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

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Collaborators

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- Yosi Yeshurun (Bar-Ilan)
- Shreya Mukherjee, Christos Lampropoulos, George Christou (UF)
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Outline

I. Introduction

-Motivation: study for long range order in Mn_{12}-ac

-Energy scales in Mn_{12}-acetate

II. Experiment

-Setup/measurements

-Susceptibility data

-Experimental phase diagram

III. Models

-Comparison to MFT

-Why randomness is needed?

-Our random field model

IV. Recent Results: Hall bar array, SQUID results

V. Summary/Perspectives

Long Range Order due to Dipolar Interactions in Mn_{12}-Ac.

Potential realization of a transverse field Ising system

LRO ⟷ Quantum Fluctuations

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

<u>A ferromagnetic phase was predicted:</u>

-Fernandez and Alonso, PRB 2000
-Garanin and Chudnovsky, PRB 2008

Interesting ferromagnetic domain dynamics predicted

<u>Neutron scattering data shows low-T ferromagnetic order:</u>

-Luis *et al.*, PRL 2005

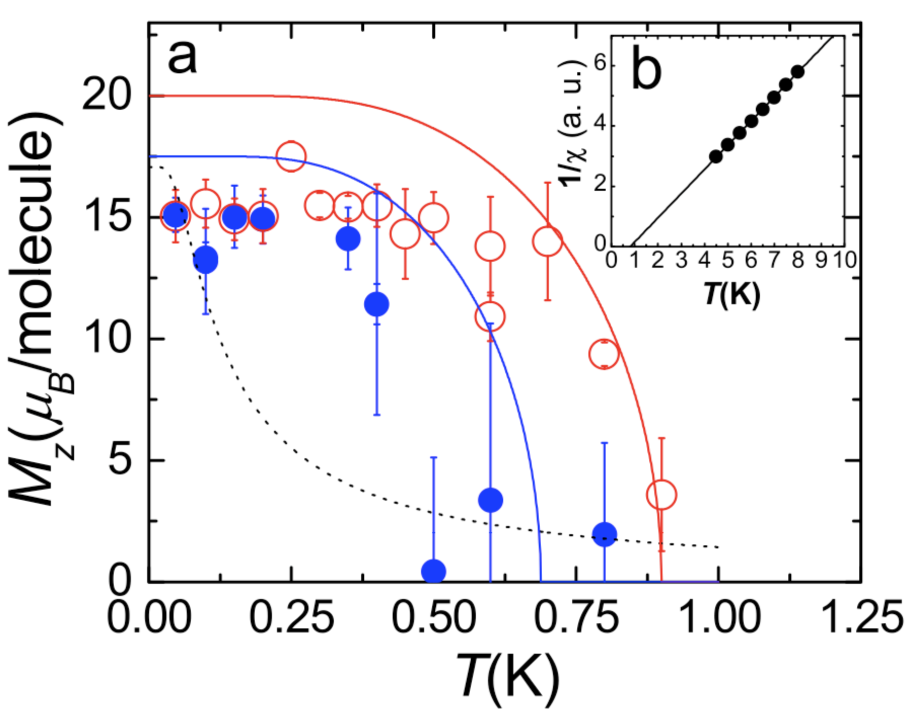
<u>Magnetic susceptibility had not been studied as a function of transverse field</u>

