Spin Dynamics in Single Molecule Magnets

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Collaborators:

- Gregoire de Loubens, Enrique del Barco
- Stephen Hill
- Dmitry Garanin
- Myriam Sarachik, Yosi Yeshurun
- Vladimir Krymov, Gary Gerfen
- George Christou, David Hendrickson

Sponsor

Outline

I. Introduction

- Quantum Tunneling of Magnetization
- Single molecule magnets

II. Mn_{12}-acetate

- Spin Hamiltonian
- Crossover from Thermally Assisted to Pure Quantum Tunneling

III. Spin-Relaxation in Ni_4

- EPR and micromagnetometry on a chip
- Spin-phonon relaxation mechanisms

IV. Summary and Perspectives

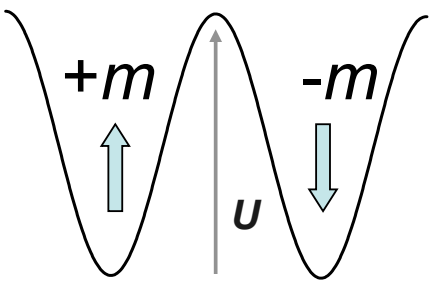
Quantum Tunneling of Magnetization

VOLUME 60 22 FEBRUARY 1988 NUMBER 8

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)

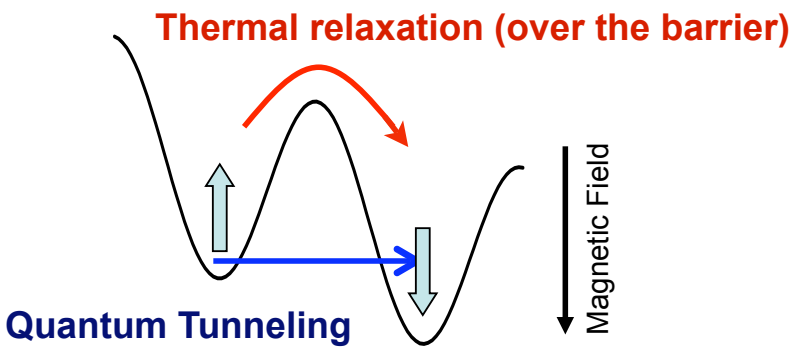
The probability of tunneling of the magnetization in a single-domain particle through an energy barrier between easy directions is calculated for several forms of magnetic anisotropy. Estimated tunneling rates prove to be large enough for observation of the effect with the use of existing experimental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

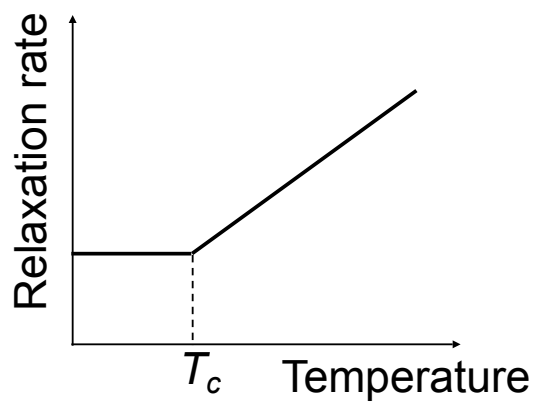


Thermal $\Gamma \sim e^{-U/k_B T}$

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

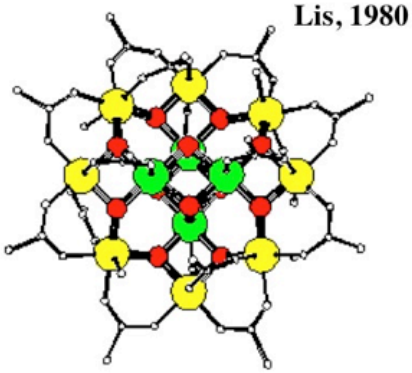
$$T_c = U/k_B B(0)$$





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

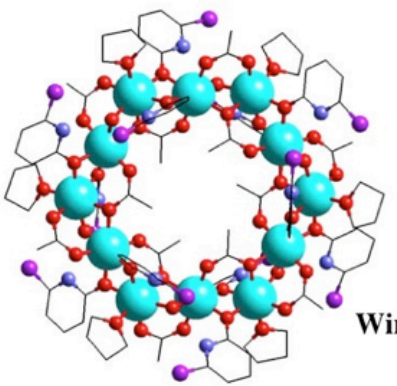
Single Molecule Magnets



Lis, 1980

Mn_{12} S = 10

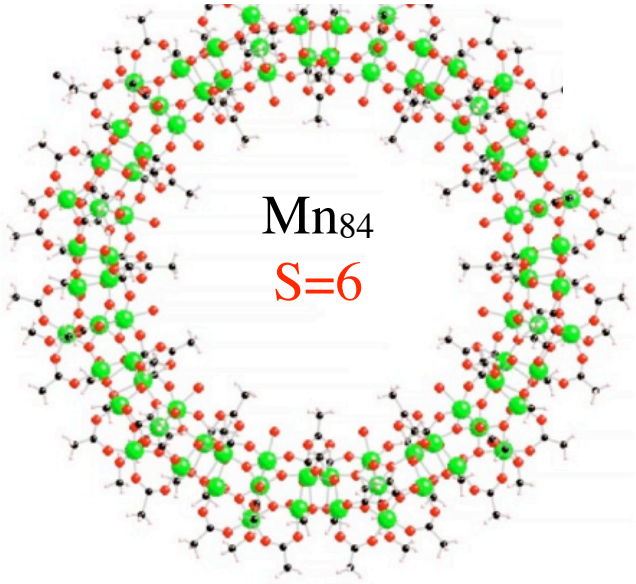
Ni_{12} S = 12



Winpenny, 1999

Physics

-Individual molecule can be n
magnetic hysteresis 1993
-Quantum Tunneling of Magn
-Quantum Phase Interference
-Quantum Coherence 2008



Mn_{84}
S=6

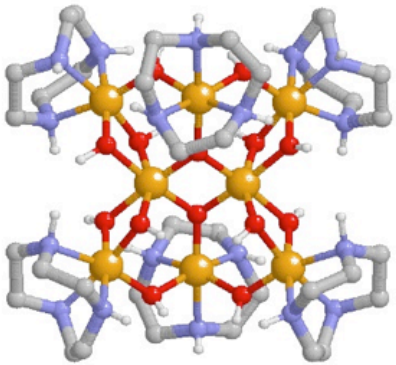
Christou, 2004

Wiegart, 1984

SMM Characteristics

- Molecules
- High spin ground state
- Uniaxial anisotropy
- Single crystals
- Synthesized in solution
- Modified chemically
  - Peripheral ligands
  - Oxidized/reduced
  - Soluble
  - Bonded to surfaces

Fe_8 S = 10



First SMM: Mn_{12}-acetate

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

Magnetic Core

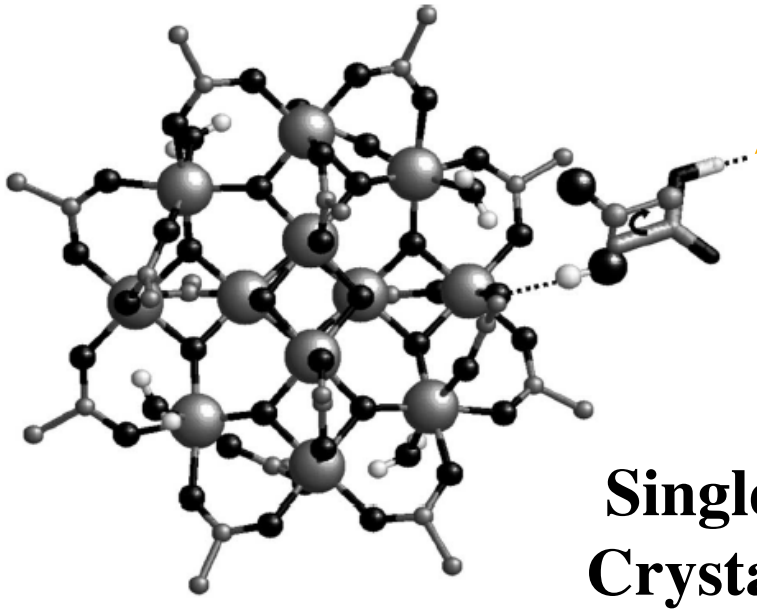
8 Mn^{3+} S=2
4 Mn^{4+} S=3/2

Competing AFM Interactions →

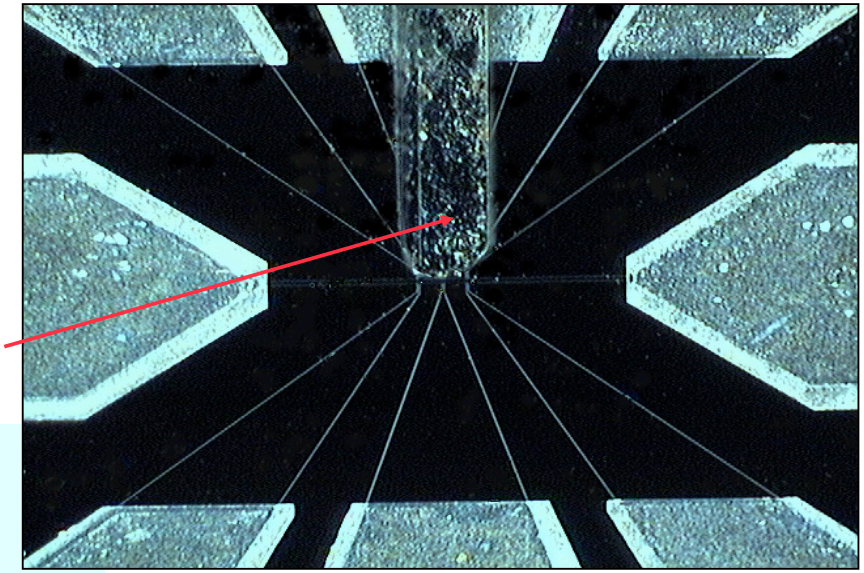
Ground state
S=10

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 dipole interactions (~0.1 K)**

