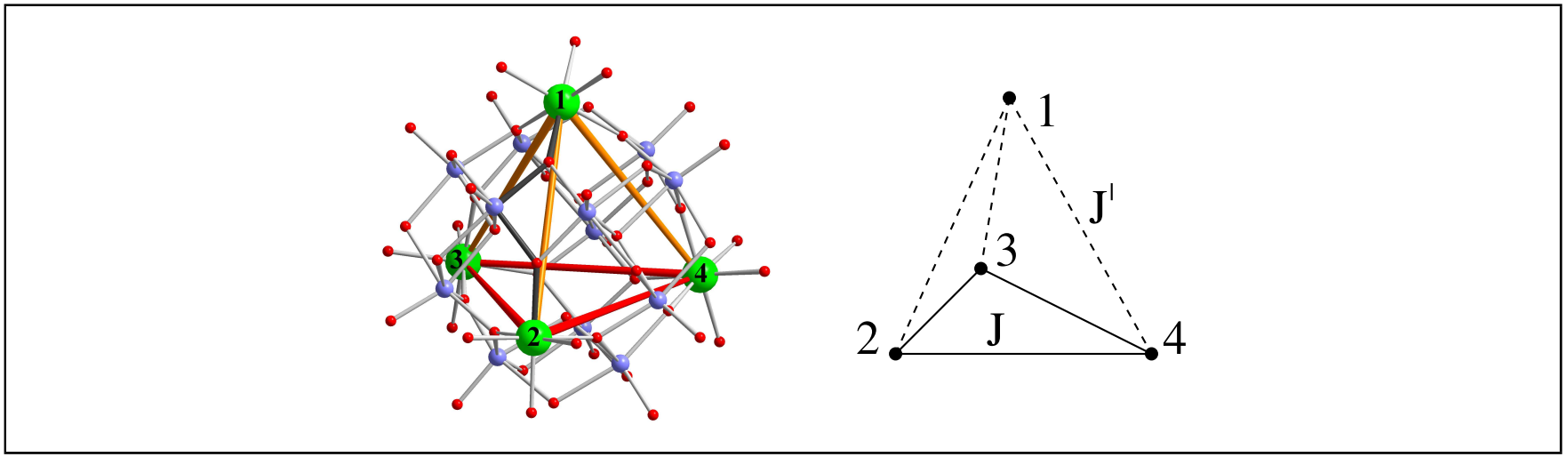


$\{Ni_4Mo_{12}\}$

1. $[Mo^{V}_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}(H_2O)_3\}_4]$
2. Anisotropic Molecules
3. Advanced ITO & Point Groups
4. www.molmag.de

[Mo$^{V}_{12}$O$_{30}$(μ_2-OH)$_{10}$H$_2${Ni^{II}(H$_2$O)$_3$}$_4$]

$[Mo^{V}_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}(H_2O)_3\}_4] = \{Ni_4Mo_{12}\}$



- Synthesis and structure of $\{Ni_4Mo_{12}\}$ (1)
- Ni-Ni distances: $d_{12} = 6.700(5)$ Å, $d_{13} = d_{14} = 6.689(1)$ Å, $d_{23} = d_{24} = 6.616(1)$ Å, $d_{34} = 6.604(1)$ Å.
- Superexchange interactions J' and J represented by dashed and solid lines.

(1) A. Müller, C. Beugholt, P. Kögerler, H. Bögge, S. Bud'ko, and M. Luban, Inorg. Chem. **39**, 5176 (2000)

$\{\mathbf{Ni_4Mo_{12}}\}$: naive expectations

Hamiltonian for almost perfectly tetrahedral symmetry and $s = 1$ (1)

