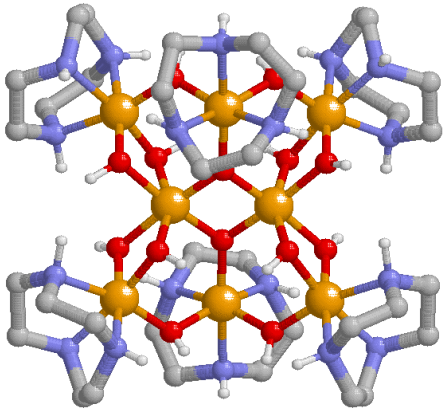
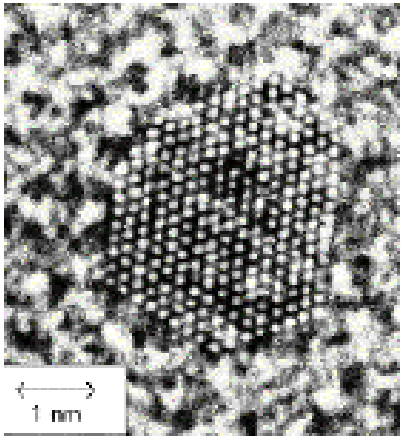
From the atom to magnetic nanoparticles



S = 1/2 to ~ 30

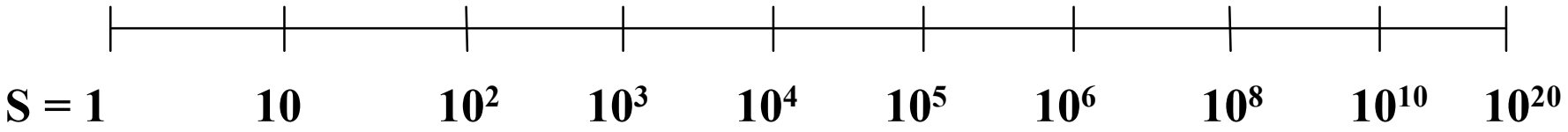
Edgar Bonet
Laboratoire Louis Néel
CNRS – Grenoble

Brasov, september 2003



S = 10^2 to 10^6

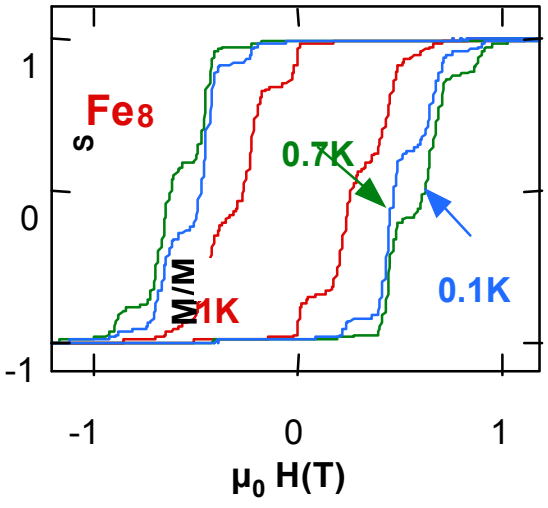
Magnetic scales

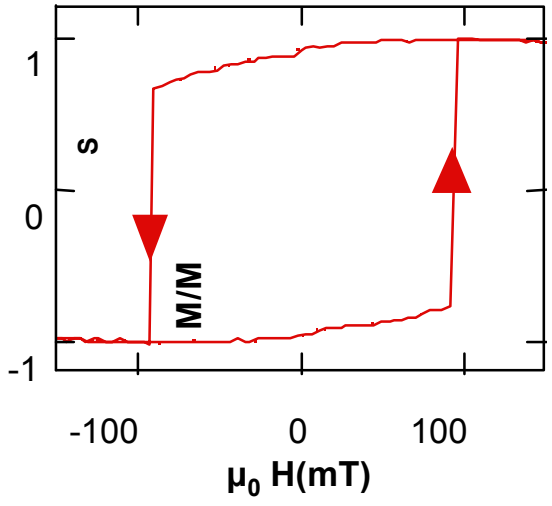


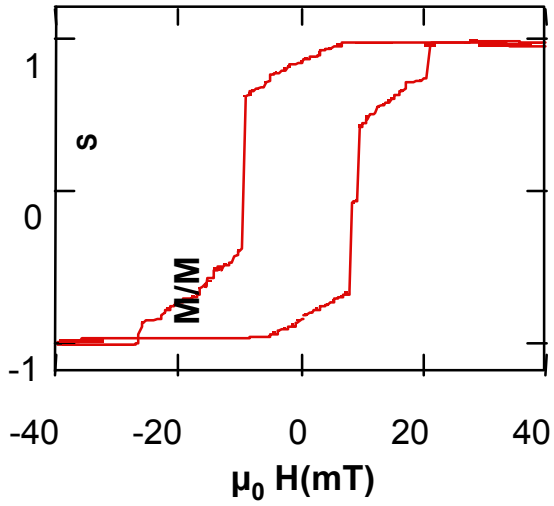
giant spin
quantum tunneling,
quantization
quantum interference

single - domain
uniform rotation
curling

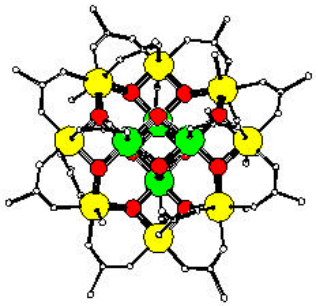
multi - domain
nucleation, propagation and
annihilation of domain walls



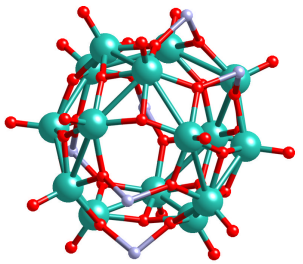




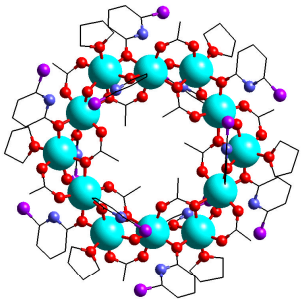
Giant spin molecules



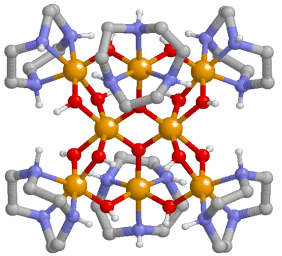
Mn_{12} (S = 10)



V_{15} (S = ½)



Ni_{12} (S = 12)



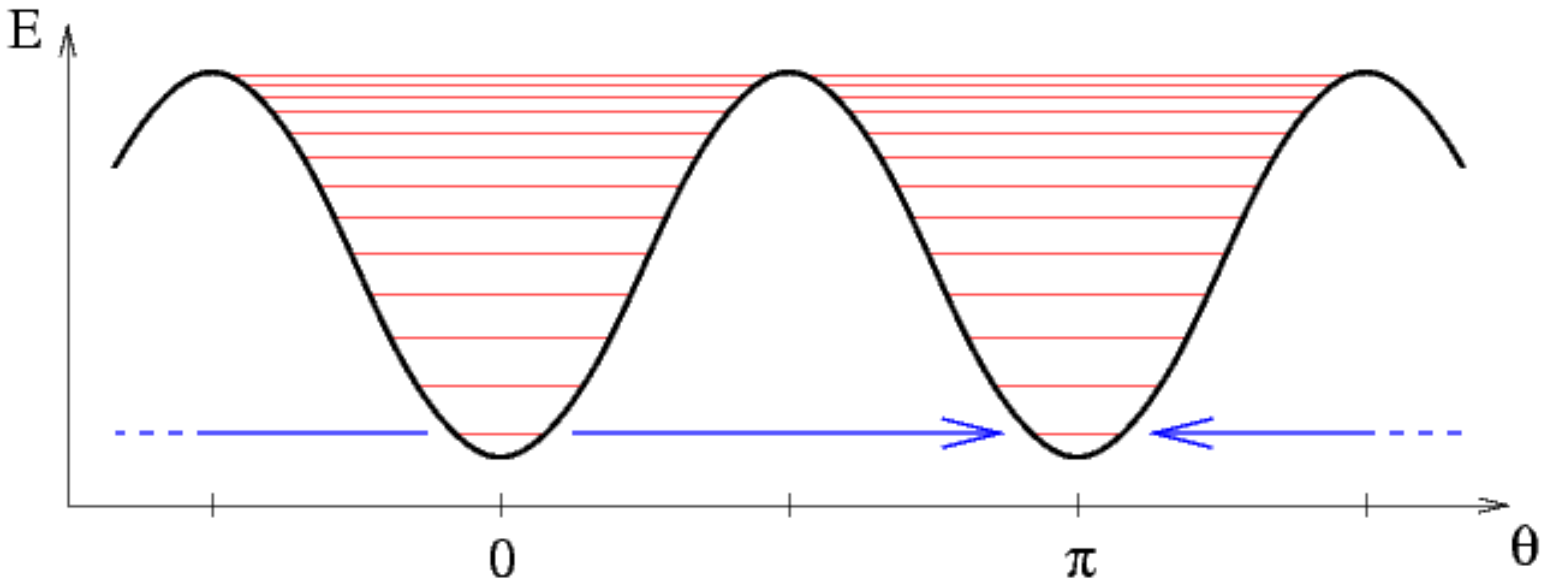
Fe_8 (S = 10)

- Single crystals
- high intra-molecular couplings
- low inter-molecular couplings

Collection of
identical quantum systems

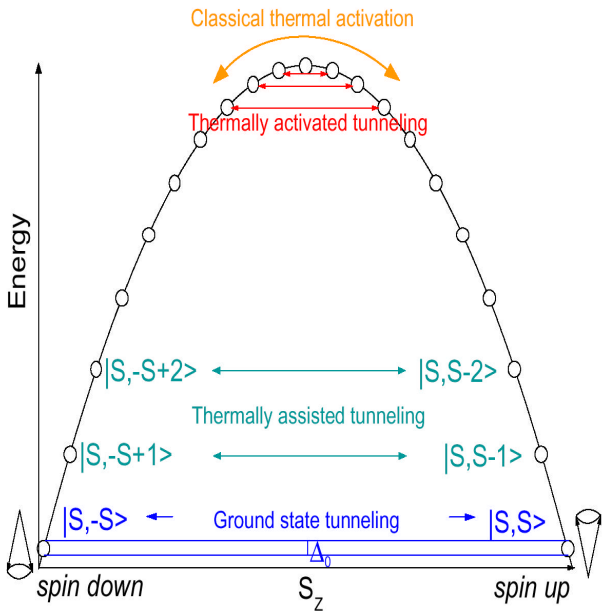
Giant spin model

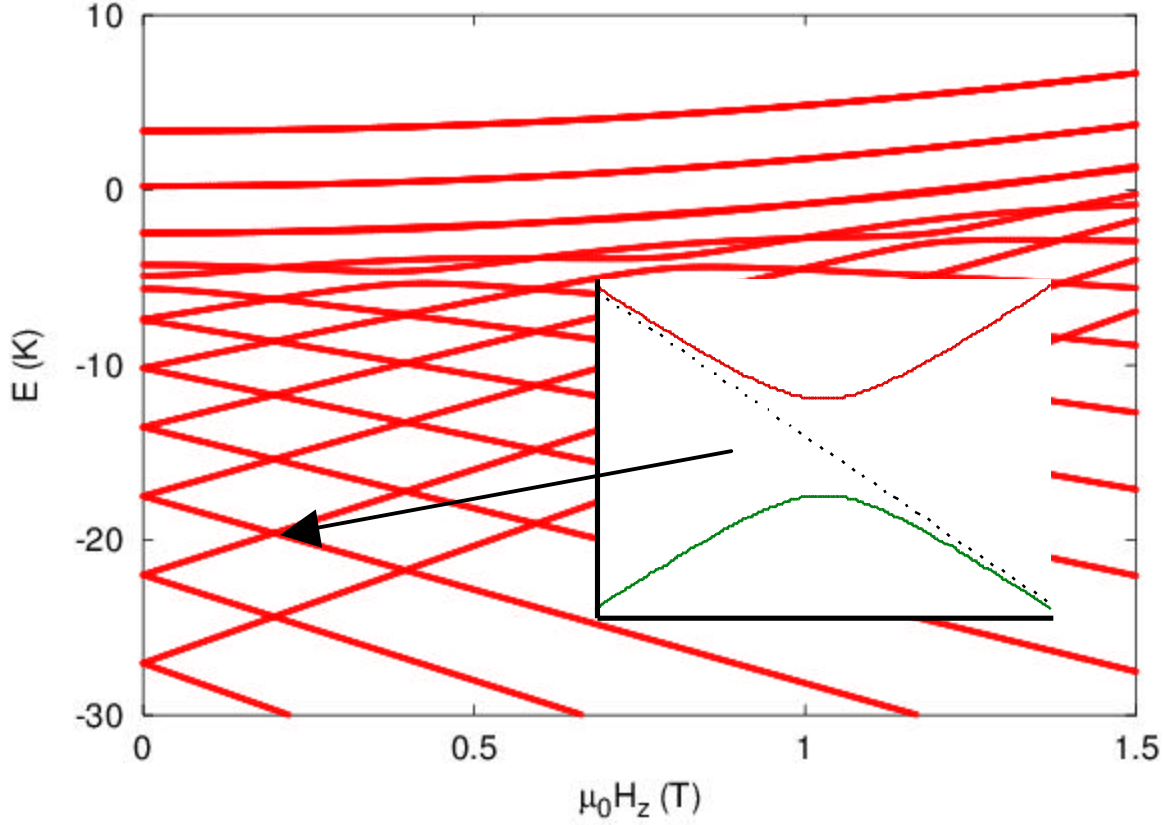
$$\mathcal{H} = -DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B\mu_0\mathbf{S}\cdot\mathbf{H}$$



