Diffraction sous conditions extrêmes ou atypiques: traitement et outils avancés

ANF ЯÉCIPROCS 04-08 juin 2018
Centre CAES du CNRS
La Vieille Perrotine - Oléron

DIFFRACTION DES ELECTRONS

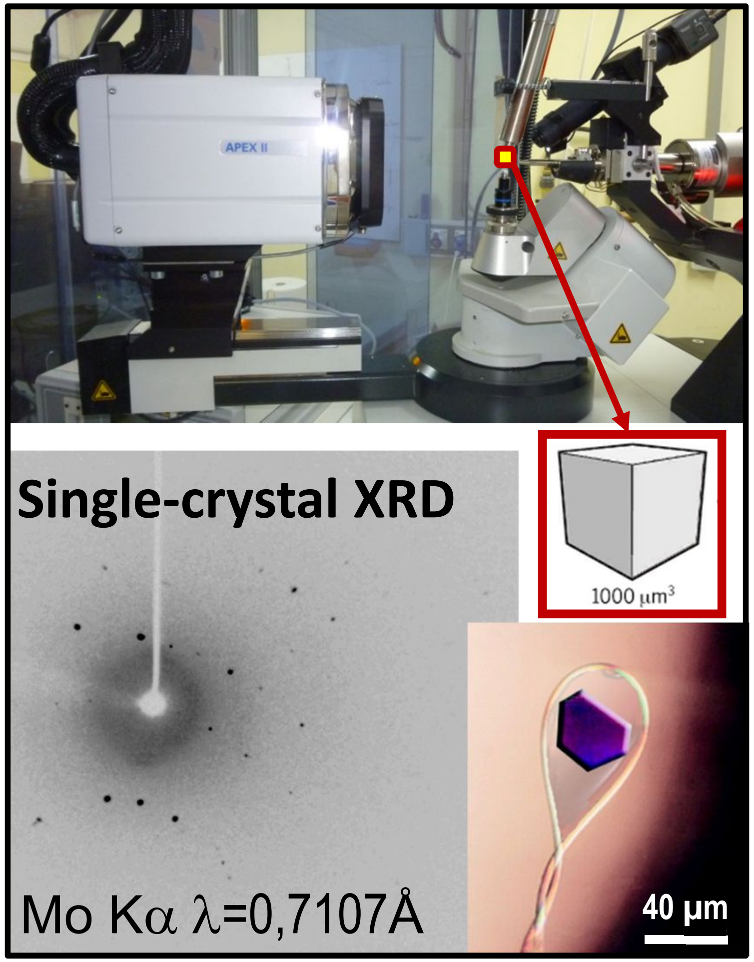
application à la cristallographie structurale

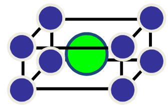
- Préambule
- Diffraction des électrons
- Precession Electron Diffraction Tomographie (PEDT)
- Traitement et outils pour l'analyse des données PEDT

Philippe BOULLAY – DR CNRS
CRISMAT UMR 6508, ENSICAEN, CNRS, Caen, France

Solving the structure of an unknown compound ?

Single crystal X-ray diffraction (SC-XRD)



- ✓ Weak interaction ► $I \propto |F|^2$ ► 
- ✓ dedicated instruments (*desk XRD ↔ synchrotron*)
- ✓ numerous users and software
- ✓ +100 years of use (*materials science ↔ biology*)

Structure determination in the absence of single-crystal data ?

see L.B. McCusker, Acta Cryst. A47 (1991) 297-311

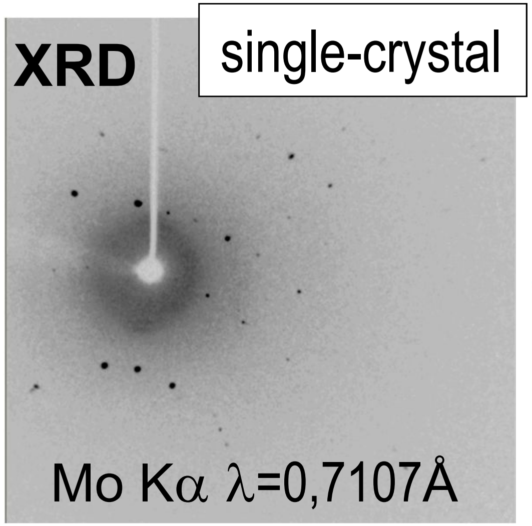
Solving the structure of an unknown compound ?

X-ray and neutron powder diffraction (XRPD and NPD)

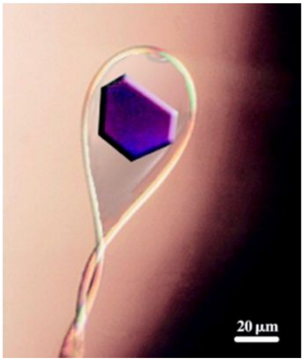
single-crystal

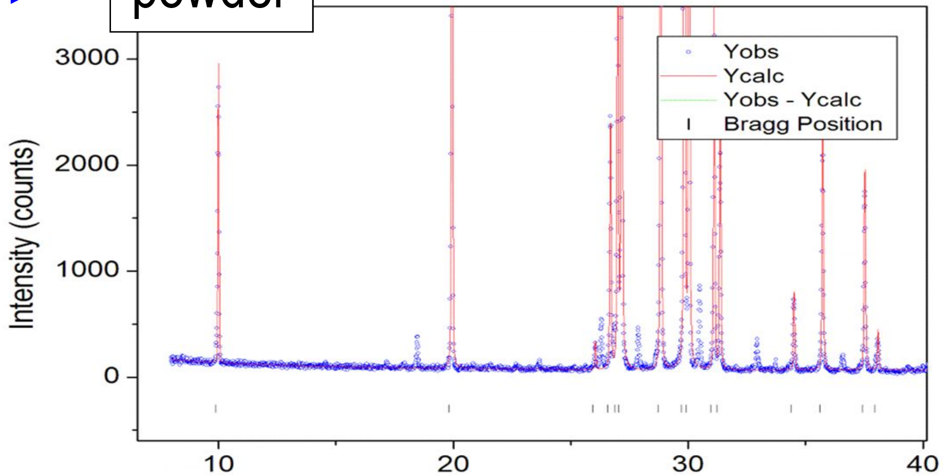
◄ **tens of micrometer** ►

powder



cell, symmetry and structure





phase identification, structure and microstructure

(size, shape, texture)

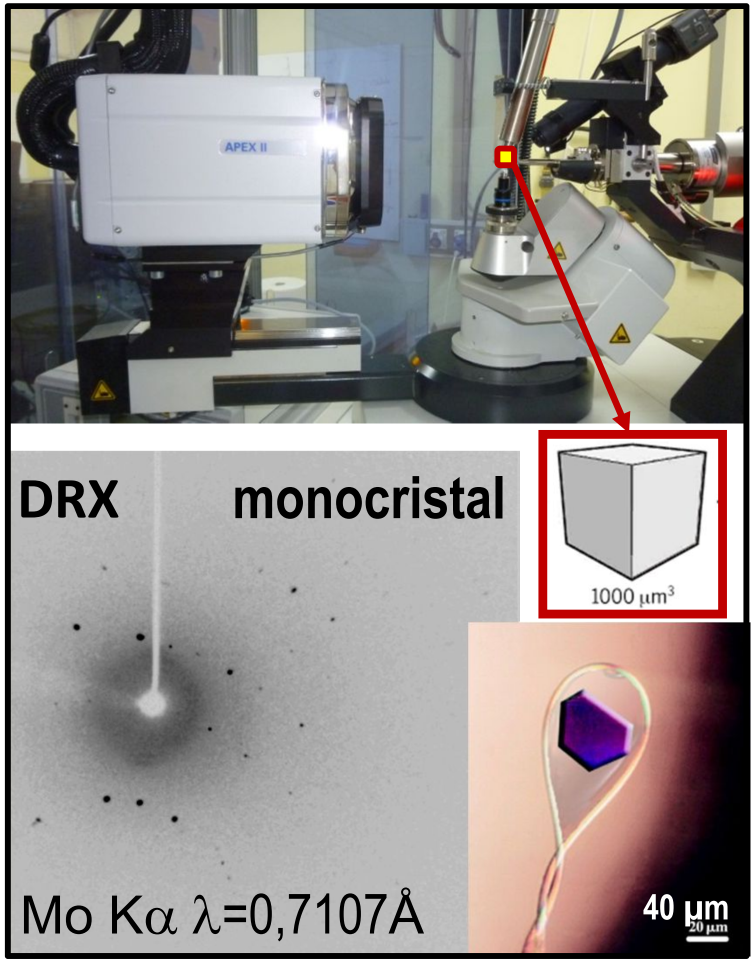
✓ Progresses in structure solution from powder diffraction patterns

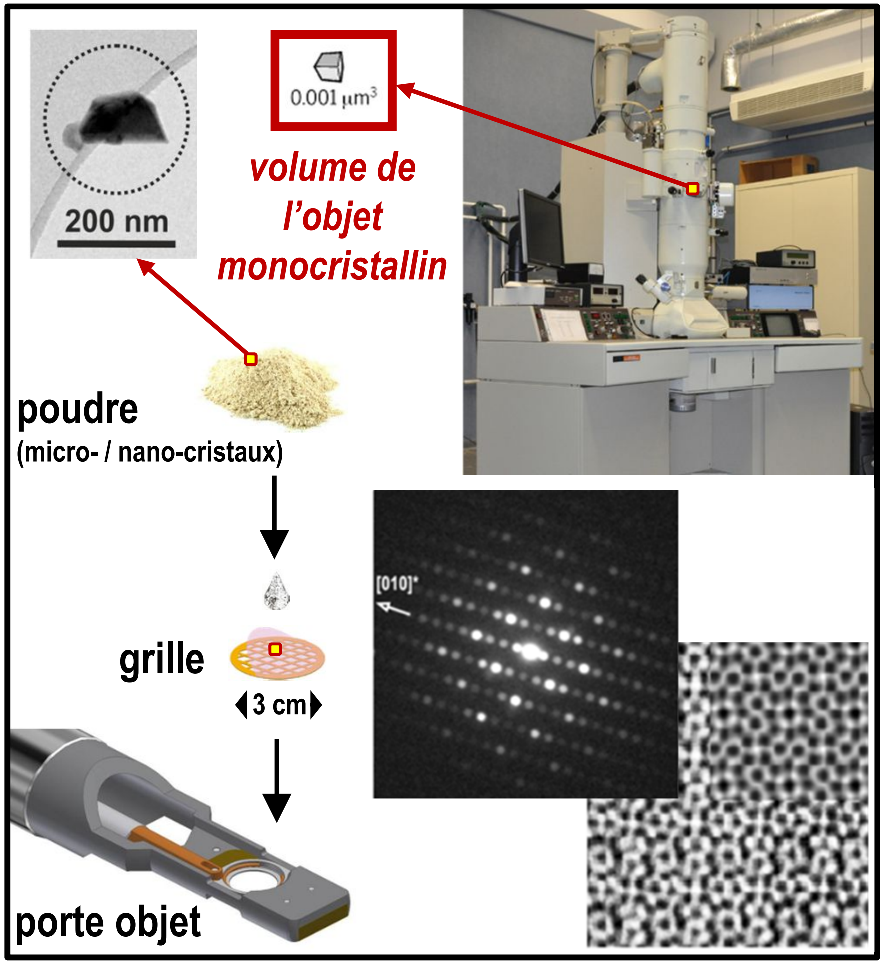
✗ Not always successful: phases mixture, large volume cell, aperiodic phases, thin films

Problem of convolution of peaks and/or small diffracting volumes

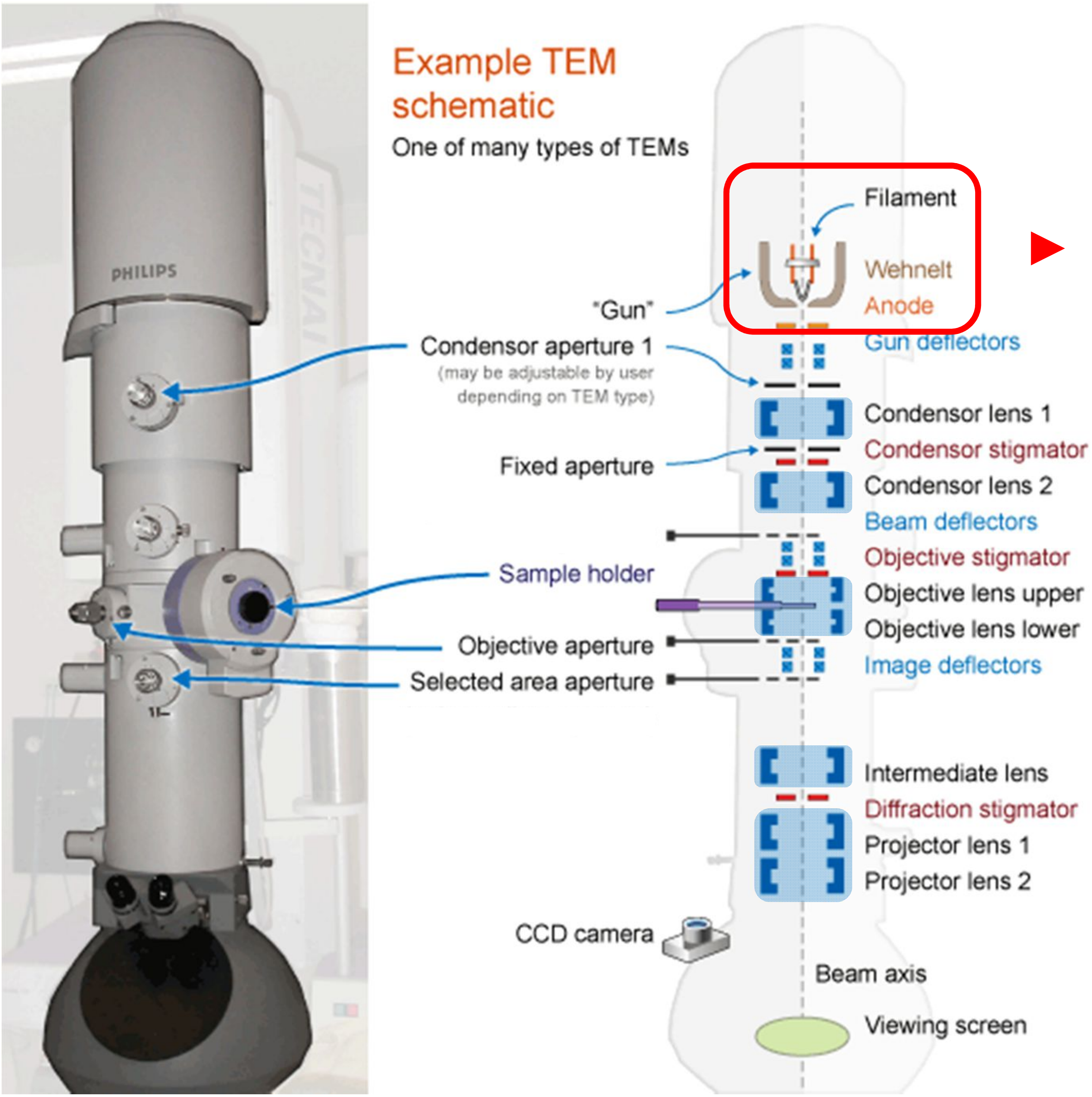
Solving the structure of an unknown compound ?

