

The role of orbital, spin, charge and geometric ordering in resonant x-ray scattering experiments performed on oxides

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Outline

I - Some generalities about x-ray absorption spectroscopy

II - About the calculation

III - X-ray directional dichroism of a polar ferrimagnet

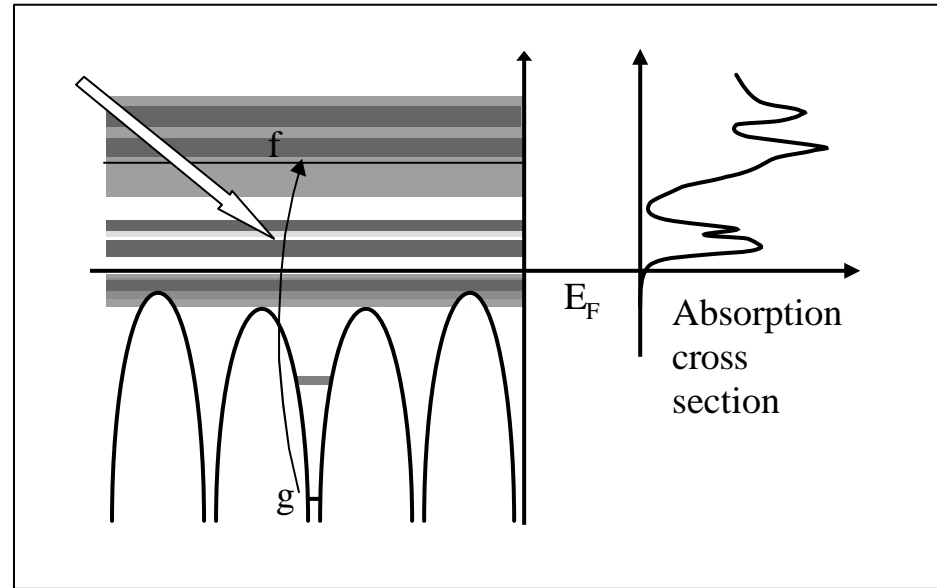
IV - Charge ordering in Fe_3O_4

V - Spin and orbital ordering in V_2O_3

I - Some generalities about x-ray absorption spectroscopy

Electronic transition between a core and a non occupied electronic level

The signal amplitude is related to the empty electronic levels (specific projection of the density of states)

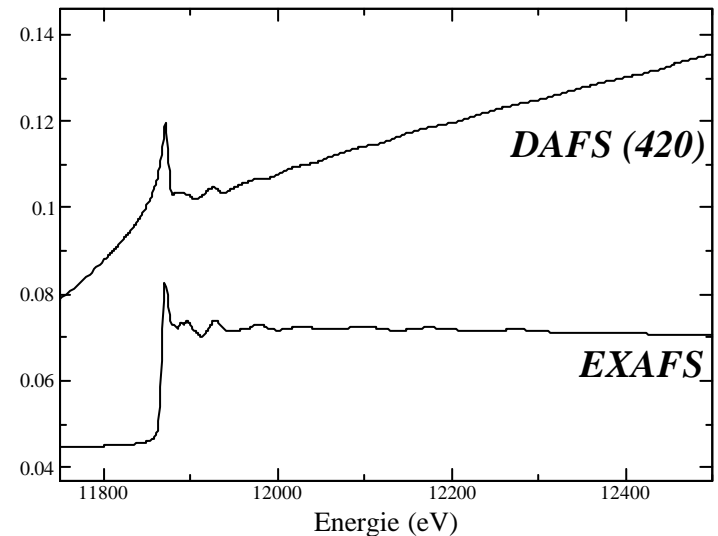
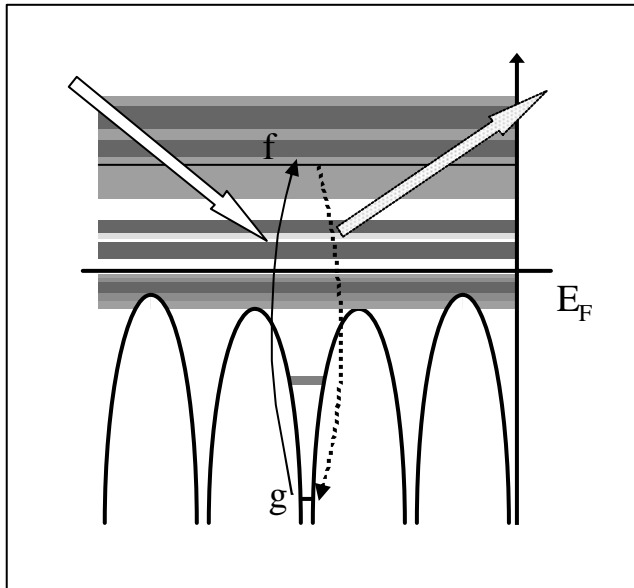


Absorption spectroscopies probe the surroundings of the absorbing atom. They are sensitive to the occupied and non occupied electronic states of the material

These electronic states are closely related to the geometrical structure of the material

Resonant x-ray spectroscopy (RXS, DAFS, DANES) and x-ray absorption spectroscopy (XAFS, XANES, EXAFS)

Resonant process where the photon is absorbed, the electron goes up to an empty level, then immediately goes back to its initial core state, emitting another photon which can have another polarization

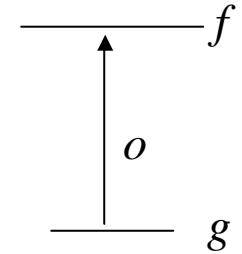


InAs

RXS is closely connected to the real x-ray absorption

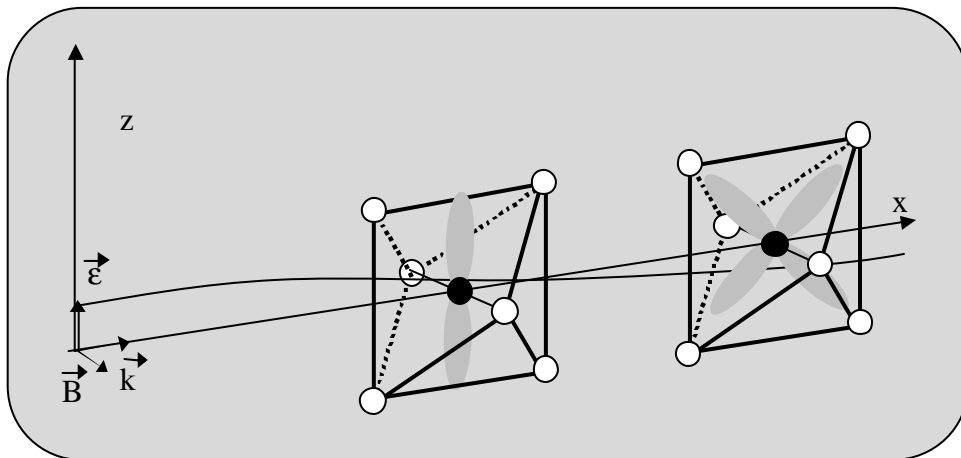
Signal depends on the transition matrices (Fermi golden rule)

$$\langle f | \vec{e} \cdot \vec{r} \left(1 - \frac{i}{2} \vec{k} \cdot \vec{r} \right) | g \rangle = \langle f | \vec{e} \cdot \vec{r} | g \rangle - \frac{i}{2} \langle f | \vec{e} \cdot \vec{r} \vec{k} \cdot \vec{r} | g \rangle$$



K edge case : dipole component and polarization along z :

- one probes the p_z states projected onto the absorbing atom
- quadrupole component, polarization along z , wave vector along x :
- one probes the d_{xz} states projected onto the absorbing atom



