

Quick reminder about magnetism

Laurent Ranno
Institut Néel CNRS-Univ. Grenoble Alpes

laurent.ranno@neel.cnrs.fr

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Magnetism : Why ?

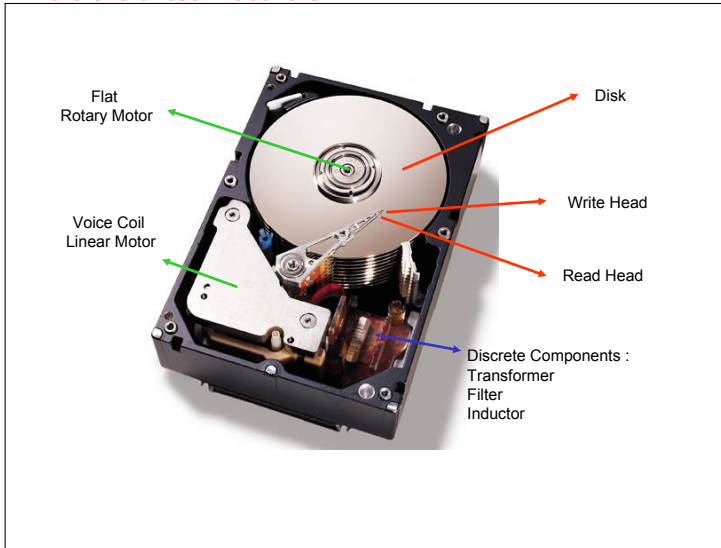
What is special about magnetism ?

All electrons are magnetic

Vast quantity of magnetic materials

Many magnetic configurations and magnetic phases
and wide range of applications

Where are these materials?



Many **different materials** are used : oxides, elements, alloys, films, bulk

Many **different effects** are exploited : high coercivity, evanescent anisotropy, magnetoresistance, antiferromagnetism, exchange bias

...

All need to be understood in detail

- to improve the material properties
- to imagine/discover new materials / new effects / new applications
- to test ideas in great detail

You can build a model magnetic system to test your ideas.

In this lecture I will review some basic concepts to study magnetism

- Origin of atomic magnetic moments
- Magnetic moments in a solid
- Interacting Magnetic moments
- Ferromagnetism and Micromagnetism

Atomic Magnetism

Electrons are charged particles (fermions) which have an intrinsic magnetic moment (the spin).

Electronic magnetism is the most developed domain but **nuclear magnetism** is not forgotten :

Negligible nuclear magnetisation but ...

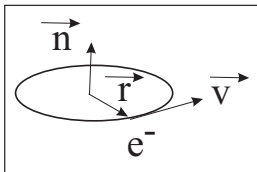
it has given birth to **NMR, MRI** which have a huge societal impact

A **neutron beam** (polarised or not) is a great tool to study magnetism (see Laurent Chapon's lecture)

Today I will restrict my lecture to electronic magnetism

Orbital Magnetic Moment

Electrons are charged particles :



one electron on its atomic orbit = current loop = coil

Its **orbital magnetic moment** $\vec{\mu}_{orb}$ is :

$$\vec{\mu}_{orb} = S \cdot I \vec{n} = \pi r^2 \cdot \frac{-ev}{2\pi r} \vec{n} = -\frac{rve}{2} \vec{n}$$

Its **angular momentum** is $\vec{\sigma}_l$:

$$\vec{\sigma}_l = \vec{r} \wedge \vec{p} = \vec{r} \wedge m\vec{v} = mrv\vec{n}$$

the orbital magnetic moment and the angular momentum are proportional :

$$\vec{\mu}_{orb} = -\frac{e}{2m}\vec{\sigma}_l = \gamma\vec{\sigma}_l$$

They point in opposite directions.

γ is the **gyromagnetic factor**

First source of atomic magnetism : the orbital motion

Spin Magnetic Moment

The electron is a quantum particle :

$$\frac{\hbar^2}{2m} \nabla^2 |\Psi(t)\rangle + V |\Psi(t)\rangle = i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle \quad \text{Schrödinger equation}$$

A proper quantum calculation does not modify the previous result

However moments are **quantified**

$$\vec{L} = \vec{r} \wedge \vec{p} \text{ gives } L^2 |\Psi\rangle = l(l+1)\hbar^2 |\Psi\rangle$$

To properly describe the electron, one needs the relativistic Dirac equation, which introduces a new quantity without classical equivalent : **the spin**

Second origin for atomic magnetism : spin

From one electron magnetism to atom magnetism

To define an **atomic electronic state** 4 quantum numbers are required :

n_i : the **main quantum number**

Each n_i corresponds to an electronic **shell** named K, L, M, N ...

l_i is the **orbital angular momentum quantum number**

l_i can be chosen between 0 and $n_i - 1$

l_i characterises the **electronic sub-shell**

l_i	0	1	2	3
	s	p	d	f

m_l is the magnetic quantum number

$$-l \leq m_l \leq l$$

Finally

s is the spin quantum number

For an electron (fermion $s=1/2$) it can be : $\sigma_z |\Psi\rangle = \pm \frac{1}{2} \hbar |\Psi\rangle$

Each electronic state is characterised by its 4 quantum numbers

To describe the atom, the filling of each electronic state has to be defined.

