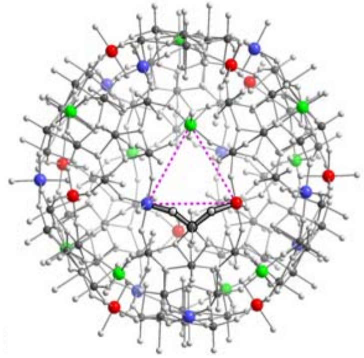
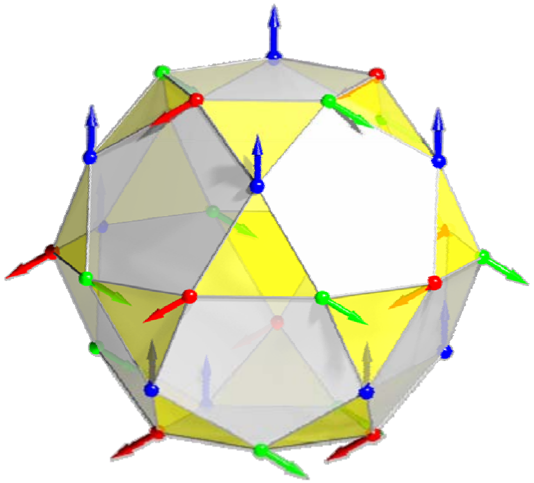
Multiple nearest-neighbor exchange constants in the frustrated magnetic molecules $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}Cr_{30}\}$





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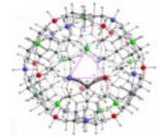
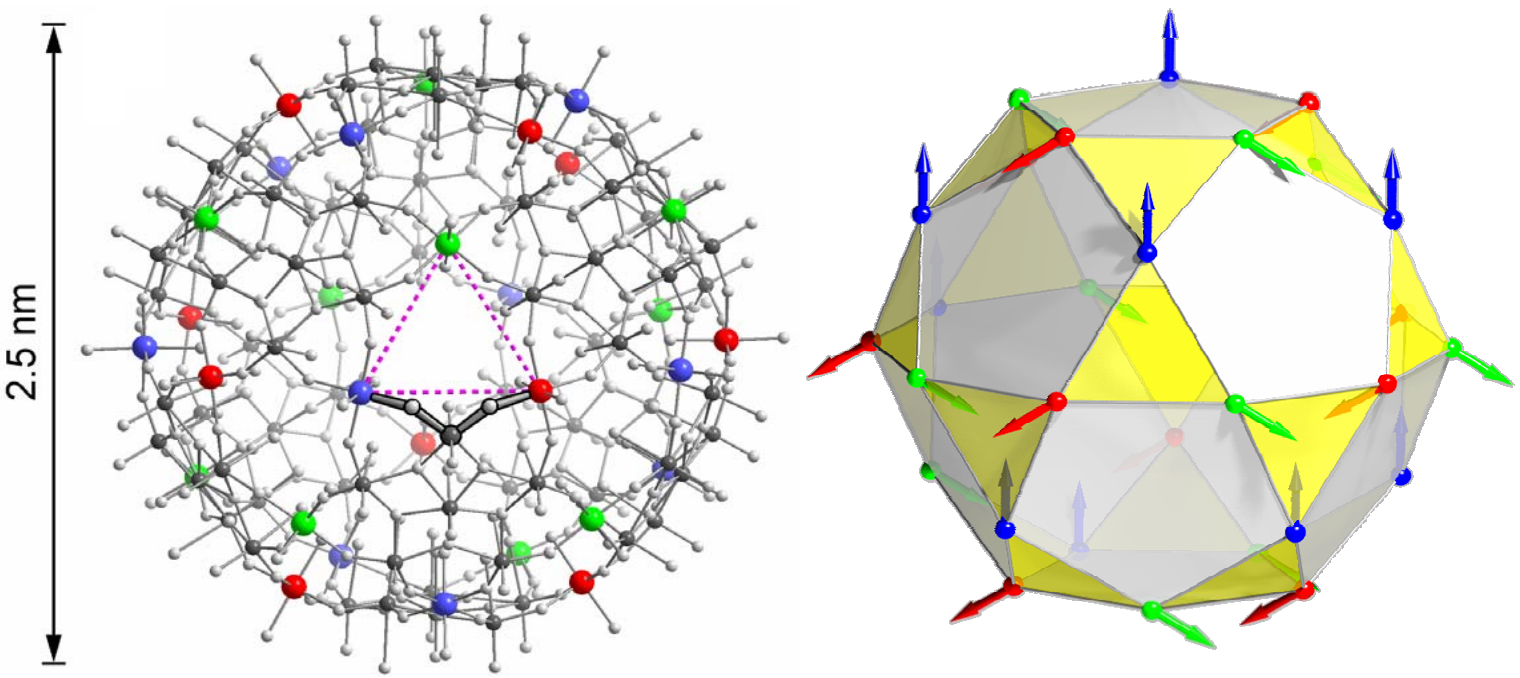
in collaboration with
R. Prozorov, H. Nojiri, and M. Luban

