Nanomagnetismo molecolare : dalla fisica classica alla meccanica quantistica

Pavia, 07/06/16

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MAGMA Net
NETWORK OF EXCELLENCE

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**FIRB "Nuove sfide nel nanomagnetismo molecolare:
dalla dinamica di spin al quantum-information processing"
(resp. S. Carretta, UNIPR. UNIPV : D. Gerace**

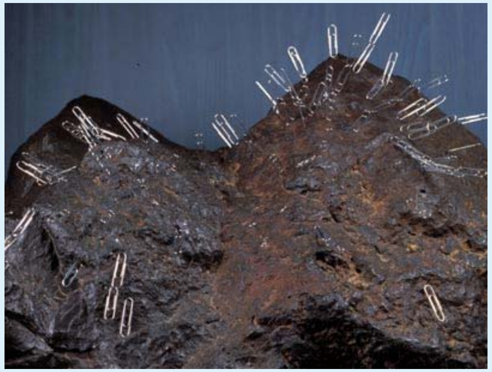
Outline

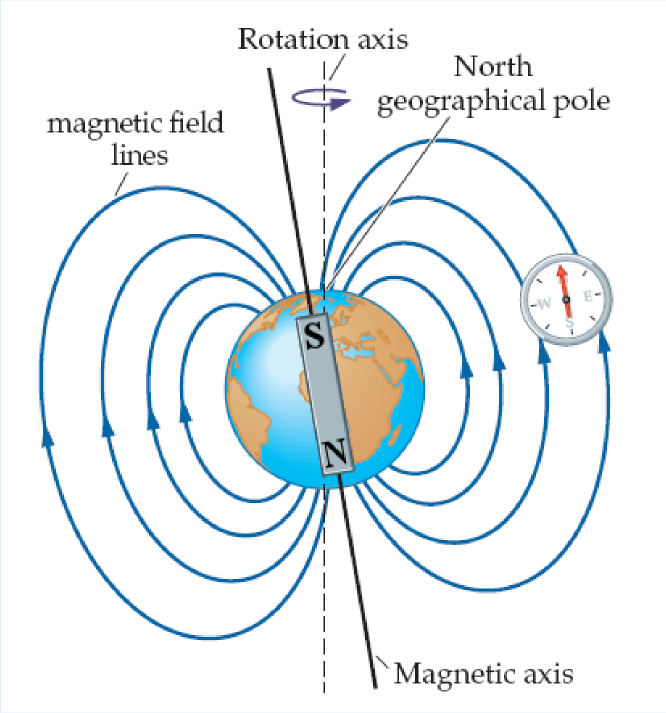
- Few words on magnetic field and magnetic systems
- Nanosystems. The case of molecular nanomagnets
- “Classical” effects
- Quantum effects and applications

Magnetism & magnetic field

Natural examples : rock magnetism and earth’s field

Earth's magnetic field changes over time because it is generated by a geodynamo (in Earth's case, the motion of molten iron alloys in its outer core).





The North and South magnetic poles wander widely over geological time scales, but sufficiently slowly for ordinary compasses to remain useful for navigation. However, at irregular intervals averaging several hundred thousand years, the Earth's field reverses and the North and South Magnetic Poles relatively abruptly switch places. These reversals of the geomagnetic poles leave a record in rocks that are of value to paleomagnetists in calculating geomagnetic fields in the past. Such information in turn is helpful in studying the motions of continents and ocean floors in the process of plate tectonics.

$$B_{earth} = 0.25 - 0.65 \text{ Gauss}$$

Il campo magnetico

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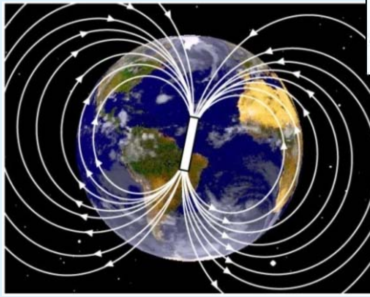
- Esiste sempre **UNA "sorgente" di campo magnetico**. Tipico esempio : la calamita
- **Sorgenti** di campo magnetico **di interesse** : elettromagneti , magneti superconduttori, magneti in genere
- E' **all'origine della forza magnetica (e/o viceversa)** fra due o più oggetti
- Ad oggi esistono **molti esempi quotidiani** di utilizzo del campo magnetico



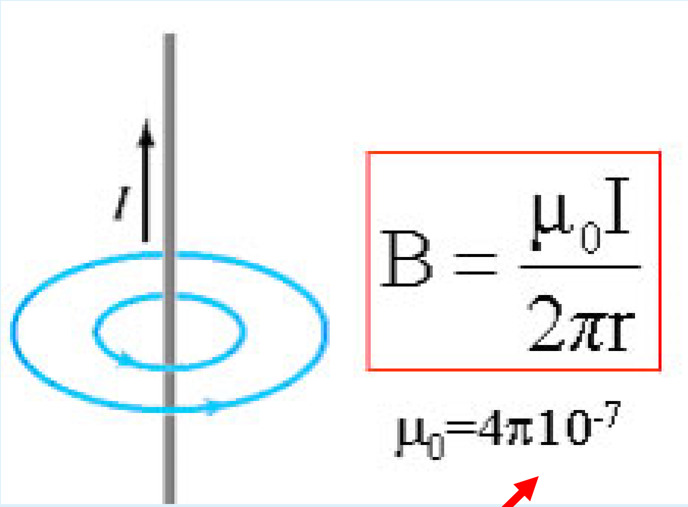
Il "più grande" magnete del mondo (CERN)

Levitazione diamagnetica della rana in alti campi magnetici (10 Tesla ; il campo terrestre è 0.00005 Tesla)

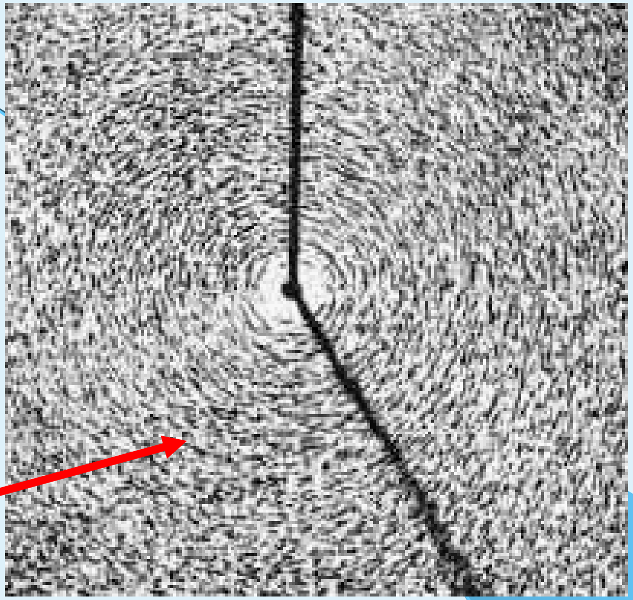
Levitazione dovuta a superconduttori ad alta temperatura critica

Treno a levitazione magnetica

Il campo magnetico dovuto a cariche elettriche circolanti

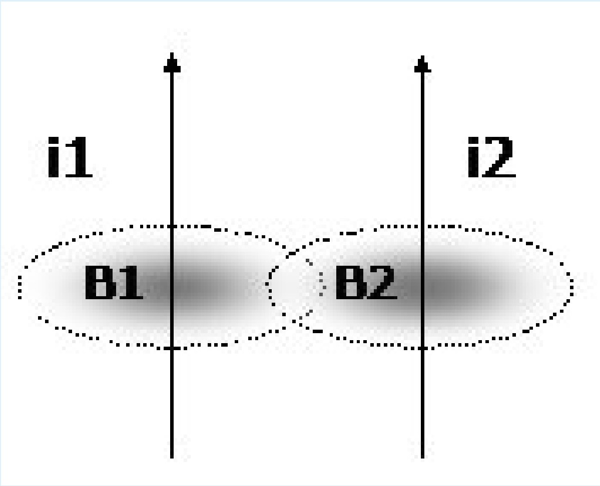


Filo elettrico percorso da corrente : legge di Biot-Savart



La limatura di ferro fornisce la direzione del campo magnetico generato dalla corrente che percorre il filo (vista dall'alto)

Fra due fili percorsi da corrente : forza magnetica

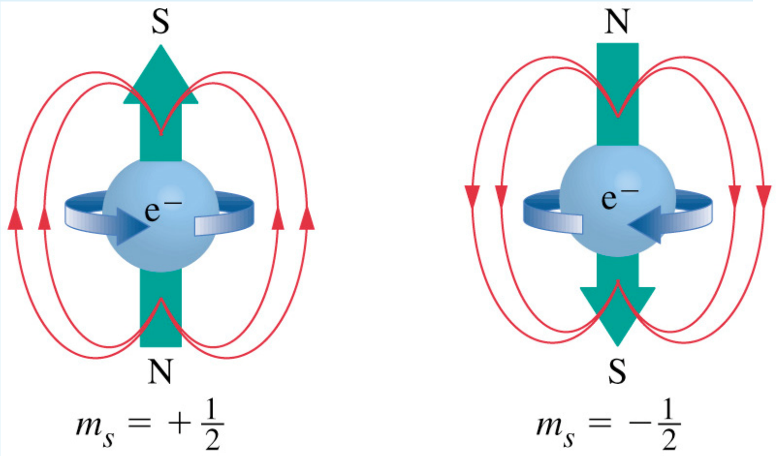


Il campo magnetico dovuto a cariche elettriche che ruotano su se stesse

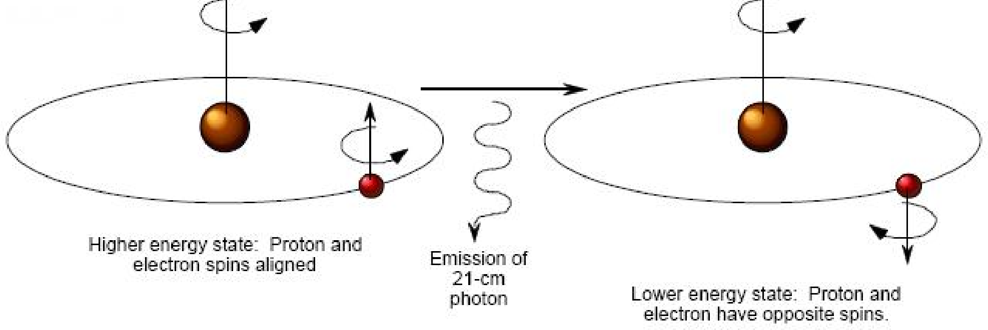
Origine del campo magnetico : particelle aventi carica elettrica in moto

Altro tipo di moto di carica che genera un campo magnetico :

rotazione di una carica elettrica intorno a un asse



Formation of the 21-cm Line of Neutral Hydrogen



Rotazione (spinning) dell'elettrone su se stesso : piccola calamita !!

Rotazione dell'elettrone e del nucleo su se stessi

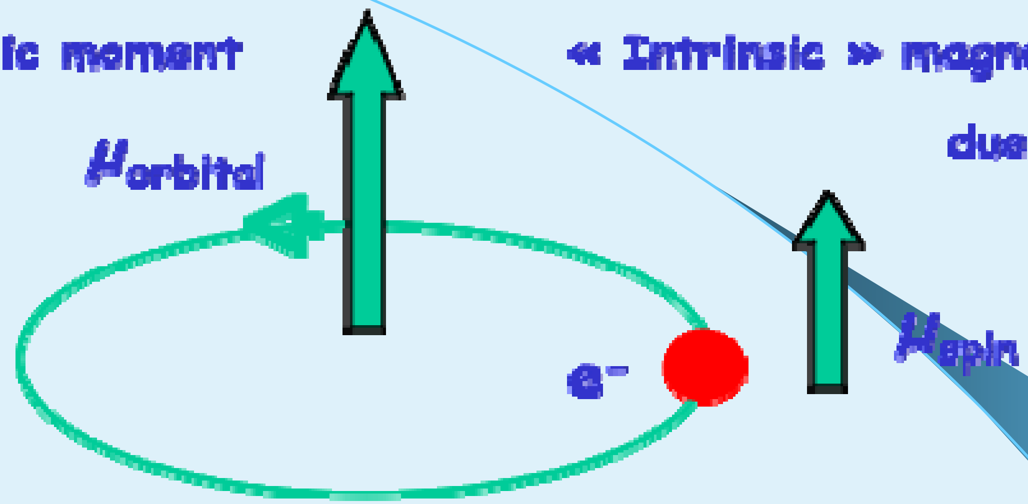
Magnetism in materials has atomic origin !!

« Orbital » magnetic moment

« Intrinsic » magnetic moment

due to the spin

$s = \pm 1/2$



$\mu_{orbital} = g_l \times \mu_B \times \ell$

$\mu_{spin} = g_s \times \mu_B \times s \approx \mu_B$

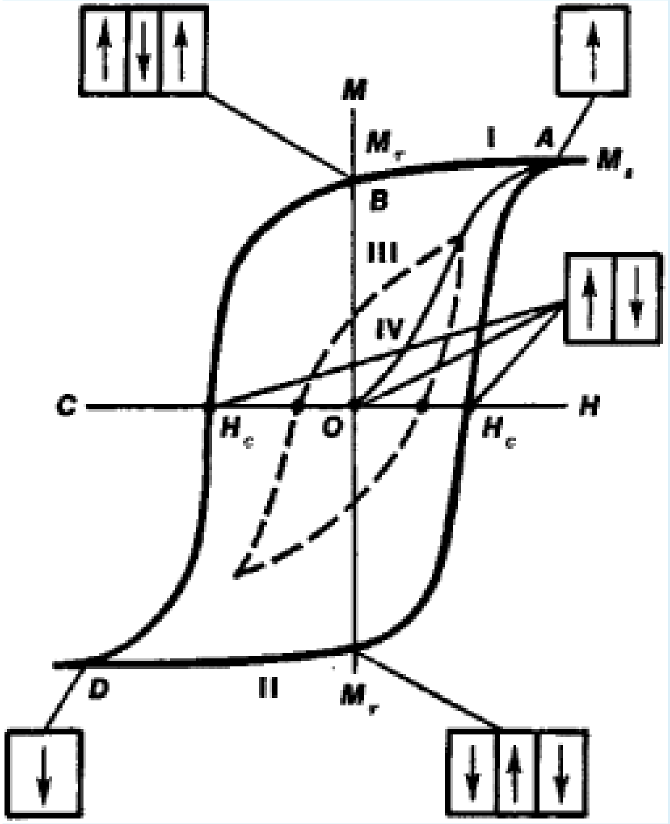
$$\mu_{total} = \mu_{orbital} + \mu_{spin}$$

$M = (1/V)\Sigma_i \, m_i = (1/V) \, \Sigma_i \, \mu_{orb} + \mu_{spin}$ <u>**Magnetization**</u>

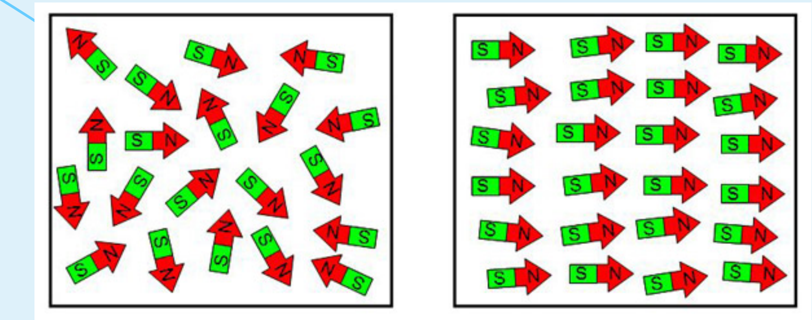
In MM, often $\mu_{orb} \sim 0 \Rightarrow$

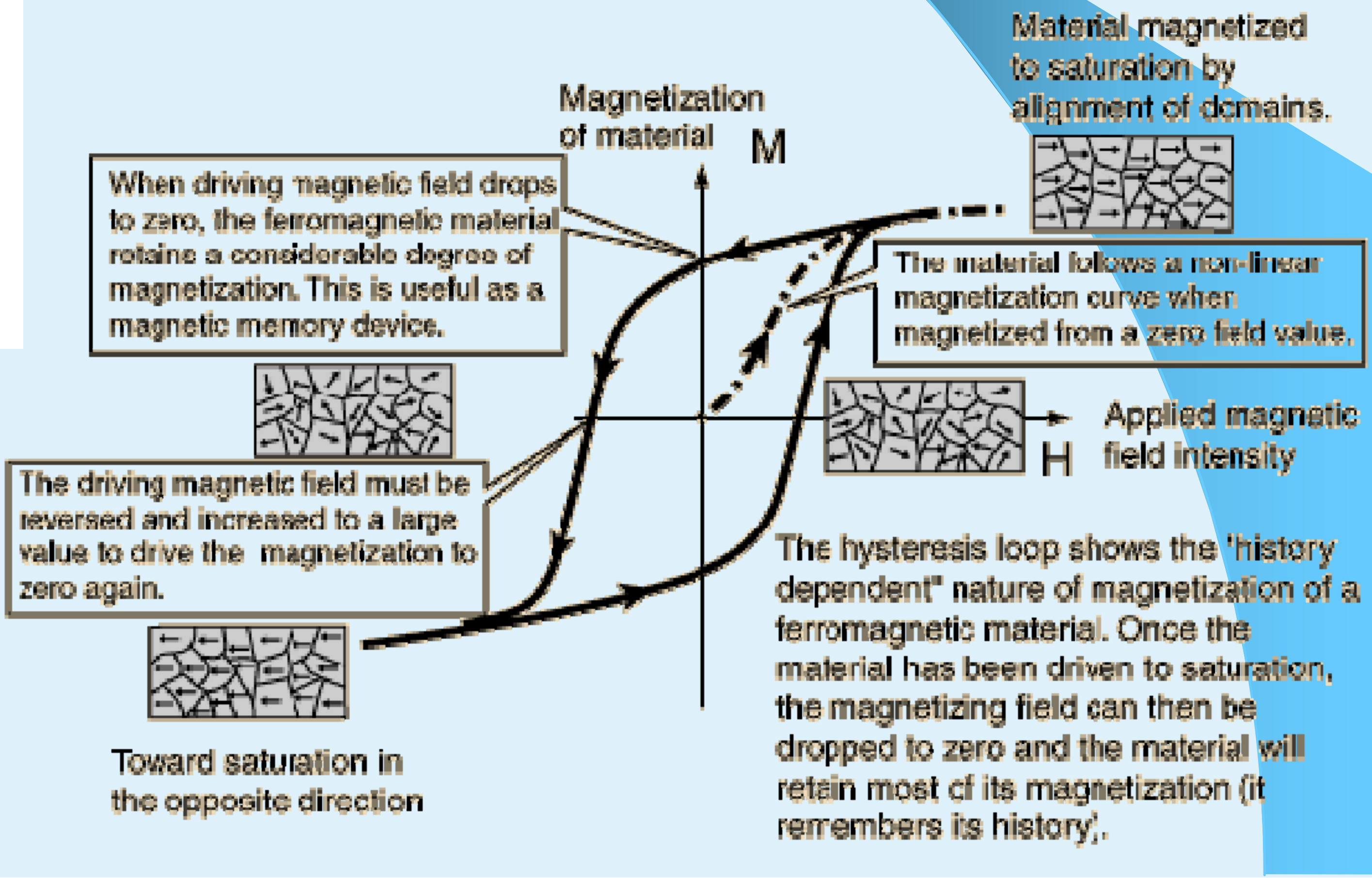
magnetism given by μ_{spin}

“Std” magnetic systems : hysteresis and domain walls



Bulk ferromagnet





Material magnetized to saturation by alignment of domains.

When driving magnetic field drops to zero, the ferromagnetic material retains a considerable degree of magnetization. This is useful as a magnetic memory device.

The material follows a non-linear magnetization curve when magnetized from a zero field value.

The driving magnetic field must be reversed and increased to a large value to drive the magnetization to zero again.

Toward saturation in the opposite direction

The hysteresis loop shows the "history dependent" nature of magnetization of a ferromagnetic material. Once the material has been driven to saturation, the magnetizing field can then be dropped to zero and the material will retain most of its magnetization (it remembers its history).

….. toward….

“Nano” - physics

i.e.

reducing the size of the systems to nm scale

Few examples of "nano" Magnetism applications

Information Technology

Data storage

Quantum computing

Energy

Transportation

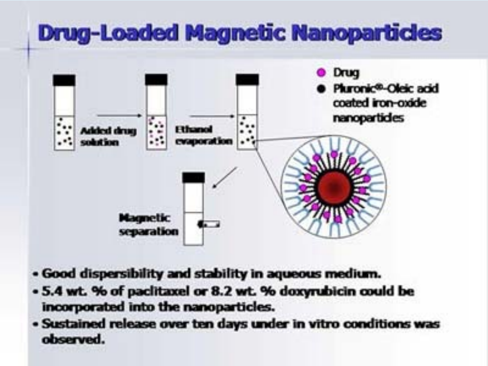
Energy storage

Biomedicine

Magnetic Resonance Imaging
(diagnosis)

Magnetic Fluid Hyperthermia
(tumour therapy)

Magnetic (drug) delivery



Drug-Loaded Magnetic Nanoparticles

- Good dispersibility and stability in aqueous medium.
- 5.4 wt. % of paclitaxel or 8.2 wt. % doxyrubicin could be incorporated into the nanoparticles.
- Sustained release over ten days under in vitro conditions was observed.

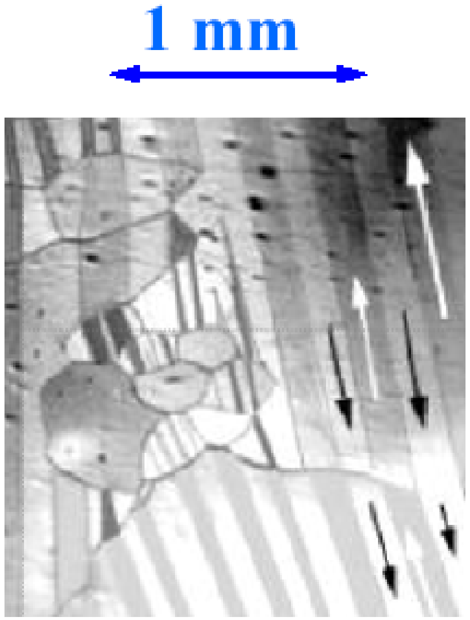
Magnetic structures

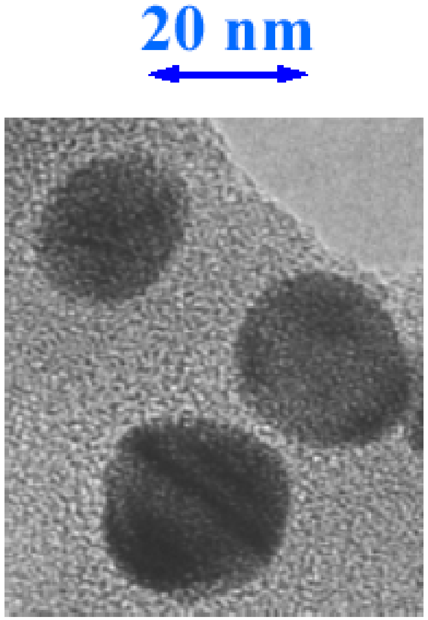
← *macroscopic* *atomic* →

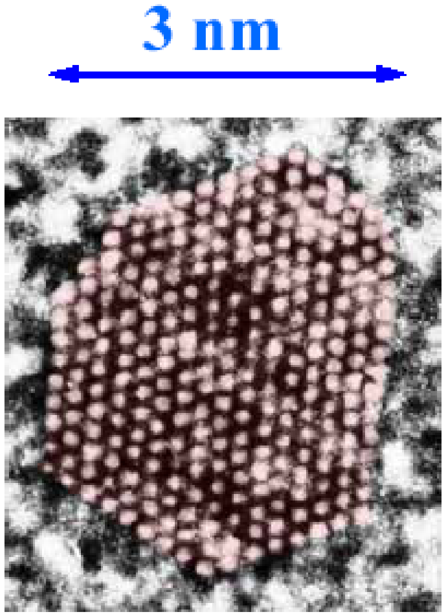
permanent magnets | micron particles | nanoparticles | clusters | molecular clusters | atoms

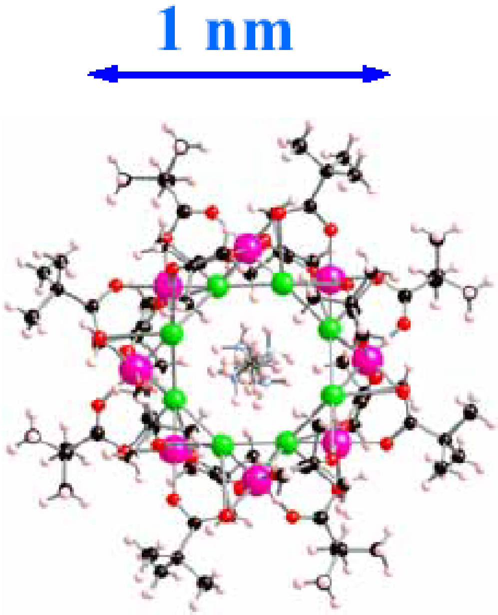
S = 10^{20} 10^{10} 10^{8} 10^{6} 10^{5} 10^{4} 10^{3} 10^{2} 10 1

multi - domains ***single - domains*** ***spins***









MESOSCOPIC MAGNETISM

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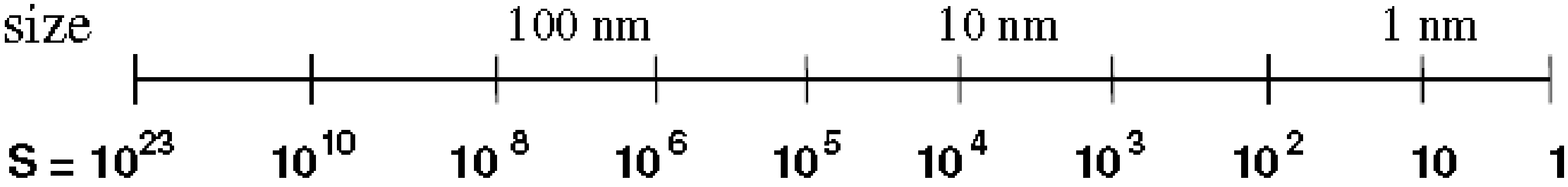
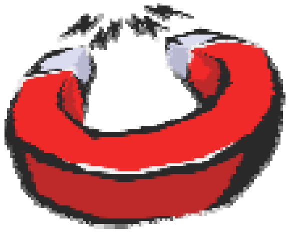
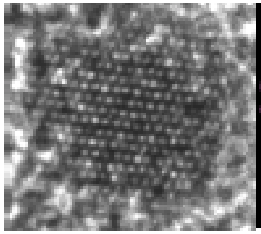
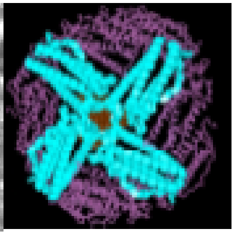
Classical ←→ Quantum

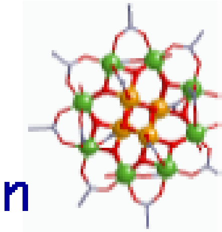








Ferritin



Mn_{12}-ac

multi - domain

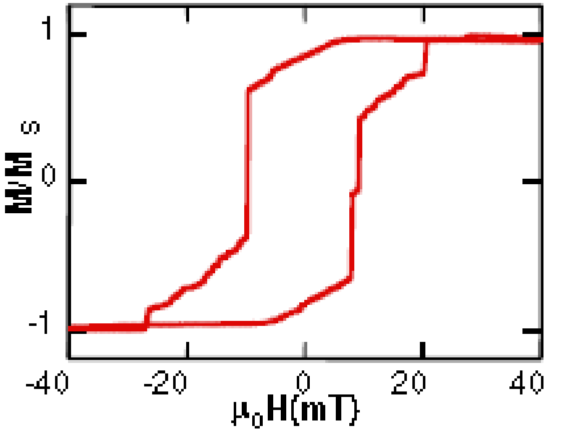
nucleation, propagation and annihilation of domain walls

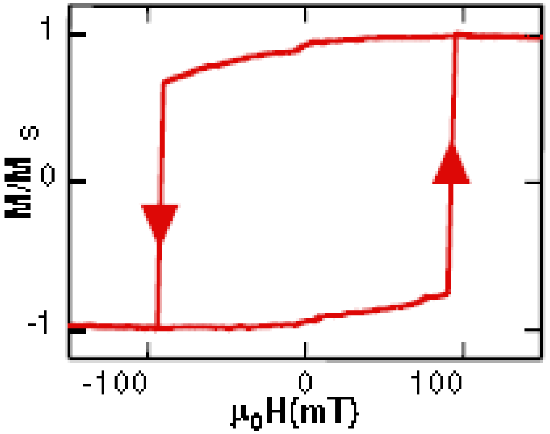
single - domain

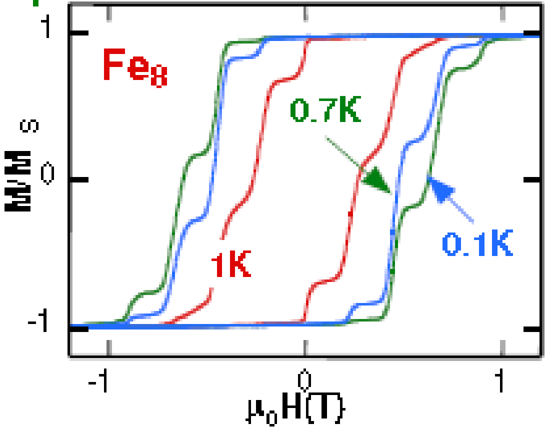
uniform rotation

Single molecule

quantum tunneling, quantum interference



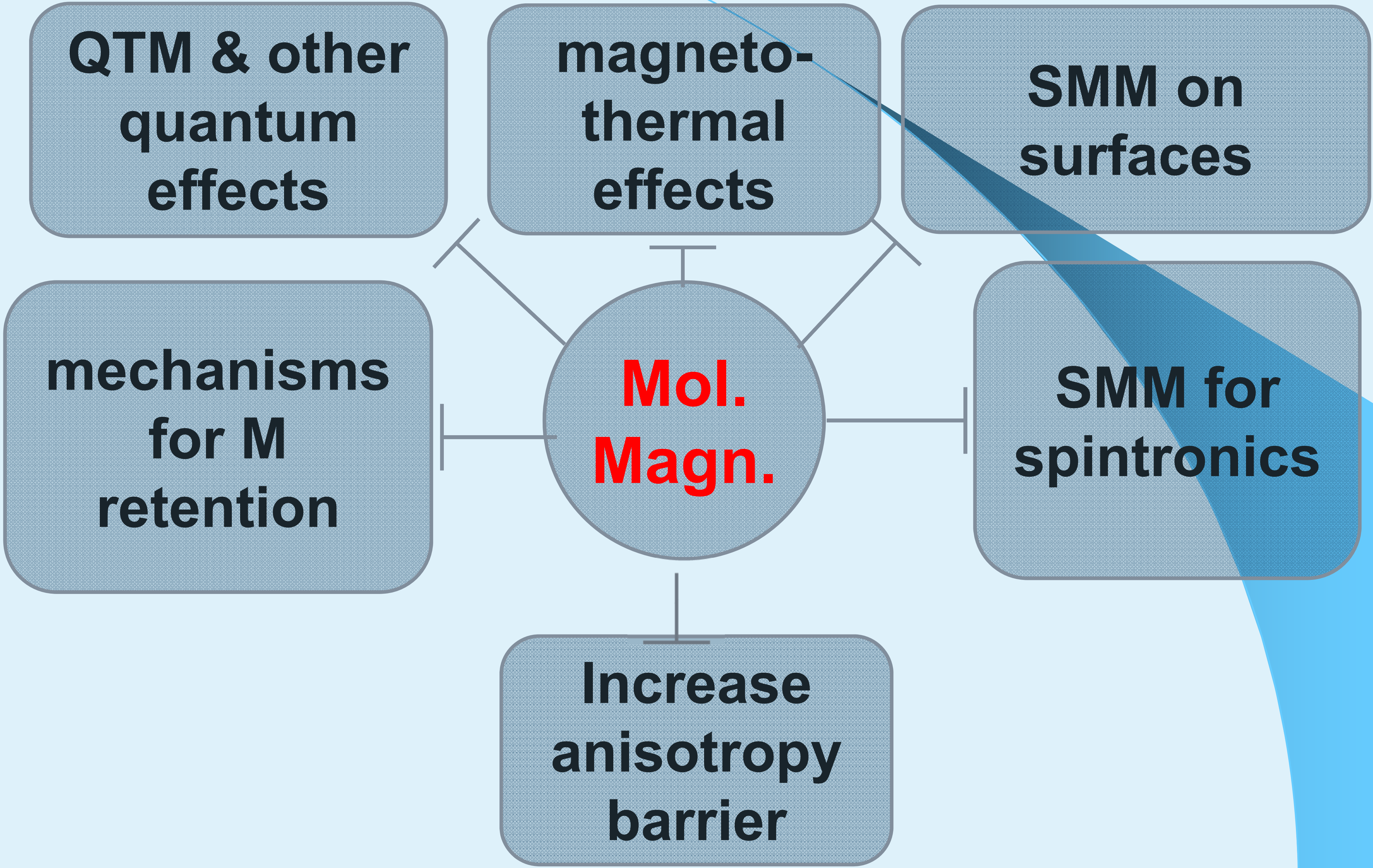




Basic dates in history of Molecular magnets or "single-molecule magnets"

- 1993 early magnetic studies on Mn12
- 1996 QTM in Mn12
- 1997 QTM in Fe8
- 2000 Mn12 on surface
- 2002 Agilent Technology Award to Sessoli, Gatteschi, Barbara, Wernsdorfer, Friedman
- 2004 TbPc2 (phtalocyanines)
- 2007 Mn6
- 2009 Fe4 on surface
- 2015 Zavoisky award to Prof. D. Gatteschi

Related research activities



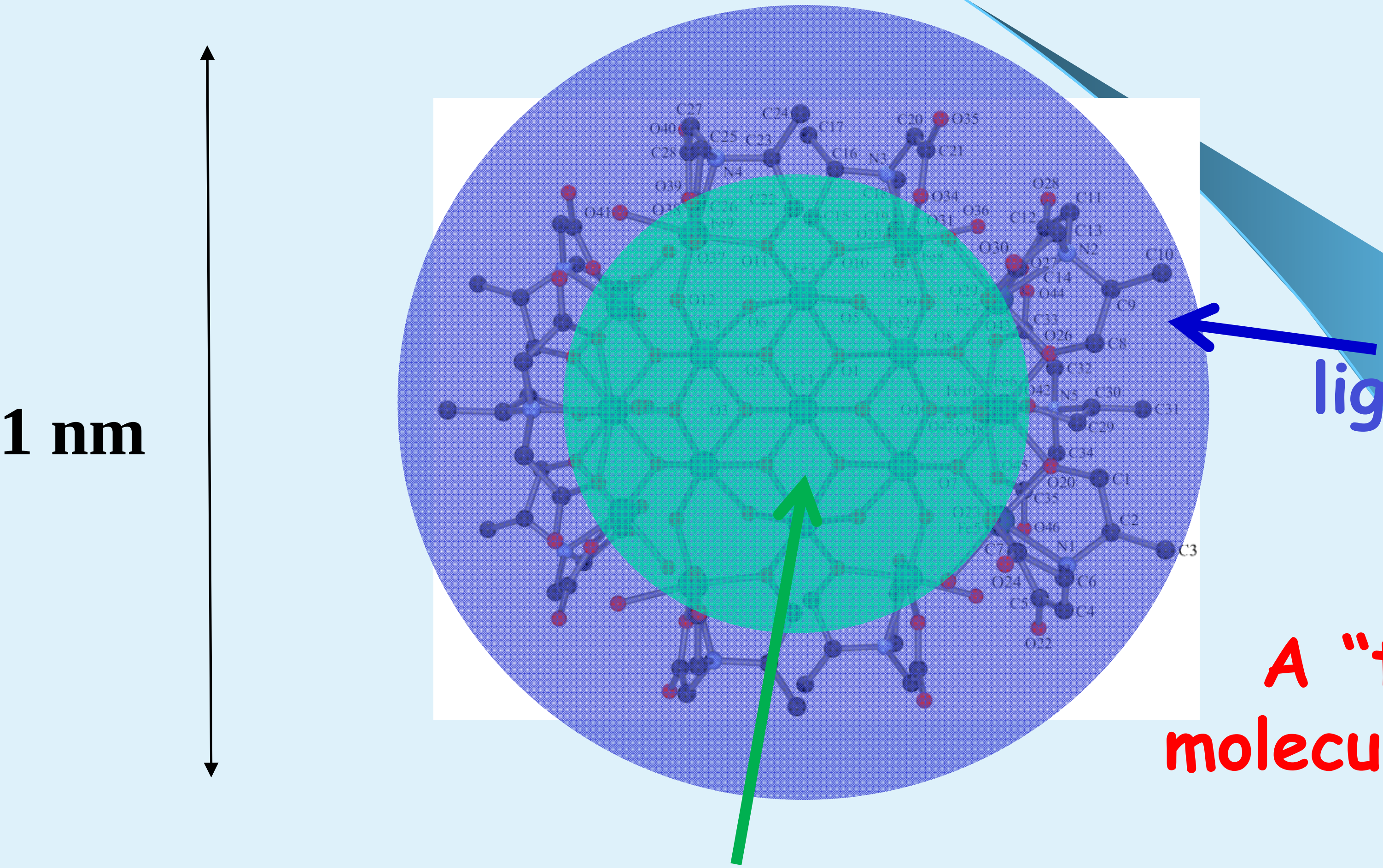
Mol. Magn.

