Polarization and dichroism

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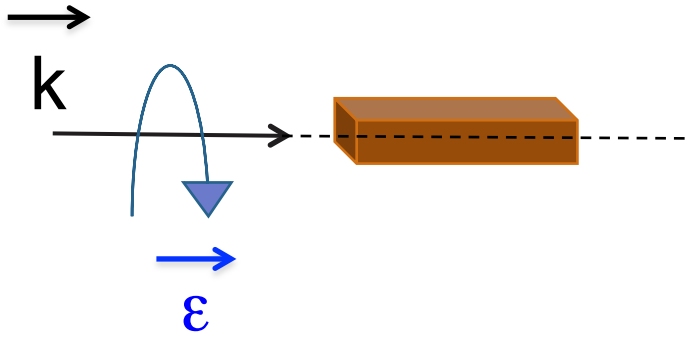
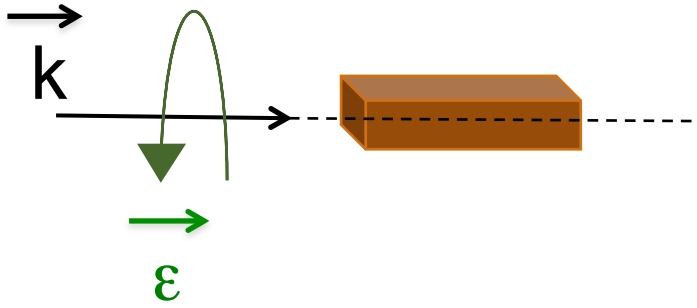
« Dichroism » (« two colors ») describes the dependence of the absorption measured with two orthogonal polarization states of the incoming light:

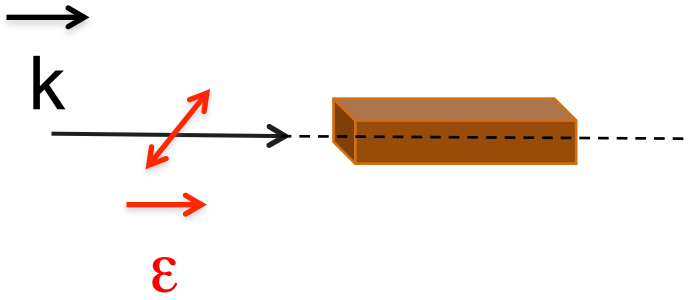
Circular left



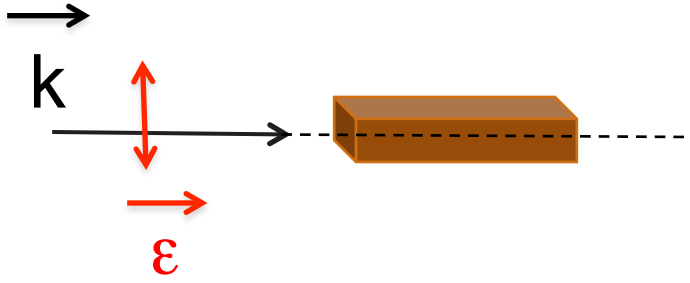
Circular right



Linear horizontal



Linear vertical



By extension, « dichroism » also includes similar dependence phenomena, such as:

- Low symmetry crystals show a trichroic dependence with linear light
- Magneto-chiral dichroism (MχD) is measured with unpolarized light
- Magnetic Linear Dichroism (MLD) is measured by changing the direction of magnetic field and keeping the linear polarization fixed **…**

Dichroism describes an angular and /or polarization behaviour of the absorption

Linear dichroism (LD) : difference measured with linearly polarized light

Circular dichroism (CD) : difference measured with left / right circularly polarized light.

Natural dichroism (ND) : time-reversal symmetry is conserved

Non-Reciprocal (NR): time-reversal symmetry is not conserved

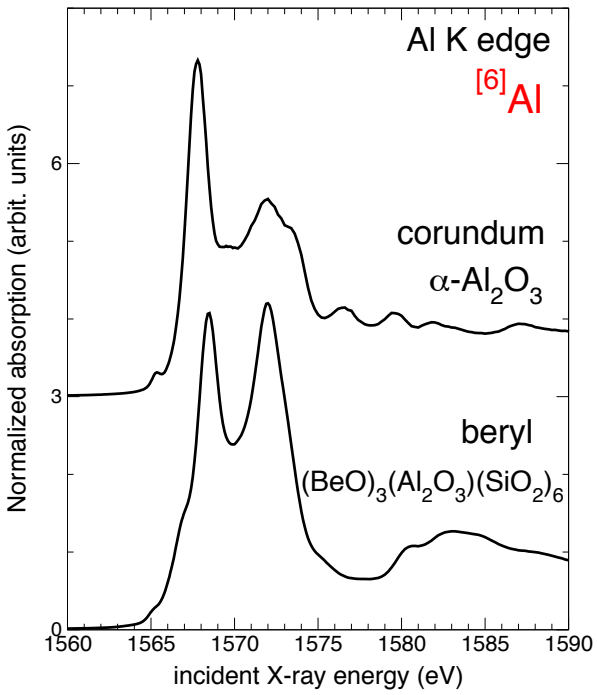
Magnetic dichroism (MD) : measured in (ferro, ferri or antiferro) magnetic materials

Dichroism	Time reversal symmetry	Parity symmetry
Natural Linear (NLD)	+	+
Magnetic Linear (MLD)	+	+
Non Reciprocal Linear (NRLD)	-	-
Natural Circular (NCD)	+	-
Magnetic Circular (MCD)	-	+
Magneto-optical (MχD)	-	-

The measurement of dichroism is often challenging…

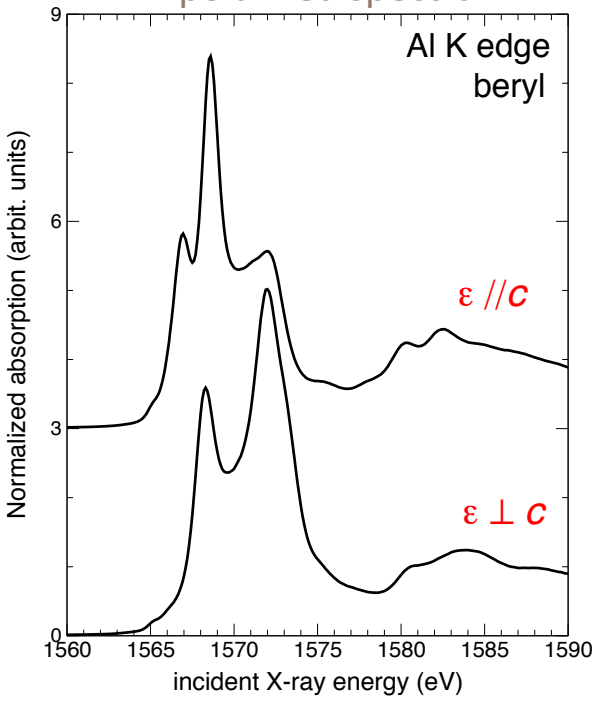
… but provides access to properties that cannot be measured in another way

isotropic spectra



Average signature

polarized spectra



Access to polarization dependent states

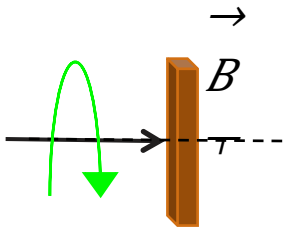
The corresponding « sum rules » relate dichroism to a ground state moment:

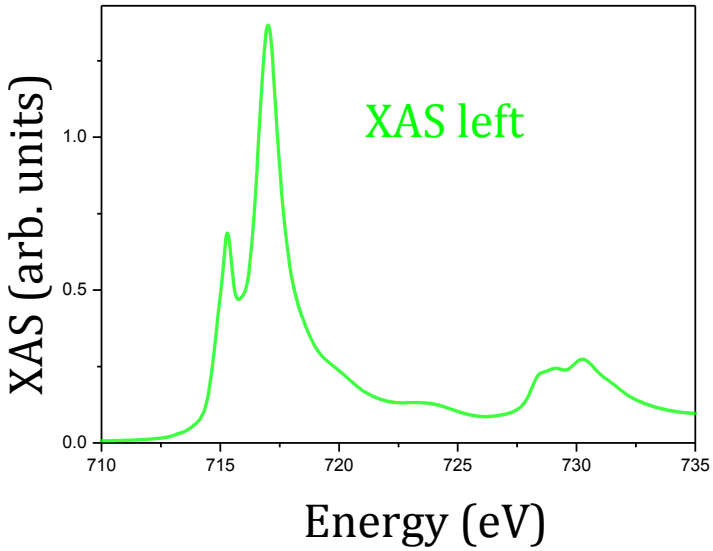
Widely applied in XMCD, less applied in other types of dichroisms

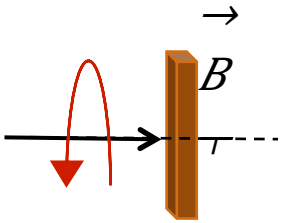
XMCD : average value of <M> the local magnetic moment of the absorber

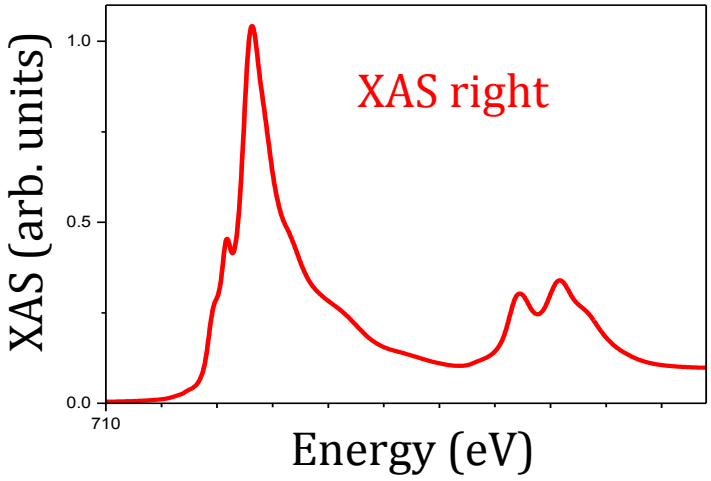
XMCD

Can be measured in ferri / ferromagnetic materials (XMCD = 0 in antiferromagnets)
XAS measured with circularly polarized x-rays on a sample magnetically polarized by external magnetic field

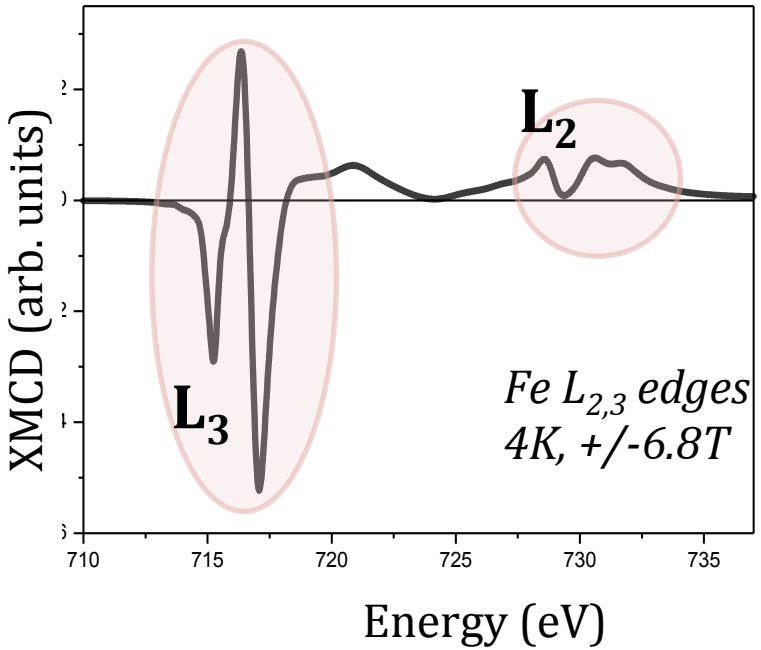








XMCD = XAS right – XAS left



XMCD sum rules

Magnetic field B is set along the *Z* axis

VOLUME 68, NUMBER 12 PHYSICAL REVIEW LETTERS 23 MARCH 1992

X-Ray Circular Dichroism as a Probe of Orbital Magnetization

B. T. Thole,[1] Paolo Carra,[2] F. Sette,[2] and G. van der Laan[3]

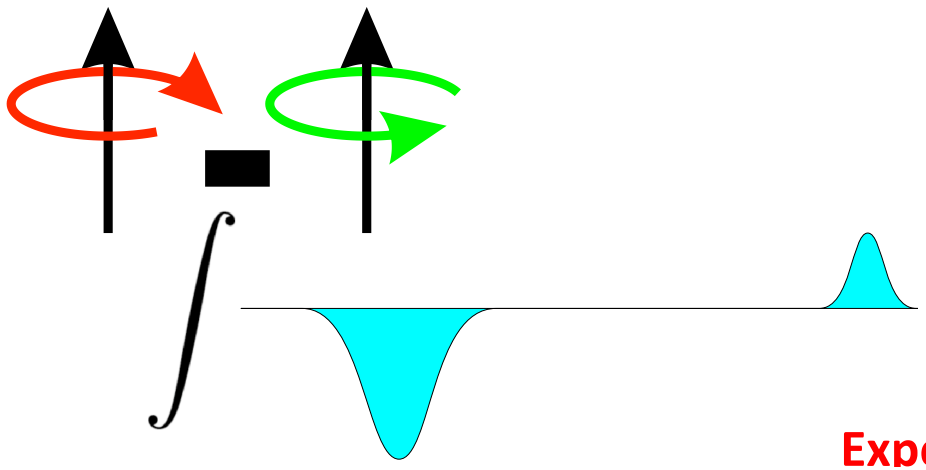
VOLUME 70, NUMBER 5 PHYSICAL REVIEW LETTERS 1 FEBRUARY 1993

X-Ray Circular Dichroism and Local Magnetic Fields

Paolo Carra,[1] B. T. Thole,[1,2] Massimo Altarelli,[1] and Xindong Wang[3]

$$(\mathcal{I}_{-1}^{c+\frac{1}{2}} - \mathcal{I}_{1}^{c+\frac{1}{2}}) - \frac{l}{l-1}(\mathcal{I}_{-1}^{c-\frac{1}{2}} - \mathcal{I}_{1}^{c-\frac{1}{2}}) = \frac{2}{3\underline{n}}\mathbf{S}_z + \frac{2(2l+3)}{3l\underline{n}}\mathbf{T}_z$$

$$\mathcal{I}_{-1} - \mathcal{I}_{1} = \frac{1}{\underline{n}}\sum_{m,\sigma}\underline{n}_{m\sigma}\frac{-m}{l} = \frac{\mathbf{L_z}}{l\underline{n}}$$



$\propto$ $\langle L_z \rangle = \langle i | L_Z | i \rangle$

Expectation value of L_Z

(*Z* component of orbital momentum operator)

