The painful Ni_4 story and other horrible tales

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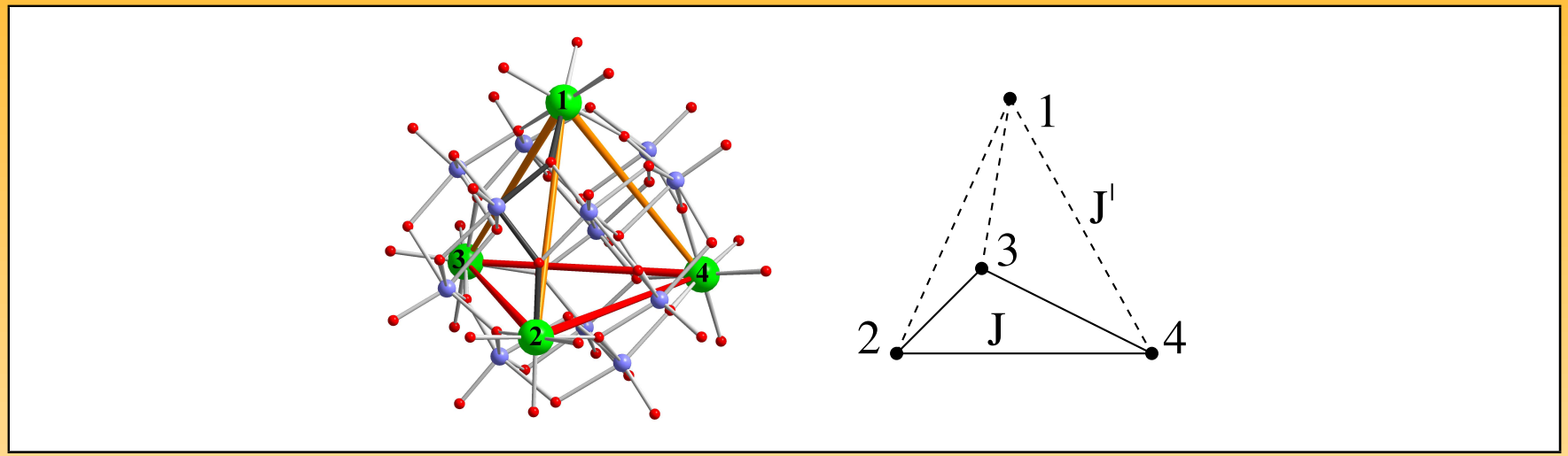
“The worldwide Ames group”

- K. Bärwinkel, H.-J. Schmidt, J. S., M. Allalen, M. Brüger, D. Mentrup, M. Exler, P. Hage, F. Hesmer, K. Jahns, F. Ouchni, R. Schnalle, P. Shechelokovskyy, S. Torbrügge (Uni Osnabrück);
- M. Luban, P. Kögerler, D. Vaknin (Ames Lab, Iowa, USA); J. Musfeldt (U. of Tennessee, USA);
- Chr. Schröder (FH Bielefeld & Ames Lab, Iowa, USA);
- R.E.P. Winpenny (Man U); L. Cronin (University of Glasgow);
- H. Nojiri (Tohoku University, Japan); N. Dalal (Florida State, USA);
- J. Richter, J. Schulenburg, R. Schmidt (Uni Magdeburg);
- S. Blügel, A. Postnikov (FZ Jülich); A. Honecker (Uni Braunschweig).
- E. Rentschler (Uni Mainz); U. Kortz (IUB); A. Tennant (HMI Berlin).

