Quantum Tunneling of Magnetization in Molecular Magnets

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Tutorial T2: Molecular Magnets, March 12, 2006

Outline

1. Introduction
- –Nanomagnetism
- –Quantum Tunneling of Magnetization
- –Initial discoveries

2. Magnetic Interactions, Energy Scales, Spin Hamiltonian

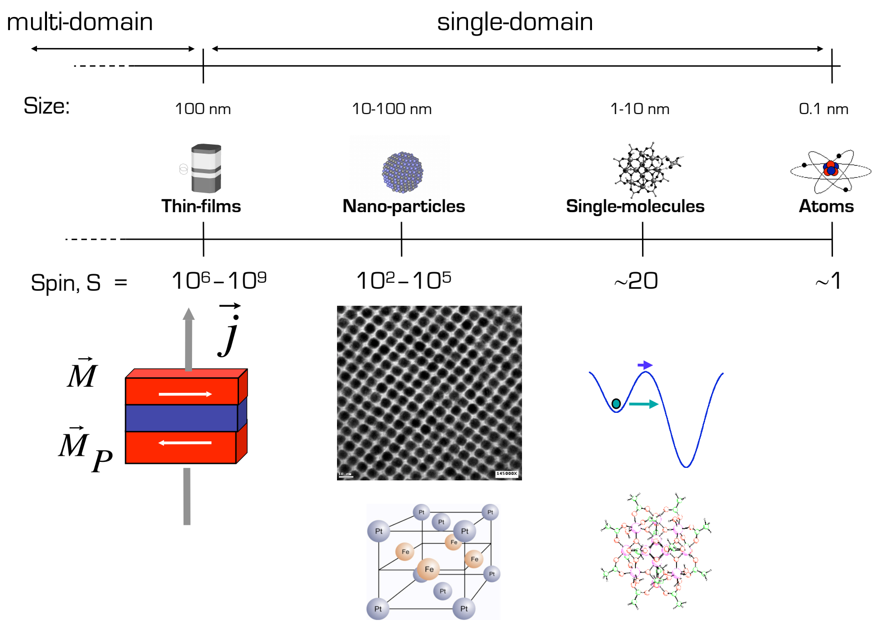
3. Experimental Techniques
- –Micro-magnetometry
- –High Frequency EPR

4. Resonant Quantum Tunneling of Magnetization
- –Thermally activated, thermally assisted and pure
- –Crossover between regimes
- –Berry Phase and Landau-Zener Method

5. High Spin Superposition States
- –SMM Ni_4: microwave spectroscopy and magnetometry
- –Photon induced transitions between superposition states
- –Decoherence rate
- –Longitudinal (energy) relaxation times

6. Perspectives

Nanomagnetism



Quantum Tunneling of Magnetization

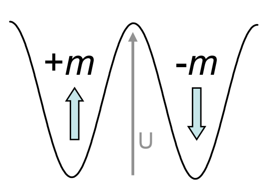
PHYSICAL REVIEW LETTERS 22 February 1988

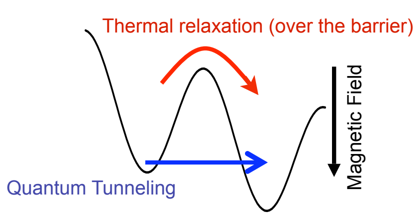
Quantum Tunneling of Magnetization in Small Ferromagnetic Particles

E. M. Chudnovsky and L. Gunther

Department of Physics and Astronomy, Tufts University, Medford, Massachusetts 02155
(Received 29 October 1987)

The probability of tunneling of the magnetization in a single-domain particle through an energy barrier between easy directions is calculated for several forms of magnetic anisotropy. Estimated tunneling rates prove to be large enough for observation of the effect with the use of existing experimental techniques.

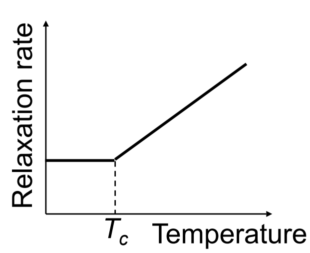




Thermal $\Gamma \sim e^{-U/k_B T}$

Quantum $\Gamma \sim e^{-B(0)} = e^{-U/k_B T_C}$

$T_c = U/k_B B(0)$

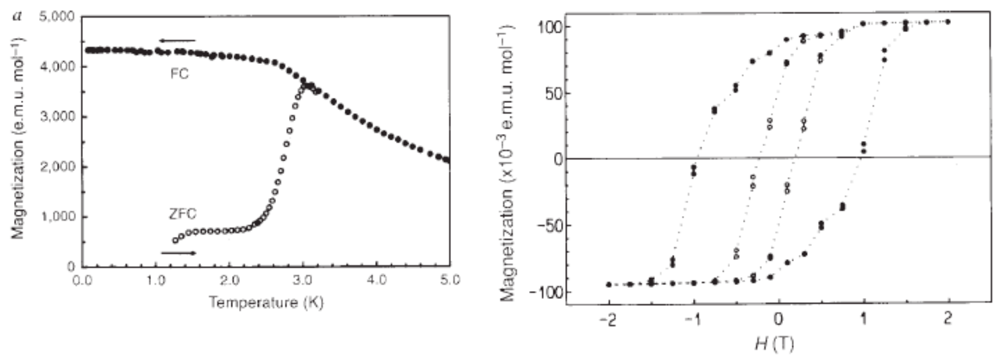


also, Enz and Schilling, van Hemmen and Suto (1986)

Magnetic Bistability in a Molecular Magnet

Magnetic bistability in a metal-ion cluster

R. Sessoli*, D. Gatteschi*‡, A. Caneschi* & M. A. Novak‡§ Nature 1993, and Sessoli et al., JACS 1993



Magnetic hysteresis at 2.8 K and below (2.2 K)
S=10 ground state spin

Quantum Tunneling in Single Molecule Magnets

Macroscopic Measurement of Resonant Magnetization Tunneling in High-Spin Molecules

Jonathan R. Friedman and M. P. Sarachik
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J. Tejada
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R. Ziolo
Wilson Center for Research and Technology, Xerox Corporation, Webster, New York 14580
(Received 1 November 1995)

We report the observation of steps at regular intervals of magnetic field in the hysteresis loop of a macroscopic sample of oriented $Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$ crystals. The magnetic relaxation rate increases substantially when the field is tuned to a step. We propose that these effects are manifestations of thermally assisted, field-tuned resonant tunneling between quantum spin states, and attribute the observation of quantum-mechanical phenomena on a macroscopic scale to tunneling in a large (Avogadro's) number of magnetically identical molecules. [S0031-9007(96)00131-7]

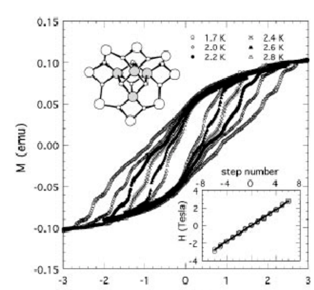
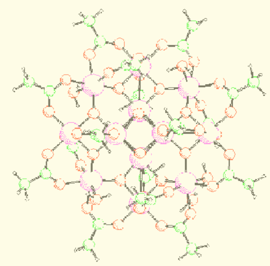


FIG. 1. Magnetization of Mn_{12} as a function of magnetic field at six different temperatures, as shown (field sweep rate of 67 mT/min). The inset shows the fields at which steps occur

Single crystal studies of Mn_{12}: L. Thomas, et al. Nature 383, 145 (1996)
Susceptibility studies: J.M. Hernandez, et al. EPL 35, 301 (1996)

Single Molecule Magnets

- Molecules with a large spin ground state (S~10)
- Large (Ising-like) uniaxial magnetic anistropy
- Single crystals: ordered 3D arrays of weakly interacting (almost identical) molecules
- Well defined discrete set of magnetic quantum states
- Chemical control of quantum energy levels
  - •Molecule Spin
  - •Molecule Symmetry
  - •Magnetic Anisotropy
  - •Intermolecular Interactions



Basic Properties

- Individual molecules can be magnetized and exhibit magnetic hysteresis
- Quantum tunneling of the magnetization