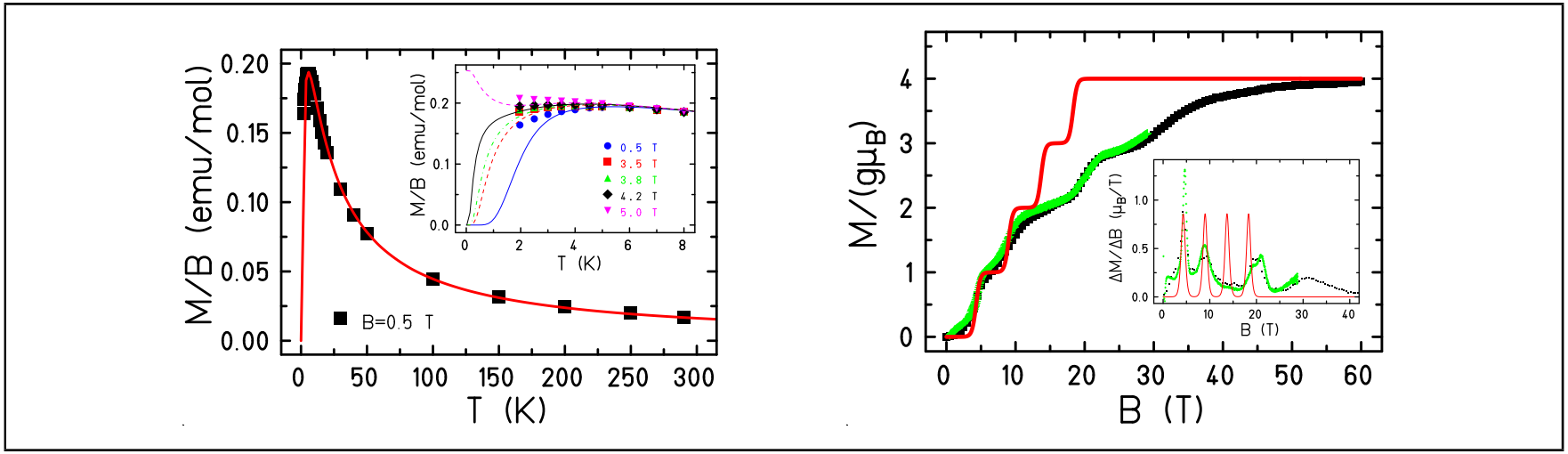
$$\underset{\sim}{H} = -2J \sum_{u<v} \underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v) + g\mu_B \vec{B} \cdot \sum_u \underset{\sim}{\vec{s}}(u) = -J \left[\underset{\sim}{\vec{S}}^2 - 4s(s+1) \right] + g\mu_B B \, \underset{\sim}{S}_z$$

Low-temperature magnetization curve $\mathcal{M}(B)$ should display four steps at

$$B_{S \to (S+1)} = -\frac{2J}{g\mu_B}(S+1)$$

(1) A. Müller, C. Beugholt, P. Kögerler, H. Bögge, S. Bud'ko, and M. Luban, Inorg. Chem. **39**, 5176 (2000)

