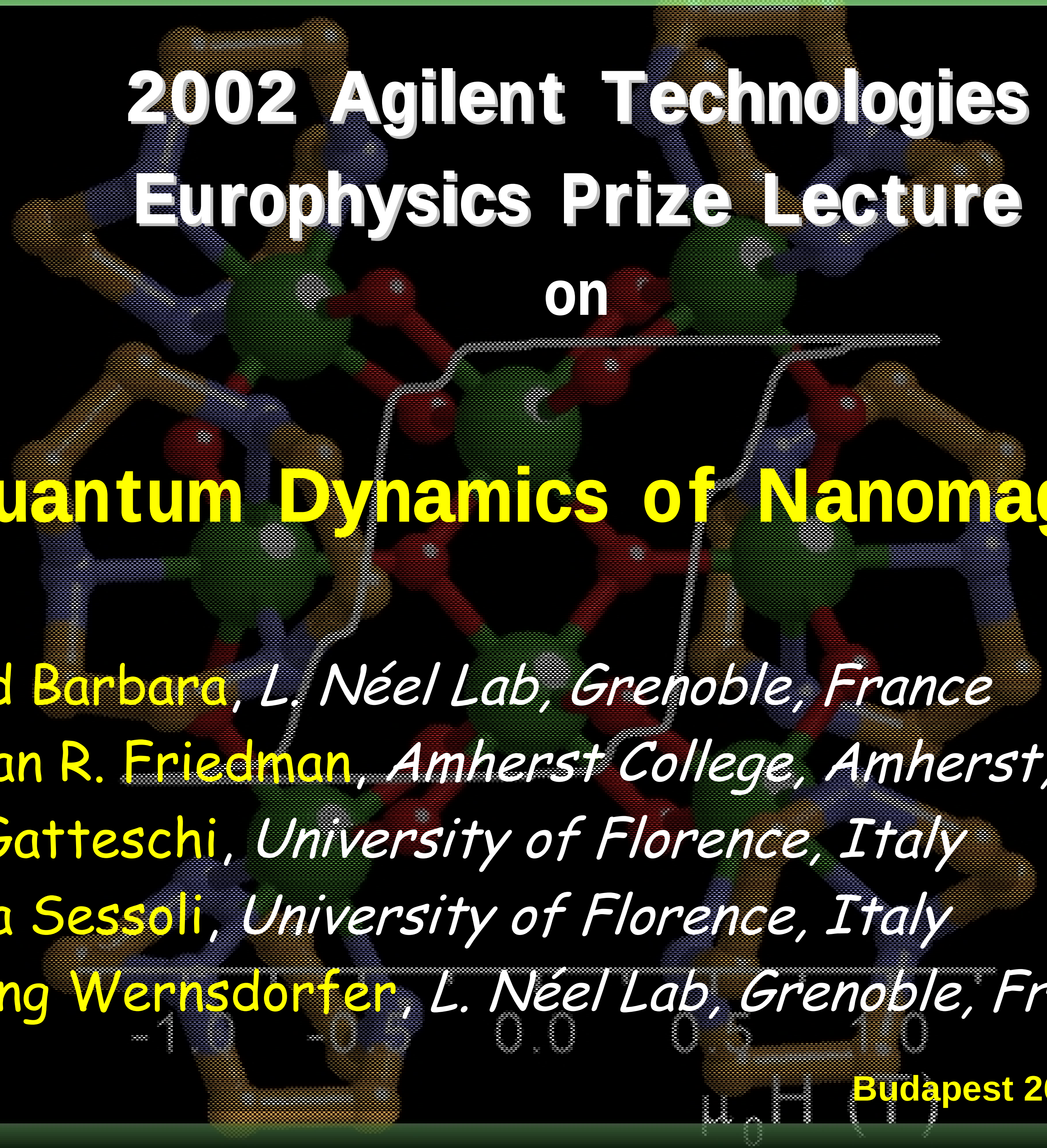
2002 Agilent Technologies Europhysics Prize Lecture

on

Quantum Dynamics of Nanomagnets



Bernard Barbara, *L. Néel Lab, Grenoble, France*

Jonathan R. Friedman, *Amherst College, Amherst, MA, USA*

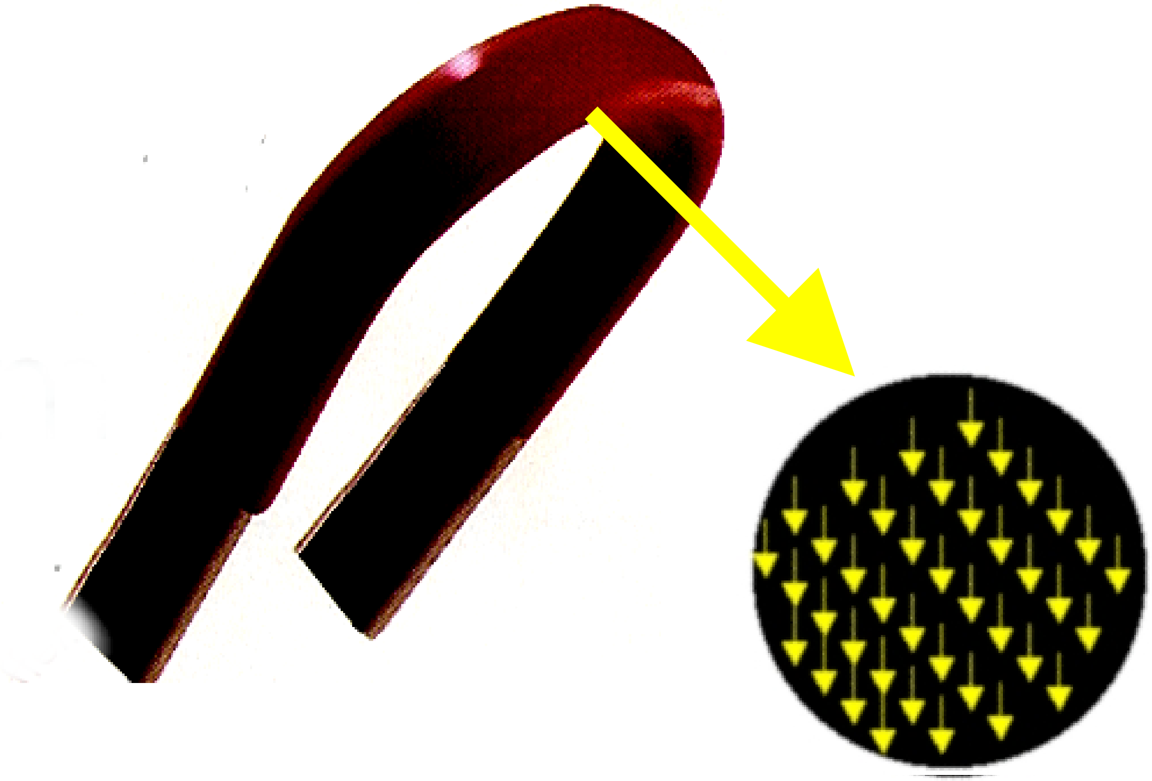
Dante Gatteschi, *University of Florence, Italy*

Roberta Sessoli, *University of Florence, Italy*

Wolfgang Wernsdorfer, *L. Néel Lab, Grenoble, France*

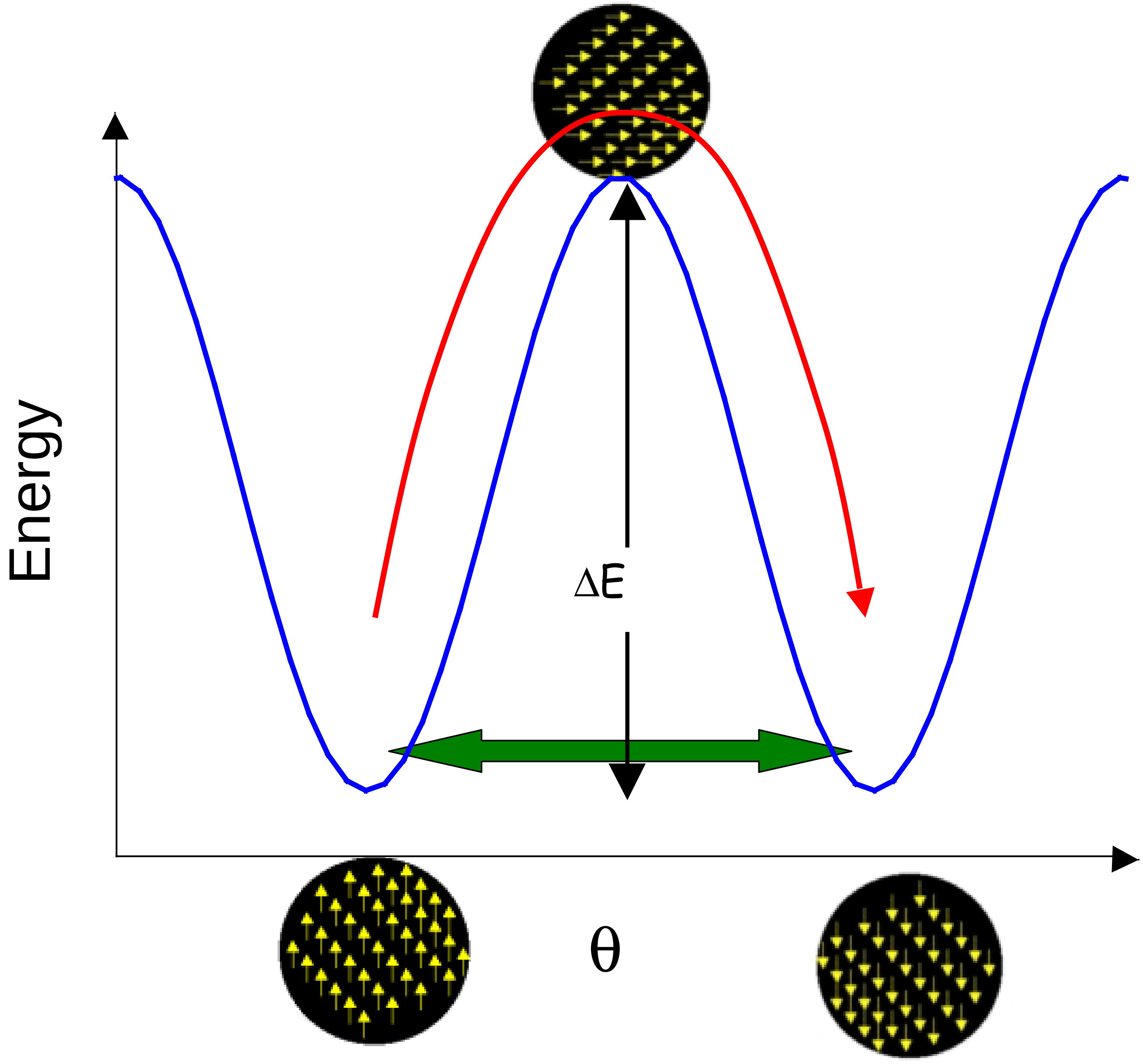
Budapest 26/08/2002

the miniaturization process



Single Domain Particles

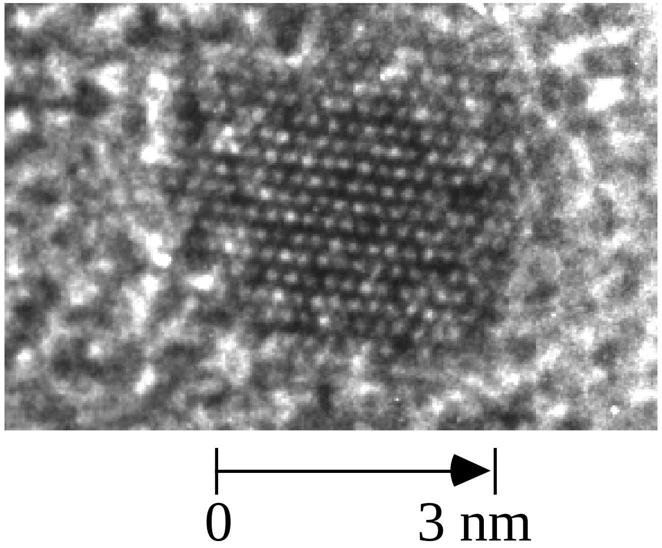
coherent rotation of all the spins


Energy
ΔE
θ

Quantum effects in the dynamics of the magnetization

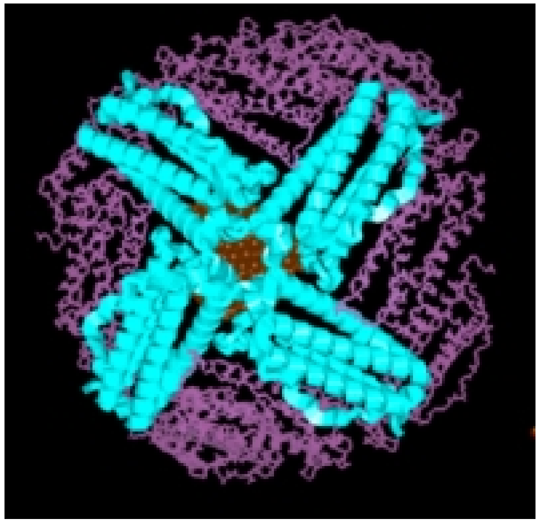
- First evidences of Quantum Tunneling in nanosized magnetic particles

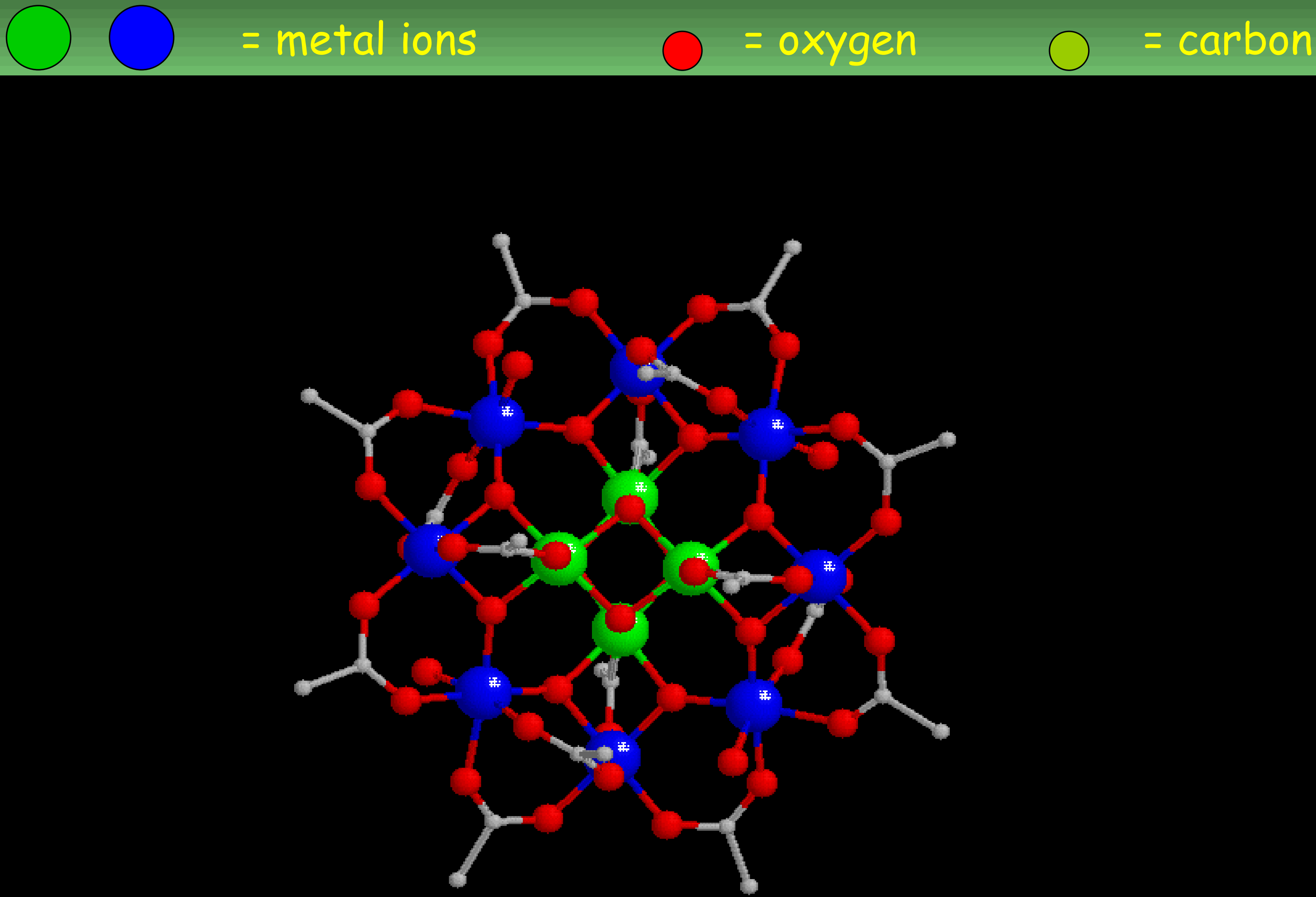
  (difficulties due to size distribution)

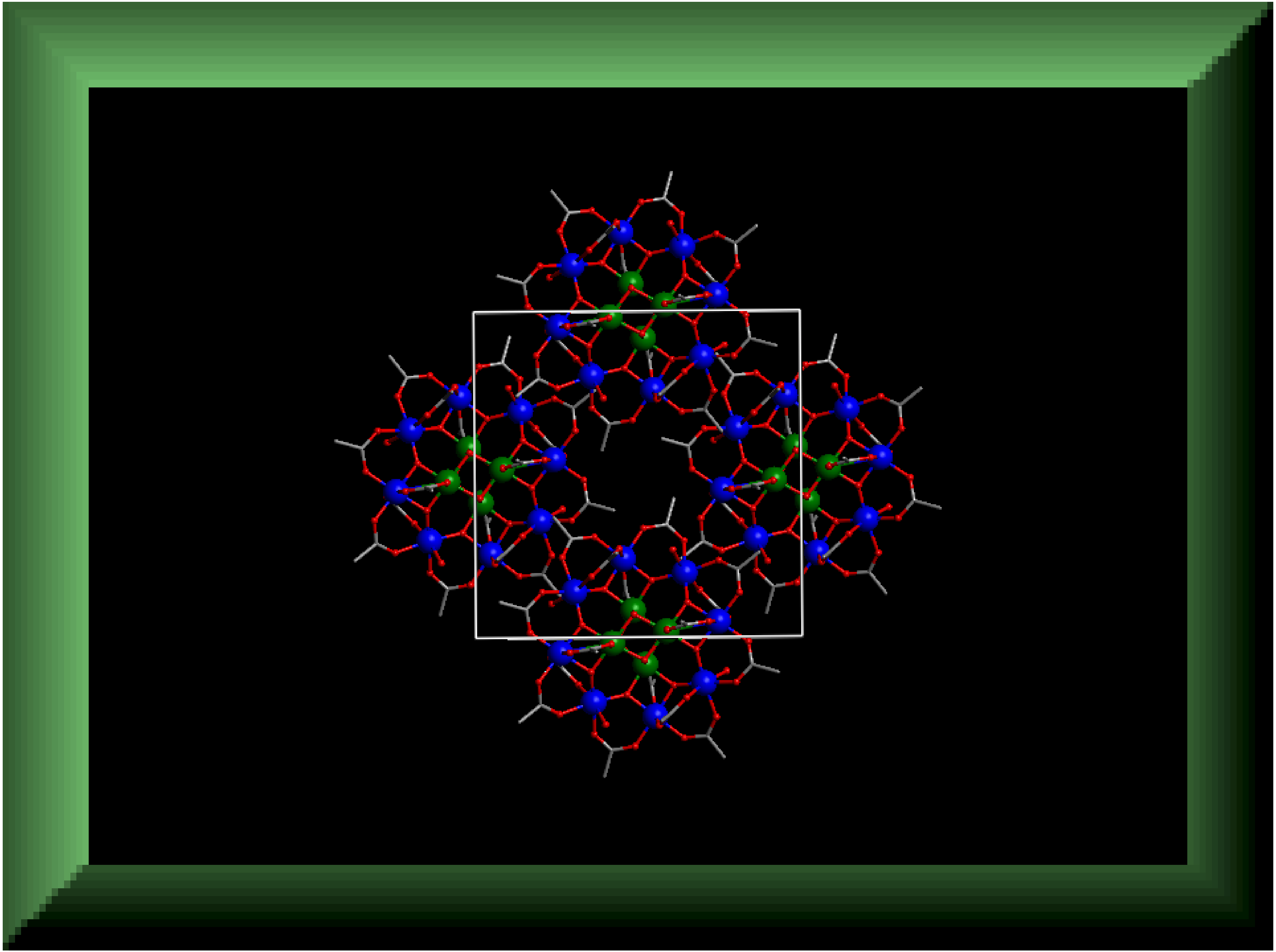


- Quantum Coherence in ferrihydrite confined in the ferritin mammalian protein

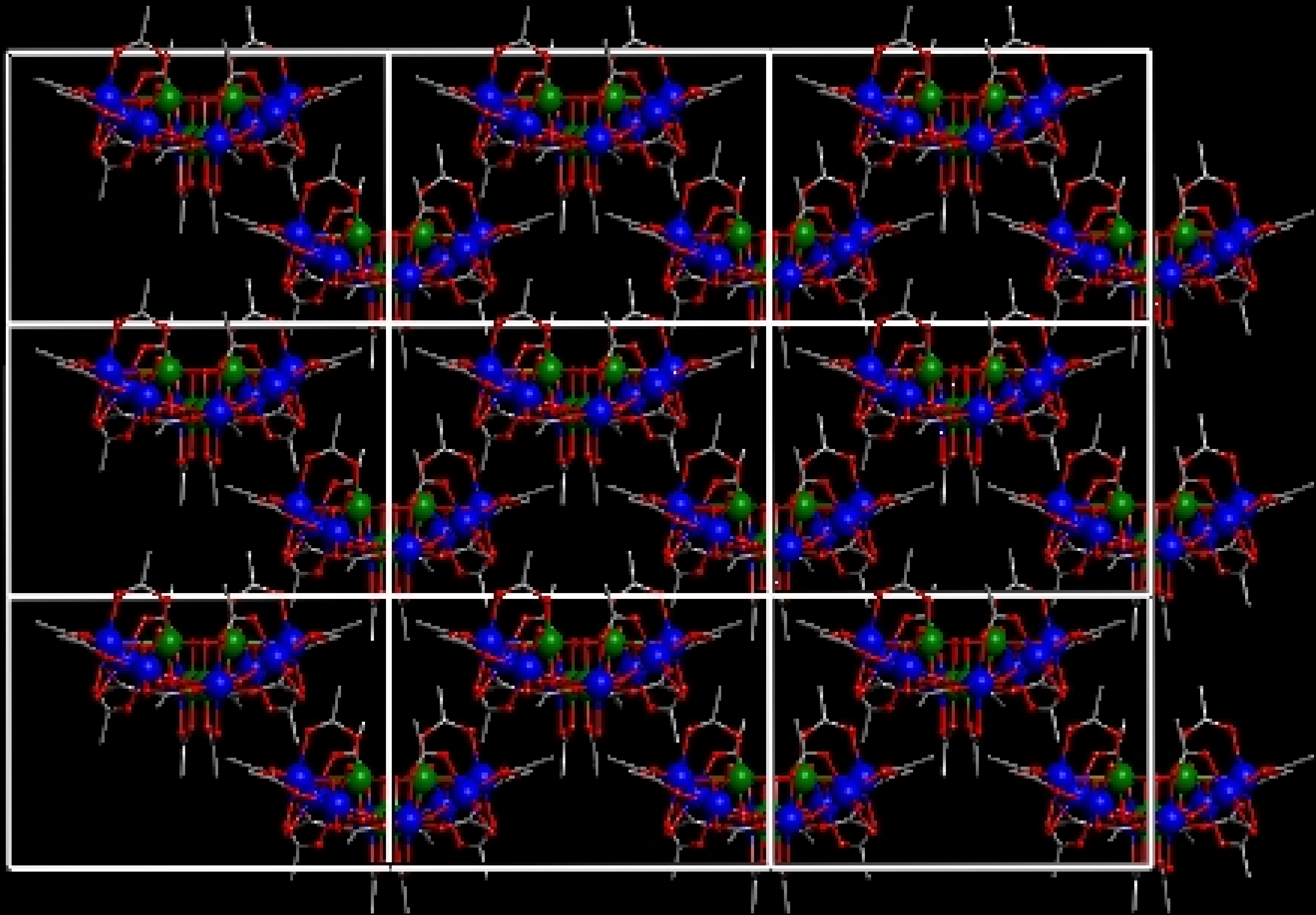
  (inconclusive due to distribution of iron load)