Resonant Quantum Tunneling of Magnetization

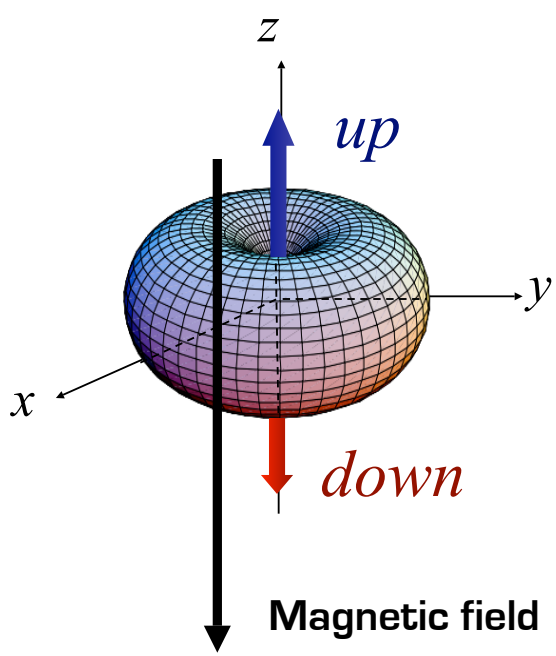
$$H = -DS_z^2 - g\mu_B S_z H_z$$

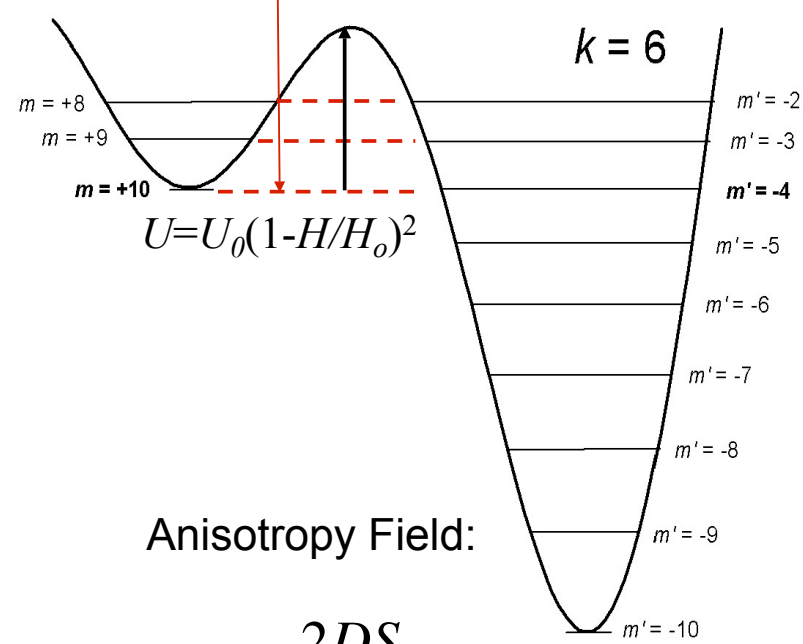
with Zeeman term

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

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

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

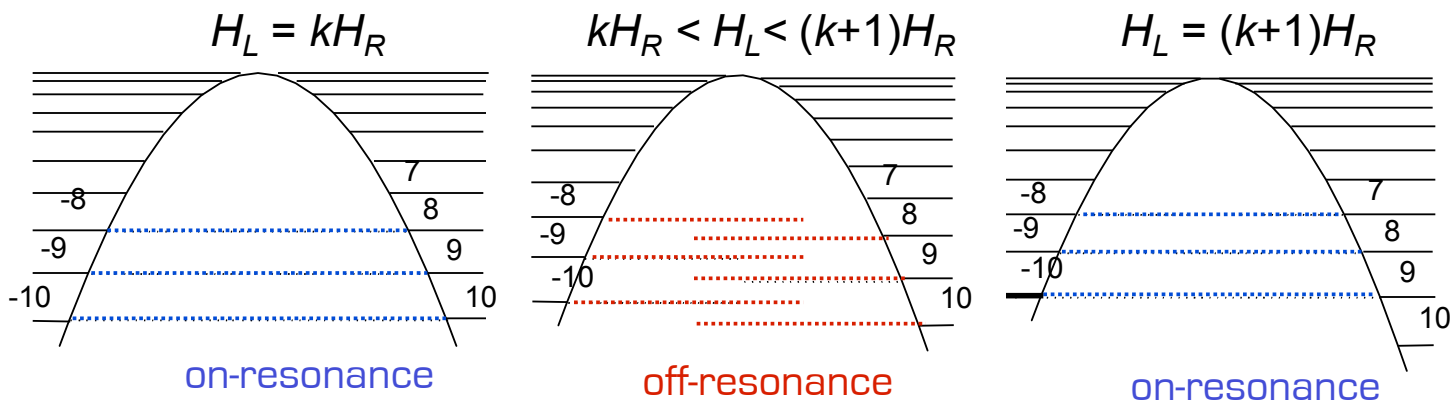


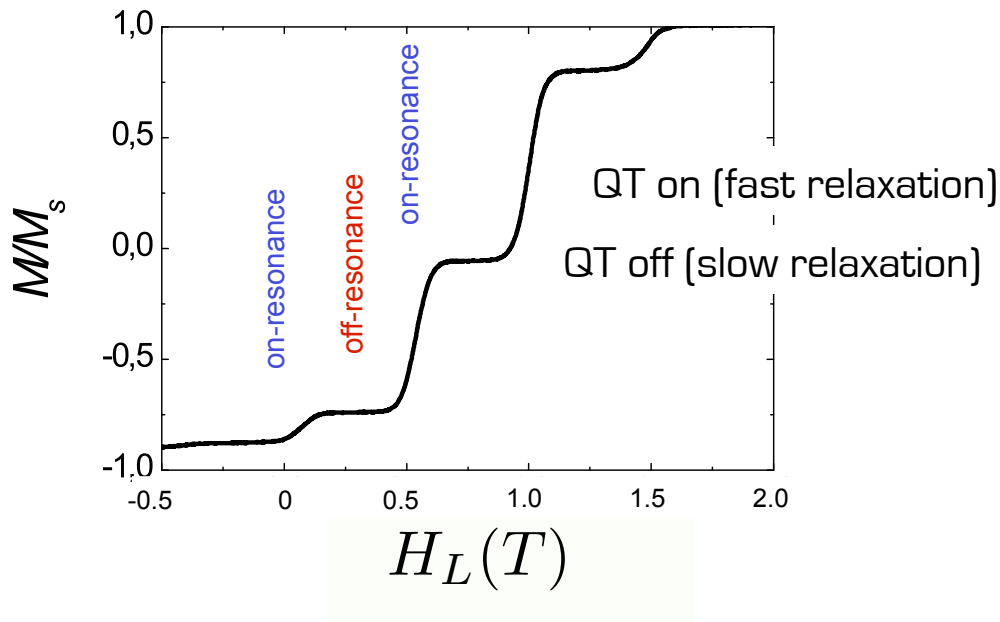


Anisotropy Field:

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

Resonant Quantum Tunneling of Magnetization





VOLUME 79, NUMBER 22 PHYSICAL REVIEW LETTERS 1 DECEMBER 1997

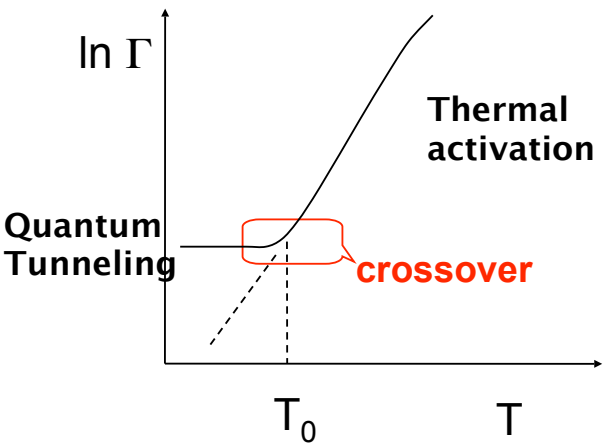
First- and Second-Order Transitions between Quantum and Classical Regimes for the Escape Rate of a Spin System

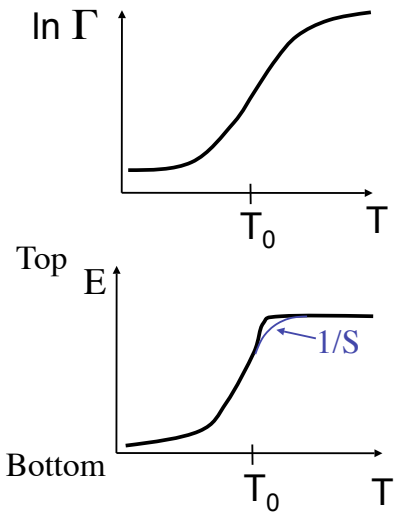
E. M. Chudnovsky* and D. A. Garanin†

Department of Physics and Astronomy, City University of New York-Lehman College, Bedford Park Boulevard West, Bronx, New York 10468-1589

