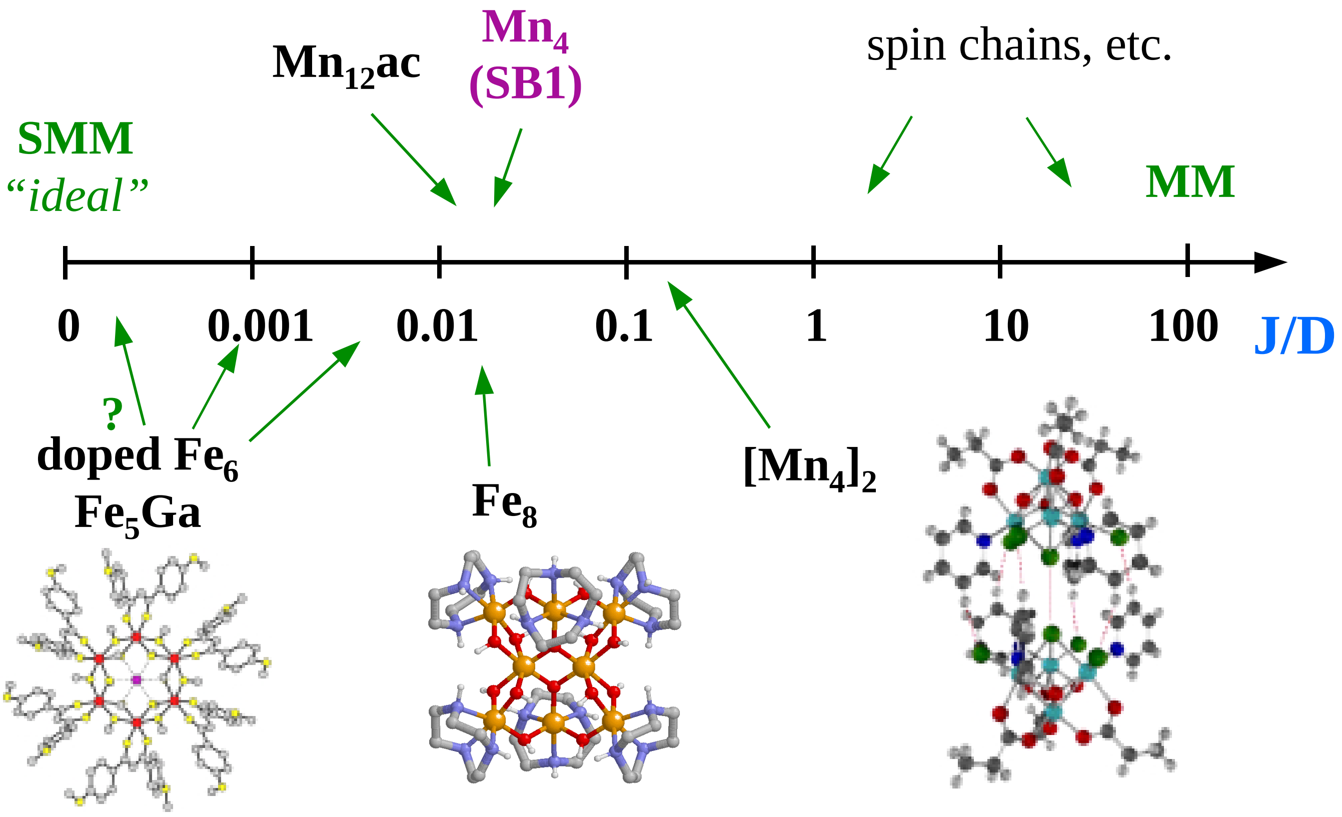
# Intermolecular interactions

*(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**

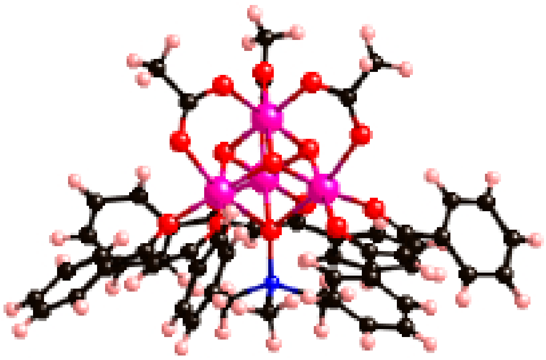
**?**
**doped $Fe_6$**
**$Fe_5Ga$**

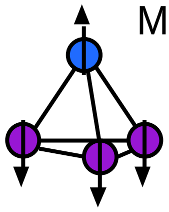
**$Fe_8$**

**$[Mn_4]_2$**

# $Mn_4$ single-molecule magnet

**$Mn_4O_3(OSiMe_3)(O_2CMe)_3(dbm)_3$**





$Mn^{IV}$ $S_1 = 3/2$

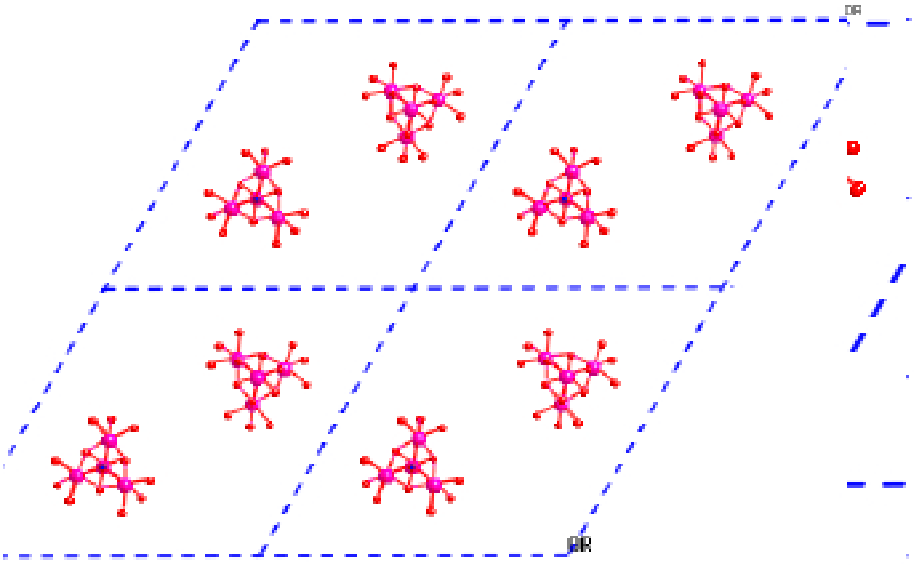
$Mn^{III}$ $S_2 = 2$

**$S = 9/2$**

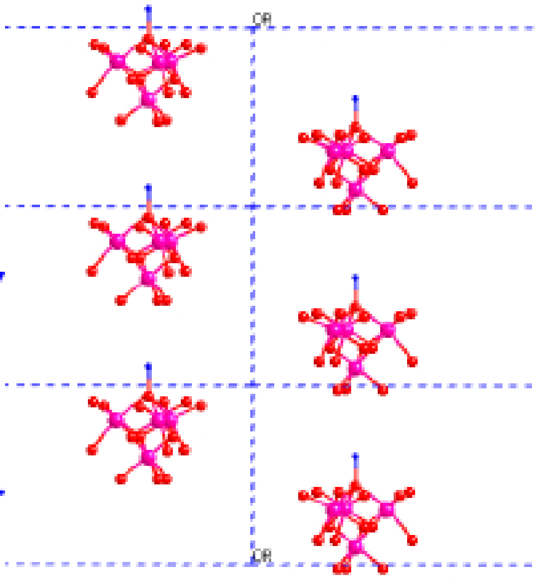
# $Mn_4O_3(OSiMe_3)(O_2CMe)_3(dbm)_3$ **(SB1)**

## Symmetry space group: P6(3)

*Top view*



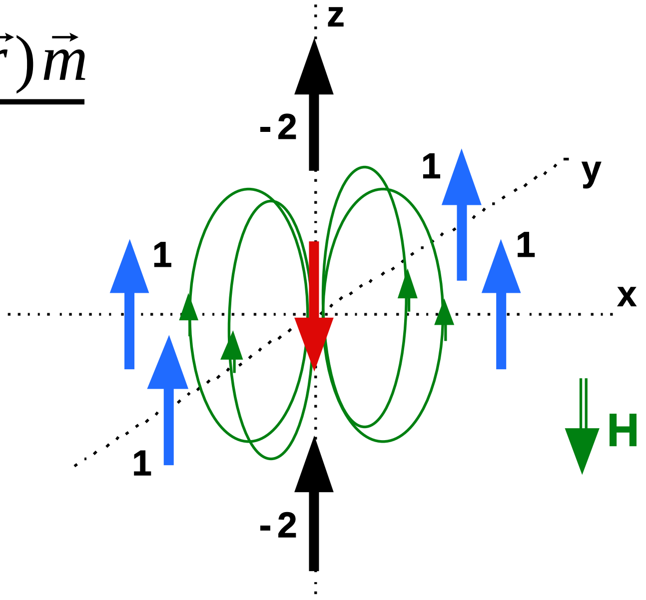
*Side view*



# Dipolar coupling

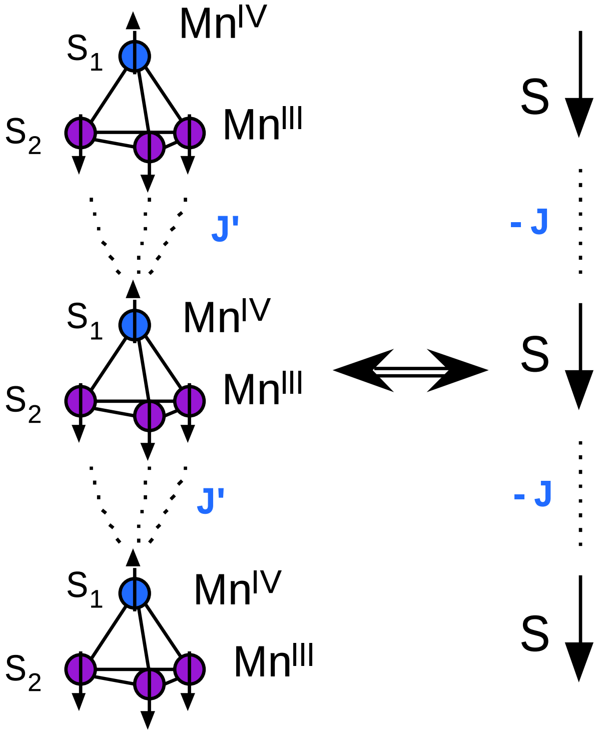
$$\vec{B}(\vec{r}) = \frac{\mu_0}{4\pi}\,\frac{3(\vec{m}\;\vec{r})\vec{r} - (\vec{r}\;\vec{r})\vec{m}}{r^5}$$