= metal ions
= oxygen
= carbon



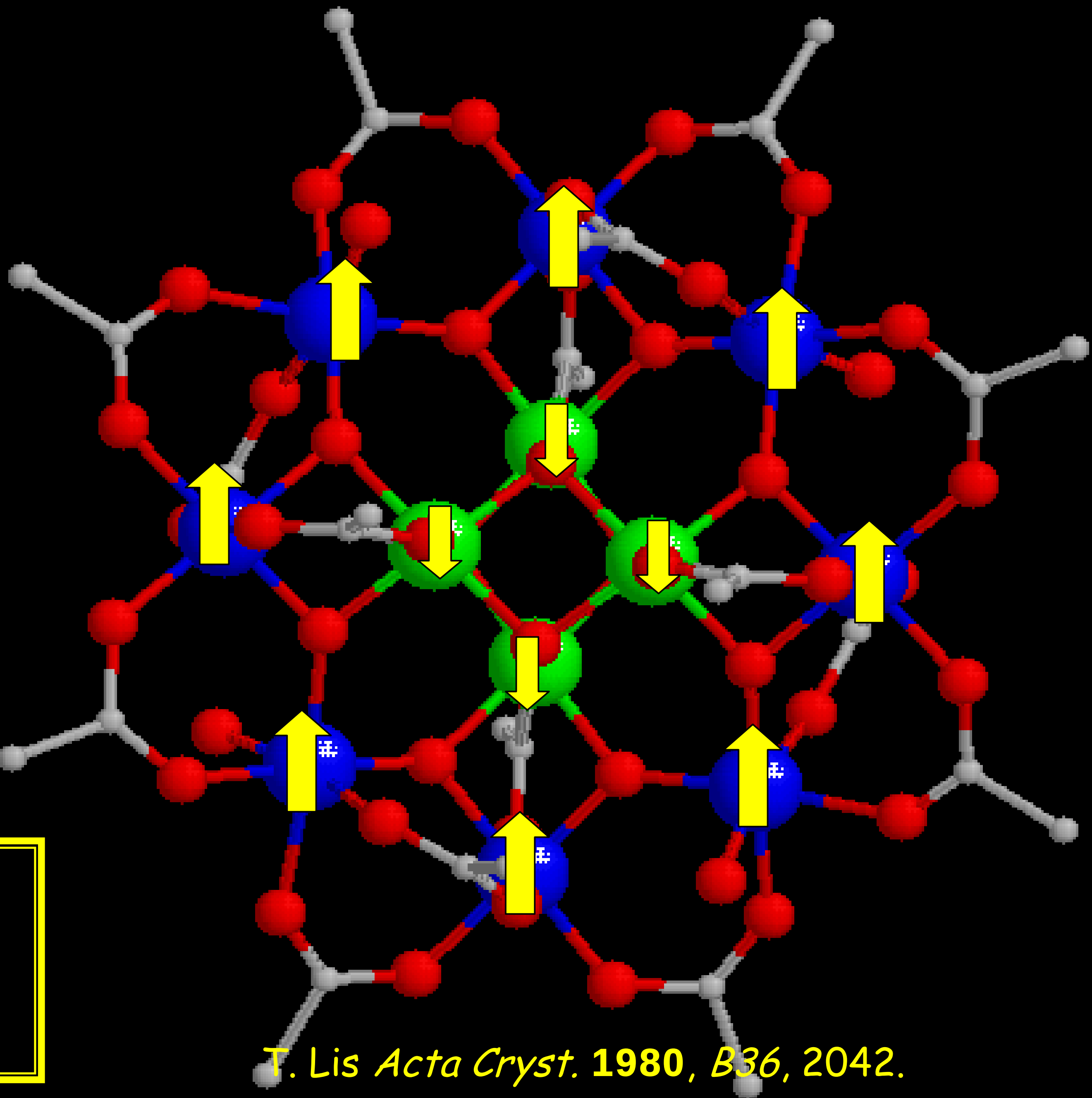
The molecules are regularly arranged in the crystal



