

Crystal structure solution from powder diffraction data.

Erik Elkaïm

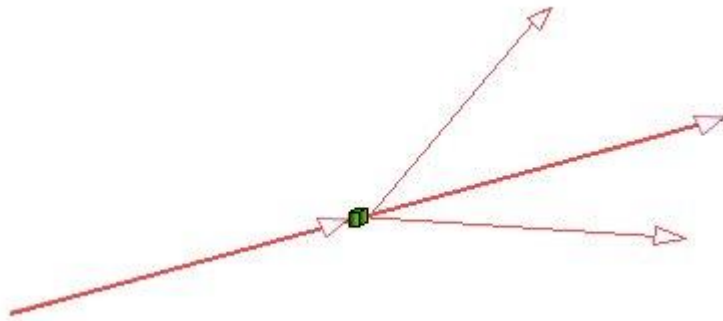
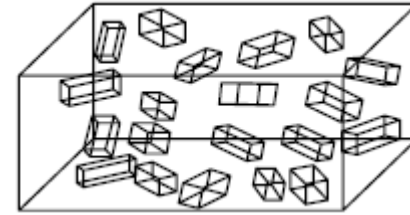


Ecole de Cristallographie CGE 4-8 Novembre 2024

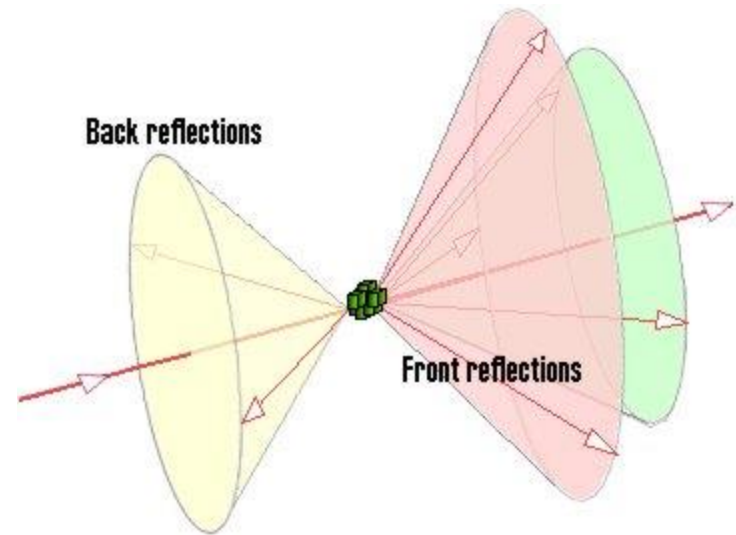
The main steps

- Diagram recording /measurement
- Indexing
- Space group determination
- Bragg intensities extraction
- Search for a structure
- Refinement
- Structure description

Powder –Single crystal diffraction

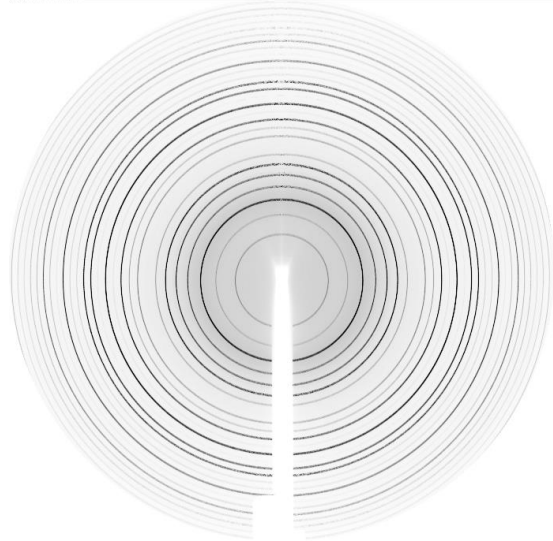


Single Crystal

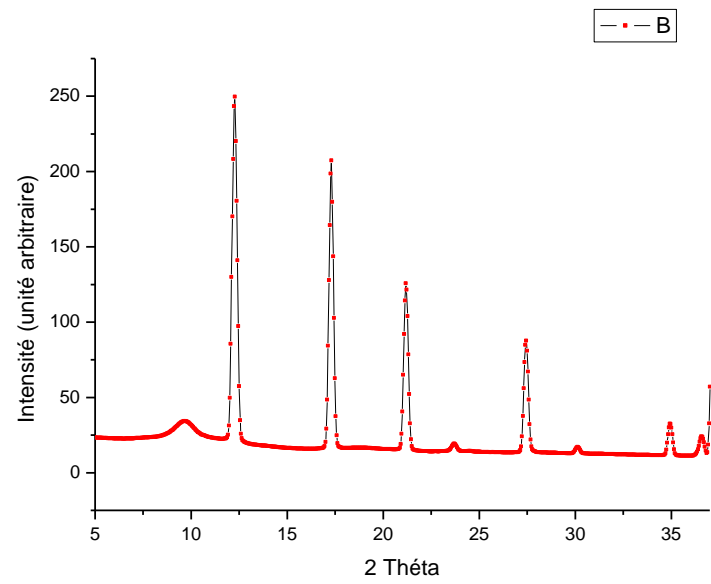


Powder

2D detector



Diagram

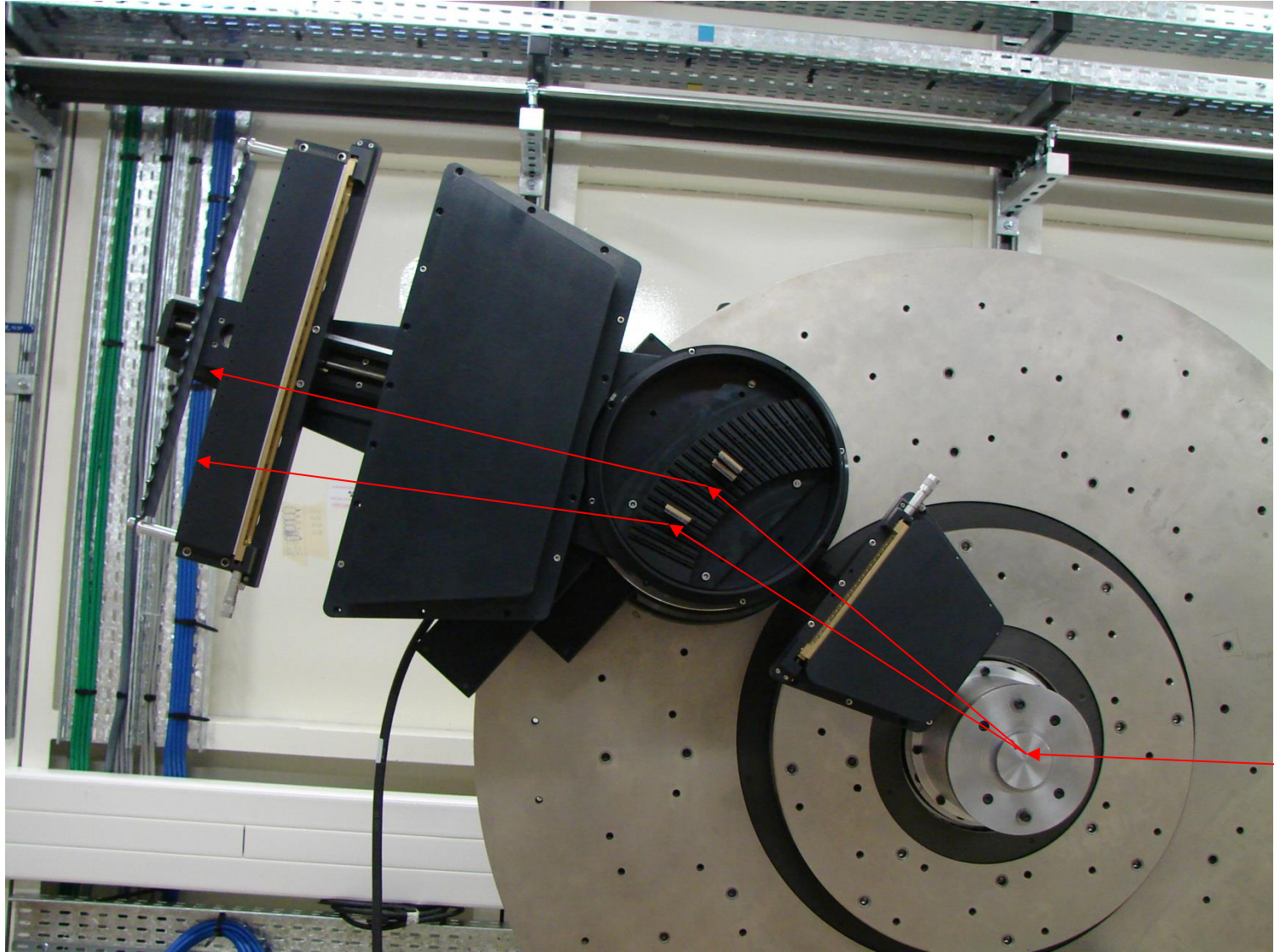


Structure solution

- If possible, single crystal diffraction: more extensive experimental data
- If no single crystal, powder is the only way...
- In recent years, electron diffraction has become an alternative for solving structures (interaction with e- about $10^6 * R_x$).
- Methods initially used are very similar to those used for single crystals.
- Better adapted methods have been developed.
- Also, measurement improvements.
 - Détectors and x-ray sources.

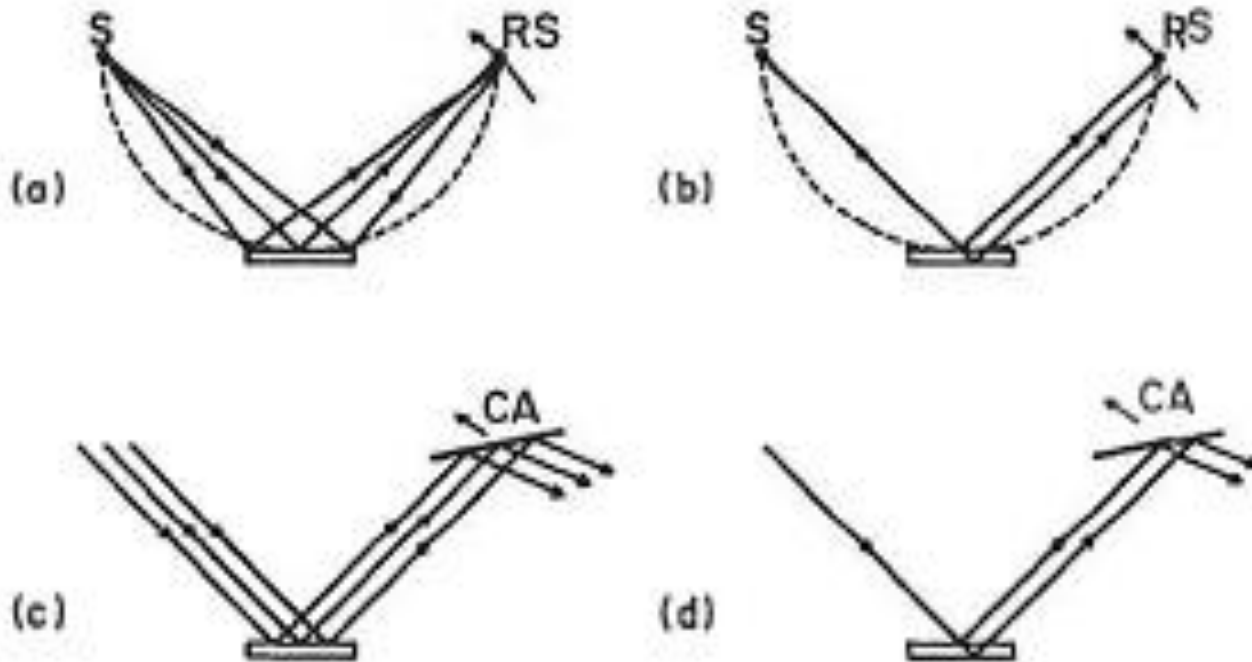
Pattern recording

- Choice of the source
 - Laboratory x-ray tubes
 - Competitive, thanks to new detectors
 - Not adapted if too many overlapping peaks or strong absorption...
 - Synchrotron
 - Well suited if narrow peaks, small amount of powder
 - Energy choice
 - « Parallel beam » setup with crystal analyser
 - Neutrons
 - Light atoms positions (hydrogens):
 - Thermal motion, site occupancy
- Data collection
 - High $\sin\theta/\lambda$
 - Better statistics at high angles
 - Fast sample spinning (capillary)
 - Reduce preferential orientation
 - More crystallites in diffracting conditions



X rays

Parallel beam setup



Advantages:

Angular analysis: less sensitive

Eliminates fluorescences → better signal/background ratio

High angular resolution

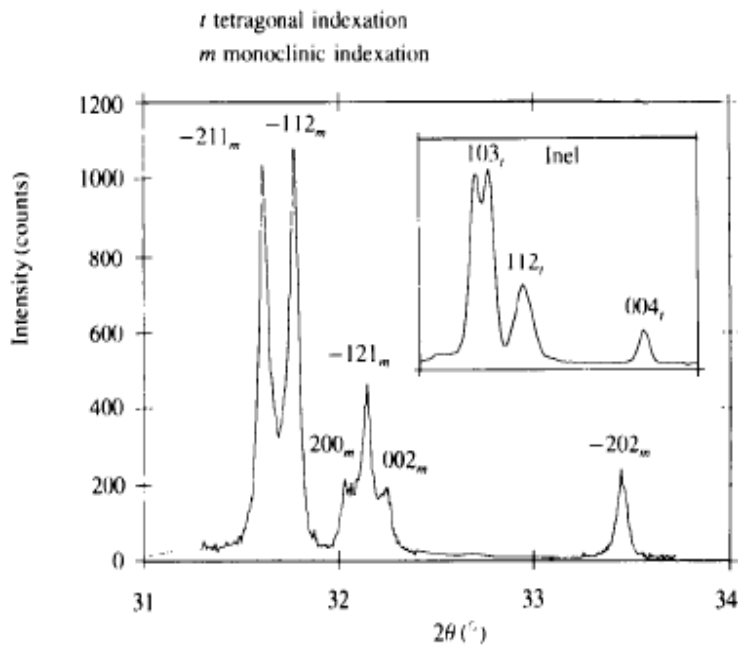


Fig. 1. Synchrotron and conventional X-ray diffraction profiles of selected peaks.