XANES and RIXS are very sensitive to the 3D environment

XANES case : real absorption

$$s(\omega) = 4p^2 a \hbar \omega \sum_{f,g} |\langle f | o | g \rangle|^2$$

The density of states is included in the f

RXS case : virtual absorption

Emitted and incident photon can have different polarizations

During the process, difference on the energy conservation given by $\Delta E \Delta t = \hbar$

Scattering amplitude from one atom :

$$f'(\omega) + if''(\omega) = -m_e \omega^2 \int_{E_{Fermi}}^{\infty} \frac{\sum_{f,g} \langle g | o_e^* | f \rangle \langle f | o_i | g \rangle}{\underbrace{E - E_g - \hbar \omega}_{DE} + i \frac{\Gamma}{2}} dE$$

outgoing photon
incoming photon

broadening

The imaginary part is proportional to the absorption cross section

XANES case

$$\mathbf{s}_{tot} = \sum_{atoms} \mathbf{s}_a = \sum_{\substack{non \\ equivalent \\ atoms}} \sum_{symetry} S(\mathbf{s}_a)$$

RXS case

Summation over the atoms with the Bragg factor + Thomson (non resonant) term :

$$I = \frac{K}{V^2} \left| \sum_{atoms} e^{i\vec{Q} \cdot \vec{R}_a} (f_{0a} + f'_a(\mathbf{w}) + if''_a(\mathbf{w})) \right|^2$$

The resonant scattering amplitude depends on the polarization and wave vector orientations, thus the scattering is not scalar (spherical) but tensorial (anisotropic)

Special interest on the forbidden reflections:

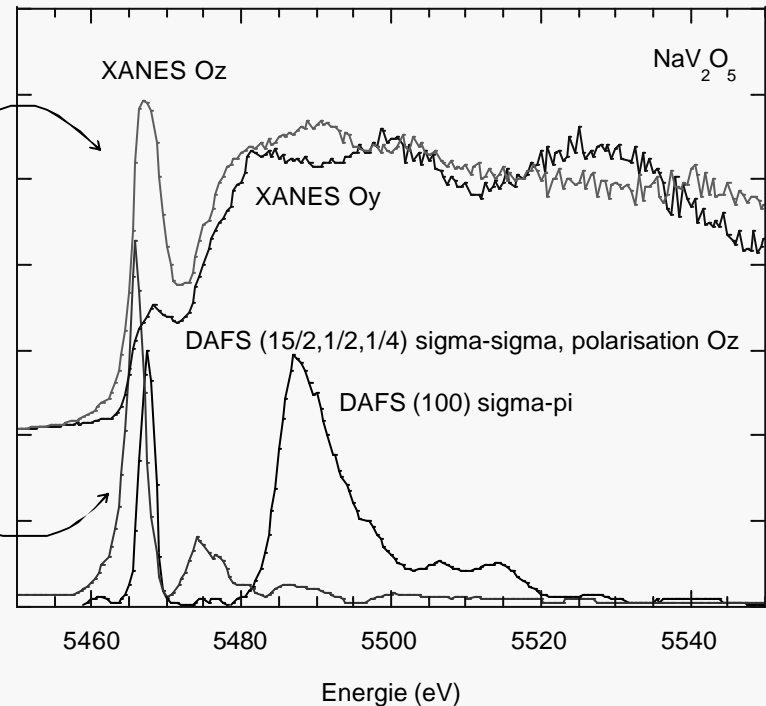
$$I_Q \approx |f_a - f_b|^2$$

More sensitive than XANES !

Example : NaV_2O_5

The XANES spectra present a linear dichroism with a pre-edge

Some reflections present spectra around the edge with a strong energy and angular dependency



Tensor approach

$$\langle f|o_i|g\rangle = \overset{\text{Dipole}}{\downarrow} D_i - i \frac{k}{2} \overset{\text{Quadrupole}}{\downarrow} Q_i + \dots$$

Signal amplitude :

$$\langle g|o_e|f\rangle \langle f|o_i|g\rangle = D_e^* D_i - i \frac{k}{2} (D_e^* Q_i - Q_e^* D_i) + \frac{k^2}{4} Q_e^* Q_i + \dots$$

Dipole-
Dipole
rank 2
tensor

Dipole-
Quadrupole
rank 3
tensor

Quadrupole
Quadrupole
rank 4
tensor

Signal amplitude:

$$\sum_{aa'} \mathbf{e}_a^{s*} \mathbf{e}_{a'}^e D_{aa'} + i \sum_{aa'a''} \mathbf{e}_a^{s*} \mathbf{e}_{a'}^e (k_{a''}^e I_{aa'a''} - k_{a''}^s I_{a'aa''}^*) + \sum_{aa'a''a'''} \mathbf{e}_a^{s*} \mathbf{e}_{a'}^e k_{a''}^s k_{a'''}^e Q_{aa''a'''} + \dots$$

$a = x, y \text{ ou } z$

Each component probes a specific projection of the density of state

For the K-edge, the dipole-quadrupole tensor probes the hybridized p - d states (non centro-symmetric material)

Cartesian tensor

$$\sum_{aa'} \mathbf{e}_a^{s*} \mathbf{e}_a^e D_{aa'} + i \sum_{aa'a''} \mathbf{e}_a^{s*} \mathbf{e}_a^e (k_a^e I_{aa'a''} - k_a^s I_{a''aa}^*) + \sum_{aa'a''a'''} \mathbf{e}_a^{s*} \mathbf{e}_a^e k_a^s k_a^e Q_{aa''a'a'''}$$

Spherical tensor

$$\sum_{\substack{\ell=0,2 \\ m=-\ell,\ell}} (-1)^{\ell+m} T_\ell^m D_\ell^m + i \sum_{\substack{\ell=1,3 \\ m=-\ell,\ell}} (-1)^{\ell+m} T_\ell^m I_\ell^m + \sum_{\substack{\ell=0,4 \\ m=-\ell,\ell}} (-1)^{\ell+m} T_\ell^m Q_\ell^m$$

l		dipole-dipole	dipole-quadrupole		quadrupole-quadrup.
0	monopole	charge r_p ++			charge r_d ++
1	dipole	moment m_p +- -	axial +- toroidal moment n	polar -- toroidal moment t	moment m_d -+
2	quadrupole	++	(t,m) +- -	(n,m) --	++
3	octupole		(n,m,m) +- -	(t,m,m) --	-+
4	hexadecapole				++

electric
 magnetic

Sign under time reversal, inversion : ++, +-, -+, -- 10

II - About the calculation

First principal calculation (fully relativistic with spin-orbit), but:

- on a wide energy range
- broadening due to the core-hole and photoelectron life times

As in most electronic structure calculations the choice of the potential is important

One body calculation = local density approximation (LDA)

