QUANTUM SPIN DYNAMICS OF RARE-EARTHS IONS

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Collaborations with other groups

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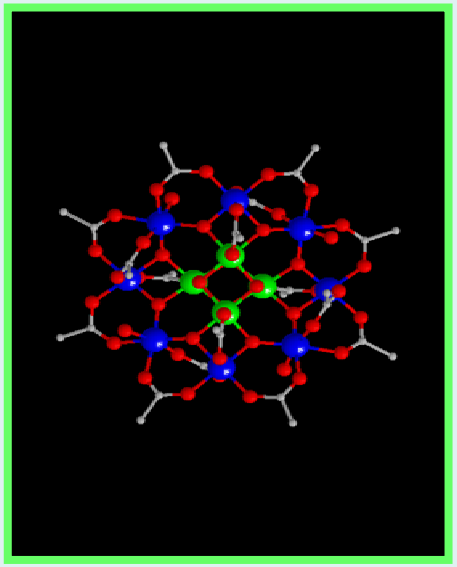
A. Müller (Bielefeld)

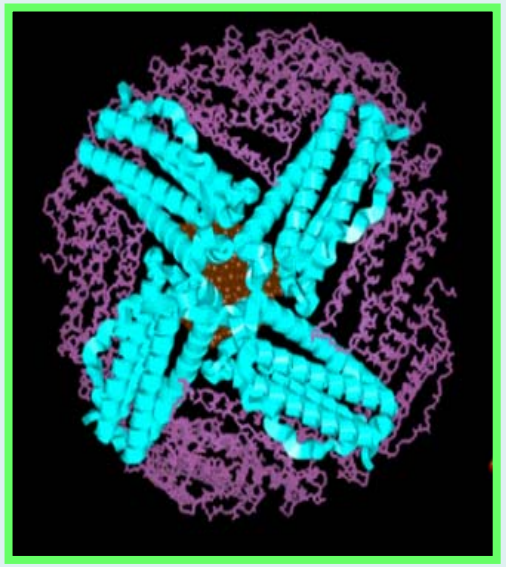
D. Mailly (LPN, Marcoussis)

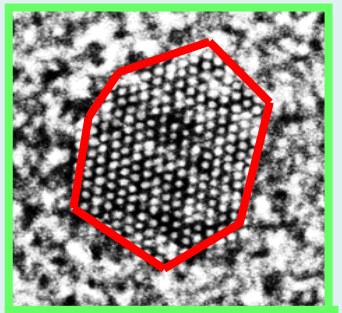
Nanometer scale

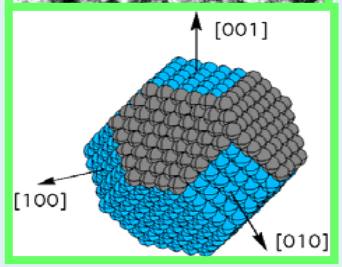
S = 10 50 10^3 10^6

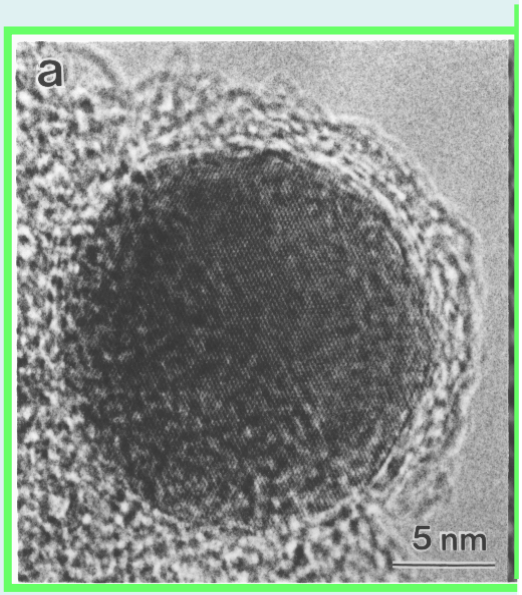
Single Molecule | Magnetic Protein | Cluster | Nanoparticle





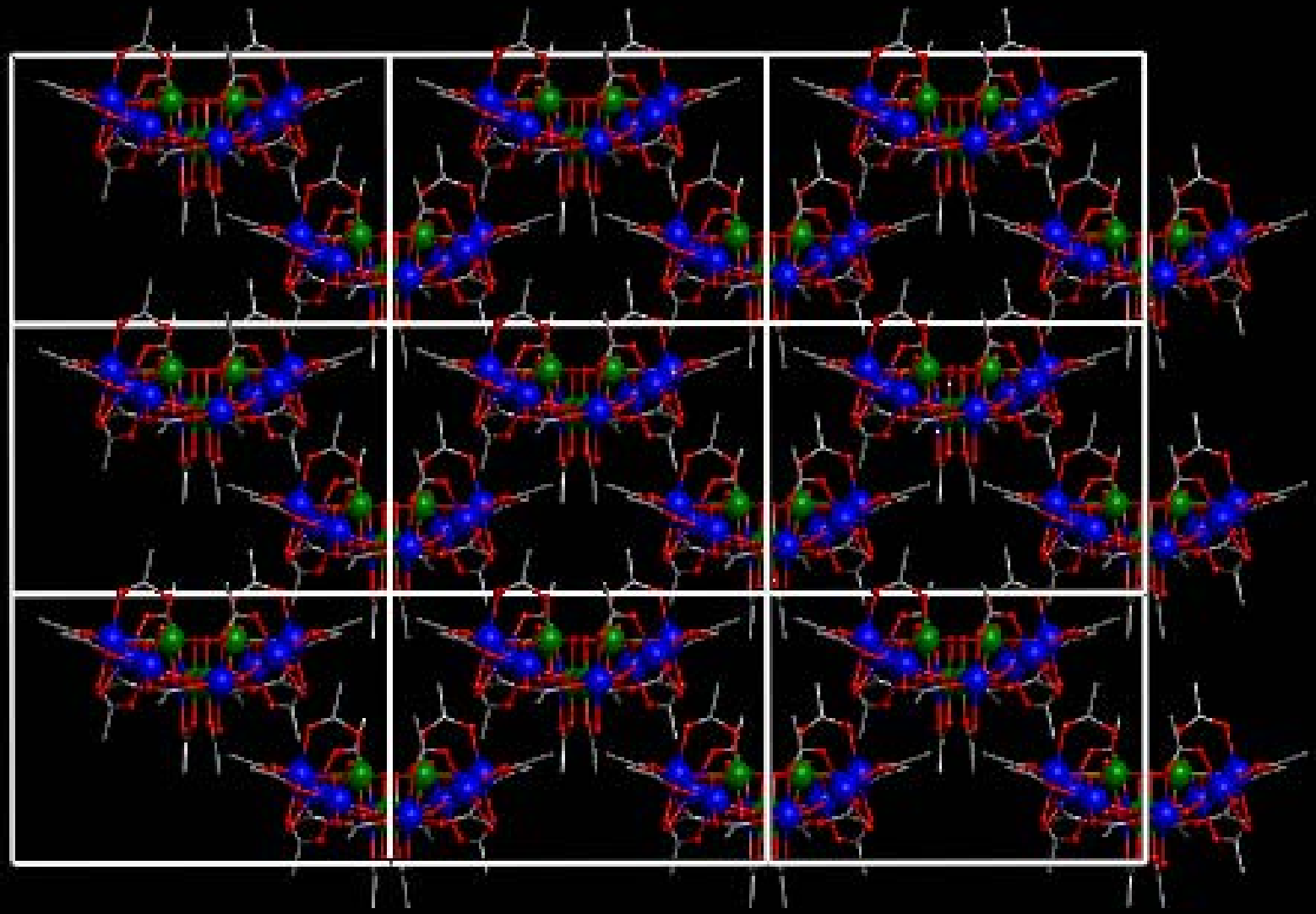






1 nm | 2 nm | 3 nm | 20 nm

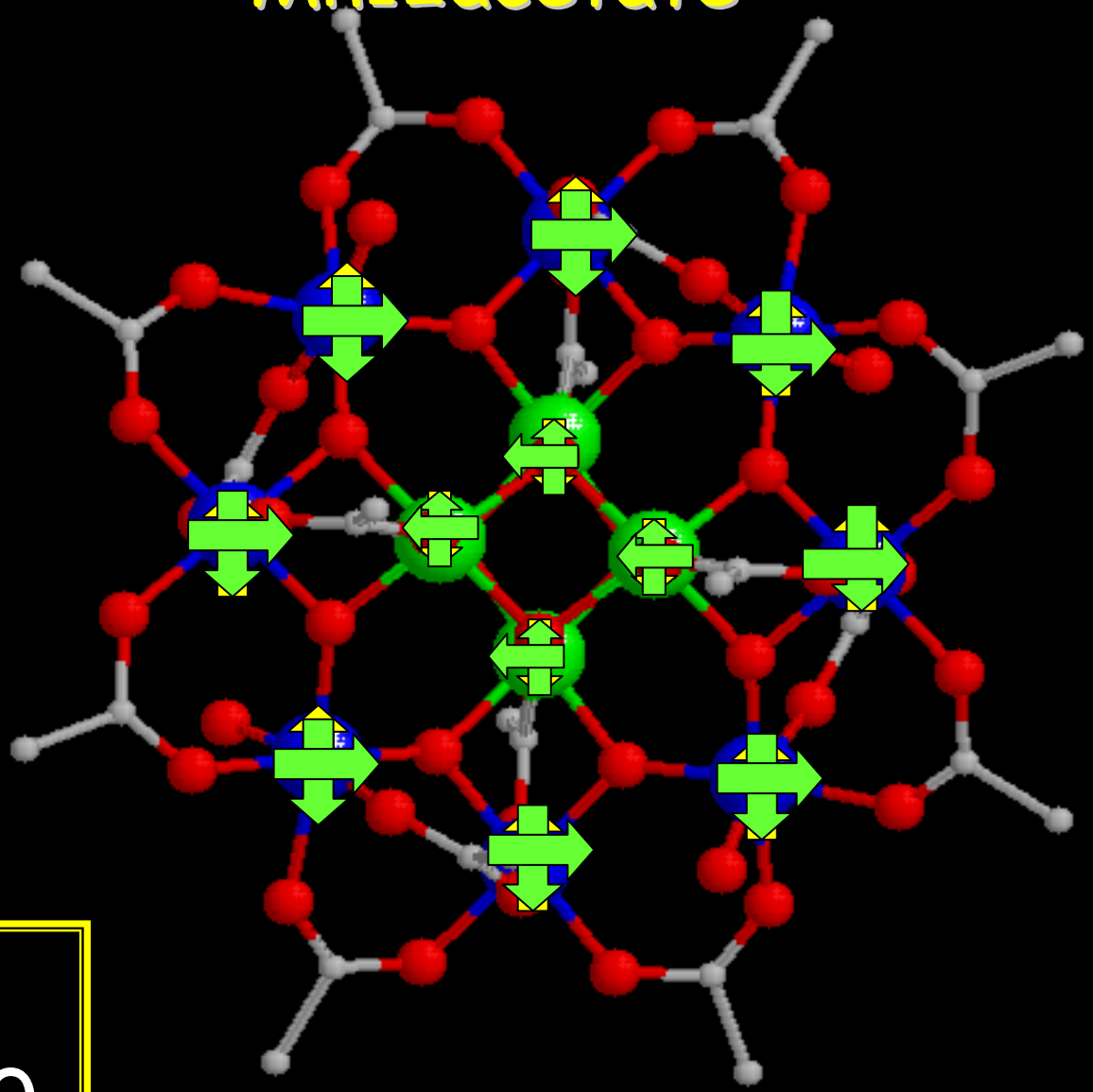
The molecules are regularly arranged in the crystal