(Received 7 July 1997)

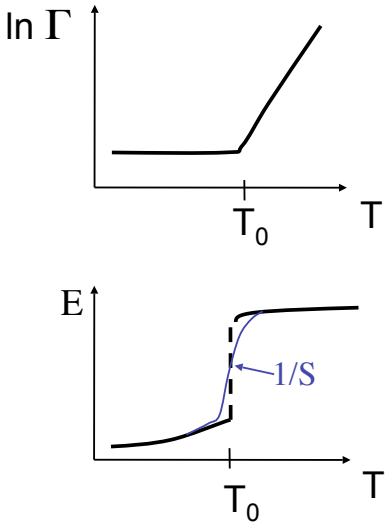
We have found a novel feature of the bistable large-spin model described by the Hamiltonian $\mathcal{H} = -DS_z^2 - H_x S_x$. The crossover from thermal to quantum regime for the escape rate can be either first ($H_x < SD/2$) or second ($SD/2 < H_x < 2SD$) order, that is, sharp or smooth, depending on the strength of the transverse field. This prediction can be tested experimentally in molecular magnets like $Mn_{12}Ac$. [S0031-9007(97)04645-0]





Second order crossover
Larkin and Ovchinnikov '83

$$U(x) = -x^2 + x^4 - x^2 \pm x^3$$



First order crossover
Chudnovsky '92

$$U(x) = -x^2 - x^4 \pm x^5$$

Chudnovsky and Garanin '97
Uniaxial nanomagnets for small transverse magnetic fields!!!

NYU

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

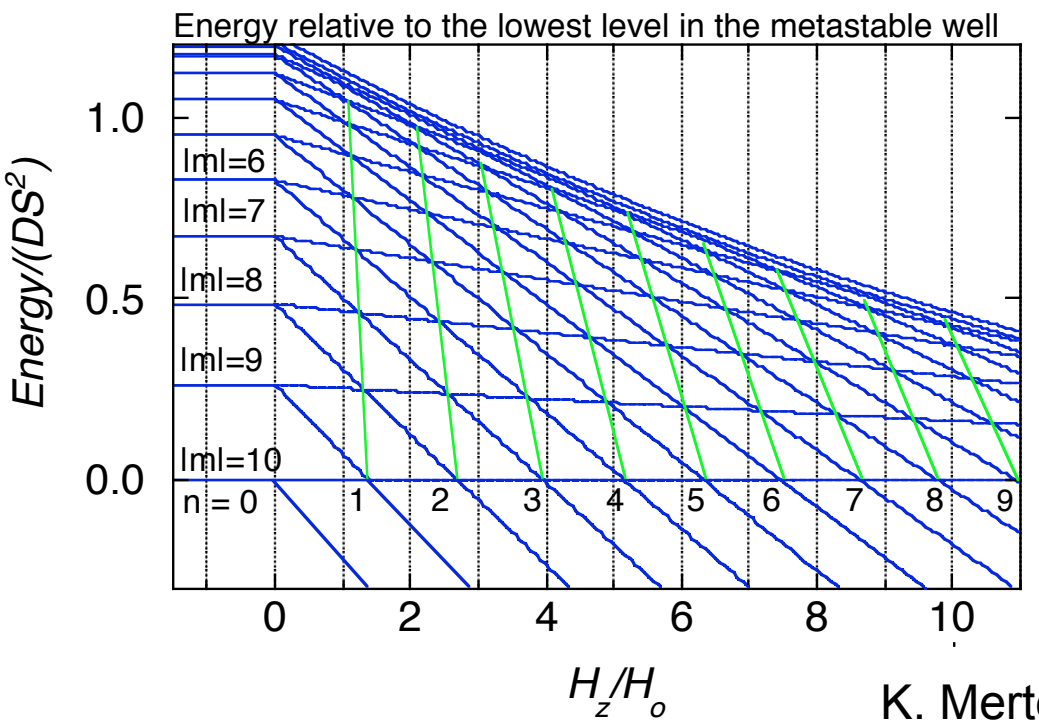
Louisa Bokacheva and Andrew D. Kent
Department of Physics, New York University, 4 Washington Place, New York, New York 10003

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

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

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

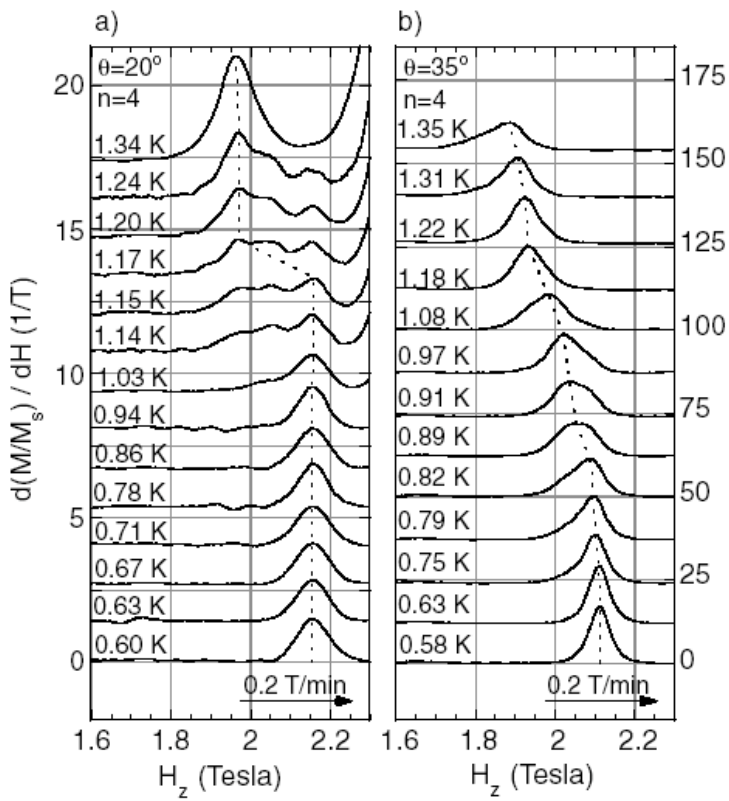
D=0.548(3) K g_z=1.94(1) **H_0= D/$g_z\mu_B$ = 0.42 T**
B=1.17(2) × 10^{-3} K (EPR: Barra et al., PRB 97)



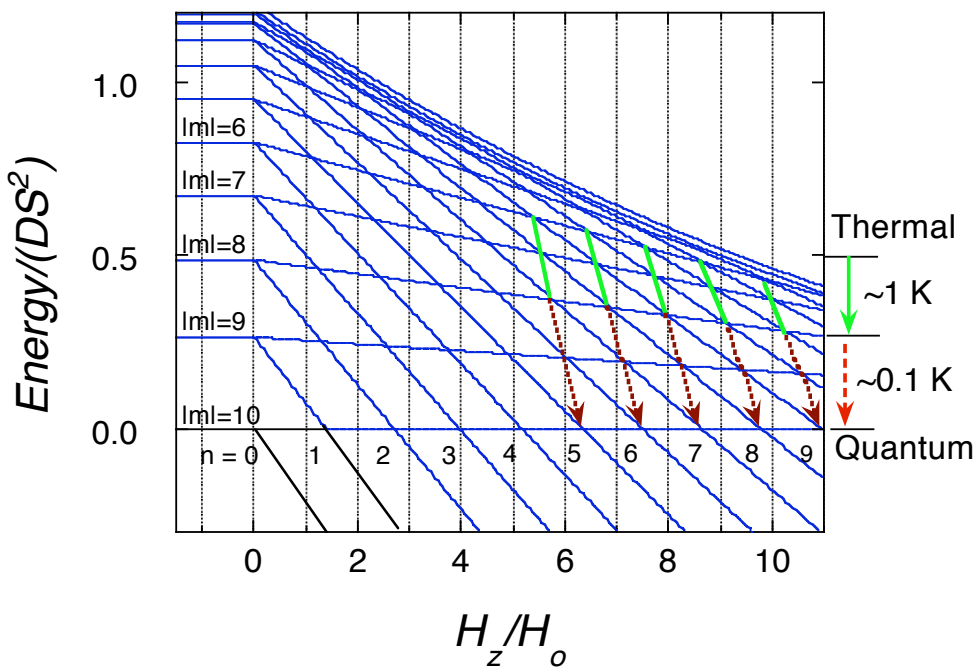
K. Mertes et al. PRB 2001

Experiments on the Crossover to Pure QTM in Mn12-acetate

dM/dH versus H_z



Schematic: dominant levels as a function of temperature

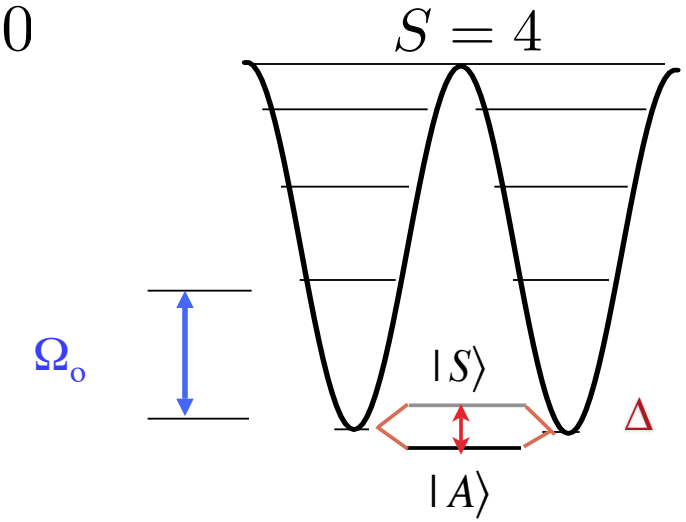


ADK *et al.* EPL 2000
L. Bokacheva, PRL 2001
K. Mertes *et al.* PRB 2001
W. Wernsdorfer *et al.* PRL 2006

Spin Relaxation between Low Lying Spin-States of Ni_4

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

$D > 0$



$$\Omega_o \gg \Delta > kT, E_o$$

First condition: consider just 2 lowest energy states

Second condition: mainly the ground state is populated

E_o typical energy width of nuclear spin multiplet

➡What are the spin-relaxation mechanisms at low temperature?