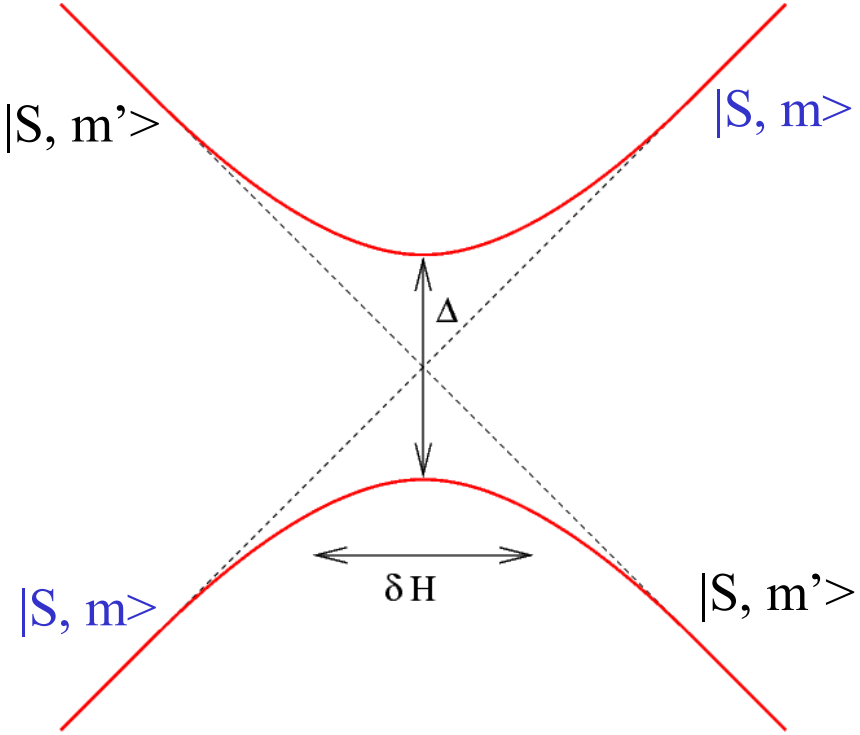
Giant spin model

$$\mathcal{H} = -DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B\mu_0\mathbf{S}\cdot\mathbf{H}$$





Landau-Zener tunneling



$$\delta H = \frac{\Delta}{g\mu_B\mu_0|m-m'|}$$

- Oscillation time

$$\tau_\Delta = \hbar/\Delta$$

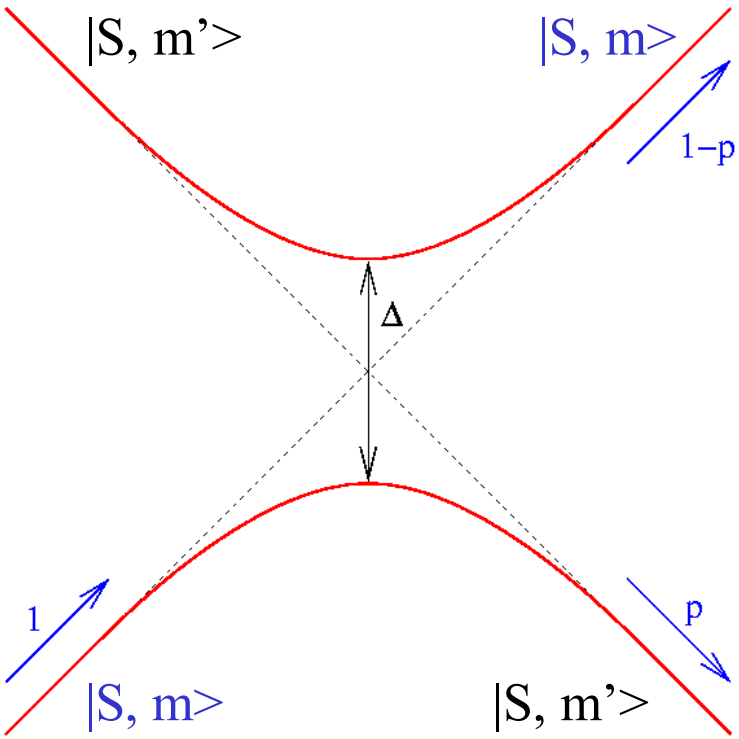
- crossing time

$$\tau_H = \frac{\delta H}{\mathrm{d}H/\mathrm{d}t}$$

$$\frac{\tau_H}{\tau_\Delta} = \frac{\Delta^2}{\hbar g\mu_B\mu_0|m-m'|\mathrm{d}H/\mathrm{d}t}$$

- $\tau_H \ll \tau_\Delta$ keeps the same state
- $\tau_H \gg \tau_\Delta$ follows energy level

Landau-Zener tunneling



$$P = 1 - \exp\left(-c\frac{\Delta^2}{\mathrm{d}H/\mathrm{d}t}\right)$$

$$c = \frac{\pi}{2\hbar g\mu_B\mu_0|m-m'|}$$

- general result for a single level crossing

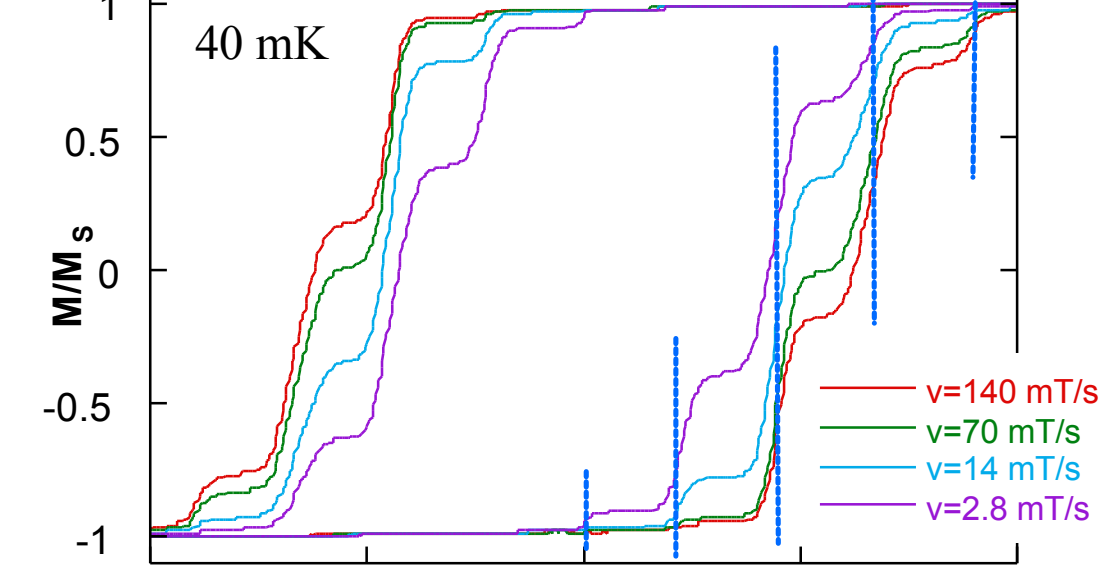
$$\mathcal{H} = \begin{pmatrix} A + g\mu_B\mu_0 mH & \Delta/2 \\ \Delta/2 & B + g\mu_B\mu_0 m'H \end{pmatrix}$$

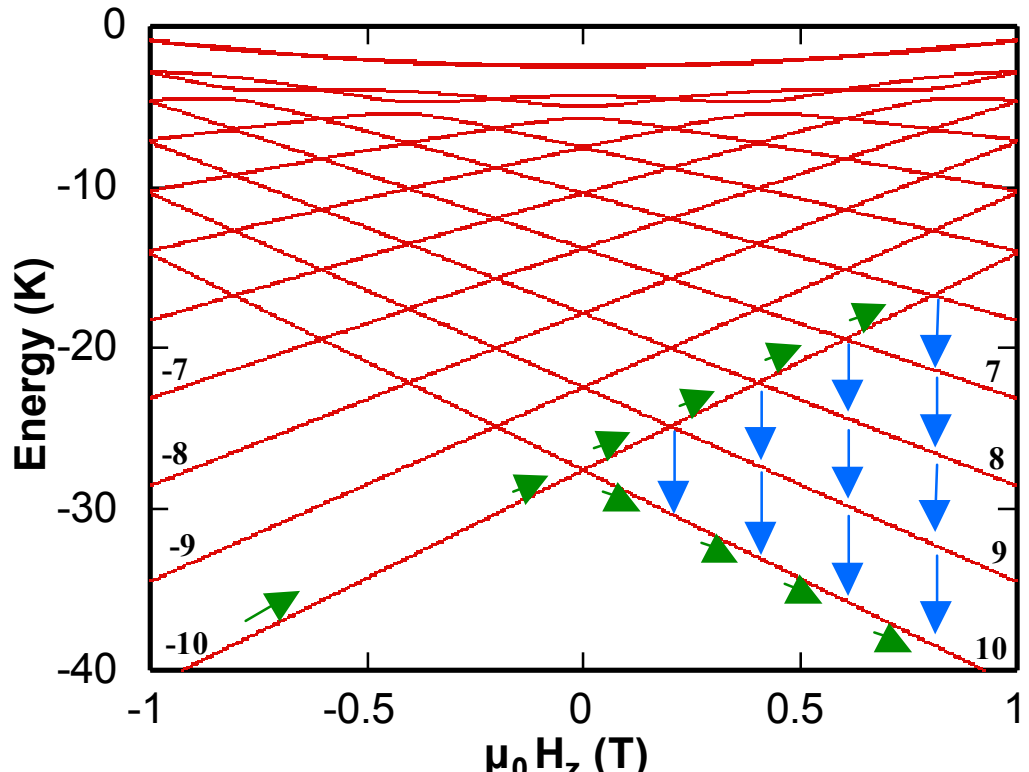
- solution of the Schroedinger equation

$$\mathcal{H}|\psi\rangle = i\hbar\frac{\partial}{\partial t}|\psi\rangle$$

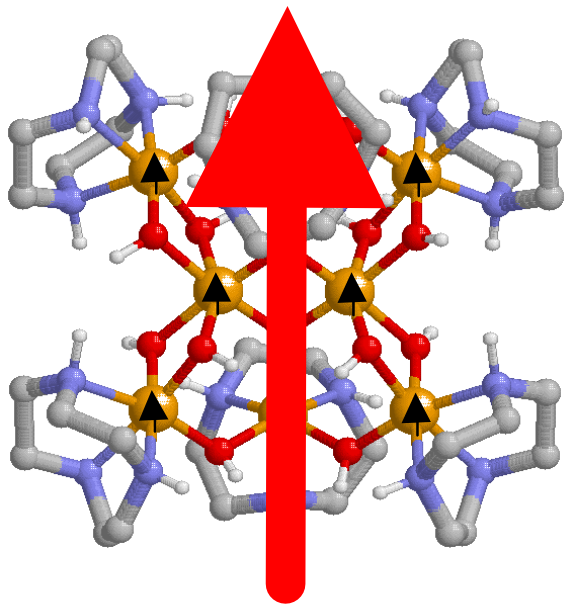
L. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932); **C. Zener**, *Proc. R. Soc. London, Ser. A* **137**, 696, (1932); **E.C.G. Stückelberg**, *Helv. Phys. Acta* **5**, 369 (1932); **S. Miyashita**, *J. Phys. Soc. Jpn.* **64**, 3207 (1995); **V.V. Dobrovitski and A.K. Zvezdin**, *Euro. Phys. Lett.* **38**, 377 (1997); **L. Gunther**, *Euro. Phys. Lett.* **39**, 1 (1997); **G.Rose and P.C.E. Stamp,** Low Temp. Phys. 113, 1153 (1999); **M. Leuenberger and D. Loss**, Phys. Rev. B 61, 12200 (2000); **M. Thorwart, M. Grifoni, and P. Hänggi**, Phys. Rev. Lett. 85, 860 (2000); …

Magnetization steps





Fe_8 $S = 10$



$$\mathcal{H} = -DS_z^2 + E(S_x^2 - S_y^2) + g\mu_B\mu_0\mathbf{S}\cdot$$

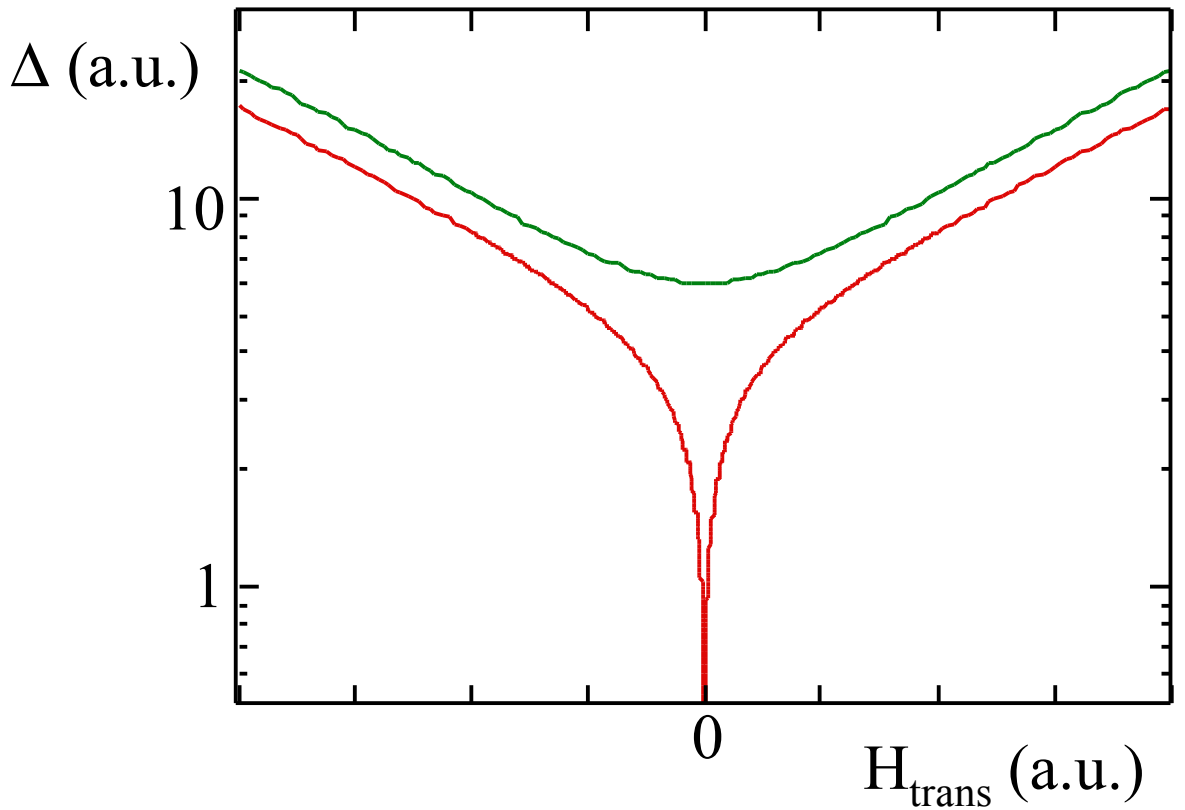
with S = 10, D = 0.27 K, E = 0.046K
A.-L. Barra et al. EPL (1996)