SC-XRD ◄ tens of micrometer ► Electron diffraction

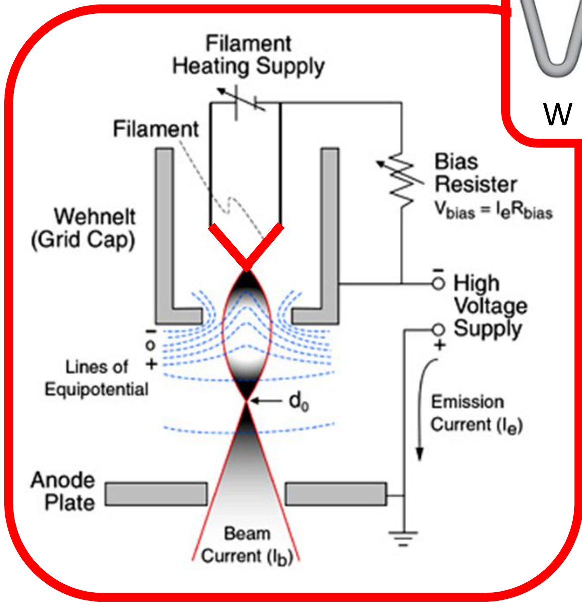




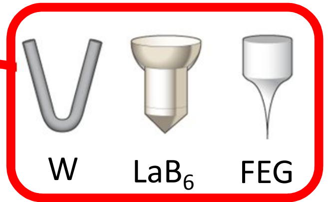
Transmission Electron Microscope (TEM)

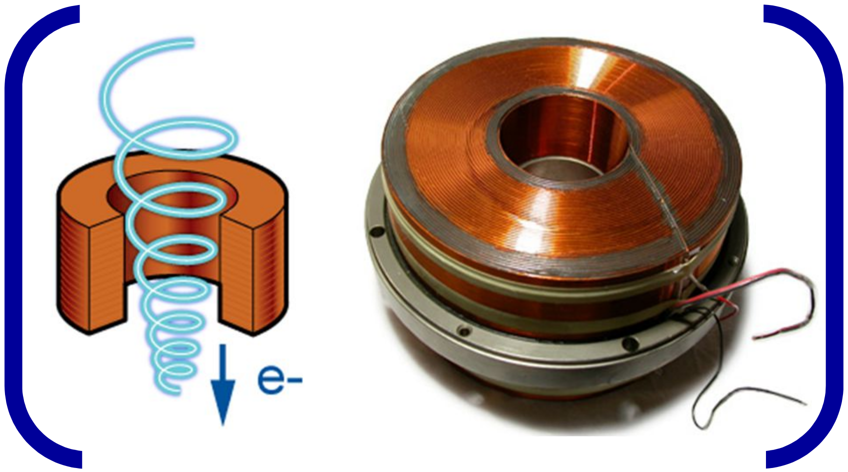


electron gun



filament

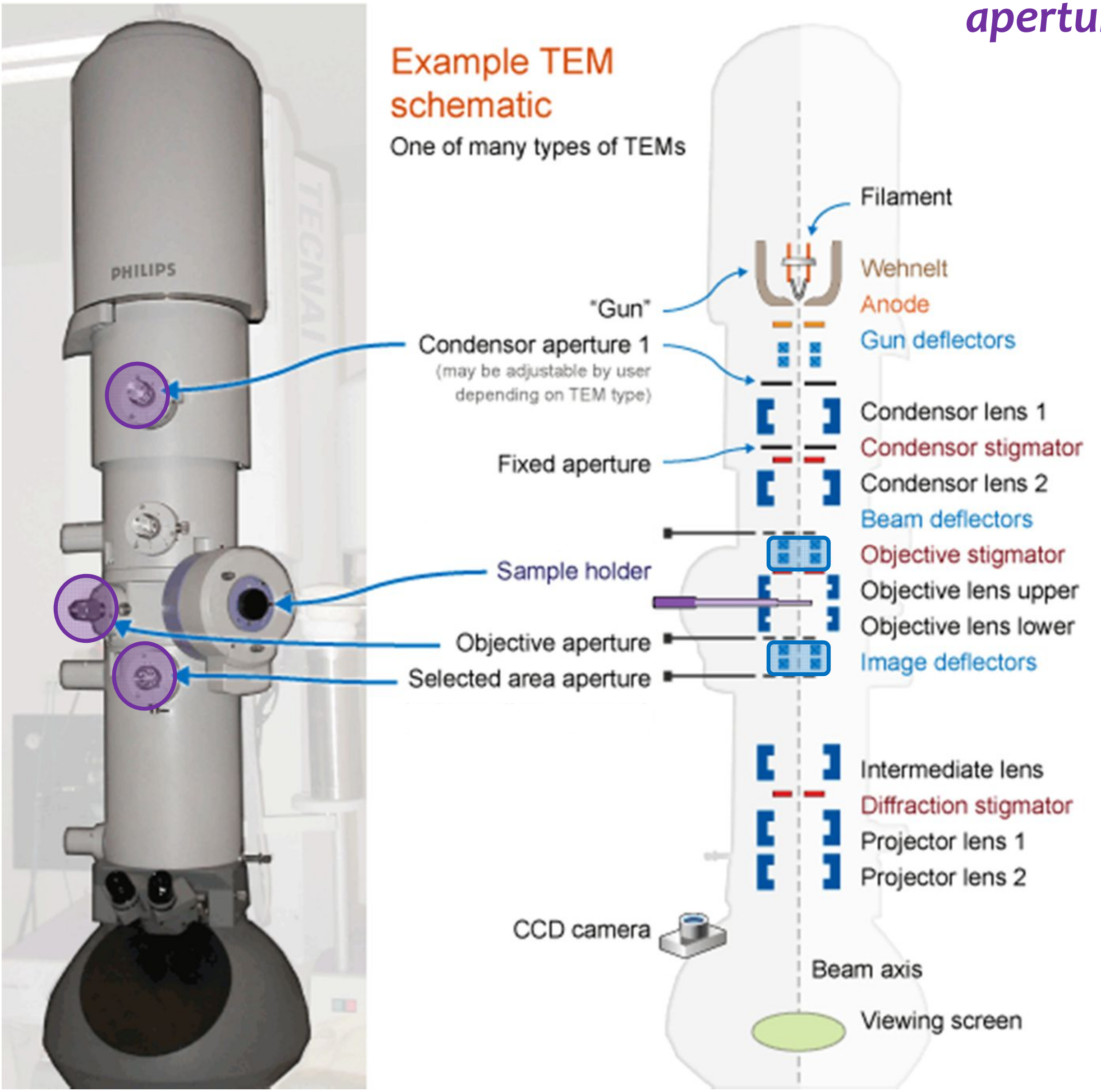




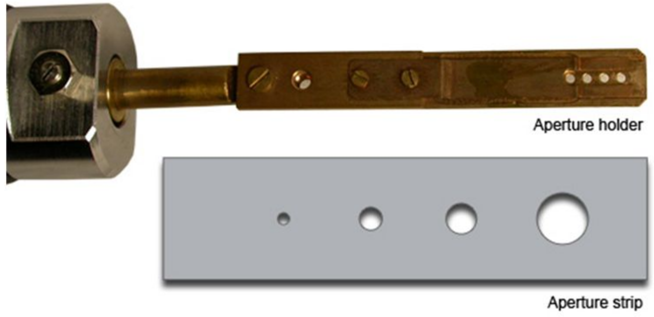
electromagnetic lens

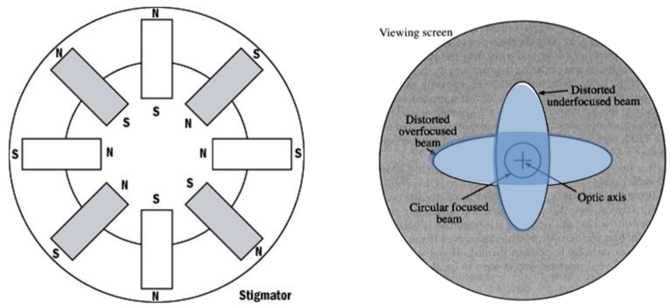
http://www.ammrf.org.au/myscope

Transmission Electron Microscope (TEM)