SMMs

- Fundamental studies of nanomagnets
  - Study of resonant QTM (Friedman, et al; Thomas et al. CNRS 1995)
  - Magnetization reversal and relaxation
    - Crossover from classical thermal activation to quantum tunneling (Sangregorio, et al. 1997, Bokacheva and ADK, PRL 2000)
    - Modeling from a microscopic point of view (Pederson et al., Harmon et al.)
  - Interference effects in magnetic quantum tunneling (W. Wernsdorfer and R. Sessoli, *Science* 1999)
  - Effects of nuclear spins on quantum tunneling
  - Study of decoherence of quantum systems

Potential Applications:

- Magnetic Data Storage (1 bit/molecule in 2D: 100 tera-bit/in^2)
- Magnetic Cooling
- Millimeter and sub-millimeter wave devices
- Quantum information storage (Leuenberger and Loss 2001)

Quantum information storage and quantum computing

letters to nature

Quantum computing in molecular magnets

Michael N. Leuenberger & Daniel Loss

Department of Physics and Astronomy, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland

Shor and Grover demonstrated that a quantum computer can outperform any classical computer in factoring numbers[1] and in searching a database[2] by exploiting the parallelism of quantum mechanics. Whereas Shor's algorithm requires both superposition and entanglement of a many-particle system[3], the superposition of single-particle quantum states is sufficient for Grover's algorithm[4]. Recently, the latter has been successfully implemented[5] using Rydberg atoms. Here we propose an implementation of Grover's algorithm that uses molecular magnets[6–10], which are solid-state systems with a large spin; their spin eigenstates make them natural candidates for single-particle systems. We show theoretically that molecular magnets can be used to build dense and efficient memory devices based on the Grover algorithm. In particular, one single crystal can serve as a 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 10^{-10} seconds. We show that our proposal should be feasible using the molecular magnets Fe_8 and Mn_{12}.

Nanotechnology 12 (2001)

Magnetic qubits as hardware for quantum computers

J Tejada[1,4], E M Chudnovsky[2], E del Barco[1], J M Hernandez[1] and T P Spiller[3]

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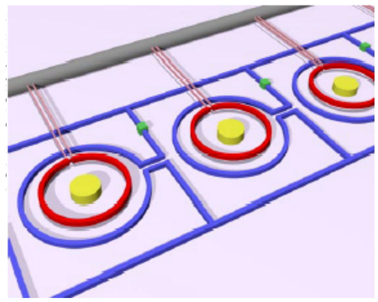


Magnetic Interactions

- Energy scales
  - Exchange
  - Magnetic anisotropy
  - Dipolar
  - Hyperfine
- Spin-Hamiltonian

First SMM: Mn_{12}-acetate

$[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4].2CH_3COOH.4H_2O$

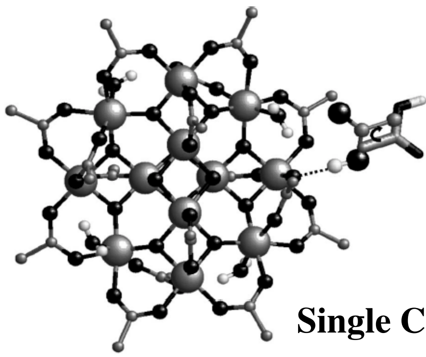
Magnetic Core

8 Mn^{3+} S=2
4 Mn^{4+} S=3/2

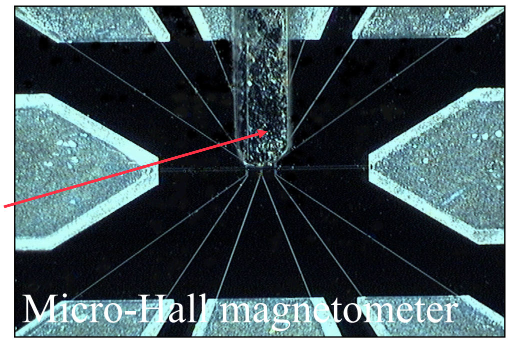
Competing AFM Interactions → Ground state S=10

Organic Environment

2 acetic acid molecules
4 water molecules

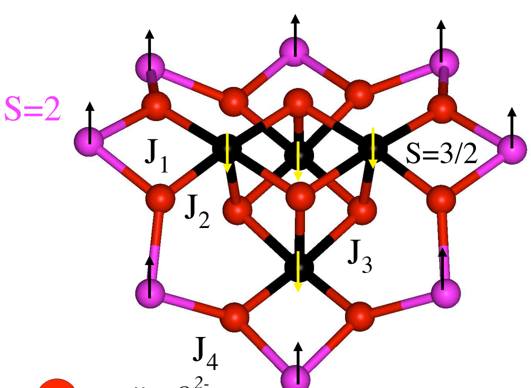


Single Crystal



- **S_4 site symmetry**
- **Tetragonal lattice a=1.7 nm, b=1.2 nm**
- **Strong uniaxial magnetic anisotropy (~60 K)**
- **Weak intermolecular interactions (~0.1 K)**

Intra-molecular Exchange Interactions



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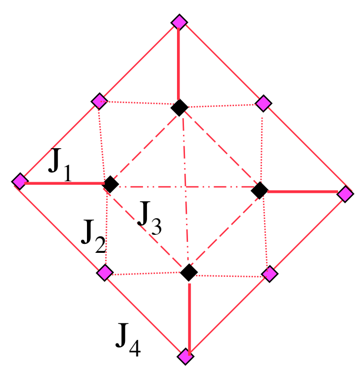


= μ_3-O^{2-}

= *Mn(IV)*

= *Mn(III)*

$J_1 \sim 215$ K
$J_2, J_3 \sim 85$ K
$J_4 \sim 45$ K

$$H = \sum_{<ij>} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_i \vec{S}_i \cdot D_i \cdot \vec{S}_i + \ldots$$

$(2S_1+1)^8(2S_2+1)^4=10^8 \Rightarrow$ S=10 and 2S+1=21

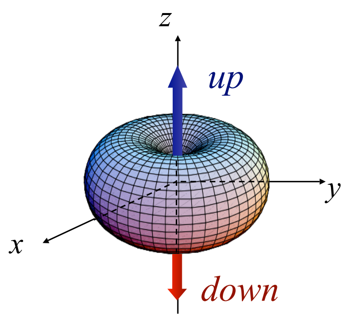
Magnetic Anisotropy and Spin Hamiltonian

Spin Hamiltonian

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

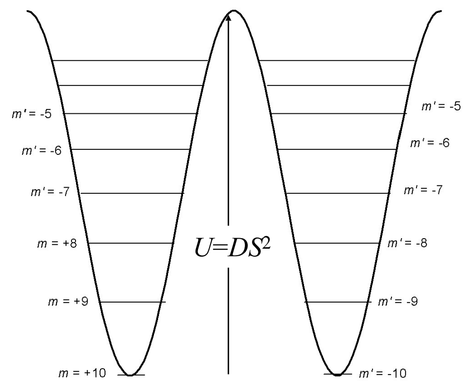
$$S_z|m> = m|m>$$

$$E_m = -Dm^2$$



(Ising-like) Uniaxial anisotropy

$2S+1$ spin levels



Experimental Techniques

- Magnetometry
  - Micro-Hall Effect Magnetometry
  - Micro-Squid
- Spectroscopy
  - EPR
  - Neutron Scattering
- NMR
- Specific Heat

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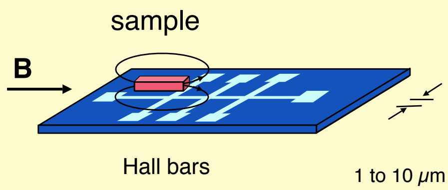
Micromagnetometry

- *μ*-Hall Effect



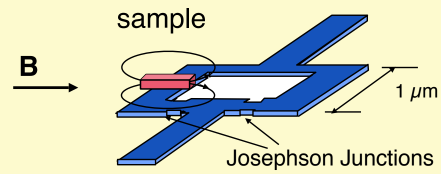
  - Based on Lorentz Force
  - Measures magnetic field