Potential = Coulomb potential + exchange-correlation potential

Depends just on the electron density

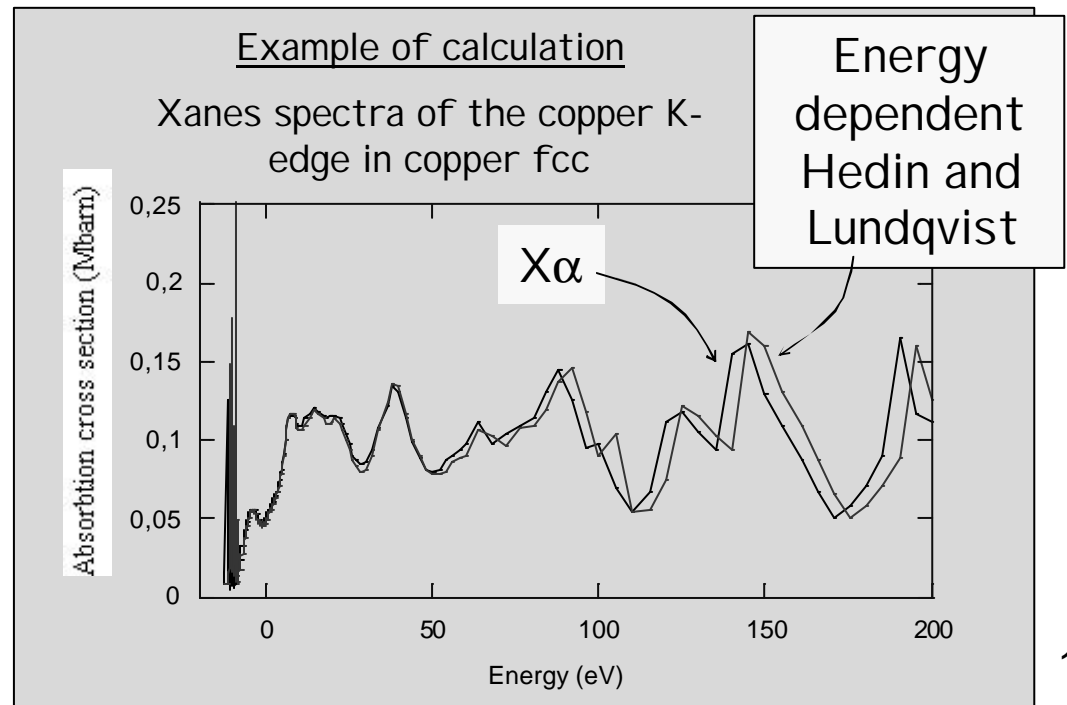
Different theories

$X\alpha$

Hedin and Lundqvist

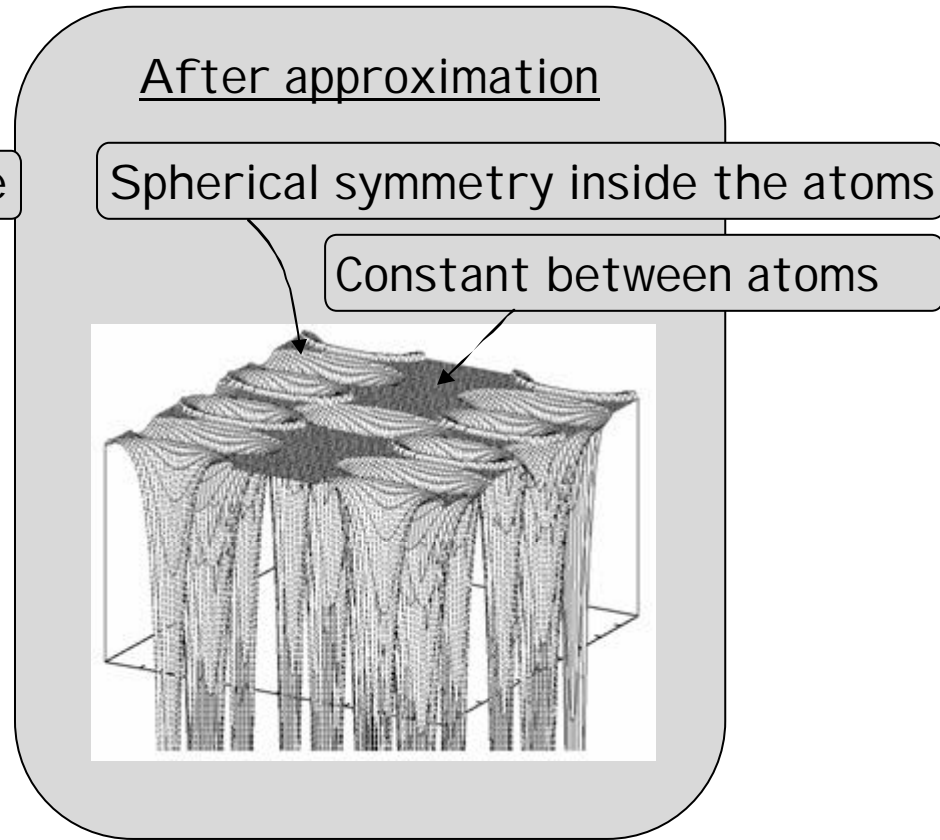
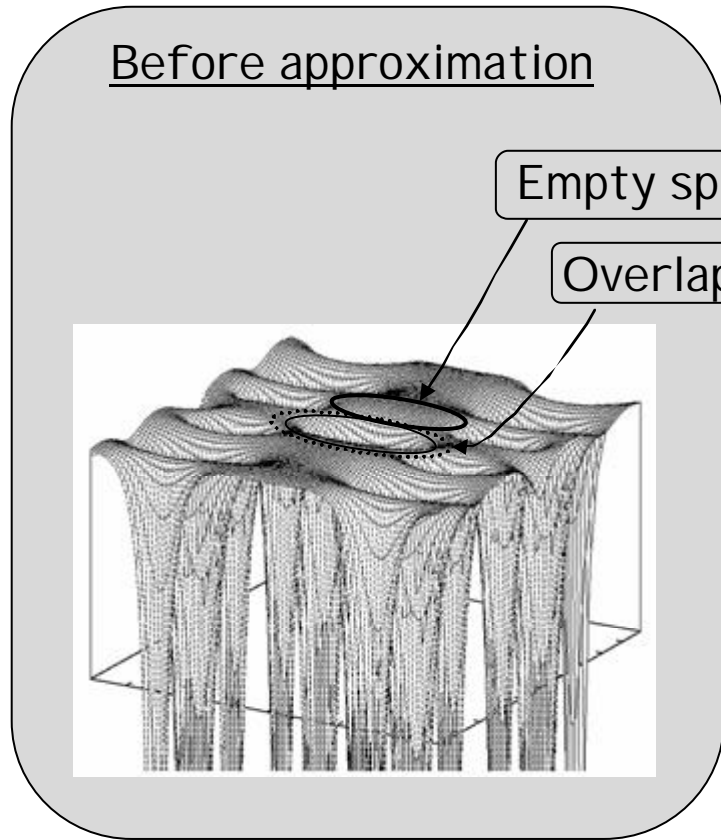
.....

Depends also on the electron kinetic energy



And about the shape of the potential

The muffin-tin approximation \longrightarrow the MT of the LMTO program
(quite) always used in the multiple scattering theory



With the muffin-tin, there are always 2 parameters : overlap and interstitial constant

Calculation of the final states

The final states are calculated with different techniques :

- the multiple scattering theory
- the finite difference method
- other methods

- With self consistency

- Without self consistency

multi-electronic
but mono-atomic

multiplet

In a cluster approach

Feff

GNXAS

Continuum ...

Fdmnes

Using the 3D periodicity

Band structure
calculations

Wien-2k

KKR (Ebert)...

Multi-atomic but
mono-electronic

III - X-ray directional dichroism of a polar ferrimagnet

GaFeO₃

M. Kubota et al., Phys. Rev. Lett. **92**, 137401 (2004)

Space group : $Pc2_1n$

Magnetic point group : $m'2'm$

$T_c \sim 205\text{ K}$

Magnetic field along c : +/-

(1) Polarization along b

$$\mathbf{s}_b^+ - \mathbf{s}_b^- \propto \text{Im}(p_y d_{xy})$$

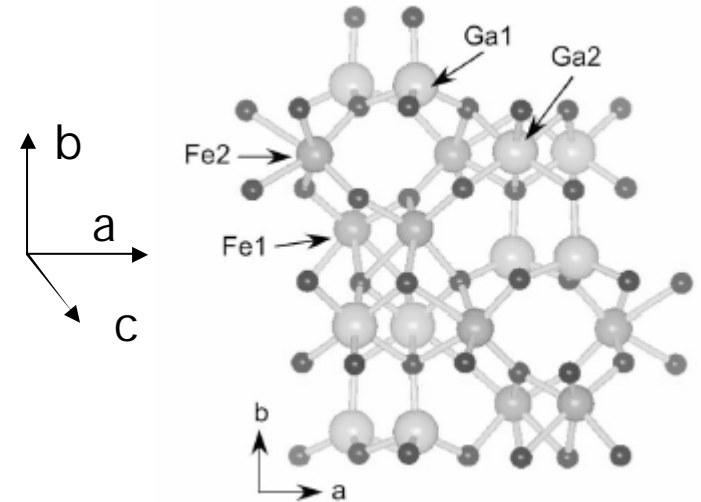
(2) Polarization along c

$$\mathbf{s}_c^+ - \mathbf{s}_c^- \propto \text{Im}(p_z d_{xz})$$

Dipole-dipole (p density of state),

Quadrupole-quadrupole (d density of state),

Real part of dipole-quadrupole (natural dichroism) are eliminated...