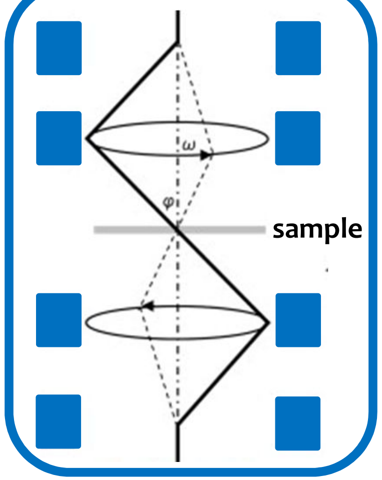


aperture





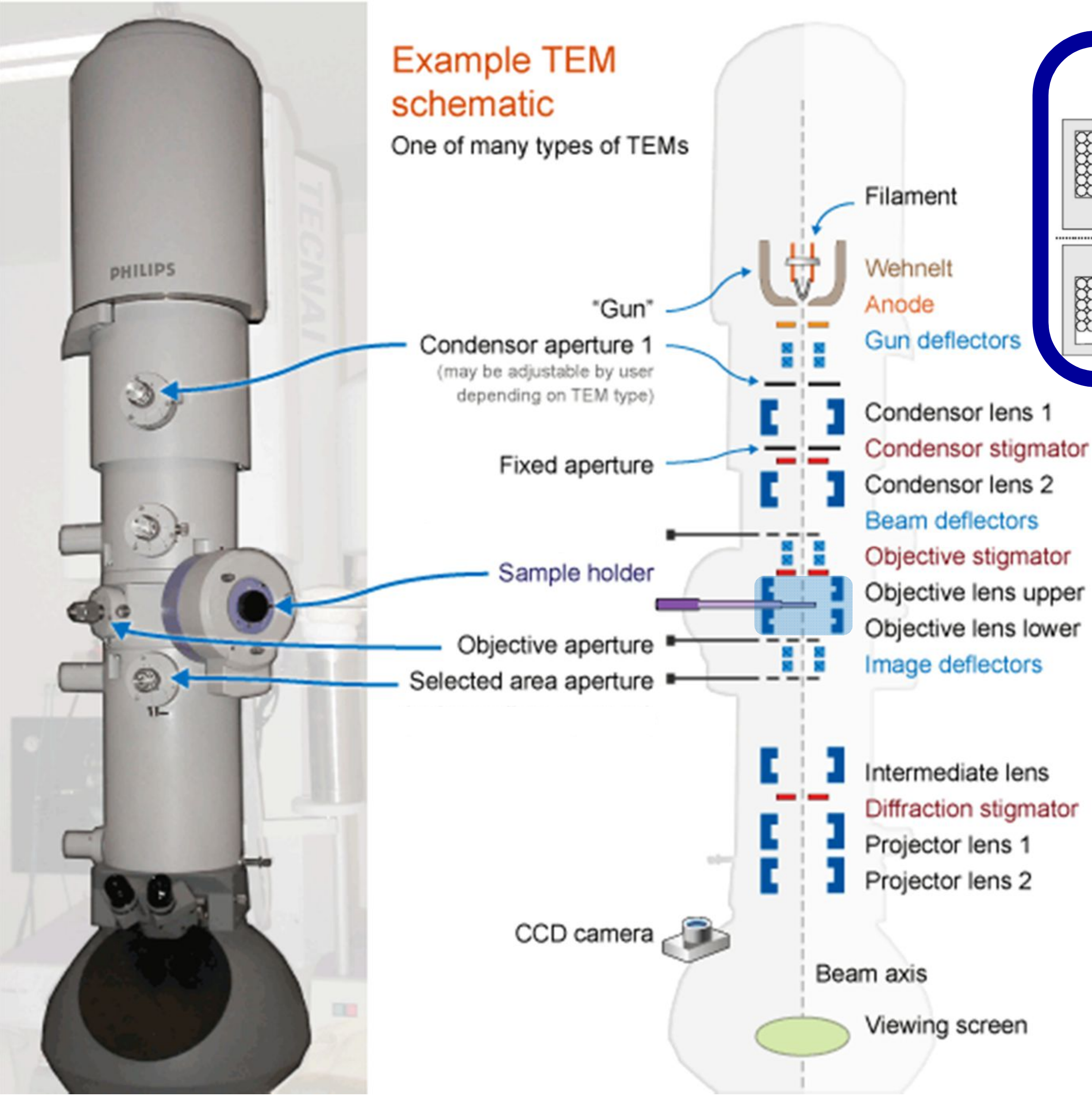
stigmator



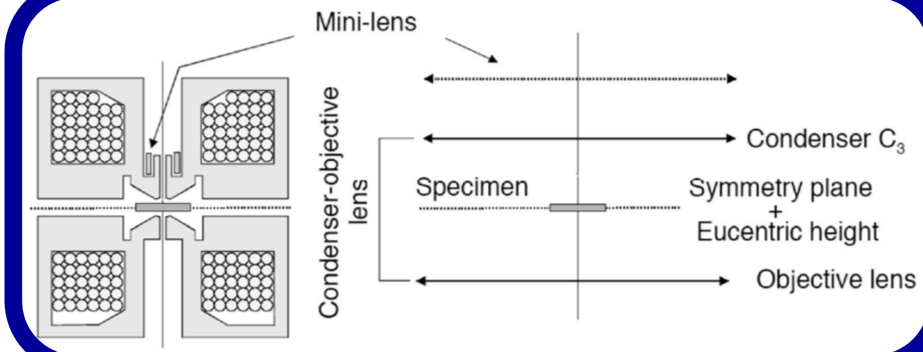
deflection coil

http://www.ammrf.org.au/myscope

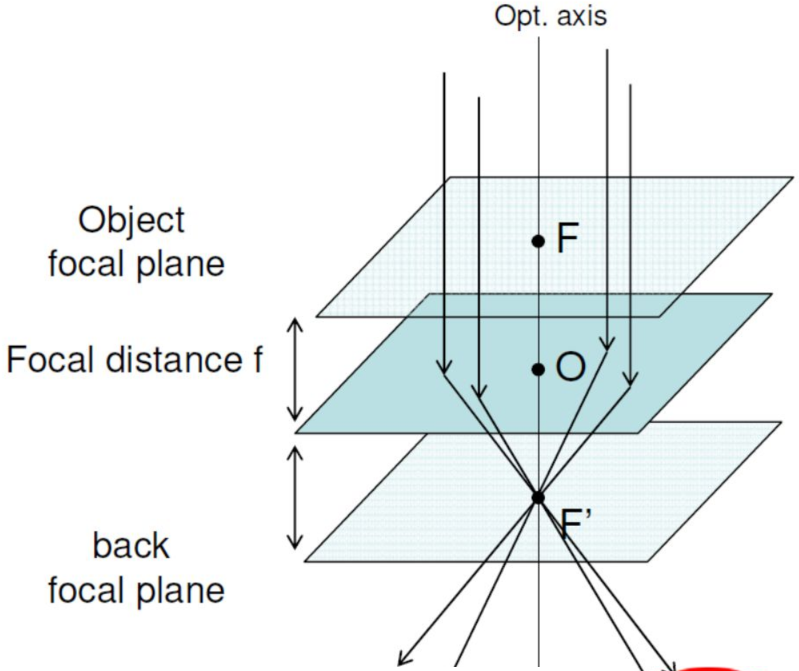
Transmission Electron Microscope (TEM)



objective lens : twin lens



thin converging lens

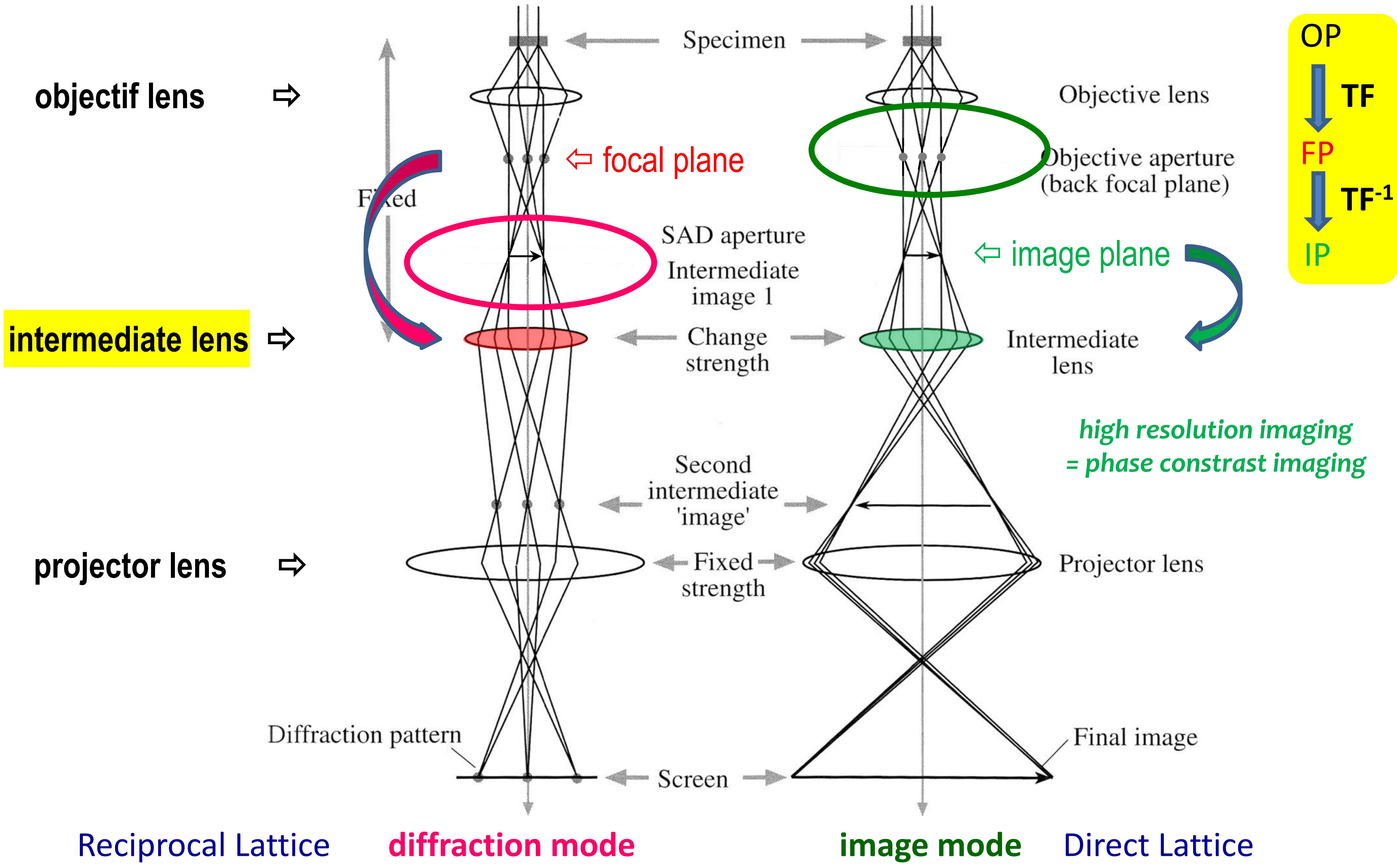


http://www.ammrf.org.au/myscope

from D. Jacob - CrystElec2018

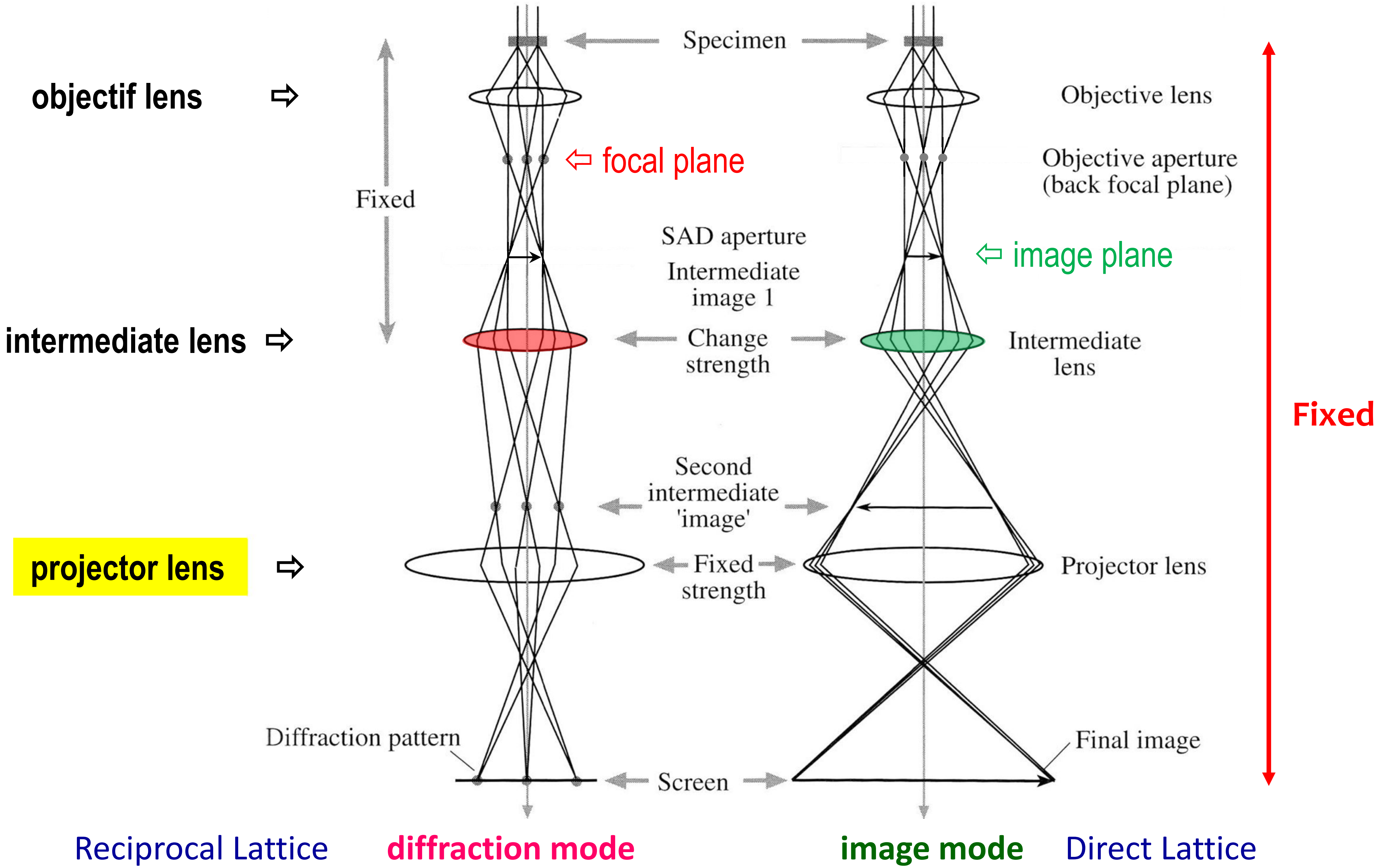
Electron Diffraction

Fraunhoffer diffraction ⇨ observation at an infinite distance



Electron Diffraction

Fraunhoffer diffraction ⇨ observation at an infinite distance



Electron-matter interactions = strong coulomb interactions

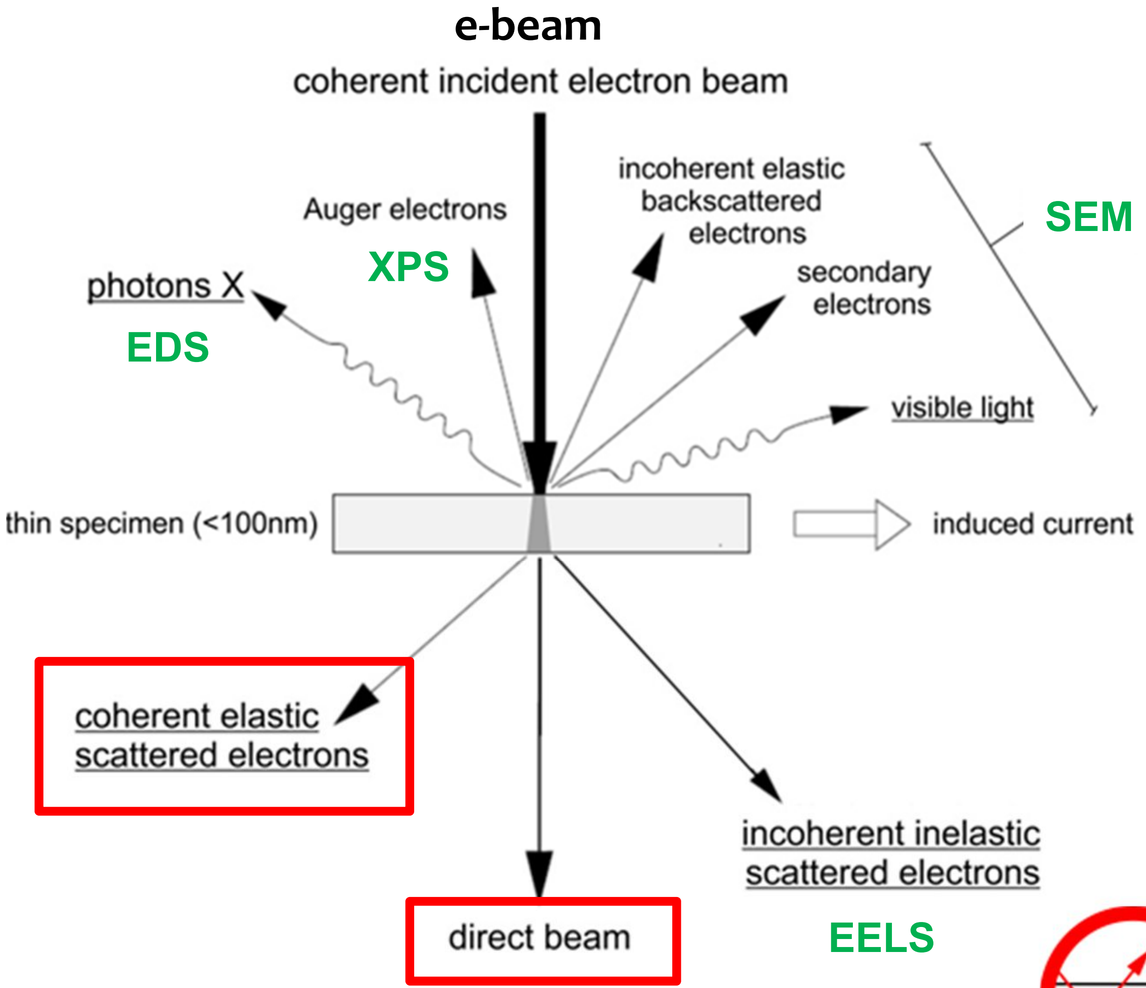
Electrons interact with the electrostatic potential of the crystal (electrons + nucleus)

diffraction

coherent elastic scattering

no energy or wavelength change

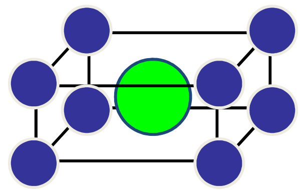
of the incident wave



Amplitude scattered by a crystal

$$A(\vec{s}) = \sum f_j(\vec{g}) . e^{i2\pi(\vec{r_j}.\vec{g})}$$

transmission function



in " 3D "