Contents

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



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

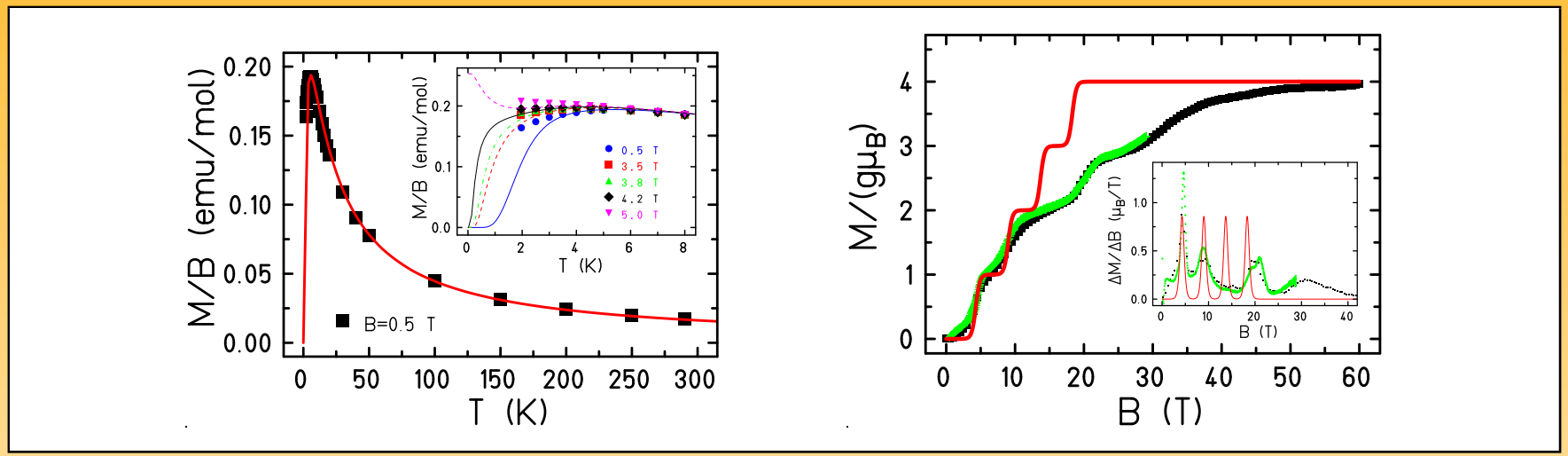
$$\underset{\sim}{H} = -2J \sum_{u<v} \underset{\sim}{\vec{s}}(u) \cdot \underset{\sim}{\vec{s}}(v) + g\mu_B \vec{B} \cdot \sum_u \underset{\sim}{\vec{s}}(u) = -J \left[\underset{\sim}{\vec{S}}^2 - 4s(s+1) \right] + g\mu_B B \, \underset{\sim}{S}_z$$

Low-temperature magnetization curve $\mathcal{M}(B)$ should display four steps at (2)

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

(1) A. Müller, C. Beugholt, P. Kögerler, H. Bogge, S. Bud'ko, and M. Luban, Inorg. Chem. **39**, 5176 (2000)
(2) 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, submitted, cond-mat/0509476

$\{Ni_4Mo_{12}\}$: 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.

(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, submitted, cond-mat/0509476

$\{Ni_4Mo_{12}\}$: options

How should we deal with such a problem?

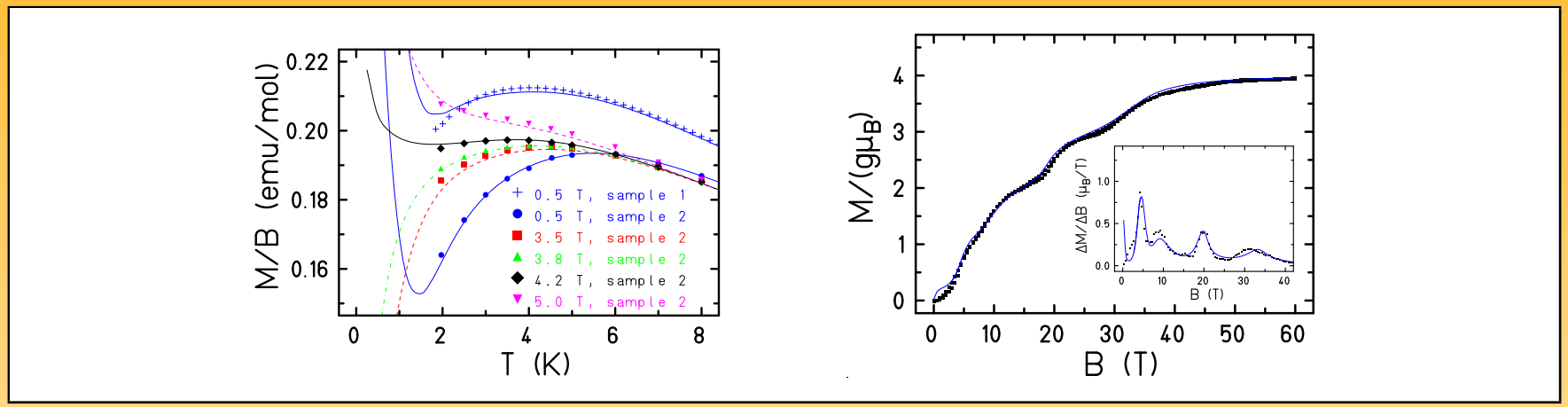
- If experimental data do not comply with theory, destroy the data! and Enough research will tend to support your theory! (Murphy)
- Set up to most general Hamiltonian.
- If this fails new concepts have to be considered.

