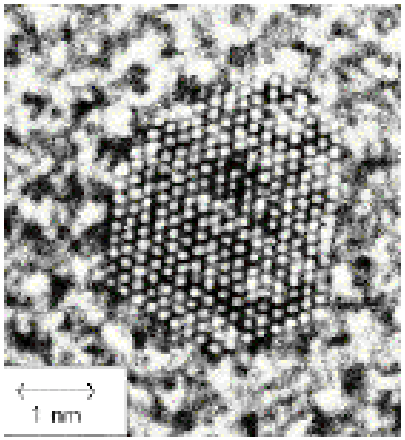
Quantum dynamics in Single-Molecule Magnets

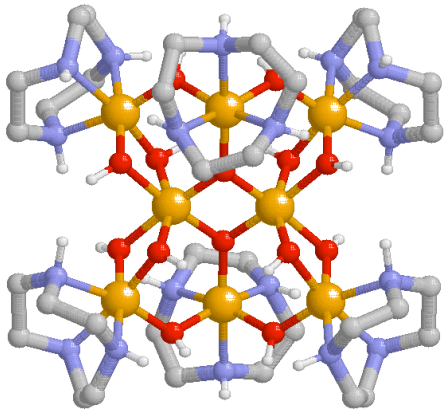


$S = 10^2$ to 10^6

Wolfgang Wernsdorfer

Laboratoire de Magnétisme Louis Néel

C.N.R.S. - Grenoble



$S = 1/2$ to ≈ 30

Laboratoire Louis Néel

CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE

MAGMA Net NETWORK OF EXCELLENCE

NanoSciences RHÔNE-ALPES

GRENOBLE 1 UNIVERSITE JOSEPH FOURIER SCIENCES, TECHNOLOGIE, MEDECINE

Magnetic structures

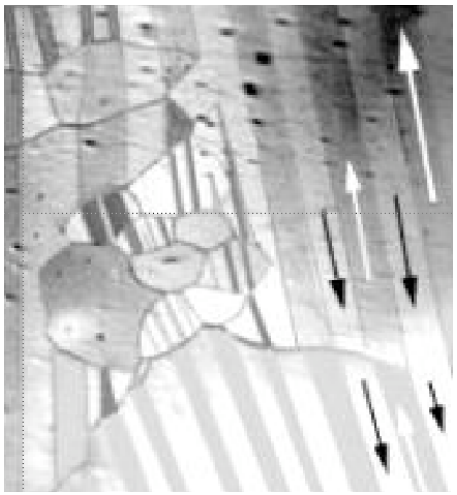
macroscopic ← → *atomic*

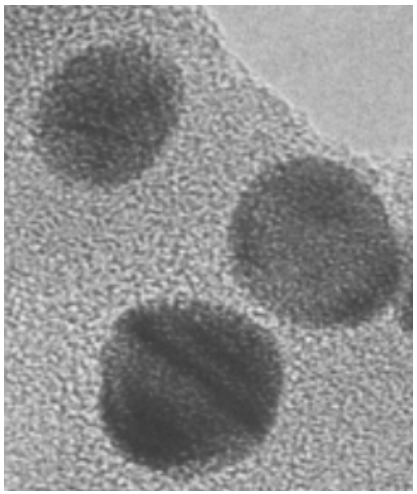
permanent magnets	micron particles	nanoparticles	clusters	molecular clusters	atoms

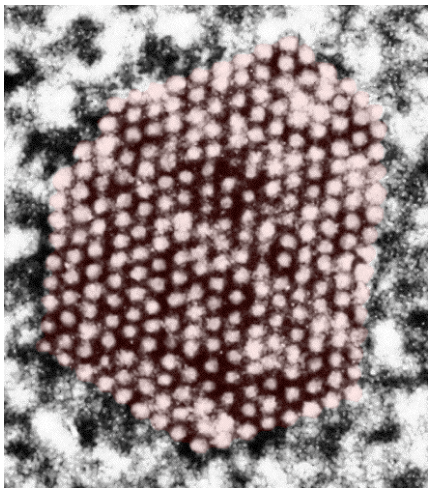
$S = 10^{20}$ 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1

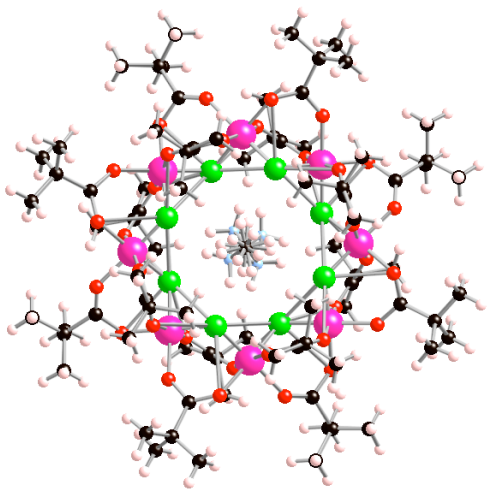
multi - domains ***single - domains*** ***spins***

1 mm **20 nm** **3 nm** **1 nm**









Magnetization reversal in magnetic structures

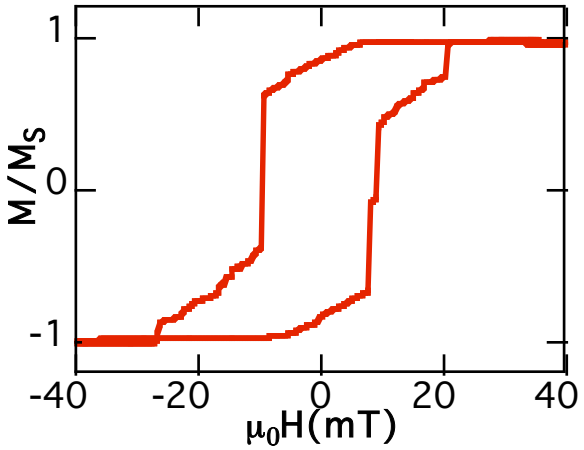
macroscopic ← → *atomic*

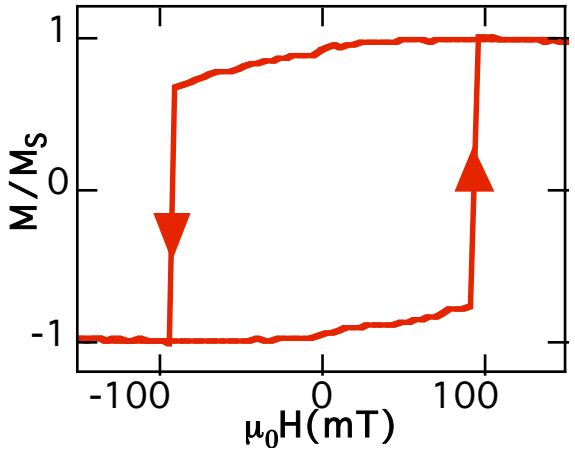
permanent magnets	micron particles	nanoparticles	clusters	molecular clusters	atoms
$S = 10^{20}$	10^{10}	10^{8}	10^{6}	10^{5}	10^{4}	10^{3}	10^{2}	10	1

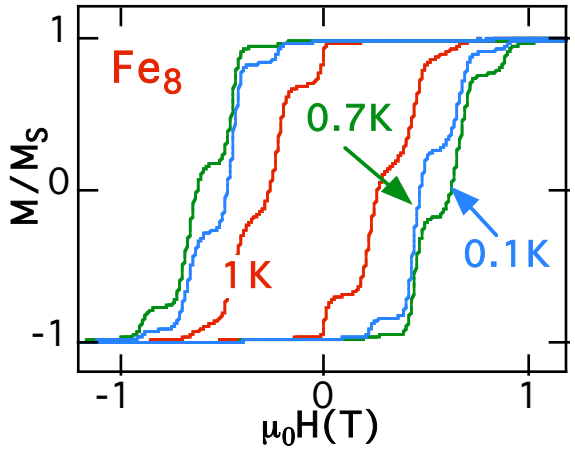
multi - domains — nucleation, propagation and annihilation of domain walls

single - domains — uniform rotation, curling, etc.

spins — quantum tunneling, interference, coherence







Magnetization reversal in 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***

nucleation, propagation and annihilation of domain walls

uniform rotation, curling, etc.

quantum tunneling, interference, coherence

"Classical" magnetism

Micromagnetics

Landau Lifshitz Gilbert equation

Quantum magnetism

Schrödinger equation

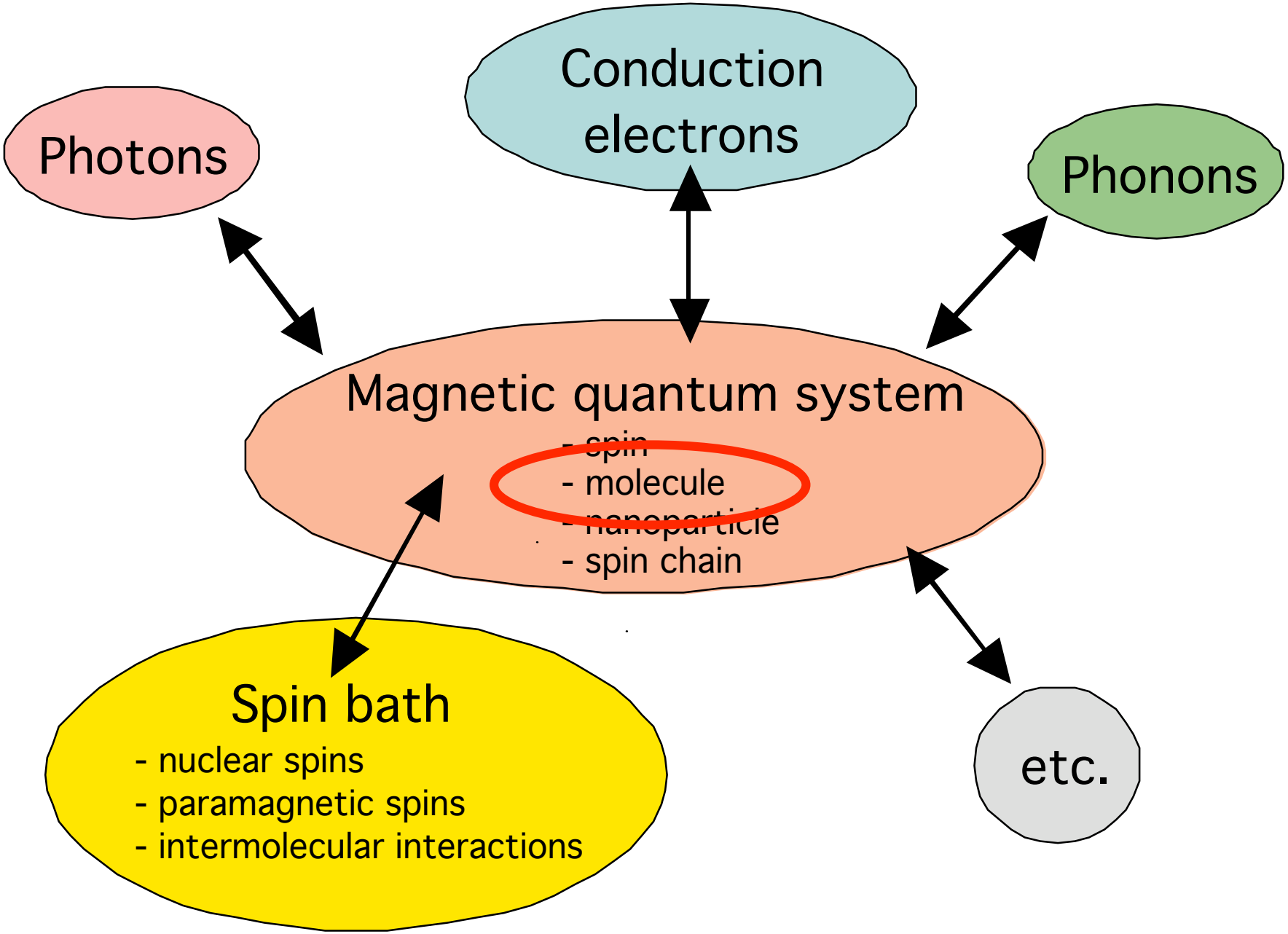
Operator formalism

Path intergrals

ab-initio calulations

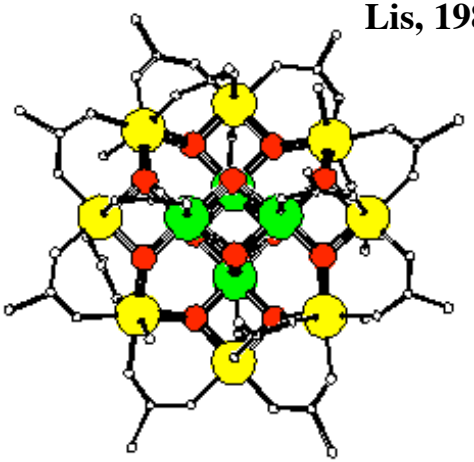
etc.

Interactions in magnetic quantum systems (decoherence)



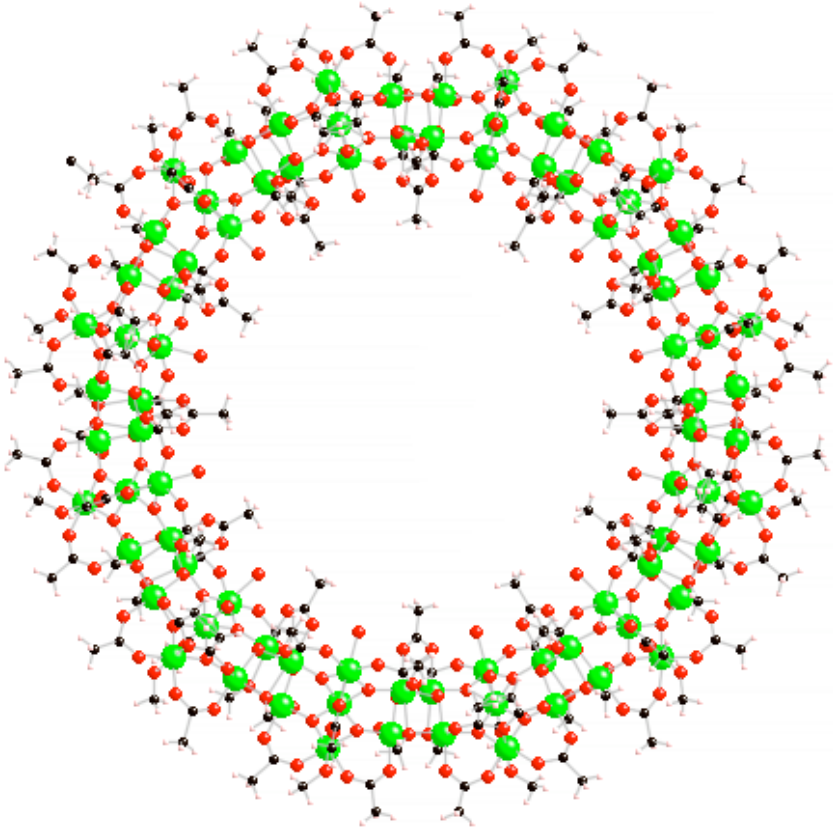
Single-molecule magnets (SMM)

Giant spins



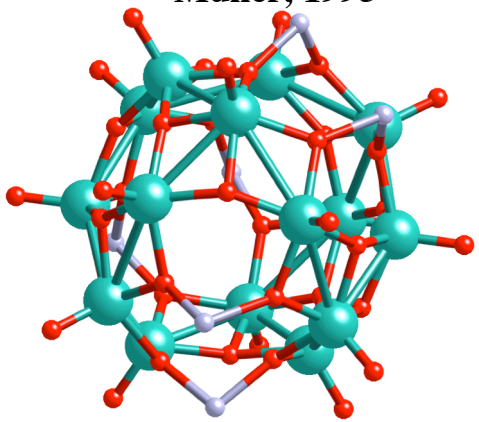
Lis, 1980

Mn_{12} S = 10



Christou, 2004

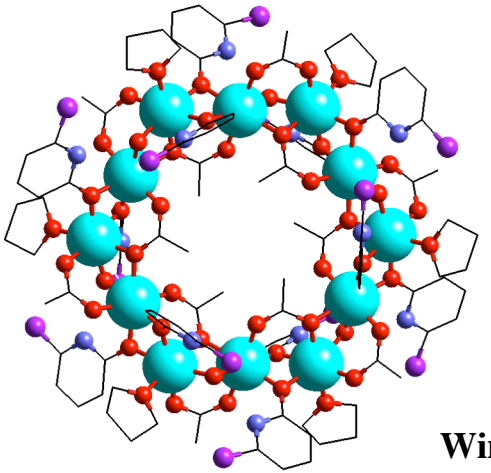
Mn_{84}
S ≈ 6



Müller, 1993

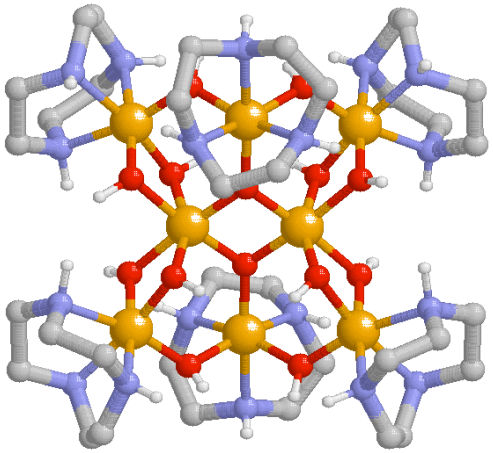
V_{15} S = 1/2

Ni_{12} S = 12



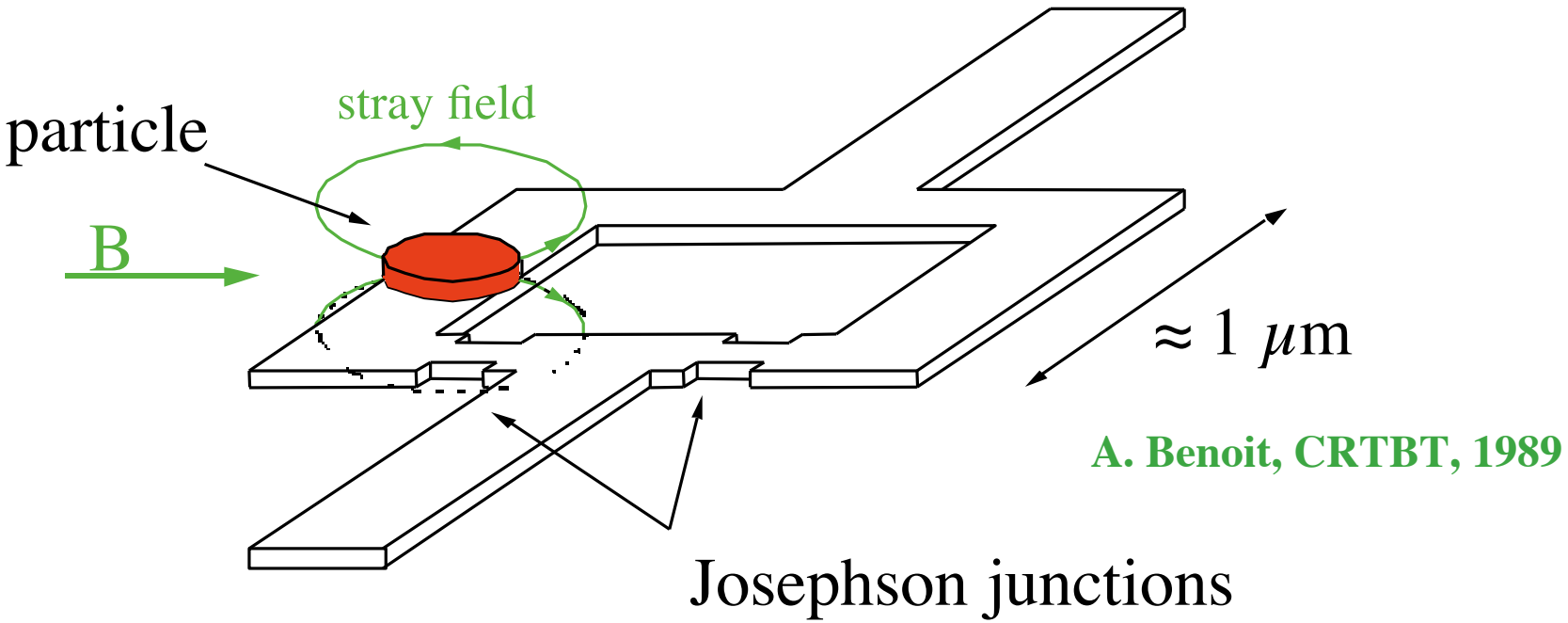
Winpenny, 1999

Fe_8 S = 10

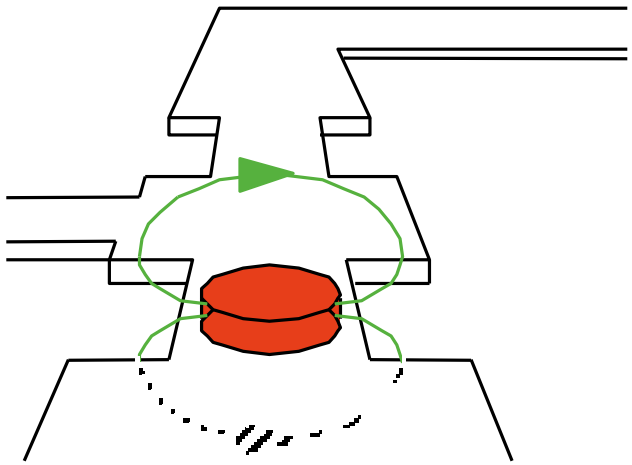


Wiegart, 1984

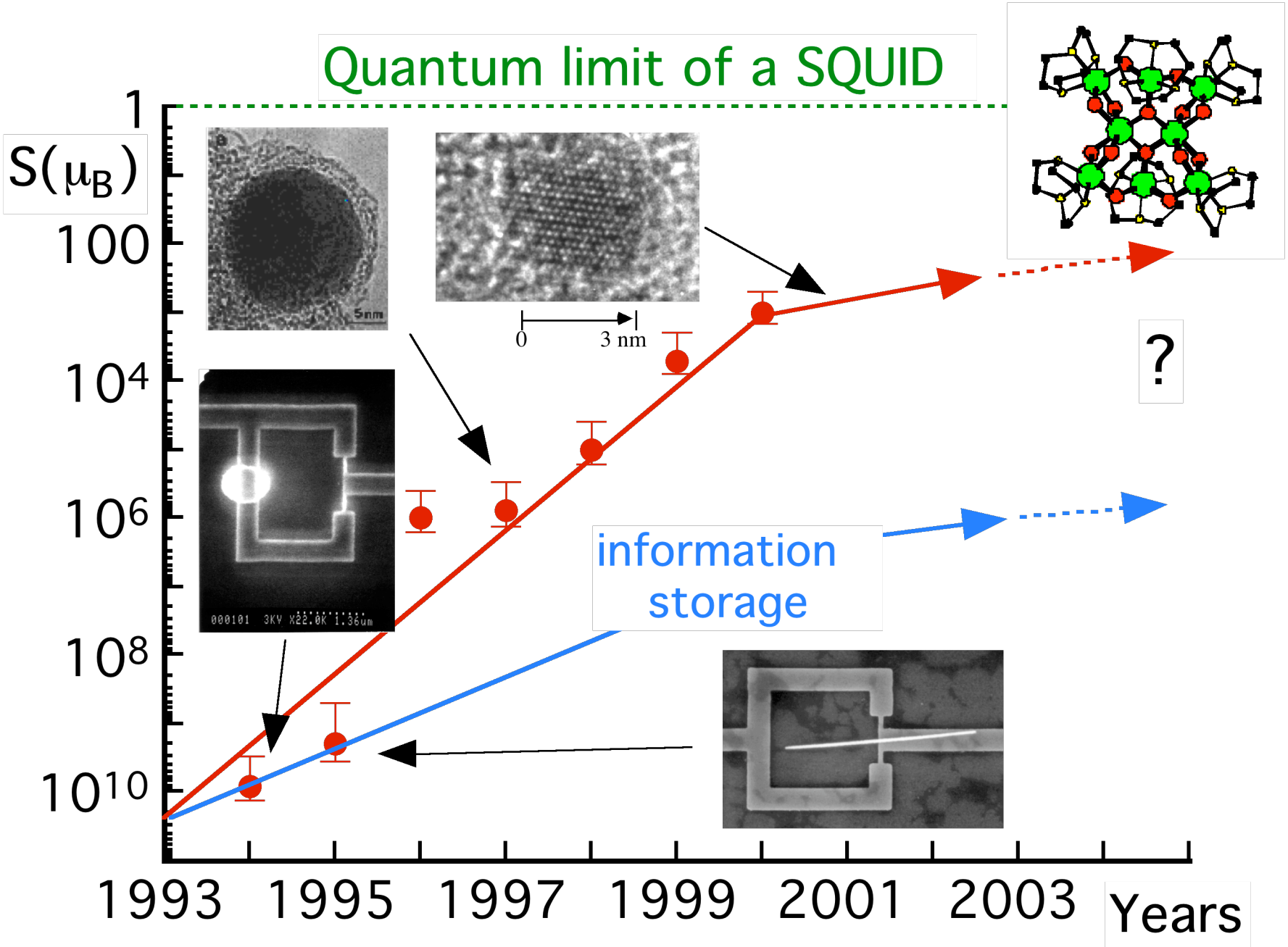
Micro-SQUID magnetometry



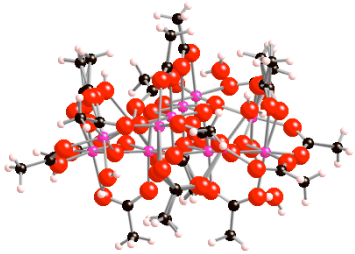
- fabricated by electron beam lithography
  (D. Mailly, LPN, Marcoussis - Paris)
- sensitivity : 10^{-4} F_0
  - ≈ 10^2 - 10^3 μ_B i.e. (2 nm)^3 of Co
  - ≈ 10^{-18} - 10^{-17} emu