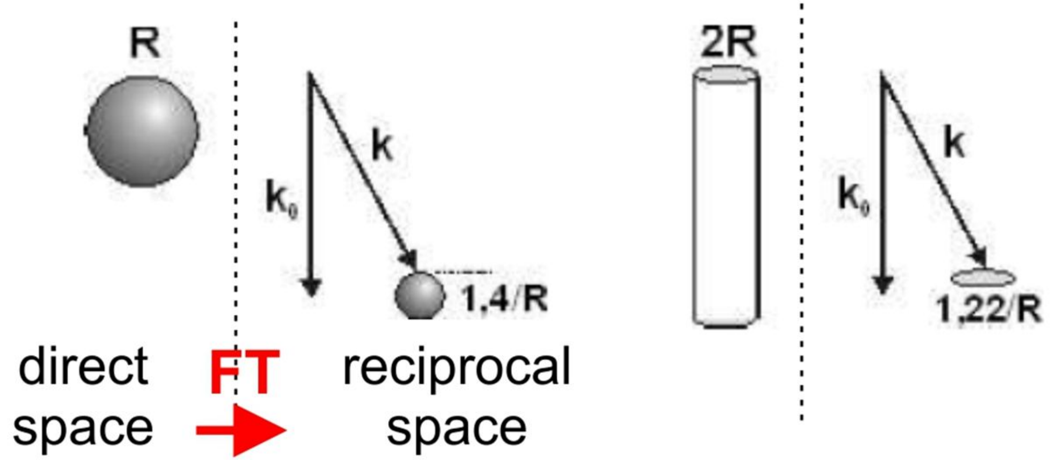
$$A(\vec{g}) = \sum_j f_j(\vec{g}) . e^{i2\pi(\vec{r_j}.\vec{g})} = F_{hkl}(\vec{g}) . \sum_m e^{i2\pi(\vec{r_m}.\vec{g})}$$

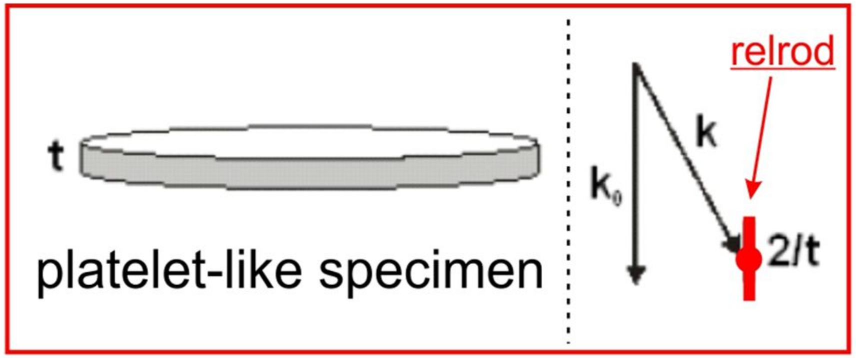
with $\vec{r_j} = \vec{r_n} + \vec{r_m}$

atoms in the elementary unit cell

crystal form factor

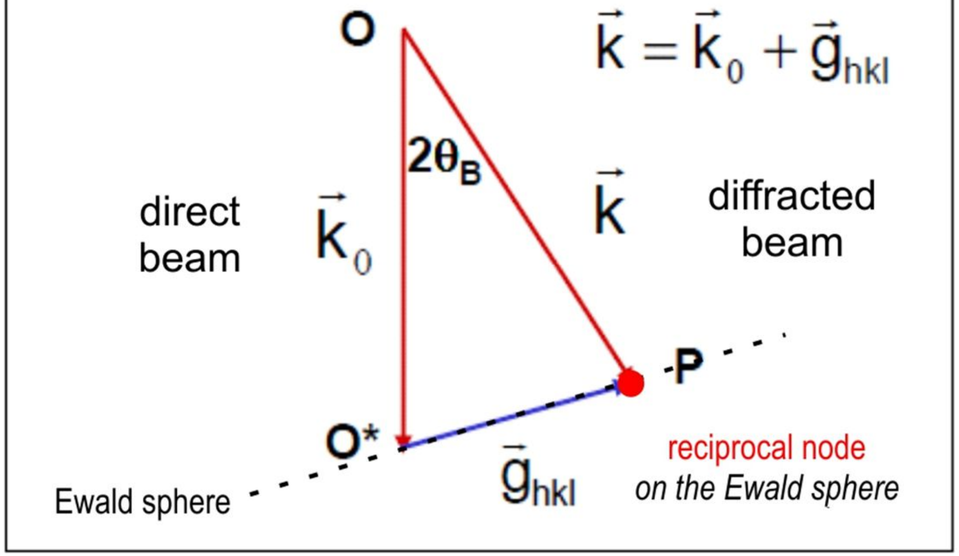
Amplitude scattered by a crystal (finite size effects)



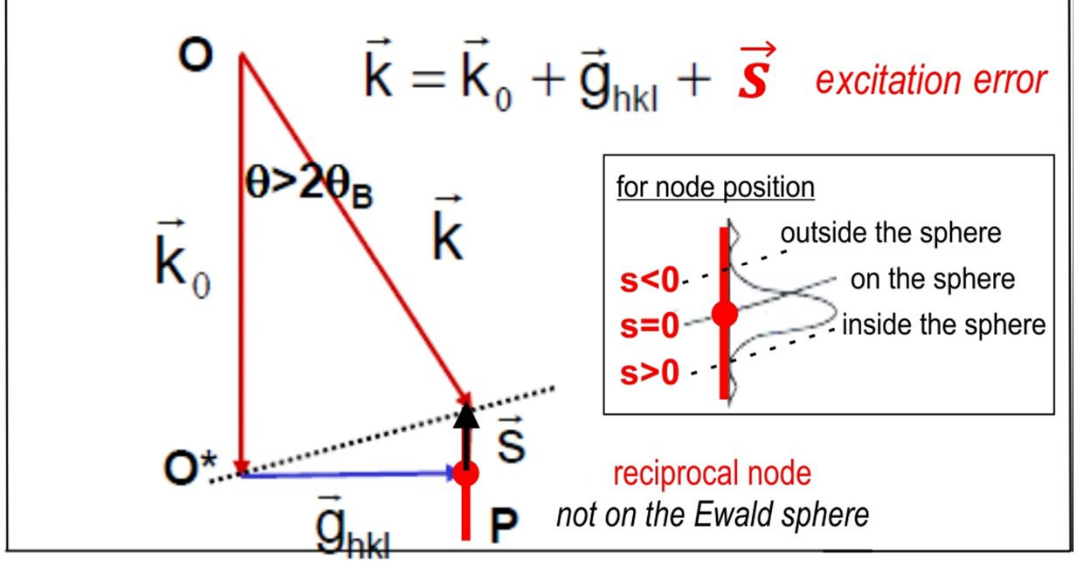


electron diffraction

exact Bragg condition



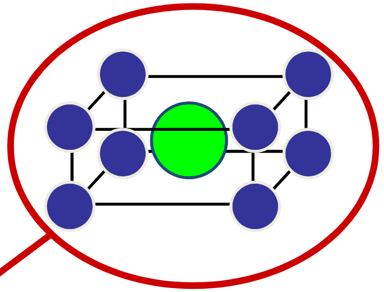
relaxed Bragg condition



Amplitude scattered by a crystal

$$A(\vec{s}) = \sum f_j(\vec{g}).e^{i2\pi(\vec{r_j}.\vec{g})}$$

transmission function



in " 3D "

$$A(\vec{g}) = \sum_j f_j(\vec{g}).e^{i2\pi(\vec{r_j}.\vec{g})} = F_{hkl}(\vec{g}).\sum_m e^{i2\pi(\vec{r_m}.\vec{g})} \quad \text{with} \quad \vec{r_j} = \vec{r_n} + \vec{r_m}$$

atoms in the elementary unit cell

$$F_{hkl}(\vec{g}) = \sum_n f_n(\vec{g})e^{i2\pi(\vec{r_n}.\vec{g})} = \sum_n f_n(\vec{g})e^{i2\pi(h.x_n+k.y_n+l.z_n)}$$

atomic scattering factors

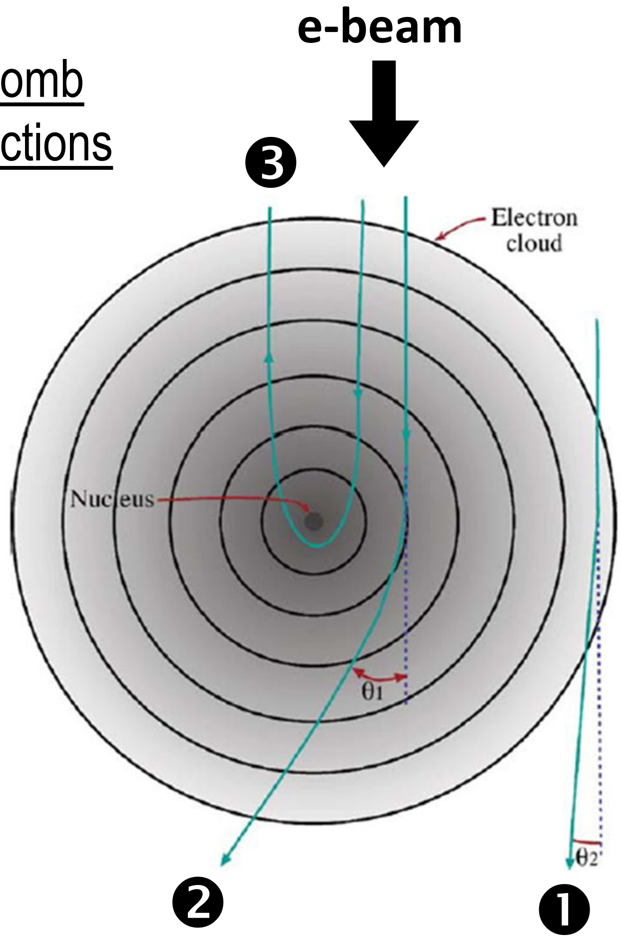
Electron case : electrons interact with the electrostatic potential of the crystal (electrons + nucleus)

➡ $V_n(\vec{r})$ electrostatic potential of atom (ion) n

X-ray case : photons are scattered by the electron cloud and the contribution from the nucleus is neglectable

➡ $\rho_n(\vec{r})$ electron density of atom (ion) n

coulomb interactions



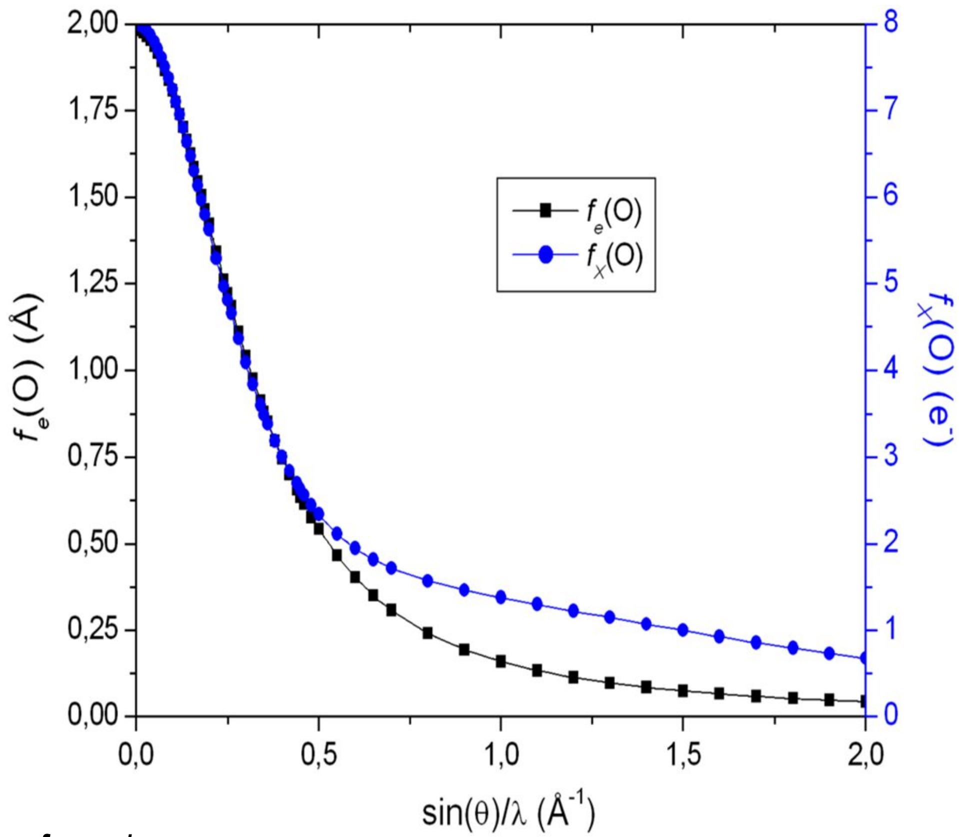
elastic e- / e- repulsion ⇨ low scattering angles ❶
e- / nucleus attraction ⇨ higher scattering angles ❷
⇨ backscattering ❸

