Quantum Tunneling of Magnetization in Molecular Magnets

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Nanomagnetism

Size:
- 100 nm
- 10-100 nm
- 1-10 nm
- 0.1 nm

Spin, \( S \)
- \( 10^6 - 10^9 \)
- \( 10^3 - 10^5 \)
- \(~20\)
- \(~1\)

Multi-domain
- Single-domain

Magnetic Field

Quantum Tunneling

Thermal Relaxation (over the barrier)

Relaxation rate

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

Quantum Tunneling of Magnetization

Physical Review Letters
25 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 20 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. Important tunneling rates prove to be large enough for observation of the effect with the use of existing experimental techniques.

\[ \Gamma \sim e^{-U/k_B T} \]
\[ \Gamma \sim e^{-B(0)} = e^{-U/k_B T_c} \]

also, Enz and Schilling, van Hemmen and Suto (1986)
Magnetic Bistability in a Molecular Magnet

Magnetic bistability in a metal-ion cluster


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

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(Received 1 November 1993)

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_{8}CH_{2}COOCH_{2}H_{2}OH 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 isolated molecules. [E010-000591-00013/7]

FIG. 1. Magnetization of Mn_{12} as a function of magnetic field at six different temperatures, as shown (field sweep rate of 80 mT/min). The inset shows the fields at which steps occur

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

Magnetic Interactions

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

- Spin-Hamiltonian

Magnetic qubits as hardware for quantum computers

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First SMM: Mn\textsubscript{12}-acetate

\[\text{[Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4].2\text{CH}_3\text{COOH.4H}_2\text{O}}\]

Magnetic Core

- 8 Mn\textsuperscript{3+} S=2
- 4 Mn\textsuperscript{4+} S=3/2
- Competing AFM Interactions
- Ground state S=10

Organic Environment

- 2 acetic acid molecules
- 4 water molecules

Single Crystal

- S\textsubscript{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

- S=2
- \(J_1 \sim 215\) K
- \(J_2,J_3 \sim 85\) K
- \(J_4 \sim 45\) K

\[H = \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_i \vec{S}_i \cdot D_i \cdot \vec{S}_i + ...\]

\((2S_1+1)^8(2S_2+1)^4=10^8 \Rightarrow S=10 \text{ and } 2S+1=21\]
Magnetic Anisotropy and Spin Hamiltonian

Spin Hamiltonian
\[ H = -DS_z^2 - g\mu_B S \cdot H \]

\[ S_z |m > = m|m > \]

\[ E_m = -Dm^2 \]

(Ising-like) Uniaxial anisotropy

2\(S+1\) spin levels

Experimental Techniques

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

• \(\mu\)-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 \(\sim 10^2 \mu_B\)

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

W. Wernsdorfer, JMMM 1995

• \(\mu\)-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 \(\sim 1 \mu_B\)

High Frequency EPR

S. Hill, UF, Gainsville

Cylindrical TE01n (\(Q \sim 10^4 - 10^5\))

\[ f = 16 \rightarrow 300 \text{ GHz} \]

Single crystal \(1 \times 0.2 \times 0.2 \text{ mm}^3\)

\(T = 0.5\) to 300 K, \(\mu_0 H\) up to 45 tesla

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

Reminder: field $\parallel z$, $S_4$-axis

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

\[ E(m_s) = -|D|m_s^2 + g\mu_B Bm_s \]

• 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, $B \parallel z$

\[ \hat{H}_o = D\hat{S}_z^2 + \mu_B \vec{B} \cdot \vec{g} \cdot \hat{S} \]

$S = 9/2$

\[ B \parallel z \text{-axis of molecule} \]
HFEP for high symmetry ($C_{3v}$) Mn$_4$ cubane; $S = \frac{9}{2}$

$[\text{Mn}_4\text{O}_3(\text{OSiMe}_3)(\text{O}_2\text{CET})_3(\text{dbm})_3]$

Cavity transmission (arb. units - off)

Magnetic field (tesla)

