Nano Quantum Magnetism

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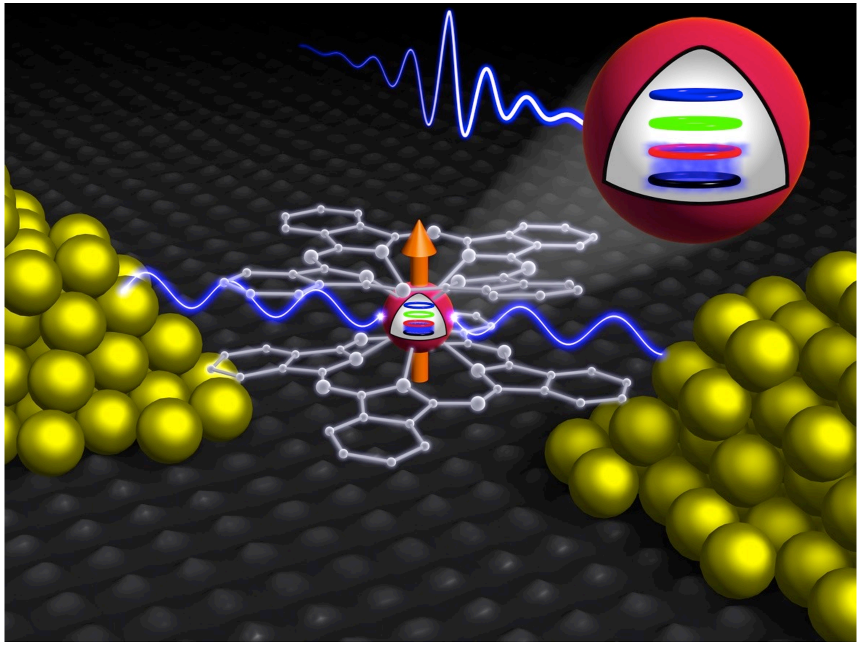


Lecture 9

Magnetic structures

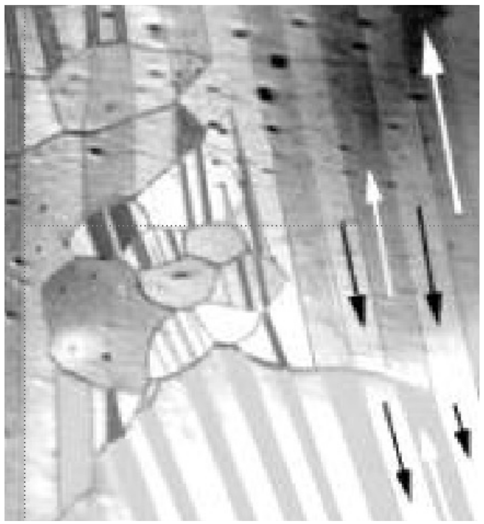
macroscopic ← → atomic

permanent magnets | micron particles | nanoparticles | clusters | molecular clusters | atoms

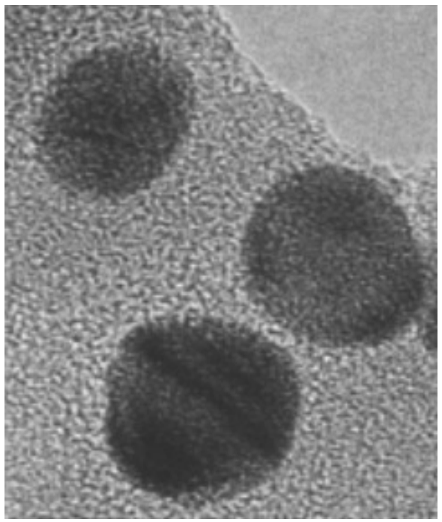
$S = 10^{20}$ 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1

multi - domains ***single - domains*** ***spins***

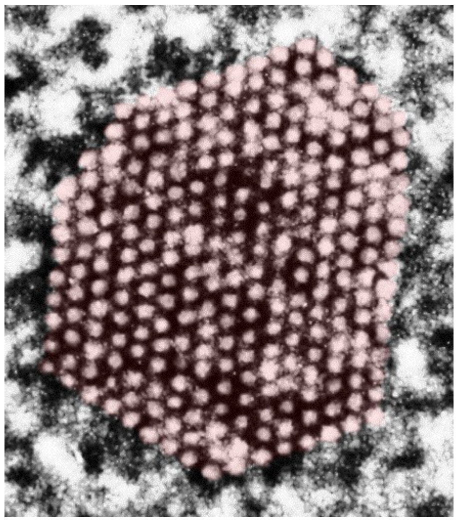
1 mm



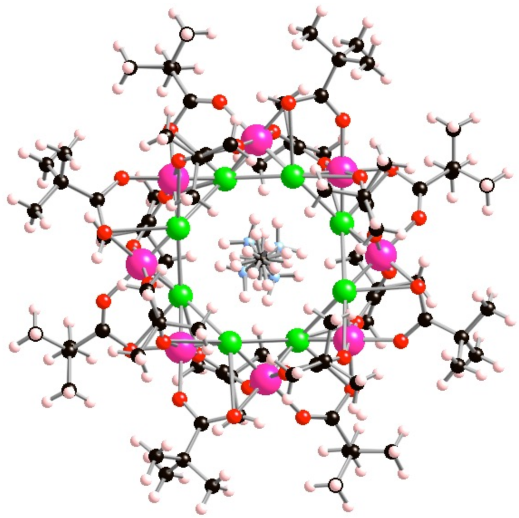
20 nm



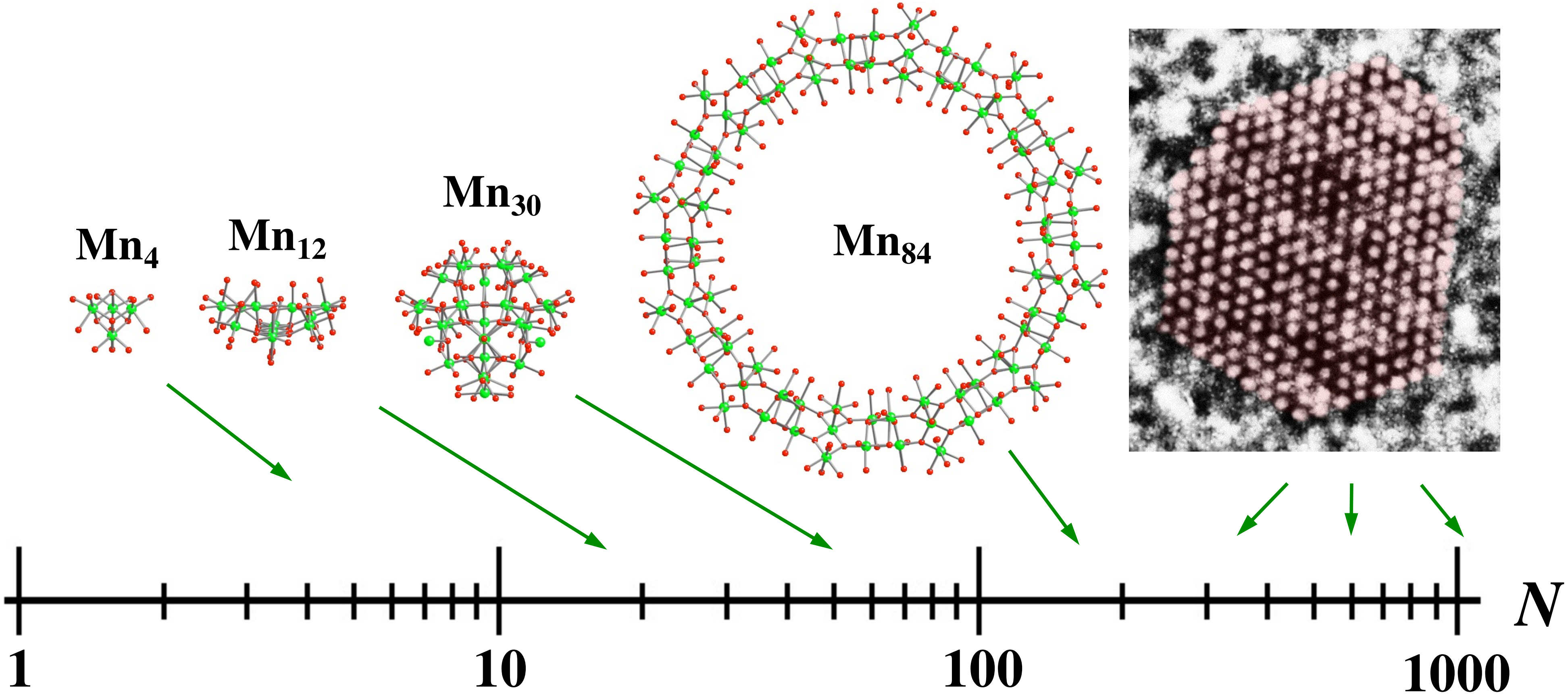
3 nm



1 nm



This lecture



Quantum world ↔ Classical world

Molecular (bottom-up) approach ↔ Classical (top-down) approach

Angew. Chem. Int. Ed. 43, 2117 (2004)

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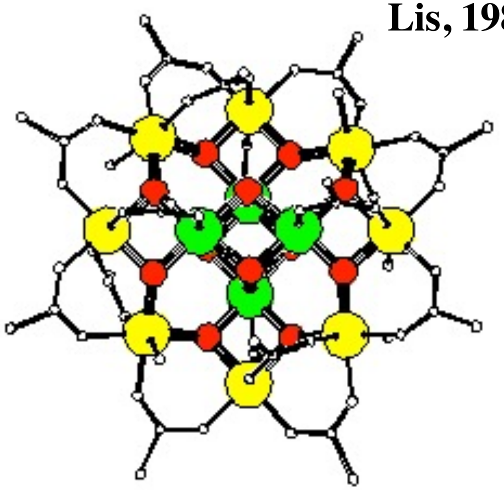
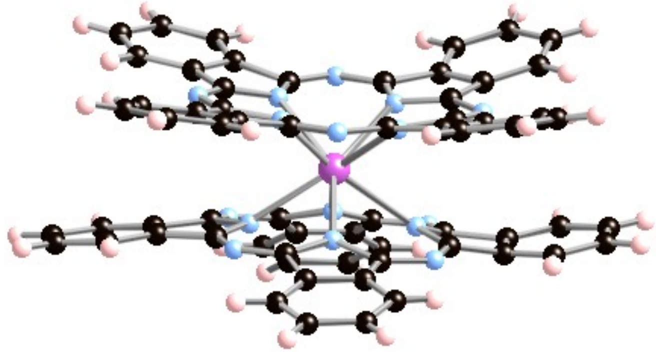
Single-molecule magnets (SMM)

