What is Responsible for Magnetism?

from Atom-based Magnets to Molecule-based Magnets

Shadi Amiri

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Introduction

Fe_3O_4 Magnetit **(800 BC)**

Metal Alloys

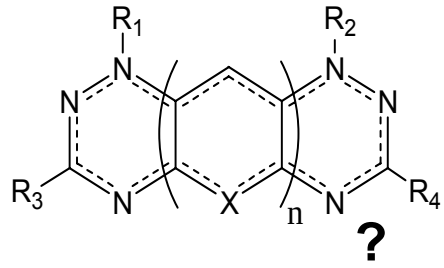
Bohr, Leeuwen: the first theorem about magnetism as a **classical** phenomenon **(1911, 1919)**

Heisenberg: magnetism as a purely **quantum mechanical** effect: exchange **(1928)**

$H = 2J\, S_i S_j$

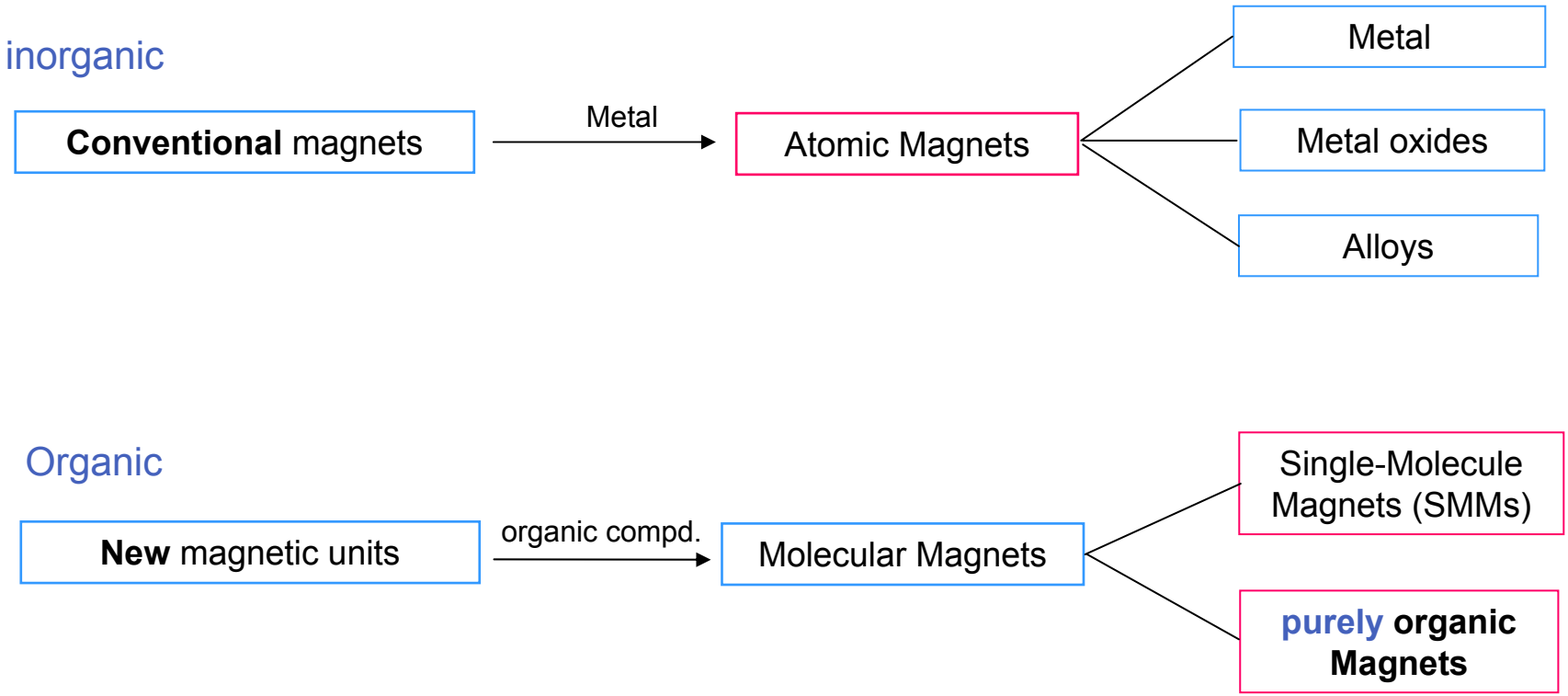
Lis: The first **s**ingle **m**olecule **m**agnet: $\underline{Mn_{12}\text{-acetate}}$ **(1980)**

Kinoshita: Carbon Magnets ? **(1991)**



Heisenberg, W. **1928** *Z. Phys*. *49*, 205; Falkoff, David, L. *American Journal of Physics,* **1950***, 18*, 30; Lis, T. et al.; *Acta Crystallog.* **1980**, *B36*, 2042; Kinoshita, M. et al. *Chem. Phys. Lett.* **1991**, *186*, 401;

Introduction / Content

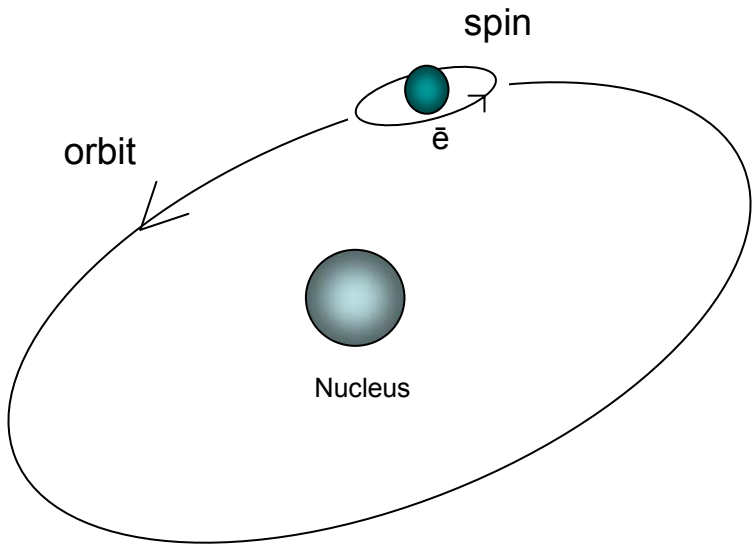


1- Conventional magnets based on

Elements
and
Simple compounds

e.g., Fe, Fe_3O_4, MnO, $LaMnO_3$, $Sr_{14-x}Ca_xCu_{24}O_{21}$, . . .

1- Conventional magnets



The processes which create **magnetic fields** in an atom are:

- Nuclear spin
- Electron spin
- Electron orbital motion

1- Conventional magnets

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

- **most of isolated atoms and ions are magnetic:**

  79 elements are magnetic in atomic state

- **Only a few of them are magnetic in solid state (15 atoms)** $J = L \pm S = 0$ (filled shells)

  1) crystal field effect (d) and Spin-Orbit Coupling (f) modifies the ground state

  2) Other interactions may be important: anisotropy, Jahn-Teller effect….

1- Conventional magnets

Conventional magnetic systems based on *elements* and *simple (or not so simple) compounds*

H																He
Li	Be										B	C	N	O	F	Ne
Na	Mg										Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac														
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Only 15 elements are magnetically ordered in the solid stated

Metal oxides e.g. Fe, MnO, $LaMnO_3$, $Sr_{14-x}Ca_xCu_{24}O_{21}$,...

Alloys

1- Conventional magnets

- Biological systems tend to use a different approach: *Very complex, big molecules based around carbon*

(e.g., Ferritin)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

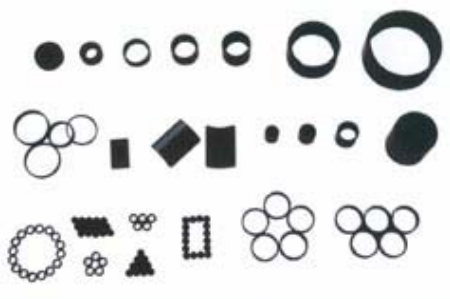
- There is another Reason too:

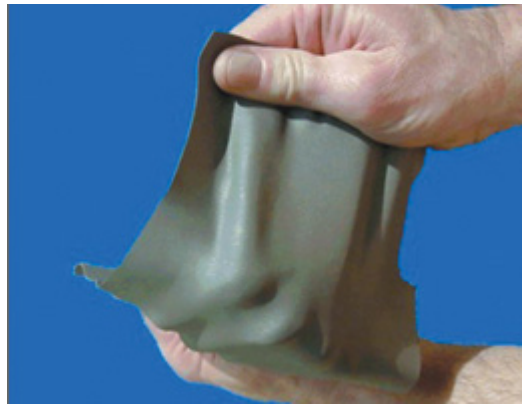
A modified Magnet with desired qualities …

1- Conventional magnets

A modified Magnet with desired qualities …

„Bonded“ Magnets



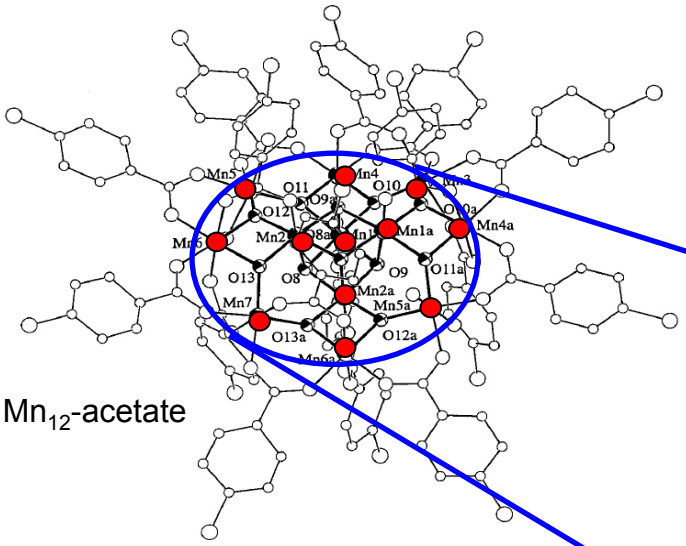


e.g., R−T−B

2- Single-Molecule Magnets (SMMs)

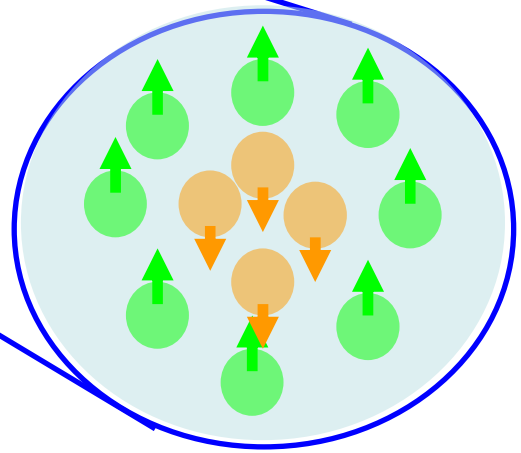
2- **S**ingle **M**olecule **M**agnets (SMMs)