$$B_z \qquad \frac{1-3\cos\theta}{r^3}$$



**$Mn_4$ (SB1)** **≈ 10 mT**

# Intermolecular exchange coupling

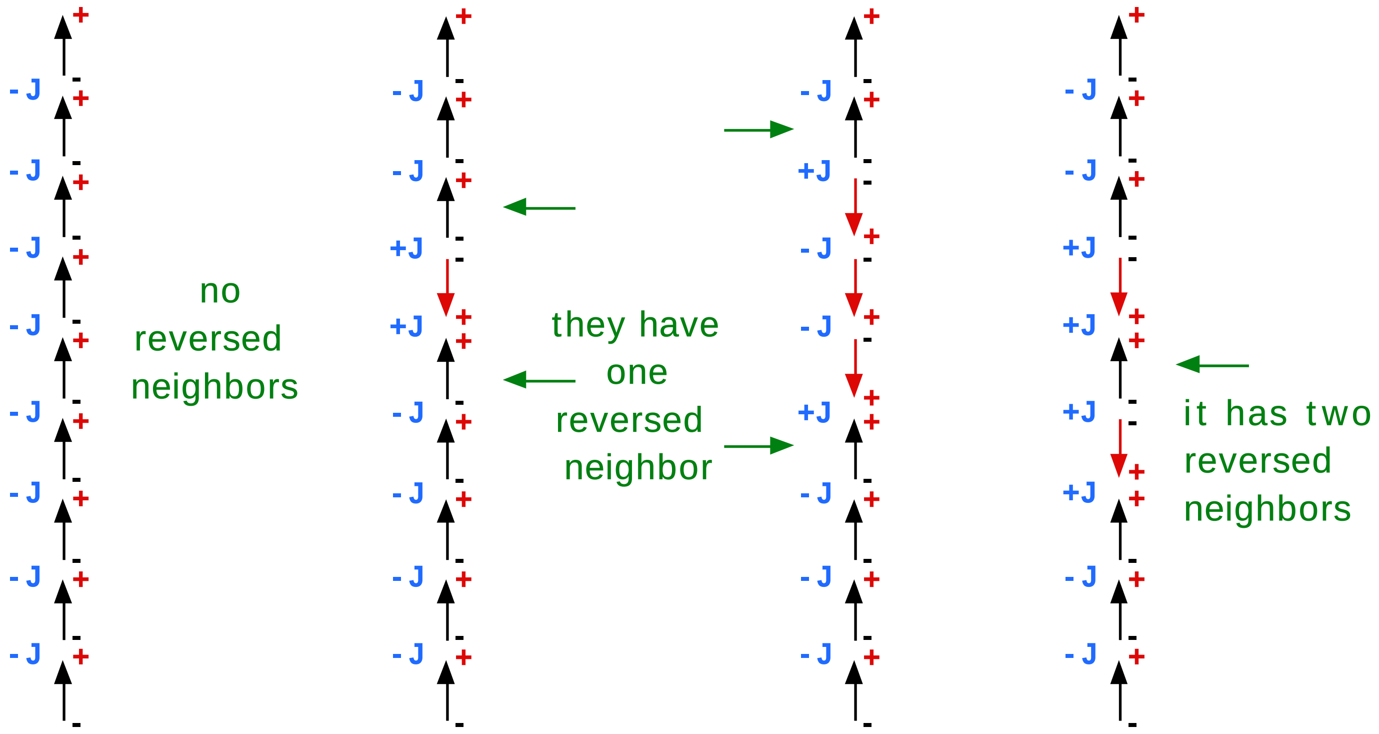


**dipolar**
**&**
**exchange**
**coupling**

**Mn4 (SB1)**
**≈ 36 mT**

# Chain-like dipolar & exchange coupling

*Case 1* *Case 2* *Case 3*



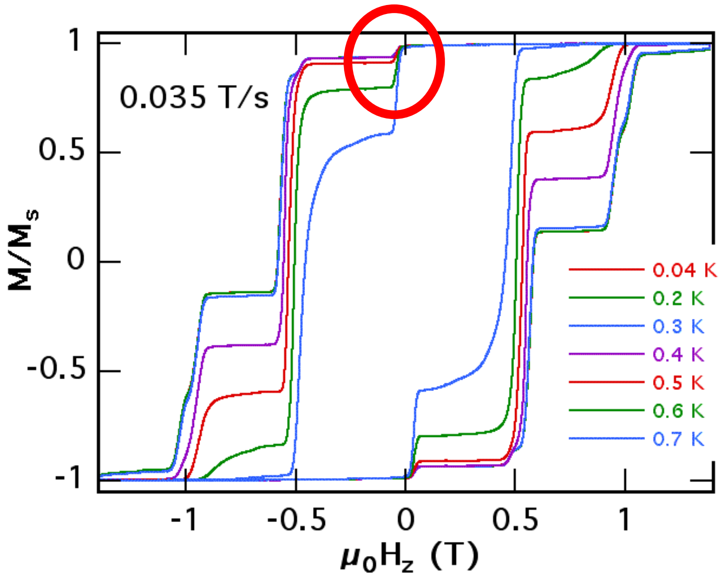
no reversed neighbors

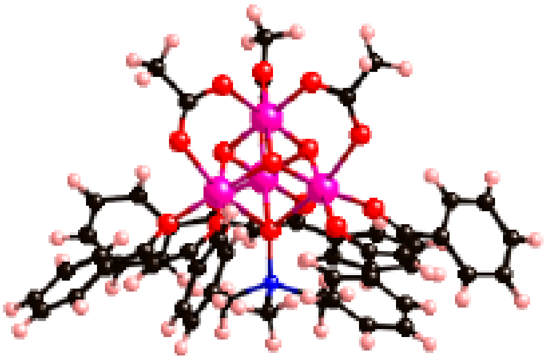
they have one reversed neighbor

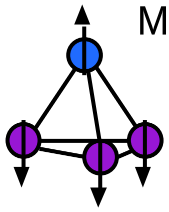
it has two reversed neighbors

# Hysteresis loops of a $Mn_4$ single-molecule magnet

## $Mn_4O_3(OSiMe_3)(O_2CMe)_3(dbm)_3$





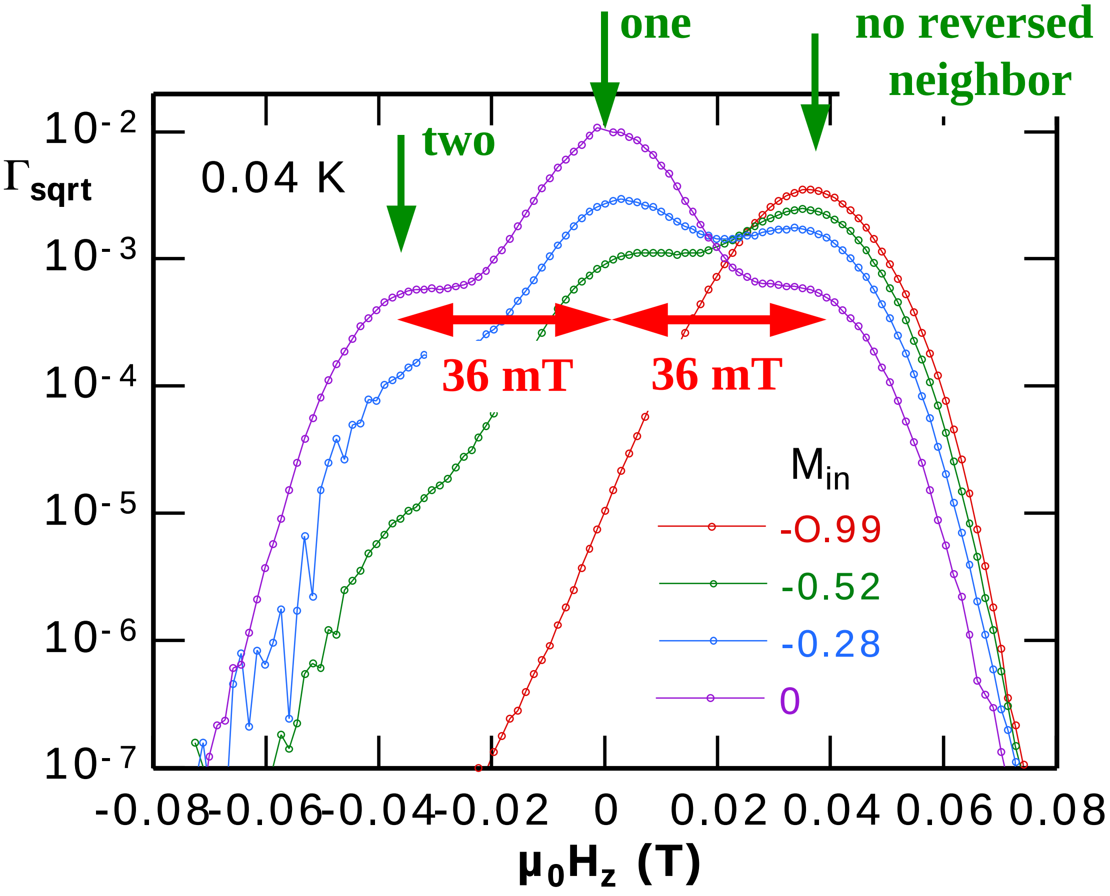


$Mn^{IV}$ $S_1 = 3/2$

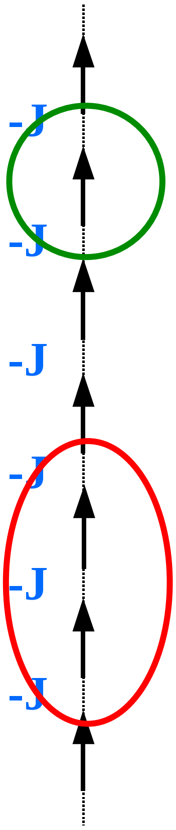
$Mn^{III}$ $S_2 = 2$

**S = 9/2**

# Distribution of internal fields



# Collective quantum phenomena



*One-body tunnel transitions*

*Two-body tunnel transitions*

**$JS^2 \approx 0.2$ K**
**$S = 9/2$**

# Two coupled SMM of S = 9/2

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

$(2S_i + 1)$ energy states

$S_i = 9/2$ : **10** energy states

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

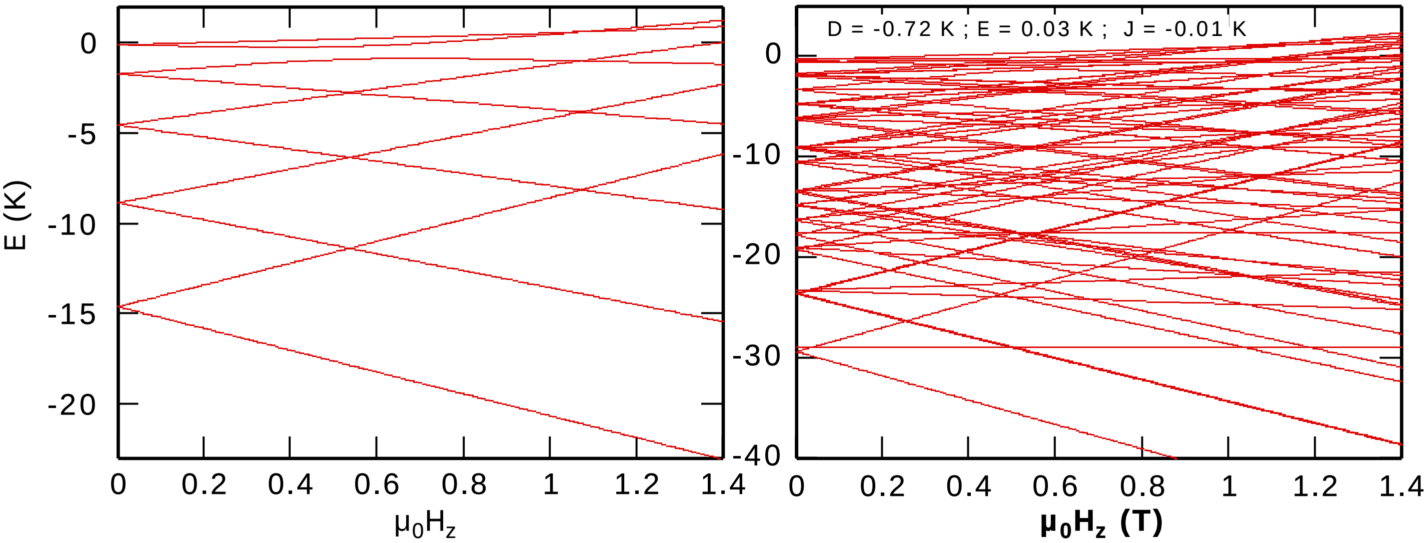
$$\mathbf{H} = \mathbf{H}_1 + \mathbf{H}_2 + J\,\vec{S}_1\vec{S}_2$$