Mn12acetate

Mn(III)
S=2

Mn(IV)
S=3/2

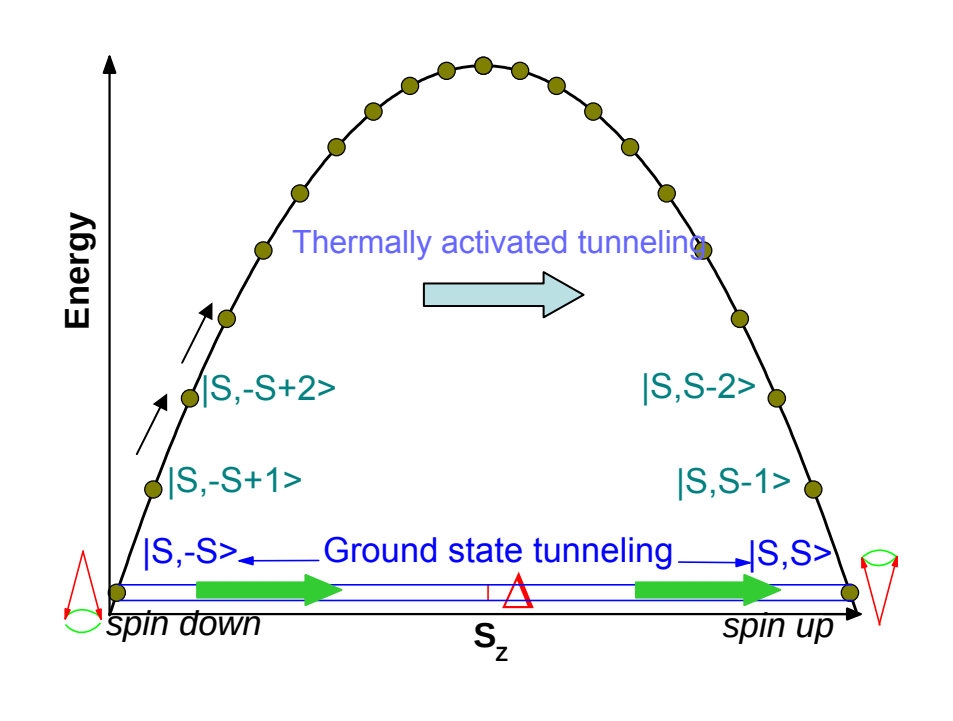


Total
Spin =10

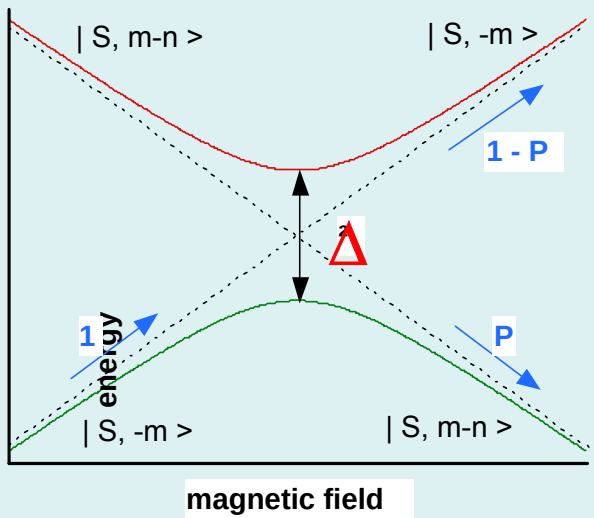
SINGLE MOLECULE « MAGNET »

Energy barrier in zero field (symmetrical)

$$H = -DS_z^2 - BS_z^4 - E(S_+^2 + S_-^2) - C(S_+^4 + S_-^4)$$



Simplified picture of an isolated spin: Landau-Zener model



If applied field // **-M**

⇓

non-symmetrical barrier

New resonances at $g\mu_B H_n = nD$

Molecular magnets (S. Miyashita) large spins give extremely small splittings

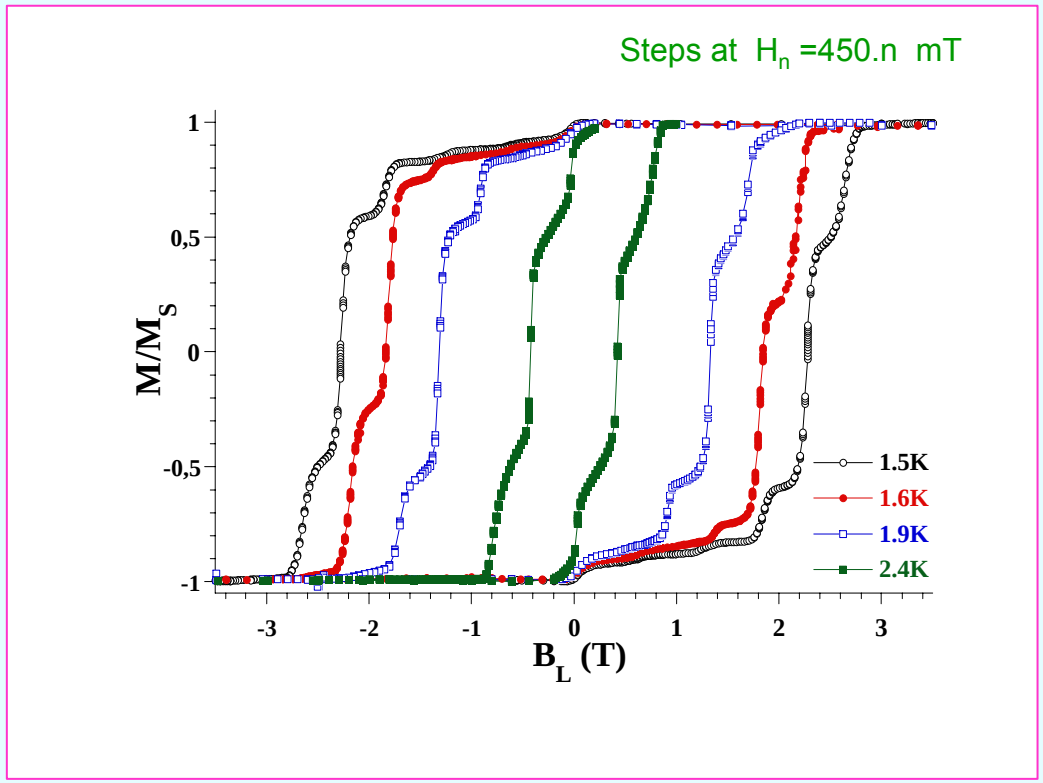
Tunneling probability:

$$P_{LZ} = 1 - \exp[-\pi(\Delta/\hbar)^2/\gamma c]$$

$$c = dH/dt$$

Tunneling of magnetization in Mn_{12}-ac:

« Technical » hysteresis loop + resonant tunneling



ICM'94 Barbara et al, JMMM (1995); NATO-ASI, QTM'94 ed. Gunther and Barbara;
Thomas et al Nature (1996); Friedman et al, PRL (1996);

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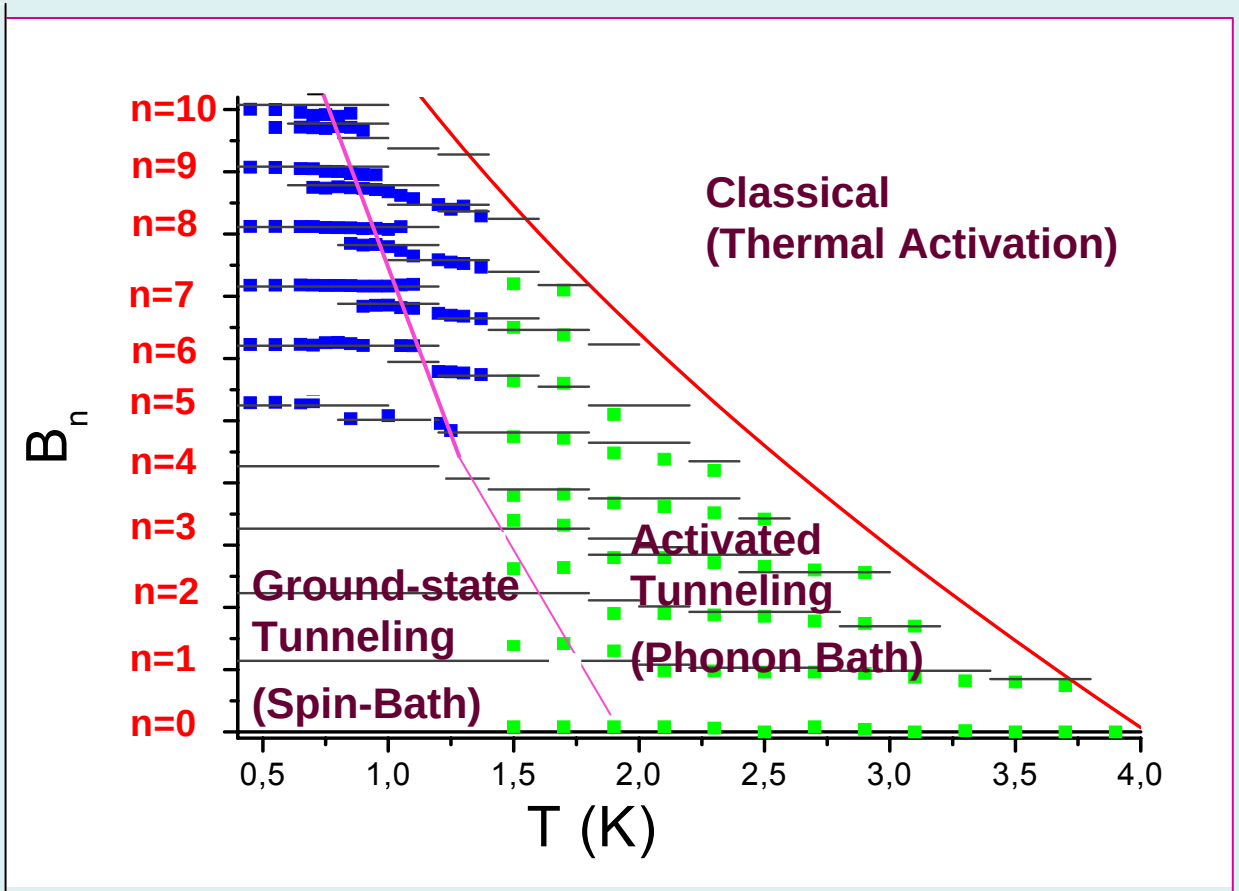
.... Slow quantum spin dynamics of molecule magnets….

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



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

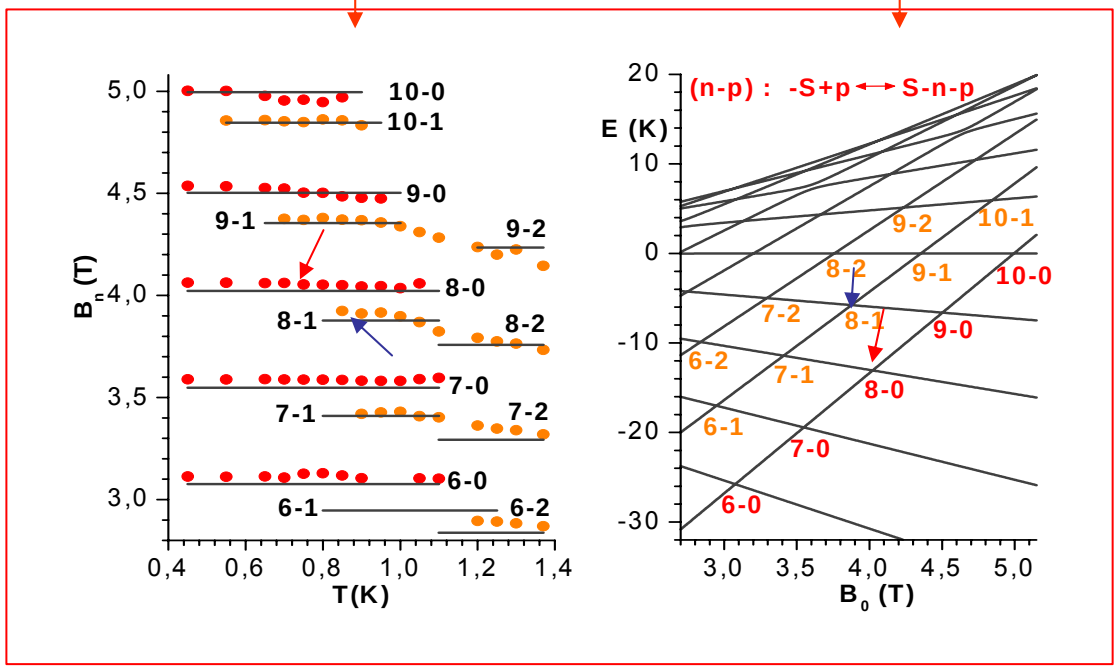
Barbara et al, JMMM 140-144, 1891 (1995) and J. Phys. Jpn. 69, 383 (2000)
Paulsen, et al, JMMM 140-144, 379 (1995); NATO, Appl. Sci. 301, Kluwer (1995)