$\{Ni_4Mo_{12}\}$: the reality



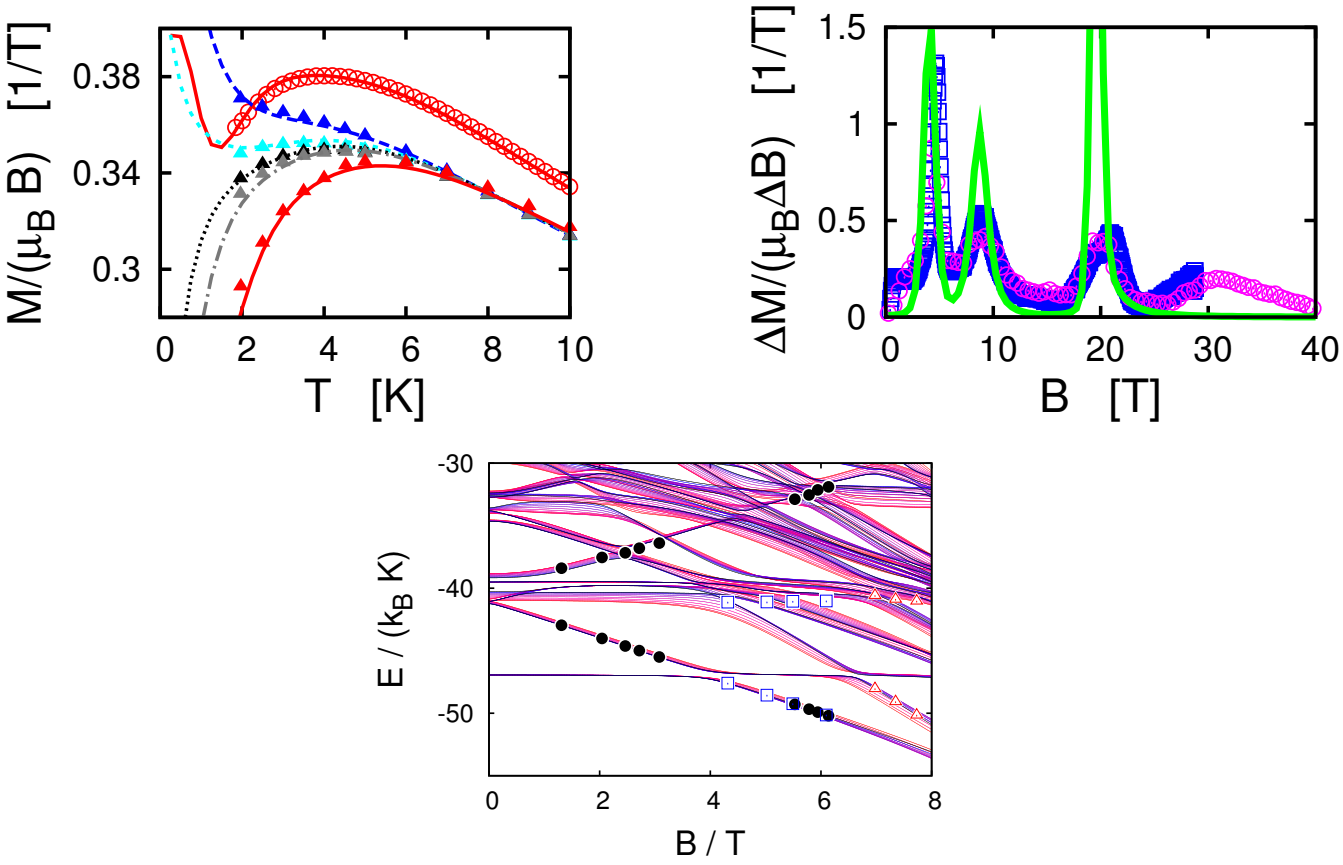
- Susceptibility reasonably well reproduced, finer details wrong.
- Magnetization deviates substantially: steps at 4.5, 8.9, 20.1, and 32 T.
- Use of two different exchange constants cannot account for the behavior.

$\{Ni_4Mo_{12}\}$: most general Hamiltonian

$$
\begin{aligned}
\underset{\sim}{H} &= \underset{\sim}{H}_{\mathsf{H}} + \underset{\sim}{H}_{\mathsf{ani}} + \underset{\sim}{H}_{\mathsf{biq}} + \underset{\sim}{H}_{\mathsf{Z}} \text{ , where} \\
\underset{\sim}{H}_{\mathsf{H}} &= -2 \sum_{u<v} J_{uv} \underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v) \\
\underset{\sim}{H}_{\mathsf{ani}} &= D \left[\sum_{u} \left(\vec{e}_r(u) \cdot \underset{\sim}{\vec{s}}(u) \right)^2 - \frac{8}{3} \right] \\
\underset{\sim}{H}_{\mathsf{biq}} &= \sum_{t,u,v,w} j_{tuvw} \left(\underset{\sim}{\vec{s}}(t) \cdot \underset{\sim}{\vec{s}}(u) \right) \left(\underset{\sim}{\vec{s}}(v) \cdot \underset{\sim}{\vec{s}}(w) \right) \\
\underset{\sim}{H}_{\mathsf{Z}} &= g \, \mu_B \, \vec{B} \cdot \sum_{u} \underset{\sim}{\vec{s}}(u)
\end{aligned}
$$

(1) J. Schnack, M. Brüger, M. Luban, P. Kögerler, E. Morosan, R. Fuchs, R. Modler, Hiroyuki Nojiri, Ram C. Rai, Jinbo Cao, J.L. Musfeldt, and Xing Wei, Phys. Rev. B **73**, 094401 (2006)

$\{Ni_4Mo_{12}\}$: results



(1) M. Brüger, Ph.D. thesis, Osnabrück University, 2008.
(2) U. Kortz, A. Müller, J. van Slageren, J. Schnack, N.S. Dalal, M. Dressel, Coord. Chem. Rev. (2009), accepted.

