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Energy Agency

SMR.1664 - 7

Conference on Single Molecule Magnets and Hybrid Magnetic Nanostructures

27 June - 1 July 2005

Quantum Dynamics in Single-Molecule Magnets Triggered by Microwave Pulses

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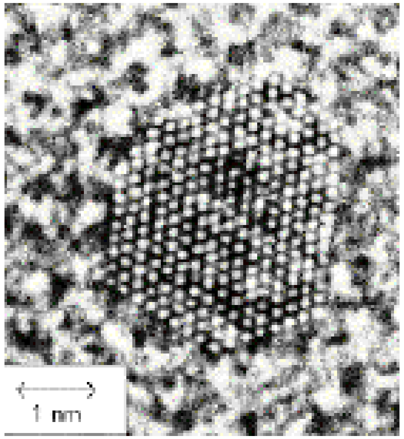
38042 Grenoble Cedex 9
FRANCE

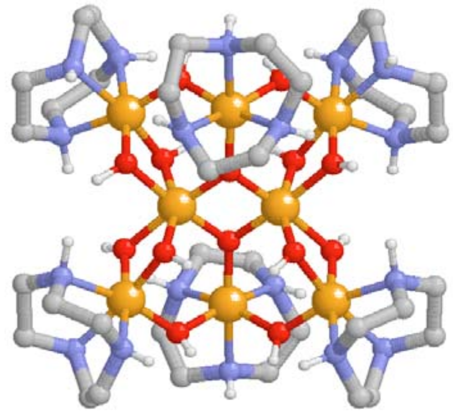
Quantum Dynamics in Single-Molecule Magnets Triggered by Microwave Pulses



$S = 10^2$ to 10^6

W. Wernsdorfer
K. Petukhov, S. Bahr, B. Barbara
Laboratoire de
Magnétisme Louis Néel
C.N.R.S. - Grenoble

A.-L. Barra
LCMI - CNRS, Grenoble



$S = 1/2$ to ≈ 30

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Magnetic structures

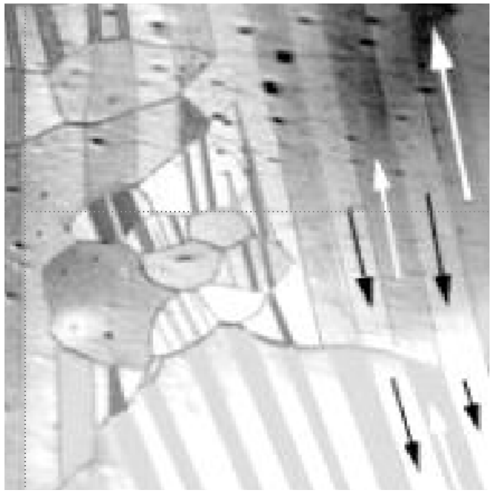
← *macroscopic* | *atomic* →

permanent magnets	micron particles	nanoparticles	clusters	molecular clusters	atoms

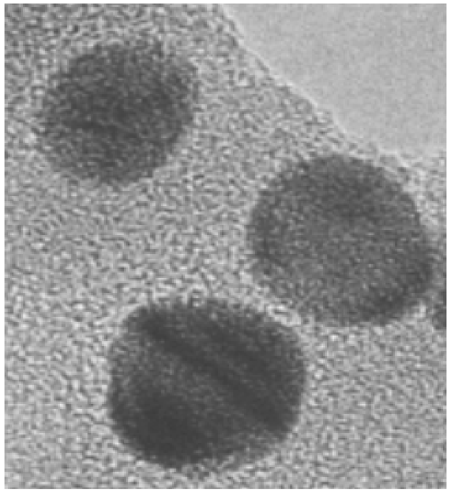
$S = 10^{20}$ | 10^{10} | 10^{8} | 10^{6} | 10^{5} | 10^{4} | 10^{3} | 10^{2} | 10 | 1

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

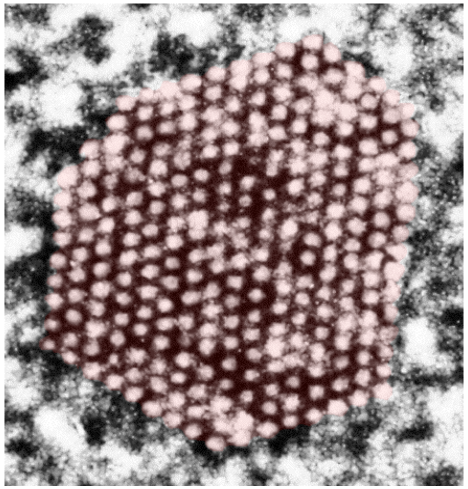
1 mm



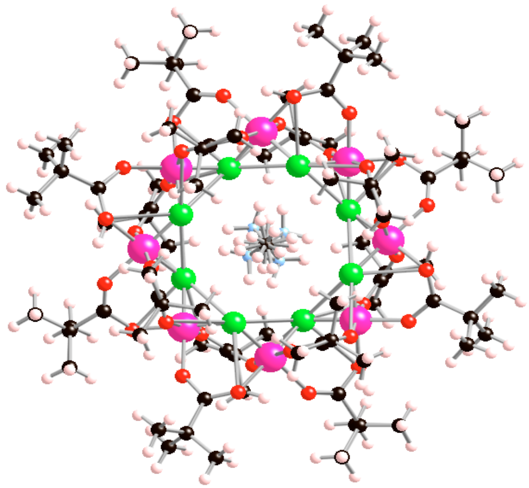
20 nm



3 nm



1 nm



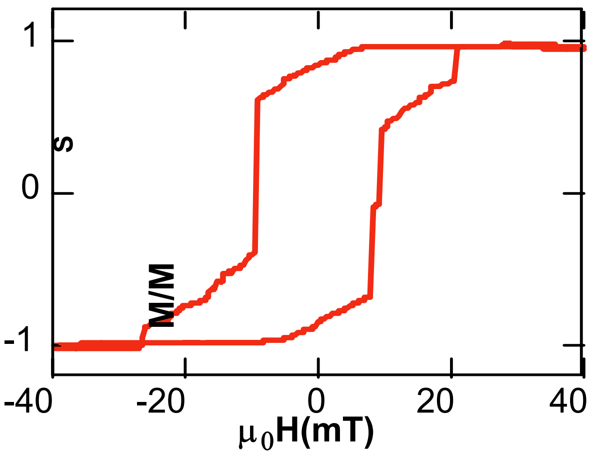
Magnetization reversal in magnetic structures

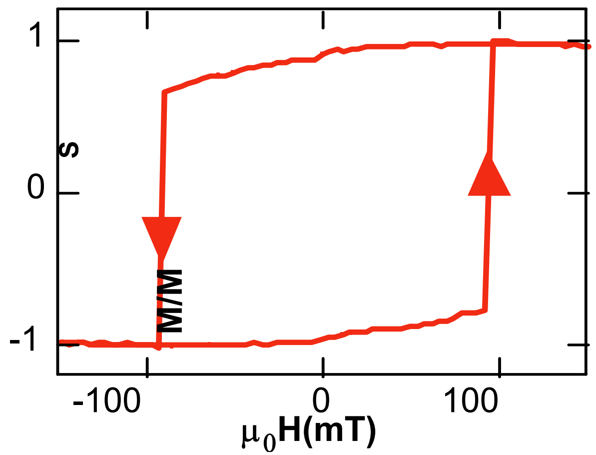
← *macroscopic* | *atomic* →

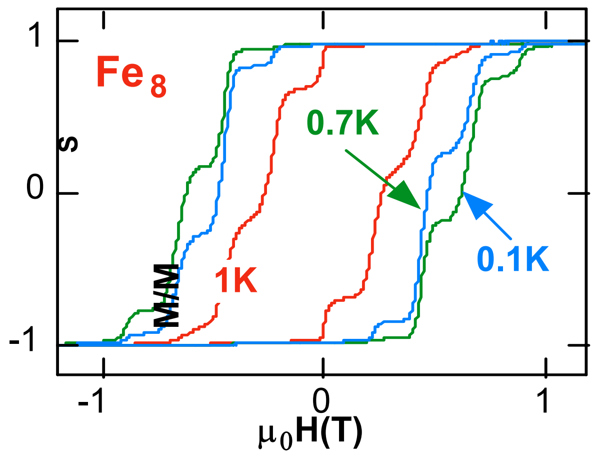
permanent magnets	micron particles	nanoparticles	clusters	molecular clusters	atoms

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

multi - domains	***single - domains***	***spins***
nucleation, propagation and annihilation of domain walls	uniform rotation, curling, etc.	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

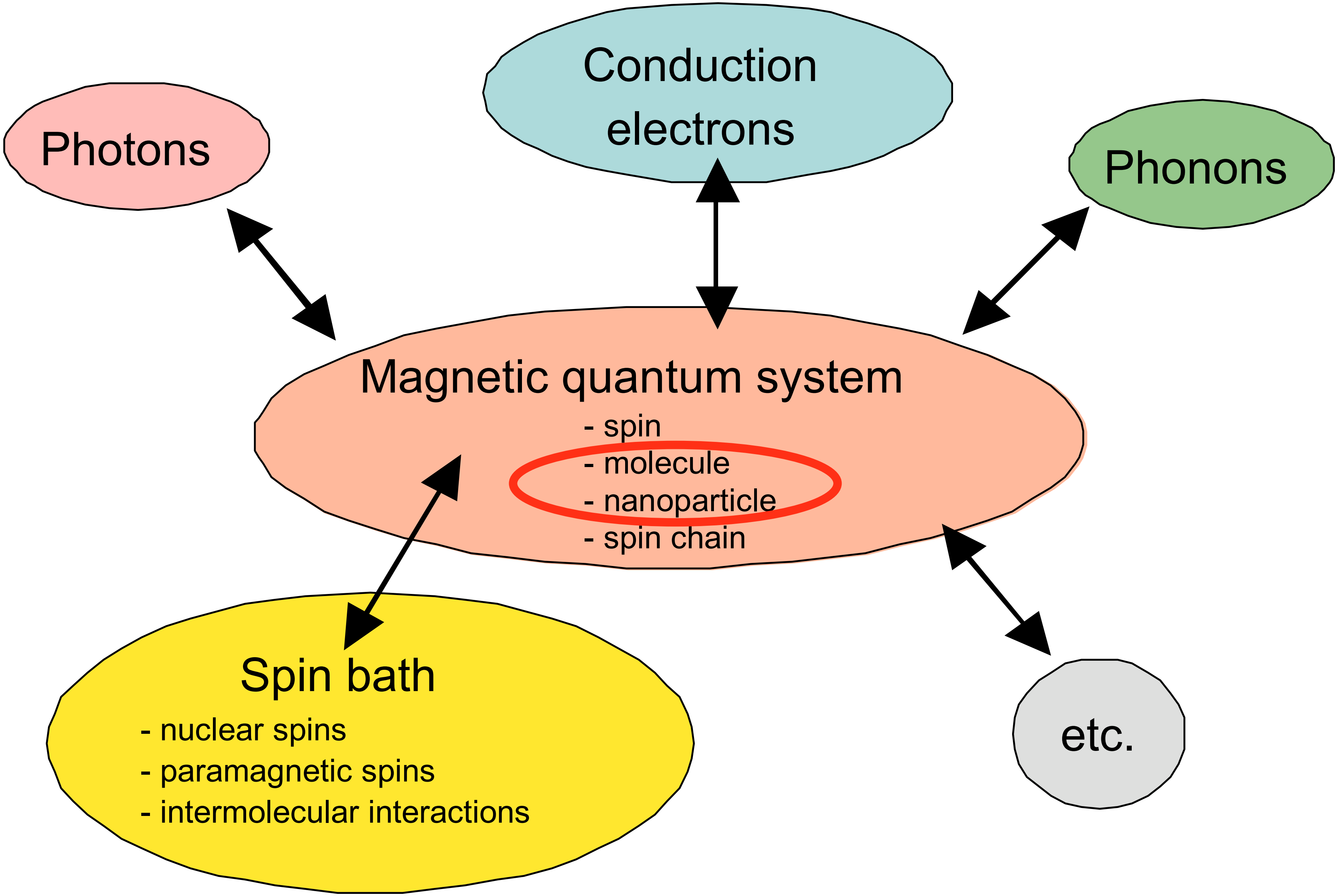
Operator formalism

Path intergrals

ab-initio calulations

etc.

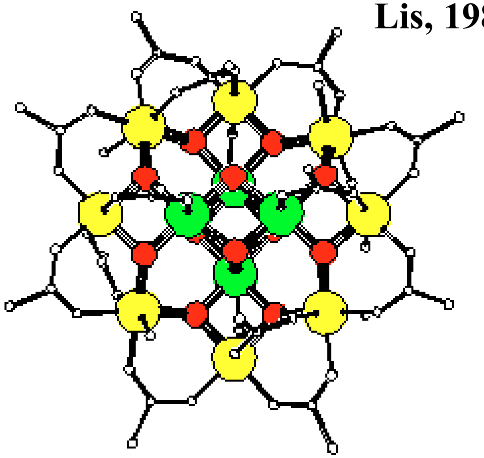
Interactions in magnetic quantum systems (decoherence)



Single-molecule magnets (SMM)

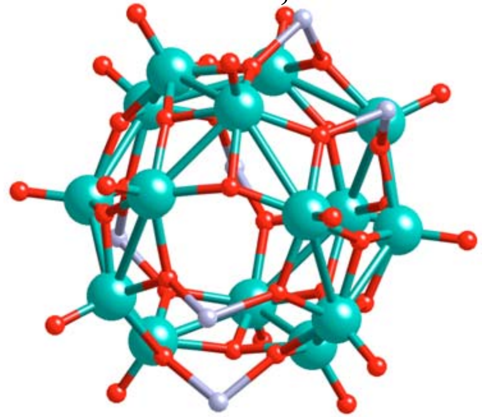
Giant spins

Lis, 1980

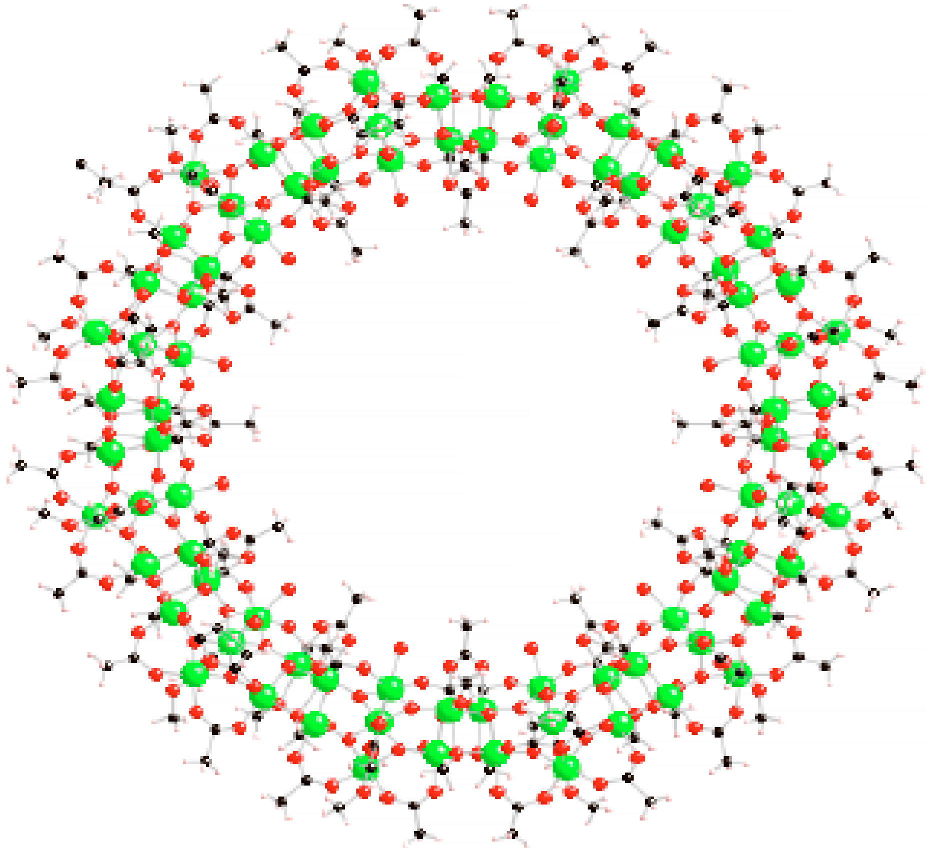


Mn_{12} $S = 10$

Müller, 1993



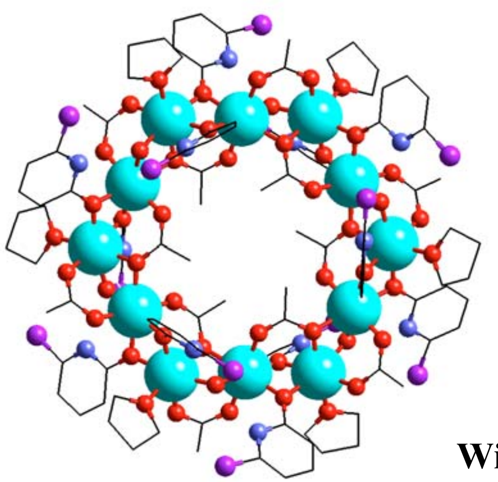
V_{15} $S = 1/2$



Christou, 2004

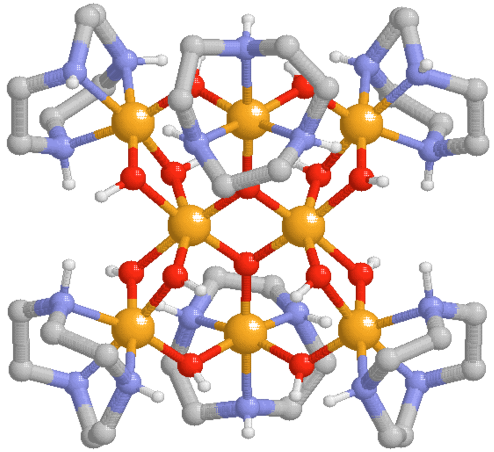
Mn_{84} $S \approx 6$

Ni_{12} $S = 12$



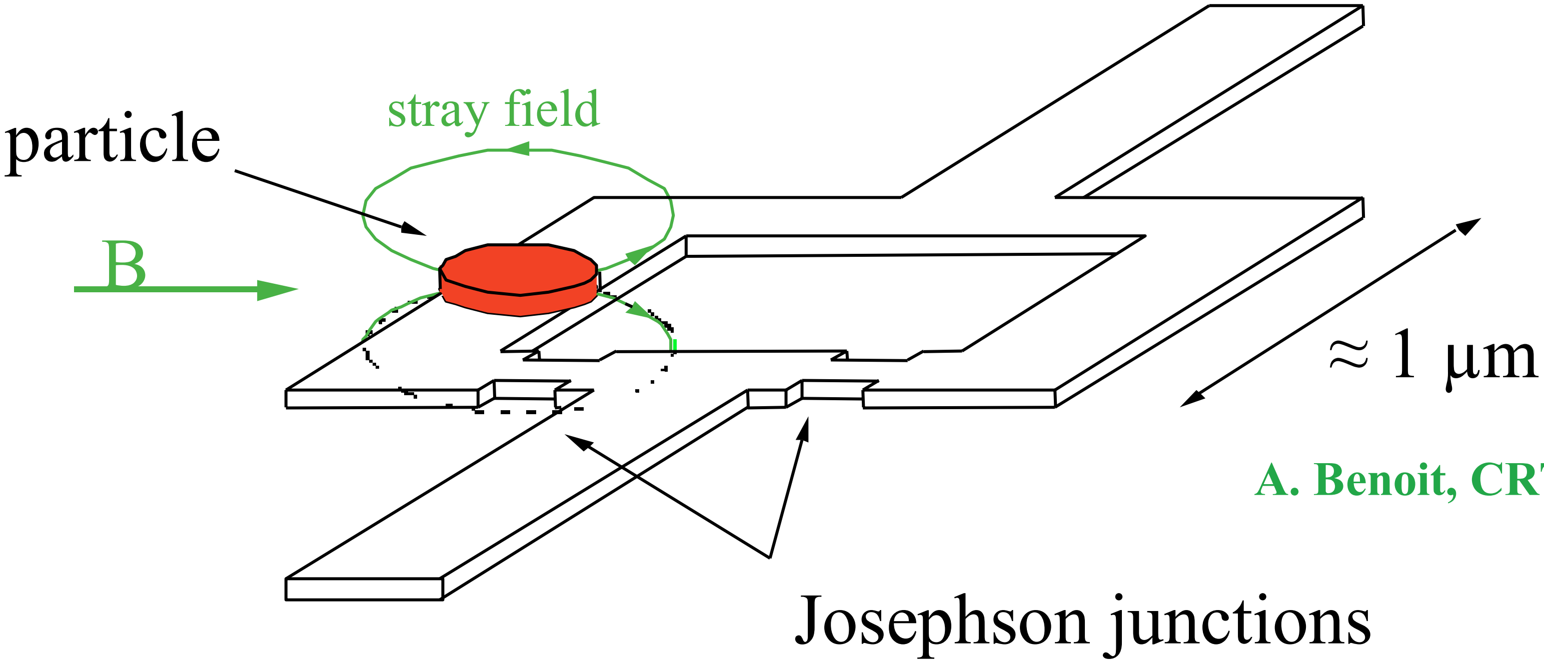
Winpenny, 1999

Fe_8 $S = 10$



Wiegart, 1984

Micro-SQUID magnetometry



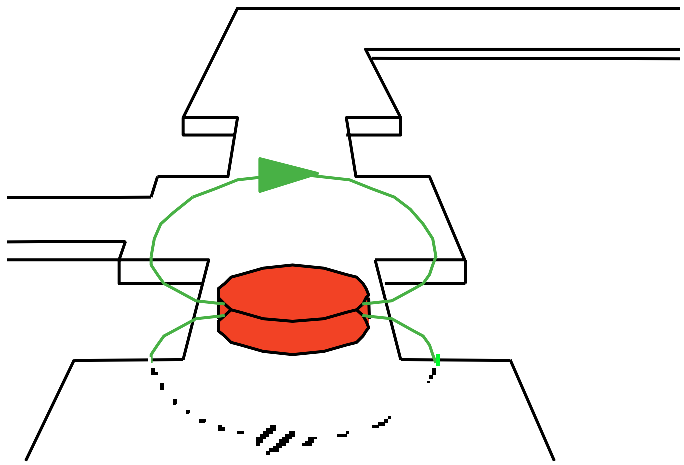
A. Benoit, CRTBT, 1989

- **fabricated by electron beam lithography**
  (D. Mailly, LPN, Marcoussis - Paris)

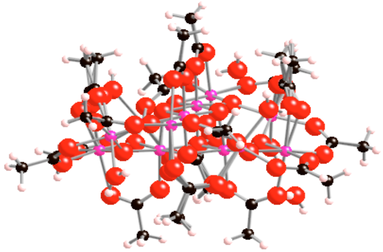
- **sensitivity :** $10^{-4}\ \Phi_o$

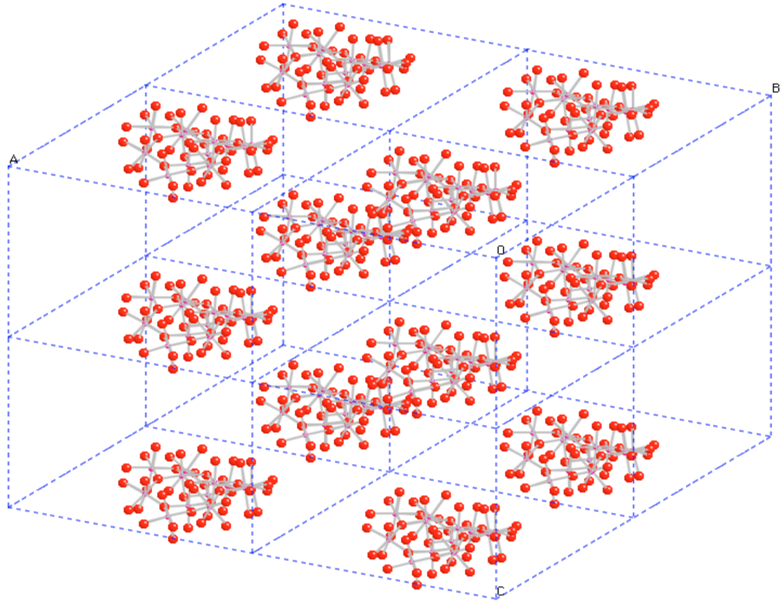
  $\approx 10^{2} - 10^{3}\ \mu_B$ **i.e.** $(2\ \text{nm})^3$ **of Co**