➡Is it possible to measure the direct single-spin-phonon relaxation rate in SMMs?

Chudnovsky: Universal lower bound on the decoherence rate: all parameters can be measured

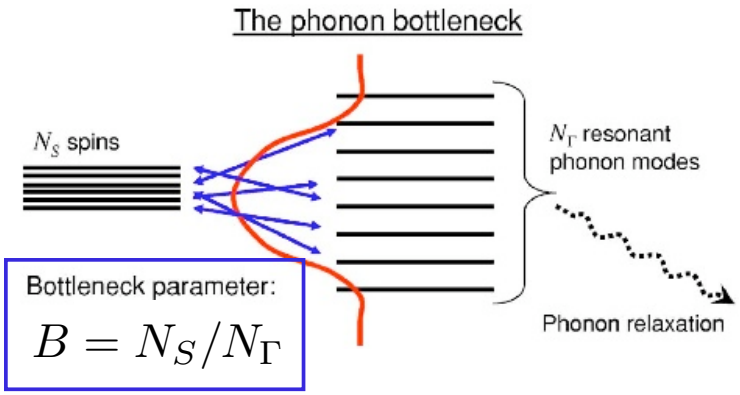
$$\tau_1^{-1} = \Gamma_1 = \frac{S^2 \Delta^2 \omega^3}{12\pi\hbar^2 \rho c_t^5} coth(\frac{\hbar\omega}{2kT})$$

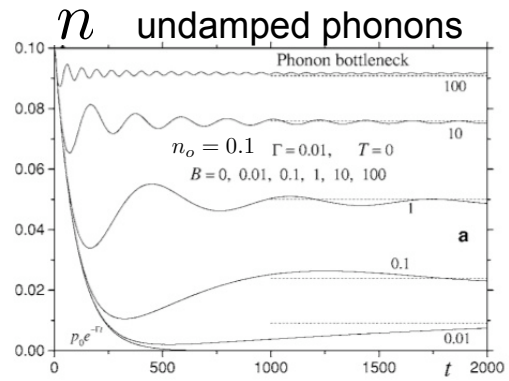
Stamp: for dephasing rate due to nuclear spins

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

Collective Spin Phonon Relaxation

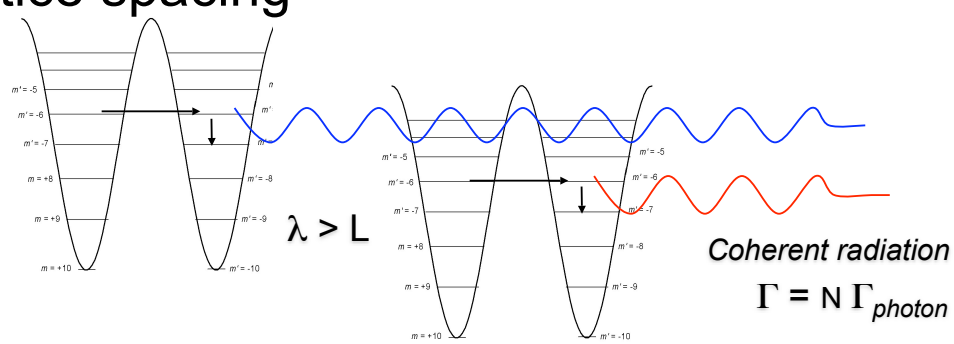
» Spin and phonon DOF are strongly coupled





Microscopic model of the bottleneck, Garanin PRB 2007, 2008

» Phonon wavelength is much greater than the lattice spacing



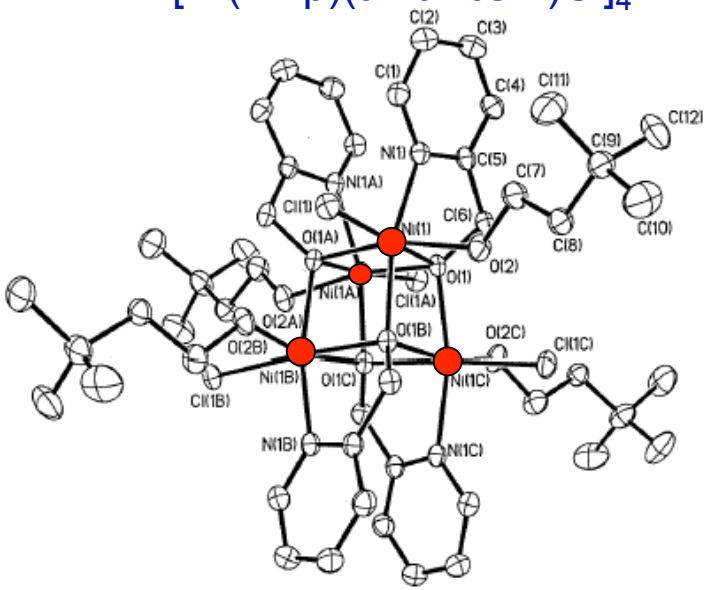
Chudnovsky & Garanin, PRL 2004

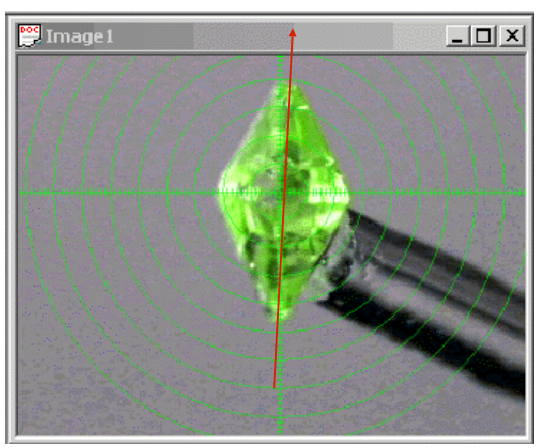
Description of Ni_4

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

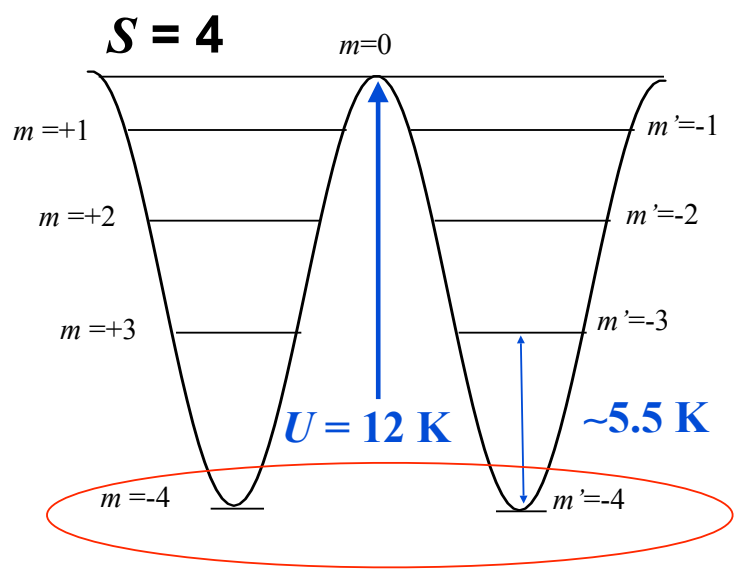
$[Ni(hmp)(t\text{-}BuEtOH)Cl]_4$

Crystals $I4_1/a$ space group





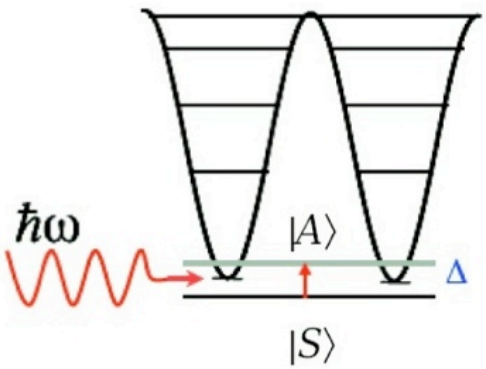
S_4 site symmetry
No solvate molecules!
No nuclear spin on Ni sites*
*at 1 % level--^{61}Ni



