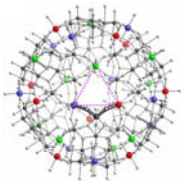
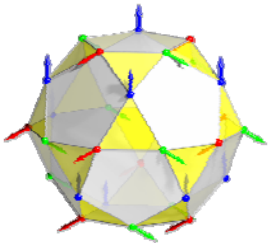
News from the Keplerate Front





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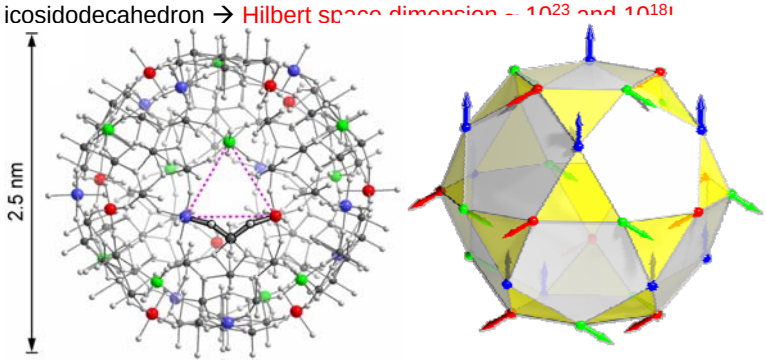
The Keplerate molecules ...

The fancy molecules $\{Mo_{72}Fe_{30}\}$[1] and $\{Mo_{72}Cr_{30}\}$[2] ($\{Mo_{72}V_{30}\}$ not considered here → Marshall's talk!)

- 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)

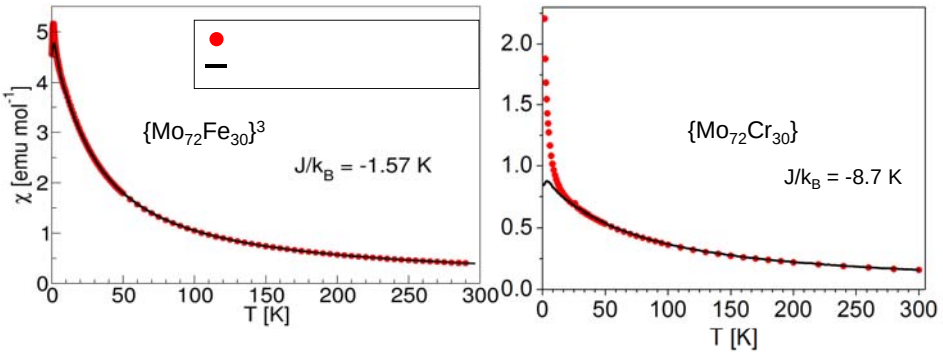
[2] A. M. Todea, A. Merca, H. Bögge, J. van Slageren, M. Dressel, L. Engelhardt, M. Luban, T. Glaser, M. Henry, and A. Müller, Angew. Chem. Int. Ed. **46**, 6106 (2007)

... and what we soon learnt about them!

!!!

[Source: advertisement of a well-known German discounter]

Basic thermodynamic properties – beautiful!

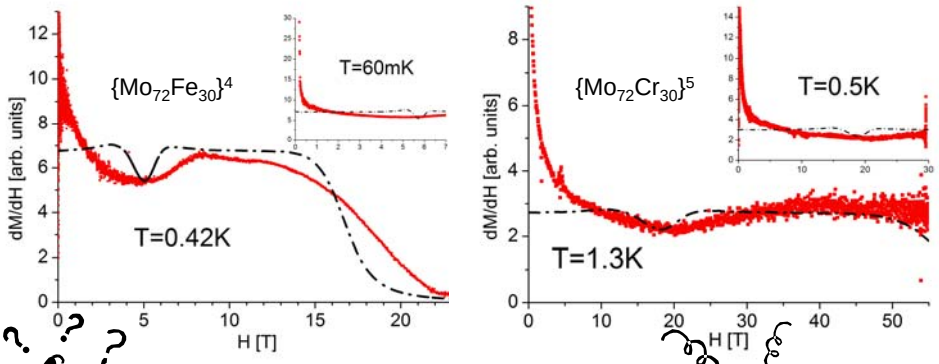


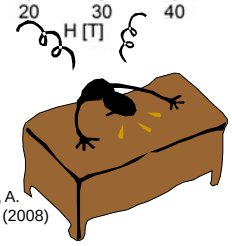
Excellent fit to a classical, single-J, nearest-neighbor Heisenberg model

