ESRF
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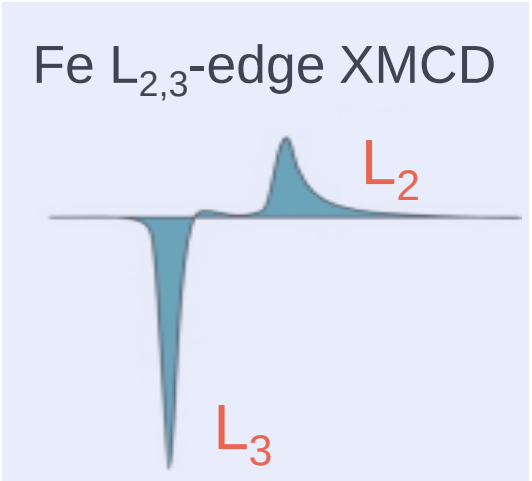
X-Ray Dichroism and Magnetism

Raffaella Torchio

postdoc ID24 BM23
torchio@esrf.fr



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Recipe:

X-RAY DICHROISM AND MAGNETISM

ingrediants:

1. electronic and magnetic structure of atoms and solids
2. X-ray absorption

directions:

what information can I get from X-ray absorption?

how do x-rays become sensitive to magnetism?

what is dichroism?

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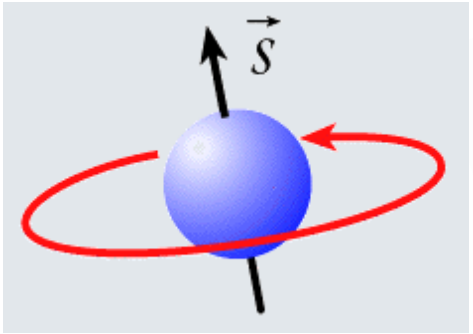
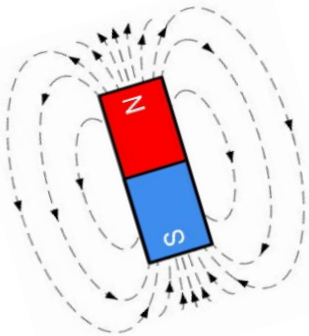
WHY CAN MATERIALS BE MAGNETIC?

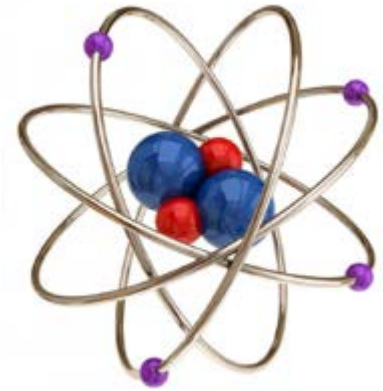
Each electron carries a magnetic moment, i.e. it behaves like a little magnet.

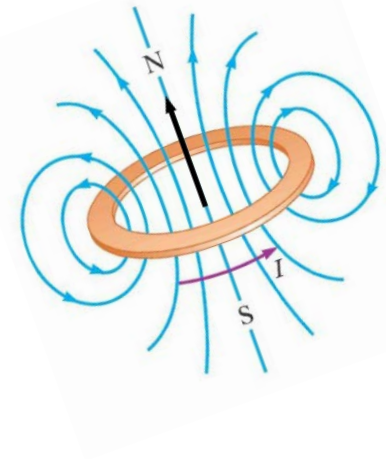
intrinsic magnetic moment: spin

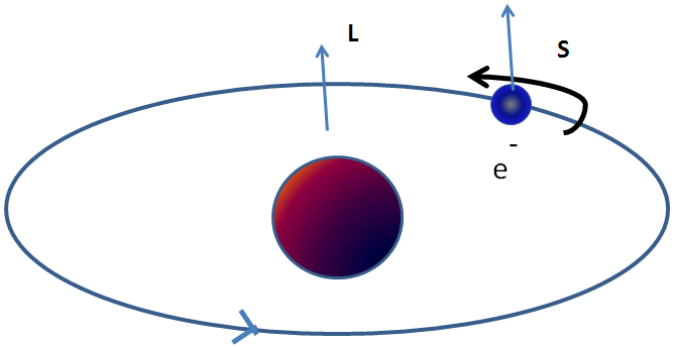
orbital moment











Quantum mechanics:

the electrons in free atoms occupy sharply defined energy levels or ‘shells’

one shell or quantum state is defined by quantum numbers:

n,	l,	m_l,	s,	m_s
pricipal number defines the energy level 1,2,,,,n	orbital angular momentum, shape 0- (n-1) s, p, d, f, g, …	angular momentum projection on a fixed axis (-l, l)	spin angular momentum 1/2	spin momentum projection on a fixed axis +1/2, -1/2

$j = s+l$ total angular momentum

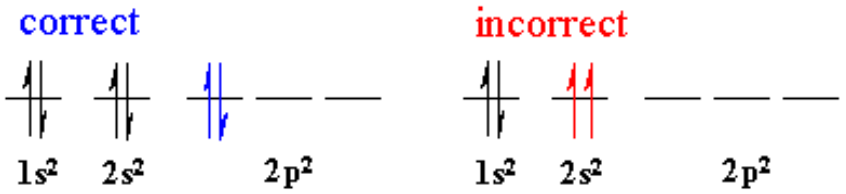
m_j projection on a fixed axis

(s-l; j+l)

many electrons:

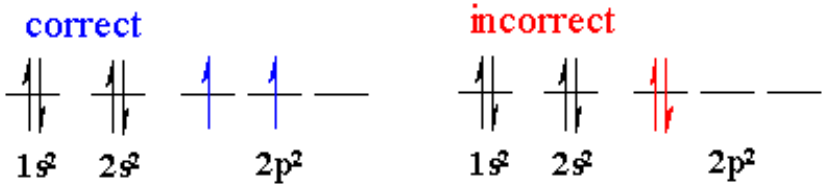
$L, M_L, S, M_S, J, M, M_J$

FILLING UP THE ORBITALS



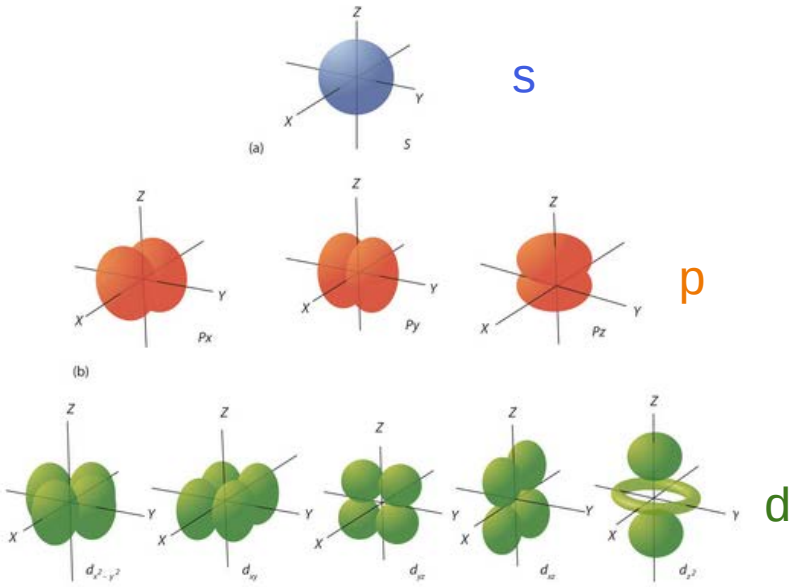
The Pauli exclusion principle

two electrons in an atoms cannot have the same set of quantum numbers

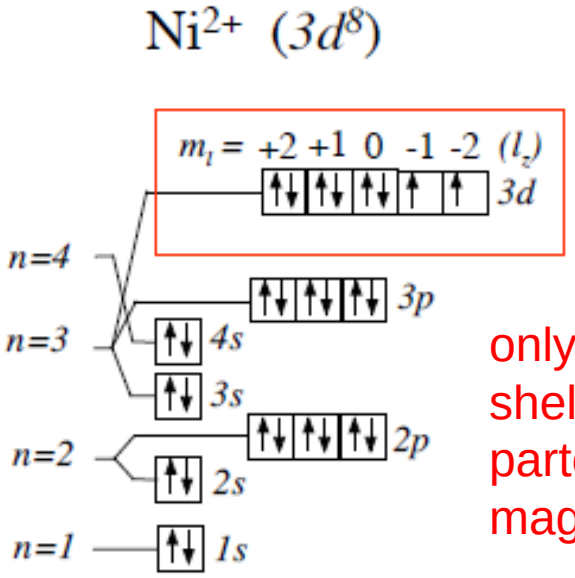


Hund's rule of Maximum Multiplicity

single electrons are placed into each degenerate orbital before they are paired with another electron in the same orbital.



orbital spatial distribution

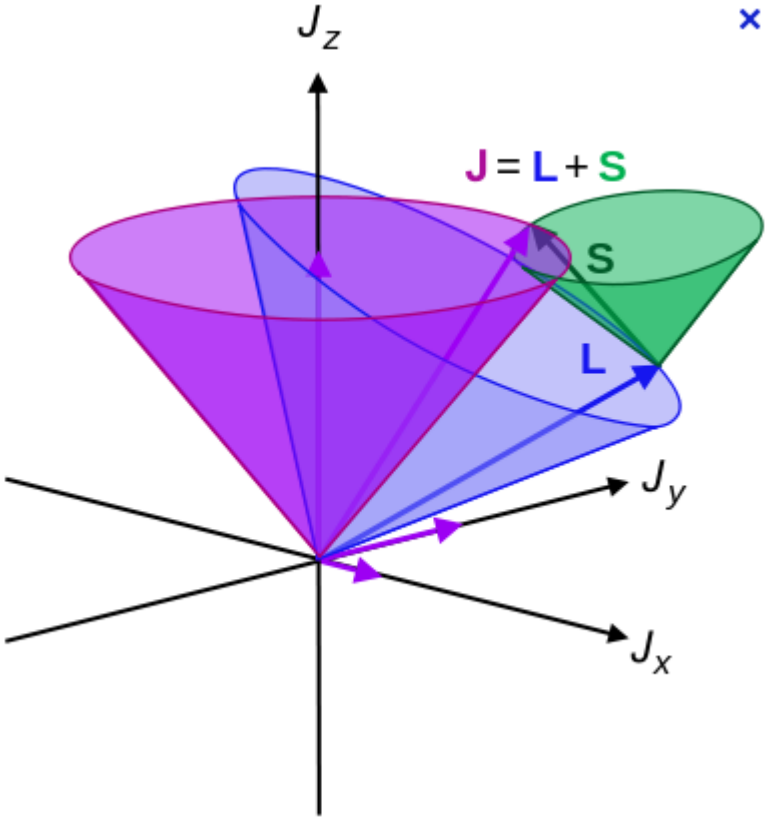


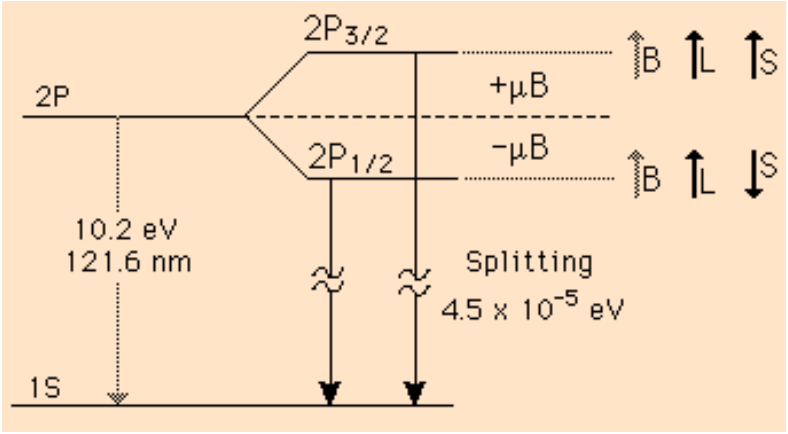
only unfilled shells partecipate to magnetism

SPIN ORBIT INTERACTION

the **spin–orbit interaction** (or **spin–orbit coupling**) is an interaction of a particle's spin with its motion.