  $\approx 10^{-18} - 10^{-17}$ **emu**

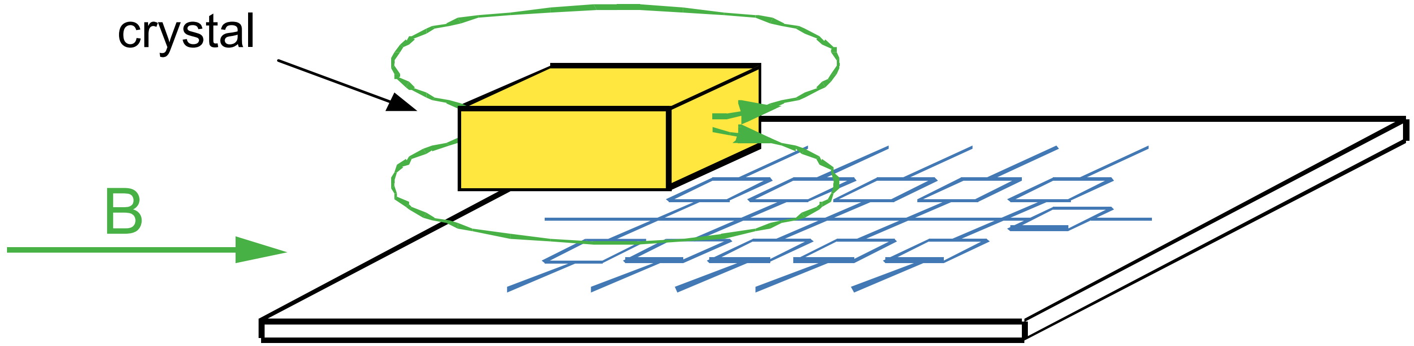


Crystal of SMMs

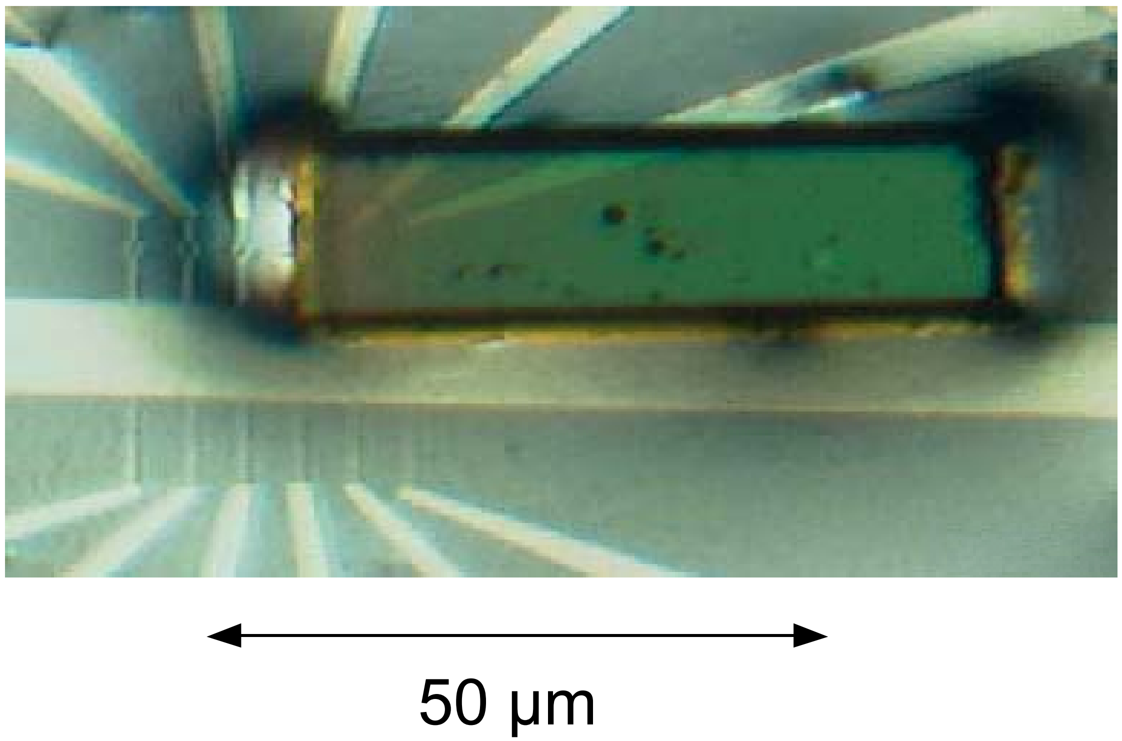




Micro-SQUID array

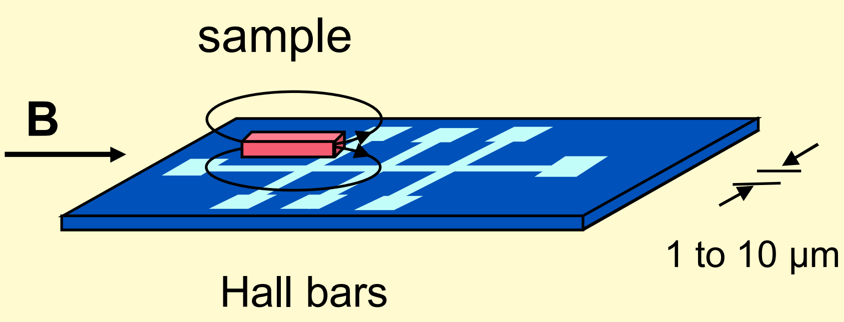


- crystal size > few µm
- 10^{-12} to 10^{-17} emu
- temperature 0.03 - 7 K
- field < 1.4 T and < 20 T/s
- rotation of field
- transverse field
- several SQUIDs at different positions



Micro-magnetometry

- μ-Hall Effect



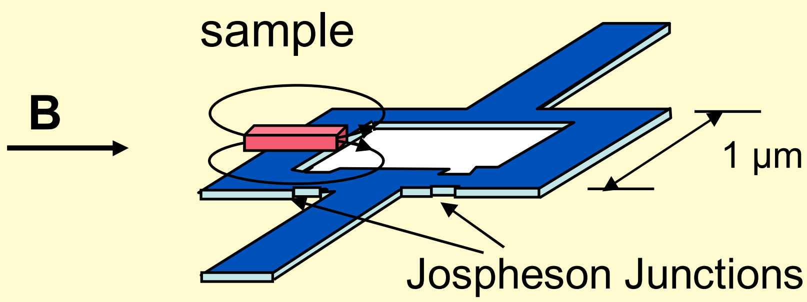
  - Based on Lorentz Force
  - Measures magnetic field

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

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

Andy Kent

- μ-SQUID



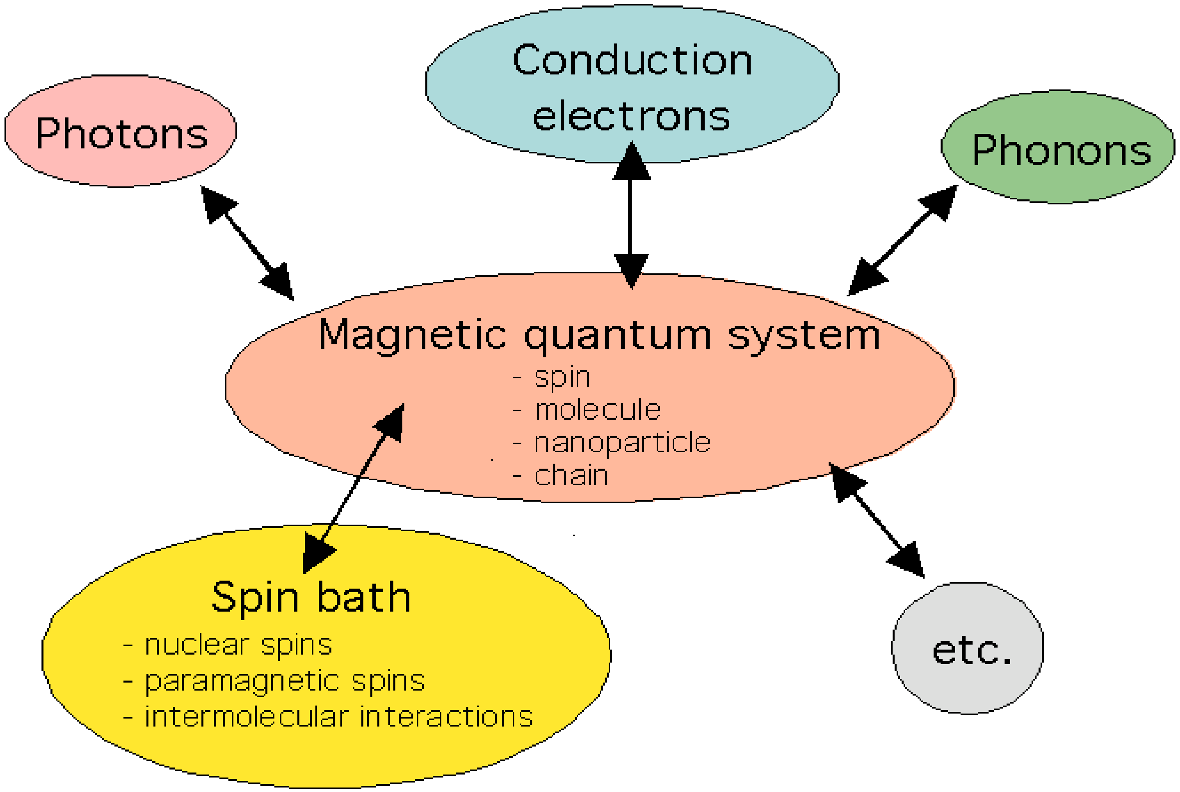
  - Based on flux quantization
  - Measures magnetic flux
  - Applied fields below the upper critical field (~1 T)
  - Low temperature (below T_c)
  - Single magnetic particles
  - Ultimate sensitivity ~1 μ_B

Outline

I. A simple tunnel picture

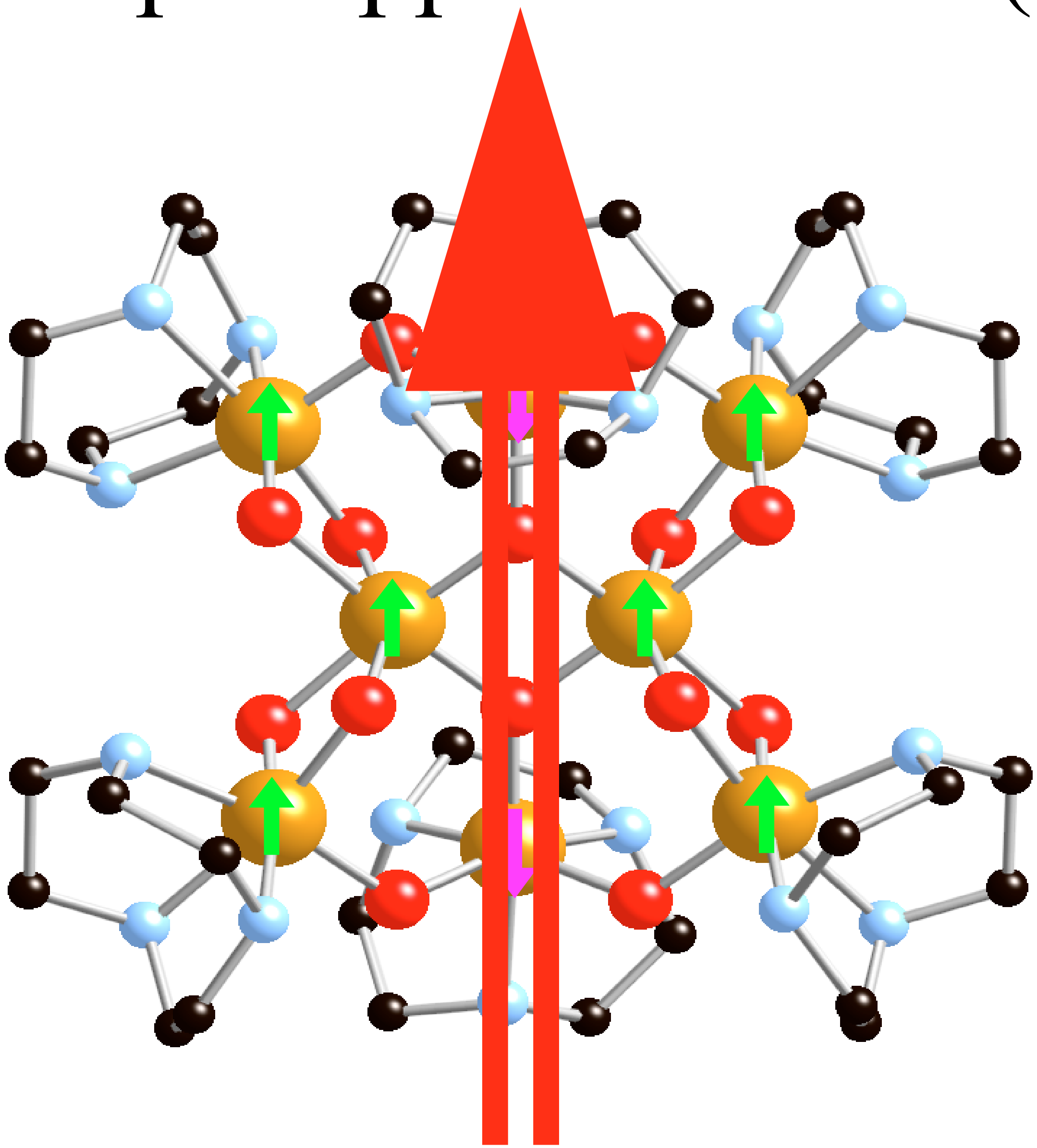
- Giant spin model
- Landau Zener tunneling
- Berry phase

II. Coupling with environment



Giant spin approximation (Fe_8)

$S = 10$



Fe^{III}:

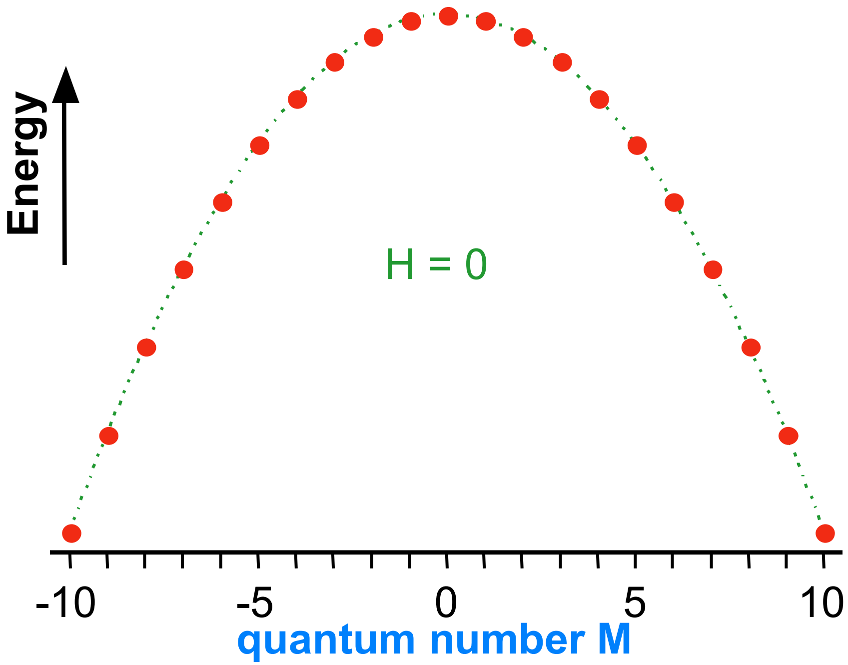
$s = 5/2$

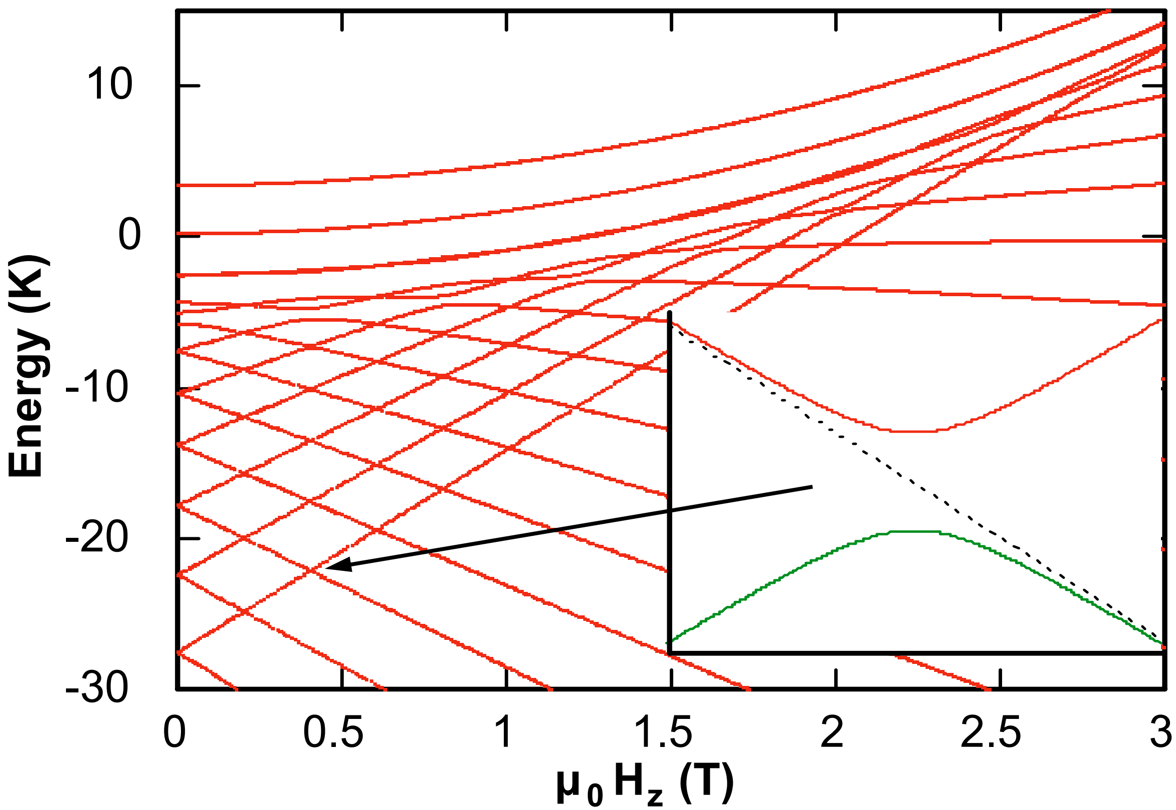
Giant spin model

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: $M = -S, -S+1, \ldots, S$

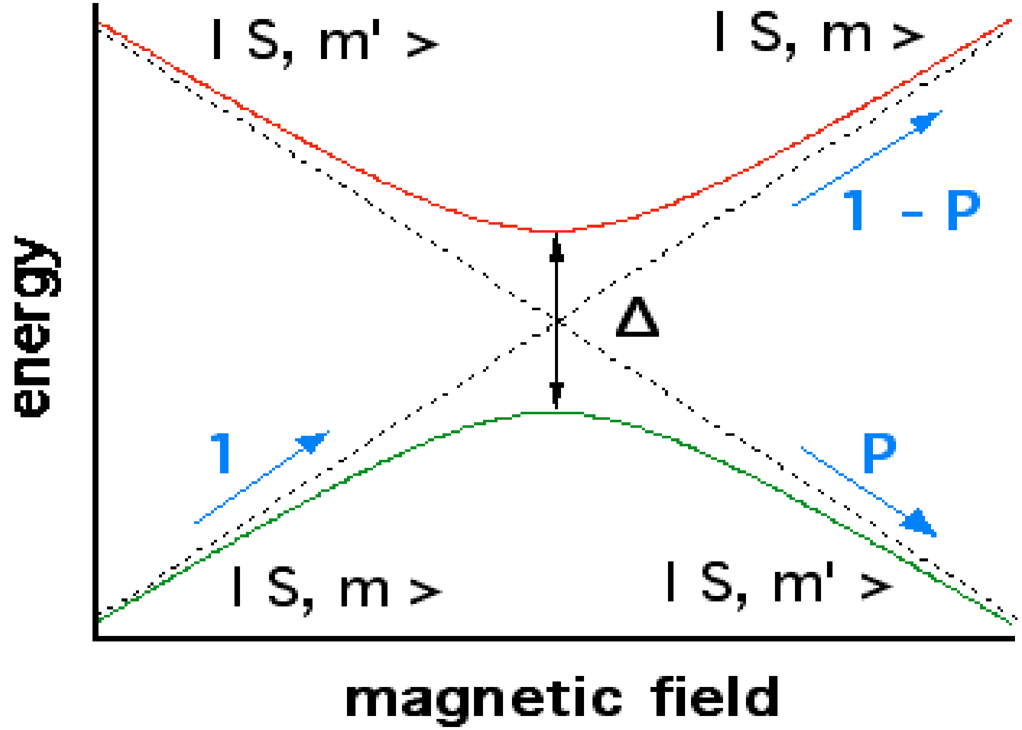
Energy levels: Zeeman diagram





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

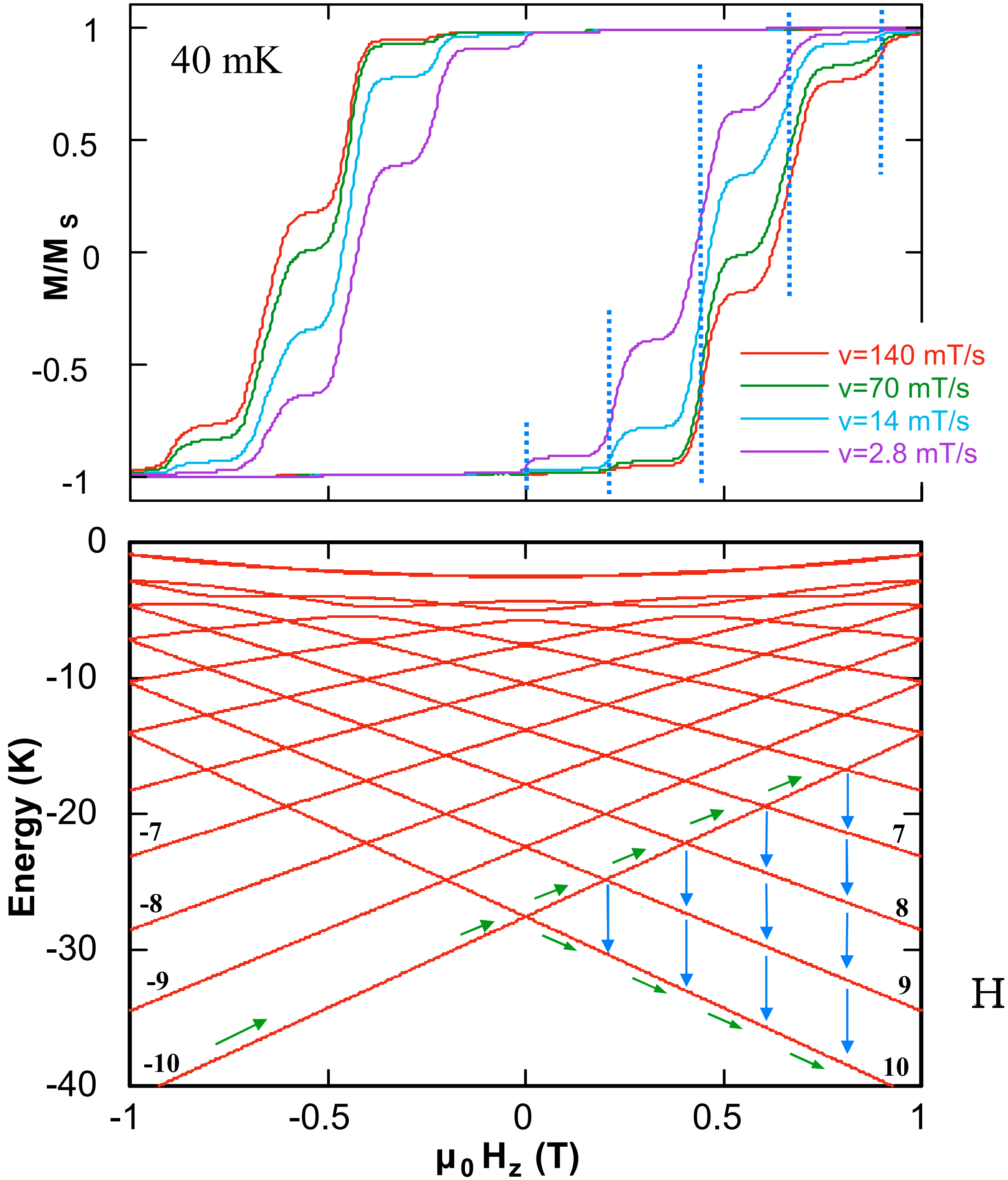
Tunneling probability at an avoided level crossing
Landau-Zener model (1932)



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

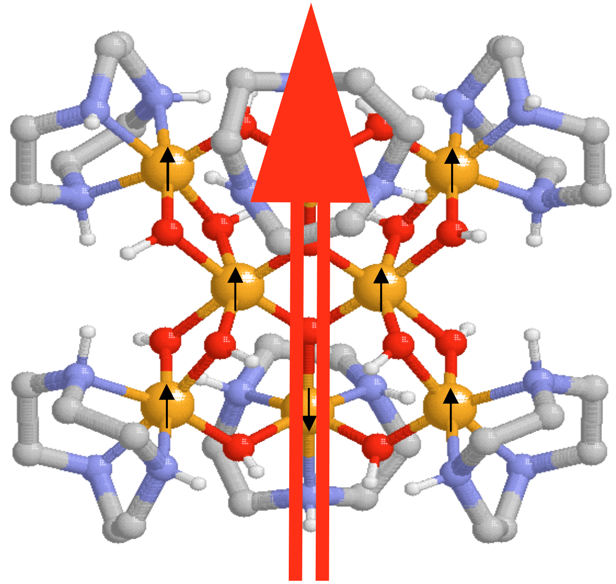
$$c = \frac{\pi}{2\hbar\, g\mu_B |m - m'| \mu_0}$$

