A lecture proposed by

SPP Molekular Magnetismus (DFG)

# How molecules go magnetic …

Michel Verdaguer, Françoise Villain,
Ruxandra Gheorghe, Fabrice Pointillart
Université Pierre et Marie Curie, Paris

# Why experiments ?

because …

- experiment arises curiosity
- experiment is speaking …
- experiment is demonstrating …
- experiment can be beautiful !

# Why experiments in magnetism ?

because …

- it is an important phenomenon …
- it arises curiosity …
- it needs to be demystified and explained
- and experiments are beautiful !

# Why experiments in molecular magnetism ?

because …

- our live relies on it and nobody knows …
- it is badly known or unknown …
- it can be explained simply …
- and experiments are beautiful !

# Goals ?

1) Citizen awareness
2) Attract good students
   to our discipline
3) Here : convincing you that
   such experiments are possible
to realize during Science Festivals ..

# Comments about a possible …

# LECTURE

(abridged …)

Bad Durkheim, SPP Molecular Magnetismus (DFG) 6-9 may 2007


Publicity Campaign, Barcelona, 2004


**This is NOT**

**the question**

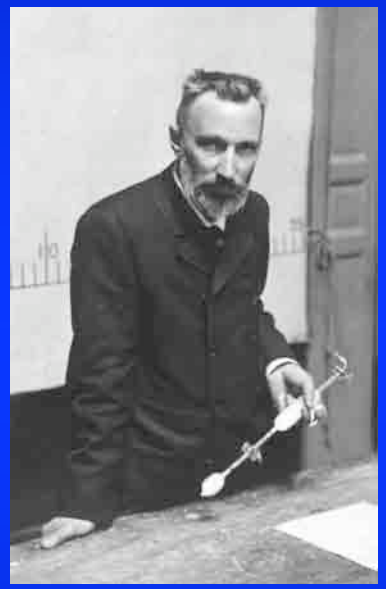
**or not ?**

# Everything is magnetic

… How ?

## Everything is magnetic …

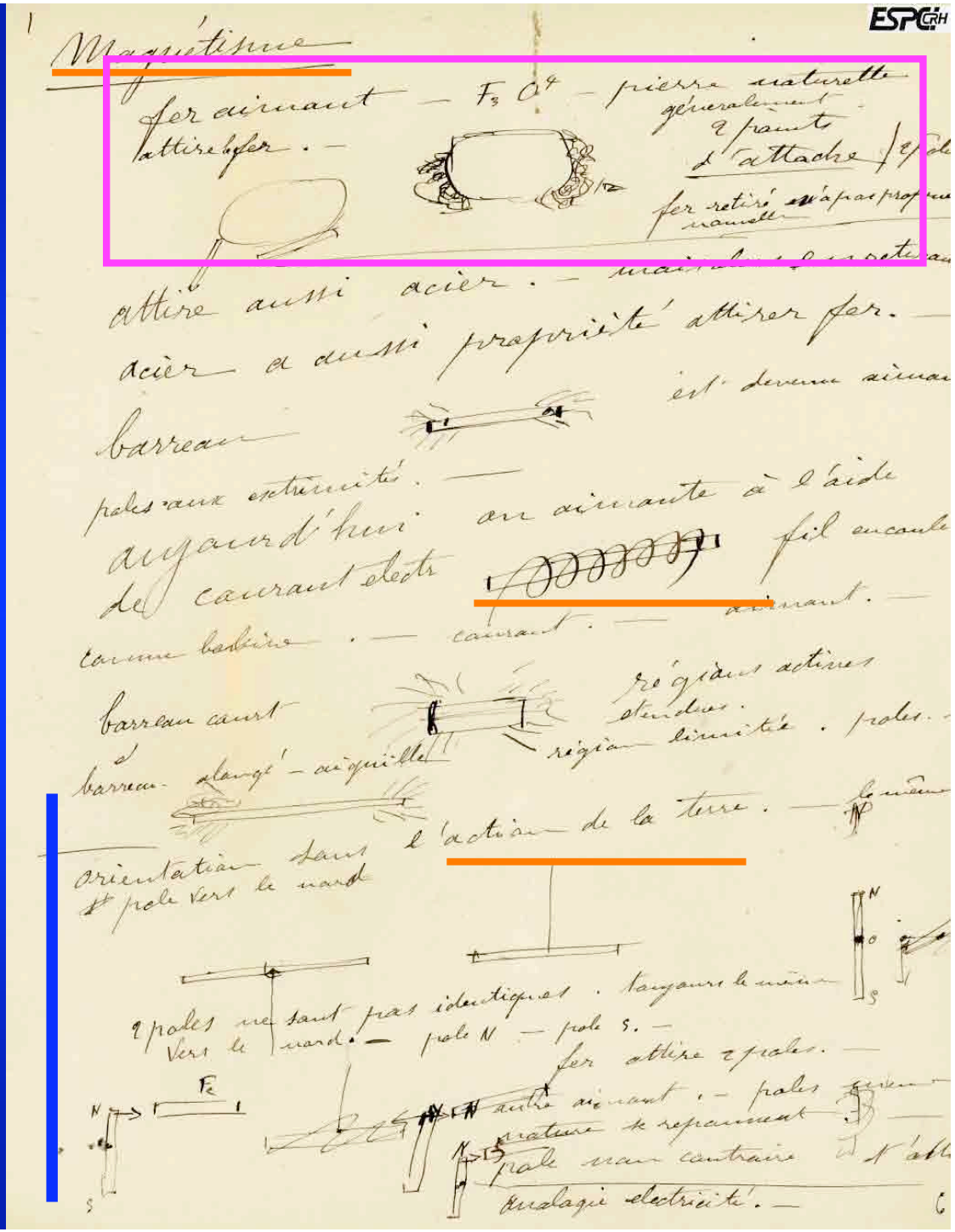
## … How ?



**Pierre Curie**

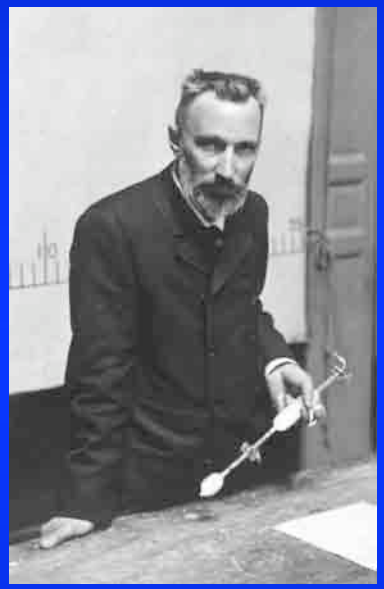
**Lectures Notes**

Fonds documentaire ESPCI



## Everything is magnetic …

## … How ?



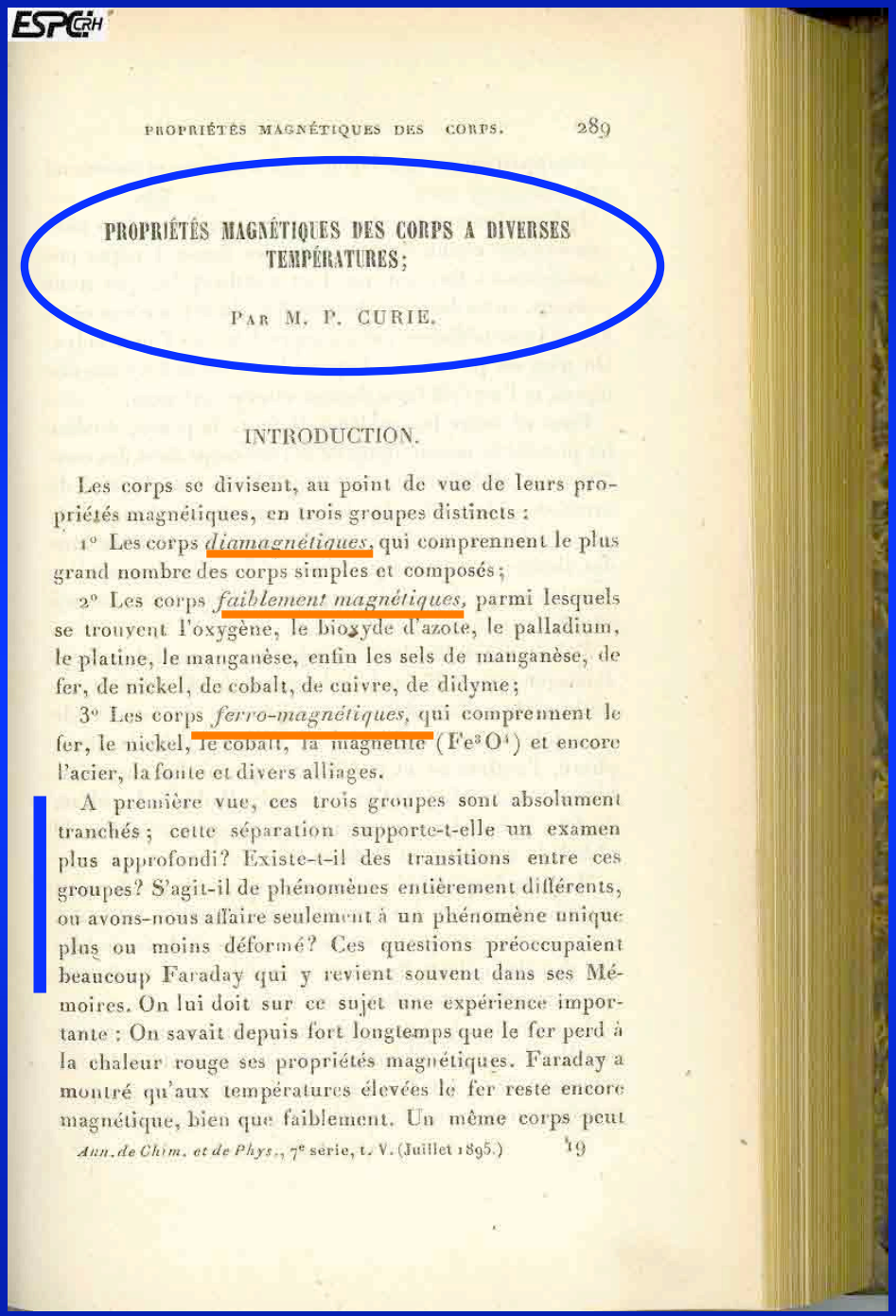
**Pierre Curie**

**Annales de Chimie**

**7ème série, V, 1895, 289**

**(Thèse de P. Curie)**

Fonds documentaire ESPCI





# PROPRIÉTÉS MAGNÉTIQUES DES CORPS A DIVERSES TEMPÉRATURES;

PAR M. P. CURIE.

## INTRODUCTION.

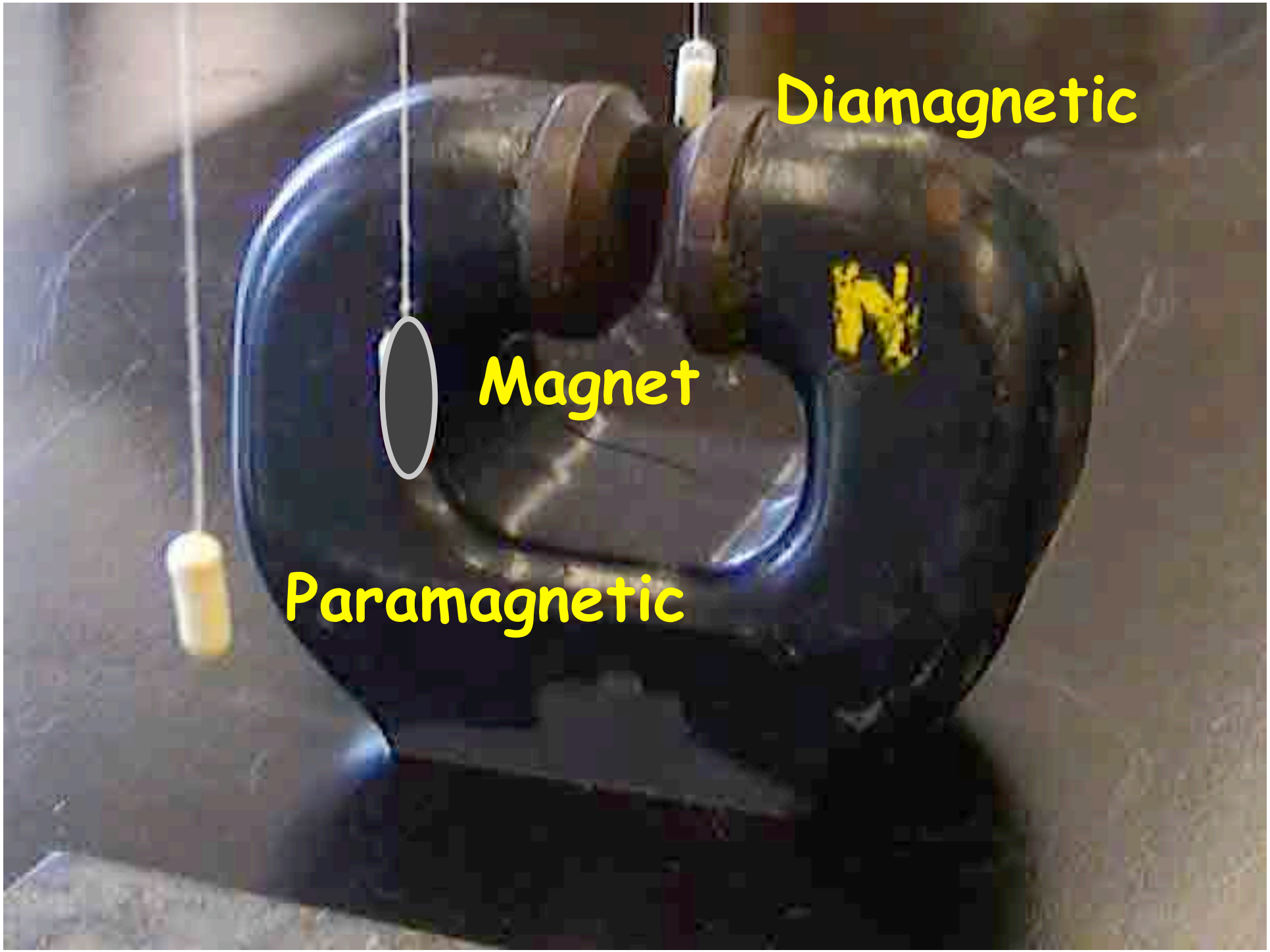
Les corps se divisent, au point de vue de leurs propriétés magnétiques, en trois groupes distincts :

1° Les corps *diamagnétiques*, qui comprennent le plus grand nombre des corps simples et composés;

2° Les corps *faiblement magnétiques*, parmi lesquels se trouvent l'oxygène, le bioxyde d'azote, le palladium, le platine, le manganèse, enfin les sels de manganèse, de fer, de nickel, de cobalt, de cuivre, de didyme;

3° Les corps *ferro-magnétiques*, qui comprennent le fer, le nickel, le cobalt, la magnétite ($Fe^3O^4$) et encore l'acier, la fonte et divers alliages.

A première vue, ces trois groupes sont absolument tranchés; cette séparation supporte-t-elle un examen plus approfondi? Existe-t-il des transitions entre ces groupes? S'agit-il de phénomènes entièrement différents, ou avons-nous affaire seulement à un phénomène unique plus ou moins déformé? Ces questions préoccupaient beaucoup Faraday qui y revient souvent dans ses Mémoires. On lui doit sur ce sujet une expérience importante : On savait depuis fort longtemps que le fer perd à la chaleur rouge ses propriétés magnétiques. Faraday a montré qu'aux températures élevées le fer reste encore magnétique, bien que faiblement. Un même corps peut


Diamagnetic
Magnet
Paramagnetic
N

**macroscopic world**

**atomic or molecular world**

**« wonder » world**

**macro**


Cais do Sodre Metro Station Lisboa, Antonio Dacosta

**quantum**

Everyday life
is full of useful *magnets*
which traditionally take the form
of three-dimensional solids,
oxides, metals and alloys

# Magnets in our world

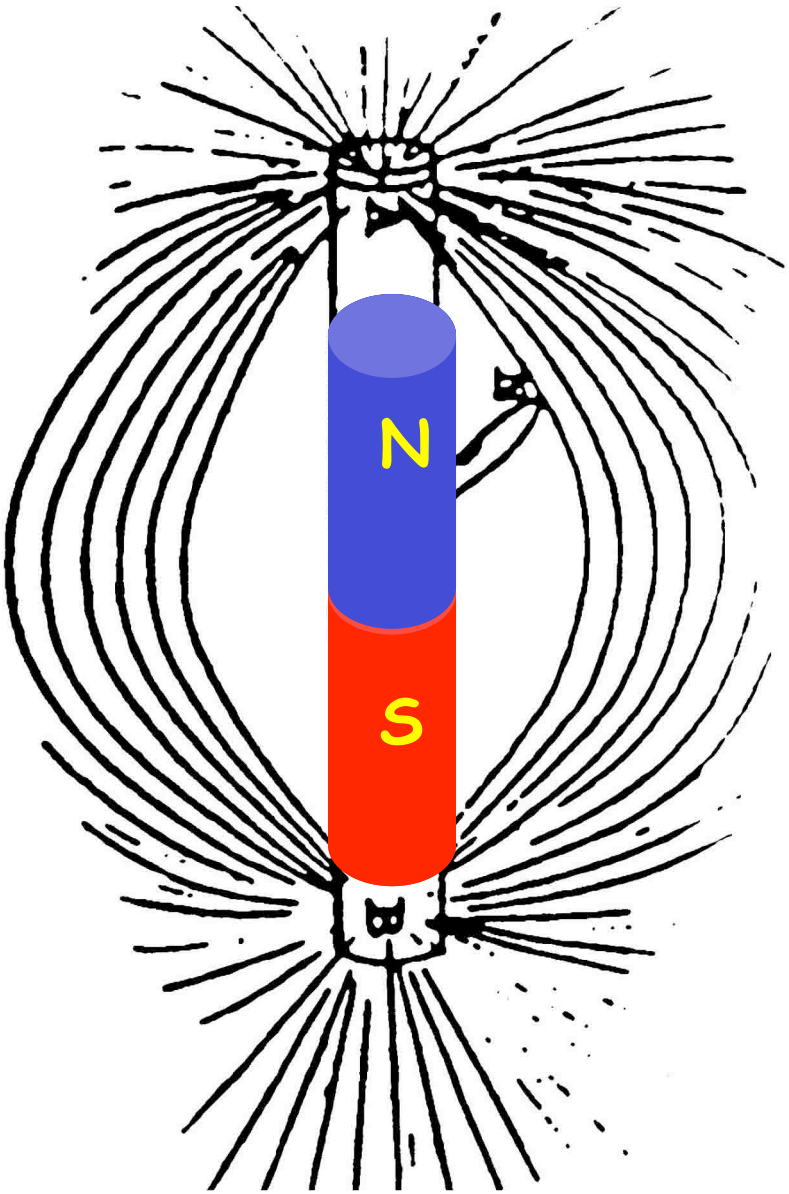
We are in a real world, at our size

# M. Faraday

Courtesy Prof. Frank James, the RI

# macroscopic world

A pioneering experiment
by M. Faraday
« Faraday lines of forces »
about magnetic flux




Courtesy Prof. Peter Day, the RI ; See also :
The Philosopher's Tree, The Institute of Physics Publishing, Bristol, 19999

A *magnet* creates a magnetic field

# « Lines of field »

What is a *magnet* ?

What is NOT a magnet ?

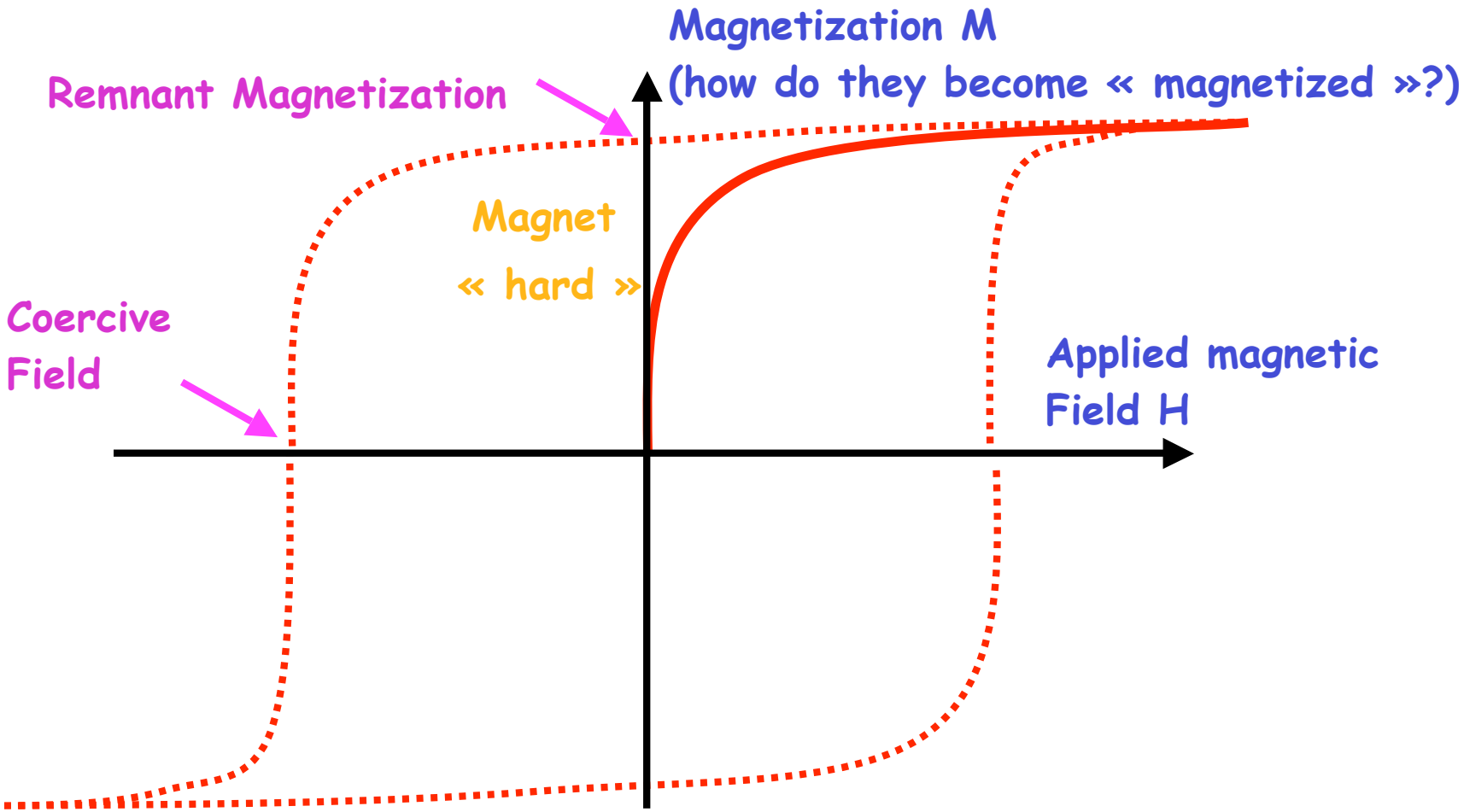
# Magnetization

macro

# Magnetization :

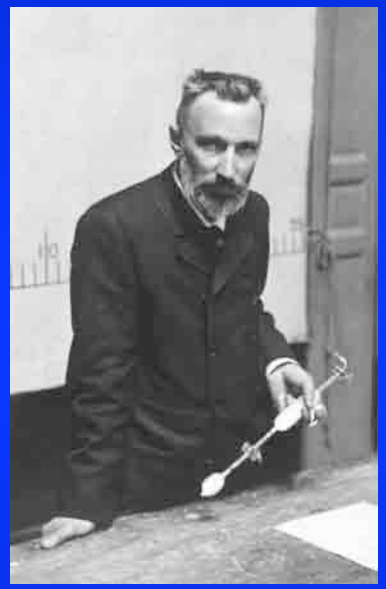
## How behave objects in a magnetic field ?

macro



## Tout est magnétique

## … Comment ?



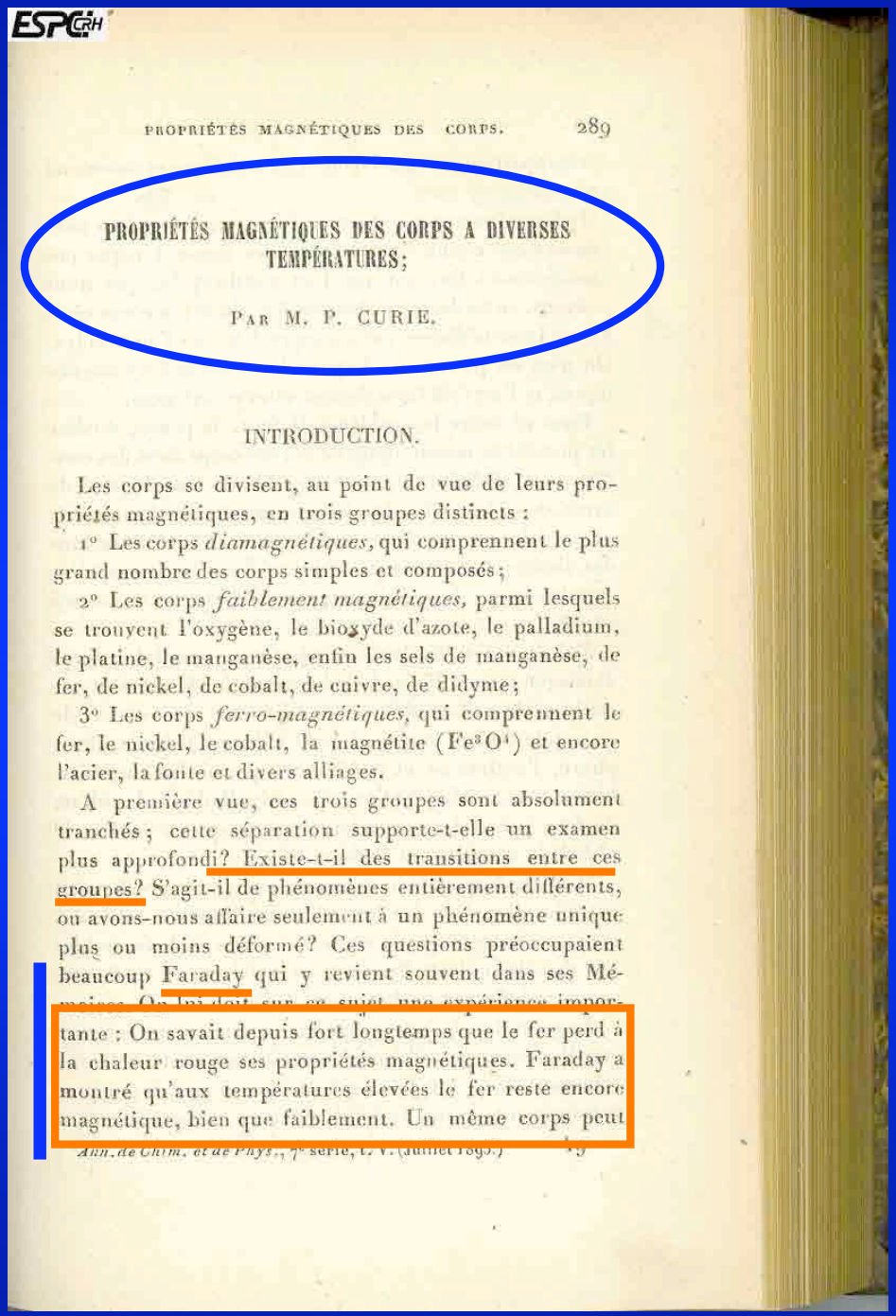
**Pierre Curie**

**Annales de Chimie**

**7ème série, V, 1895, 289**

**(Thèse de P. Curie)**

Fonds documentaire ESPCI





### PROPRIÉTÉS MAGNÉTIQUES DES CORPS A DIVERSES TEMPÉRATURES;

PAR M. P. CURIE.

#### INTRODUCTION.

Les corps se divisent, au point de vue de leurs propriétés magnétiques, en trois groupes distincts :

1° Les corps *diamagnétiques*, qui comprennent le plus grand nombre des corps simples et composés;

2° Les corps *faiblement magnétiques*, parmi lesquels se trouvent l'oxygène, le bioxyde d'azote, le palladium, le platine, le manganèse, enfin les sels de manganèse, de fer, de nickel, de cobalt, de cuivre, de didyme;

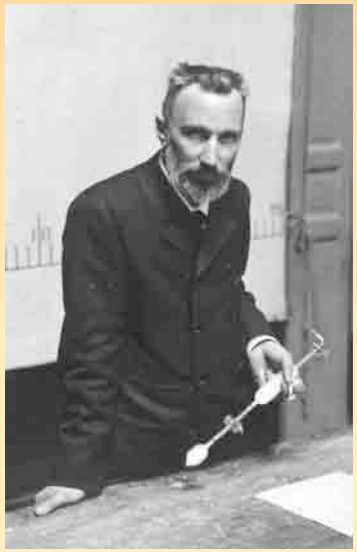
3° Les corps *ferro-magnétiques*, qui comprennent le fer, le nickel, le cobalt, la magnétite ($Fe^3O^4$) et encore l'acier, la fonte et divers alliages.