Giant spins

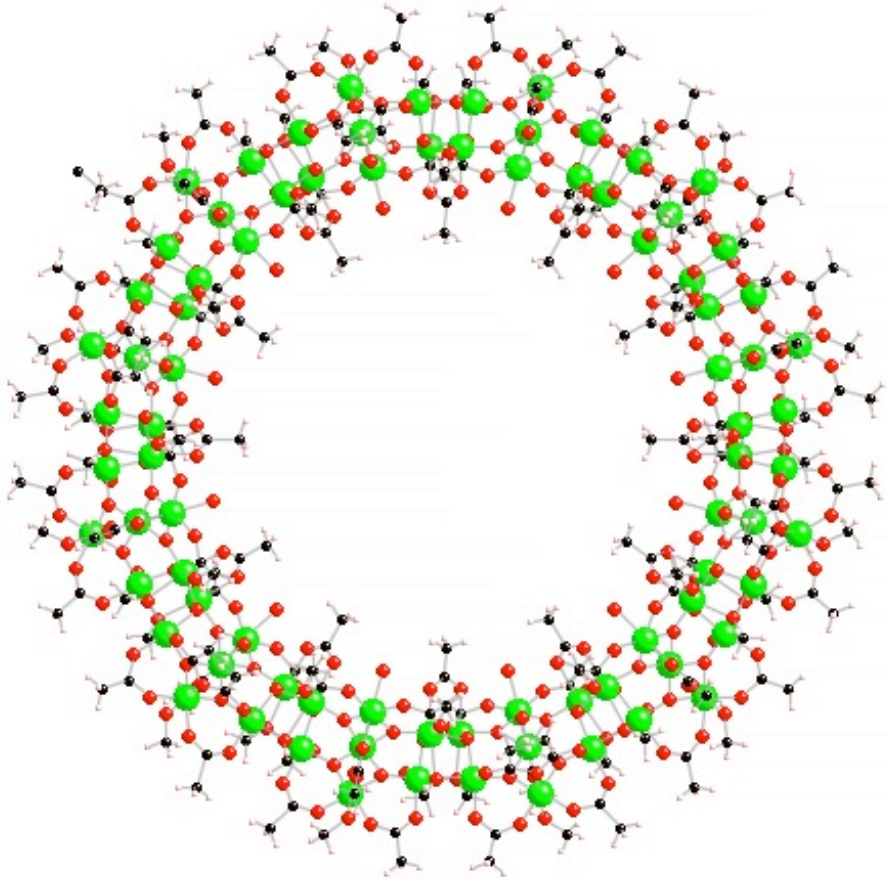
Lis, 1980



Mn_{12} $S = 10$



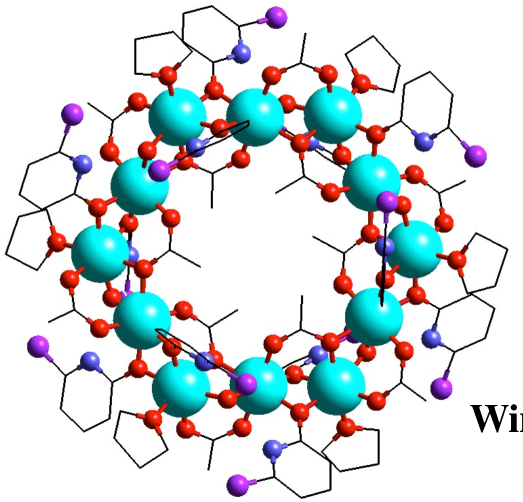
Tb $J = 6$



Mn_{84} $S \approx 6$

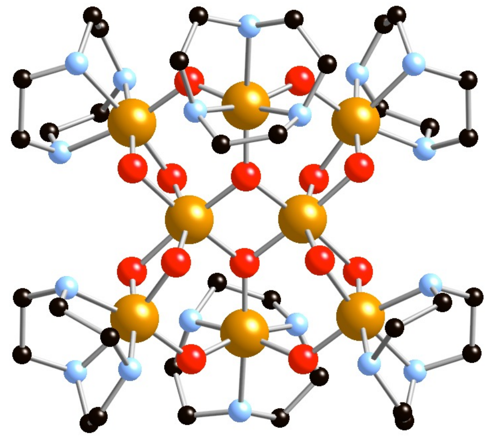
Christou, 2004

Ni_{12} $S = 12$



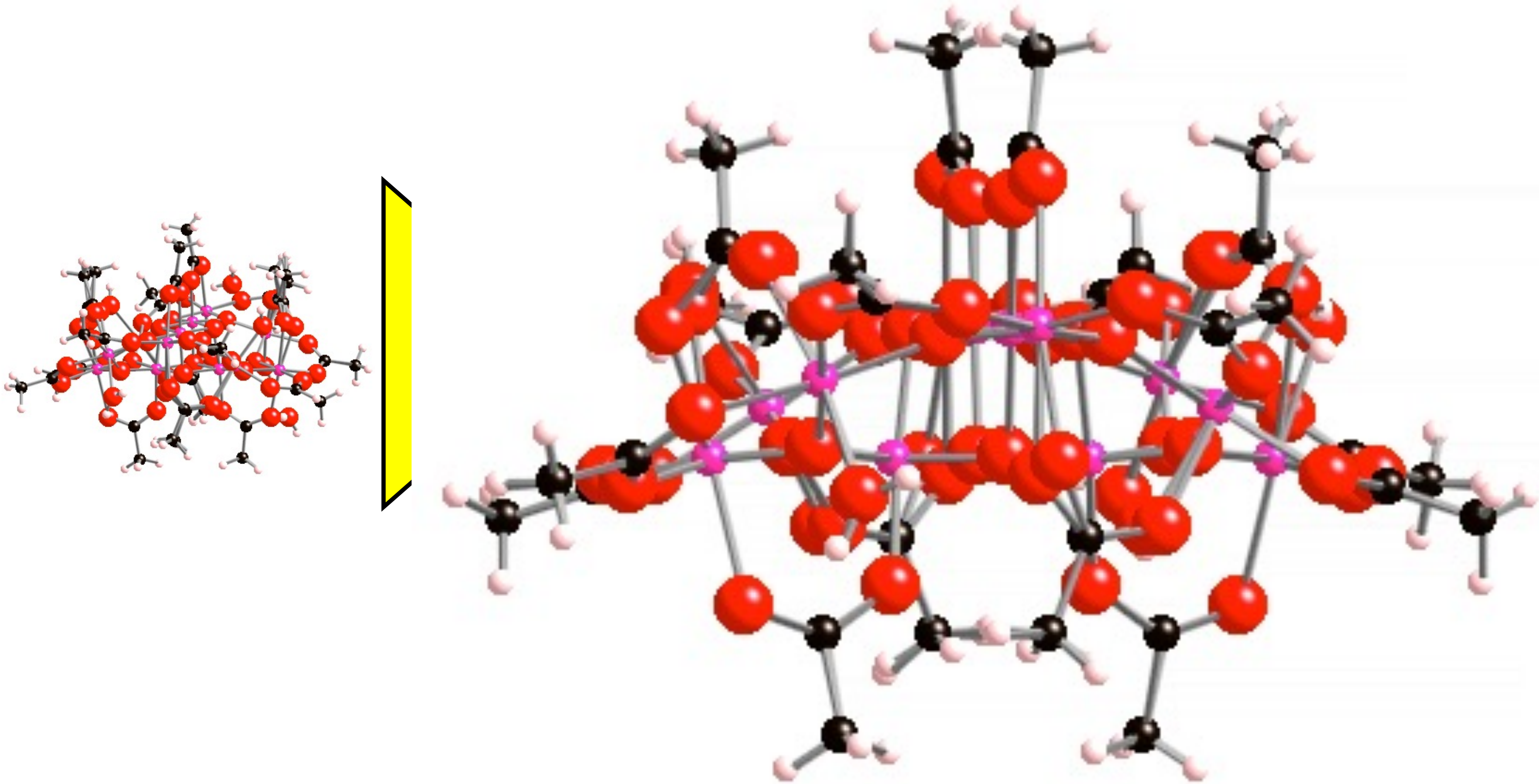
Winpenny, 1999

Fe_8 $S = 10$

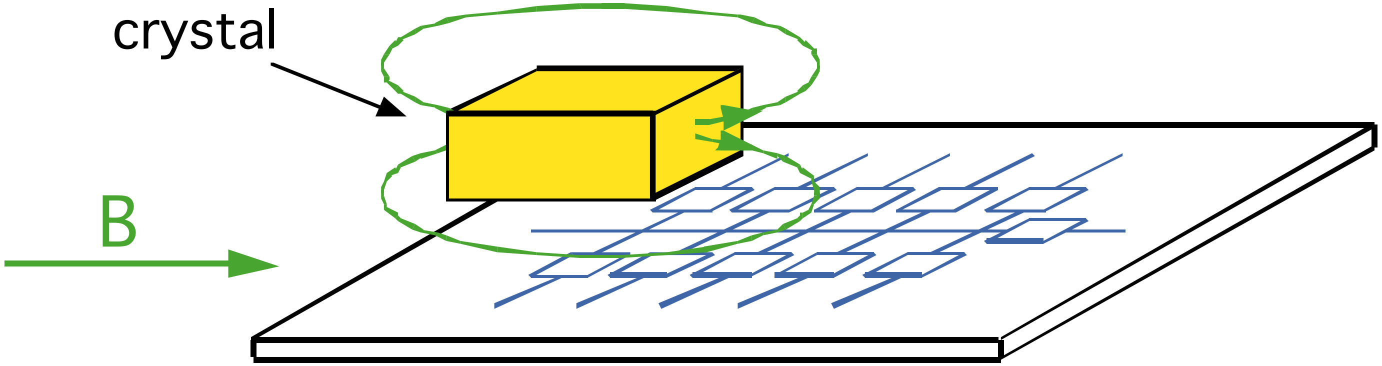


Wiegart, 1984

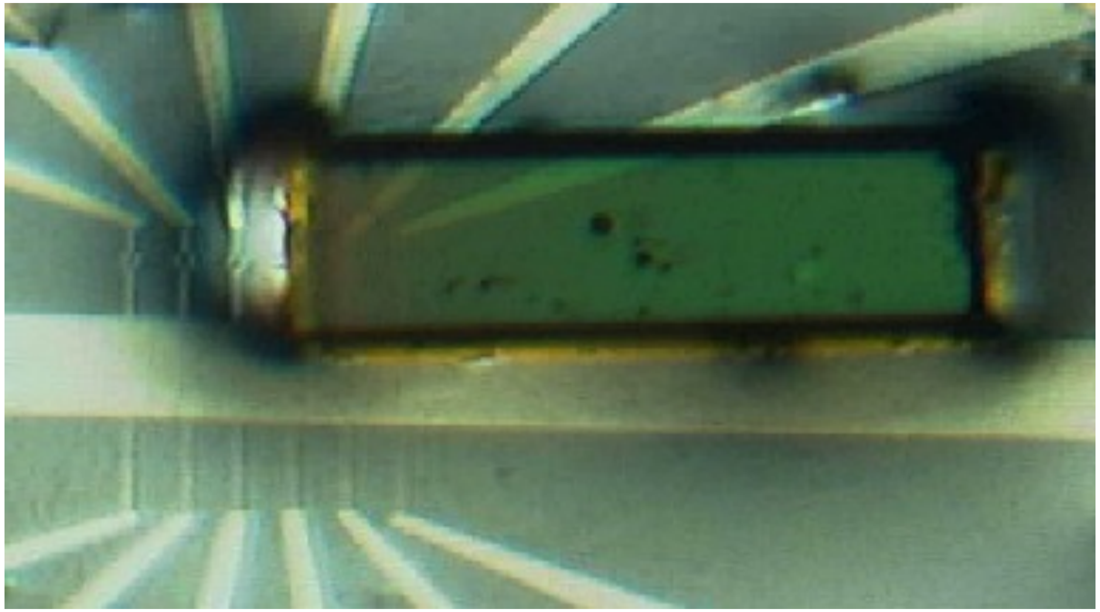
Crystal of SMMs



Micro-SQUID array



- **crystal size > few μm**
- **10^{-12} to 10^{-17} emu**
- **temperature 0.03 - 7 K**
- **field < 1.4 T and < 20 T/s**
- **rotation of field**
- **transverse field**
- **several SQUIDs at different positions**

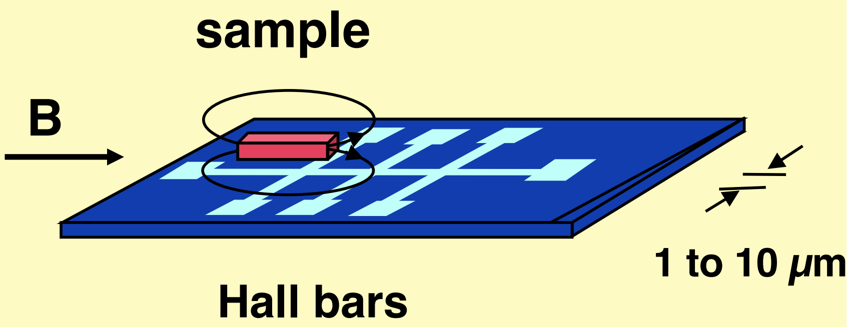


50 μm

W.W. *Adv. Chem. Phys.* 118, 99 (2001)

Micro-magnetometry

- μ-Hall Effect

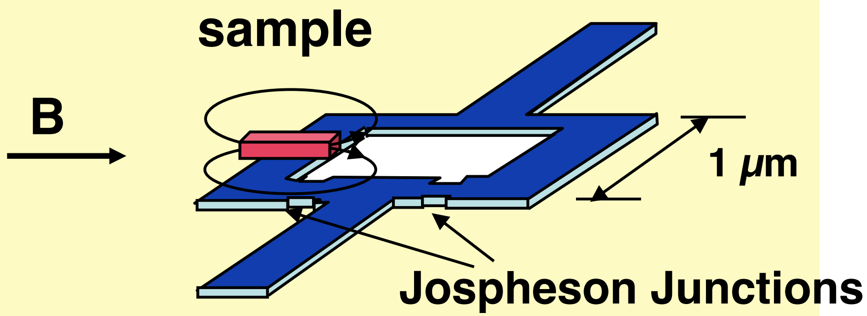


  - Based on Lorentz Force
  - Measures magnetic field

$$V_H = \frac{\alpha I}{ne} M$$

  - Large applied in-plane magnetic fields (>20 T)
  - Broad temperature range
  - Single magnetic particles
  - Ultimate sensitivity ~10^2 μ_B

- μ-SQUID



  - Based on flux quantization
  - Measures magnetic flux
  - Applied fields below the upper critical field (~1 T)
  - Low temperature (below T_c)
  - Single magnetic particles
  - Ultimate sensitivity ~1 μ_B

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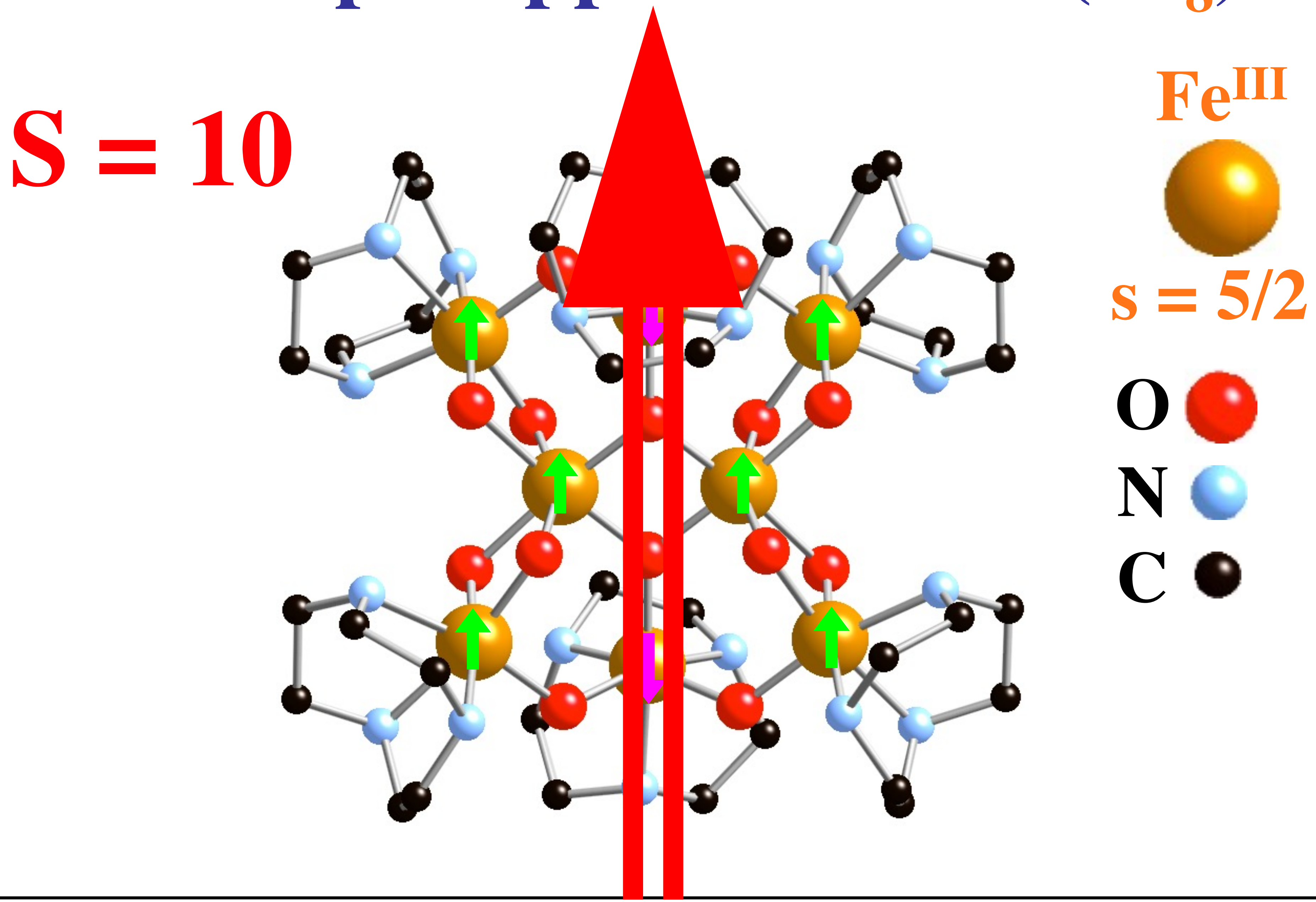
Giant spin approximation (Fe_8)



Giant Spin Hamiltonians

Nanoparticle:

$$\mathbf{E} = -K_{||} \cos^2\theta + K_{\perp} \sin^2\theta \cos^2\phi + \ldots + \mu_0 \vec{M} \vec{H}$$

$$E = E_0 (\vec{m}) - \mu_0 M_S \vec{m} \vec{H}$$

(Stoner and Wohlfarth)

Single spin model:

$$H = -D S_z^2 + E S_x^2 + \ldots + g\mu_B \mu_0 \vec{S} \vec{H}$$

(Schroedinger, Heisenberg)

***Semi-classical* spin**

$$Z = \oint D\{\cos\theta\} D\{\phi\} \exp\left[-\frac{1}{\hbar} \int_0^{\hbar/T} d\tau \, S\dot{\phi}(\cos\theta - 1) - H(\theta, \phi) \right]$$

(Path intergral formalism of Feynman)

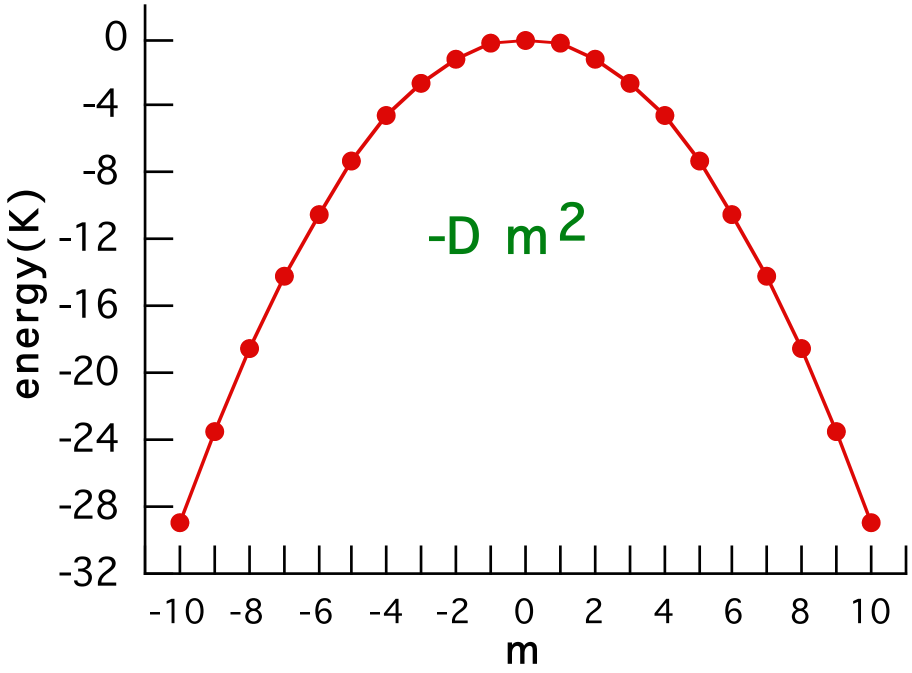
Single spin model

$$\mathrm{H} = -D\, S_z^2 + E\, S_x^2 + \ldots + g\mu_B\, \vec{S}\, \vec{H}$$

Choice of quantification axis: Sz – direction

Choice of the base $|S,m\rangle$ ***with m = -S, -(S-1), ..., S***

Matrix elements: $E_{m,n} = \langle S,m | H | S,n \rangle$



Diagonalisation:

- ***eigen-values (energy levels)***
- ***eigen-vectors***
- ***transition amplitudes***
- ***expectation values***

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Single spin model

$$\mathrm{H} = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B\,\vec{S}\,\vec{H}$$

using the spin raising and lowering opertators $S_{\pm} = S_x \pm i\,S_y$

$$\mathrm{H} = -D\,S_z^2 + E/2\left(S_+^2 + S_-^2\right) + g\mu_B\,\vec{S}\,\vec{H}$$

$$S_z^n\left|S,m\right\rangle = m^n\left|S,m\right\rangle$$

$$S_{\pm}\left|S,m\right\rangle = \sqrt{S\left(S+1\right) - m\left(m\pm 1\right)}\left|S,m\pm 1\right\rangle$$

$$S_{\pm}^2\left|S,m\right\rangle = \sqrt{\left[S\left(S+1\right) - m\left(m\pm 1\right)\right]\left[S\left(S+1\right) - \left(m\pm 1\right)\left(m\pm 2\right)\right]}\left|S,m\pm 2\right\rangle$$

Single spin model

$$E_{m,n} = \langle S,m | H | S,n \rangle$$

$$H = \begin{bmatrix}
\alpha_{+10} & \beta_{+10} & \gamma_{+9} & & & & & & & \\
\beta_{+10} & \alpha_{+9} & * & * & & & & & & \\
\gamma_{+9} & * & * & * & * & & & \mathbf{O} & & \\
 & * & * & * & * & * & & & & \\
 & & * & * & * & * & * & & & \\
 & & & * & * & * & * & * & & \\
 & & & & * & * & * & * & * & \\
 & & \mathbf{O} & & & * & * & * & * & \gamma_{-9} \\
 & & & & & & * & * & \alpha_{-9} & \beta_{-10} \\
 & & & & & & & \gamma_{-9} & \beta_{-10} & \alpha_{-10}
\end{bmatrix}$$

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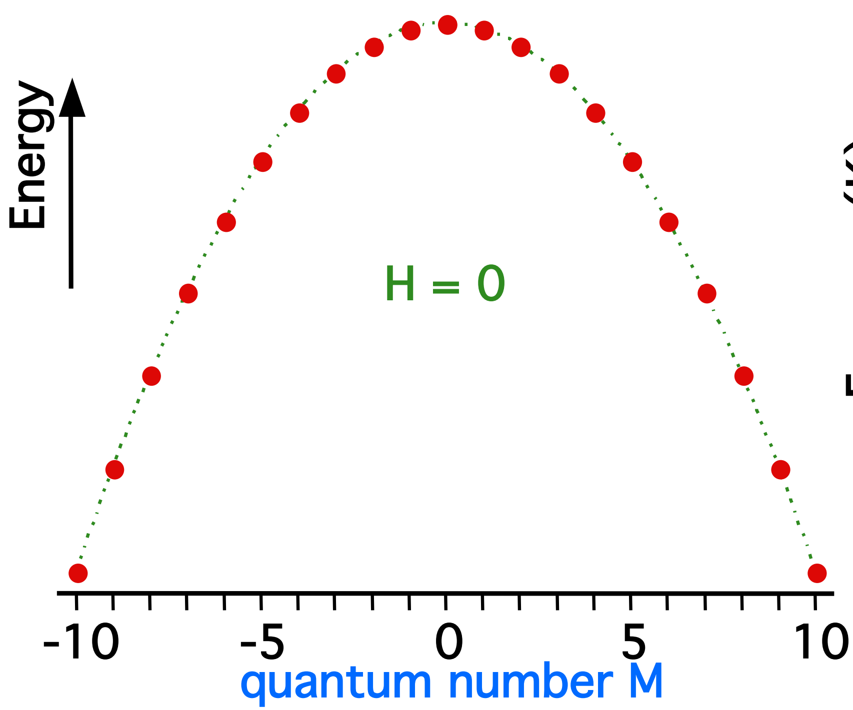
Giant spin model

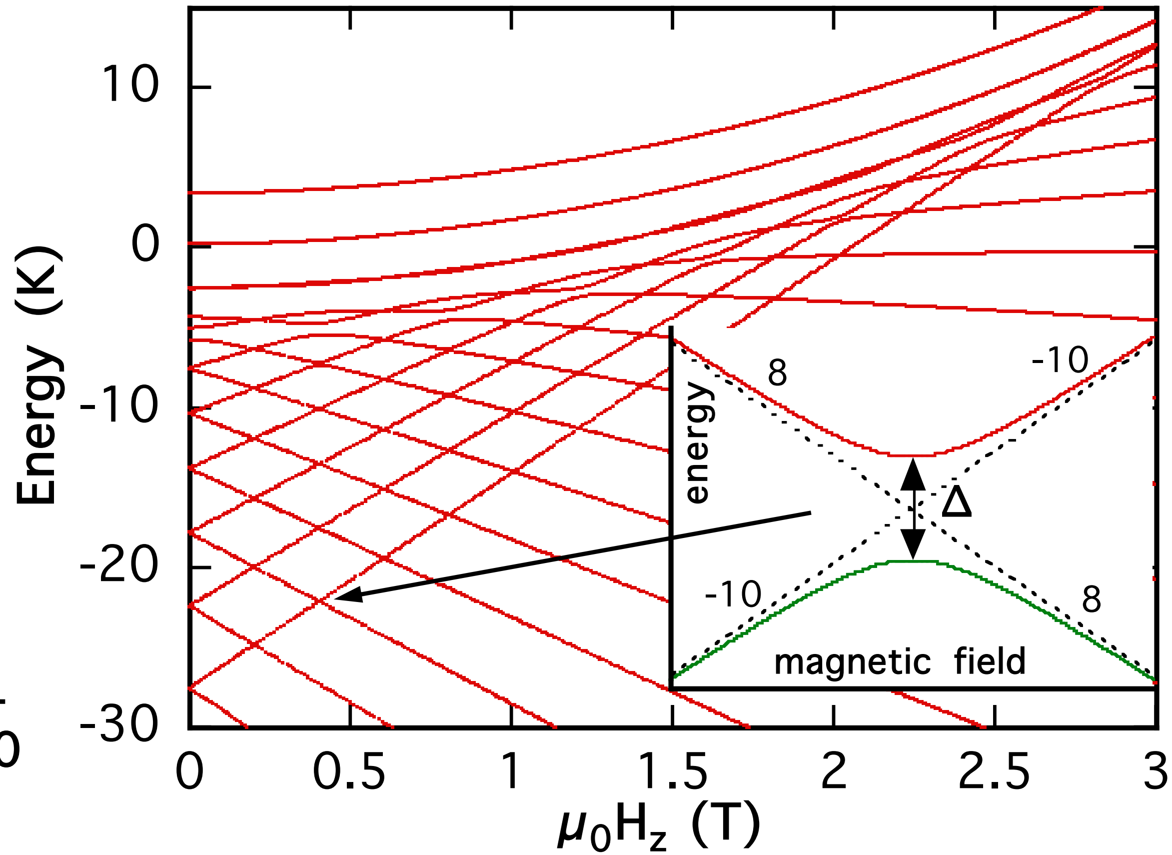
Spin Hamiltonian: $H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B \vec{S}\,\vec{H}$

(2S + 1) energy states: M = -S, -S+1, …, S

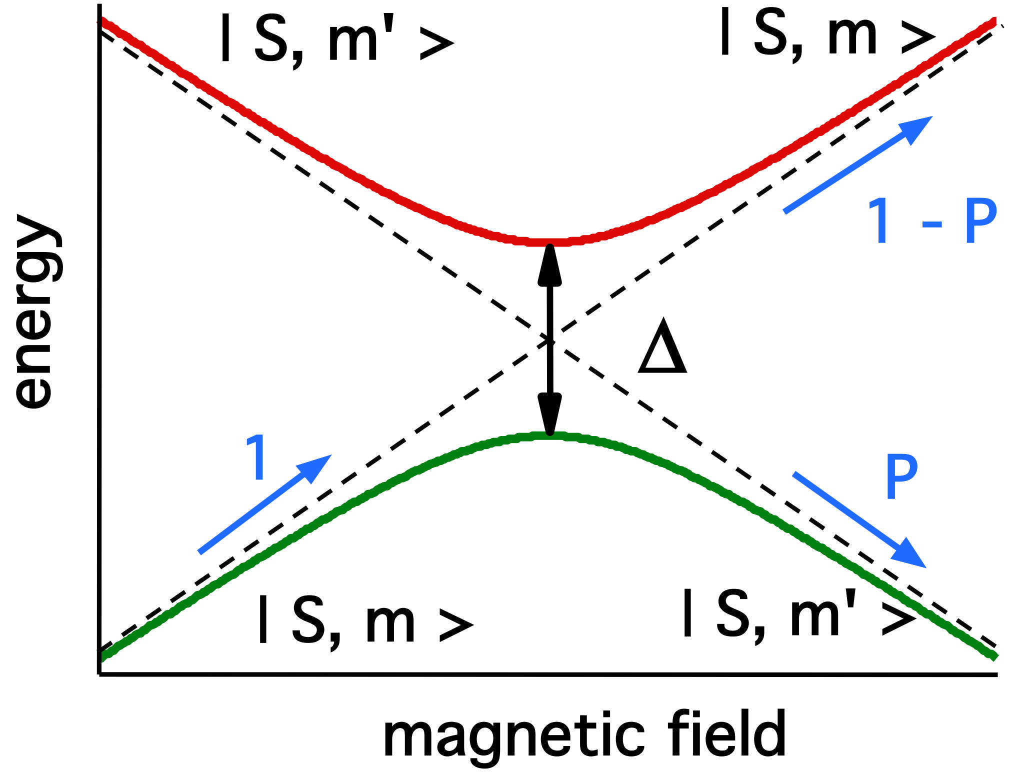
magnetic anisotropy **Zeeman energy**

Energy levels: Zeeman diagram





Tunneling probability at an avoided level crossing
Landau-Zener model (1932)



- *general result for a single level crossing*

$$H = \begin{pmatrix} A - h & \Delta \\ \Delta & B - h \end{pmatrix}$$

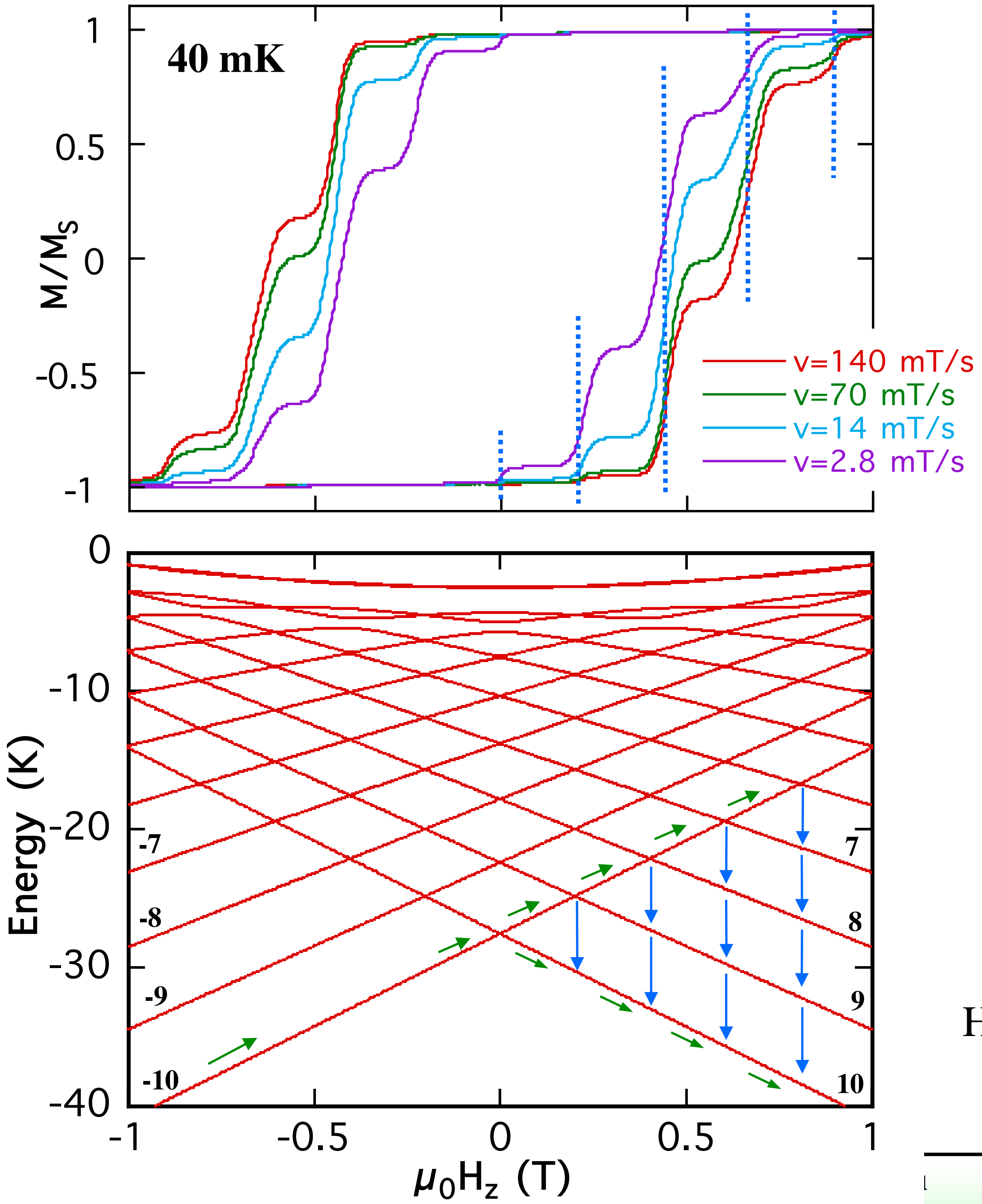
- *solution of the Schroedinger equation*

$$H|\ \rangle = i\hbar \frac{\partial}{\partial t}|\ \rangle$$

$$P = 1 - \exp\left[-c \frac{\Delta^2}{dH/dt}\right]$$

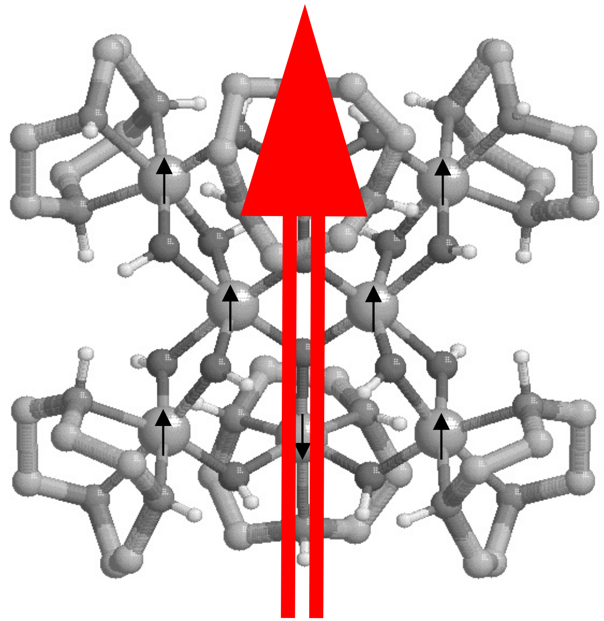
$$c = \frac{\pi}{2\hbar\, g\mu_B |m - m'| \mu_0}$$