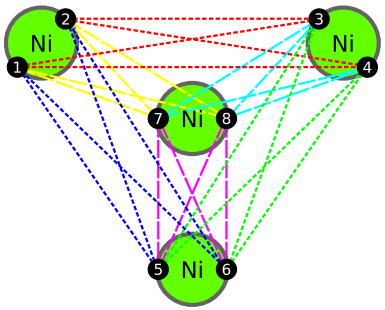
$\{Ni_4Mo_{12}\}$: interpretation

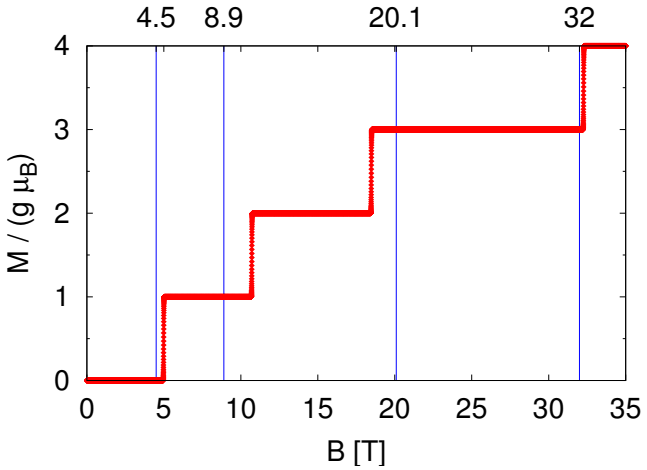
Interpretation of the generalized fourth-order terms:

- Higher order terms in the derivation of a spin Hamiltonian from the Hubbard model (1)
- Higher order terms in the derivation of a spin Hamiltonian from a spin-phonon Hamiltonian (2)
- Which scenario is valid? Maybe both!
- In the spin-phonon scenario the appearance of these terms means that the prefactors are not small. Since the prefactors are given by matrix elements of the Hesse matrix, this is equivalent to soft bonds! $\Rightarrow$ MAGNETOSTRICTION!
- These terms naturally lead to non-equidistant steps in the magnetization.

(1) V. V. Kostyuchenko, Phys. Rev. B **76**, 212404 (2007)
(2) M. Brüger, Ph.D. thesis, Osnabrück University, 2008.

$\{Ni_4Mo_{12}\}$: Hubbard model

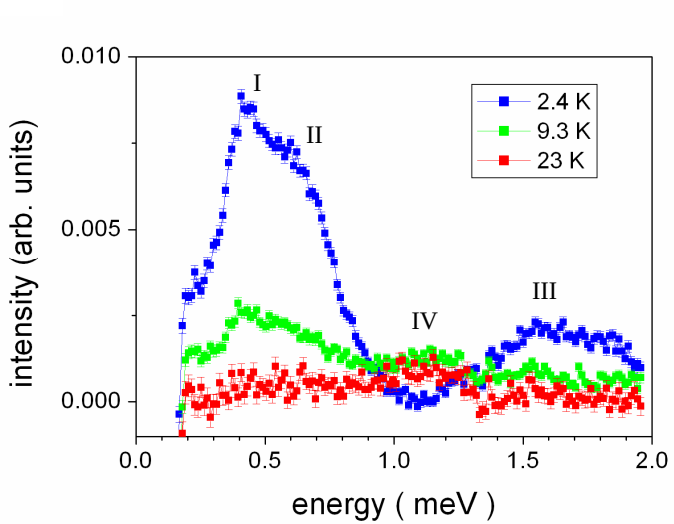




- Ref. (1) claims that magnetization steps can be obtained with a Hubbard model.
- $\underset{\sim}{H} = \sum_{i,j;\sigma} t_{ij} \underset{\sim}{c}^{\dagger}_{i,\sigma} \underset{\sim}{c}_{j,\sigma} + U \sum_i \underset{\sim}{n}_{i,\uparrow} \underset{\sim}{n}_{i,\downarrow} + g\mu_B B \underset{\sim}{S}^z$
- Result: Hubbard model does not explain the magnetization steps (2).
- Even additional two-band terms did not yield a good fit.

(1) V. V. Kostyuchenko, Phys. Rev. B **76**, 212404 (2007).
(2) M. Höck, Diploma thesis, Bielefeld University, 2008.