The electromagnetic interaction between the electron's spin and the magnetic field generated by the electron's orbit around the nucleus causes a splitting of energy levels.





$J = L + S$

$M_j = L+S;\ L-S$

example: 2P L=1 S= $\pm\frac{1}{2}$

$\rightarrow M_j = \frac{1}{2}; \frac{3}{2}$

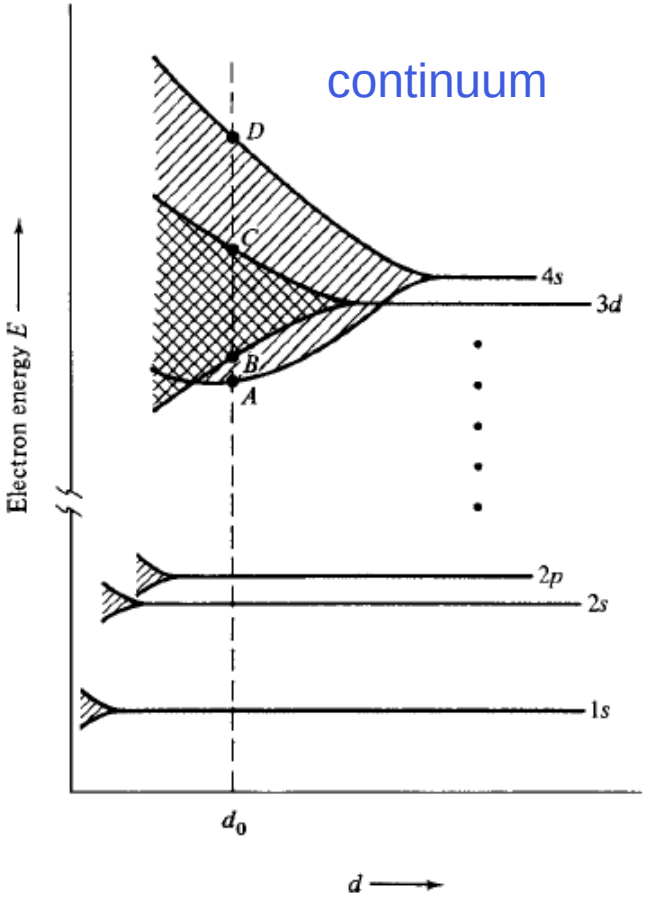
2P → $2P_{\frac{3}{2}}$, $2P_{\frac{1}{2}}$

BAND STRUCTURE: SOLIDS

When N atoms are brought close together to form a solid each level of the free atom must split into N levels, because of the Pauli principle.

The extent of the splitting is different for different levels. In the 3d metals, for example, the outermost electrons are the 3d and 4s; these electron clouds are the first to overlap as the atoms are brought together, and at the equilibrium distance, the 3d and 4s levels are spread into a band.

These bands contain so many energy levels to constitute almost a continuum of allowed energy



MAGNETIC SUSCEPTIBILITY

All materials possess the property of becoming magnetized, or polarized, in the presence of an applied magnetic field, thus altering the applied field.

This property is called magnetic susceptibility χ

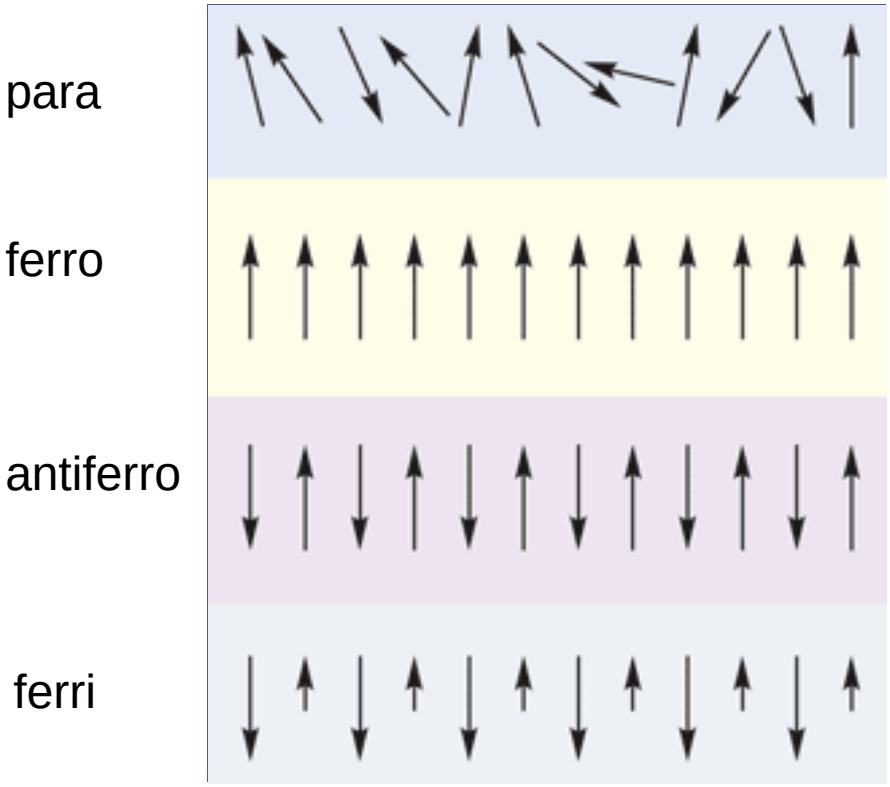
$$M = \chi H$$

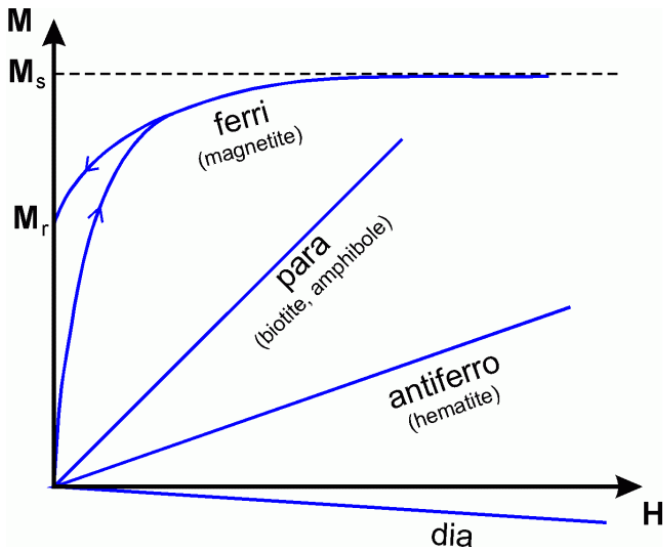
In weak fields, like the Earth's magnetic field, the magnetization is approximately linearly proportional to the magnetizing field H

The magnetization adds to the external field **H**, making the total magnetic induction:

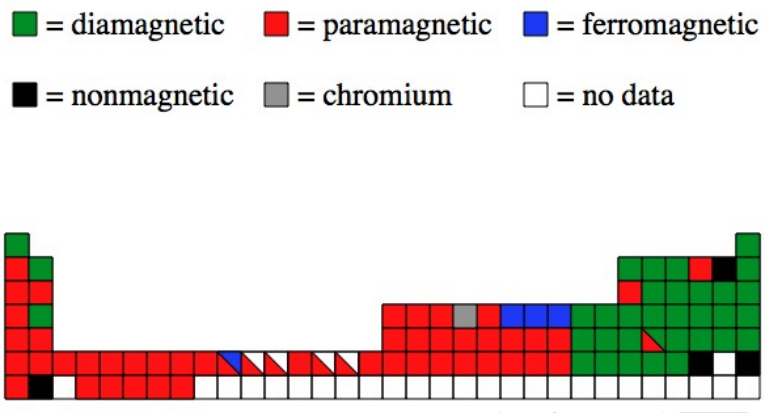
$$B = \mu_0 (H + M)$$

TYPES OF MAGNETISM





Magnetic Behavior	Value of χ
Diamagnetic	small and negative
Paramagnetic	small and positive
Ferromagnetic	large and positive
Antiferromagnetic	small and positive

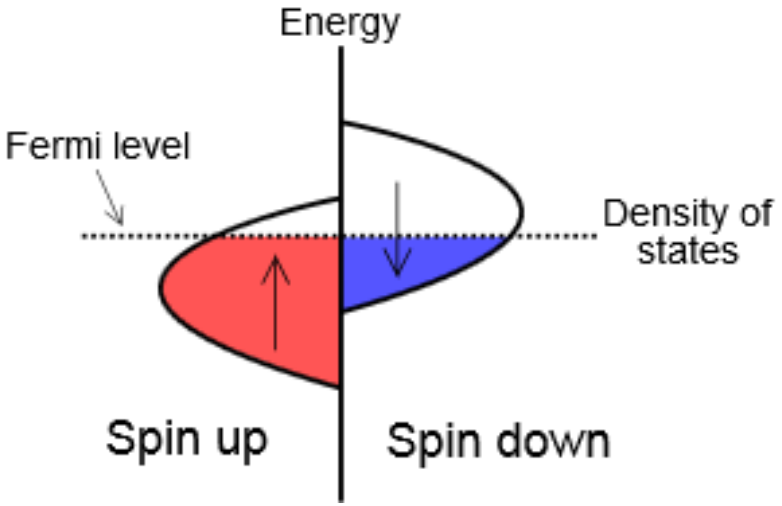


STONER MODEL FOR FERROMAGNETS

Electron bands can spontaneously split into up and down spins subbands.

