NYU

Spins Dynamics in Nanomagnets

Andrew D. Kent

Department of Physics, New York University

Lecture 1: Magnetic Interactions and Classical Magnetization Dynamics

Lecture 2: Spin Current Induced Magnetization Dynamics

Lecture 3: Quantum Spin Dynamics in Molecular Nanomagnets

Outline

I. Introduction
- Quantum Tunneling of Magnetization
- Initial Discoveries
- Single molecule magnets

II. Magnetic Interactions in SMMs
- Energy Scales, Spin Hamiltonians
- Mn_{12}-acetate

III. Resonant Quantum Tunneling of Magnetization
- Thermally activated, thermally assisted and pure
- Crossover between regimes
- Quantum Phase Interference

IV. Experimental Techniques
- Micromagnetometry
- SQUIDs and Nano-SQUIDs
- EPR

Magnetic Nanostructures

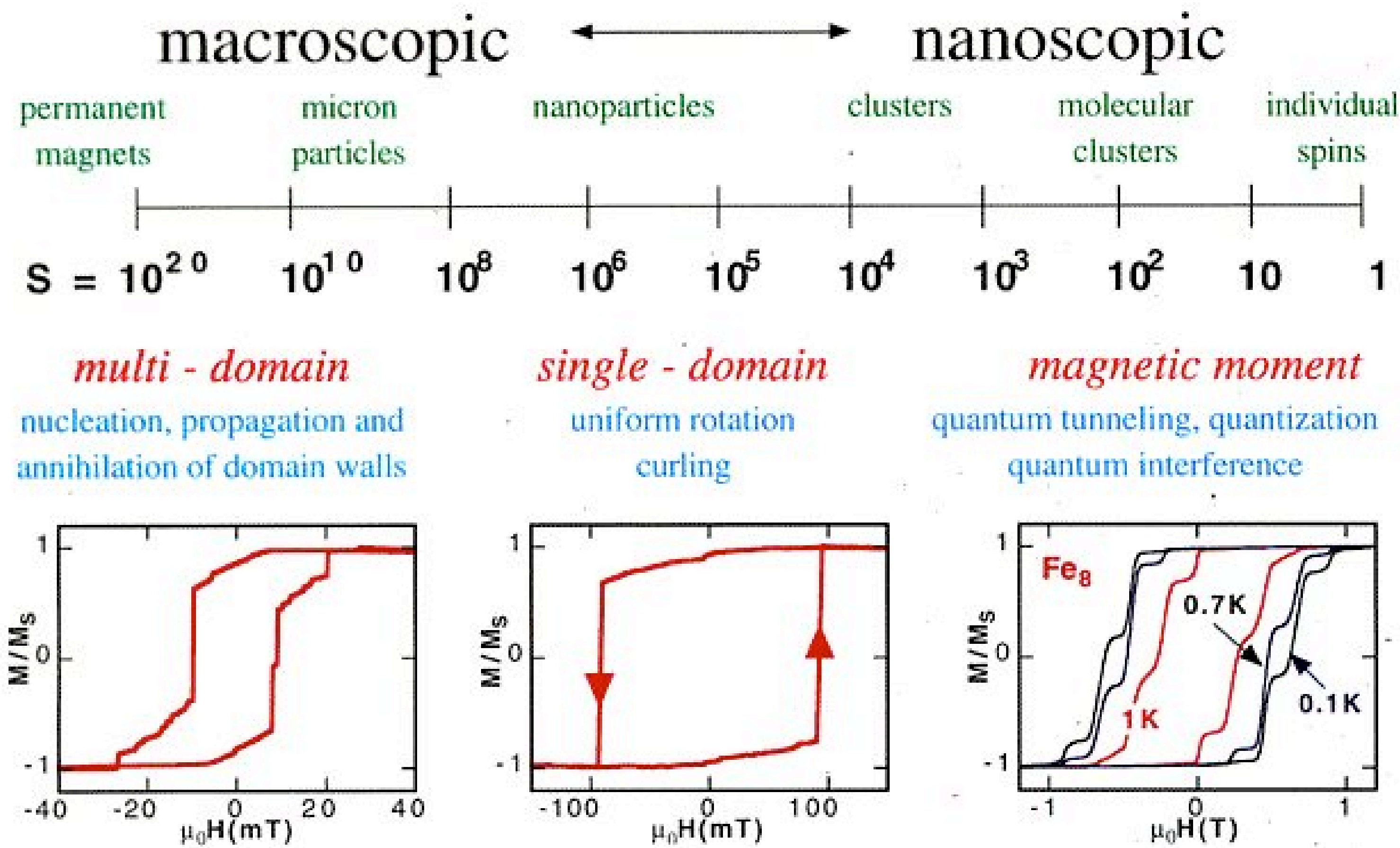


Image from, W. Wernsdorfer, Advances in Chemical Physics 2001 and ArXiv:0101104

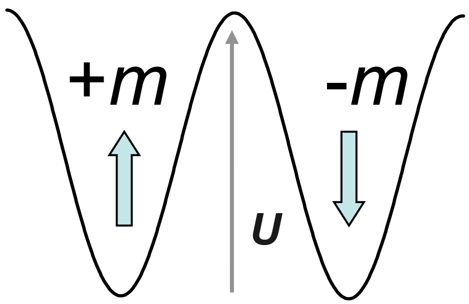
Quantum Tunneling of Magnetization

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)

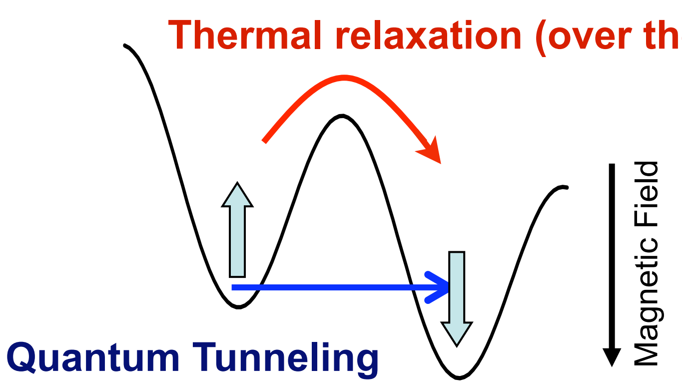
The probability of tunneling of the magnetization in a single-domain particle through an energy barrier between easy directions is calculated for several forms of magnetic anisotropy. Estimated tunneling rates prove to be large enough for observation of the effect with the use of existing experimental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

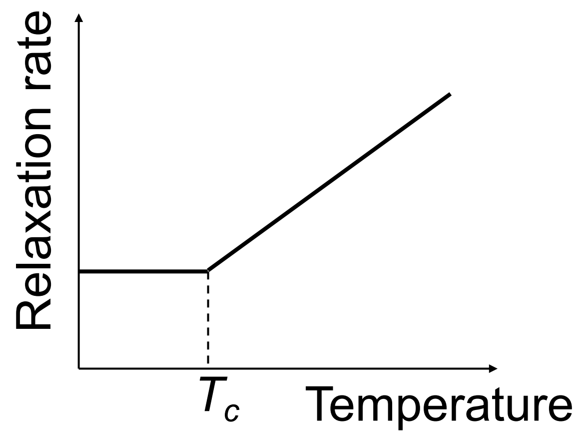


Thermal $\Gamma \sim e^{-U/k_B T}$

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

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



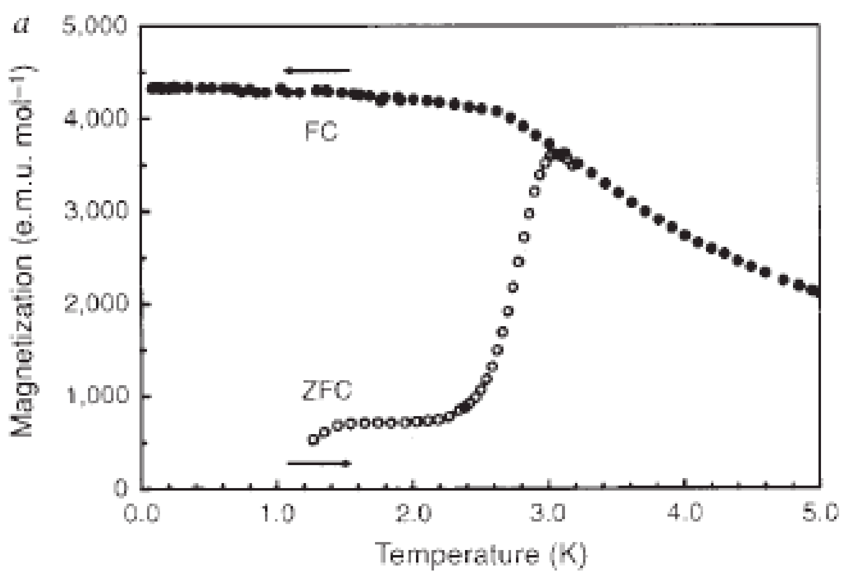


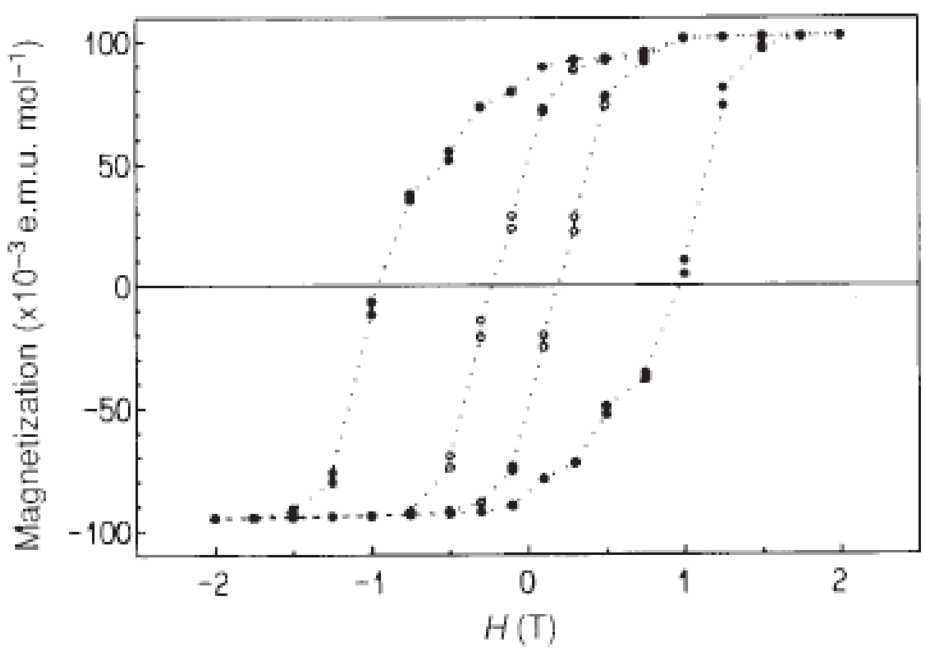
also, Enz and Schilling, van Hemmen and Suto (1986)