$\{Ni_4Mo_{12}\}$: Inelastic Neutron Scattering



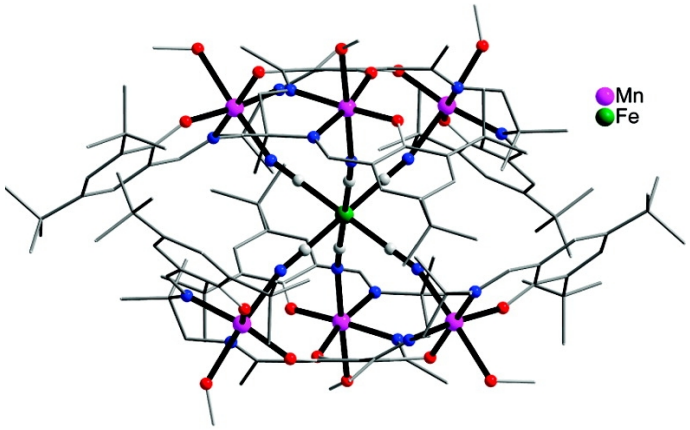
- Zero-field Inelastic Neutron Scattering for various temperatures;
- Data by O. Waldmann and J. Nehrkorn (1);
- Temperature dependence of peaks not compatible with general Hamiltonian . . .

(1) O. Waldmann, J. Nehrkorn, M. Brüger, M. Höck, J. Schnack, in preparation.

. . . will be continued.

Anisotropic Molecules

Anisotropic Molecules I



Rational design of strict C_3 symmetry:

- Idea of Thorsten Glaser:
  C_3 symmetric alignment of local easy axes
  (easy axis $\equiv$ Jahn-Teller axis);
- Various ions can be used so far,
  e.g. Mn_6Cr (1), Mn_6Fe (2), ...
- Problem: numerical simulation;
  Hilbert space dimensions large.

(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).