SMMs: "nanoscale magnetic particles "



e.g., Mn_{12}-acetate

Molecular compounds based on macromolecules, each containing a core of magnetic ions surrounded by organic ligands, and assembled in an insulating crystalline structure



Caneschi, A. et al., *J. Am. Chem. Soc*. **1991**, *113*(15), 5873

Hendrickson, D. et al., *J. Am. Chem. Soc*. **1996**, *118*, 7746

2- **S**ingle **M**olecule **M**agnets (SMMs)

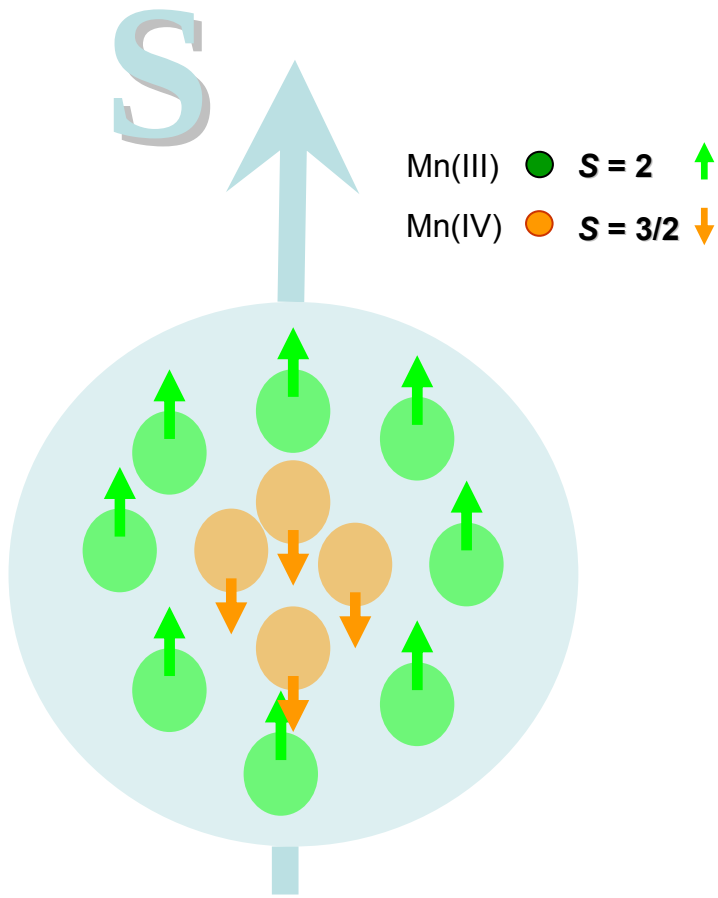
- **The whole cluster behaves as a nanometer-size magnet, because of:**

1- Well defined **giant spin** (*S* =10) at low temperatures (T<35 K)

$$S = 8_{\uparrow}2 - 4_{\downarrow}3/2 = 10$$

2- **Easy-axis anisotropy** due to Jahn -Teller distortion on Mn (III)

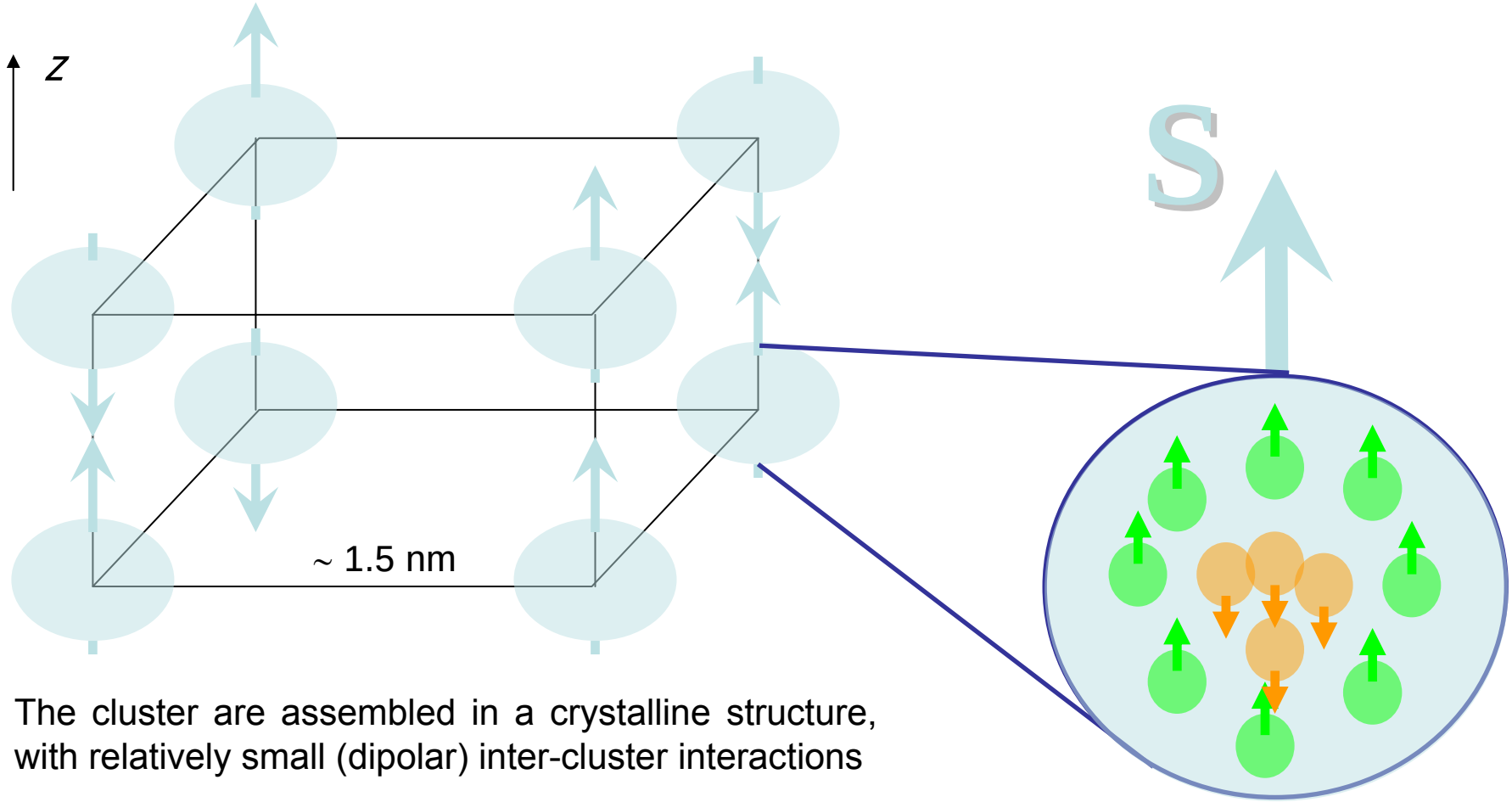
3- Organic ligands ("chicken fat") **isolate the ions**



$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_20$

D. Gatteschi et al., *Science*,**1994**, *265*, 1054
R. Sessoli et al., *JACS*, **1993**, *115*, 1804

2- **S**ingle **M**olecule **M**agnets (SMMs)

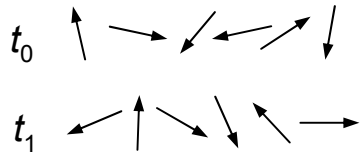


The cluster are assembled in a crystalline structure, with relatively small (dipolar) inter-cluster interactions

The magnetic interactions have been controlled in SMMs

D. Gatteschi et al., *Science*, **1994**, *265*, 1054

Spin Configurations in Solids

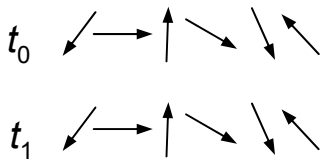


Paramagnet

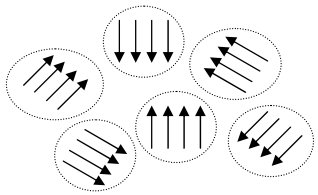
Ferromagnet

Antiferromagnet

Ferrimagnet

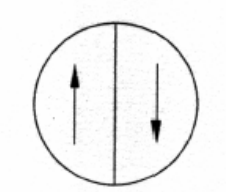


Spin Glass



Cluster Glass

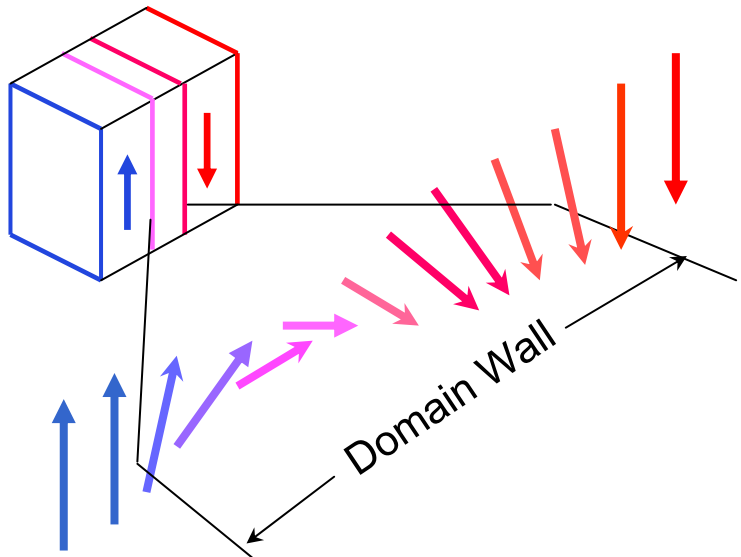
Uniaxial



2- **S**ingle **M**olecule **M**agnets (SMMs)

Domain Wall Width:

in traditional ferromagnetic materials, several easy axis
$\Rightarrow$ several domains corresponding the different directions