A family of famous magnetic molecules ...



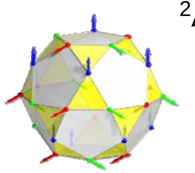
The fancy molecules $\{Mo_{72}Fe_{30}\}$[1] and $\{Mo_{72}Cr_{30}\}$[2] ($\{Mo_{72}V_{30}\}$ not considered here)

- 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}!

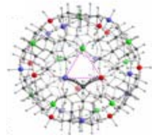


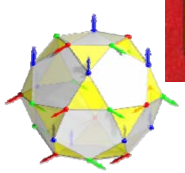
[1] A. Müller, S. Sarkar, S.Q.N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. Trautwein, and V. Schünemann, Angew. Chem., Int. Ed. Engl. **38**, 3238 (1999)

[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)

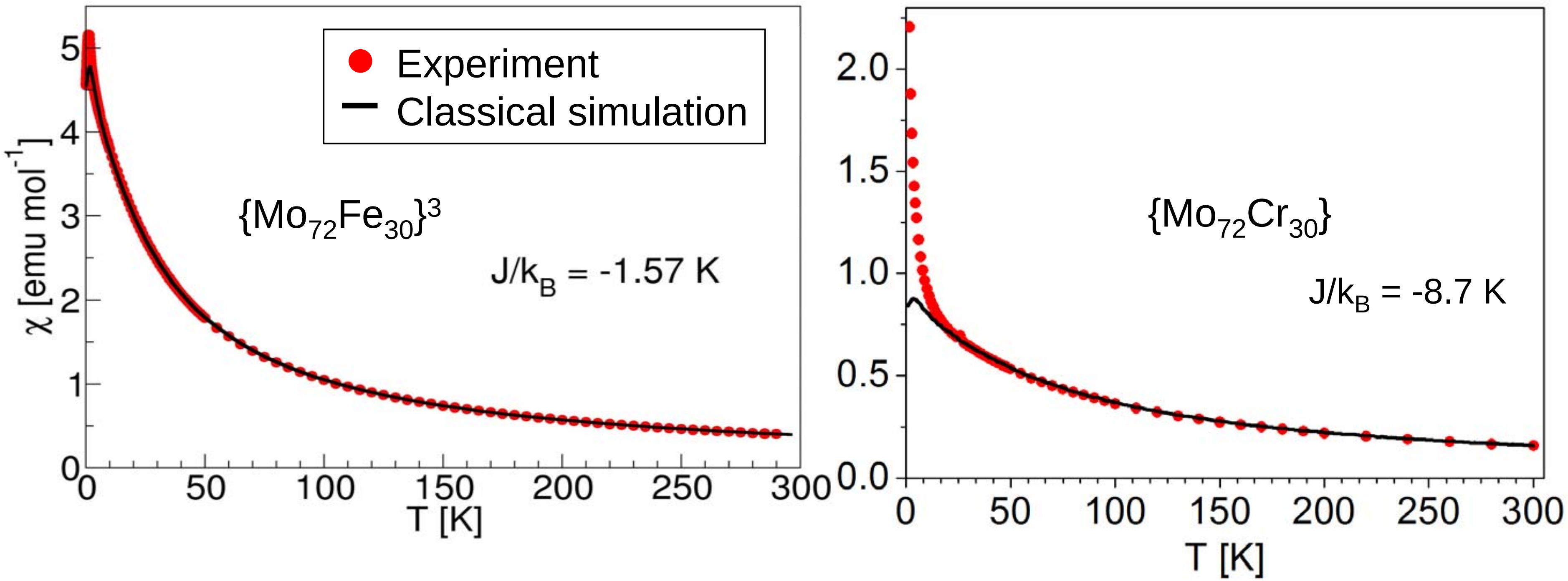


A family of **famous** magnetic molecules ...



