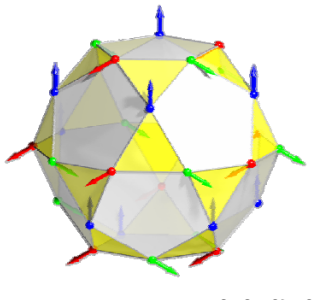
Spin freezing and slow magnetization dynamics in geometrically frustrated magnetic molecules with exchange disorder



Christian Schröder

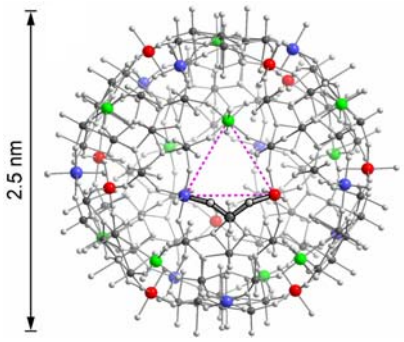
University of Applied Sciences, Bielefeld
& Ames Laboratory, Ames, Iowa, USA

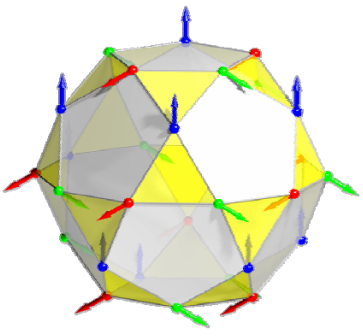
in collaboration with
Luban, R. Prozorov, F. Borsa, and K. Kumagai

A family of famous magnetic molecules

The fancy "Keplerate" molecules $\{Mo_{72}Fe_{30}\}$[1] and $\{Mo_{72}Cr_{30}\}$[2] ($\{Mo_{72}V_{30}\}$ not considered here)

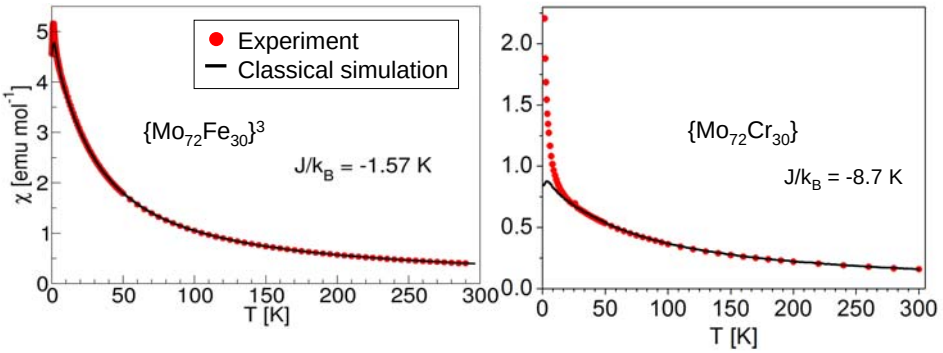
- 30 paramagnetic Fe^{3+} or Cr^{3+} ions (S = 5/2 or 3/2) embedded on the vertices of an icosidodecahedron → Hilbert space dimension ~ 10^{23} and 10^{18}!





[1] A. Müller, S. Sarkar, S.Q.N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. Trautwein, and V. Schünemann, Angew. Chem., Int. Ed. Engl. **38**, 3238 (1999)
[2] A. M. Todea, A. Merca, H. Bögge, J. van Slageren, M. Dressel, L. Engelhardt, M. Luban, T. Glaser, M. Henry, and A. Müller, Angew. Chem. Int. Ed. **46**, 6106 (2007)

Basic thermodynamic properties

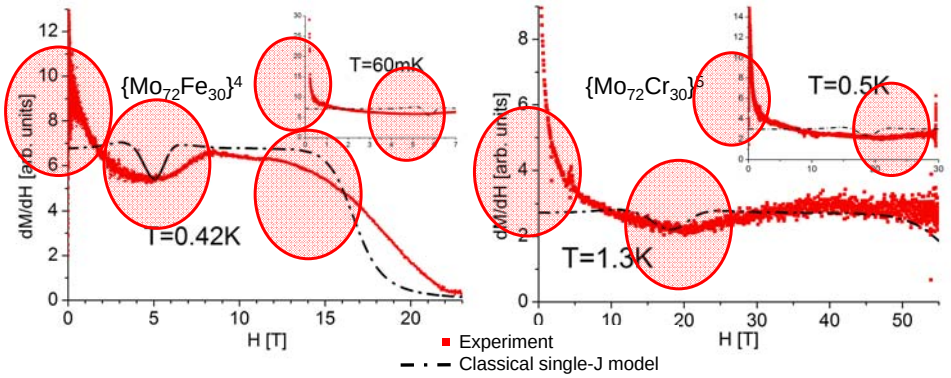


Excellent fit to a classical, single-J, nearest-neighbor Heisenberg model with AF exchange

$$\tilde{H} = J_C \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j + g\mu_B \vec{H} \cdot \sum_i \vec{S}_i$$

[3] A. Müller, M. Luban, C. Schröder, R. Modler, P. Kögerler, M. Axenovich, J. Schnack, P. C. Canfield, S. Budko, and N. Harrison, ChemPhysChem **2**, 517 (2001)

Low T *dM/dH vs. H* measurements reveal



→ Characteristic ***disagreement*** between theory and experiment in ***both*** molecules at low temperatures!