Resonance width and tunnel window

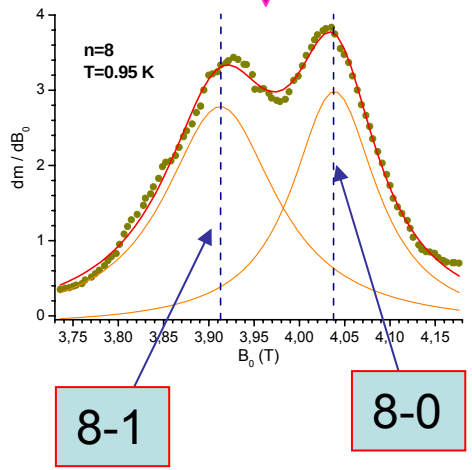
Effects of magnetic couplings and hyperfine Interactions

Data points and calculated lines

Level Scheme



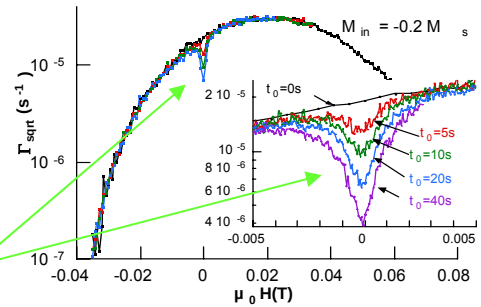
Inhomogeneous dipolar broadening and the electronic spin-bath



- 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 the tunnel window by nuclear spins:

Prokofiev and Stamp (1998)



Weak HF coupling:

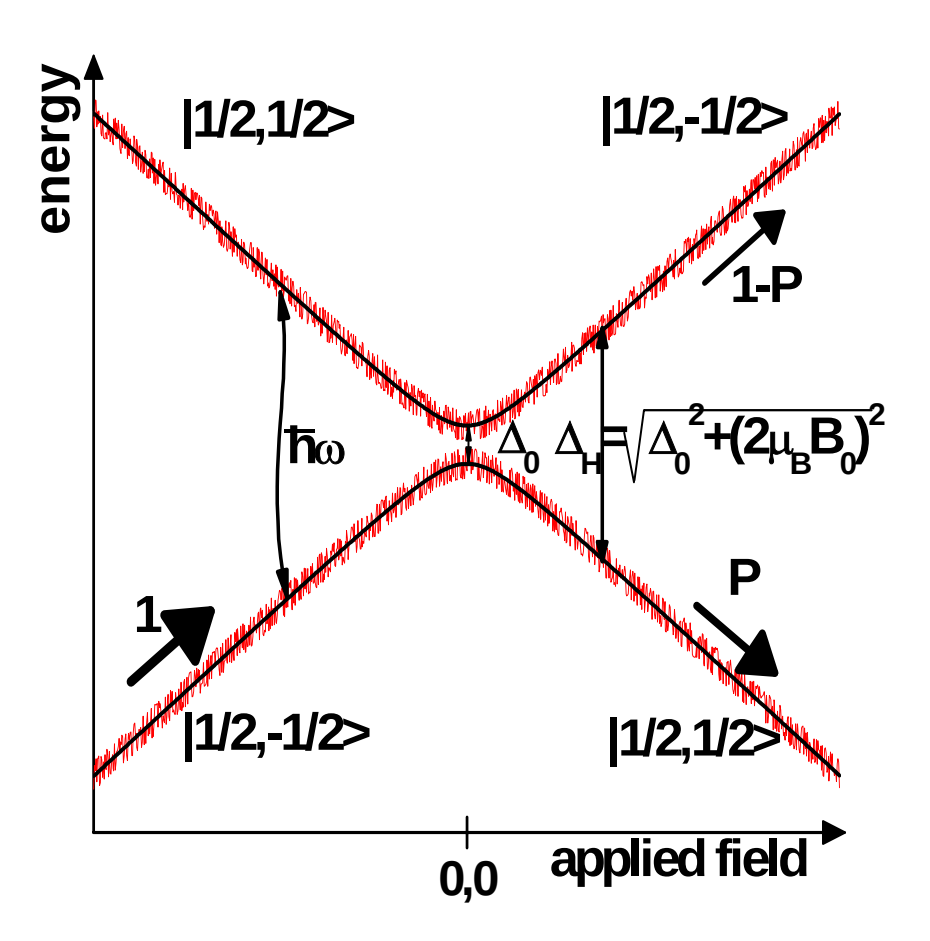
Broadens the tunnel window (10^5)

Decoherence mechanisms

Landau-Zener model

For an ensemble of spins

$H = -DS_z^2 - BS_z^4 - E(S_+^2 + S_-^2) - C(S_+^4 + S_-^4) - g\mu_B S_z H_z$



Tunneling probability:

$P_{LZ} = 1 - \exp[-\pi(\Delta/\hbar)^2/\gamma c]$

$c = dH/dt$

Single Molecule Magnets: large spins

↓

very small tunnel splittings: $\Delta \sim (E/D)^{-2S}$

↓

very small tunnel probabilities:

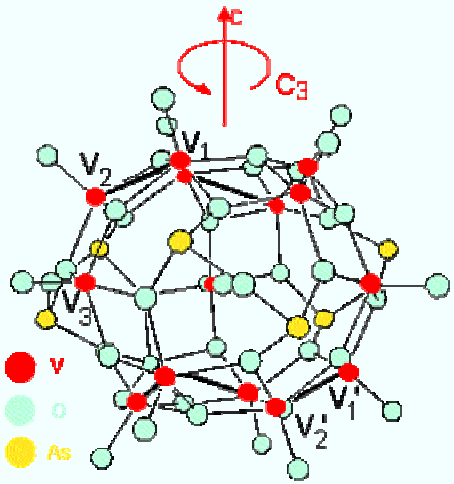
$P_{LZ} \sim \Delta^2/c \sim (E/D)^{4S}/c$

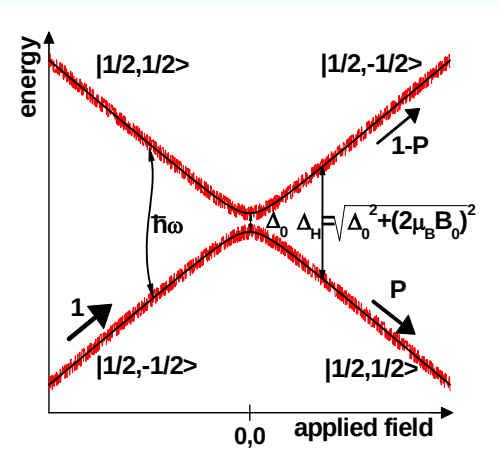
$P_{PS} \sim (\Delta^2/\omega_0)e^{-|\xi|/\xi_0}$

Larger tunneling rate
Strong decoherence

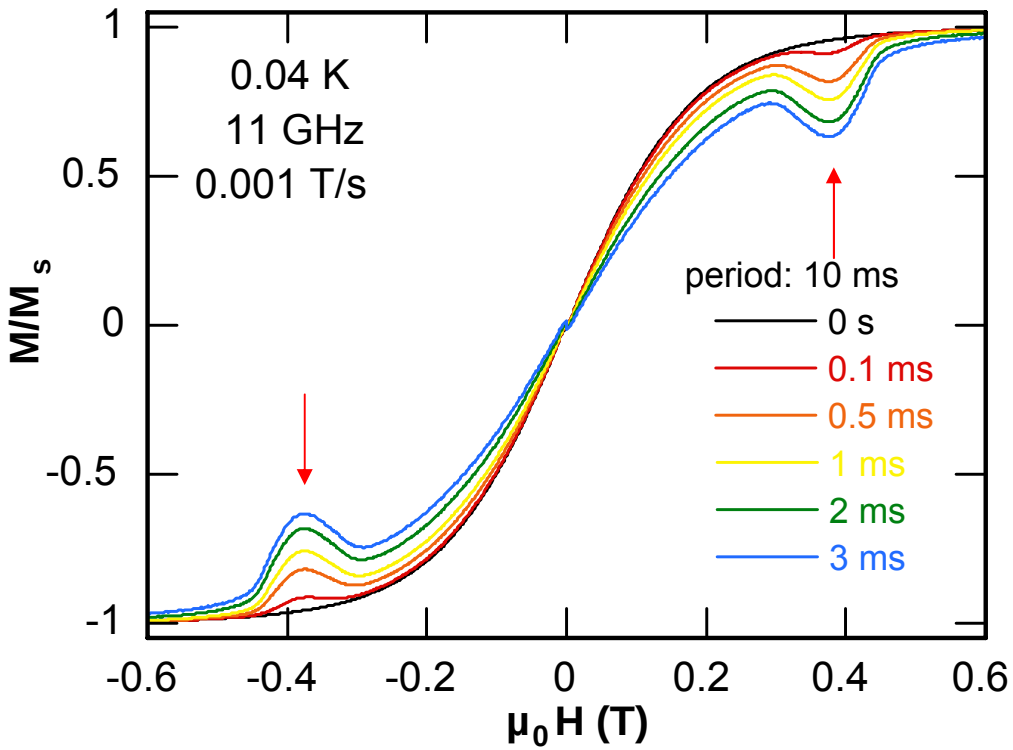
V_{15} , a molecule with S=1/2

Dipolar interactions 10^3 times smaller but I=7/2





Absorption of sub-centimetric waves



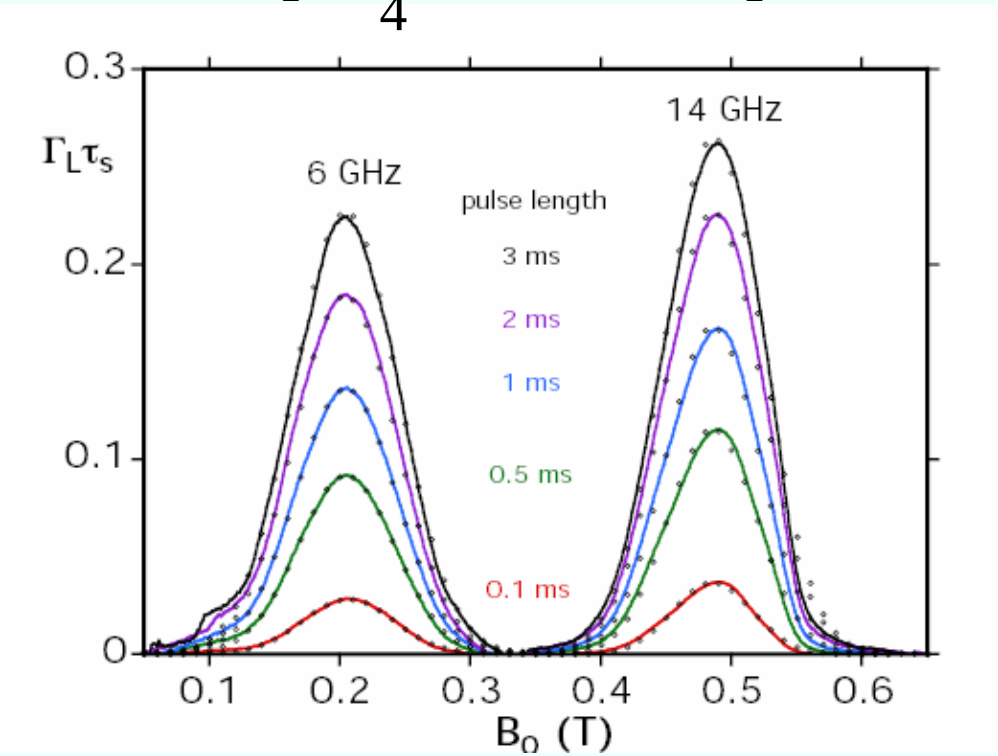
$$\frac{\Delta M(B)}{M_{eq}(B)} = \frac{2\Gamma(B)\tau_1}{1+2\Gamma(B)\tau_1}$$

$\Gamma_{Max} \sim 5\ s^{-1}$

I. Chiorescu, W. Wernsdorfer, A. Müller, H. Boggë, and B. Barbara et al, PRL (2000)
W. Wernsdorfer, D.Mailly, A. Müller, and B. Barbara, EPL, 2004

Gaussian absorption lines

$$\Gamma_L = \frac{\pi}{4}(\gamma b)^2 f(\nu = \gamma B_L)$$



Important broadening by nuclear spins and other molecule spins → Loss of coherence

$$P = \frac{(\gamma b)^2}{(\gamma B - \omega)^2 + (\gamma b)^2} \sin^2\left\{\frac{1}{2}\left[(\gamma B - \nu)^2 + (\gamma b)^2\right]^{\frac{1}{2}} t\right\}$$

$\Omega_R \sim \gamma b \sim 30$ kHz $<< 1/\tau_2 \sim \gamma\sigma \sim 0.2$ GHz

Rabi oscillations, require much larger *b*.