→ Measurement of the toroidal moment...(non reciprocal activity)

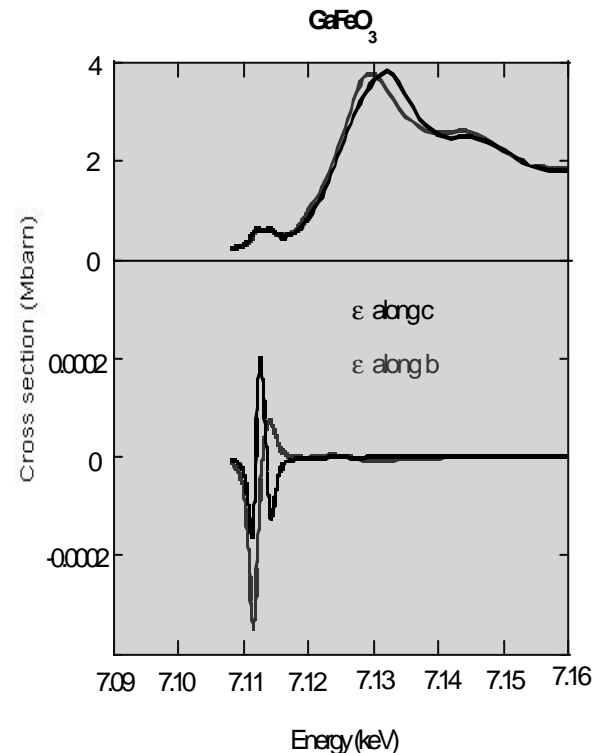
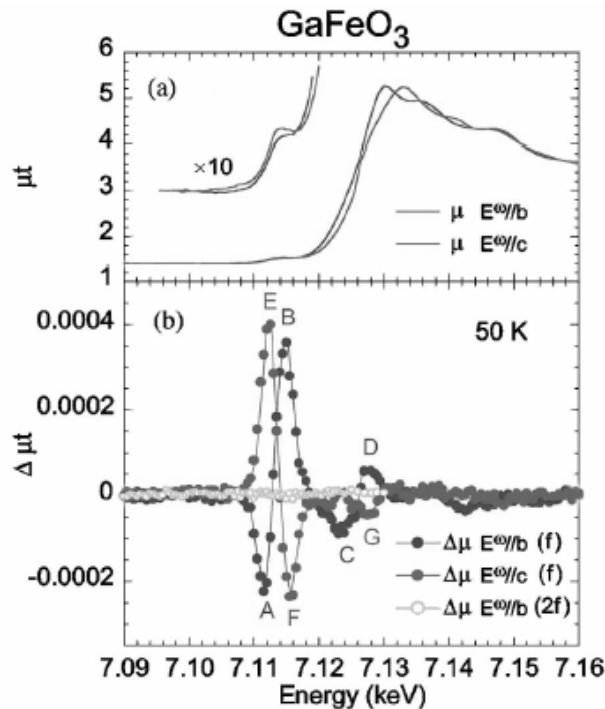


FIG. 2 (color). Spectra of (a) the x-ray absorption μt and (b) the XNDD $\Delta \mu t$ of a GaFeO₃ crystal at 50 K for $E^\omega \parallel b$ (red) and $E^\omega \parallel c$ (blue). $\Delta \mu t$ is defined as the difference of absorption coefficients when a magnetic field is applied parallel ($H +$) and antiparallel ($H -$) to the c axis. In (b) the spectrum of the second-harmonic component of the magnetic-field modulation for $E^\omega \parallel c$ is also shown with open circles.

Even with a relatively crude calculation, it is possible to check the origin of very thin experimental features !

IV - Charge ordering in Fe_3O_4

Verwey transition (1939)

LT

120 K

HT

Insulating
monoclinic (Cc)

$$\sqrt{2}a \times \sqrt{2}a \times 2a$$

~ Orthorhombic

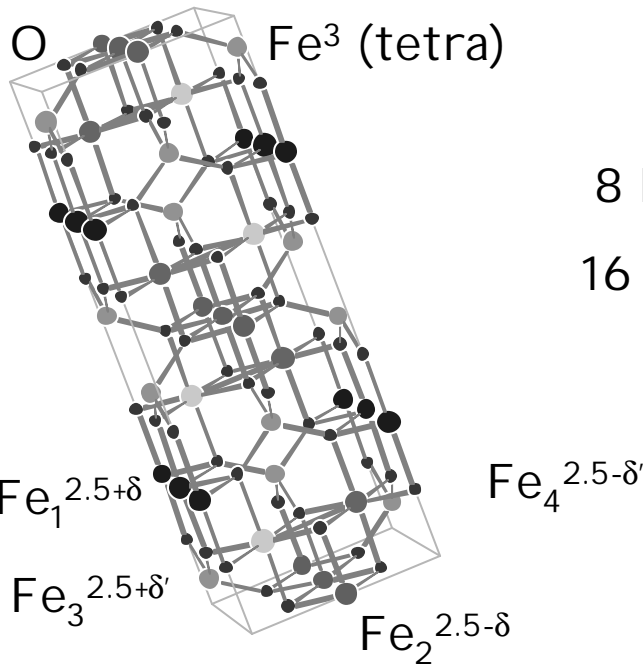
$$\frac{a}{\sqrt{2}} \times \frac{a}{\sqrt{2}} \times 2a$$

Charge ordering

$\text{Fe}^{2+}/\text{Fe}^{3+}$ octa



along 001



Metal

Cubic

8 Fe^{3+} tetrahedral site
16 $\text{Fe}^{2.5+}$ octahedral site

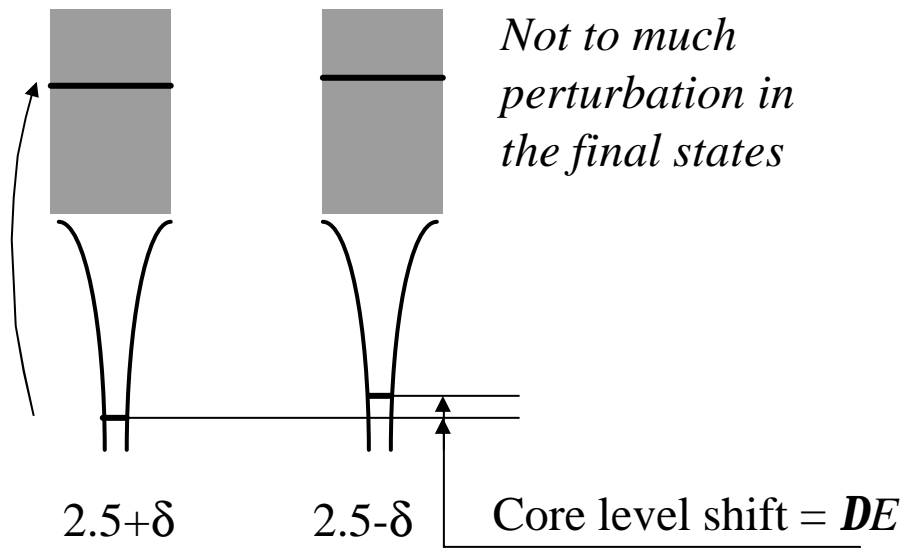
PowderCell 2.0

J.Wright *et al.*, Phys. Rev. Lett. 87, 266401 (2001)