Mn12acetate

Mn(III)
S=2

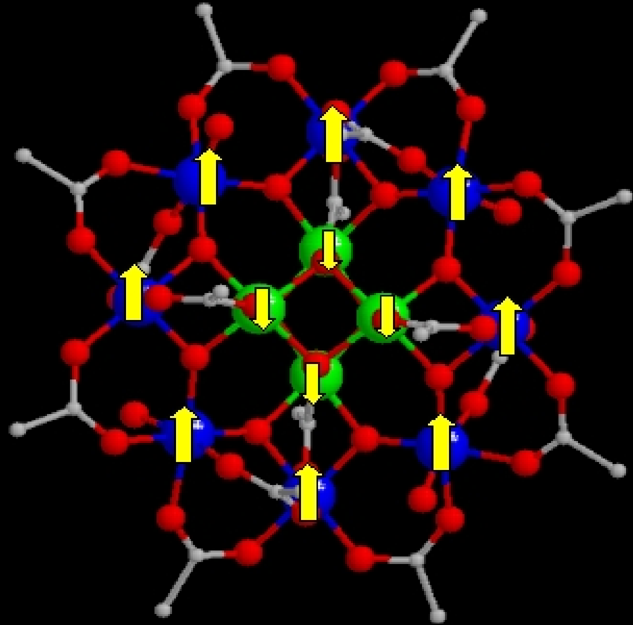
Mn(IV)
S=3/2



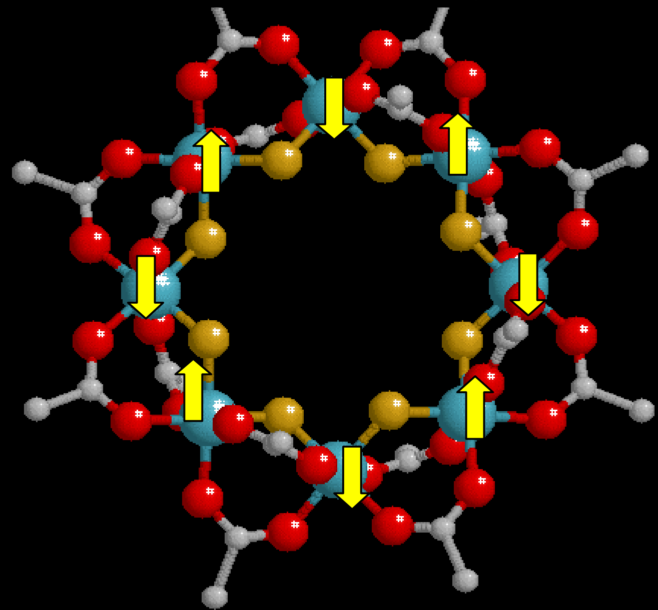
Total Spin
=10

T. Lis *Acta Cryst.* **1980**, *B36*, 2042.

high spin molecules



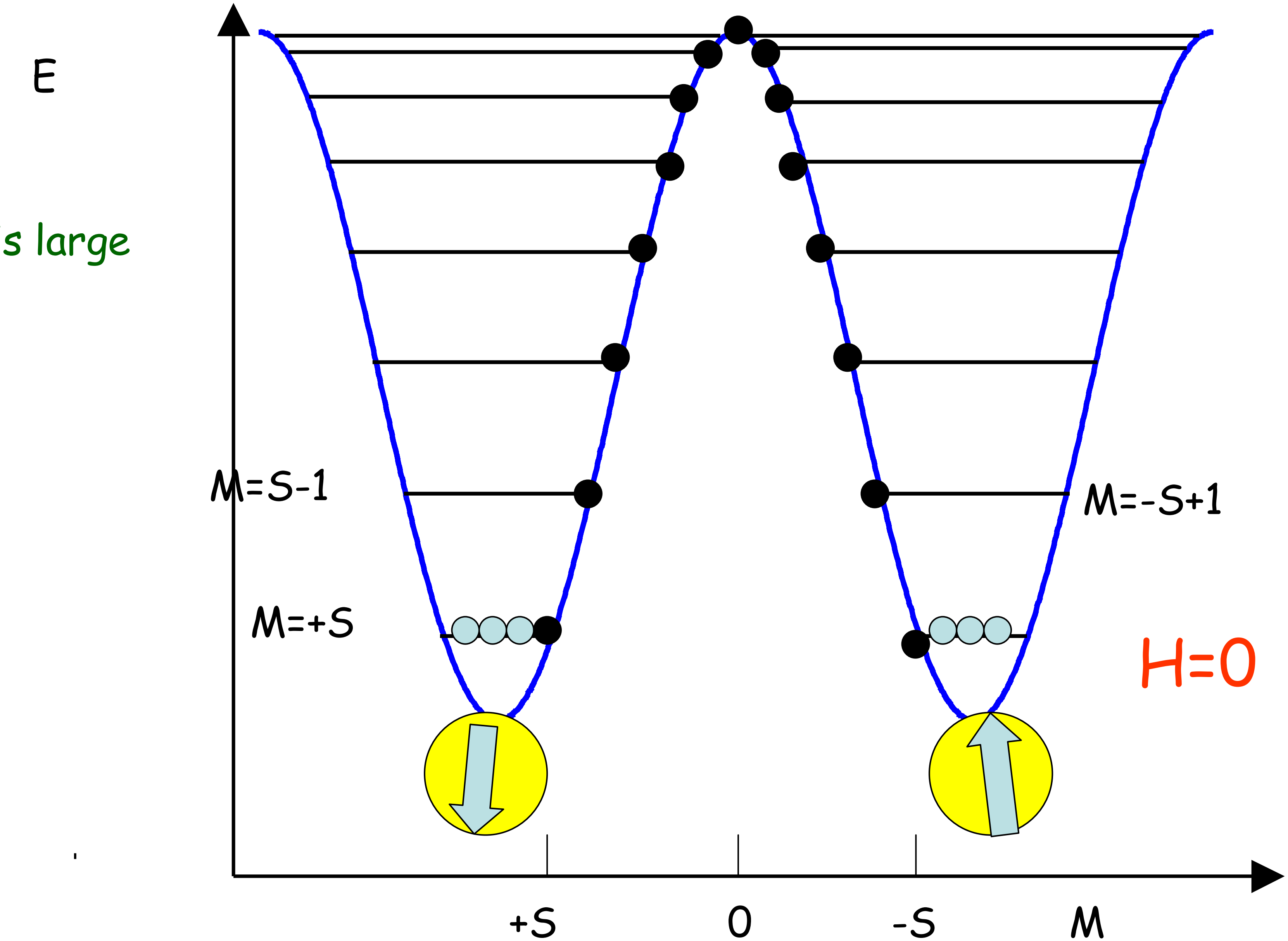
and low spin molecules



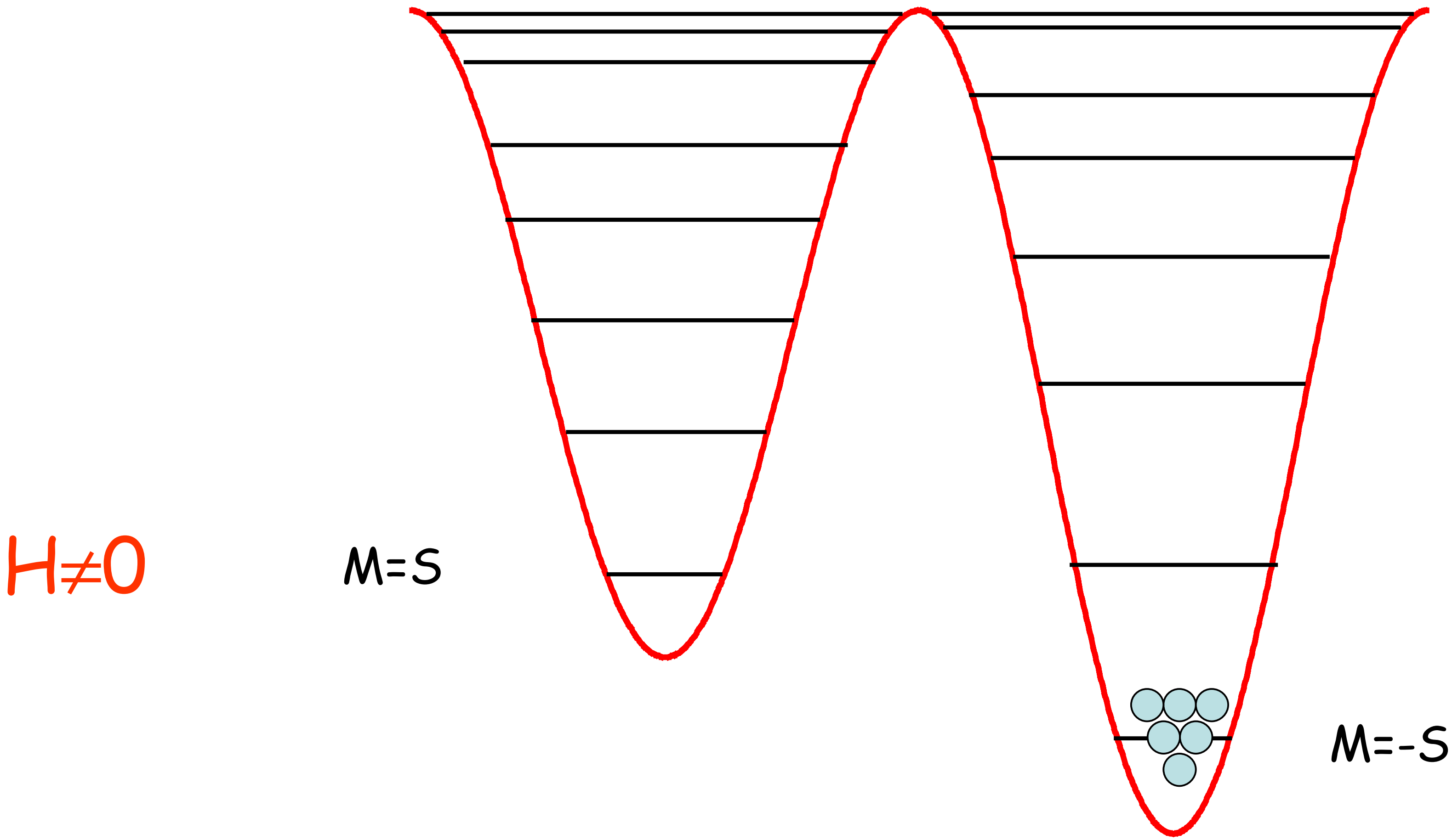
Uniaxial magnetic anisotropy

$$\mathcal{H} = -DS_z^2$$

If S is large

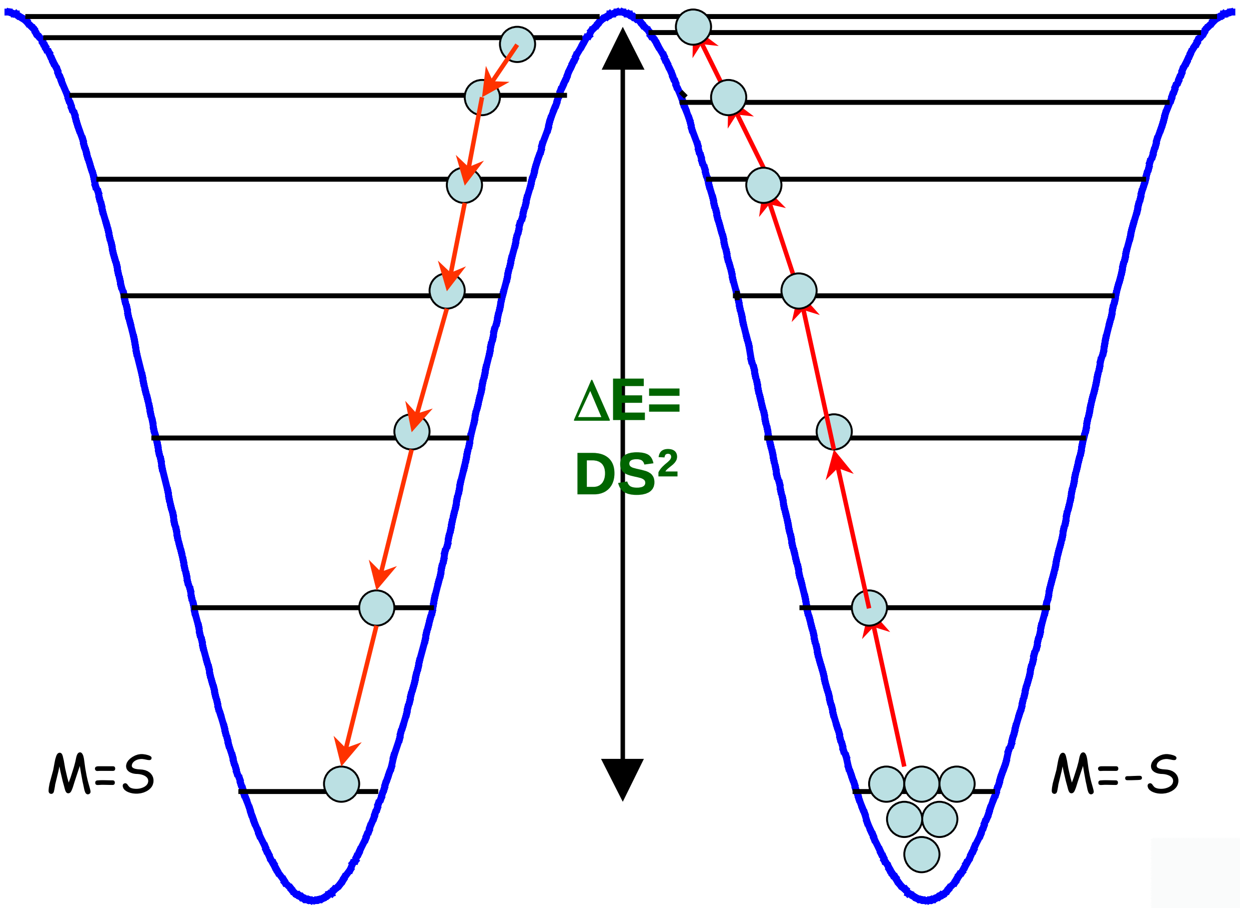


$$\mathcal{H} = -DS_z^2 + g\mu_B H_z S_z$$



return to the equilibrium

thermal activated mechanism



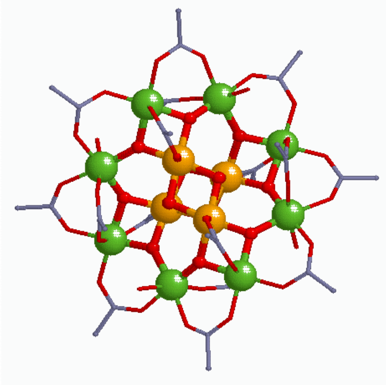
H=0

time=0

$\tau=\tau_0\exp(\Delta E/k_BT)$

$\tau_0 \approx 10^{-7}$

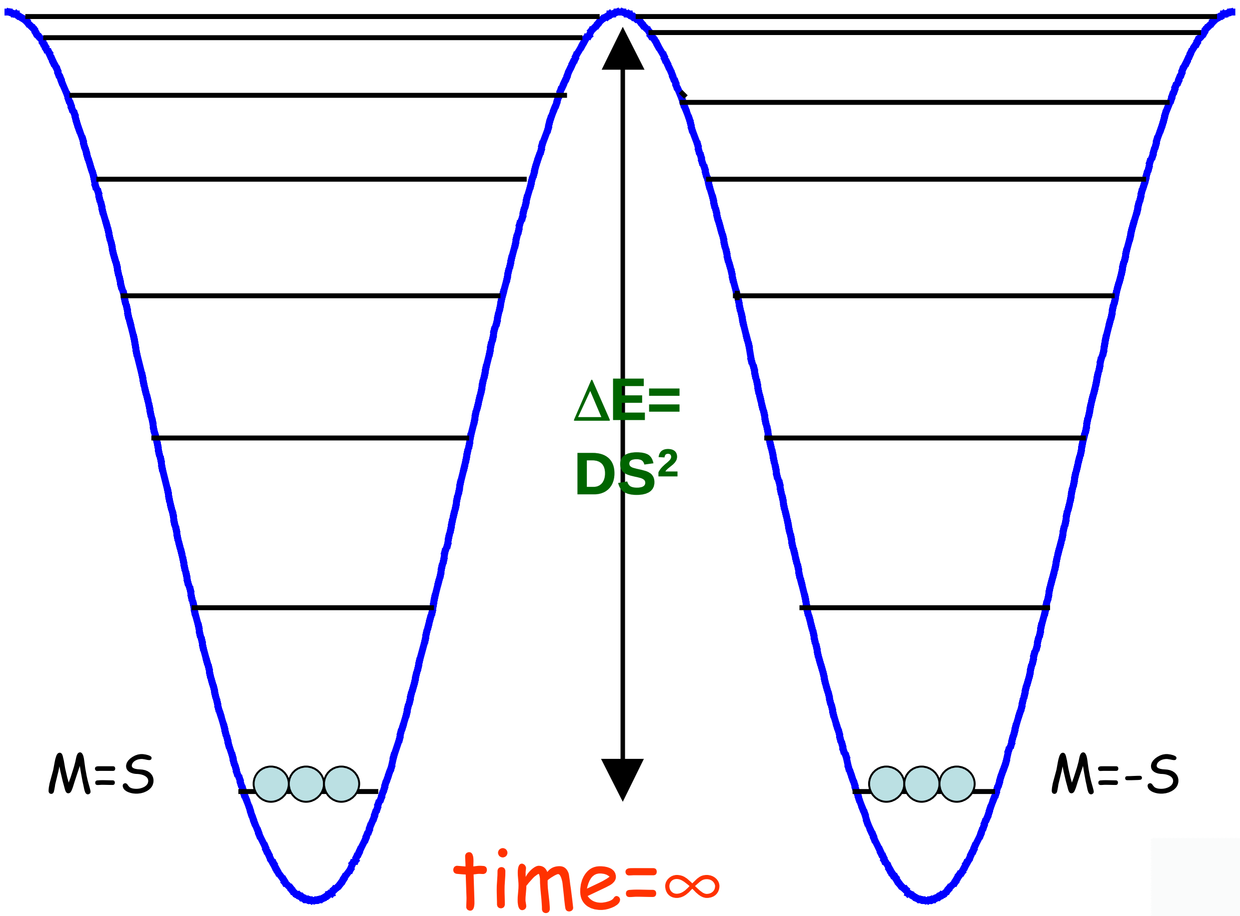
$\Delta E = 63$ K



J. Villain et al. *Europhys. Lett.* **1994**, *27*, 159

return to the equilibrium

thermal activated mechanism



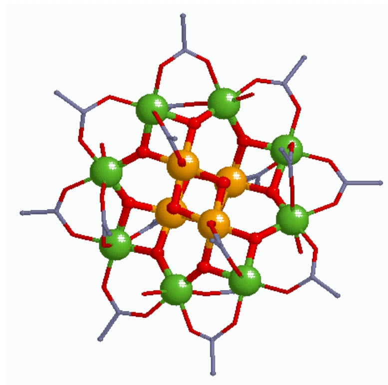
H=0

time=∞

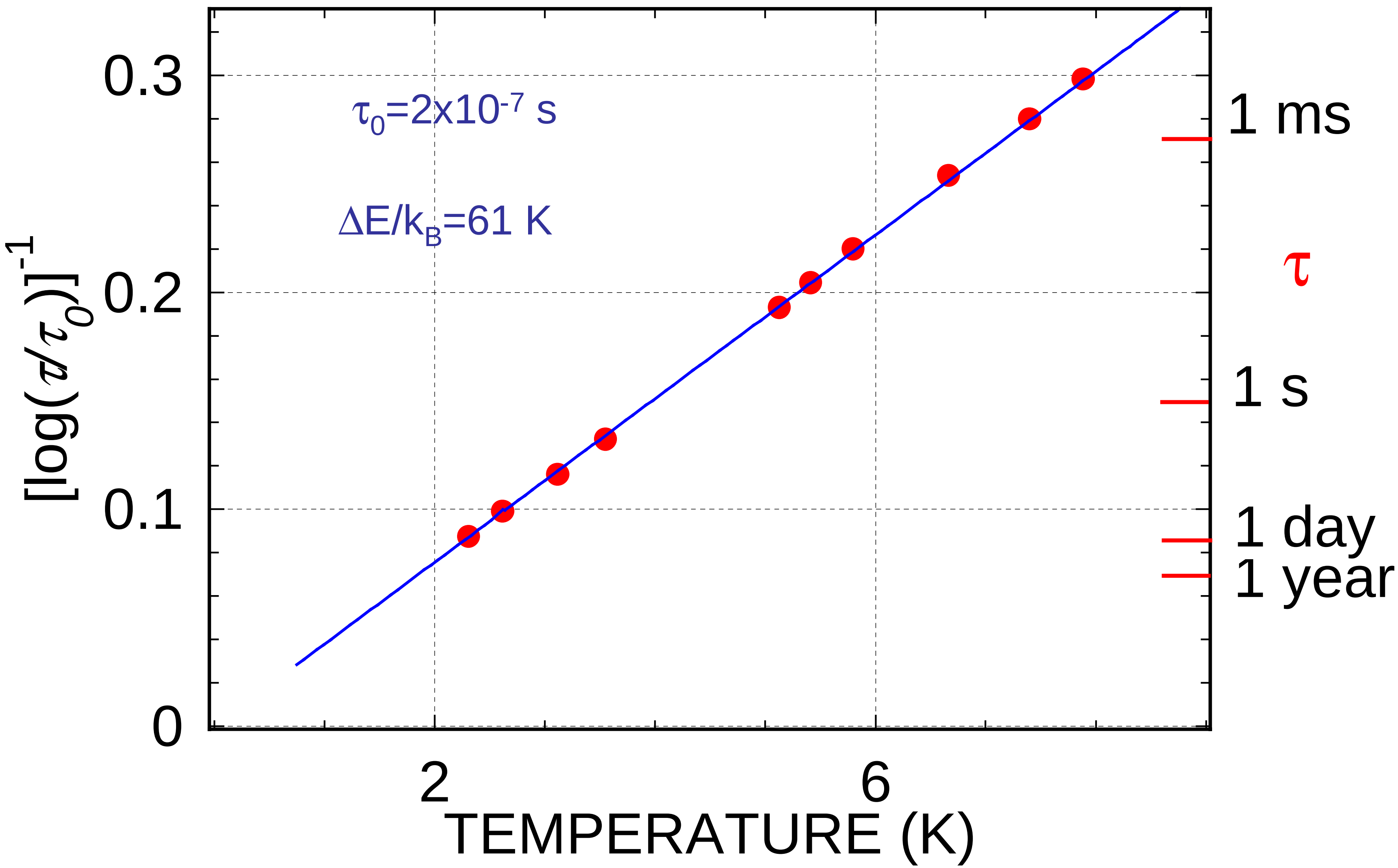
$\tau=\tau_0 \exp(\Delta E/k_B T)$

$\tau_0 \approx 10^{-7}$

$\Delta E = 63$ K

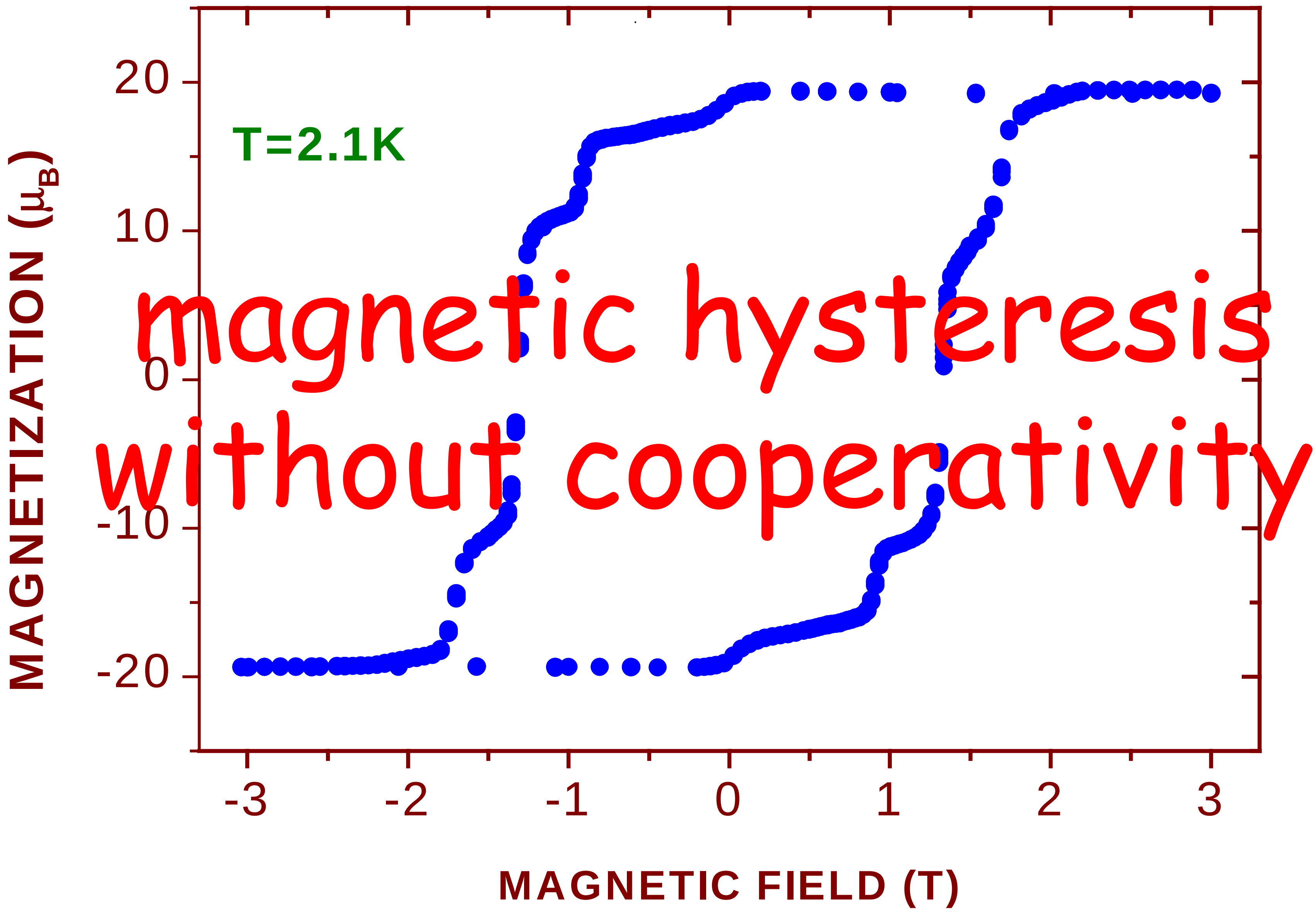


Temperature dependence of the relaxation time of Mn12acetate

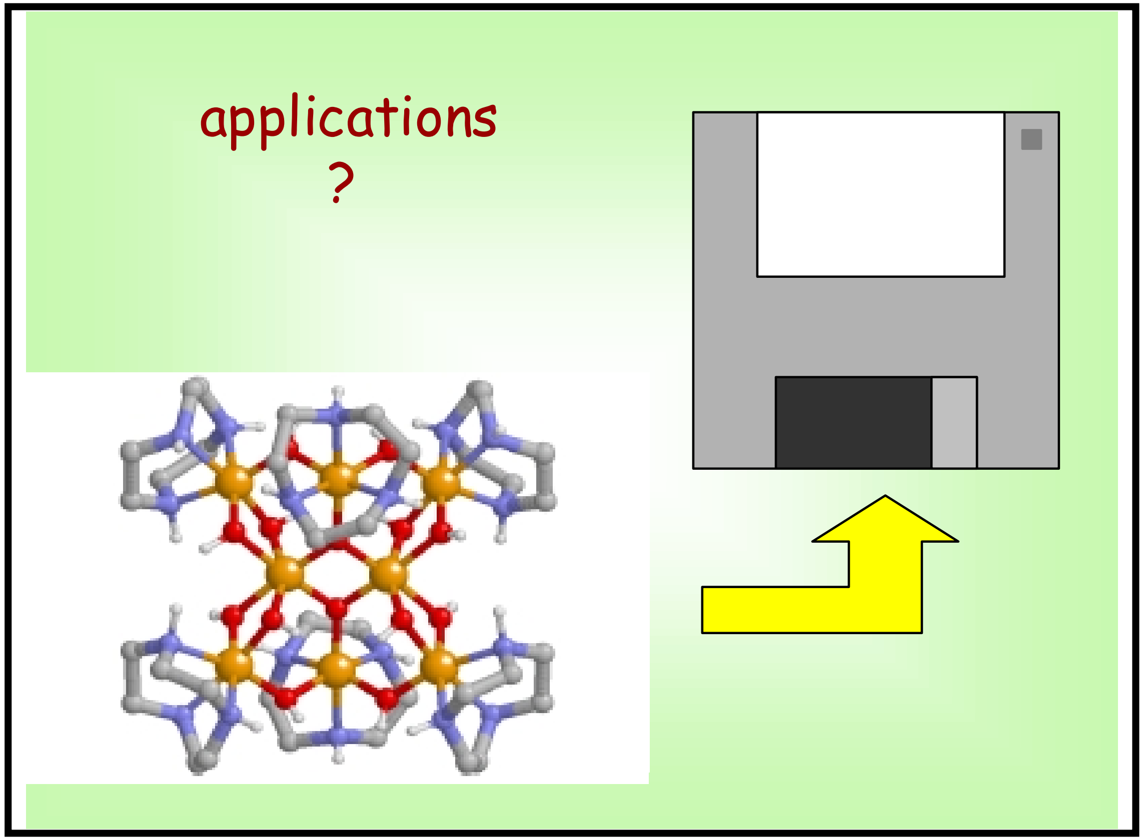


Sessoli et al. *Nature* **1993**, *365*, 141

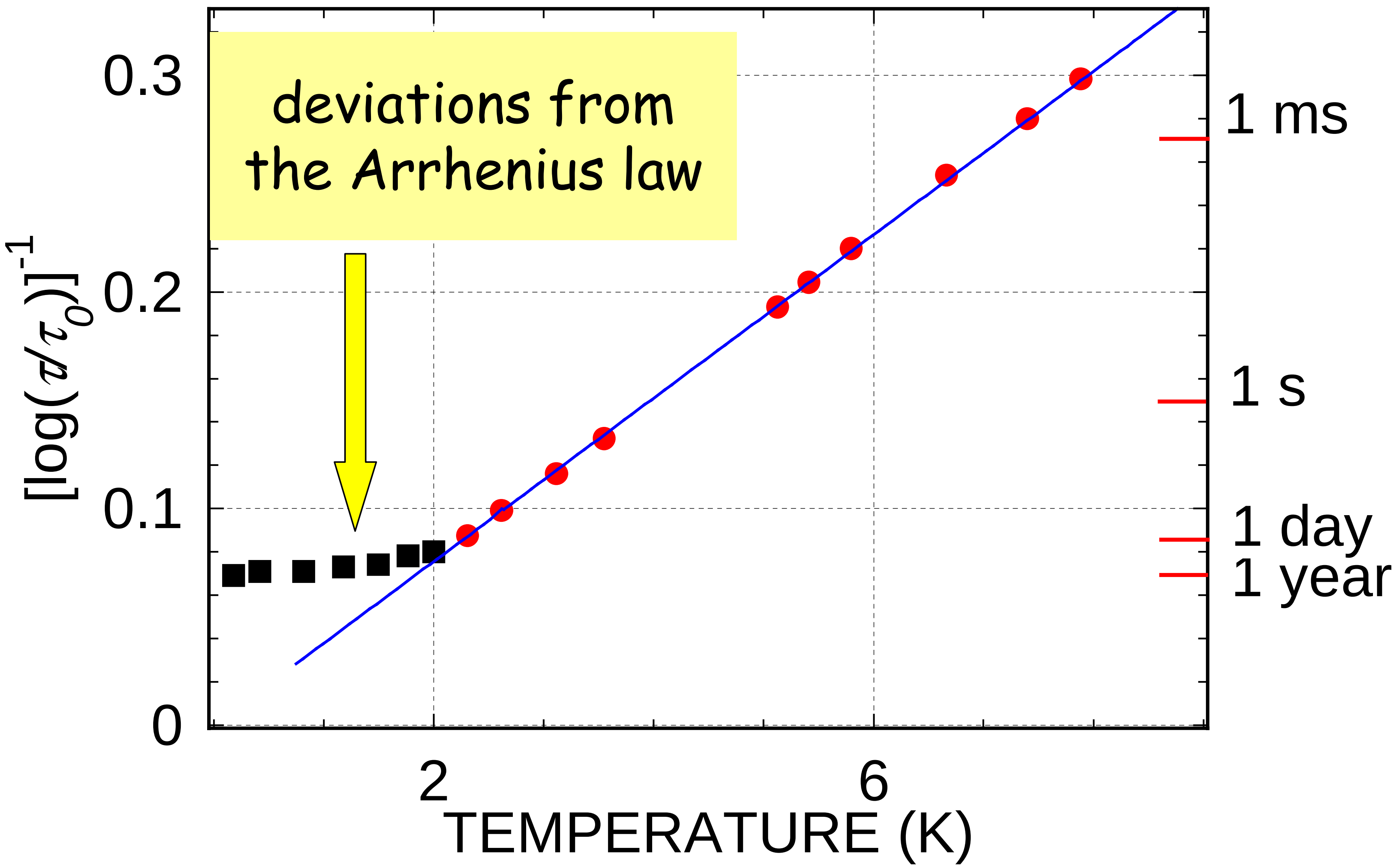
Mn12acetate: Hysteresis loop



High Spin Clusters



Single Molecule Magnets

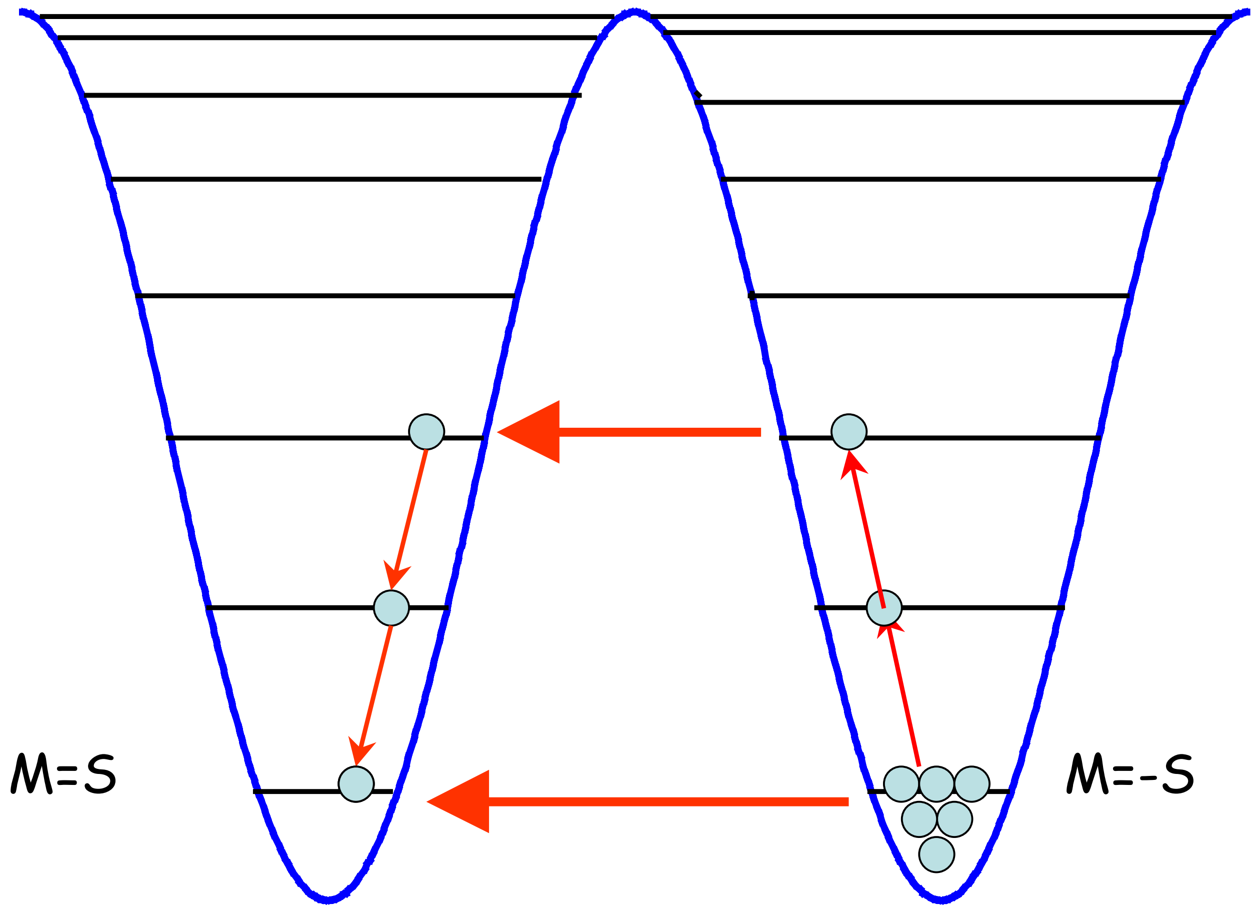