$\mu = 138 \text{ GHz}$

Fit to easy axis data - yields diagonal crystal field terms

$$\hat{H}_o = D\hat{S}_z^2 + B_4^0\hat{C}_4^0 + \mu_B g_{zz}B\hat{S}_z,$$

where $\hat{C}_4^0 = \alpha\hat{S}_z^2\hat{S}_z^2 + \beta\hat{S}_z^4$

Frequency (GHz)

Magnetic field (tesla)

$S = 9/2$

$D = -0.484 \text{ cm}^{-1}$

$B_4^0 = -0.000062 \text{ cm}^{-1}$

$g_z = 2.00(1)$
In high-field limit \((g\mu_B B > DS)\), \(m_s\) represents spin-projection along the applied field-axis.

\[
\hat{H} = DS_z^2 + \hat{H}_T + g\mu_B B \cdot \hat{S}
\]

\[
E(m_s) = \left\{ -\frac{D}{2} \pm |H_T| \right\} m_s^2 + g\mu_B m_s B
\]

\[
\hat{H}_{xy} = DS_z^2 + \hat{H}_T + g\mu_B B \cdot \hat{S}
\]

Resonant Quantum Tunneling of Magnetization

\[
H = -DS_z^2 - g\mu_B S_z H_z
\]

\[
S_z |m> = m|m>
\]

\[
E_m = -Dm^2 - g\mu_B H_z m
\]

“Resonance” fields where antiparallel spin projections are coincident, \(H_j = kD/g\mu_B\), levels \(m\) and \(m'; k=m+m'\)

Anisotropy Field:

\[
H_A = \frac{2DS}{g\mu_B}
\]

Magnetic field
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at high temperature

\[ U = U_0(1 - H/H_o)^2 \]

\[ \Gamma \sim e^{-U/kT} \]
Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at intermediate temperature

Thermally assisted tunneling

$$\Gamma_{TAT} = f(T)$$

$$U = U_0(1 - H/H_0)^2$$

Resonant Quantum Tunneling of Magnetization

Relaxation processes in SMMs

Magnetic relaxation at low temperature

Pure quantum tunneling

$$\Gamma_q = f(T)$$
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 \[ \Delta_{m,m'} \propto D \left( \frac{H_z}{H_A} \right)^{m+m'} \]

Upper levels
Large splitting
Low Boltzmann population

Lowest levels
Small splitting
High Boltzmann population

Relaxation pathway = \( f(T) \)

Crossover: Chudnovsky & Garanin, PRL 1997

Crossover between Thermally Assisted and Pure Quantum Tunneling in Molecular Magnet Mn12-Acetate

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

\[ H(n, m_{\text{csc}}) = nH_0 \left\{ 1 + B/D[m_{\text{csc}}^2 + (m_{\text{csc}} - n)^2] \right\} \]

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

Energy relative to the lowest level in the metastable well

K. Mertes et al. PRB 2001
High Spin Superposition States

- SMM Ni\textsubscript{4}; microwave spectroscopy and magnetometry
- Photon induced transition between superposition states
- Decoherence rate
- Longitudinal (energy) relaxation times
Coherent QTM: Microwave Spectroscopy and Magnetometry

![Diagram](image)

**Limit** \( \Omega_o \gg \Delta \gg kT, E_o \)

- **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

\[
\Gamma_\phi = \frac{E_o^2}{\Delta}
\]

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

\[
\tau^{-1} = \Gamma_1 = \frac{S^2 \Delta^{3} \omega^3}{12 \pi \hbar^2 \rho c^2} \coth \left( \frac{\hbar \omega}{2kT} \right)
\]

**Experiment**

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

- Photon induced transition between superposition states combined with magnetization measurements

\![Diagram](image)

- Monitor spin-state populations while performing microwave spectroscopy
- Pulsed and CW microwave fields
- High magnetic sensitivity: \( \sim 10^5 \) spins/Hz\(^{1/2} \)
- High magnetic fields
- Time resolved magnetic measurements (~GHz)
**Description of SMM Ni\(_4\)**

