Rotational band structure of low-lying excitations in small Heisenberg systems

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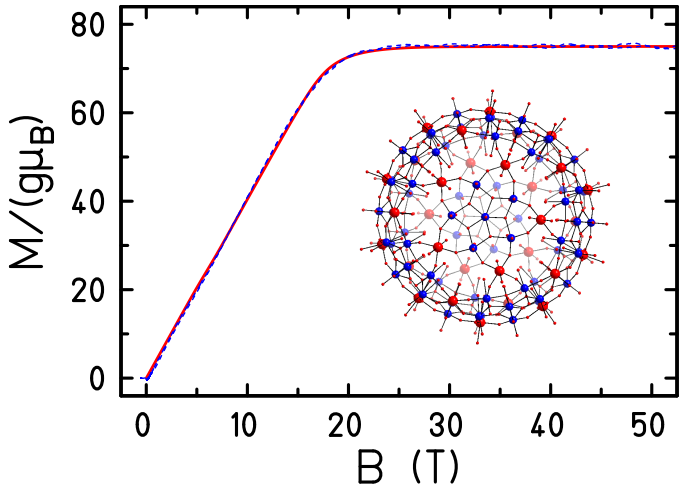
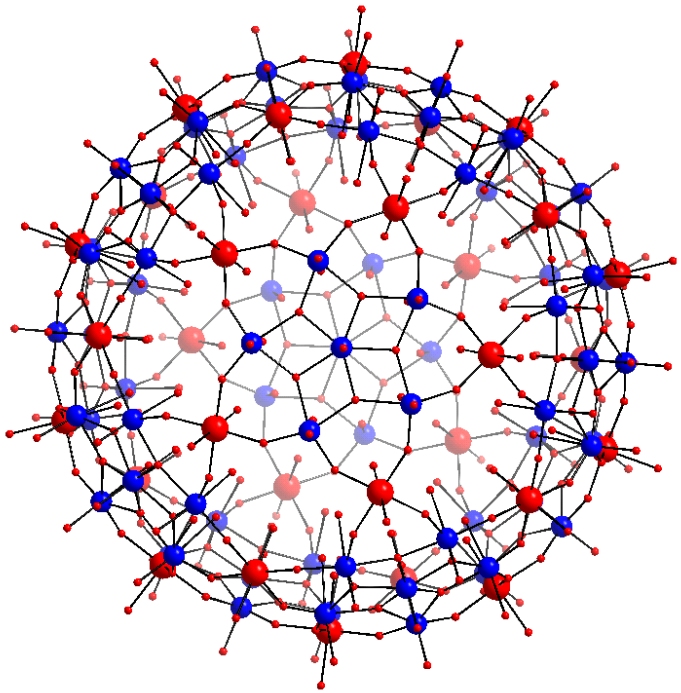


http://obelix.physik.uni-osnabrueck.de/∼schnack/

Structure of $\{Mo_{72}Fe_{30}\}$



- largest magnetic molecule synthesised to date[a];
- small red balls – oxygen, big red balls – iron, blue balls – molybdenum;
- 30 iron ions ($s = 5/2$), four next neighbours each;
- dimension of the Hilbert space $(2s+1)^N \sim N_A$;
- rather small next-neighbour coupling, $J \approx 0.78$ K;
- perfect icosidodecahedron;
- displayed viewing along a fivefold symmetry axis.

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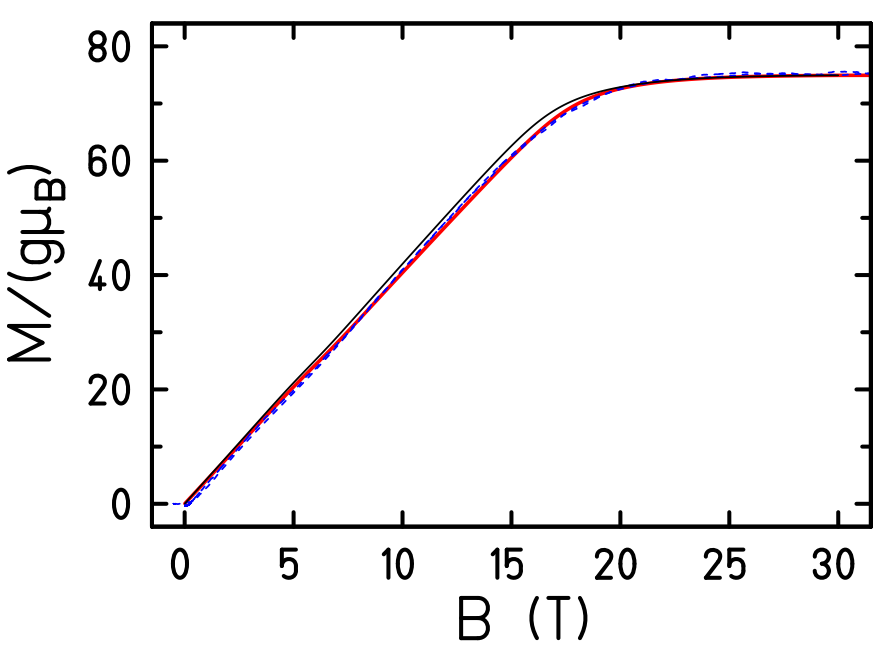
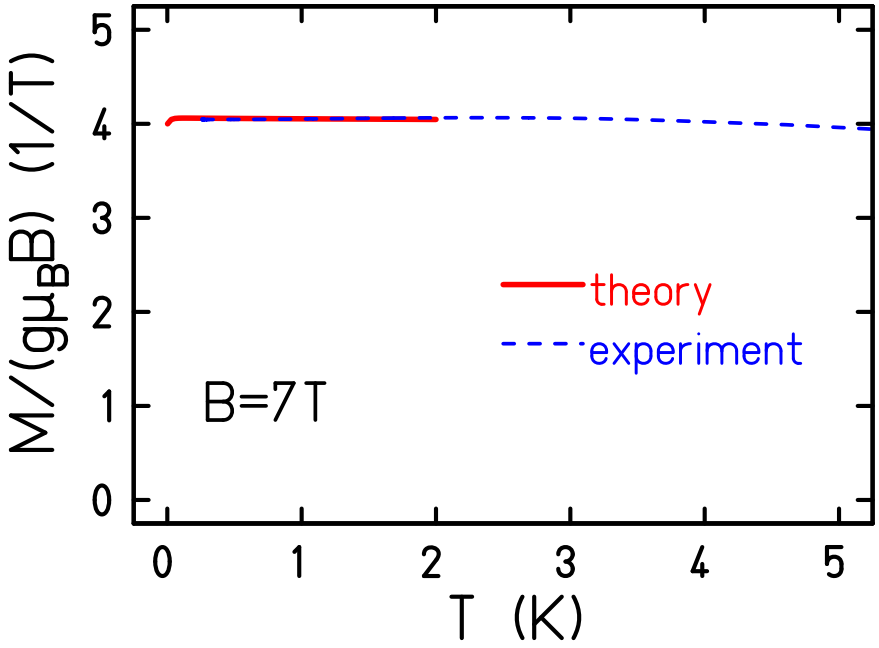
[a] A. Müller et al., *Archimedean synthesis and magic numbers: "Sizing" giant molybdenum-oxide-based molecular spheres of the Keplerate type*, Angew. Chem. Int. Ed. Engl. **38** (1999), 3238.

