Random Fields in Molecular Magnets

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Supported by NSF-DMR

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OUTLINE

I - Background

(a) Molecular Magnets: Mn_{12}-acetate, Fe-8
(b) Blocking (spin reversal by tunneling, avalanches)

II - Random Field Ising Ferromagnetism (RFIFM)

(a) Ferromagnetism in Mn-12?
(b) Suppression of T_c by transverse magnetic field
(c) RFIFM – whence the randomness?
(d) Comparison with LiHoF

III – Dipole interactions?

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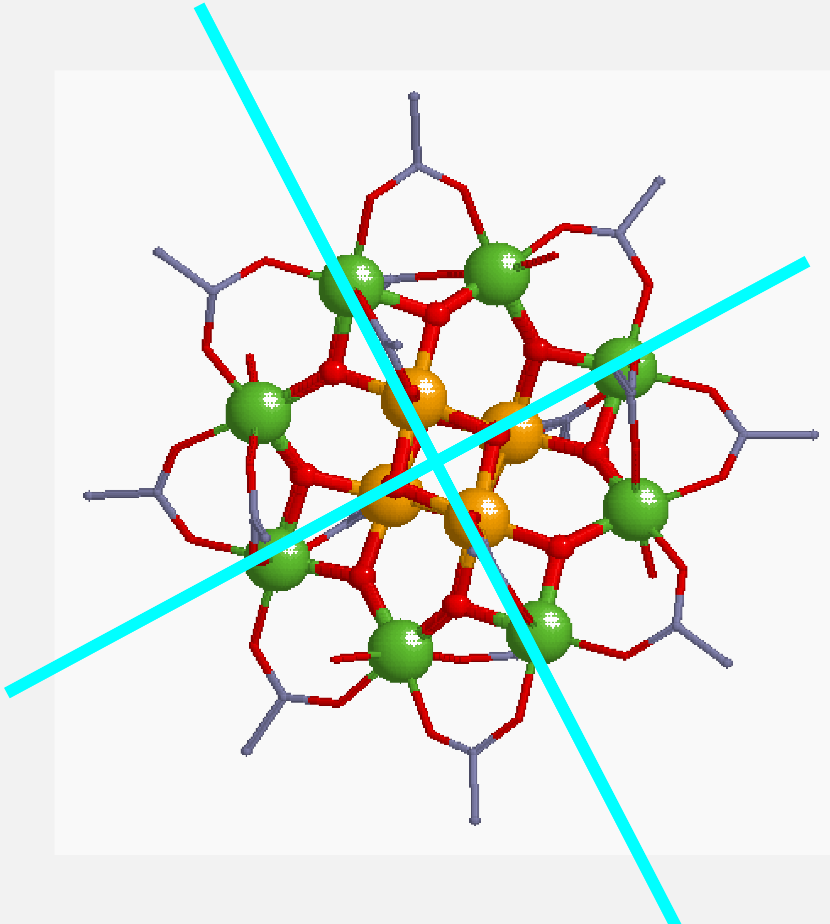
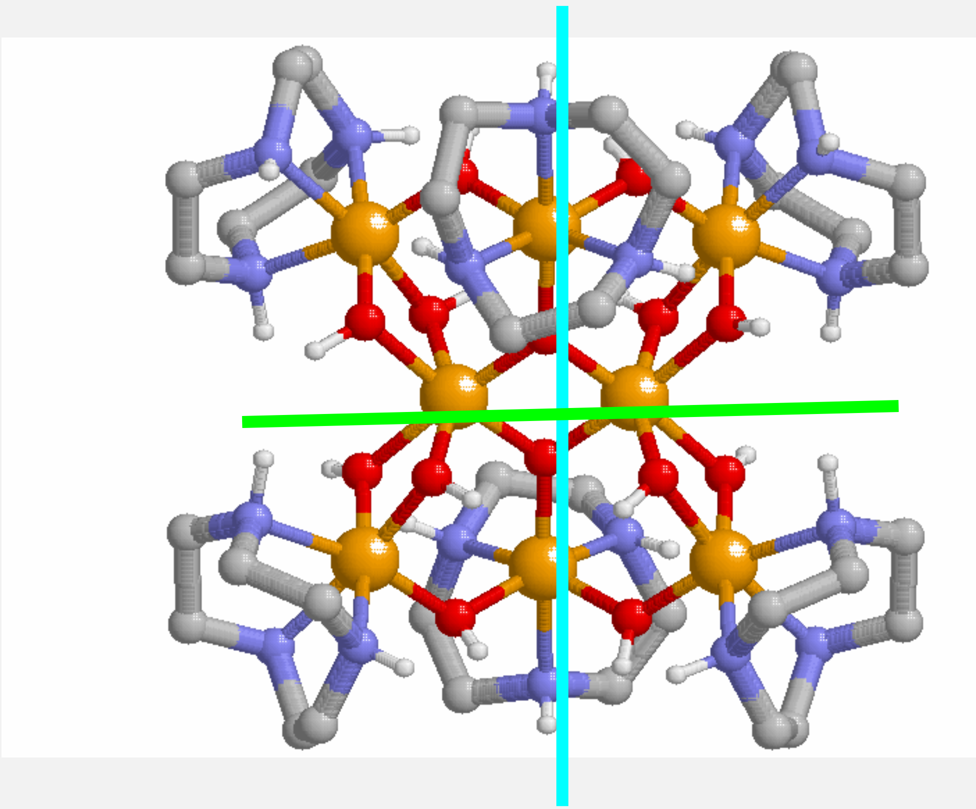
Mn12 S=10 Fe8





Four fold axis

Two fold axis

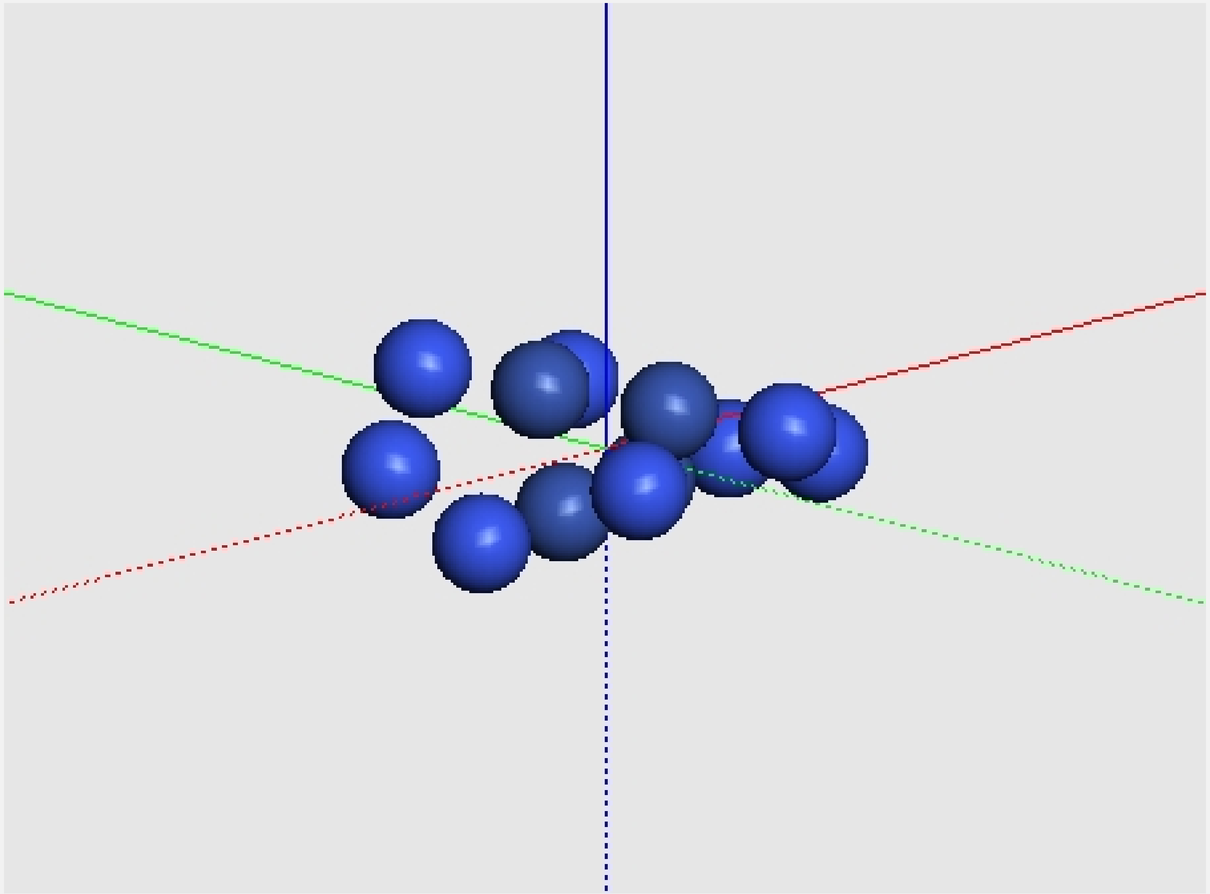
Mn_{12} Acetate Complex

A tetragonal crystal containing a large (Avogadro's) number of weakly interacting magnetically identical spin-10 molecules.

$$Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$$

Uniaxial crystal, large anisotropy ≈ 60 K

Molecular Structure of Mn_{12}-acetate

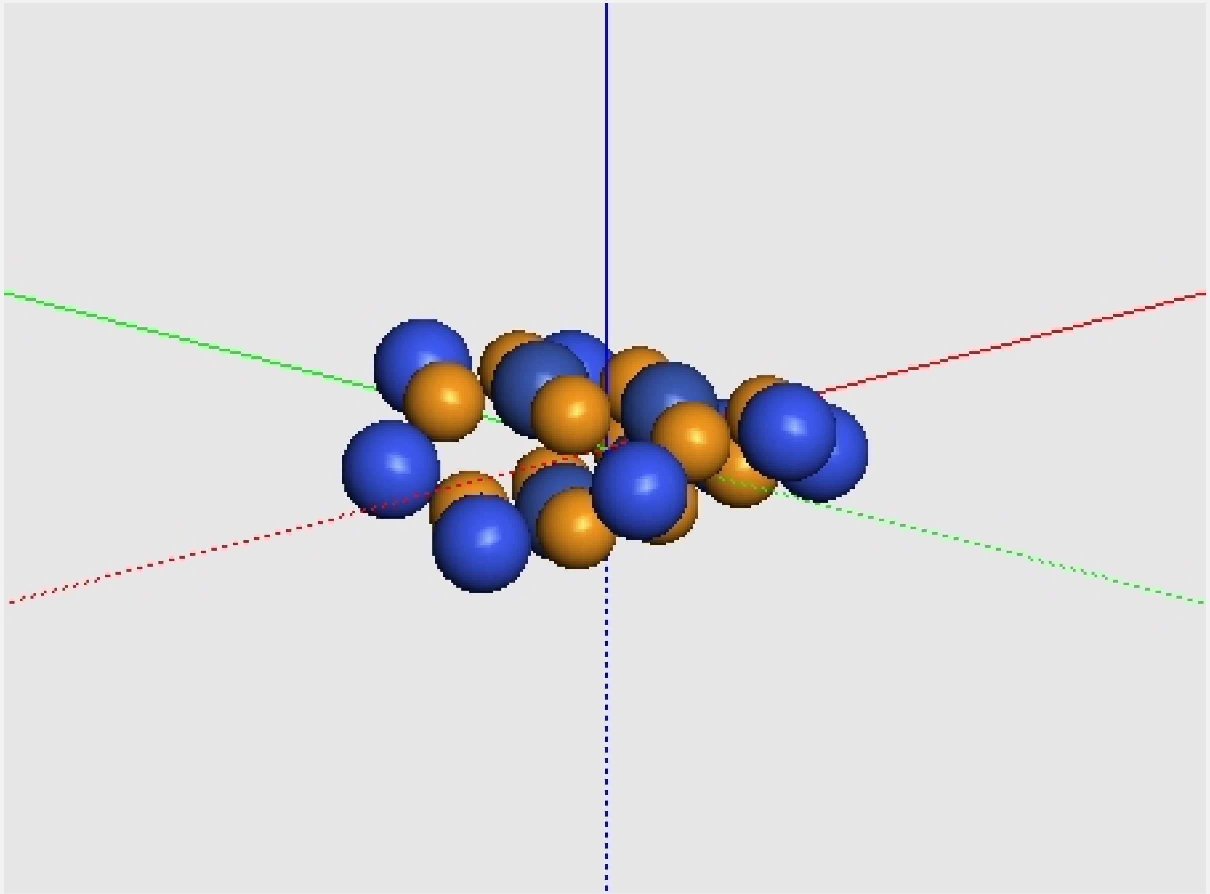


Magnetic Core

- 12 Manganese Atoms

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$

Molecular Structure of Mn_{12}-acetate

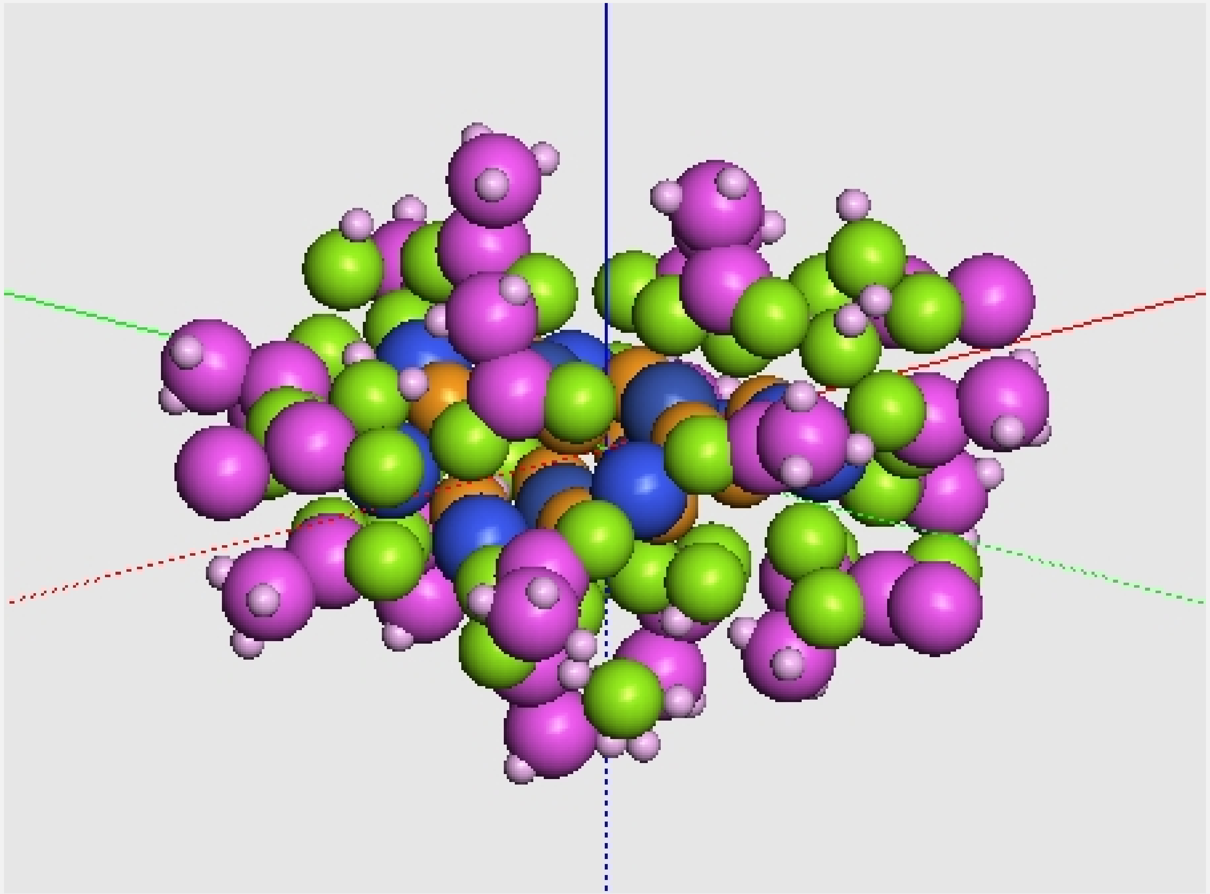


Magnetic Core

- 12 Manganese Atoms
- 12 Oxygen Atoms

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$

Molecular Structure of Mn_{12}-acetate



Magnetic Core

- 12 Manganese Atoms
- 12 Oxygen Atoms

Non-magnetic Ligands

- Acetic Acid
- Water

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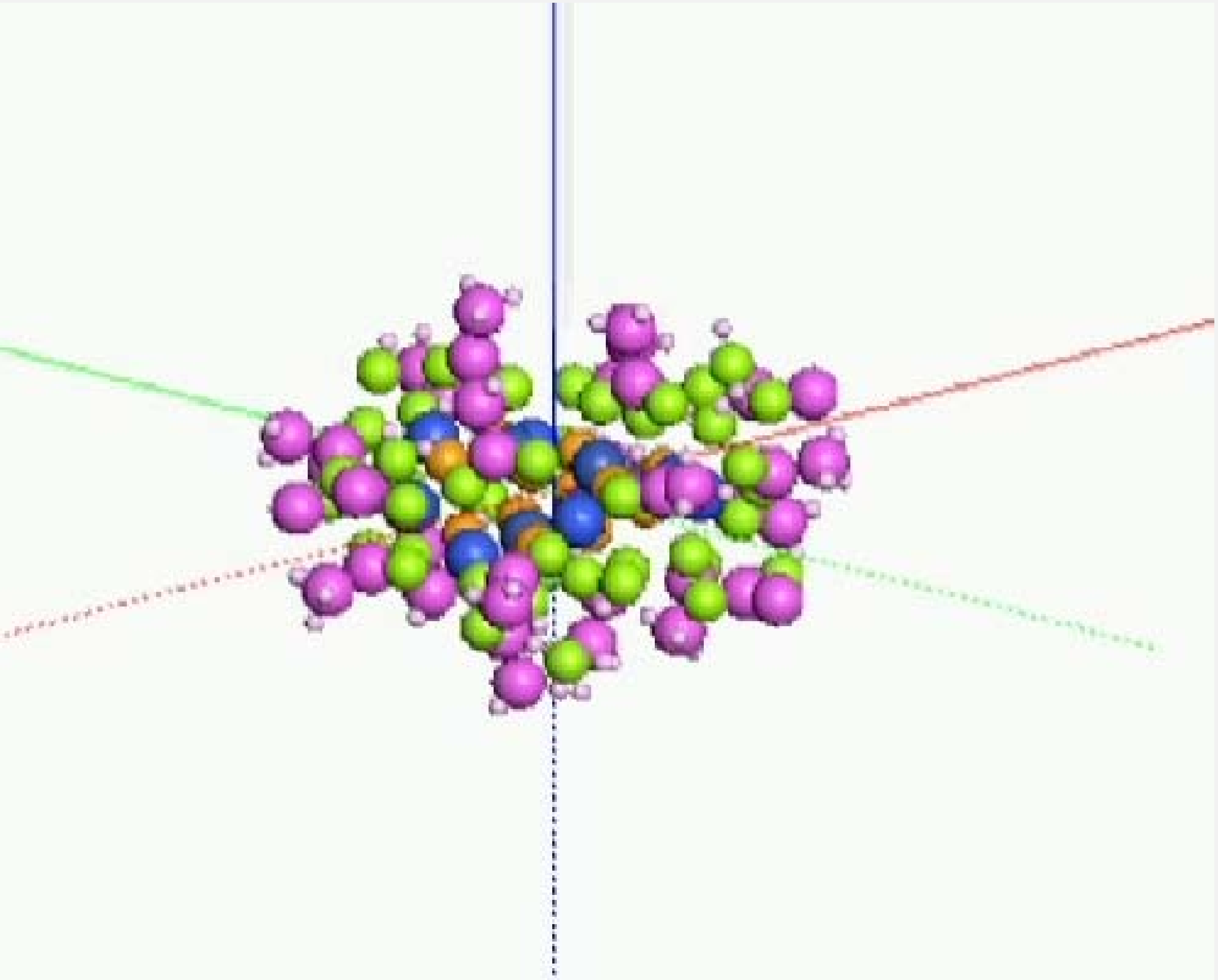
Molecular Structure of Mn_{12}-acetate