- QTM & other quantum effects
- magneto-thermal effects
- SMM on surfaces
- mechanisms for M retention
- SMM for spintronics
- Increase anisotropy barrier

Some applications

- Memory storage
- Magneto-thermal effects
- molecules on surfaces (read and write)
- Information Storage & Processing:
  - molecular spintronics
  - quantum computation
  - hybrid cavities

Typical Magnetic Molecule



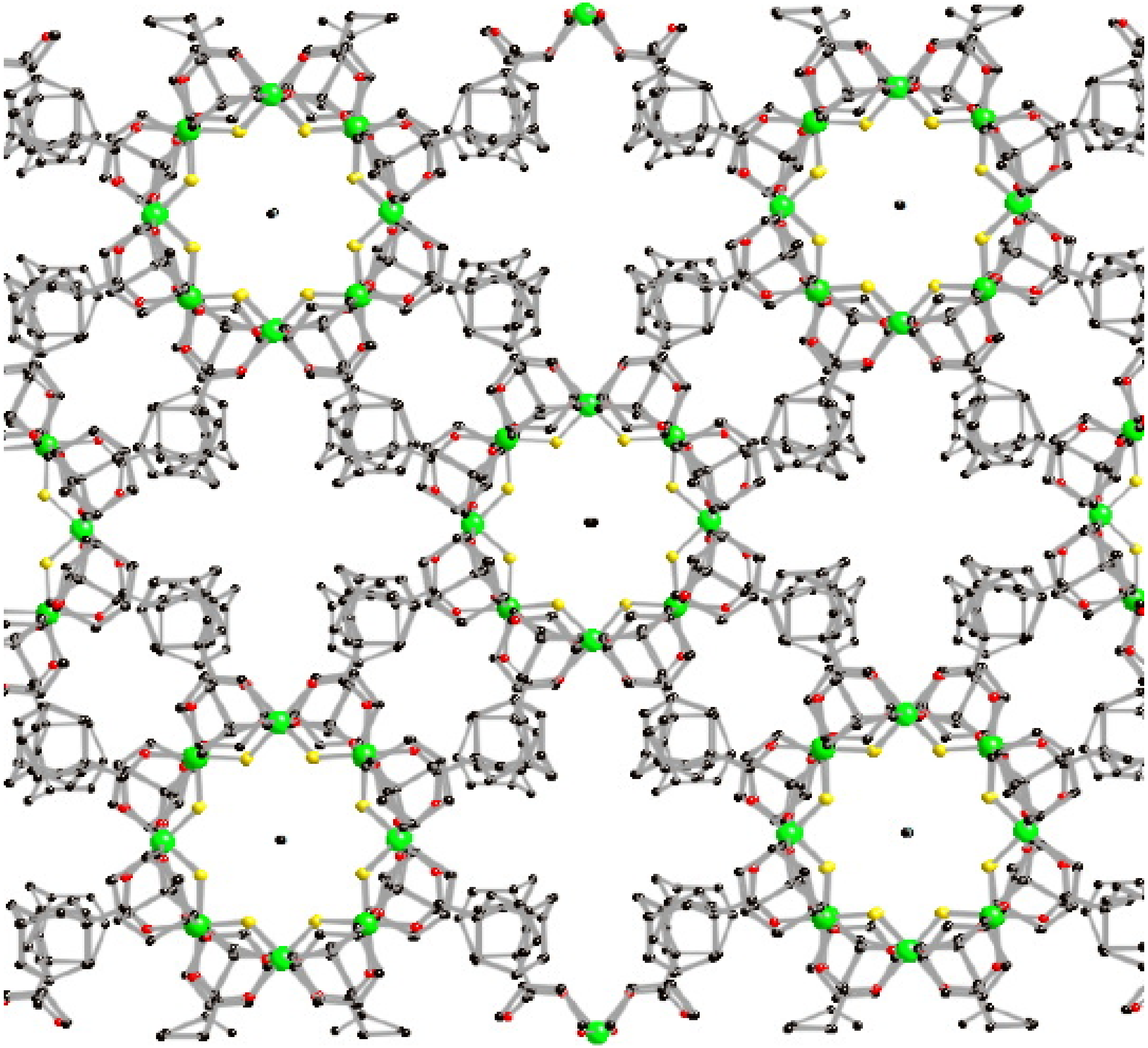
1 nm

ligand

A “total” molecular spin

magnetic core

Molecular engineering to design nanomagnets

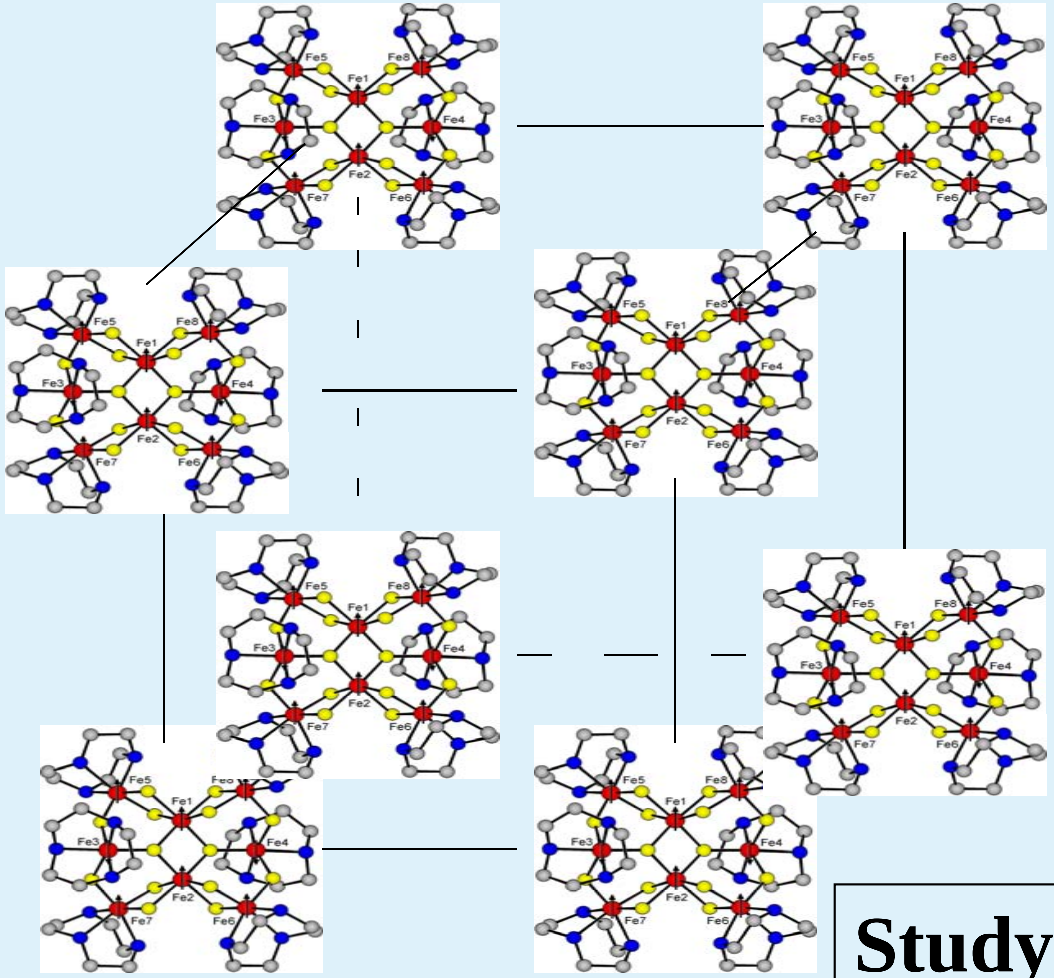


Cr8

A single crystal is a collection of identical nanomagnets well separated one another and perfectly oriented

Another example of nanomagnet: crystal of Fe8

Few magnetic ions per molecule



Unit repeated over all the crystal

Negligible magnetic interactions

among molecules

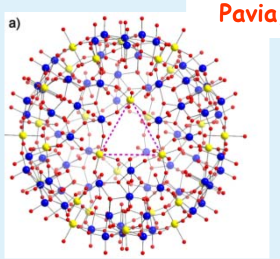
i.e.

Molecular nanomagnets or single molecule magnets

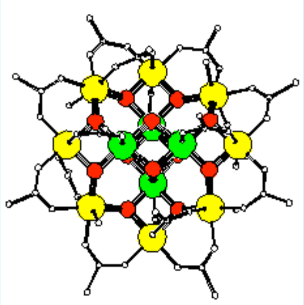
↓

Studying the bulk ⇒ Investigating the single molecule

Molecular Nanomagnets (MNM)



Wide variety : rings (Fe10, Fe6, Cu8, Cu6, Cr8…..)

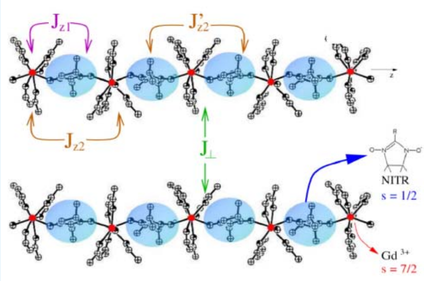


"clusters" , Single Molecule Magnets (Mn12, Fe8, Ni10, Cr4 ,Fe4…)

chains , Single Chain Magnets (CoPhOMe, Dy-Ph, Gd-R, ….)

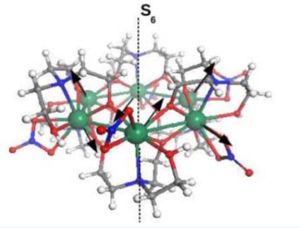
- Crystals made up of **very weakly interacting molecules**

⇒ **magnetic properties** determined by **single molecule**



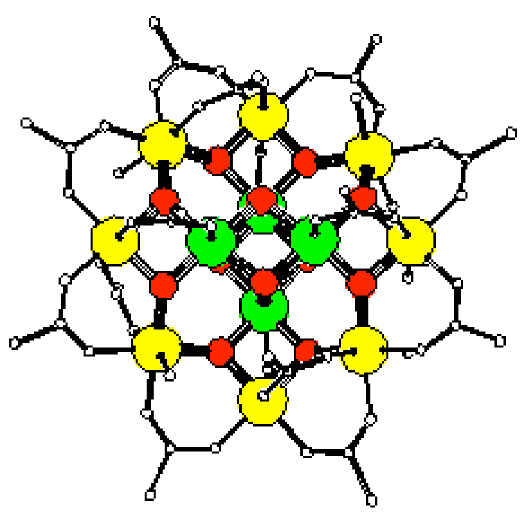
- Clusters and rings can be **designed at will** :

  - number of interacting magnetic ions (spins) ÷ geometric spatial arrangement of the ions
  - single ion spin dimension (s=1/2……s=5/2)
  - exchange interaction J (AF, FM)

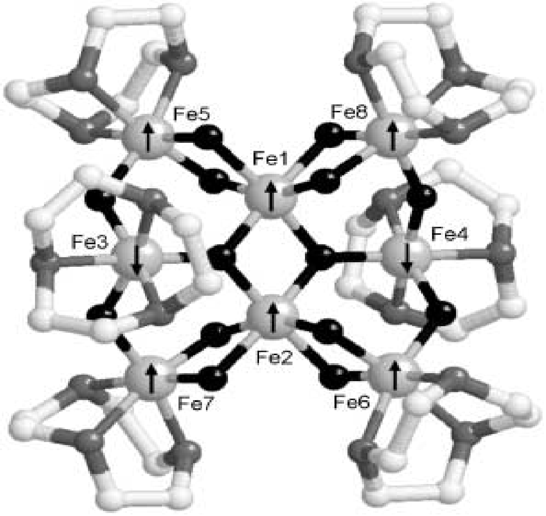


Example:
High-spin
Molecular magnets

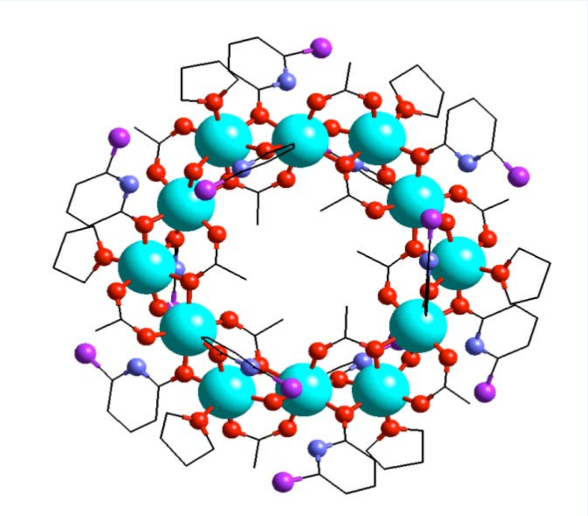
Some high spin nanomagnets



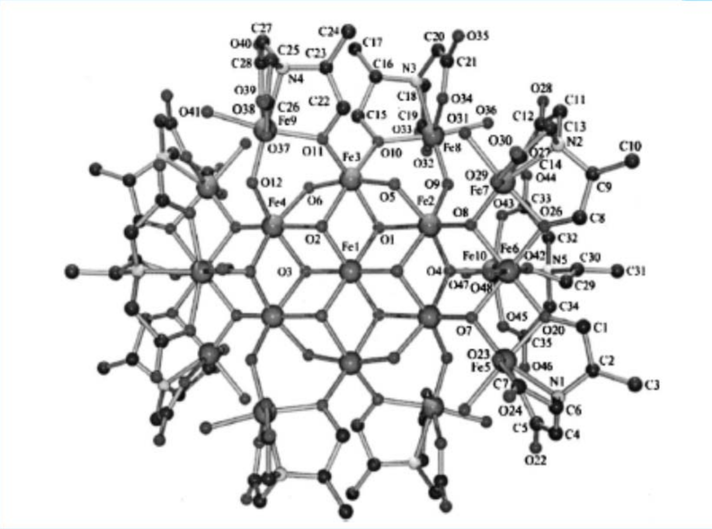
Lis, 1980 **Mn12** **S = 10**



Fe8 **S = 10** Wieghardt, 1984



Winpenny, 1999 **Ni12** **S = 12**



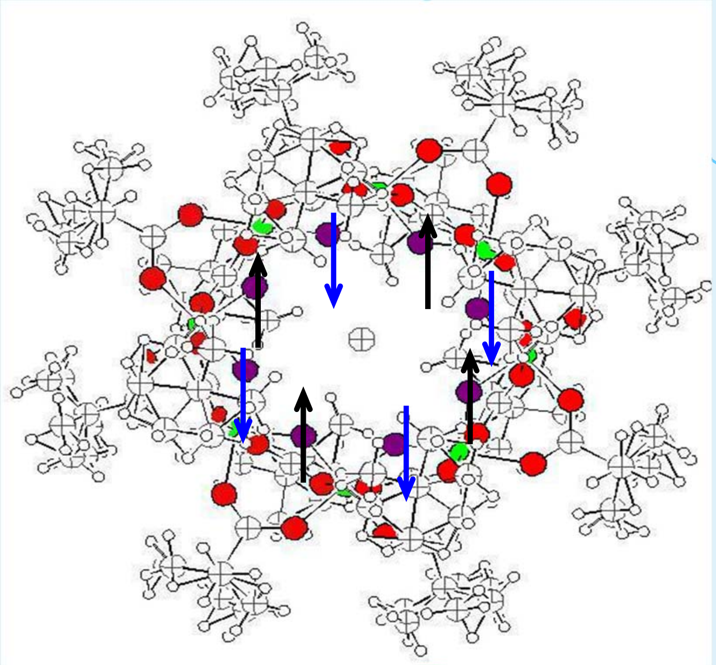
Fe19 **S=33/2** Powell, 2000

Example :
Low-spin
Molecular magnets

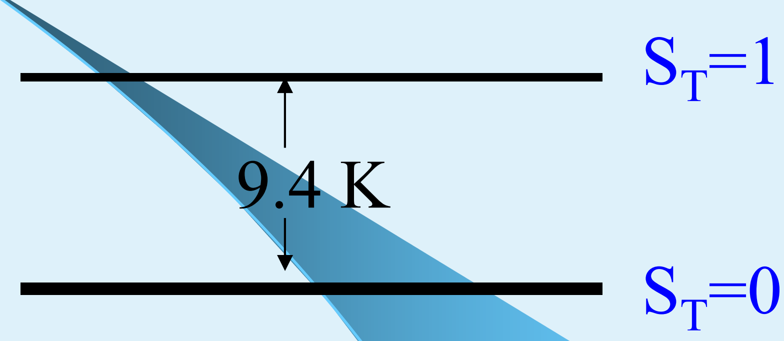
Some AF ring-like $S_T=0$ nanomagnets

Cr(III) s = 3/2
AF ground state
(total spin $S_T = 0$)

$J \approx 17.2$ K
$\Delta_{0\rightarrow1} \approx$ 9.4 K

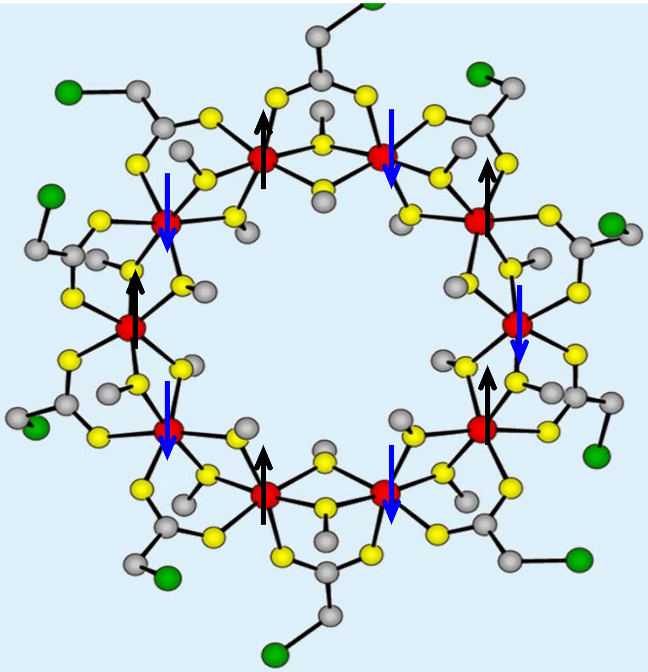


Cr8

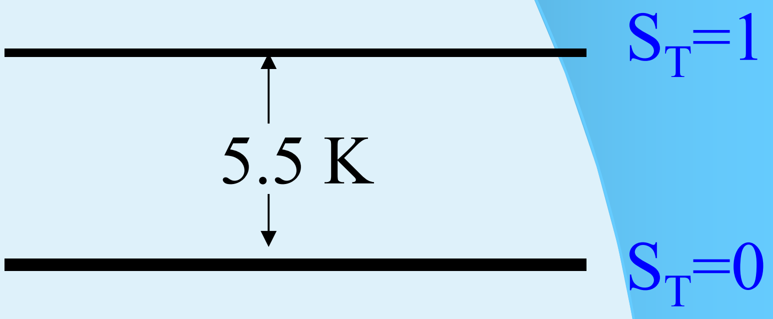


Fe(III) s = 5/2
AF ground state
(total spin $S_T = 0$)

$J \sim 13.8$ K
$\Delta_{0\rightarrow1} \sim$ 5.5 K

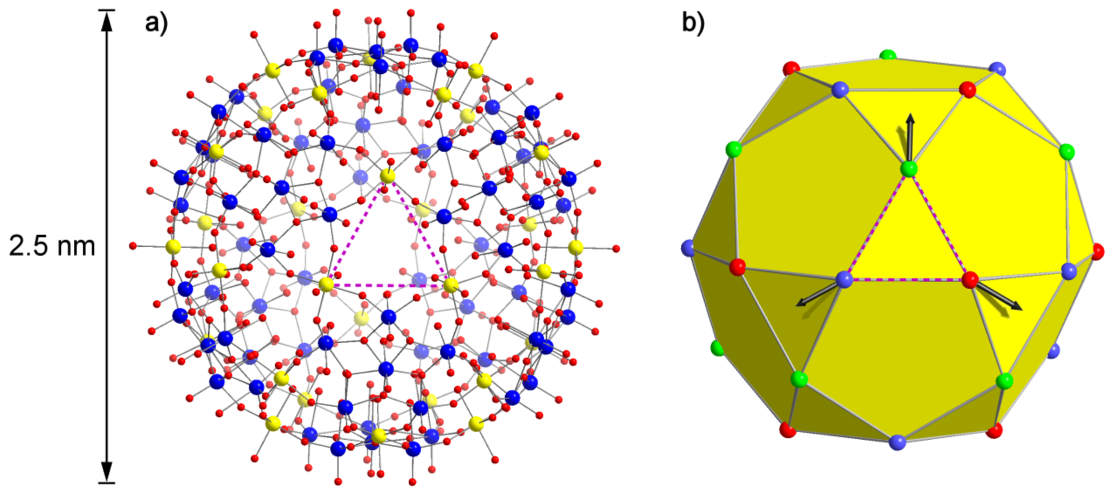


Fe10

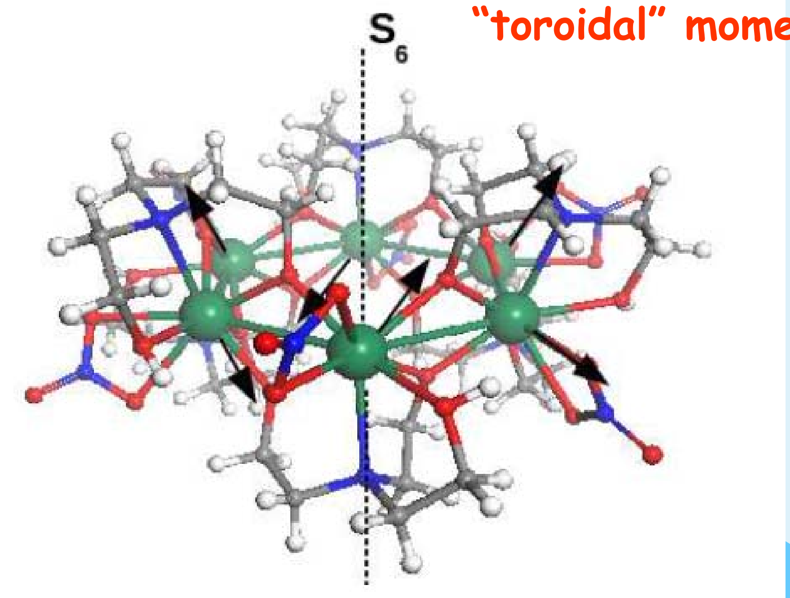


Other nanomagnets…..

Fe30

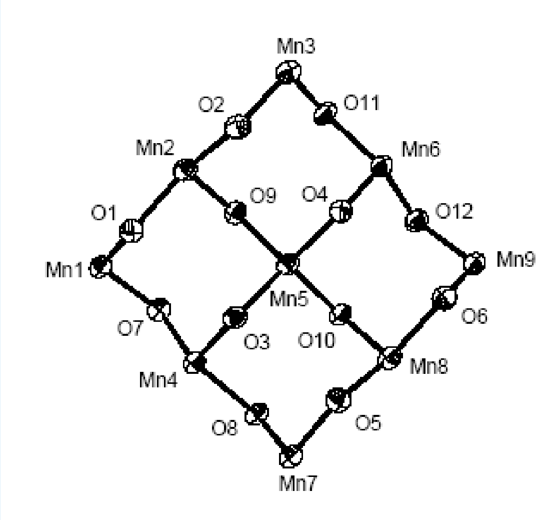


Dy6

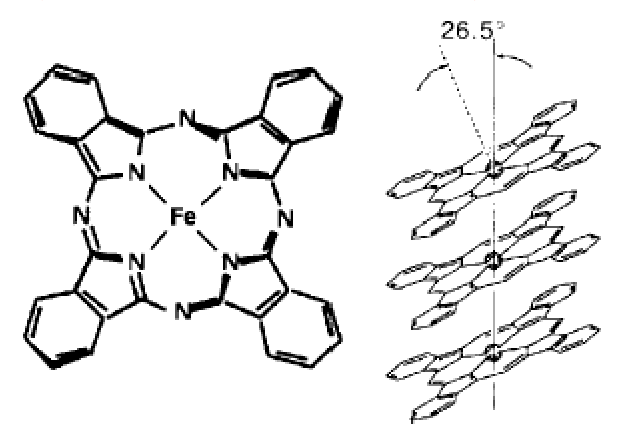


"toroidal" moment

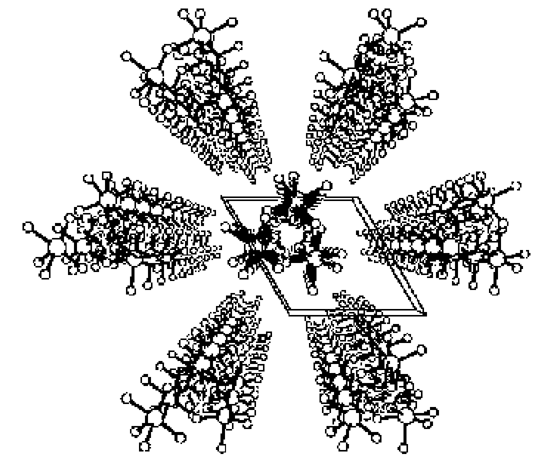
Mn 3x3 grid



Phtalocyanines-based (double deckers)



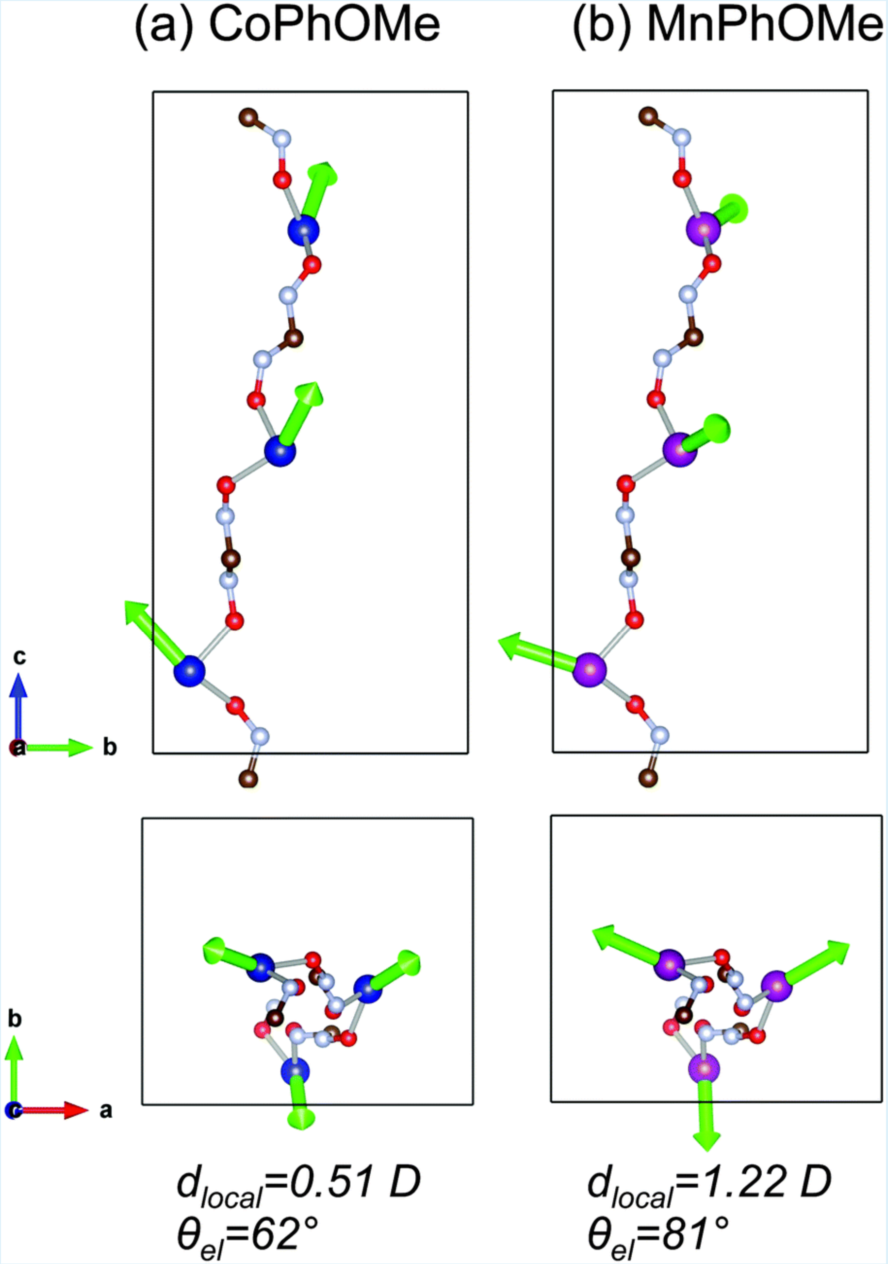
Single-chain magnets (1D magnetic nanowires)



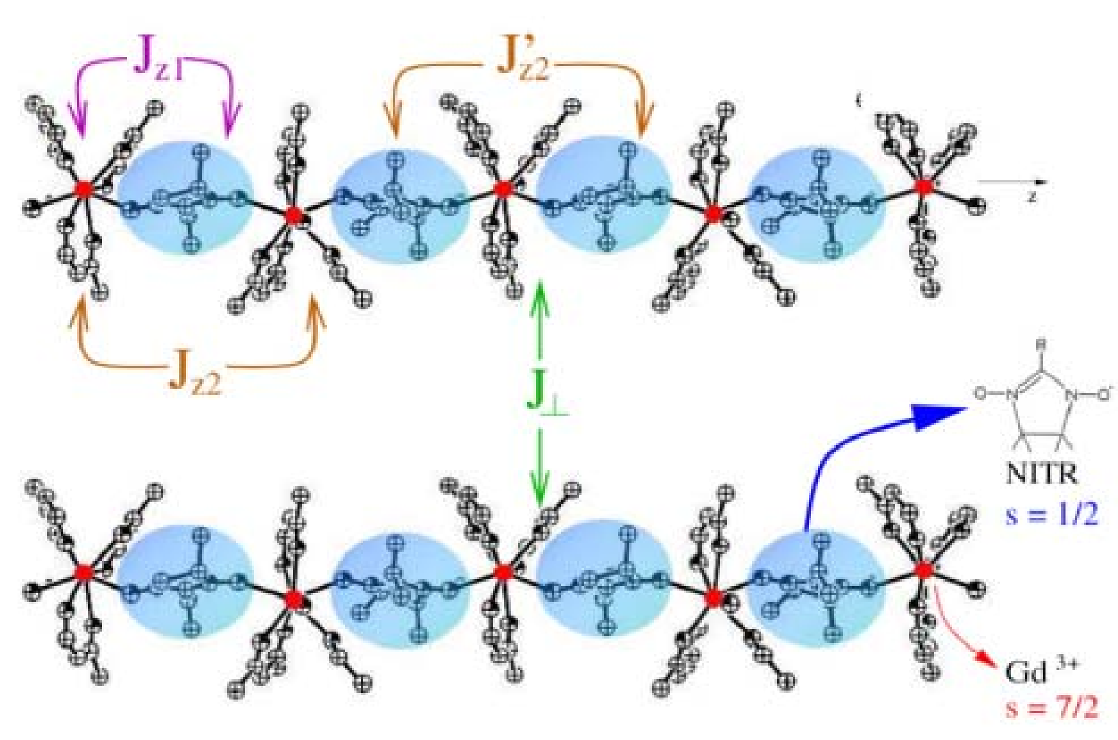
Example : Molecular chains

Examples of molecular chains

single chain magnets



Gd-R chain. Villain's conjecture



Why Physics of Molecular magnets is so interesting ?