Spin-parity dependent quantum tunneling

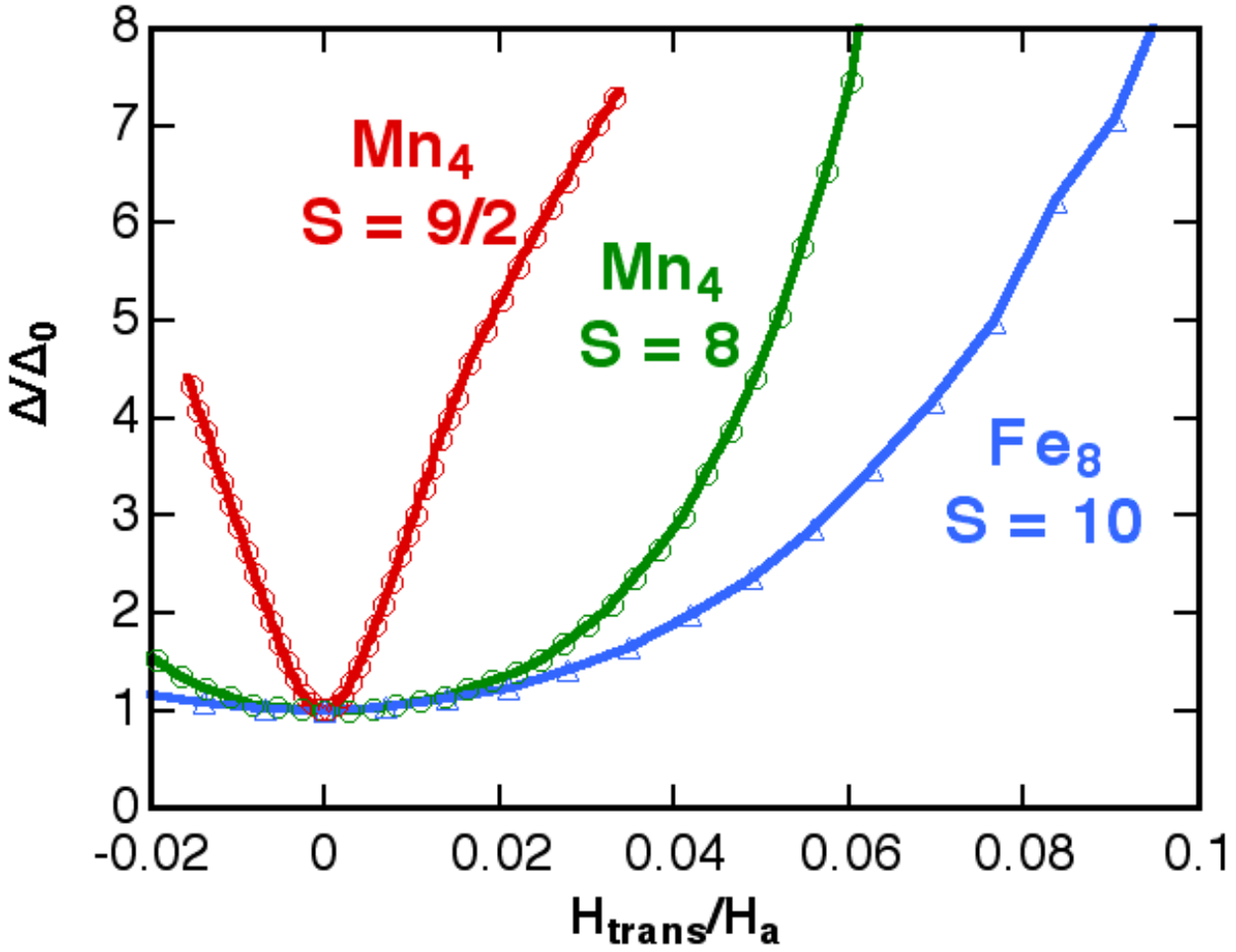
Kramers theorem: No matter how unsymmetric the crystal field, a system possessing an odd number of electrons must have a ground state that is at least doubly degenerate, even in the presence of crystal fields and spin-orbit interactions
H. A. Kramers, Proc. Acad. Sci. Amsterdam 33, 959 (1930)

Mesoscopic systems:

M. Enz and R. Schilling R.,J.Phys.C ,19 (1986) L711
J.L. Van Hemmen and S. Süto, Europhys. Lett. 1, 481 (1986)
D. Loss, D.P. DiVincenzo, and G. Grinstein, Phys. Rev. Lett., 69, 3232 (1992)
J. von Delft and C. L. Hendev. Phvs. Rev. Lett.. 69. 3236 (1992)



Spin-parity dependent quantum tunneling



S = 9/2
H_a = 4.6 T
$D_0 = 1.9*10^{-7}$ K

S = 8
H_a = 5.1 T
$D_0 = 0.28*10^{-7}$ K

S = 10
H_a = 4.0 T
$D_0 = 0.94*10^{-7}$ K

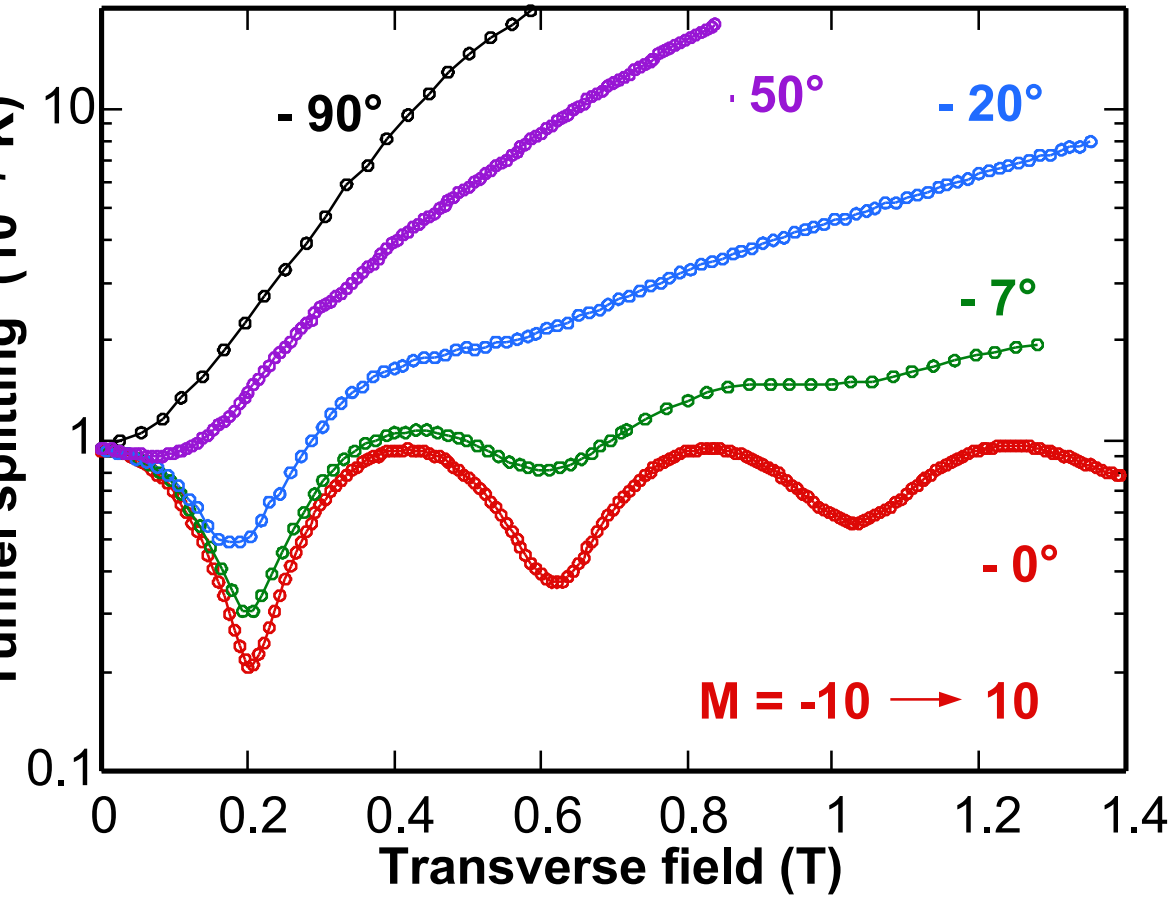
Environnemental effects

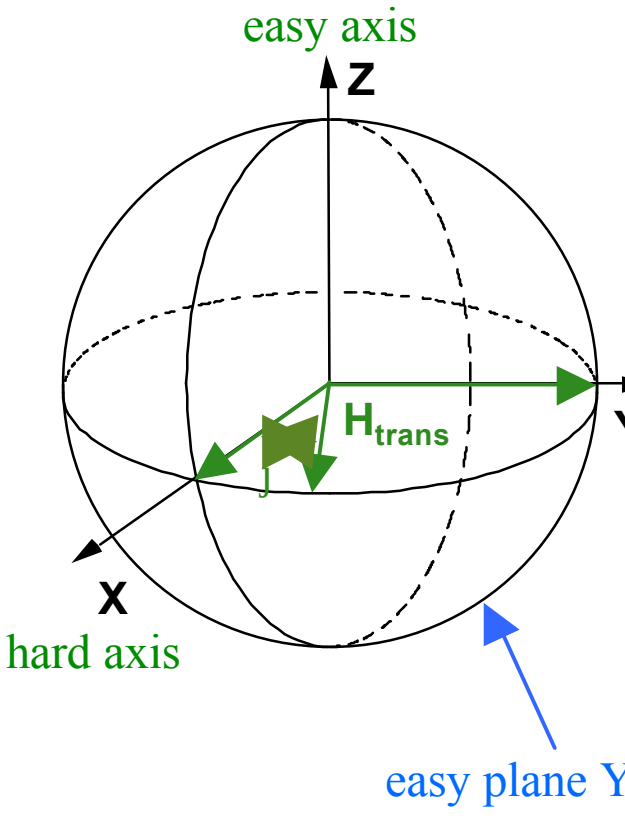
- hyperfine interaction (nuclear spins)
- dipolar interaction between molecules
- exchange interaction between molecules

etc

Phys. Rev. B 65, 180403 (2002)

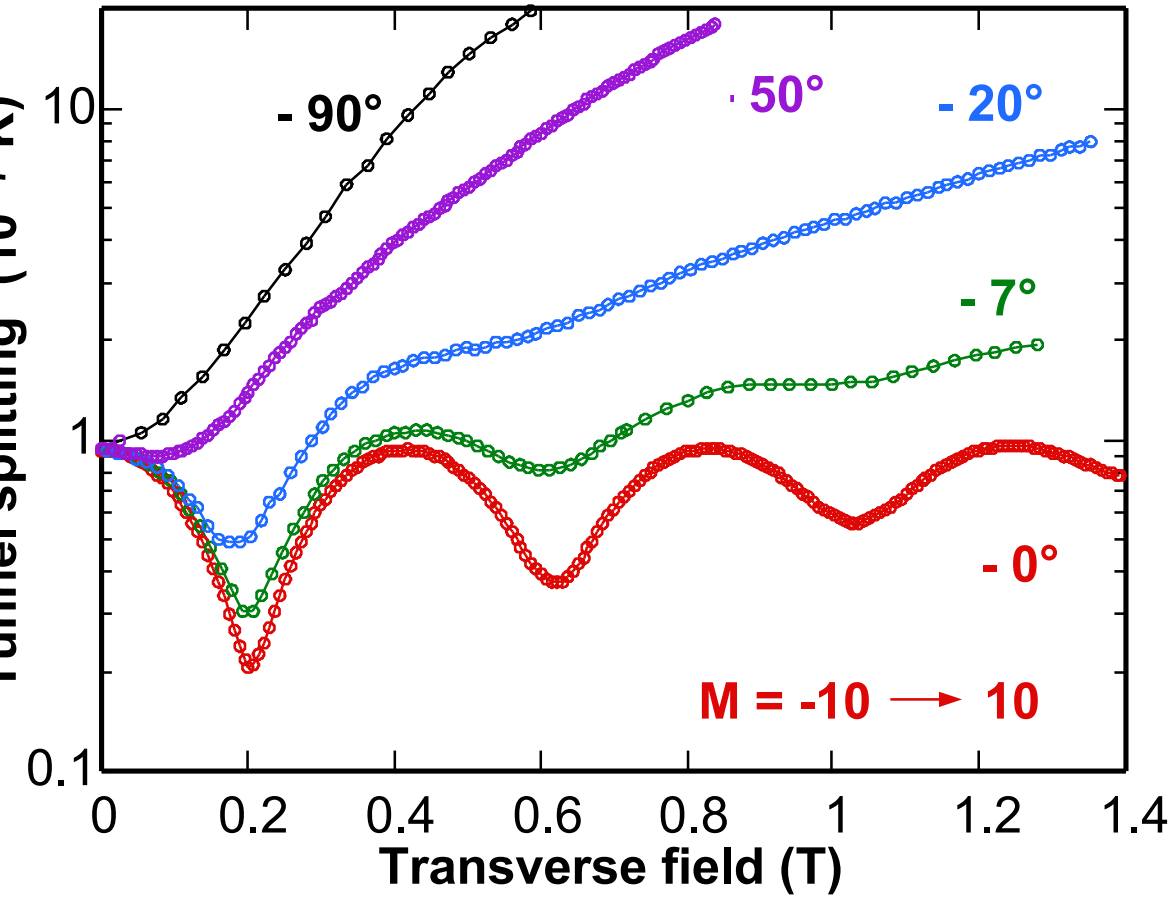
Quantum phase interference (Berry phase) in single-molecule magnets