Pauli Exclusion Principle

How to fill the electronic states ?

The lowest energy configuration must obey :

Pauli principle(1925)

Electrons are fermions, so one electron at most in each quantum state $(n_i, l_i, m_i, \sigma_i)$.

Hund's rules (1927)

One defines the **atomic spin moment** S

$$\vec{S} = \sum_i \vec{\sigma}_i$$

1st Hund's rule : **S maximum**, taking Pauli principle into account.
(=minimizing Coulomb interaction between electrons)

The **atomic orbital momentum** L

$$\vec{L} = \sum_i \vec{m}_i$$

2nd Hund's rule **L maximum**, keeping Pauli and 1st rule.

Hund's rules

Tb^{+3} is $4f^8$

m_i	-3	-2	-1	0	1	2	3
$\sigma = \frac{1}{2}$	↑	↑	↑	↑	↑	↑	↑
$\sigma = -\frac{1}{2}$	↓						

so $L=3$ and $S=3$

Not enough to get the **total atomic angular momentum**

$$\vec{J} = \vec{L} + \vec{S}$$

The **3rd** Hund's rule couples \vec{L} and \vec{S}

Physical origin : **spin-orbit coupling** $H = \lambda \vec{L} \cdot \vec{S}$, $\lambda \propto \frac{\partial V_{elec}}{r \partial r}$

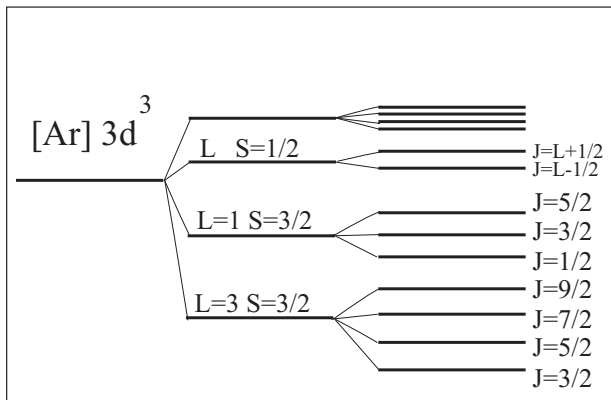
\vec{L} and \vec{S} are antiparallel, i.e.

$$J = |L - S| \text{ for a filling } < 50\%$$

\vec{L} et \vec{S} parallel, i.e.

$$J = L + S \text{ for a filling } > 50\% \text{ (here } J=6)$$

Multiplets



The ground state is occupied, often the excited states are very/too high in energy.

If the excited state can be thermally populated : T-dependent J number

Bohr magneton

Using classical mechanics

$$\vec{\mu}_{orb} = -\frac{e}{2m}\vec{\sigma}_l$$

Quantification of the momentum :

$$\vec{\sigma}_l = \hbar\vec{l}$$

Leads to **quantification** of the orbital **magnetic moment** :

$$\vec{\mu}_l = -\frac{e\hbar}{2m}\vec{l} = -\mu_B\vec{l}$$

μ_B is the **Bohr magneton**, it is the smallest possible value for an electron magnetic moment.

$$\Rightarrow 1\mu_B = 9.27 \cdot 10^{-24} \text{ Am}^2$$

It is the relevant unit to measure atomic magnetic moments.

Orbital :

$$\vec{\sigma}_l = \hbar \vec{l}$$

$$\vec{\mu}_l = -\mu_B \vec{l}$$

Spin :

$$\vec{\sigma}_s = \hbar \vec{s}$$

$$\vec{\mu}_s = -2\mu_B \vec{s}$$

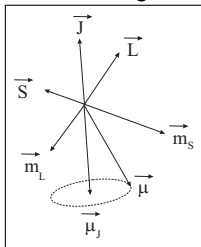
Spin and orbit do not have the same gyromagnetic factor

Atomic magnetic moments

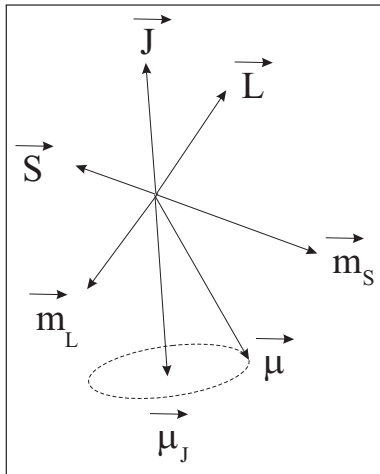
For an atom (L, S, J), there is :

an atomic orbital magnetic moment $\vec{m}_L = -\mu_B \vec{L}$

an atomic spin magnetic moment $\vec{m}_S = -2\mu_B \vec{S}$



Atomic magnetic moments



$$\vec{m}_L + \vec{m}_S = -\mu_B(\vec{L} + 2\vec{S})$$

$\vec{m}_L + \vec{m}_S$ is not colinear with $\vec{J} = \vec{L} + \vec{S}$

The total atomic magnetic moment is not proportional to \vec{J}

J is a good quantum number for the Hamiltonian.