M. Izumi *et al.*, Acta Cryst B38, 2121 (1982)

Resonant scattering can be more precise than XANES because for some reflections it measures the difference between sites and not just the sum

It is well to check charge discrepancy :



$$f^{2.5+d}(E) \approx f^{2.5}\left(E + \frac{\Delta E}{2}\right)$$

$$f^{2.5+d} \approx f^{2.5} + \frac{\partial f^{2.5}}{\partial E} \frac{\Delta E}{2}$$

$$f^{2.5-d} \approx f^{2.5} - \frac{\partial f^{2.5}}{\partial E} \frac{\Delta E}{2}$$

$$F = f^{2.5+d} - f^{2.5-d} \approx \frac{\partial f^{2.5}}{\partial E} \Delta E$$

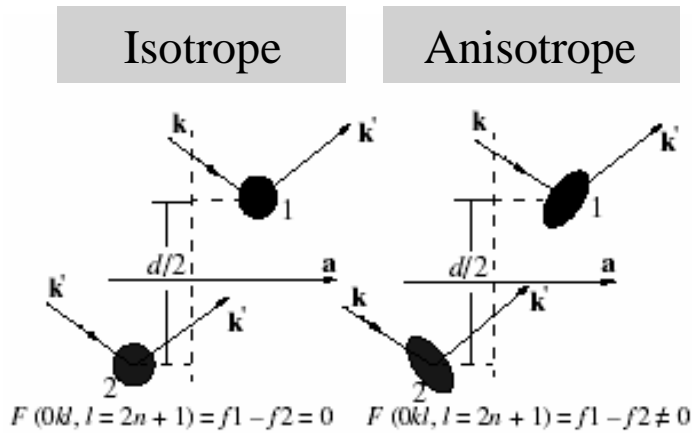
Some reflections show a typical derivative line-shape !

Some others do not show any modification when passing through the charge ordering transition !

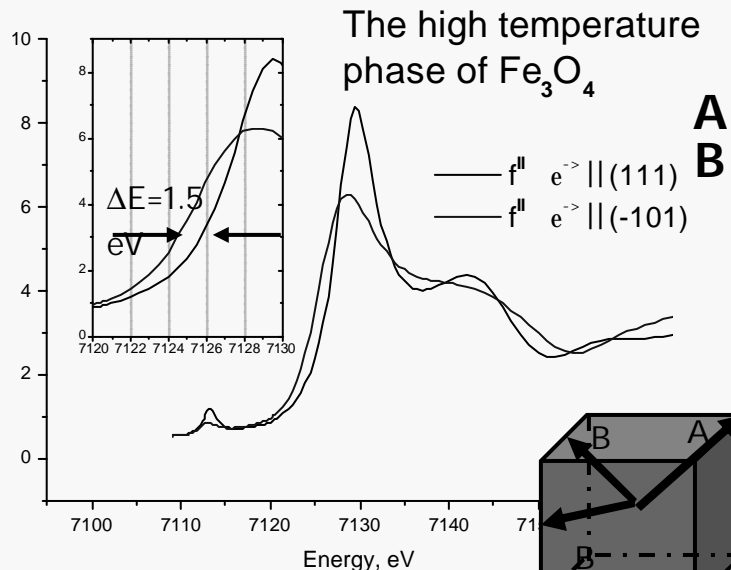
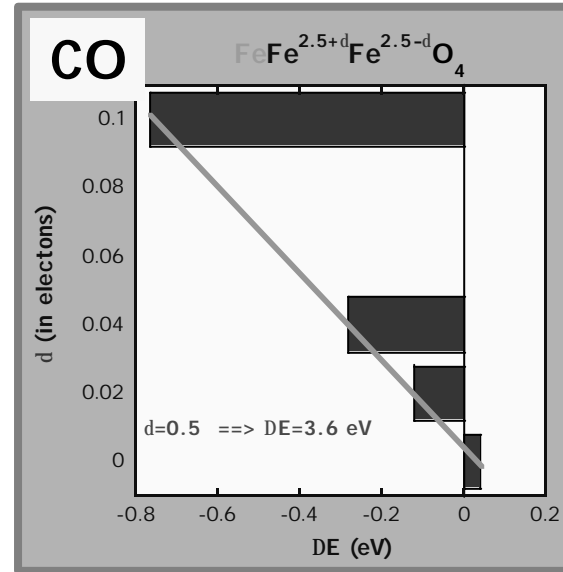
Does the charge ordering phenomenon exist ?

Is it possible to measure it with RXS ?

Linear dichroism



Charge ordering



Linear dichroism makes that intensity is not zero at the forbidden reflections.

Both phenomena can look as an energy shift !

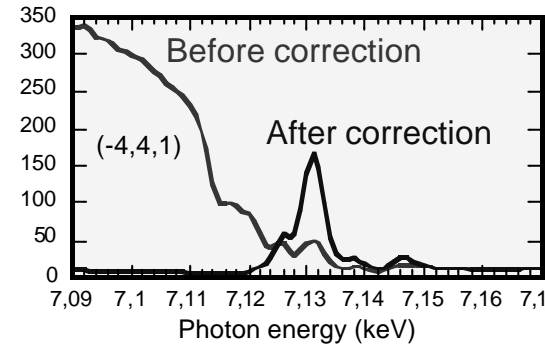
Thus, it is complicated...

Moreover :

The optimized structure is an approximation

Experimental difficulties :

- low signal with a lot of absorption
- multi-diffraction
- twinning



- 1) Measurement of many reflections (Xmas, ESRF)
- 2) Realistic calculations on big cluster (up to 8 Å) with the better structure possible
- 3) Use of R-factors (metric distances) to compare with experiment