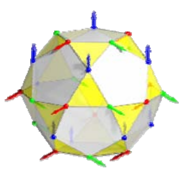


... and their thermodynamic properties



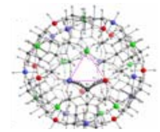
Excellent fit to a classical, single-J, nearest-neighbor Heisenberg model

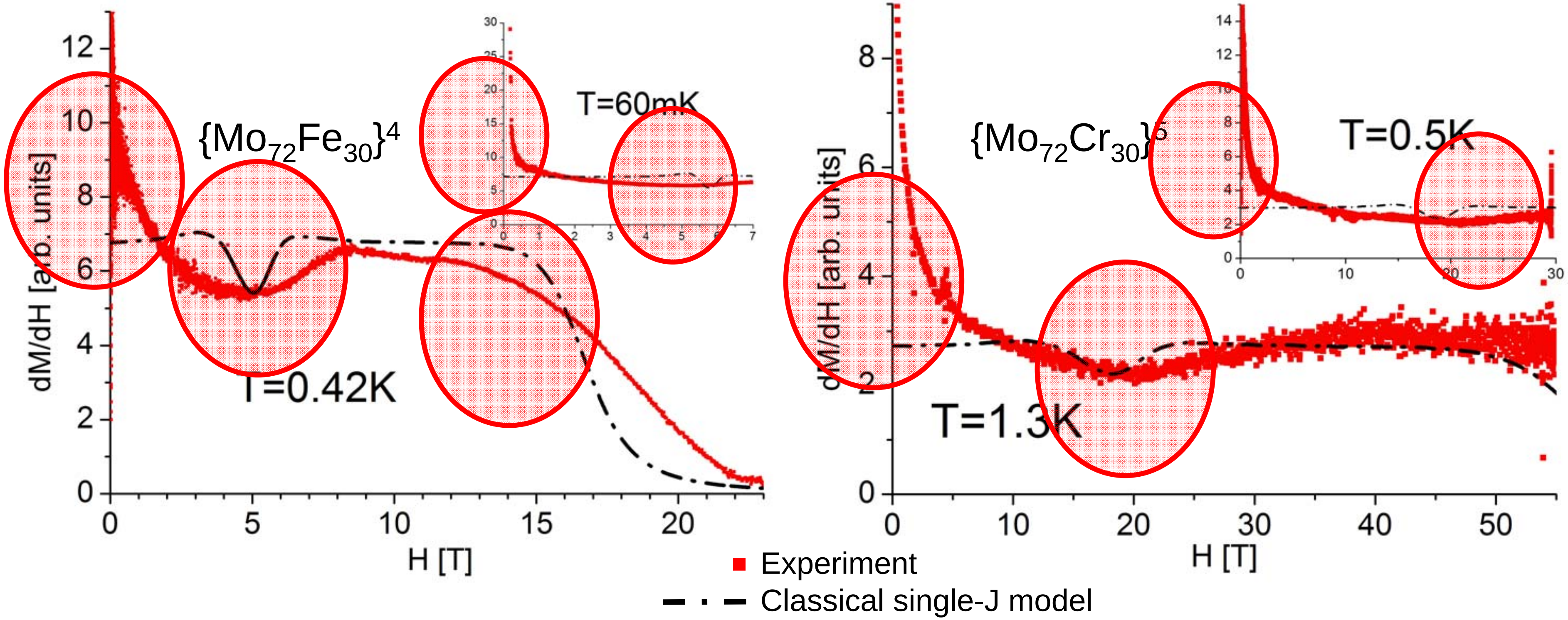
$$\tilde{H} = J_C \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j + g\mu_B \vec{H} \cdot \sum_i \vec{S}_i$$



[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 revealed

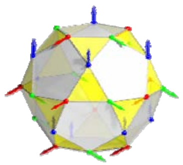




→ Characteristic ***disagreement*** between theory and experiment in ***both*** molecules!

→ Can one find a proper theoretical description that can solve these problems ***all at once***?

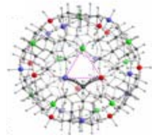
→ Is there a common physical origin?