Magnetisation of $\{Mo_{72}Fe_{30}\}$



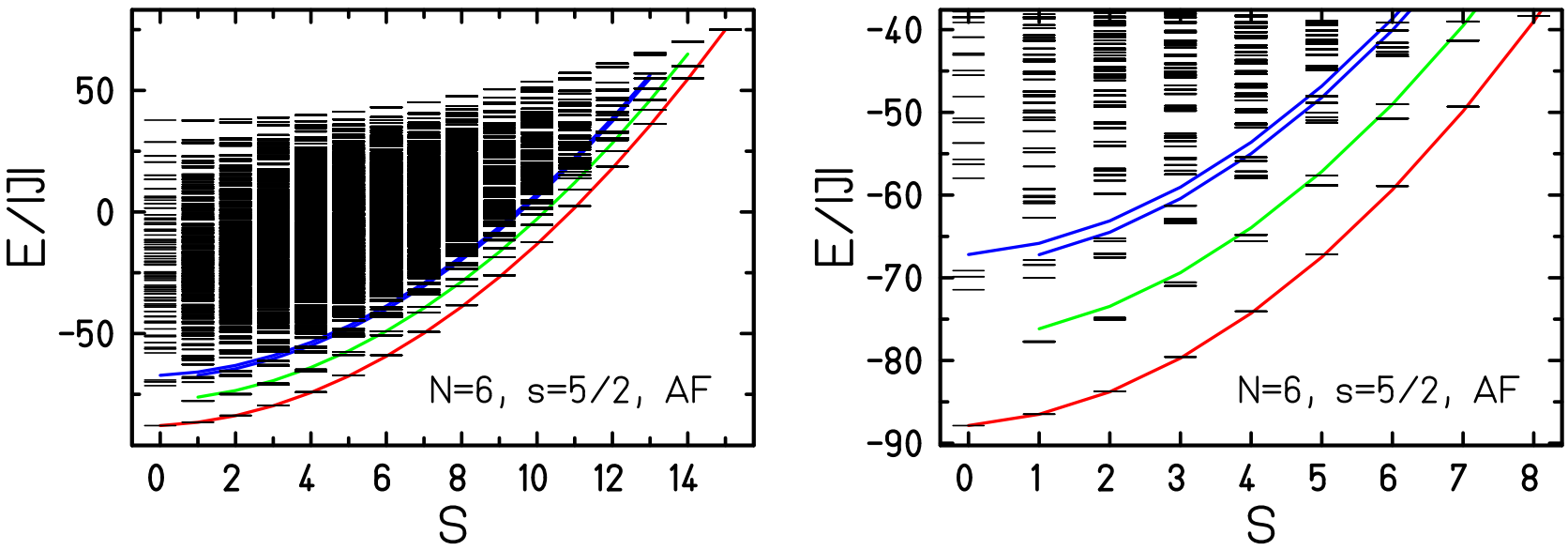


How to describe $\{Mo_{72}Fe_{30}\}$?

- Heisenberg model seems to be appropriate;
- structure suggests isotropic next-neighbour interaction;
- single coupling constant J determined from high temperature susceptibility;
- dimension of the Hilbert space $(2s+1)^N \sim 10^{23}$!

$\Rightarrow$ model low-temperature behaviour by using **rotational band structure**

Rotational bands in AF Heisenberg rings



Ground state rotational band known and used for rings of even N[a],

but seems to be a general property of AF Heisenberg systems

[a] A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996); G. L. Abbati *et al.*, Inorg. Chim. Acta **297**, 291 (2000); O. Waldmann, Phys. Rev. B (submitted).

Heisenberg model

Hamilton operator (AF: $J < 0$, F: $J > 0$)

$$\begin{aligned} \underset{\sim}{H} &= -\sum_{(u,v)} J(u,v) \left\{ \underset{\sim}{s}^3(u)\,\underset{\sim}{s}^3(v) + \frac{\gamma}{2}\left[\underset{\sim}{s}^+(u)\,\underset{\sim}{s}^-(v) + \underset{\sim}{s}^-(u)\,\underset{\sim}{s}^+(v) \right] \right\} \\ &\quad + g\,\mu_B\,B \sum_u^N \underset{\sim}{s}^3(u) \end{aligned}$$

$\gamma = 0$ – Ising model; $\gamma = 1$ – Heisenberg model.