- Conventional setup vs high resolution setup with rear analyser.
- Improves the available information and facilitates indexing

Other geometries/setup

From Bob He (Fundamentals of 2D X-ray diffraction)

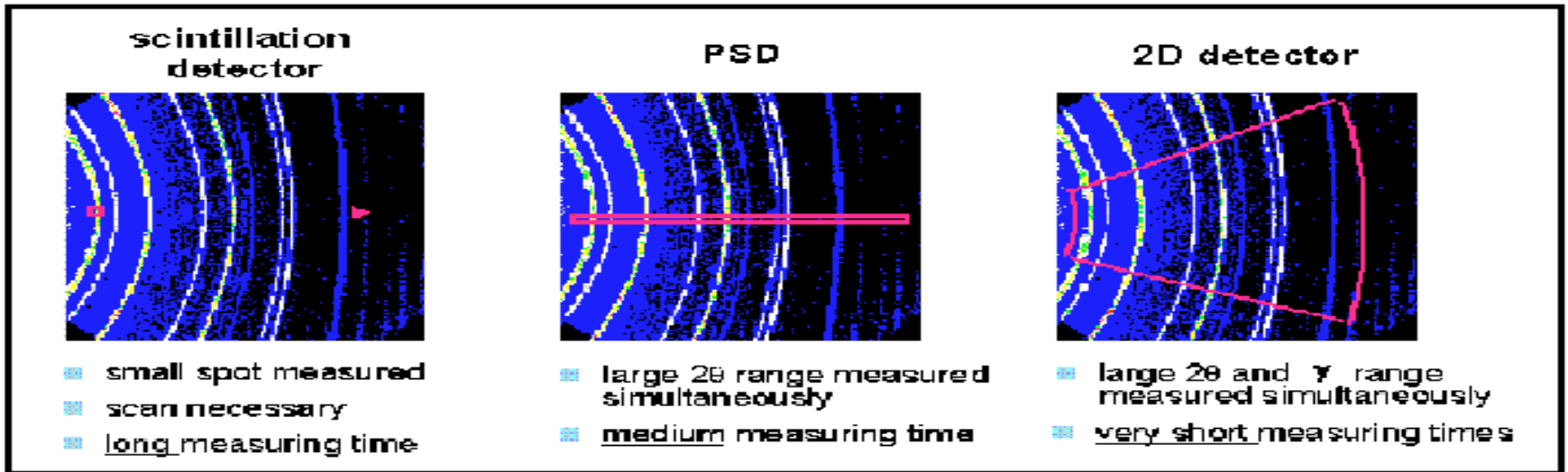
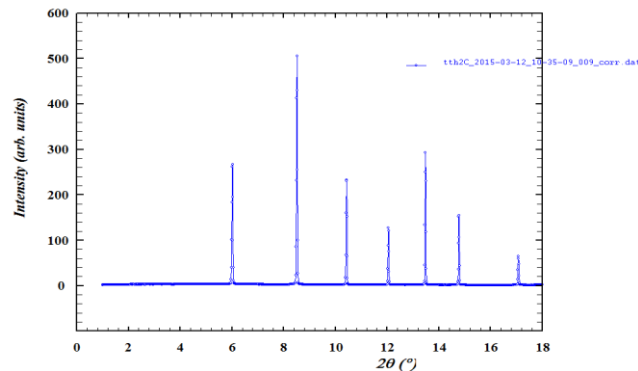


Figure 4. Comparison of diffraction pattern coverage between point (0D), linear PSD (1D), and area (2D) detectors.



Powder diffraction diagram: Intensity = $f(2\theta)$

diagram from a 2D detector scan

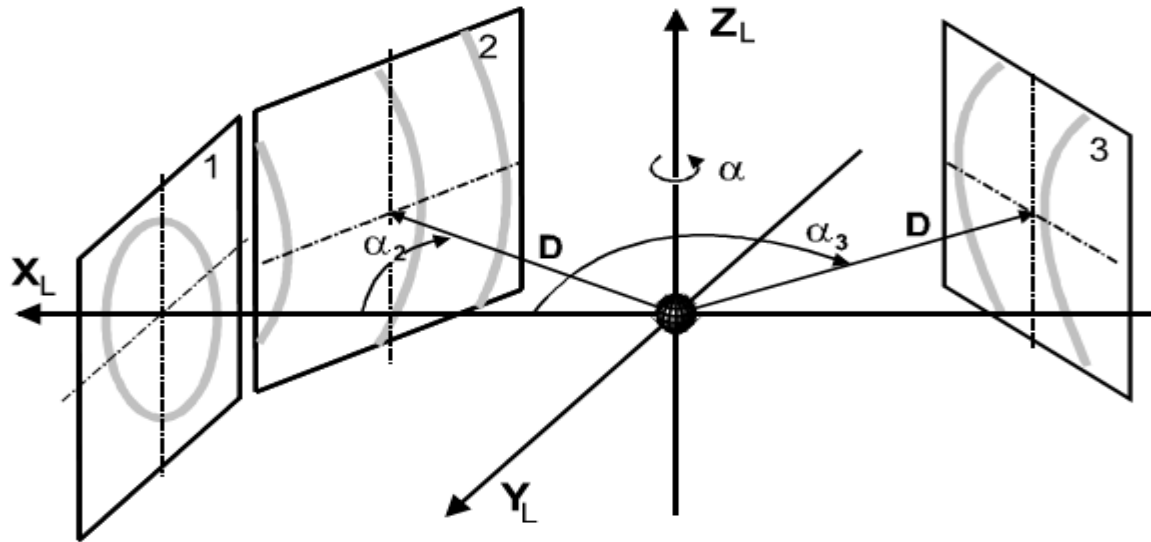
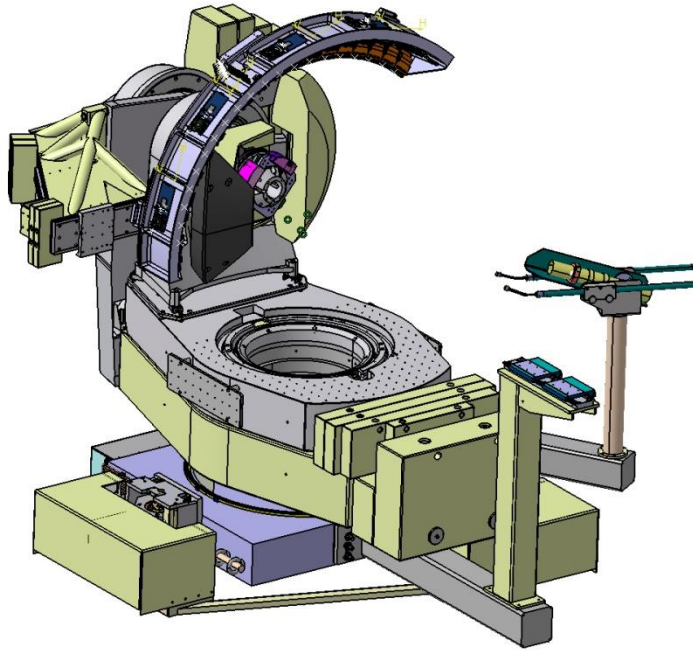
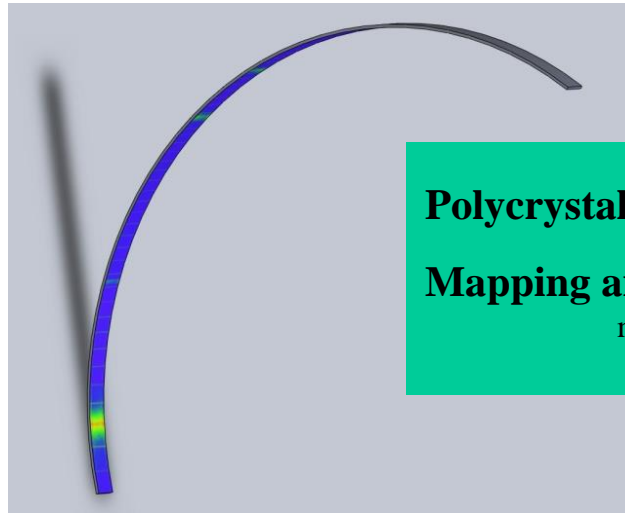


Figure 8. Detector position in the laboratory system $X_L Y_L Z_L$: D is the sample-to-detector distance; α is the swing angle of the detector.

Cirpad detector: curved and 2D



Static mode



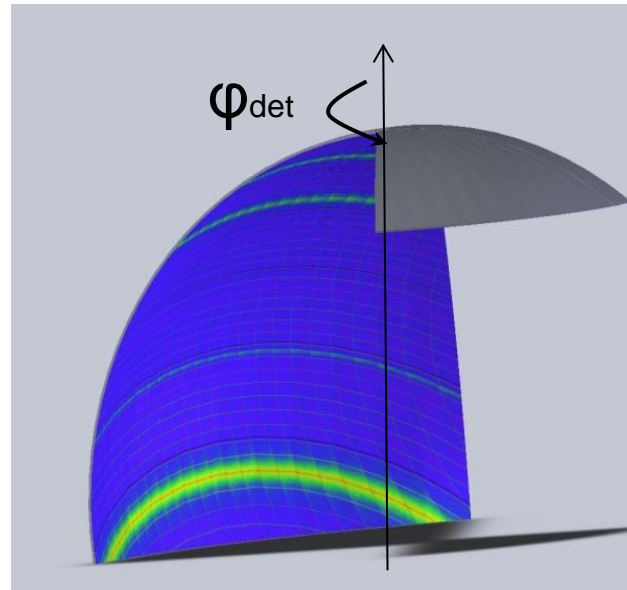
Polycrystalline & desorded materials

Mapping and kinetics

minimum acquisition time : ~ 2 msec

Readout time : ~ 1 msec

Scanning mode



Textured materials

Fast pole figures

$\sin^2(\psi)$ method

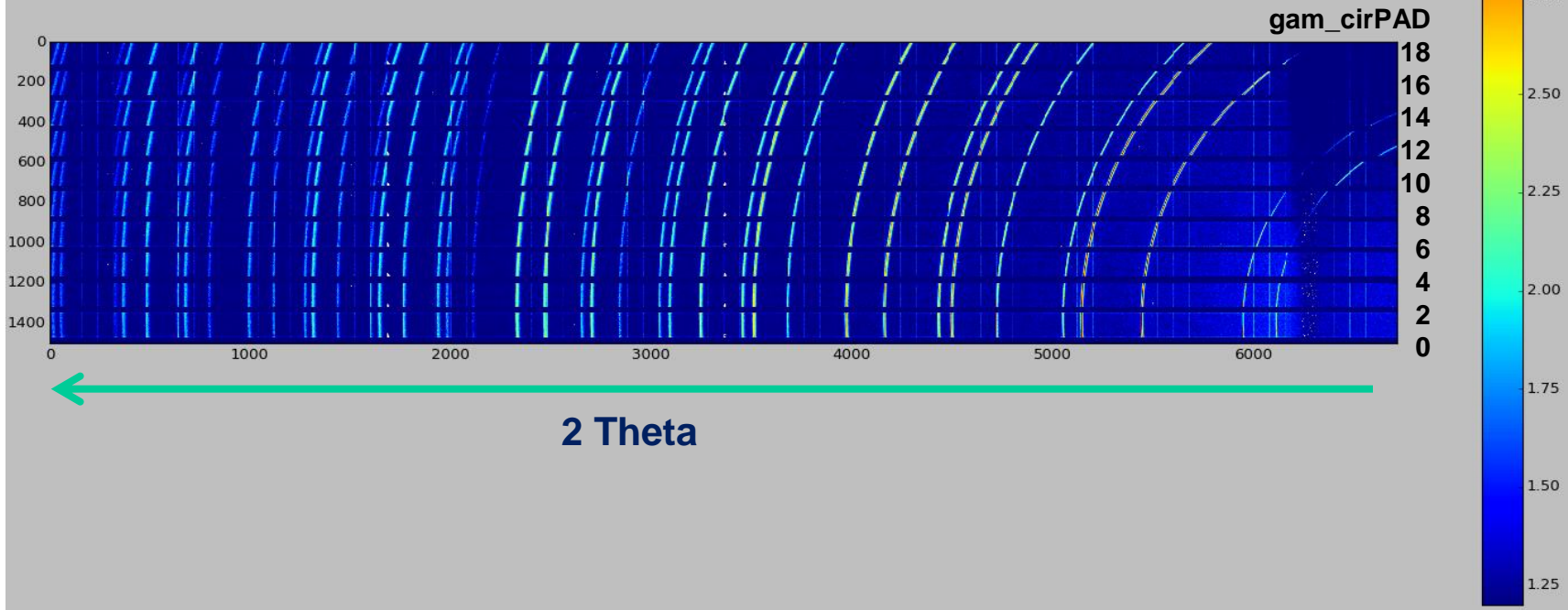


Tests at 18keV with CeO_2 powder

20 modules : 11200×120 pixels (H \times V), 1 module= 560



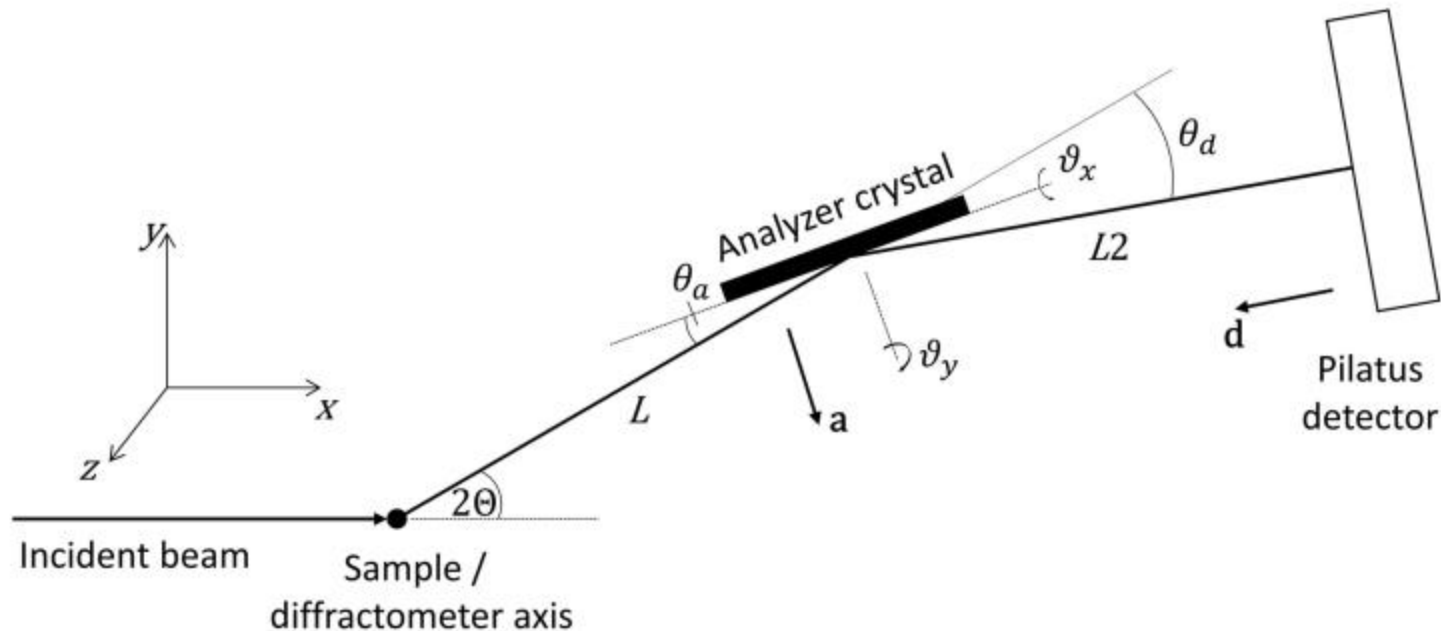
Representation des 12 premiers modules, coordonnées en pixels
(i.e. 2th max $\sim 81^\circ$, pour différentes positions en gamma (pas de 2°))



Another geometry

2D Detector 2D behind a multianalyser

C. Dejoie et A. Fitch, J. Appl. Cryst. (2021), **54**, 1088-1099
beamline ID22 (ESRF)



Diffraction rings curvature taken into account

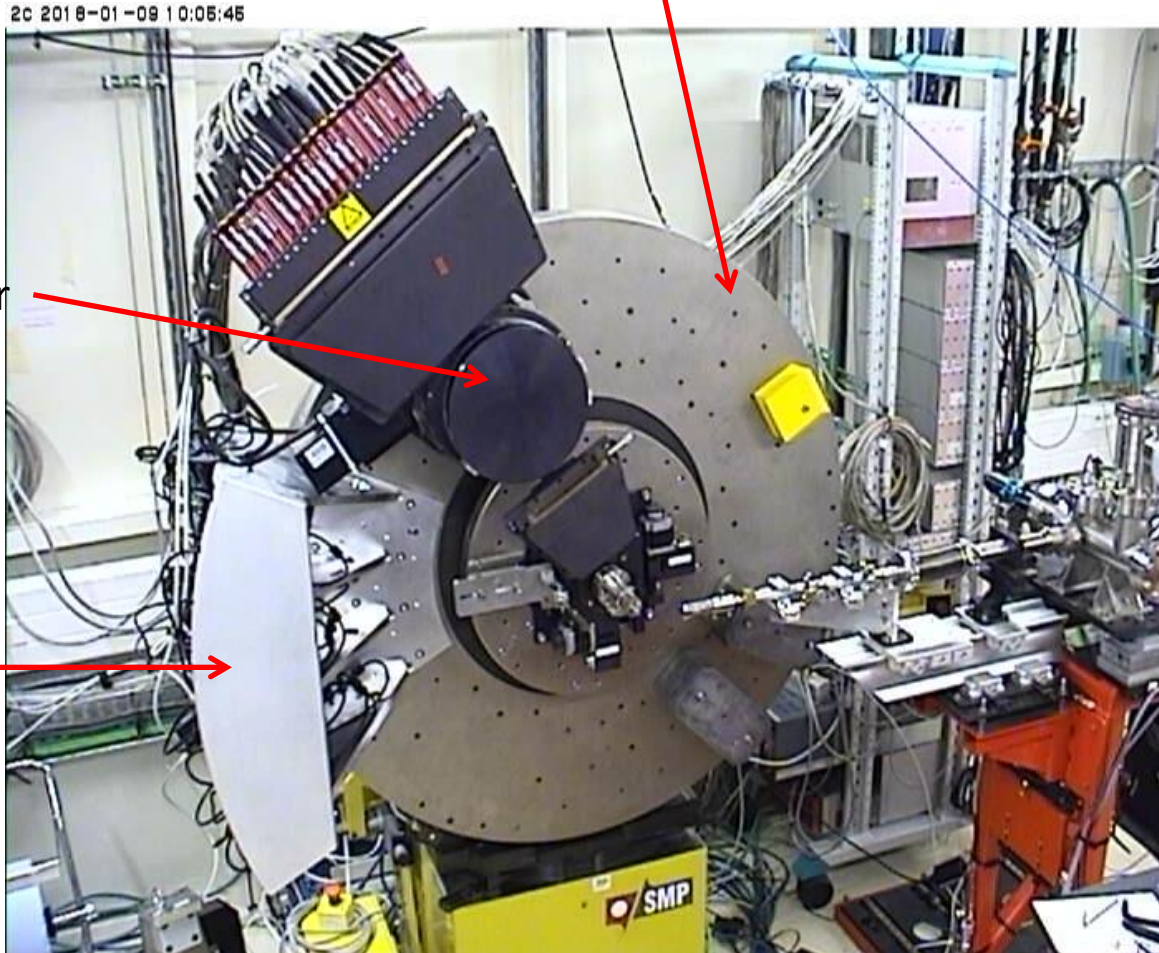
→ more efficient as the integrated ring portion increases

Beamline CRISTAL: 2 detectors mounted on the 2C diffractometer 2theta disk.