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

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

see, A. D. Kent et al., Journal of Applied Physics 1994

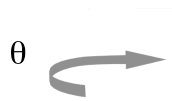
- *μ*-SQUID



  - 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

W. Wernsdorfer, JMMM 1995

High Frequency EPR



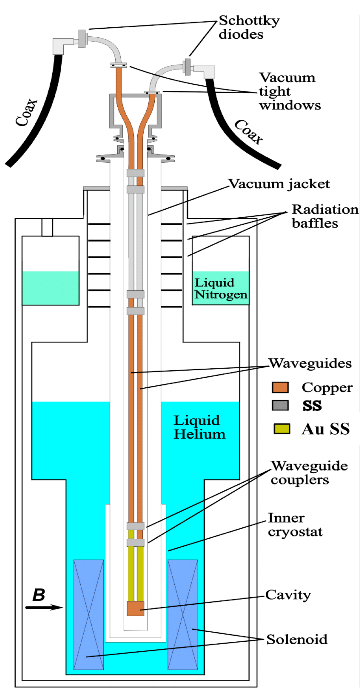
S. Hill, UF, Gainsville

Cylindrical TE01*n* (*Q* ~ 10^4 - 10^5)

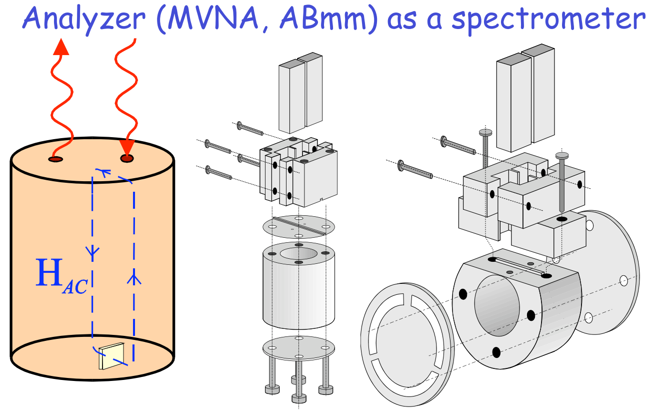
f = 16 → 300 GHz

Single crystal 1 × 0.2 × 0.2 mm³

T = 0.5 to 300 K, μ_oH up to 45 tesla

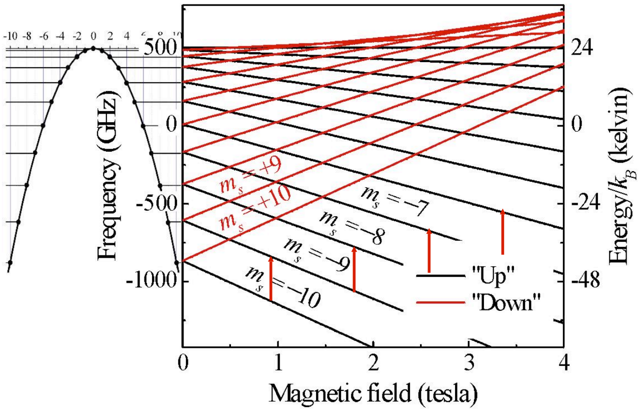


•We use a Millimeter-wave Vector Network Analyzer (MVNA, ABmm) as a spectrometer

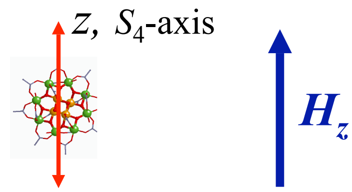


M. Mola *et al*., Rev. Sci. Inst. **71**, 186 (2000)

Single-crystal, high-field/frequency EPR



Reminder: field//z



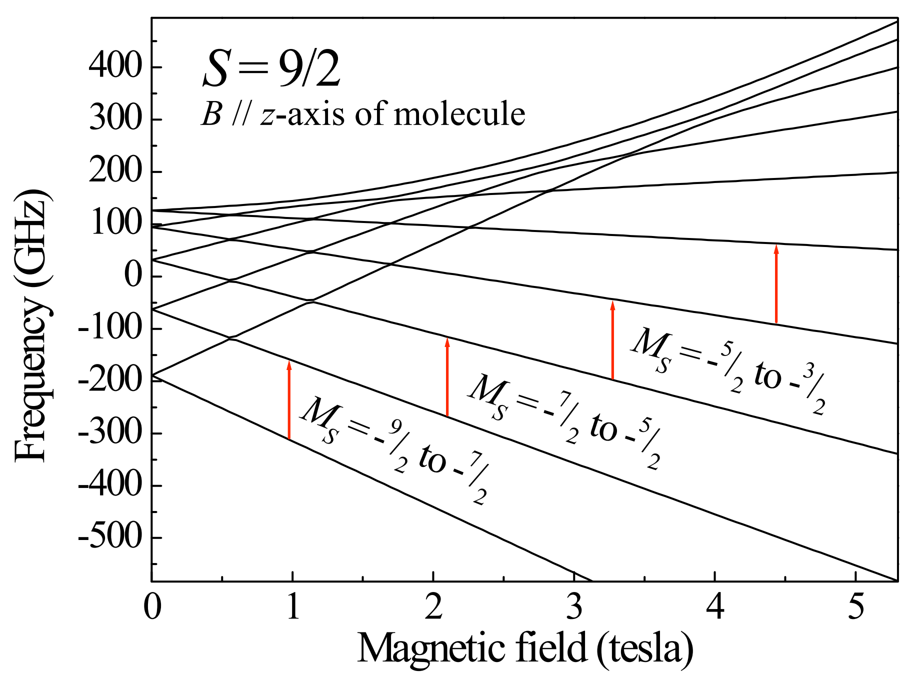
m_s represents spin-projection along the molecular 4-fold axis

$$E(m_s) = -|D|m_s^2 + g\mu_B B m_s$$

- Magnetic dipole transitions ($\Delta m_s = \pm 1$) - note frequency scale!
- EPR measures level spacings directly, unlike magnetometry methods

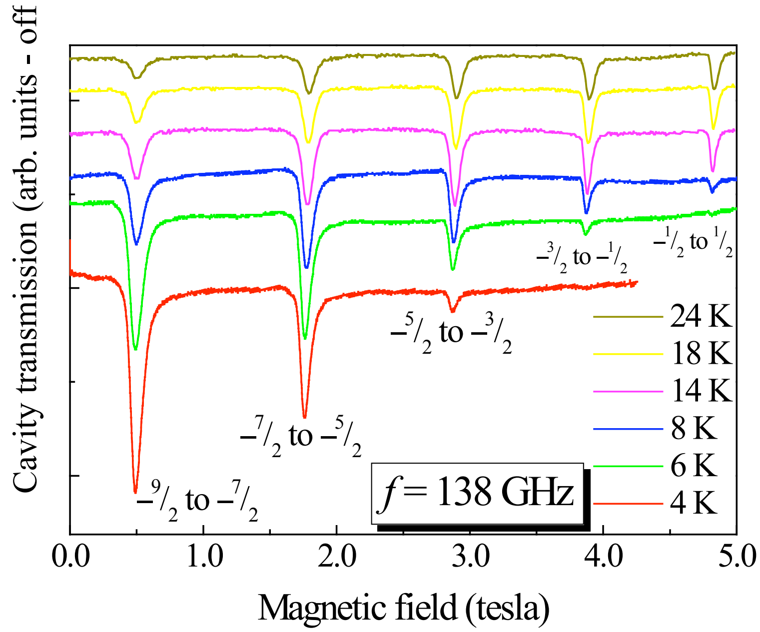
Energy level diagram for D < 0 system, B//z

$$\hat{H}_o \cong D\hat{S}_z^2 + \mu_B \vec{B}.\vec{g}.\hat{S}$$



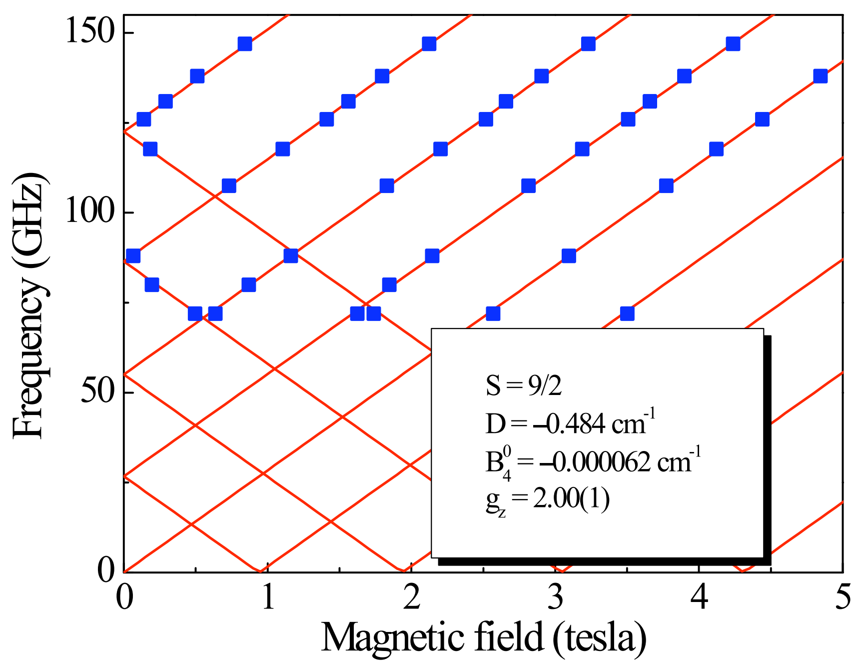
HFEPR for high symmetry (C_{3v}) Mn_4 cubane; $S = {}^9/_2$