$(2S_1 + 1)(2S_2 + 1)$ energy states

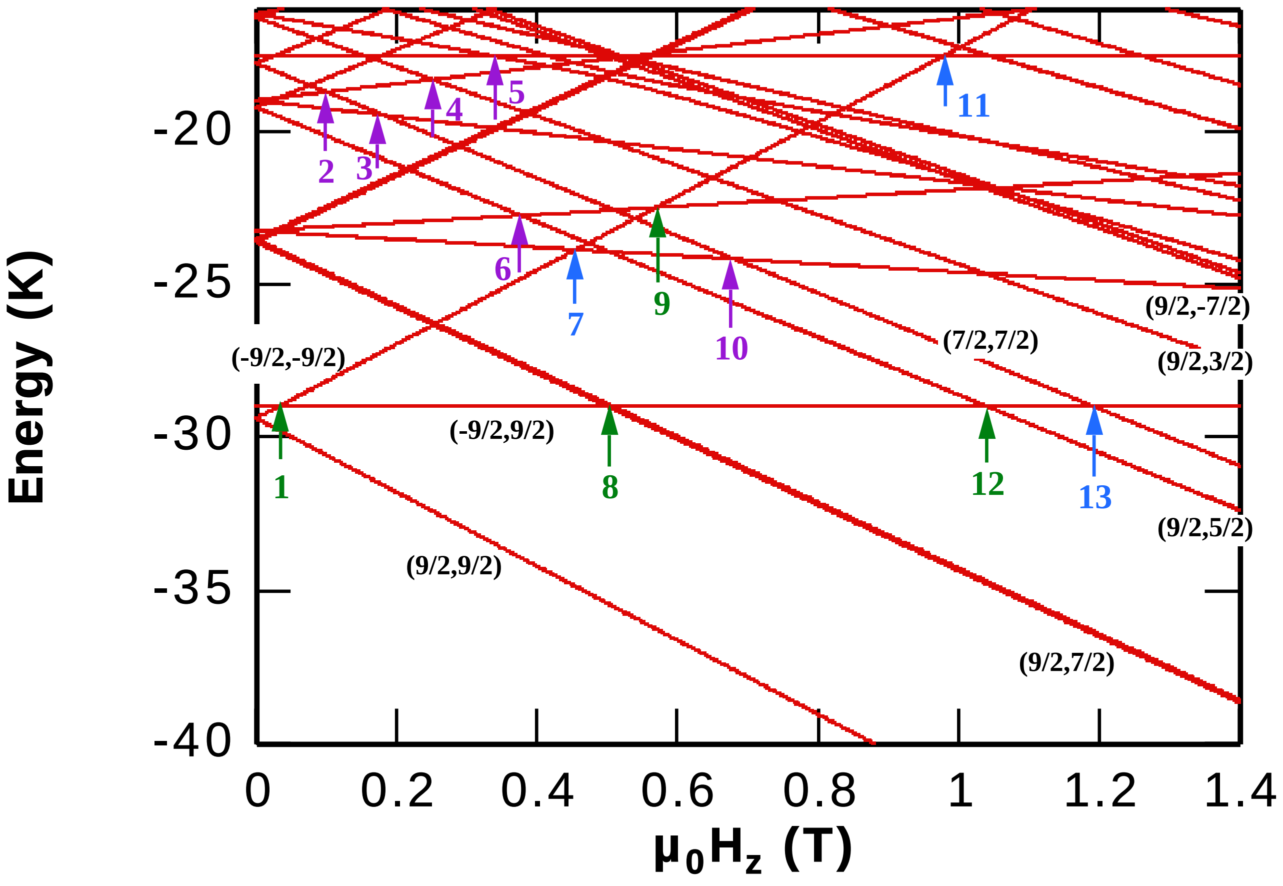
$S_i = 9/2$ : **100** energy states

$M_1 = -S_1, -S_1+1, \ldots, S_1$

$M_2 = -S_2, -S_2+1, \ldots, S_2$



# Zeeman diagram of two coupled SMM of S = 9/2



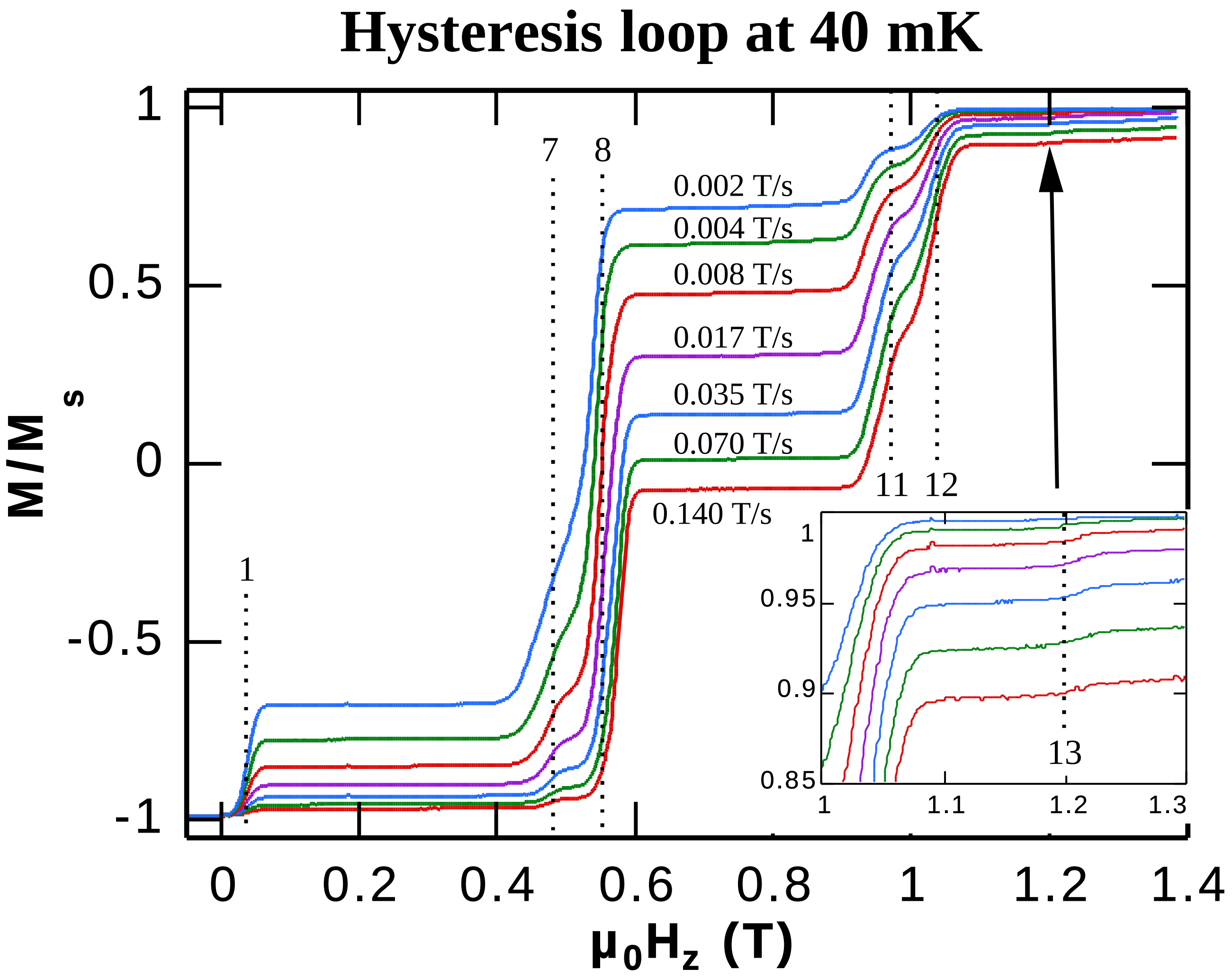
# Spin-spin cross-relaxation

## *“the happy collaboration of two spins”*

**Examples:**

**Transition 7**
Initial state: (-9/2,-9/2)
After tunneling: (-7/2,+9/2)
Final state: (-9/2,+9/2)

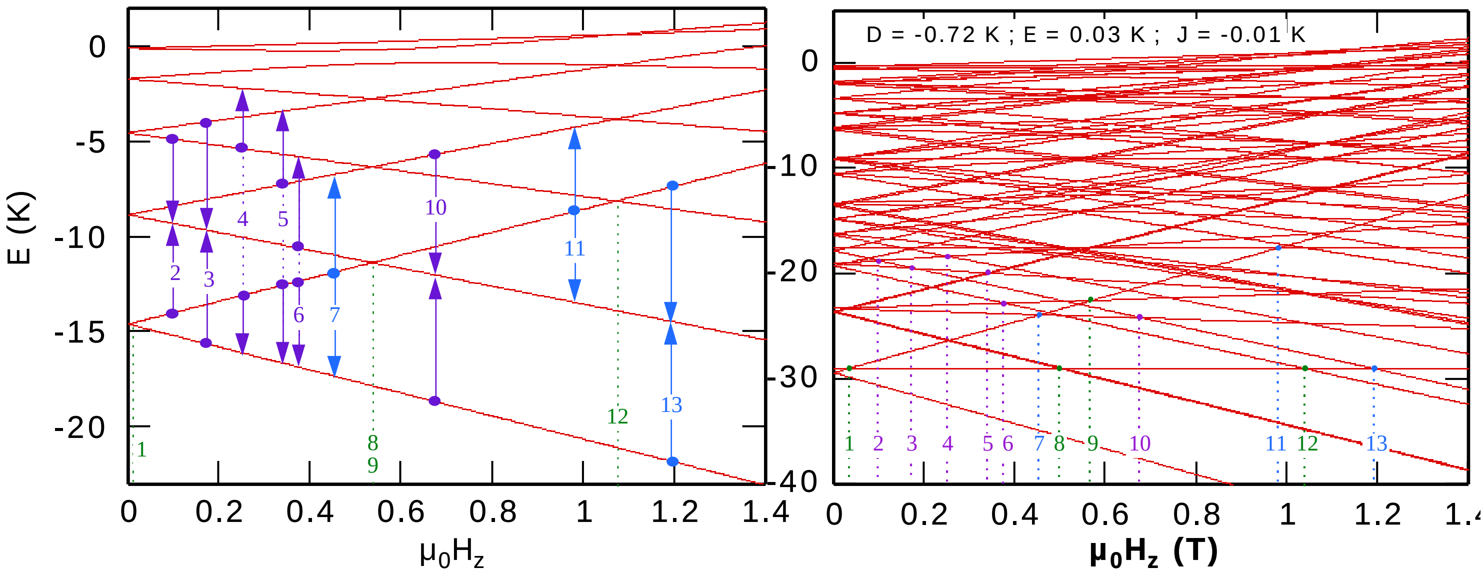
**Transition 13**
Initial state: (-9/2,+9/2)
After tunneling: (+7/2,+7/2)
Final state: (+9/2,+9/2)


Hysteresis loop at 40 mK
M/M$_s$
$\mu_0 H_z$ (T)
1
0.5
0
-0.5
-1
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1
7
8
11
12
0.002 T/s
0.004 T/s
0.008 T/s
0.017 T/s
0.035 T/s
0.070 T/s
0.140 T/s
1
0.95
0.9
0.85
1
1.1
1.2
1.3
13

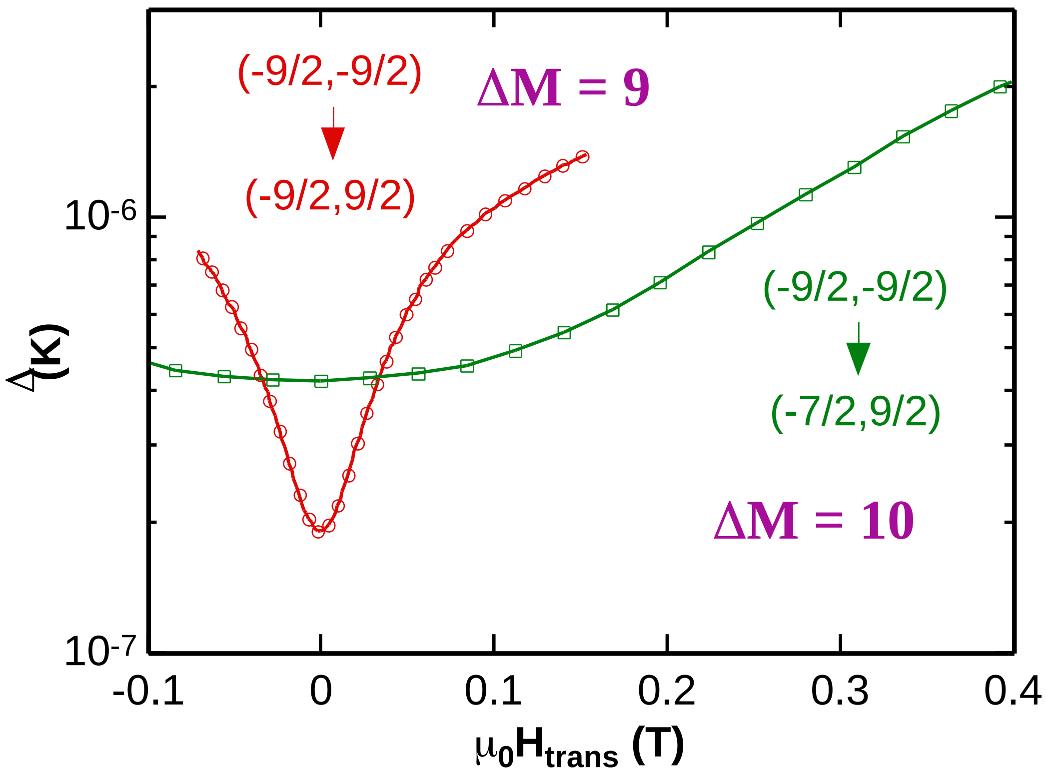
# Virtual phonon transitions

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

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



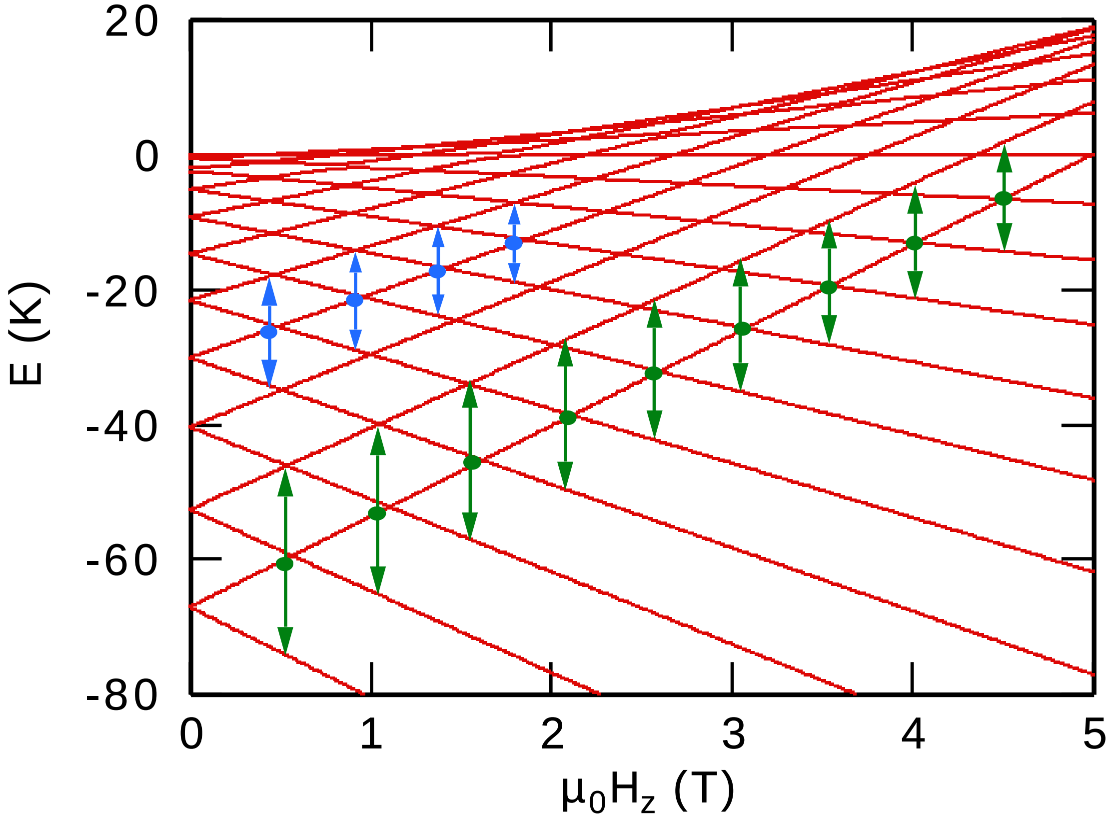
# Parity of level crossing



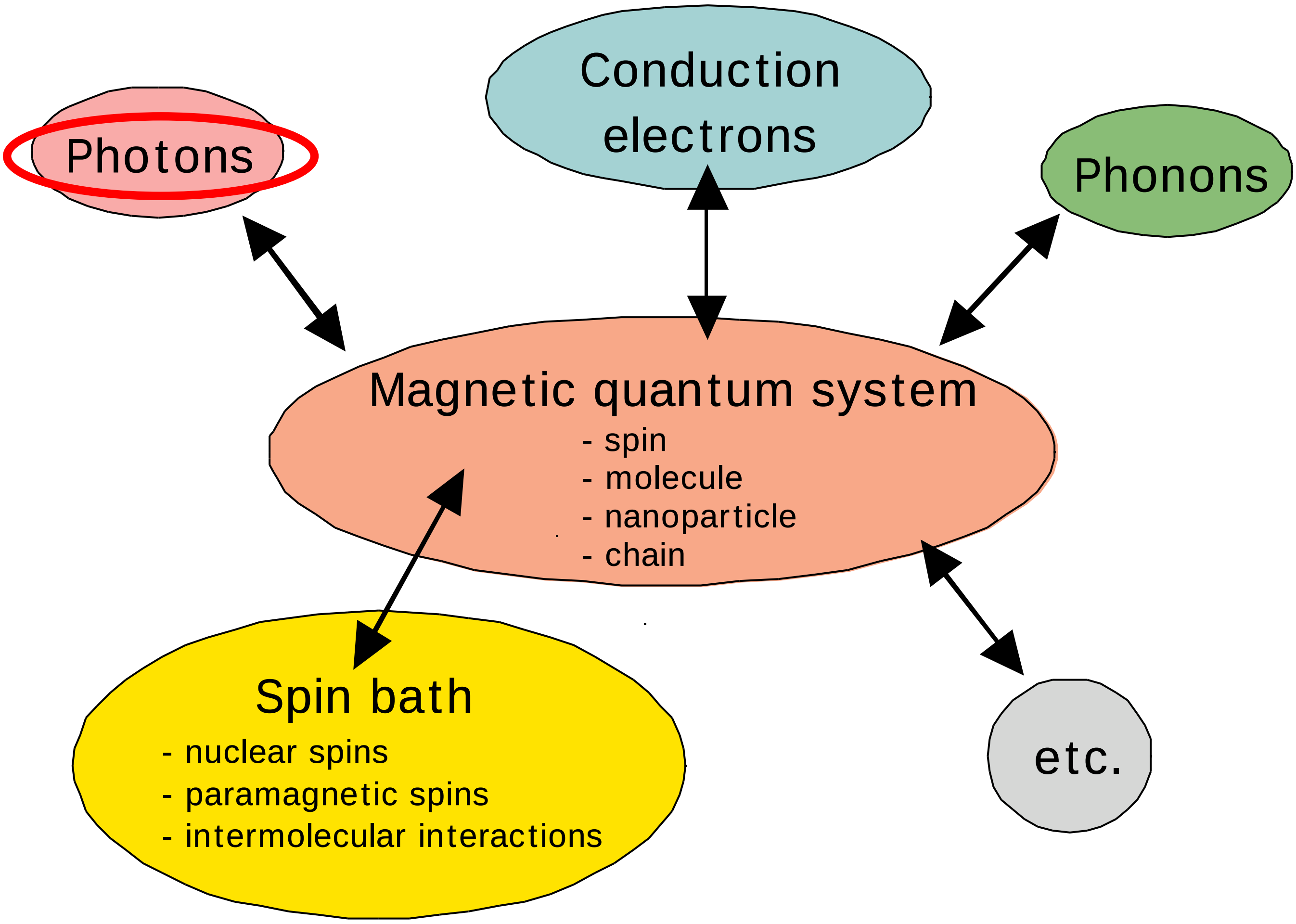
**total quantum number:**

**$M = m1 + m2$**

# Spin-spin cross-relaxation in $Mn_{12}$-ac



# Decoherence in magnetic mesoscopic systems



Photons

Conduction electrons

Phonons

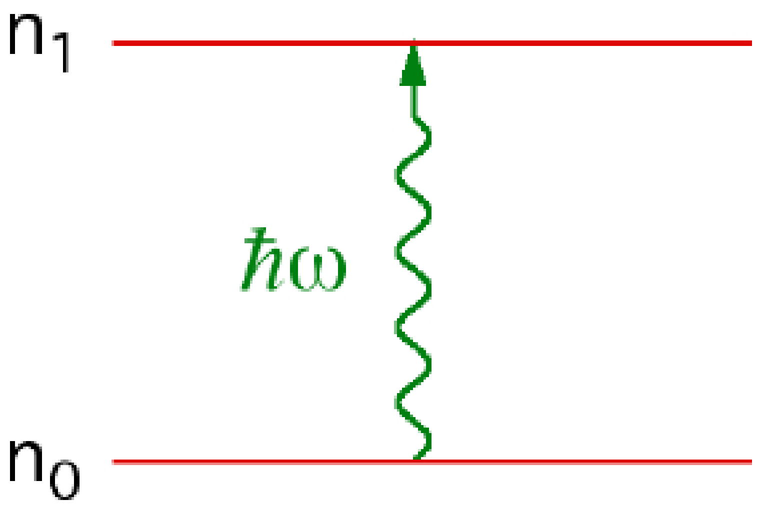
Magnetic quantum system
- spin
- molecule
- nanoparticle
- chain

Spin bath
- nuclear spins
- paramagnetic spins
- intermolecular interactions

etc.