This is due to the exchange interaction between spins:

$$H_{Heisenberg} = -2J\vec{S}_1 \cdot \vec{S}_2$$



which in turn is related to the Pauli exclusion principle

The magnetic moment ***m*** is given by the difference in the number of electrons (or holes) in the majority and minority bands:

$$m = \mu_B(N_e^{maj} - N_e^{min}) = \mu_B(N_h^{maj} - N_h^{min})$$

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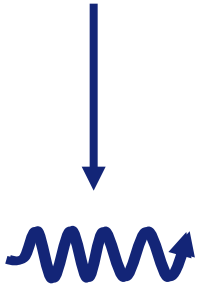
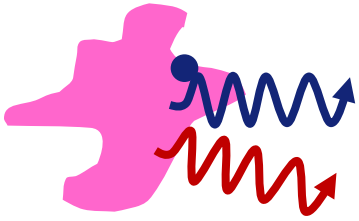
X-RAY SPECTROSCOPY

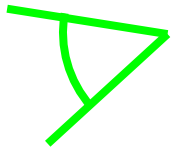
different ways to study matter with X-rays (where are the atoms, how they vibrate. .etc..)

photon: packet of light

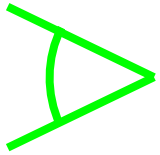




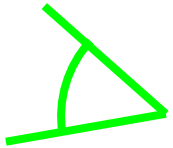
electrons



transmitted photons



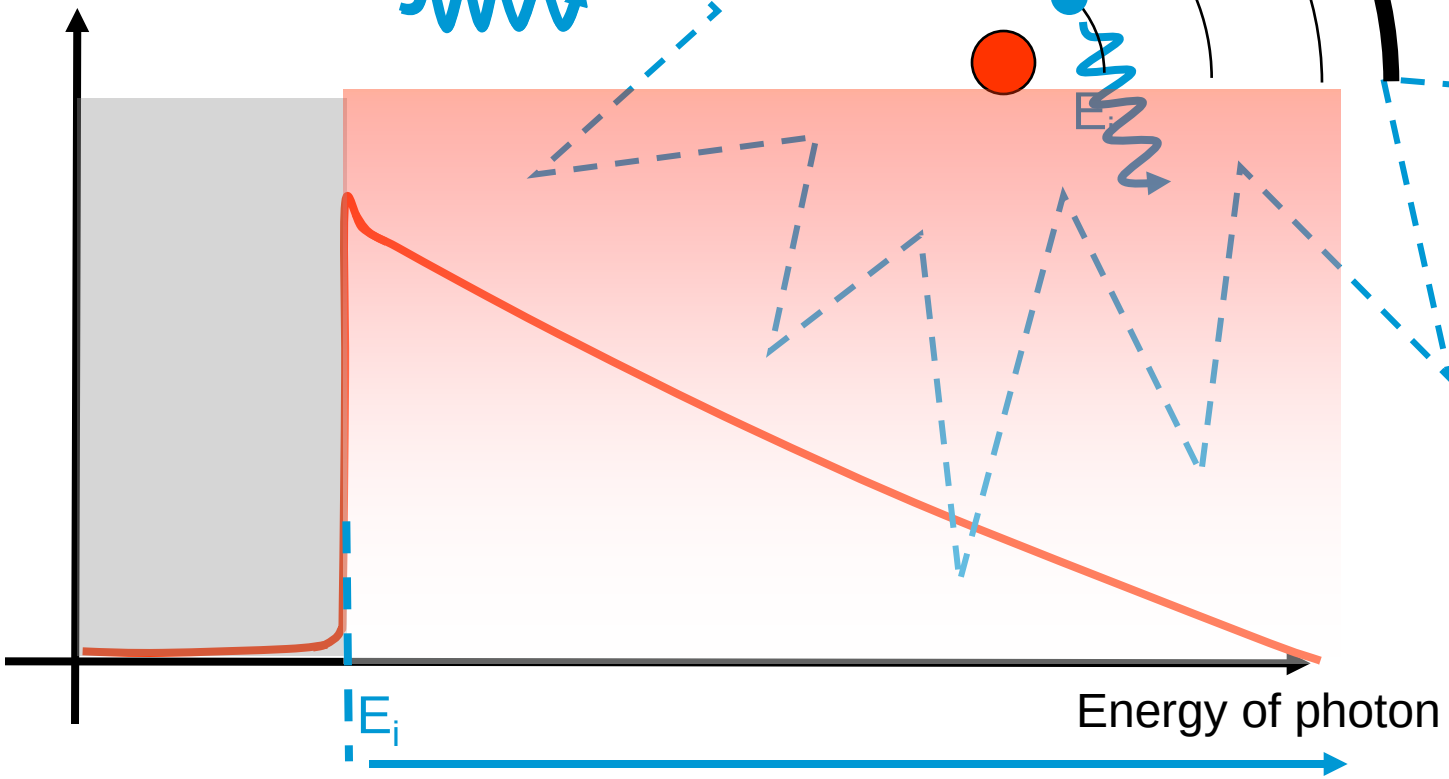
fluorescence photons



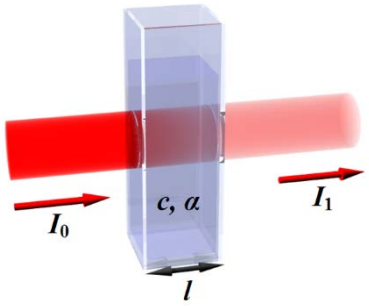
in X-ray absorption we record the transmitted photons

X-RAY ABSORPTION SPECTROSCOPY

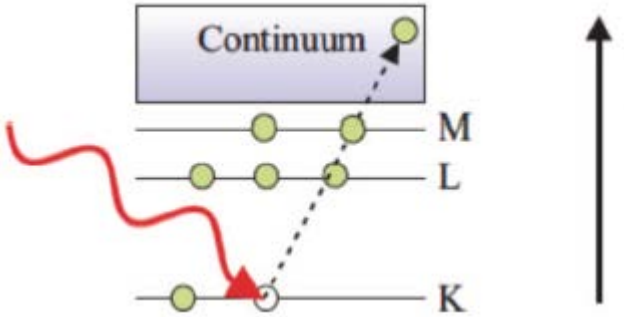
Probability of absorption
(or absorption spectrum)



ABSORPTION COEFFICIENT AND SELECTION RULES



$$I_1 = I_0 e^{-\mu l}$$



$$\mu \propto n \sum_f W_{fi}$$

the absorption coefficient is proportional to the sample density and to the transition probability of the absorbing atom from initial state to possible final states

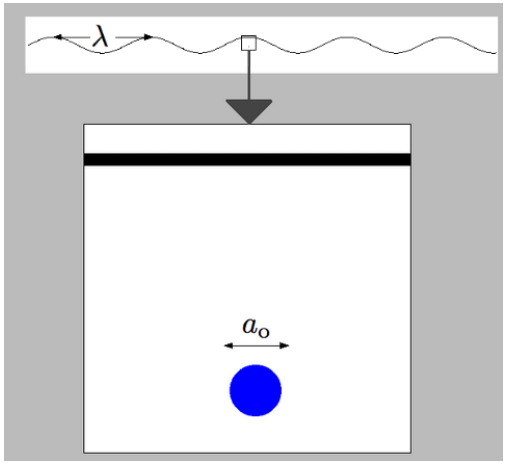
the calculation of W_{fi} is very complex unless we do some approximation:

- photon-electron interaction is weak
  Fermi Golden Rule

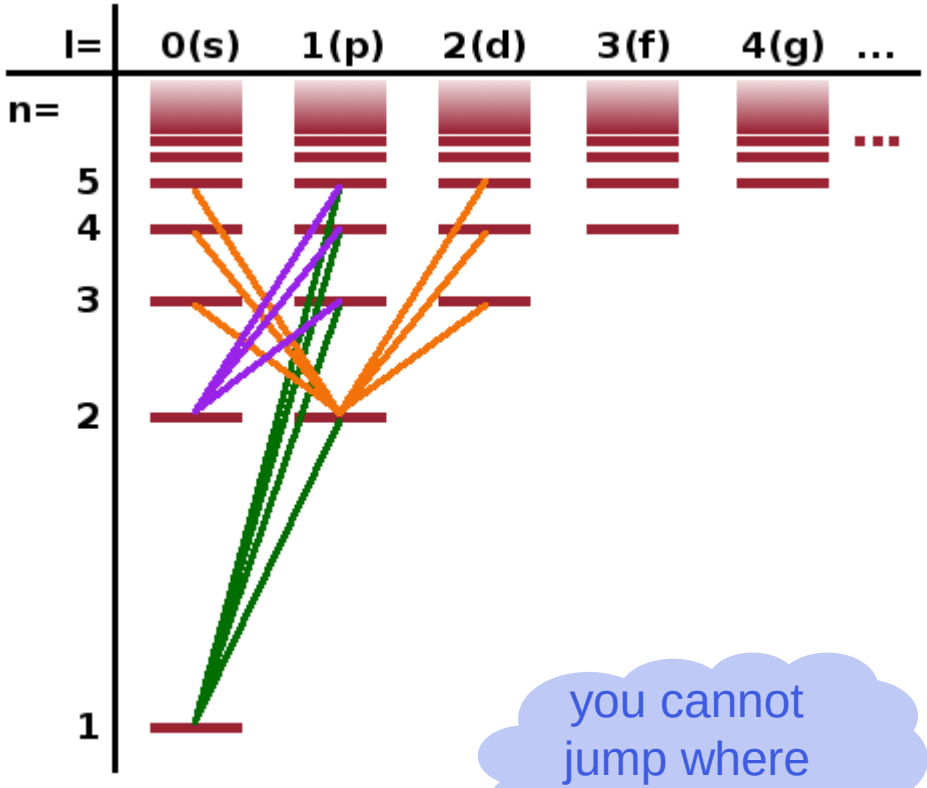
- sudden approximation: the other electrons ‘don’t care’ about the photoemitted electron

CONSEQUENCES OF DIPOLE APPROXIMATION: SELECTION RULES

dipole approximation:
the photon wave is constant over the atomic scale

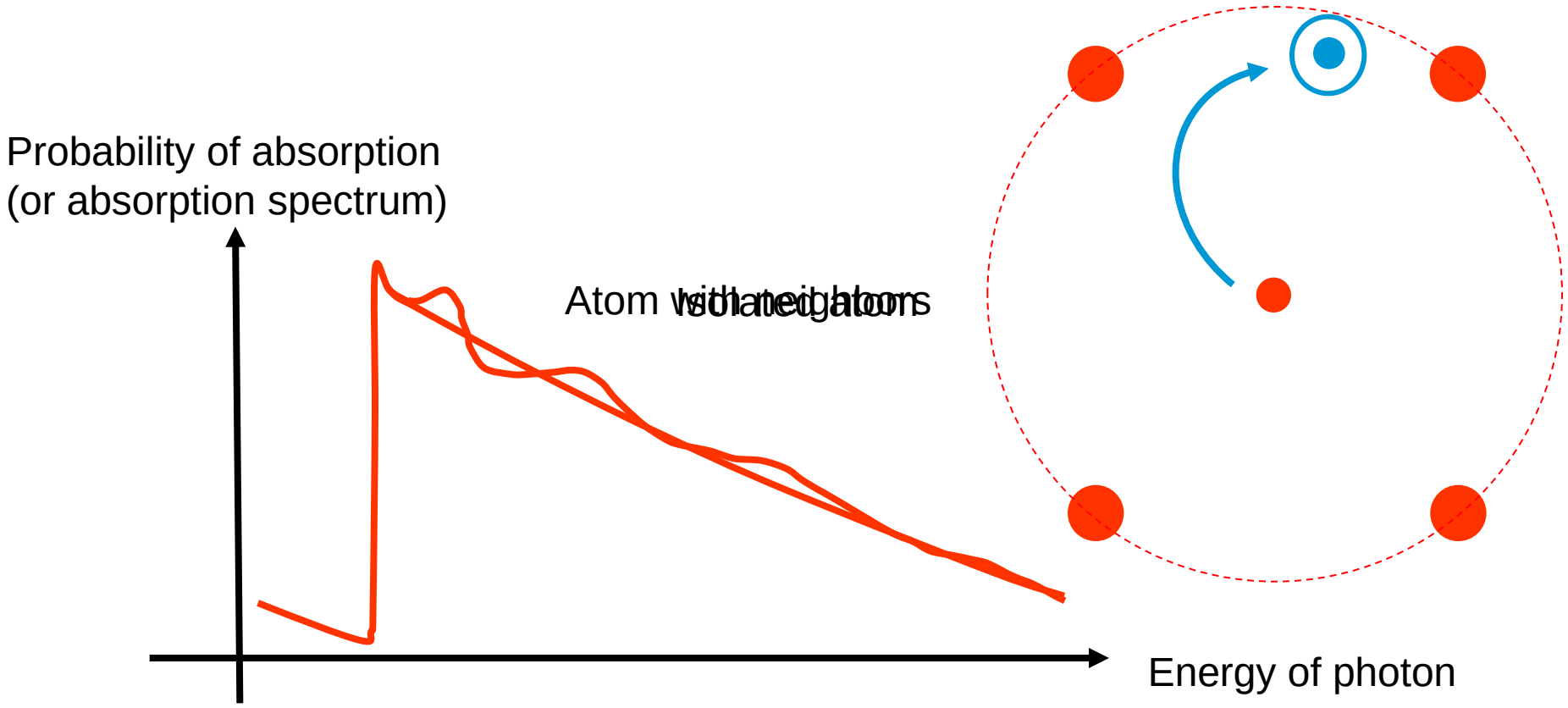


$\Delta l = \pm 1$
$\Delta s = 0$
$\Delta j = \pm 1$
$\Delta m = 0$



you cannot jump where you want!

