Resonant Diffraction on Powders

- Site Selective Spectroscopy - Chemical Selective Diffraction

H. Palancher, S. Bos, Ch. Pichon, J. Lynch, B. Rebours,

E. Lorenzo, J.-F. Berar, J.-L. Hodeau

Lab. Cristallographie-CNRS - GRENOBLE - (F)

& experiments at the ESRF - GRENOBLE - (F)

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Outline

Introduction

- some basis of resonant diffraction

Application using Resonant Diffraction

Selective Site Spectroscopy

DAFS, DANES

↳ charge order in La4Mn5Si4O22 powder via

- **"site selective f' refinement"**.

Anisotropy of Resonant Diffraction,

↳ site symmetry information : not on powders

Chemical Selective Diffraction

MAD, SAD,

↳ phase of structure factors

Resonant Contrast Diffraction,

↳ direct localization of atoms in zeolites via

- **"anomalous differential patterns"**,
- **"dispersive difference maps"**.

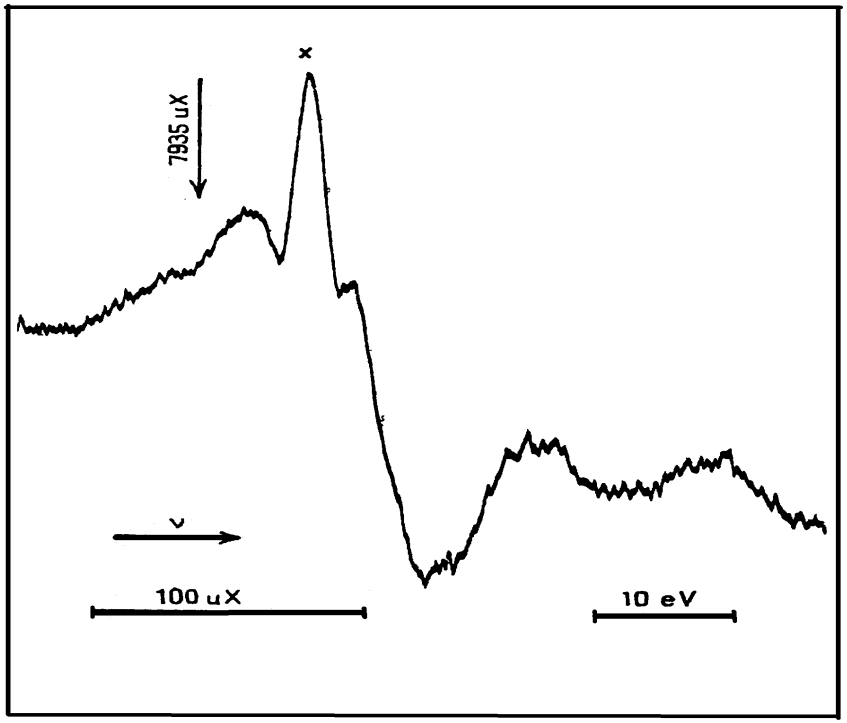
Historic Measurement

“ Distribution spectrale dans les régions d’absorption propres de divers cristaux ”

Y. Cauchois, Compte Rendus Acad. des Sciences, CRAS, 242, 100 (1956)

Bragg intensity

Energy dispersive spectra with a bent crystal analysor (Mica)
Energie : Al K- edge, Reflection (002)



“ … l'apparition possible, a côté de raies blanches, de raies noires … ”

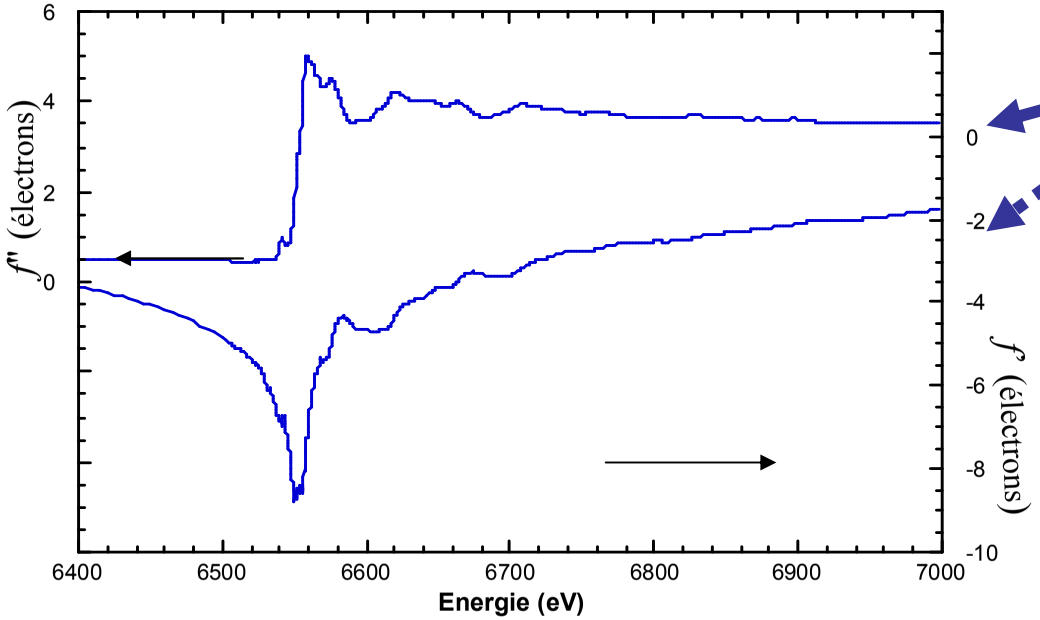
“ … Ces anomalies d'intensité, différentes d'absorptions banales, semblent attribuables au comportement exceptionnel des facteurs de structure dans les régions "anomales" … ”

Relation between *intensities* and *f'(E), f''(E)*

Intensity ∝ structure factor square modulus

$$F(\mathbf{Q},E) = \sum_i f_i(\mathbf{Q},E)\exp\left(i\mathbf{Q}.\mathbf{r_i}\right)\exp\left(-B_i Q^2\right)$$

$$f_i(\mathbf{Q},E) = f_{0_i}(\mathbf{Q}) + f_i'(E) + if_i''(E)$$



Anomalous scattering factors

f_0 Thomson scattering amplitude

$f''(E)$ proportional to $E.\mu(E)$

f' ←Kramers-Kronig relation→ f''

$$f'(E) = \frac{2}{\pi}\int_0^\infty \frac{E.f''(E)}{E^2 - E^2}dE$$

Resonant Diffraction : Diffracted intensity measurement *versus* the energy near the absorption edge of a native atom

Absorption → local environment of absorbing atoms

Diffraction → crystallographic structure

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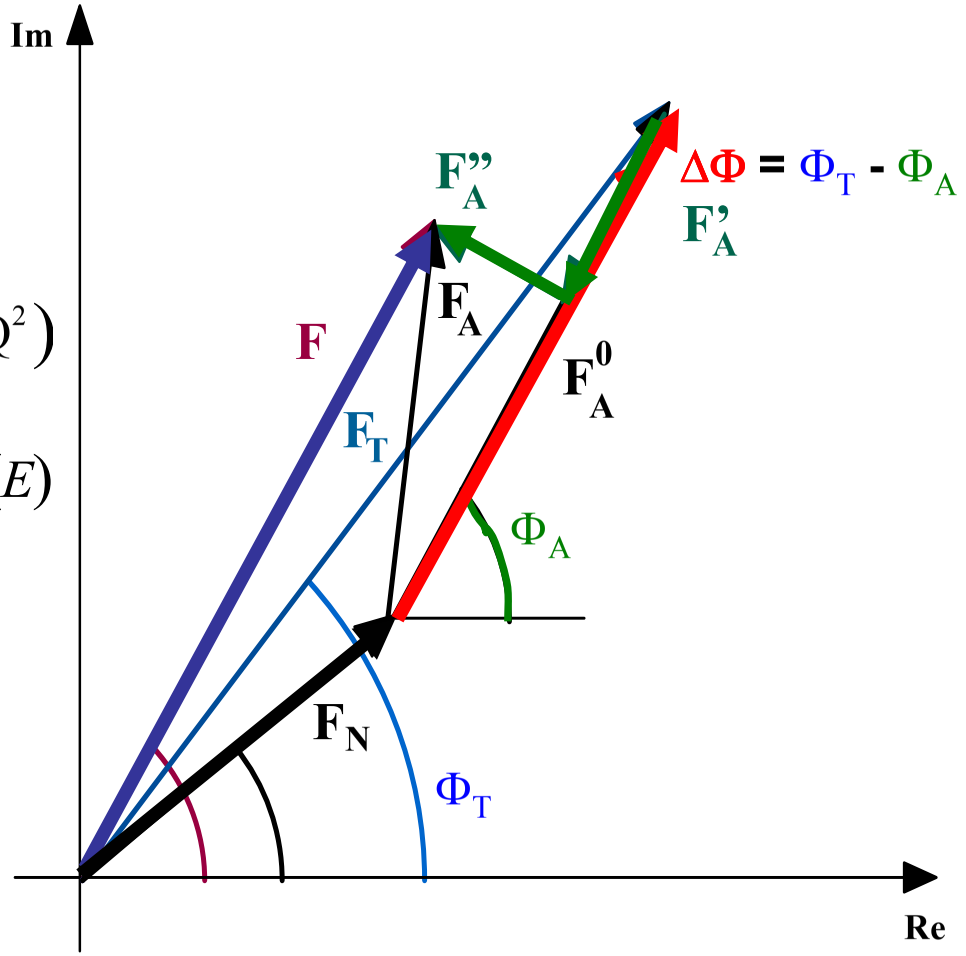


F_N non anomalous atoms
F_A anomalous atoms
$\Delta\Phi = \Phi_T - \Phi_A$

$$I(h,\lambda) = Abs.LP.\lambda^3.\ (|F_T|^2+(f'_A{}^2+f''_A{}^2)|F_A|^2/f^o_A{}^2+2|F_T||F_A|(f'_A\cos(\Delta\Phi)+f''_A\sin(\Delta\Phi))/f^o_A)$$

Application using Resonant Diffraction

based on structure factor selectivities

$$F(\mathbf{Q},E) = \sum_i f_i(\mathbf{Q},E)\exp(i\mathbf{Q}.\mathbf{r_i})\exp(-B_i Q^2)$$

Chemical selectivity — **Site selectivity**

we can combine diffraction and spectroscopy information

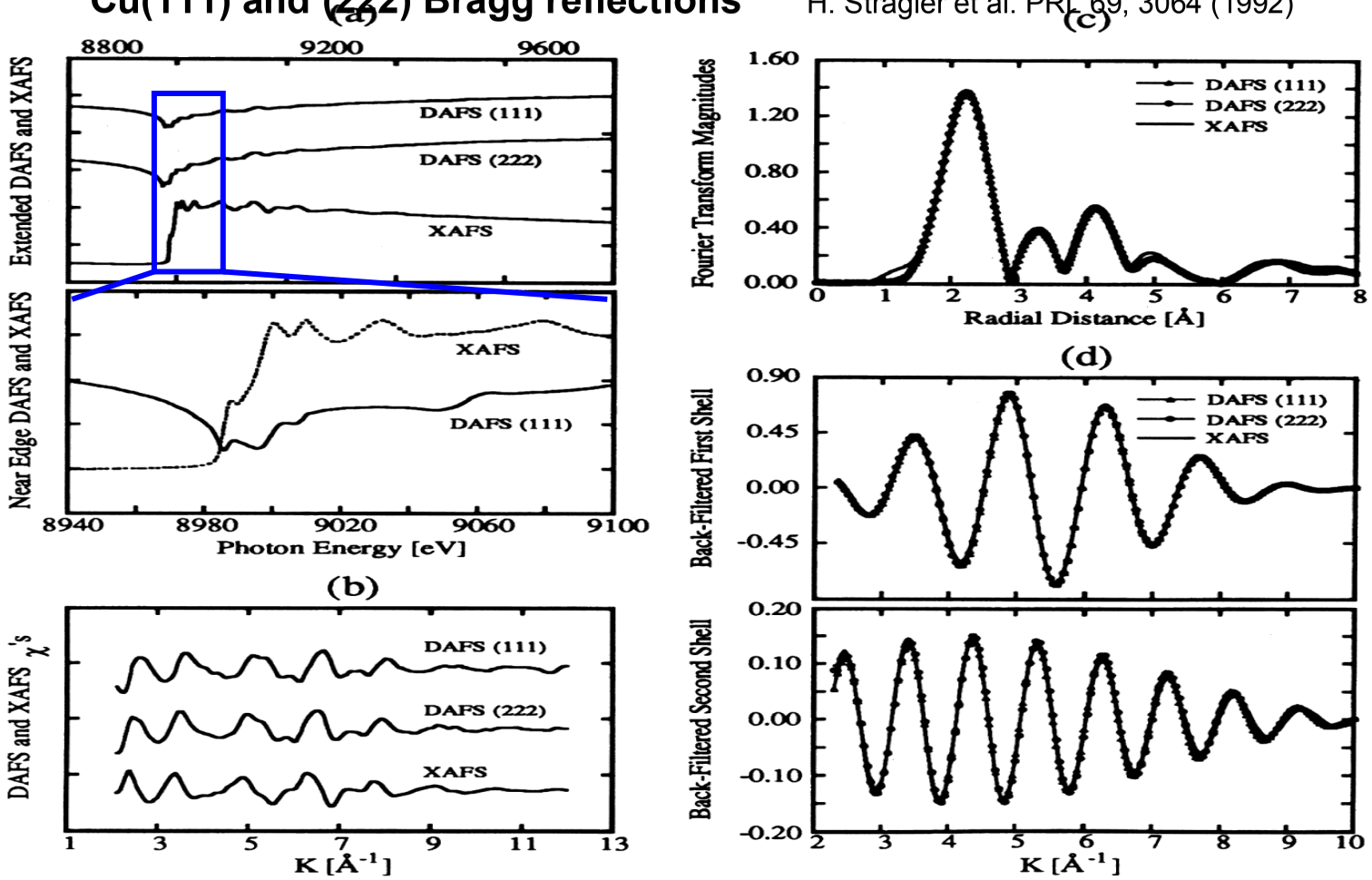
- Selective Site Spectroscopy : **DAFS, DANES**
- **Anisotropy of Resonant Scattering**

we can vary the contribution of one specific atom on diffracted intensity

- **Structure Factor Phase Solution : MAD**
- **Element Selective Diffraction : Contrast**

Site Selective Spectroscopy : DAFS

Cu(111) and (222) Bragg reflections H. Stragier et al. PRL 69, 3064 (1992)



↳ **same Fourier transform**
(only different phase shifts for DAFS or XAFS)

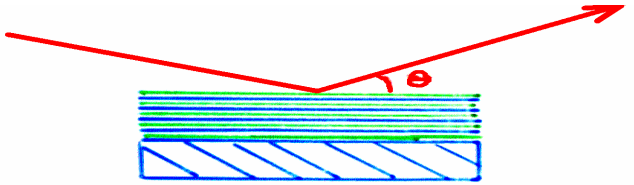
↳ **Site selective distance information**

XAFS : atom selective local information

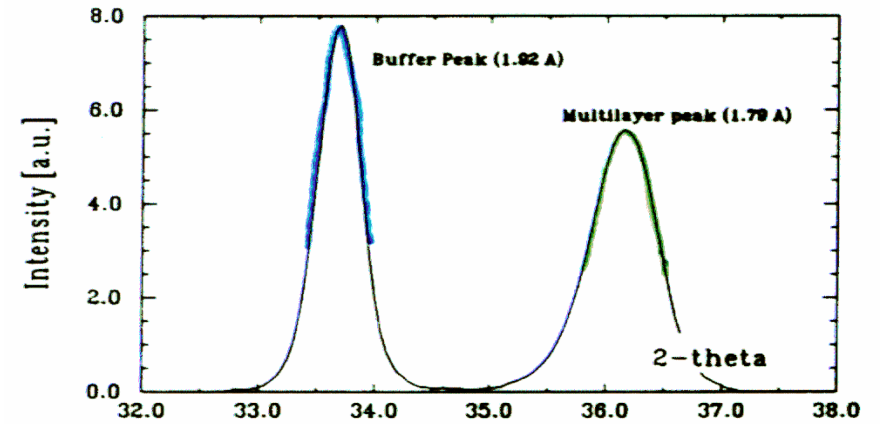
DAFS : atom and site or phase selective local information