Atomic scattering factor

X-ray case : photons are scattered by the electron cloud and the contribution from the nucleus is neglectable

$$f_n{}^X\left(\frac{\sin\theta}{\lambda}\right) = \sum_{i=1}^{4} a_i\, e^{-b_i \frac{\sin^2\theta}{\lambda^2}} + c \qquad f_n{}^X(0) = Z_n$$

Electron case : electrons interact with the electrostatic potential of the crystal (electrons + nucleus)



$$f_n{}^e(\vec{g}) = \frac{me^2}{2h^2}\left(\frac{\lambda}{\sin\theta}\right)^2 \left(Z_n - f_n{}^X(\vec{g})\right)$$ *Mott–Bethe formula*

h *Planck's constant (6.626 x 10^{-34} J s)*

m *electron mass (9.109 x 10^{-31} kg)*

e *electronic charge (1.60 x 10^{-19} C)*

$$f_n^e(0) = \frac{4\pi^2 me^2}{3h^2} Z_n \langle r^2 \rangle$$ *Ibers formula*

r *atomic radius*

Wavelength of the incident electron beam

$$\lambda = \frac{h}{\sqrt{2meV}} \frac{1}{\sqrt{1+\frac{eV}{2mc^2}}}$$

relativistic effects

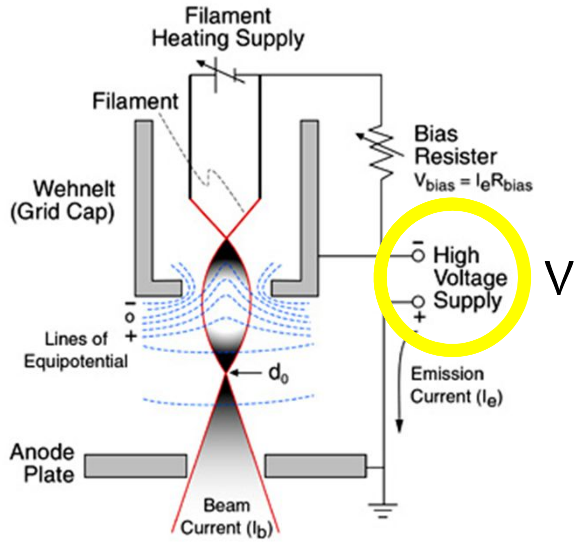
V ⇔ λ

120 kV = 0.0335Å

200 kV = 0.0251Å

300 kV = 0.0197Å

electron gun



The Ewald sphere radius (1/λ) is large in electron diffraction:

- ⇨ can be assimilated to a plane
- ⇨ diffraction condition verified for several reciprocal nodes
- ⇨ direct observation of undistorted reciprocal planes (**zone axis patterns**)

Zone Axis Patterns (ZAP)

Several (h_i k_i l_i) planes intersect along the direction [uvw] *(zone axis)* of the crystal.

When the incident e-beam goes through the crystal along [uvw], these planes are close to Bragg's condition $\Rightarrow$ **diffraction.**

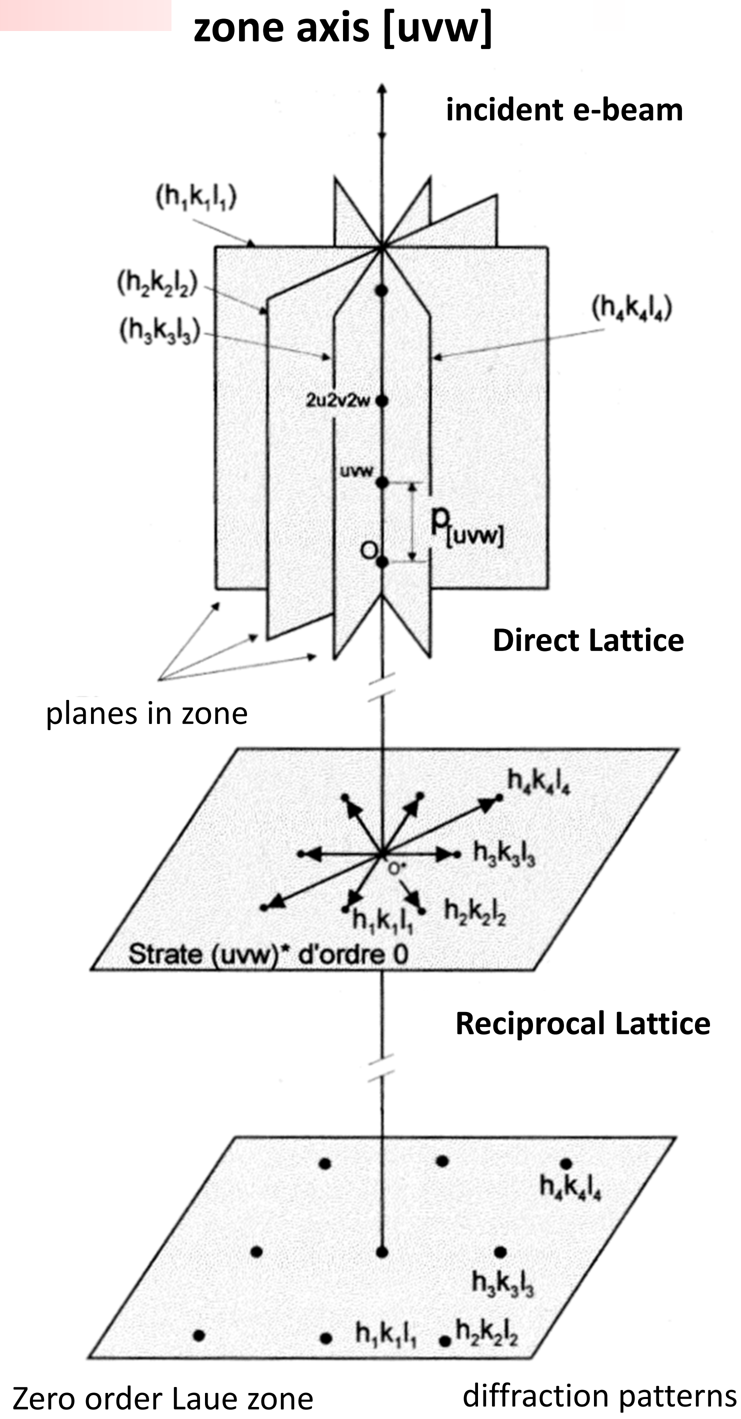
these planes obey the relation:

$$hu + kv + lw = 0$$

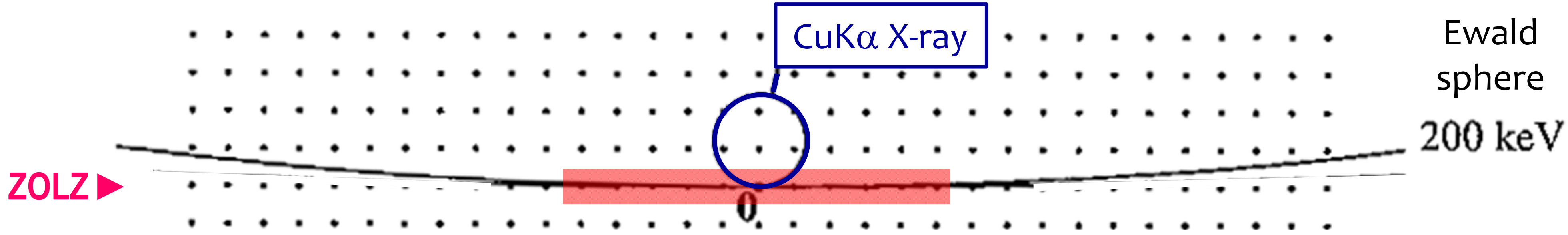
$$(uvw)^* \perp [uvw]$$

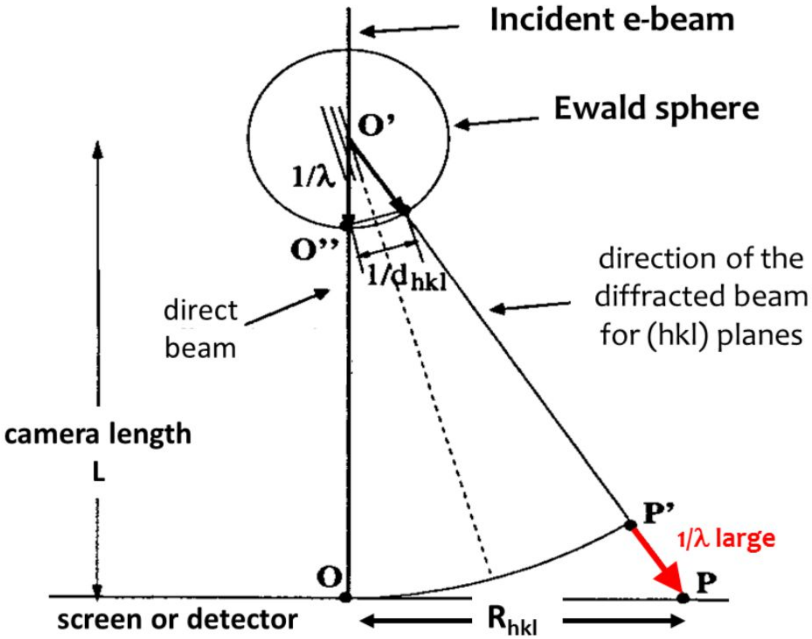
The Ewald sphere is tangent to the reciprocal lattice plane passing by the origin and containing all $h_ik_il_i$ spots (RL nodes) forming the

Zero Order Laue Zone (ZOLZ).