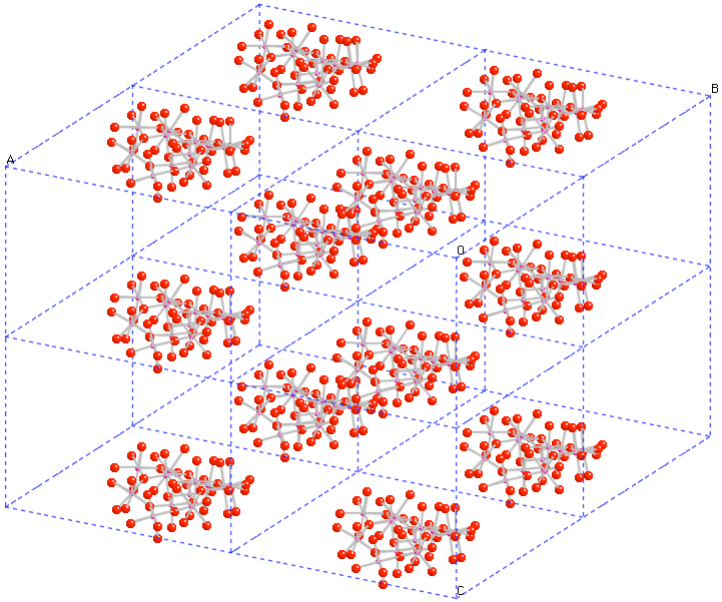


Roadmap of the micro-SQUID technique

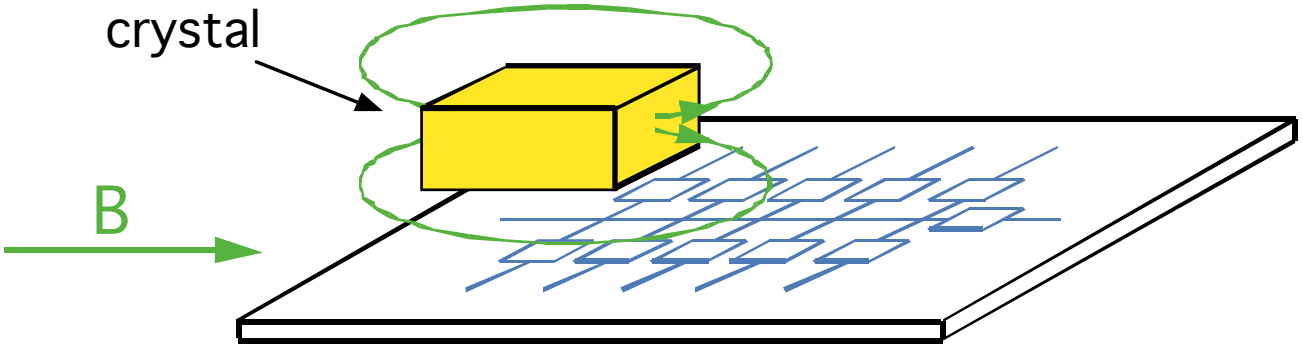


Crystal of SMMs

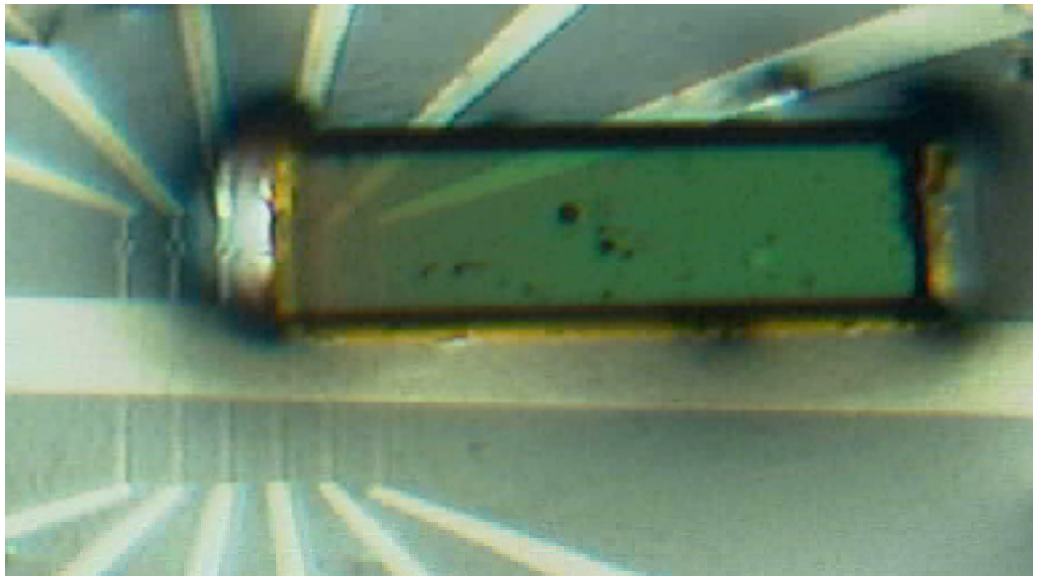




Micro-SQUID array



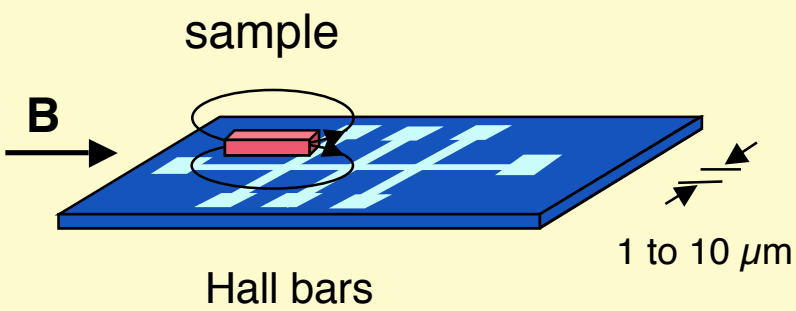
- crystal size > few μm
- 10^{-12} to 10^{-17} emu
- temperature 0.03 - 7 K
- field < 1.4 T and < 20 T/s
- rotation of field
- transverse field
- several SQUIDs at different positions



50 μm

Micro-magnetometry

- μ-Hall Effect

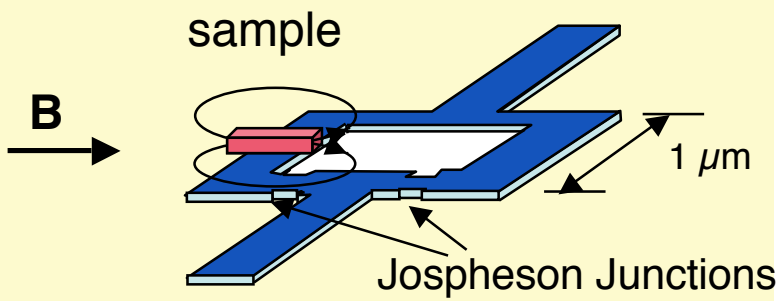


  - Based on Lorentz Force
  - Measures magnetic field

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

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

- μ-SQUID



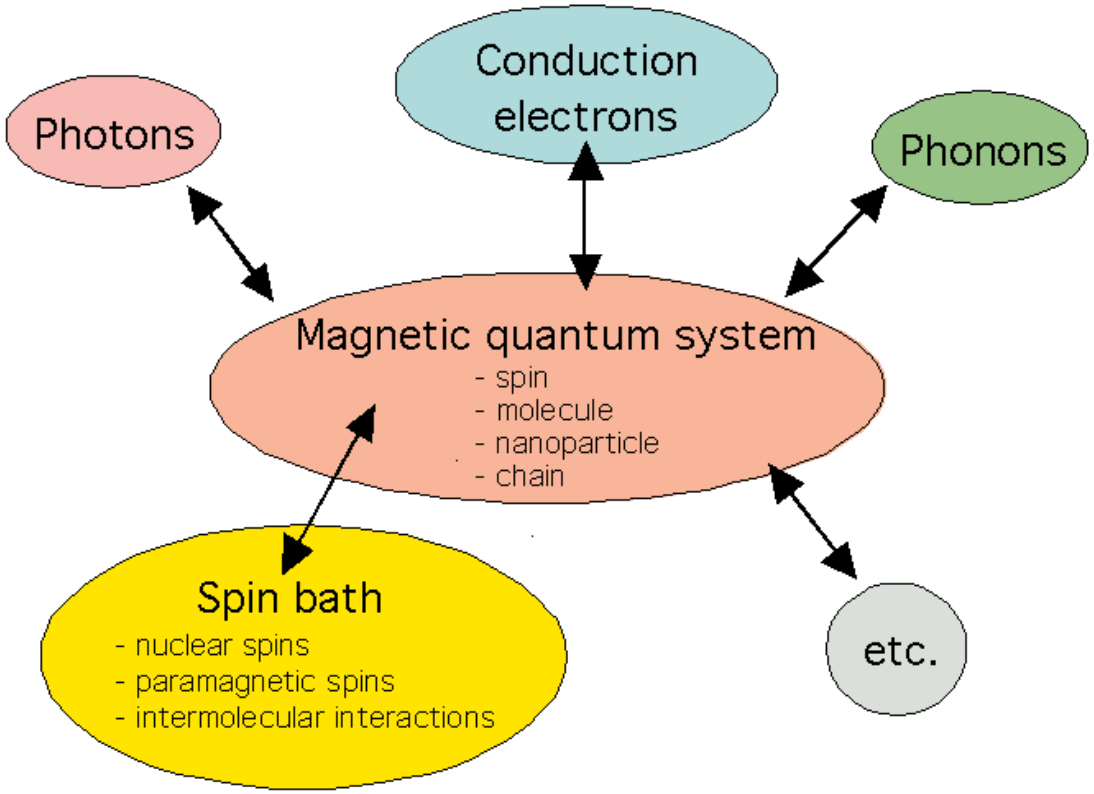
  - Based on flux quantization
  - Measures magnetic flux
  - Applied fields below the upper critical field (~1 T)
  - Low temperature (below T_c)
  - Single magnetic particles
  - Ultimate sensitivity ~1 μ_B

Outline

I. A simple tunnel picture (Mn_{12}, Fe_8)

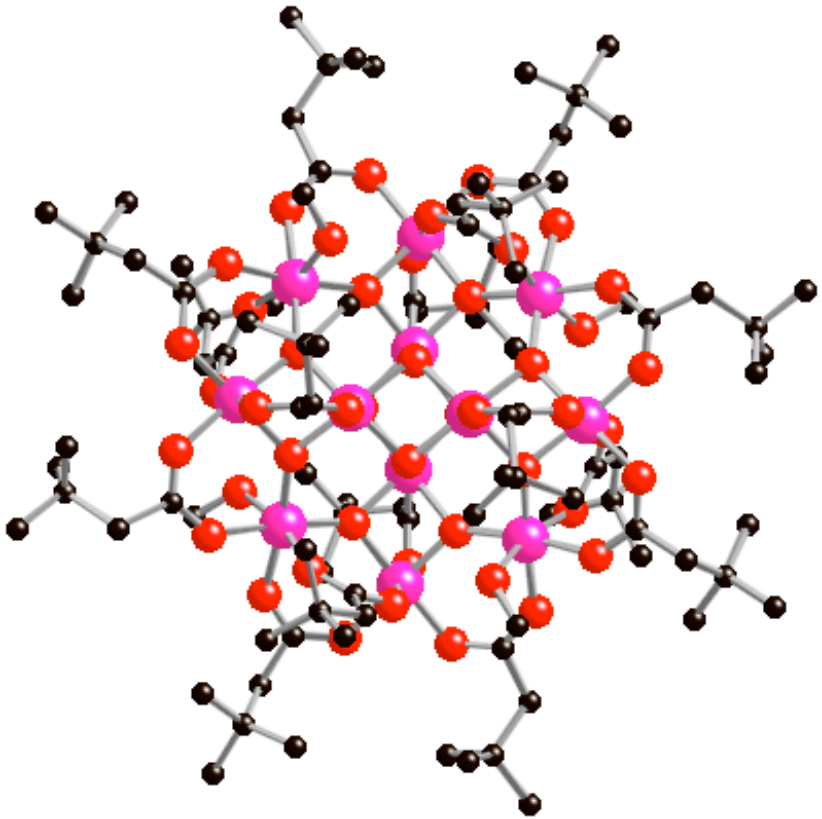
- Giant spin model
- Landau Zener tunneling
- Berry phase

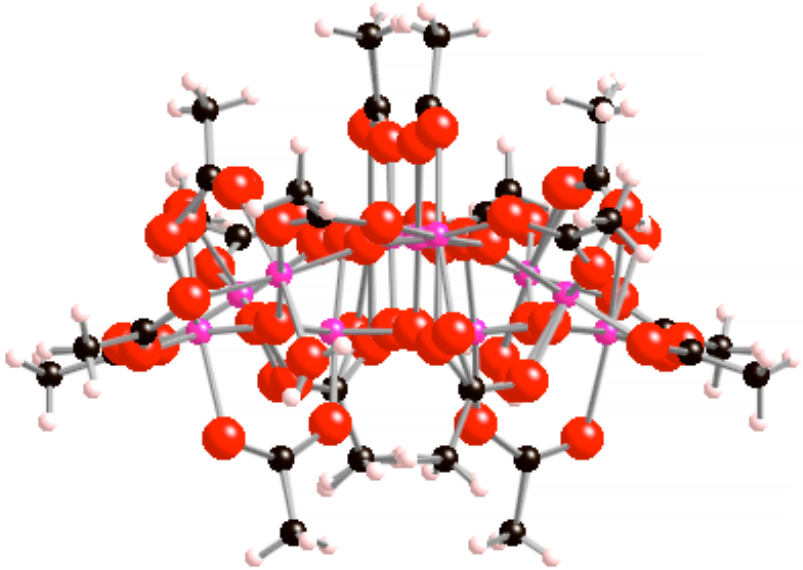
II. Coupling with environment



Mn_{12}-*t*BuAc

$[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(CH_3OH)_4].CH_3OH$





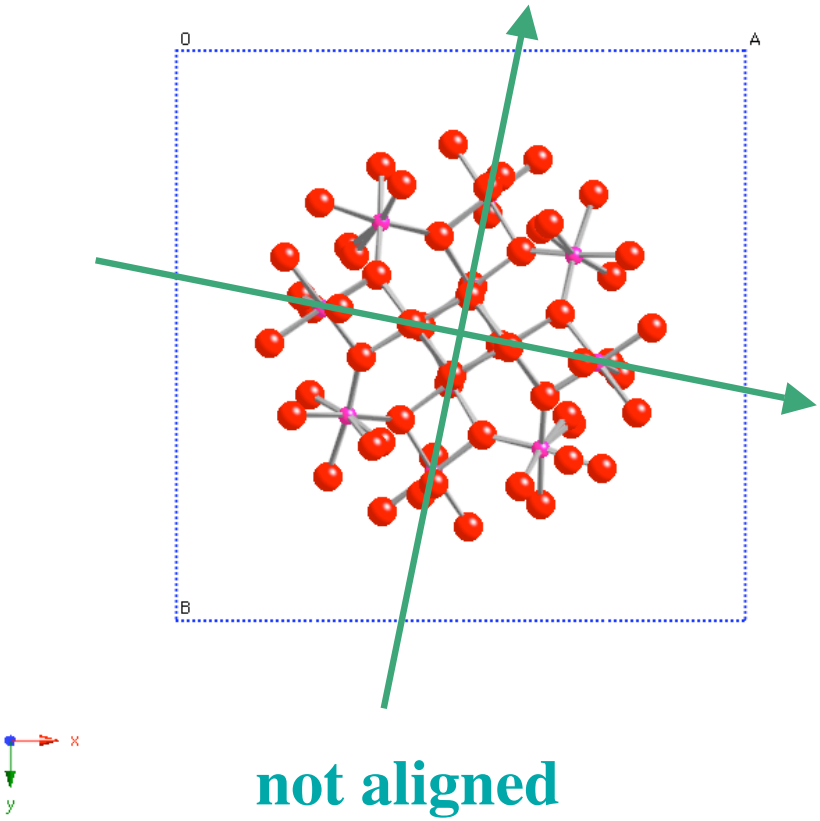
Mn^{III}: s = 2

Mn^{IV}: s = 3/2

Comparison between

Mn_{12}-Ac

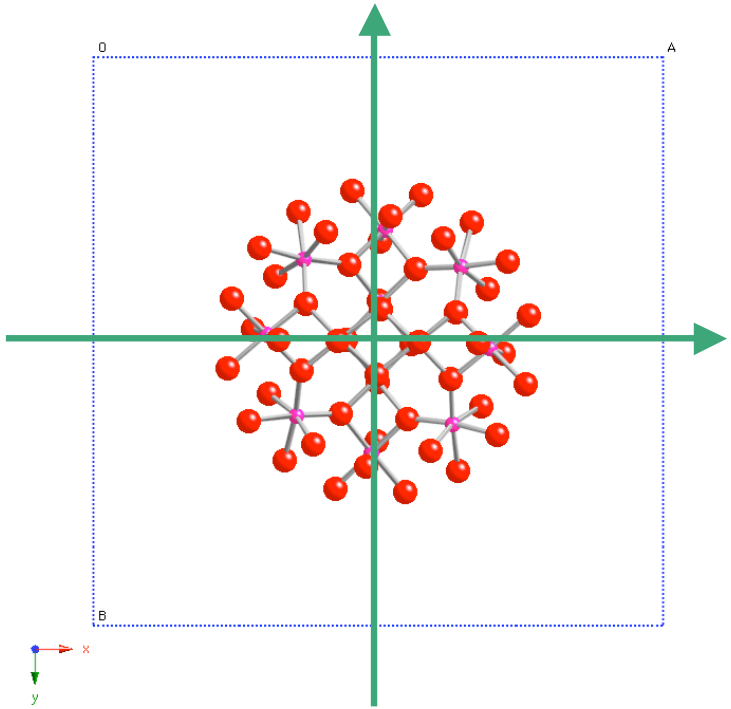
$[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4].2CH_3CO_2H.4H_2O$



not aligned

Mn_{12}-*t*BuAc

$[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(CH_3OH)_4].CH_3OH$



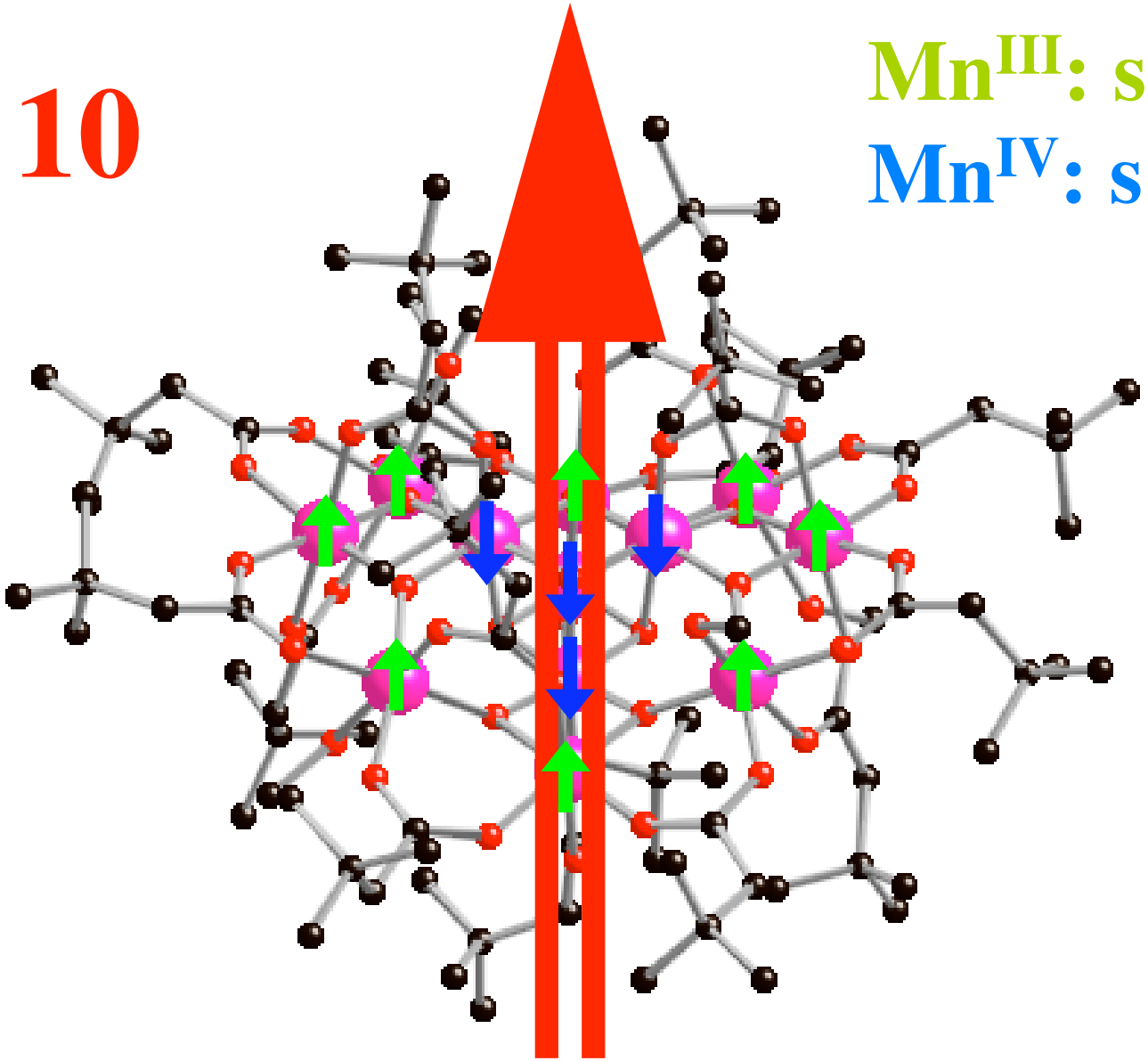
- **well aligned !!**
- **larger unit cell**
- **less disorder**

Giant spin approximation (Mn_{12})

