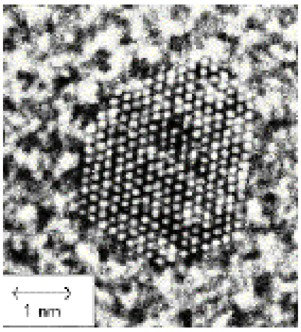
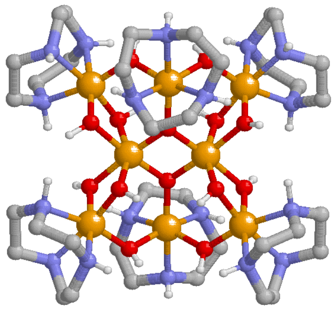
# Magnetization reversal in nanostructures:
# *Quantum dynamics in nanomagnets and single-molecule magnets*




$S = 10^2$ to $10^6$

**Wolfgang Wernsdorfer,**
**Laboratoire de Magnétisme Louis Néel**
**C.N.R.S. - Grenoble**

*Second lecture*



$S = 1/2$ to $\approx 30$

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

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# Mesoscopic physics in magnetism

*macroscopic* *nanoscopic*

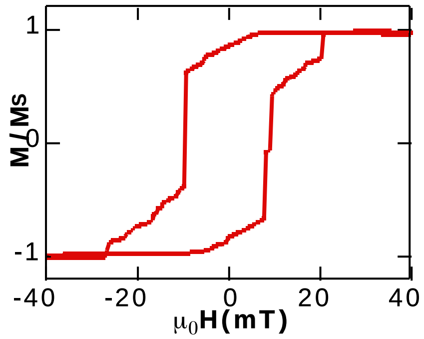
| permanent magnets | micron particles | nanoparticles | clusters | molecular clusters | individual spins |
|---|---|---|---|---|---|

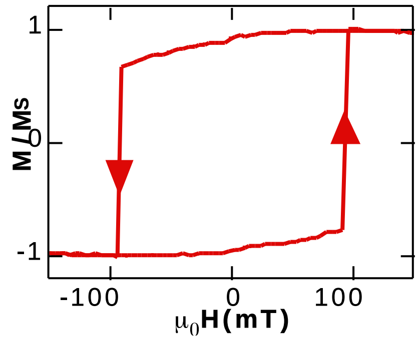
S = $10^{20}$ $10^{10}$ $10^{8}$ $10^{6}$ $10^{5}$ $10^{4}$ $10^{3}$ $10^{2}$ 10 1

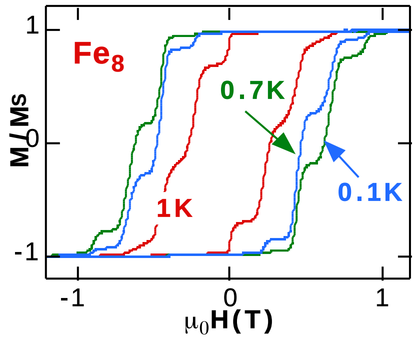
*multi - domain*
nucleation, propagation and annihilation of domain walls

*single - domain*
uniform rotation
curling

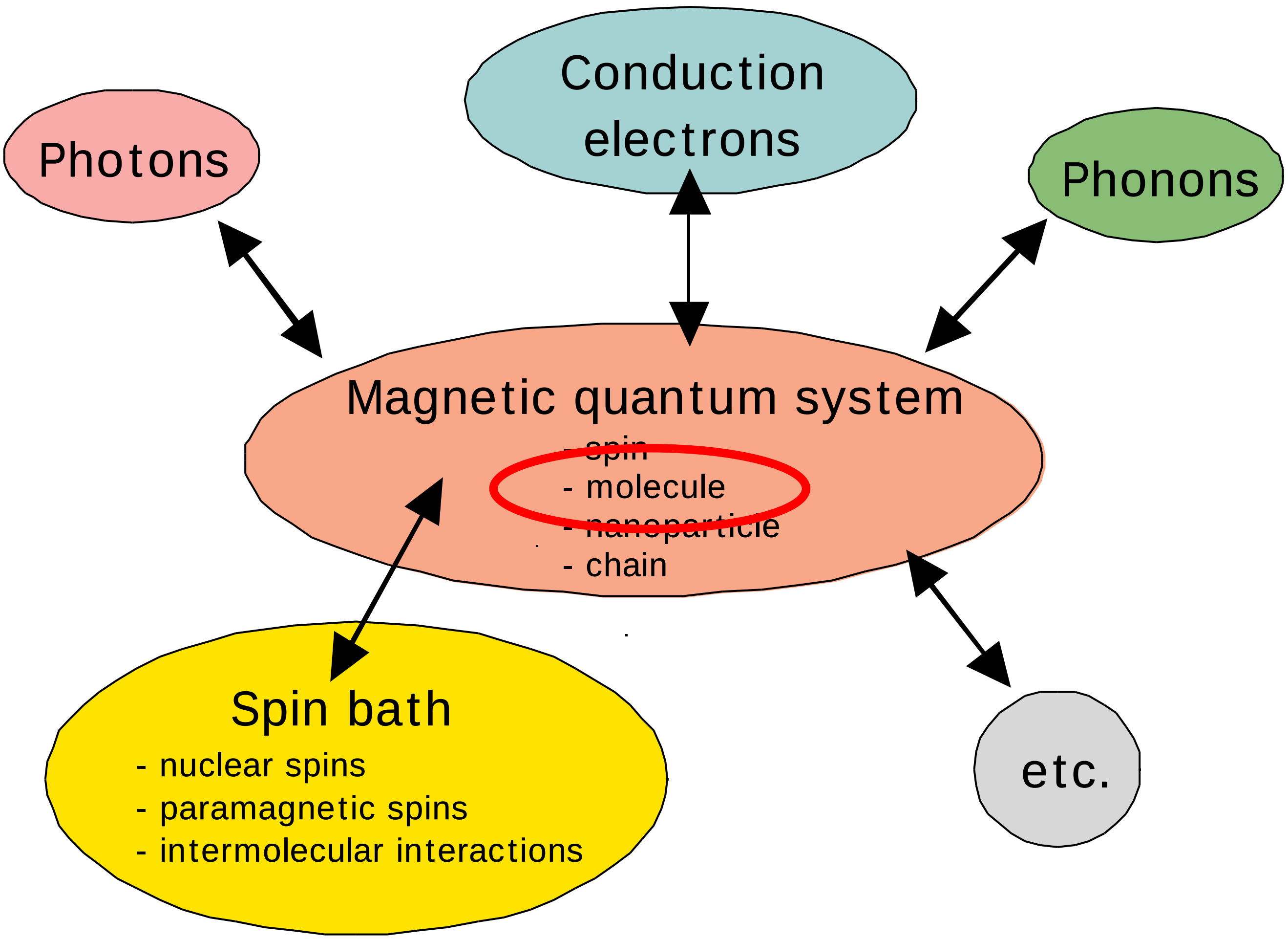
*giant spin*
quantum tunneling,
quantization
quantum interference

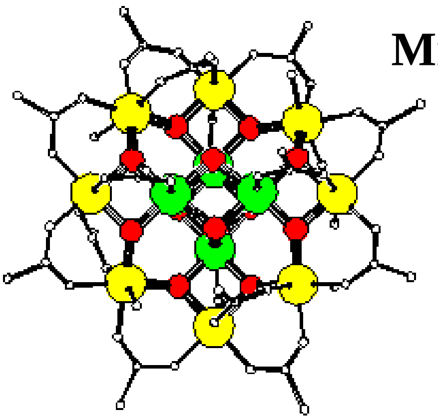


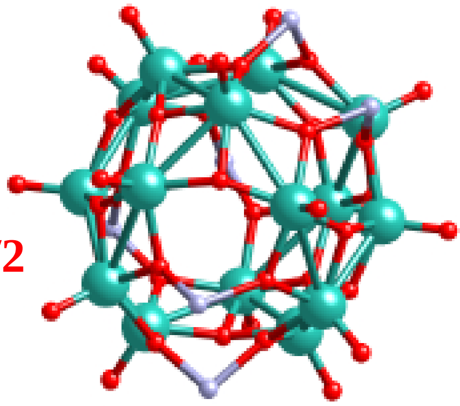
## Interactions in magnetic mesoscopic systems





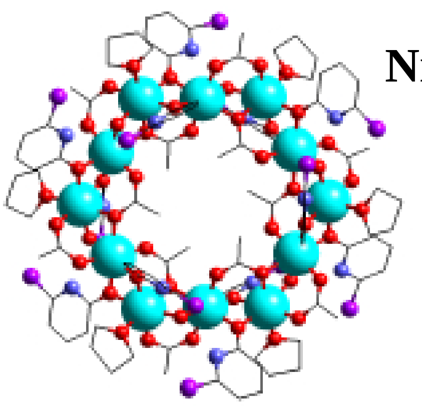
**$Mn_{12}$ S = 10**

**$V_{15}$ S = 1/2**



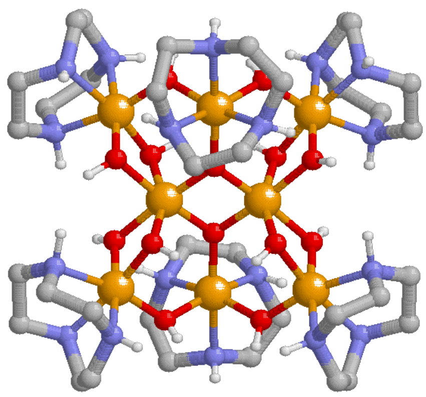
# Single-molecule magnets (SMM)