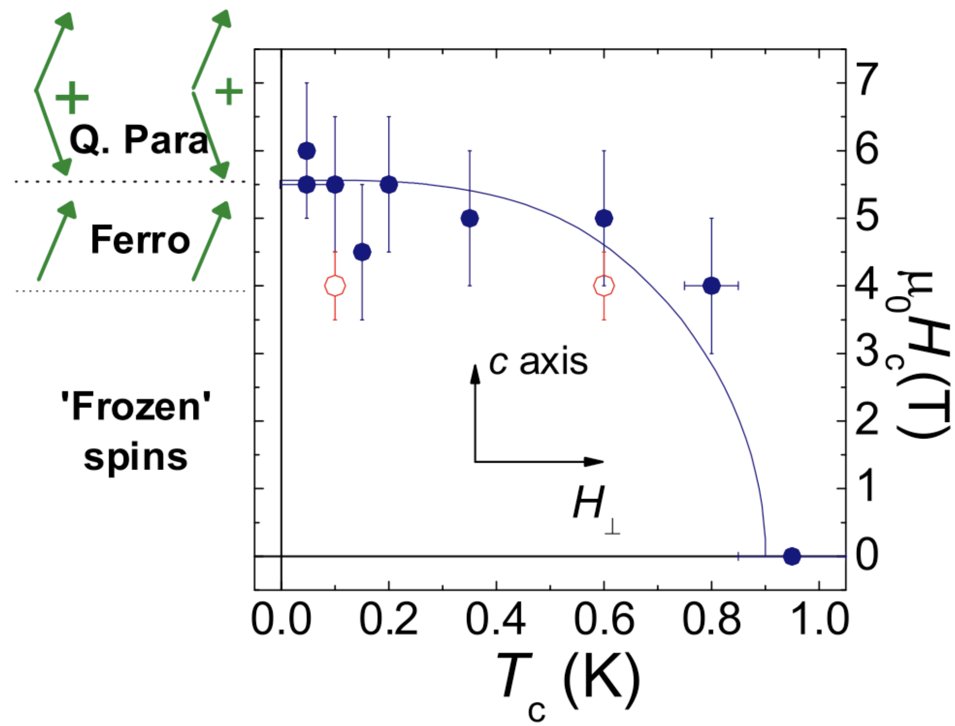
Neutron Scattering Study

PRL **95,** 227202 (2005) PHYSICAL REVIEW LETTERS week ending 25 NOVEMBER 2005

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

F. Luis,[1,*] 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_{12}-acetate

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

Magnetic Core

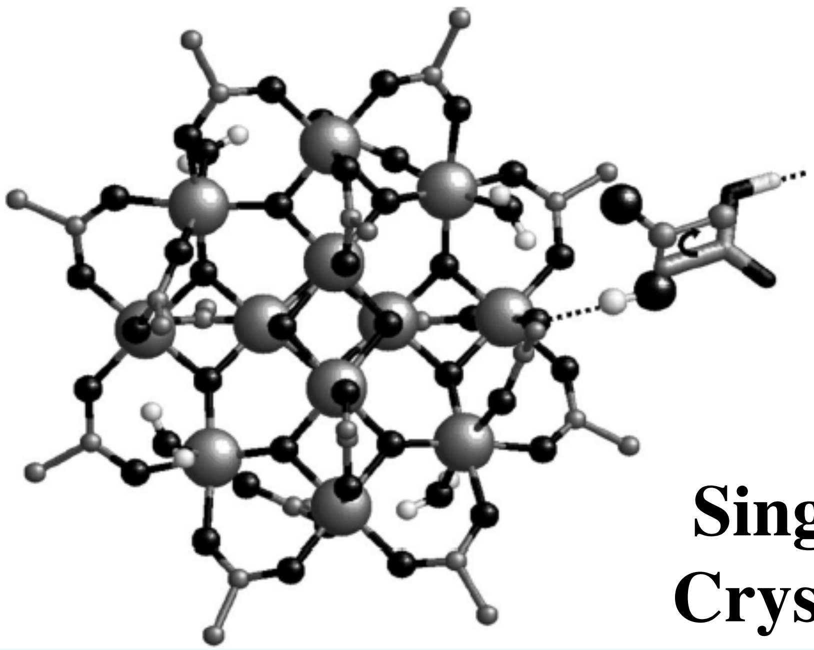
8 Mn^{3+} S=2
4 Mn^{4+} S=3/2

Competing AFM Interactions

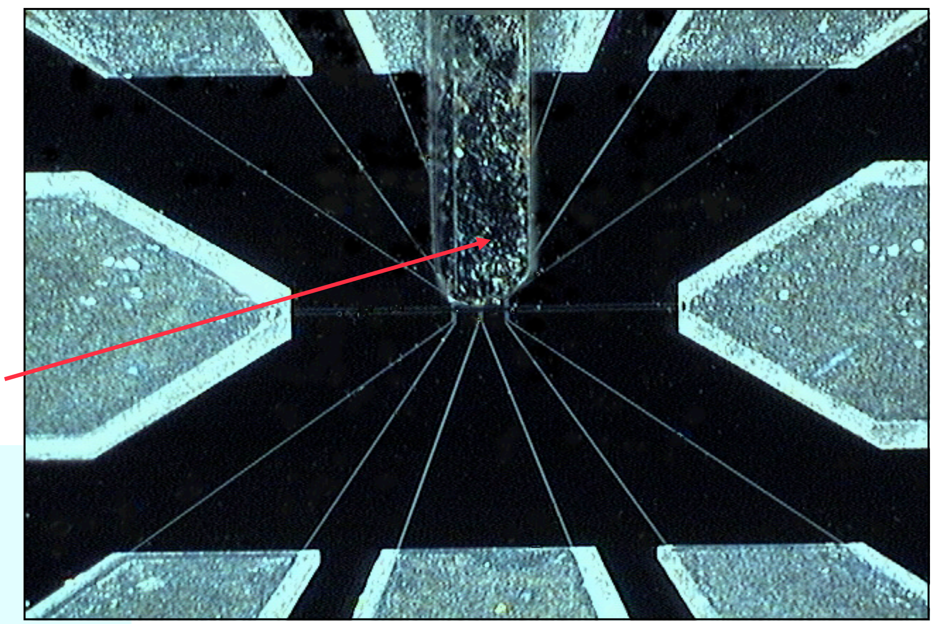
Ground state S=10

Organic Environment

2 acetic acid molecules
4 water molecules



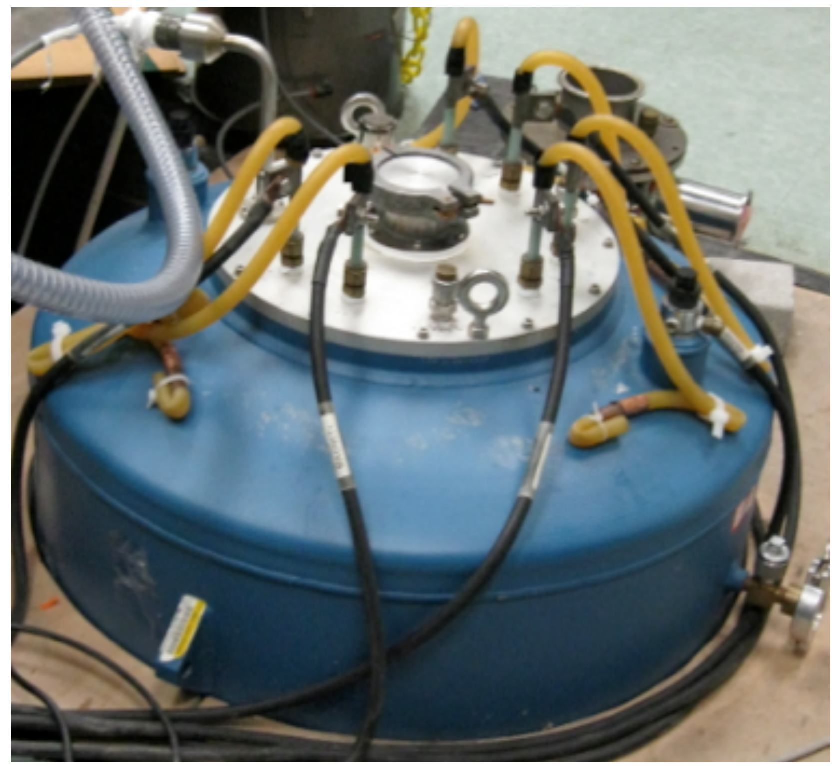
Single Crystal



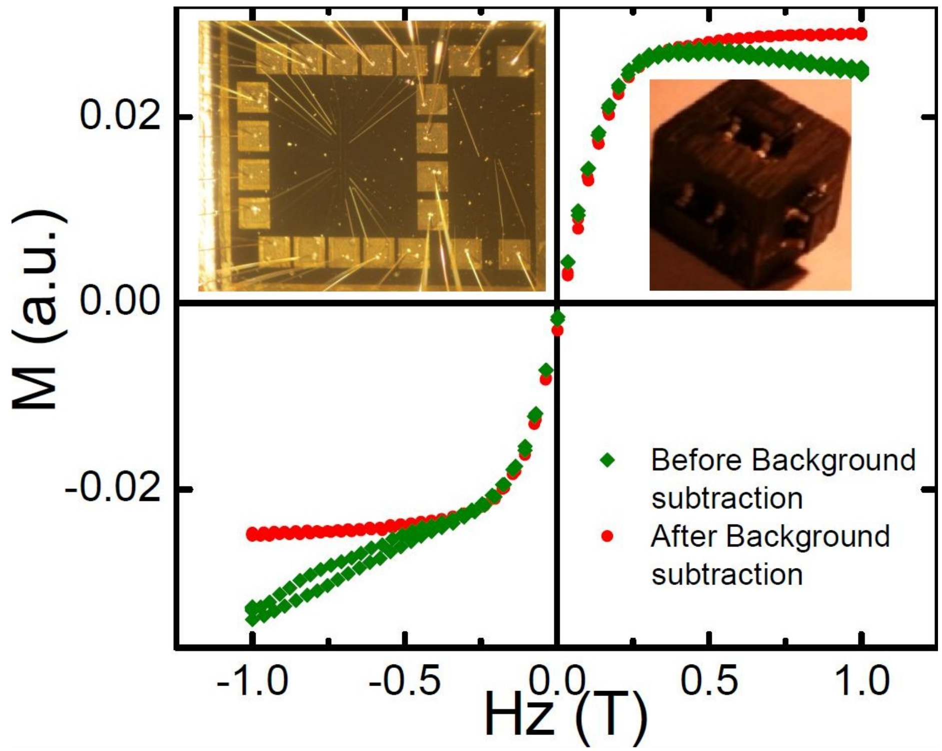
- S_4 site symmetry
- Body centered tetragonal lattice a=1.7 nm, b=1.2 nm
- Strong uniaxial magnetic anisotropy (~60 K)
- Weak intermolecular dipole interactions (~0.1 K)
- Discrete disorder

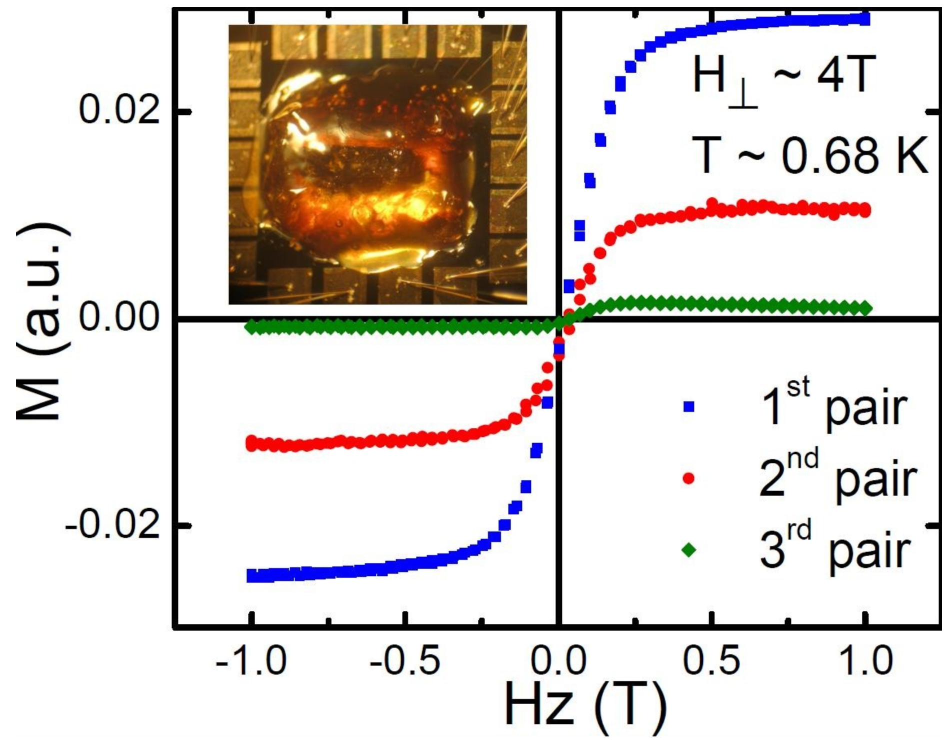
Experimental Setup

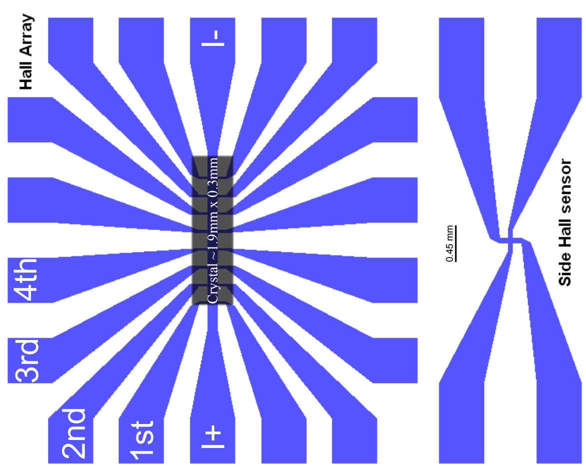
Measurements taken between 0.4 K to 6 K in a ^{3}He refrigerator with a 3D superconducting vector magnet.



Experimental Setup







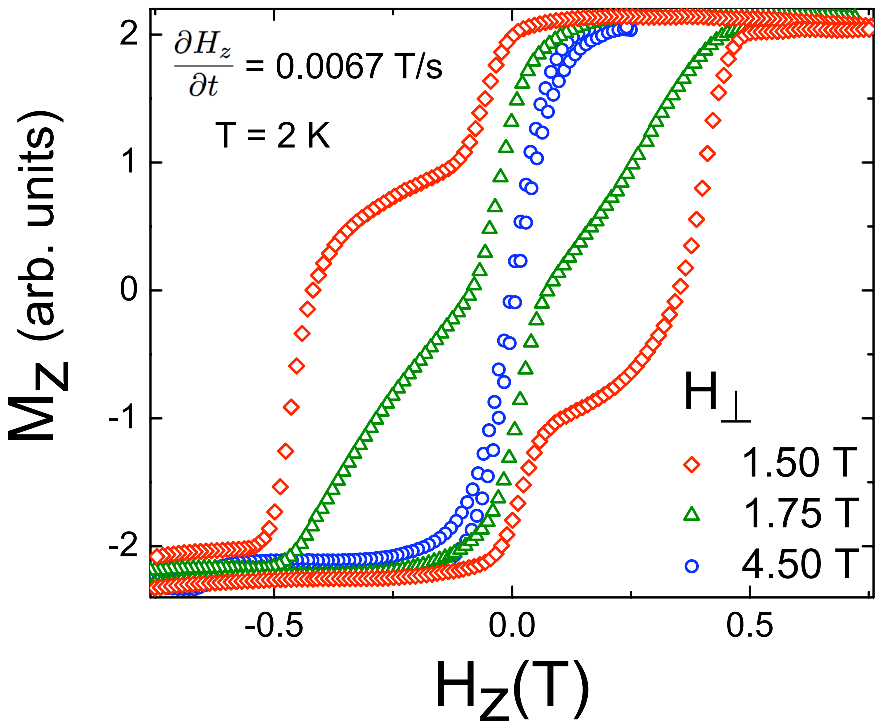
Crystal dimensions

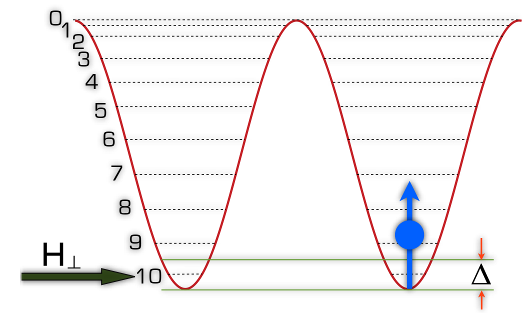
$\sim 0.4 \times 0.4 \times 2.17\ \mathrm{mm}^3$

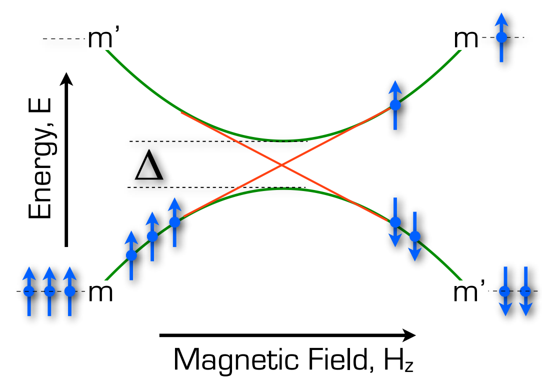
New to experimental setup:

1) Hall bar array
2) Reference Hall bar
3) Measure the applied field

Quantum Tunneling of Magnetization

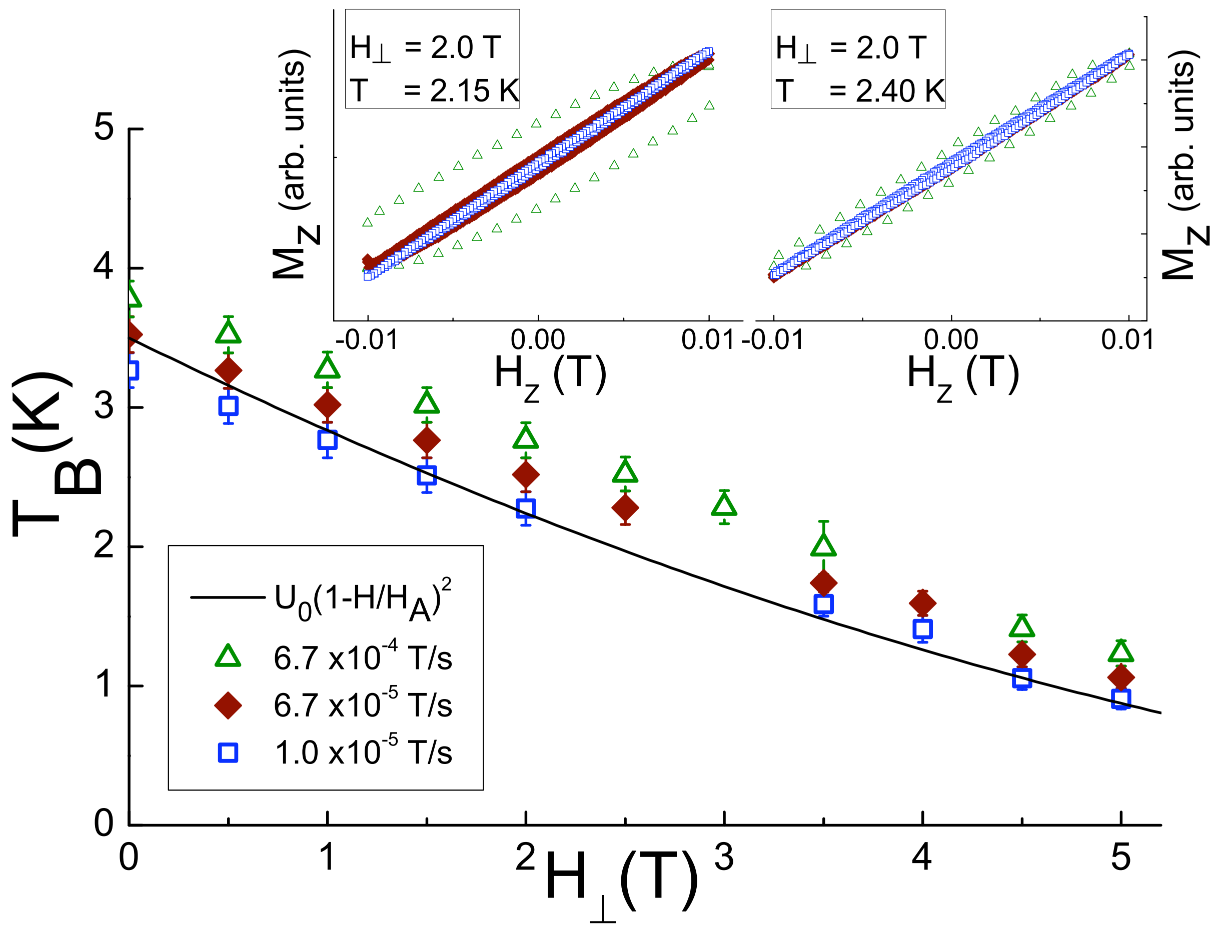






- Applying $H_\perp$ breaks the symmetry and lifts the degeneracies by mixing the eigenstates of $\hat{S}_z$.
- Increasing $H_\perp$ promotes quantum tunneling, accelerating the relaxation towards thermal equilibrium.

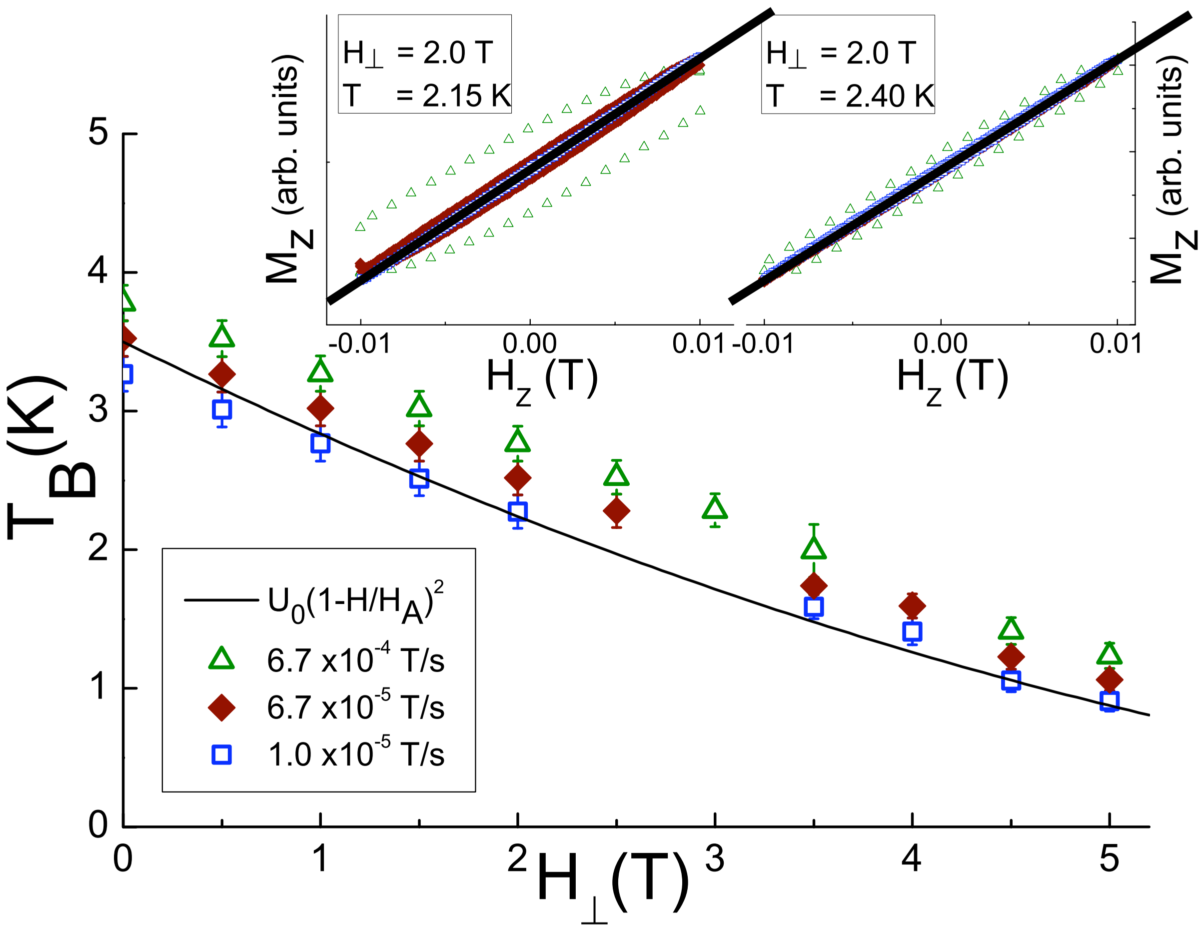
Blocking Temperature



- T_B depends on sweep rate and transverse field.
- $T_B = \dfrac{U}{k_B \ln\left(\frac{t_m}{\tau_0}\right)}$

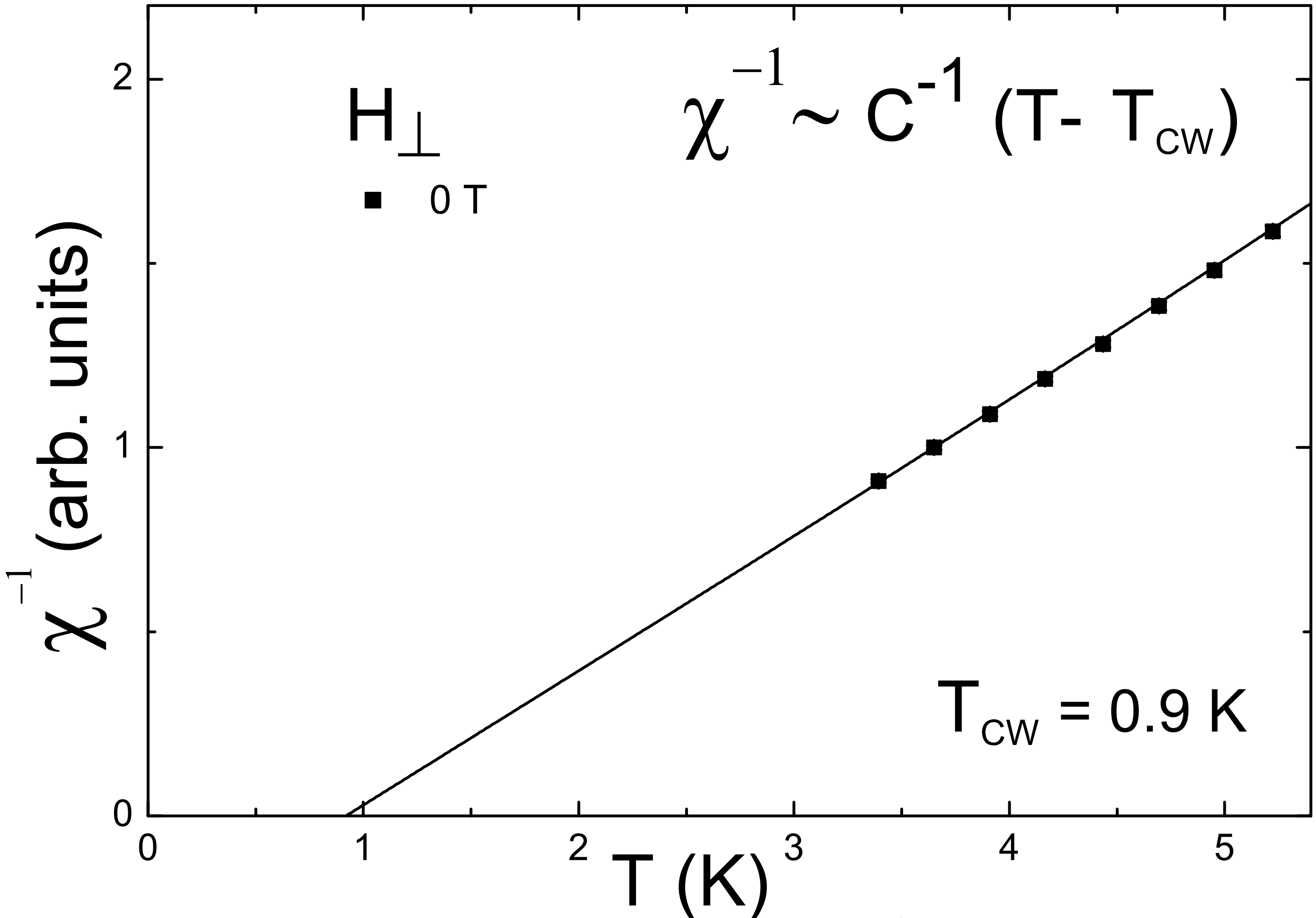
-The equilibrium susceptibility can be measured for $T > T_B(H_\perp)$

Blocking Temperature



- T_B depends on sweep rate and transverse field.
- $T_B = \dfrac{U}{k_B \ln\left(\frac{t_m}{\tau_0}\right)}$
- $\chi = \partial M_z / \partial H_z |_{H_z=0}$ in equilibrium.