XMCD sum rules

Magnetic field B is set along the *Z* axis

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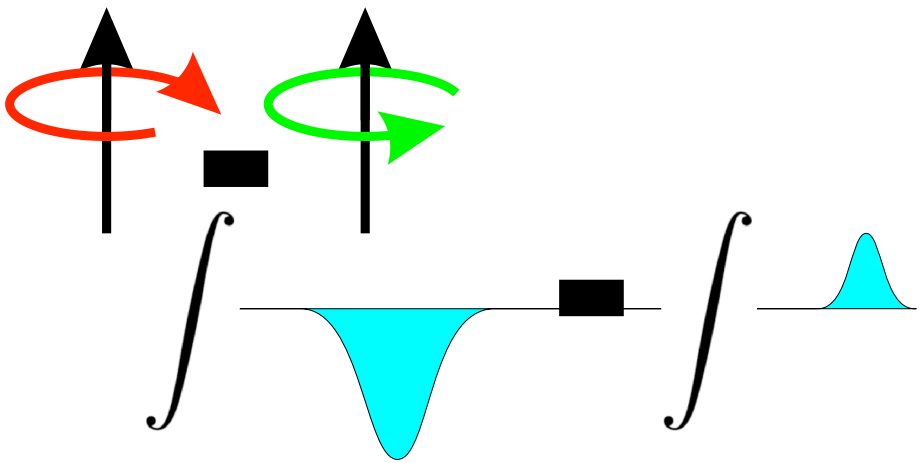


$\propto$ $\langle S_Z \rangle = \langle i | S_Z | i \rangle$

$(+ \langle T_Z \rangle = \langle i | T_Z | i \rangle)$

magnetic dipole operator

The corresponding « sum rules » relate dichroism to a ground state moment:

Widely applied in XMCD, less applied in other types of dichroisms

XMCD : average value of <M> the local magnetic moment of the absorber

XMLD : average value of $<M^2>$

XNCD : mixture between states with different parity (orbital pseudodeviator)

XNLD : anisotropy of charge distribution (quadrupole / hexadecapole moments)

Dichroism is not straightforward to predict / calculate…

Let's start with X-ray Natural Linear Dichroism (XNLD)

The XAS cross-section

$$\sigma(\omega) = 4\pi^2 \alpha \hbar \omega \sum_{f,i} \left| \left\langle f \left| \hat{O} \right| i \right\rangle \right|^2 \delta\left(\hbar\omega - E_f + E_i\right)$$

$$\hat{O} = \left(\boldsymbol{p}.\boldsymbol{\varepsilon} + i\frac{\hbar}{2}\boldsymbol{\sigma}.\boldsymbol{k} \times \boldsymbol{\varepsilon} + \frac{i\omega\hbar}{4mc^2}\boldsymbol{\sigma}.\boldsymbol{p} \times \boldsymbol{\varepsilon} \right) e^{i\boldsymbol{k}.\boldsymbol{r}}$$

Photon polarization Photon wave vector

$$\left\langle f \left| \left(\boldsymbol{p}.\boldsymbol{\varepsilon} + i\frac{\hbar}{2}\boldsymbol{\sigma}.\boldsymbol{k} \times \boldsymbol{\varepsilon} + \frac{i\omega\hbar}{4mc^2}\boldsymbol{\sigma}.\boldsymbol{p} \times \boldsymbol{\varepsilon} \right) e^{i\boldsymbol{k}.\boldsymbol{r}} \right| i \right\rangle$$
$$= i\frac{m}{\hbar}(E_f - E_g)\langle f | o_{E1} + o_{E2} + o_{E3} + o_{M1} + o_{M2} + o_{SP} \ldots | i \rangle$$

Electric operators

$$o_{E1} = \boldsymbol{\varepsilon}.\boldsymbol{r}$$
$$o_{E2} = \frac{i}{2}\boldsymbol{\varepsilon}.\boldsymbol{r}\boldsymbol{k}.\boldsymbol{r}$$
$$o_{E3} = -\frac{1}{6}\boldsymbol{\varepsilon}.\boldsymbol{r}(\boldsymbol{k}.\boldsymbol{r})^2$$

Magnetic operators

$$o_{M1} = c_m \boldsymbol{k} \times \boldsymbol{\varepsilon}.(\boldsymbol{L} + 2\boldsymbol{S})$$
$$o_{M2} = i c_m \boldsymbol{k} \times \boldsymbol{\varepsilon}.\left(\frac{2}{3}\boldsymbol{L} + 2\boldsymbol{S}\right)(\boldsymbol{k}.\boldsymbol{r})$$

Negligible for X-rays

Dipole spin position operator

$$o_{SP} = i\Omega\boldsymbol{\sigma}.\boldsymbol{\varepsilon} \times \boldsymbol{r}$$

Sizeable for K edge XMCD

N. Bouldi, PRB 96 (2017)

quadrupole octupole

$$\left\langle f\left|\vec{\varepsilon}.\vec{r}\left(1+\frac{i}{2}\vec{k}.\vec{r}-\frac{1}{6}\left(\vec{k}.\vec{r}\right)^2\right)\right|i\right\rangle = \left\langle f\left|\vec{\varepsilon}.\vec{r}\right|i\right\rangle + i\frac{k}{2}\left\langle f\left|\vec{\varepsilon}.\vec{r}\vec{u}.\vec{r}\right|i\right\rangle - \frac{k^2}{6}\left\langle f\left|\vec{\varepsilon}.\vec{r}\left(\vec{u}.\vec{r}\right)^2\right|i\right\rangle$$

$$\vec{u} = \frac{\vec{k}}{k} \qquad k = \tfrac{1}{2}\alpha\hbar\omega$$

Photon energy in Rydberg

Fine structure constant $\cong \frac{1}{127}$

Selection rules

The expansion of $\vec{\varepsilon}.\vec{r}$ and $\vec{u}.\vec{r}$ in real spherical harmonics gives :

$$\vec{\varepsilon}.\vec{r} = (-1)^m \sqrt{\frac{4\pi}{3}} r Y_1^m(\Omega) \qquad \Omega = (\theta, \varphi)$$

For example, polarization along z, wave vector along x :

$$\vec{\varepsilon}.\vec{r} = z = r\cos\theta = \sqrt{\tfrac{4\pi}{3}} r Y_1^0 = c_{10} r Y_1^0 \longrightarrow \ell_o = 1 \quad m_o = 0$$

$$\vec{\varepsilon}.\vec{r}\,\vec{u}.\vec{r} = zx = r^2 \sin\theta\cos\theta\cos\varphi = c_{21} r^2 (Y_2^{-1} - Y_2^1) \longrightarrow \ell_o = 2 \quad m_o = +1 \text{ and } -1$$

The transition matrix is :

$$\langle f | o | i \rangle = c_{\ell_o m_o} \sum_{\ell,m} a_{\ell m}^f(E) \left(\int_0^R b_\ell(r,E)\, g_{\ell_i}(r)\, r^{2+\ell_o}\, dr \right) \left(\iint_{Sphere} Y_\ell^m(\Omega)\, Y_{\ell_o}^{m_o}(\Omega)\, Y_{\ell_i}^{m_i}(\Omega)\, d\Omega \right)$$

Radial integral

Gaunt coefficient

Non zero, only for some ℓ and m → gives the selection rules

Case of *K*-edge (1s initial state): $\ell_i = 0 = m_i$

dipole component and polarization along z : $\ell_o = 1$ $m_o = 0$

the only non-zero matrix element is for $\ell = 1$ $m = 0$

→ one probes the p_z final states projected onto the absorbing atom

dipole component and polarization along y : $\vec{\varepsilon}.\vec{r} = y = c_{11} r (Y_1^1 + Y_{-1}^1)$

→ one probes the p_y final states projected onto the absorbing atom

If p_z and p_y electron density are different : one can measure XNLD

→XNLD is due to anisotropy in charge distribution

Case of *K*-edge (1s initial state): $\ell_i = 0 = m_i$

quadrupole component, polarization along z, wave vector along x :

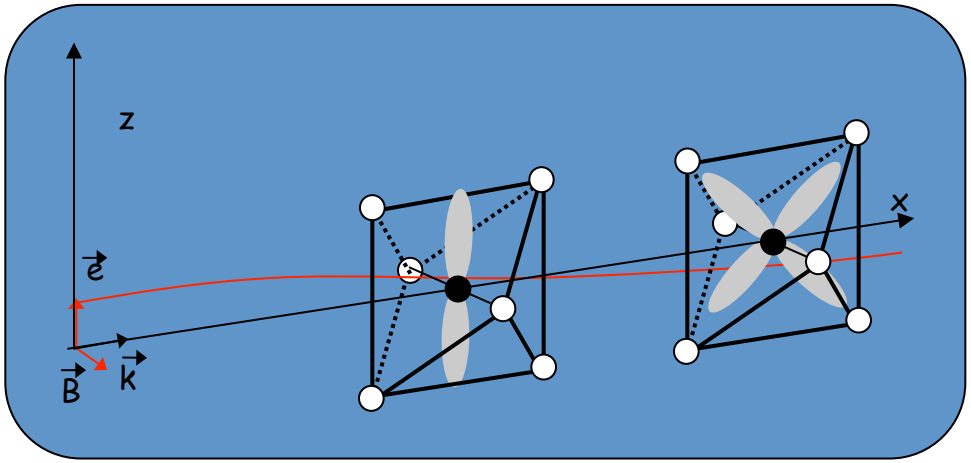
one probes the d_{xz} final states projected onto the absorbing atom

quadrupole component, polarization along (x+y)/sqrt(2),

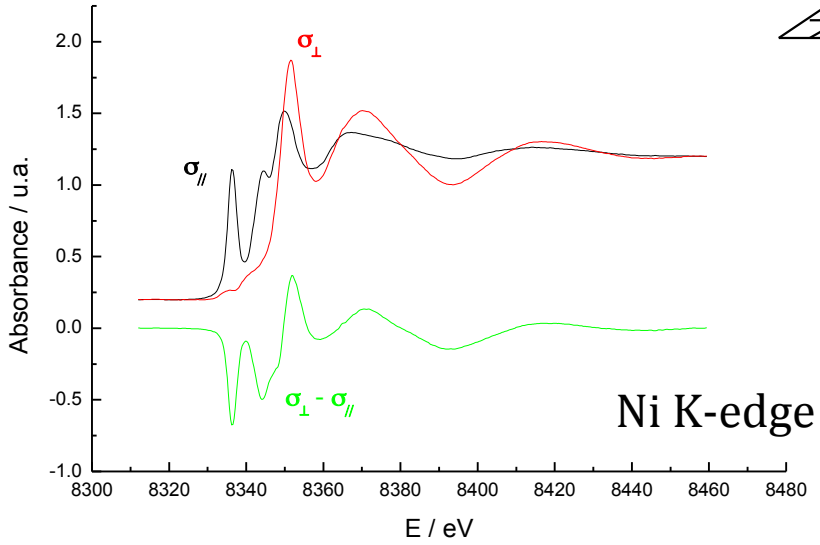
wave vector along (x-y)/sqrt(2)

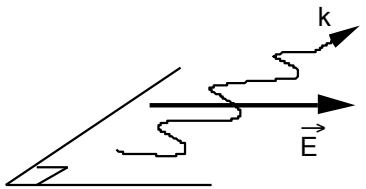
one probes the d_{x2-y2} final states projected onto the absorbing atom

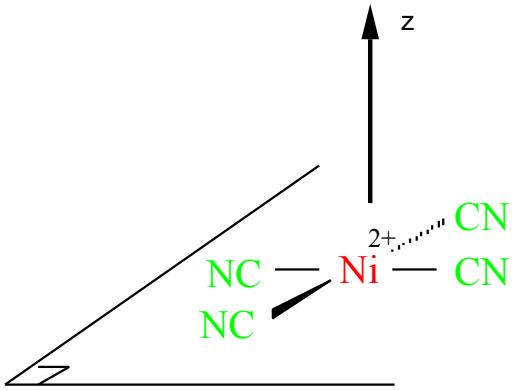
If the d_{xz} and d_{x2-y2} electron densities are different, one can measure XNLD

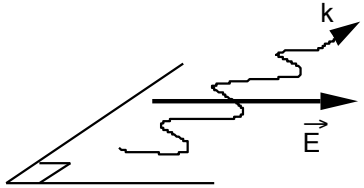


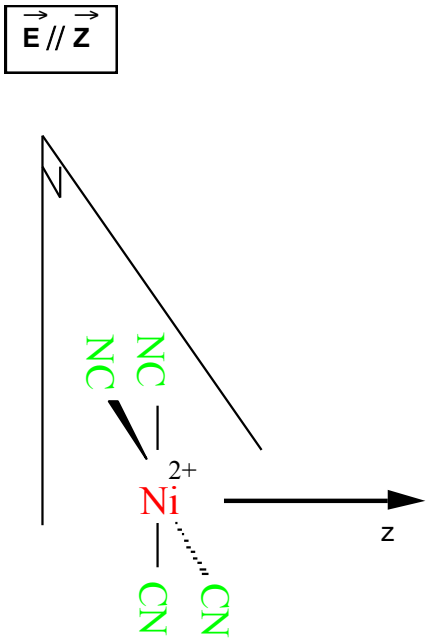
Example : s-p transitions in square planar *3d* complex





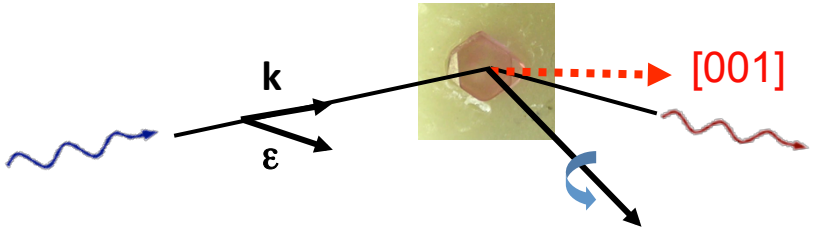




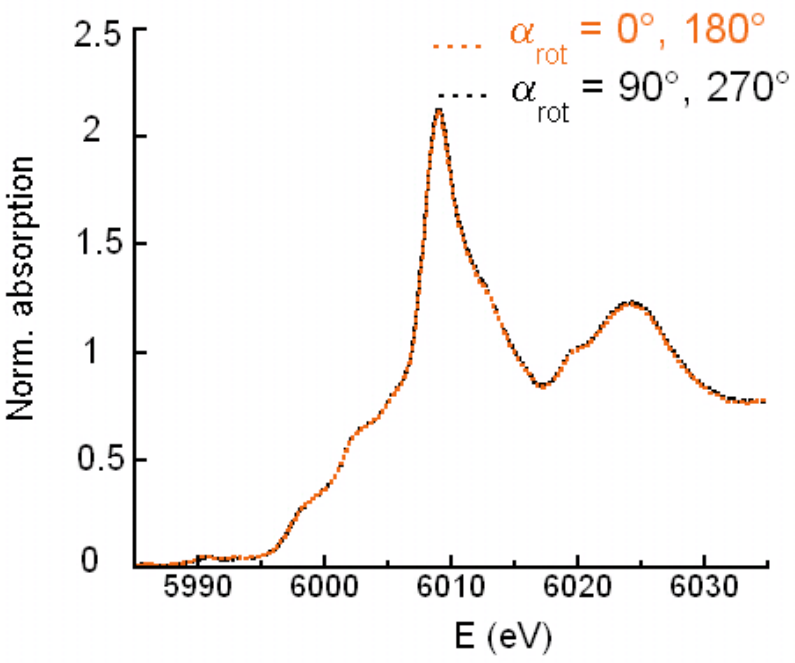


Dipole versus quadrupole transitions

Octahedral Cr^{3+} ions in $MgAl_2O_4$



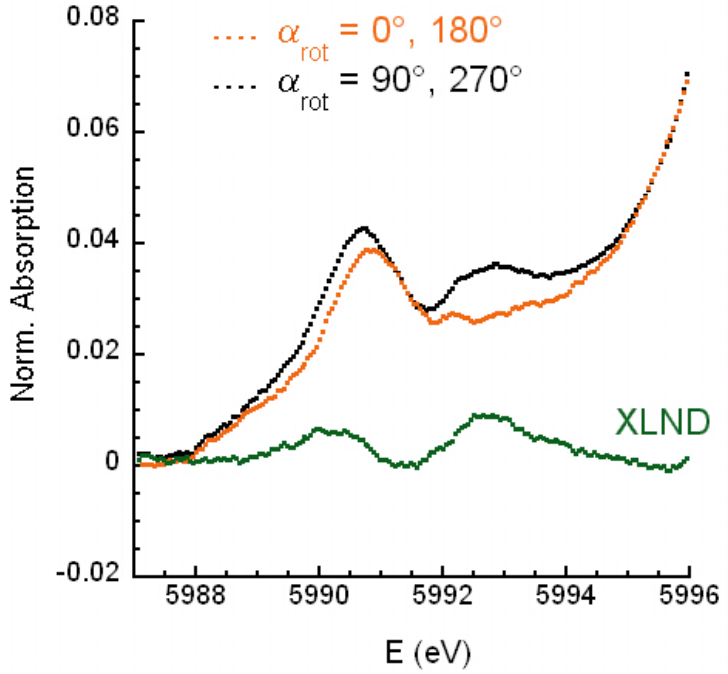
Cr K-edge



electric dipole 1s→p transitions

No XNLD

Cr K pre-edge



electric quadrupole 1s→3d transitions

XNLD

Same crystal but different angular dependence

One absorbing site versus whole crystal

$$\sigma(\omega) = 4\pi^2 \alpha \hbar\omega \sum_{f,i} \left| \langle f | o | i \rangle \right|^2 \delta(\hbar\omega - E_f + E_i)$$