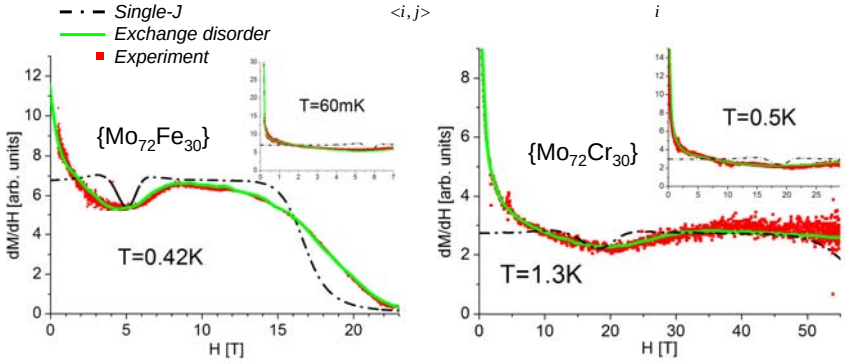
→ Can one find a theory that can solve these problems ***all at once***?

[4] C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, P. Kögerler, Phys. Rev. Lett. **94**, 017205 (2005)
[5] C. Schröder, R. Prozorov, P. Kögerler, M. D. Vannette, X. Fang, M. Luban, A. Matsuo, K. Kindo, A. Müller, A. Maria Todea, Phys. Rev. B **77** (22), 224409 (2008)

Exchange disorder model

- We proposed[5] an ***exchange disordered*** nearest neighbor Heisenberg Hamiltonian with the 60 interactions J_{ij} characterized by a ***two-parameter probability distribution***

$$\tilde{H} = \sum_{<i,j>} J_{ij}\,\vec{S}_i \cdot \vec{S}_j + g\mu_B \vec{H} \cdot \sum_i \vec{S}_i$$



[5]C. Schröder, R. Prozorov, P. Kögerler, M. D. Vannette, X. Fang, M. Luban, A. Matsuo, K. Kindo, A. Müller, A. Maria Todea, Phys. Rev. B **77** (22), 224409 (2008)

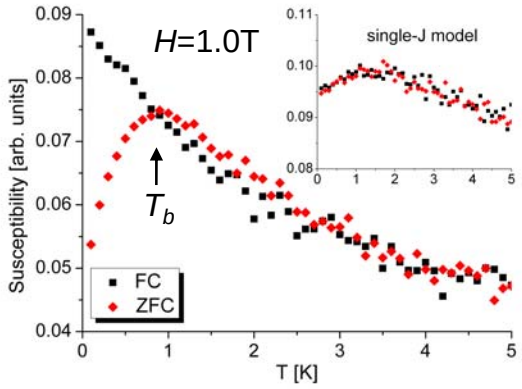
Further implications

- The exchange disorder model of the Keplerate molecules $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}Cr_{30}\}$ combines two important aspects:
  - (Geometric) ***frustration***
  - ***Randomness*** (exchange disorder)
- The combination of both aspects lead to
  - highly degenerate free-energy landscapes with a
  - distribution of barriers between different metastable states
- resulting in broken ergodicity below a characteristic spin freezing temperature T_f ("rough free-energy landscape").
- **These are the necessary ingredients for spin glass models[6]!**

[6]K. Binder and A. P. Young, Rev. Mod. Phys **58**, 801 (1986)

Stochastic spin dynamics simulations I

- FC and ZFC susceptibility for $\{Mo_{72}Fe_{30}\}$



- Single-*J* model: no difference between FC and ZFC curve

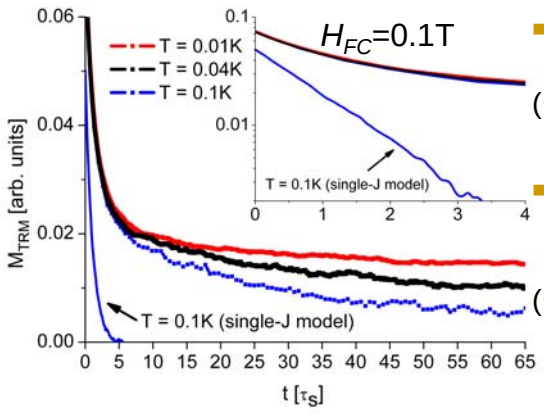
(→ flat free-energy landscape)

- Exchange disorder model: branching of FC and ZFC curve;
  - branching temperature T_b decreases for increasing external field values H

(→ rough free-energy landscape)