S = 10

Mn^{III}: s = 2

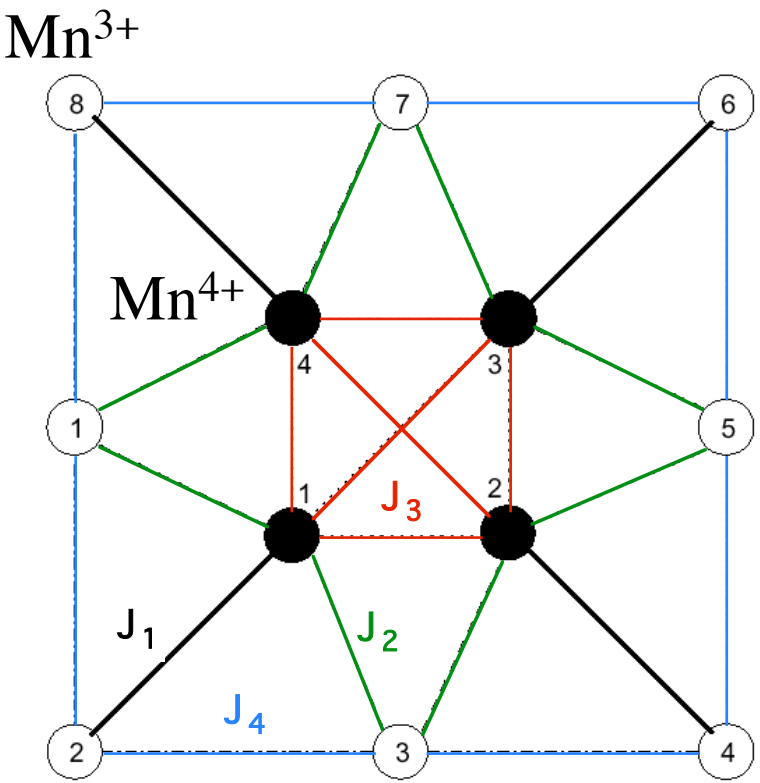
Mn^{IV}: s = 3/2

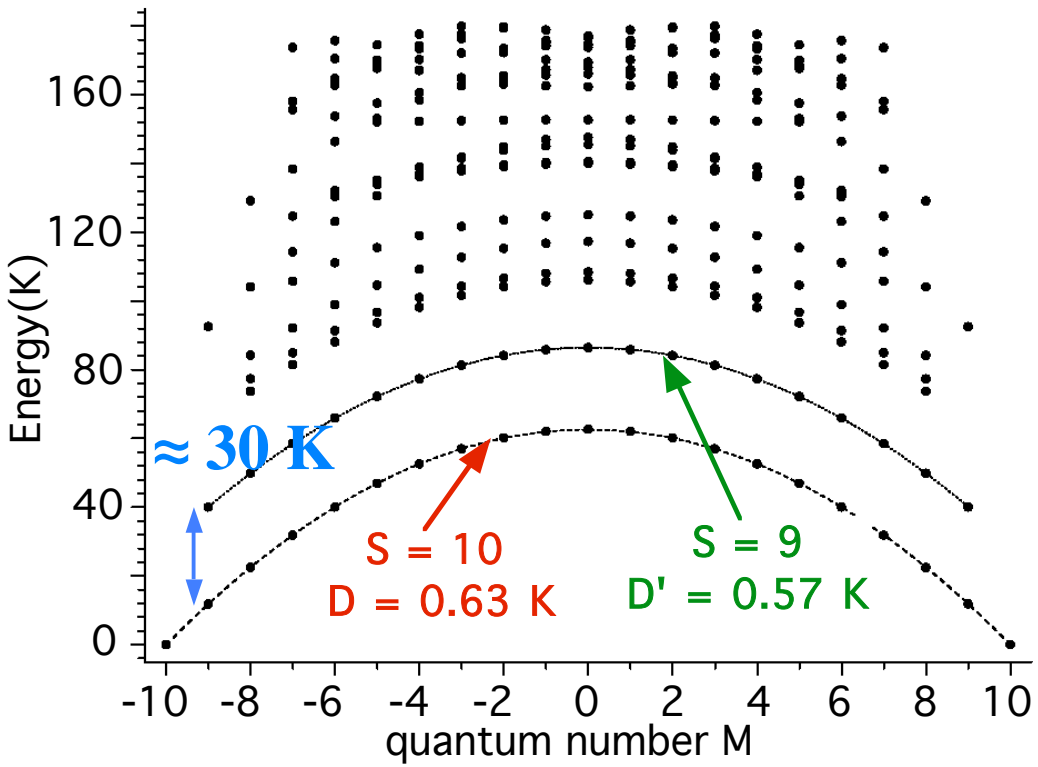


Giant spin approximation

Example: Mn12-ac

Hilbert space: $(2x2 + 1)^8(2x3/2 + 1)^4 \approx 10^8$





$J_1 \approx$ -215 K

$J_2 \approx J_3 \approx$ -86 K

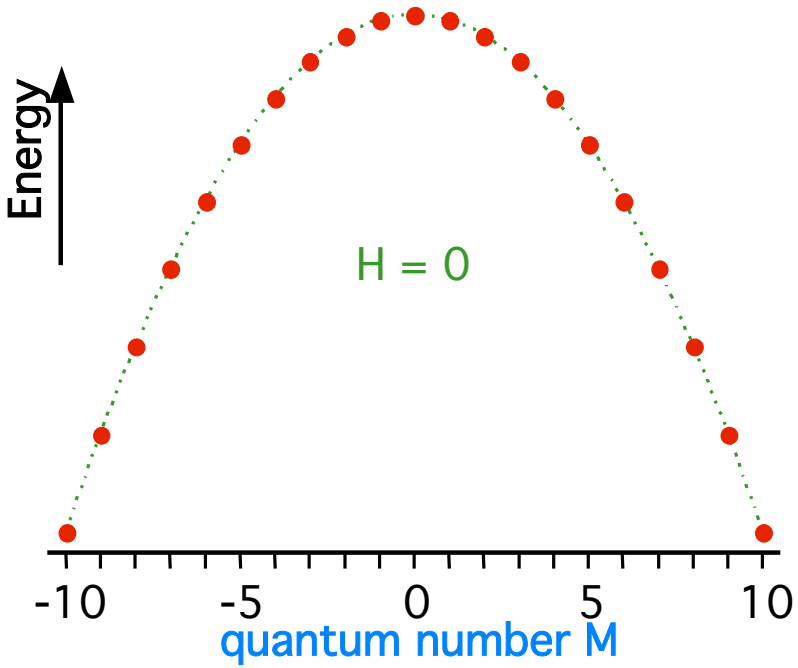
$J_4 <$ 43 K

I. Tupitsyn (2000)

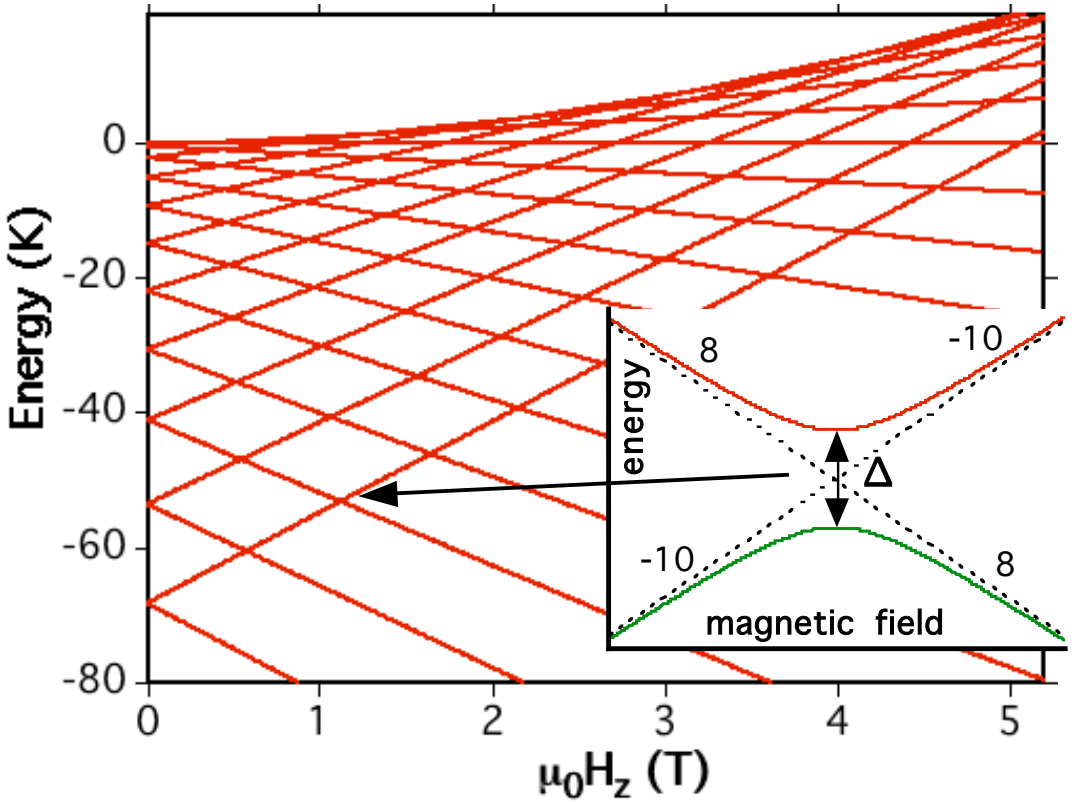
Giant spin model

Spin Hamiltonian: $H = -D\,S_z^2 - B\,S_z^4 + H_{tr} - g\mu_B\,\vec{S}\,\vec{H}$

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

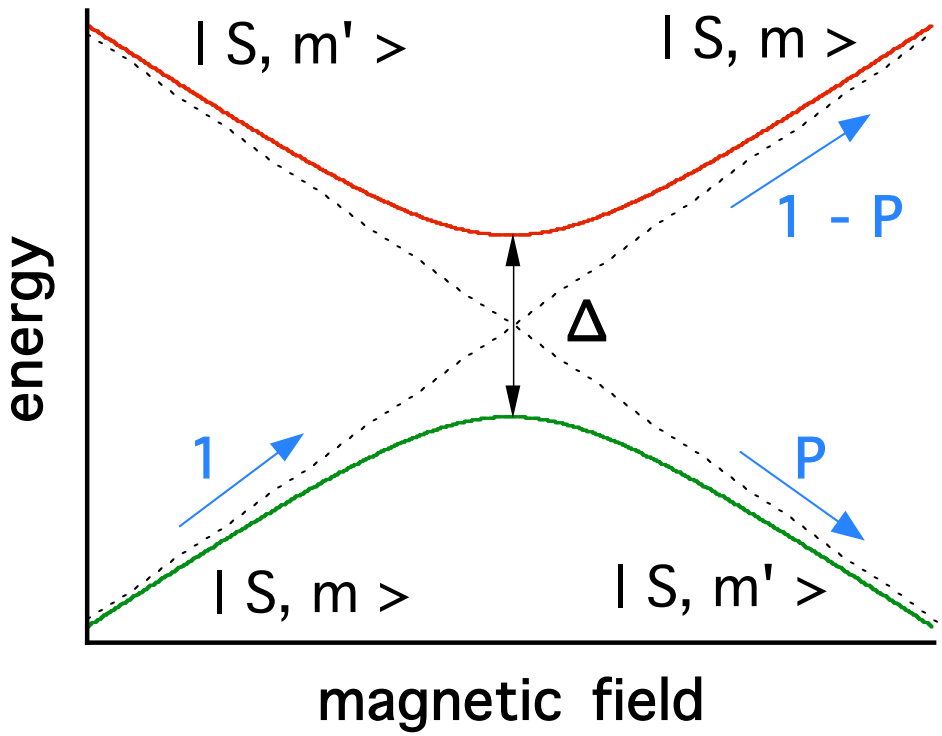


Energy levels: Zeeman diagram



with S = 10, D = 0.56 K, B = 1.5 mK

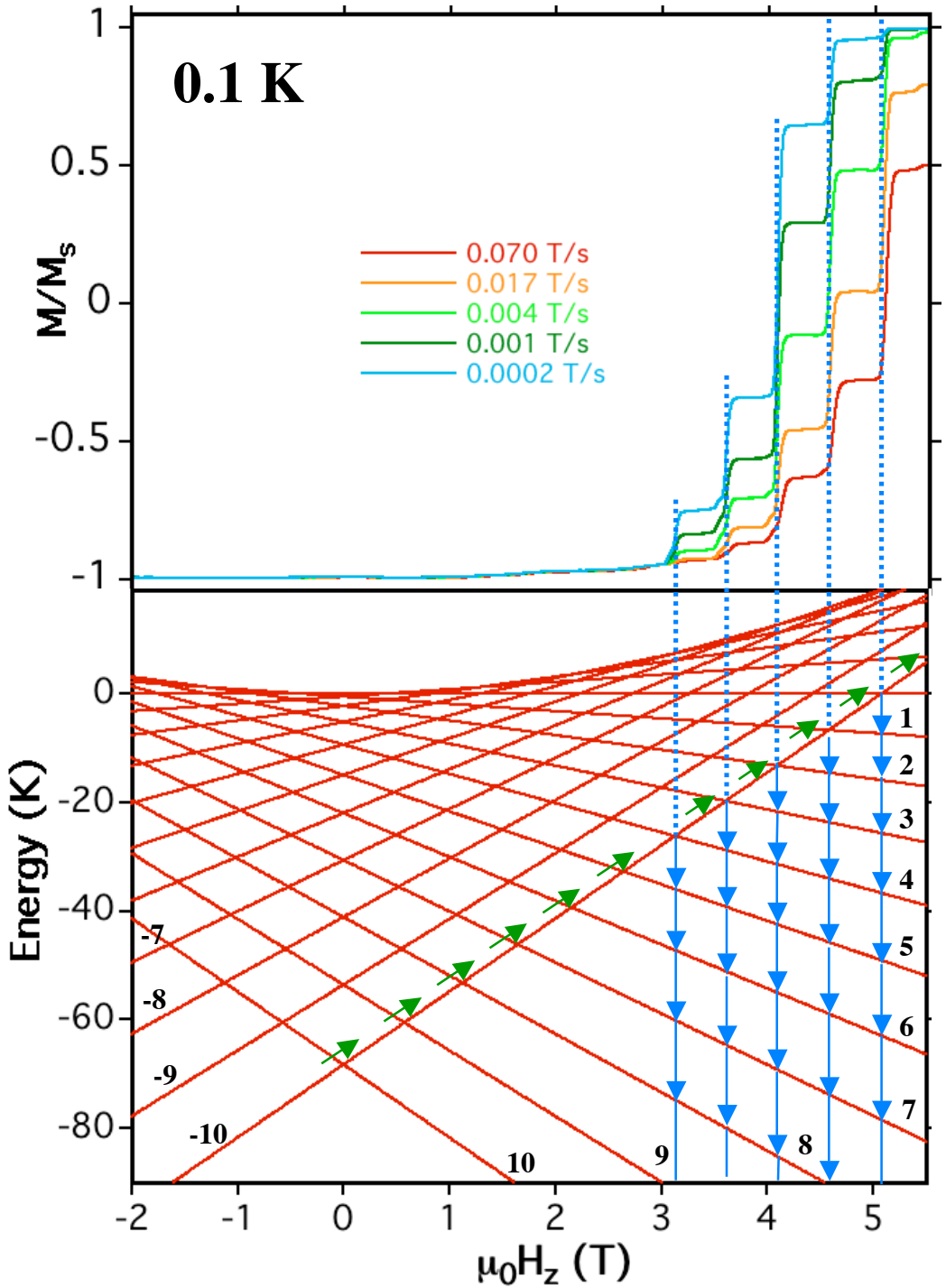
Tunneling probability at an avoided level crossing
Landau-Zener model (1932)



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

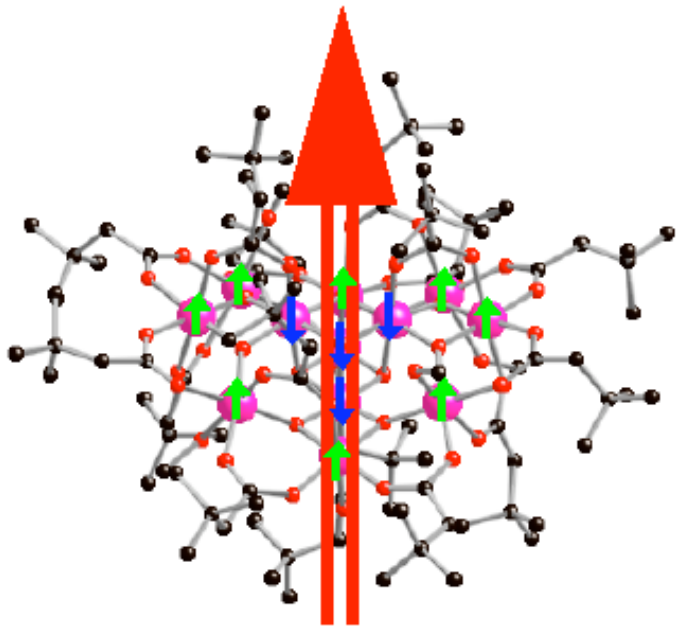
$$c = \frac{\pi}{2\hbar\, g\mu_B |m - m'| \mu_0}$$

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

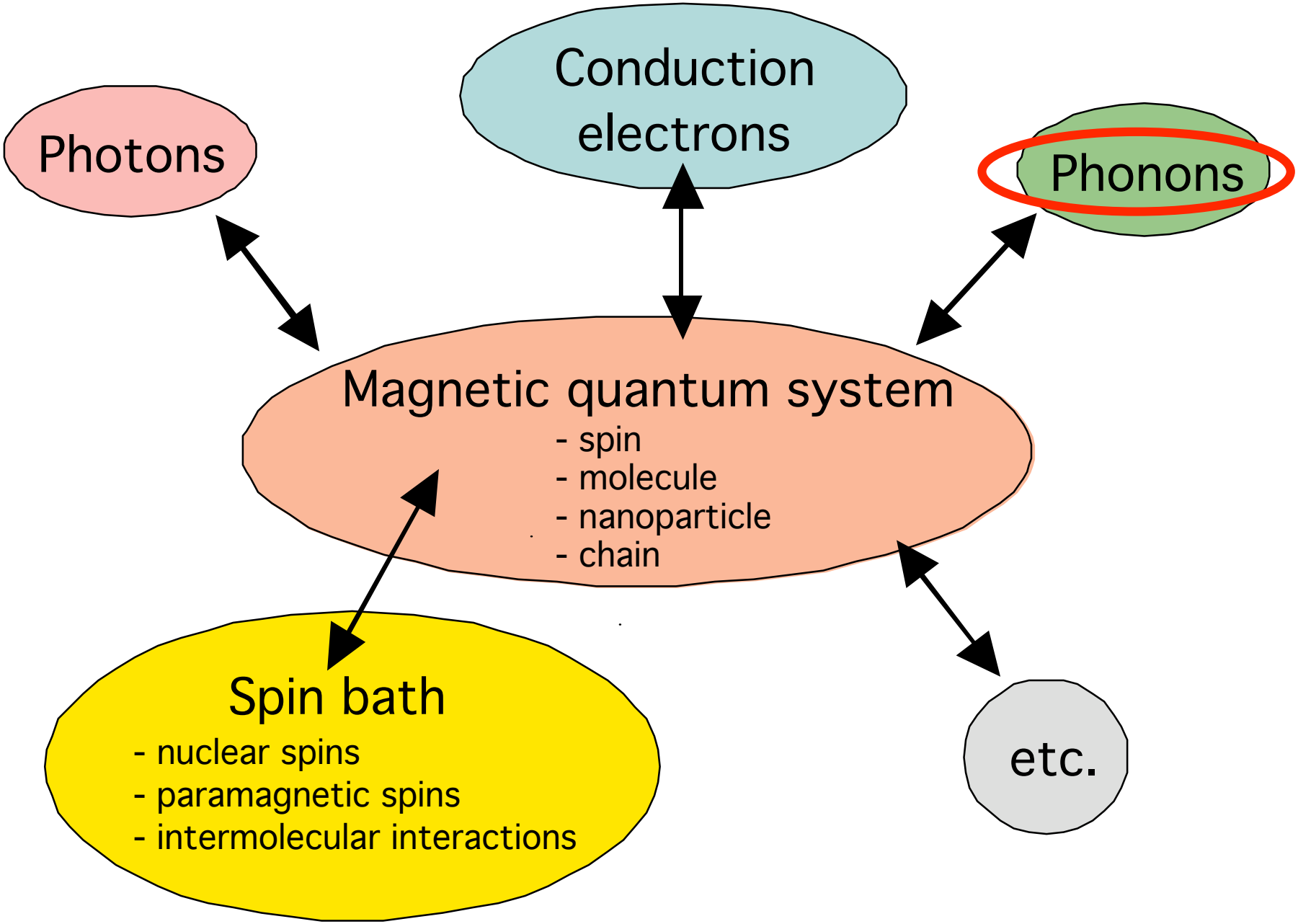
Mn_{12} S = 10



$$H = -D\,S_z^2 - B\,S_z^4 + H_{tr} - g\mu_B\,\vec{S}\,\vec{H}$$

with D = 0.56 K, B = 1.5 mK

Interactions in magnetic quantum systems (decoherence)

