Random-Field Ferromagnetism in Single Crystals of Molecular Magnet Mn_{12}-acetate

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I. Introduction
- Motivation: study for long range order in Mn$_{12}$-ac
- Energy scales in Mn$_{12}$-acetate

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- Why randomness is needed?
- Our random field model

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Potential realization of a transverse field Ising system

\[ H = - \sum_{ij} J_{ij} S_i^z S_j^z - h \sum_i S_i^x \]

A ferromagnetic phase was predicted:
- Fernandez and Alonso, PRB 2000
- Garanin and Chudnovsky, PRB 2008

Interesting ferromagnetic domain dynamics predicted

Neutron scattering data shows low-T ferromagnetic order:
- Luis et al., PRL 2005

Magnetic susceptibility had not been studied as a function of transverse field
Neutron Scattering Study

Long-Range Ferromagnetism of Mn$_{12}$ Acetate Single-Molecule Magnets under a Transverse Magnetic Field

F. Luis,$^{1,\ast}$ J. Campo,$^1$ J. Gómez,$^2$ G. J. McIntyre,$^3$ J. Luzón,$^1$ and D. Ruiz-Molina$^2$

-Blue points are at 4 T
-Red points are at 0 T data taken after applying 6 T before setting the above fields.
Mn\textsubscript{12}-acetate

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

**Magnetic Core**
- 8 Mn\textsuperscript{3+} S=2
- 4 Mn\textsuperscript{4+} S=3/2

**Organic Environment**
- 2 acetic acid molecules
- 4 water molecules

**Single Crystal**
- \( S_4 \) site symmetry
- Body centered tetragonal lattice \( a=1.7 \text{ nm}, b=1.2 \text{ nm} \)
- Strong uniaxial magnetic anisotropy (~60 K)
- Weak intermolecular dipole interactions (~0.1 K)
- Discrete disorder

Competing AFM Interactions
Ground state
\( S=10 \)
Experimental Setup

Measurements taken between 0.4 K to 6 K in a $^3$He refrigerator with a 3D superconducting vector magnet.
New to experimental setup:
1) Hall bar array
2) Reference Hall bar
3) Measure the applied field
Quantum Tunneling of Magnetization

Applying $H_\perp$ breaks the symmetry and lifts the degeneracies by mixing the eigenstates of $\hat{S}_z$.

Increasing $H_\perp$ promotes quantum tunneling, accelerating the relaxation towards thermal equilibrium.
Blocking Temperature

- The equilibrium susceptibility can be measured for $T > T_B(H_\perp)$

$T_B$ depends on sweep rate and transverse field.

$$T_B = \frac{U}{k_B \ln \left( \frac{t_m}{\tau_0} \right)}$$
Blocking temperature

- Temperature below which the crystal shows hysteretic behavior.

$$T_B = \frac{U}{k_B \ln \left( \frac{tm}{\tau_0} \right)}$$

$$\chi = \frac{\partial M_z}{\partial H_z} \bigg|_{H_z=0}$$ in equilibrium.
Data follows a Curie-Weiss law*: \( \chi^{-1} \sim C^{-1} (T - T_{cw}) \)

\( T_{cw} = 0.9 \text{ K} \)

*as shown in F. Luis et al., PRL 2005
NYU QCPS-III Workshop in Orlando

Susceptibility

In MFT: \( T_c \sim c \)
Susceptibility

\[ \chi^{-1} \text{ (arb. units)} \]

\[ T \text{ (K)} \]

\[ H_\perp \]

MFT

- 0 T
- 1 T
- 2 T
- 3 T
- 4 T
- 5 T
Phase Diagram

$T_{CW}$ decreases much more rapidly than predicted by MFT*

*MFT due to Garanin and Chudnovsky PRB 2008 & Millis et al. PRB 2010
Mean Field Theory

\[ H = - \sum_{ij} J_{ij} S_i^z S_j^z - h \sum_i S_i^x \]

\[ T_c \text{ suppressed for } \Delta \approx J \]

Quantum fluctuations destroy LRO
Diluted (x<1): not all sites are magnetic

- Randomness in spin-spin interactions, $J_{ij}$
  (for $x<0.2$ no longer a FM)
- Presence of a transverse field canting, $\langle S_x \rangle \neq 0$

Random field on $S_{zi}$
Disorder in the solvent molecules generates a discrete set of isomers with second order anisotropy and easy axis tilts


\[ \pm E(S_x^2 - S_y^2) \]

a. Most probable \( E \neq 0 \)
b. Equal populations of:

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

\[ -E(S_x^2 - S_y^2) \]

S. Takahashi et al., PRB 2004
E. del Barco, ADK, S. Hill et al., JLTP 2005

→ Easy axis tilts up to 1.7 deg
Randomness in $\text{Mn}_{12}$-acetate

- Applied transverse magnetic field, $H_{\perp}$, is perpendicular to the crystal c-axis but NOT the spin quantization axis of the tilted molecules.