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
Department of Physics, The City College of the City University of New York, New York, New York 10031

J. Tejada
Facultat de Física, Universitat de Barcelona, 08028 Barcelona, Spain

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]

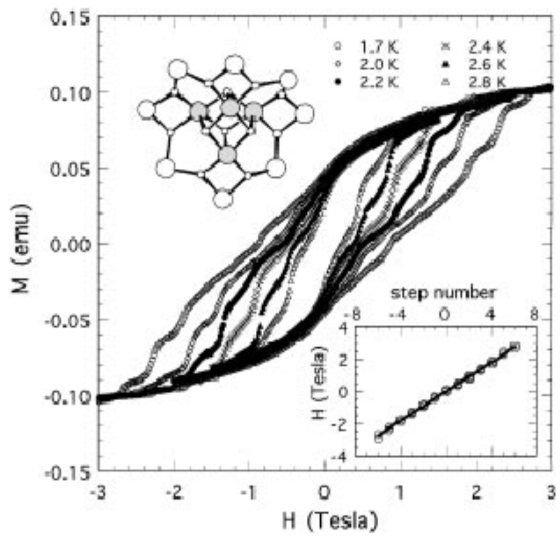


FIG. 1. Magnetization of Mn_{12} as a function of magnetic field at six different temperatures, as shown (field sweep rate of 67 mT/min). The inset shows the fields at which steps occur

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

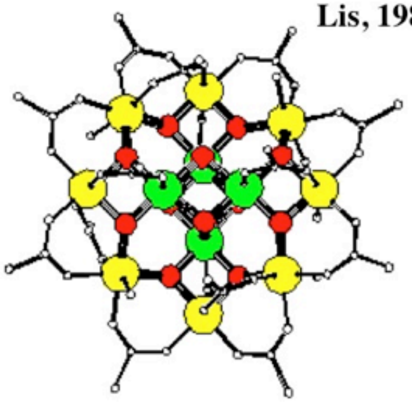
Physics

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

SMM Characteristics

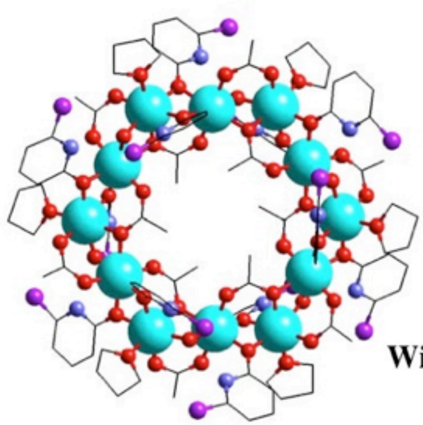
- Molecules
- High spin ground state
- Uniaxial anisotropy
- Single crystals
- Synthesized in solution
- Modified chemically
  - Peripheral ligands
  - Oxidized/reduced
  - Soluble
  - Bonded to surfaces