# Interaction with photons

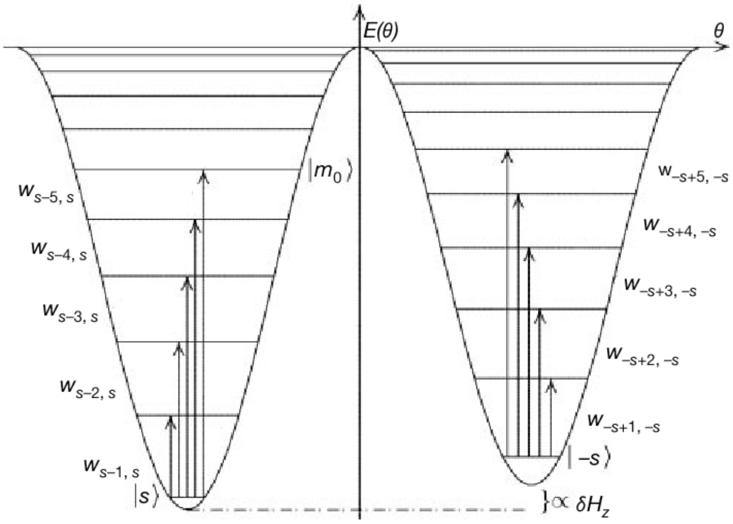
(microwaves: 1 to 115 GHz)

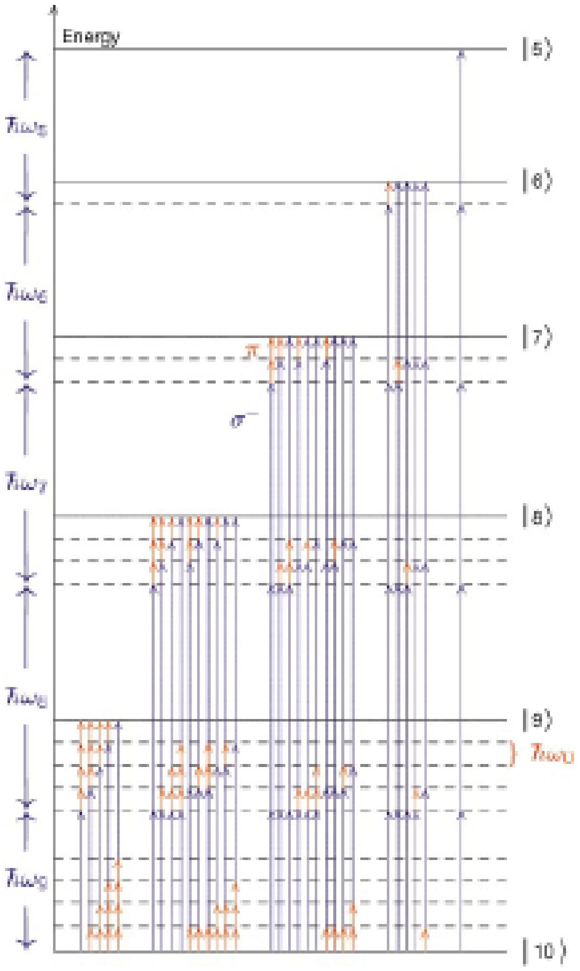


# Quantum computing in molecular magnets

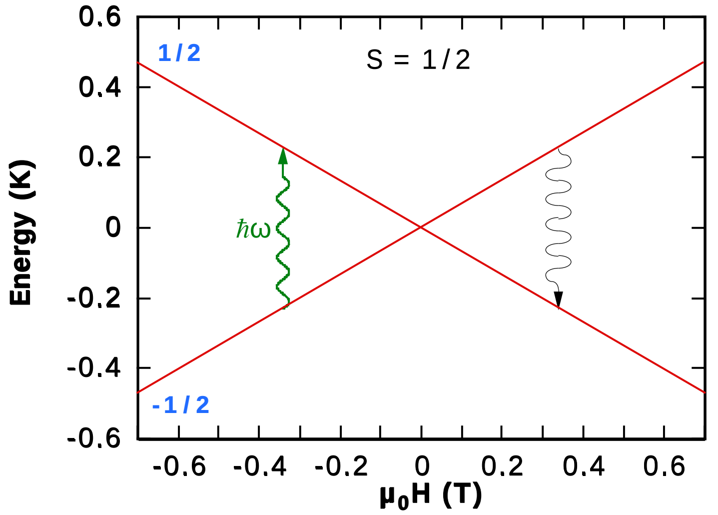
**Michael N. Leuenberger & Daniel Loss**
NATURE, 410, 791 (2001)

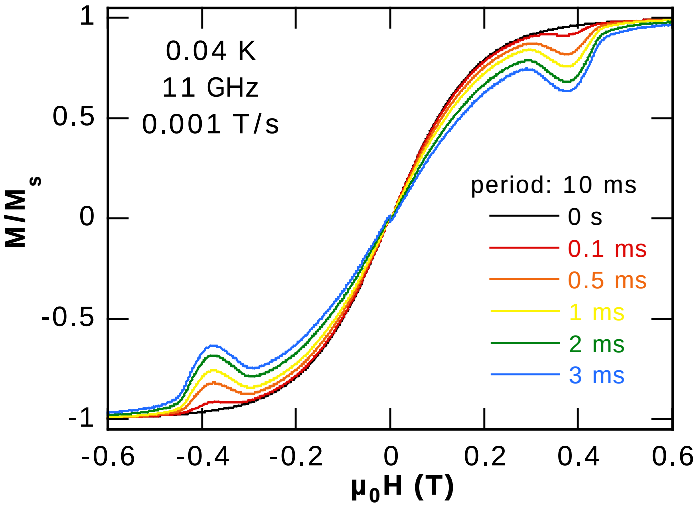
- implementation of Grover's algorithm
- storage unit of a dynamic random access memory device.
- fast electron spin resonance pulses can be used to decode and read out stored numbers of up to $10^5$ with access times as short as 0.1 nanoseconds.