## Giant spins

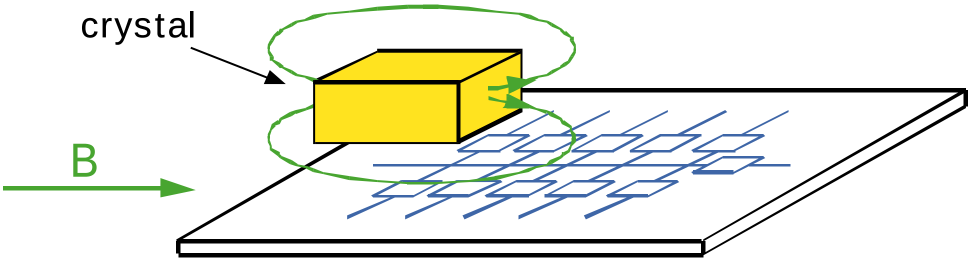


**$Ni_{12}$ S = 12**

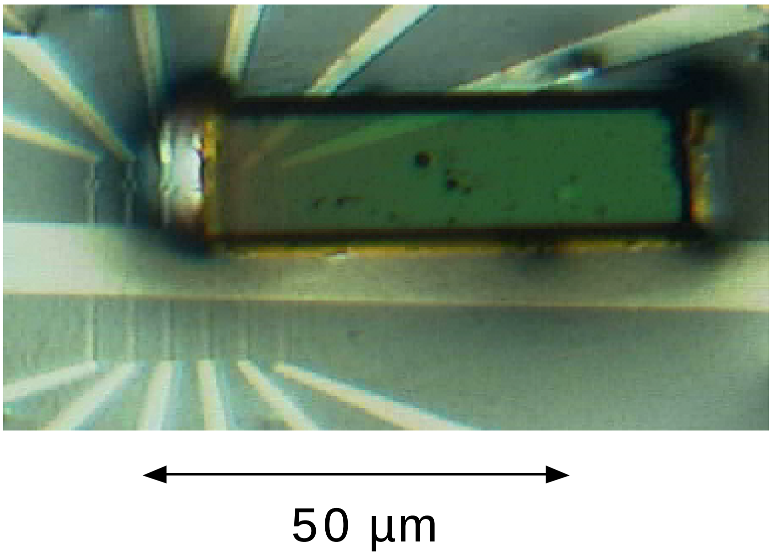
**$Fe_8$ S = 10**



# Micro-SQUID array

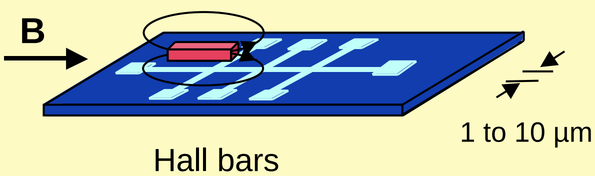



- crystal size > few µm
- $10^{-12}$ to $10^{-17}$ emu
- temperature 0.03 - 7 K
- field < 1.4 T and < 20 T/s
- rotation of field
- transverse field
- several SQUIDs at different positions



# Micro-magnetometry

- μ-Hall Effect

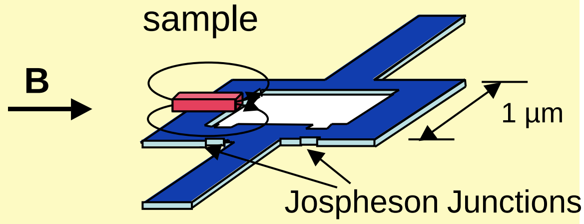



  - Based on Lorentz Force
  - Measures magnetic field

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

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

- 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 $\mu_B$

*Slide: A. Kent, NY*

# Outline

Micro-SQUID technique

1. A simple tunnel picture
   - Giant spin model
   - Landau Zener tunneling
   - Spin parity
   - Berry phase
2. Interactions with the environment
   - Intermolecular interactions
   - Interaction with photons

Conclusion

# Giant Spin Hamiltonians

**Nanoparticle:**

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

(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)

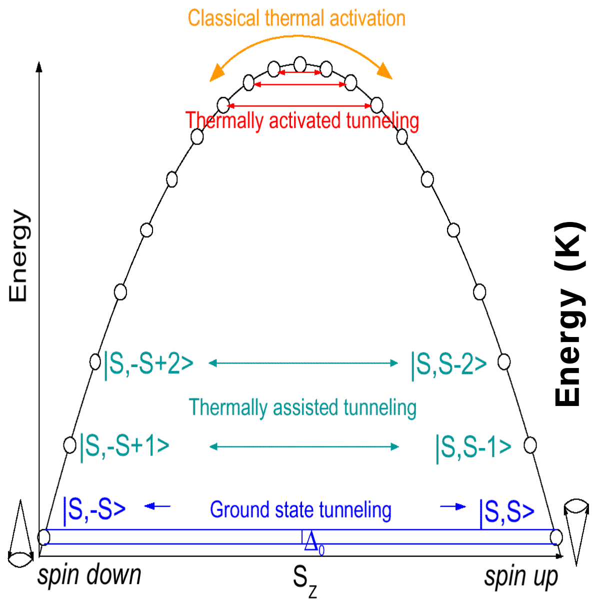
# Giant spin model

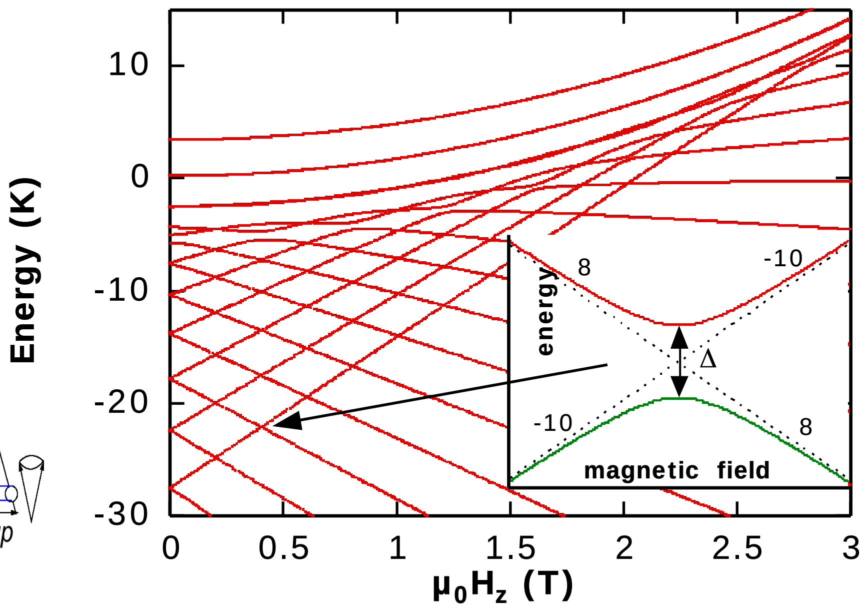
**Spin Hamiltonian:** $\mathrm{H} = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B\,\vec{S}\,\vec{H}$