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

[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

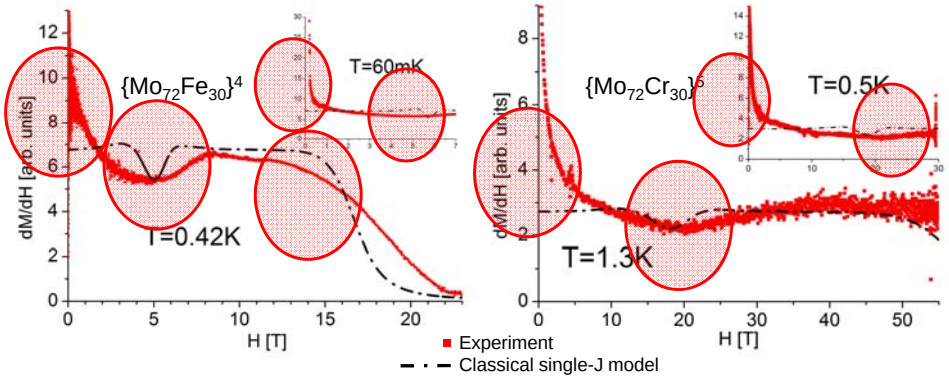




[4]C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, P. Kögerler, Phys. Rev. Lett. **94**, 017205 (2005)

[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)

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, Phys. Rev. B **77** (22), 224409 (2008)

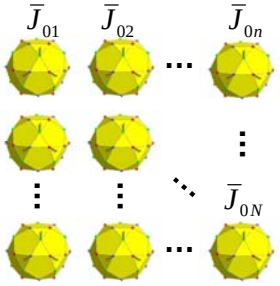
Multiple nearest neighbor exchange model

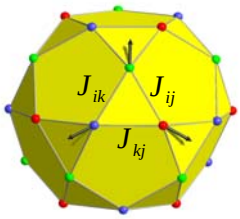
- We propose a ***multiple-J*** nearest neighbor Heisenberg Hamiltonian

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

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

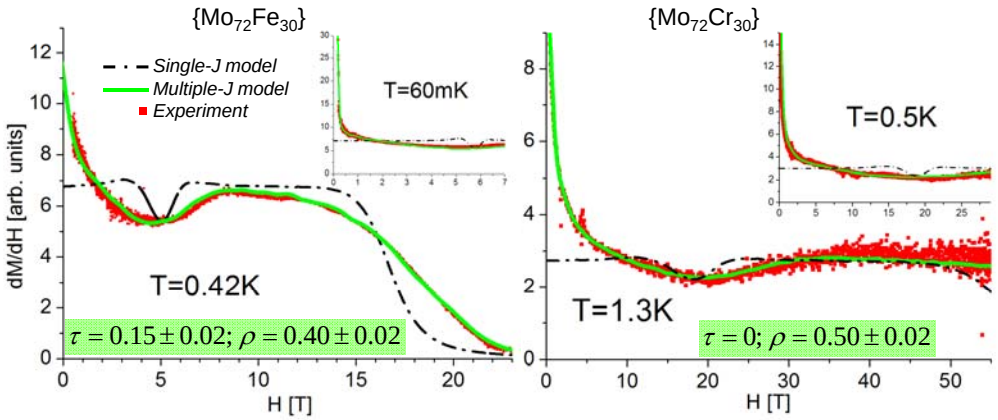
1. Assign a single average exchange value to each molecule of the ensemble $\bar{J}_{0n} \in \{(1-\tau)J_0, (1+\tau)J_0\}$ with equal probability, where J_0 is determined by high-temperature susceptibility measurements using the *single-J* model.
2. For the *n*th system, the individual values for the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

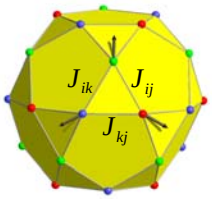


[5] C. Schröder, R. Prozorov, P. Kögerler, M. D. Vannette, X. Fang, M. Luban, A. Matsuo, K. Kindo, A. Müller, A. Maria Todea, Phys. Rev. B **77** (22), 224409 (2008)

Results I

Why two distributions?

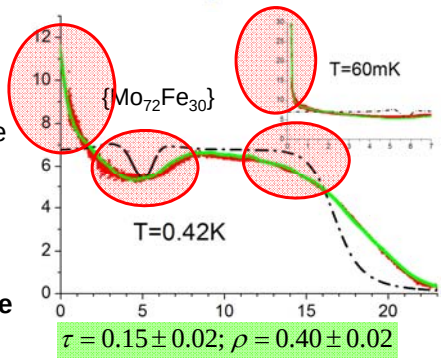
- For $\rho \neq 0$ there exists a distribution of 60 *different* exchange constants in a given molecule
  - the corner-sharing spin triangles are of **isosceles-type** rather than equilateral-type!