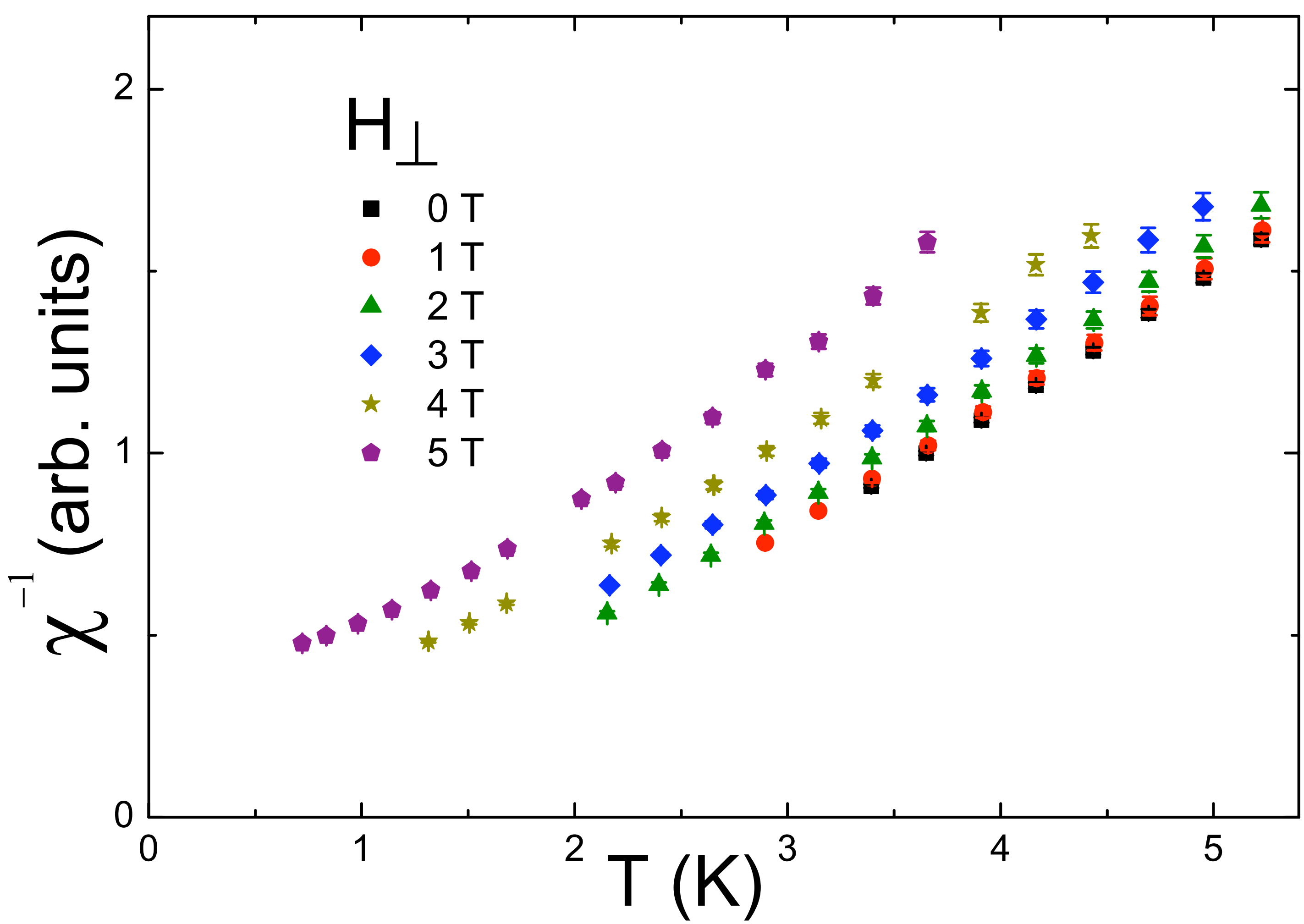
Susceptibility



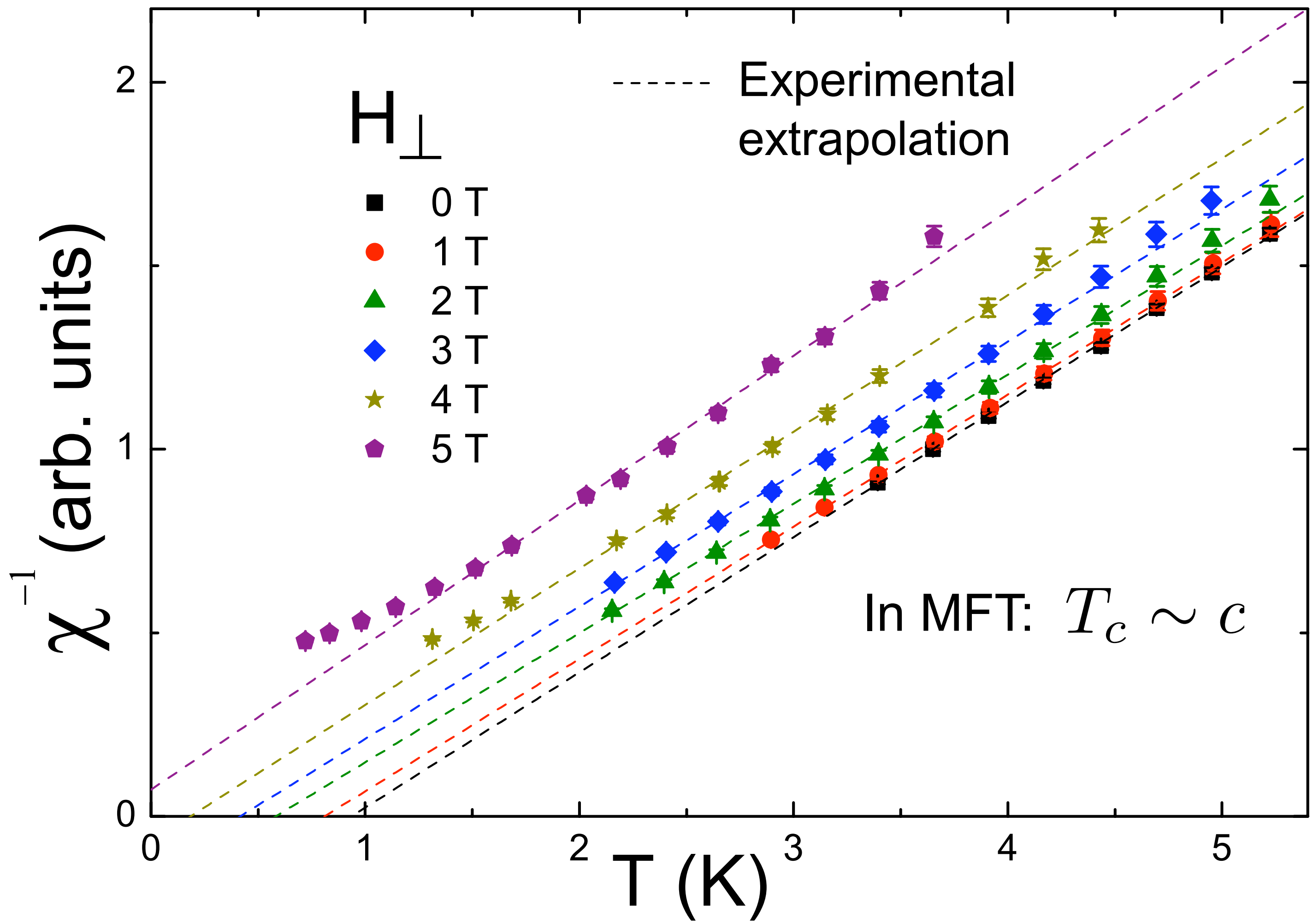
Data follows a Curie-Weiss law* $\chi^{-1} \sim C^{-1}\,(T - T_{CW})$

*as shown in F. Luis et al., PRL 2005

Susceptibility



Susceptibility



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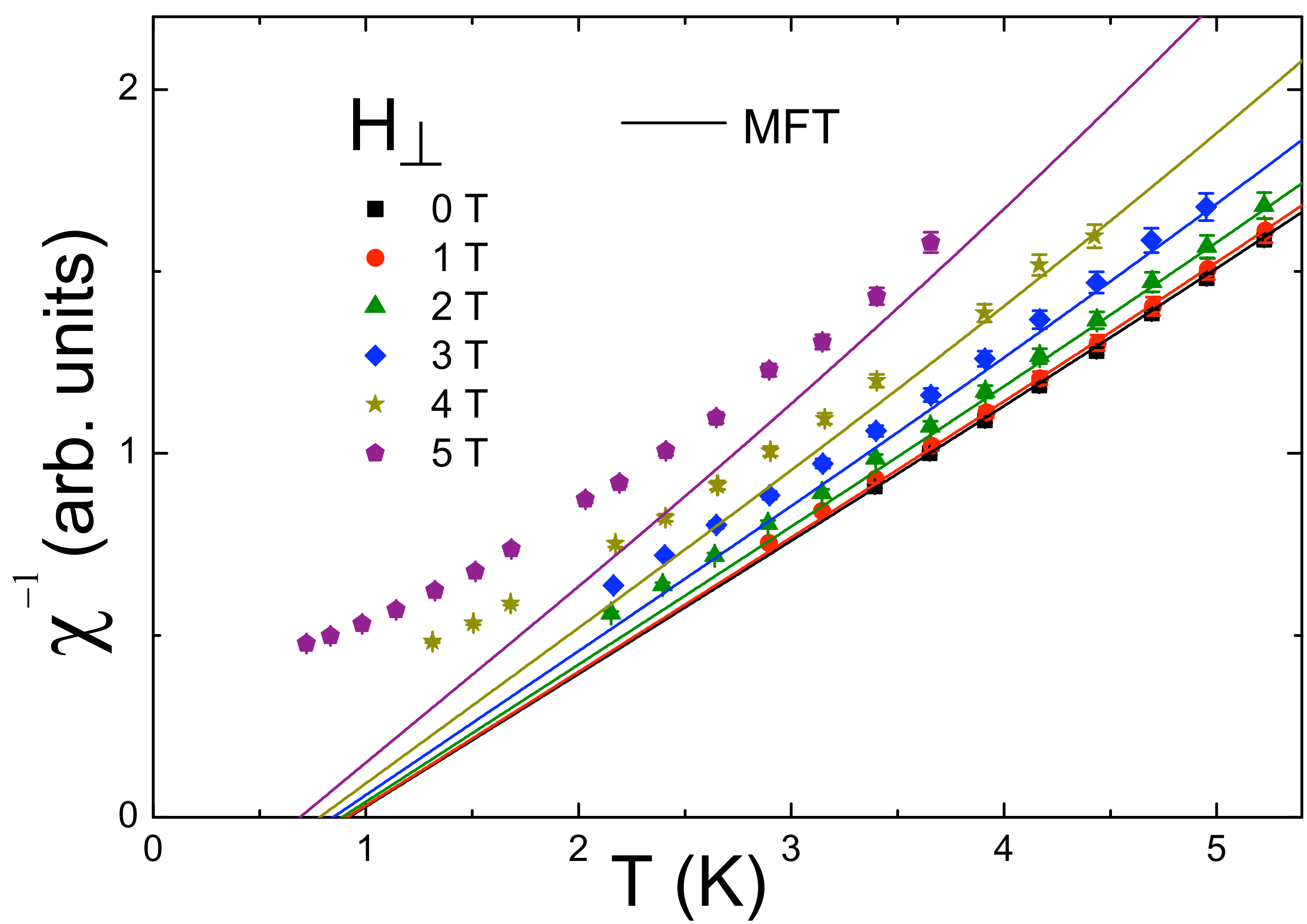
Susceptibility



