Temperature Change During Molecular Magnet Tunneling and its Implications to the Landau-Zener theory

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Outline

- Fe8 Single Molecule Magnet (SMM).
- Magnetization relaxation in Fe8 SMM:
  - Quantum Tunneling of Magnetization (QTM).
  - Magnetic Deflagration.
- Previous work:
  - Deflagration velocity.
  - Thermal diffusivity.
- Temperature measurements during magnetization reversal.
- Conclusions.
Fe8 SMM

- 8 Fe$^{3+}$ ions ($S = 5/2$):
  - 2 ions with spin down: $S = 5$
  - 6 ions with spin up: $S = 15$
  - Total $S = 10$ below $T=20K$.

- There are 4 different exchange interactions.
  $J_1 = -147$ K $J_2 = -173$ K $J_3 = -22$ K $J_4 = -50$ K

Fe8 SMM

- We grow the single crystals.
- Crystal dimensions- several mm long.
- Parallelogram shape.
- Strong Magnetic Anisotropy- directional dependence of magnetic properties.
Fe8 SMM Hamiltonian:

\[ H = S \cdot D \cdot S \]

\[ D = D_{zz} - \frac{1}{2} (D_{xx} + D_{yy}) \quad E = \frac{1}{2} (D_{xx} - D_{yy}) \]

\[ D \approx -0.29 \text{ K} \quad \begin{vmatrix} E \\ D \end{vmatrix} \approx 0.16 \]

\[ H = DS_z^2 + E(S_x^2 - S_y^2) \]

\[ H_{S=1} = \begin{pmatrix} D & 0 & E \\ 0 & 0 & 0 \\ E & 0 & D \end{pmatrix} \]
Fe8 SMM

Eigenstates for $S=1$ and $E=0$:

$$H = DS_z^2 \Rightarrow$$ Double Potential Well problem.

$$|left\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, |middle\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, |right\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$\left| \langle left | e^{-\frac{H\tau}{\hbar}} | right \rangle \right|^2 = 0$$
Fe8 SMM

Eigenstates for \( S=1 \) and \( E\neq 0 \):

\[
H = D S_z^2 + E (S_x^2 - S_y^2)
\]

\[
|1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \end{pmatrix},
|2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix},
|3\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}
\]

Quantum Tunneling of Magnetization ‘QTM’

\[
\left| \langle \text{left} | e^{-\frac{iHt}{\hbar}} | \text{right} \rangle \right|^2 = \frac{1 - \cos(\frac{2Et}{\hbar})}{2} = \frac{1 - \cos(\frac{\Delta_t t}{\hbar})}{2}
\]

\( E_2 = D + E \)
\( E_1 = D - E \)
\( E_c = 0 \)
\( \Delta_t = 2E \)  
Tunnel Splitting
Fe8 SMM
Eigenstates for $S=10$, magnetic field and small perturbation $H'$ where $[H', S_z] \neq 0$:

$$H = DS_z^2 + g\mu_B H_z S_z + H'$$

$H_z = 0$

$H_z < 0$

'Matching Fields'

$$|H_z| = \frac{nD}{g\mu_B} \approx n0.225T$$

Quantum tunneling

Decay
Fe₈ SMM

Eigenvalues vs magnetic field in $\hat{z}$ direction: $H = D S_z^2 + g \mu_B H_S S_z + H'$

QTM leads to magnetization change of the crystal.

W. Wemsdorfer, R. Sessoli, A. Caneschi, D. Gatteschi, A. Comia, and D. Mailly. Landau zener method to study quantum phase interference of Fe₈ molecular nanomagnets
Magnetic Relaxation

‘Blocking temperature’ $T_B \sim 500$ mK, the limit between pure QTM regime and thermal assisted transitions regime.