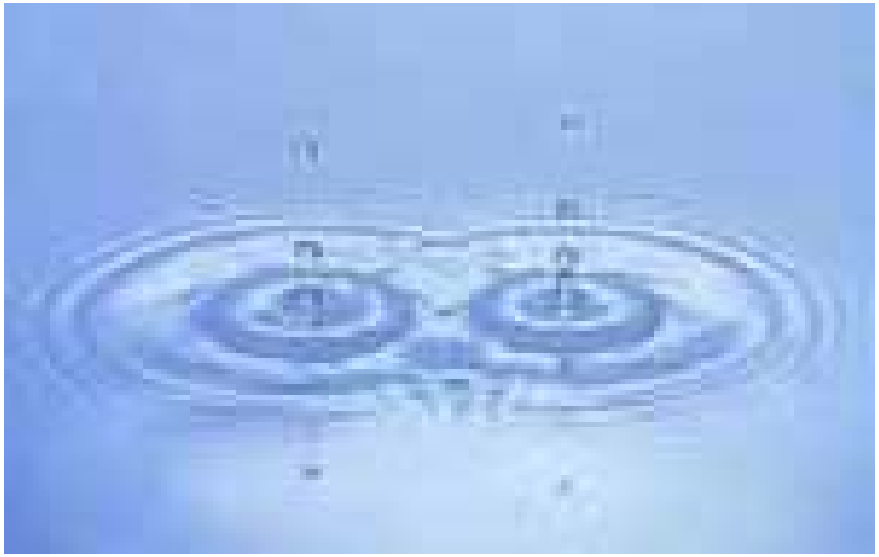
EXTENDED X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY (EXAFS)



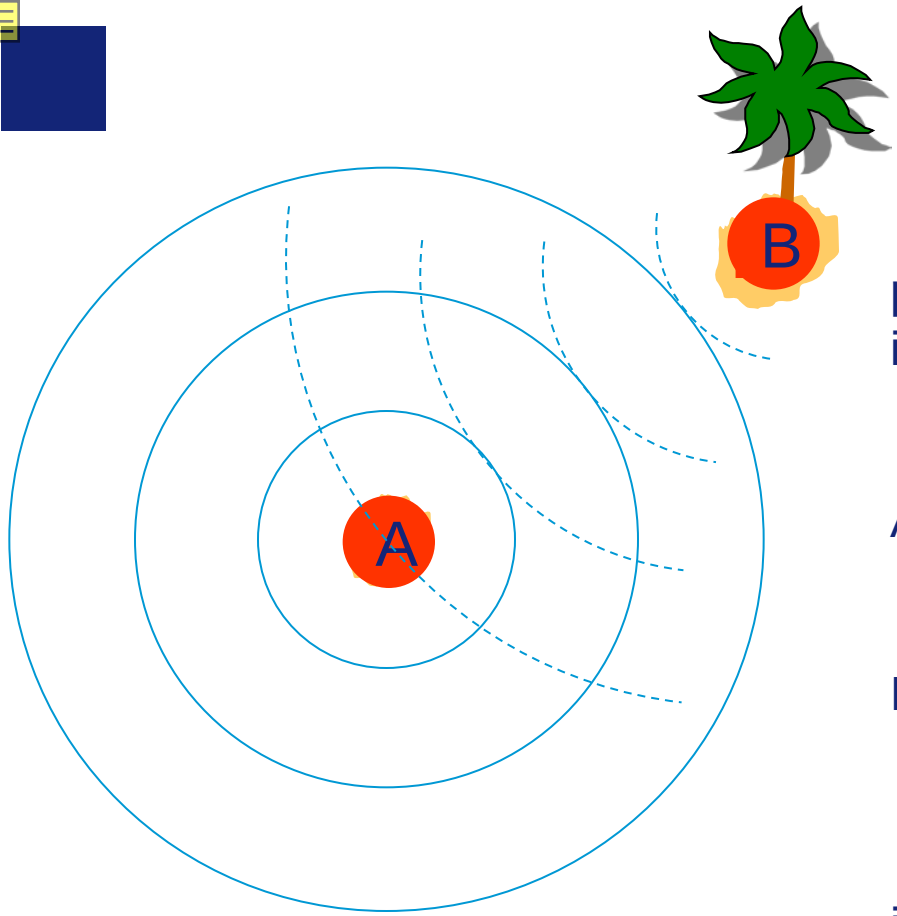
The probability of absorption oscillates

WHY ?

UNDERSTANDING EXAFS



The photoelectron behaves as a wave…



Amount of water in center of A is:

probability of photoelectron presence
i.e. of photon absorption

- zero if there is no B (no incoming wave)

A is an isolated atom

- little (a lot) if B is small (big)

B is a weak (strong) scatterer (i.e. C or Pb)

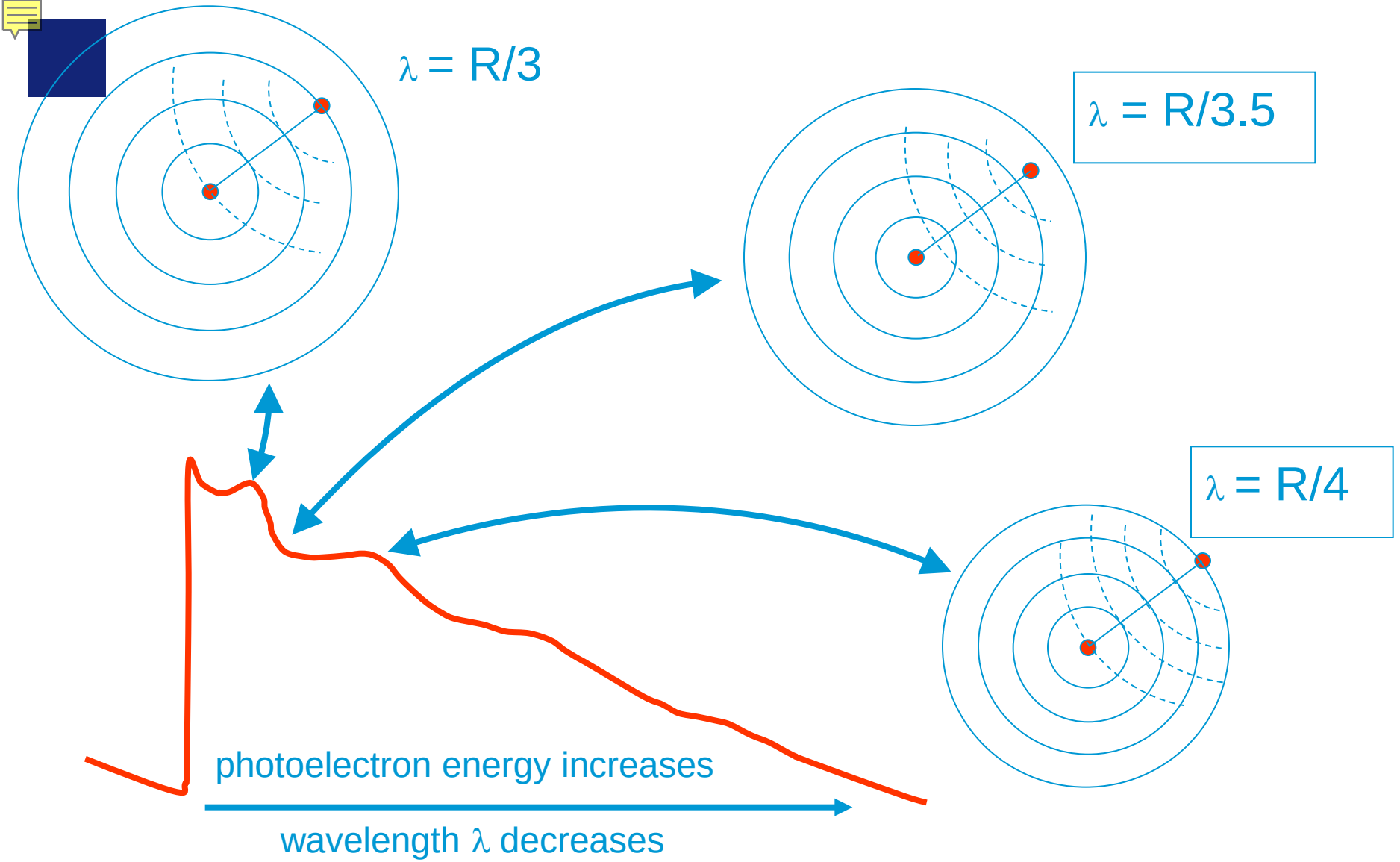
- very much if incoming and outgoing wave crests coincide

if R_{AB} is an integer multiple of wavelength

By measuring the amount of water in center of A, we learn:
By measuring the probability of X-ray absorption, we learn:

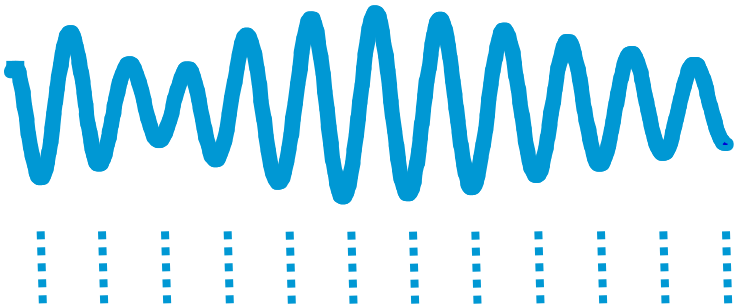
1. How far are the closest islands
2. How many and how big they are

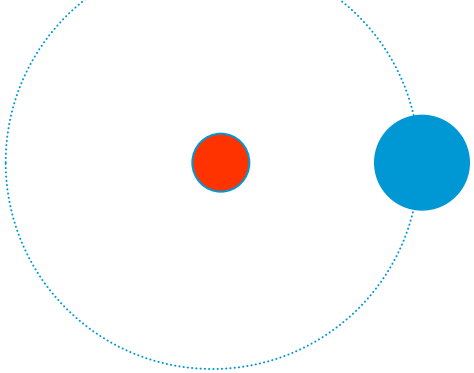
1. Nearest neighbour distances
2. Number and type of neighbours