Spin operators

$$\left[\underset{\sim}{s}^a(u), \underset{\sim}{s}^b(v) \right] = i\,\epsilon_{abc}\,\underset{\sim}{s}^c(u)\,\delta_{uv} \quad , \quad \underset{\sim}{s}^\pm(u) = \underset{\sim}{s}^1(u) \pm i\,\underset{\sim}{s}^2(u)$$

Very often all individual spin quantum numbers are the same, like in the iron rings.

Typical observables in the canonical ensemble

Mean energy and specific heat

$$\langle\langle\ \underset{\sim}{H}\ \rangle\rangle \;=\; \frac{1}{Z}\,\mathrm{tr}\left\{\underset{\sim}{H}\,e^{-\beta\underset{\sim}{H}}\right\} \quad , \quad Z=\mathrm{tr}\left\{e^{-\beta\underset{\sim}{H}}\right\} \quad , \quad \beta=\frac{1}{kT}$$

$$C \;=\; \frac{d}{dT}\,\langle\langle\ \underset{\sim}{H}\ \rangle\rangle = \frac{1}{kT^2}\left(\langle\langle\ \underset{\sim}{H}^2\ \rangle\rangle - \langle\langle\ \underset{\sim}{H}\ \rangle\rangle^2\right)$$

Magnetisation and magnetic susceptibility

$$\mathcal{M} \;=\; g\mu_B\left(\frac{1}{Z}\,\mathrm{tr}\left\{\underset{\sim}{S}^3\mathrm{e}^{-\beta\underset{\sim}{H}}\right\}\right)$$

$$\chi \;=\; \left(\frac{\partial\,\mathcal{M}}{\partial\,B}\right) = g^2\mu_B^2\beta\left(\langle\langle\ \left(\underset{\sim}{S}^3\right)^2\ \rangle\rangle - \langle\langle\ \underset{\sim}{S}^3\ \rangle\rangle^2\right)$$

Symmetries I

Heisenberg Hamilton operator & Zeeman term

$$\underset{\sim}{H} \quad = \quad -\sum_{(u,v)} J(u,v)\ \vec{\underset{\sim}{s}}(u) \cdot \vec{\underset{\sim}{s}}(v) + g\,\mu_B\,B \sum_{u}^{N} \underset{\sim}{s}^3(u)$$

Symmetry about the 3-axis, good quantum number M

$$\left[\underset{\sim}{H}, \underset{\sim}{S}^3\right] = 0 \quad , \quad \underset{\sim}{S}^3 = \sum_{u}^{N} \underset{\sim}{s}^3(u)$$

Rotational symmetry, good quantum number S

$$\left[\underset{\sim}{H}, \vec{\underset{\sim}{S}}^2\right] = 0 \quad \& \quad \left[\vec{\underset{\sim}{S}}^2, \underset{\sim}{S}^3\right] = 0$$

Symmetries II
Translational invariance of rings

Cyclic shift operator $\underset{\sim}{T}$

$$\underset{\sim}{T}\,|\,m_1,\ldots,m_{N-1},m_N\,\rangle \quad = \quad |\,m_N,m_1,\ldots,m_{N-1}\,\rangle$$

$$\left[\underset{\sim}{H},\underset{\sim}{T}\right]=0 \quad \& \quad \left[\underset{\sim}{T},\underset{\sim}{\vec{S}}\right]=0$$

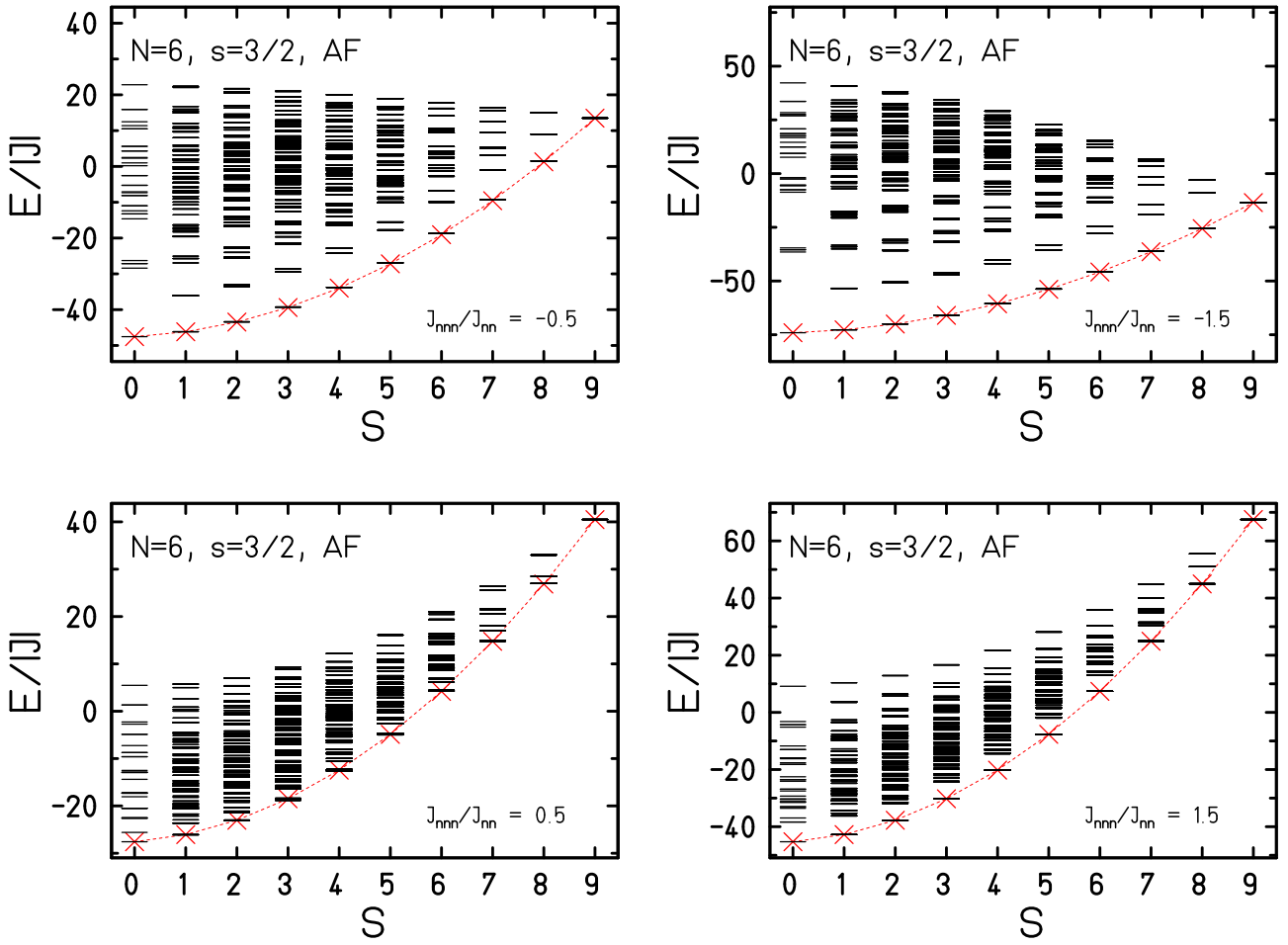
use appropriate symmetry operator for other spin topologies

