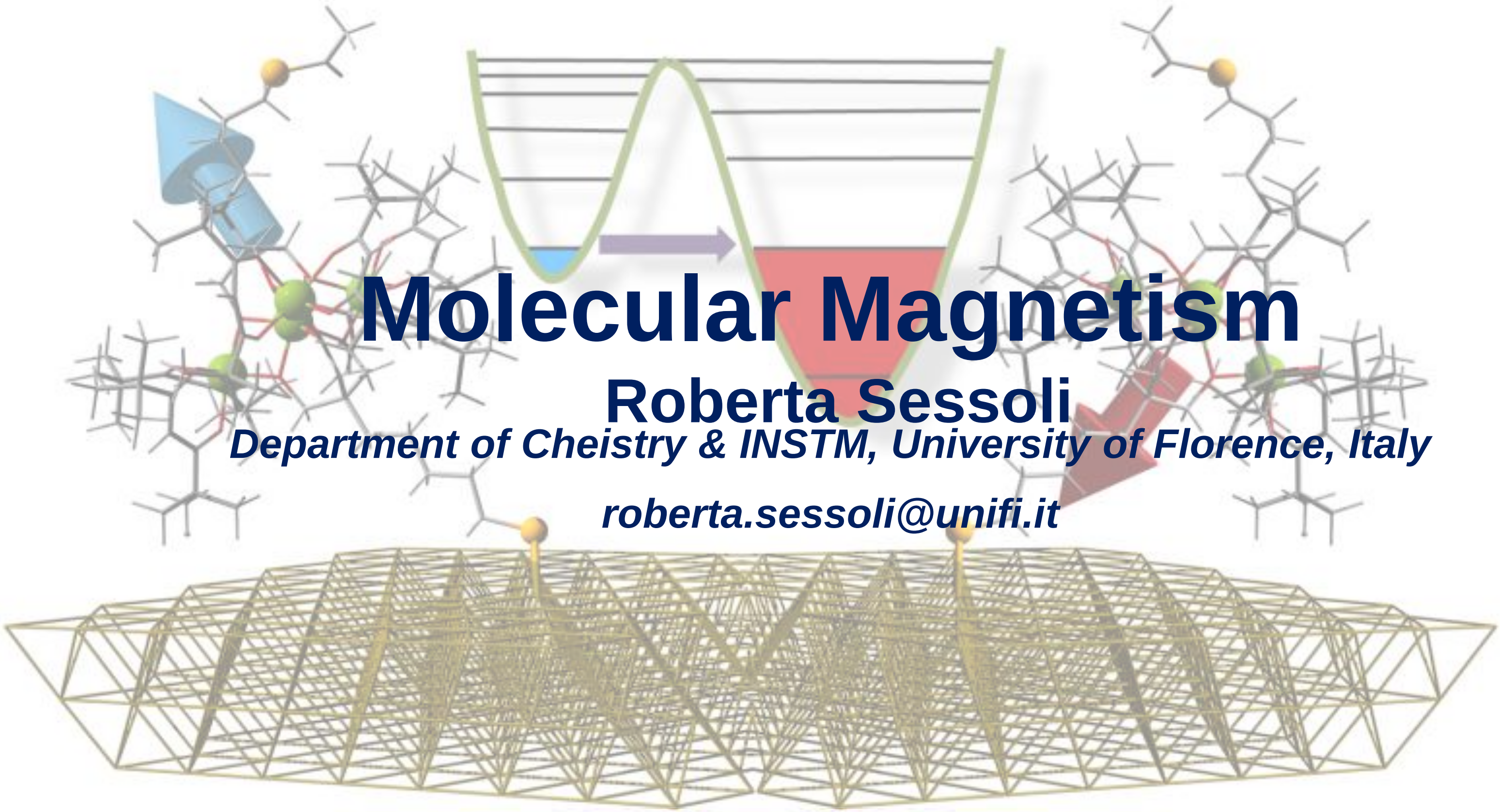

Molecular Magnetism

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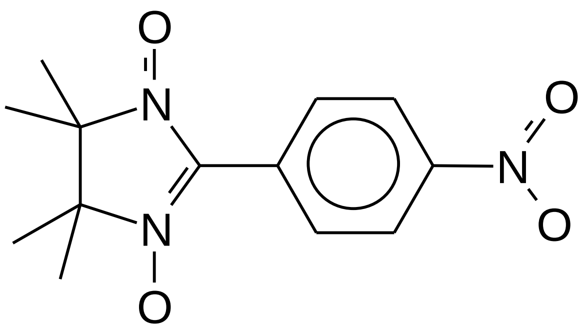
Outline

- Introduction
- 0d Materials (Single Molecule Magnets)
  - Reversal of the magnetization: thermal process
  - Reversal of the magnetization: quantum process
  - Rational Design of SMMs
- 1d materials (Single Chain Magnets)
- Addressing individual molecules
  - SMMs on surfaces
  - SMMs in transport expertiments

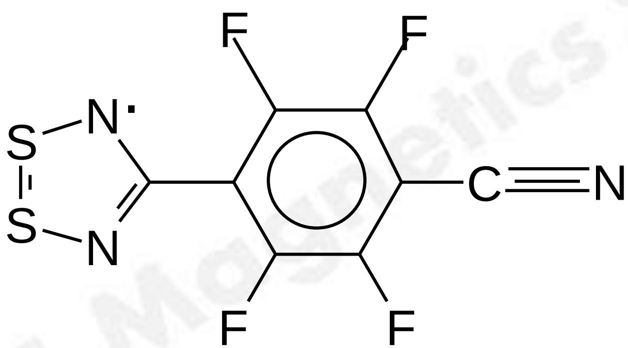
Organic ferromagnets

Magnetism of S=1/2 for each molecule, not of “impurities”



the first one (1991)

Tc= 0.6 K



the highest Tc

Tc=36 K

Magnetic Exchange in Molecular Materials

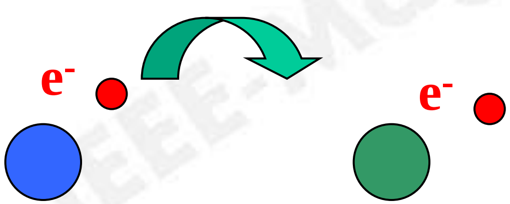
$$H = \mathbf{S}_A \cdot \mathbf{J} \cdot \mathbf{S}_B \qquad \mathbf{J} = \begin{pmatrix} J_{xx} & J_{xy} & J_{xz} \\ J_{yx} & J_{yy} & J_{yz} \\ J_{zx} & J_{zy} & J_{zz} \end{pmatrix}$$

$$H = J\,\mathbf{S}_A \cdot \mathbf{S}_B + \mathbf{S}_A \cdot \mathbf{D}_{AB} \cdot \mathbf{S}_B + \mathbf{d}_{AB} \cdot (\mathbf{S}_A \times \mathbf{S}_B)_A$$

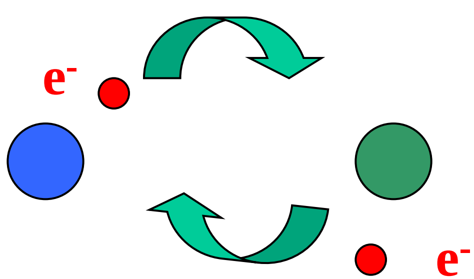
Isotropic (Heisenberg) $J = 1/3\,\mathrm{Tr}(\mathbf{J})$

Anisotropic (traceless matrix)

Antisymmetric (Dzyaloshinsky-Moriya)



Favours AF interaction



Favours F interaction

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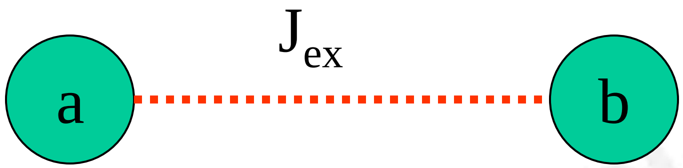
Isotropic Exchange in a pair



$H = J_{ex}\underline{\mathbf{S}}_a\underline{\mathbf{S}}_b$

$\underline{S} = \underline{S}_a + \underline{S}_b$

$\underline{S}^2 = (\underline{S}_a + \underline{S}_b)^2 = \underline{S}_a^2 + \underline{S}_b^2 + 2\underline{S}_a\,\underline{S}_b$

$\underline{S}_a\,\underline{S}_b = ½(\underline{S}^2 - \underline{S}_a^2 - \underline{S}_b^2)$

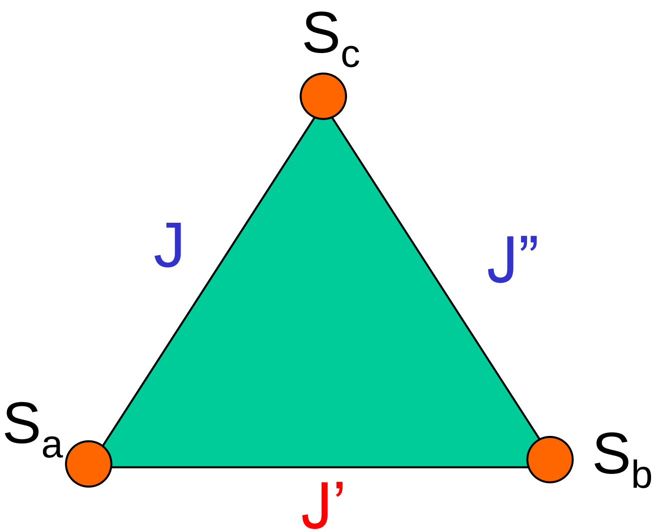
$H = J_{ex}/2(\underline{S}^2 - \underline{S}_a^2 - \underline{S}_b^2)$

$E(S, S_a, S_b) = J_{ex}/2(S(S+1) - S_a(S_a+1) - S_b(S_b+1))$

Lande's rule for the intervals: E(S) - E(S-1) = JS

$$\chi_M = 1/3\,\frac{N\mu_B^2 g^2}{kT}\,\frac{\Sigma_S S(S+1)(2S+1)\exp(-E(S)/kT)}{\Sigma_S (2S+1)\exp(-E(S)/kT)}$$

Beyond the pair of spins



$$\mathcal{H} = \sum_{i,j>l}^{N} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j$$

1) **St**^{2} commutes with $\mathcal{H}$,

2) **S**tz commutes with $\mathcal{H}$,

3) In zero field and zero anisotropy each St state is (2St+1) degenerate

4) The base is defined by n-1 intermediate spin states plus St

e. g. : |Sa,Sb,Sc,Sab,St,M>

5) $\mathcal{H}$ does not commute with intermediate spin states (e.g. Sab)

$\mathcal{H}$ =J**S**a•**S**c+J’**S**a•**S**b+J”**S**b•**S**c

St=(**S**a+**S**b)+**S**c=**S**a+(**S**b+**S**c)=
=(**S**a+**S**c)+**S**b

Magnetic anisotropy in molecular materials

The magnetic anisotropy is mainly associated to the asymmetry of the crystal field

$$\mathcal{H}_{\mathrm{CF}} = \sum_{N,k} B_N^k \mathbf{O}_N^k$$

with $N = 2, 4, 6, \ldots, 2S.$
and $-N \leq k \leq +N$

Stevens operators

The O_n^m operators are defined as:

$$O_2^0 = 3S_z^2 - s(s+1)$$

$$O_2^2 = \frac{1}{2}(S_+^2 + S_-^2)$$

$$O_4^0 = 35S_z^4 - [30s(s+1) - 25]S_z^2 + 3s^2(s+1)^2 - 6s(s+1)$$

$$O_4^2 = \frac{1}{4}[7S_z^2 - s(s+1) - 5](S_+^2 + S_-^2) + \frac{1}{4}(S_+^2 + S_-^2)[7S_z^2 - s(s+1) - 5]$$

$$O_4^3 = \frac{1}{4}S_z(S_+^3 + S_-^3) + \frac{1}{4}(S_+^3 + S_-^3)S_z$$

$$O_4^4 = \frac{1}{2}(S_+^4 + S_-^4).$$

Alternative notations commonly used

$$\mathcal{H}_{\rm CF} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \quad = D_{xx}S_x^2 + D_{yy}S_y^2 + D_{zz}S_z^2$$

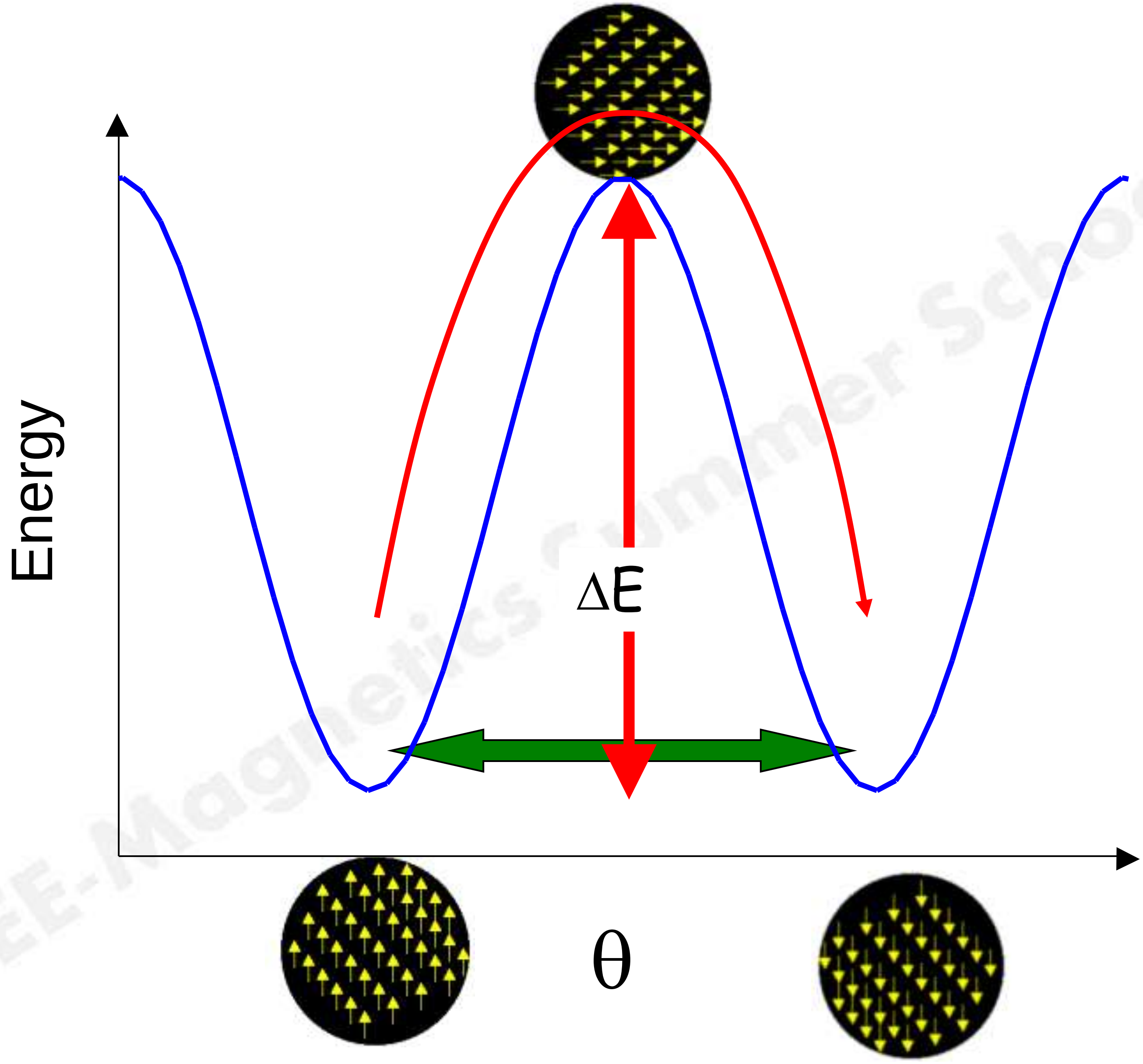
$$D = D_{zz} - \frac{1}{2}D_{xx} - \frac{1}{2}D_{yy}; E = \frac{1}{2}(D_{xx} - D_{yy}).$$

$$\mathcal{H}_{\rm CF} = D\left[S_z^2 - \frac{1}{3}S(S+1)\right] + E(S_x^2 - S_y^2).$$ with $-1/3 \leq E/D \leq +1/3.$

$$\mathcal{H}_{\rm CF} = -D'S_z^2 + BS_x^2$$

with $\breve{B} = 2E$ and $D' = -(D + B/2)$

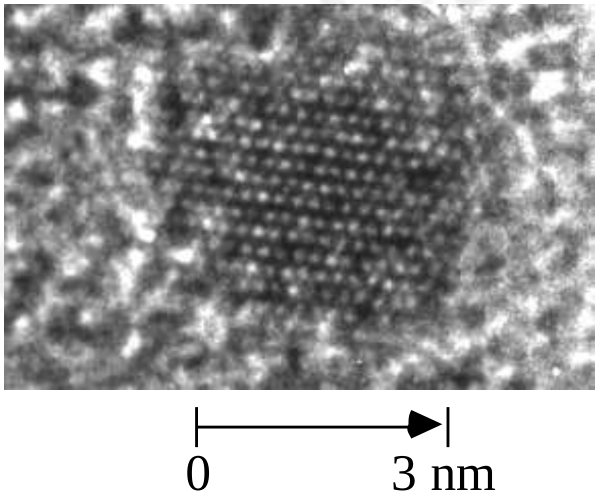
Single Domain Nanoparticles



Quantum Tunneling of Magnetization

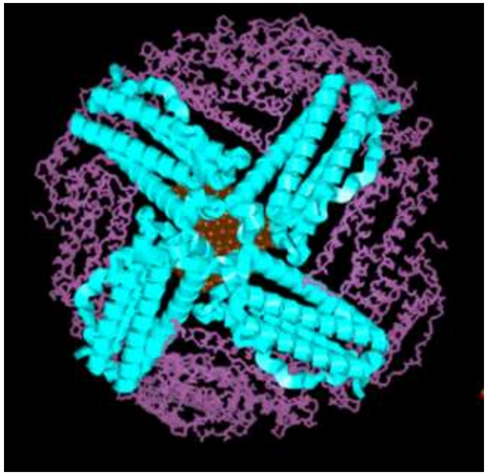
- First evidences of Quantum Tunneling in nanosized magnetic particles

  (difficulties due to size distribution)



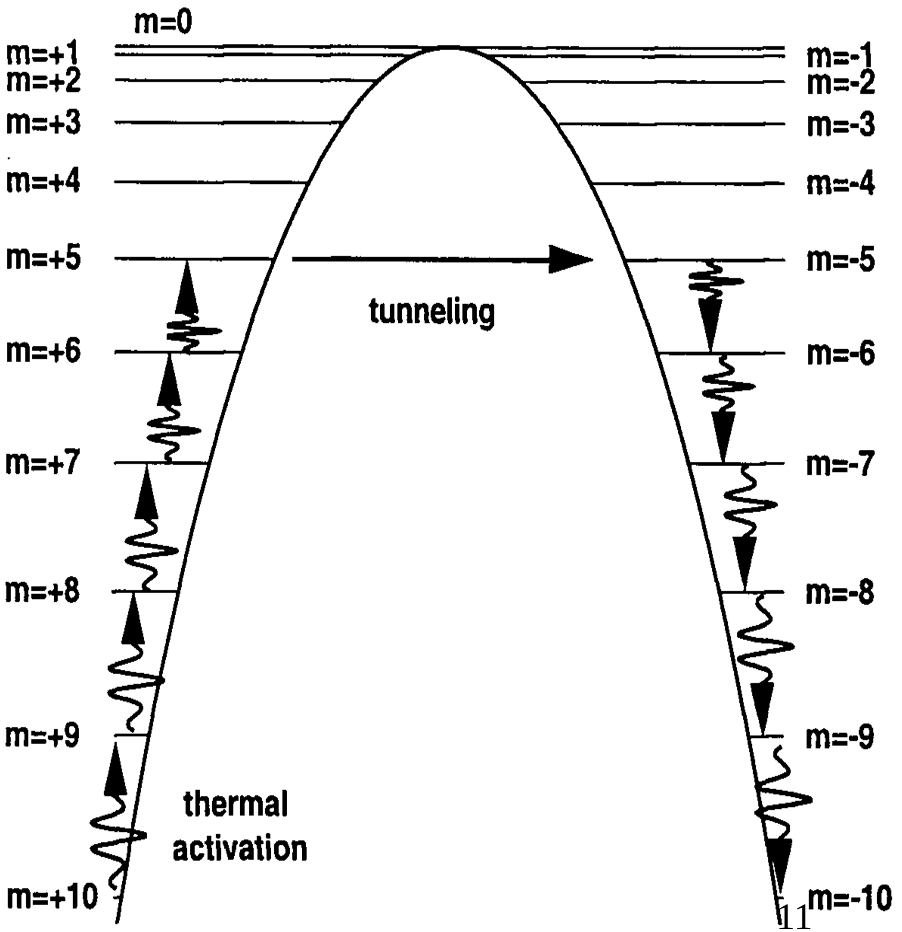
- Quantum Coherence in ferrihydrite confined in the ferritin mammalian protein

  (inconclusive due to distribution of iron load)



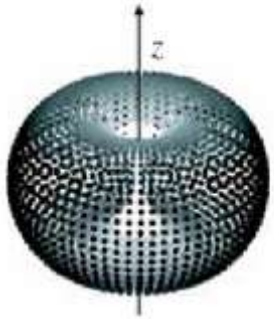
Reducing further the size …

- The continuum of levels within the potential wells breaks down and quantum size effects, like tunneling, are observed: this is the exciting region for new properties



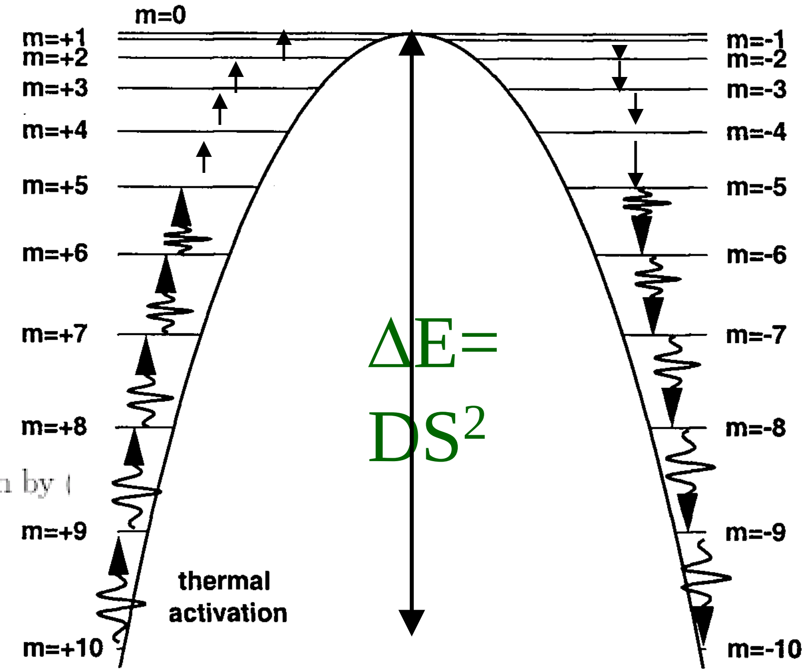
Single Molecule Magnets

$$\mathcal{H}_{\rm an} = DS_z^2$$



$$S_z \mid m\rangle = m \mid m\rangle$$

$$E_m = -|D|m^2$$



At equilibrium, the probability p_m^0 that the spin is in state $|m\rangle$ is given by

$$p_m^0 = (1/Z)\exp[-\beta(E_m)]$$

Intuitively, it may be expected that the relaxation rate $1/\tau$ is proportional to the probability to be at the top of the barrier.

$$1/\tau = (1/\tau_0)p_0^0 = (1/Z)(1/\tau_0)\exp(-\beta E_0) \approx$$

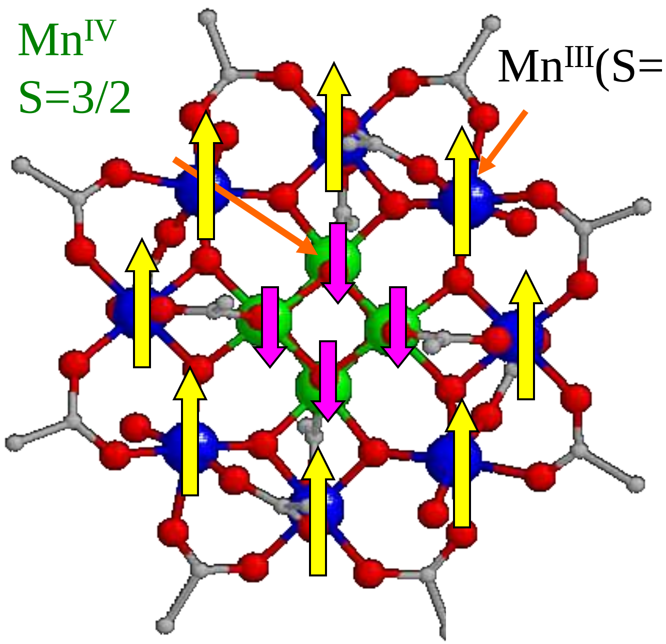
$$\approx (1/\tau_0)\exp[-\beta(E_0 - E_s)] \approx (1/\tau_0)\exp(-\beta|D|s^2)$$

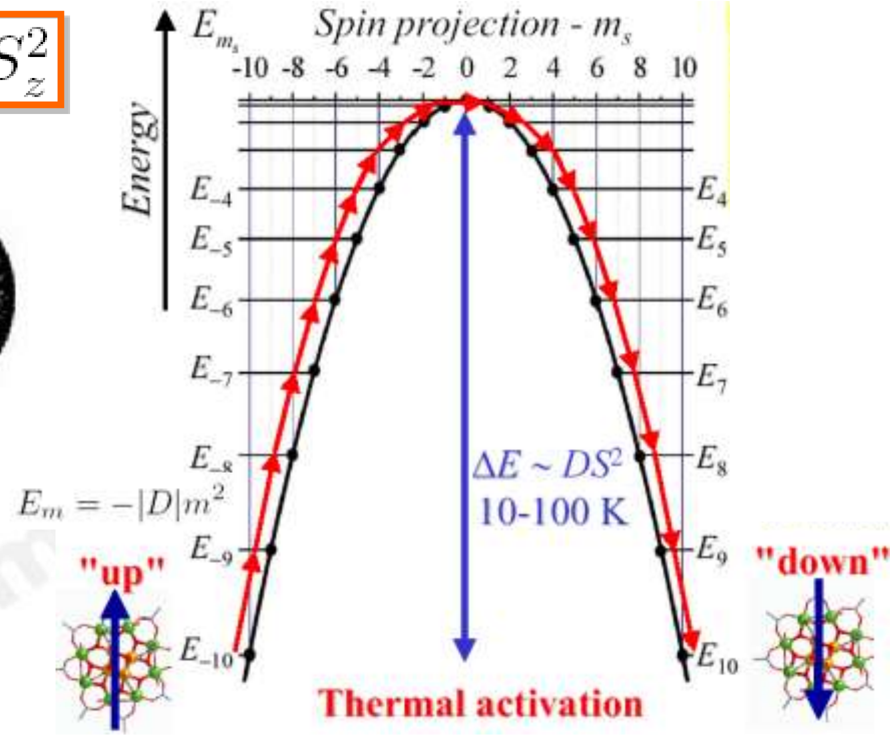
$$\tau=\tau_0\exp(\Delta E/k_BT)$$

Single Molecule Magnets: a school of physics

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

$$\mathcal{H}_{an} = DS_z^2$$

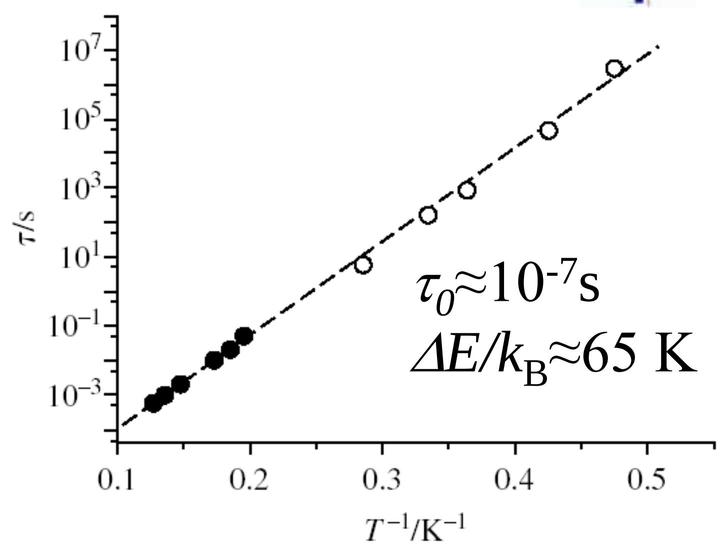




$\tau = \tau_0 \exp(\Delta E/k_B T)$

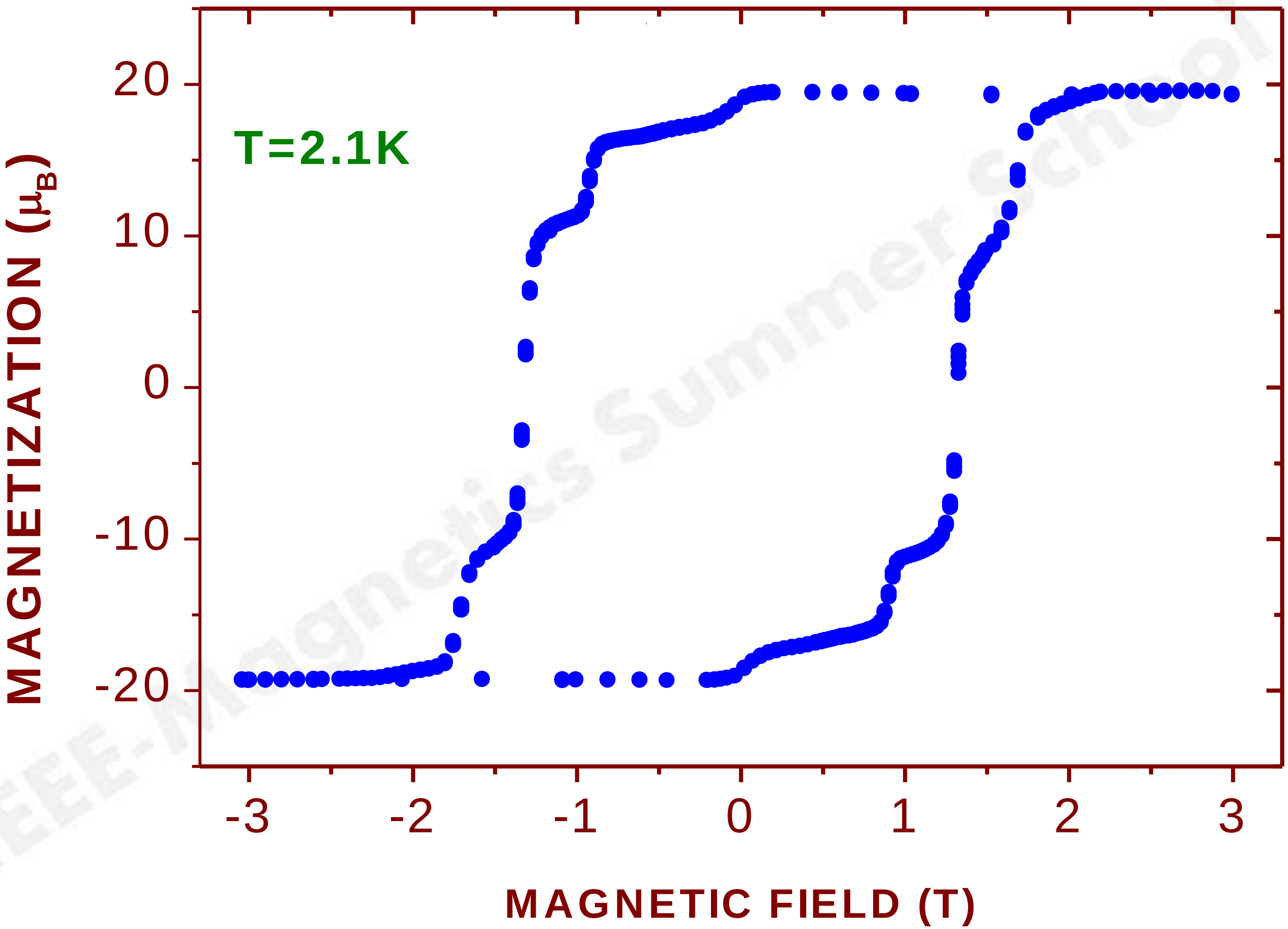
$S_{tot}=10$

$D\approx$-0.7 K



Sessoli et al. Nature 1993

Hysteresis loop of molecular origin



Master equation and transition probability

The time evolution of the population of the |m> state is given by:

$$\frac{d}{dt}p_m(t) = \sum_q \left[\gamma_q^m p_q(t) - \gamma_m^q p_m(t)\right]$$

Where γ are the transition probabilities independent from each other (Markov process) And are related to spin-phonon interactions.

A trivial solution is that at equilibrium: $p_m^0 = (1/Z)\exp(-\beta E_m)$

$$\sum_q \left[\gamma_q^m p_q^0 - \gamma_m^q p_m^0\right] = 0$$

The detailed balance principle tell us that also each term of the sum vanishes at equilibrium $\gamma_m^{m'} p_m^0 = \gamma_{m'}^m p_{m'}^0$

$$\gamma_m^{m'}/\gamma_{m'}^m = p_{m'}^0/p_m^0 = \exp[\beta(E_m - E_{m'}]$$

Solution of the master equation

In a more general case (biaxial anisotropy, transverse field)

$$| m^* \rangle = \sum_{m'} \varphi_{m'}^{(m)} | m' \rangle$$

With *k*=0,1, 2..,2s.
The population of each state varies exponentially:

$$p_m(t) = \varphi_m^{(k)} \exp(-t/\tau_k)$$

And substituting in $\frac{d}{dt} p_m(t) = \sum_q \left[\gamma_q^m p_q(t) - \gamma_m^q p_m(t) \right]$

$$\frac{1}{\tau_k} \varphi_m^{(k)} = \sum_q \left[\gamma_q^m \varphi_q^{(k)} - \gamma_m^q \varphi_m^{(k)} \right] = \sum_q \left[\gamma_q^m - \delta_q^m \sum_{q'} \gamma_m^{q'} \right] \varphi_q^{(k)}$$

where the Kronecker symbol δ_q^m (=1 if $q = m$, while $\delta_q^m = 0$ if $q \neq m$) has been introduced.