Magnetic Core

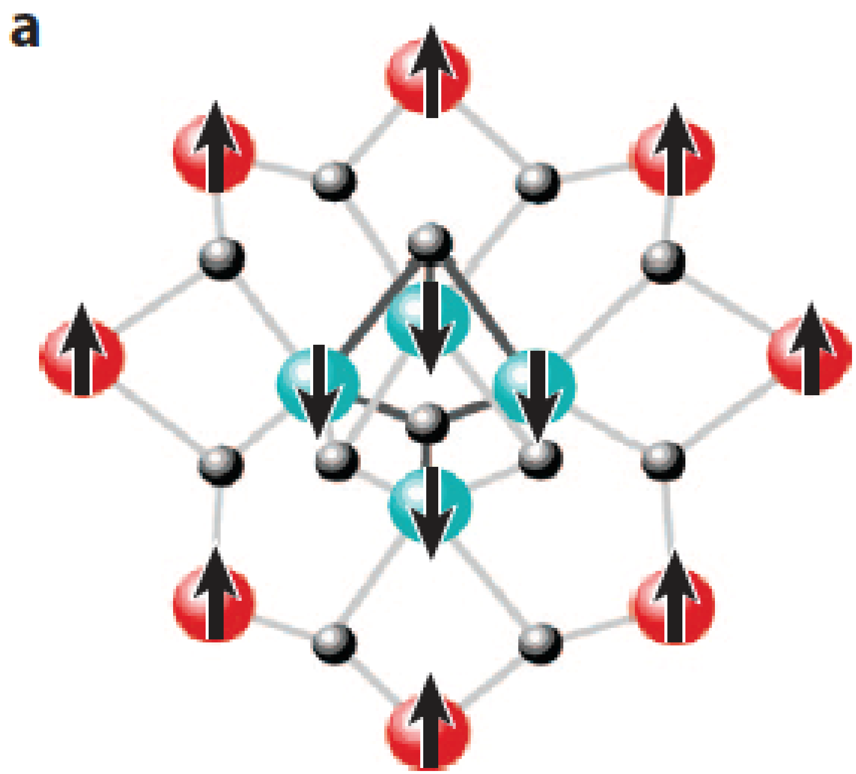
- 12 Manganese Atoms
- 12 Oxygen Atoms

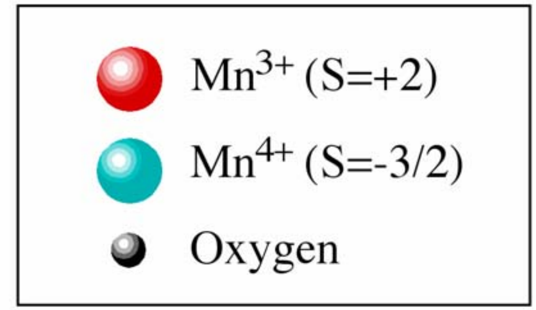
Non-magnetic Ligands

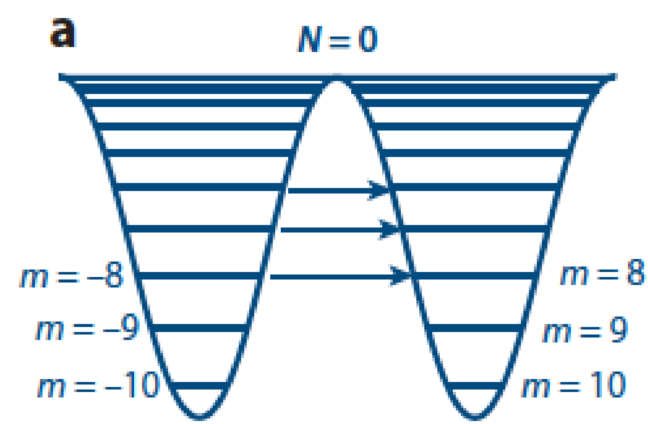
- Acetic Acid
- Water

Symmetry: S_4

$$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$$



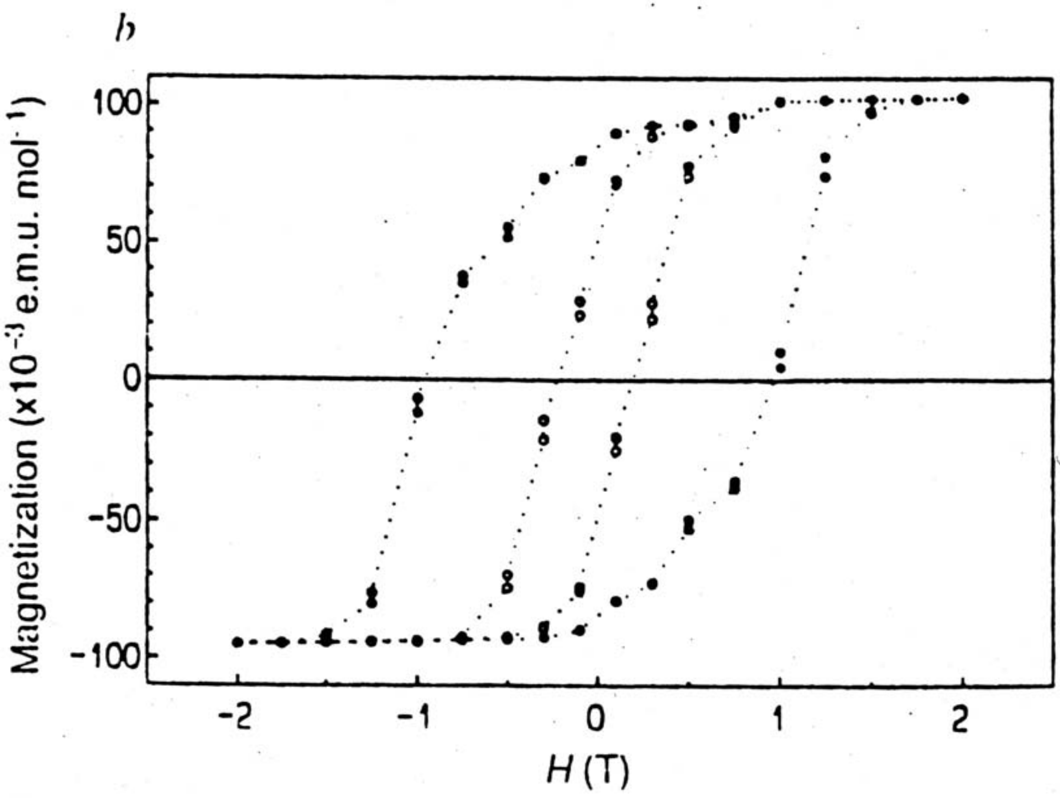


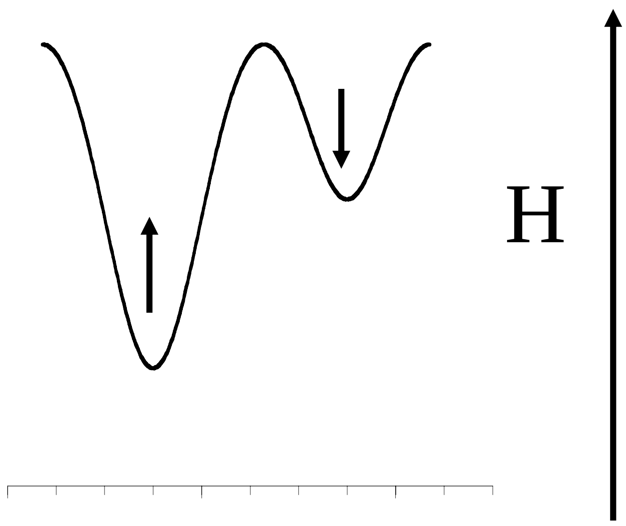


- S=10 ground state
- Large uniaxial anisotropy; bistable
- Negligible intercluster exchange

$$H = -DS_z^2 - BS_z^4 + \ldots$$

Blocking Temperature

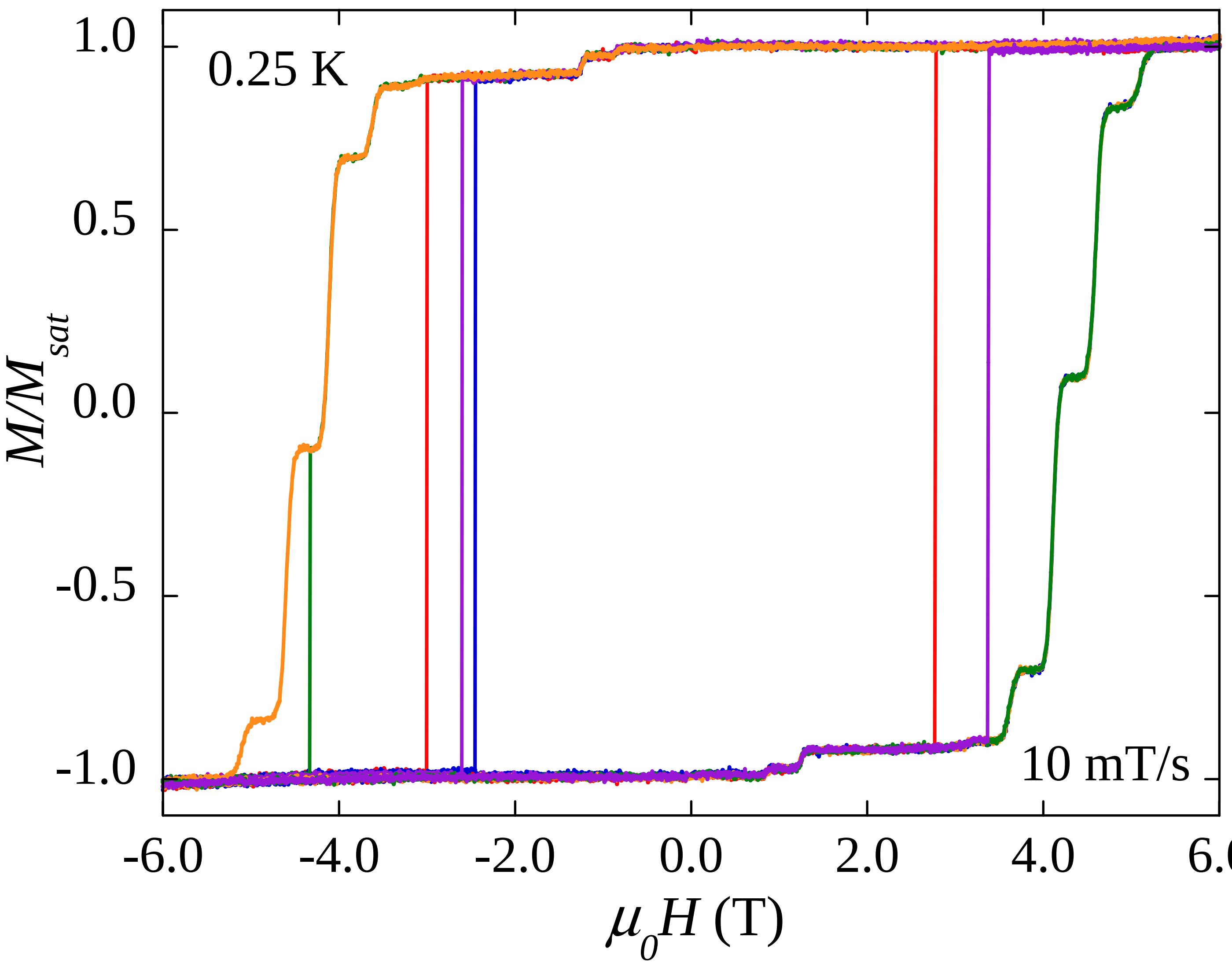




$$H = -DS_z^2 - BS_z^4 + g\mu_B H_z S_z \ldots$$

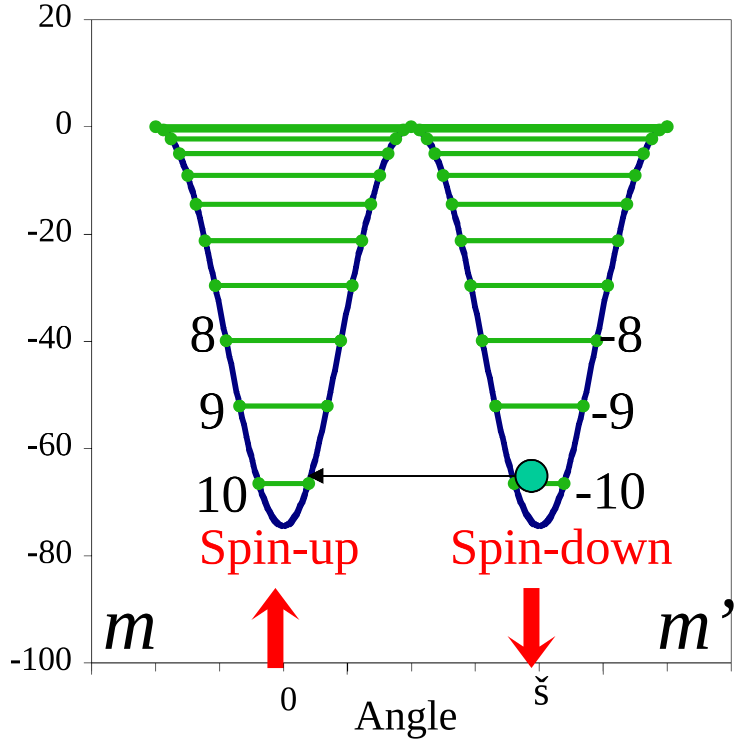
R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature **365**, 141 (1993).

Spin Reversal: Tunneling and Avalanches



Spin Reversal by Tunneling

$$\hat{\mathcal{H}} = -D\hat{S}_z^2 - A\hat{S}_z^4 - g_z\mu_B H_z\hat{S}_z + \hat{\mathcal{V}}_T$$



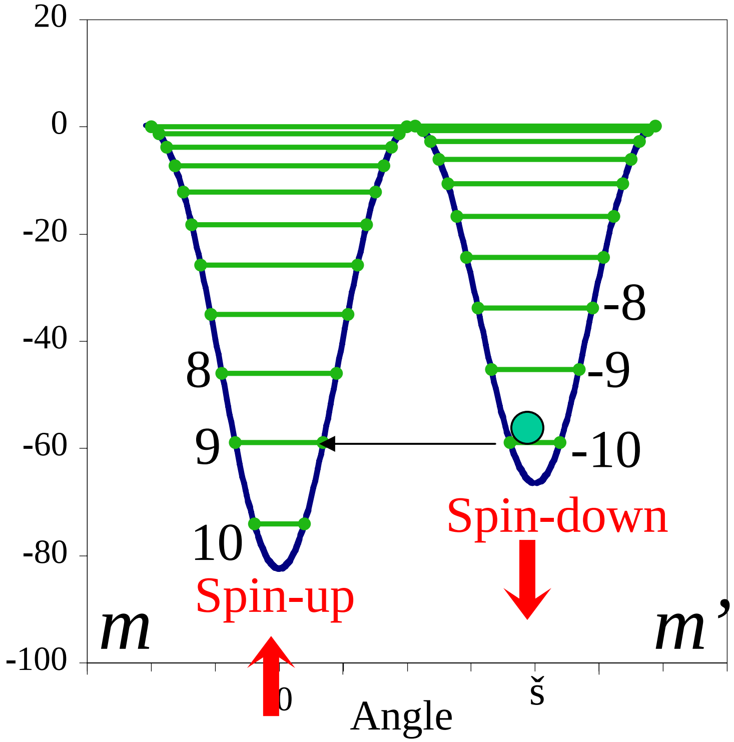
$H_z = 0$

Resonance Number,

$N = -(m + m') = 0$

Spin Reversal by Tunneling

$$\hat{\mathcal{H}} = -D\hat{S}_z^2 - A\hat{S}_z^4 - g_z\mu_B H_z\hat{S}_z + \hat{\mathcal{V}}_T$$



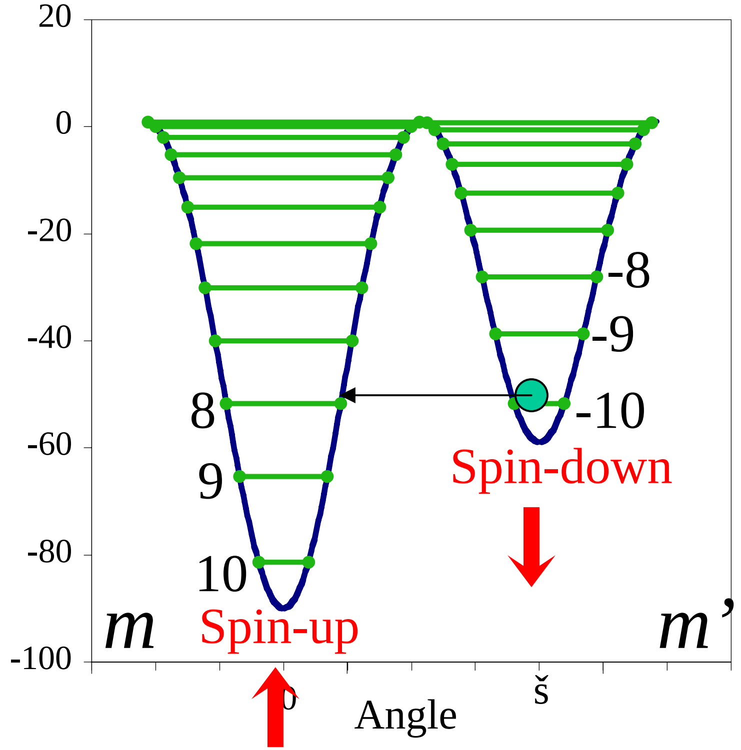
$H_z > 0$

Resonance Number,

$N = -(m + m') = 1$

Spin Reversal by Tunneling

$$\hat{\mathcal{H}} = -D\hat{S}_z^2 - A\hat{S}_z^4 - g_z\mu_B H_z\hat{S}_z + \hat{\mathcal{V}}_T$$



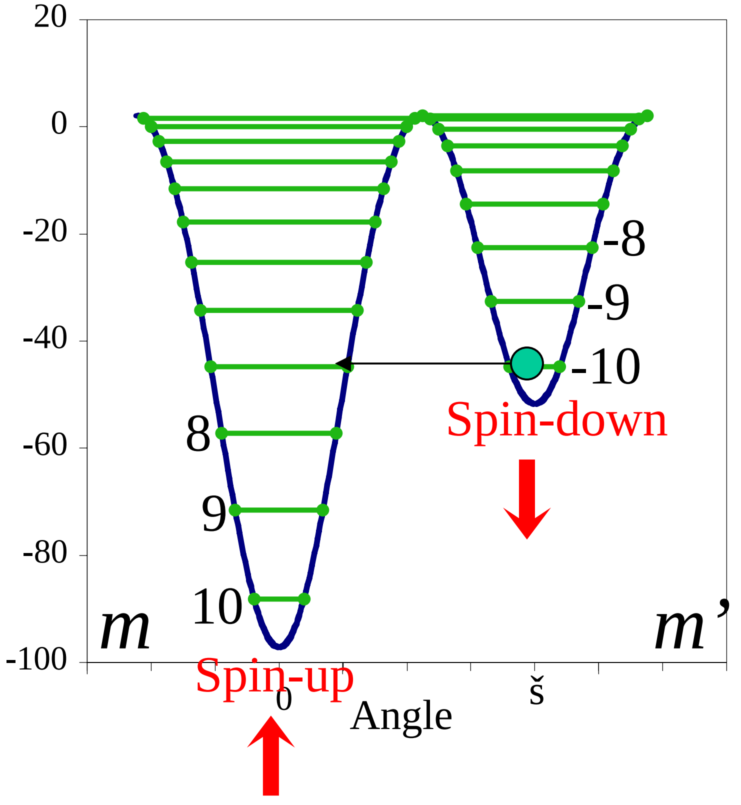
$H_z > 0$

Resonance Number,

$N = -(m + m') = 2$

Spin Reversal by Tunneling

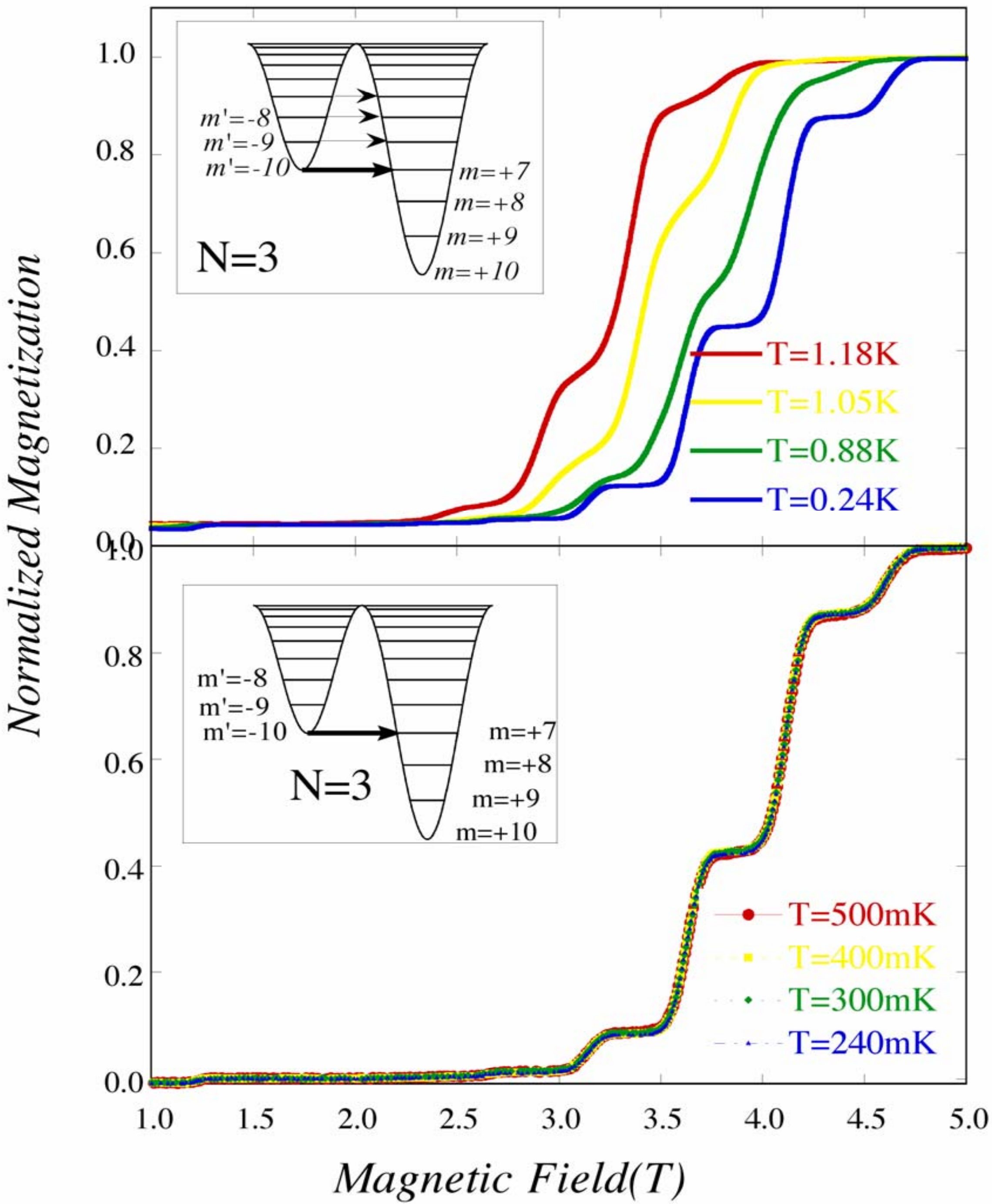
$$\hat{\mathcal{H}} = -D\hat{S}_z^2 - A\hat{S}_z^4 - g_z\mu_B H_z \hat{S}_z + \hat{\mathcal{V}}_T$$