What we measure :

XAS signal from the crystal (sum over atoms) : symmetry of the material (space group)

What we directly calculate with an atomic code :

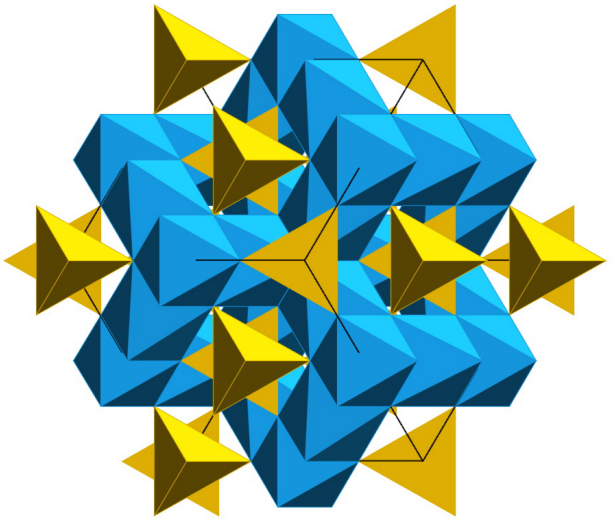
XAS signal from one atom : symmetry of the atomic site (point group symmetry)

lower than crystal symmetry

How to make connection between crystal properties and site properties ?

One absorbing site versus whole crystal

Our example for today : spinel $MgAl_2O_4$



- Fd-3m space group (#227):
  cubic system
  m-3m point group

- Cubic unit cell contains 32 octahedral sites :
  16 are occupied, with Wyckoff position 16c

Do we need to perform 16 calculations ?
Can we simplify the problem ?

Wyckoff Positions of Group 227 (*Fd*-3*m*) [origin choice 2]

Multiplicity	Wyckoff letter	Site symmetry	Coordinates
			(0,0,0) + (0,1/2,1/2) + (1/2,0,1/2) + (1/2,1/2,0) +
192	i	1	(x,y,z) (-x+3/4,-y+1/4,z+1/2) (-x+1/4,y+1/2,-z+3/4) (x+1/2,-y+3/4,-z+1/4) (z,x,y) (z+1/2,-x+3/4,-y+1/4) (-z+3/4,-x+1/4,y+1/2) (-z+1/4,x+1/2,-y+3/4) (y,z,x) (-y+1/4,z+1/2,-x+3/4) (y+1/2,-z+3/4,-x+1/4) (-y+3/4,-z+1/4,x+1/2) (y+3/4,x+1/4,-z+1/2) (-y,-x,-z) (y+1/4,-x+1/2,z+3/4) (-y+1/2,x+3/4,z+1/4) (x+3/4,z+1/4,-y+1/2) (-x+1/2,z+3/4,y+1/4) (-x,-z,-y) (x+1/4,-z+1/2,y+3/4) (z+3/4,y+1/4,-x+1/2) (z+1/4,-y+1/2,x+3/4) (-z+1/2,y+3/4,x+1/4) (-z,-y,-x) (-x,-y,-z) (x+1/4,y+3/4,-z+1/2) (x+3/4,-y+1/2,z+1/4) (-x+1/2,y+1/4,z+3/4) (-z,-x,-y) (-z+1/2,x+1/4,y+3/4) (z+1/4,x+3/4,-y+1/2) (z+3/4,-x+1/2,y+1/4) (-y,-z,-x) (y+3/4,-z+1/2,x+1/4) (-y+1/2,z+1/4,x+3/4) (y+1/4,z+3/4,-x+1/2) (-y+1/4,-x+3/4,z+1/2) (y,x,z) (-y+3/4,x+1/2,-z+1/4) (y+1/2,-x+1/4,-z+3/4) (-x+1/4,-z+3/4,y+1/2) (x+1/2,-z+1/4,-y+3/4) (x,z,y) (-x+3/4,z+1/2,-y+1/4) (-z+1/4,-y+3/4,x+1/2) (-z+3/4,y+1/2,-x+1/4) (z+1/2,-y+1/4,-x+3/4) (z,y,x)
96	h	..2	(0,y,-y) (3/4,-y+1/4,-y+1/2) (1/4,y+1/2,y+3/4) (1/2,-y+3/4,y+1/4) (-y,0,y) (-y+1/2,3/4,-y+1/4) (y+3/4,1/4,y+1/2) (y+1/4,1/2,-y+3/4) (y,-y,0) (-y+1/4,-y+1/2,3/4) (y+1/2,y+3/4,1/4) (-y+3/4,y+1/4,1/2) (0,-y,y) (1/4,y+3/4,y+1/2) (3/4,-y+1/2,-y+1/4) (1/2,y+1/4,-y+3/4) (y,0,-y) (y+1/2,1/4,y+3/4) (-y+1/4,3/4,-y+1/2) (-y+3/4,1/2,y+1/4) (-y,y,0) (y+3/4,y+1/2,1/4) (-y+1/2,-y+1/4,3/4) (y+1/4,-y+3/4,1/2)
96	g	..m	(x,x,z) (-x+3/4,-x+1/4,z+1/2) (-x+1/4,x+1/2,-z+3/4) (x+1/2,-x+3/4,-z+1/4) (z,x,x) (z+1/2,-x+3/4,-x+1/4) (-z+3/4,-x+1/4,x+1/2) (-z+1/4,x+1/2,-x+3/4) (x,z,x) (-x+1/4,z+1/2,-x+3/4) (x+1/2,-z+3/4,-x+1/4) (-x+3/4,-z+1/4,x+1/2) (x+3/4,x+1/4,-z+1/2) (-x,-x,-z) (x+1/4,-x+1/2,z+3/4) (-x+1/2,x+3/4,z+1/4) (x+3/4,z+1/4,-x+1/2) (-x+1/2,z+3/4,x+1/4) (-x,-z,-x) (x+1/4,-z+1/2,x+3/4) (z+3/4,x+1/4,-x+1/2) (z+1/4,-x+1/2,x+3/4) (-z+1/2,x+3/4,x+1/4) (-z,-x,-x)
48	f	2.m m	(x,1/8,1/8) (-x+3/4,1/8,5/8) (1/8,x,1/8) (5/8,-x+3/4,1/8) (1/8,1/8,x) (1/8,5/8,-x+3/4) (7/8,x+1/4,3/8) (7/8,-x,7/8) (x+3/4,3/8,3/8) (-x+1/2,7/8,3/8) (7/8,3/8,-x+1/2) (3/8,3/8,x+3/4)
32	e	.3m	(x,x,x) (-x+3/4,-x+1/4,x+1/2) (-x+1/4,x+1/2,-x+3/4) (x+1/2,-x+3/4,-x+1/4) (x+3/4,x+1/4,-x+1/2) (-x,-x,-x) (x+1/4,-x+1/2,x+3/4) (-x+1/2,x+3/4,x+1/4)
16	d	.-3m	(1/2,1/2,1/2) (1/4,3/4,0) (3/4,0,1/4) (0,1/4,3/4)
16	c	.-3m	(0,0,0) (3/4,1/4,1/2) (1/4,1/2,3/4) (1/2,3/4,1/4)
8	b	-43m	(3/8,3/8,3/8) (1/8,5/8,1/8)
8	a	-43m	(1/8,1/8,1/8) (7/8,3/8,3/8)

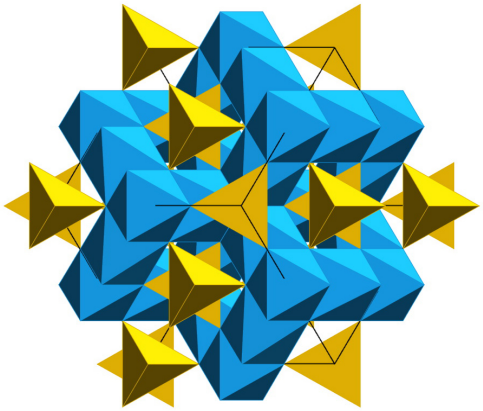
3 translations

4 equivalent sites by rotation

3 x 4 = 12

One absorbing site versus whole crystal

Our example for today : spinel $MgAl_2O_4$



- Fd-3m space group (n°227):
  cubic system
  m-3m point group

- Cubic unit cell contains 32 octahedral sites :
  16 are occupied, with Wyckoff position 16c : D_{3d} or -3m symmetry

- Only 4 are crystallographic equivalent (translations do not matter for XAS)

Symmetry elements in O_h point group

Orientation XYZ

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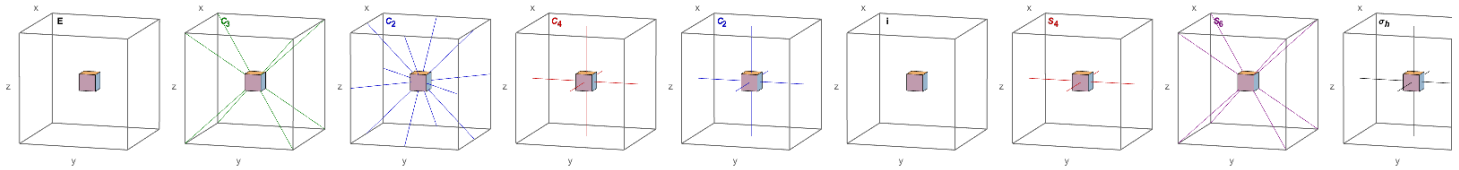
Symmetry Operations

In the Oh Point Group, with orientation XYZ there are the following symmetry operations



Operator	Orientation
E	$\{0,0,0\}$,
C_3	$\{1,1,1\}$, $\{1,1,-1\}$, $\{1,-1,1\}$, $\{-1,1,1\}$, $\{-1,-1,1\}$, $\{-1,1,-1\}$, $\{1,-1,-1\}$, $\{-1,-1,-1\}$,
C_2	$\{1,1,0\}$, $\{1,-1,0\}$, $\{1,0,-1\}$, $\{1,0,1\}$, $\{0,1,1\}$, $\{0,1,-1\}$,
C_4	$\{0,0,1\}$, $\{0,1,0\}$, $\{1,0,0\}$, $\{0,0,-1\}$, $\{0,-1,0\}$, $\{-1,0,0\}$,
C_2	$\{0,0,1\}$, $\{0,1,0\}$, $\{1,0,0\}$,
i	$\{0,0,0\}$,
S_4	$\{0,0,1\}$, $\{0,1,0\}$, $\{1,0,0\}$, $\{0,0,-1\}$, $\{0,-1,0\}$, $\{-1,0,0\}$,
S_6	$\{1,1,1\}$, $\{1,1,-1\}$, $\{1,-1,1\}$, $\{-1,1,1\}$, $\{-1,-1,1\}$, $\{-1,1,-1\}$, $\{1,-1,-1\}$, $\{-1,-1,-1\}$,
σ_h	$\{1,0,0\}$, $\{0,1,0\}$, $\{0,0,1\}$,
σ_d	$\{1,1,0\}$, $\{1,-1,0\}$, $\{1,0,-1\}$, $\{1,0,1\}$, $\{0,1,1\}$, $\{0,1,-1\}$,

Symmetry elements in D_{3d} point group

Orientation 111

Table of Con

This orientation is non-standard, but related to the orientation of the Oh pointgroup, which normally would be orientated with the C3 axes in the 111 direction. We only show one of the options of the D3d subgroups of the Oh group with orientation XYZ.

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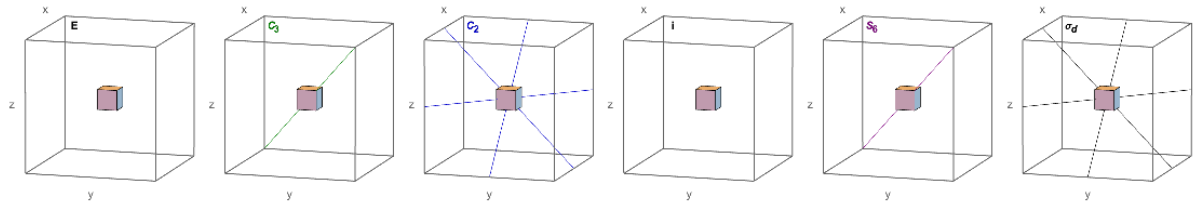
Symmetry Operations

In the D3d Point Group, with orientation 111 there are the following symmetry operations

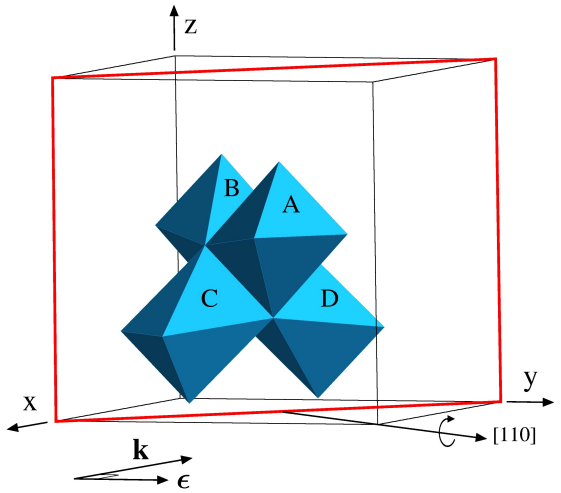


Operator	Orientation
E	$\{0,0,0\}$,
C_3	$\{1,1,1\}$, $\{-1,-1,-1\}$,
C_2	$\{1,-1,0\}$, $\{0,1,-1\}$, $\{1,0,-1\}$,
i	$\{0,0,0\}$,
S_6	$\{1,1,1\}$, $\{-1,-1,-1\}$,
σ_d	$\{1,-1,0\}$, $\{0,1,-1\}$, $\{1,0,-1\}$,

The C_3 axis in D_{3d} is one of the C_3 axis in O_h

One absorbing site versus whole crystal

Our example for today : spinel $MgAl_2O_4$



- Fd-3m space group (n°227):
  cubic system
- Cubic unit cell
- There are four D_{3d} sites crystallographic equivalent, with their respective C_3 axis along

$$[111]\ [\bar{1}11]\ [1\bar{1}1]\ [11\bar{1}] \quad \text{directions}$$

A, B, C and D sites are not « equivalent» for XAS :

A priori they yield different cross-sections !

$$\sigma^{cube} = \sigma^{A} + \sigma^{B} + \sigma^{C} + \sigma^{D}$$

Issues related to XNLD calculations

1. Can we predict the angular dependence based on the crystal structure ?

2. Is there an analytical expression of the XAS cross-section :

   for electric dipole transitions ?
   for electric quadrupole transitions ?