Site Selective Spectroscopy : DAFS

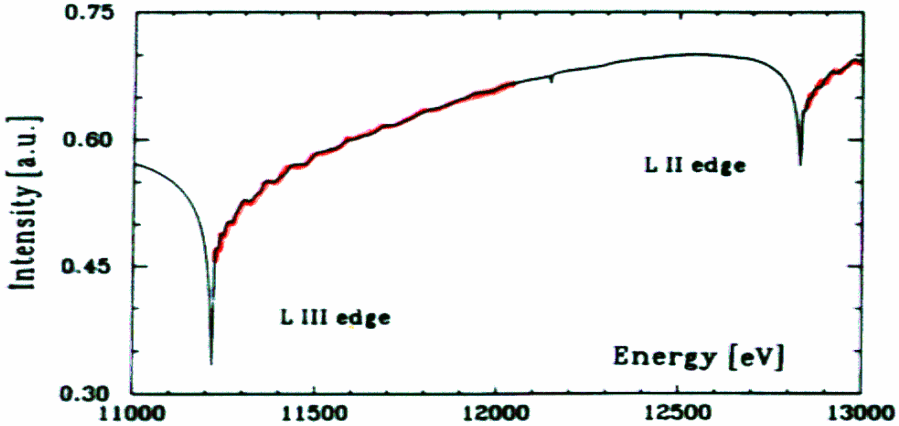
DAFS method on multilayers

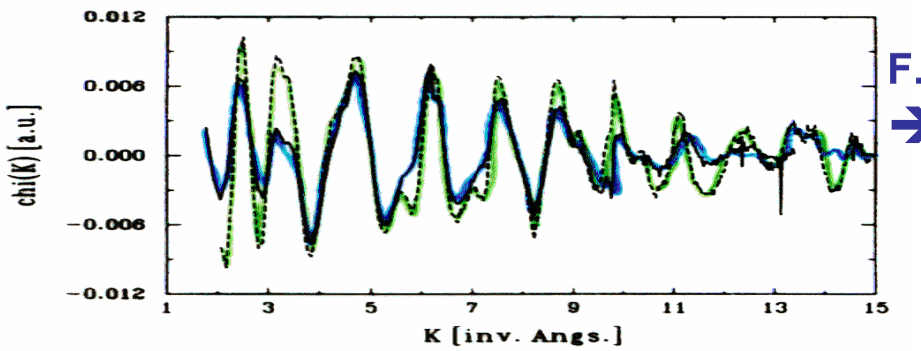


Ir buffer & Ir/Fe multilayer Bragg reflections

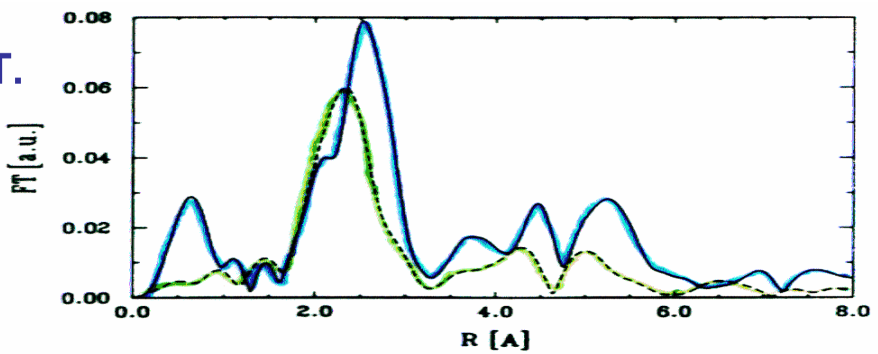


Multilayer Bragg intensity at Ir L_{III} edge





F.T. ➔



- Ir buffer and Ir/Fe multilayer : different DAFS signals
- selective of Ir buffer and Ir/Fe multilayer — H. Renevier et al., Physica B 208-209, 217, (1995)
- first neighbor shells of Fe at the Ir-Fe interfaces — H. Renevier et al., PRL 78, 2775, 1997

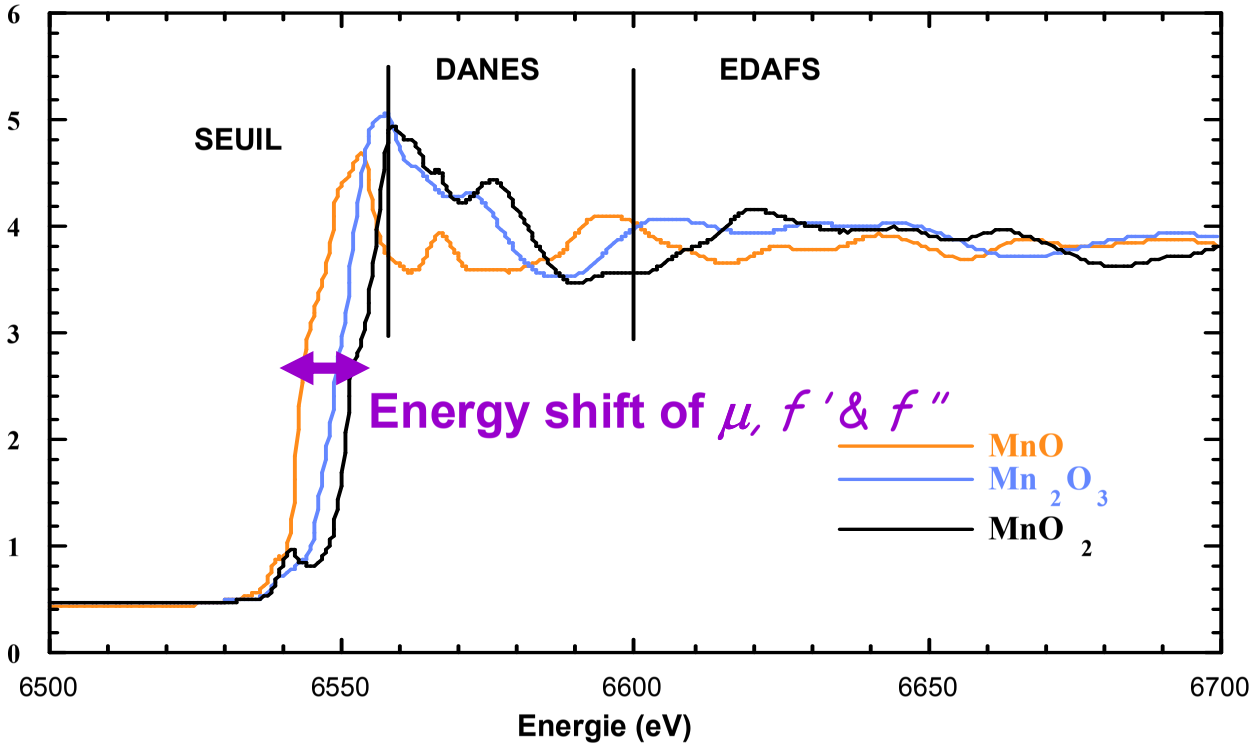
Study of sites with different valence

Chemical & site selectivities: *via* structure factor contributions

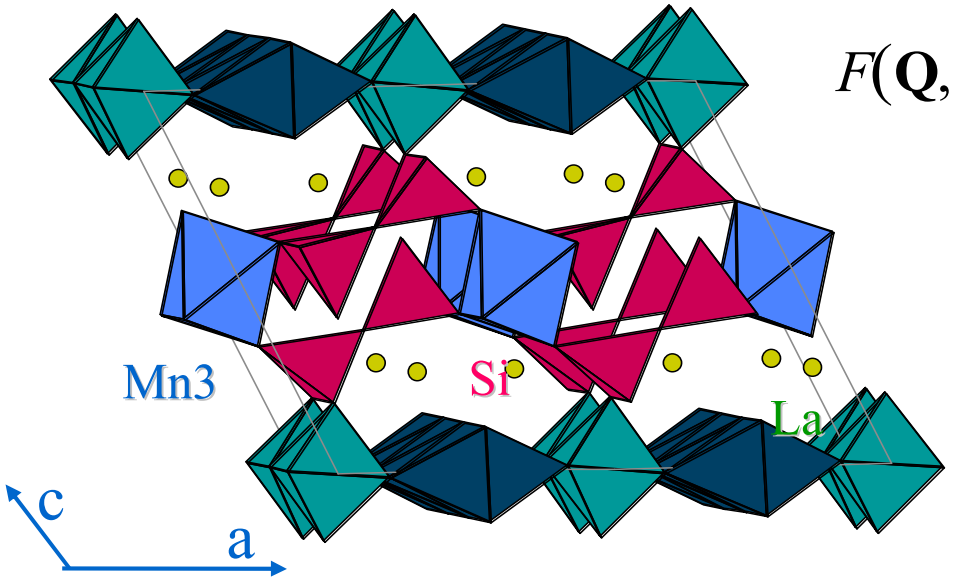
$$F(\mathbf{Q},E)=\sum_i f_i(\mathbf{Q},E)\exp(i\mathbf{Q}.\mathbf{r_i})\exp(-B_i Q^2)$$

Chemical selectivity — **Site selectivity**

Valence sensitivity of Resonant Diffraction due to XANES sensitivity of f' & f''



Mn valence states on $La_4Mn_5Si_4O_{22}$ powder



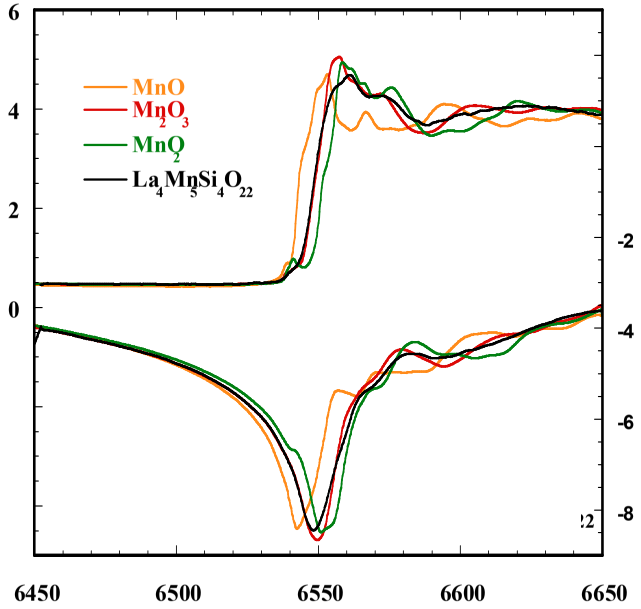
$La_4Mn_5Si_4O_{22}$
known structure

$$F(\mathbf{Q},E) = \sum_i f_i(\mathbf{Q},E)\exp(i\mathbf{Q}.\mathbf{r_i})\exp(-B_i Q^2)$$

$$f_i(\mathbf{Q},E) = f_{0_i}(\mathbf{Q}) + f_i'(E) + if_i''(E)$$

Chemical selectivity for Valence studies

***f'* et *f''* variation close to the edge**
Refinement of f' (and f'' using KK)



Which valence state for the three sites ?

Mn^{4+} ⇨ Mn1, Mn^{3+} ⇨ Mn2, Mn^{2+} ⇨ Mn3

Different strategies for DANES measurements on powders

Measurement of **complete spectra** (BM16-ESRF)

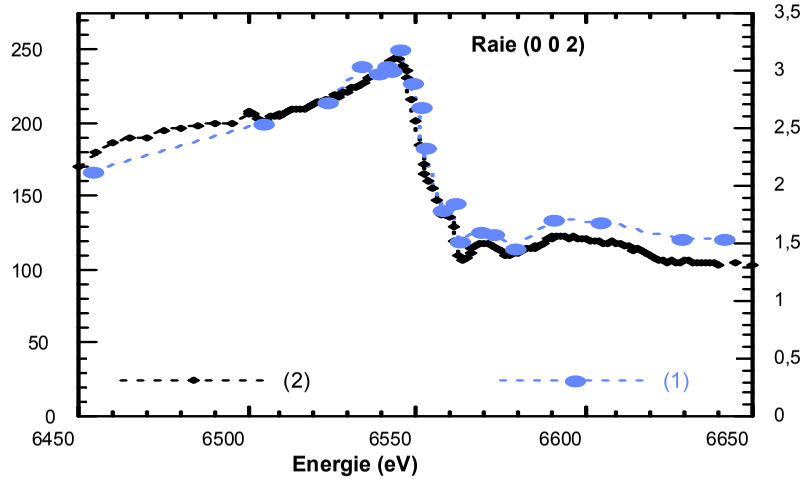
- large angular domain **2θ** (ex :**50°)**
- **21** energies distributed around the Mn K edge (6539 eV)

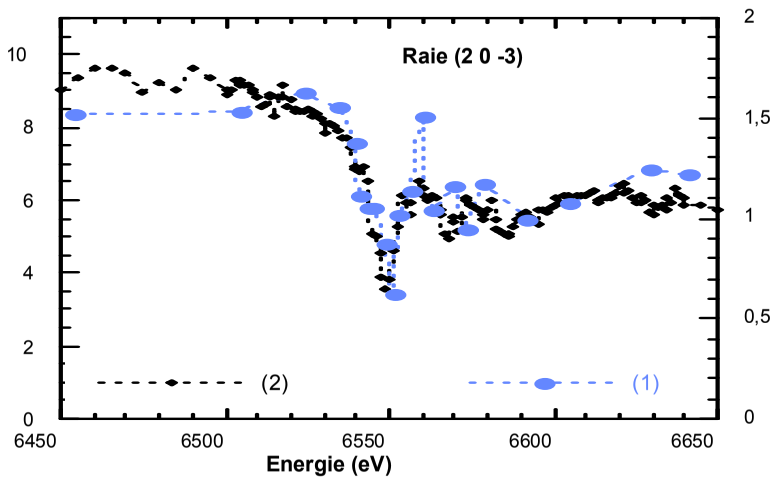
↳ Intégration of diffracted refections

Continuous scan of **diffracted peaks *versus* energy** (BM2-ESRF)

- mosaïc analyser (0.2°)
- background & fluorescence measurements
- sampling in ω : "ω scans "

↳ continuous scans of 9 reflections : 6450 < E < 6750eV

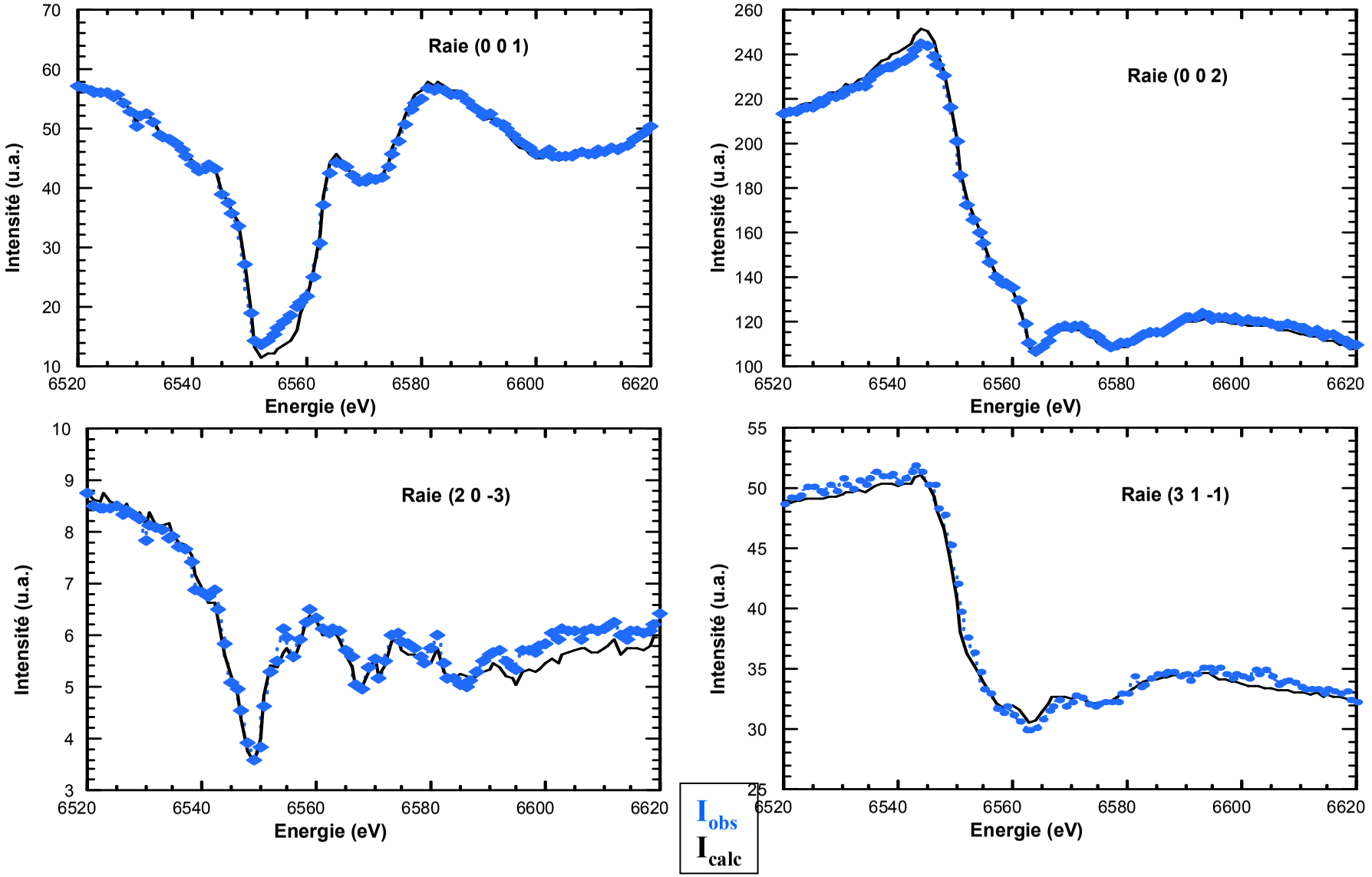




Conclusion on the experimental strategies:

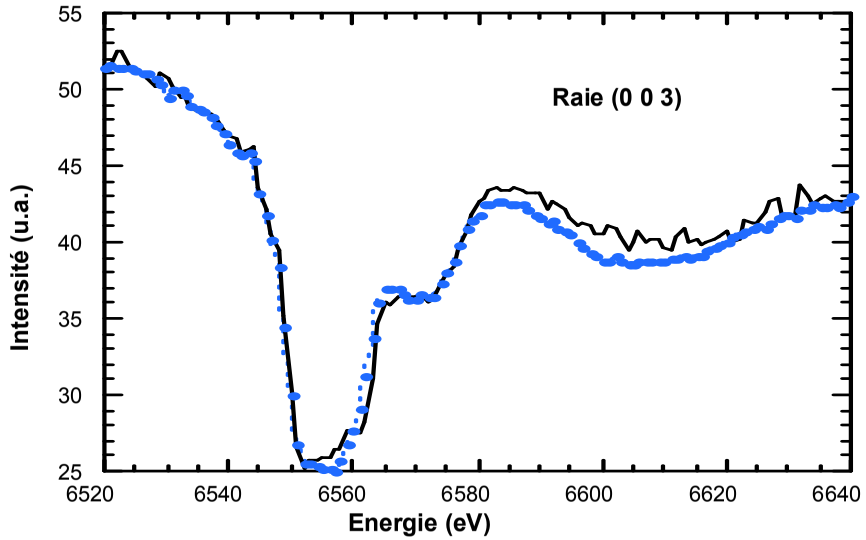
- continuous energy scans I(E)
  - ↳ better accuracy
- complete spectra measurements (3 energies)
  - ↳ analysis of reflection shapes and sampling

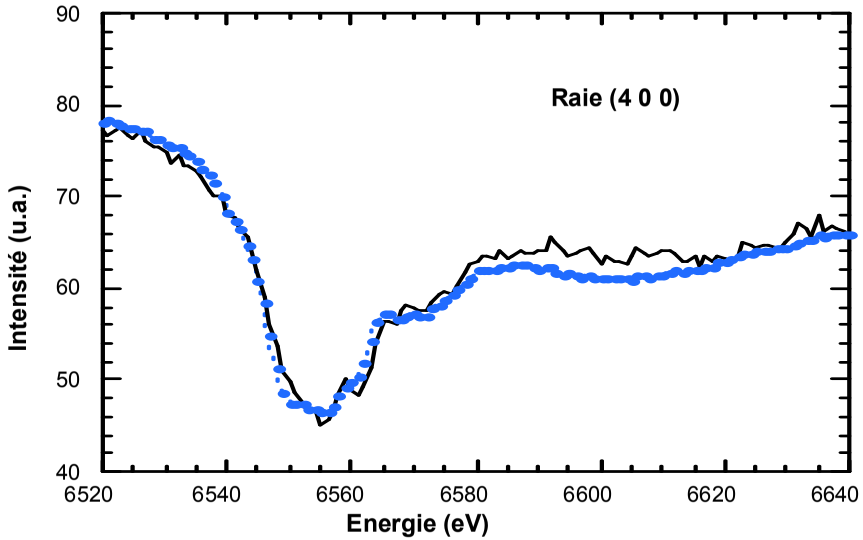
Refinement **of f' resonant scattering factors for the** 3 Mn sites using known crystalline struture

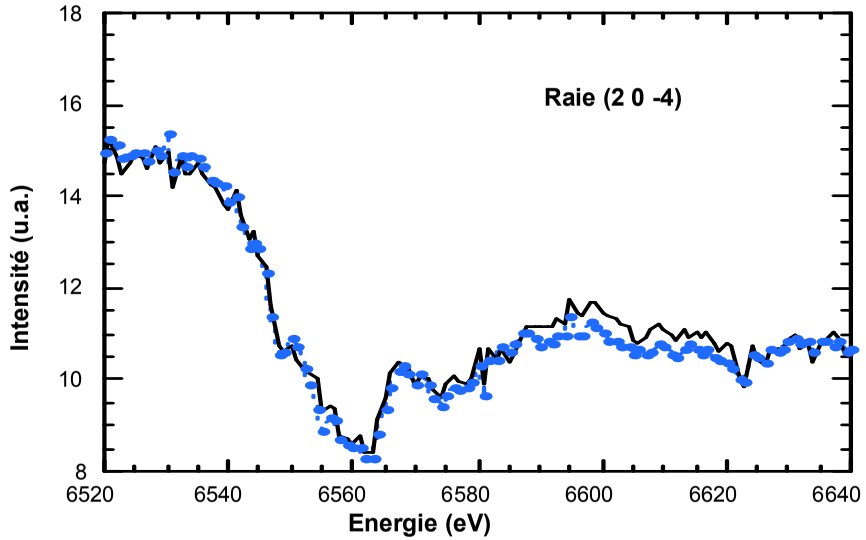


S. Bos et al., unpublished

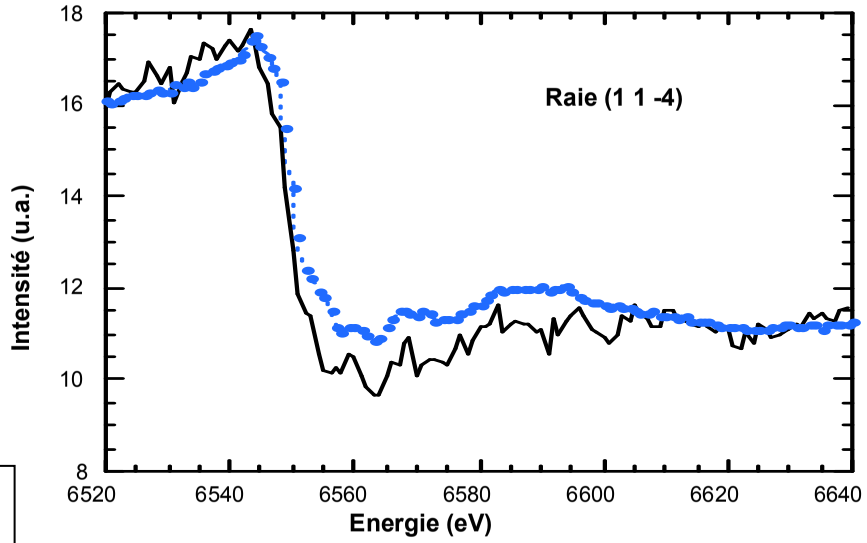
Refinement **of f' resonant scattering factors for the** 3 Mn sites using known crystalline struture







I_{obs}
I_{calc}



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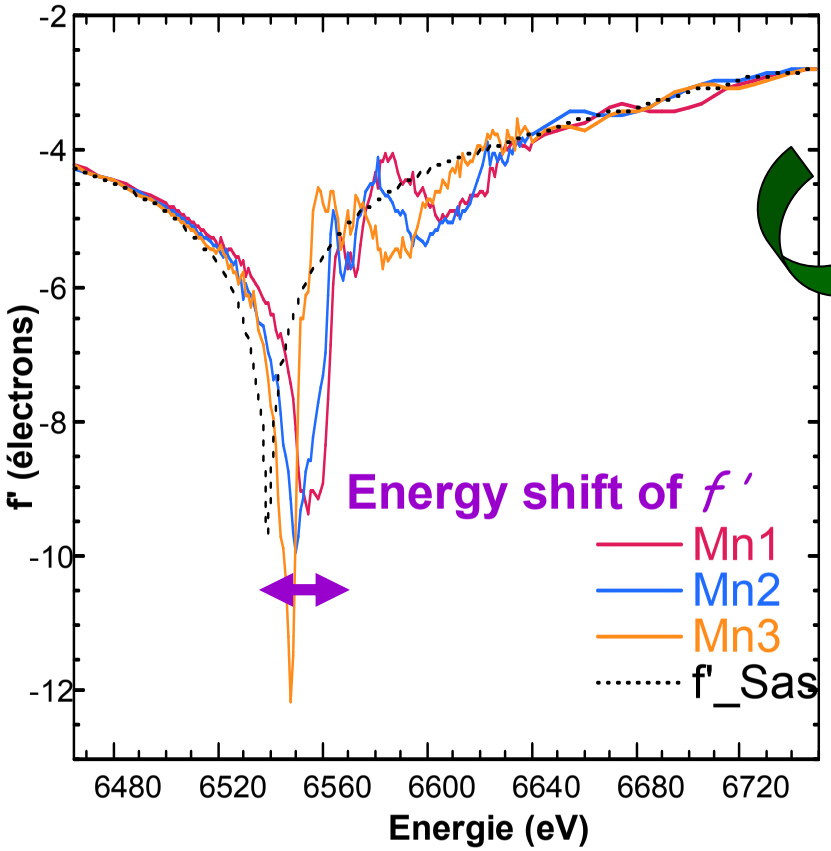
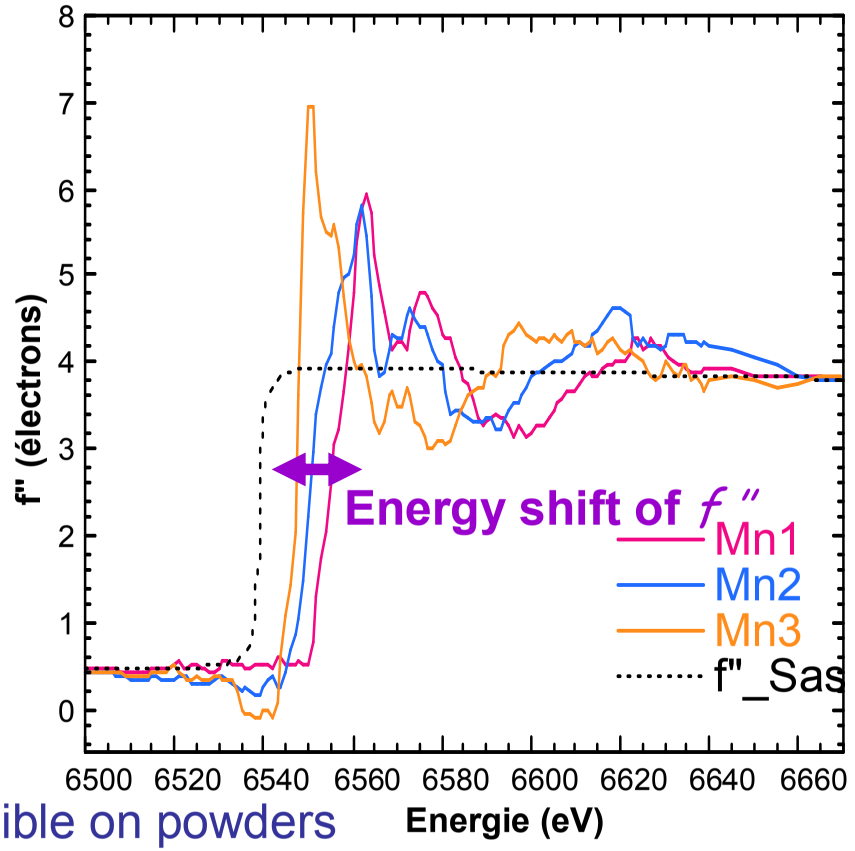
Refinement **of resonant scattering factors for the** 3 Mn sites



KK Transformation



Conclusion on the method itself

↳ Resonant Diffraction and DANES is possible on powders

Conclusion on the **resonant contribution** refinement

↳ different edge shifts for the 3 Mn sites corresponding to **3 valence states**

S. Bos et al., unpublished

Application using Resonant Diffraction

based on structure factor selectivities

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Chemical selectivity — **Site selectivity**

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- **Selective Site Spectroscopy : DAFS, DANES**
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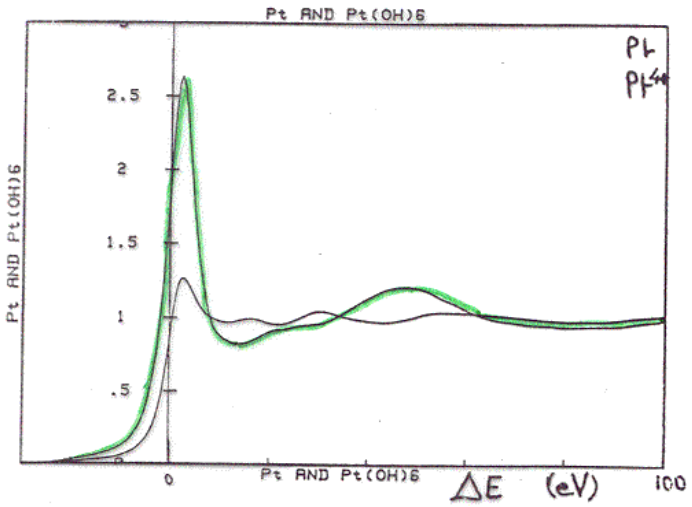
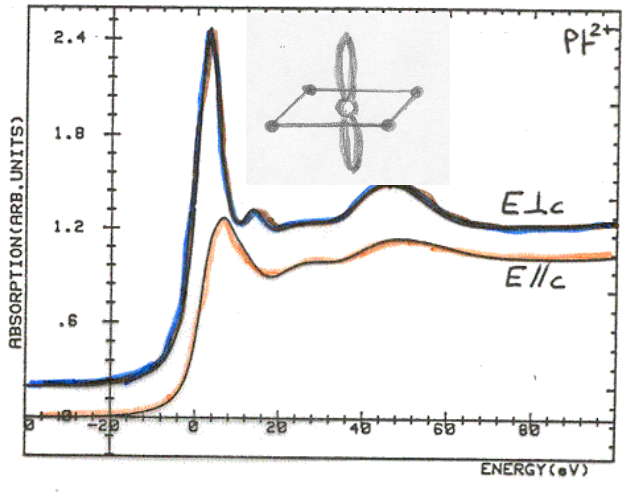
X-ray Dichroïsm: Anisotropy of Anomalous Scattering

Low local site symmetry

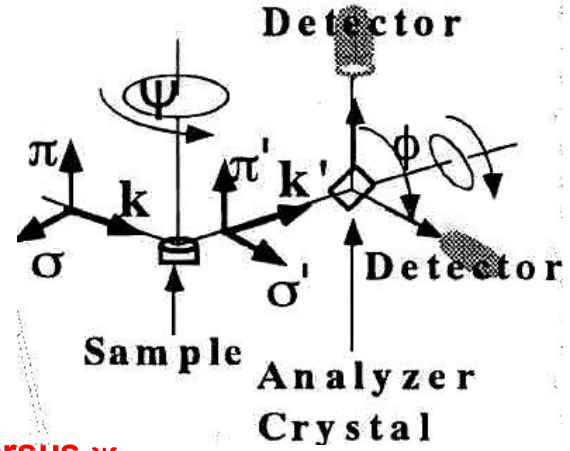
- **Absorption is sensitive to directions of polarization**

ex. **of Platinum Pt^{2+}**





- **Anomalous scattering terms f' and f'' vary for different directions of polarization → tensor properties ***
- **Diffracted intensities vary with polarization direction and azimuthal angle ***
- **Intensities ≠ 0 for forbidden reflections (2_1, 4_1, .., n, c, d,..)**