The magnetic moment measurable value is its projection along \vec{J}

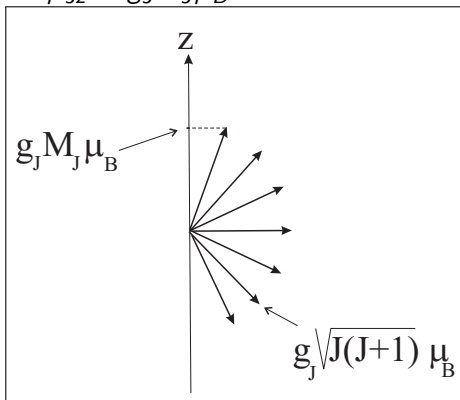
One can define the **Landé factor** g_J

$$\vec{\mu}_J = -g_J\mu_B\vec{J}$$

$$g_J = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

Degeneracy of moment

Possible value for $\mu_{Jz} = g_J M_J \mu_B$ are :



M_J between $-J$ and $+J$

degeneracy = $2J+1$

Atom in a magnetic field

To lift the degeneracy, a **magnetic field** can be applied.

When an electromagnetic field is applied, the electron Hamiltonian has to be modified

$$H = \frac{p^2}{2m} \text{ becomes } H = \frac{1}{2m}(\vec{p} - q\vec{A})^2 + q\phi$$

One can expand :

$H =$ kinetic energy + Zeeman term + diamagnetic term

Atom in a magnetic field

$$H = \frac{1}{2m}(\vec{p} - q\vec{A})^2 + q\phi$$

In a uniform field ($\parallel z$) we can choose $\vec{A} = -\frac{1}{2}\vec{r} \wedge \vec{B}$

H = kinetic energy + Zeeman term + diamagnetic term

Zeeman $H_{Zeeman} = \frac{-q}{2m}\vec{L} \cdot \vec{B} = -\vec{\mu} \cdot \vec{B}$ + similar expression for spin.

and **diamagnetic** $H_{dia} = \frac{q^2}{2m}A^2 = \frac{q^2 B^2}{8m}(x^2 + y^2)$

The diamagnetic part explains the magnetic response of non magnetic materials (e.g. silicon) ($\chi < 0$, proportional to electron number and orbit area, T-independent).

Special atomic configurations

maximum moment that can be measured : $g_J J \mu_B$

For a filled sub-shell :

$S=0$, $L=0$ so $J=0$

No magnetic moment

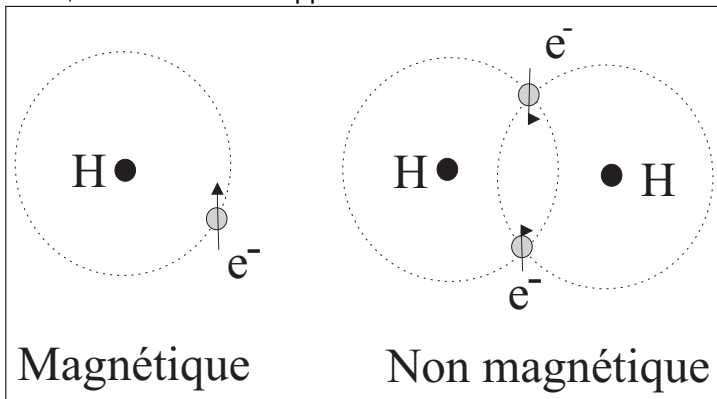
For a half-filled subshell :

$L=0$, $J=S$

No orbital moment

Atom to Solid

In a solid, chemical bonds appear



Elements magnétiques à l'état solide
ordre à basse température

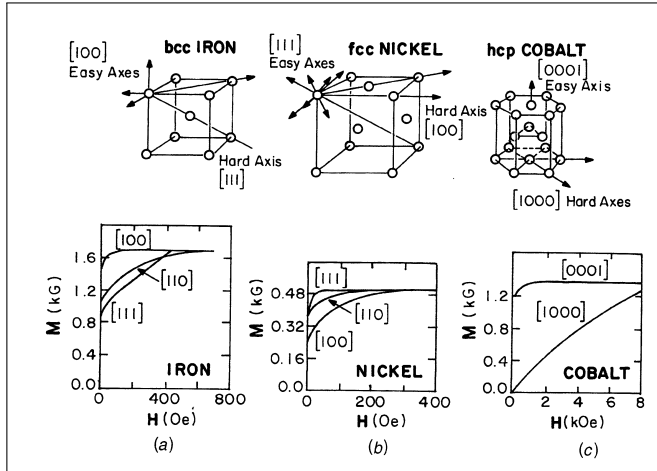
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
* Lanthanides			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
** Actinides			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