Molecular Nanomagnets (MNM)

Classical Physics involved

- Physics of low-dimensional systems (how magnetism depends on crystal and spin dimensionality
- Spin dynamics : how spins move when T and H are varied
- system's dynamics, e.g. Brownian motion (due to temperature effect)

Quantum Physics involved

Due to finite number of magnetic ions ⇒ discrete energy levels

- gapped ground state : level crossing effects
- "macroscopic" quantum tunneling and/or tunneling of the Neel vector (after D.Loss et al.)
- spin dynamics in zero dimension
- measurement of the decoherence time (quantum computation)
- quantum entanglement

The switch from classical (physics) to quantum mechanical depends often on temperature region of operation

"Classical" (not trivial !!) physics :

Nanoparticles

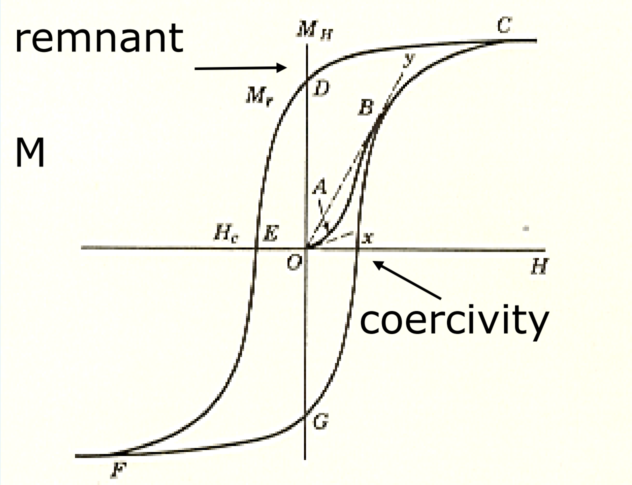
Molecular nanomagnets at "high" temperature

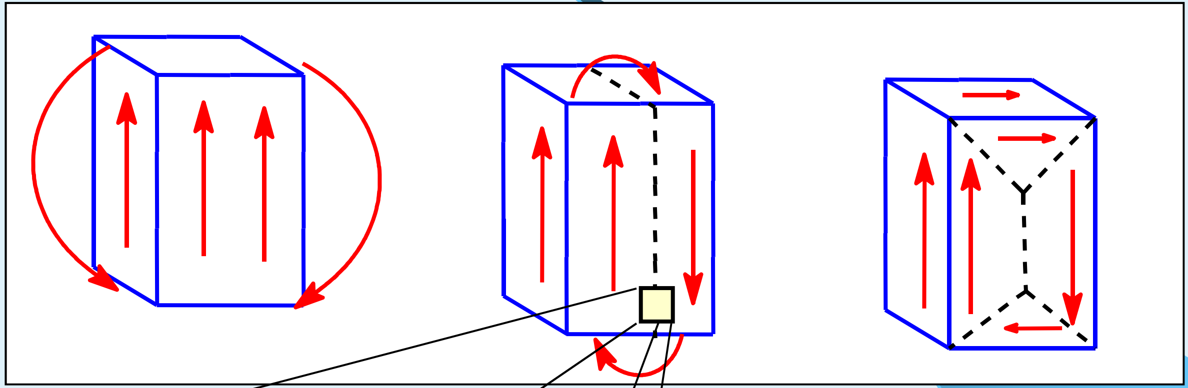
Nanomagnetism for “classical” NPs

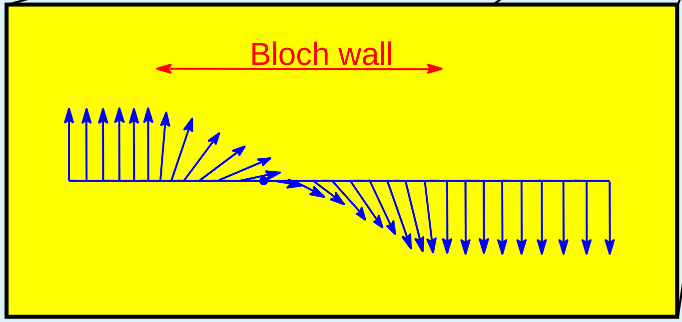
Below a critical temperature, T_C, some materials exhibit spontaneous magnetization (ferro- and ferrimagnetism). Demagnetizing field induces domain formation (i.e. uniformly magnetizated regions of different shape and size are formed).

$$E = E_{ex} + E_k + E_\lambda + E_D$$

E_{ex} exchange energy, E_k magnetocrystalline anisotropy energy, E_λ magnetoelastic energy, E_D magneto-static energy







Typical values of domain wall width are in the 10-100 nm range.

The width of the domain wall depends on the anisotropy and exchange coupling and

$$\delta = \pi\sqrt{A/K}$$

A = exchange energy density (J/m^2)

K = magnetic anisotropy energy density (J/m^2)

Single Domain Nanoparticles

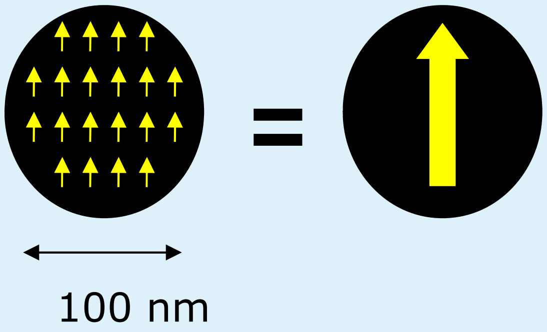
Total wall energy per area unit: $E_\sigma=2(AK)^{1/2}$

Reducing the dimensions of the crystal: competition among E_σ and the magnetostatic energy, E_λ . But E_λ scales with the volume, E_σ with the surfaces

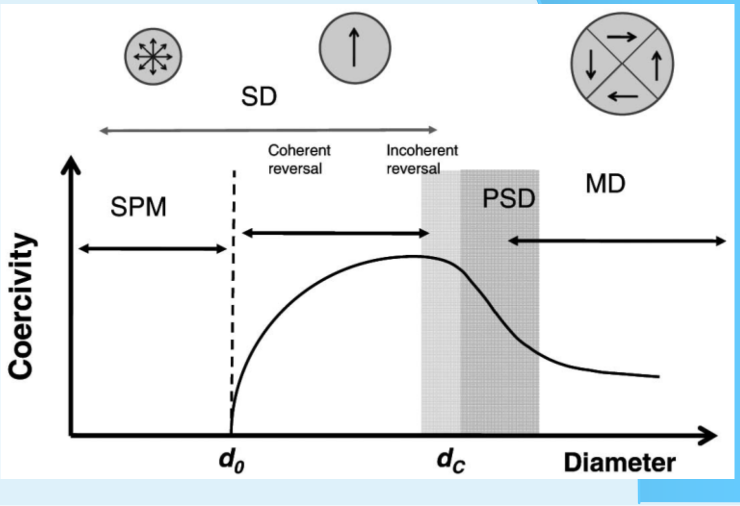
⇒ There exists a lower limit in size, D, corresponding to the single domain state.

Typical *D* values:	
Fe	15 nm
Co	70 nm
Ni	55 nm
NdFeB	100 nm
Fe_3O_4	128 nm
γ-Fe_2O_3	166 nm

$$D=18\,E_\sigma\,/\,\mu_0 M_S^2$$



When D<δ all the spins are coupled (Exchange Energy is constant). The inversion of M occurs through a coherent movement of all the spins of the particle.

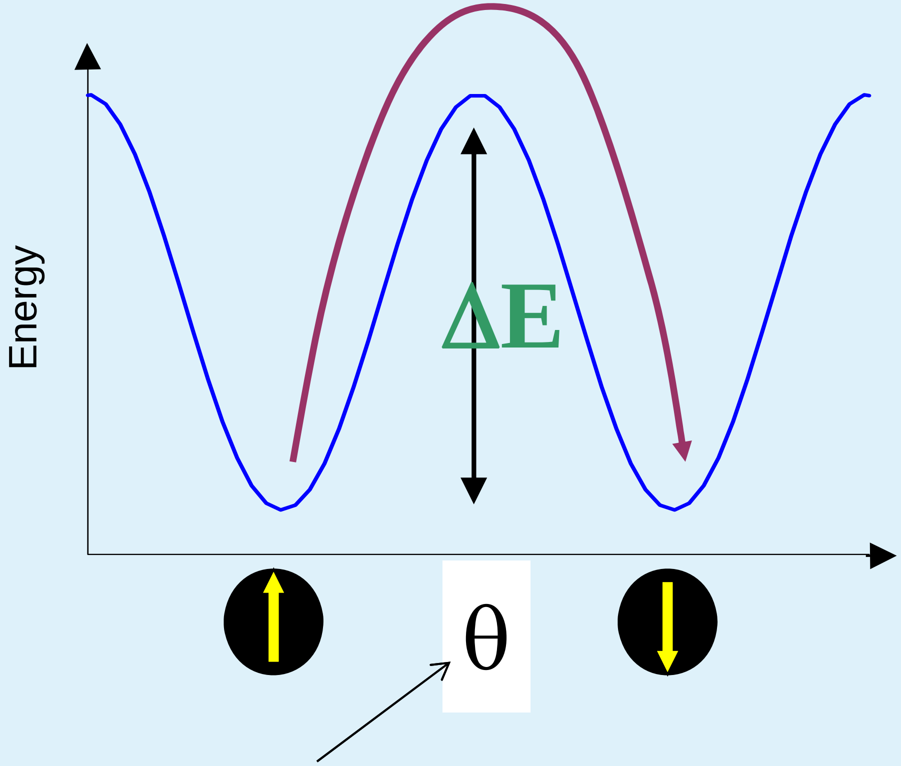


Single Domain Nanoparticles

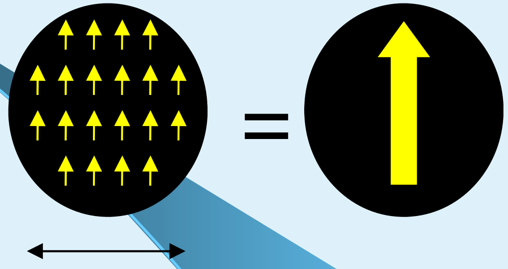
(small ferromagnets under critical diameter d_c)

Superparamagnetism (giant spin)

Stoner-Wolhfarth model:



z = easy-axis of M, θ=angle (z,M)



d_c= 20-100 nm

The inversion of M occurs through a **coherent movement** of all the spins of the particle

Energy barrier $\Delta E = k_A V$

k_A= anisotropy constant, **V**= particle volume

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

Neel correlation time

If NPs interact : Vogel-Fulcher model, $\tau_N = \tau_0 \exp[\Delta E / k_B (T - T_0)]$

Also in MM for studying the fundamental physical processes and for the applications we need to follow the typical times of the systems

For example some MM are superparamagnetic

How to detect the dynamics typical of systems ?

The (extended) “resonance” concept

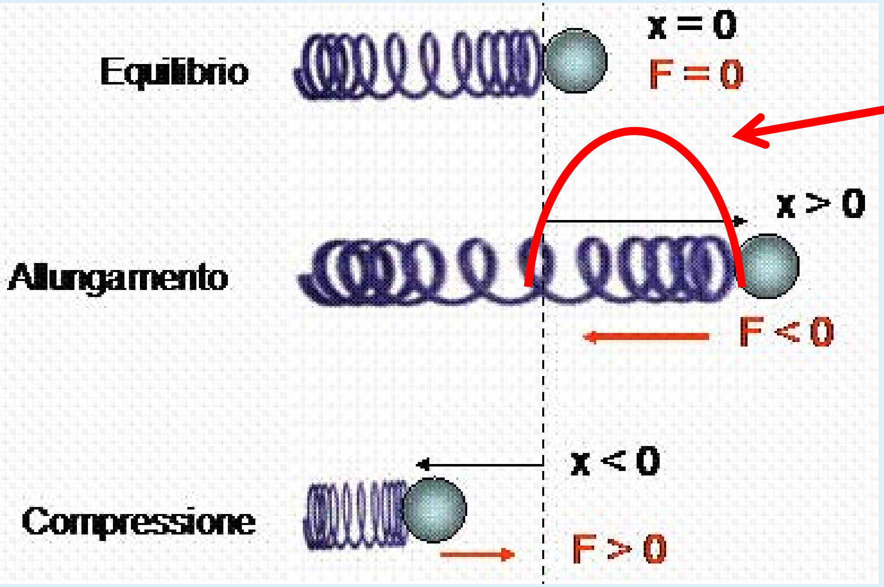
Il fenomeno della risonanza

- Consiste in una risposta "aumentata" dei sistemi
(molla, chitarra/microfono, ponti, nuclei, elettroni, molecole,…)
sollecitati da una azione esterna agente a frequenze proprie dei sistemi stessi

Quando si ha risonanza

c'è un picco nella risposta del sistema

Il fenomeno della risonanza



AMPIEZZA DELLA MOLLA (MAX ALLUNGAMENTO)

<u>RISONANZA DELLA MOLLA</u>

Se la molla viene "forzata" dall'esterno alla sua frequenza, <u>aumenta l'ampiezza</u> della sua oscillazione

Il fenomeno della risonanza

RISONANZA SONORA : effetto Larsen in chitarre amplificate

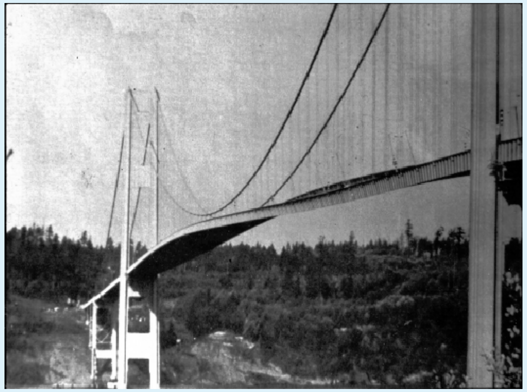
20 Hz – 500 Hz

Time 2.00 & 3.15

Il fenomeno della risonanza

RISONANZA MECCANICA :

Ponte di Tacoma che oscilla e poi crolla causa vento a circa 67 km/h




Conditions for observing a resonance typical of motions inside the investigated system :

stimulate the system with
a frequency ω_{meas}
near a typical system frequency $\nu_c = 1/\tau_c$:

$$\omega_{meas}\,\tau_c \approx 1$$

Possible motions : spin motion,
Brownian motion, molecular motion

FOR THIS PURPOSE

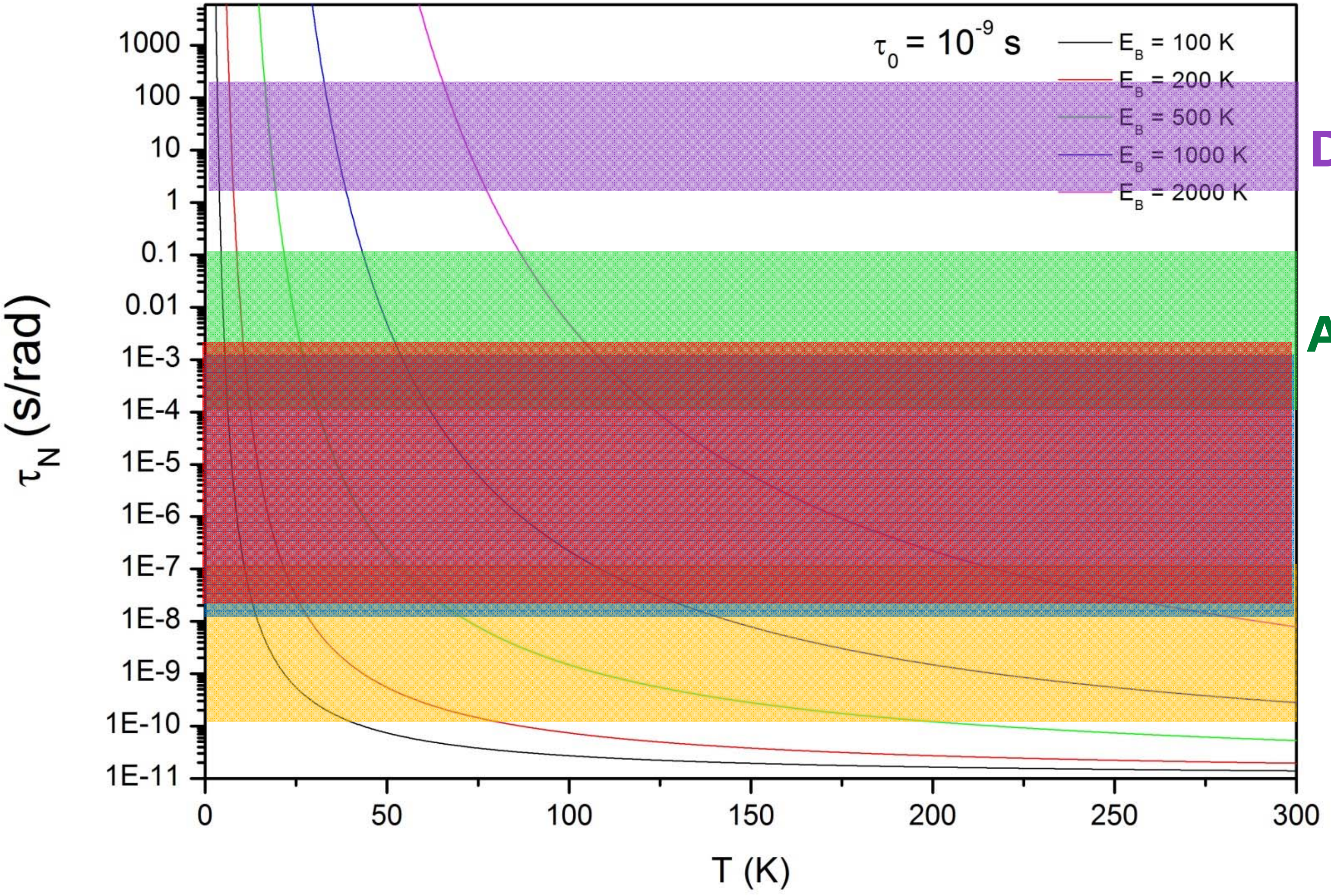
ONE CAN USE DIFFERENT TECHNIQUES ABLE TO DETECT MAGNETIC PROPERTIES

Concept of response function

(e.g. specific heat, magnetic susceptibility)

Typical times/frequencies : how to observe the dynamics

Pavia, 07/06/16



DC Magnetometry

AC Susceptibility

MUSR

NMR

Mössbauer Spectroscopy

SPM particle blocking is noticeable when $\tau_m = \tau_N$ at a given temperature

Some response functions

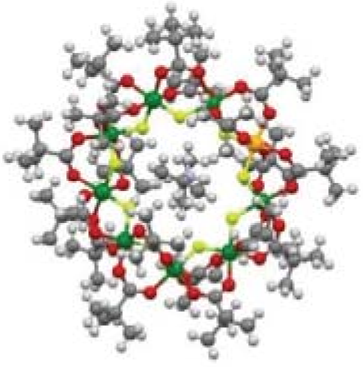
(to the externl stimuli)

Molecular magnets

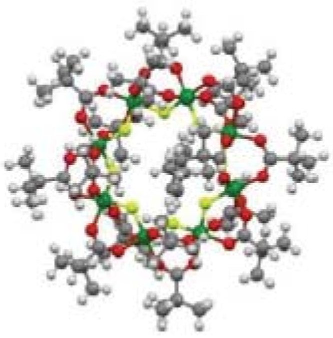
DC susceptibility : Curie law for T>100K

RINGS

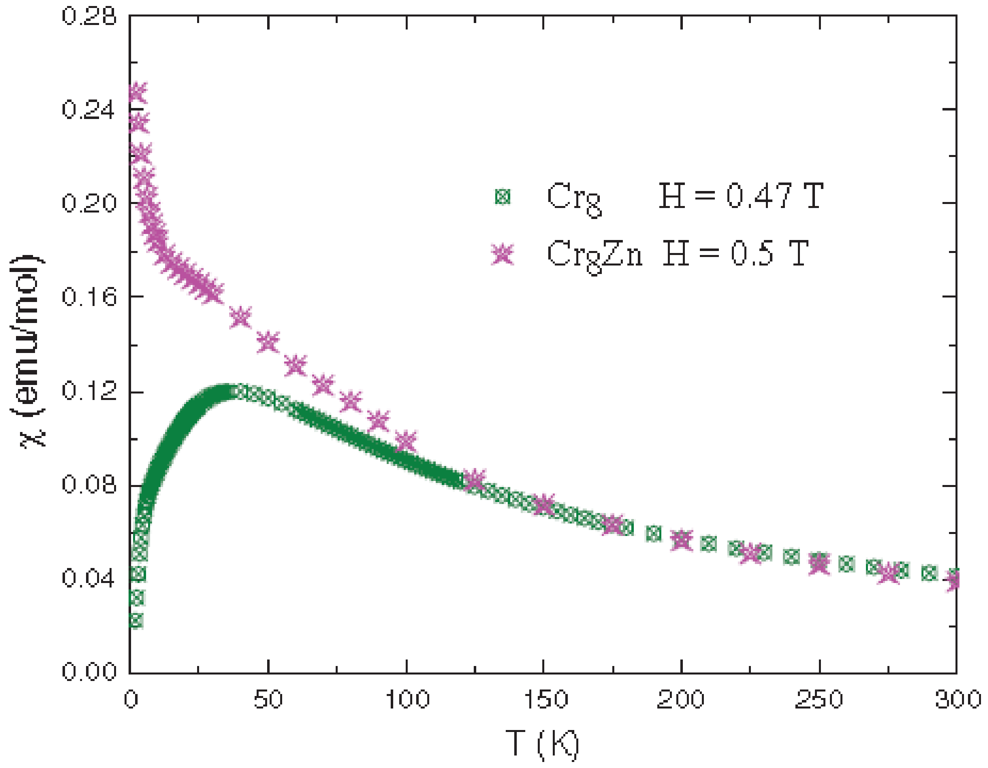
Just one atom makes the difference !!



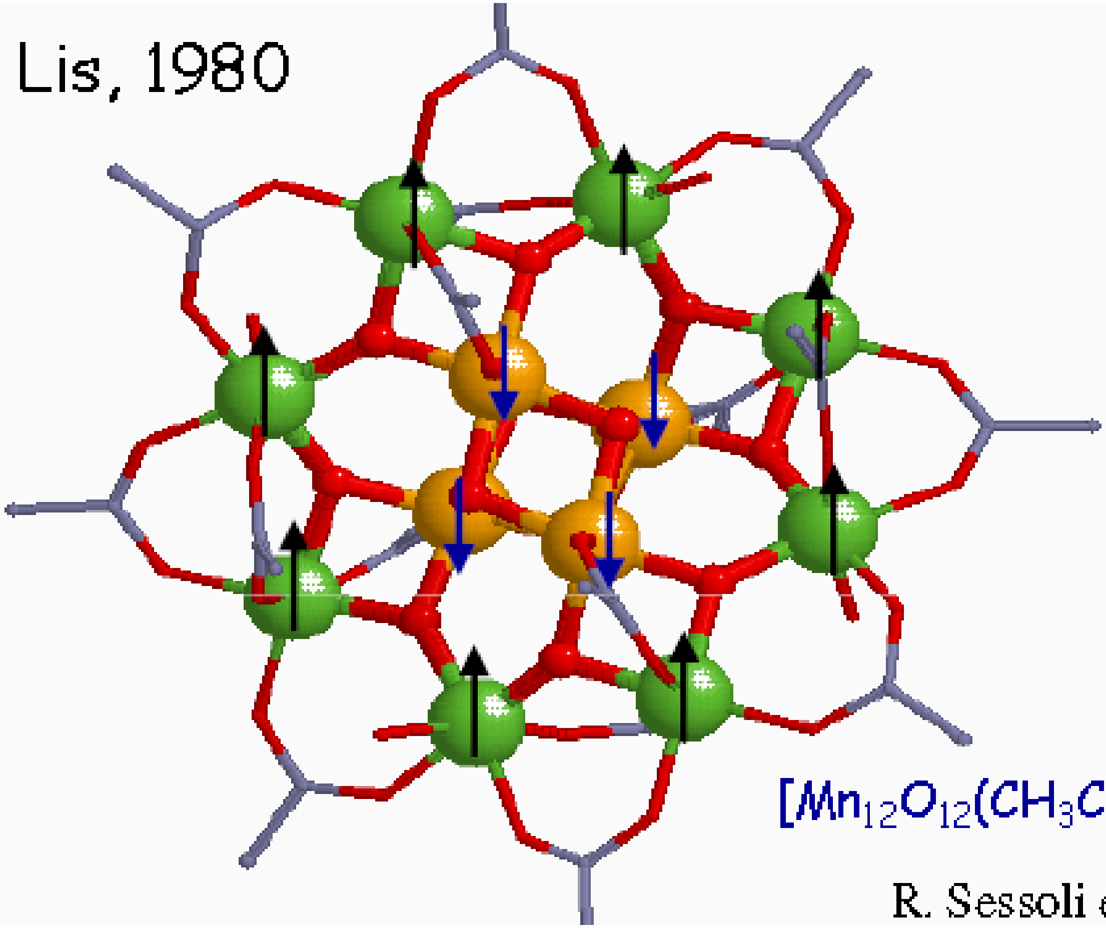
Cr_8Zn "Open Ring"



Cr_8 "Closed Ring"



The first single molecule magnet: Mn_{12}-acetate



Lis, 1980

Mn(III) ● $S = 2$ ↑

Mn(IV) ● $S = 3/2$ ↓

Oxygen ●

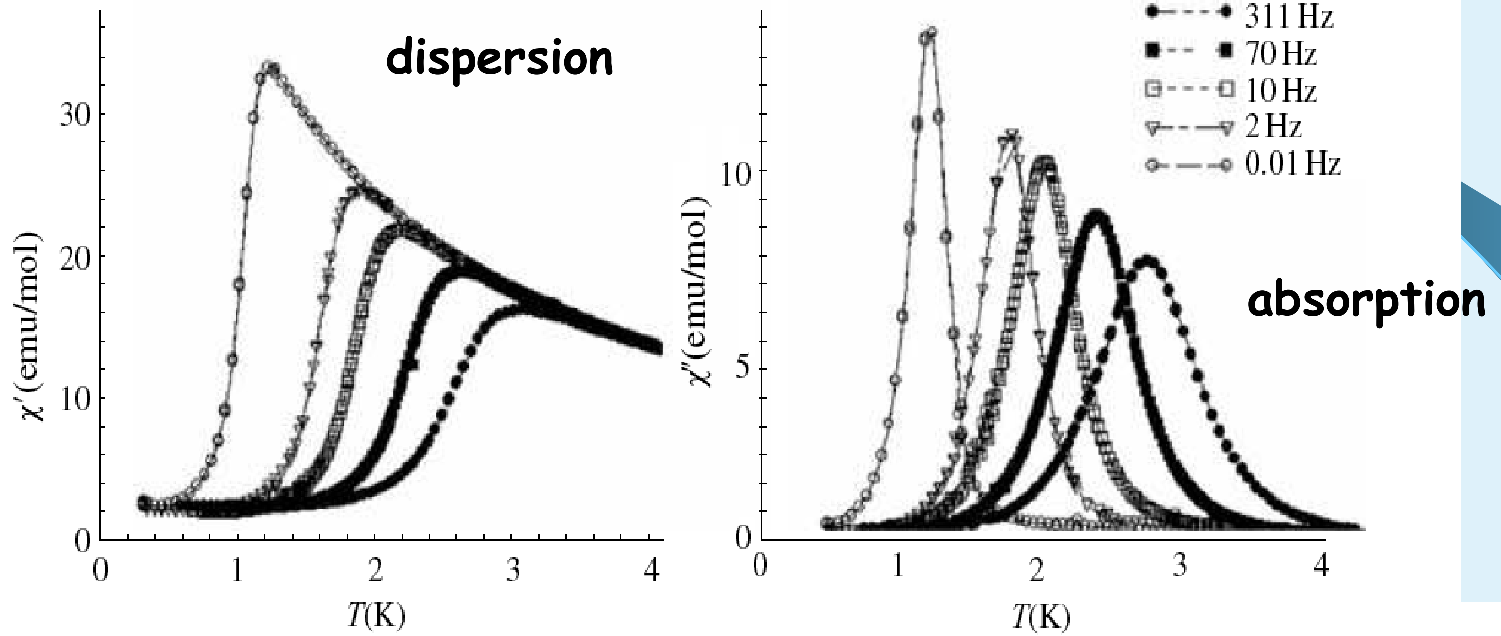
Carbon ●

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

R. Sessoli et al. JACS **115**, 1804 (1993)

AC susceptibility typical data : varying the frequency

Spin block : “Blocking” temperature

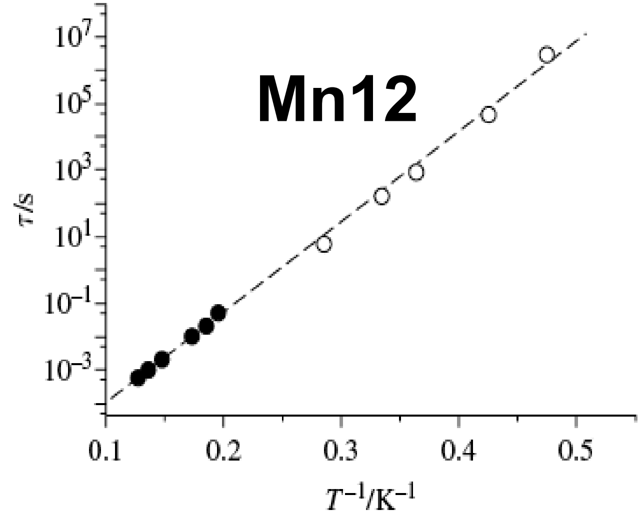


Maximum (response) for

$\omega_{AC}\tau = 1$

τ= correlation time of spins

i.e. Neel time !



Another "source" for understanding the response function.

An historical technique for Pavia:

Nuclear Magnetic Resonance

An historical technique for Pavia: Nuclear Magnetic Resonance

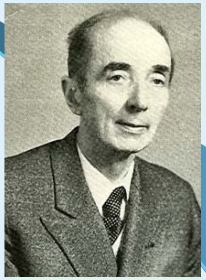
Pavia, 07/06/16

1944

Isidor Isaac Rabi

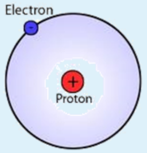
The Nobel Prize in Physics 1944 was awarded to Isidor Isaac Rabi *"for his resonance method for recording the magnetic properties of atomic nuclei"*.