The Master matrix

$$\frac{d\vec{N}}{dt} = \tilde{\Gamma}\vec{N}$$

$$\Gamma_q^m = \gamma_q^m - \delta_q^m \sum_{m'} \gamma_{m'}^m$$

$$\tilde{\Gamma} = \begin{pmatrix} -\sum_{m'\neq 1}\gamma_1^{m'} & \gamma_2^1 & \cdot & \cdot & \gamma_{2s+1}^1 \\ \gamma_1^2 & -\sum_{m'\neq 2}\gamma_2^{m'} & \cdot & \cdot & \gamma_{2s+1}^2 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \gamma_1^{2s+1} & \gamma_2^{2s+1} & \cdot & \cdot & -\sum_{m'\neq s}\gamma_{2s+1}^{m'} \end{pmatrix} \qquad \vec{N} = \begin{pmatrix} N_1 \\ N_2 \\ \cdot \\ \cdot \\ N_{2S+1} \end{pmatrix}$$

There are 2s+1 solution of $(\det\Gamma-\lambda)=0$

One solution is $\lambda=0$, corresponding to $\tau=\infty$ (the equilibrium)

The relaxation rate at low temperature is

$$\tau = \max_{\lambda_i\neq 0}\left\{-\frac{1}{\lambda_i}\right\}$$

Transition probabilities

The allowed transitions for spin-phonon coupling have

|m-m'|=1,2

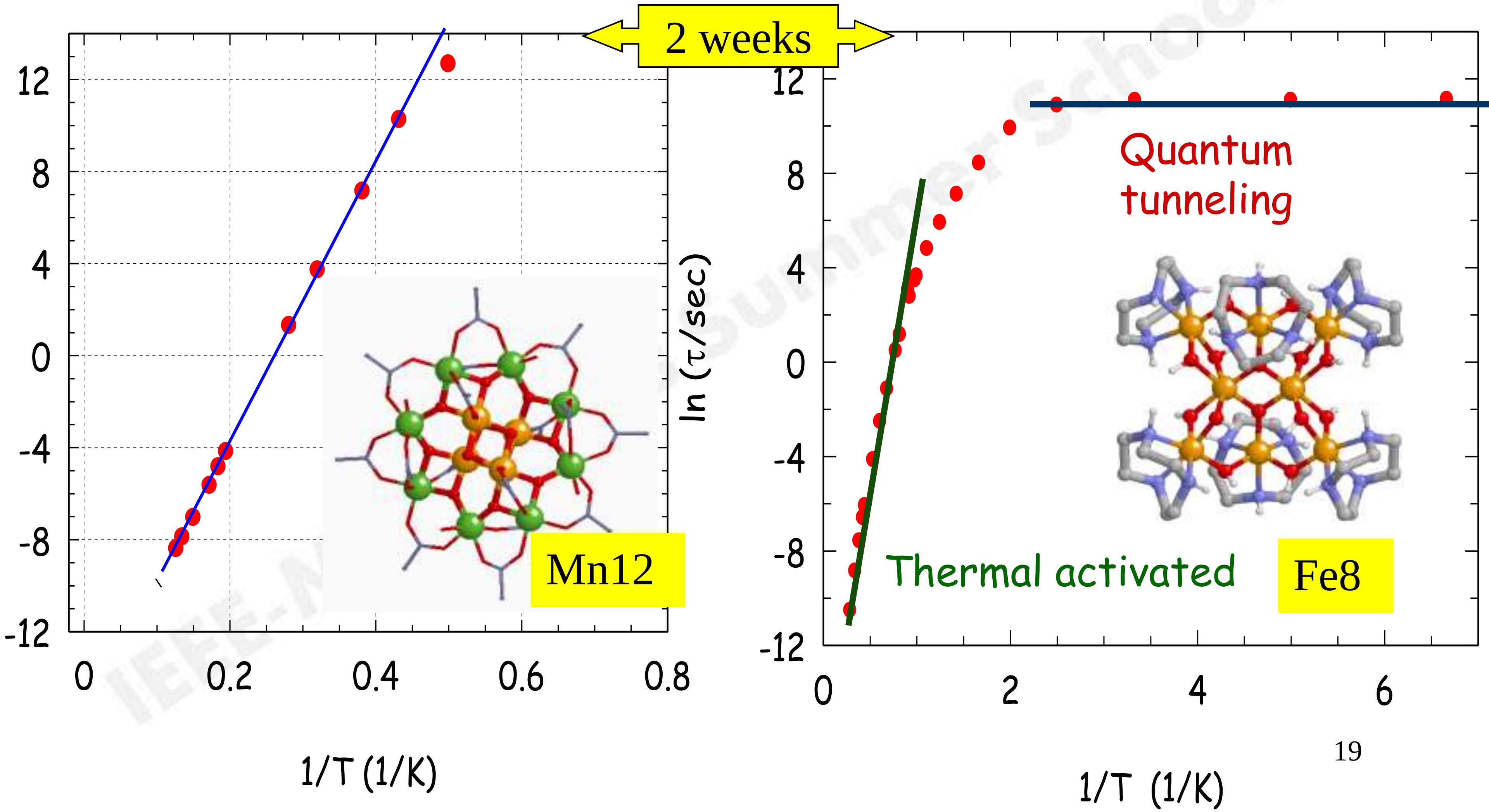
$$\gamma_m^p = \frac{3}{2\pi\rho\hbar^4 c^5}\frac{\left(E_p - E_m\right)^3}{e^{\beta(E_p - E_m)}-1}\left\{g_a\left[\left(S_+^2\right)_{mp}^2 + \left(S_-^2\right)_{mp}^2\right] + g_b\left[\left(\{S_+, S_z\}\right)_{mp}^2 + \left(\{S_-, S_z\}\right)_{mp}^2\right]\right\}$$

When (E_m-E_p) is small (which also corresponds to the top of the barrier) the transition probability is small because of the factor $(E_m - E_p)^3$, which mainly reflects the fact that there are few phonon states of very low energy.

$$\tau = \tau_0 \exp(\Delta E / k_B T)$$

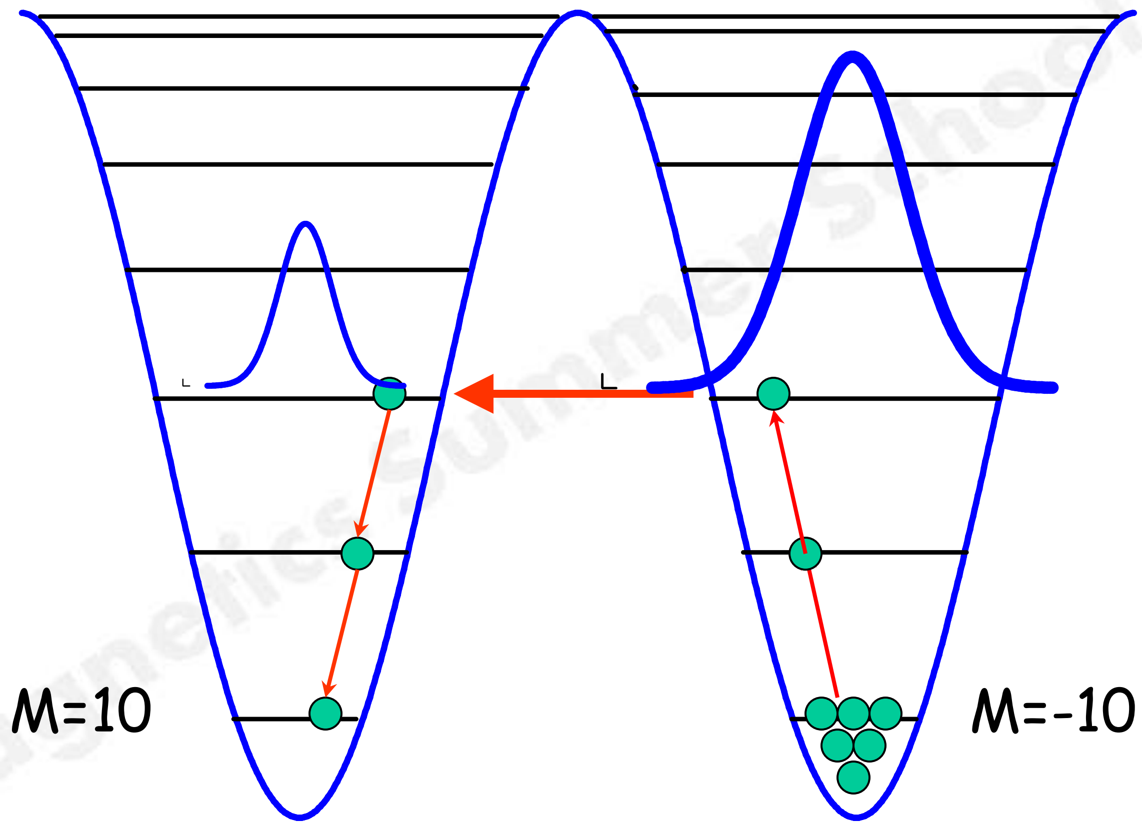
$$\tau_0(\mathrm{SMM}) > \tau_0(\mathrm{MNP})$$

Low temperature dynamics

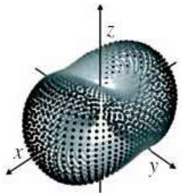


Tunnel mechanism & return to equilibrium

H=0



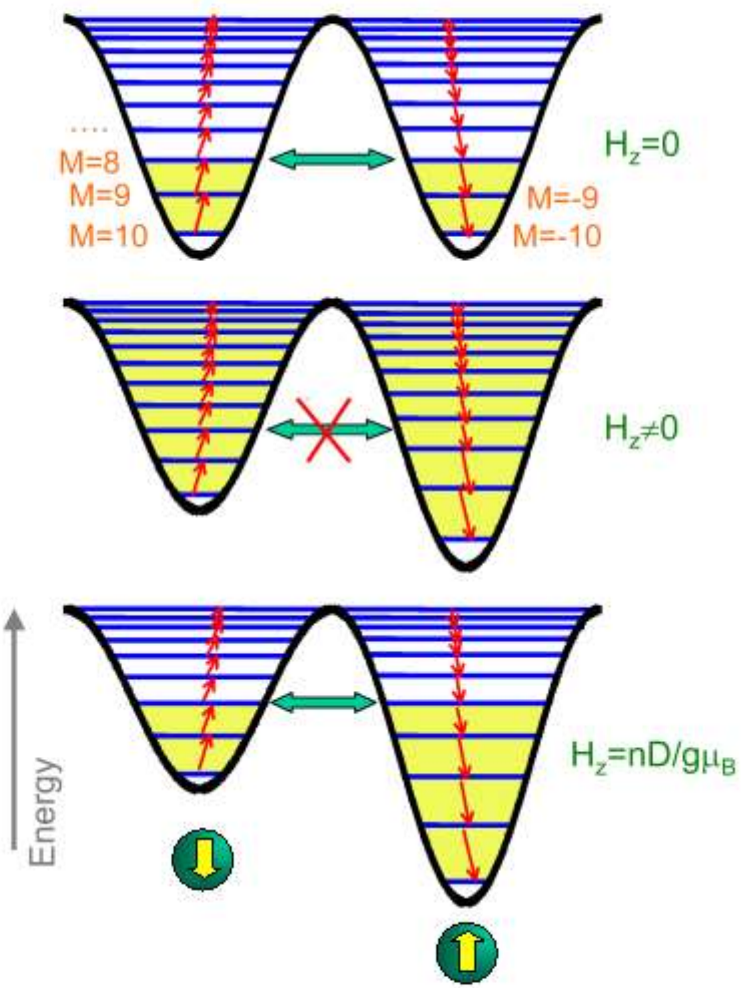
Resonant Quantum Tunneling of the Magnetization

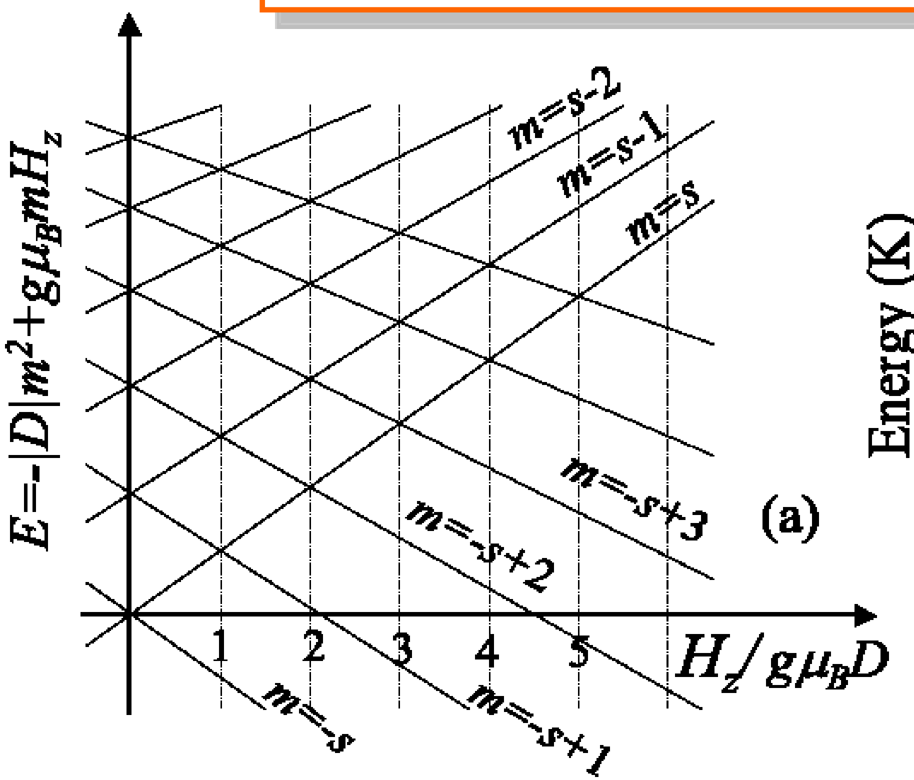


$$\mathcal{H}_{\mathrm{CF}} = DS_z^2 + E(S_x^2 - S_y^2)$$

$$E_m^{(0)} - E_{m'}^{(0)} = 0$$

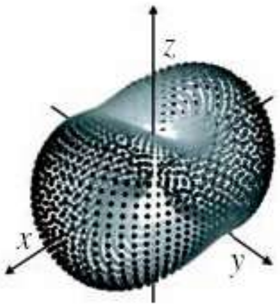
$$g\mu_B H^{(mm')} = |D|(m + m')$$

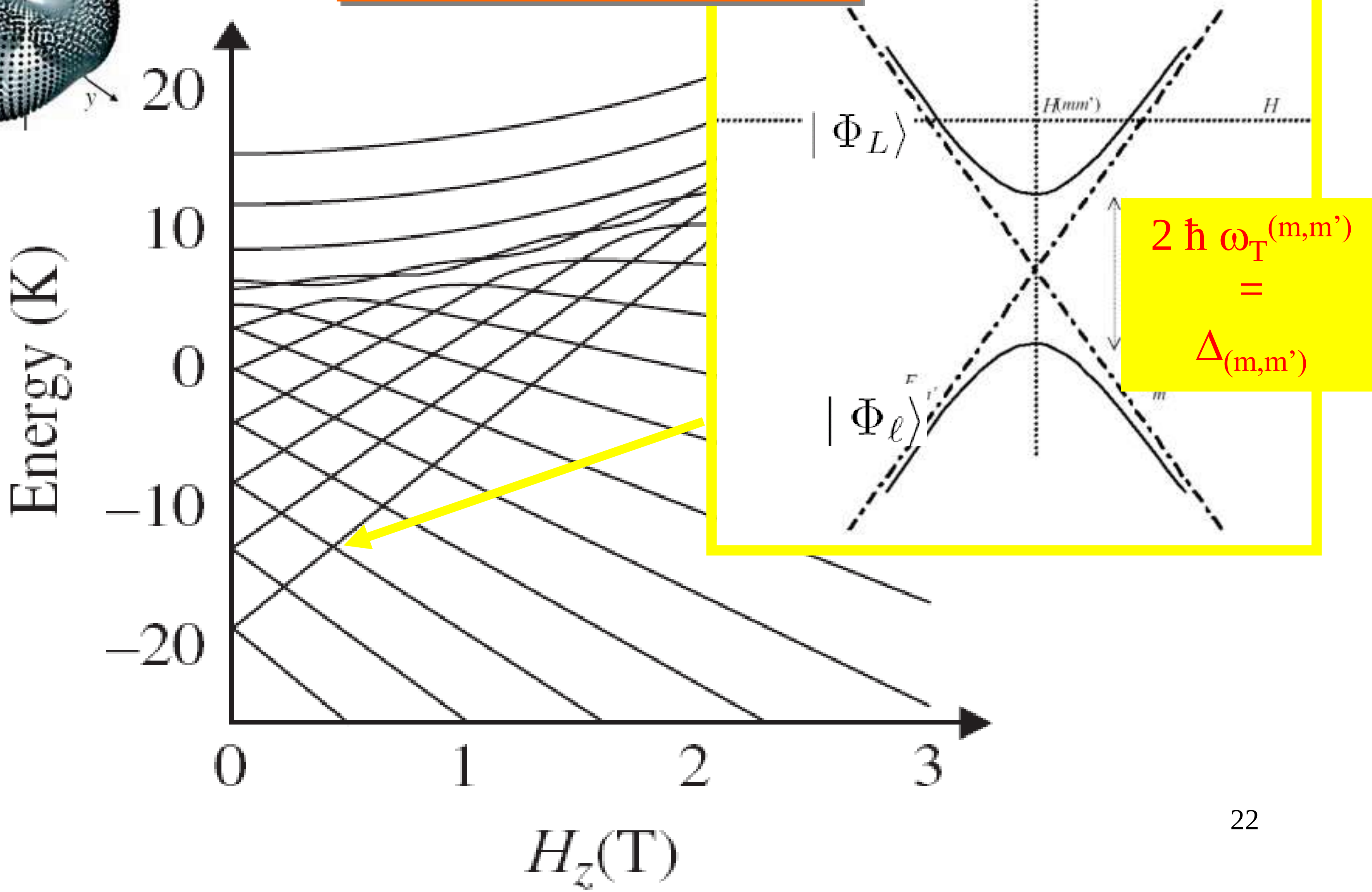




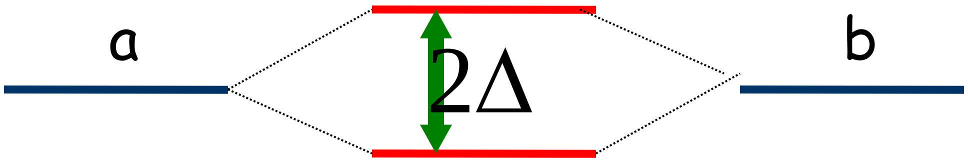
Resonant Quantum Tunneling of the Magnetization

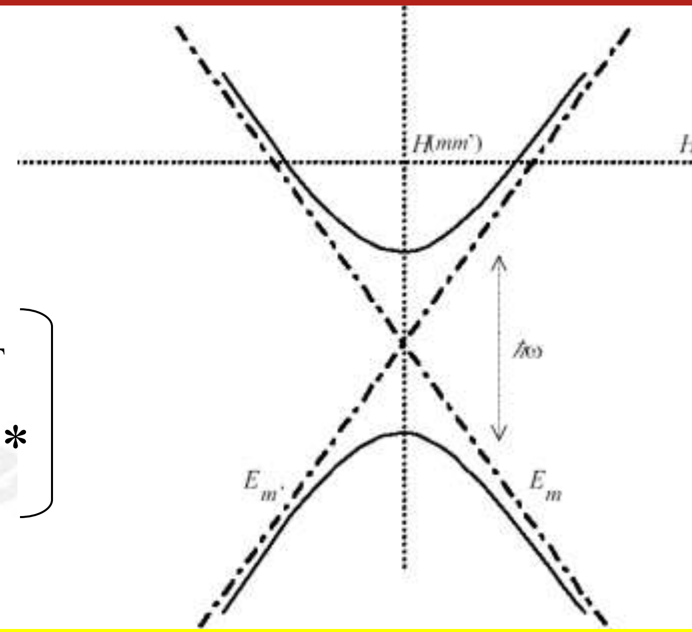
$$\mathcal{H}_{CF} = DS_z^2 + E(S_x^2 - S_y^2)$$





Two levels description





Diagonal terms $\propto S_z$

Out of diagonal terms $\propto S_{x,y}$

$$\begin{pmatrix} Em^* & \hbar\omega_T \\ \hbar\omega_T & Em'^* \end{pmatrix}$$

$$\Delta = \frac{\langle m^* | \mathcal{H} | m^* \rangle - \langle m'^* | \mathcal{H} | m'^* \rangle}{2} \approx g\mu_B (m - m')\delta H_z/2$$

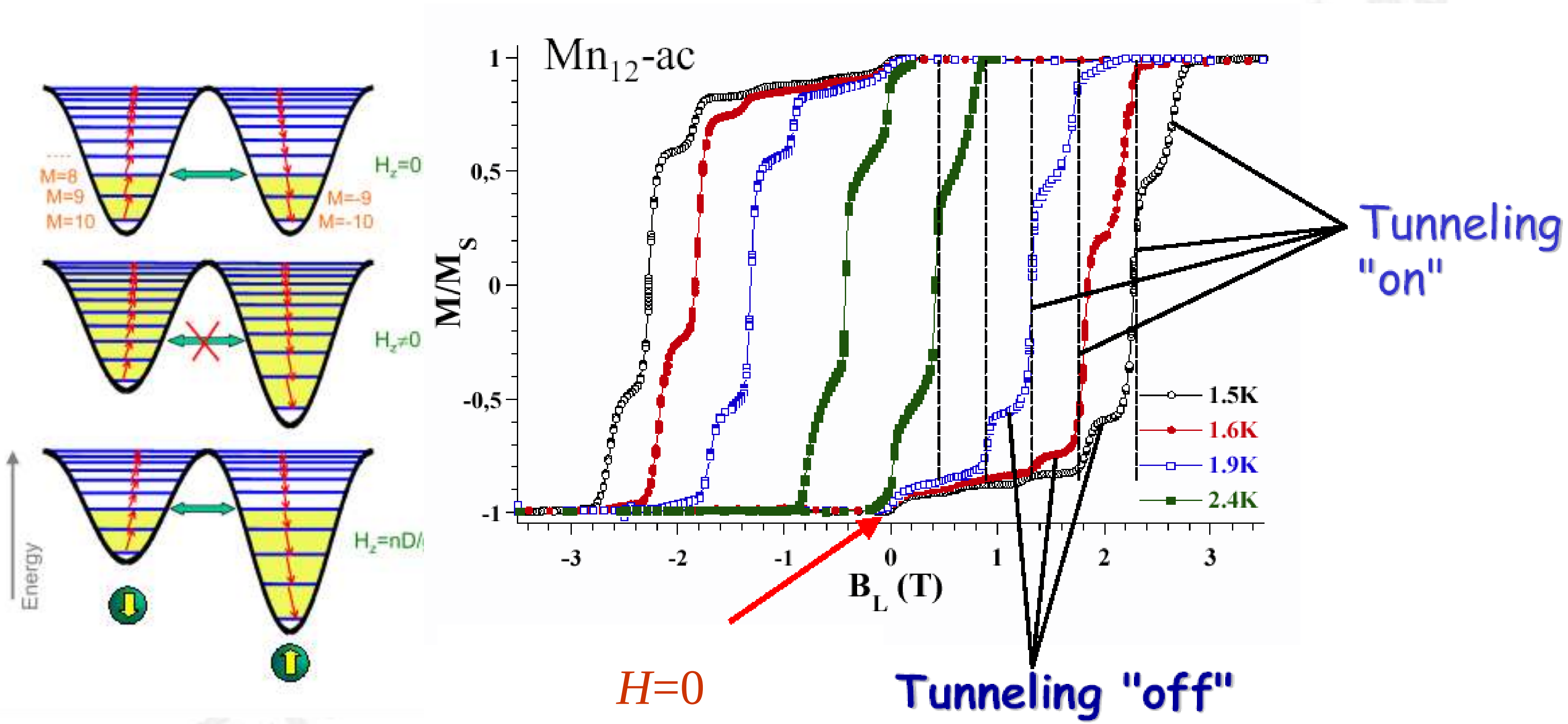
$$\delta E = \pm\sqrt{\Delta^2 + \hbar^2\omega_T^2}$$

$$|\,\Phi_\ell\rangle = |\,m^*\rangle \cos\phi + |\,m'^*\rangle \sin\phi$$

$$|\,\Phi_L\rangle = -|\,m^*\rangle \sin\phi + |\,m'^*\rangle \cos\phi$$

$$|\tan\phi| = \frac{\hbar\omega_T}{|\delta E - \Delta|}$$

Resonant Quantum Tunneling of the Magnetization



Thomas et al., *Nature 1996*
Friedman et al., *PRL 1996*

Classical anisotropy potential

Axial Rhombic Tetragonal

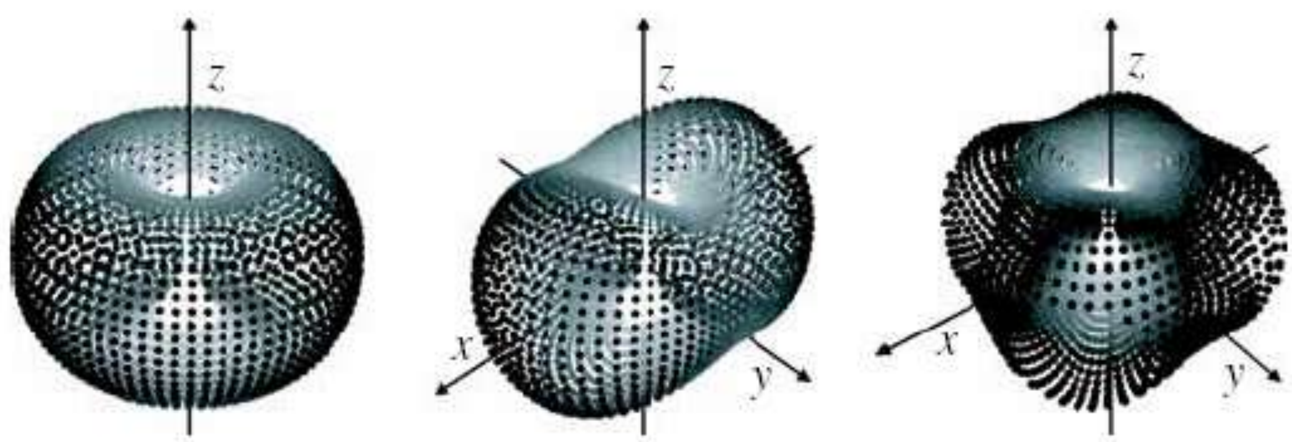


FIG. 2.2. The distance of the surface from the origin represents the classical potential energy of a spin experiencing a uniaxial crystal field with negative D (left), the same including a transverse second-order term (middle), or a transverse fourth-order term (right).

$$\mathcal{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + \ldots\ldots\ldots$$

Tunneling and symmetry

$$\mathcal{H} = \mathcal{H}_0 + \delta\mathcal{H} \qquad \mathcal{H}_0 = -|D|S_z^2 + g\mu_B H_z$$

- Biaxial anisotropy (rhombic symmetry, x≠y ≠z)

$$\delta\mathcal{H} = (B/4)(S_+^2 + S_-^2)$$

$\langle m | \mathcal{H} | m' \rangle \neq 0$ only when |m-m'| is even

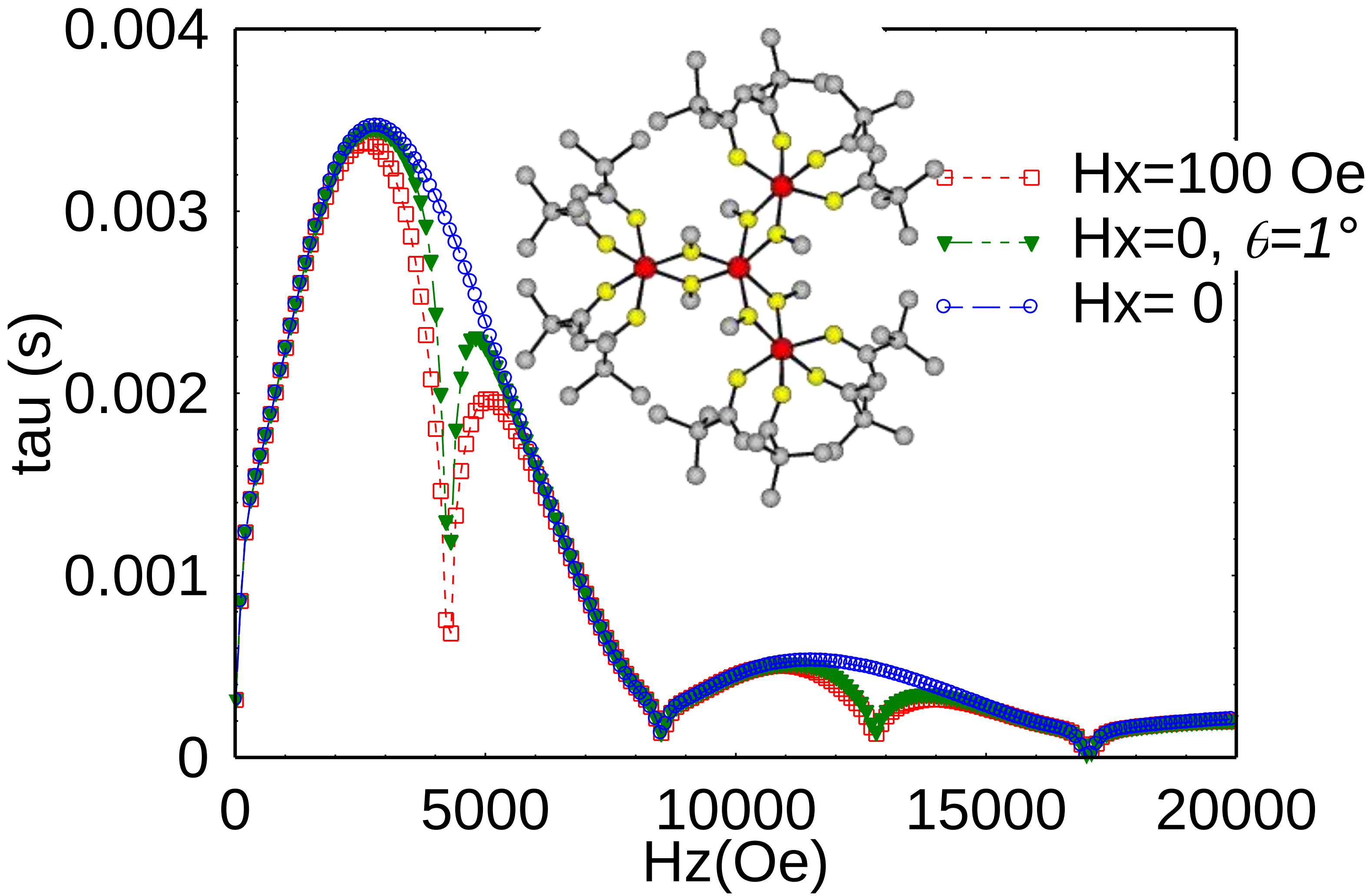
$$|\Psi\rangle = \sum_p \varphi(s-2p)\,|s-2p\rangle$$

$$|\Psi\rangle = \sum_p \varphi(s-2p-1)\,|s-2p-1\rangle$$

$$\boxed{m - m' = 2k}$$

Simulated relaxation time

Relaxatiom time for a Fe4 star: S=5 D=-0.4 cm^{-1} E=0.04



Tunneling and symmetry

$$\mathcal{H} = \mathcal{H}_0 + \delta\mathcal{H} \qquad \mathcal{H}_0 = -|D|S_z^2 + g\mu_B H_z$$

- Uniaxial symmetry (e.g. tetragonal symmetry, x=y ≠z)

$$\delta\mathcal{H} = C(S_+^4 + S_-^4)$$

$\langle m | \mathcal{H} | m' \rangle \neq 0$ only when |m-m'| is 4n

$$|\Psi\rangle = \sum_p \varphi(s - 4p)\,|\,s - 4p\rangle$$

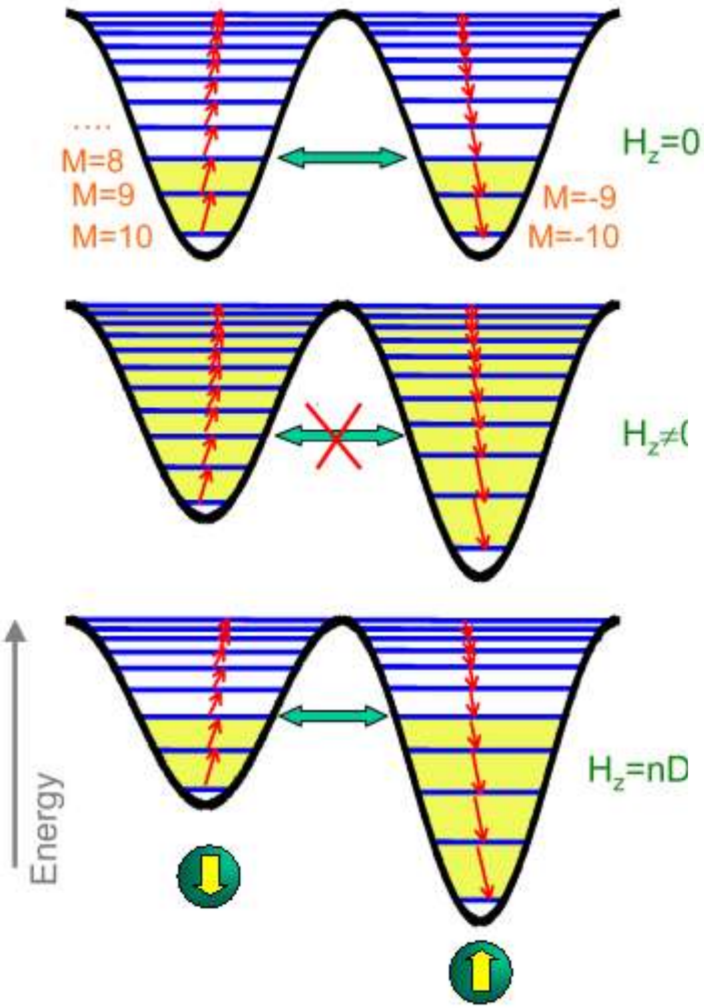
$$m - m' = 4k$$

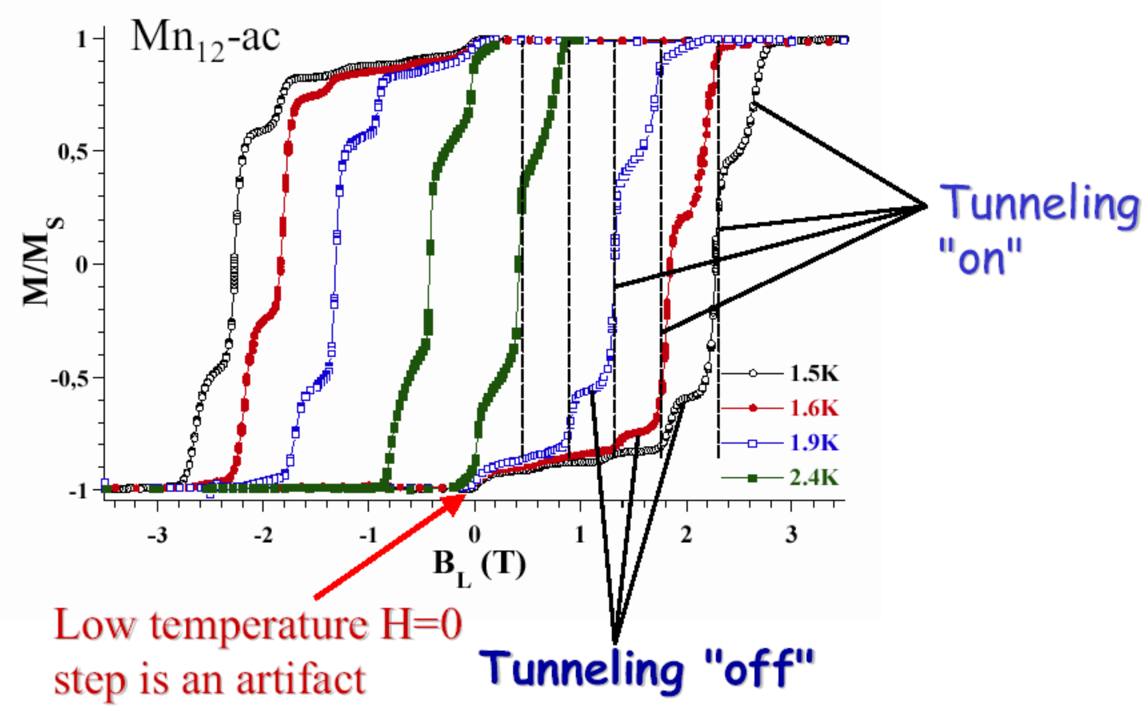
$$|\Psi\rangle = \sum_p \varphi(s - 4p - 1)\,|\,s - 4p - 1\rangle$$

For any symmetry tunneling in zero field is not allowed for an half-integer spin state

The Karmers' degeneracy

Relaxed selection rules





Thomas et al., *Nature 1996*
Friedman et al., *PRL 1996*

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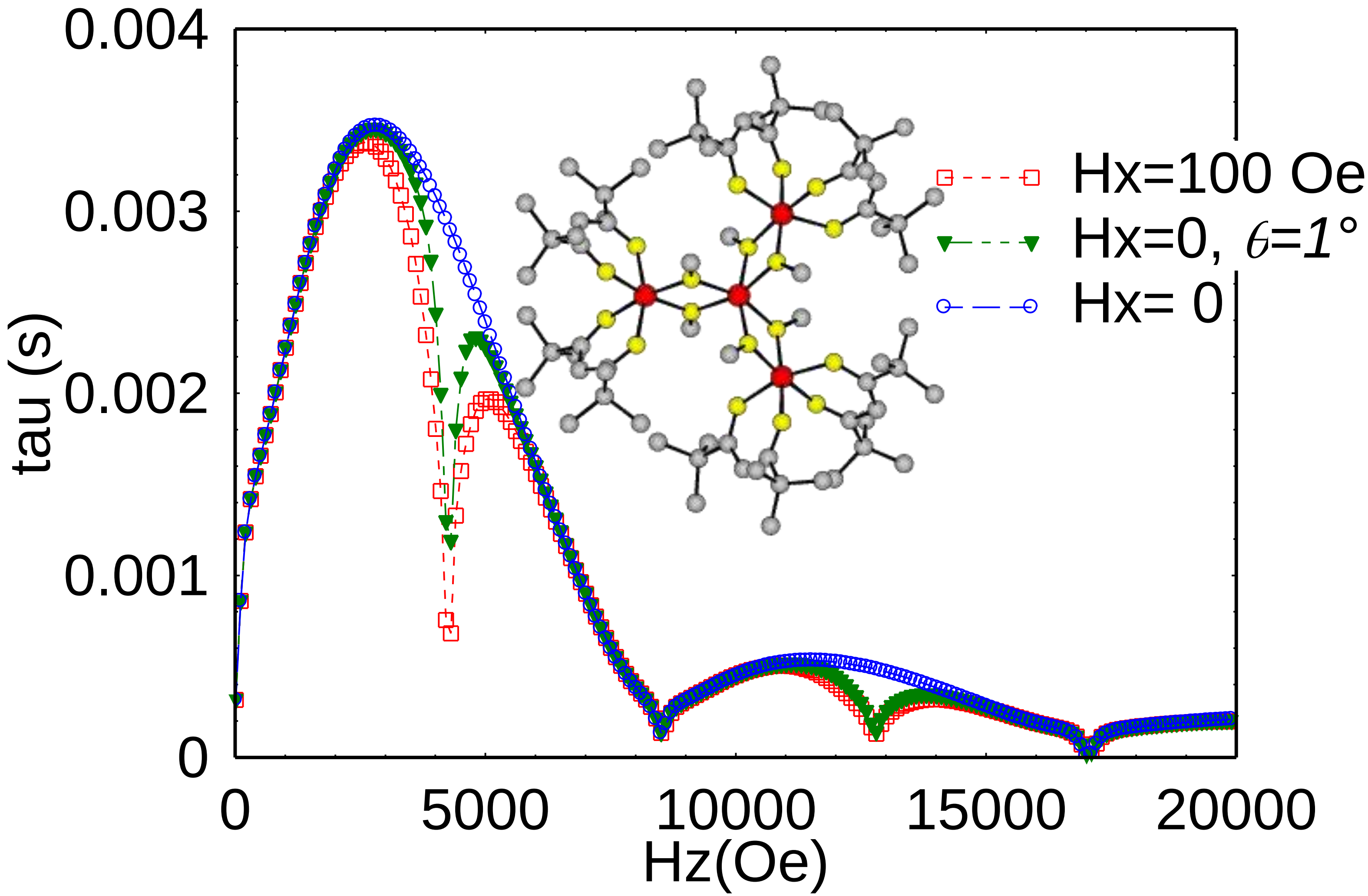
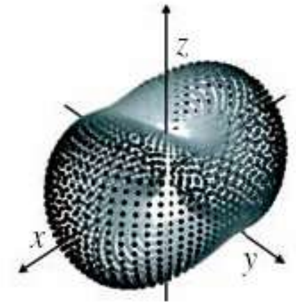
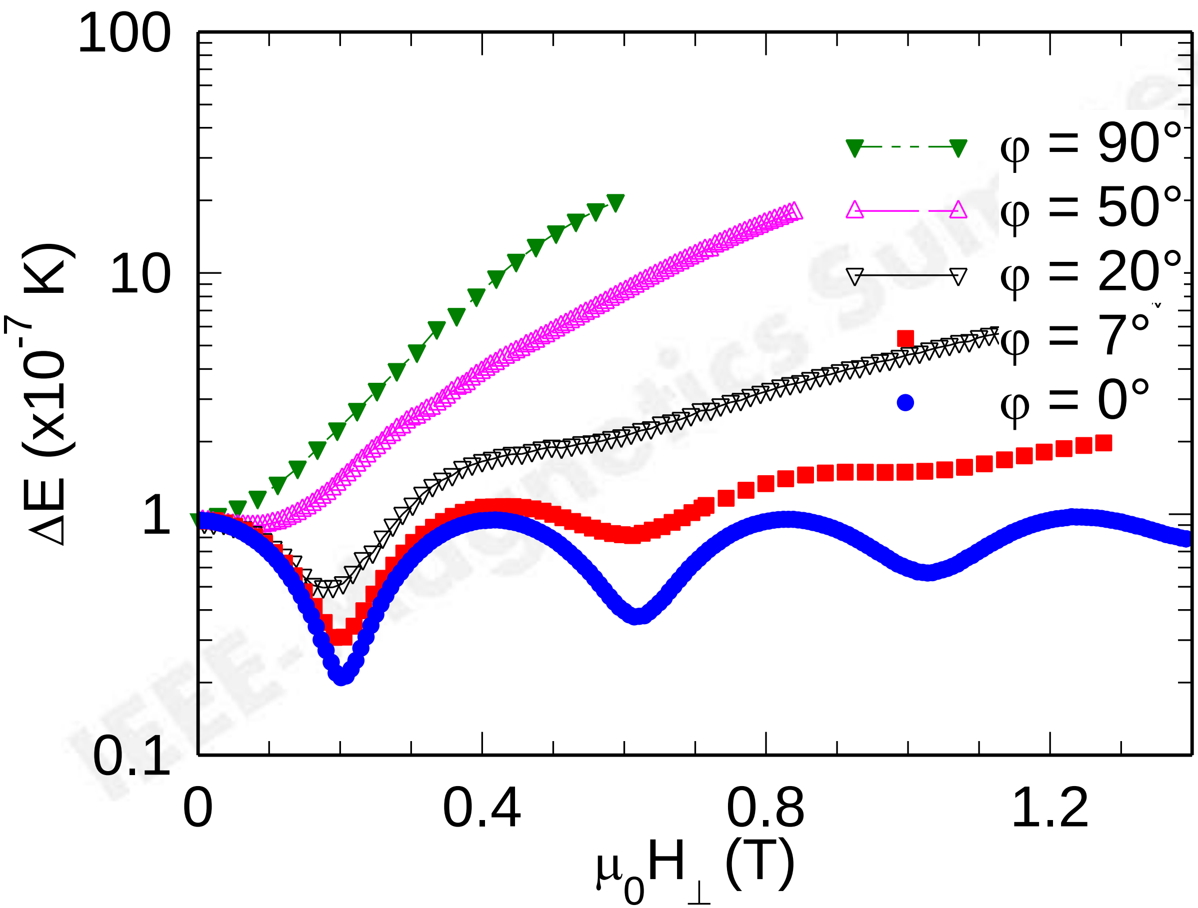