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

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

(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, submitted, cond-mat/0509476

$\{Ni_4Mo_{12}\}$: 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, submitted, cond-mat/0509476

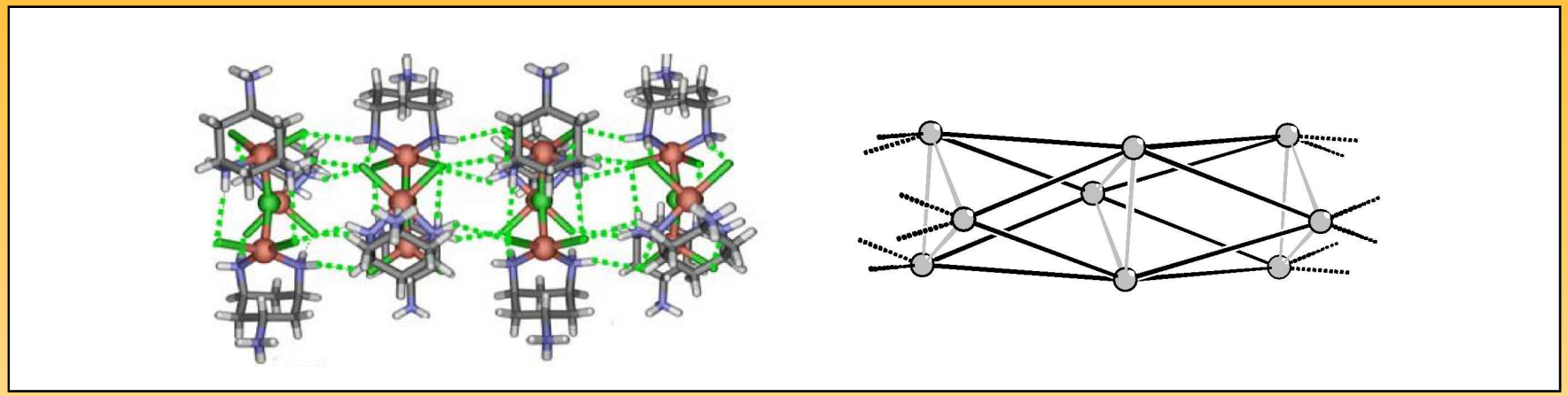
$\{Ni_4Mo_{12}\}$: things to do

There is still a lot to do!