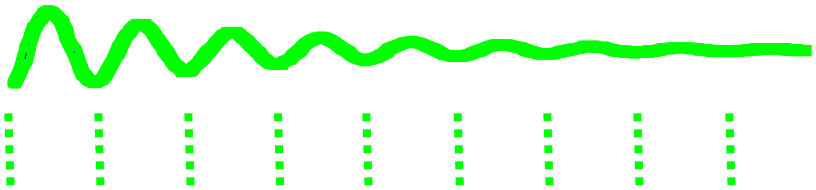
The probability of absorption oscillates due to constructive and destructive interference

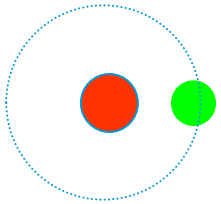
Lead
(82 electrons)

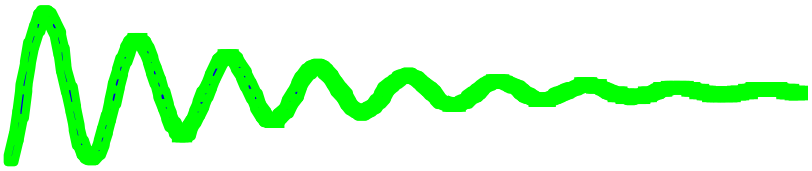


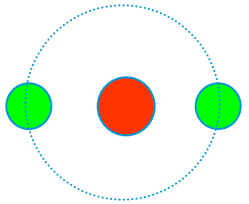


Carbon
(6 electrons)







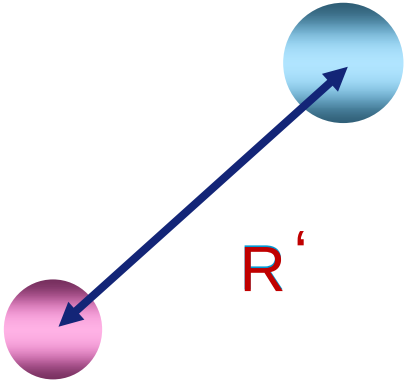


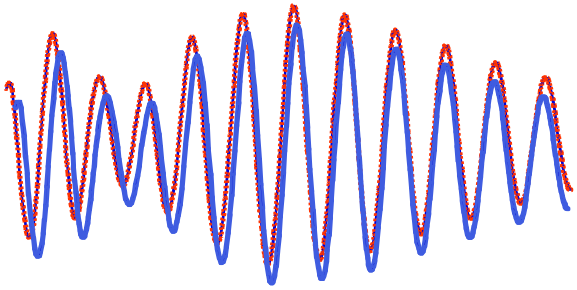
frequency	➡	interatomic distance	R
shape	➡	type of neighbor atoms	
amplitude	➡	number of neighbor atoms	N, σ^2

EXAFS PROPERTIES

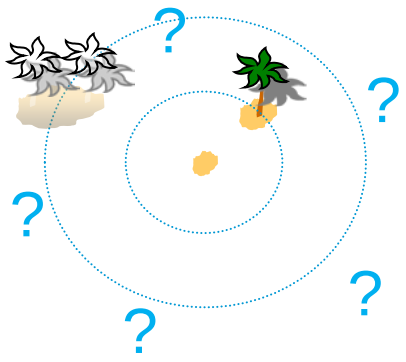
EXAFS çan measure tiny atomic displacements

we can extract: R, N, σ^2



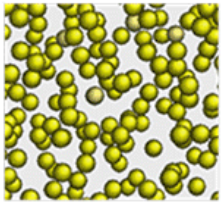


EXAFS is « shortsighted »



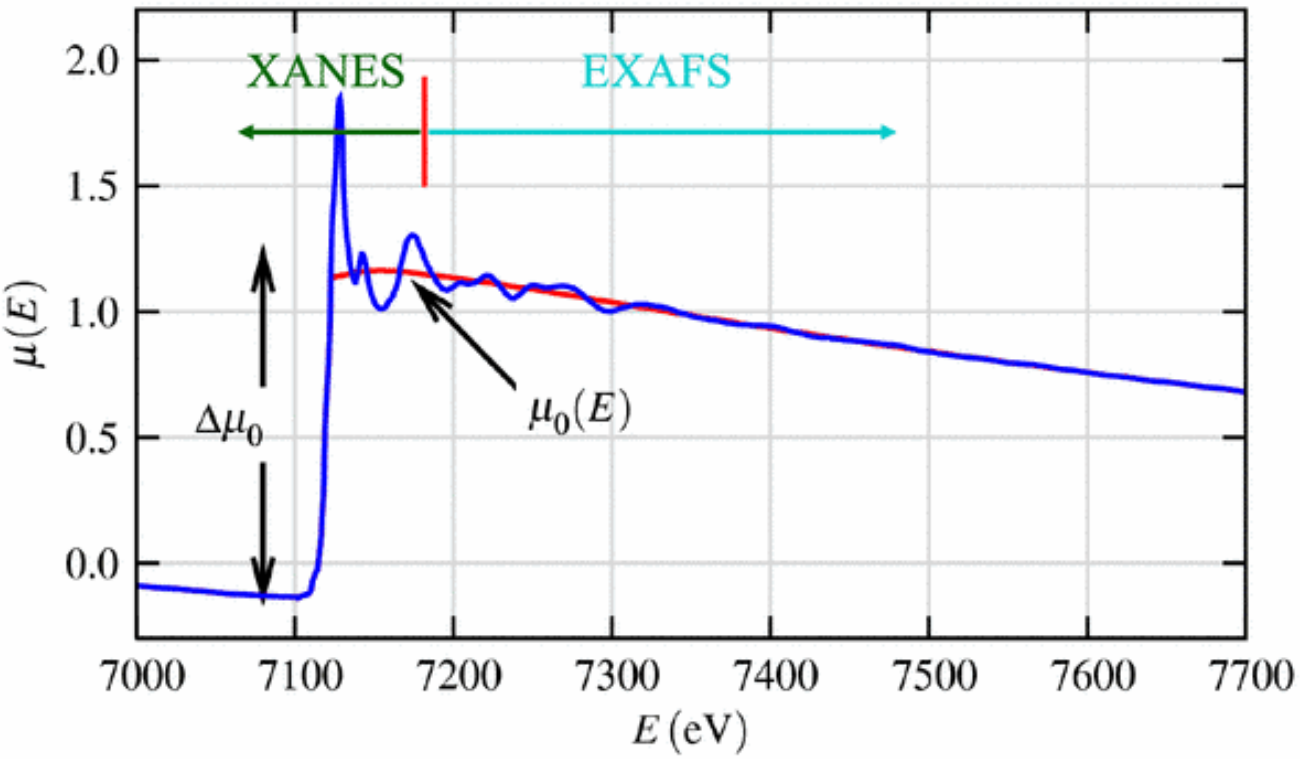
It doesn't care whether there is long range order.

It allows to investigate condensed matter in all its states (gas, liquid, solid) and also amorfous matter, chemically disordered systems, messy systems



It looks only at the surroundings of the selected chemical species

X-RAY ABSORPTION NEAR EDGE STRUCTURE (XANES)



INFORMATION

local site symmetry and geometry

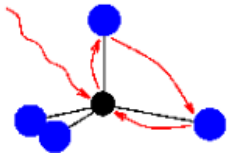
electronic structure

oxidation state

chemical coordination

ORIGIN

Transition to unfilled bound states, nearly bound states, continuum multiple scattering



analytical description not available

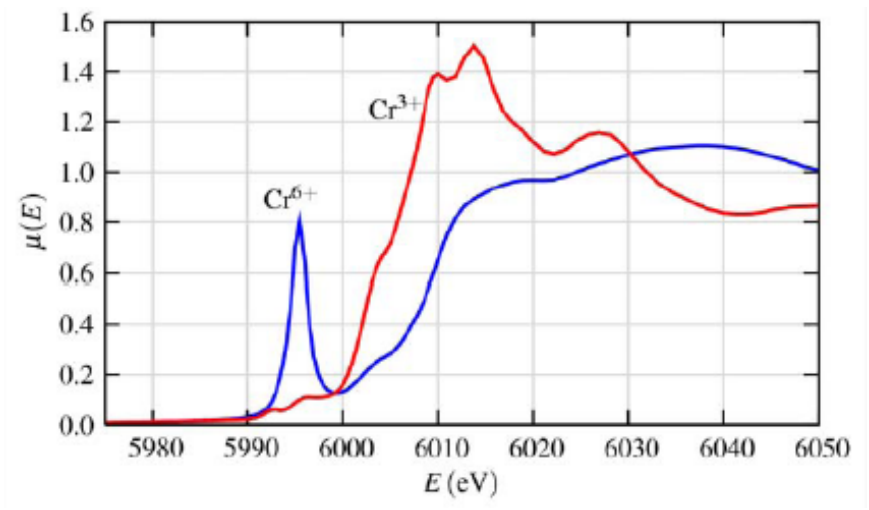
can be described *qualitatively* in terms of