$H_z > 0$

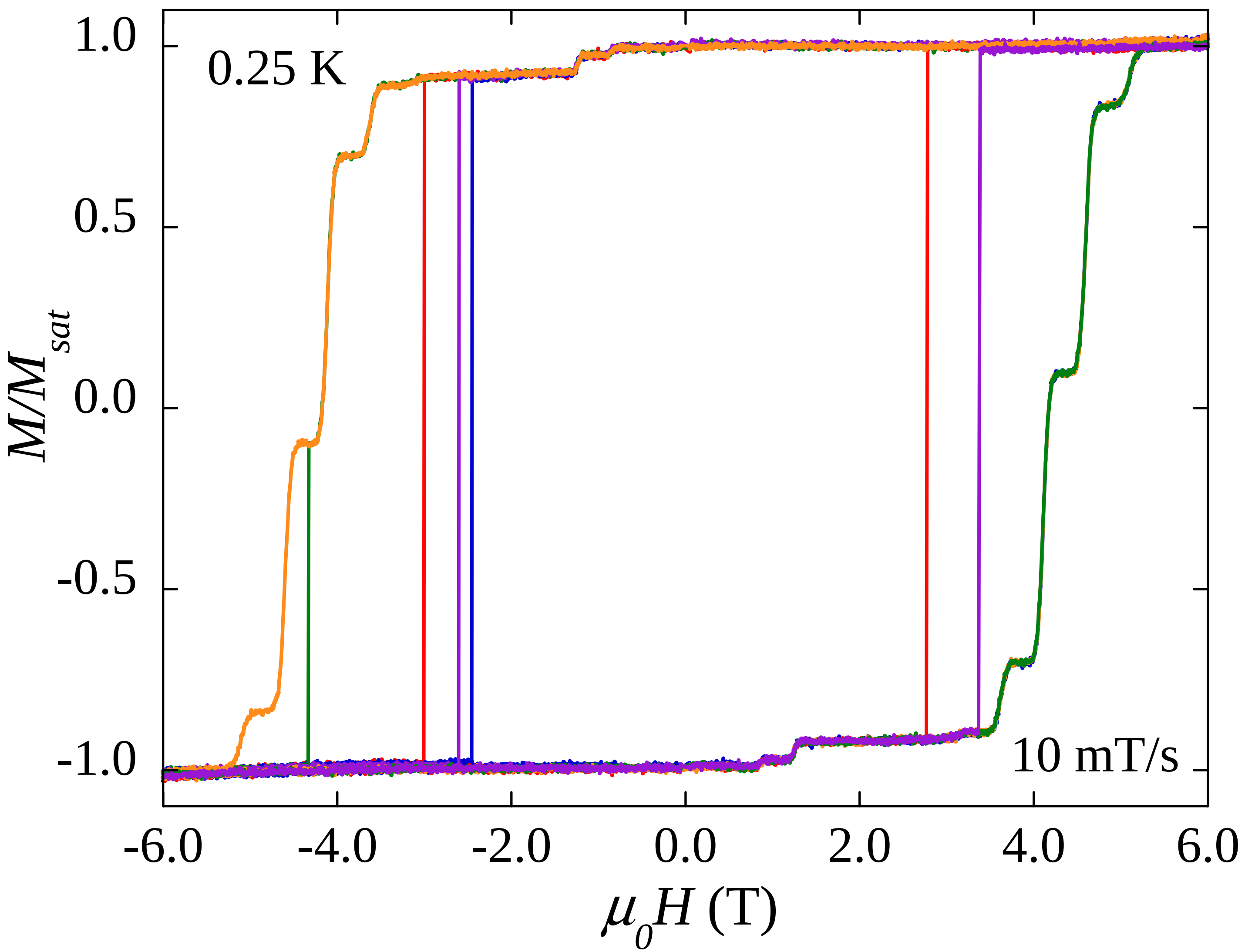
Resonance Number,

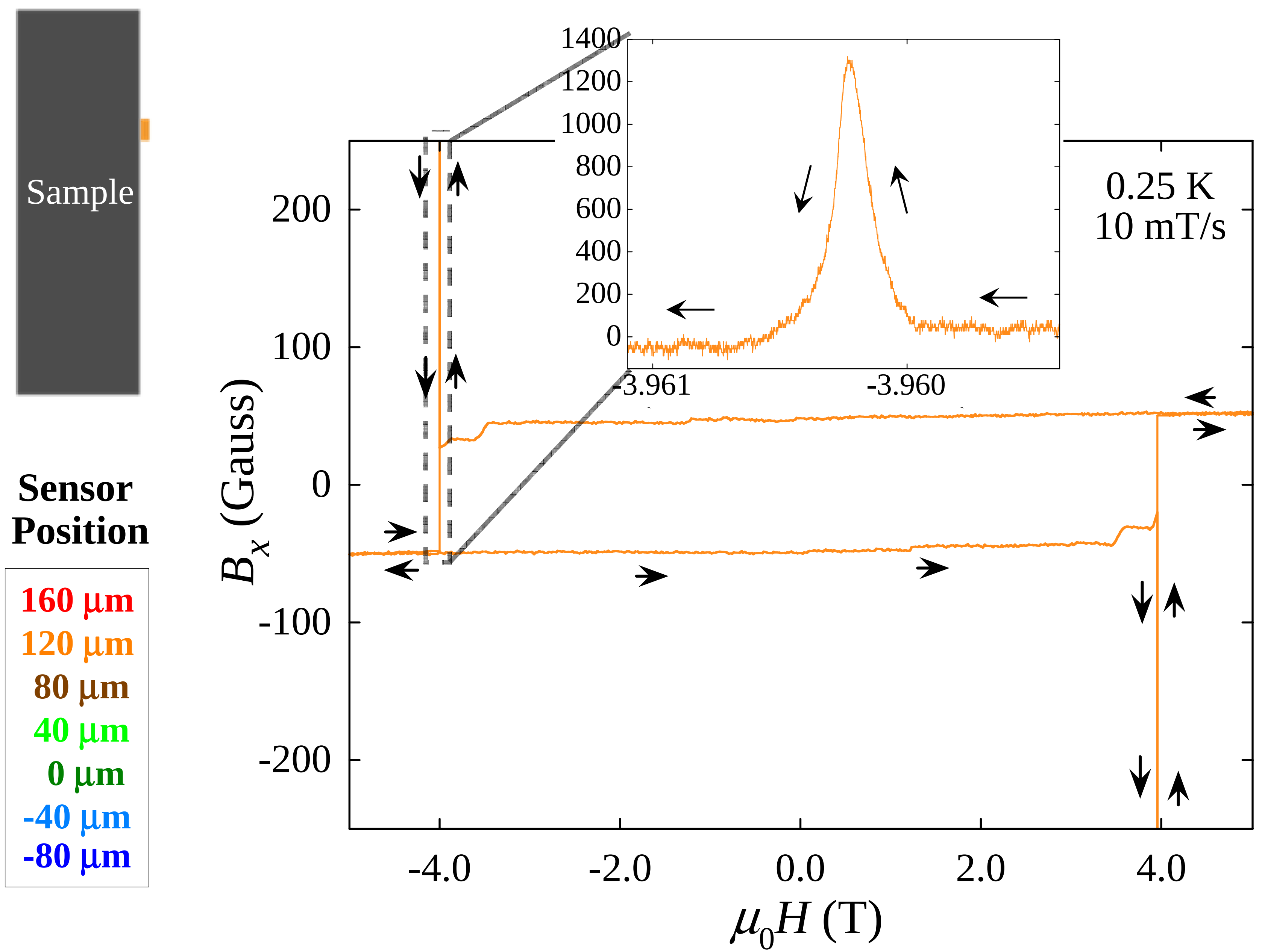
$N = -(m + m') = 3$



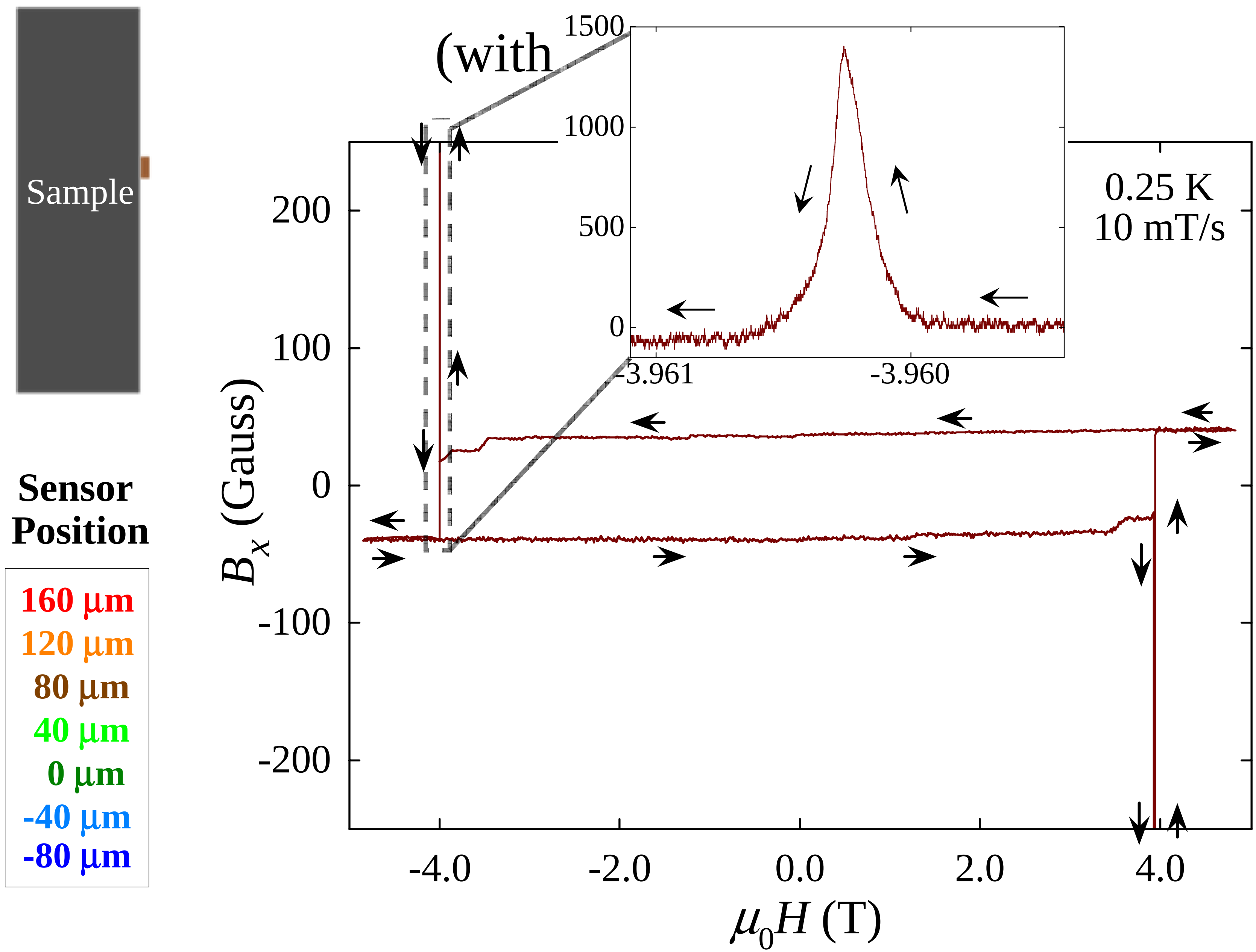
N=3
m'=-8
m'=-9
m'=-10
m=+7
m=+8
m=+9
m=+10
T=1.18K
T=1.05K
T=0.88K
T=0.24K
T=500mK
T=400mK
T=300mK
T=240mK
Normalized Magnetization
Magnetic Field(T)
0.0
0.2
0.4
0.6
0.8
1.0
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

Spin Reversal via Avalanches





Sample
Sensor Position
160 μm
120 μm
80 μm
40 μm
0 μm
-40 μm
-80 μm
0.25 K
10 mT/s
B_χ (Gauss)
$\mu_0 H$ (T)
200
100
0
-100
-200
-4.0
-2.0
0.0
2.0
4.0
1400
1200
1000
800
600
400
200
0
-3.961
-3.960



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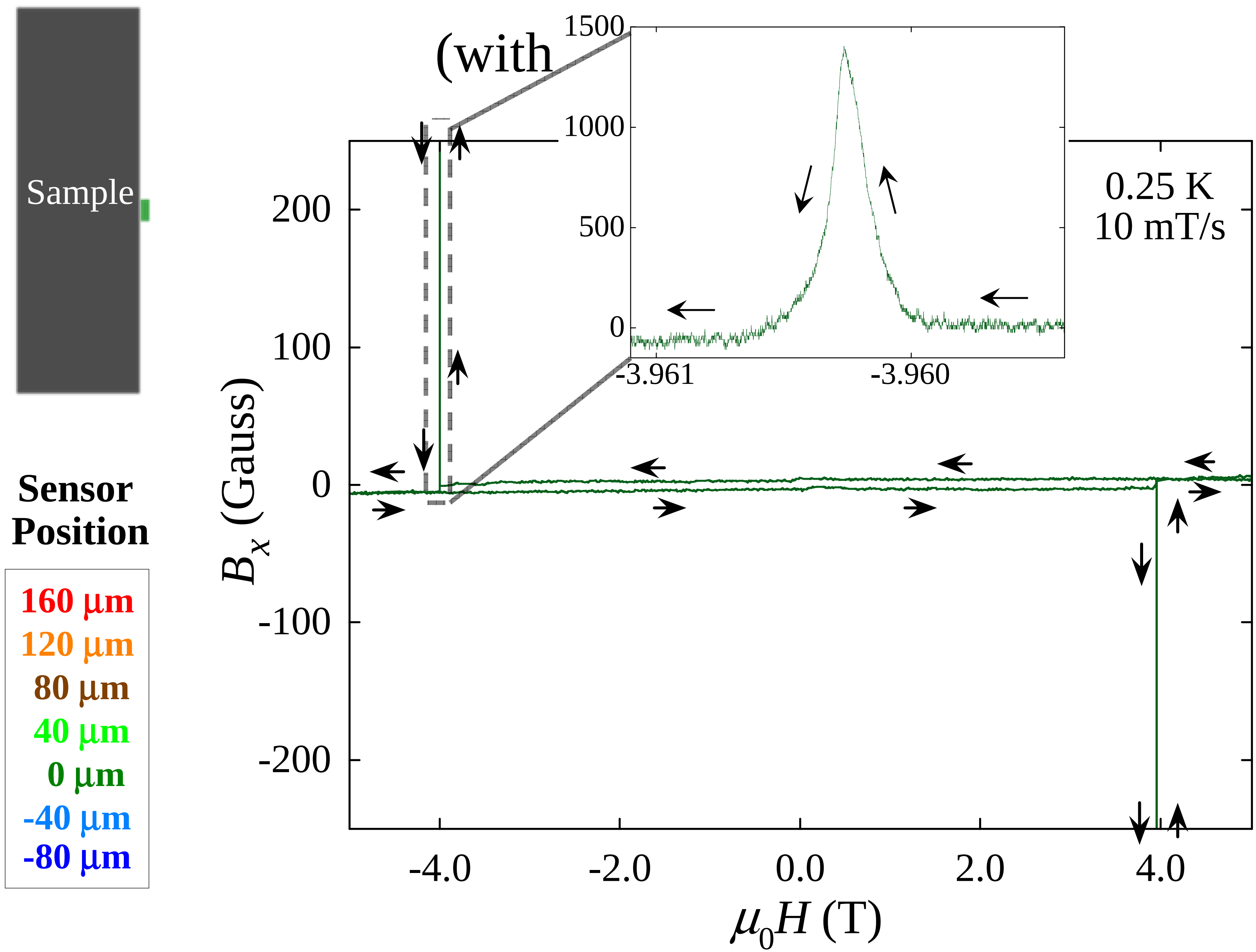
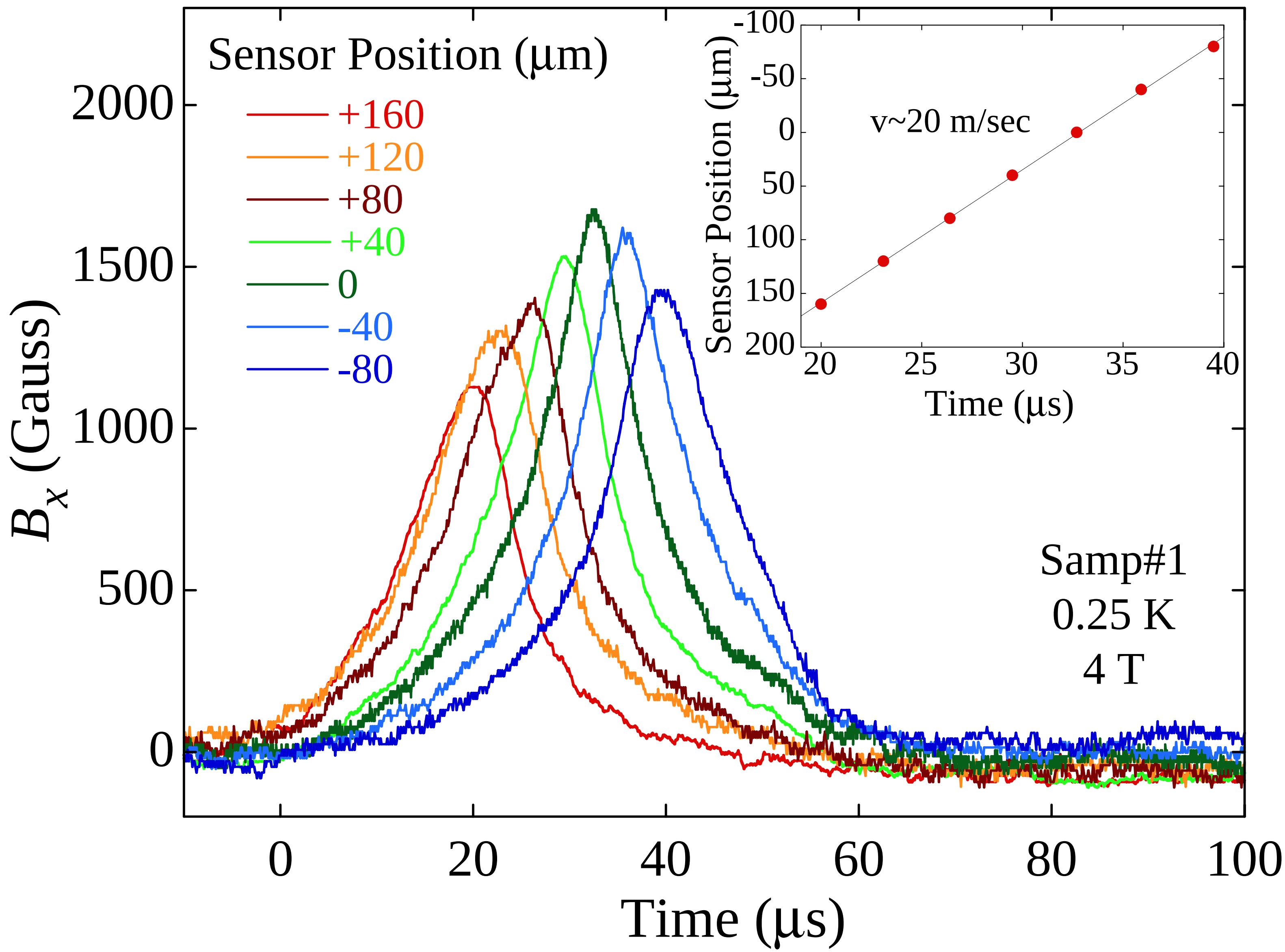
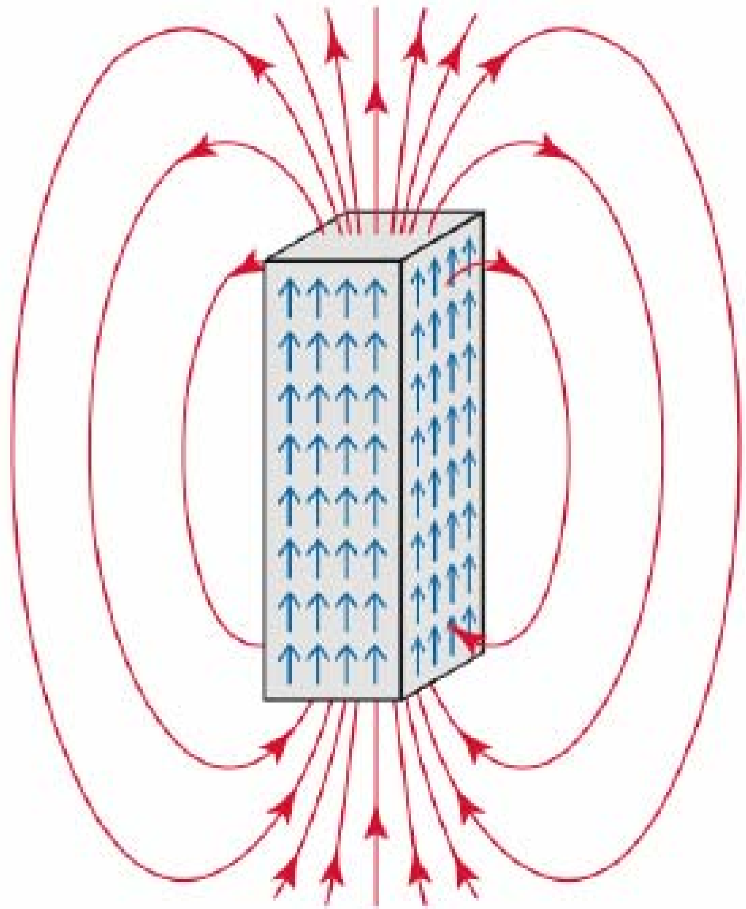
-200
-4.0
-2.0
0.0
2.0
4.0
1500
1000
500
0
-3.961
-3.960



Sample
(with
1500
1000
500
0
-3.961
-3.960
0.25 K
10 mT/s
200
100
0
-100
-200
B_x (Gauss)
-4.0
-2.0
0.0
2.0
4.0
$\mu_0 H$ (T)
Sensor Position
160 μm
120 μm
80 μm
40 μm
0 μm
-40 μm
-80 μm