A première vue, ces trois groupes sont absolument tranchés; cette séparation supporte-t-elle un examen plus approfondi? Existe-t-il des transitions entre ces groupes? S'agit-il de phénomènes entièrement différents, ou avons-nous affaire seulement à un phénomène unique plus ou moins déformé? Ces questions préoccupaient beaucoup Faraday qui y revient souvent dans ses Mémoires. On lui doit sur ce sujet une expérience importante : On savait depuis fort longtemps que le fer perd à la chaleur rouge ses propriétés magnétiques. Faraday a montré qu'aux températures élevées le fer reste encore magnétique, bien que faiblement. Un même corps peut

Everyday life
is full of useful *magnets*
which traditionally take the form
of three-dimensional solids,
oxides, metals and alloys

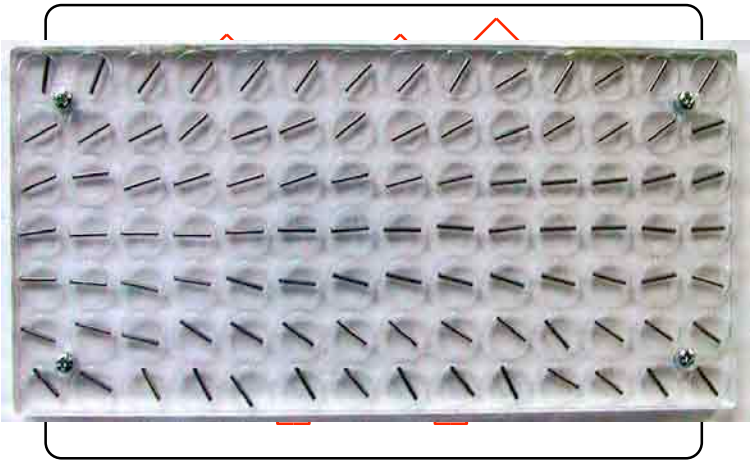
# Curie Temperature

macro



# The magnetic moments order at Curie temperature

A set of molecules / atoms :



$T_C$

$\rightleftharpoons$

$kT \approx J$

Magnetic Order Temperature or Curie Temperature

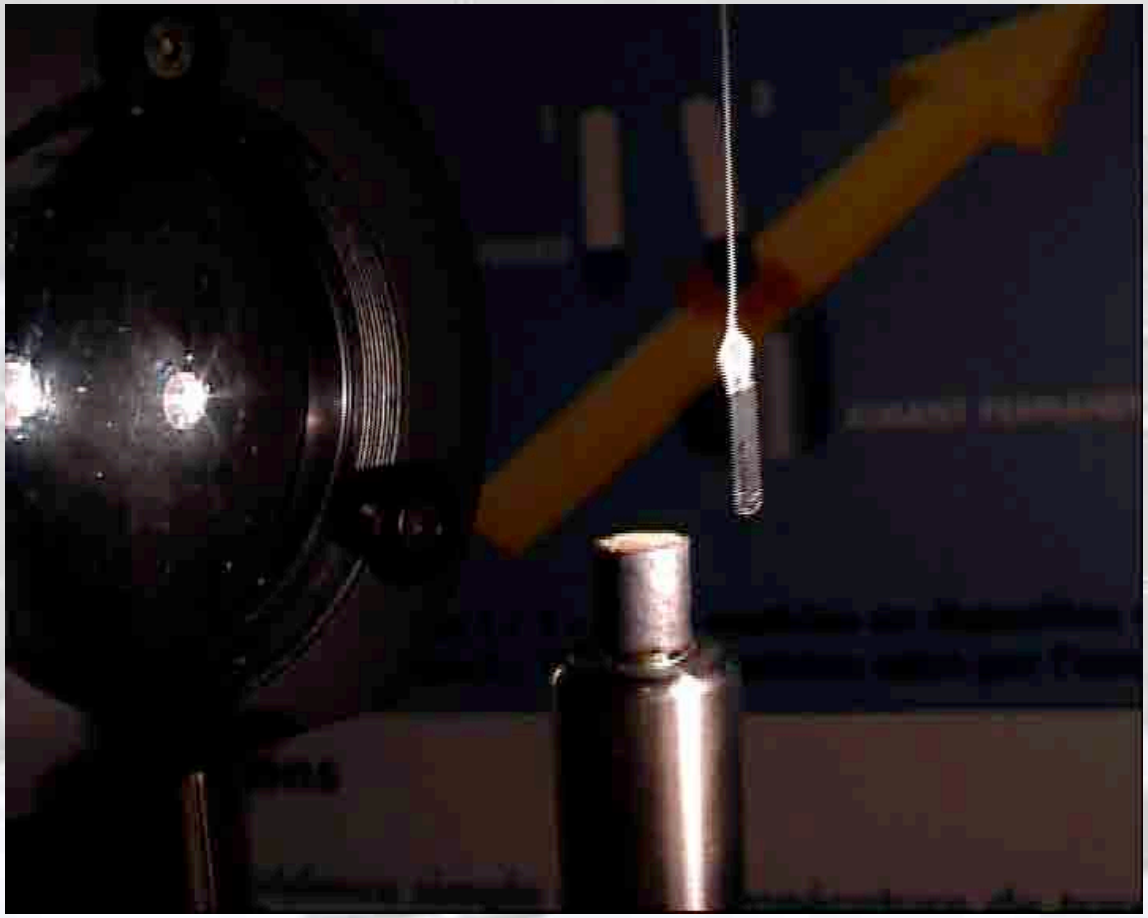
**Solid, Magnetically Ordered**
thermal agitation (kT) weaker than the interaction (J) between molecules

$kT << J$

… **Paramagnetic solid** :
thermal agitation (kT) larger than the interaction (J) between molecules

$kT >> J$

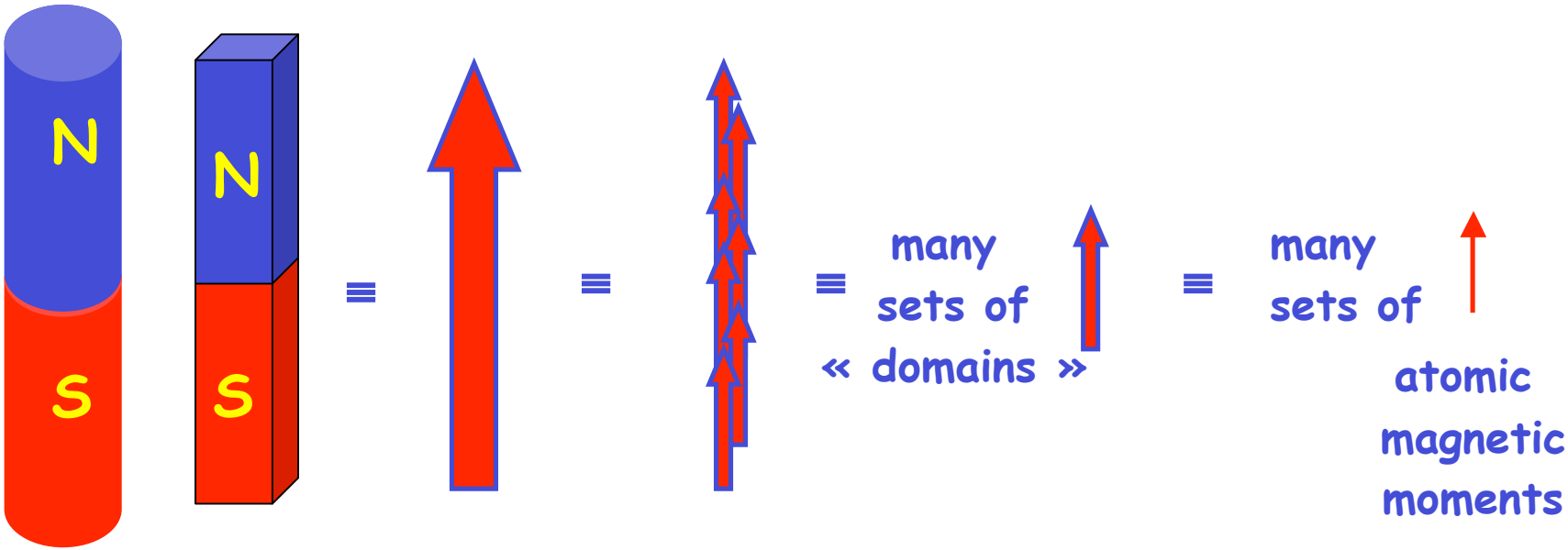
# Magnetic ordering : Curie Temperature …



… a demonstrator

# from macroscopic to atomic world

looking closer to smaller and smaller magnets

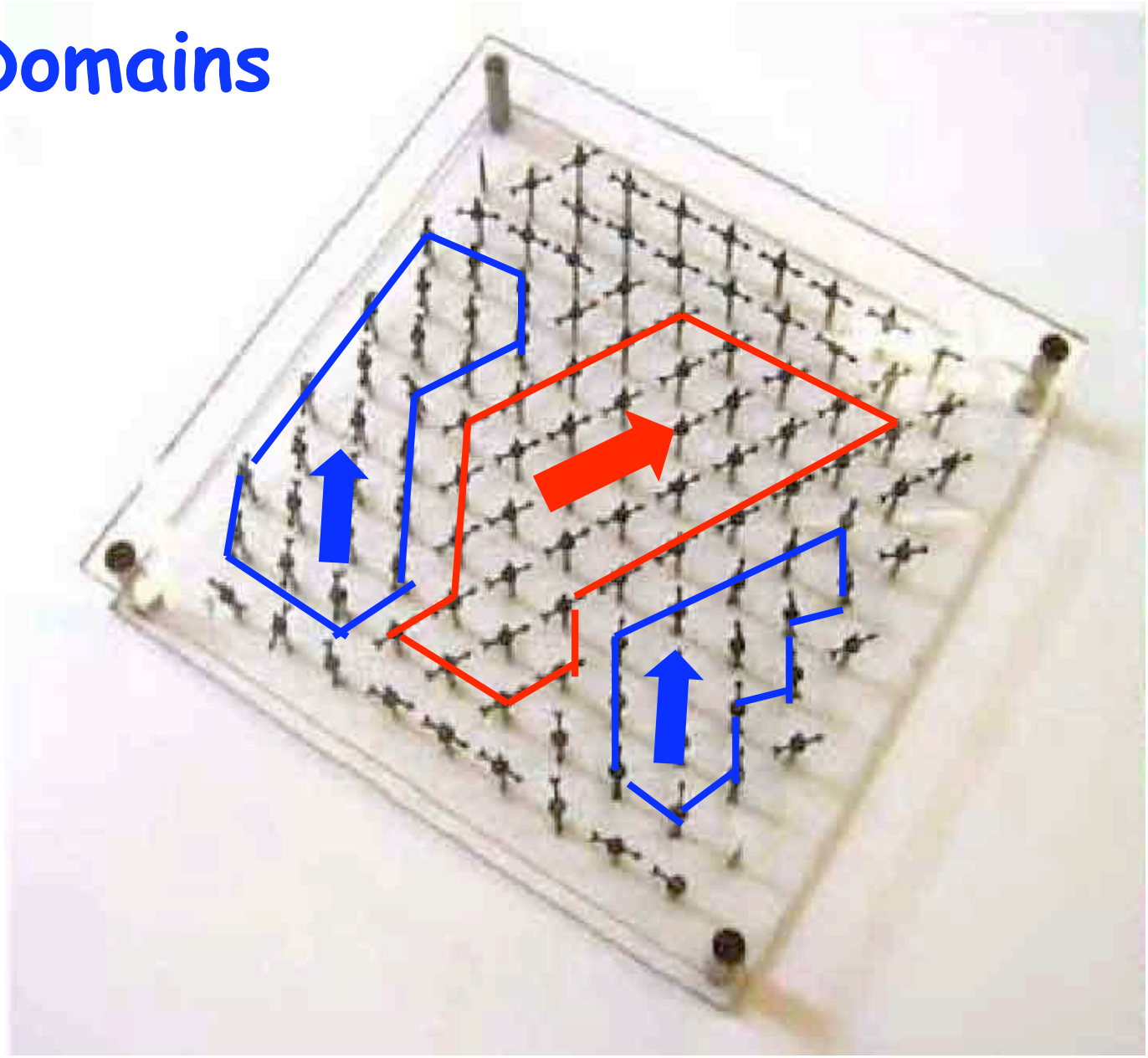


How *magnets* behave ?

# Domains

macro

# Domains



*Physics : Macroscopic* *Mesoscopic* *Nanoscopic*

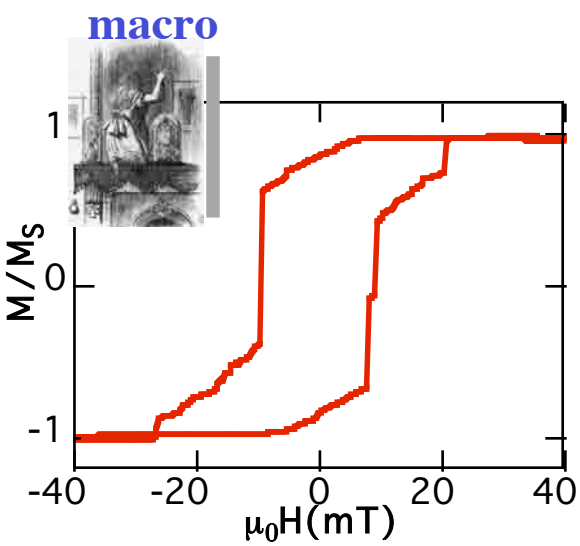
permanent magnets | micron particles | nanoparticles | clusters | molecular clusters | individual spins

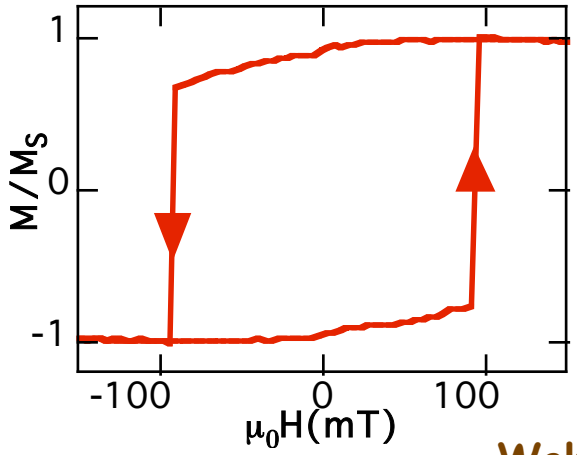
$S = 10^{20}$ $10^{10}$ $10^{8}$ $10^{6}$ $10^{5}$ $10^{4}$ $10^{3}$ $10^{2}$ 10 1

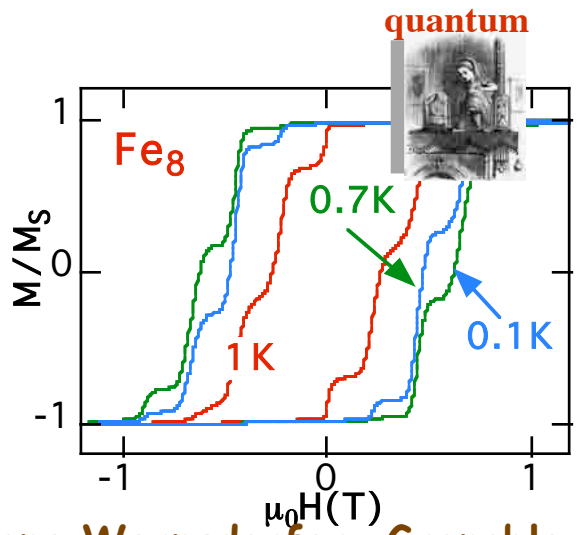
*multi - domain*
nucleation, propagation and annihilation of domain walls

*single - domain*
uniform rotation
curling

*magnetic moment*
quantum tunneling,
quantization
quantum interference



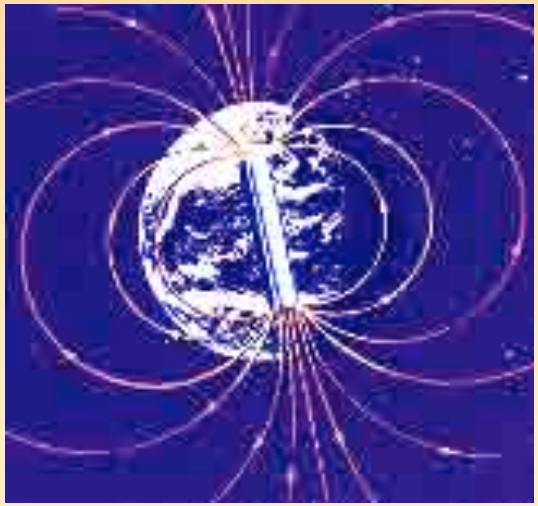




Wolfgang Wernsdorfer, Grenoble

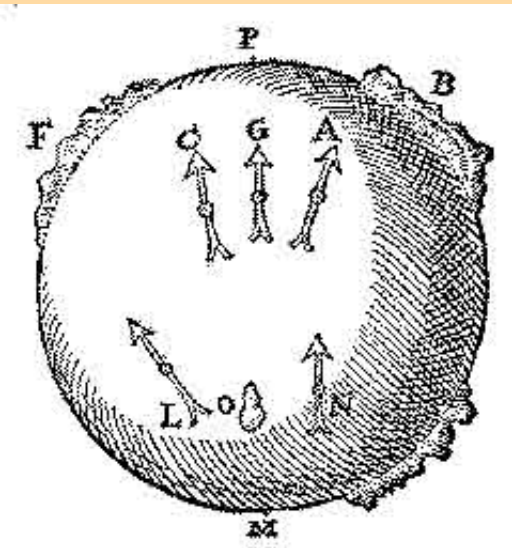
Everyday life
is full of useful *magnets*

# Compasses

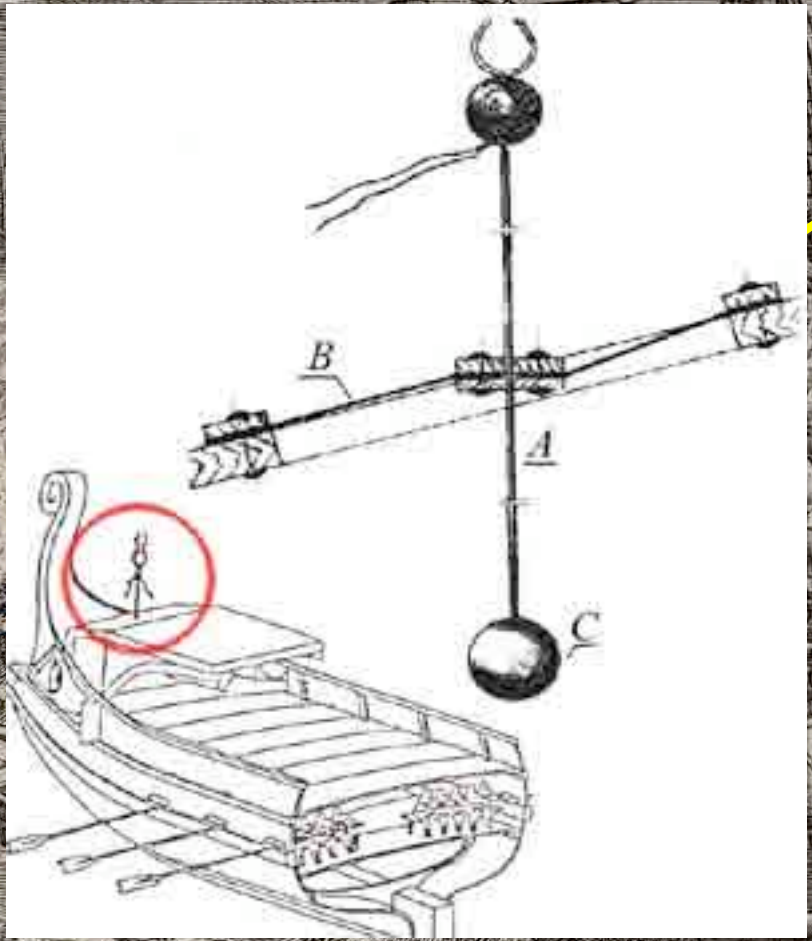
*Magnetic Earth*



*1600*
*William Gilbert*
*De Magnete*



Jan van der Straet (Giovanni Stradanus), Bruges, 1523 ; Florence, 1605
Nova Reperta, vers 1620-1630 , 14 planches gravées par Jérôme Wierix et Adriaen Collaert, éditées par Philippe Galle



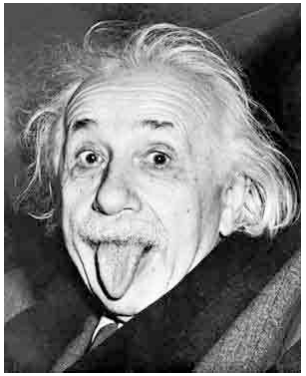

Calcul de la longitude, Burin 22 x 28 cm around 1600 Inv. n° 11786

16.

ORBIS LONGITVDINES REPERTÆ E MAGNETIS A POLO DECLINATIONE.

Magnete paulum vtique sæpe acuta Dat inuenire portum vtique Plancius.

Compasses, Jiangomen station, Beijing



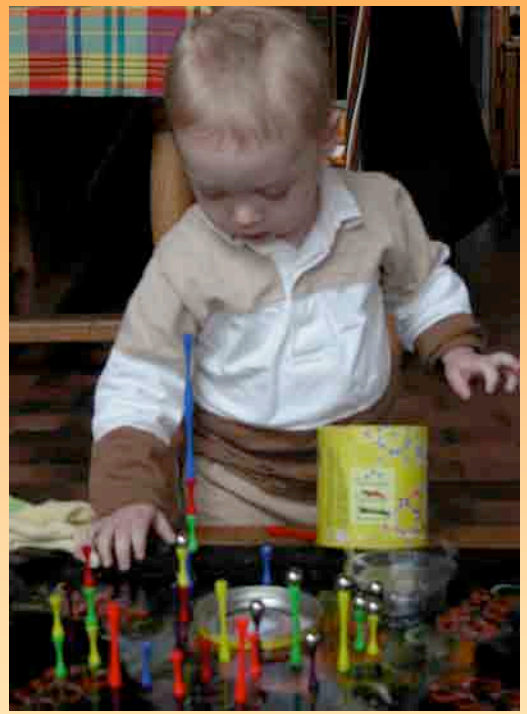
## The fascination of *magnets* on children

« A wonder of such nature I experience as a child of 4 or 5 years, when my father showed me a compass. That this needle behaved in such a determined way did not at all fit into the nature of events which could find a place in the unconscious world of concepts (effects connected with direct « touch »). I can still remember – or at least believe I can remember – that *this experience made a deep and lasting impression upon me*.
Something deeply hidden had to be behind things. »

A. Einstein

Quoted by Livingston, J. D. In *Driving Force: The Natural Magic of Magnets*. Cambridge, MA: Harvard University Press, 1996. ISBN: 0674216458.

Everyday life
is full of useful *magnets*



# Toys

macro

Everything is magnetic

… thanks to electrons …

# Origin of *Magnetism*

## … the electron *

I am an electron

- rest mass $m_e$,
- charge $e^-$,
- magnetic moment $\mu_B$

quantum

everything, tiny, elementary

* but do not forget nuclear magnetism !

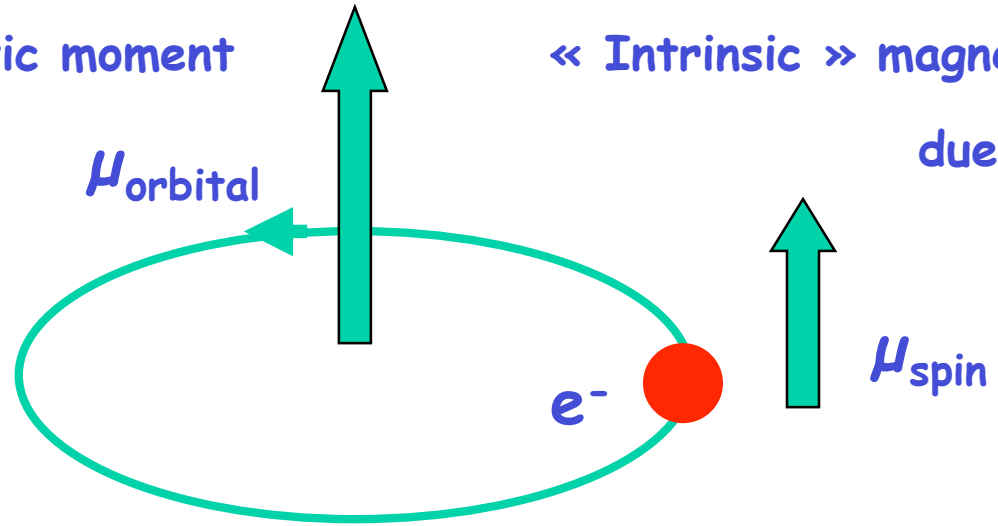
# Origin of *Magnetism*

« Orbital » magnetic moment

« Intrinsic » magnetic moment

due to the spin

$s = \pm 1/2$



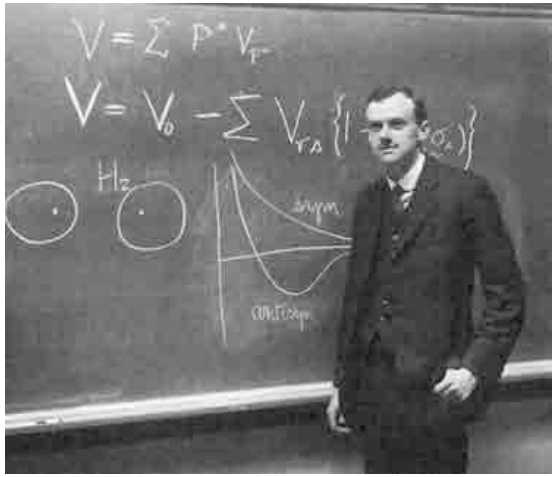

$$\mu_{orbital} = g_l \times \mu_B \times \ell$$

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

quantum

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

# Dirac Equation



The Principles of Quantum Mechanics, 1930

Nobel Prize 1933

$$(E'+e\varphi)\psi = [\frac{1}{2m}(\mathbf{p}+\frac{e}{c}\mathbf{A})^2 + \frac{e\hbar}{2mc}\boldsymbol{\sigma}\bullet\nabla\times\mathbf{A} - \frac{p^4}{8m^3c^2} - \frac{e\hbar^2}{8m^2c^2}\nabla\bullet\nabla\varphi - \frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\bullet\nabla\varphi\times\mathbf{p}]\psi$$

1905

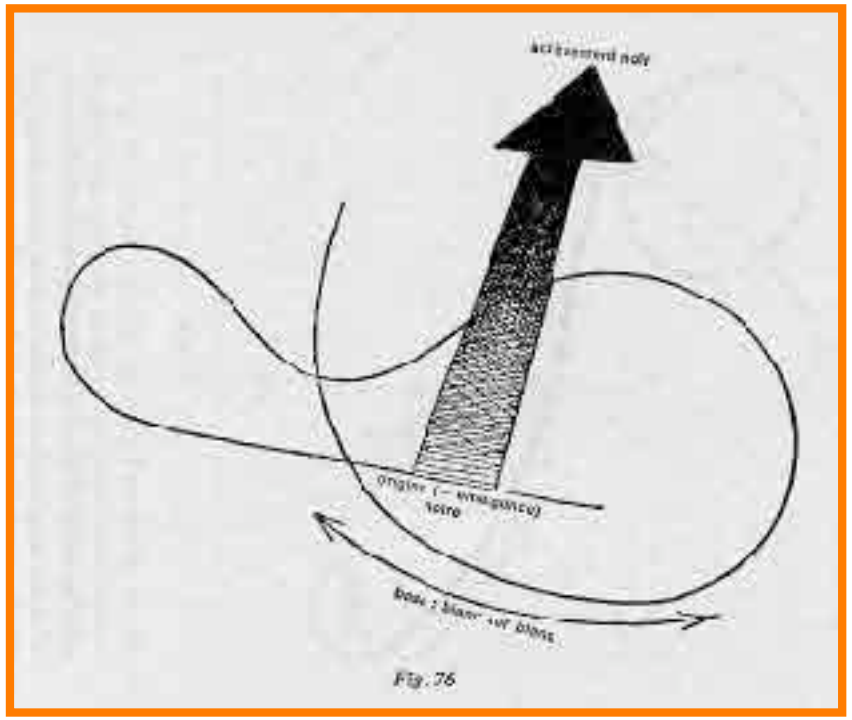
1928

http://www-history.mcs.st-and.ac.uk/history/PictDisplay/Dirac.html

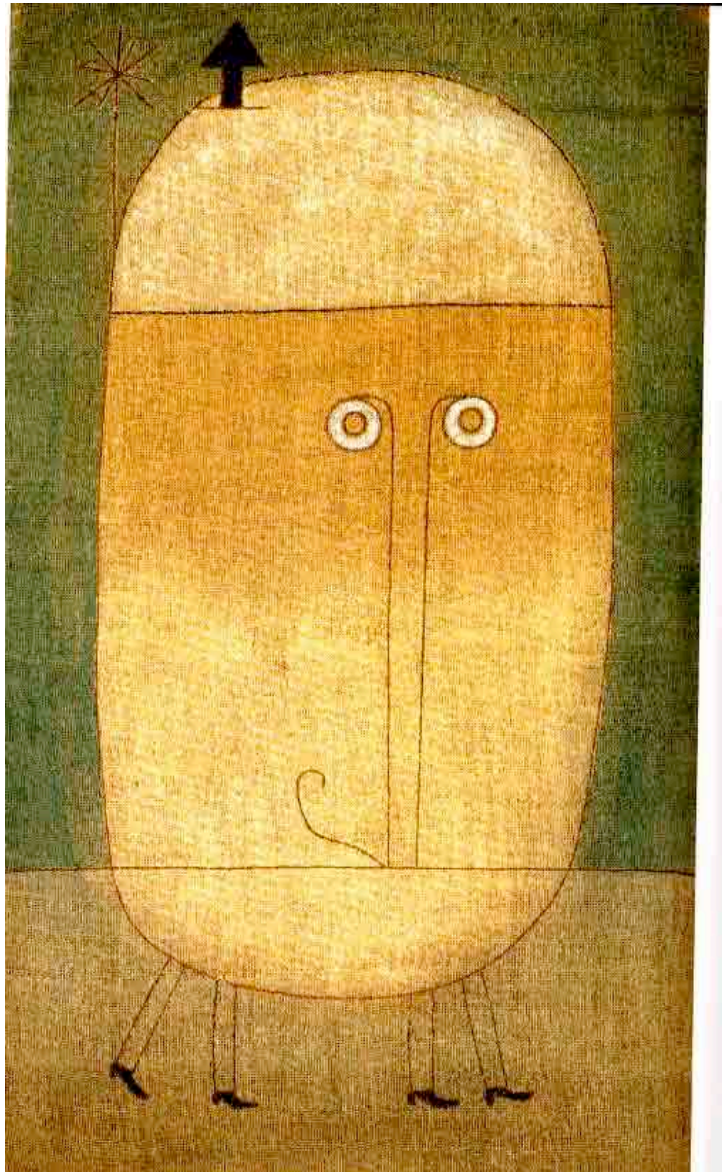
About what are we speaking ?