$N = B_{Max}/2\pi\sigma = \gamma B \tau_2/2\pi \sim 20$

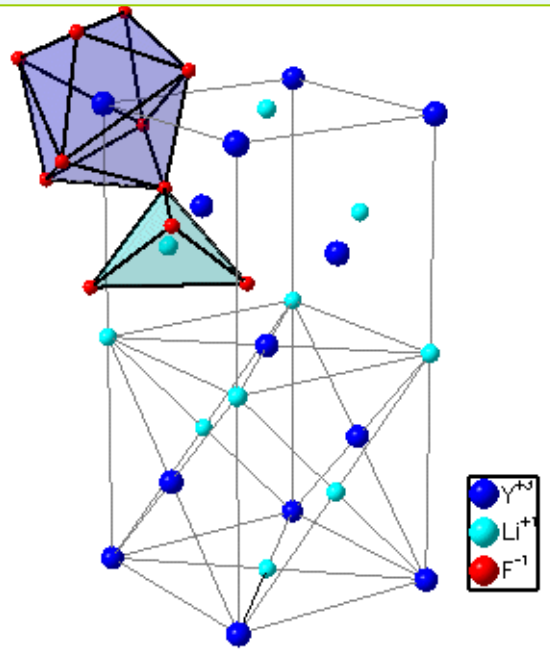
Precession ~ 20 turns

W. Wernsdorfer, D.Mailly, A. Müller, and B. Barbara, EPL, 2004

Tunneling of the angular momentum of Isolated Rare-earths ions

(ensemble measurements of « paramagnetic » ions)

An extention of the slow quantum dynamics studies of SMM
to the cases of strong spin-orbit and hyperfine coupling



0.2 % Ho^{3+} in substitution of Y^{3+}
In $YLiF_4$
Tetragonal symmetry (Ho in S4);
($J = L+S = 8$; $g_J=5/4$)

Dipolar interactions

~ 20 mK << 200 mK (levels separation)

CF levels and energy barrier of Ho^{3+} in $Y_{0.998}Ho_{0.002}LiF_4$

$$H_{CF} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^4 O_4^4 + B_6^4 O_6^4$$

Strong mixing

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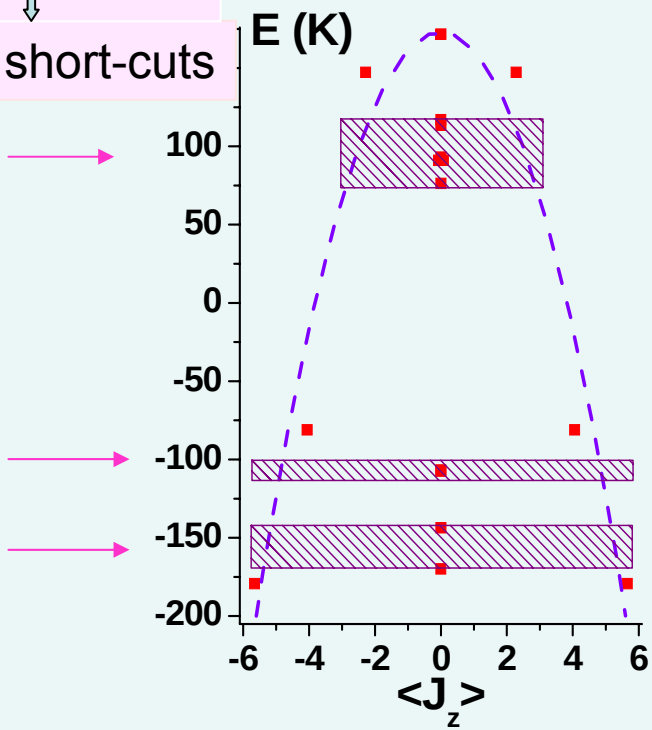
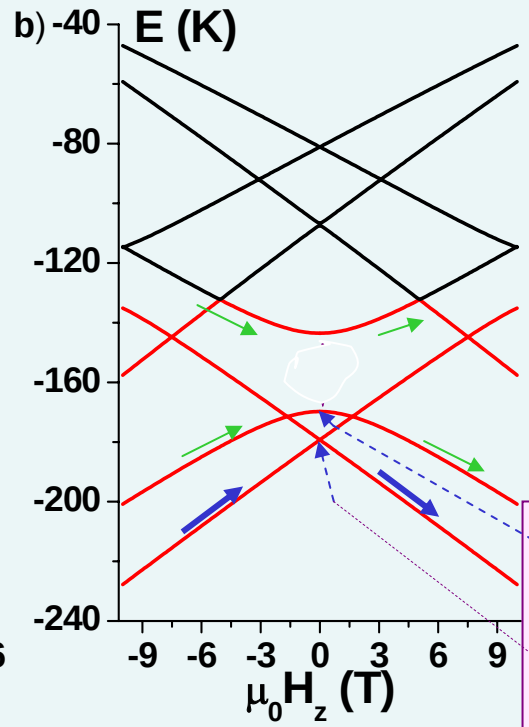
Barrier short-cuts





Singlet excited state
+
Doublet ground-state
+
Large τ_1 (Orbach process)

⇩

Energy barrier
(~ 10 K)

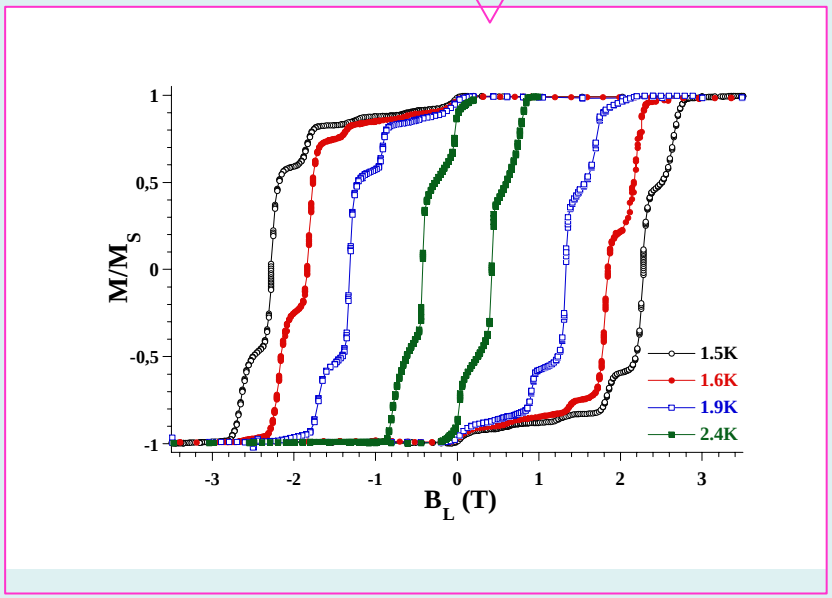
R. Giraud, W. Wernsdorfer, D. Mailly, A. Tkachuk, and B. Barbara, PRL, 87, 057203-1 (2001)

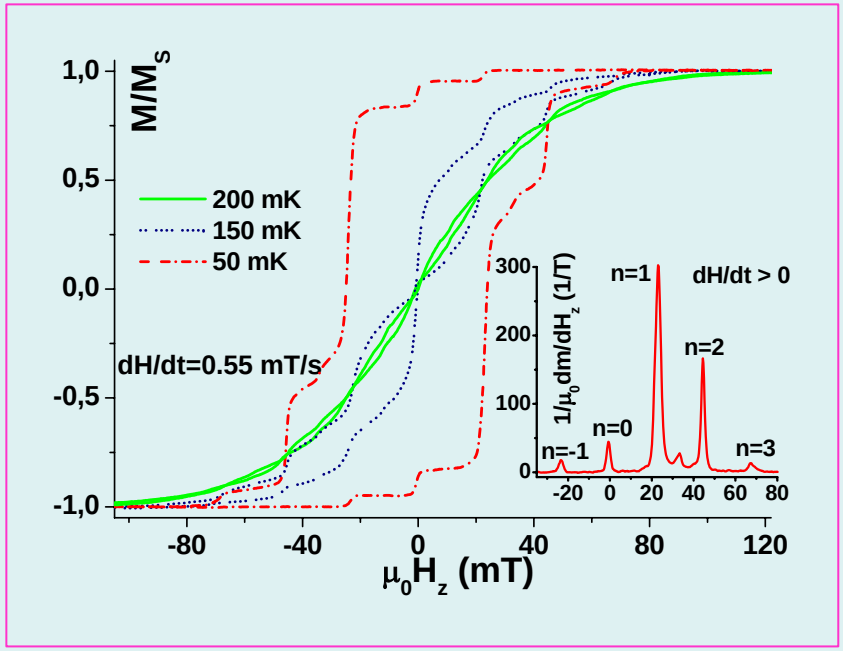
B20 = 0.606 K, B40 = -3.253 mK, B44 =- 42.92 mK, B60 =-8.41mK, B64 =- 817.3mK
Sh. Gifeisman et al, Opt. Spect. (USSR) 44, 68 (1978);
N.I. Agladze et al, PRL, 66, 477 (1991)

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

Comparison with Mn12-ac

Many steps !





L.Thomas, F. Lionti, R. Ballou, R. Sessoli, D. Gatteschi,and B. Barbara, Nature, 1996.