→ **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** $H \approx 0$

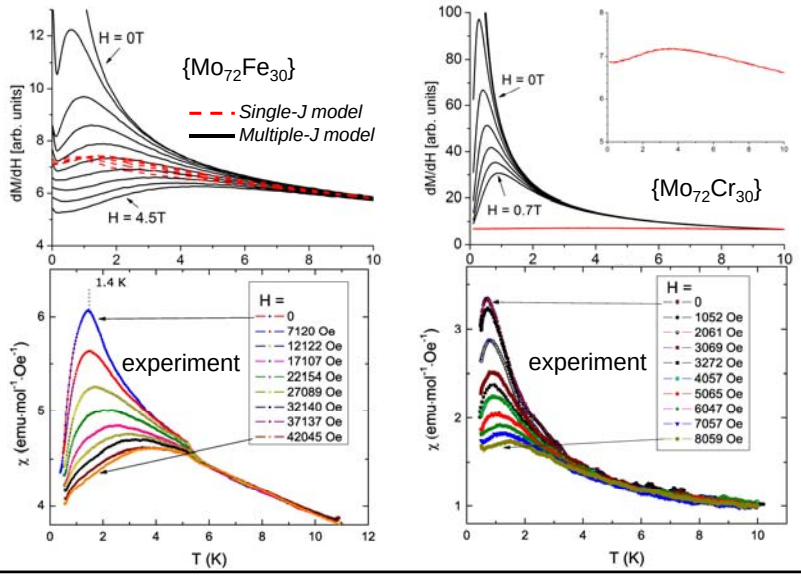
- For $\tau \neq 0$ the *mean value* of the exchange constants within each molecule *in the ensemble* is different
  - saturation field H_{sat} varies
  - the dip position at $H_{sat}/3$ *varies as well!*

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



Results II

Predictions for dM/dH vs. T and experimental results



Summary I

- 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 rectangular 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 I

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 I

- 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.

More Predicitons!

- The multiple-J model of the Keplerate molecules $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}Cr_{30}\}$ combines two important aspects:

1. (Geometric) ***frustration***
2. ***Randomness*** (i.e. the distribution of J values)

These are the necessary ingredients for spin glass models[7]!!!

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

Are the Keplerates classical spin glasses???

- A characteristic feature of a spin glass is the hysteretic behavior in the field-cooled (FC) and zero-field-cooled (ZFC) magnetization measurements leading to the so-called "λ"-curve.
- Experimental procedure:

1. Cool down from T_{max} to T_{min} in zero field
2. Turn on the external field
3. Heat up from T_{min} to T_{max} and measure *M(T)* (ZFC curve)
4. Cool down again from T_{max} to T_{min} with applied field and measure *M(T)* (FC curve)

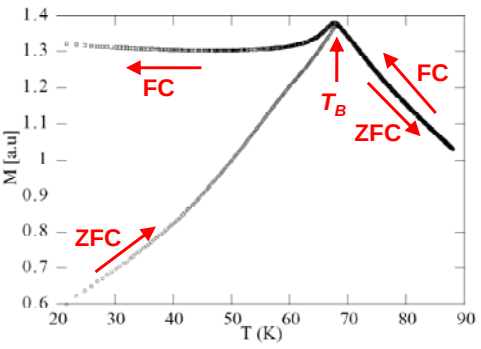
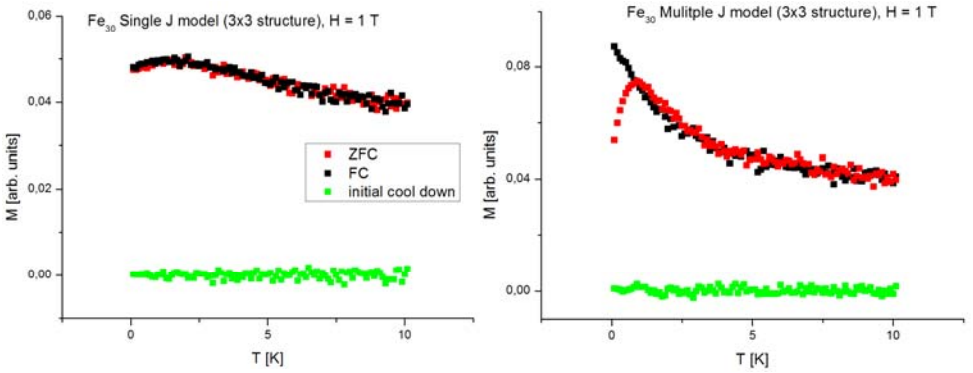


FIG. 1. FC- and ZFC-magnetisation vs. temperature of Cu(Mn13.5at%), H =1 Oe.