Transverse field dependence of the tunnel-splitting

Fe_8 SMM
biaxial symmetry





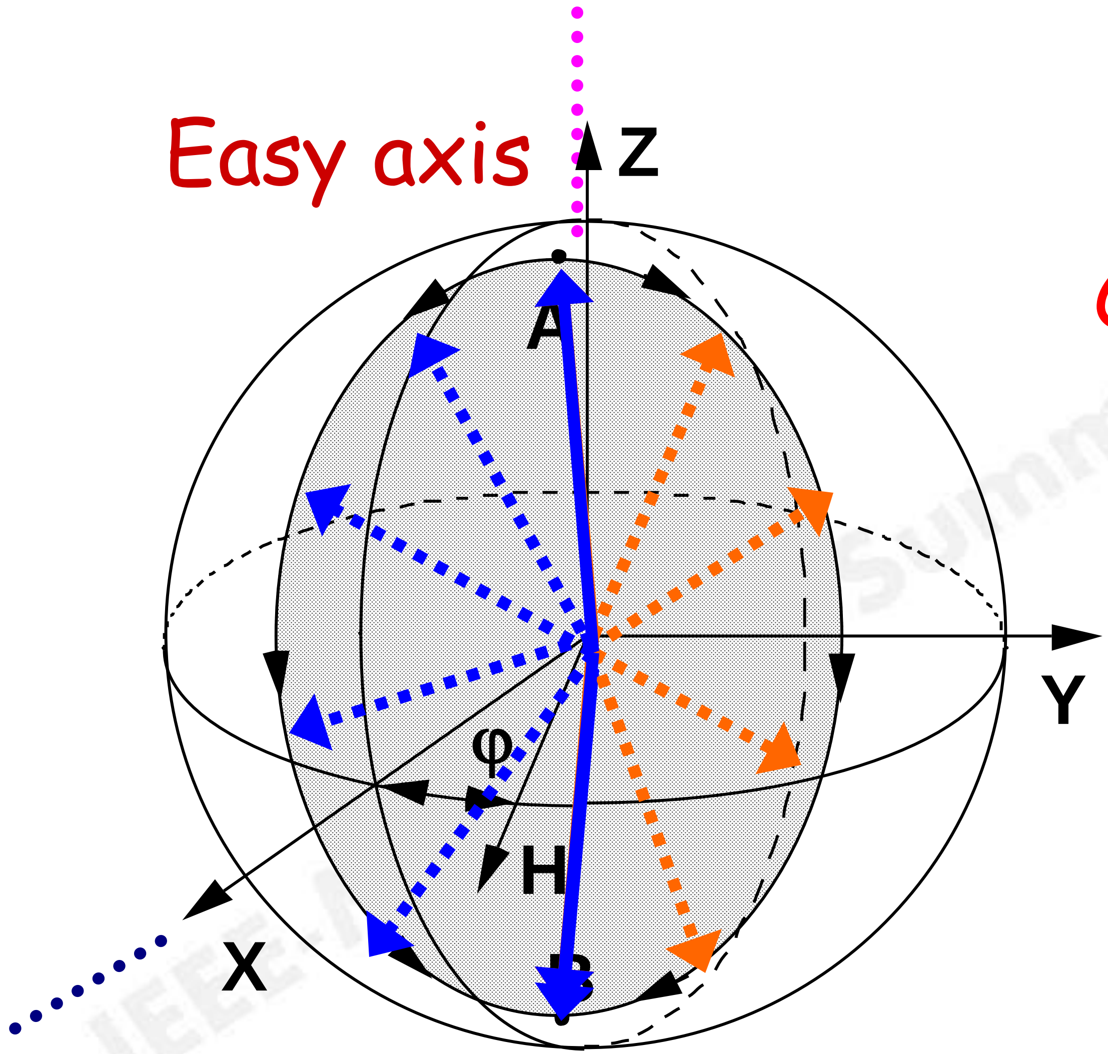
φ=90°

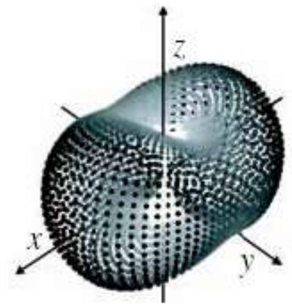
intermediate axis

φ=0°

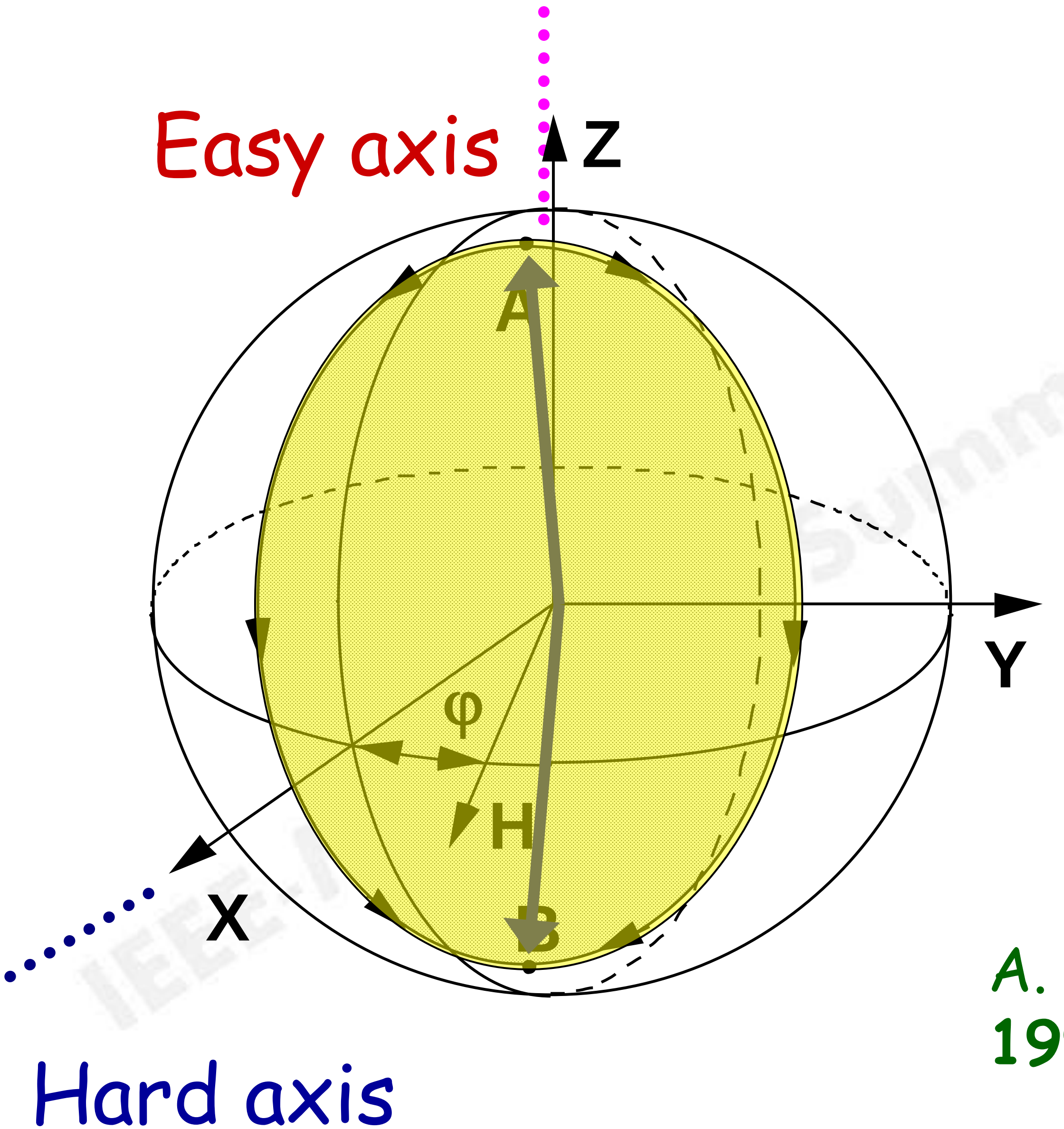
hard axis

A semiclassical picture





Destructive Topological Interferences



destructive if

$A=k\pi/S$ (k odd)

$\Delta H_x =$

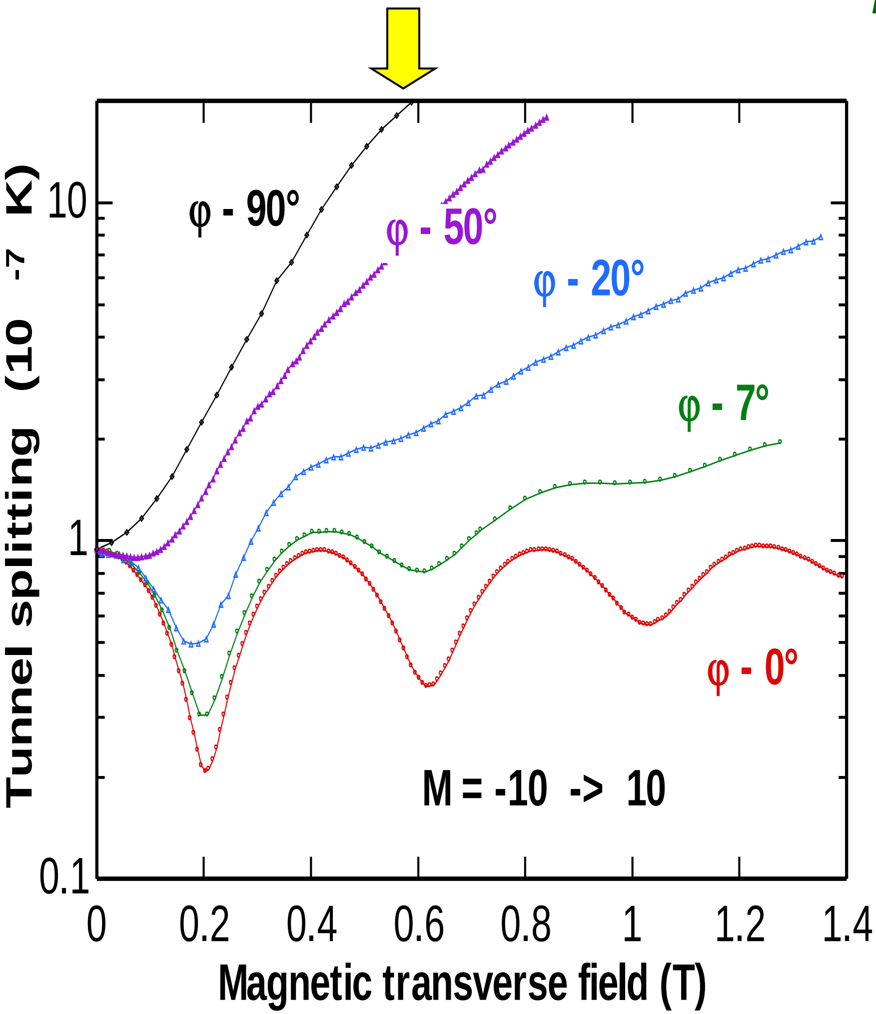
$2/g\mu_B\sqrt{2E(E-D)}$

A. Garg. *Europhys. Lett.* **1993**, *22*,205

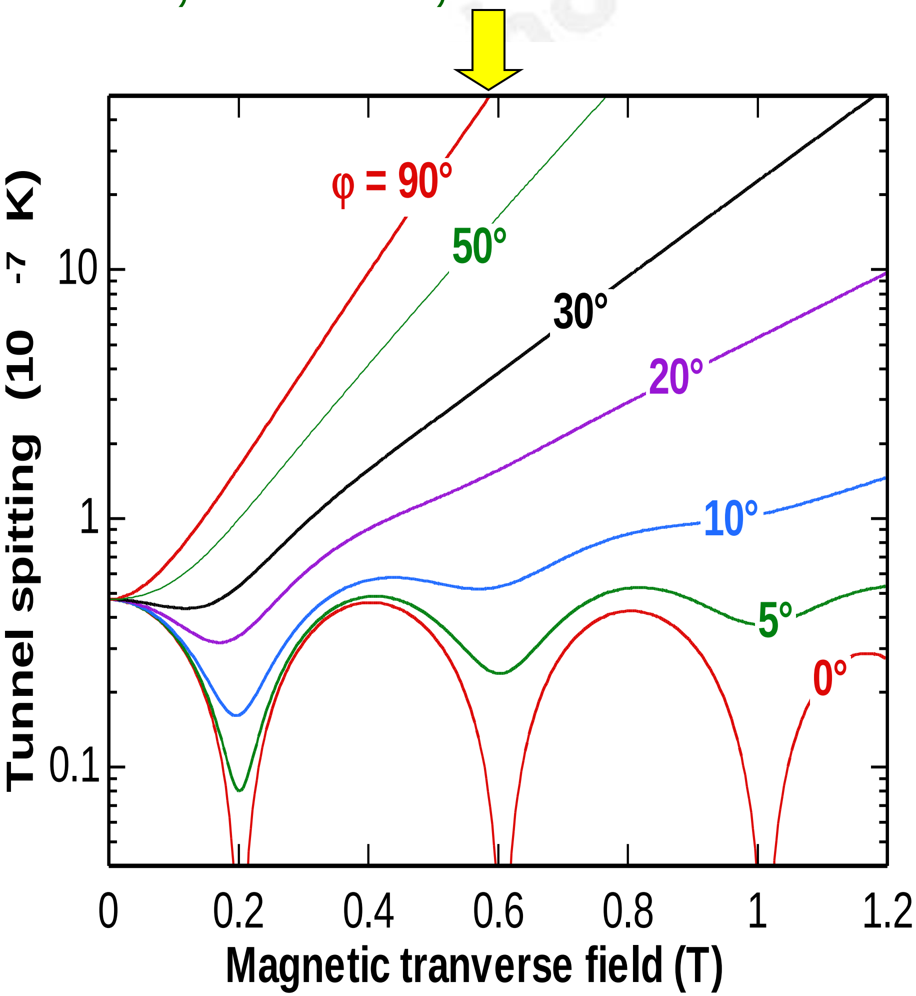
Destructive Topological Interferences

$$H = DS_z^2 + E(S_x^2 - S_y^2) + C\,(S_+^4 -+ S_-^4)$$

experimental

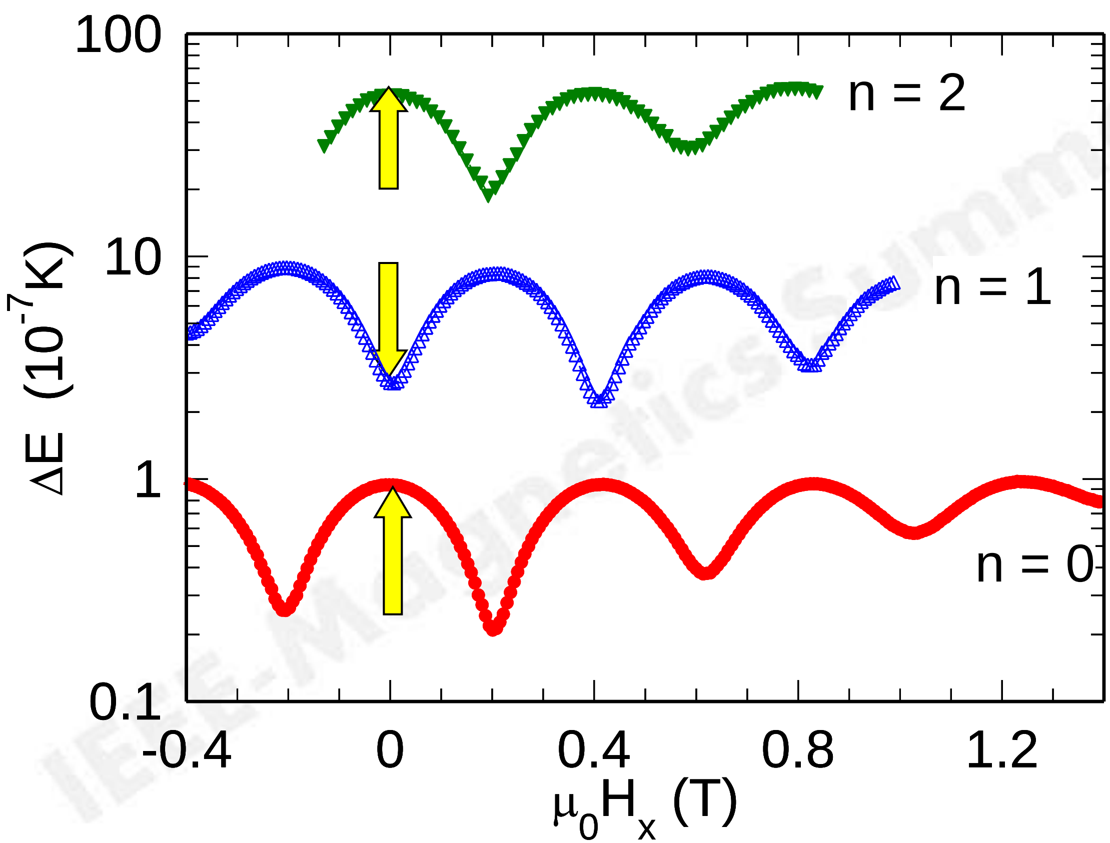


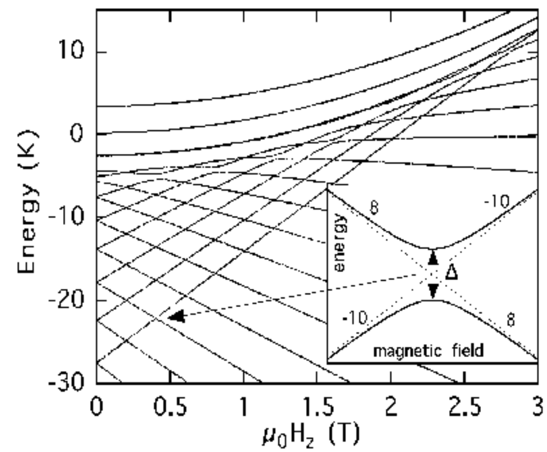
calculated with
D=-0.29,E=0.046,C=-2.9x10^{-5} K



Parity effect on the topological interference

Tunnel resonance $|m_s=10\rangle \leftrightarrow |m_s=-10+\mathbf{n}\rangle$

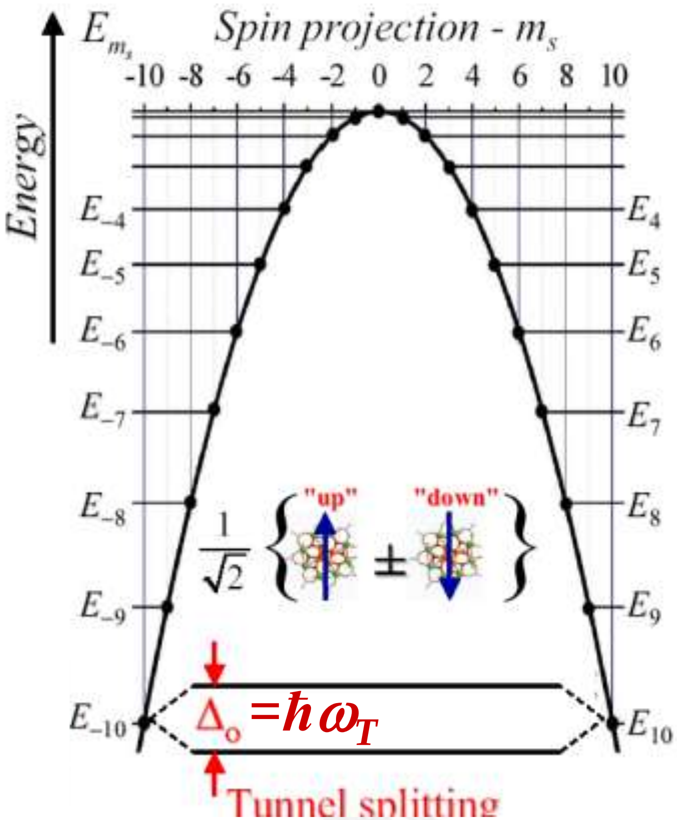




The effect of the transverse field is different for allowed and forbidden quantum resonances

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

Why high order Spin Hamiltonian terms are important ?



Tunnel splitting according to perturbation theory

$\mathcal{H} = \mathcal{H}_0 + \delta\mathcal{H}$ $\qquad$ $\mathcal{H}_0 = -|D|S_z^2 + g\mu_B H_z$

1. at order 2s if $\delta\mathcal{H}$ is H_x

$$\hbar\omega_T = 4|D|s^2\left(\frac{g\mu_B H_x}{2|D|}\right)^{2s}\frac{1}{(2s)!}$$

Zeeman

2. at order s if $\delta\mathcal{H} = (B/4)(S_+^2 + S_-^2)$

$$\hbar\omega_T = 4|D|s^2\left(\frac{B}{16|D|}\right)^{s}\frac{(2s)!}{(s!)^2}$$

2^{th} order

3. At order s/2 if $\delta\mathcal{H} = C(S_+^4 + S_-^4)$

$$\hbar\omega_T = 4|D|s^2\left(\frac{C}{16|D|}\right)^{s/2}\frac{(2s)!}{[(s/2)!]^2}$$

4^{th} order

$$s! \simeq s^{s+1/2}e^{-s}\sqrt{2\pi}.$$

From the single spin to the pair

$$\mathcal{H}_{\mathrm{SS}} = -J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2$$

$$|S_1 - S_2| \le S \le S_1 + S_2$$

$$W(S) = -(J_{12}/2)[S(S+1) - S_1(S_1+1) - S_2(S_2+1)]$$

$$\mathbf{g}_S = c_1\mathbf{g}_1 + c_2\mathbf{g}_2$$

$$\mathbf{D}_S = d_1\mathbf{D}_1 + d_2\mathbf{D}_2 + d_{12}\mathbf{D}_{12}$$

$$c_1 = (1+c)/2; c_2 = (1-c)/2$$

$$d_1 = (c_+ + c_-)/2; d_2 = (c_+ - c_-)/2$$

$$d_{12} = (1 - c_+)/2$$

and

$$c = \frac{S_1(S_1+1) - S_2(S_2+1)}{S(S+1)}$$

$$c_+ = \frac{3[S_1(S_1+1) - S_2(S_2+1)]^2 + S(S+1)[3S(S+1) - 3 - 2S_1(S_1+1) - 2S_2(S_2+1)]}{(2S+3)(2S-1)S(S+1)}$$

$$c_- = \frac{4S(S+1)[S_1(S_1+1) - S_2(S_2+1)] - 3[S_1(S_1+1) - S_2(S_2+1)]}{(2S+3)(2S-1)S(S+1)}.$$

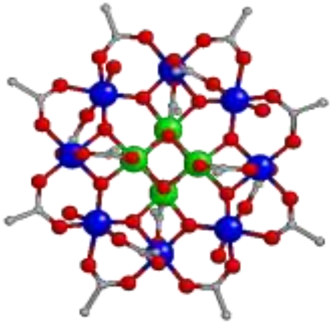
Magnetic anisotropy of spin clusters

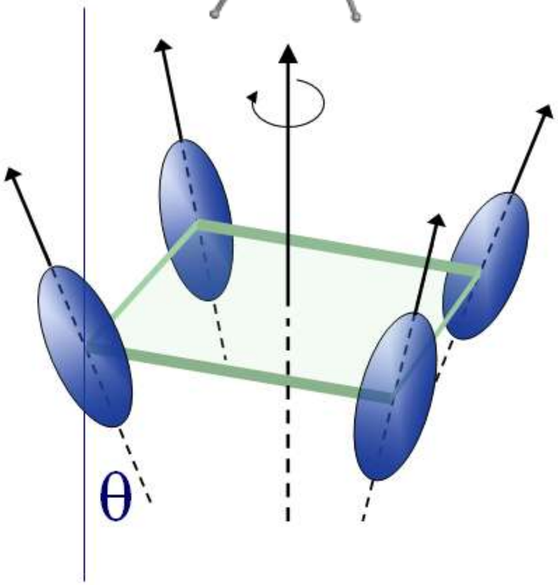
$$\boldsymbol{D}_S = \sum_i d_i \boldsymbol{D}_i + \sum_{i<j} d_{ij} \boldsymbol{D}_{ij}$$

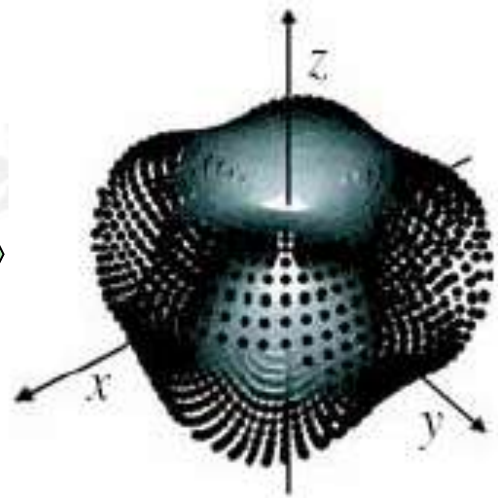
Single Ion

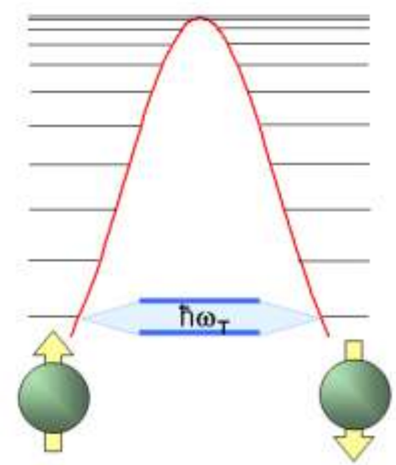
Exchange anisotropy

I-4









Non-collinearity is a key ingredient in molecular magnets

Non-collinearity of magnetic anisotropy

- High Order Transverse Anisotropy is a key factor in Quantum Tunneling of the Magnetization
- Its major source is the multispin nature of SMMs
- Non-collinearity of the anisotropy is necessary to observe transverse anisotropy in axial molecules

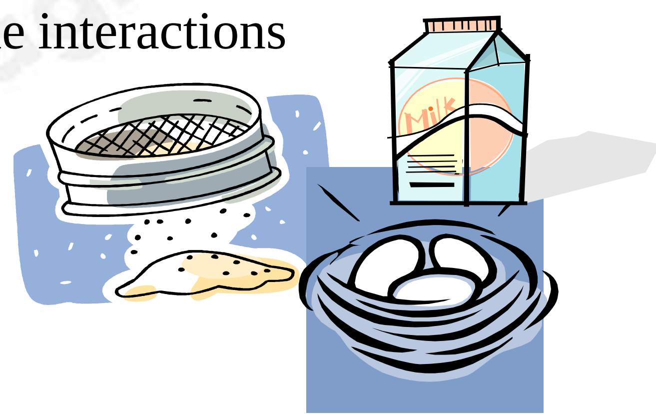
Why spin non-collinearity is so important in Molecular Magnetism?

- The use of organic ligand reduces the symmetry on the metal ion
- Most organic compounds crystallize in the monoclinic or orthorhombic systems
- If the symmetry of the magnetic center is lower than that of the space group INEVITABILY more than one non-magnetically equivalent center are present (metal ions not in special Wyckoff positions)

Mid-term goals:

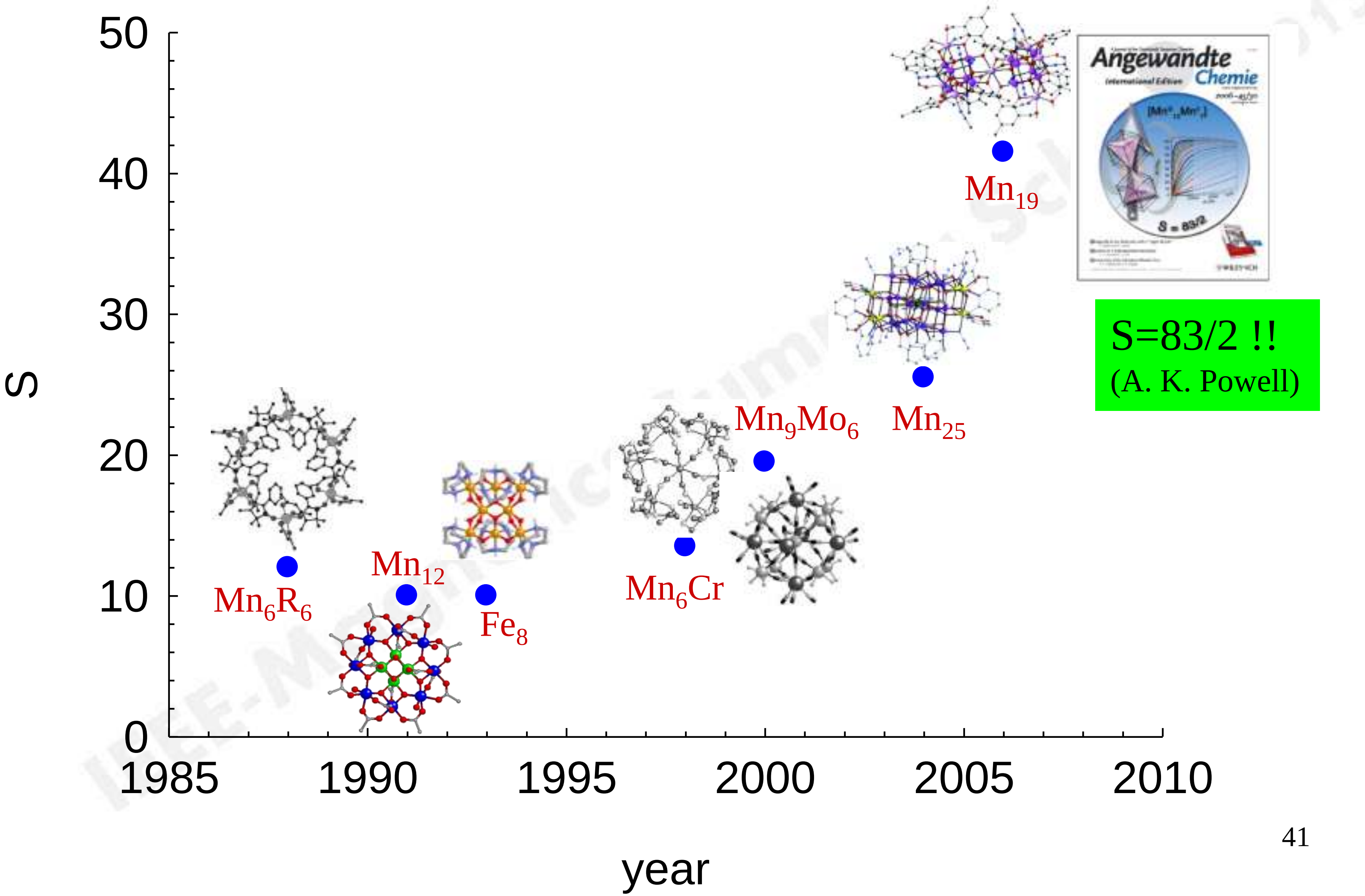
- Increase the blocking temperature

  - ☑ Total Spin (intra-molecular interactions)
  - ☑ Axial Magnetic Anisotropy
  - ☑ Transverse Magnetic Anisotropy
  - ☑ Inter-molecular interactions
  - ☑ Hyperfine interactions

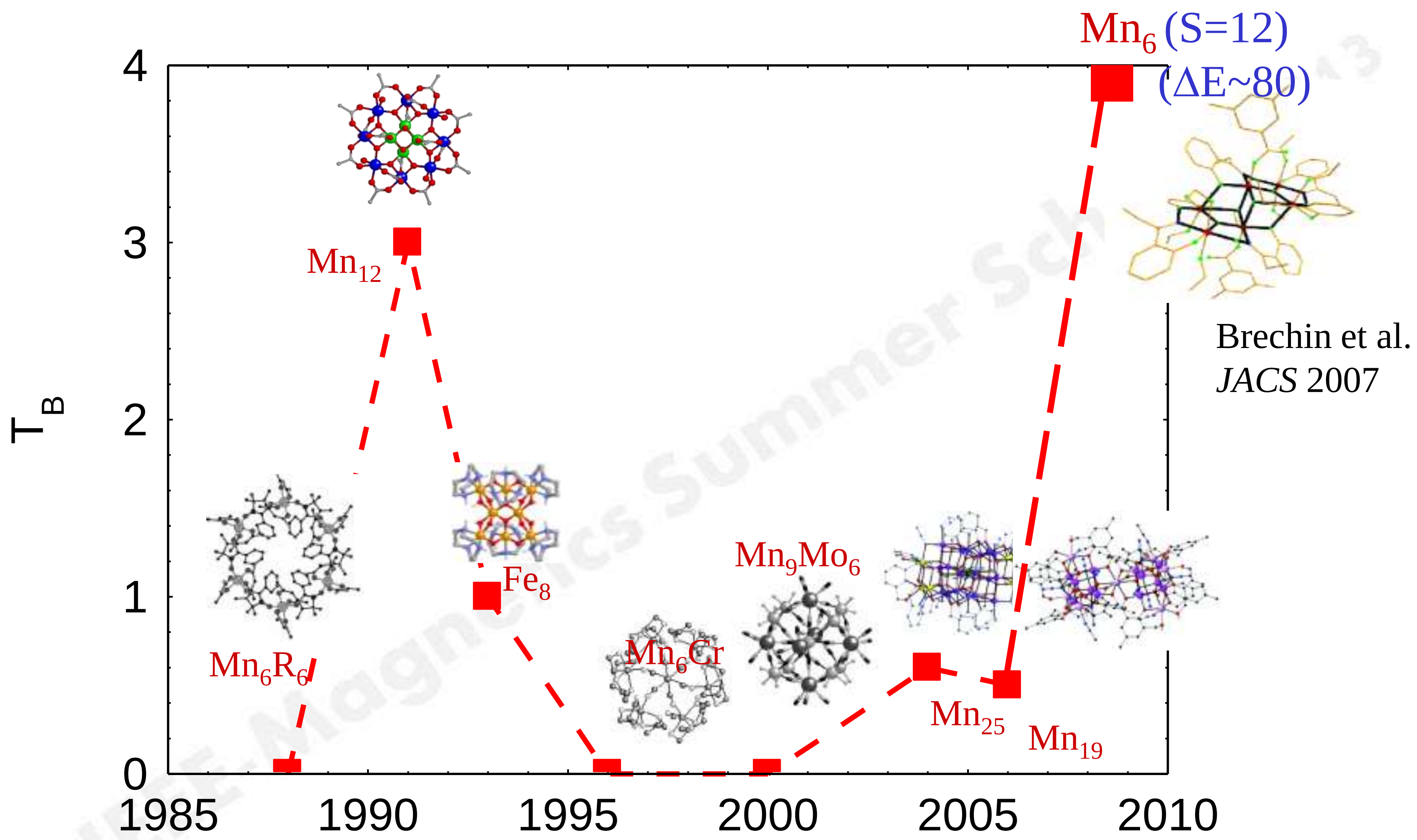


→ ?