$[Mn_4O_3(OSiMe_3)(O_2CEt)_3(dbm)_3]$



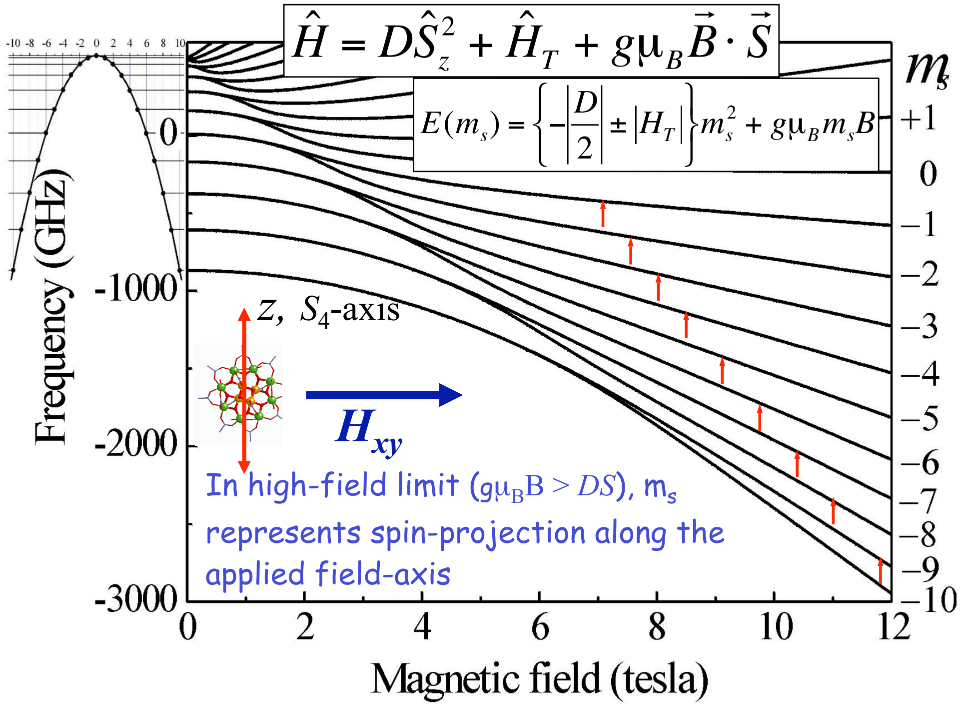
Fit to easy axis data - yields diagonal crystal field terms

$$\hat{H}_o = D\hat{S}_z^2 + B_4^0\hat{O}_4^0 + \mu_B g_{zz} B\hat{S}_z, \text{ where } \hat{O}_4^0 = \alpha\hat{S}^2\hat{S}_z^2 + \beta\hat{S}_z^4$$



Single-crystal, high-field/frequency EPR

Rotate field in *xy*-plane and look for symmetry effects



Resonant Quantum Tunneling of Magnetization

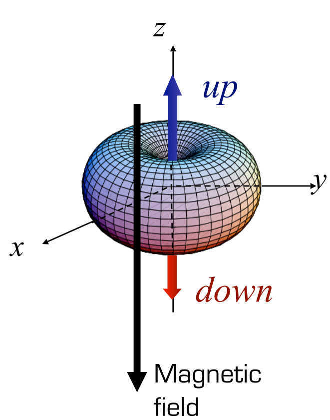
$$H = -DS_z^2 - g\mu_B S_z H_z$$

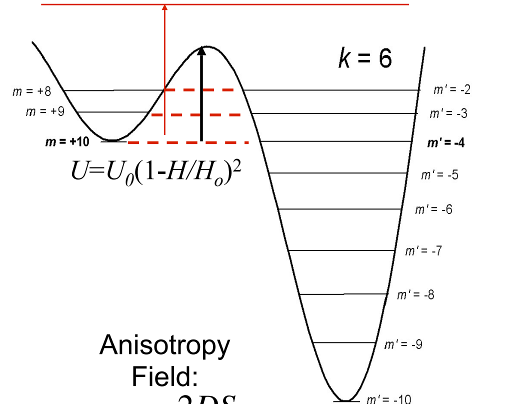
$$S_z|m> = m|m>$$

$$E_m = -Dm^2 - g\mu_B H_z m$$

with Zeeman term

"Resonance" fields where antiparallel spin projections are coincident, $H_k = kD/g\mu_B$, levels m and m'; k=m+m'

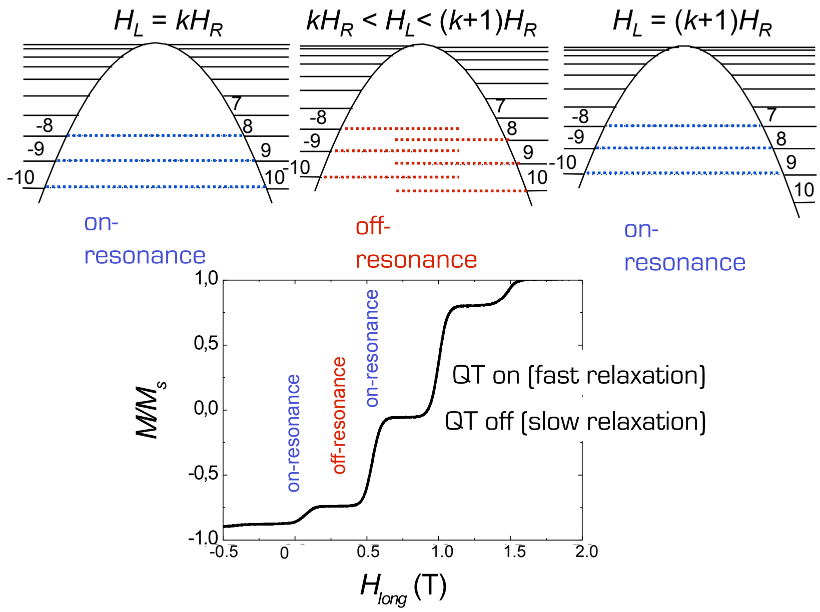




Anisotropy Field:

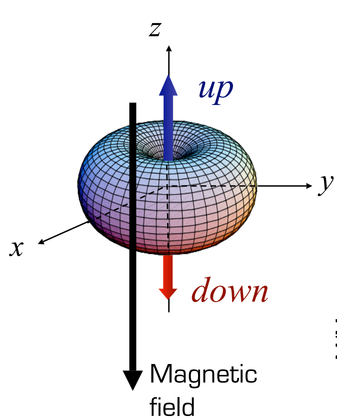
$$H_A = \frac{2DS}{g\mu_B}$$

Resonant Quantum Tunneling of Magnetization



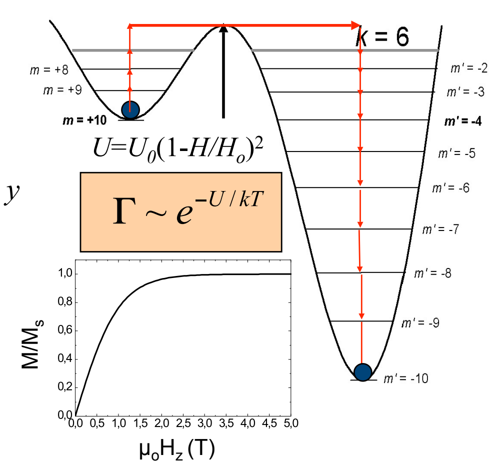
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs



Magnetic relaxation at high temperature

Thermal activation (over the barrier)

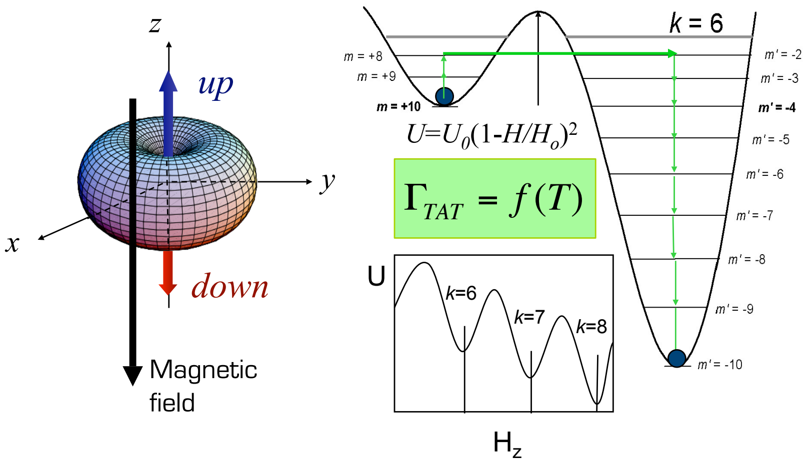


Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at intermediate temperature

Thermally assisted tunneling

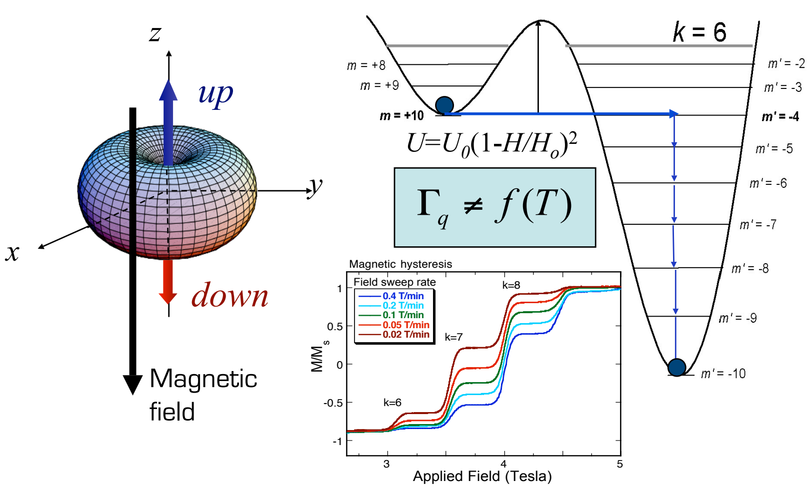


Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at low temperature

Pure quantum tunneling



Crossover from Thermally Assisted to Pure QTM

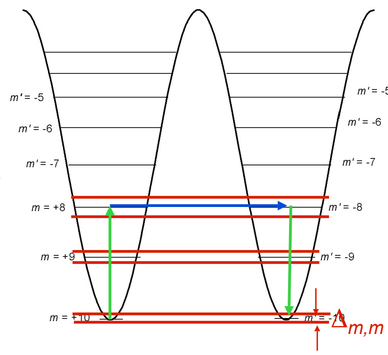
$$H = -DS_z^2 - g\mu_B S_z H_z - g\mu_B S_x H_x$$

Tunnel splitting on resonance $\Delta_{m,m'} \propto D\left(\frac{H_x}{H_A}\right)^{m-m'}$

Upper levels
Large splitting
Low Boltzmann population

Relaxation pathway = $f(T)$

Lowest levels
Small splitting
High Boltzman population



Theory of thermally assisted tunneling: Villian (1997), Leuenberger & Loss (2000) and Chudnovsky & Garanin (1999)
Crossover: Chudnovsky & Garanin, PRL 1997

Crossover between Thermally Assisted and Pure Quantum Tunneling in Molecular Magnet Mn_{12}-Acetate

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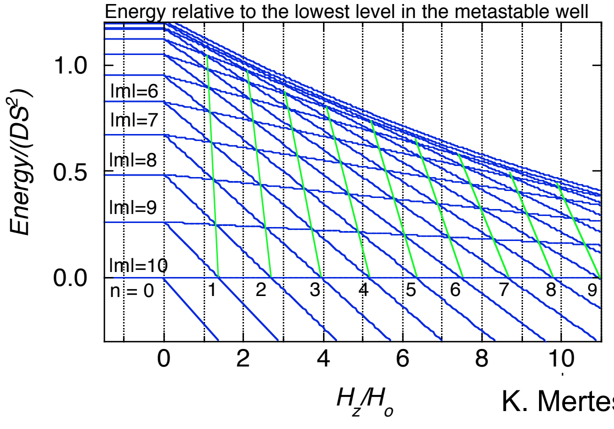
Marc A. Walters
Department of Chemistry, New York University, 31 Washington Place, New York, New York 10003
(Received 19 June 2000)

$$\mathcal{H} = -DS_z^2 - BS_z^4 - g_z\mu_B S_z H_z + \mathcal{H}'.$$

$$H(n, m_{esc}) = nH_0\{1 + B/D[m_{esc}^2 + (m_{esc} - n)^2]\}$$

D=0.548(3) K g_z=1.94(1) **H_0= $D/g_z\mu_B$ = 0.42 T**
B=1.17(2) × 10^{-3} K (EPR: Barra et al., PRB 97)

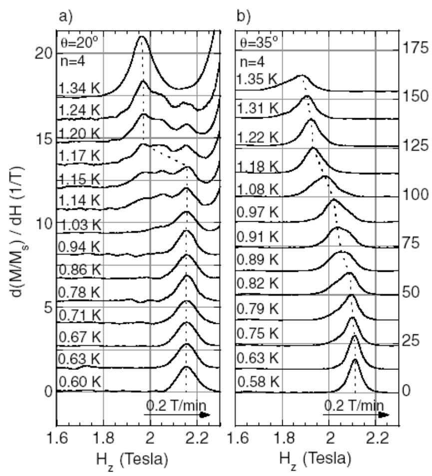
Energy relative to the lowest level in the metastable well



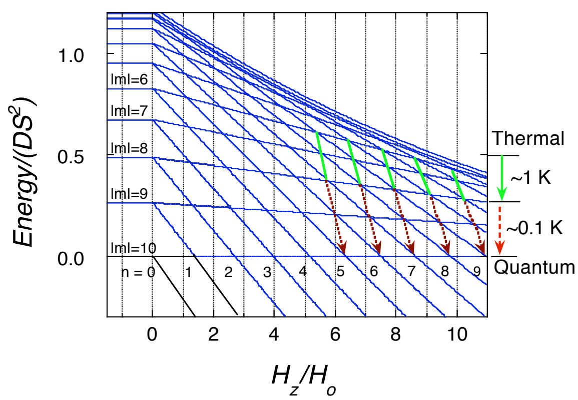
K. Mertes et al. PRB 2001

Experiments on the Crossover to Pure QTM in Mn_{12}-acetate

dM/dH versus H_z



Schematic: dominant levels as a function of temperature

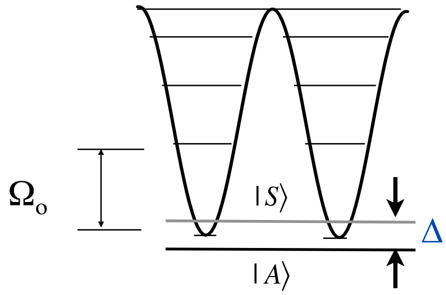


L. Bokacheva, ADK, M. Walters, PRL 2001

High Spin Superposition States

- SMM Ni_4; microwave spectroscopy and magnetometry
- Photon induced transition between superposition states
- Decoherence rate
- Longitudinal (energy) relaxation times