Barbara et al. *J. Magn. Magn. Mat.* **1995**, *140-144*, 1825

return to the equilibrium

tunnel mechanism

H=0

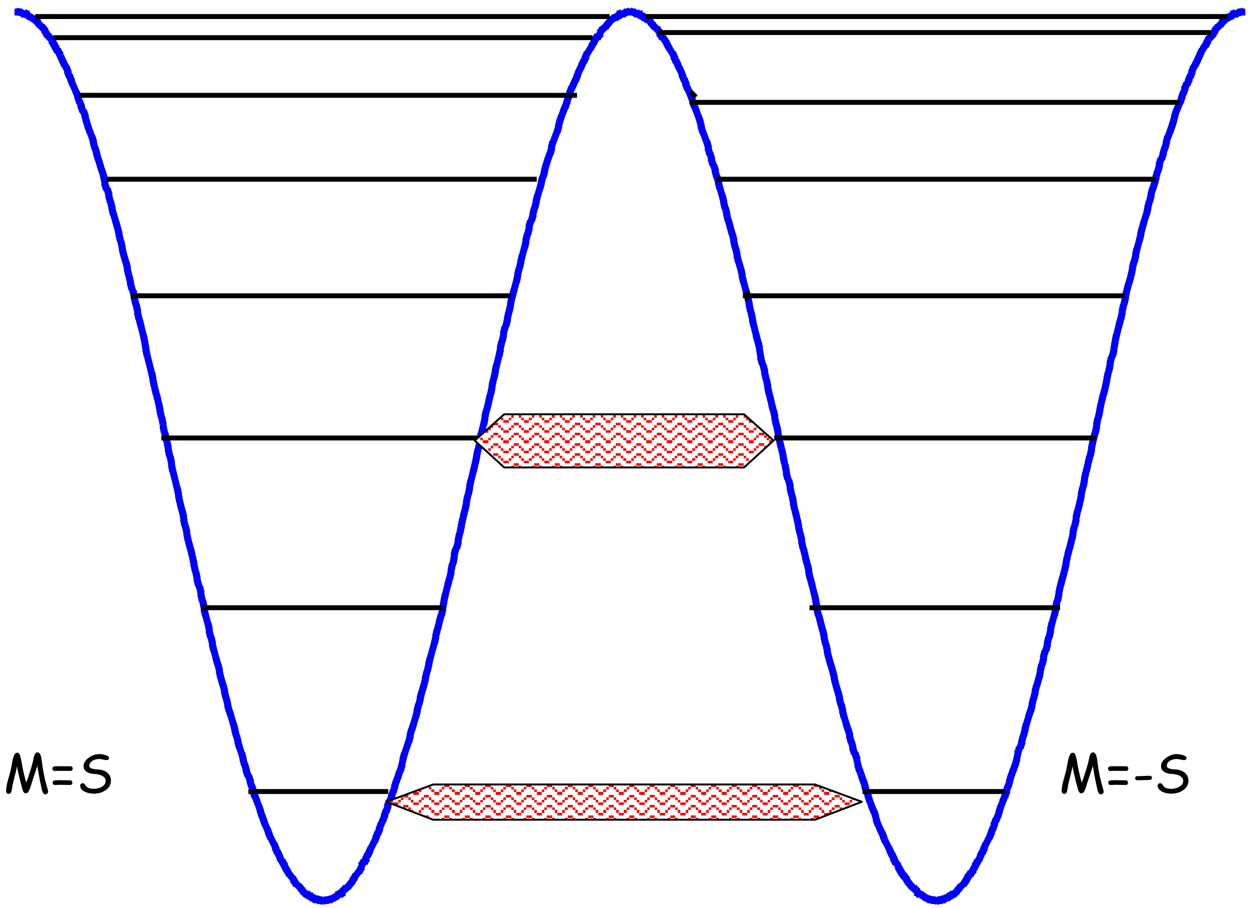


terms in S_x and S_y of the spin Hamiltonian

return to the equilibrium

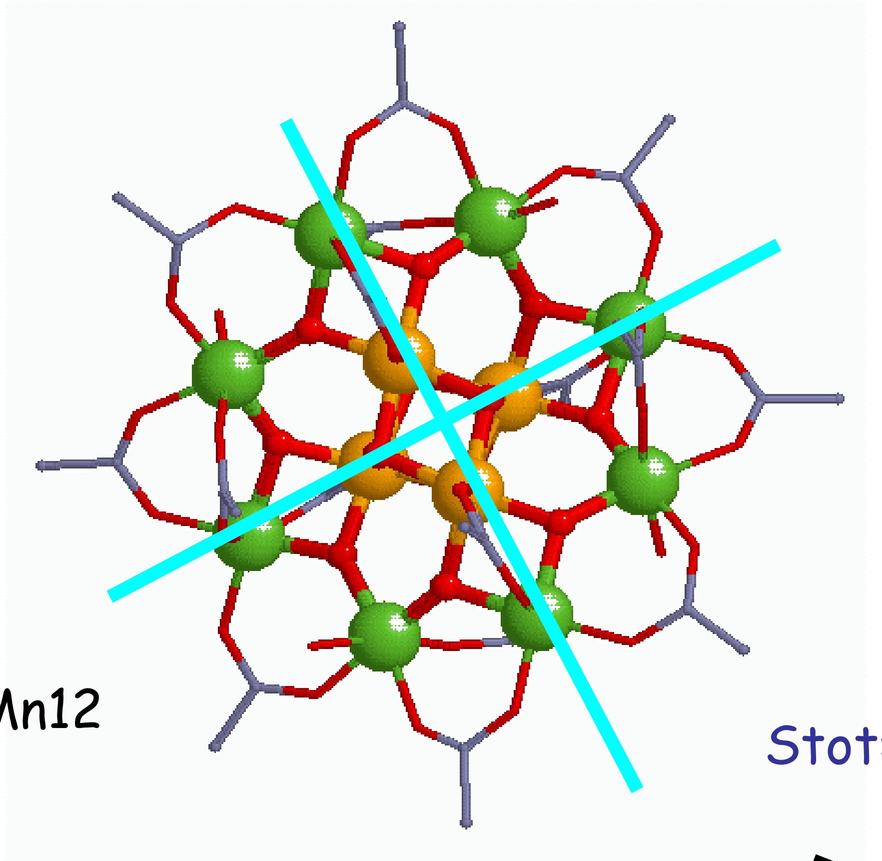
tunnel mechanism

H=0



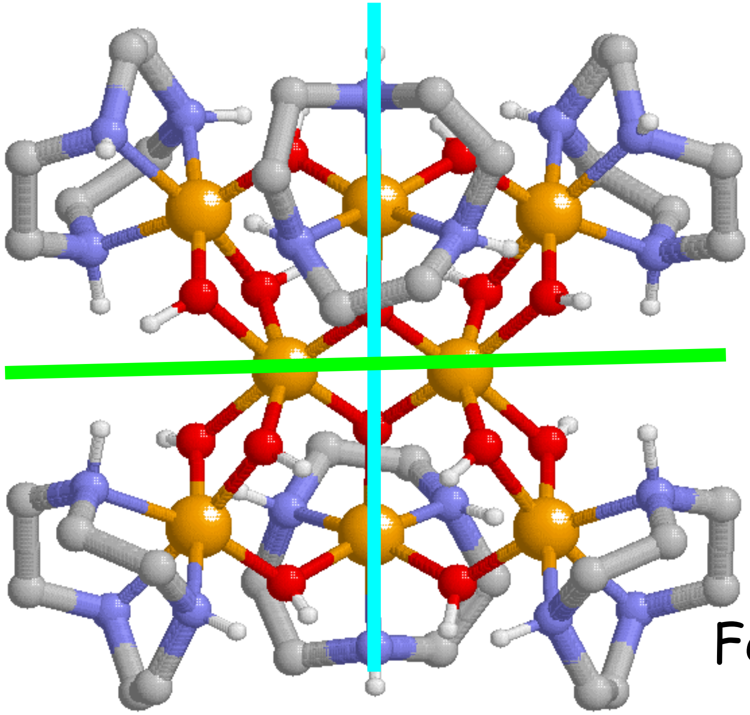
terms in S_x and S_y of the spin Hamiltonian

What is the difference ?



Mn12

Stot=10

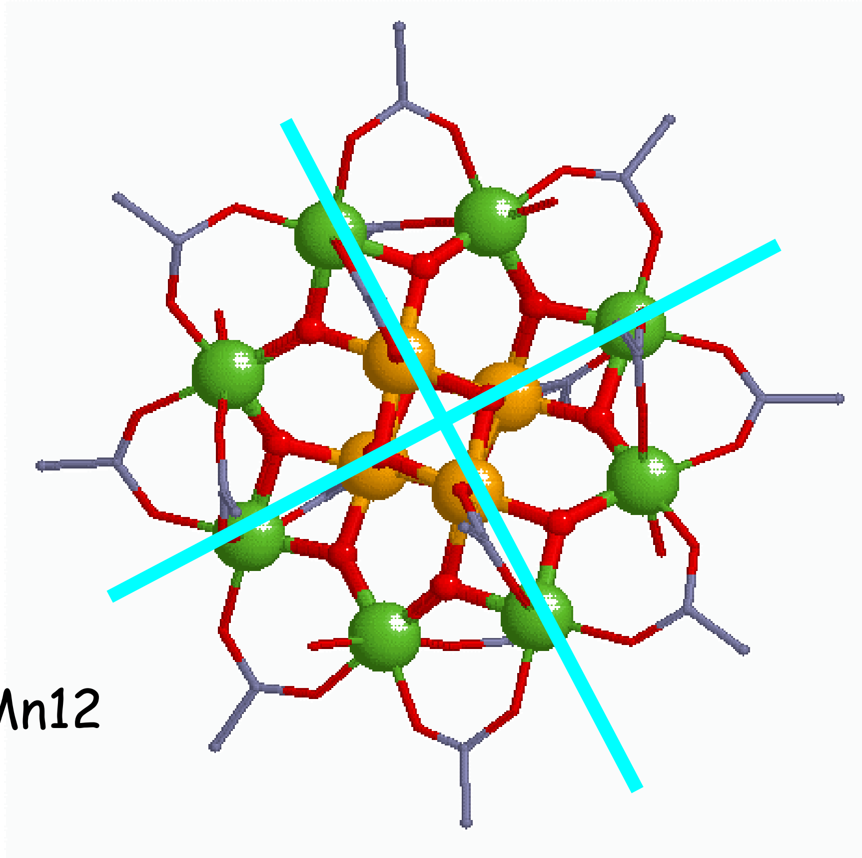


Fe8

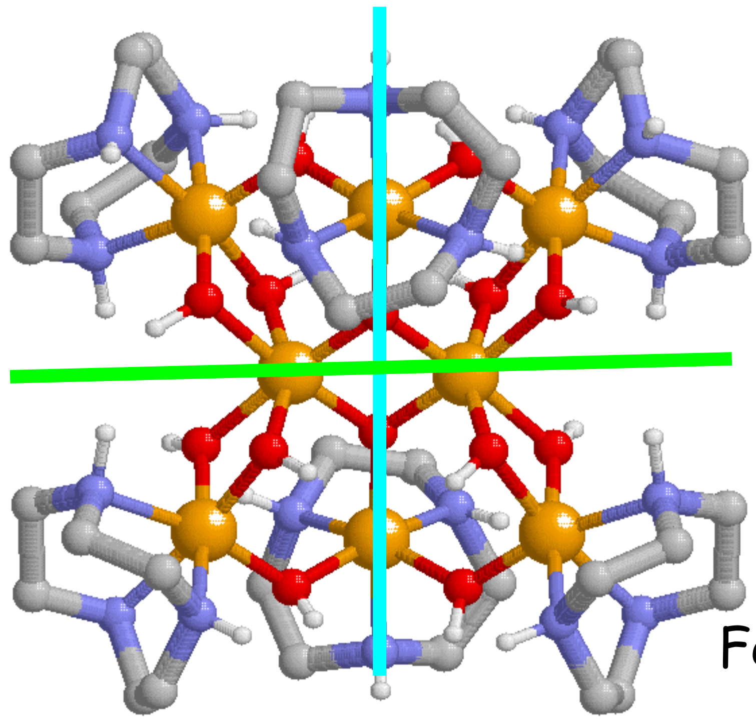
$$\mathcal{H} = \mu_B \mathbf{S.g.B} - D\,\mathbf{S}_z^2 + E\,(\mathbf{S}_x^2 - \mathbf{S}_y^2) + B\,\mathbf{S}_z^4 + C\,(\mathbf{S}_+^4 + \mathbf{S}_-^4)$$

Four fold axis
Tetragonal (E=0)

What is the difference ?



Mn12



Fe8

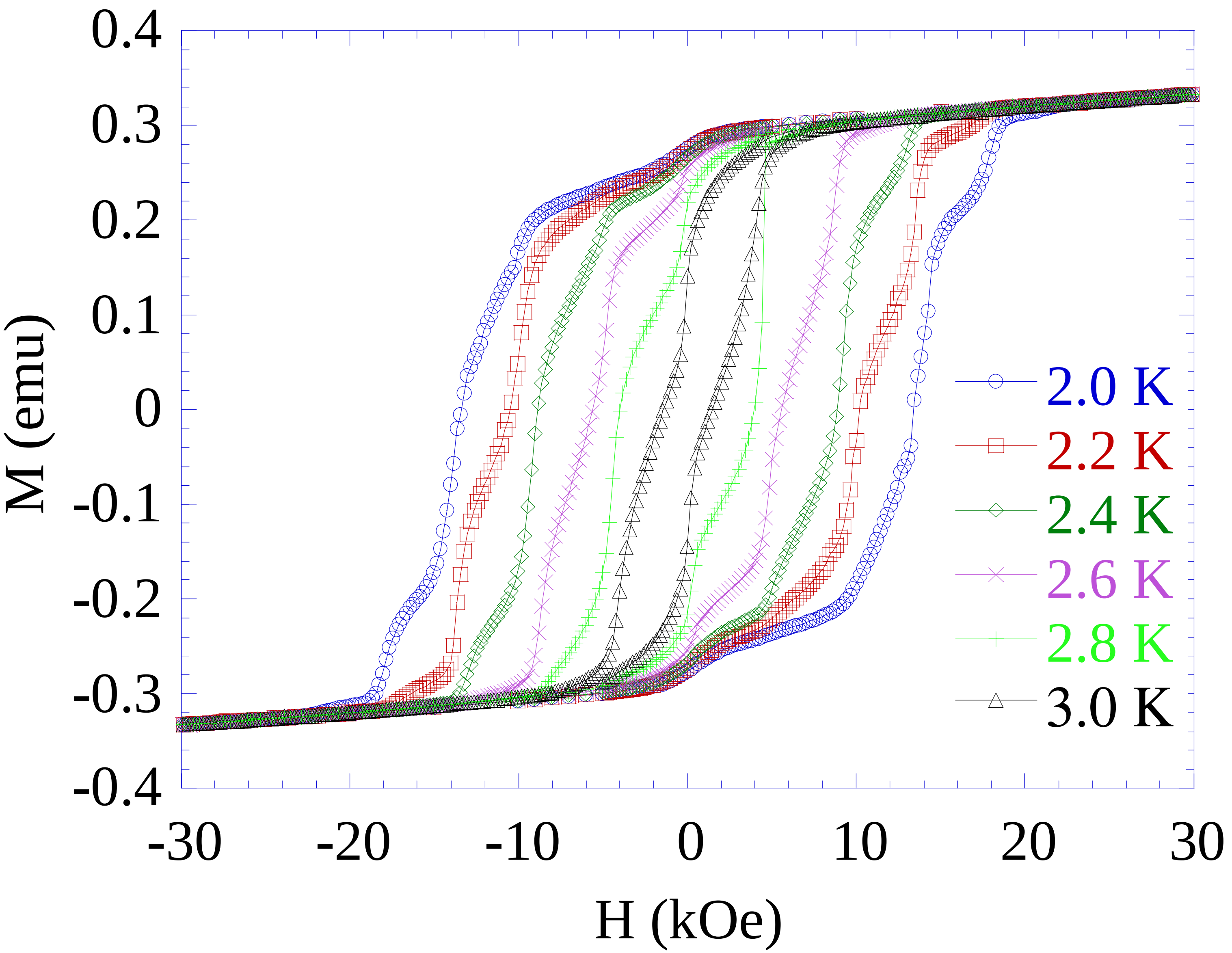
$$\mathcal{H} = \mu_B \mathbf{S.g.B} - D\,\mathbf{S}_z^2 + E\,(\mathbf{S}_x^2 - \mathbf{S}_y^2) + B\mathbf{S}_z^4 + C\,(\mathbf{S}_+^4 + \mathbf{S}_-^4)$$

Four fold axis
Tetragonal (E=0)

Two fold axis
Rhombic (E≠0)

Hysteresis loops for Mn_{12}

Friedman et al., PRL, 1996; Hernandez et al, EPL, 1996; Thomas et al., Nature, 1996



Hysteresis loops for Mn_{12}

Friedman et al., PRL, 1996;
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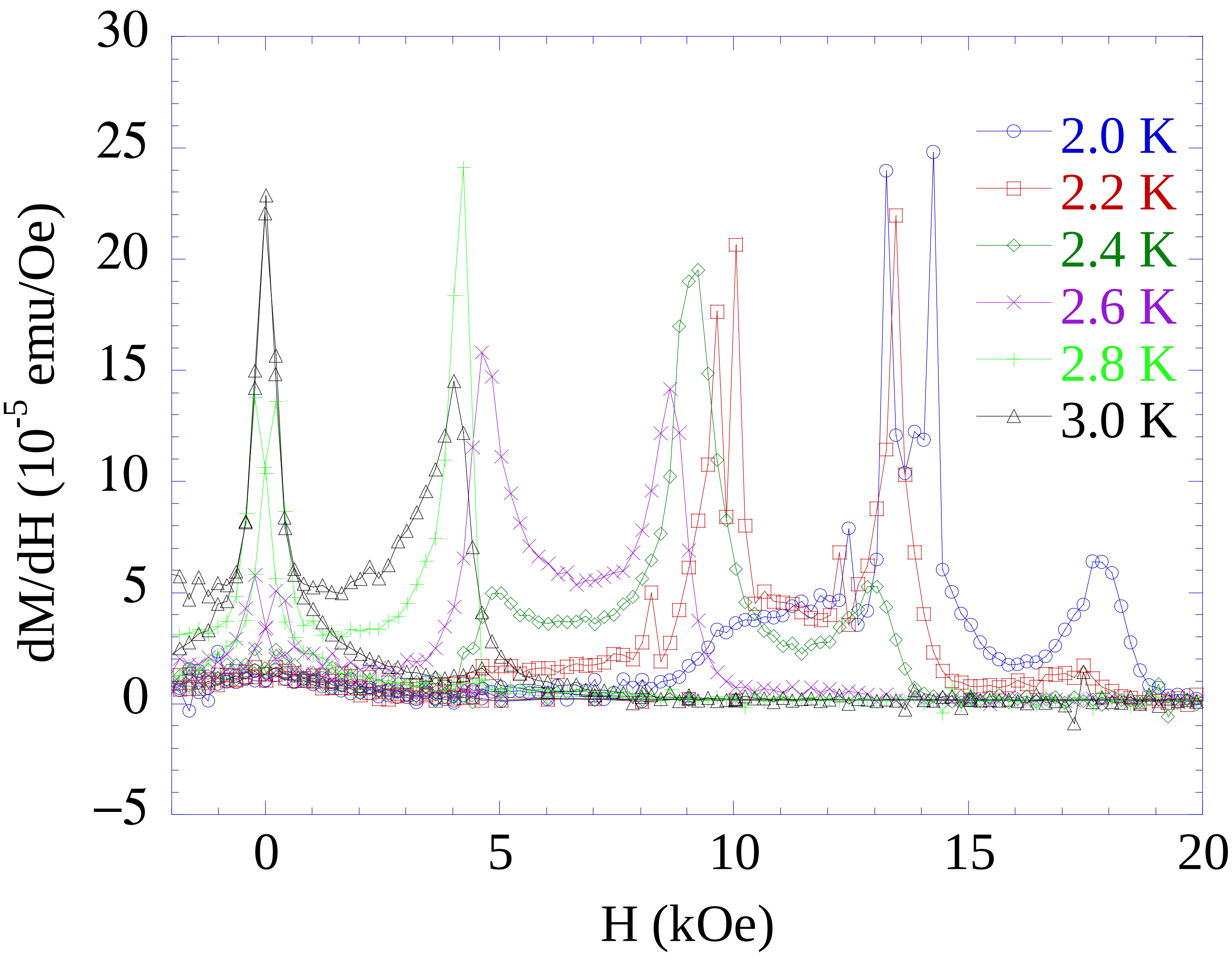
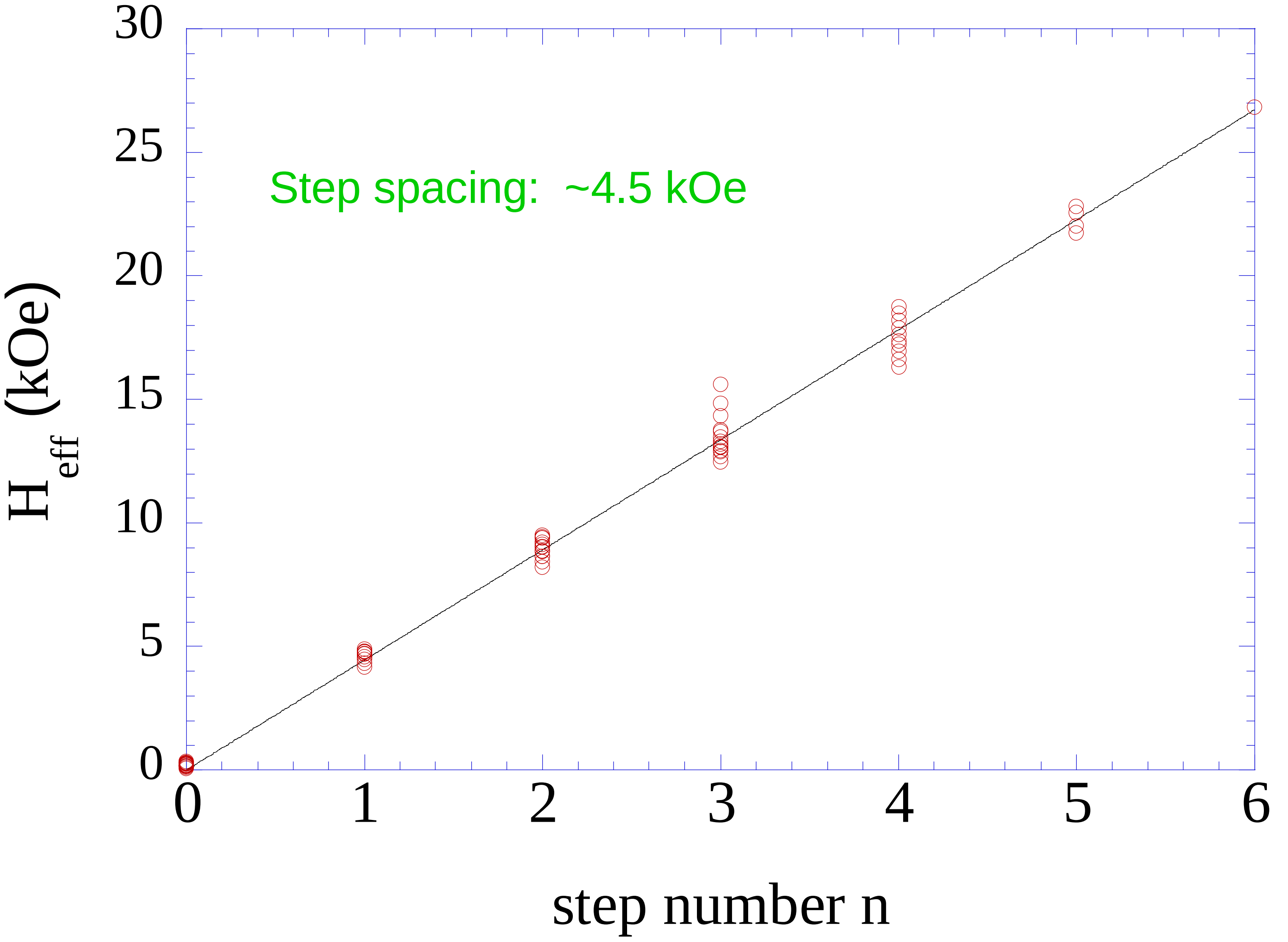
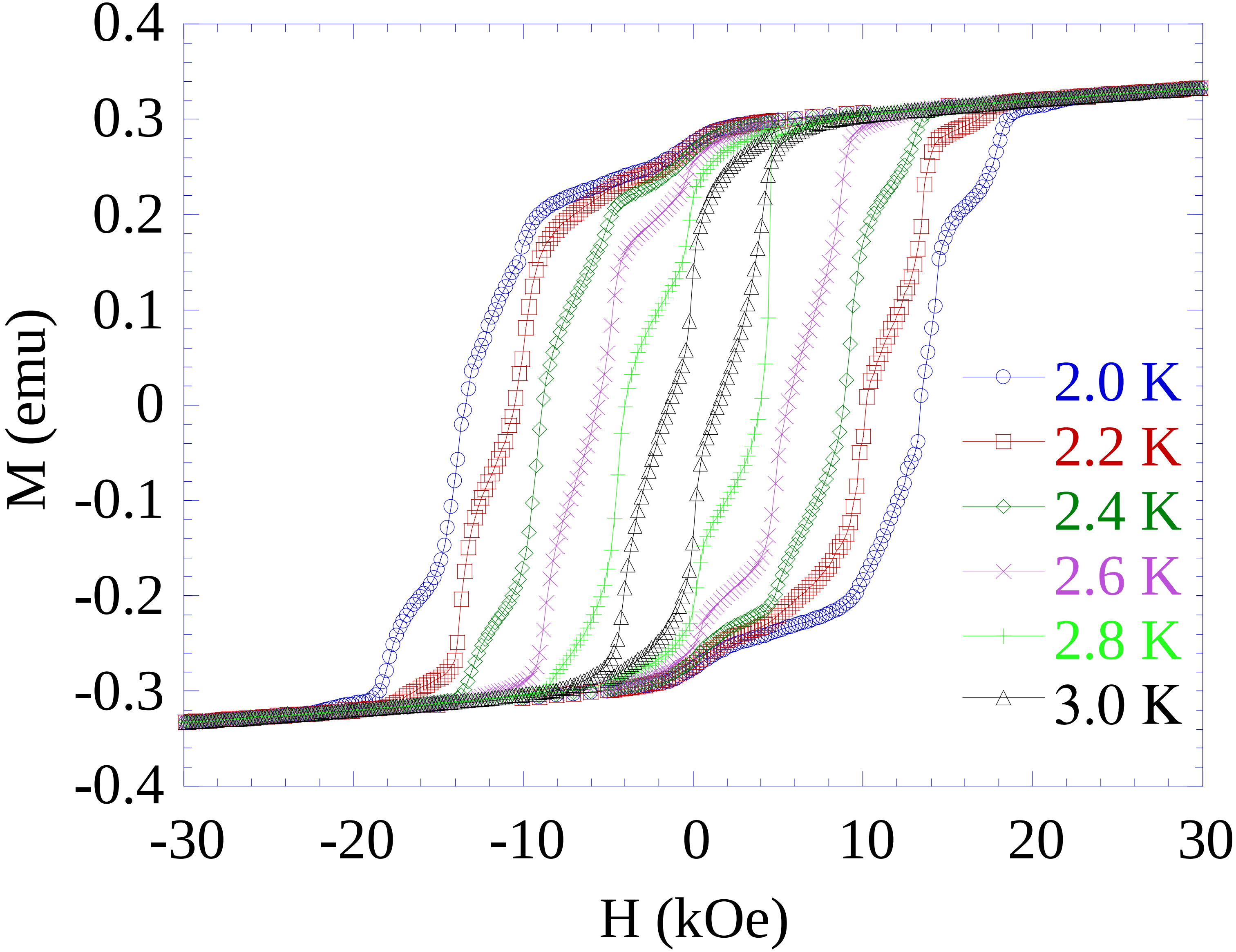