Eigenvalues of $\underset{\sim}{T}$, good quantum number k

$$z=\exp\left\{-i\frac{2\pi k}{N}\right\} \quad , \quad k=0,1,\ldots,N-1$$

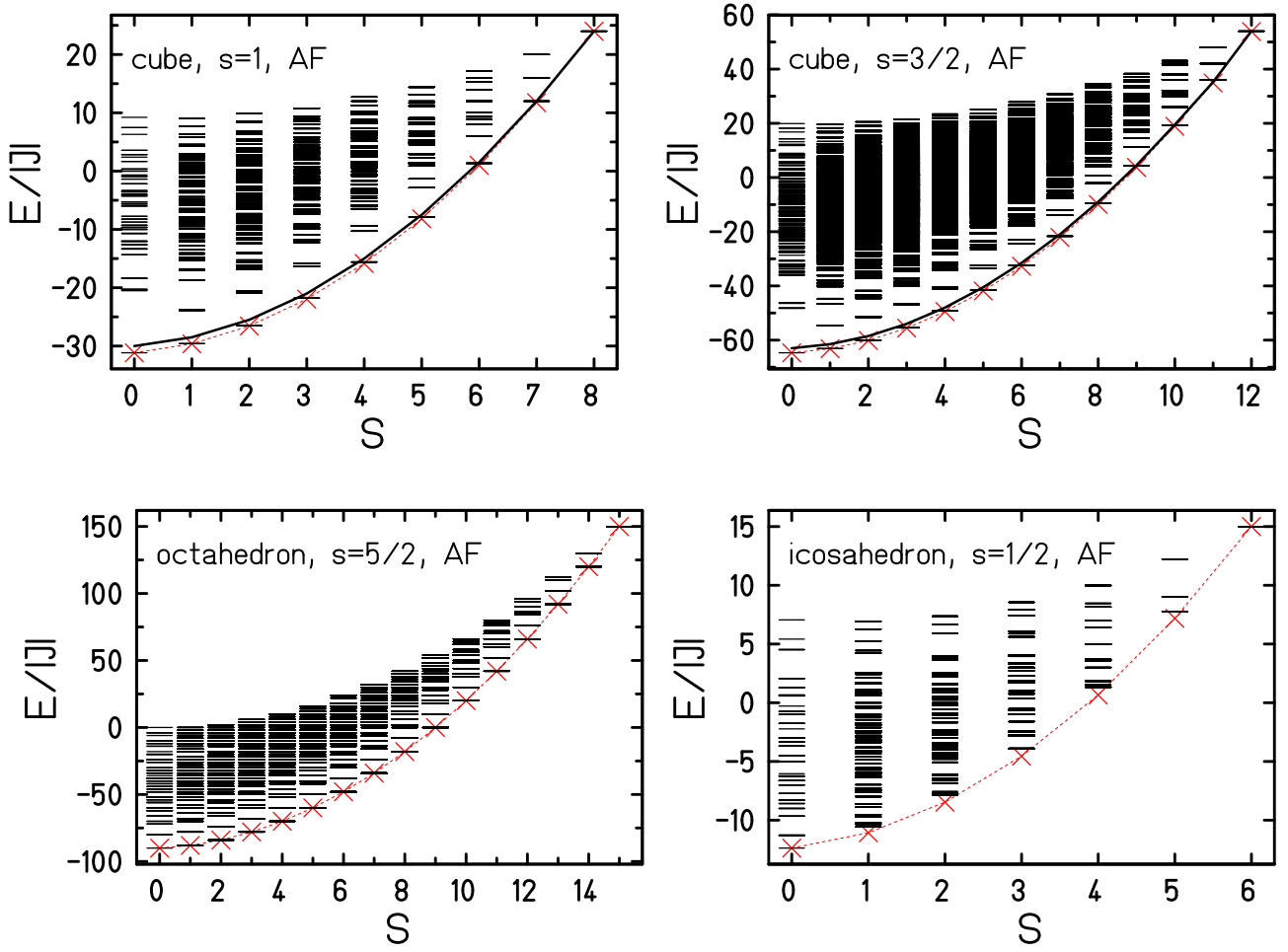
Evaluation of eigenvalues and eigenstates of the Hamilton operator in Hilbert subspaces $\mathcal{H}(S,M,k)$ with good quantum numbers S, M and k.