# Representations,
# Models,
# Analogies …

# Analogy : spin and arrow

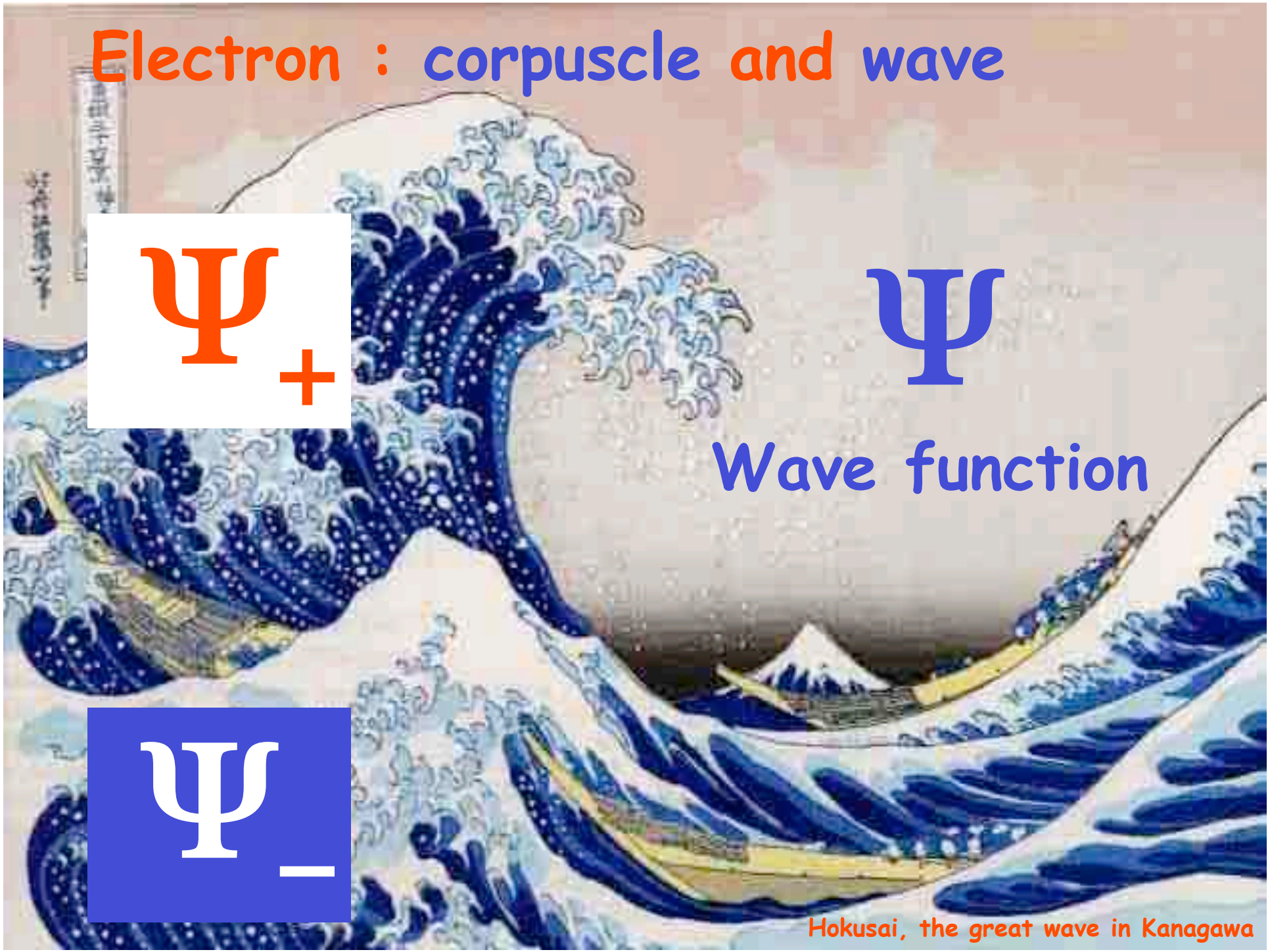



Paul Klee, Théorie de l'art, Denoël, Paris



An isolated spin …

# Electron : corpuscle and wave



$\Psi_+$

$\Psi$

Wave function

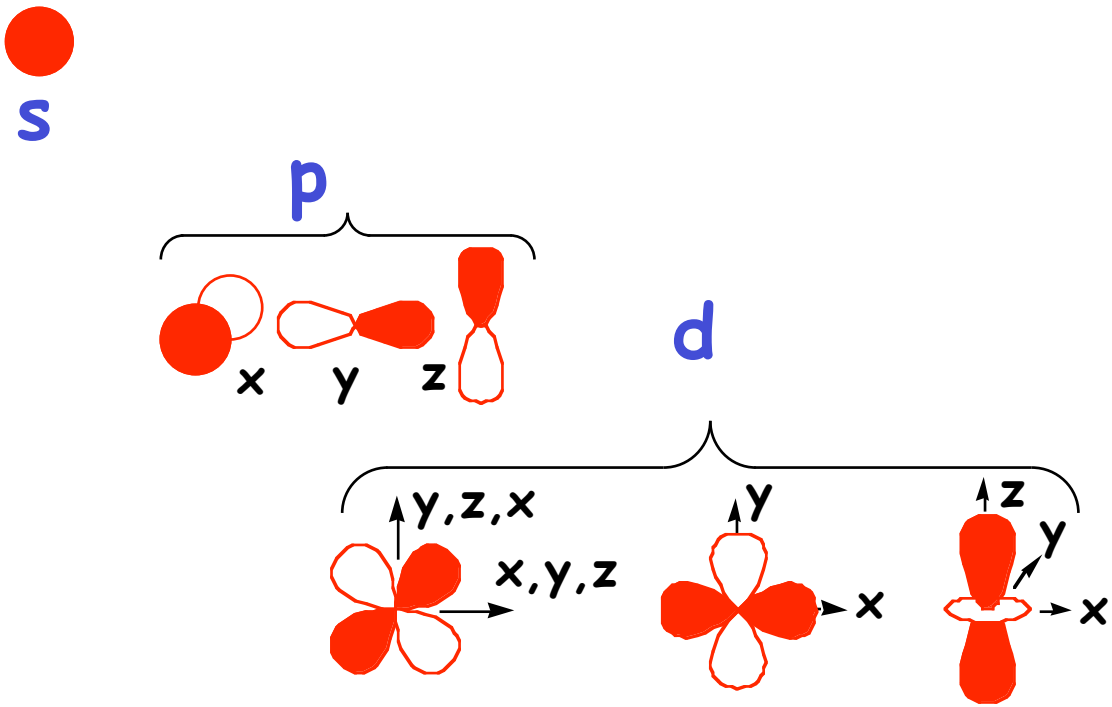
$\Psi_-$

Hokusai, the great wave in Kanagawa

# Electron : corpuscle and wave

Wave function or « orbital » $\Psi_{n,\ l,\ m_l\ \ldots}$

l = 0 1 2 3

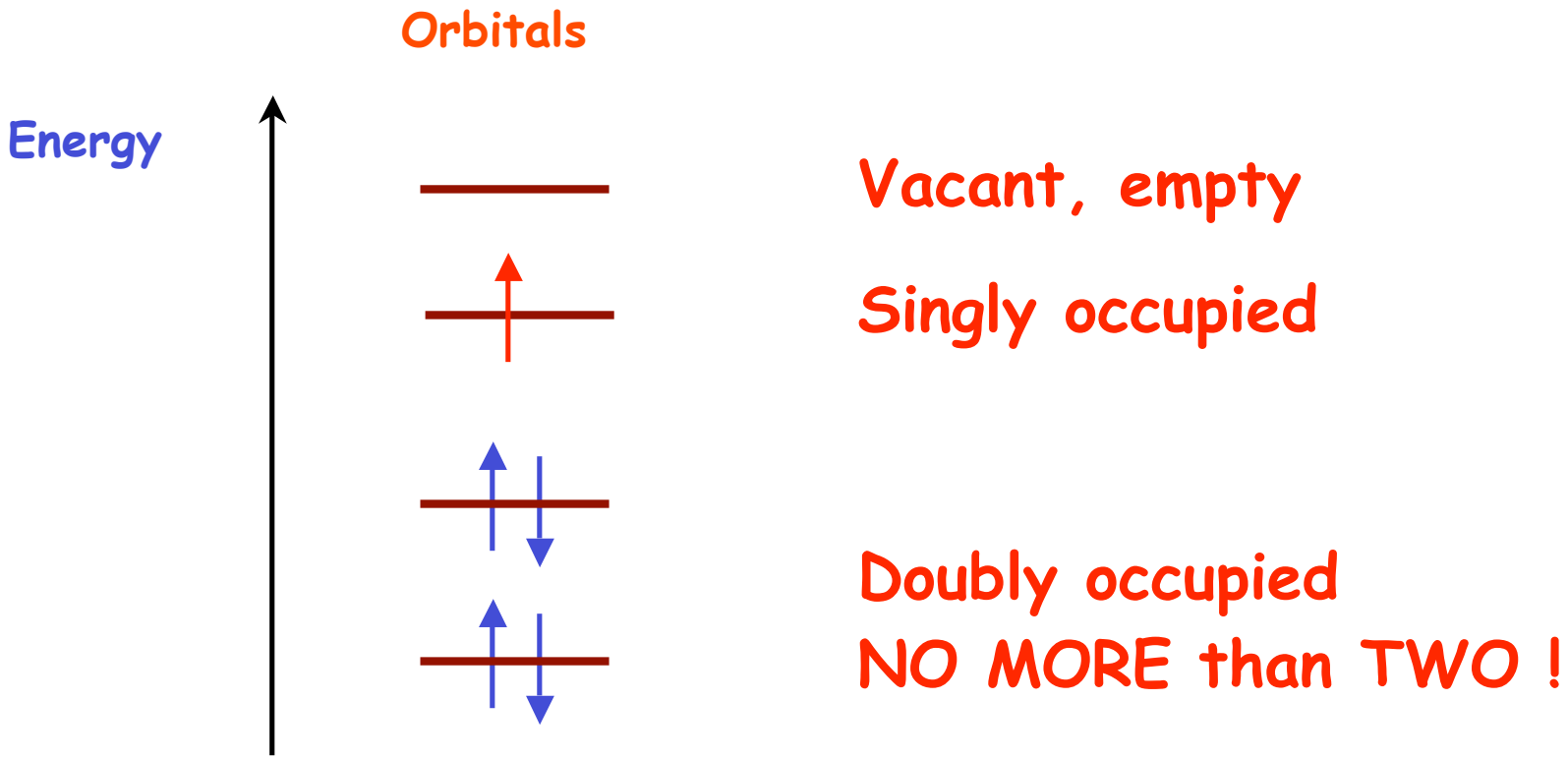




angular representation

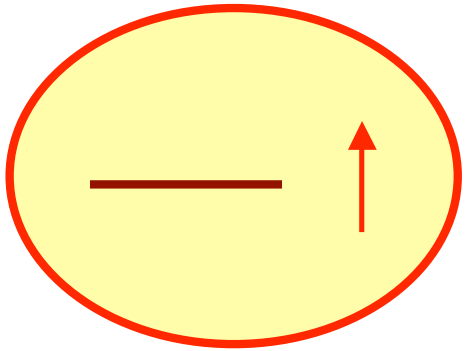

# Electron : also an energy level

## Energy Diagramme (« ladder »)




**Principle 1 : fill from the bottom (aufbau)**

# Electron : orbital and spin !

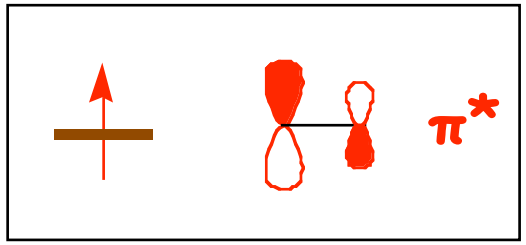
Up

Down

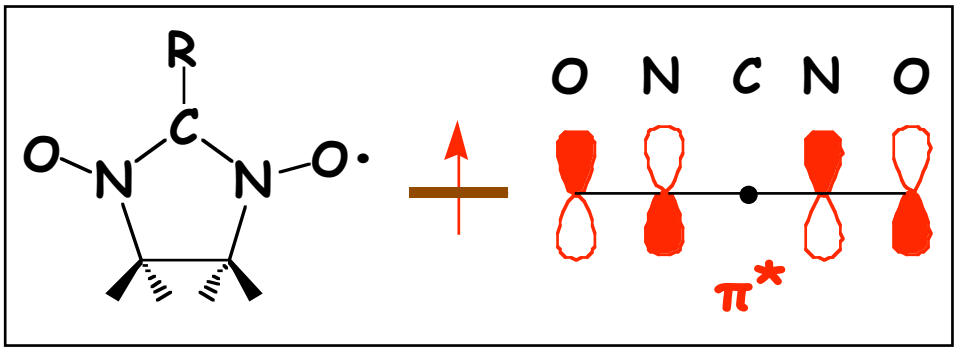
Singly occupied

« Paramagnetic »

$m_S = \pm 1/2$

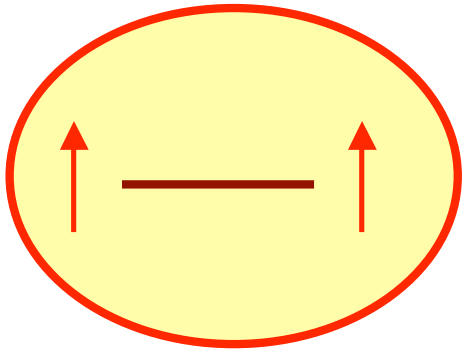


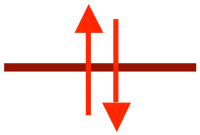

Nitrogen oxide NO·




Nitronylnitroxyde


# Electron : orbital and spin !





Doubly occupied

S = 1/2 - 1/2 = 0

« Diamagnetic »

## Principle 2 : no more than TWO electrons per level (orbital) with different spins !

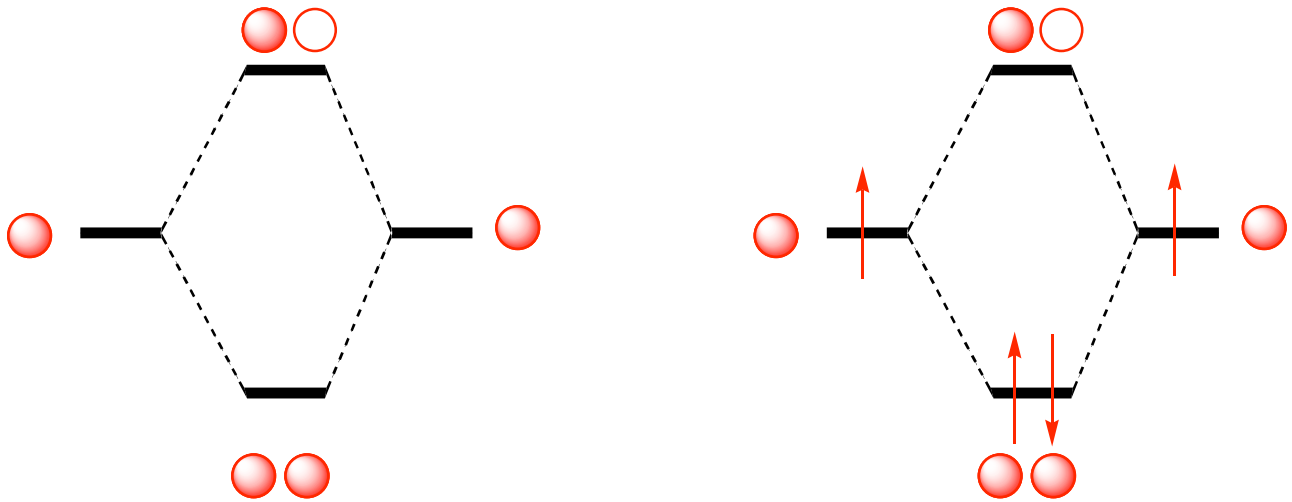
(Pauli's exclusion principle)

# Molecules

are most often regarded

as isolated, non magnetic, creatures

## Dihydrogen



quantum

**Diamagnetic**

Spin S = 0

# $N_2$ Diamagnetic

macro

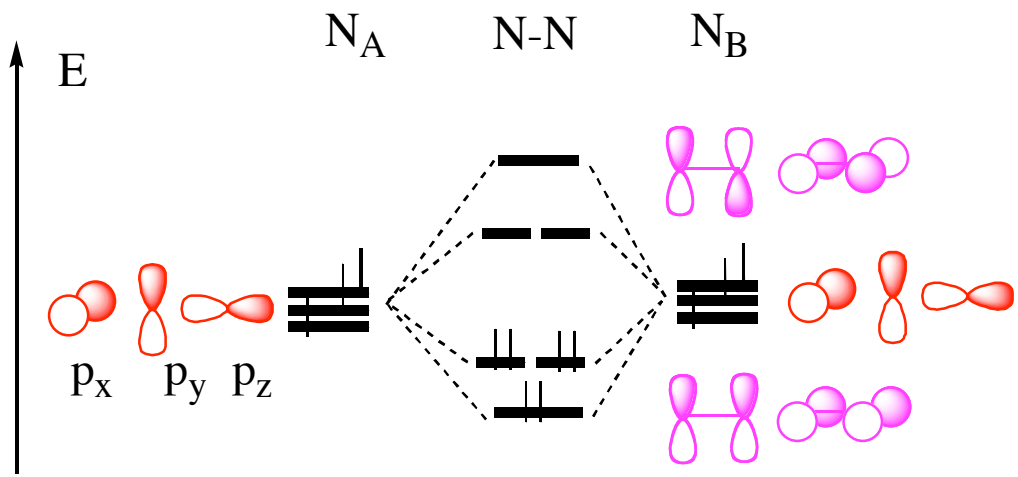
## Pouring liquid dinitrogen

liquid dinitrogen
does NOT stick

diamagnetic

# the *dinitrogen*

## is a dia*magnetic molecule*




**diamagnetic, spin S = 0**

All electrons are paired in bonds, very stable molecule

when dioxygen is in its ground state
it is a triplet (spin S=1)
and its reactivity is weak

# Paramagnetic $O_2$

macro

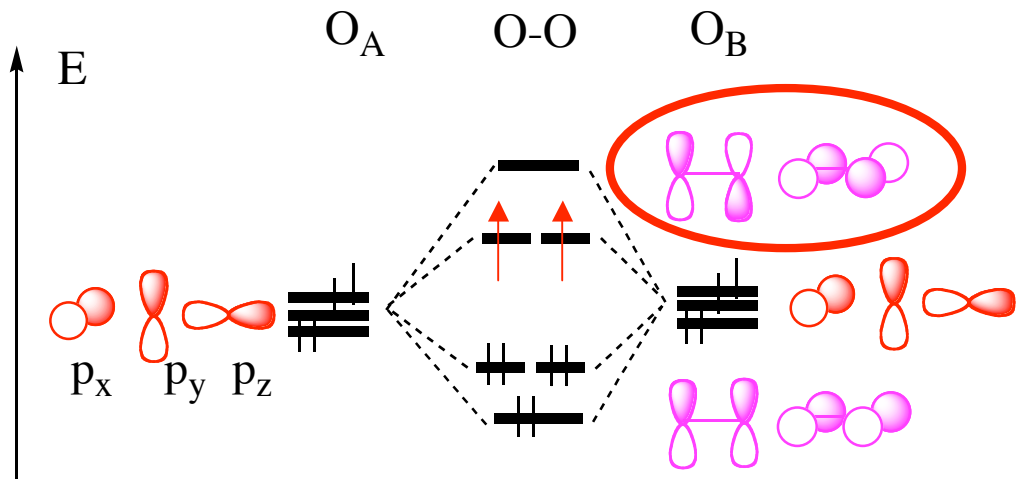
Liquid $O_2$


liquid dioxygen
does stick
$O_2$ is paramagnetic

# the *dioxygen*

## that we continuously breathe

## is a *magnetic molecule*



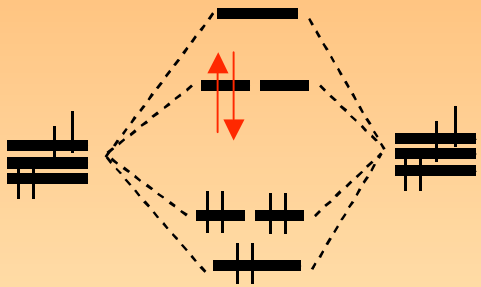

orthogonal π molecular orbitals

**paramagnetic, spin S =1**

Two of its electrons have parallel magnetic moments that shapes aerobic life and allows our existence as human beings

when dioxygen is in an excited state
it can becomes a singlet (spin S=0)
and strange reactivity appears
sometines useful (glow-worm ...)

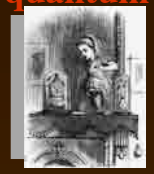
# Singlet dioxygen




## Luminol Light

# dioxygen singlet (spin S=0)

quantum




luminol

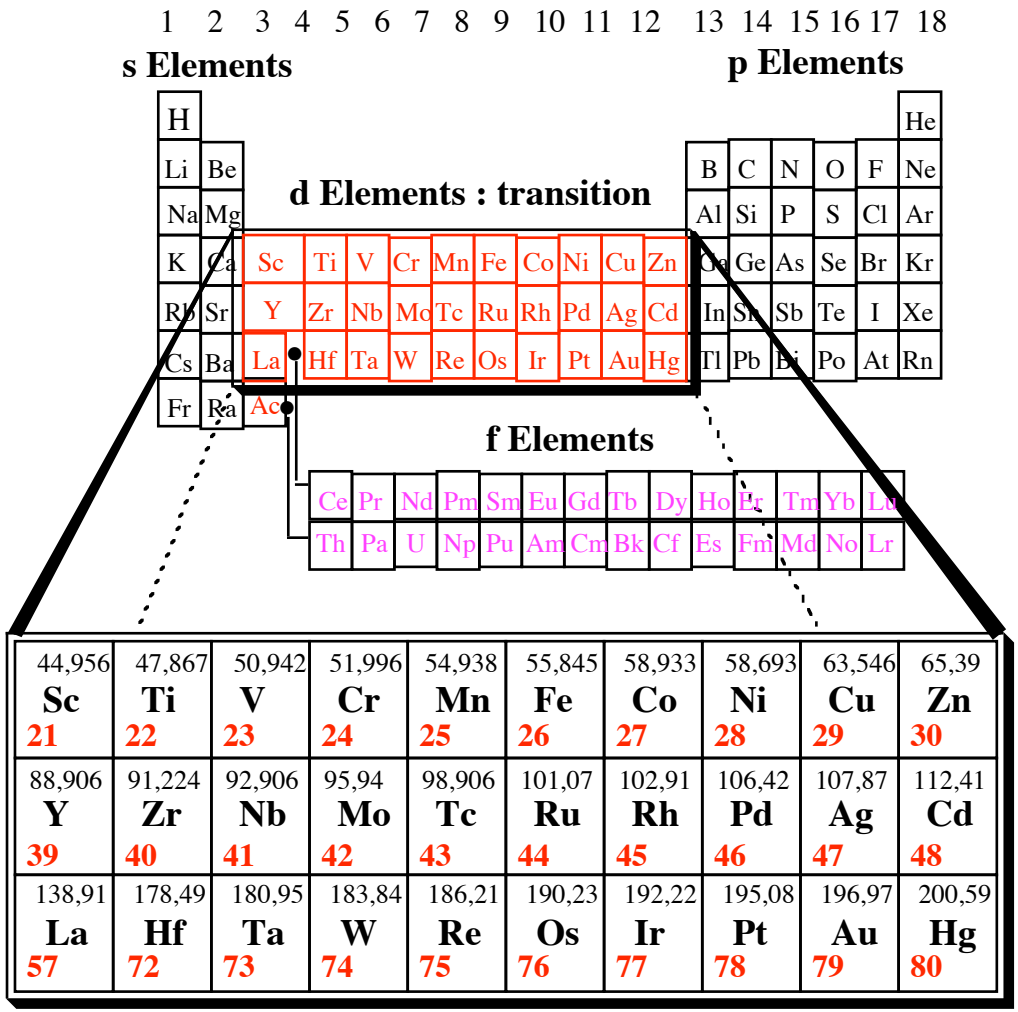

macro

glow-worm ...

Documents from Nassau and Alvarez

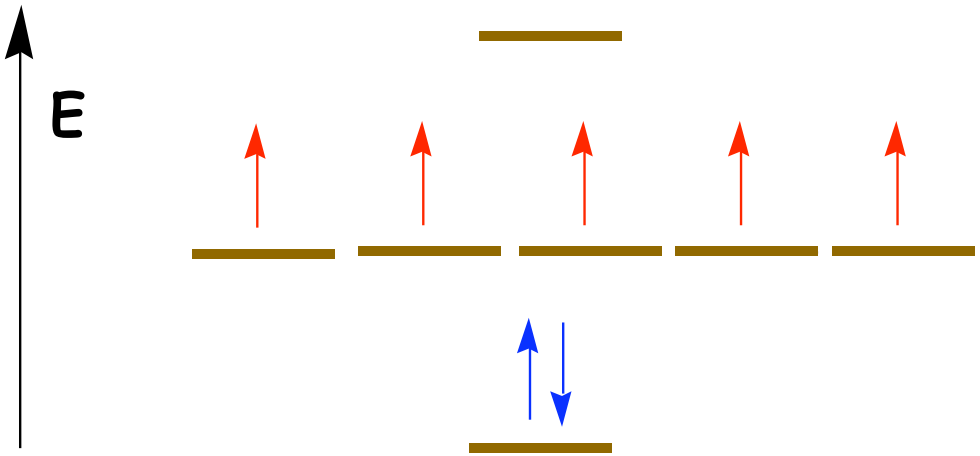
More complex molecular frameworks
called metal complexes
built from transition metal and molecules
are able to bear up to five or seven electrons
with aligned magnetic moments (spins)

# Il sistema periodico … (Primo Levi)




**È bello raccontare i guai passati …**

# Transition Elements



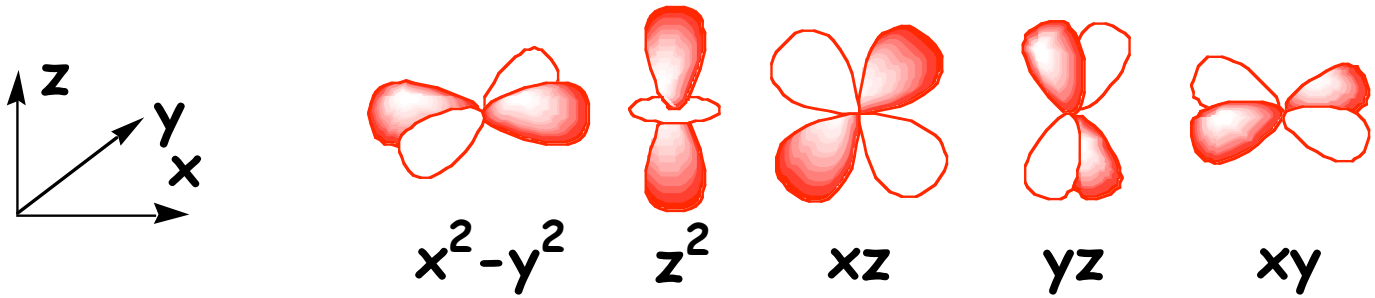

**5 d orbitals**

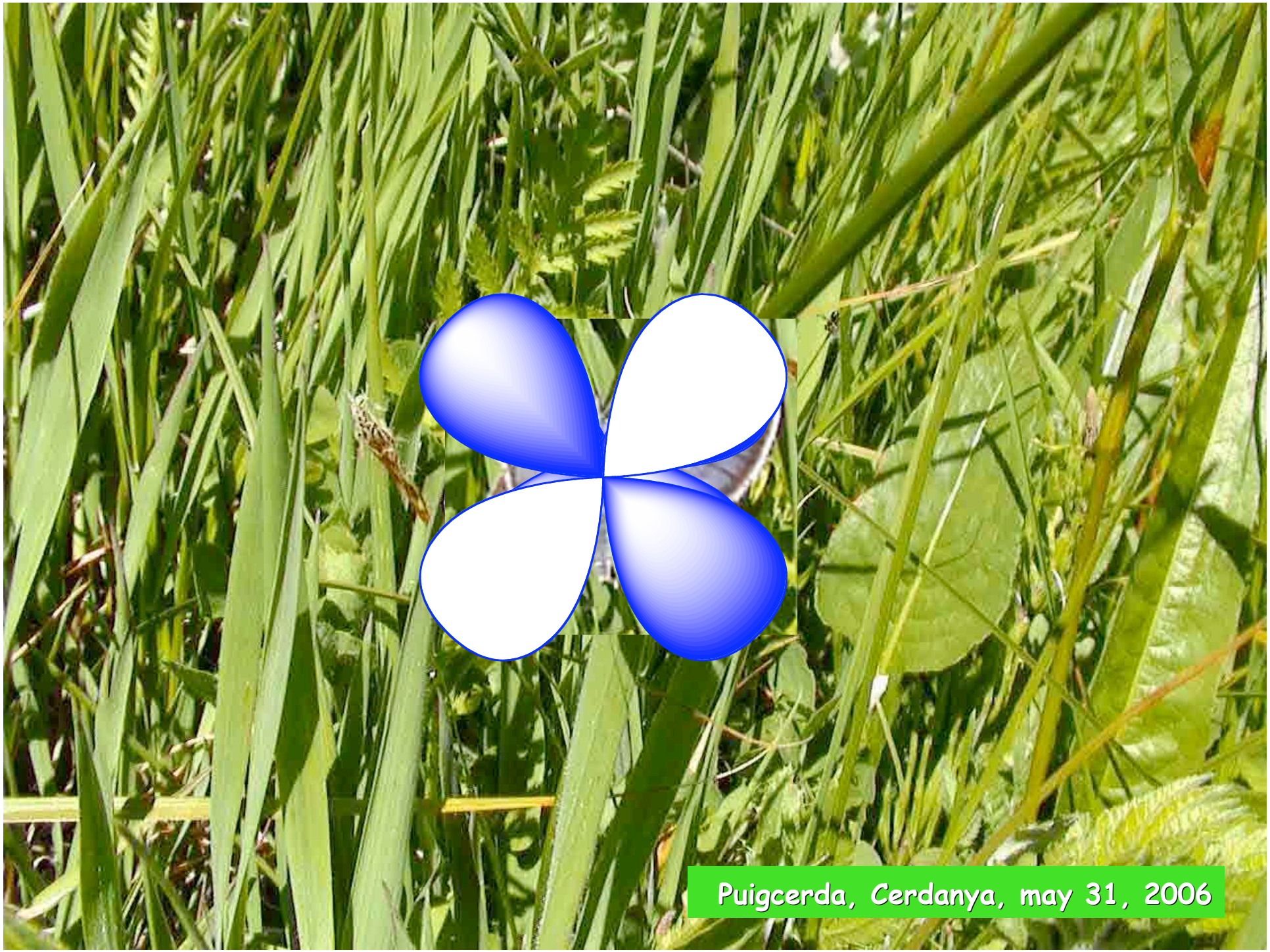
⇩

Unpaired Electrons

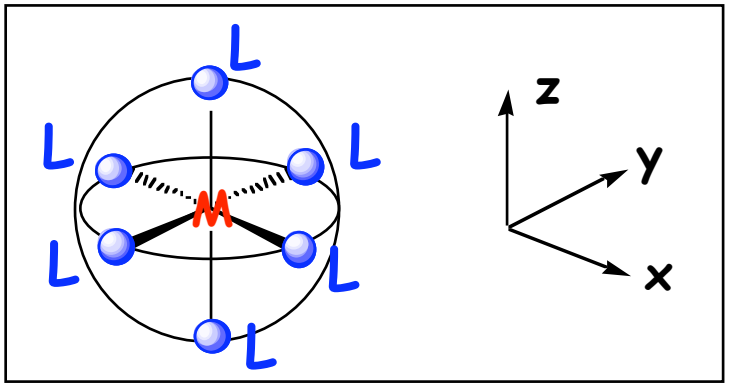
⇩

Partial Ocupancy
Paramagnetism
Conductivity

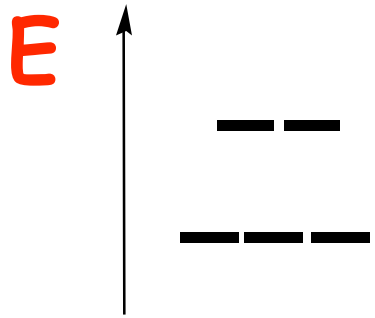




Puigcerda, Cerdanya, may 31, 2006

# Mononuclear complex $ML_6$

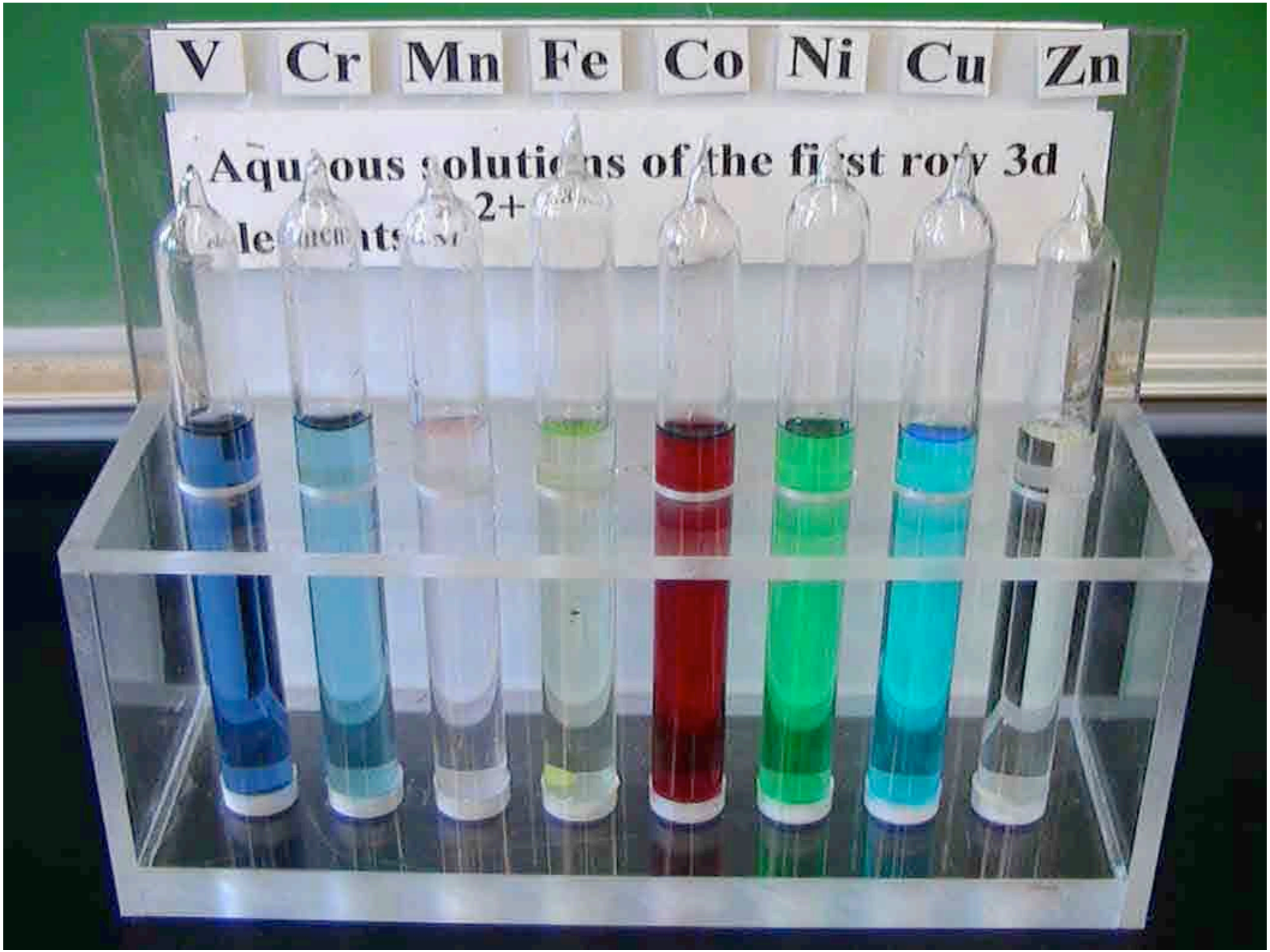



Splitting of the energy levels

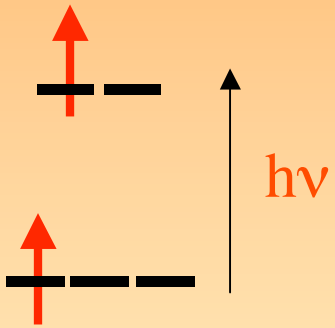


Electrons …
WANTED !

