The painful Ni$_4$ story and other horrible tales

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“The worldwide Ames group”

- 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).
1. $[\text{Mo}^V_{12}\text{O}_{30}(\mu_2-\text{OH})_{10}\text{H}_2\{\text{Ni}^{\text{II}}(\text{H}_2\text{O})_3\}_4]$, a lifetime’s project  
   (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)

2. $[(\text{CuCl}_2\text{tachH})_3\text{Cl}]\text{Cl}_2$, a special triangular molecule-based spin tube  
   (J. Schnack, Hiroyuki Nojiri, P. Kögerler, G.J.T. Cooper, and L. Cronin)
\[ [\text{Mo}^{V}_{12}\text{O}_{30}(\mu_{2}-\text{OH})_{10}\text{H}_{2}\{\text{Ni}^{II}(\text{H}_{2}\text{O})_{3}\}_{4}] = \{\text{Ni}_{4}\text{Mo}_{12}\} \]

- \[ [\text{Mo}^{V}_{12}\text{O}_{30}(\mu_{2}-\text{OH})_{10}\text{H}_{2}\{\text{Ni}^{II}(\text{H}_{2}\text{O})_{3}\}_{4}] = \{\text{Ni}_{4}\text{Mo}_{12}\} \text{ (1)} \]

- Ni-Ni distances: \( d_{12} = 6.700(5) \text{ Å}, d_{13} = d_{14} = 6.689(1) \text{ Å}, d_{23} = d_{24} = 6.616(1) \text{ Å}, d_{34} = 6.604(1) \text{ Å} \).

- Superexchange interactions \( J' \) and \( J \) represented by dashed and solid lines.

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

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

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

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

\{Ni_{4}Mo_{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.

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.
\( \{ \text{Ni}_4\text{Mo}_{12} \} : \) most general Hamiltonian

\[
H \sim = H_H + H_{\text{ani}} + H_{\text{biq}} + H_Z , \text{ where}
\]

\[
H_H = -2 \sum_{u < v} J_{uv} \vec{s}(u) \cdot \vec{s}(v)
\]

\[
H_{\text{ani}} = D \left[ \sum_u (\vec{e}_r(u) \cdot \vec{s}(u))^2 - \frac{8}{3} \right]
\]

\[
H_{\text{biq}} = -2 \sum_{u < v} j_{uv} \left( \vec{s}(u) \cdot \vec{s}(v) \right)^2
\]

\[
H_Z = g \mu_B \vec{B} \cdot \sum_u \vec{s}(u)
\]

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\textsuperscript{II} ions applied.

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

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

- \([(\text{CuCl}_2\text{tachH})_3\text{Cl}]\text{Cl}_2\), tach = \text{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.

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···H-N-Cu super-exchange; Cu-Cu distance is 6.82 Å.

- Conjecture: weakly coupled triangles, i.e. $|J_2| \ll |J_1|$ ⇒ independent triangles at high $T$; effective spin-1/2 chain at low $T$: wrong!

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

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
Finite size extrapolation problem?

Rojo boundary (1) can be numerically tested for singlet-singlet gap $\Delta_0 - 0 \approx 6$ K.

Apart from these problems the real chain will be further investigated experimentally. 😎 Cu ⇒ Ni?

Interesting physics can be done with magnetic molecules.

And, the future is wide open.