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

Fe_8 $S = 10$



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

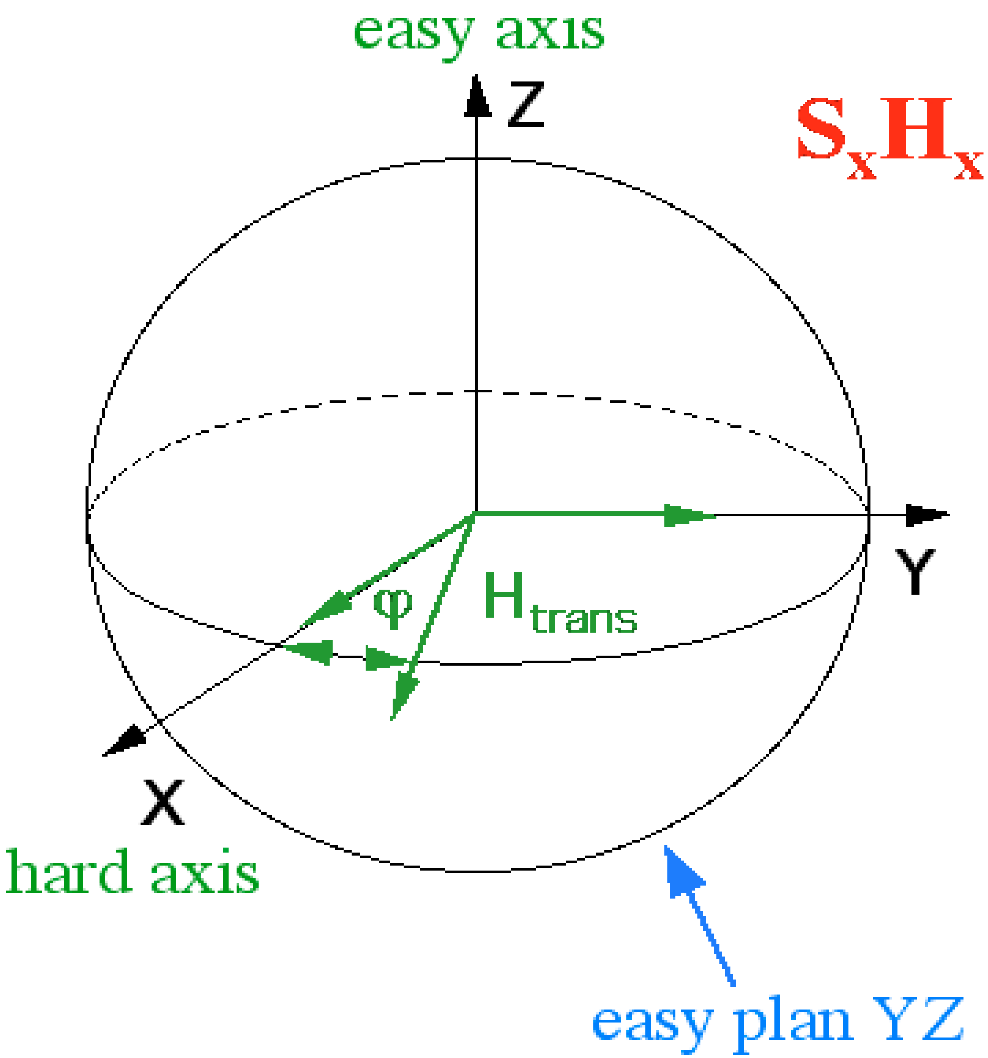
with S = 10, D = 0.27 K, E = 0.046K

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

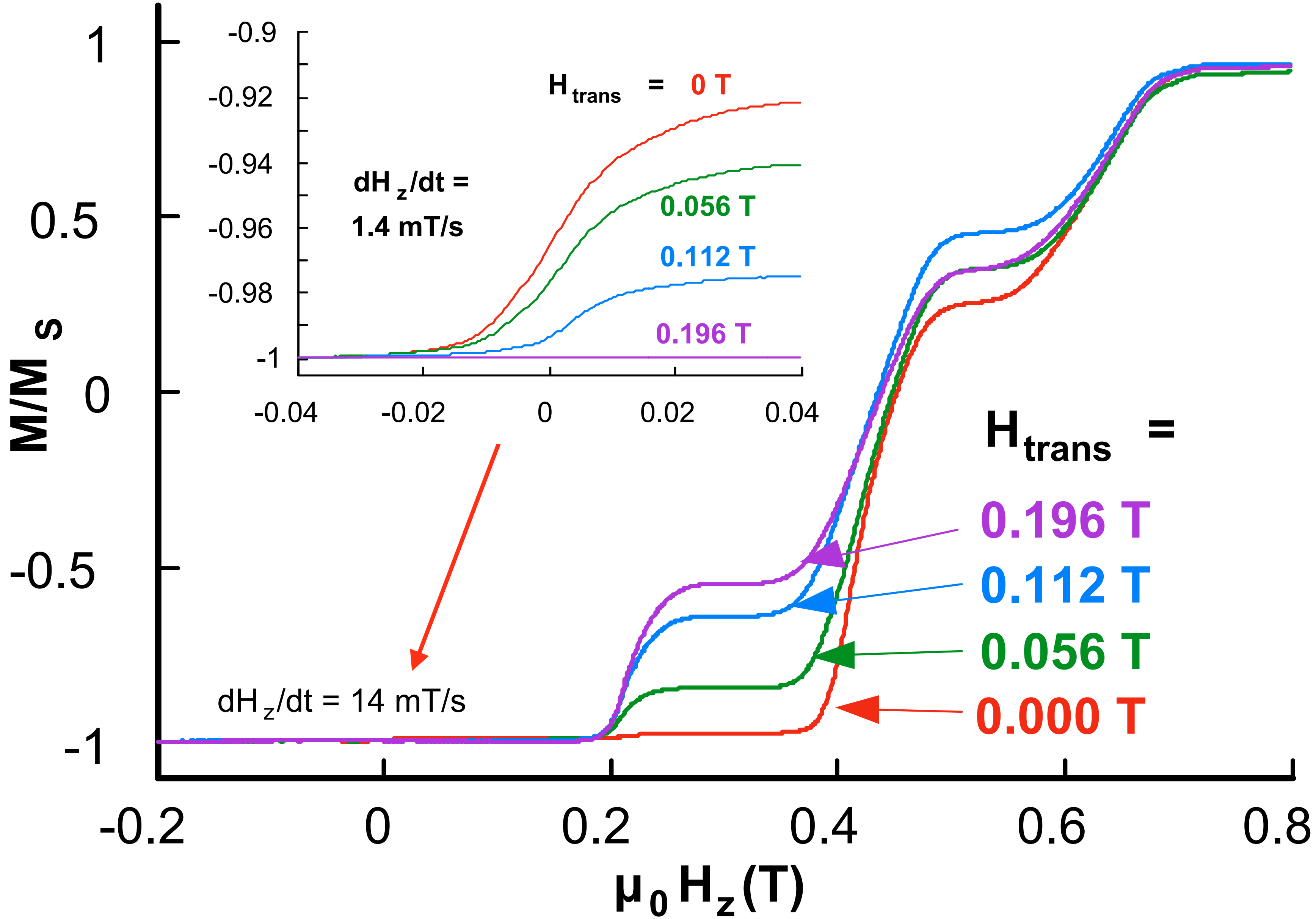
Giant spin Hamiltonian of Fe_8

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

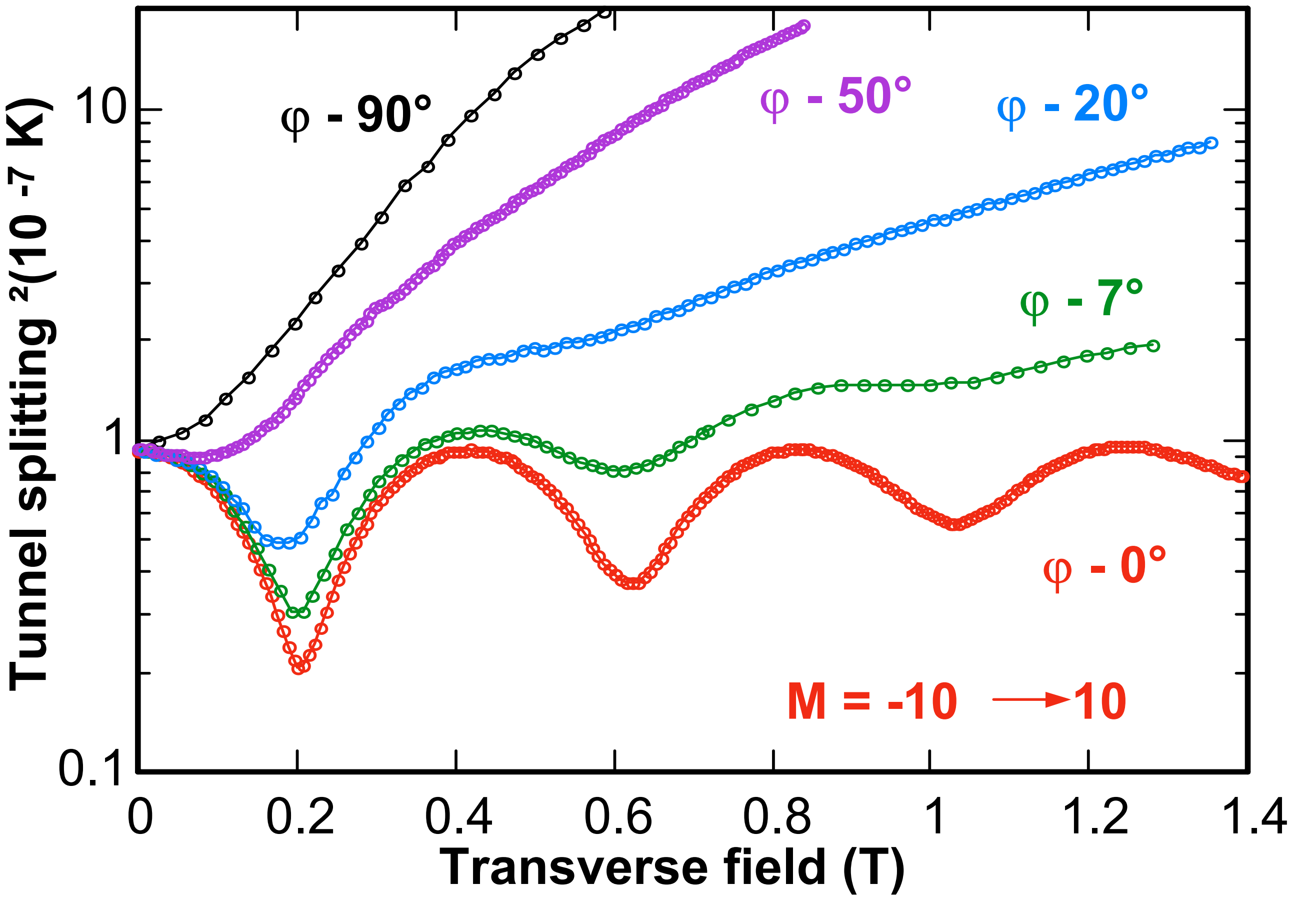
$$S_xH_x + S_yH_y + S_zH_z$$

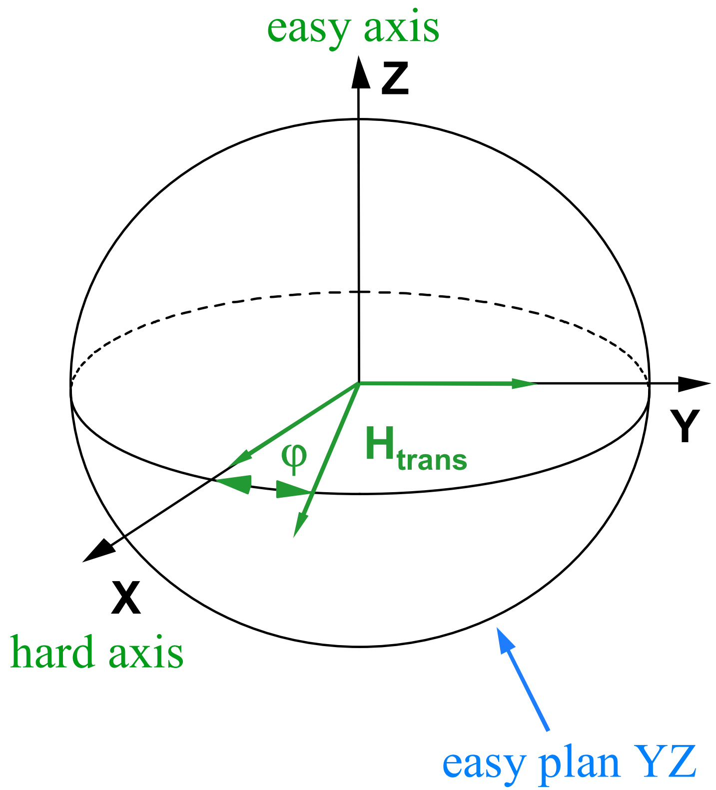


Hysteresis loops at different transverse fields



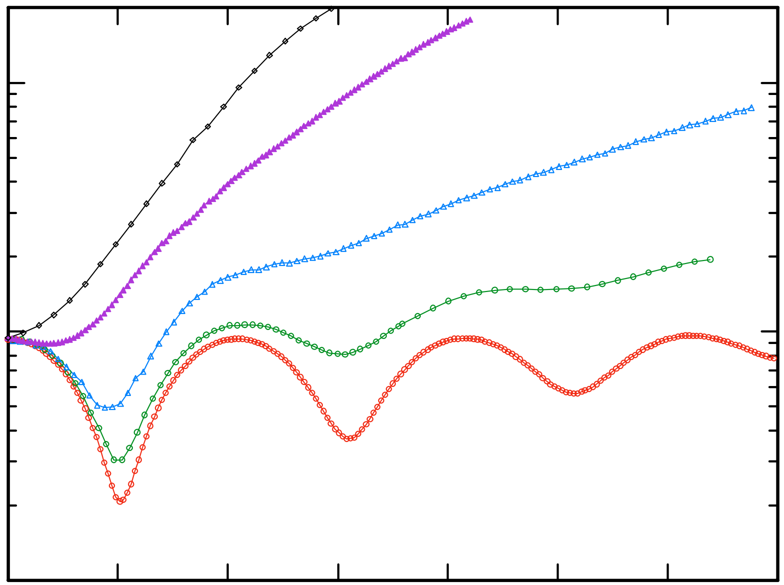
Quantum phase interference (Berry phase) in single-molecule magnets

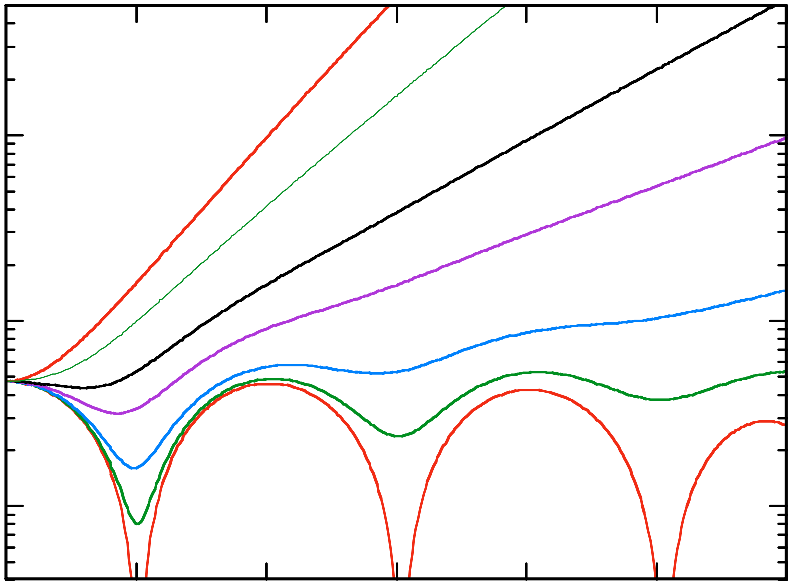




Transverse field dependence of tunnel splitting

(operator formalism)





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

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

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

Path integrals (Feynman)

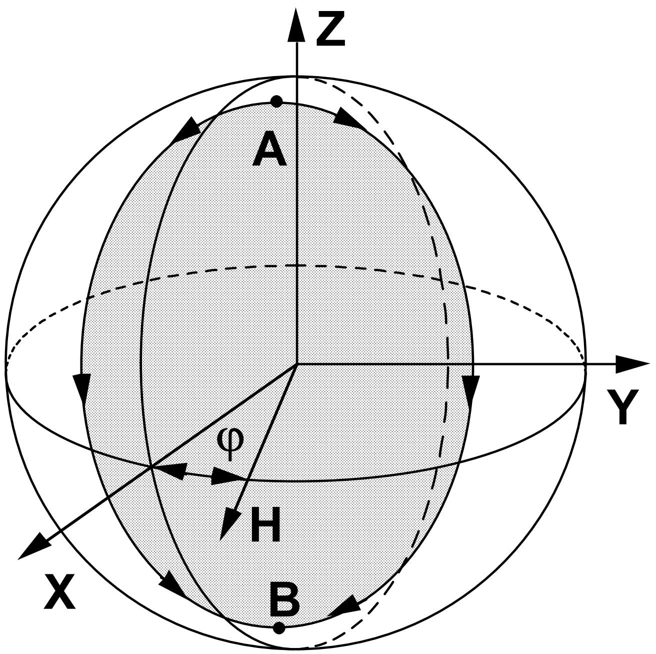
Path-integral partition function:

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

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

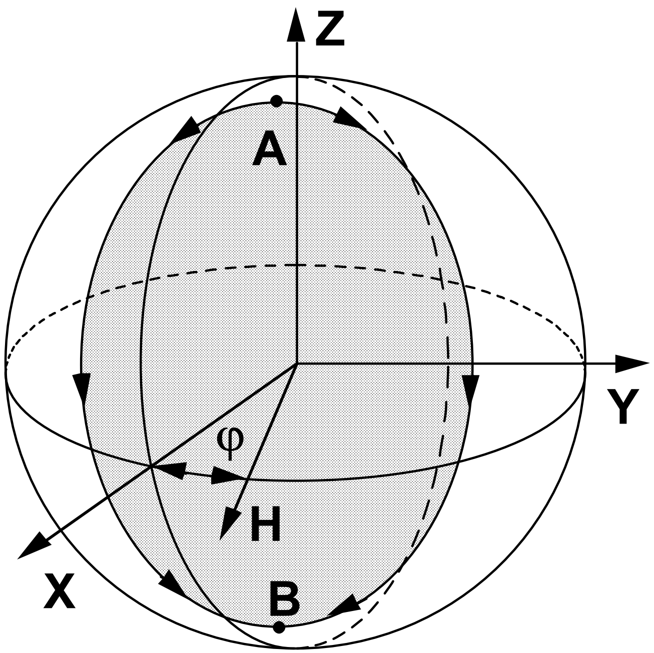


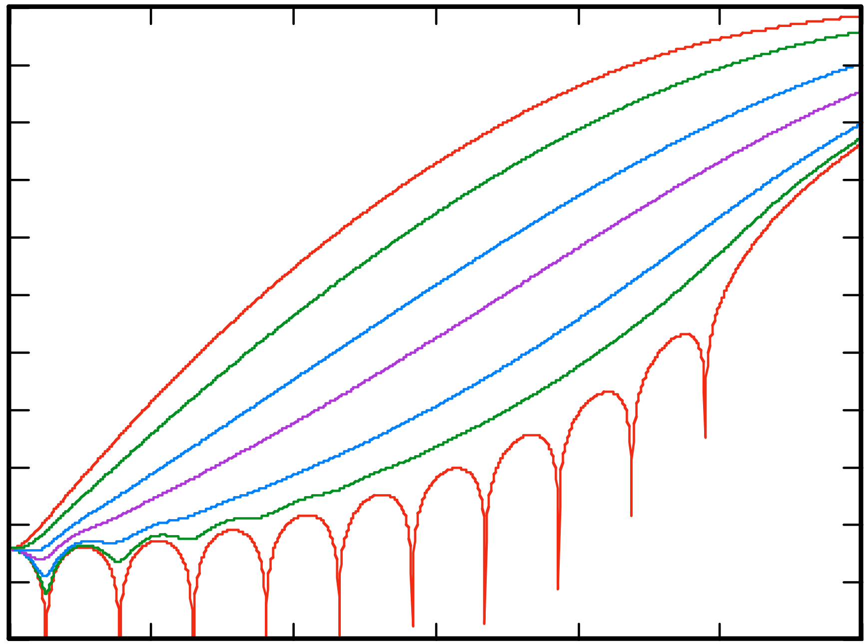
destructive interference occures whenever the shaded area is kπ/S, for odd k.

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

Transverse field dependence of tunnel splitting

(path integrals formalism)



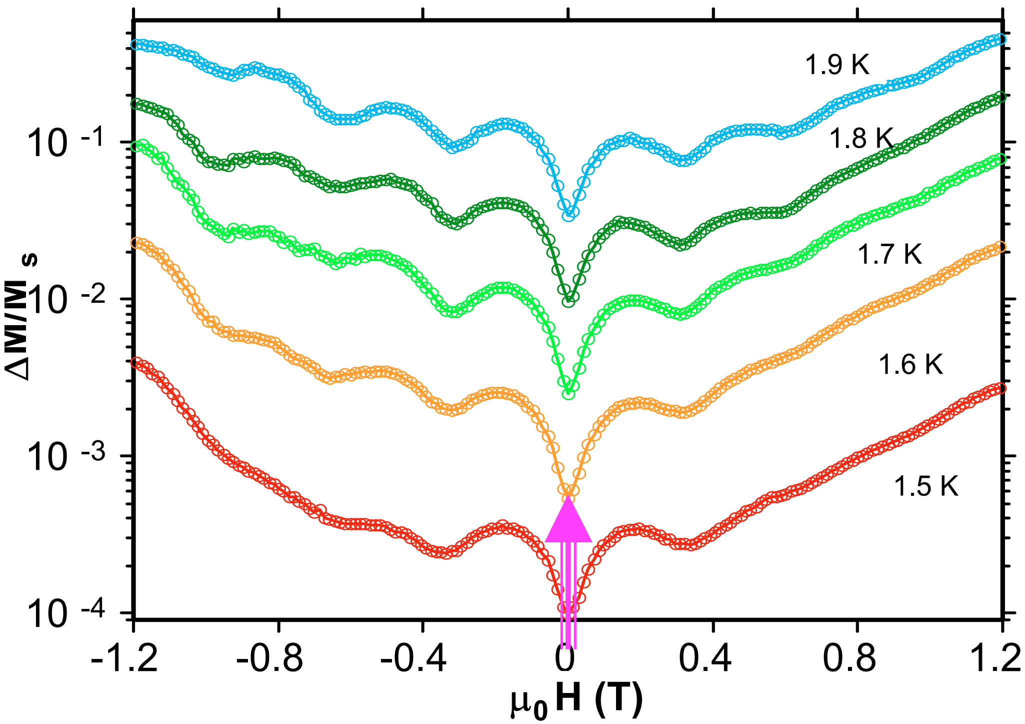


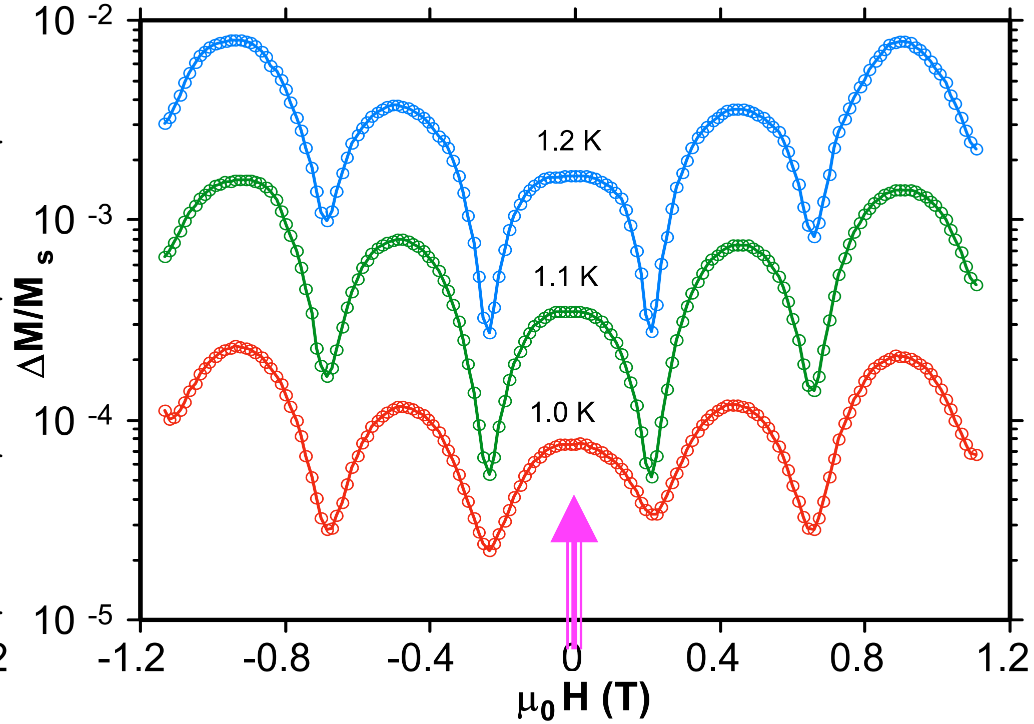
$$H = -D\,S_z^2 + E\left(S_x^2 - S_y^2\right) + g\mu_B \vec{S}\,\vec{H}$$

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

Quantum phase interference and spin parity in Mn_{12}

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





W. Wernsdorfer, N. E. Chakov, G. Christou, PRL (July 2005)
cond-mat/0503193

Magnetization reversal in magnetic structures

← *macroscopic* | *atomic* →

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

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

Tunneling splitting

$$\Delta \sim \left(\frac{E}{D}\right)^{S} \qquad E << D$$

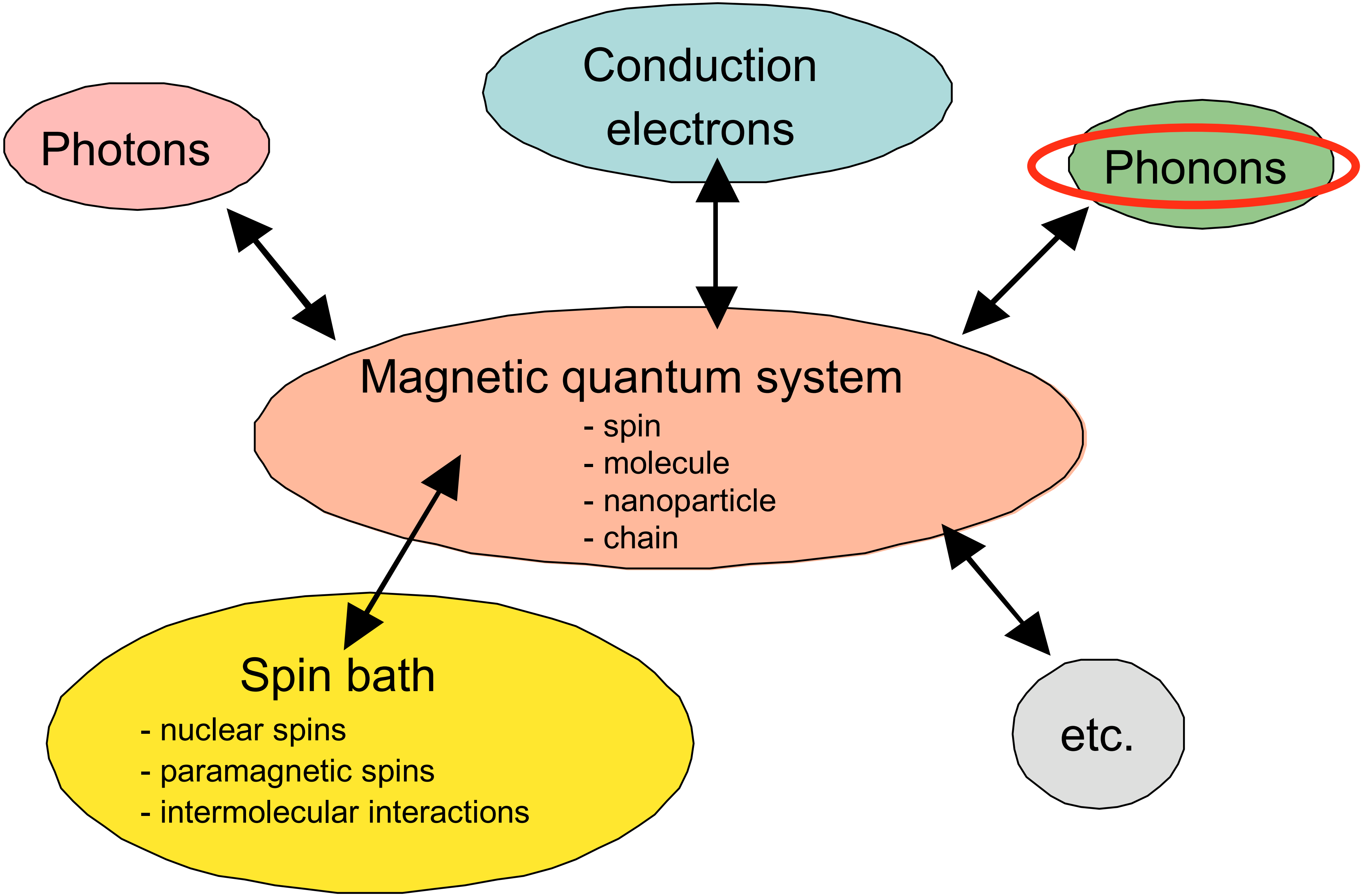
$$\Delta \sim \left(\frac{H_x}{D}\right)^{2S}$$

Tunneling probability

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

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

Interactions in magnetic quantum systems (decoherence)