* A. Kirfel et al., Acta Cryst. A47,180 (1991); A48, 247 (1992); A49, 35 (1993)
* V.E. Dmitrienko et al., Acta Cryst. A61, 481 (2005)
* D.H. Templeton & L.K. Templeton, Acta Cryst. A41, 133 (1985)

- **on Powders : superposition of reflections of diffrents grains versus ψ**

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Structure factor phase solution (MAD & SAD methods)

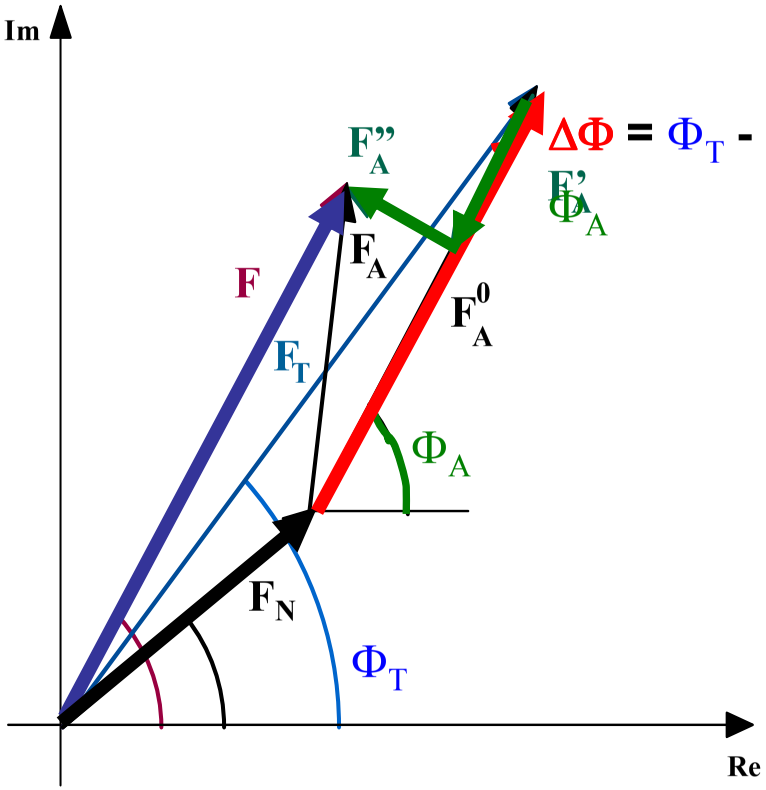
$$F(\mathbf{Q},E) = \sum_i f_i(\mathbf{Q},E)\exp(i\mathbf{Q}.\mathbf{r_i})\exp(-B_i Q^2)$$

$$I(h,\lambda) = Abs.LP.\lambda^3.\ (|F_T|^2+(f'_A{}^2+f''_A{}^2)|F_A|^2/f^o_A{}^2+2|F_T||F_A|(f'_A\cos(\Delta\Phi)+f''_A\sin(\Delta\Phi))/f^o_A)$$

F_N non anomalous atoms

F_A anomalous atoms

$\Delta\Phi = \Phi_T - \Phi_A$



Intensity variation for the same structure versus the energy or for Friedel pairs

Multi-wavelength Anomalous Dispersion & Single Anomalous Dispersion

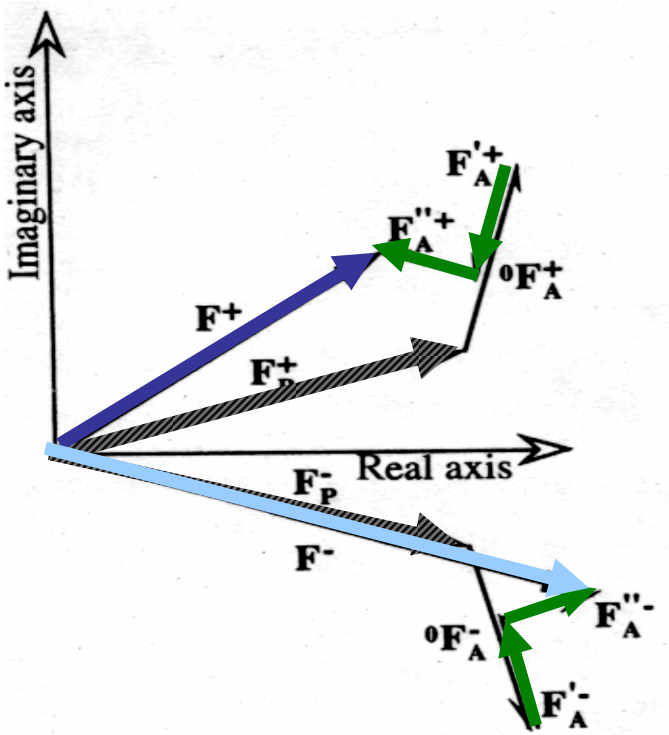
Methods MAD & SAD used in **Biocrystallography** (very large cell)

Structure factor phase solution and Contrast

Effect of anomalous dispersion on diffracted intensity of **(hkl) and (-h-k-l) reflections**

$$I^+ \alpha |F_T|^2 + ((f_a'^2+f_a''^2)/f_{oa}^2)|F_A|^2 + 2(f_a'/f_{oa})|F_T||F_A|\cos(\delta\Phi) + 2(f_a''/f_{oa})|F_T||F_A|\sin(\delta\Phi)$$

$$I^- \alpha |F_T|^2 + ((f_a'^2+f_a''^2)/f_{oa}^2)|F_A|^2 + 2(f_a'/f_{oa})|F_T||F_A|\cos(\delta\Phi) - 2(f_a''/f_{oa})|F_T||F_A|\sin(\delta\Phi)$$

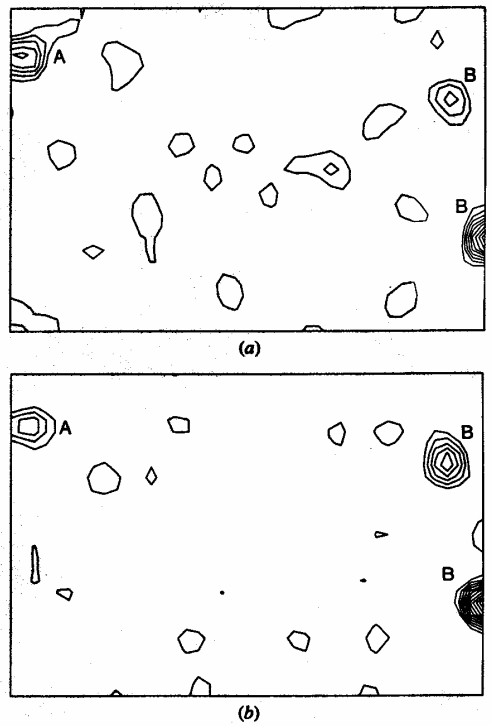


⇨ **Bijvoet differences :**

$I^+ - I^-$ proportional to f'' and $\sin(\delta\Phi)$

⇨ **Dispersive differences :**

$I_{E1} - I_{E2}$ depends mainly on $f'_{E1} - f'_{E2}$ and $\cos(\delta\Phi)$



*Bromine positions in a brominated oligonucleotide crystal as shown by Patterson map ****

* Karle J. Int. J of Quantum Chemistry. 7, 356 (1991)

** Hendrickson, Science 254, 51, ((1991)

*** Peterson et al. J. Syn. Rad. 3, 24, (1996)

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Resonant Contrast Diffraction : on powder diffraction

use the **chemical contrast** to retrieve the **localisation of a specific atom**

Effect of anomalous dispersion on a diffracted intensity :

$$I^+ \alpha |F_T|^2 + ((f_a'^2+f_a''^2)/f_{oa}^2)|F_A|^2 + 2(f_a'/f_{oa})|F_T||F_A|\cos(\delta\Phi) + 2(f_a''/f_{oa})|F_T||F_A|\sin(\delta\Phi)$$

$$I^- \alpha |F_T|^2 + ((f_a'^2+f_a''^2)/f_{oa}^2)|F_A|^2 + 2(f_a'/f_{oa})|F_T||F_A|\cos(\delta\Phi) - 2(f_a''/f_{oa})|F_T||F_A|\sin(\delta\Phi)$$

Bijvoet differences : $I^+ - I^-$ *proportional to* f''

But on powder diffraction :

- overlapping of I + and I - reflections
- hudge absorption effect

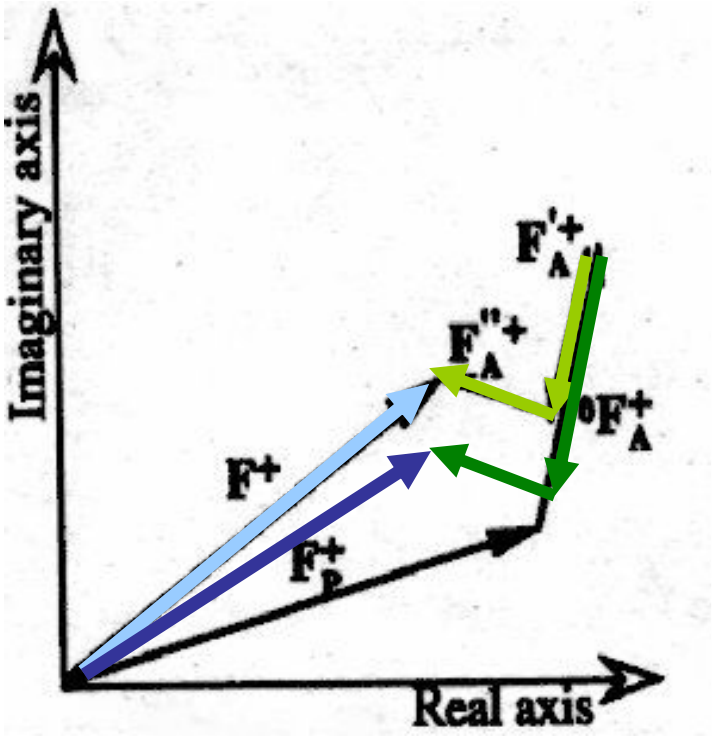
weak variation with f " hudge fluorescence scattering

Dispersive differences : *proportional to* $f'_{\lambda 1} - f'_{\lambda 2}$

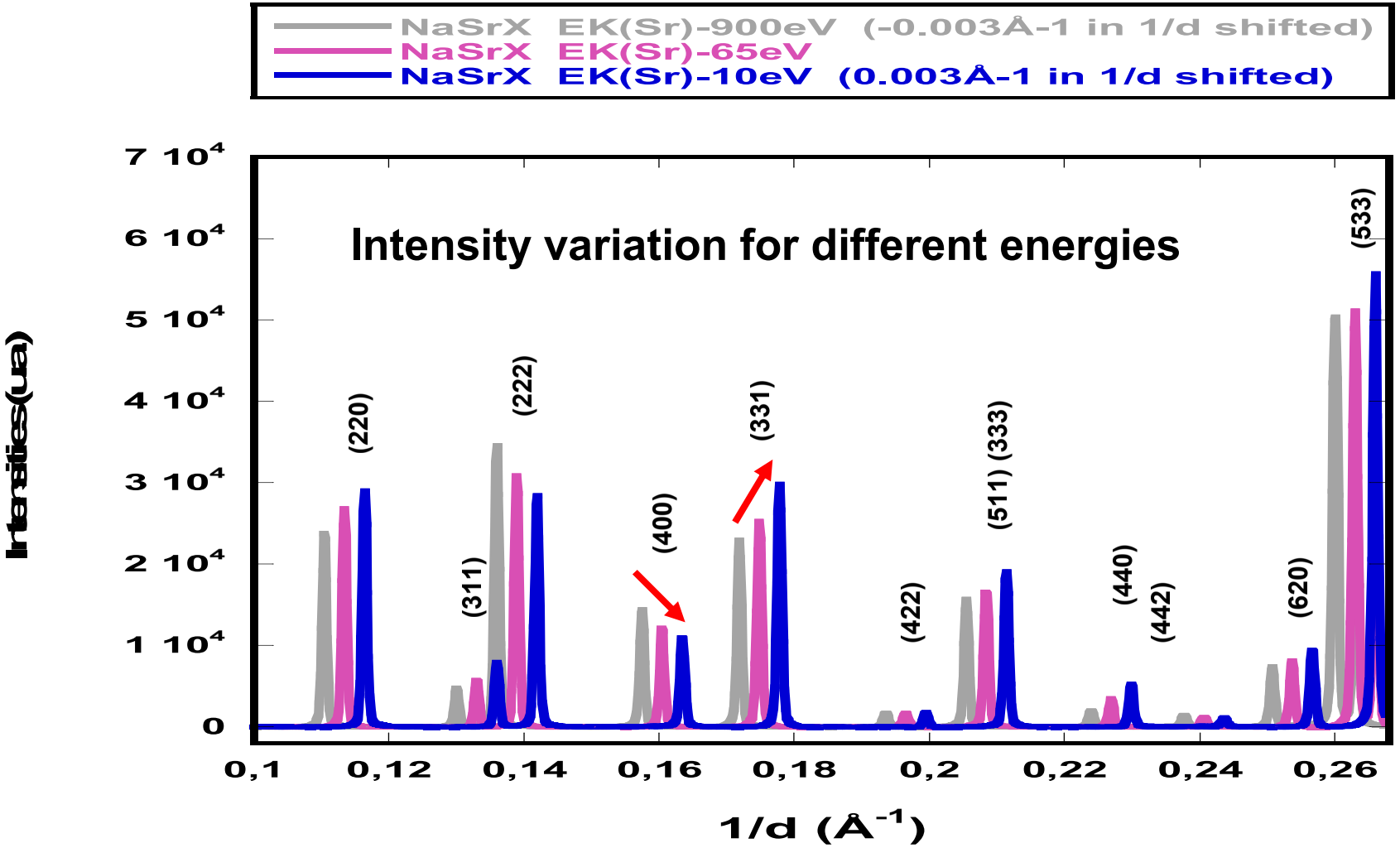
on powder diffraction :

- the intensity variation is seen
- weak absorption is possible

larger variation with f ' weaker fluorescence scattering



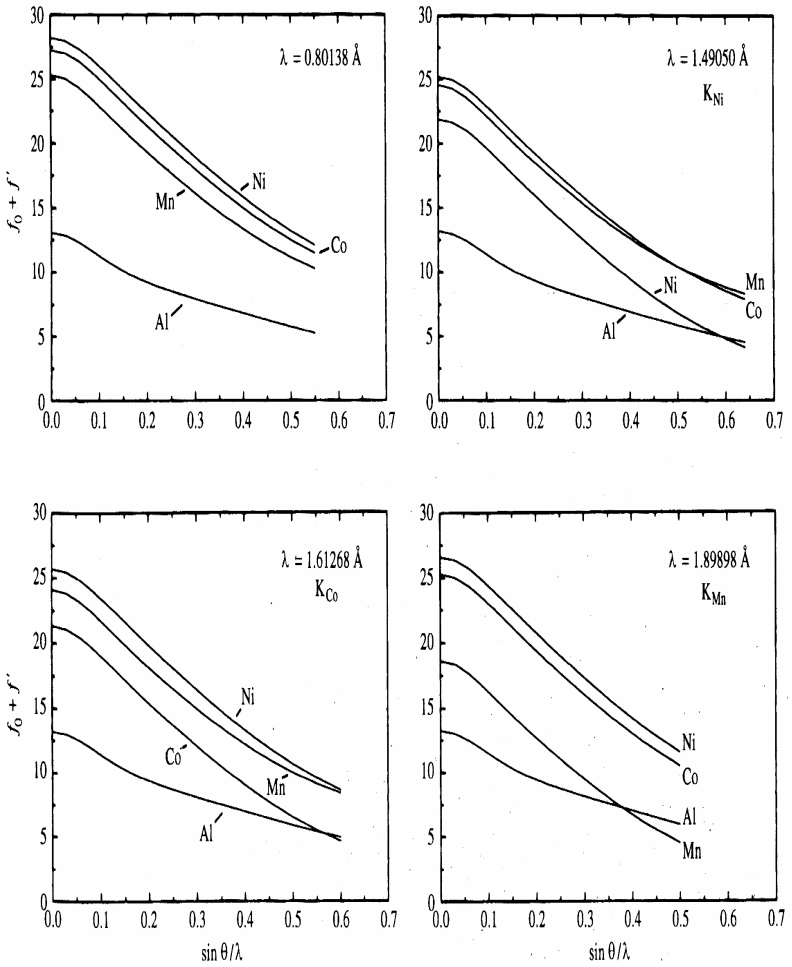
Resonant Contrast Diffraction : effect on Bragg intensities