Coherent QTM: Microwave Spectroscopy and Magnetometry



- **Limit** $\Omega_o >> \Delta >> kT, E_o$

First condition: consider just 2 lowest energy states

Second condition: insures dephasing by phonons and nuclear spins is small

E_o typical energy width of nuclear spin multiplet

- **Predictions** (Stamp) for dephasing rate due to nuclear spins in an applied field

$$\Gamma_\phi = \frac{E_o}{\Delta}^2$$

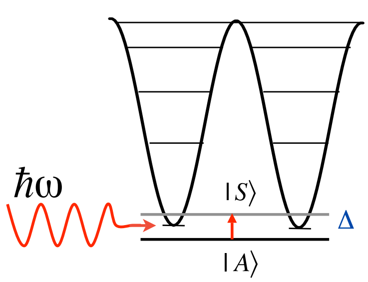
(Chudnovsky) spin-phonon interaction: universal lower bound on decoherence

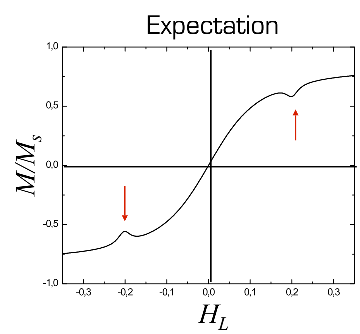
$$\tau_1^{-1} = \Gamma_1 = \frac{S^2\Delta^2\omega^3}{12\pi\hbar^2\rho c_t^5} coth(\frac{\hbar\omega}{2kT})$$

Experiment

Study: Magnetization Dynamics Induced by Microwaves (cw and pulsed)

- Photon induced transition between superposition states combined with magnetization measurements



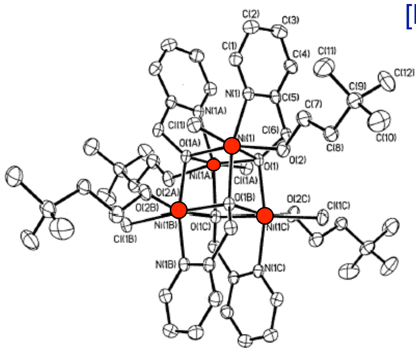


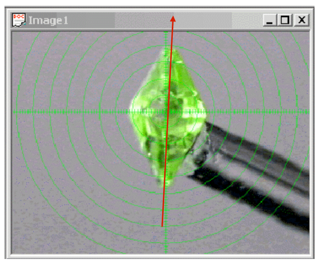
- Monitor spin-state populations while performing microwave spectroscopy
- Pulsed and CW microwave fields
- High magnetic sensitivity: ~10^5 spins/$Hz^{1/2}$
- High magnetic fields
- Time resolved magnetic measurements (~GHz)

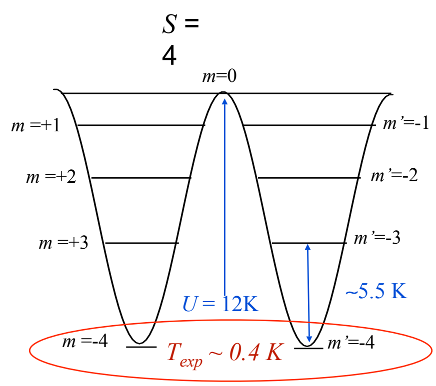
Description of SMM Ni_4

$$H = -DS_z^2 + C\left(S_+^4 + S_-^4\right) - g\mu_B S_z H_z - g\mu_B S_x H_x$$

$[Ni(hmp)(t\text{-}BuEtOH)Cl]_4$



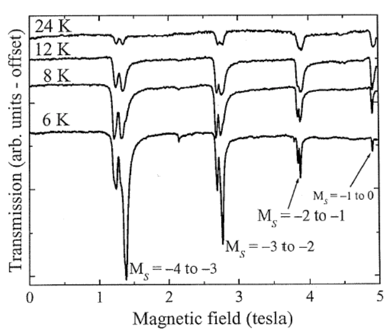


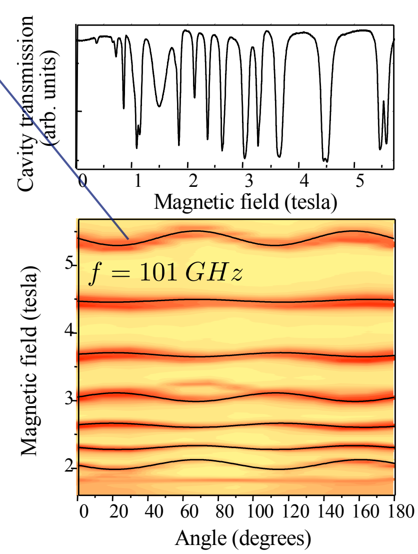


Description of SMM Ni_4

High frequency EPR: *Stephen Hill, UF - Gainesville, FL*

$$H = -DS_z^2 + C\left(S_+^4 + S_-^4\right) - g\mu_B S_z H_z - g\mu_B S_x H_x$$



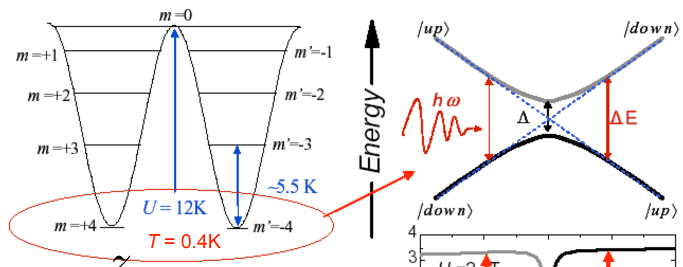


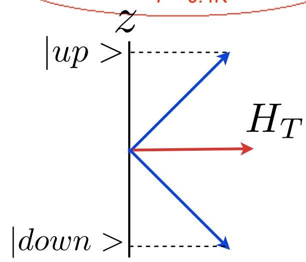
$$D_L = -0.863\ K$$
$$D_U = -0.830\ K$$
$$B_4^0 = -1.7 \times 10^{-4}\ K$$
$$B_4^4 = -5.8 \times 10^{-4}\ K$$

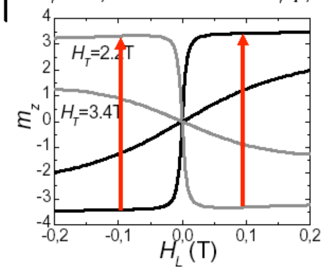
$g_z = 2.30 \qquad g_x = g_y = 2.23$

Multiple but narrow peaks – "molecular environments" with slightly different D values