$T_{exp} \sim 0.4\ K$

Experiment

Magnetization dynamics induced by microwaves

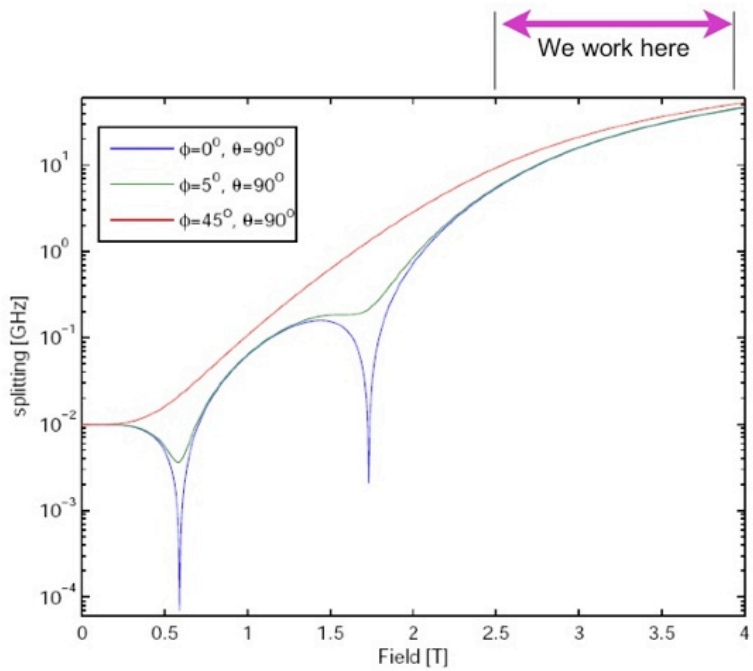


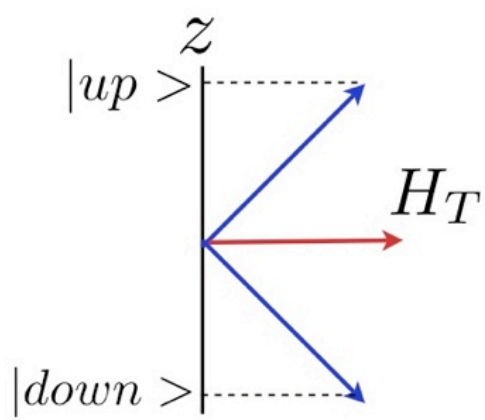
$$|S\rangle = \frac{1}{\sqrt{2}}\left(|up\rangle + |down\rangle\right)$$

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

Transverse field used to tune the tunnel splitting $\Delta > k_B T$

$\rightarrow$ coherent QTM





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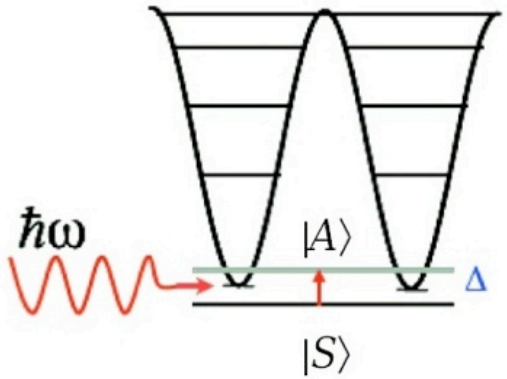

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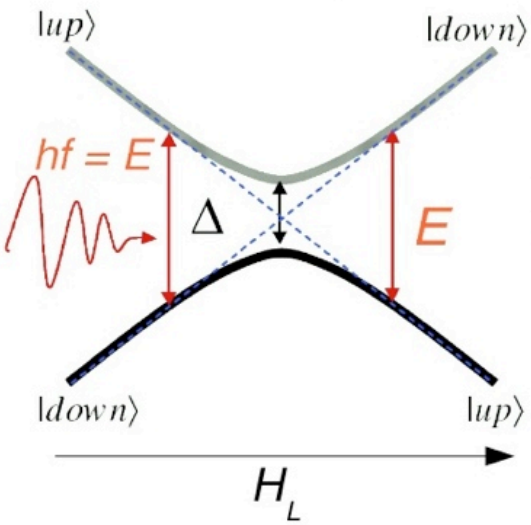
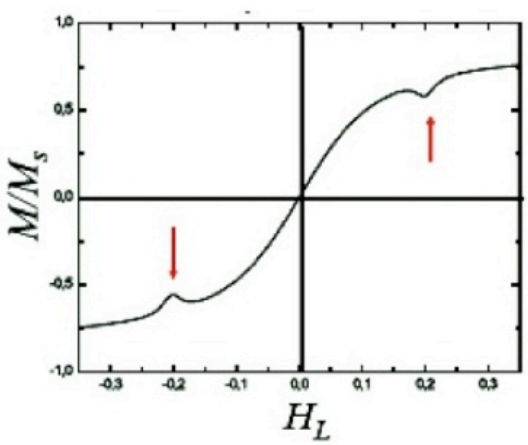
$$|A\rangle = \frac{1}{\sqrt{2}}\left(|up\rangle - |down\rangle\right)$$

Transverse field used to tune the tunnel splitting $\Delta > k_B T$

$\rightarrow$ coherent QTM

Photon absorption $\rightarrow$ Magnetization changes

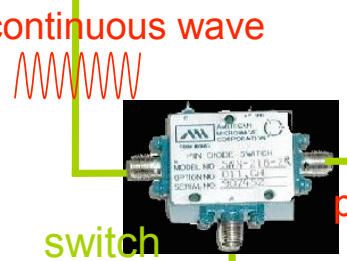


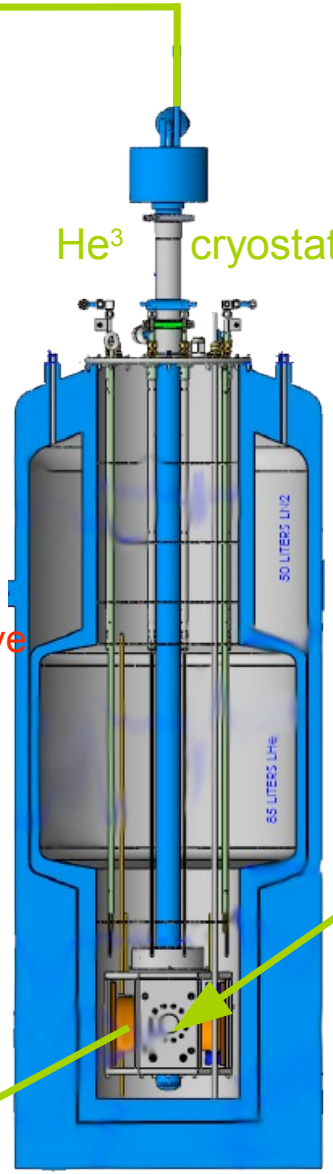


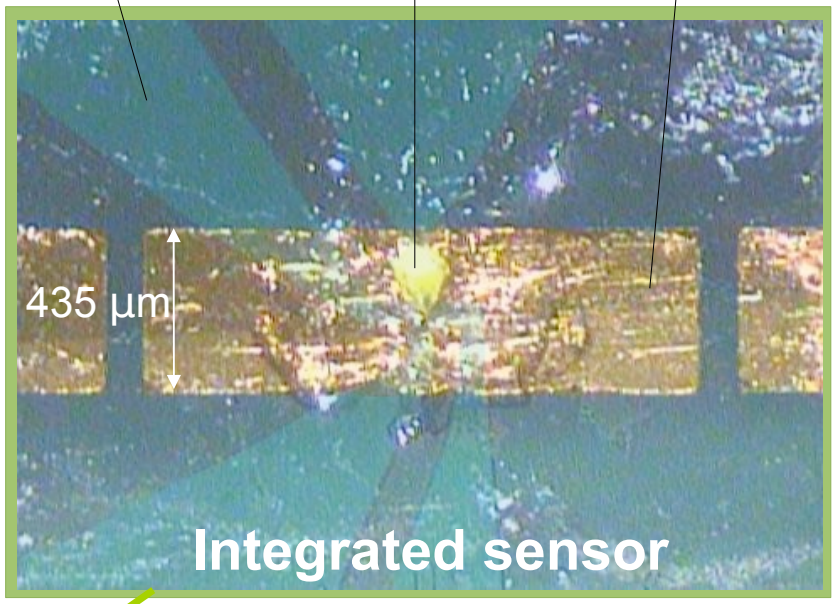
Photon induced transition between superposition states combined with magnetization measurements.