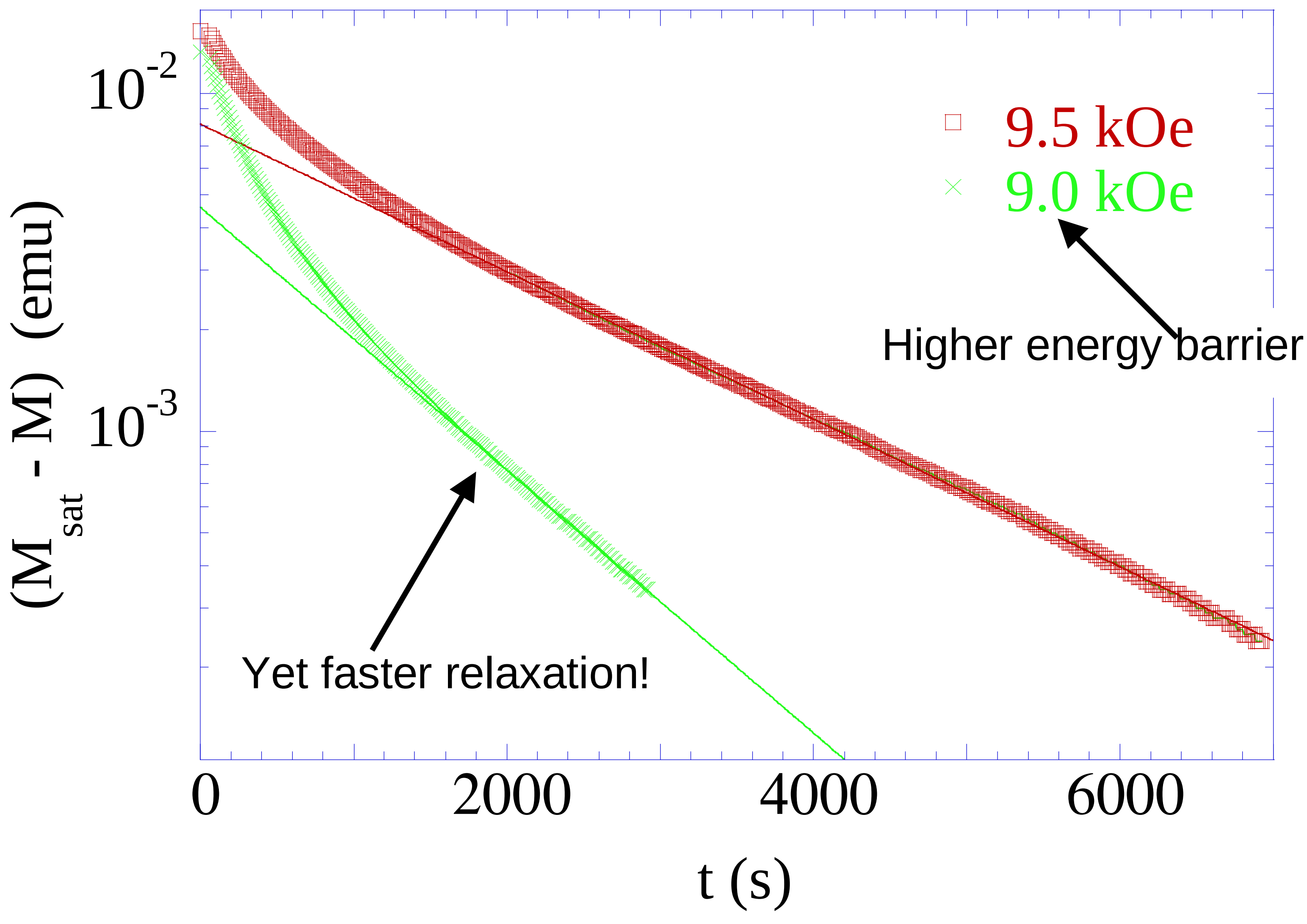
Uniform spacing between steps



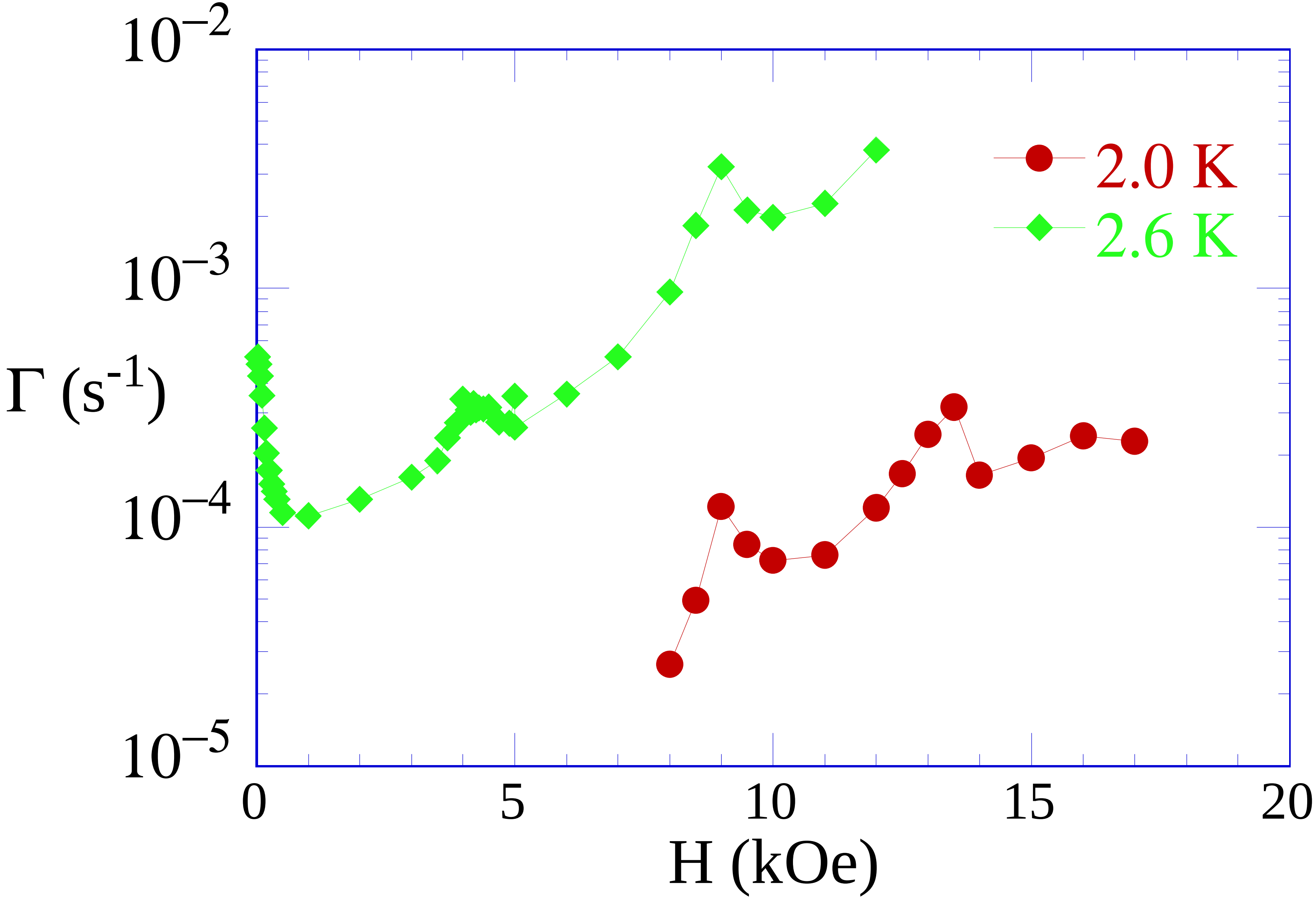
Hysteresis loops for Mn_{12}



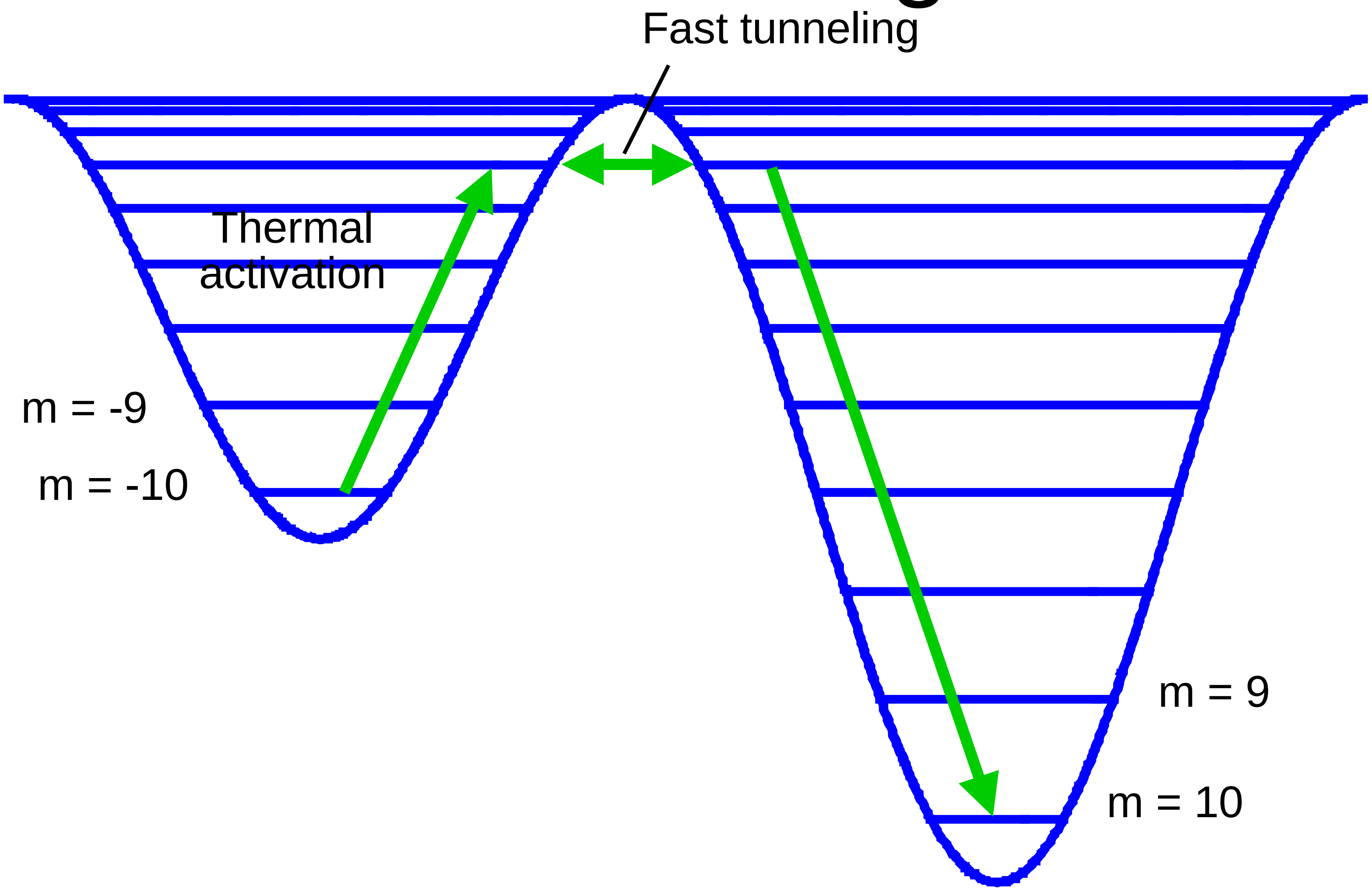
Enhanced Relaxation at Step Fields



Enhanced Relaxation at Step Fields



Thermally Assisted Resonant Tunneling



Tunneling occurs when levels in opposite wells align.

Hamiltonian for Mn_{12}

$$= -DS_z^2 - g\mu_B \mathbf{S}\cdot\mathbf{H}$$

The field at which $|m\rangle$ (in the left well) crosses $|-m+n\rangle$ (in the right well):

$$H_{m,-m+n} = \frac{-Dn}{g\mu_B}$$

Steps occur at regular intervals of field, as observed.

Step occurs every 4.5 kOe $\Rightarrow$ D/g = 0.31 K

Compare with ESR data:

D = 0.56 K, g = 1.93 **D/g = 0.29 K**

(Barra et al., PRB, 1997)

Hamiltonian for Mn_{12}

$$= -DS_z^2 - g\mu_B \mathbf{S}\cdot\mathbf{H} - BS_z^4$$

Spectroscopic studies revealed a 4th-order longitudinal anisotropy term B ~ 1.1 mK. (ESR: Barra et al., PRB, 1997 and Hill et al., PRL, 1998; INS: Mirebeau et al., PRL, 1999, Zhong et al., JAP, 2000 and Bao et al., cond-mat, 2000)

$\Rightarrow$Different pairs of levels cross at slightly different fields.

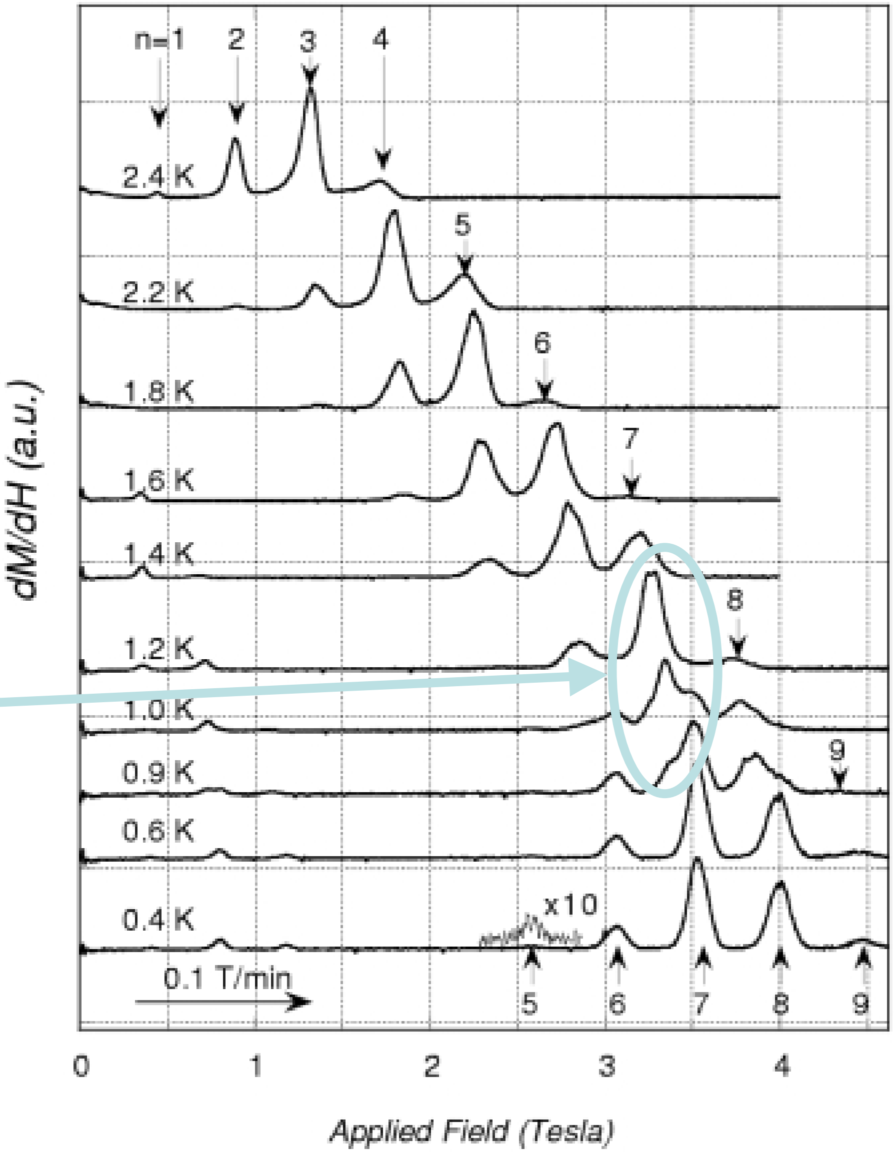
$\Rightarrow$Allows for the Examination of the Crossover from Thermally Assisted to Pure Quantum Tunneling.

Crossover to Ground-state Tunneling

Level crossing fields:

$$H_{m,m'} = \frac{Dn}{g\mu_B}\left[1+\frac{B}{D}(m^2+m'^2)\right]$$

Abrupt "first-order" transition between thermally assisted and ground state tunneling.



Theory: Chudnovsky and Garanin, PRL, 1997; Exp't: Kent, et al., EPL, 2000, Mertes et al., JAP, 2001.

Fe_8 Hamiltonian in Zero Field

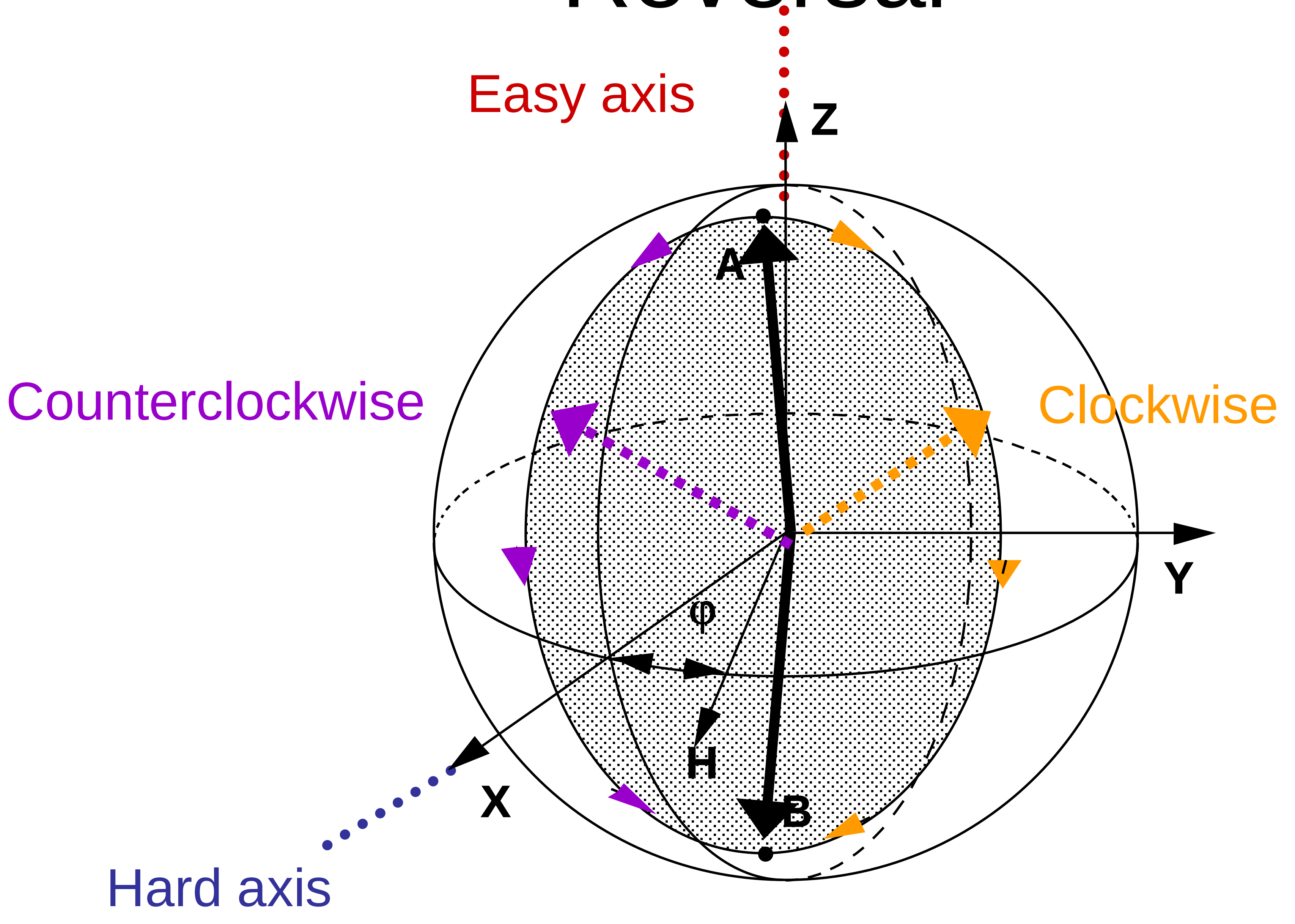
$$= -DS_z^2 + E(S_x^2 - S_y^2) + C(S_+^4 + S_-^4)$$

Easy Axis

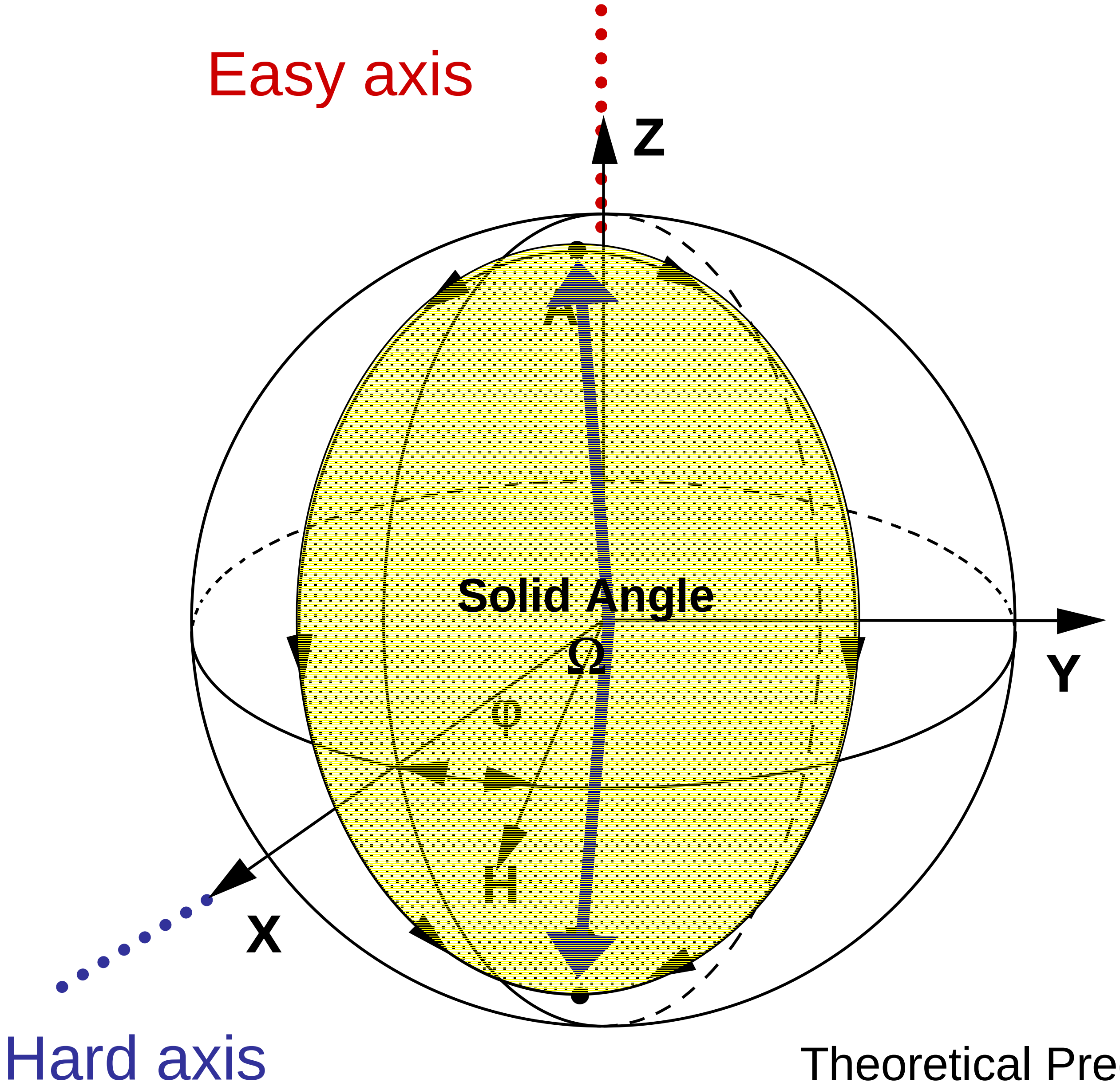
Hard Axis

Spin wants to rotate in the y-z plane

Two Paths for Magnetization Reversal



Destructive Topological Interference



Equivalence between paths is maintained when **H** is applied along the Hard Axis.