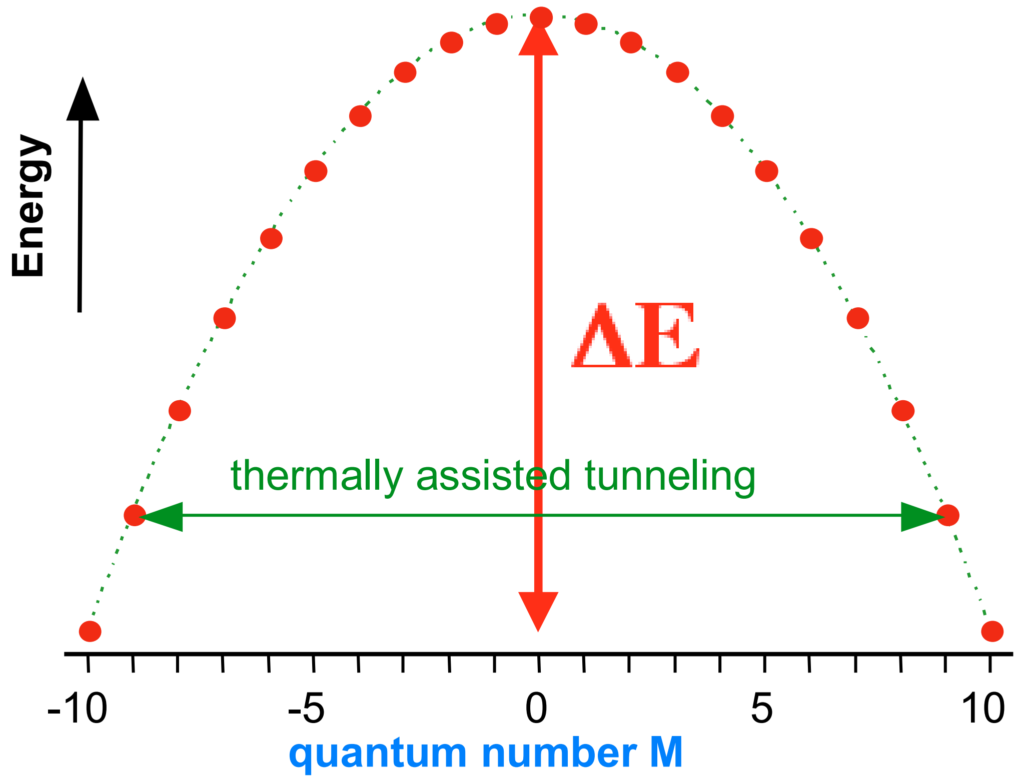


Giant spin model

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: $M = -S, -S+1, \ldots, S$

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



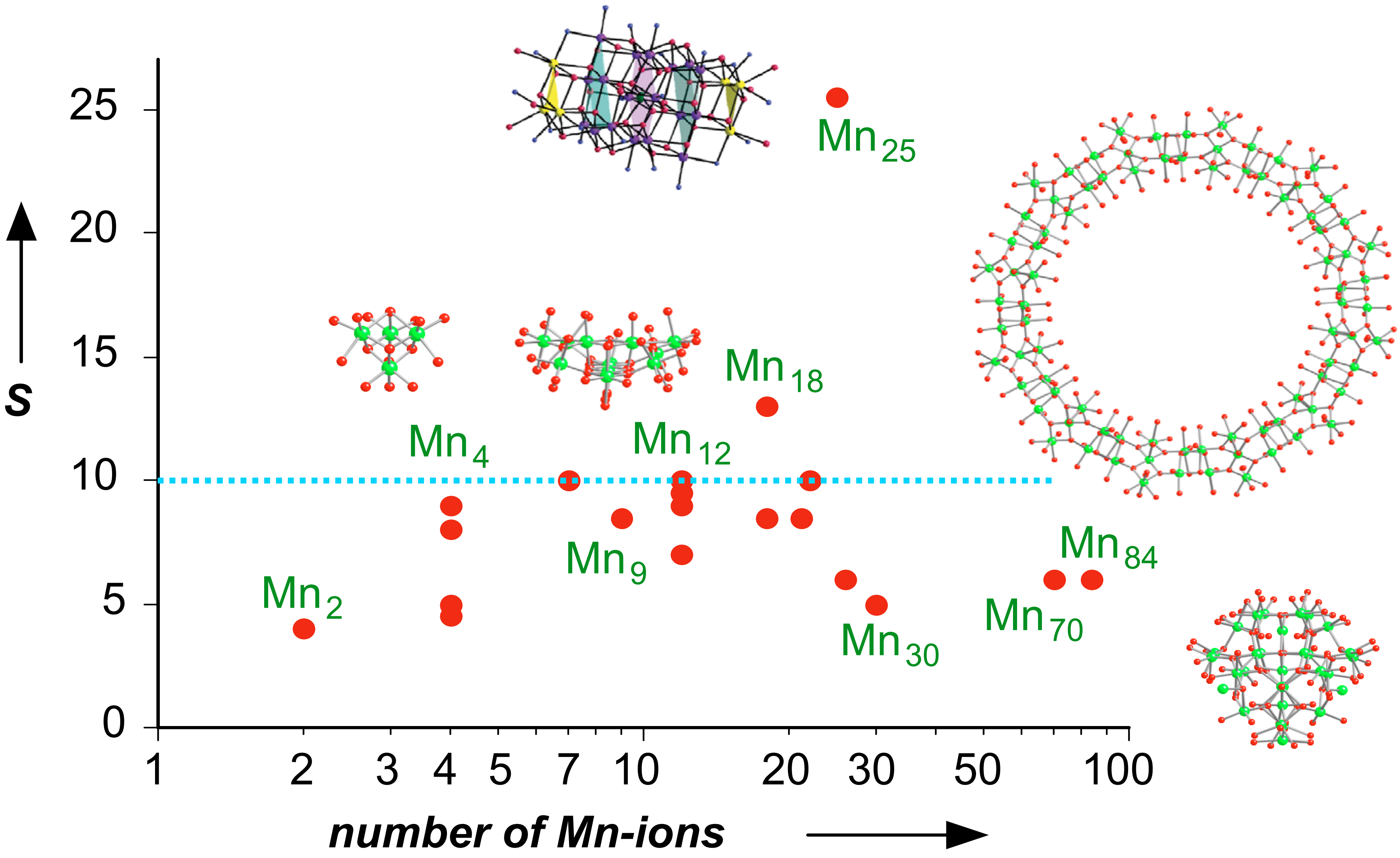
Anisotropy barrier

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

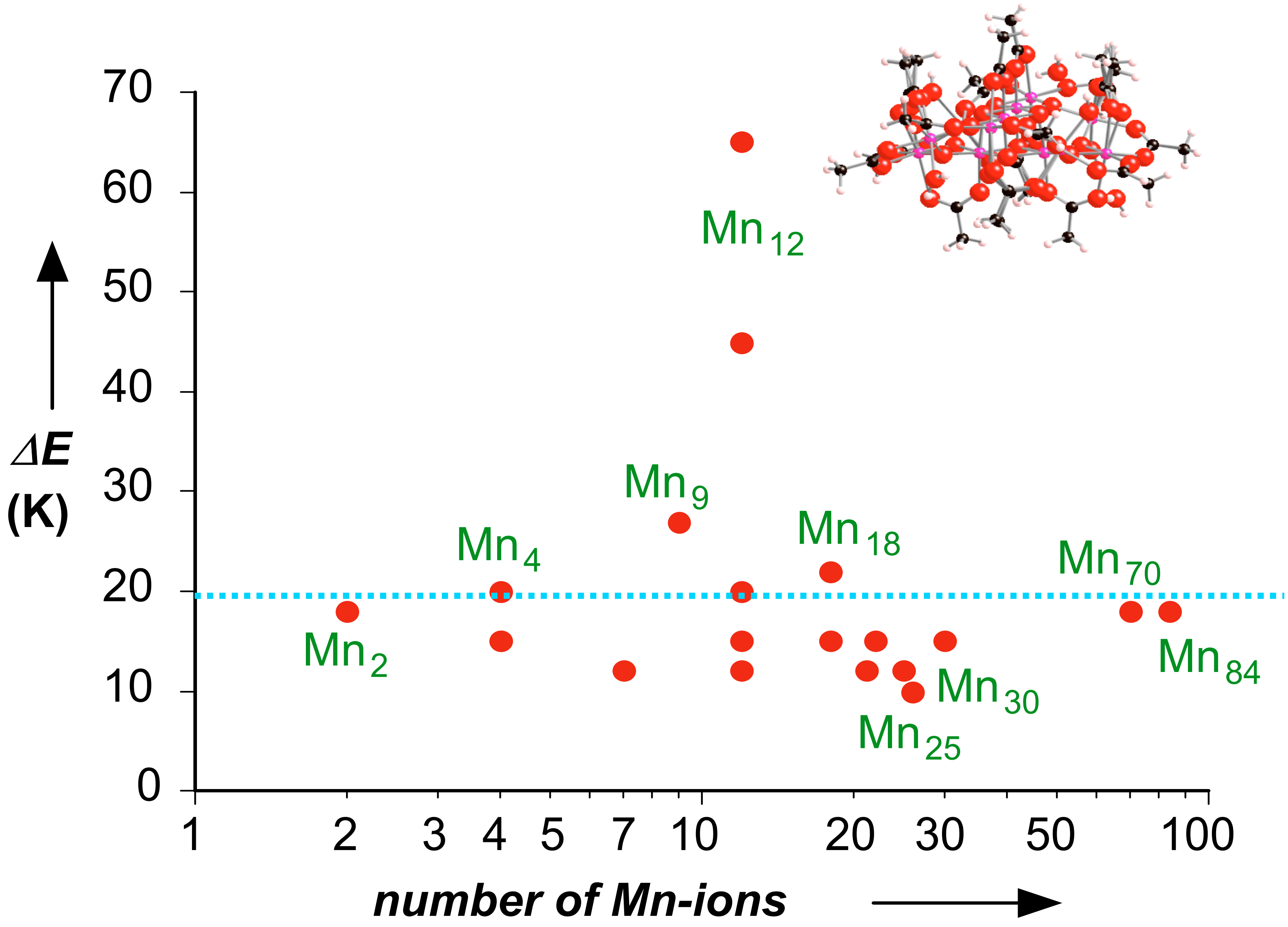
Anisotropy constant

Spin

Spin ground states of Mn based SMMs



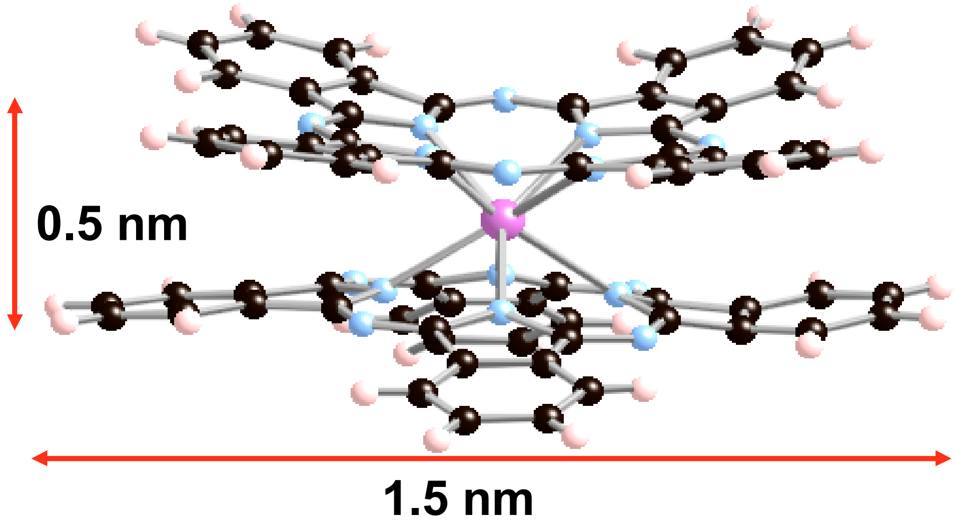
Anisotropy barriers of Mn based SMMs

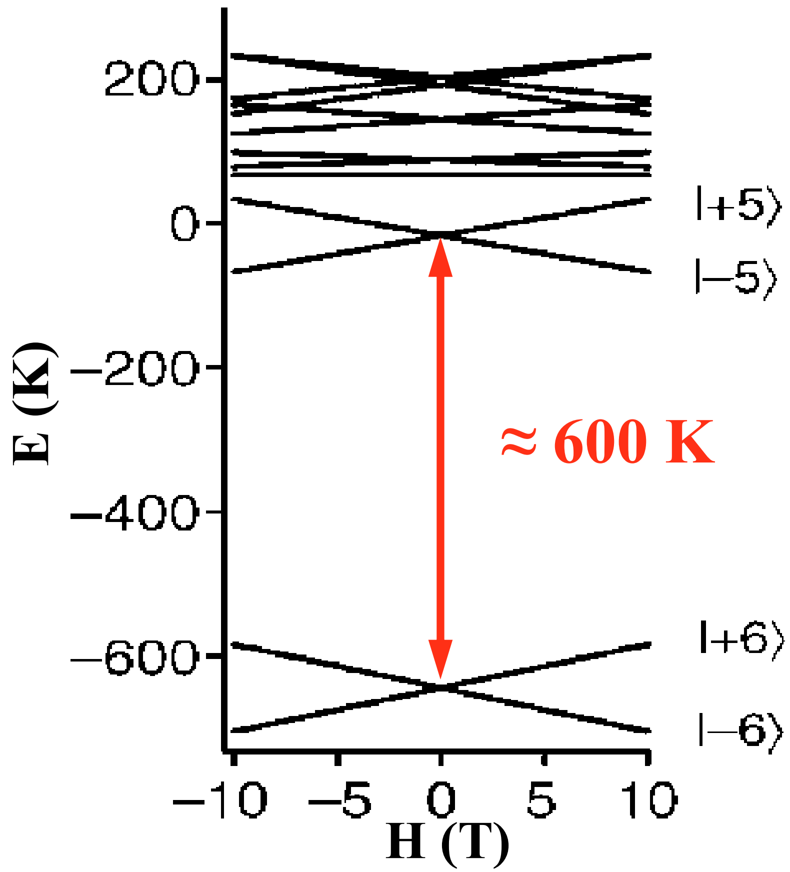


Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets

Bis(phthalocyaninato)terbium

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



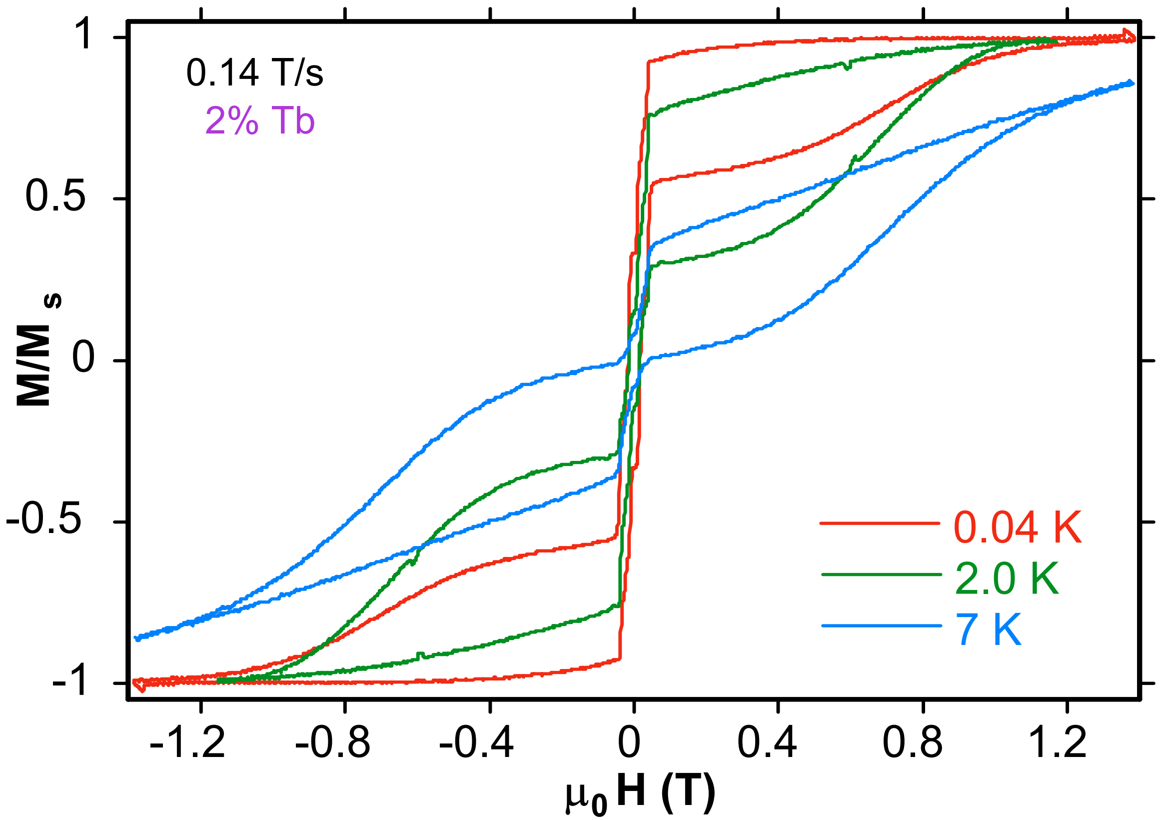


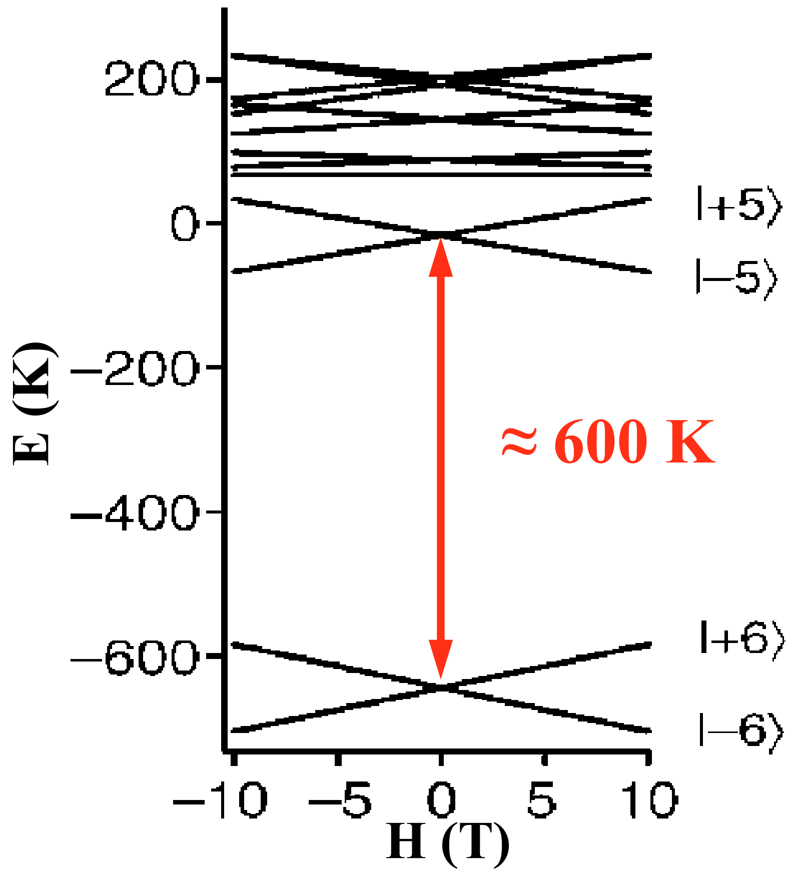
N.Ishikawa, et al.,
J.Phys.Chem. A 106, 9543 (2002)
J. Am.Chem.Soc. 125, 8694 (2003)
Inorg.Chem. 42, 2440 (2003)
J.Phys.Chem. A 107, 9543 (2003)
J. Phys.Chem.B 108, 11265 (2004)

Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets

Bis(phthalocyaninato)terbium

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

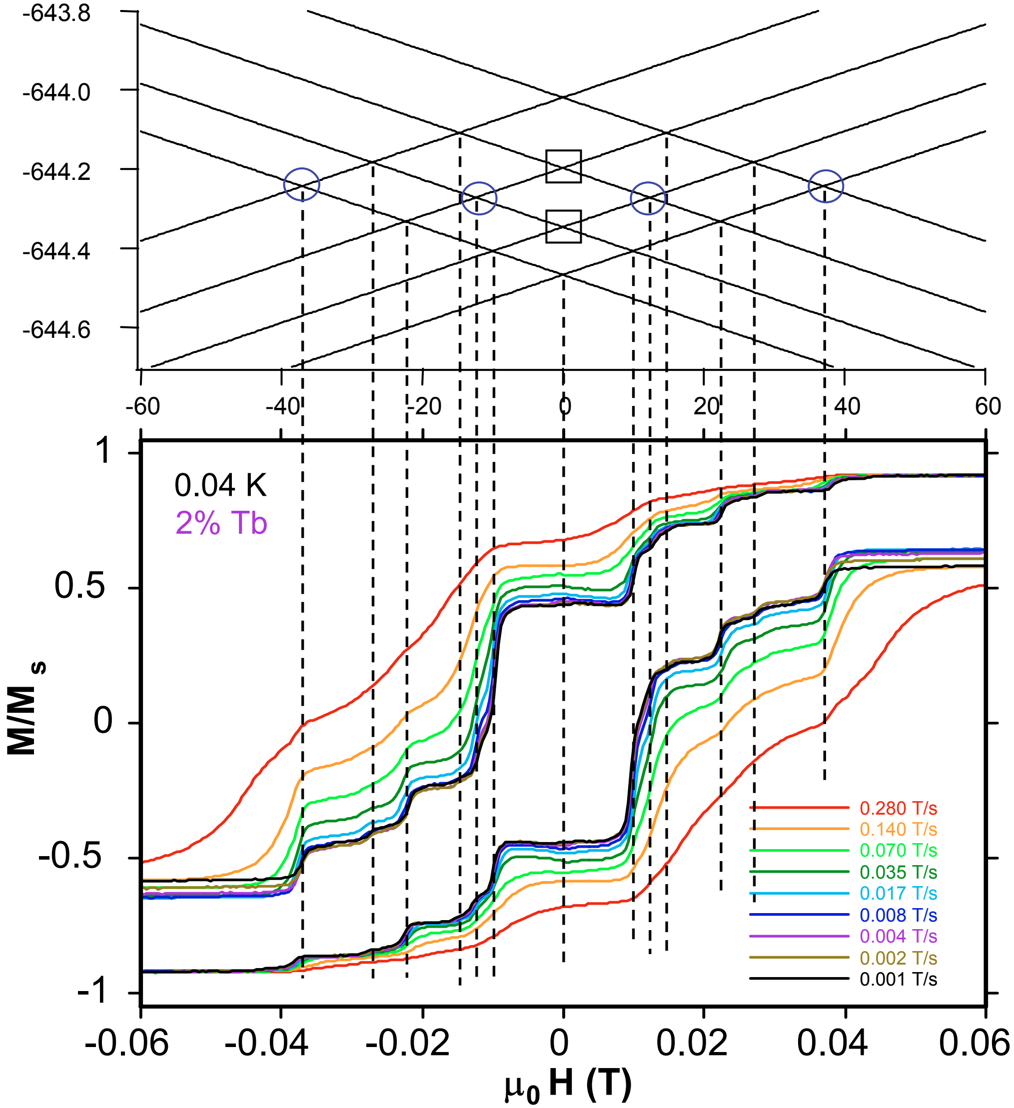




N. Ishikawa, M. Sugita, W. Wernsdorfer, Angew. Chem. Int. Ed. 44 ,2 (2005)

N. Ishikawa, M. Sugita, W. Wernsdorfer, J. Am. Chem. Soc. 127, 3650 (2005)

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



$A_{hf}=0.0173\text{cm}^{-1}$

$P_{quad}=0.010\text{cm}^{-1}$

○ :avoided crossing occurs by off-diagonal LF term

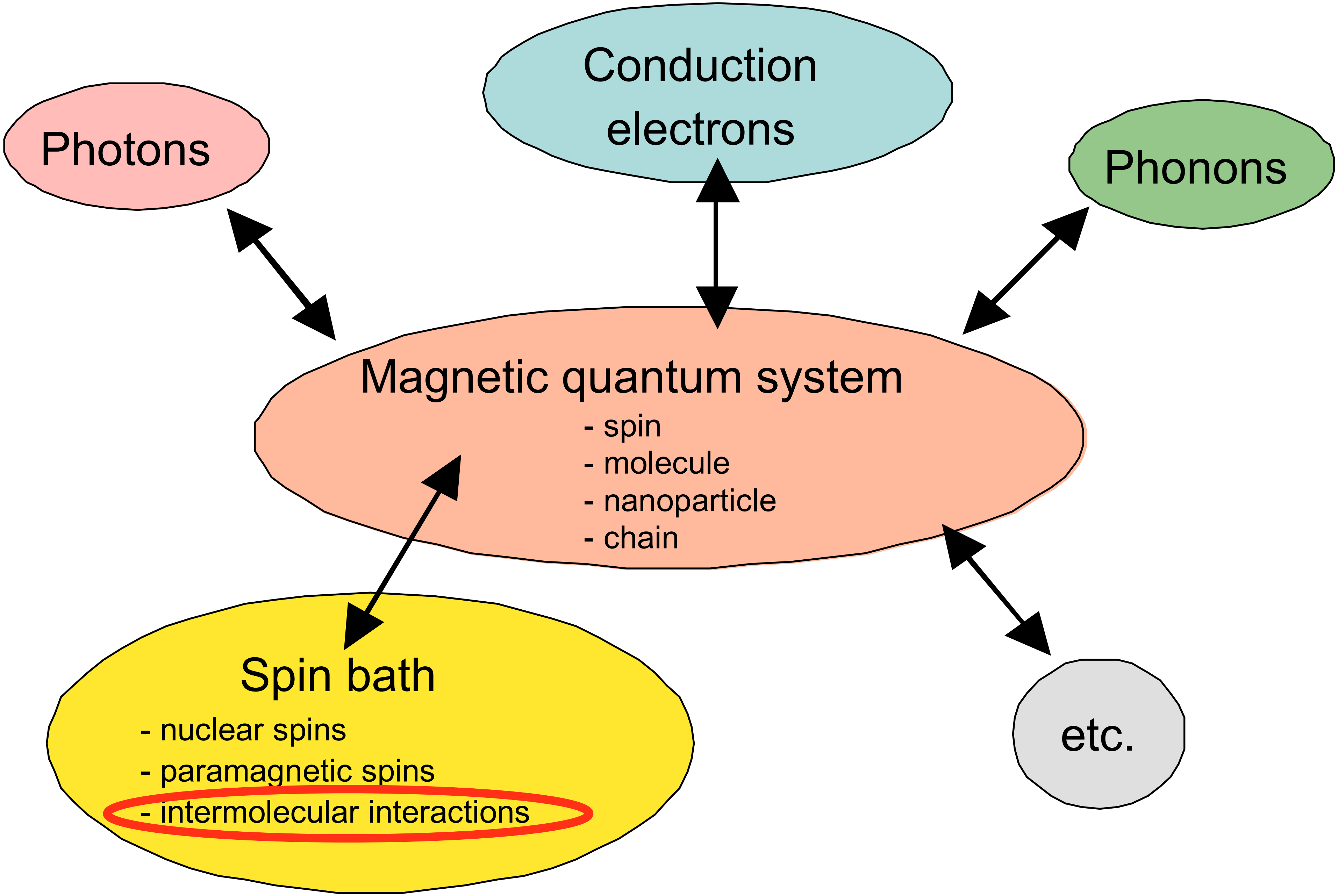
□ :avoided crossing occurs by transverse field

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)

