Field-dependent magnetic parameters in $\{Ni_4Mo_{12}\}$: Magnetostriction at the molecular level?

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Models and Theory for Molecular Magnetism

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unilogo-m-rot.jpg

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Entering new territory

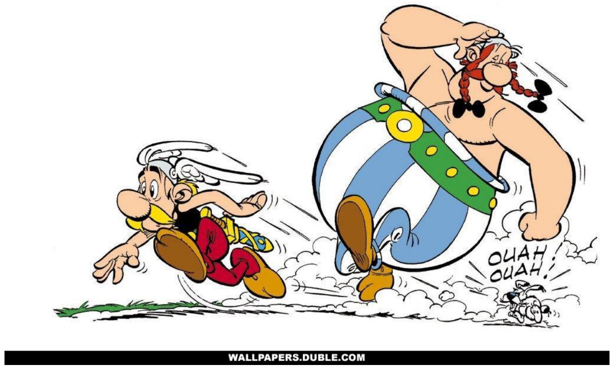
can be dangerous!

Proven with four examples from history and science.

Entering new territory

1. France 50 B.C.
2. Germany 9 AD
3. Hysteresis without anisotropy
4. Molecular magnetostriction!?

France 50 B.C.



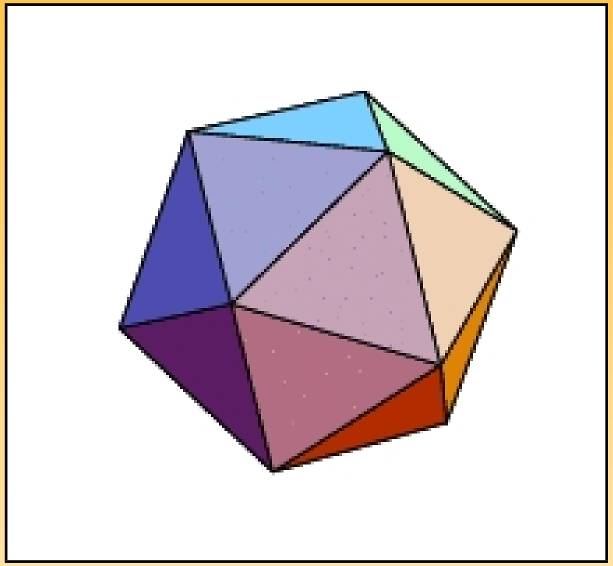
Nous sommes en 50 avant Jésus-Christ. Toute la Gaule est occupée par les Romains... Toute? Non! Un village peuplé d'irréductibles Gaulois résiste encore et toujours à l'envahisseur. Et la vie n'est pas facile pour les garnisons de légionnaires romains des camps retranchés de Babaorum, Aquarium, Laudanum et Petitbonum...

(The year is 50 B.C. Gaul is entirely occupied by the Romans. Well not entirely! One small village of indomitable Gauls still holds out against the invaders. And life is not easy for the Roman legionaries who garrison the fortified camps of Totorum, Aquarium, Laudanum and Compendium...)

Germany 9 AD


- Varus battle (9 AD) in *Kalkriese* close to Osnabrück, over 20.000 Romans killed;
- “Quintilius Varus, give me back my legions.” (Augustus)
- Proven due to coins from LUGDUNUM (Lyon), only coins before 9 AD found;
- Osnabrück remained barbarian: $\Rightarrow$ University founded not until 1974!