[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, submitted to Phys. Rev. B (2008)

Multiple nearest neighbor exchange model

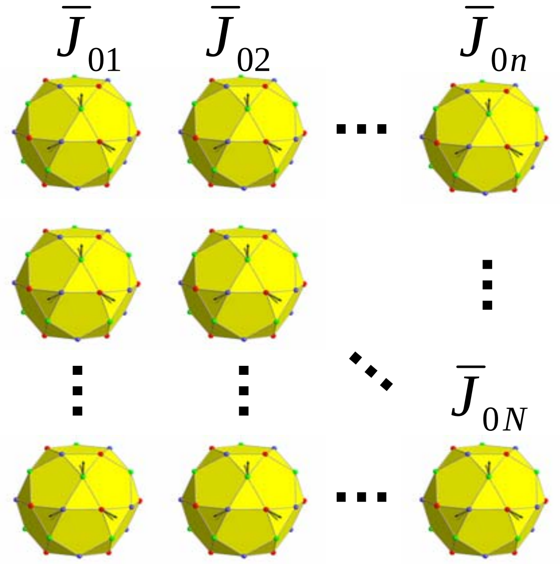


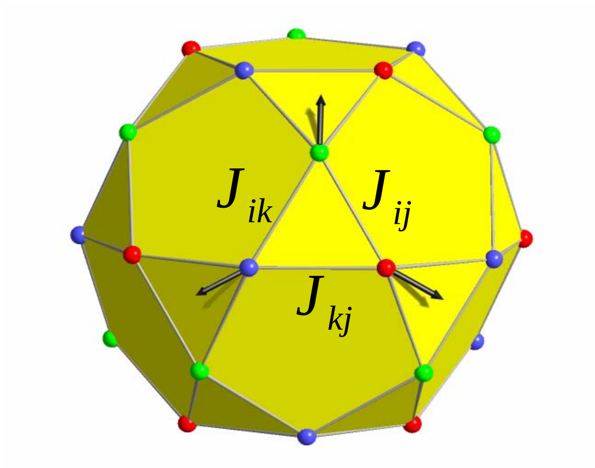
- We propose a ***multiple-J*** nearest neighbor Heisenberg Hamiltonian

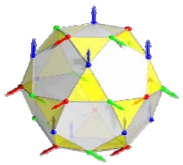
$$\tilde{H} = \sum_{<i,j>} J_{ij} \vec{S}_i \cdot \vec{S}_j + g\mu_B \vec{H} \cdot \sum_i \vec{S}_i$$

with the interactions J_{ij} characterized by a ***probability distribution*** for an ***ensemble of independent molecules*** according to the following receipe*:*

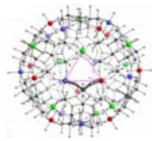
1. Assign a single average exchange value to each molecule of the ensemble $\bar{J}_{0n} \in \{(1-\tau)J_0, (1+\tau)J_0\}$ with equal probability, where J_0 is determined by high-temperature susceptibility measurements using the *single-J* model.
2. For the *n*th system, the individual values for the 60 classical exchange constants are chosen from the interval $J_{ij} \in \{(1-\rho)\bar{J}_{0n}, (1+\rho)\bar{J}_{0n}\}$ with equal probability.