Rotational bands: numerical findings I



J. Schnack and M. Luban, Phys. Rev. B **63** (2001), 014418.

Rotational bands: numerical findings II



J. Schnack and M. Luban, Phys. Rev. B **63** (2001), 014418.

Rotational bands: justification I

Fourier decomposition according to sublattice structure[a], applied to rings of even N

$$\underset{\sim}{H} = -2\,J \sum_{u=1}^{N} \vec{\underset{\sim}{s}}(u) \cdot \vec{\underset{\sim}{s}}(u+1) = -2\,J \sum_{p \in \widehat{G}} e^{ip}\, \vec{\underset{\sim}{S}}_p \cdot \vec{\underset{\sim}{S}}_{-p} = \sum_{p \in \widehat{G}} \underset{\sim}{H}_p$$

$$\forall u : s(u) = s \ , \ \vec{\underset{\sim}{S}}_p := \frac{1}{\sqrt{N}} \sum_{u=1}^{N} e^{ipu}\, \vec{\underset{\sim}{s}}(u) \ , \ p \in \widehat{G} = \left\{ \frac{2\pi k}{N}, \ k = 0, \ldots, N-1 \right\}$$

$$\underset{\sim}{H}_0 + \underset{\sim}{H}_\pi = -\frac{2\,J}{N} \left(\sum_{u=1}^{N} \vec{\underset{\sim}{s}}(u) \right)^2 + \left(\sum_{u=1}^{N} (-1)^u\, \vec{\underset{\sim}{s}}(u) \right)^2 = -\frac{4\,J}{N} \left[\vec{\underset{\sim}{S}}^2 - \vec{\underset{\sim}{S}}_A^2 - \vec{\underset{\sim}{S}}_B^2 \right]$$

other $\underset{\sim}{H}_p$ small in ground state band; $\vec{\underset{\sim}{S}}_A, \vec{\underset{\sim}{S}}_B$ sublattice spins.

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[a] B. Bernu, P. Lecheminant, C. Lhuillier, and L. Pierre, Phys. Rev. B **50**, 10048 (1994).

Rotational bands: justification II

Bounding and approximating parabolas[a]

$$\underset{\sim}{H} \quad = \quad \sum_{\mu\nu} J_{\mu\nu}\, \underset{\sim}{\vec{s}}_\mu \cdot \underset{\sim}{\vec{s}}_\nu \quad , \quad J_{\mu\nu} = J_{\nu\mu} \qquad J_{\mu\mu} = 0,$$

$$\text{consider only cases where} \quad j \equiv \sum_\nu J_{\mu\nu},$$

evaluate eigenvalues of $\mathbb{J} \equiv (J_{\mu\nu})$; dimension $N \times N$.

$$\frac{j - j_{\min}}{N}\, \underset{\sim}{\vec{S}}^2 + j_{\min} N s(s+1) \leq \underset{\sim}{H} \leq \frac{j - j_{\max}}{N}\, \underset{\sim}{\vec{S}}^2 + j_{\max} N s(s+1)$$

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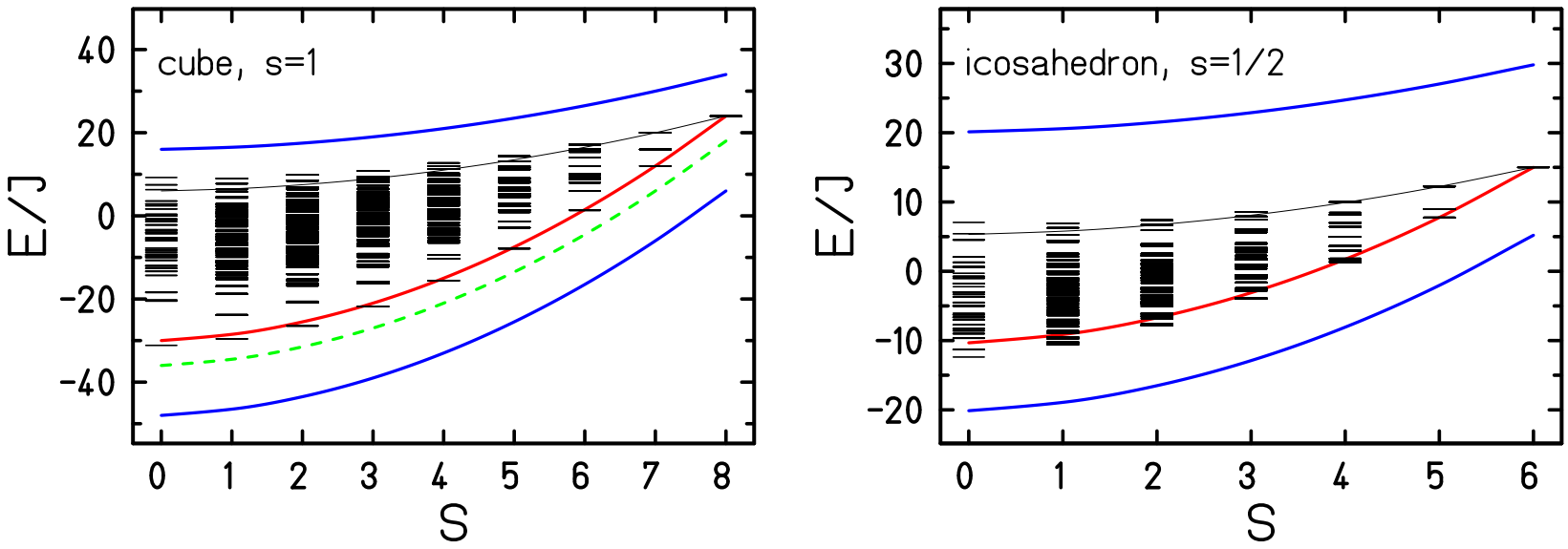
[a] H.-J. Schmidt, J. Schnack, M. Luban, *Bounding and approximating parabolas for the spectrum of Heisenberg spin systems*, submitted to Europhysics Letters, cond-mat/0101228.