Introduction

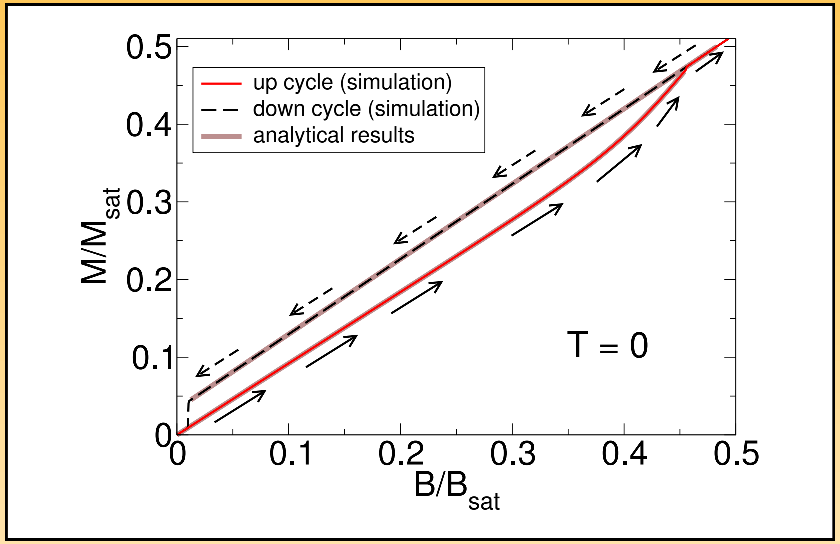


- Investigate antiferromagnetically coupled spins mounted on the vertices of an icosahedron.
- Isotropic Heisenberg exchange + applied magnetic field.
- Classical realization: magnetization jump, 1st order phase transition, hysteresis, metastability.
- Quantum realization: with increasing s unusual jumps of the magnetization.

Classical First Order $(T = 0)$ Phase Transition[1]

(1) If you feel the urge to discuss the term "phase transition", please let's do it during the coffee break. I will bring Ehrenfest along with me.

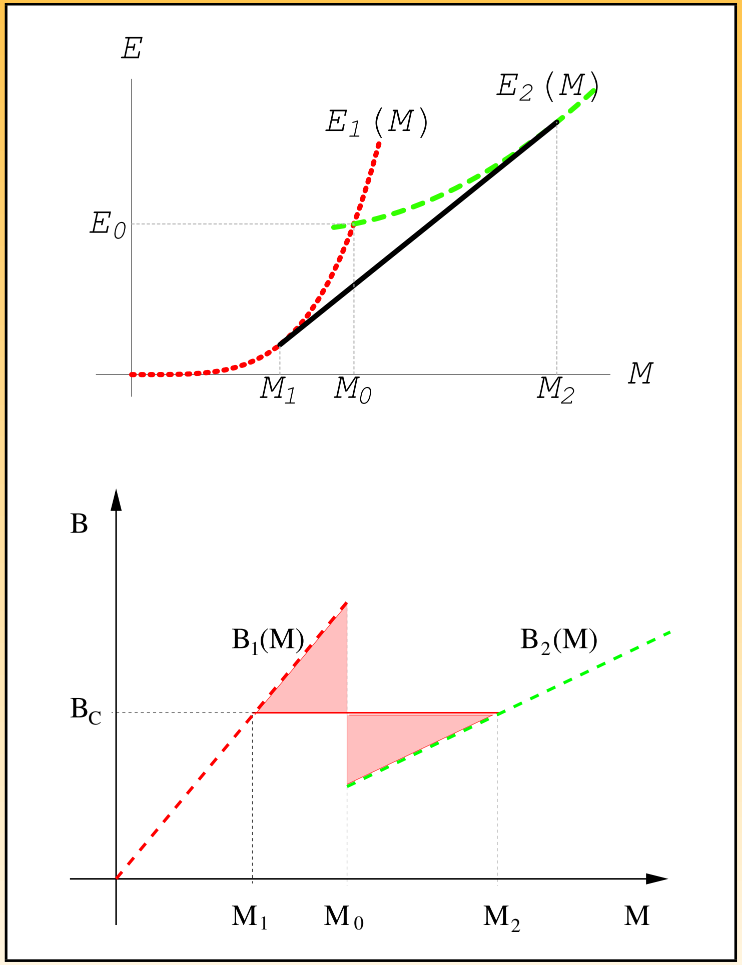
Metamagnetic phase transition I
Hyteresis without anisotropy



- Heisenberg model with isotropic nearest neighbor exchange
- Hysteresis behavior of the classical icosahedron in an applied magnetic field.
- Classical spin dynamics simulations (thick lines).
- Analytical stability analysis (grey lines).