Evolution of SMMs



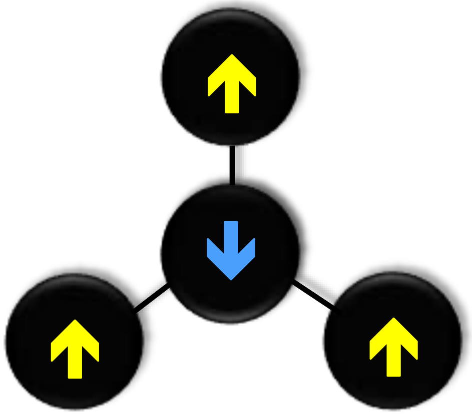
Evolution of SMMs



Why do SMMs work only at low temperature?

$\Delta E \sim |D| S_{tot}^{2}$

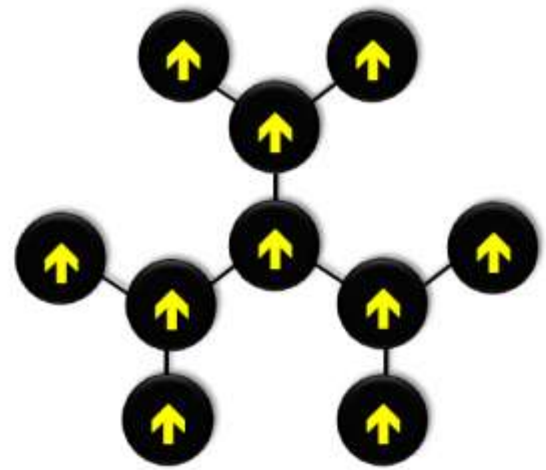
Increase S_{tot} through ferromagnetic interaction



$$D = \sum_i c_i d_i \quad \text{but} \quad c_i \propto \frac{1}{S_{tot}^2}$$

ΔE does not increase with S_{tot}

Increase S_{tot} by the n° of interacting spins



$$D = \sum_i c_i d_i \quad \text{but} \quad c_i \propto \frac{1}{n_{spin}}$$

ΔE increases as S_{tot}

O. Waldmann *Inorg. Chem.* 2007

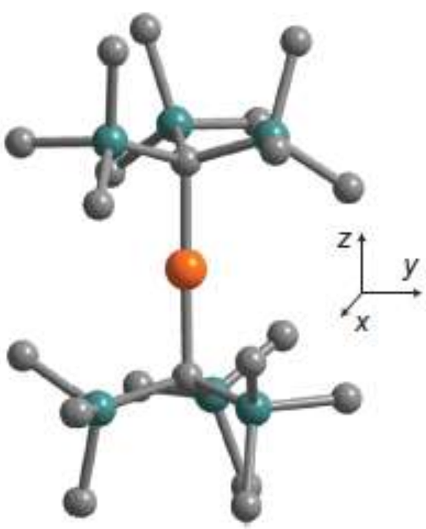
Gatteschi et al. *Molecular Nanomagnets,OUP 2006*

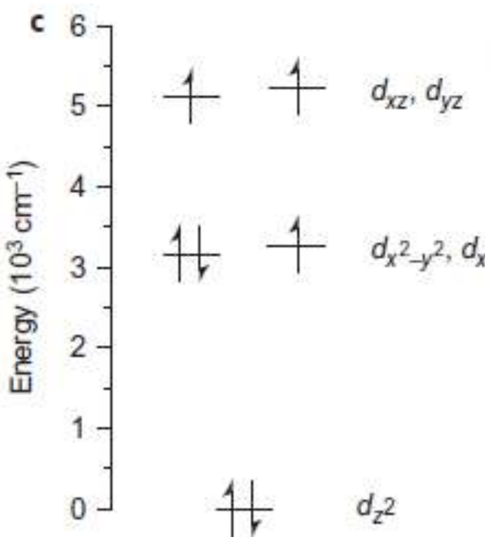
Increase orbital contribution in 3d metal ions

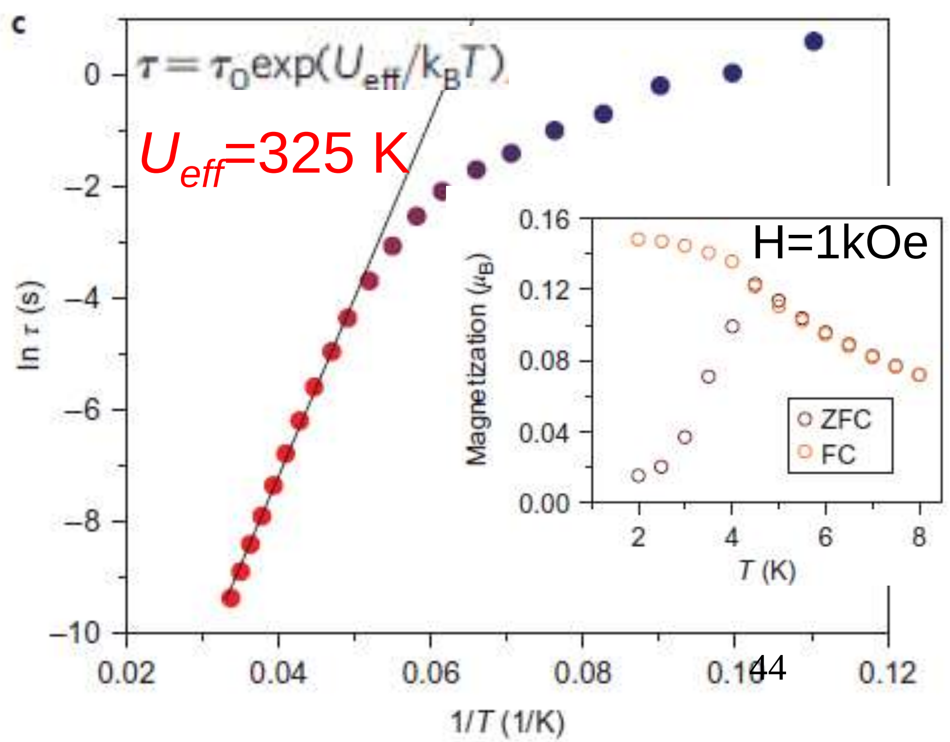
nature chemistry | ARTICLES
PUBLISHED ONLINE: 5 MAY 2013 | DOI: 10.1038/NCHEM.1630

Magnetic blocking in a linear iron(I) complex

Joseph M. Zadrozny[1], Dianne J. Xiao[1], Mihail Atanasov[2,3], Gary J. Long[4], Fernande Grandjean[4], Frank Neese[3] and Jeffrey R. Long[1]*



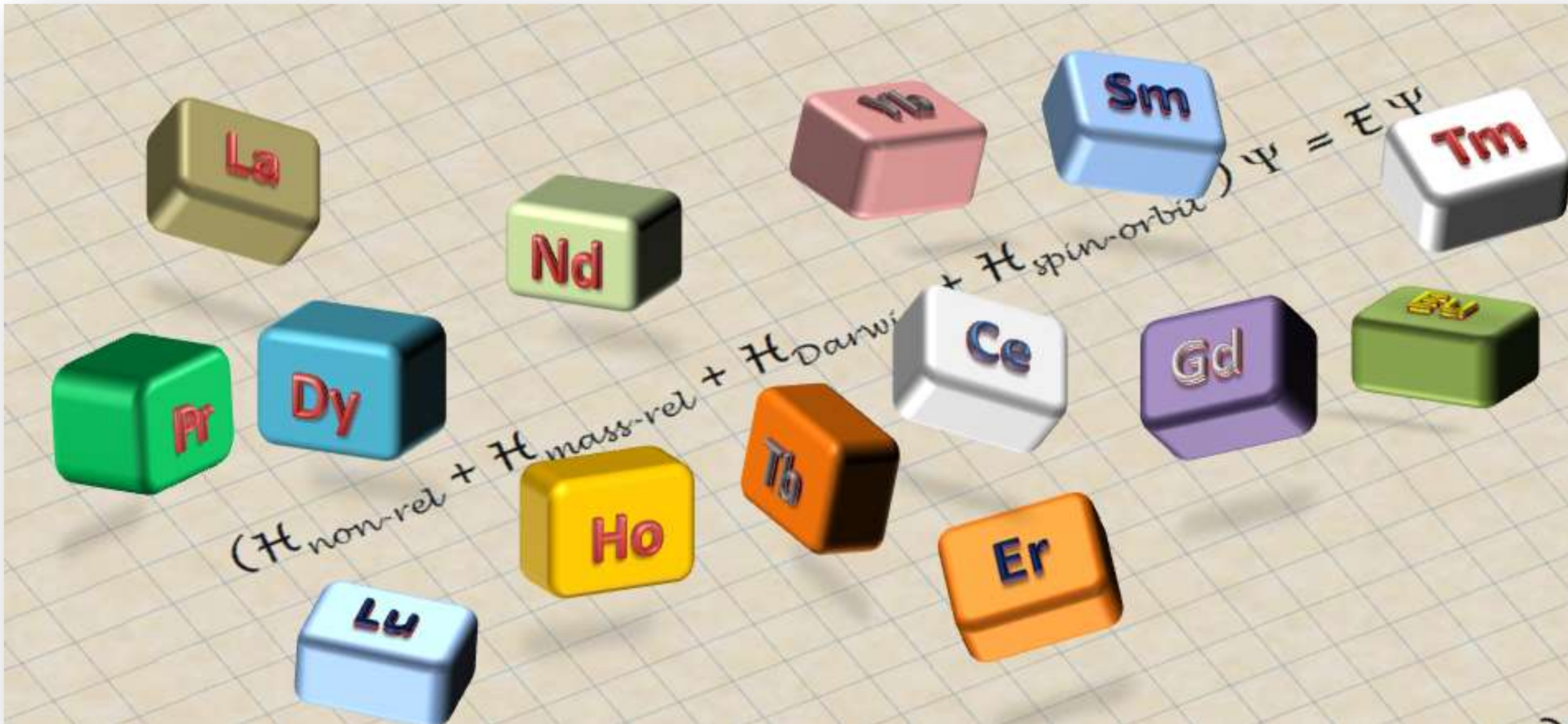




Fe(I) in linear coordination

J=7/2

Lanthanides: a source of magnetic anisotropy



Dalton Transactions

Dynamic Article Links

Cite this: DOI: 10.1039/c2dt31388j

www.rsc.org/dalton

PERSPECTIVE

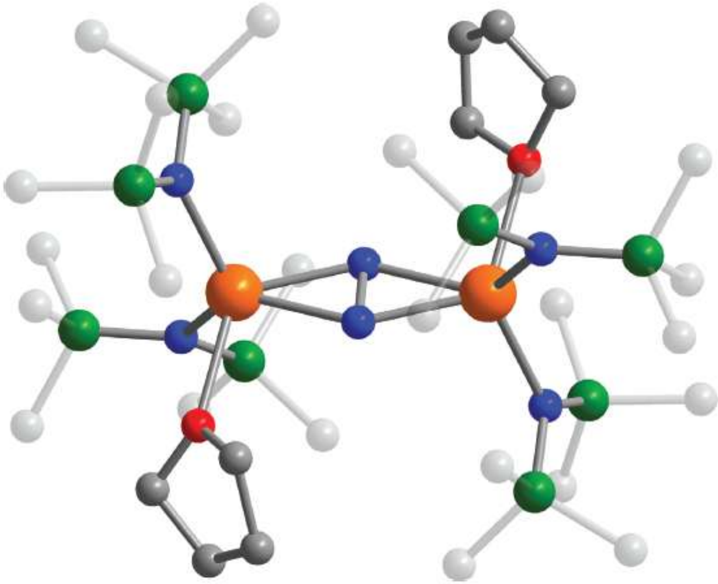
Lanthanides in molecular magnetism: so fascinating, so challenging†

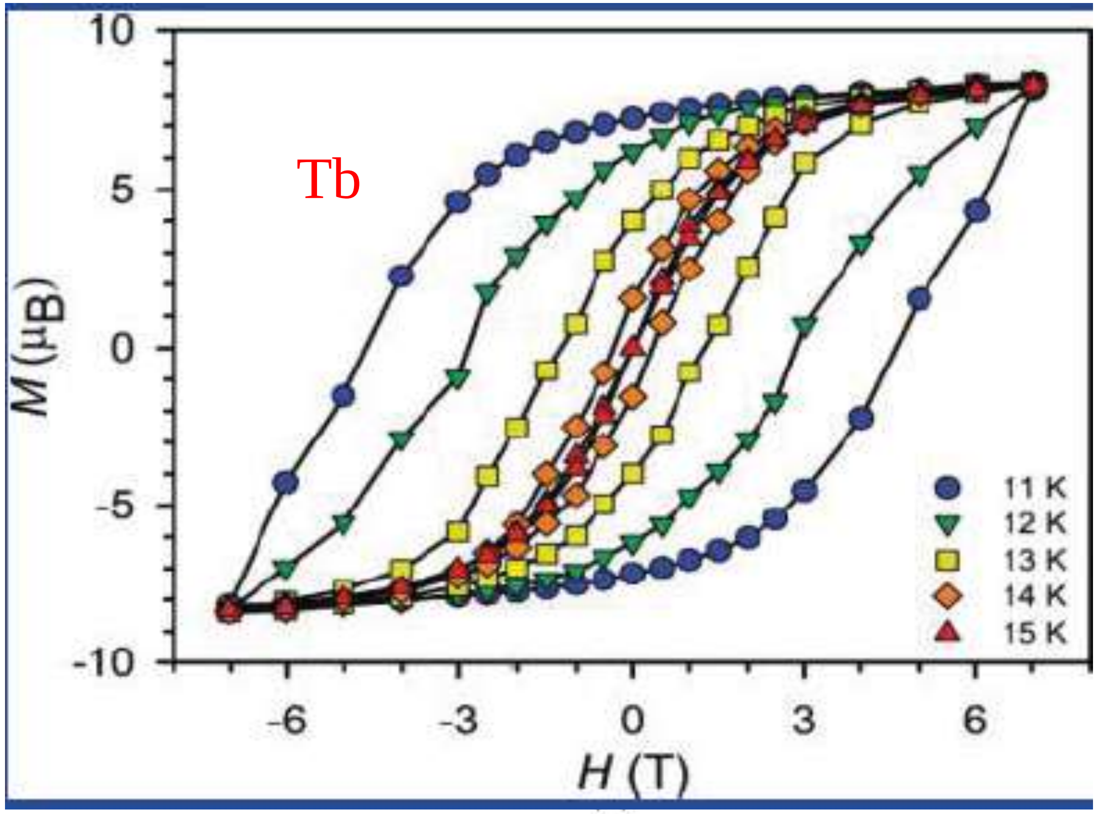
Javier Luzon[a,b] and Roberta Sessoli*[c]

† Dedicated to the memory of Ian J. Hewitt.

Record Blocking Temperature in a RE SMM

$[\{[(Me_3Si)_2N]_2Dy(THF)\}_2(\mu\text{-}N_2)]^-$





N_2^{3-} S=1/2

J(R-Gd) = 27 cm^{-1}
Anti-Ferromagnetic
S_{tot}=13/2

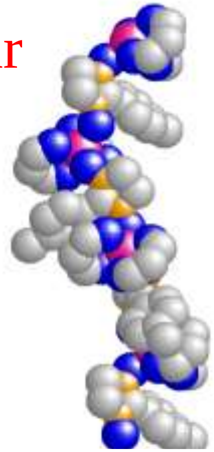
ARTICLES
PUBLISHED ONLINE: 22 MAY 2011 | DOI: 10.1038/NCHEM.1063
nature chemistry

Strong exchange and magnetic blocking in N_2^{3-}-radical-bridged lanthanide complexes

Jeffrey D. Rinehart[1], Ming Fang[2], William J. Evans[2]* and Jeffrey R. Long[1]*

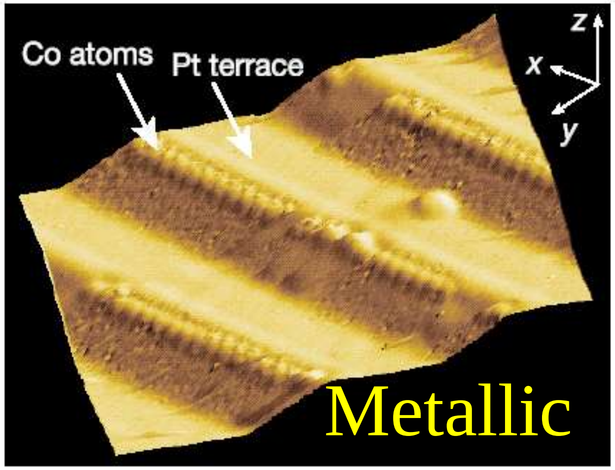
From 0d to 1d: Single Chain Magnets

Molecular

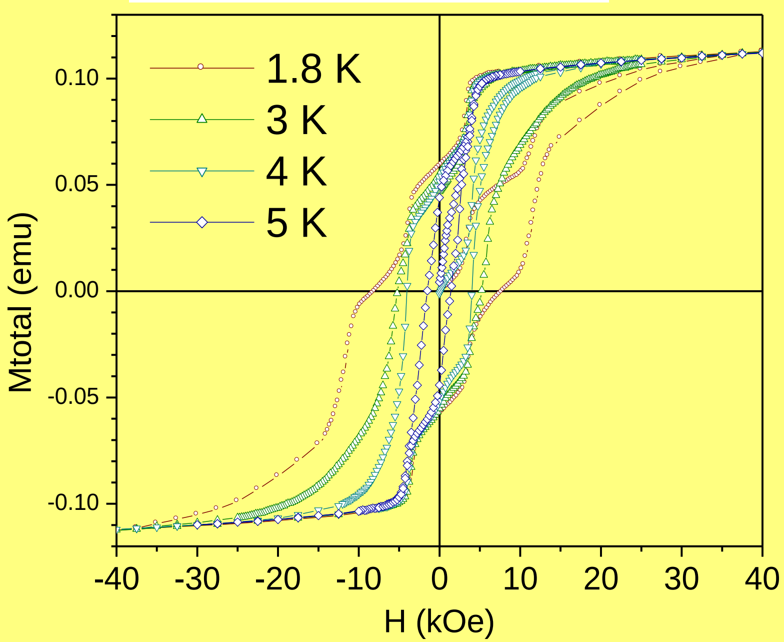


Caneschi et al.

Angew. Chem. 2001



P. Gambardella et al.
Nature 2002



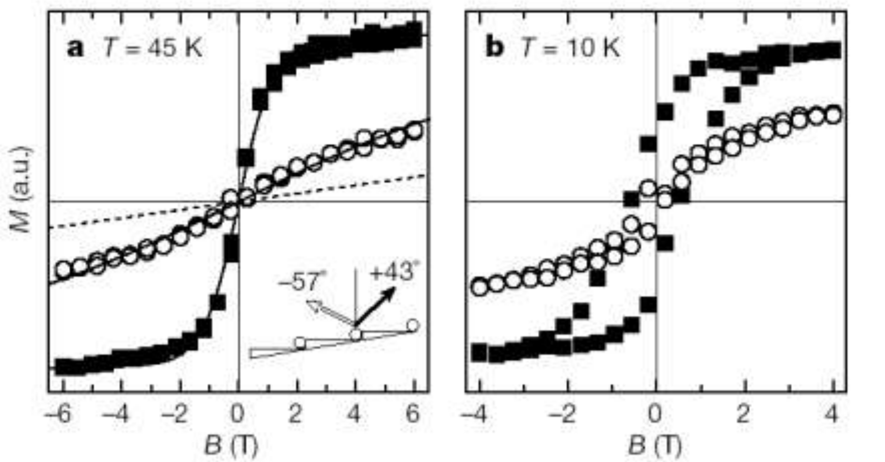
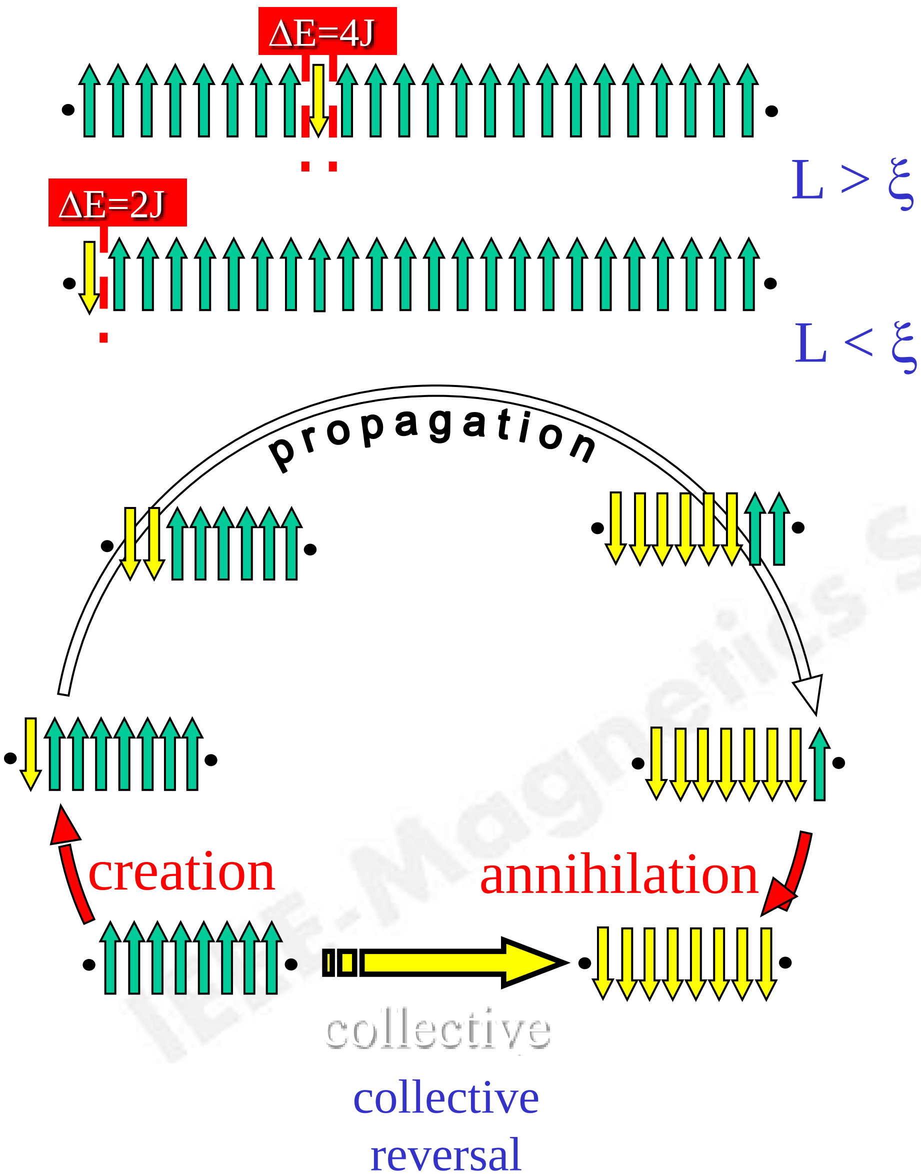


Figure 3 Magnetization of a monatomic wire array recorded at the L_3 Co edge. **a**, *M* as a function of the applied field at *T* = 45 K measured along the easy direction (filled squares) and at 80° away from the easy direction (open circles) in the plane perpendicular

Spin Dynamics in Single Chain Magnets



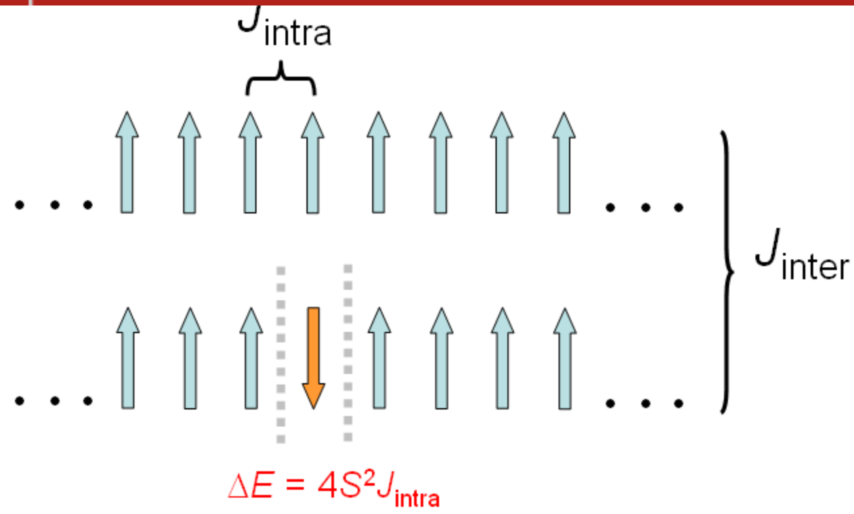
$$M(t) = M_{sat}\exp(t/\tau)$$

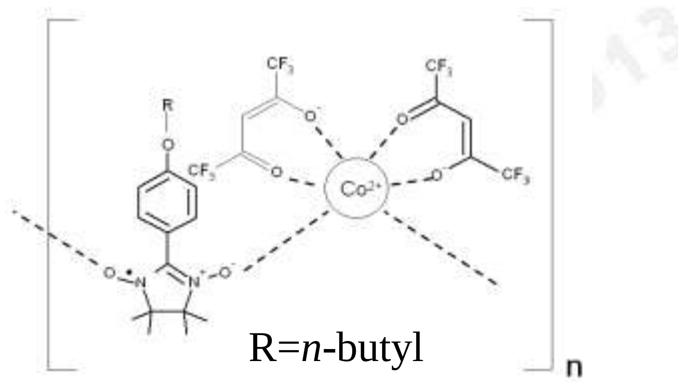
$$\tau = \tau_0 \exp(4J/k_BT)$$

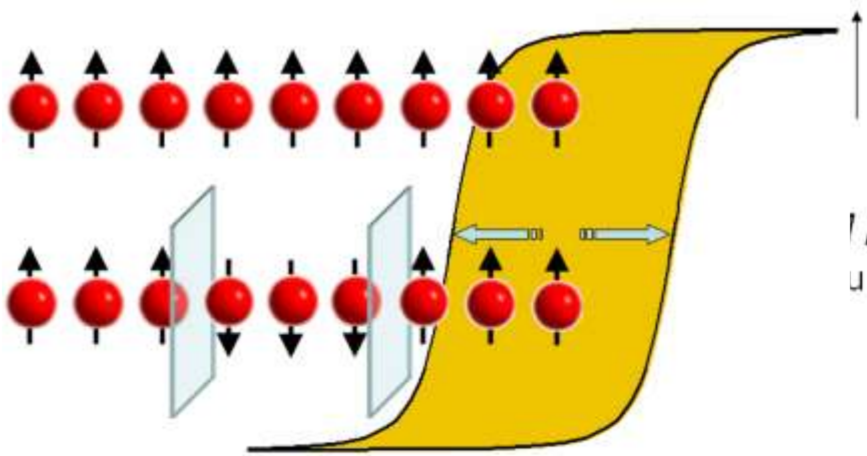
$$\xi_{Ising} \propto (2J/k_BT)$$

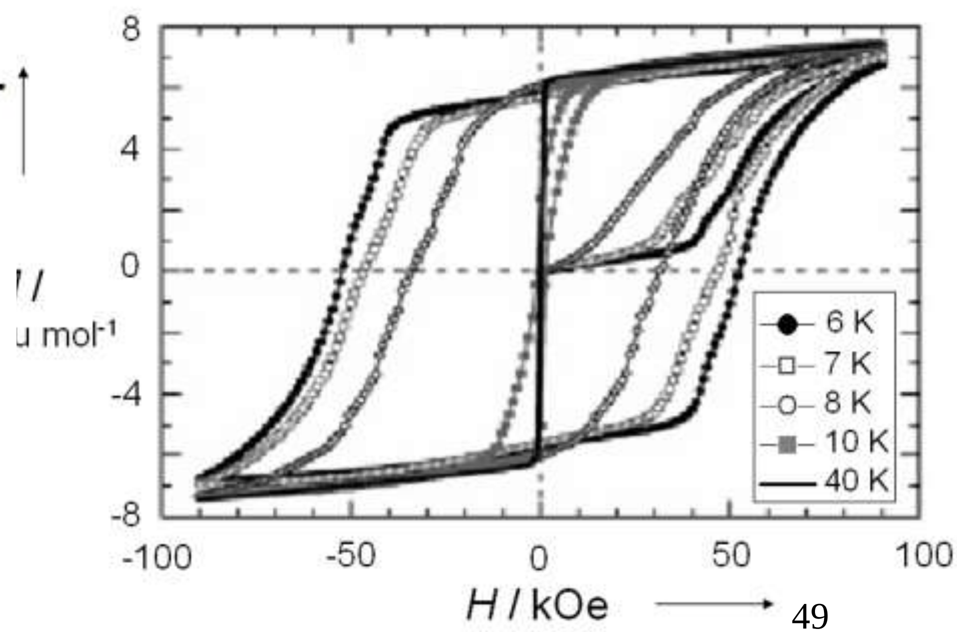
The relaxation time diverges at low temperature as ξ^2

High Coercitivity in SCMs



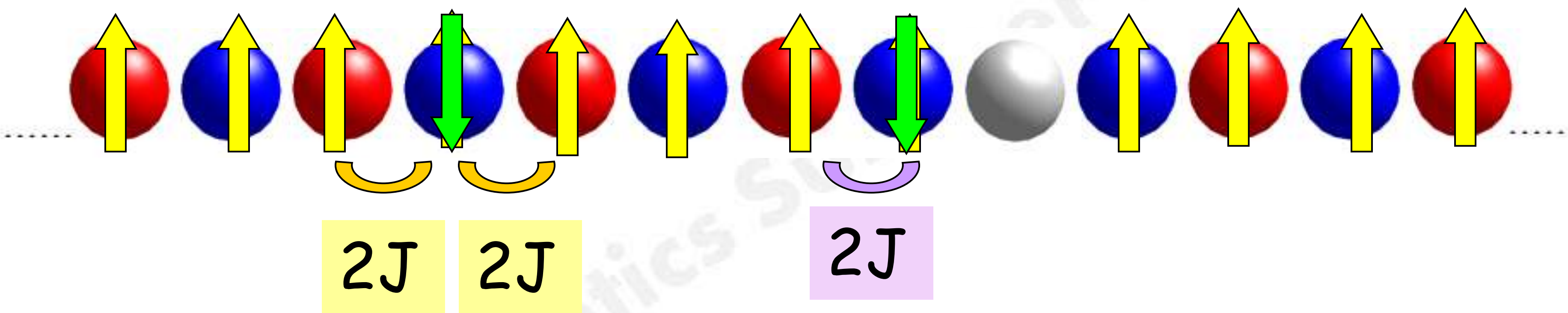






N. Ishii, et al.*J. Am. Chem. Soc.* 2008, *130*, 24.

The role of diamagnetic defects in the dynamics



J. K. L. da Silva et al. *Phys. Rev. E* 52 (1995) 4527

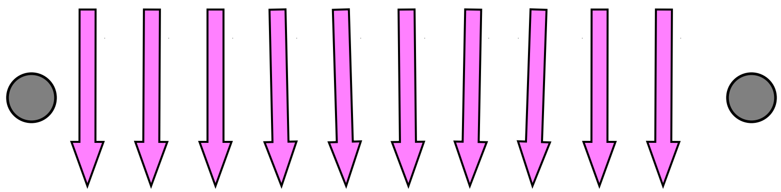
$$\tau \propto \xi^2 \approx \exp(4J/k_BT) \text{ if } L \gg \xi_{th}$$

$$\tau \propto \xi \approx \exp(2J/k_BT) \text{ if } L \ll \xi_{th}$$

Finite size effects in SCMs

in the $\xi > \overline{N}$ regime

ΔE=2J



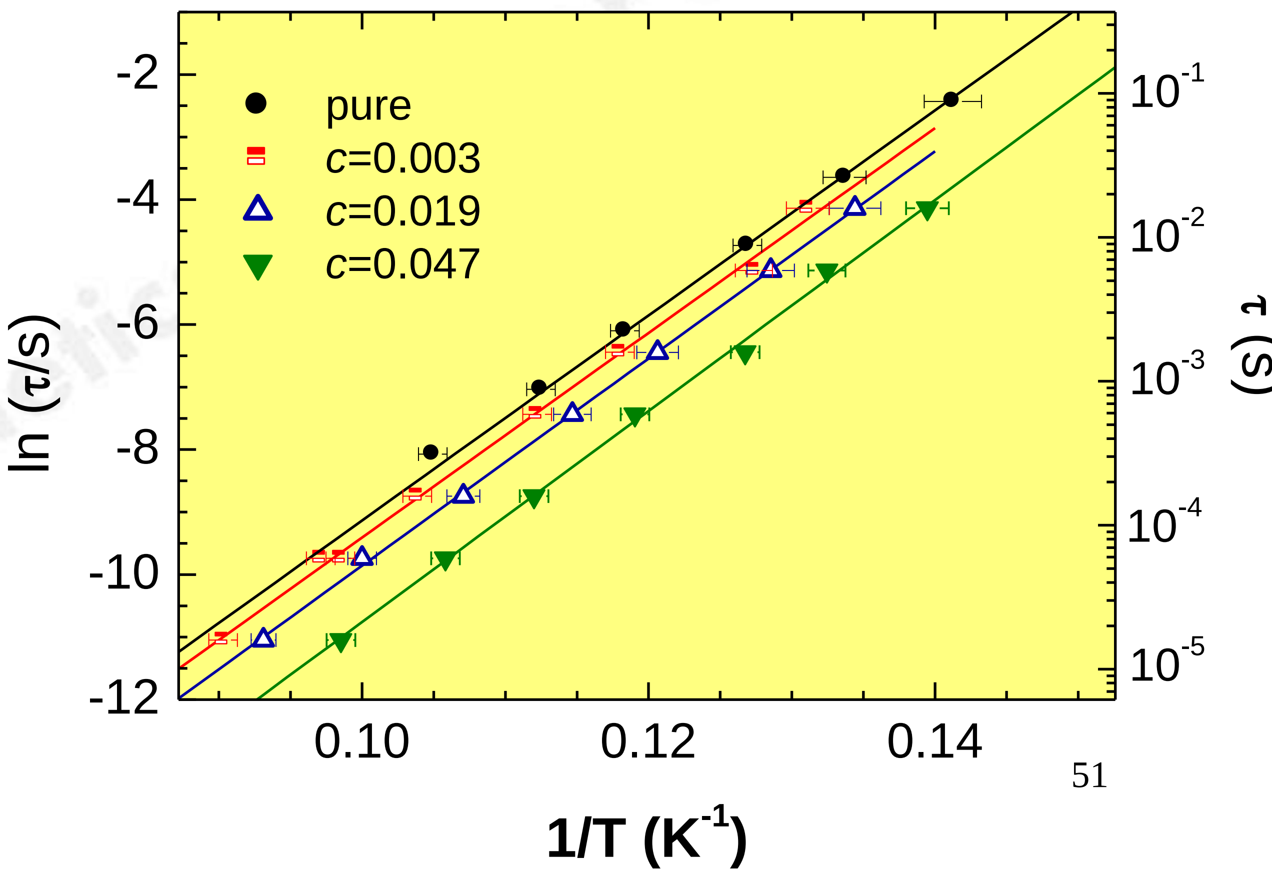
The domain wall motion is a classical random walk:

propagation ~ $\frac{1}{N-1}$

$$\lambda_1 \approx \frac{2q\alpha}{N-1}\exp\left(-\frac{2J}{k_B T}\right)$$

$$\tau_1 \propto (N-1)\exp\left(\frac{2J}{k_B T}\right)$$

τ_0 shifting



Finite size effects in SCMs

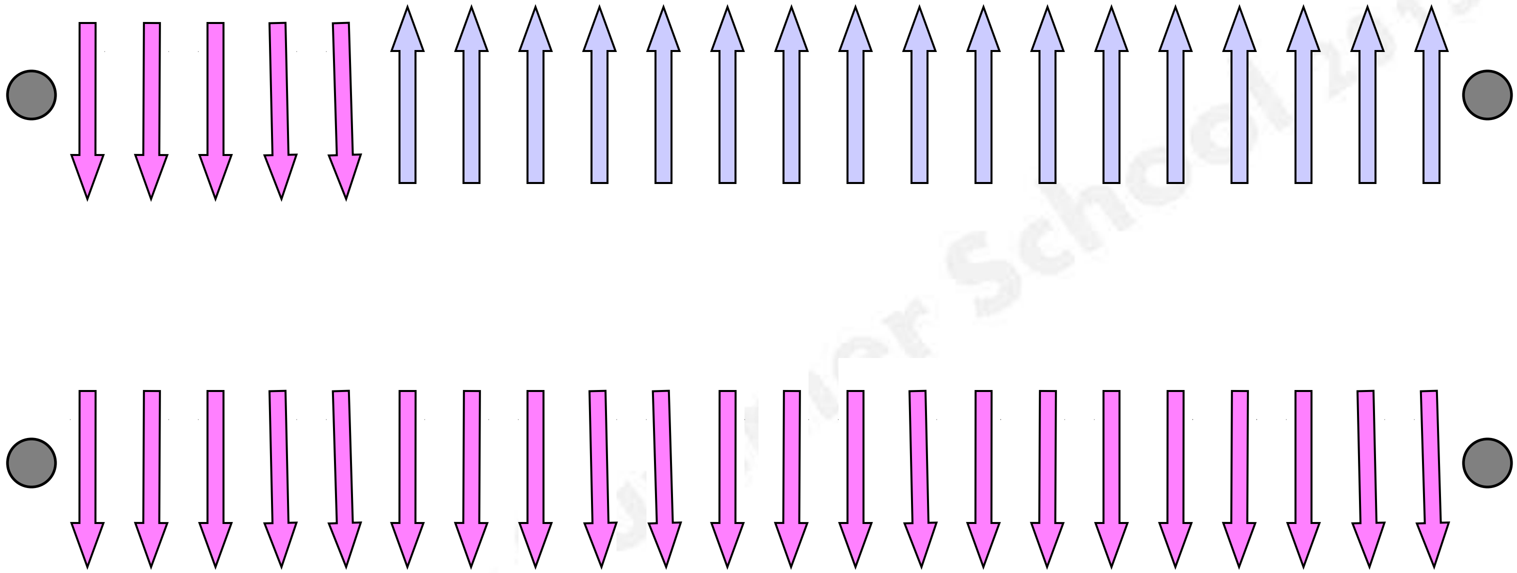
…taking into account multiple events…

$\Delta E = 2J$

Prob ~ q^5

$\Delta E = 0$

Prob ~ q^N

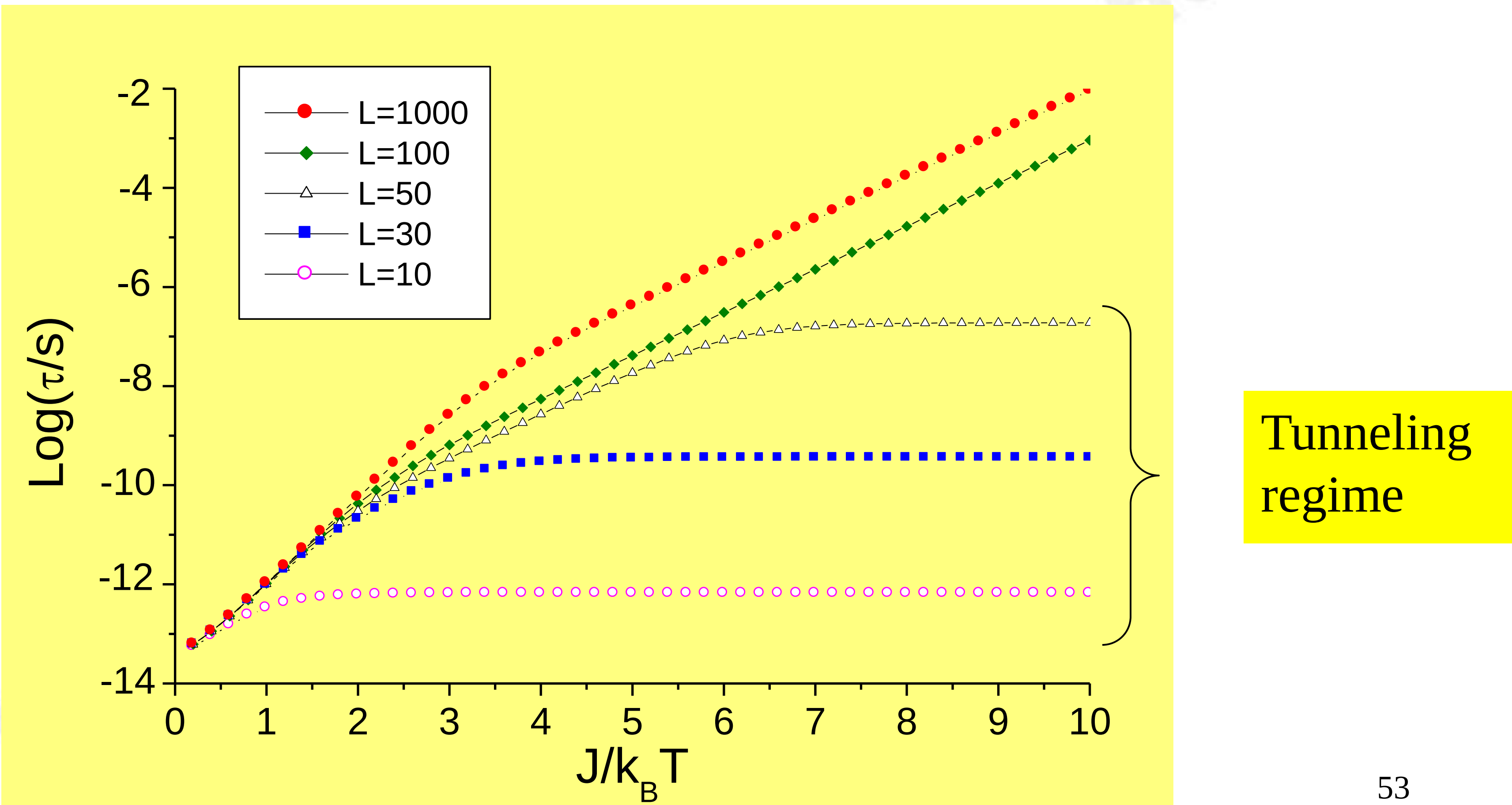


For short segments
the UNDERBARRIER process can become faster than any thermally activated mechanism

$$\frac{1}{\tau(N)} = \frac{1}{\tau_1} + \alpha\, q^N$$

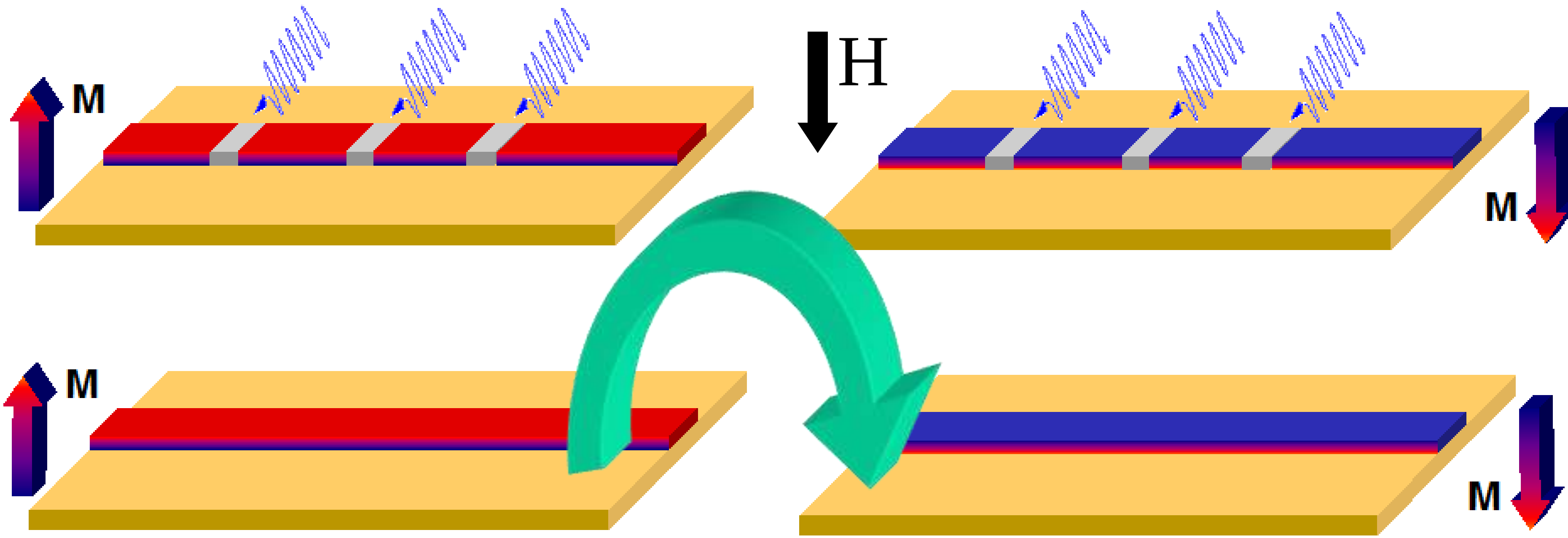
Transition from SCM to SMMs behavior

If *q* is temperature independent the cross-over to tunneling regime depends on the the length *L*



A perspective: switching from SCM to SMM

Perturbed state □ short segments:
the magnetization can reverse
(collective reversal of the spins)



Unperturbed state □ long segments:
the magnetization is frozen
(Glauber's dynamics)

Light-induced magnetic relaxation

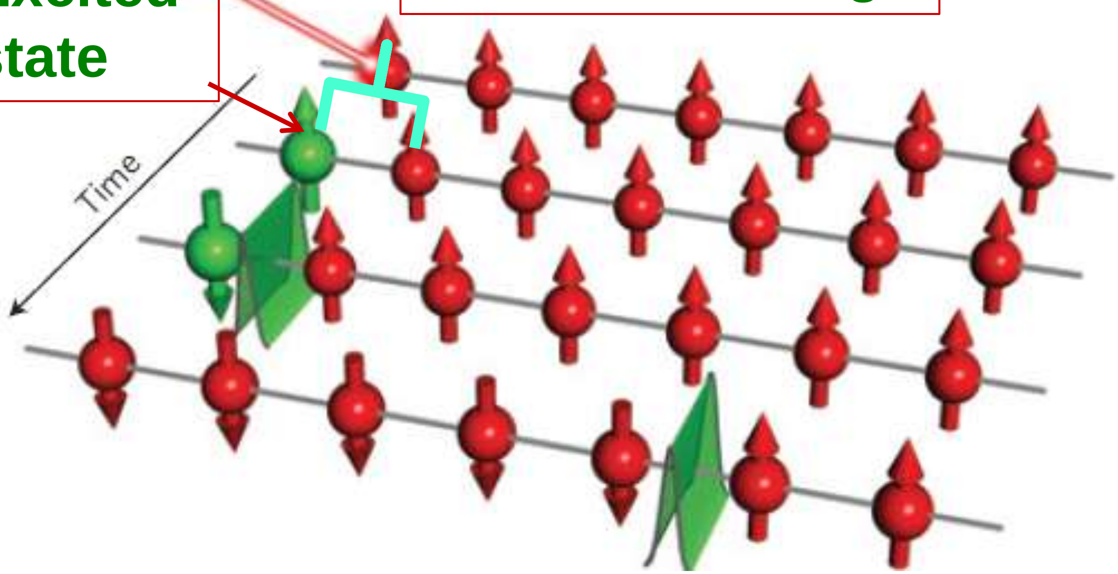
nature materials
LETTERS
PUBLISHED ONLINE: 2 DECEMBER 2012 | DOI: 10.1038/NMAT3498

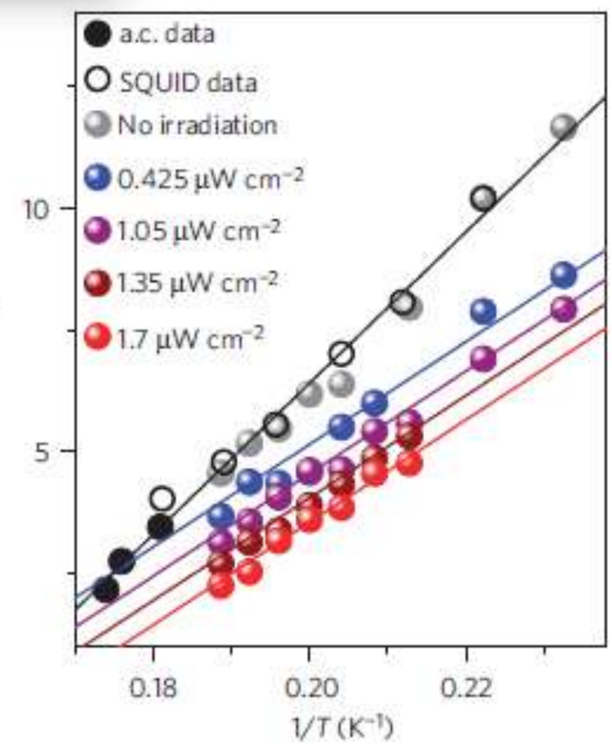
Dynamic control of magnetic nanowires by light-induced domain-wall kickoffs

Eric Heintze[1], Fadi El Hallak[1], Conrad Clauß[1], Angelo Rettori[2,3], Maria Gloria Pini[4], Federico Totti[5], Martin Dressel[1] and Lapo Bogani[1]*

Excited state

Weaker exchange

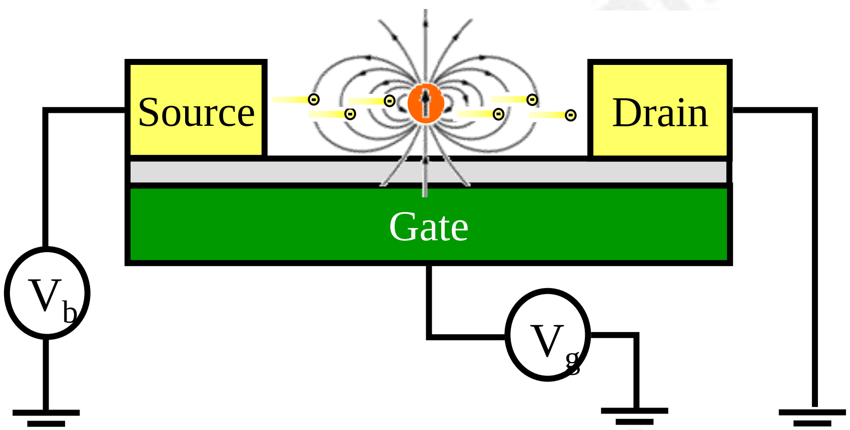




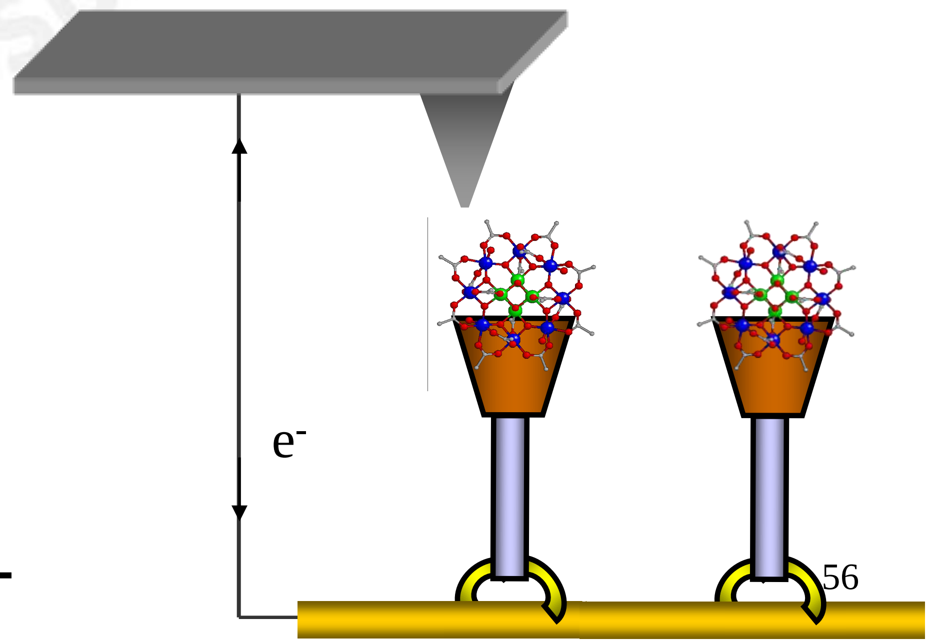
Why magnetic molecule @ surfaces ?

- Electric field can be much more “local”
- Address individual molecules

Molecules in nano-junctions



Scanning Probe Microscopies

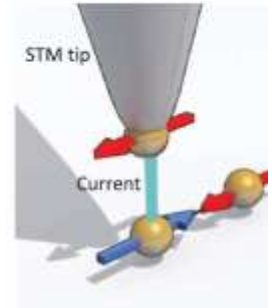


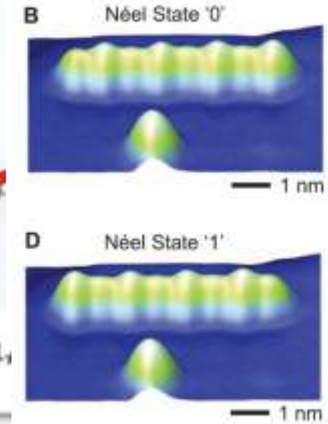
SP-STM Detection of Magnetic Bistability

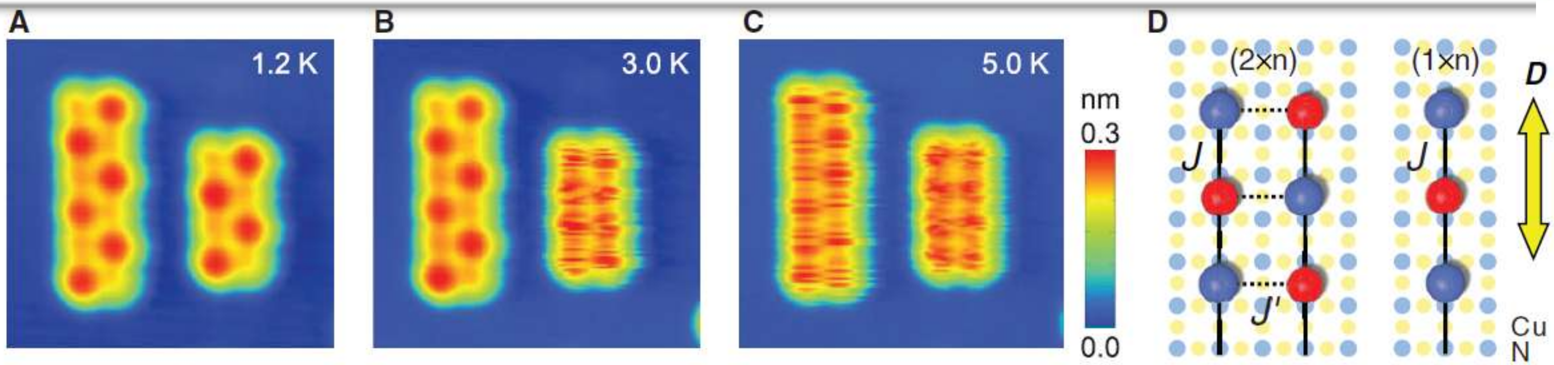
REPORTS

Bistability in Atomic-Scale Antiferromagnets

Sebastian Loth,[1,2]* Susanne Baumann,[1,3] Christopher P. Lutz,[1] D. M. Eigler,[1] Andreas J. Heinrich[1]

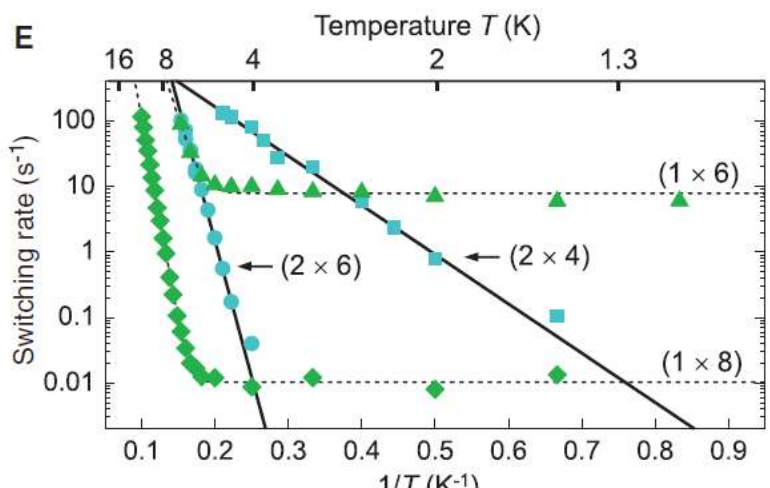






Fe_n
@
Cu_2N
@
Cu(100)

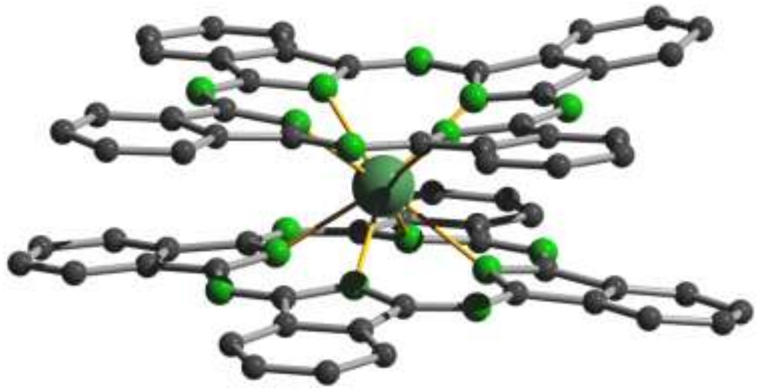
Fig. 3. Thermal stability of AFM arrays. (**A** to **C**) STM images of (2×6) and (2×4) arrays of Fe atoms. (A) 1.2 K. Both arrays have stable Néel states. (B) 3.0 K. The smaller array switched rapidly during the image. (C) 5.0 K. Both arrays switched rapidly. Image size, 7.7 × 7.7 nm. Image was taken at 2 mV and 3 pA, and image acquisition time was 52 s. (**D**) Schematic of the atomic positions of Fe and Cu_2N substrate atoms in (2×*n*) and (1×*n*) arrays. Cu atoms, yellow; N atoms, light blue. Ball colors depict the spin alignment of one Néel state, with red being parallel and blue antiparallel with the tip's spin. (**E**) Arrhenius plot of the switching rates for the arrays of (A) and a (1×8) and (1×6) chain (fig. S5). The determination of switching rates is explained in fig. S3. Magnetic field was 3 T. Fig. S4 shows comparison to a 1-T field. Fit parameters are given in table S1.



IBM Research Division, Almaden Research Center

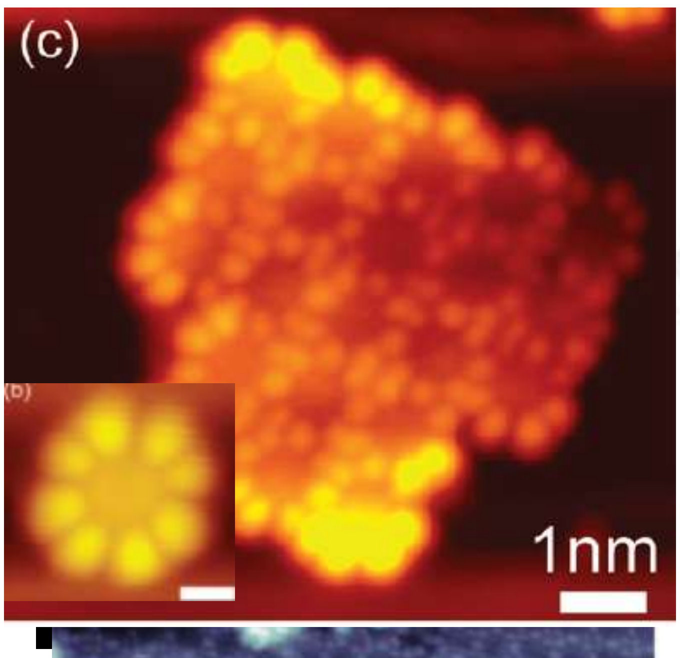
UNIVERSITÀ DEGLI STUDI FIRENZE
DIPARTIMENTO DI CHIMICA "UGO SCHIFF"

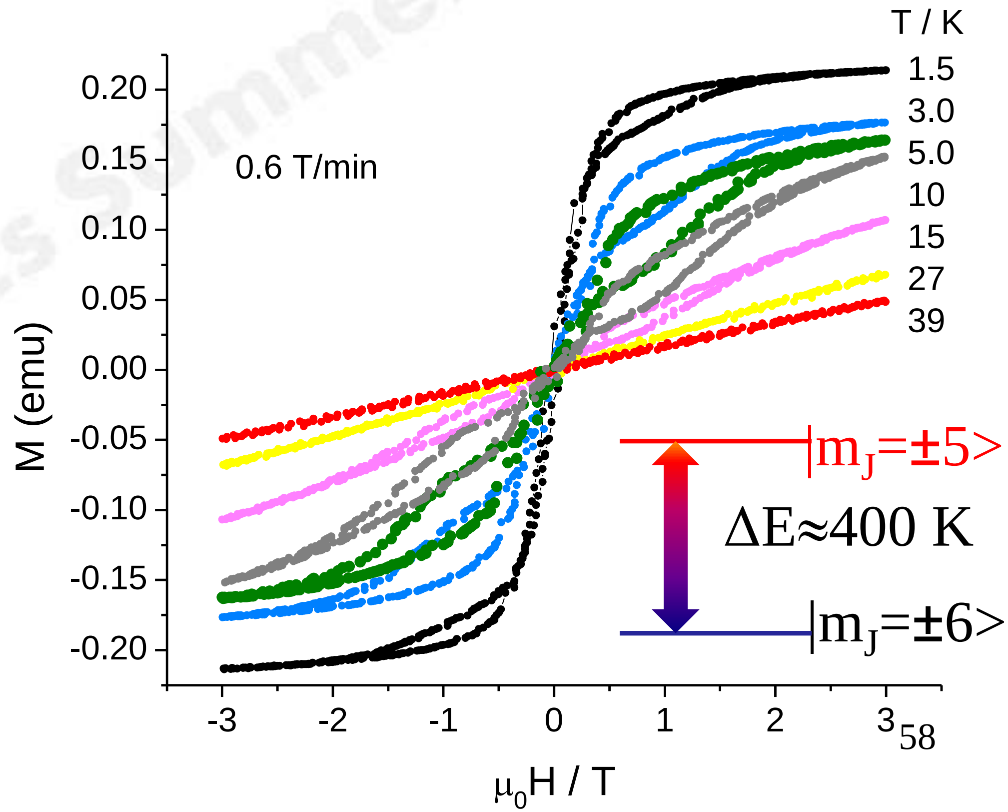
$TbPc_2$: a single ion SMM



Tb^{3+}
L=3
S=3
} J=6

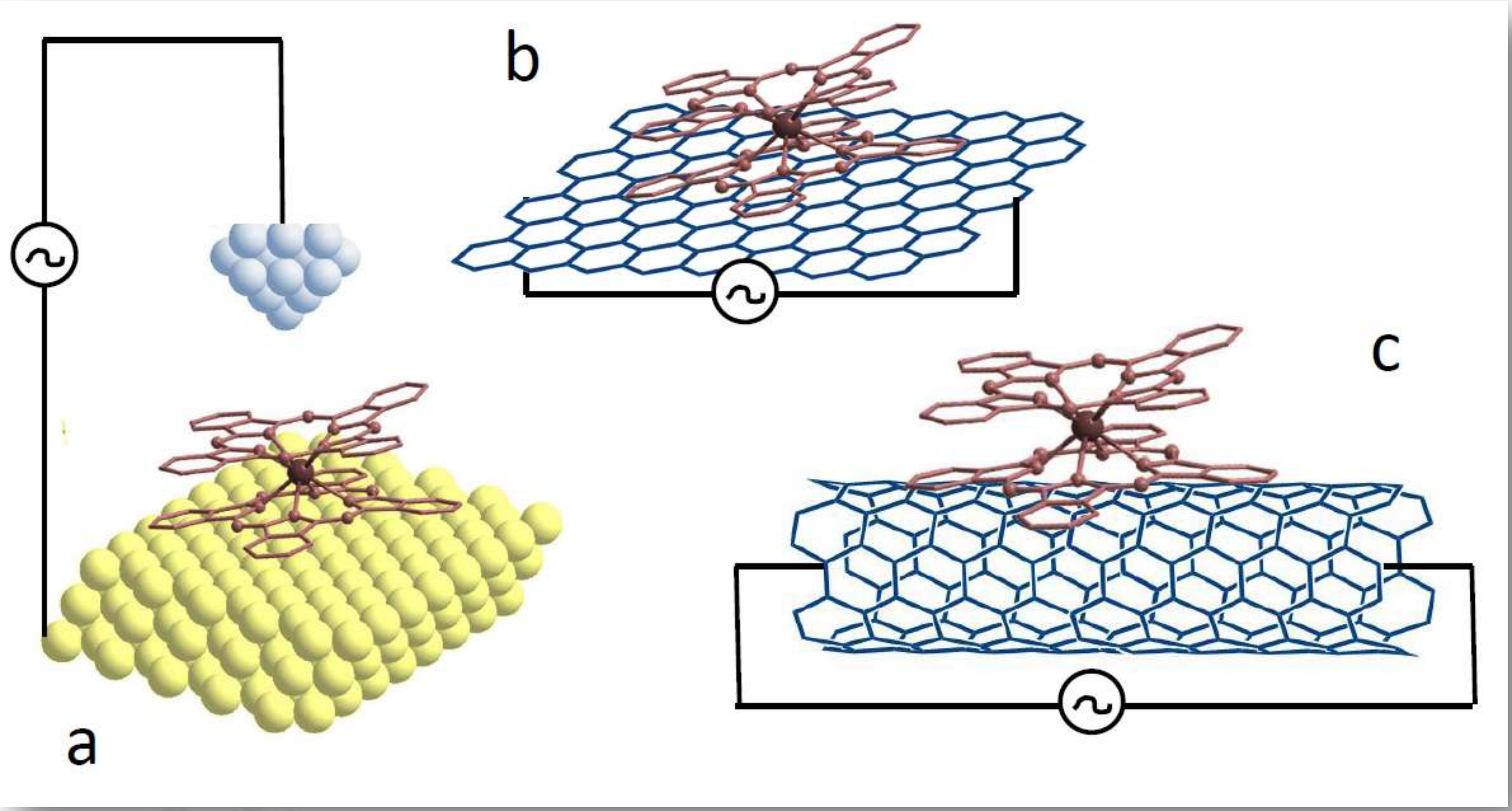
- Thermally Evaporable
- Flat
- Large magnetic moment
- Large anisotropy
- High T_B





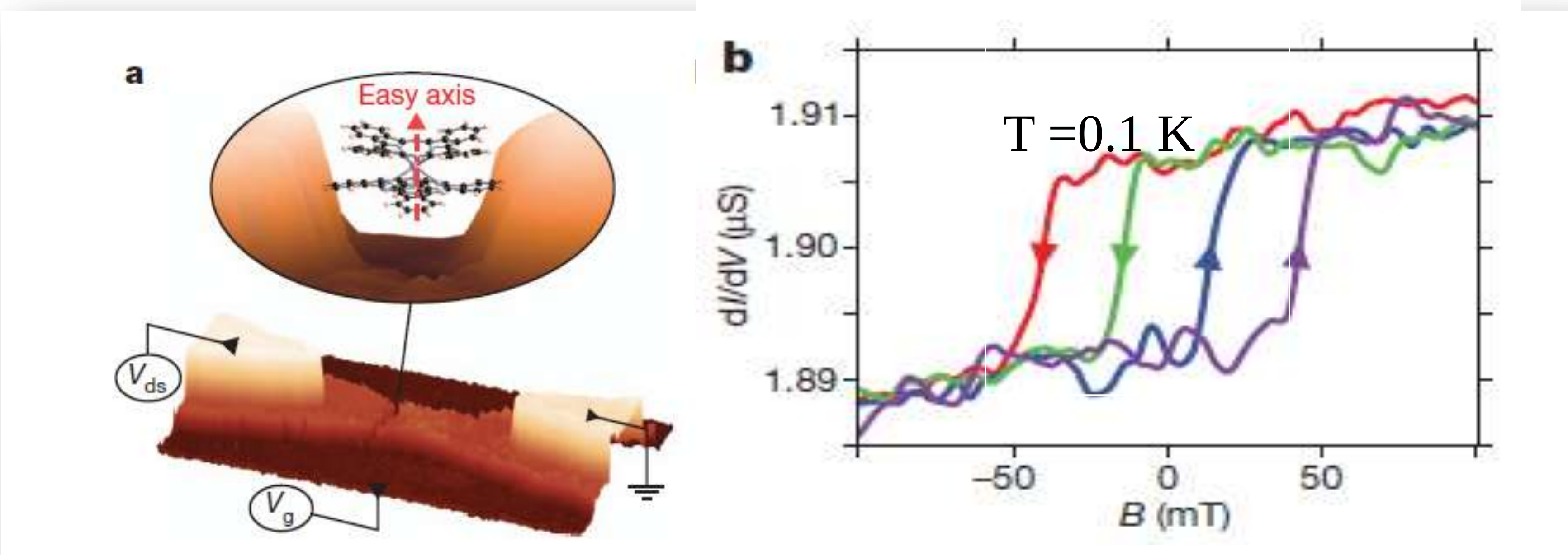
Komeda et al. 2009
Kern et al., Nano Lett. 2008
Hietschol et al. JACS 2011

Spintronics architectures based on $TbPc_2$



a) Komeda et al. *Nature Commun.* 2011
b) Candini et al. *Nanoletters* 2011
c) Urdampilleta et al. *Nature Materials* 2011

Spintronics architectures based on $TbPc_2$



16 AUGUST 2012 | VOL 488 | NATURE | 357
doi:10.1038/nature11341

Electronic read-out of a single nuclear spin using a molecular spin transistor

Romain Vincent[1], Svetlana Klyatskaya[2], Mario Ruben[2,3], Wolfgang Wernsdorfer[1] & Franck Balestro[1]

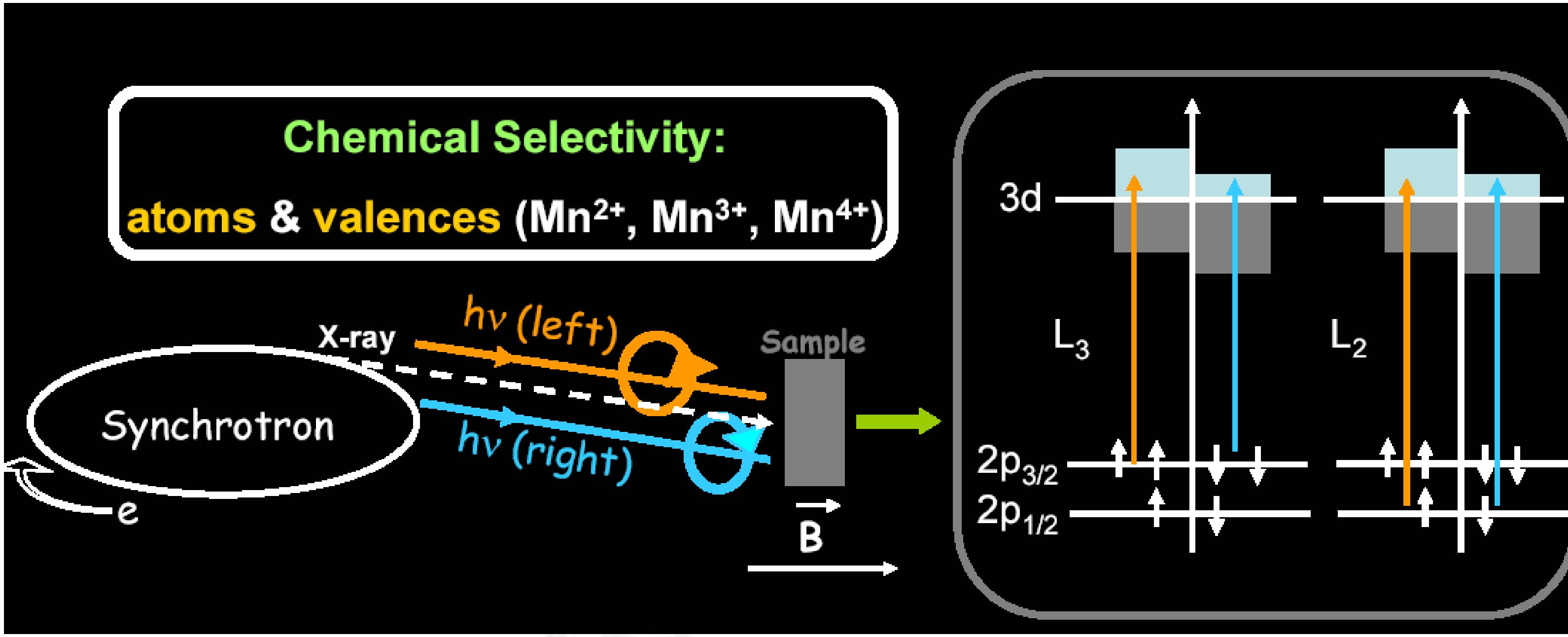
UNIVERSITÀ DEGLI STUDI FIRENZE
DIPARTIMENTO DI CHIMICA "UGO SCHIFF"

Challenges

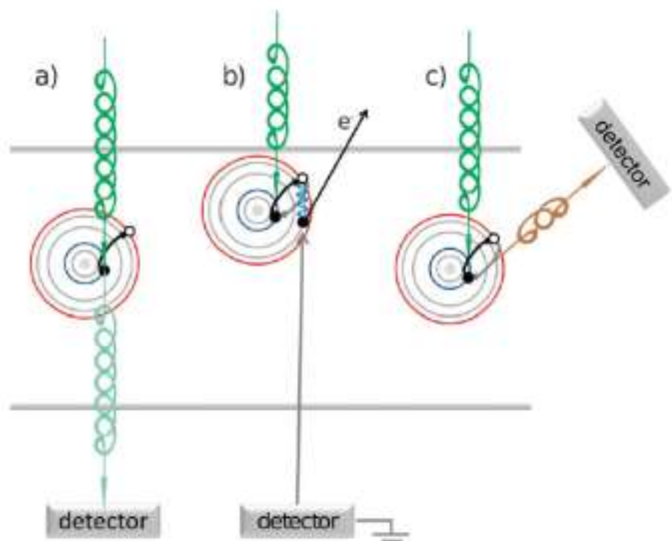
- Chemical stability on surfaces
- Robustness of SMM behavior

X-ray Magnetic Circular Dichroism

- Element & valence selectivity



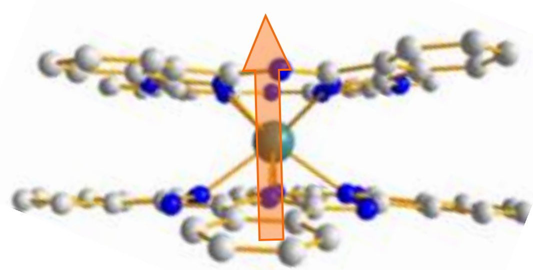
- Surface sensitivity when absorption is detected as Total Electron Yield (b)



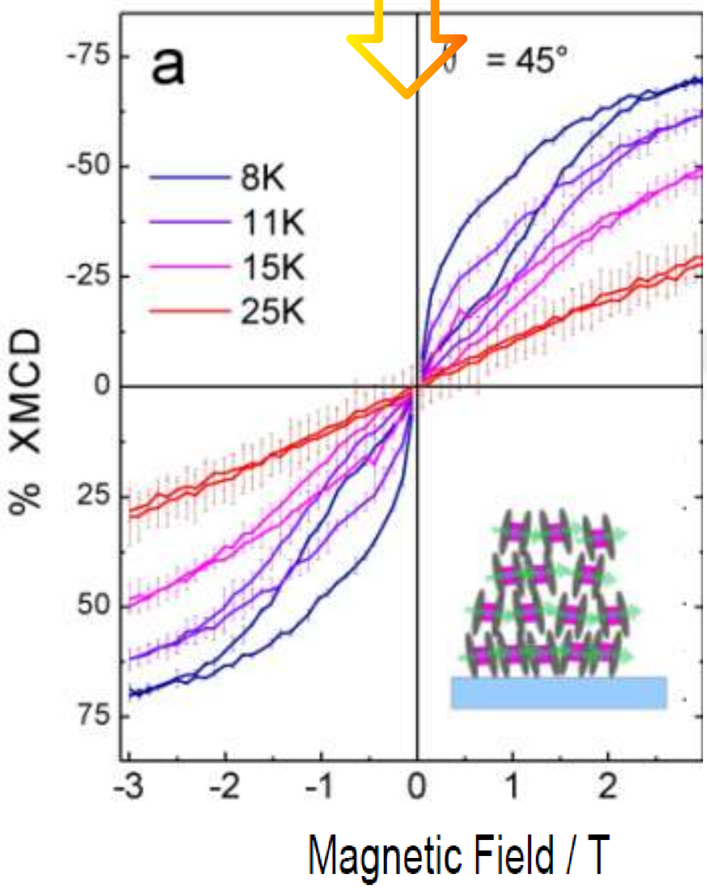
- a) absorption
- b) T. E. Y
- c) Fluorescence

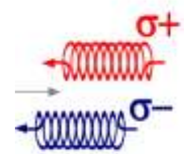
SMM behavior is sensitive to nanostructure

$TbPc_2$
Terbium bis-phthalocyaninato

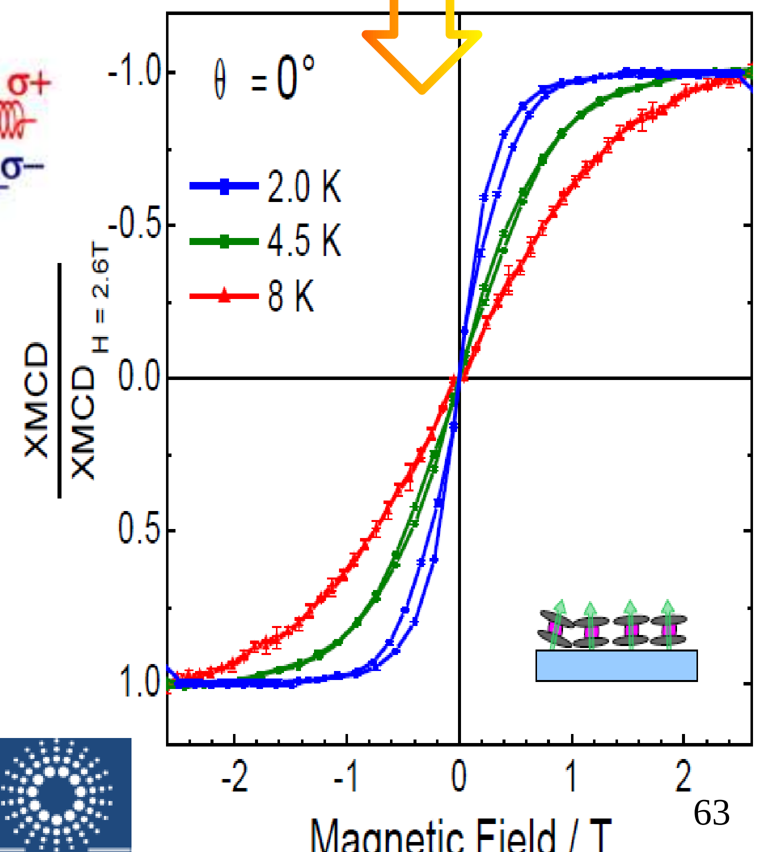


thick film





Monolayer
@ Au(111)



ID8@ ESRF

Implanted probes ($^8Li^+$, μ^+)

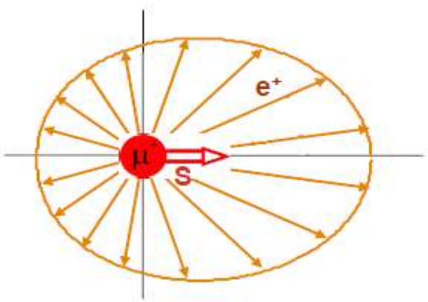
In muon spin relaxation muons are employed like local probe of magnetic field.

