Spin Dynamics in Single Molecule Magnets

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Quantum Tunneling of Magnetization in Small Ferromagnetic Particles

E. M. Chudnovsky and L. Gunther

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(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.

\[ \Gamma \sim e^{-U/k_B T} \]

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

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

Thermal

Quantum

also, Enz and Schilling, van Hemmen and Suto (1986)
Single Molecule Magnets

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

**Examples**
- $\text{Mn}_{12}$ \( S = 10 \)
- $\text{Ni}_{12}$ \( S = 12 \)
- $\text{Mn}_{84}$ \( S = 6 \)
- $\text{Fe}_8$ \( S = 10 \)
First SMM: Mn$_{12}$-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$^{3+}$ S=2
- 4 Mn$^{4+}$ S=3/2

Ground state

- Competing AFM Interactions
- S=10

Organic Environment

- 2 acetic acid molecules
- 4 water molecules

• 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)

Single Crystal
Resonant Quantum Tunneling of Magnetization

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

\[ S_z |m \rangle = m |m \rangle \]

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

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

\[ H_L = kH_R \]

\[ kH_R < H_L < (k+1)H_R \]

\[ H_L = (k+1)H_R \]

\[ H_L(T) \]

\[ M/M_s \]

QT on [fast relaxation]

QT off [slow relaxation]
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 10468-1389

(Received 7 July 1997)

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

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

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

Chudnovsky and Garanin '97
Uniaxial nanomagnets for small transverse magnetic fields!!!
Crossover between Thermally Assisted and Pure Quantum Tunneling in Molecular Magnet Mn$_{12}$-Acetate

Louisa Bokacheva and Andrew D. Kent

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Marc A. Walters

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(Received 19 June 2000)

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

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

\[ D = 0.548(3) \text{ K} \quad g_z = 1.94(1) \quad H_0 = D/g_z \mu_B = 0.42 \text{ T} \]

\[ B = 1.17(2) \times 10^{-3} \text{ K} \quad \text{(EPR: Barra et al., PRB 97)} \]

Energy relative to the lowest level in the metastable well

Energy/\((DS^2)\)

- \(l_m = 6\)
- \(l_m = 7\)
- \(l_m = 8\)
- \(l_m = 9\)
- \(l_m = 10\)

\(n = 0, 1, 2, 3, 4, 5, 6, 7, 8, 9\)

\(H_z/H_o\)

K. Mertes et al. PRB 2001
Experiments on the Crossover to Pure QTM in Mn12-acetate

**dM/dH versus H_z**

![Graph showing dM/dH versus H_z with energy levels as a function of temperature.]

**Schematic: dominant levels as a function of temperature**

![Schematic diagram showing energy levels versus Hz/H_o with temperature markers.]

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 Ni₄

\[ H = -DS^2_z + H_T + g\mu_B \vec{H} \cdot \vec{S} \]

\( D > 0 \)

\[ S = 4 \]

\[ \Omega_o \]

\[ |S\rangle \]

\[ |A\rangle \]

\[ \Omega_o \gg \Delta > kT, E_o \]

**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:

\[ \tau^{-1}_1 = \Gamma_1 = \frac{S^2 \Delta^2 \omega^3}{12\pi \hbar^2 \rho c^5} \coth\left(\frac{\hbar \omega}{2kT}\right) \]

Stamp: for dephasing rate due to nuclear spins

\[ \Gamma_\phi = \frac{E_o}{\hbar \Delta} \]
Collective Spin Phonon Relaxation

» Spin and phonon DOF are strongly coupled

\[ B = \frac{N_S}{N_\Gamma} \]

Microscopic model of the bottleneck, Garanin PRB 2007, 2008

» Phonon wavelength is much greater than the lattice spacing

\[ \lambda > L \]

Coherent radiation

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

Chudnovsky & Garanin, PRL 2004
Description of Ni$_4$

\[ H = -DS^2_z + C(S^4_+ + S^4_-) - g\mu_B S_z H_z - g\mu_B S_x H_x \]