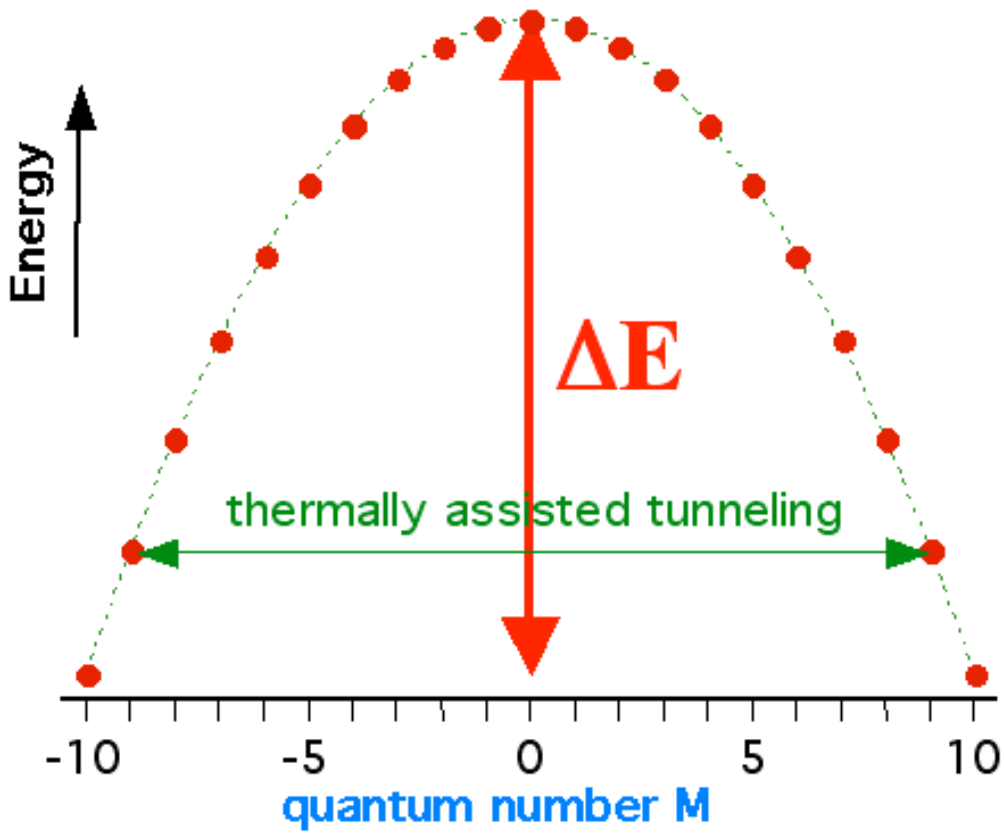


Giant spin model & temperature

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

Spin-phonon coupling : $\Delta M = \pm 1, \pm 2$

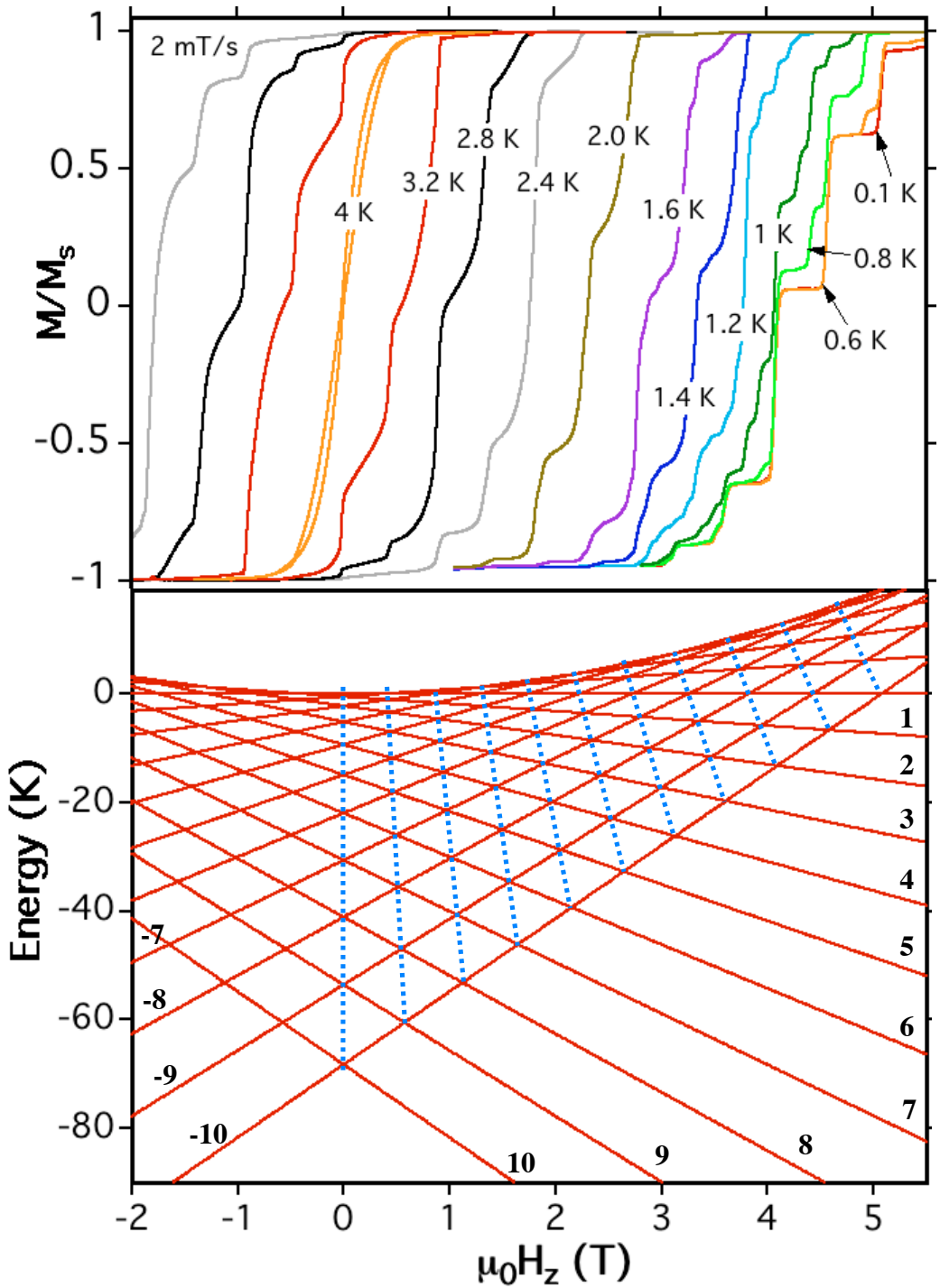


Anisotropy barrier

$$\Delta E \approx D\,S^2$$

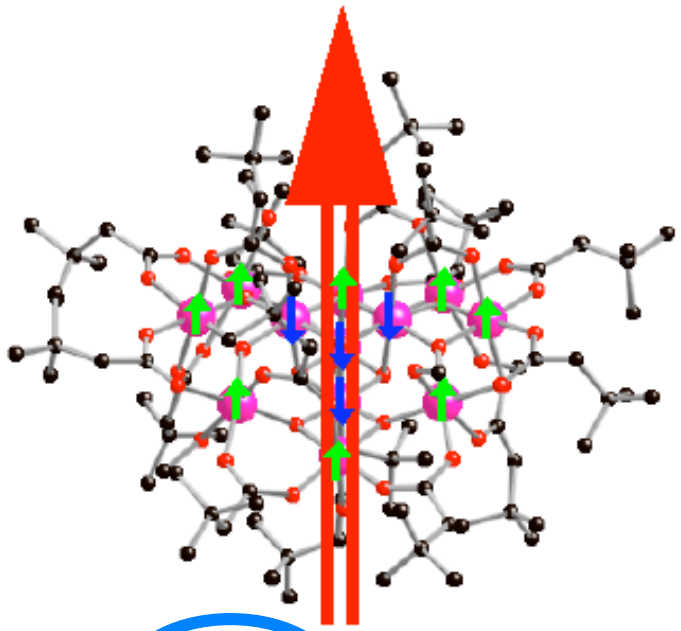
Anisotropy constant

Spin



Landau-Zener tunneling & temperature

Mn_{12} S = 10

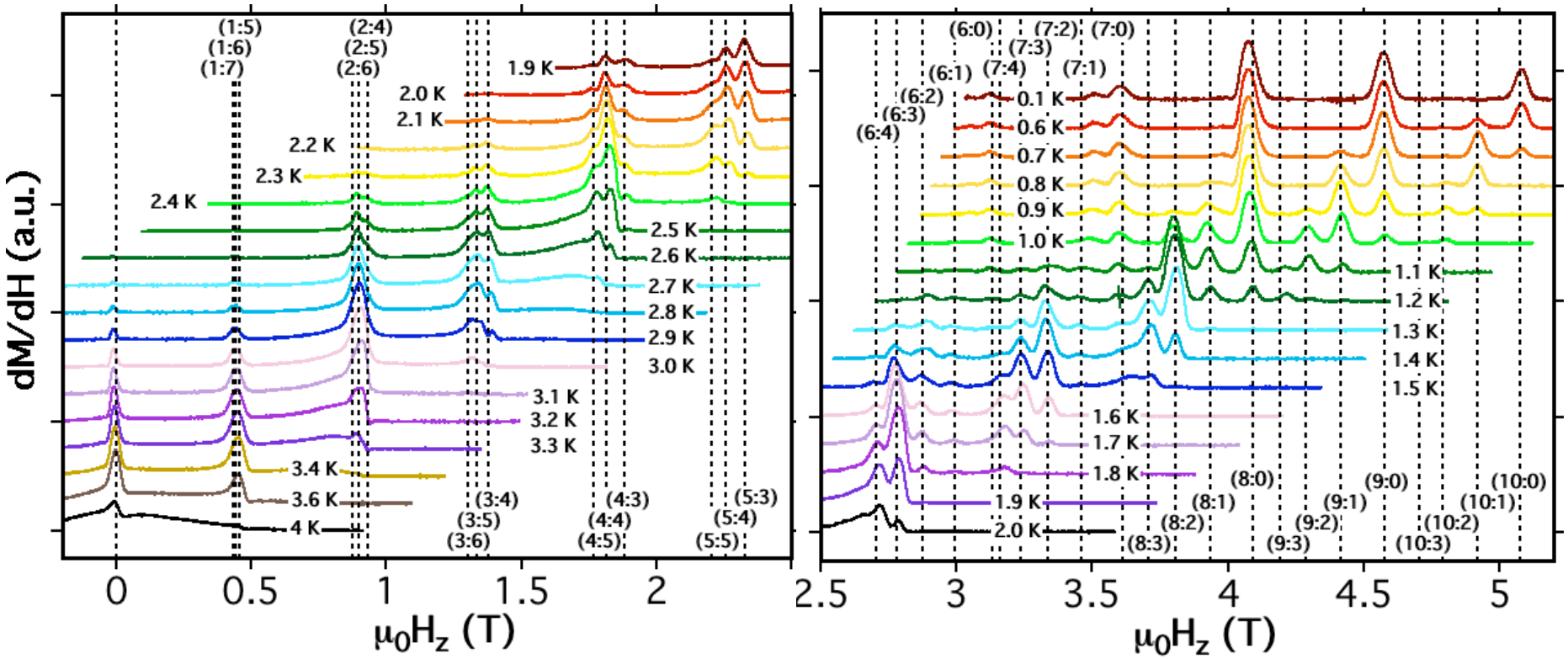


$$H = -D\,S_z^2 - B\,S_z^4 + H_{tr} - g\mu_B\,\vec{S}\,\vec{H}$$

with D = 0.56 K, B = 1.5 mK

Field derivative of M(H) at different temperatures

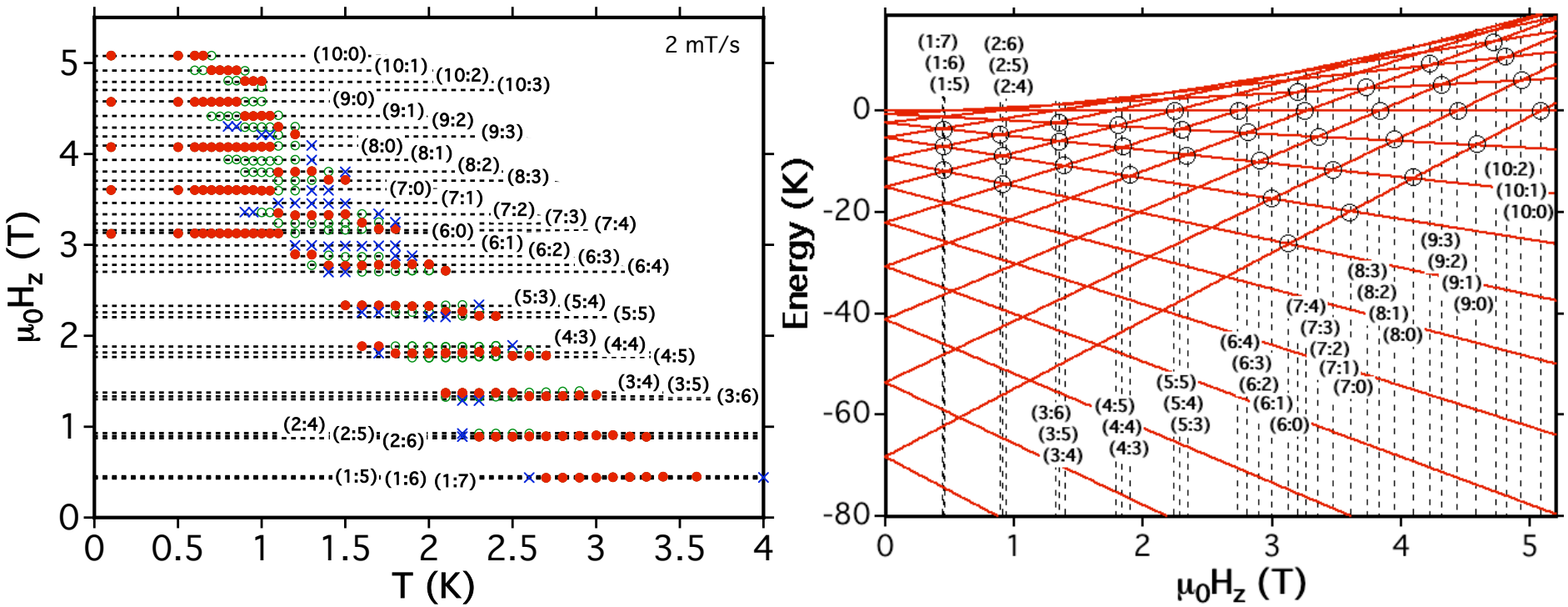
Mn_{12}-*t*BuAc



W. Wernsdorfer, M. Murugesu,
G. Christou, cond-mat/0508437

Temperature dependence of the peak positions of dM/dH

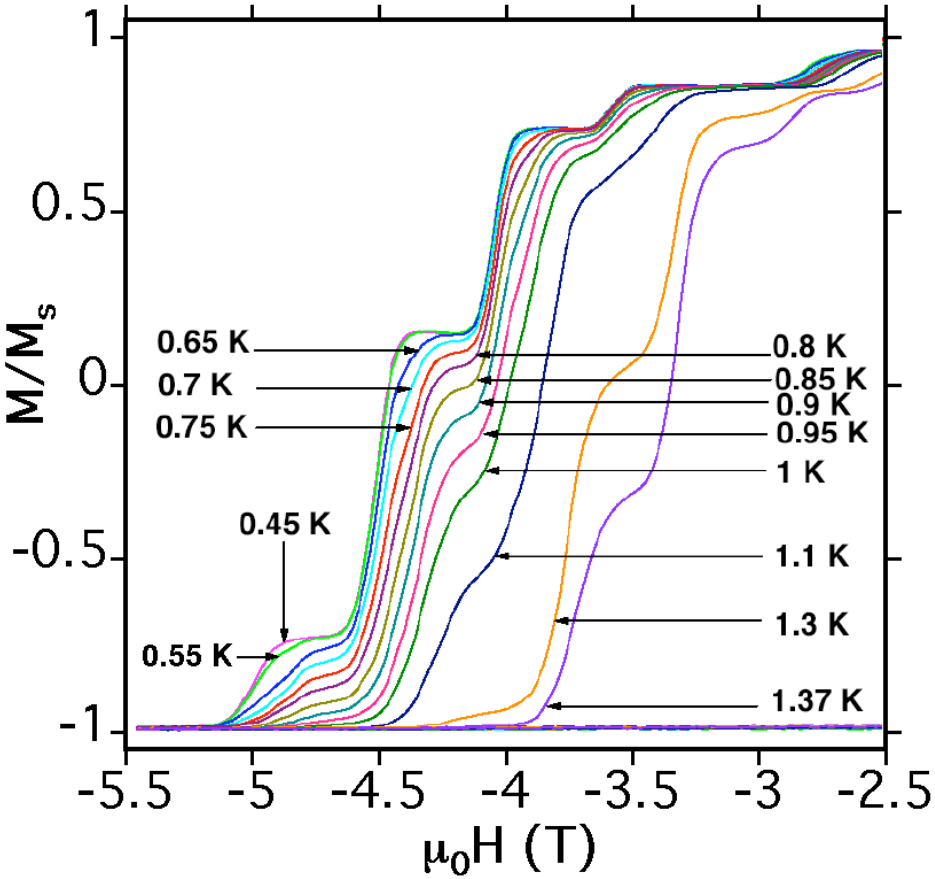
Mn_{12}-*t*BuAc



W. Wernsdorfer, M. Murugesu,
G. Christou, cond-mat/0508437

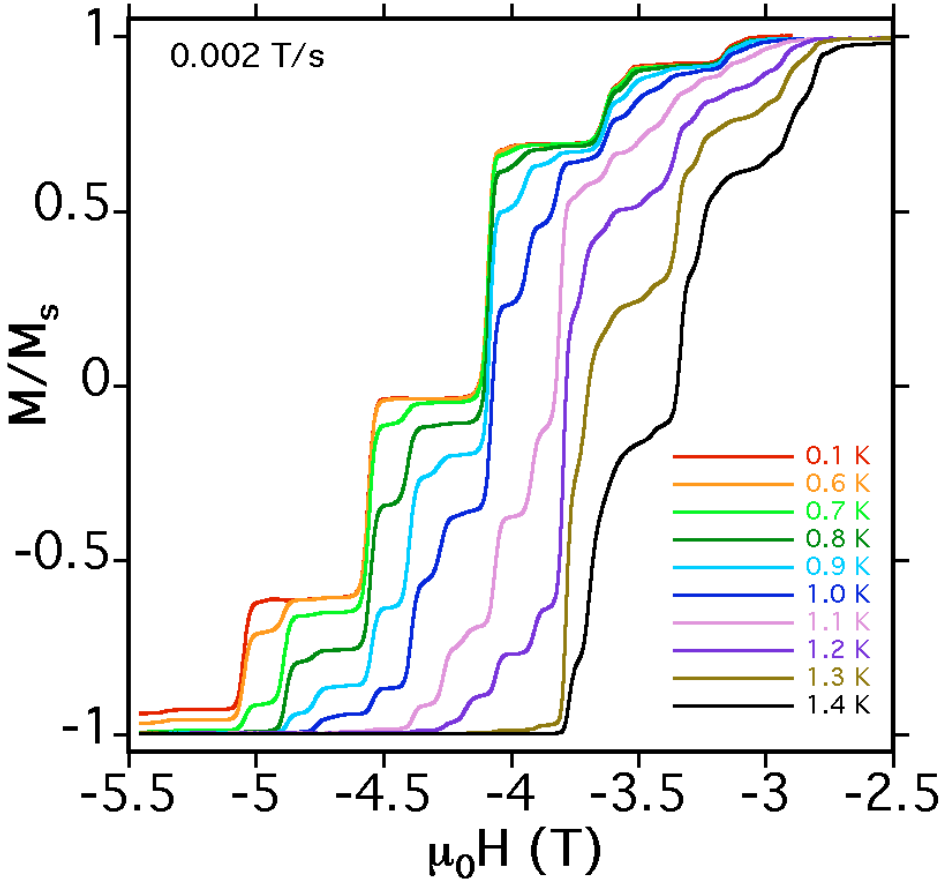
Comparison between

Mn_{12}-Ac



I. Chiorescu, B. Barbara, et al.,
Phys. Rev. Lett. 85, 4807 (2000)

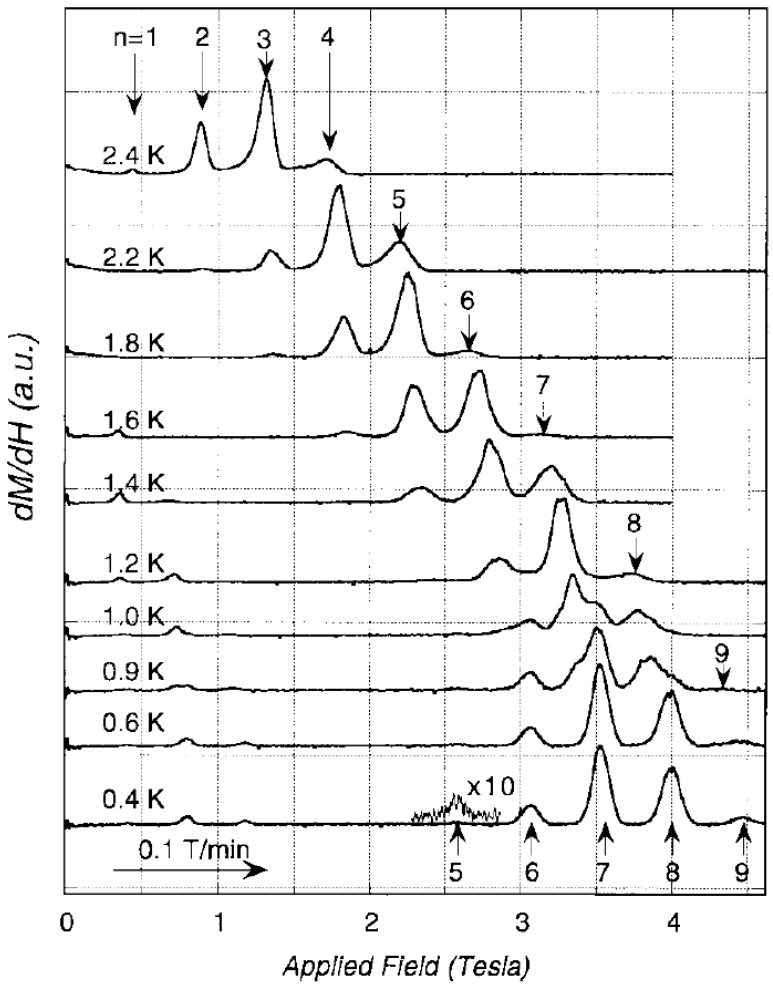
Mn_{12}-*t*BuAc



W. Wernsdorfer, M. Murugesu,
G. Christou, cond-mat/0508437

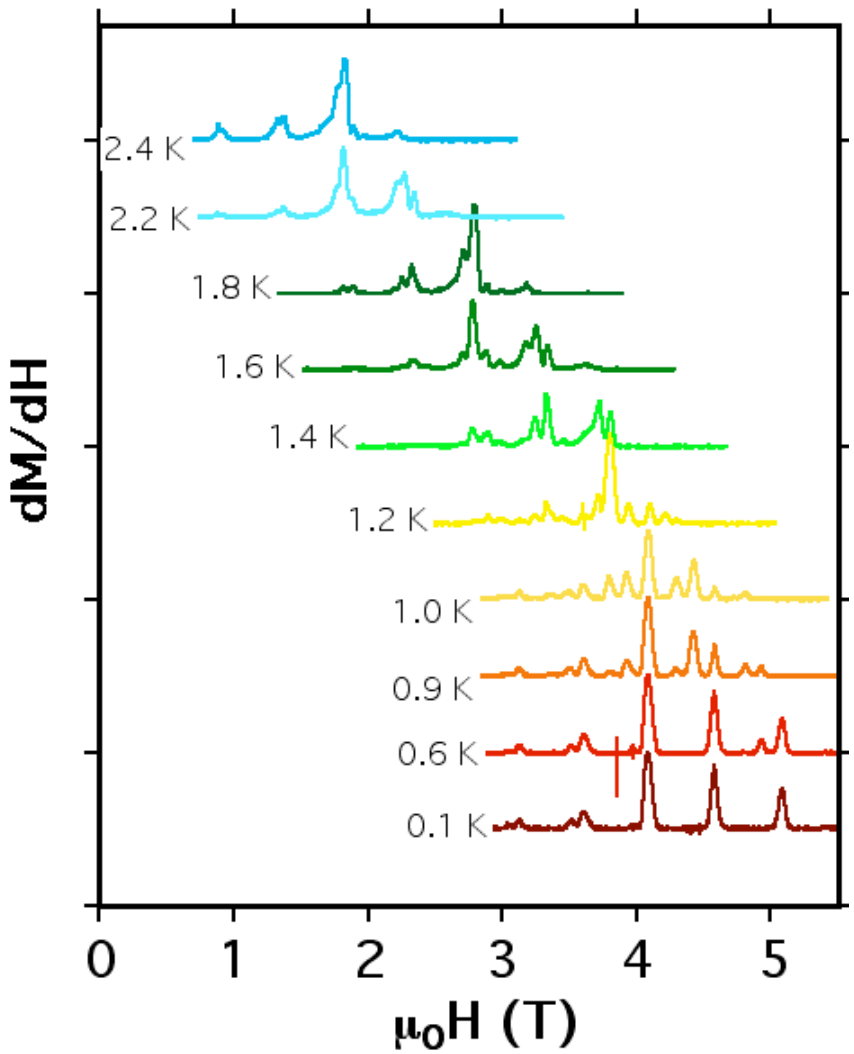
Comparison between

Mn_{12}-Ac



A. D. Kent, et al., EPL 49, 521 (2000) and J. Appl. Phys. 87, 5493 (2000)

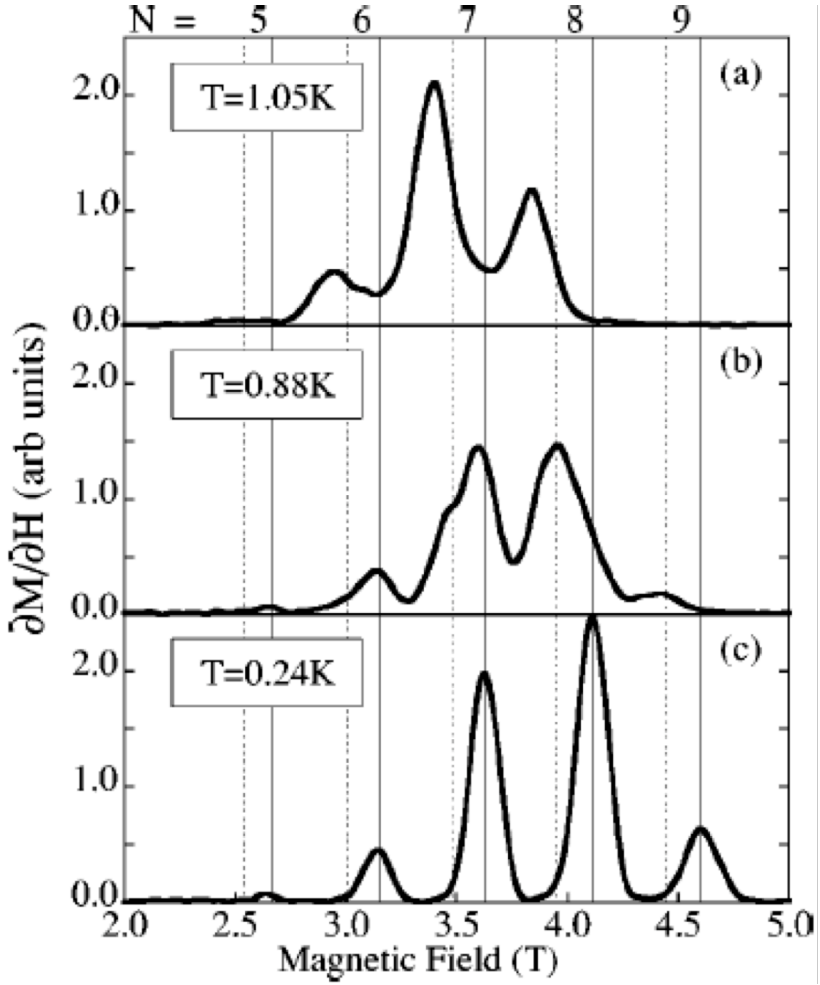
Mn_{12}-*t*BuAc



W. Wernsdorfer, M. Murugesu, G. Christou, cond-mat/0508437

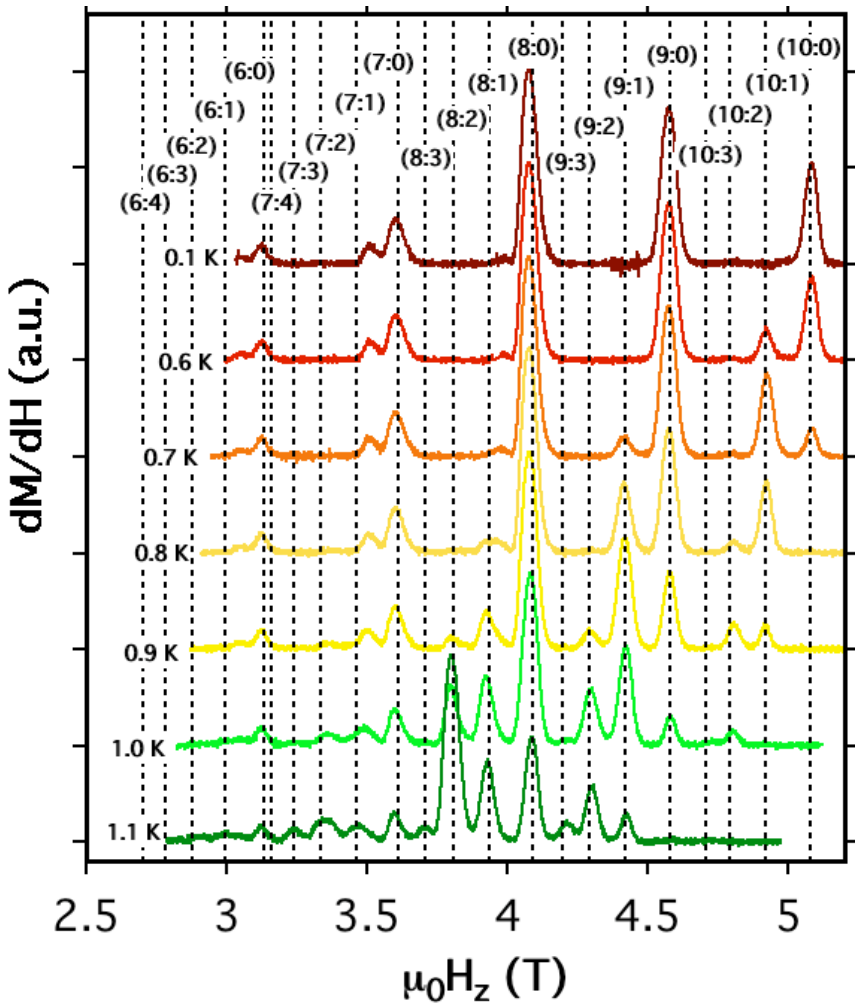
Comparison between

Mn_{12}-Ac



K. M. Mertes, M. P. Sarachik, et al.
Phys. Rev. B 65, 212401 (2002)

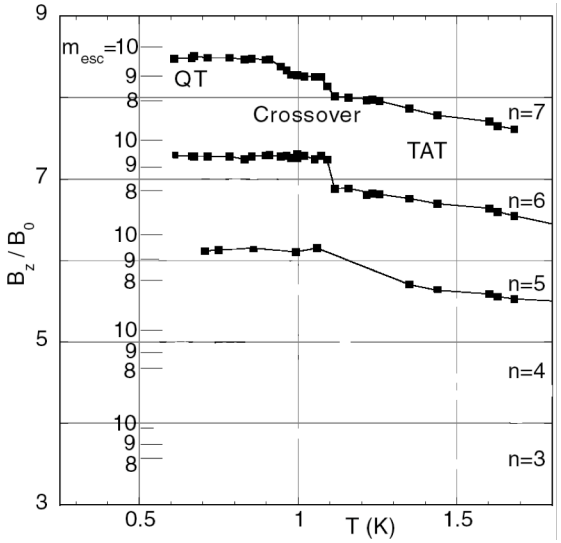
Mn_{12}-*t*BuAc

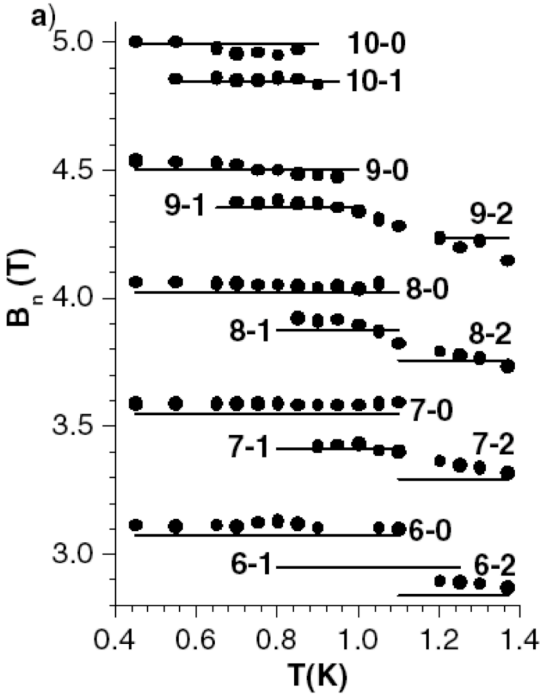


W. Wernsdorfer, M. Murugesu,
G. Christou, cond-mat/0508437

Comparison between

Mn_{12}-Ac





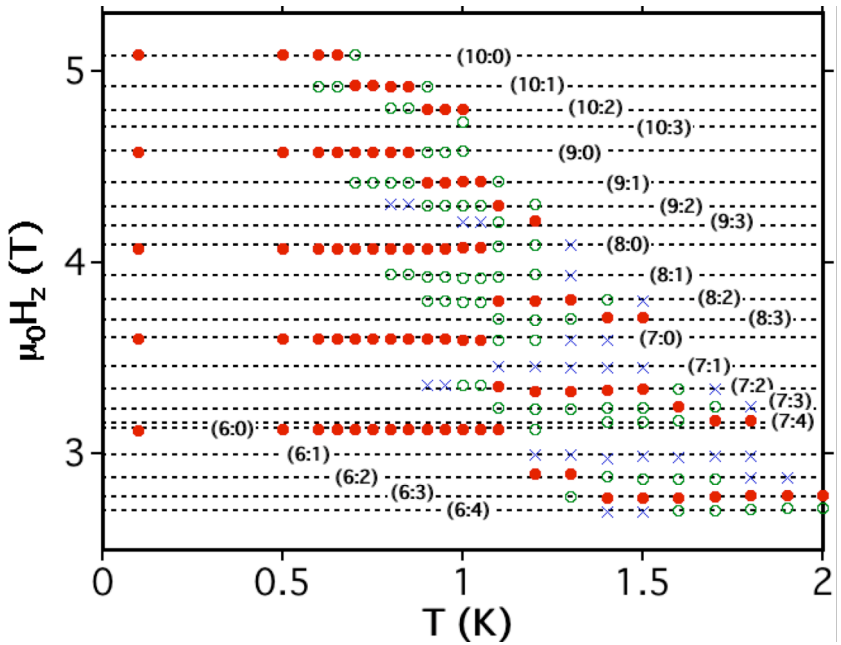
"sharp" crossover

L. Bokacheva,
A. D. Kent, et al.,
PRL 85, 4803 (2000)

"smooth" crossover

I. Chiorescu,
B. Barbara, et al.,
PRL 85, 4807 (2000)

Mn_{12}-*t*BuAc



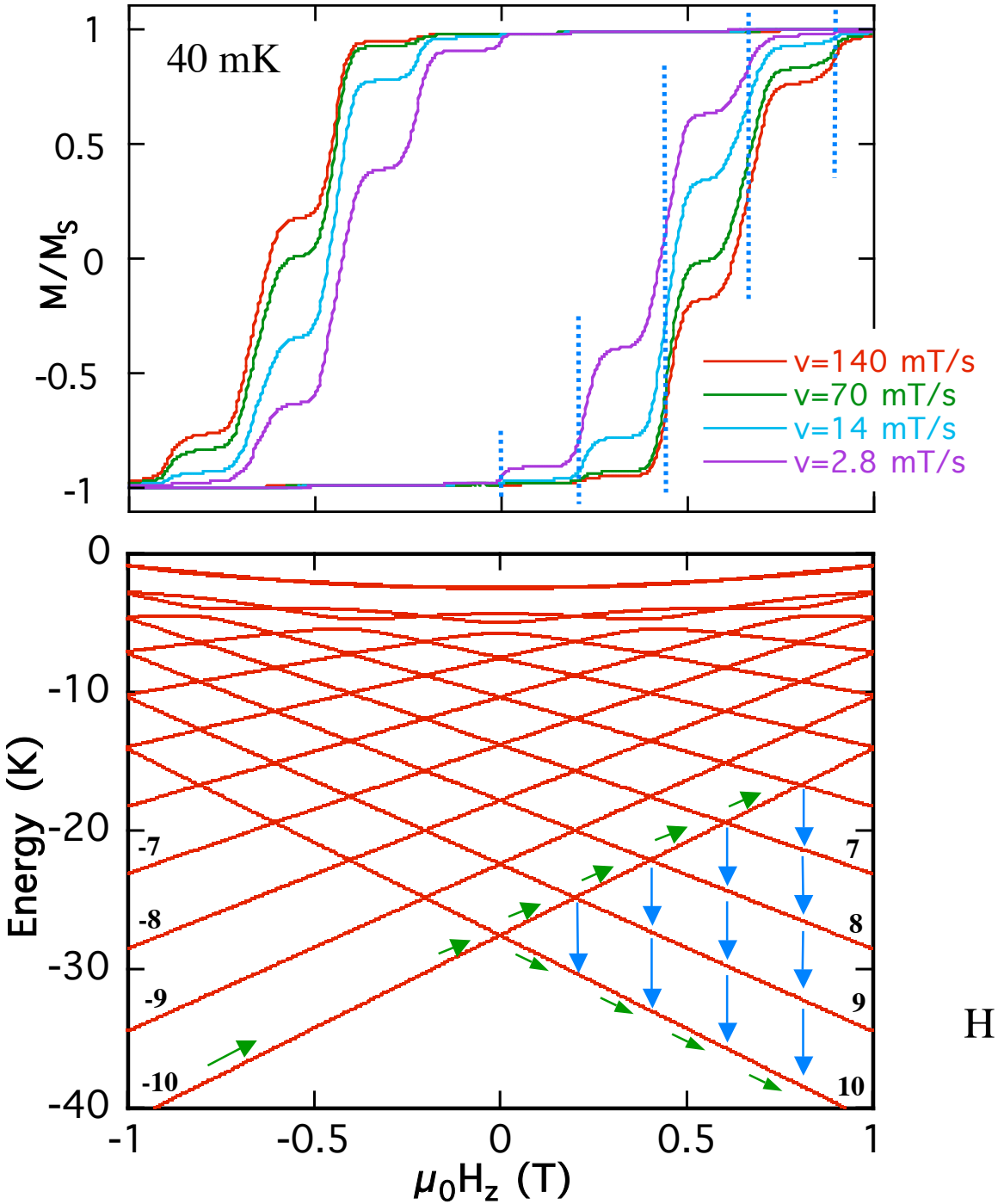
W. Wernsdorfer, M. Murugesu,
G. Christou, cond-mat/0508437