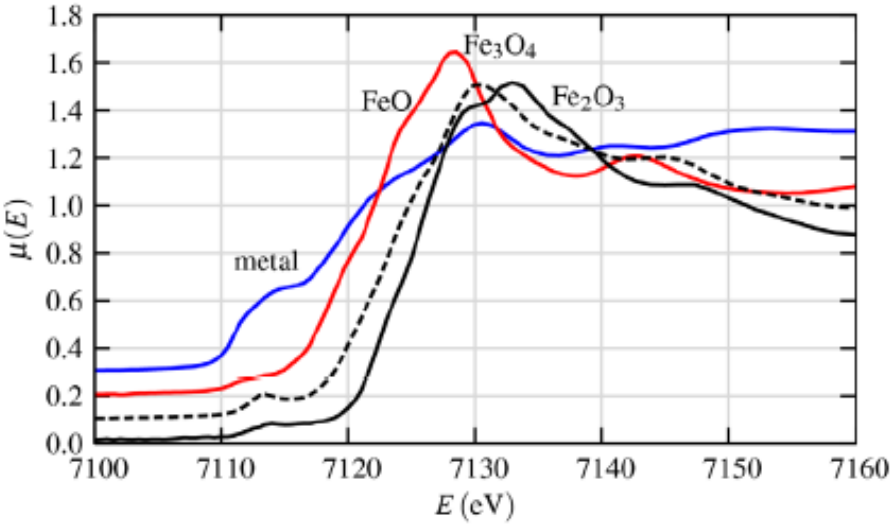
coordination chemistry

molecular orbitals

band-structure

multiple scattering



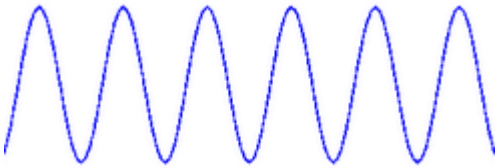


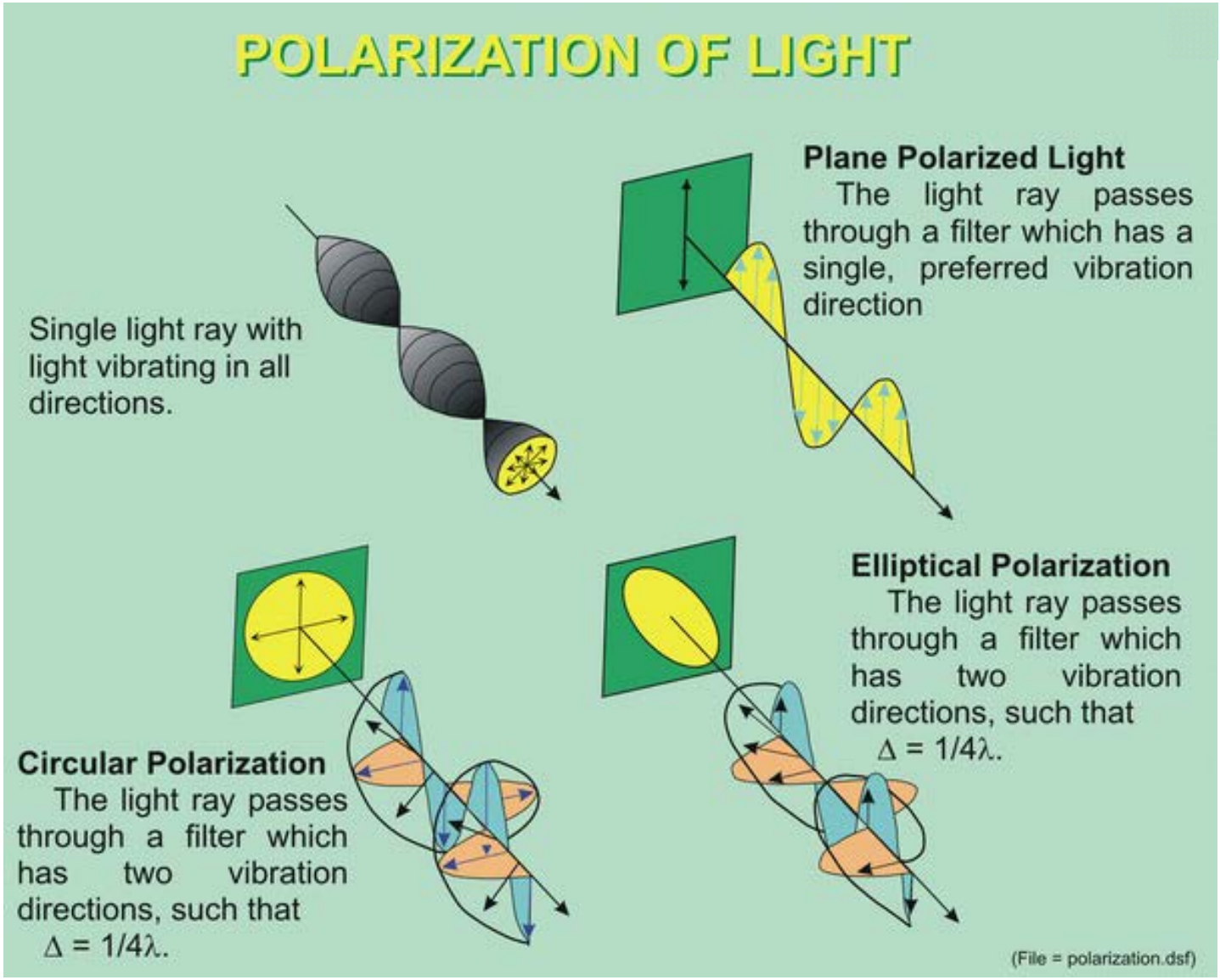
XANES can be used simply as a fingerprint of phases and oxidation state.
linear combinations of known spectra to get compositional fraction of the components.

HOW CAN ABSORBED X-RAY BECOME SENSITIVE TO MAGNETISM ?

EXAFS → local structure: R, N

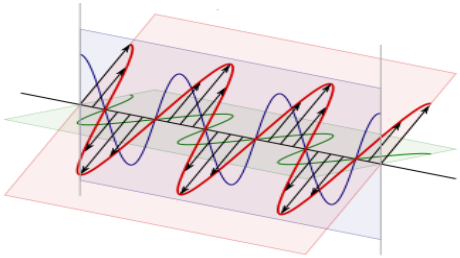
XANES → electronic structure, oxidation state
chemical coordination



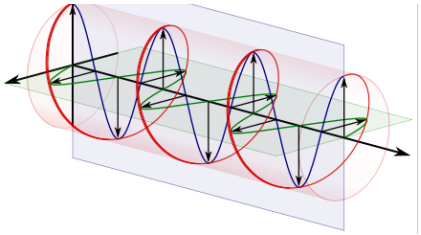

POLARIZATION OF LIGHT
Single light ray with light vibrating in all directions.
Plane Polarized Light
The light ray passes through a filter which has a single, preferred vibration direction
Circular Polarization
The light ray passes through a filter which has two vibration directions, such that
Δ = 1/4λ.
Elliptical Polarization
The light ray passes through a filter which has two vibration directions, such that
Δ = 1/4λ.
(File = polarization.dsf)

DICHROISM

DICHROISM: property of a sample to absorb with different cross section photon beams with different polarization



LINEAR : difference in absorption between two mutually perpendicular linear polarized beams



CIRCULAR: difference in absorption between right and left polarized photons

origin: breaking of spherical symmetry in the process of photoabsorption

structural anisotropy of e^- density → natural

magnetic anisotropy (FM or AF) → XMD

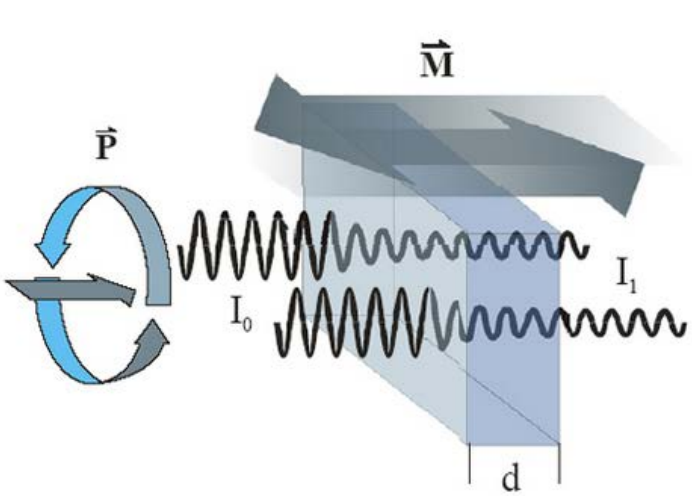
X-RAY MAGNETIC CIRCULAR DICHROISM (XMCD)

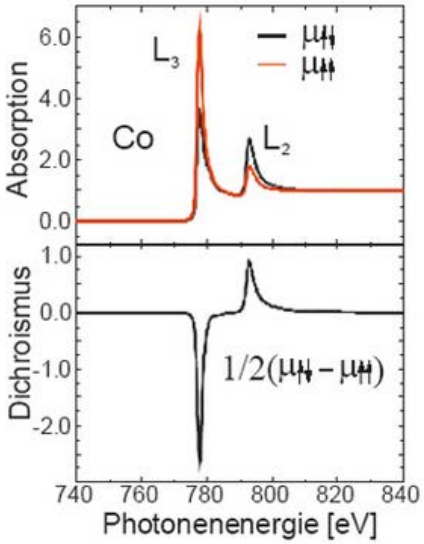
measures the dependence of X-ray absorption on the circular left and right polarization of incident beam by a magnetic material

$$XMCD = \mu^{L} - \mu^{R}$$

brings information on spin and orbital moment in magnetic materials

- To make the absorption process spin dependent:
  - circularly polarized photons
  - because they can transfer their angular momentum to photoelectron





CONSERVATION OF THE ANGULAR MOMENTUM

a polarized photon can transfer its elicity (angular momentum) to an absorber

Let's consider an atom in an initial pure quantum state:

$$M = \boldsymbol{J} \cdot \boldsymbol{m}$$

J= total angular momentum, M= projection of J along the preferred magnetic axis defined by the unit vector m

and a photon with angular momentum **σ** in the direction of propagation

$$\boldsymbol{\sigma} = \sigma\, \boldsymbol{q}$$

once the photon is absorbed by the atom, using the rules of vector addiction:

$$\boldsymbol{J}' = \mathbf{J} + \boldsymbol{\sigma}$$

$$M' = \boldsymbol{J}' \cdot \boldsymbol{m} = (\boldsymbol{J} + \boldsymbol{\sigma}) \cdot \boldsymbol{m} = M + \sigma\, (\boldsymbol{q} \cdot \boldsymbol{m})$$

CONSERVATION OF ANGULAR MOMENTUM

$$\Delta M = M' - M = \sigma(\boldsymbol{q} \cdot \boldsymbol{m}) = \pm 1 \quad \text{if } \boldsymbol{q} \,//\, \boldsymbol{m}$$

±1 for circular polarization

the change in angular momentum projection is ±1 depending on wheter the photon helicity is parallel or antiparallel to the sample magnetization

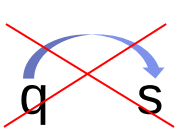
selection rule: $\Delta M = \pm 1$

preferred geometry for XMCD

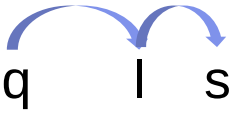
If the absorption coefficient for circularly left and right polarized photon are different, the atom exibit magnetic dichroism

2 STEP-MODEL

1. a circularly polarized photon excites a photoelectron from a core level transferring its helicity (angular momentum) to the photoelectron;
   If the photoelectron is excited from a spin–orbit split level, the helicity of the photon can be partly transferred to the spin through the spin–orbit coupling



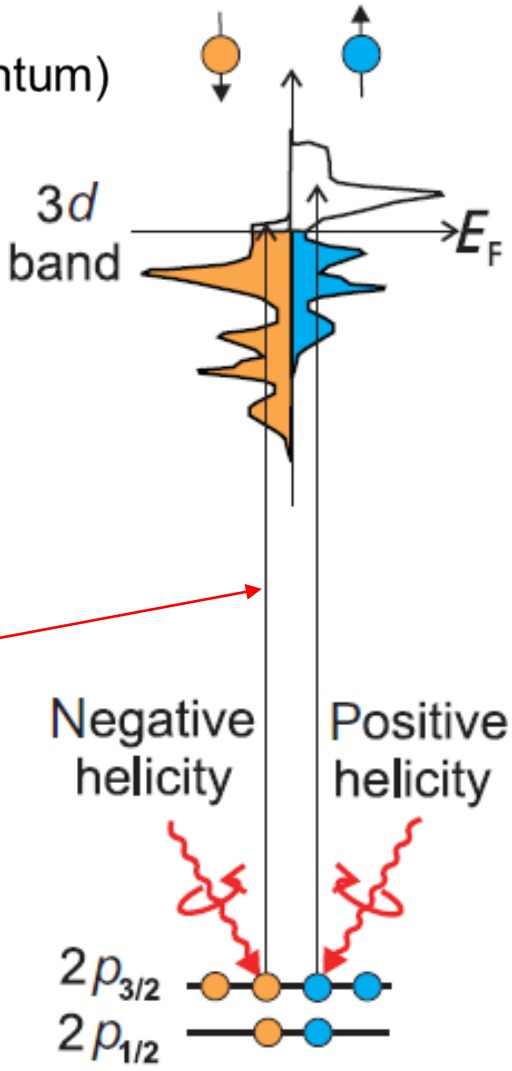
because ΔS=0 but



➡ excited photoelectrons are spin polarized

$\propto P_{circ}$

2. the photoelectron is captured into an unoccupied valence state. The transition rate depends on the number of available final states with spin // to the photoelectron spin (ΔS=0) $\propto \boldsymbol{m}$