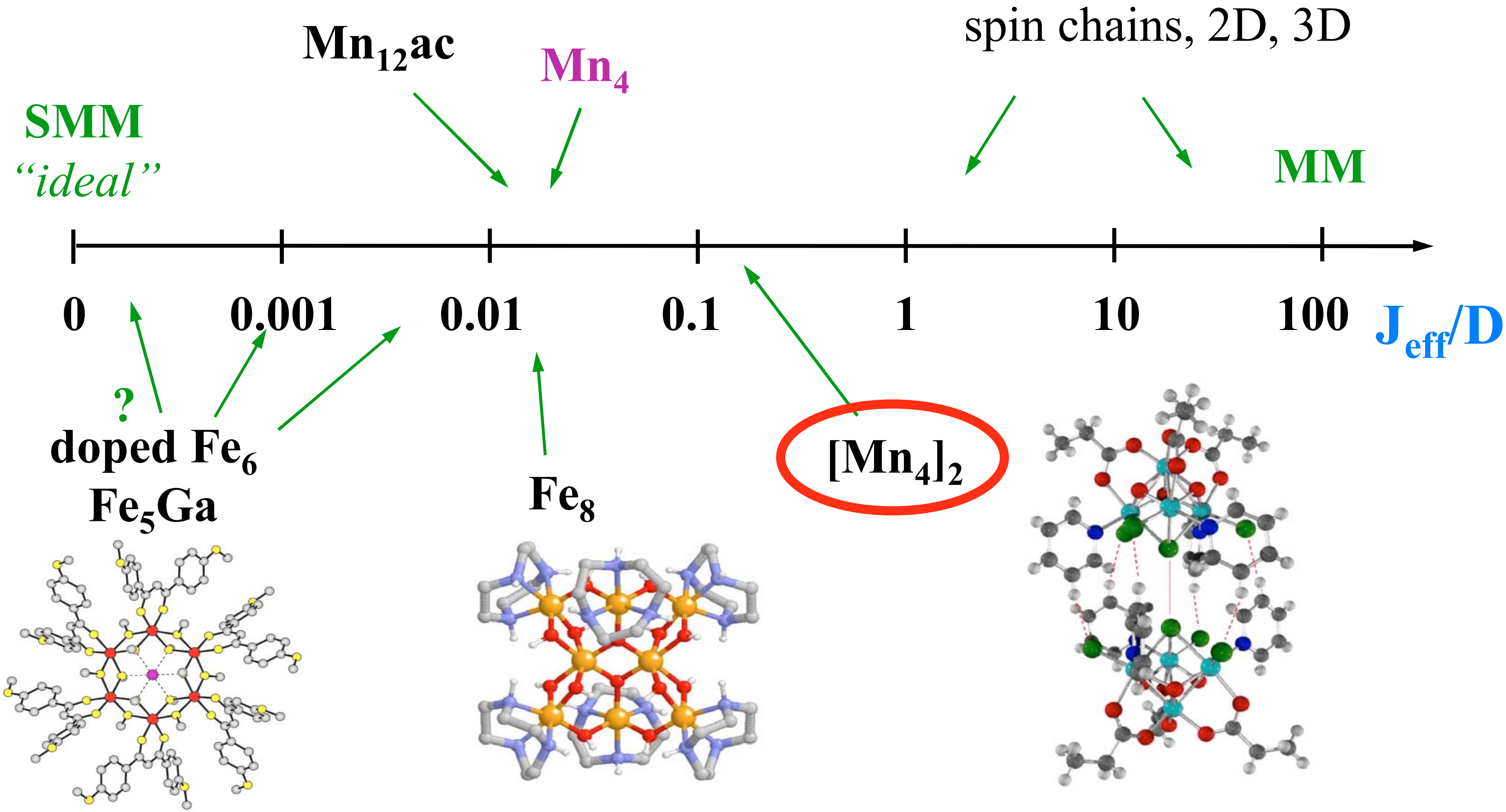
N. Ishikawa, M. Sugita, W. Wernsdorfer, J. Am. Chem. Soc. 127, 3650 (2005)

Interactions in magnetic quantum systems (decoherence)



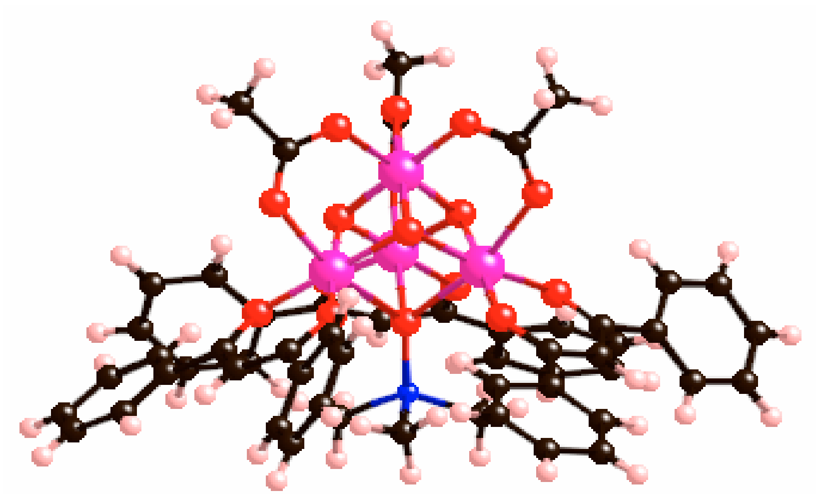
Intermolecular interactions J_{eff}

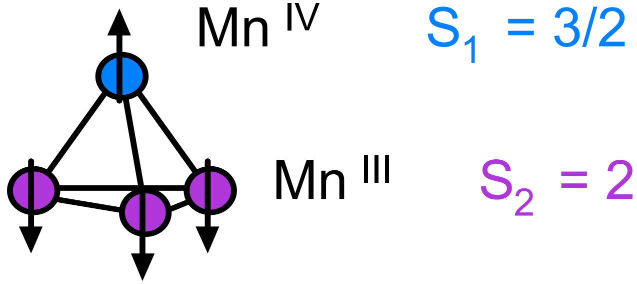
(dipolar and exchange)



Mn_4 single-molecule magnet

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



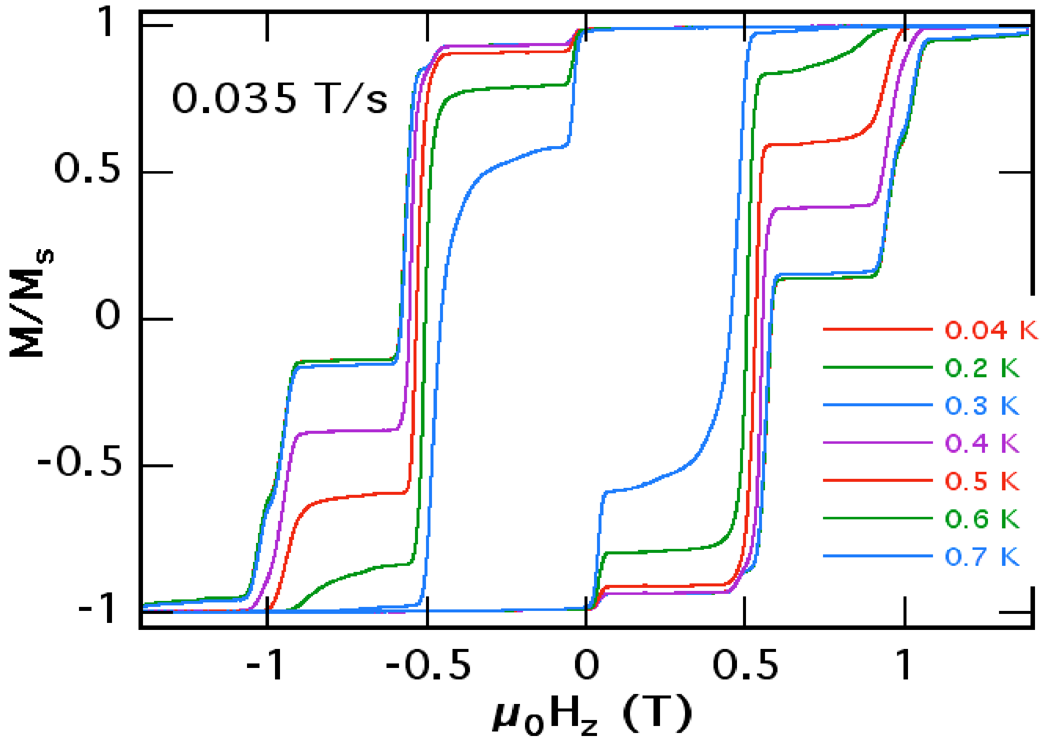


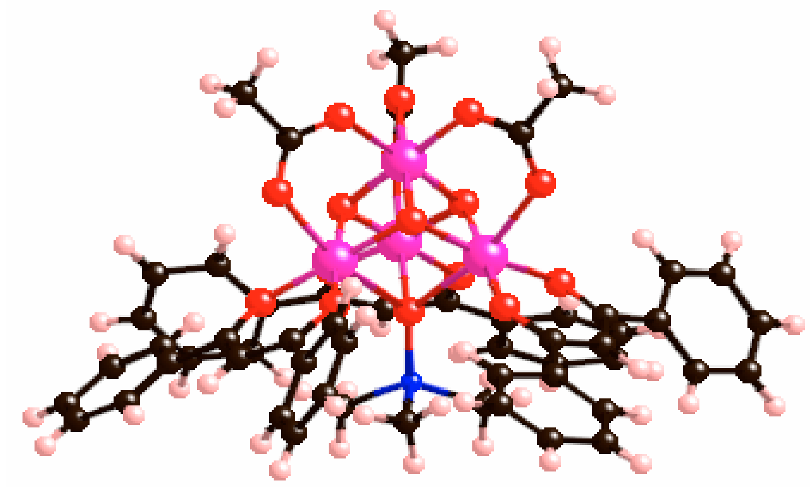
S = 9/2

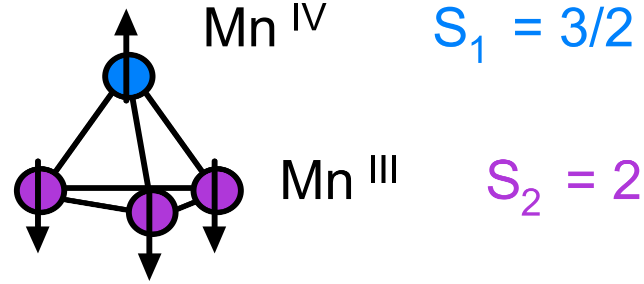
Group of G. Christou

Hysteresis loops of a Mn_4 single-molecule magnet

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



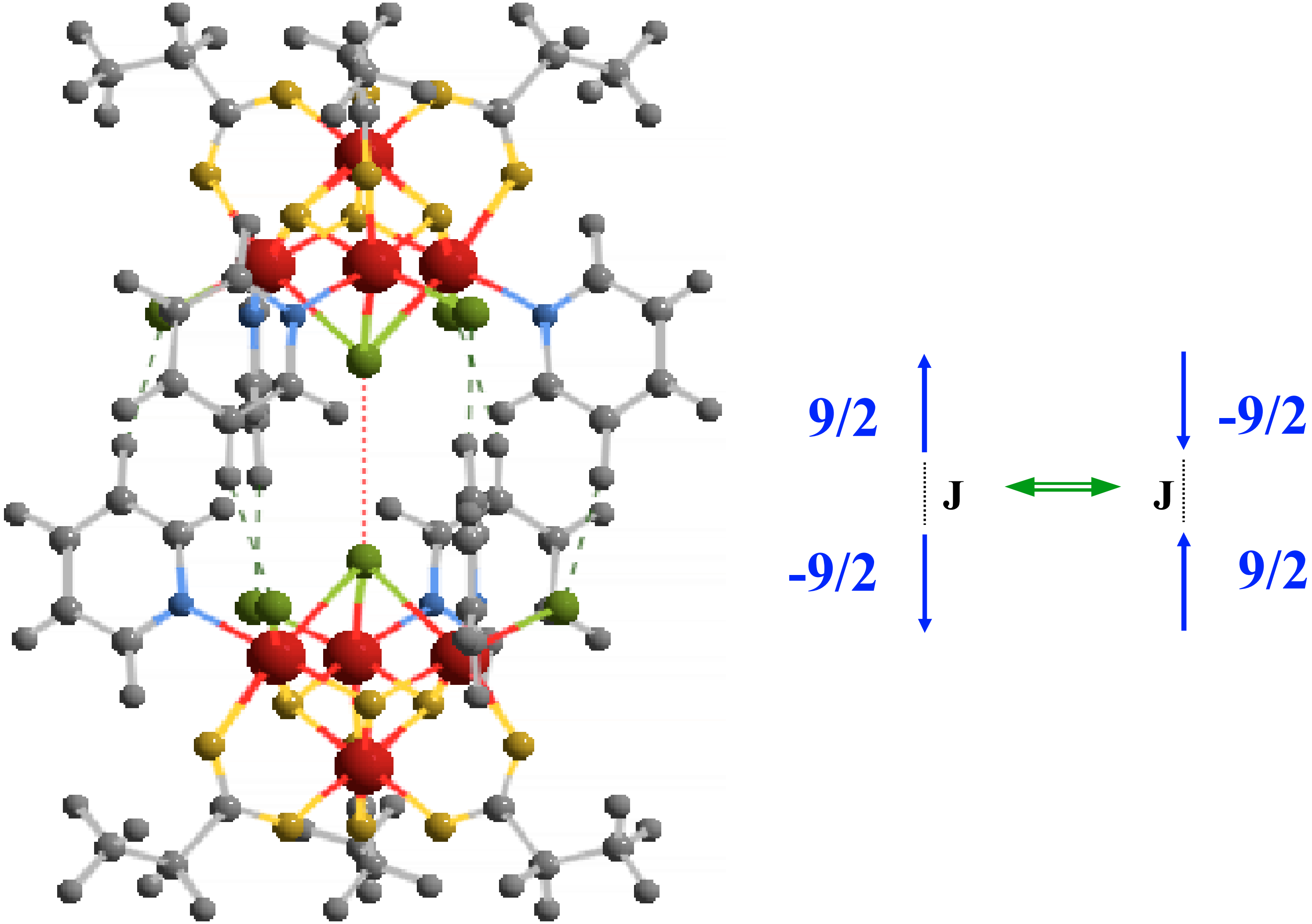




W. Wernsdorfer, S. Bhaduri, R. Tiron, D.N. Hendrickson, G. Christou, Phys. Rev. Lett. 89 (2002) 197201.

$S = 9/2$

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



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

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

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

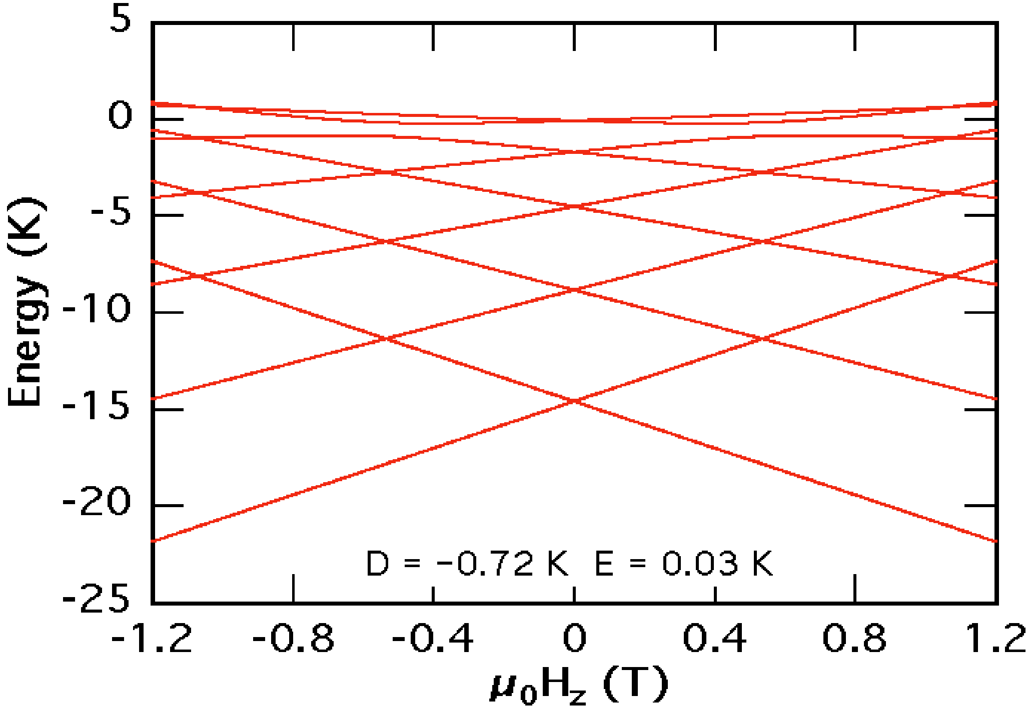
$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + J\,\vec{S}_1\vec{S}_2$$

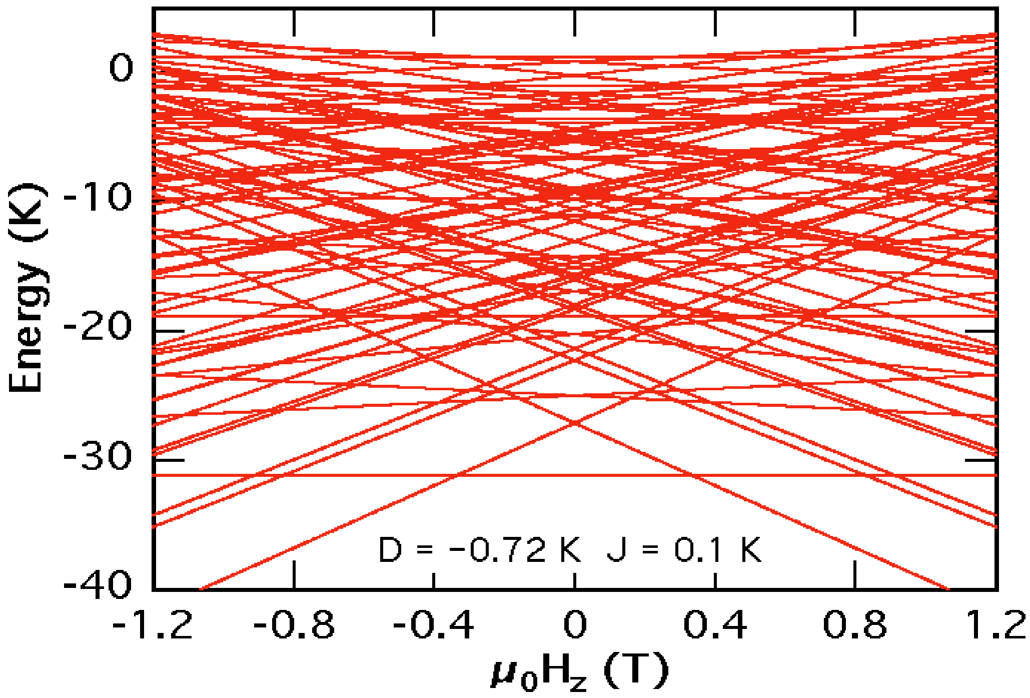
$(2S_1 + 1)(2S_2 + 1)$ energy states

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

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

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



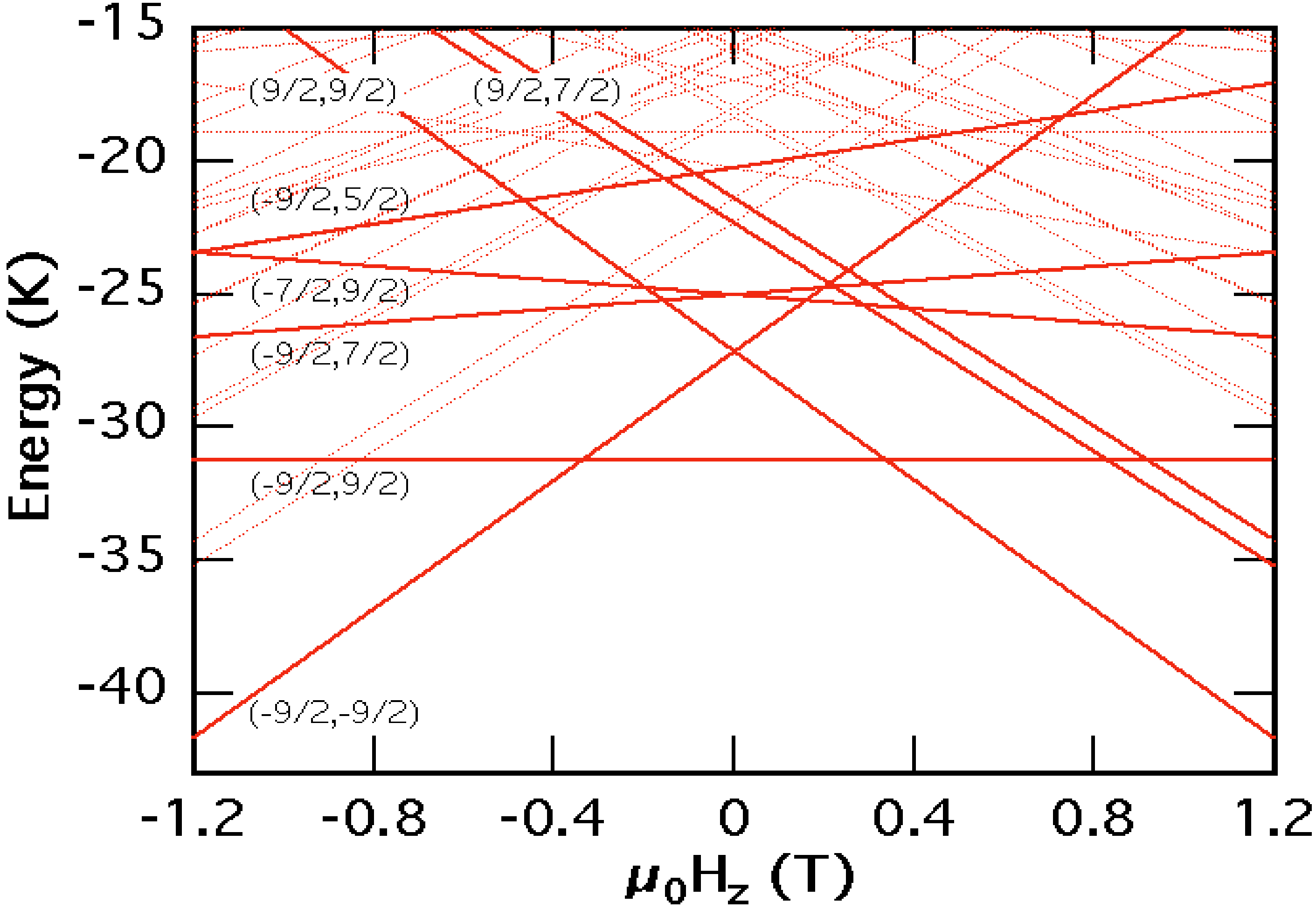


Exchange coupled dimer of S = 9/2

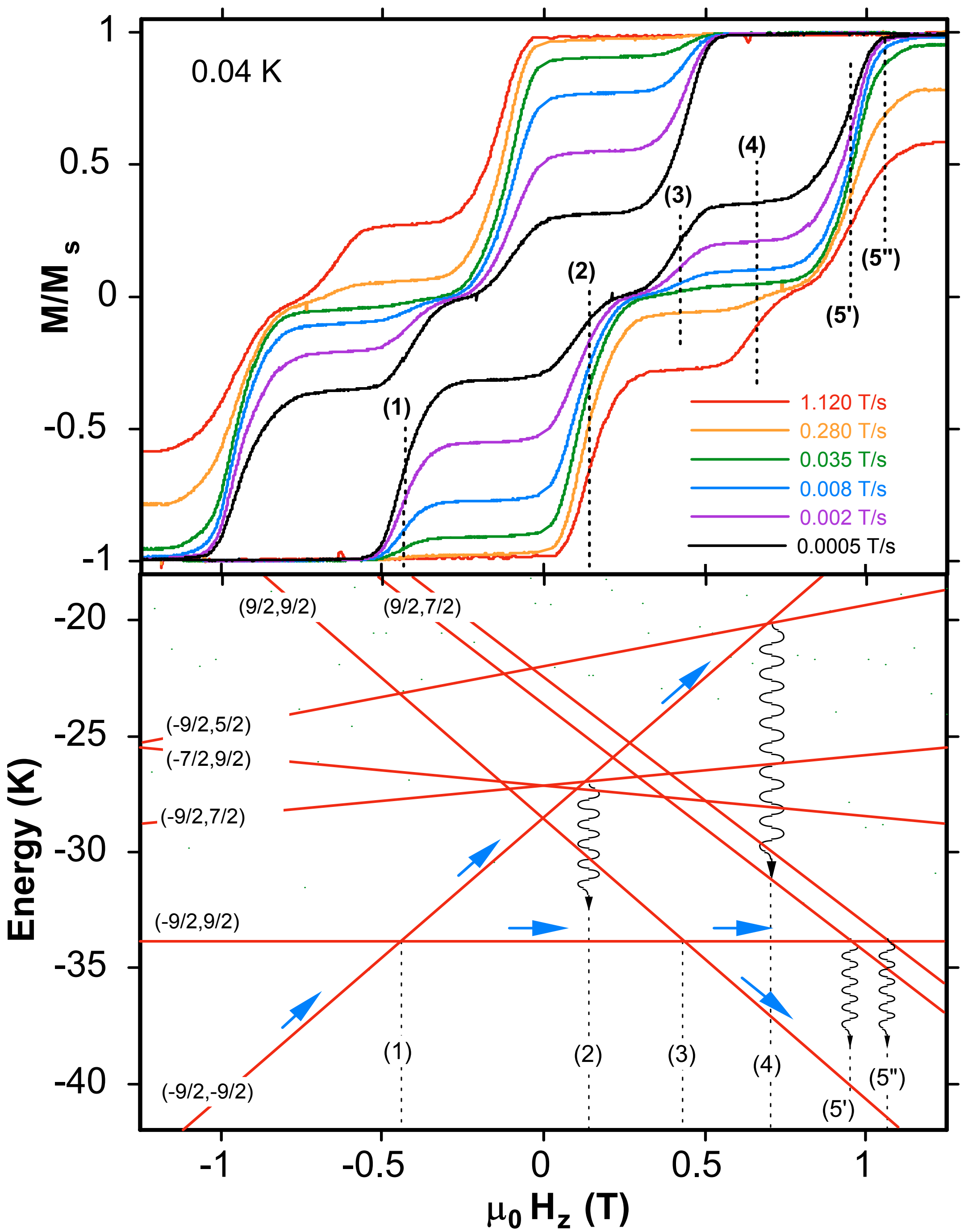
$$H = H_1 + H_2 + J\,\vec{S}_1\vec{S}_2$$

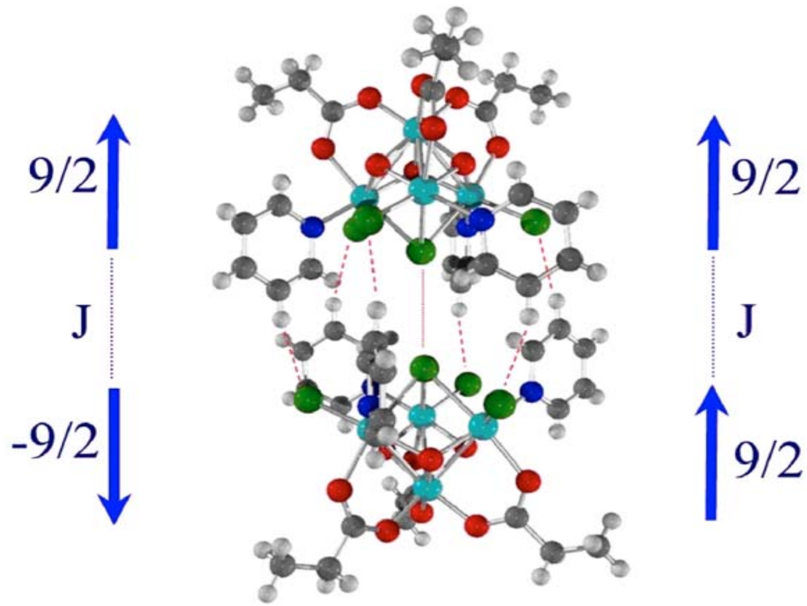
$$H_i = -D\,S_{i,z}^2 + H_i^{trans} + g\mu_B\mu_0\,\vec{S}_i\,\vec{H}$$

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



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

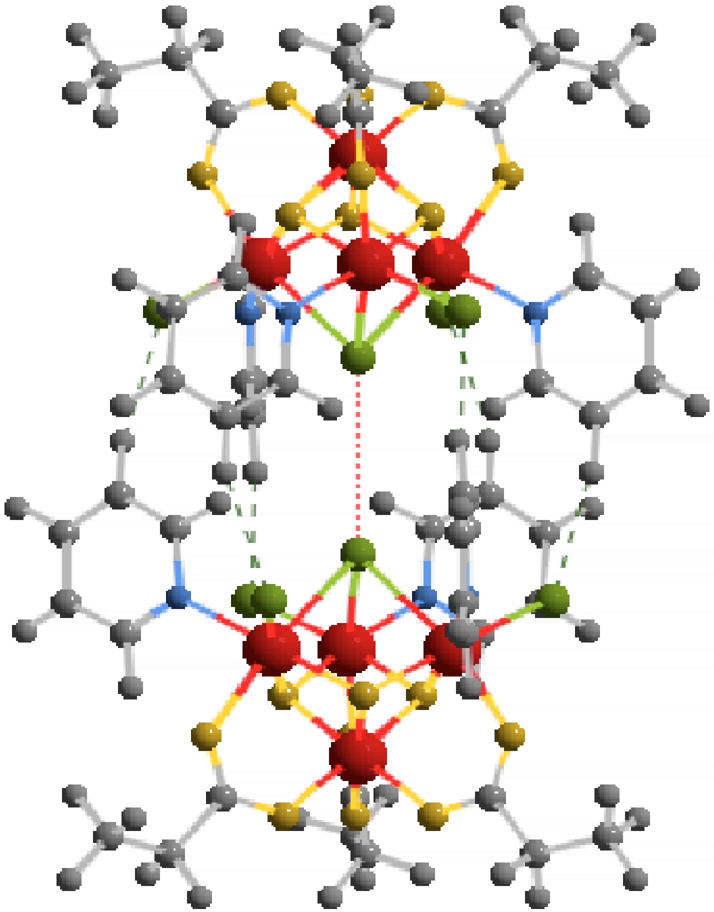


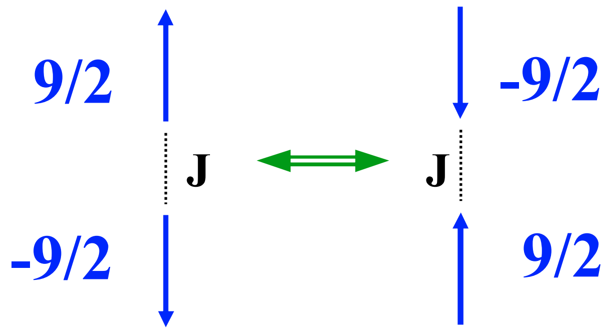


W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson & G. Christou
Nature **416**, 406 (28 March 2002)

Why is this dimer so interesting ?