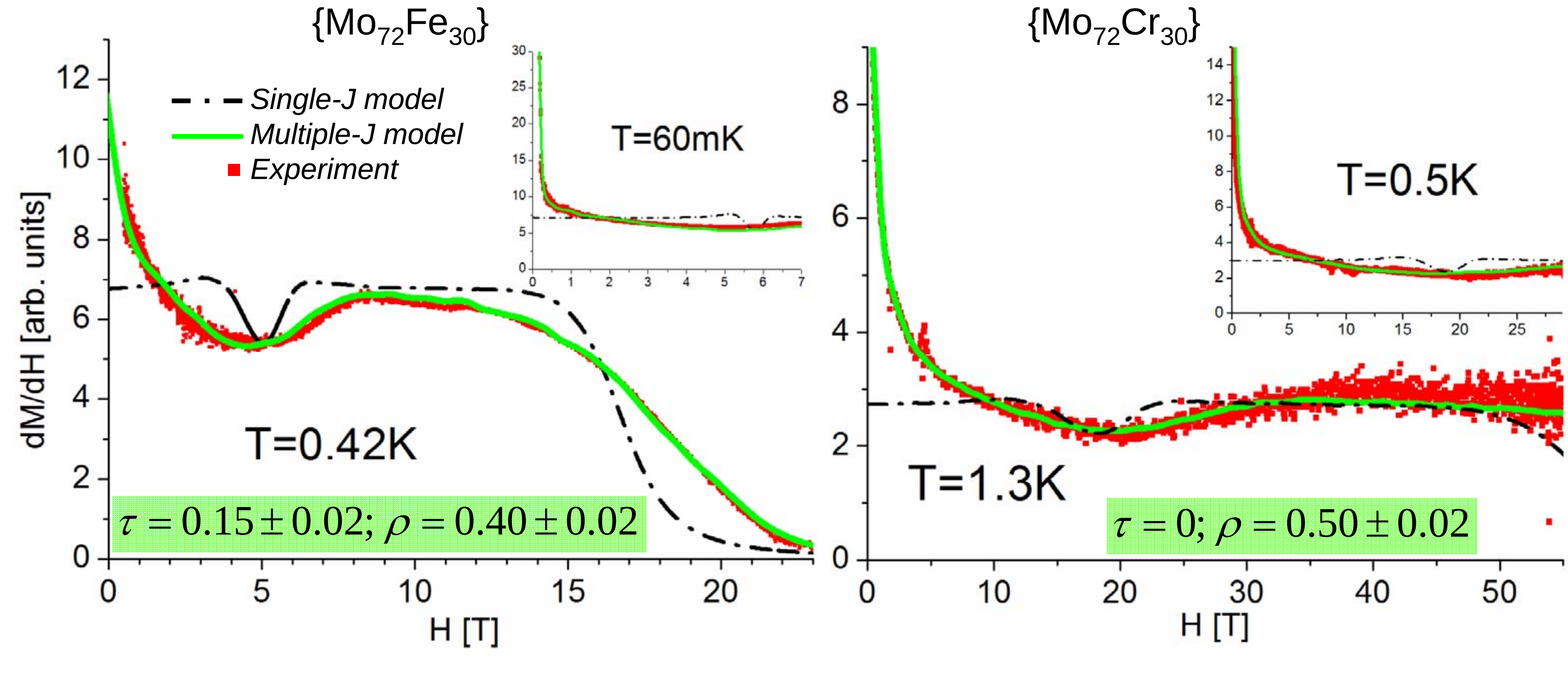


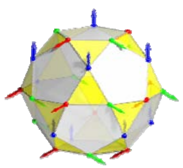


Results I



- We have considered ensembles of up to 100 molecules and performed classical Monte Carlo simulations[5] in the parameter space of (τ, ρ)



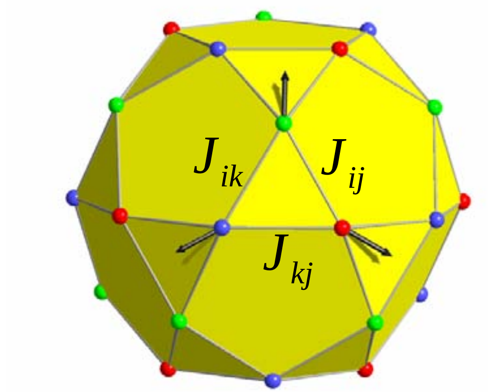


[5]C. Schröder, R. Prozorov, P. Kögerler, M. D. Vannette, X. Fang, M. Luban, A. Matsuo, K. Kindo, A. Müller, A. Maria Todea, submitted to Phys. Rev. B (2008)

Results I

Why two distributions?