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)

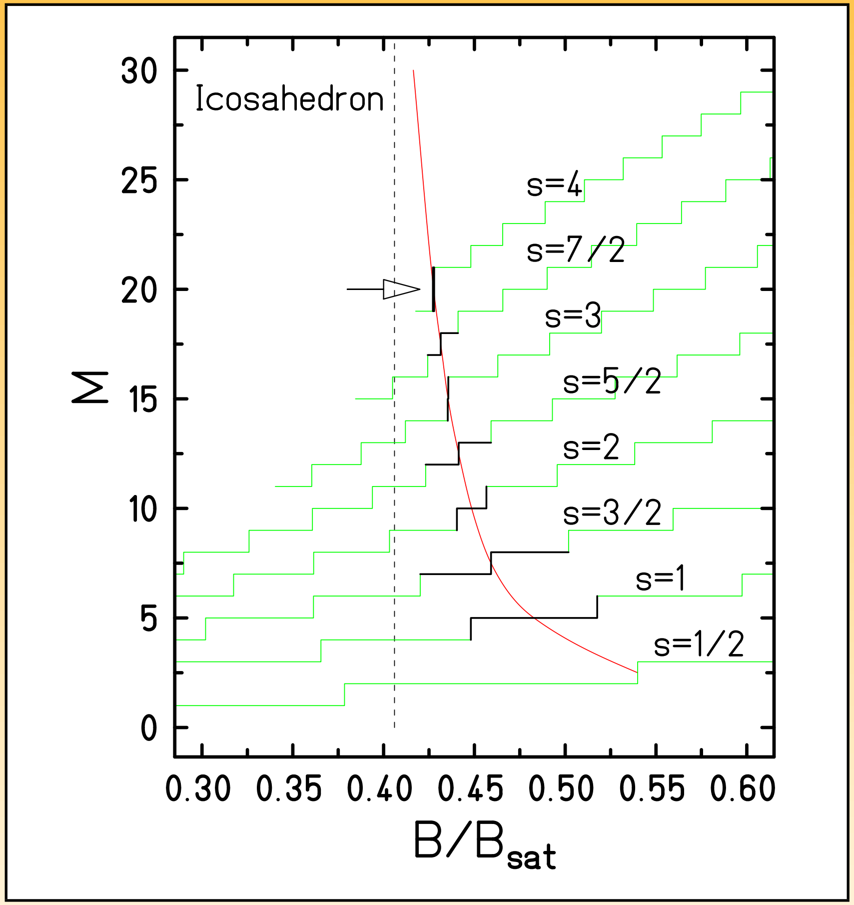
Metamagnetic phase transition II
Non-convex minimal energy



- Minimal energies realized by two families of spin configurations (1): $E_1(M)$ – "4-θ-family", $E_2(M)$ – "decagon family"
- Overall minimal energy curve is not convex.
- Maxwell construction yields ($T=0$) 1st order phase transition at B_c (1,2,3)
- ($T=0$)–magnetization dynamics extends into metastable region.

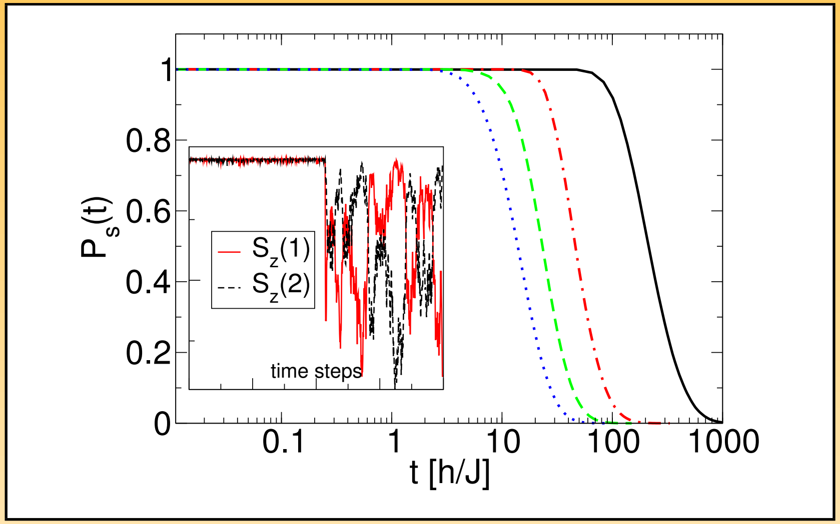
(1) C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)
(2) D. Coffey and S.A. Trugman, Phys. Rev. Lett. **69**, 176 (1992)
(3) C. Lhuillier and G. Misguich, in *High Magnetic Fields*, Eds. C. Berthier, L. Levy, and G. Martinez, Springer (2002) 161-190

Metamagnetic phase transition III
Quantum icosahedron



- Quantum analog:
  Non-convex minimal energy levels
  $\Rightarrow$ magnetization jump of $\Delta M > 1$.
- Lanczos diagonalization for various s.
- True jump of $\Delta M = 2$ for $s = 4$.
- Polynomial fit in $1/s$ yields the classically observed transition field.