Speed of Propagation

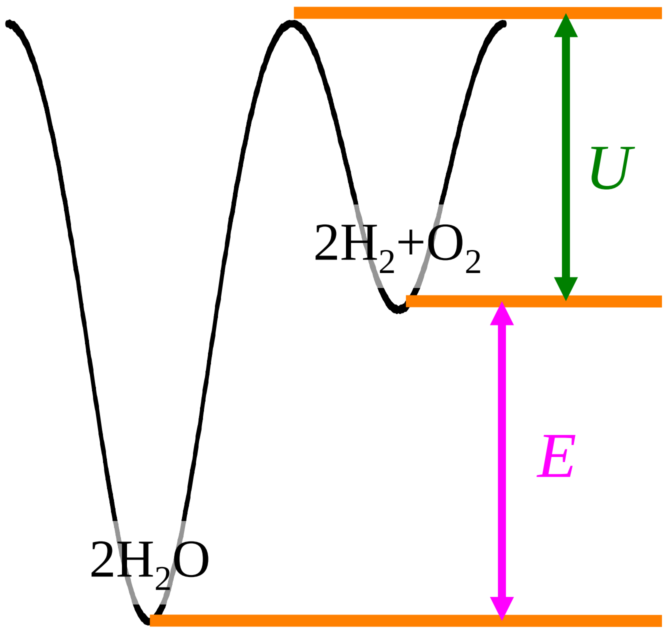




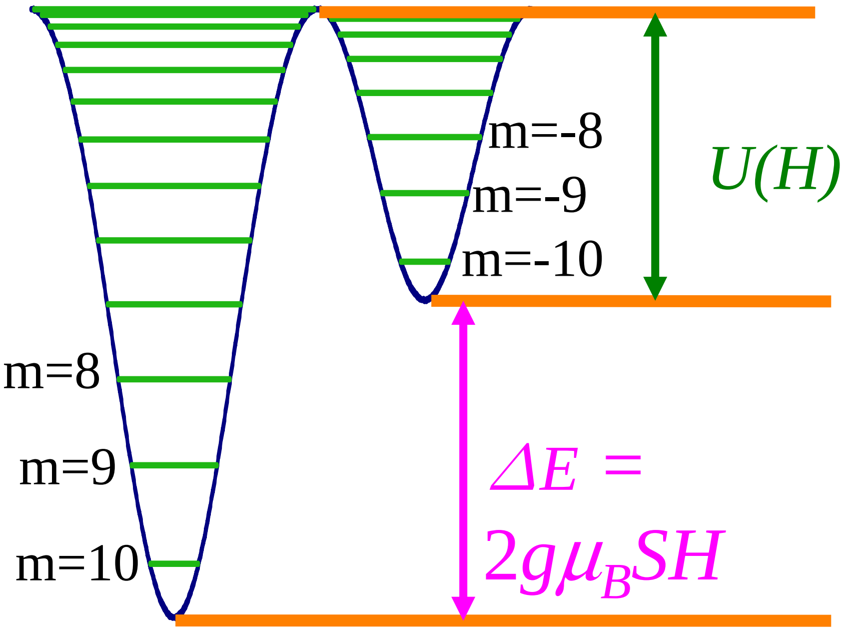
Magnetic Deflagration

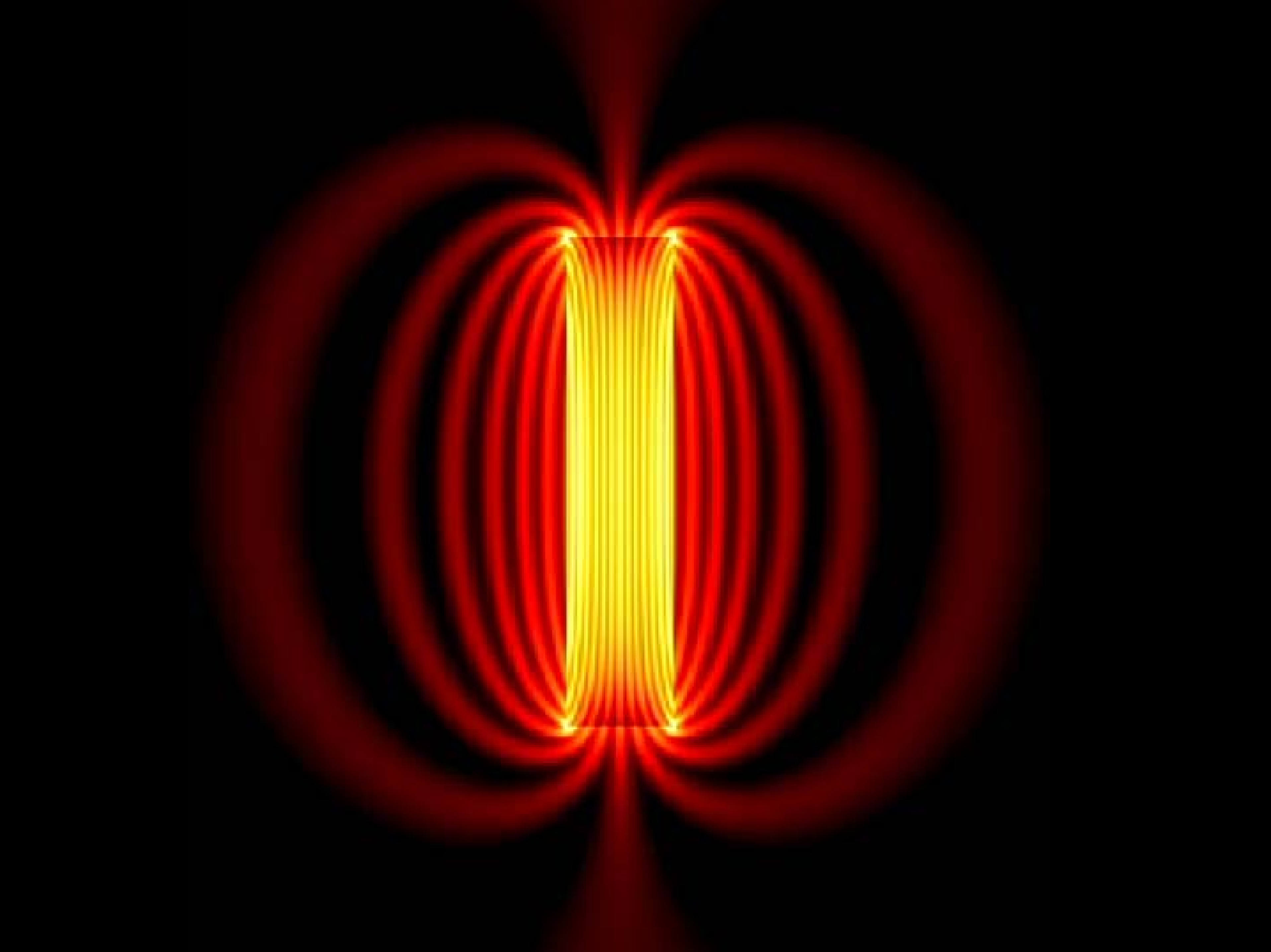
Chemical Deflagration

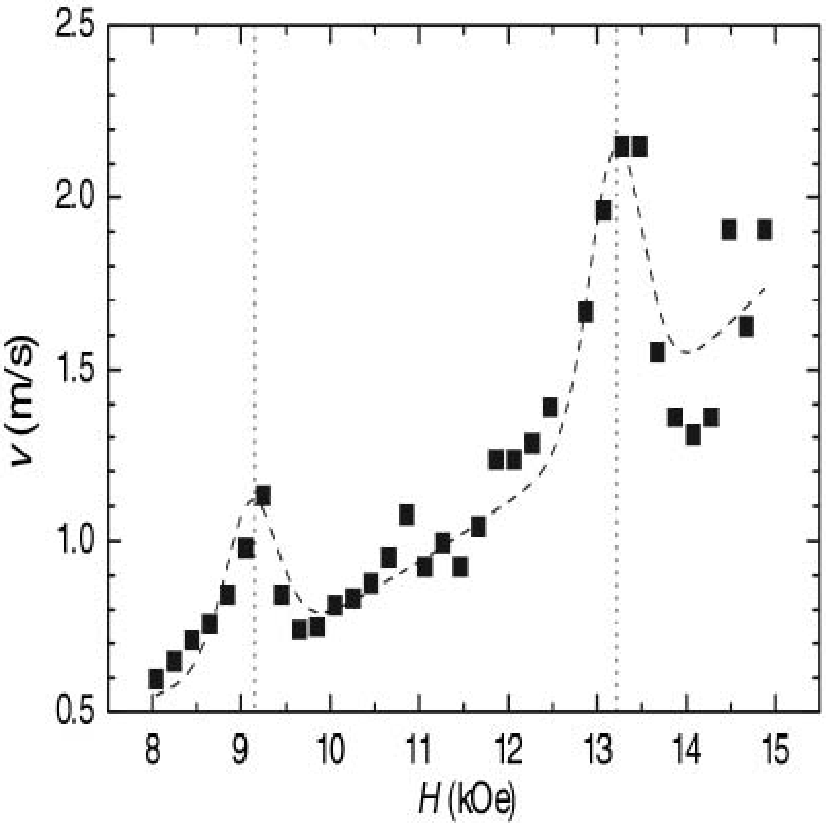
Chemical Reaction

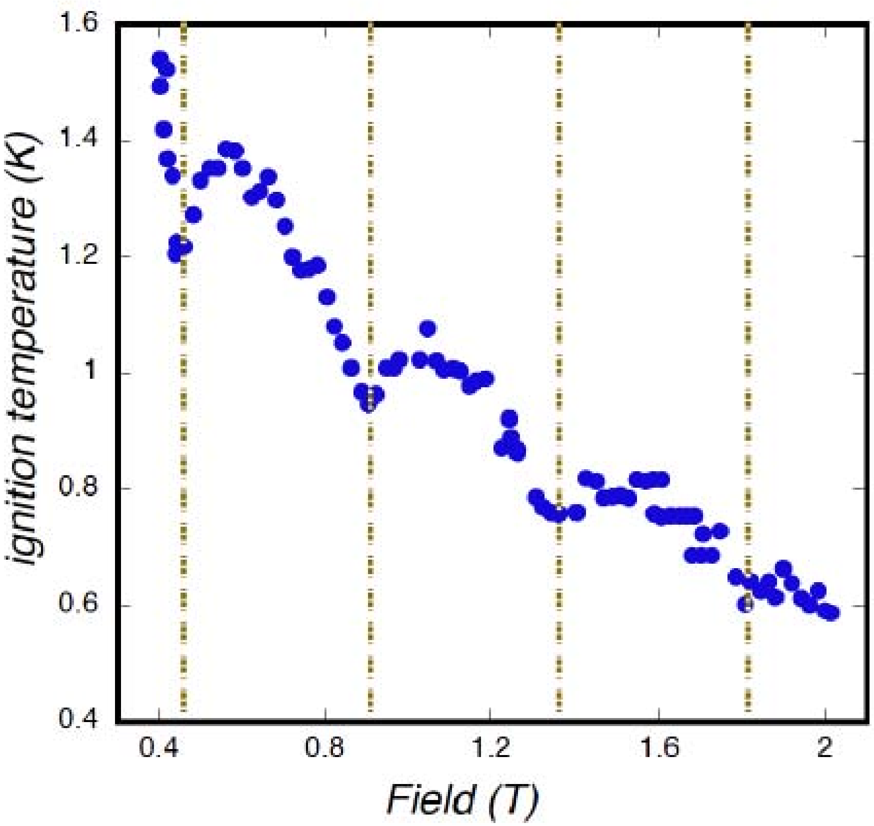


Spin Reversal









J. Tejada's group

Quantum mechanics: at resonant fields (where leve
increased velocity of propagation, dips in ignition te

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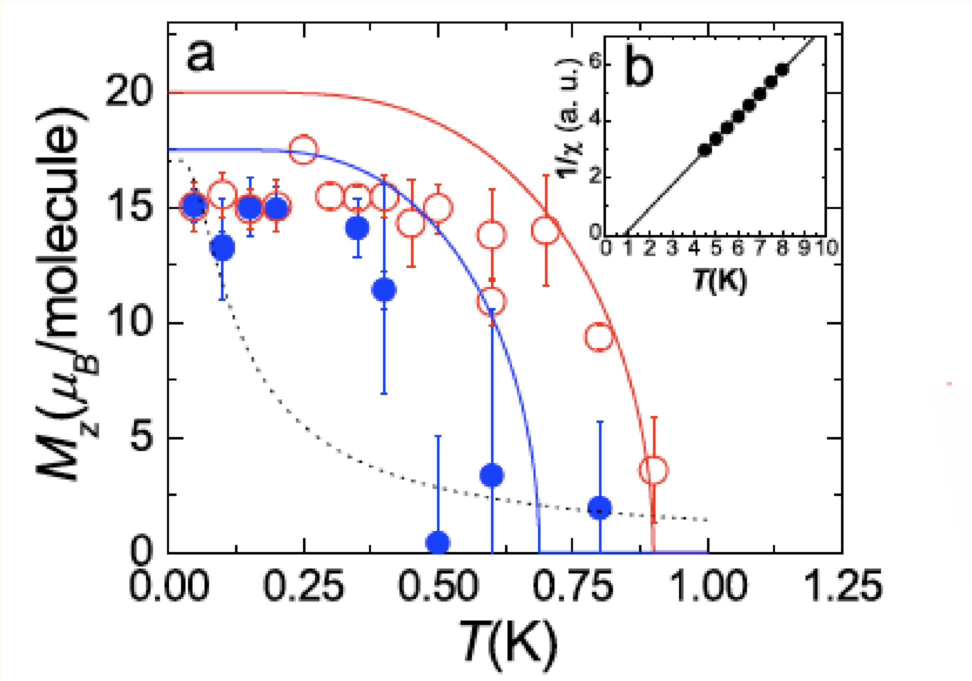
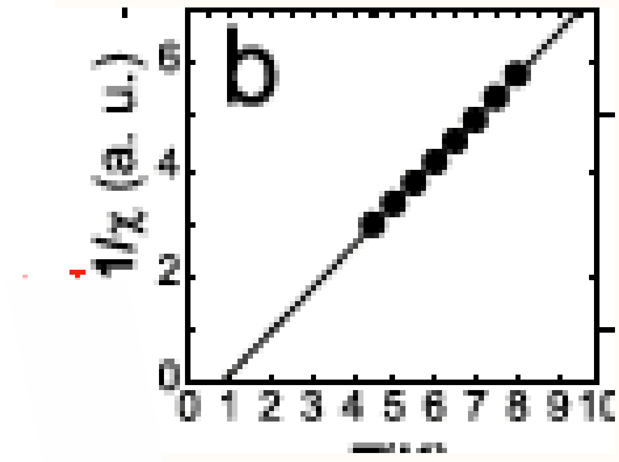
(d) Comparison with LiHoF

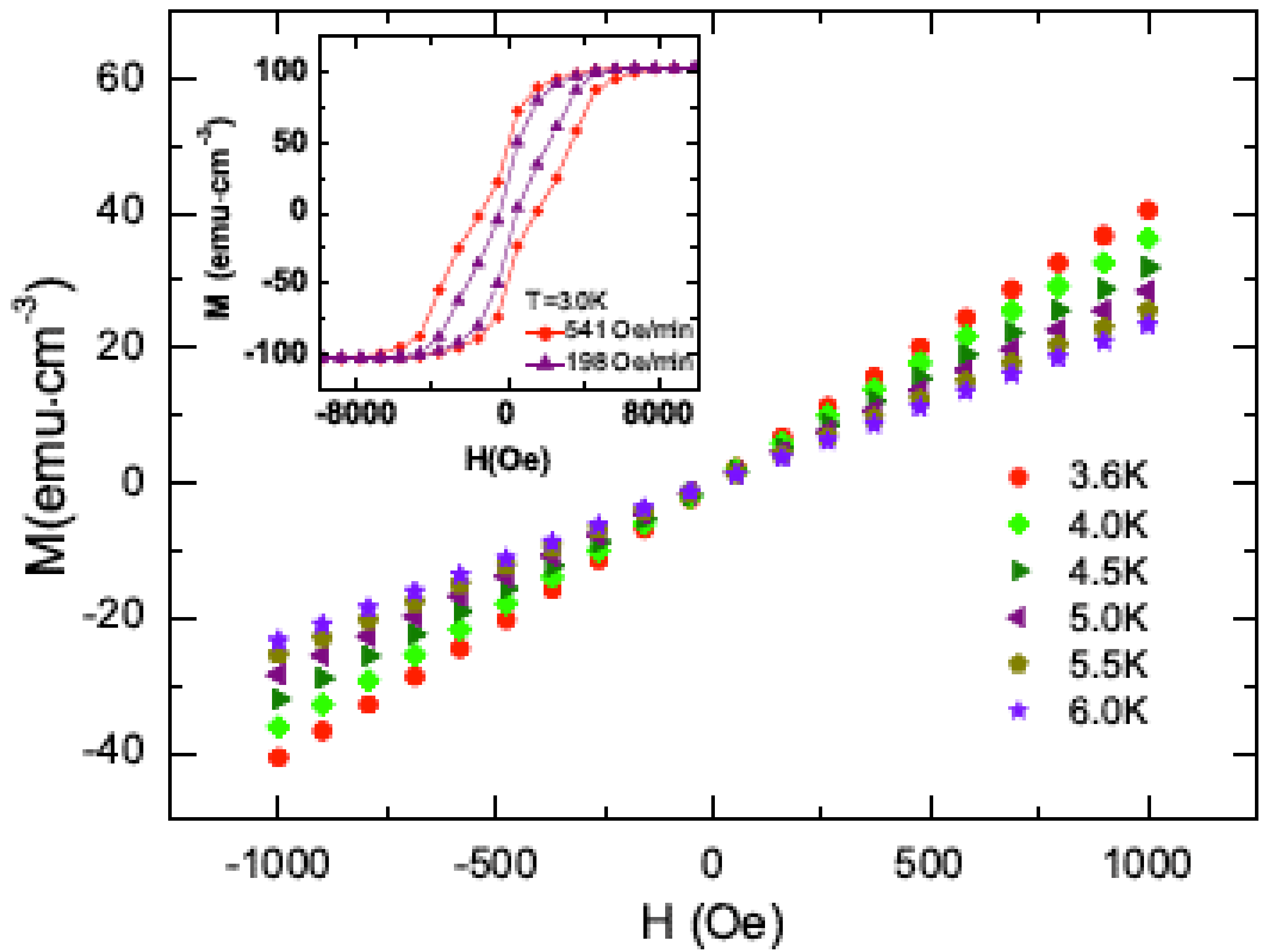
III – Dipole interactions?

DIPOLAR(?) FERROMAGNETISM IN MN-12



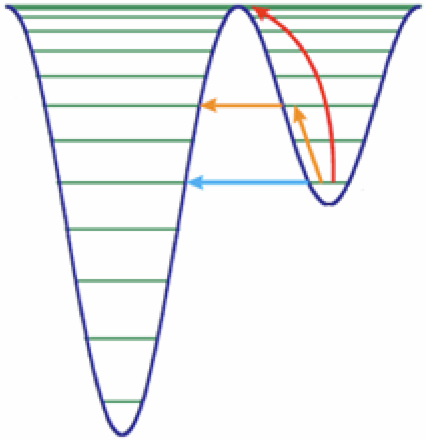


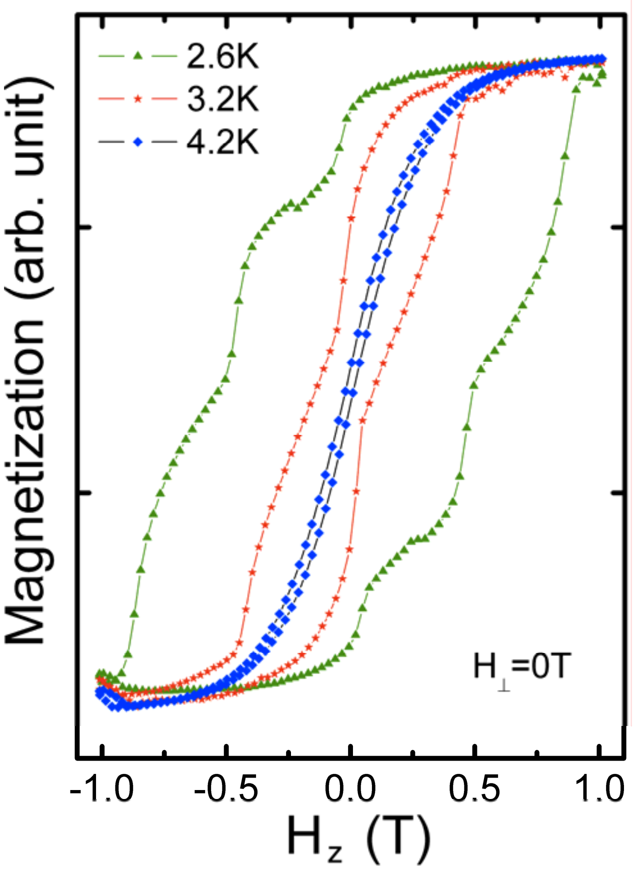
F. Luis, et *al.* PRL **95**, 227212 (2005)



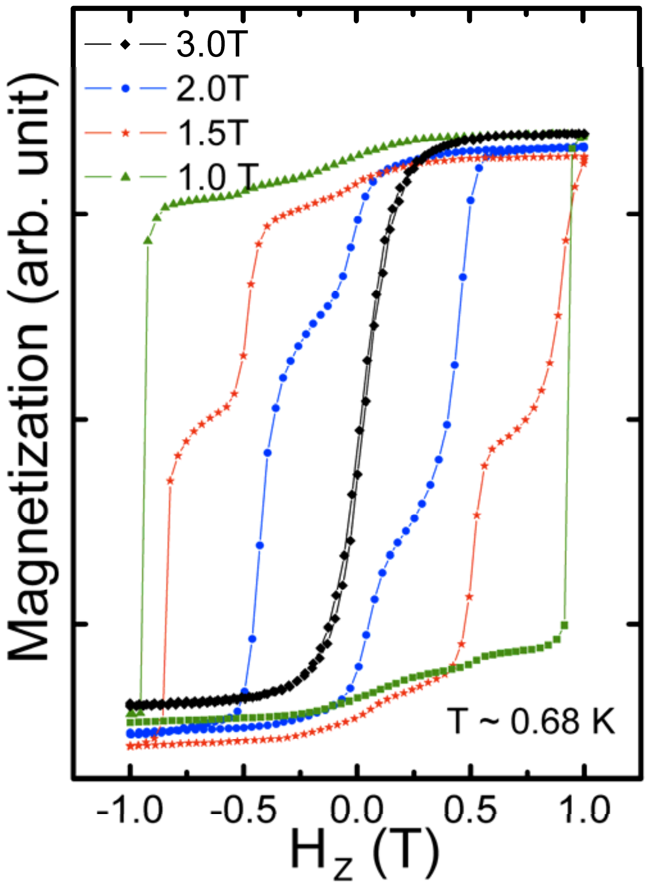
M(emu·cm^{-3})
H (Oe)
60
40
20
0
-20
-40
-1000
-500
0
500
1000
3.6K
4.0K
4.5K
5.0K
5.5K
6.0K
M (emu-cm^{-3})
H(Oe)
100
50
0
-50
-100
-8000
0
8000
T=3.0K
541 Oe/min
198 Oe/min