An indirect manifestation of the presence of unpaired electrons : the colour

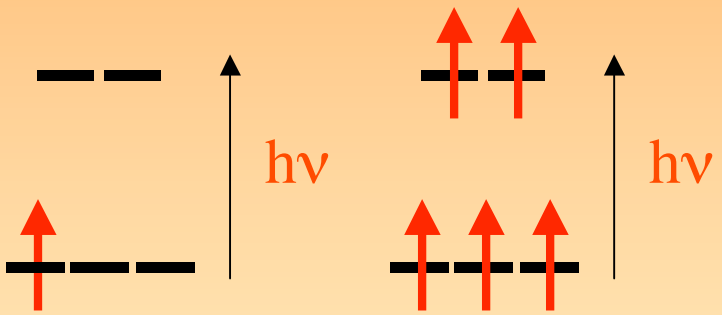

V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Aqu ous solutions of the first row 3d
2+
le ments

Complexes of transition metal ions
often display beautiful colours
essentially to d levels splitting




Colours in water
Geometrical Changes
Spin Changes

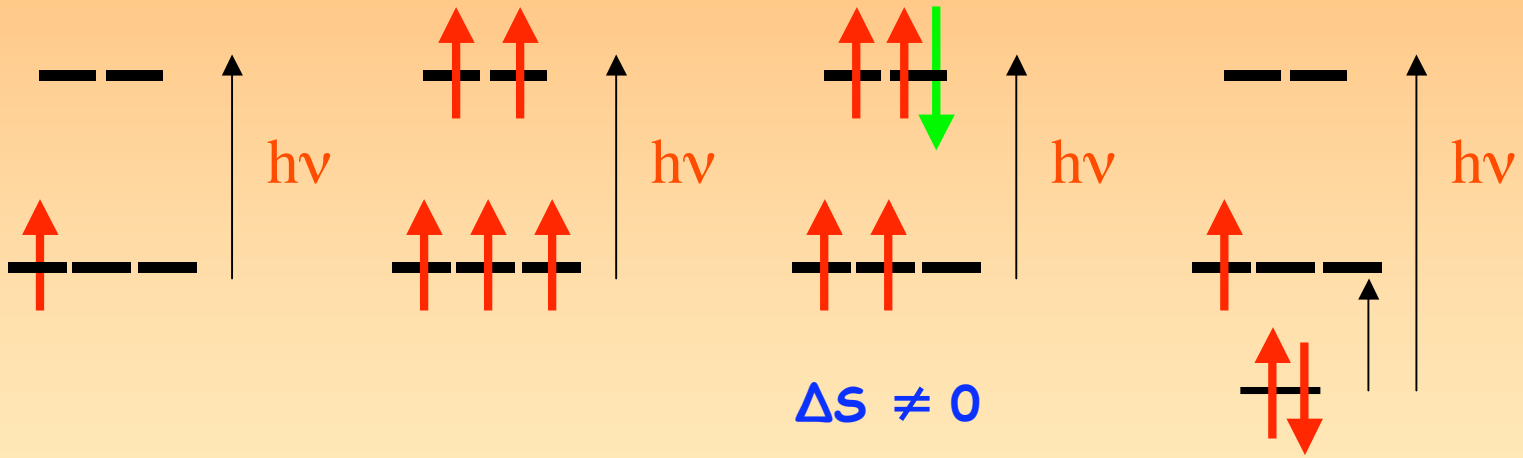
The complexes of transition metal present often delicate and beautiful colours depending mostly on the splitting of the d orbitals




quantum

macro

Complexes of transition metal ions
often display beautiful colours
essentially to d levels splitting




Colours in water
Geometrical Changes
Spin Changes

quantum

macro

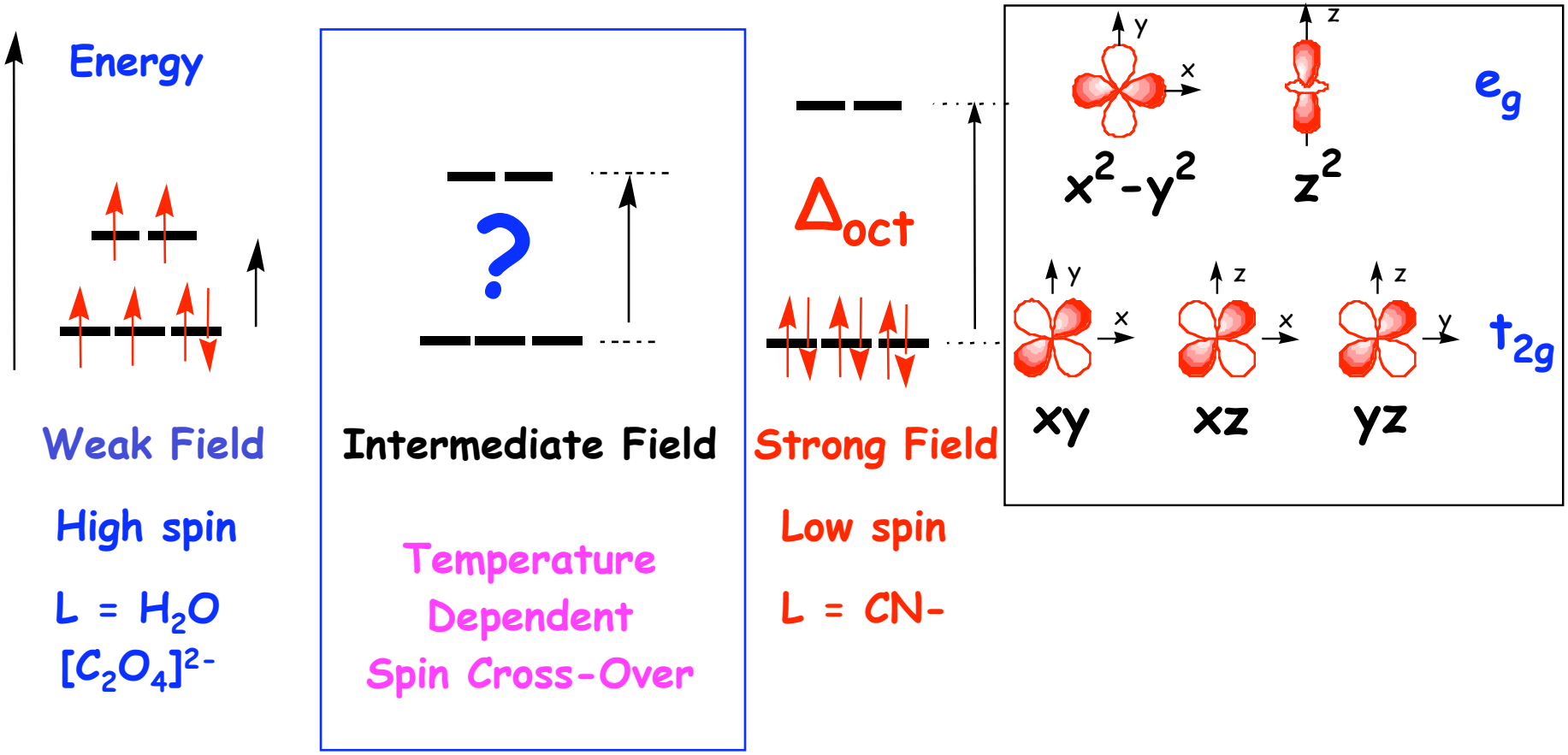
Electrons …

WANTED !

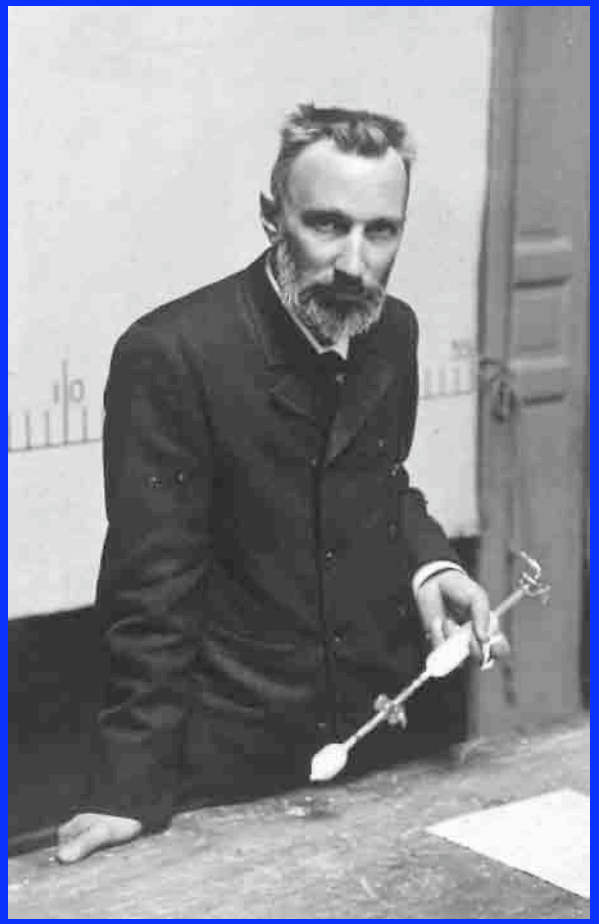
# A direct manifestation of the presence of unpaired electrons : the magnetism

or interaction with a magnetic field

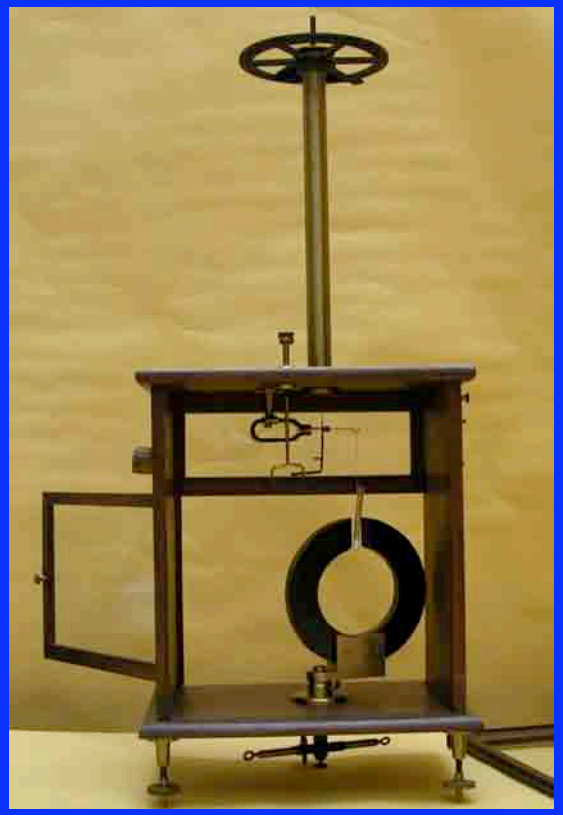
# How large is the splitting ?



# Curie Law

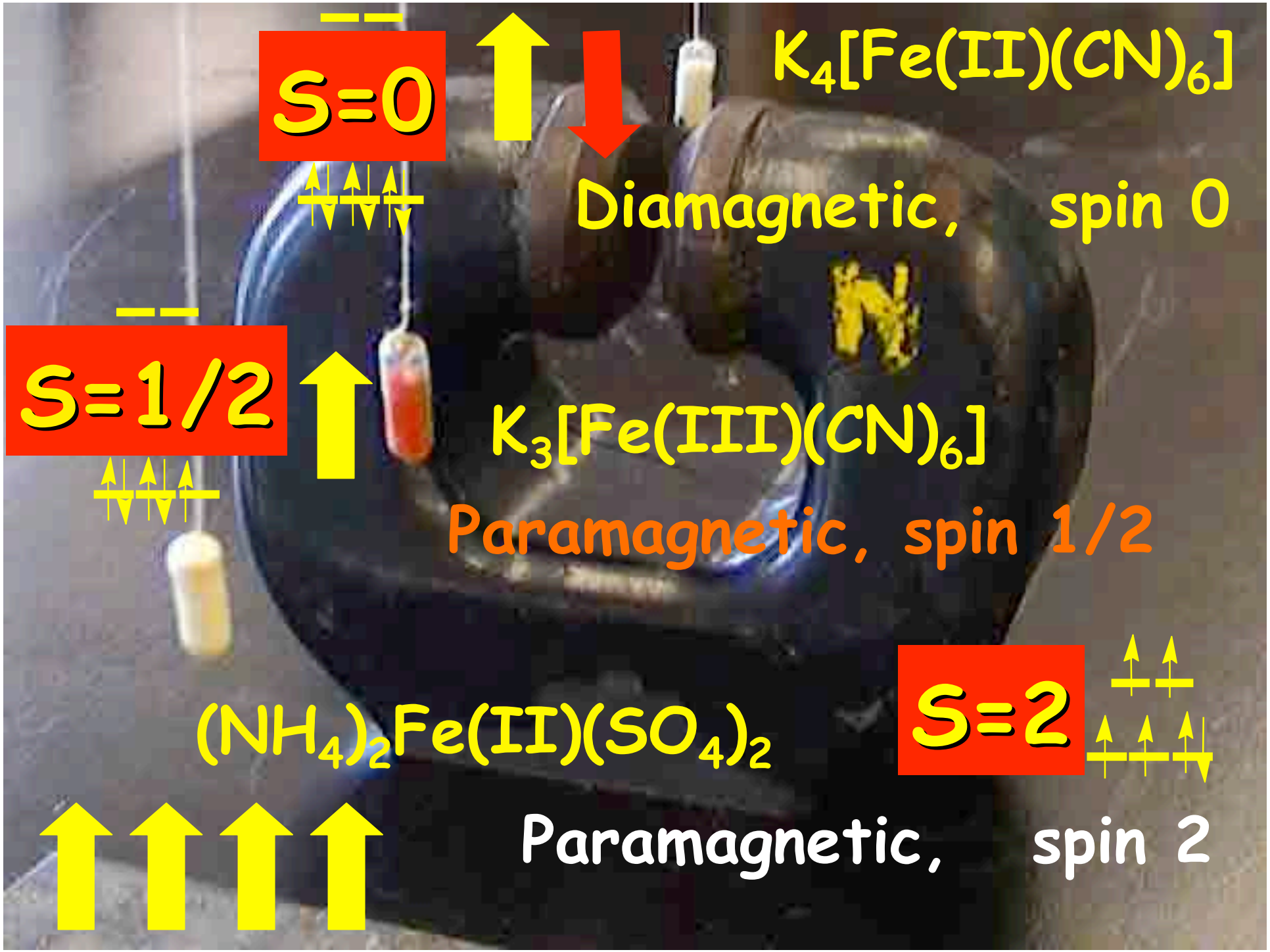


Pierre Curie, 1900 Paris

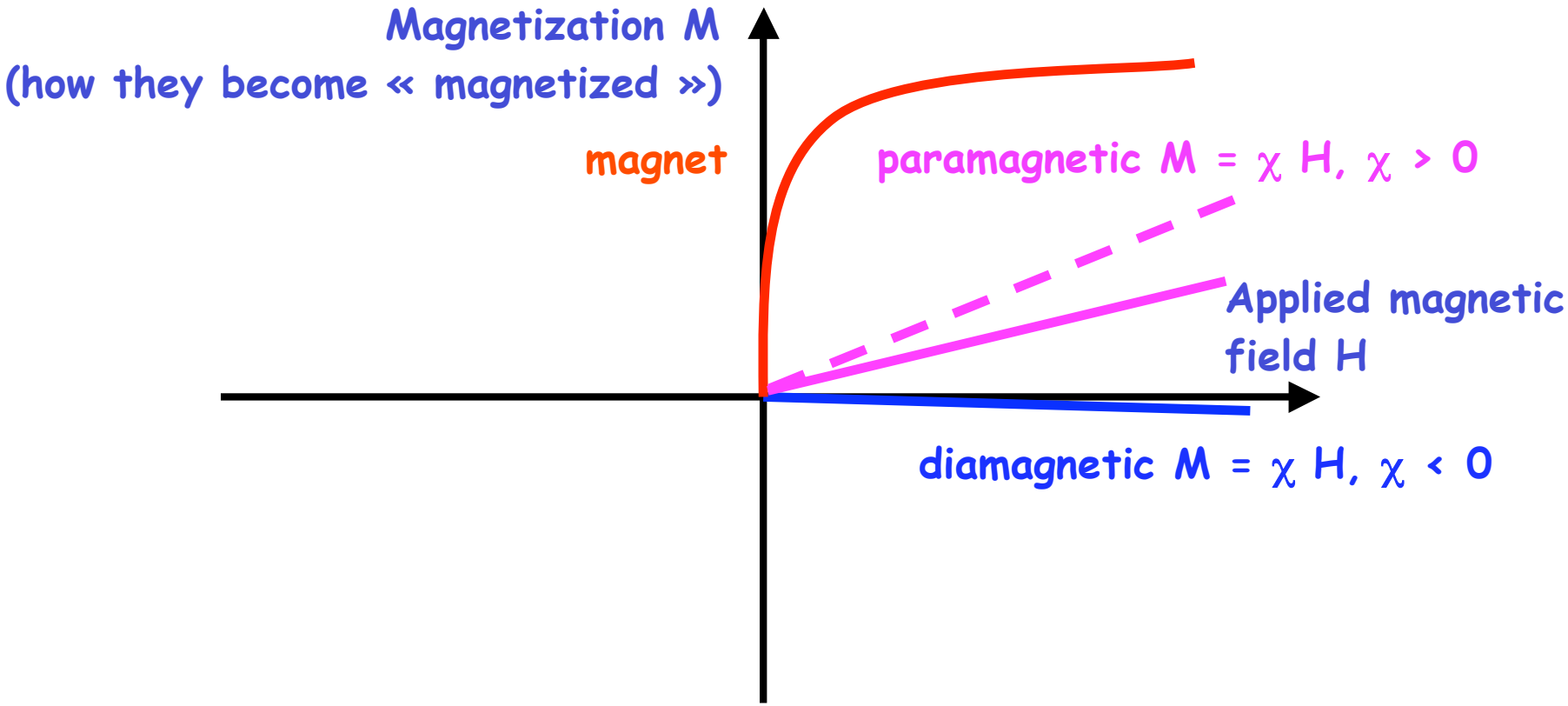


Curie Balance

$$\chi_M T = \text{Constant}$$


S=0
$K_4[Fe(II)(CN)_6]$
Diamagnetic, spin 0
S=1/2
$K_3[Fe(III)(CN)_6]$
Paramagnetic, spin 1/2
S=2
$(NH_4)_2Fe(II)(SO_4)_2$
Paramagnetic, spin 2

# Magnetization : how objects behave in a magnetic field ?

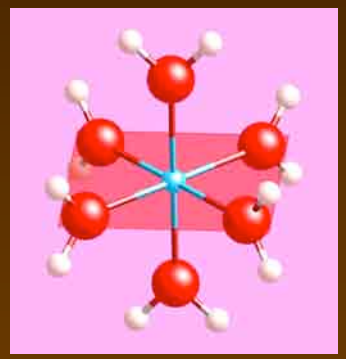



macro

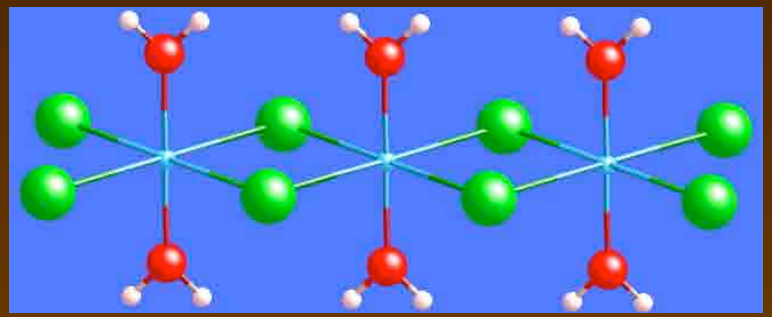
Playing with ligands,
the chemist is able
to control
the geometry
and symmetry
of complexes (colour, magnetism)

# $Co(II)Cl_2$, $6H_2O$ : from octahedral to tetrahedral

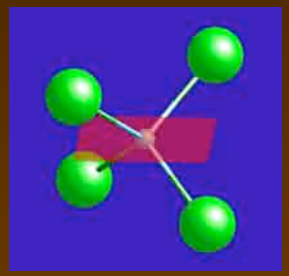
$Co^{2+}$



Heat



+ $Cl^-$



- $Cl^-$

+ $H_2O$

2 $Cl^-$

macro

quantum

Playing with ligands,
the chemist is able
to control
the spin state

Hysteresis

allows bistability of the system

and use in display, memories …

# Spin and colour changes

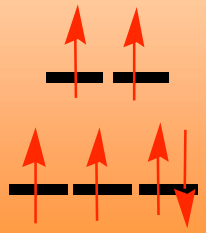
macro

$[Fe^{II}(H_2O)_6]^{2+}$
pale green

$Fe^{II}(o\text{-}phen)_3]^{2+}$
bright red

macro

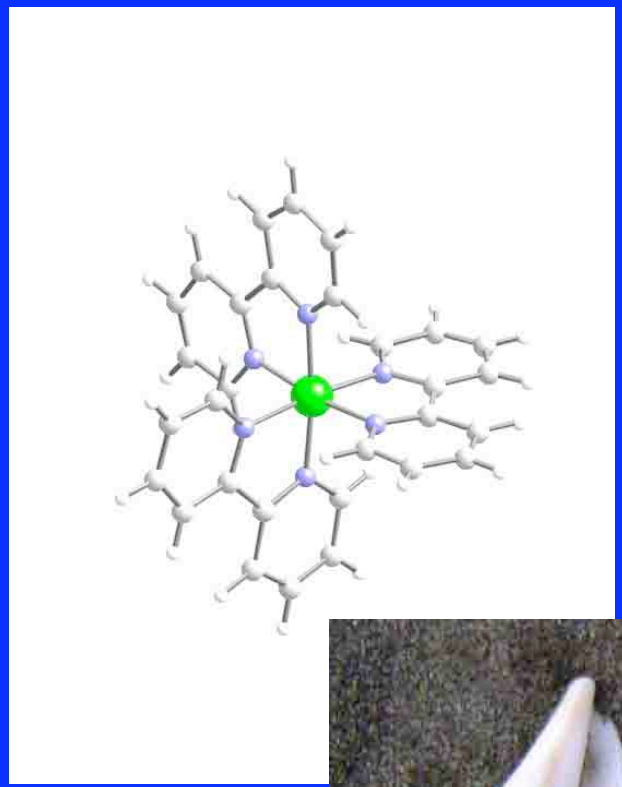
S=2

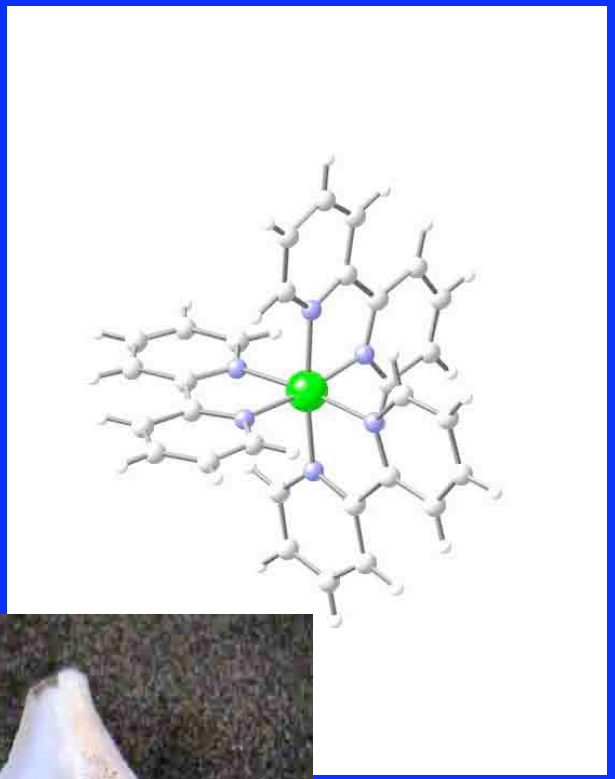


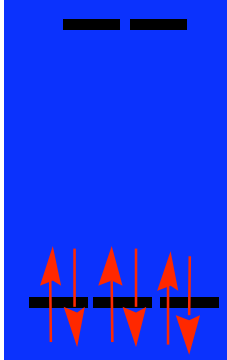
S=0

quantum

# Low spin, chiral, $Fe^{II}(bipyridine)_3]^{2+}$







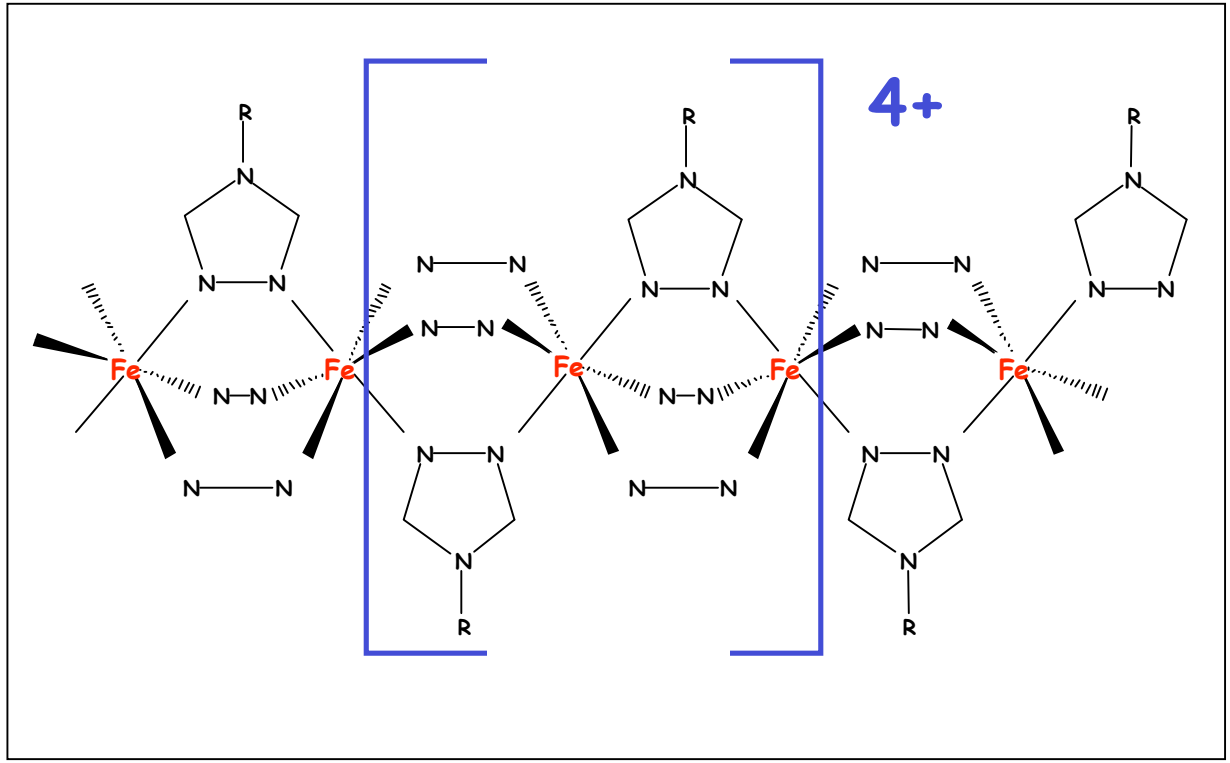
Λ

Δ

Playing with ligands,
the chemist is able
to control
the spin state

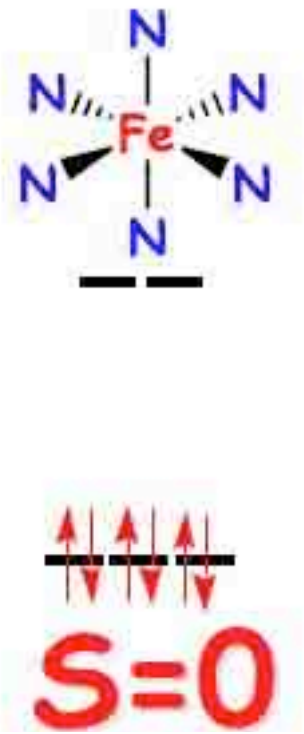
# Spin Cross-Over

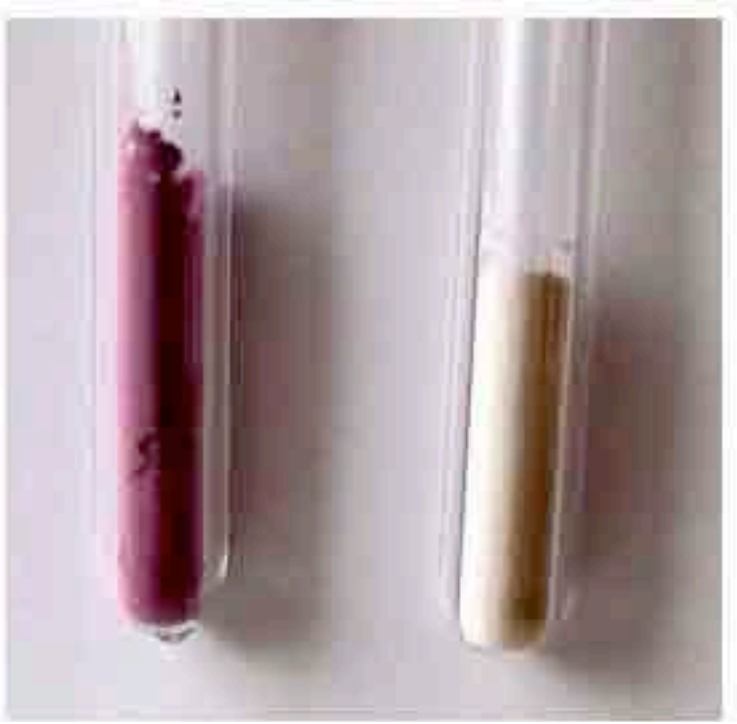
## A Fe(II) « Chain » with spin cross-over