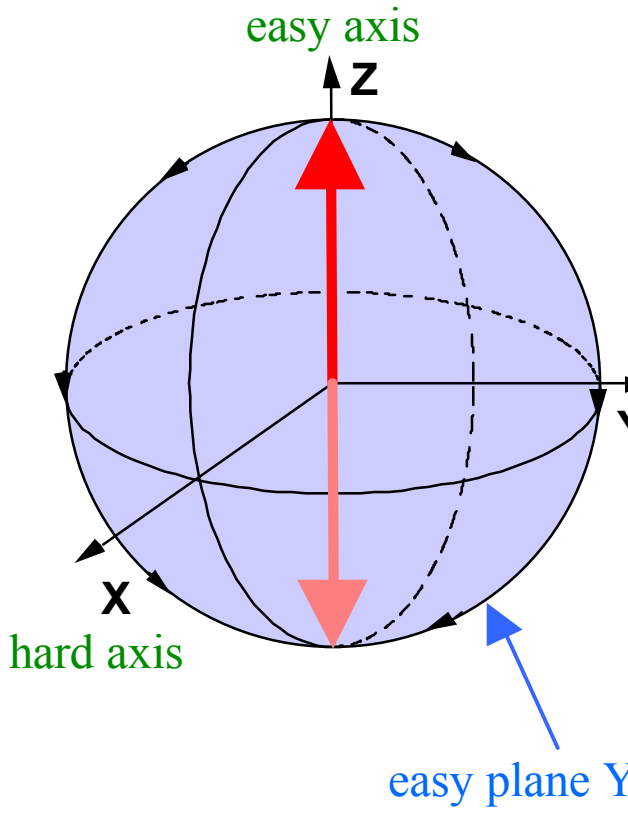




Quantum phase interference (Berry phase) in single-molecule magnets

W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)
Theory: A. Garg, Europhys. Lett. 22, 205 (1993)





Quantum phase interference (Berry phase) in single-molecule magnets

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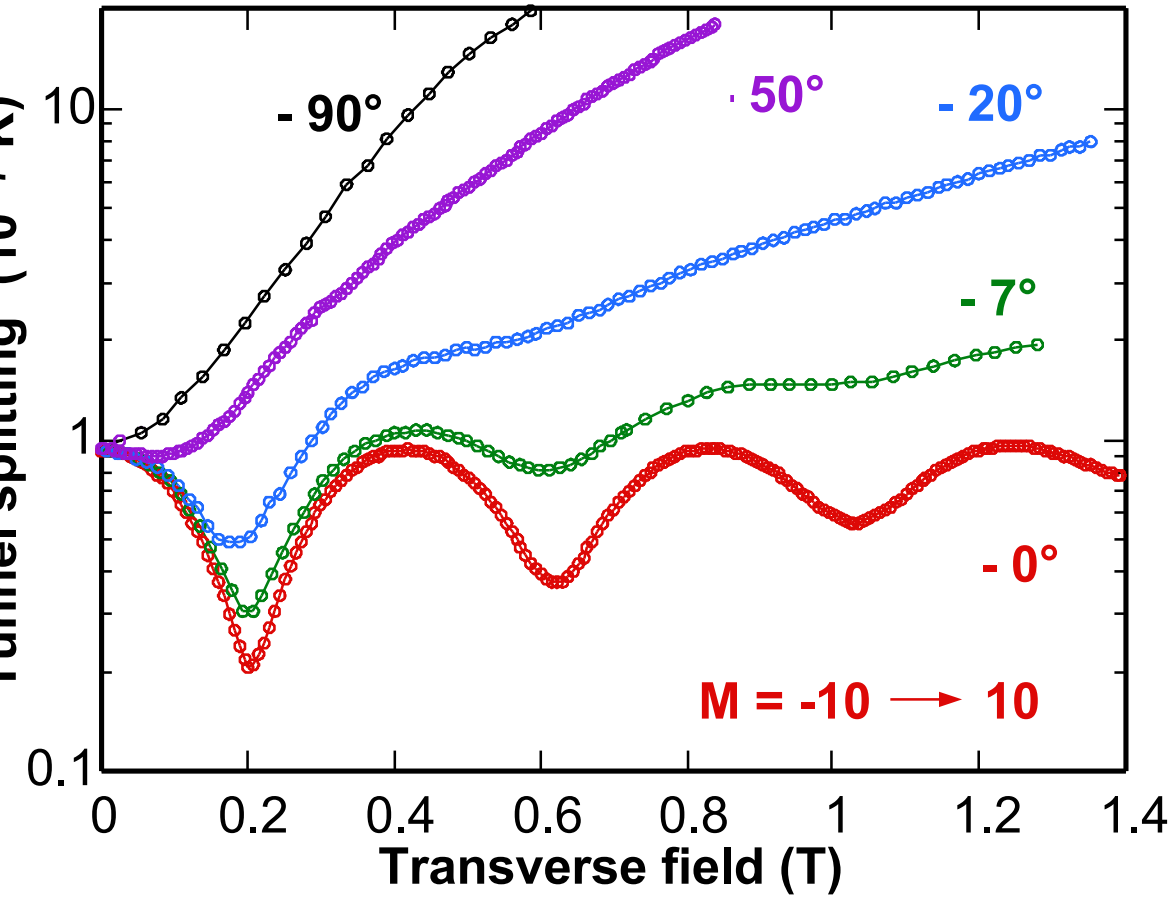
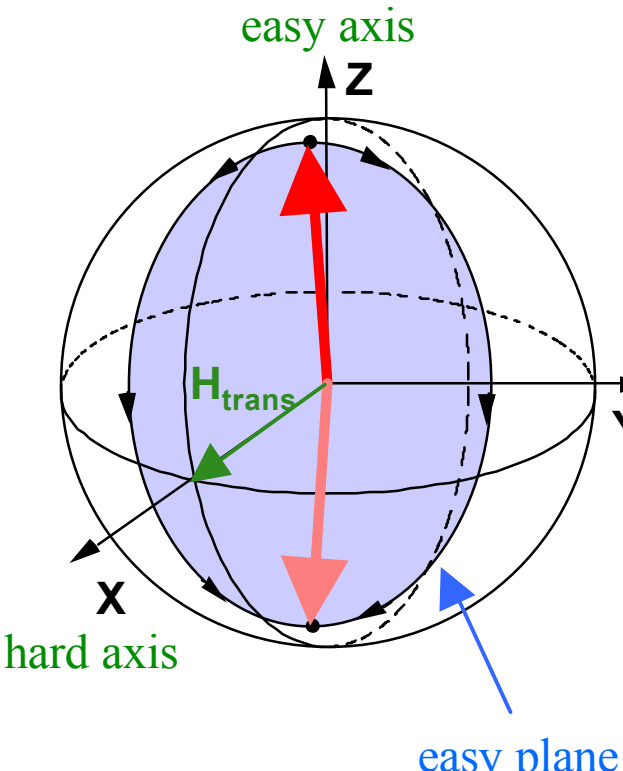
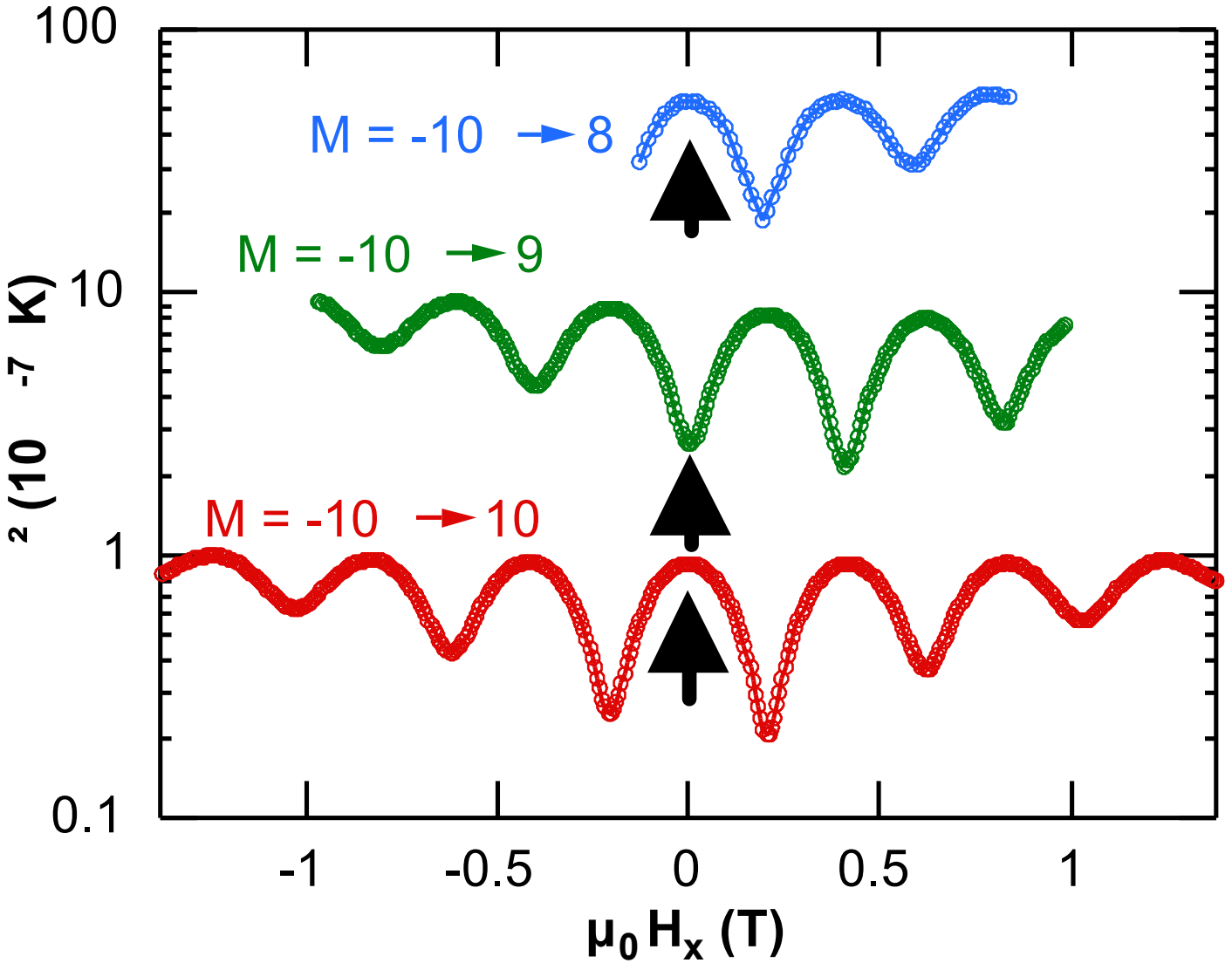




Parity of level crossings



W. Wernsdorfer and R. Sessoli, *Science* 284, 133 (1999)

Intermolecular interactions

(dipolar and exchange)

SMM
"ideal"

Mn_{12}ac

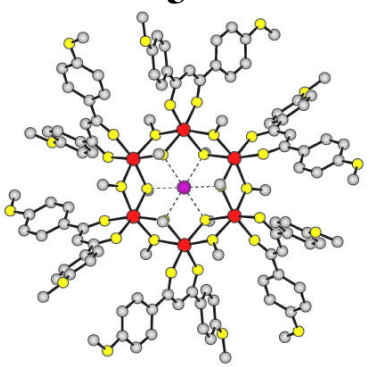
Mn_4 (SB1)

spin chains, etc.

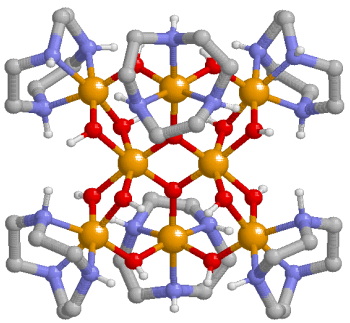
MM

0 **0.001** **0.01** **0.1** **1** **10** **100** **J/D**

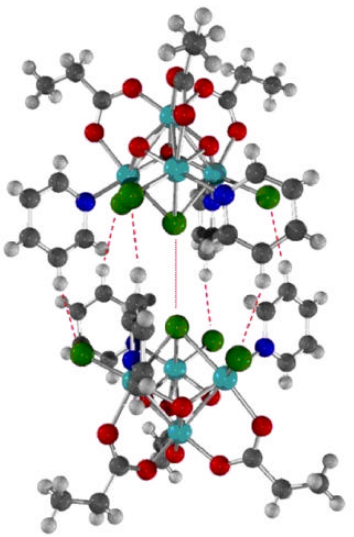
?
doped Fe_6
Fe_5Ga



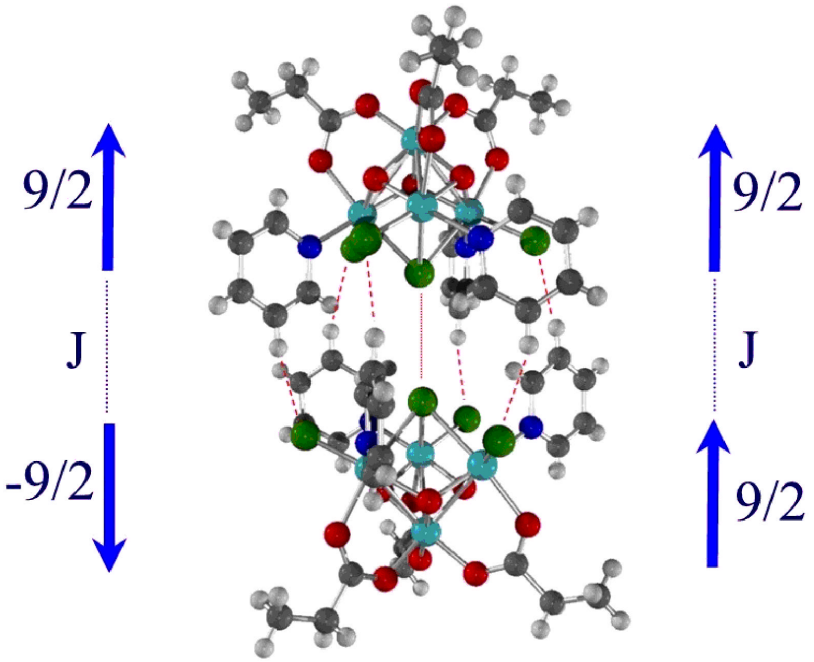
Fe_8

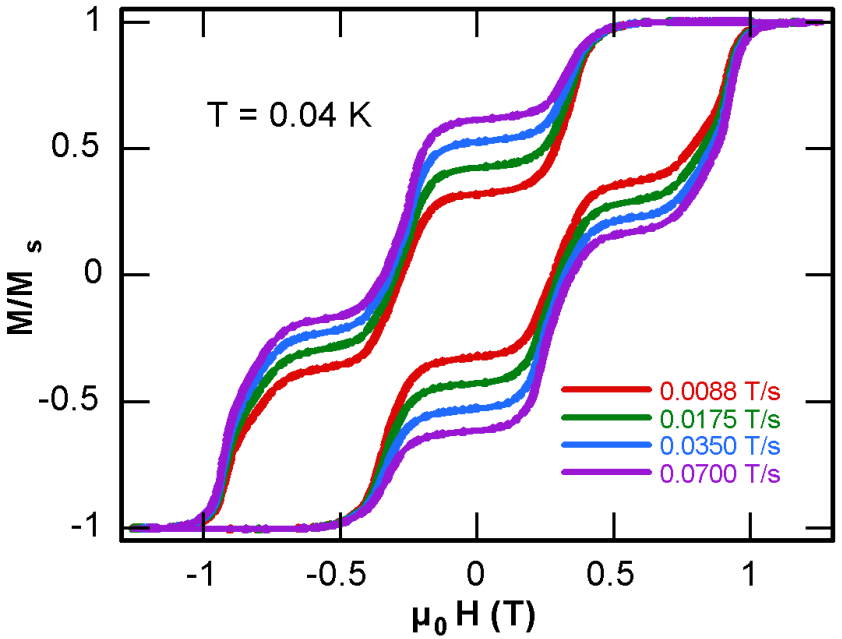


$[Mn_4]_2$



Molecular dimers





R. Tiron,W. Wernsdorfer, C. Thirion, R. Giraud, E. Bonet, B. Barbara (LLN, CNRS, Grenoble, France), **A. Benoit** (CRTBT, CNRS, Grenoble, France), **D. Mailly** (LPN, CNRS, Marcoussis, France), **N. Aliaga, S. Bhaduri, C. Boskovic, C. Canada, M. Soler, G. Christou** (Dept. of Chemistry, Uni. of Florida, USA), **E. Yang, E. M. Rumberger, D. N. Hendrickson** (Dept. of Chemistry, Uni. of California at San Diego, USA)