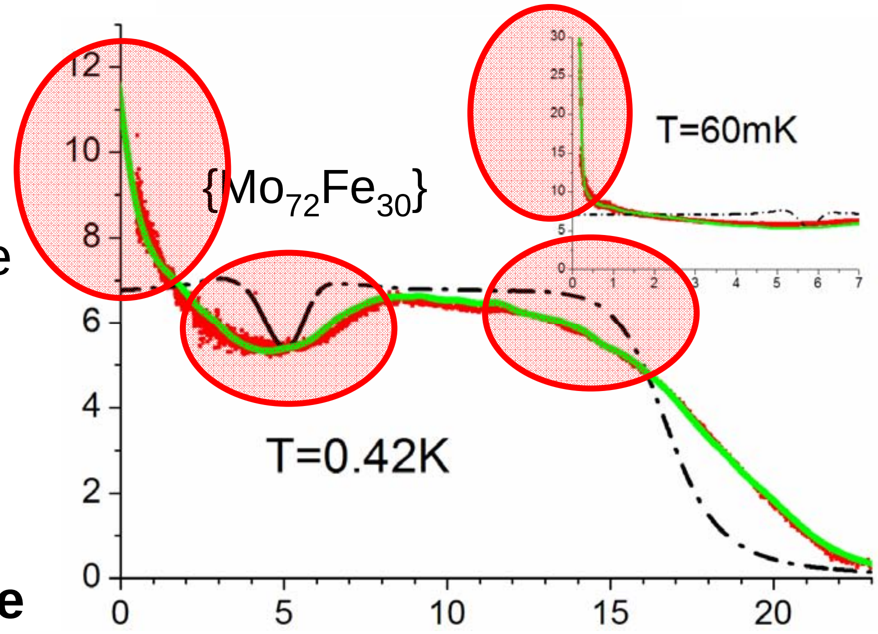
- For $\rho \neq 0$ there exists a distribution of 60 *different* exchange constants in a given molecule
  - the corner-sharing spin triangles are of **isosceles-type** rather than equilateral-type!



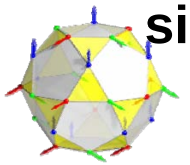
→ **non-analytic behavior (i.e. a jump) of** $M(T=0, H=0)$ **and hence a strong sensitivity of** $dM/dH(T \approx 0)$ **for** $H \approx 0$

- For $\tau \neq 0$ the *mean value* of the exchange constants within each molecule *in the ensemble* is different
  - saturation field H_{sat} varies
  - the dip position at $H_{sat}/3$ *varies as well!*

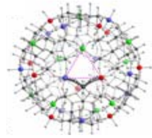
→ **relatively sharp features occuring in the single-J model are smeared out**



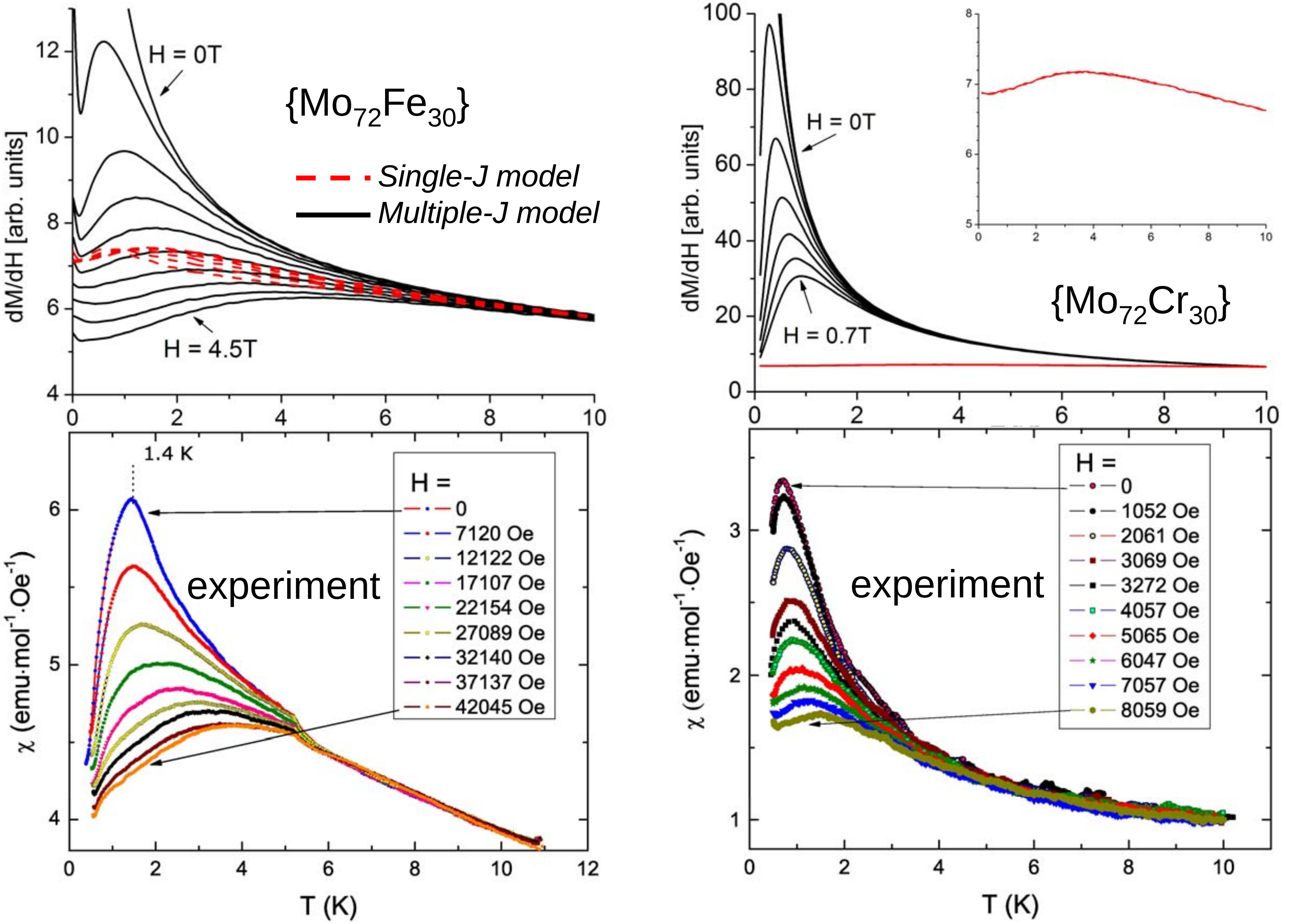
$\tau = 0.15 \pm 0.02; \rho = 0.40 \pm 0.02$