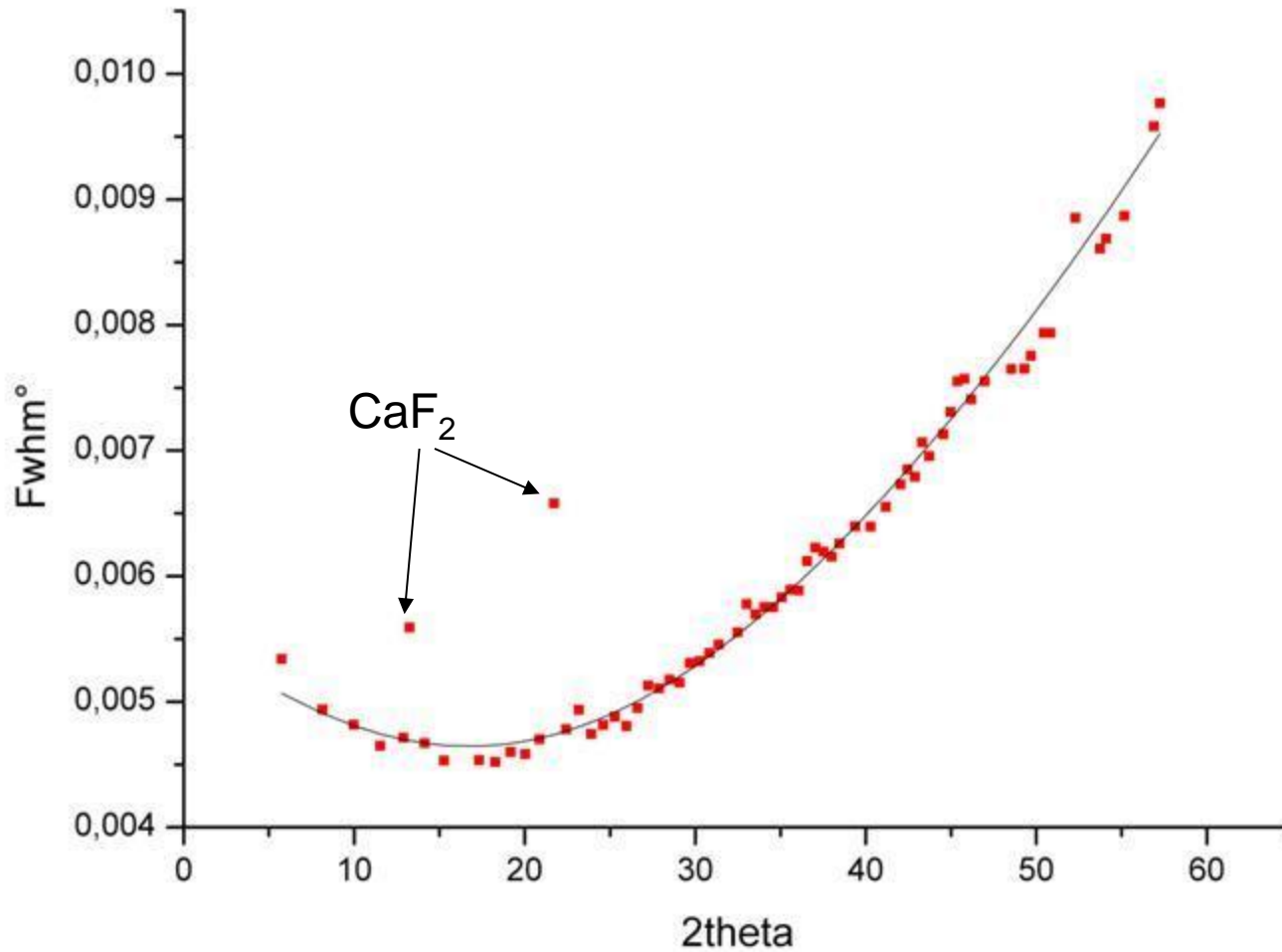
Disque 2Θ

Multianalyseur

Mythen



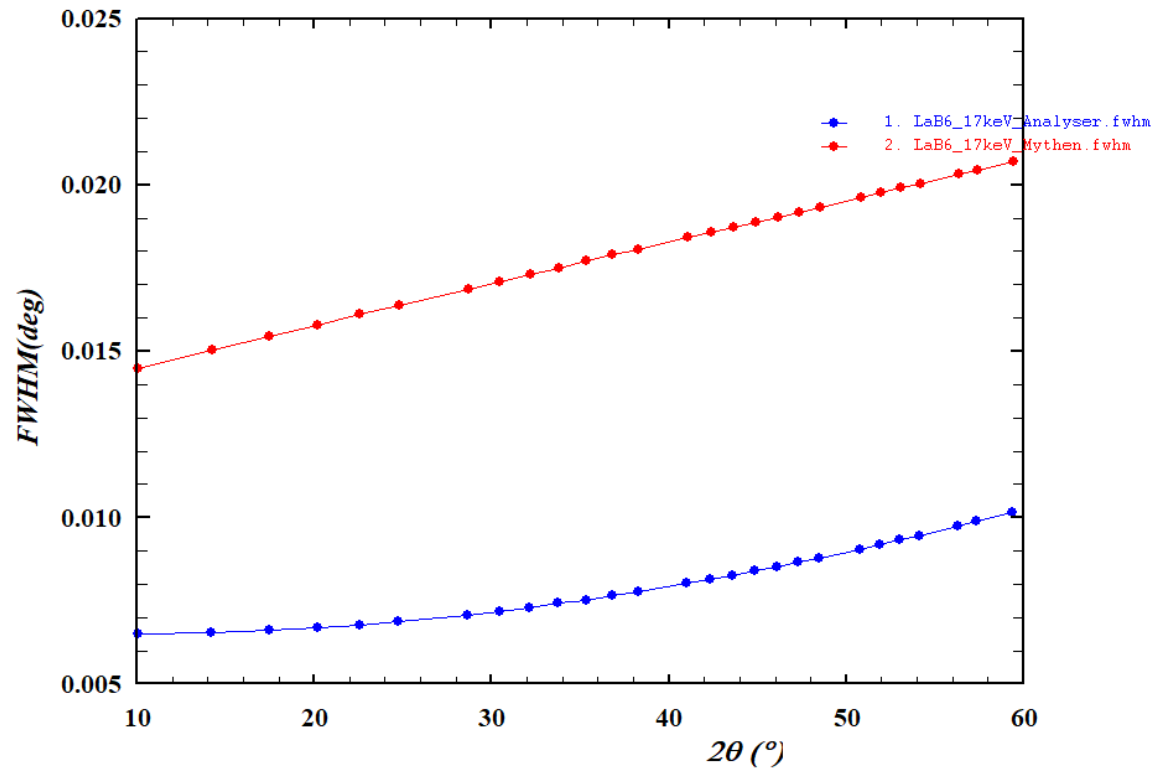
$\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ at 17keV



Instrumental resolution function (IRF)

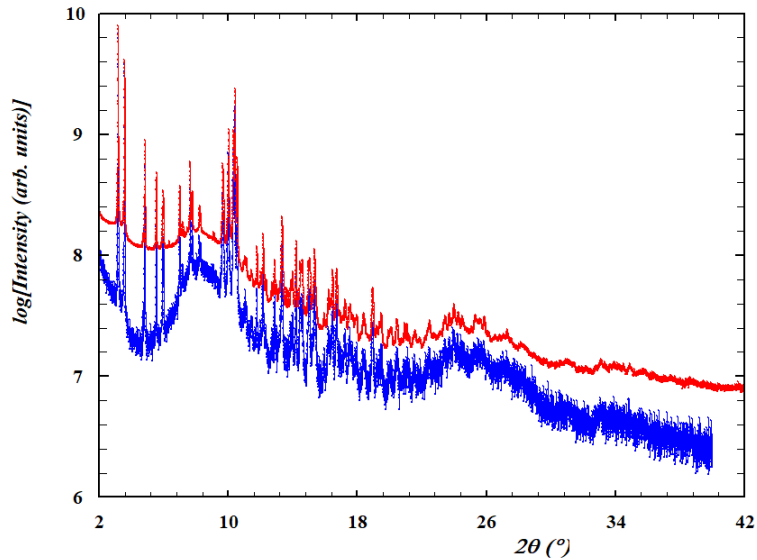
Instrumental Resolution Function

Instrument Resolution Function (LaB6@17keV)

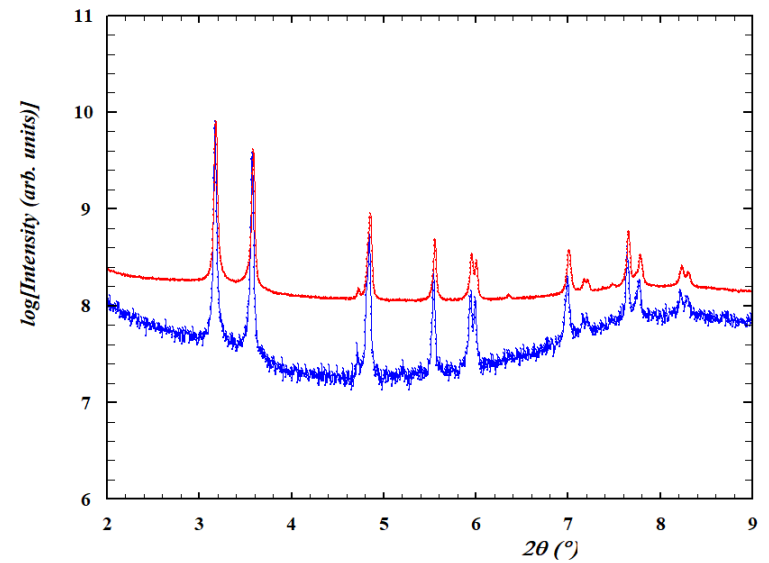


Intensity comparison

Analyser (1h) and Mythen (5mn)



Analyser (1h) and Mythen (5mn)



Data reduction softwares

(Images → Diagrams)

- Geometry (detector, position, angle)
- Masques (defective pixels, beamstop etc..)
 - Fit2D (Hammersley, ESRF)
 - ImageReducer ou Foxtrot (Girardot, Ounsy, Perez, Viguier, SOLEIL)
 - PyFAI (Kieffer et al., ESRF)
 - Others...

ImageReducer-Foxtrot (Soleil)

Image processing software for 2D detectors

Nexus files reading (Images stack)

Masks drawing

Region of interest (ROI)

Superimposition of calculated lines (simulation)

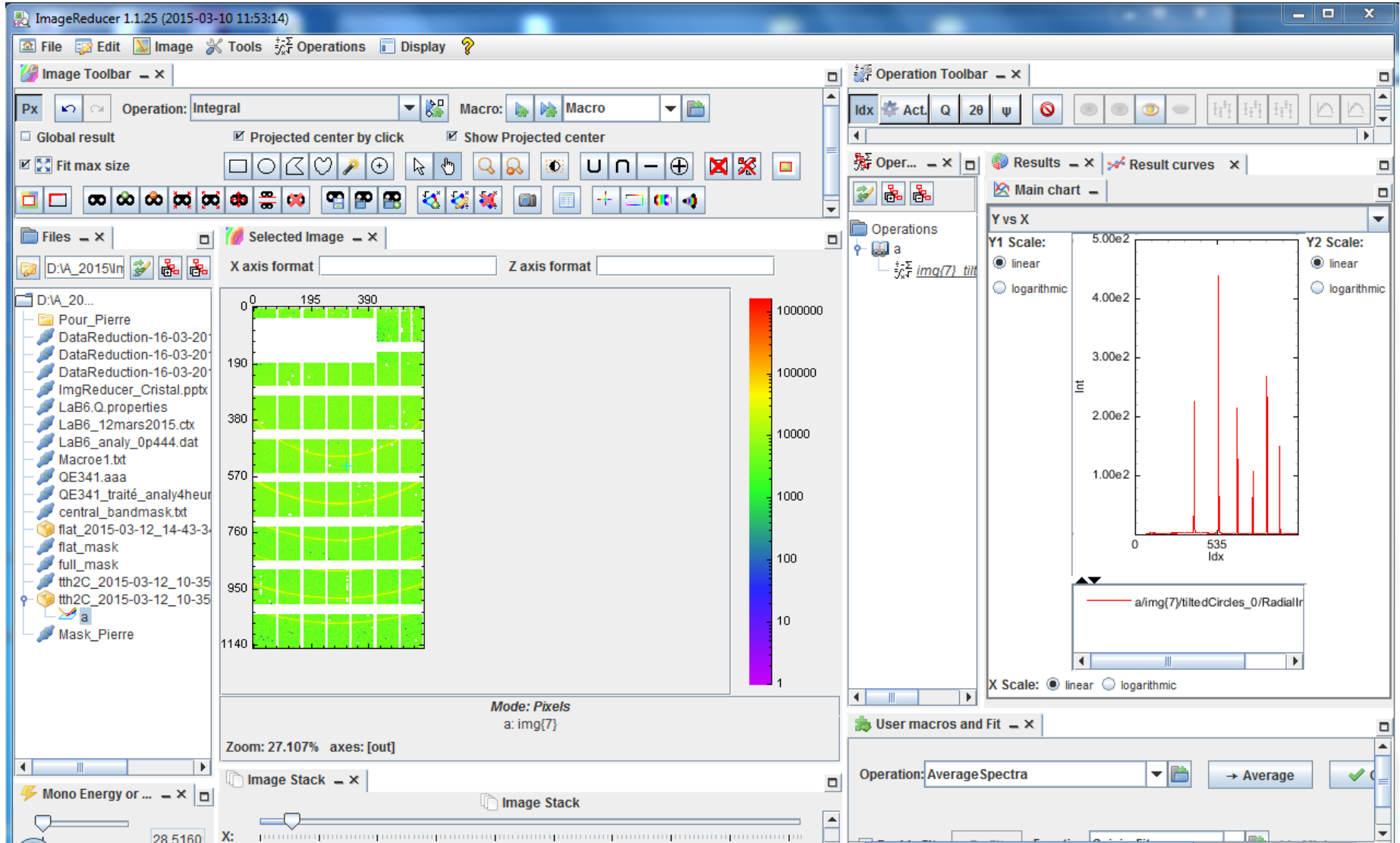
Geometry calibration based on a standard