R. Giraud, W. Wernsdorfer, D. Mailly, A.Tkachuk, and B. Barbara, PRL, 2001

Steps at $B_n = 450.n$ (mT)

Steps at $B_n = 23.n$ (mT)

… Nuclear spins…

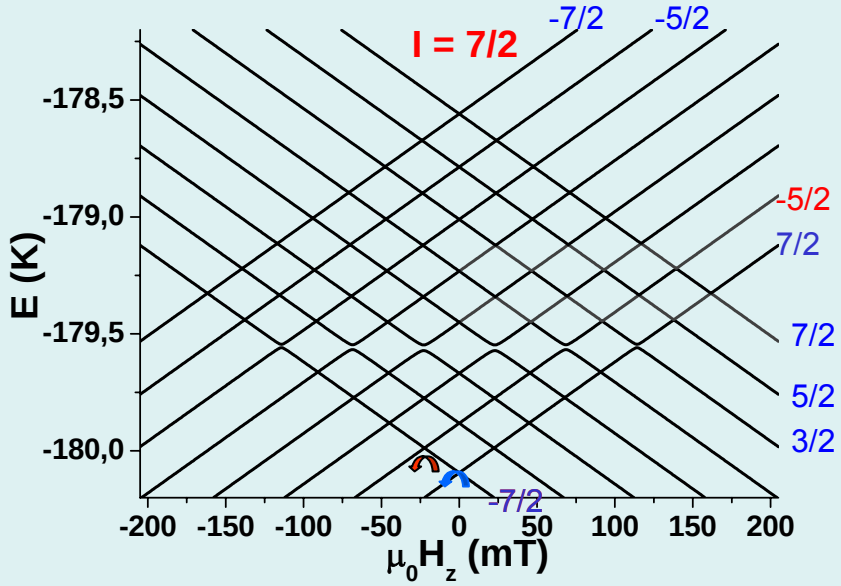
Tunneling of Mn_{12}-ac Molecules

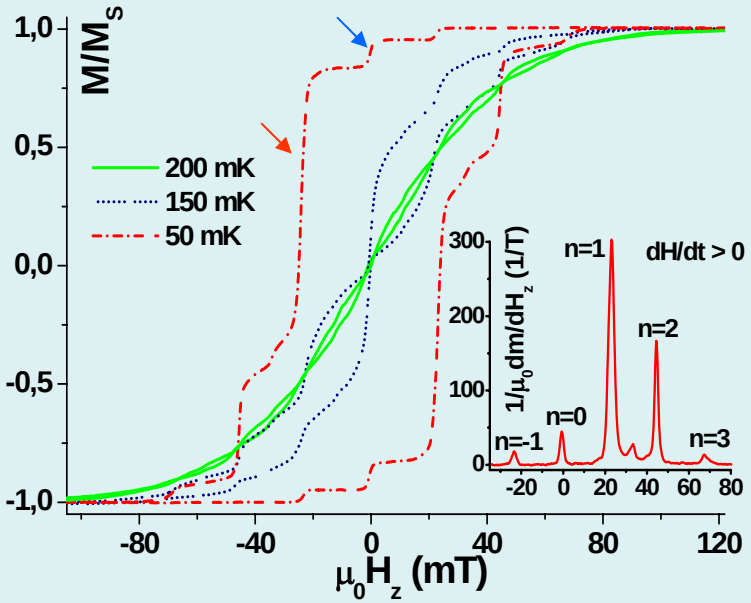
Tunneling of Ho^{3+} ion

Quasi-Ising CF Ground-state + Hyperfine Interactions

$$H = H_{CF\text{-}Z} + A\{J_z I_z + (J^+ I^- + J^- I^+)/2\}$$

The ground-state doublet ⟹ $2(2 \times 7/2 + 1) = 16$ states





$g_J \mu_B H_n = n.A/2$

A = 38.6 mK, Linewidth ~ 10 mK ~ Dip. Int.

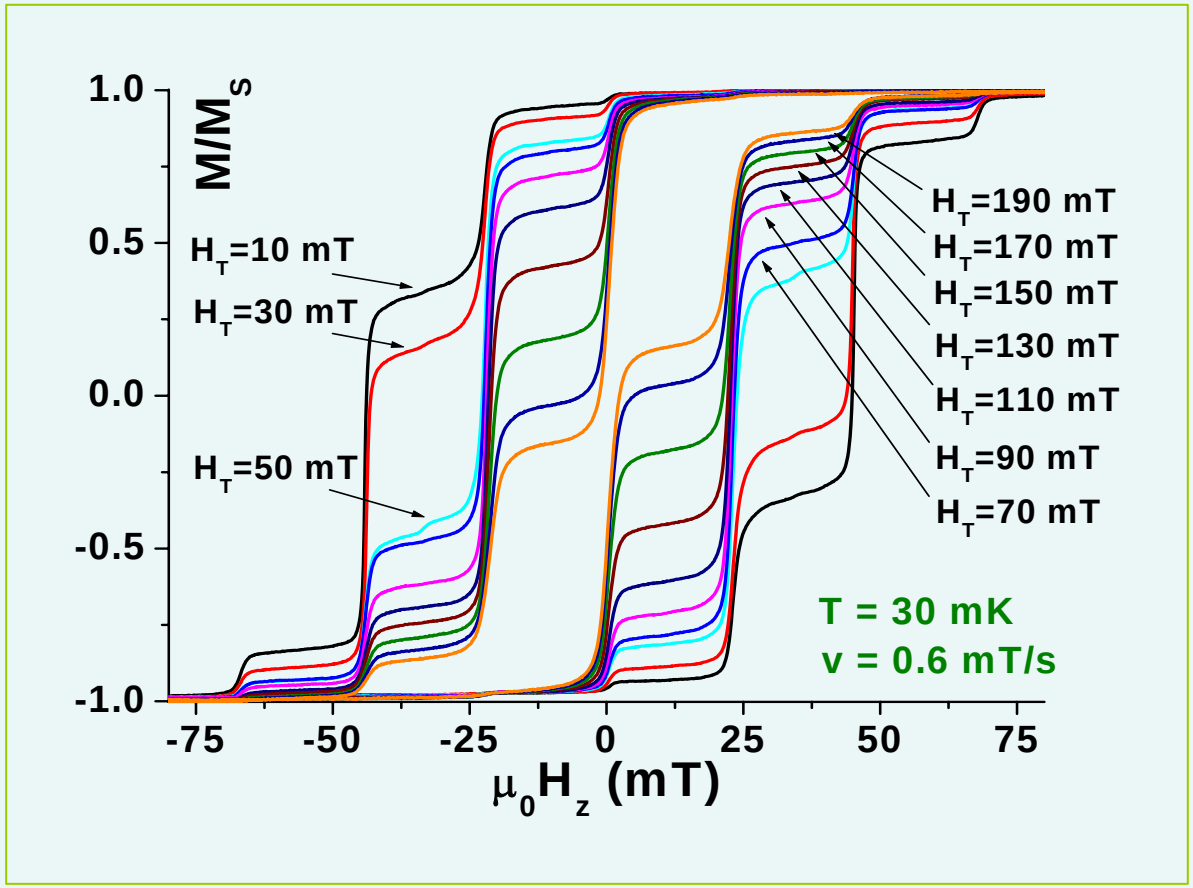
Avoided Level Crossings between $|\Psi^-, I_z\rangle$ and $|\Psi^+, I_z'\rangle$ if $\Delta I = (I_z - I_z')/2 =$ odd

Co-Tunneling of electronic and nuclear momenta:

Electro-nuclear entanglement (2-bodies)

Application of a transverse magnetic field:

(slow sweeping field: sample at the cryostat temperature)



Acceleration of quantum dynamics → the remanent magnetization vanishes

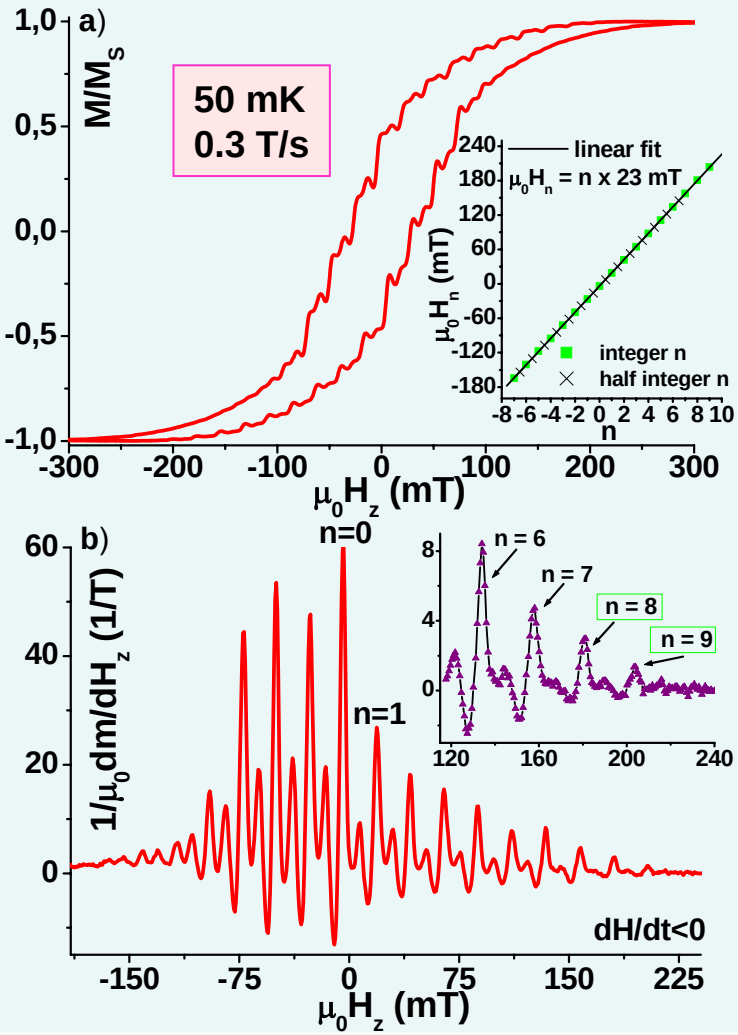
Quantum fluctuations destroy the local moment

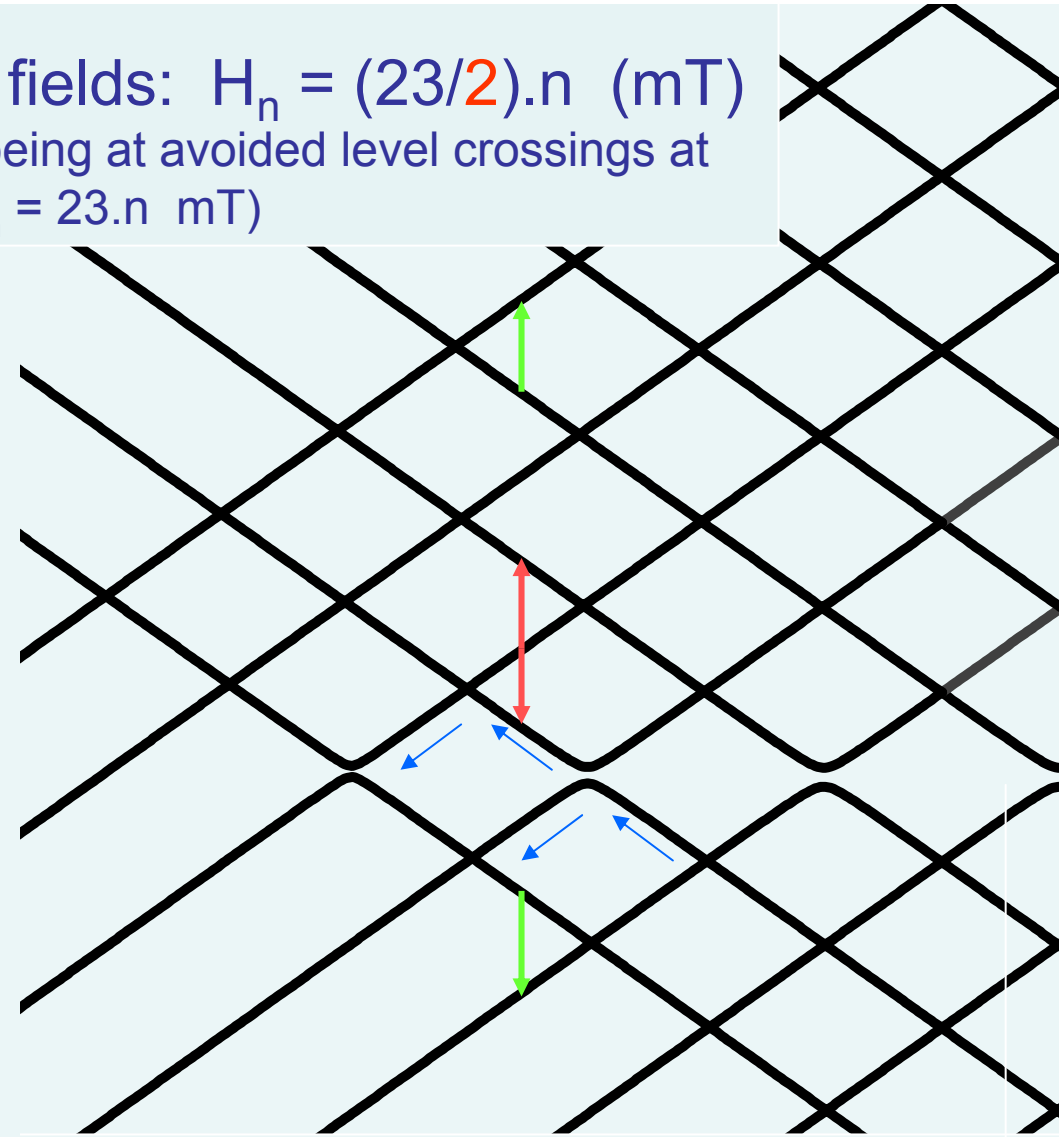
Transition from « Classical » to Quantum Paramagnet (QPT)