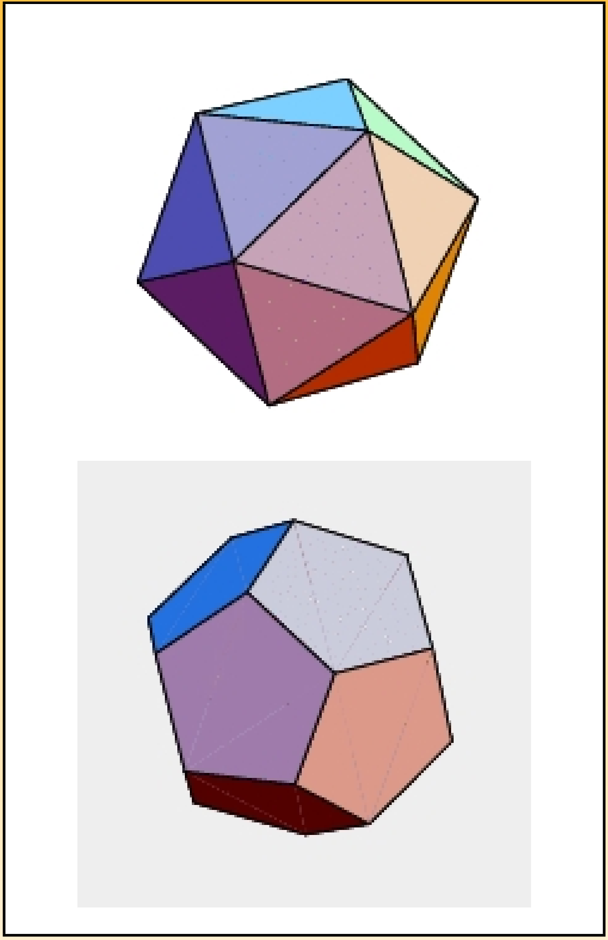
Metamagnetic phase transition IV
Metastability



- Classical spin dynamics simulations (Christian Schröder).
- Survival probability $P_s(t)$ for the metastable decagon phase subject to an external field $B/B_{sat} = 0.27$ for temperatures $k_BT/J = 0.025, 0.015, 0.005, 0.0005$ (left to right).
- Inset: Example trajectory of the system's time evolution at finite temperature.

C. Schröder, H.-J. Schmidt, J. Schnack, M. Luban, Phys. Rev. Lett. **94**, 207203 (2005)

Similar transitions



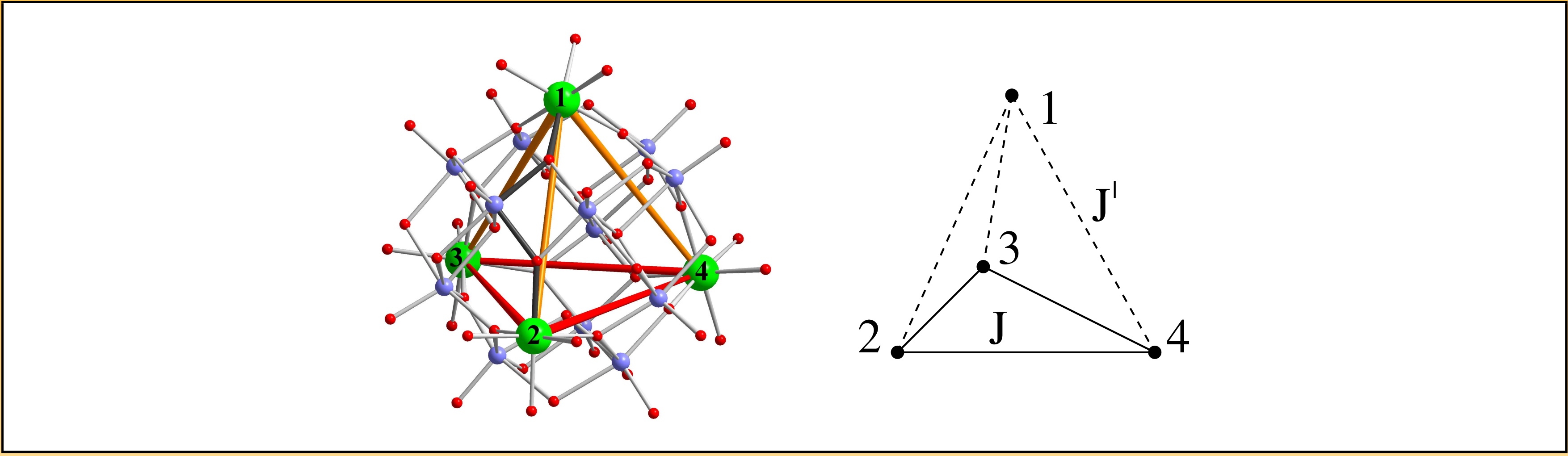
- First noticed in the context of the Buckminster fullerenes C_{20} and C_{60} (1).
- It seems to be important that the ground state is not coplanar and spins do not fold umbrella-like in field. The symmetry of low-field and high-field ground states needs to be different;
  Counter examples: $\{Mo_{72}Fe_{30}\}$, kagome lattice.
- This phase transition exists for many polytopes with icosahedral symmetry: numerical investigations for $20 \leq n \leq 720$ by N.P. Konstantinidis (2).