"sharp" crossover

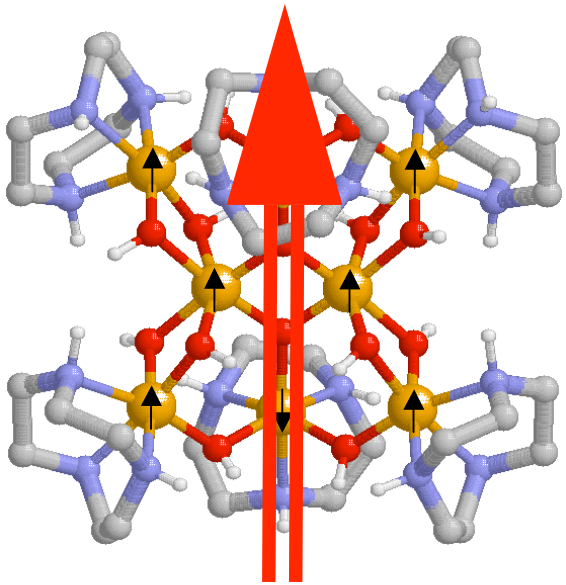
in agreement with theory

E. M. Chudnovsky and D. A. Garanin,
Phys. Rev. Lett. 79, 004469 (1997)

Application of Landau-Zener tunneling



Fe_8 S = 10



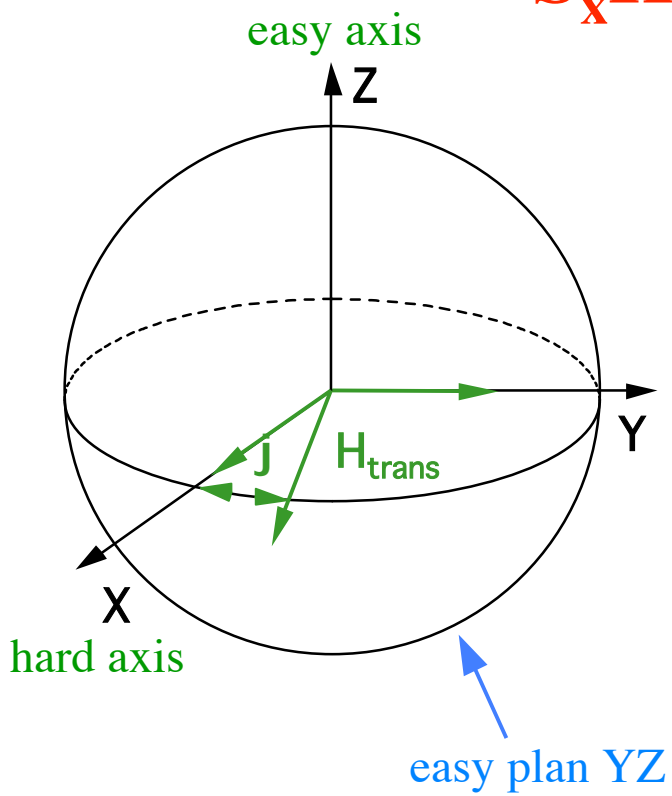
$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B\,\vec{S}\,\vec{H}$$

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

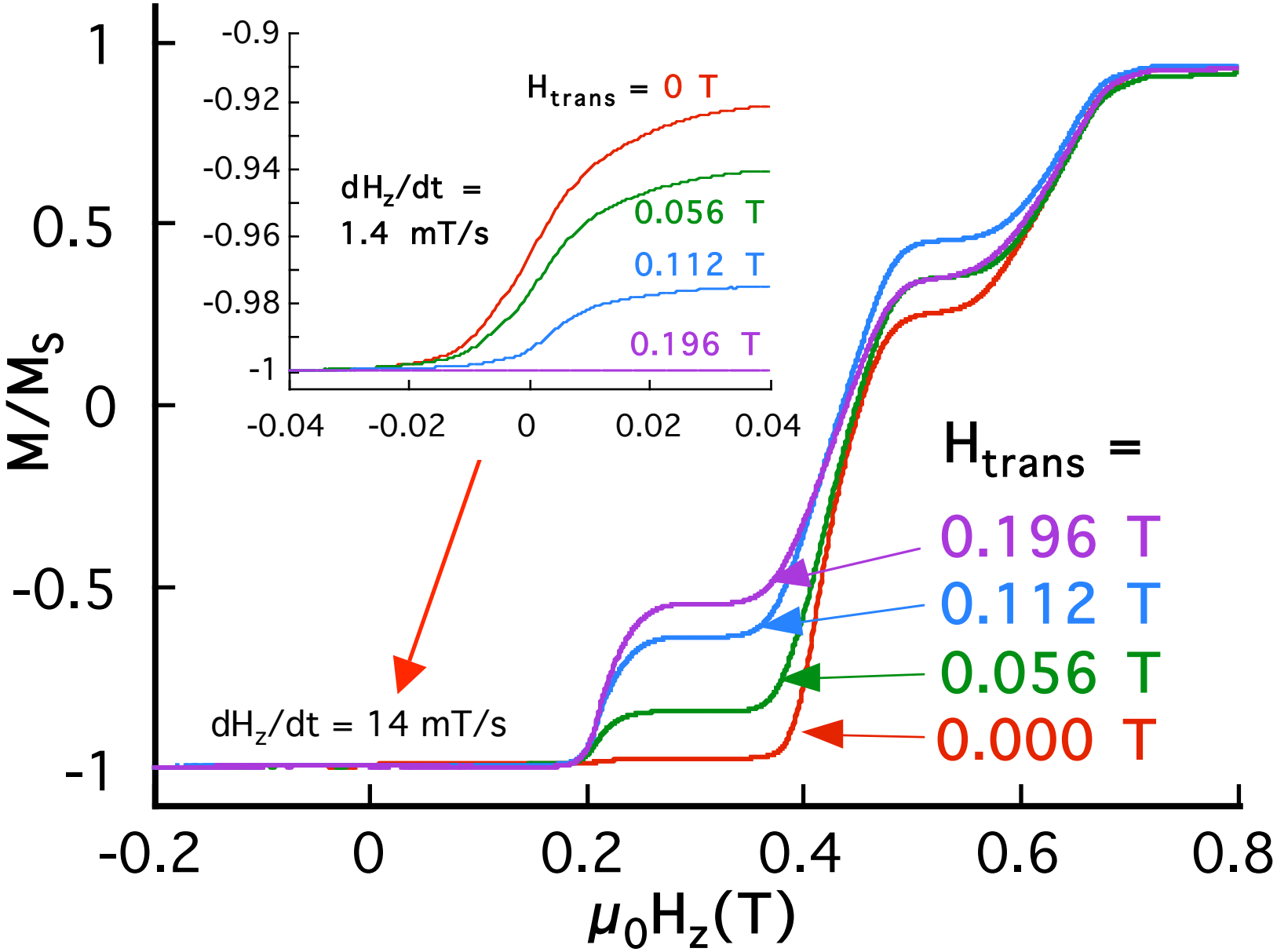
A.-L. Barra et al. EPL (1996)

Giant spin Hamiltonian of Fe_8

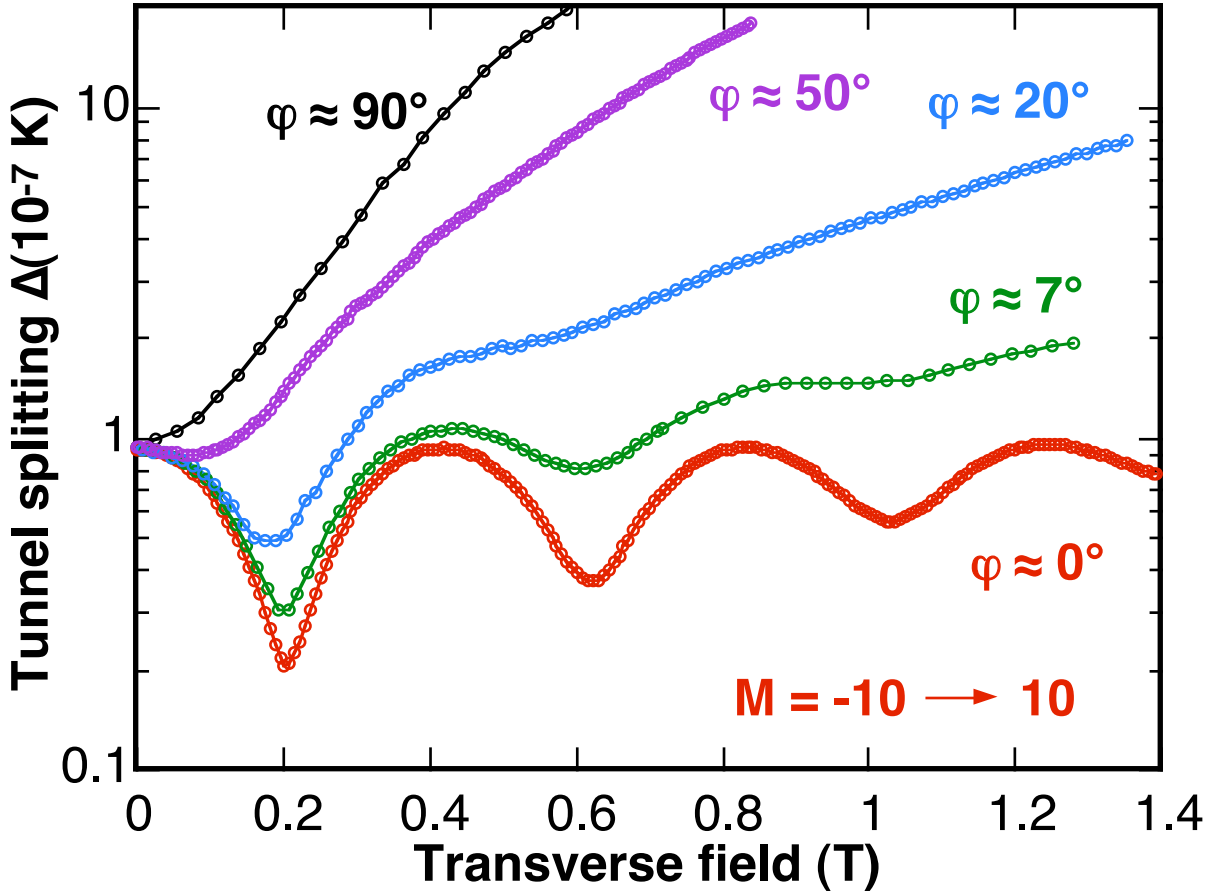
$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B \underbrace{\vec{S}\,\vec{H}}_{S_xH_x + S_yH_y + S_zH_z}$$

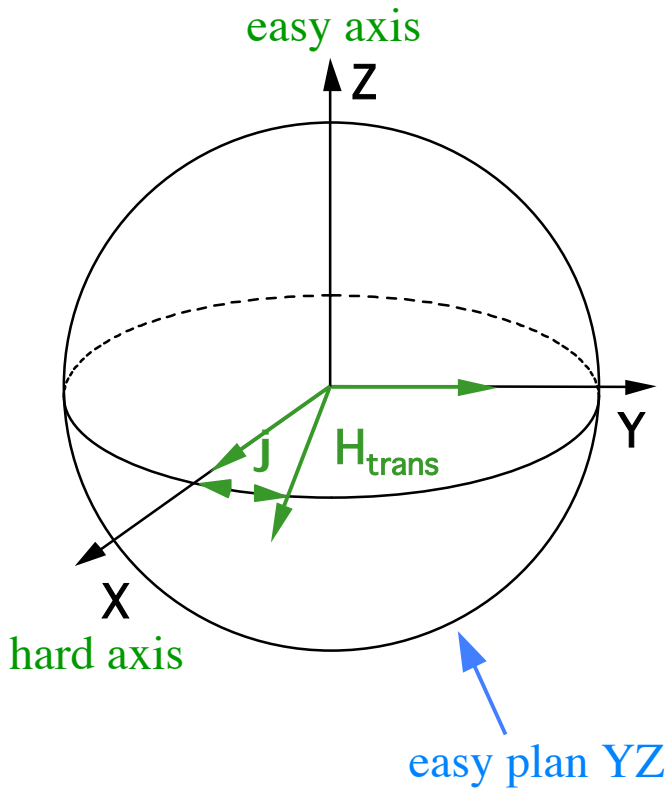


Hysteresis loops at different transverse fields



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

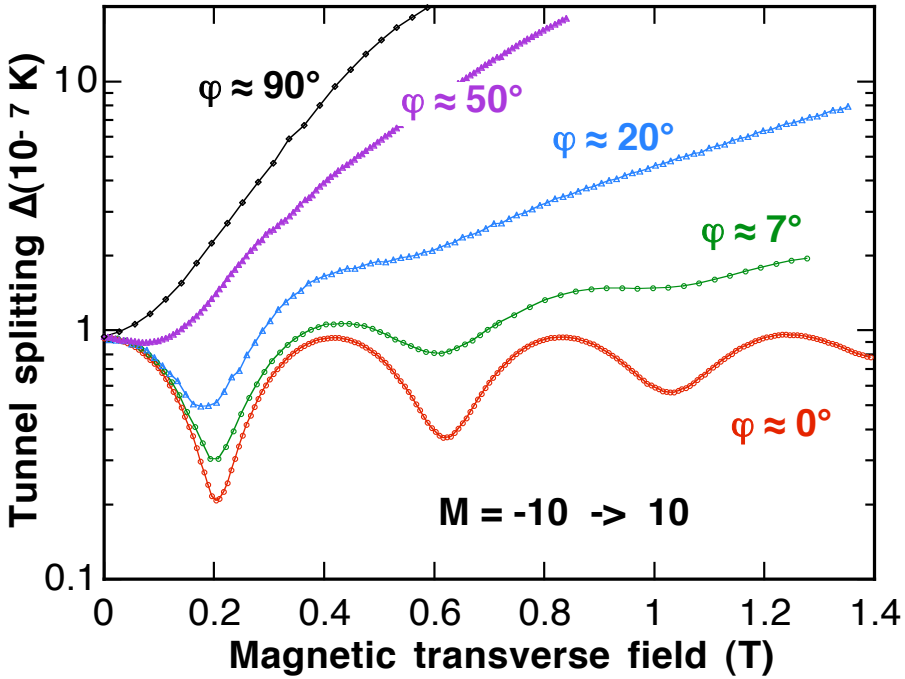


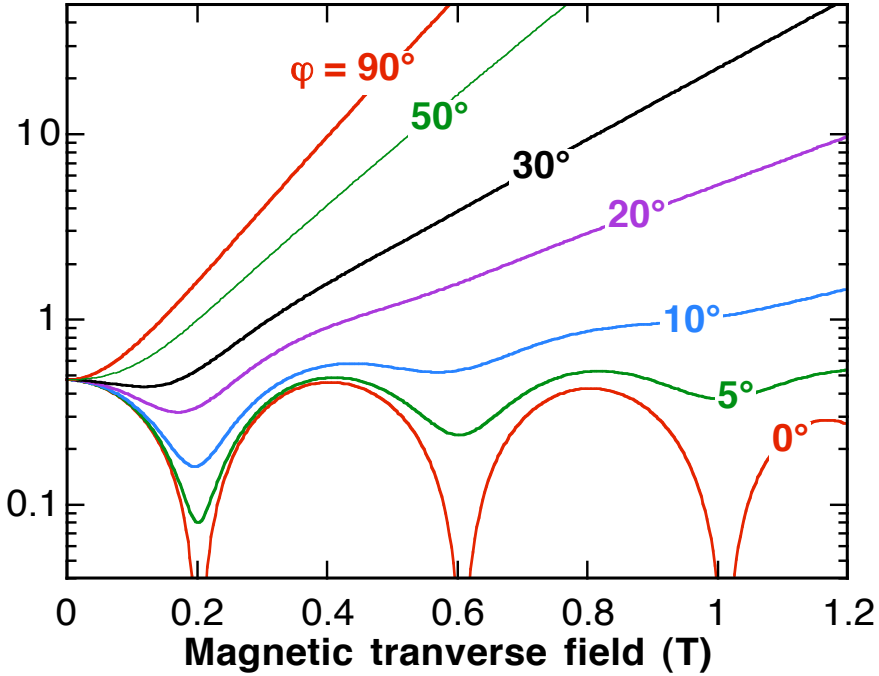


W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

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)

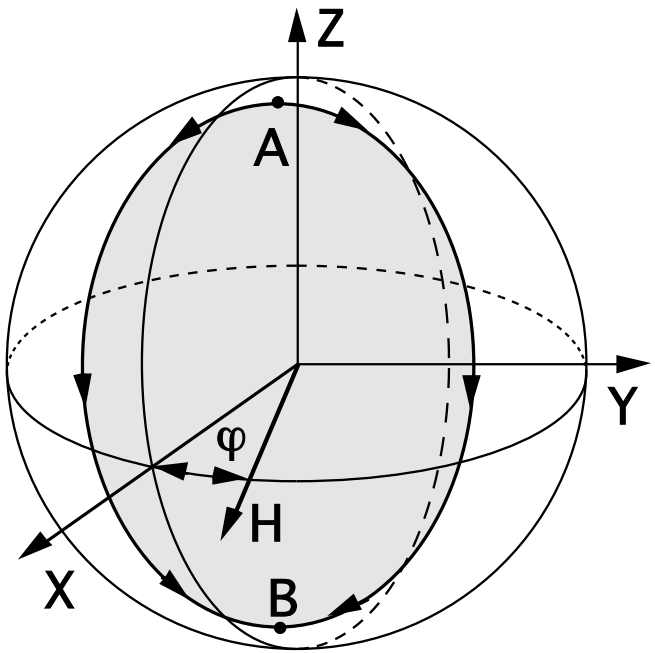
Path-integral partition function:

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

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

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

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

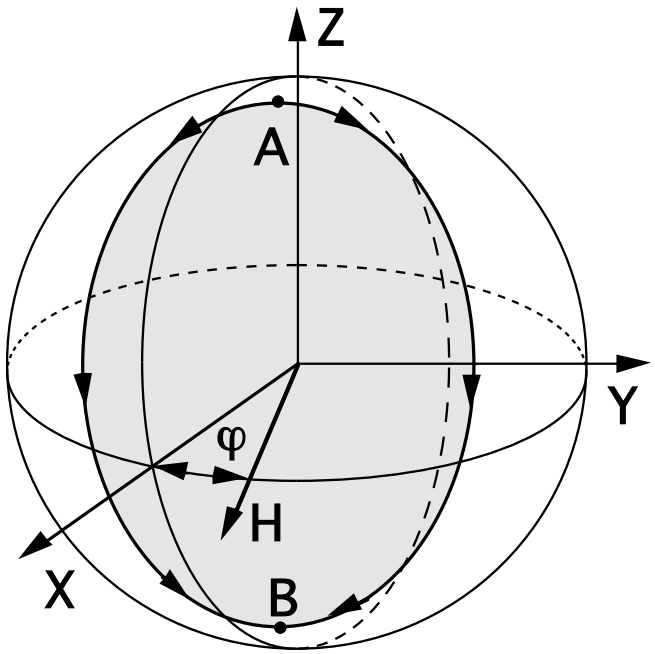


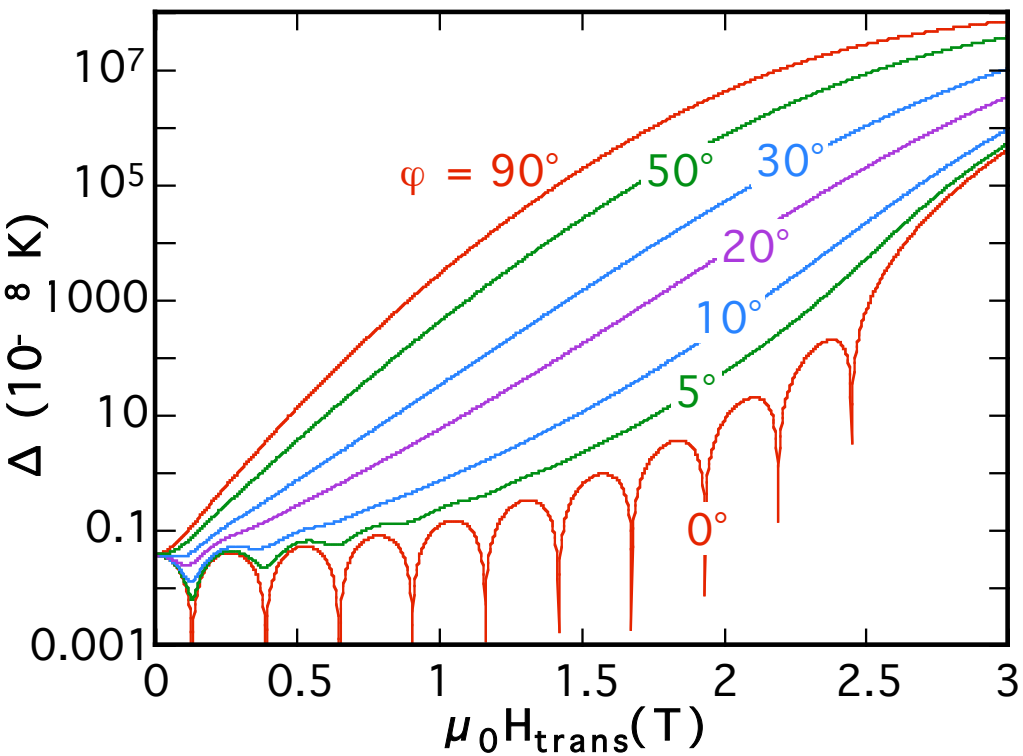
destructive interference occures whenever the shaded area is kp/S, for odd k.