Topological (Berry's) phase depends on solid angle Ω enscribed by the two paths.

Complete destructive interference occurs for certain discrete values of Ω.

Theoretical Prediction: A. Garg., 1993.

Destructive Topological Interference

Modulation of Tunnel Splitting:

$$\Delta = \cos(S\Omega),$$

where Ω depends on the field along the Hard Axis.

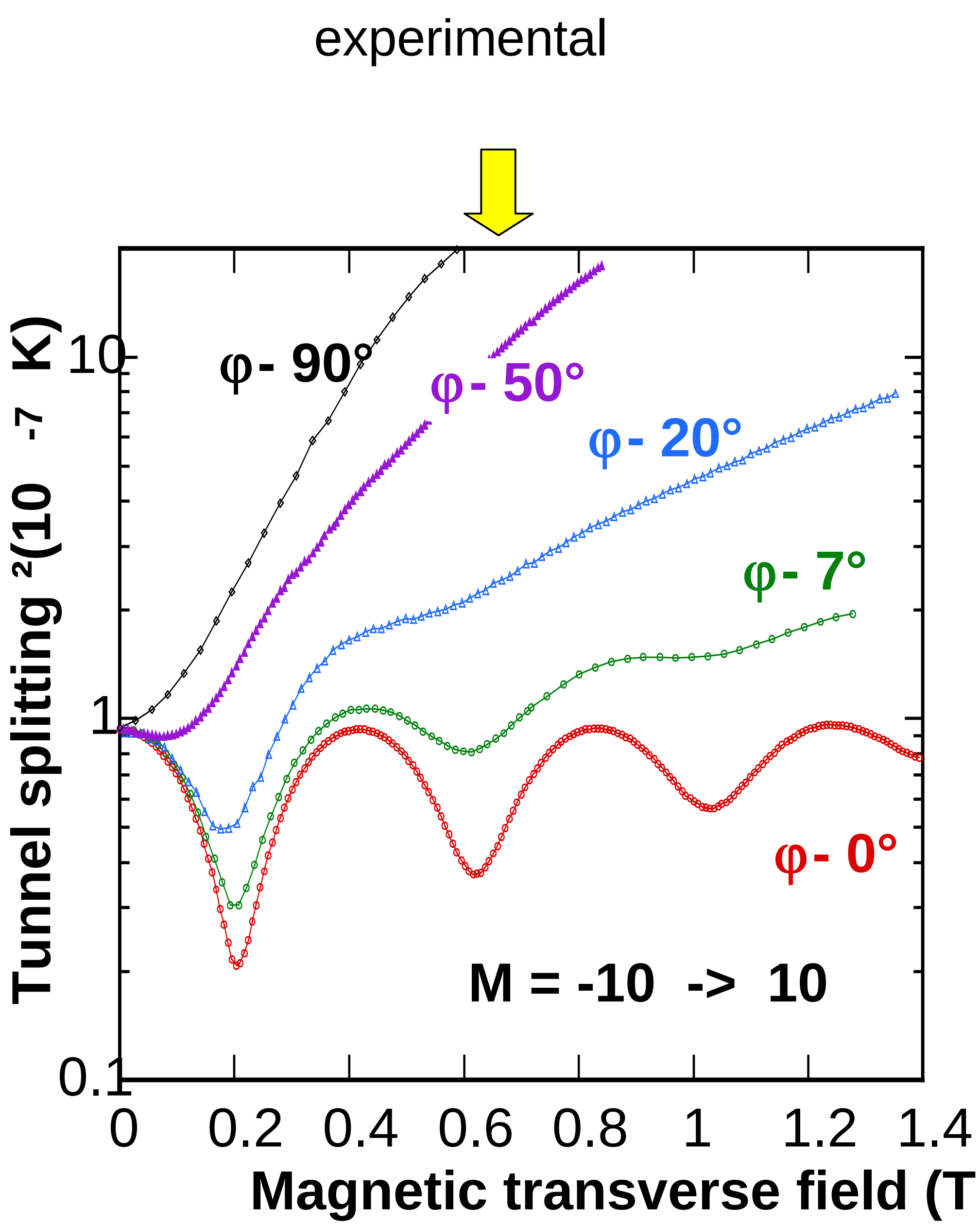
When $S\Omega = \pi/2, 3\pi/2, 5\pi/2\ldots$, tunneling is completely suppressed!

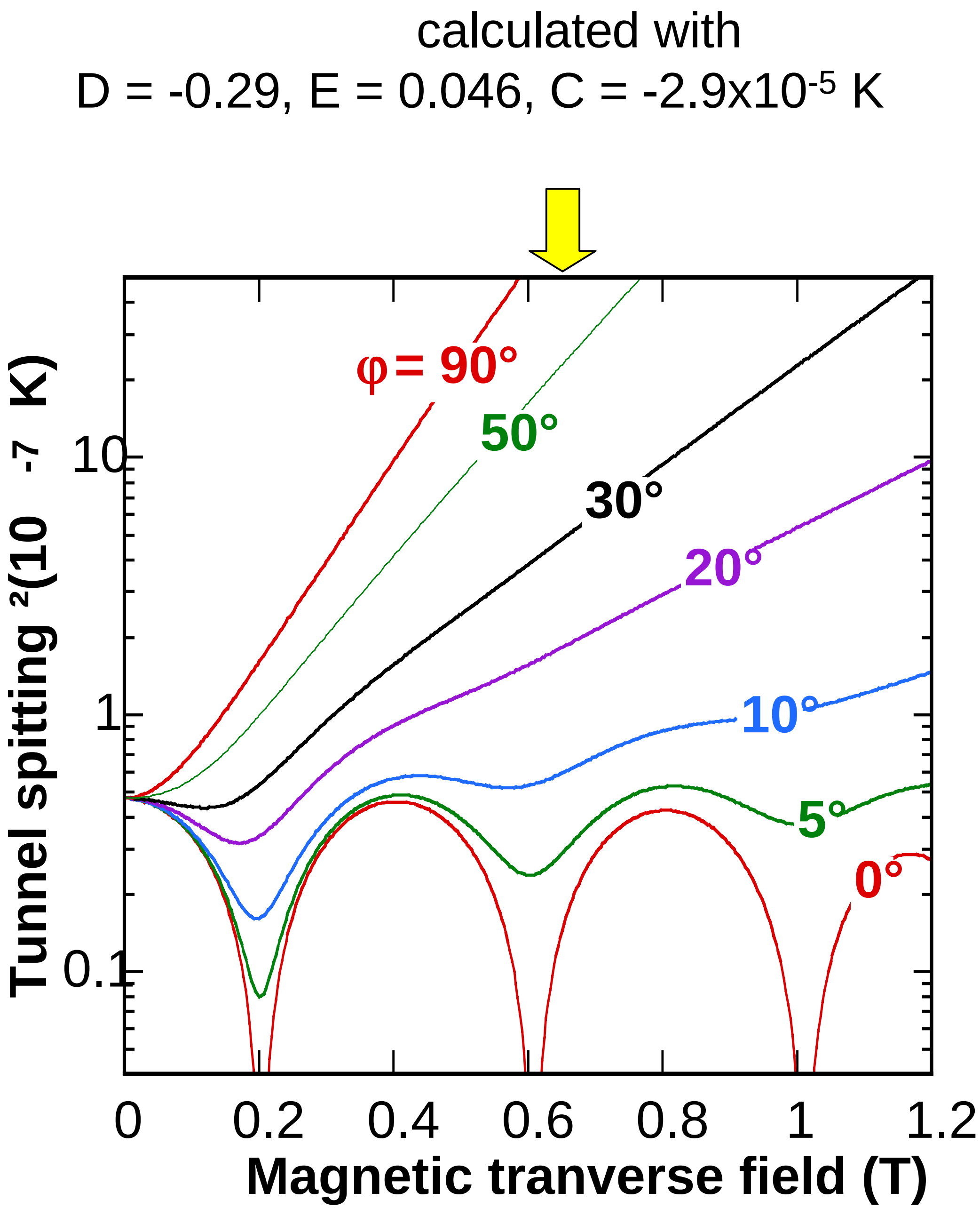
Interval between such destructive interference points:

$$\Delta H = \frac{2}{g\mu_B}\sqrt{2E(E+D)}$$

A. Garg., 1993.

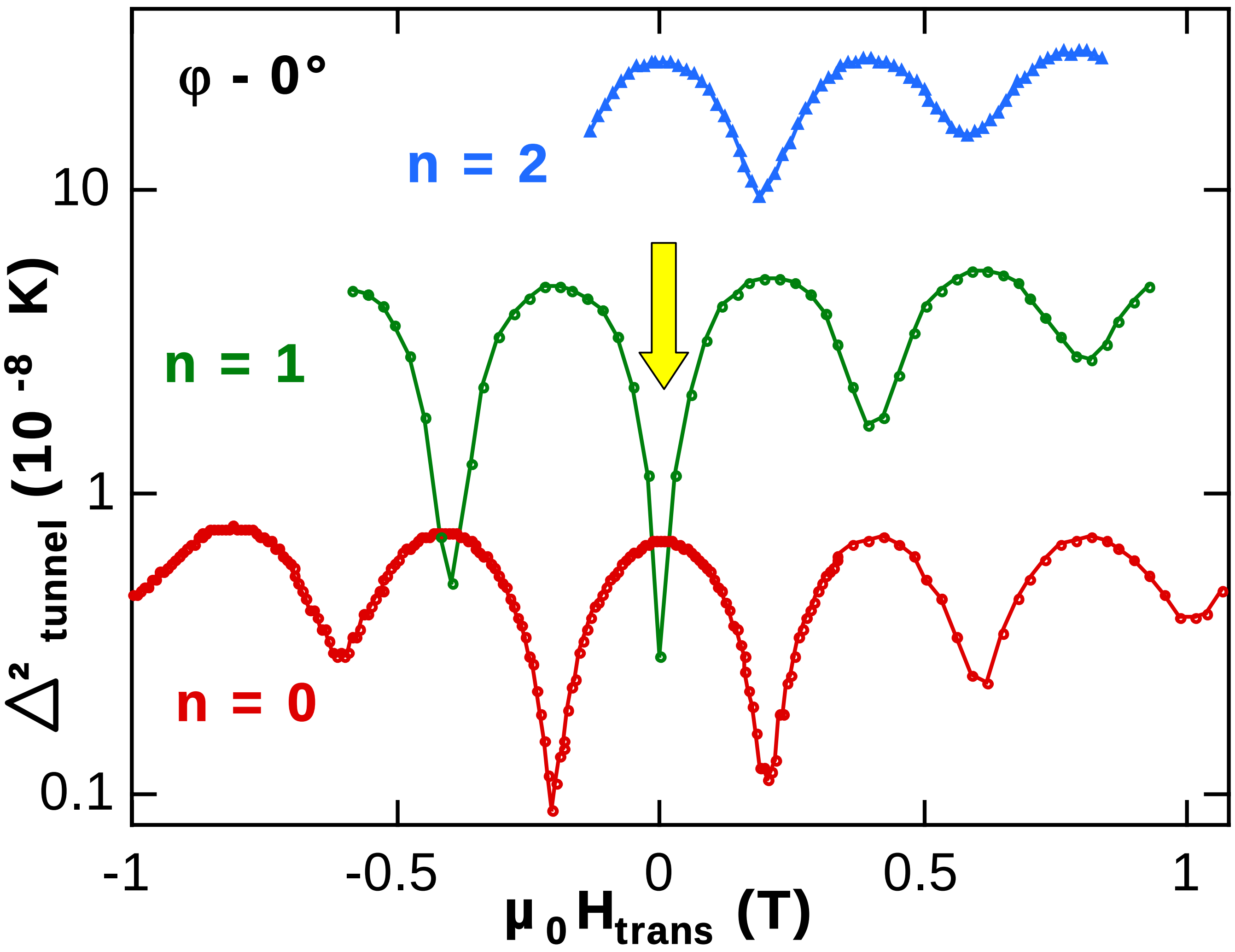
Measured Tunnel Splitting





W. Wernsdorfer and R. Sessoli, Science, 1999.

Parity Effect: Odd vs. Even Resonances



W. Wernsdorfer and R. Sessoli, Science, 1999.

What Causes Tunneling and Why the Parity Effect in Fe_8

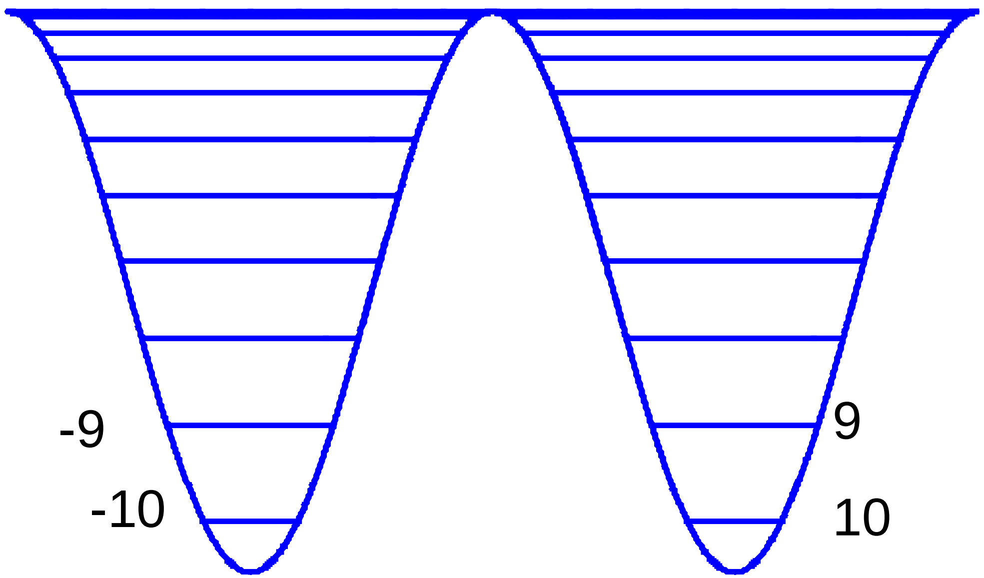
- Tunneling is produced by terms in the Hamiltonian that do not commute with S_z.
- For Fe_8, these terms are

$$E(S_x^2 - S_y^2) = \frac{E}{2}(S_+^2 + S_-^2)$$

- Selection rule: $\Delta m = \pm 2p \quad (p = 1,2,3,\ldots)$
- Every other tunneling resonance is forbidden!

What Causes Tunneling and Why the Parity Effect in Fe_8

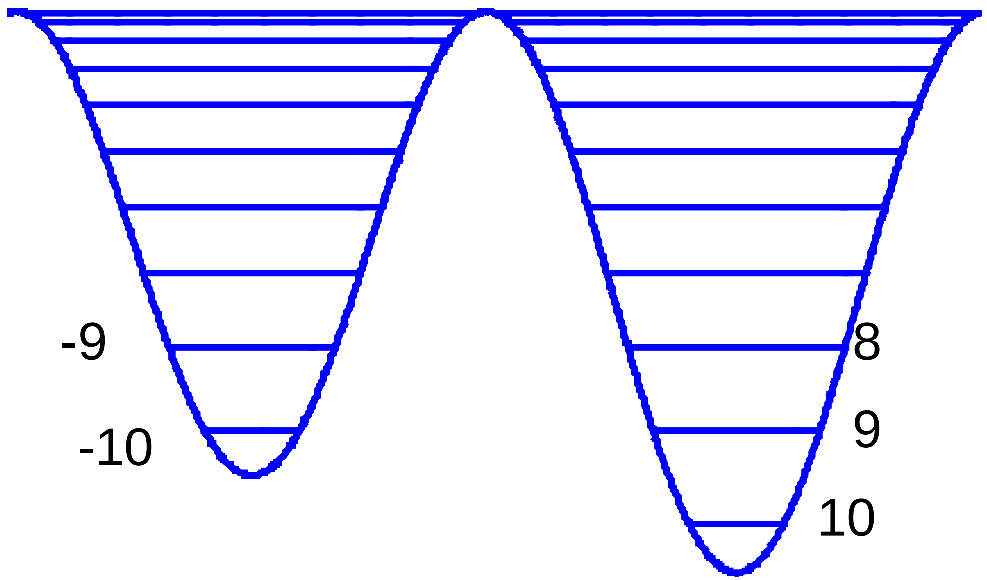
n = 0



$$\Delta m = \pm 2p$$

Tunneling Allowed

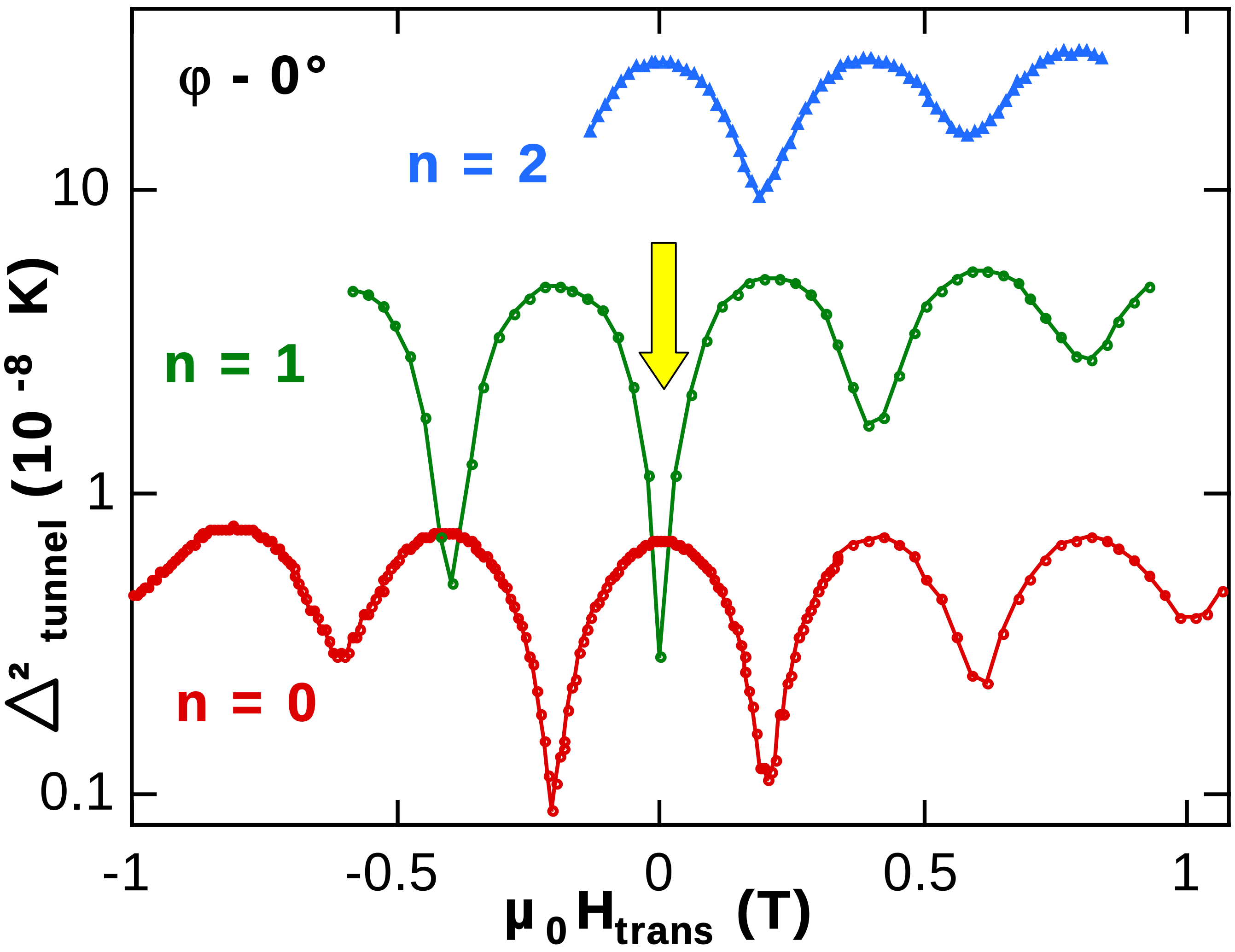
n = 1



$$\Delta m \neq \pm 2p$$

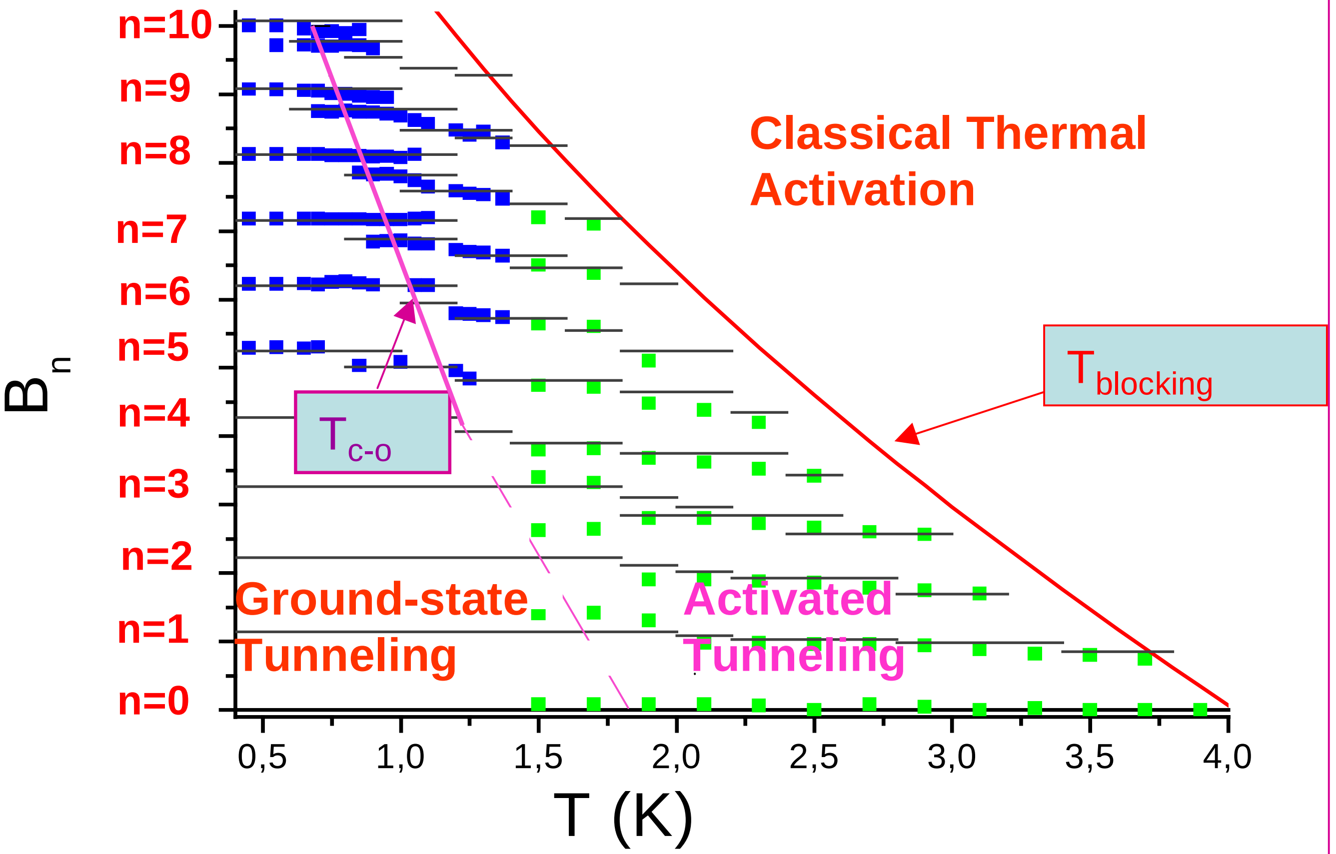
Tunneling Forbidden

Parity Effect: Odd vs. Even Resonances



W. Wernsdorfer and R. Sessoli, Science, 1999.

Crossover From Classical to Quantum Regime
(Mn_{12}-ac)