Reaching Equilibrium

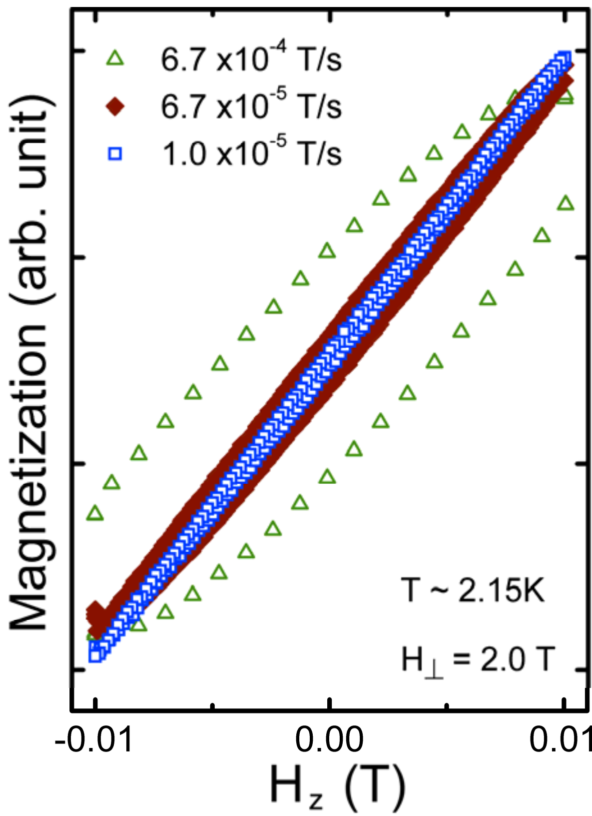




Temperature

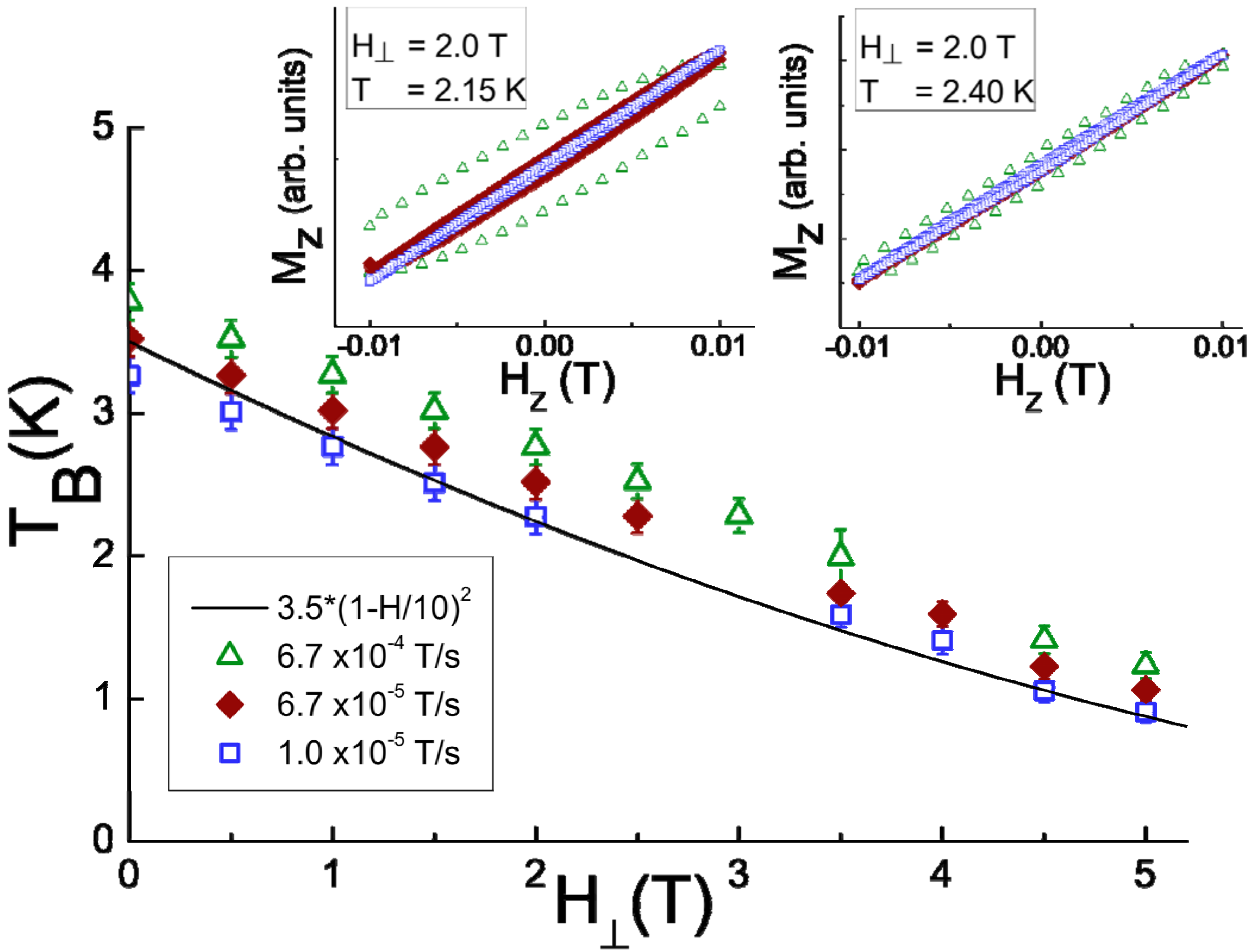


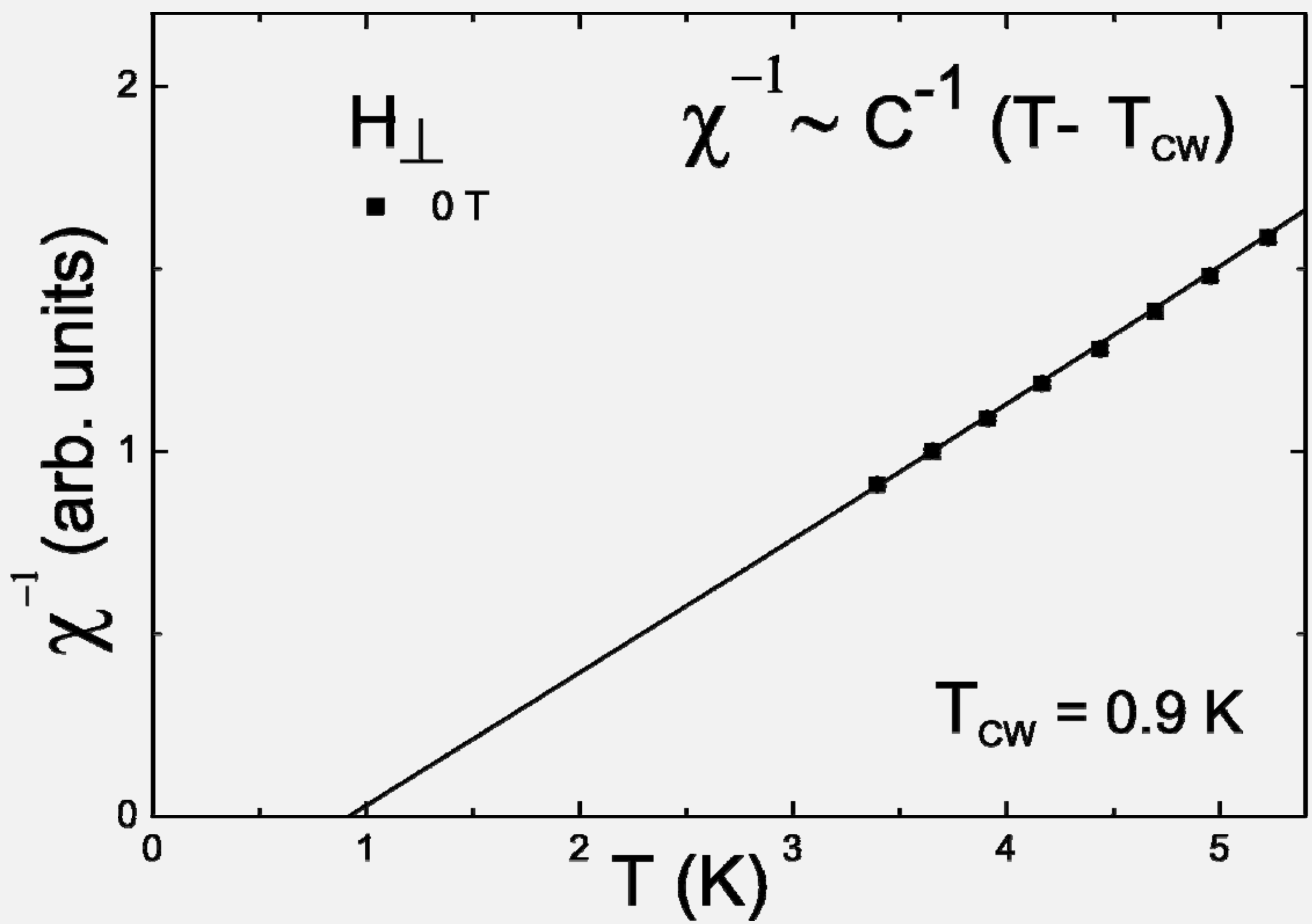
Transverse field



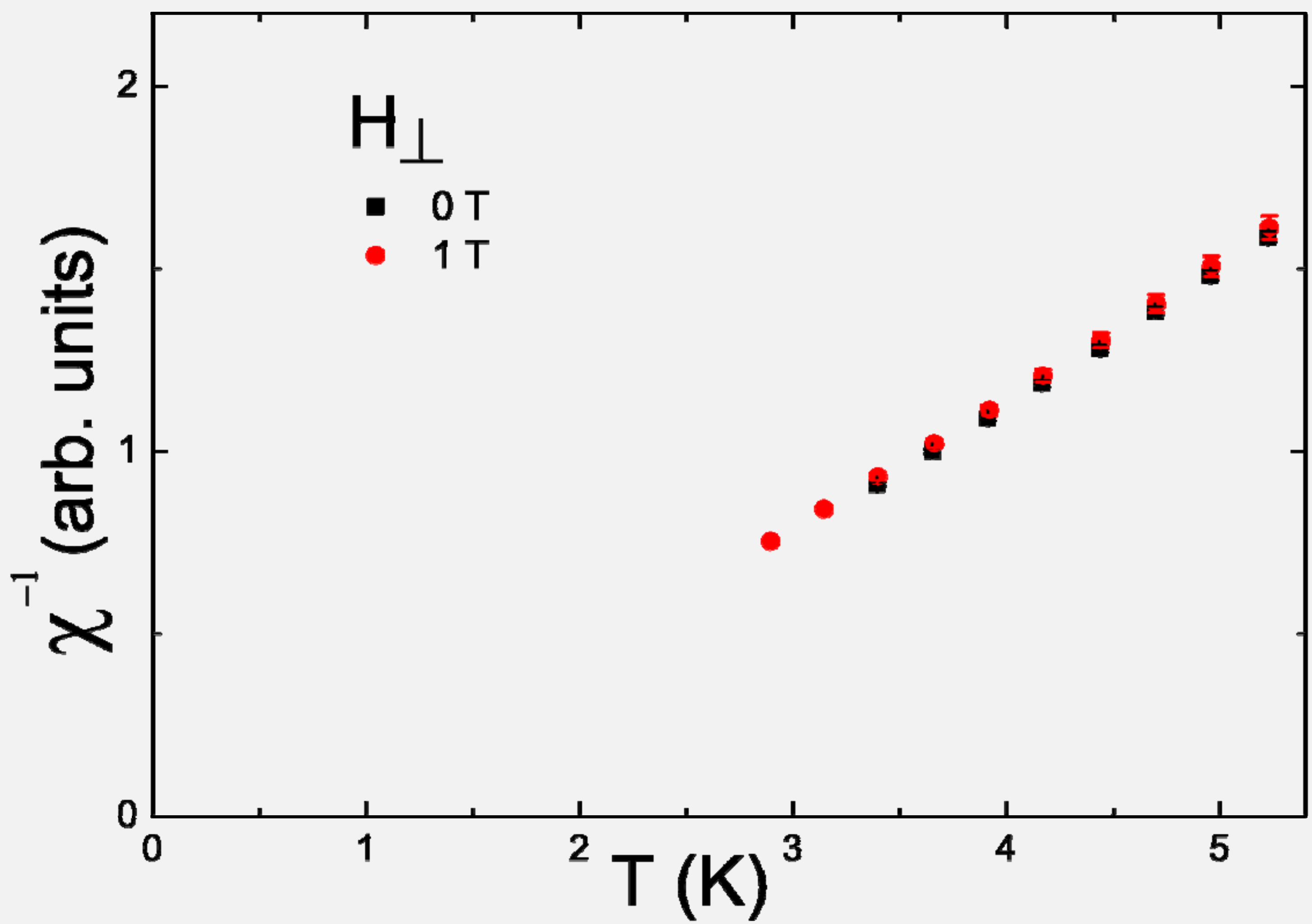
Time

- Measurements of susceptibility in equilibrium

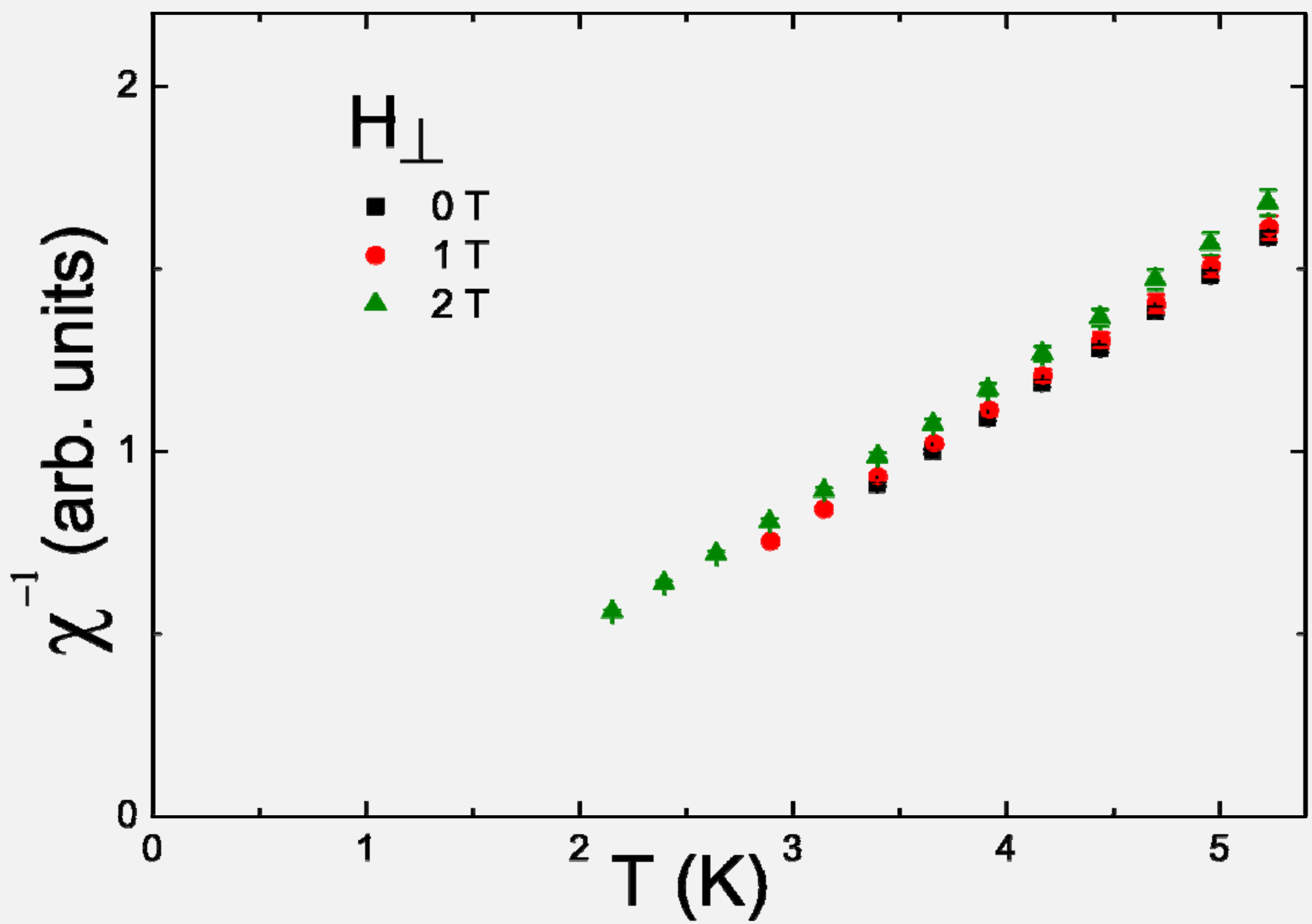




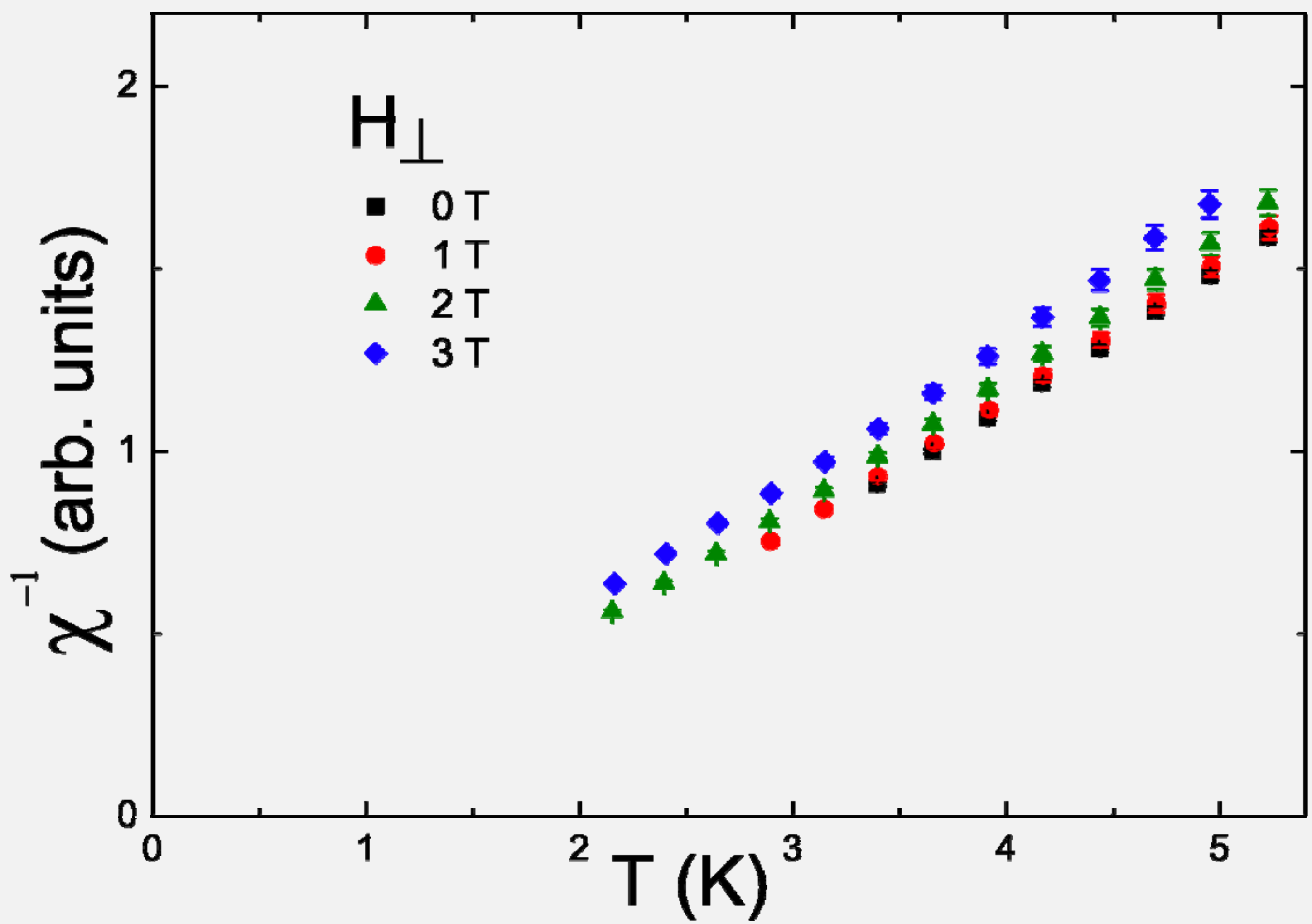
$H_\perp$
0 T
$\chi^{-1} \sim C^{-1} (T - T_{CW})$
$T_{CW} = 0.9$ K
χ^{-1} (arb. units)
T (K)
0
1
2
3
4
5
0
1
2