- Is direct evidence via field-dependent x-ray possible? Single crystals?
- Anisotropic exchange, Dzyaloshinskii-Moriya interaction?
- Model the EPR spectra taken by Hiroyuki.
- 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)

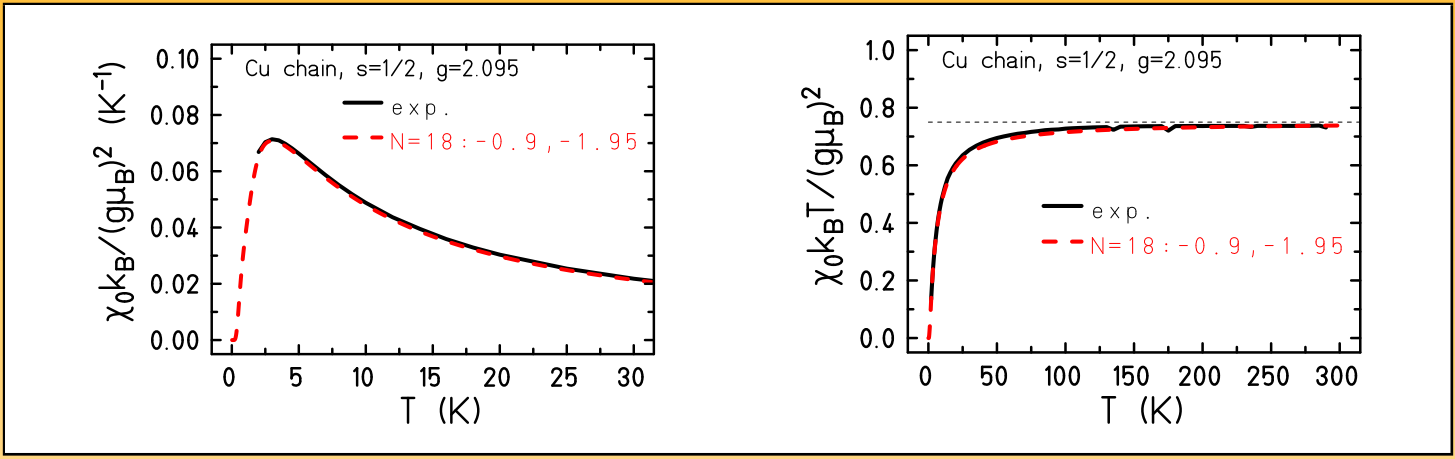
A frustrated triangular Cu chain



- $[(CuCl_2tachH)_3Cl]Cl_2$, tach $=$ *cis,trans*-1,3,5-triamino-cyclohexane (1)
- One-dimensional stack of antiprisms of af coupled equilateral copper(II) triangles: three-leg ladder with frustrated rung boundary condition.
- Intra-triangle couplings J_1 – grey lines, inter-triangle couplings J_2 – black lines.

(1) G. Seeber, P. Kögerler, B.M. Kariuki, and L. Cronin, Chem. Commun. (Cambridge) **2004**, 1580 (2004).