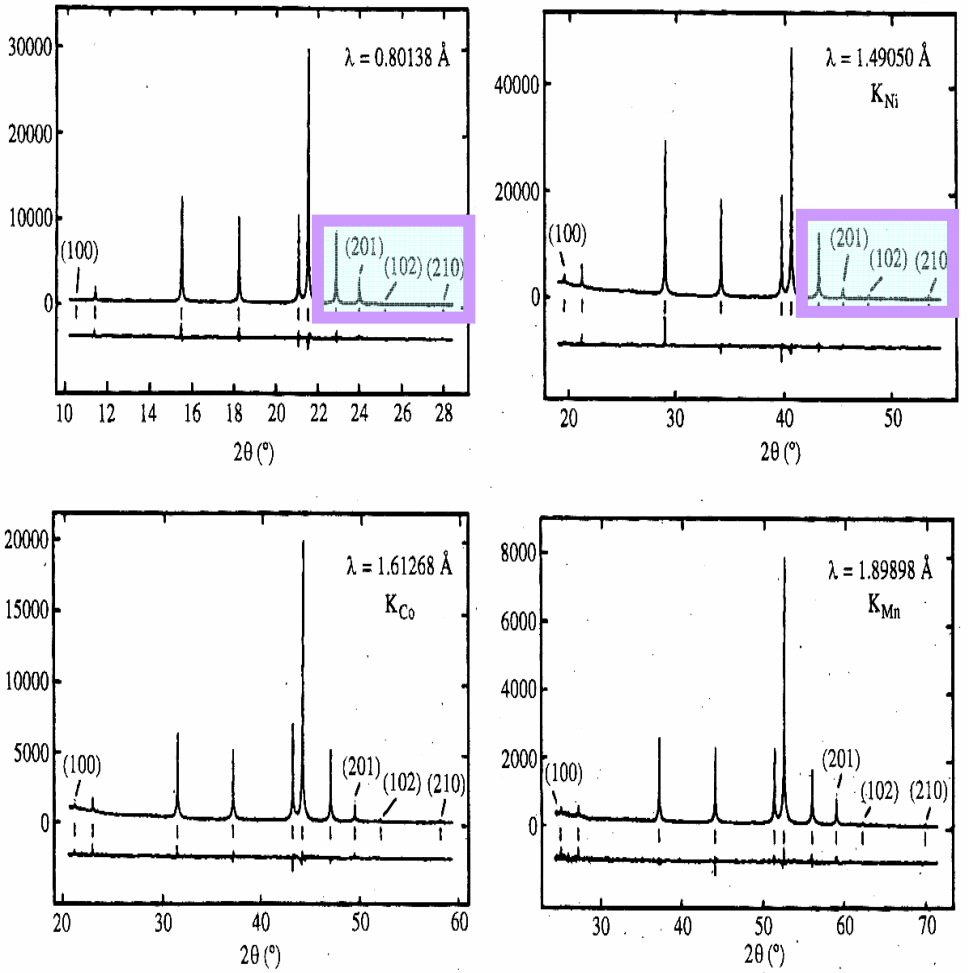
Resonant effects on powder diffraction diagram

Variations of **(400)** and **(331)** Bragg raw intensity different with energy closed to E_K(Sr).

Variation of scattering due to resonant scattering and *f'(E)*



Real scattering power (fo + f') of Ni, Co, Mn and Al as a function of q for energies far and close to K edges of Ni, Co and Mn atoms

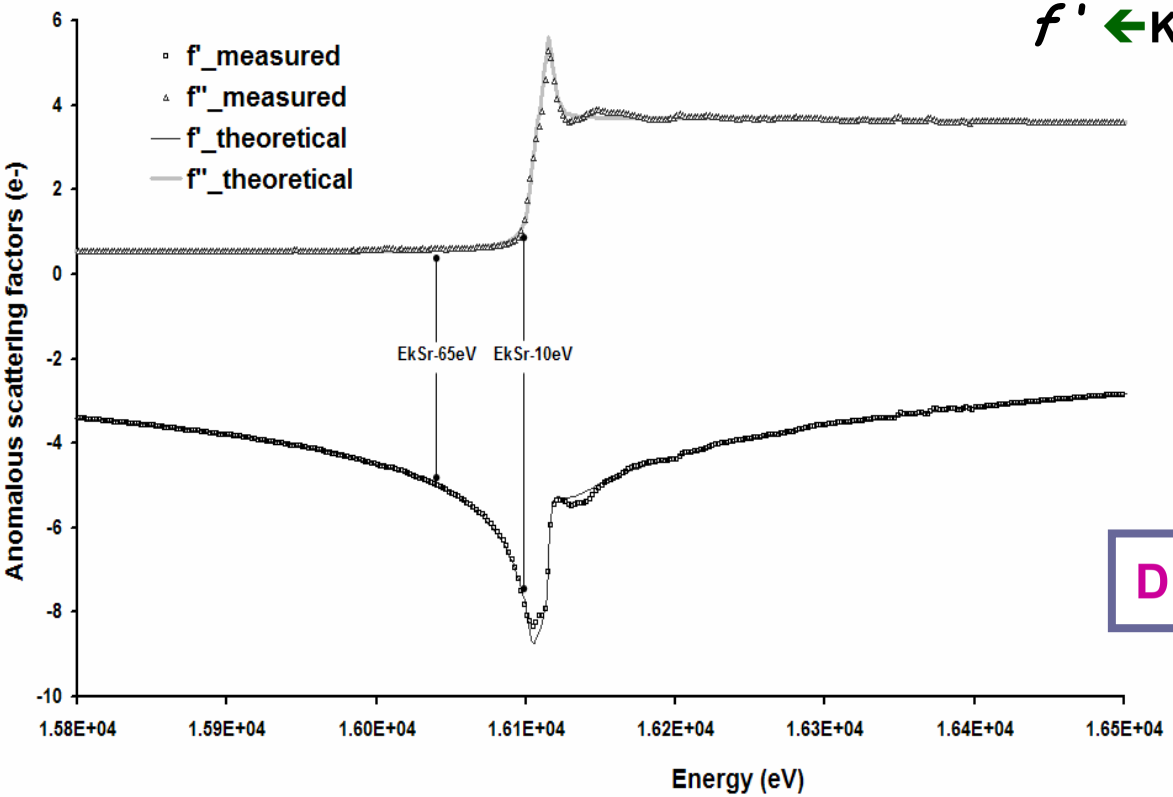


Low 2θ angle part of the observed and refined diffraction patterns of LaNi3.55Mn0.4Al0.3Co0.75 for the same wavelengths or energies

Joubert, J.M.; Cerny, R.; Latroche, M.; Percheron-Gueguan, A.; Yvon. K. *J. Appl. Cryst*. 1998, *31*, 327

Accurate determination of $f'(E), f''(E)$ on the sample itself

Sr K absorption edge



f''(E) proportional to E.μ(E)

f' ← **Kramers-Kronig relation** → f''

$$f'(\omega_0) = \frac{2}{\pi} P\int_0^\infty \frac{\omega f''(\omega_0)}{\omega^2 - \omega_0^2} d\omega$$

$$f''(\omega_0) = \frac{2}{\pi} P\int_0^\infty \frac{f'(\omega_0)}{\omega^2 - \omega_0^2} d\omega$$

Direct measurement of f''

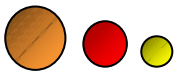
Softwares: **DiffKK** (Cross, J.O. (1998) Phys. Rev. **B58**, 11215).

CHOOCH (Evans, G. & Pettifer, R. (2001) J. Appl. Cryst. **34**, 82).

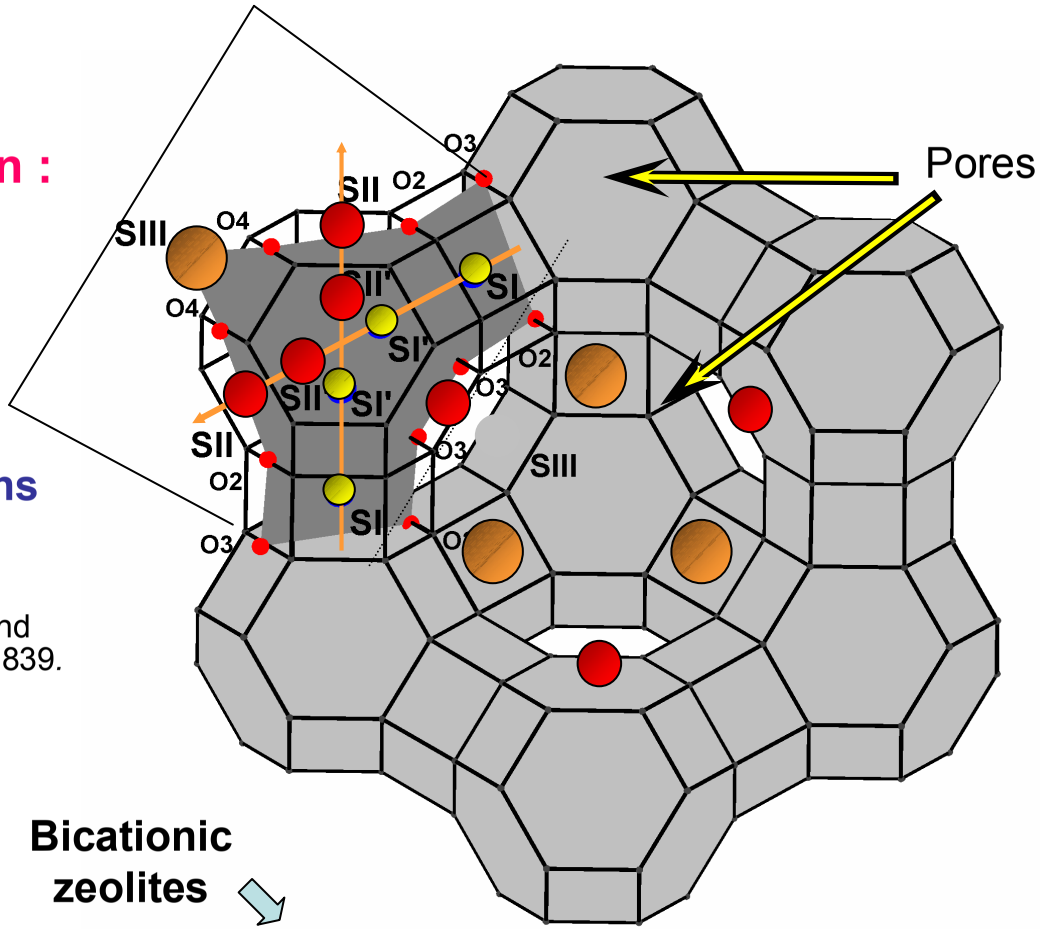
+ Introduction of a correction for white line

Adsorption selectivity in zeolites driven by cation distributions

Cation distributions determination :



SIII, SII, SI



Strong evolution of cation distributions with measurements conditions

Example in dehydration process:

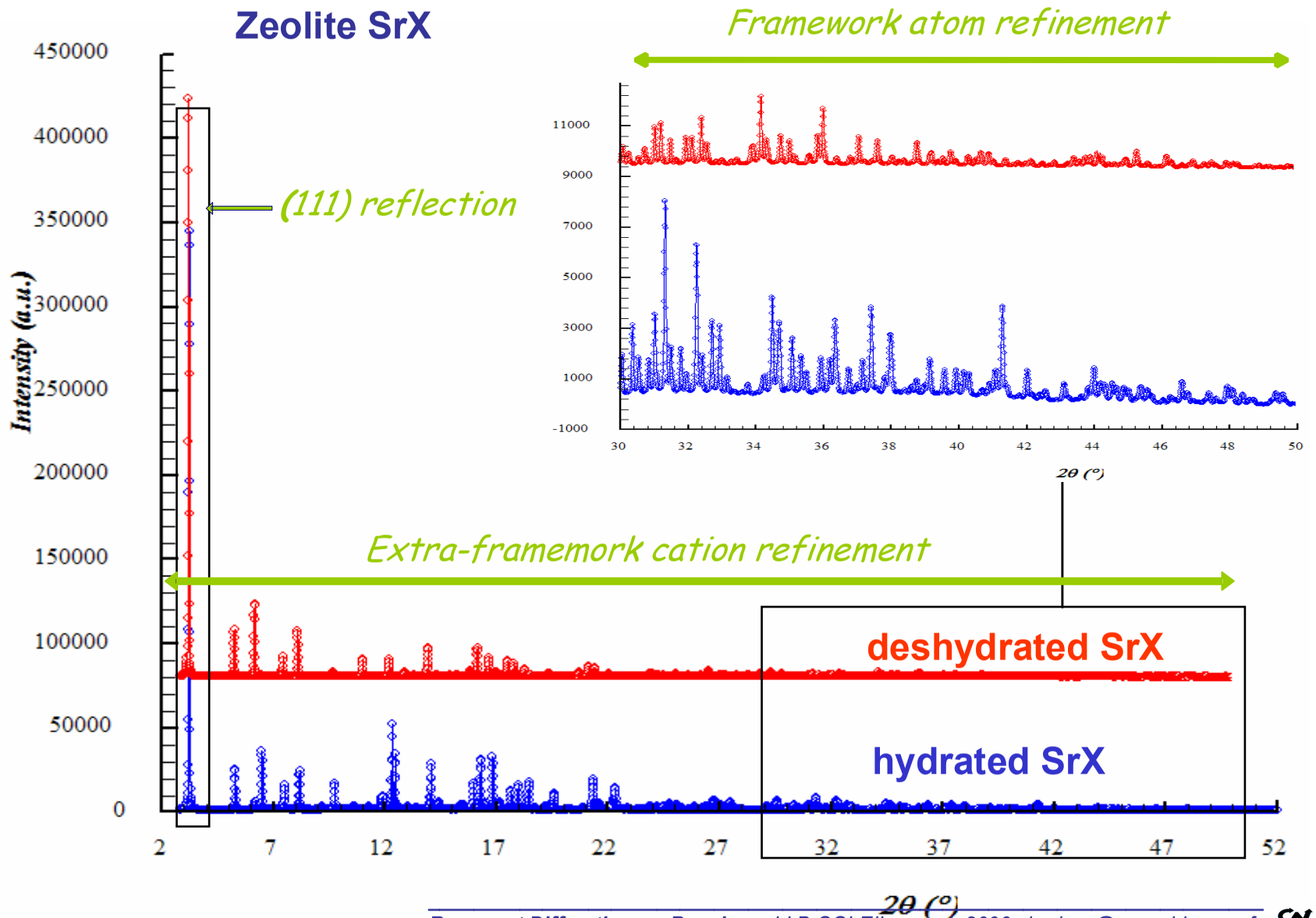
Norby, P., Poshni, F.I., Gualtieri, A.F., Hanson, J.C. and C.P. Grey (1998) *J. Phys. Chem.* **B102**, 839.