Detector orientation and distance

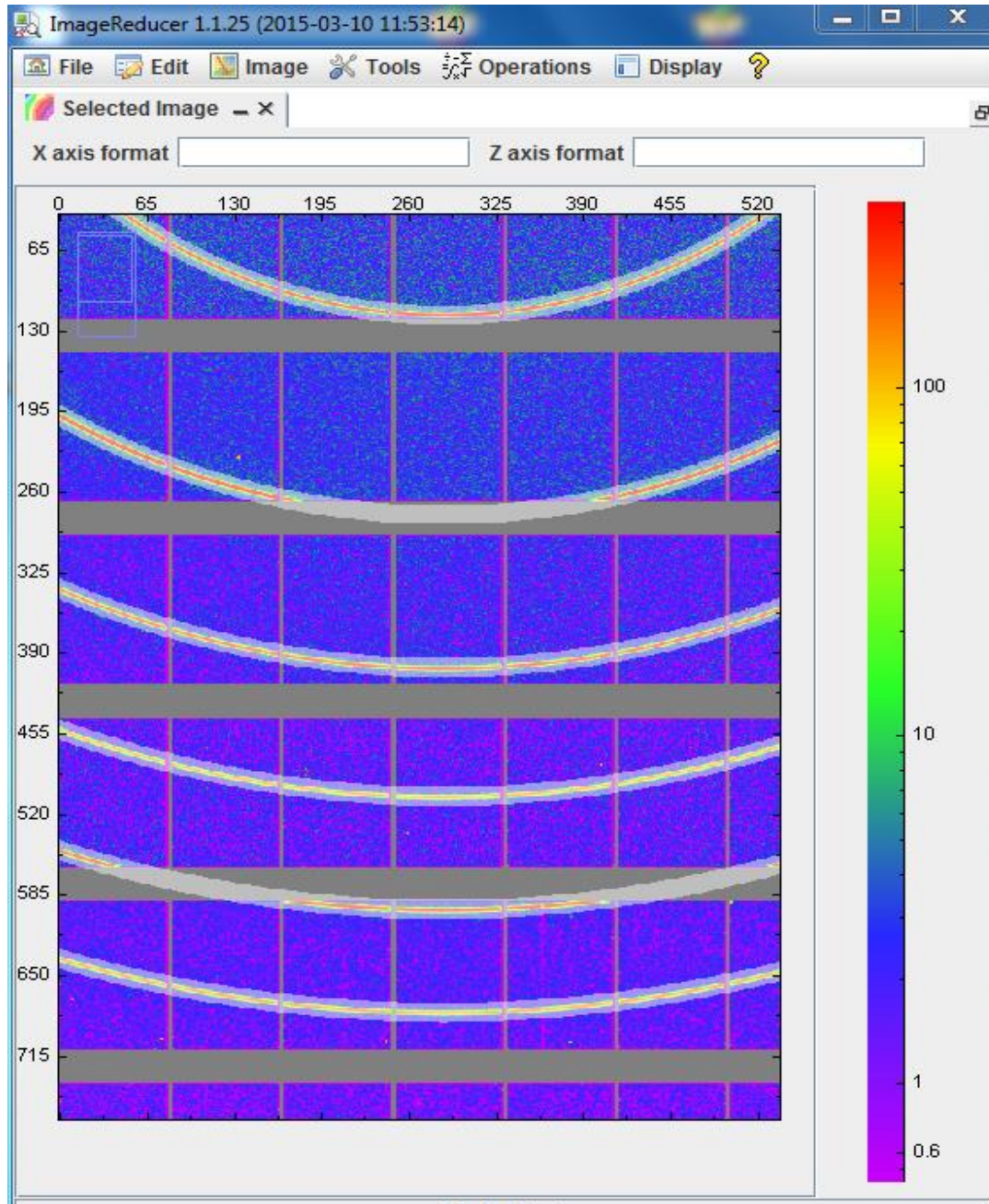
Radial and azimuthal integration

Exporting diagrams

Radial integration(ellipse)



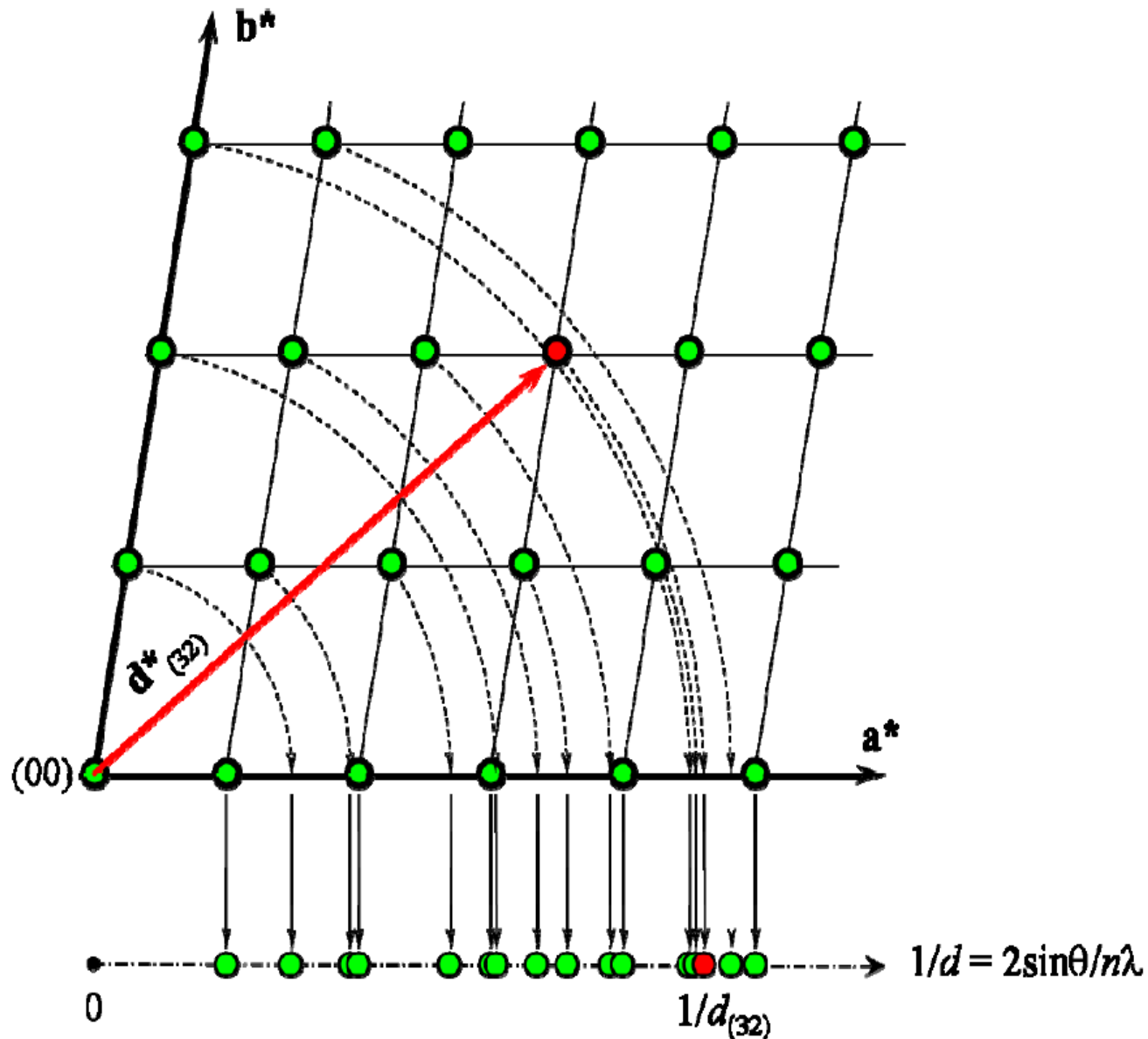
Simulation



Indexation

- Finding the crystal lattice
- Difficult problem, especially for non-orthogonal lattices:
 - In the past, intuitive methods: nowadays, many programs exist.
- Additional difficulty if impurities or absent lines

Why Powders more difficult than Single Crystal?



From R.Cerny

Indexation

- Determination of Bragg peaks positions: d_{hkl}
- $n_{hkl}^2 = 1/d_{hkl}^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^* \cos \gamma^* + 2klb^*c^* \cos \alpha^* + 2hla^*c^* \cos \beta^*$
- $Q_{hkl} = h^2 A + k^2 B + l^2 C + 2hkD + 2klE + 2hlF$
- Simplifications
 - Cubic: $Q_{hkl} = (h^2 + k^2 + l^2)A$
 - Tetragonal: $Q_{hkl} = (h^2 + k^2)A + l^2C$
 - Hexagonal: $Q_{hkl} = (h^2 + hk + k^2)A + l^2C$
 - Orthorombic: $Q_{hkl} = h^2 A + k^2 B + l^2 C$
 - Monoclinic: $Q_{hkl} = h^2 A + k^2 B + l^2 C + 2hlF$
 - Rhombohedral: $Q_{hkl} = (h^2 + k^2 + l^2)A + 2(hk + kl + hl)D$
- Indexing means finding A, B, C...F and h, k, l
- Solving linear equations in A, B, C..F

Indexing methods and figures of merit

- **Trials and errors:** Treor (Werner), then N-Treor (Altomare et al)
 - Assignment of (small) indices to the few first reflections then resolution of linear equations with unknown A,B,C,..F
 - Test if these parameters allow the indexing of the following lines. Methode sensitive to the presence of impurities.
- **Monte Carlo:** (MacMaille: A. LeBail)
 - Random generation of cells, calculation of Qhkl and comparison with the position of the observed lines. Observed intensities can also be used.
- **Dichotomie:**(Dicvol: Boultif et Louer)
 - Variation of the cell parameters (a,b,c, α ..) between min and max values per constant step. A domain is retained if for each line observed there is a hkl such that Qhkl min and max surround Qobs. This domain is in turn divided into subdomains etc... until you get a candidate cell.
- **Figures of merit** allow you to compare the different solutions found: M_N (De Wolff) and F_N (Smith et Snyder)
 - $M_{20} = Q_{20} / (2 \langle \Delta Q \rangle N_{20})$
 - $F_N = (1 / \langle \Delta 2\theta \rangle) (N / N_{calc})$

Determining the Space Group

- Manually after indexing
 - Absent peaks at low angles
 - Ambiguity
 - Superposition
- During extraction or even during structure resolution

Extraction of intensities

- Essentially by LeBail's method (see Rietveld's refinement):
 - Global adjustment of profiles without a structure model. (Full pattern matching).
 - Positions of the lines are constrained by the lattice parameters.
 - A profile broadening function is determined/refined
 - The intensity of each superimposed line massif is distributed among its components (hkl lines), starting point of the search for the structure.
 - Warning: intensities of hkl are not reliable if superposition of peaks: tendency to divide the massif in equal parts

Reminders

- $F_{hkl} = \int_{\text{cell}} \rho(\mathbf{u}) e^{2\pi i \mathbf{h} \cdot \mathbf{u}} d\mathbf{u} = \sum_i f_i e^{2\pi i (hx_i + ky_i + lz_i)} e^{-T}$ avec
 $T = B_i^2 / (\sin\theta/\lambda)^2$
→ $F_{hkl} = |F| e^{i\Phi}$
- $\rho(x, y, z) = 1/V \sum_H F_{hkl} e^{-2\pi i (hx + ky + lz)}$
- For a powder
 - $I_{hkl} = k L_P m_{hkl} A |F|^2$
- Structure $\approx \rho(x, y, z)$ in the unit cell
- So, we have to find the F with their phases

Crystal structure solution different methods

- Direct methods
 - Direct determination of the phase of the structural factors and then electron density obtained by FT
- Patterson method
- Direct space methods
 - Especially if known fragments
 - Random displacement of fragments in the lattice, calculation of the diagram and comparison with observations (MonteCarlo, simulated annealing, etc.)
- Other methods
 - Charge flipping, Artificial Intelligence?

Direct methods

- Based on a good estimate of the $|F_{hkl}|$
- Normalized structure factors
- Statistical methods for determining the phase from the distribution of intensities:
 - But the intensities evaluated are not as reliable as for single crystals
 - Adapted Methods for Powder Diagrams (Program EXPO2014: A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni et al. *J. Appl. Cryst.* **46**, 1231-1235)
- Phase relationships of Fs arise from atomicity and electronic density positivity
 - For example, relationships between triplet phases of reflections.

Direct methods: intensity statistics

- Normalized (E) and unitary (U) structure factors

– $|E\mathbf{h}| = |\mathbf{F}\mathbf{h}|/\sqrt{\sum f_j^2}$ and $|U\mathbf{h}| = |\mathbf{F}\mathbf{h}|/\sqrt{\sum f_j}$, $\langle |E\mathbf{h}| \rangle = 1$, $|U\mathbf{h}| < 1$

	Centrosymétrique	Non-centrosymétrique
$\langle E^2 \rangle$	1.00	1.00
$\langle E^2-1 \rangle$	0.968	0.736
$\langle E \rangle$	0.798	0.886
% $ E > 1.0$	31.7	36.8
% $ E > 2.0$	4.6	1.8
% $ E > 3.0$	0.3	0.01

Direct methods: relationships between phases

- Structure invariants

- Phases combinations which are origin independent

- $F(\mathbf{h}) = \sum_j^N f_j \exp(2\pi i \mathbf{h} \cdot \mathbf{r}_j) = |F(\mathbf{h})| \exp(i\Phi\mathbf{h})$

- If origin displaced of \mathbf{r}_0 ,

- $F(\mathbf{h}) = \sum_j^N f_j \exp(2\pi i \mathbf{h} \cdot (\mathbf{r}_j - \mathbf{r}_0)) = |F(\mathbf{h})| \exp(i\Phi\mathbf{h} - 2\pi i \mathbf{h} \cdot \mathbf{r}_0)$ or

$$\Phi' \mathbf{h} = \Phi \mathbf{h} - 2\pi i \mathbf{h} \cdot \mathbf{r}_0$$

If $\mathbf{h} + \mathbf{k} + \mathbf{l} = \vec{\mathbf{0}}$ then $\Psi_3 = \Phi\mathbf{h} + \Phi\mathbf{k} + \Phi\mathbf{l}$ is an invariant.

Also, $\Psi_4 = \Phi\mathbf{h} + \Phi\mathbf{k} + \Phi\mathbf{l} + \Phi\mathbf{m}$ invariant if $\mathbf{h} + \mathbf{k} + \mathbf{l} + \mathbf{m} = \vec{\mathbf{0}}$

- Invariants depend only on the structure and not on the origin choice while $\Phi\mathbf{h}$, $\Phi\mathbf{h}..$ depend on the origin choice.

- There are also semi-invariants: for example, for space group P-1, if origin on one of the centers of symmetry, reflections $2h, 2k, 2l$ keep the same phase.