L. Landau, *Phys. Z. Sowjetunion* 2, 46 (1932); C. Zener, *Proc. R. Soc. London, Ser. A* 137, 696, (1932); E.C.G. Stückelberg, *Helv. Phys. Acta* 5, 369 (1932); S. Miyashita, *J. Phys. Soc. Jpn.* 64, 3207 (1995); V.V. Dobrovitski and A.K. Zvezdin, *Euro. Phys. Lett.* 38, 377 (1997); L. Gunther, *Euro. Phys. Lett.* 39, 1 (1997); G.Rose and P.C.E. Stamp, Low Temp. Phys. 113, 1153 (1999); M. Leuenberger and D. Loss, Phys. Rev. B 61, 12200 (2000); M. Thorwart, M. Grifoni, and P. Hänggi, Phys. Rev. Lett. 85, 860 (2000); …



Application of Landau-Zener tunneling

Fe_8 S = 10



$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B \vec{S}\,\vec{H}$$

with S = 10, D = 0.27 K, E = 0.046K

A.-L. Barra et al. EPL (1996)

Field sweep rate dependence of Landau-Zener tunneling

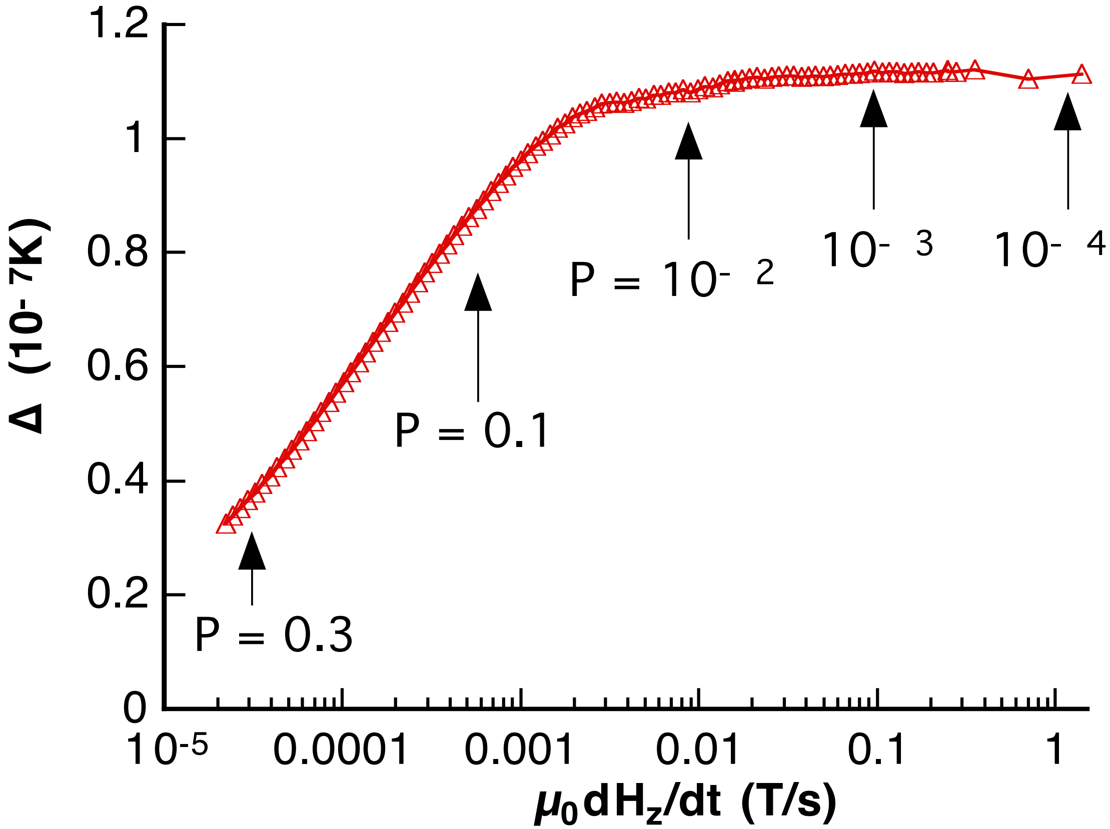
Landau-Zener tunneling probability P

$$P = 1 - \exp\left[-\frac{\pi \Delta^2}{4\hbar\, g\mu_B S\, dH/dt}\right]$$

$$\Rightarrow \Delta = \sqrt{-\frac{4\hbar\, g\mu_B S}{\pi}\frac{dH}{dt}\ln[1-P]}$$

$$\Rightarrow \Delta \neq f\left(\frac{dH}{dt}\right)$$

fullfilled for P < 0.04



Jie Liu, Biao Wu, Li-Bin Fu, R.B. Diener, and Qian Niu
cond-mat/0105497, PRB' 02

Field sweep rate dependence of Landau-Zener tunneling

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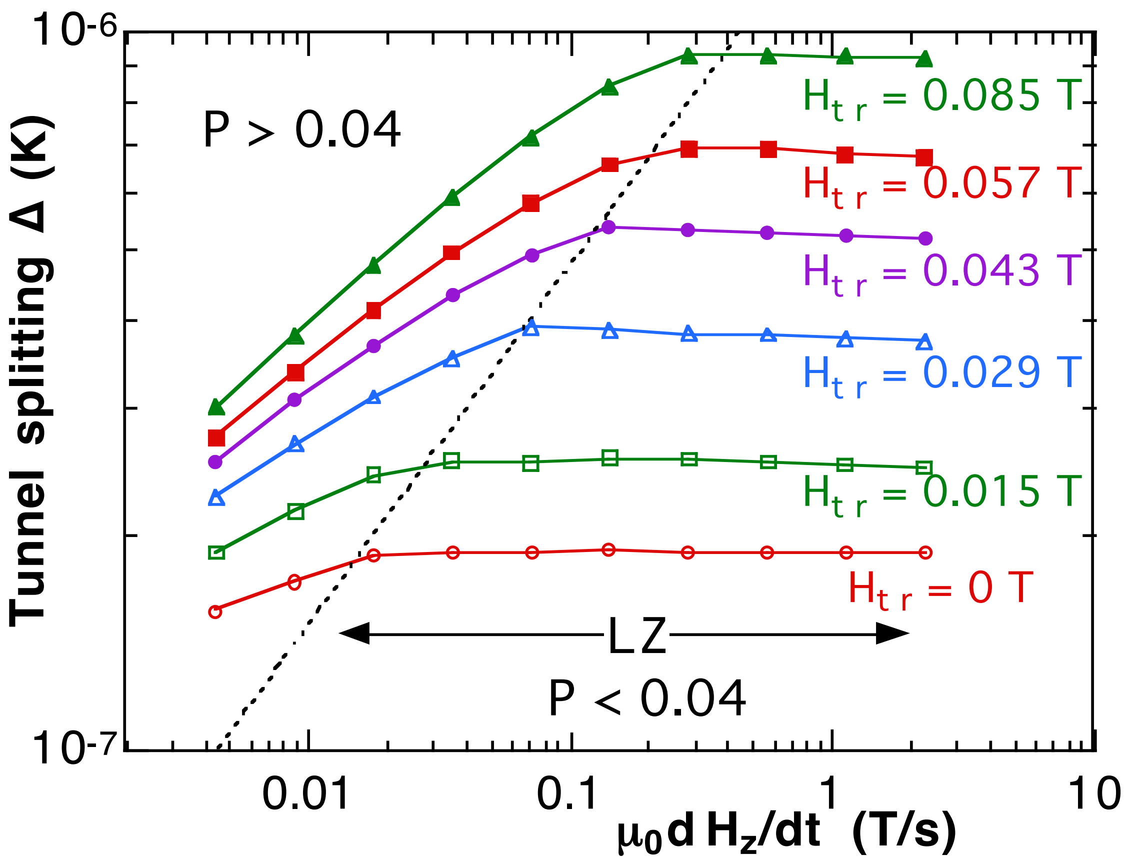
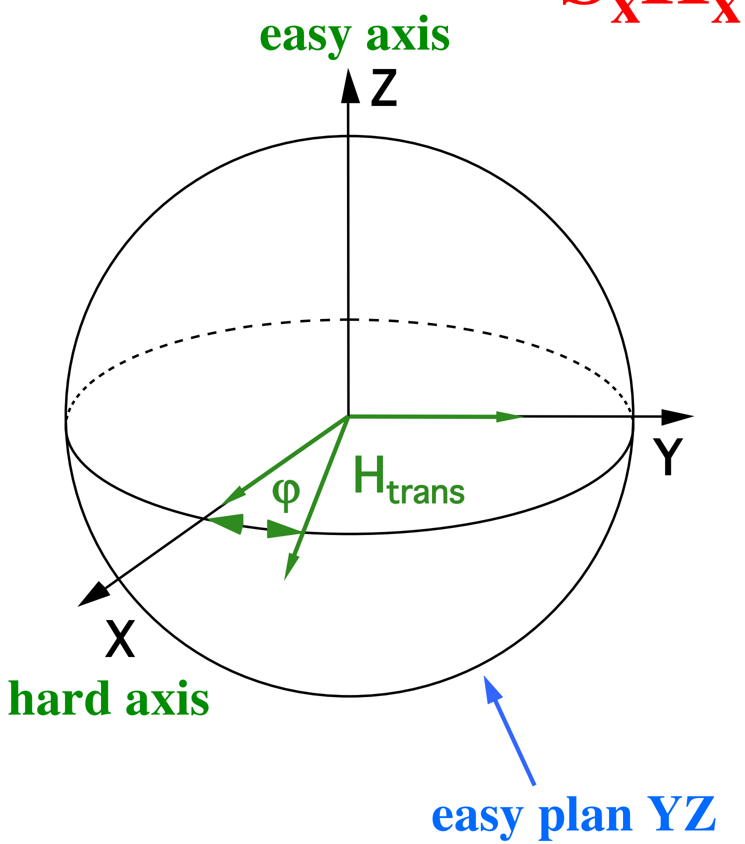