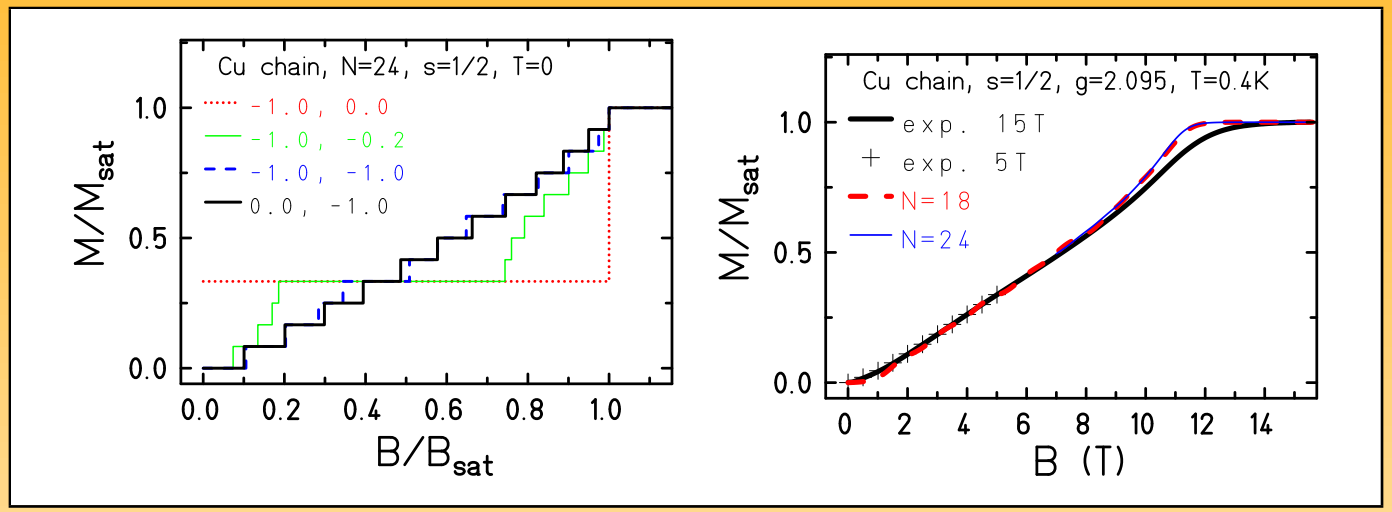
Triangular Cu chain: susceptibility



- Intra-triangle exchange J_1: bridging chloro ligand and hydrogen bonds; Cu-Cu distance is 4.46 Å.
- Inter-triangle exchange J_2: hydrogen-bonded Cu-Cl$\cdots$H-N-Cu super-exchange; Cu-Cu distance is 6.82 Å.
- Conjecture: weakly coupled triangles, i. e. $|J_2| \ll |J_1|$
  $\Rightarrow$ independent triangles at high T; effective spin-$1/2$ chain at low T: wrong!

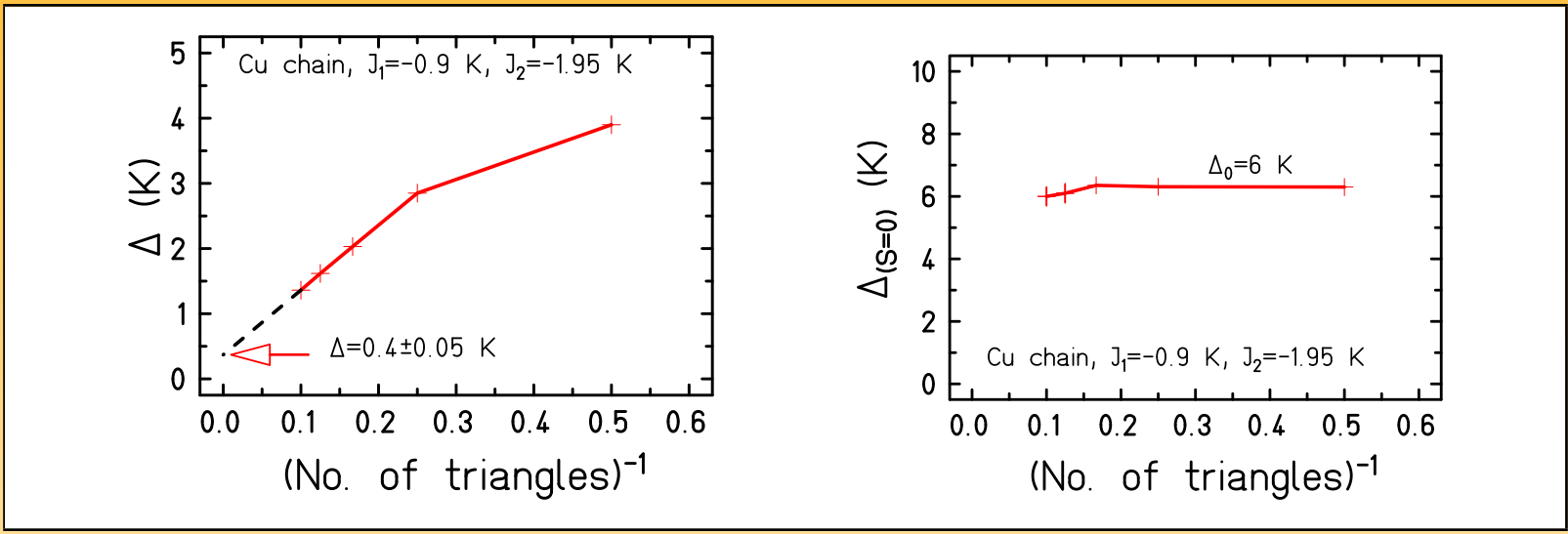
(1) J. Schnack, Hiroyuki Nojiri, P. Kögerler, G.J.T. Cooper, L. Cronin, Phys. Rev. B **70**, 174420 (2004)