3. How does one calculate the spectrum for the whole crystal using a single atom model ?

Expression of the angular dependence of XAS, RIXS etc…

Many physical properties can be described by a tensor : for example :

electric dipole transition amplitude in XAS : tensor of rank 1 (= a vector) :
$3^1 = 3$ components

electric dipole transition intensity in XAS : tensor of rank 2 (= a matrix)
$3^2 = 9$ components

A tensor of rank N is the generalized form : 3^N components

Two formalisms can be used to describe the same physical property :

- Cartesian Tensors
- Spherical Tensors

Expression of the angular dependence of XAS, RIXS etc…

Take a Cartesian tensor of rank 2 and apply a transformation :

its components will transform linearly into themselves

Now we limit ourselves to rotations

It is possible to make « special » linear combinations the 9 components and from « groups » where they transform into themselves

One is invariant : a scalar (a 0^{th} rank tensor)

A group of 3 transform into themselves : a vector (a 1^{st} rank tensor)

A group of 5 transform into themselves : a 2^{nd} rank tensor

It is not possible to make smaller groups : we call them *irreducible tensors*

Expression of the angular dependence of XAS, RIXS etc…

Ex : Spherical harmonics Y_ℓ^m are irreducible tensors

By analogy, irreducible tensors are labeled : T_ℓ^m with $m = -\ell, \ldots, \ell$ and rank ℓ

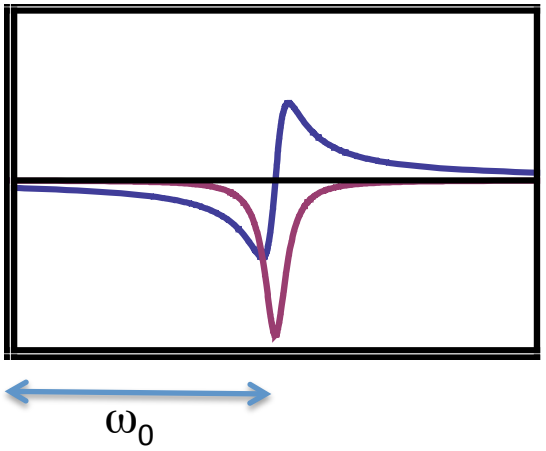
It is easy to rotate or multiply them.

XAS cross-section in Cartesian coordinates : (1) electric dipole transitions

In Quanty (which uses Green function formalism) the **electric dipole** XAS cross-section is calculated as the Imaginary part of the « conductivity tensor » σ :

$$\text{Absorption} = -\text{Im}[\varepsilon.\sigma.\varepsilon]$$

ε : polarization



Real

Imaginary = XAS

→ The conductivity tensor is calculated once

→ The absorption cross-section can then very easily be calculated for any ε

XAS cross-section in Cartesian coordinates : (1) electric dipole transitions

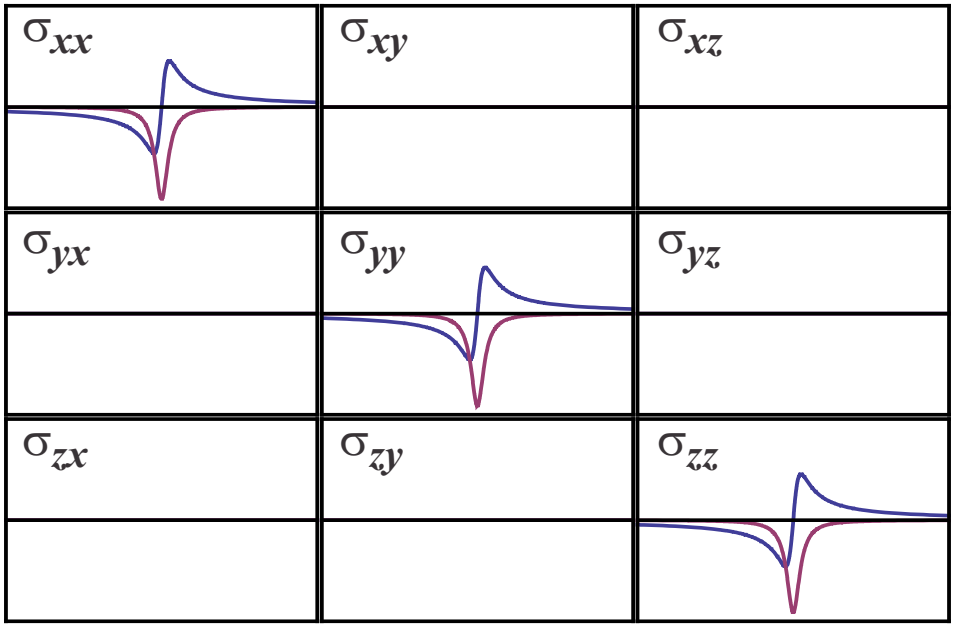
- For linearly polarized x-rays, this conductivity tensor writes :

$$\sigma^D(\epsilon) = \sum_{ij} \epsilon_i \epsilon_j \sigma_{ij}, \qquad \text{with}$$

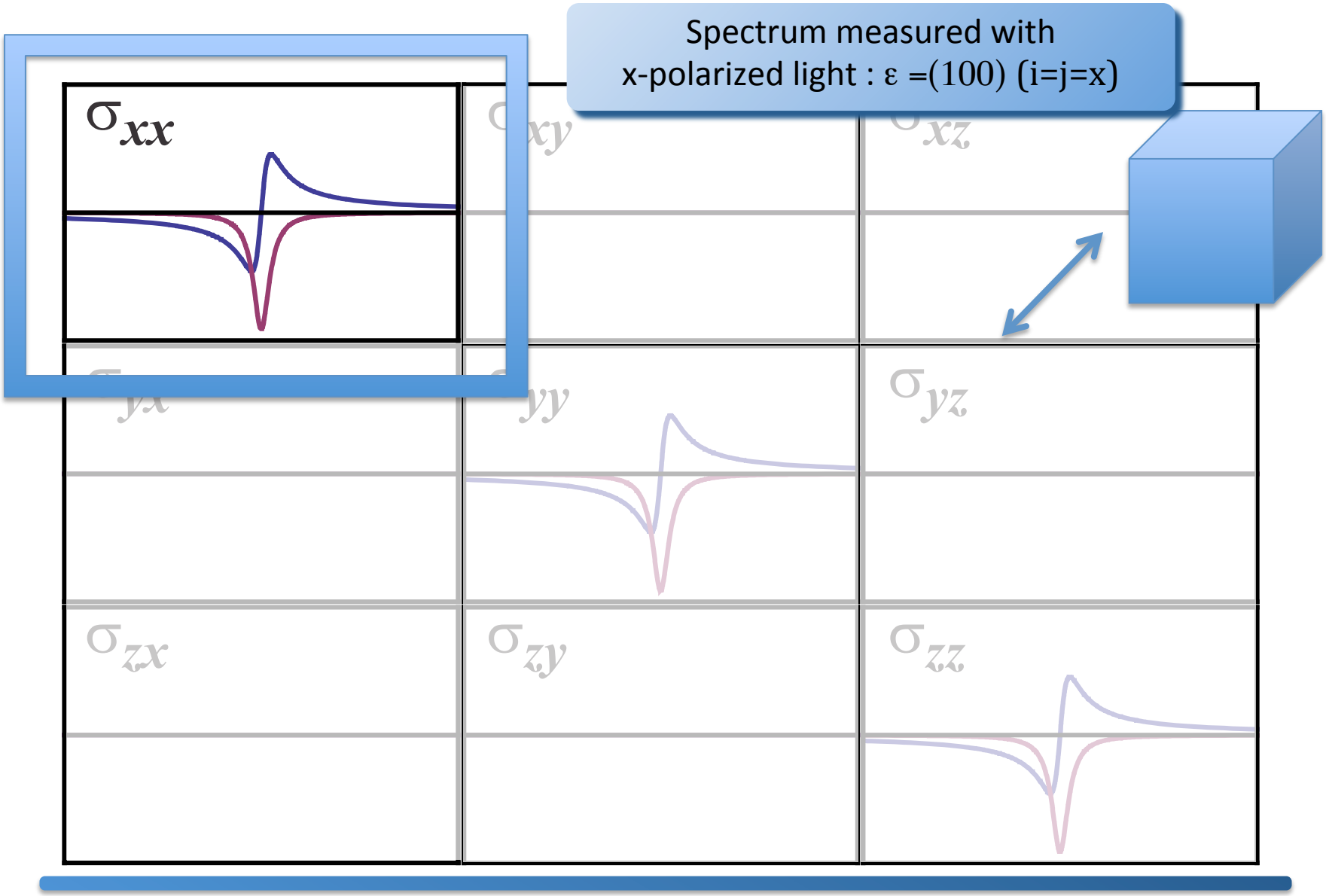
$$\sigma_{ij} = 4\pi^2 \alpha_0 \hbar\omega \sum_f \langle i|\mathbf{r}_i|f\rangle\langle f|\mathbf{r}_j|i\rangle \delta(E_f - E_i - \hbar\omega). \qquad i = x,y,z \;\; ; j = x,y,z$$

→ The « conductivity tensor » σ_{ij} = a Cartesian tensor of rank 2 (= a matrix):