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

Crystals I4$_1$/a space group

S$_4$ site symmetry
No solvate molecules!
No nuclear spin on Ni sites*
*at 1% level$^{61}$Ni

\[ U = 12 \text{ K} \]
\[ T_{\text{exp}} \sim 0.4 \text{ K} \]
Experiment

Magnetization dynamics induced by microwaves

\[ |S\rangle = \frac{1}{\sqrt{2}} (|\text{up}\rangle + |\text{down}\rangle) \]

\[ |A\rangle = \frac{1}{\sqrt{2}} (|\text{up}\rangle - |\text{down}\rangle) \]

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

\[ \rightarrow \text{coherent QTM} \]

We work here

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Experiment

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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

- Vector Network Analyzer
- Hall sensor
- Ni\textsubscript{4} crystal (\(10^{14}\) to \(10^{15}\) molecules)
- microstrip resonator
- He\textsubscript{3} cryostat
- Switch
- Pulsed microwave
- Pattern generator
- Superconducting 3D magnet

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

Experiment: mapping in \((H_z \text{ and } H_T)\)

- Linewidth \(\rightarrow T_2^* \sim 0.2 \text{ ns} \) (inhomogeneous broadening, lower bound for the coherence time)
- Analysis of peak amplitude: Fermi golden-rule

\[ \Gamma = \frac{\pi}{2} \left( \frac{g\mu_B}{\hbar} \right)^2 \left| \langle S | S_z | A \rangle \right|^2 f(\omega) \]
$P_{\text{abs}}, \Delta M$ and the Relaxation Rate in Steady State

Absorption rate $\Lambda$ vs. relaxation rate $\Gamma$

Steady State

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

Energy balance

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

Population difference

$N_0 = N_a - N_b$

In equilibrium

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

In equilibrium

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

Simultaneous measurement of $P_{\text{abs}}$ and $\Delta M$ yields $\Gamma$
Simultaneous CW Absorption and Magnetization Measurements

\[ \Delta H \simeq 0.1 \, \text{T} \]

\[ T_2 > 0.25 \, \text{ns} \]
Temperature Dependence

2-state model

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

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

Relaxation rate

\[
\Gamma = \frac{(m_b - m_a)}{\Delta M} \frac{P_{abs}}{\hbar \omega_0}
\]
Temperature Dependence of Relaxation Rate

- Moderate increase with increasing \( T \) below \( \sim 0.8 \) 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

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

\[ Q \approx 1 \text{ for } SH_z < H_\perp \]

Direct process
(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

\[
\Gamma_T = \frac{\Gamma_{ph}}{B_{\omega_0}} \coth^2 \left( \frac{\hbar \omega_0}{2k_B T} \right) + \sum_i \Gamma_{0i} \exp \left( \frac{-E_i}{k_B T} \right)
\]

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

\[
\approx 180,000 \text{ at } 10 \text{ GHz}
\]

\[
\approx 24,000 \text{ at } 27.8 \text{ GHz}
\]

\[
\rightarrow \mathcal{T}_{ph} \approx 0.5 \mu s \quad \rightarrow l_{ph} \approx 500 \mu m
\]

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

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

Lowest rate governing the relaxation:

\[
\Lambda^- \approx \frac{\Gamma_{ph} \Gamma_{sp, T}}{B_{\omega_0, T} \Gamma_{sp, T} + \Gamma_{ph}}
\]

where \( B_{\omega_0, T} = B_{\omega_0} \tanh^2 (\hbar \omega_0 / (2k_B T)) \)
Relaxation Mechanisms

Phonon bottleneck + Orbach mechanism

\[
\Gamma_T = \frac{\Gamma_{ph}}{B\omega_0} \coth^2 \left( \frac{\hbar \omega_0}{2k_B T} \right) + \sum_i \Gamma_{0i} \exp \left( \frac{-E_i}{k_B T} \right)
\]

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 $B\omega_0 \Gamma_{sp,T} \ll \Gamma_{ph}$, $T_{ph} \ll 10$ 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.
Single Molecule Magnets

**Physics**
- Individual molecule can be magnetized and exhibit magnetic hysteresis 1993
- Quantum Tunneling of Magnetization 1995
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**Open Questions/Research Directions**
- 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...