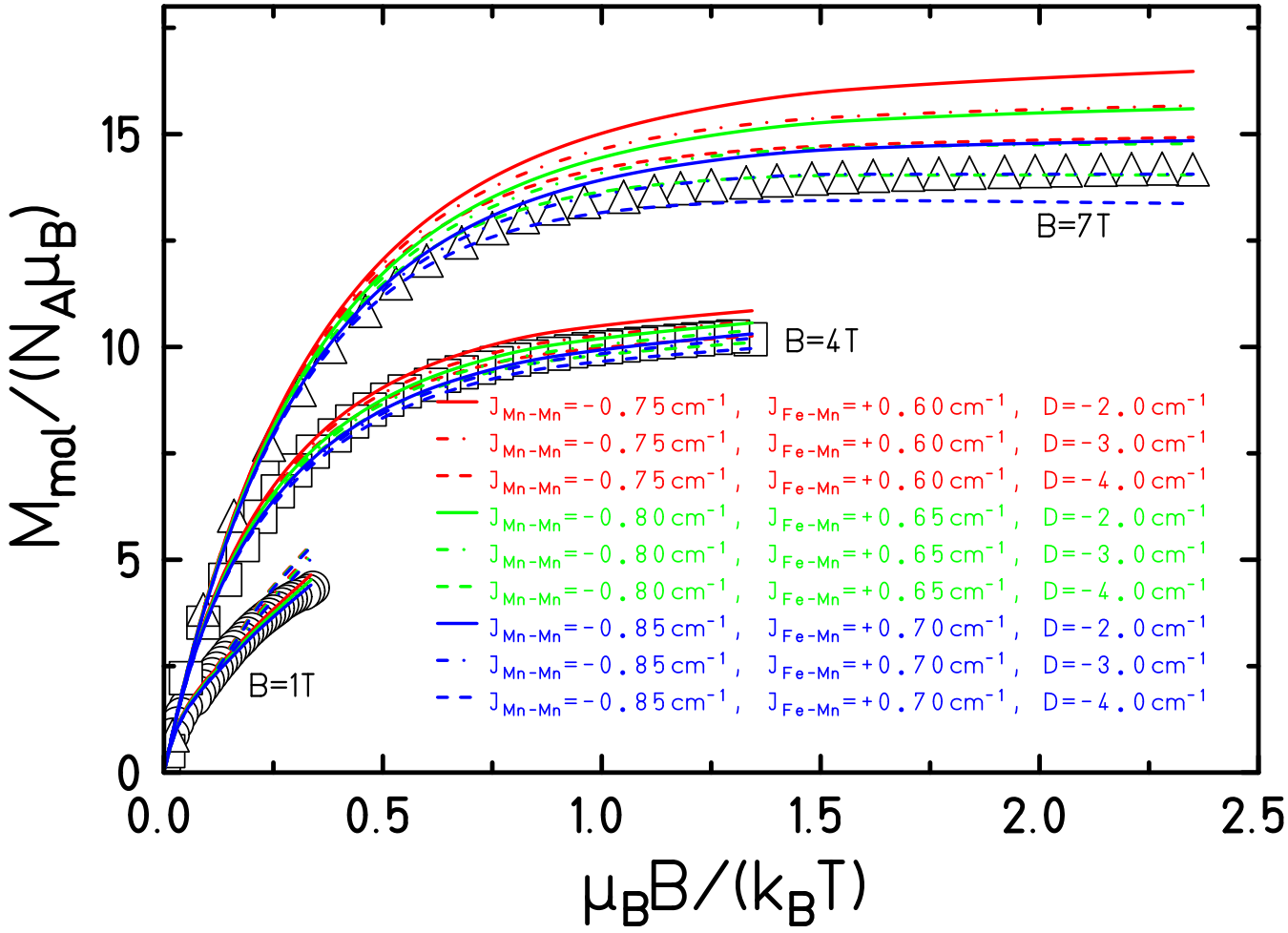
Anisotropic Molecules II – Theory

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

- $\left[\underset{\sim}{H}, \vec{\underset{\sim}{S}}^2\right] \neq 0, \left[\underset{\sim}{H}, \underset{\sim}{S}_z\right] \neq 0$
- You have to diagonalize $\underset{\sim}{H}(\vec{B})$ for every field (direction and strength)!
  $\Rightarrow$ Orientational average (Lebedev-Laikov grids (1)).
- If you are lucky, point group symmetries still exist. Use them!
- Easy: $\dim(\mathcal{H}) < 30000$; possible: $30000 < \dim(\mathcal{H}) < 140000$

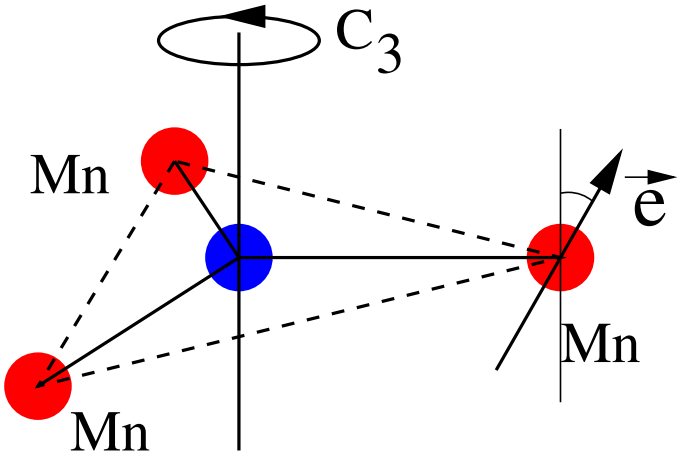
(1) V. I. Lebedev and D. N. Laikov, Dokl. Akad. Nauk **366**, 741 (1999); and link to program on `www.molmag.de`