Above $T_B$, QTM is negligible, over barrier transitions: $M(t) = M_0 \exp\left(-\frac{t}{\tau}\right)$

Below $T_B$, no temperature dependence: $M(t) = M_0 \exp\left((\frac{t}{\tau})^\alpha\right)$

$\alpha \in [0,1]$
Magnetic Relaxation

Above $T_B$, the relaxation time is according to Arrhenius low:

$$\tau(U) = \tau_0 \exp\left(\frac{U}{k_B T}\right)$$

\[\tau_0 = 3.4 \times 10^{-8} \text{ sec}\]

However, below $T_B$, relaxation time is constant in temperature but has field dependence:

![Graph 1](image1.png)

![Graph 2](image2.png)

Magnetic Relaxation

Hamiltonian for a linear time dependent magnetic field:

$$H(t) = DS_z^2 + g\mu_B\alpha_z S_z t + H'$$

$$\frac{dH_z}{dt} = \alpha_z$$

According to Landau - Zener theory:

$$C_{LZ} = \langle + | u(t) | + \rangle$$

$$u(t) = e^{\frac{i}{\hbar} \int_{-\infty}^{t} H(t) dt}$$

$$P_{mm'} = 1 - \exp\left(\frac{-\pi \Delta_{mm'}^2}{2\hbar(m - m')g\mu_B\alpha_z}\right)$$

Magnetic Relaxation

Magnetization measurements at different temperatures and constant sweep rate:

- Hysteresis loop.
- Equally separated steps can be seen at matching fields – QTM.
- No temperature dependence below 0.4 K (pure QTM).
- For high Temperatures QTM and hysteresis vanish due to over barrier transitions.

Magnetization Reversal

Tunnel splitting in a linear time dependent magnetic field:

The probability to have tunneling while sweeping the field around $H_z \approx 0$ T:

$$P_{10,-10} = 1 - \exp\left(\frac{-\pi \Delta^2}{4 \hbar g \mu_B \alpha_z}\right)$$


Tunnel splitting cannot be sweep rate dependent – LZ theory does not describe the experiment well.
Magnetic Relaxation

Magnetization measurements for different sweep rates at constant temperature 50 mK:

- Hysteresis loop.
- Sweep rate dependence of stairs height can be seen.
- We count three steps during QTM.
- For high rates (above 5 mT/s) there is a total reversal of magnetization at the first matching field – we call this phenomena ‘Magnetic Deflagration’.

What is Magnetic Deflagration?

Magnetic Deflagration is the case where the sample magnetization is flipped in the form of spin reversal front which propagates along the sample in a constant subsonic velocity.
Magnetic Relaxation

Magnetic Deflagration theory:

\[ U \text{ Activation Energy} \]

\[ \Delta E \text{ Zeeman Energy} \]

\[ S_z = -10 \]

\[ S_z = 10 \]

\[ H_z \approx 0.22 \, T \]
Magnetic Relaxation

Magnetic Deflagration theory:

Ignition of deflagration:
the heat loss through the sample boundaries is insufficient to balance the heat released - the sample temperature can rise and the ignition of a self-supporting burning process as deflagration.
Magnetic Relaxation

Magnetic Deflagration theory:

Fronts of deflagration:
- Flat Front propagates in subsonic velocity.
- Flame area – up and down spins.
- The flame area is accompanied by a magnetic field in the xy plane.
- Flame temperature:
  \[ T_f \propto \frac{\Delta E}{C_{ph}} \]
Magnetic Relaxation

Magnetic Deflagration equations:

Heat equation:
\[
\frac{dT}{dt} = \nabla \kappa(T) \nabla T - T_f \frac{dn}{dt}
\]

Metastable state population:
\[
\frac{dn}{dt} = -\frac{1}{\tau} (n - n^{eq})
\]

Front velocity:
\[
v = \sqrt{\frac{\kappa}{\tau_0} \exp\left(-\frac{U(H)}{2k_B T_f}\right)}
\]
**Previous Work**

**Velocity measurements:**

The magnetic field lines as spins reverse direction during avalanche traveling along the sample.

When the front passes a given Hall sensor there is a Hall voltage peak. From the time difference between the sensors' peaks we can find the fronts velocity.
Previous Work

Velocity measurements:

Hall voltages vs time:

\[ v \leq 0.6 \frac{m}{s} \]

Previous Work

Velocity measurements:

- Velocity increases with sweep rate.
- Velocity of the order of $v \approx \frac{m}{s}$.
- It looks like the velocity saturates for high sweep rates.