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

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

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

\(D_L = -0.863 K\)
\(D_U = -0.830 K\)
\(B_4^0 = -1.7 \times 10^{-4} K\)
\(B_4^4 = -5.8 \times 10^{-4} K\)
\(g_z = 2.30\quad g_x = g_y = 2.23\)
**Experiment**

\[ |up > \]
\[ |down > \]

\[ \frac{1}{\sqrt{2}}(|up> + |down>) \]

\[ \frac{1}{\sqrt{2}}(|up> - |down>) \]

**Experimental Setup**

[Diagram showing experimental setup with Vector Network Analyzer, switch, Superconducting magnet, He3 cryostat, continuous wave, pulsed microwave, pattern generator, and Hall-sensor.]
Results: Photon Induced Transitions between Superposition States

Magnetization with microwaves

\[ f = 39.42 \text{ GHz} \]

\[ H_L(T) \]

\[ M / M_\sigma \]

\[ T = 0.45 \text{ K} \quad \Delta T < 0.01 \text{ K} \text{ in the peaks} \]

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

\[ |\text{up}\rangle \quad |\text{down}\rangle \]
**Results: Photon Induced Transitions between Superposition States**

![Curvature graph]

**Approach to saturation and Ni$_4$ ‘micro-environments’**

As a function of mw power – cw radiation

\[ H_T = 3.2 \text{ T} \quad f = 39.4 \text{ GHz} \quad P_{\text{loss-in-coax}} = 15 \text{ dB} \]

![Graph showing variations]

*We observe variations up to 90% for higher fields and lower frequencies*
Decoherence time lower bound

\[ H_T = 3.2 \text{ T} \quad f = 39.4 \text{ GHz} \]

Results: Transverse relaxation rate \((\tau_2)\) – decoherence \((\tau_\phi)\)

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

\[ A = \frac{M - M_{eq}}{M_{eq}} \]

\[ H_L(T) \]

\[ \Delta M = (T_{\text{on}} - T_{\text{off}}) \]

\[ f = 40 \text{ GHz} \quad H_L = 3.2 \text{ T} \]

\[ \alpha = 0.01 \text{ T/min} \]

\[ \text{d.c.} = 50\% \]

\[ \tau = 30s \]

Results: Longitudinal relaxation rate \((\tau_1)\)

Pulsed mw experiments
Results: Longitudinal relaxation rate ($\tau_1$)

Pulsed radiation experiments

Energy relaxation increases with freq.

Longitudinal relaxation effects in cw experiments
Spin-Phonon Relaxation

Relaxation rate:
\[ \tau_1^{-1} = \Gamma_1 = \frac{S^2 \Delta^2 \omega^3}{12 \pi \hbar \rho c_i} \coth \left( \frac{\hbar \omega}{2kT} \right) \]

Chudnovsky, PRL 2004

\[ c_i = 10^3 m/s \quad \Delta / \hbar = 20 \text{ GHz} \]

\[ \tau_1 = 10^{-3} \text{ sec} \]

Upper limit on the relaxation time!

Phonon-laser effect:
\[ \Gamma_L \sim \omega^{-3} \]

Chudnovsky and Garanin, PRL 2004

Other levels important?

Summary (Ni₄)

- 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 \( \tau_\phi > 0.5 \text{ ns} \)
  - Similar to that observed in the Mn₄-dimer through EPR measurements a system with strong intermolecular exchange interactions

- Determination of the longitudinal relaxation times \( \tau \sim 10-20 \text{ s} \)
  - Characterized \( \tau \) as a function of longitudinal field and frequency
Perspectives

Coherent oscillations of the magnetization; Rabi and Spin Echo experiments

\[ \frac{\pi}{2} \quad t_{\text{delay}} \quad \pi \quad t_{\text{delay}} \quad \frac{\pi}{2} \]

High radiation power is needed for measurable Rabi periods

Ex: \( \pi \)-pulse \( \gamma H_{1} T_{\text{pulse}} = \frac{\pi}{2} \), \( H_{1} = 1 \mu T \), \( T_{\text{pulse}} = 5 \mu s \)

\( H_{1} = 100 \mu T \), \( T_{\text{pulse}} = 50 \text{ ns} \)

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


Predicted by Chudnovsky and Garanin

\[ \lambda > L \]

Coherent radiation

\[ \Gamma = N \Gamma_{\text{photon}} \]