Single molecule vs. Dimer

$$\mathbf{H}_i = -D\, S_{i,z}^2 + \mathbf{H}_i^{trans} + g\mu_B\mu_0\, \vec{S}_i\, \vec{H}$$

$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + J\, \vec{S}_1 \vec{S}_2$$

$(2S_i + 1)$ energie states

$S_i = 9/2$: **10** levels

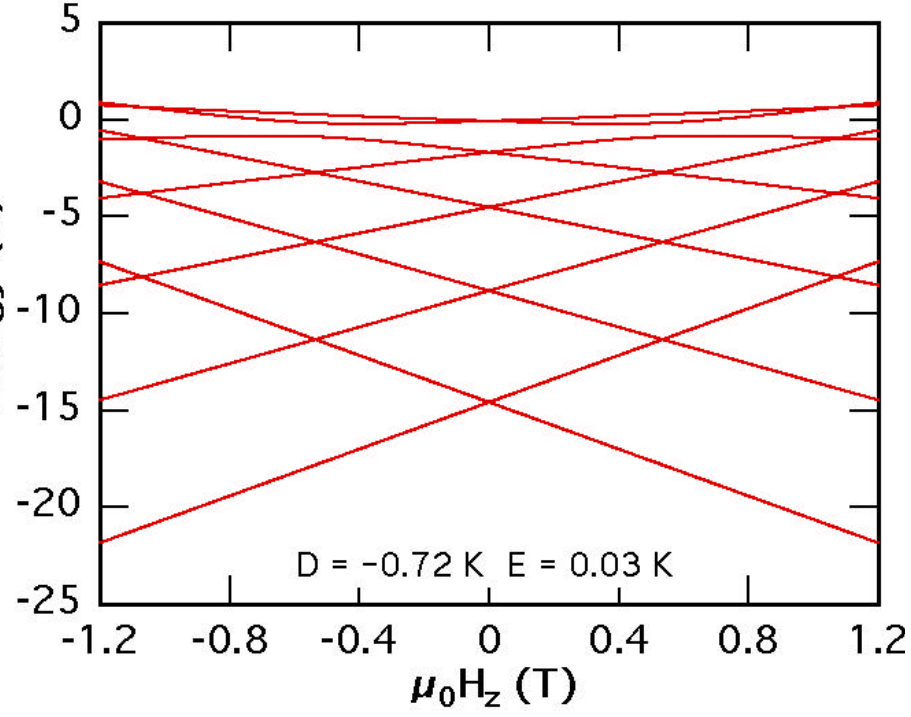
$m_i = -S_i, -S_i+1, \ldots, S_i$

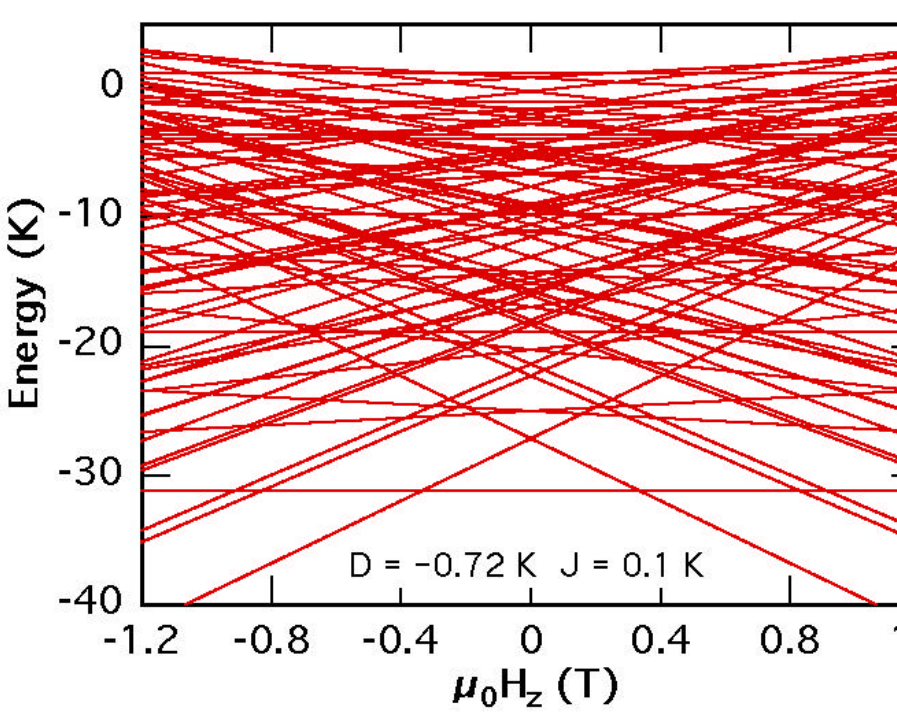
$(2S_1 + 1)(2S_2 + 1)$ energie state

$S_i = 9/2$: **100** levels

$m_1 = -S_1, -S_1+1, \ldots, S_1$

$m_2 = -S_2, -S_2+1, \ldots, S_2$



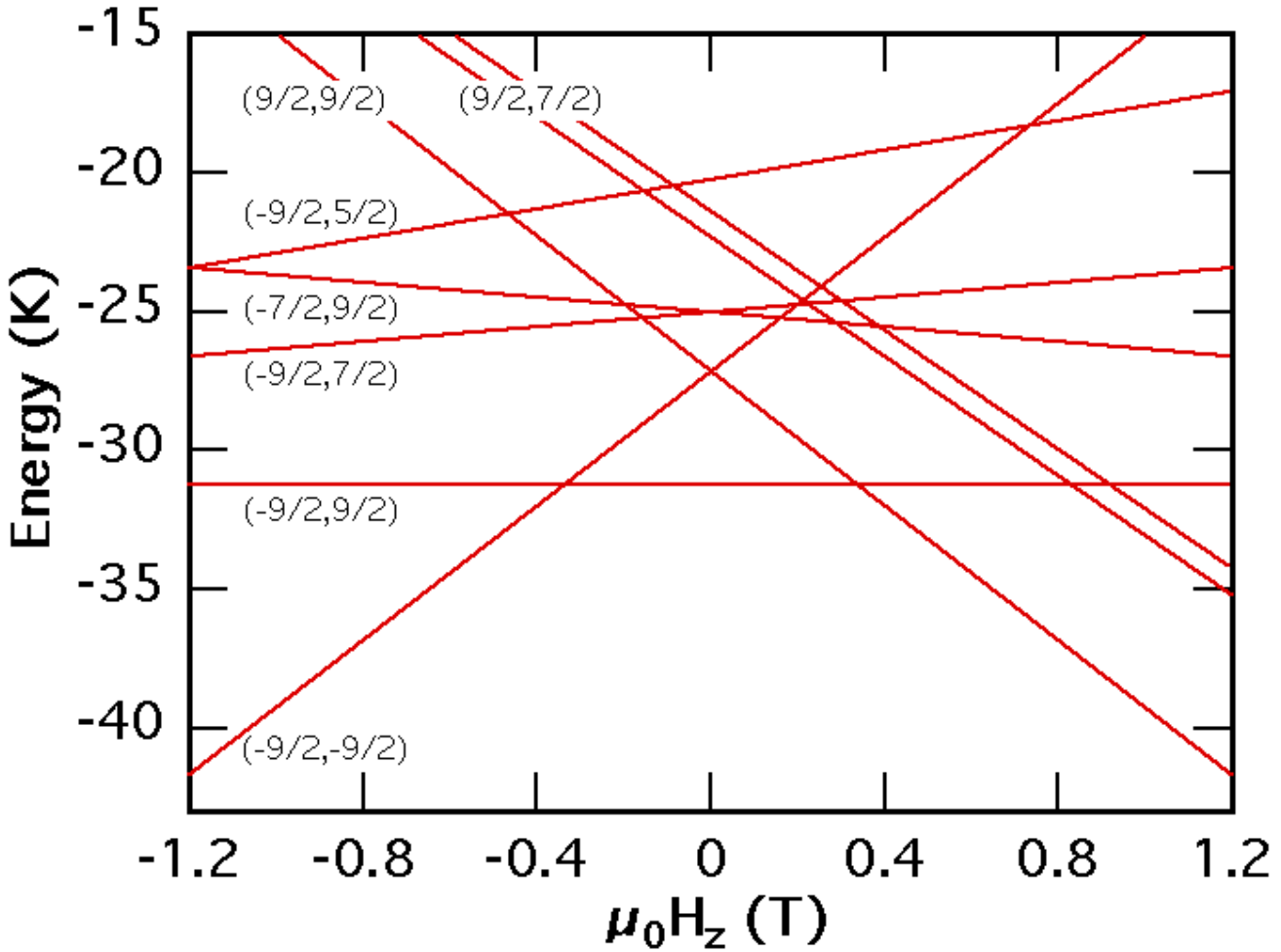


Zeeman Diagram for the S = 9/2 dimer

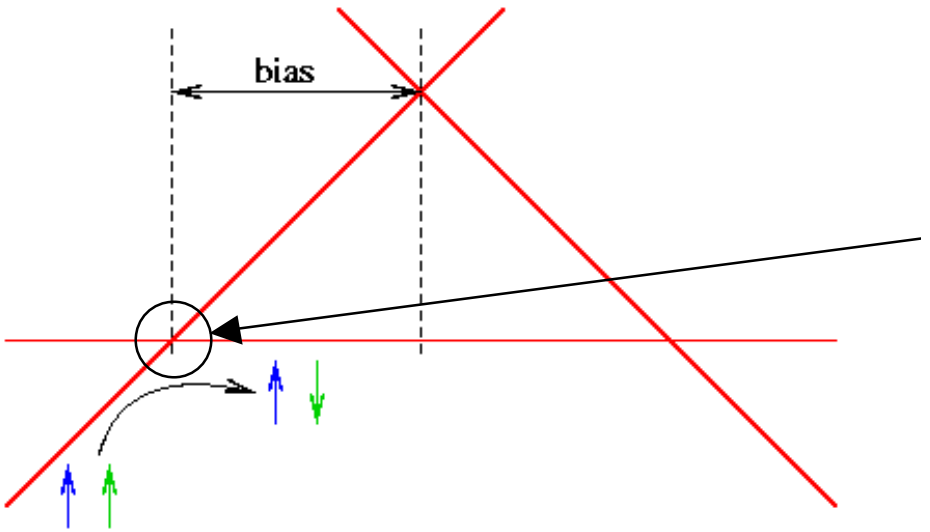
$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + J\,\hat{S}_1\hat{S}_2$$

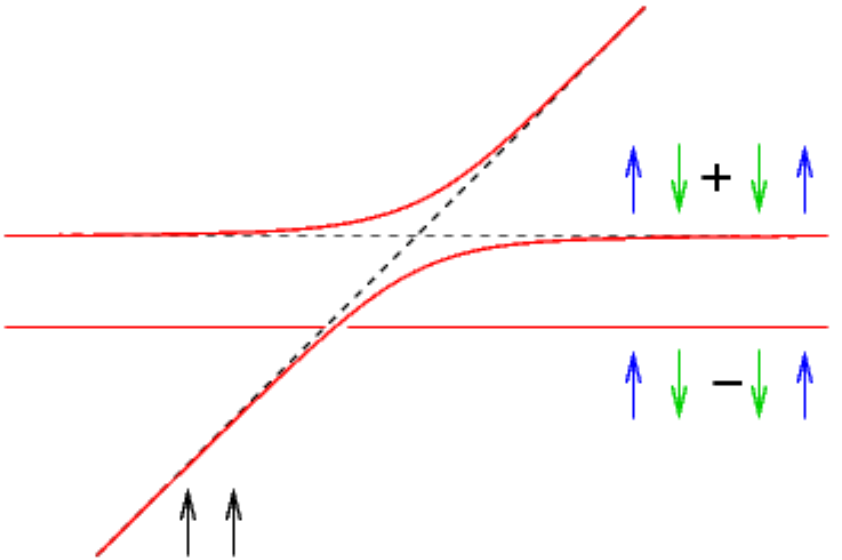
$$\mathbf{H}_i = -D\,S_{i,z}^2 + \mathbf{H}_i^{trans} + g\mu_B\mu_0\,\hat{S}_i\,\hat{H}$$

100 energy states (m_1,m_2)