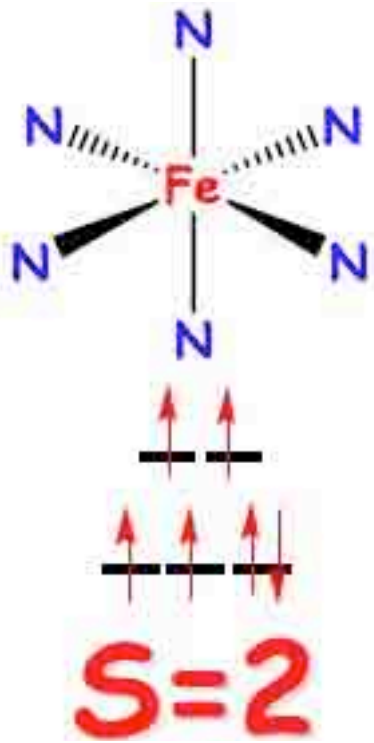



**Triazole substituted Ligand (R) ; insulated by counter-anions**

Many groups : Leiden, Mainz, Kojima, O. Kahn, C. Jay, Y. Garcia, ICMC Bordeaux





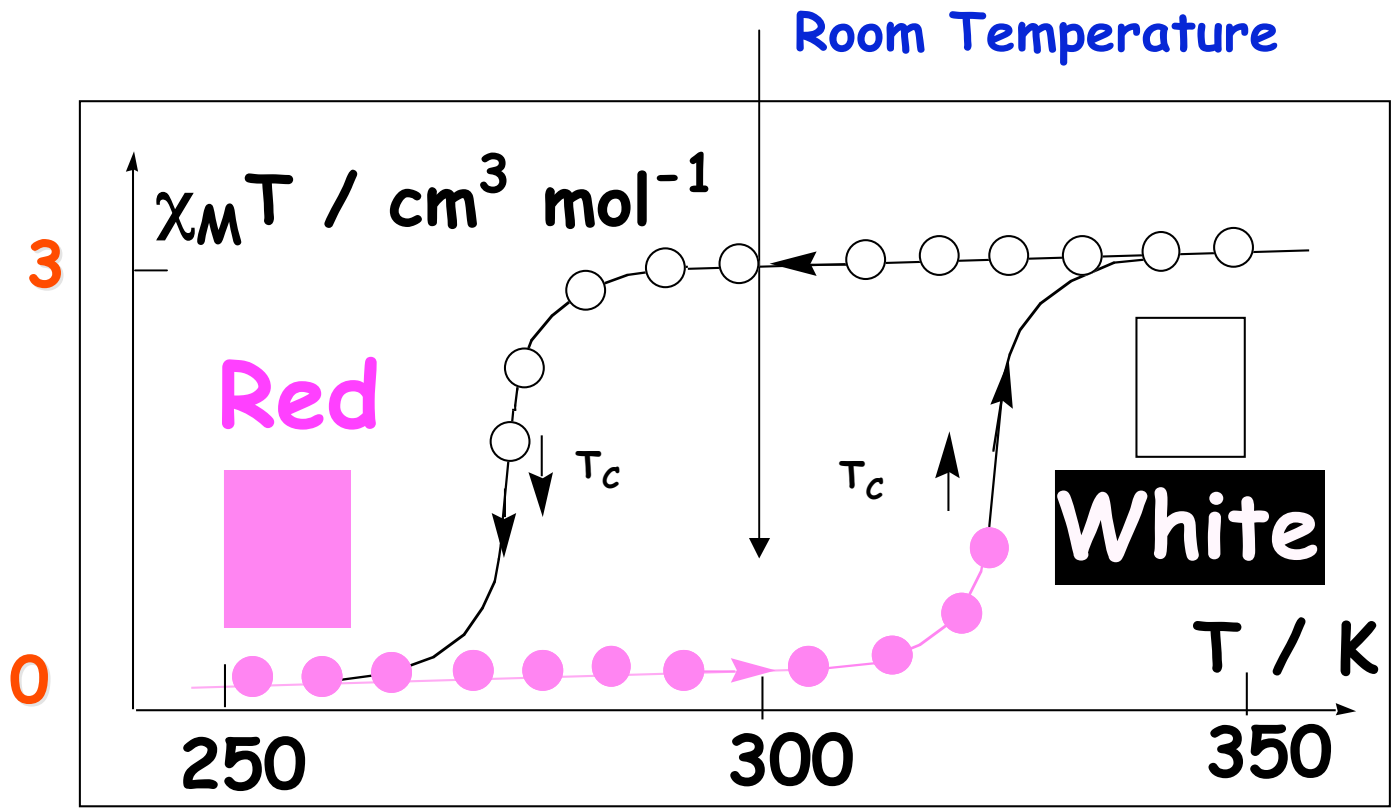

Sample coming from Low T

Sample coming from High T

Transition Cross-over Demonstrator by Jean-François Letard
The very samples presented were synthesized by students in Paris during practical works
Courtesy Prof. C. Roux, C. Train, A. Proust

# Spin Cross-Over

## Bistability Domain




The system « remembers » its thermal past !

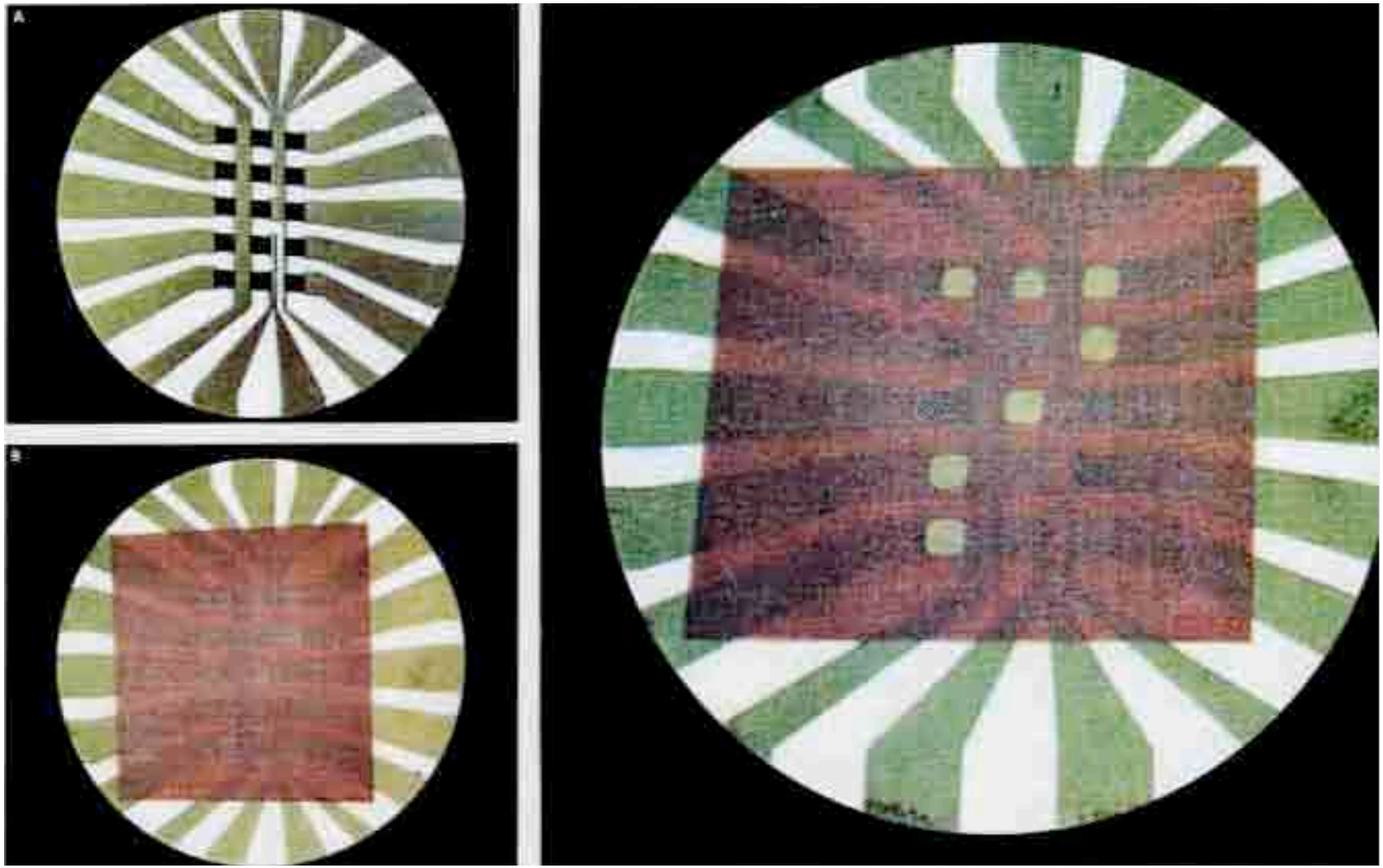
O. Kahn, C. Jay and ICMC Bordeaux

# Then, memory ?

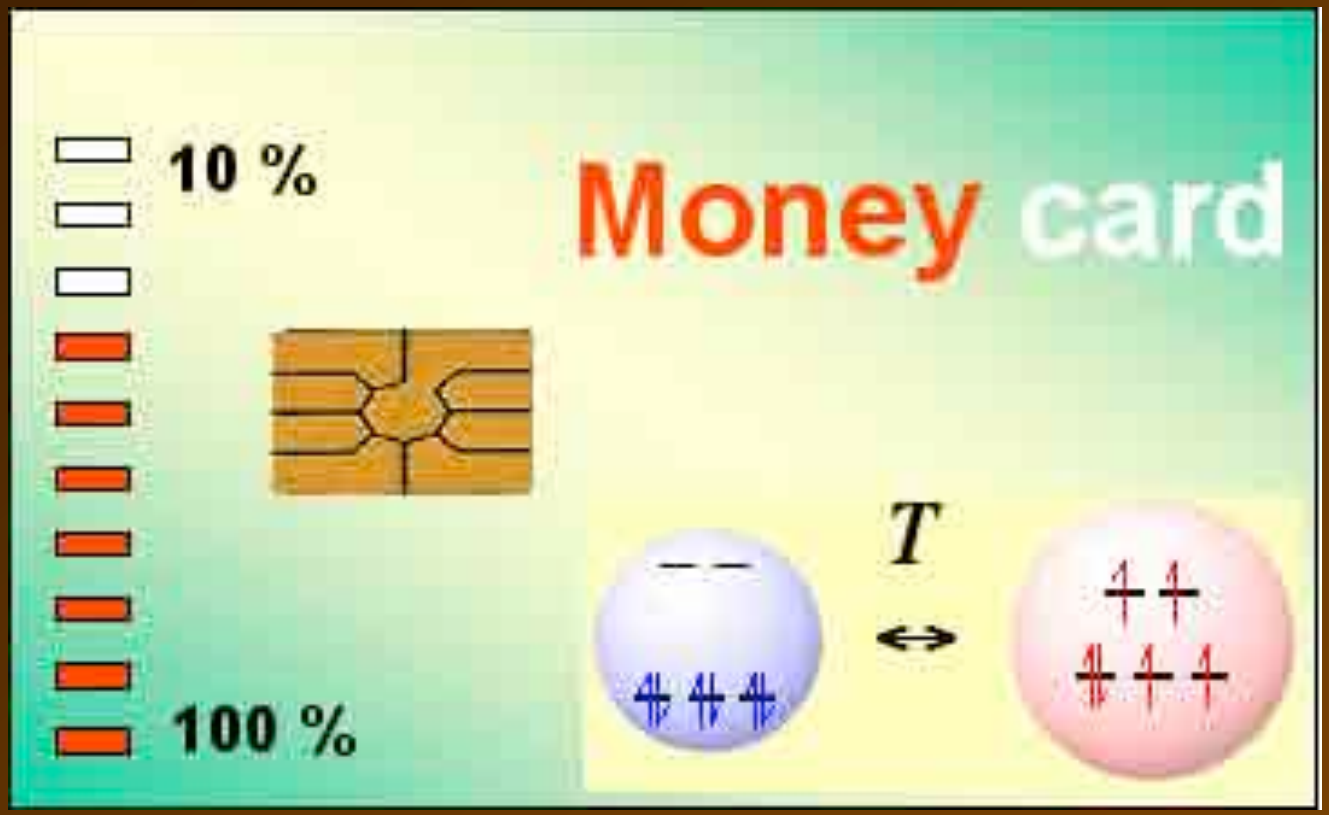
« It is an essential character of living being that the sensation leaves traces.
There is nothing comparable in material world
It is a real joke to name « memory » the hysteresis phenomenon. » …

Paul Langevin, Discussion sur la matière vivante,
10ème semaine internationale de synthèse, 1938, PUF, 1943, 219-223

# From the molecule to the material and to the device …



O. Kahn, C. Jay and ICMC Bordeaux




O. Kahn, Y. Garcia, Patent

May we go further

and dream of *molecular magnets*

i.e. low density,

biocompatible

transparent

or colourful magnets ?

Do the chemists
know how
to align the spins
of electrons
in molecules,
parallel or antiparallel ?

to get magnetic compounds …

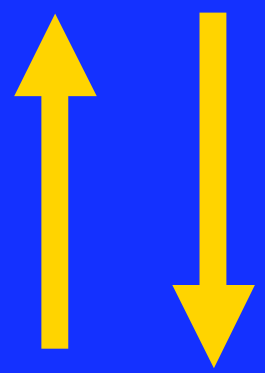
# Understanding …

why the spins of two neighbouring electrons (S = 1/2) become :

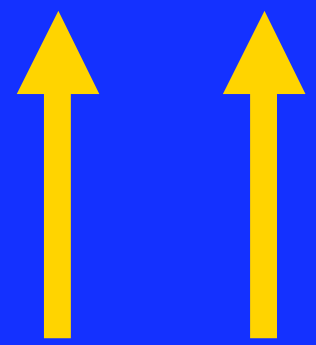
antiparallel ?

or parallel ?

S=0



Singlet



Triplet

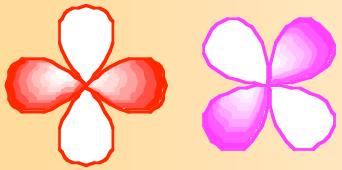
S=1

$$J = 2k + \cancel{4\beta S}$$

$>0$ $\quad$ $<0$

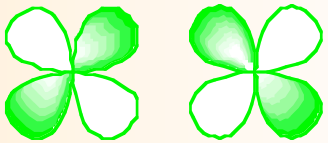
if $S = 0$

Orthogonality



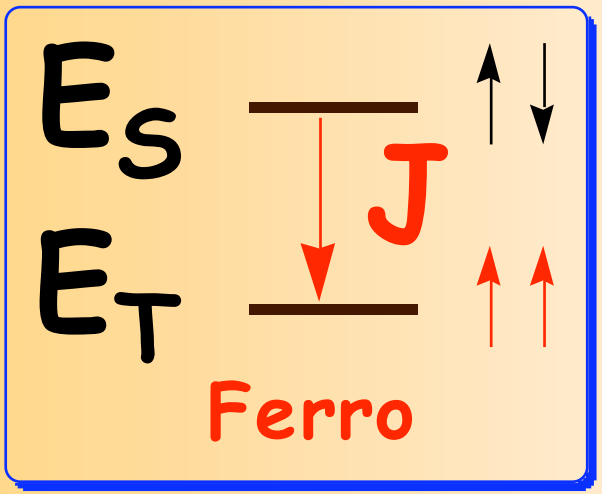
if $S \neq 0; |\beta S| >> k$

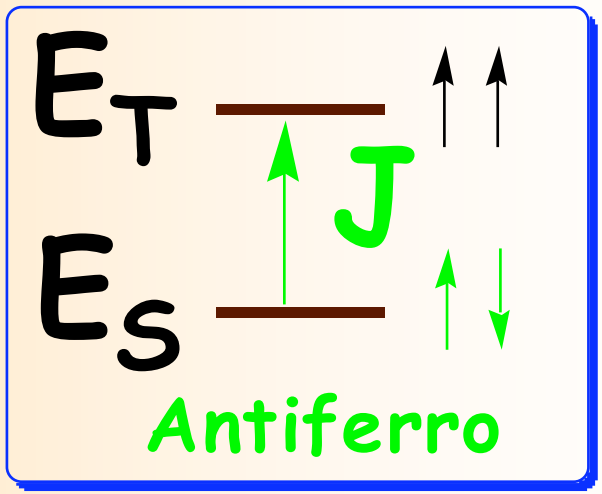
Overlap



$O_2$

Hund




$H_2$

Aufbau

# Tell it with flowers

(find the orbital)

isolated

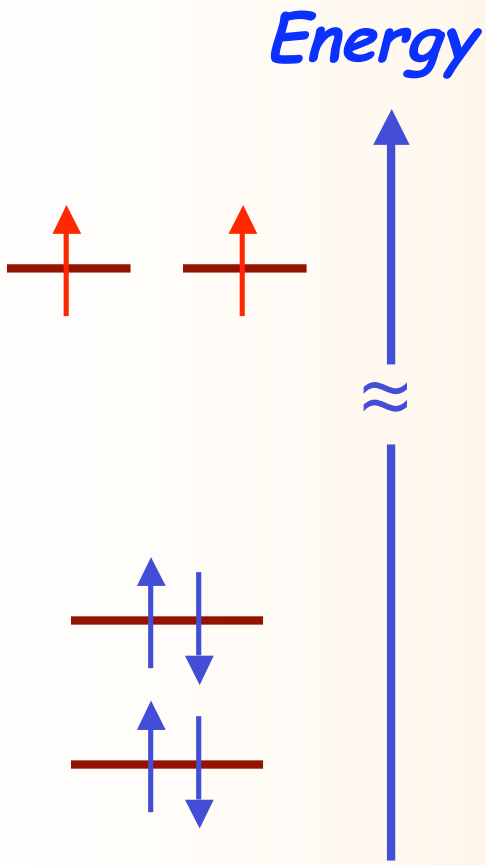
Overlap ($\sigma$)

Overlap ($\pi$)

Orthogonality

Flowers from the garden
of the Gulbenkian's Foundation
Lisbon

# Exchange interactions can be very weak …




**Exchange interactions**

*order of magnitude :*
*$cm^{-1}$ or Kelvins …*

**« Chemical » bonds**
**Robust !**

*order of magnitude :*
*>> 150 kJ $mol^{-1}$ …*

Michelangelo, Sixtin Chapel, Rome

Please, avoid pairing electrons into bonds …

## Avoid …

# $NO_2$ Dimerisation

… to pair
the « magnetic »
électrons

macro

# Interpretation(s)

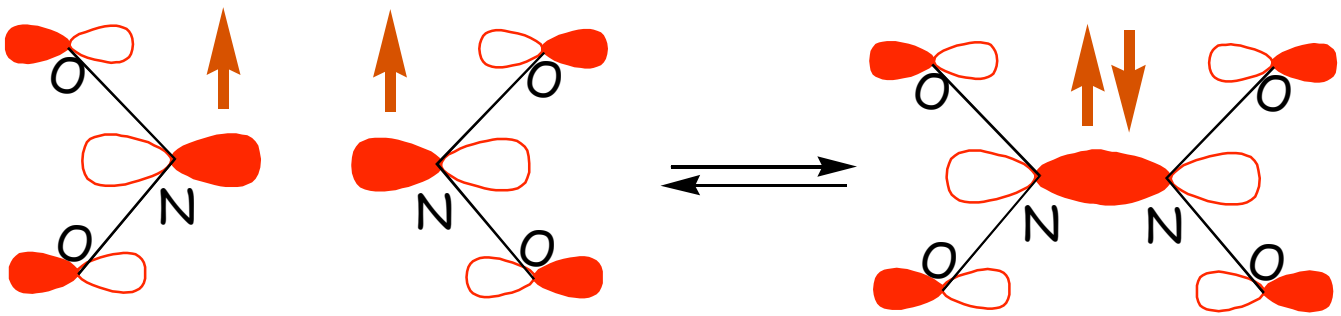
## Thermodynamics (Le Chatelier ...)

*Equilibrium* : $2\ NO_2 \underset{2}{\overset{1}{\rightleftharpoons}} N_2O_4$ + Heat

Brown

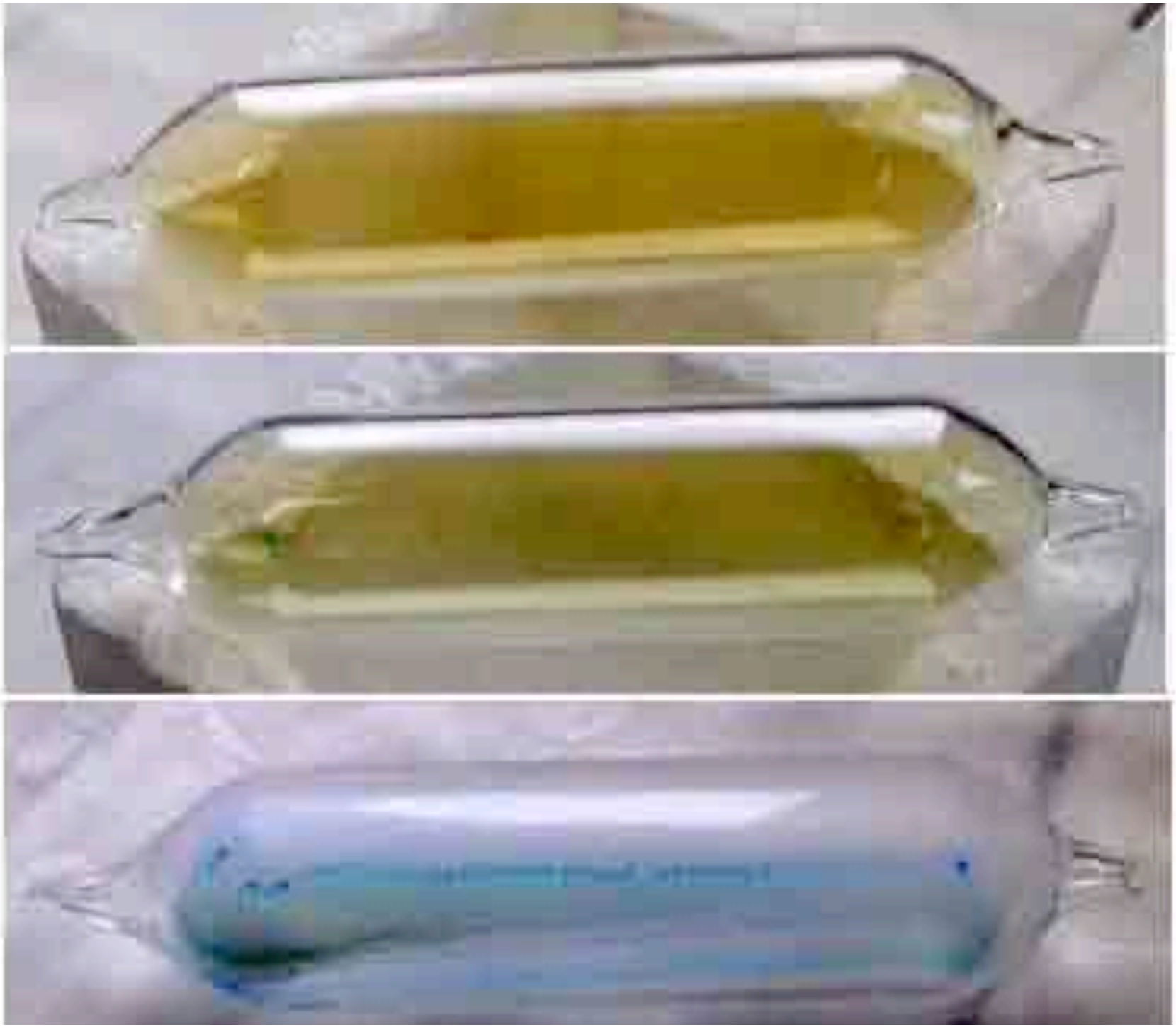
colorless

## Orbital




Pairing of electrons, bonding

DIA-magnetic !

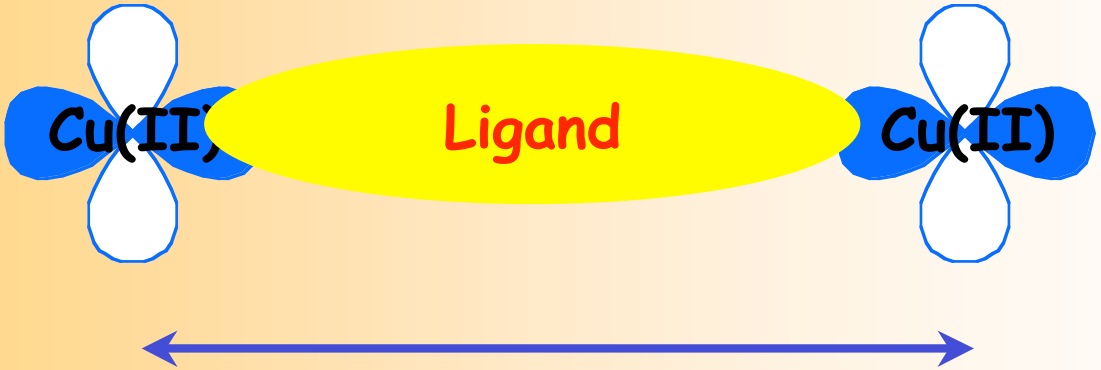


# A beautiful artefact

When some residual NO is present in the vessel :

*Reaction :* $NO_2 + NO \underset{2}{\overset{1}{\rightleftharpoons}} N_2O_3$

Brown colorless Blue green




≈ 5 Å

Orbital Interaction …

# Which ligand ? Why not …

- Cyanide, $CN^-$ ?