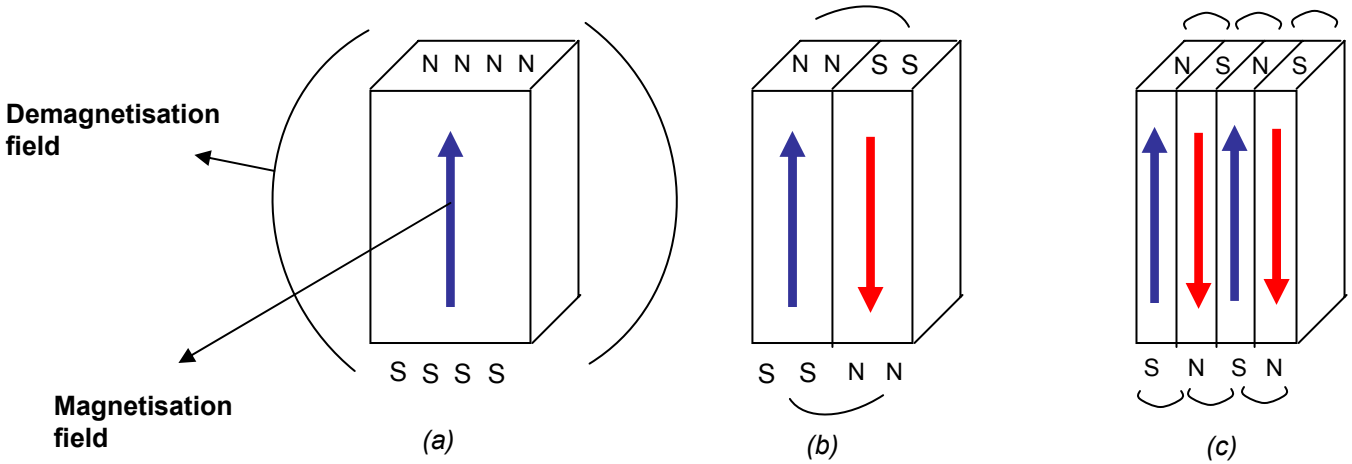


Schematic representation of a 180° domain wall

2- **S**ingle **M**olecule **M**agnets (SMMs)

2-1- Domain

The break up of the magnetisation into N domains reduces the magnetostatic energy by a factor of 1/N



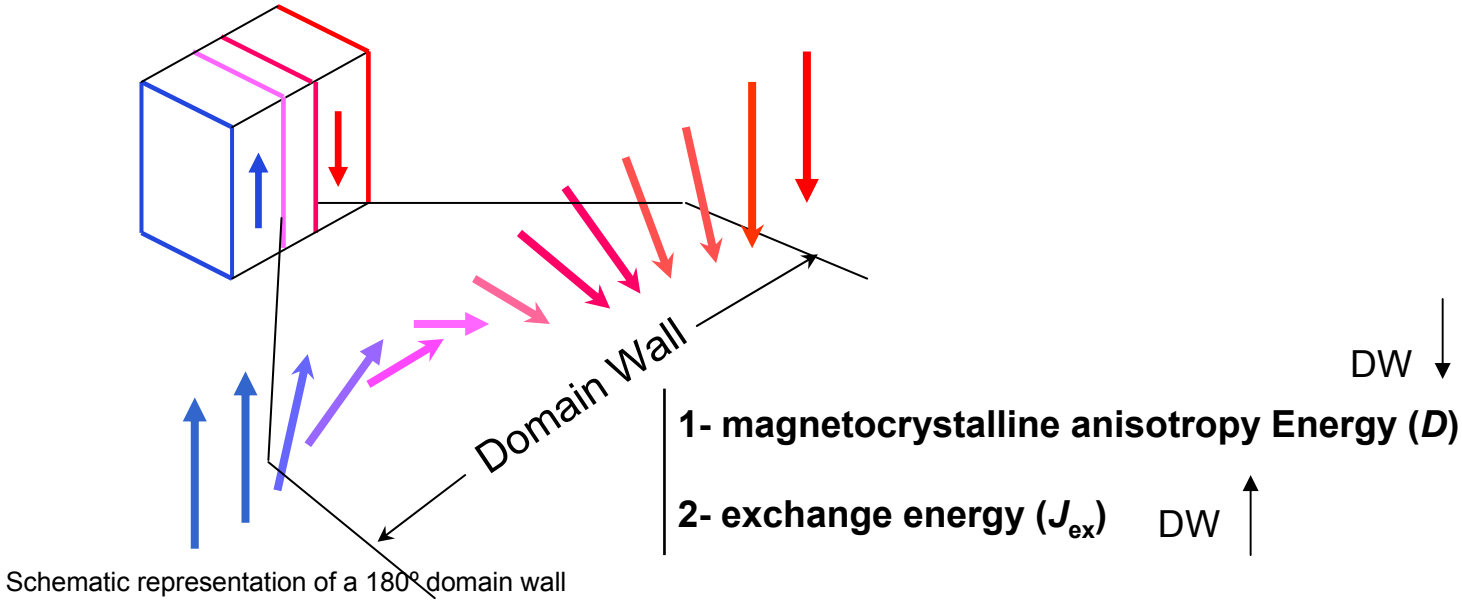
Schematic illustration of the break up of magnetisation into domains
(a) single domain, *(b)* two domains,*(c)* four domains

2- **S**ingle **M**olecule **M**agnets (SMMs)

2-2- Domain Wall

Domain Wall Width:

in ferromagnetic materials, several easy axis
$\Rightarrow$ several domains corresponding the different directions



Schematic representation of a 180° domain wall

Domains are separated by domain walls where the magnetization rotates gradually

2- **S**ingle **M**olecule **M**agnets (SMMs)

2-1- Domain Wall

2-1-2-Exchange

Domain wall Width depends on

1- Anisotropy

2- Exchange → **Superexchange**

In a three-dimentional network of SMMs,

macroscopic Quantum tunneling

major Mechanism for magnetic interactions …

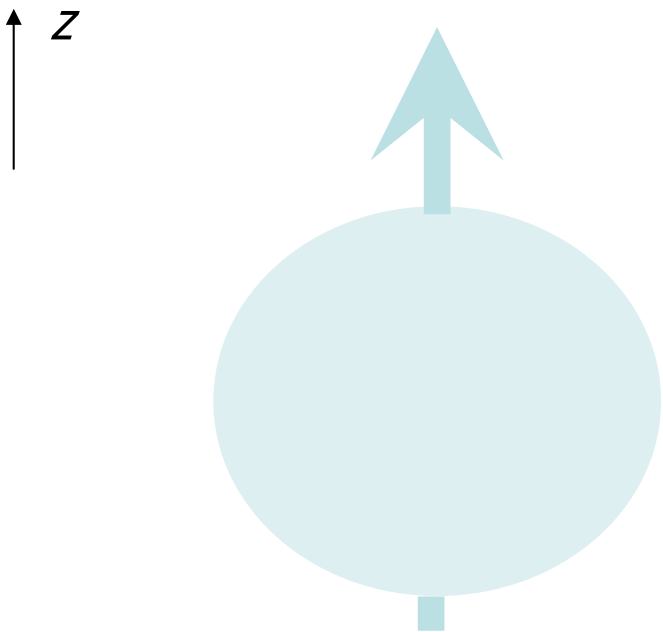
Christou,G., et al. *Phys. Rev. B*. **2003**, *68*, 140407; J. R. Friedman, M. P. Sarachik, J. Tejada, R. Ziolo, *Phys. Rev. Lett.***1996**, 76, 3830 **;** J. M. Hernandez *et al., Europhys. Lett.* **1996**, *35*, 301**;** L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli and B. Barbara**,** *Nature,* **1996,** *383*,145

2- **S**ingle **M**olecule **M**agnets (SMMs)

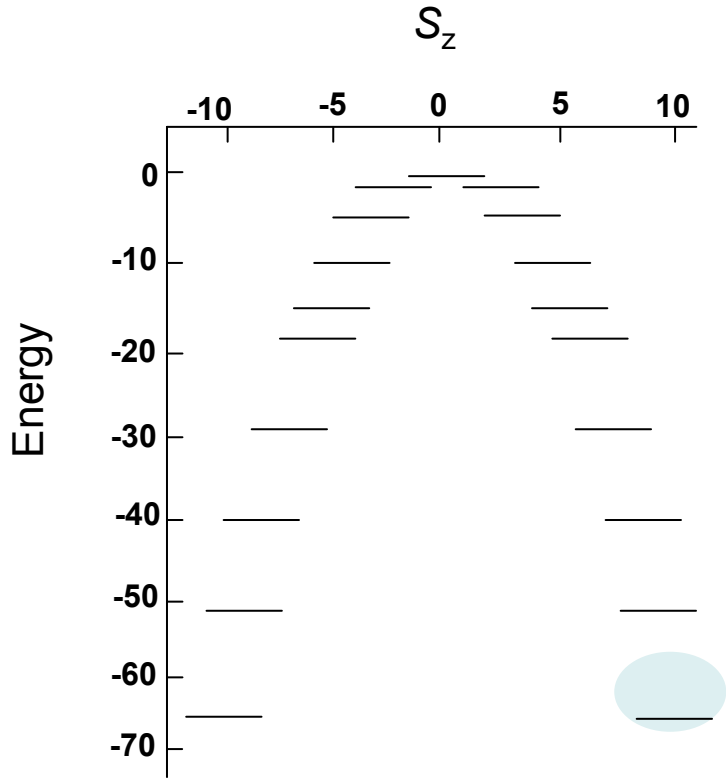
2-1- Domain Wall

2-1-2- Exchange

2-1-2-Thermally activated relaxation



$$\mathcal{H} = -DS_z^2$$



The magnetic moment of the molecule is preferentially aligned along the z – axis.

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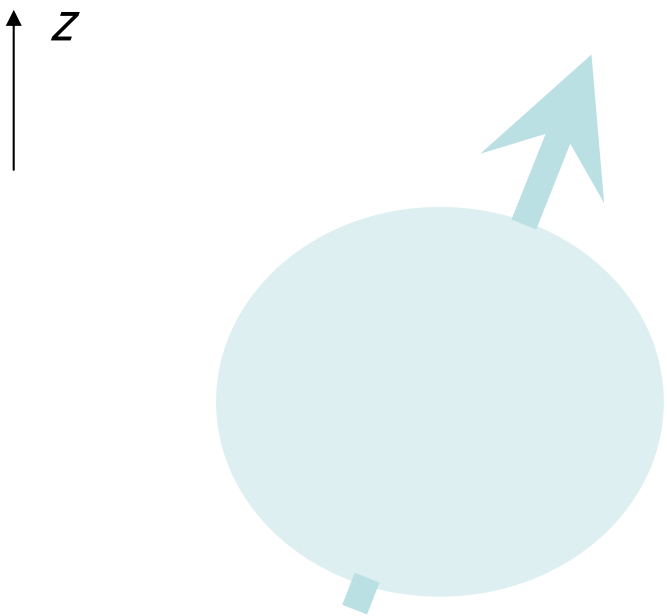