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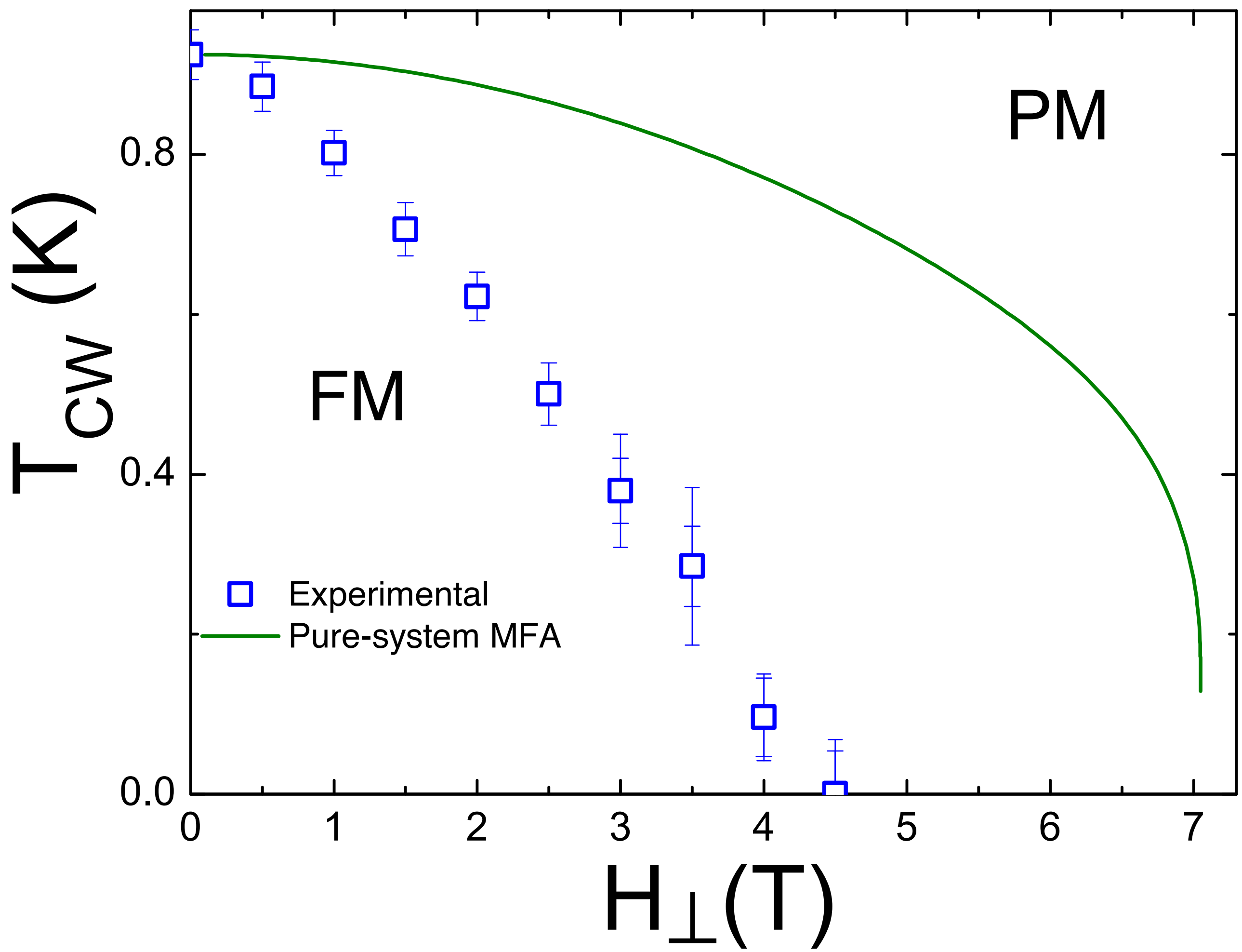
Phase Diagram



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

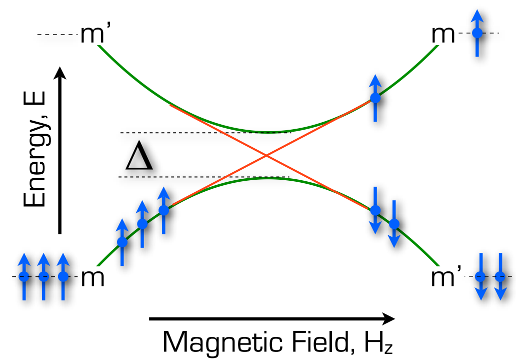
*MFT due to Garanin and Chudnovsky PRB 2008 & Millis et al. PRB 2010

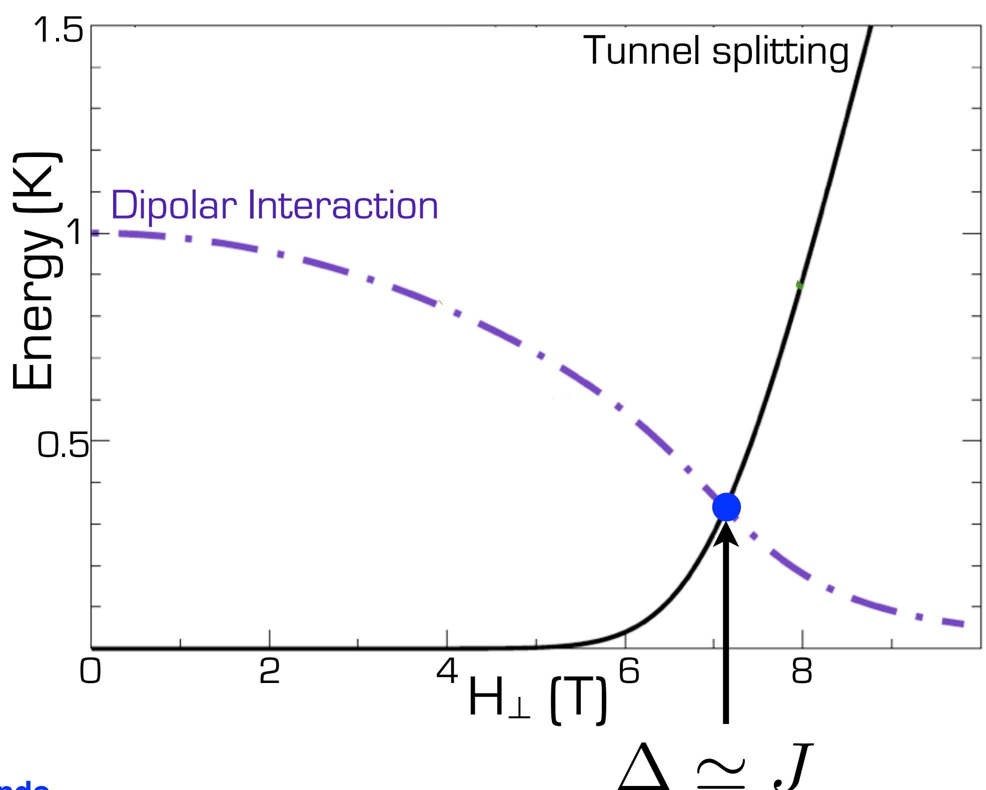
Mean Field Theory

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

T_c suppressed for $\Delta \simeq J$

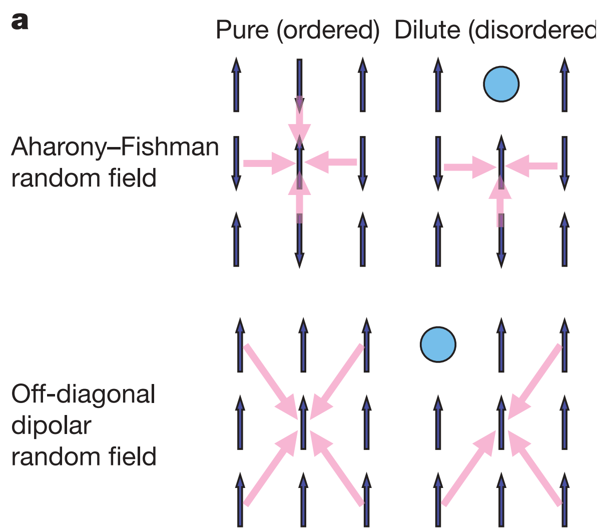
Quantum fluctuations destroy LRO

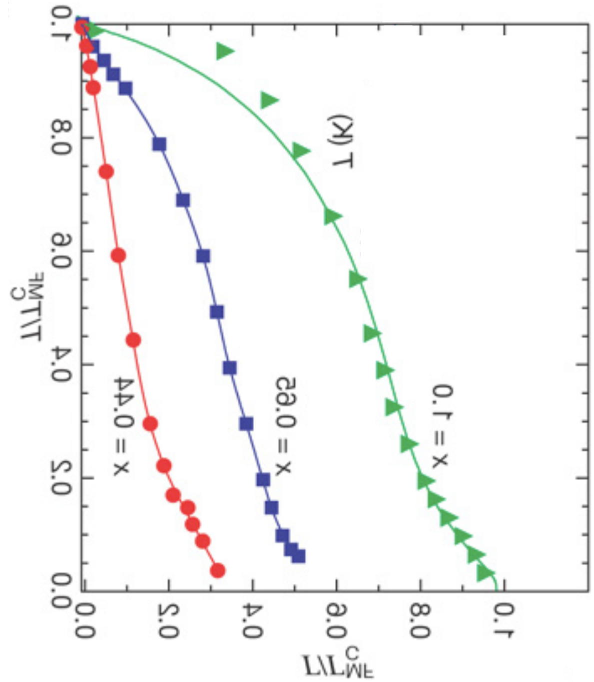




Ordering due to Dipole Interactions

Phase diagram is similar to that of $LiHo_xY_{1-x}F_4$





<u>Diluted (x<1)</u>: not all sites are magnetic

- Randomness in spin-spin interactions, J_{ij}

  (for $x<0.2$ no longer a FM)

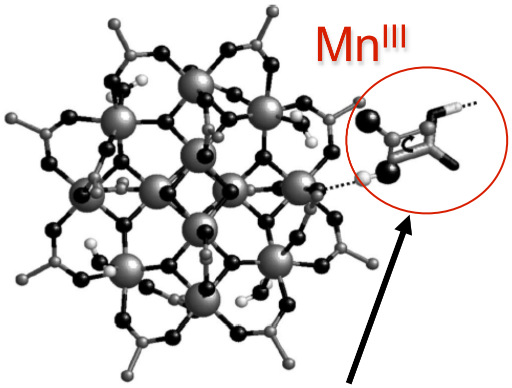
- Presence of a transverse field canting, $<S_x>\neq 0$

  Random field on S_{zi}

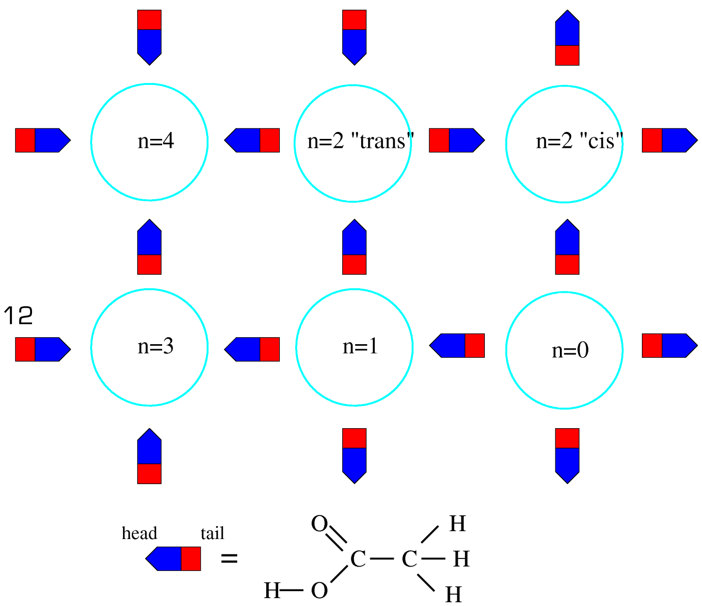
Randomness in Mn_{12}-acetate

Disorder in the solvent molecules generates a discrete set of isomers with second order anisotropy and easy axis tilts

A. Cornia *et al.*, *Phys. Rev. Lett.* **89**, 257201 (2002)



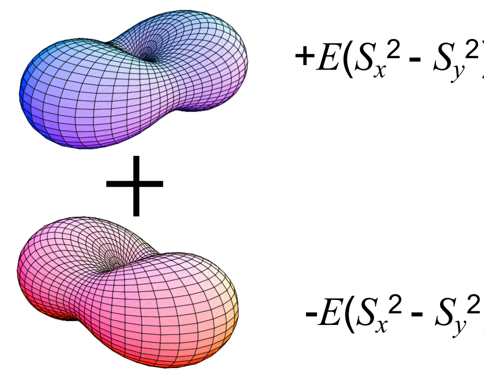
average of 2 CH_3COOH molecules per Mn_{12} with 4 possible positions