Nature of the mixing: *entangled electro-nuclear* states

Additional steps at fields: $H_n = (23/2).n$ (mT)

(single Ho^{3+} tunneling being at avoided level crossings at $H_n = 23.n$ mT)



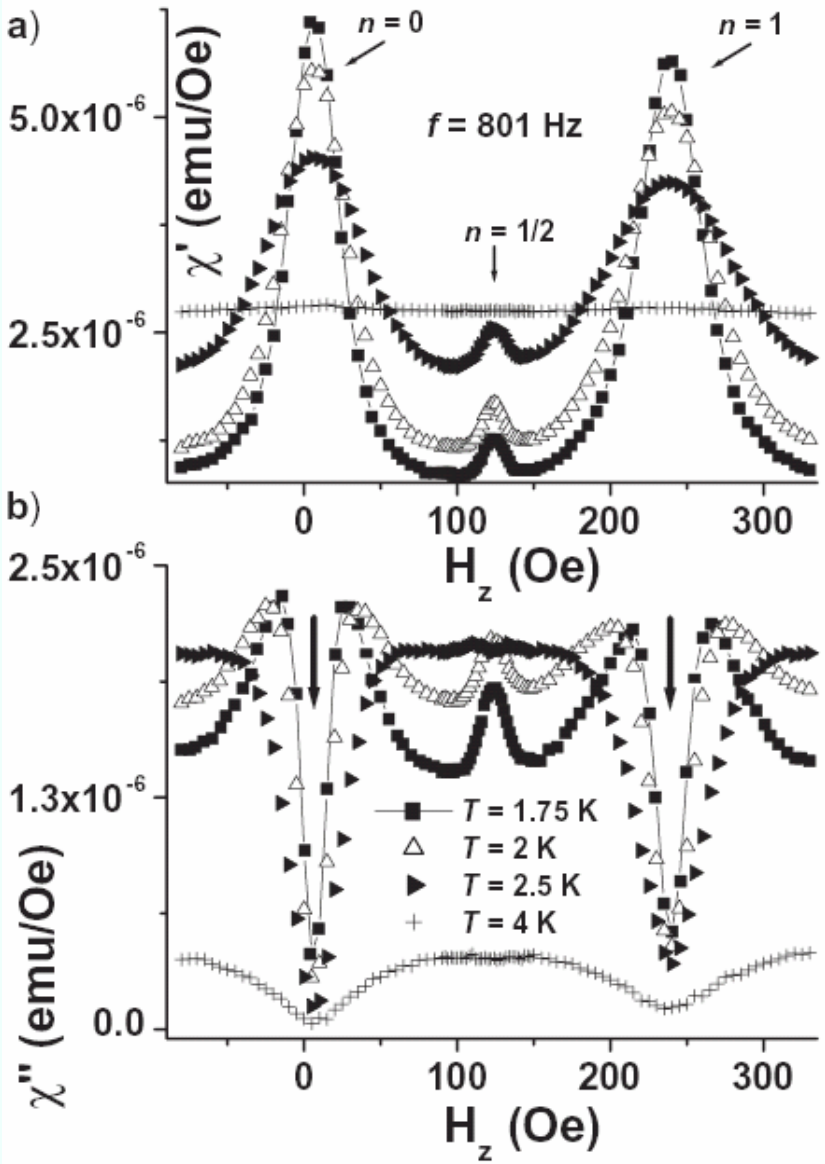


Giraud et al, PRL 87, 057203 1 (2001)

Simultaneous tunneling of Ho^{3+} pairs due to dipolar interactions (4-bodies entanglement)

Two Ho^{3+} Hamiltonian ⟹ avoided level crossings at $H_n = (23/2).n$

Ac susceptibility (SQUID measurements)

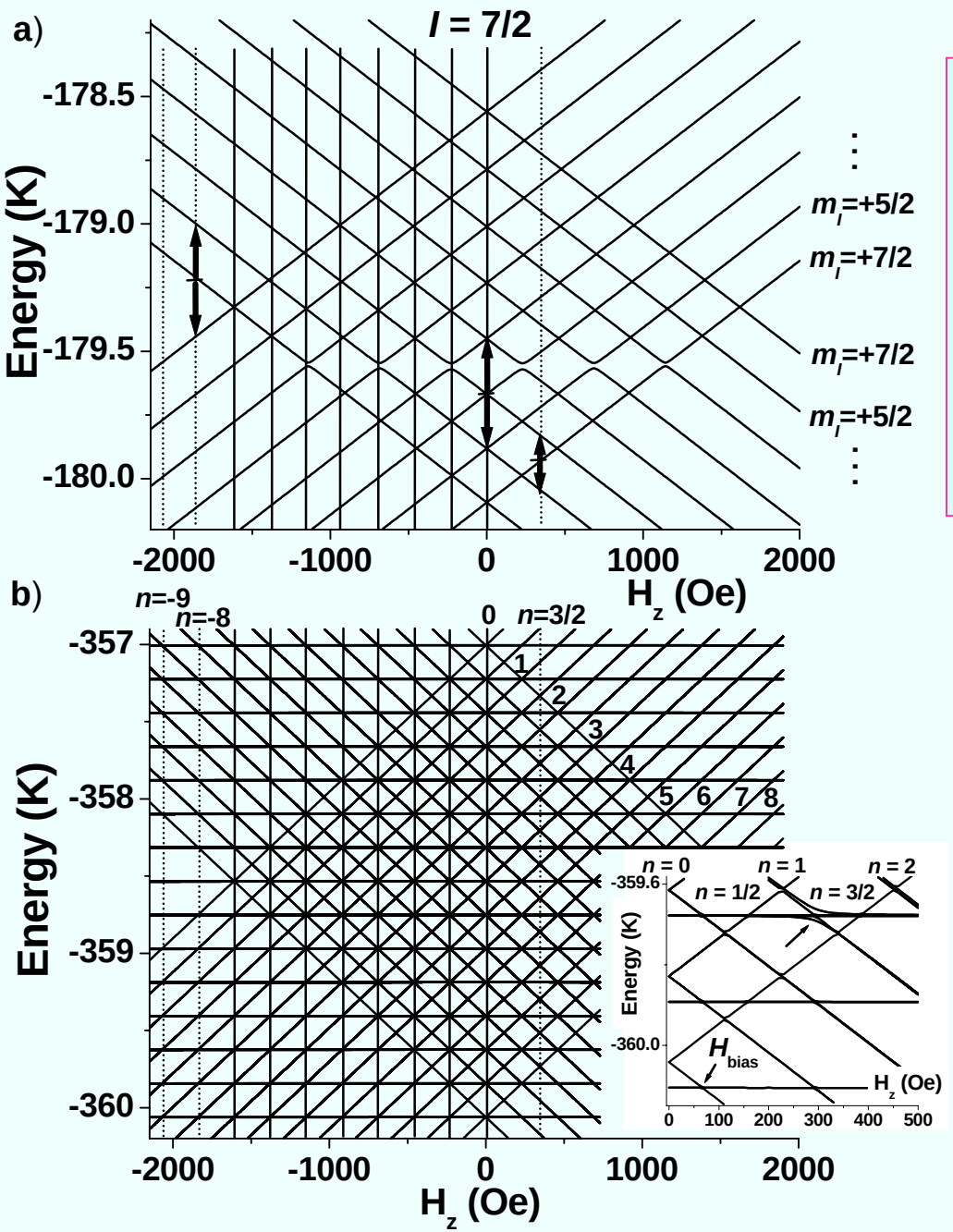


Single-ion and dipolar-bias Tunneling

Co-tunneling

Tunneling rates and ac measurement frequency

R. Giraud, A. Tkachuk, B. Barbara, PRL, 2003.



Single-ion level structure

$$E_n = \Delta E \pm g\mu_B H_n$$

Tunneling: $g\mu_B H_n = (n'-n)A/2$

Co-tunneling: $g\mu_B H_n = (n'-n+1/2)A/2$

(A= Ho hyperfine constant)

Two-ions Level structure

Electronic Spin-bath:

Co-tunneling

Biais tunneling

Diffusive tunneling

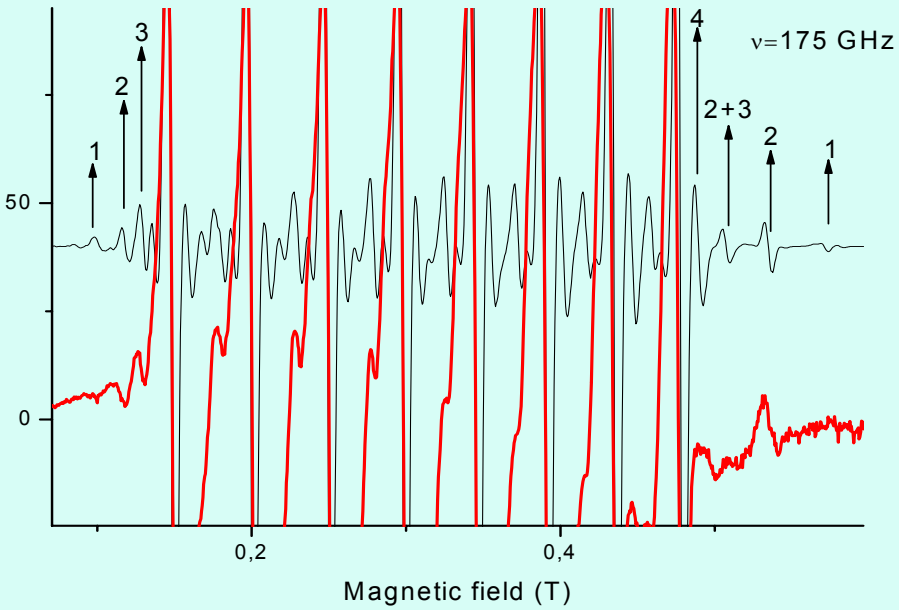
Nuclear spin-bath (Li, F, Y):

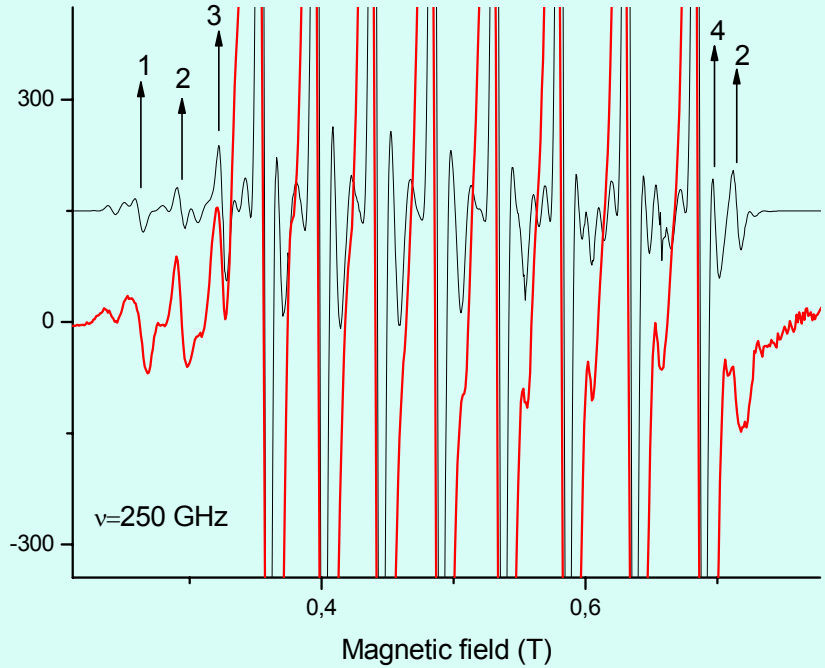
Linewidths

R. Giraud, A. Tkachuk, and B. Barbara PRL (2003).

Ho-dimer satellites in the EPR signal in ^{7}LiYF4 (1% Ho): Bias-tunneling transitions only