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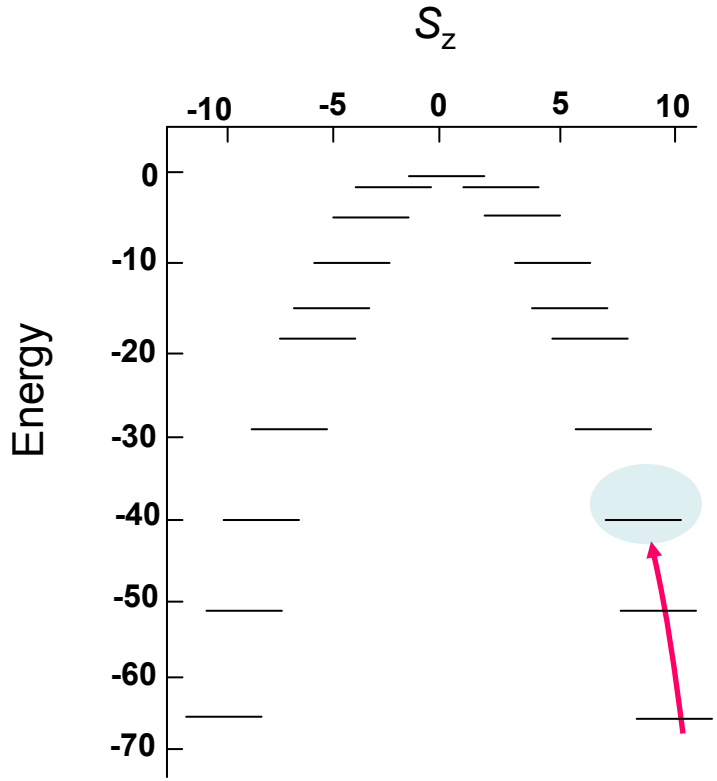

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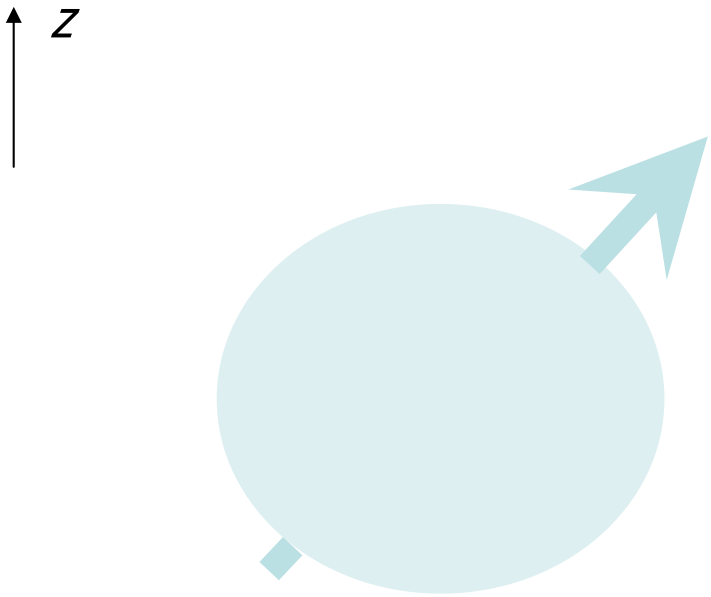

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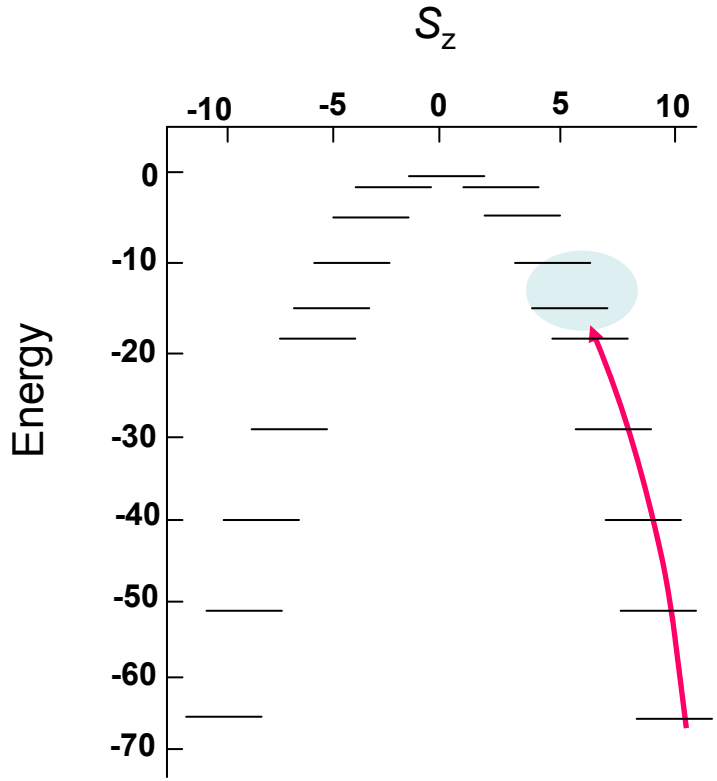

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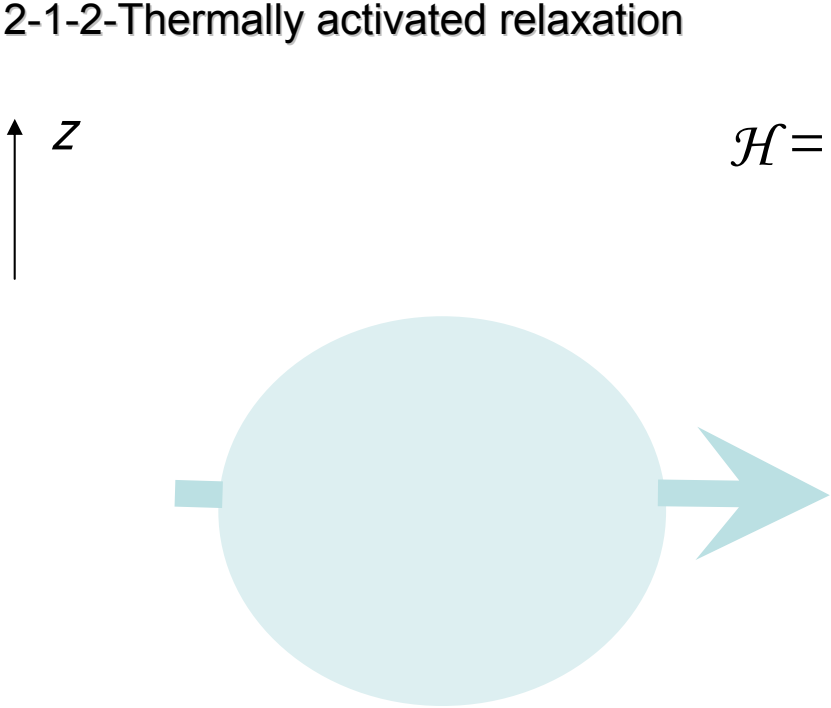

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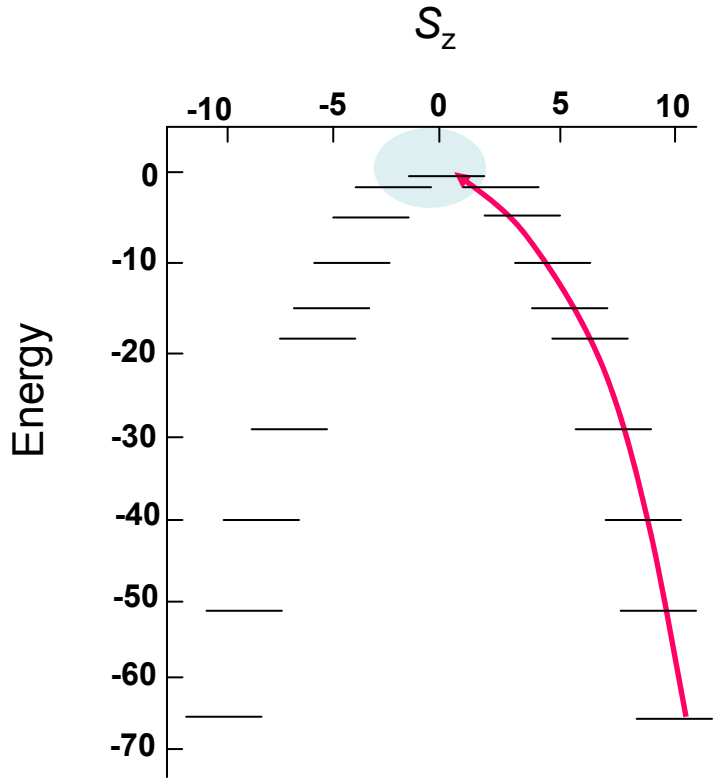

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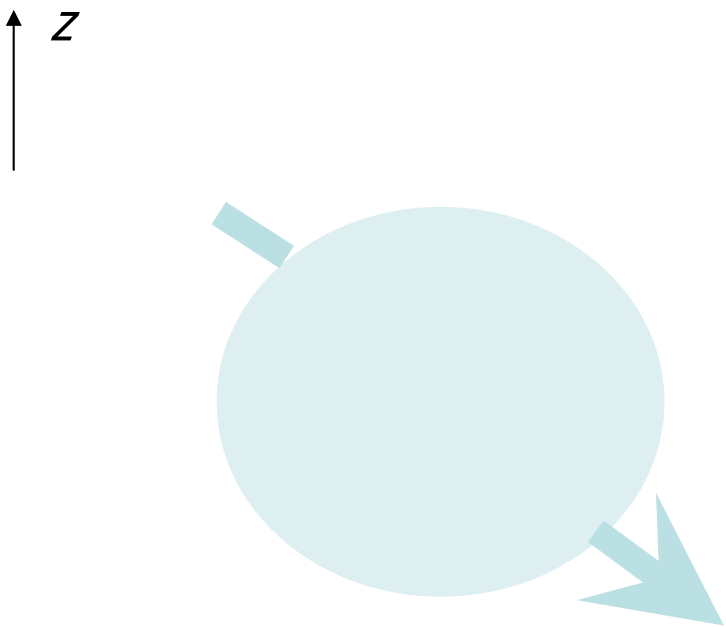

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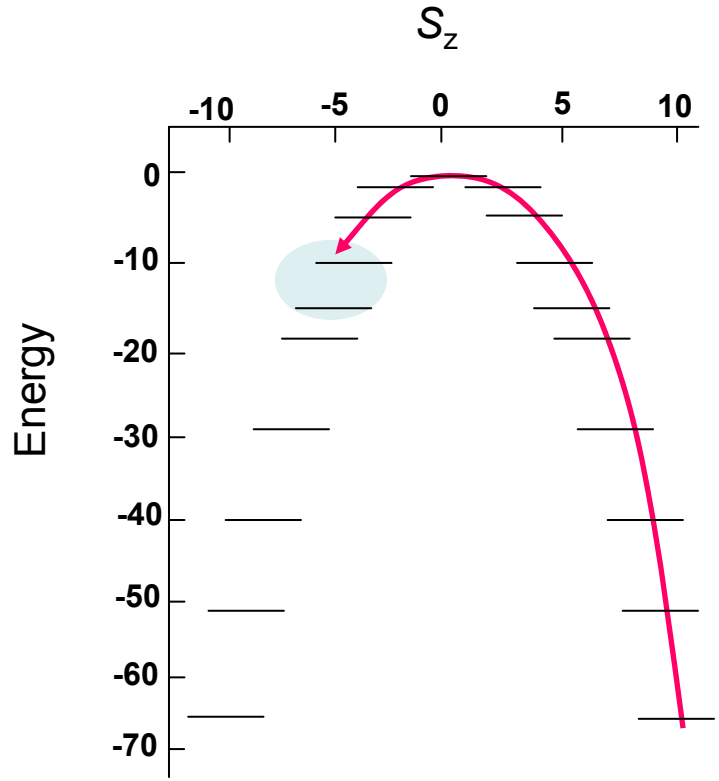