Triangular Cu chain: magnetization



- Weakly coupled triangles: pronounced plateau at $1/3$ of the saturation magnetization. Magnetization measurement shows no plateau.
- Solution: isotropic Heisenberg model with antiferromagnetic exchange parameters $J_1 = -0.9$ K and $J_2 = -1.95$ K and $g = 2.095$ (average of small g-anisotropy).
- Deviations at high field: g-anisotropy and DM-interaction (?); deviations at low field: singlet-triplet gap overestimated in finite systems.

Triangular Cu chain: our gaps

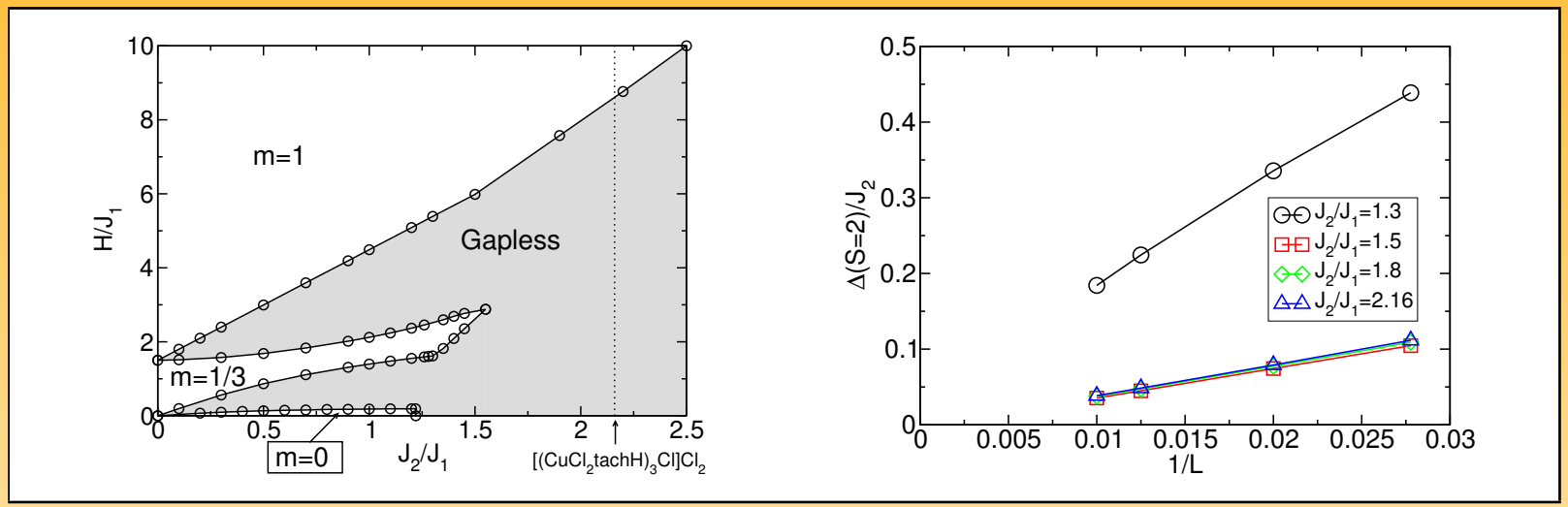


- Ground state non-degenerate (1),
  whereas should be twofold degenerate for weakly coupled triangles (2).