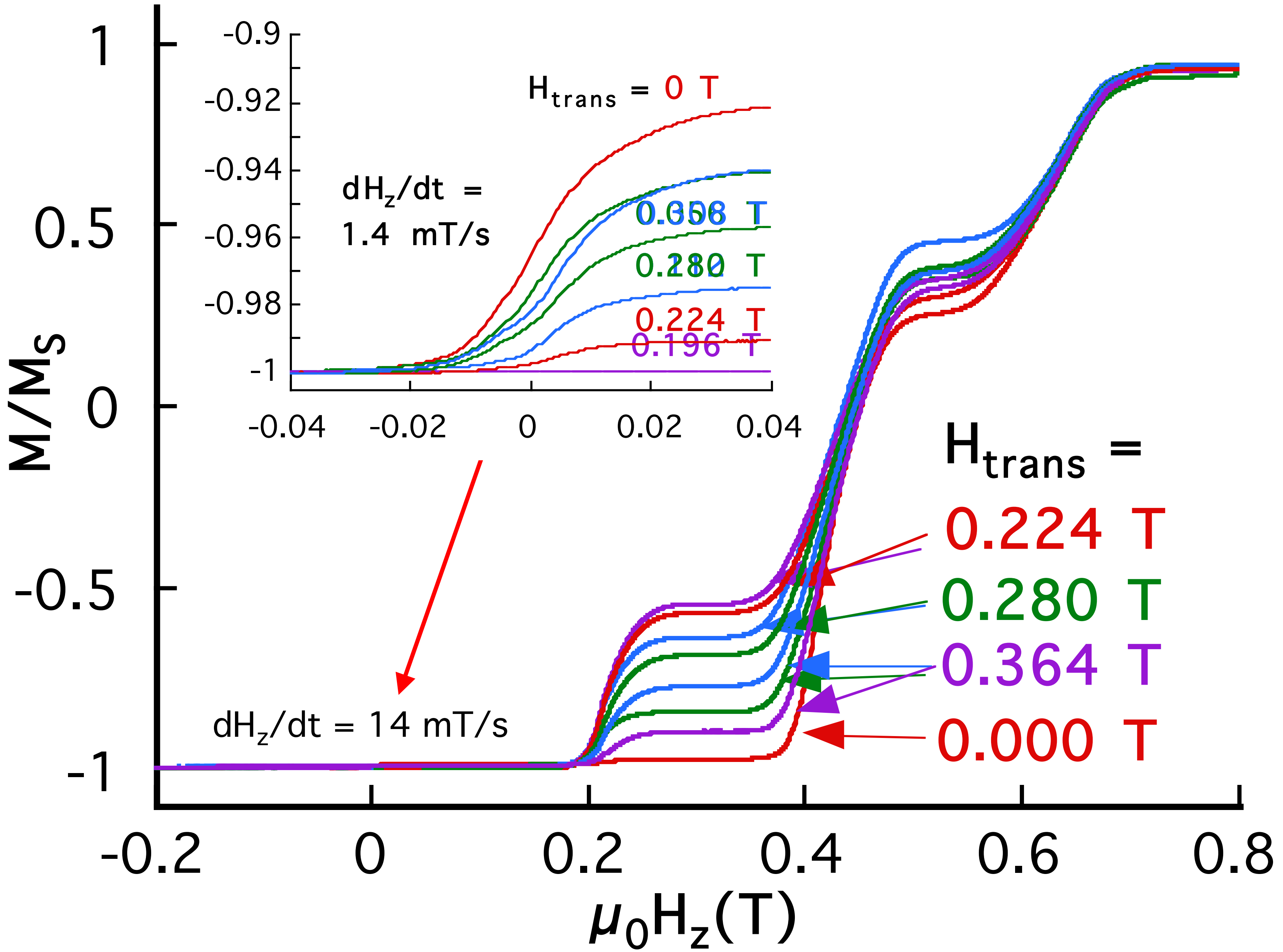
Giant spin Hamiltonian of Fe_8

$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B \vec{S}\,\vec{H}$$

$$\vec{S}\,\vec{H} = S_xH_x + S_yH_y + S_zH_z$$



Hysteresis loops at different transverse fields



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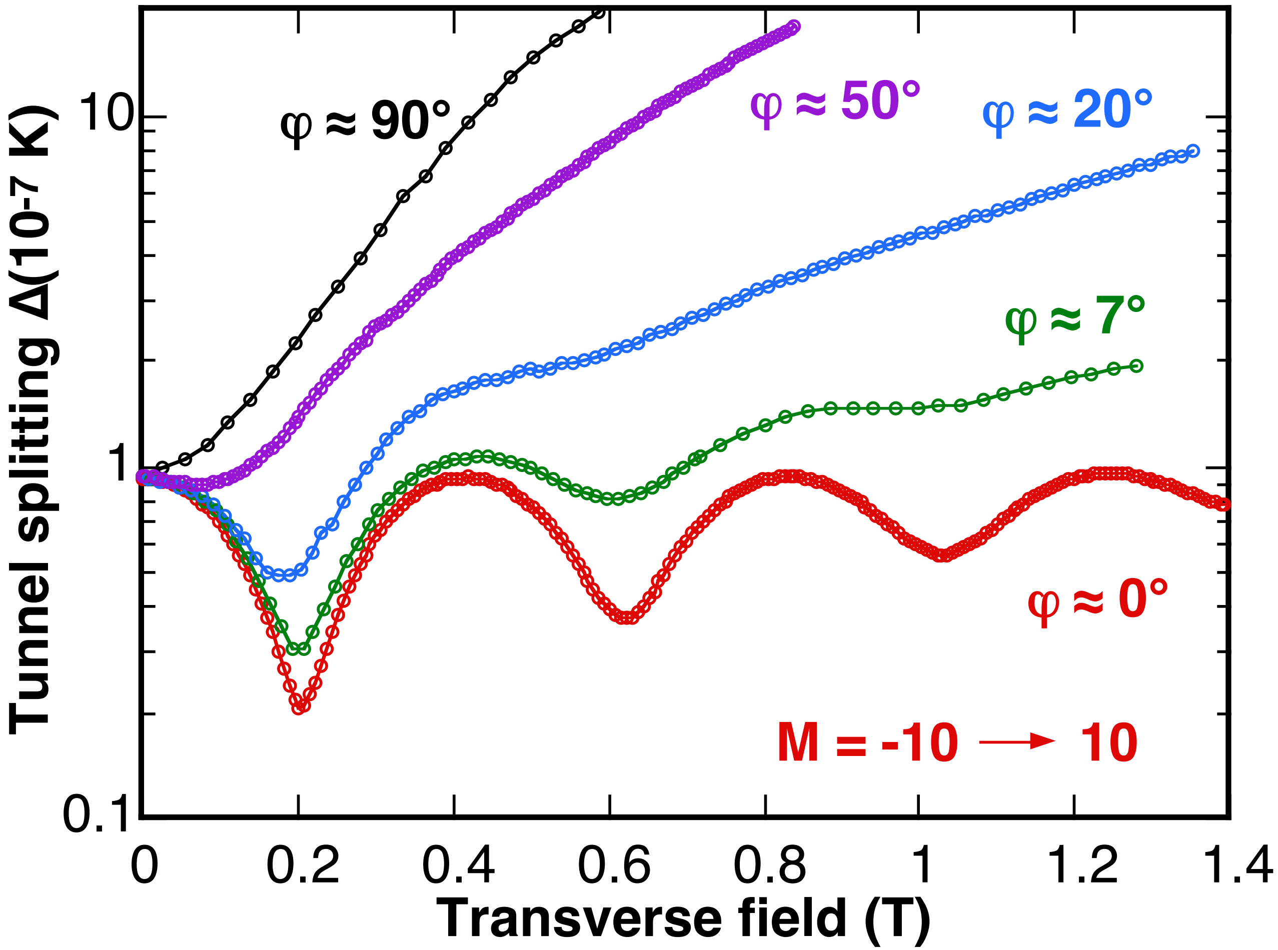
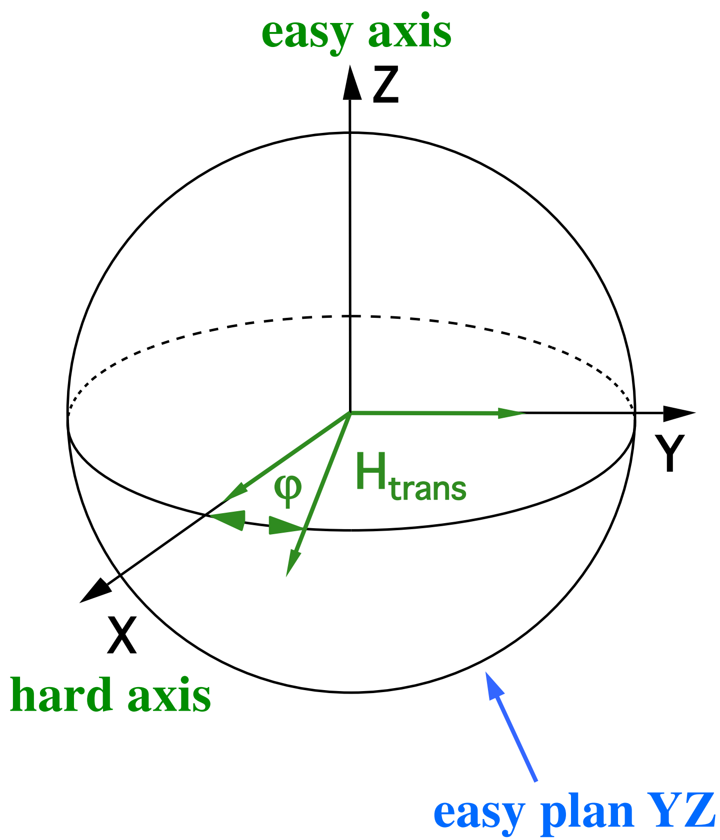
Quantum phase interference (Berry phase) in single-molecule magnets





W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

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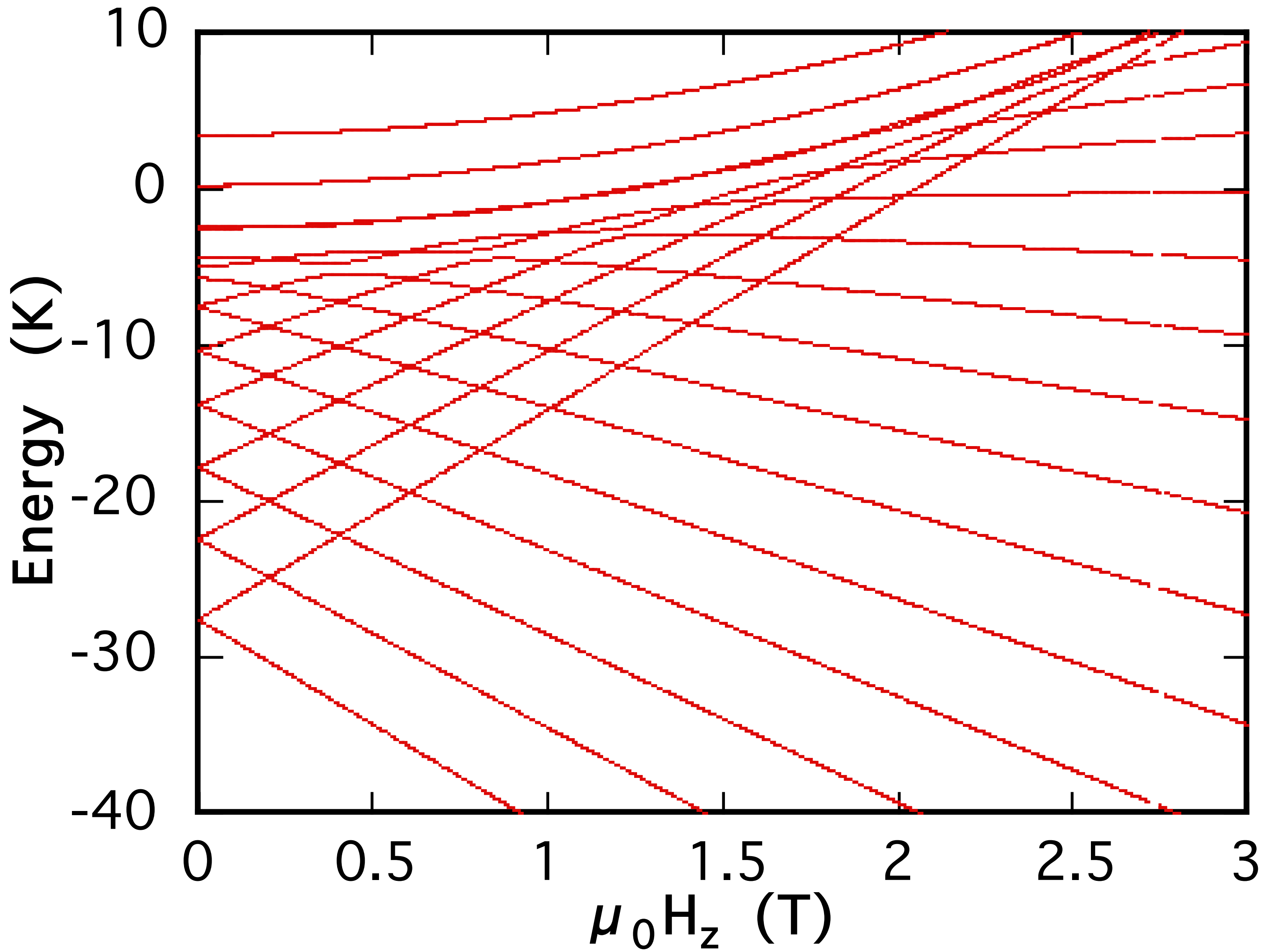
Giant spin model

Spin Hamiltonian: $\mathrm{H} = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B \vec{S}\,\vec{H}$



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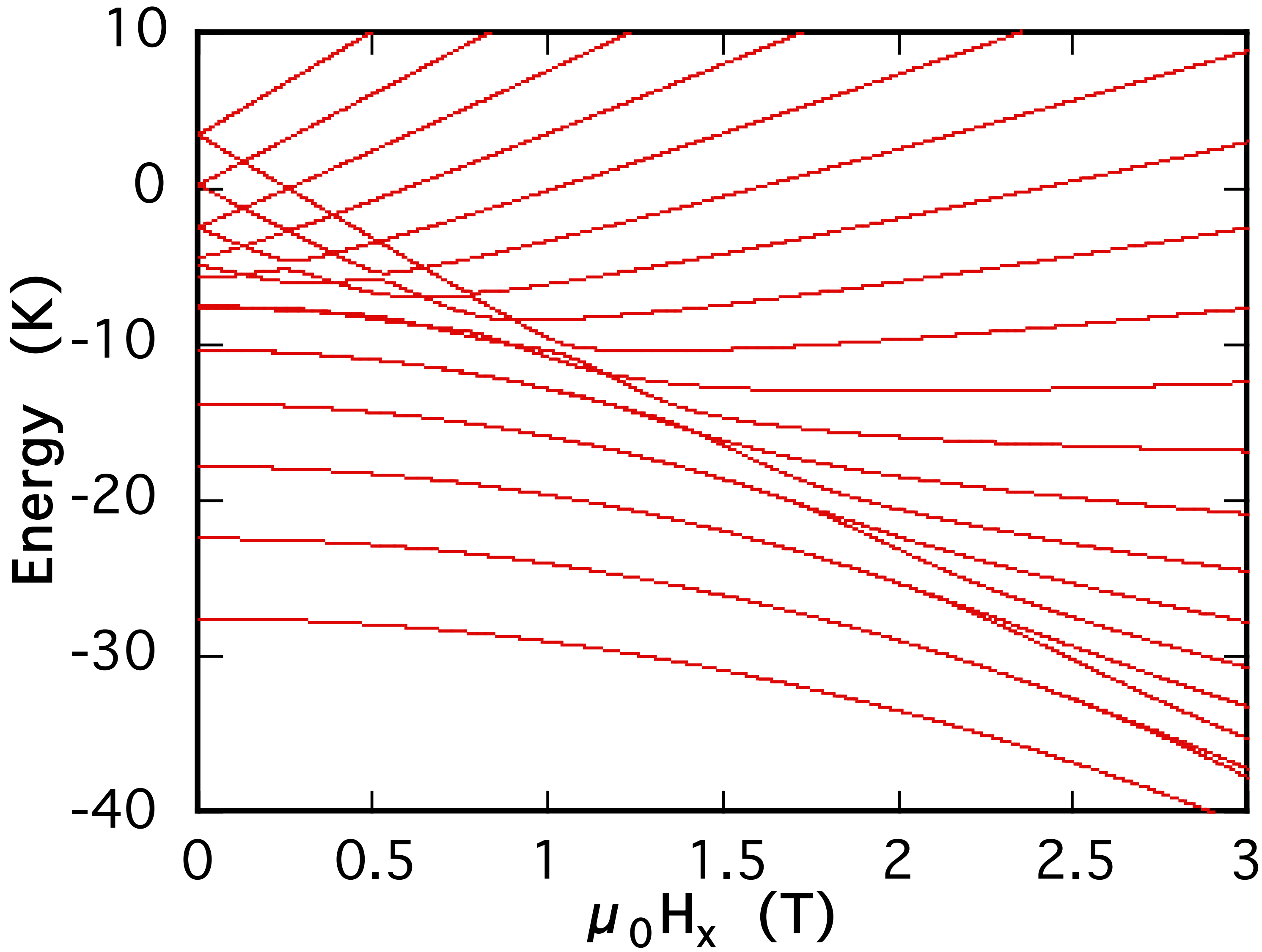
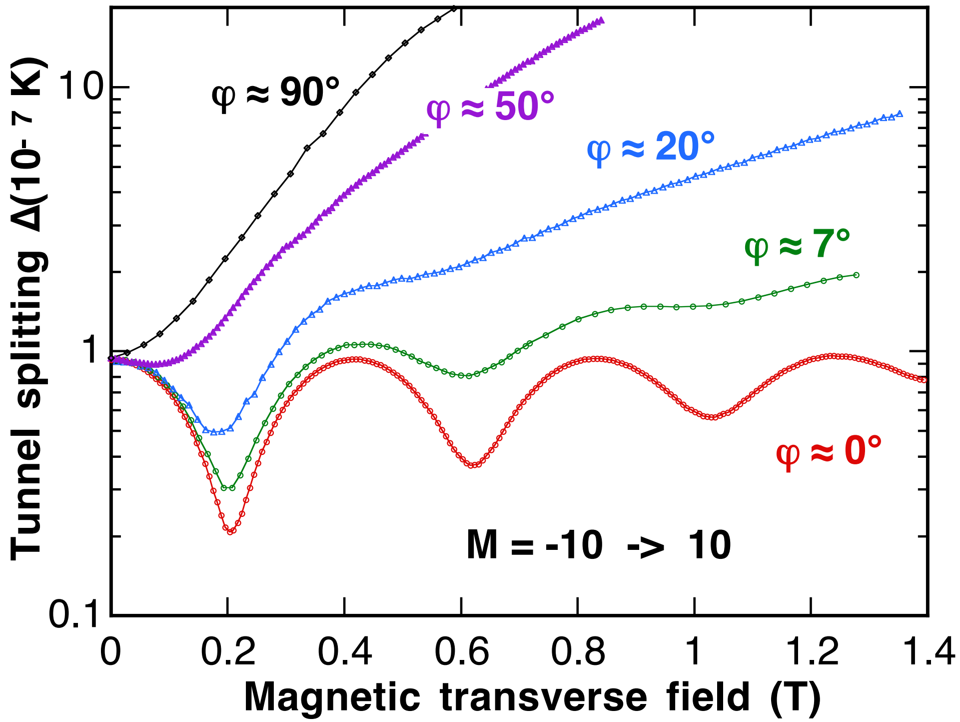
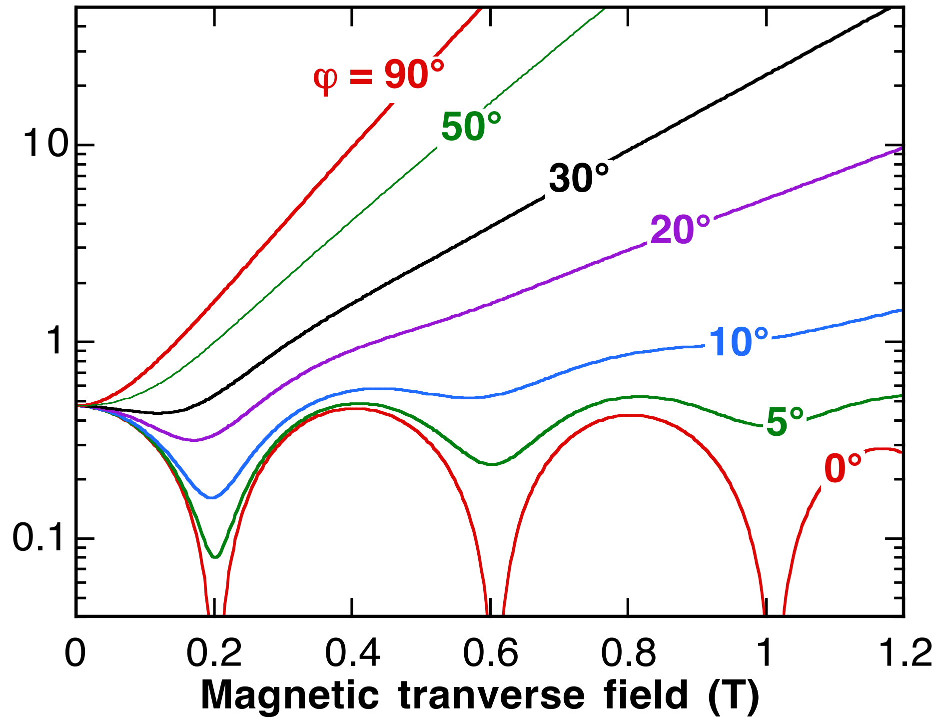