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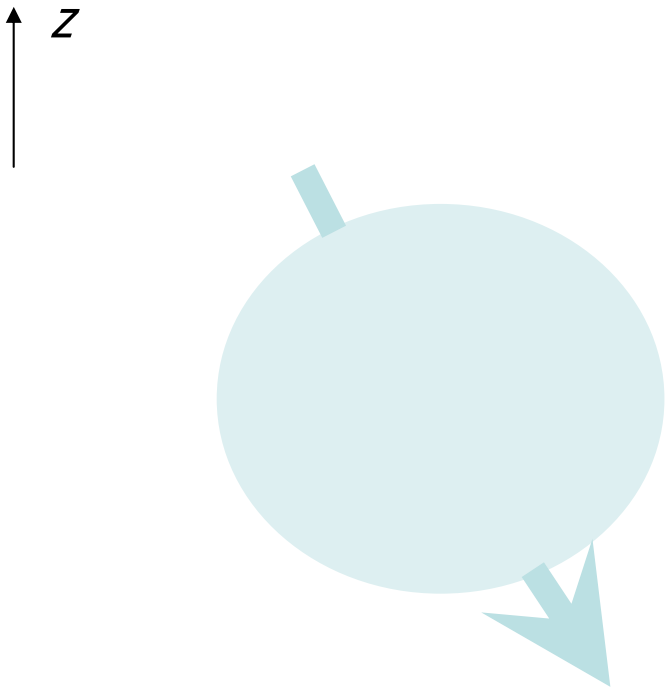

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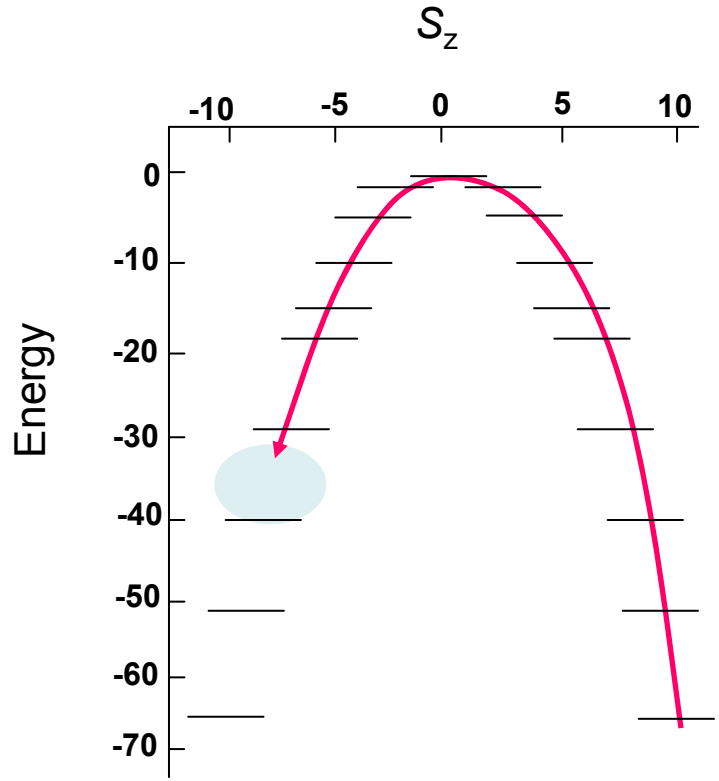

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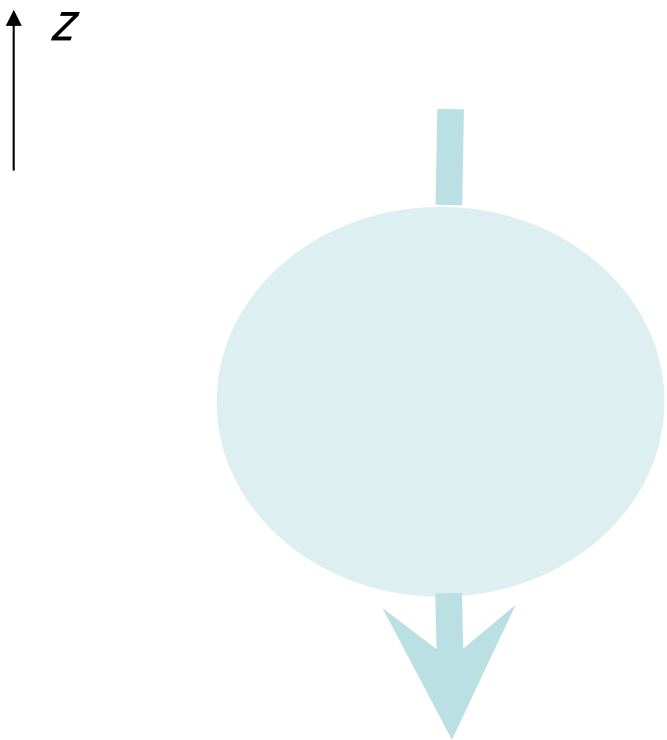

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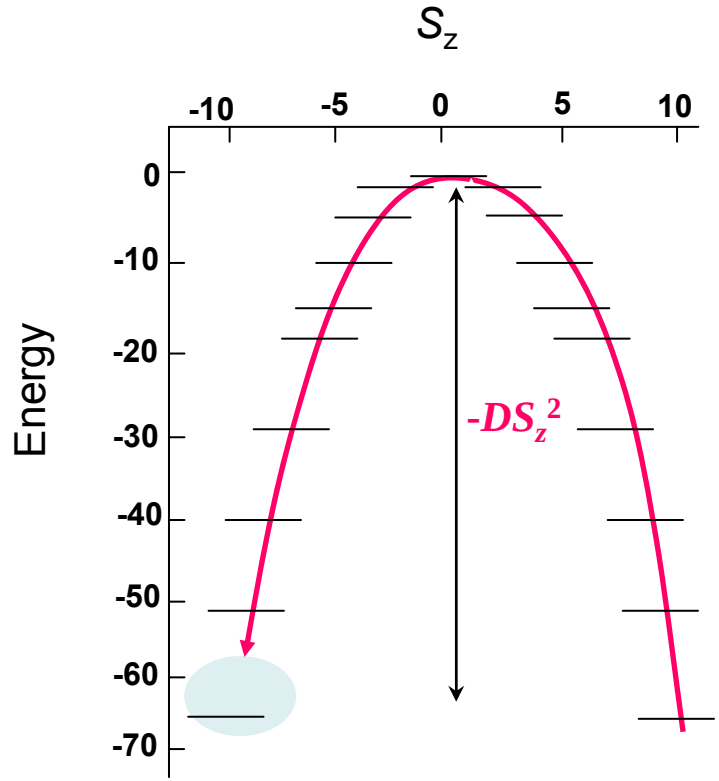


Classically, it takes an energy ~ 65 K to reverse the spin.

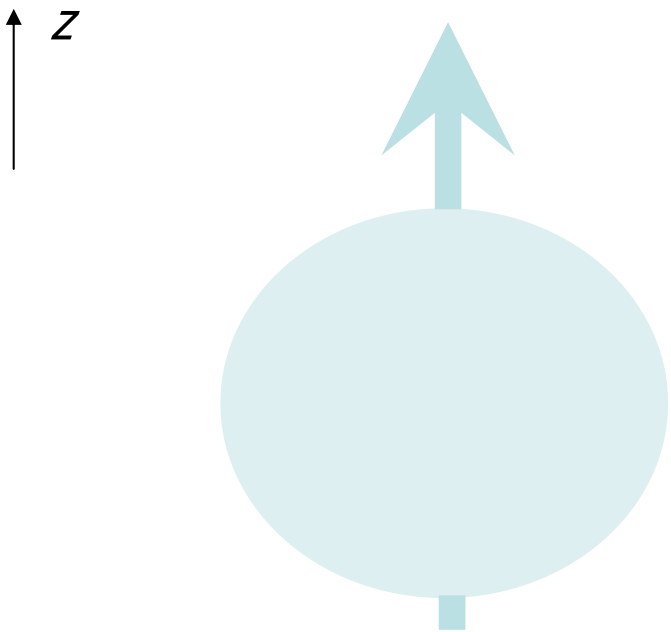
Barrier against magnetic relaxation

2- **S**ingle **M**olecule **M**agnets (SMMs)

2-1- Domain Wall

2-1-2- Superexchange

2-1-2-Quantum tunneling of magnetization



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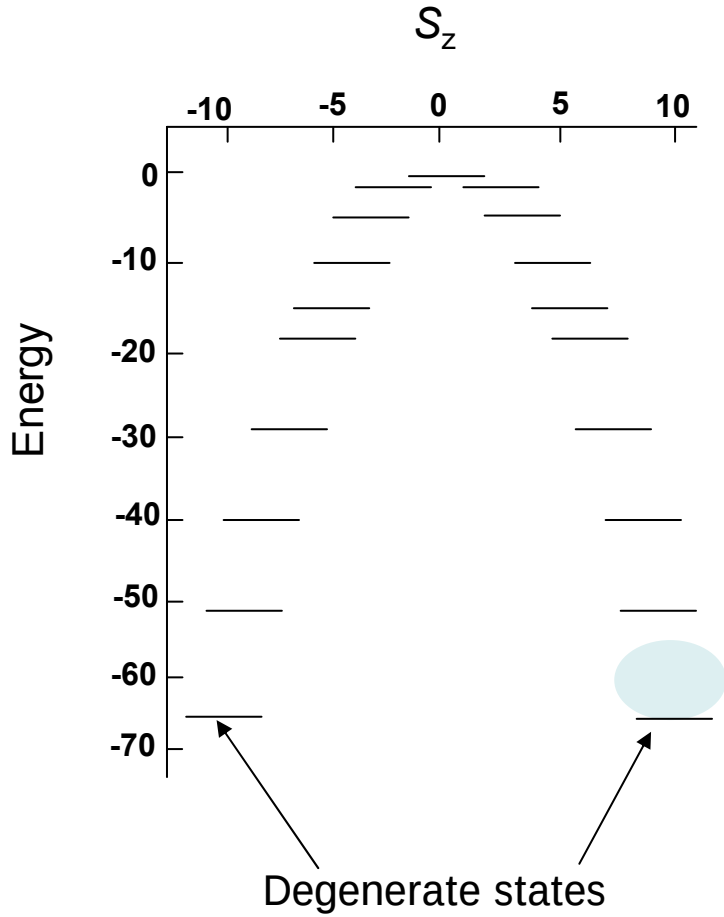

Spin tunneling (M. Sarachik)