E. del Barco, ADK, et al. PRL 2004

Experimental Setup



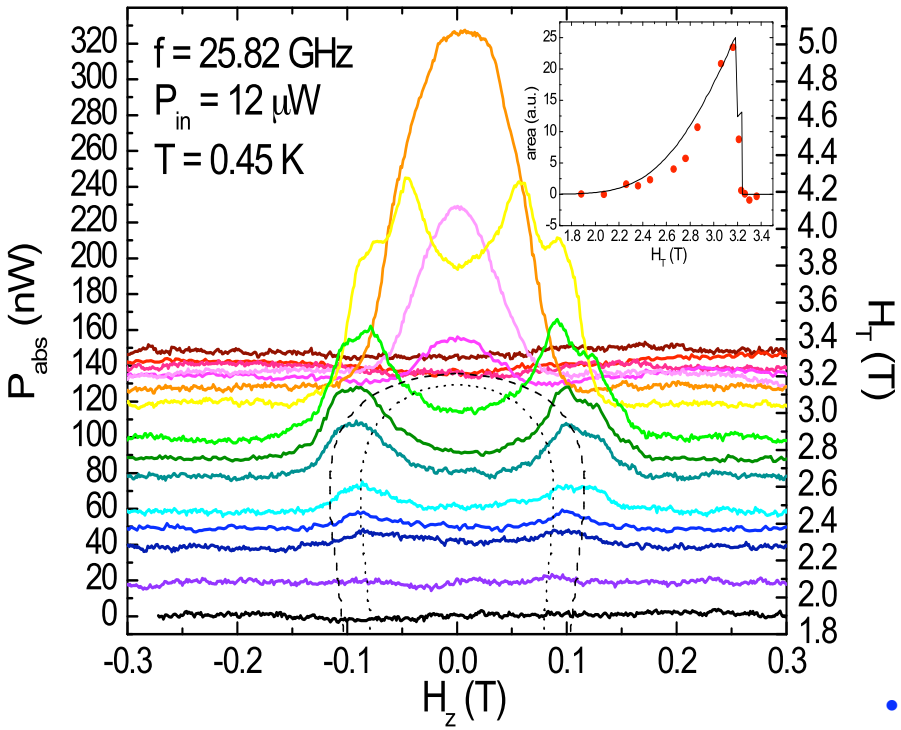




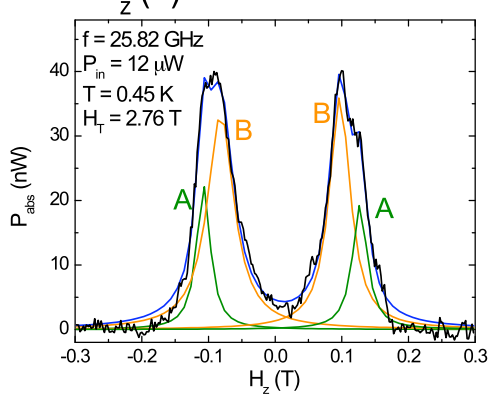
- Resonator: high calibrated rf magnetic field, max h_{ac} ~ 1 Oe @ 30 GHz, large filling factor
- GaAs/GaAlAs heterostructure: high spin sensitivity, fast response (>1MHz)

EPR Spectroscopy: Level Dispersion

Experiment: mapping in (H_z and H_T)

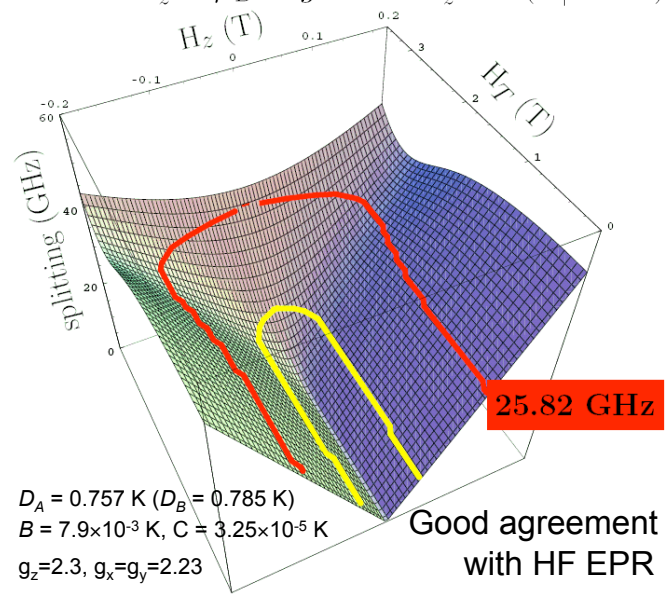


Multiple but narrow peaks: "molecular environments" with slightly different D values



Direct Diagonalization of the Hamiltonian

$$\mathcal{H} = -DS_z^2 - \mu_B \boldsymbol{H}.\hat{g}.\boldsymbol{S} - BS_z^4 + C(S_+^4 + S_-^4)$$



D_A = 0.757 K (D_B = 0.785 K)
B = 7.9×10^{-3} K, C = 3.25×10^{-5} K
g_z=2.3, g_x=g_y=2.23

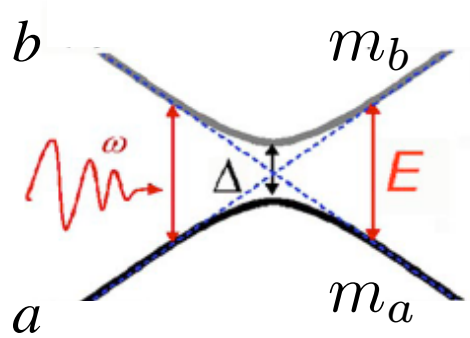
Good agreement with HF EPR

- Linewidth → T_2^* ~ 0.2 ns (inhomogeneous broadening, lower bound for the coherence time)
- Analysis of peak amplitude: Fermi golden-rule

$$\Gamma = \frac{\pi}{2}\left(\frac{g\mu_B}{\hbar}h_{ac}\right)^2 |\langle S|S_z|A\rangle|^2 f(\omega)$$

P_{abs}, ΔM and the Relaxation Rate in Steady State

absorption rate Λ
vs.
relaxation rate Γ



Population difference

$$N_0 = N_a - N_b$$

In equilibrium

$$N_0^{\text{eq}} = N_S \tanh\left(\frac{E}{2k_B T}\right)$$

Steady State

$$P_{\text{abs}} = \Lambda \hbar \omega N_o$$

$$N_o = \frac{N_o^{\text{eq}}}{1 + 2\Lambda/\Gamma}$$

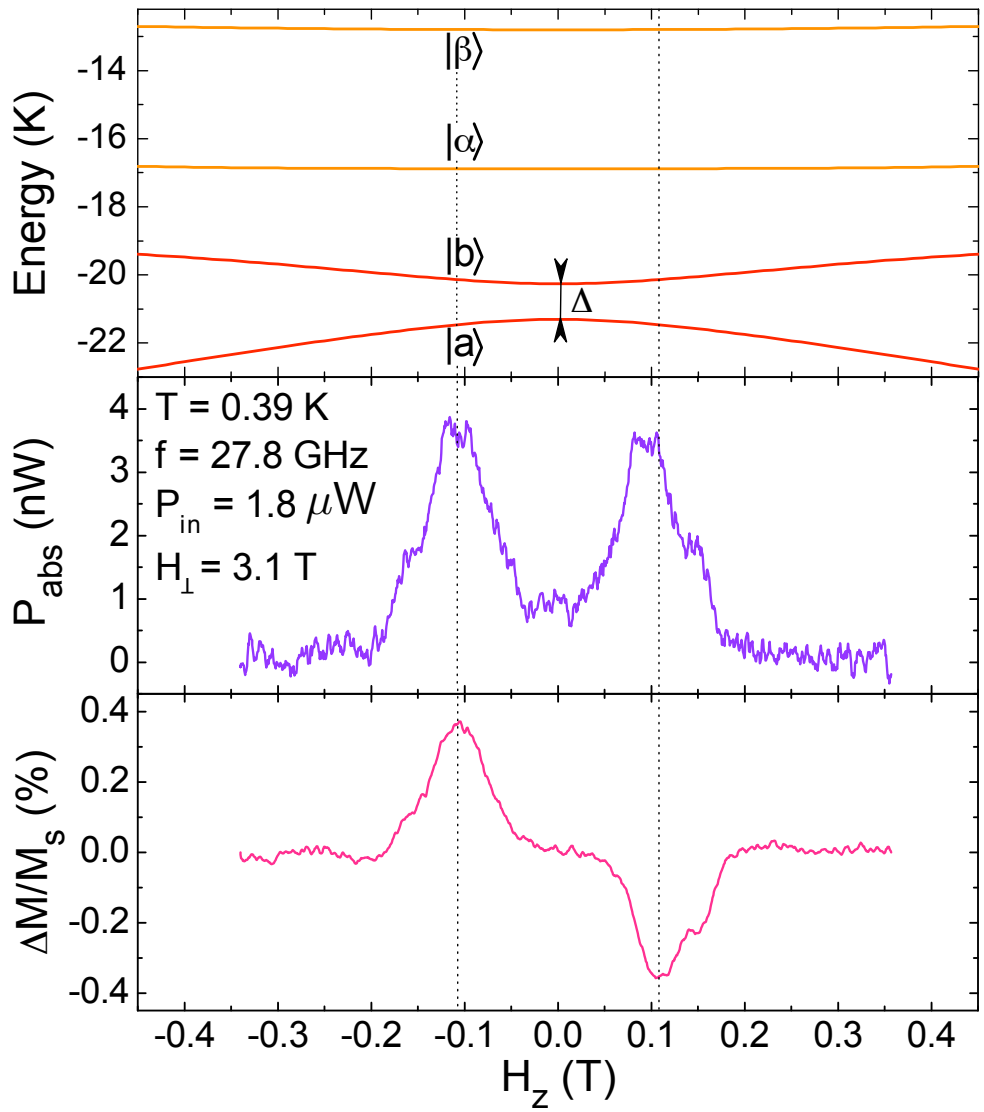
$$M = N_a m_a + N_b m_b$$
$$= M^{\text{eq}} + \Delta M$$