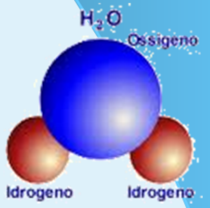
Esperimenti RMN di
Luigi Giulotto (Università di Pavia)

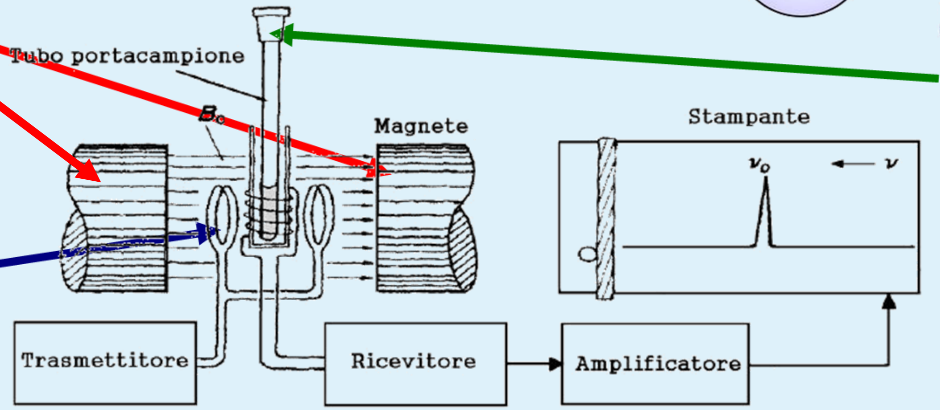


1948/50

Il **primo esperimento** di Risonanza Magnetica Nucleare
nella materia condensata (nucleo dell'atomo di idrogeno)







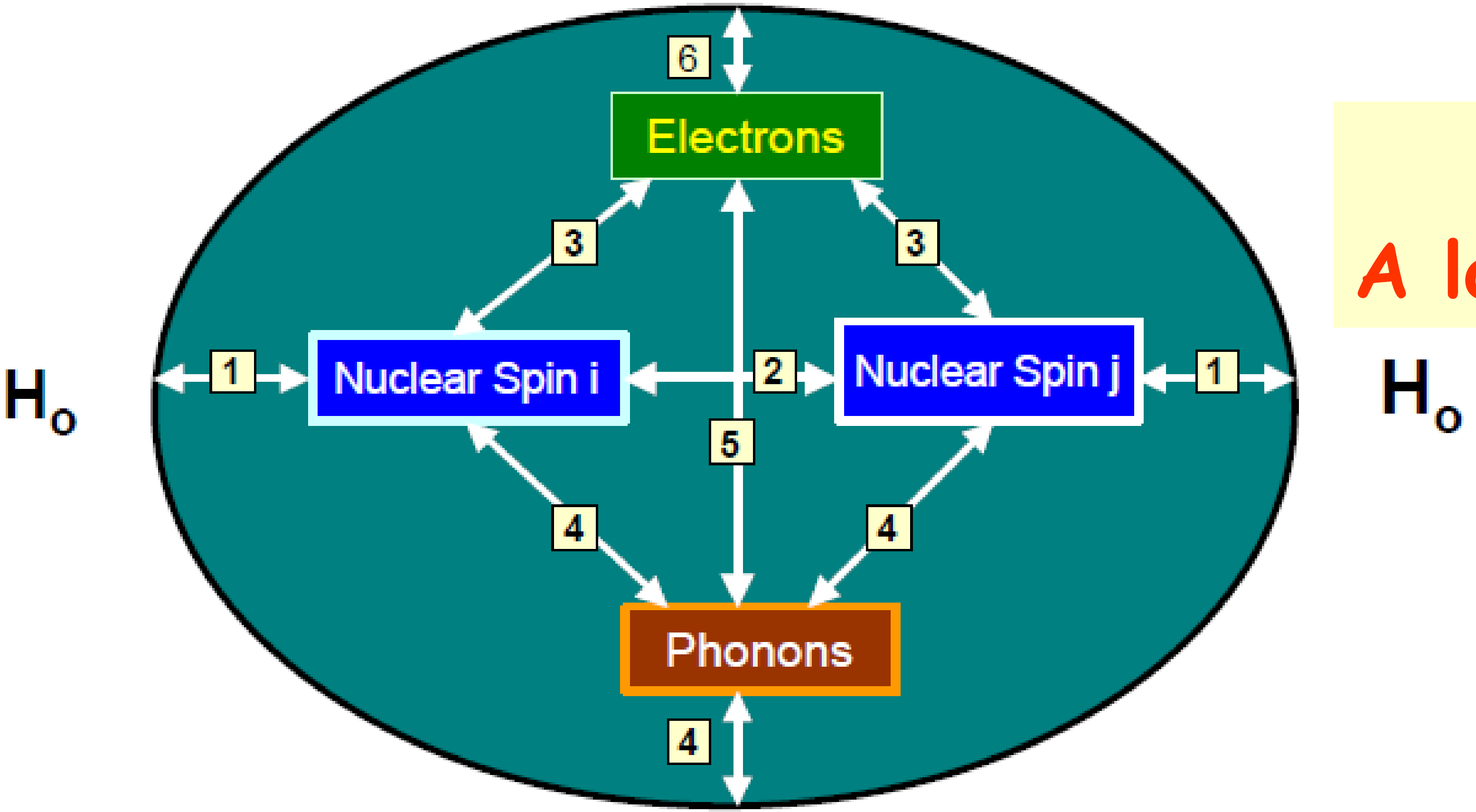
Magnete che genera un campo magnetico statico

Bobine che generano un campo magnetico a radiofrequenza

Campione di H_2O

1945/46 : Bloch - Purcell

Basic Nuclear Spin Interactions



NMR.
A local probe

$H = H_z + H_D + H_{CS} + H_Q + H_{hyp} + H_J + H_{ce}$

H_Z = Zeeman interaction , path 1 ($\propto B_0 \sim 10^{9}$)

H_D = Dipolar interactions among nuclear spins, path 2,3 ($\propto I \cdot S \cdot r^{-3} \sim 10^{3-5}$)

H_{CS} = Chemical shielding interaction, path 6 and 3 ($\sim 1 - 10^{5}$)

H_Q = Quadrupolar interaction (nuclei $I > 1/2$) with surrounding ∇E), path 3 ($10^{3} - 10^{7}$)

H_{hyp} (paramagnetic shift) = hyperfine e-n dipolar (pseudocontact) and contact interactions, path 3 (influenced by 5)

H_J = J-coupling, path 2 via path 3

H_{ce}= interaction of nuclei with conduction electrons (e.g. nuclei, Knight shift), path 3

NMR

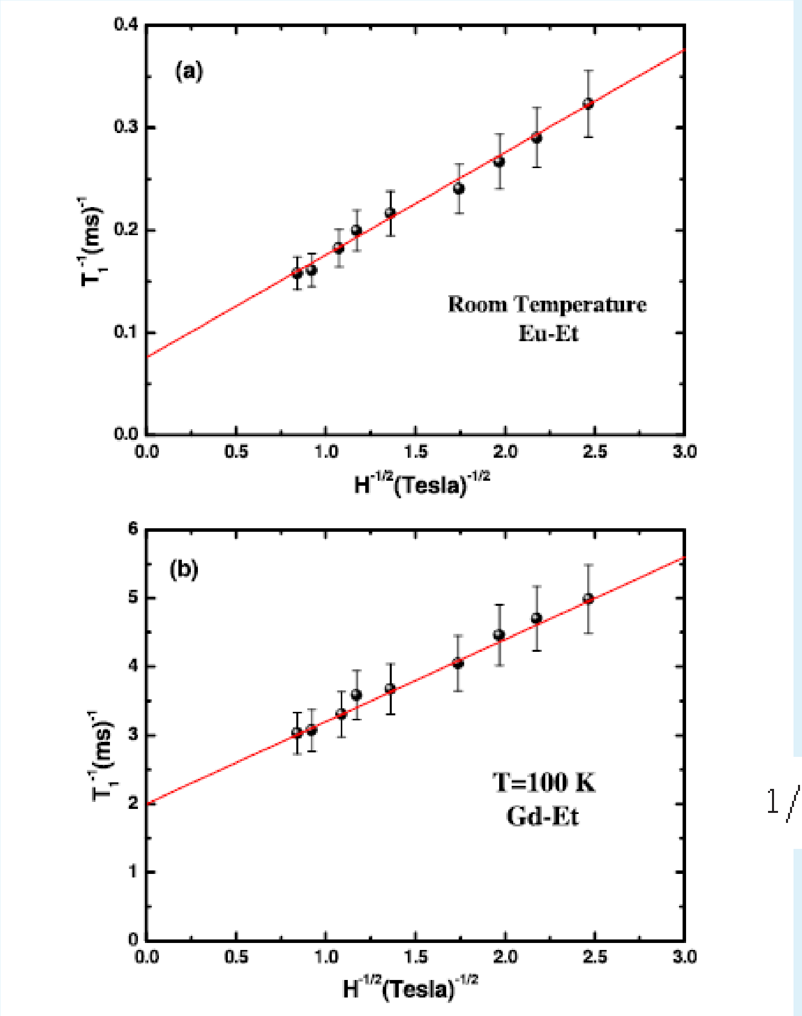
- Absorption spectra (almost static response)
- Nuclear time to reach equilibrium $1/T_1$:

  nuclear dynamical response
- Also T_2

EXAMPLE AT ROOM TEMPERATURE

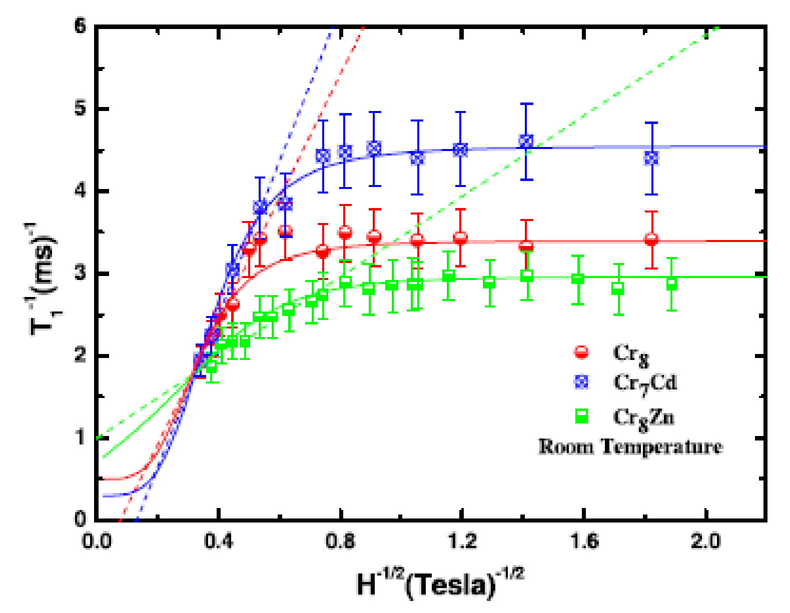
Pavia, 07/06/16

1D spin diffusion
Molecular chians



$$1/T_1 = PH^{\ 1/2} + Q.$$

No spin diffusion
Molecular rings



$$1/T_1 = A/(1 + (H/H_c)^2) + C \ (\mathrm{ms}^{\ 1})$$

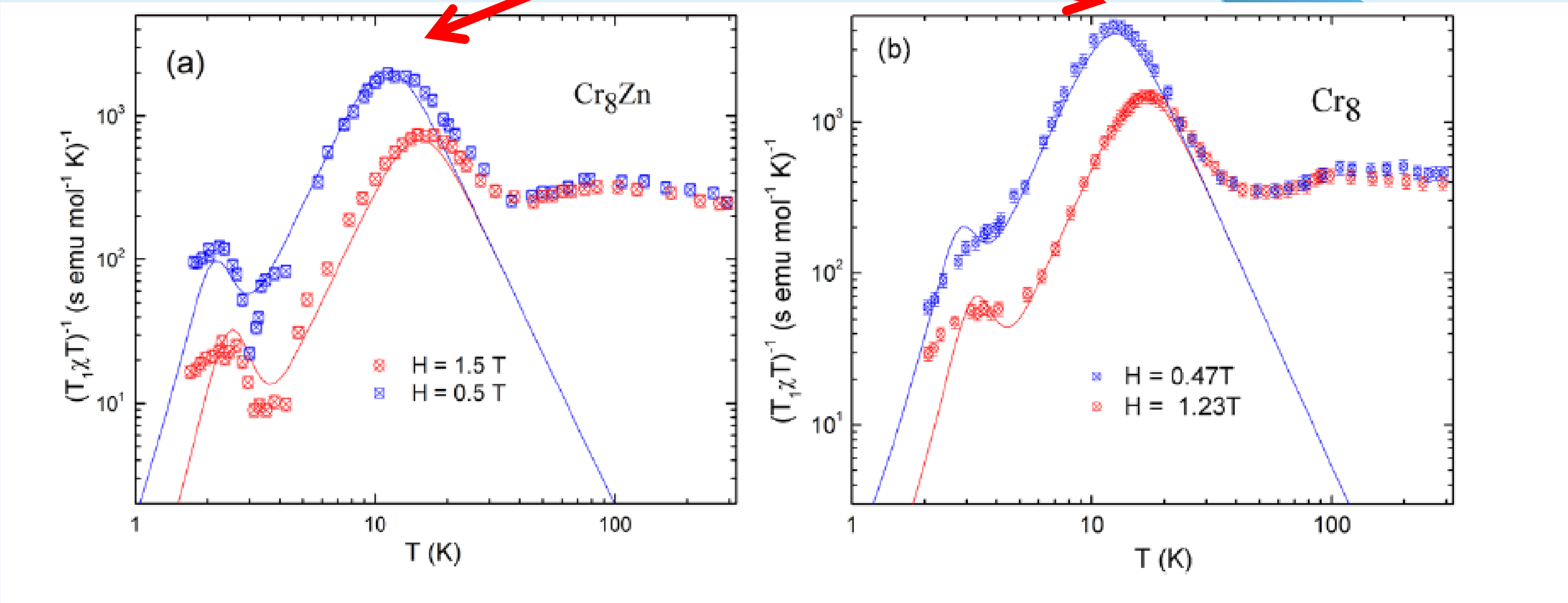
AGAIN "CLASSICAL" BEHAVIOUR DETECTING SPIN MOTION

Pavia, 07/06/16

Vs temperature behaviour

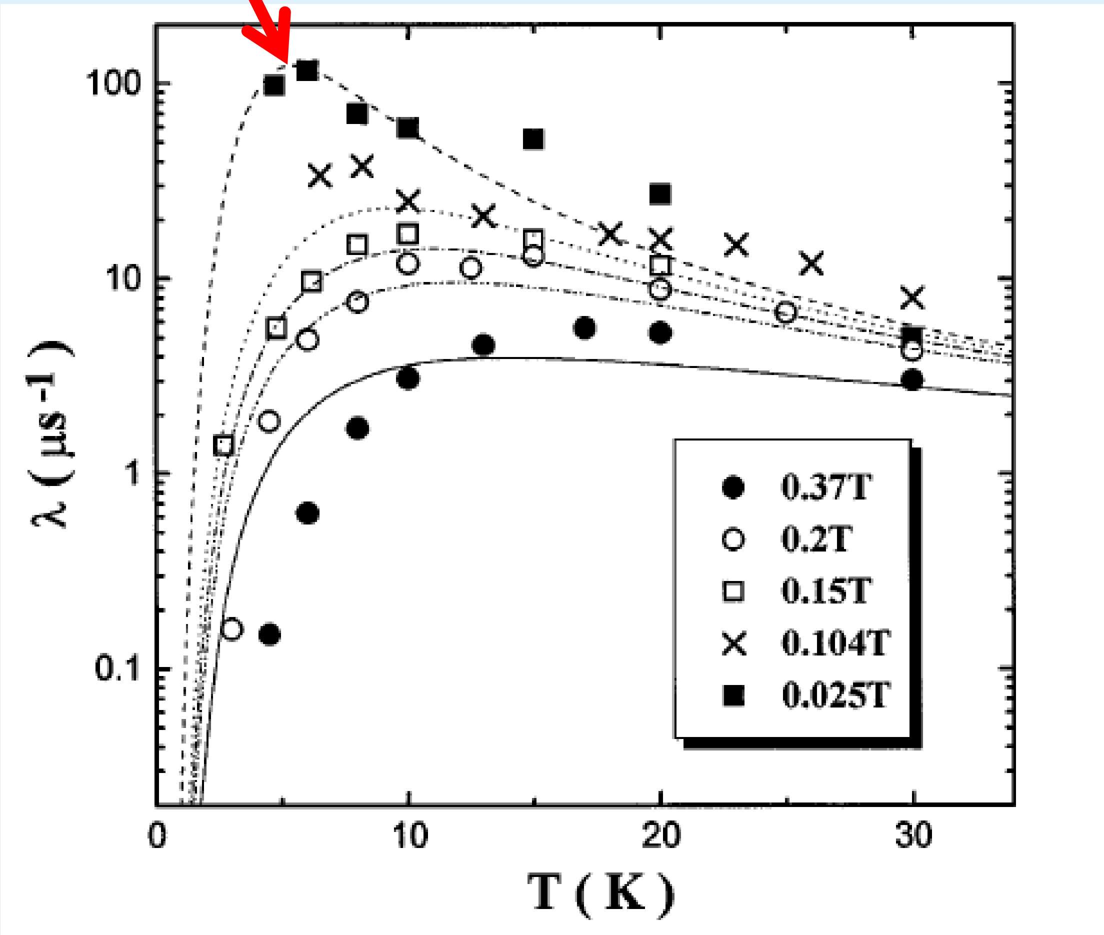
Peaks → max resp. function at

$$\frac{1}{T_1\chi T} = A\left\{\frac{\lambda_1\omega_{c1}(T)}{\omega_{c1}^2(T)+\omega_L^2} + \frac{\lambda_2\omega_{c2}(T)}{\omega_{c2}^2(T)+\omega_L^2}\right\}$$



"Quasi-classical" effect : Muon Spin Resonance, a local technique similar to NMR

Peaks at $\omega_{meas}\tau \approx 1$



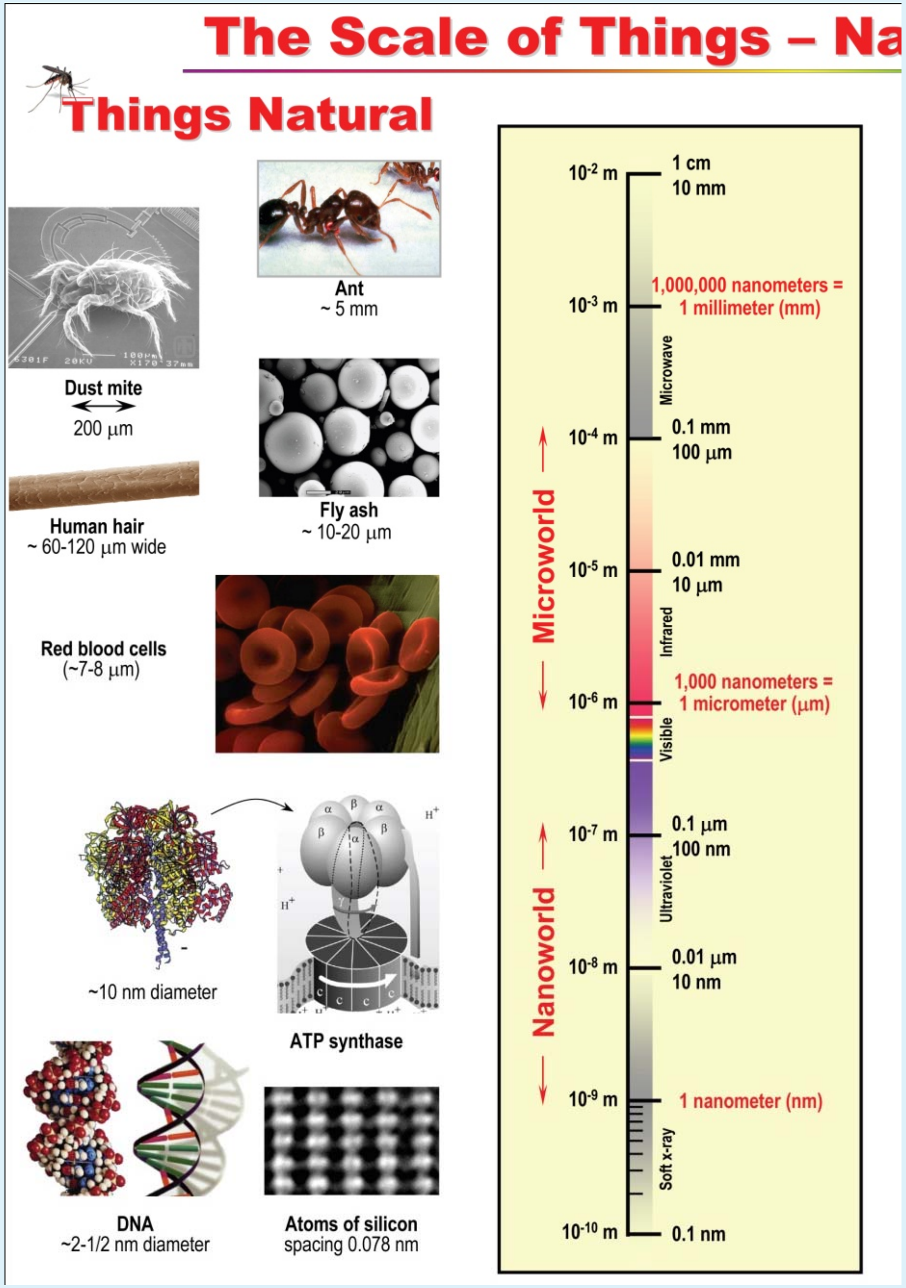
Mn12

max when $\omega_{meas}\tau_c \approx 1$

In this case a bit more complicate due to quantum structure of energy levels

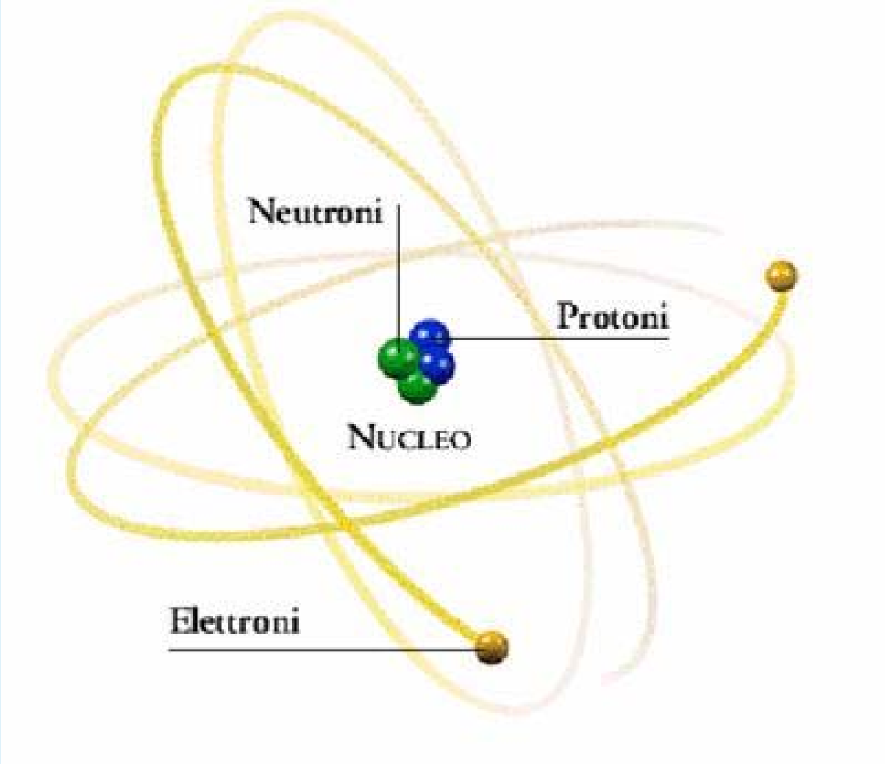
… going to quantum world

Struttura atomica e nucleare

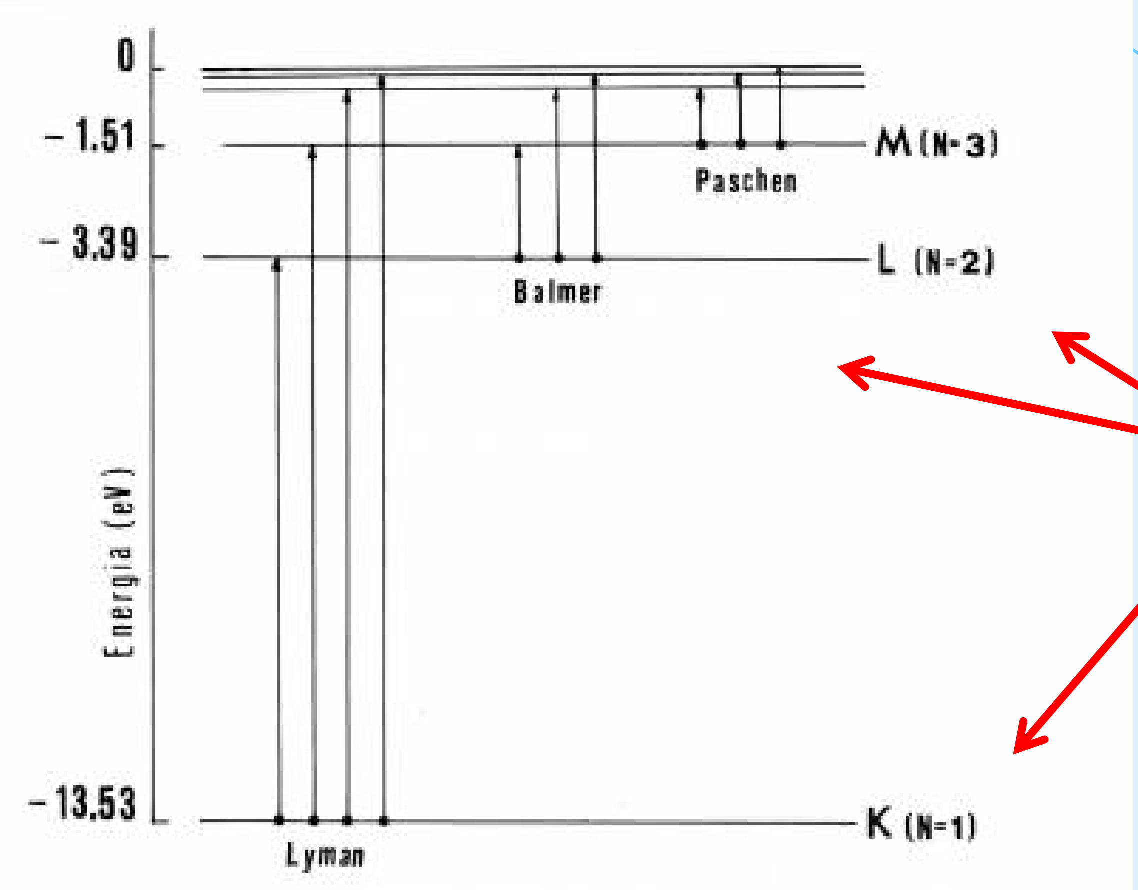


Organi → tessuti → molecole → Atomi → nuclei

Particelle atomiche e subatomiche



Struttura atomica e nucleare



Quantizzazione dei Livelli energetici

Esempio : atomo di idrogeno

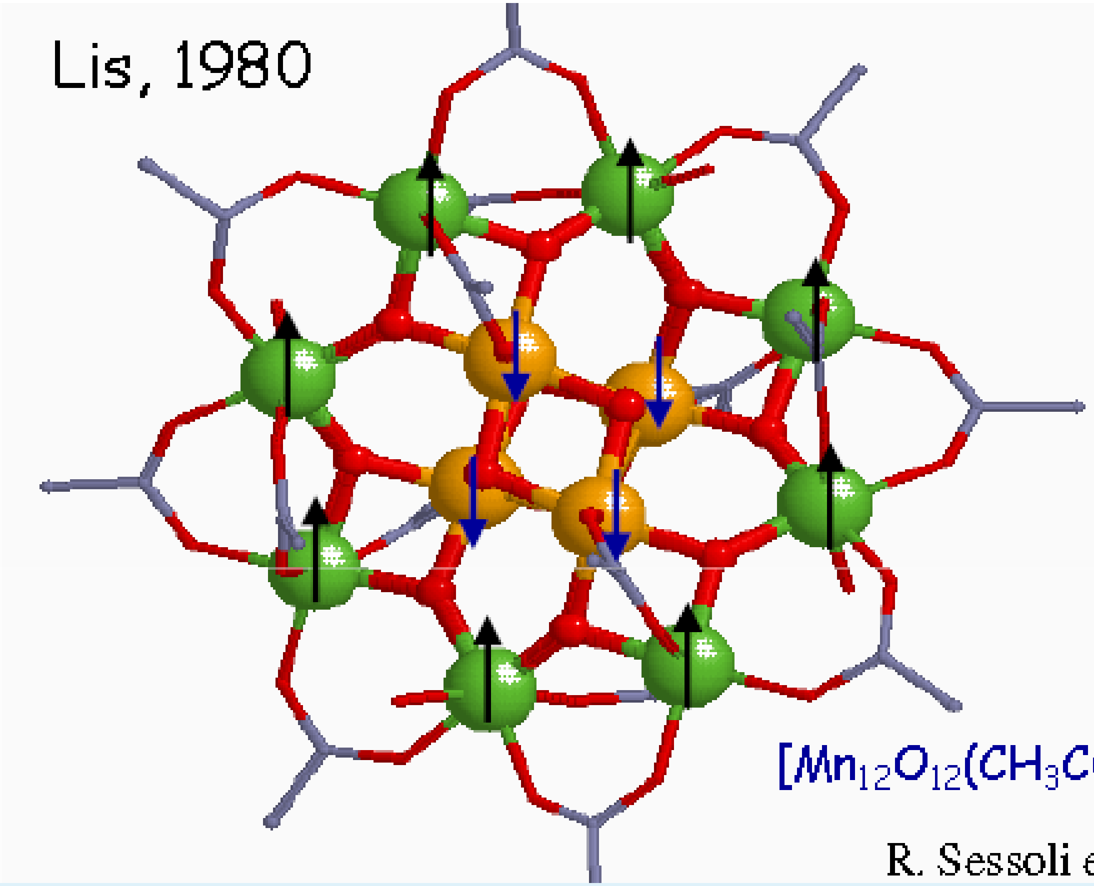
ATOMI E NUCLEI SONO SISTEMI QUANTISTICI

Un sistema quantistico non può assumere (in modo continuo) tutti i valori di energia

Quantum Physics of Mn12

Few N spins : $(2s+1)^N$ levels

The first single molecule magnet: Mn_{12}-acetate



Mn(III) ● $S = 2$ ↑

Mn(IV) ● $S = 3/2$ ↓

Oxygen ●

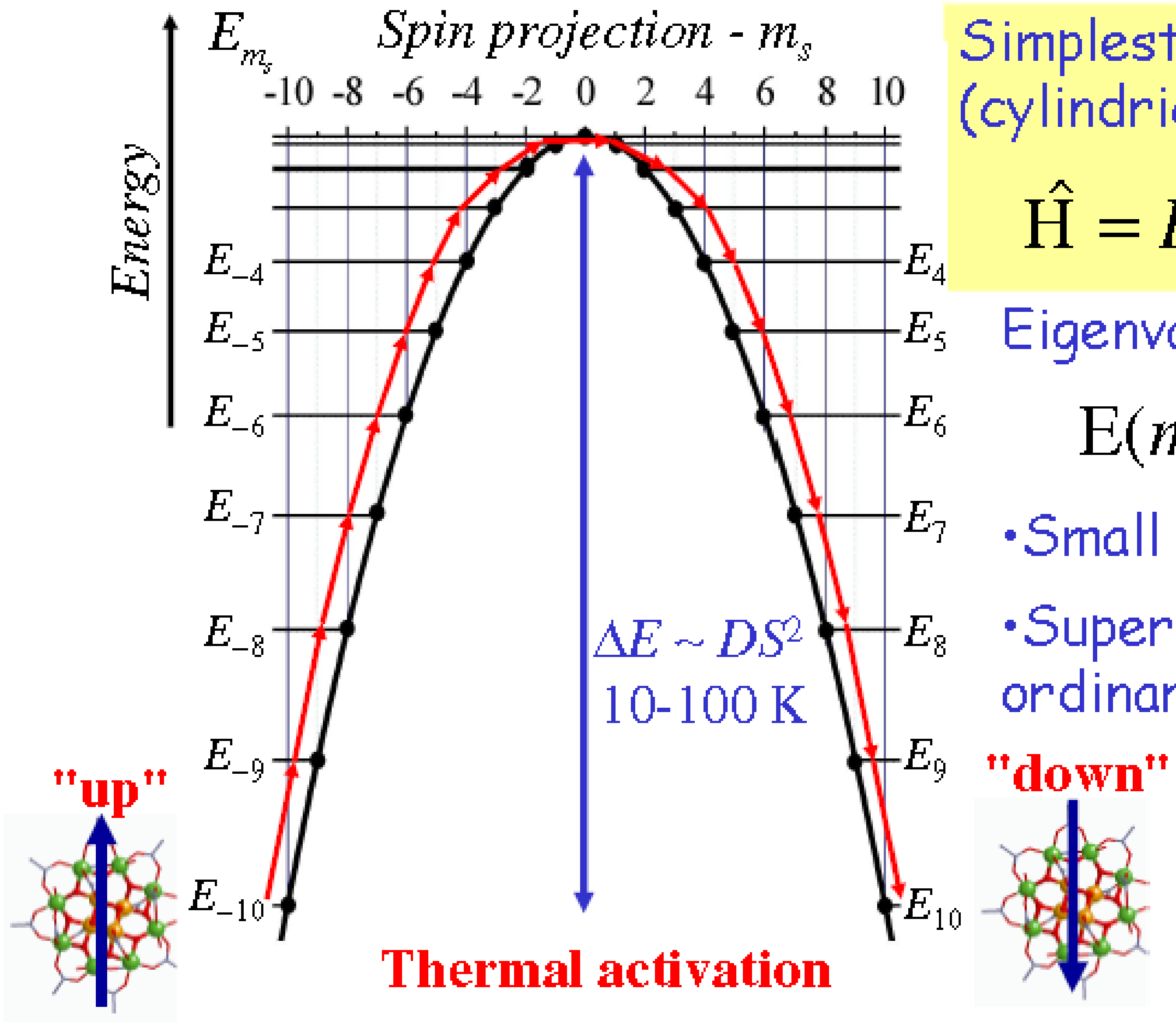
Carbon ●

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

R. Sessoli et al. JACS **115**, 1804 (1993)

Discrete levels. Superparamagnetic behaviour

Quantum effects at the nanoscale ($S = 10$)



Simplest case: axial (cylindrical) crystal field

$$\hat{H} = D\hat{S}_z^2 \qquad (D < 0)$$

Eigenvalues given by:

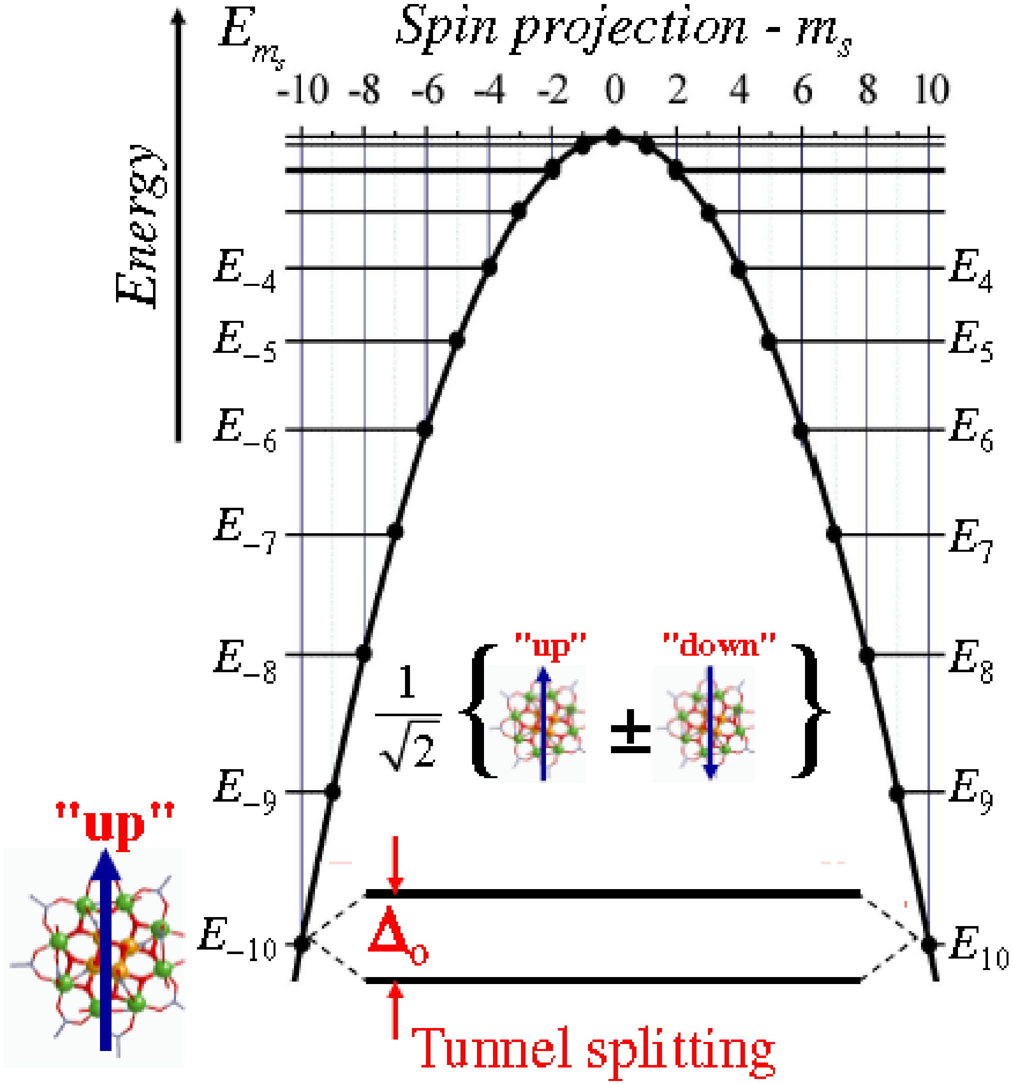
$$E(m_s) = -|D| m_s^2$$

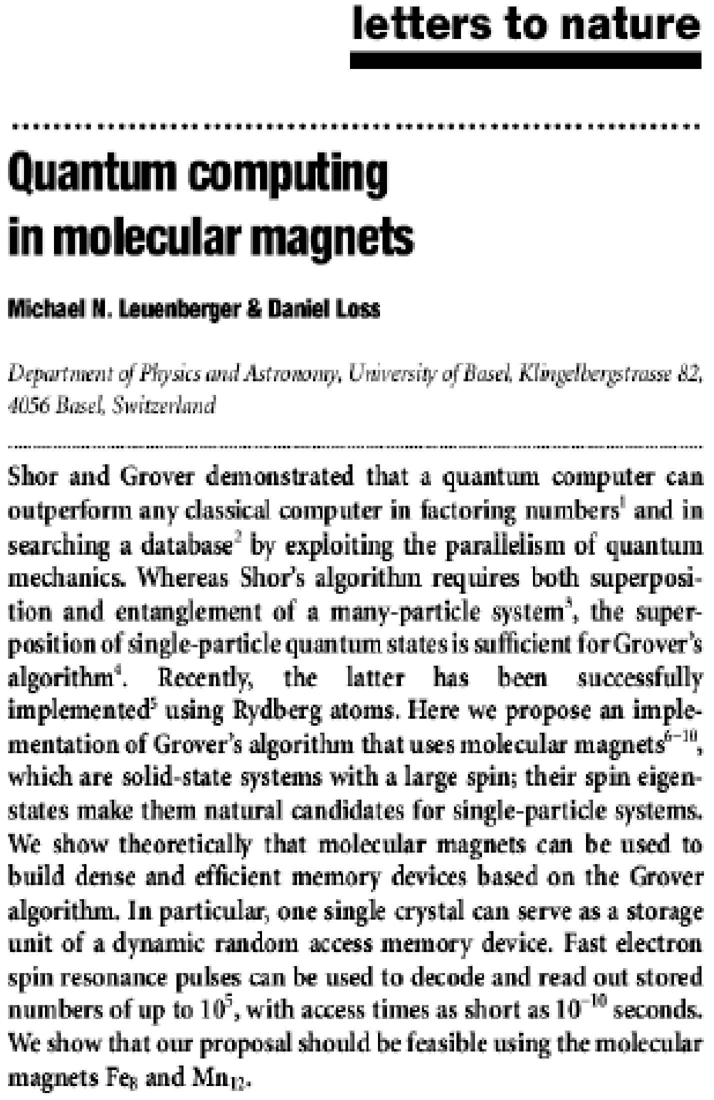
- Small barrier - DS^2
- Superparamagnet at ordinary temperatures

$|D| \sim 0.1 - 1$ K for a typical single molecule magnet

Quantum tunneling of the magnetization (QTM)

Quantum effects at the nanoscale (S = 10)





letters to nature

Quantum computing in molecular magnets

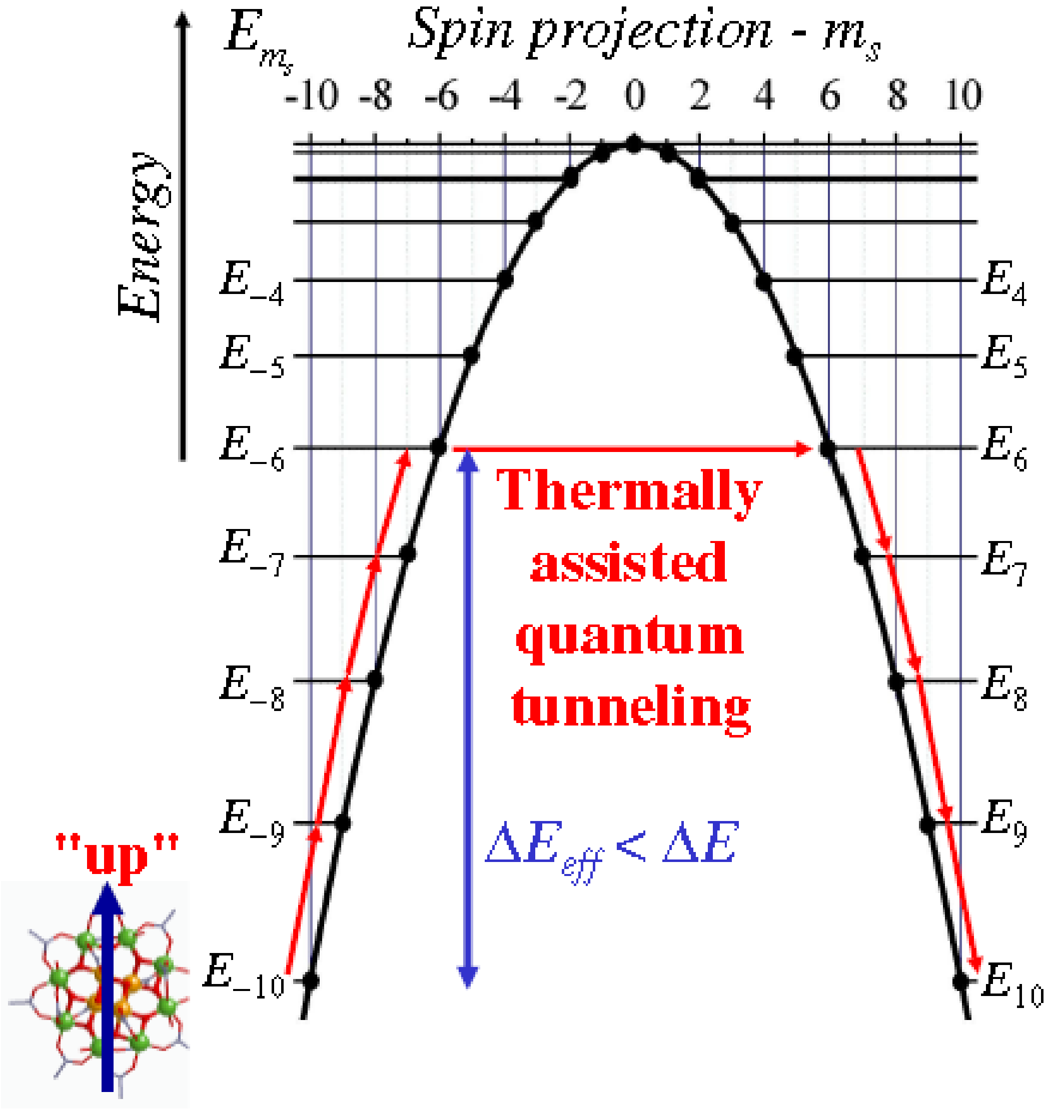
Michael N. Leuenberger & Daniel Loss

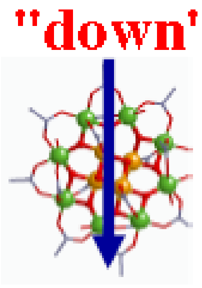
Department of Physics and Astronomy, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland

Shor and Grover demonstrated that a quantum computer can outperform any classical computer in factoring numbers[1] and in searching a database[2] by exploiting the parallelism of quantum mechanics. Whereas Shor's algorithm requires both superposition and entanglement of a many-particle system[3], the superposition of single-particle quantum states is sufficient for Grover's algorithm[4]. Recently, the latter has been successfully implemented[5] using Rydberg atoms. Here we propose an implementation of Grover's algorithm that uses molecular magnets[6–10], which are solid-state systems with a large spin; their spin eigenstates make them natural candidates for single-particle systems. We show theoretically that molecular magnets can be used to build dense and efficient memory devices based on the Grover algorithm. In particular, one single crystal can serve as a 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 10^{-10} seconds. We show that our proposal should be feasible using the molecular magnets Fe_8 and Mn_{12}.

Thermally assisted Quantum Tunneling

Quantum effects at the nanoscale ($S = 10$)





Break axial symmetry:

$$\hat{H} = D\hat{S}_z^2 + \hat{H}_T$$

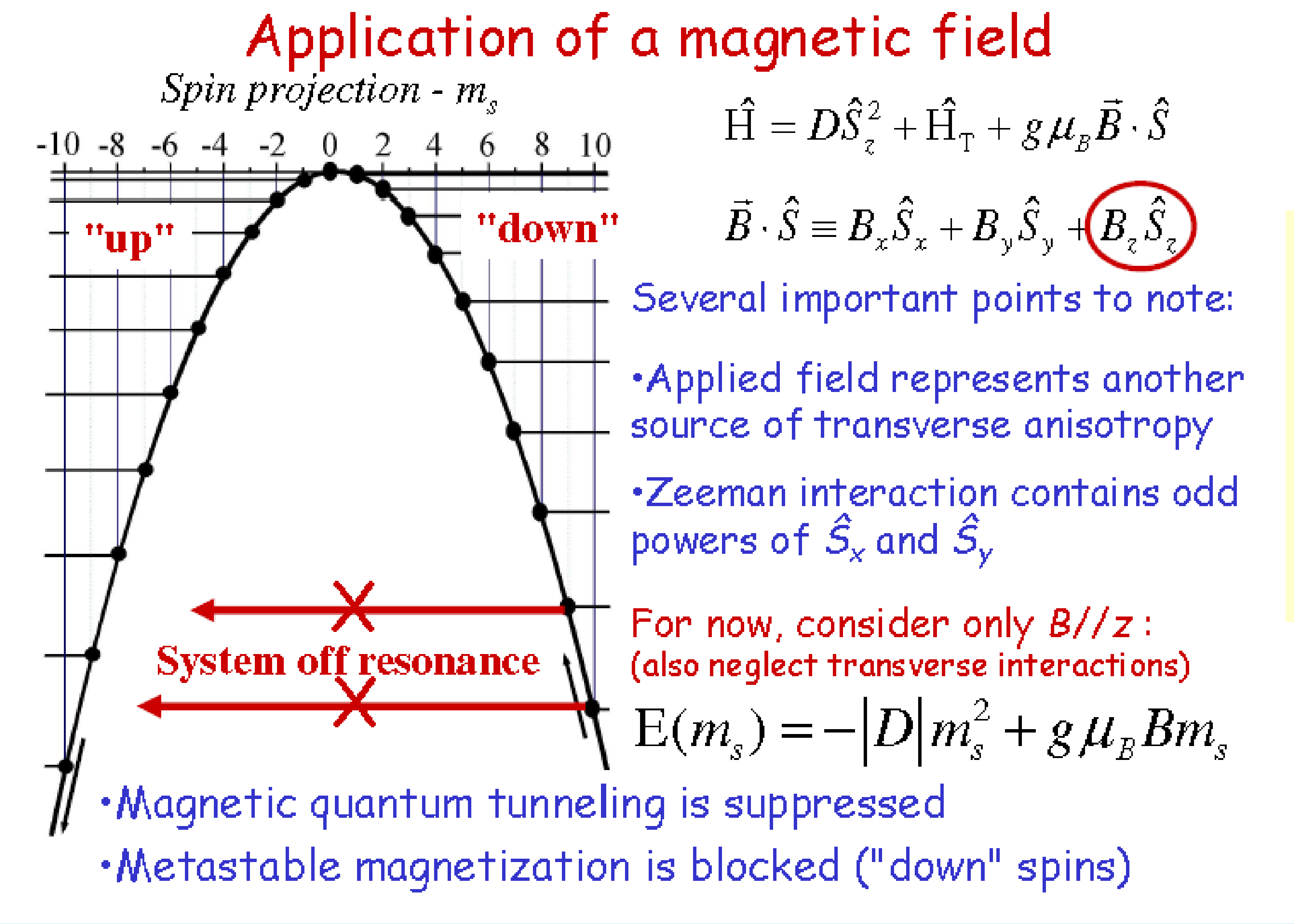
$H_T \Rightarrow$ interactions which do not commute with $\hat{S}_z$

- m_s **not** good quantum #
- Mixing of m_s states

$\Rightarrow$ resonant tunneling (of m_s) through barrier

- Lower effective barrier

Applying a field : levels change (Zeeman effect)



Application of a magnetic field

$$\hat{H} = D\hat{S}_z^2 + \hat{H}_T + g\mu_B\vec{B}\cdot\hat{S}$$

$$\vec{B}\cdot\hat{S} \equiv B_x\hat{S}_x + B_y\hat{S}_y + \boxed{B_z\hat{S}_z}$$

Several important points to note:

- Applied field represents another source of transverse anisotropy
- Zeeman interaction contains odd powers of $\hat{S}_x$ and $\hat{S}_y$

For now, consider only $B//z$:
(also neglect transverse interactions)

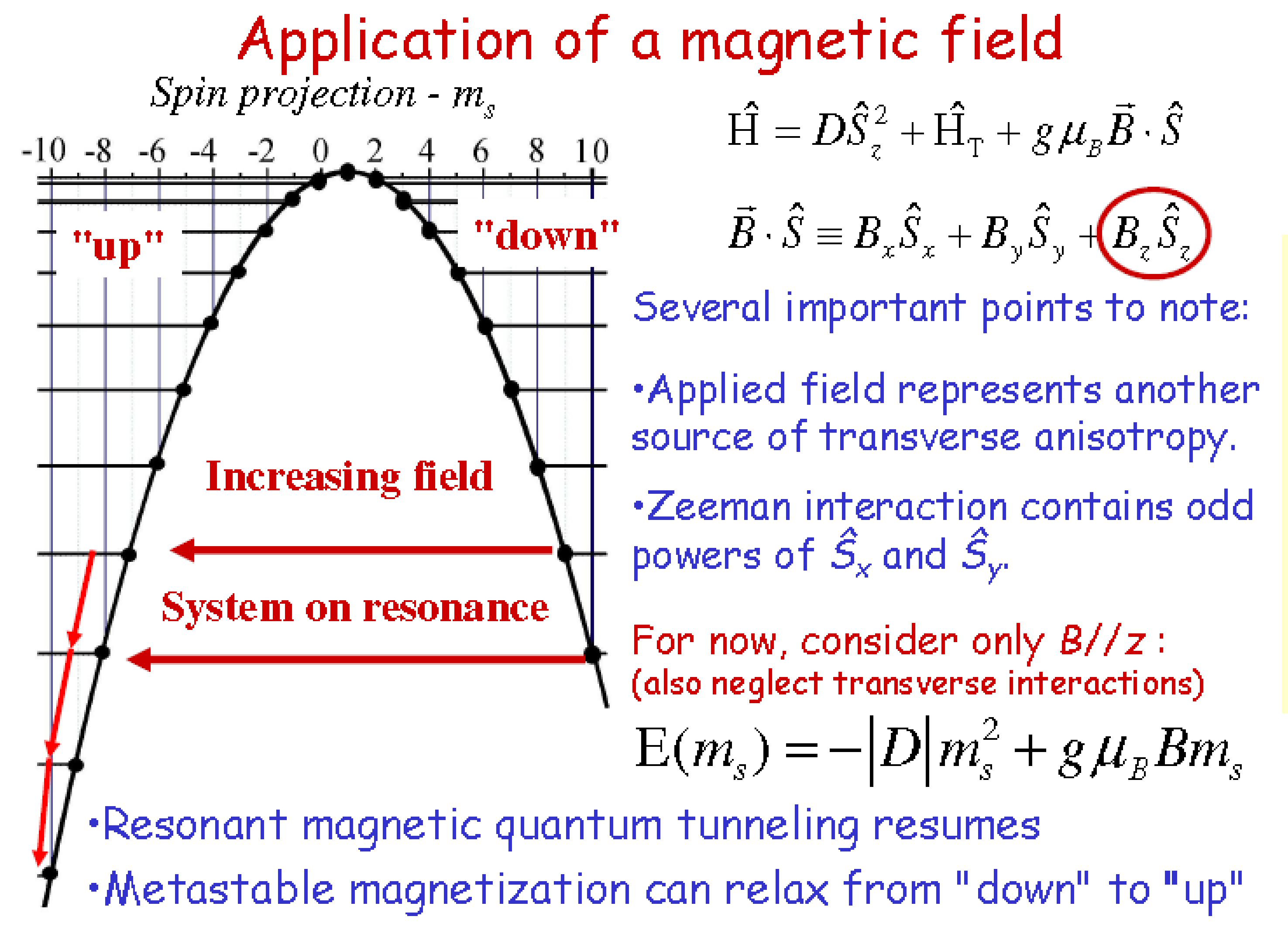
$$E(m_s) = -|D|m_s^2 + g\mu_B B m_s$$

- Magnetic quantum tunneling is suppressed
- Metastable magnetization is blocked ("down" spins)

OFF Res

QTM OFF

Applying a field : levels change (Zeeman effect)



Application of a magnetic field

$$\hat{\mathrm{H}} = D\hat{S}_z^2 + \hat{\mathrm{H}}_\mathrm{T} + g\mu_B\vec{B}\cdot\hat{S}$$

$$\vec{B}\cdot\hat{S} \equiv B_x\hat{S}_x + B_y\hat{S}_y + \boxed{B_z\hat{S}_z}$$

Several important points to note:

- Applied field represents another source of transverse anisotropy.
- Zeeman interaction contains odd powers of $\hat{S}_x$ and $\hat{S}_y$.

For now, consider only $B//z$:
(also neglect transverse interactions)

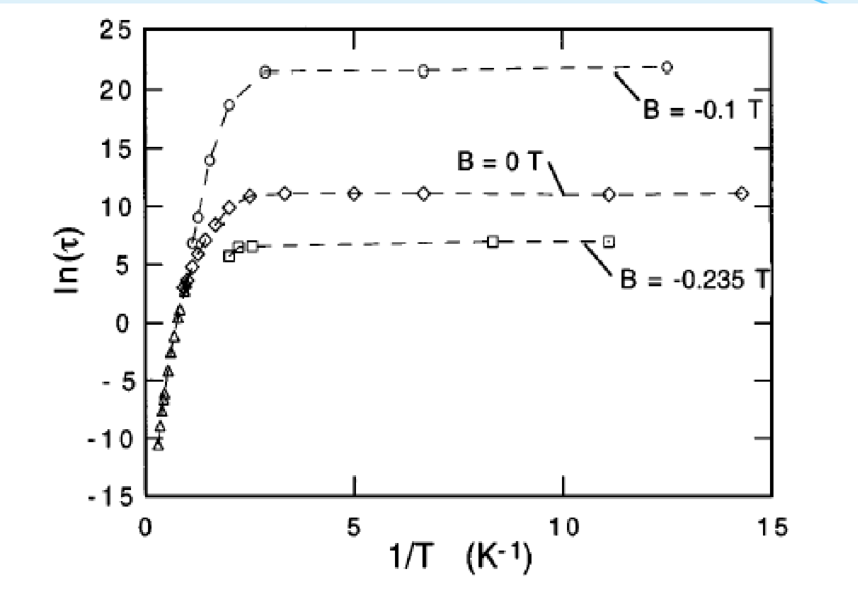
$$\mathrm{E}(m_s) = -|D|m_s^2 + g\mu_B B m_s$$

- Resonant magnetic quantum tunneling resumes
- Metastable magnetization can relax from "down" to "up"

ON
Res

QTM
ON

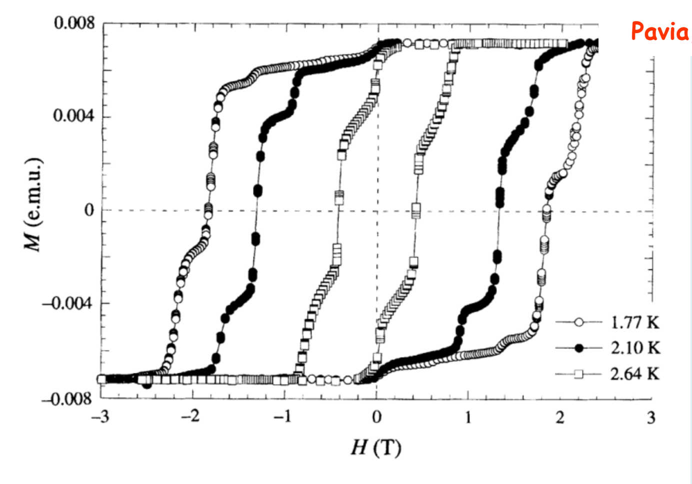
EXPERIMENTAL EVIDENCES of QTM



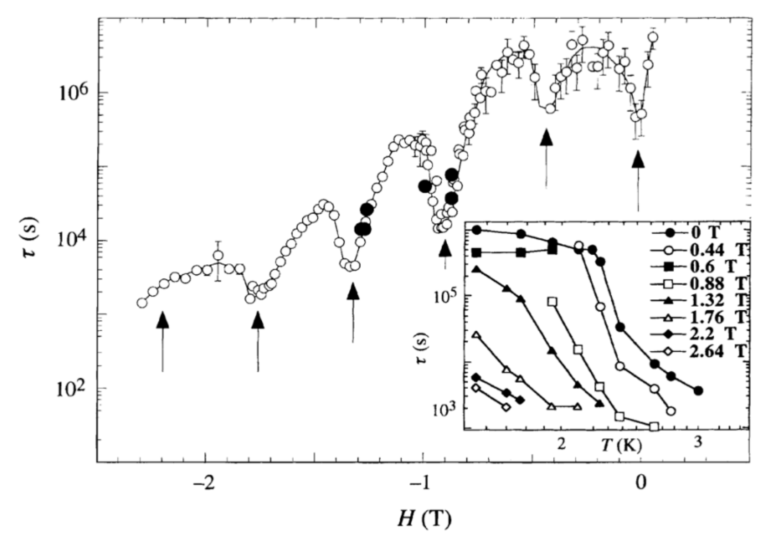
the relaxation time becomes T-independent

Nature 383, 145.

appearence of step-like hysteresis loop of M



vertical steps for H_z values corresponding to the LA



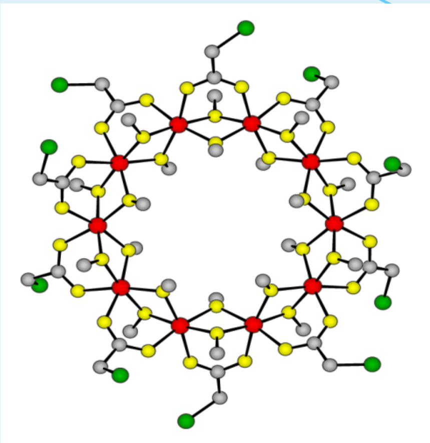
drop of the relaxation time in proximity of LA

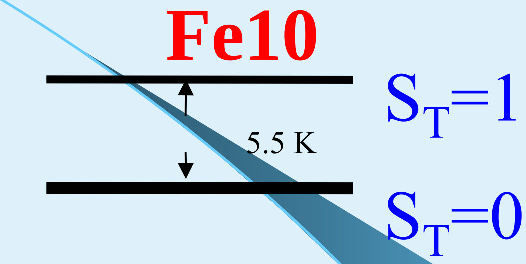
Quantum energy level crossing

The S_T=0 homometallic ring-like systems

Fe(III)   s = 5/2
AF ground state
(total spin S_T = 0)

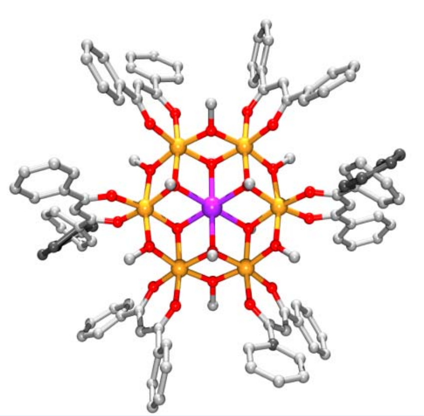
J ≈ 13.8 K
$\Delta_{0\to1}$ ≈ 5.5 K

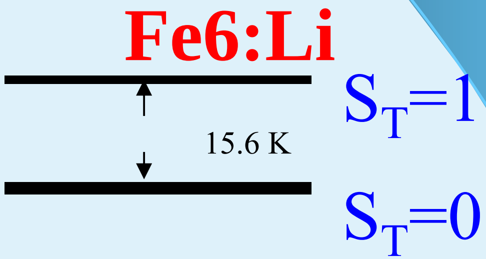




Fe(III)   s = 5/2
AF ground state
(total spin S_T = 0)

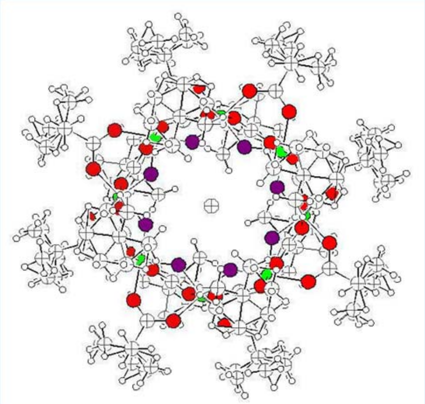
J ≈ 21 K
$\Delta_{0\to1}$ ≈ 15.6 K

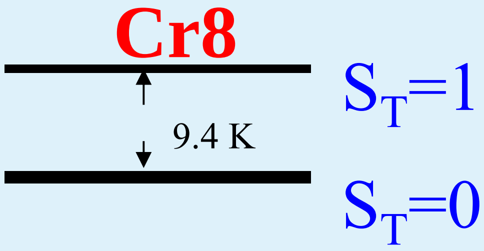




Cr(III)   s = 3/2
AF ground state
(total spin S_T = 0)

J ≈ 17.2 K
$\Delta_{0\to1}$ ≈ 9.4 K





Hamiltonian – energy levels

Hamiltonian for ring nanomagnets :

$$\Sigma_i J\ \mathbf{s}_i \cdot \mathbf{s}_{i+1} + \Sigma_i U(\mathbf{s}_i) + \Sigma_{ij} U_{i,j}(\mathbf{s}_i,\mathbf{s}_j) + g\, \mu_B\, \mathbf{B} \cdot \Sigma_i\, \mathbf{s}_i$$

$U(\mathbf{s}_i)$ = *crystal field anisotropies*

$U_{i,j}(\mathbf{s}_i,\mathbf{s}_j)$ = *intramol.dipolar interactions, hyperfine couplings, D-M interact., higher order exch., etc.*

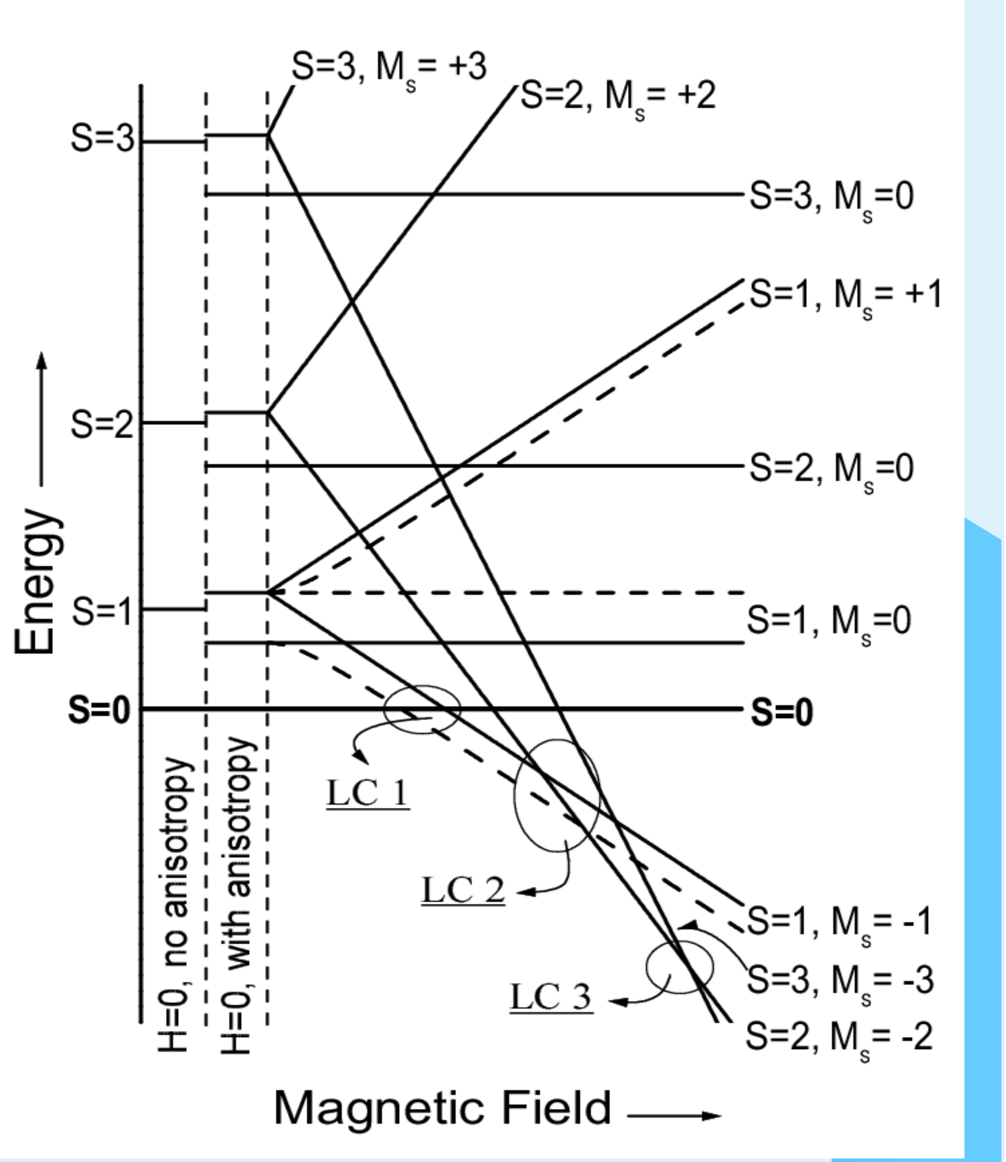
Approximate energy levels (Landè rule) :

$$E(S_{TOT}) = P/2\ S_{TOT}\ (S_{TOT} + 1) \qquad P = 4\ J\ /\ N$$

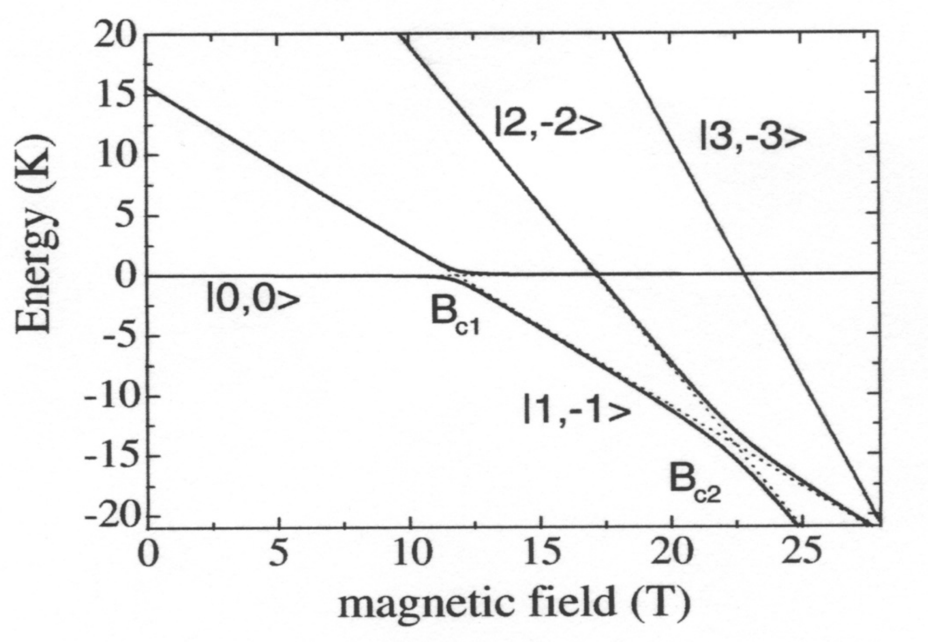
N = number of magnetic ions in the ring

- Level crossing fields depend on the angle θ between field and molecular axis z
- ***POSSIBLE LEVEL REPULSION AT CROSSING FIELDS (LEVEL ANTICROSSING)***

Diagram of energy levels (scheme)



ANTICROSSING OR AVOIDED LEVEL CROSSING (ALC)



ALC means mixing of wave-functions of two different levels

example case of energy levels of Fe6:Li

IN SOME RINGS THERE IS EXPERIMENTAL EVIDENCE FOR LEVEL REPULSION AT CROSSING FIELDS (ALC).