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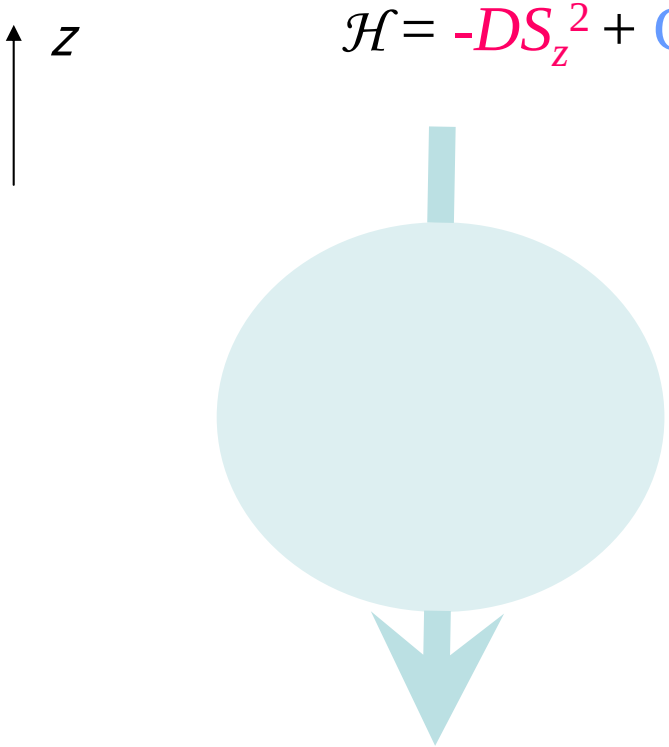
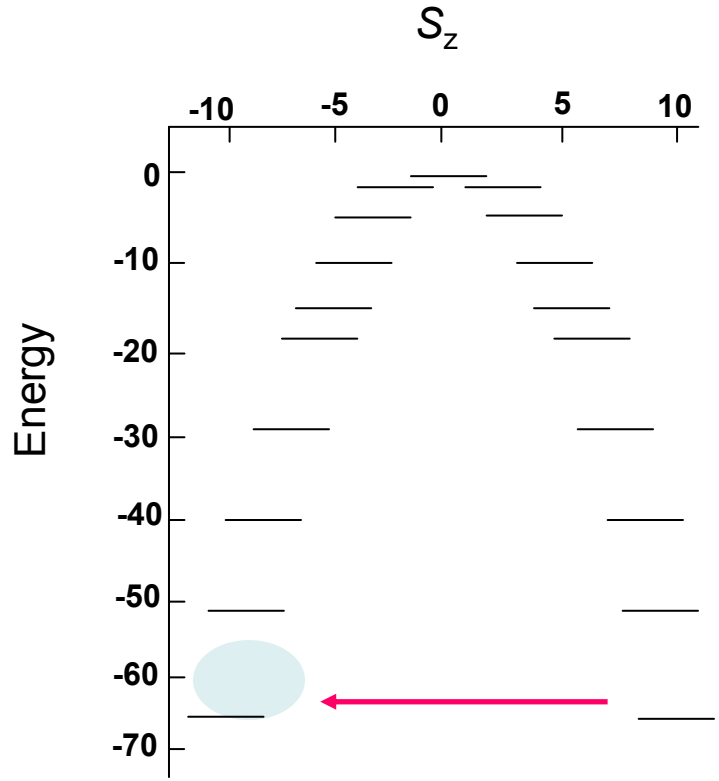
2-1-2- Superexchange

2-1-2-Quantum tunneling of magnetization



$$\mathcal{H} = -DS_z^2 + C(S_+^4 + S_-^4)$$



Quantum mechanically, the spin of the molecule can be reversed by tunneling through the barrier

L. Thomas et al., *Nature* **1996**, *383*, 145

2- **S**ingle **M**olecule **M**agnets (SMMs)

Bistability

Uniaxial anisotropy

up = 1

down = 0

Bistable

magnetic materials

Particle units

for

magnetic memory

as magnetic molecular qubits for quantum information and computation processes

M. N. Leuenberger, D. Loss, *Nature*, **2001**, *410*, 789; J. Tejada, E. M. Chudnovsky, E. del Barco, J. M. Hernandez, *Nanotechnology*, **2001**, *12*, 181; Koo, H.; Krafft, C.; Gomez, R. D. *Appl. Phys. Lett,* **2002**, *81*, 862

2- **S**ingle **M**olecule **M**agnets (SMMs)

Summery:

Requirements for a single-molecule magnet

1. **Large Molecules – Little intermolecular interaction**

2. **Well defined giant spin ground state** S
   - Clusters of transition metal oxides: Mn, Fe, Ni, Co, etc..

3. **Large uniaxial (negative) magnetoanisotropy** $D < 0$

Other considerations....

4. **Symmetry**
   - Quantum tunneling is extremely sensitive to SMM symmetry

$$\hat{\mathrm{H}}_{zfs} = D\hat{S}_z^2 + \hat{\mathrm{H}}_{\mathrm{T}} \qquad e.g. \qquad \hat{\mathrm{H}}_{\mathrm{T}} = E\left(S_x^2 - S_y^2\right)$$

5. **The environment**
   - Intermolecular interactions, nuclear hyperfine interactions, etc.
   - Disorder (ligand disorder)

2- **S**ingle **M**olecule **M**agnets (SMMs)

Mn: **Christou Group** (University of Florida)

Fe: **Winpenny Group** (University of Manchester)

Many other examples: Ni, V and Co Clusters

3-Purely Organic Magnets

Only carbon based molecular spesies,

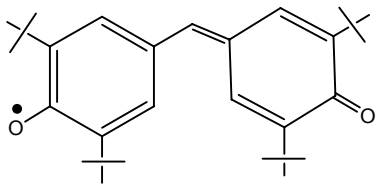
which bear an *unpaired spin*

Is it possible?

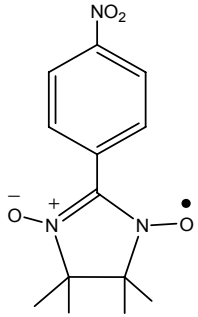
„ Making Ferromagnetism in materials containing only ***s*** and ***p*** electrons ! “

„C“ doesn‘t have a spontaneous „magnetic moment“ in any of ist allotropes

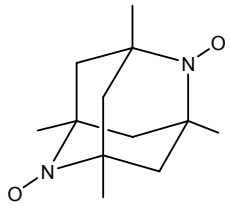
3- **Organic-Based Magnets**



galvinoxyl



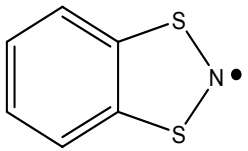
p-NPNN



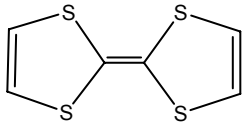
adamantane

fullerene

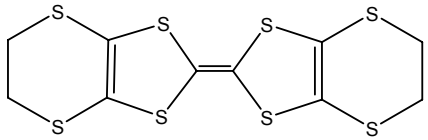
1) nitronyl nitroxides



BDTA



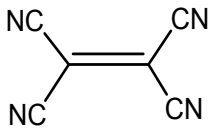
TTF



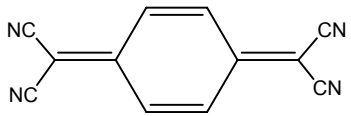
BEDT-TTF

2) TTF

3) carbens

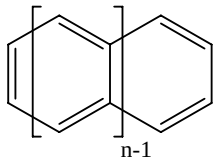


TCNE

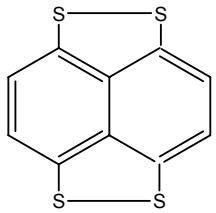


TCNQ

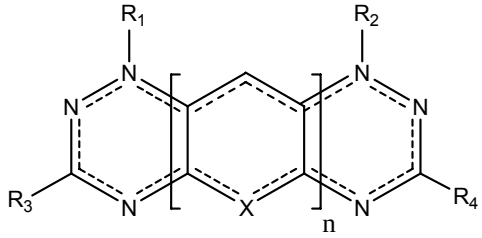
4) fullerens



acene



TTN



5) acenes

Blundell, S. J.; Pratt, F. L.. *J, Phys.: Condens. Matter,* **2004**, *16*, R771; Wudl, F.; Bendikov, M. *Chem. Rev*. **2004**, *104*, 4891; Houk, K. N. et al.; *J. Org. Chem.* **2001**, *66*, 5517; Langer, P.; Schreiner; P. R. *Angew. Chem.* **2005**, *117*, 5389; Houk, K. N.; Winkler; M. *JACS*, **2007** published on web

3- **Organic-Based Magnets**

What make having organic magnets in *crystalline structure* impossible?

Two main reasons

1- not enough *stability* of organic systems with unpaired spins (open-shell)

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→ aligning antiferromagnetically

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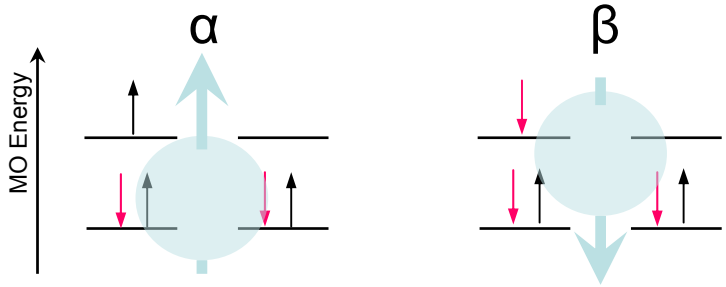

Intermolecular overlaps of SOMOs will tend to lead to a state with the character of a ***bonding orbital***

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→

aligning antiferromagnetically

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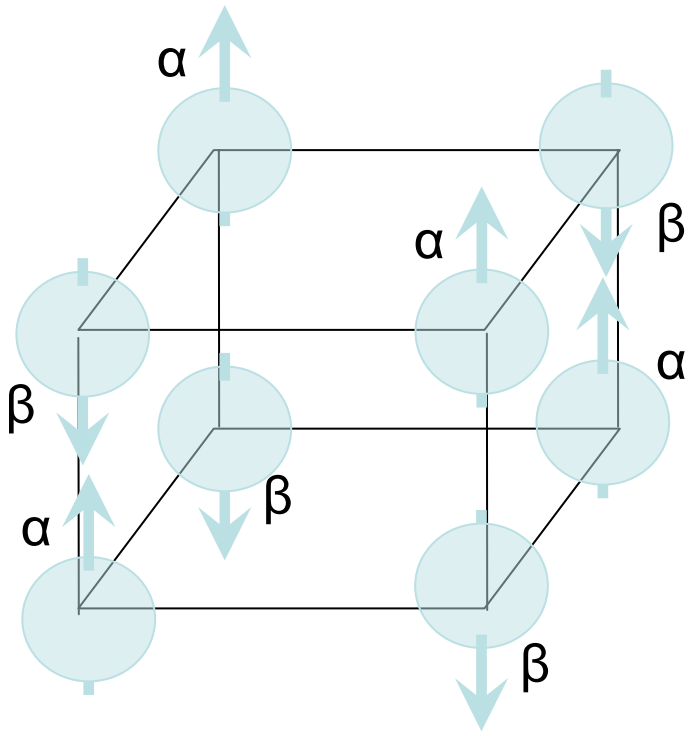