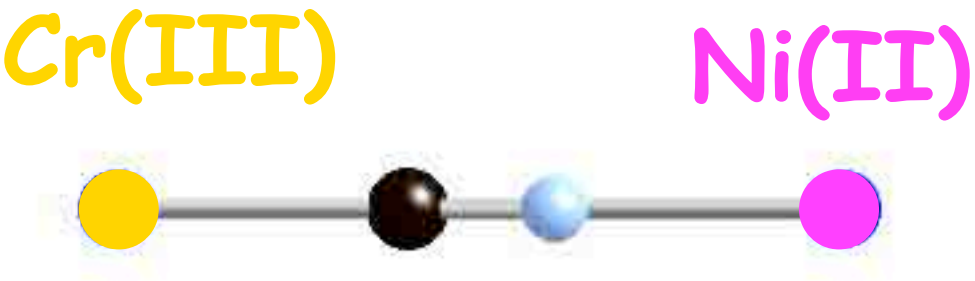
Museo nacional dos azulejos, Lisboa

$C{\equiv}N^-$

# Cyanide Ligand

Friendly ligand : small, dissymetric, forms stable complexes

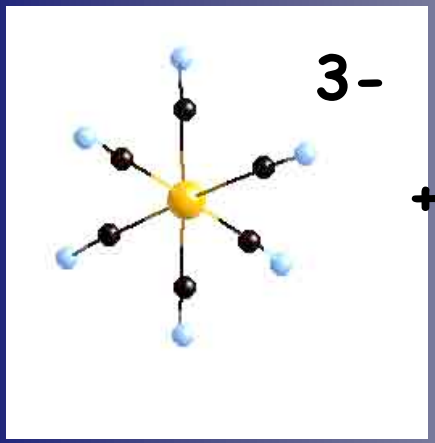
Warning : dangerous, in acid medium gives HCN, lethal



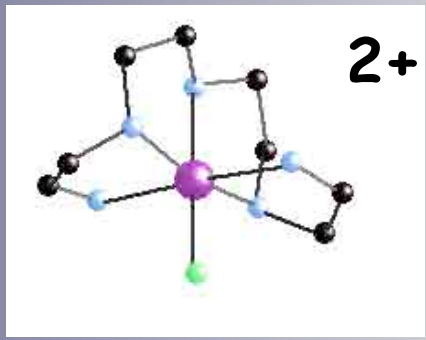

# Dinuclear μ-cyano heterometallic complexes

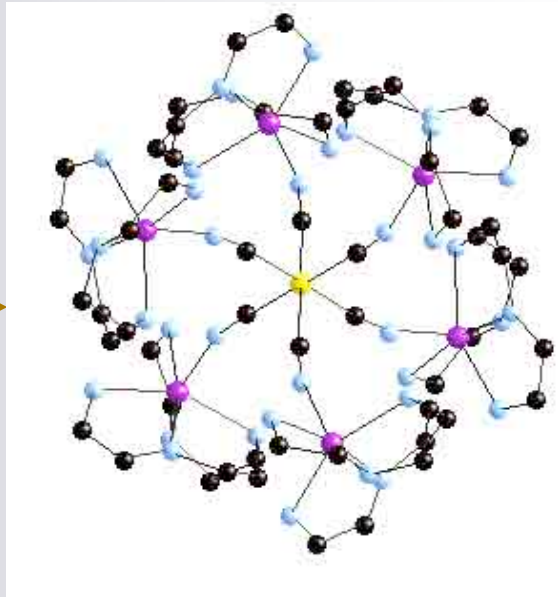
NB : A dissymetric ligand helps to get stable heterometallic complexes …
« Birds of the same feathers flock together » …

# Polynuclear complex, synthetic strategy




+ 6



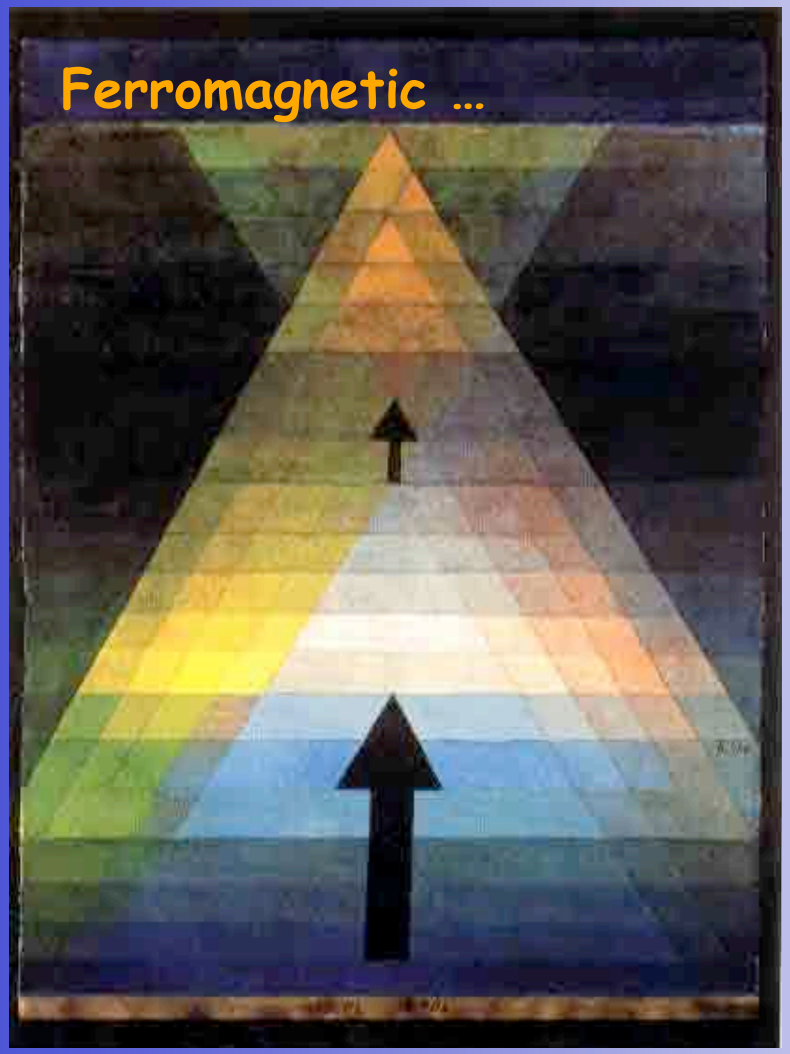

Hexacyanometalate "Heart"
Lewis Base

Mononuclear Complex
Lewis Acid

Polynuclear Complex

macro

macro

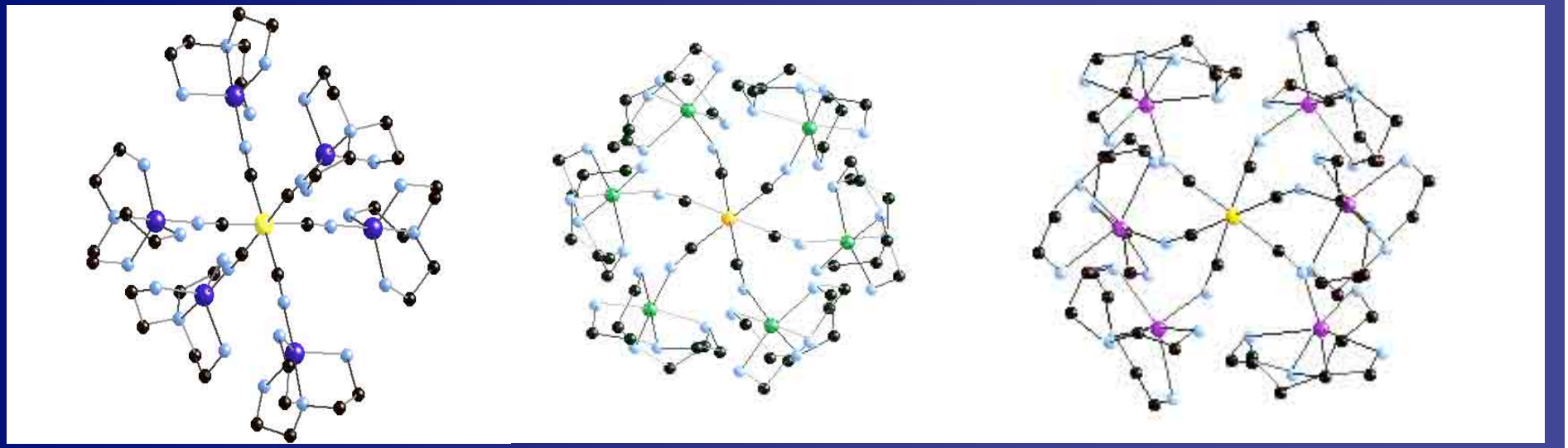



Eros


Nocturnal separation, 1922

Paul KLEE

# … High Spin Heptanuclear Complexes



**CrCu6**

**S = 9/2**

Hexagonal R -3
a = b = 15,27 Å; c = 78,56 Å
a = b= 90°; g = 120°; V = 4831 Å$^3$

**CrNi6**

**S = 15/2**

Hexagonal R -3
a = b = 15,27 Å; c = 41,54 Å
a = b= 90°; g = 120°; V = 8392 Å$^3$

**CrMn6**

**S = 27/2**

Hexagonal R -3
a = b = 23,32 Å; c = 40,51 Å
a = b= 90°; g = 120°; V = 19020 Å$^3$

Marvaud et al., Chemistry, 2003, *9*, 1677 and 1692

electrons …

WANTED !

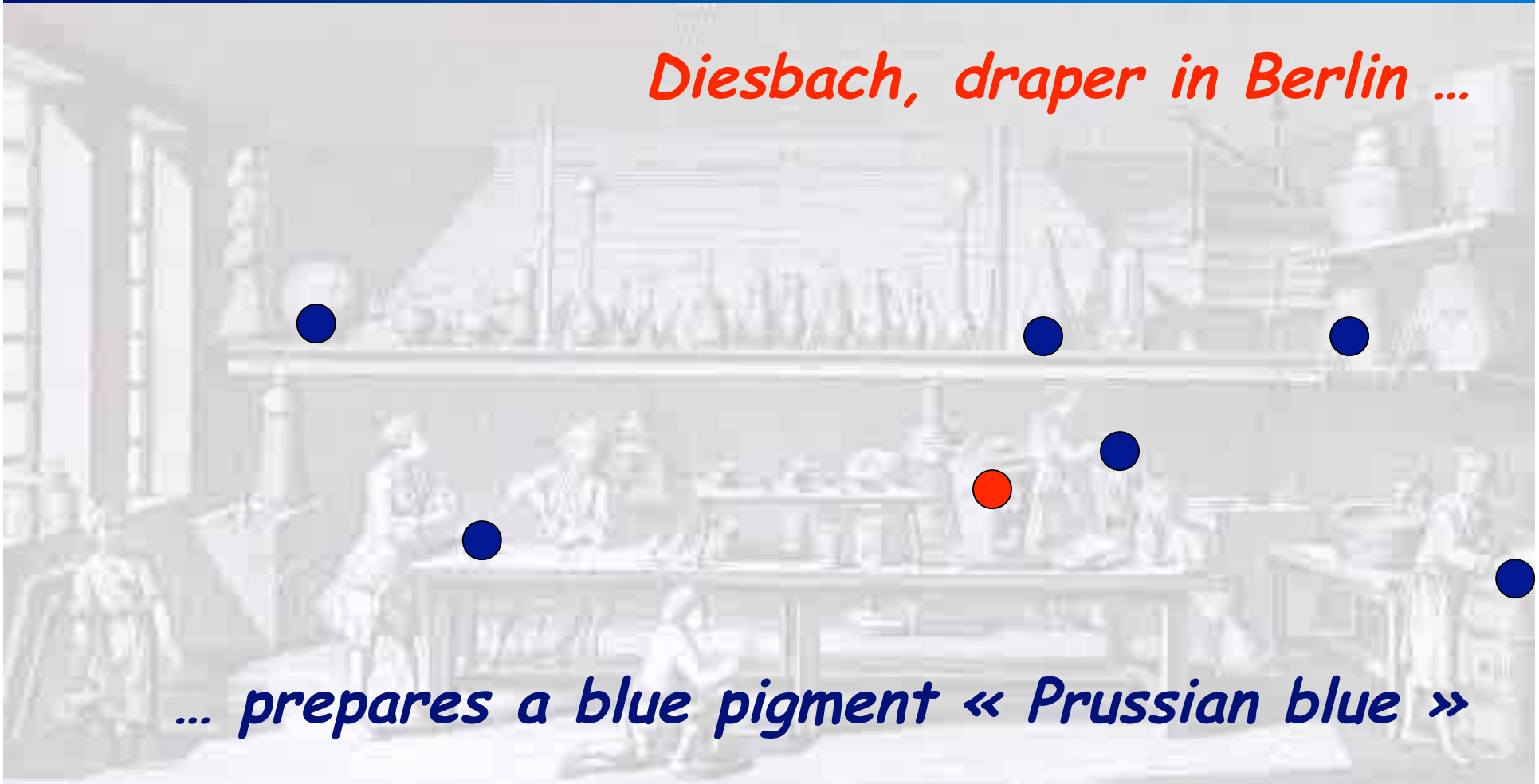
# How to manipulate electrons *between* molecules ?

## Towards magnets

The saga of high $T_c$ Prussian Blues Analogues

# 1704 … 2004 : 300th anniversary !

Diesbach, draper in Berlin …

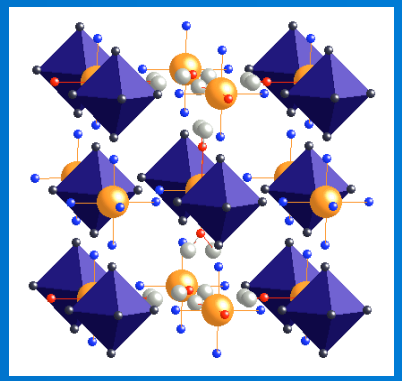


… prepares a blue pigment « Prussian blue »

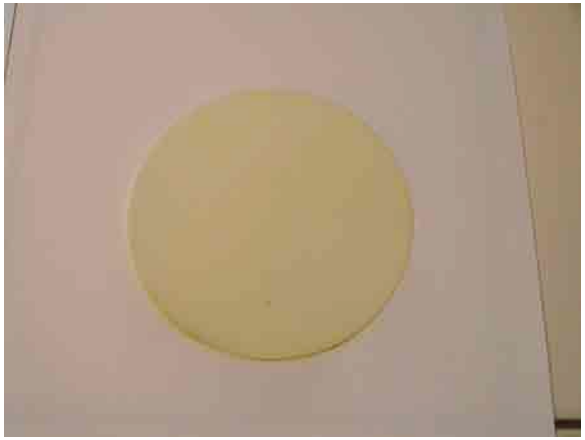
… said to be the first coordination compound

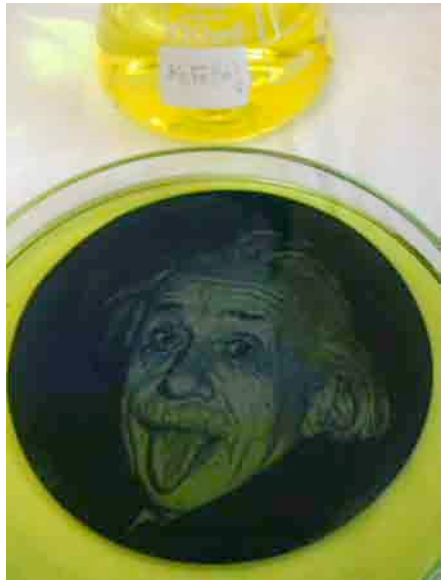
# *Classical Coordination Chemistry…*

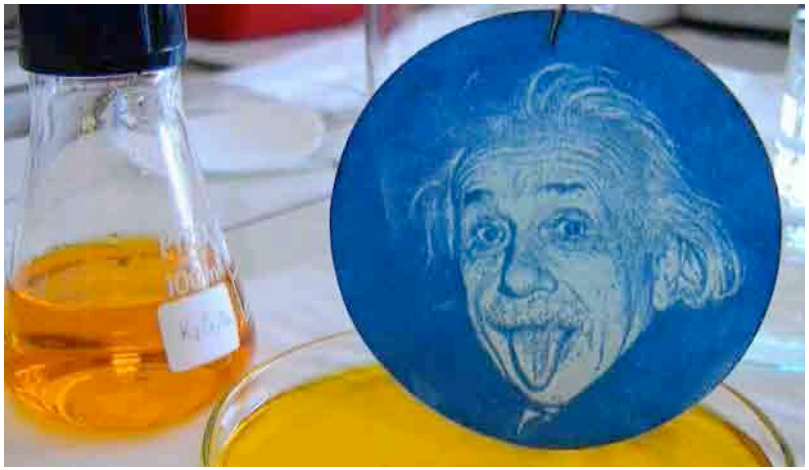
$$3[Fe(CN)_6]^{4-}{}_{aq} + 4Fe^{3+}{}_{aq} \longrightarrow \{Fe_4[Fe(CN)_6]_3\}^0 \cdot 15H_2O$$

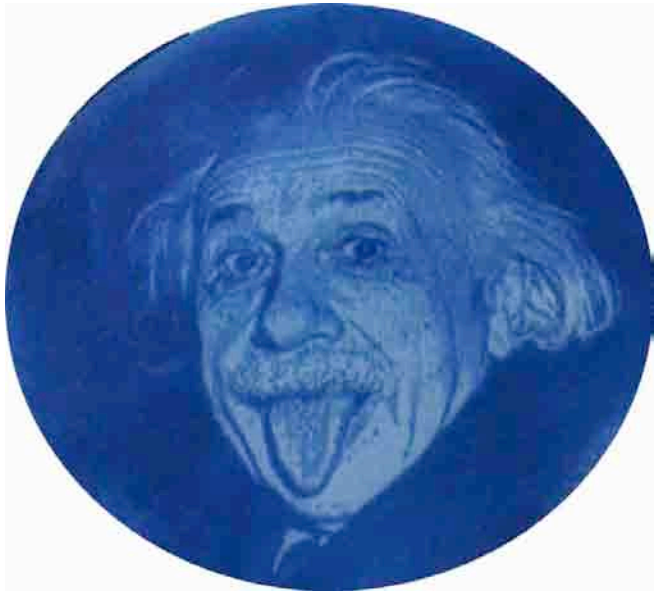


# Cyanotypes









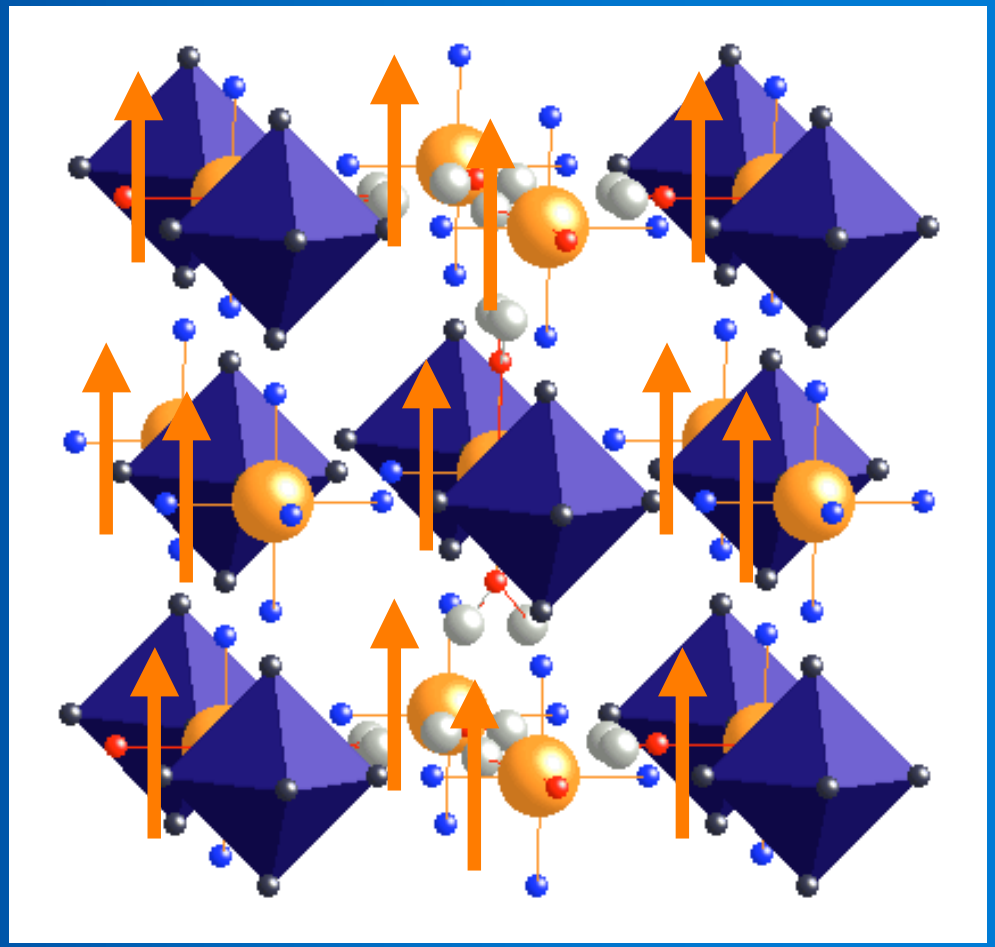
Einstein a portrait, Cyanotypes by F. Villain, CIM2, UPMC

# Magnetic Properties of Prussian Blue

$$T_c \propto z\,|J|$$

z : number of magnetic neighbours
|J| : coupling constant between nearest neighbours

$$T_c = 5.6\ K$$



Néel, 1948

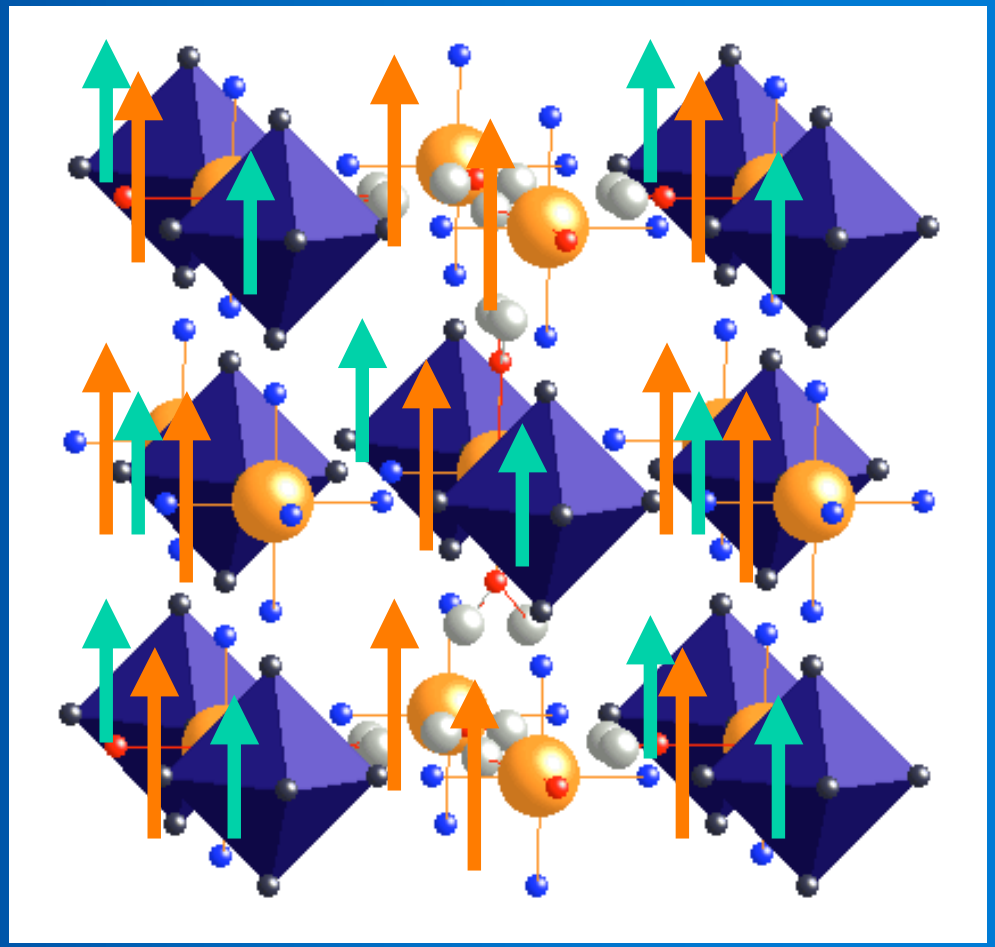
# Ferromagnetic Prussian blue analogues …

$T_c \propto z\,|J|$

$J_{Ferro} > 0$

Orthogonality

$T_c >> 5.6$ K



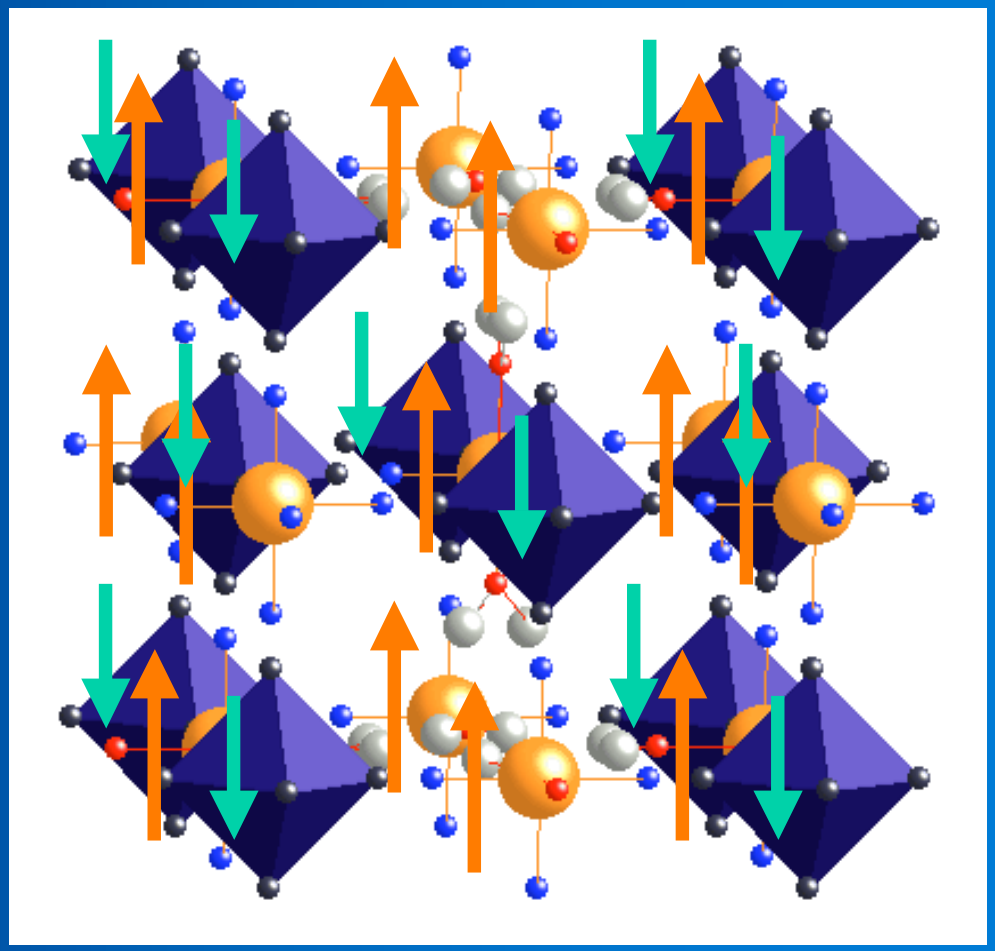
# Ferrimagnetic Prussian blue analogues ...

$T_C \propto z\,|J|$

$J_{Antiferro} < 0$

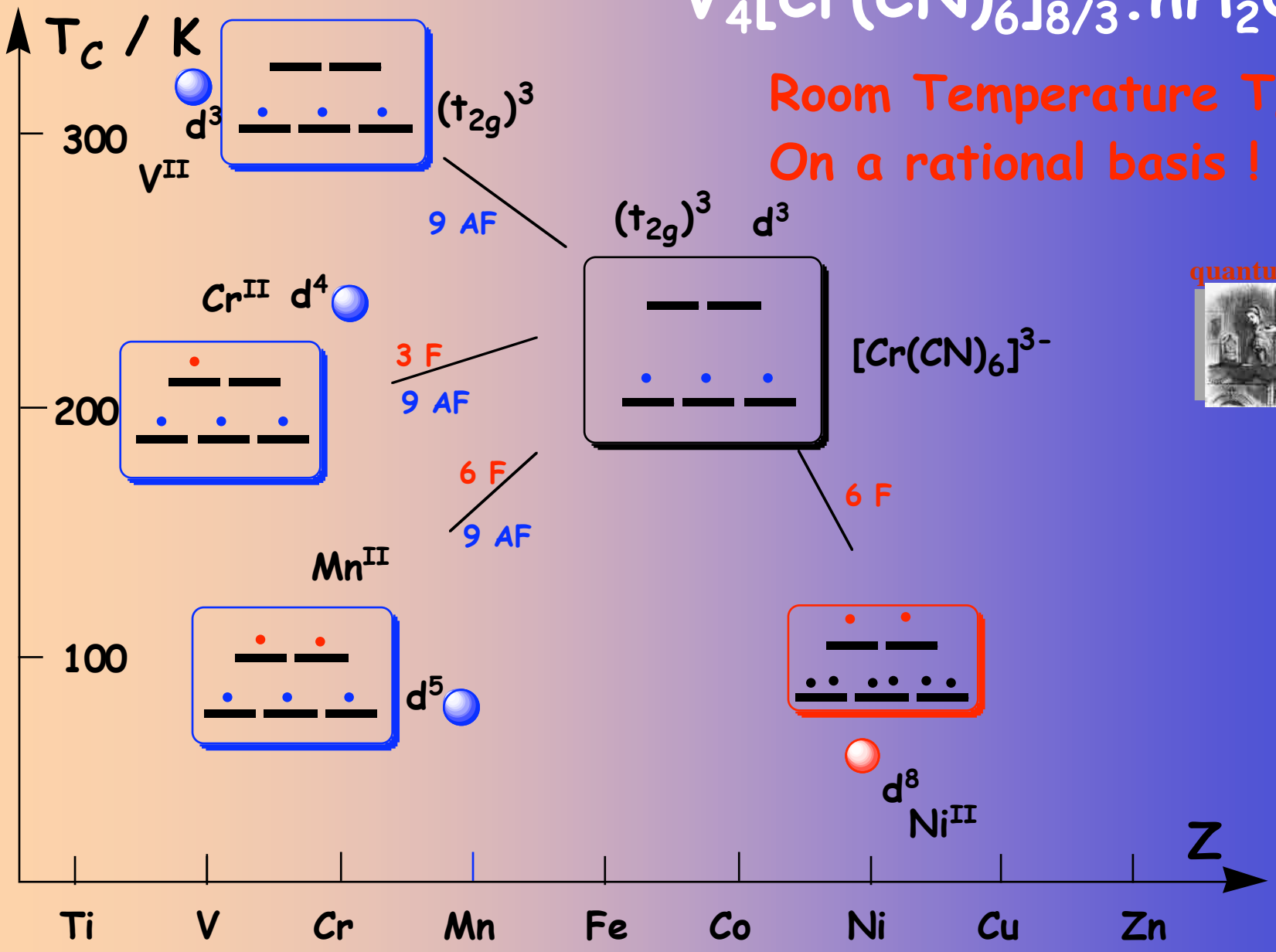
Overlap ...