Boris Malkin group, Kazan





In the ^{7}Li 0.1% sample the width of single ions ~3.5 mT and of dimers ~ 2mT

G. Shakurov, B. Malkin, B. Barbara, Appl. Magn. Res. 2005

Toy model of two coupled effective spins, with $g_z / g_x >> 1$

$$H/J = \Sigma_{ij} S_i^z S_j^z + \alpha \Sigma_{ij} (S_i^+ S_j^- + S_j^+ S_i^-)/2 + \beta \Sigma_{ij} (S_i^+ S_j^+ + S_j^- S_i^-)$$

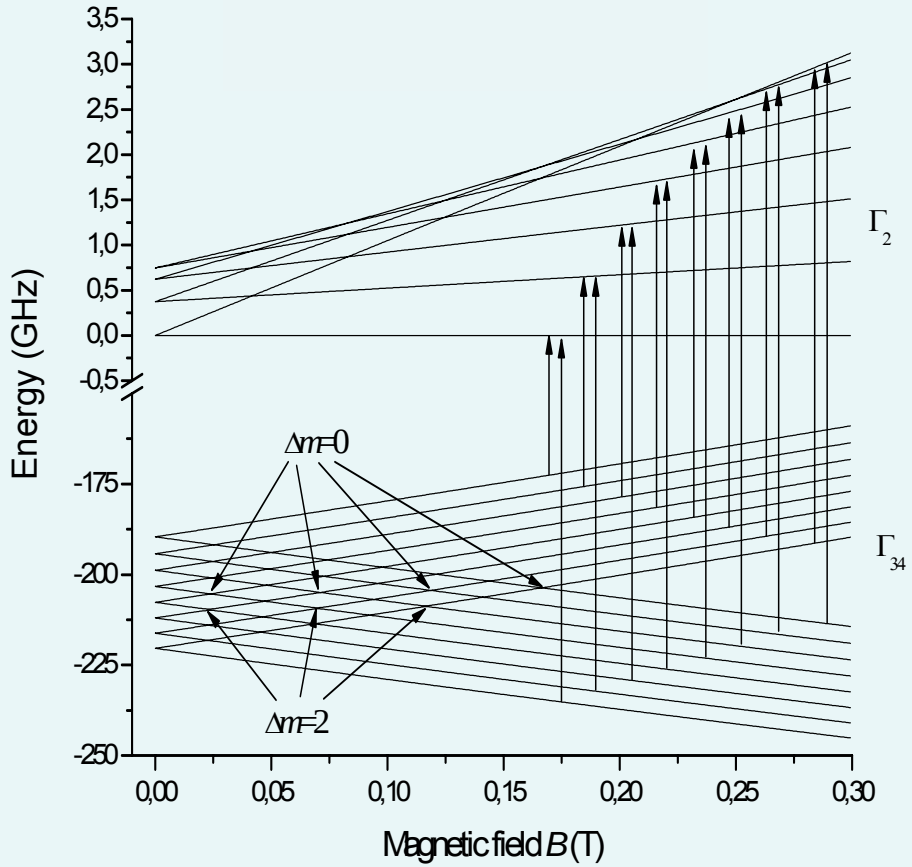
with

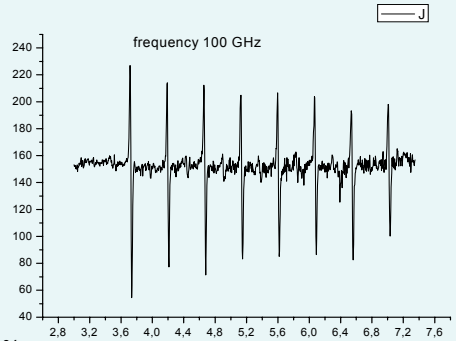
$\alpha = (J_x + J_y)/4J$ $\Downarrow$ **Diffusive tunneling**

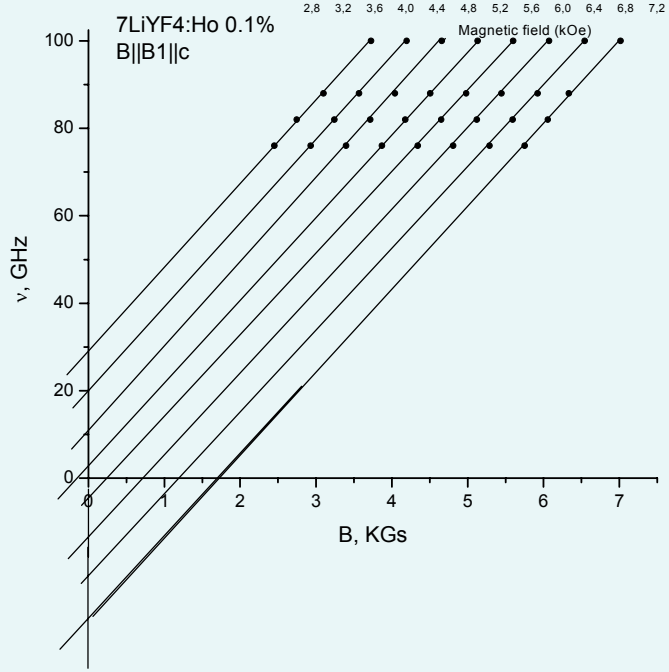
$\beta = (J_x - J_y)/4J$ $\Downarrow$ **Co-tunneling**

This is why dipolar interactions induce co-tunneling

Direct check of hyperfine sublevels from EPR In Ho:$YLiF_4$ (B. Malkin group)



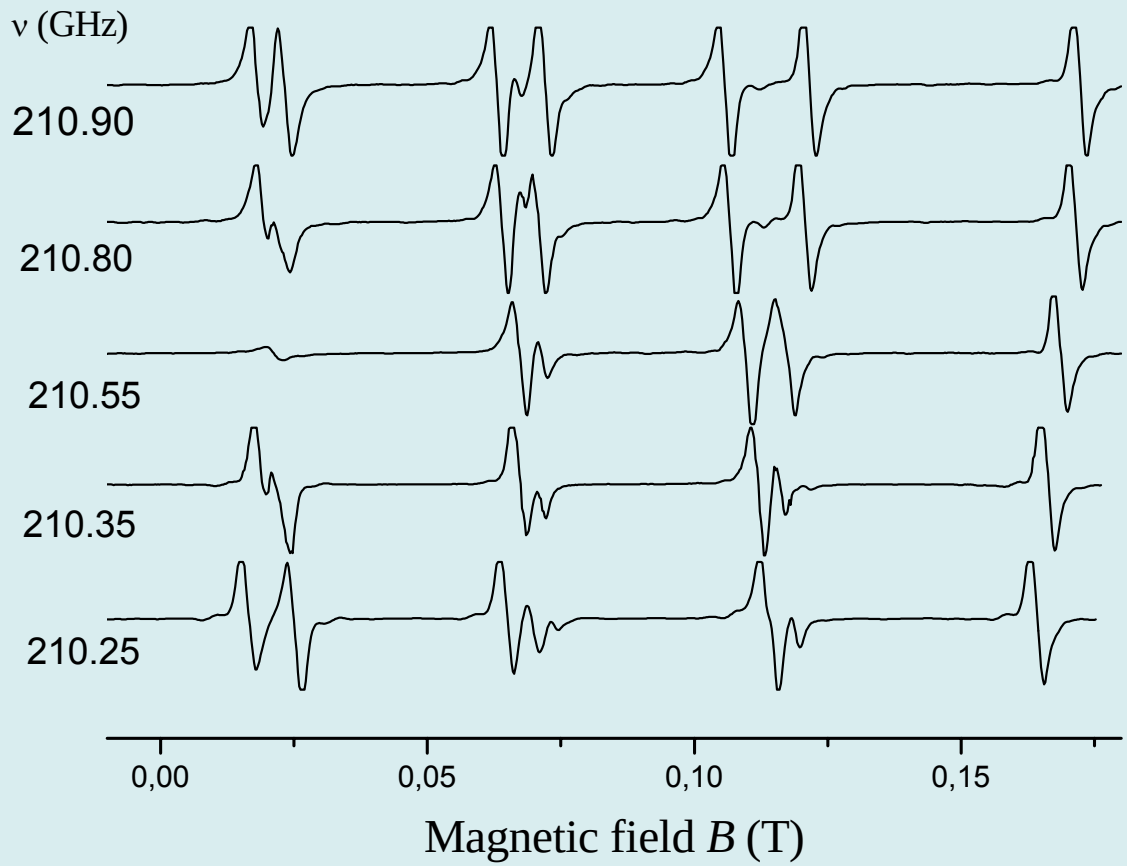




G. Shakurov, B. Malkin, B. Barbara, Appl. Magn. Res. 2005

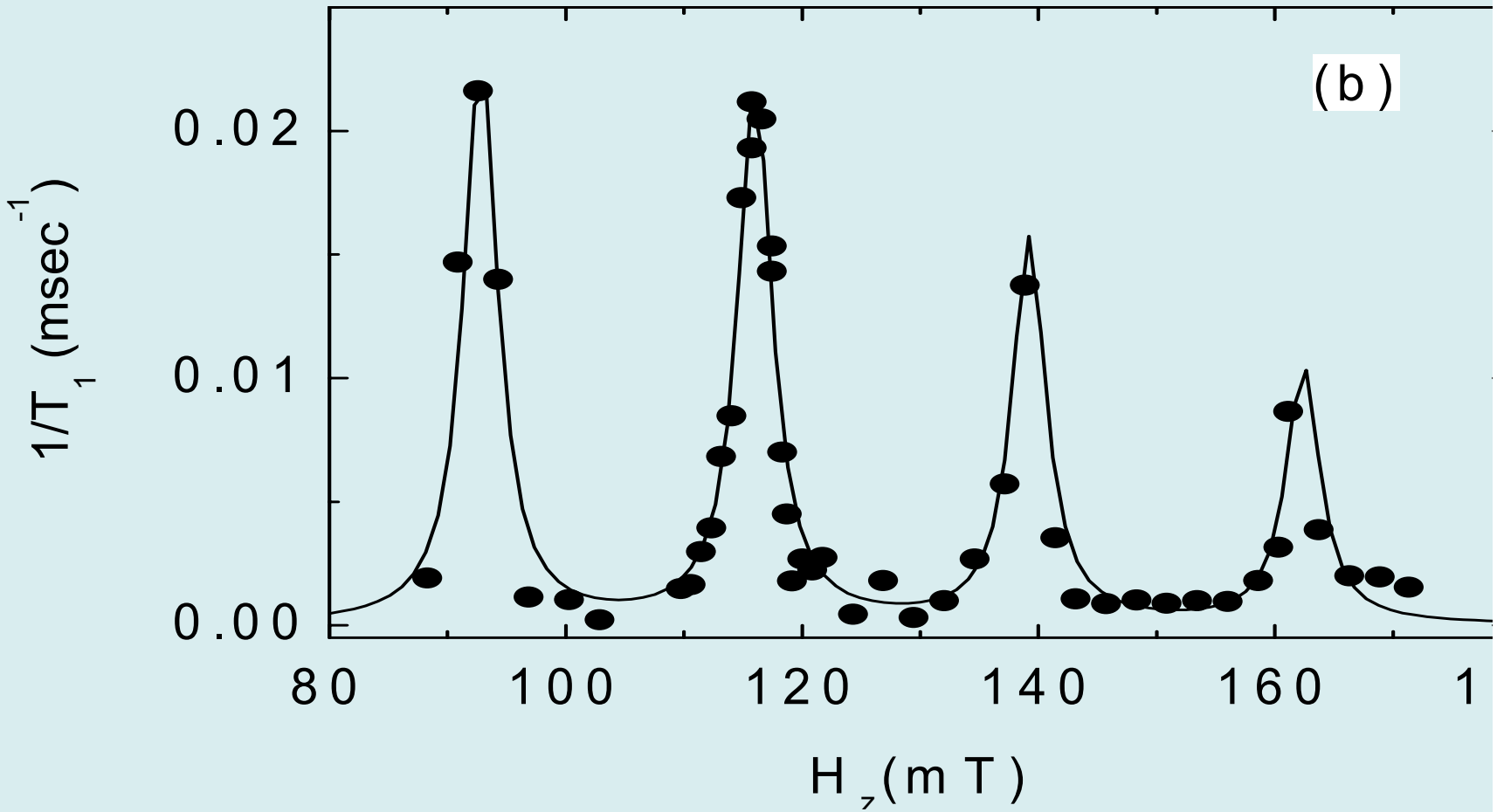
Direct observation of levels repulsions

Hyperfine sublevels ($\Delta m=2$) in the EPR spectra



G. Shakurov, B. Malkin, B.Barbara, Appl. Magn. Res. 2005

^{19}F_NMR M. J. Graf, A. Lascialfari, F. Borsa, A. M. Tkachuk, and B. Barbara (cond-ma