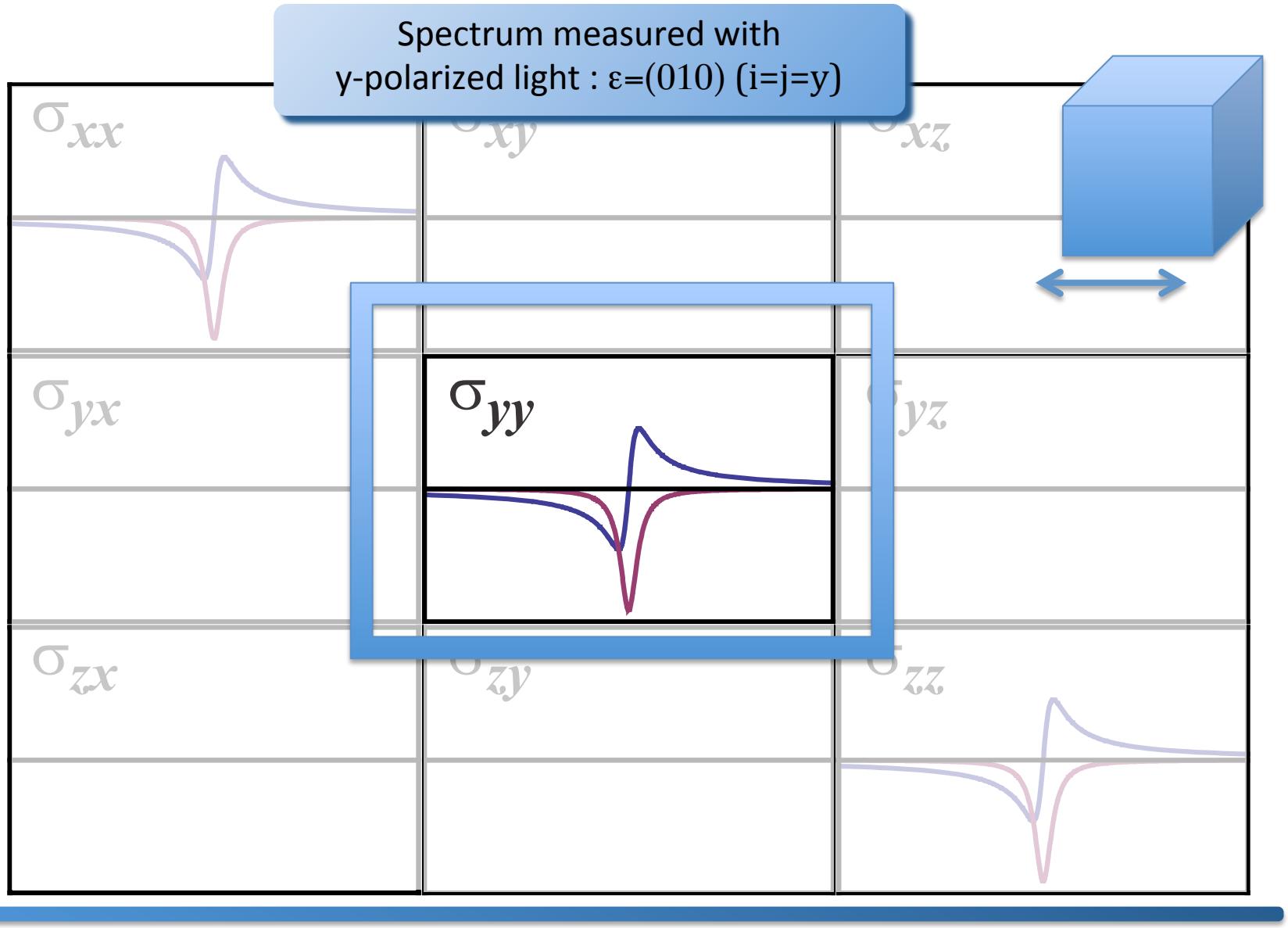
3 x 3 = 9 components

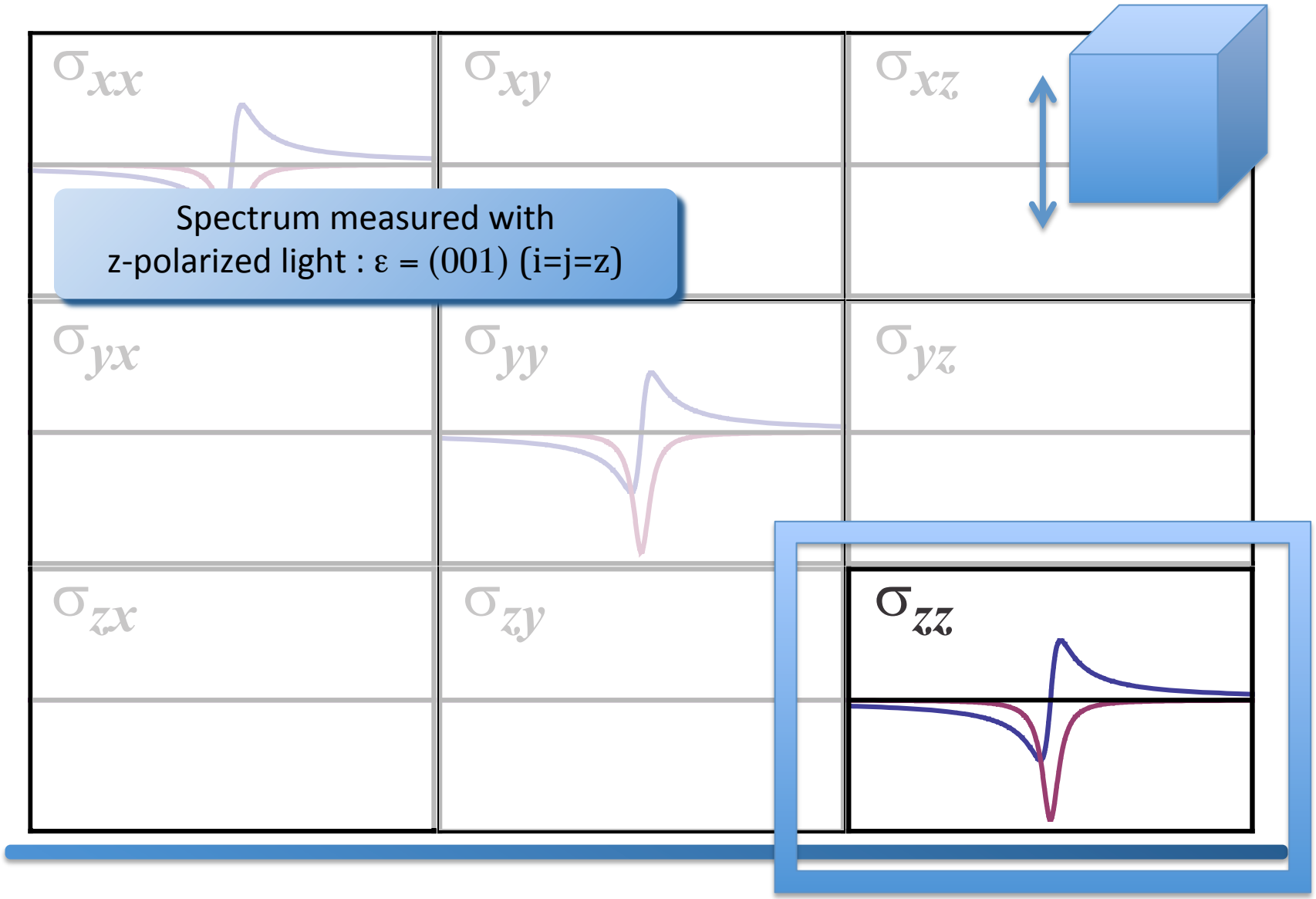


XAS cross-section in Cartesian coordinates : (1) electric dipole transitions



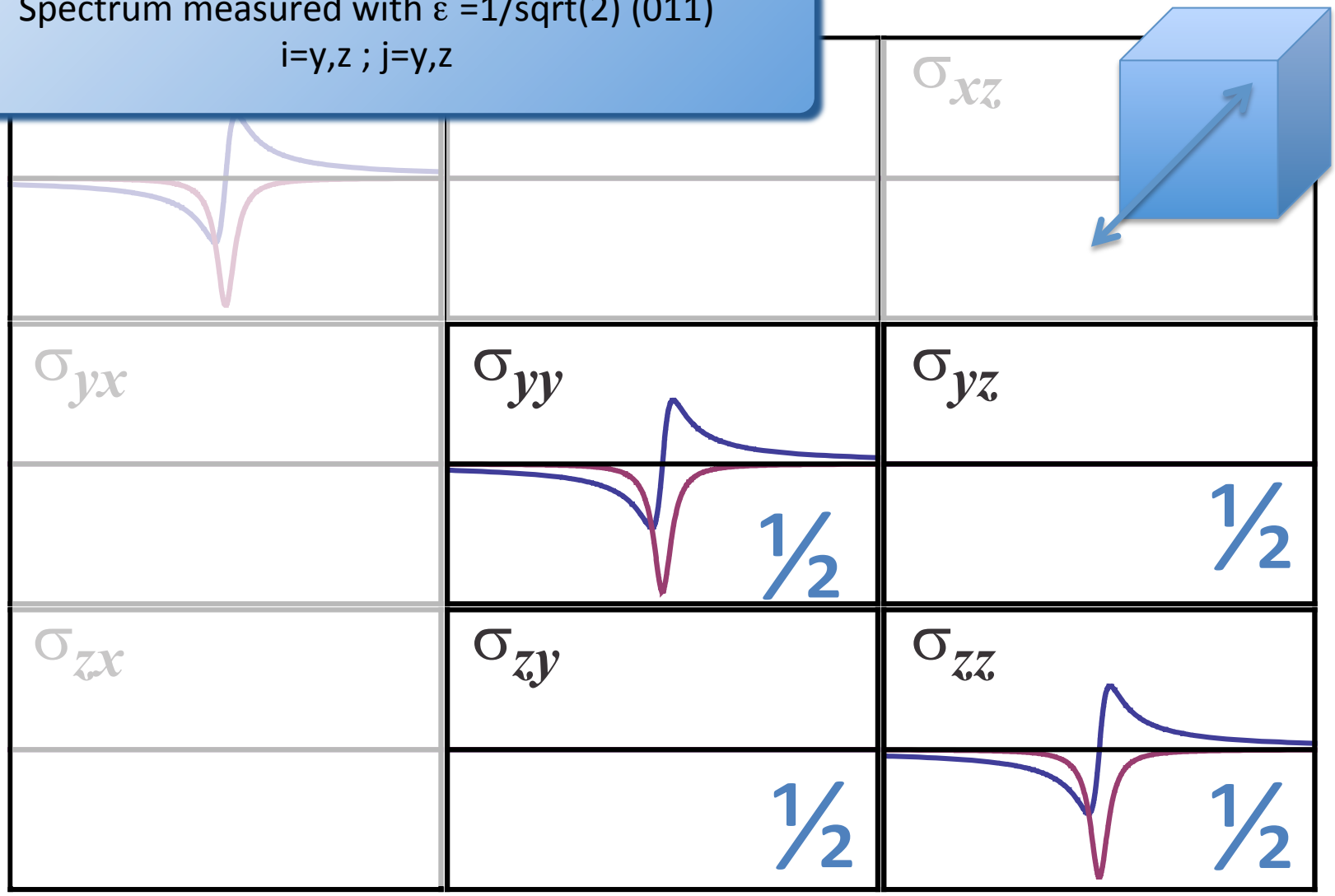
XAS cross-section in Cartesian coordinates : (1) electric dipole transitions




σxx
σxy
σxz
Spectrum measured with
z-polarized light : ε = (001) (i=j=z)
σyx
σyy
σyz
σzx
σzy
σzz

But the conductivity tensor (σ) is a TENSOR

Spectrum measured with ε =1/sqrt(2) (011)
i=y,z ; j=y,z



XAS cross-section in Cartesian coordinates : (1) electric dipole transitions

- Simplification is possible by considering the symmetry group G of the sample

For any operation S in G, $\sigma(\varepsilon)=\sigma[S(\varepsilon)]$

σ is symmetrized (averaged over all S symmetry operations)

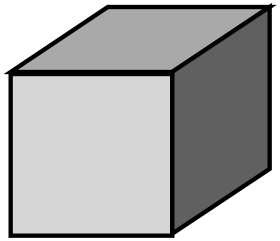
→ <u>Spherical average : the case of a powder :</u>

$$\langle \sigma^{D}(\epsilon) \rangle = \tfrac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}).$$

The isotropic spectrum is the trace of the conductivity tensor in any (x,y,z) frame

→ The case of cubic symmetry

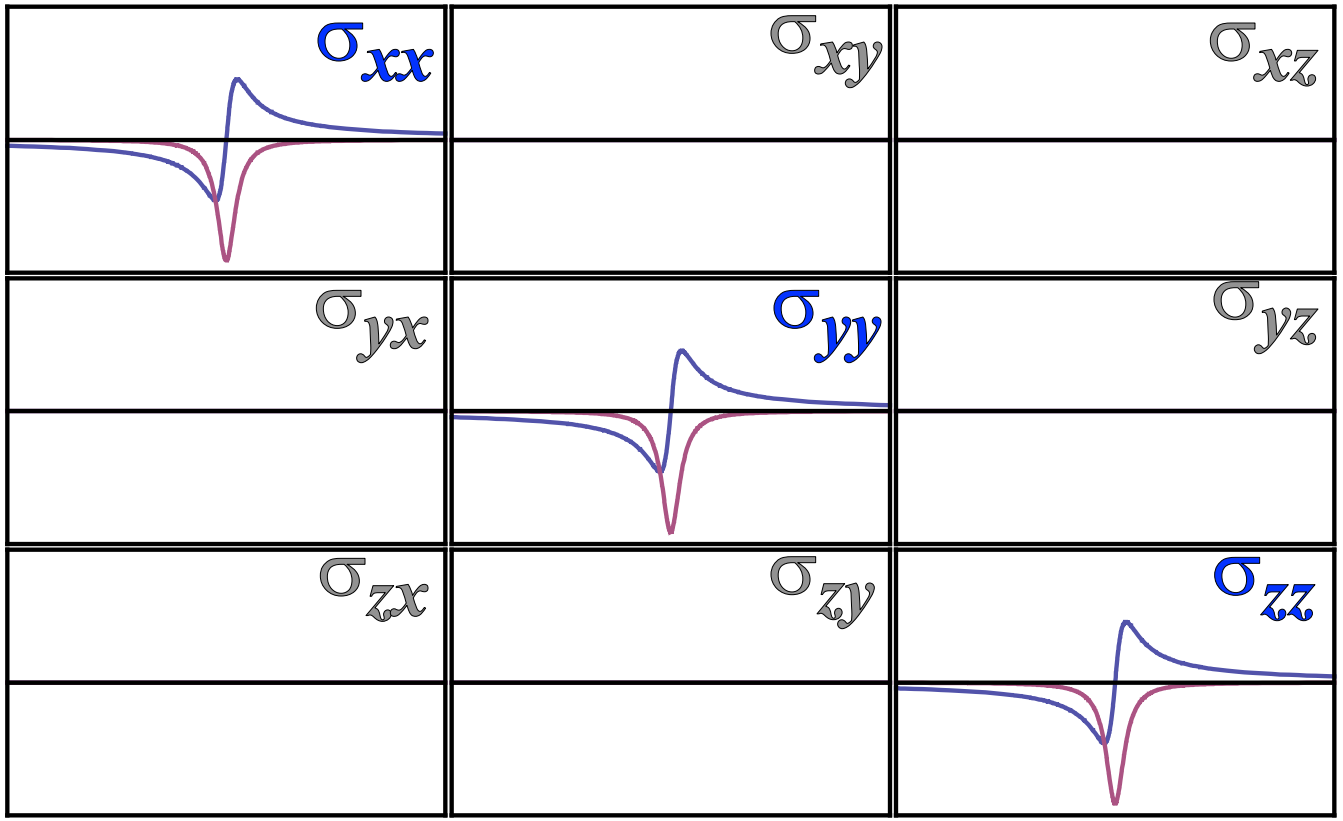
In the cubic (xyz) frame the conductivity tensor writes :



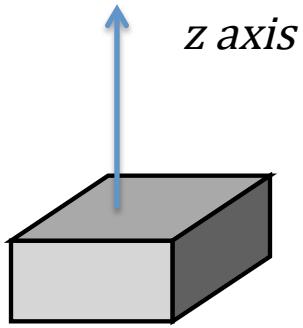
$\sigma_{xx} = \sigma_{yy} = \sigma_{zz}$

isotropic

Other components are zero



→ The case of tetragonal symmetry

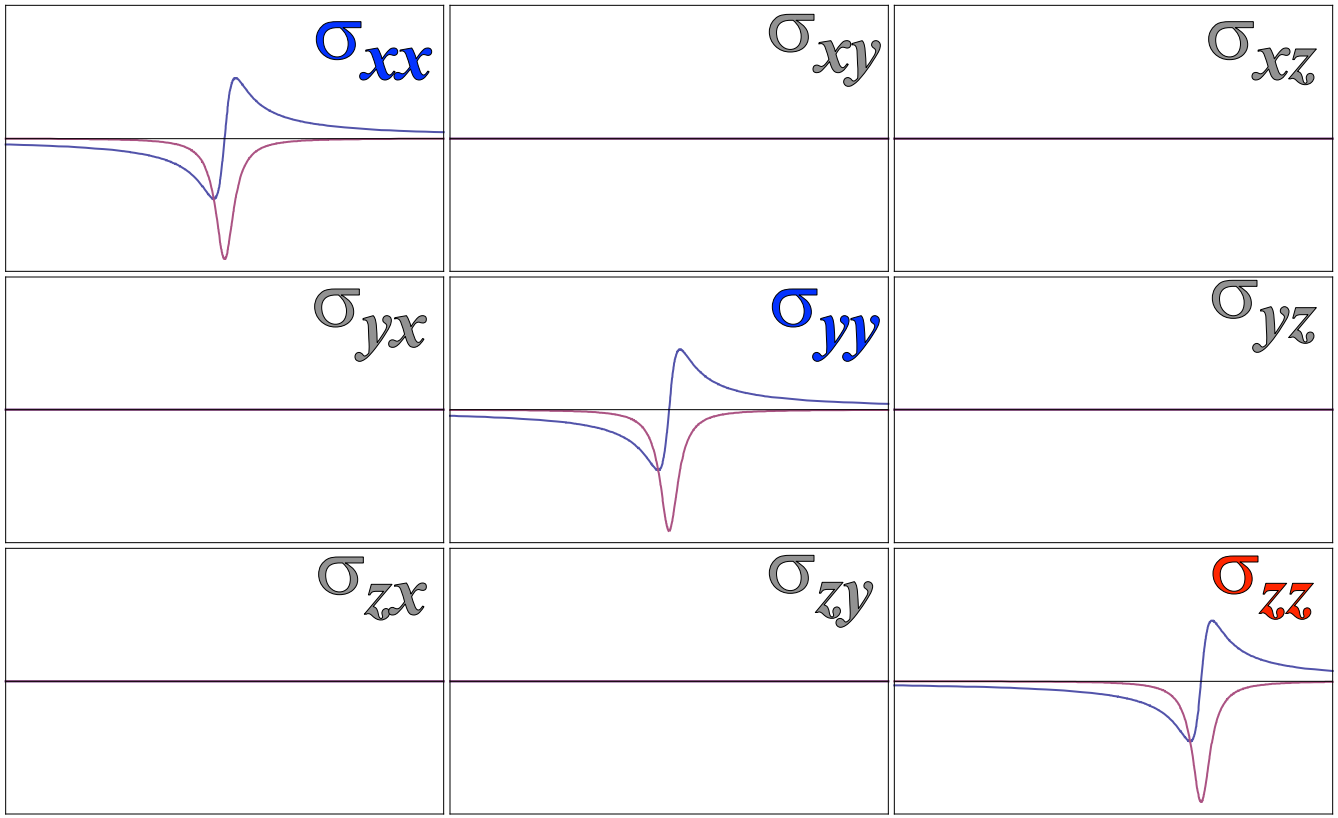


In the (xyz) tetragonal frame where z is the fourfold axis the conductivity tensor writes :

$\sigma_{xx} = \sigma_{yy} \neq \sigma_{zz}$

dichroism

Other components are zero



Other (equivalent) expressions from the literature for a dichroic crystal :

A crystal with a high symmetry axis z : trigonal or tetragonal system

The conductivity tensor can be written in the principal axis

$$\sigma^D(\hat{\epsilon}) = {}^t\hat{\epsilon}. \begin{pmatrix} \sigma_\perp^D & 0 & 0 \\ 0 & \sigma_\perp^D & 0 \\ 0 & 0 & \sigma_\parallel^D \end{pmatrix} .\hat{\epsilon}.$$