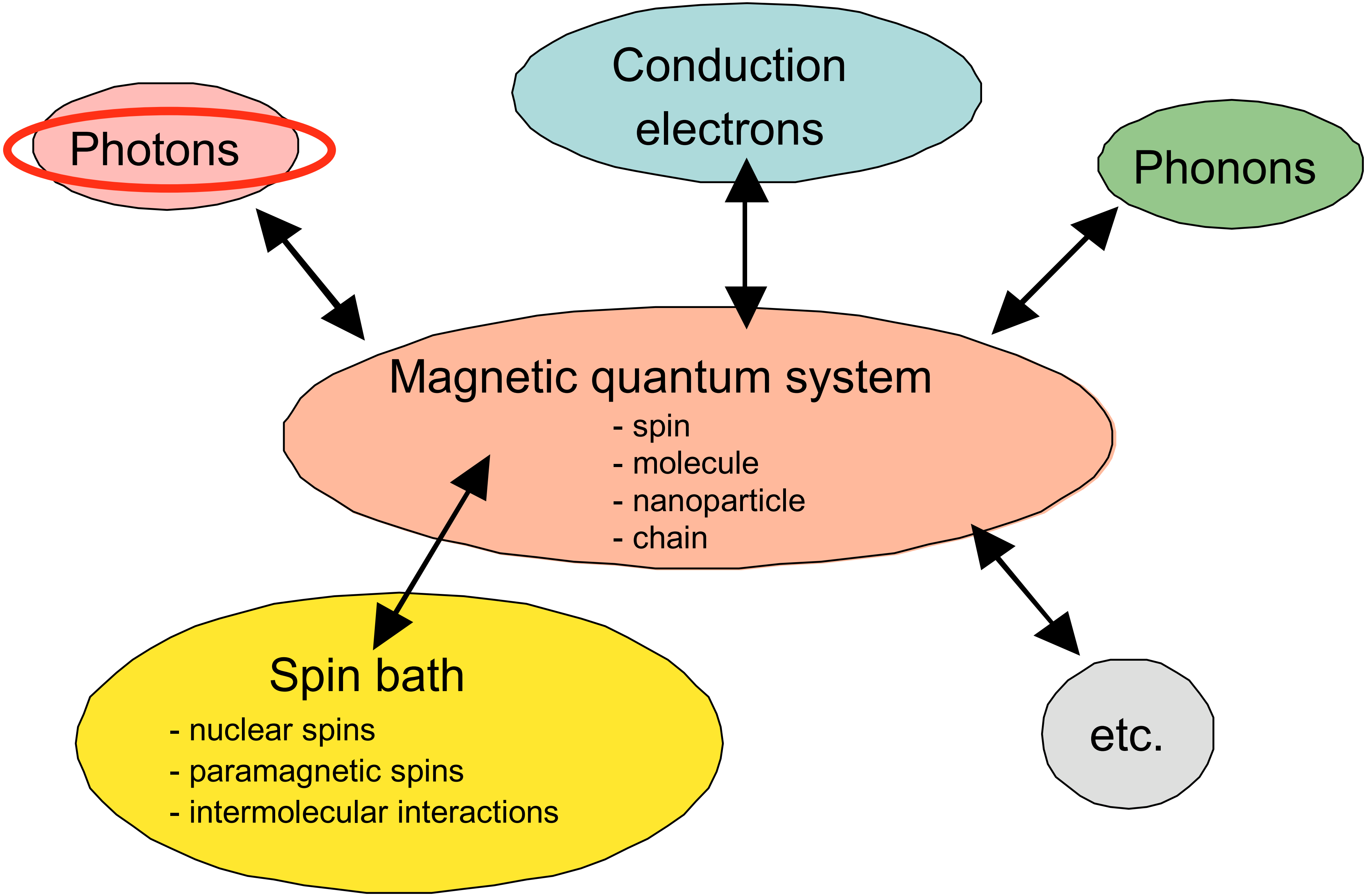
- Possibility of tuning quantum properties (resonance positions)
- Coupled mesoscopic quantum system
- Model system for tunneling in mesoscopic antiferromagnets
- Important step towards coupled quantum bits





W. Wernsdorfer, N. Aliaga-Alcalde,
D. N. Hendrickson & G. Christou
Nature **416**, 406 (2002)
R. Tiron, et al.,
Phys. Rev. Lett. 91, 227203 (2003)

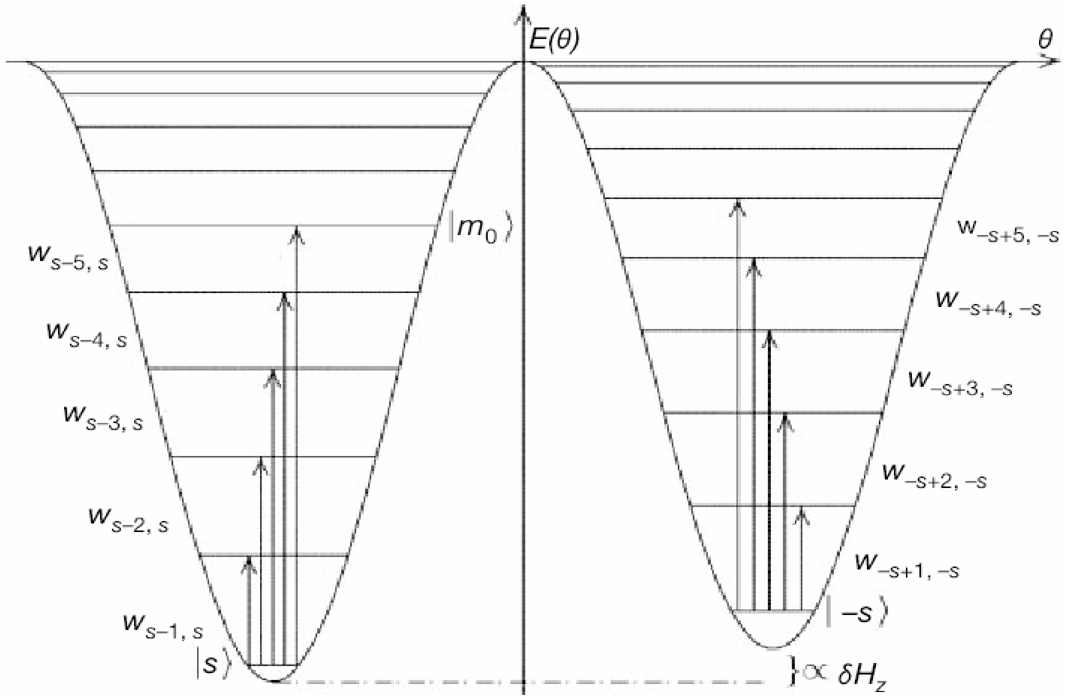
Interactions in magnetic quantum systems (decoherence)

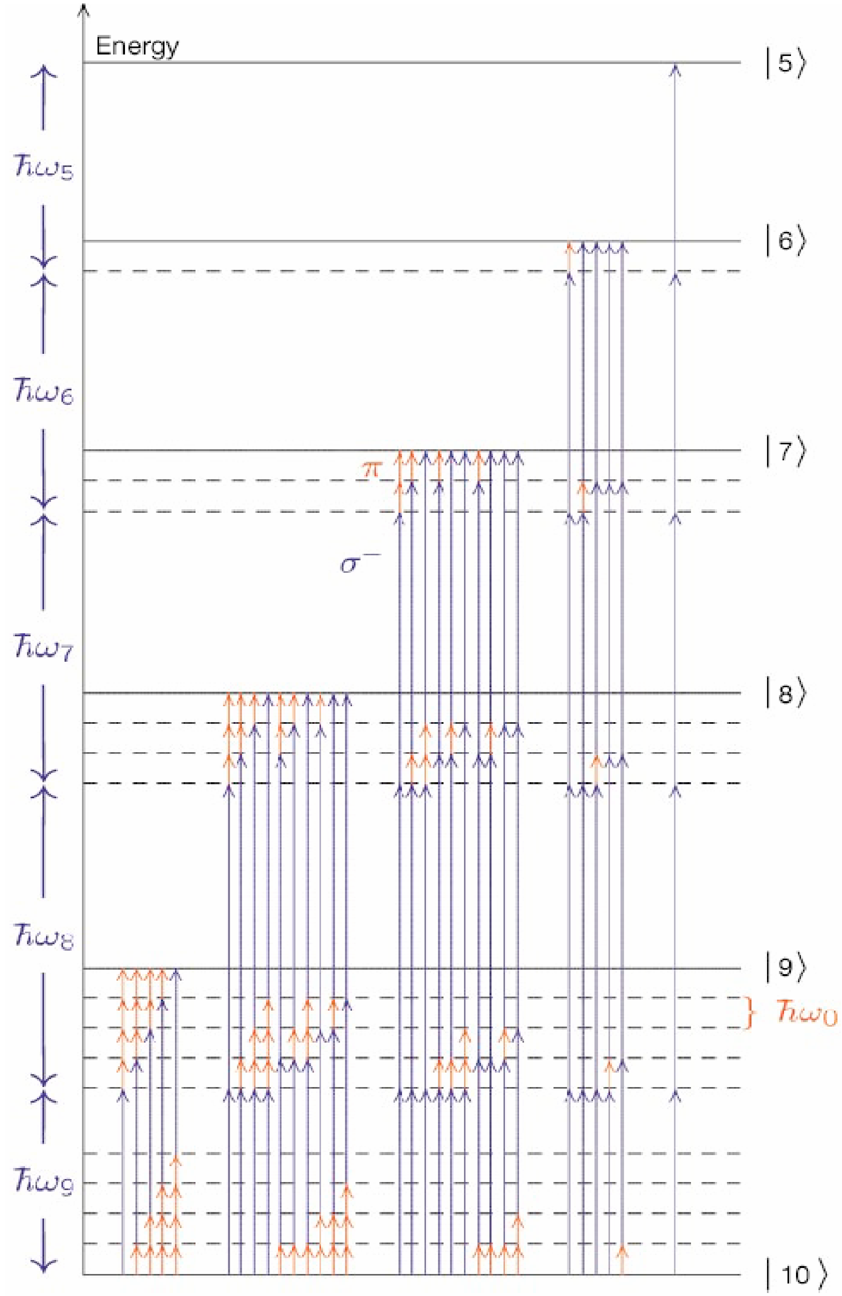


Quantum computing in molecular magnets

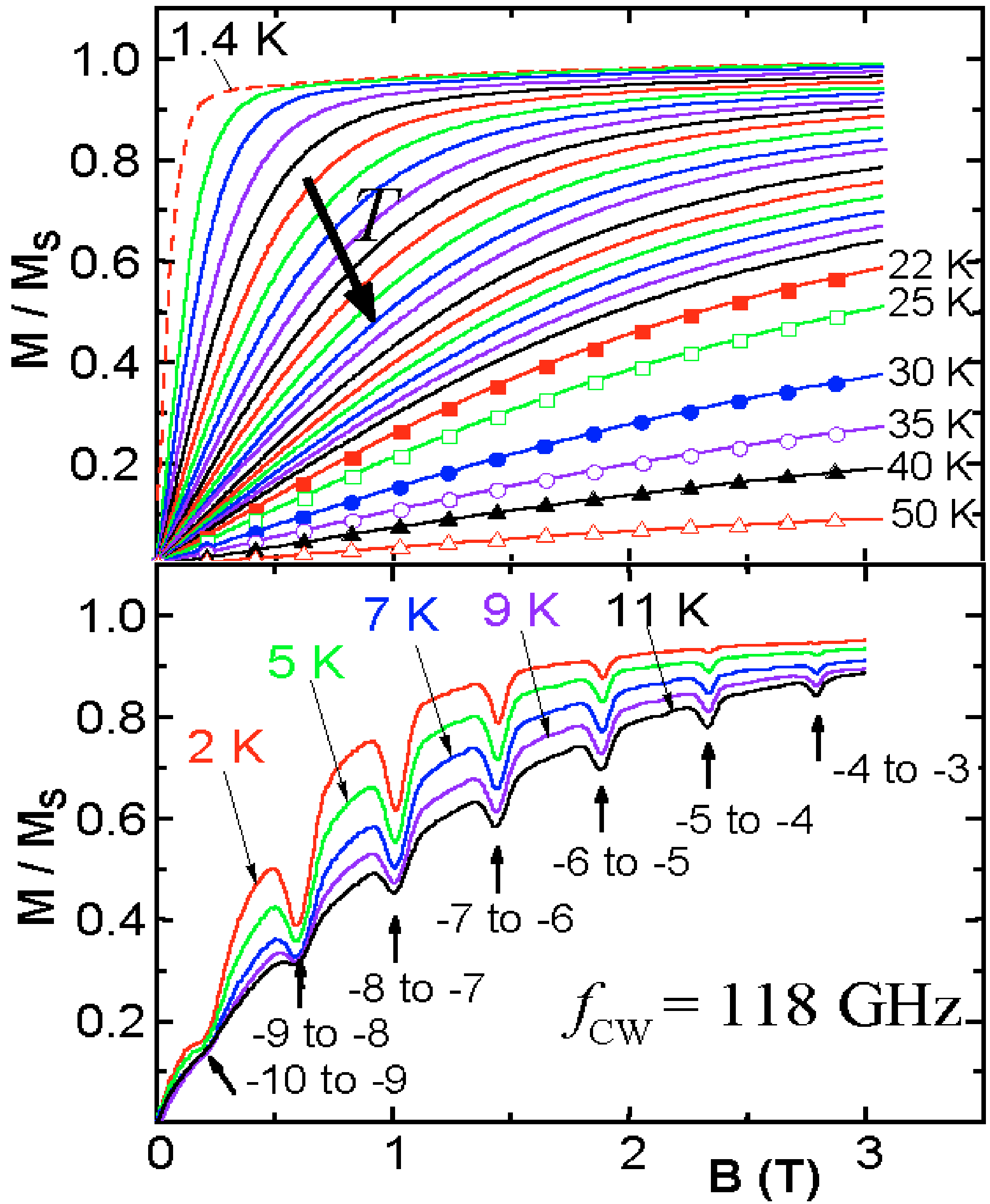
Michael N. Leuenberger & Daniel Loss NATURE, 410, 791 (2001)

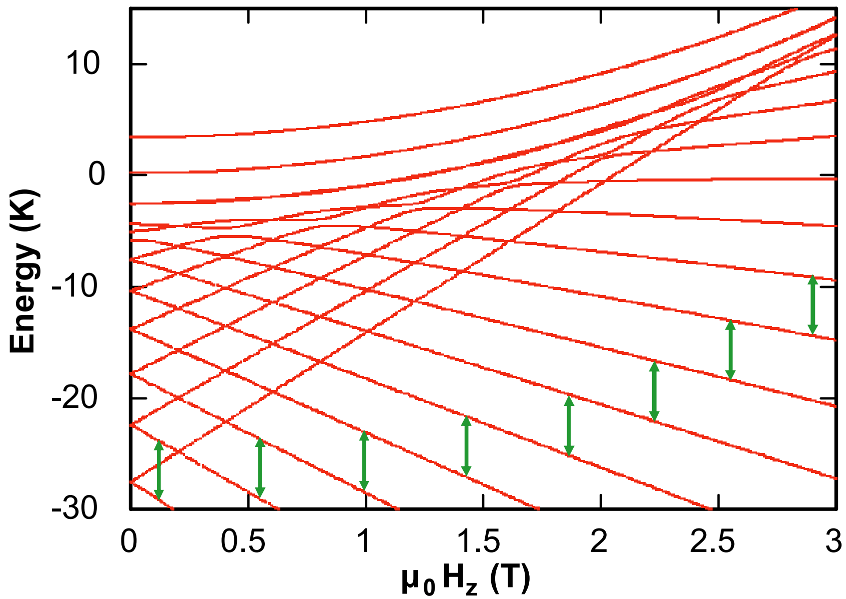
- implementation of Grover's algorithm
- storage unit of a dynamic random access memory device.
- fast electron spin resonance pulses can be used to decode and read out stored numbers of up to 10^5 with access times as short as 0.1 nanoseconds.





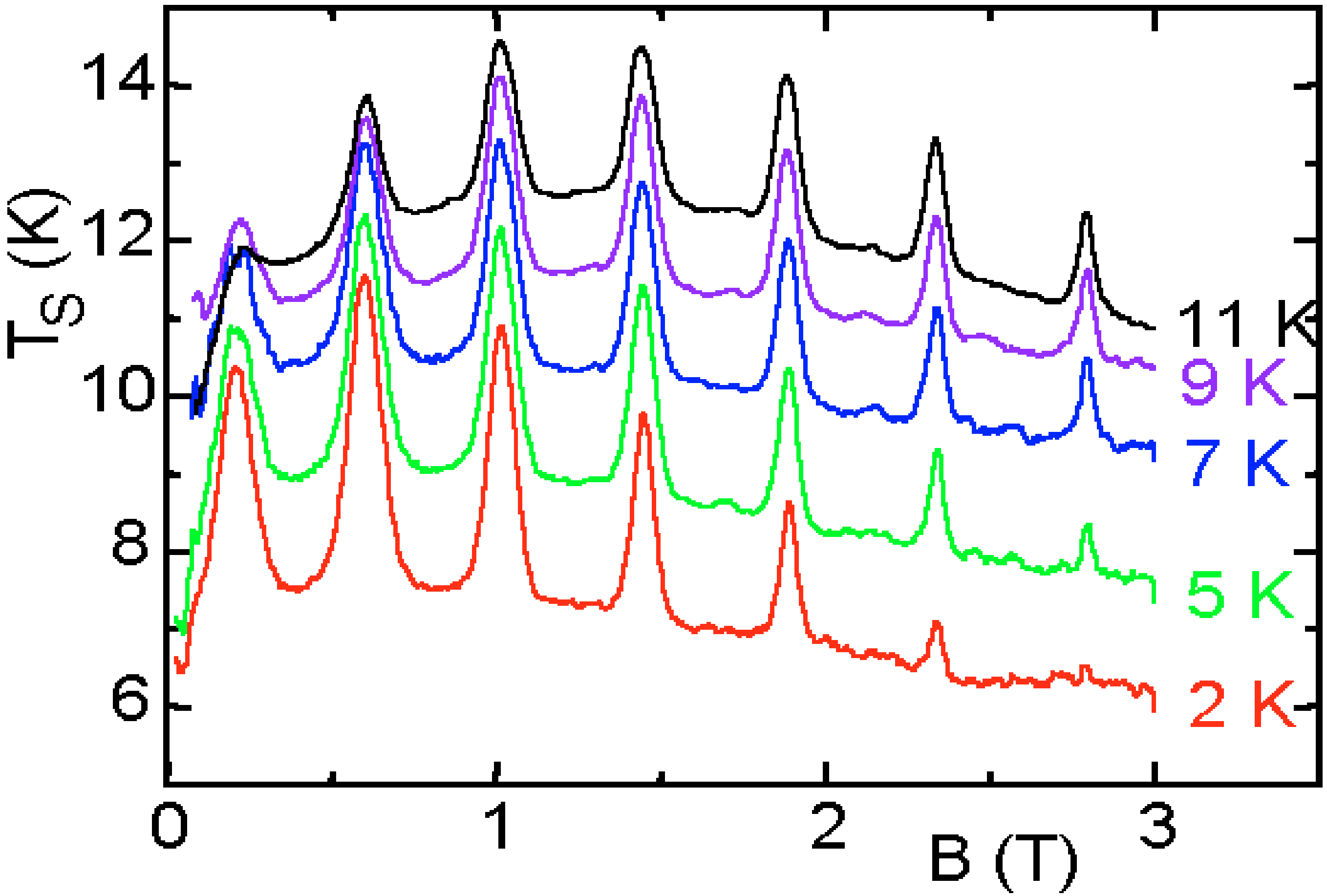
Resonant photon absorption in Fe_8 detected via magnetization measurements