ferro antiferro ferri

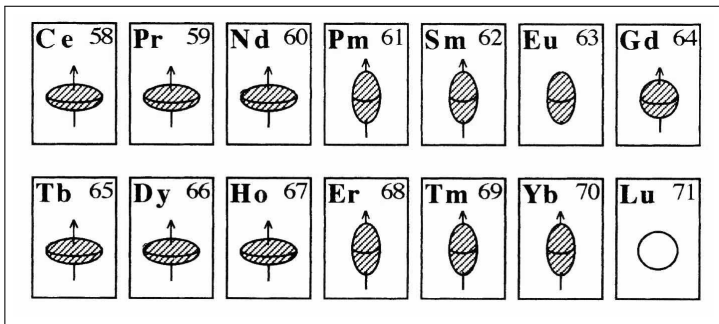
Two series are mostly studied : 3d transition metals and 4f rare-earths but also 4d (Pd, Ru), 5d (Pt, Re), 5f (U) ...

Magnetic Atoms in a Solid

For a sphere of magnetic material (= isotropic shape) experimentally, there exists : **easy axes** to magnetise and **hard axes**



Crystal Electric Field



Partially filled electronic shell \Rightarrow **non spherical sub-shell.**

Effect of the crystalline environment (Coulomb repulsion) =
Crystal Electric Field (CEF)

Preferred crystallographic axes to rotate the electronic density (the
orbits)

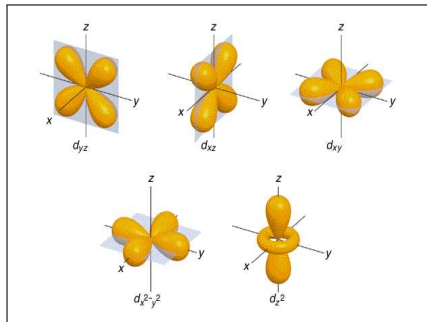
Spin-orbit coupling $\Rightarrow \vec{S}$ also rotates to easy axes
CEF modifies the configuration (lift sub-shell degeneracy)

Atomic orbitals

3d orbitals

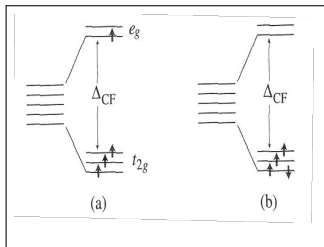
Spherical harmonics $Y_m^l(\theta, \phi)$ is a good base for isotropic environments.

The e_g, t_{2g} base is more suitable for a cubic CEF.



The two e_g (bottom) and three t_{2g} (top) orbitals. g stands for inversion symmetry, e and t come from group theory.

Atomic orbitals



Degeneracy is lifted in a cubic charged environment.

High spin or **Low spin** configuration depending on CEF vs U.

Since $\langle e_g | L_z | e_g \rangle = \langle t_{2g} | L_z | t_{2g} \rangle = 0$, there is **quenching** of the orbital moment

True for 3d atoms (not for 4f rare earths because 4f is an inner subshell, less influence from neighbours)

Magnetocrystalline energy is described using a formalism adapted to the **crystallographic symmetry**. It can be written using a complete basis (Stevens operators) or a phenomenological expression (a few K_i ; **magnetocrystalline coefficients** dependent on available data)

Cubic symmetry :

$$E_{an.mc.}(directioncosines) = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2\alpha_1^2\alpha_2^2\alpha_3^2$$

Uniaxial symmetry :

$$E_{an.mc.}(\theta) = K_1 \sin^2 \theta + K_2 \sin^4 \theta$$

Interacting moments

Experimentally, magnetic order appears in some solids
magnetic moments interact

What are the possible interactions ?

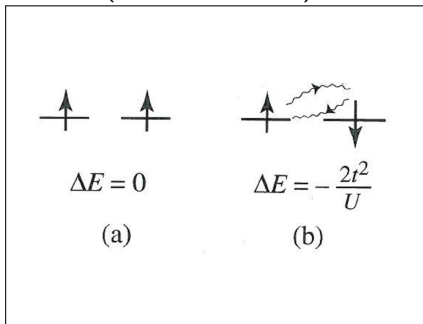
- dipolar (dipole-dipole : $1\mu_B$ creates $\approx 1\text{ Tesla} \approx 1\text{K}$)
- exchange

insulators (localised magnetic moments = **localised magnetism**)
will not be modelled the same way as metals (band magnetism =
itinerant magnetism)

Exchange can be **direct** or **indirect** : oxygen atoms Fe-O-Fe
(**super-exchange, double exchange**), conduction band to couple
localised spins in rare-earth metals (**RKKY like**),
Dzyaloshinskii-Moriya chiral 90° interaction)