// means parallel to z ($=\sigma_{zz}$)
$\perp$ means perpendicular to z ($=\sigma_{xx}$, σ_{yy})

2 fundamental spectra only are needed in order to know everything

Analytical expression of dipole cross-section for a trigonal or tetragonal crystal :

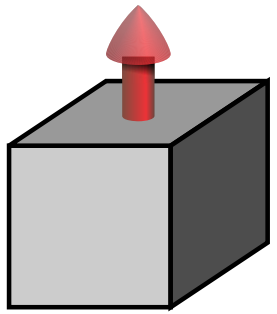
$$\begin{aligned} \sigma^D(\hat{\epsilon}) &= \sigma_\perp^D \sin^2\theta + \sigma_\parallel^D \cos^2\theta. \\ &= \sigma_{iso}^D + \tfrac{1}{3}\sigma_{dic}^D(3\cos^2\theta - 1), \end{aligned}$$

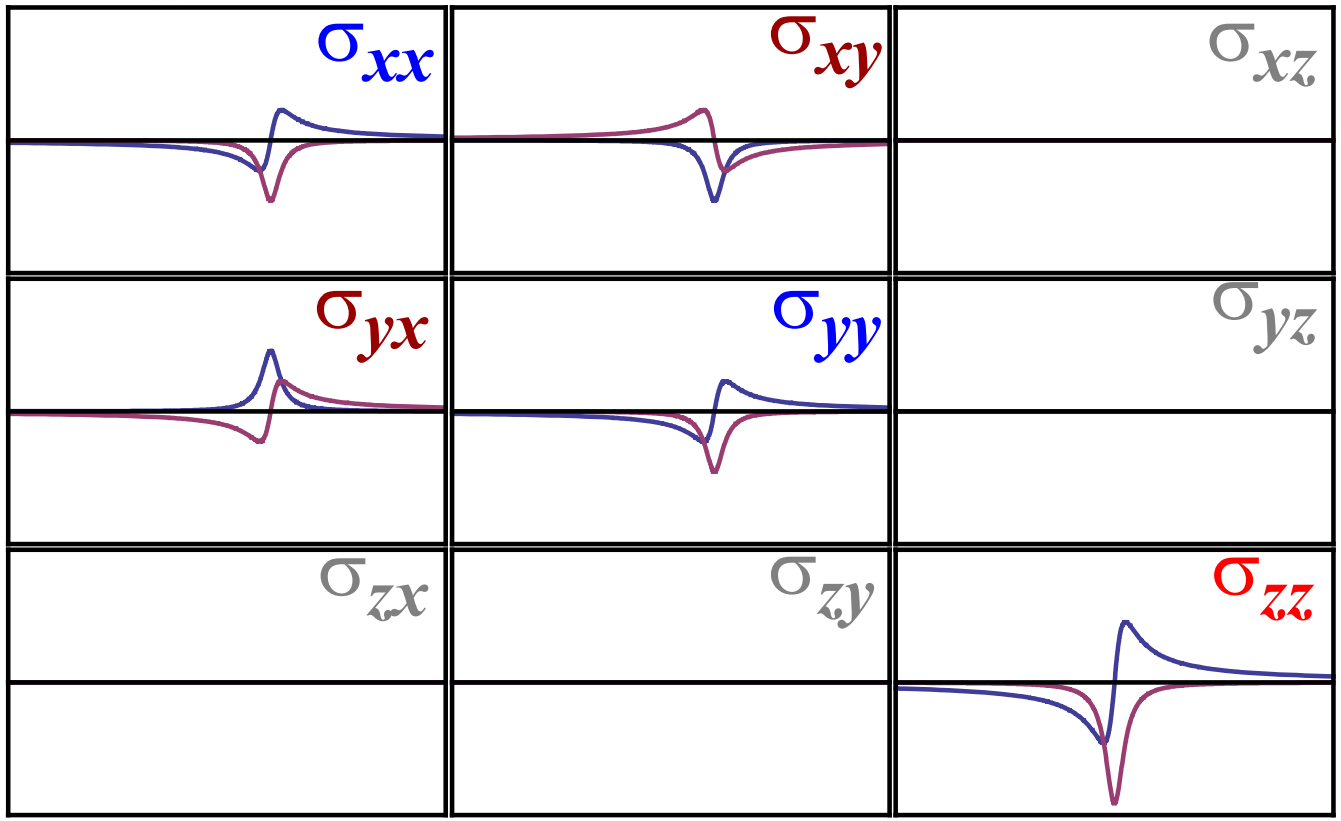
$$\hat{\boldsymbol{\varepsilon}} = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$$

At magic angle (54.7 ° between ε and z) : one measures the isotropic spectrum

→ The case of cubic symmetry + magnetic field

Magnetic field along z



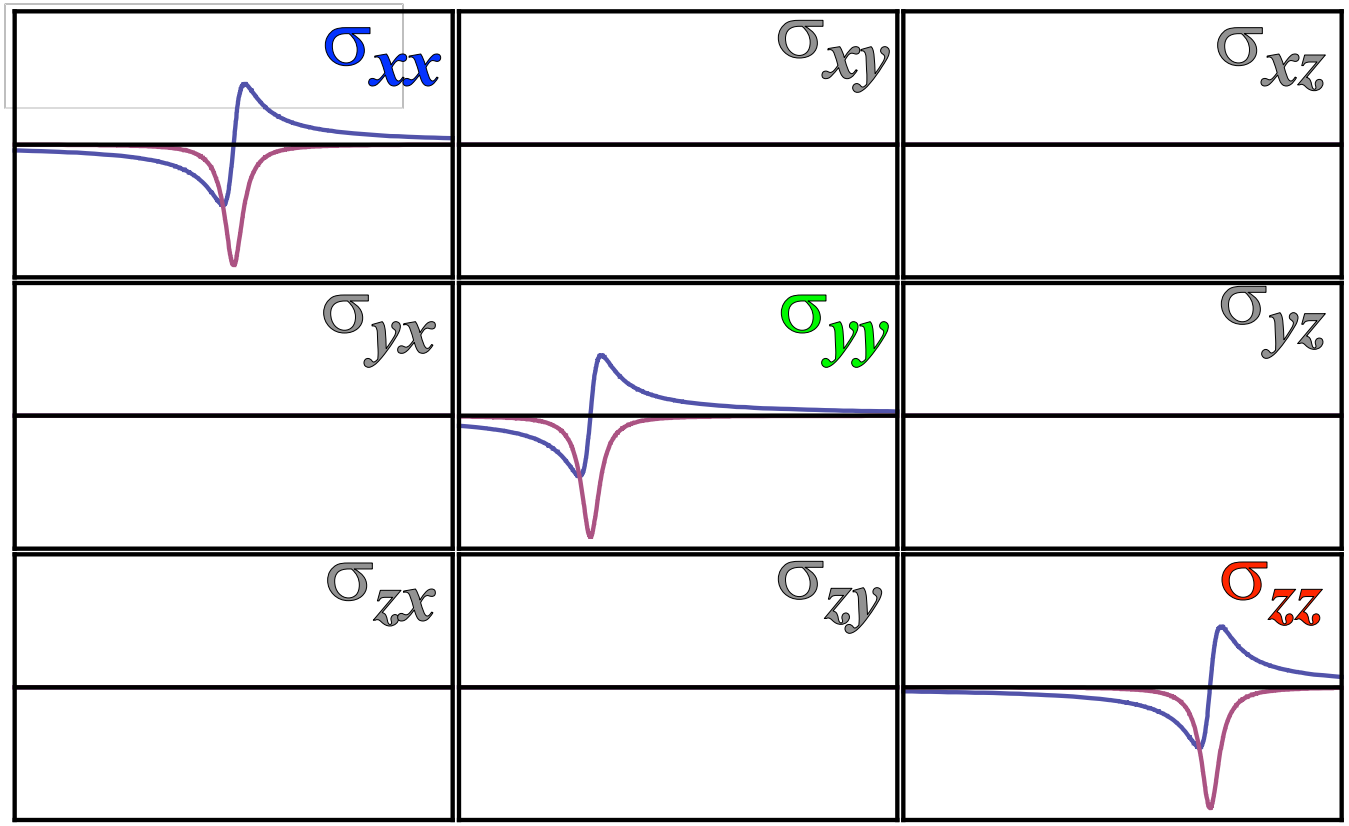


→ The case of orthorhombic symmetry

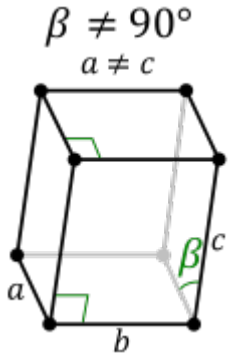
In the (xyz) orthrhombic frame the conductivity tensor writes :

$\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$

Other components are zero



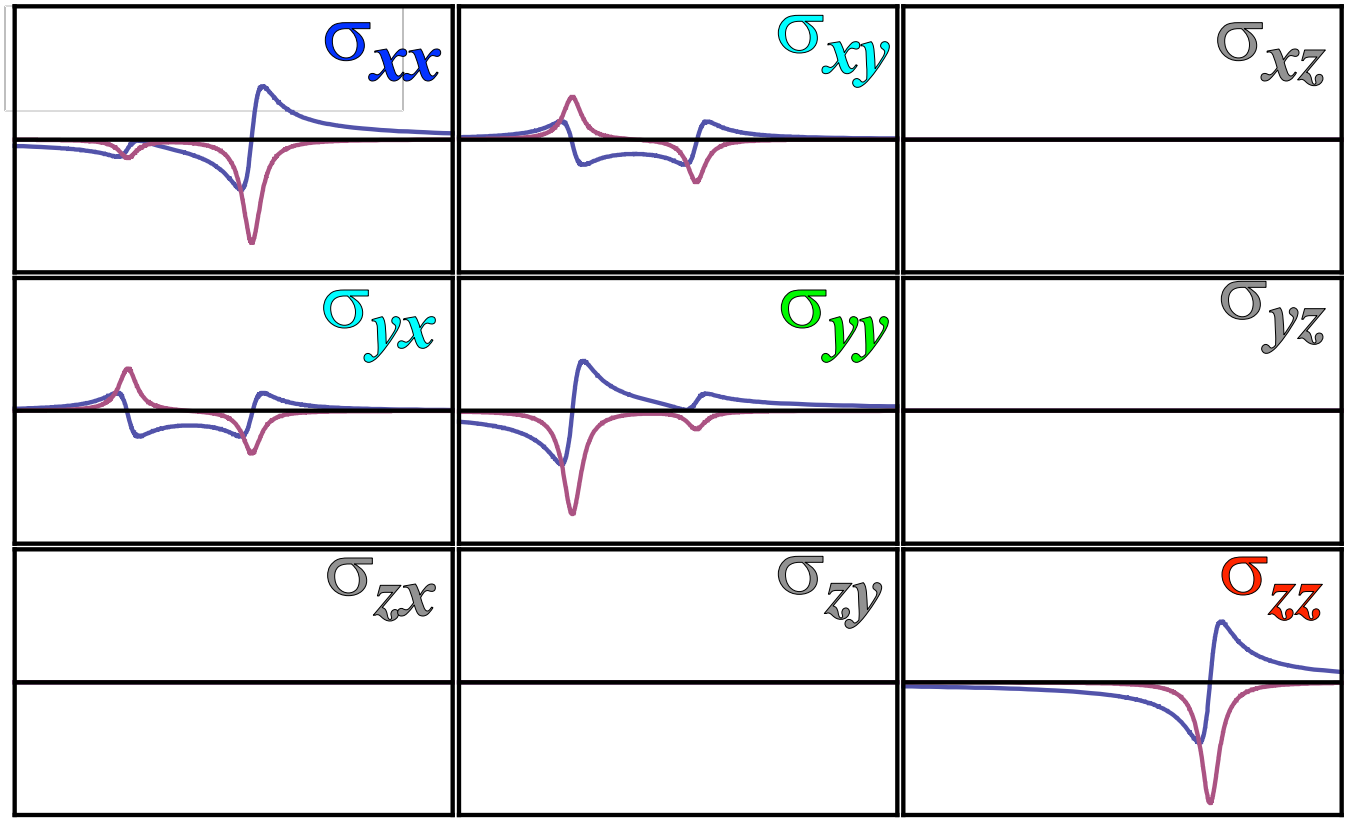
→ The case of monoclinic symmetry



In the (xyz) monoclinic frame the conductivity tensor writes :

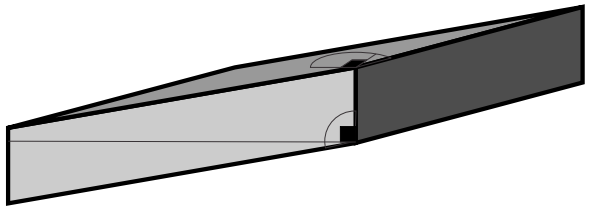
$\sigma_{xx} \neq \sigma_{yy} \neq \sigma_{zz}$

σ_{xy} and σ_{yx} are non-zero

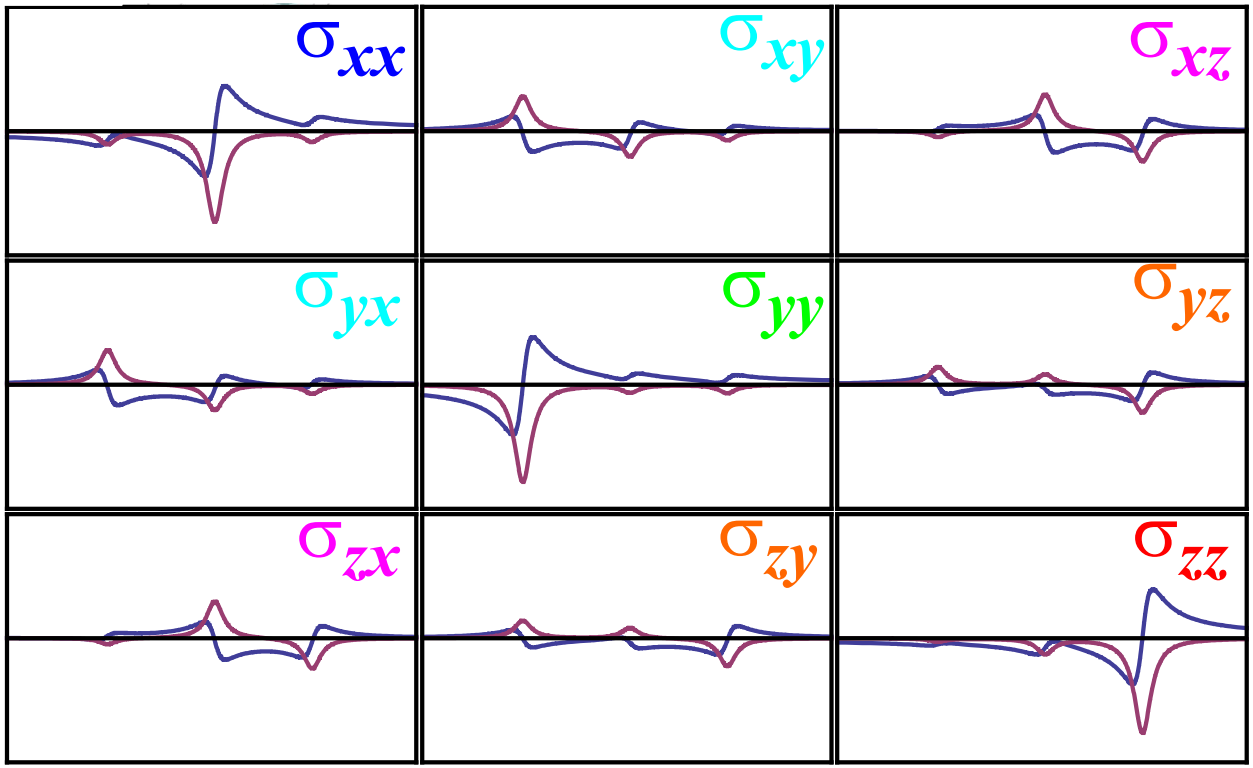


→ The case of triclinic symmetry

In the (xyz) triclinic frame the conductivity tensor writes :