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

Transverse field dependence of tunnel splitting

(path integrals formalism)



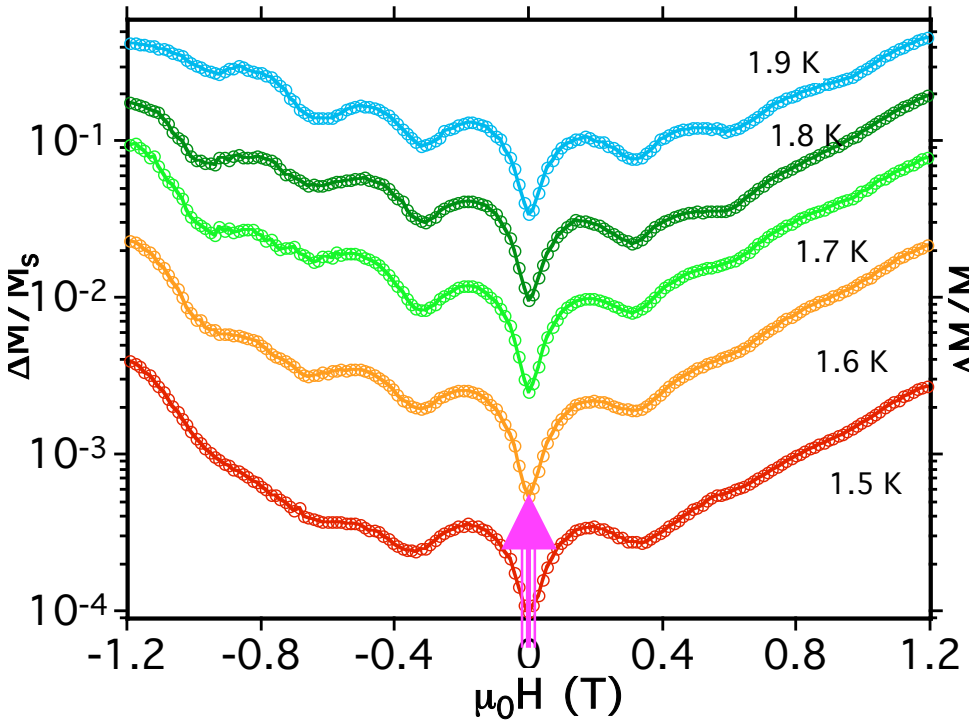


$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B\,\vec{S}\,\vec{H}$$

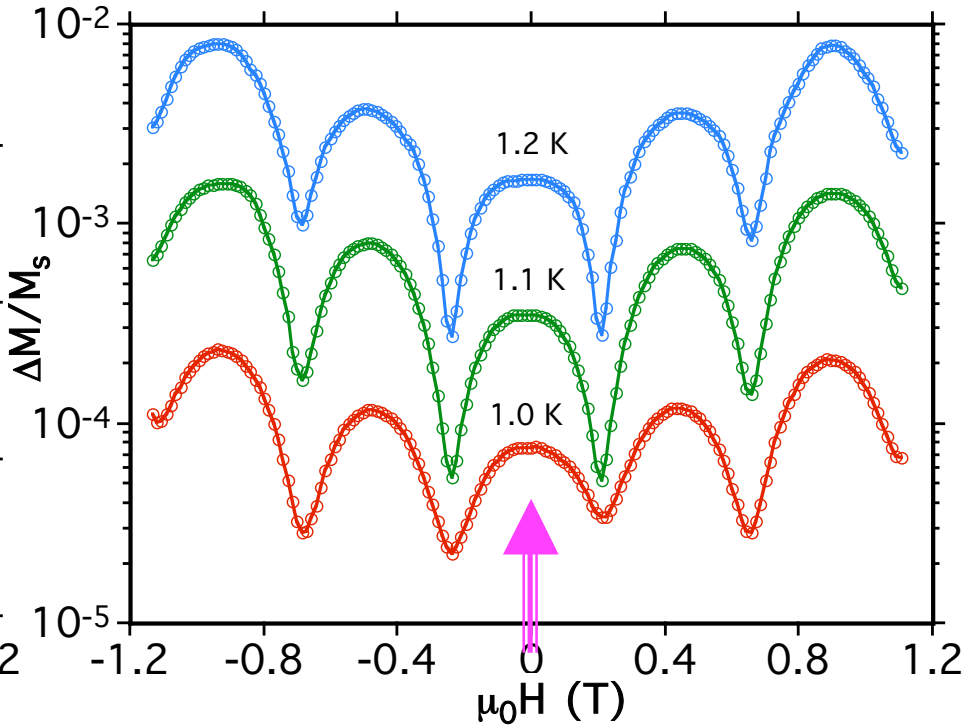
A. Garg, Europhys. Lett. **22**, 205 (1993)

Quantum phase interference and spin parity in Mn_{12}

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



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



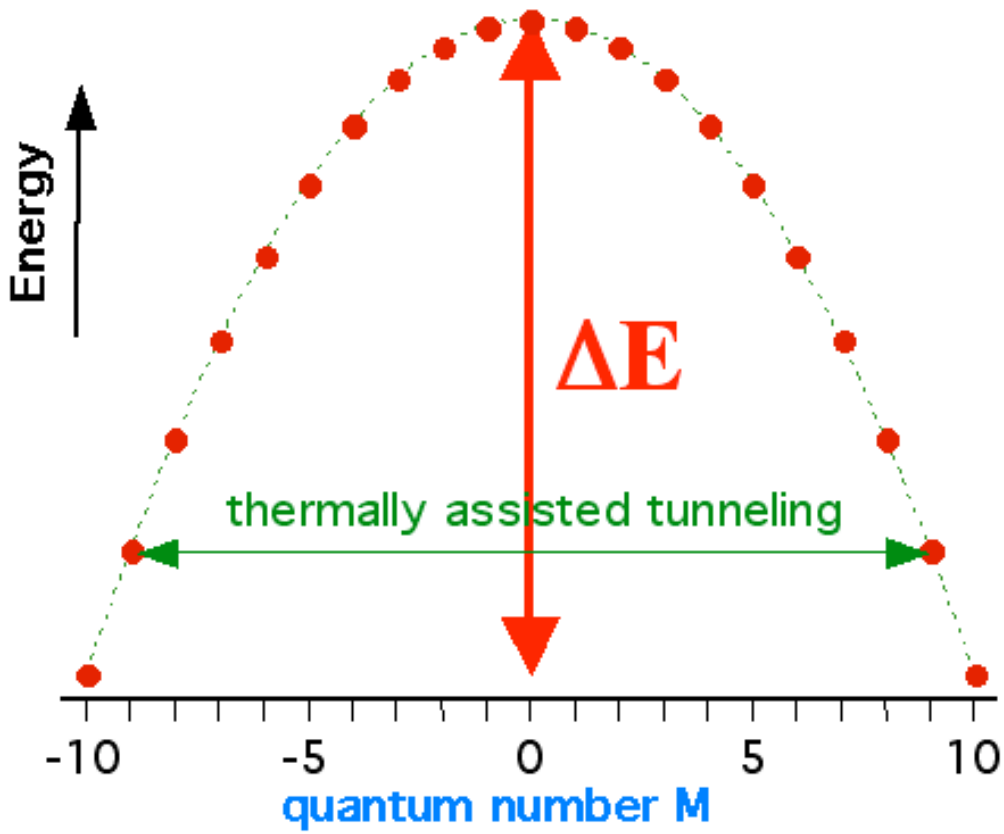
W. Wernsdorfer, N. E. Chakov, G. Christou,
PRL 95, 037203 (2005)

Giant spin model & temperature

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

Spin-phonon coupling : $\Delta M = \pm 1, \pm 2$



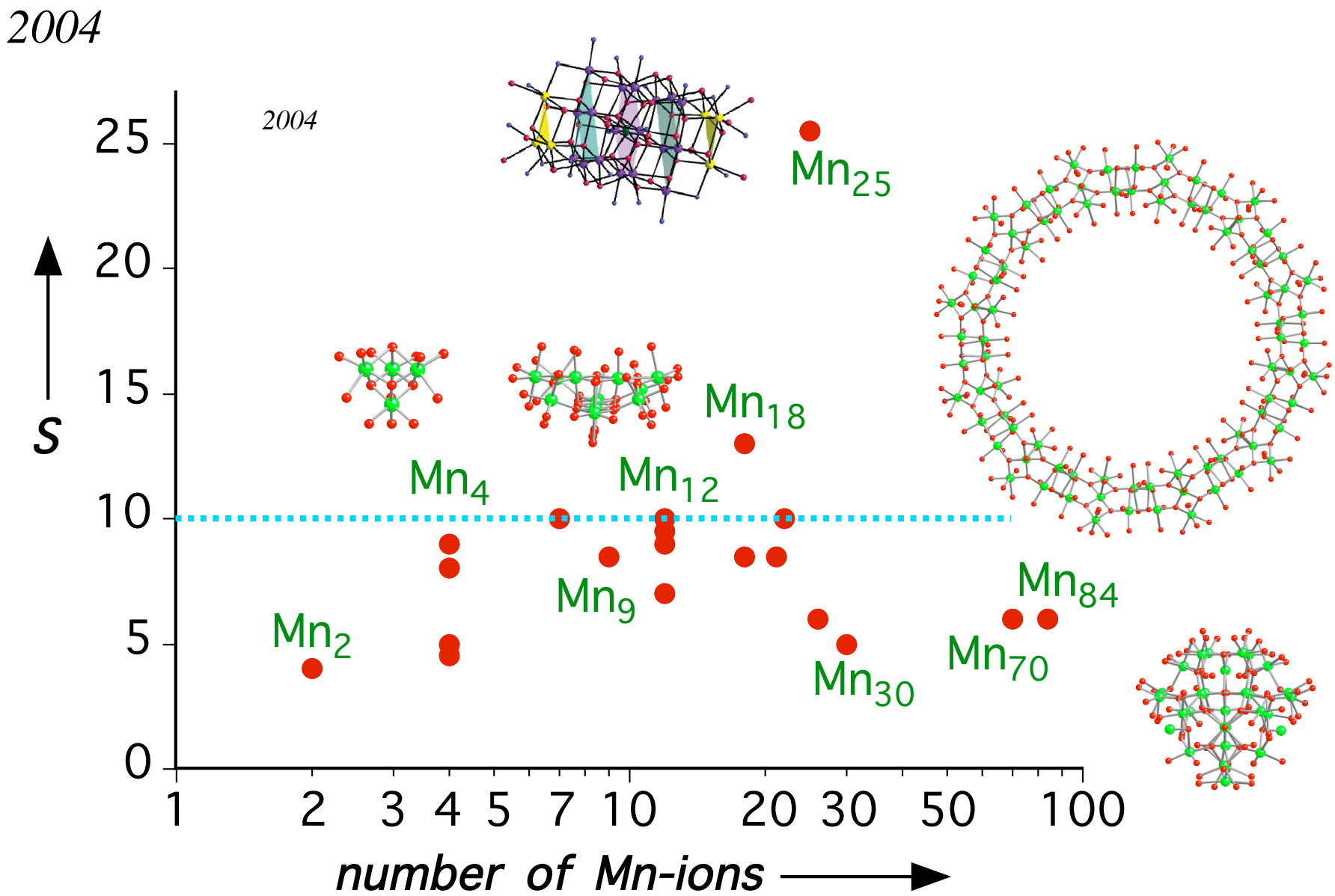
Anisotropy barrier

$$\Delta E \approx D\,S^2$$

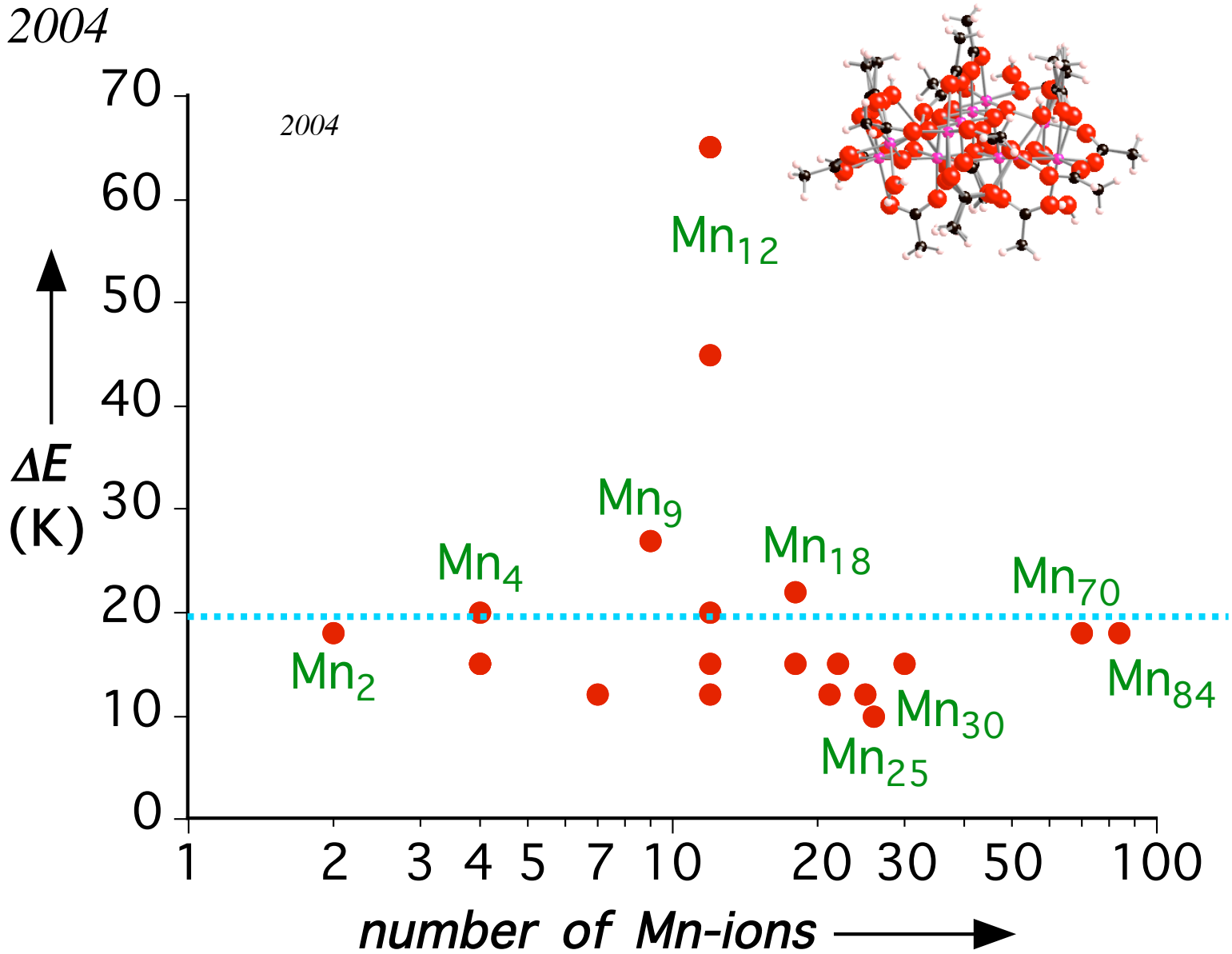
Anisotropy constant

Spin

Spin ground states of Mn based SMMs



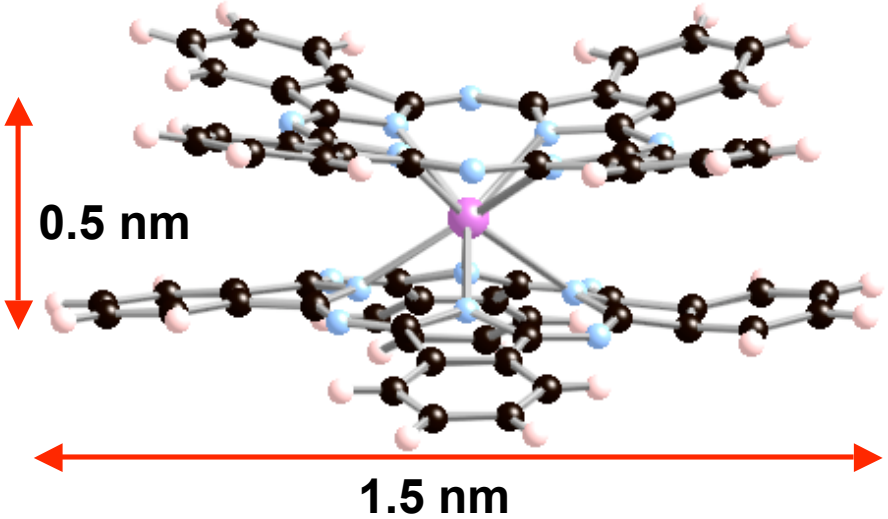
Anisotropy barriers of Mn based SMMs

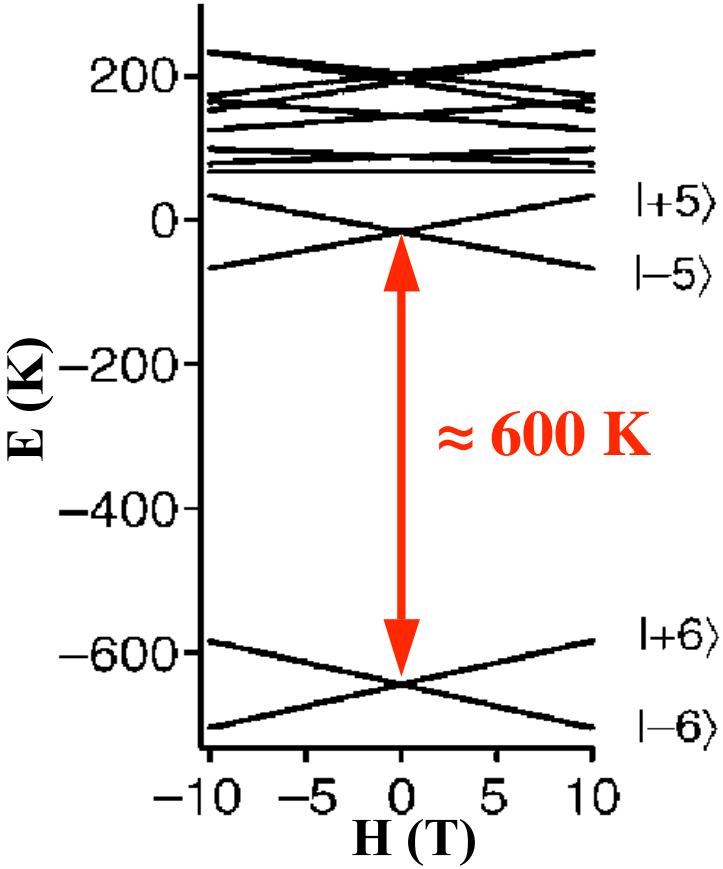


Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets

Bis(phthalocyaninato)terbium

Naoto Ishikawa, Department of Applied Chemistry, Chuo University, Tokyo



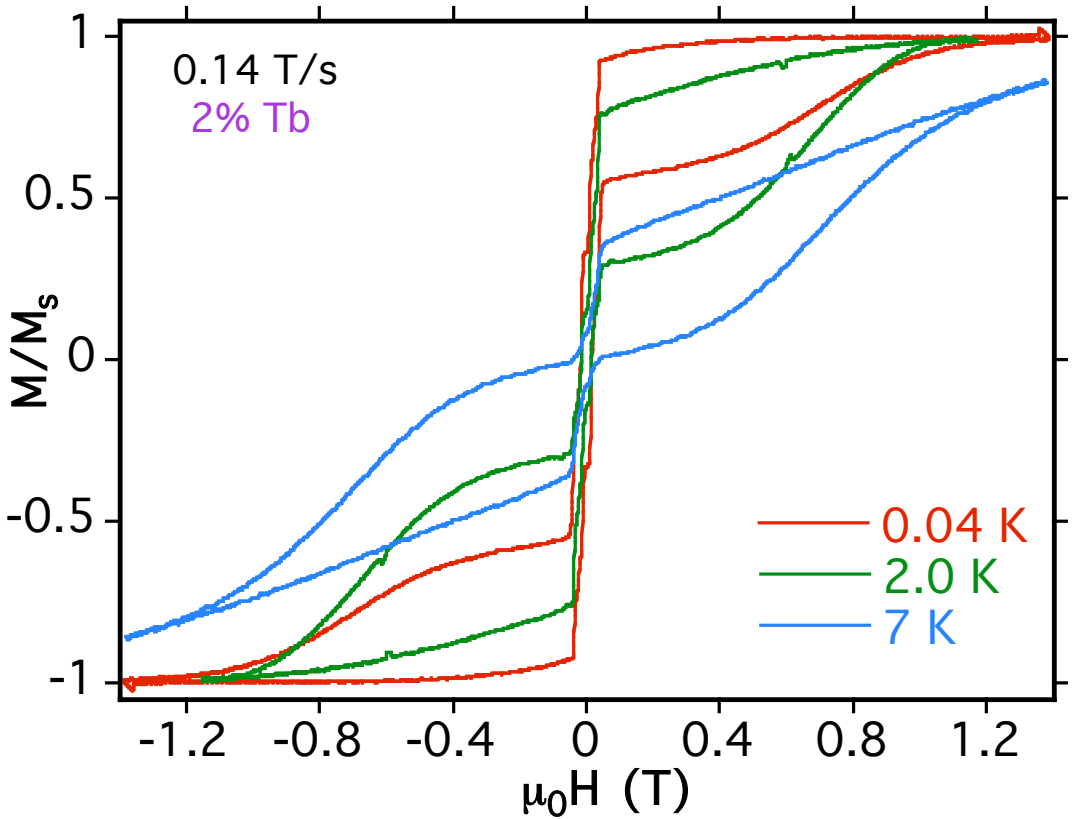


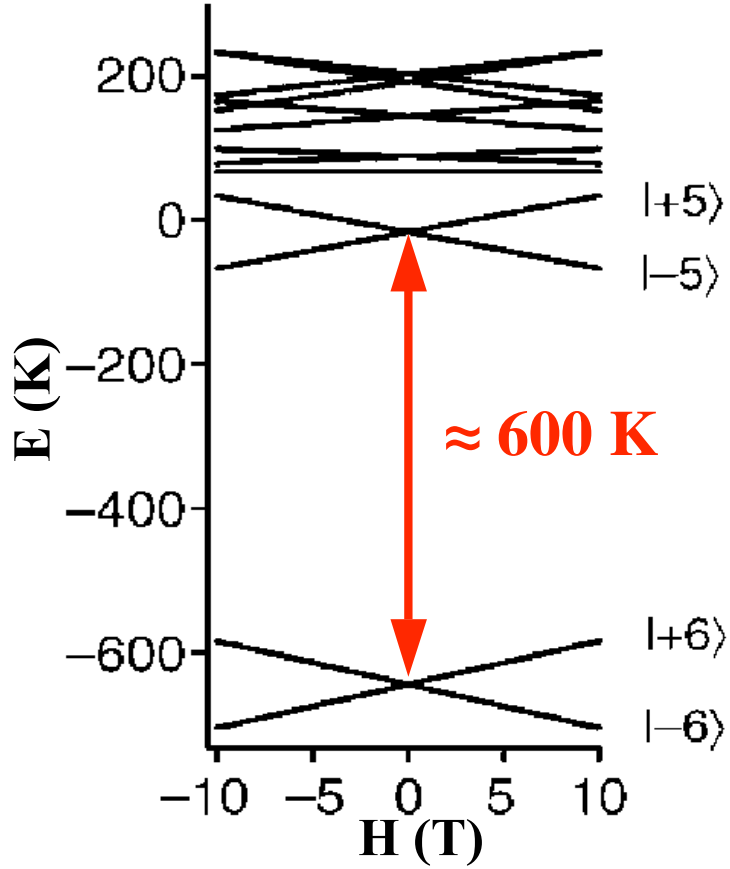
N.Ishikawa, et al.,
J.Phys.Chem. A 106, 9543 (2002)
J. Am.Chem.Soc. 125, 8694 (2003)
Inorg.Chem. 42, 2440 (2003)
J.Phys.Chem. A 107, 9543 (2003)
J. Phys.Chem.B 108, 11265 (2004)

Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets

Bis(phthalocyaninato)terbium

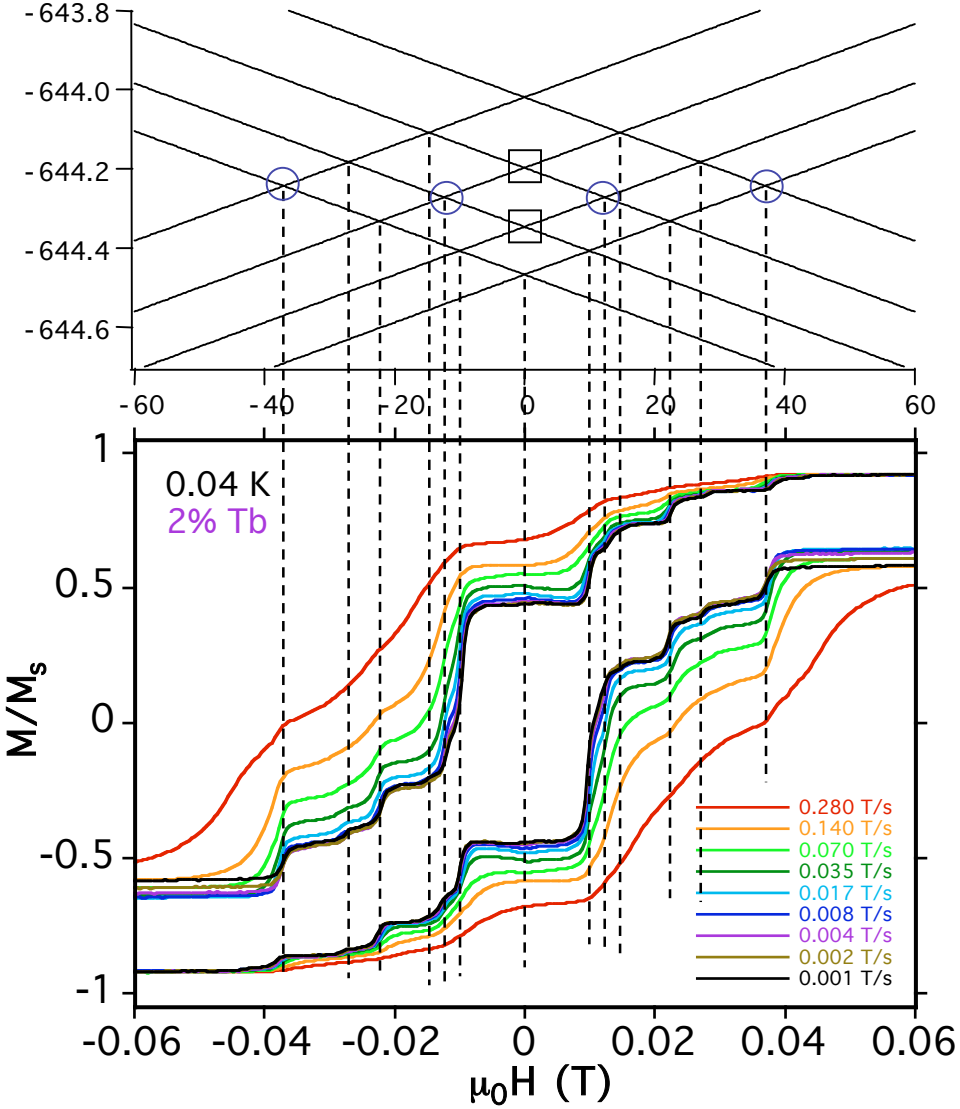
Naoto Ishikawa, Department of Applied Chemistry, Chuo University, Tokyo





N. Ishikawa, M. Sugita, W. Wernsdorfer, Angew. Chem. Int. Ed. 44 ,2 (2005)
N. Ishikawa, M. Sugita, W. Wernsdorfer, J. Am. Chem. Soc. 127, 3650 (2005)

$$H = \text{Zeeman} + \text{LF term} + A_{hf} J \cdot I + P_{quad}\{I_z^2 + (1/3)I(I+1)\}$$