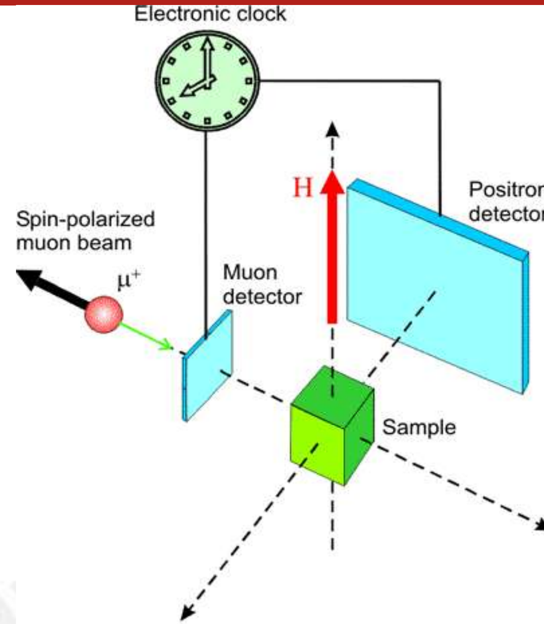
Muon: S=1/2

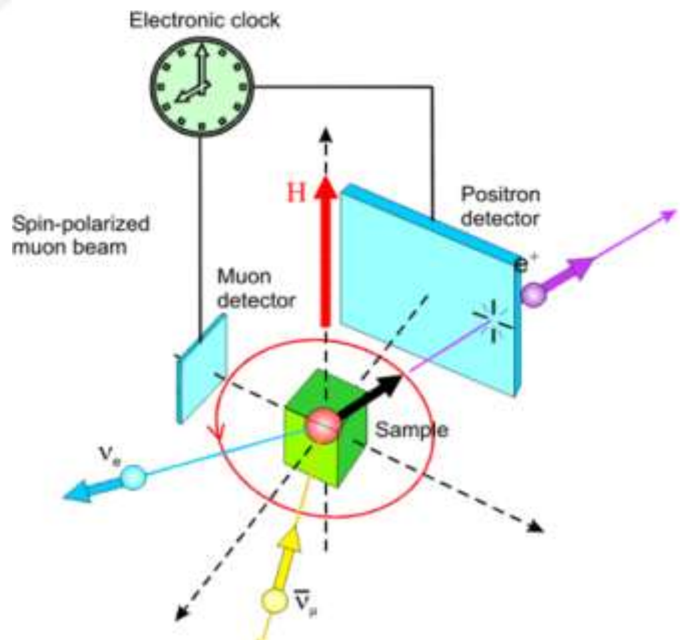
Muon decay (life time 2.2 μs)

$$\mu^+ \longrightarrow e^+ + \nu_\mu + \nu_e$$

Positrons are preferentially emitted along muon spin

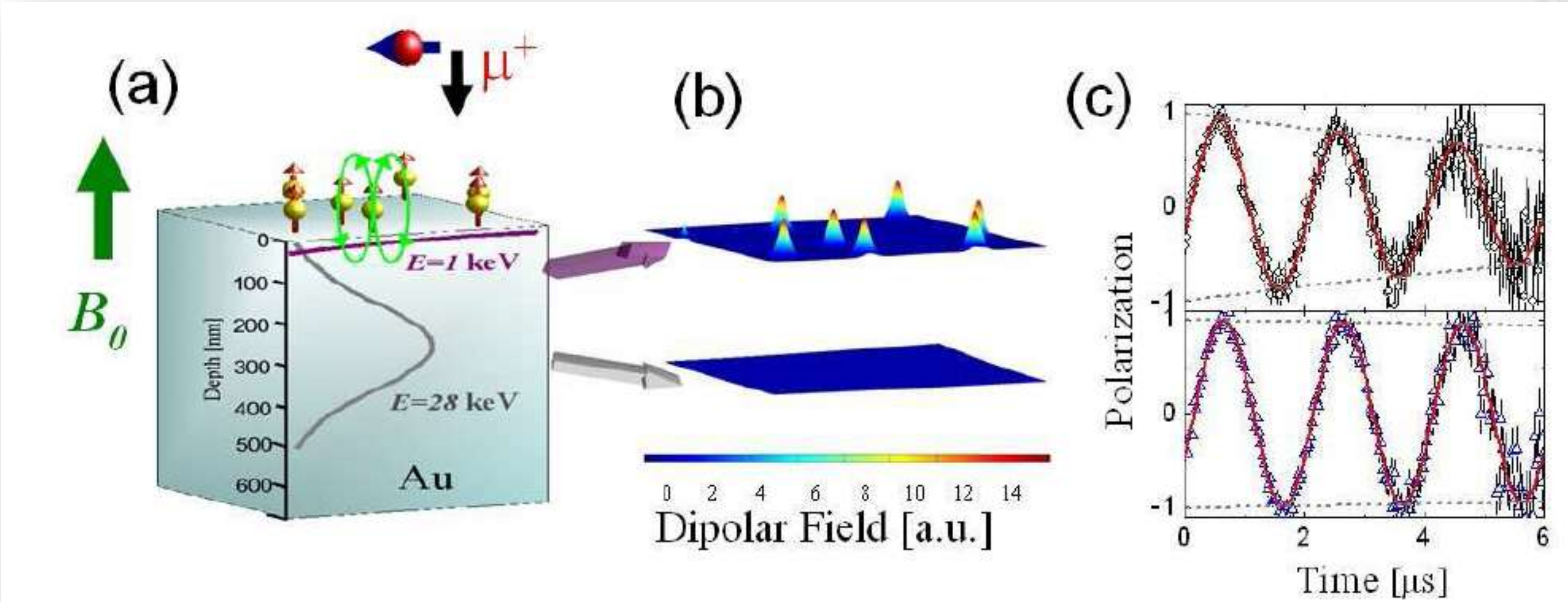






Measuring the varation of the spatial distribution of positrons emitted in the time it's possible to obtain information about the local magnetic fields experienced by the muons.

Implanted probes ($^8Li^+$, μ^+)



Muon: S=1/2

Muon decay (life time 2.2 μs)

$\mu^+ \longrightarrow e^+ + \nu_\mu + \nu_e$

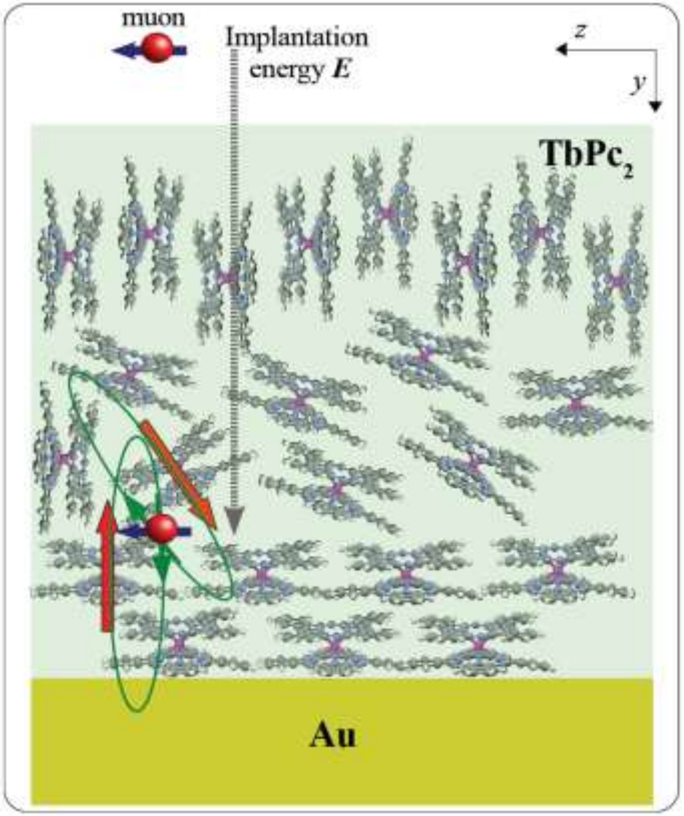
Positrons are preferentially emitted along muon spin

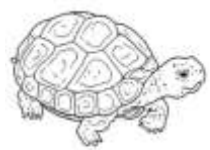
Low energy muons

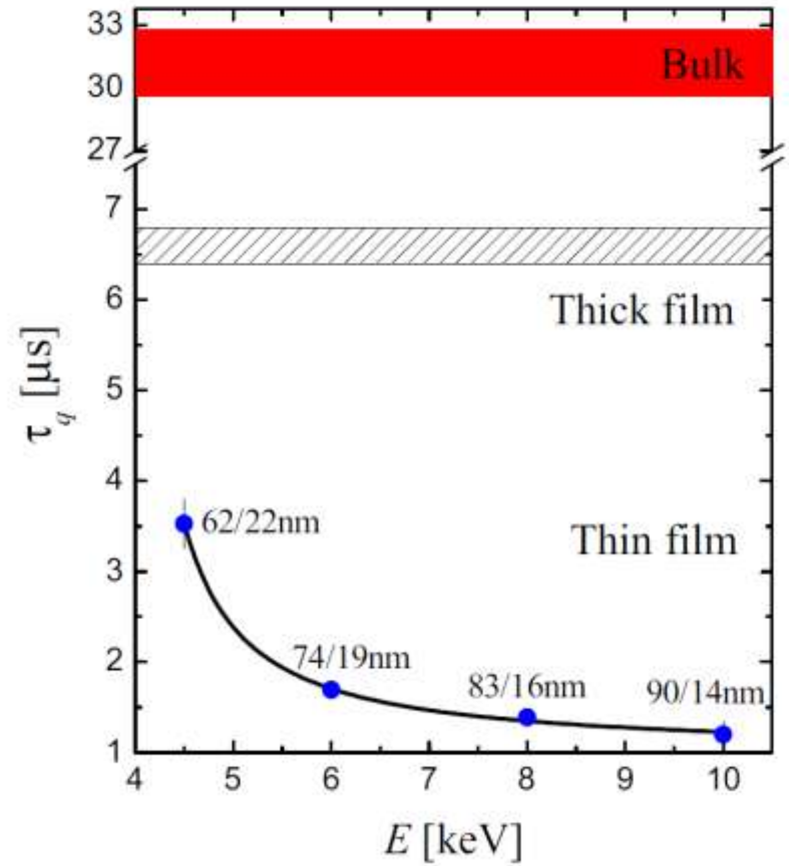
In collaboration with Zaher Salman @ PSI

$TbPc_2$ SMM films: implanted muons studies

Gradual increase of the relaxation time on increasing the distance from the Au substrate







Molecular packing is more important than electronic interaction with the substrate

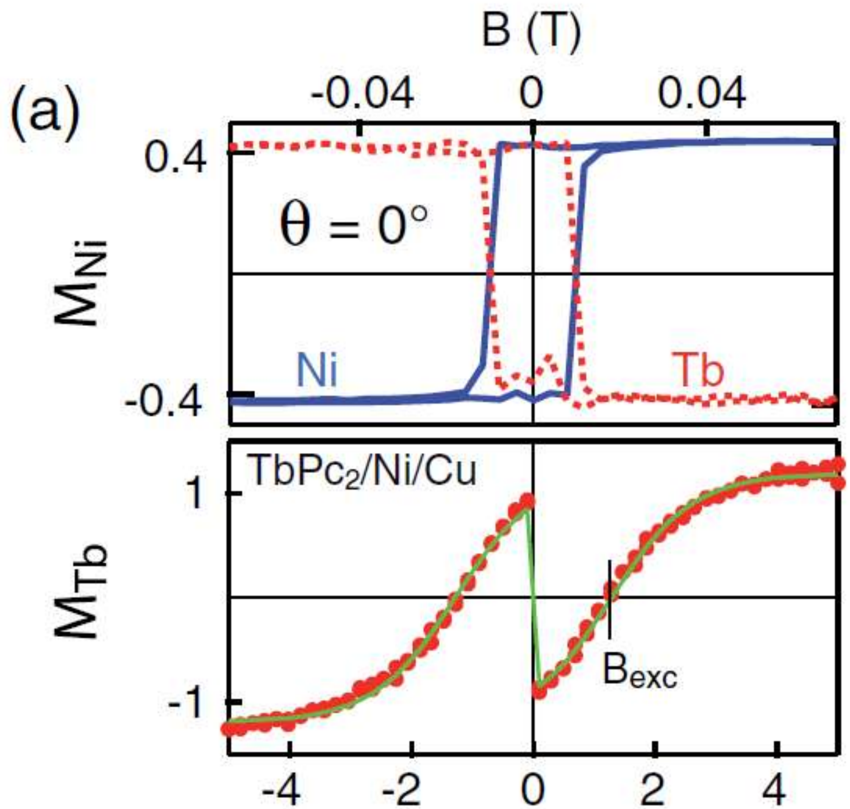
Hofmann & al *ACS Nano*
doi:10.1021/nn3031673

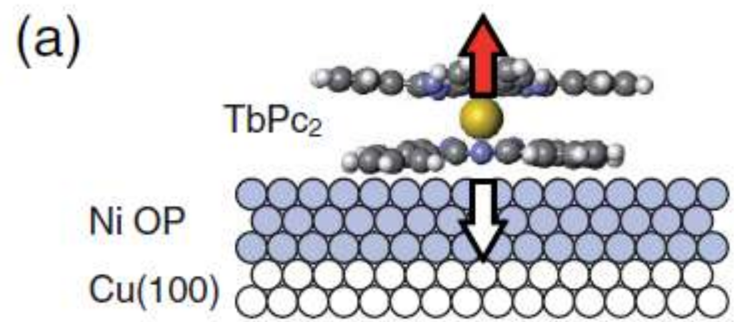
$TbPc_2$ on a magnetic substrate

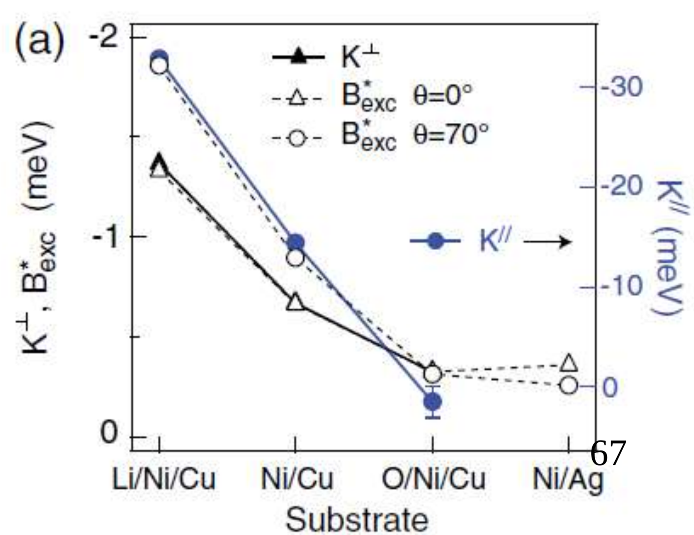
PRL **107,** 177205 (2011)

Coupling Single Molecule Magnets to Ferromagnetic Substrates

A. Lodi Rizzini,[1] C. Krull,[1] T. Balashov,[1] J. J. Kavich,[1] A. Mugarza,[1] P. S. Miedema,[2] P. K. Thakur,[3] V. Sessi,[3] S. Klyatskaya,[4] M. Ruben,[4,5] S. Stepanow,[6] and P. Gambardella[1,7,8]



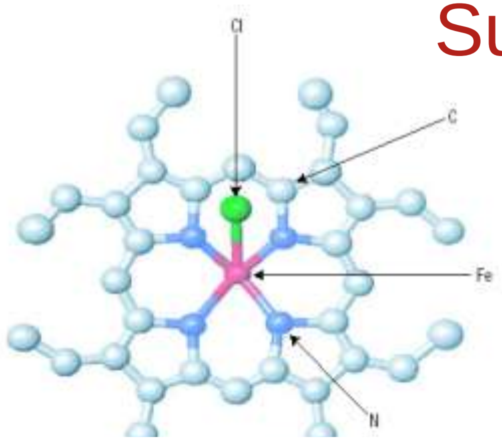




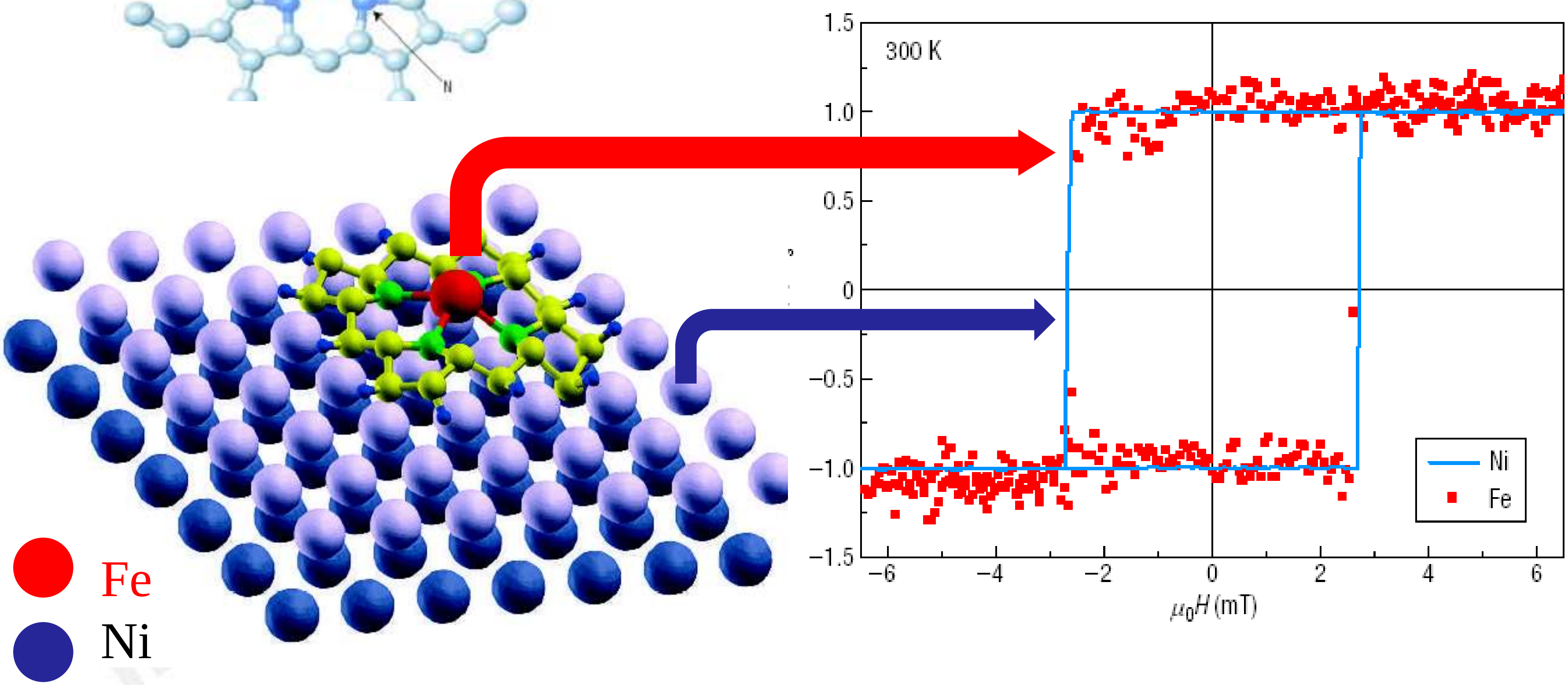
MODERATE AF INTERACTION

Magnetic molecules on a magnetic surface

Surface induced hysteresis @ 300 K

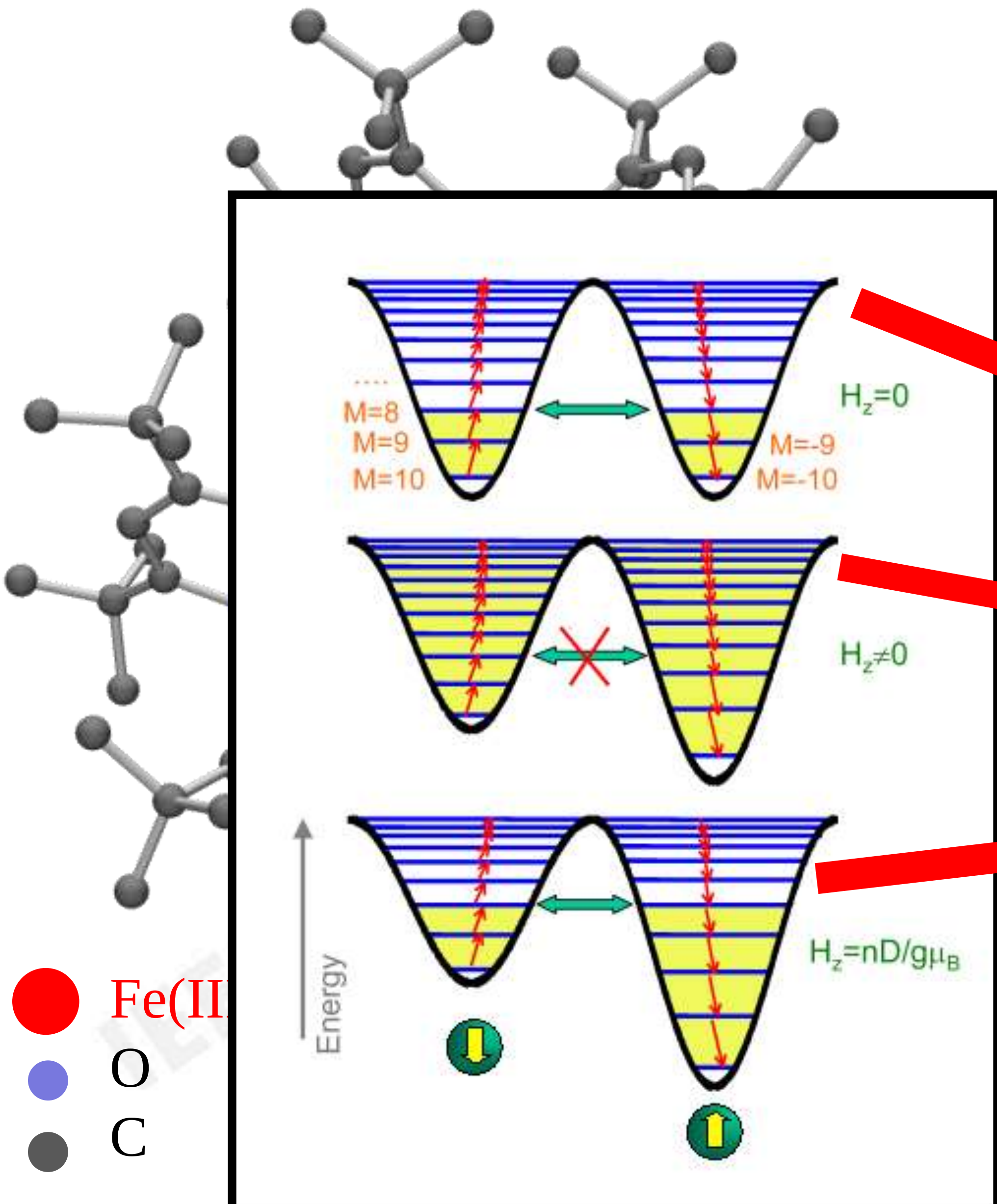


Fe octaethylporphyrin (OEP) chloride molecule
Sublimated on Co or Ni films on Cu(100)



Wende et al. *Nature Materials* VOL 6 JULY 2007, p. 516

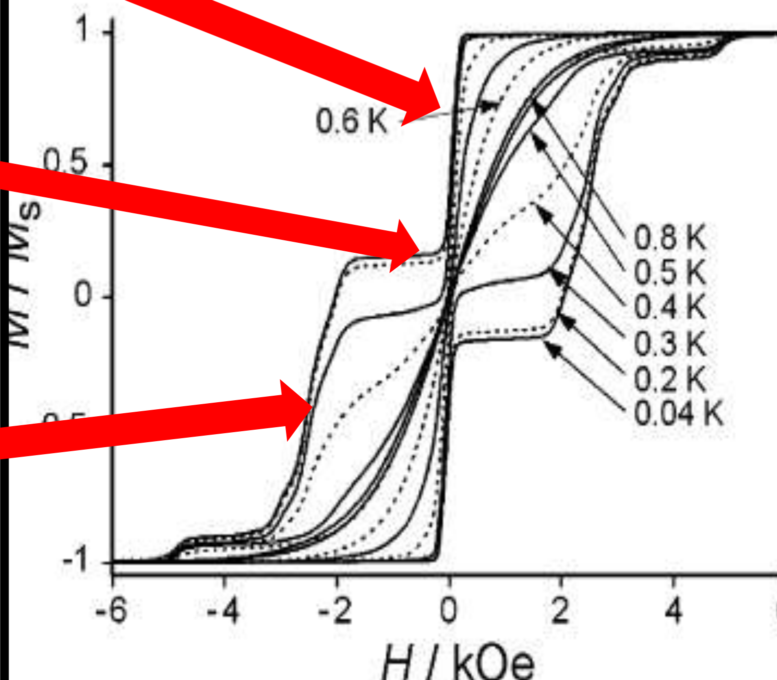
Fe_4: another robust SMM



$S_T=3x5/2-5/2=5$

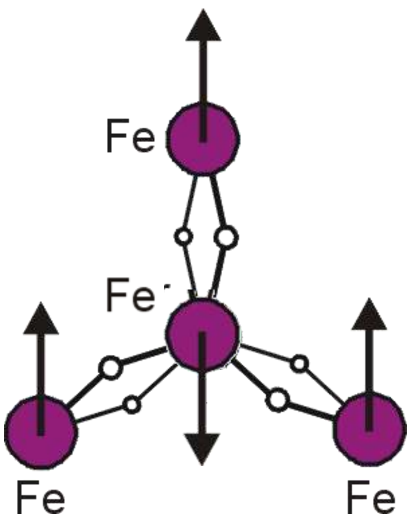
↓

Lower T_B than Mn_{12}

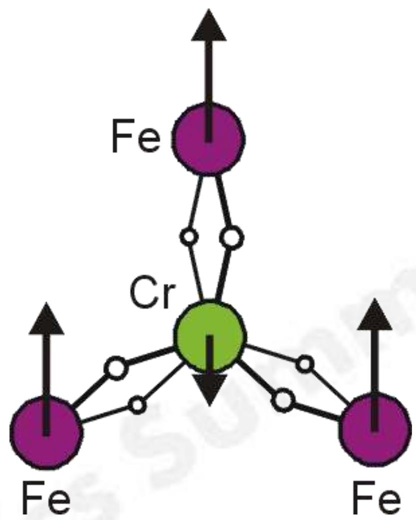


- Fe(II
- O
- C

Fe_3M propellers

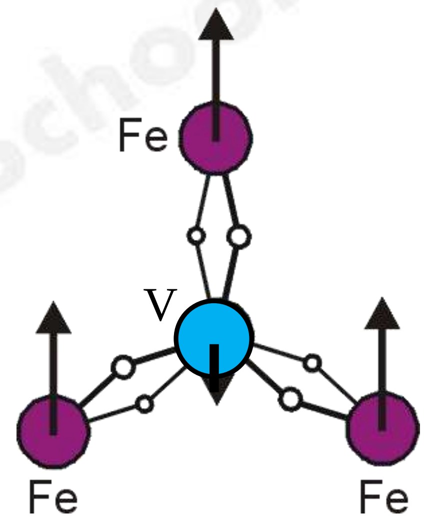


S = 5
D = -0.45 cm^{-1}
ΔE ~15 K



S = 6
D = -0.16 cm^{-1}
ΔE ~8 K

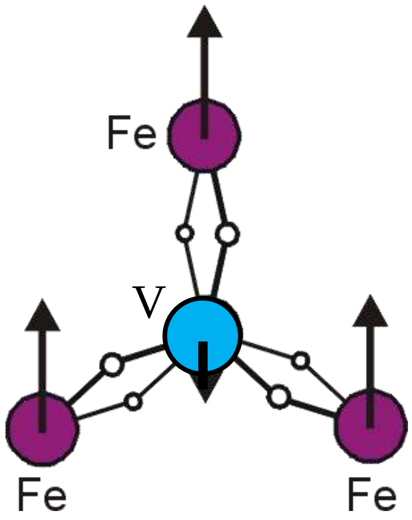
100% pure

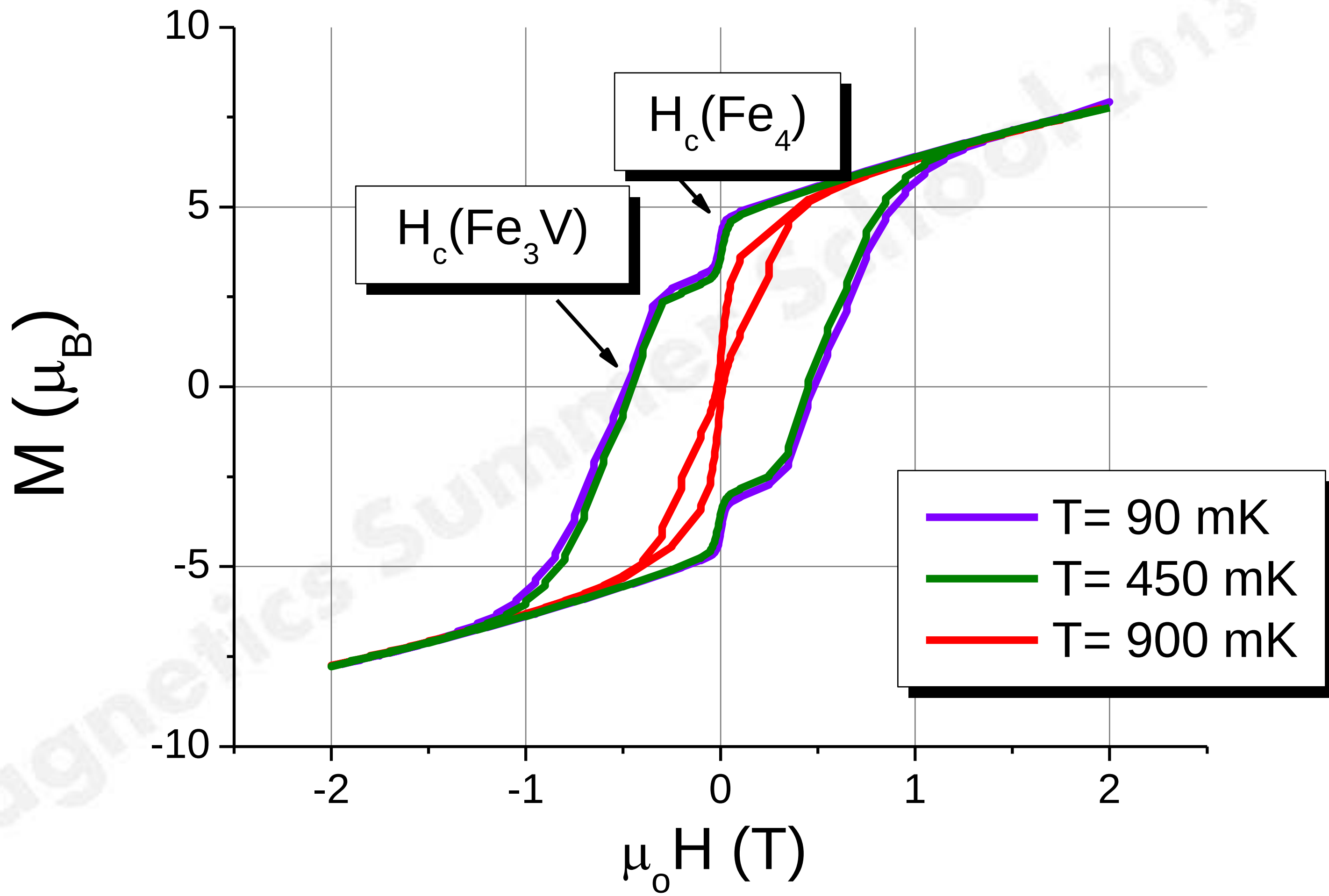


S = 13/2
D ~ -0.35 cm^{-1}
ΔE ~21 K

Small impurity of Fe_4

Adding remnant magnetization by chemical design



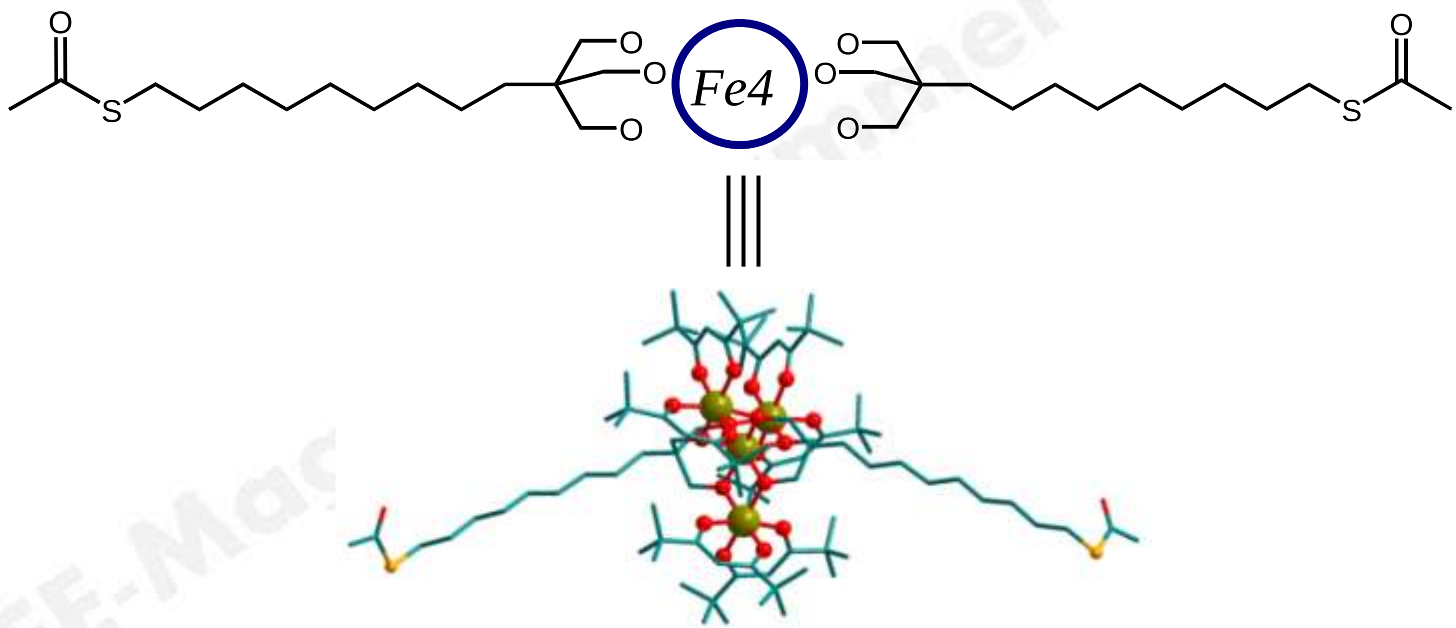


Zero Field Tunneling is less efficient for S=13/2

In collaboration with Dr. Carley Paulsen @ CNRS, Grenoble

Functionalization of Fe_4 clusters

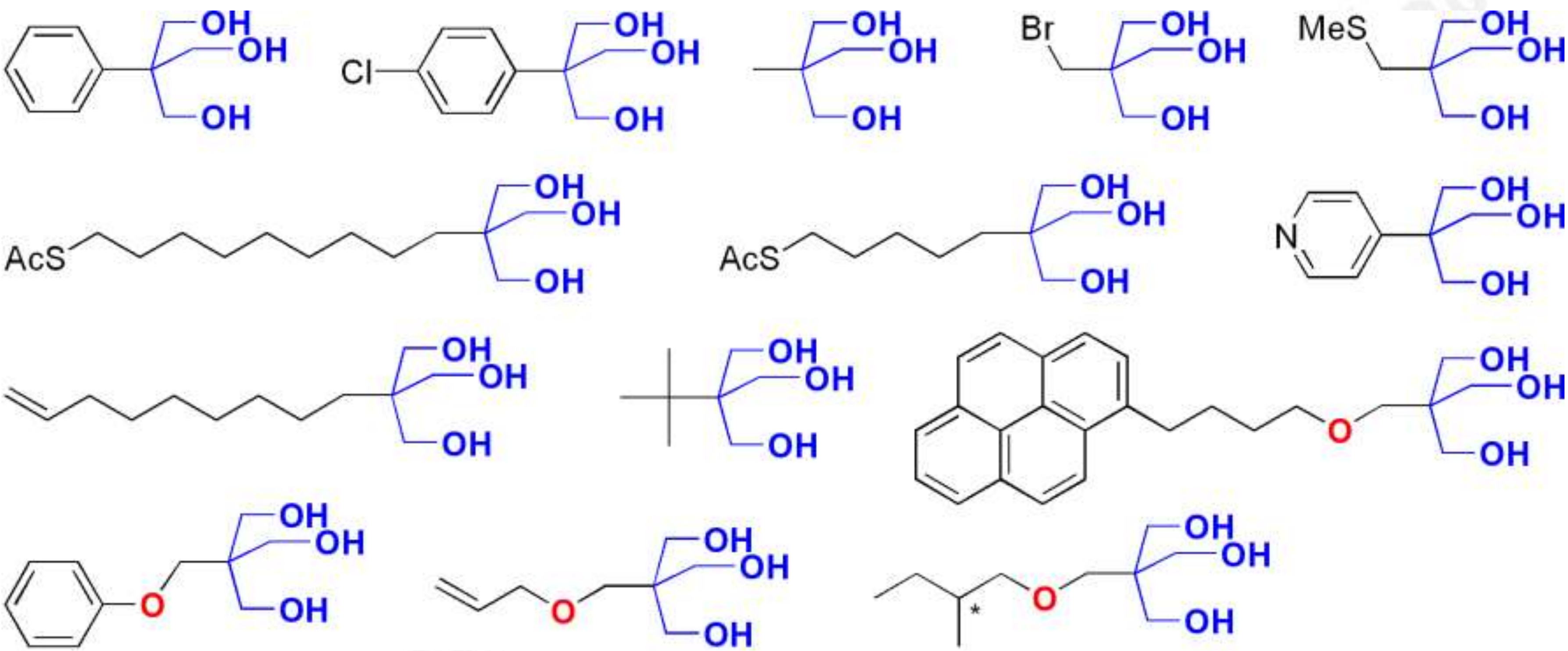
- *Functionalization by means of ligand exchange*
- *Two triol ligands take the place of six methoxides*
- *Sulphur-based functional groups make cluster bind to gold surfaces*