(1) D. Coffey and S.A. Trugman, Phys. Rev. Lett. **69**, 176 (1992).
(2) N.P. Konstantinidis, unpublished.

Magnetostriction

at the molecular level!?

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



- $[Mo^V_{12}O_{30}(\mu_2\text{-}OH)_{10}H_2\{Ni^{II}(H_2O)_3\}_4] = \{Ni_4Mo_{12}\}$ (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. Bogge, S. Bud'ko, and M. Luban, Inorg. Chem. **39**, 5176 (2000)

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

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

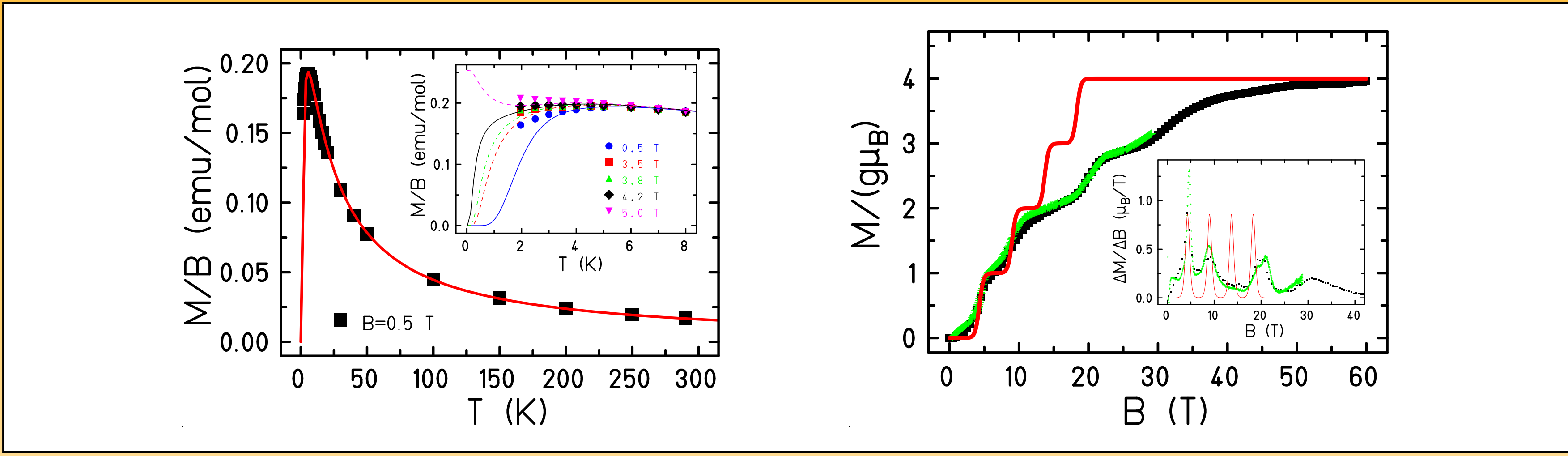
$$\underset{\sim}{H} = -2J \sum_{u<v} \underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v) + g\mu_B \vec{B} \cdot \sum_u \underset{\sim}{\vec{s}}(u) = -J\left[\underset{\sim}{\vec{S}}^2 - 4s(s+1)\right] + g\mu_B B\, \underset{\sim}{S}_z$$