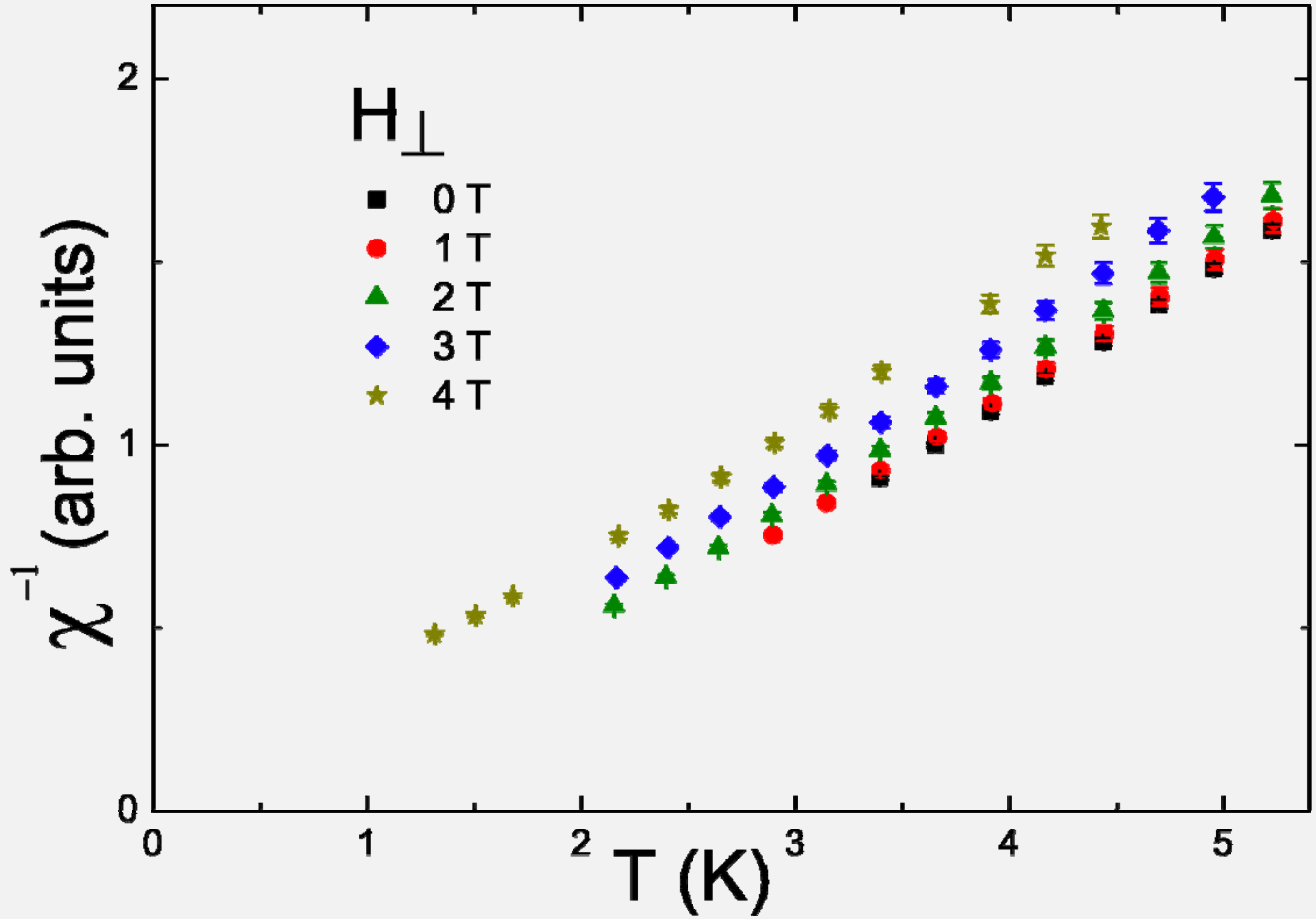
H⊥
0 T
1 T
χ⁻¹ (arb. units)
T (K)
0
1
2
3
4
5
0
1
2



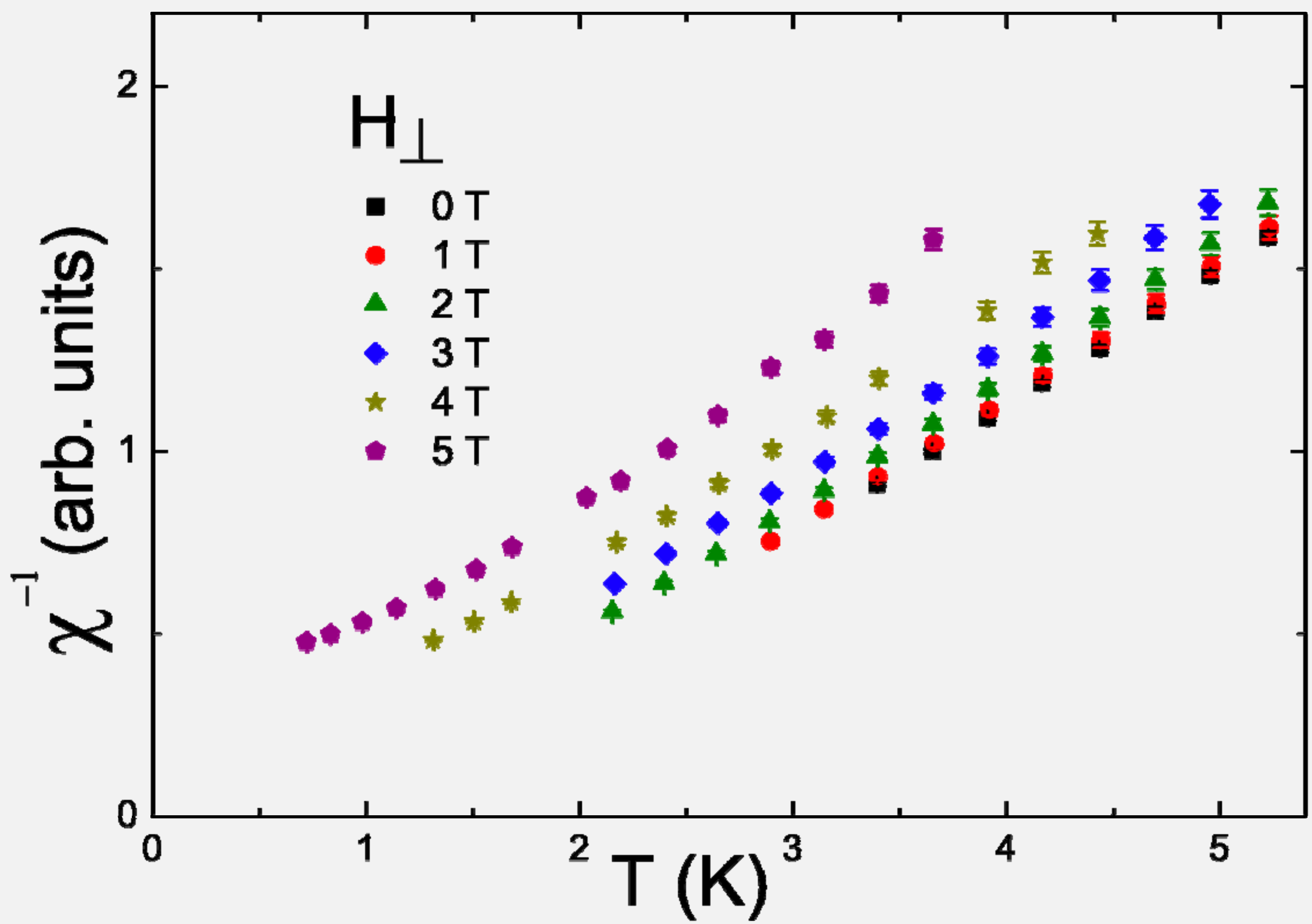
H⊥
0 T
1 T
2 T
χ^{-1} (arb. units)
T (K)
0
1
2
0
1
2
3
4
5



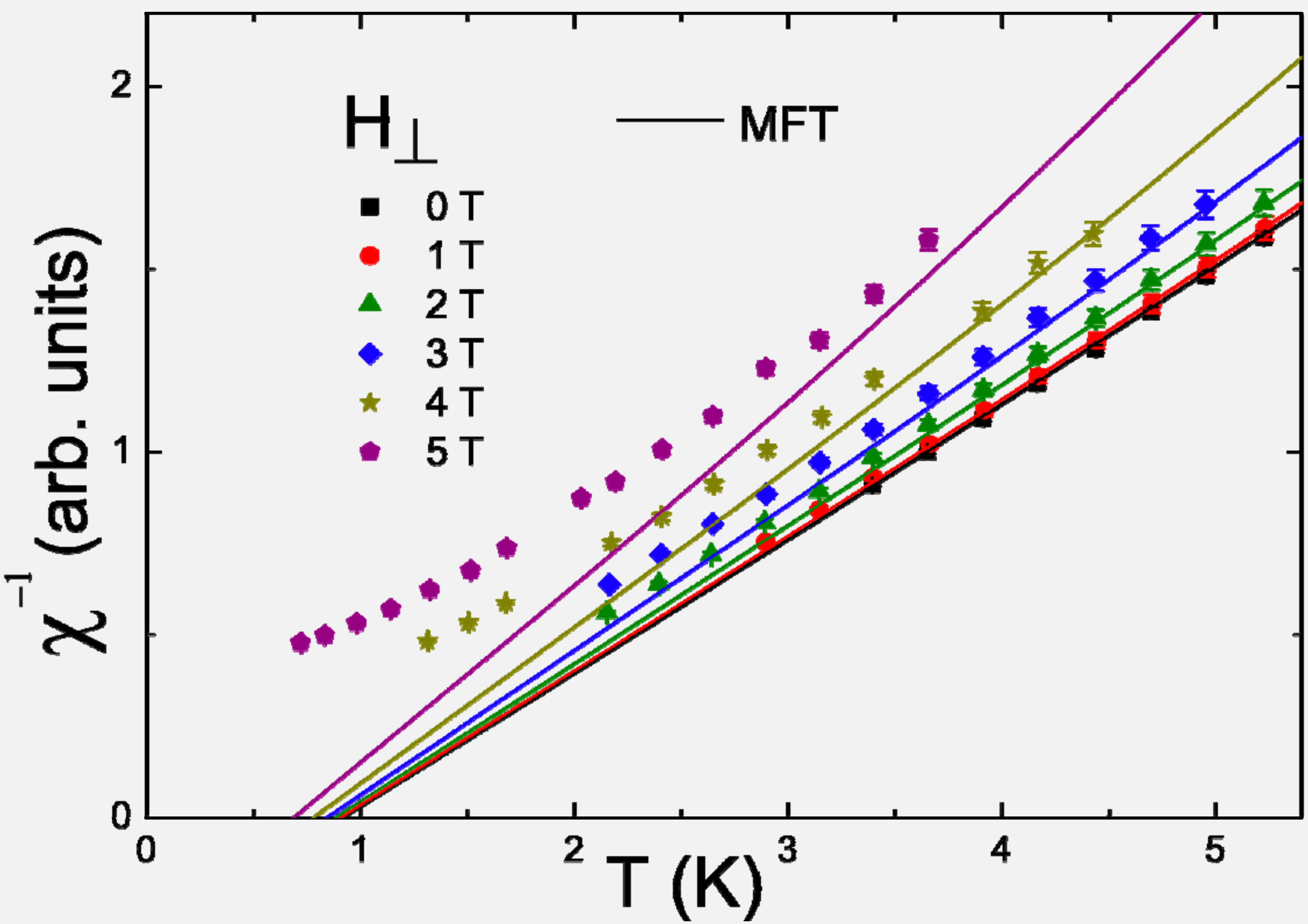
$H_\perp$
0 T
1 T
2 T
3 T
χ^{-1} (arb. units)
T (K)
0
1
2
3
4
5
0
1
2



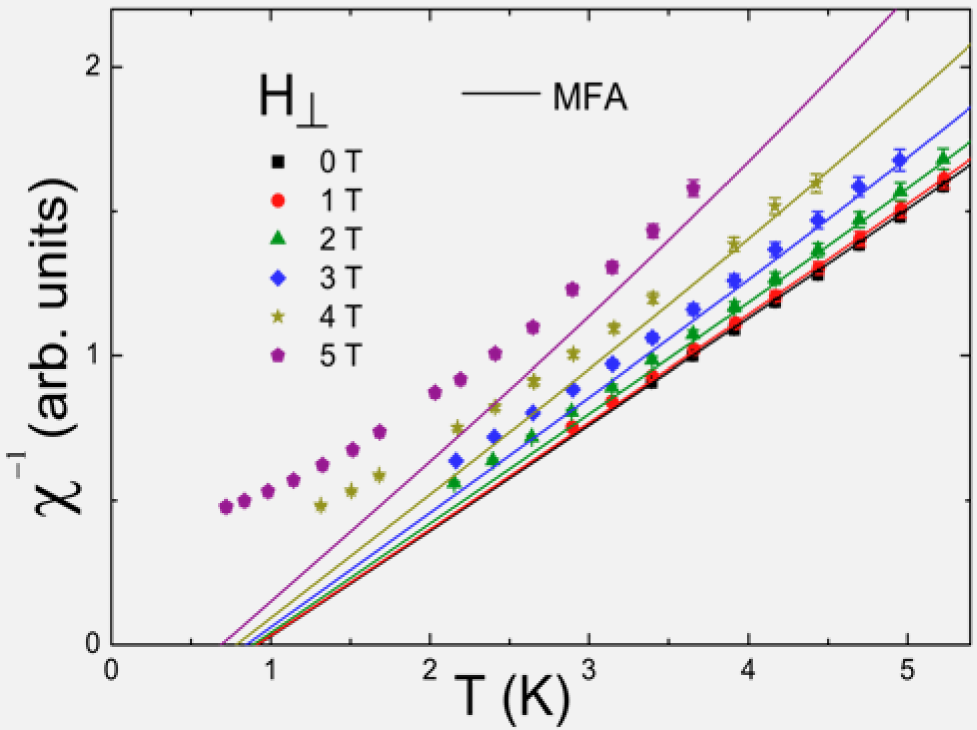
H⊥
0 T
1 T
2 T
3 T
4 T
χ^{-1} (arb. units)
T (K)
0
1
2
3
4
5

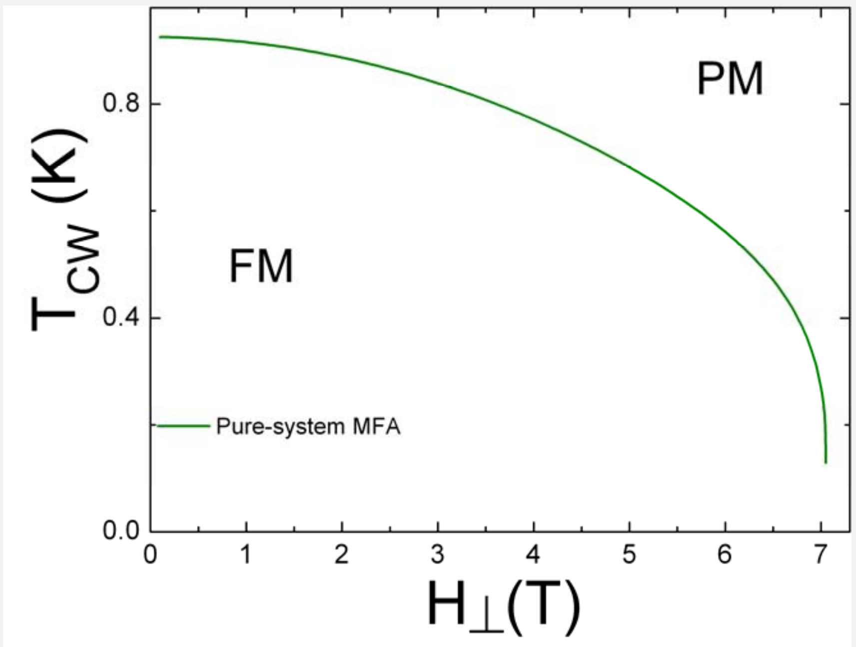


$H_{\perp}$
0 T
1 T
2 T
3 T
4 T
5 T
χ^{-1} (arb. units)
T (K)
0
1
2
0
1
2
3
4
5



$$\mathcal{H} = \mathcal{H}_{molecule} + g\mu_B \vec{H}_\perp \cdot \vec{S}_\perp + \mathcal{H}_{dipole}$$

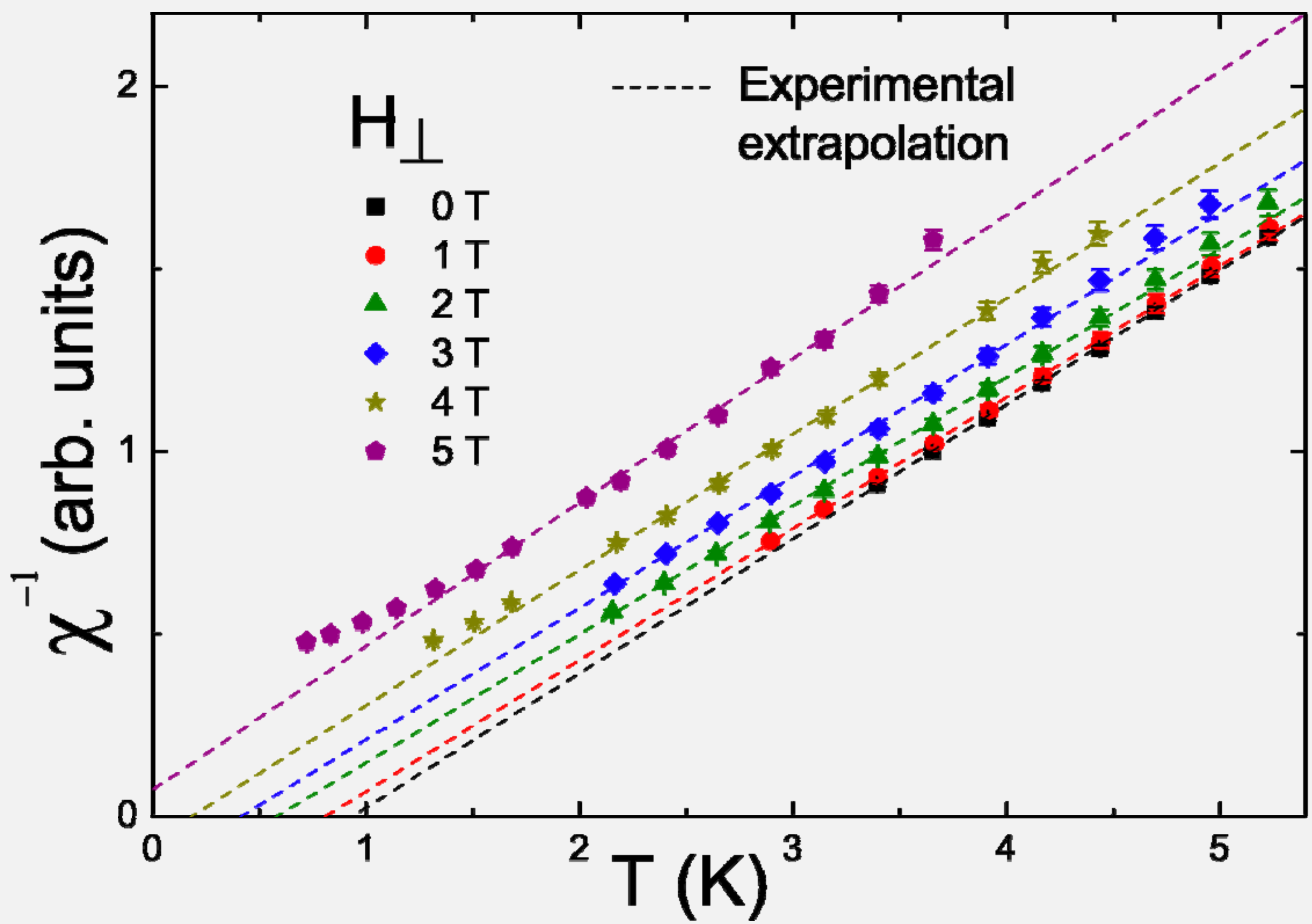




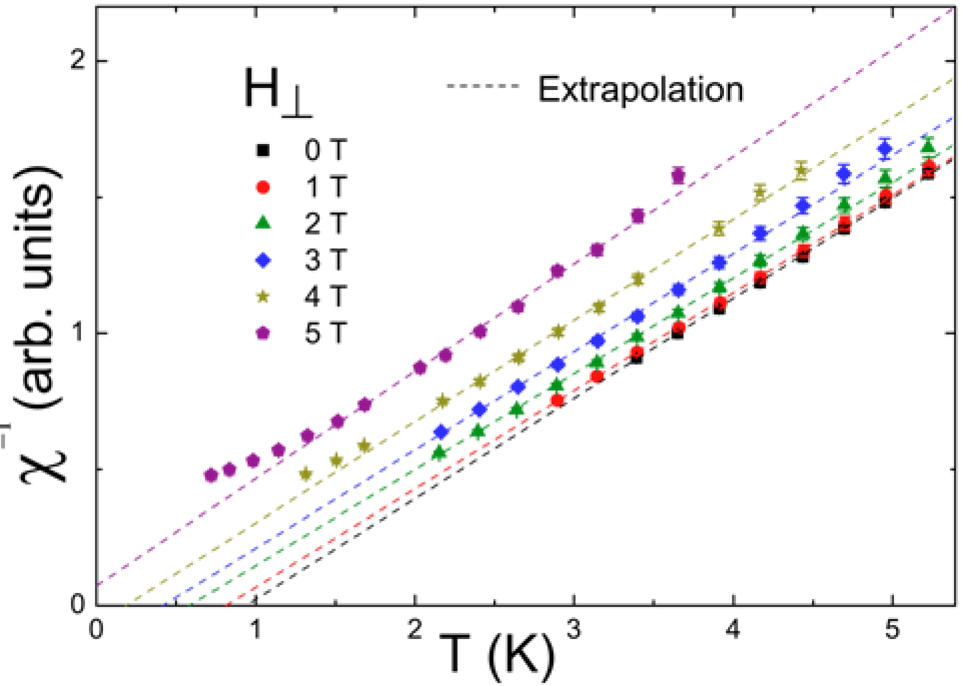
Mean field calculation of transition temperature for a pure dipolar Ising ferromagnet in transverse field.
[Millis *et al*, PRB 81, 024423 (2010)]

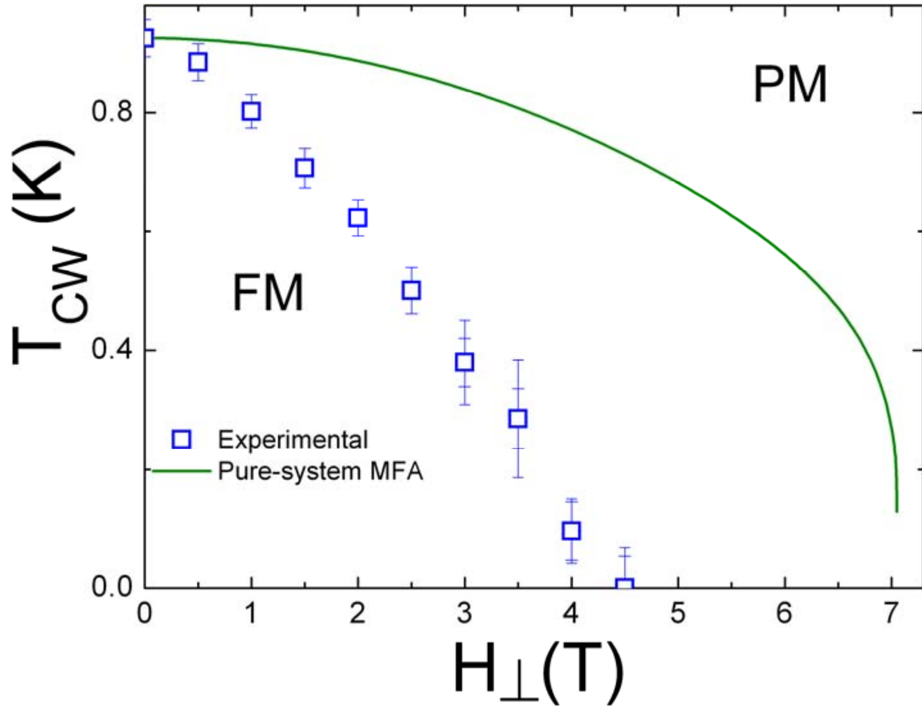
T_C decreases due to quantum fluctuation (spin canting).