Phenomenological fit:

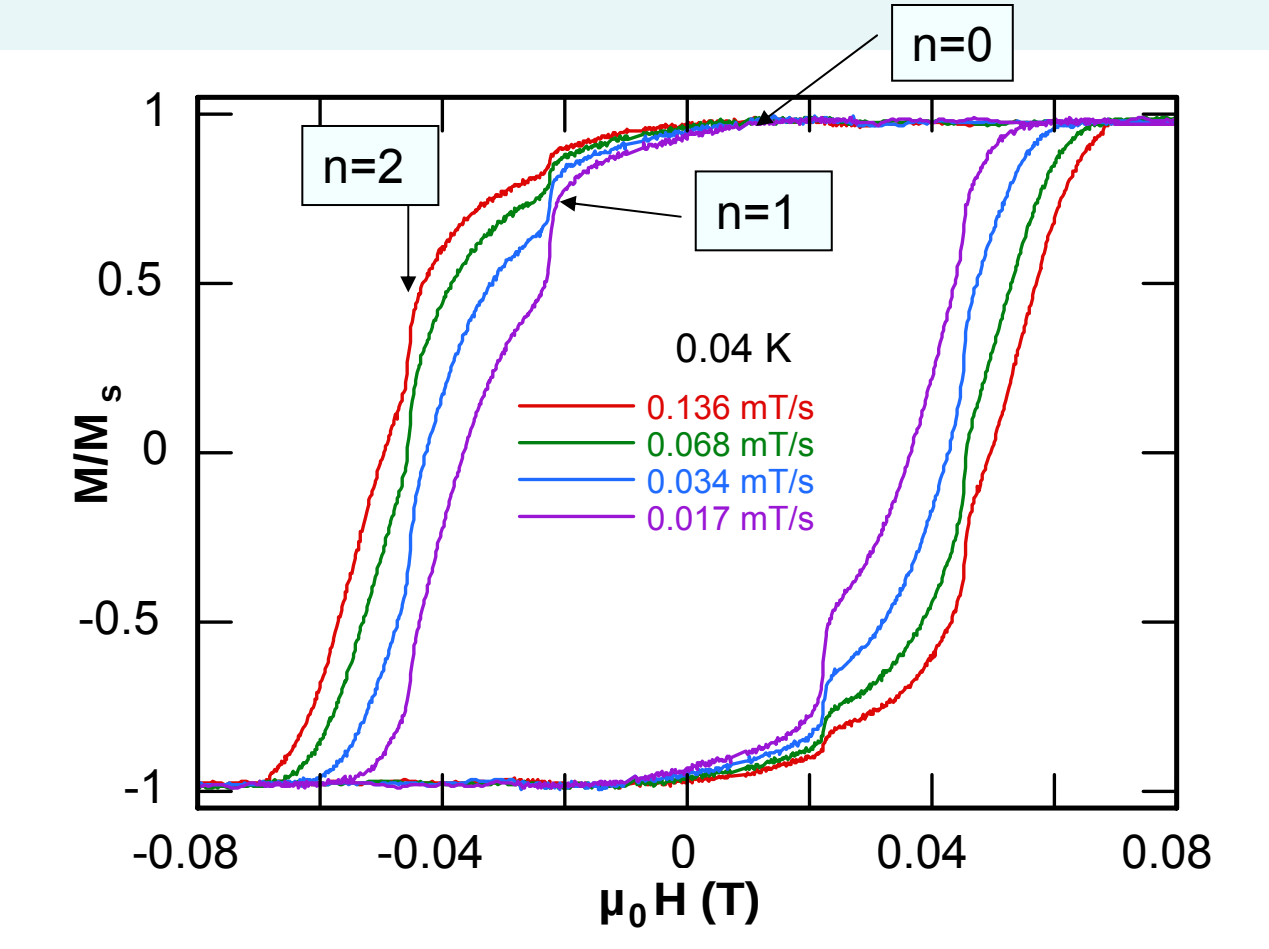
$1/T_1 = B^2 W / [W^2 + (\omega_N - \Delta)^2]$, $\Delta = [1.3\text{x}10^{18} (H-23n)^2 + \Delta_n^2]^{1/2}$ with Δ_n ~20 mK,

Levels broadening at crossing is extremely small (~ 2 mT):

Decoherence strongly suppressed : possible to measure directly level repulsion

Case of a metallic matrix:

Ho^{3+} ions in $Y_{0.999}Ho_{0.001}Ru_2Si_2$



These steps come from tunneling transitions of **J+I** of single Ho^{3+} ions, in a sea of free electrons.

B. Barbara, R. Giraud, W. Wernsdorfer, D. Mailly, A. Tkachuk, H. Suzuki, ICM-Rome, JMMM (2004)

CONCLUSION

Molecular magnets

Coexistence of classical hysteresis loop and resonant quantum tunneling

non-adiabatic Landau-Zener (single-ion picture)
Observation of tunneling made possible by environmental spins (nuclear spins)
Spin tunneling asssited by photons (photons bath)
Strong decohrence by environmental spins (nuclear spins)

Highly diluted Ho^{3+} in $LiYF_4$

Tunneling of the total angular momentum J = L+S of Ho^{3+} single ions

two-bodies entanglement
Quasi-isolated Ho^{3+} ions: J and I tunnel simultaneously (in a metal also: Ho in YSi_2Ru_2).
Relevant quantum number of Ho^{3+} is not J but I+J (Kramers, QPT…).

Co-tunneling, bias-tunneling, spin-diffusion in Ho^{3+} dimmers

four-bodies entanglements, Co-tunneling of dimmers is observed.
Crucial role of the anisotropic character of dipolar interactions.
Microscopic basis for the study of QPT (concentrated systems) and coherent quantum dynamics.

…. Molecular magnets with Rare-Earths

R-E Double-Deckers also show single-ion tunneling on electro-nuclear states

(M. Ruben)

Some perspectives

Higher order many-body tunneling and **decoherence by the environment**
(quantum phase transitions)

Spin-echo experiment and Rabi oscillations on electronic states of

- **Molecular magnets**
  (intra-molecules hyperfine interactions ~10 mK)

- **Entangled E-N pairs of Ho^{3+}**
  (dipolar interactions, hyperfine interactions ~1 mK)

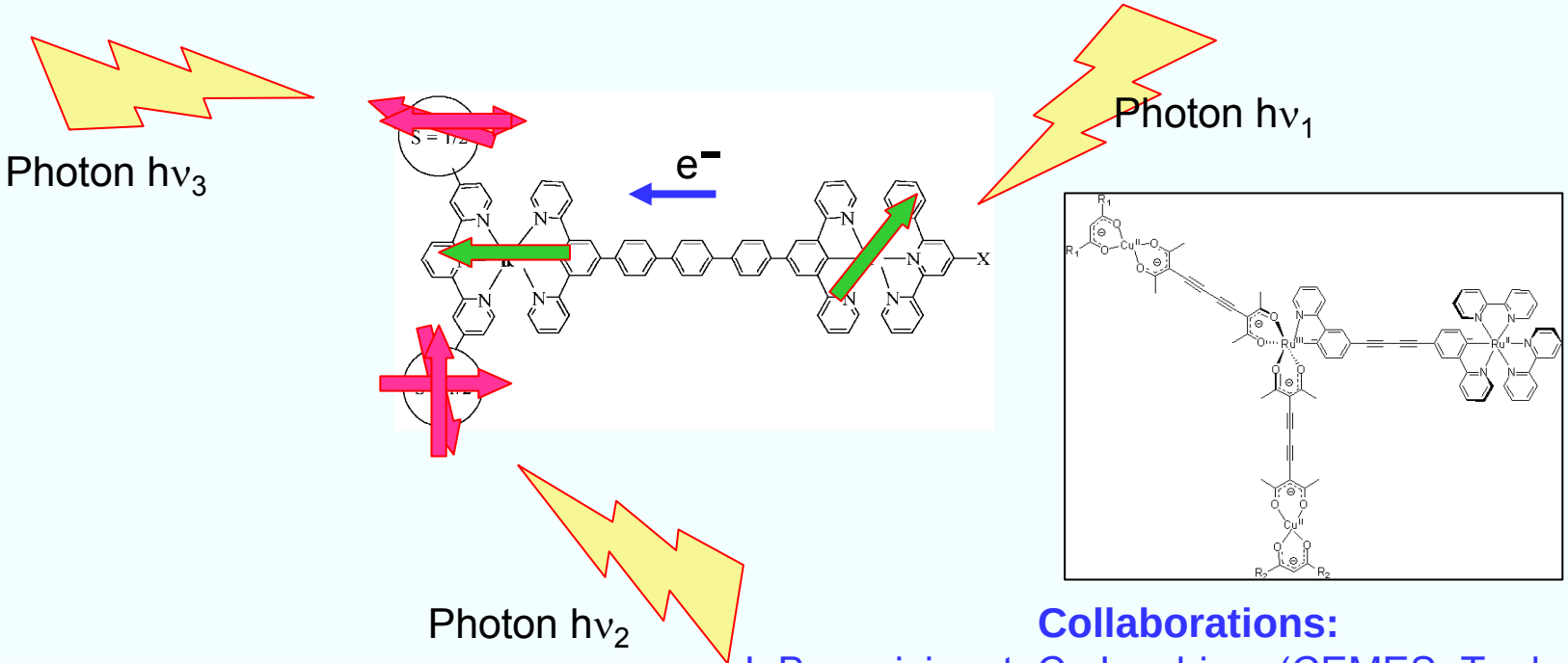
Metallic systems : Decoherence by free carriers on spin tunneling in meta
Injection of polarized spins..

(Tunneling, Kondo, Heavy fermions, Spintronics)

Spin qubits manipulated by photons

Manipulating the exchange interactions between two spins

Qubit de spins coupled by the injection of an electron and manipulated by transfert of photo-electrons



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Far infra-red : variations of charges (**S**)

Sub-centimeter: variations of spin projections(m_S)

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MANY THANKS

FOR

YOUR ATTENTION !

Mesoscopic Magnetism

Nano-magnetism

Tunneling of narrow DWs in highly anisotropic systems (Dy_3Al_2, SmCoCu)

Nanomagnetism on distributions (deposited clusters, BaFeO nanoparticles…)

Single-particles nano-magnetism (micro-SQUIDs)
nanoparticles, clusters (10 nm): thermally activated reversal (SW, NB models…)

Quantum nano-magnetism
single molecule magnets (1 nm): reversal by tunneling, slow quantum dynamics
with different environments: inhomogeneous and homogeneous baths
(spin, phonon, radiation, free carriers...)

Sub-nanometer scale

Atomic magnets (Quantum)
Rare-Earths ions (0.1 nm): Crucial role of nuclear spins