C. Djurberg, K. Jonason, P. Nordblad, Eur. Phys. J. B **10**, 15 (1998)

Are the Keplerates classical spin glasses???

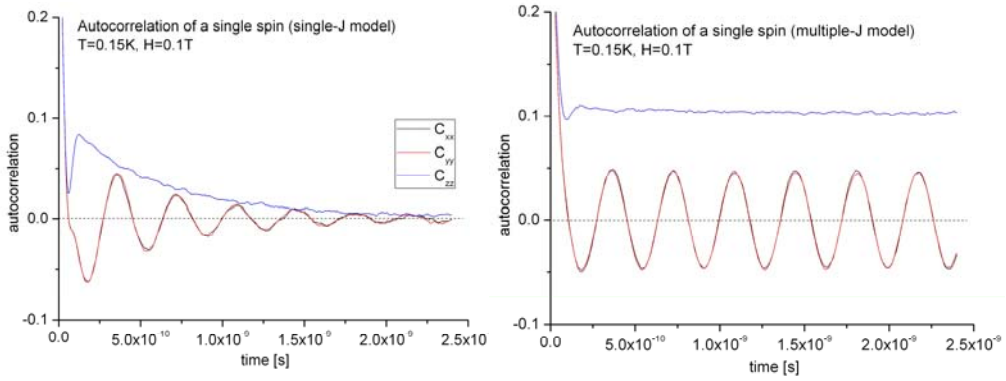
- Using a stochastic spin dynamics approach one can ***directly simulate*** such experiments!



→ The multiple-J model clearly shows hysteretic behavior reminiscent of a classical spin glass model whereas the single-J model does not!

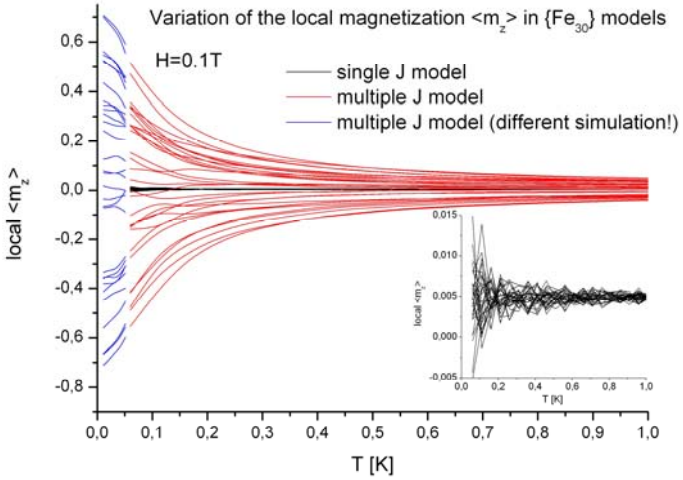
Are the Keplerates classical spin glasses???

- Another characteristic feature of a spin glass: slow "glassy" dynamics and spin freezing



→ The multiple-J model clearly shows slow "glassy" dynamics (in fact the autocorrelation plateaus) in contrast to the single-J model (→ Marshall's talk!)!

Are the Keplerates classical spin glasses???



→ The multiple-J model clearly shows "freezing out" of – different(!) – spin configurations with non zero value of the local spin components in the ground state at very low temperatures and magnetic field.

Summary II & Discussion II

- The multiple-J model provides the ingredients for a classical spin glass description, namely frustration and randomness.
- Classical simulations clearly show "glassy" behavior and spin freezing for the multiple-J model → this is absent in the single-J model!!!
- Experimental "proof"???
  - ZFC and FC measurements
  - NMR (as a local probe that is sensitive directly to the local spin components of the Fe magnetic moments) (→ Yuji Furukawa, Ferdinando Borsa, Marshall Luban)
  - Mössbauer spectroscopy
- **Leaving us with the interesting question: Are the Keplerate molecules $\{Mo_{72}Fe_{30}\}$ and $\{Mo_{72}Cr_{30}\}$ – zero dimensional – spin glasses???**

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

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