Lis, 1980

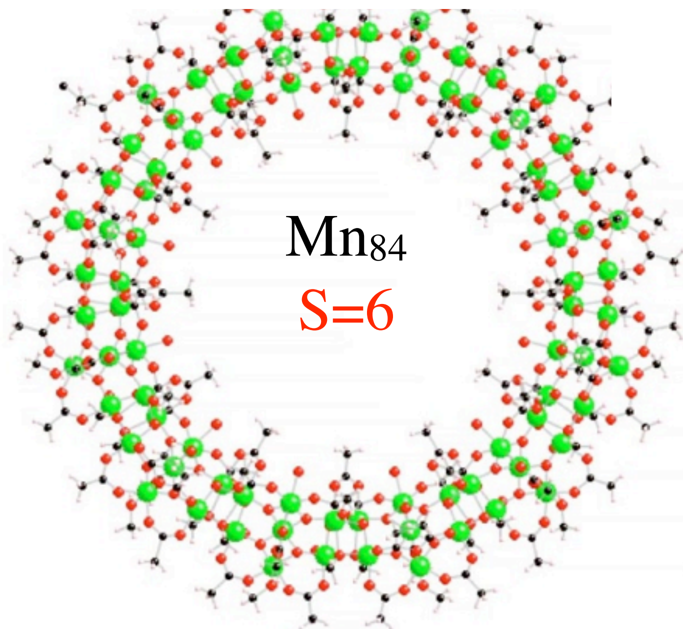


Mn_{12} S = 10

Ni_{12} S = 12



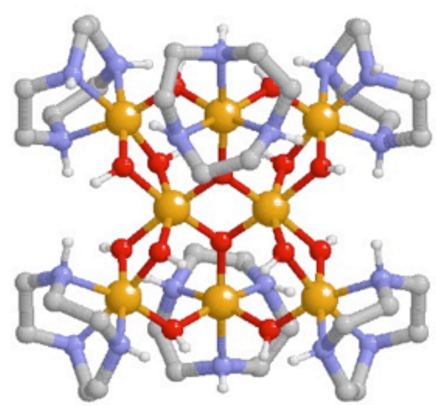
Winpenny, 1999



Mn_{84}
S=6

Christou, 2004

Fe_8 S = 10



Wiegart, 1984

NYU

First SMM: Mn_{12}-acetate

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

Magnetic Core

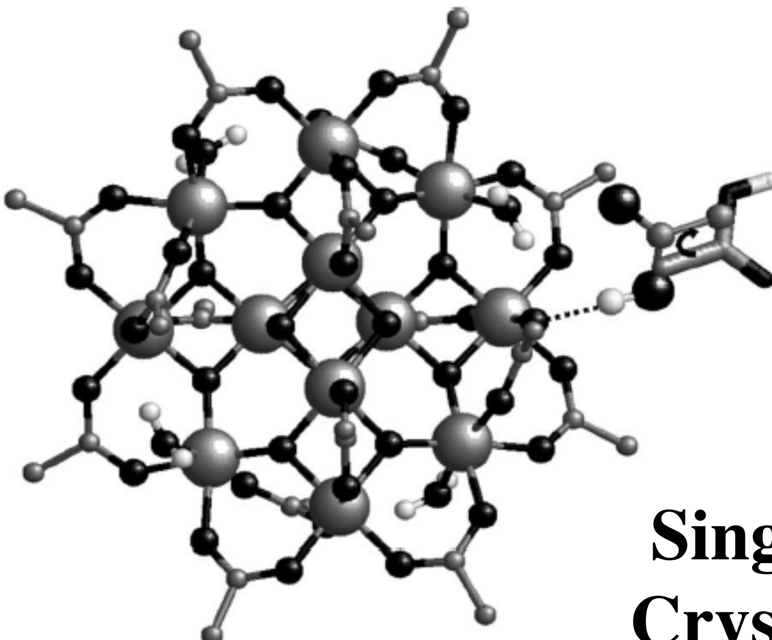
8 Mn^{3+} S=2
4 Mn^{4+} S=3/2

Competing AFM Interactions

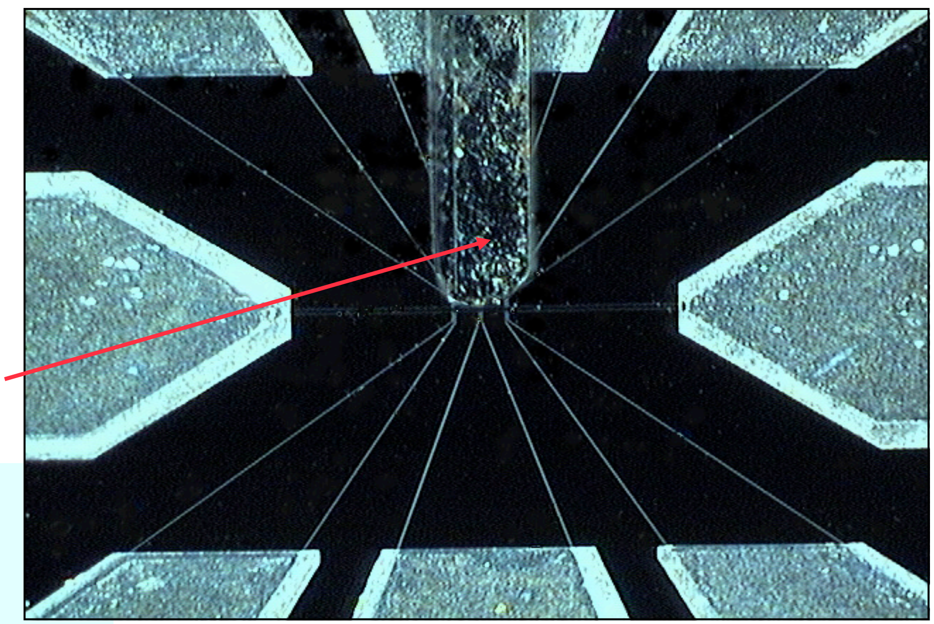
Ground state S=10

Organic Environment

2 acetic acid molecules
4 water molecules

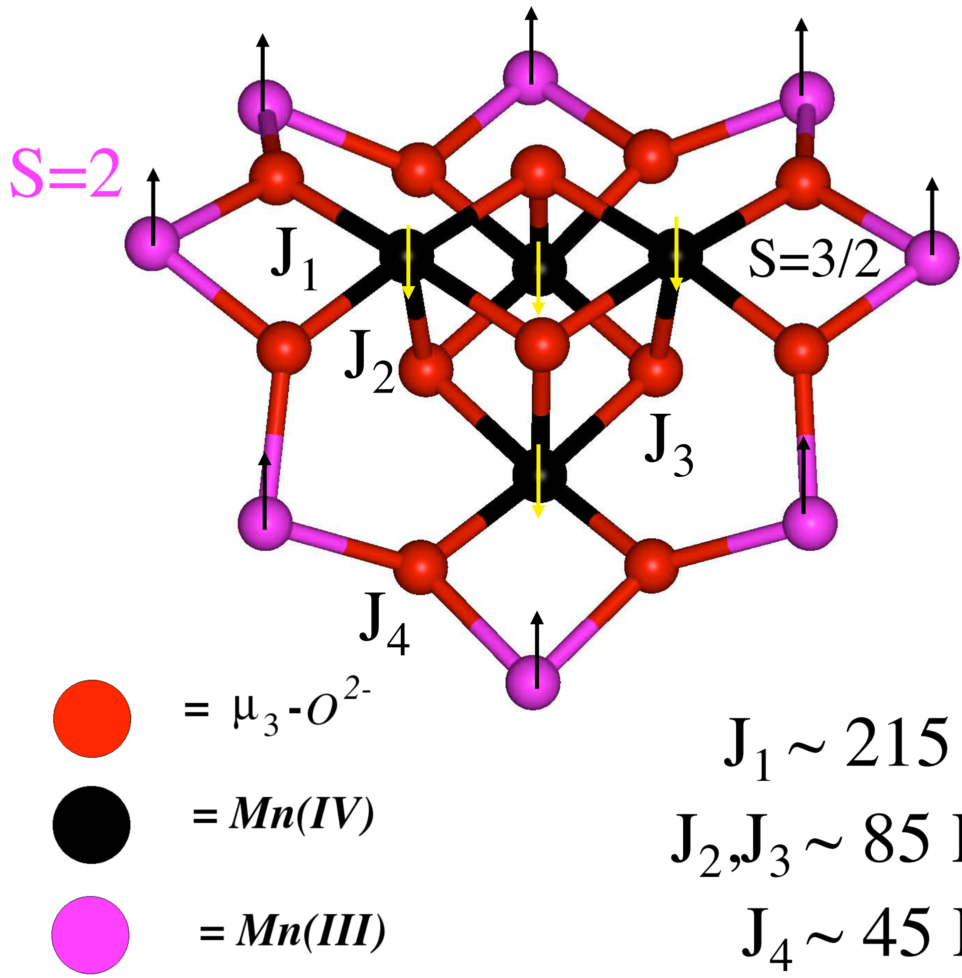


Single Crystal

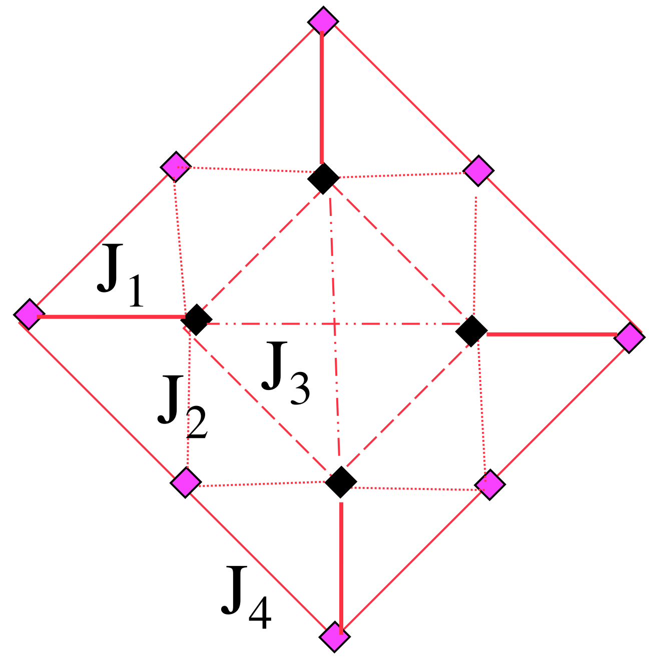


- **S_4 site symmetry**
- **Tetragonal lattice a=1.7 nm, b=1.2 nm**
- **Strong uniaxial magnetic anisotropy (~60 K)**
- **Weak intermolecular dipole interactions (~0.1 K)**

Intra-molecular Exchange Interactions



≡



$J_1 \sim 215$ 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 $2S+1=21$

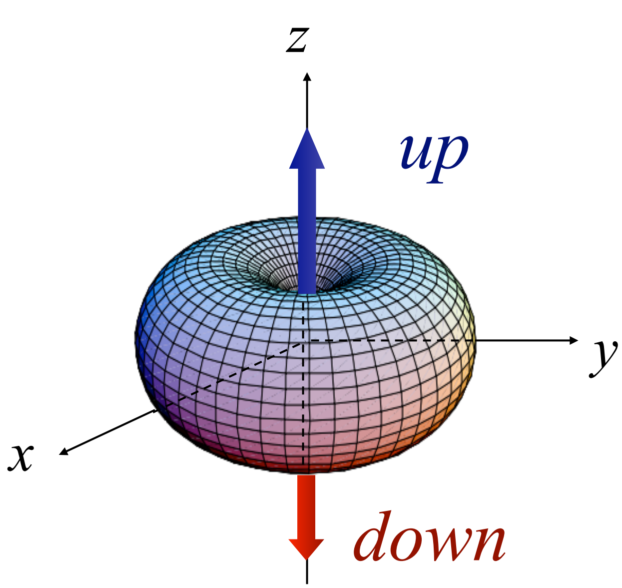
Magnetic Anisotropy and Spin Hamiltonian

Spin Hamiltonian

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

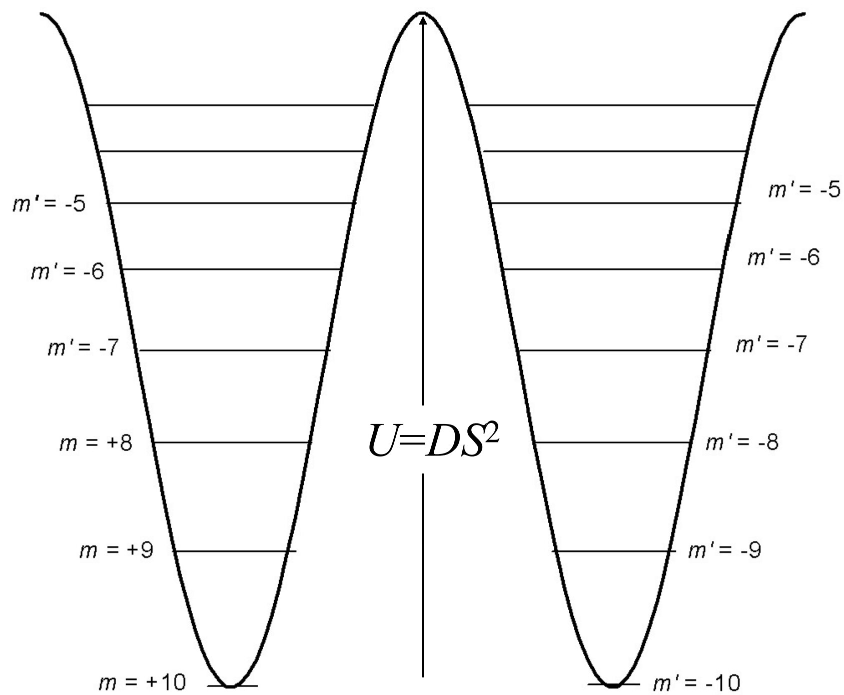
$$S_z|m>= m|m>$$

$$E_m = -Dm^2$$



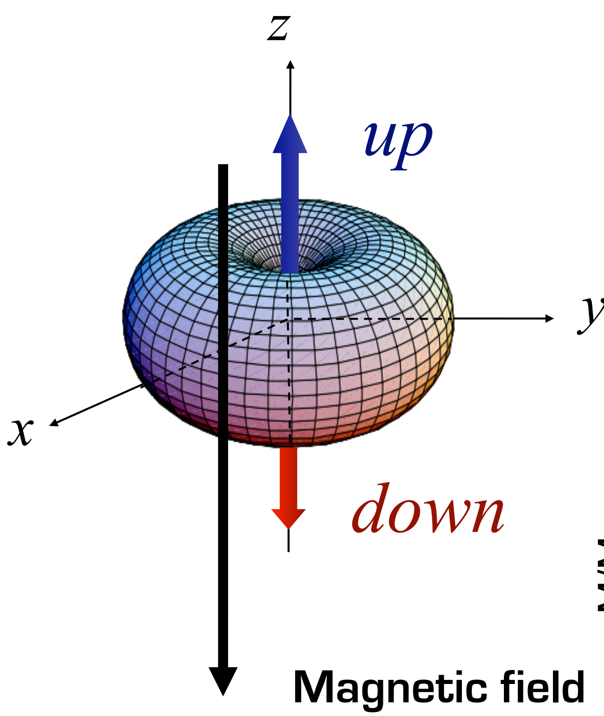
(Ising-like) Uniaxial anisotropy

$2S+1$ spin levels



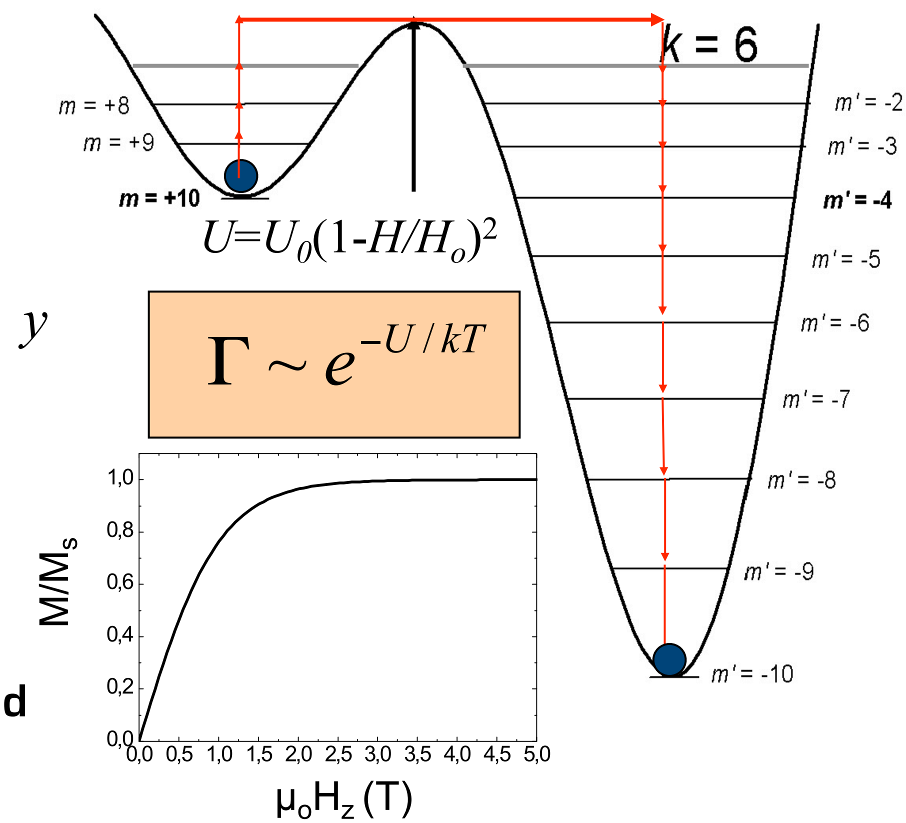
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs



Magnetic relaxation at high temperature

Thermal activation (over the barrier)



$$U=U_0(1-H/H_o)^2$$

$$\Gamma \sim e^{-U/kT}$$

NYU

Resonant Quantum Tunneling of Magnetization

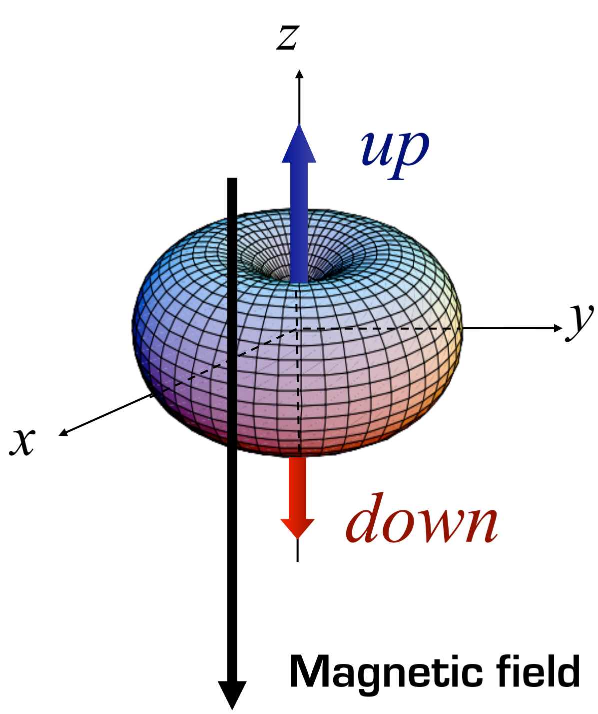
$$H = -DS_z^2 - g\mu_B S_z H_z$$

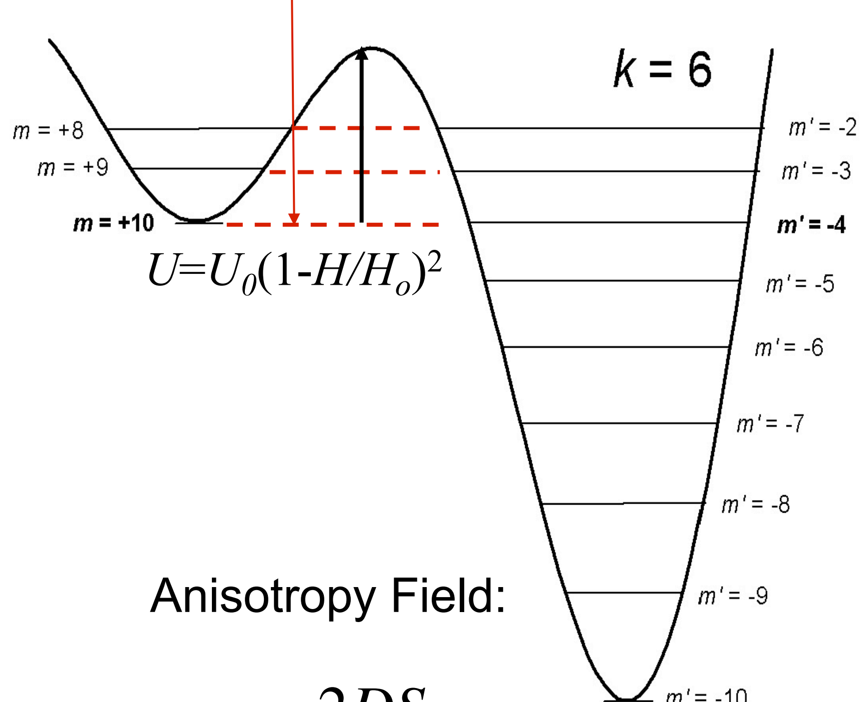
$$S_z|m> = m|m>$$

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

with Zeeman term

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

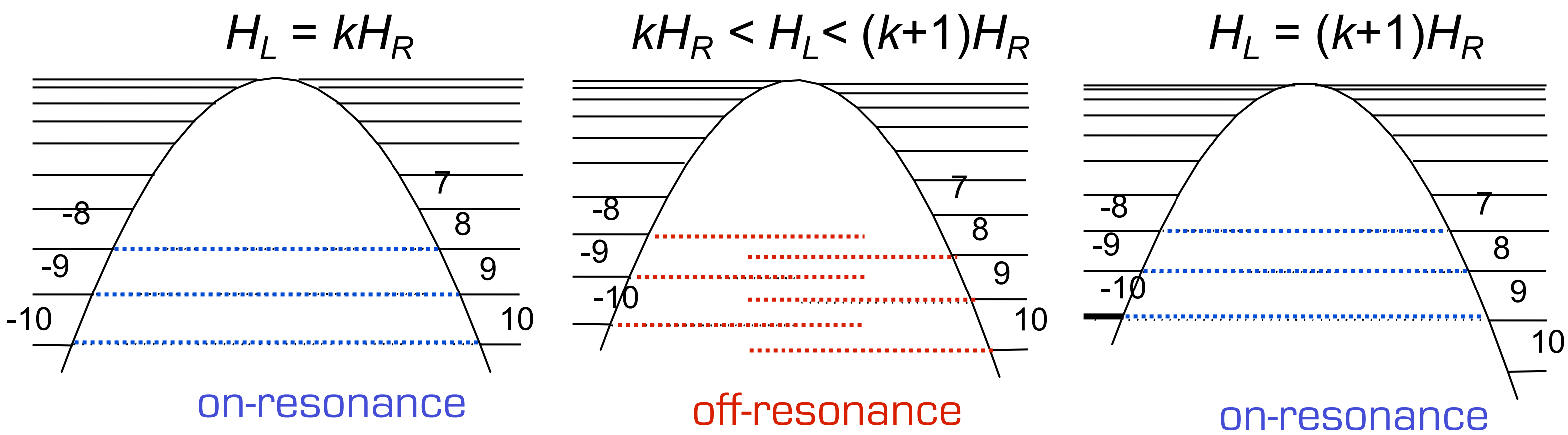


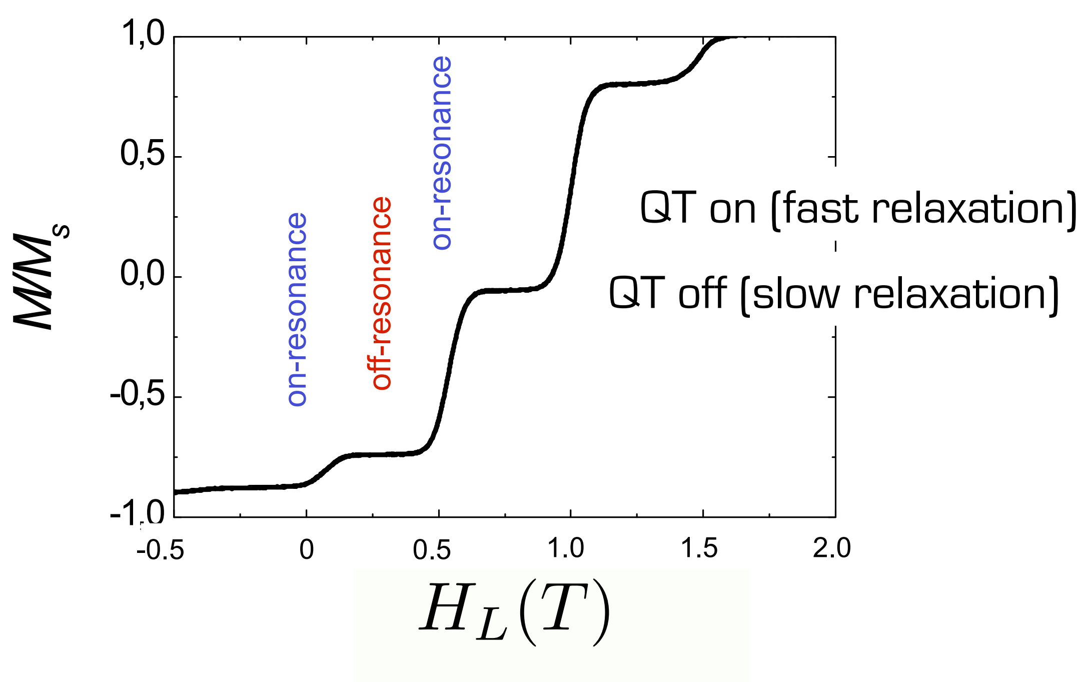


Anisotropy Field:

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

Resonant Quantum Tunneling of Magnetization



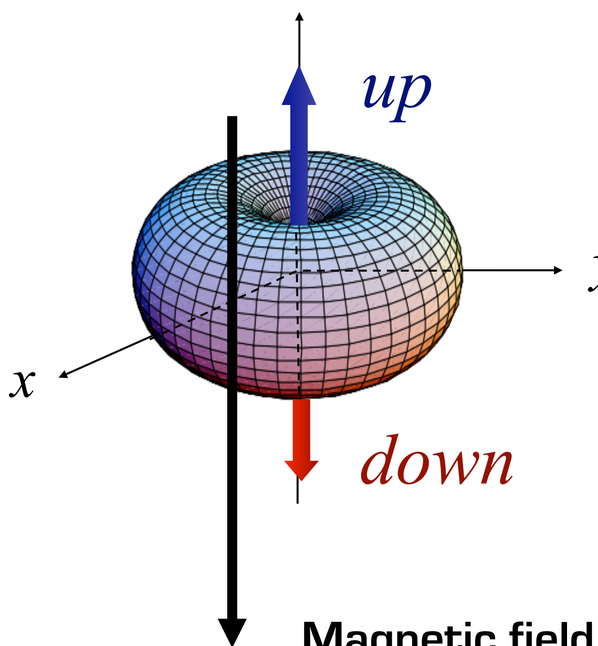


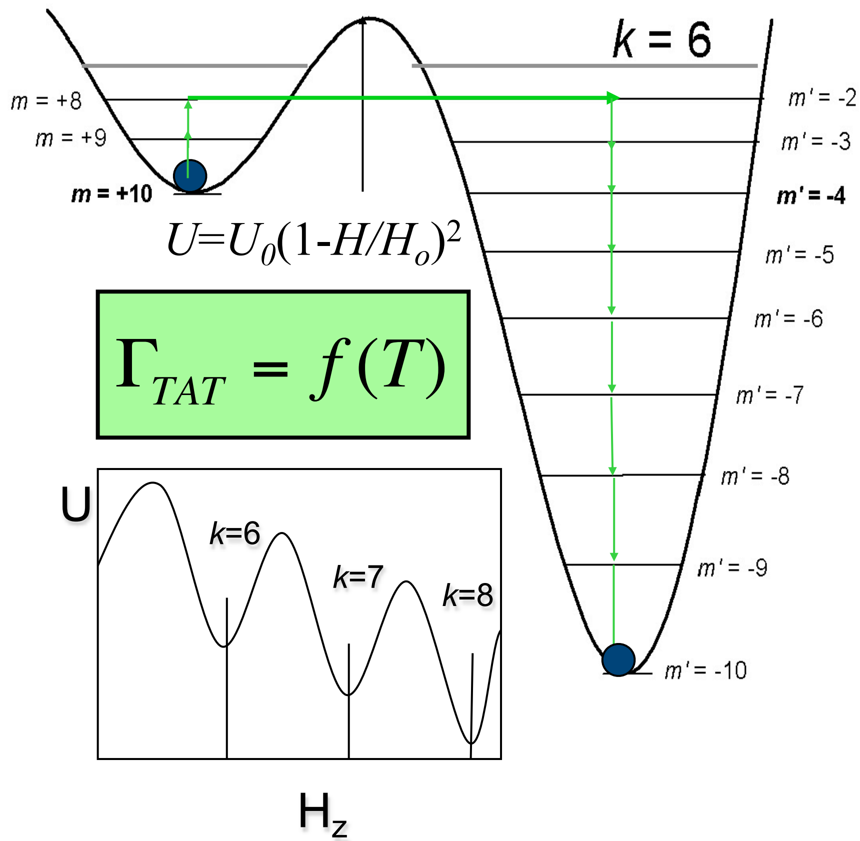
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at intermediate temperature

Thermally assisted tunneling



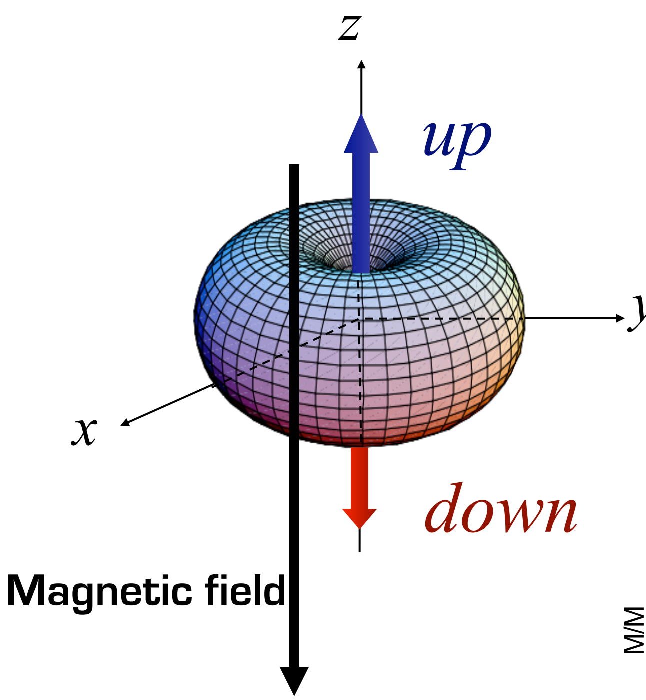


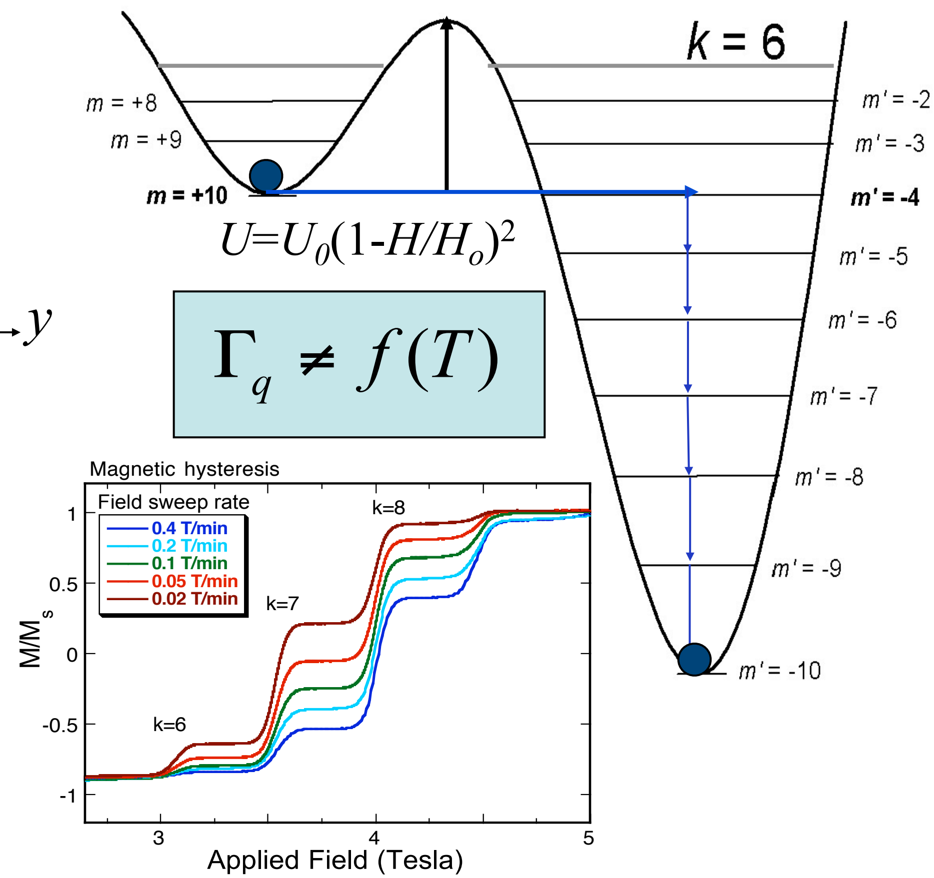
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at low temperature

Pure quantum tunneling





VOLUME 79, NUMBER 22 PHYSICAL REVIEW LETTERS 1 DECEMBER 1997

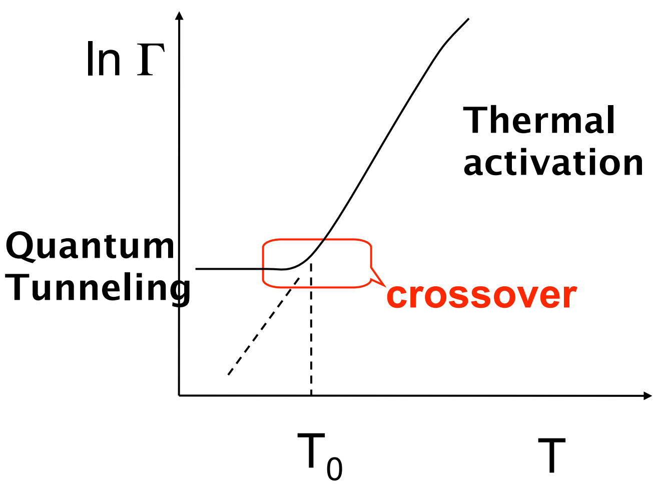
First- and Second-Order Transitions between Quantum and Classical Regimes for the Escape Rate of a Spin System

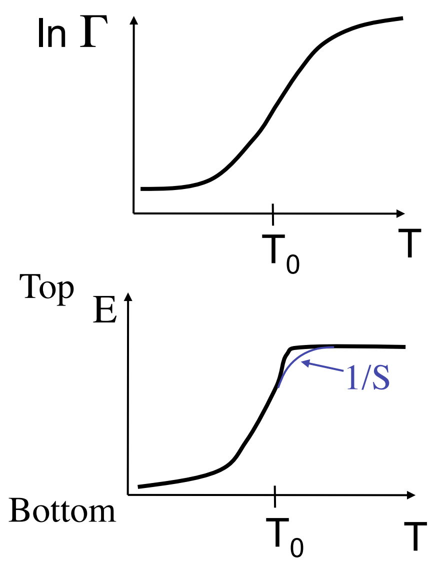
E. M. Chudnovsky* and D. A. Garanin†

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)

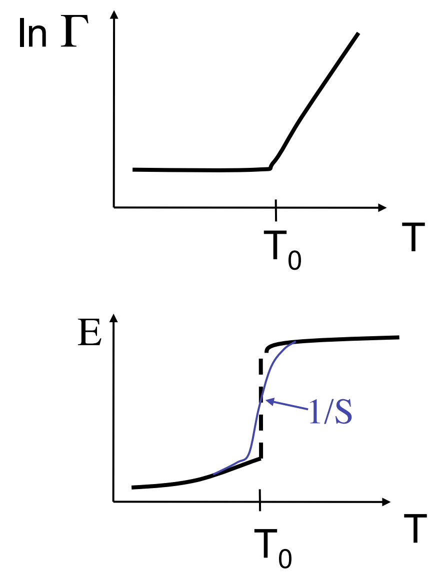
We have found a novel feature of the bistable large-spin model described by the Hamiltonian $\mathcal{H} = -DS_z^2 - H_x S_x$. The crossover from thermal to quantum regime for the escape rate can be either first ($H_x < SD/2$) or second ($SD/2 < H_x < 2SD$) order, that is, sharp or smooth, depending 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