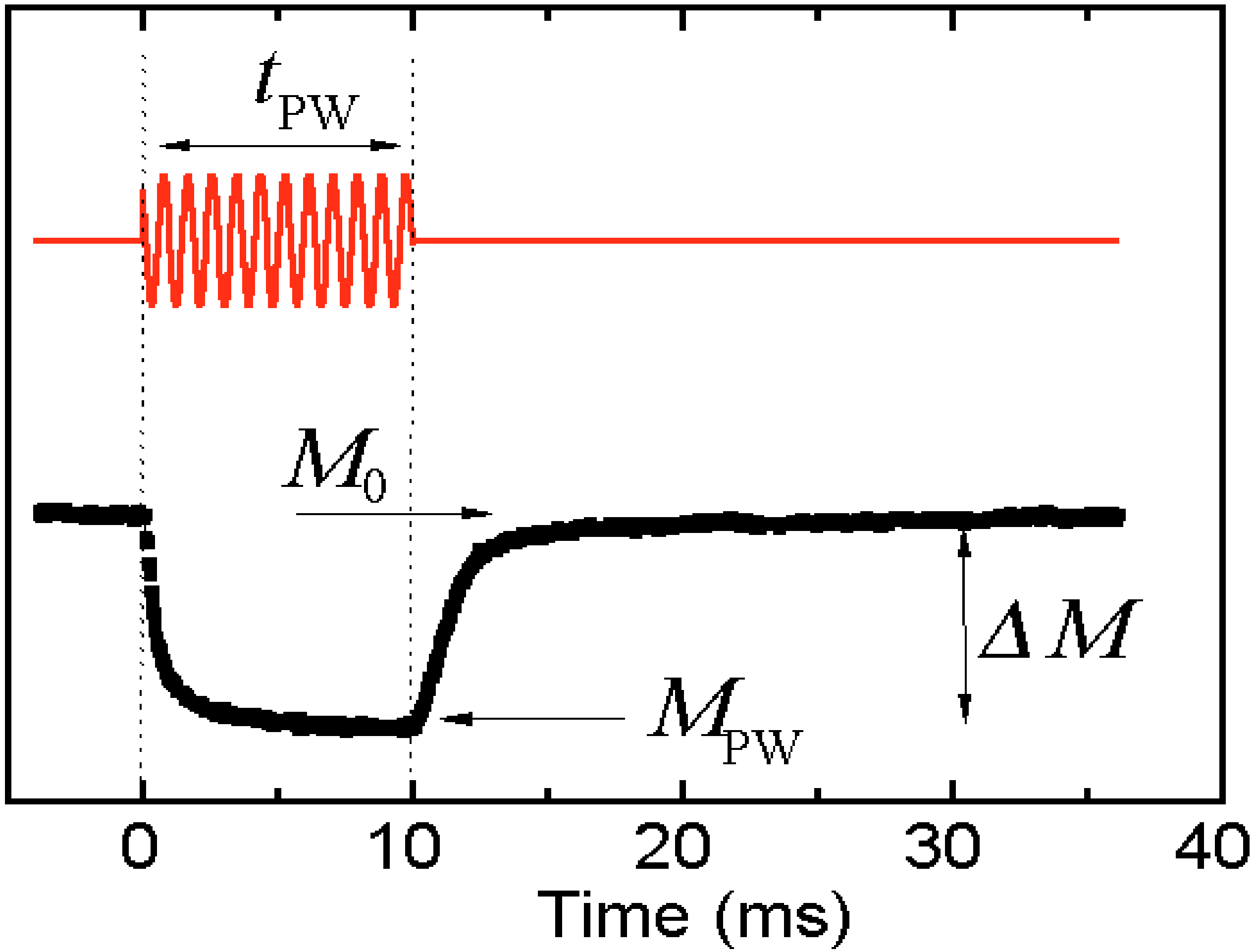
➤ *like HF-EPR*

Spin temperature TS versus applied field calculated using a mapping procedure

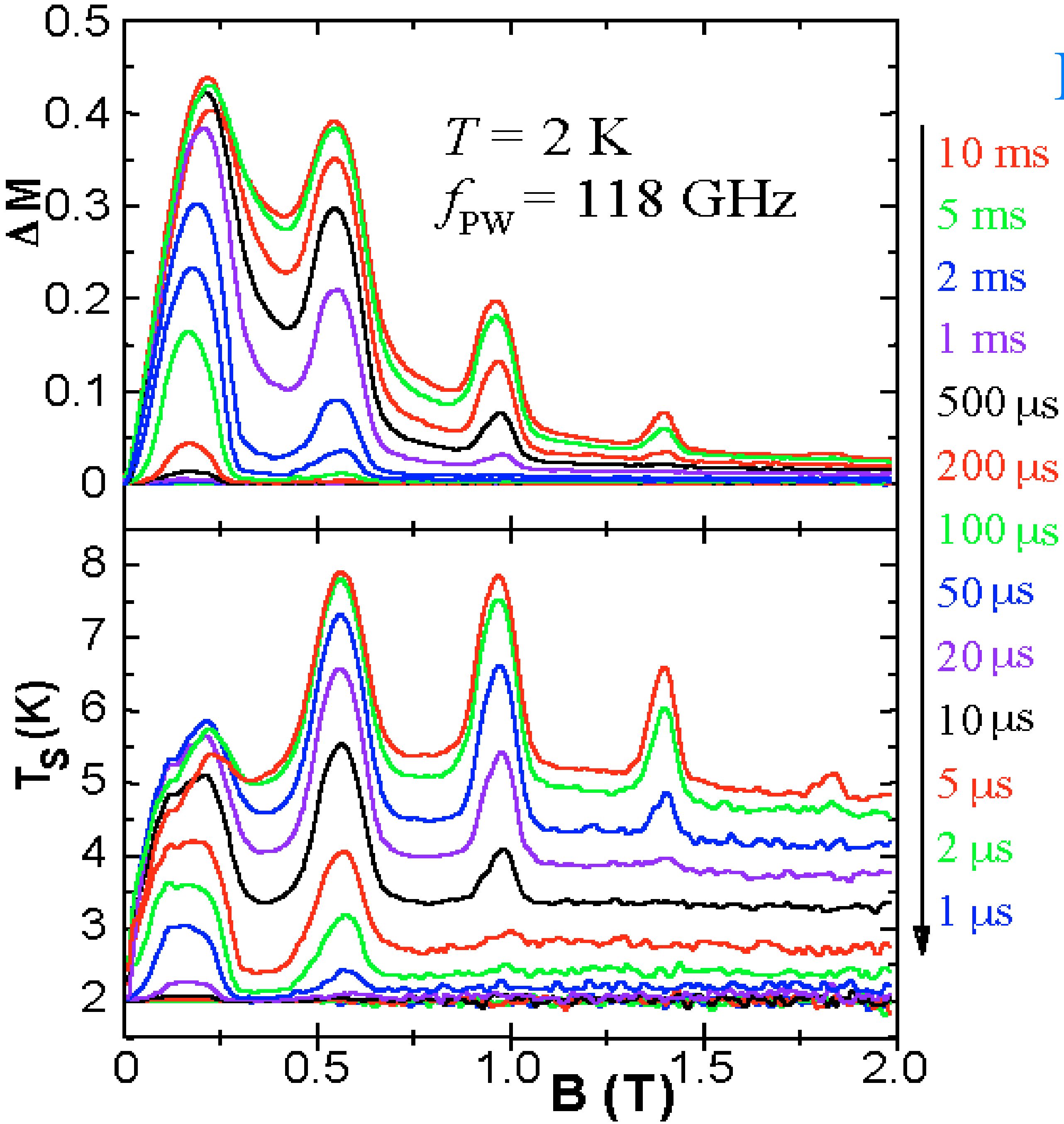


➢ ***quantitative HF-EPR***

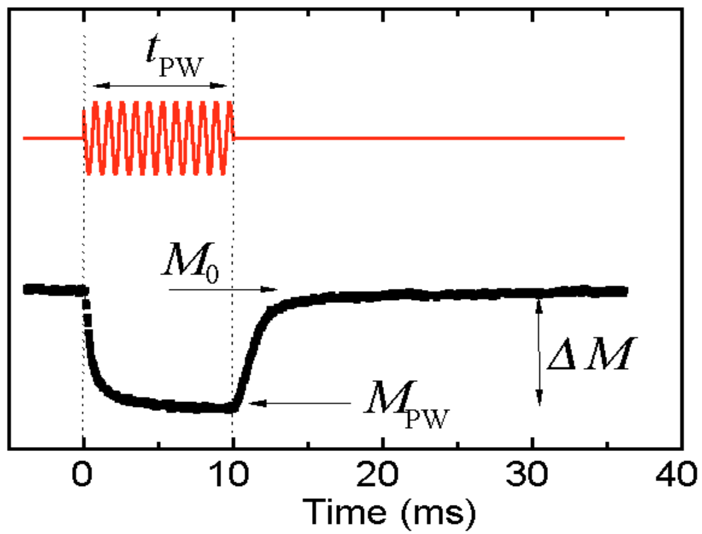
Pulsed microwave irradiation



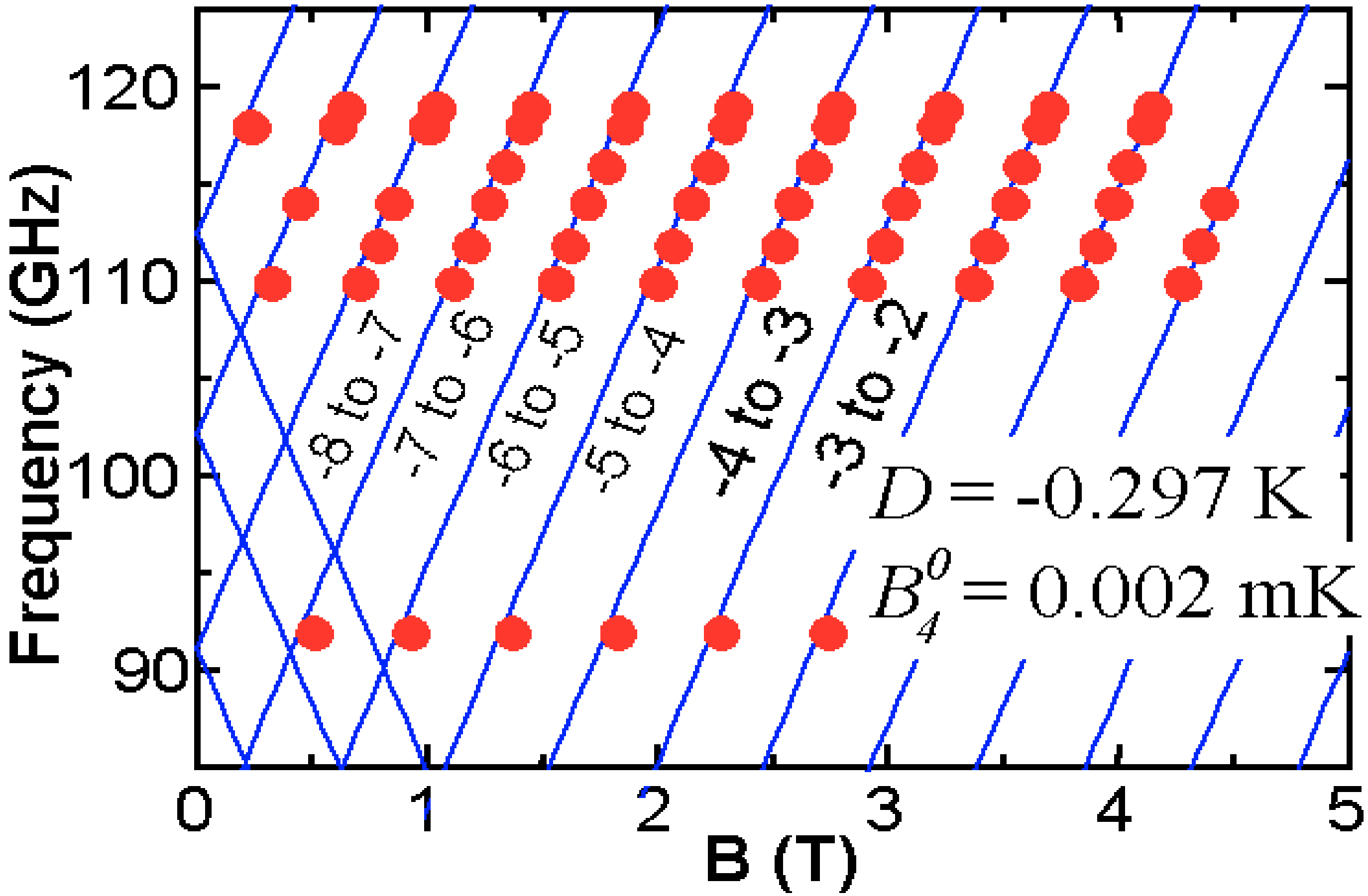
Pulsed microwave irradiation



> ➢ *quantitative HF-EPR*



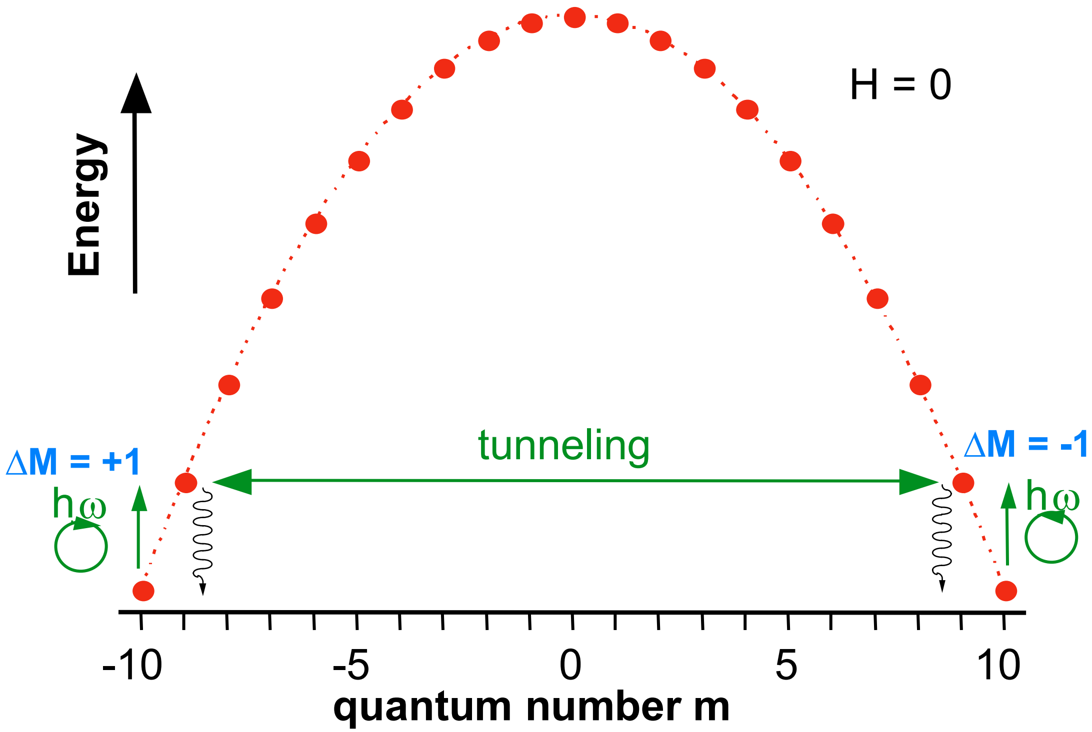
Resonant photon absorption in Fe_8 detected via magnetization measurements

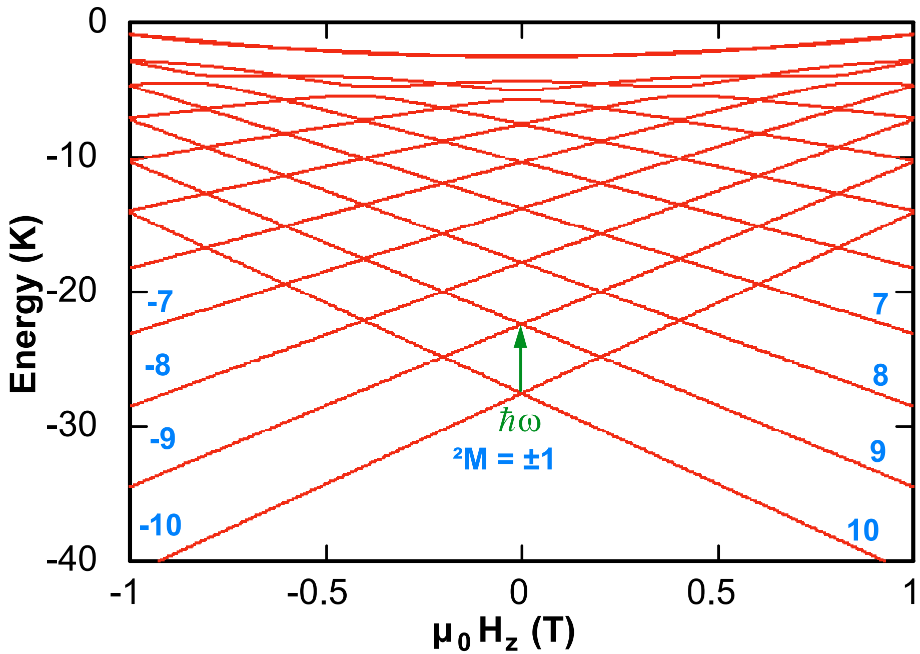


➢ *Simultanously hysteresis and EPR studies on the same micro crystal*

Photon assisted tunneling

Absorption of circular polarized microwaves

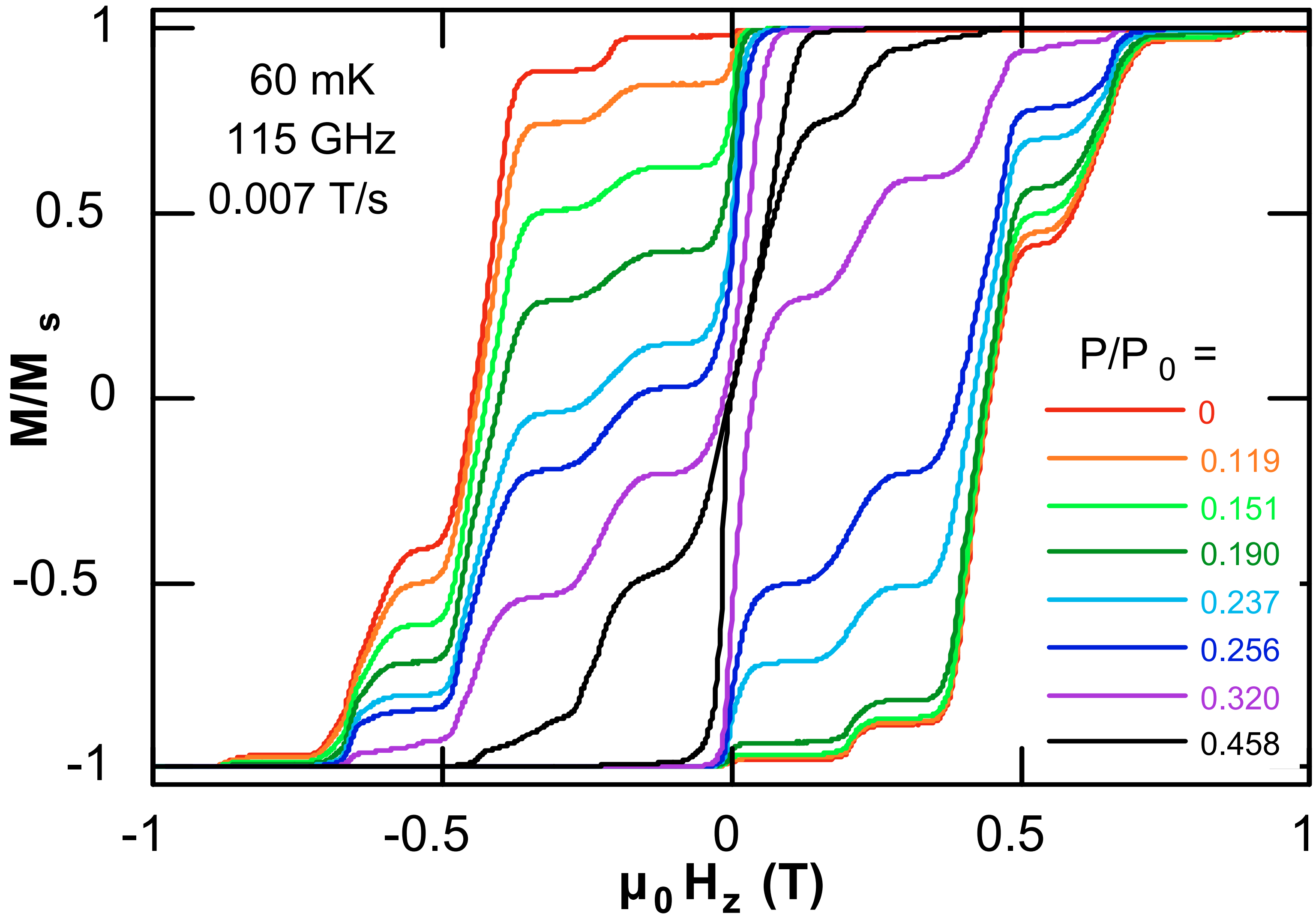




PRB 68, 220407(R) (2003)

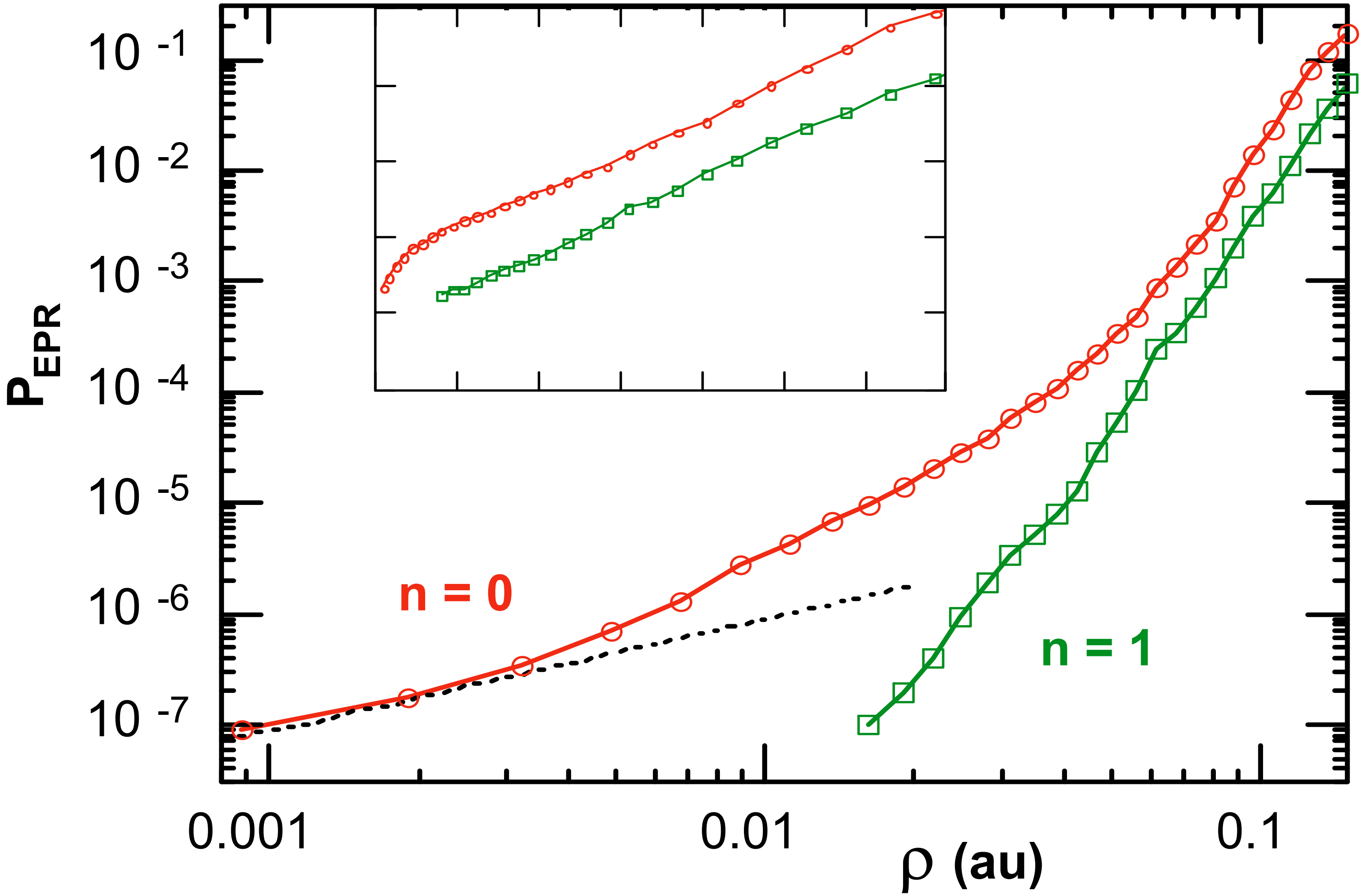
Absorption of circular polarized microwaves (115 GHz)

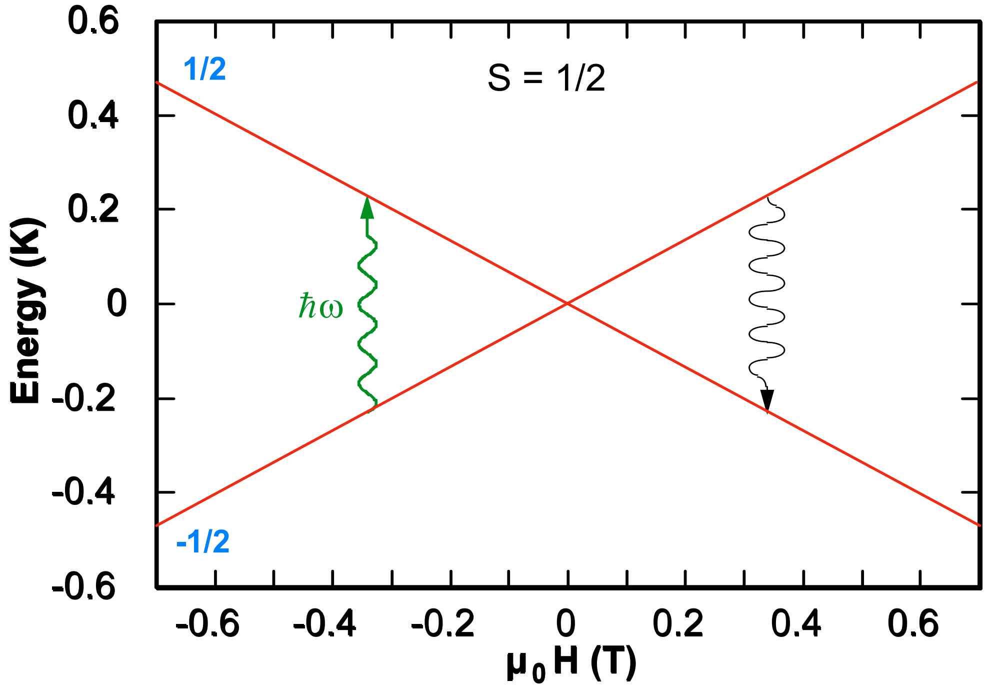
PRB 68, 220407(R) (2003)