9 components are different



XAS cross-section in Cartesian coordinates : (2) electric quadrupole transitions

For linearly polarized x-rays, the **electric quadrupole** XAS cross-section writes :

$$\sigma(\boldsymbol{\epsilon}, \mathbf{k}) = \sum_{ijlm} \epsilon_i k_j \epsilon_l k_m \sigma_{ijlm}, \qquad \text{with}$$

$$\sigma_{ijlm} = \pi^2 \alpha_0 \hbar\omega \sum_f \langle i|\mathbf{r}_i \mathbf{r}_j|f\rangle\langle f|\mathbf{r}_l \mathbf{r}_m|i\rangle \delta(E_\mathrm{f} - E_\mathrm{i} - \hbar\omega),$$

→ Conductivity tensor : a Cartesian tensor of rank 4 :
more complicated than a matrix !
3 x 3 x3 x 3 = 81 components

Note that Quanty calculates only a 5x5 matrix (25 well-chosen wrt symmetry) components

→ For a powder :

$$\langle\sigma(\boldsymbol{\epsilon}, \mathbf{k})\rangle = \frac{k^2}{15}(\sigma_{xxxx} + \sigma_{yyyy} + \sigma_{zzzz} + 3\sigma_{xyxy} + 3\sigma_{xzxz} + 3\sigma_{yzyz} - \sigma_{xxyy} - \sigma_{xxzz} - \sigma_{yyzz}).$$

= the isotropic quadrupole spectrum

Expressing the angular dependence with Cartesian tensors quickly becomes heavy :

for electric quadrupole transitions
when symmetry is low

What about with spherical tensors ?

Expressions for all symmetry groups (dipole and quadrupole operators) are given in :

C. Brouder, « Angular dependence of x-ray absorption spectra »,
J. Phys. Condens. Matter 2 701 (1990)

XAS cross-section in spherical coordinates : (1) electric dipole transitions

For linearly polarized x-rays, the electric dipole XAS cross-section writes :

$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0) - \sqrt{8\pi/5} \sum_{m=-2}^{2} Y_2^{m*}(\hat{\varepsilon}) \sigma^{D}(2,m).$$ with

isotropic

angular coefficient

anisotropic tensor components
= fundamental spectra
= energy-dependent functions

→ The symmetry of the crystal restricts the possible values of σ(2,m).

Angular dependence	Point groups
Isotropy (i)	O_h (m3m), T_d ($\bar{4}$3m), O (432), T_h (m3), T (23)
Dichroism (ii)	$D_{\infty h}$(∞/mm), $C_{\infty v}$ (∞m), D_{6h} (6/mmm), D_{3h} ($\bar{6}$m2), C_{6v} (6mm), D_6 (622), C_{6h}(6/m), C_{3h} ($\bar{6}$), C_6 (6), D_{3d} ($\bar{3}$m), C_{3v} (3m), D_3 (32), S_6 ($\bar{3}$), C_3 (3), D_{4h} (4/mmm), D_{2d} ($\bar{4}$2m), C_{4v} (4mm), D_4 (422), C_{4h} (4/m), S_4 ($\bar{4}$), C_4 (4)
Trichroism (iii*a*)	D_2 (222), C_{2v} (mm2), D_{2h} (mmm)
Trichroism (iii*b*)	C_2 (2), C_s (m), C_{2h} (2/m)
Trichroism (iii*c*)	C_1 (1), C_i ($\bar{1}$)

XAS cross-section in spherical coordinates : (1) electric dipole transitions

Examples

$$\hat{\varepsilon} = \begin{pmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{pmatrix}$$

z axis defined as high symmetry axis of the crystal

Cubic

$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0).$$

$$= \sigma_{xx} = \sigma_{yy} = \sigma_{zz}$$

isotropic : 1 spectrum to measure / calculate

Trigonal / Tetragonal

dichroism : 2 spectra to measure / calculate

$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0) - (1/\sqrt{2})(3\cos^2\theta - 1)\sigma^{D}(2,0)$$

similar to : $\sigma^{D}_{iso} + \frac{1}{3}\sigma^{D}_{dic}(3\cos^2\theta - 1)$

Triclinic

$$\begin{aligned}\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0) &- \sqrt{3}\sin^2\theta[\cos 2\varphi\,\sigma^{Dr}(2,2) + \sin 2\varphi\,\sigma^{Di}(2,2)] \\ &+ 2\sqrt{3}\sin\theta\cos\theta[\cos\varphi\,\sigma^{Dr}(2,1) + \sin\varphi\,\sigma^{Di}(2,1)] \\ &- (1/\sqrt{2})(3\cos^2\theta - 1)\sigma^{D}(2,0)\end{aligned}$$

trichroism

6 spectra to measure / calculate

XAS cross-section in spherical coordinates : (2) electric quadrupole transitions

For linearly polarized x-rays, the electric quadrupole XAS cross-section writes :

1 isotropic

$$\sigma^{Q}(\hat{\varepsilon},\boldsymbol{k}) = \sigma^{Q}(0,0) + \sum_{m}\Big((-2/9)\sqrt{14\pi}[Y_2^{m*}(\hat{\varepsilon}) + Y_2^{m*}(\hat{k})] - 8\pi/(9\sqrt{5}) \times \sum_{\alpha\beta}(2\alpha 2\beta|2m)Y_2^{\alpha*}(\hat{\varepsilon})Y_2^{\beta*}(\hat{k})\Big)\sigma^{Q}(2,m) + \sum_{m}\Big(16\pi/(3\sqrt{5}) \times \sum_{\alpha\beta}(2\alpha 2\beta|4m)Y_2^{\alpha*}(\hat{\varepsilon})Y_2^{\beta*}(\hat{k})\Big)\sigma^{Q}(4,m)$$

with

5 +9 = 14 anisotropic tensor components

15 independent fundamental spectra (energy-dependent functions) in order to determine (= measure or calculate) σ for any (ε,k)

XAS cross-section in spherical coordinates : (2) electric quadrupole transitions

Examples

$$\hat{\varepsilon} = \begin{pmatrix} \sin\theta\cos\varphi \\ \sin\theta\sin\varphi \\ \cos\theta \end{pmatrix} \qquad \hat{k} = \begin{pmatrix} \cos\theta\cos\varphi\cos\psi - \sin\varphi\sin\psi \\ \cos\theta\sin\varphi\cos\psi + \cos\varphi\sin\psi \\ -\sin\theta\cos\psi \end{pmatrix}.$$

spherical coordinates

(xyz) frame : z axis defined as high symmetry axis of the crystal
x and y are defined according Tables of Crystallography

Cubic

$$\sigma^{Q}(\hat{\varepsilon},\hat{k}) = \sigma^{Q}(0,0) + (1/\sqrt{14})[35\sin^2\theta\cos^2\theta\cos^2\psi + 5\sin^2\theta\sin^2\psi - 4 + 5\sin^2\theta(\cos^2\theta\cos^2\psi\cos 4\varphi - \sin^2\psi\cos 4\varphi - 2\cos\theta\sin\psi\cos\psi\sin 4\varphi)]\sigma^{Q}(4,0).$$

XNLD is not zero for a cubic crystal !
2 spectra to measure / calculate

Trigonal

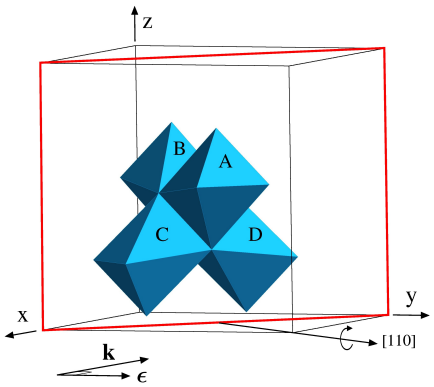
$$\sigma^{Q}(\hat{\varepsilon},\hat{k}) = \sigma^{Q}(0,0) + \sqrt{5/14}(3\sin^2\theta\sin^2\psi - 1)\sigma^{Q}(2,0) + 1/\sqrt{14}(35\sin^2\theta\cos^2\theta\cos^2\psi + 5\sin^2\theta\sin^2\psi - 4)\sigma^{Q}(4,0) - \sqrt{10}\sin\theta[(2\cos^2\theta\cos^2\psi - 1)\cos\theta\cos(3\varphi) - (3\cos^2\theta - 1)\sin\psi\cos\psi\sin(3\varphi)]\sigma^{Qr}(4,3).$$

4 spectra to measure / calculate

Triclinic

15 spectra to measure / calculate

Coming back to our example : how to calculate XNLD in practice ?



$$\sigma(\omega) = 4\pi^2\alpha\hbar\omega\sum_{f,i}\left|\left\langle f\left|\varepsilon.r + \frac{I}{2}\varepsilon.rk.r\right|i\right\rangle\right|^2\delta\left(\hbar\omega - E_f + E_i\right)$$

$$\sigma(\omega) = 4\pi^2\alpha\hbar\omega\sum_{f,i}\left|\langle f|\varepsilon.r|i\rangle\right|^2\delta\left(\hbar\omega - E_f + E_i\right) + \pi^2\alpha\hbar\omega\sum_{f,i}\left|\langle f|\varepsilon.rk.r|i\rangle\right|^2\delta\left(\hbar\omega - E_f + E_i\right)$$

dipole

quadrupole

Cubic crystal

$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0).$$

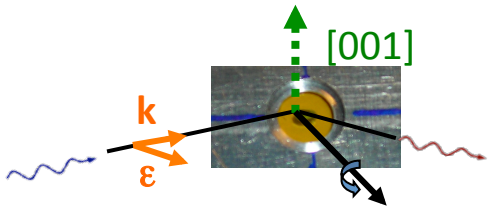
$$\sigma^{Q}(\hat{\varepsilon},\hat{k}) = \sigma^{Q}(0,0) + (1/\sqrt{14})[35\sin^2\theta\cos^2\theta\cos^2\psi + 5\sin^2\theta\sin^2\psi - 4 + 5\sin^2\theta(\cos^2\theta\cos^2\psi\cos 4\varphi - \sin^2\psi\cos 4\varphi - 2\cos\theta\sin\psi\cos\psi\sin 4\varphi)]\sigma^{Q}(4,0).$$

One spectrum to calculate :
any orientation of ε is possible

Two spectra to calculate :
two independent sets of (ε,k)

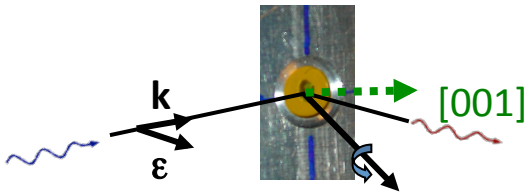
quadrupole

Two spectra to calculate :
two independent sets of (ε,k)



$\hat{\boldsymbol{\varepsilon}}$	$\hat{\mathbf{k}}$	θ	ϕ	ψ
$(0,1,0)$	$(-1,0,0)$	$\frac{\pi}{2}$	$\frac{\pi}{2}$	$\frac{\pi}{2}$

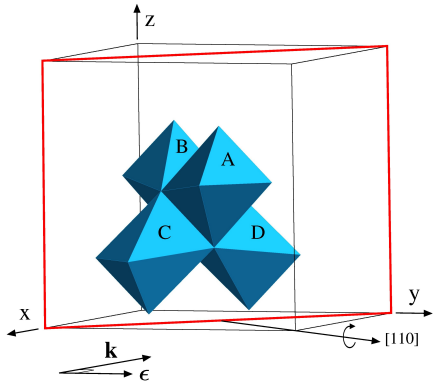
$$\sigma^{Q}_{\mathrm{cub}}(\alpha_{\mathrm{rot}}=0^{\circ})=\sigma^{Q}_{0}-\frac{4}{\sqrt{14}}\sigma^{Q}_{\mathrm{cub}}(4,0).$$



$\hat{\boldsymbol{\varepsilon}}$	$\hat{\mathbf{k}}$	θ	ϕ	ψ
$(0,\frac{1}{\sqrt{2}},-\frac{1}{\sqrt{2}})$	$(0,\frac{1}{\sqrt{2}},\frac{1}{\sqrt{2}})$	$\frac{3\pi}{4}$	$\frac{\pi}{2}$	π

$$\sigma^{Q}_{\mathrm{cub}}(\alpha_{\mathrm{rot}}=90^{\circ})=\sigma^{Q}_{0}+\frac{7}{2\sqrt{14}}\sigma^{Q}_{\mathrm{cub}}(4,0).$$

Coming back to our example : how to calculate XNLD in practice ?



$$\sigma(\omega) = 4\pi^2\alpha\hbar\omega\sum_{f,i}\left|\left\langle f\left|\varepsilon.r + \frac{I}{2}\varepsilon.rk.r\right|i\right\rangle\right|^2\delta\left(\hbar\omega - E_f + E_i\right)$$

dipole

quadrupole

Cubic crystal

$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0).$$

isotropic

$$\sigma^{Q}(\hat{\varepsilon},\hat{k}) = \sigma^{Q}(0,0) + (1/\sqrt{14})[35\sin^2\theta\cos^2\theta\cos^2\psi + 5\sin^2\theta\sin^2\psi - 4 + 5\sin^2\theta(\cos^2\theta\cos^2\psi\cos 4\varphi - \sin^2\psi\cos 4\varphi - 2\cos\theta\sin\psi\cos\psi\sin 4\varphi)]\sigma^{Q}(4,0).$$

Dichroism : 2 fundamental spectra

One D_{3d} site

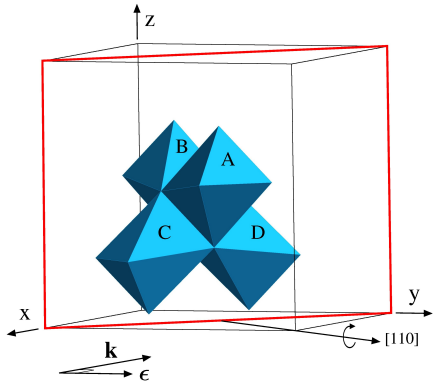
$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0) - (1/\sqrt{2})(3\cos^2\theta - 1)\sigma^{D}(2,0)$$

Dichroism : 2 fundamental spectra

$$\sigma^{Q}(\hat{\varepsilon},\hat{k}) = \sigma^{Q}(0,0) + \sqrt{5/14}(3\sin^2\theta\sin^2\psi - 1)\sigma^{Q}(2,0) + 1/\sqrt{14}(35\sin^2\theta\cos^2\theta\cos^2\psi + 5\sin^2\theta\sin^2\psi - 4)\sigma^{Q}(4,0) - \sqrt{10}\sin\theta[(2\cos^2\theta\cos^2\psi - 1)\cos\theta\cos(3\varphi) - (3\cos^2\theta - 1)\sin\psi\cos\psi\sin(3\varphi)]\sigma^{Qr}(4,3).$$