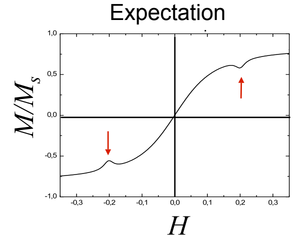
Experiment







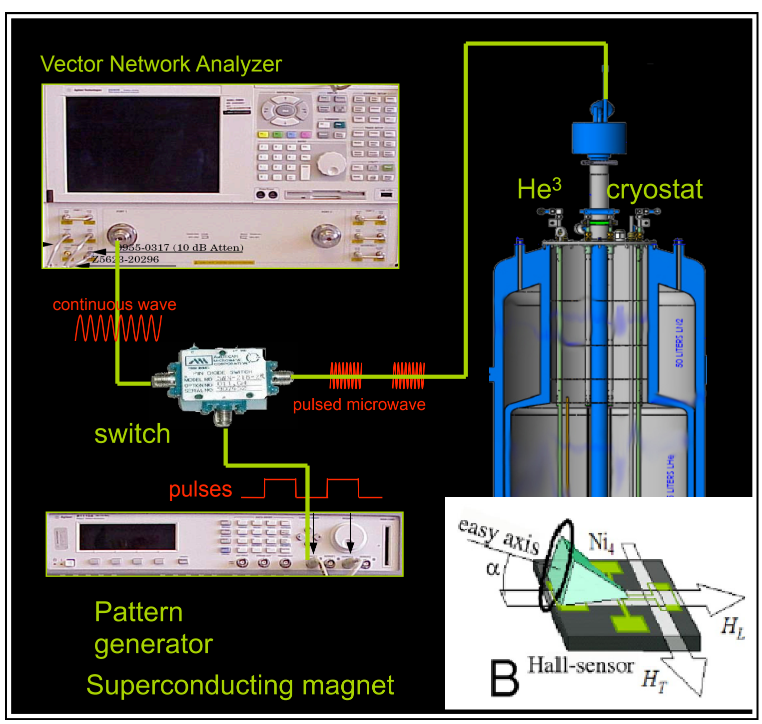
Expectation



$$|S\rangle = \frac{1}{\sqrt{2}}\left(|up\rangle + |down\rangle\right)$$

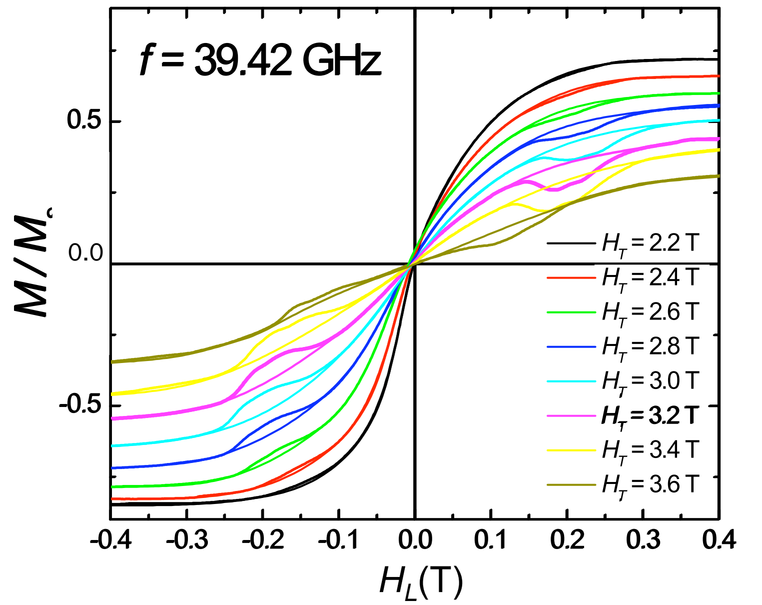
$$|A\rangle = \frac{1}{\sqrt{2}}\left(|up\rangle - |down\rangle\right)$$

Experimental Setup



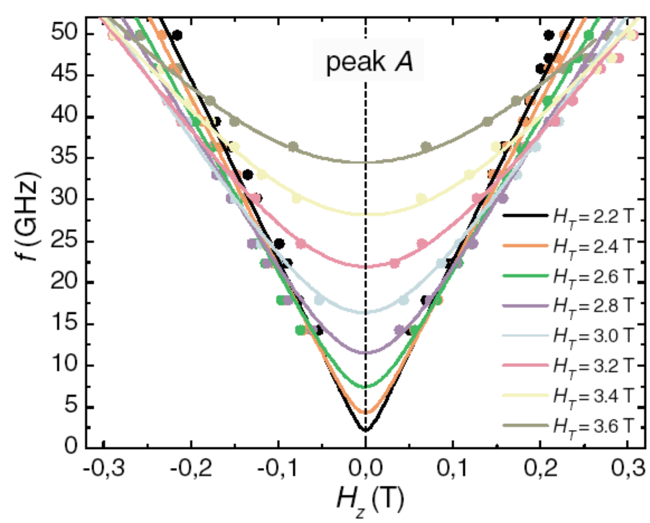
Results: Photon Induced Transitions between Superposition States

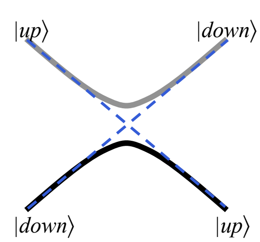
Magnetization with microwaves



T = 0.45 K ΔT < 0.01 K in the peaks

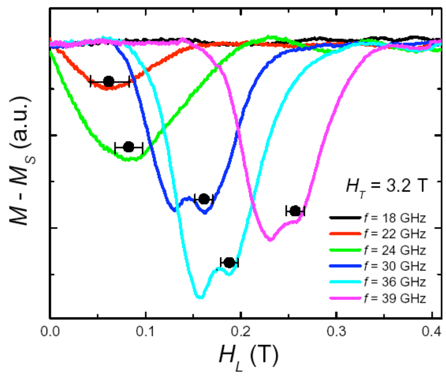
Results: Photon Induced Transitions between Superposition States



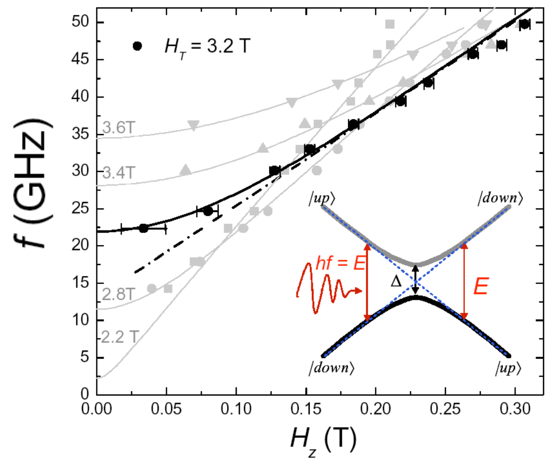


Level Repulsion: Observation of quantum superposition of high spin states with opposite magnetization

Results: Photon Induced Transitions between Superposition States



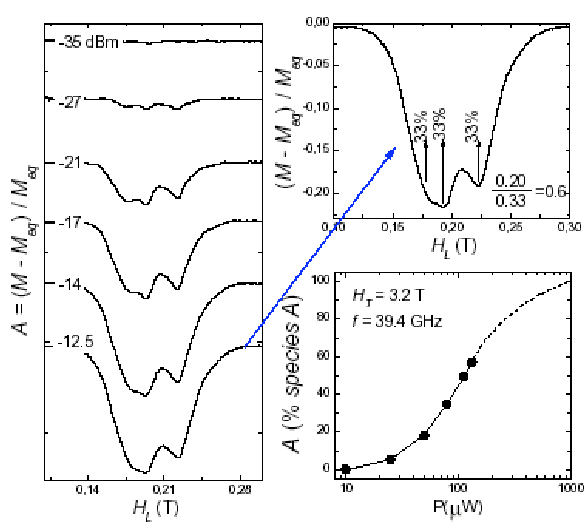
Curvature



Approach to saturation and Ni_4 'micro-environments'

As a function of mw power – cw radiation

H_T = 3.2 T *f* = 39.4 GHz $P_{loss-in-coax}$= 15 dB

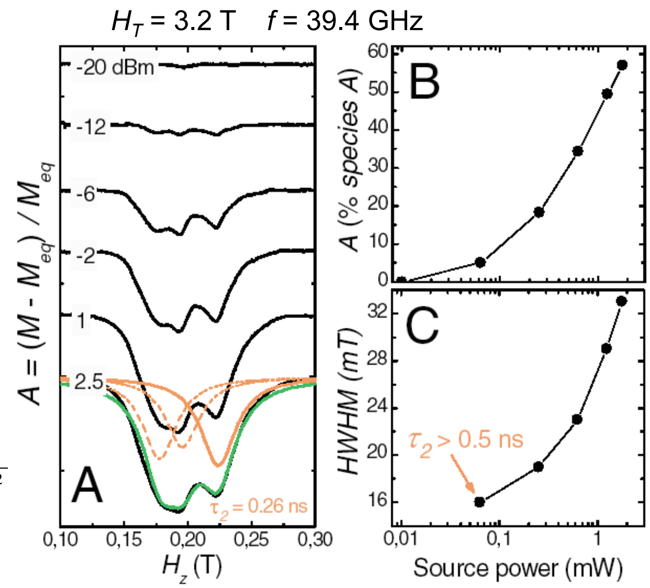


We observe variations up to 90% for higher fields and lower frequencies

Results: Transverse relaxation rate (τ_2) – decoherence (τ_ϕ)