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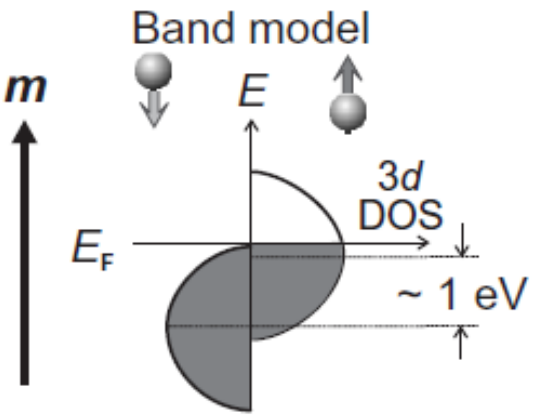
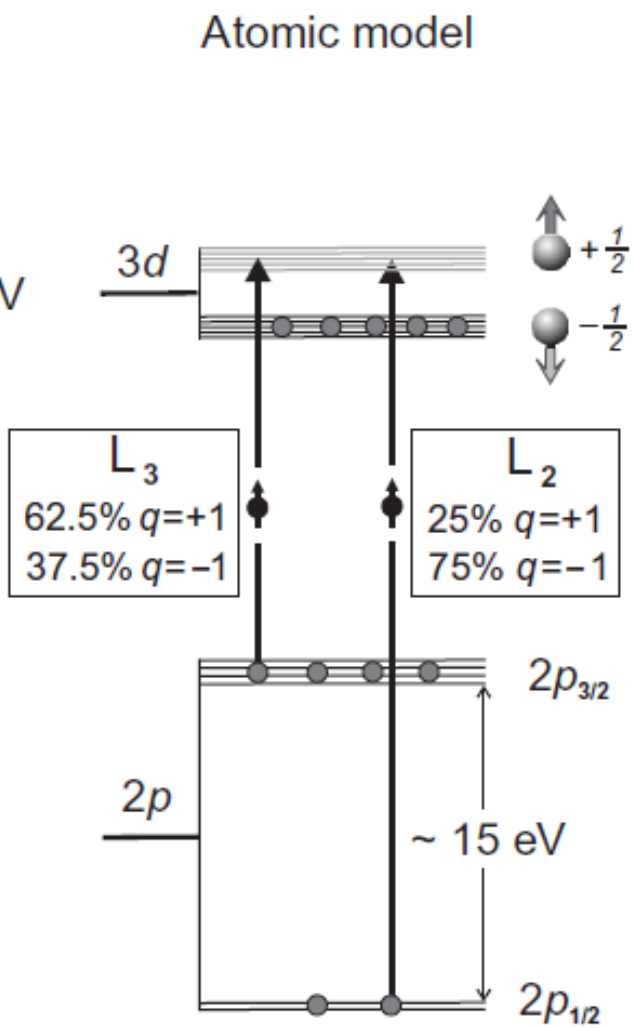
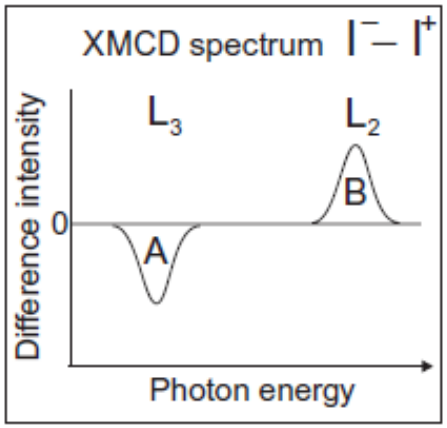
AN EXAMPLE

only spin up photoelectrons can be excited from the 2p core level to the unfilled spin up valence band since the dipole operator does not act on spin: ΔS=0





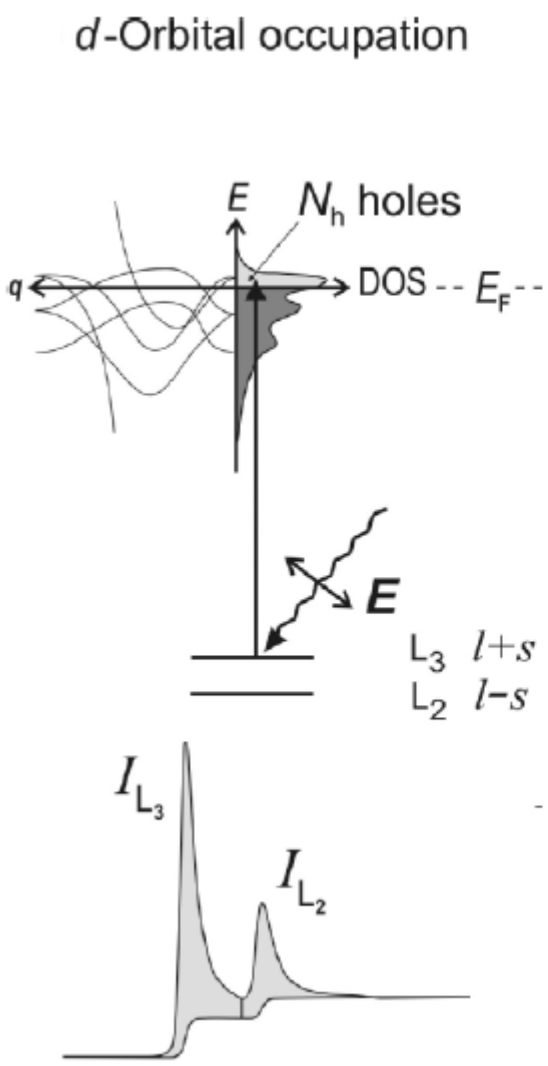
62,5% • 4 + 25% • 2 = 3
37.5% • 4 + 75% • 2 = 3



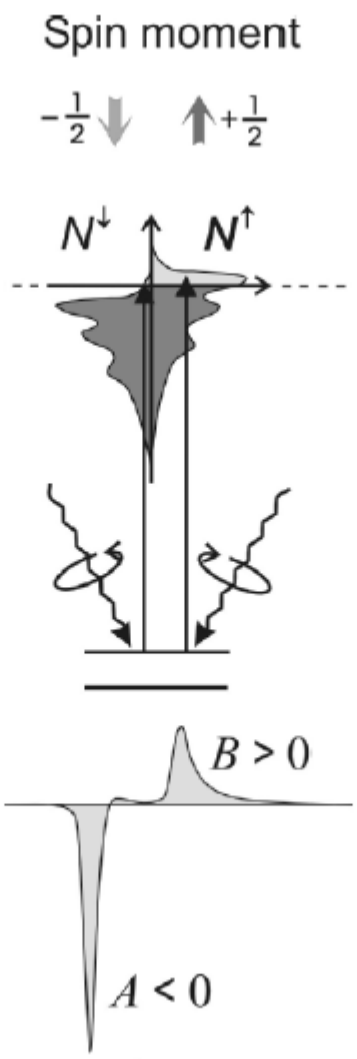
$$XMCD = \mu^L - \mu^R$$
$$\propto P_{circ}\,\rho_s\,cos\theta$$
$$\propto P_{circ}\,\boldsymbol{m}\,cos\theta$$

P_{circ} = degree of circular photon polarization
ρ_s = spin polarized density of states of the valence shell
θ = angle between the photon angular momentum and the sample magnetic moment

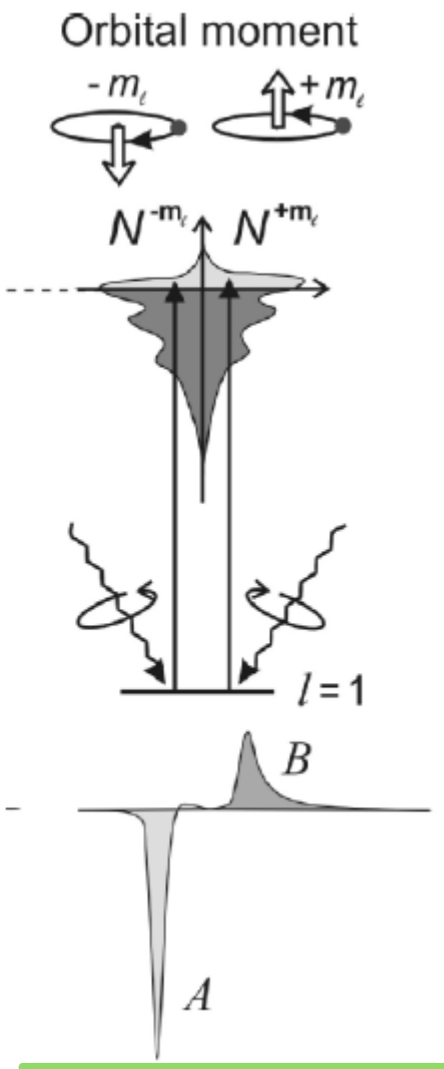
SUM RULES



$$\langle I_{L_3} + I_{L_2} \rangle = C N_h$$



$$\langle -A + 2B \rangle = \frac{C}{\mu_B} m_s$$



$$-\langle A + B \rangle = \frac{3C}{2\mu_B} m_o$$

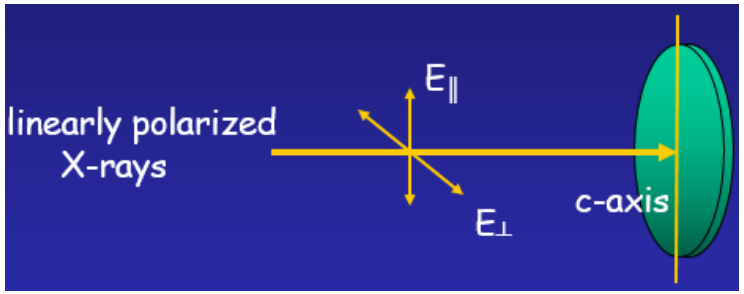
X-RAY LINEAR DICHROISM

dependence of absorption on the relative orientation between linear x-ray polarization and crystallographic axis

$$XLD = \frac{\mu^{//} - \mu^{\perp}}{\mu^{//} + \mu^{\perp}}$$

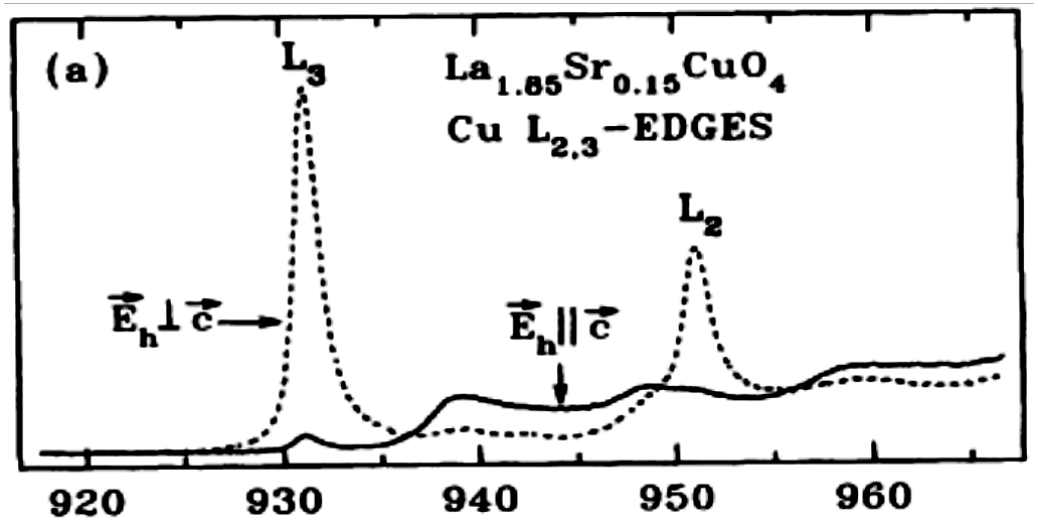
$\mu^{//} : \vec{E} \,//\, \vec{c}$

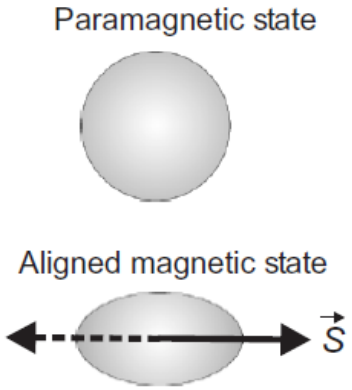
$\mu^{\perp} : \vec{E} \perp \vec{c}$

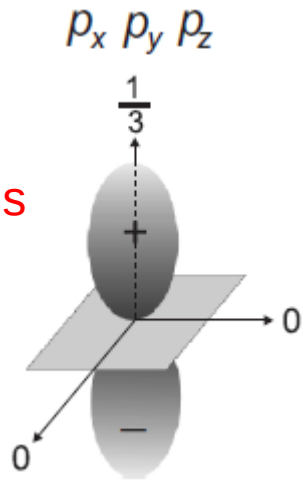


In nonmagnetic systems the anisotropy arises from an anisotropic charge distribution about the absorbing atom caused by bonding.