Trichroism : 4 fundamental spectra

Coming back to our example : how to calculate XNLD in practice ?



$$\sigma(\omega) = 4\pi^2 \alpha \hbar\omega \sum_{f,i} \left| \left\langle f \left| \varepsilon.r + \frac{I}{2} \varepsilon.rk.r \right| i \right\rangle \right|^2 \delta\left(\hbar\omega - E_f + E_i\right)$$

dipole

quadrupole

Cubic crystal

$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0).$$

isotropic

$$\sigma^{Q}(\hat{\varepsilon},\hat{k}) = \sigma^{Q}(0,0) + (1/\sqrt{14})[35\sin^2\theta\cos^2\theta\cos^2\psi + 5\sin^2\theta\sin^2\psi - 4 + 5\sin^2\theta(\cos^2\theta\cos^2\psi\cos 4\varphi - \sin^2\psi\cos 4\varphi - 2\cos\theta\sin\psi\cos\psi\sin 4\varphi)]\sigma^{Q}(4,0).$$

dichroism : 2 fundamental spectra

Average over A, B, C and D sites

Average over A, B, C and D sites

One D_{3d} site

$$\sigma^{D}(\hat{\varepsilon}) = \sigma^{D}(0,0) - (1/\sqrt{2})(3\cos^2\theta - 1)\sigma^{D}(2,0)$$

dichroism : 2 fundamental spectra

$$\sigma^{Q}(\hat{\varepsilon},\hat{k}) = \sigma^{Q}(0,0) + \sqrt{5/14}(3\sin^2\theta\sin^2\psi - 1)\sigma^{Q}(2,0) + 1/\sqrt{14}(35\sin^2\theta\cos^2\theta\cos^2\psi + 5\sin^2\theta\sin^2\psi - 4)\sigma^{Q}(4,0) - \sqrt{10}\sin\theta[(2\cos^2\theta\cos^2\psi - 1)\cos\theta\cos(3\varphi) - (3\cos^2\theta - 1)\sin\psi\cos\psi\sin(3\varphi)]\sigma^{Qr}(4,3).$$

trichroism : 4 fundamental spectra

Be careful :

the fundamental spectra (tensor components)of the crystal are not necessarly the same as for a single site.

Here it can be shown that :

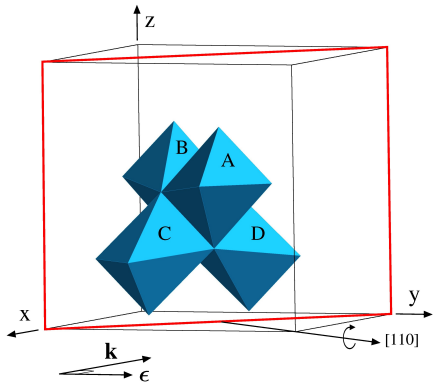
crystal

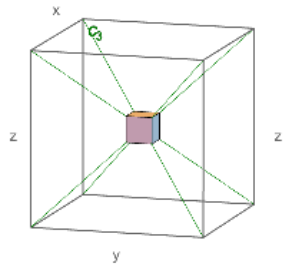
$$\sigma_D^{cube}(0,0) = \sigma_D^{D_{3d}}(0,0)$$

$$\sigma_Q^{cube}(0,0) = \sigma_Q^{D_{3d}}(0,0)$$

$$\sigma_Q^{cube}(4,0) = -\frac{1}{18}\left(7\sigma_Q^{D_{3d}}(4,0) + 2\sqrt{70}\sigma_Q^{D_{3d}}(4,3)\right)$$

site





$rot_B = R_z(\pi/2)$

site A → site B

$\sigma_D(\varepsilon)$ $\quad$ $\sigma_D(rot_B^{-1}(\varepsilon))$

$\sigma_Q(\varepsilon,k)$ $\quad$ $\sigma_Q(rot_B^{-1}(\varepsilon), rot_B^{-1}(k))$

$rot_C = R_z(3\pi/2)$

site A → site C

$\sigma_D(\varepsilon)$ $\quad$ $\sigma_D(rot_C^{-1}(\varepsilon))$

$\sigma_Q(\varepsilon,k)$ $\quad$ $\sigma_Q(rot_C^{-1}(\varepsilon), rot_C^{-1}(k))$

$rot_D = R_z(\pi)$

site A → site D

$\sigma_D(\varepsilon)$ $\quad$ $\sigma_D(rot_D^{-1}(\varepsilon))$

$\sigma_Q(\varepsilon,k)$ $\quad$ $\sigma_Q(rot_D^{-1}(\varepsilon), rot_D^{-1}(k))$

$$\sigma_D^{cube} = \sigma_D^A + \sigma_D^B + \sigma_D^C + \sigma_D^D$$

$$\sigma_Q^{cube} = \sigma_Q^A + \sigma_Q^B + \sigma_Q^C + \sigma_Q^D$$

Site A

$\hat{\boldsymbol{\varepsilon}}$	$\hat{\mathbf{k}}$
$(0,1,0)$	$(-1,0,0)$

$$|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}\hat{\mathbf{k}}\cdot\mathbf{r}| = |R^{-1}_{\pi/2}(\hat{\boldsymbol{\varepsilon}})\cdot\mathbf{r}R^{-1}_{\pi/2}(\hat{\mathbf{k}})\cdot\mathbf{r}| \quad \text{Site B}$$

$$= |R^{-1}_{\pi}(\hat{\boldsymbol{\varepsilon}})\cdot\mathbf{r}R^{-1}_{\pi}(\hat{\mathbf{k}})\cdot\mathbf{r}| \quad \text{Site D}$$

$$= |R^{-1}_{3\pi/2}(\hat{\boldsymbol{\varepsilon}})\cdot\mathbf{r}R^{-1}_{\pi/2}(\hat{\mathbf{k}})\cdot\mathbf{r}| = xy. \quad \text{Site C}$$

$$\sigma^{Q}_{\text{cub}}(\hat{\boldsymbol{\varepsilon}},\hat{\mathbf{k}}) = \sigma^{Q}_{A}(\hat{\boldsymbol{\varepsilon}},\hat{\mathbf{k}}). \quad \text{1 calculation}$$

$\hat{\boldsymbol{\varepsilon}}$	$\hat{\mathbf{k}}$
$(0,\frac{1}{\sqrt{2}},-\frac{1}{\sqrt{2}})$	$(0,\frac{1}{\sqrt{2}},\frac{1}{\sqrt{2}})$

Site A

$$|\hat{\boldsymbol{\varepsilon}}\cdot\mathbf{r}\hat{\mathbf{k}}\cdot\mathbf{r}| = |R^{-1}_{\pi}(\hat{\boldsymbol{\varepsilon}})\cdot\mathbf{r}R^{-1}_{\pi}(\hat{\mathbf{k}})\cdot\mathbf{r}| = |z^2/2-(x-y)^2/4| \quad \text{Site D}$$

$$|R^{-1}_{\pi/2}(\hat{\boldsymbol{\varepsilon}})\cdot\mathbf{r}R^{-1}_{\pi/2}(\hat{\mathbf{k}})\cdot\mathbf{r}| \quad \text{Site B}$$

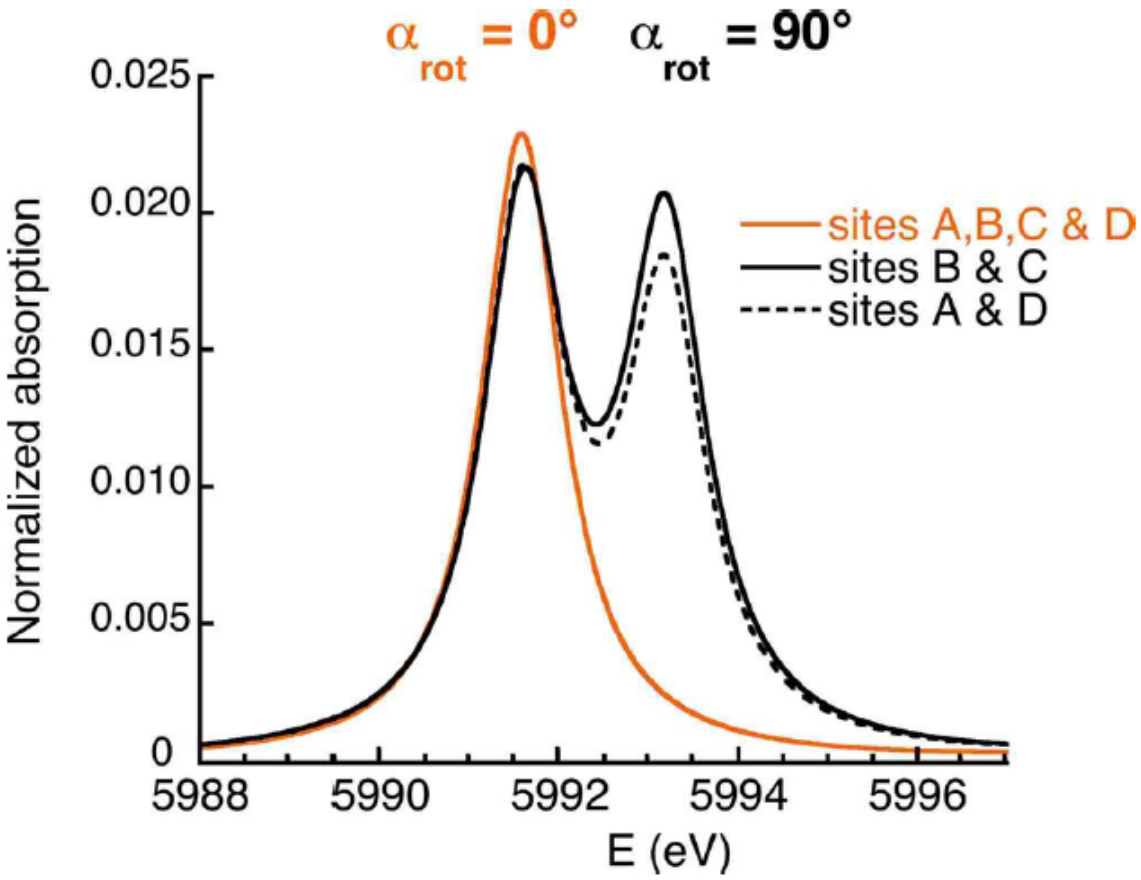
$$= |R^{-1}_{3\pi/2}(\hat{\boldsymbol{\varepsilon}})\cdot\mathbf{r}R^{-1}_{\pi/2}(\hat{\mathbf{k}})\cdot\mathbf{r}| = |z^2/2-(x+y)^2/4|. \quad \text{Site C}$$

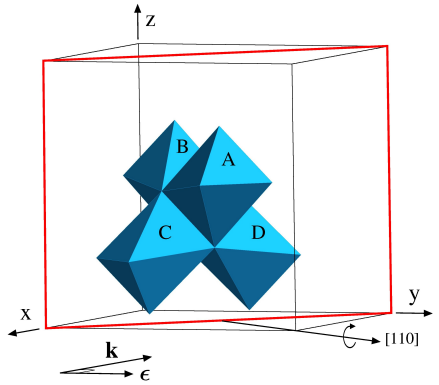
$$\sigma^{Q}_{\text{cub}}(\hat{\boldsymbol{\varepsilon}},\hat{\mathbf{k}}) = \frac{\sigma^{Q}_{A}(\hat{\boldsymbol{\varepsilon}},\hat{\mathbf{k}}) + \sigma^{Q}_{C}(\hat{\boldsymbol{\varepsilon}},\hat{\mathbf{k}})}{2}. \quad \text{2 calculations}$$

For quadrupole XNLD, the number of calculations to do has been reduced from :

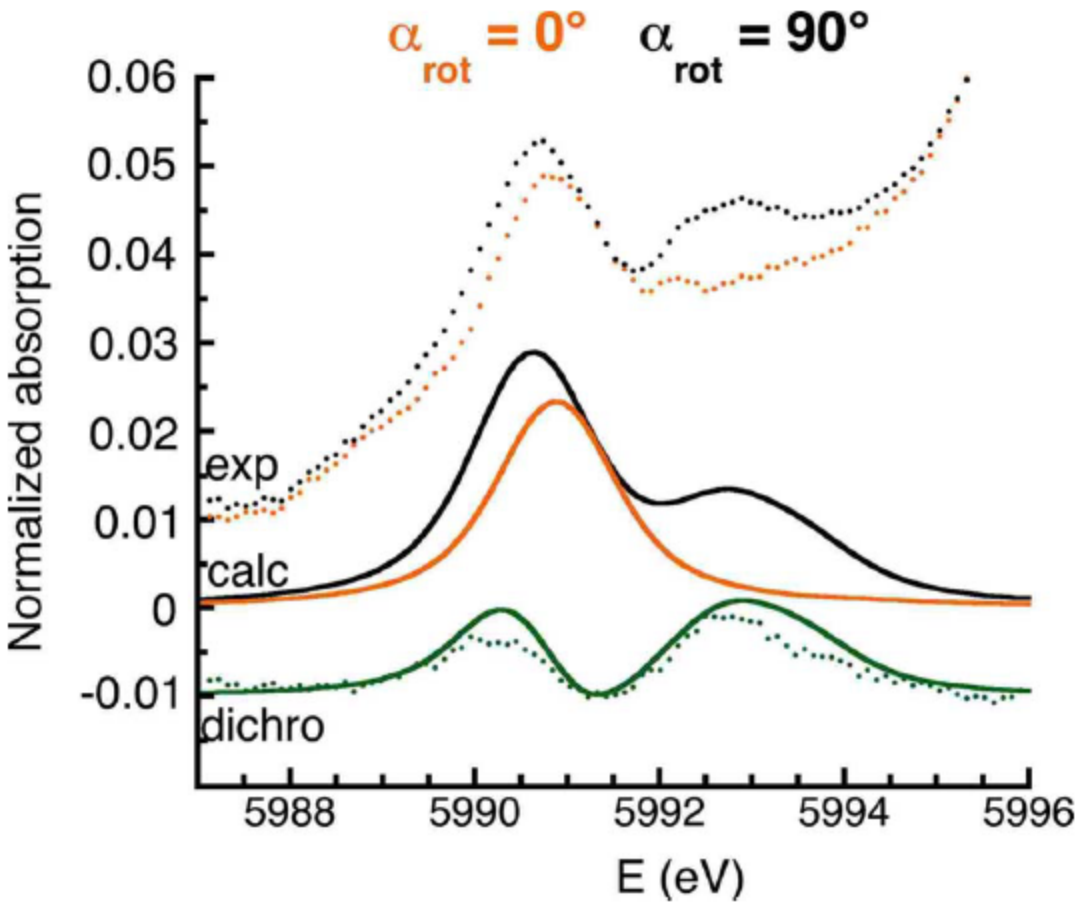
16 (sites) x 15 (components) to 3 by symmetry considerations

Conclusion : Always look first for symmetries !





DFT calculations



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Phys. Rev. B 78, 195103 (2008)

Conclusion

- Symmetry considerations and tensor expressions are very helpful :

- to reduce the number of calculations / experiments needed
- to know what angular dependence to expect

- XNLD in XAS is well understood

- XNLD in RIXS, XMLD, XNCD… are much more difficult