Magnetic order

Microscopic mechanism (Hubbard model)



$$H = -\sum t_{ij} \cdot c_{i\sigma}^+ c_{j\sigma} + U \sum n_{i\uparrow} n_{i\downarrow}$$

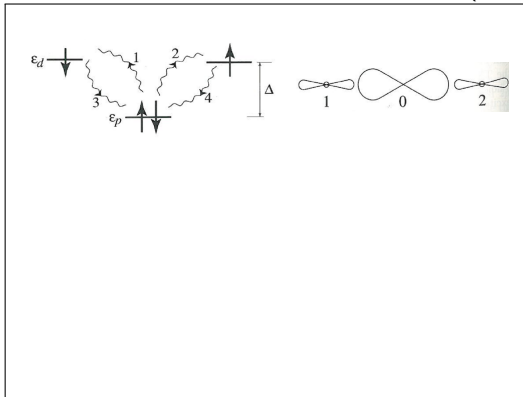
hopping t ($\Delta x \cdot \Delta p > h$, more delocalised = less kinetic energy)
and Coulomb repulsion U

One can then build an Effective Heisenberg Hamiltonian :

$$H = J \sum S_i S_j$$

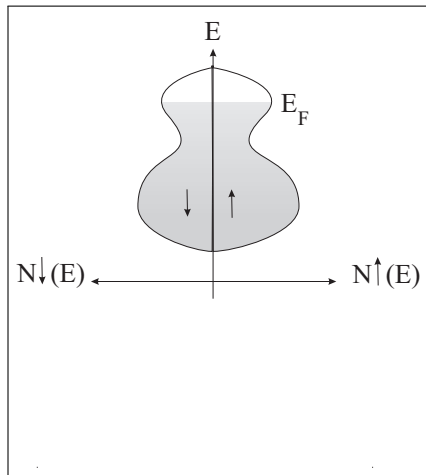
Superexchange

In oxides **indirect coupling** between two magnetic ions will depend on the geometry of the M-O-M bond (i.e. **orbital overlaps**).

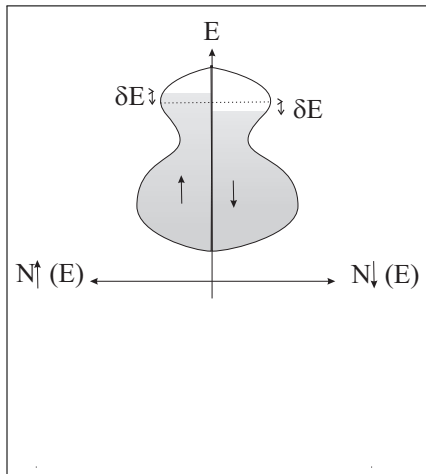


Non magnetic band structure

For a non magnetic metal



Magnetic band structure



$$\Delta m = 2\mu_B \mathcal{N}(E_F) \delta E$$

$$\Delta m = 2\mu_B \mathcal{N}(E_F) \delta E$$

If δE is created by applying a magnetic field H_0 then the magnetic susceptibility is :

$$\chi = \frac{\Delta m}{H} = 2\mu_0 \mu_B^2 \mathcal{N}(E_F)$$

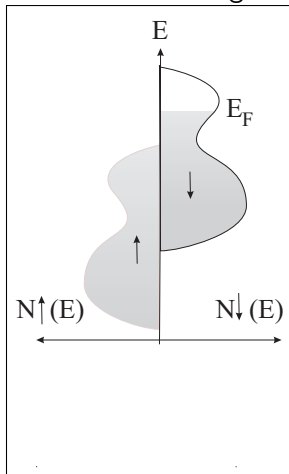
Such a susceptibility does not depend on temperature but on the density of conduction electrons (**Pauli paramagnetism**).

A spin-dependent electron interaction can also create δE .

If the interaction gain is larger than the kinetic energy loss then the metal is magnetic.

Band structure : nickel

Band ferromagnetism creates a non integer magnetic moment.



Ni up : 5 electrons and Ni down 4.4 electrons $\Rightarrow 0.6\mu_B$

When one band is full : **strong ferromagnet**

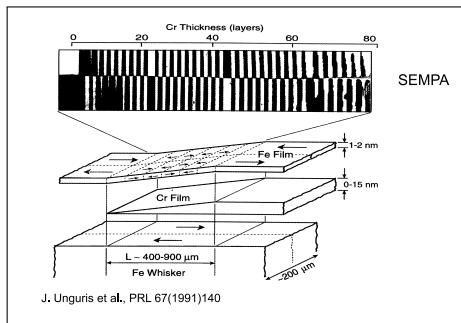
Interlayer coupling : RKKY

Indirect exchange coupling in a metallic system : **RKKY interaction** spin-polarised conduction band will propagate the spin information to a second spin or layer through a non magnetic medium.

$$J = \frac{\cos(2.k_F.r)}{r^3}$$

oscillating coupling through a metallic spacer. lengthscale k_F finite, discrete thickness effect, period becomes a few monolayers.