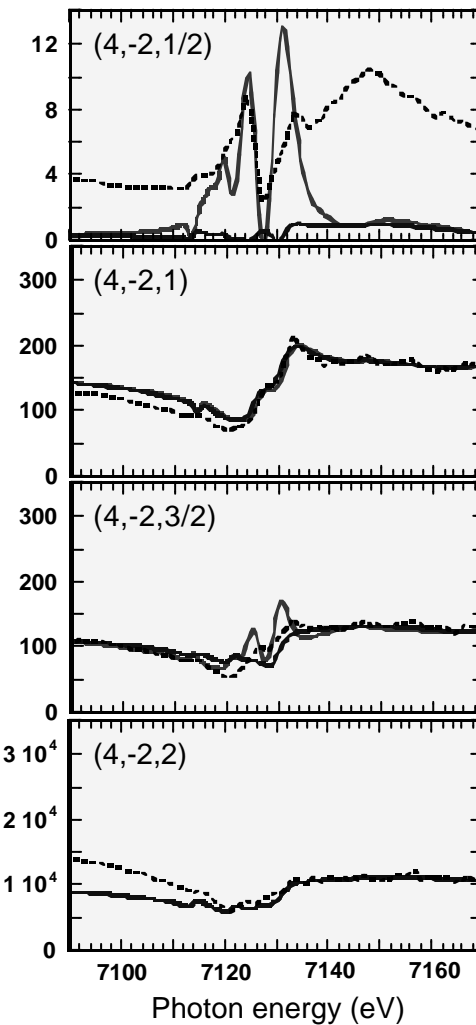
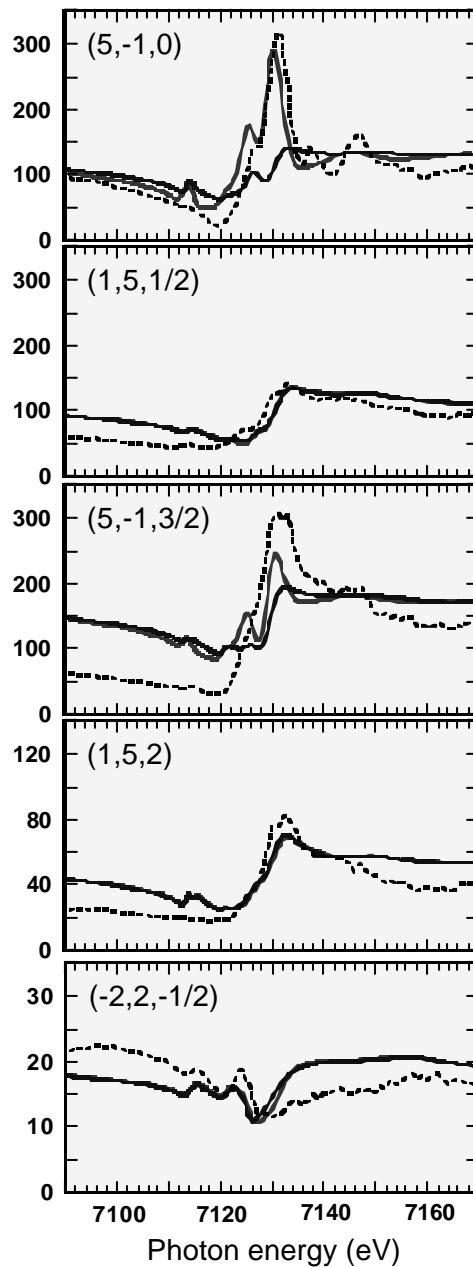
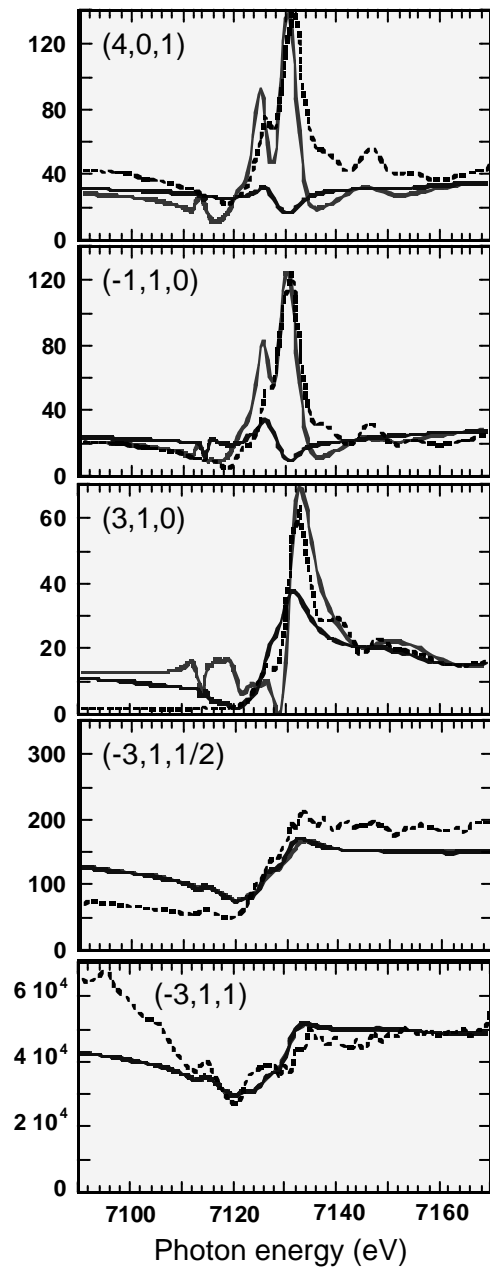
$$D_i = \frac{1}{2} \int \left| \frac{1}{c_i^{th}} I_i^{th}(E) - \frac{1}{c_i^{ex}} I_i^{ex}(E) \right| dE \quad c_i = \int_{E_{min}}^{E_{max}} I_i(E) dE$$

$$D = \frac{1}{n} \sum_{i=1,n} D_i$$

→ fit of the charge ordering

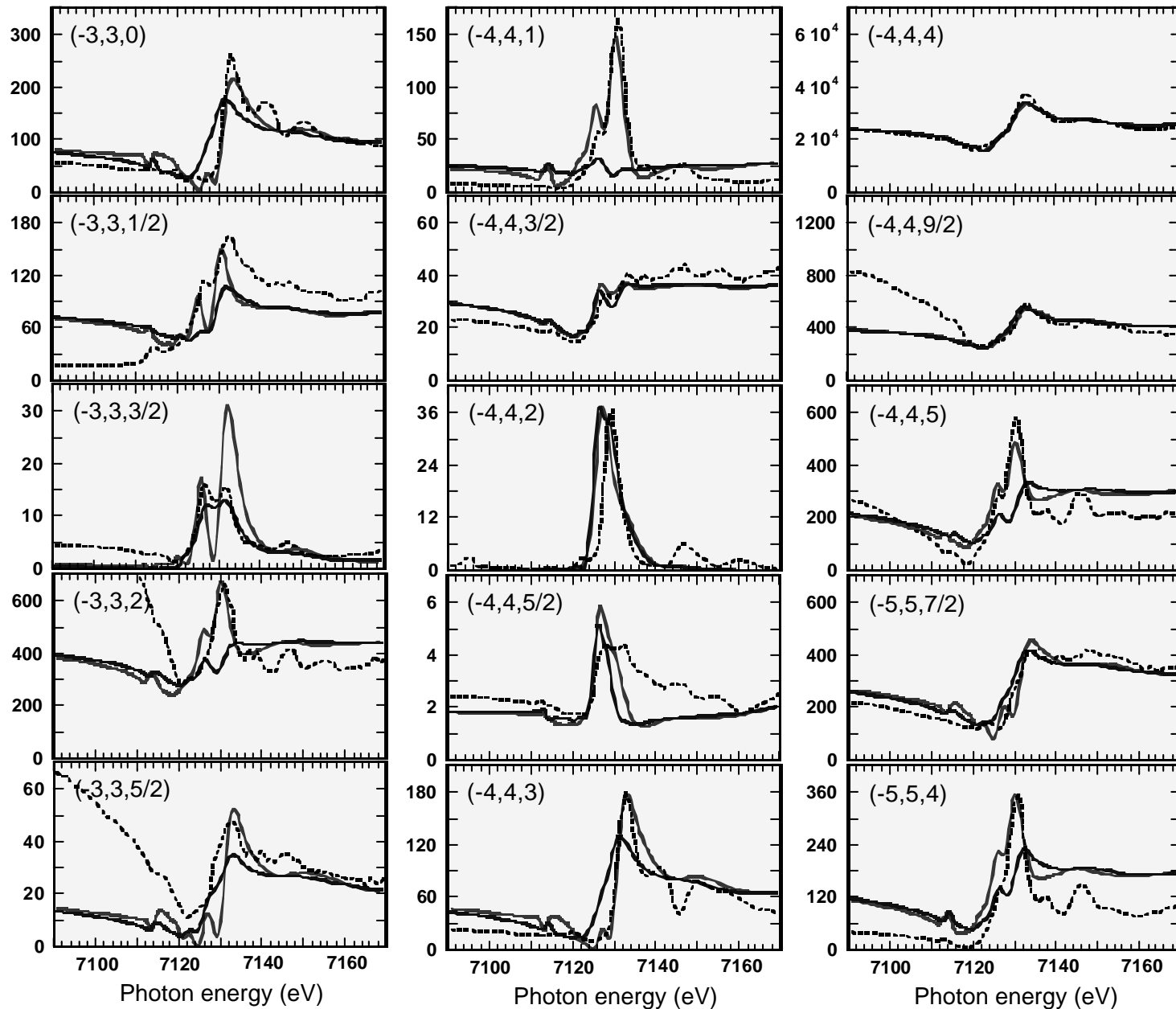
d occupancy rates taken as parameters

Reflection intensity (nbr of elec²)