Monocationic zeolites ↘ **Conventional diffraction**

Bicationic zeolites ↘ **Resonant or anomalous diffraction**

performed with *in situ* measurements

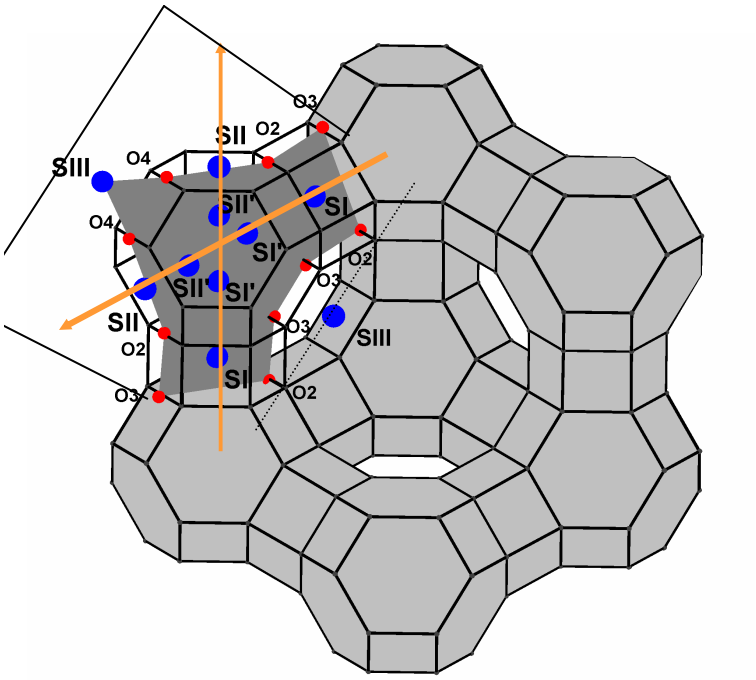
XRD powder patterns of hydrated & deshydrated zeolites



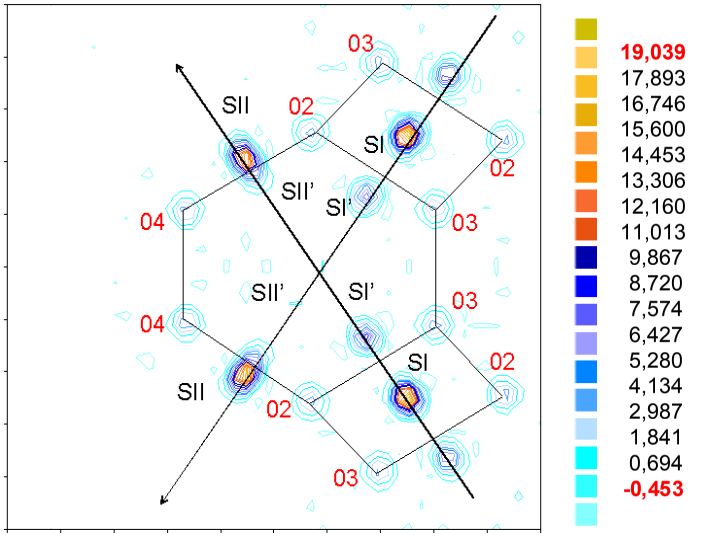
Cation distribution visualized in *direct space*

Electron density (ρ) in a chanel plane of SrX-D

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}} F(\mathbf{H})\exp\{-2\pi\, i(\mathbf{H}\cdot\mathbf{r})\}$$

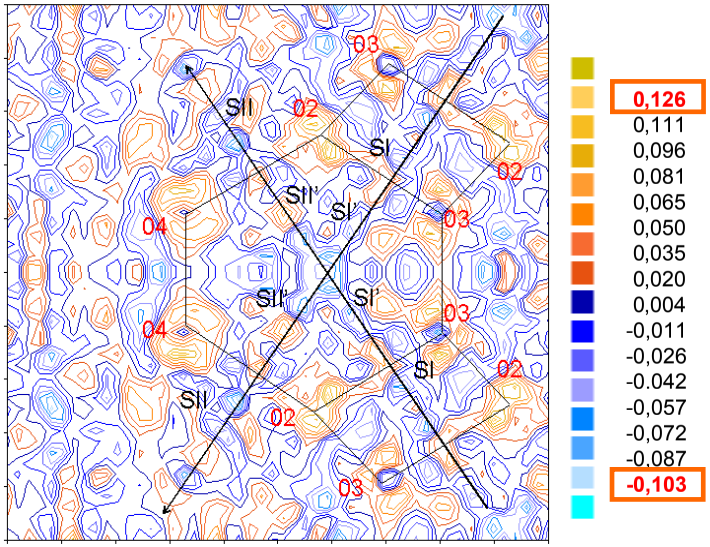


ρ_{obs}



ρ_{obs}-ρ_{calc}

(I_{diff} = **1,2 %** × I_{obs} (max))

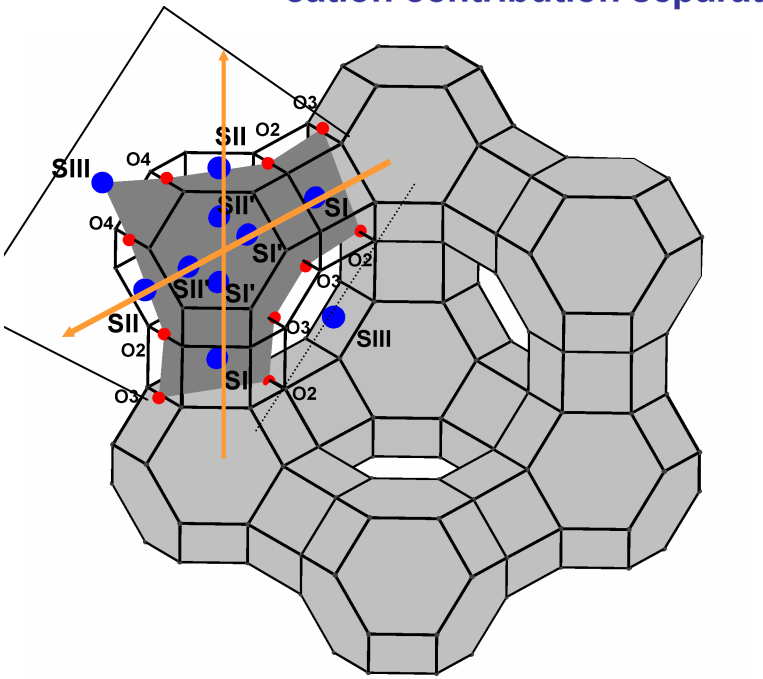


Cation distribution visualized in *direct space*

Electron density (ρ) in a chanel plane

in bicationic zeolites:

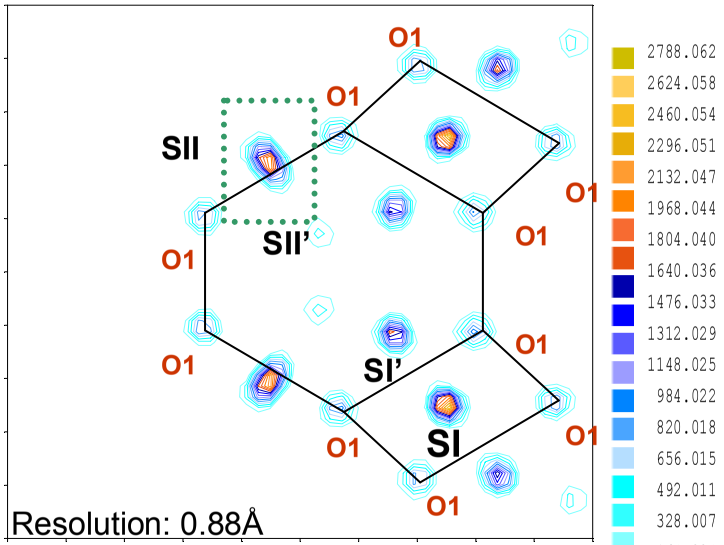
- two cations may occupy the same site,
- Improvement of resolution does not always lead to cation contribution separation



$Sr_{22}\ Ca_{18}\ X$

$r_{Sr^{2+}}$ =1.18Å

$r_{Ca^{2+}}$ =1.00Å



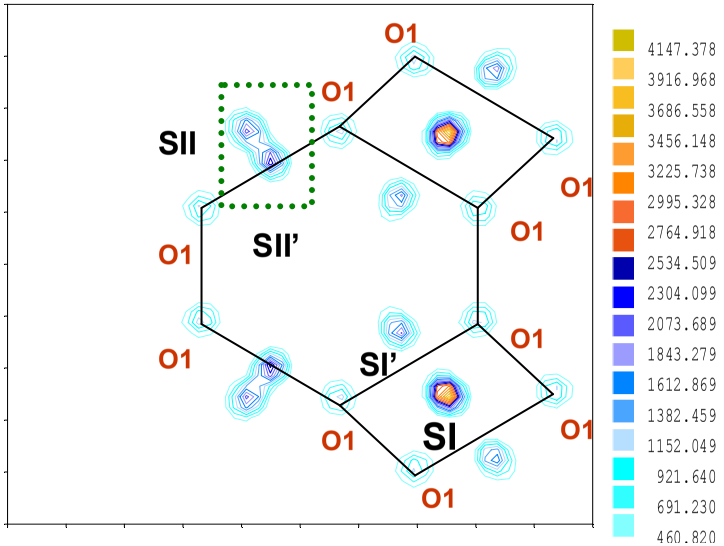
$Sr_{25}\ Rb_{16}\ X$

$r_{Sr^{2+}}$ =1.18Å

$r_{Rb^{+}}$ =1.52Å

Rb^{+} = 36 e^{-}

Sr^{2+} = 36 e^{-}



Need of a selective probe : Resonant Diffraction

Energy selection & determination of *f'(E), f''(E)* on powder

f' **and** ***f''*** **variations close to absorption edge $E_{K(Sr)}$ for cation Sr in SrRbX**

$Rb^+ = 36e^-$, $Sr^{2+} = 36e^-$

⇨ sensitivity to chemical state and environment

↳ **measurement of the absorption on the sample itself**

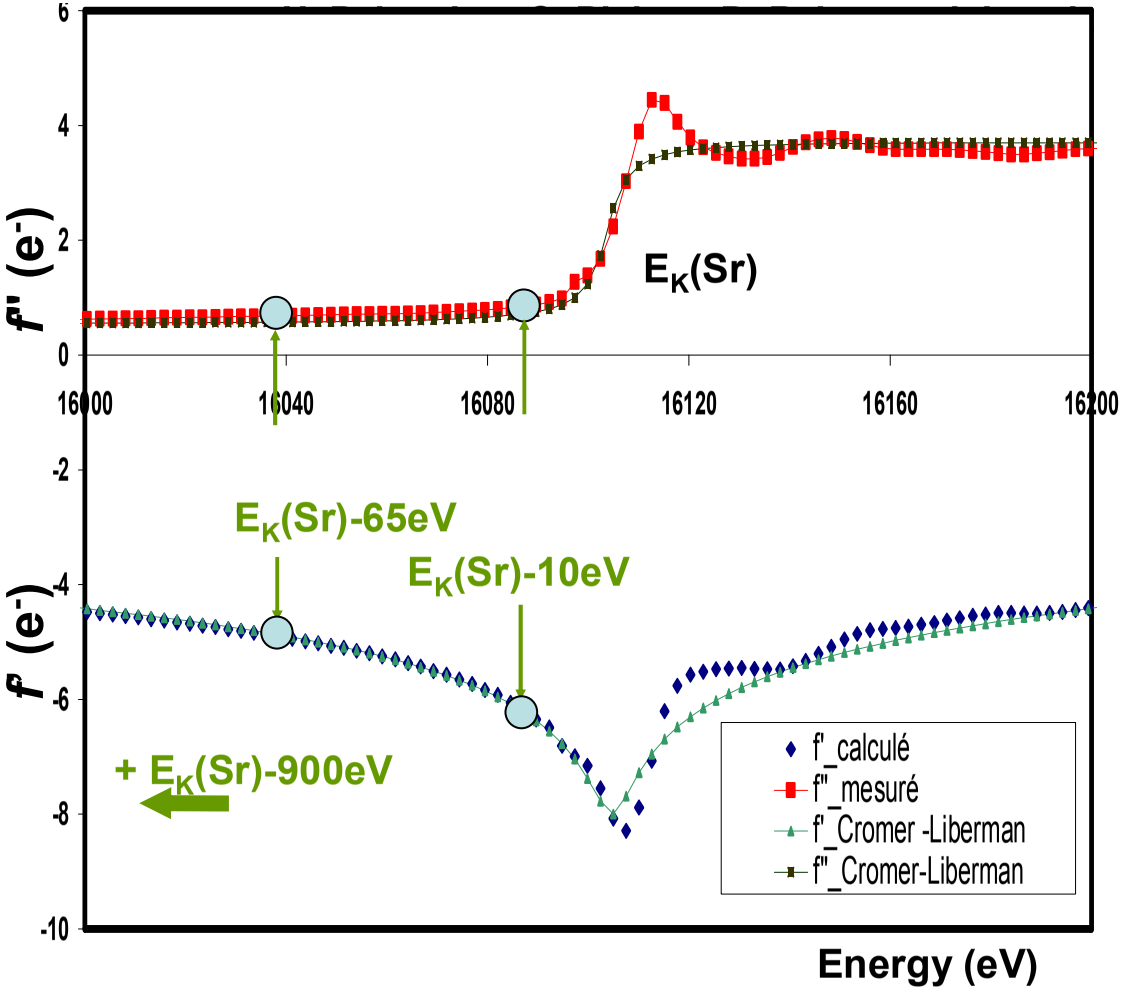
↳ **determine f' by using Kramers Kronig relation**

⇨ optimization of the energies

E_K(Sr)-900eV **f' = - 2.55 e^-**

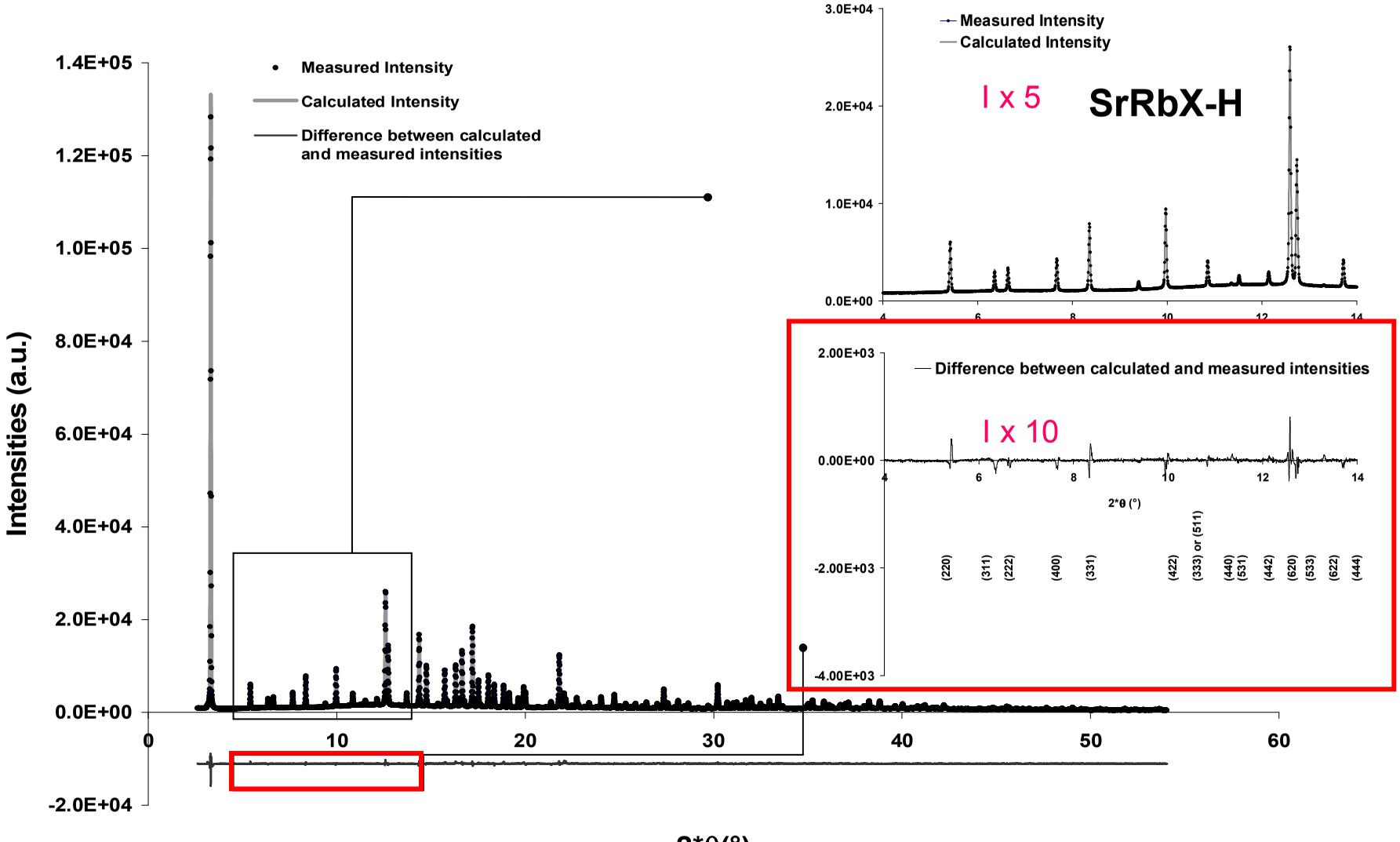
E_K(Sr)-65eV **f' = - 4.94 e^-**

E_K(Sr)-10eV **f' = - 6.79 e^-**

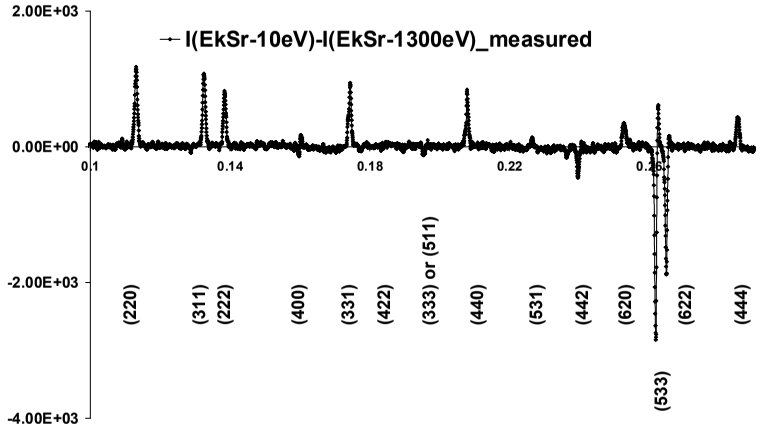


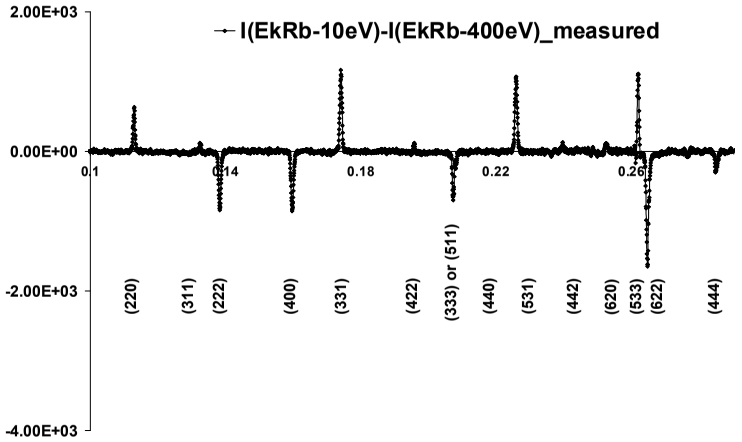
Cation distribution visualized in *reciprocal space*