Interlayer coupling : RKKY



Oscilating spin polarisation will create undirect exchange between spins.

It can lead to noncolinear orders. It is the exchange mechanism in metallic rare-earths.

Used also to create **artificial antiferromagnet** : Co/Ru/Co

Mean Field Model : Paramagnetism

Independent localised spins at temperature T (Brillouin paramagnetism)

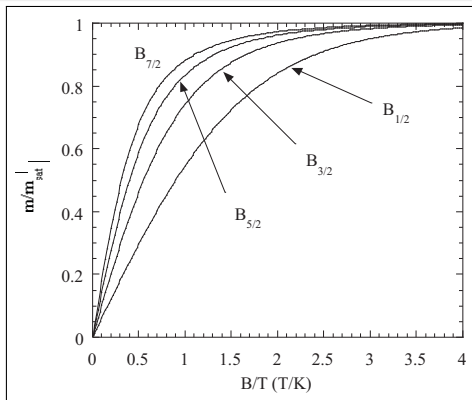
When applying a magnetic field, the probability to fill the different magnetic states follows a Maxwell distribution given by the ratio Zeeman energy/Thermal energy

$$M = M_{sat} B_J(x) \text{ avec } M_{sat} = Ng_J J \mu_B \text{ and } x = \frac{g_J J \mu_0 \mu_B H}{kT}$$

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\frac{x}{2J}$$

Brillouin function

Mean Field Model : Brillouin Paramagnetism



$$\chi = \frac{M}{H} = \frac{C}{T}$$

$$\chi = \frac{m}{H_0} = Ng_J^2 J(J+1) \frac{\mu_B^2 \mu_0}{3kT}$$

Curie law, C is the Curie constant

With interactions : The interaction from the other atomic moments is proportional to their magnetisation mean value.

$$\vec{H}_m = \lambda \cdot \langle S \rangle$$

$$\text{and } x = \frac{g_J J \mu_0 \mu_B H_i}{kT} \text{ with } H_i = H + H_m$$

$$\text{so } x = \frac{g_J J \mu_0 \mu_B (H + \lambda M)}{kT}$$

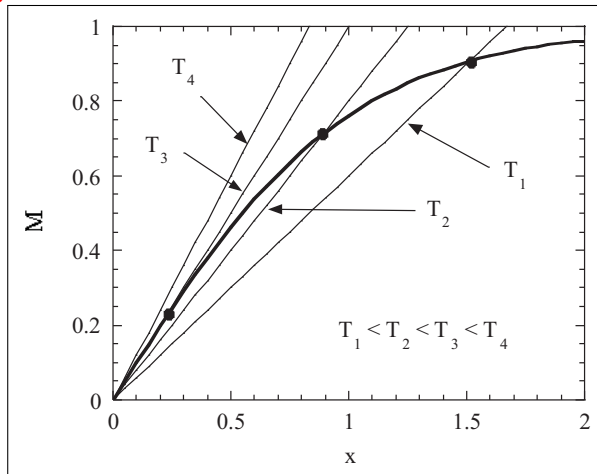
At fixed temperature T and field H , $M(H,T)$ is given by the simultaneous resolution of both equations :

$$M = M_{sat} B_J(x) \quad (1)$$

$$M = \frac{kT}{\lambda g_J J \mu_0 \mu_B} x - \frac{H}{\lambda} \quad (2)$$

Graphical resolution

When $H = 0$, the line goes through zero. Depending on T ($T < T_{critical}$) it allows to get a **spontaneous magnetisation** and a **ferromagnetic order**



Identifying initial slopes, one gets T_c

$$T_c = \lambda C$$

T_c is proportional to λ and to Curie constant C

When $T=0$ one gets the saturation magnetisation

$$M_{sp}(T = 0) = M_{sat} = Ng_J J \mu_B$$

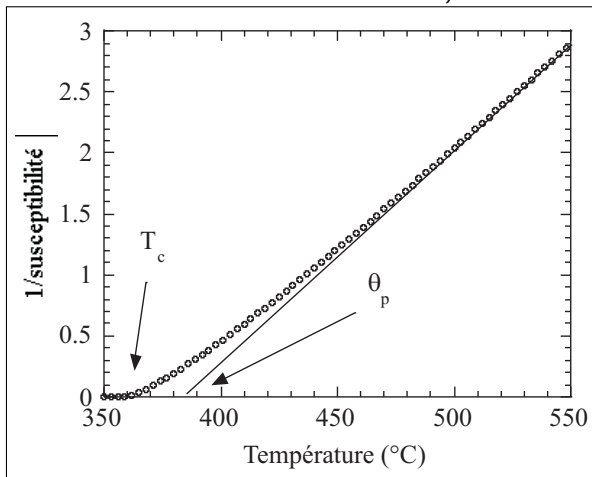
When H is not zero, even at high T , there is a non zero magnetisation. Susceptibility is χ