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

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

(1) A. Müller, C. Beugholt, P. Kögerler, H. Bogge, 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

$$\underset{\sim}{H} = \underset{\sim}{H}_{\text{H}} + \underset{\sim}{H}_{\text{ani}} + \underset{\sim}{H}_{\text{biq}} + \underset{\sim}{H}_{\text{Z}} \, , \text{ where}$$

$$\underset{\sim}{H}_{\text{H}} = -2 \sum_{u<v} J_{uv} \underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v)$$

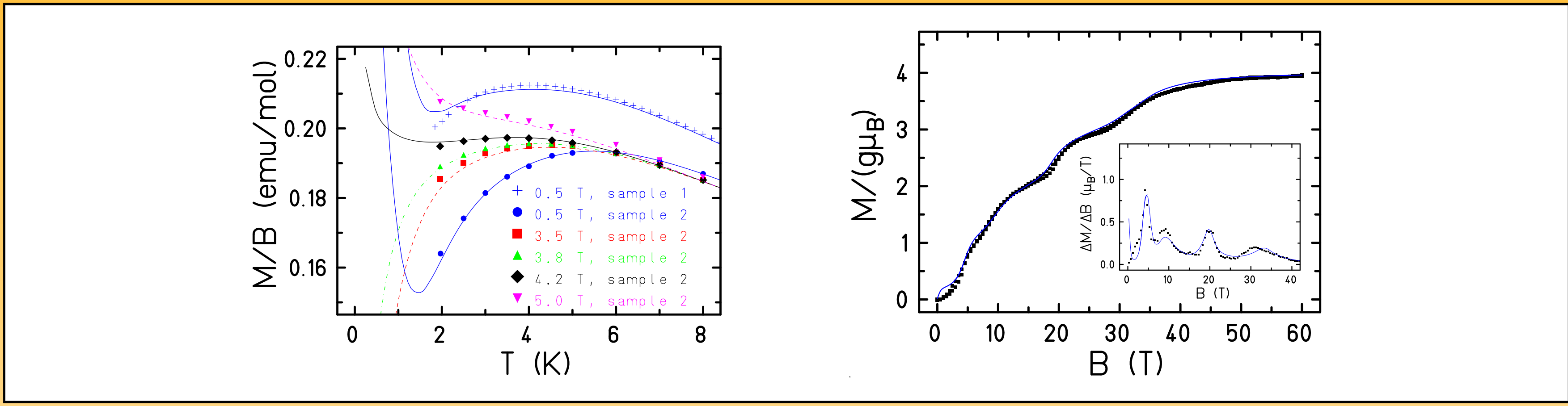
$$\underset{\sim}{H}_{\text{ani}} = D \left[\sum_{u} \left(\vec{e}_r(u) \cdot \underset{\sim}{\vec{s}}(u) \right)^2 - \frac{8}{3} \right]$$

$$\underset{\sim}{H}_{\text{biq}} = -2 \sum_{u<v} j_{uv} \left(\underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v) \right)^2$$

$$\underset{\sim}{H}_{\text{Z}} = g \, \mu_B \, \vec{B} \cdot \sum_{u} \underset{\sim}{\vec{s}}(u)$$