Far from the edges, good fit but no chemical discrimination between Sr^{2+} and Rb^{+}



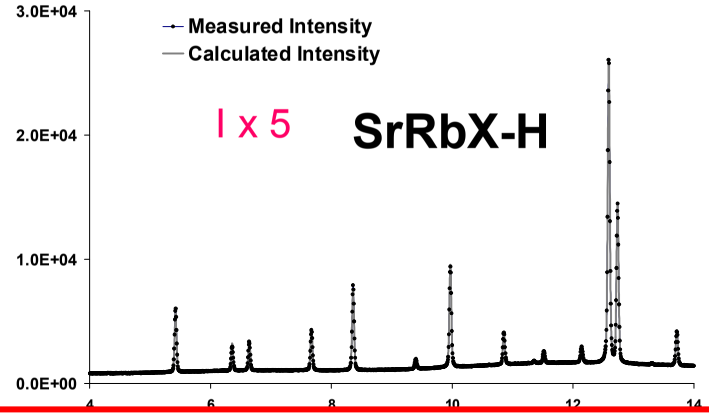
Visualization in *reciprocal space* of resonant effects near the edge *via* "anomalous differential pattern"

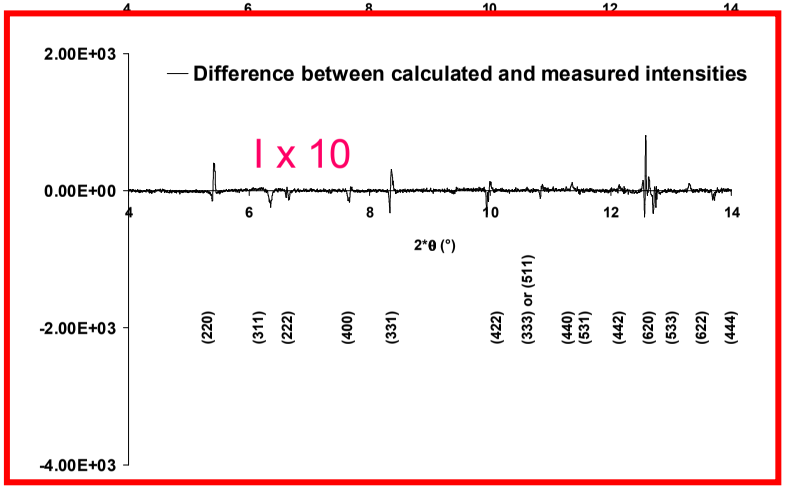




Sr K edge

Rb K edge





⇨ **Significant anomalous signal even in powders**

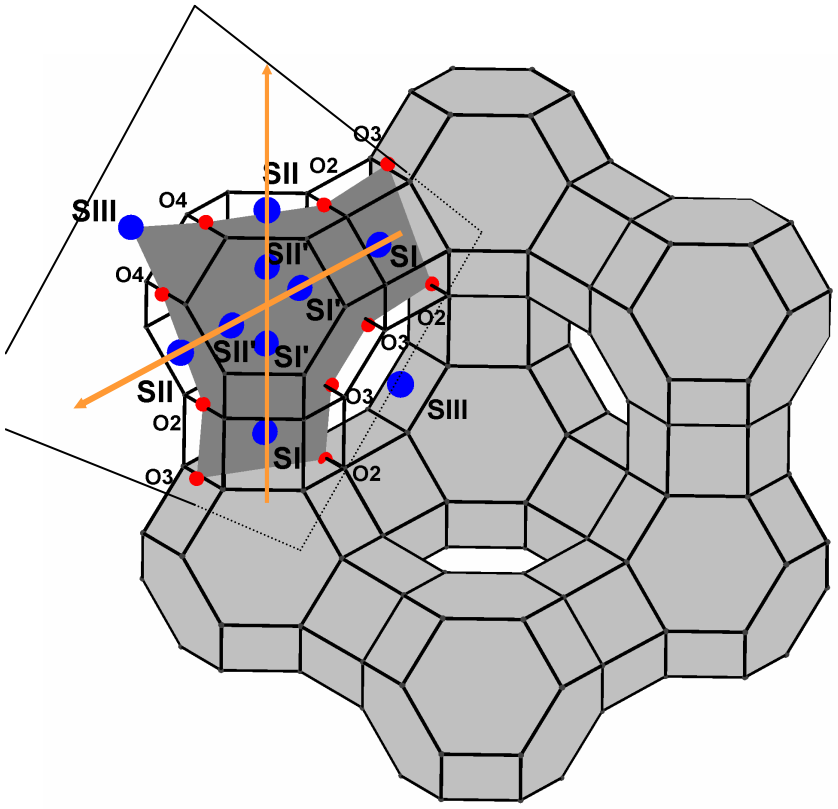
⇨ **Close to the edges: cation discrimination**

Cation distribution visualized in *direct space*

Localisation of cations with close Z

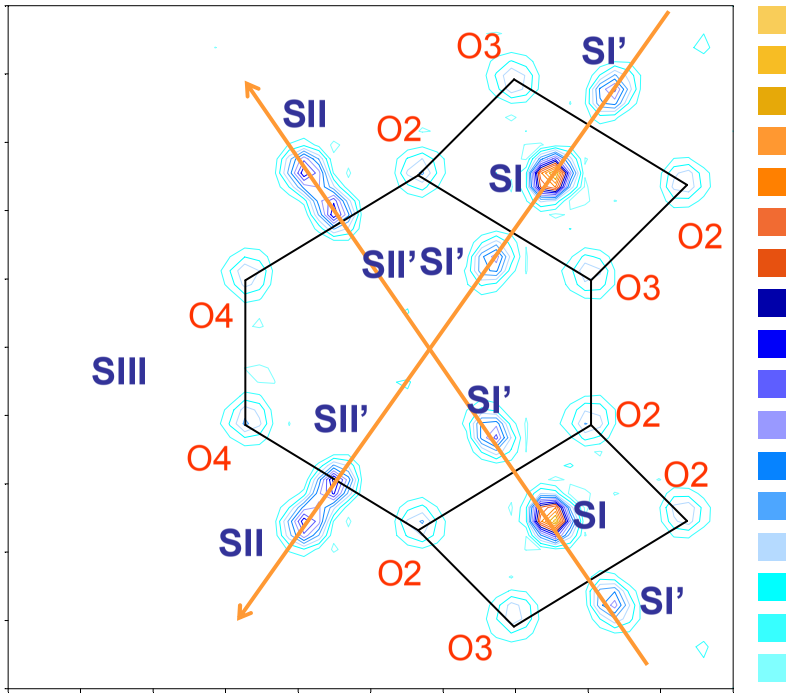
Rb^{+} = 36e^{-}, Sr^{2+} = 36e^{-}

X or Y zeolite structure



Electron density (ρ) maps calculated by Fourier transform

$$\rho(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{H}} F(\mathbf{H})\exp\{-2\pi\, i(\mathbf{H}\cdot\mathbf{r})\}$$



Sr_{25} Rb_{16} X

H. Palancher et al. Angew. Chem. Int. Ed. (2005) 44, 11, 1725.

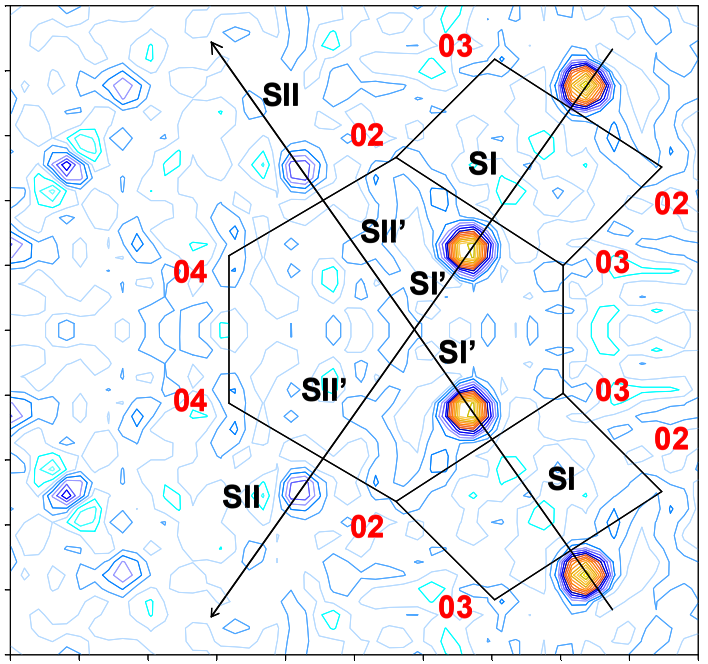
Visualization in *direct space* of resonant effects near the edge *via* "dispersive difference maps"

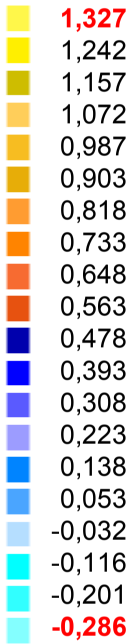
in situ characterisation of cationic distributions in bicationic SrRbX-H zeolite

Difference between anomalous data and calculated one with $\Delta f'$ = 0

$Z(Sr^{2+}) = Z(Rb^{1+}) = 36e^-$

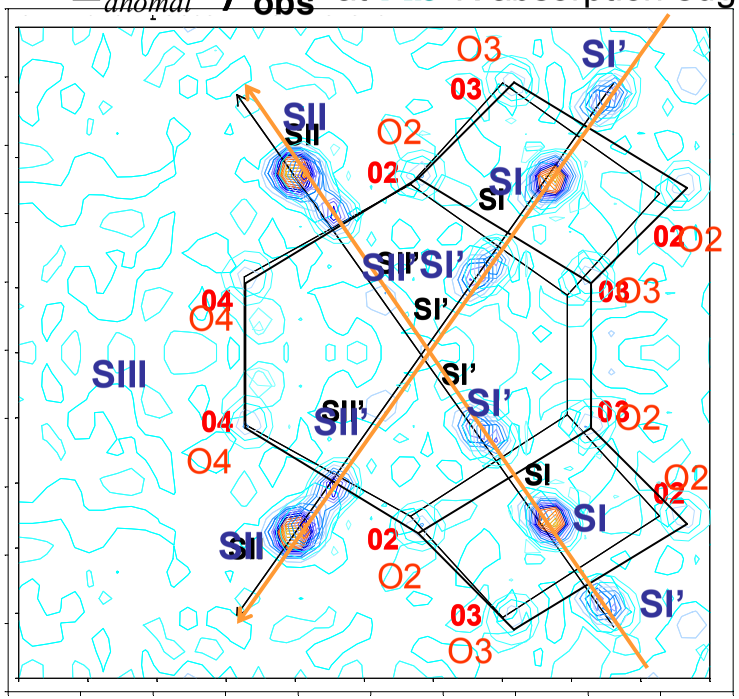
Δ^{ffE-nE}_{anomal} ρ_{obs} at Sr K absorption edge

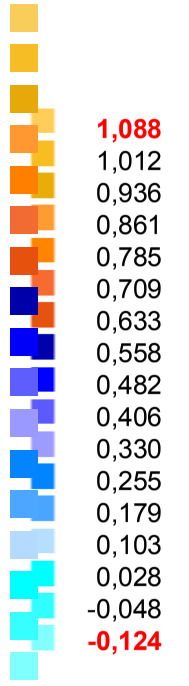




Sr^{2+} cation location and quantification

Δ^{ffE-nE}_{anomal} ρ_{obs} at Rb K absorption edge





Rb^{+} cation location and quantification

$Sr_{25}Rb_{16}X$

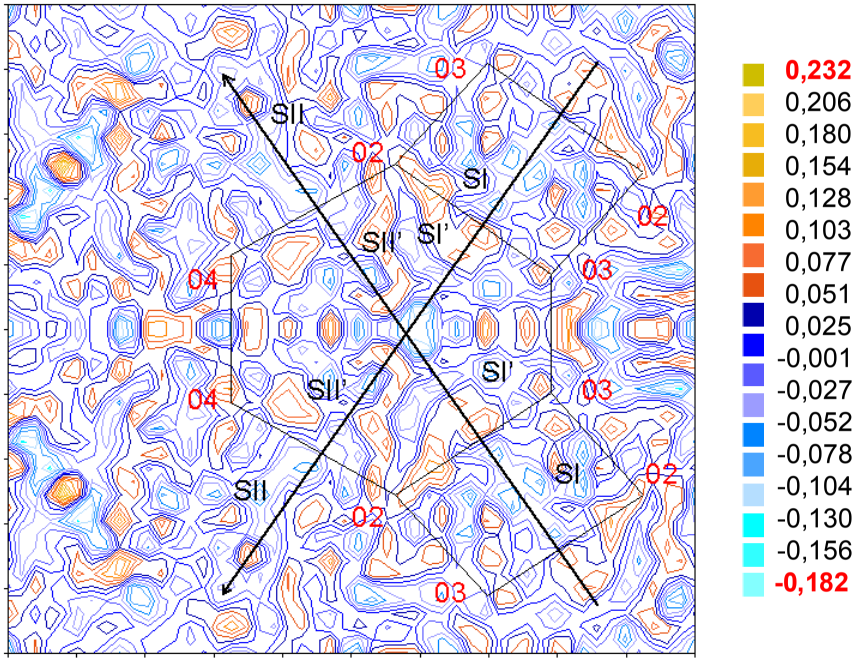
H. Palancher et al. Angew. Chem. Int. Ed. (2005) 44, 11, 1725.