- Singlet-triplet gap $\Delta_{0-1} \gtrapprox 0.4$ K; singlet-singlet gap $\Delta_{0-0} \approx 6$ K

(1) J. Schnack, Hiroyuki Nojiri, P. Kögerler, G.J.T. Cooper, L. Cronin, Phys. Rev. B **70**, 174420 (2004)
(2) A. Lüscher, R. M. Noack, G. Misguich, V. N. Kotov, and F. Mila, Phys. Rev. B **70**, 060405(R) (2004)

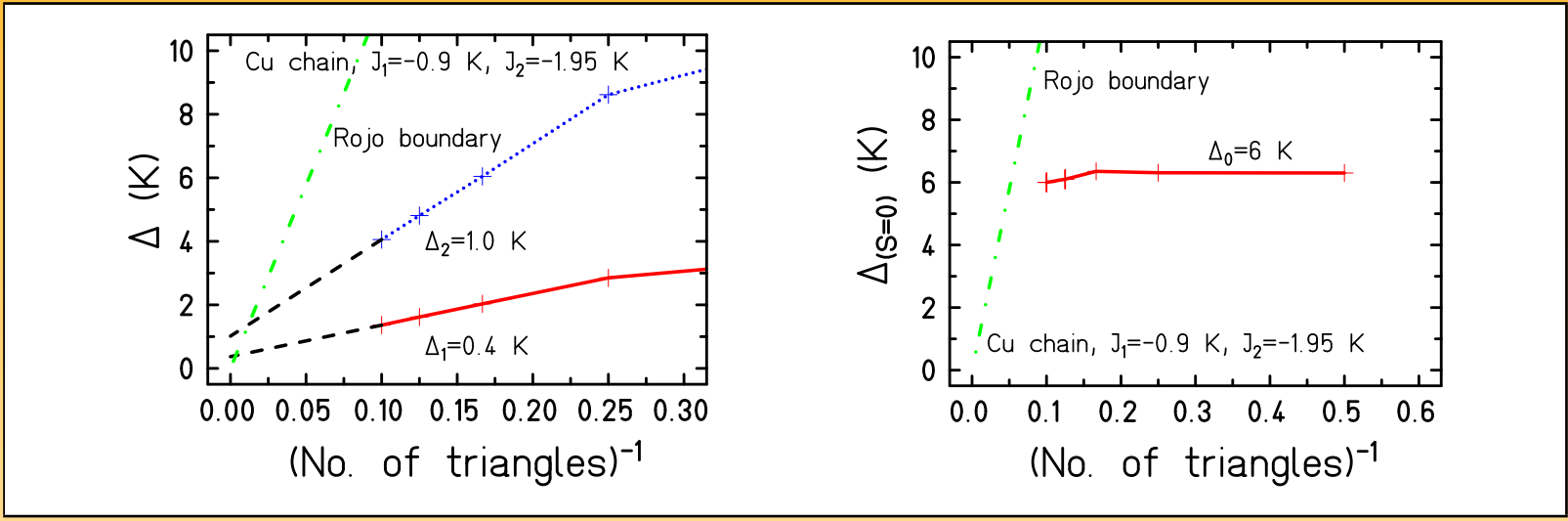
Triangular Cu chain: their gaps – no gaps!



- Chain can be mapped on either effective $s = 1/2$ chain with chirality for weak intertriangle coupling (degenerate ground state) or on a gapless effective $s = 3/2$ chain for strong intertriangle coupling (2). In addition, all three-lag ladders with half-integer spin are gapless or have a degenerate ground state (3)!

(1) J.-B. Fouet, A. Läuchli, S. Pilgram, R.M. Noack, F. Mila, cond-mat/0509217
(2) A. Lüscher, R.M. Noack, G. Misguich, V.N. Kotov, and F. Mila, Phys. Rev. B **70**, 060405(R) (2004)
(3) A.G. Rojo, Phys. Rev. B **53**, 9172 (1996)

Triangular Cu chain: our gaps II



- Finite size extrapolation problem?
- Rojo boundary (1) can be numerically tested for singlet-singlet gap $\Delta_{0-0} \approx 6$ K.
- Apart from the these poblems the real chain will be further investigated experimentally. Cu $\Rightarrow$ Ni?

(1) A.G. Rojo, Phys. Rev. B **53**, 9172 (1996)

Summary

Interesting physics can be done with magnetic molecules.

And, the future is wide open.