**easy axis tilts $\Rightarrow$ random field**

- Some of the tilted molecules experience a field, $H_{||}$, along their easy axis.
- Isomers are distributed randomly.
- Random distribution gives rise to random-field along the easy axis of tilted molecules.
Randomness in Mn$_{12}$-acetate

- Transverse field leads directly to a random field longitudinal field on misaligned sites (red spins)
- These spins “freeze-out” (become ‘slave’ to the random field for $h_{\text{rand}} \sim J_{ij}$) and cannot participate in the LRO
- This leads to an effective dilution which reduces $T_c$ and produces an additional random field
Including Randomness in Theory

\[ H = - \sum_{ij} J_{ij} S_i^z S_j^z - \hbar \sum_i S_i^x - \sum_i h_{i}^{\text{rand}} S_i^z \]

\[ h_{\text{rand}} \neq 0 \quad T_c \text{ suppressed when } h_{\text{rand}} \sim J \]

3 T \sin (1^\circ) \simeq 50 \text{ mT}

McHugh et al., PRB 79, 052404 (2009)
Model Hamiltonian

Hamiltonian for interacting Ising spins in transverse field that includes random fields

\[
\mathcal{H} = \mathcal{H}_{mol}^0 + \mathcal{H}_{mol}^{ran,i} + \mathcal{H}_{dipole}
\]

[Millis et al. PRB 81, 024423(2010)]

\[
\mathcal{H}_{mol}^0 = -DS_z^2 - BS_z^4 + C \left( S_+^4 + S_-^4 \right) + g\mu_B \vec{H}_\perp \cdot \vec{S}_\perp
\]

\[
\mathcal{H}_{mol}^{ran,i} = \theta_i \cos(\phi_i + \phi_H) g\mu_B H_\perp S_z + E_i \left( S_x^2 - S_y^2 \right)
\]

where,

\[
\mathcal{H}_{mol}^0
\]

is a single-molecule Hamiltonian.

\[
\mathcal{H}_{mol}^{ran,i}
\]

is a site-dependent random field Hamiltonian.

\[
\theta, \phi
\]

are polar and azimuthal tilt angles.

\[
D = 0.548 \text{ K}, \quad B = 0.0012 \text{ K}, \quad C = 1.44 \times 10^{-5} \text{ K}
\]
Comparison to Experimental Data

\[ H \]_

\[ \chi^{-1} \text{ (arb. units)} \]

\[ T \text{ (K)} \]

- Pure-system
- Random-field

\[ z^* \]
Comparison to the experimental data

\[ \chi^{-1} - \chi_0^{-1}(\text{a.u.}) \]

- Cornia model (25% untilted sites)
- Cornia model with 0.2θ tilt on untilted sites

\[ T(K) \]

\[ H_\perp \]

5 T
Phase Diagram and Curie-Weiss Temperature

![Phase Diagram](image)

- **T_{CW} (K)**
- **H_\perp (T)**

- **FM**
- **PM**

- **Experimental**
- **Pure-system MFA**
- **Random-field MFA**

**Introduction**

**Experimental Setup**

**Preliminary Results**

**Theoretical Model**

**Perspectives**
Recent Results

Hall bar array

Blocking Temperature

BT cliff!

1st pair

$T_{cw} \approx 0.54$

Data now at:
- spatially resolved
- higher+lower T
Effective intermolecular spin-spin interaction position dependent crystal field

\( J_F = E_{dip} \left[ 2J_{SR} \left( \frac{c}{a} \right) + \frac{8\pi}{3} - 2\Lambda \right] \)

short-range \( J_{SR}(0.7) \approx 1.23 \)

long-range

demagnetization factor \( \Lambda(\vec{r}) \)

A. J. Millis et al., PRB 2010

\( \chi \) (arb. units)

\( T \) (K)

\( H_\perp = 0 \) T

- 1st Pair: \( \sim 0.56 \) K
- 2nd Pair: \( \sim 0.97 \) K
- 3rd Pair: \( \sim 0.98 \) K

1st Pair: \( \sim 0.54 \) K
2nd Pair: \( \sim 0.88 \) K
3rd Pair: \( \sim 1.15 \) K

Spatially Resolved Susceptibility Measurements
SQUID Data

\[ \theta = \theta_{cw}(c/a) - CN_m(lc/la) \]

\[ H_\perp = 0 \ T \]

S. Li et al., PRB 82, 174405 (2010)
LiHo$_x$Y$_{1-x}$F$_4$ – Mn$_{12}$-acetates

• Dilution
  - random interactions
    (“SG” behavior for x<0.2)

• Transverse field
  - spin-canting+dipole interactions produces a random field along the Ising axis
    randomly located spins that are uniformly polarized along x
    produce a random field along z.

• Hyperfine interactions ~ dipolar interactions

• Critical behavior can be studied experimentally

• No dilution
  - In zero-transverse field Mn$_{12}$-ac is essentially a pure Ising system

• Transverse field
  - random field along the Ising axis of misaligned molecules
    large random fields
    misaligned spins `slave’ to random field and do not order
    randomly located and randomly polarized `slave’ spins produce an additional random field along the Ising axis*

• Weak hyperfine interactions

• Slow QTM relaxation
  prevents study of the critical behavior (at least for now).

*not included in mft (i.e. Millis et al, ArXiv:2009)
Summary

• $\text{Mn}_{12}$-ac is an experimental realization of random field Ising ferromagnetism (RFIFM) in SMMs
• From the susceptibility’s dependence on the transverse magnetic field and temperature, we can get quantitative information about the strength and the distribution of the random field
• The random field can be externally tunable via the transverse field.

A. J. Millis et al., PRB 81, 024423 (2010)
B. Wen et al., PRB 82, 014406 (2010)
S. Li et al., PRB 82, 174405 (2010)
Open Questions/Research Directions in RFIFM

- Test model of disorder in Mn_{12}-ac.
- SMM with larger quantum fluctuations to enable study of the of PM->FM phase transition and the quantum critical point
- Vary the scale of the random fields
- Examine the domain structure and relaxation into FM phase
- Vary lattice parameters c/a to vary intermolecular interactions (including exchange interactions).