Transverse field dependence of tunnel splitting

(operator formalism)





$$H = -D\,S_z^2 + E\left(S_+^2 + S_-^2\right) + C\left(S_+^4 + S_-^4\right) + g\mu_B\,\vec{S}\,\vec{H}$$

$$D = 0.292\,\mathrm{K}, \quad E = 0.046\,\mathrm{K}, \quad C = -2.9\times10^{-5}\,\mathrm{K}$$

W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

Path integrals (Feynman)

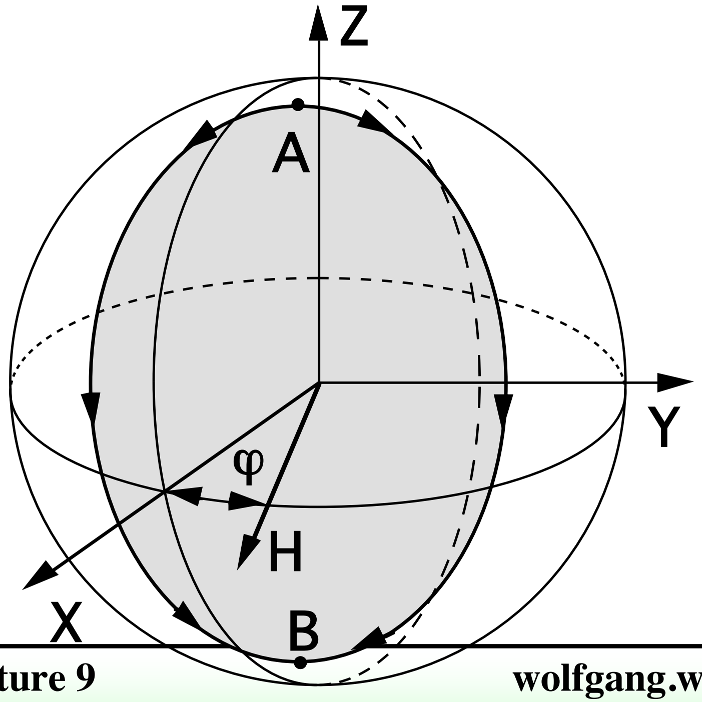
Path-integral partition function:

$$Z = \oint D\{\theta\} D\{\phi\} \exp\left[-\frac{1}{\hbar} \int_0^{\hbar/T} d\tau\, L_E \right]$$

where L_E is the Euclidean magnetic Lagrangian related to the real-time Lagrangian L through $L_E = - L(t \quad -i\tau)$

$$Z = \oint D\{\cos\theta\} D\{\phi\} \exp\left[-\frac{1}{\hbar} \int_0^{\hbar/T} d\tau\, S\dot{\phi}(\cos\theta - 1) - H(\theta, \phi) \right]$$

- **extremal trajectories that minimize the Euclidian action, at T = 0**



destructive interference occures whenever the shaded area is kπ/S, for odd k.

A. Garg, Europhys. Lett. 22, 205 (1993)

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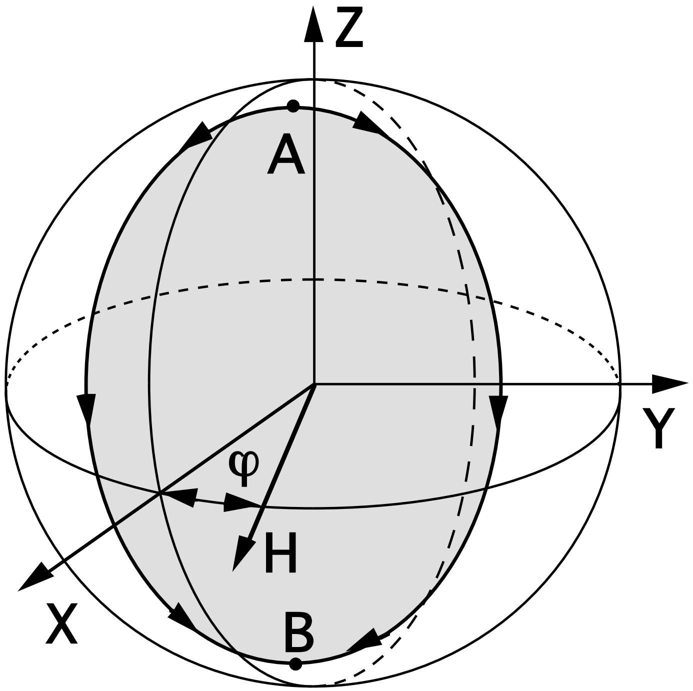
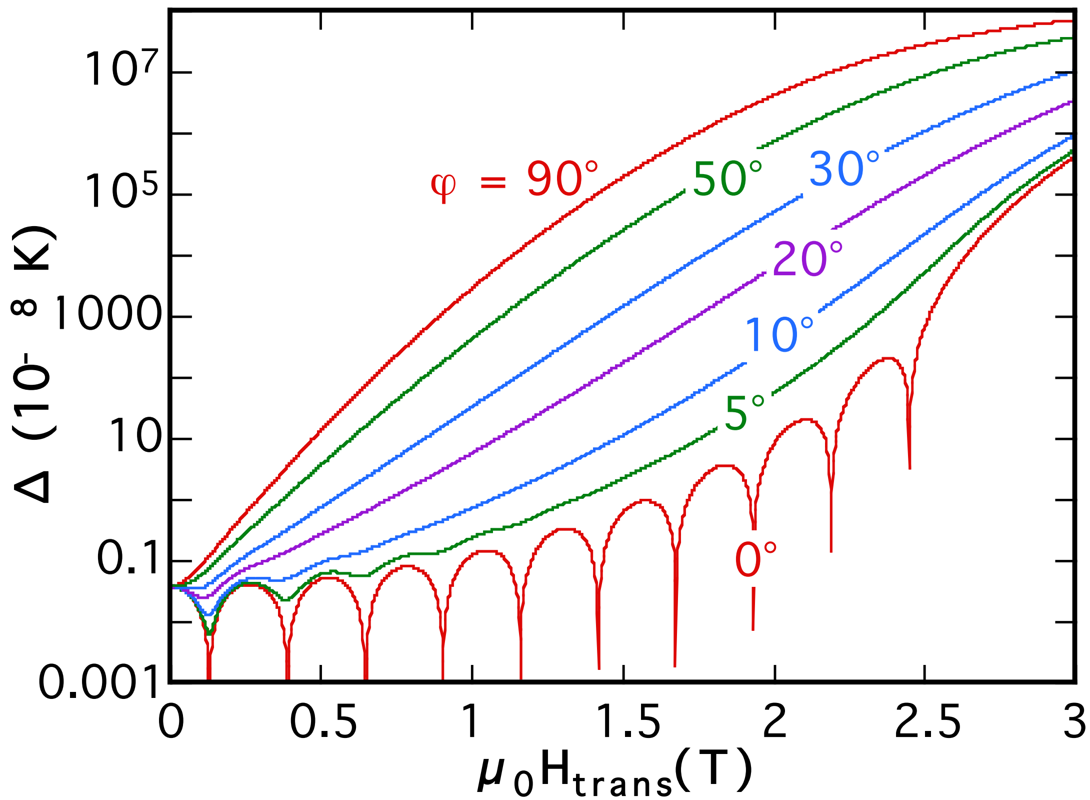
Transverse field dependence of tunnel splitting

(path integrals formalism)





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A. Garg, Europhys. Lett. 22, 205 (1993)

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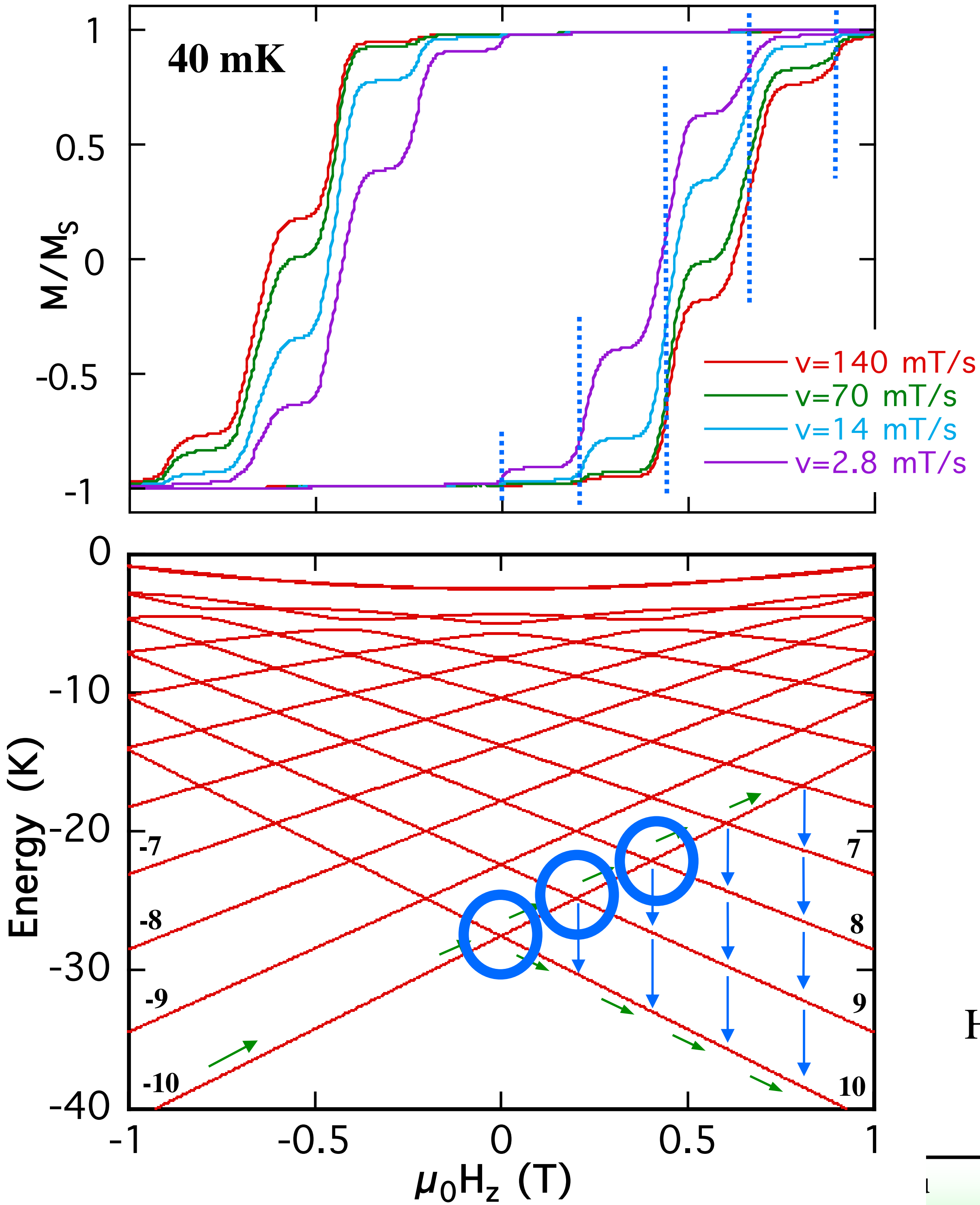
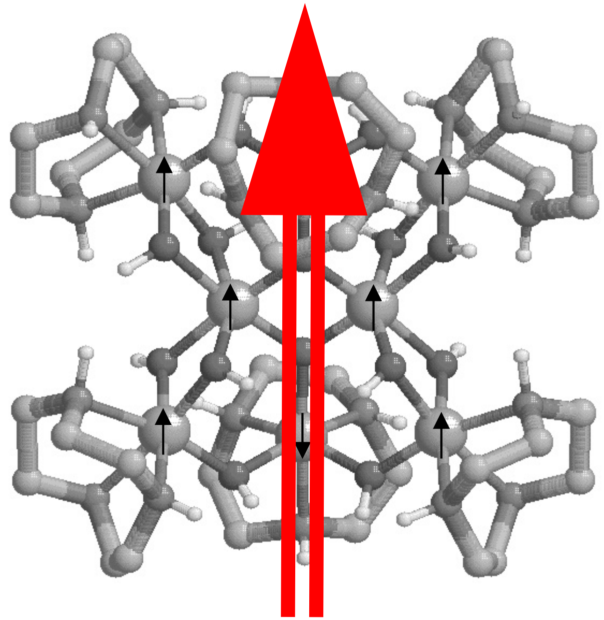


Application of Landau-Zener tunneling

Fe_8 **S = 10**



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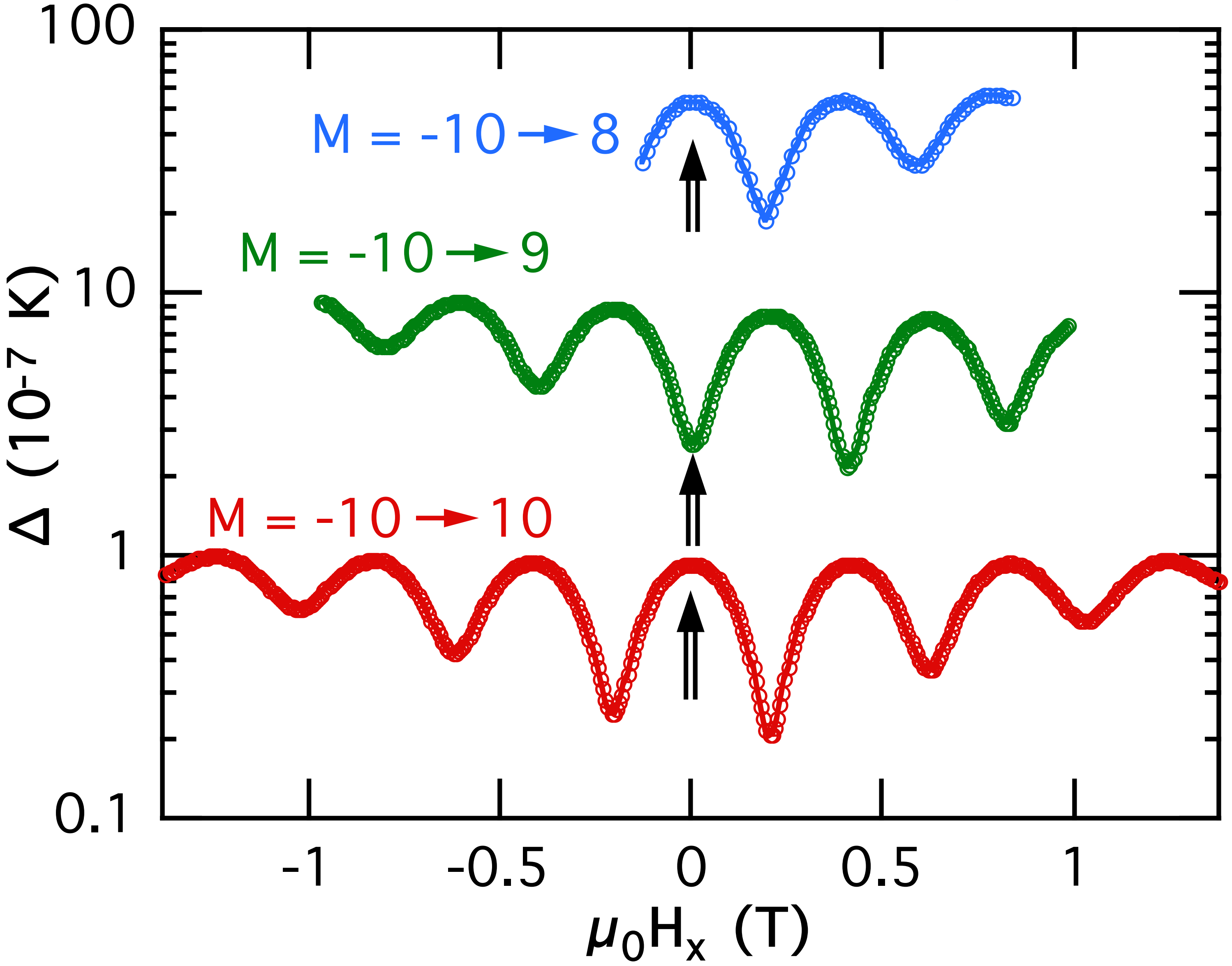
with S = 10, D = 0.27 K, E = 0.046K