Zone Axis Patterns and ZOLZ

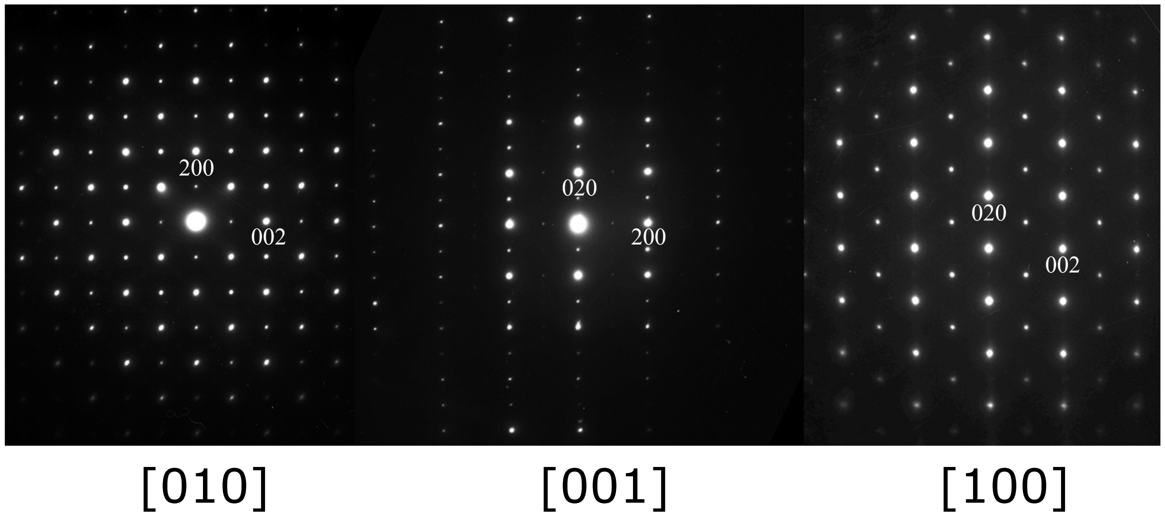




$$d_{hkl} = \frac{\lambda L}{R_{hkl}}$$

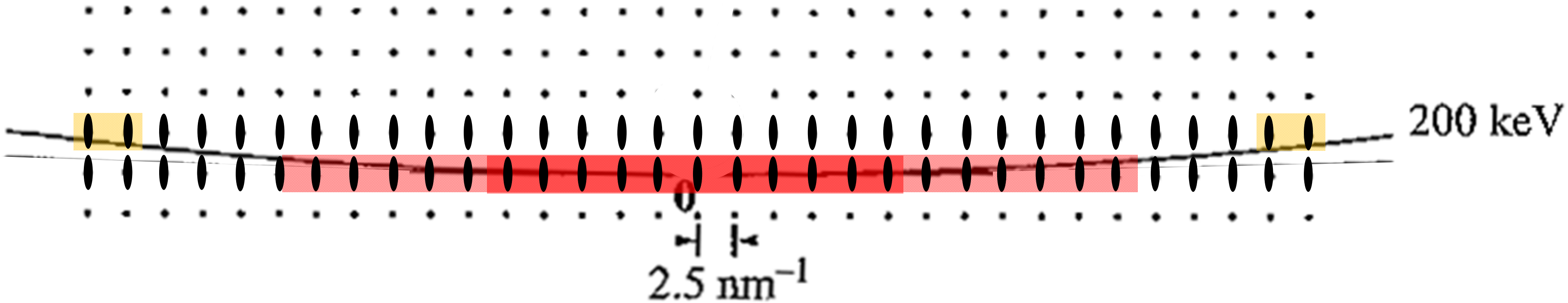
Zone Axis Patterns for La_2NiMnO_6

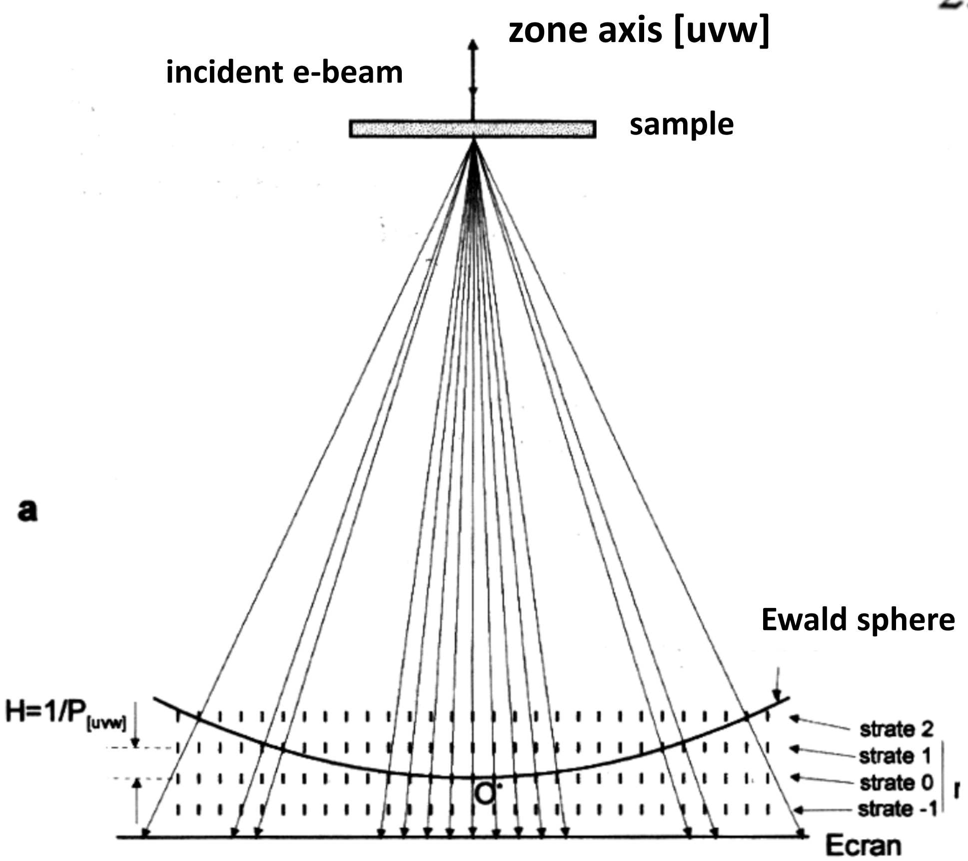
Pnma (*a*≈5.50Å, *b*≈7.70Å and *c*≈5.50Å)

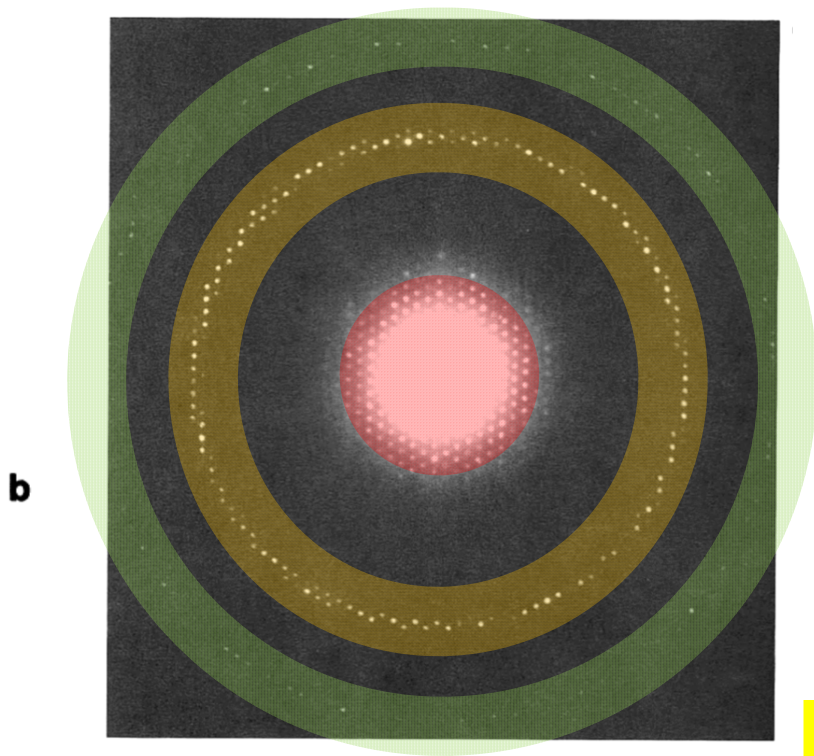


► lattice parameters and symmetry determination

Zone Axis Patterns and Higher Order Laue Zones (HOLZ)







Laue Zones
▼

Zero Order
(ZOLZ)

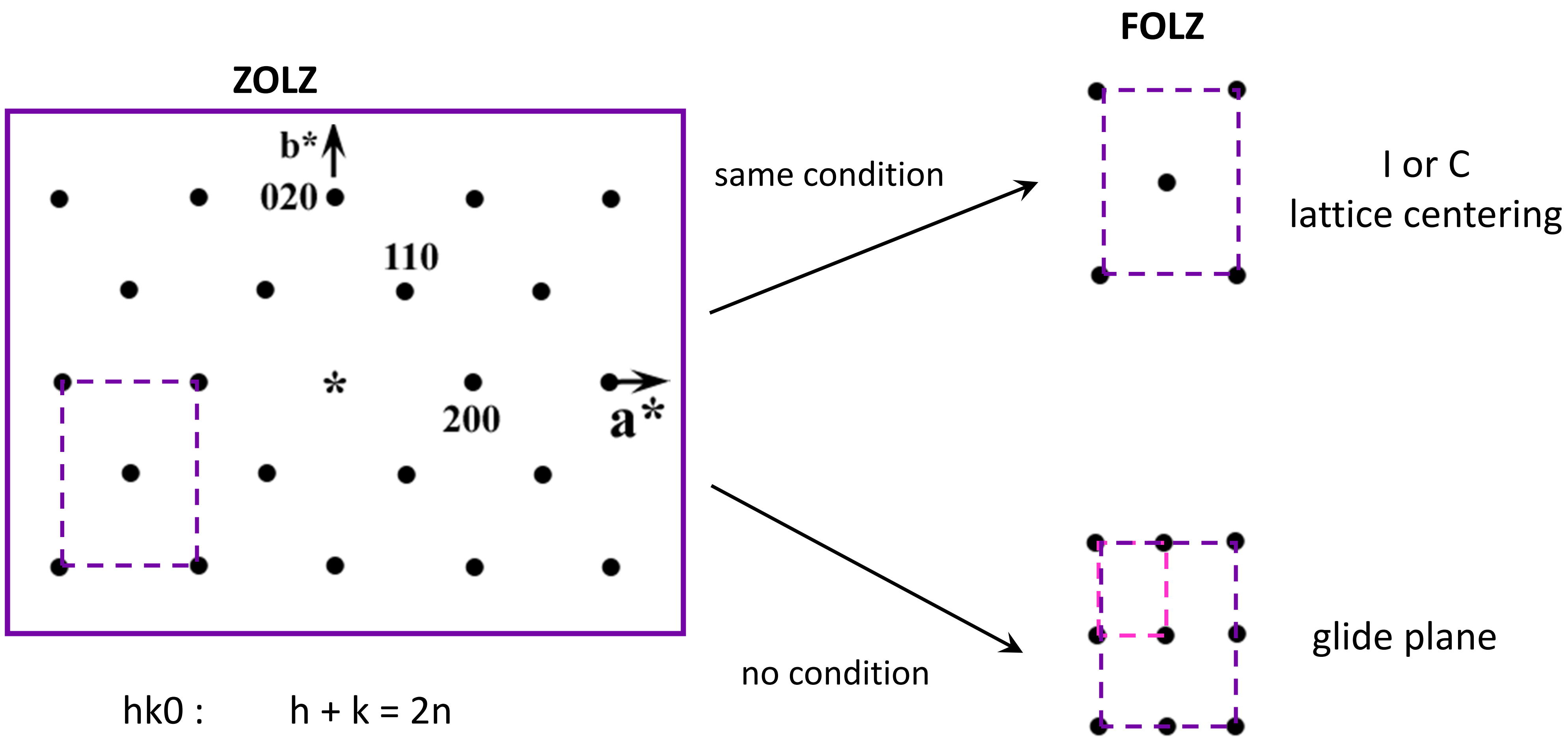
First Order
(FOLZ)

Second Order
(SOLZ)

...

2D ⇨ 3D

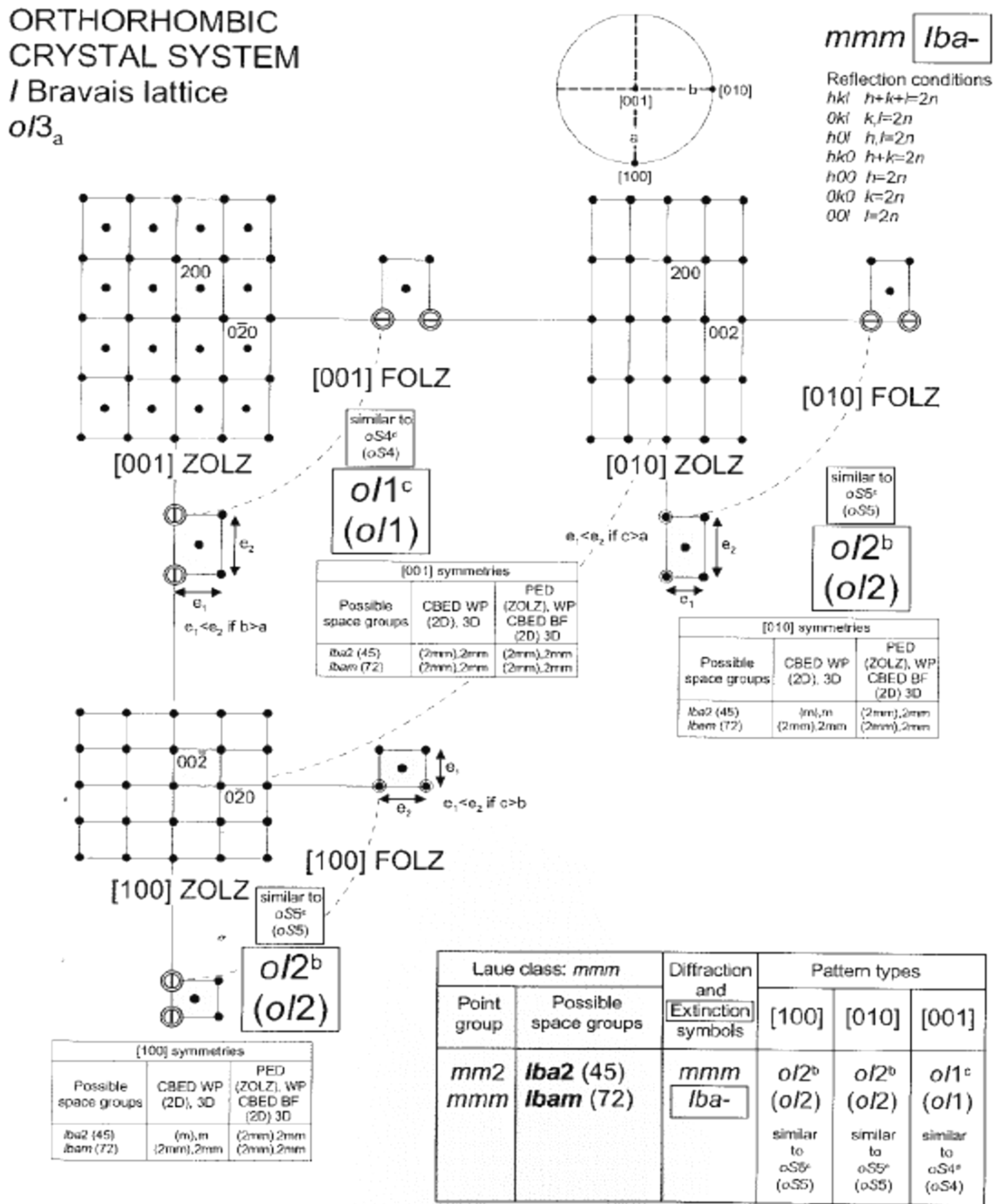
Symmetry determination from zone-axis patterns



hk0 : h + k = 2n

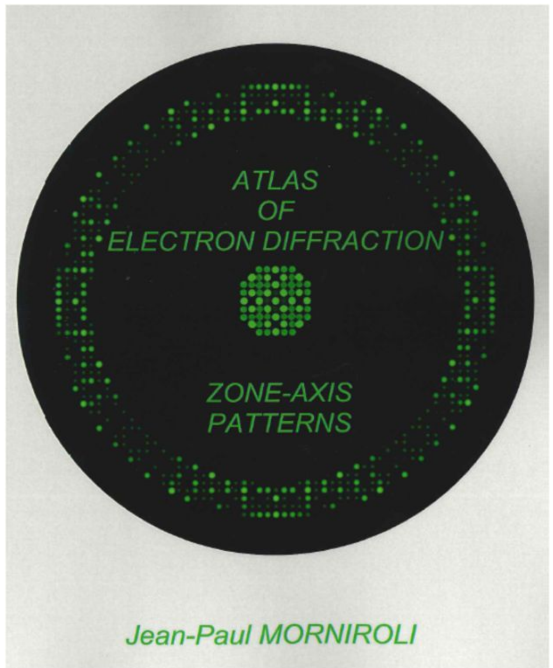
I or C lattice centering or glide plane n ⊥ c