Fe4C9SAc

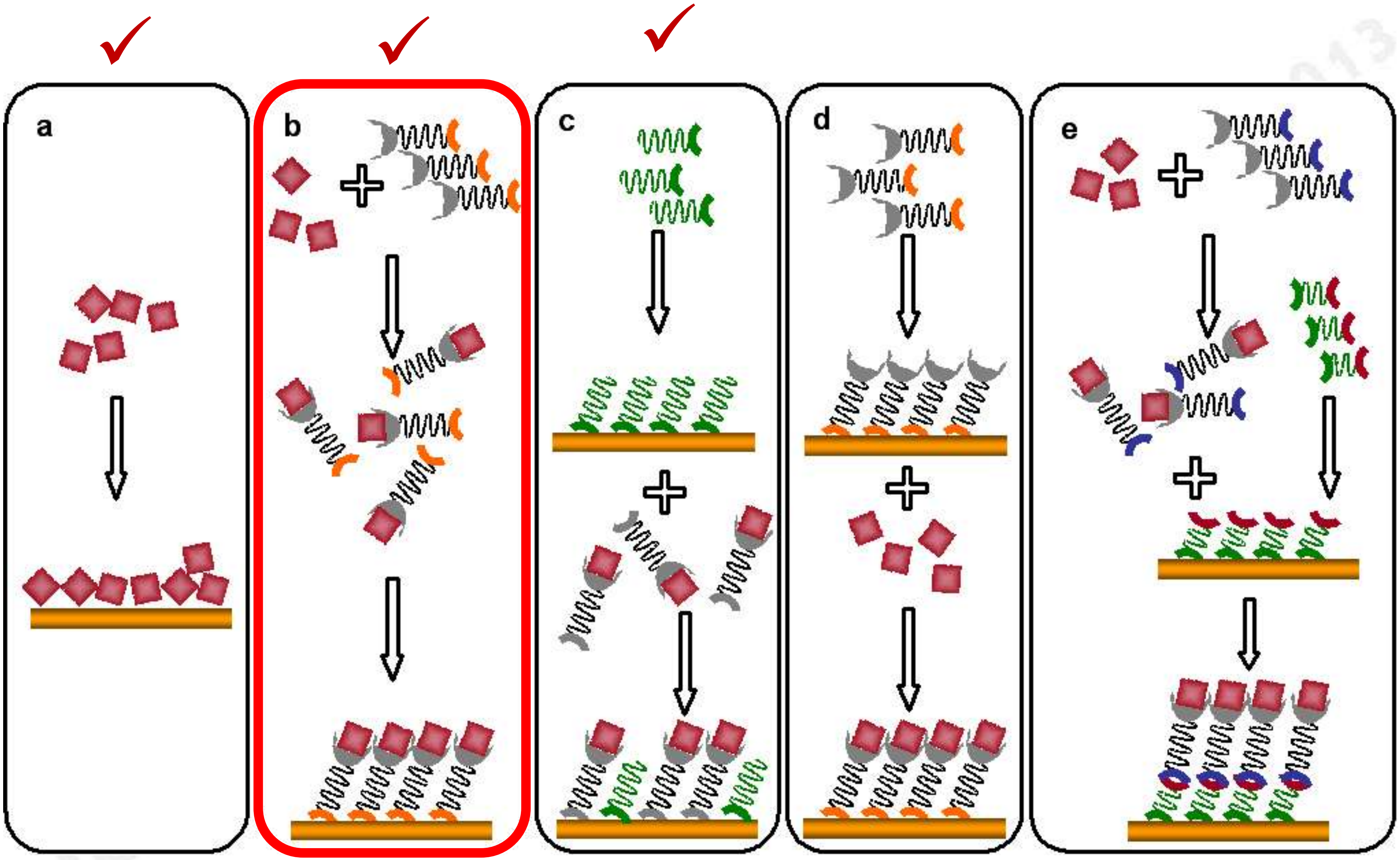
By Andrea Cornia, University of Modena , Italy

Functionalization of Fe_4 clusters



By Andrea Cornia, University of Modena , Italy

Deposition of molecules on surfaces



X-ray Magnetic Circular Dichroism at low temperature

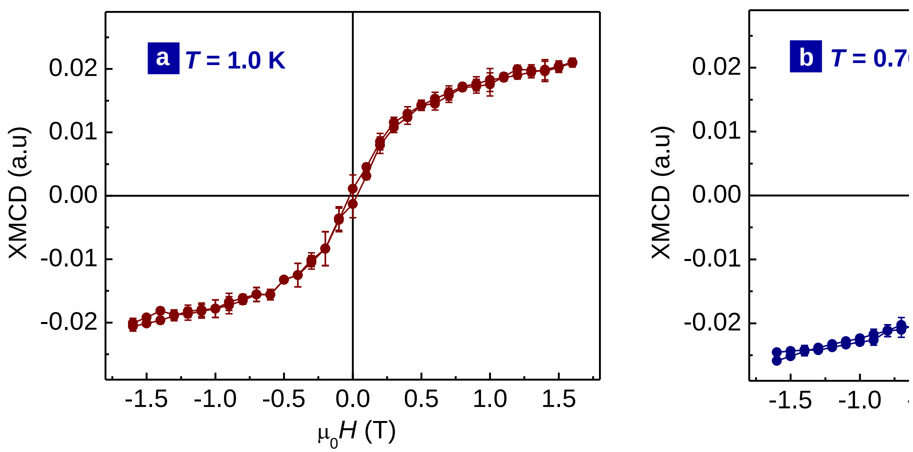
French End-Station (TBT)
setup by
J.-P. Kappler
(IPCMS, Strasbourg)
&
Ph. Sainctavit
(IMPMC. Paris)

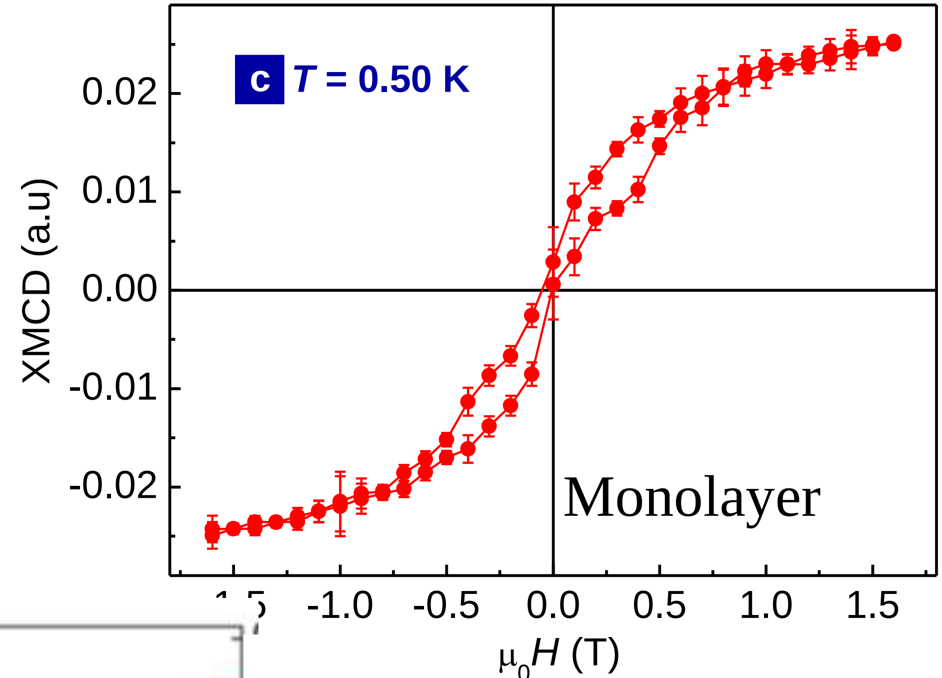
- UHV, bakeable
- ^3He-^4He dilution refrigerator:

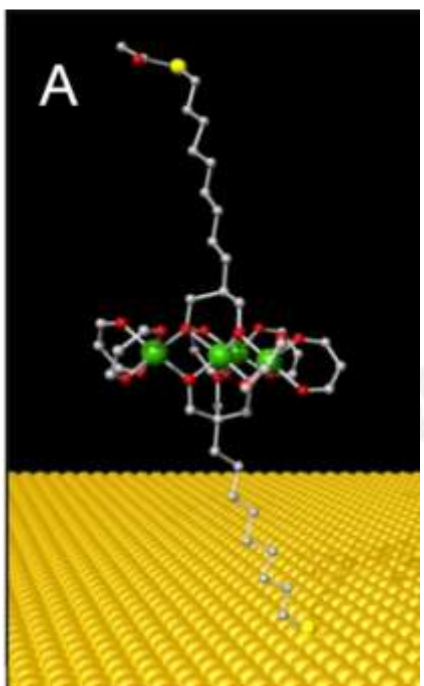
  T ≈ 500 mK
- Superconducting coil :

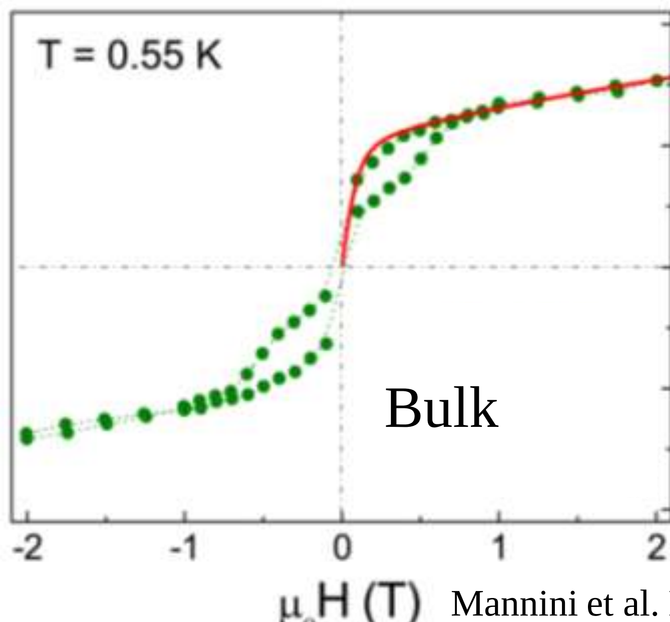
  -7 T < B < +7 T

Magnetic hysteresis of Fe_4 wired to a gold surface



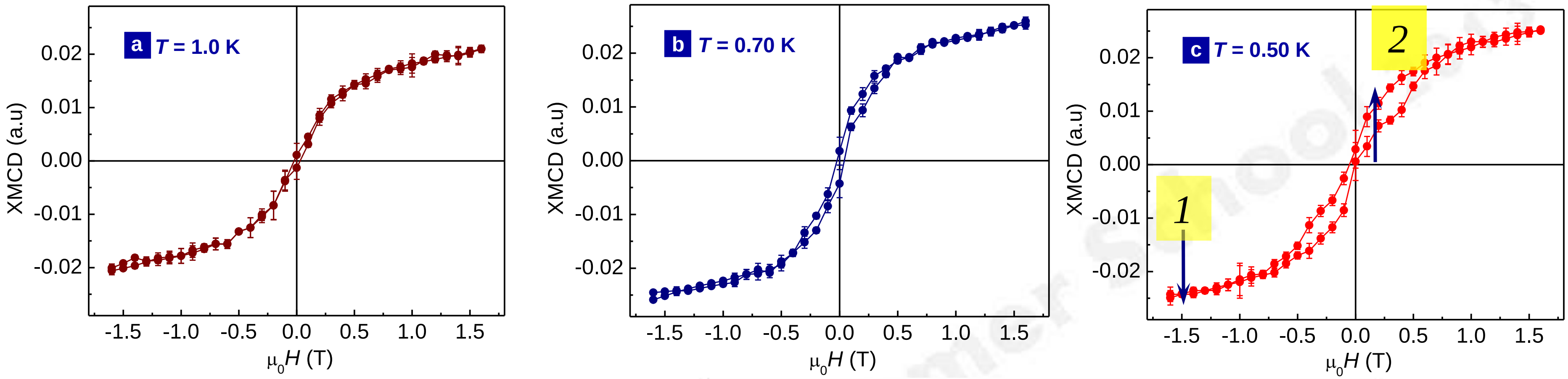


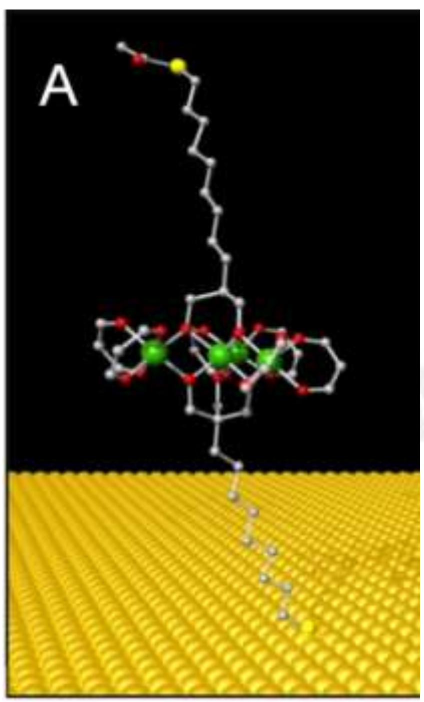


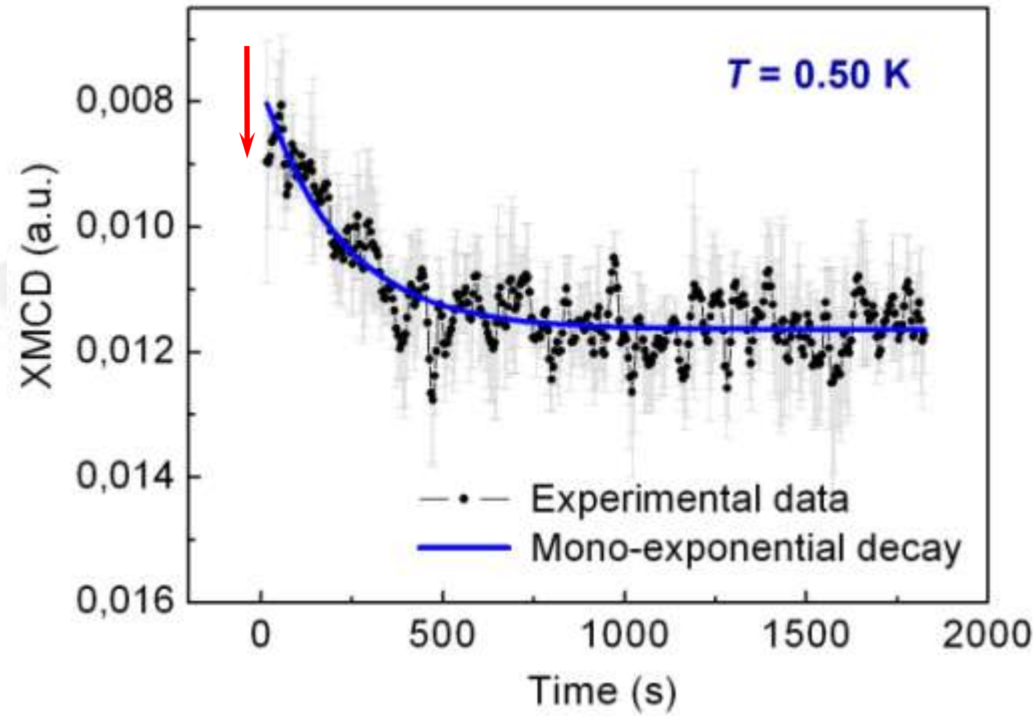


Mannini et al. Nature Mat 2009: doi:10.1038/NMAT2374

Magnetic hysteresis of Fe_4 wired to a gold surface

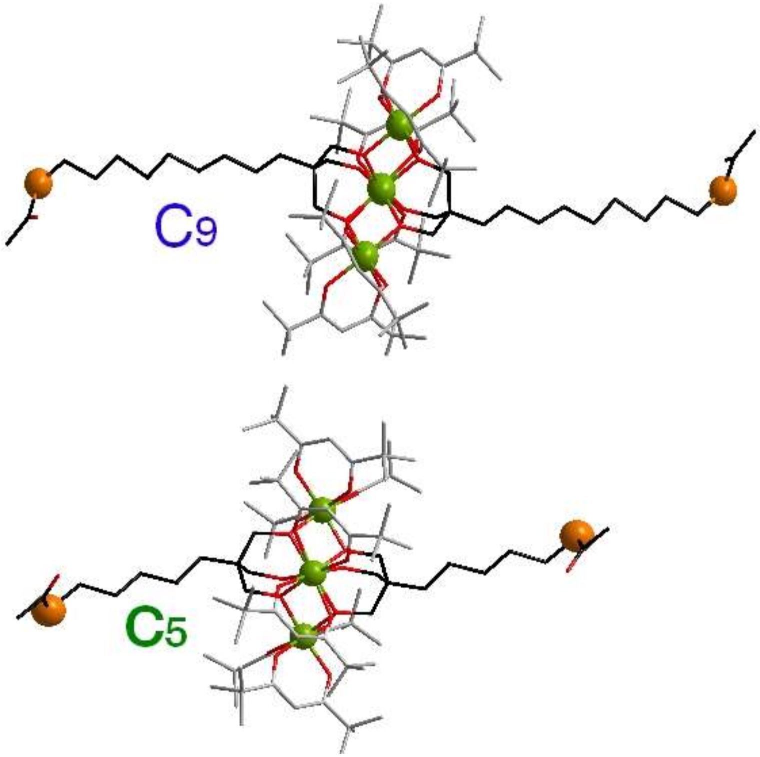


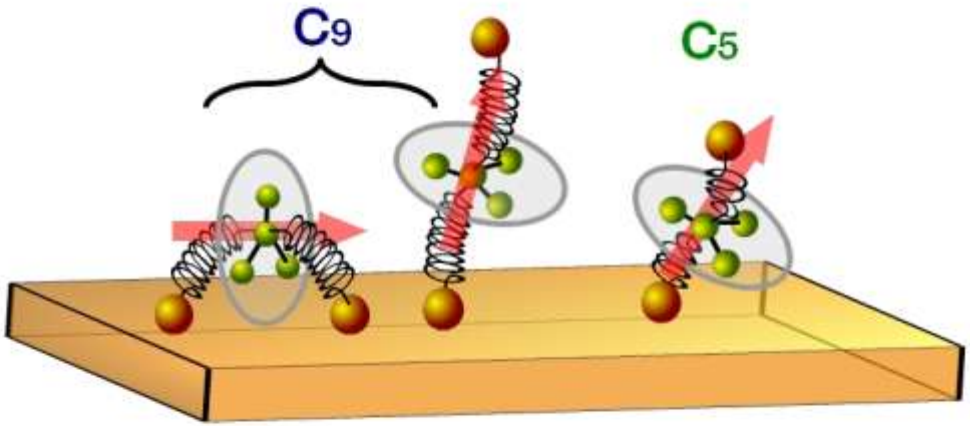


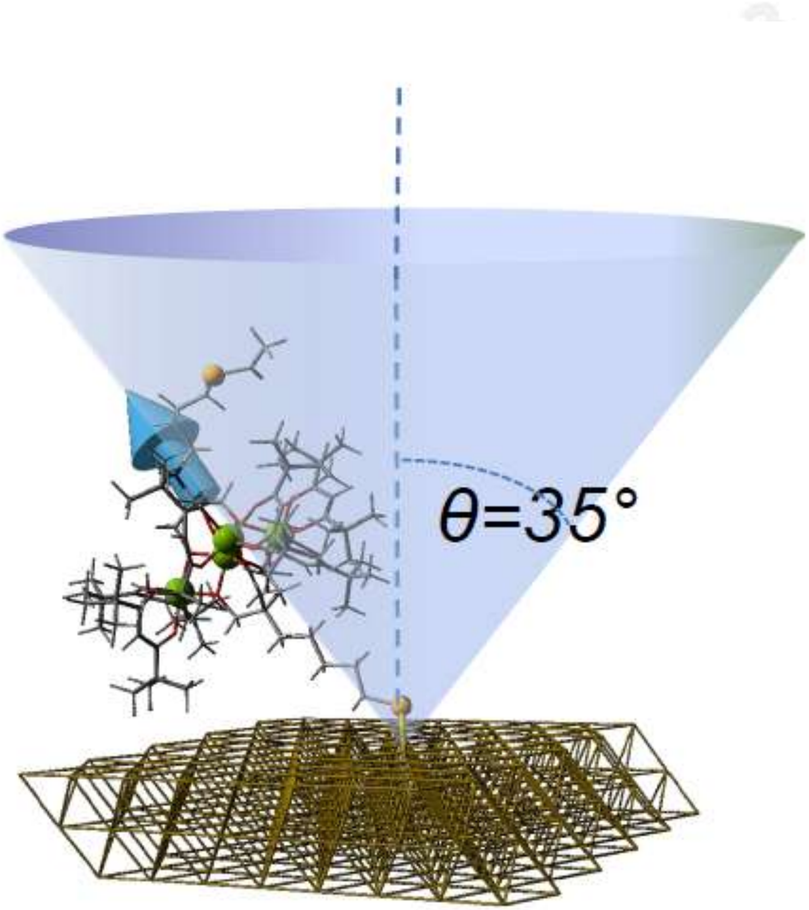


Mannini et al. Nature Mat 2009: doi:10.1038/NMAT2374

Control of the orientation on the surface

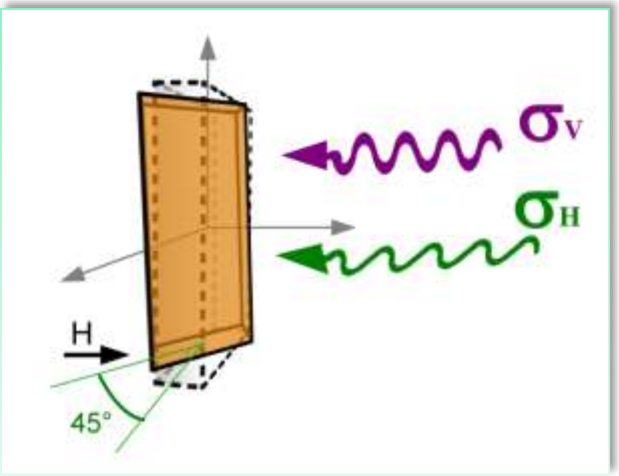




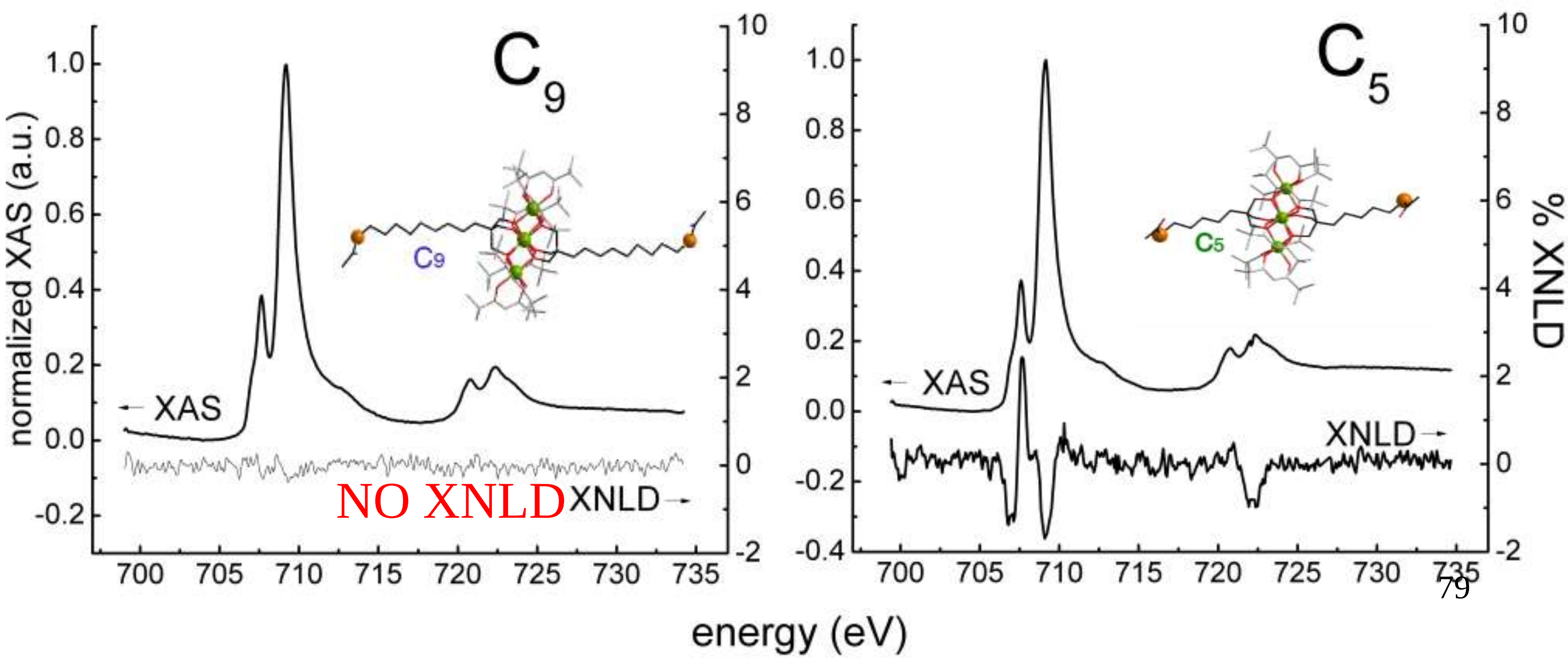


DFT calculations by Federico Totti

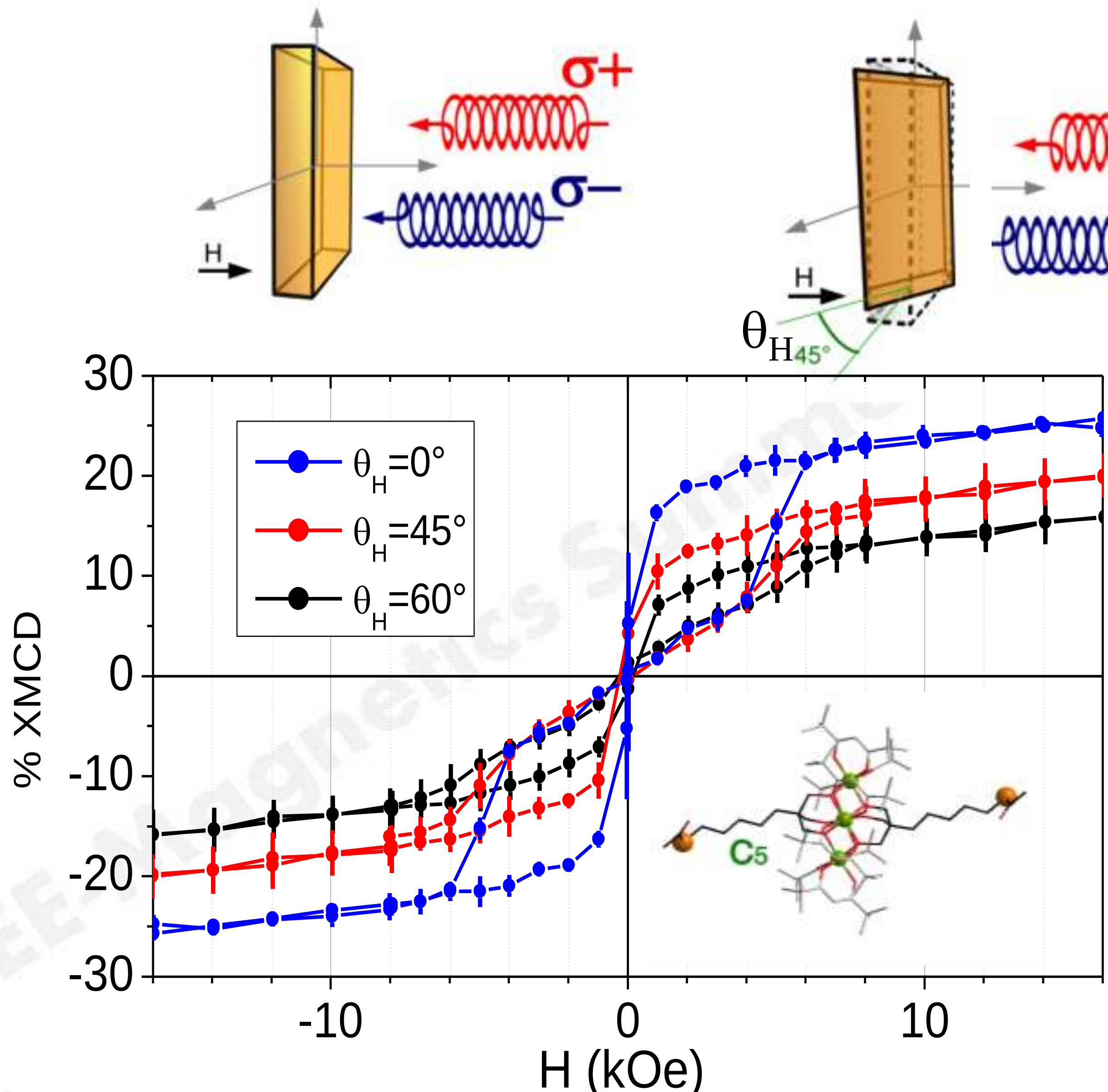
Natural Linear Dichroism @ Fe – L edge



XNLD: An experimental technique sensitive to the orientation of molecules on the surface



Angular Dependence of the Magnetic Hysteresis



T=650 mK

Mannini et al. *Nature* 2010, *468*, 417

SMM: Quantum Master Matrix Approach

$$\frac{d\vec{N}}{dt} = \tilde{\Gamma}\vec{N}$$

$$\Gamma_q^m = \gamma_q^m - \delta_q^m \sum_{m'} \gamma_{m'}^m$$

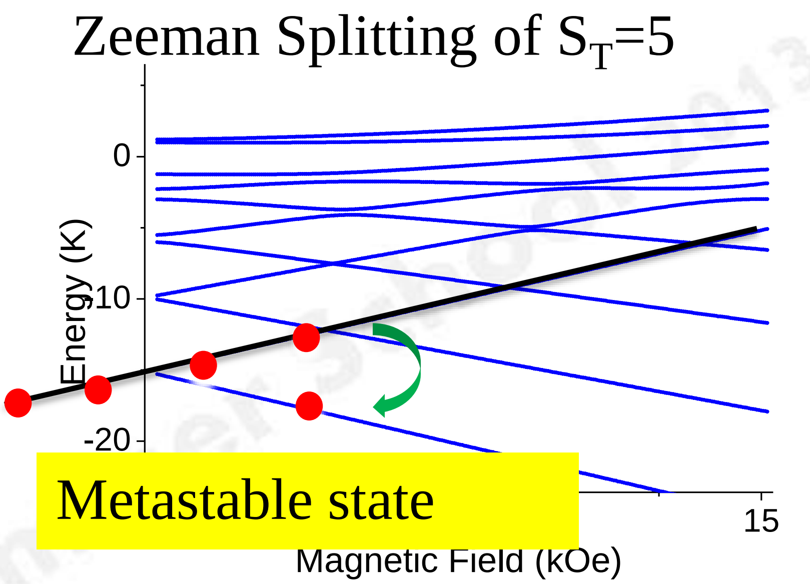
$$\tilde{\Gamma} = \begin{pmatrix} -\sum_{m'\neq 1}\gamma_1^{m'} & \gamma_2^1 & \cdot & \cdot & \gamma_{2s+1}^1 \\ \gamma_1^2 & -\sum_{m'\neq 2}\gamma_2^{m'} & \cdot & \cdot & \gamma_{2s+1}^2 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \gamma_1^{2s+1} & \gamma_2^{2s+1} & \cdot & \cdot & -\sum_{m'\neq s}\gamma_{2s+1}^{m'} \end{pmatrix} \qquad \vec{N} = \begin{pmatrix} N_1 \\ N_2 \\ \cdot \\ \cdot \\ N_{2S+1} \end{pmatrix}$$

$$\gamma_q^p = \frac{3}{\pi\hbar^4\rho c_s^5}\frac{\left(E_p - E_q\right)^3}{\left[e^{(E_p-E_q)/k_BT} - 1\right]}\left|\left\langle\varphi_p \,|\, \mathcal{H}_{S-Ph} \,|\, \varphi_q\right\rangle\right|^2$$