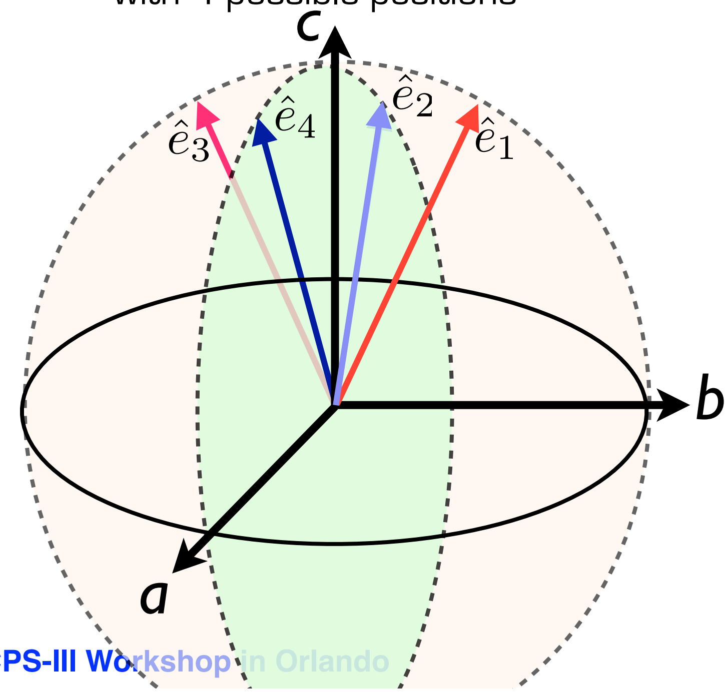


$$\pm E(S_x^2 - S_y^2)$$

a. Most probable $E \neq 0$

b. Equal populations of:





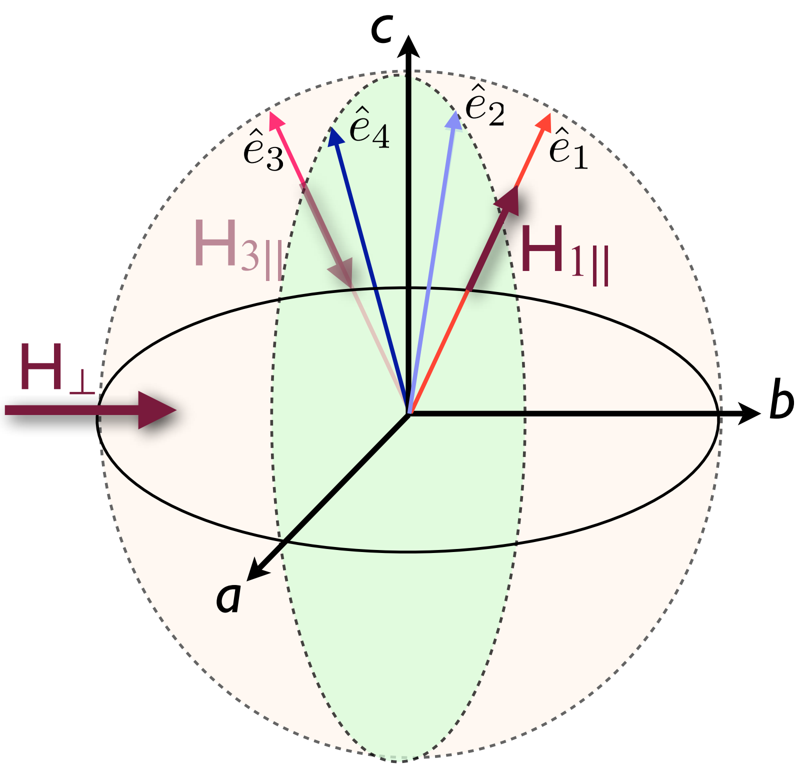
S. Takahashi *et al.*, PRB 2004

E. del Barco, ADK, S. Hill *et al.*, JLTP 2005

→ Easy axis tilts up to 1.7 deg

Randomness in Mn_{12}-acetate

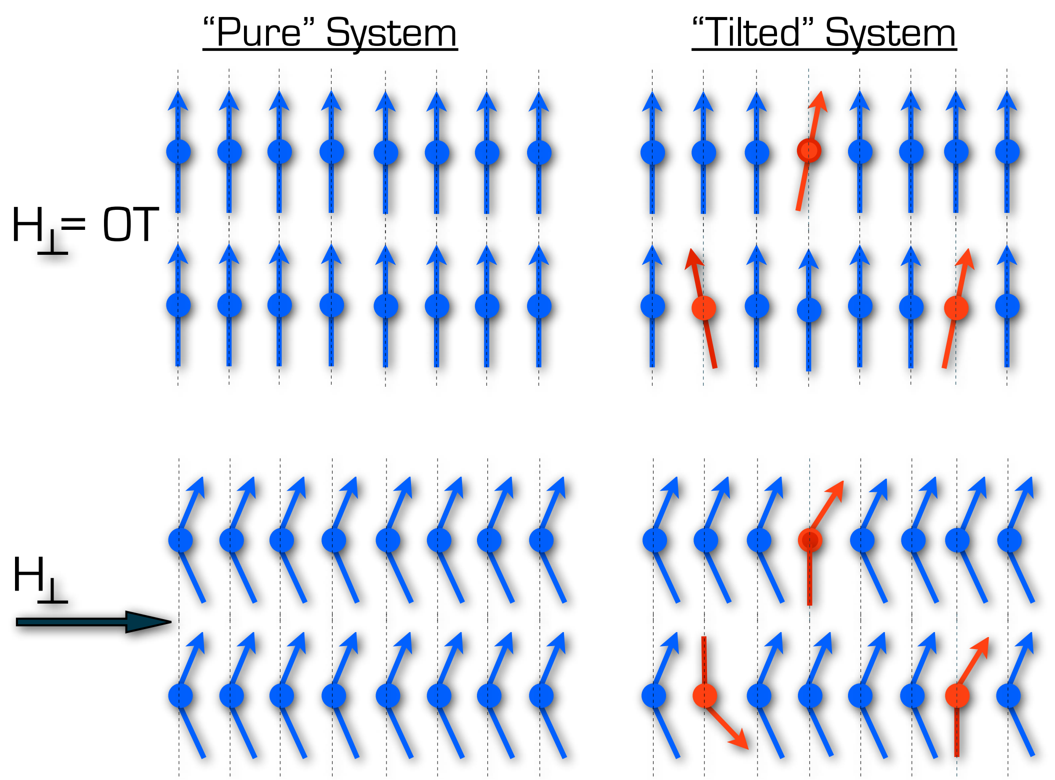
- Applied transverse magnetic field, $H_\perp$, is perpendicular to the crystal c-axis but NOT the spin quantization axis of the tilted molecules.



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

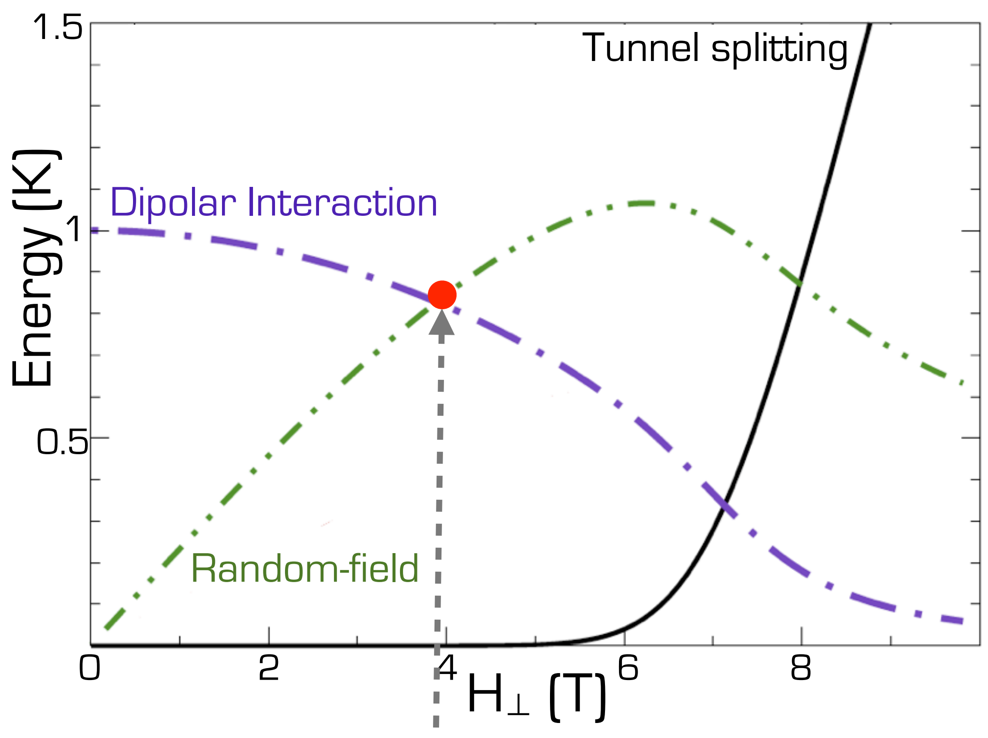


- Transverse field leads directly to a random field longitudinal field on misaligned sites (red spins)
- These spins "freeze-out" (become 'slave' to the random field for $h_{rand} \sim J_{ij}$) and cannot participate in the LRO
- This leads to an effective dilution which reduces T_c and produces an additional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

Including Randomness in Theory

$$H = -\sum_{ij} J_{ij} S_i^z S_j^z - h \sum_i S_i^x - \sum_i h_i^{\text{rand}} S_i^z$$

<u>$h^{\text{rand}} \neq 0$</u> T_c suppressed when $h^{\text{rand}} \simeq J$



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

$h^{\text{rand}} \simeq J$

McHugh *et al.*, PRB **79**, 052404 (2009)

Model Hamiltonian

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

$$\mathcal{H} = \mathcal{H}^0_{mol} + \mathcal{H}^{ran,i}_{mol} + \mathcal{H}_{dipole}$$ [Millis *et al.* *PRB* **81,** 024423(2010)]