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



χ^{-1} (arb. units)
T (K)
$H_\perp$
0 T
1 T
2 T
3 T
4 T
5 T
Experimental extrapolation
0
1
2
3
4
5
0
1
2



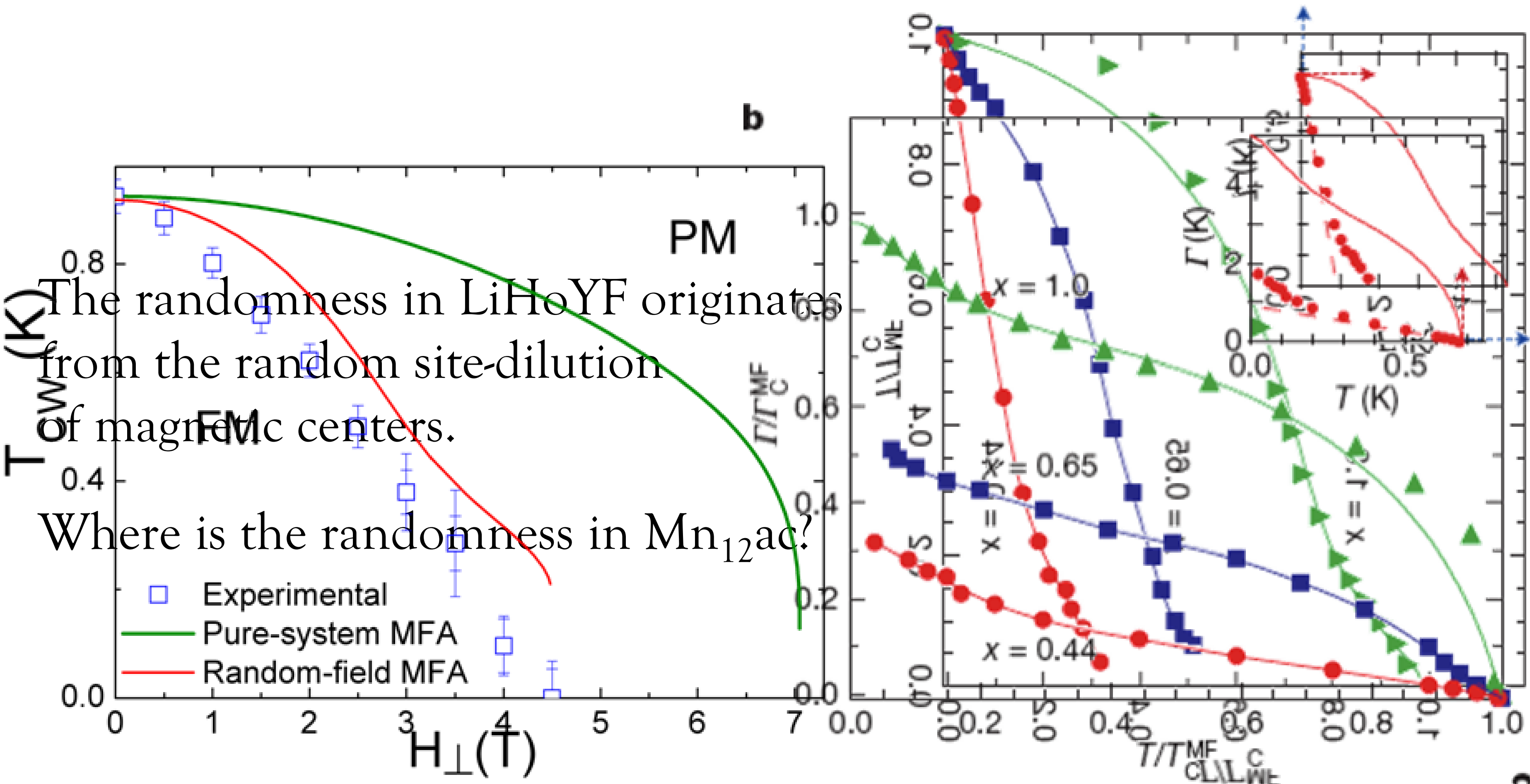


The intercept is suppressed by the transverse magnetic field much more strongly than expected.

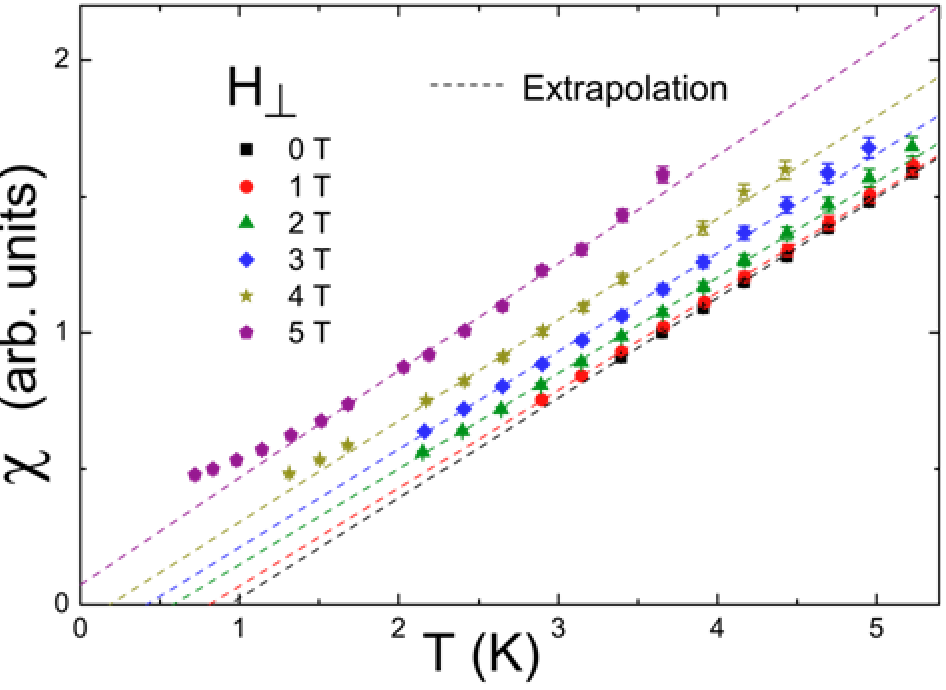
Behavior similar to $LiHo_xY_{1-x}F_4$

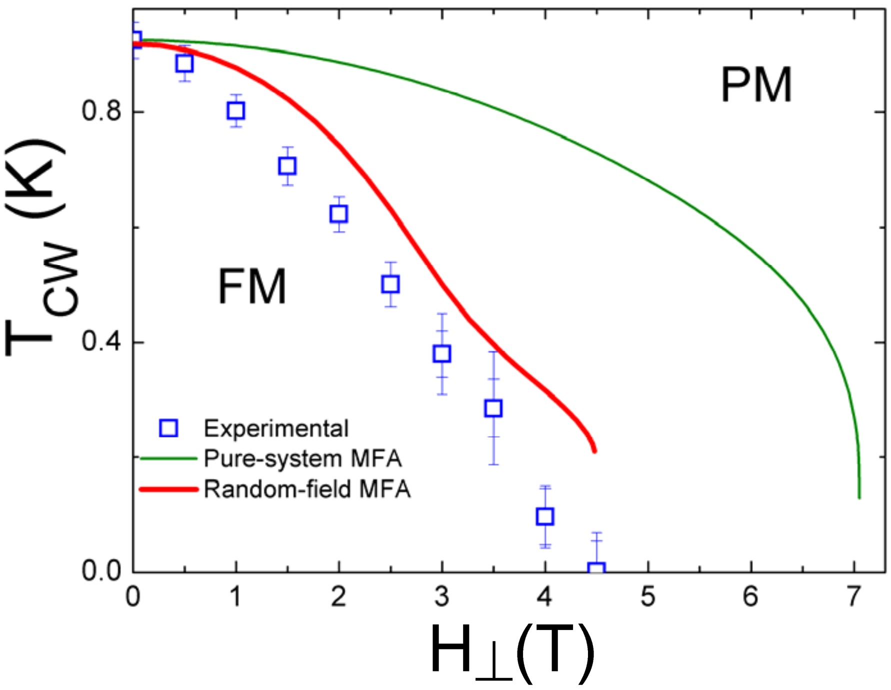
Silevitch *et al.* (Nature, **448**, 06050 (2007))

Random Field Ising Ferromagnetism (RFIFM)



- The randomness in LiHoYF originates from the random site-dilution of magnetic centers.
- Where is the randomness in $Mn_{12}ac$?





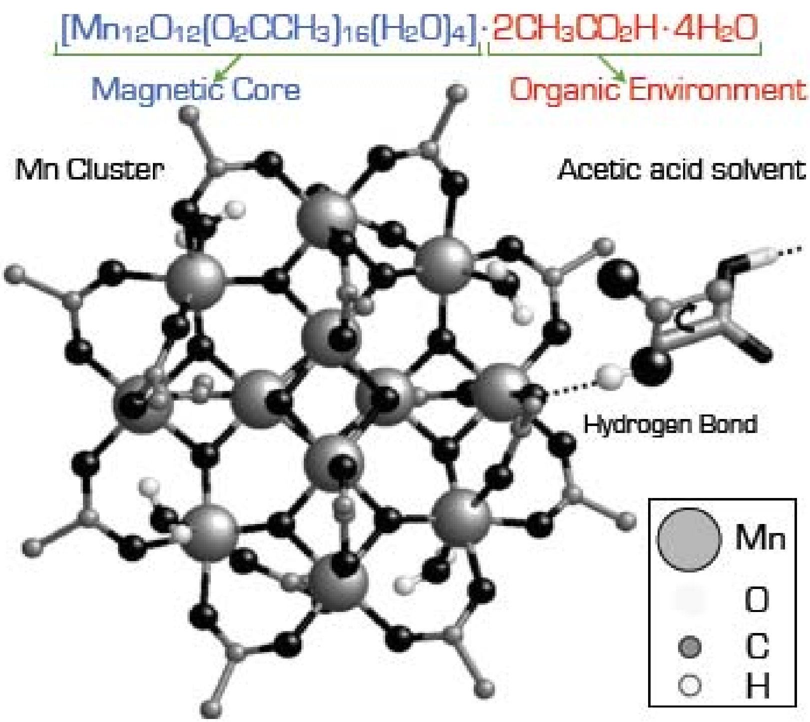
Random fields established by transverse field in the presence of isomer disorder

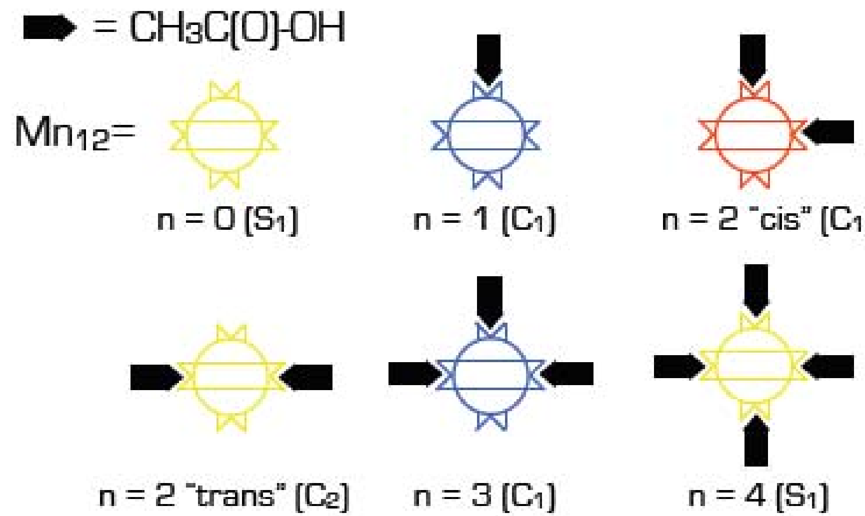
$$H_{mol} = H^0_{mol} + H^{ran,i}_{mol}.$$

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

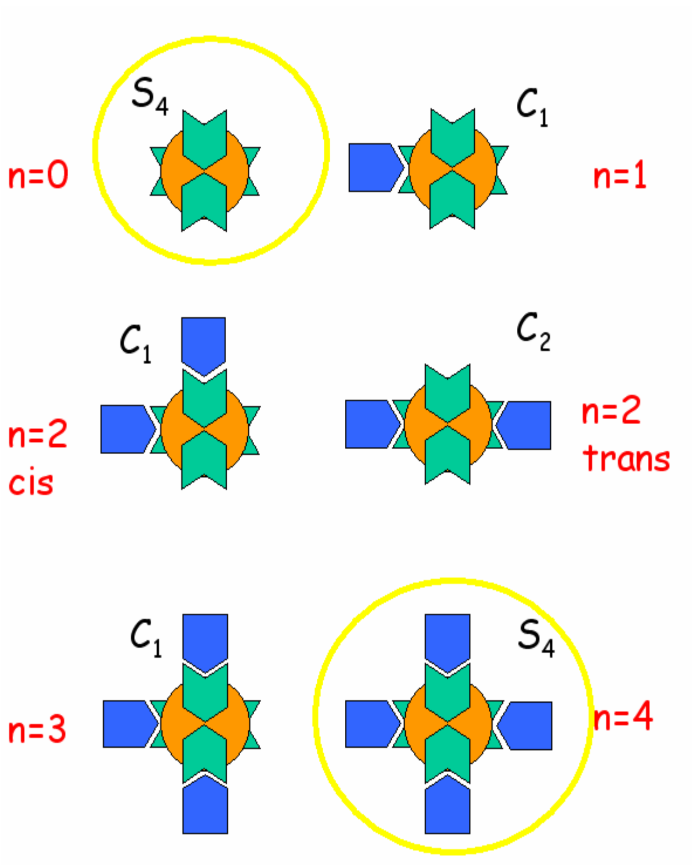
Millis, Kent, Sarachik, Yeshurun PRB **81**, 024423, 2010

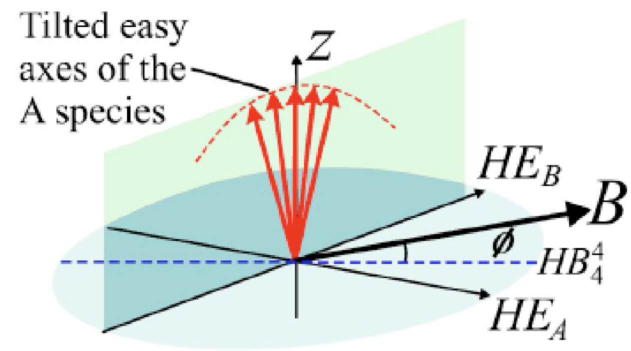
The distribution of random fields arises physically from a distribution of isomers of the host acetate material.

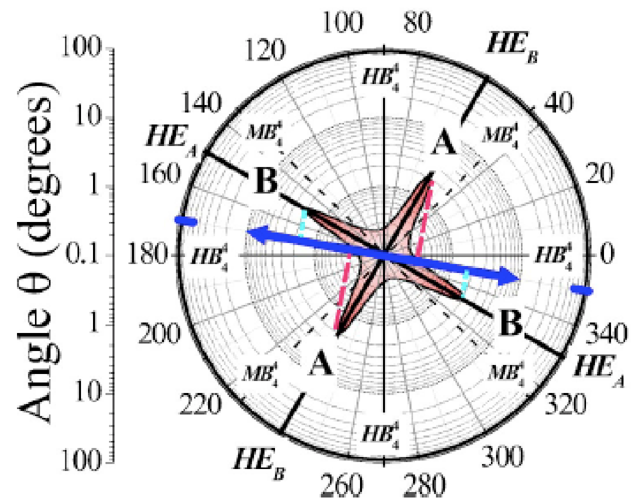




6 Different Isomers of Mn_{12}







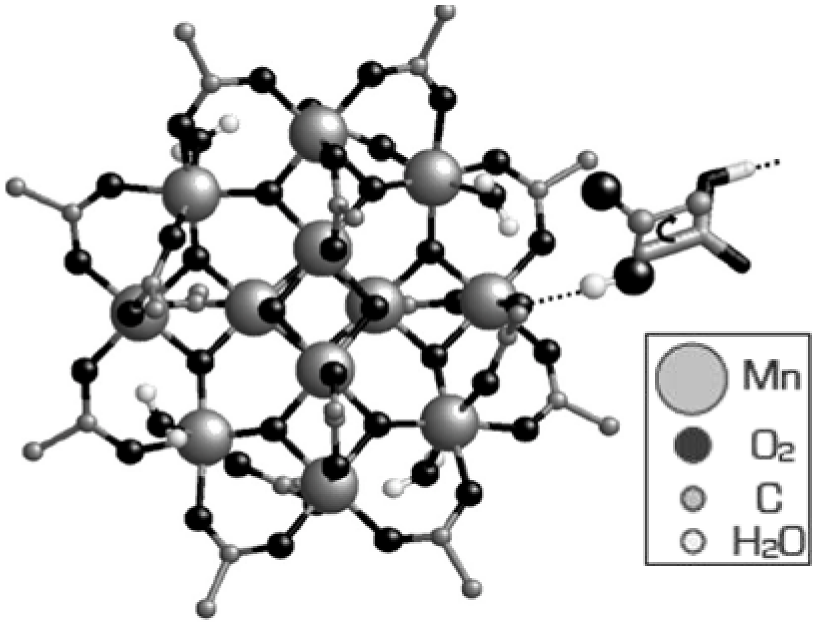
Six different isomers

Cornia et al. PRL 2002;
del Barco et al. JLTP 2005

Isomer disorder causes the easy axis of some of the molecules to tilt away from the crystal *c* axis by a small angle $\theta \sim 0.5$ to 1.7 degrees

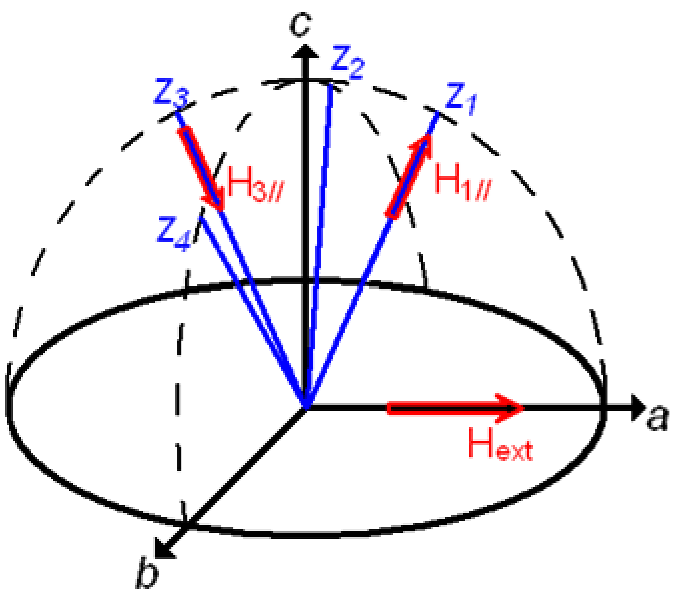
isomer disorder → easy axis tilt

- The external magnetic field is applied transverse to the crystal c-axis, NOT perpendicular to the easy axis of the tilted molecules.



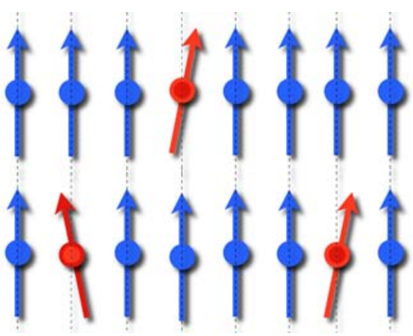
- The tilted molecules experience a field along their Ising axis.

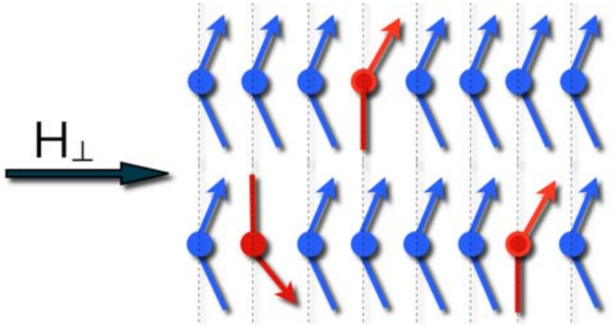
- The projection become comparable to the dipolar interactions when $H_\perp$ = 5T, the tilted spins are frozen and do not order. This leads to an effective dilution.