Direct methods: relationships between phases

- Harker-Kasper inequalities (Acta. Cryst **1**, 70, 1948)

- For centrosymmetric structures

1) $U_h^2 < \frac{1}{2}(1+U_{2h}) \rightarrow U_{2h} > 0$ if $|U_h| > 0.707$

- Remark: even if $|U_h| < 0.707$ U_{2h} can be sometimes determined

Ex: $|U_{222}| = 0.6$ and $|U_{111}| = 0.5$ then U_{222} positive

$$[|U_h| + |U_k|]^2 \leq [1 + s(\mathbf{h})s(\mathbf{k})s(\mathbf{h}+\mathbf{k}) U_{\mathbf{h}+\mathbf{k}}] \times [1 + s(\mathbf{h})s(\mathbf{k})s(\mathbf{h}-\mathbf{k}) U_{\mathbf{h}-\mathbf{k}}]$$

- Equality relation : D. Sayre (Acta.Cryst **5**, 60, 1952)

- $F(\mathbf{h}) = \theta_h / V \sum_k F(\mathbf{k})F(\mathbf{h} - \mathbf{k})$ (exact relation if identical atoms)
- Same relation between E_h : if $|E_h|$, $|E_k|$, $|E_{h-k}|$ large , dominate the sum and

we get $\Phi_{\mathbf{h}} \sim \Phi_{\mathbf{k}} + \Phi_{\mathbf{h}-\mathbf{k}}$ (see triplet $\Phi_{-\mathbf{h}} + \Phi_{\mathbf{k}} + \Phi_{\mathbf{h}-\mathbf{k}} \sim 0$)

Direct methods: relationships between phases

- Tangent formula: Karle-Hauptman (Acta.Cryst 9, 635, 1956)

$$\tan(\Phi_{\mathbf{h}}) \sim \frac{\sum_k |E(\mathbf{k})E(\mathbf{h}-\mathbf{k})| \sin(\Phi_{\mathbf{k}} + \Phi_{\mathbf{h}-\mathbf{k}})}{\sum_k |E(\mathbf{k})E(\mathbf{h}-\mathbf{k})| \cos(\Phi_{\mathbf{k}} + \Phi_{\mathbf{h}-\mathbf{k}})}$$

corresponds to $\Phi_{\mathbf{h}} \sim$ phase of $[\sum_k E(\mathbf{k})E(\mathbf{h}-\mathbf{k})]$

- Formula used to propagate phases from a few initial phases
- Probability of phase $\Phi_{\mathbf{h}}$: $\mathbf{P}(\Phi_{\mathbf{h}})$

- $\mathbf{P}(\Phi_{\mathbf{h}}) = \frac{1}{2\pi I_0(G_{\mathbf{h}\mathbf{k}})} \exp(G_{\mathbf{h}\mathbf{k}} \cos \Phi_{\mathbf{h}\mathbf{k}})$ with $I_0(x)$ zero order modified Bessel function
and $G_{\mathbf{h}\mathbf{k}} = \frac{2}{\sqrt{N}} |E_{\mathbf{h}} E_{\mathbf{k}} E_{\mathbf{h}-\mathbf{k}}|$ for identical atoms. (even more complicated for unequal atoms!!)

Usually process starts with phases of the largest E_s

Direct methods: relationships between phases

- In summary, the steps of the procedure are:
 - Normalisation and then use of E
 - Find invariants and fix the origin by assigning phases to 2 or 3 structure factors with high E
 - Select a set of reflections with the strongest E
 - Assigning arbitrary phases to a few additional reflections of this set and calculating the phases of the other reflections via the tangent formula until convergence, then probabilistic calculation of figures of merit to evaluate the quality of the starting phases. Swap these starting phases and calculate figures of merit.
 - The set of phases with the best figures of merit is used to calculate a map of density

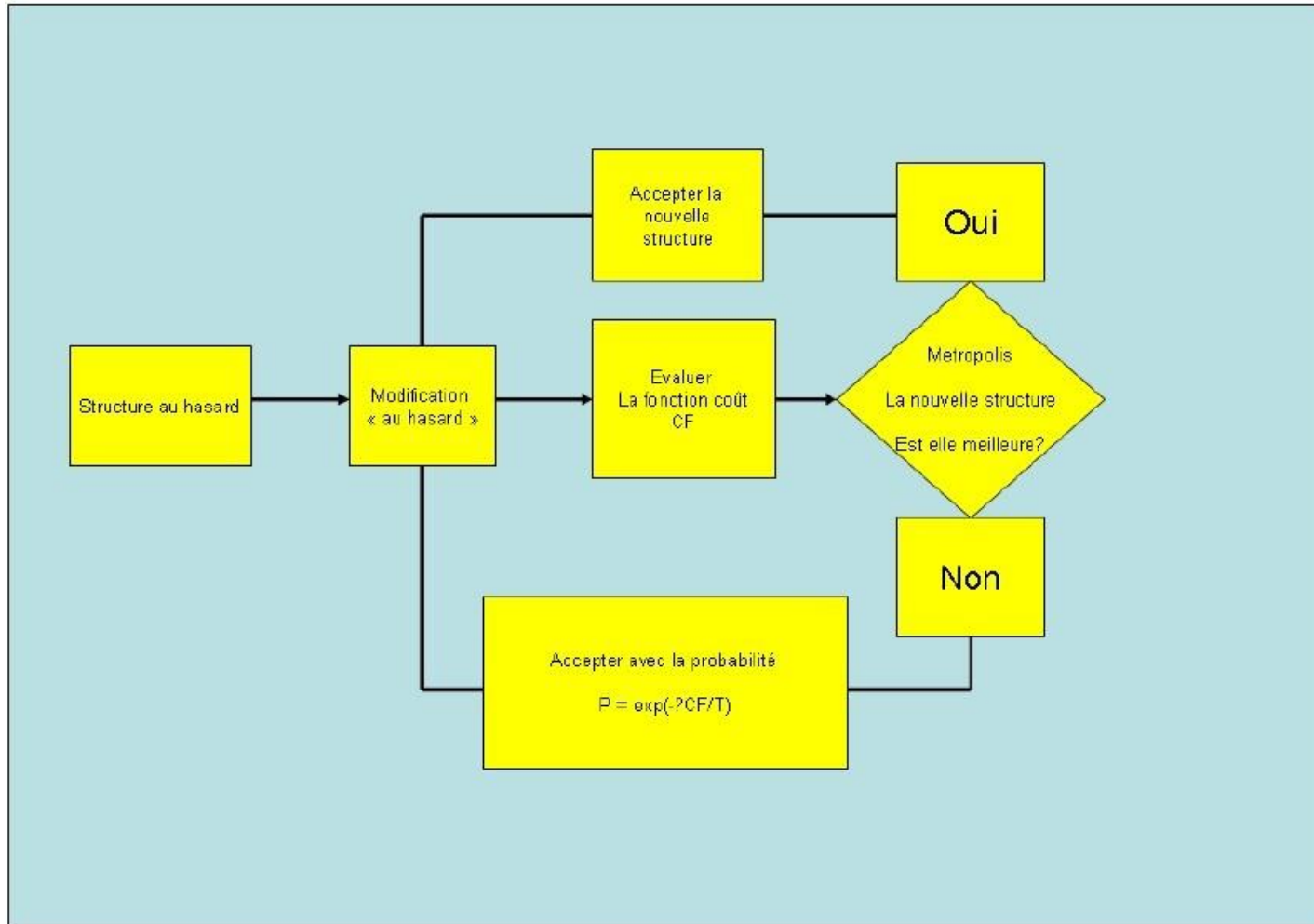
Patterson's method

- $P(\mathbf{u}) = \int_V \rho(\mathbf{r}) \rho(\mathbf{r} + \mathbf{u}) d\mathbf{u}$ autocorrelation function of density
- It can be shown that $P(\mathbf{u}) = (1/V) \sum_{\mathbf{h}} |F_{\mathbf{hkl}}|^2 e^{-2\pi\mathbf{h}\cdot\mathbf{u}}$
- Positions of max of $P(\mathbf{u})$ correspond to interatomic vectors
- Max Intensity $\sim Z_i * Z_j$
- If heavy atoms, the strongest peaks allow these atoms to be placed.
- Then use Fourier-difference maps to complete the structure.

Structure solution in direct space

- Monte Carlo or simulated annealing methods
 - Model of the molecule moved in the cell
 - Can also work ab-initio
 - Only cell content
 - FOX program (R. Cerny, V. Favre-Nicolin)
 - EXPO program (A. Altomare et al.)

Solution in direct space



Algorithme pour la méthode d'optimisation par 'recuit simulé':

Often, slower than direct methods

Solution in direct space

- Information from other analysis techniques
 - EXAFS: environment of an atom, number of neighbors..
 - NMR
 - Infrared spectroscopy
 -
- Calculations
 - Fragments

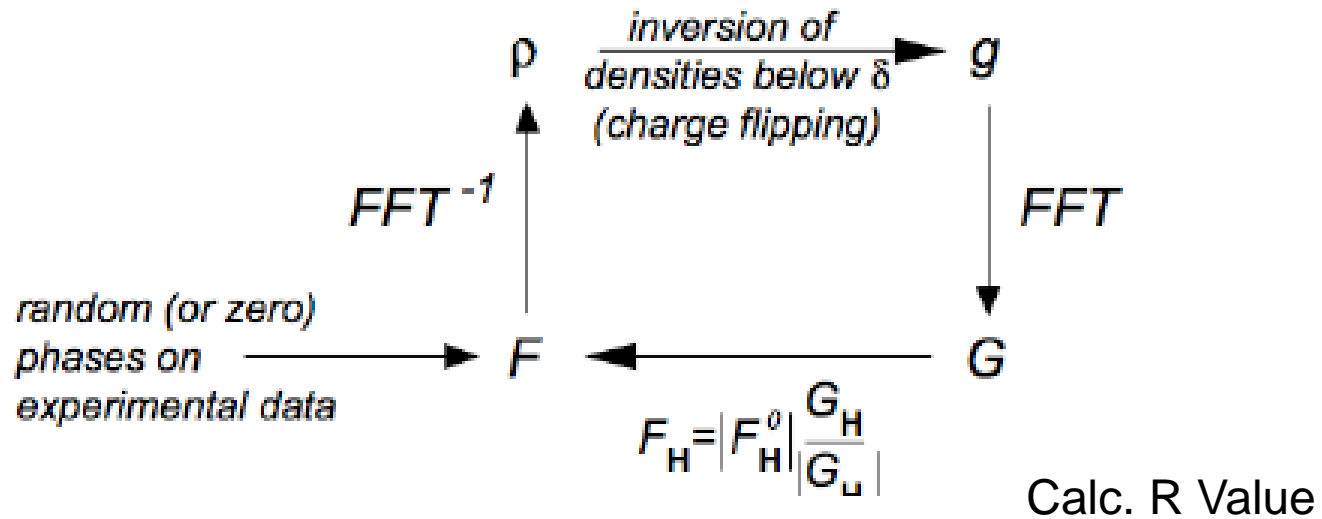
Charge flipping

Oszlanyi et al. (Acta.Cryst. A60 p.134, **2004**)

L. Palatinus (Acta.Cryst. B p.1, **2013**)

- Hybrid method (in direct and reciprocal spaces)
- Assign Phases to $|F_{obs}|$ (reciprocal space)
- By FT get a density map (Direct Space)
- Change the signs (flipping) si $\rho < \delta$ ($\delta > 0$, δ small)
- By FT calculate the F with the new phases
- Remplacer the $|F|$ by $|F_{obs}|$ with phases obtained
- Cycle until convergence(phases no longer evolve)

Charge flipping



- See demo (N.Schoeni and G.Chapuis) at <http://escher.epfl.ch/flip/>

Charge flipping

- Methode advantages
 - In principle, ab-initio resolution
 - No need for composition or space groupx
 - A posteriori determination of the space group
- Disadvantages
 - Need for high-resolution measurements($\text{high } \sin\Theta/\lambda$)
 - Few overlapping peaks

Fourier maps

- $F_{hkl} = \int_{\text{cell}} \rho(\mathbf{u}) e^{2\pi i \mathbf{h} \cdot \mathbf{u}} d\mathbf{u} = \sum_i f_i e^{2\pi i (hx_i + ky_i + lz_i)} e^{-T}$
- $\rho(x, y, z) = 1/V \sum_H F_{hkl} e^{-2\pi i (hx + ky + lz)}$
- $\Delta\rho(x, y, z) = 1/V \sum_H (F_{hkl}(\text{obs}) - F_{hkl}(\text{calc})) e^{-2\pi i (hx + ky + lz)}$
- Maximums of $\Delta\rho$ (difference maps) correspond (in principle) to missing atoms but sometimes difficult to interpret...
- Phases of F_{calc} attributed to F_{obs} ..

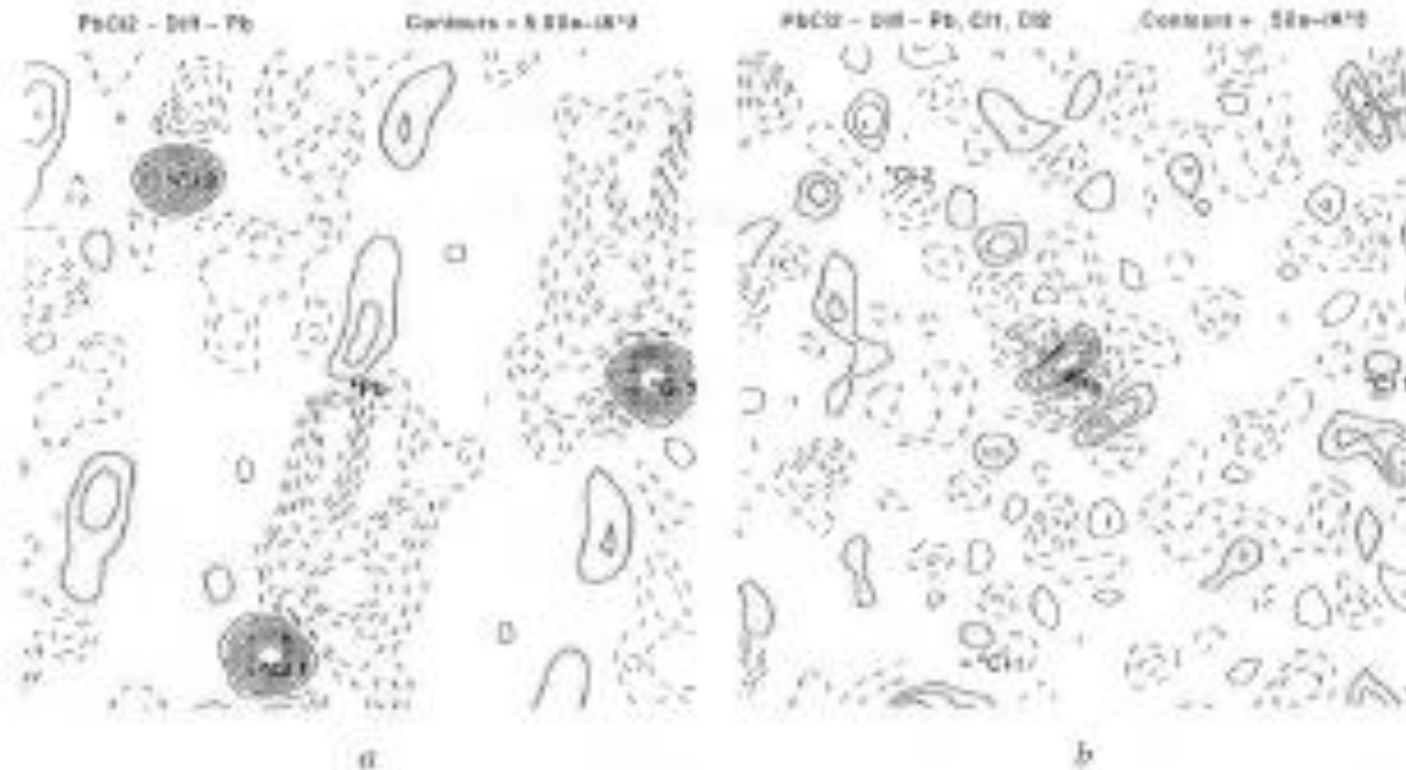


Figure 7.6 Séries de Fourier « différence » dans le composé $PbCl_2$.

À gauche : Série de Fourier « différence » intermédiaire. Coefficients de la série : $x_j(Pb) (H) |F_o(H)| - x_j(Pb)(H) |F_o(Pb) (H)|$. Contours : $5 e/\text{Å}^2$. À droite, série « différence » résiduelle. Coefficients de la série : $x_j(Cl1,Cl2) (H) |F_o(H)| - x_j(Cl1,Cl2) (H) |F_o(Pb) (H)|$. Contours : $0.5 e/\text{Å}^2$.