A.-L. Barra et al. EPL (1996)

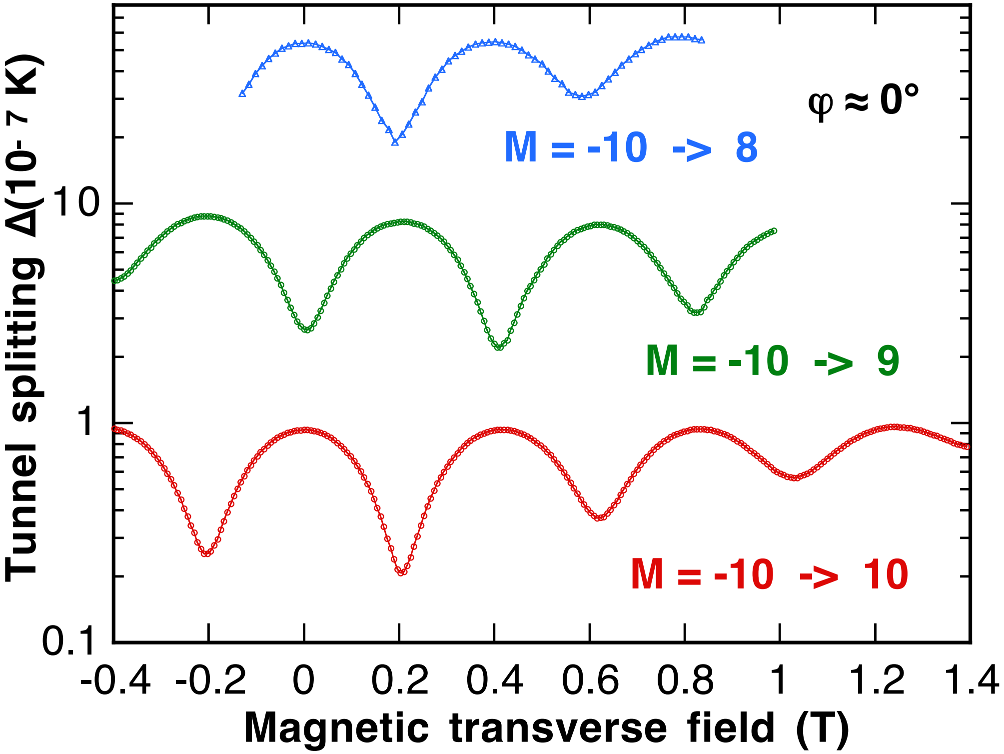
Parity of level crossings

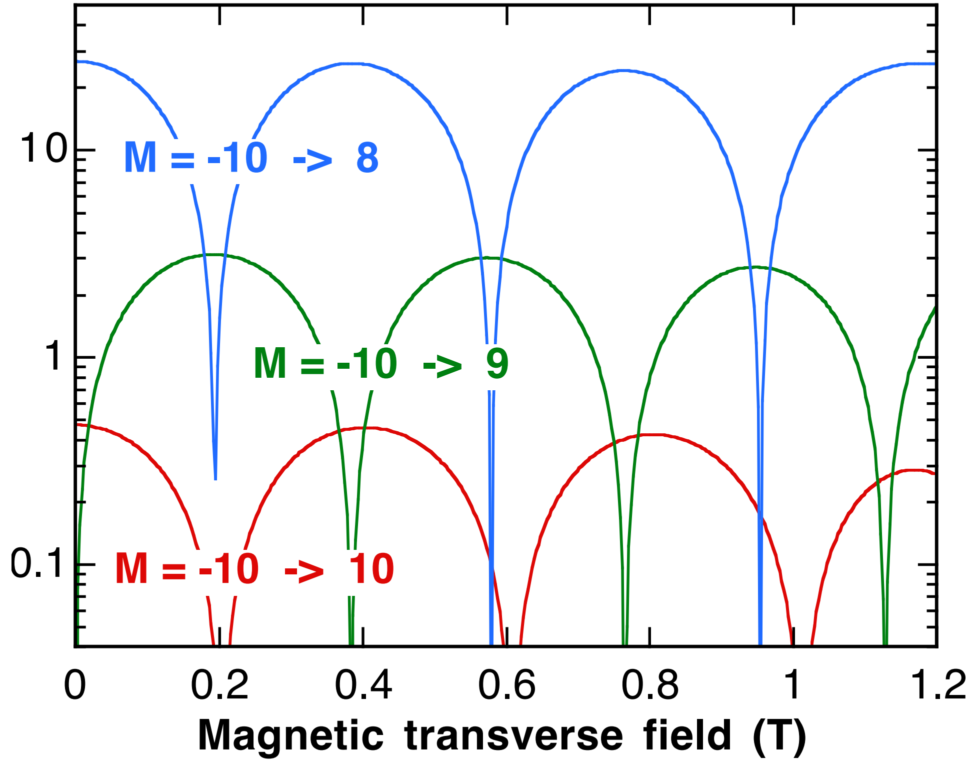


W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

Parity of level crossings

(operator formalism)





$$H = -D S_z^2 + E\left(S_+^2 + S_-^2\right) + C\left(S_+^4 + S_-^4\right) + g\mu_B \vec{S}\vec{H}$$

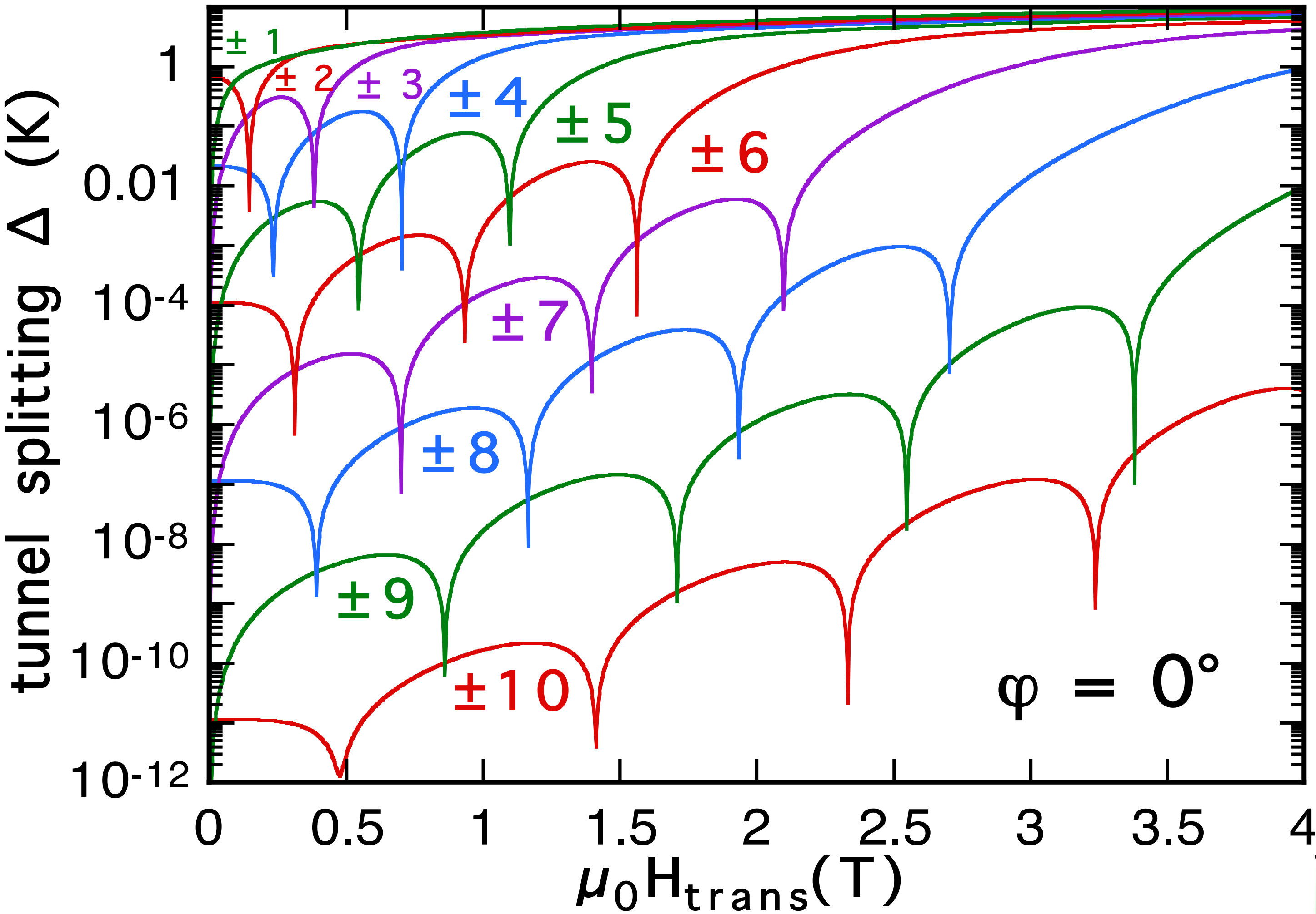
$$D = 0.292K, \quad E = 0.046K, \quad C = -2.9 \times 10^{-5} K$$

W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

Transverse field dependence of tunnel splitting of Mn12 acetate

$$H = A\, S_z^2 + B\, S_z^4 + C\left(S_+^4 + S_-^4\right) + g\,\mu_B\, S_z\, H$$

HF-EPR (Barra et al. EPL'96): $A = -0.56K$ $B = -1.1\ 10^{-3}K$ $C = 2.9\ 10^{-5}K$



KIT

Spin-parity dependent quantum tunneling

Kramers theorem: ***No matter how unsymmetric the crystal field, a system possessing an odd number of electrons must have a ground state that is at least doubly degenerate, even in the presence of crystal fields and spin-orbit interactions***

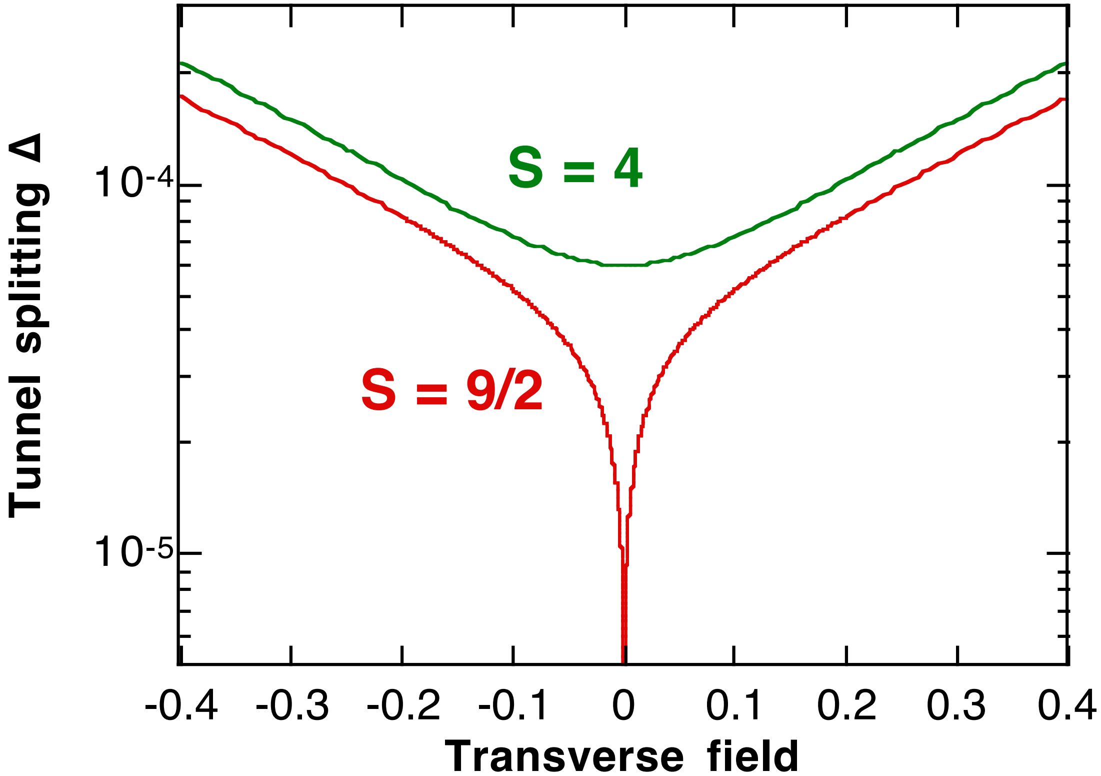
H. A. Kramers, Proc. Acad. Sci. Amsterdam 33, 959 (1930)

Mesoscopic systems:

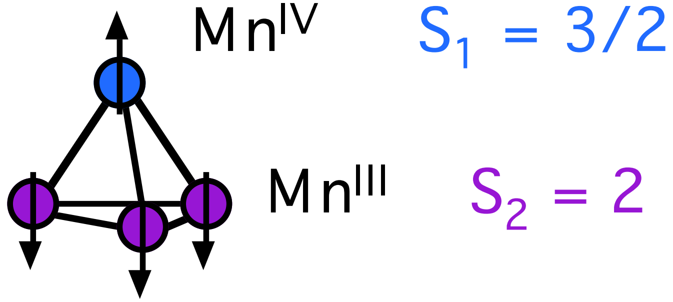
J.L. Van Hemmen and S. Süto, Europhys. Lett. 1, 481 (1986)

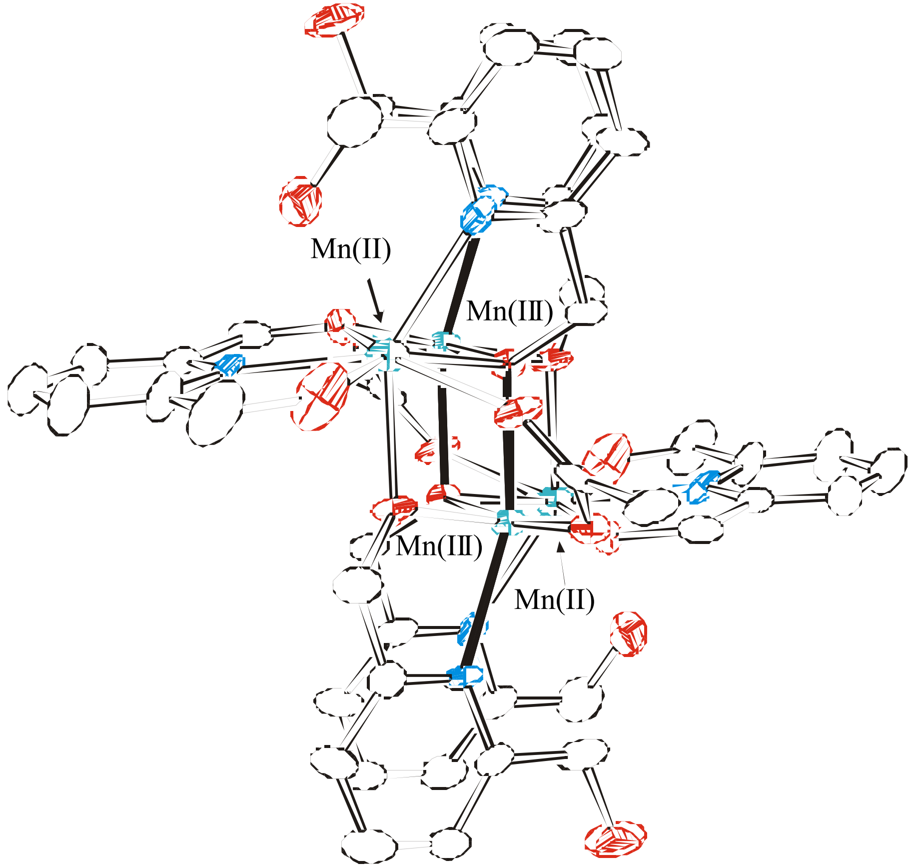
D. Loss, D.P. DiVincenzo, and G. Grinstein, Phys. Rev. Lett., 69, 3232 (1992)