The polarization dependence gives the symmetry of the empty orbitals

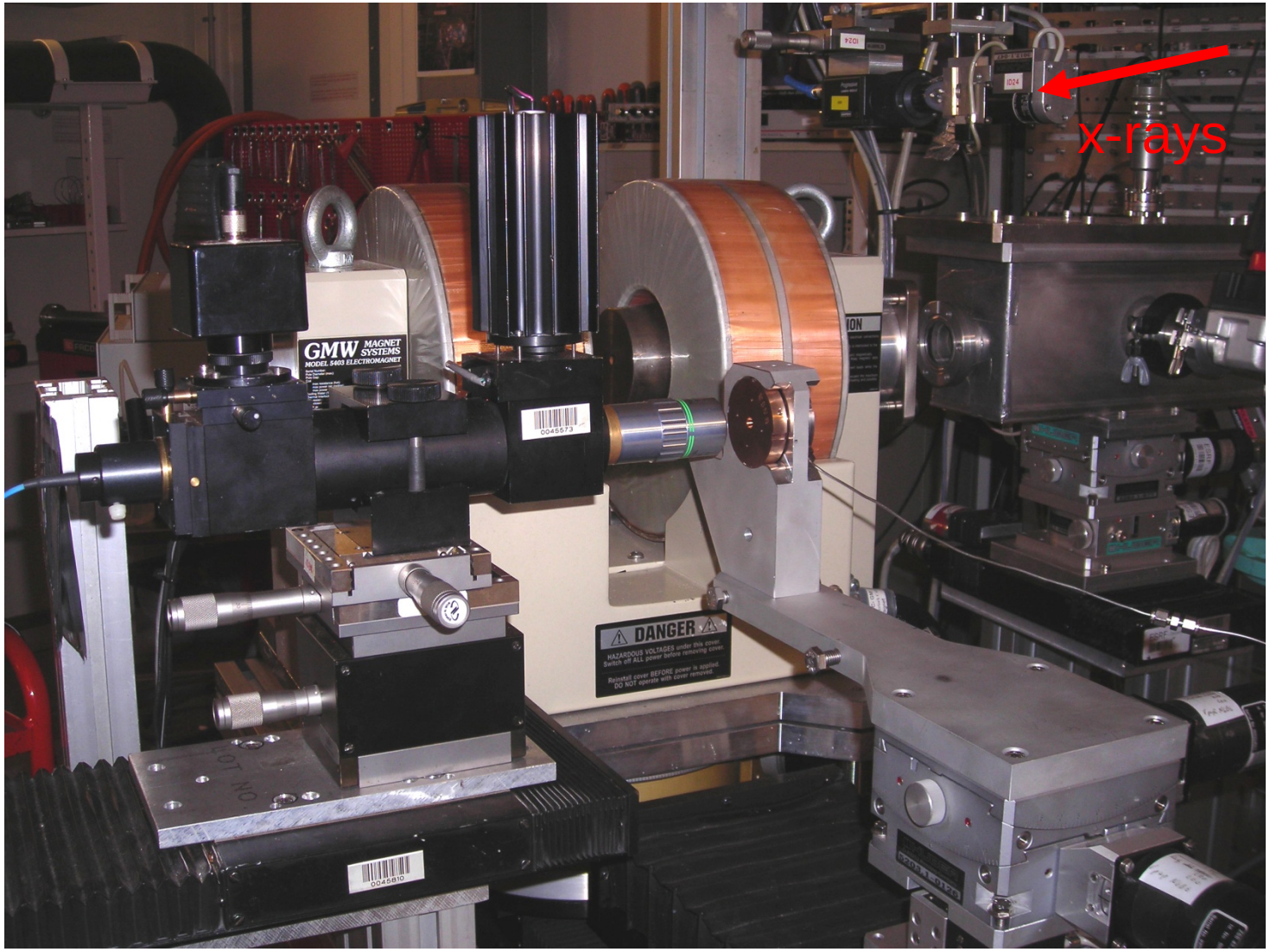




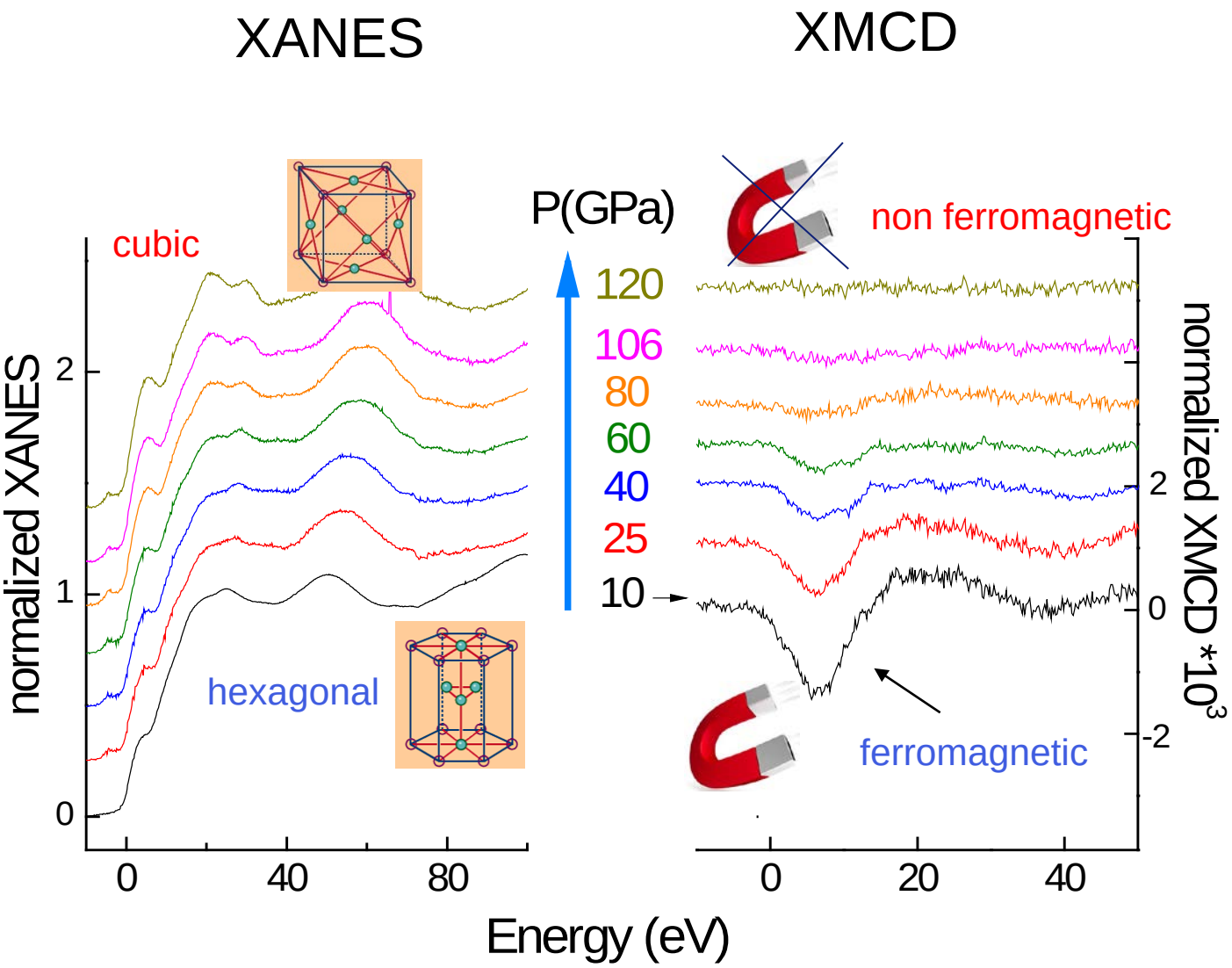


2p → 3d dipole allowed transition

EXAMPLE: XMCD UNDER HIGH PRESSURE @ID24



COBALT MAGNETISM AND STRUCTURE AT HIGH PRESSURE



at 120 GPa Cobalt transforms from hexagonal FM to cubic non FM

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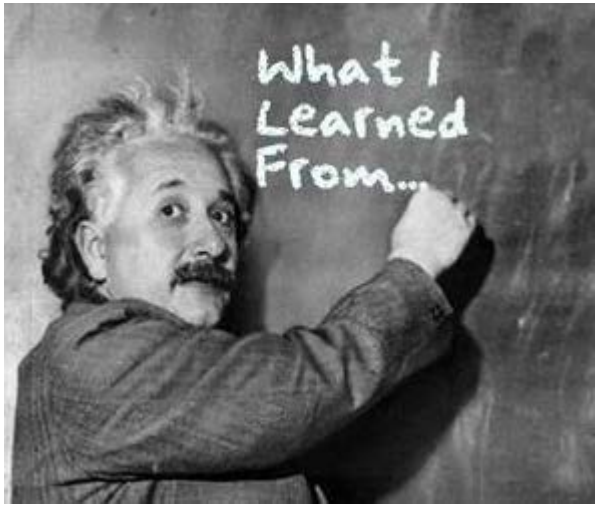
TAKE HOME MESSAGE

XAS is a very powerful technique

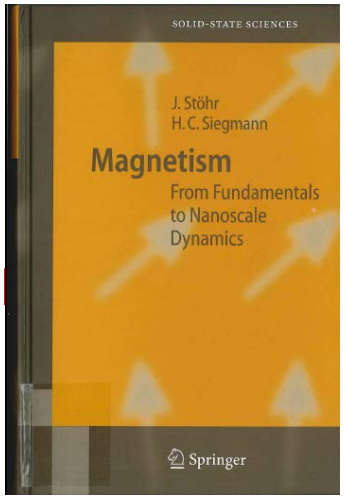
which can bring information about



local structure of solid and amorphous (EXAFS)

electronic structure, oxidation state and
chemical coordination (XANES)

and if x-rays are polarized it can also becomes sentitive to

magnetic arrangments: ferromagnetism, ferrimagnetism (X
and antiferromagnetism (XMLD)

symmetry of empty orbitals (XND)