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

**magnetic anisotropy** **Zeeman energy**

**Energy levels: Zeeman diagram**



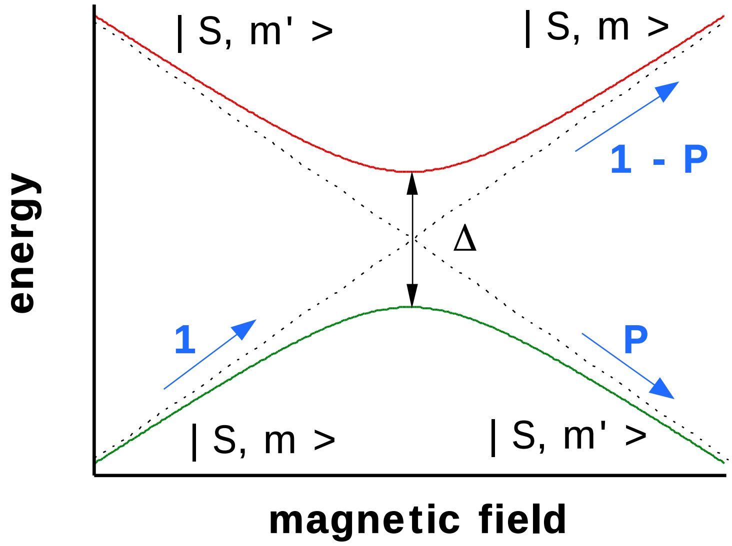

with S = 10, D = 0.27 K, E = 0.046K

# Landau-Zener tunneling (1932)

## Tunneling probability at an avoided level crossing

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

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



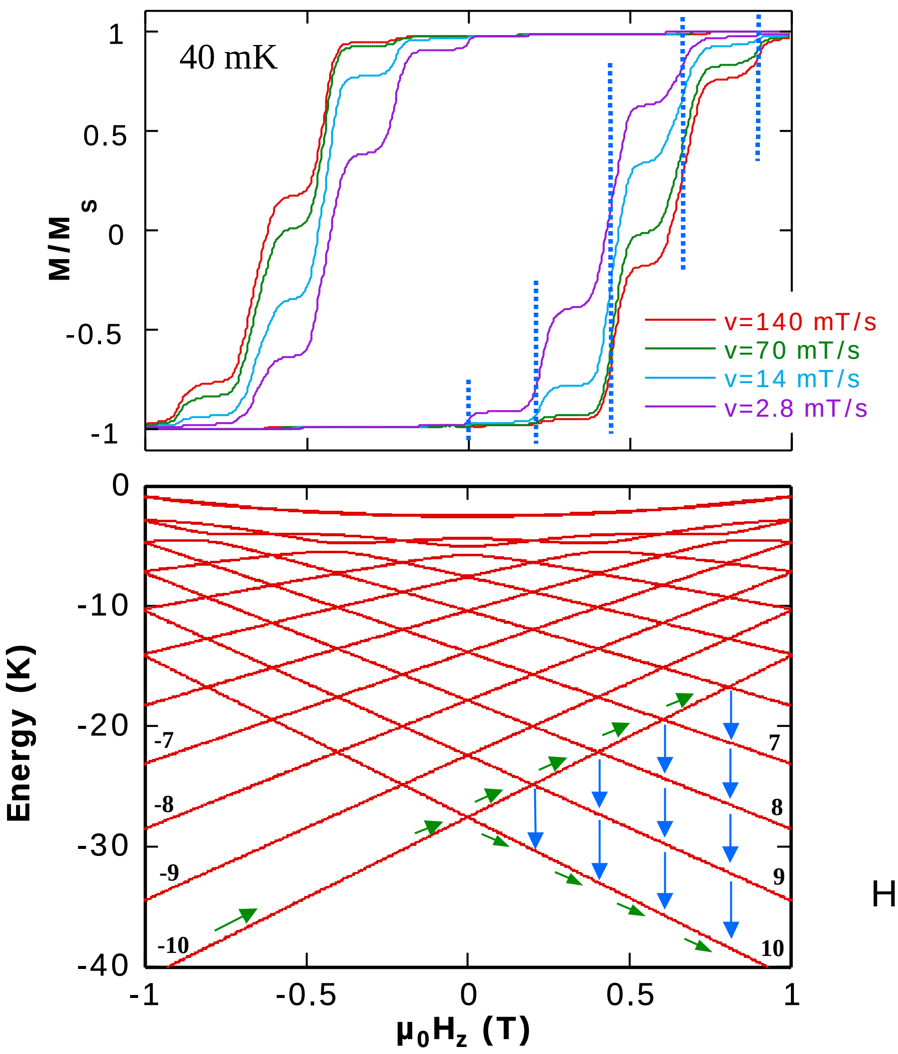

- general result for a single level crossing

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

- solution of the Schroedinger equation

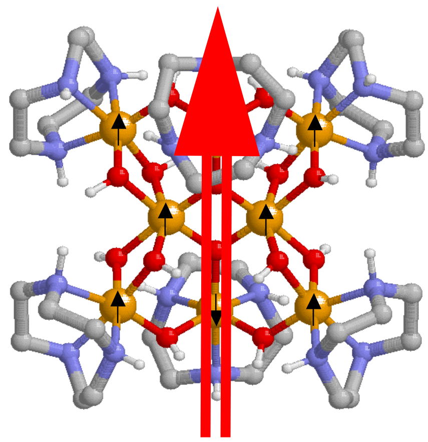
$$H|\ \rangle = i\hbar \frac{\partial}{\partial t}|\ \rangle$$


**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

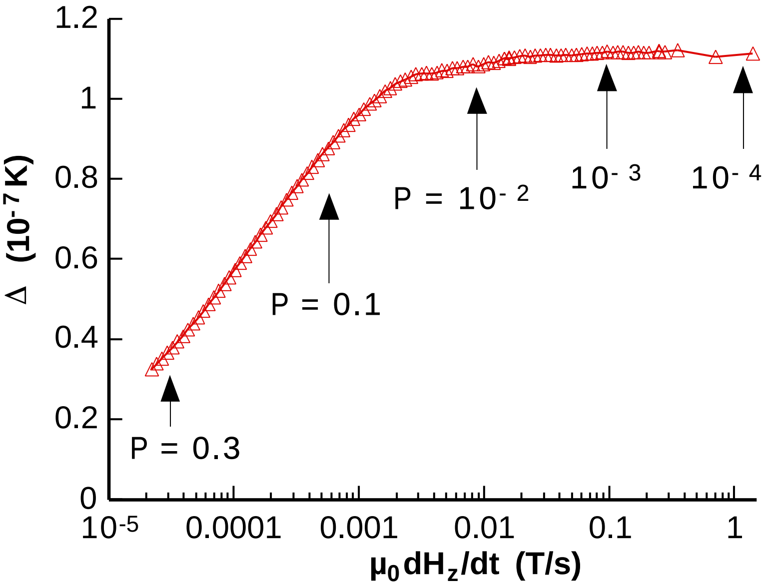
**Landau-Zener tunneling probability P**

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

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

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

**fullfilled for P < 0.04**





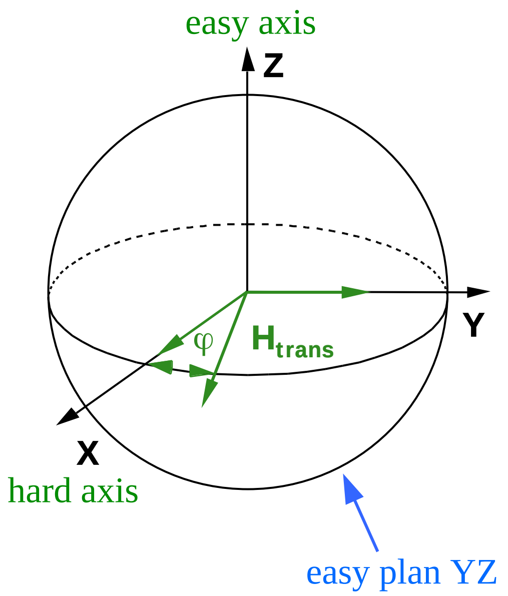
**Jie Liu, Biao Wu, Li-Bin Fu, R.B. Diener, and Qian Niu**



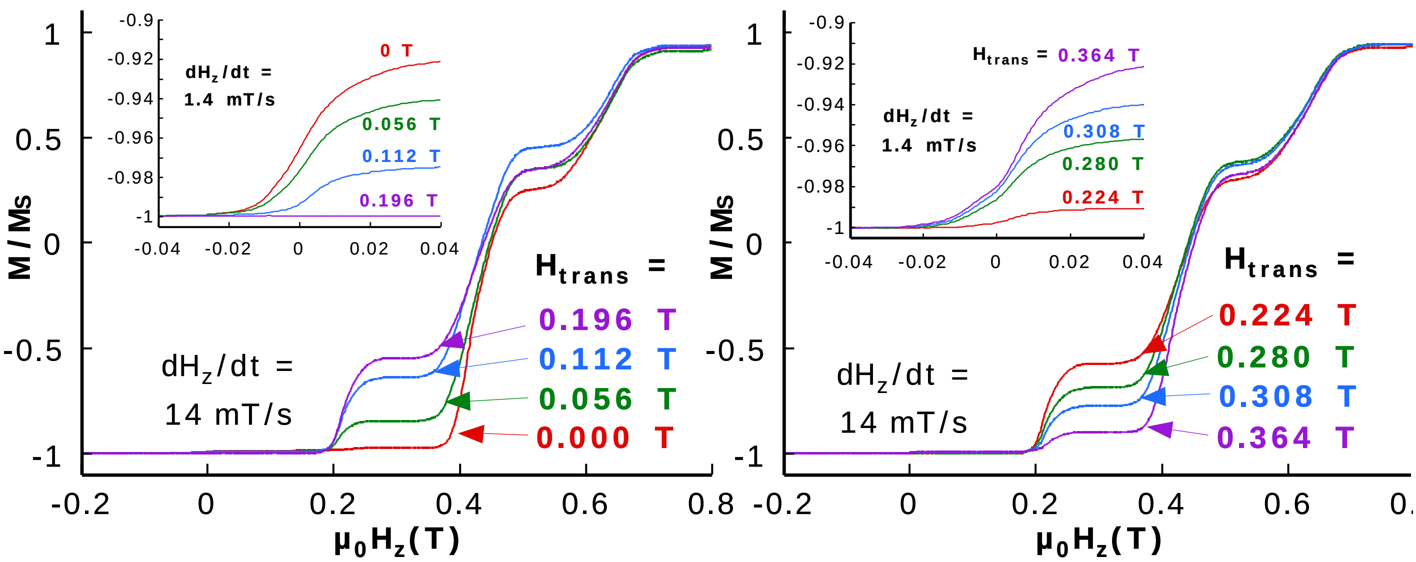
**cond-mat/0105497, PRB'02**

# Giant spin Hamiltonian of $Fe_8$

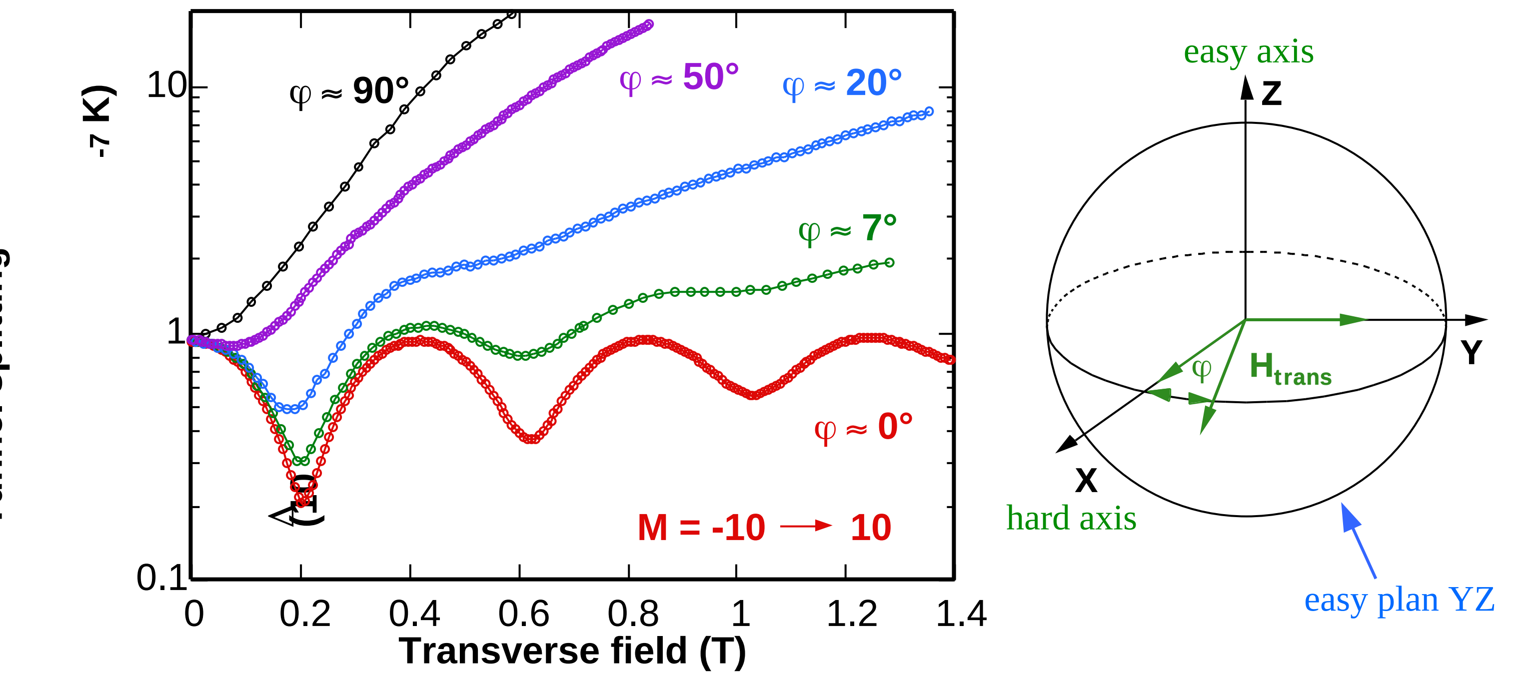
$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B\,\vec{S}\,\vec{H}$$