Previous Work

Thermal diffusivity measurements:

Recording the thermistors voltages after applying a voltage pulse in the heater resistor.

Cold Finger
Heater
RuO$_2$ Hot
Fe8 Crystal
RuO$_2$ Cold
Teflon Holder

320 mK
**Previous Work**

**Thermal diffusivity measurements:**

Heat equation:

\[
\frac{\partial T(x,t)}{\partial t} - \kappa \frac{\partial^2 T(x,t)}{\partial x^2} = 0
\]

Solution:

\[
\Delta T_{cs}(t) = c \int_0^t \frac{x \exp\left(\frac{-x^2}{4\kappa(t-s)}\right)}{\left(4\pi\kappa\right)^{\frac{3}{2}}(t-s)^{\frac{3}{2}}} \Delta T_{hs}(s) ds
\]

Previous Work

Flame temperature estimation according to previous work:

\[
T_f = \frac{U(H)}{k_B \ln\left(\frac{\kappa}{v^2 \tau_0}\right)}
\]

\[
U(H^{1}_{res}) = 24.5 K \\
\kappa = 2 \cdot 10^{-6} \frac{m^2}{s} \\
v = 0.5 \frac{m}{s} \\
\tau_0 = 3.4 \cdot 10^{-8} s
\]

\[T_f \approx 5 K\]
Temperature Measurements

Experimental setup:

Recording the thermistors voltages while sweeping the magnetic Field from +1 to -1 T.
**Temperature Measurements**

**Calibration:**

- Cool down the system from 9 to 0.3 K for over an hour.
- Temperature measurement according to the system thermometer near the sample location.
- Voltage increases for low temperatures.

\[
T = T_0 + T_1 \left(1 - \exp\left(-\frac{V}{V_1}\right)\right) + T_2 \left(1 - \exp\left(-\frac{V}{V_2}\right)\right)
\]
Temperature Measurements

Background measurements - without sample:

- Temperature rise at both sides for zero field due to super-conductivity phase of solders in the experimental setup.
- Cold side warming during the sweep as a result of Eddy currents in the copper cold finger attached to the themistor.
- Both sides have the same temperature at the beginning of the sweep - calibration is working.
Temperature Measurements

Results:

Sample 1:

- Two main heat burst can be seen. (and almost unseen small bump between them). Not a magnetic deflagration.
- The temperature rises occur at matching fields.
- No sweep rate dependence.

Maximal temperature is \( \sim 1.7 \) K.
Temperature Measurements

Results:

Sample 2:

- One heat burst at $\sim -0.6 \, \text{T}$ simultaneously in both sides of the sample - All the spins flip together. Not a magnetic deflagration.
- No sweep rate dependence.

Maximal temperature is $\sim 2.2 \, \text{K}$. 
Temperature Measurements

Results:

Sample 3:

- Sweep rate dependence: For panels a. and b. only the hot side shows heat burst. The cold side is too hot to allow quantum behavior. For panels c. and d. one heat burst can be seen in both sides. Time delay due to long time response of the thermistors.
- This sample is a candidate for magnetic deflagration.

*Maximal temperature is \( \sim 1.8 \) K.*
Conclusions:

T < 2.2K. This is lower than estimates from deflagration.

\[ T_f = \frac{U(H)}{k_B \ln\left(\frac{\kappa}{v^2 \tau_0}\right)} \]

However in previous work we have never seen more than three steps in magnetization measurements.

Therefore, we suggest that the effective barrier height for tunneling is somewhere between the 7th and 6th levels, namely, U ~ 10 K for the first resonant field. Using this effective height the flame temperature is:

\[ T_f \leq 2.5K \]

In agreement with direct measurements.
Conclusions:

- $T < 2.2 \text{ K}$, and is lower than level spacing.
- Because $T < \text{ level spacing}$ only the ground state should be included.
- Up until now the magnetic steps were analyzed by LZ theory which doesn’t take into account the decay to the ground state. We hope to develop a three states LZ formula to analyze magnetization jumps in molecular magnets.