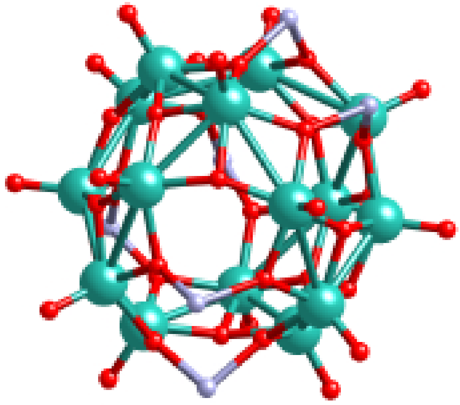


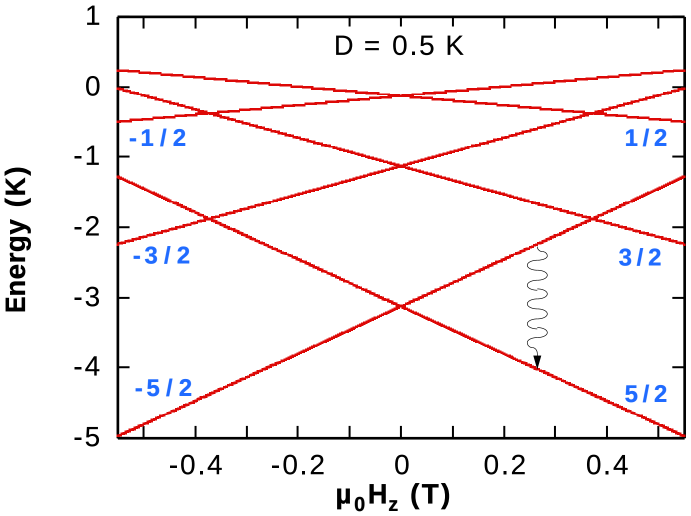
# Absorption of microwaves

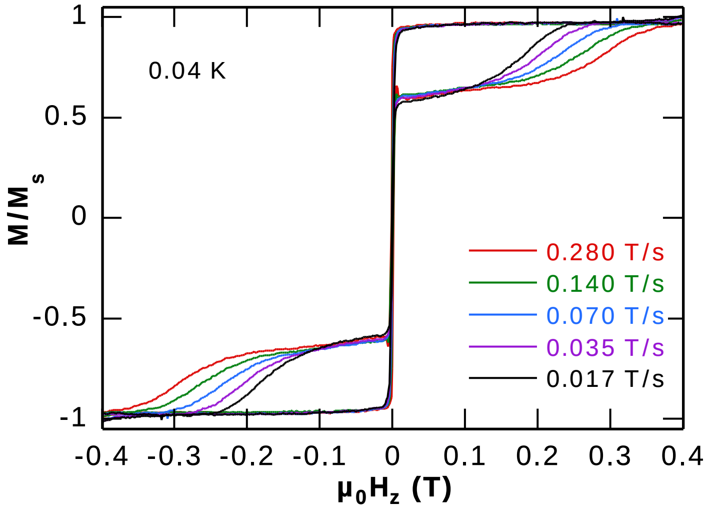




$V_{15}$ S = 1/2

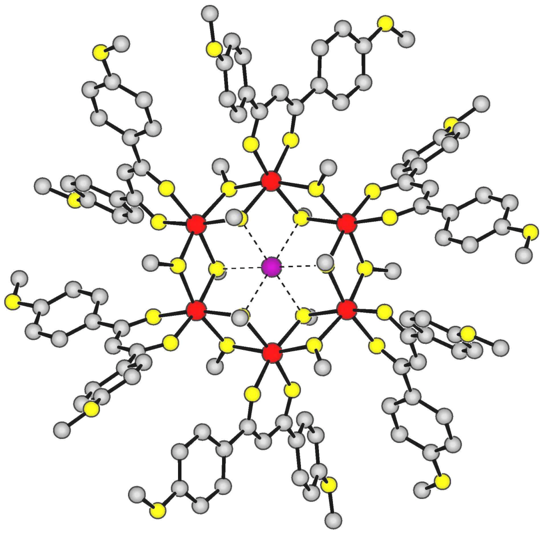






**Reducing intermolecular couplings**

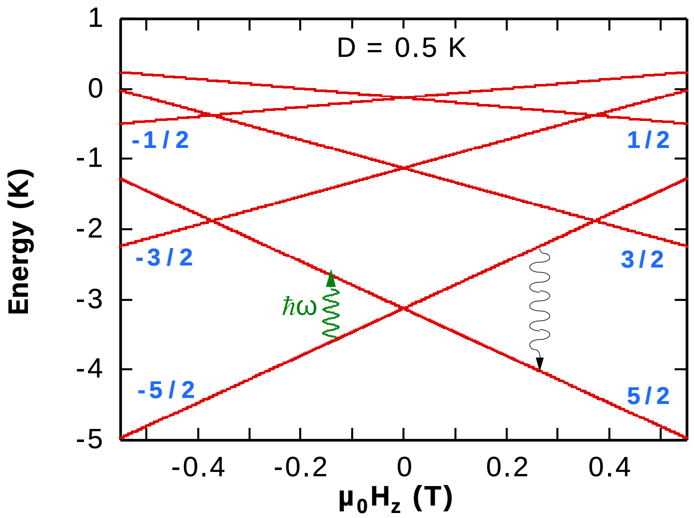
**Fe$_6$ wheels: S = 0**

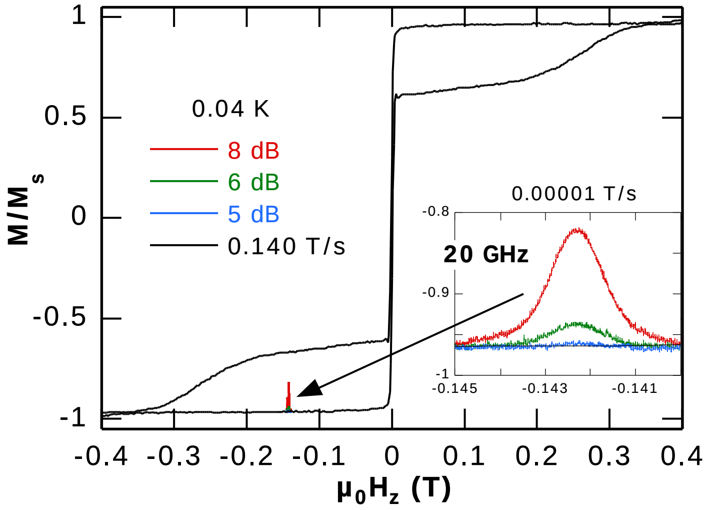


**Doping with Ga**

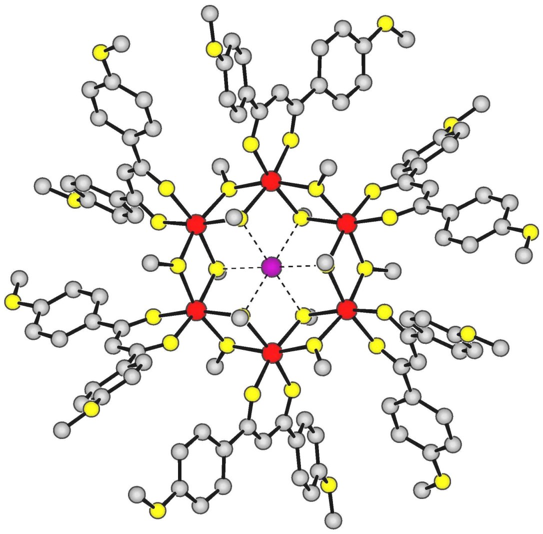
**Fe$_5$Ga : S = 5/2**

# Reducing intermolecular couplings





**Fe$_6$ wheels: S = 0**

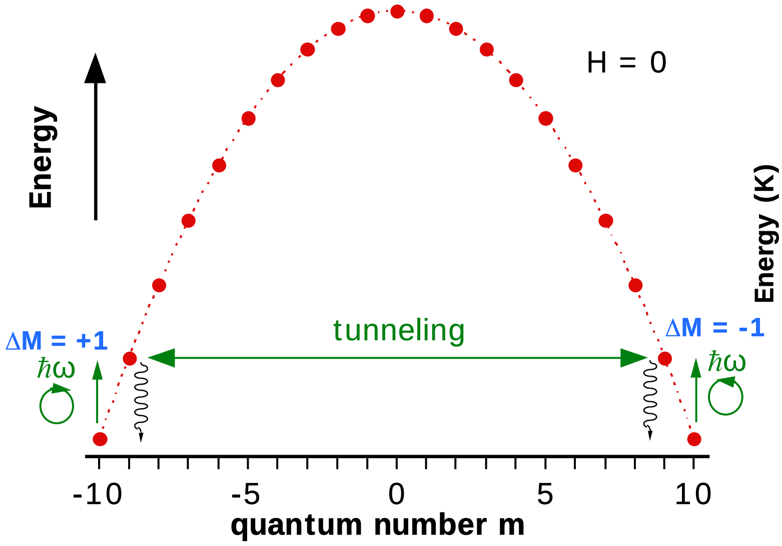


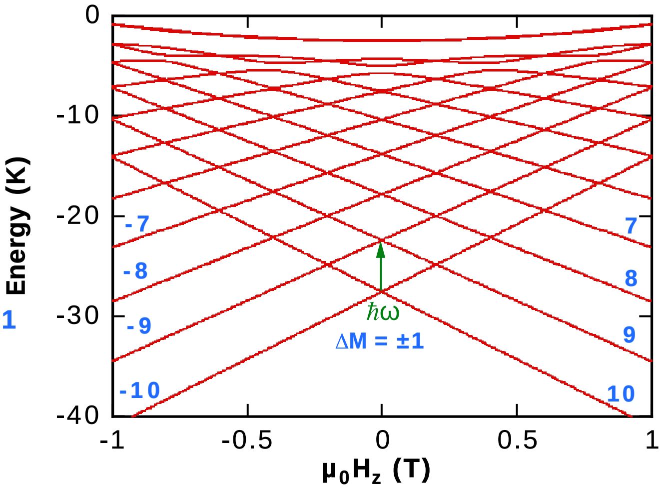
**Doping with Ga**

**Fe$_5$Ga : S = 5/2**

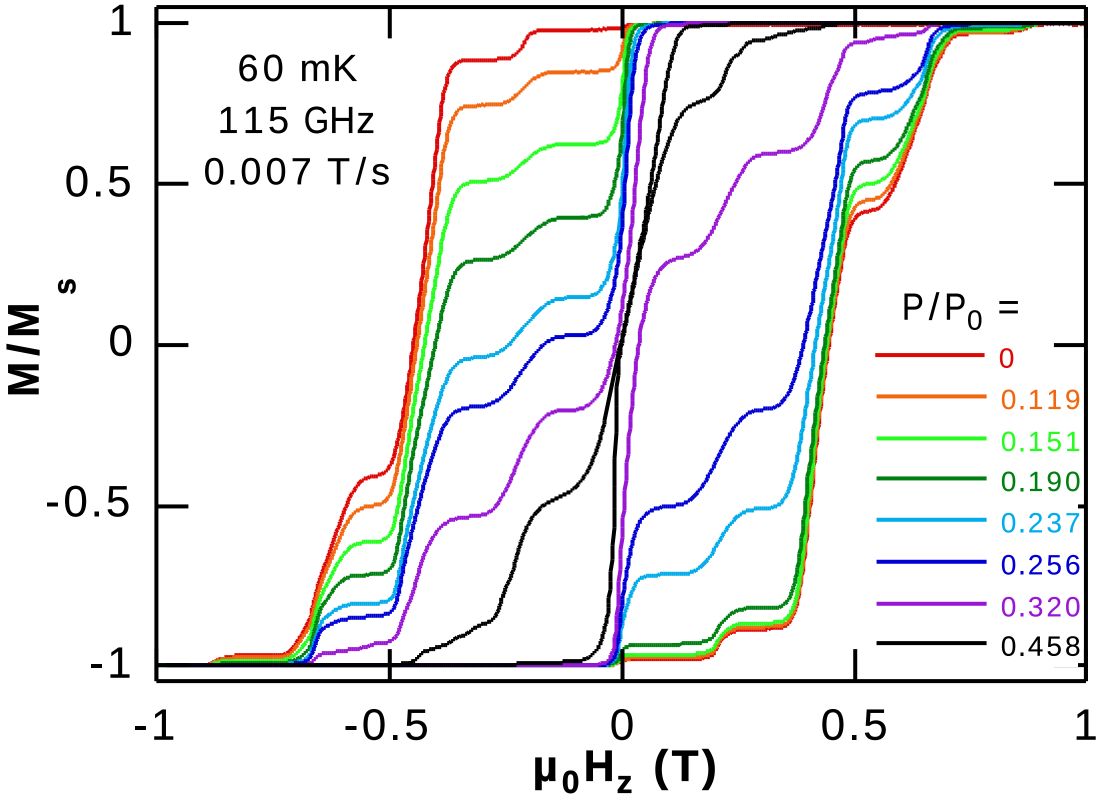
# Photon assisted tunneling

## Absorption of circular polarized microwaves

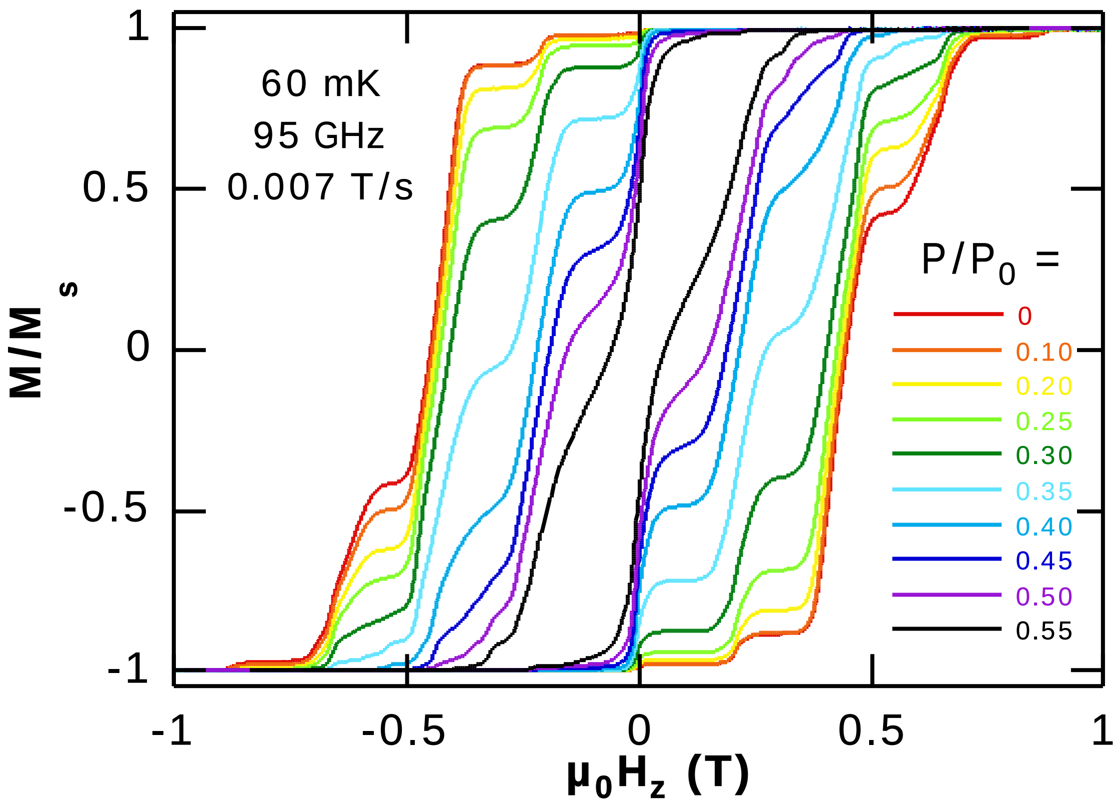




# Absorption of circular polarized microwaves
# (115 GHz)

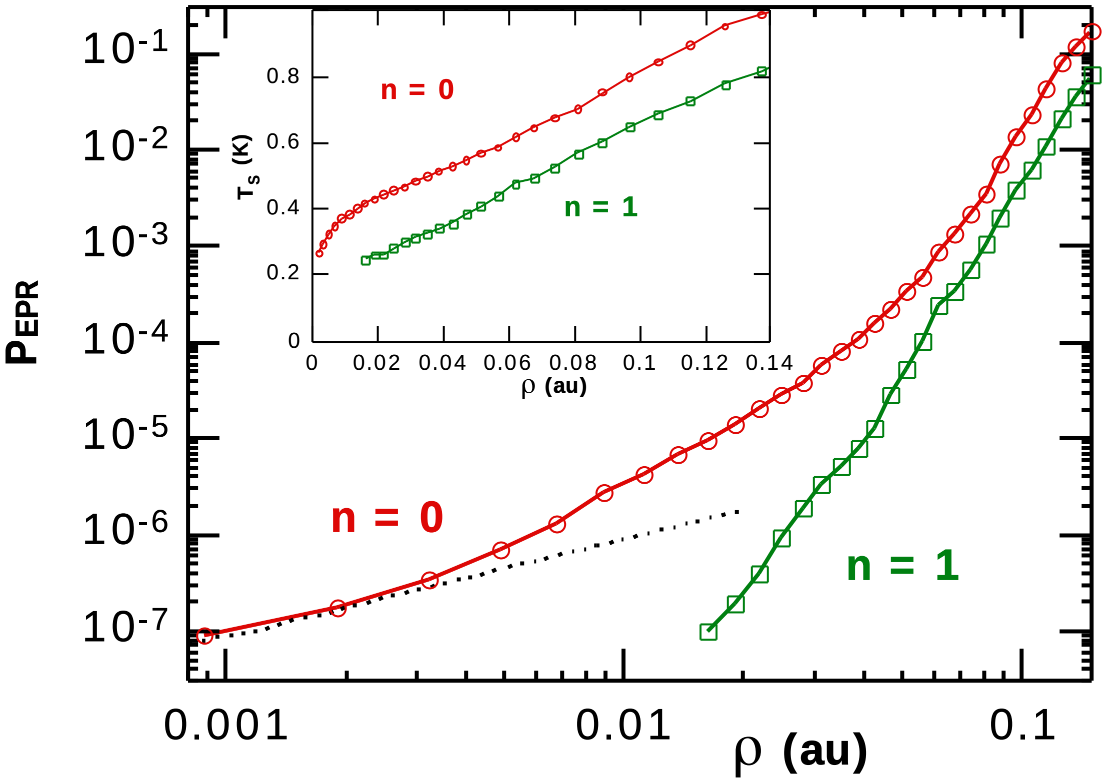


# Absorption of circular polarized microwaves
# (95 GHz)



# Photon induced tunnel probability

$$P_{EPR} = P - n_{\pm10}P_{\pm10}$$

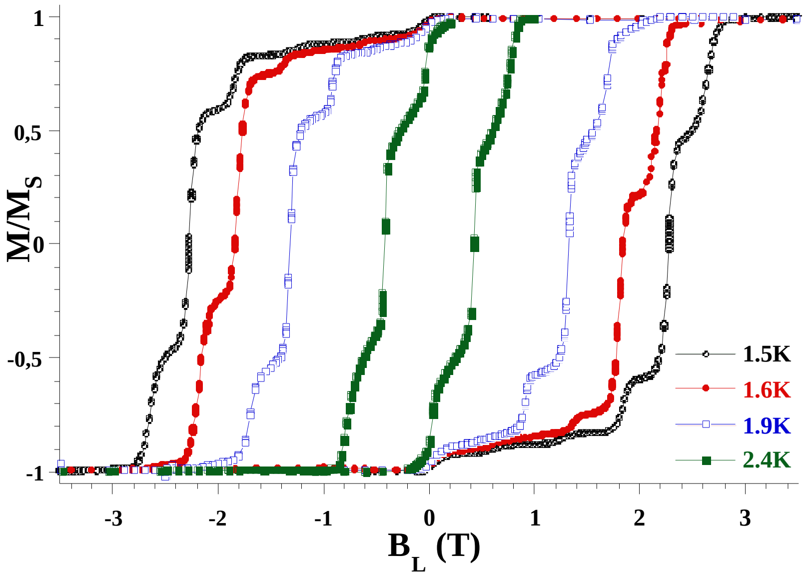


# Perspectives concerning microwave experiments

- **Quantum dynamic: spin-echo like experiments**

# Conclusion

## Beginning: $Mn_{12}$-ac



L. Thomas, B. Barbara, *et al.*, Nature (1996)

**R. Sessoli, D. Gatteschi, D. Hendrikson, G. Christou, *et al.* (1993)**
**M. Novak, C. Paulsen, B. Barbara, *et al.* (1994)**
**J. Friedman, M. Sarachik, *et al.*, PRL (1996)**
**L. Thomas, B. Barbara *et al.*, Nature (1996)**

# Followed by: 130 systems

**Mn, $Mn_2$, $Mn_3$, $Mn_4$, $[Mn_4]_2$, $Mn_5$, $Mn_6$, $Mn_7$, $Mn_8$, $Mn_9$, $Mn_{10}$, $Mn_{11}$, $Mn_{12}$, $Mn_{13}$, $Mn_{16}$, $Mn_{18}$, $Mn_{21}$, $Mn_{24}$, $Mn_{26}$, $Mn_{30}$**

**$Fe_2$, $Fe_3$, $Fe_4$, $Fe_5$, $Fe_6$, $Fe_7$, $Fe_8$, $Fe_{10}$, $Fe_{11}$, $Fe_{13}$, $Fe_{17/19}$, $Fe_{19}$**

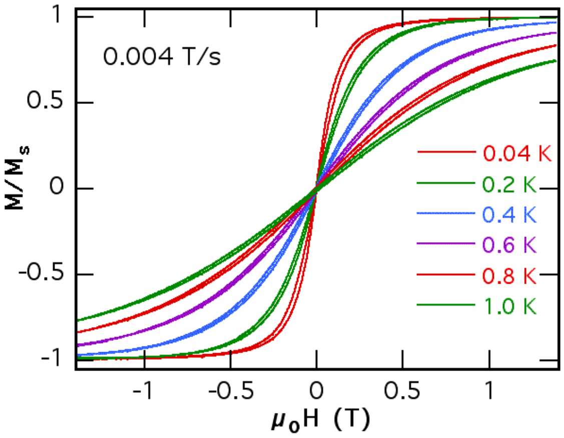
**$Ni_4$, $Ni_5$, $Ni_6$, $Ni_8$, $Ni_{12}$, $Ni_{21}$, $Ni_{24}$**

**$Co_4$, $Co_6$, $Co_{10}$**

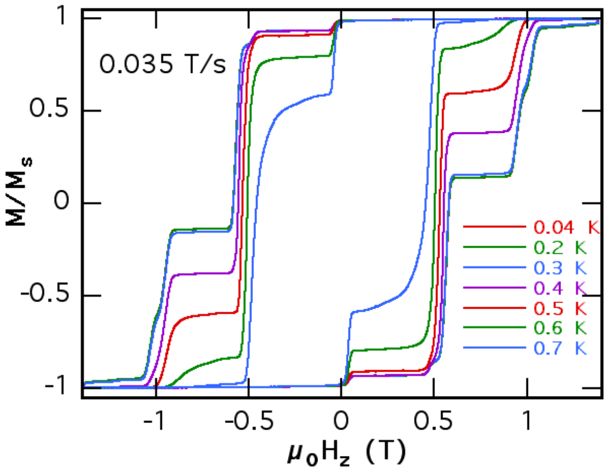
**$Co_2Gd_2$, $Co_2Dy_2$, $Cr_{12}$, $CrNi_6$, $CrNi_2$, $CrCo_3$, $Fe_{10}Na_2$, $Fe_2Ni_3$, $Mn_2Dy_2$, $Mn_2Nd_2$, $V_{15}$, Ho, ...**