# Hysteresis loops at different transverse fields

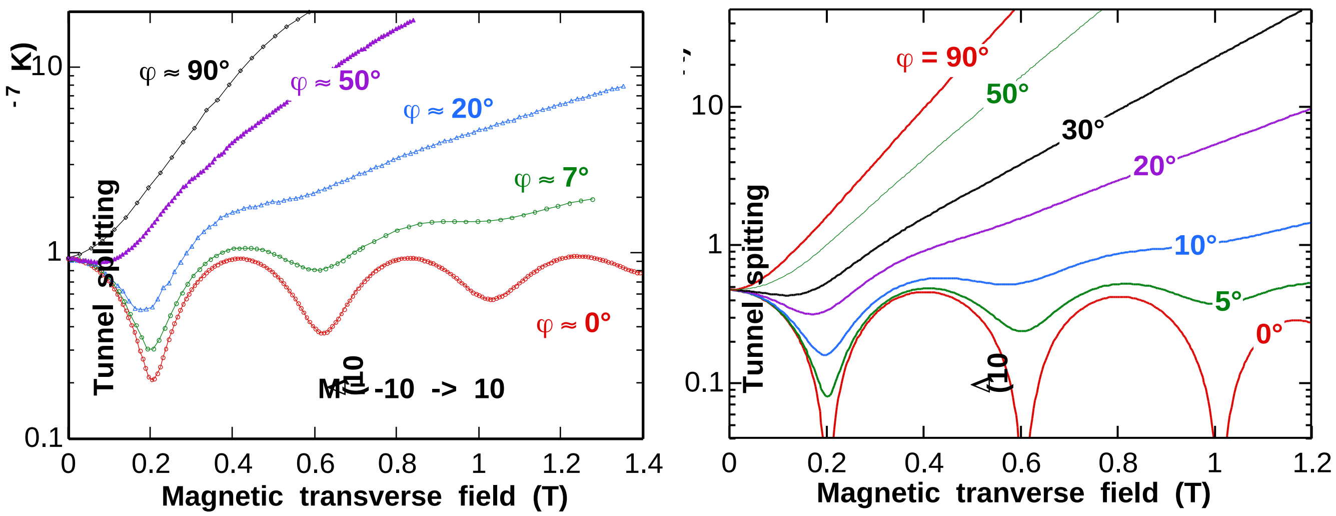


# Quantum phase interference (Berry phase) in single-molecule magnets



# Transverse field dependence of tunnel splitting

(operator formalism)




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

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

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

# **Path integrals** (Feynman)

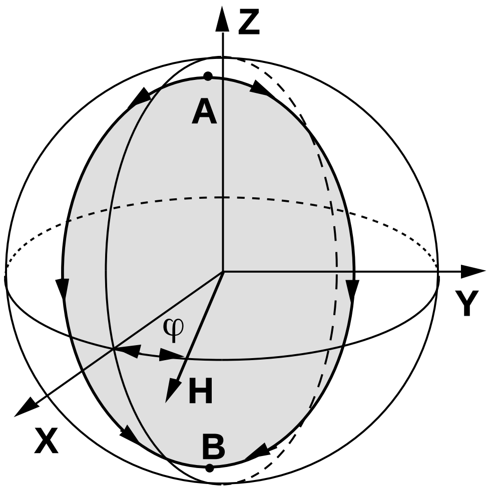
Path-integral partition function:

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

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

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

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

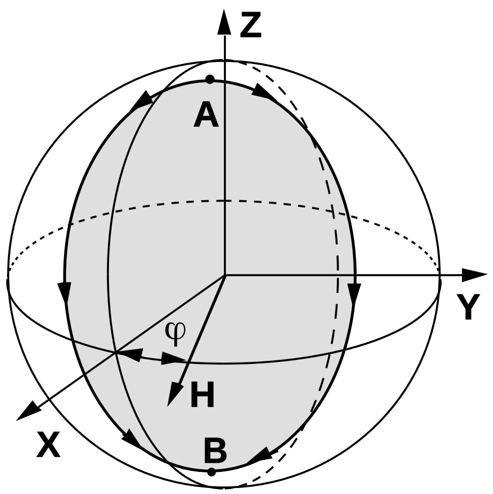


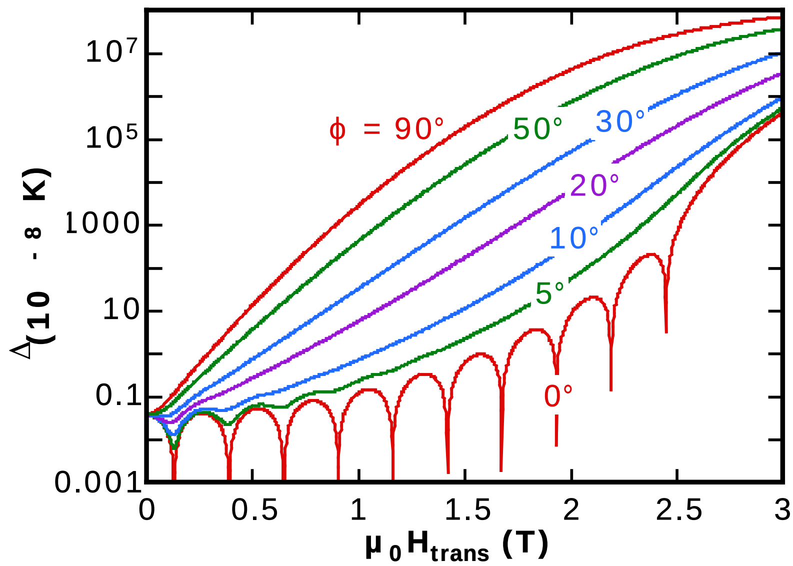

destructive interference occures whenever the shaded area is $k\pi/S$, for odd k.

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

# Transverse field dependence of tunnel splitting

**(path integrals formalism)**




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

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# Transverse field dependence of tunnel splitting
## (path integrals formalism)