$T_C >> 5.6$ K



# $V_4[Cr(CN)_6]_{8/3}.nH_2O$

**Room Temperature $T_c$**
**On a rational basis !**





Ferlay et al. *Nature*, 1995 Mallah et al. Science 1993 Gadet et al., J.Am. Chem. Soc. 1992

$$2[Cr^{III}(CN)_6]^{3-} + 3V_{aq}^{2+} \longrightarrow [V_3[Cr^{III}(CN_6)]_2]^0$$

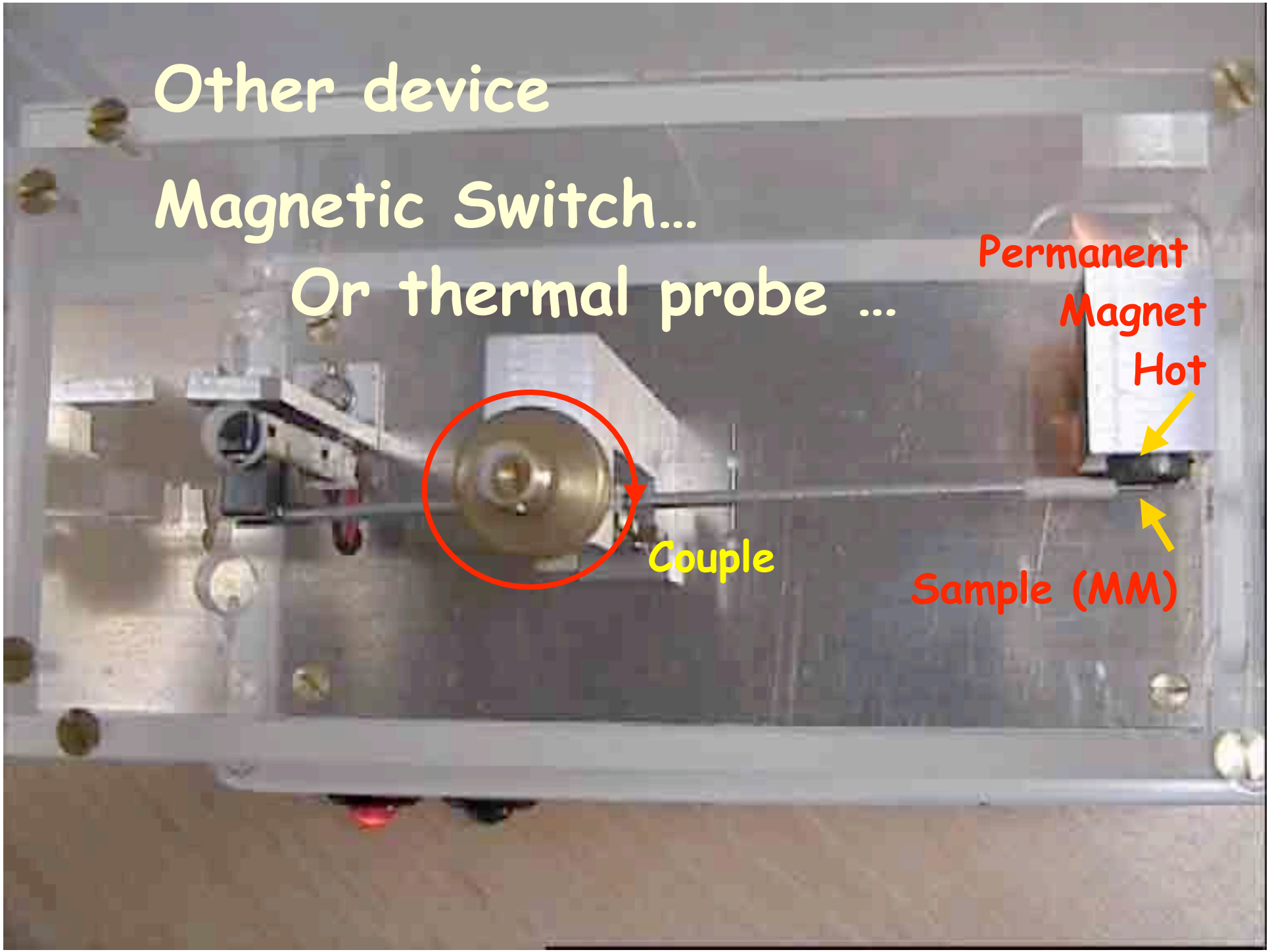
macro

A blue, transparent, low density magnet at room temperature

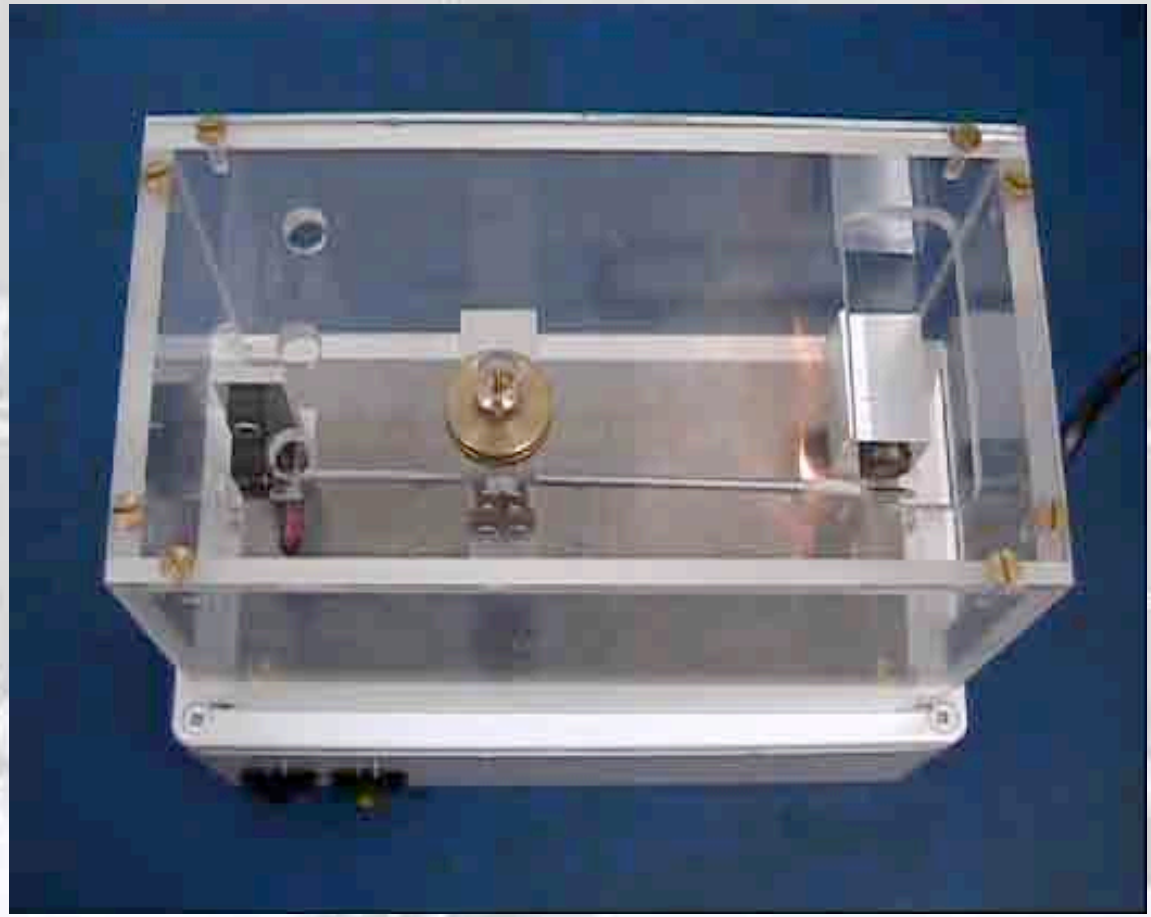
# Devices

Based on Room temperature Magnets

Prussian blue analogues


Other device
Magnetic Switch…
Or thermal probe …
Permanent
Magnet
Hot
Couple
Sample (MM)

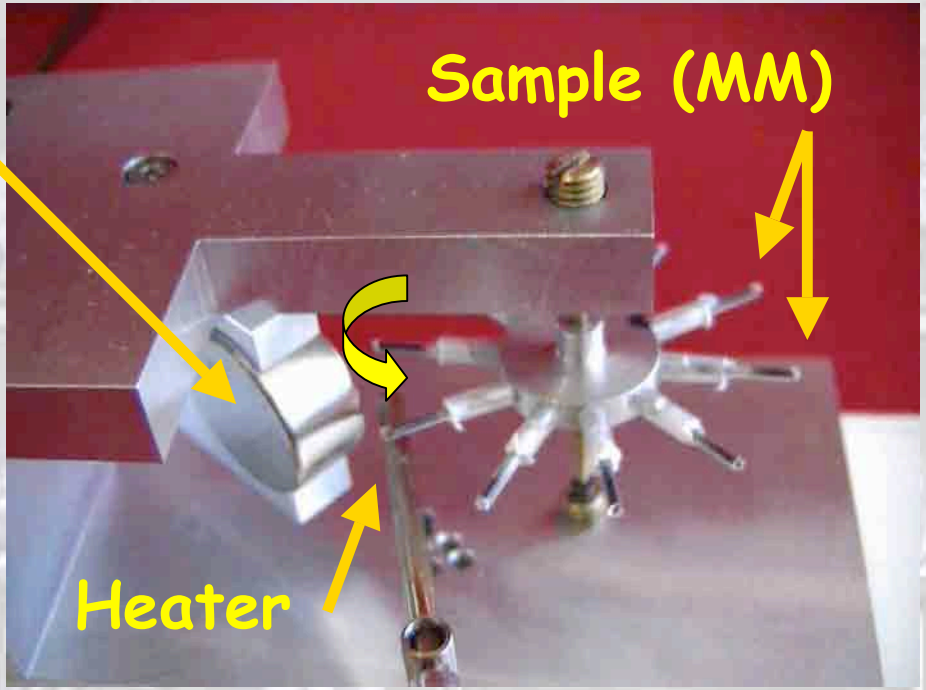
# Up to 2004 … magnetic analogues used as …



macro

… devices and demonstrators

# … another demonstrator

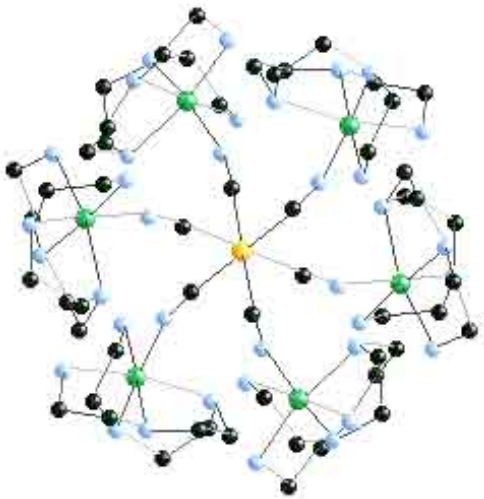


# … another demonstrator

Chemists have managed
to *transform*
isolated *single molecules*
*into magnets*

# Single Molecule Magnets

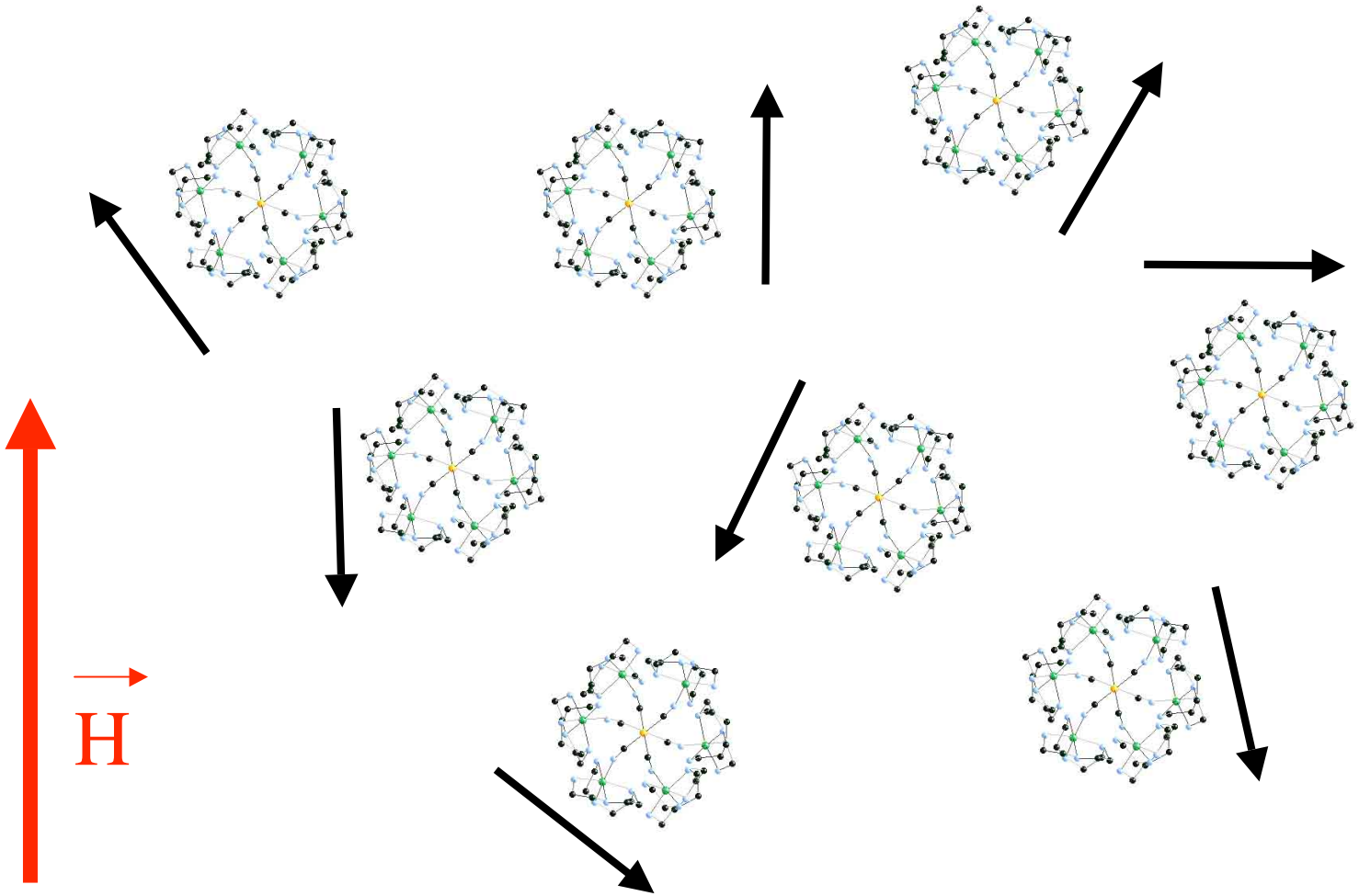
# What is named Single Molecule Magnet ?



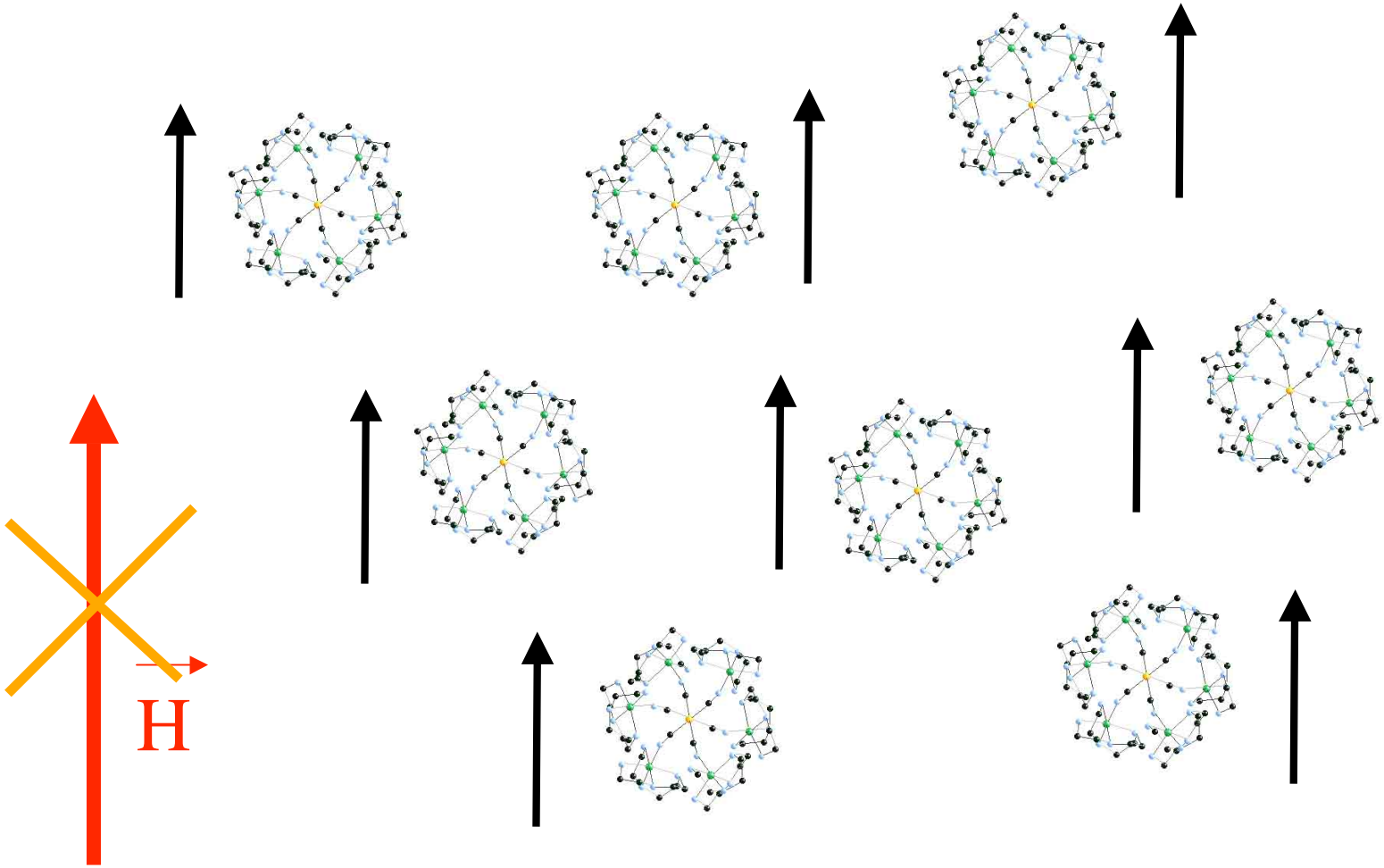
=

High Spin
Anisotropic

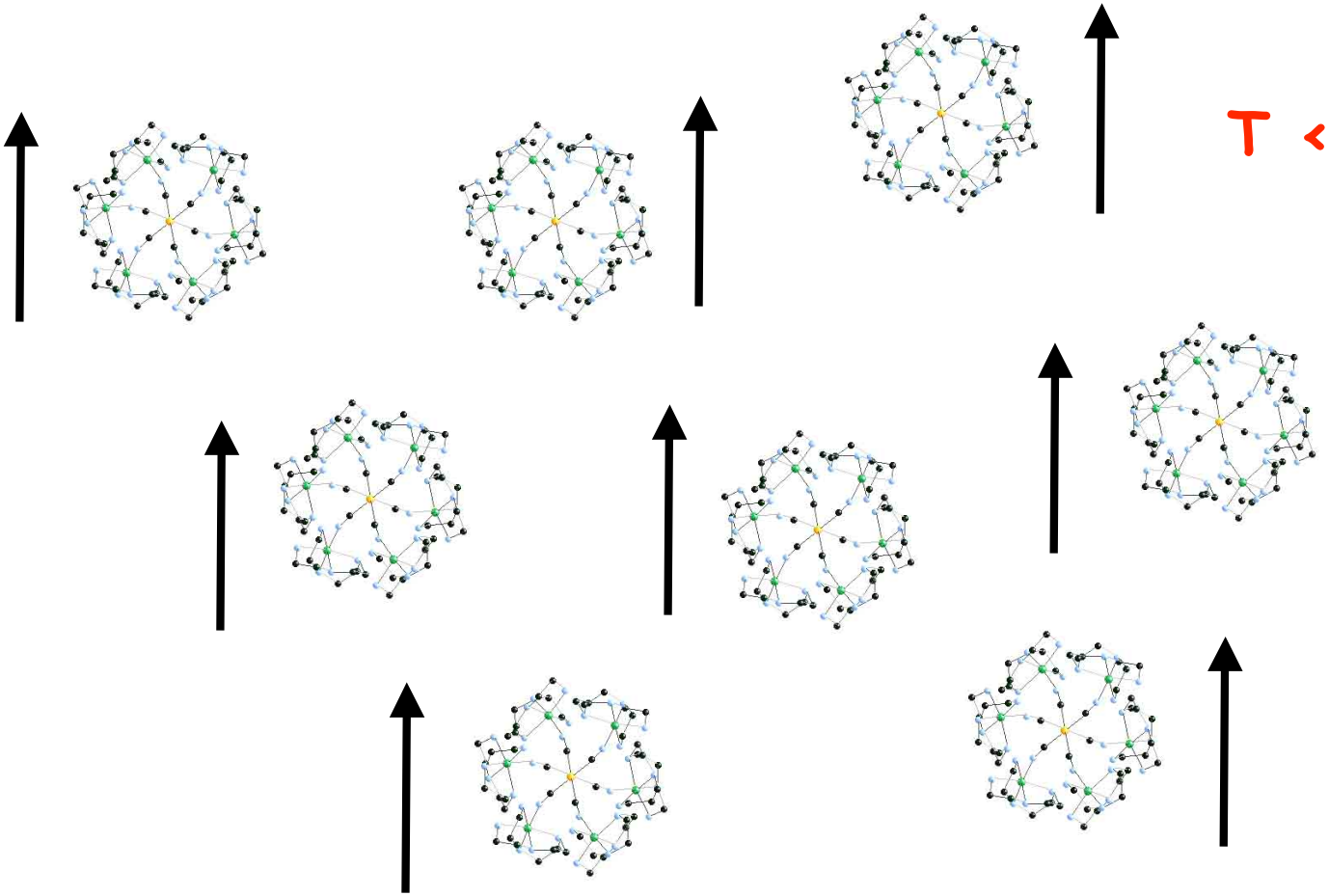
# High Spin Paramagnetic Molecule



# Single Molecule Magnet



# Single Molecule Magnet

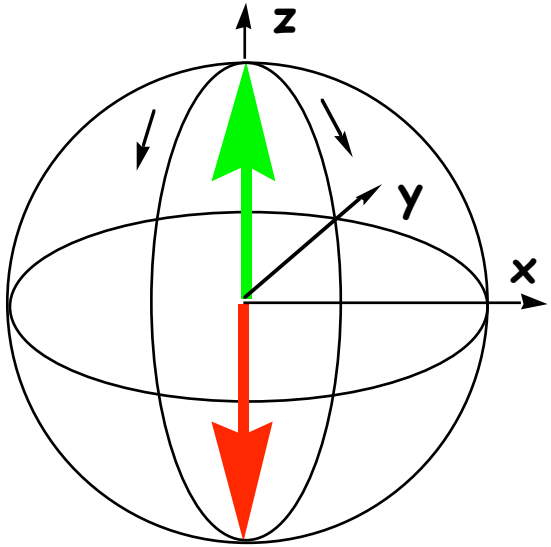


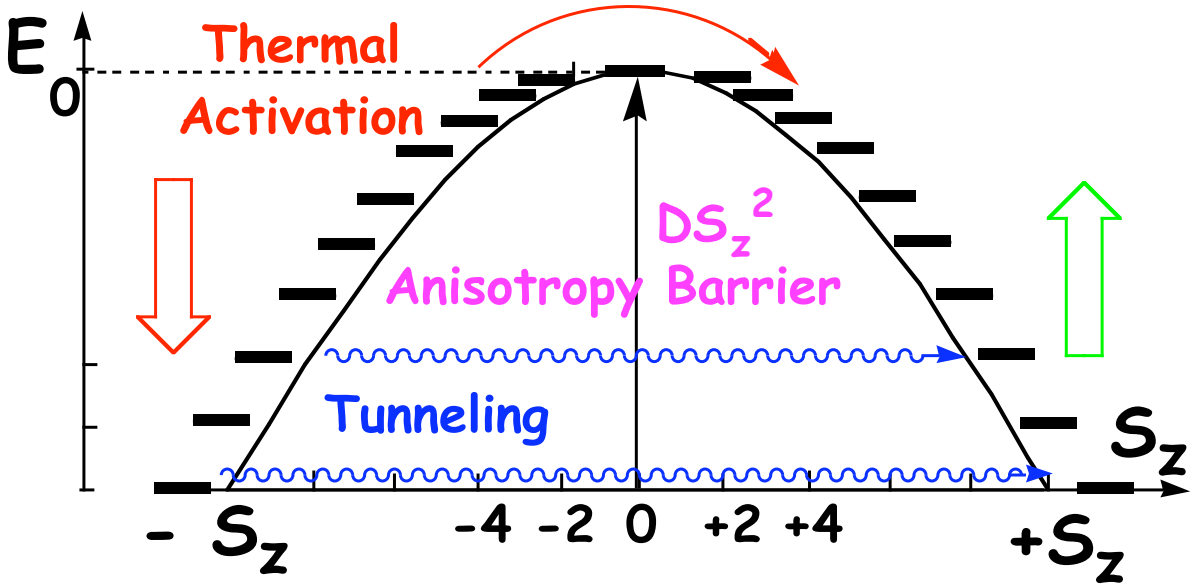
if

$T < T_{Blocking}$

Towards information storage at the molecular level ?