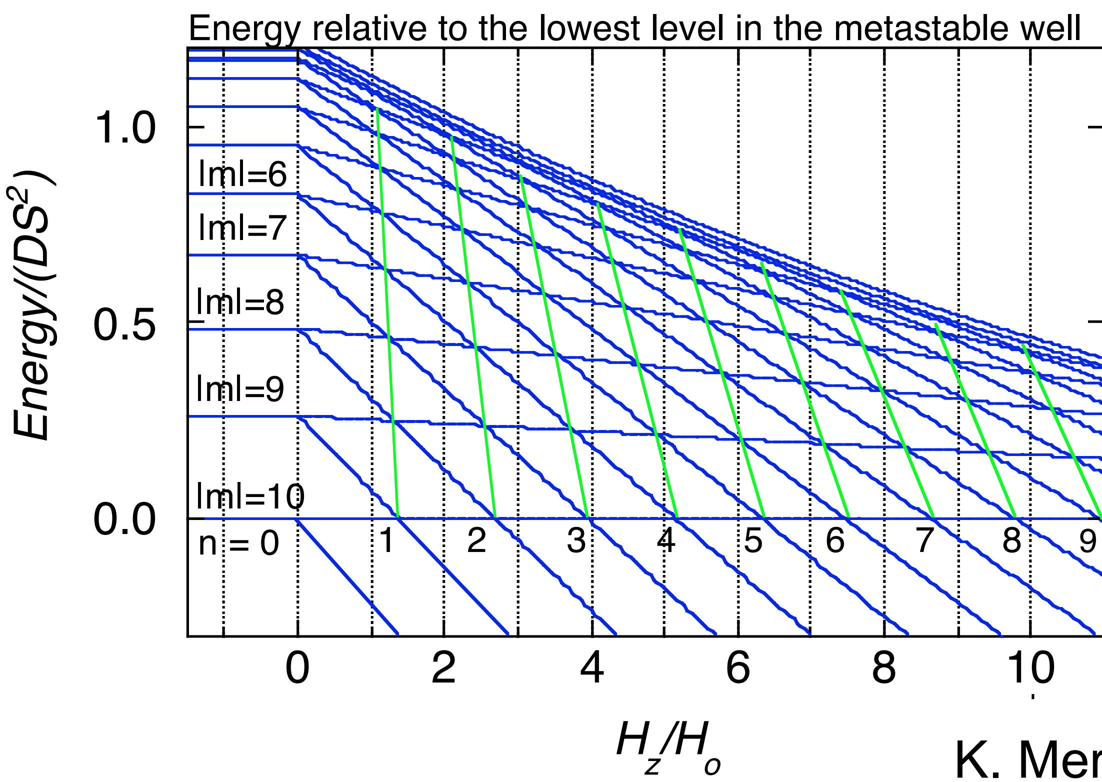
Marc A. Walters
Department of Chemistry, New York University, 31 Washington Place, New York, New York 10003
(Received 19 June 2000)

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

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

D=0.548(3) K g_z=1.94(1) **H_0= $D/g_z\mu_B$ = 0.42 T**

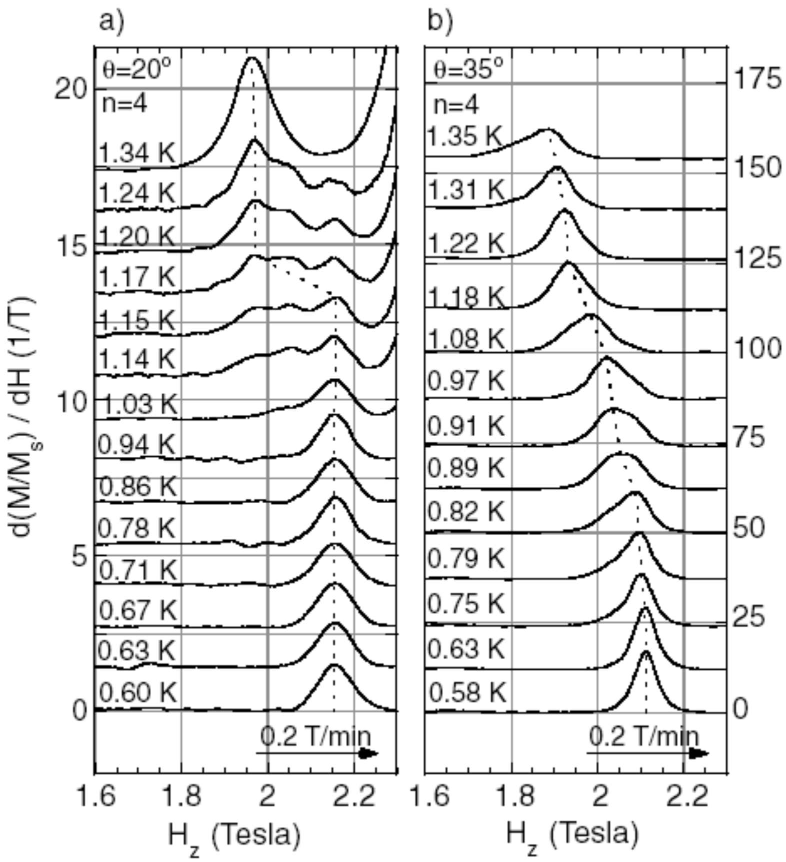
B=1.17(2) × 10^{-3} K (EPR: Barra et al., PRB 97)



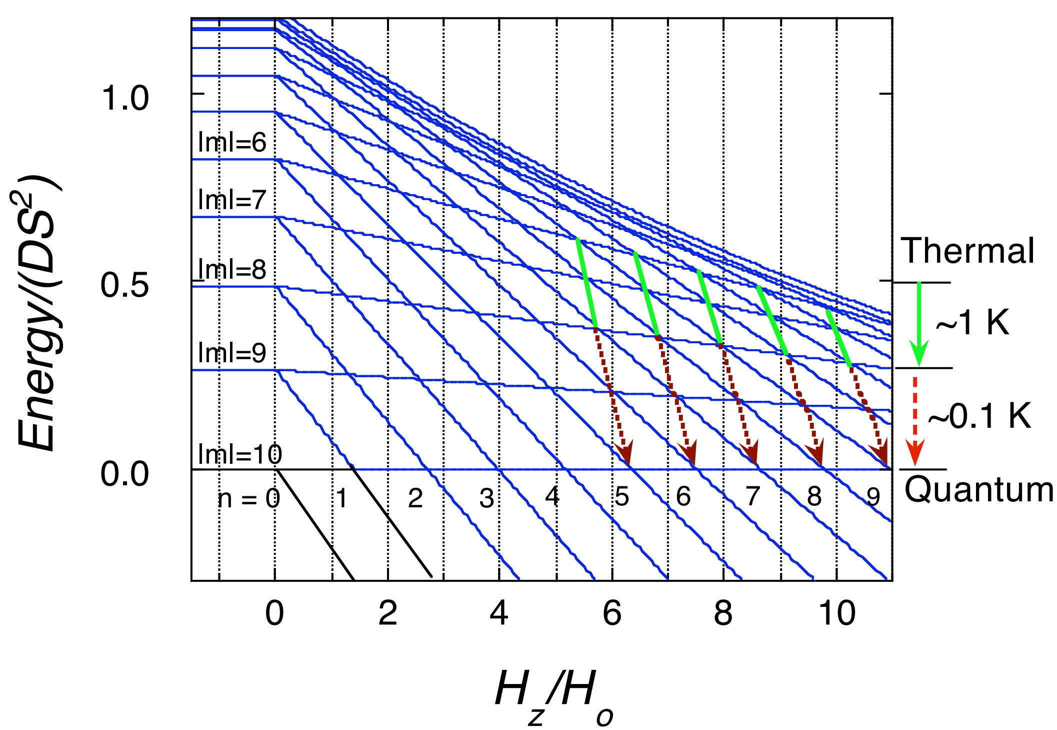
K. Mertes et al. PRB 2001

Experiments on the Crossover to Pure QTM in Mn12-acetate

dM/dH versus H_z



Schematic: dominant levels as a function of temperature



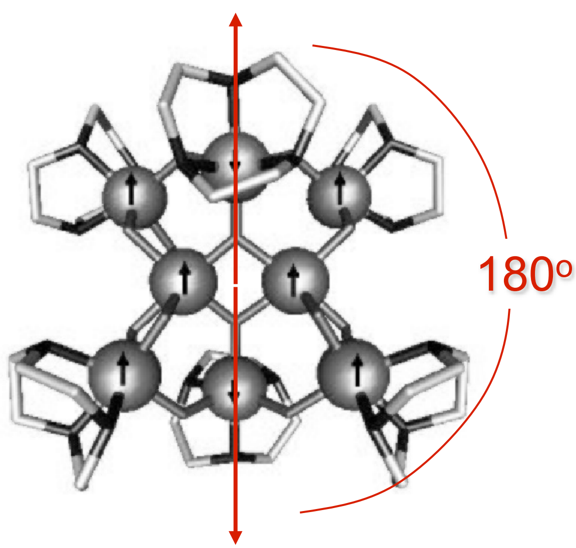
ADK *et al.* EPL 2000
L. Bokacheva, PRL 2001
K. Mertes *et al.* PRB 2001
W. Wernsdorfer *et al.* PRL 2006