Rietveld's refinement

- Refinement of structural and profiles parameters on the experimental diagram (Fullprof – J.Rodriguez-Carvajal)
- Structural parameters
 - For each atom
 - Position (x,y,z), Thermal motion(B or Bij), occupancy factor
- Other parameters
 - Scale factor, cell parameters, preferred orientation
 - Profile function, broadening function with 2θ , asymmetry x
 - Background noise

Intensity diffracted by a powder

- Integrated intensity $I_h \sim (I_0 \lambda^3 / R) m_h L p O A |F_h|^2$
 - $L = 1/(\sin\theta_B \sin 2\theta_B)$ Lorentz factor
 - $p = (1-t) + t \cos^2 2\theta$ polarisation factor $t \sim 0.05$ for synchrotron beam (vertical geometry)
 - A, O absorption and preferential orientation factors
 - R distance Sample-Detector distance
 - m_h multiplicity of peak hkl
- $I_h \sim k m_h L p A |F_h|^2$, with k scale factor
- For a single peak $y(2\theta) = y_i = I_h \Phi(2\theta - 2\theta_B, \Gamma) + b_i$
 - $\Phi(2\theta - 2\theta_B, \Gamma)$ normalized profile function of width Γ

The refinement

- We try to minimize $M = \sum_i w_i [y_i(\text{obs}) - y_i(\text{calc})]^2$
- $Y_i(\text{calc}) = \sum_{\text{hkl}} (I_{\text{hkl}} \Phi(2\theta_i - 2\theta_{\text{B,hkl}}, \Gamma) + b_i)$
 - Often used, $\Phi = \eta L + (1 - \eta)G$ pseudo-voigt function
 - $\eta = \eta_0 + X \cdot 2\theta$ shape parameter
 - $\Gamma^2(2\theta) = W + V \tan(\theta) + U \tan^2(\theta) + Ig / \cos^2(\theta)$ simplest broadening function
 - U, V, W, Ig et X refinable parameters
- Remarks:
 - Other formulations with more "physical" parameters are used.
 - The profile measured is the convolution of the "sample" profile with the instrumental profile.
 - Reminders:
 - Scherrer's formula $\beta(2\theta) \sim 0.9 \lambda / L \cos\theta$
 - Microdeformation $\Delta 2\theta \sim 4\varepsilon \tan(\theta)$

Factors of agreement

For Profiles

$$R_{wp} = [\sum w_i (y_{obs,i} - y_{calc,i})^2]^{0.5} / [\sum w_i (y_{obs,i})^2]^{0.5}$$

- $R_p = [\sum |y_{obs,i} - y_{calc,i}|] / [\sum |y_{obs,i}|]$
- $R_{exp} = [N - P]^{0.5} / [\sum w_i (y_{obs,i})^2]^{0.5}$
- $G.O.F = R_{wp} / R_{exp}$
- Recalculated only on areas containing reflections
- Are also calculated without background

Factors of agreement

For the structure

- $R_B = [\sum_k |I_{obs,k} - I_{calc,k}|] / [\sum_k |I_{obs,k}|]$
- $R_F = [\sum_k |F_{obs,k} - F_{calc,k}|] / [\sum_k |F_{obs,k}|]$

Avec

– $I_{obs,k} = I_{calc,k} \sum_i \Phi(2\theta_i - 2\theta_{B,k})(y_{obs,i} - b_i) / (y_{calc,i} - b_i)$ not directly measured.

- All the agreement factors must be considered
- Look at the difference plot

Results

- Agreement factors
- Drawing of the obs ,calc diagrams and difference
- Structure drawing, stacking
- Atomic positions, distances and angles
 - Control of these distances
 - Coordination polyhedra
- Typical atomic thermal motion factors
- Eventually, microstructure

XRD and IR structural investigations of a special breathing effect in the MOF-type gallium terephthalate MIL-53(Ga).

Christophe Volkringer, Thierry Loiseau, Nathalie Guilloua, Gérard Férey, Erik Elkaim and Alexandre Vimont
Institut Lavoisier (Versailles) and Laboratoire de catalyse et spectrochimie (Caen).

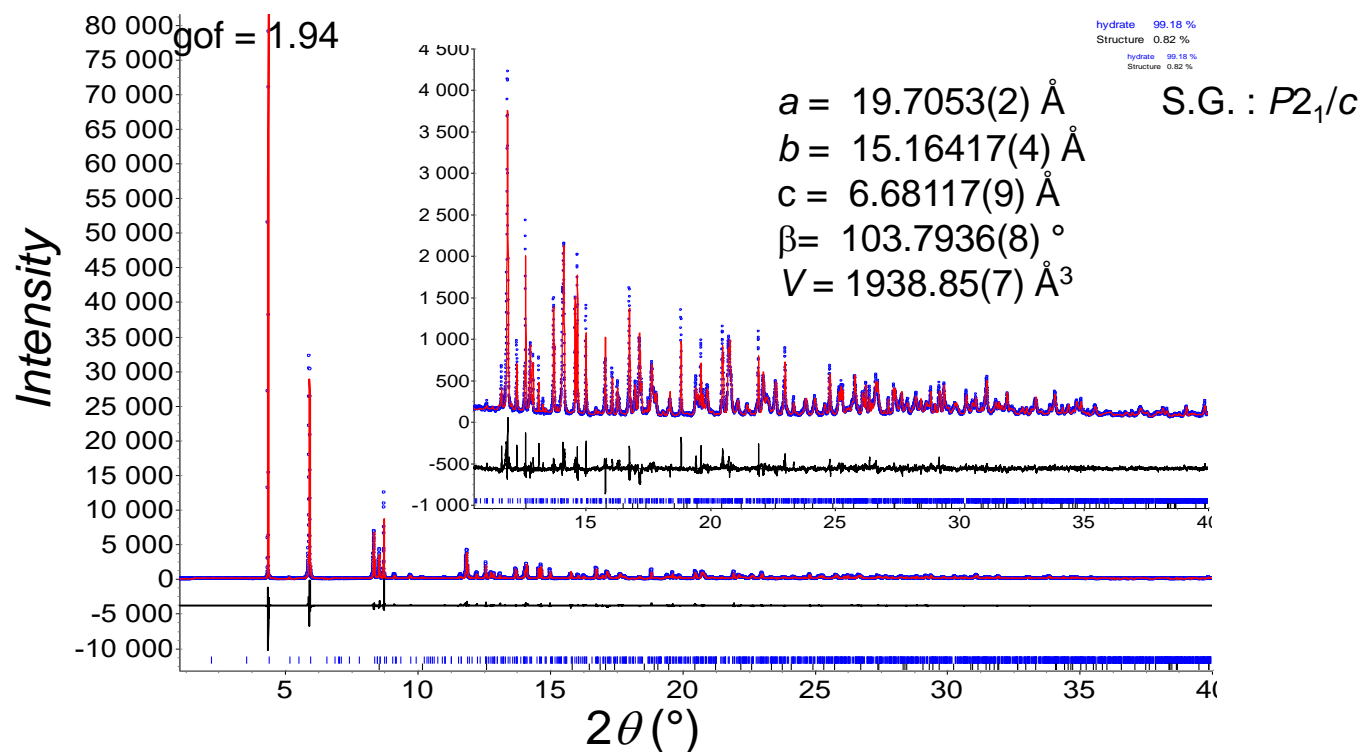
Dalton Trans., 2009, 2241–2249

$$R_B = 4.01 \%$$

31 independant non-hydrogen atoms

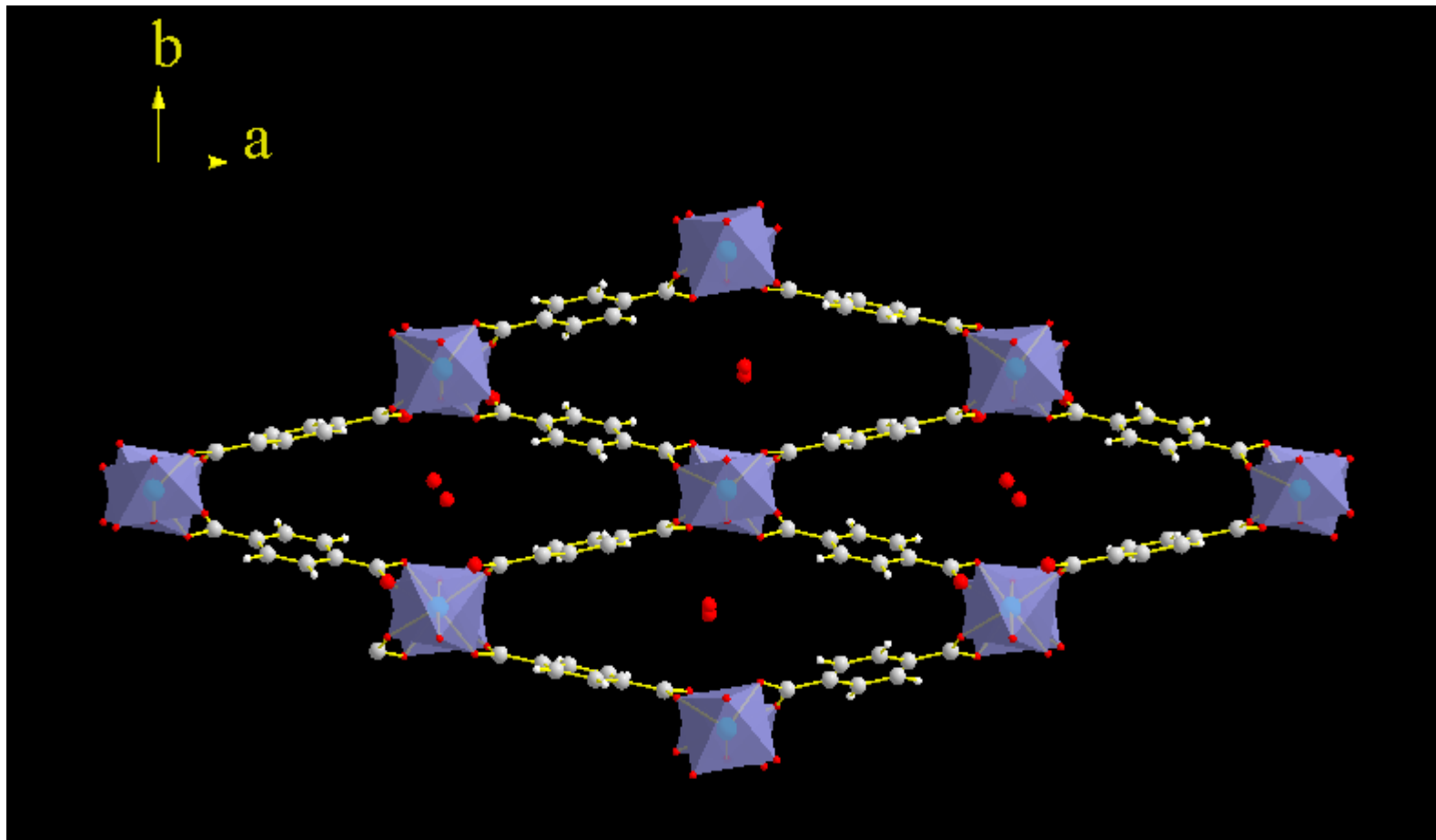
$$R_{wp} = 12.18 \%$$

treated as rigid bodies



Affinement Rietveld

nano-porous compound



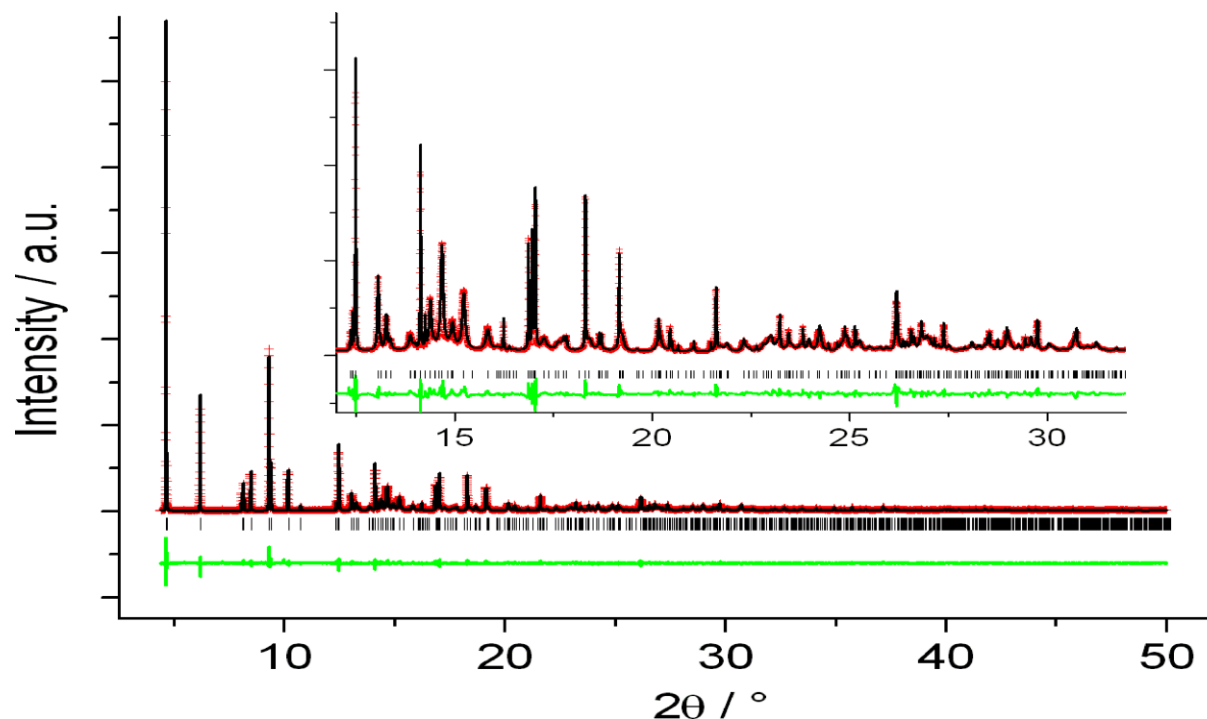
T. Loiseau and N. Guillou (Institut Lavoisier - Versailles)

Structure of $\text{Mn}_3(\text{OH})_2(\text{C}_6\text{H}_2\text{O}_4\text{S})_2$

Romain Sibille^{*,a}, Thomas Mazet^a, Erik Elkaim^b, Bernard Malaman^a and Michel François^a

Inorganic Chemistry, 2013, 52(2): 608–616

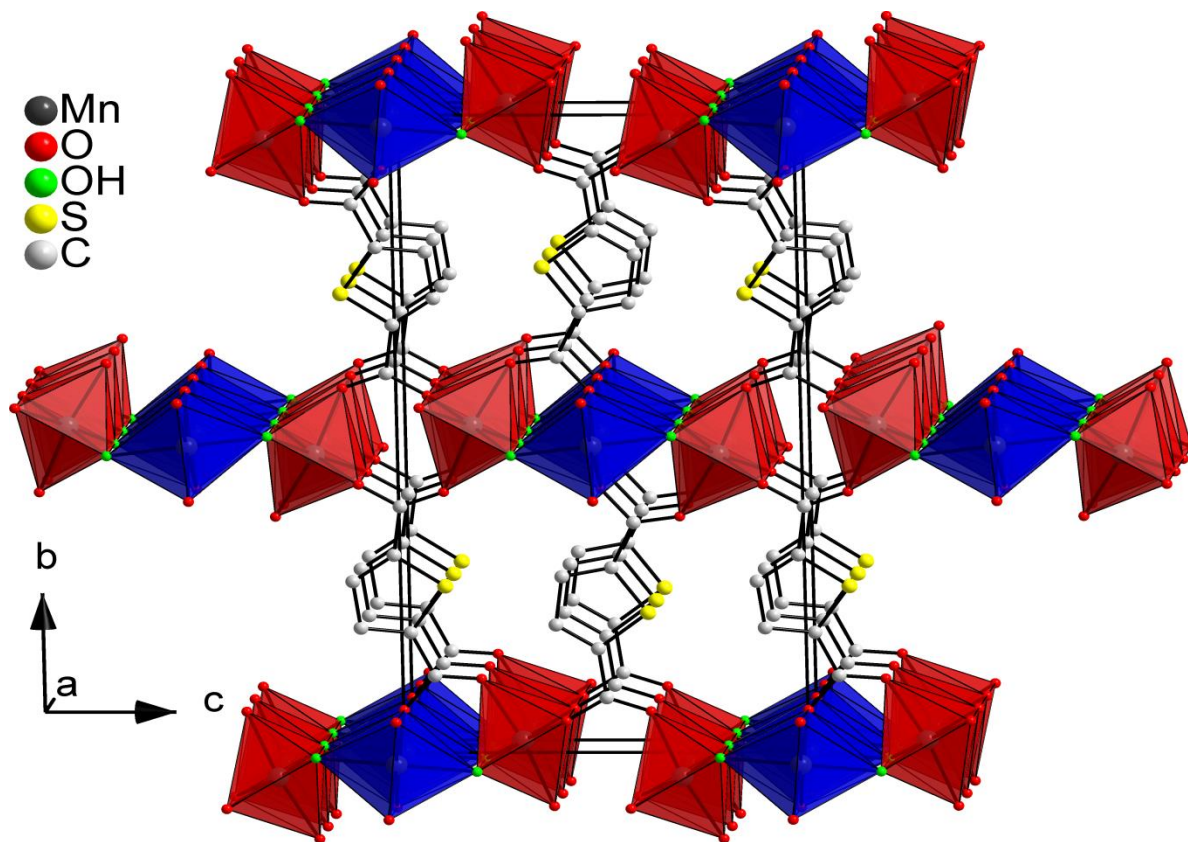
High angular resolution diagram collected at Cristal ($\lambda = 0.7775 \text{ \AA}$)