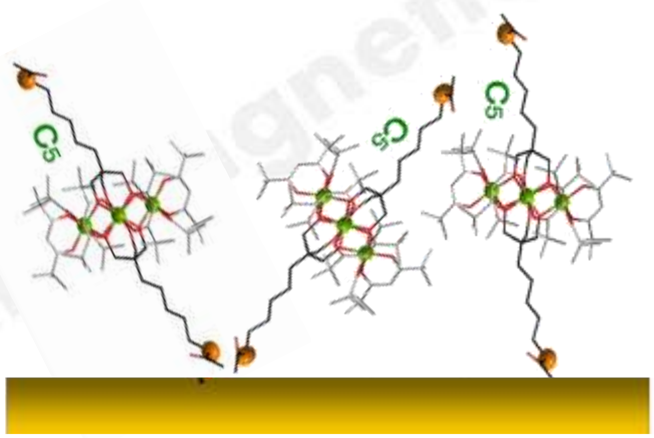
$$M(t) = \sum_m p_m(t)\frac{dE_m}{dH}$$

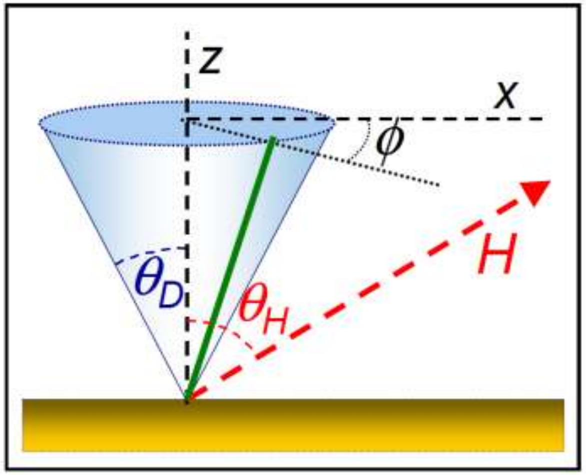
$$\frac{d}{dt}p_m(t) = \sum_q\left[\gamma_q^m p_q(t) - \gamma_m^q p_m(t)\right]$$

Numerical Simulation of the Magnetic Hysteresis



Quantum Master Matrix

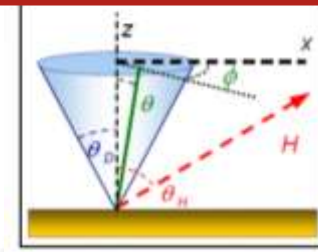




Numerical Simulation of the Magnetic Hysteresis

Spin-Hamiltonian Matrix Calculation

Integration over all permitted orientations



Diagonalization

Eigen-Values & Pn(t=∞)

Eigen-Vectors

$$|\varphi_q\rangle = \sum_{m=-S}^{S} \lambda_m^q \, |m\rangle$$

Calculation of transition probabilities γ_n^q

Diagonalization of Master equation & Calculation of τ

Calculation of the change in population

$$\frac{d}{dt} p_m(t) = \sum_q \left[\gamma_q^m p_q(t) - \gamma_m^q p_m(t)\right]$$

H'=H+dH

Calculation of the magnetization

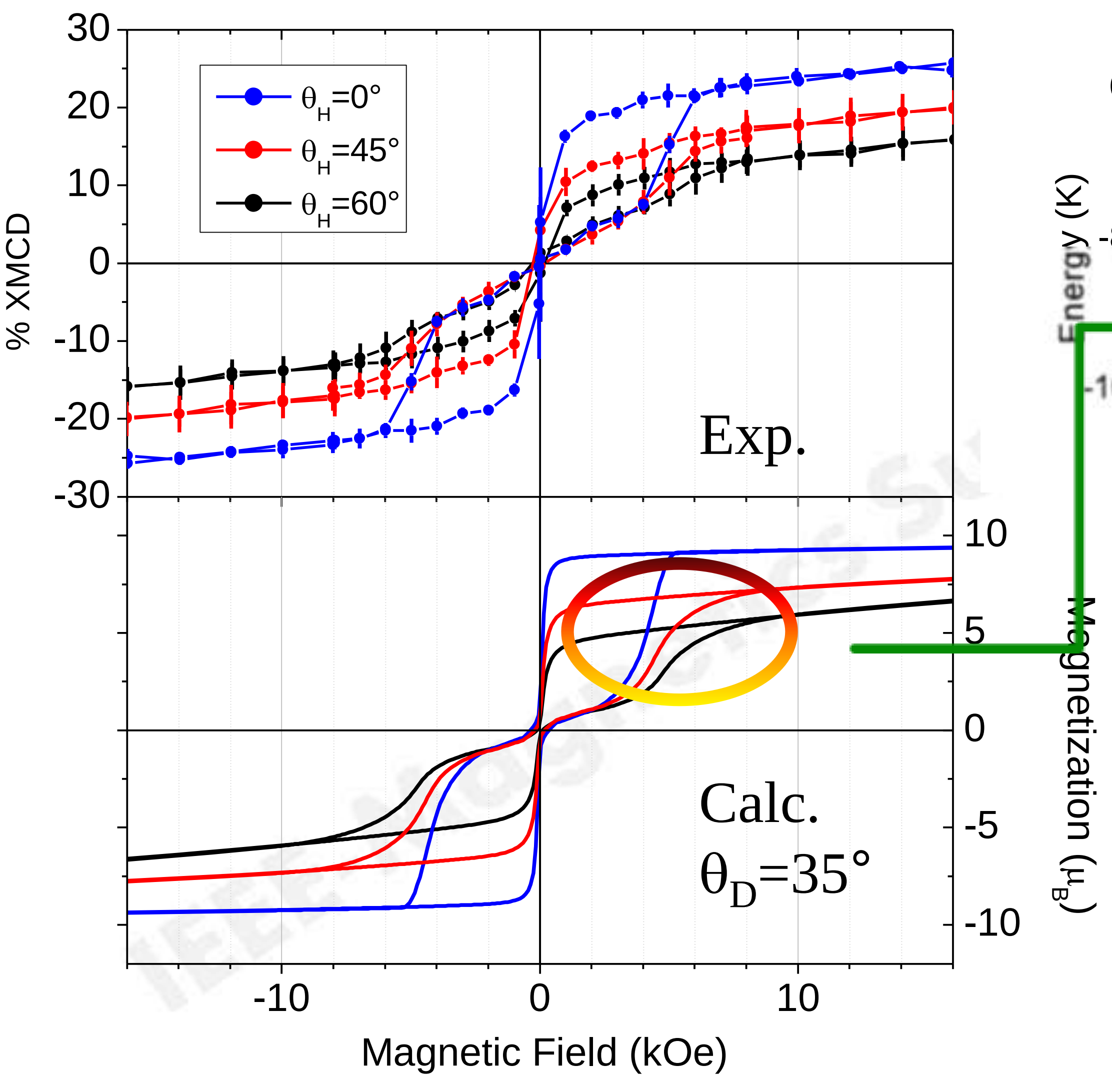
$$M(t) = -\sum_m p_m(t) \frac{dE_m}{dH}$$

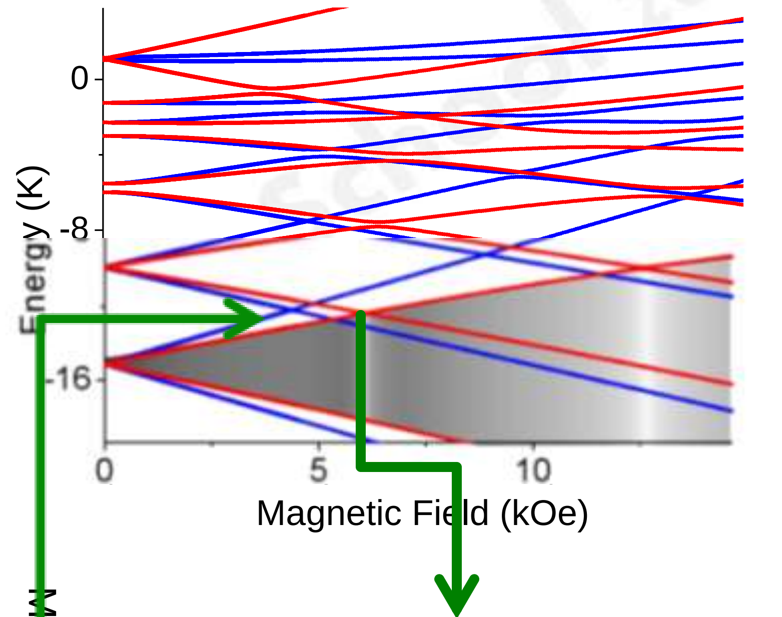
To have a statistical average: *γ'=γ/10000* and is cycled over *n* cycle

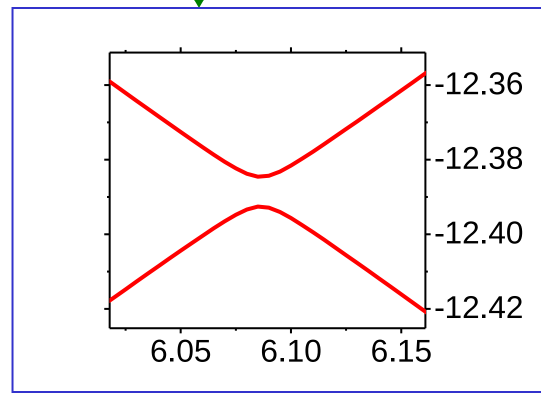
n & *dH* are chosen to correspond to experimental sweeping time

Numerical Simulation of the Magnetic Hysteresis

T=650 mK

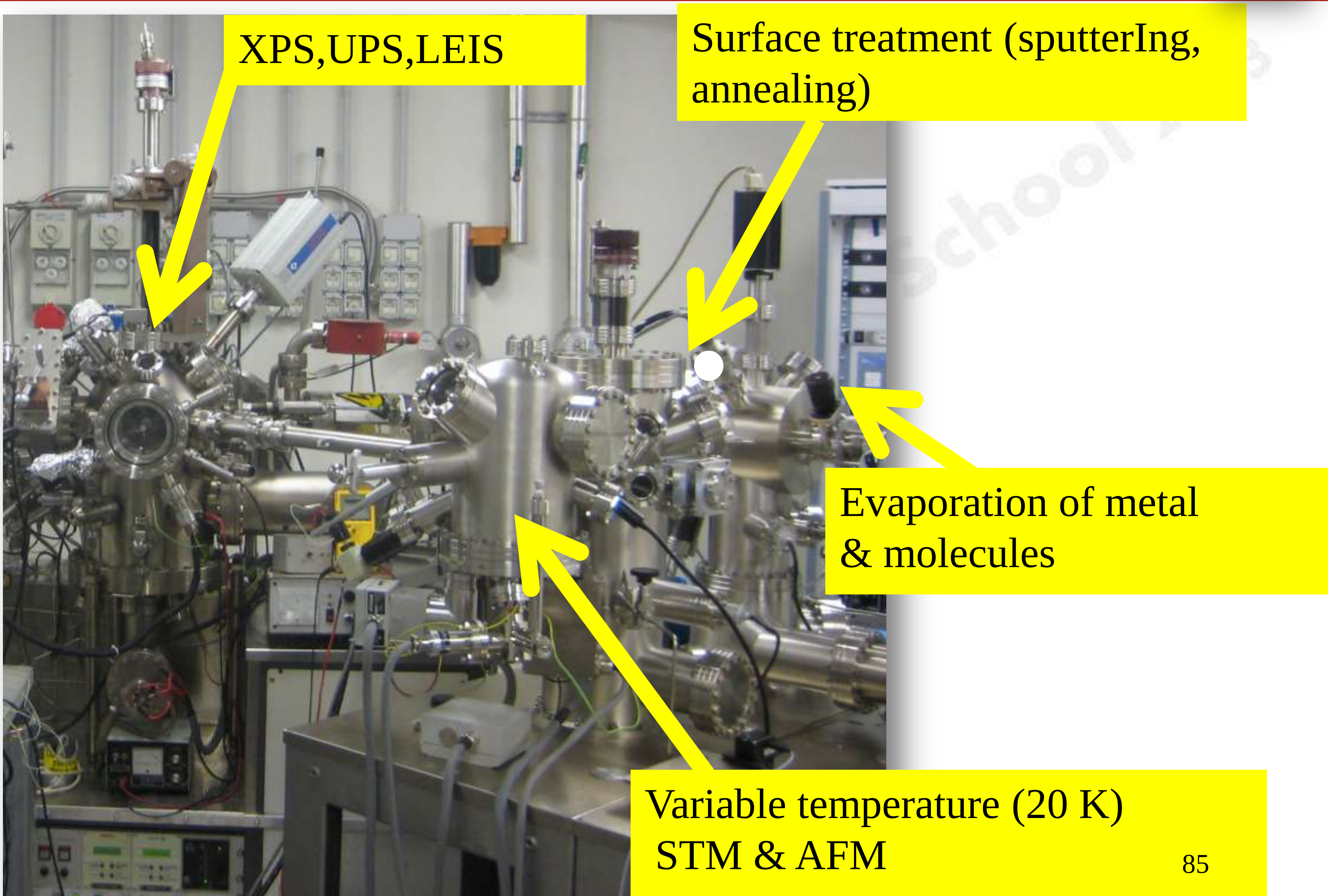




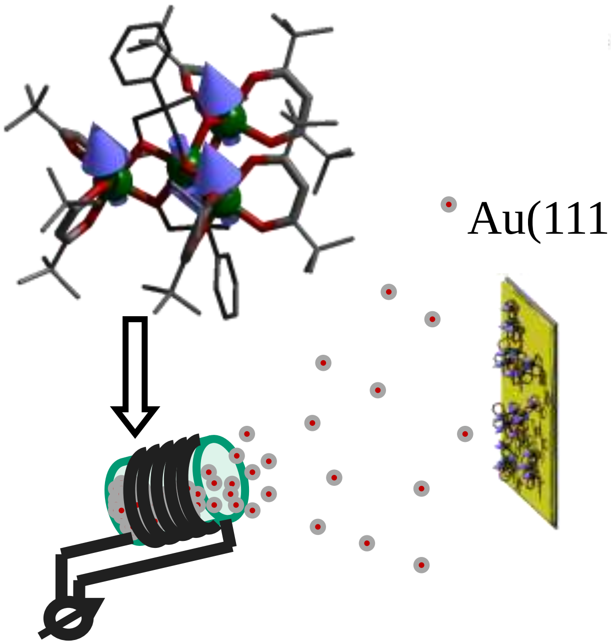


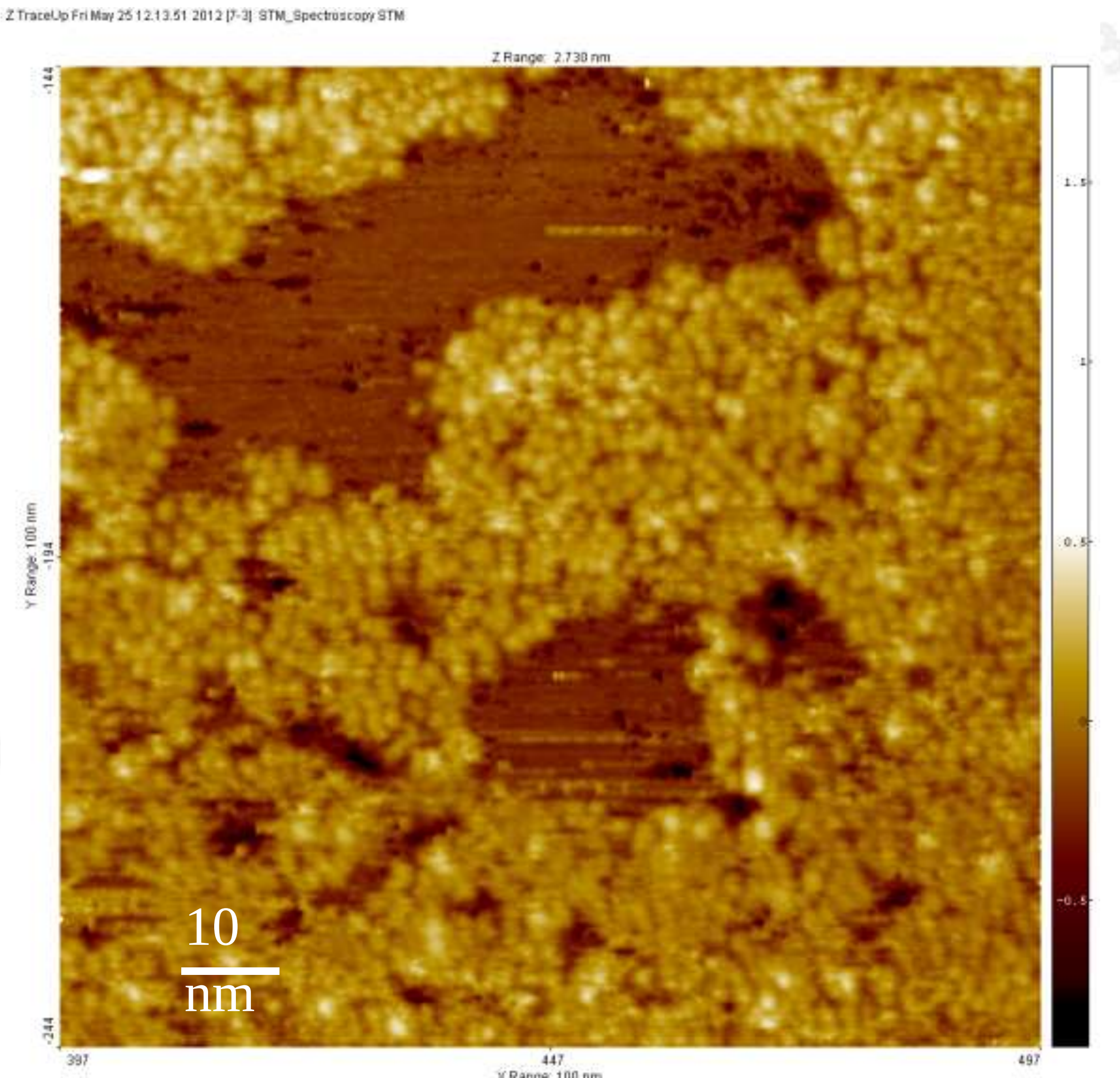
$\Delta E_{QT} \sim 10$ mK

UHV-Preparation & characterization facilities



STM image of Fe_4Ph evaporated on Au(111)



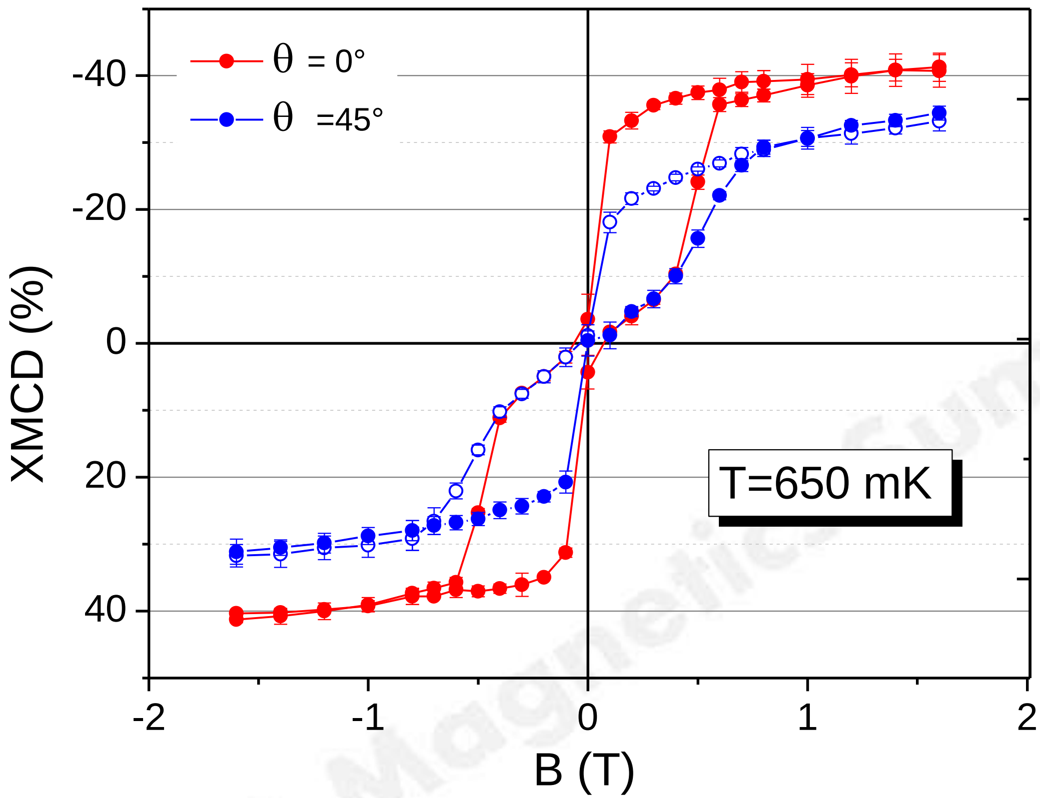


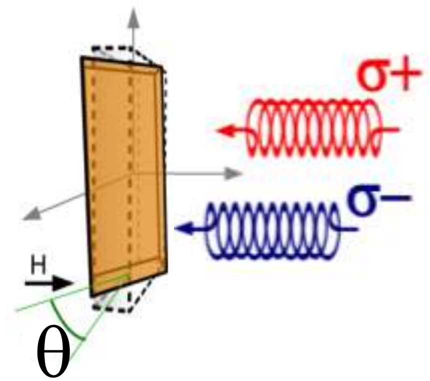
Fe_4Ph is weakly bound to Au but does not form multilayer aggregates

Malavolti et al.in preparation

XMCD of Fe_4Ph evaporated on Au(111)

Fe_4@Au; Fe L_2edge





angular dependent hysteresis

⇩

preferential orientation on the surface

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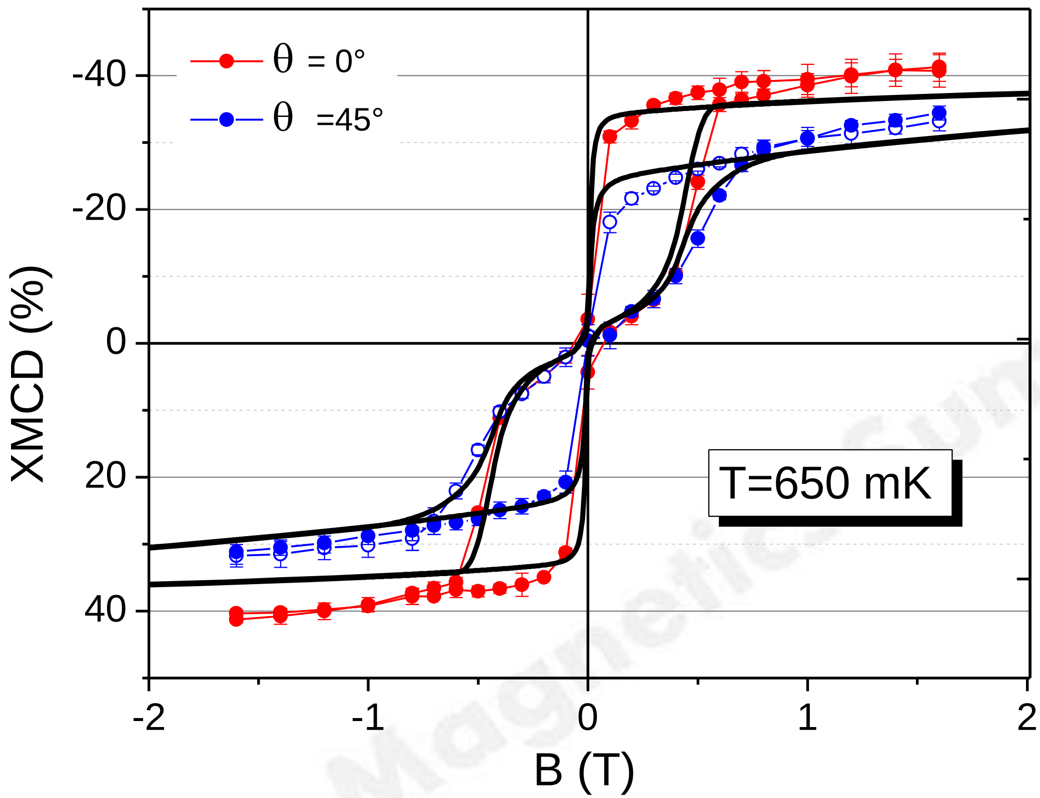
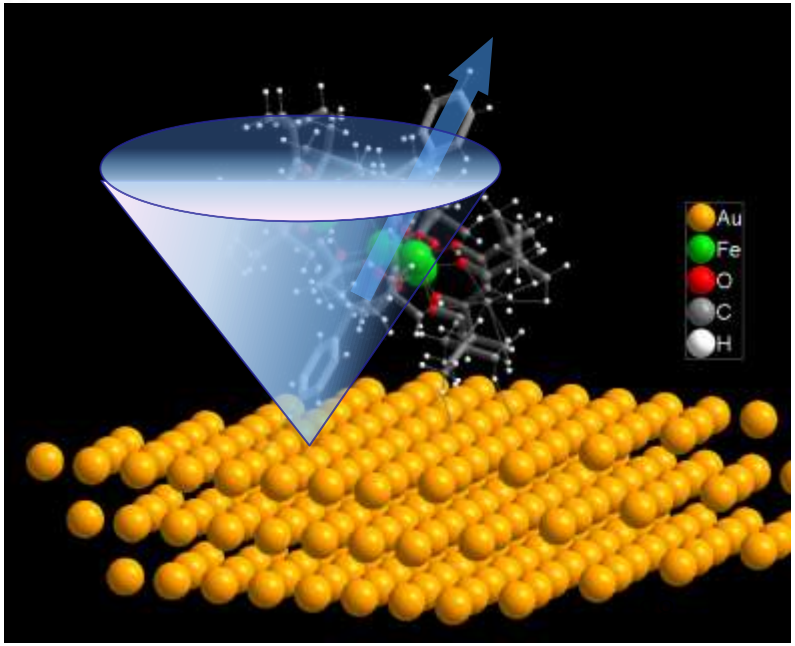
DIPARTIMENTO DI CHIMICA "UGO SCHIFF"

XMCD of Fe_4Ph evaporated on Au(111)

Fe_4@Au; Fe L_2edge

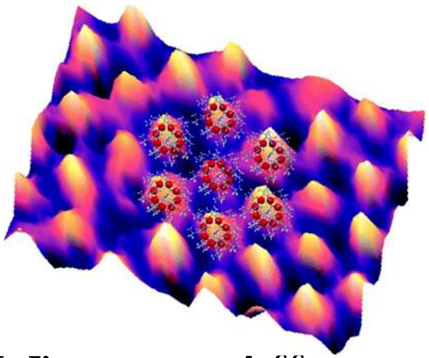


Simulated Hysteresis using a 45° cone



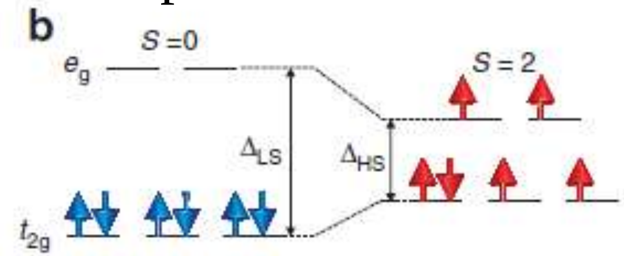
Beyond SMM

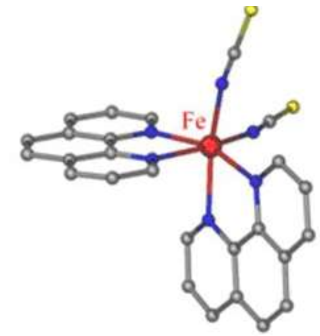
Molecular Q-bit



Winpenny, Affronte
ACS Nano 2012

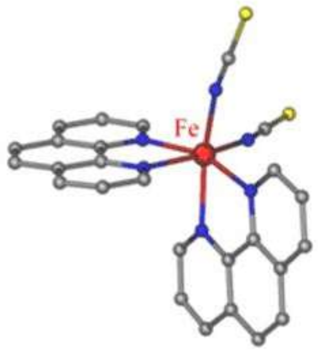
Spin cross-over





Evergreen spin crossover compounds

$Fe^{II}(phen)_2(NCS)_2$

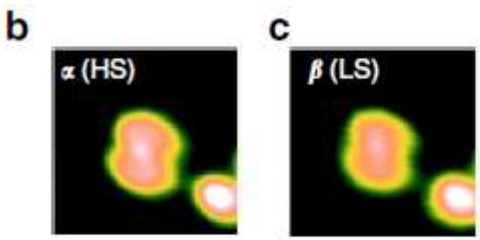


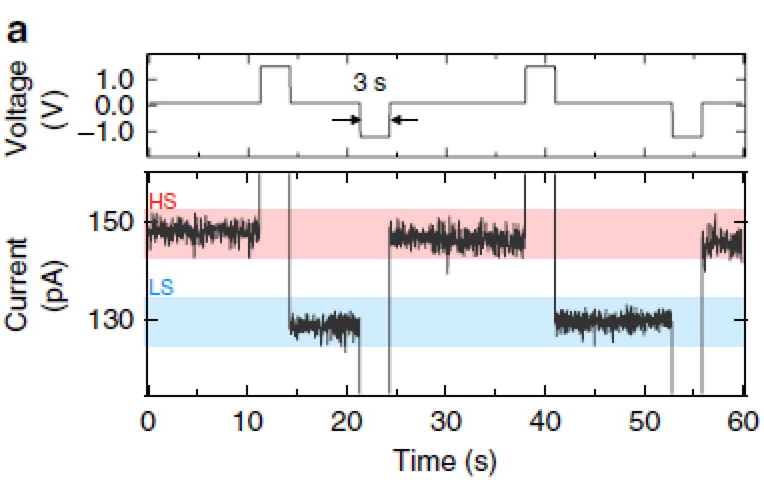
nature COMMUNICATIONS
DOI: 10.1038/ncomms1940

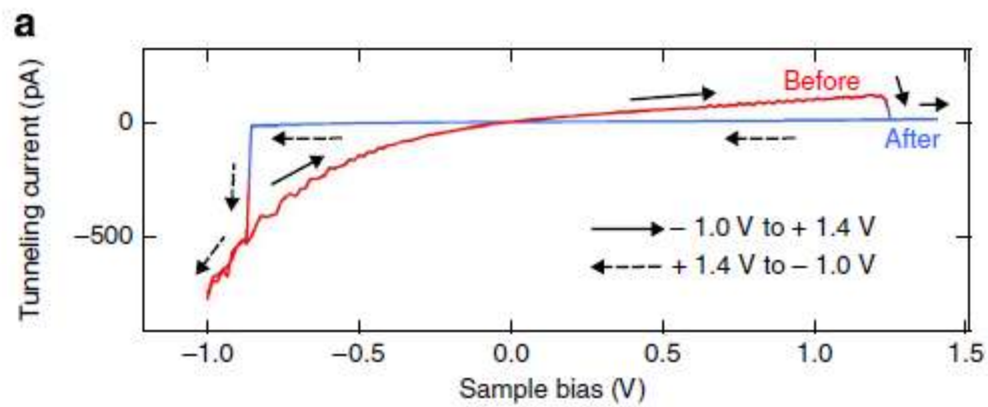
Robust spin crossover and memristance across a single molecule

Toshio Miyamachi[1,2], Manuel Gruber[1,3], Vincent Davesne[1,3], Martin Bowen[3], Samy Boukari[3], Loïc Joly[3], Fabrice Scheurer[3], Guillaume Rogez[3], Toyo Kazu Yamada[1,4], Philippe Ohresser[5], Eric Beaurepaire[3] & Wulf Wulfhekel[1,2]

Evaporated @ CuN/Cu







The bias applied with an STM tip can change the spin state in a reversible way

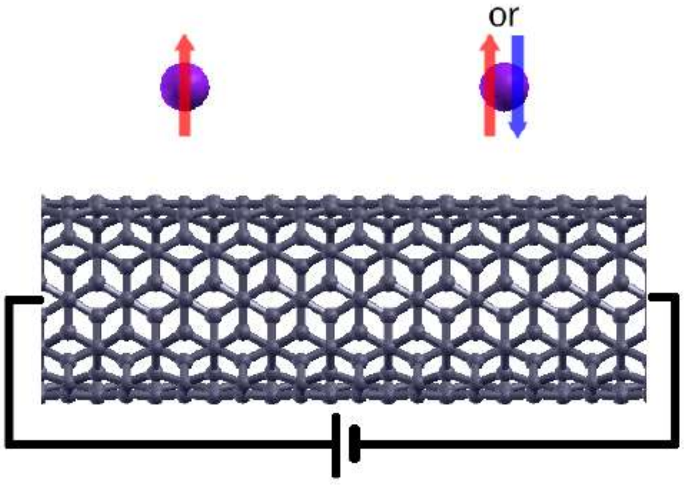
Magnetoresistance without magnetic electrodes

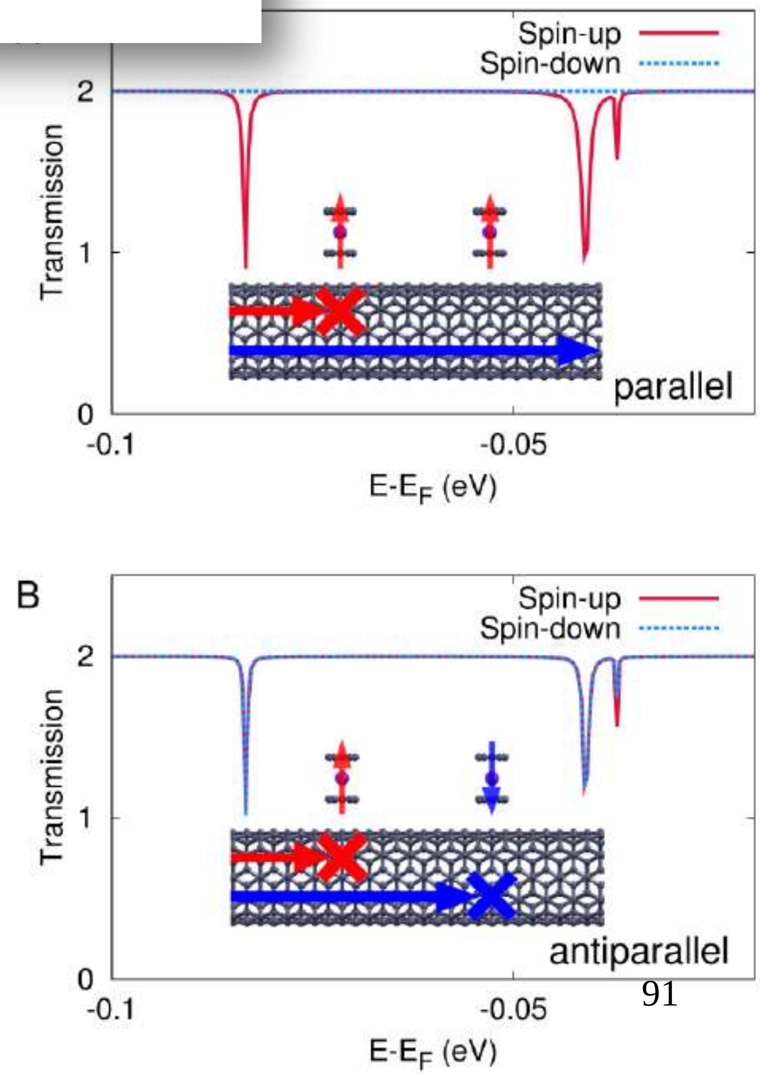
Molecular Spintronics

DOI: 10.1002/anie.201208816

Fano-Resonance-Driven Spin-Valve Effect Using Single-Molecule Magnets**

*Kwangwoo Hong and Woo Youn Kim**

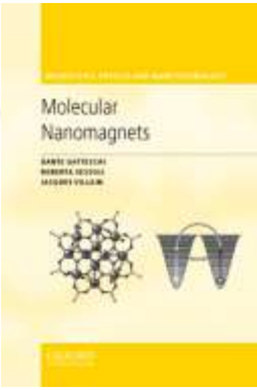




Further reading

SMM & Quantum Tunneling:

Molecular Nanomagnets
D. Gatteschi, R. Sessoli, J. Villain
Oxford University Press 2006



SMM & surfaces

Struct Bond (2006) [redacted]: 1–x
DOI 10.1007/430_029
© Springer-Verlag Berlin Heidelberg 2006
Published online: [redacted] 2006

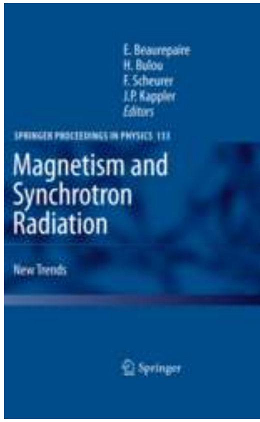
Vol 122

Preparation of Novel Materials Using SMMs

Andrea Cornia[1] (✉) · Antonio Fabretti Costantino[1] · Laura Zobbi[1] ·
Andrea Caneschi[2] · Dante Gatteschi[2] · Matteo Mannini[2] · Roberta Sessoli[2]

Magnetism & surfaces

Magnetism and Synchrotron Radiation,
Springer Proceeding in Physics



Single Chain Magnets

Coulon, C.; Miyasaka, H.; Clerac, R. *Structure and Bonding*; Springer: Berlin, 2006; Vol. 122, pp 163-206.

Contributions

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- Surface Science

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- Theory

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POST-DOCTORAL POSITION AVAILABLE

In the frame of an ERC Advanced Grant awarded to the University of Florence, Department of Chemistry, for the research project

Molecular Nanomagnets at Surfaces:
Novel Phenomena for Spin Based Technologies

a **POST-DOCTORAL** position (one year, renewable) is available for a highly motivated and talented young researcher with experience in the area of **surface science and magnetism** and/or **scanning probe microscopies**. Experience on molecular materials and/or cryogenics would be particularly appreciated. The applicant will work in the stimulating ambience of the Laboratory of Molecular Magnetic Materials (http://www.unifi.it/lamm/index_English.html) on a new UHV thermal deposition set-up equipped with a variable temperature **Omicron VT-STM/AFM** and all main facilities for in-situ preparation and characterization. A **low temperature – 9T magnetic field AFM-MFM** set-up is also available.

Please send your CV (with names of senior coworkers we could contact for recommendation) or contact Prof. Roberta Sessoli roberta.sessoli@unifi.it for more information.