Symmetry determination from zone-axis patterns

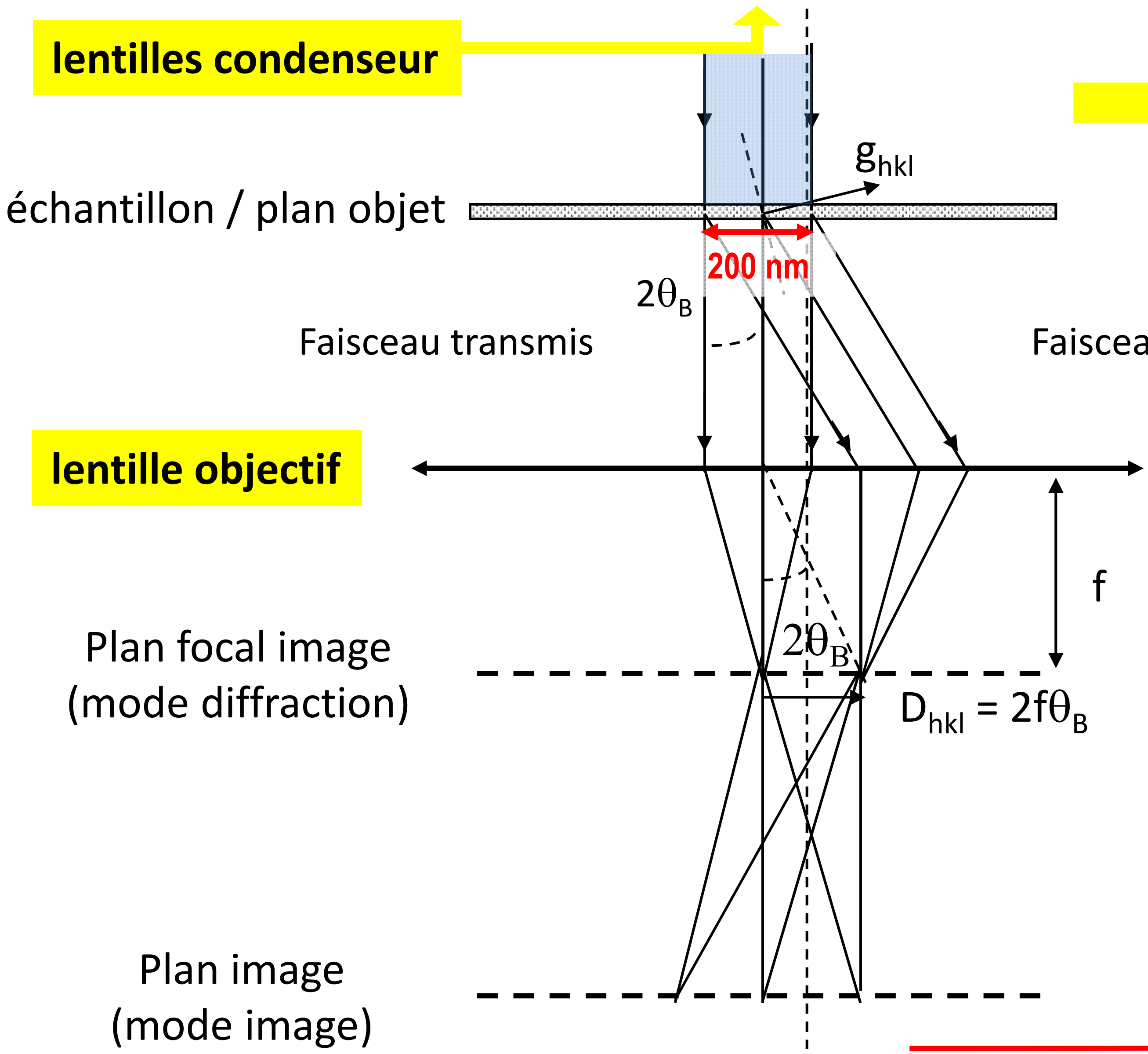


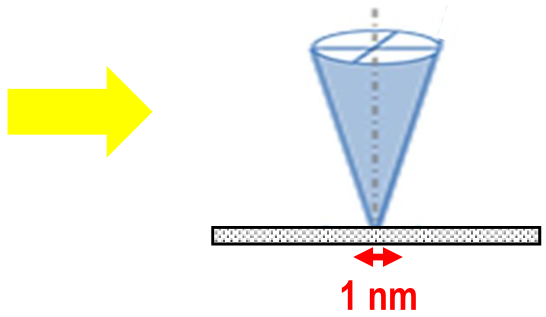
“This atlas contains all the useful theoretical zone-axis electron diffraction patterns drawn for each of the 187 extinction symbols. Comparison of these theoretical patterns with experimental Precession Electron Diffraction (PED) patterns and Convergent-Beam Electron Diffraction (CBED) patterns allows, through a systematic method, an easy unambiguous identification of the space group of a crystal.”

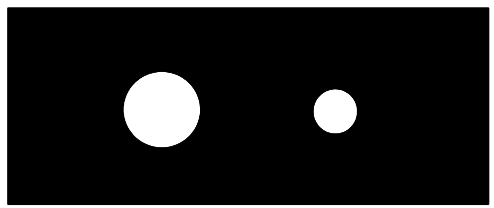
Jean-Paul Morniroli



Diffraction en faisceaux parallèle ► cliché de points

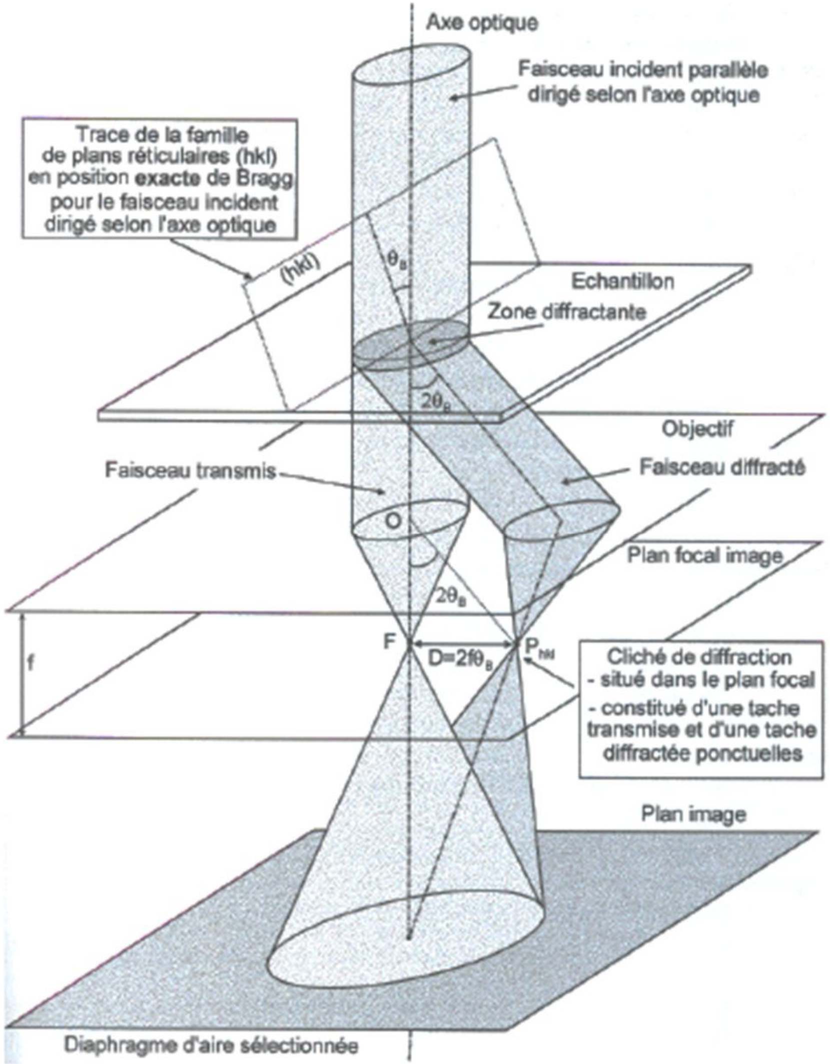




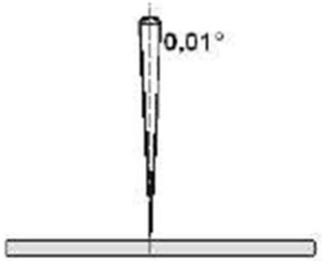


⇒ Cliché de points (deux-ondes)

en faisceau parallèle ← - - - - - - - - → **en faisceau convergent**

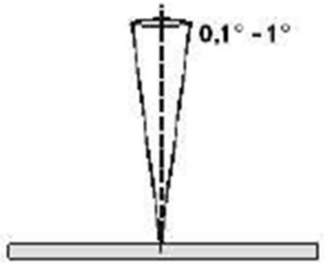


Diffraction électronique en sélection d'aire
Selected Area Electron Diffraction

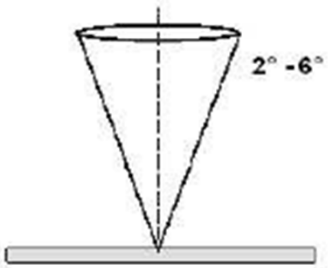


microdiffraction

Convergent Beam Electron Diffraction

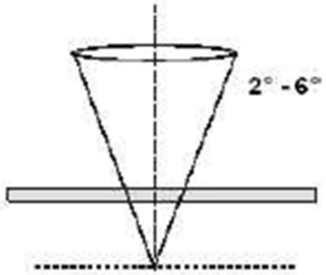


CBED



Kossel

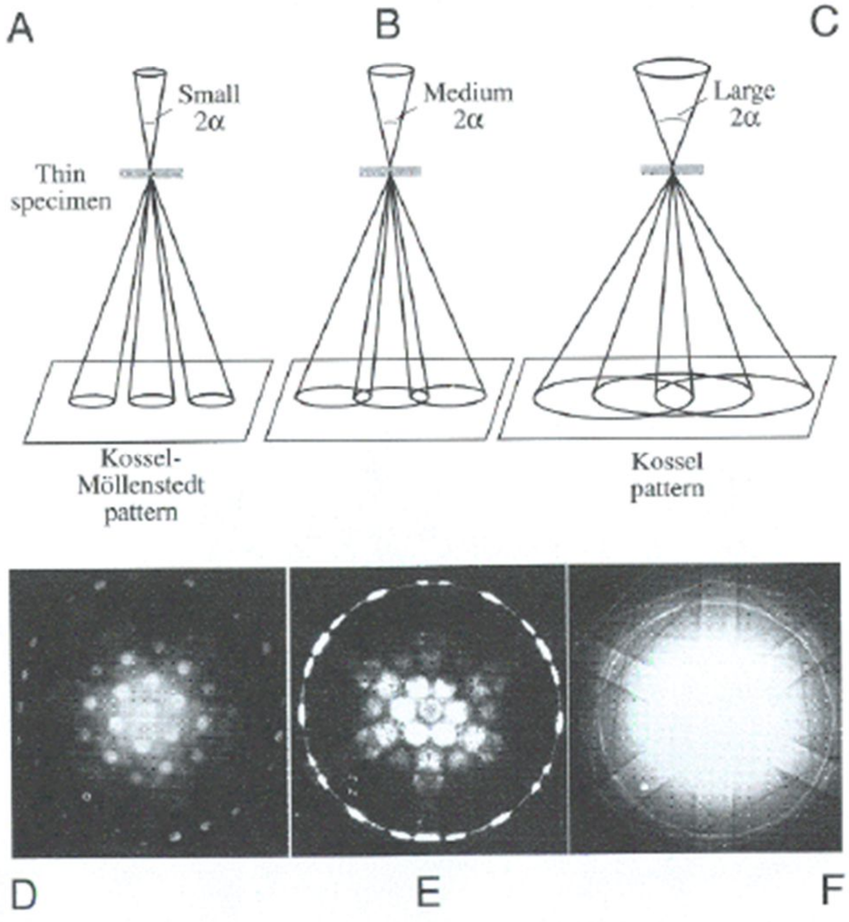
Large Angle Convergent Beam Electron Diffraction