M. Enz and R. Schilling R.,J.Phys.C ,19 (1986) L711
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)

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M.N. Leuenberger and D. Loss, Phys. Rev. B 61, 12200 (2000).
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Rong Lü, Hui Hu, Jia-Lin Zhu, Xiao-Bing Wang, Lee Chang, and Bing-Lin Gu, Phys. Rev. B 61, 14581 (2000).
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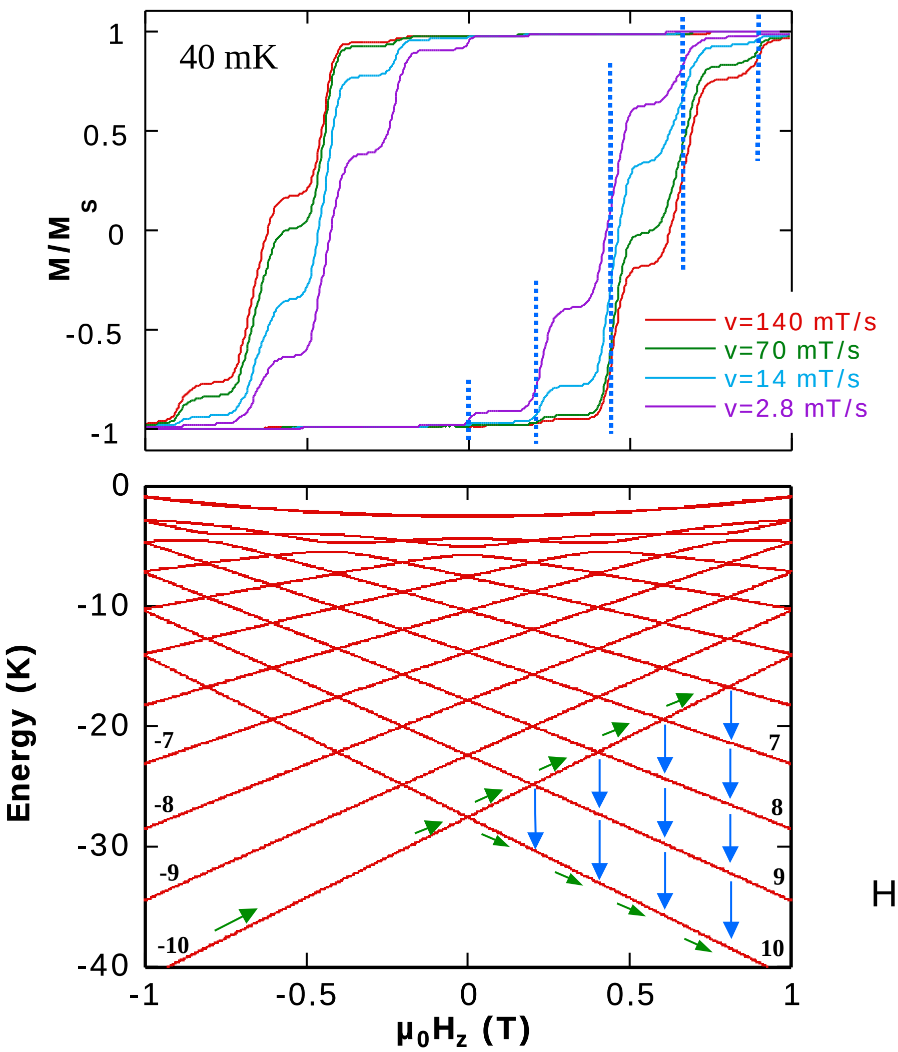
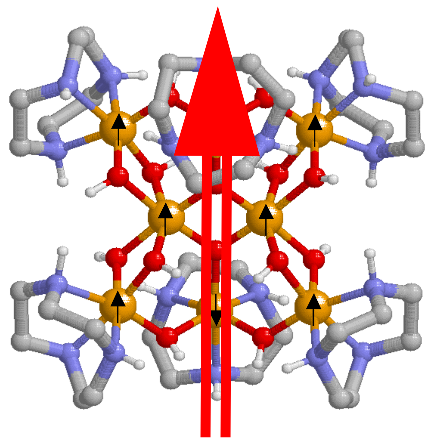
Rong Lü, Jia-Lin Zhu, Yi Zhou, and Bing-Lin Gu, Phys. Rev. B 62, 11661 (2000).
Y.-B. Zhang, J.-Q. Liang, H.J. W. Müller-Kirsten S.-P. Kou, X.-B. Wang, and F.-C. Pu, Phys. Rev. B 60, 12886 (2000).
Yan-Hong Jin, Yi-Hang Nie, J.-Q. Liang, Z.-D. Chen, W.-F. Xie, and F.-C. Pu, Phys. Rev. B 62, 3316 (2000).
E.M. Chudnovsky and X.Martines Hidalgo, EuroPhys. Lett. 50, 395 (2000).


**etc.**




# Application of Landau-Zener tunneling

**$Fe_8$ S = 10**

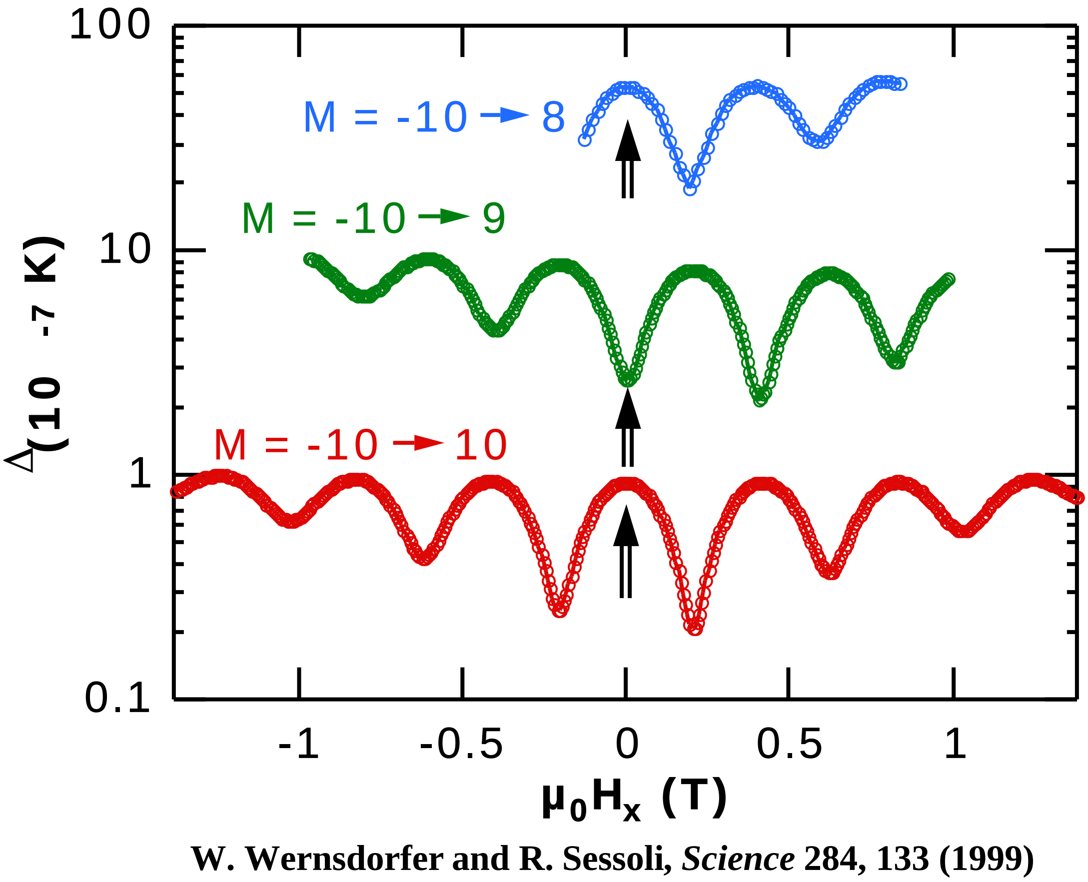


$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B \vec{S}\,\vec{H}$$

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

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

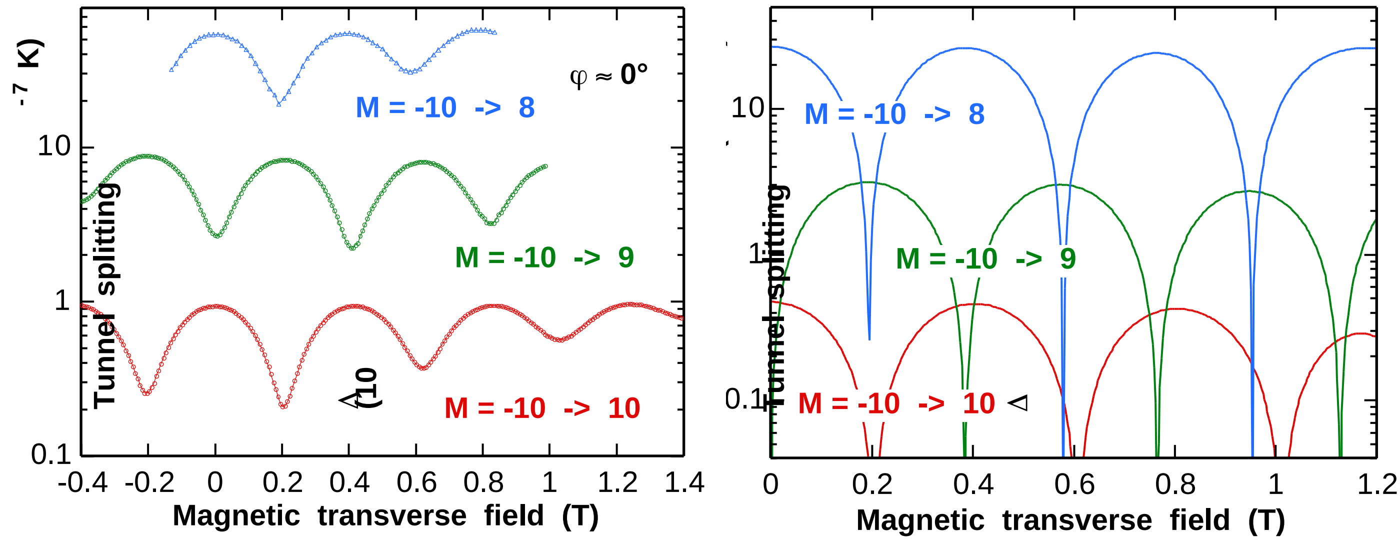
# Parity of level crossings




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

# Parity of level crossings

(operator formalism)




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

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

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

# 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:**

M. Enz and R. Schilling R.,J.Phys.C ,19 (1986) L711

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)