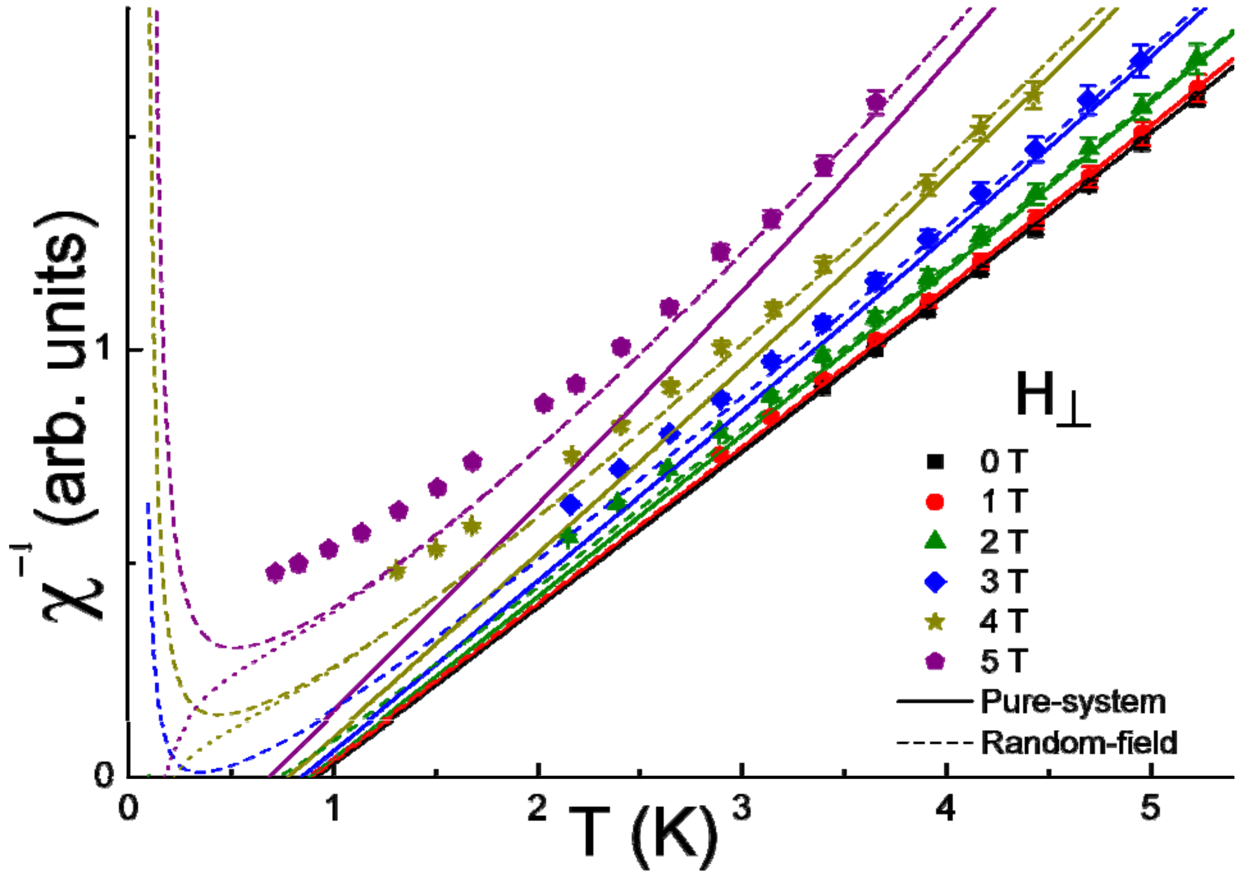
easy axis tilt ➔ random field

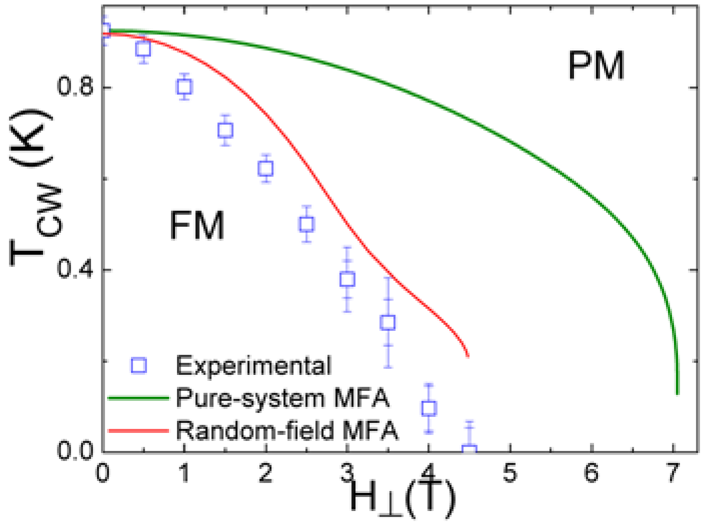
- At zero $H_\perp$, tilting changes dipolar interaction very little.
- For untilted molecules, the two longitudinal orientations are equal, even in $H_\perp$.
- For tilted molecules, the projection of transverse field makes one orientation preferred over the other.



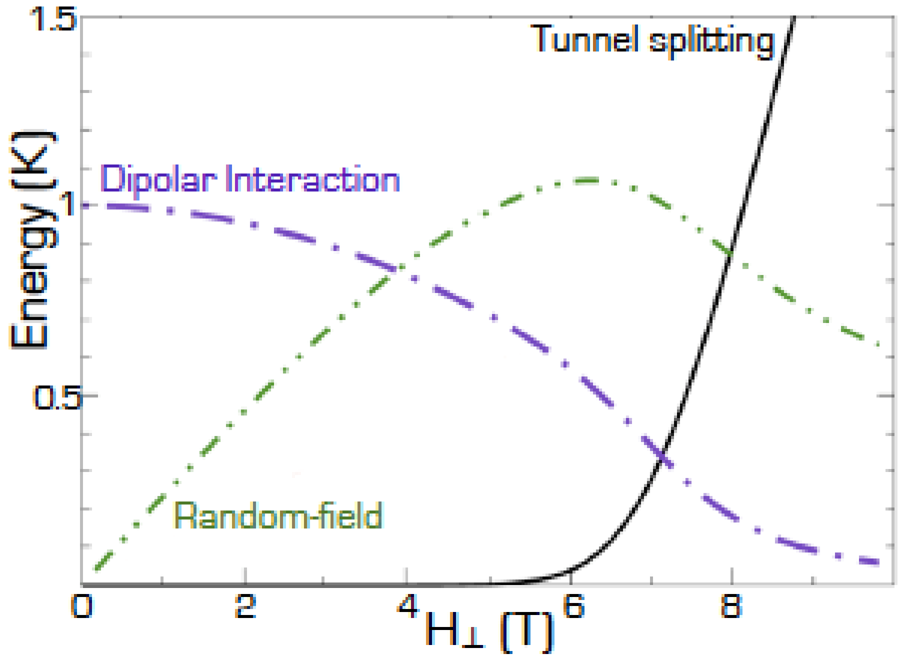


Random Field Ising Ferromagnetism





PM
FM
T_{CW} (K)
0.0
0.4
0.8
0
1
2
3
4
5
6
7
$H_\perp$(T)
Experimental
Pure-system MFA
Random-field MFA



Tunnel splitting
Dipolar Interaction
Random-field
Energy (K)
1.5
1
0.5
0
2
4
6
8
$H_\perp$ (T)

$LiHo_xY_{1-x}F_4$ – 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)

OUTLINE

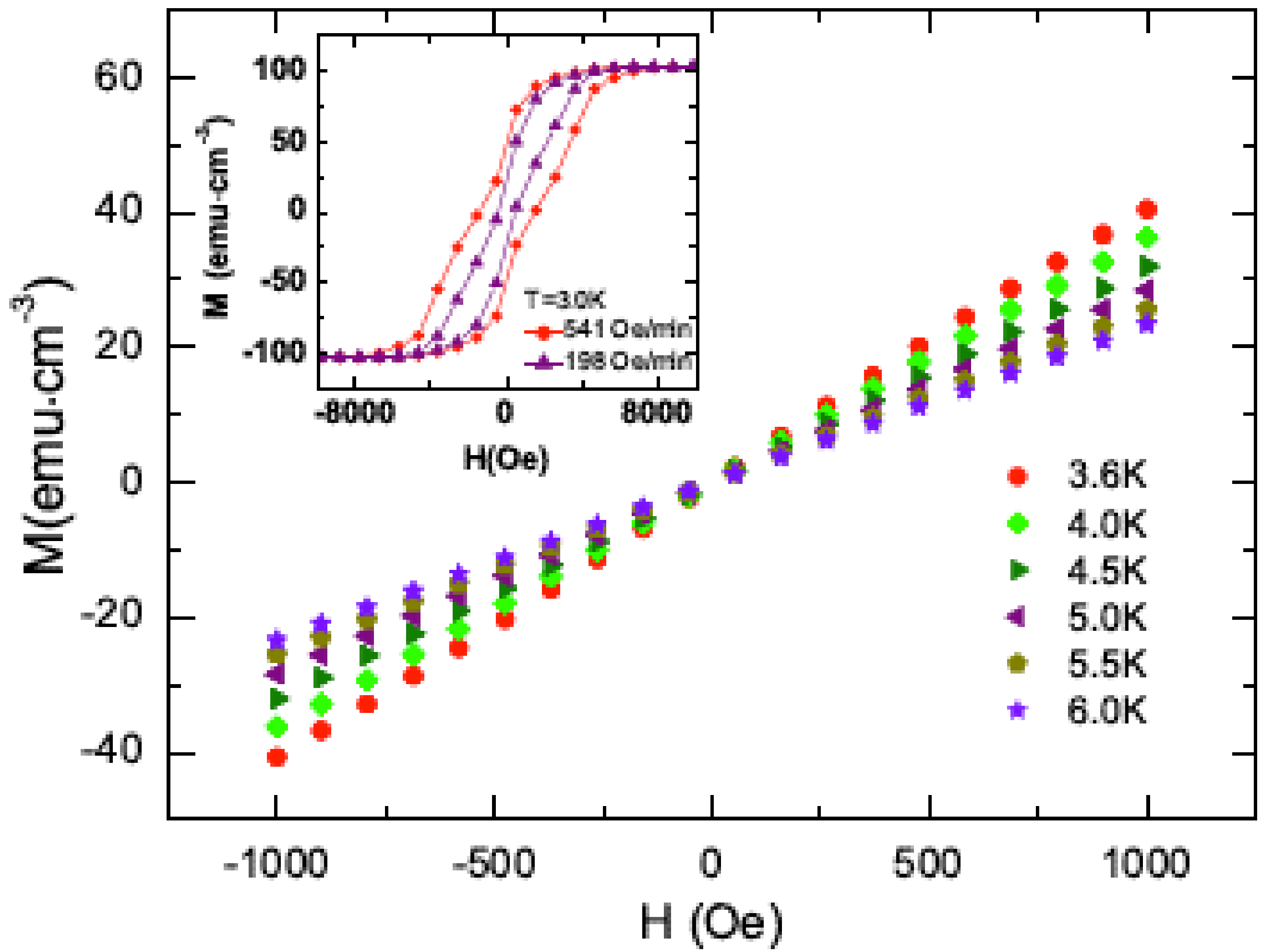
I - Background

(a) Molecular Magnets: Mn_{12}-acetate, Fe-8
(b) Blocking (spin reversal by tunneling, avalanches)

II - Random Field Ising Ferromagnetism (RFIFM)

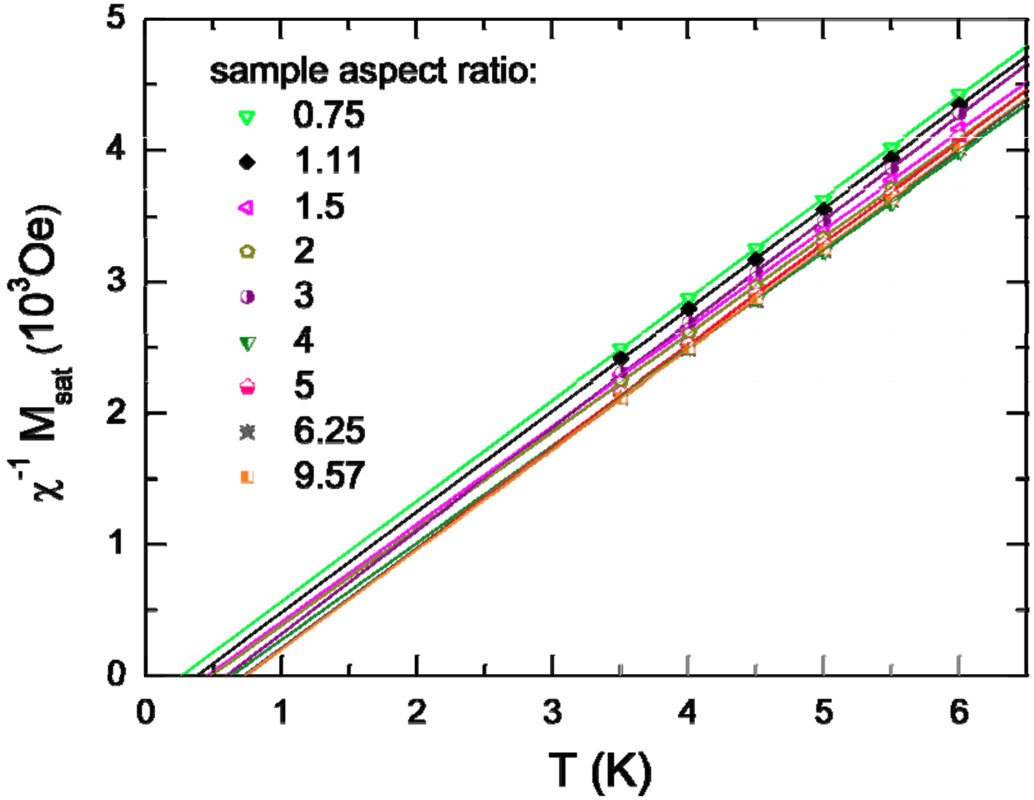
(a) Ferromagnetism in Mn-12?
(b) Suppression of T_c by transverse magnetic field
(c) RFIFM – whence the randomness?
(d) Comparison with LiHoF

III – Dipole interactions?



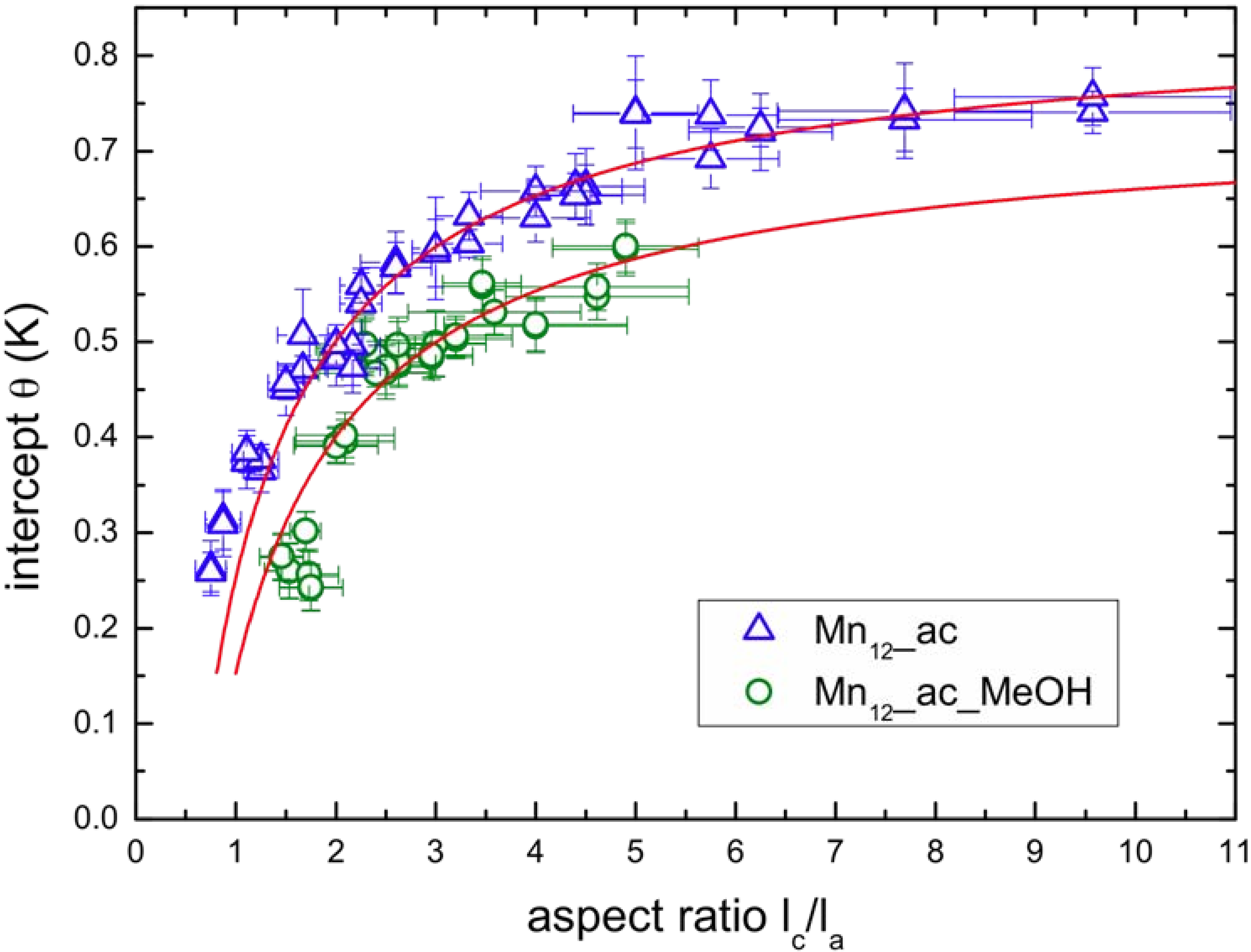
M(emu·cm^-3)
H (Oe)
3.6K
4.0K
4.5K
5.0K
5.5K
6.0K
M (emu·cm^-3)
H(Oe)
T=3.6K
541 Oe/min
198 Oe/min

Determination of Curie-Weiss θ of Mn_{12}-ac and Mn_{12}-ac -MeOH

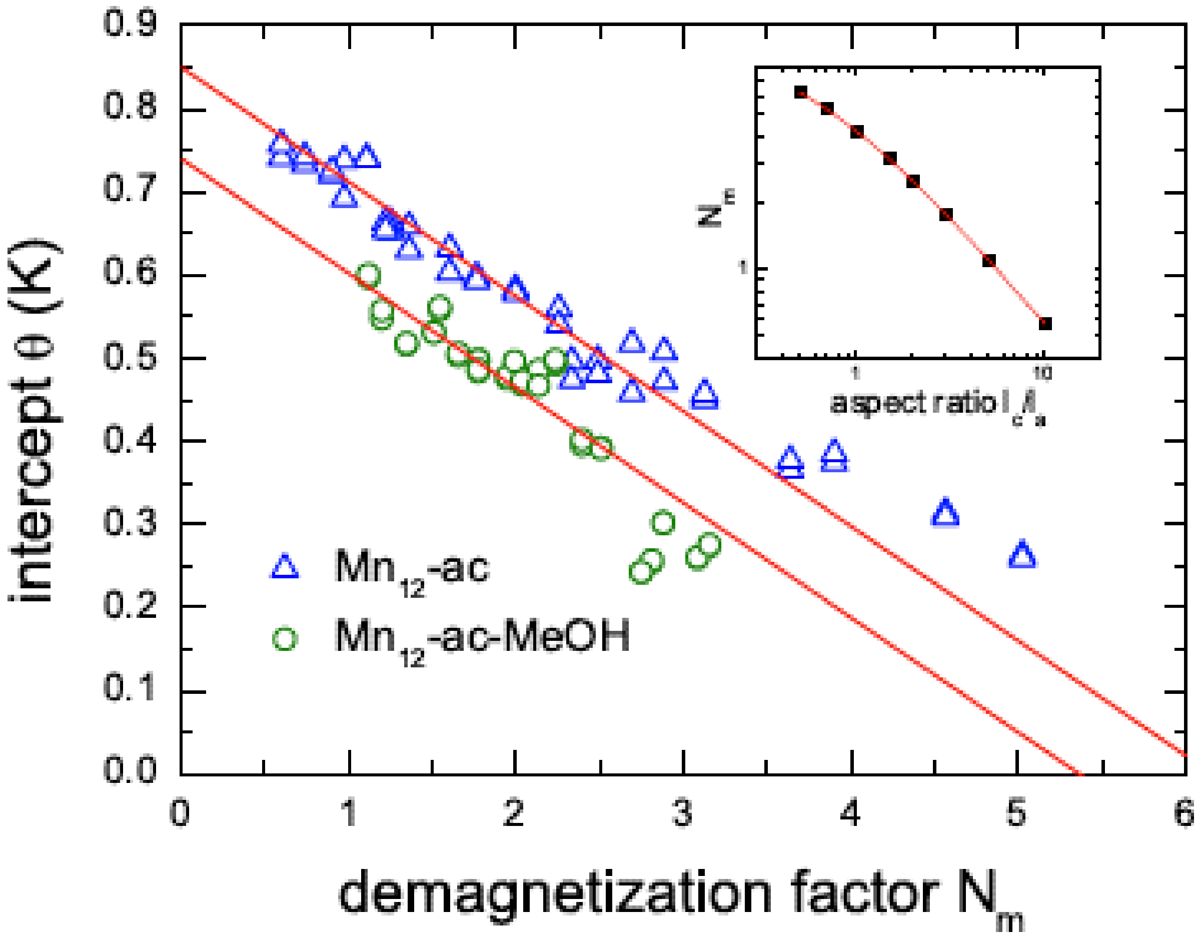


Nearly identical lattice constants and unit cell volumes

Different ligands



intercept θ (K)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
1
2
3
4
5
6
7
8
9
10
11
aspect ratio l_c/l_a
Mn_{12}_ac
Mn_{12}_ac_MeOH



In addition to dipolar interactions,
a non-dipolar (superexchange) contribution.

Summary

I - *Background – molecular magnets*

II - We have found an experimental realization of random field Ising ferromagnetism (RFIFM) in Mn12-ac, a prototypical molecular magnet.

III - The randomness is introduced, and can be tuned, by external magnetic field.

III – The interactions are not purely dipolar and depend on the crystal ligands.