Stochastic spin dynamics simulations II

- TRM (thermoremanent dc magnetization) time decay of the FC magnetization for $\{Mo_{72}Fe_{30}\}$



- Single-*J* model: fast exponential decay

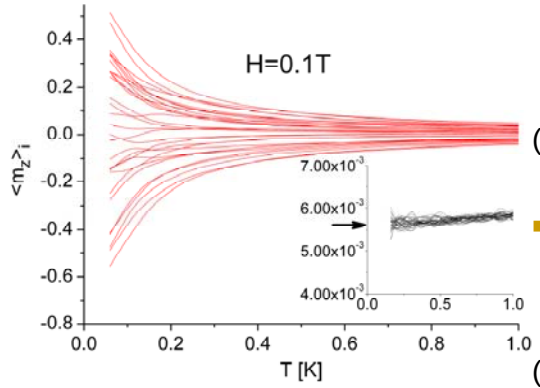
(→ flat free-energy landscape)

- Exchange disorder model: very slow non-exponential decay (approx. log(*t*) for long times)

(→ rough free-energy landscape)

Monte Carlo simulations

- Thermal average for each of the 30 ***local Fe moments*** $\langle m_z \rangle_i$ of a $\{Mo_{72}Fe_{30}\}$ molecule in a weak external field



- Single-*J* model: no dispersion, convergence to exact *T*=0 results (coplanar antiferromagnetic groundstate)

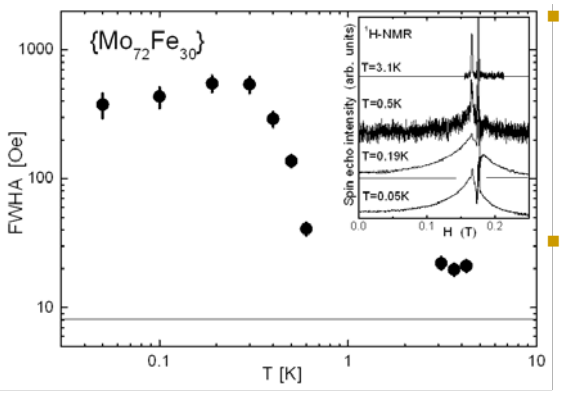
(→ flat free-energy landscape)

- Exchange disorder model: strong dispersion, „freezing out" of a non-coplanar spin configuration.

(→ rough free-energy landscape)

Experimental NMR results for $\{Mo_{72}Fe_{30}\}$

- NMR provides a ***local probe*** sensitive to the local spin components of the magnetic moments via the nuclear-electron dipolar interaction.



- Dramatic broadening of the proton line width below 600 mK (even at H=0T)!

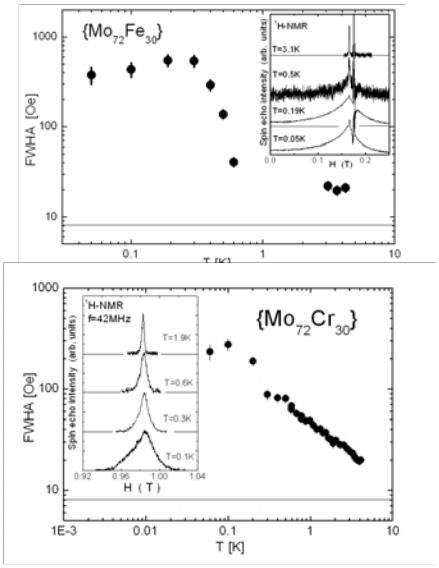
→ direct evidence for a non-zero value of the local Fe moments $\langle m_z \rangle_i$

- Broadening would be absent for the single-*J* scenario!

→ local Fe moments $\langle m_z \rangle_i$ are the same and very small at each lattice site.

Experimental NMR results for $\{Mo_{72}Fe_{30}\}$

- NOTE: Broadening does NOT originate from three dimensional magnetic ordering!
  (→ susceptibility measurements do not show any anomaly around 600 mK!)
- We conclude that the fluctuation frequency of Fe spin moments at low temperatures is much slower than the MHz range, corresponding to spin freezing!



Summary

- The pair of magnetic molecules $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}Cr_{30}\}$ display spin freezing and slow low temperature dynamics reminiscent of spin glass behavior due to disorder of the intra-molecular exchange interaction.
- Our theoretical calculations predict a low-temperature, low-field variation of the local magnetic moments which is consistent with the results of our proton NMR measurements.
- Our calculations strongly suggest that the free-energy landscape for the spin configurations in a single molecule consists of a distribution of barriers between different metastable states.
- As a consequence we predict that measurements of the TRM decay-times and the FC and ZFC susceptibility would show spin glass behavior.

Thank you for your attention!

christian.schroeder@fh-bielefeld.de

We thank the thousands of volunteers participating in the public resource computing facility, Spinhenge@home [http://spin.fh-bielefeld.de]. The large-scale Monte Carlo simulations necessary for the present research were made possible due to the availability of their personal computers.