Anisotropic Molecules III – Mn_6Fe



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

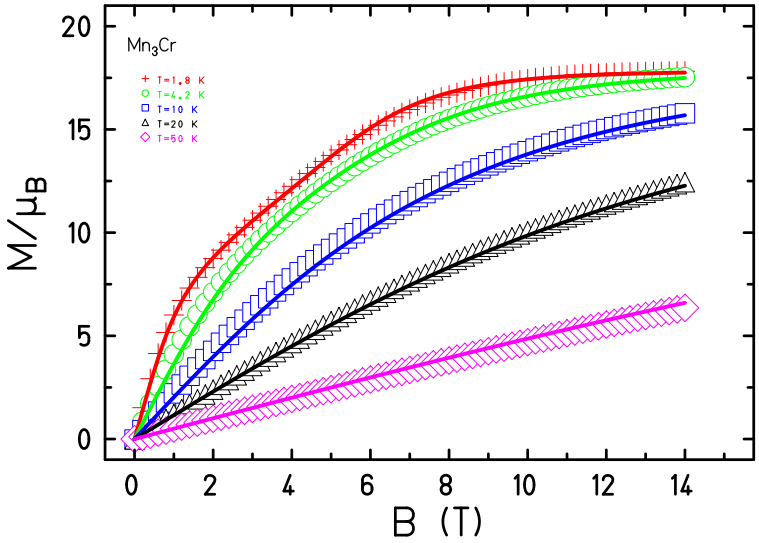
Anisotropic Molecules IV – Mn_3Cr Model

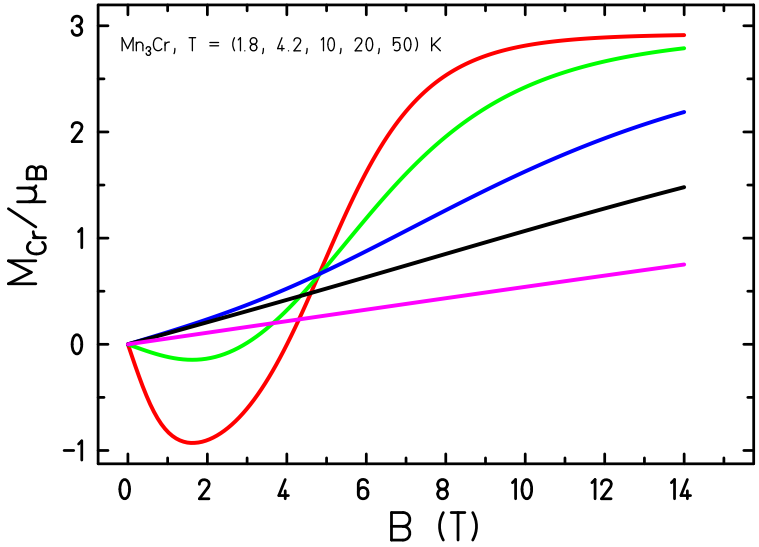


- Gross properties of Mn_3Cr in (1);
- Assume C_3 symmetry;
- Two couplings: J_1 to central Cr, J_2 between Mn; Mn: s=5/2, g=2.0; Cr: s=3/2, g=1.95.
- Model Mn anisotropy by local axis $\vec{e}(\vartheta, \phi)$. Due to C_3 symmetry $\vartheta_{\text{Mn1}} = \vartheta_{\text{Mn2}} = \vartheta_{\text{Mn3}}$. Only relative angle $\phi = 120°$ determined.
- Model Cr anisotropy by local axis $\vec{e}(\vartheta, \phi)$. Due to C_3 symmetry $\vartheta_{\text{Cr}} = 0$.

(1) S. Khanra, B. Biswas, C. Golze, B. Büchner, V. Kataev, T. Weyhermüller, P. Chaudhuri, Dalton Trans. 481 (2007).

Anisotropic Molecules V – Mn_3Cr Results



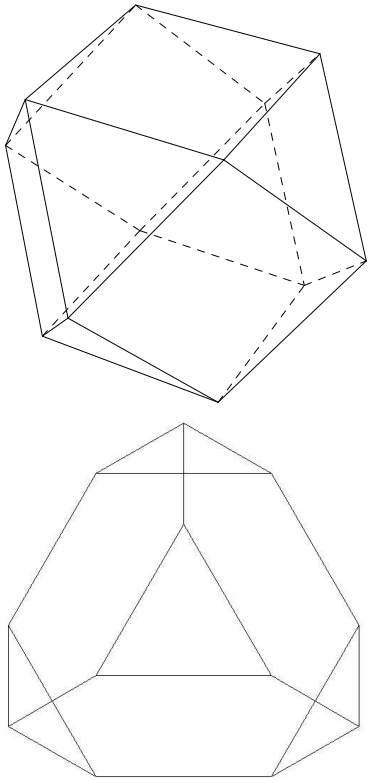


Result: $J_1 = -0.29$ cm^{-1}, $J_2 = -0.08$ cm^{-1},
$d_{\mathrm{Mn}} = -1.21$ cm^{-1}, $\vartheta_{\mathrm{Mn}} = 22°$, $d_{\mathrm{Cr}} = +0.17$ cm^{-1}.

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.

Advanced ITO & Point Groups

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 (2009), submitted; arXiv:0812.4126v1.