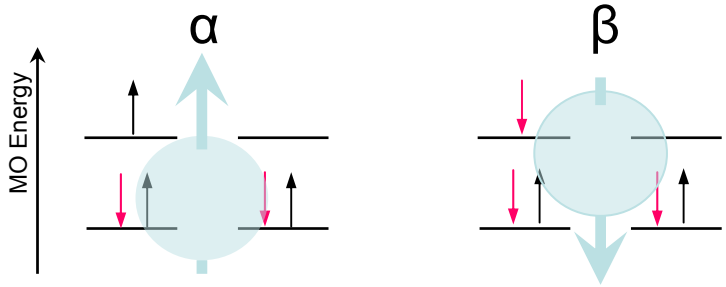

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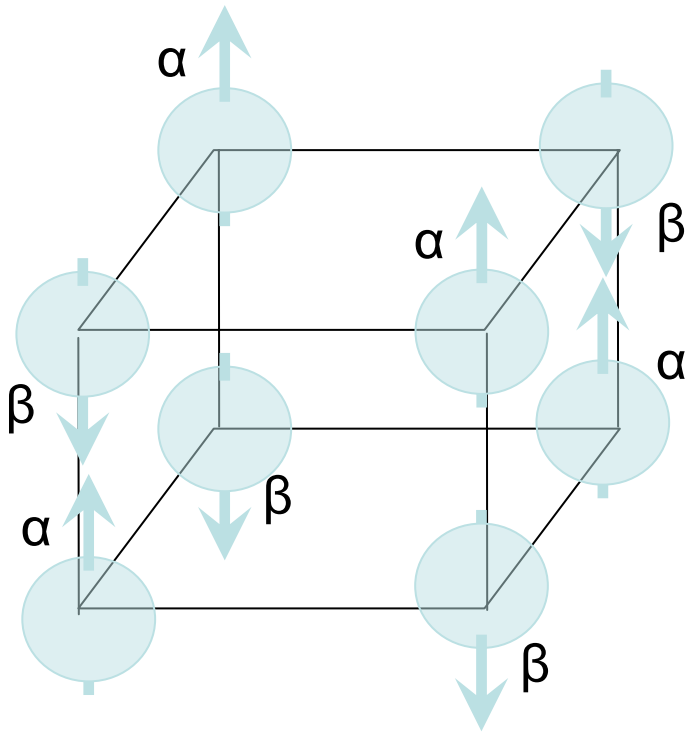
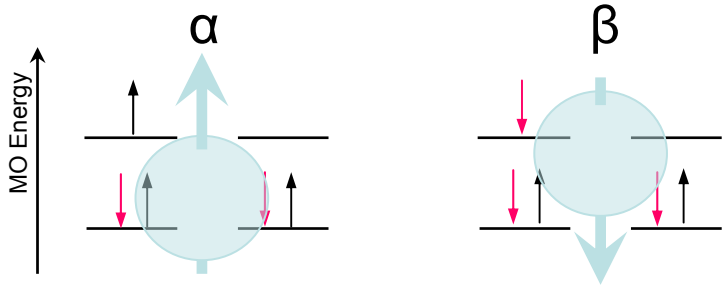
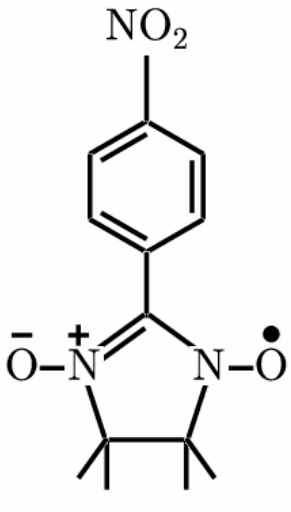




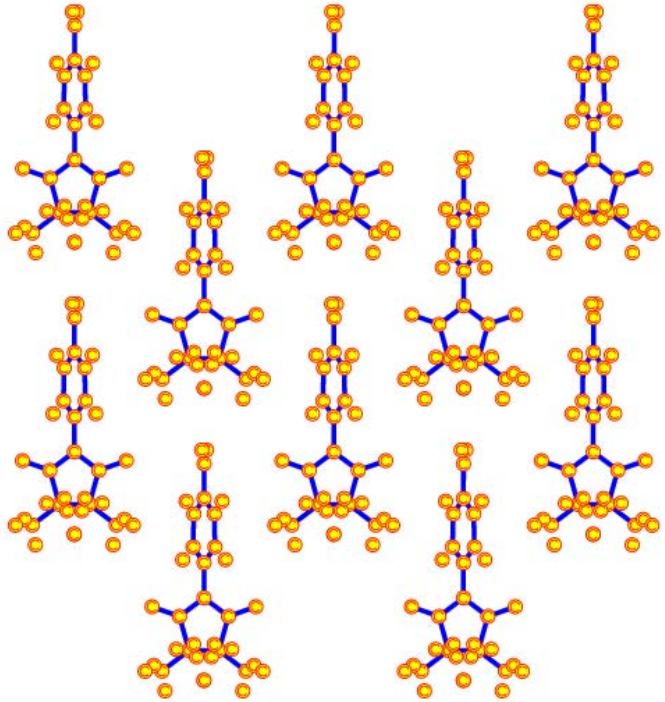
Is ferromagnetic aligning impossible?

3- **Organic-Based Magnets**



p-NPNN

Minora Kinoshita, Japan, 1991



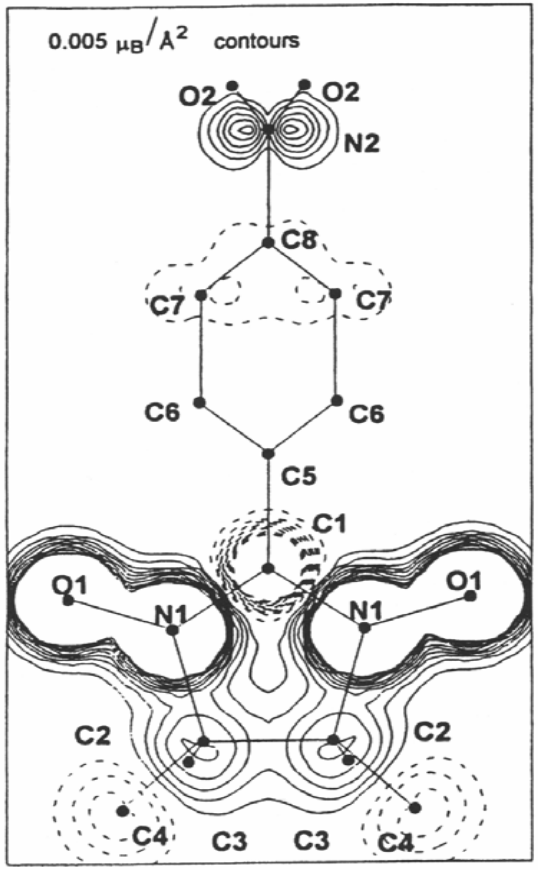
The first organic ferromagnet with T_c=0.67 K

Only the *β*-phase of *p*-NPNN is ferromagnetic

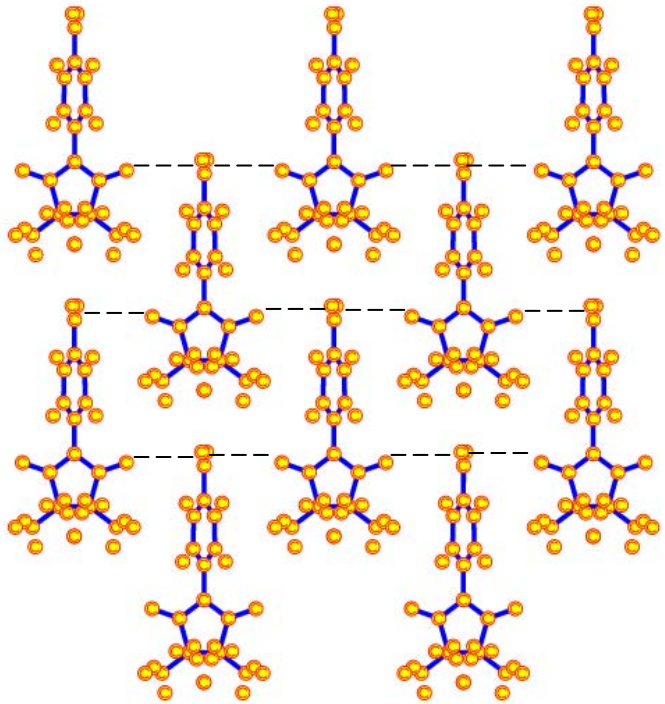
Kinoshita, M. et al.; *Chem. Phys. Lett.* **1991**, *186*, 401

3- **Organic-Based Magnets**

Spin density map of *p*-NPNN



β-phase

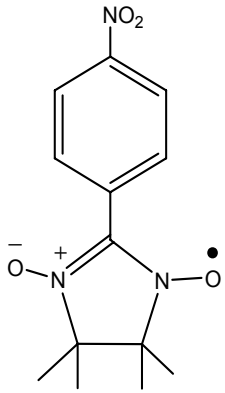


Tc=0.67 K

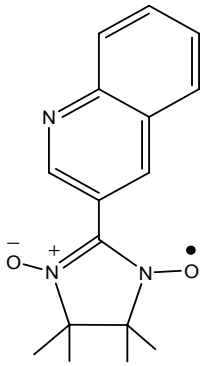
Zheludev A, Ressouche E, Schweitzer J, Wan M and Wang H. *J. Magn. Magn. Mater.* **1994,** *135,* 147