Visualization in *direct space* of resonant effects near the edge *via* "dispersive difference maps"

in situ **characterisation of cationic distributions in bicationic SrRbX-H zeolite**

Difference between anomalous data and calculated one with true $\Delta f'$

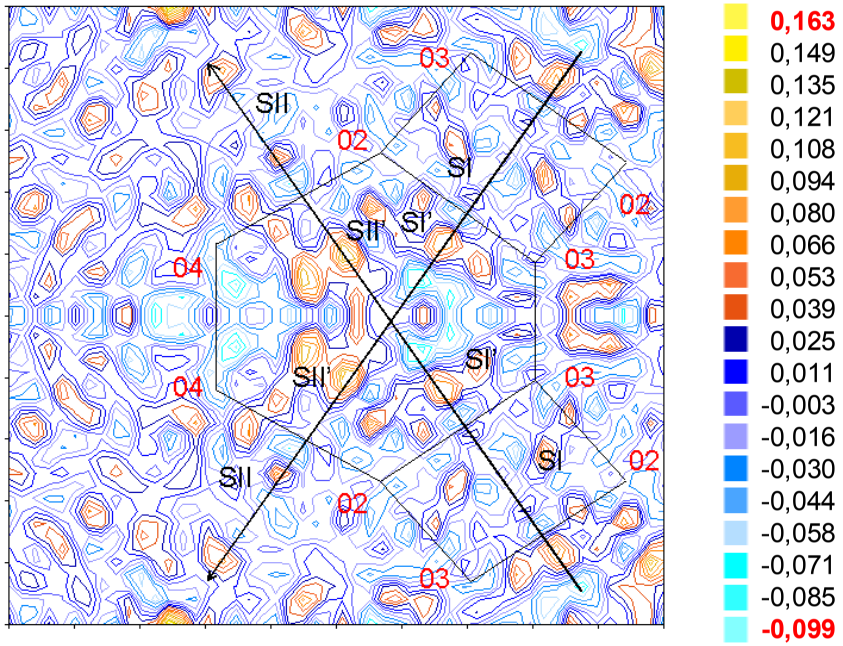
$\Delta^{ffE-nE}_{anomal}(\rho_{obs} - \rho_{calc})$ $\Delta f'$(Sr) = **- 4,6 e-**



residual at **Sr** K absorption edge

no residuals !

$\Delta^{ffE-nE}_{anomal}(\rho_{obs} - \rho_{calc})$ $\Delta f'$(Rb) = **- 4,3 e-**



residual at **Rb** K absorption edge

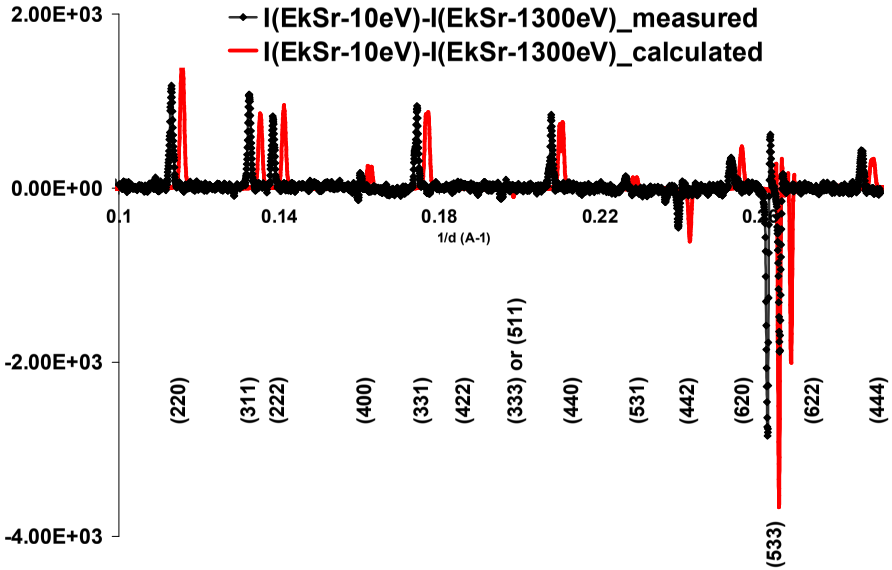
H. Palancher et al. Angew. Chem. Int. Ed. (2005) 44, 11, 1725.

Visualization in *reciprocal space* of resonant effects near the edge *via* "anomalous differential pattern"

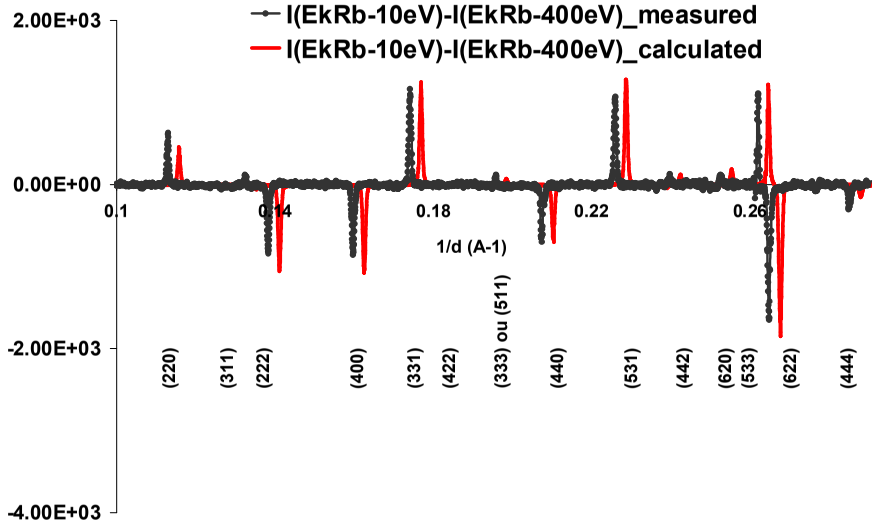
Evaluation in reciprocal space, of the quality of determined structural model

at **Sr** absorption edge

SrRbX-H



at **Rb** absorption edge

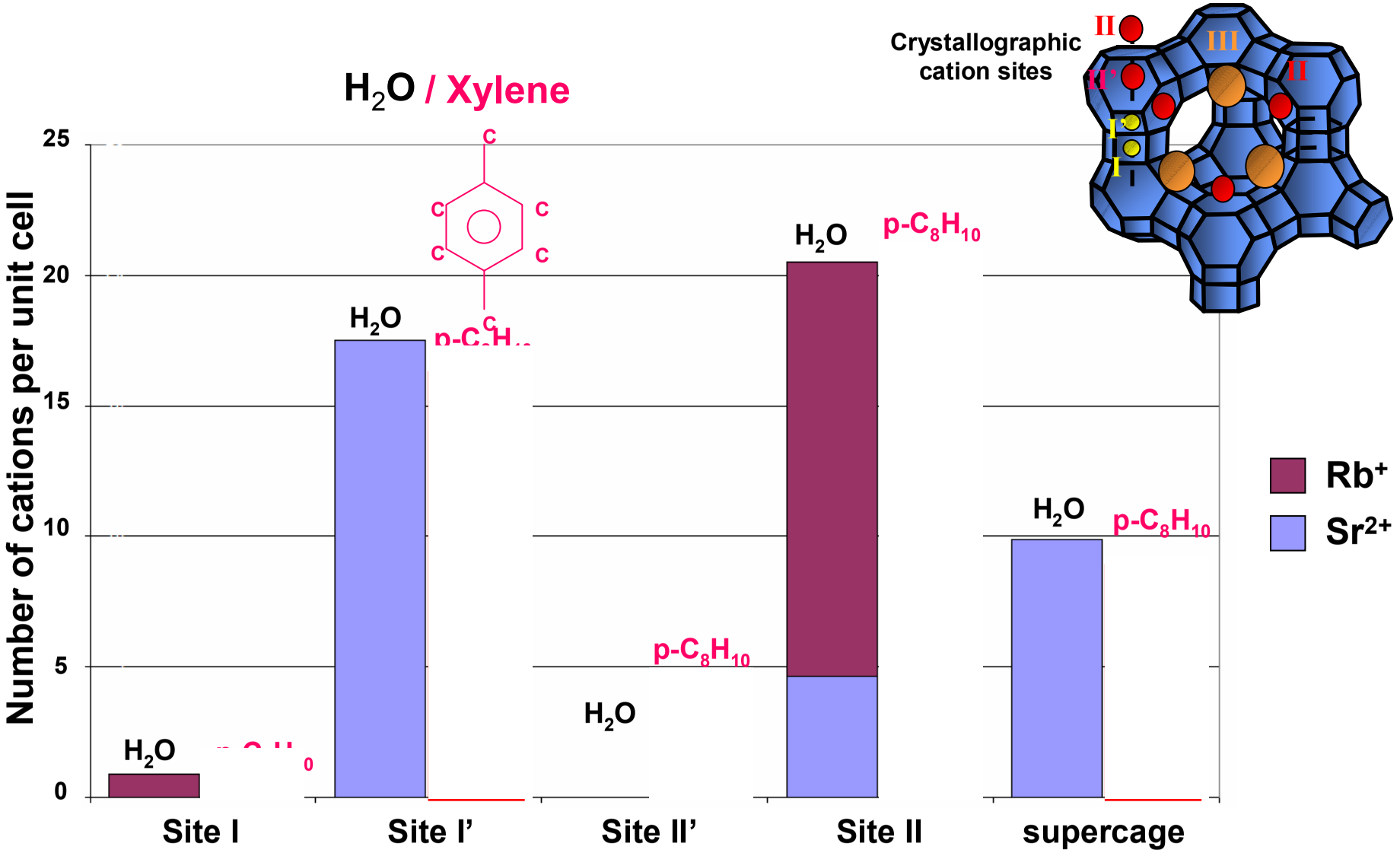


➡ Agreement in intensity between calculated and measured resonant differential patterns

➡ Implementation of this calculation in the FullProf software

H. Palancher et al. Angew. Chem. Int. Ed. (2005) 44, 11, 1725.

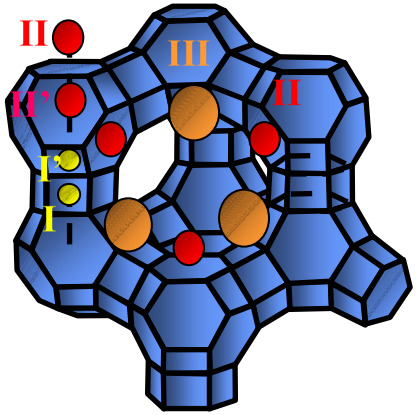
Importance of contrast measurements for direct atom localization for *in-situ* studies



Efficiency of Resonant Contrast Diffraction for atom localization

Chemical composition of SrRbX:

		Resonant diffraction on dehydrated SrRbX
Cation amount (per unit cell)	Sr^{2+}	**29.5 ± 2.5**
	Rb^{1+}	**13.8 ± 0.9**
	Na^{1+}	4



Electric charges	Negative charges of the framework (elementary analysis)	Positive charges (Anomalous diffraction)
	78.7	**80.8**

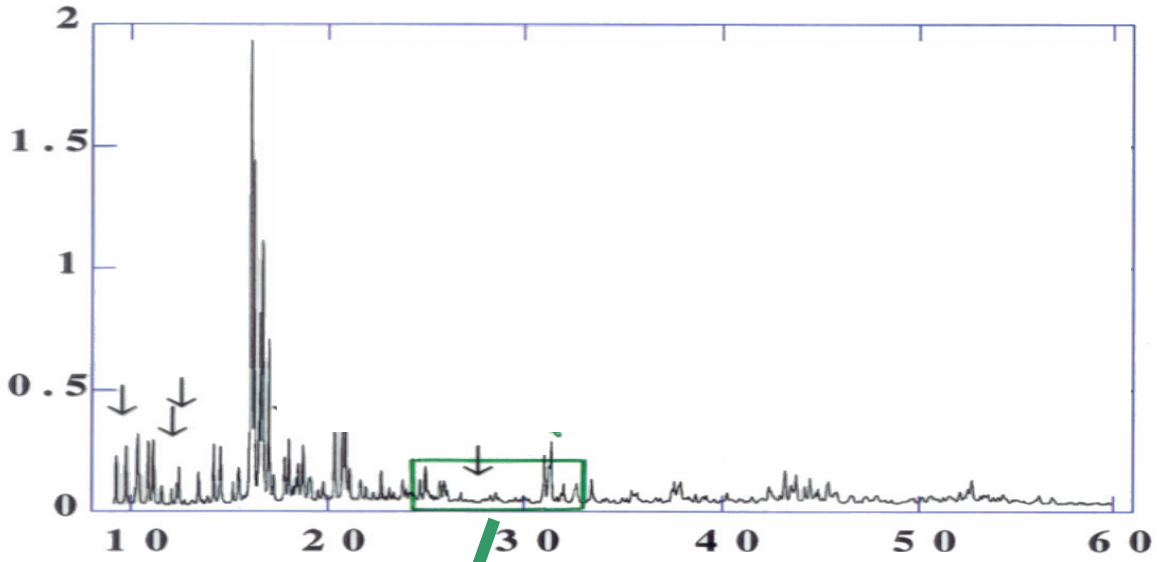
Resonant Contrast Diffraction on powders :
good efficiency via the use of
- "anomalous differential patterns",
- "dispersive difference maps"

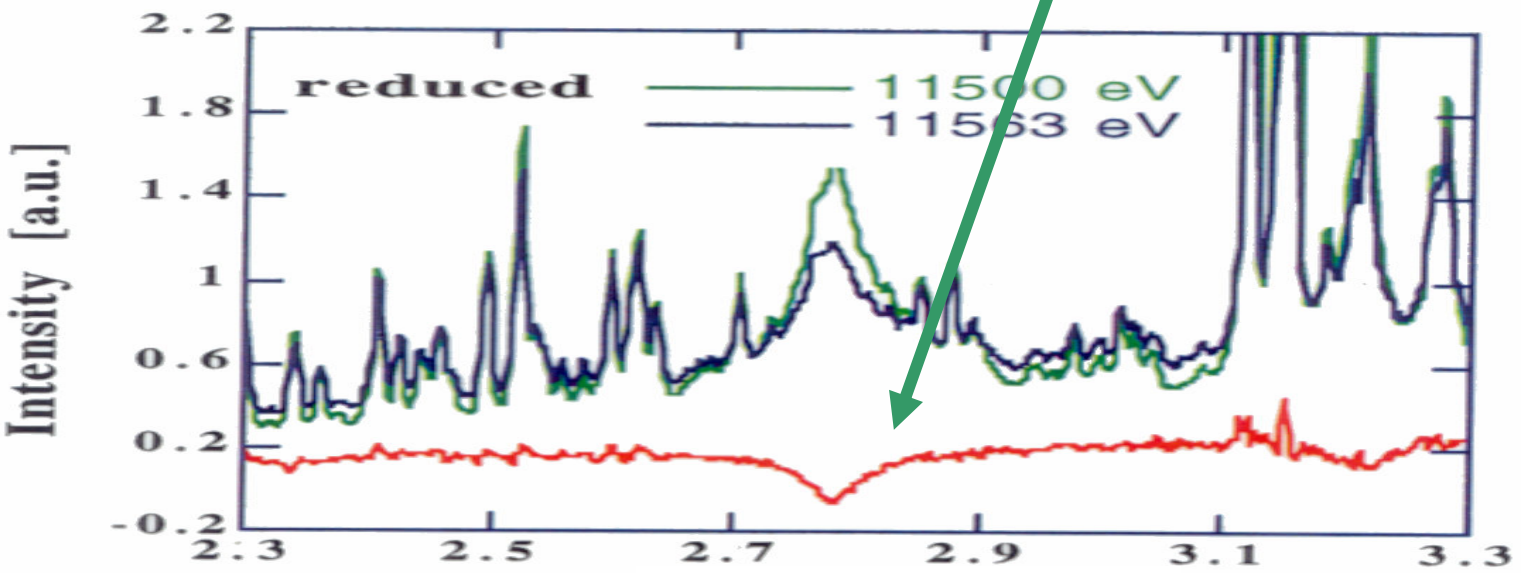
Study of mixed phases with different crystallinity,

ZMS-5 zeolites (3 wt% Pt)

- Differential anomalous pattern

- ⇨ differentiate interzeolite and intrazeolite particles
- ⇨ localization of fcc metallic Pt





Resonant Diffraction on Powders

we can combine diffraction and spectroscopy information

- **Selective Site Spectroscopy : DAFS & DANES**
- **Anisotropy of Resonant Scattering**

we can vary the contribution of one specific atom on diffracted intensity

- **Structure Factor Phase Solution : MAD**
- **Element Selective Diffraction : Contrast**

Resonant Diffraction is an extremely selective probe for :

- atomic local environment
- nano systems
- modulated structure
- Distortion studies
- Charge Ordering studies
- Structure determination
- Atom localization in complex systems

Thanks to H. Palancher, Ch Pichon, J. Lynch, B. Rebours, S. Bos, E. Lorenzo, J.F. Berar