**……**

**$S = 0, 1/2, 1, 3/2, 2, 5/2, 4, 9/2, 5, \ldots\ldots\ldots\ldots 33/2$**

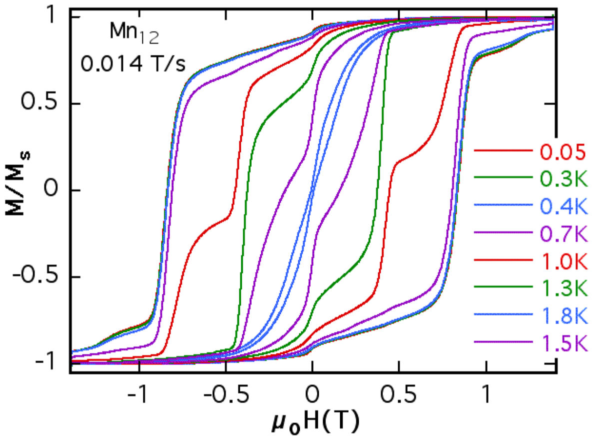


[$Mn_3O(OAc)_6(py)_3$]py

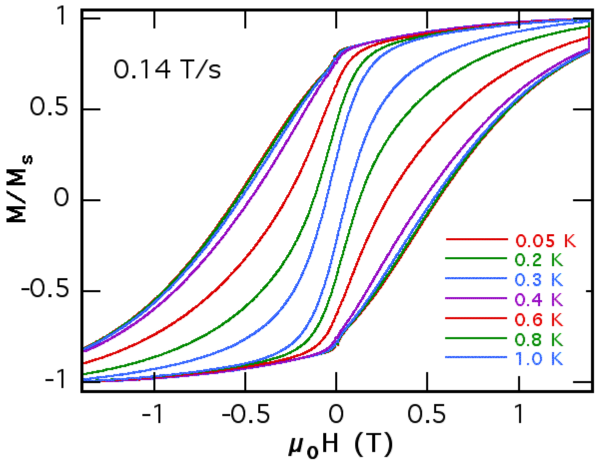


$Mn_4O_3(OSiMe_3)(O_2CMe)_3(dbm)_3$

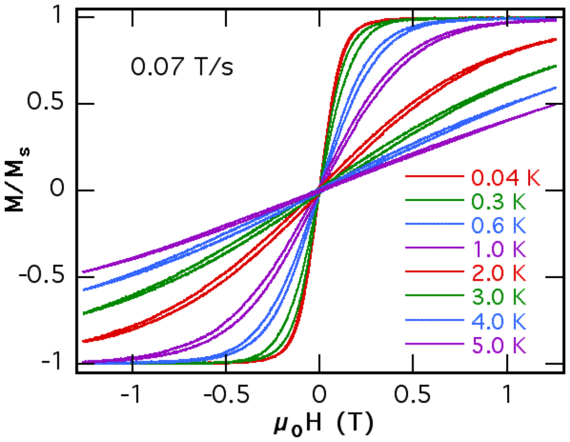
## Size dependence ?



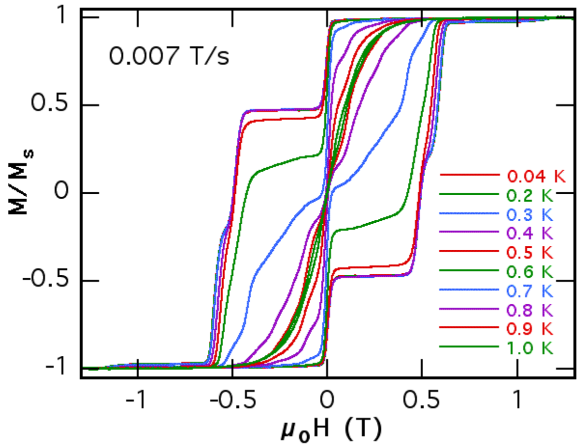
$(PPh_4)_2[Mn_{12}O_{12}(O_2CCH_2Cl)_{16}(H_2O)_3]$



$Mn_{30}O_{24}(OH)_8(O_2CCH_2C(CH_3)_3)_{32}(H_2O)_2(CH_3NO_2)$



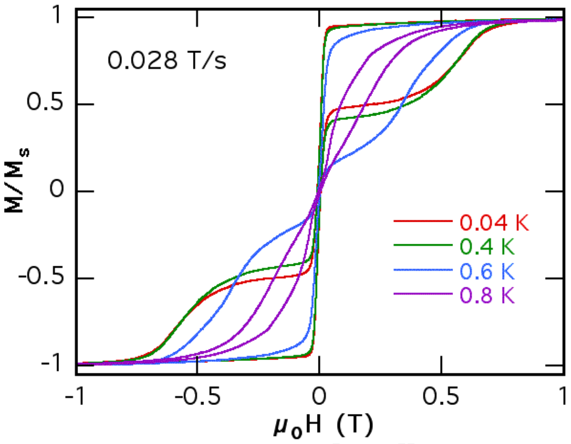
$Mn_4O_3(O_2CEt)_4(dbm)_3$



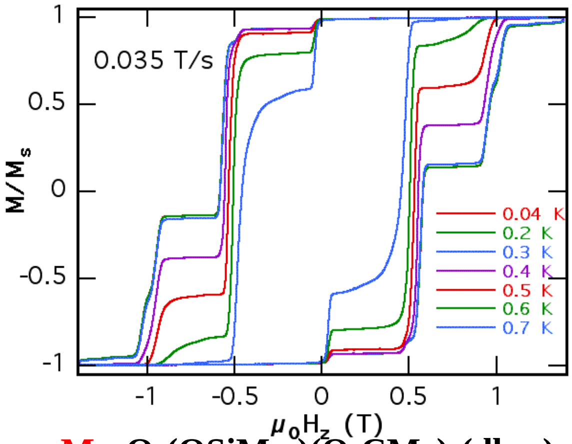
$Mn_4O_3Cl(OAC)_3(dbm)_3$

**Control / origin of the magnetic anisotropy ?**

**$S = 9/2$**

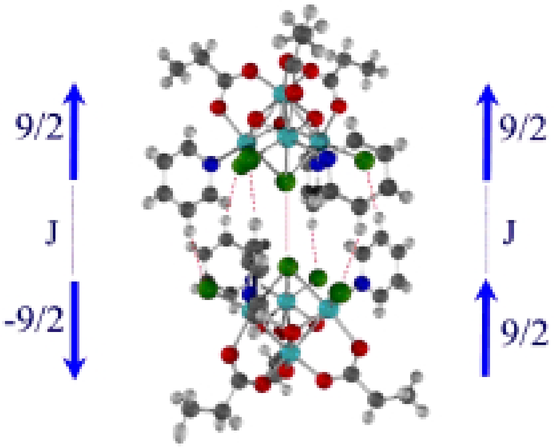


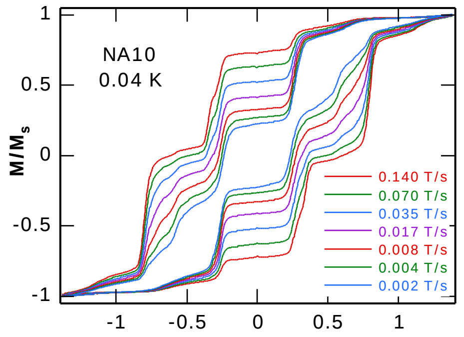
$Mn_4O_3(O_2CPh)_4(dbm)_3$

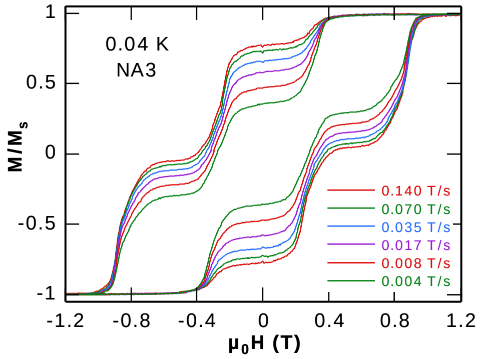


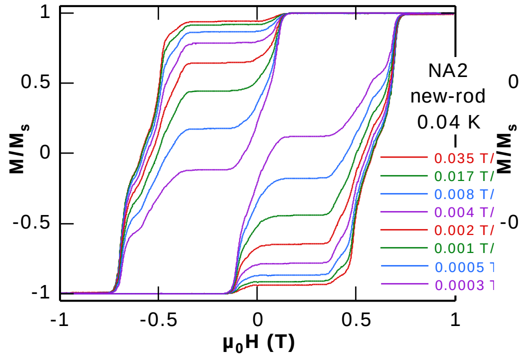
$Mn_4O_3(OSiMe_3)(O_2CMe)_3(dbm)_3$

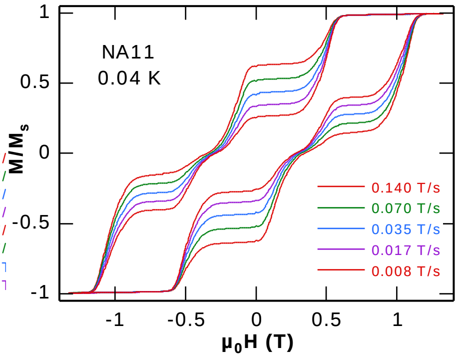
# Exchange biased $Mn_4$

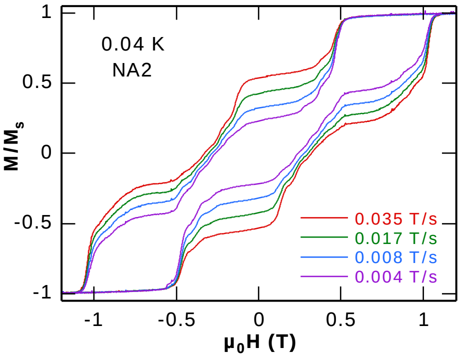






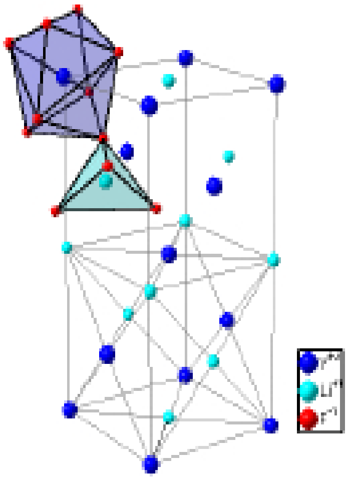






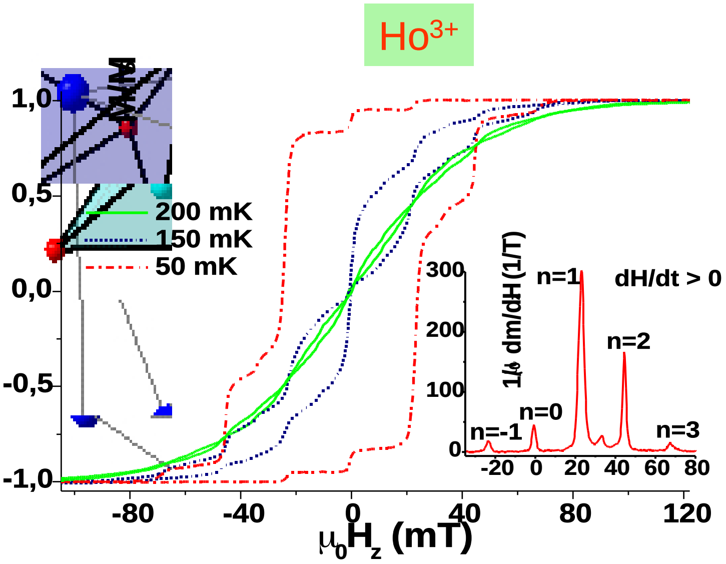
# Rare-earth ions: Ho$^{3+}$ in $Y_{0.998}Ho_{0.002}LiF_4$

## Effects of Strong Hyperfine Interactions



Tetragonal symmetry
(Ho in S4)

J = L+S = 8;     $g_J$=5/4

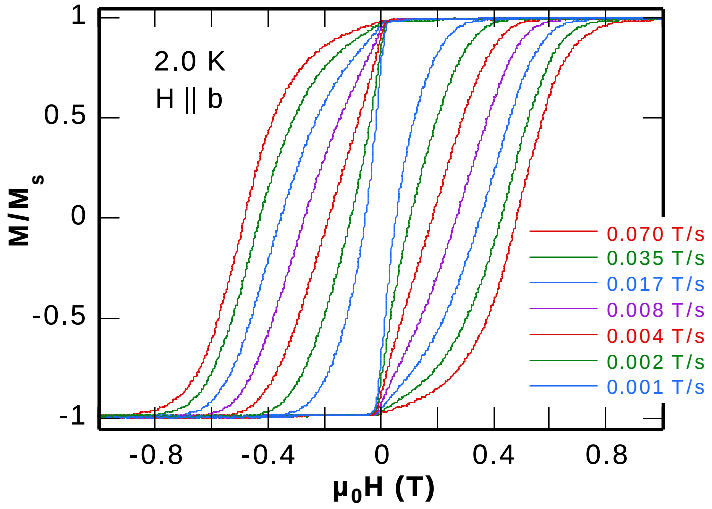


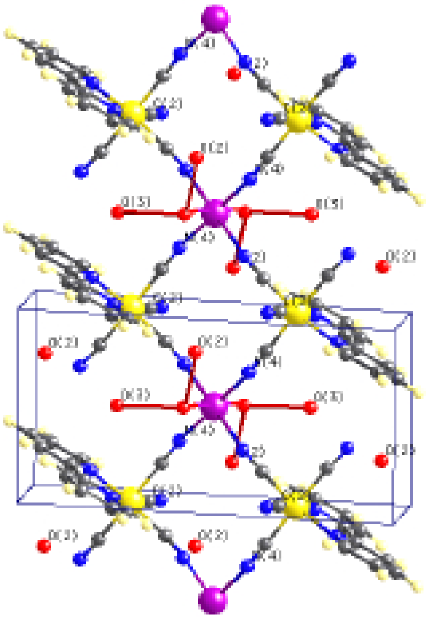
R. Giraud, W. Wernsdorfer, A.~M. Tkachuk, D. Mailly, and B. Barbara, *Phys. Rev. Lett.* **87**, 057203 (2001).