Exchange bias





fixed

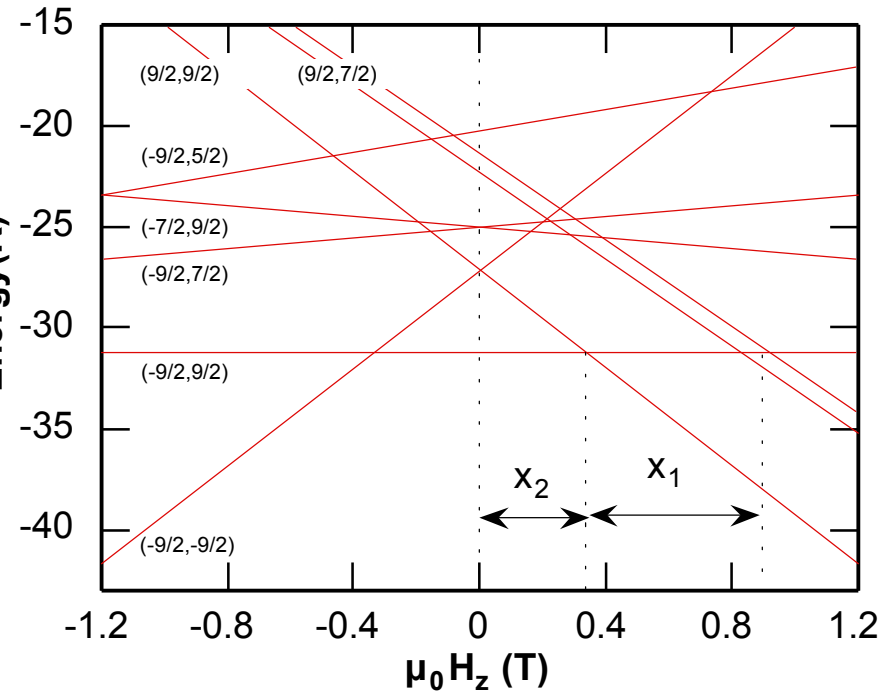
$$\mathcal{H} = -DS_{1z}^2 + E(S_{1x}^2 - S_{1y}^2) + g\mu_B\mu_0 \mathbf{S_1}\cdot\mathbf{H}$$
$$-DS_{2z}^2 + E(S_{2x}^2 - S_{2y}^2) + g\mu_B\mu_0 \mathbf{S_2}\cdot\left(\mathbf{H} + \frac{J}{g\mu_B\mu_0}\mathbf{S}_1\right)$$

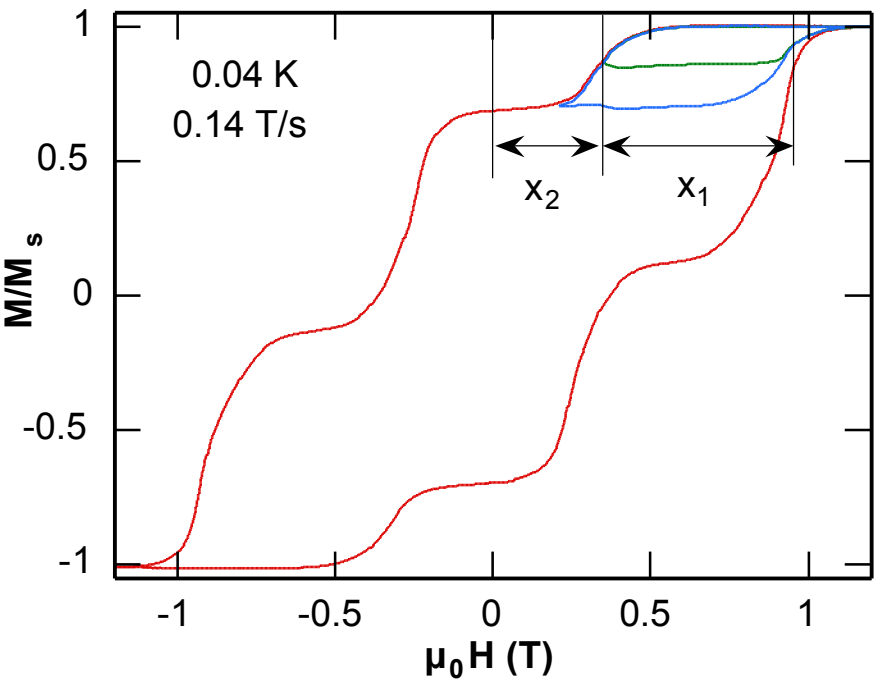
bias

Anisotropy & intermolecular coupling

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2 + J\mathbf{S}_1 \cdot \mathbf{S}_2$$

$$\mathcal{H}_i = -DS_{iz}^2 + E(S_{ix}^2 - S_{iy}^2) + g\mu_B\mu_0\mathbf{S}_i \cdot \mathbf{H}$$





$D = g * \mu_B/k_B * \mathbf{X_1} = 2 * 0.928/1.38 * \mathbf{0.58} = 0.75$ K

$J_{tot} = g * \mu_B/k_B * \mathbf{X_2} / S = 2 * 0.928/1.38 * \mathbf{0.34} / 4.5 = 0.10$ K

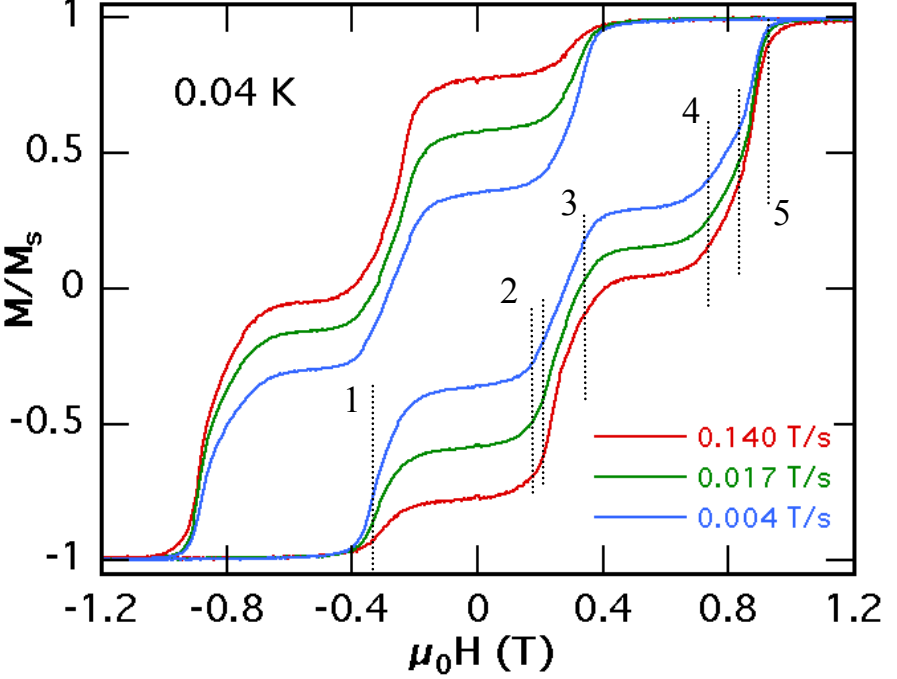
D = anisotropy constant; J_{tot} = coupling constant

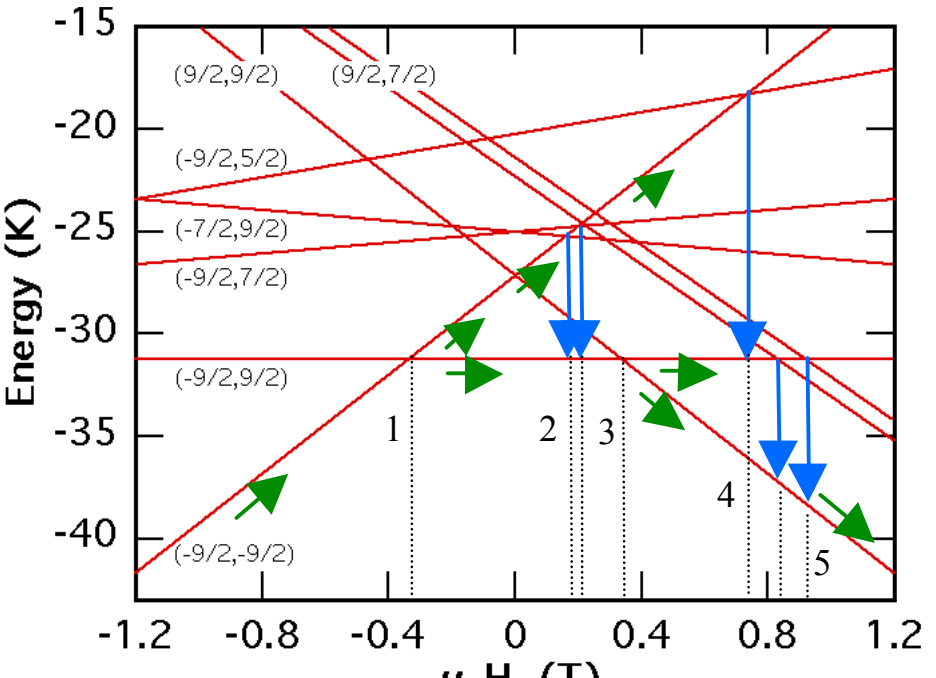
Tunneling in the dimer

Transitons

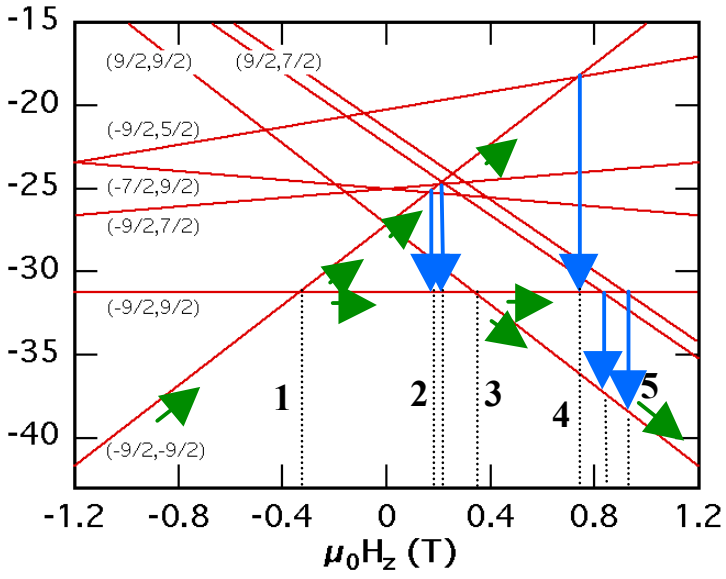
(1) (-9/2,-9/2) ? (-9/2, 9/2) ;
(2) (-9/2,-9/2) ? (-9/2, 7/2)
relaxes ? (-9/2, 9/2) ;
(3) (-9/2, 9/2) ? (9/2, 9/2) ;
(4) (-9/2,-9/2) ? (-9/2, 5/2)
relaxes ? (-9/2, 9/2) ;
(5) (-9/2, 9/2) ? (7/2, 9/2)
relaxes ? (9/2, 9/2).

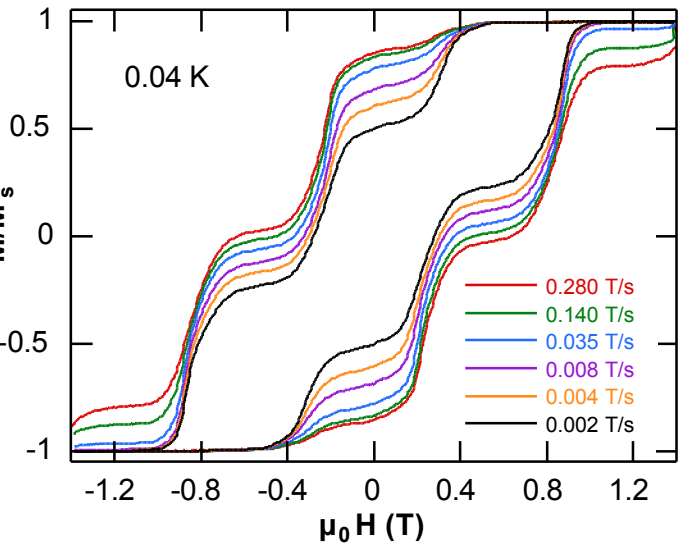
(1) and **(3)** are symmetric relative to the origin;



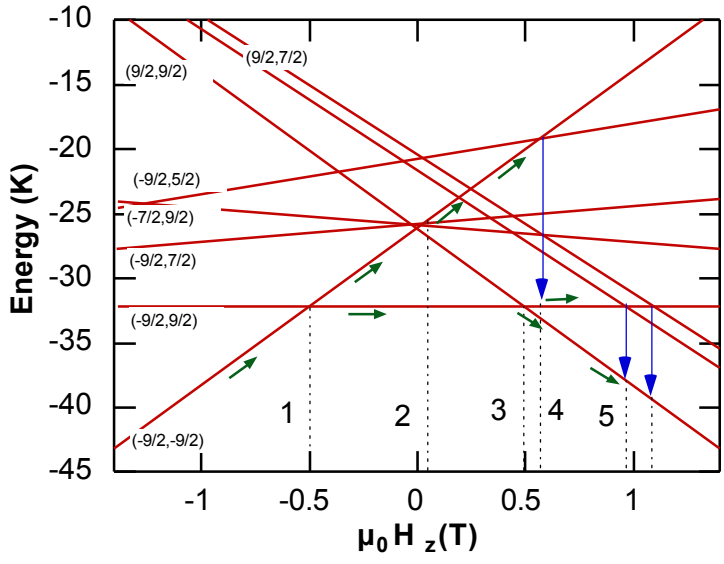


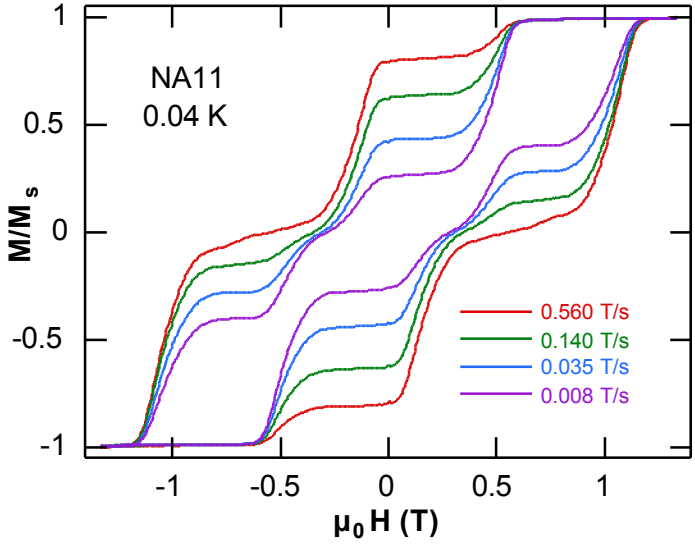
2x $Mn_4O_3Cl_4(O_2CEt)_3(py)_3$ NA3





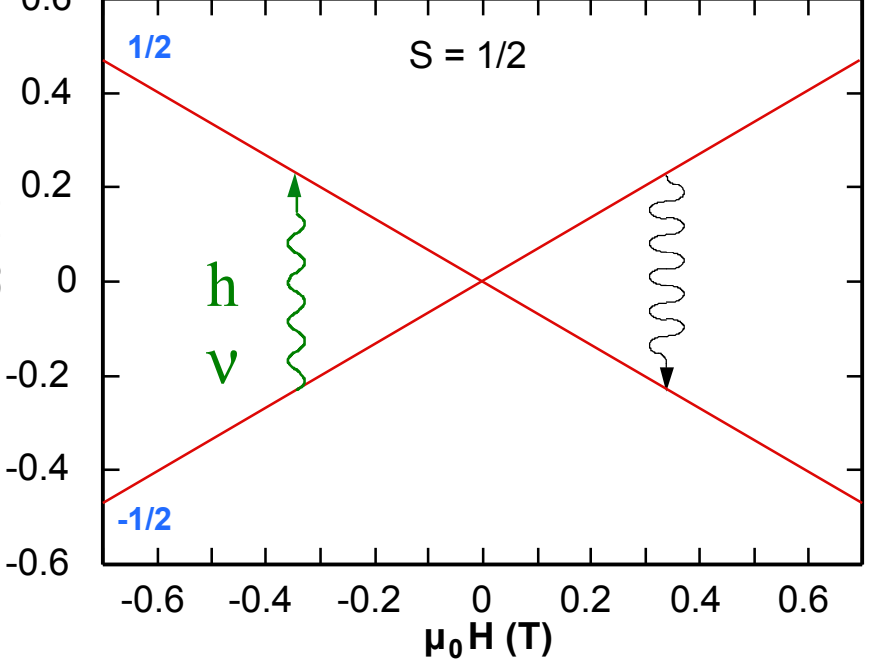
2x $Mn_4O_3Cl_4(O_2CH_2Cl_2)_3(py)_3$ NA11