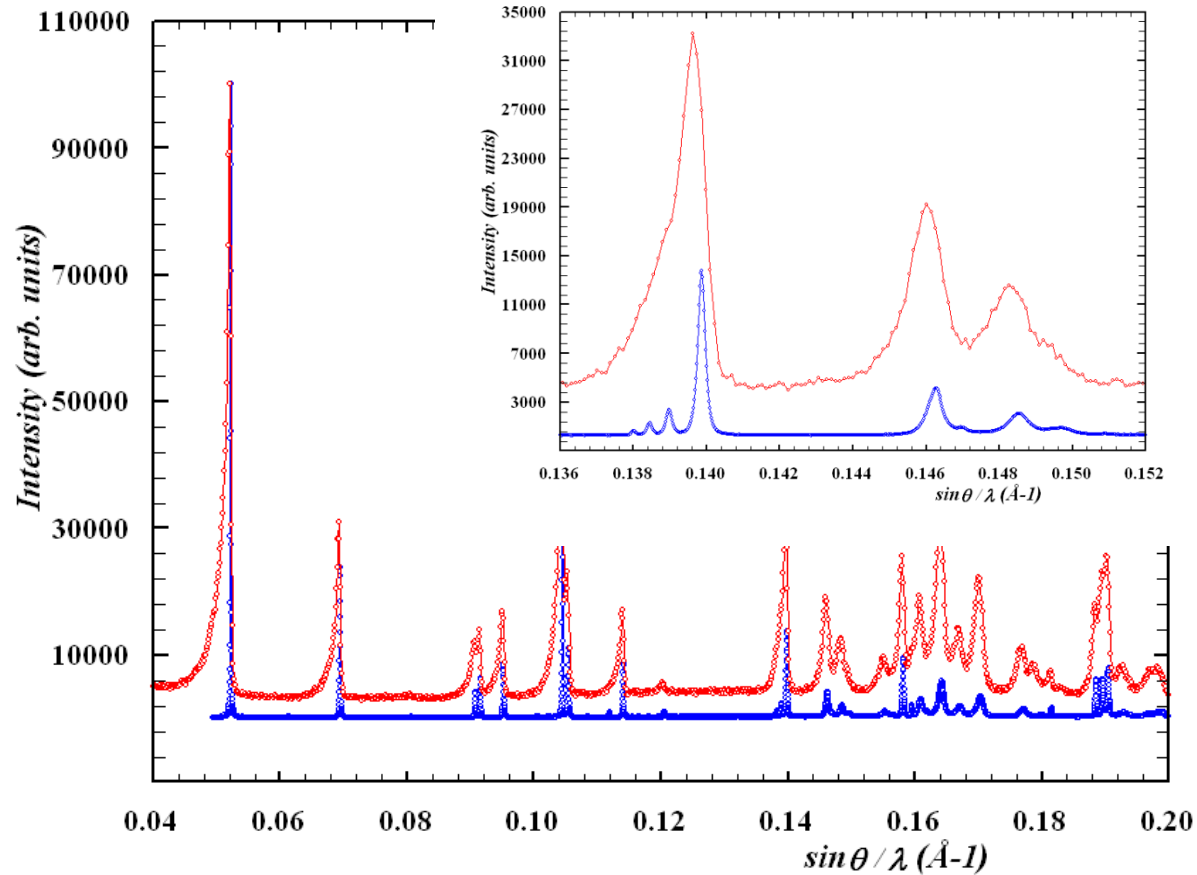
Indexation $\rightarrow P2_1/c$ $a = 3.4475 \text{ \AA}$, $b = 19.1368 \text{ \AA}$, $c = 11.0146 \text{ \AA}$ and $\beta = 97.455^\circ$

Resolution with program FOX (V. Favre-Nicolin)

Structure



Comparison Labo - Synchrotron



High resolution also allows study of the microstructure (size, deformation)

Multi-Diagram Refinement

- Ability to refine on multiple diagrams
 - Neutrons and X-rays
 - Synchrotron radiation at several wavelengths (anomalous effect)
 $f = f_0 + f' + if''$
 - Hydrogens positions
 - Partial occupancy of 2 elements with close atomic numbers.

Anomalous scattering factors f' et f''

Values of anomalous coefficients: extracted from DABAX (ESRF Grenoble)

Two sets of data can be displayed according to Brenann and Cowan: $2 < Z < 92$, or Sasaki: $2 < Z < 83$ and $Z=92$
Energy range limited to [4 - 40 Kev]

Two elements maximum can be selected together
Click left mouse button to select

Select the author

Brenann and Cowan data

Sasaki data

Del. Selection

Draw

Mouse position

Elem.	E (Ev)	lambda (Å)	f'	f''
Fe	7100.1	1.7462	-6.221	0.469
Co	7100.1	1.7462	-2.269	0.551

Absorption edges energies (Bearden and Burr, 1967)

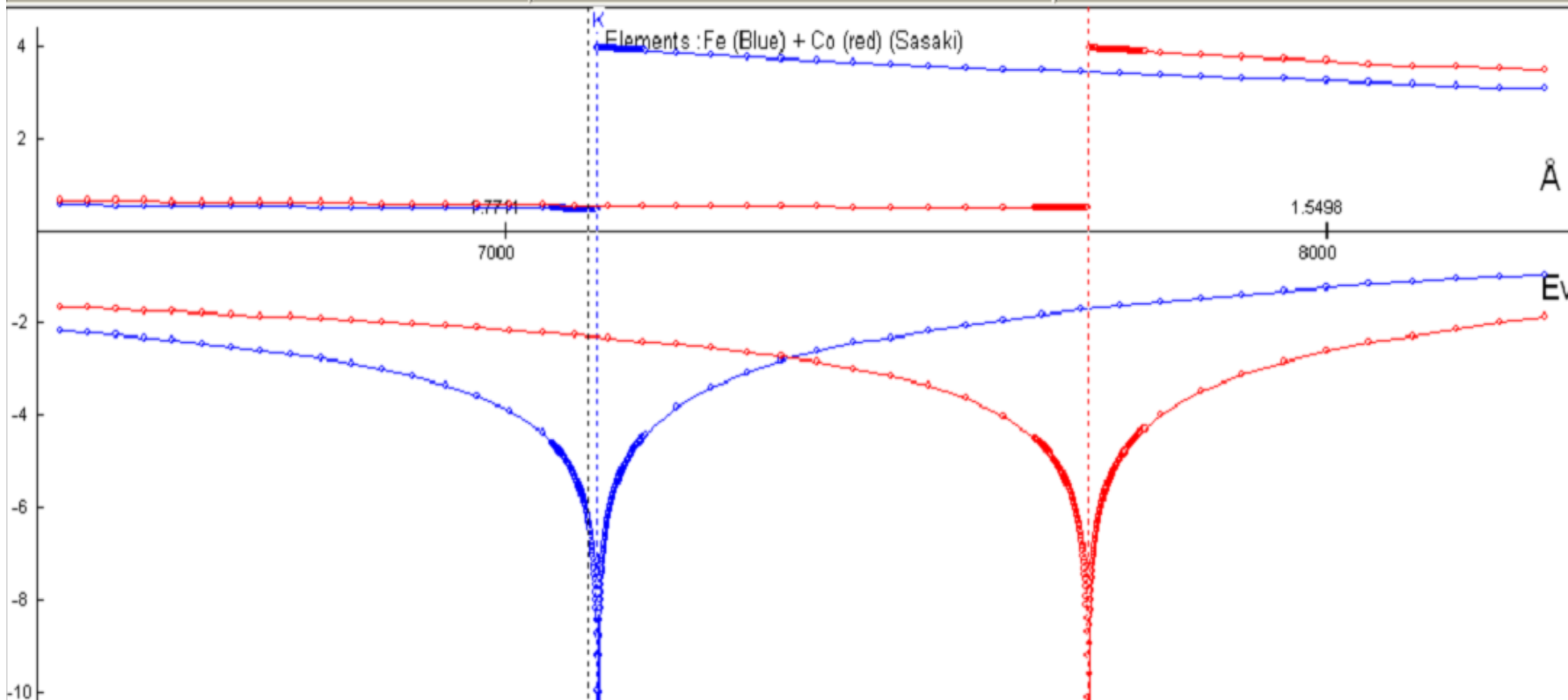
Elem.	K	L1	L2	L3	M1	M2
Fe	7112.0	846.1	721.1	708.1	91.3	0.0
Co	7708.9	925.6	793.8	778.6	101.0	0.0

Enter a value of λ : Å or energy: Ev.

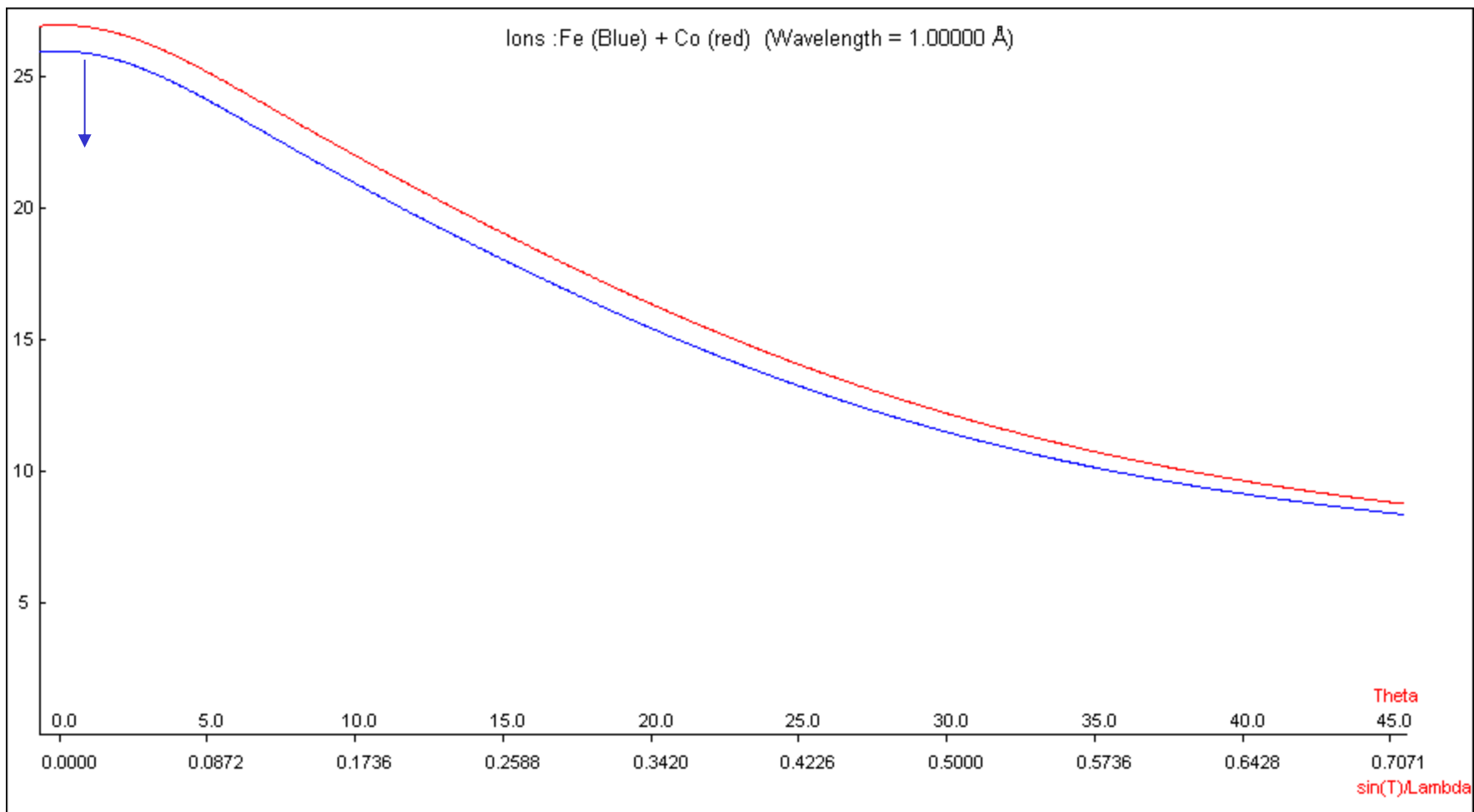
Elem.	E (Ev)	lambda (Å)	f'	f''
Fe	7125.54	1.7399	-6.148	3.937
Co	7125.5	1.7399	-2.329	0.545

To display the anomalous factors, enter the energy or the wavelength and press the "Tab" or "Enter key"

Warning:
The values of the nearest energy listed in the ".ano file are displayed (not interpolated). Edit the result file for more accurate information.