(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** (2006) 094401

$\{Ni_4Mo_{12}\}$: new concept – magnetostriction



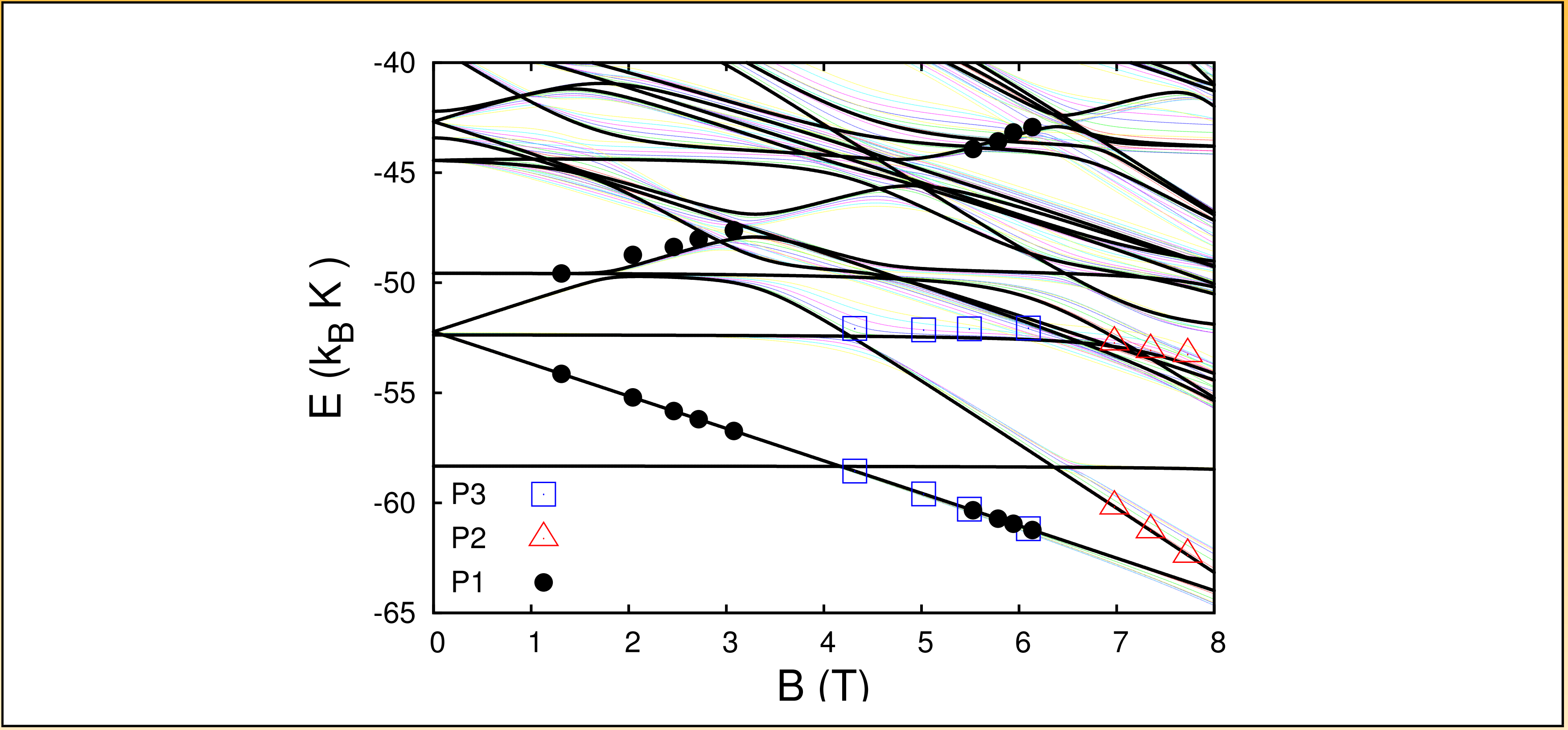
- Magnetic observables can only be understood when assuming that parameters of the Hamiltonian depend on field via field-induced structural changes (1).

- Two low-field parametrizations & a free Ni^{II} ions applied.

- High-field parametrization of the form $J(B) = J_0 \exp\left(\frac{|B|}{\gamma}\right)$.

(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** (2006) 094401

{Ni$_4$Mo$_{12}$}: EPR – a foretaste



The "spaghetti" Hamiltonian is in good agreement with Hiroyuki's EPR data. Nevertheless, extensive calculations are needed to simulate the powder sample.

{Ni_4Mo_{12}}: things to do

There is still a lot to do!

- Is direct evidence via field-dependent x-ray possible? Single crystals?
- Anisotropic exchange, Dzyaloshinskii-Moriya interaction?
- Infrared and Raman measurements by J. Musfeldt.
- Investigate the isostructural compounds containing Fe^{II} with $s = 2$ and Co^{II} with $s = 3/2$ instead of Ni^{II}.
- Can we advance Density Functional Theory (DFT) calculations to give a definite answer (1)?

(1) A.V. Postnikov, M. Brüger, and J. Schnack, Phase Transitions **78**, 47 (2005)

Thank you very much for your attention.

www.molmag.de

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