Tunneling Selection Rules

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

Form of H_A determined by the site symmetry of the molecule

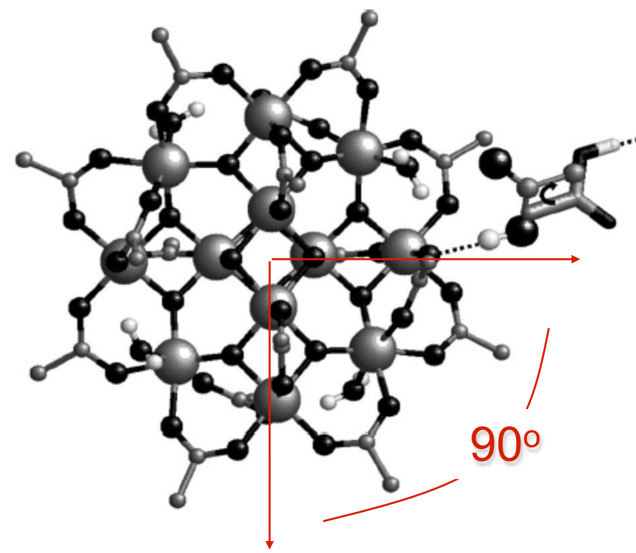
Fe_8



C_2-site symmetry (rhombic)

$$\mathbf{H_A} = E(S_x^2 - S_y^2)$$

Mn_{12}-acetate

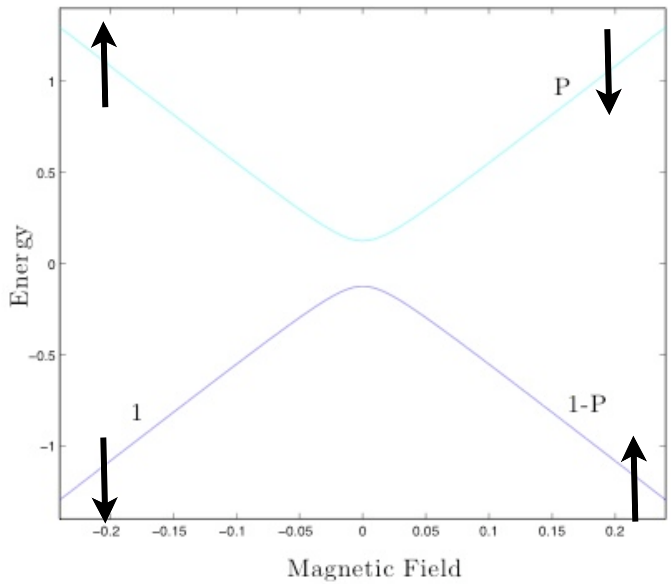


S_4-site symmetry (tetragonal)

$$\mathbf{H_A} = C(S_+^4 + S_-^4)$$

Hysteresis Loops as a Function of Transverse Magnetic Field

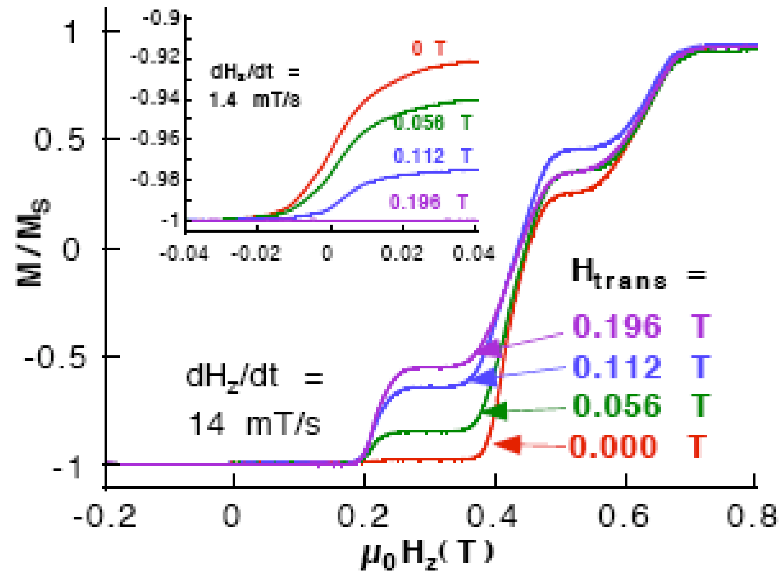
Landau-Zener Transitions

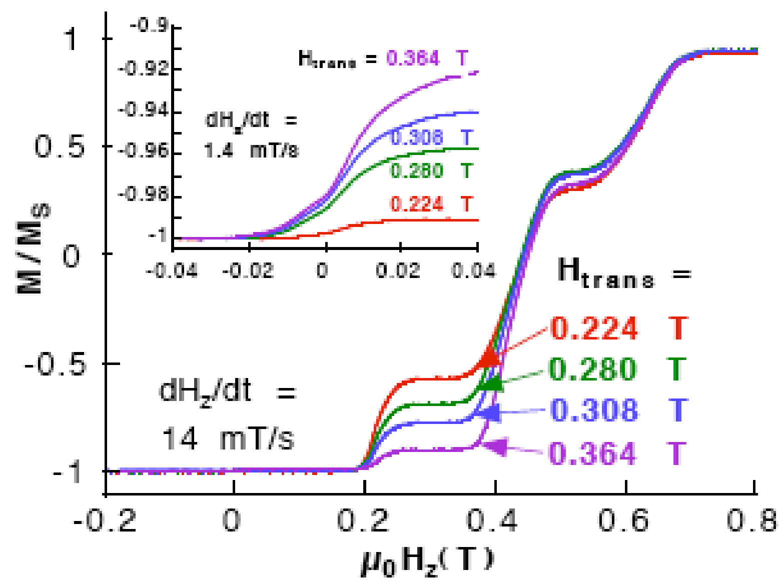


$$P = e^{-\epsilon}$$

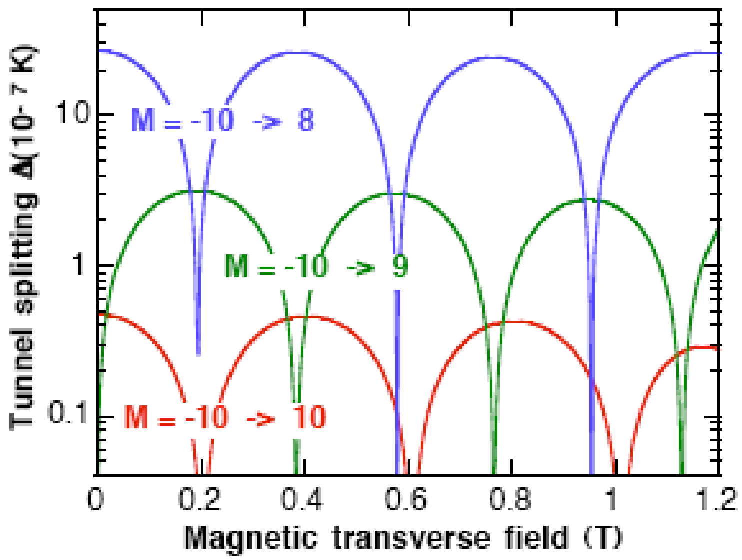
$$\epsilon = \pi\Delta^2/(2\hbar v)$$

$$v = 2Sg\mu_B dB_z/dt$$



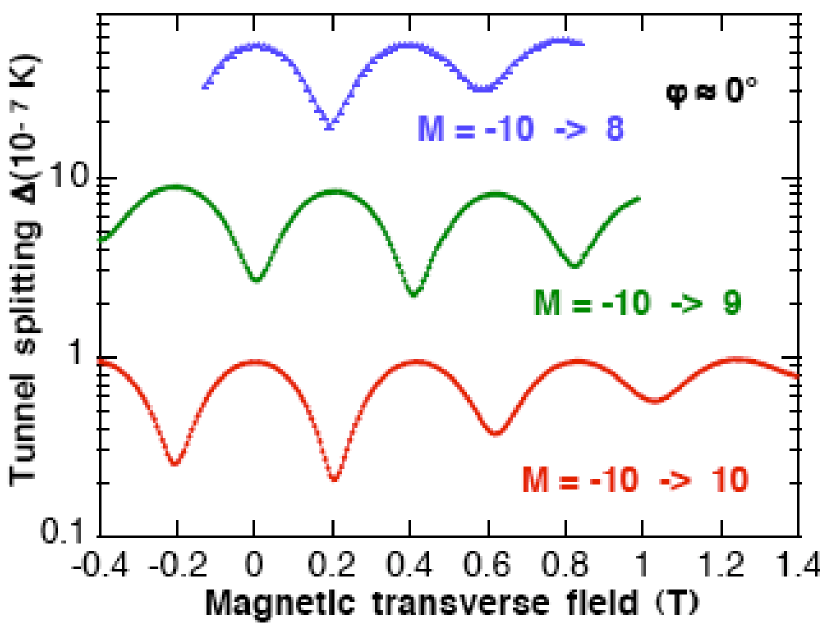


Oscillations and Parity Effect in the Tunnel Splitting



Spin-parity effects in QTM:
Loss et al., 1992
von Delft & Henley, 1992

Predicted for a biaxial system by Garg 1992!



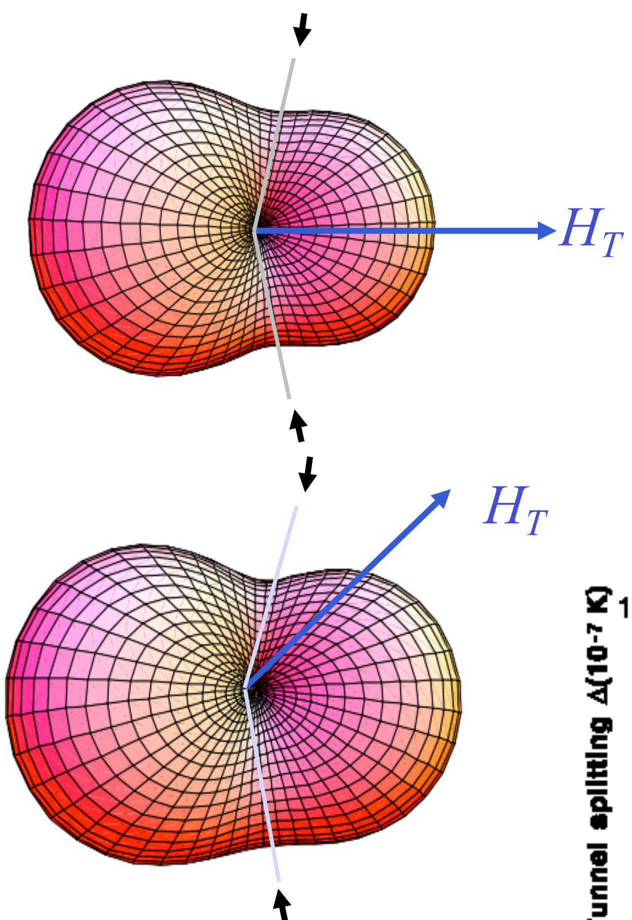
W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

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

$$D = 0.292\text{K}, \quad E = 0.046\text{K}, \quad C = -2.9\times10^{-5}\text{K}$$