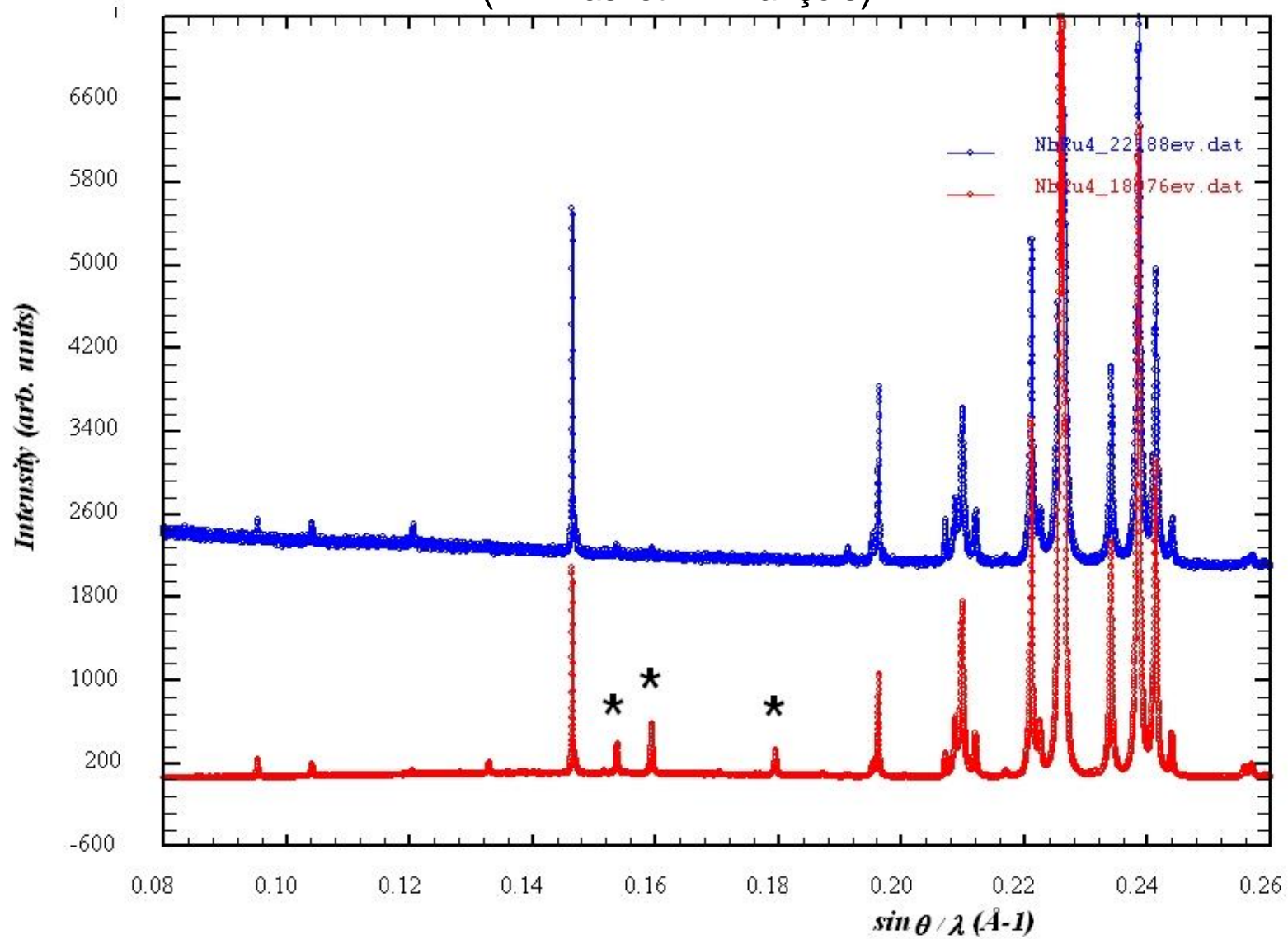


Ions : Fe (Blue) + Co (red) (Wavelength = 1.00000 Å)



Anomalous diffraction of an NbRu alloy

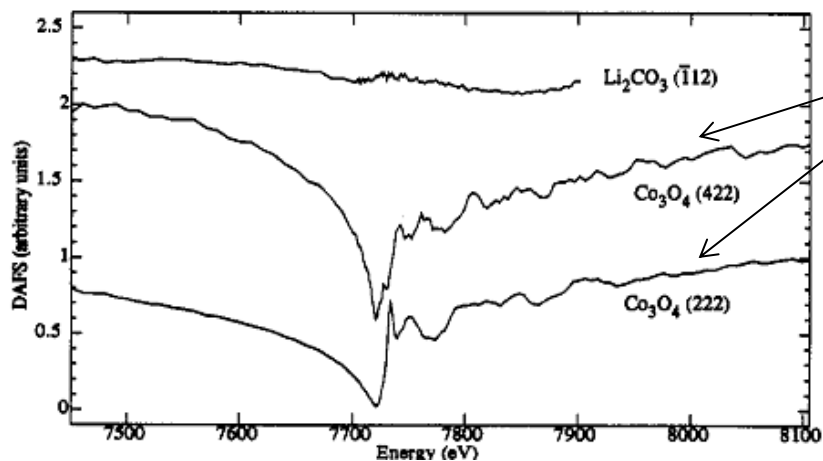
(M. Vilasi et M. François)



Resonant diffraction: DAFS

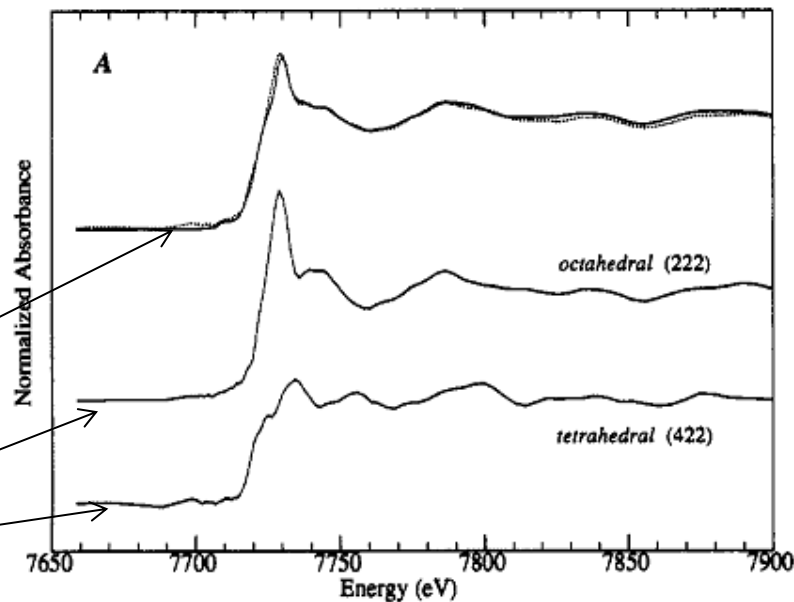
Diffraction Anomalous Fine Structure= Spectroscopy under diffraction conditions

Pickering et al. J. Am. Chem. SOC. 1993,115, 6302-6311



Spectra (DAFS) of reflections 422 et 222

A) Sum $2 \cdot \text{octa} + 1 \cdot \text{tétra}$ absorption spectra extracted from DAFS measurements



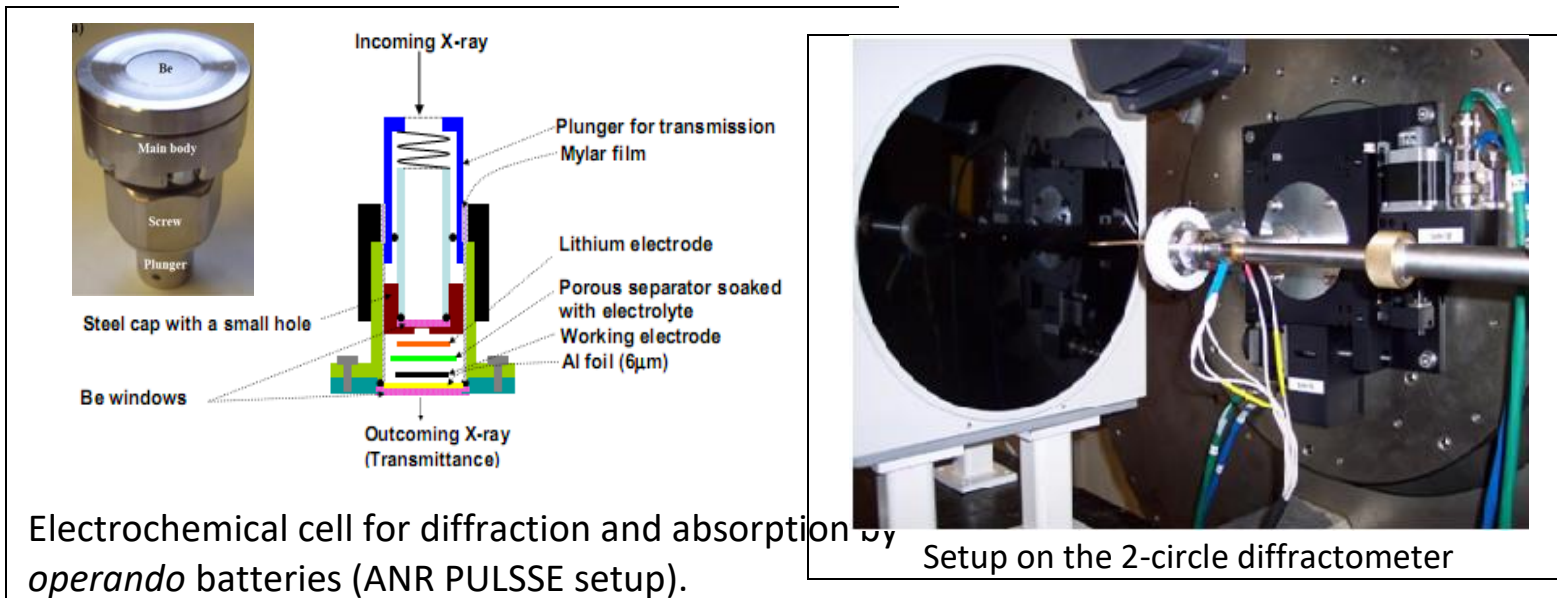
Operando studies of Lithium batteries

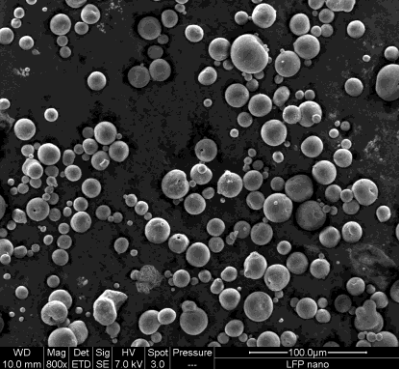
Collaboration with LRCS (Amiens) ,IMN (Nantes) and SOLEIL (XAS beamlines)

(ANR funded : PULSSE project)

Slow kinetics study to follow charge (discharge) of the battery with a time resolution of a 2-3mn

- Use of an imaging plate detector (MAR345)
- Design and construction of an electrochemical cell



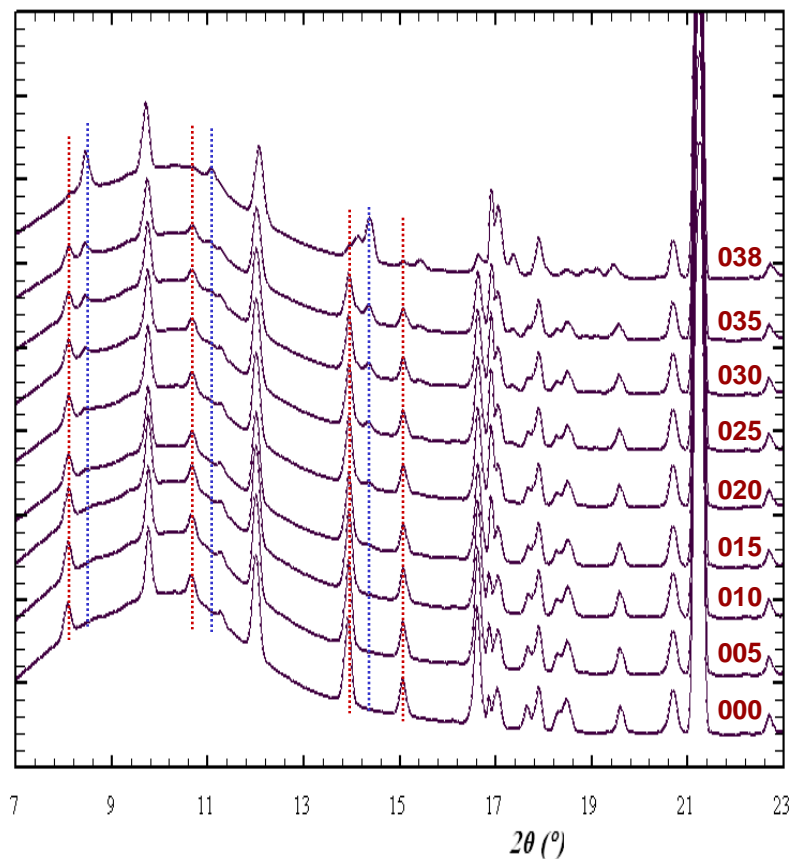
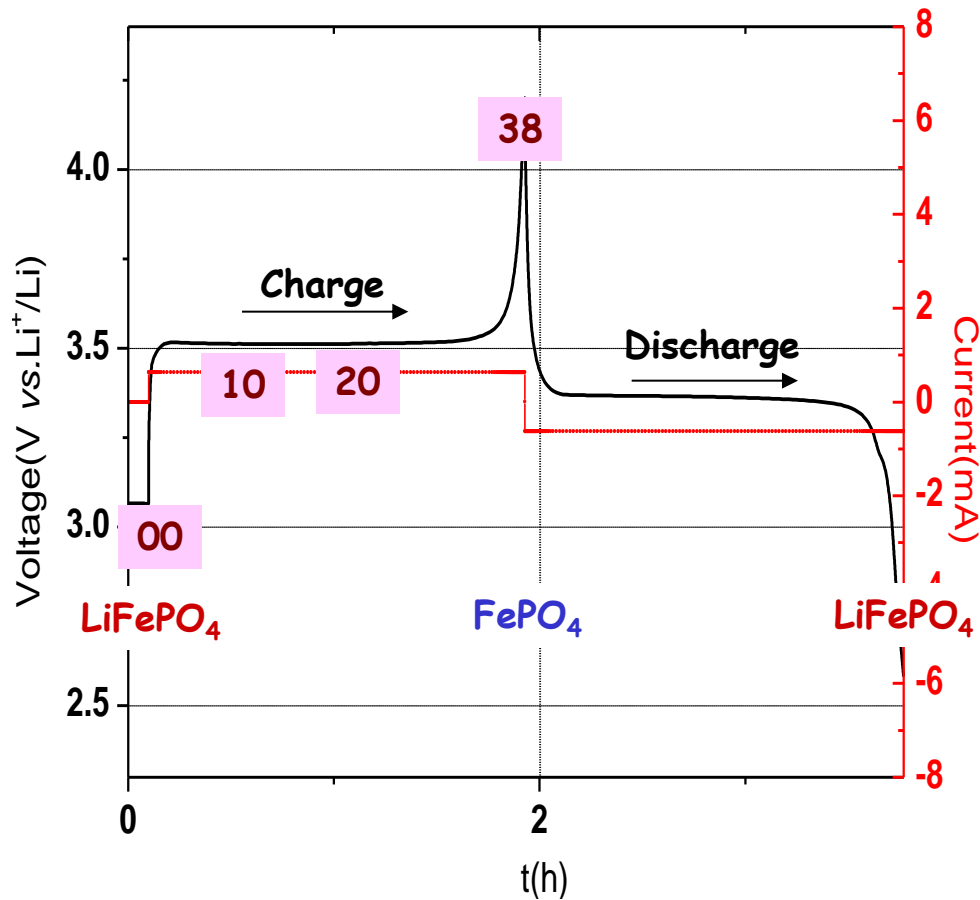


Batteries Li / Electrolyte / LiFePO₄

ANR PULSSE IMN(Nantes), LCRS(Amiens), SOLEIL

One XRD pattern (recorded within 10 sec.) every 3 min.

Wavelength : $\lambda = 0.727 \text{ \AA}$



two-phase reaction

Other experimental methods

Multi-grains crystallography

Use of 2D detectors and single-crystal type measurements.

Diffraction images of only a few dozen grains (beam size/grain size ratio)

Searching for individual spots (position and intensity) helps reduce overlaps

Counting the number of peaks and their sum for each 2θ

Histogram number_pics = $f(2\theta)$ information on multiplicity.

Best case: orientation of each crystal is obtained after treatment for single crystal.

Otherwise reconstruction of a high-resolution powder diagram

See: serial crystallography: Beyerlein et al Powder Diffr. (2014), vol30 (s25)

J. Wright (ID11, ESRF)

General Bibliography

- Crystal Structure Analysis (W. Clegg et al., Oxford University Press)
- Diffraction des rayonnements (J. Protas, Dunod)
- Fundamentals of Crystallography (C. Giacovazzo)

Structure solution and refinement from x-rays or neutrons diffraction data

E.Elkaim and B. Baptiste

- Sample: Strontium Oxalate
- Indexing synchrotron diagram
- Space group
- Structure solution by Direct Methods (EXPO)
- Refinement by Rietveld method (Fullprof)
- Structure solution par simulated annealing (EXPO or FOX)
- Structure visualisation (VESTA)
- (Neutron data refinement)
- Gfourier: position the H (Deuterium)
- Fullprof Studio

From a powder diffraction diagram to structure solution : the main steps

Erik Elkaim

- Diagram recording /measurement
- Indexing
- Space group determination
- Bragg intensities extraction
- Search for a structure
- Refinement
- Structure description