Advanced ITO & Point Groups II

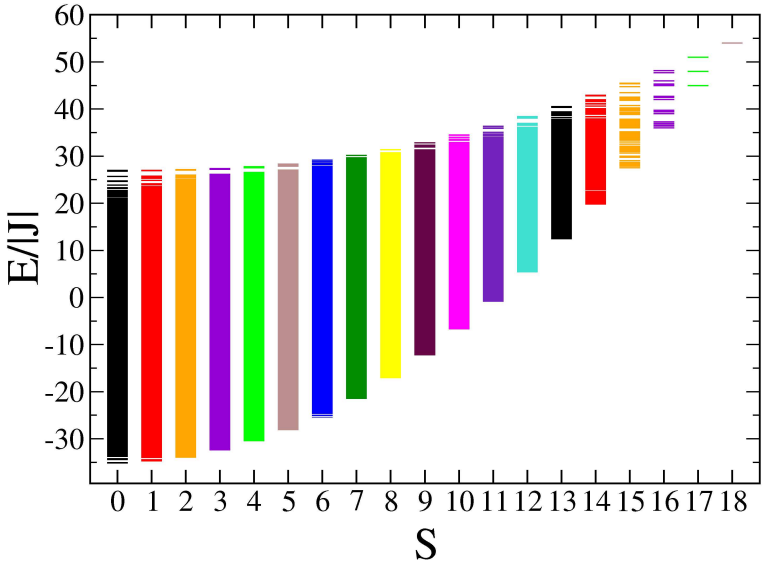
$$\underset{\sim}{G}(R)\,|\,\alpha\,S\,M\,\rangle_a = \sum_{\alpha'} |\,\alpha'\,S\,M\,\rangle_a\;{}_a\langle\,\alpha'\,S\,M\,|\,\alpha\,S\,M\,\rangle_b$$

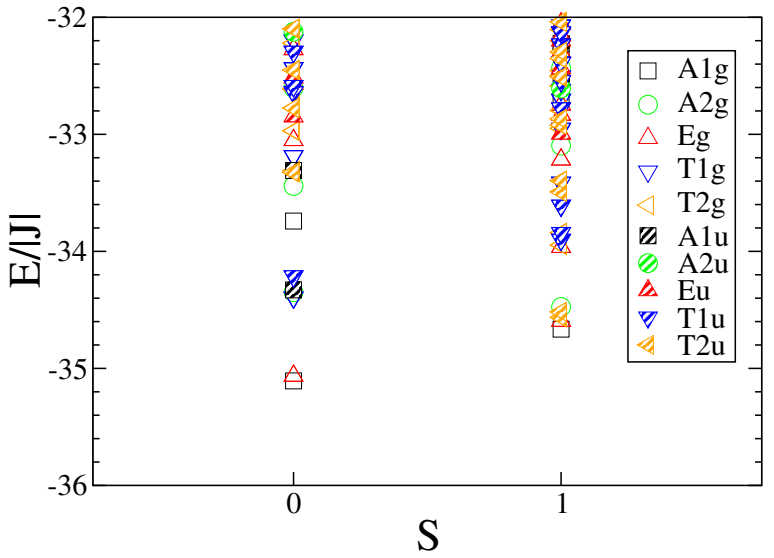
Problem: Recoupling

- 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) V. Fack, S. N. Pitre, and J. van der Jeugt, Comp. Phys. Comm. **101**, 155 (1997);
V. Fack, S. N. Pitre, and J. van der Jeugt, Comp. Phys. Comm. **86**, 105 (1995).

Advanced ITO & Point Groups III





Cuboctahedron, $s = 3/2$, Hilbert space dimension 16777216; symmetry O_h (1).
Evaluation of recoupling coefficients very time consuming. (1,2)

(1) J. Schnack and R. Schnalle, Polyhedron (2009), in press; arXiv:0810.2165v1;
(2) R. Schnalle and J. Schnack, Phys. Rev. B (2009), submitted; arXiv:0812.4126v1.

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www.molmag.de

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Dec 2008	536	356	167	59	909	4140113	1857	5206	11055	16626
Nov 2008	730	516	238	74	1173	6858040	2228	7166	15500	21917
Oct 2008	725	515	246	73	1100	5535402	2268	7646	15968	22502
Sep 2008	470	354	155	51	693	2768395	1535	4672	10641	14121
Aug 2008	405	248	137	49	497	6152376	1541	4277	7710	12567
Jul 2008	430	261	151	58	770	6577675	1812	4696	8103	13335
Jun 2008	469	287	173	78	929	7321311	2356	5192	8627	14088
May 2008	438	307	183	74	896	3259109	2301	5678	9546	13605
Apr 2008	422	292	168	62	746	3126317	1887	5054	8776	12675
Mar 2008	450	310	164	50	769	3456918	1572	5084	9611	13976
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