# Single molecule magnets

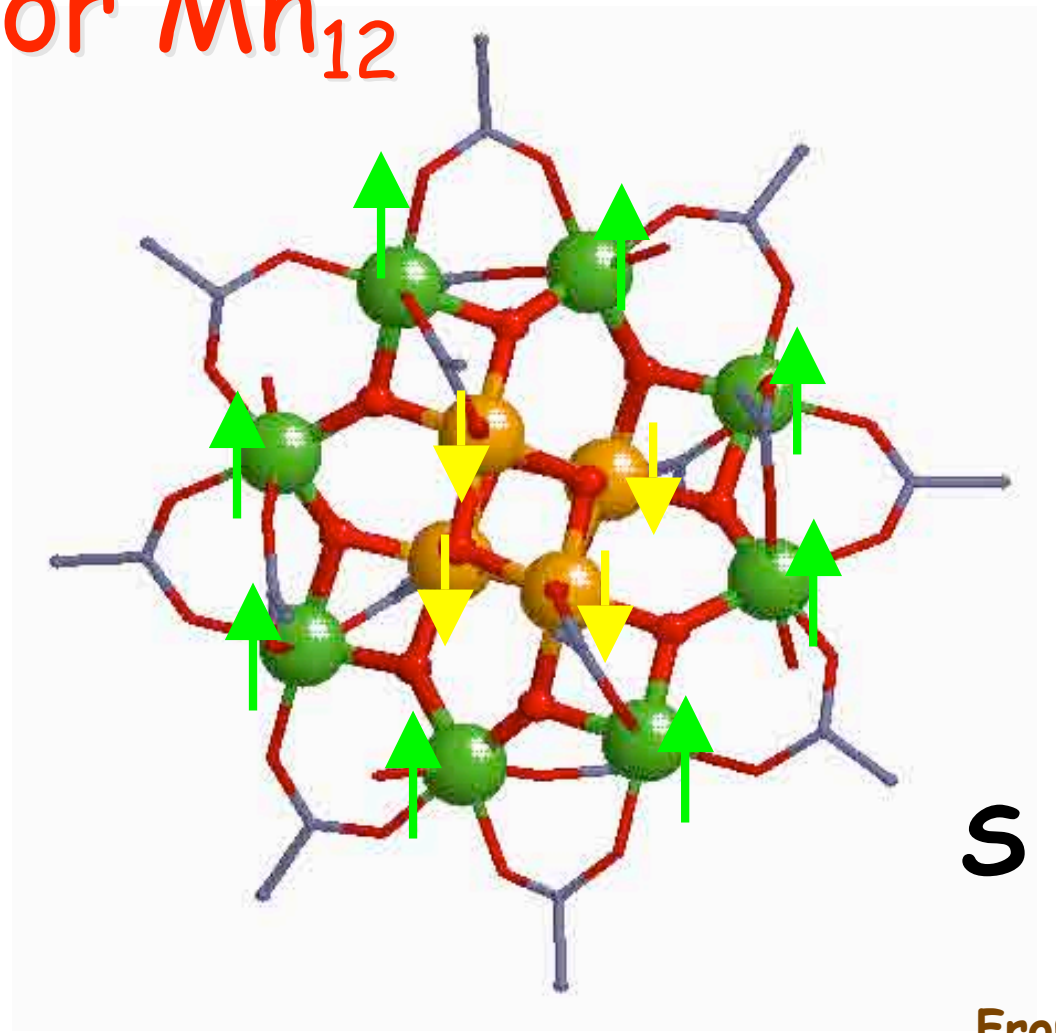



quantum

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

## or $Mn_{12}$



Mn(III) S=2

Mn(IV) S=3/2

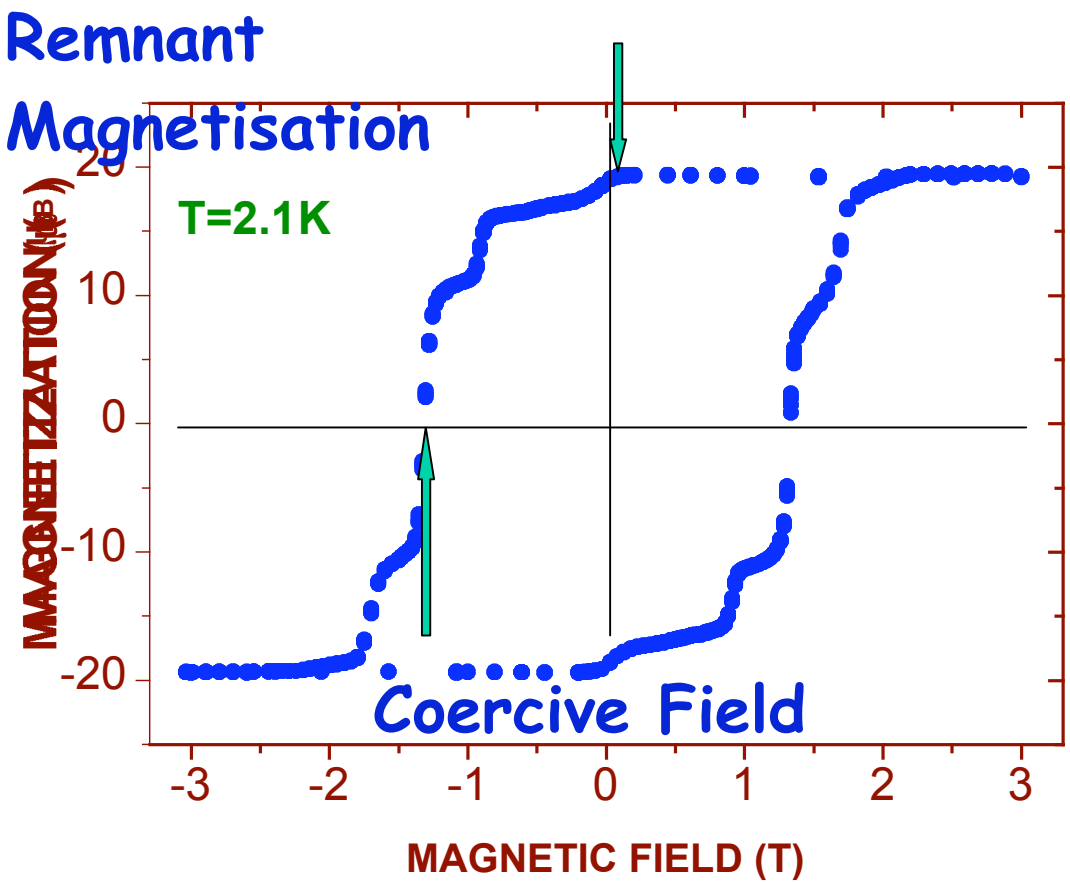
Ion Oxyde

Carbone

**S** =8x2 -4x3/2 = **S=10**

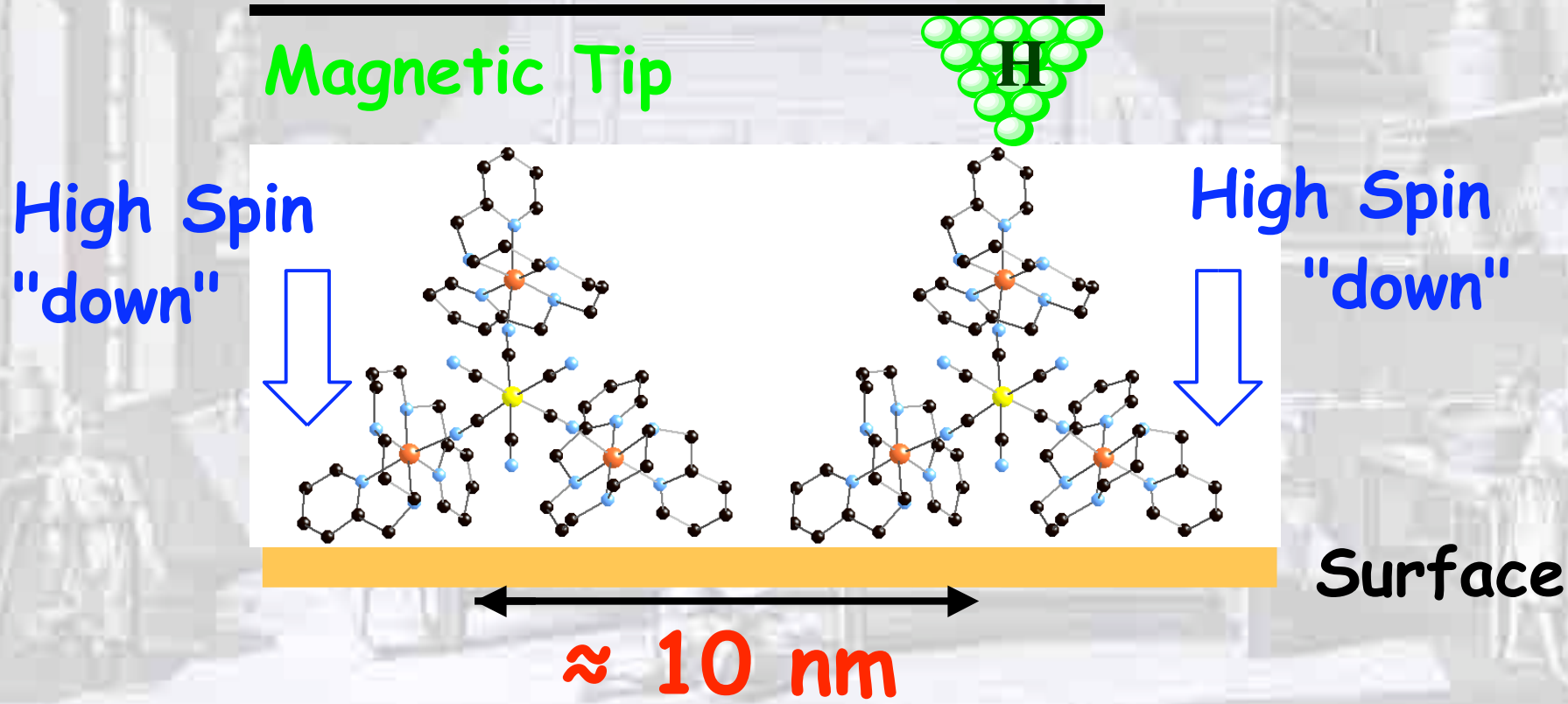
From D.Gatteschi and R. Sessoli

# Mn12 is a hard magnet



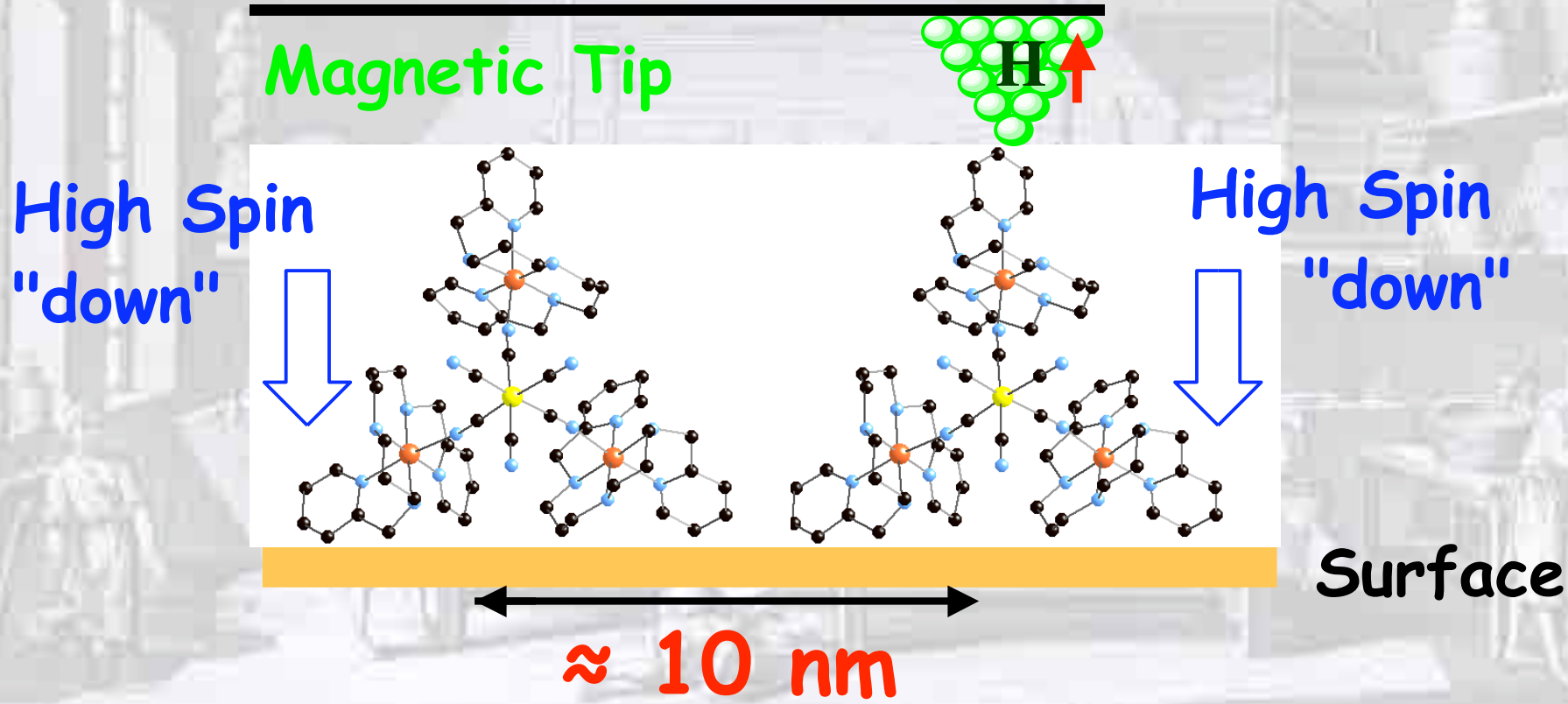

Bistability : in zero field the magnetisation can be positive or negative depending of the story of the sample

# The dream ...




quantum

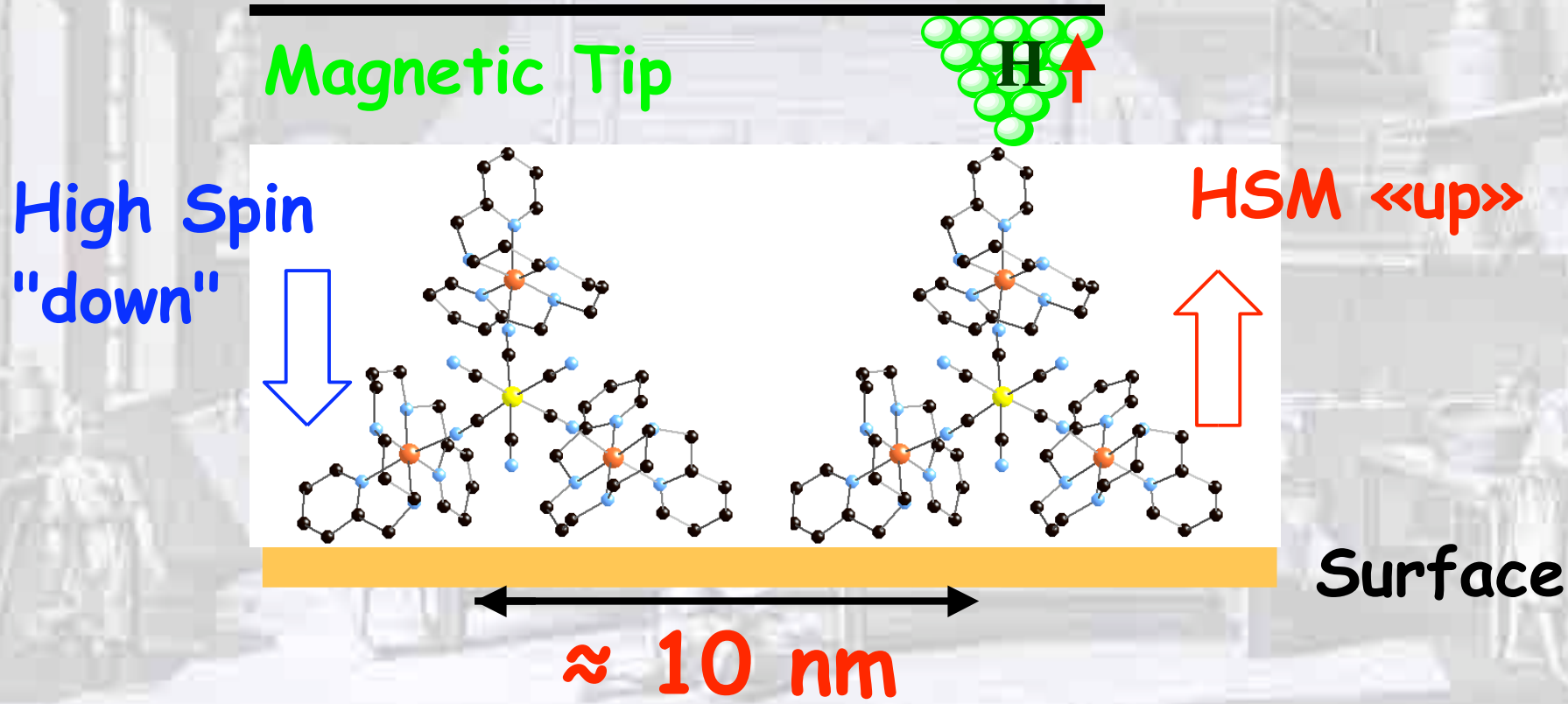
macro




quantum

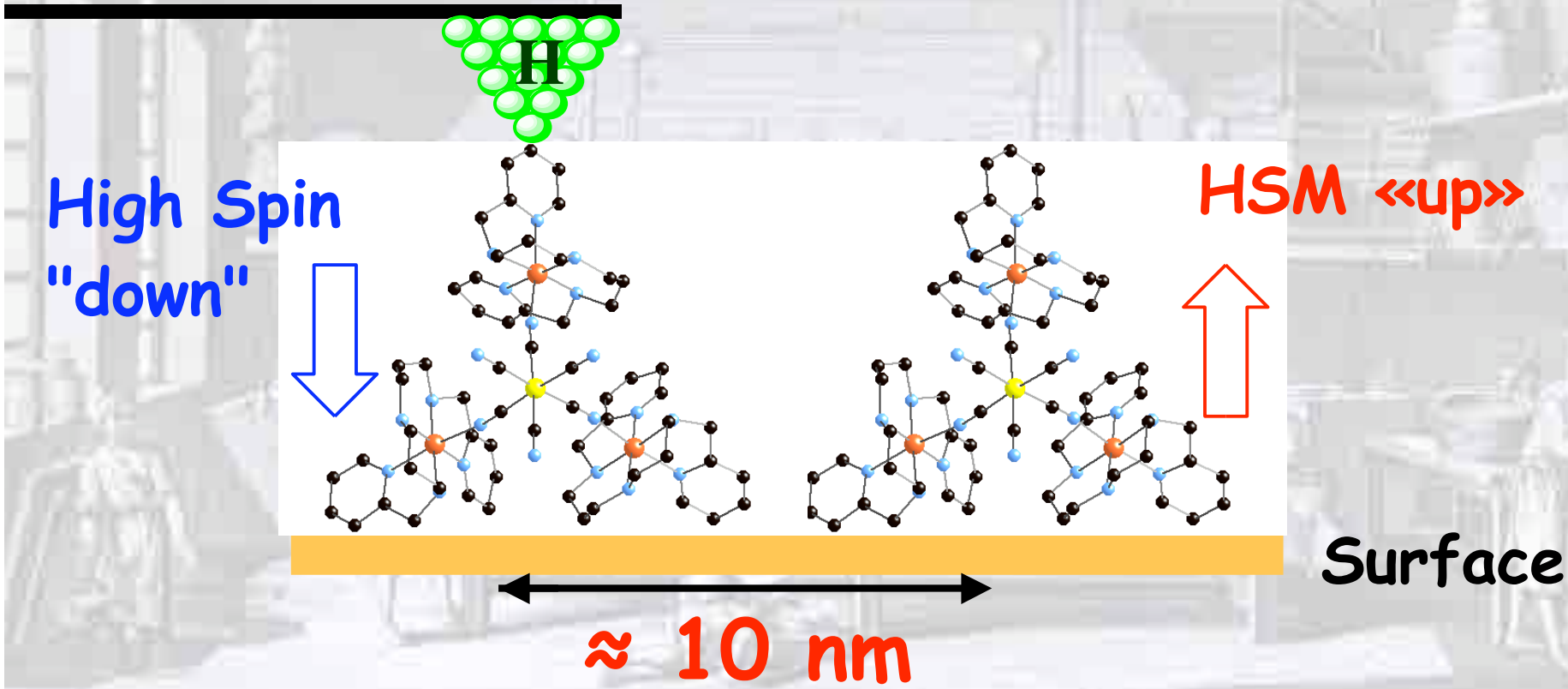
macro

# The dream …




… information storage at the molecular level !

# Nanosciences ...




... a challenge for chemists and friends ...

The possibilities are endless …


# Another popular non scientific use of the word « magnetism »

as attractive but less recommended …

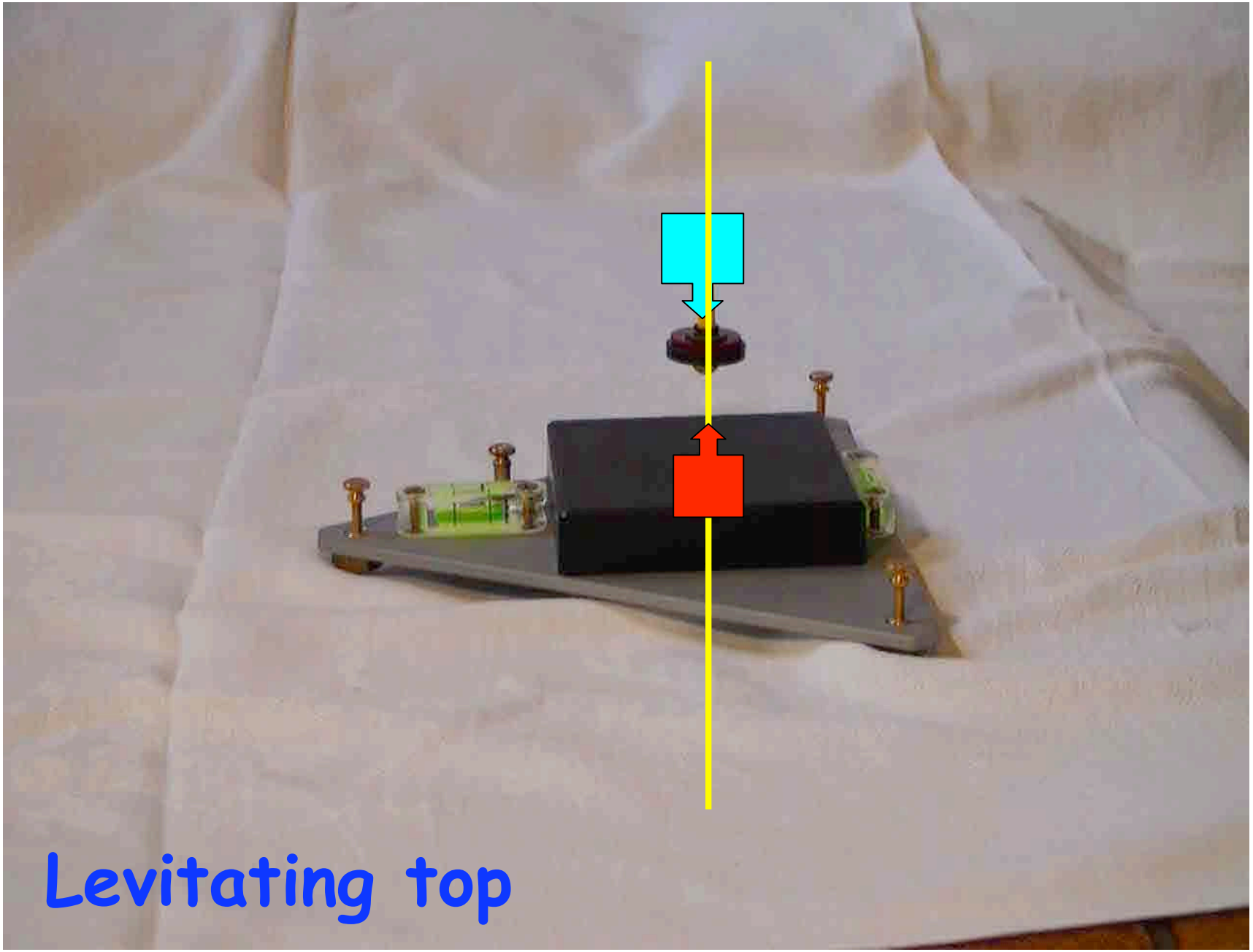
An interaction

through space

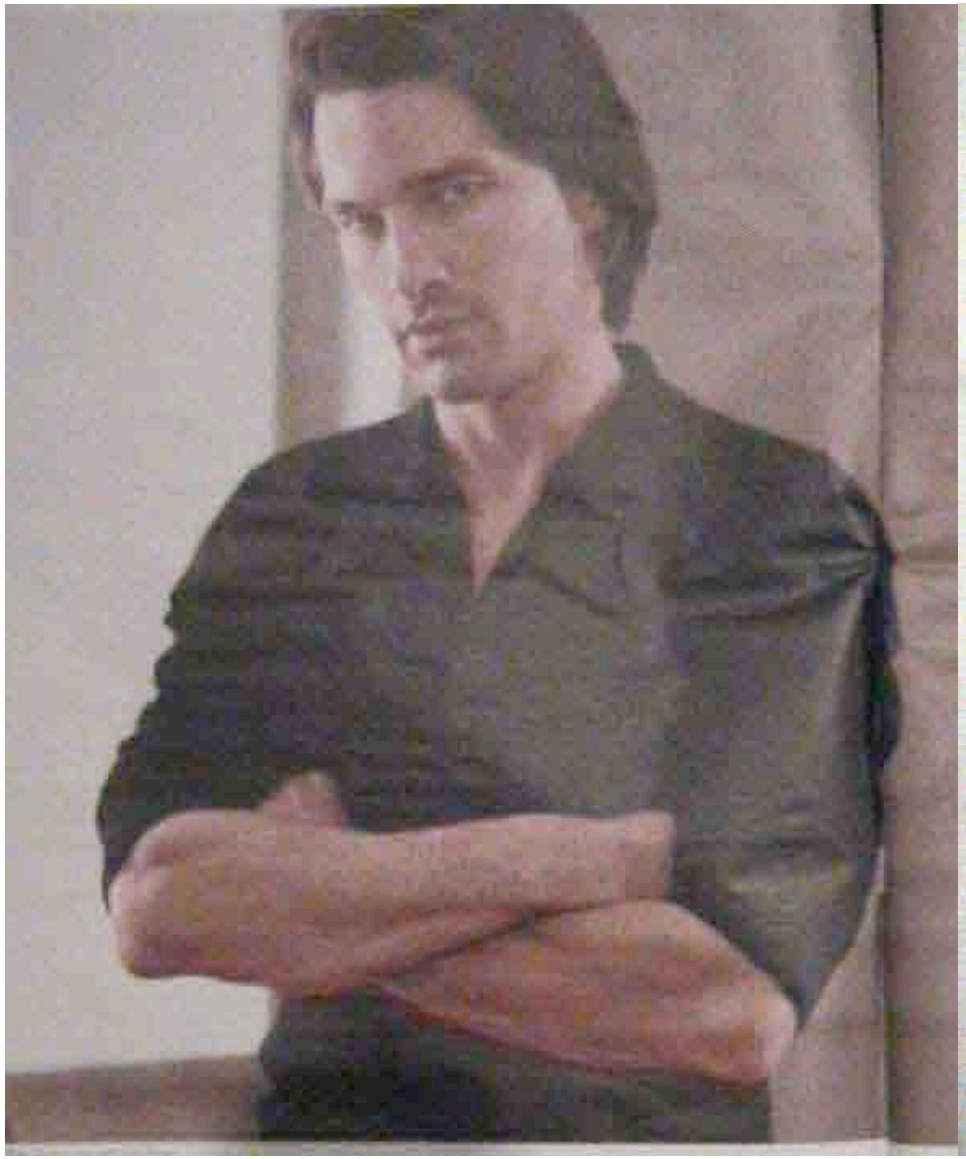
invisible, incomprehensible …

Magnetism = Magic !

To be demystified …



# Levitating top



# L'HOMME
## YVES SAINT LAURENT

SENSUEL ET MAGNÉTIQUE

*« This flask is equipped with magnets and induces in its centre an intense magnetic field which magnetizes the whole liquid.*

*Keep in the magnetic flask, tap or mineral water or any other drink, from 15mns to several hours, for an optimum magnetization.*

*Drink daily Magnetized Water : in preference, 1 cup when getting up, 1 or 2 in the morning and the afternoon and 1 cup at bedtime.*

*As a matter of fact, the body and tyhe blood are composed at 70 and 80% of water, hence magnetized water, more lively, more energetizing due to its magnetic properties, carries its energy into the whole organism.*

*Active research in hospitals, worldwide and mainly in China, have demonstrated the beneficent effects of magnetized water.*

*Some specialists foresee that ..*

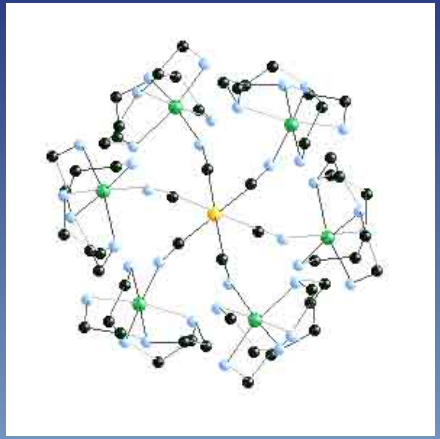
*Magnetism will play an important rôle in the world of tomorrow.*

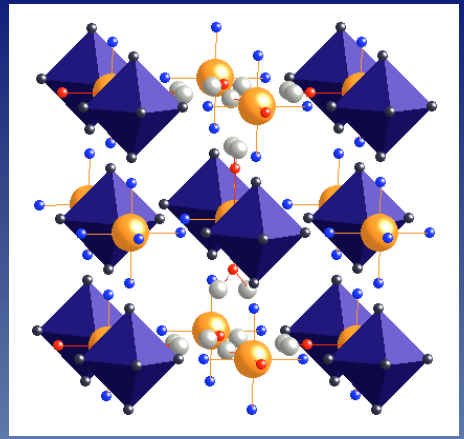

*M. Noyori, Hanoi, october 2003*

*To day*
*the chemist is able*
*to synthesize*
*any molecule*
*at will*

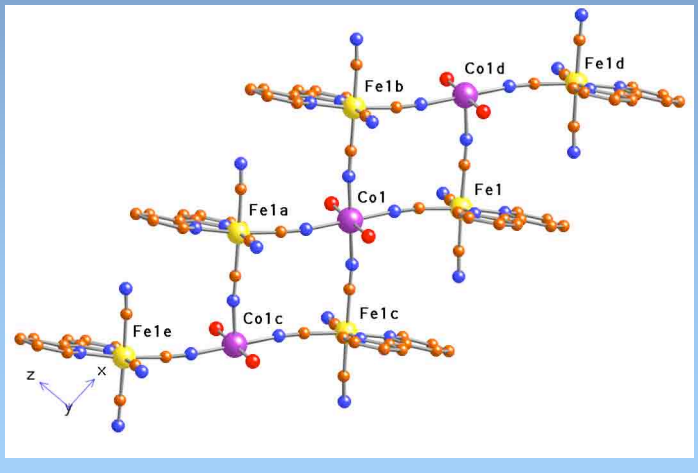
# NEW MAGNETIC OBJECTS

High spin Molcules

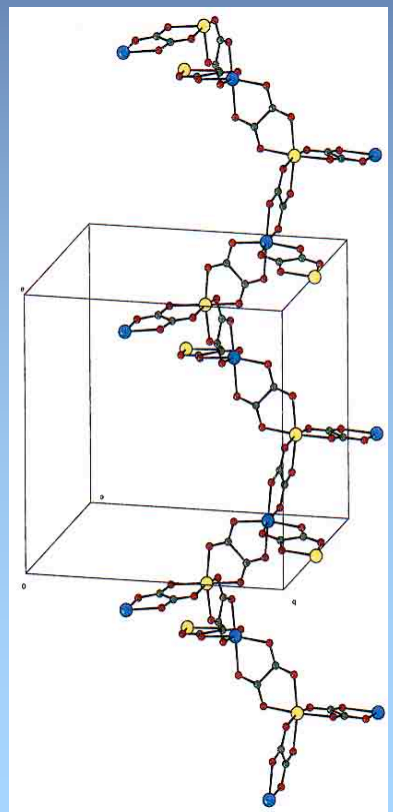




High $T_c$ Magnets Photo-Magnets

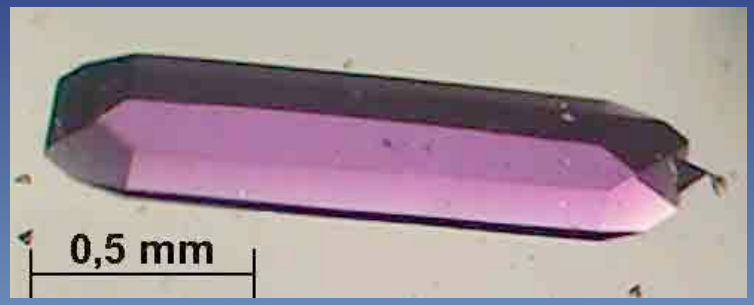



Single Chain Magnets



Chiral Magnets

High spin
Molcules



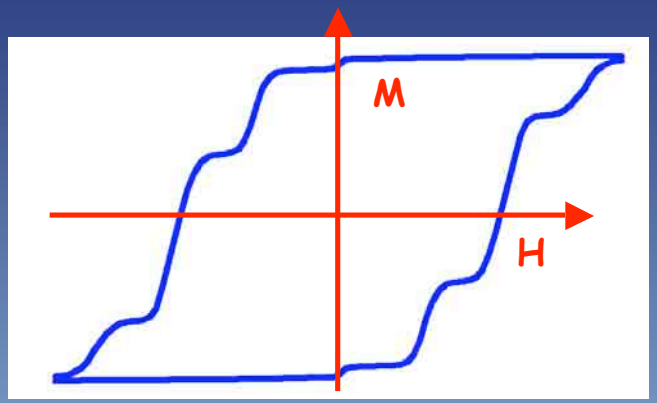

High $T_c$
Magnets
Photo-Magnets

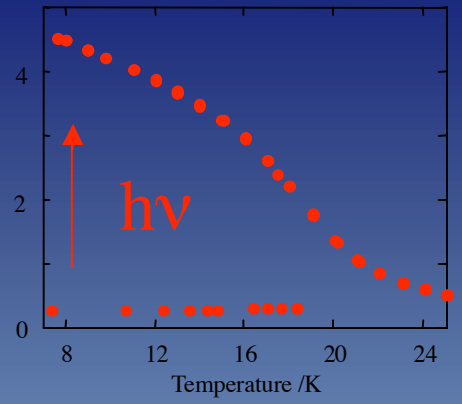
# BEAUTIFUL OBJECTS

Single Chain Magnets

Chiral
Magnets

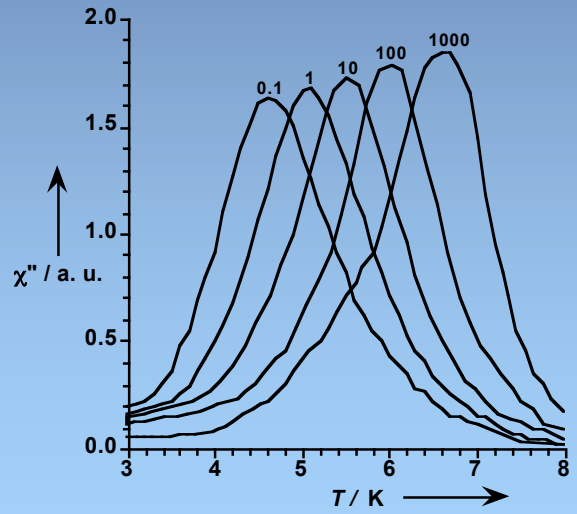
High spin
Molcules



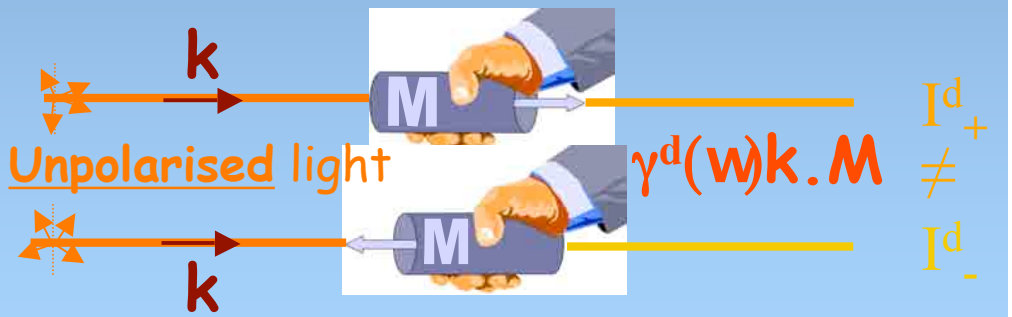




High $T_c$
Magnets
Photo-Magnets

# NEW PROPERTIES

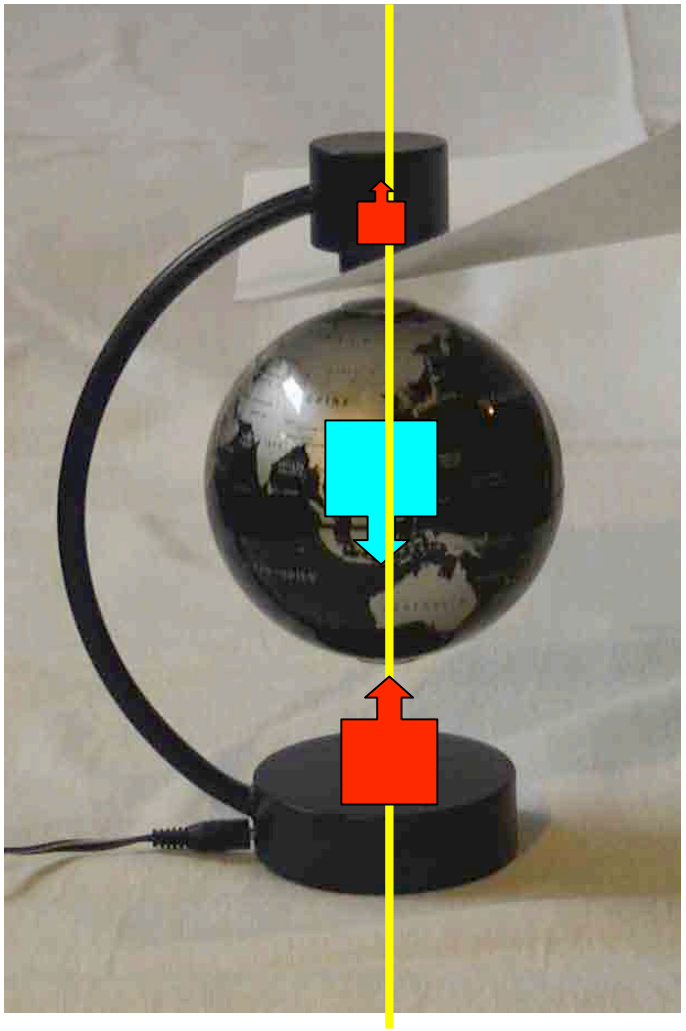



Single Chain Magnets




Chiral
Magnets

# Earth needs care ….



# Science for peace … (Vincenzo Balzani)


Pablo Picasso
Child with a dove, 1901
oil on canvas, 73x54 cm
Private collection
on loan to National Gallery