$Fe_1-Fe_2 \pm 0.12e^-$ —————
 $Fe_3-Fe_4 \pm 0.08e^-$ —————
 Same charge —————
 experiment

Reflection intensity (nbr of elec²)



$\text{Fe}_1\text{-Fe}_2 \pm 0.12e^-$
 $\text{Fe}_0\text{-Fe}_0 \pm 0.08e^-$

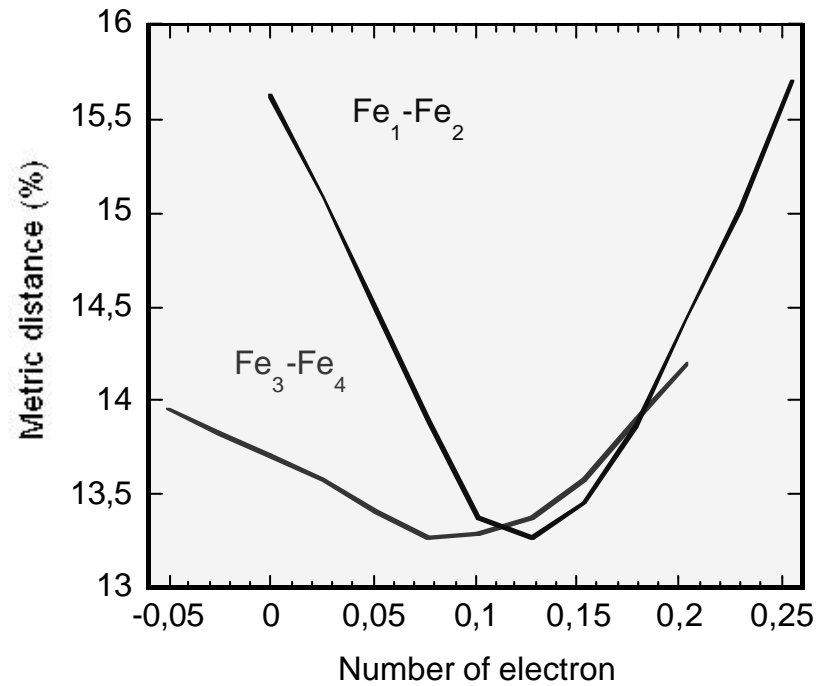
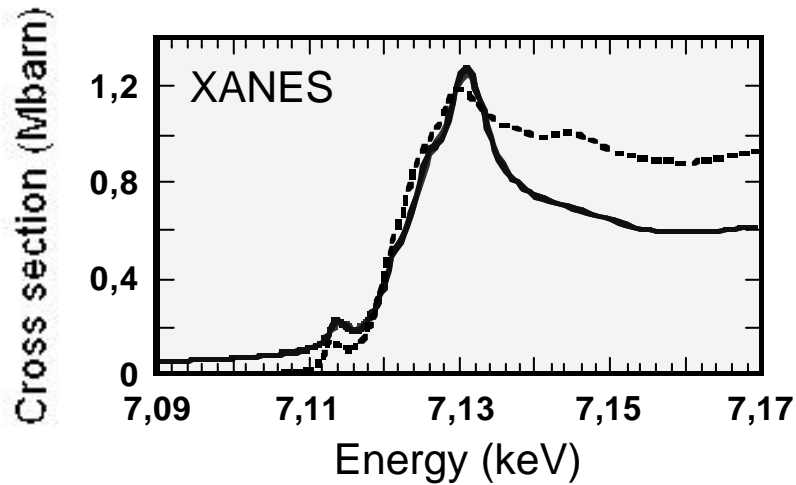


Same charge



experiment

XANES does not see anything !



Best agreement for
 ± 0.12 and ± 0.08 electron

Agreement satisfactory when intensity not too low

For reflections with very low intensity :

structural effect ?

Agreement with theoretical calculations (LSDA+U) and bond valence method

(1) : I. Leonov et al., Phys. Rev. Lett. 93, 146404 (2004) → TBLMTO

(2) : H.-T. Jeng, et al., Phys. Rev. Lett. 93, 156403 (2004) → FLAPW

	P. work	BVS	(1)		(2)	
	n_{3d}	n_{3d}	n_{3d}	M	$n_{3d}?$	M
Fe ₁	5.62	5.6	5.69	3.50	5.57	3.45
Fe ₂	5.38	5.4	5.44	3.94	5.41	3.90
Fe ₃	5.42	5.4	5.51	3.81	5.44	3.81
Fe ₄	5.58	5.6	5.69	3.48	5.56	3.39

Resonant X-ray scattering can give quantitative values of electronic parameters

Charge ordering : ± 0.12 and ± 0.08 electron for Fe₃O₄

± 0.04 for NaV₂O₅

V - Spin and orbital ordering in V_2O_3

A long story...

Interplay of orbital and spin degrees of freedom...

Experiments from Paolasini *et al.*

Phys. Rev. Lett. **82**, 4719 (1999);

J. Electron Spectrosc. Relat. Phenom. 120/1-3 (2001).

Orbital Occupancy Order in V_2O_3 : Resonant X-Ray Scattering Results

L. Paolasini,¹ C. Vettier,¹ F. de Bergevin,² F. Yakhou,¹ D. Mannix,^{1,3} A. Stunault,⁴ W. Neubeck,¹
M. Altarelli,^{1,*} M. Fabrizio,⁵ P. A. Metcalf,⁶ and J. M. Honig⁶

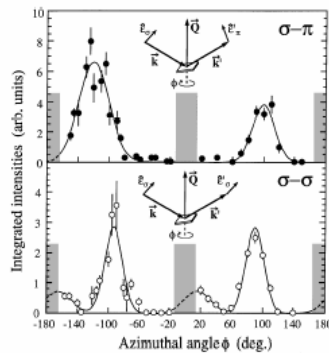


FIG. 3. Polarized integrated intensity of the (111) orbital reflection measured at different azimuthal angle Φ of rotation of the [111] plane about the (111) direction for a photon energy of 5.464 keV. The shaded areas indicate zones that were blind due to the sample mount. Lines are guides for the eyes.