A_{hf}=0.0173cm^{-1}

P_{quad}=0.010cm^{-1}

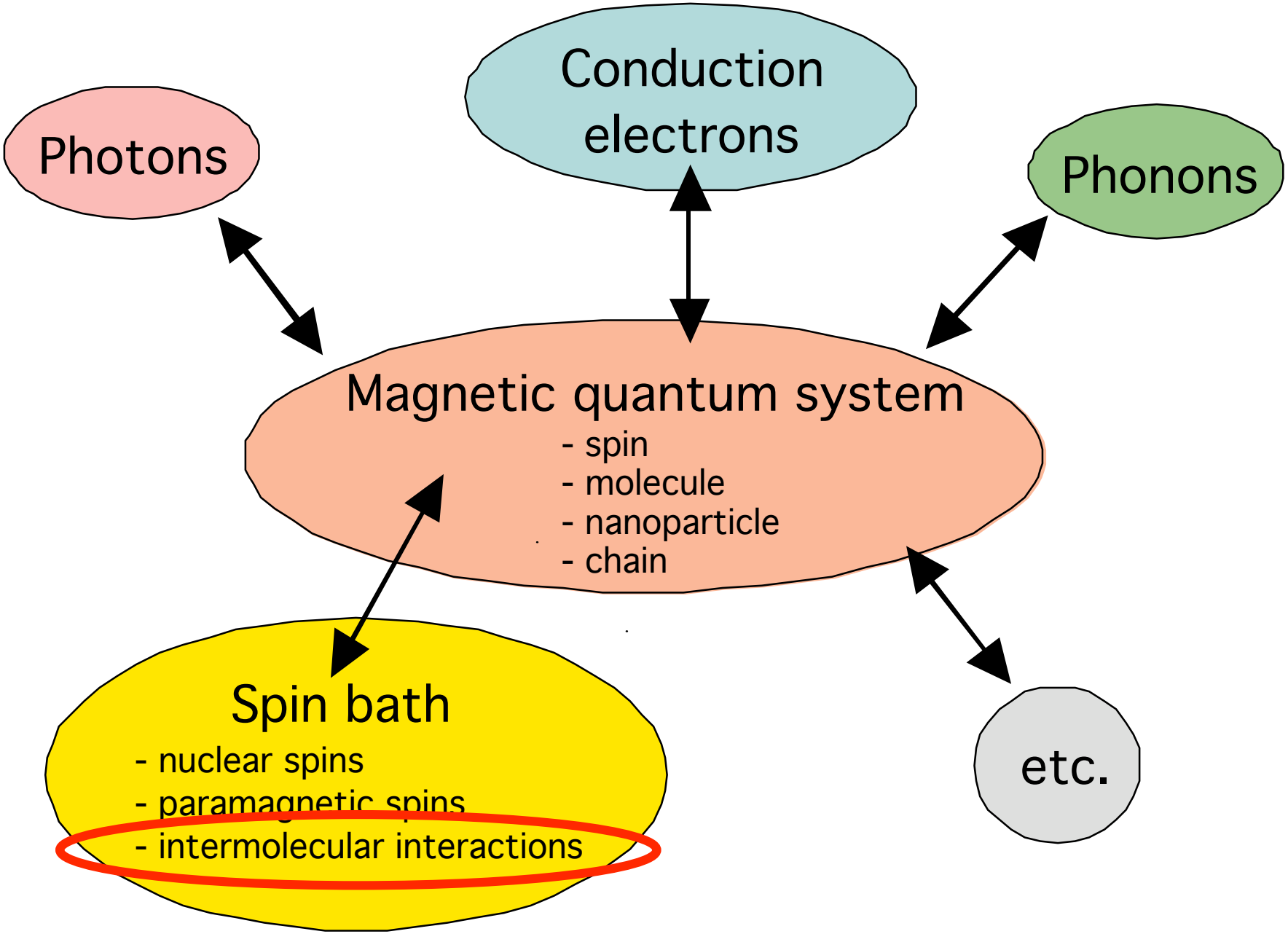
○ :avoided crossing occurs by off-diagonal LF term

□ :avoided crossing occurs by transverse field

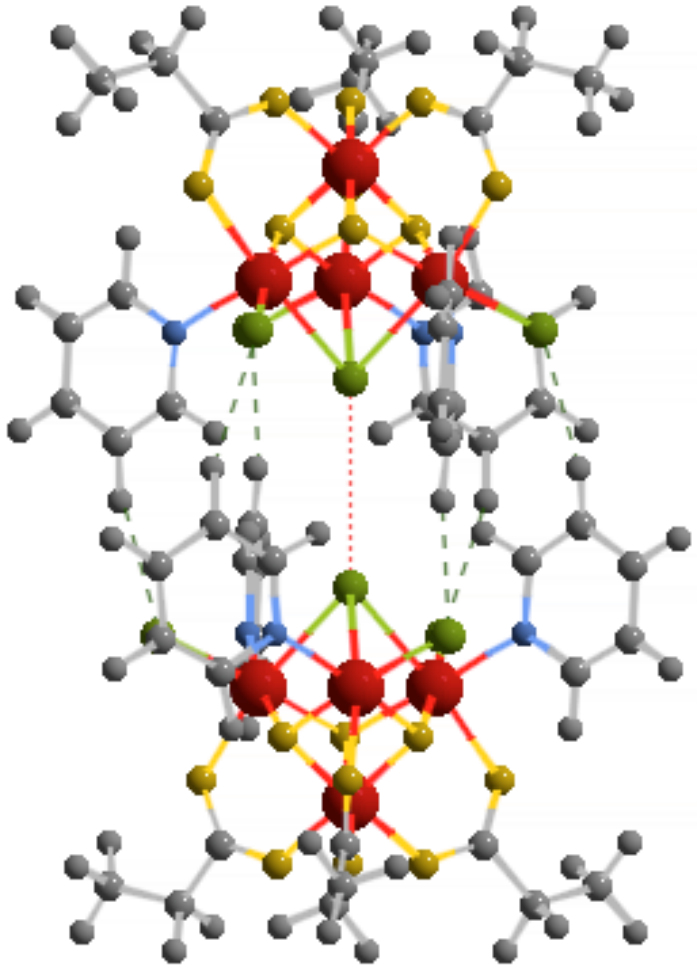
Others :avoided crossing does not occur by either LF term nor transverse field

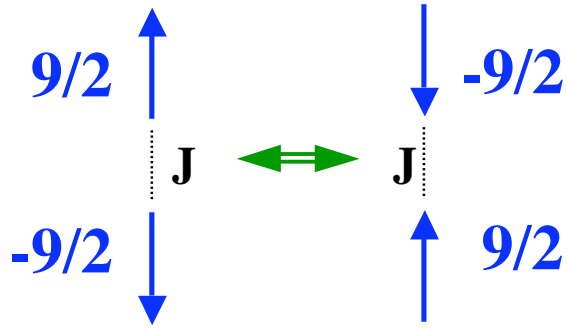
N. Ishikawa, M. Sugita, W. Wernsdorfer, Angew. Chem. Int. Ed. 44 ,2 (2005)
N. Ishikawa, M. Sugita, W. Wernsdorfer, J. Am. Chem. Soc. 127, 3650 (2005)

Interactions in magnetic quantum systems (decoherence)



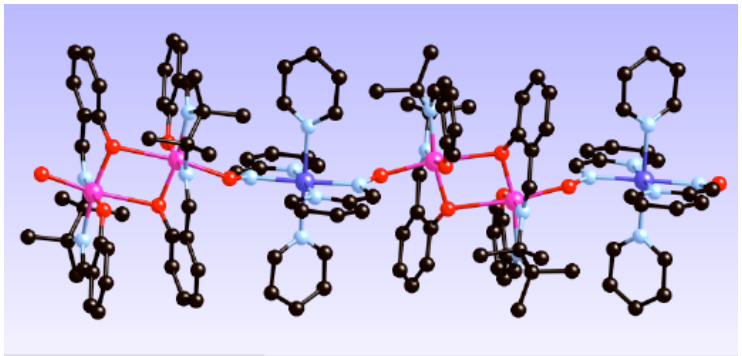
Exchange-biased quantum tunnelling in a supramolecular dimer of single-molecule magnets





W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson & G. Christou
Nature **416**, 406 (28 March 2002)

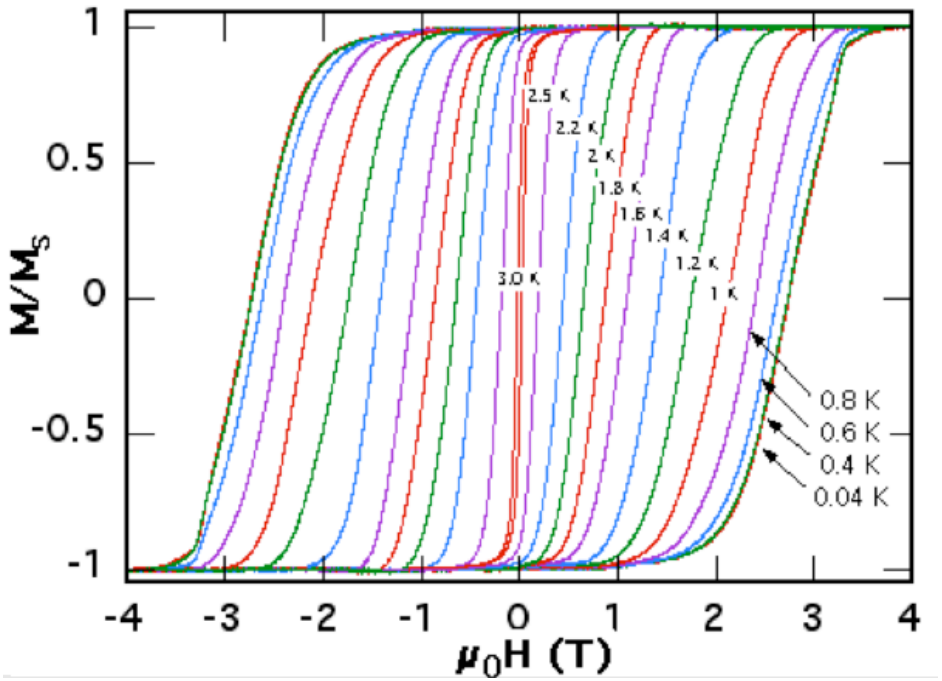
Single-chain magnets (SCM)



Mn_2Ni - chain of S = 3 units

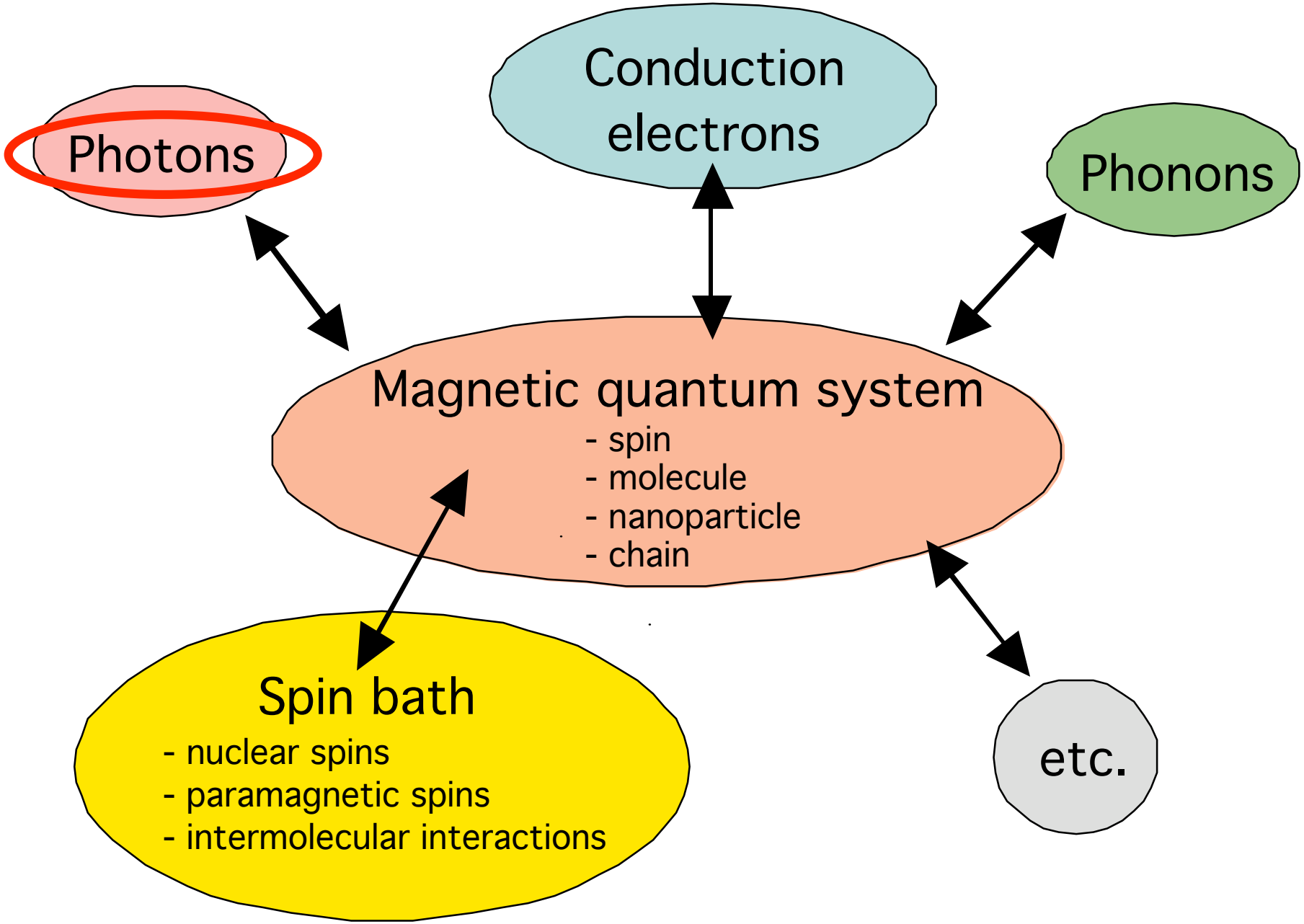
R. Clérac, H. Miyasaka, M. Yamashita, and C. Coulon,
J. Am. Chem. Soc.124, 12837 (2002).

See talk of L. Bogani Monday, 16:15



Quantum nucleation in a single-chain magnet
WW et al.
cond-mat/0509309

Interactions in magnetic quantum systems (decoherence)

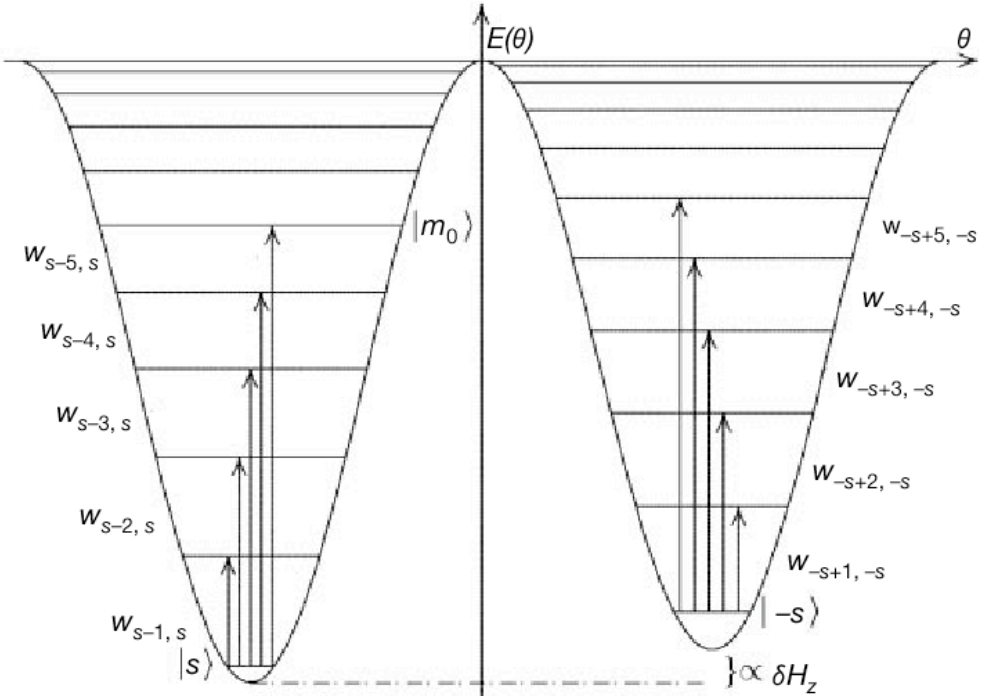


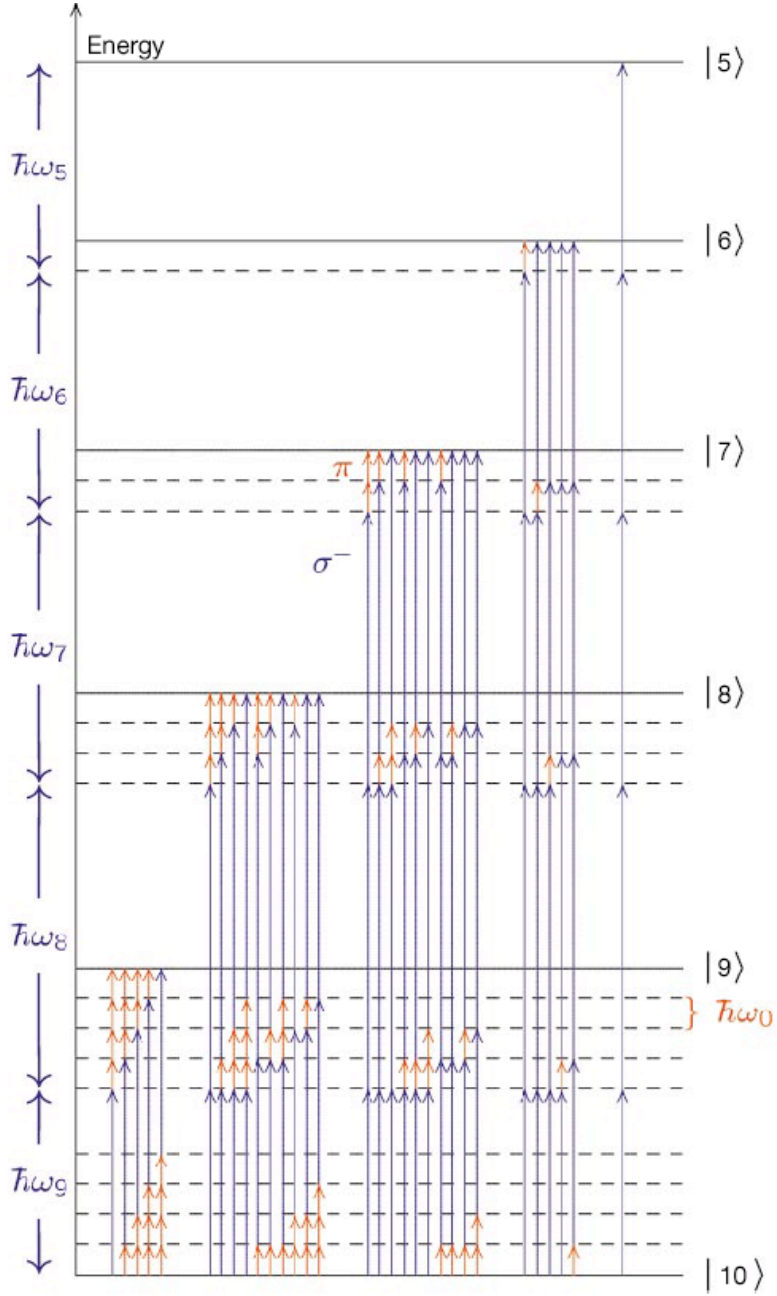
Quantum computing in molecular magnets

Michael N. Leuenberger & Daniel Loss

NATURE, 410, 791 (2001)

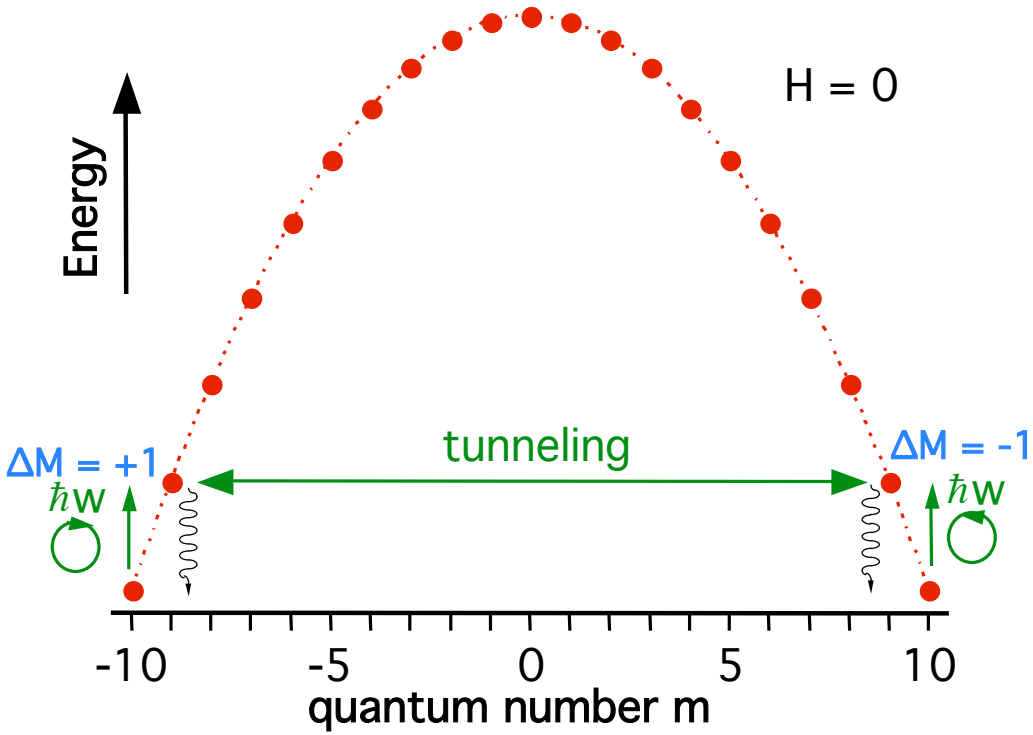
- implementation of Grover's algorithm
- storage unit of a dynamic random access memory device.
- fast electron spin resonance pulses can be used to decode and read out stored numbers of up to 10^5 with access times as short as 0.1 nanoseconds.