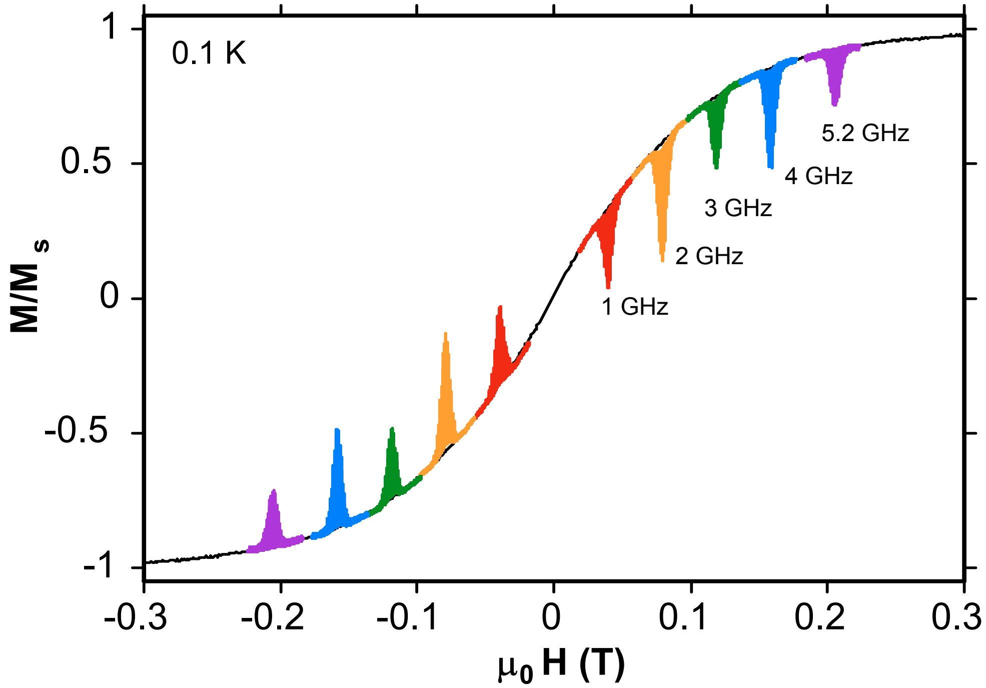


Photon induced tunnel probability

$$P_{EPR} = P - n_{\pm 10}P_{\pm 10}$$

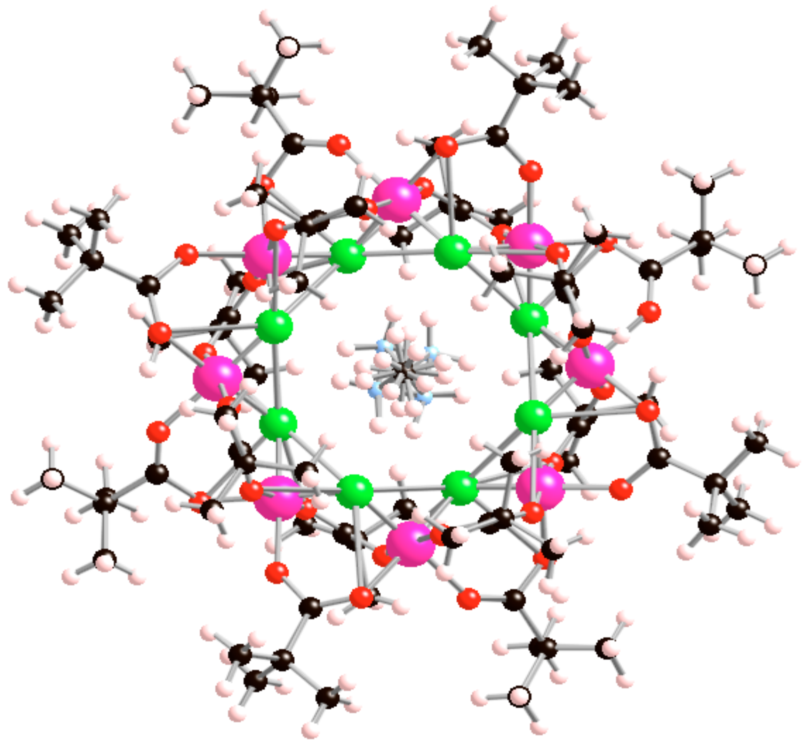






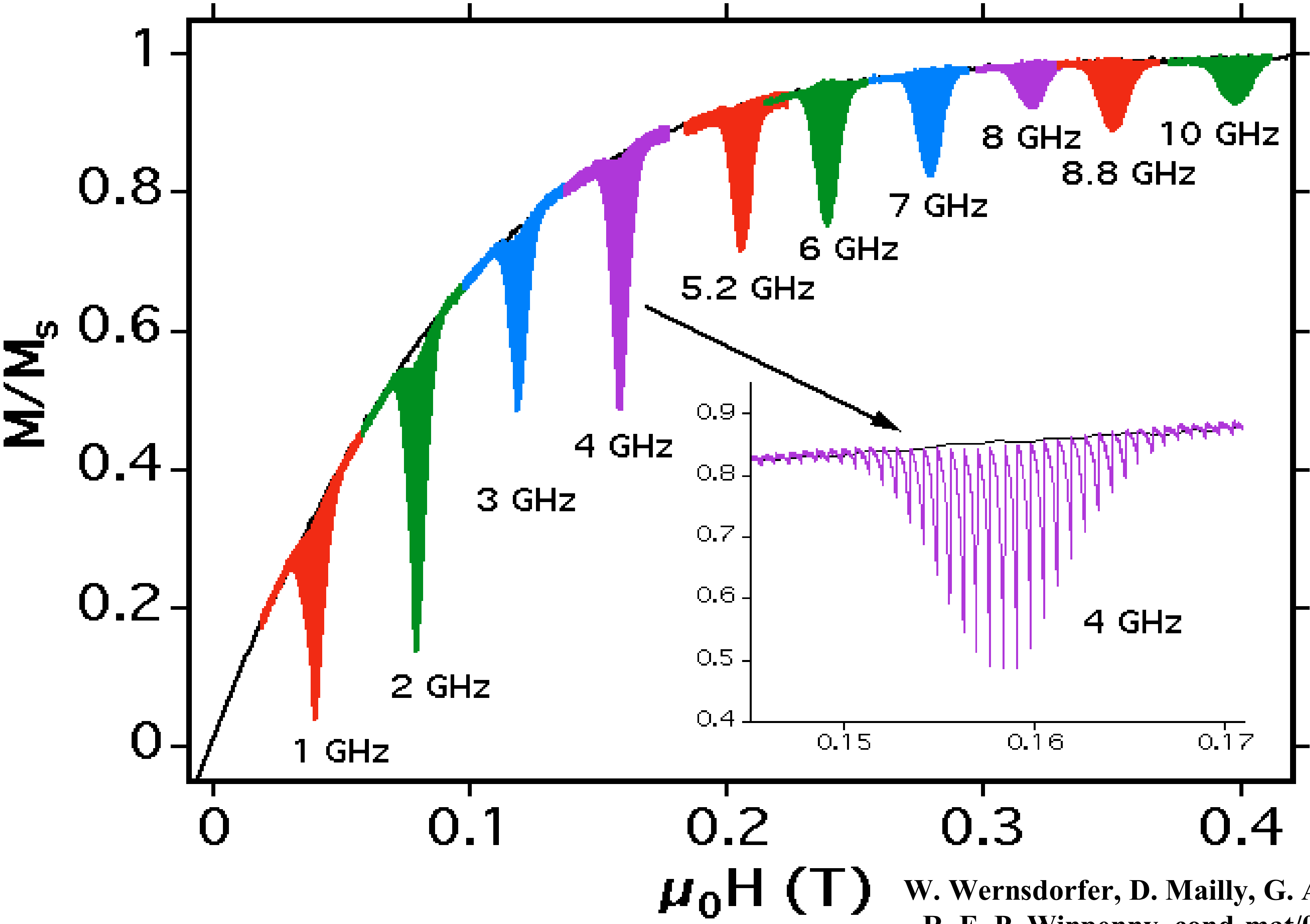
Absorption of microwaves

Cr_7Ni S = 1/2



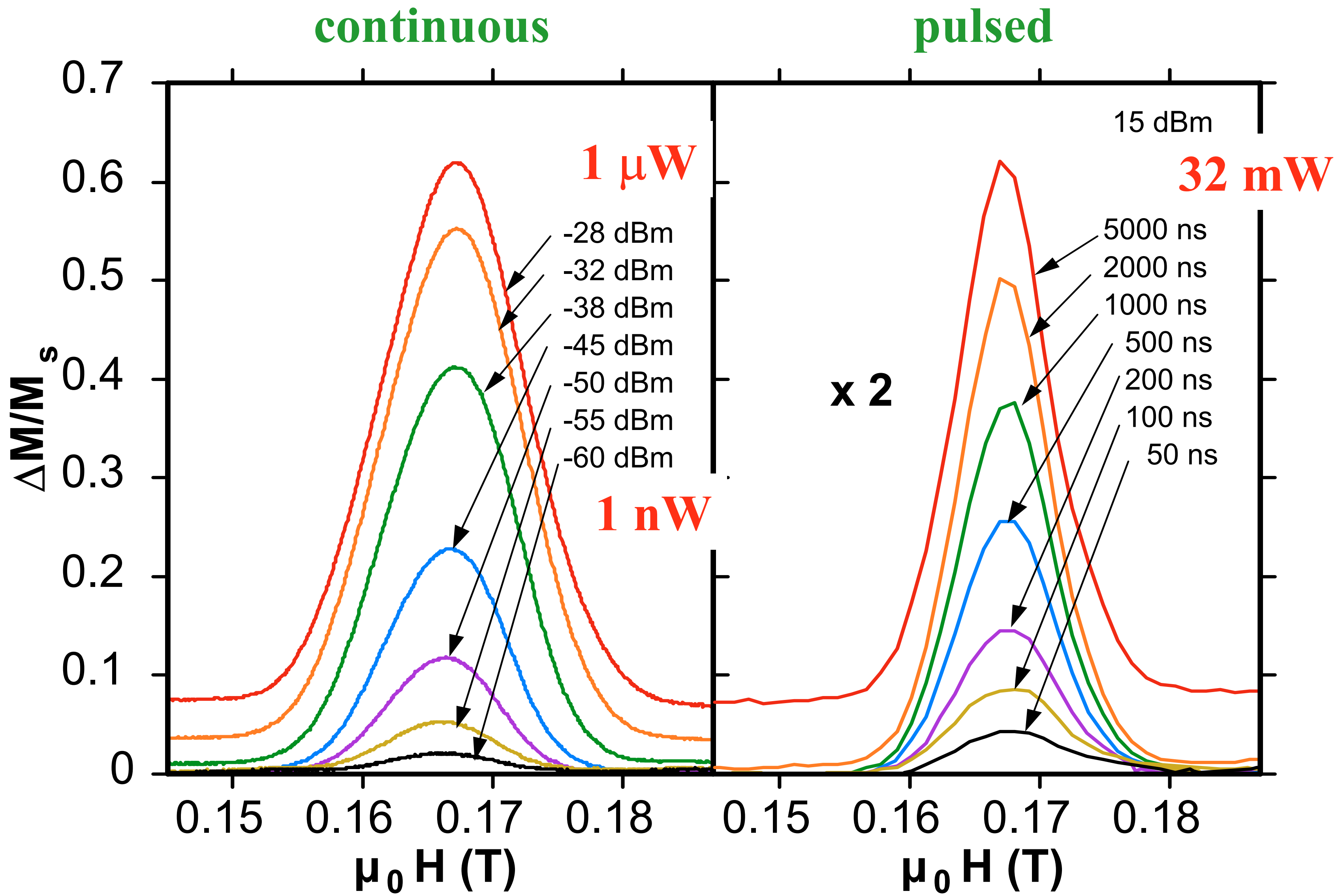
W. Wernsdorfer, D. Mailly, G. A. Timco, R. E. P. Winpenny, cond-mat/0504416

Absorption of microwaves: Cr_7Ni



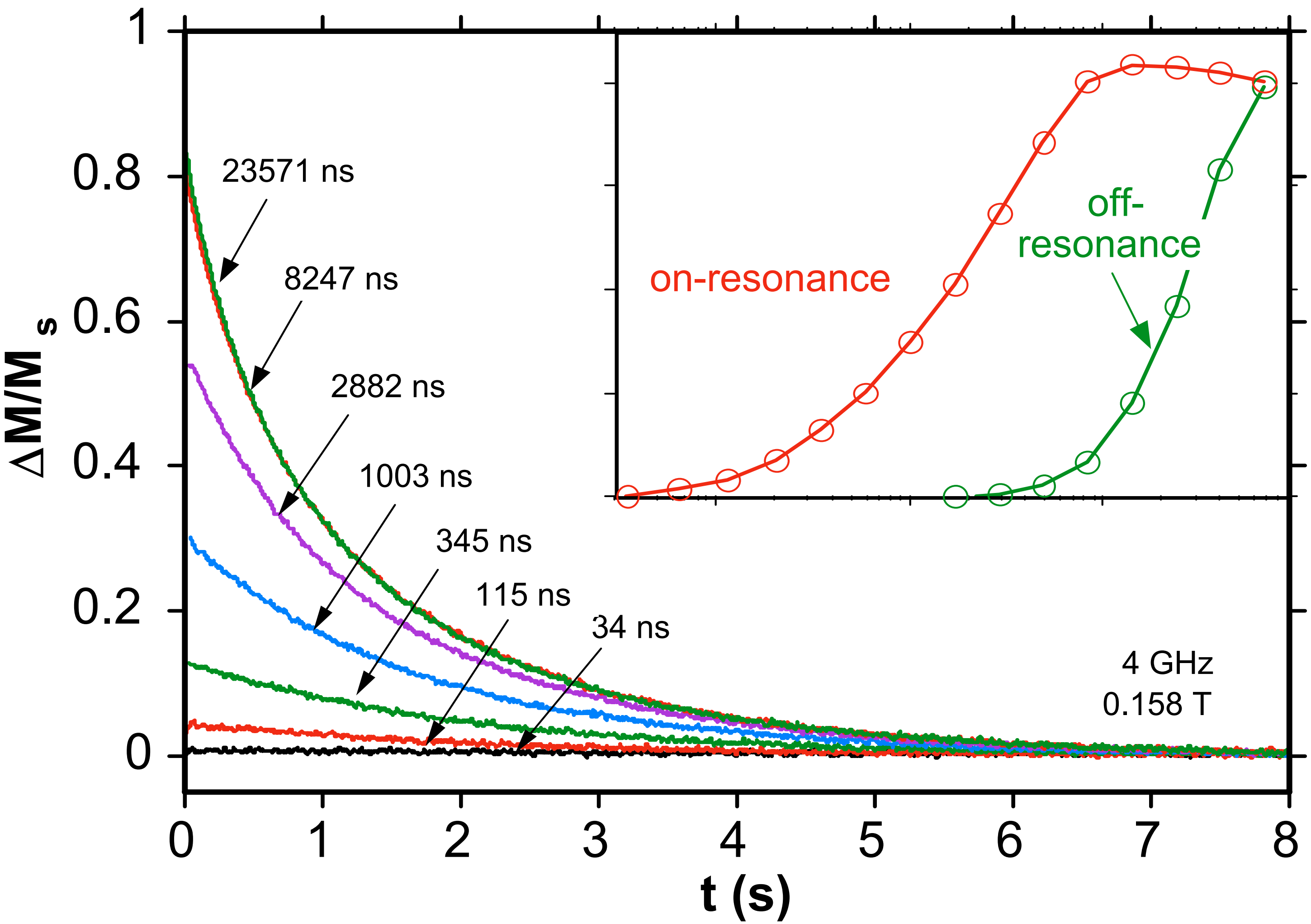
W. Wernsdorfer, D. Mailly, G. A. Timco, R. E. P. Winpenny, cond-mat/0504416

Comparison of line widths



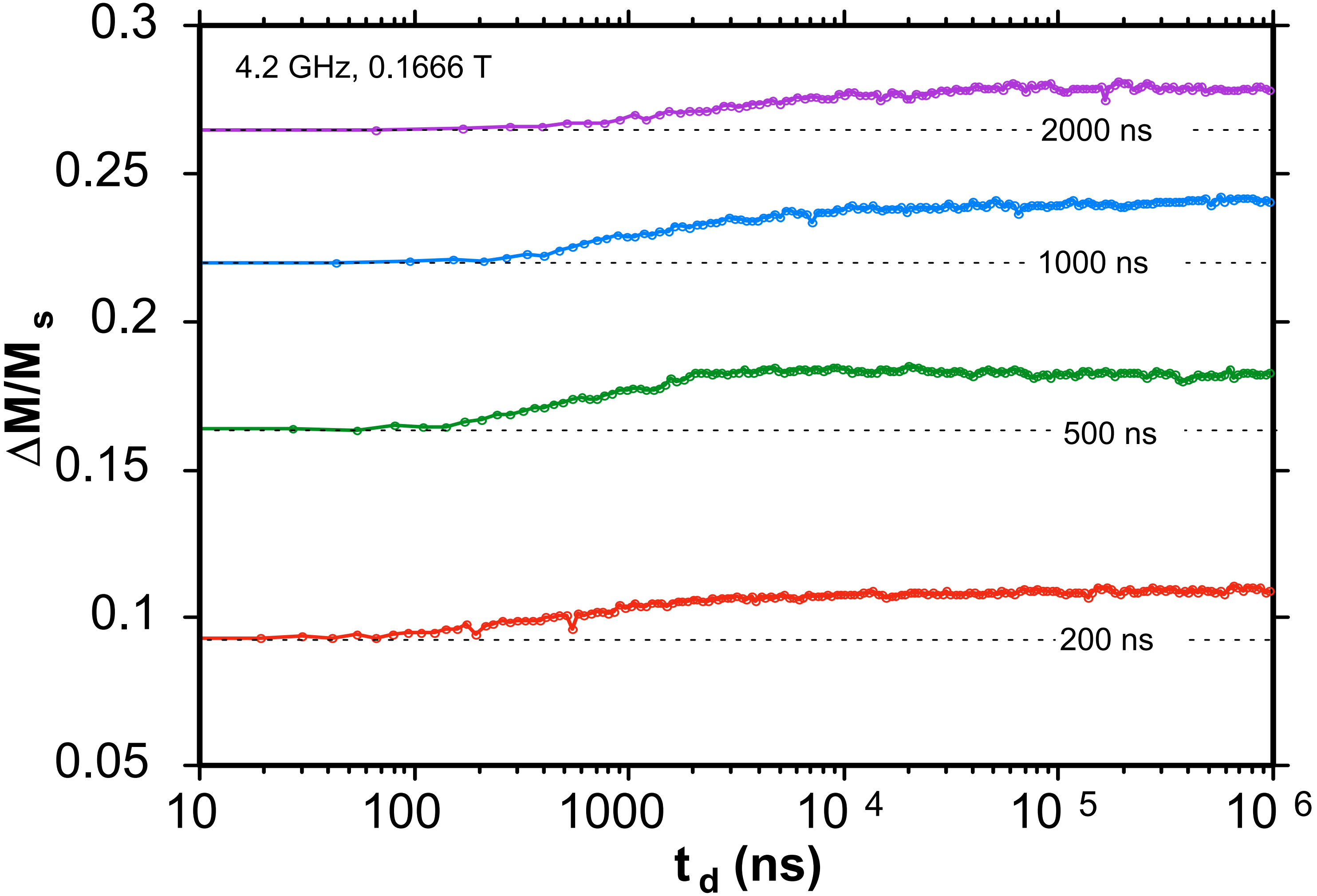
W. Wernsdorfer, D. Mailly, G. A. Timco, R. E. P. Winpenny, cond-mat/0504416

Relaxation after pulse



W. Wernsdorfer, D. Mailly, G. A. Timco,
R. E. P. Winpenny, cond-mat/0504416

Two pulse hole-digging method



➢ ***Energy diffusion time of about 1000 ns***

W. Wernsdorfer, D. Mailly, G. A. Timco, R. E. P. Winpenny, cond-mat/0504416

Project concerning microwave experiments

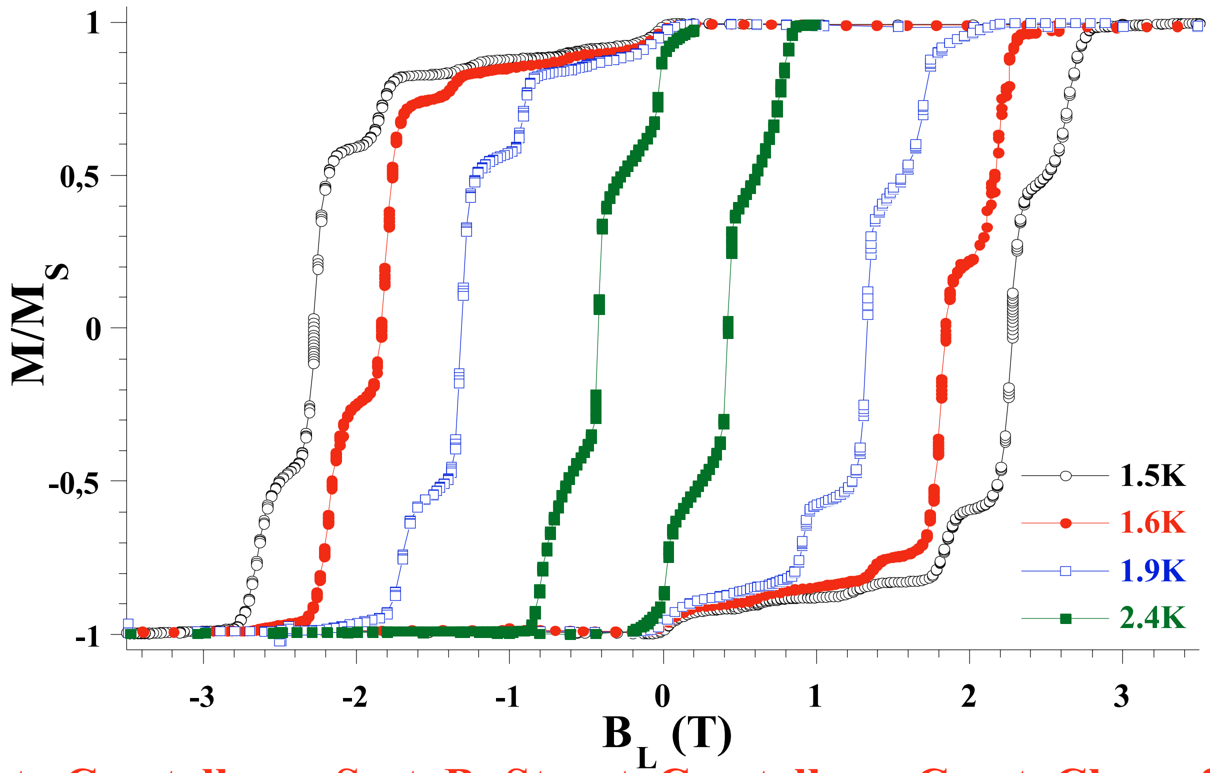
- **Quantum dynamic: spin-echo experiments**

Main problem: decoherence

P. C. E. Stamp and I. S. Tupitsyn, Phys. Rev. B 69, 014401 (2004)

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: >200 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}, Fe_{11}, Fe_{13}, $Fe_{17/19}$, Fe_{19} , Fe_{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}

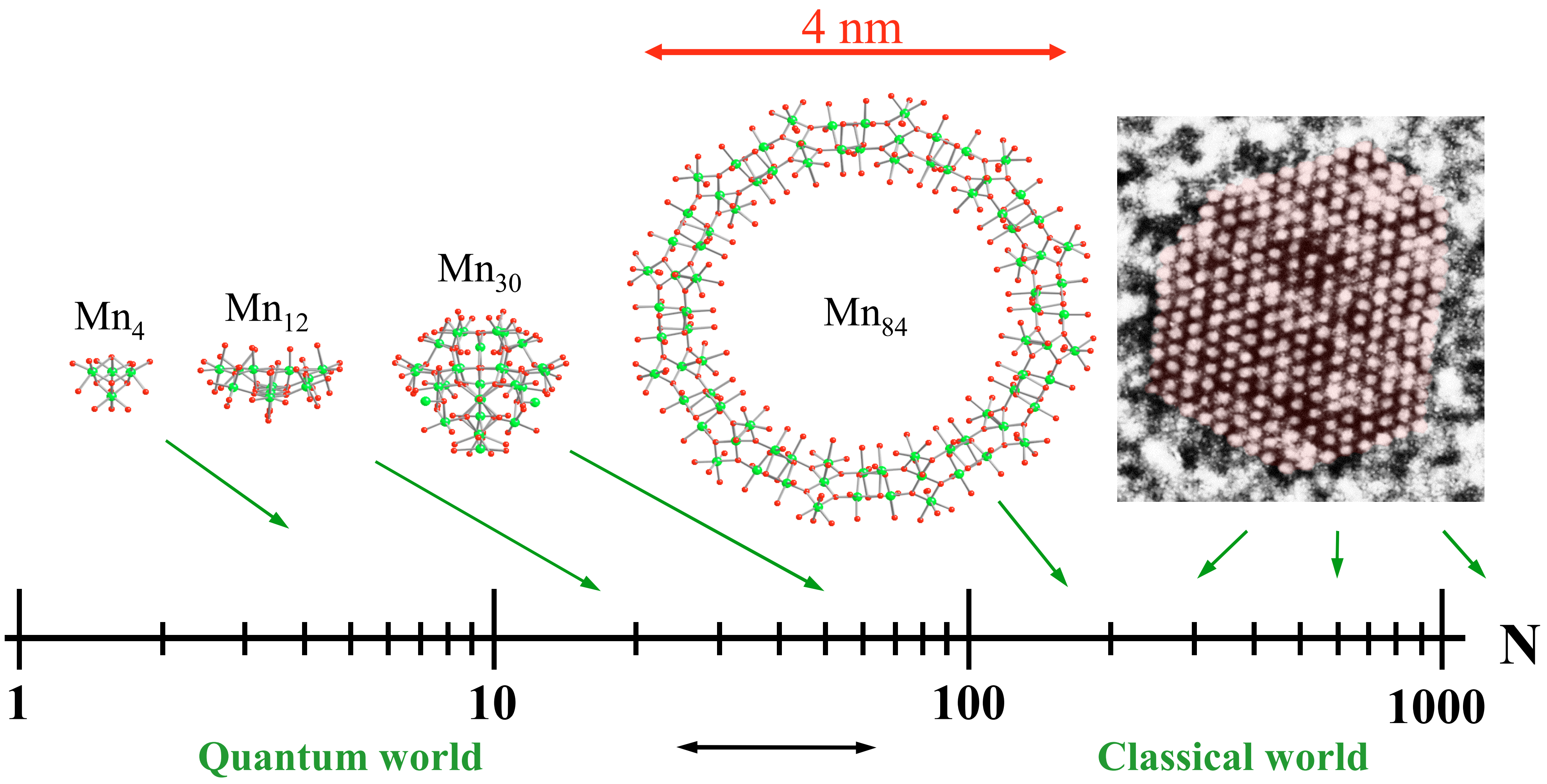
Co_2Gd_2, Co_2Dy_2, Cr_{12}, $CrNi_6$, $CrNi_2$, $CrCo_3$, $Fe_{10}Na_2$, Fe_2Ni_3, Mn_2Dy_2, Mn_2Nd_2, V_{15}, Ho, Fe_2Ho_2, $Mn_{11}Ln_4$, ...

Only few of these molecules are SMMs !!

. . . .

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

Mesoscopic Physics

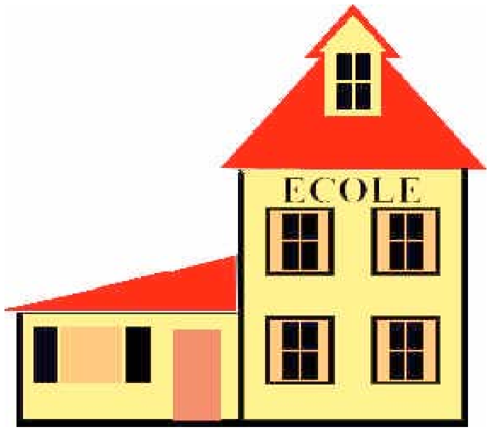


A. J.Tasiopoulos, A. Vinslava, W. Wernsdorfer, K. A.Abboud, and G. Christou,
Angew. Chem. Int. Ed., 43, 2117 (2004)

Conclusion

J. Villain: ***"… a school of physics"***

& chemistry



Collaborations (Grenoble)

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: $[Mn_4]_2$**
K. Petukhov **post-doc 2004-5: GHz**

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

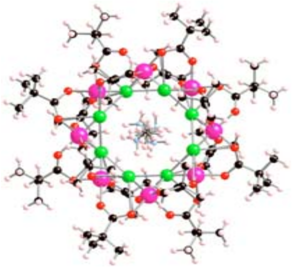
T. Ohm **PhD 1998: Fe_8**
V. Villar **PhD 2001: Fe_8, chaines**
E. Lhotel **PhD 2004: chaines**

C. Paulsen, P. Gandi, A. Sulpice, 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

Group of G. Christou, Dept. of Chemistry, Florida

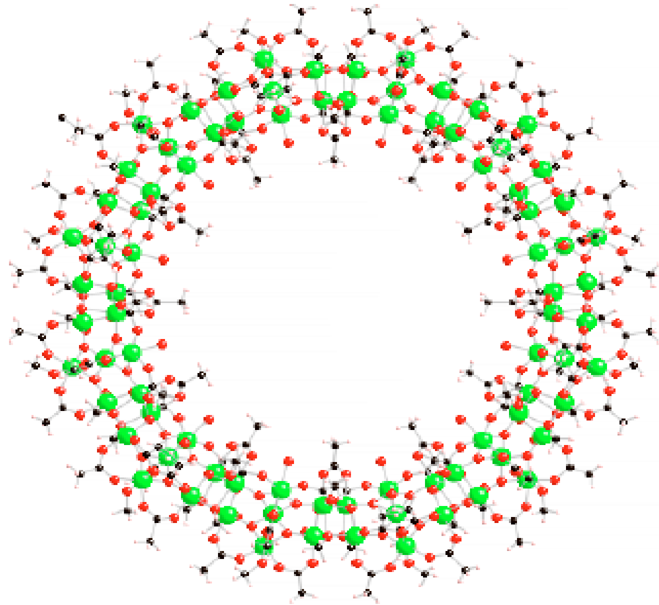
Group of R. Sessoli, D. Gatteschi, Univ. of Firenze, Italie
Group of A. Cornia, Univ. of Modena, Italie
Group of R.E.P. Winpenny, Univ. of Edinburg, UK
Group of E. Brechin, Univ. of Manchester, UK
Group of T. Mallah, Univ. Paris-Sud, Orsay, France
Group of A. Müller, Univ. of Bielefeld, Germany
Group of A. Powell, Univ. of Kahlsruhe, Germany
Group of D. Hendrickson, Dept. of Chemistry, San Diego
Group of E. Coronado, Univ. of Valence, Spain
Group of D. Luneau, Univ. of Lyon, France
Group of N. Ishikawa, Chuo Univ., Tokyo, Japan

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. of Valence, Spain

• • •

SMMs

Mn_{84}



Christou, 2004

SCMs