Quantum Phase Interference in Fe_8

$$\mathbf{H} = -DS_z^2 + E(S_x^2 - S_y^2) - g\mu_B S_x H_x$$

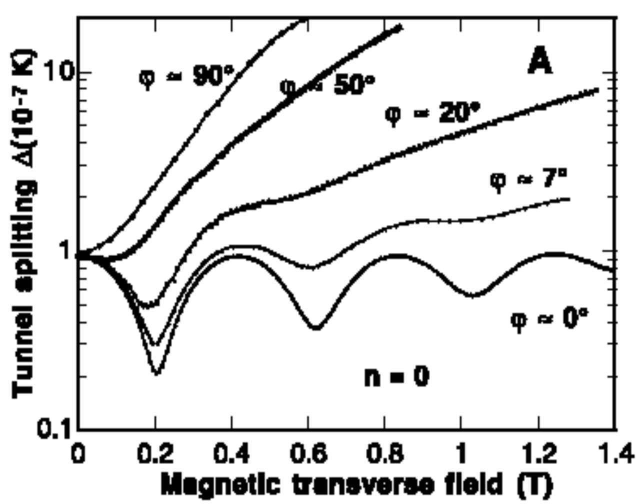


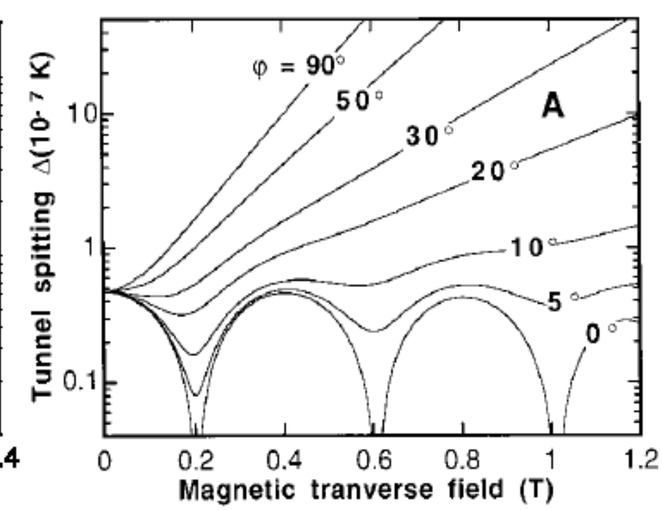
SCIENCE VOL 284 2 APRIL 1999

Quantum Phase Interference and Parity Effects in Magnetic Molecular Clusters

W. Wernsdorfer[1*] and R. Sessoli[2]

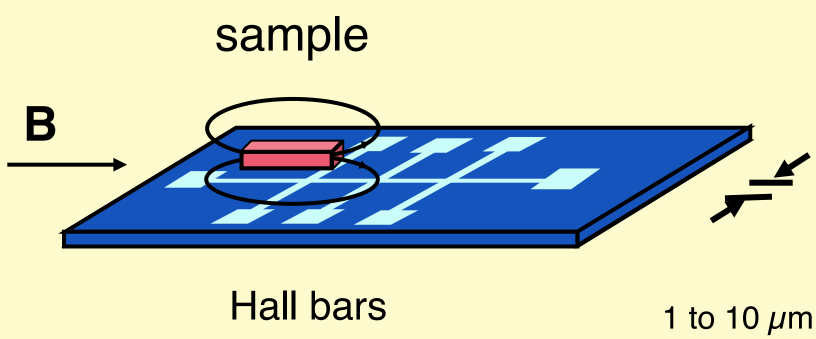
An experimental method based on the Landau-Zener model was developed to measure very small tunnel splittings in molecular clusters of eight iron atoms, which at low temperature behave like a nanomagnet with a spin ground state of $S = 10$. The observed oscillations of the tunnel splittings as a function of the magnetic field applied along the hard anisotropy axis are due to topological quantum interference of two tunnel paths of opposite windings. Transitions between quantum numbers $M = -S$ and $(S - n)$, with n even or odd, revealed a parity effect that is analogous to the suppression of tunneling predicted for half-integer spins. This observation is direct evidence of the topological part of the quantum spin phase (Berry phase) in a magnetic system.





Micromagnetometry

- *μ*-Hall Effect

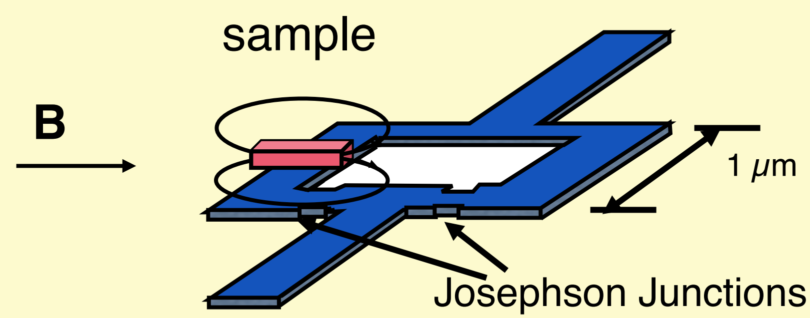


  - Based on Lorentz Force
  - Measures magnetic field

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

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

- *μ*-SQUID

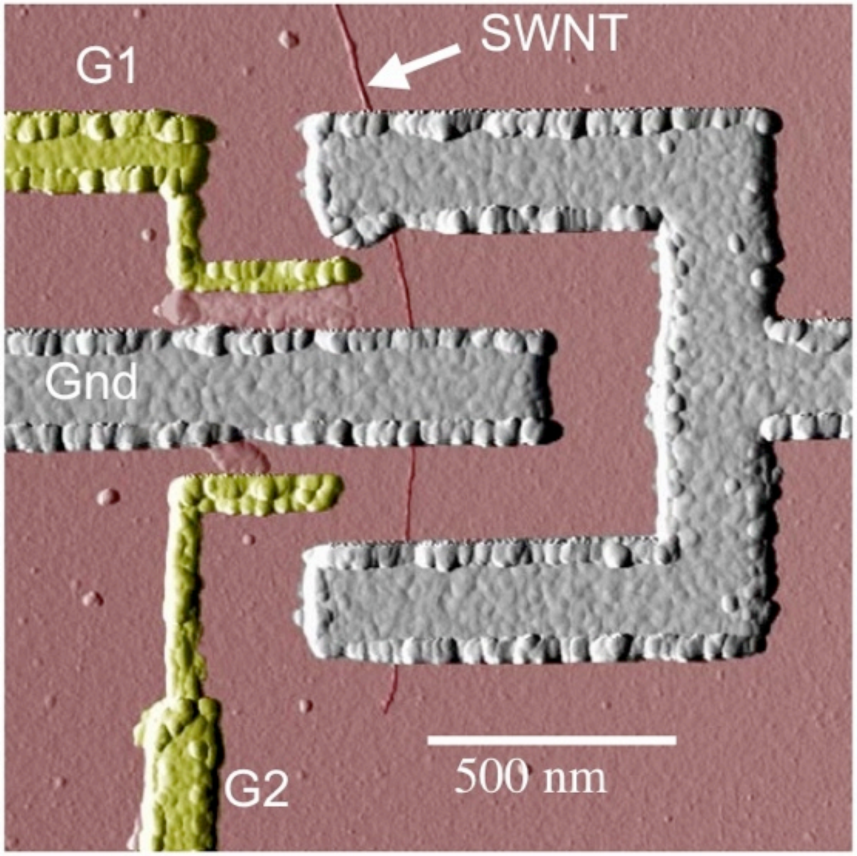


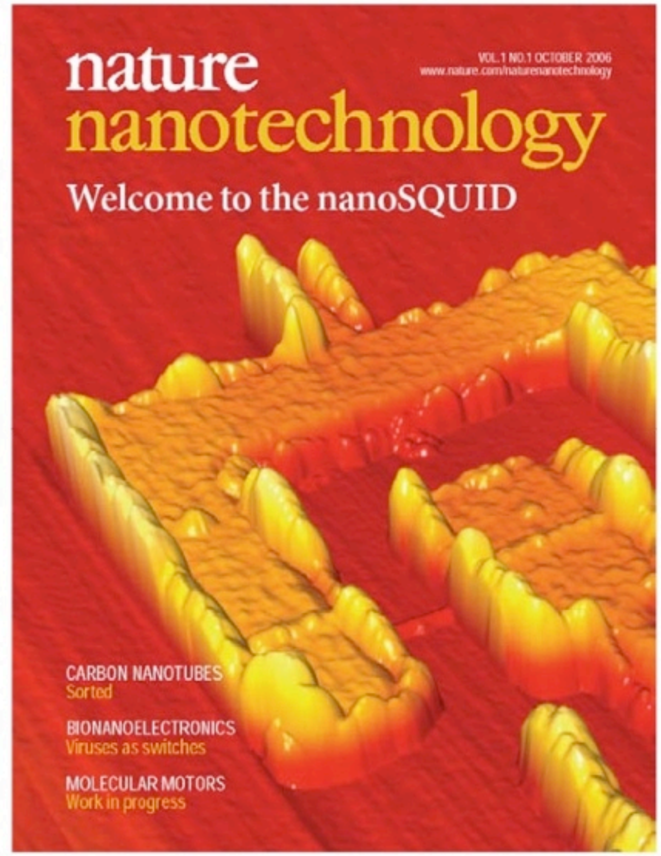
  - Based on flux quantization
  - Measures magnetic flux
  - Applied fields below the upper critical field (~1 T)
  - Low temperature (below T_c)
  - Single magnetic particles
  - Ultimate sensitivity ~1 μ_B

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

W. Wernsdorfer, JMMM 1995

Nano-SQUID





J.-P. Cleuziou, W. Wernsdorfer, V. Bouchiat, Th. Ondarçuhu, M. Monthioux, *Nature Nanotechnology*, 1, 53 (2006)

NYU

Summary

I. Introduction

Quantum Tunneling of Magnetization

Initial Discoveries

Single molecule magnets

II. Magnetic Interactions in SMMs

Energy Scales, Spin Hamiltonians

Mn_{12}-acetate

III. Resonant Quantum Tunneling of Magnetization

Thermally activated, thermally assisted and pure

Crossover between regimes

Quantum Phase Interference

IV. Experimental Techniques

Micromagnetometry

SQUIDs and Nano-SQUIDs

EPR