# Slow dynamics in spin-chains

## NC[Fe(III)(CN)Co(II)]NC

**A. R. Lescouezec, M. Julve, F. Lloret**,
Valencia University, Spain
**P. Herson, Y. Dromzée, M. Verdaguer**
Chimie Inorganique et Matériaux Moléculaires, CNRS, Paris





# Conclusion

***J. Villain:*** ***"… a school of physics"***

***& chemistry***

# Collaborations

| | |
|---|---|
| **L. Thomas** | **PhD 1996: $Mn_{12}$-ac** |
| **F. Lionti** | **PhD 1997: $Mn_{12}$-ac, $Fe_{17/19}$** |
| **I. Chiorescu** | **PhD 2000: $Mn_{12}$-ac, $V_{15}$** |
| **R. Giraud** | **PhD 2002: $Ho^{3+}$** |
| **C. Thirion** | **PhD 2003: nanoparticles, GHz** |
| **R. Tiron** | **PhD 2004: $[Mn_4]_2$ , …** |

**E. Bonet, W. Wernsdorfer, B. Barbara**
**LLN, CNRS, Grenoble**

**C. Paulsen, V. Villar, A. Sulpice, A. Benoit**
**CRTBT, CNRS, Grenoble**

**A.-L. Barra, L. Sorace,**
**LCMI - CNRS, Grenoble**

**D. Mailly**
**LPN, CNRS, Marcoussis**

# Collaborations

## Concerning SMMs and spin chains

**C. Paulsen, A. Sulpice, V. Villar, T. Ohm, CRTBT - CNRS**
**A.-L. Barra, L. Sorace, LCMI - CNRS, Grenoble**

**Group of G. Christou, Dept. of Chemistry, Florida**
**Group of D. Hendrickson, Dept. of Chemistry, San Diego**

**Group of D. Gatteschi et R. Sessoli, Univ. de Firenze, Italie**
**Group of A. Cornia, Univ. de Modena, Italie**

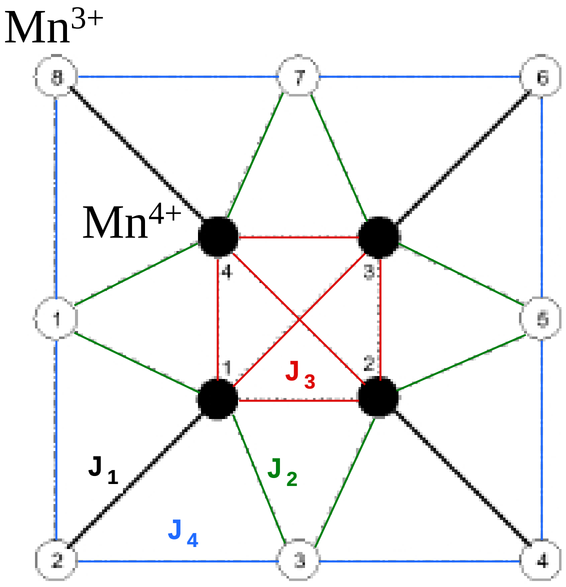
**Group of A. Müller, Univ. de Bielefeld, Germany**
**Group of A. Powell, Univ. de Kahlsruhe, Germany**
**Group of M. Verdaguer, Univ. P. et M. Curie, Paris**
**Group of M. Julve, Univ. de Valence, Spain**
**Group of R.E.P. Winpenny, Univ. de Manchester, UK**
**Group of E. Coronado, Univ. de Valence, Spain**
**Group of P. Rey et D. Luneau, CEA, Grenoble**
**• • •**

# Merci !

# Giant spin approximation

## Example: Mn12-ac

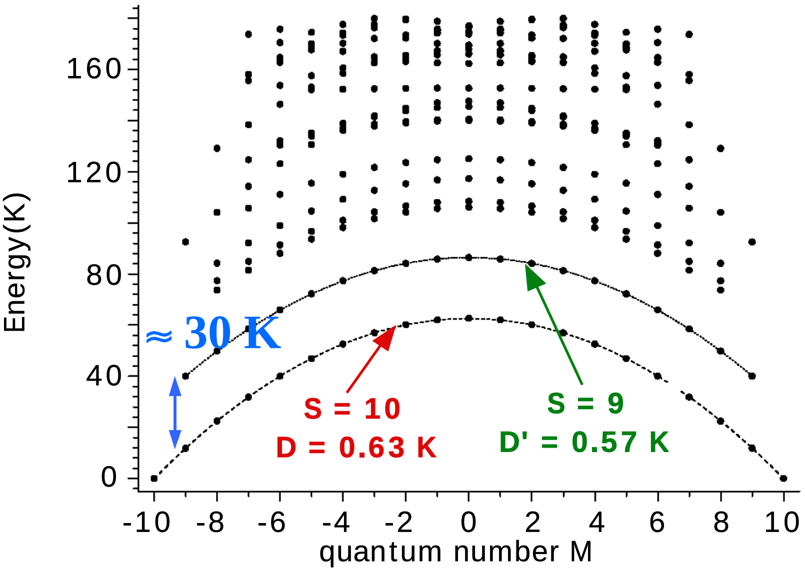
Hilbert space: $(2\text{x}2 + 1)^8(2\text{x}3/2 + 1)^4 \approx 10^8$



$J_1 \approx$ -215 K

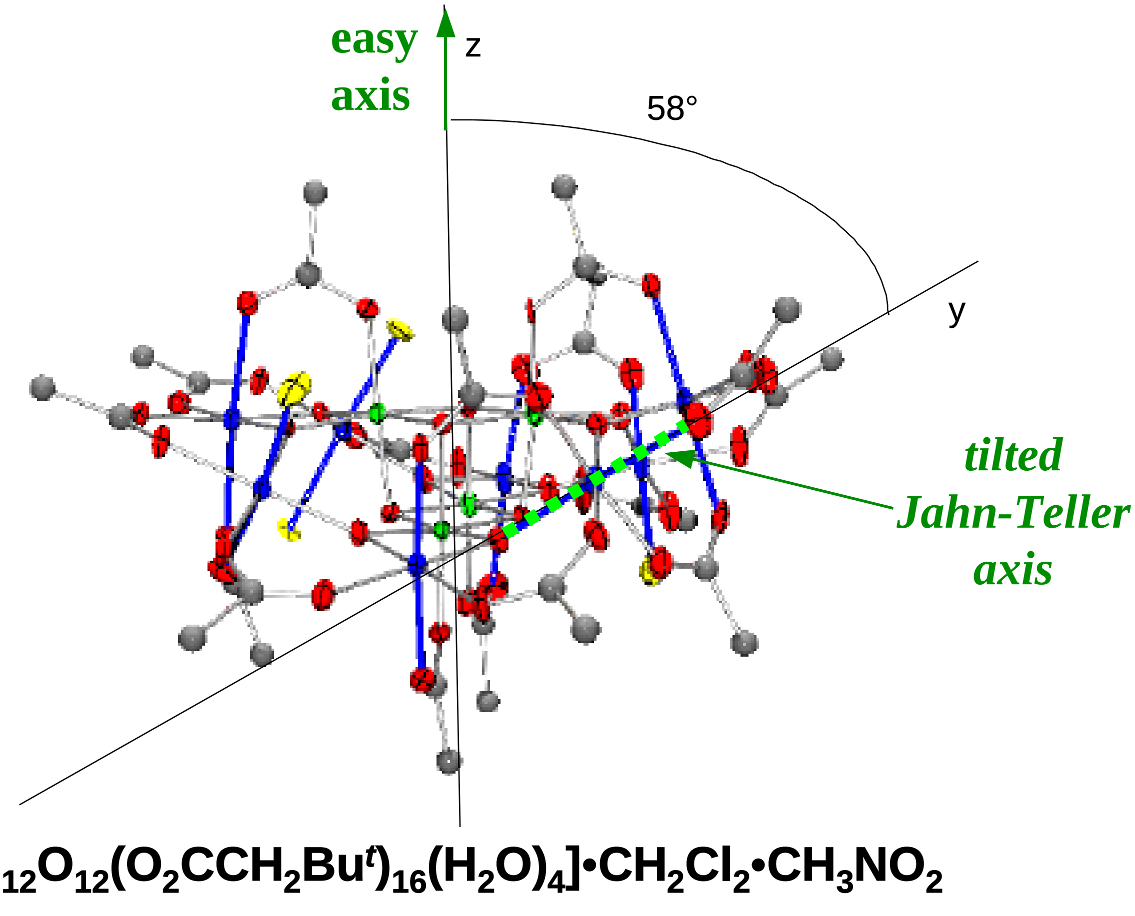
$J_2 \approx J_3 \approx$ -86 K

$J_4 <$ 43 K



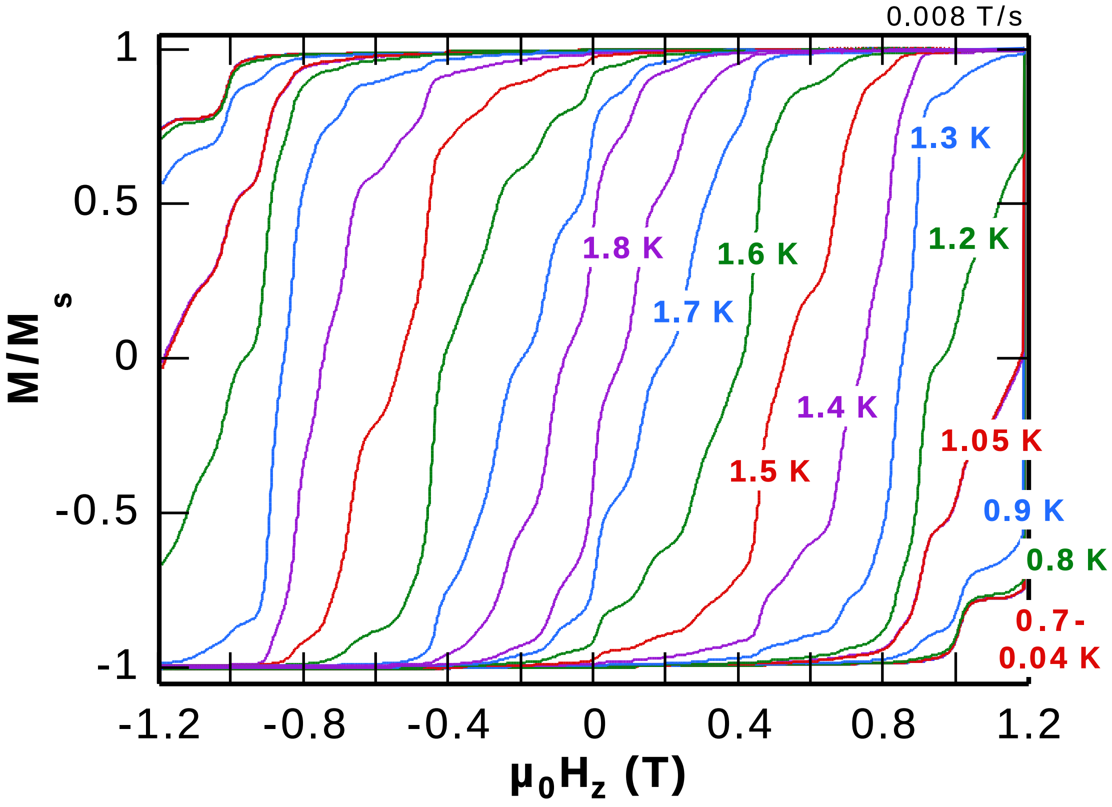
I. Tupitsyn (2000)

# “One member of the Mn12 family”

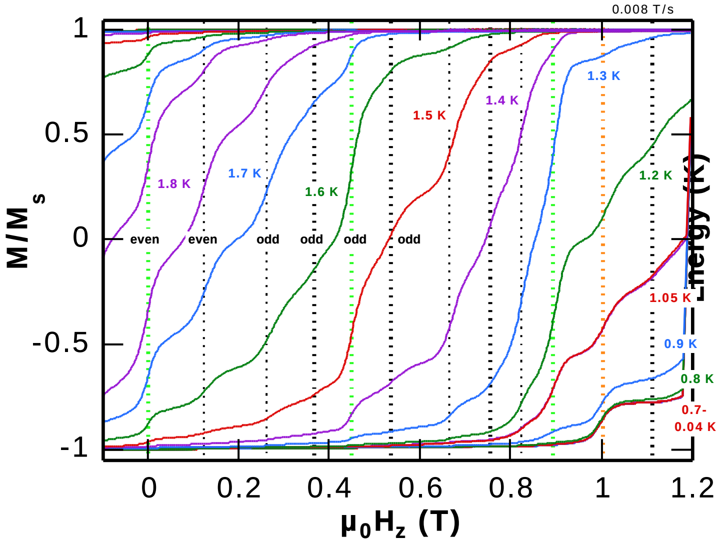


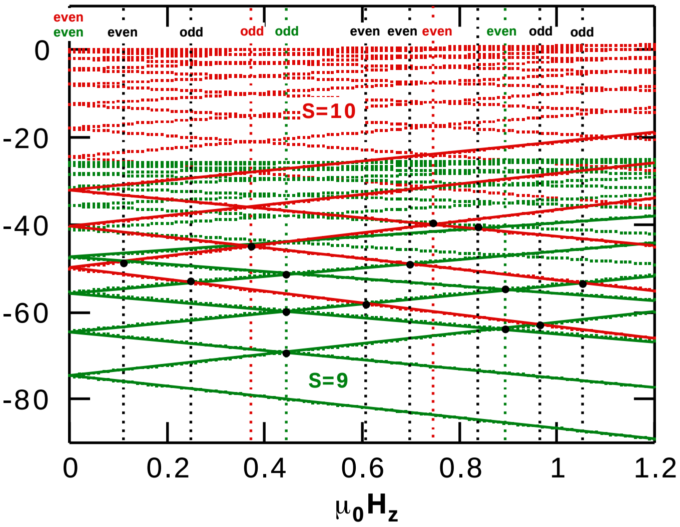
**$[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(H_2O)_4]\cdot CH_2Cl_2\cdot CH_3NO_2$**

# Hysteresis loops



## First attempt to find a model based on two spin multiplets:





S = 9, D = 0.6 K

S’ = 10, D’ = 0.5 K

# MQT Strategy of single particle measurements

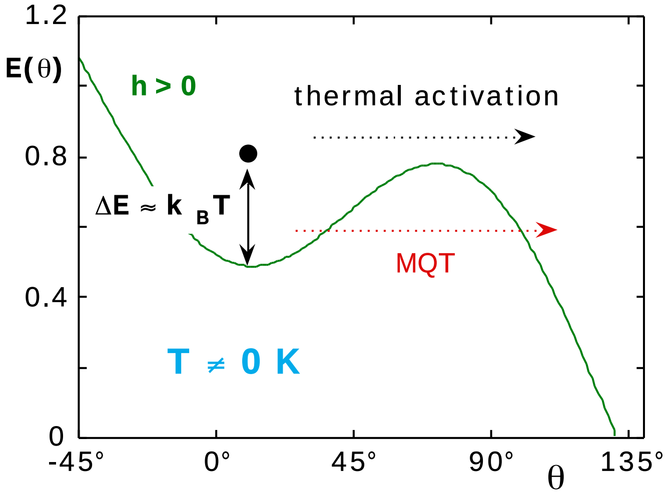
| **Quasi-static measurements** | **Dynamic measurements** |
|---|---|
| - hysteresis loops<br>- $H_{SW}(\theta,\phi)$ | - relaxation (T,H)<br>- P(T,H), $H_{SW}(T,dH/dt)$ |
| - magnetic anisotropy<br>(forme, crystalline, surface) | - activation volume<br>- damping factor |