J. von Delft and C. L. Hendey, Phys. Rev. Lett., 69, 3236 (1992)



Mn_4 single-molecule magnets





$Mn_4O_3(OSiMe_3)(O_2CMe)_3(dbm)_3$

$S = 9/2$

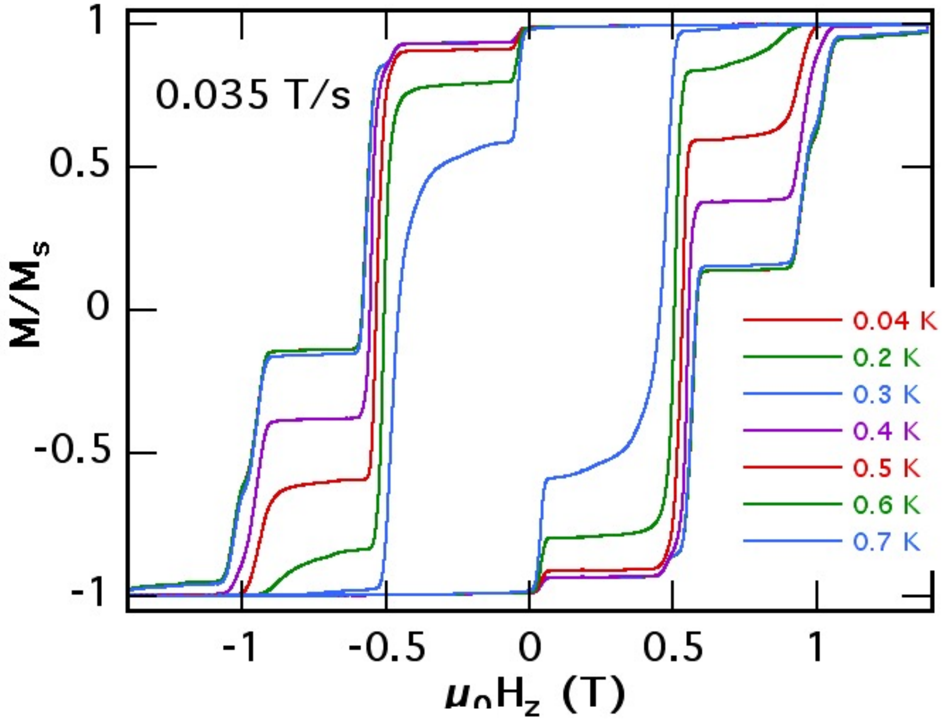
$[Mn_4(O_2CMe)_2(Hpdm)_6][ClO_4]_2$

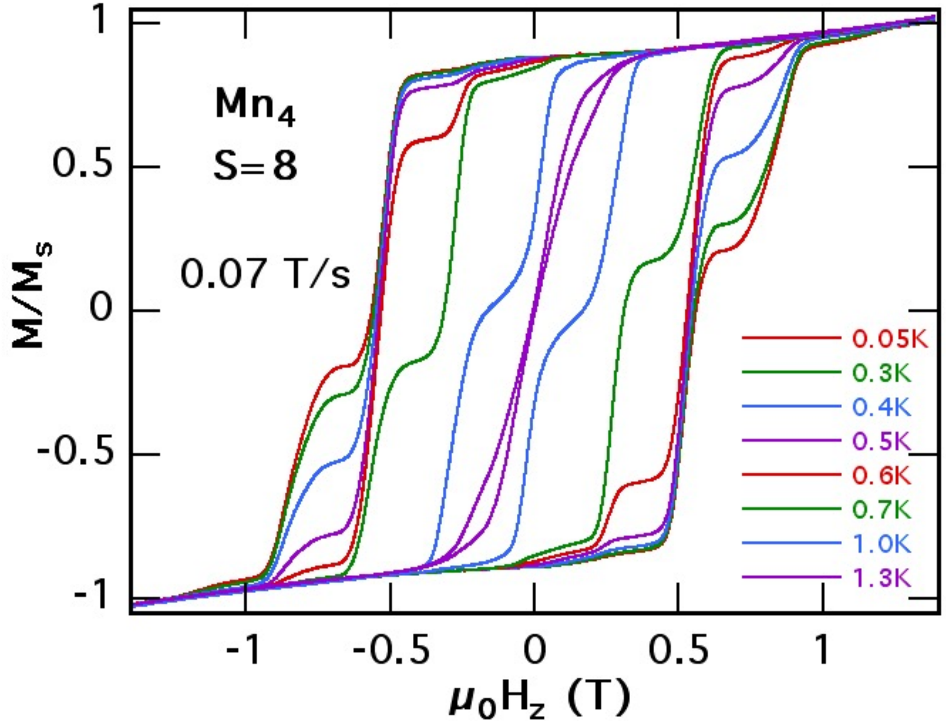
$S = 8$

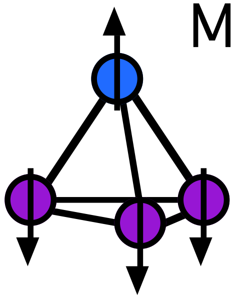
Hysteresis loops of Mn_4 single-molecule magnets

$Mn_4O_3(OSiMe_3)(O_2CMe)_3(dbm)_3$

$[Mn_4(O_2CMe)_2(Hpdm)_6][ClO_4]_2$







Mn^{IV} $S_1 = 3/2$

Mn^{III} $S_2 = 2$

S = 9/2

S = 8

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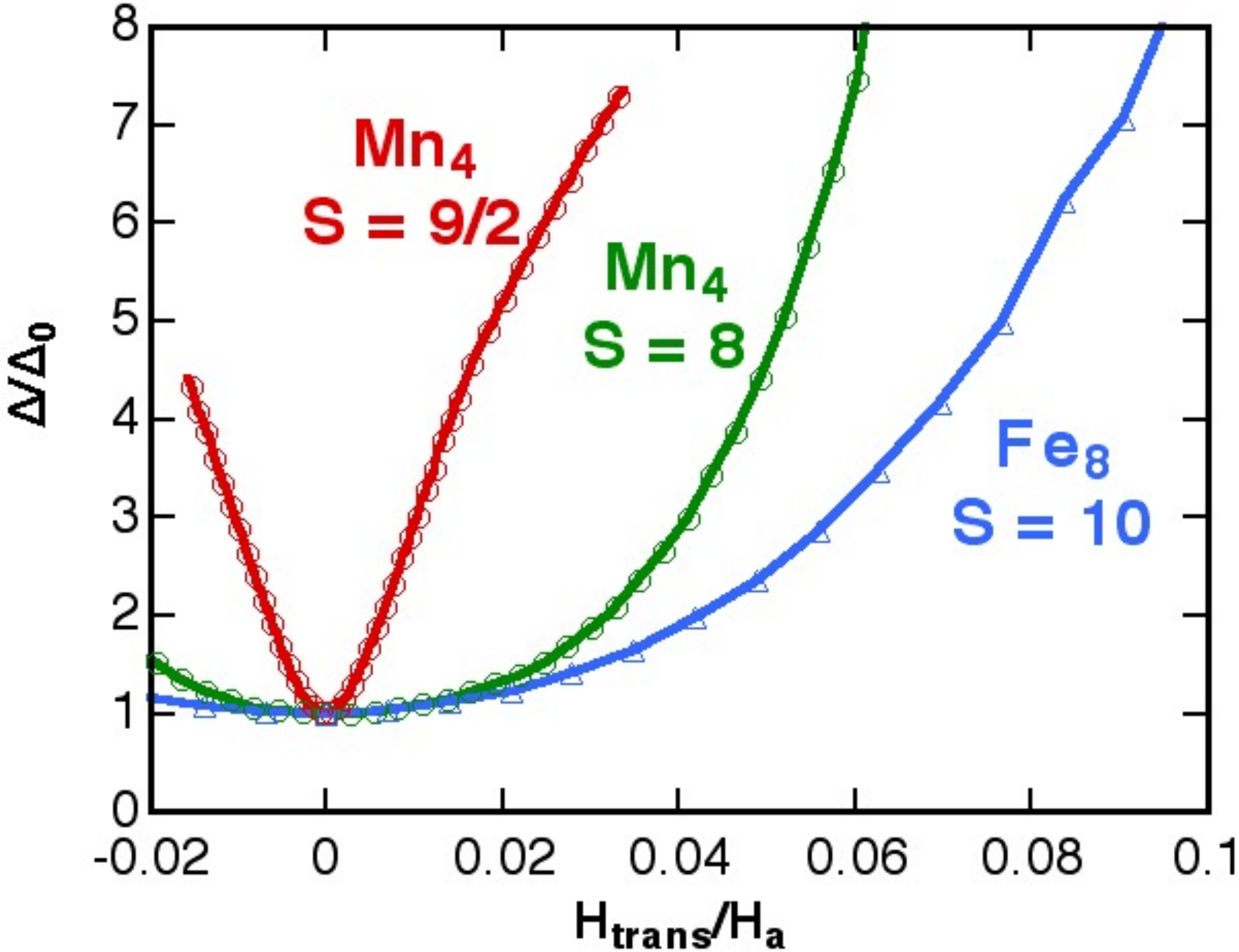
Spin-parity dependent quantum tunneling



S = 9/2
H_a = 4.6 T
$\Delta_0 = 1.9*10^{-7}$ K

S = 8
H_a = 5.1 T
$\Delta_0 = 0.28*10^{-7}$ K

S = 10
H_a = 4.0 T
$\Delta_0 = 0.94*10^{-7}$ K

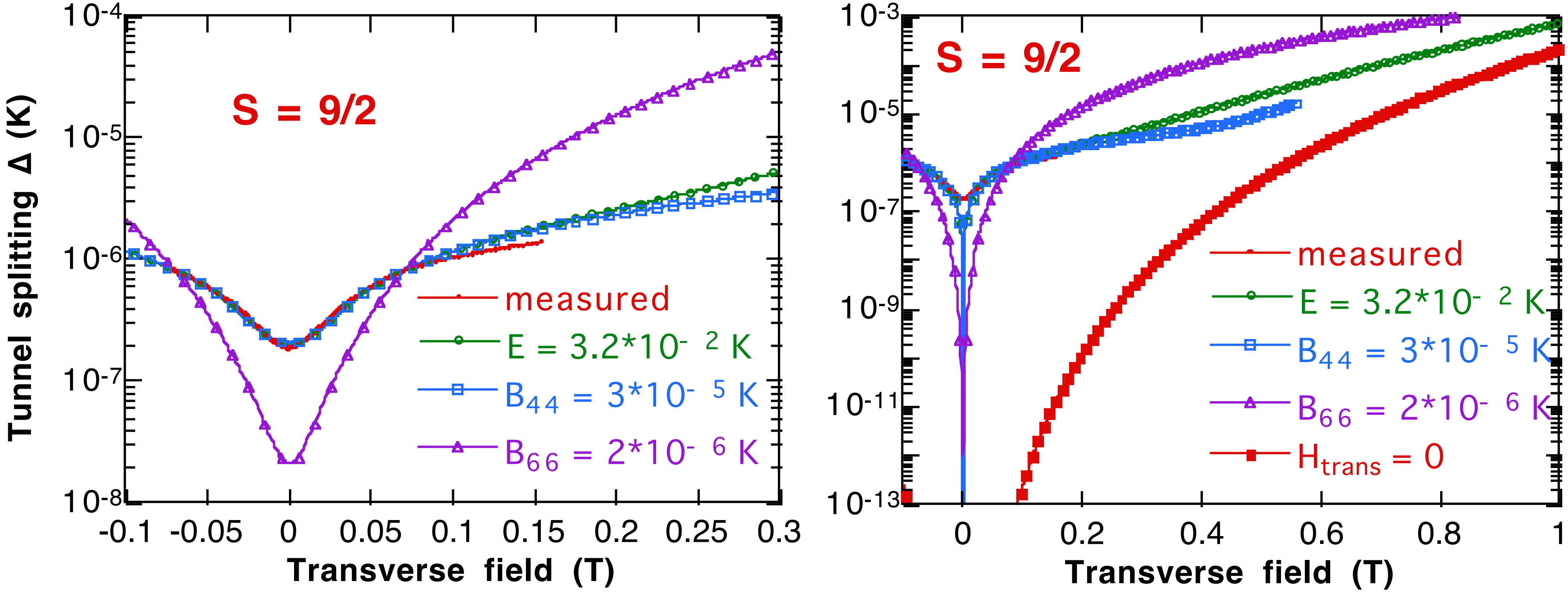
Environnemental effects

- ***hyperfine interaction (nuclear spins)***
- ***dipolar interaction between molecules***
- ***exchange interaction between molecules***

PRB 65, 180403 (2002)

Environnemental effects on the spin-parity dependent quantum tunneling

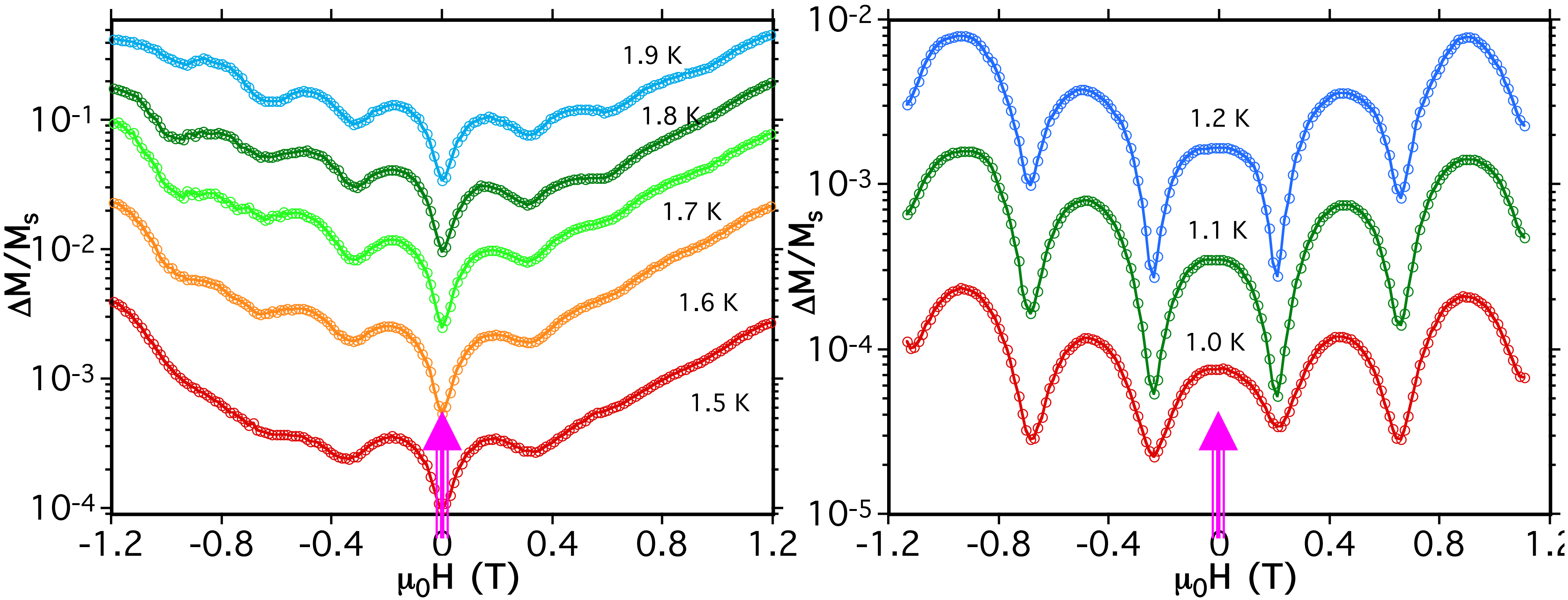
- *hyperfine interaction (nuclear spins)*
- *dipolar interaction between molecule*



=> 35 mT of dipolar fields are sufficient to explain the data for small transverse fields

Quantum phase interference and spin parity in Mn_{12}

$[Mn_{12}]^{-e}$	$[Mn_{12}]^{-2e}$
$S = 19/2$	$S = 10$



W. Wernsdorfer, N. E. Chakov, G. Christou, PRL 95, 037203 (2005)