Energy balance

$$\Gamma = \frac{(m_b - m_a)}{\Delta M} \frac{P_{\text{abs}}}{\hbar \omega_0}$$

→ Simultaneous measurement of P_{abs} and ΔM yields Γ

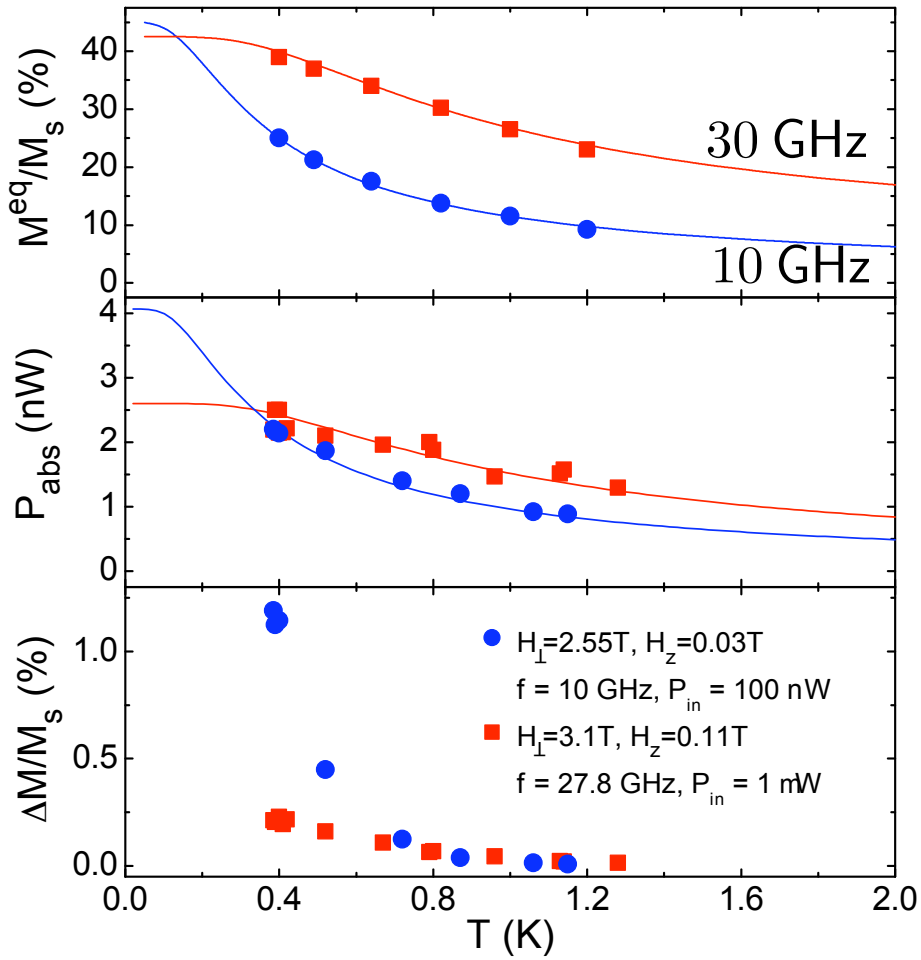
Simultaneous CW Absorption and Magnetization Measurements



$\Delta H \simeq 0.1$ T

$T_2 > 0.25$ ns

Temperature Dependence



2-state model

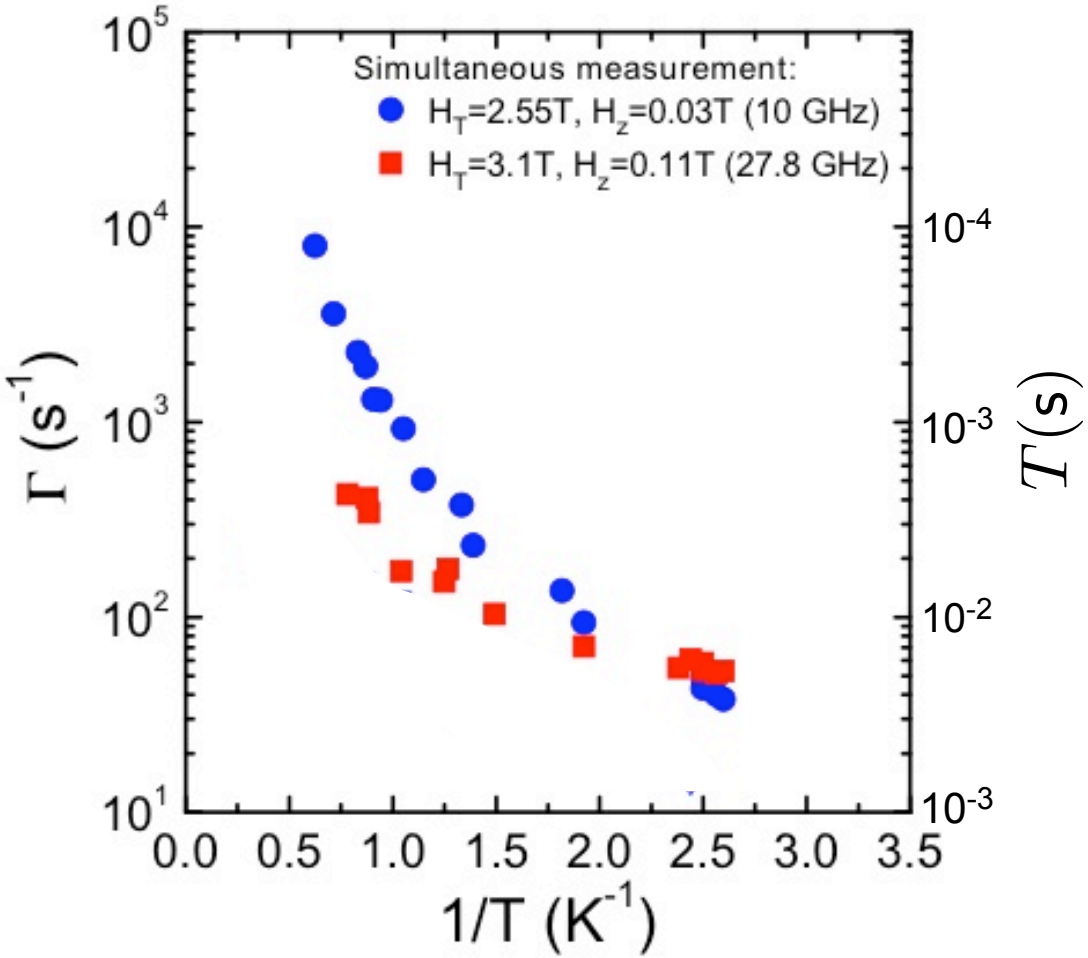
$$\frac{M^{\mathrm{eq}}}{M_s} = \frac{m_a + m_b \exp\left(-\hbar\omega_0/(k_B T)\right)}{S(1+\exp\left(-\hbar\omega_0/(k_B T)\right))}$$

$$P_{\mathrm{abs}} = \hbar\omega_0 \left(\frac{g\mu_B}{\hbar} h_{\mathrm{ac}}\right)^2 \frac{|\langle a|S_z|b\rangle|^2}{2\Gamma_2} N_S \tanh\left(\frac{\hbar\omega_0}{2k_B T}\right)$$

→ **Relaxation rate**

$$\Gamma = \frac{(m_b - m_a)}{\Delta M} \frac{P_{\mathrm{abs}}}{\hbar\omega_0}$$

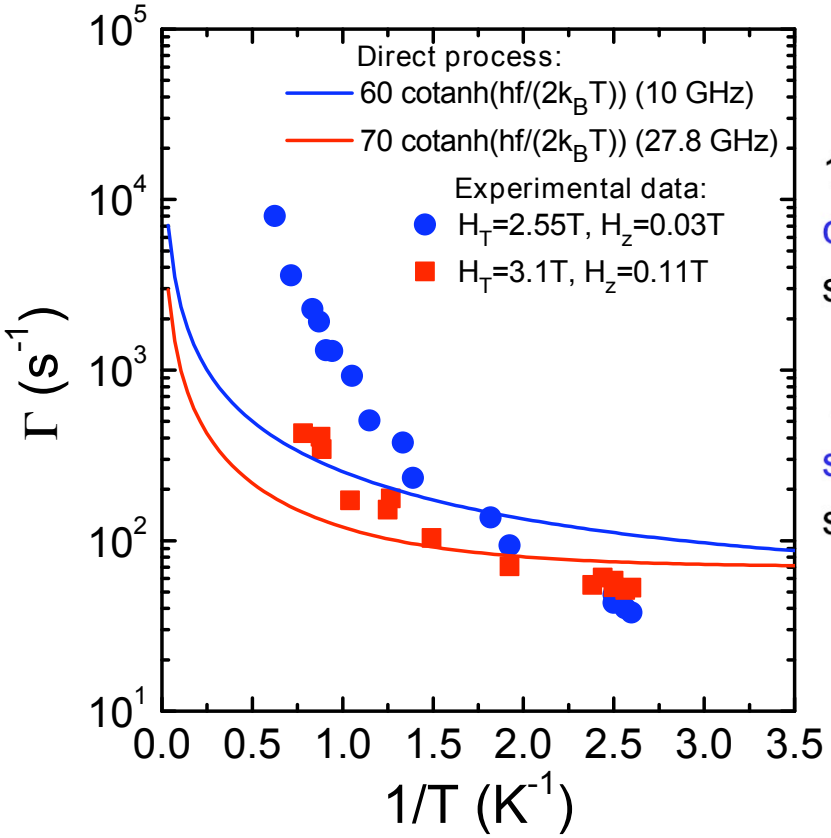
Temperature Dependence of Relaxation Rate



- Moderate increase with increasing T below ~0.8 K
- Exponential increase at high-T (>1 K)

Temperature Dependence of Relaxation Rate

comparison with direct spin-phonon relaxation form



1) The temperature dependence can not be explained by direct single-spin-phonon process