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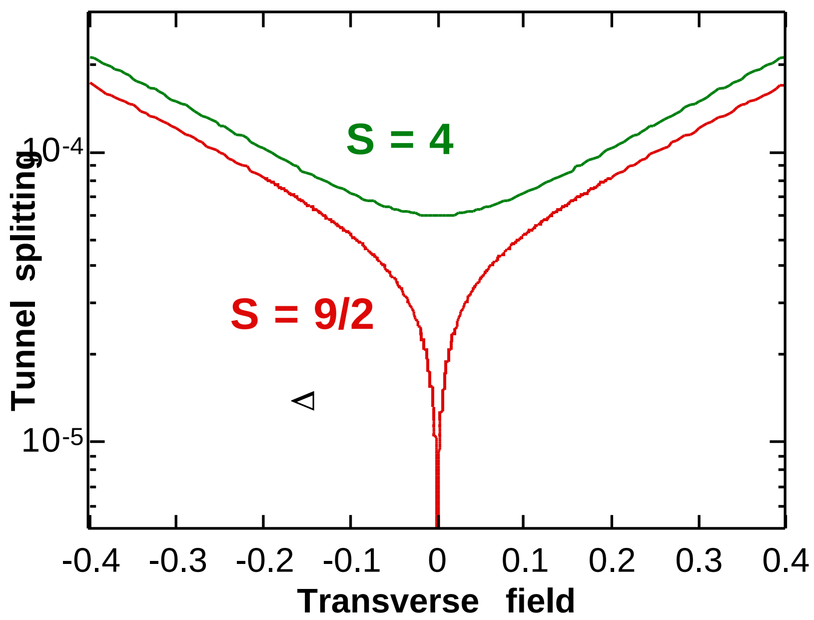
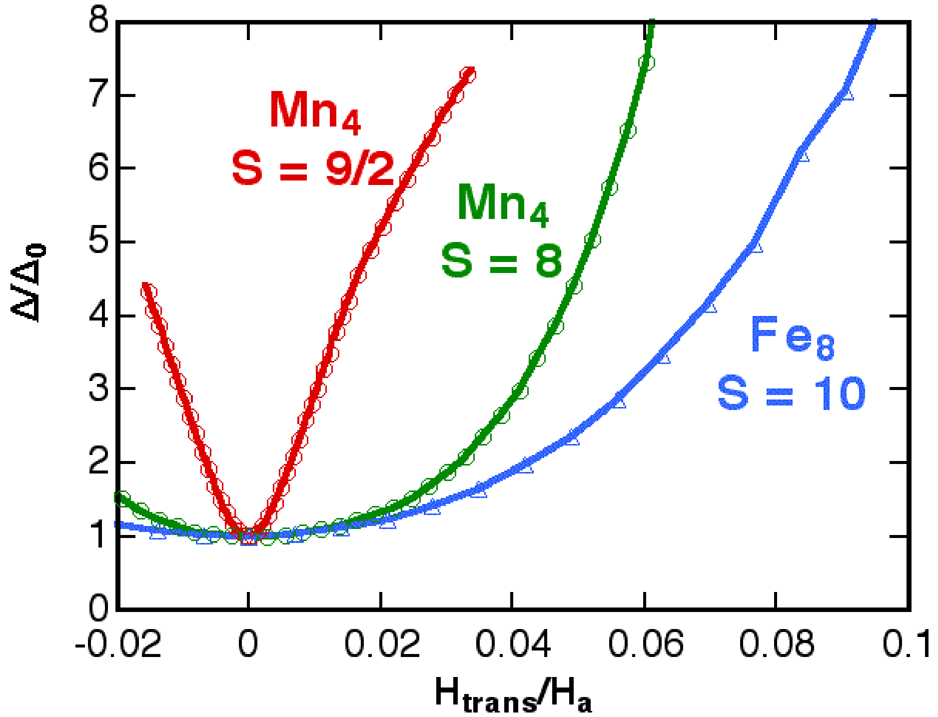