Questions (experimental) on fundamental structure of levels arise :

1) How can we distinguish LC from ALC ?

2) What is the "value" of ALC, i.e. the "gap" at the crossing ?

3) How (if) levels' lifetime affects the degree of ALC ?

4) Does any other quantum effect (e.g. QT of the Neel vector, QTNV in brief) occurs, especially near ALC or LC ?

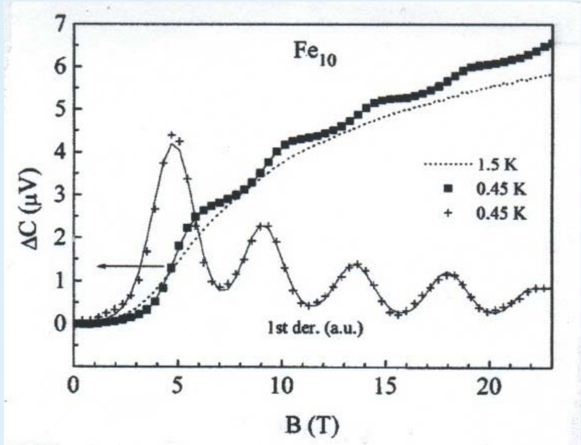
Macroscopic probes (magnetization , EPR, specific heat,….) help , but give not definitive answers

Evidences for ground state spin change & LC/LAC : torque and specific heat on single x-tals

1) Peaks of *dM/dH* at crossing fields ; **2) Plateaus** in *M(H)* corresponding to S=0, 1, 2,… states

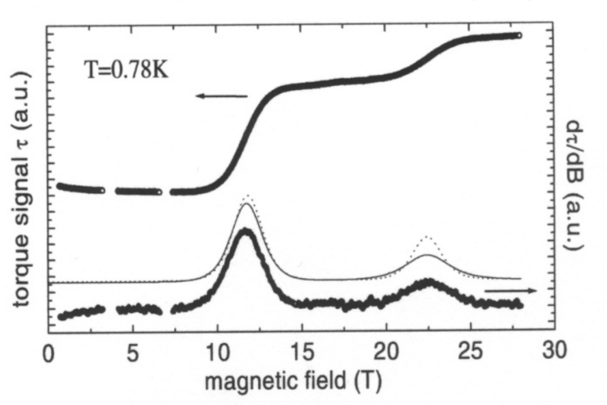
Ferric wheel Fe_{10}

[ϑ (H, unique axis) = 49.8°]

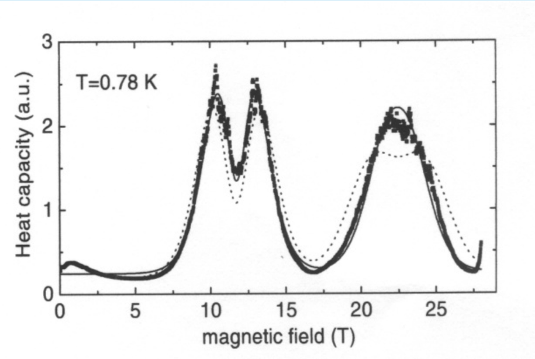


Fe6:Li

θ=(H,c)=25°

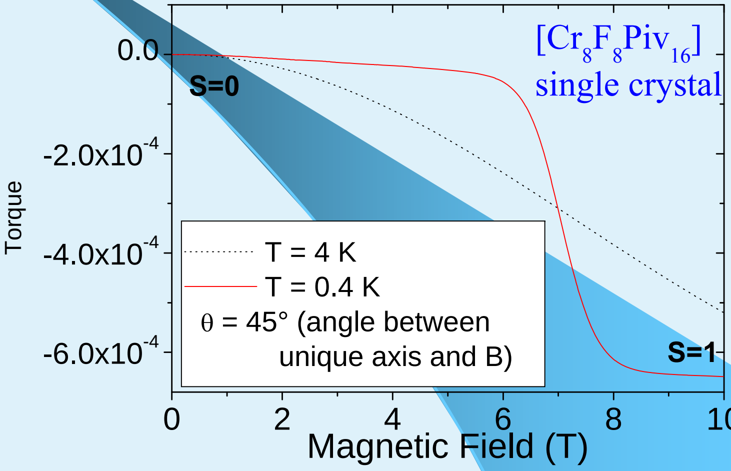


SPECIFIC HEAT

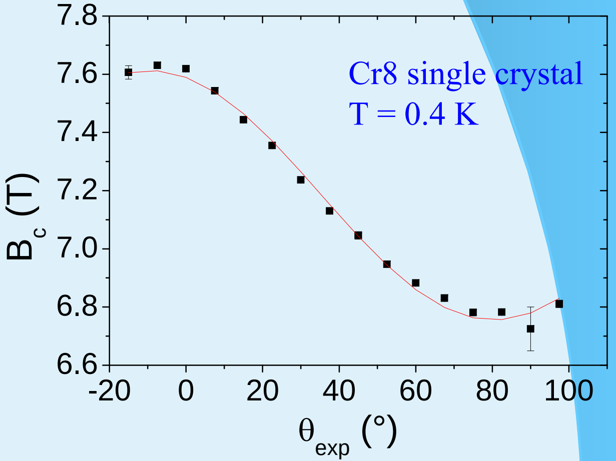


⇒ Level anti-crossing (LAC)

$Cr_8(Piv)_{16}$



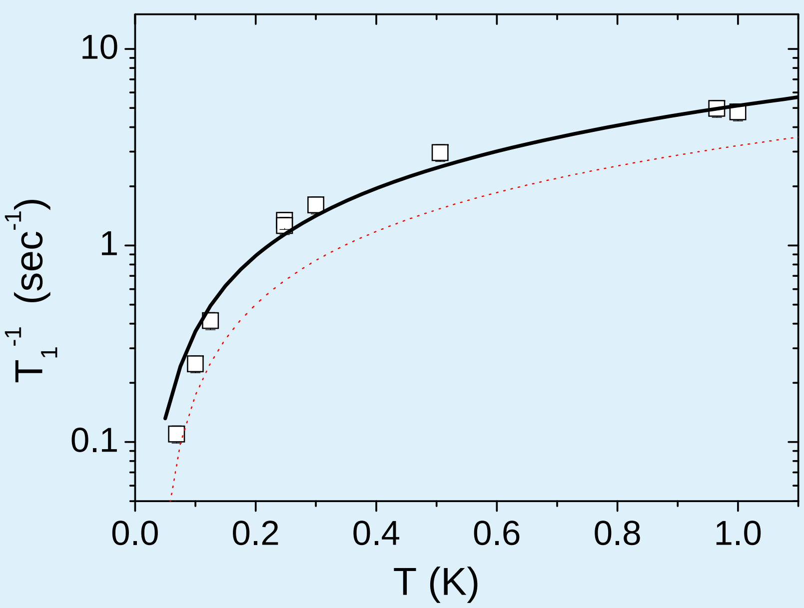
- **Angular dependence** of the crossing field

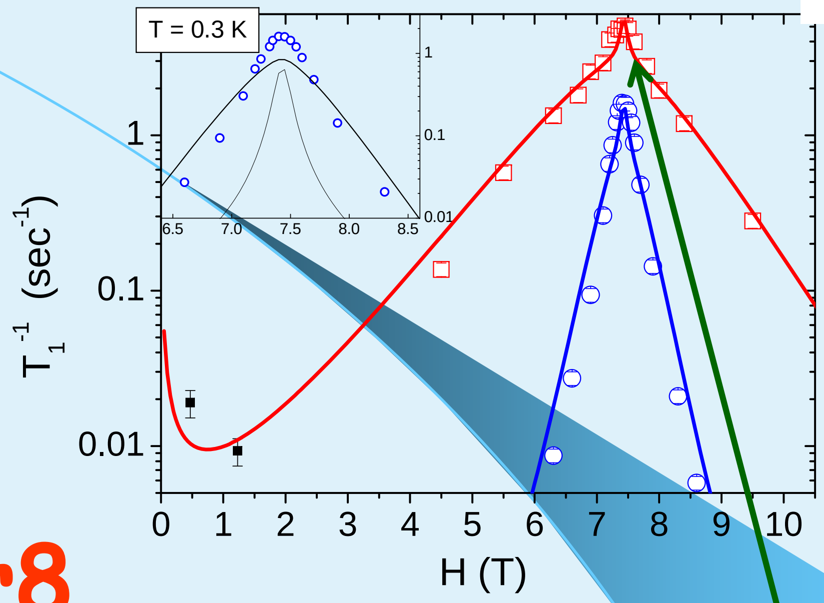


- *From specific heat : very small LAC*

1H NMR on Cr8 . T≤1K

Pavia, 07/06/16





Cr8

$$T_1^{-1} = A^2\left\{\frac{e^{-\frac{\Delta}{T}}}{1+e^{-\frac{\Delta}{T}}}\right\}\frac{\Gamma_1}{\Gamma_1^{\,2}+\omega_N^2} + B^2\frac{\Gamma_2}{\Gamma_2^{\,2}+(\hbar\omega_L-\Delta)^2}$$

$$\Delta = \sqrt{[g\mu_B(H_{c1}-H)]^2+\Delta_1^2}$$

Cross. Field H_{c1}

Quasi-elastic **Inelastic**

Fit parameters :

$\Delta_1 = 0.10\ (5)$ K , $A^2 = 9\ (1)\cdot 10^{13}$ rad^2 Hz^2 , $B^2 = 7\ (1)\cdot 10^{13}$ rad^2 Hz^2 ,

$\Gamma_1 = 4.0(3)*10^4$ H T rad Hz, $\Gamma_2 = 4.0(6)*10^6$ T rad Hz

The H and T dependences are due to direct, Raman or Orbach processes ? Between nuclei and phonons or electrons and phonons ? Does QTNV play any role ?

Looking for high anisotropy barrier

For having e.g. room temperature

Storage memories

High anisotropy Single ion Magnets: Tb-double deckers of phtalocyanines

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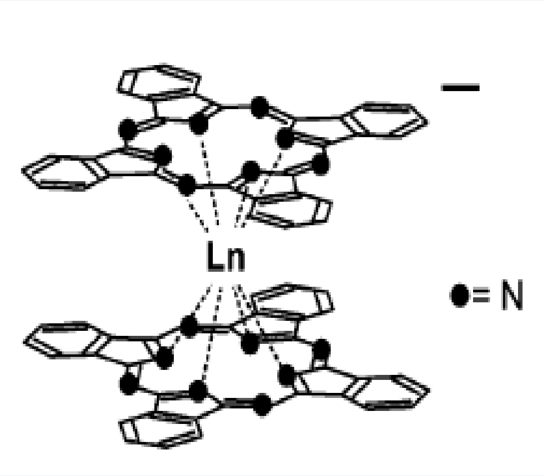
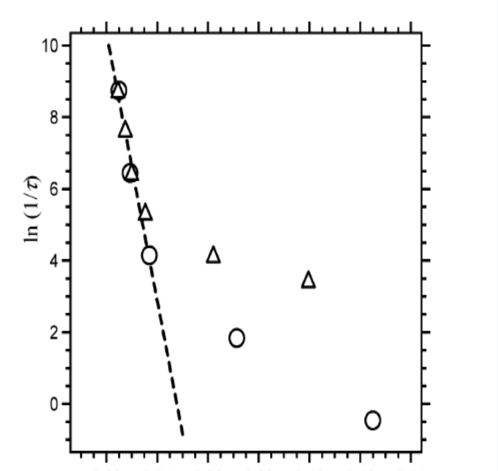
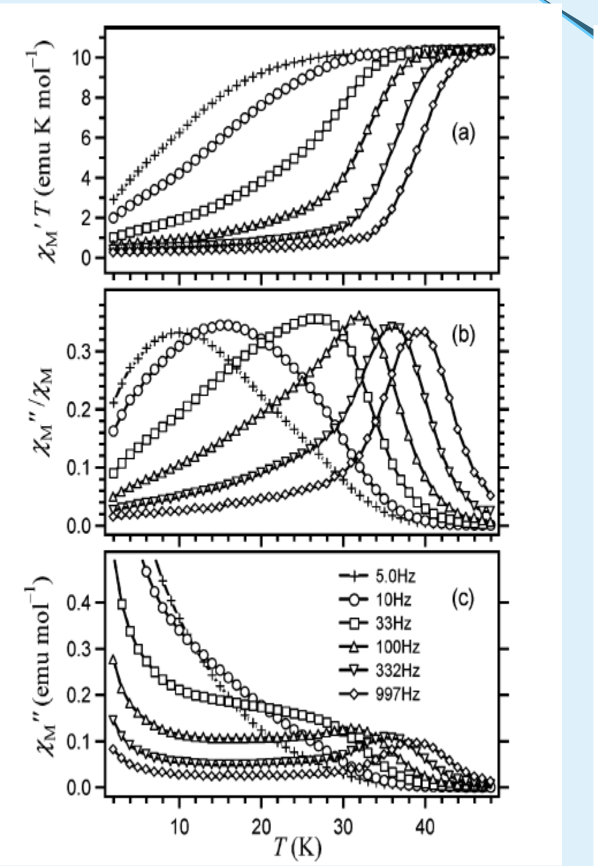
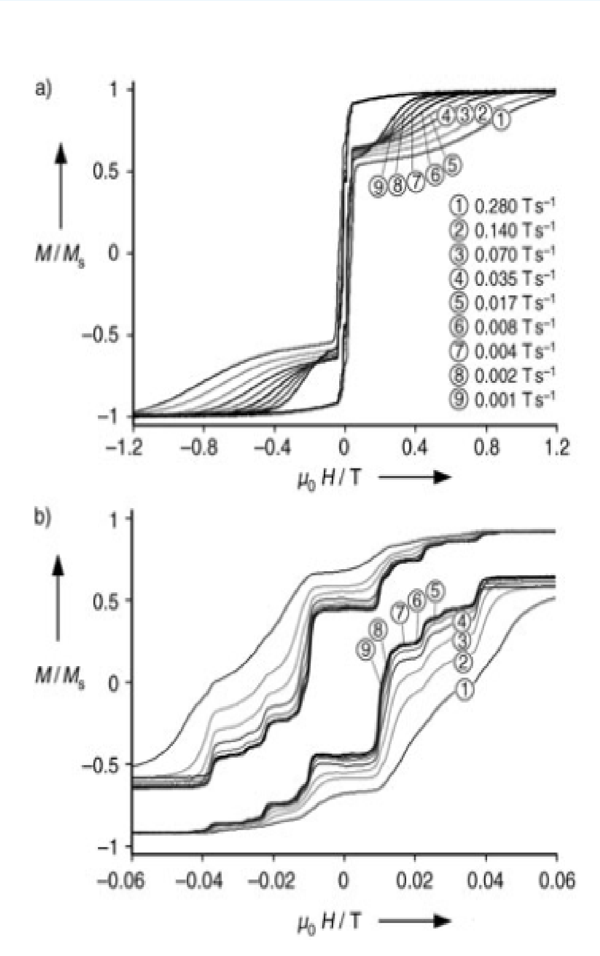




J. Phys. Chem. B **2004,** *108,* 11265−11271 [4]



AC susceptibility

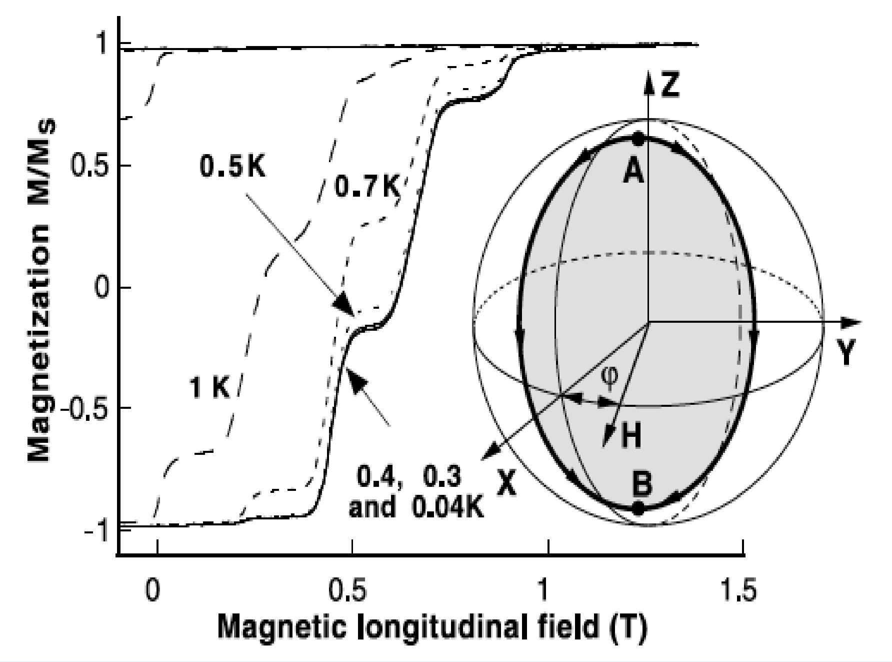


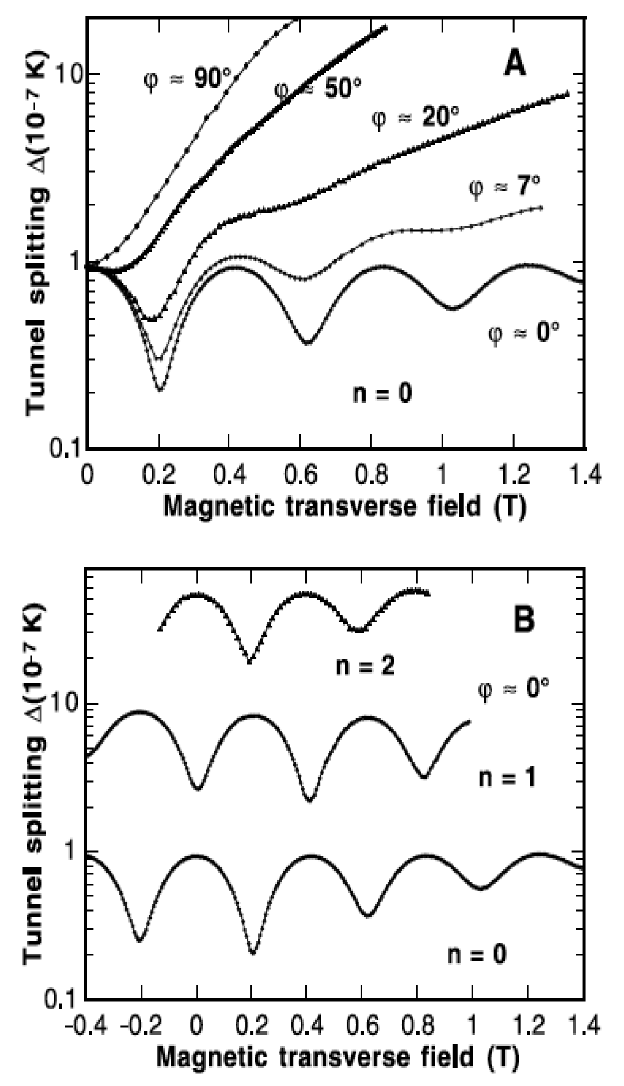
hysteresis

Tb^{3+} (J=6)=
U_{eff}/k_B=80K

Other quantum effects

Quantum phase interference (Berry phase)

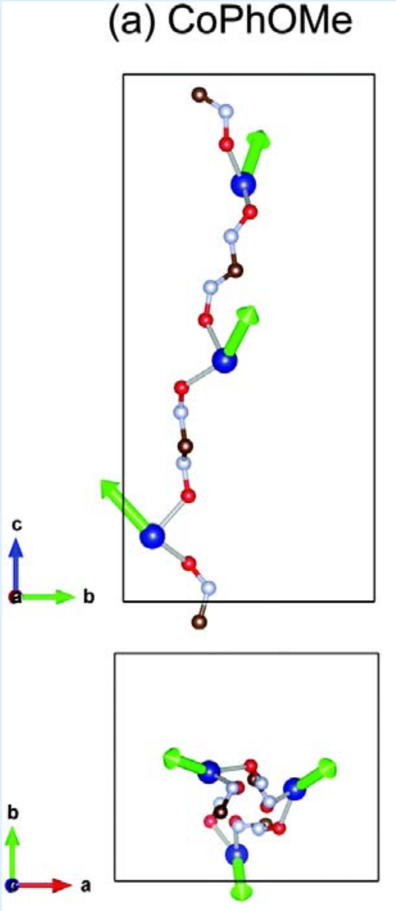




SCIENCE VOL 284 2 APRIL 1999

$$P = 1 - \exp\left[-\frac{\pi\Delta^2}{4\hbar g\mu_B S\,dH/dt}\right]$$

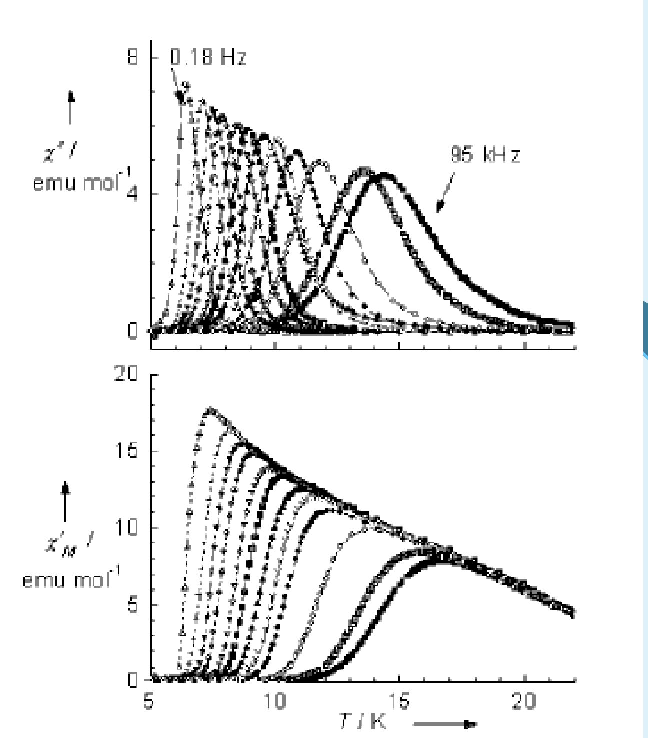
Glauber dynamics of spin chain



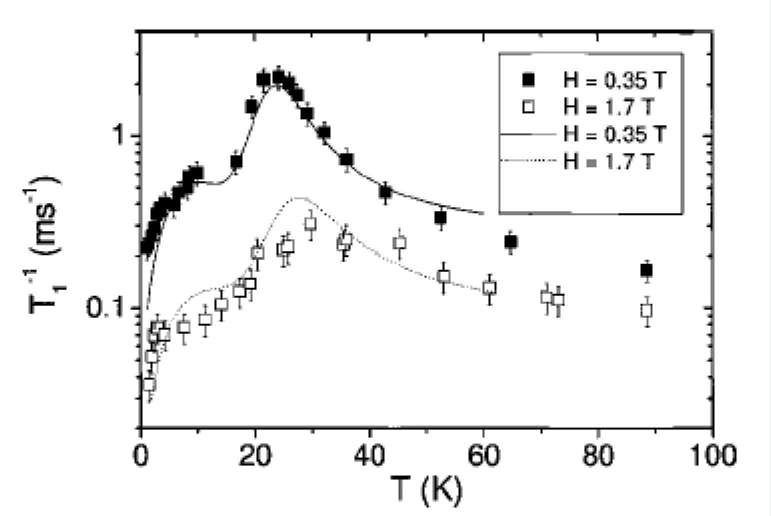
d_{local}=0.51 D
θ_{el}=62°

Single chain magnets

Angew. Chem. Int. Ed. **2001**, *40*, No. 9

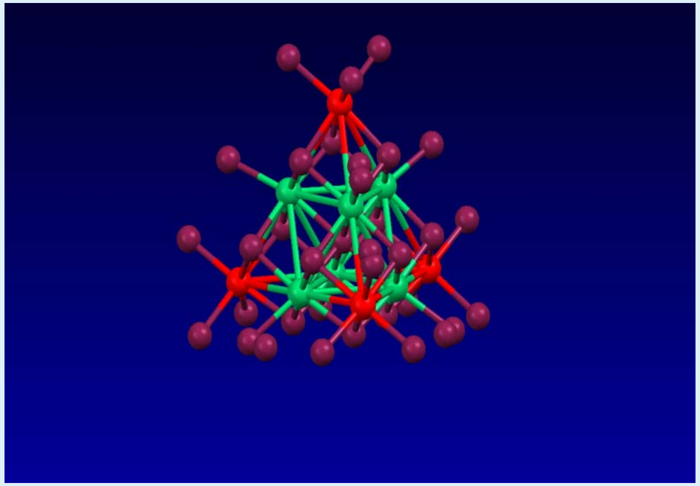


AC susceptibility

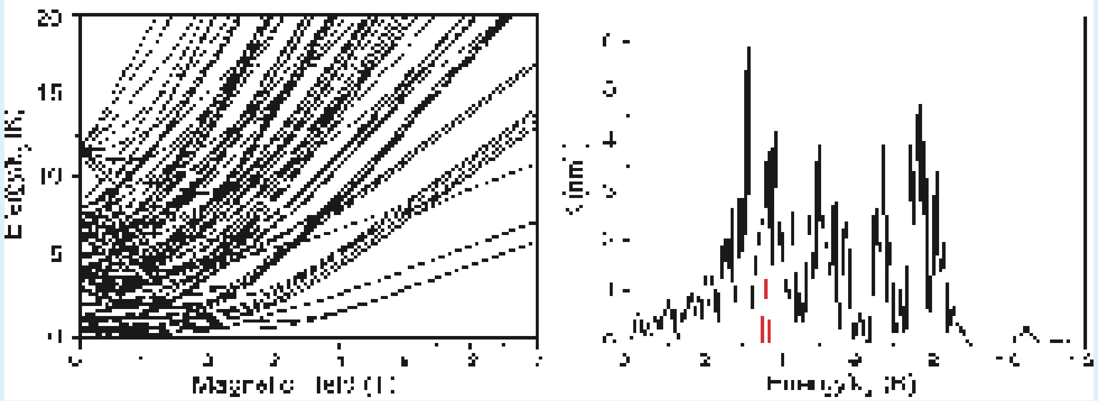


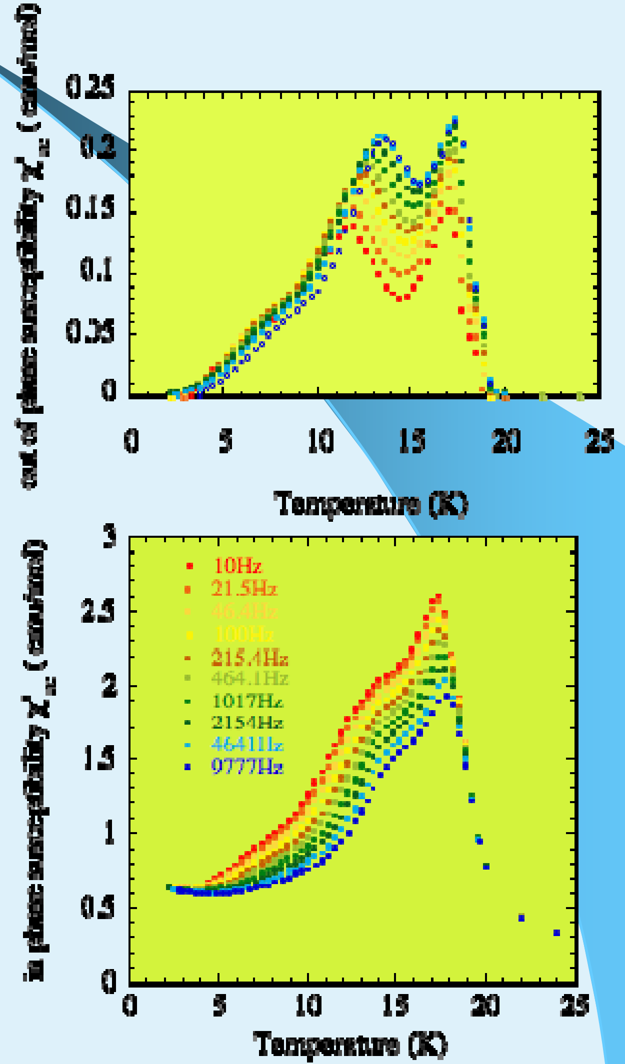
NMR

Phonon trapping in Ni10



[Ni10(O)(dbm)4(thme)4(BzO)2(ttOH)6]

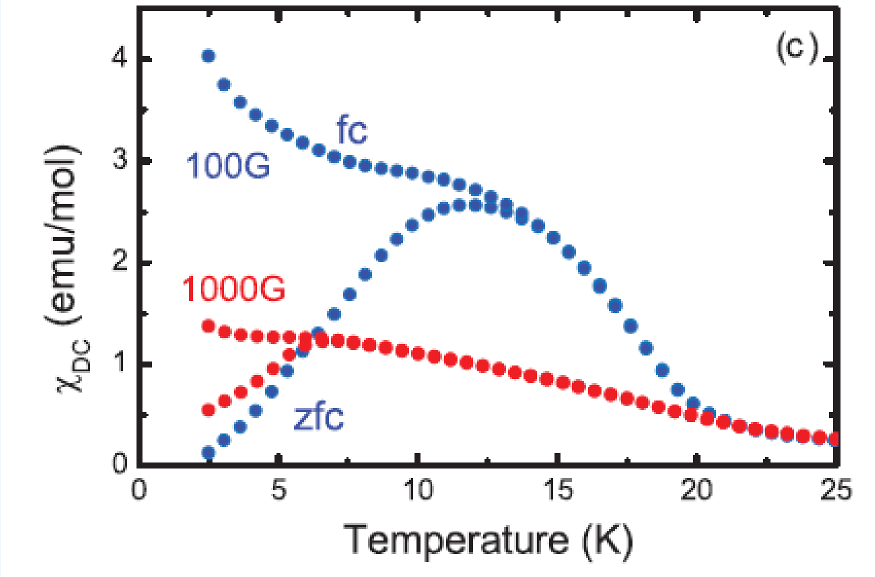




Phys. Rev. Lett. 97, 207201 (2006).