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

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

where,

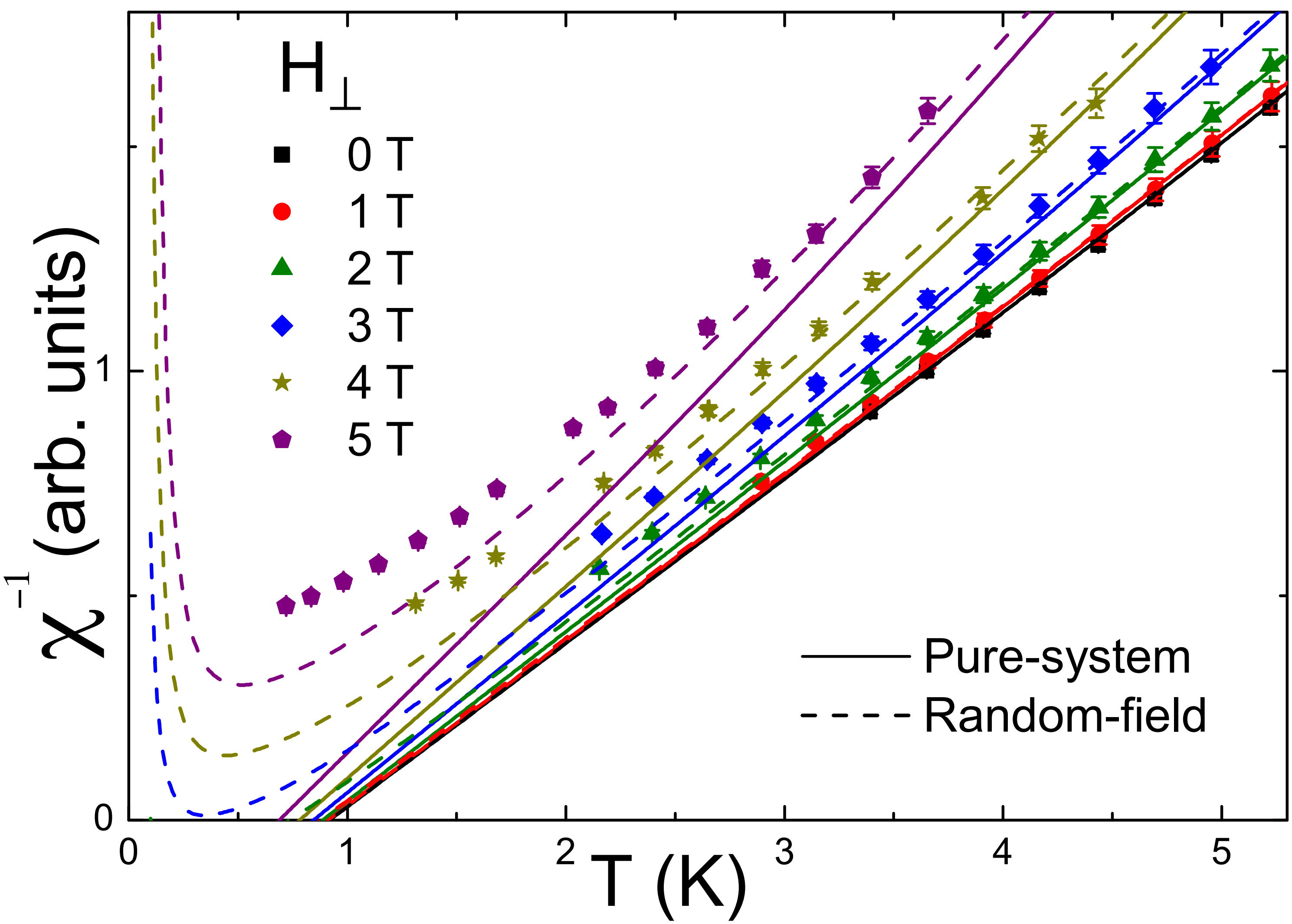
$\mathcal{H}^0_{mol}$ is a single-molecule Hamiltonian.

$\mathcal{H}^{ran,i}_{mol}$ is a site-dependent random field Hamiltonian.

θ, ϕ are polar and azimuthal tilt angles.

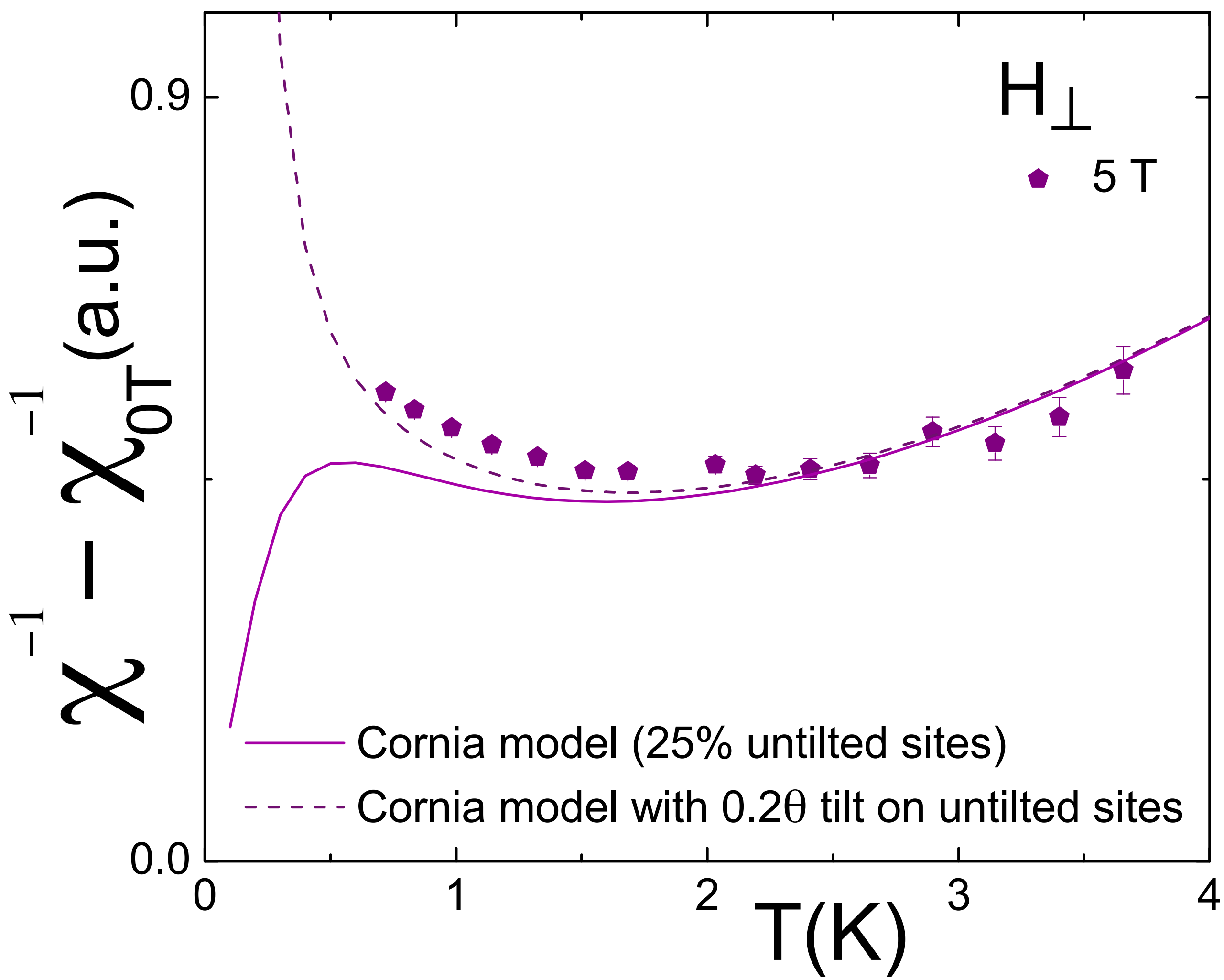
$D = 0.548$ K, $B = 0.0012$ K, $C = 1.44 \times 10^{-5}$ K