3- **Organic-Based Magnets**

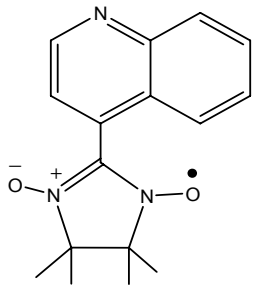
Some rational designs based on NITR



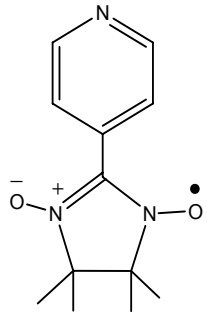
p-PYNN



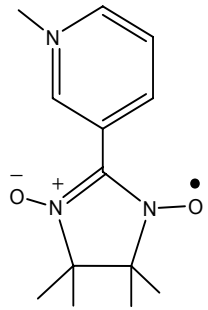
3-QNNN



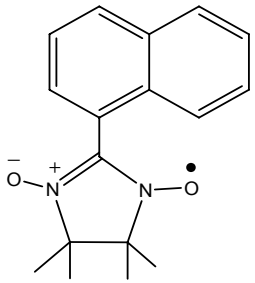
4-QNNN



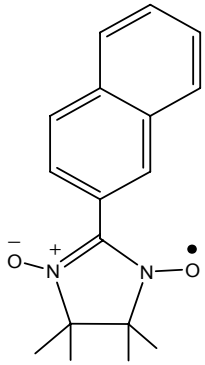
p-PYNN



m-MPYNN



1-NAPNN

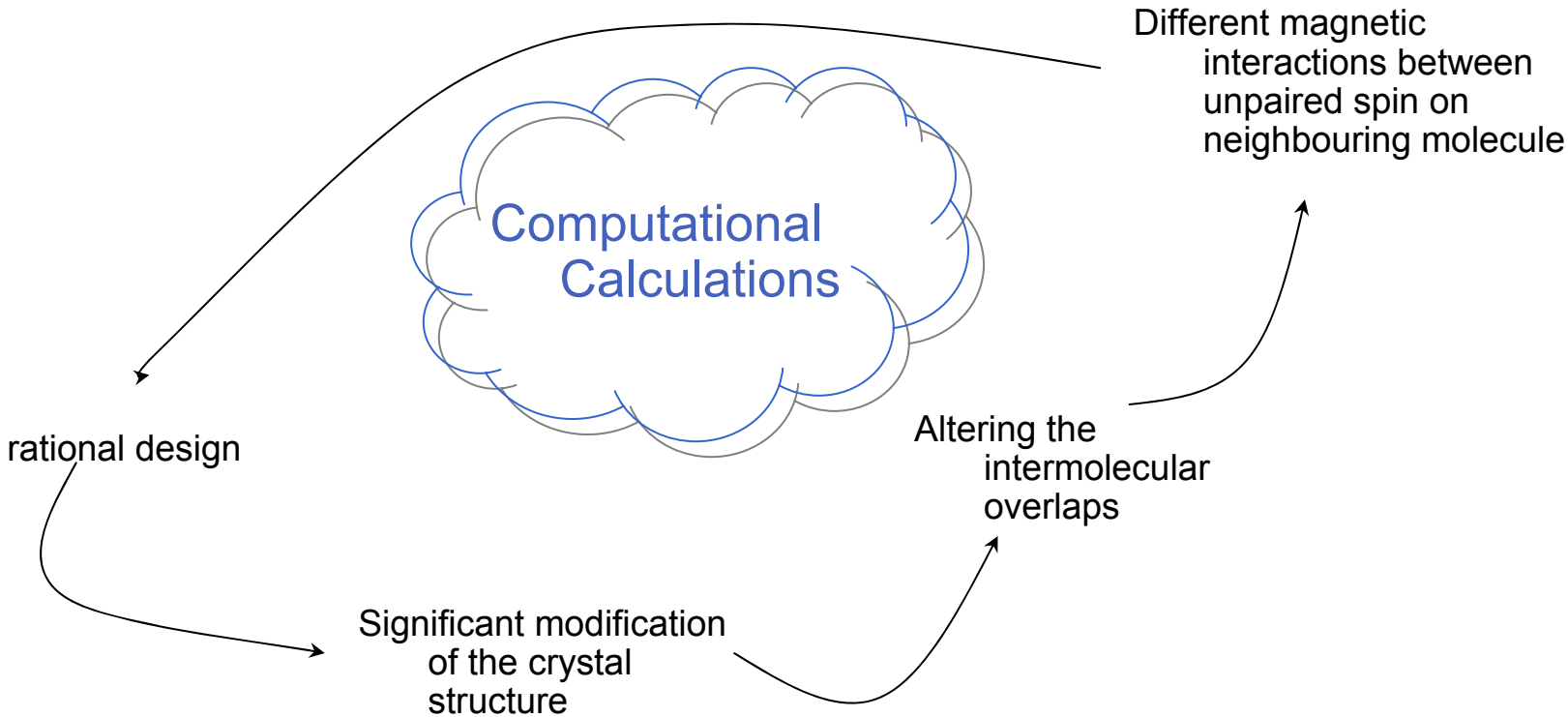


2-NAPNN

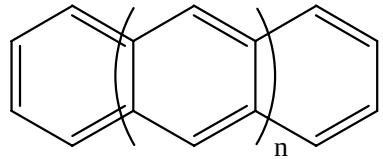
Pratt, F. L. et al., *Synth. Met.* **1993**, *61,* 171
Blundell, S. J. et al., *Hyperfine Interact.* **2001**, *133,* 169

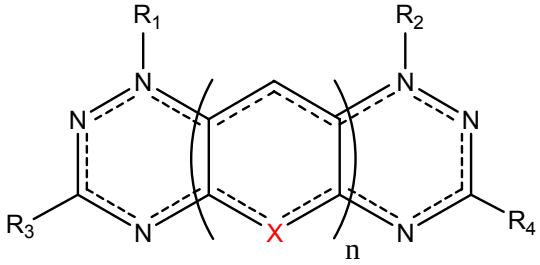
3- **Organic-Based Magnets**

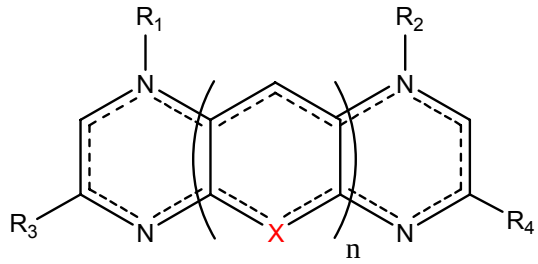
Rational Design of Organic Magnets



Promotionsthema







X = C, N

R_1, R_2, R_3, R_4 = EDG, EWG

„ Rationale Synthese und theoretisches Verständnis von zwitterionischen Oligoazaacenen-

Organische Materialien mit geringer Singulett-Triplett-Energieaufspaltung “

3- **Organic-Based Magnets**

Several angles, which need to be explored:

Primery Goals of our Research:

i. A better undrestanding of the fundamental principles, which govern macroscopic magnetic behaviors

Overlap and orthogonality effect

Spin delocalisation effect

Spin polarisation effect

A deeper undrestanding of how the electronic properties of molecular systems relate to their physical characterictics

ii. Designing new organic architectures with desired properties (based on open-shell units)

The properties of the molecule itself

Control interactions between the spin carriers (molecules)

Stability

3- **Organic-Based Magnets**

Potential applications:

Molecular Magnets As A Quantum Memory Device

- Utilize the spin eigenstates as qubits
- The Capabilities of This Device:

  „ 1 bit/molecule in 2D: 100 tera-bit/in^2 „

- Read-in, decode, read-out time of 10^{-10} s
- Limitation of technology ~ S=10,000

3- Organic-Based Magnets

Perspectives

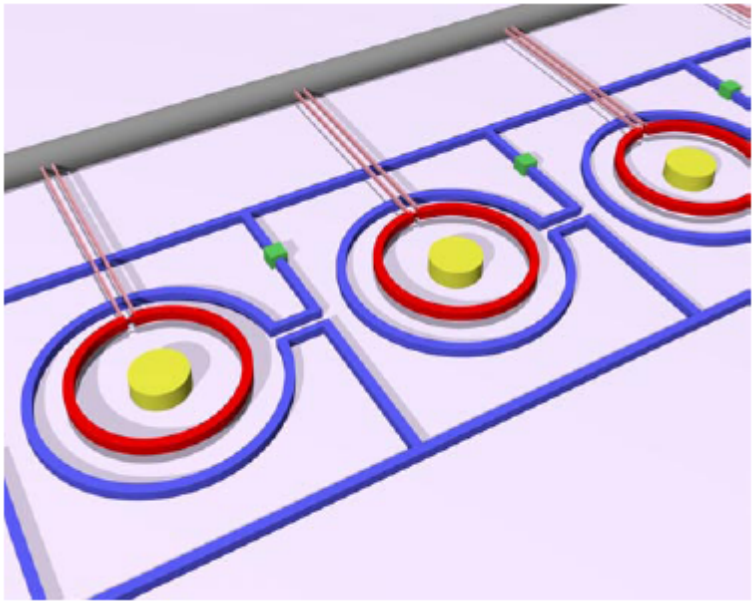


Figure 3. A schematic example of the coupled controlled qubit realization. The magnetic qubits (clusters/particles, yellow) are arranged in a one-dimensional lattice and coupled to the superconducting loops of micro-SQUID (red) circuits as shown. The coupling circuits (blue) contain Josephson switches (green). (This figure is in colour only in the electronic version, see `www.iop.org`)

quantum tunnelling of the spin of the molecular cluster/particle is suppressed. In this case the classical picture of the $|1\rangle$ state (the excited state) is the uniform precession of the magnetic

State preparation. State preparation (and indeed the operation of magnetic cluster qubits) must be realized at a temperature significantly lower than the energy gap, Δ, between the states $|0\rangle$ and $|1\rangle$. The typical gap for case (1) is of the order of a few kelvin, while in case (2) the gap may be controlled by applying an external magnetic field perpendicular to the anisotropy axis of the molecular cluster. The operation of a magnetic cluster qubit must therefore be done in the kelvin down to millikelvin temperature range. A system of case (1) qubits allowed to attain equilibrium at such a temperature is thus effectively prepared in the state $|0000\ldots\rangle$. Clearly the actual system state will be a thermal density operator, so there will be small contributions with excited qubits (and much smaller corrections with the cluster spin(s) in states outside the truncated space which forms the effective qubit(s) Hilbert space). These corrections can be calculated from the system parameters and the temperature and will be damped by an appropriate Boltzman factor.

A case (1) qubit in state $|0\rangle$ subject to a sudden change in external magnetic field perpendicular to the easy axis of the molecular cluster (which changes the tunnelling magnitude to that appropriate for case (2)) is effectively subject to a sudden basis change. In the new basis the state is an equal-weight superposition of $|0\rangle$ and $|1\rangle$. Such superposition preparation has already effectively been achieved for non-interacting ensembles [43, 44].

J. Tejada et al, Nanotechnology, **2001**, *12*, 181-186

Perspective:

Molecule-Based Magnets

- New phenomena observed, not in conventional magnets
- bio-compatible alternative to conventional magnets
- Low-cost, Light-weight, low-temperature
- flexible syntheses

- desired and multifunctional properties (magnetic, conductive, optic …)

Summery

	atom-based magnets	molecule-based magnets
Element magnet	**atoms**	**molecules**
Proporation	**Physical engineering**	**Chemical engineering**
Interactions	**Direct exchange**	**Superexchange**
Magnetic characteristic	**Soft, hard**	**Soft**
Other characteristics	**limited**	**unlimited**

Tehran

Sharif University of Technology

Tehran in night


Bible History Online

Acknowledgments

Prof. Dr. Schreiner Prof. Dr. J. Ipaktschi

AG-Prof. Schreiner Prof. Dr. D. Boghaei (Sharif University of Technology)

Thank you for your attention