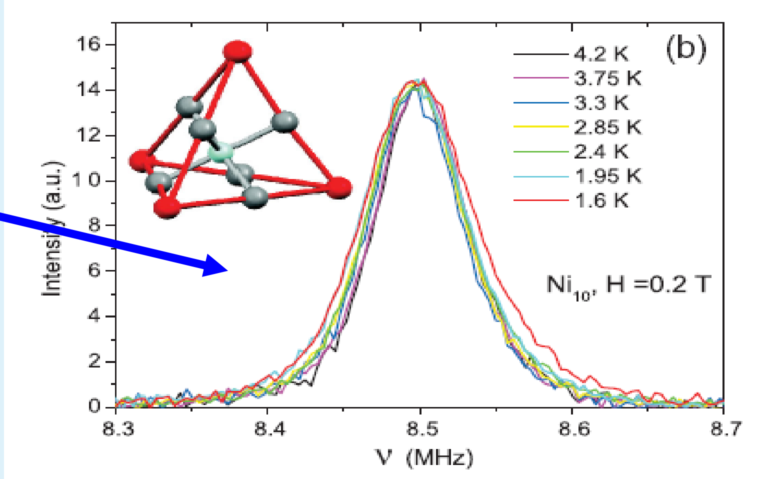
Nonequilibrium Dynamics in Ni10 powders

From SQUID : slowing down of M, i.e. **non equilibrium** situation

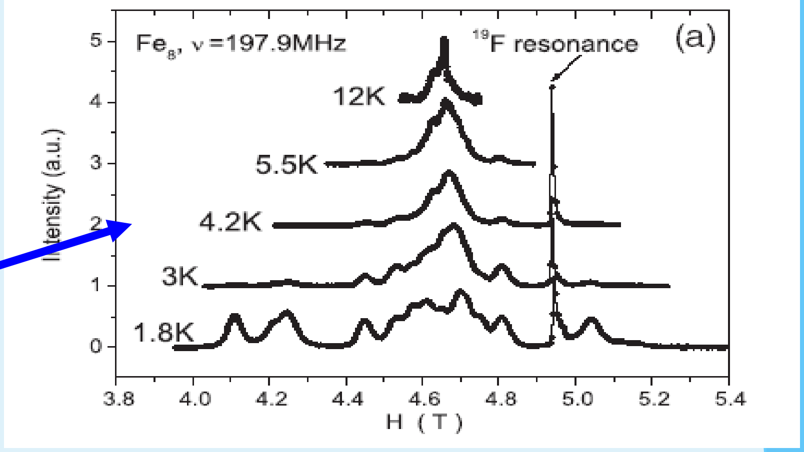


From NMR : narrow line (FWHM ~ 100 KHz) i.e. **no local field** due to “giant” S

Ni10



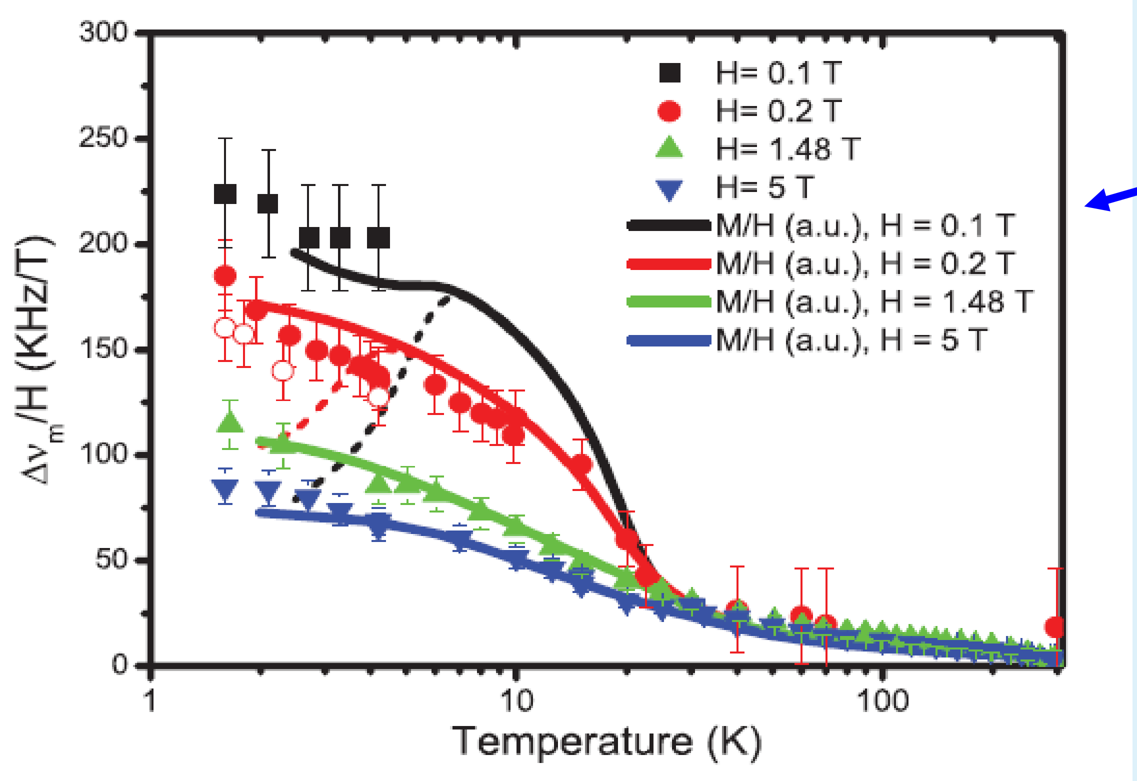
For comparison : Fe8



Solution : resonant phonon trapping

Pavia, 07/06/16

Phonons are no more a heat bath but the joint dynamics of spin+phonons dominates (phonons populations n_{ph} are not fixed solely by thermostat temperature)



Points : NMR
Lines : SQUID

$$\Delta\nu_{\rm tot}^2 = \Delta\nu_d^2 + \Delta\nu_m^2$$

$$\Delta\nu_m^2 = \sum_R \sum_{i\in R} (\langle \nu_{R,i} - \nu_0 \rangle_{\Delta t})^2 / N$$

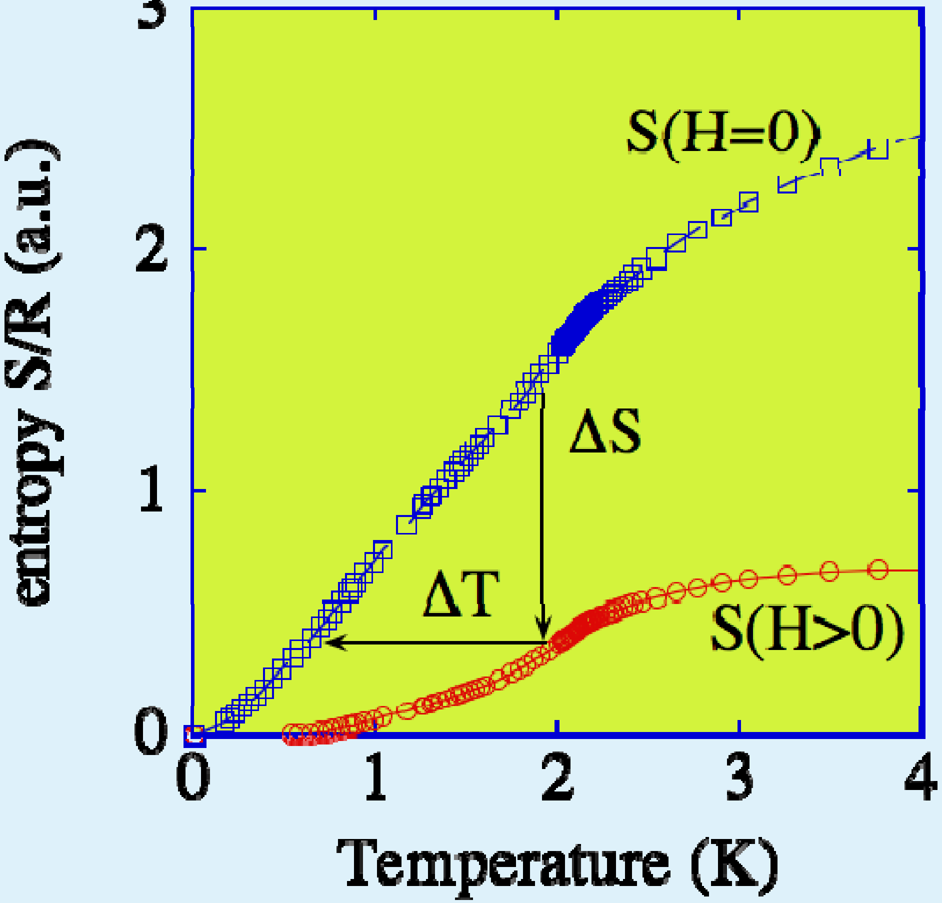
$$\sum_{i\in R} (\langle \nu_{R,i} - \nu_0 \rangle_{\Delta t})^2 \simeq \gamma^2 \sum_{i\in R} \Big[\sum_{j\in R} \frac{A(\theta_{i,j})}{r_{i,j}^3} \langle m_{z,j} \rangle_{\Delta t} \Big]^2$$

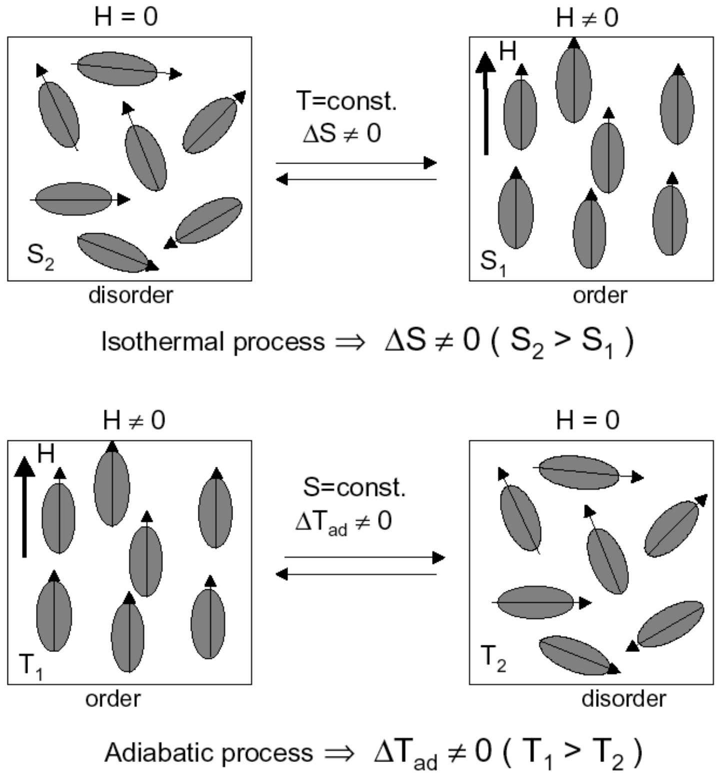
(i) The dependence of $\langle m_{z,j}\rangle_{\Delta t}$ on j is weak and can be neglected
(ii) The average molecular magnetization over Δt is nearly homogeneous

$$\longrightarrow \quad \Delta\nu_m^2 = \gamma^2 \sum_R [\langle \mu_z \rangle_{\Delta t}]^2 A/N = BM^2$$

Magnetocaloric effect: entropy of a magnetic system

$S = k \ln \Gamma$





The MagnetoCaloric Effect (MCE) is the adiabatic temperature change of a material upon application of a magnetic field

Entropy and MCE for Magnetic nanoparticles

classical case

$$Z = \left[4\pi \frac{kT}{mH} \sinh\left(\frac{mH}{kT}\right)\right]^N,$$

$$S_C = -\frac{\partial(kT \ln Z)}{\partial T}$$
$$= Nk\left[\ln(4\pi) + \ln\left(\sinh\left(\frac{mH}{kT}\right) / \left(\frac{mH}{kT}\right)\right) + 1 - \frac{mH}{kT}\coth\left(\frac{mH}{kT}\right)\right]. \quad (5)$$

$$\Delta S_C \approx \frac{-Nm^2H^2}{6kT^2} = \frac{-mM_0H^2}{6kT^2}.$$

quantum case:

$$Z = \sum_{m=-J}^{J} e^{\text{[illegible]}}$$

$$S = k_B \ln(2J + 1)$$

$$\Delta S_Q = -\frac{Ng^2\mu_B^2 J(J+1) H^2}{6kT^2}.$$

McMichael et al.

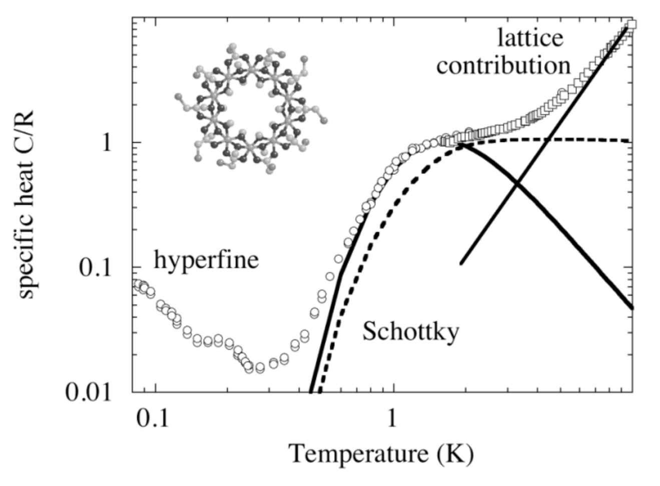
Journal of Magnetism and Magnetic Materials 111 (1992) 29–33

Scripta Materialia 46 (2002) 89–94

Determination of MCE from experiments

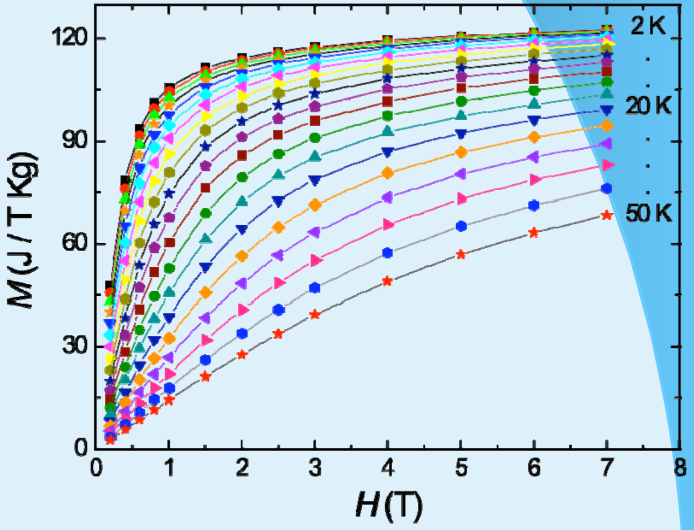
$$\Delta S = \frac{Q_{rev}}{T}$$

$$\int_A^B \left(\frac{\delta Q}{T}\right)_{\mathrm{rev}}$$



from specific heat data:

$$S(T)_H = \int_0^T \frac{C(T)_H}{T}\, \mathrm{d}T.$$



from magnetization data:

$$\Delta S_m(T)_{\Delta H} = \int_{H_i}^{H_f} \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H.$$

MCE - a comparison

	⊗Σ (ϑ/KγK)	T(K)	ΔH (T)
inter-metallic	˜3	<10K	3T→0
Mn12	˜3	˜3K	7T→0
Mn10	12	2K	3T→0
Fe14	4	6K	7T→0
PBA	1	200K	3T→0
Mn32	15	18	3T→0
Gd2	40	2K	7T→0

Recent theoretical study(2013) on MCE

- By explicitly considering Carnot refrigeration cycles, we theoretically show that the best molecules for magnetic refrigeration between T =10K and the sub-Kelvin region are **those made of strongly ferromagnetically coupled magnetic ions**, contrarily to the established belief. (E. Garlatti et al, APPLIED PHYSICS LETTERS 103, 202410 (2013)

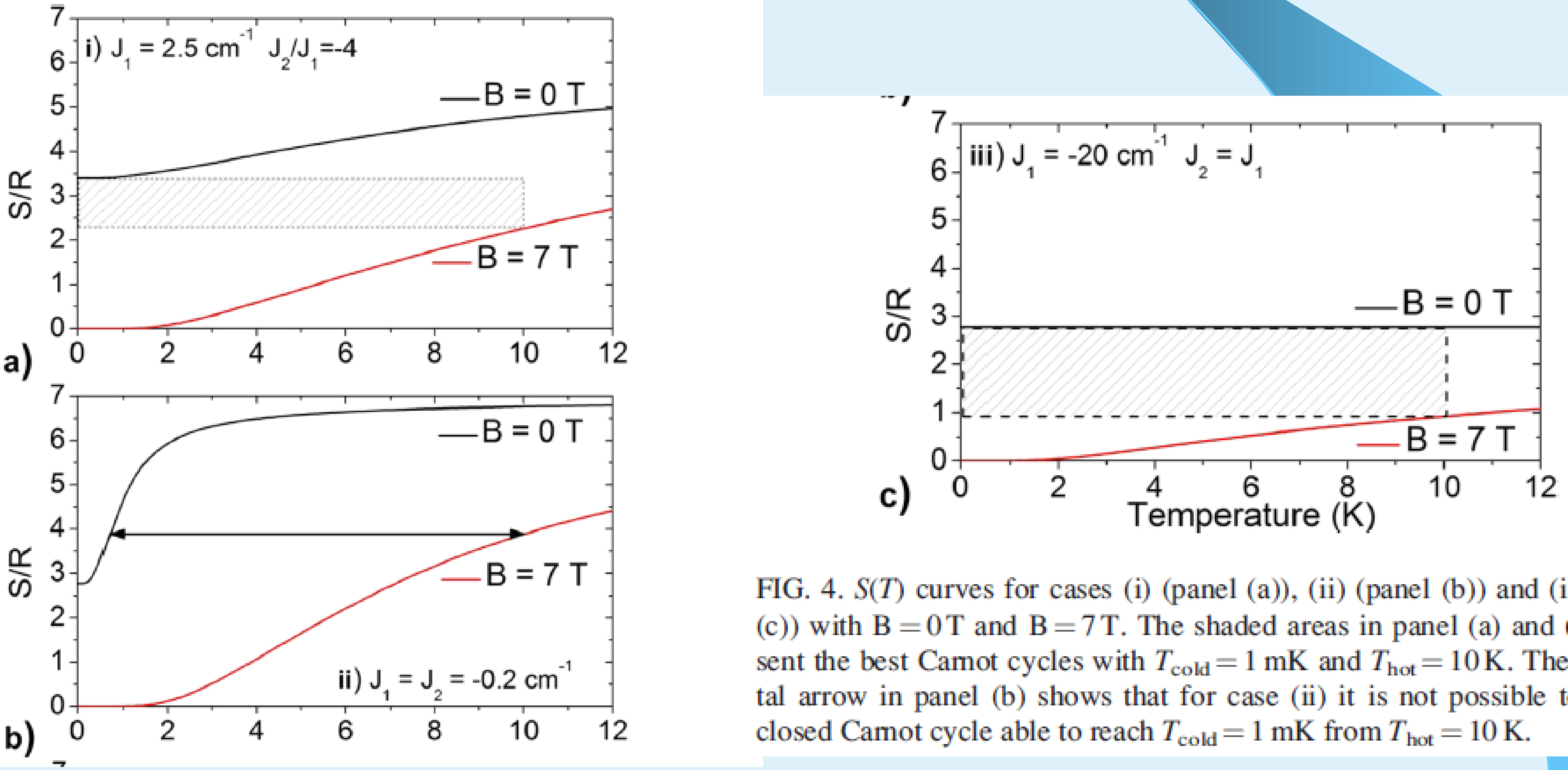
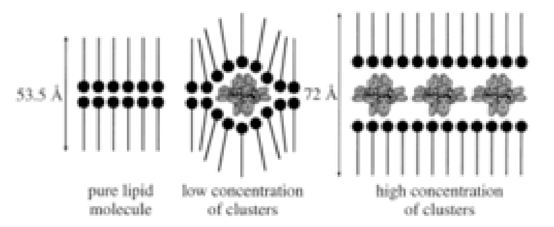
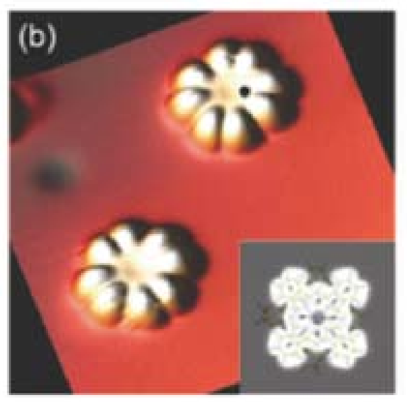


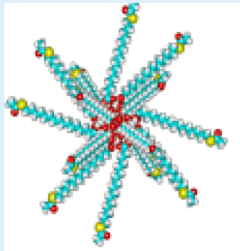
FIG. 4. $S(T)$ curves for cases (i) (panel (a)), (ii) (panel (b)) and (iii) (panel (c)) with B = 0 T and B = 7 T. The shaded areas in panel (a) and (c) represent the best Carnot cycles with $T_{\mathrm{cold}} = 1$ mK and $T_{\mathrm{hot}} = 10$ K. The horizontal arrow in panel (b) shows that for case (ii) it is not possible to build a closed Carnot cycle able to reach $T_{\mathrm{cold}} = 1$ mK from $T_{\mathrm{hot}} = 10$ K.

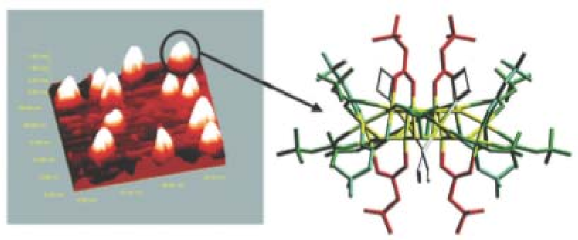
Magnetic Molecules on surfaces
Single molecule read and write

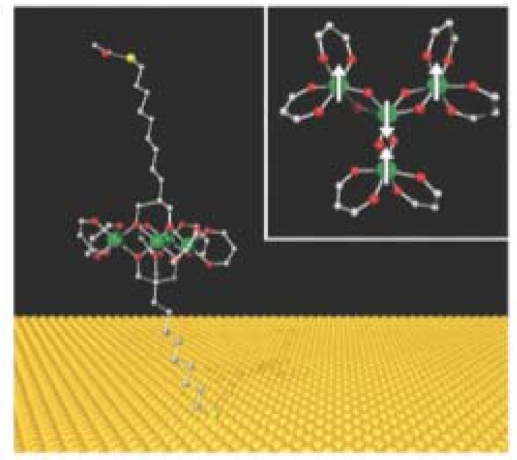
Pavia, 07/06/16

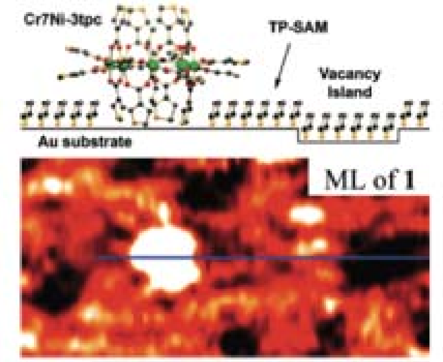


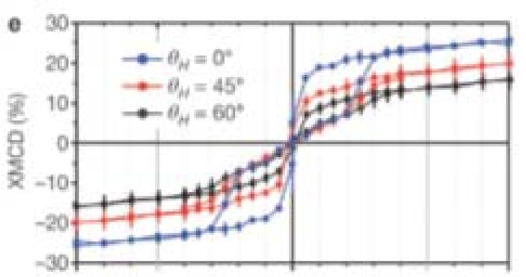


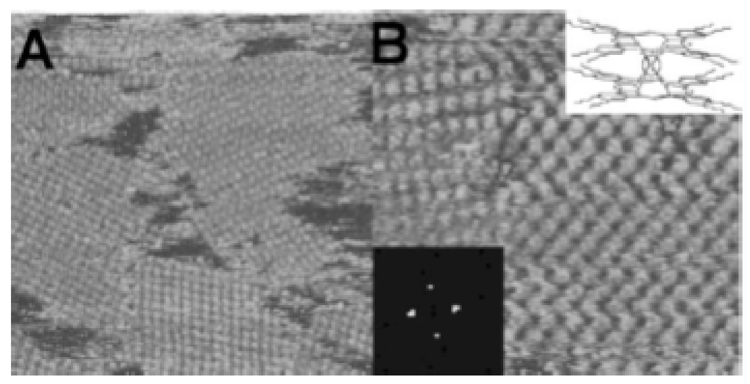


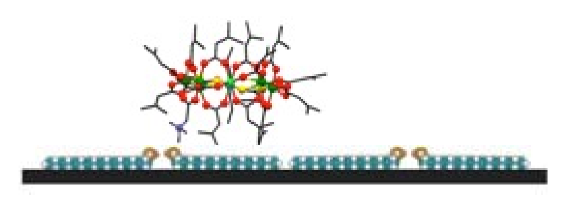








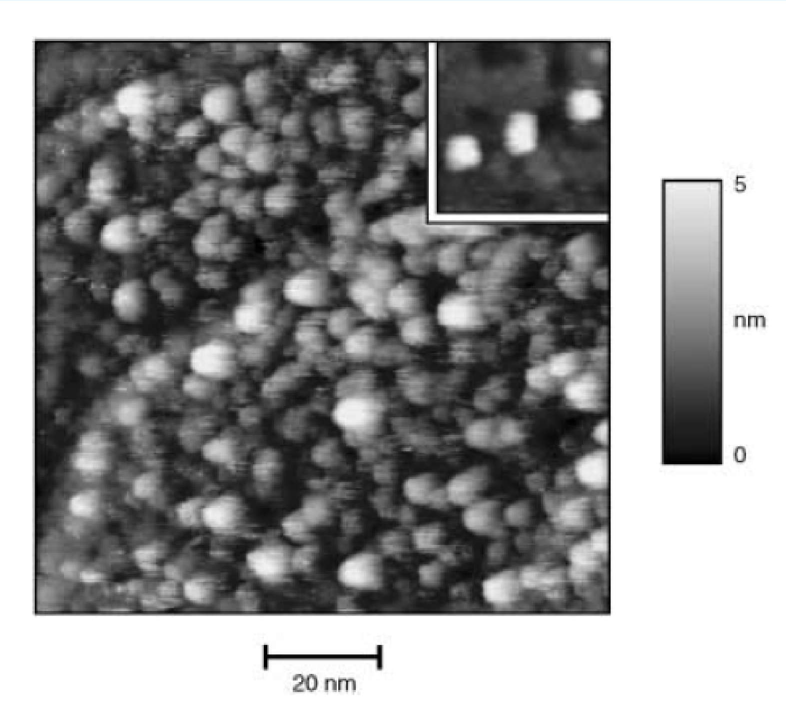




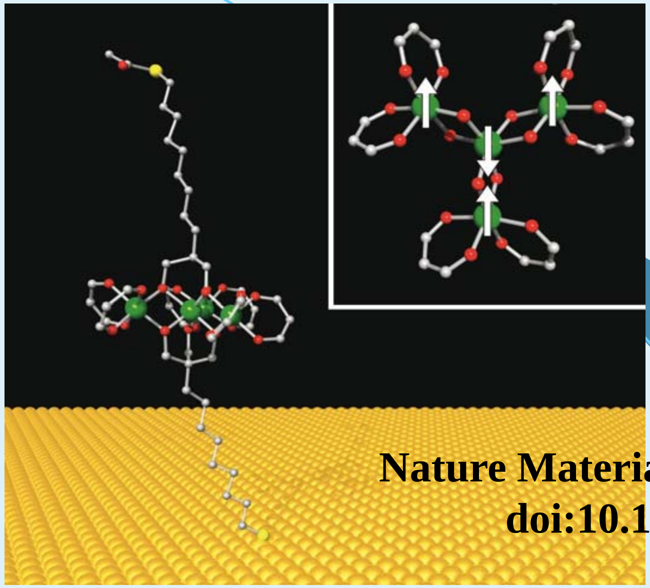
review by N. Domingo et al., Chem. Soc. Rev. 2011
A. Cornia, D. Tahlam, M. Affronte (2016)

Sunset of Mn12 & sunrise of Fe4

Pavia, 07/06/16

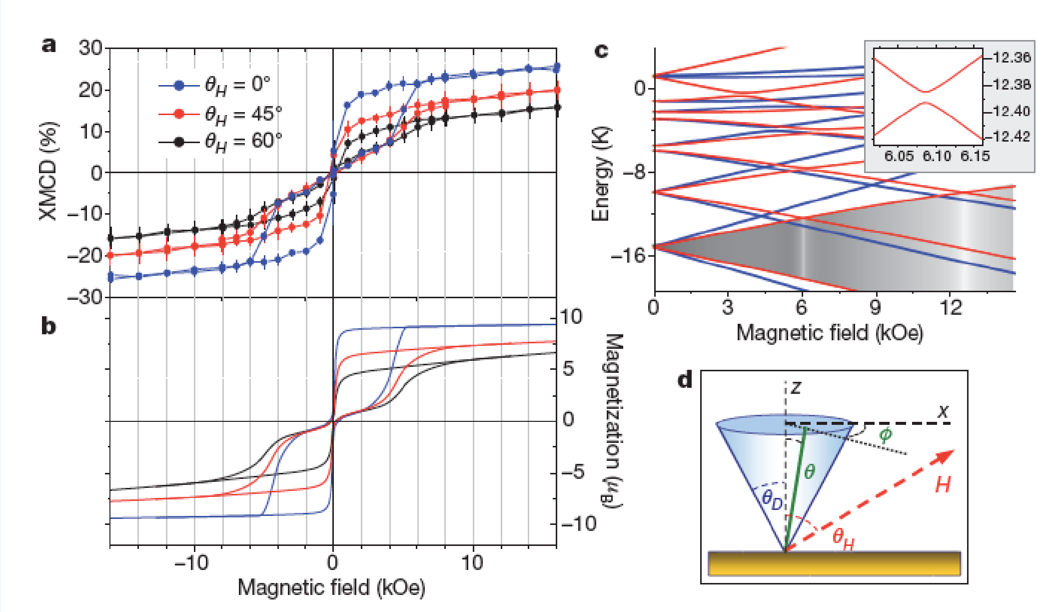


Angew. Chem. Int. Ed. **2003**, *42*, 1645–1648

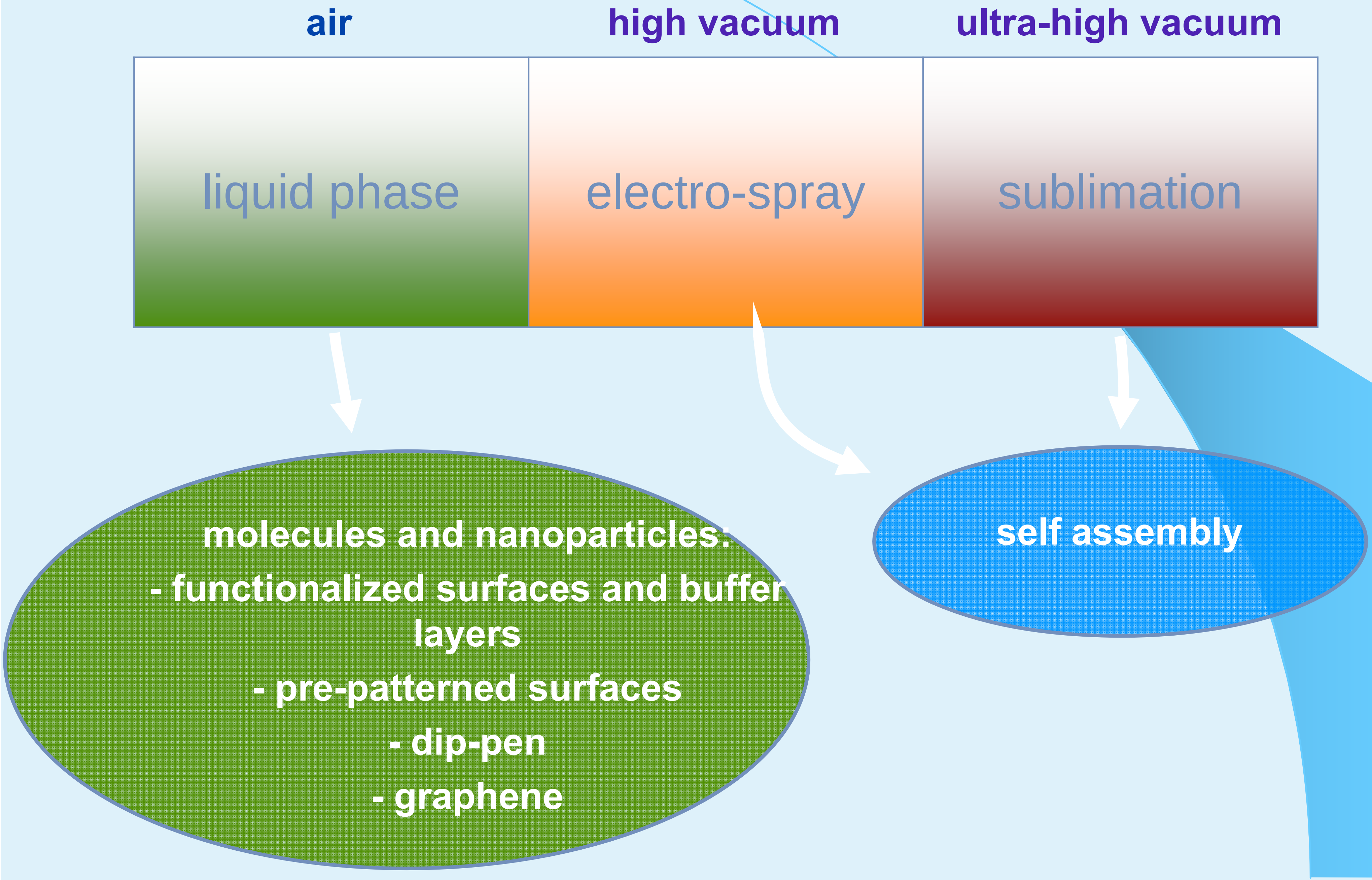


Nature Materials 8, 194 - 197 (2009)
doi:10.1038/nmat2374

doi:10.1038/nature09478



Methods of deposition



air

high vacuum

ultra-high vacuum

liquid phase

electro-spray

sublimation

molecules and nanoparticles:

- functionalized surfaces and buffer layers

- pre-patterned surfaces

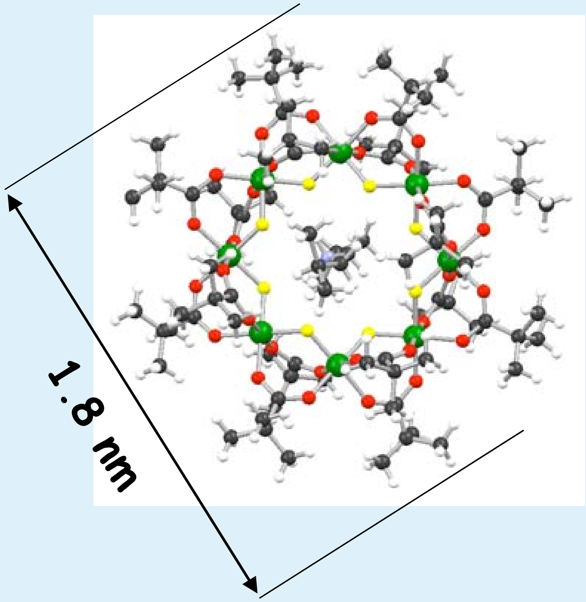
- dip-pen

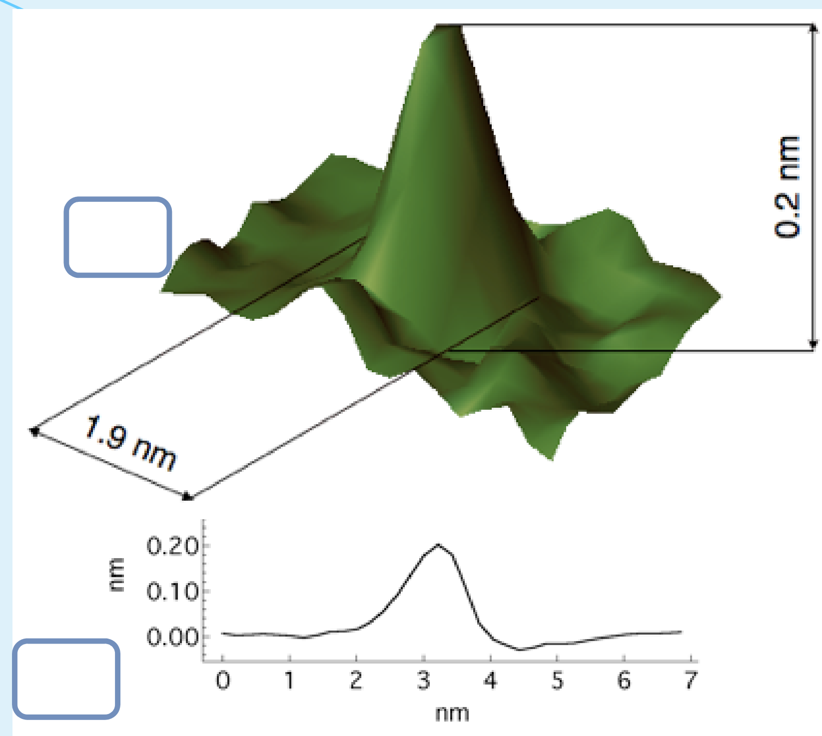
- graphene

self assembly

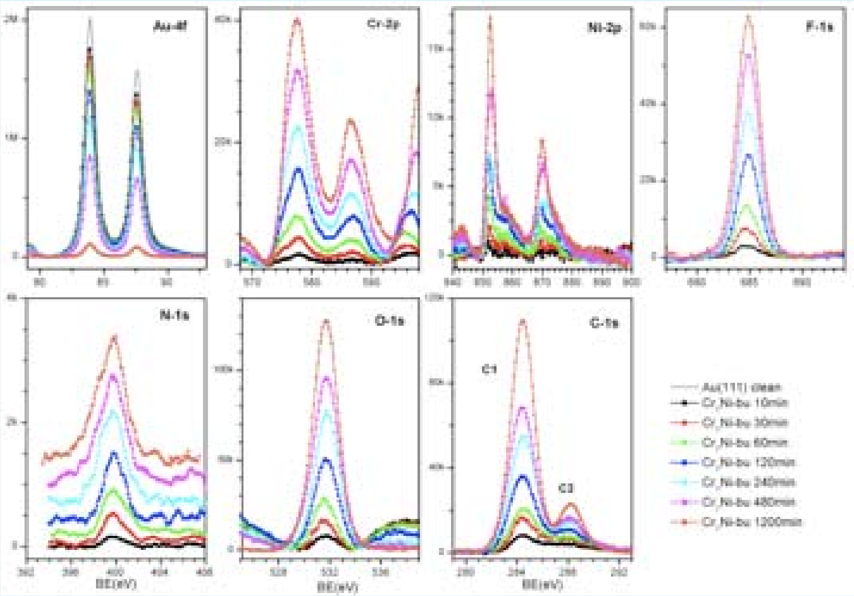
Integrity checks (also magnetic properties)

surface





STM: lateral size as expected

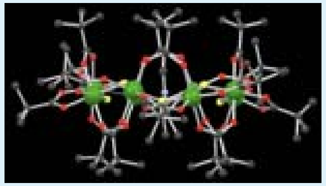


Derivative	Cr-2p/Ni-2p [7.0]	F-1s/Cr-2p [1.14]	N-1s/ 7Cr-2p [1]	S-2p/ 7Cr-2p [1]	O-1s /7Cr2p [32]	C-1s/7Cr-2p
Cr7Ni-*bu*	7.2 ± 0.5	1.17 ± 0.05	1.10 ± 0.15	-	29 ± 5	90 ± 15 [88]
Cr7Ni-*thiobu*	6.8 ± 0.5	1.13 ± 0.05	0.90 ± 0.15	1.00 ± 0.15	30 ± 5	95 ± 15 [86]

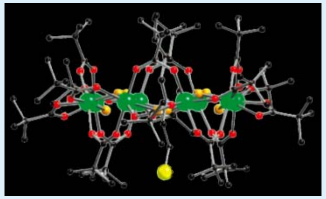
XPS: stoichiometric elemental ratios are respected

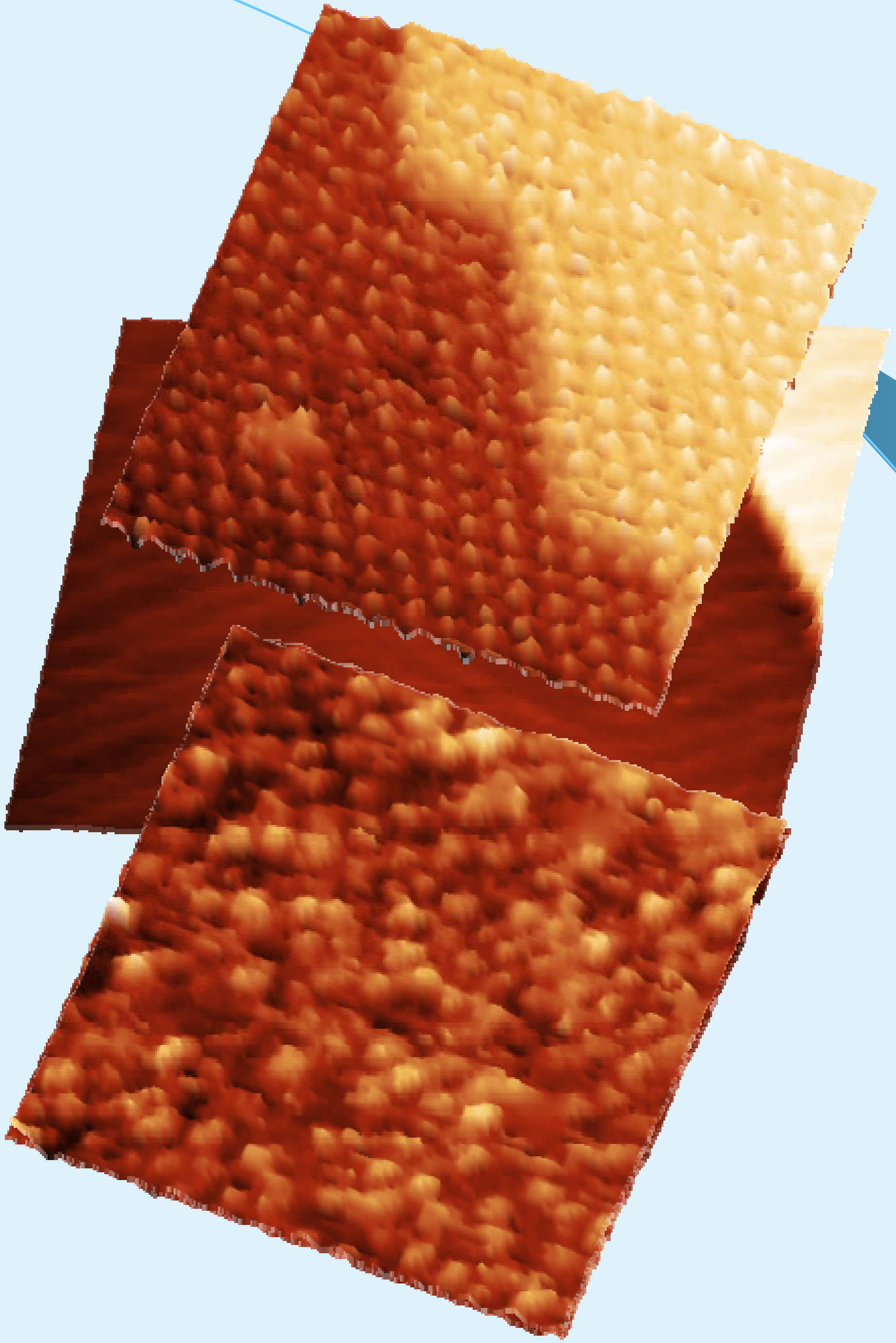
Self-assembly!

Cr7Ni-bu



Cr7Ni-thiobu





monolayer

Recently addressing Fe4 molecules

Here, we probe electrical transport through individual Fe4 SMMs using a scanning tunnelling microscope at 0.5 K. Correlation of topographic and spectroscopic information permits identification of the spin excitation fingerprint of intact Fe4 molecules. Building from this, we find that the exchange coupling strength within the molecule's magnetic core is significantly enhanced.

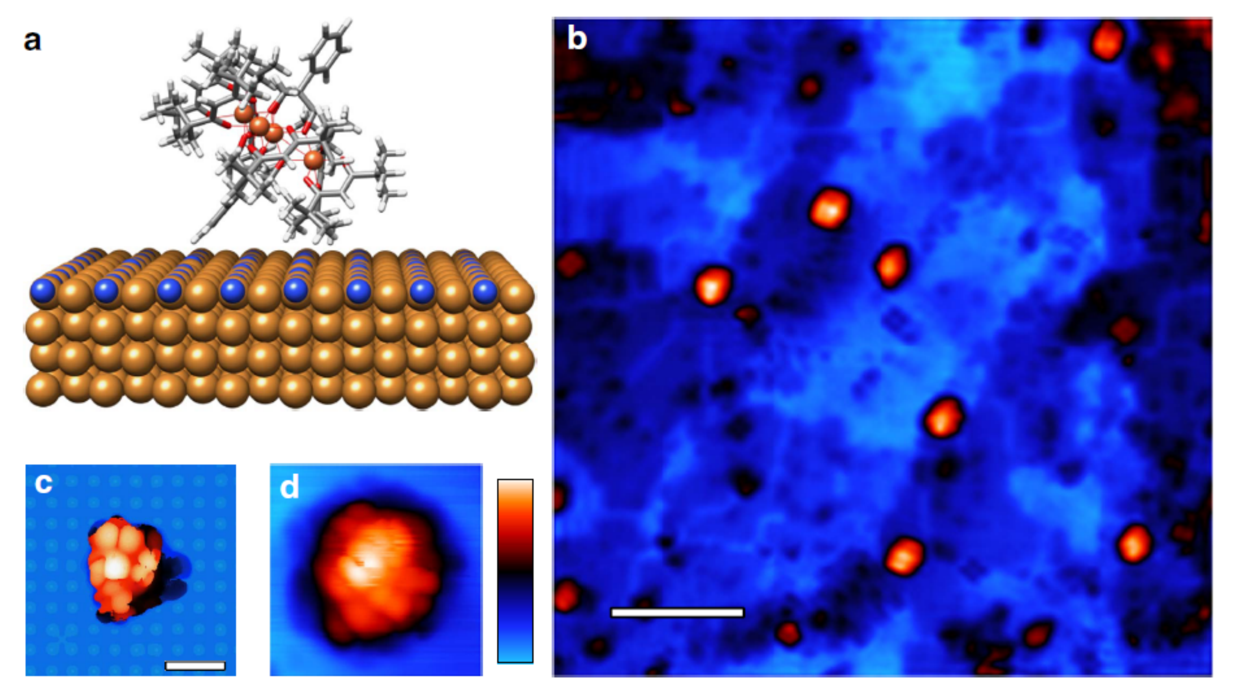
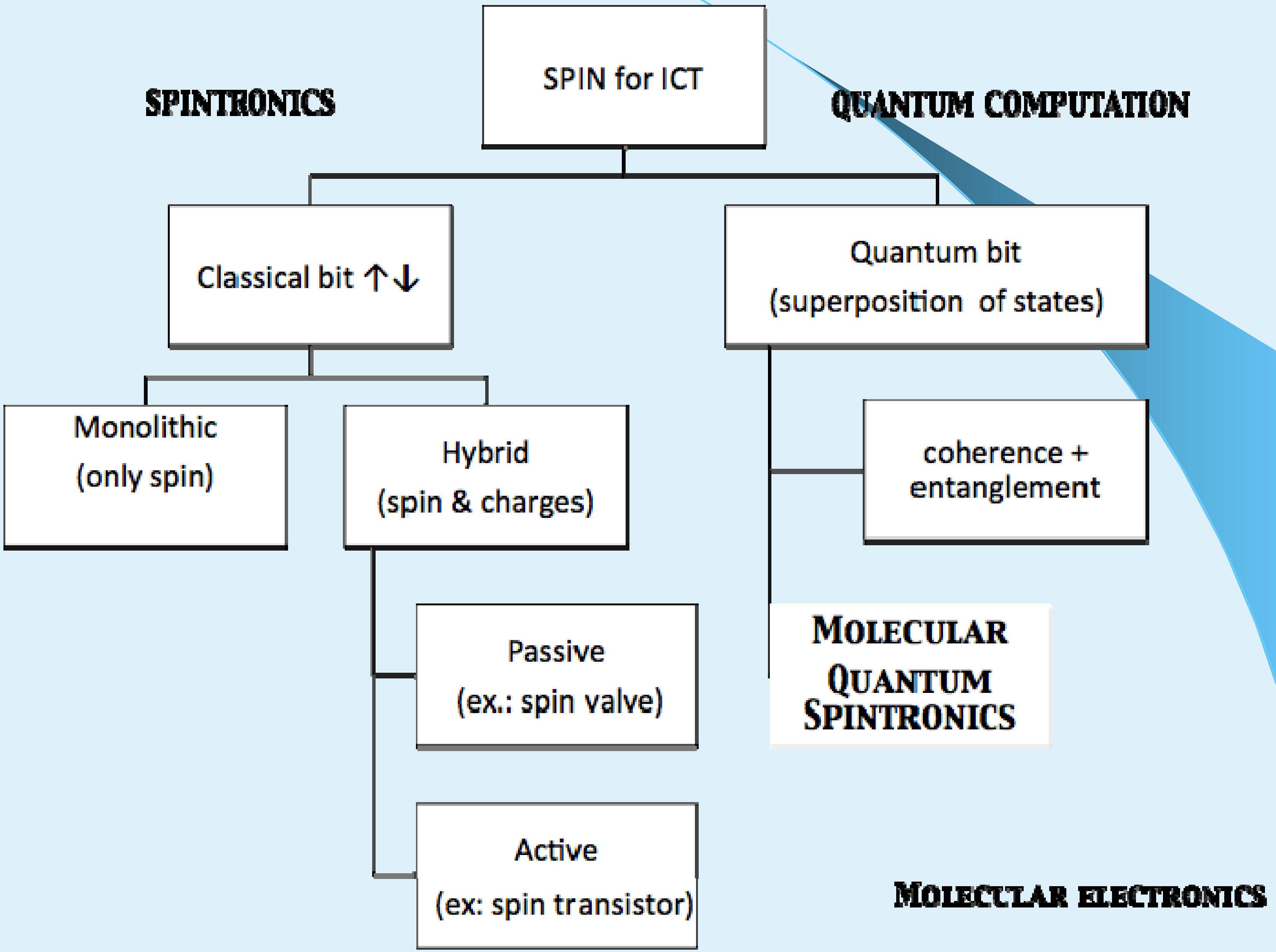


Figure 1 | Fe_4 molecule adsorbed on the Cu_2N surface. (a) $[Fe_4(L)_2(dpm)_6]$ resting on the Cu_2N surface.

Molecular spintronics and quantum computation



SPIN for ICT

SPINTRONICS

QUANTUM COMPUTATION

Classical bit ↑↓

Quantum bit
(superposition of states)

Monolithic
(only spin)

Hybrid
(spin & charges)

coherence + entanglement

Passive
(ex.: spin valve)

Active
(ex: spin transistor)

MOLECULAR QUANTUM SPINTRONICS

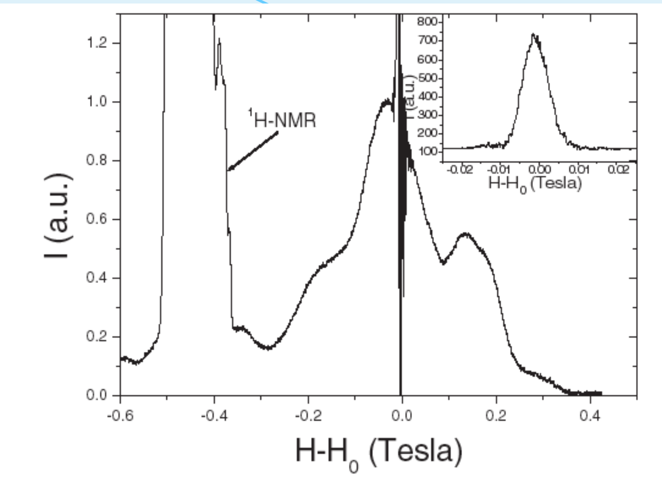
MOLECULAR ELECTRONICS

Quantum bits

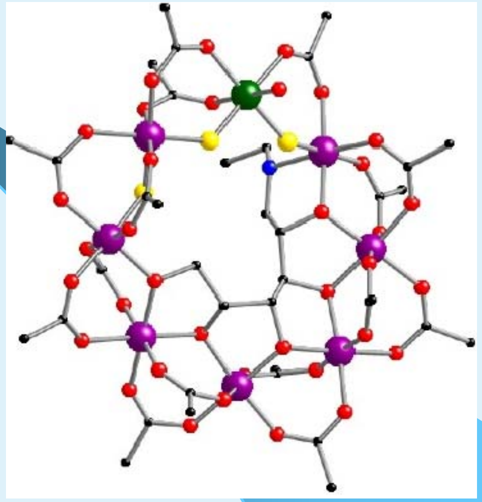
$$|\Psi\rangle = \alpha|\uparrow\rangle + \beta|\downarrow\rangle$$

Quantum coherence in antiferromagnetic rings

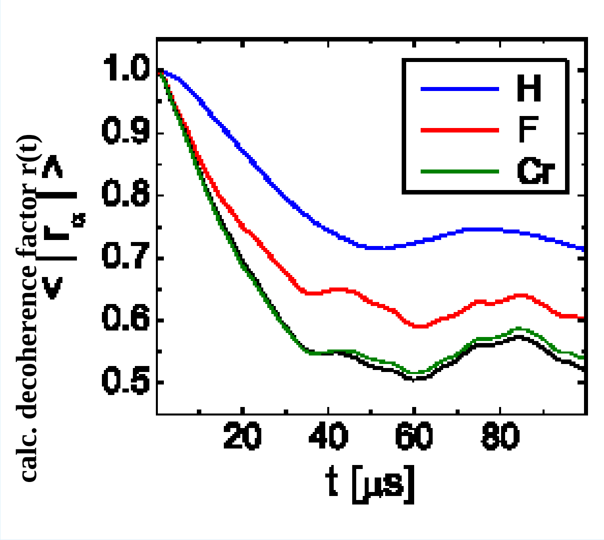
Cr7Ni



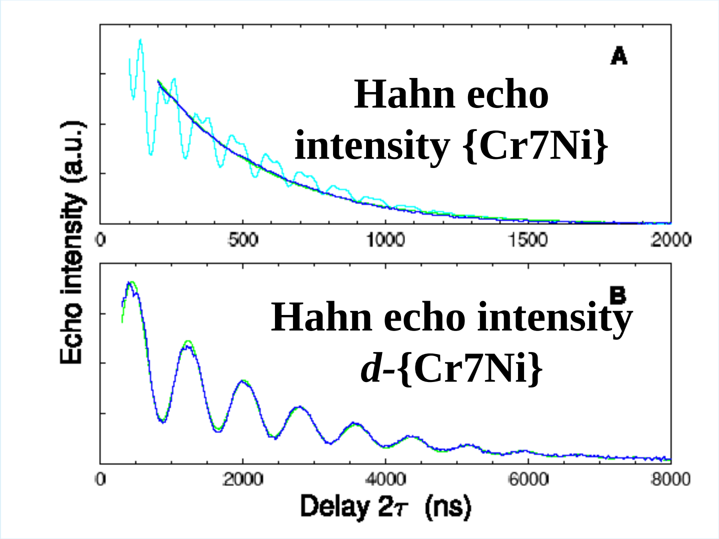
Micotti et al. PRL 97, 267204 (2006)



glued Cr7Ni in which
fluoride groups are replaced by alkoxides
G.Timco et al. Angew. Chem.2008, 47, 9681



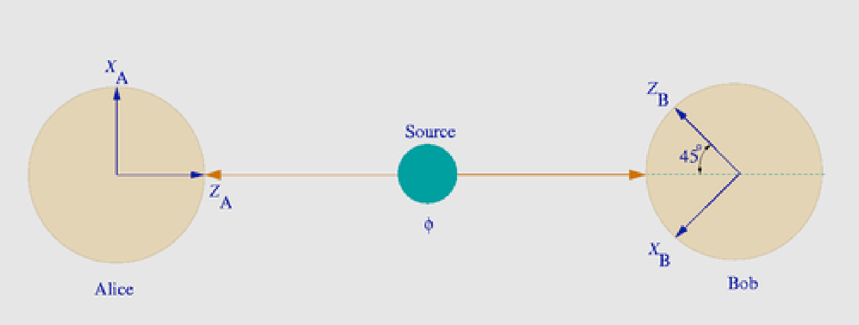
F. Troiani, V. Bellini, and M. Affronte
Physical Review B 77, 054428 (2008).



Ardavan et al. PRL 98, 057201 (2007)

Entanglement as a genuine quantum phenomenon

- separate objects with well defined states.
  - weak (initial) coupling.
- the states of each subsystem can no longer be described independently from one to another!
  - the state of the global system cannot be factorized



example of separable state:

$$|\Psi\rangle = |\uparrow_A\rangle|\downarrow_B\rangle$$

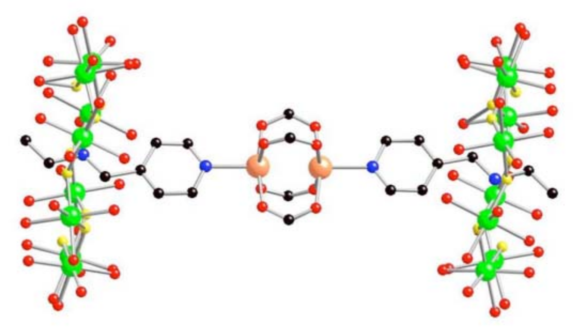
example of entangled state:
Bell (or Einstein, Podolsky, Rosen) state

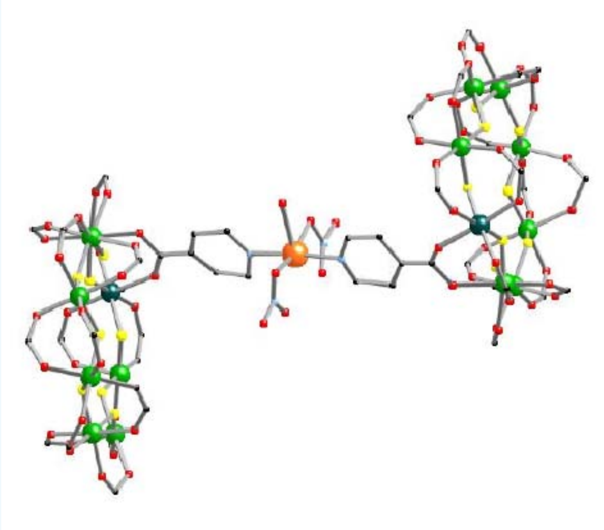
$$|\Psi\rangle = \frac{|\uparrow_A\downarrow_B\rangle \quad |\downarrow_A\uparrow_B\rangle}{\sqrt{2}}$$

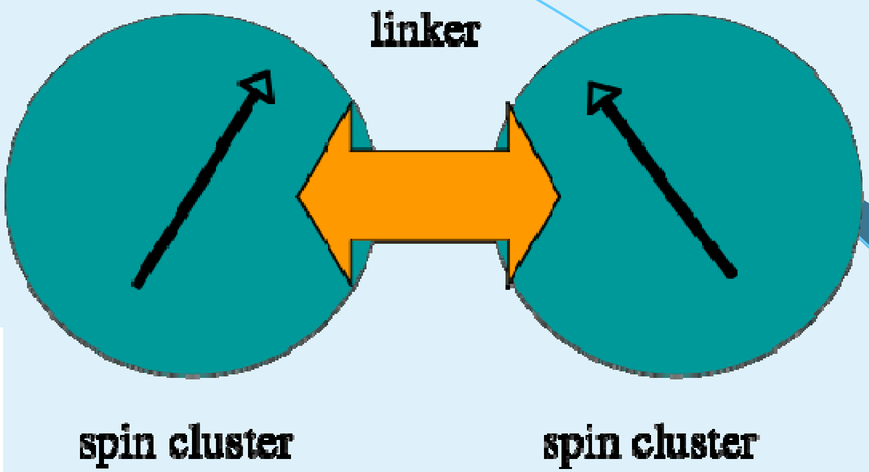
A measurement of the second qubit always gives result depending on the state of the first

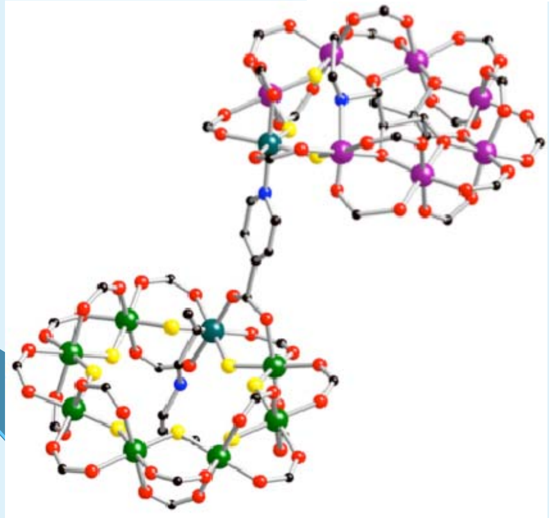
REVIEWS OF MODERN PHYSICS, VOLUME 81, p.865 APRIL–JUNE 2009, Horodecki et al.
REVIEWS OF MODERN PHYSICS, VOLUME 80, p.517 APRIL–JUNE 2008, Amico et al.

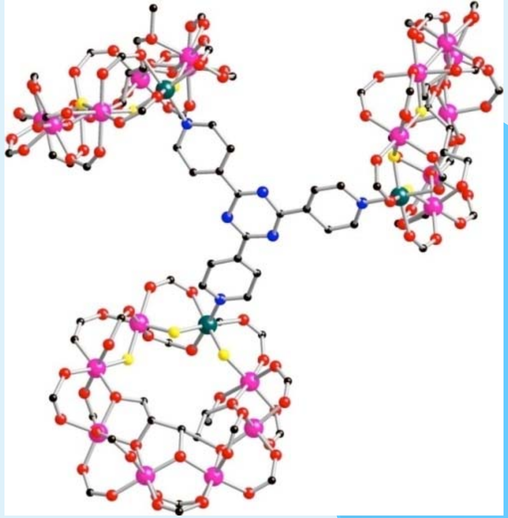
Rules of “this” game







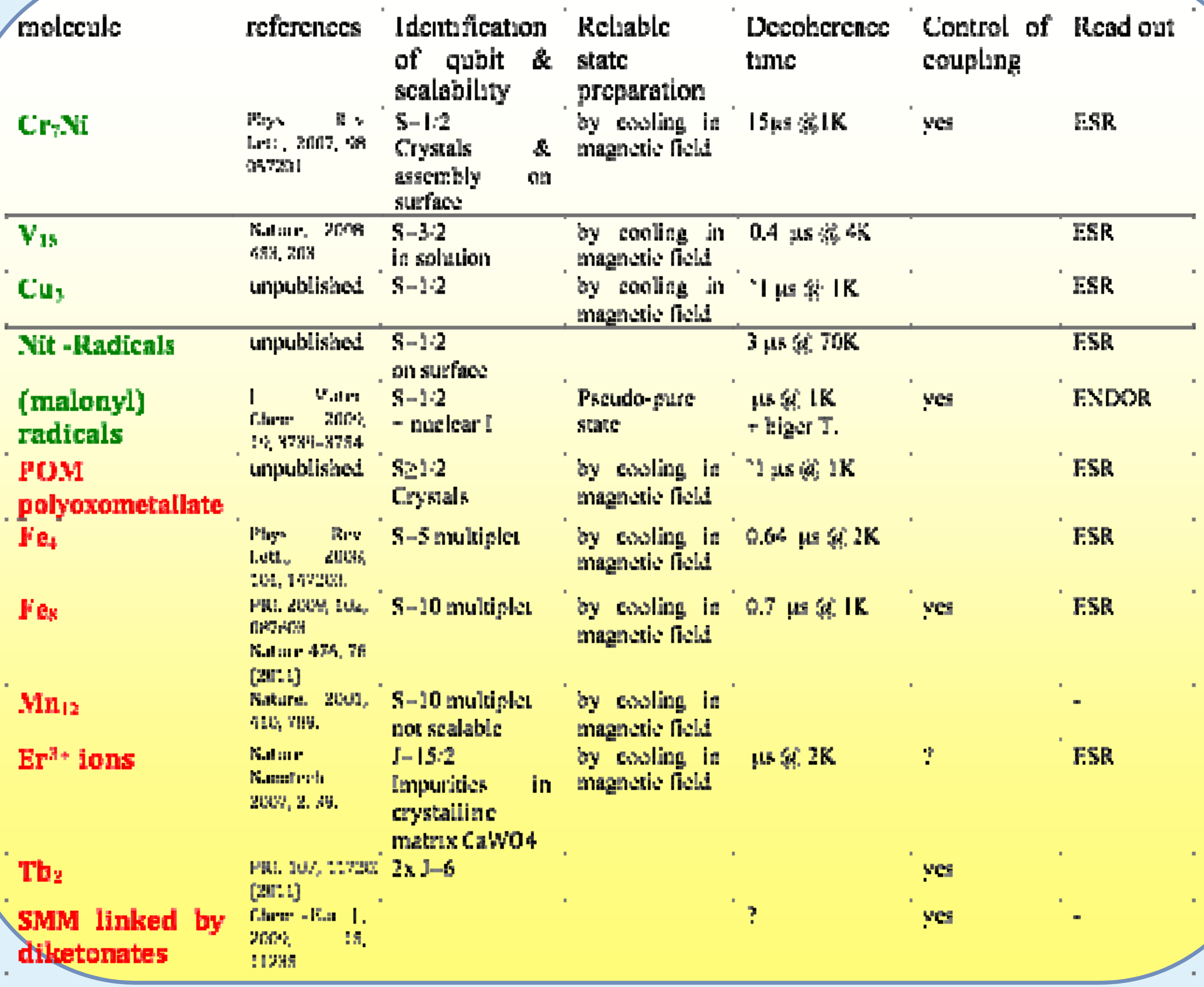




To entangle the spins of different molecular units

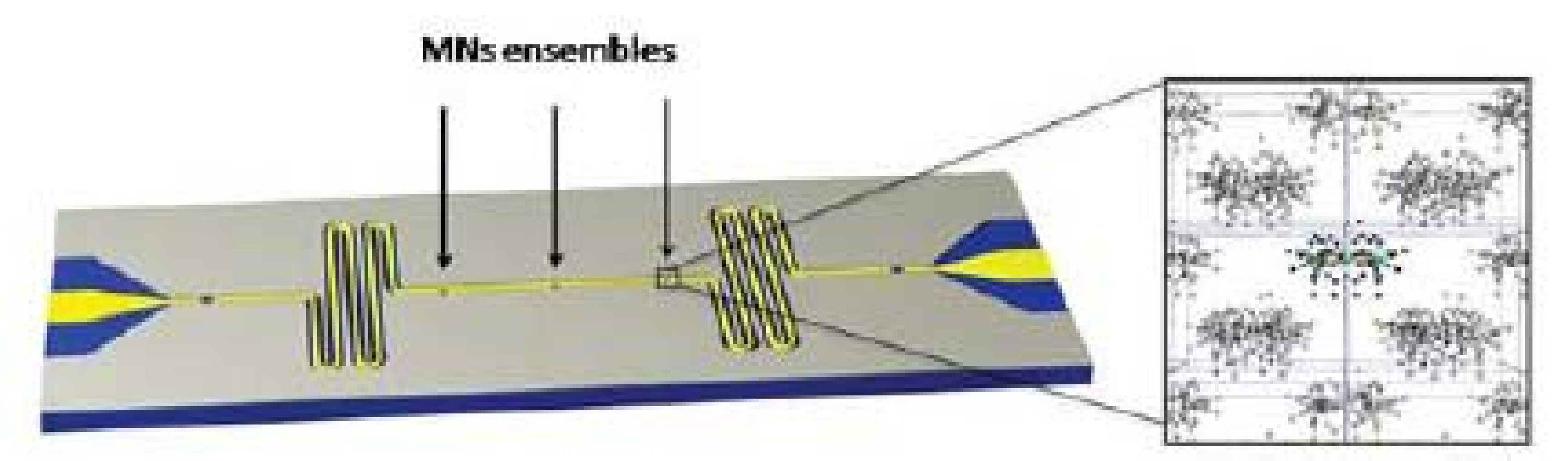
Nanotechnology 21, 274009 (2010)

Molecular spin clusters for Quantum Computation



molecule	references	Identification of qubit & scalability	Reliable state preparation	Decoherence time	Control of coupling	Read out
Cr_7Ni	Phys Rev Lett., 2007, 98 057201	S=1/2 Crystals & assembly on surface	by cooling in magnetic field	15μs @1K	yes	ESR
V_{15}	Nature, 2008 453, 203	S=3/2 in solution	by cooling in magnetic field	0.4 μs @ 4K		ESR
Cu_3	unpublished	S=1/2	by cooling in magnetic field	~1 μs @ 1K		ESR
Nit -Radicals	unpublished	S=1/2 on surface		3 μs @ 70K		ESR
(malonyl) radicals	J Mater Chem 2009, 19, 3739-3754	S=1/2 + nuclear I	Pseudo-pure state	μs @ 1K + higer T.	yes	ENDOR
POM polyoxometallate	unpublished	S≥1/2 Crystals	by cooling in magnetic field	~1 μs @ 1K		ESR
Fe_4	Phys Rev Lett., 2008, 101, 147201.	S=5 multiplet	by cooling in magnetic field	0.64 μs @ 2K		ESR
Fe_8	PRL 2009, 102, 087603 Nature 476, 76 (2011)	S=10 multiplet	by cooling in magnetic field	0.7 μs @ 1K	yes	ESR
Mn_{12}	Nature, 2001, 410, 789.	S=10 multiplet not scalable	by cooling in magnetic field			-
Er^{3+} ions	Nature Nanotech 2007, 2, 39.	J=15/2 Impurities in crystalline matrix CaWO4	by cooling in magnetic field	μs @ 2K	?	ESR
Tb_2	PRL 107, 117203 (2011)	2x J=6			yes	
SMM linked by diketonates	Chem -Eur J. 2009, 15, 11235			?	yes	-

Cavity-assisted Quantum Information Processing



superconducting resonators with Molecular Nanomagnets

In progress.

YBCO resonator already realized

The end

Any questions ??