Bounding and approximating parabolas



- appropriately shifted bounding parabola approximates ground state band very well;
- curvature parameter D uniquely defined by eigenvalues j and $j_{\min}$;
- for symmetric spin arrays result coincides with other "derivations";
- generalization; works also for non-symmetric systems.

Rotational band Hamiltonian

$$\underset{\sim}{H} = -2\,J \sum_{(u<v)} \vec{\underset{\sim}{s}}(u) \cdot \vec{\underset{\sim}{s}}(v) \quad \approx \quad -\frac{D\,J}{N} \left[\vec{\underset{\sim}{S}}^2 - \sum_{j=1}^{N_{SL}} \vec{\underset{\sim}{S}}_j^2 \right] = \underset{\sim}{H}_1^{\text{eff}}$$

$$\approx \quad -J\,\frac{D(N,s)}{N} \left[\vec{\underset{\sim}{S}}^2 - \gamma \left(\sum_{j=1}^{N_{SL}} \vec{\underset{\sim}{S}}_j^2 \right) \right] = \underset{\sim}{H}_2^{\text{eff}}$$

- N_{SL} – number of sublattices, $\vec{\underset{\sim}{S}}_j$ – sublattice spin;
  $\{\mathrm{Mo_{72}Fe_{30}}\}$[a]:
- $N_{SL} = 3$, $S_A, S_B, S_C = 0, 1, \ldots, 25$, $S = 0, 1, \ldots, 75$;
- $D = 6$ determined from "ferromagnetic ground state" or j and $j_{\min}$;
- $D(N,s) = 6.23$, $\gamma = 1.148$.

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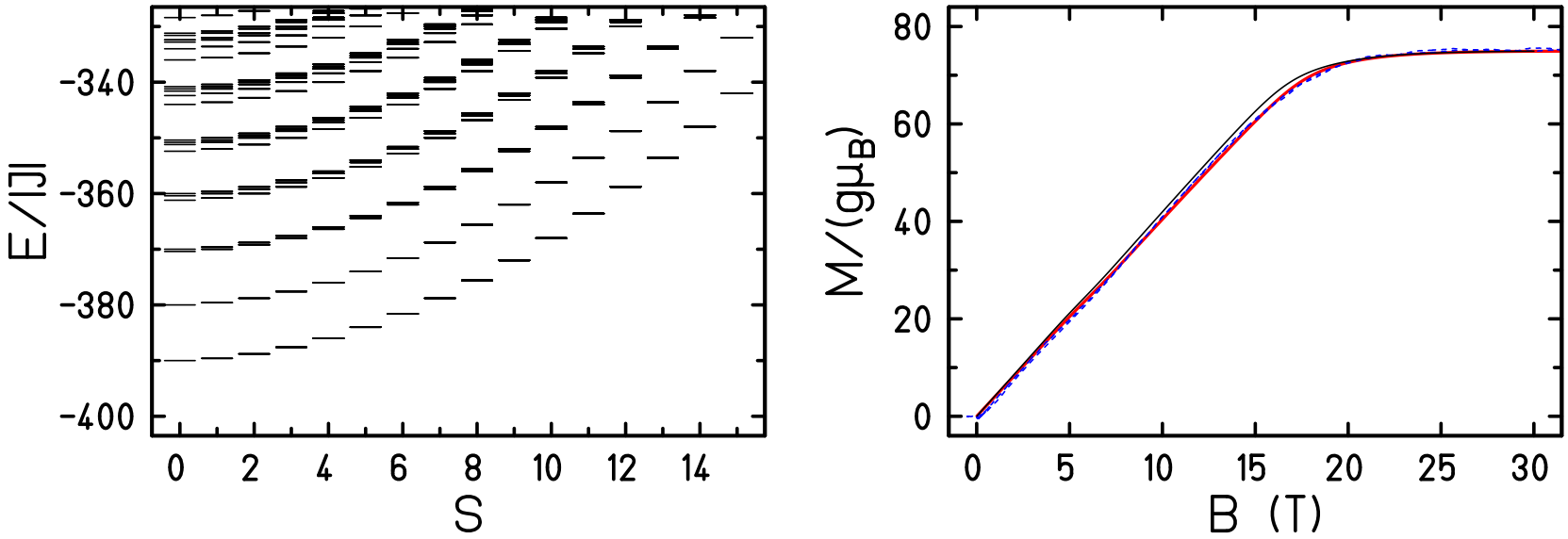
[a] M. Luban, J. Schnack, and R. Modler, *Approximate quantum model of the Heisenberg molecular magnet* $\{Mo_{72}Fe_{30}\}$, Phys. Rev. Lett. (submitted).