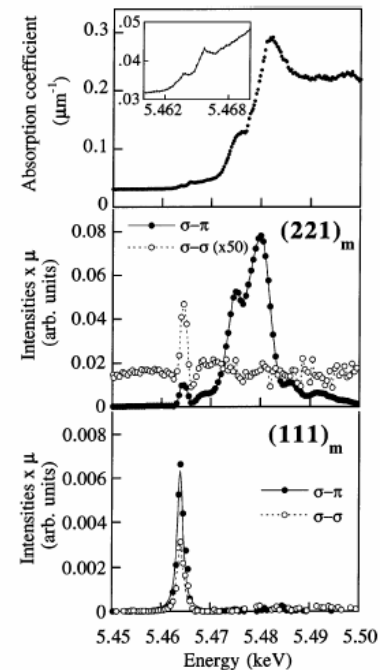
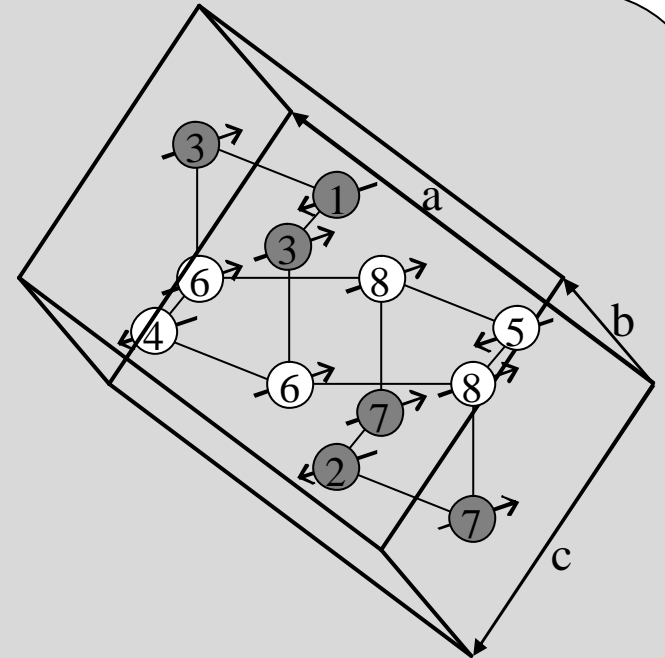


FIG. 2. Energy dependence of the (221) magnetic reflection (middle panel) and the (111) orbital peak (bottom panel) at $T = 100$ K. The two polarization channels $\sigma\text{-}\sigma$ and $\sigma\text{-}\pi$ are shown. The absorption coefficient (top panel) has been obtained from fluorescence data. The inset shows details of the spectrum near the $3d$ threshold.

Geometrical monoclinic structure from Dernier and Marezio (1970).
 Magnetic space group, $C_{2h} \otimes \hat{T}$, from Moon (1970).

atom	position	spin	Sym.	Translation
V_8	(u, v, w)	?	E	0
V_6	$(-u, -v, -w)$?	I	0
V_3	$(\frac{1}{2}+u, -v, w)$?	Tm_b	$(\frac{1}{2}, 0, 0)$
V_7	$(\frac{1}{2}-u, v, -w)$?	TC_{2b}	$(\frac{1}{2}, 0, 0)$
V_4	$(\frac{1}{2}+u, \frac{1}{2}+v, \frac{1}{2}+w)$?	T	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
V_5	$(\frac{1}{2}-u, \frac{1}{2}-v, \frac{1}{2}-w)$?	TI	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
V_2	$(u, \frac{1}{2}-v, \frac{1}{2}+w)$?	m_b	$(0, \frac{1}{2}, \frac{1}{2})$
V_1	$(-u, \frac{1}{2}+v, \frac{1}{2}-w)$?	C_{2b}	$(0, \frac{1}{2}, \frac{1}{2})$

$$u = 0.3438, v = 0.0008, w = 0.2991$$



$$F = \sum_{a=1,8} S_a (e^{i\vec{Q}\cdot\vec{R}_8} (f_8' + i f_8''))$$

$$\sum_{aa'} e_a^{s*} e_a^e D_{aa'}$$

$$+ i \sum_{aa'a''} e_a^{s*} e_a^e (k_a^e I_{aa'a''} - k_a^s I_{a'aa''}^*)$$

$$+ \sum_{aa'a''a'''} e_a^{s*} e_a^e k_a^s k_a^e Q_{aa'a''a'''}$$

Neglecting v

For $h +$ "number of y among $\alpha, \beta, \gamma, \delta$ " odd :

$$D_{\mathbf{ab}}^{hkl} = 8i \cos(hu + lw) \text{Im}(D_{\mathbf{ab}})$$

$$I_{\mathbf{abg}}^{hkl} = 8i \sin(hu + lw) R(I_{\mathbf{abg}})$$

$$Q_{\mathbf{abgd}}^{hkl} = 8i \cos(hu + lw) \text{Im}(Q_{\mathbf{abgd}})$$

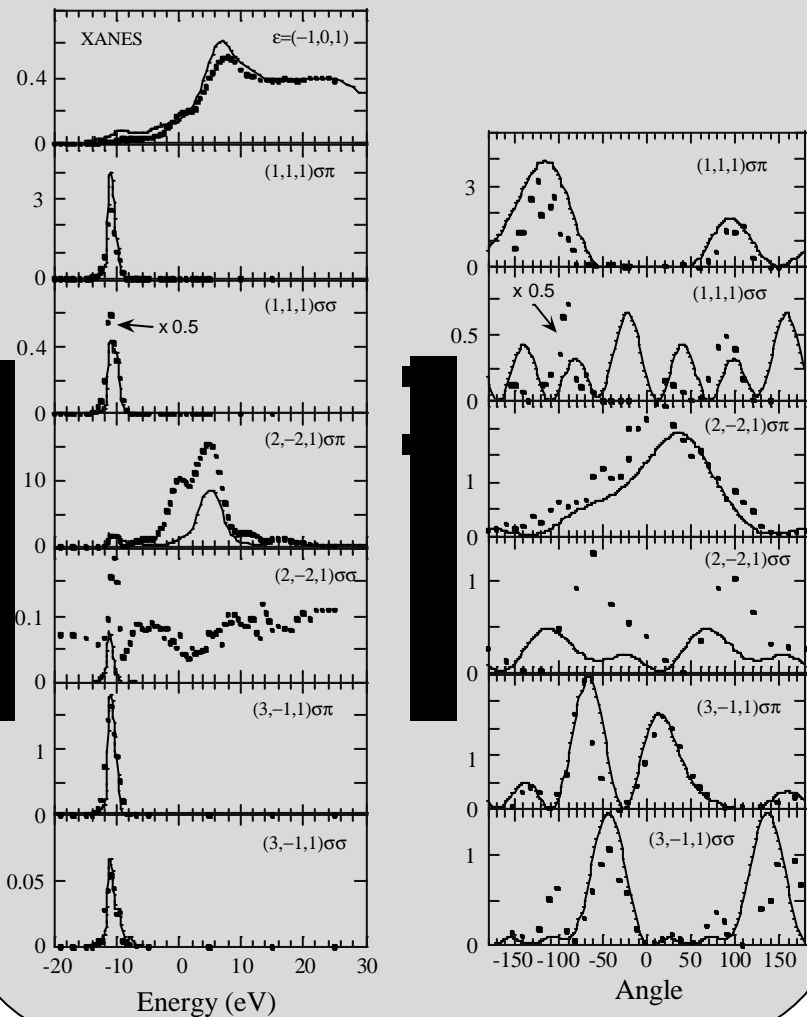
After summation over polarization and wave vector components :

→ Dipole-Dipole signal zero in σ - σ because depends on $R(D)$

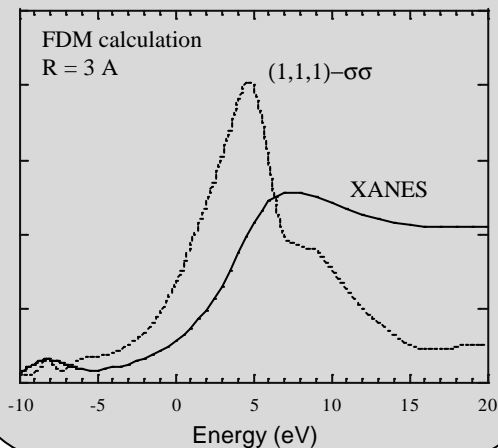
→ Dipole-Dipole signal zero in σ - π for h odd because $\text{Im}(D_{xz})$ zero

→ Dipole-Quadrupole and Quadrupole-Quadrupole not zero.

Calculation using the multiple scattering theory with the magnetic ordering



Calculation using the finite difference method to check the orbital ordering



Signal comes from the spin ordering

PR B **69**, 224401 (2004)

Resonant X-ray scattering can give information on the electronic structure of complex material