# Spin-parity dependent quantum tunneling




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

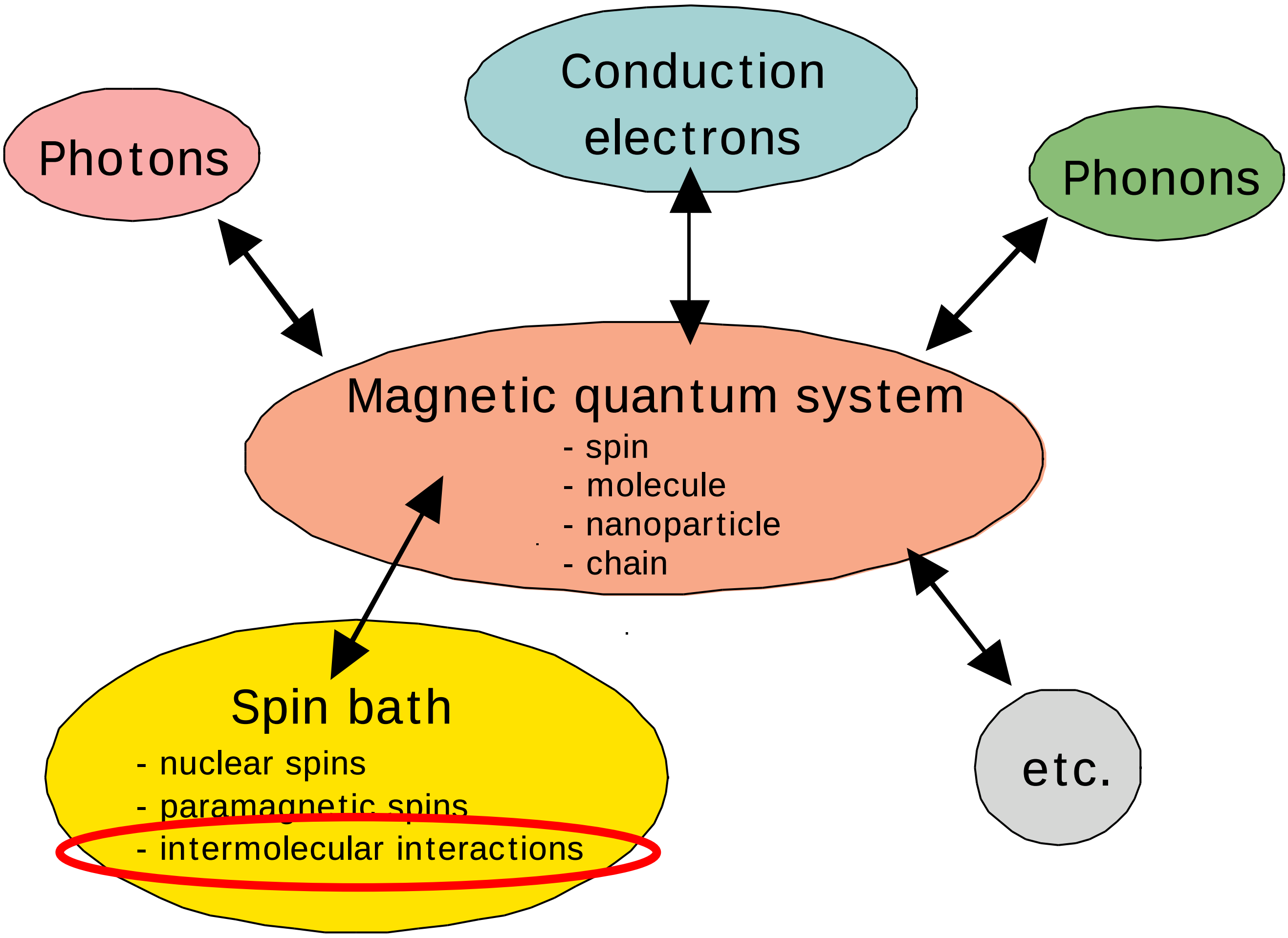
**Environnemental effects**

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

**etc.**

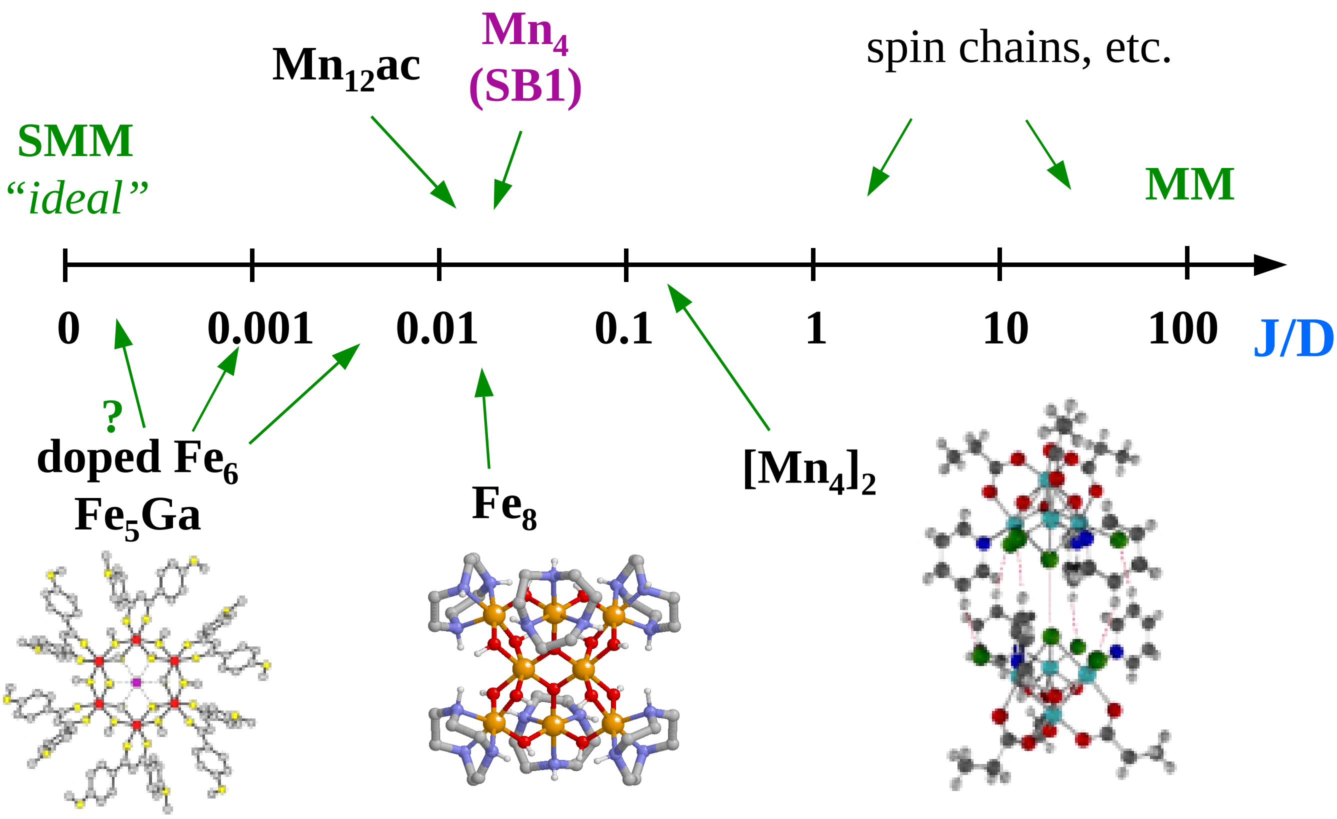
**Phys. Rev. B 65, 180403 (2002)**

Decoherence in magnetic mesoscopic systems



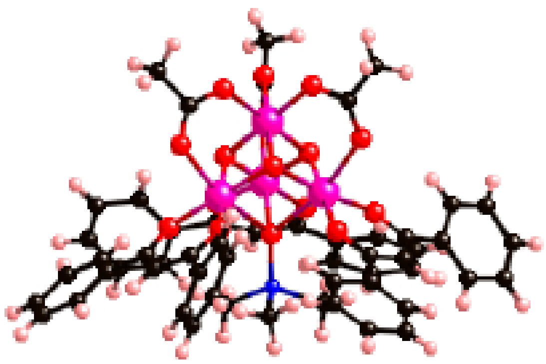
Intermolecular interactions

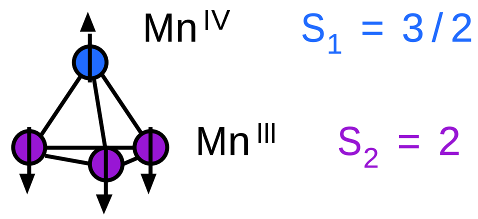
*(dipolar and exchange)*



# $Mn_4$ single-molecule magnet

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

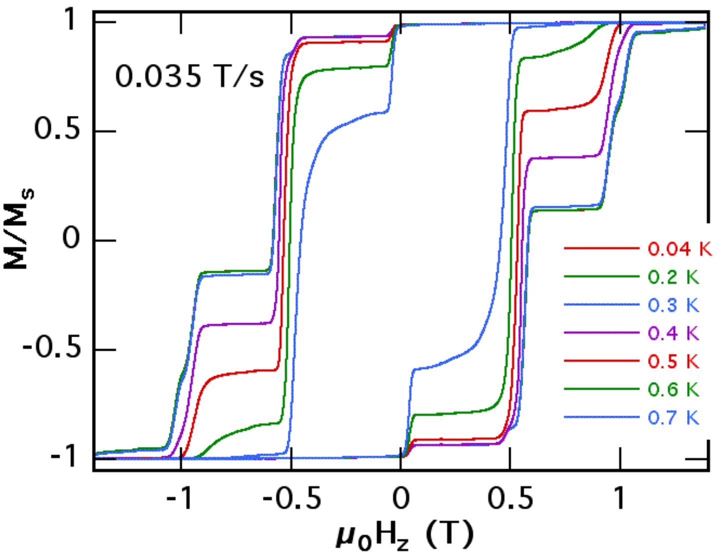


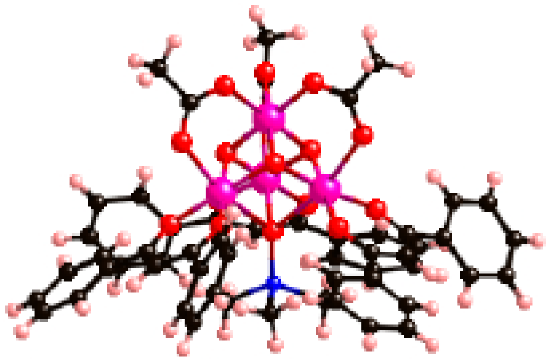


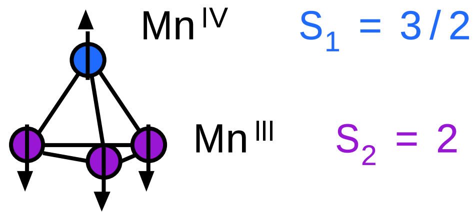

**S = 9/2**

# Hysteresis loops of a
# $Mn_4$ single-molecule magnet

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

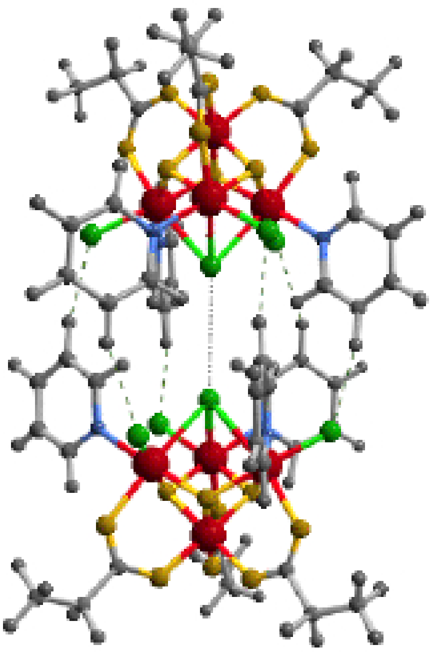


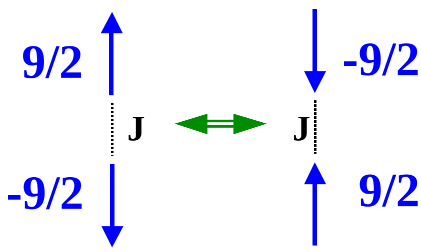






**S = 9/2**

# Exchange-biased quantum tunnelling in a supramolecular dimer of single-molecule magnets






W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson & G. Christou
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# Exchange coupled dimer of S = 9/2

$$\mathbf{H}_i = -D\,S_{i,z}^2 + \mathbf{H}_i^{trans} + g\mu_B\mu_0\,\vec{S}_i\,\vec{H}$$

(2S$_i$ + 1) energy states

$S_i$ = 9/2 : **10** energy states

$M_i = -S_i, -S_i+1, \ldots, S_i$

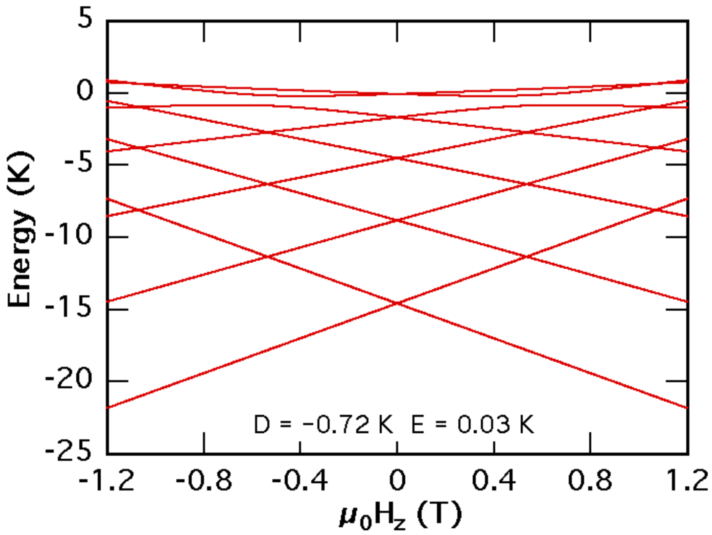
$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + J\,\vec{S}_1\vec{S}_2$$