**"all" parameters are defined in the classical regime**

**deviations for T -> 0**

**studying the crossover Tc and the escape rate $\Gamma_{QT}$**
**as a function of external parameters:**
**transverse fields, field directions, microwaves, etc.**

# Macroscopic Quantum Tunneling of magnetization



$$\Gamma_{TA} = \Gamma_0 e^{-\Delta E / k_B T} \Leftrightarrow \Gamma_{QT} = \Gamma_0' e^{-B}$$

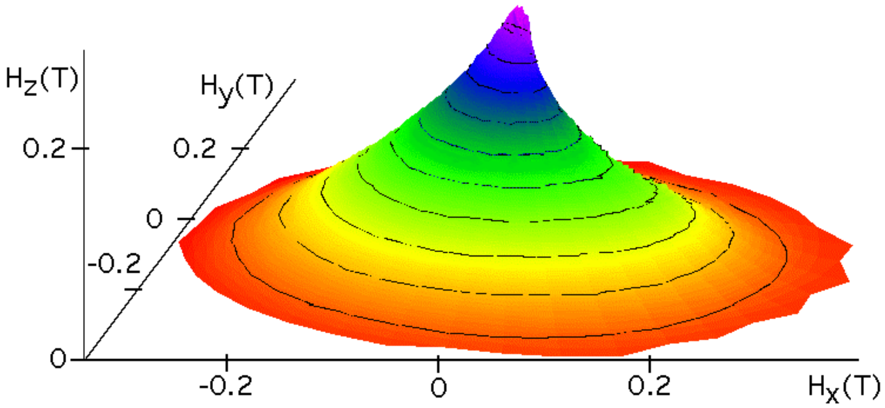
$$\frac{\Delta E}{k_B T} = \frac{E_0(\theta, \gamma)}{k_B T} \varepsilon^{3/2}$$

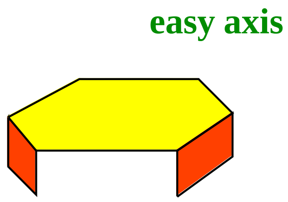
$$B \approx \frac{4 * 6^{1/4}}{9} S \varepsilon^{5/4} \frac{|\cot\theta|^{1/6}}{\sqrt{1 + \frac{K}{K_{||}}\left(1 + |\cot\theta|^{2/3}\right)}}$$

## Crossover temperature:

$$\frac{\Delta E}{k_B T_c} = B \qquad T_c = \frac{9}{4 * 6^{1/4}} \frac{E_0}{k\ S} \varepsilon^{1/4} \frac{\sqrt{1 + \frac{K}{K_{||}}\left(1 + |\cot\theta|^{2/3}\right)}}{|\cot\theta|^{1/6}}$$

**Miguel and Chudnovsky, PRB (1996)**
**Gwang-Hee Kim and Dae Sung Hwang, PRB (1997)**





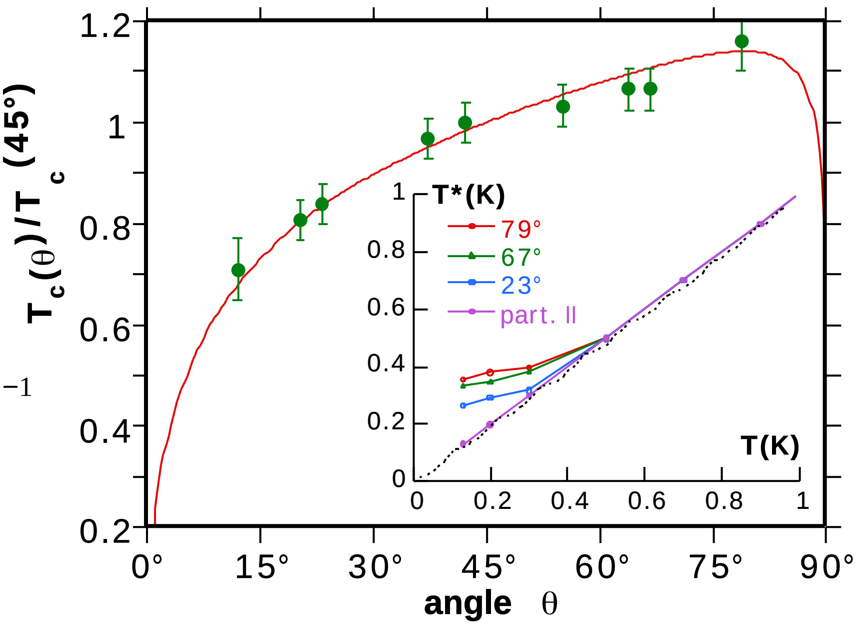
**Barium ferrite nanoparticle(10 nm)**

# Macroscopic Quantum Tunneling of Magnetization of Single Ferrimagnetic Nanoparticles of Barium Ferrite (10 nm)

**W.W. et al, PRL, 79, 4014, (1997)**

$$T_c(\theta) \quad \mu_0 H_a\, \varepsilon^{1/4} |\cot\theta|^{1/6}\left(1+|\cot\theta|^{2/3}\right)^{-1}$$

$$T_c(45°) = 0.31 \text{ K}$$

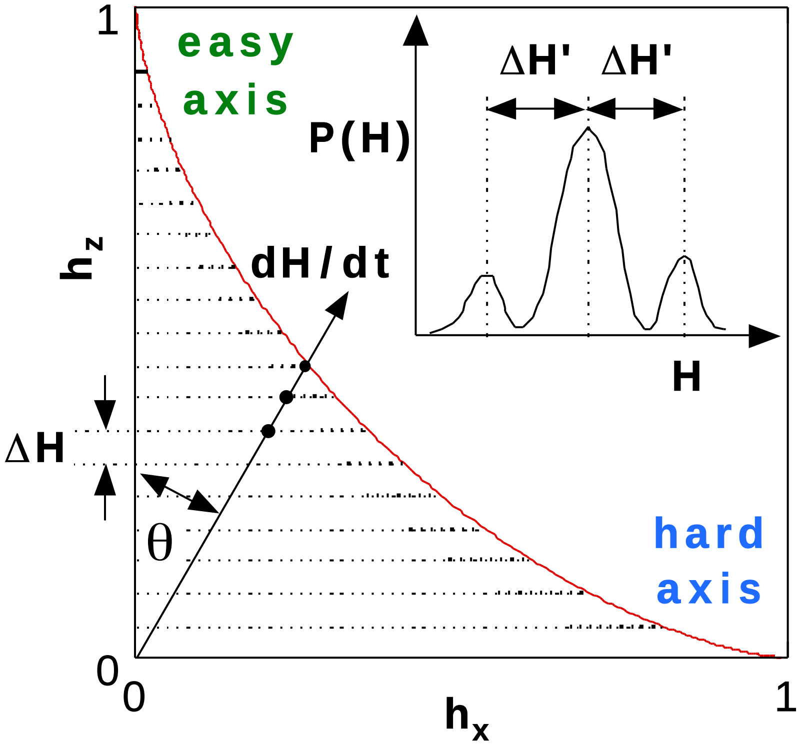


# Quantization of the magnetization

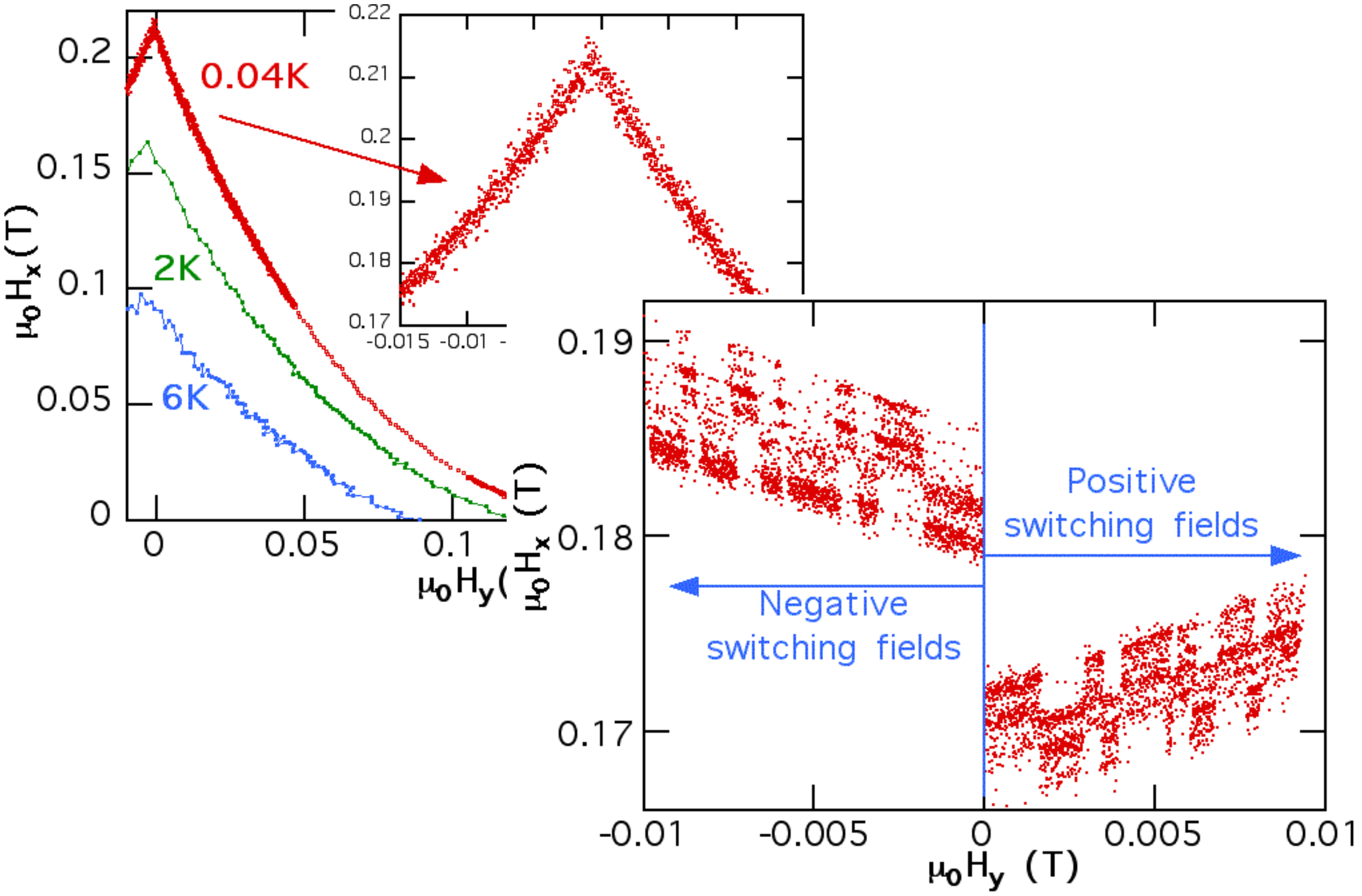
Schematic view of the resonance fields of a giant spin S. The continuous red line is the classical switching fields of Stoner-Wohlfarth.

The inset presents schematically a switching field histogram with

$$\Delta H' \approx \frac{H_a}{2S}\frac{1}{\cos\theta}$$

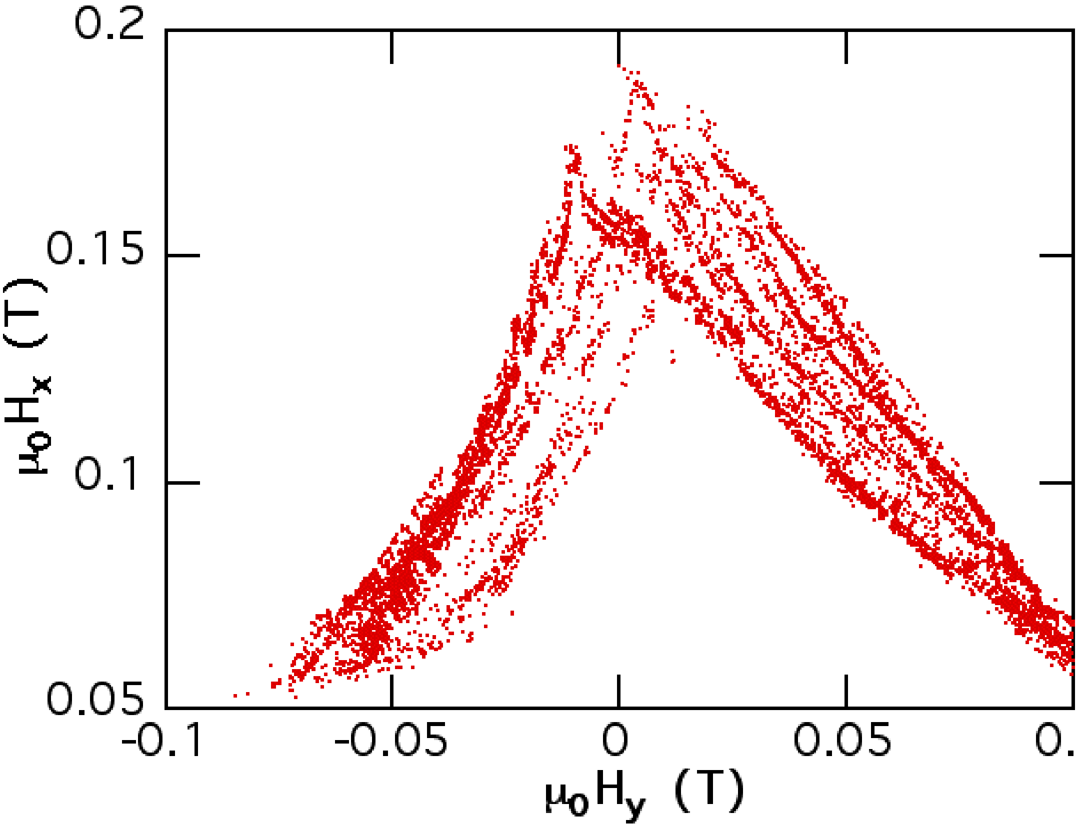


# Fe - clusters (≈3 nm)



## Fe - clusters (≈ 3 nm)

## sample oxidation ?!? surface spin frustration ?!?



# Comparison of Josephson and magnetic grain systems

| **System** | **Rf SQUID ring or current-biased junction** | **Single domain ferro- or antiferromagnetic particle** |
|---|---|---|
| Macroscopic variable | Trapped flux or Cooper pair phase | Magnetization or Néel vector |
| Control parameters **$q$** | External flux or Bias current **$I$**<br>$\varepsilon = 1 - I/I_c$<br>Critical current $I_c$<br>dissipation | Applied magnetic field **$H$**<br>$\varepsilon = 1 - H/H_{sw}^0$<br>Magnetic anisotropy field $H_{sw}^0$<br>Field directions or transverse fields<br>dissipation |
| Form of potential near instability | $\alpha q^2 - \beta q^3$ | $\alpha q^2 - \beta q^3$ or $\alpha q^2 - \gamma q^4$<br>(depending on field direction) |
| Number of particles involved in tunneling | $10^{15} - 10^{23}$ electrons (SQUID) | $1 - 10^8$ magnetic moments |