Comparison to Experimental Data

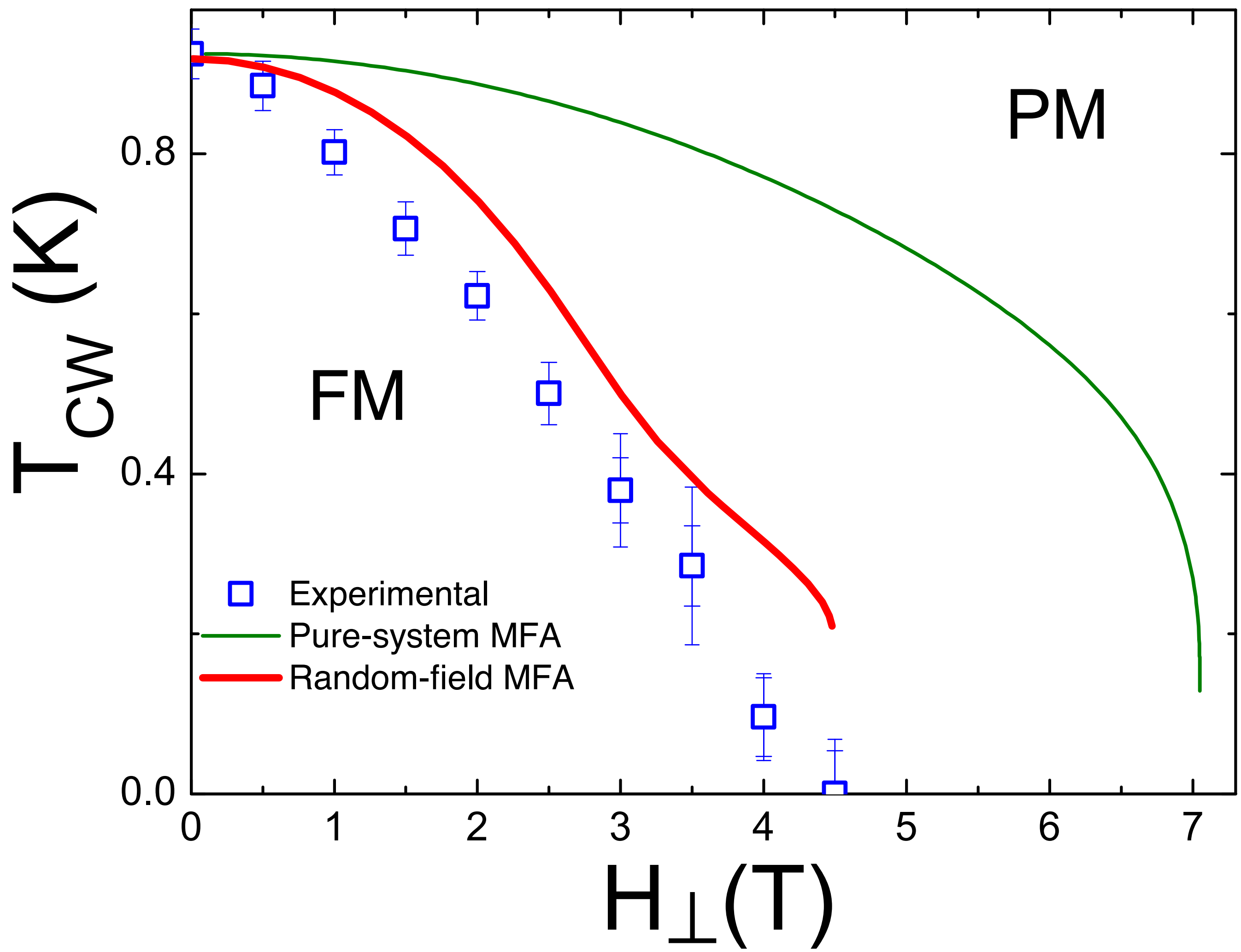


•z

Comparison to the experimental data

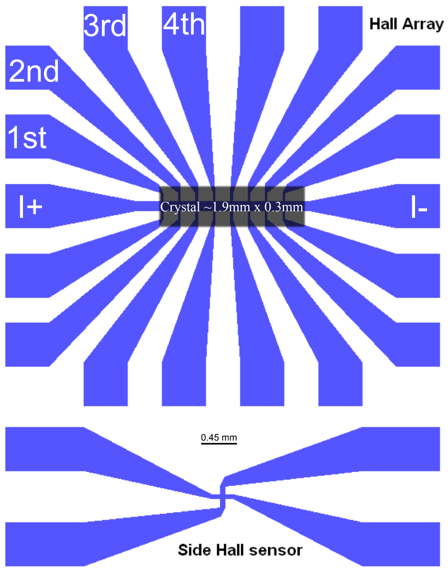


Phase Diagram and Curie-Weiss Temperature

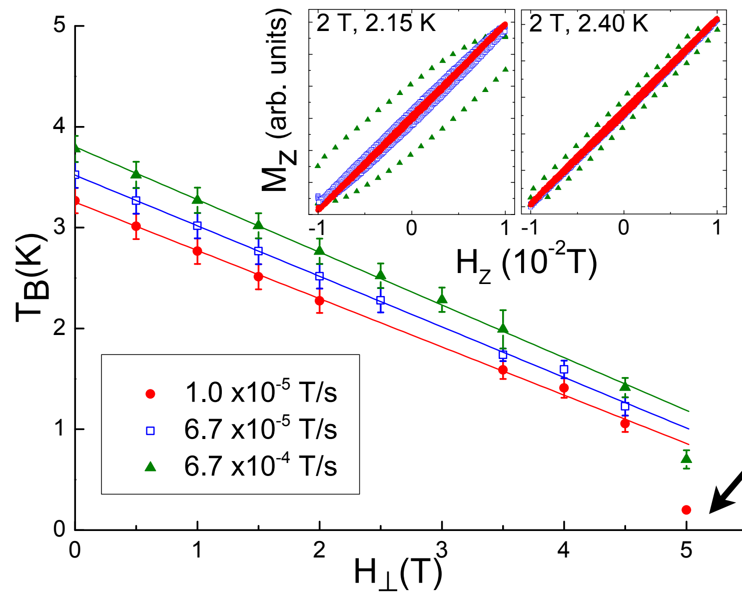


Recent Results

Hall bar array



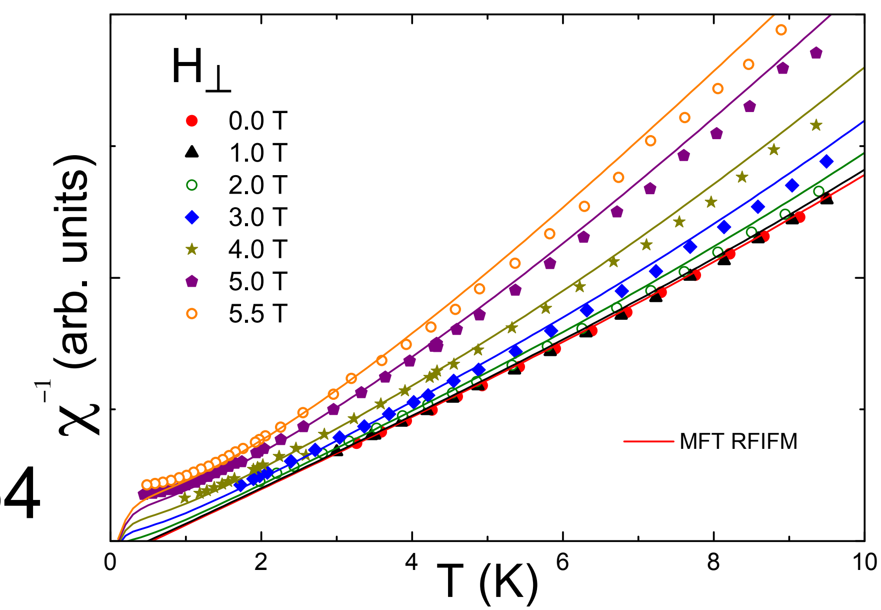
Blocking Temperature



BT cliff!

1st pair

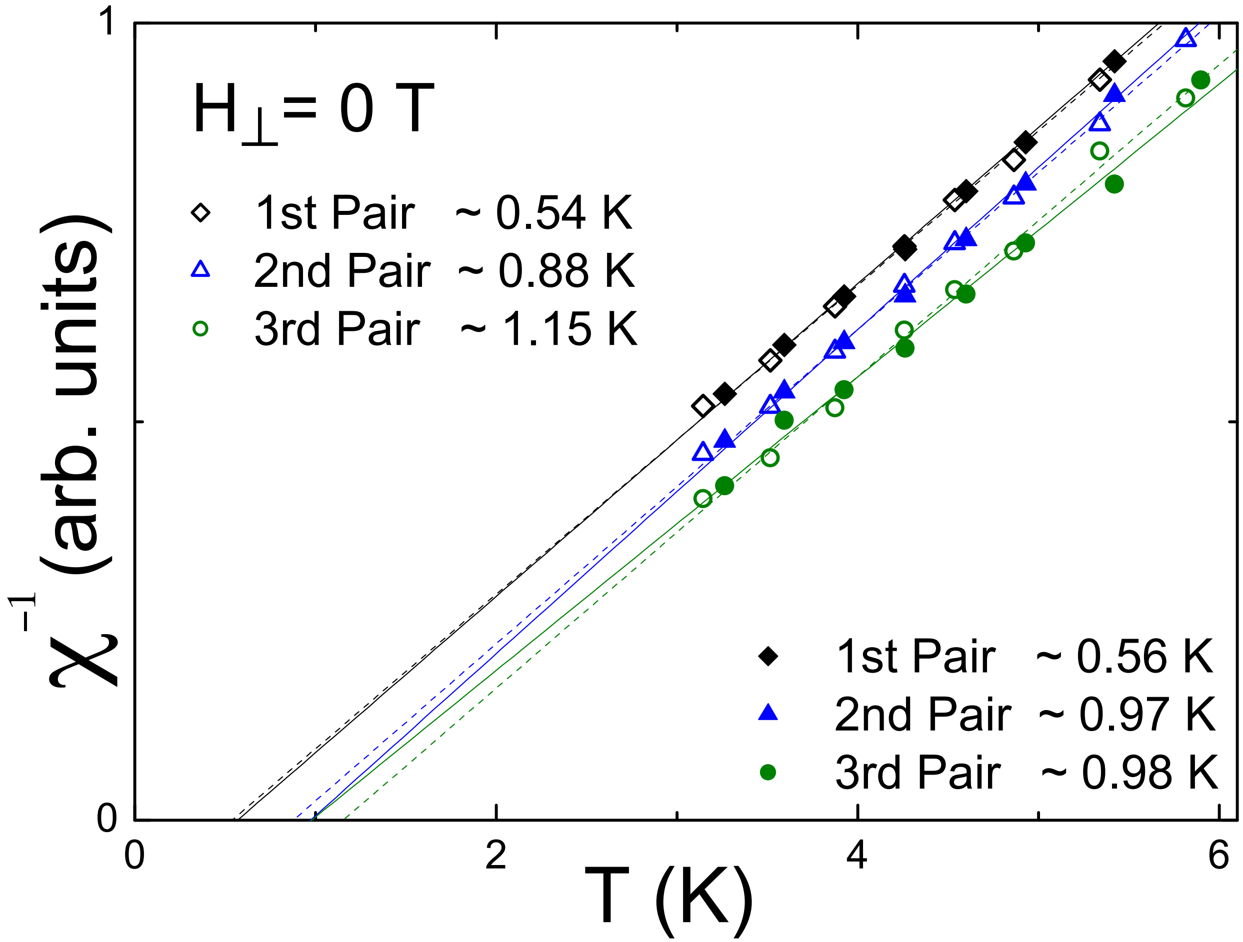
T_{cw}~0.54



<u>Data now at:</u>

-spatially resolved
-higher+lower T

Spatially Resolved Susceptibility Measurements



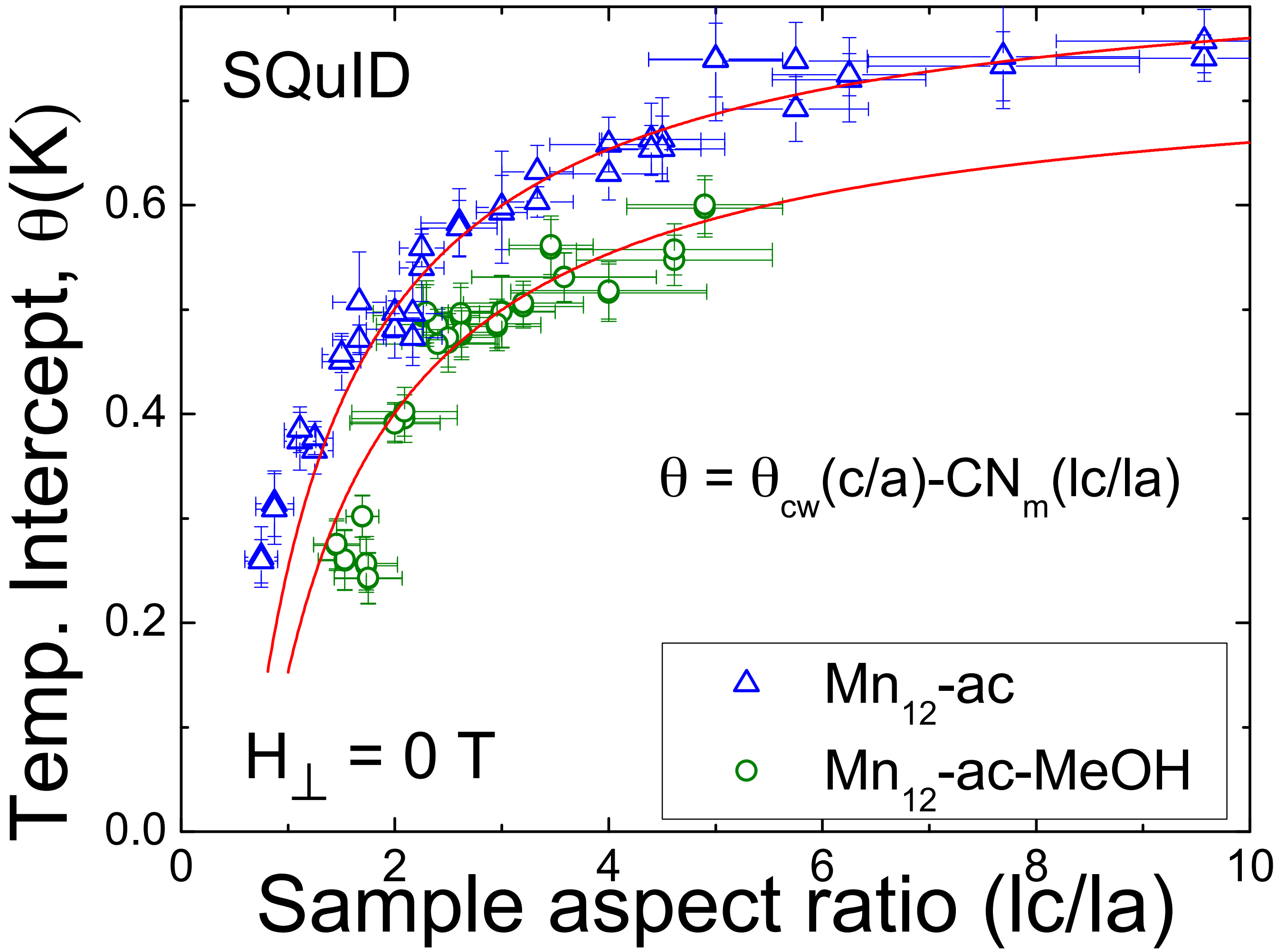
Effective intermolecule spin-spin interaction position dependent crystal

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

A. J. Millis *et al.*, PRB 2010

short-range $J_{SR}(0.7) \approx 1.23$ long-range demagnetization factor $\Lambda(\vec{r})$

SQUID Data



S. Li et al., PRB **82**, 174405 (2010)

$LiHo_xY_{1-x}F_4$ – 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)

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Summary

- 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)

Perspectives

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).