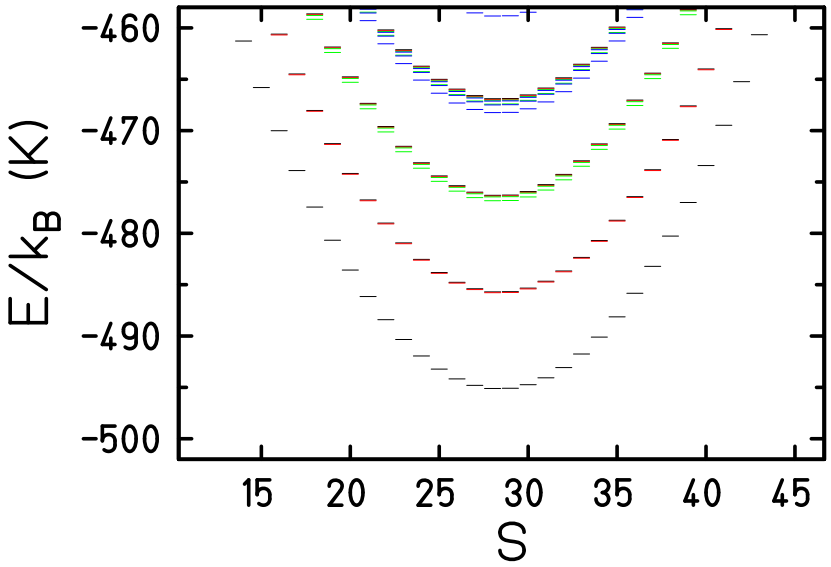
Spectrum and Magnetisation I

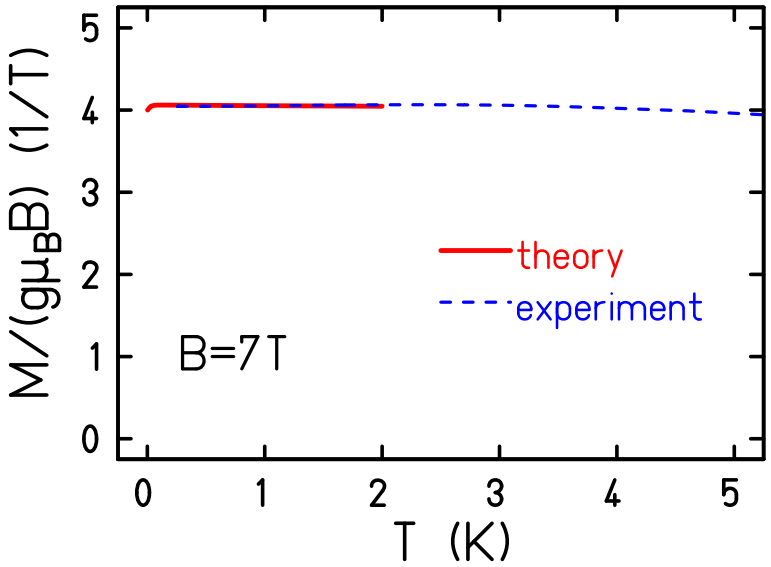


$\{Mo_{72}Fe_{30}\}$:

- 1. (lowest) band: $S_A = S_B = S_C = 25$, $S = 0, 1, \ldots, 75$;
- 2. band: $S_A = S_B = 25$, $S_C = 24$ (and permutations), $S = 0, 1, \ldots, 74$;
- 3. band: $S_A = 25$, $S_B = S_C = 24$ or $S_A = S_B = 25$, $S_C = 23$ (and permutations), $S = 0, 1, \ldots, 73$;
- magnetisation curve at low T basically given by 1. band:
  black curve – $D = 6$, red curve – $D(N, s)$, blue curve – data.

Spectrum and Magnetisation II

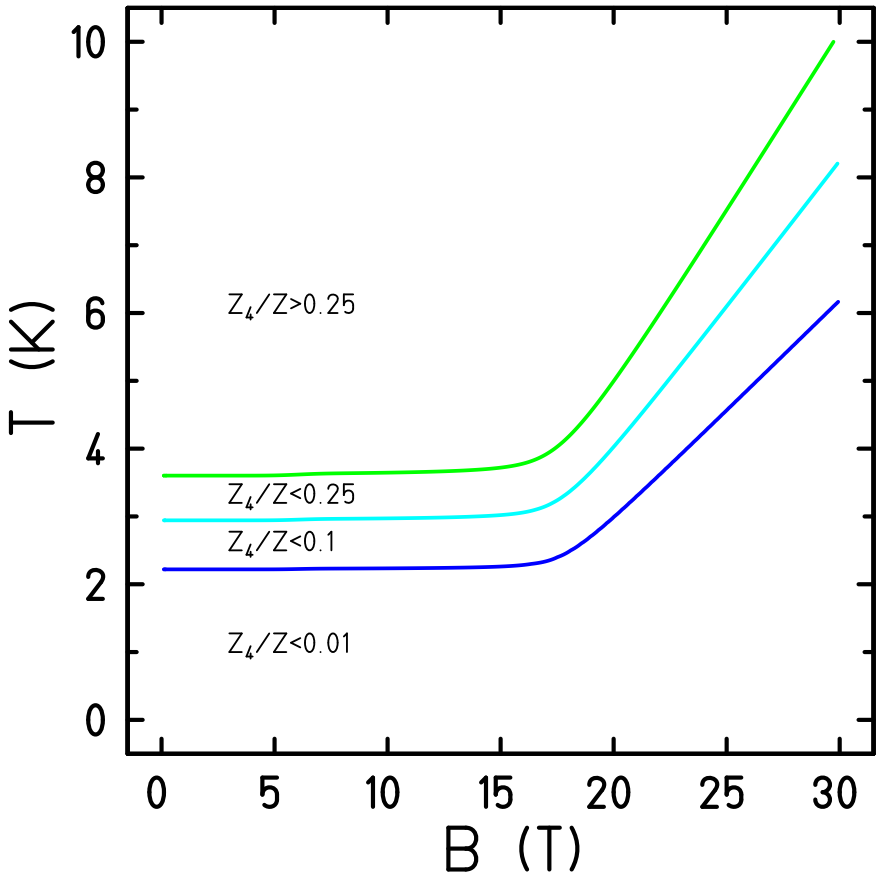




$\{Mo_{72}Fe_{30}\}$:

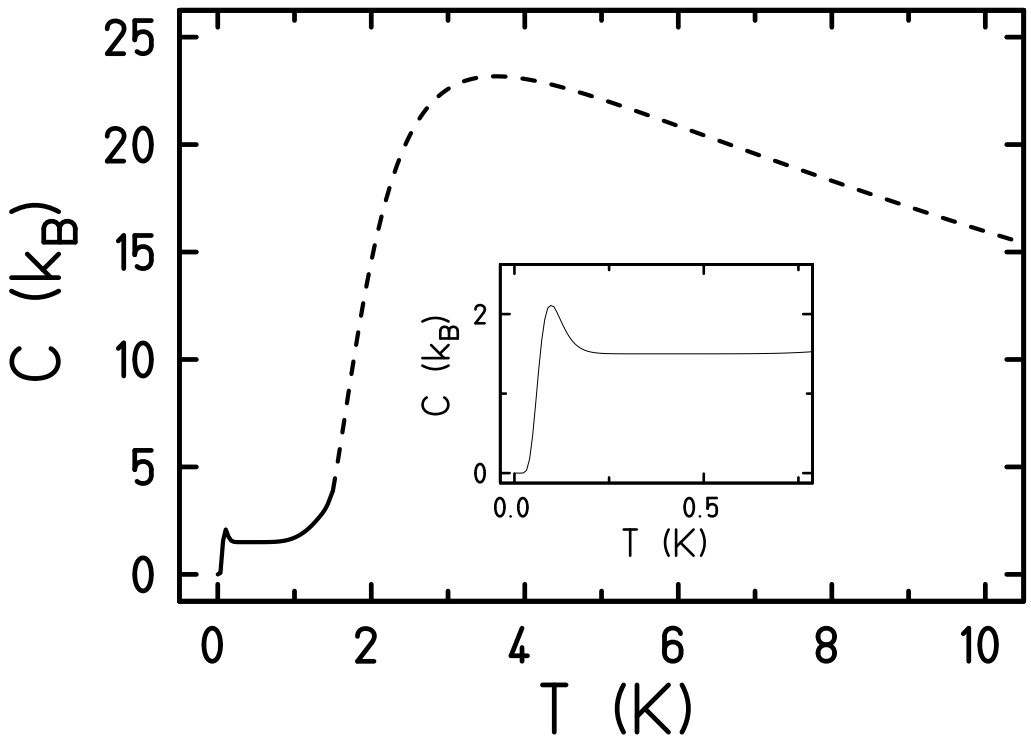
- high degeneracy within a band;
- exponentially increasing degeneracy from band to band;
- contributions from $M \neq S_0(B)$ average to $\langle\langle\ M\ \rangle\rangle \approx S_0(B)$;
- but due to exponentially increasing degeneracy a limiting temperature exists.

Limiting temperature



- contribution Z_4 of the fourth band to the partition function $Z = Z_1 + Z_2 + Z_3 + Z_4$;
- exponentially increasing degeneracy from band to band;
- partition function cannot be treated iteratively band by band above $T_L(B)$;
- above $T_L(B)$ a vast number of bands contributes.

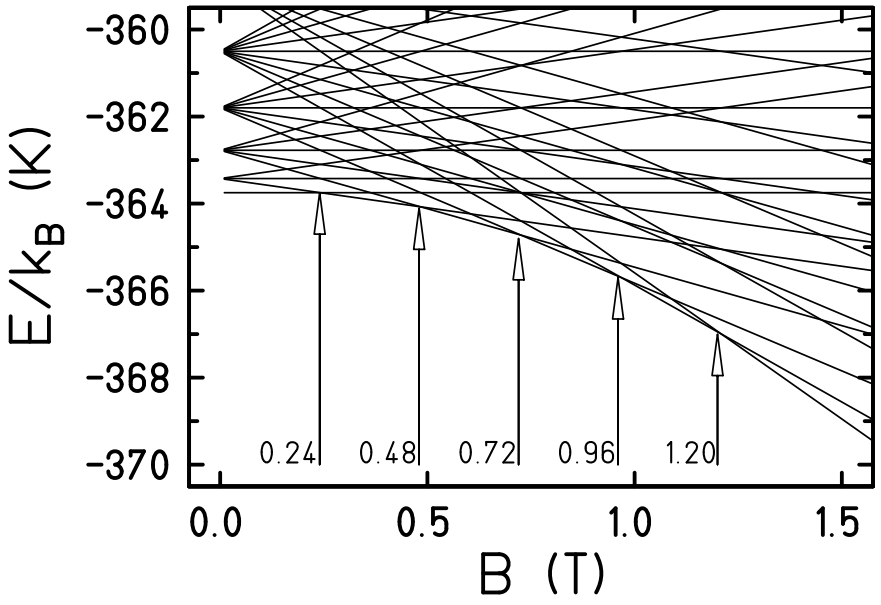
Specific heat



specific heat of $\{Mo_{72}Fe_{30}\}$:

- below $T_L(B) \approx 1.5 \ldots 2$ K rotational Hamiltonian predicts peak and classical behaviour;
- above $T_L(B)$ an interpolation connecting to the correct high temperature limit is used.

Can one detect rotational bands?



- quadratic dependence of E on S in the ground state band can be confirmed by:
- the rather straight line M vs. B below the saturating field;
- low-temperature NMR: level crossings of the ground state band at equidistant field steps ΔB;
- a measurement of $C = 3k_B/2$ for $0.25\ \mathrm{K} < T < 0.75\ \mathrm{K}$;
- the 2. band can be confirmed by:
- low-temperature ESR and neutron scattering should see the gap to the second band, $\Delta E \approx 8$ K.

Summary

Summary

- Heisenberg model with isotropic next neighbour interaction describes the spectrum of $\{Mo_{72}Fe_{30}\}$ with very good accuracy;
- additional terms seem to be rather small – zero field splitting?;
- rotational band structure is confirmed for a wide variety of spin arrays;
- low-temperature behaviour can be modeled using the first few rotational bands.

Open problems or in progress

- Confirm rotational band structure!
- Exact calculations for the icosidodecahedron of $s = 1/2$? It may be synthesised!
- Approximations for the intermediate energy levels, spin-resolved density of states.