$$\chi = \frac{M}{H} = \frac{C}{T - T_c}$$

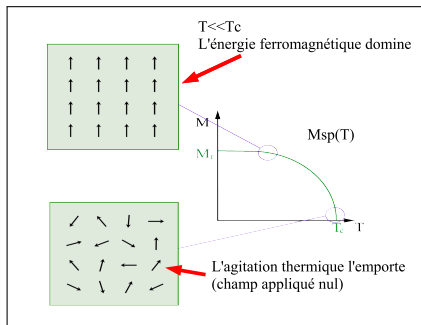
Curie-Weiss law

In this mean field model, $T_c = \theta_p$

Mean field models do not work close to transition T_c (no fluctuations in the model).



Spontaneous Magnetisation



Non equivalent sublattices may exist, competing exchange interactions, non collinear ones ...

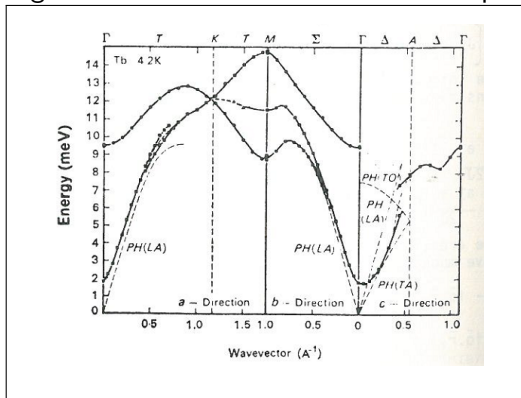
Antiferromagnetism : 2 identical lattices antiferromagnetically coupled. No net M but AF long range order up to the Néel Temp.

Ferrimagnetism : 2 (or more) non equivalent lattices, AF-coupled
Commensurate, non-commensurate, frustrated orders, helicoidal, cycloïdal, multi-q orders are observed in more complex systems.

Excitations

Excitations can disorder the magnetic saturated state (similar to phonon disordering the periodic crystal lattice).

These excitations can be modelled as **spin waves** / magnons and measured using neutron inelastic diffusion for example



Landau-Lifschitz-Gilbert equation

$$\frac{d\mathbf{M}}{dt} = \gamma \mathbf{M} \times \mathbf{H}_{\text{eff}} + \alpha \mathbf{M} \times (\mathbf{M} \times \mathbf{H}_{\text{eff}}) \quad (3)$$

γ the gyromagnetic ratio (1 T = 30 GHz precession)

α the damping constant

\mathbf{H}_{eff} the effective field :

$$\mathbf{H}_{\text{eff}} = -\frac{1}{\mu_0} \frac{\partial E}{\partial \mathbf{M}}$$

The **effective field** includes contributions from the applied field (Zeeman energy), the demagnetizing field (shape anisotropy), magnetocrystalline and exchange energies.

Electron magnetism can be studied using these GHz spectroscopies : **EPR** Electron Paramagnetic Resonance, **FMR** FerroMagnetic Resonance

(**NMR** nuclear magnetism is MHz spectroscopy)

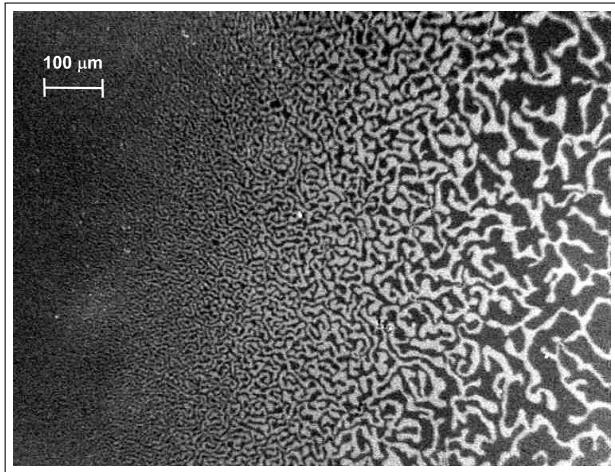
More details about the ferromagnetic state : **Micromagnetism**

For a given sample, its **magnetic configuration** (\vec{M} distribution) depends on the minimisation of the total energy which contains 4 main contributions.