Measured (■ ■) and Calculated (——) Resonance Fields

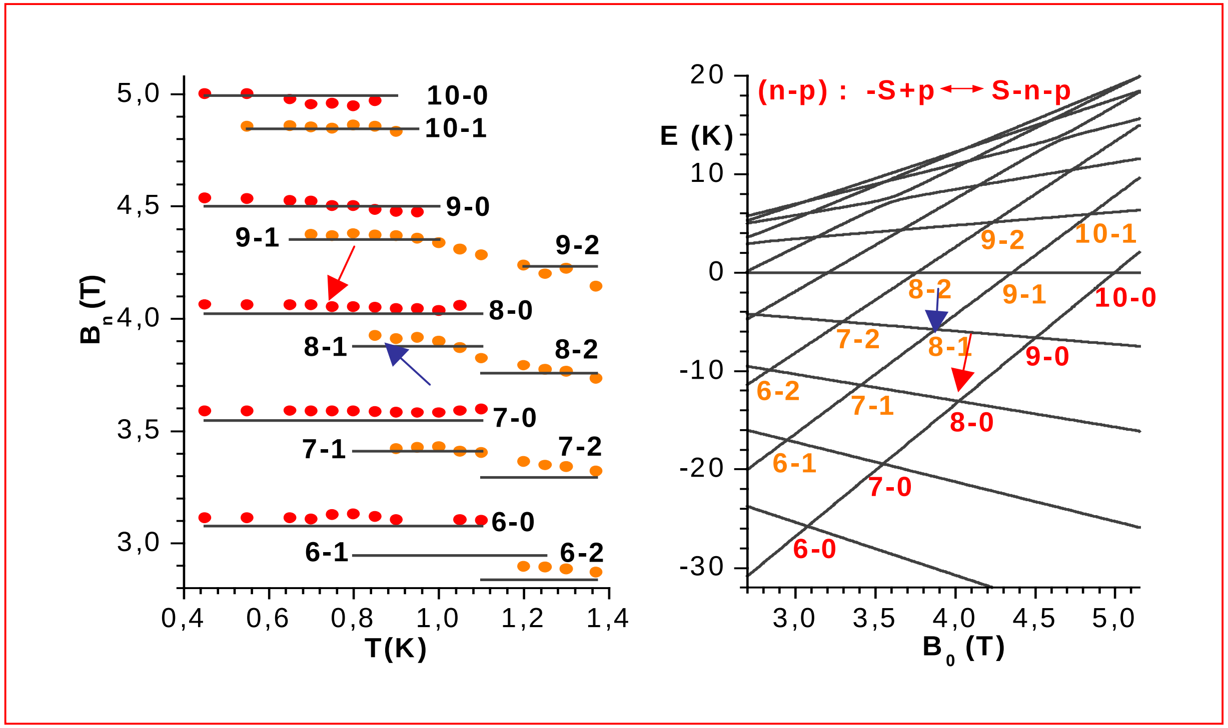
Barbara et al, JMMM 140-144, 1891 (1995) and J. Phys. Jpn. 69, 383 (2000)
Paulsen, et al, JMMM 140-144, 379 (1995); NATO, Appl. Sci. 301, Kluwer (1995)

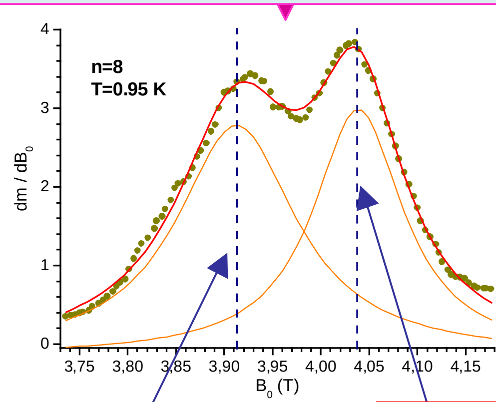
The Tunnel Window:
An effect of weak Hyperfine Interactions

Data points and calculated lines

Level Scheme

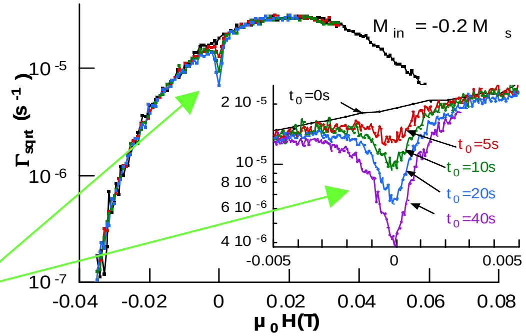
Inhomogeneous broadening of Two resonances: Dipolar fields





8-1

8-0

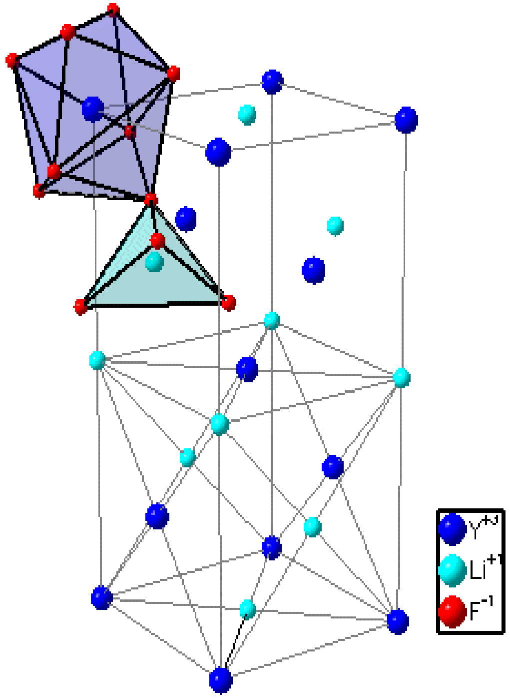


- Chiorescu et al, PRL, 83, 947 (1999)
- Barbara et al, J. Phys. Jpn. 69, 383 (2000)
- Kent et al, EPL, 49, 521 (2000)
- Wernsdorfer et al, PRL (1999)

Homogeneous broadening of nuclear spins: Tunnel window

Effects of Strong Hyperfine Interactions:

Case of Rare-earth ions: Ho^{3+} in $Y_{0.998}Ho_{0.002}LiF_4$



Tetragonal symmetry
(Ho in S_4)

$J = L+S = 8$; $g_J=5/4$

Dipolar interactions between Ho^{3+} → << mT

$$H_{CF-Z} = -B_2^0 O_2^0 - B_4^0 O_4^0 - B_4^4 O_4^4 - B_6^0 O_6^0 - B_6^4 O_6^4 - g_J \mu_B \mathbf{JH}$$

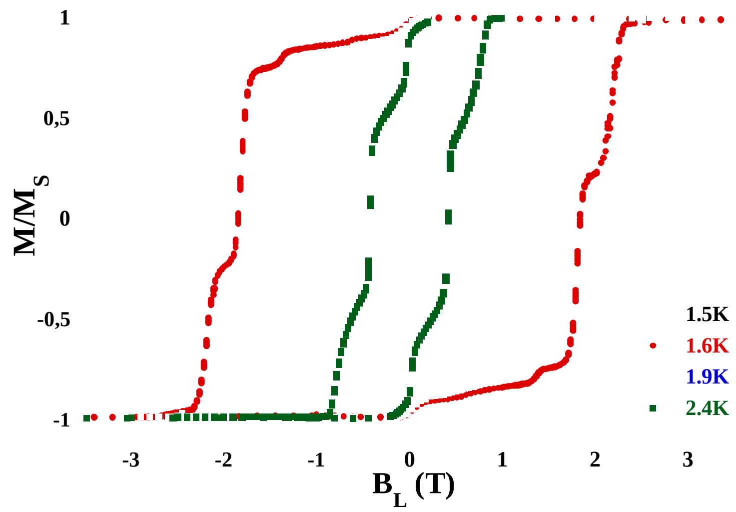
B_l^m : acurately determined by high resolution optical spectroscopy

Sh. Gifeisman et al, Opt. Spect. (USSR) 44, 68 (1978); N.I. Agladze et al, PRL, 66, 477 (1991)

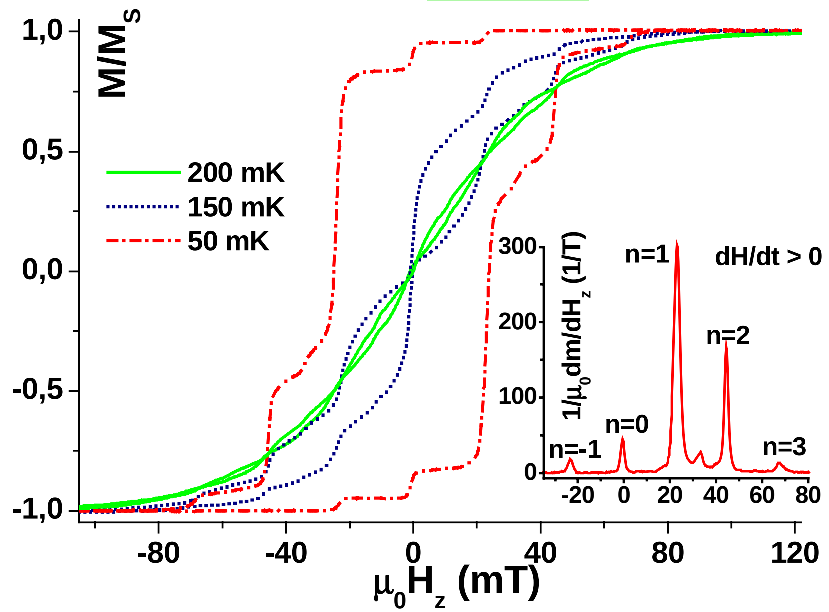
Hysteresis loop of Ho^{3+} ions in $YLiF_4$

Comparison with Mn12-ac

Mn_{12}-ac



Ho^{3+}



Thomas et al, Nature (1996)

Friedman et al, PRL (1996), Hernandez et al, EPL (1996)

Steps at Bn = 450.n (mT)

Tunneling of Mn_{12}-ac Molecules

Giraud et al, PRL, 87, 057203-1 (2001)

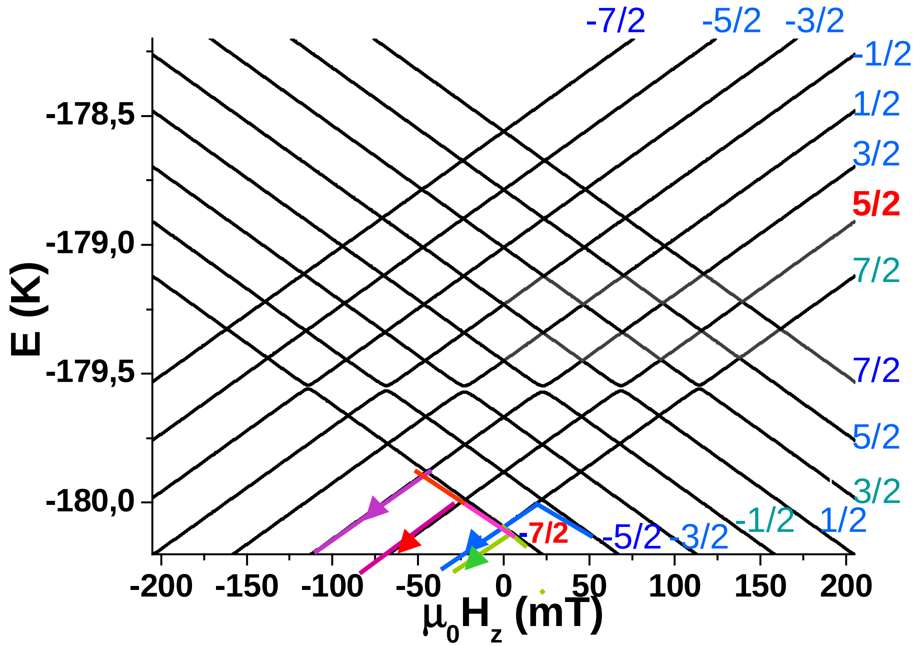
Steps at B_n = 23.n (mT)

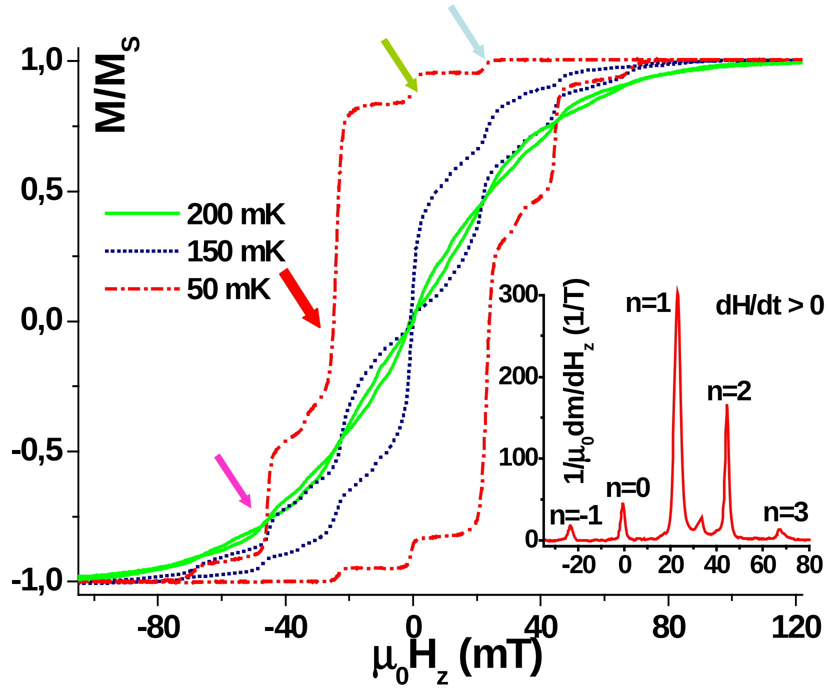
Tunneling of Ho^{3+} ion

Role of Strong Hyperfine Interactions

$$H = H_{CF-Z} + A.\mathbf{I}.\mathbf{J}$$

Induce Tunneling of Electronic Moments

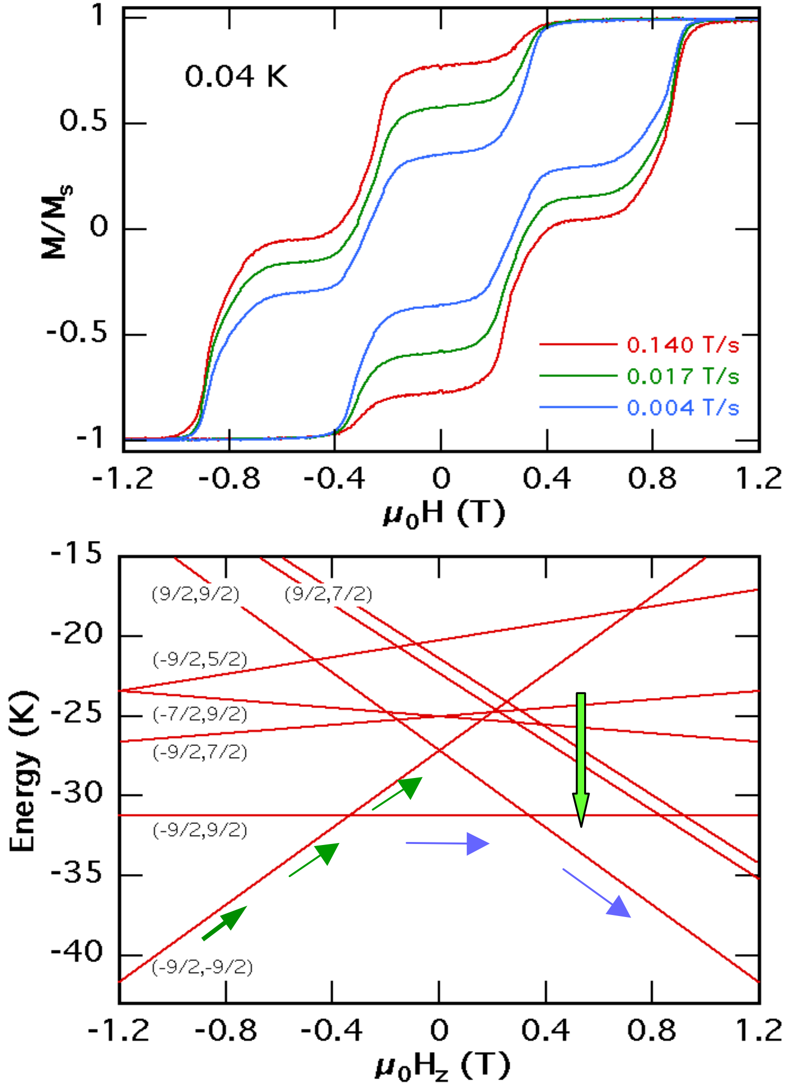


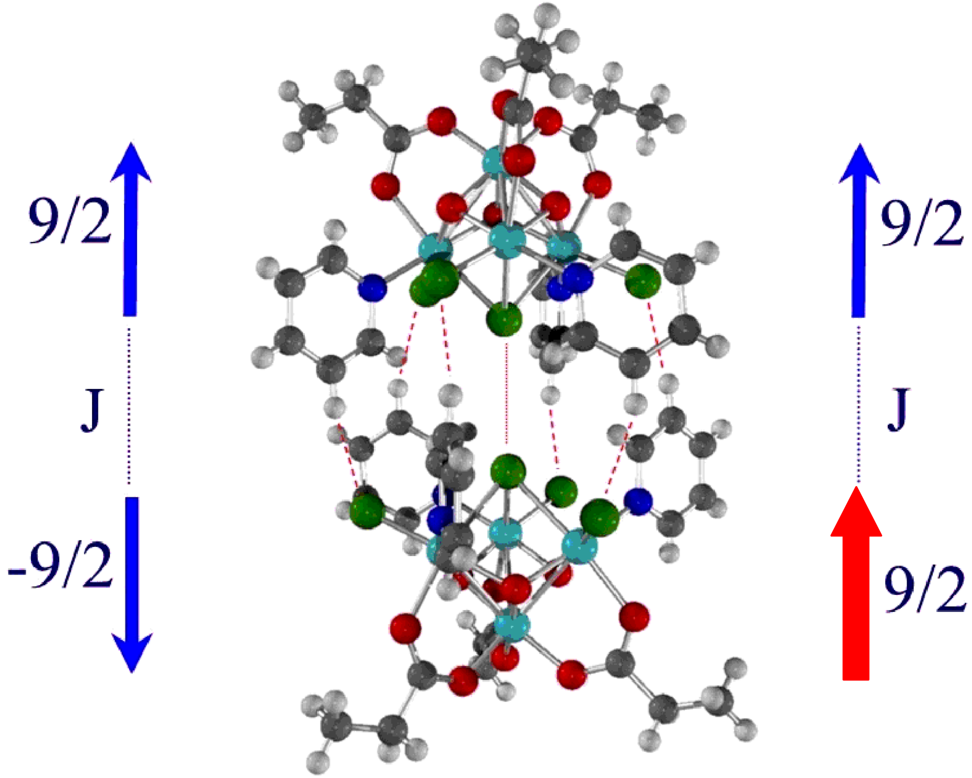


Co-Tunneling of Electronic and Nuclear Spins:
Electro-nuclear entanglement

Avoided Level Crossings between |Ψ−, Iz> and |Ψ+, Iz'> if DI= (Iz -Iz')/2 integer