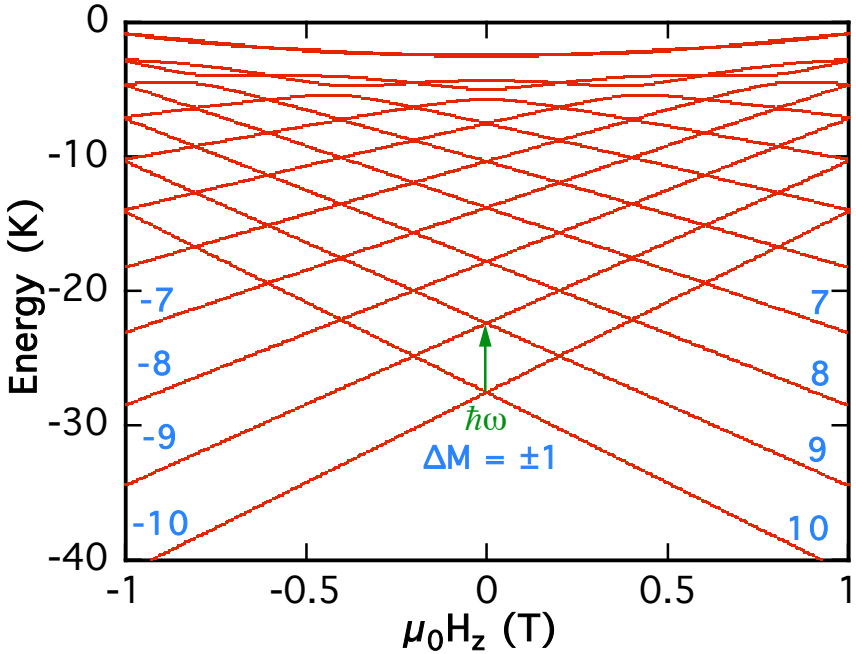




Photon assisted tunneling

Absorption of circular polarized microwaves

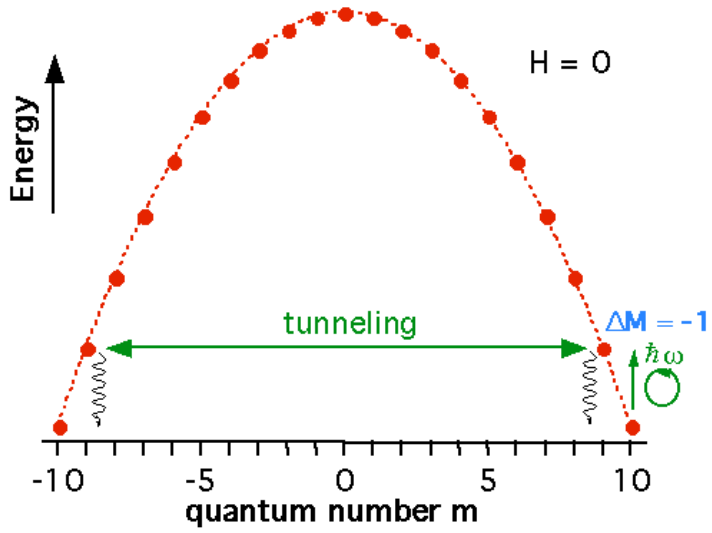


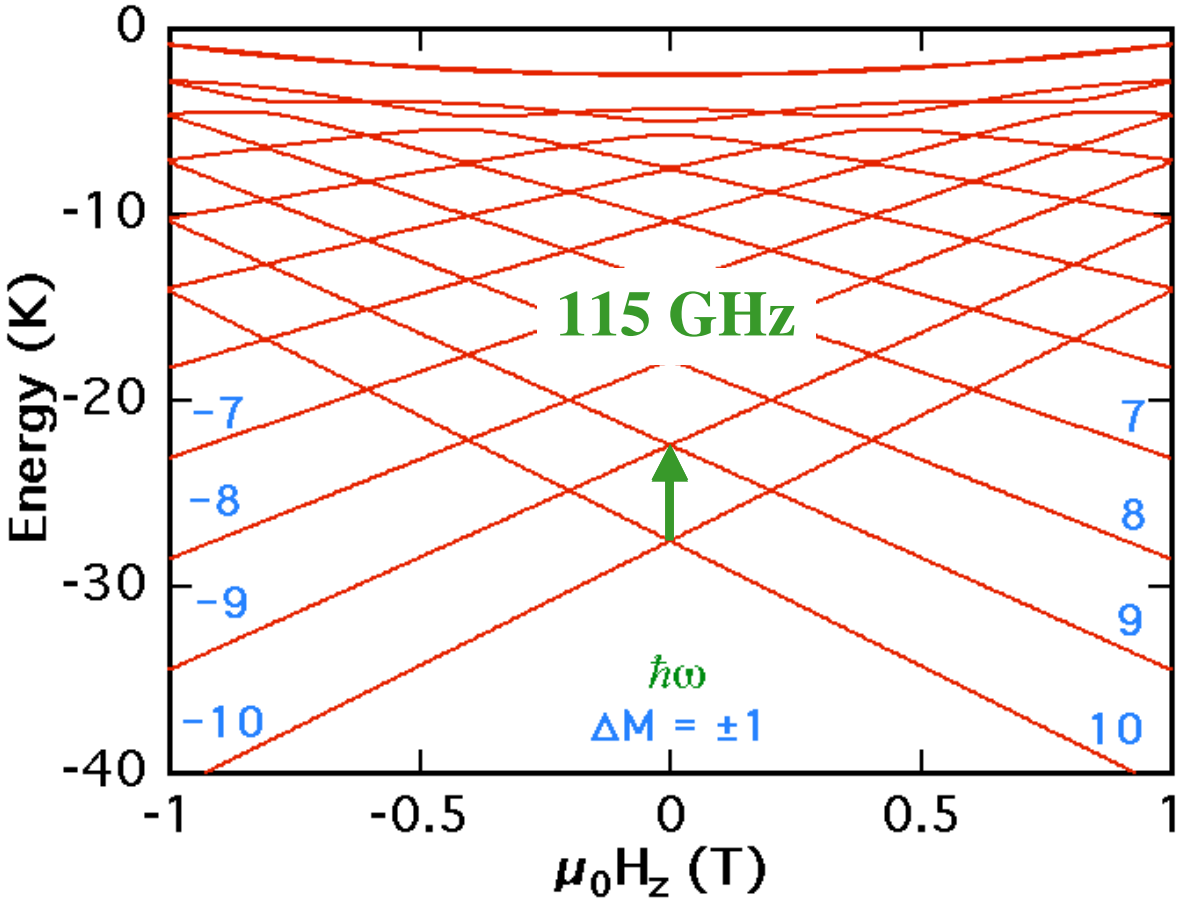


PRB 68, 220407(R) (2003)

Photon assisted tunneling

Absorption of circular polarized microwaves

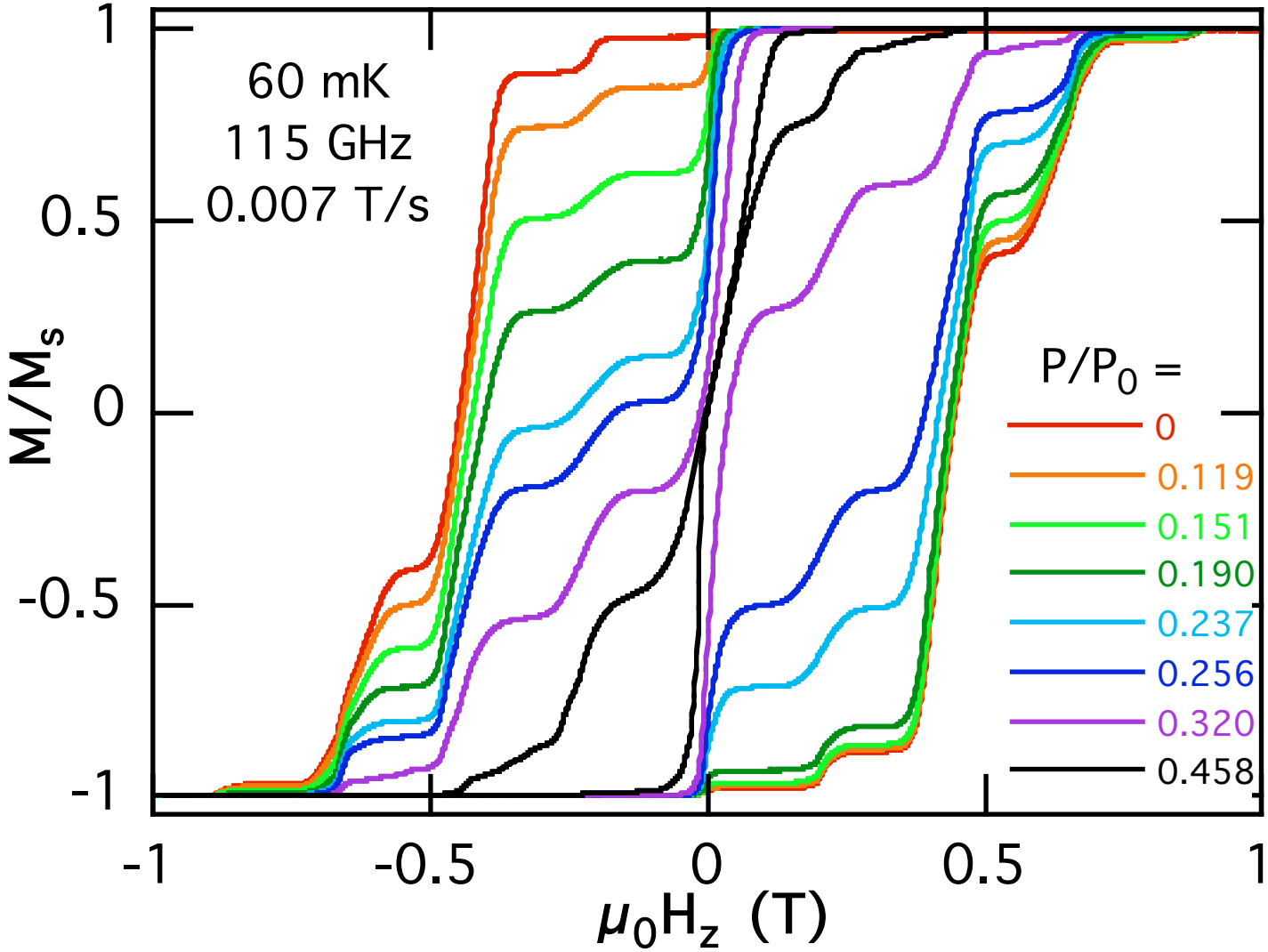




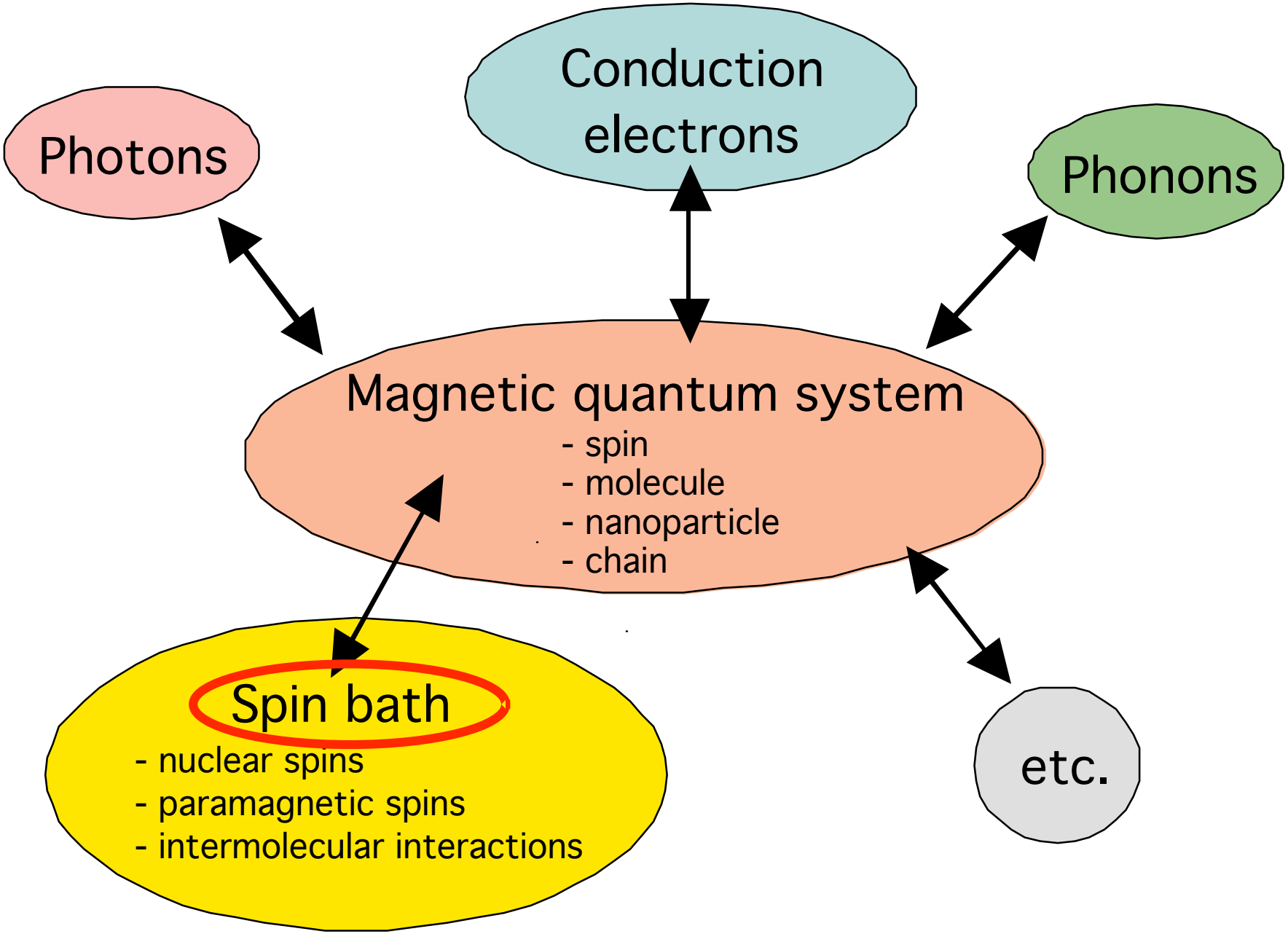
PRB 68, 220407(R) (2003)

Absorption of circular polarized microwaves (115 GHz)

PRB 68, 220407(R) (2003)

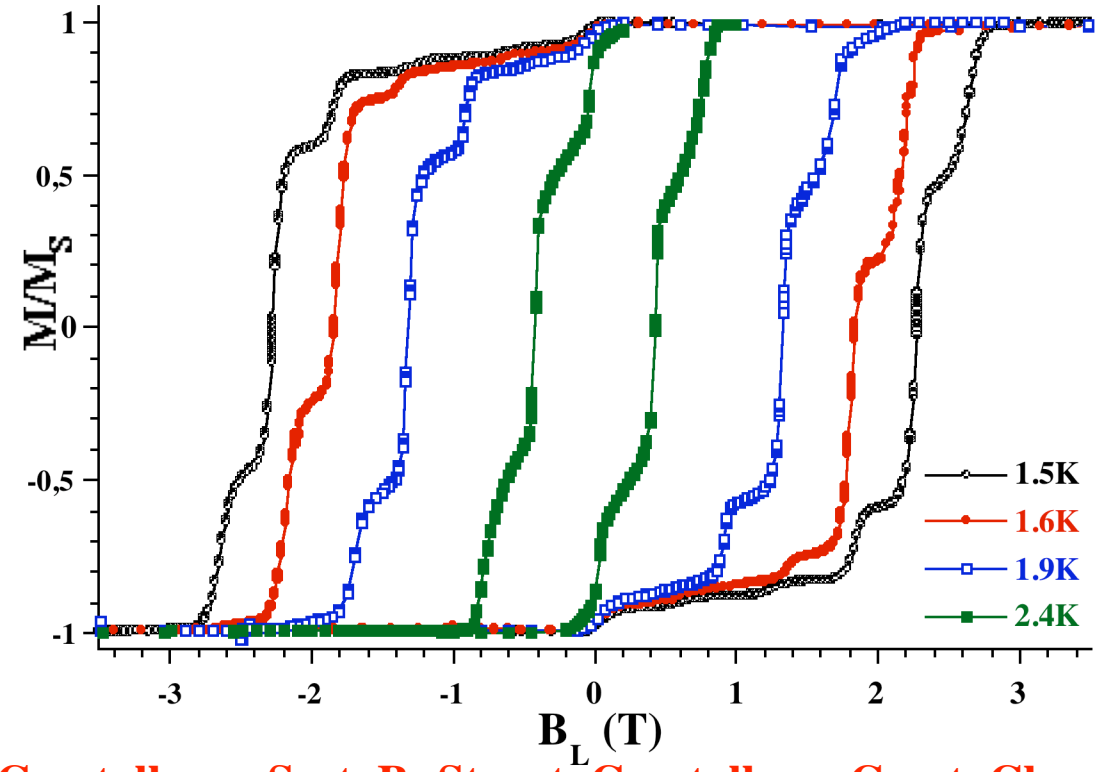


Interactions in magnetic quantum systems (decoherence)



Conclusion

Beginning: Mn_{12}-ac



L. Thomas, B. Barbara, *et al.*, Nature (1996)

T. Lis, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 36, 2042 (1980)

R. Sessoli, D. Gatteschi, M. Novak, D. Hendrikson, G. Christou, *et al.* (1989-93)

M. Novak, C. Paulsen, B. Barbara, *et al.* (1994)

J. Friedman, M. Sarachik, *et al.*, PRL (1996)

L. Thomas, B. Barbara *et al.*, Nature (1996)

Followed by: >250 systems (in our group)

Mn, Mn_2, Mn_3, Mn_4, $[Mn_4]_2$, Mn_5, Mn_6, Mn_7, Mn_8, Mn_9, Mn_{10}, Mn_{11}, Mn_{12}, Mn_{13}, Mn_{16}, Mn_{18}, Mn_{21}, Mn_{22}, Mn_{24}, Mn_{26}, Mn_{30} , Mn_{70} , Mn_{84}

Fe_2, Fe_3, Fe_4, Fe_5, Fe_6, Fe_7, Fe_8, Fe_{10}, F … e$_{30}$

Ni_4, Ni_5, Ni_6, Ni_8, Ni_{12}, Ni_{21}, Ni_{24}

Co_4, Co_5, Co_6, Co_7, Co_{10}

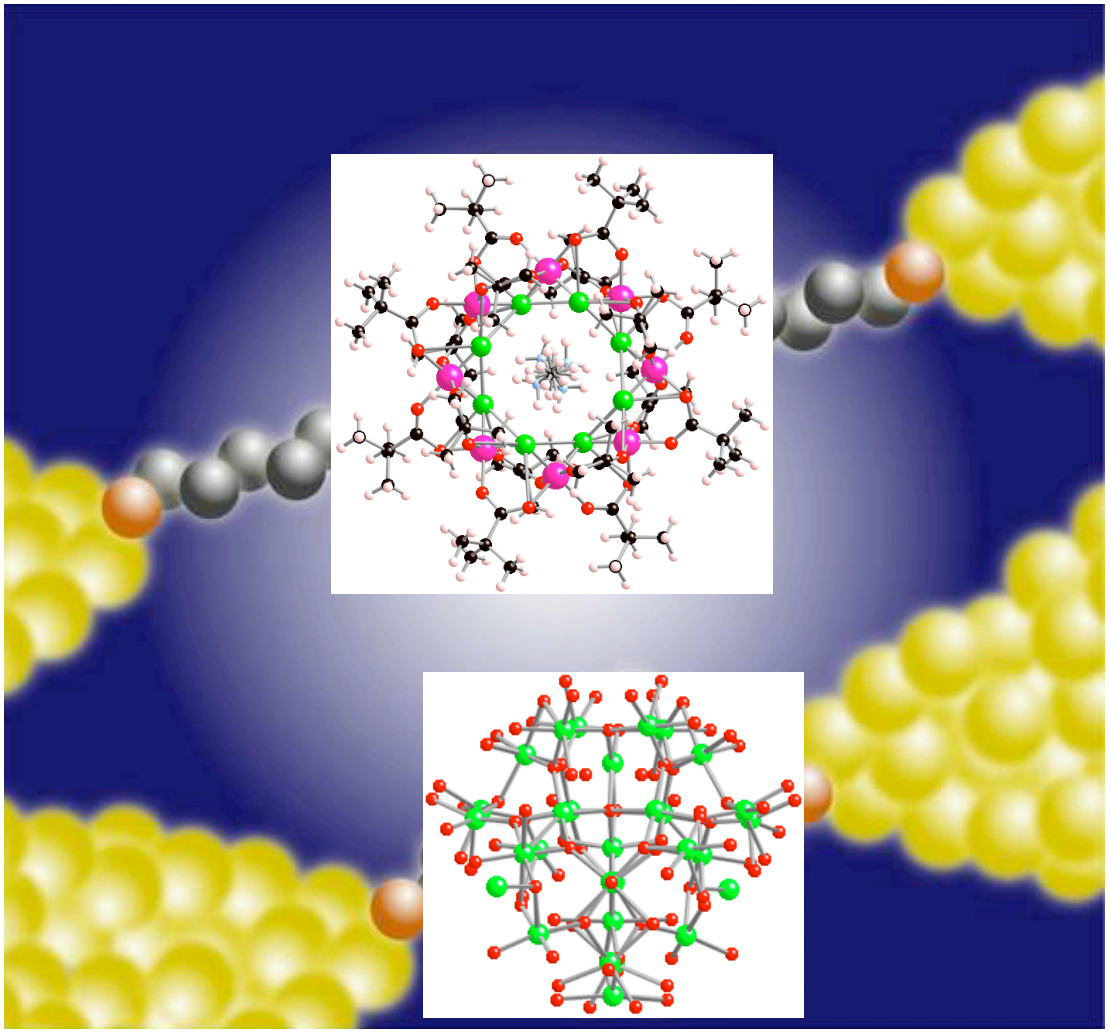
Co_2Gd_2, Co_2Dy_2, Cr_{12}, $CrNi_6$, $CrNi_2$, $CrCo_3$, $Fe_{10}Na_2$, Fe_2Ni_3, Mn_2Dy_2, Mn_2Nd_2, V_{15}, Ho, Fe_2Ho_2, $Mn_{11}Ln_4$, ..

Only few of these molecules are SMMs !!

• • • • • •

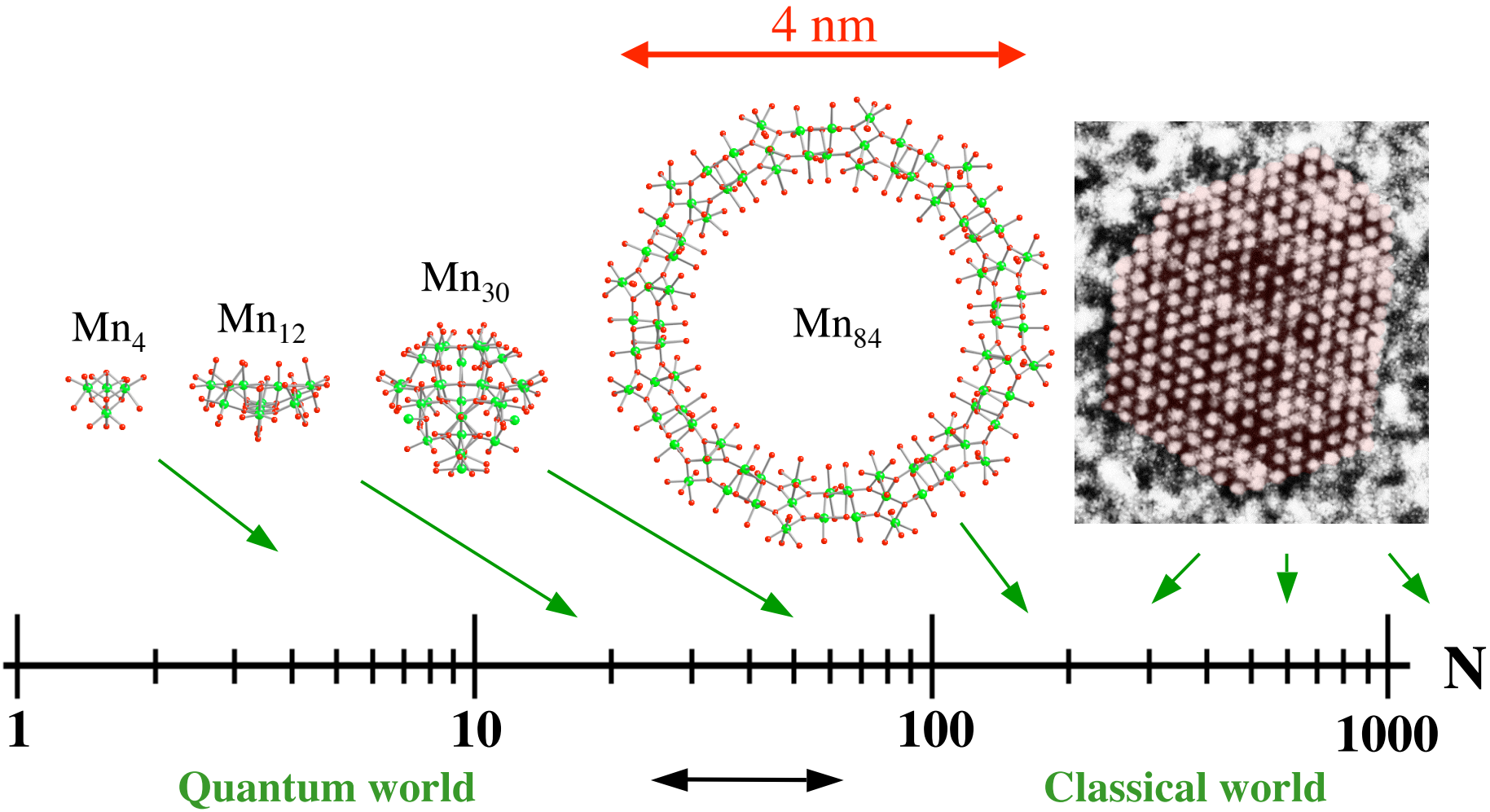
S = 0, 1/2, 1, 3/2, 2, 5/2, 4, 9/2, 5, …… 51/2

Development of molecular Spin-Electronics



APS March Meeting 2004

Mesoscopic Physics



A. J.Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A.Abboud, and G. Christou, Angew. Chem. Int. Ed., 43, 2117 (2004)

Collaborations (Physics)

L. Thomas	PhD 1996: Mn_{12}-ac
F. Lionti	PhD 1997: Mn_{12}-ac, $Fe_{17/19}$
I. Chiorescu	PhD 2000: Mn_{12}-ac, V_{15}
R. Giraud	PhD 2002: Ho^{3+}
C. Thirion	PhD 2003: nanoparticles, GHz
R. Tiron	PhD 2004: $[Mn_4]_2$
S. Bahr	PhD started 2005: GHz
K. Petukhov	post-doc 2004-5: GHz

F. Balestro, E. Bonet, W. Wernsdorfer, B. Barbara, LLN, CNRS, Grenoble

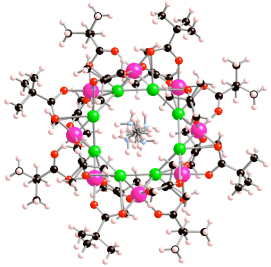
T. Ohm	PhD 1998: Fe_8
V. Villar	PhD 2001: Fe_8 , chaines
E. Lhotel	PhD 2004: chaines

V. Bouchiat, C. Paulsen, A. Benoit, CRTBT, CNRS, Grenoble

L. Sorace, post-doc 2003: GHz
A.-L. Barra, LCMI - CNRS, Grenoble

J. Villain, CEA, Grenoble

D. Mailly, LPN, CNRS, Marcoussis



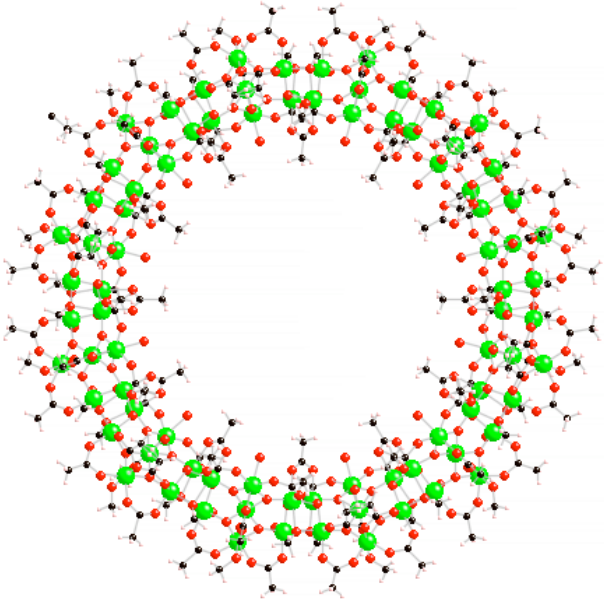
Winpenny, 2003

Collaborations (Chemistry)

SMMs

Group of G. Christou, Dept. of Chemistry, Florida
Group of R. Sessoli, D. Gatteschi, Univ. de Firenze, Italie
Group of A. Cornia, Univ. de Modena, Italie
Group of R.E.P. Winpenny, Univ. de Manchester, UK
Group of E. Brechin, Univ. de Manchester, UK
Group of T. Mallah, Orsay
Group of V. Marvaud, Univ. P. et M. Curie, Paris
Group of A. Müller, Univ. de Bielefeld, Germany
Group of A. Powell, Univ. de Kahlsruhe, Germany
Group of D. Hendrickson, Dept. of Chemistry, San Diego
Group of E. Coronado, Univ. de Valence, Spain
Group of D. Luneau, Univ. of Lyon, France
Group of G. Royal, Univ. J. Fourier, Grenoble

Mn_{84}



Christou, 2004

SCMs

Group of R. Clerac & C. Coulon, Univ. Bordeaux, Pessac
Group of H. Miyasaka, Tokyo Metropolitan Uni.
Group of M. Verdaguer, Univ. P. et M. Curie, Paris
Group of M. Julve, Univ. de Valence, Spain

• • •

MAGMA Net
NETWORK OF EXCELLENCE