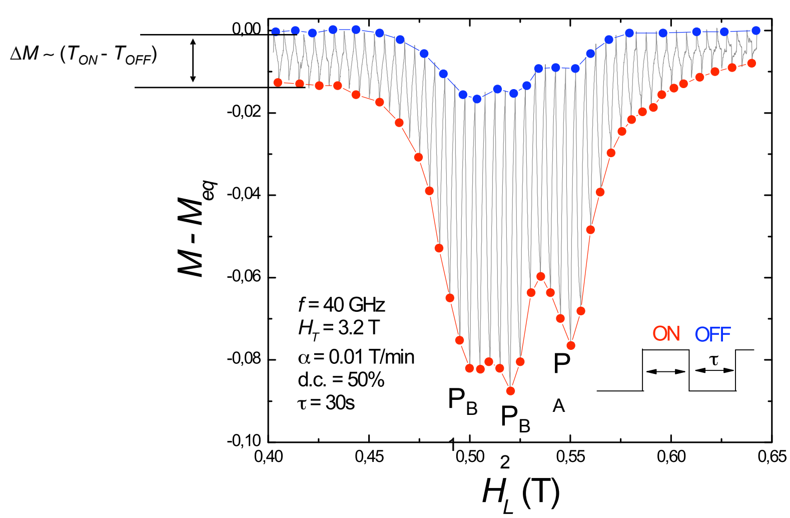
Decoherence time lower bound

$$f(\omega) = \frac{1}{\pi} \frac{\tau_2}{1 + (\omega - \omega_0)^2 \tau_2^2}$$



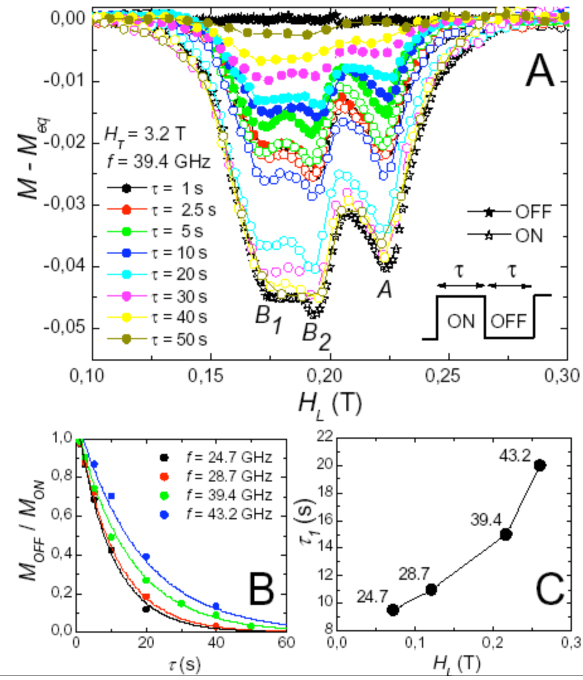
Results: Longitudinal relaxation rate (τ_1)

Pulsed mw experiments



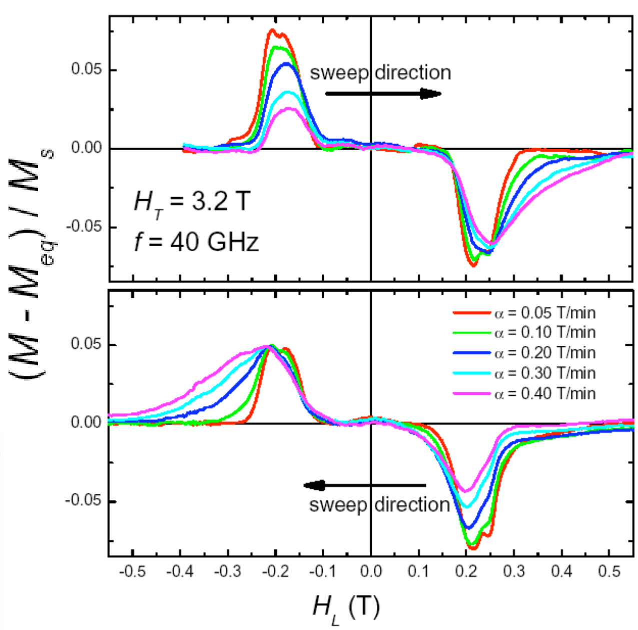
Results: Longitudinal relaxation rate (τ_1)

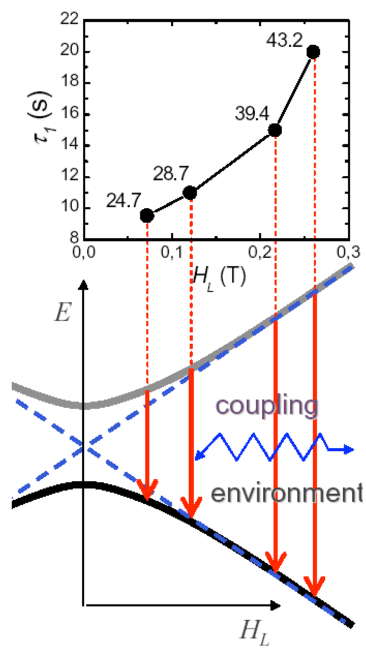
Pulsed radiation experiments



Longitudinal relaxation effects in cw experiments

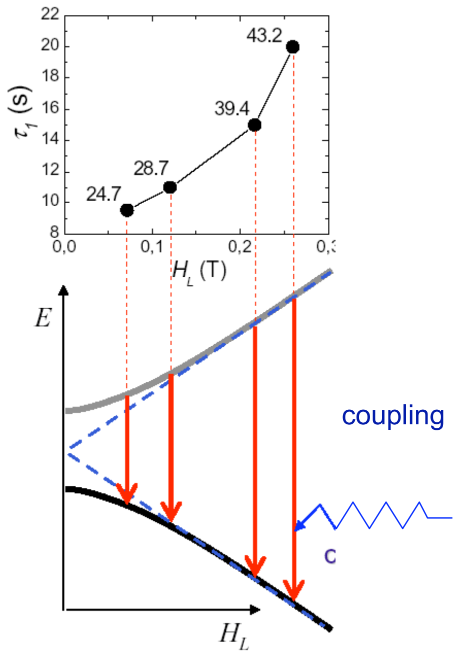
Energy relaxation increases with freq.





Spin-Phonon Relaxation

Pulsed radiation experiments



Relaxation rate:

$$\tau_1^{-1} = \Gamma_1 = \frac{S^2\Delta^2\omega^3}{12\pi\hbar\rho c_t^5} coth(\frac{\hbar\omega}{2kT})$$

Chudnovsky, PRL 2004

$c_t = 10^3 m/s, \quad f = \Delta/h = 20\,GHz$

$$\tau_1 = 10^{-3}\,sec$$

Upper limit on the relaxation time!

Phonon-laser effect:

$$\Gamma_L \sim \omega^{-3}$$

Chudnovsky and Garanin, PRL 2004

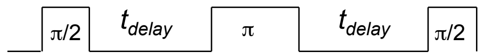
Other levels important?

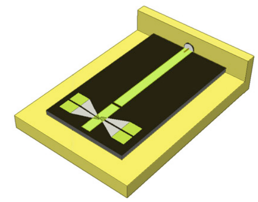
Summary (Ni_4)

- Observation of energy splittings between low-lying superpositions of high spin-states.
  - Direct measurement of the magnetization combined with microwave spectroscopy
- Lower bound for the decoherence time τ_ϕ > 0.5 ns
  - Similar to that observed in the Mn_4-dimer through EPR measurements a system with strong intermolecular exchange interactions
- Determination of the longitudinal relaxation times τ ~ 10-20 s
  - Characterized τ as a function of longitudinal field and frequency

Perspectives

- Coherent oscillations of the magnetization; Rabi and Spin Echo experiments





High radiation power is needed for measurable Rabi periods

Ex: π-pulse $\gamma H_1 S T_{pulse} = \pi$, $H_1 = 1\ \mu T$, $T_{pulse} = 5\ \mu s$

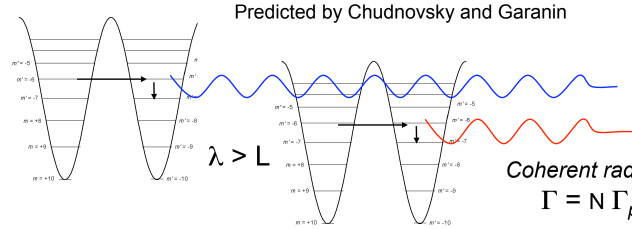
$H_1 = 100\ \mu T$, $T_{pulse} = 50\ ns$

- Open questions also relate to collective effects:
  - Intermolecular magnetic interactions—exchange and dipolar
  - Radiation and phonon fields!

Magnetic Relaxation Enhancement (Cavity) and Superradiance in Mn_{12}-acetate

Tejada et al., Phys. Rev. B, 2003 and Appl. Phys. Lett. B, 2004

Predicted by Chudnovsky and Garanin



Coherent radiation

$\Gamma = N\,\Gamma_{photon}$