Exchange-biased quantum tunnelling in a dimer of Mn_4 molecule

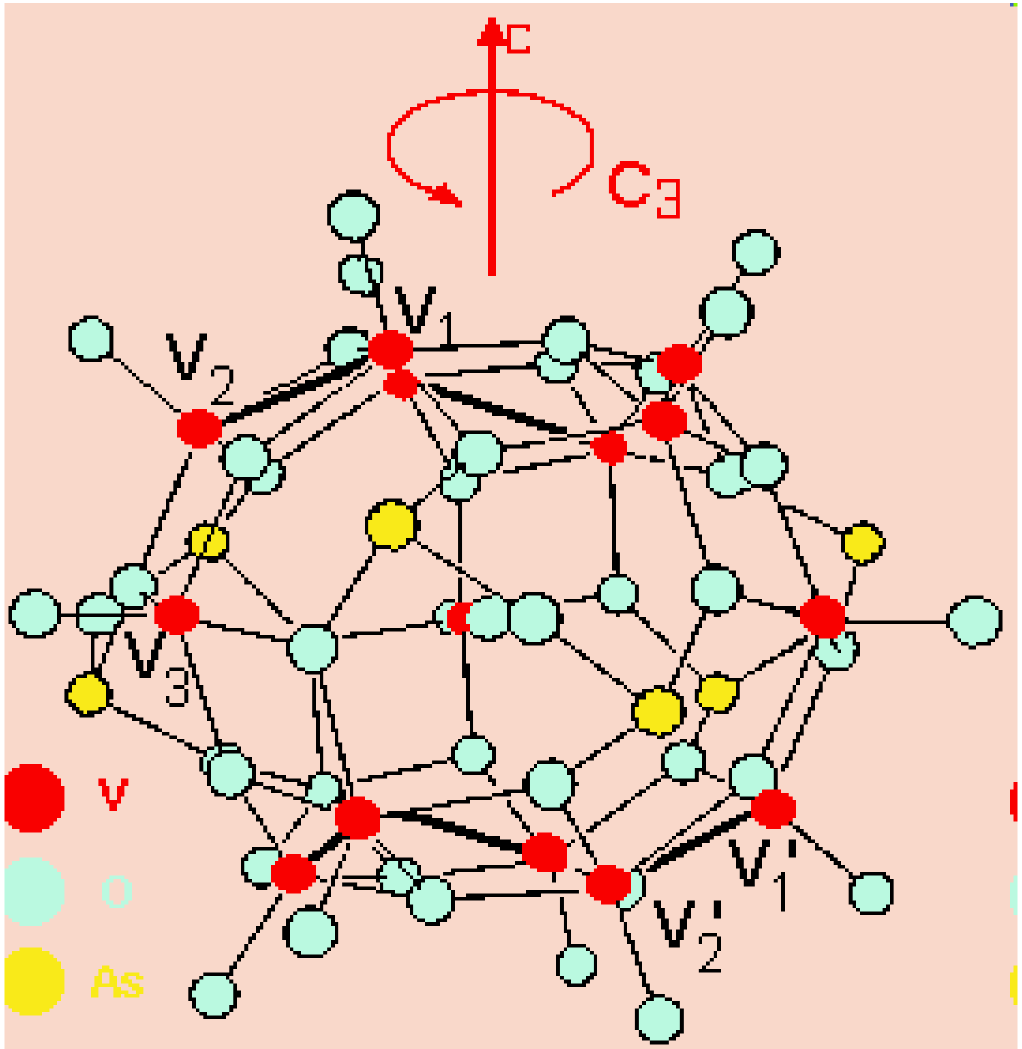




W. Wernsdorfer et al, *Nature* **416**, 406 (2002)

V_{15} : The Archetype of Low spin Molecules

A Mesoscopic Spin S=1/2



Exchange interactions:

Antiferromagnetic ~ several 10^2K

Müller, Döring, Angew. Chem. Intl. Engl., 27, 171 (1988)

Anisotropy of g-factor:

~ 0.6%

Ajiro et al, J..Low. Temp. Phys. to appear (2003)

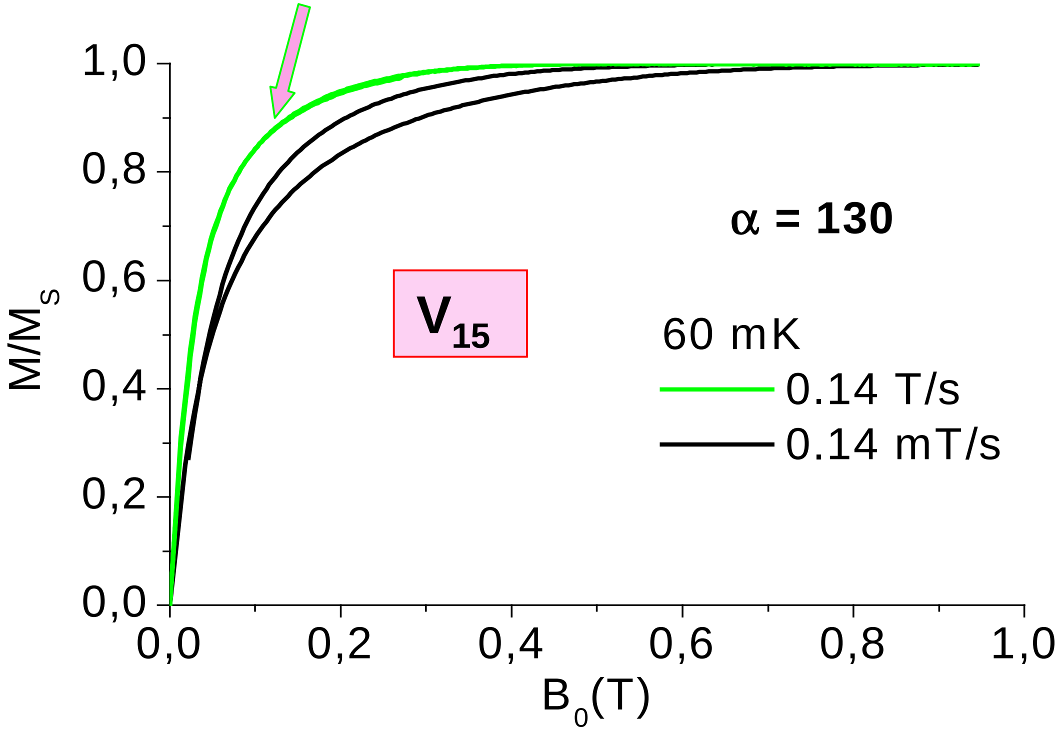
Barra et al,J. Am. Chem. Soc. 114, 8509 (1992)

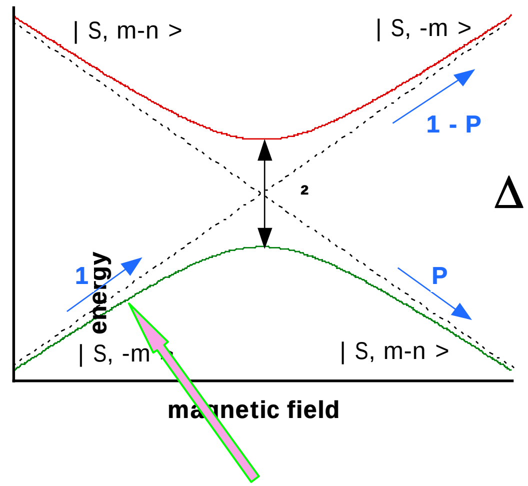
« Isolated V_{15} » :
A two-level system « without dissipation »

Fast sweeping rate / Weak coupling to the cryostat

Adiabatic Landau-Zener Spin Rotation

M(H) : Reversible and out of equilibrium





Δ ~ 80 mK

M(H) = dE(H)/dH

Nuclear Spin-Bath :
Weak Level Broadening

Barbara et al, cond-mat / 0205141 v1; submited to PRL.

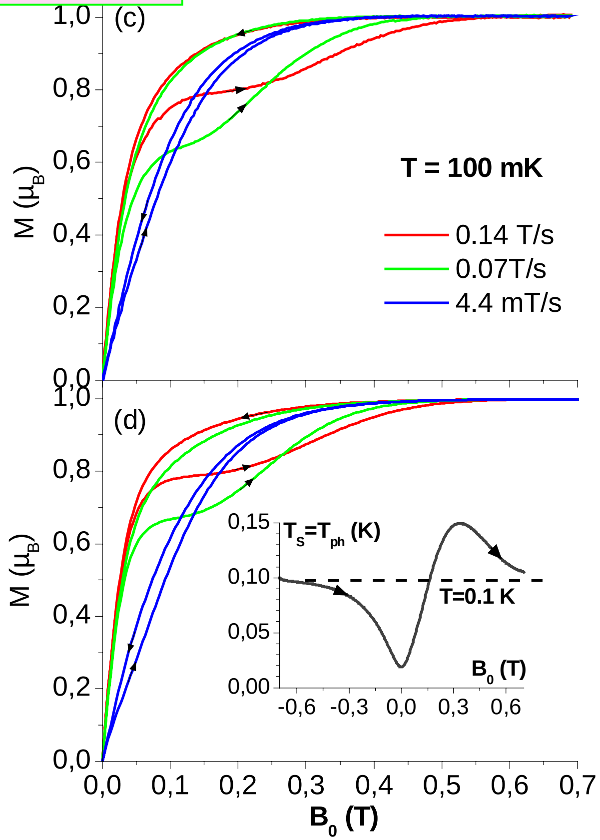
« Non-Isolated V_{15} » : A two-level system « with dissipation »

Low sweeping rate / Strong coupling to the cryostat

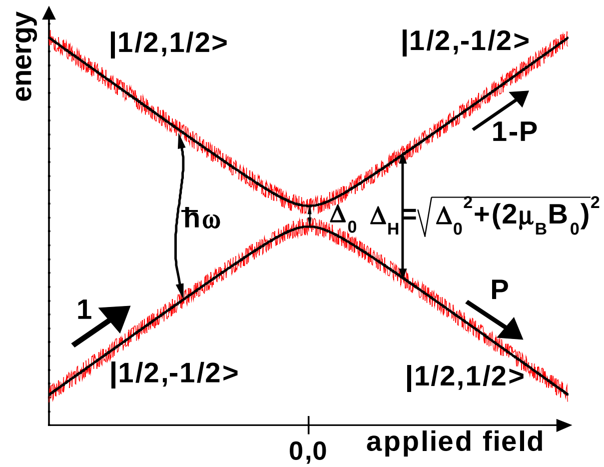
M(H): Irreversible

Measured ⇨

Calculated ⇨



LZS transition at Finite Temperature (dissipative)



<u>Phonon-bath</u> → bottleneck model

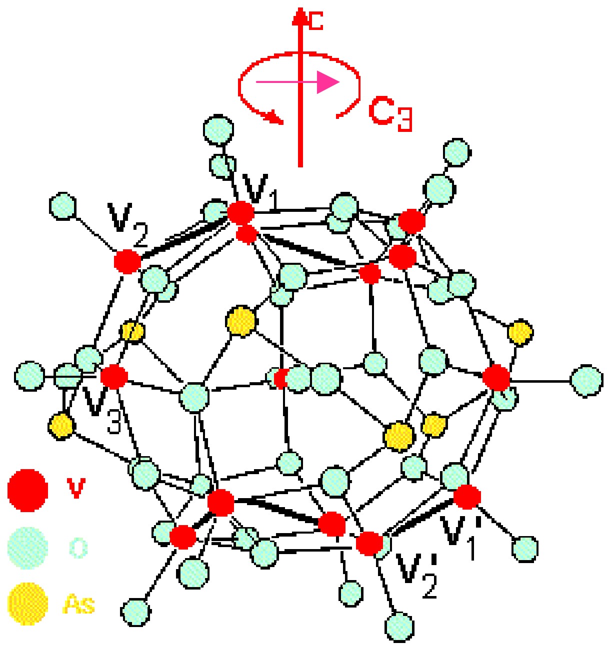
Abragam, Bleaney, 1970; Chiorescu et al, 1999.

<u>Nuclear spin-bath</u> → level broadening

Stamp, Prokofiev, 1998.

Chiorescu et al, PRL 84, 3454 (2000)

V_{15}: a Gapped Spin ½ Molecule



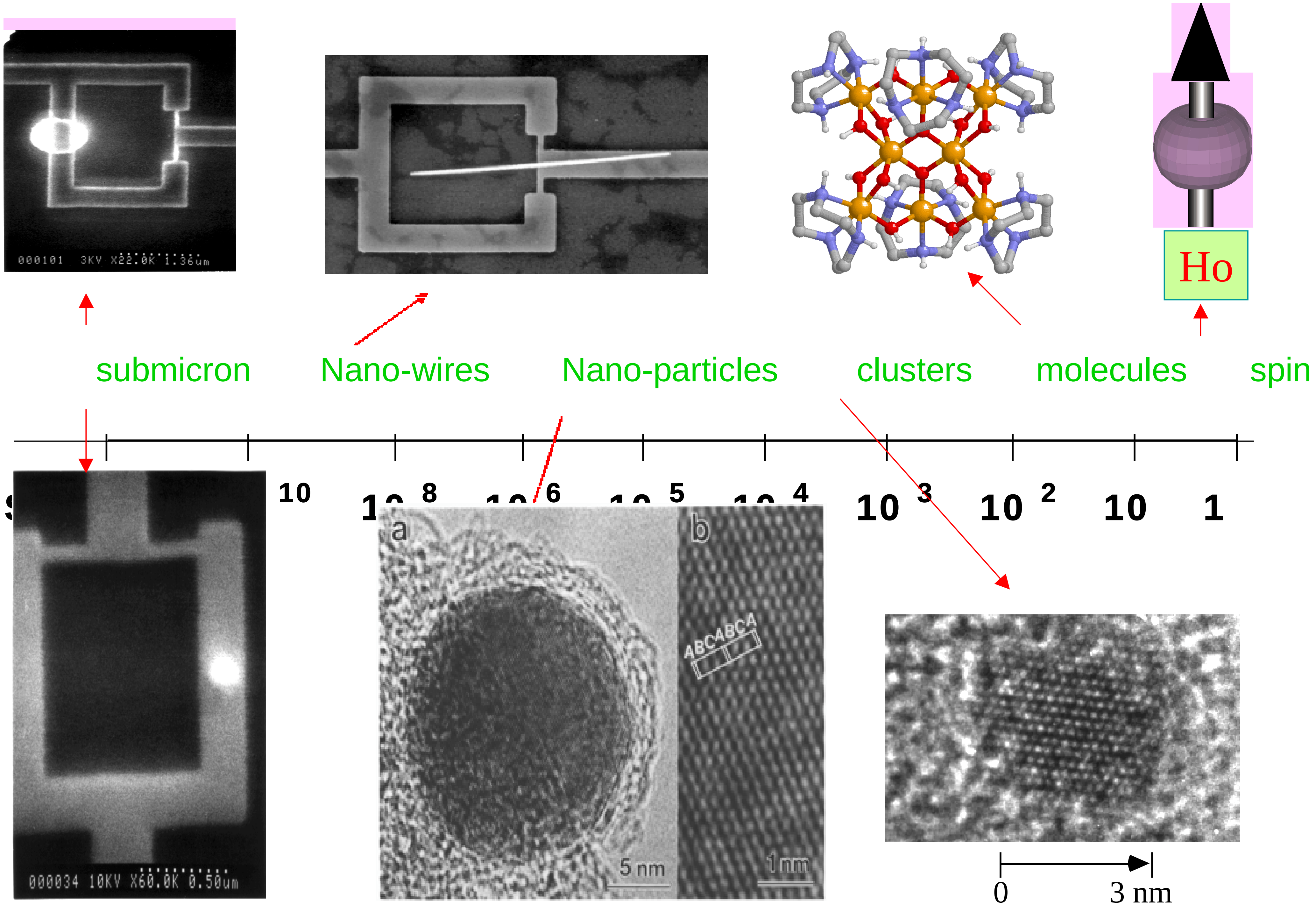
Time Reversal Symmetry → D = 0 (Kramers Theorem)

The Multi-Spin Character of the Molecule
(15 spins)

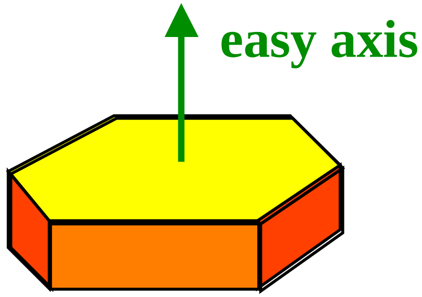
+

Dzyaloshinsky-Moriya interactions: $H_{DM} = -\Sigma\ \mathbf{D}_{ij}\mathbf{S}_i x \mathbf{S}_j$

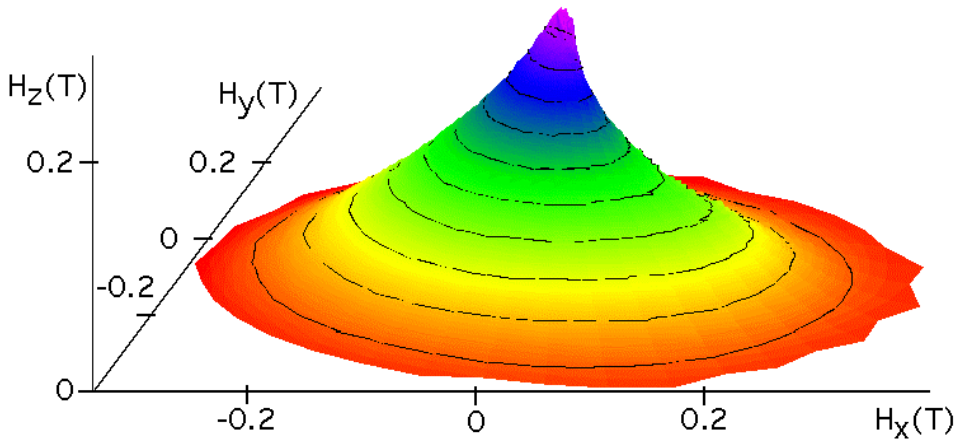
Magnetism: From Macroscopic to Single atoms



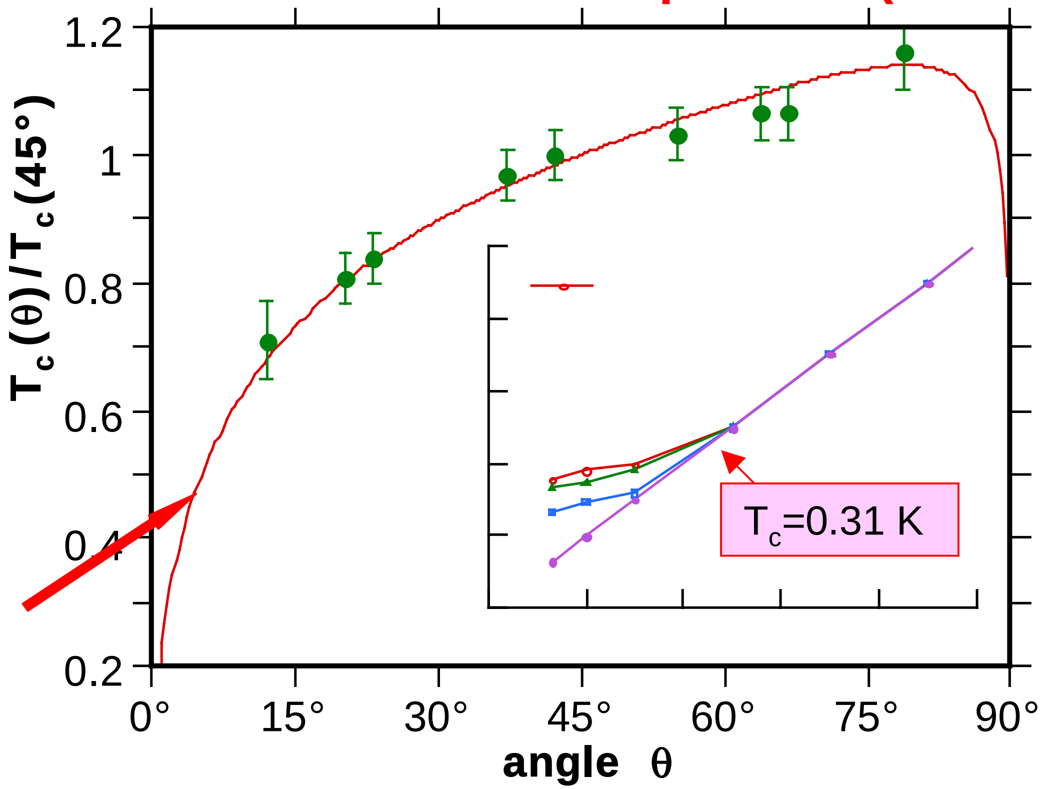
Macroscopic Quantum Tunneling of Magnetization of Single Nanoparticles



Barium ferrite Nanoparticle (10 nm)



Stoner-Wohlfarth astroid



$$T_c(\theta) \propto \mu_0 H_a \, \varepsilon^{1/4} \, |\cot\theta|^{1/6} \left(1 + |\cot\theta|^{2/3}\right)^{-1}$$

Miguel and Chudnovsky, PRB (1995)

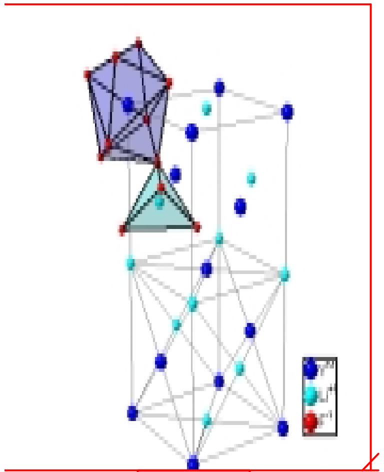
Wernsdorfer et al. et al, PRL, 79, 4014, (1997)

Conclusion and Perspectives

Quantum Tunneling at the Mesoscopic Scale
(Environmental Effects on Quantum Mechanics)

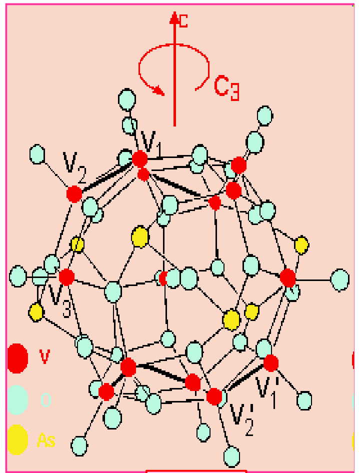
Evidence for Quantum Coherence
(τ_{ϕ}, Rabbi oscillations, …)

Manipulations of Quantum Spins, Spins Qbits
(Quantum Informations and Computers)



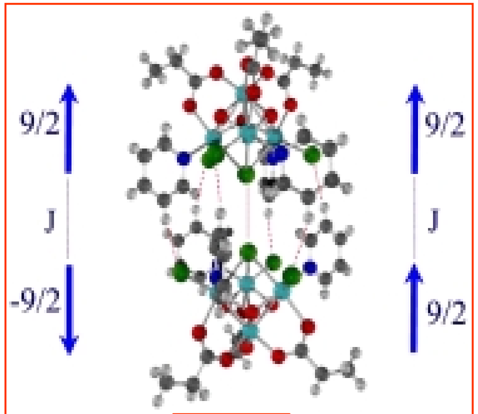
Ho^{3+}

Tunneling of single Ho^{3+} ions
Entangled I-J states



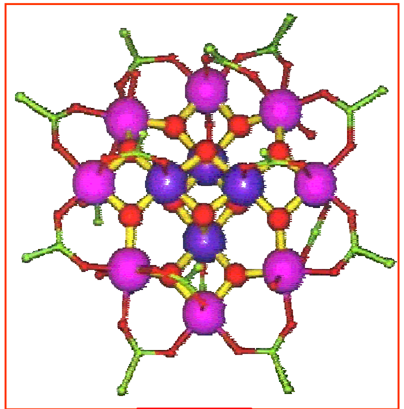
V_{15}

Dissipation control of LZS
Molecule spins 1/2 : Gapped



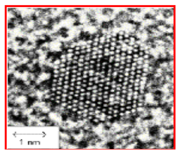
Mn_4

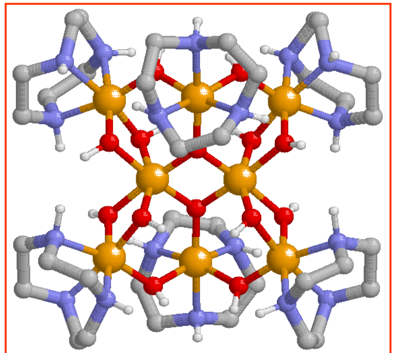
Ho^{3+} , Mn_4 pairs:
Cross-spin transitions, Co-tunneling



Mn_{12}-ac

Quantum → Classical crossover
Quantum Dynamics, Spin Bath





Fe_8

Quantum Dysnamics
Berry Phases

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