2) The zero temperature rate is slower than expected from direct single-spin-phonon process

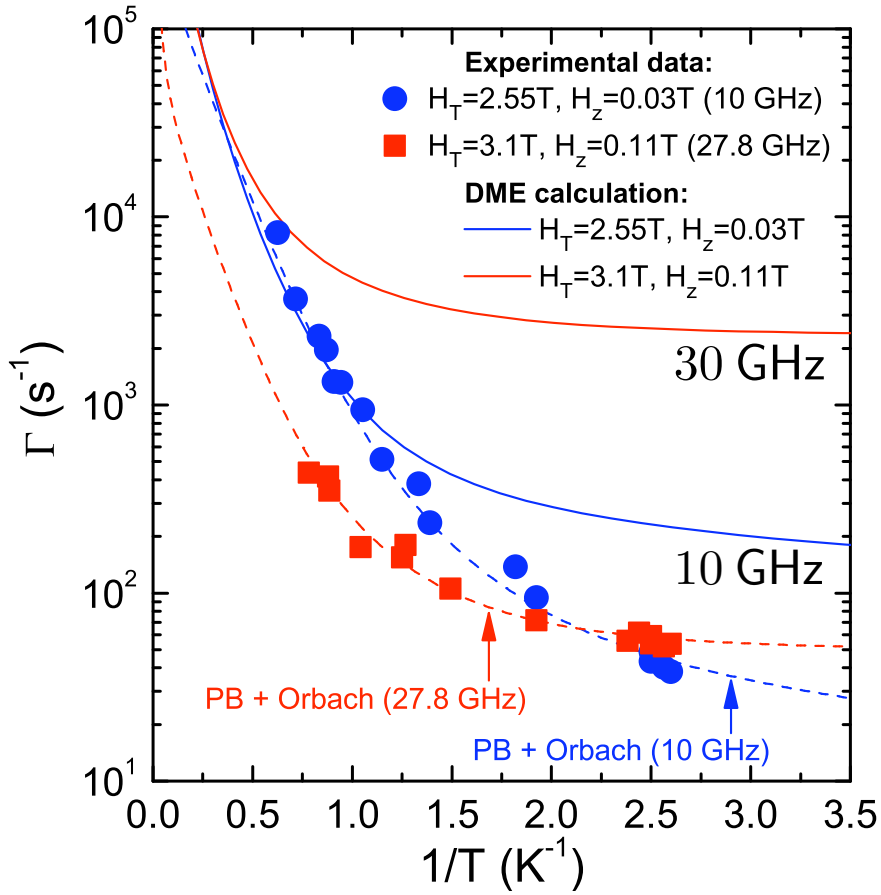
$$E_t = (\rho v_t^5 \hbar^3)^{1/4} = 76 \text{ K}$$

$$Q \cong 1 \text{ for } SH_z < H_\perp$$

<u>Direct process</u>
(Chudnovsky & Garanin 2005)

$$\Gamma_{sp,T} = QS^2 \frac{\Delta^2 \omega_0 (g\mu_B H_\perp)^2}{12\pi E_t^4} \coth\left(\frac{\hbar\omega_0}{2k_B T}\right)$$

Relaxation Mechanisms



Phonon bottleneck + Orbach mechanism

$$\Gamma_T = \frac{\Gamma_{\rm ph}}{B_{\omega_0}} \coth^2\left(\frac{\hbar\omega_0}{2k_BT}\right) + \sum_i \Gamma_{0i} \exp\left(\frac{-E_i}{k_BT}\right)$$

$$B_{\omega_0} \equiv \frac{N_S}{N}\frac{\rho_S(\omega_0)}{\rho_{\rm ph}(\omega_0)} = \frac{N_S}{N\sqrt{2\pi}}\frac{2\pi^2\tilde{\Omega}_D^3}{\omega_0^2\delta\omega_0}$$

≈ 180 000 at 10 GHz

≈ 24 000 at 27.8 GHz

→ T_{ph} ≈ 0.5 μs → $l_{\rm ph} \simeq 500\ \mu$m

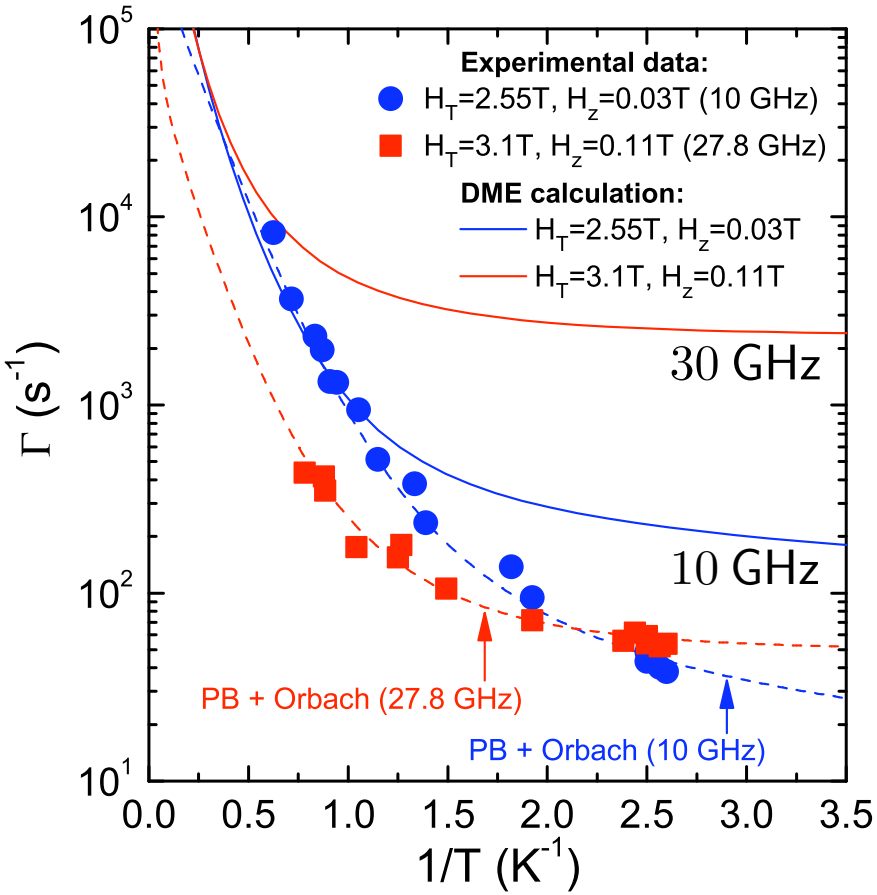
$$\dot{n}_{\omega_0} = -\Gamma_{\rm sp}\left[n_{\omega_0} + (2n_{\omega_0} - 1)\, p_{\omega_0}\right]$$

$$\dot{p}_{\omega_0} = \Gamma_{\rm ph}\left(p_{\omega_0}^{\rm eq} - p_{\omega_0}\right) - B_{\omega_0}\dot{n}_{\omega_0}$$

Lowest rate governing the relaxation: $\Lambda_- \cong \dfrac{\Gamma_{\rm ph}\Gamma_{{\rm sp},T}}{B_{\omega_0,T}\Gamma_{{\rm sp},T} + \Gamma_{\rm ph}}$,

where $B_{\omega_0,T} = B_{\omega_0}\tanh^2(\hbar\omega_0/(2k_BT))$

Relaxation Mechanisms



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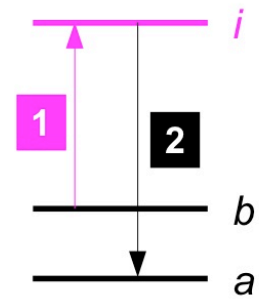

Thermally activated process: intermediate higher energy level *i*.

Density matrix equation with the relaxation terms in the universal form: full quantum mechanical calculation of the relaxation rate between *b* and *a* *without* any unknown coupling constant.

Summary

- The energy splittings between low-lying superpositions of high spin-states of Ni_4 has been measured spectroscopically
- Energy relaxation has been measured in a cw experiment in a low-excitation limit by combining magnetic and microwave data acquired simultaneously
- The temperature dependence of the energy relaxation rate in Ni_4 has been measured at two different frequencies. The data show that the spin relaxation is dominated by a phonon bottleneck at low temperatures and occurs by an Orbach mechanism at high temperature.
- To eliminate the phonon bottleneck requires $B_{\omega_0}\Gamma_{\mathrm{sp},T} \ll \Gamma_{\mathrm{ph}}$, $T_{\mathrm{ph}} \ll 10$ ns
  - Submicron scale crystals!!!
- Coherence is expected to play an important role in the collective spin-phonon relaxation in SMM crystals: The fact that the DME calculations+phonon bottleneck work so well to explain the data is somewhat surprising.
- <u>References</u>: G. de Loubens et al., Europhysics Letters 2008 & JAP 2007

Single Molecule Magnets

<u>Physics</u>

-Individual molecule can be magnetized and exhibit magnetic hysteresis 1993
-Quantum Tunneling of Magnetization 1995
-Quantum Phase Interference 1999
-Quantum Coherence 2008

<u>Open Questions/Research Directions</u>

-Understanding mechanism of decoherence and finding means to mitigate environmental effects
-Addressing individual molecules, on surfaces (STM) between electrodes (quantum dots) & by magnetometry
-Electronic transport properties: coupling between electronic and spin-dof
-Collective effects in spin-relaxation: superradiance...