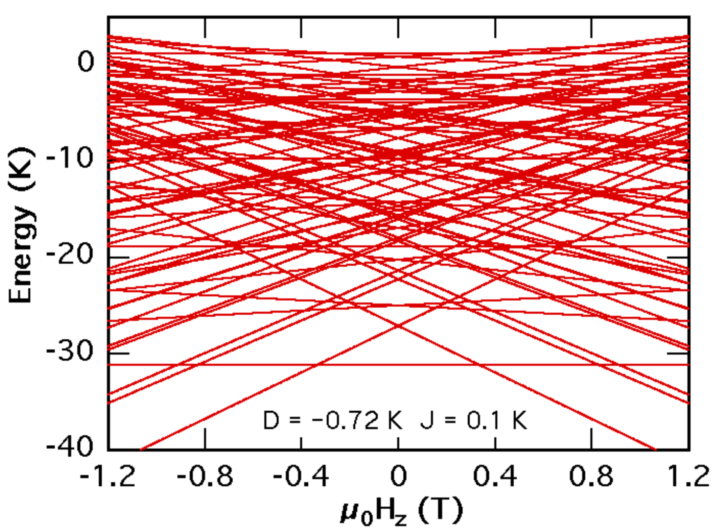
(2S$_1$ + 1)(2S$_2$ + 1) energy states

$S_i$ = 9/2 : **100** energy states

$M_1 = -S_1, -S_1+1, \ldots, S_1$

$M_2 = -S_2, -S_2+1, \ldots, S_2$



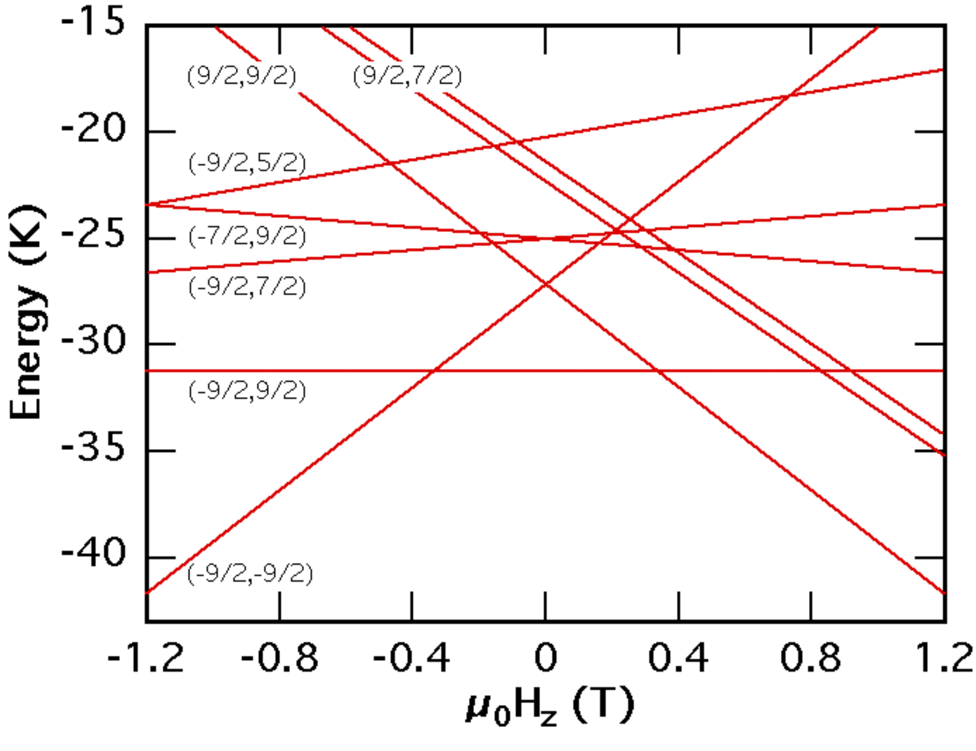



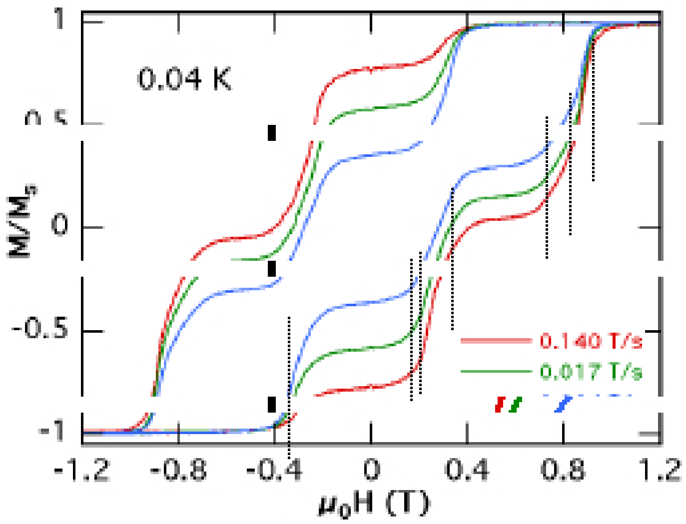
## Exchange coupled dimer of S = 9/2

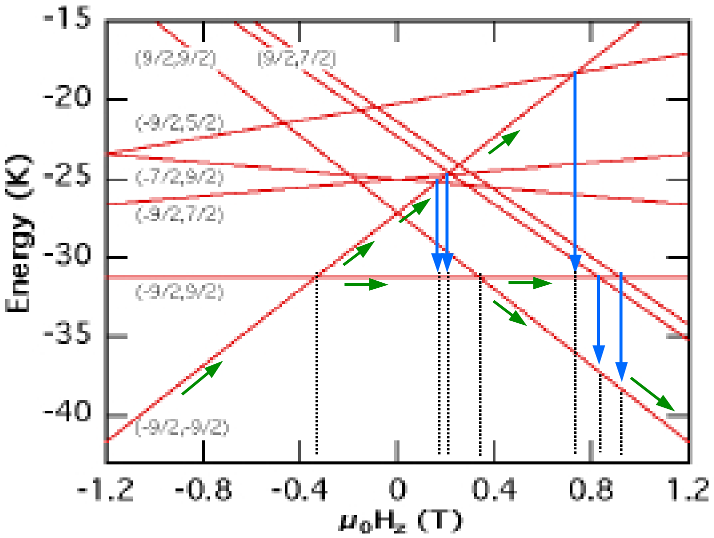
$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + J\,\vec{S}_1\vec{S}_2$$

$$\mathbf{H}_i = -D\,S_{i,z}^2 + \mathbf{H}_i^{trans} + g\mu_B\mu_0\,\vec{S}_i\,\vec{H}$$

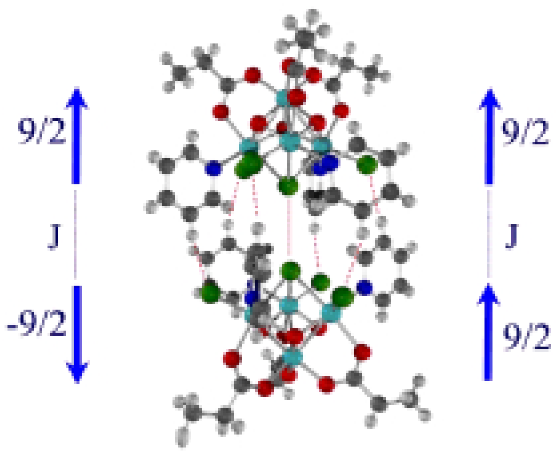
100 energy states **($M_1$,$M_2$)**






**Tunnelling in a dimer of Mn4 single-molecule magnets with S = 9/2**

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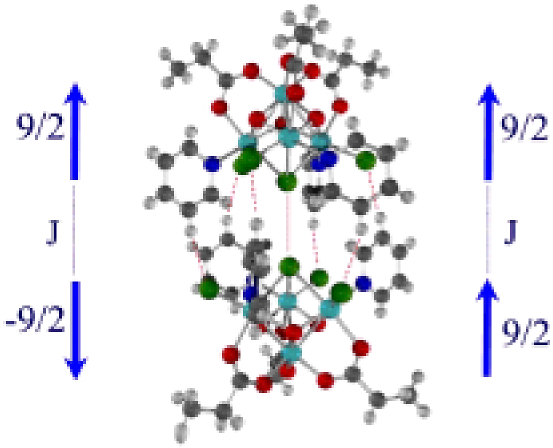
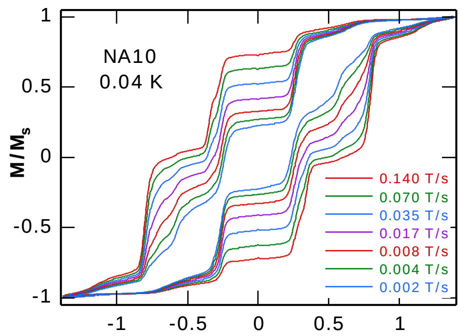
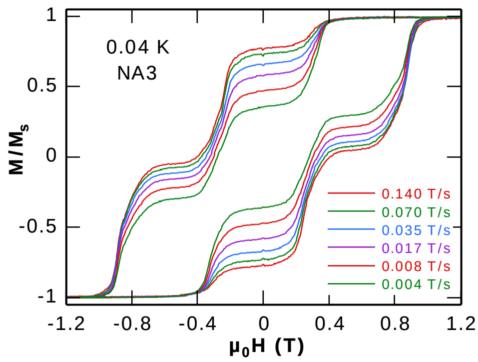
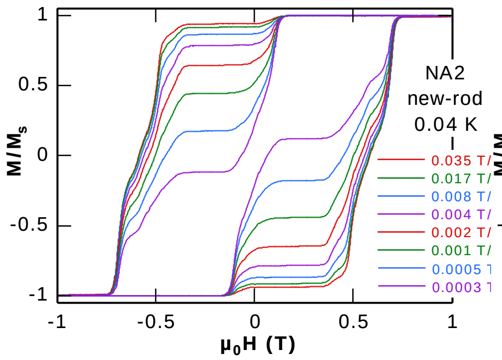
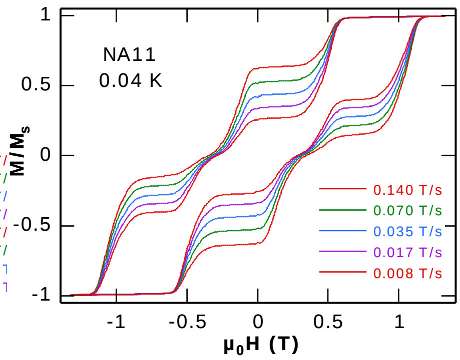
# Exchange biased $Mn_4$

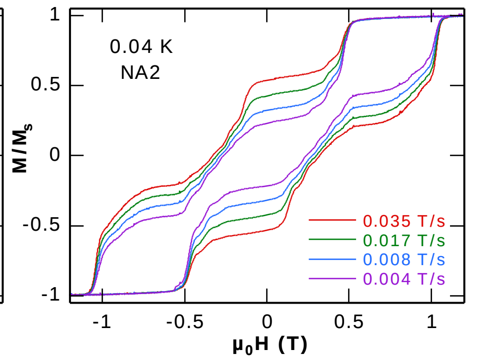


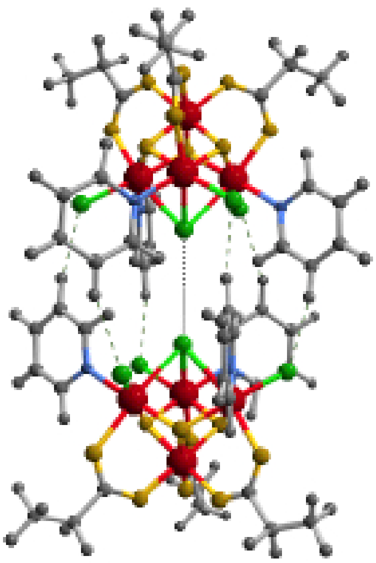



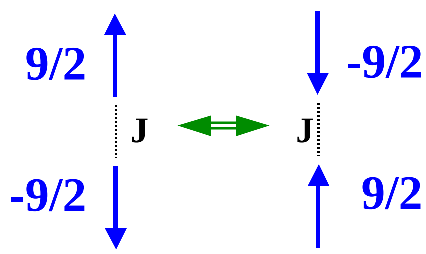



# Why is this dimer so interesting ?

- Possibility of tuning quantum properties (resonance positions)
- Coupled mesoscopic quantum system
- Model system for tunneling in mesoscopic antiferromagnets
- Important step towards coupled quantum bits



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