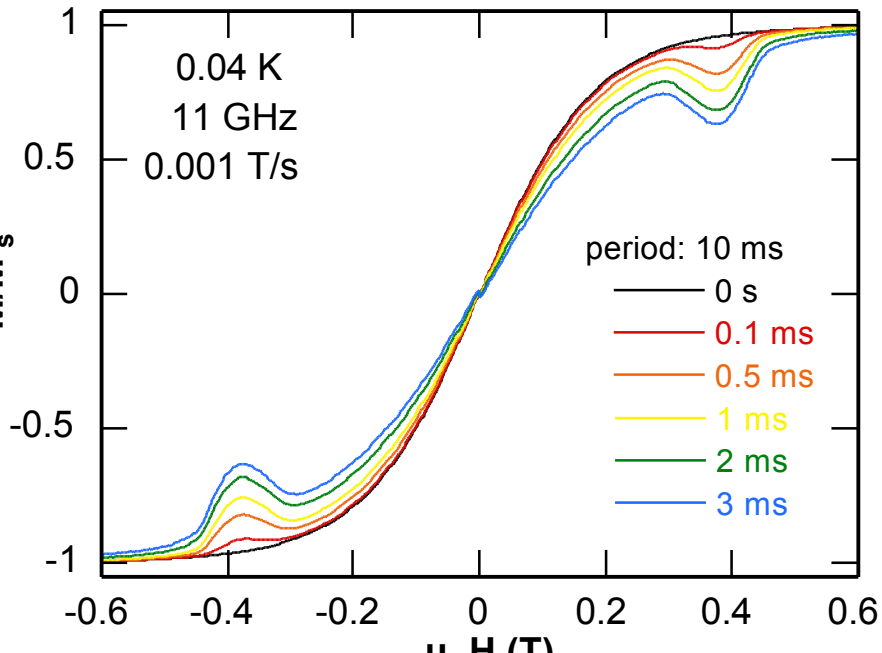




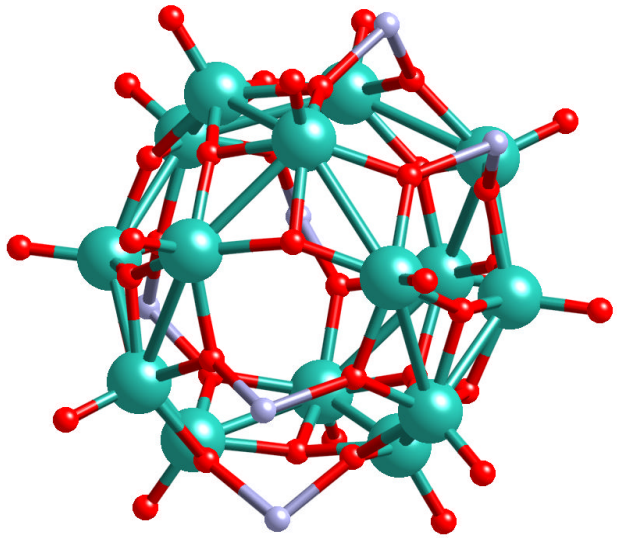
Inter-molecular coupling is stronger in NA11 than in NA3;
Easier to resolve resonances (2) from (3) and (4) from (5)

Absorption of microwaves

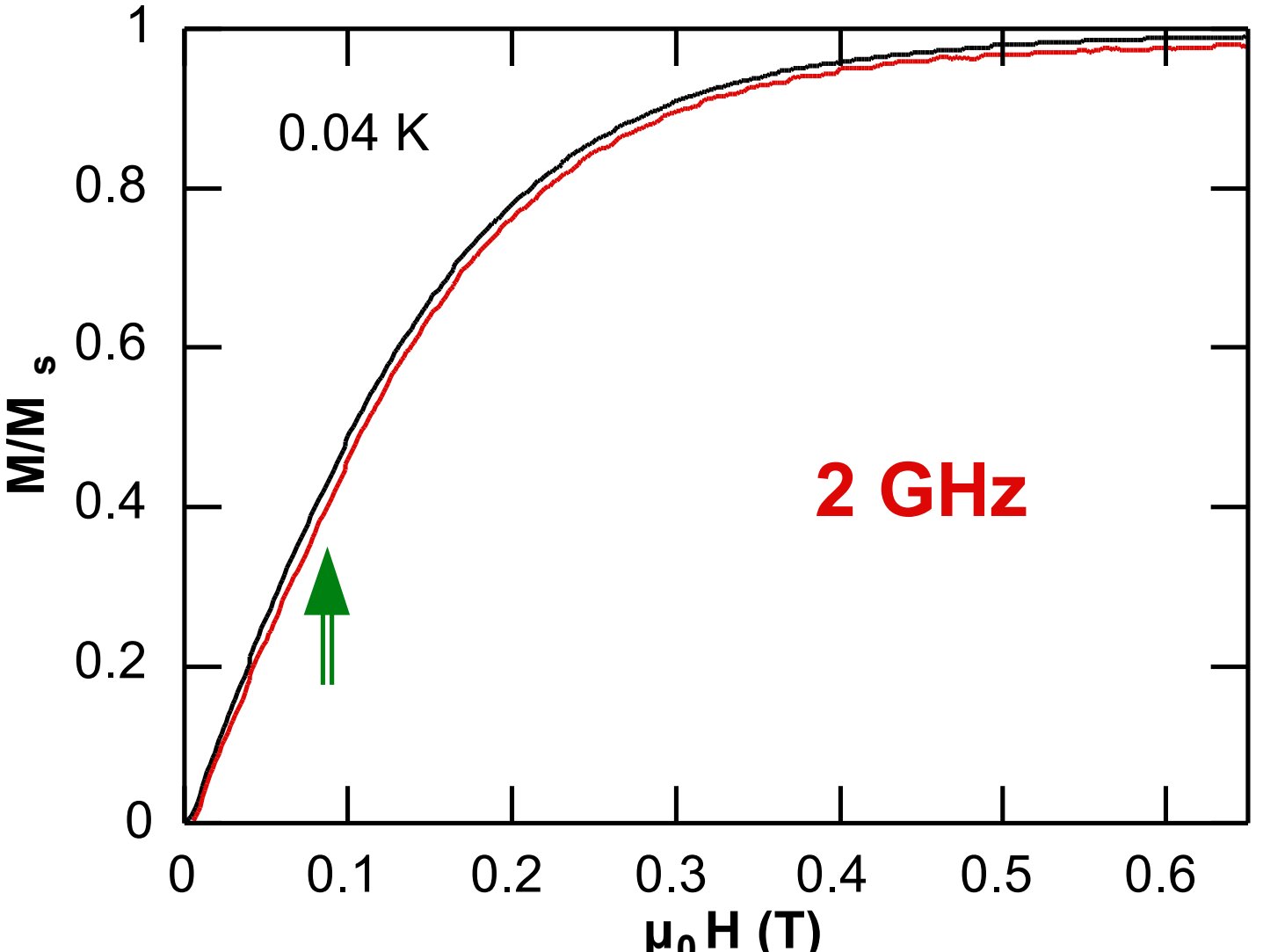


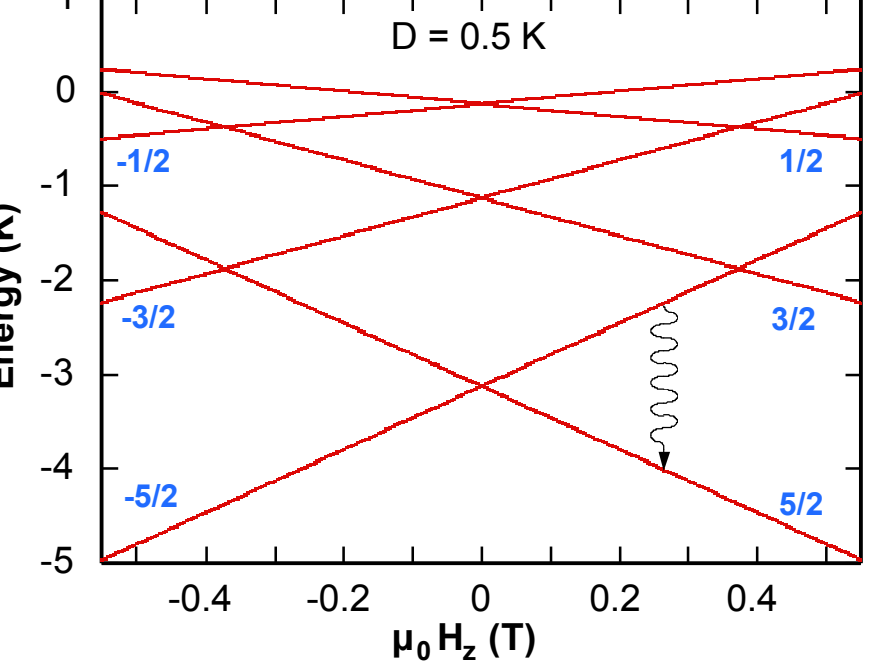


V_{15} S = 1/2



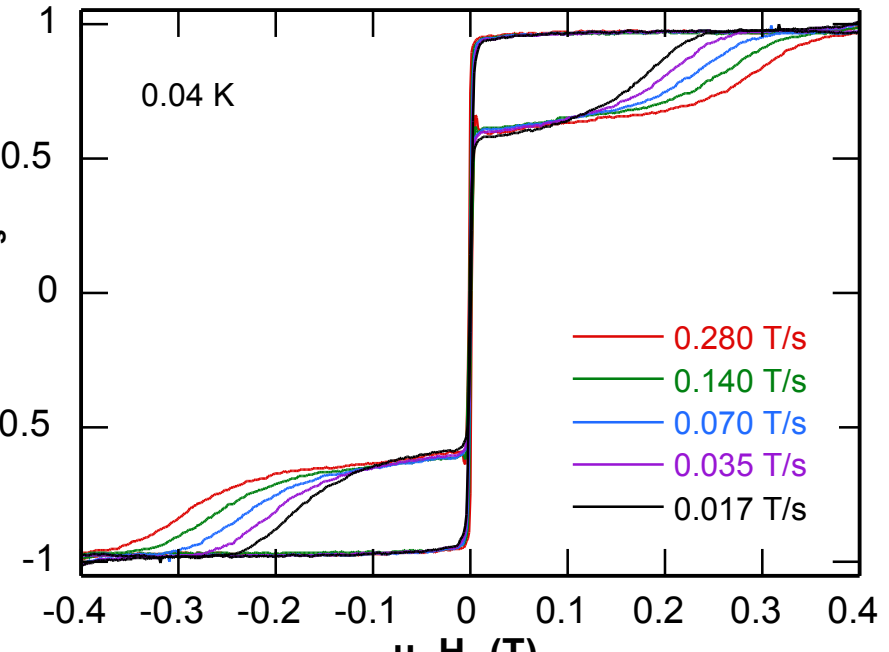
Frequency dependence of the absorption of microwaves in v