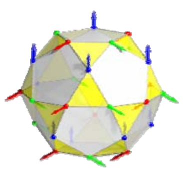


Results II

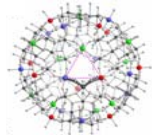


Predictions for dM / dH vs. T and experimental results





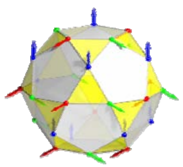
Summary



- We propose a distribution of exchange constants (*multiple-J* model) for the frustrated magnetic molecules $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}Cr_{30}\}$ based on a two-parameter probability distribution with a mean value determined by high temperature susceptibility data using a *single-J* model.

- Our classical Monte Carlo results are in excellent agreement with our experimental data for dM/dH vs. T and H in the low-T ($T < 5K$) regime for both, $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}Cr_{30}\}$.

- For higher temperatures ($T > 5K$) the results for the *multiple-J* model and the *single-J* model converge, and the *single-J* model provides a satisfactory description of each molecule.



Discussion

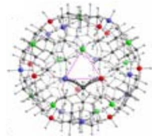
The existence of a distribution of exchange constants has several implications:

- Lifting of degeneracies and fanning out of magnetic energy levels
  → provides a reasonable explanation for three long-standing puzzling issues concerning these magnetic molecules:

  1. Classical behavior down to very low temperatures.
     - The effective temperature for the crossover from classical to quantum behavior would be considerably lower than that expected a priori for the *single-J* model.
  2. The failure of efforts to observe magnetization steps, in (static!) measurements of *M* versus *H*, in the mK temperature range.
  3. The very broad peak (maximum at 0.6 meV) that has been observed by inelastic neutron scattering on $\{Mo_{72}Fe_{30}\}$ at 65 mK[6].

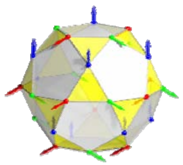
[6] V. O. Garlea, S. E. Nagler, J. L. Zarestky, C. Stassis, D. Vaknin, P. Kögerler, D. F. McMorrow, C. Niedermayer, D. A. Tennant, B. Lake, Y. Qiu, M. Exler, J. Schnack, and M. Luban, Phys. Rev. B **73**, 024414 (2006).

Discussion



- One can attribute the failure of the *single-J* model to the combined effect of a large number of diverse perturbing mechanisms that are *excluded* when one uses an idealized *single-J* description!
  - impurities, variations in the exchange-coupling geometry, weak magnetic exchange interactions of more-distant neighbors, Dzyaloshinsky-Moriya and dipole-dipole interactions, …

- A theoretical description based on a Heisenberg model where the nearest-neighbor exchange constant is chosen using a probability distribution provides a relatively simple, *phenomenological* platform for compromising between the need for microscopic realism versus practical limitations.



Thank you for your attention!

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.