- Exchange energy
- Zeeman energy
- Magnetic Anisotropy energy
- Demagnetising energy

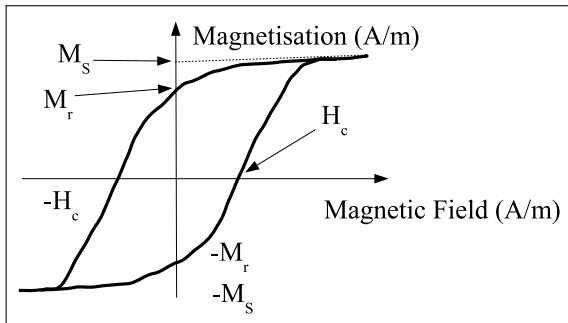
Lengthscale : domain walls

At **remanence** (Zero applied field),
A sample will **demagnetise** due to demagnetising field



Here GdCo film (perpendicular anisotropy) Kerr images

magnetisation reversal



out of equilibrium state
hysteretic in most cases

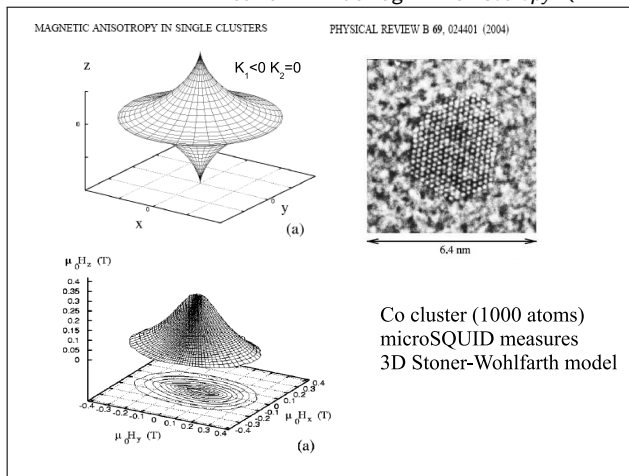
characteristic fields and magnetisation

remanent magnetisation M_r , **spontaneous** magnetisation M_s ,
coercive field H_c

Applied magnetic field H_a vs **total** magnetic field $\vec{H} = \vec{H}_a + \vec{H}_d$

magnetisation reversal : uniform

Minimise : $E = E_{Zeeman} + E_{demag} + E_{anisotropy}$ (no exchange energy)

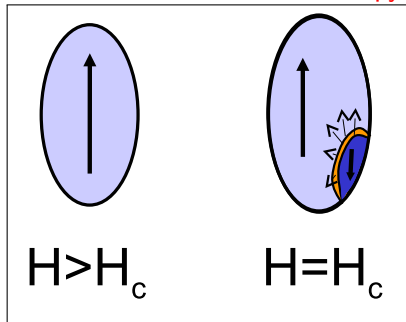


Stoner-Wohlfahrt astroid

magnetisation reversal mechanism

Brown's paradox : M reversal happens very often under applied field (H_c) much smaller than the anisotropy field.

How to overcome the **anisotropy barrier** ?

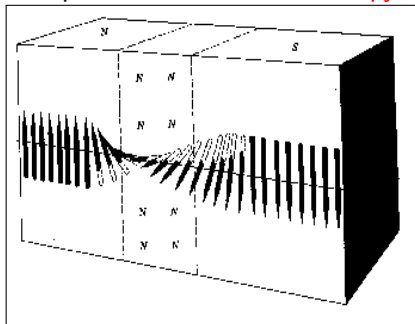


nucleation + **propagation** of a domain wall

Lengthscale : domain wall width

Between domains : a **domain wall**

Competition between **anisotropy energy** and **exchange energy**



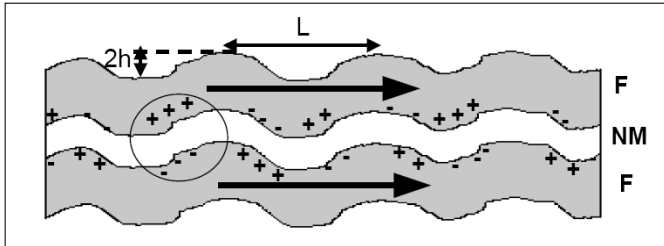
domain wall width δ and wall energy γ

$$\delta(\text{m}) = \pi \sqrt{\frac{A}{K}} \text{ and } \gamma(\text{J/m}^2) = 4\sqrt{AK} \quad (4)$$

Large anisotropy \Rightarrow narrow domain wall (down to a few nm)

Small anisotropy \Rightarrow wide domain walls (up to mm)

Interlayer coupling : Orange peel



Coupling may still exist in “uncoupled” system
orange peel=magnetostatic, **pinholes**

Units

B,H,M,m

B magnetic induction (Tesla)

H magnetic field (A/m)

$$\vec{B} = \mu_0(\vec{H} + \vec{M})$$

m = magnetic moment (Am²)

M = Magnetisation = magnetic moment / unit volume (A/m)

Maxwell equations

$$\text{div } \vec{B} = 0$$

$$\text{rot } \vec{H} = \vec{j} + d\vec{D}/dt$$

S.I. vs c.g.s

1 Tesla = 10 000 Gauss

in vacuum :

B=1 Gauss corresponds to H=1 Oersted

$$\vec{B} = \mu_0 \vec{H}$$