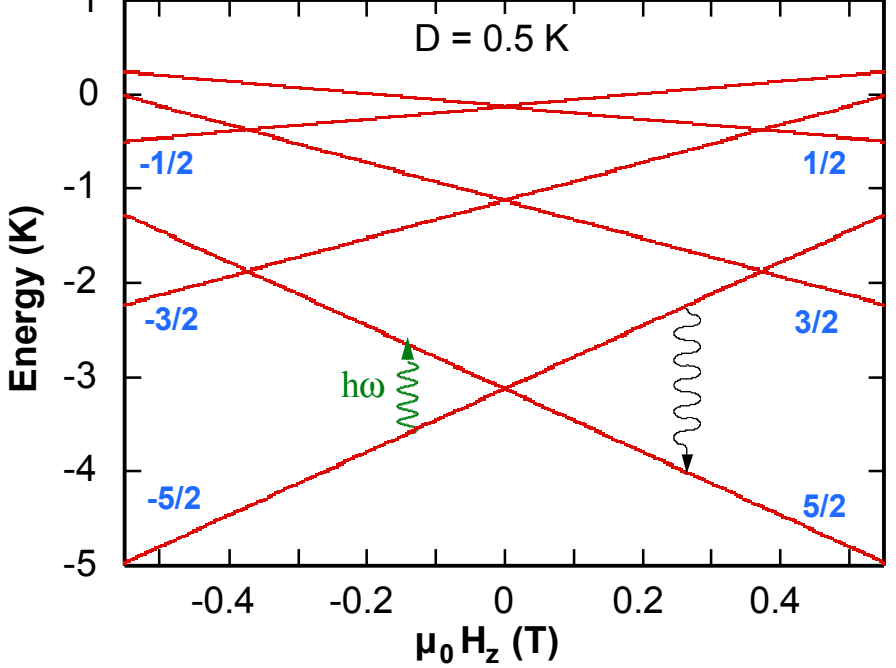
Reducing intermolecular couplings

Fe_6 wheels: S = 0



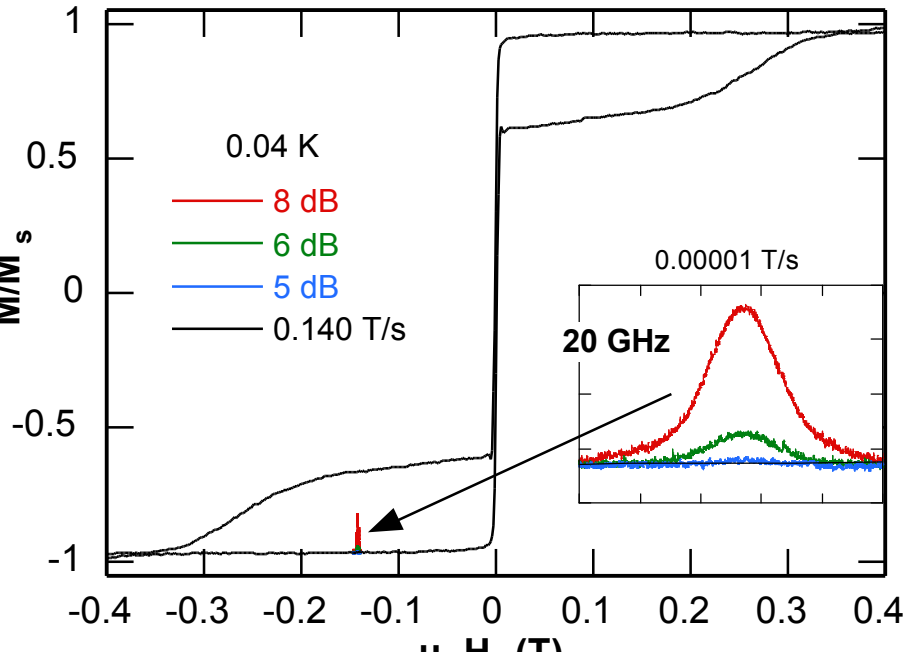
Doping with Ga

Fe_5Ga : S = 5/2



Reducing intermolecular couplings

Fe_6 wheels: S = 0

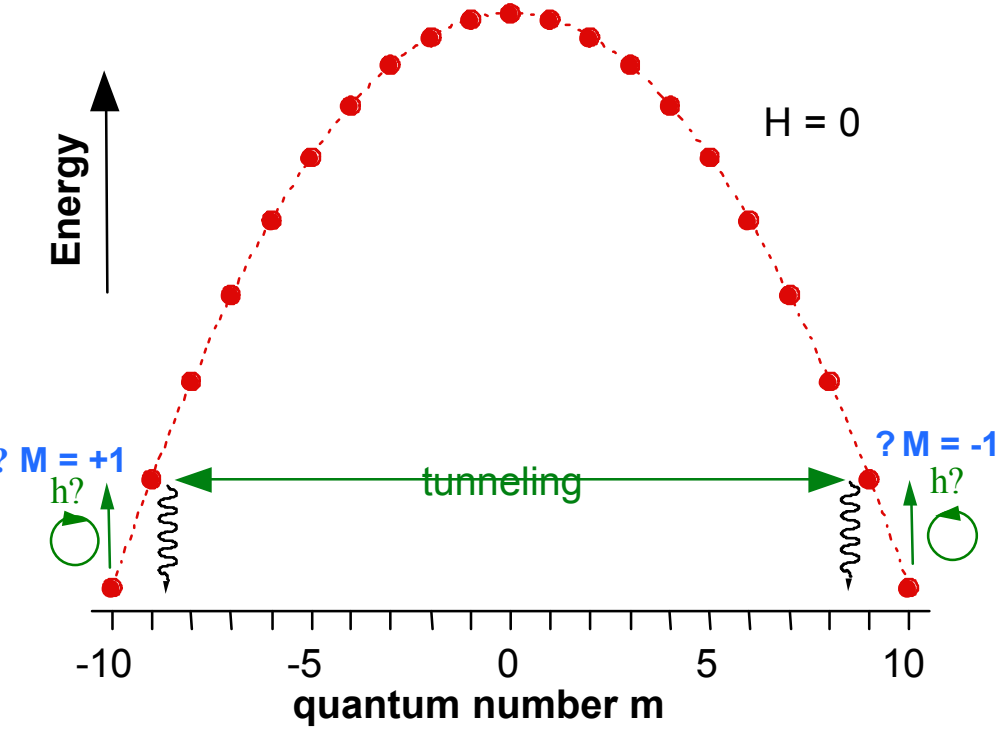


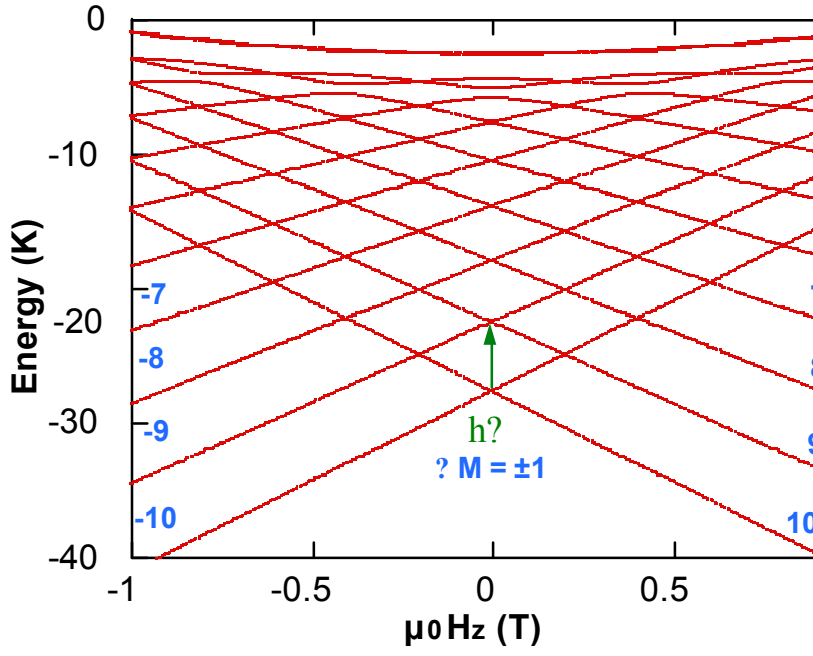
Doping with Ga

Fe_5Ga : S = 5/2

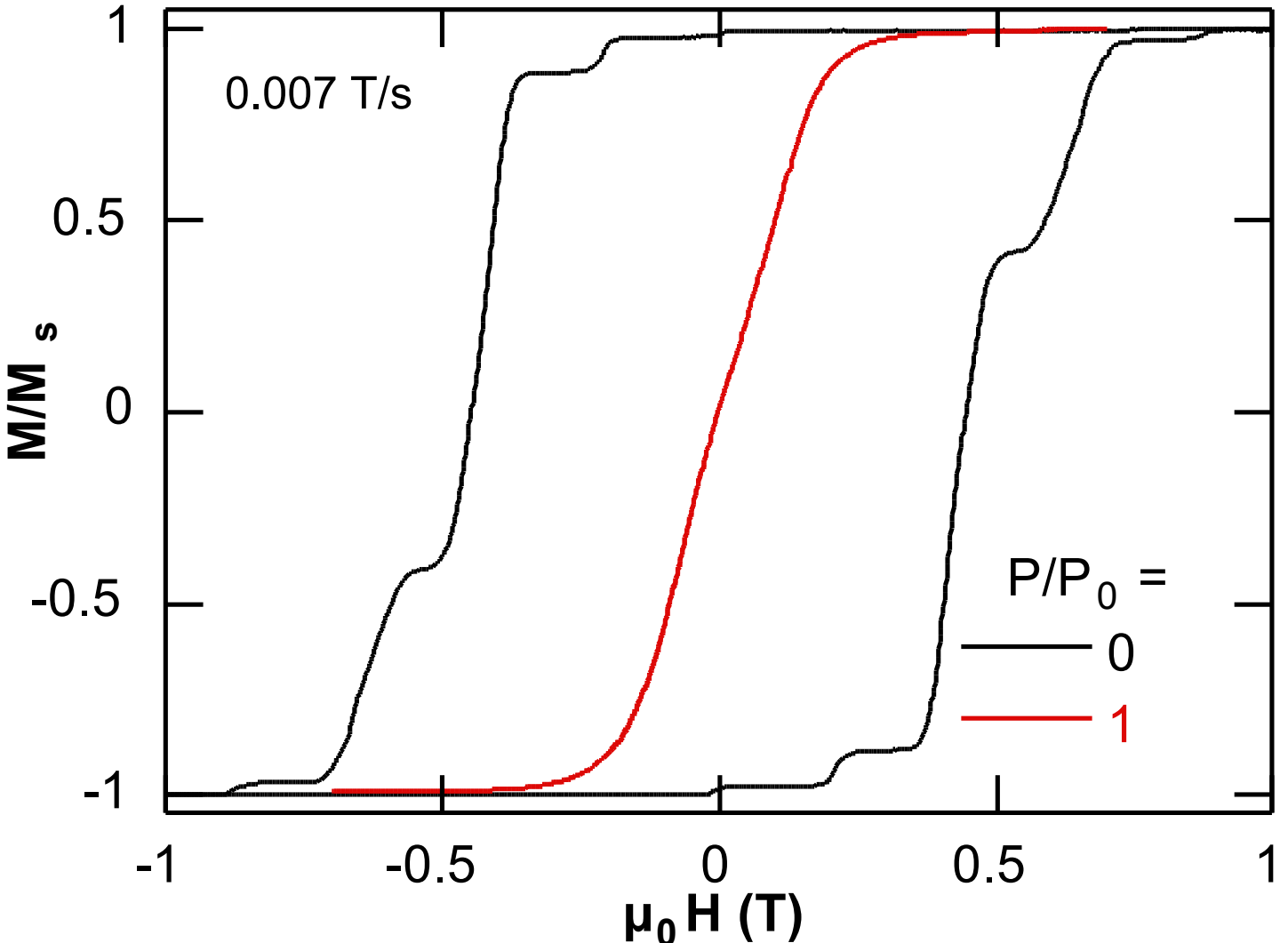
Photon assisted tunneling

Absorption of circular polarized microwaves

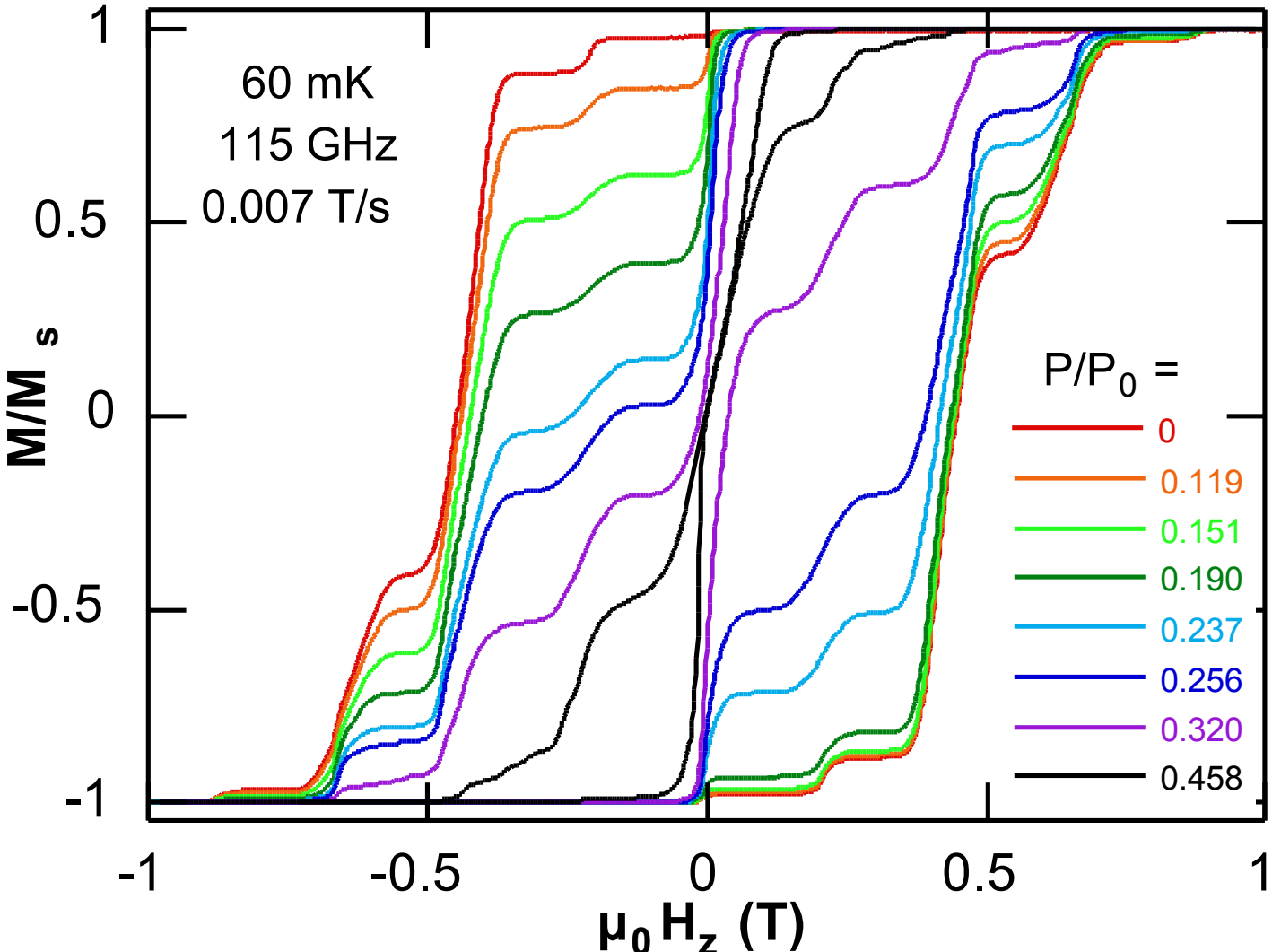




Absorption of circular polarized microwaves (115 GHz)



Absorption of circular polarized microwaves (115 GHz)



Absorption of circular polarized microwaves (95 GHz)