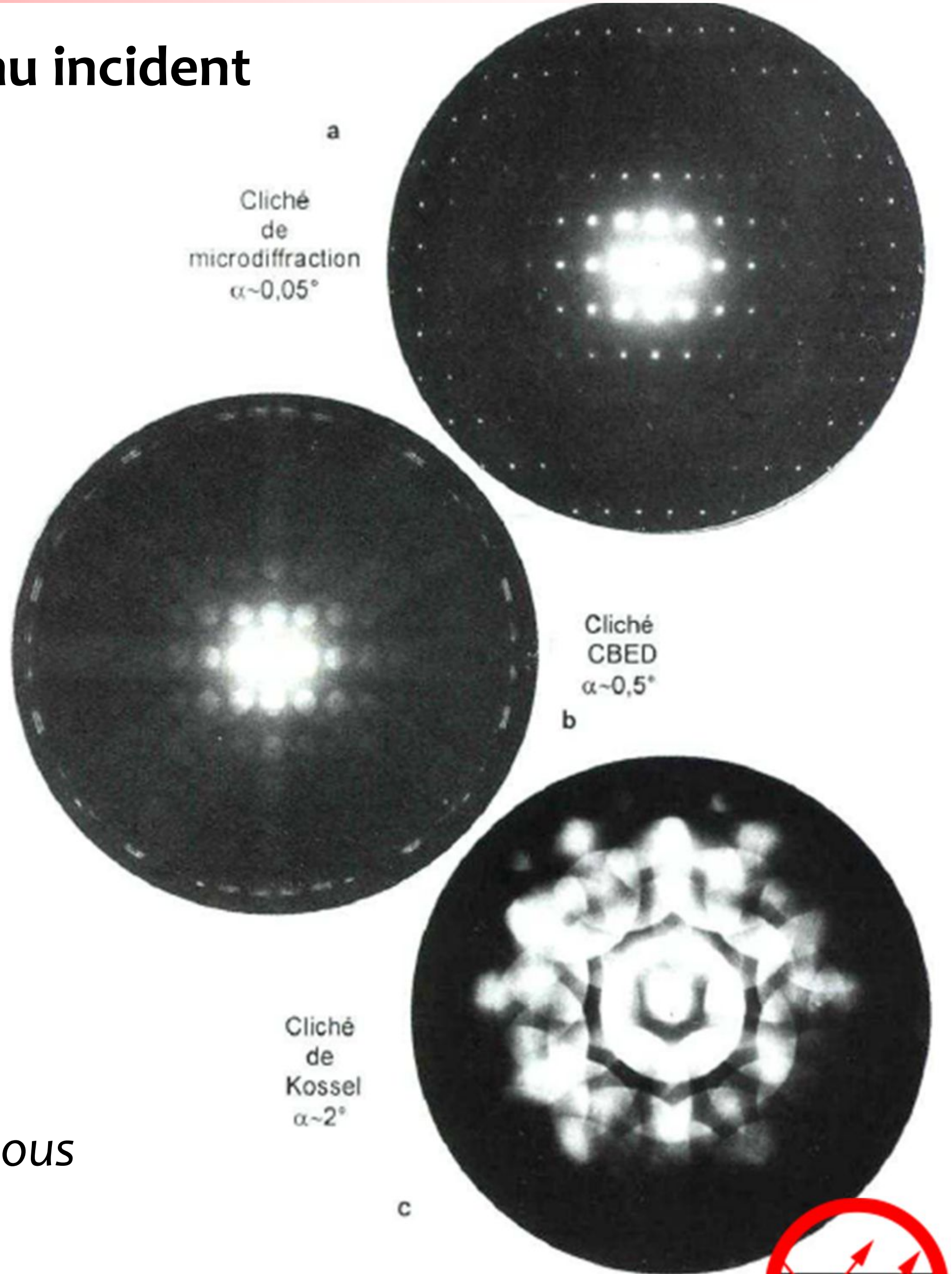


LACBED

Electron Diffraction

Effet de la convergence du faisceau incident



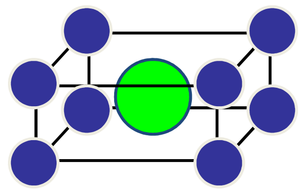


Les nœuds du réseau réciproque se présentent sous la forme de disques de plus en plus larges

Amplitude scattered by a crystal

$$A(\vec{s}) = \sum f_j(\vec{g}) . e^{i2\pi(\vec{r_j}.\vec{g})}$$

transmission function



in " 3D "

$$A(\vec{g}) = \sum_j f_j(\vec{g}) . e^{i2\pi(\vec{r_j}.\vec{g})} = F_{hkl}(\vec{g}) . \sum_m e^{i2\pi(\vec{r_m}.\vec{g})}$$

with $\vec{r_j} = \vec{r_n} + \vec{r_m}$

atoms in the elementary unit cell

crystal form factor

atomic scattering factors

$$F_{hkl}(\vec{g}) = \sum_n f_n(\vec{g}) e^{i2\pi(\vec{r_n}.\vec{g})} = \sum_n f_n(\vec{g}) e^{i2\pi(h.x_n + k.y_n + l.z_n)}$$

atomic positions

measure $I_g = ||A_g||^2$

the phase is lost

TF^{-1}

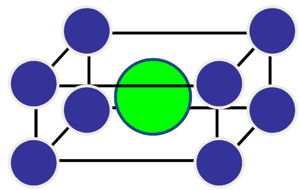
Motif de diffraction

Fraunhofer Diffraction = FT of the transmission function of the object

Amplitude scattered by a crystal

$$A(\vec{s}) = \sum f_j(\vec{g}) . e^{i2\pi(\vec{r_j}.\vec{g})}$$

transmission function



in " 3D "

$$A(\vec{g}) = \sum_j f_j(\vec{g}) . e^{i2\pi(\vec{r_j}.\vec{g})} = F_{hkl}(\vec{g}) . \sum_m e^{i2\pi(\vec{r_m}.\vec{g})}$$

with $\vec{r_j} = \vec{r_n} + \vec{r_m}$

atoms in the elementary unit cell

crystal form factor

atomic scattering factors

$$F_{hkl}(\vec{g}) = \sum_n f_n(\vec{g}) e^{i2\pi(\vec{r_n}.\vec{g})} = \sum_n f_n(\vec{g}) e^{i2\pi(h.x_n + k.y_n + l.z_n)}$$

atomic positions

measure $I_g = ||A_g||^2$

the phase is lost

solving the phase problem

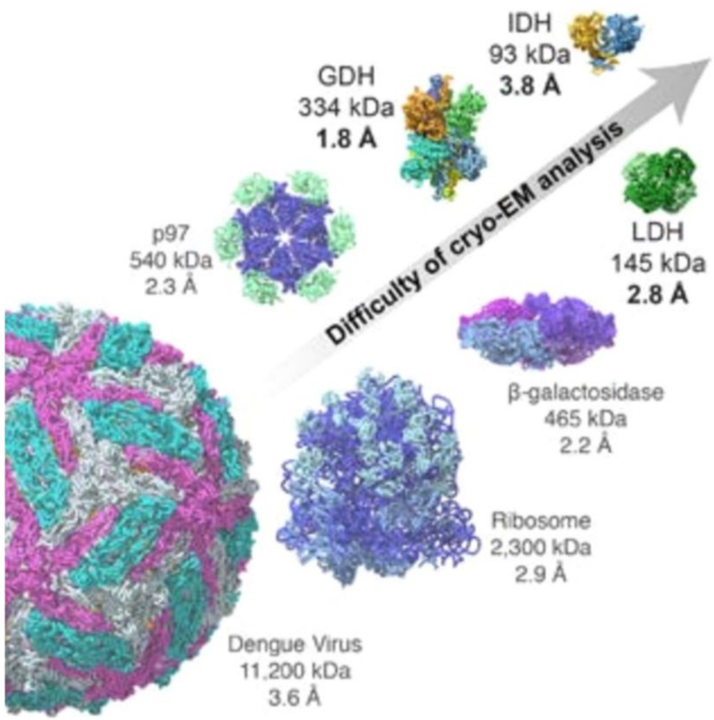
The Patterson method (heavy atom)
Direct methods
Molecular replacement
Isomorphic Replacement
Simulated annealing
Charge-flipping
...

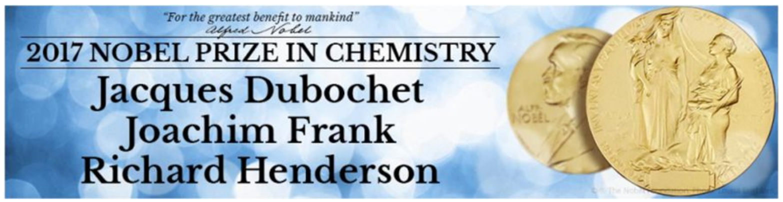
Solving the structure of an "unknown" compound ?

3b. Electron Microscopy Imaging

Cryo-Electron Microcopy

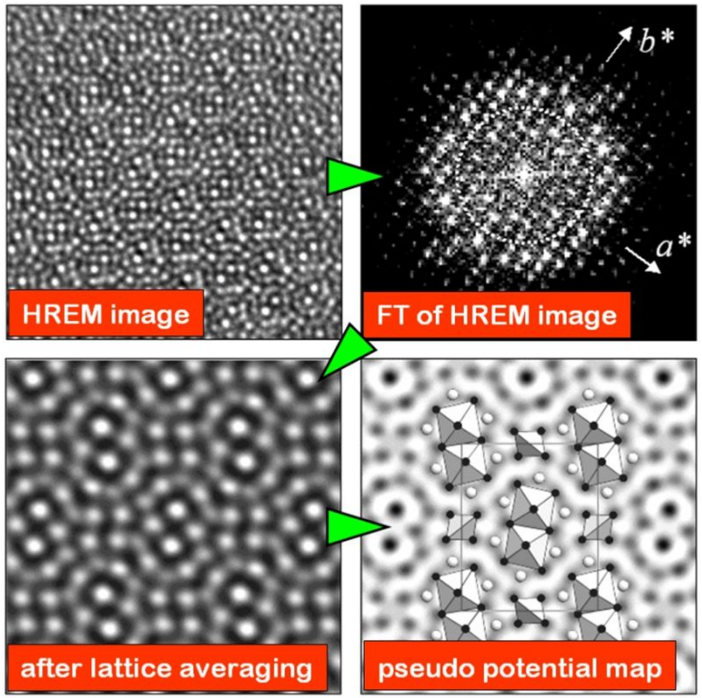
for the high-resolution structure determination of biomolecules in solution





High Resolution Electron Microscopy

from model building to ***direct phase retrieval***



see T. Weirich et al. Nature 382 (1996) 144-146

Analyse des intensitées diffractées ►► structure

Analyse simplifiée lorsque l'**approximation cinématique** est satisfaite $I \propto |F|^2$

↳ $I_{diffractée}$ est faible en comparaison de $I_{transmise}$

↳ pas de diffractions multiples des faisceaux diffractés

↳ diffraction purement élastique

N'EST PAS VERIFIEE EN DIFFRACTION ELECTRONIQUE !

Forte interaction e^- / matière ⇨ conditions dynamiques ($I_{diff.}$ 10^6 > rayons X)

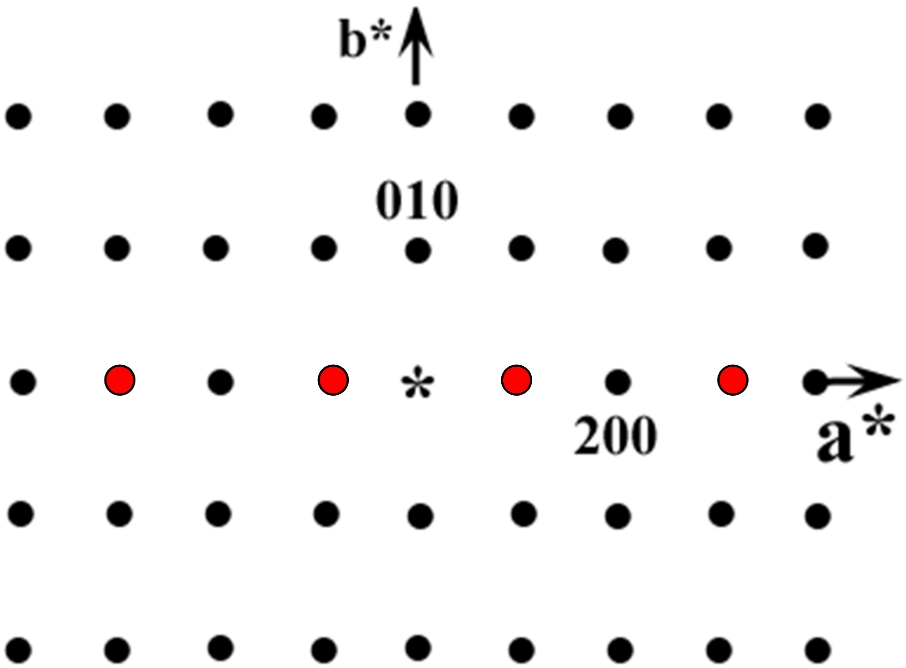
Les conditions de la diffraction en microscopie électronique sont un avantage notamment en ce qui concerne l'analyse de faible quantité de matière

… mais un désavantage en ce qui concerne la détermination structurale par les approches utilisées classiquement en diffraction des rayons X

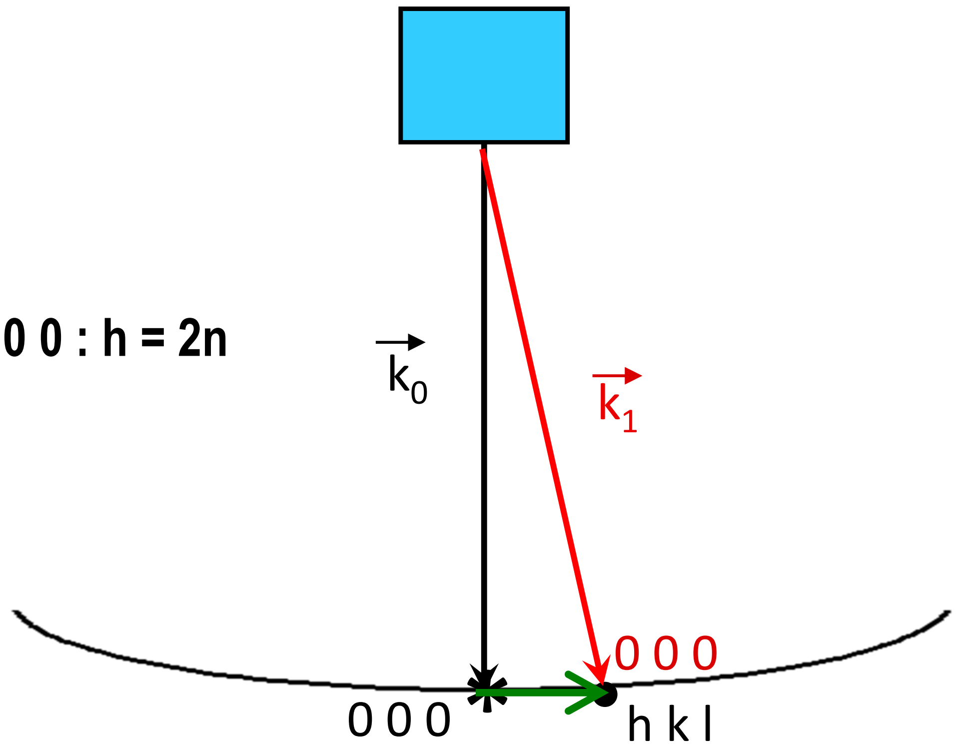
Effect of multiple scattering ► ►

A diffracted beam acts as a secondary incident beam :

visible effect ⇨ translation of the whole diffraction patterns



h 0 0 : h = 2n

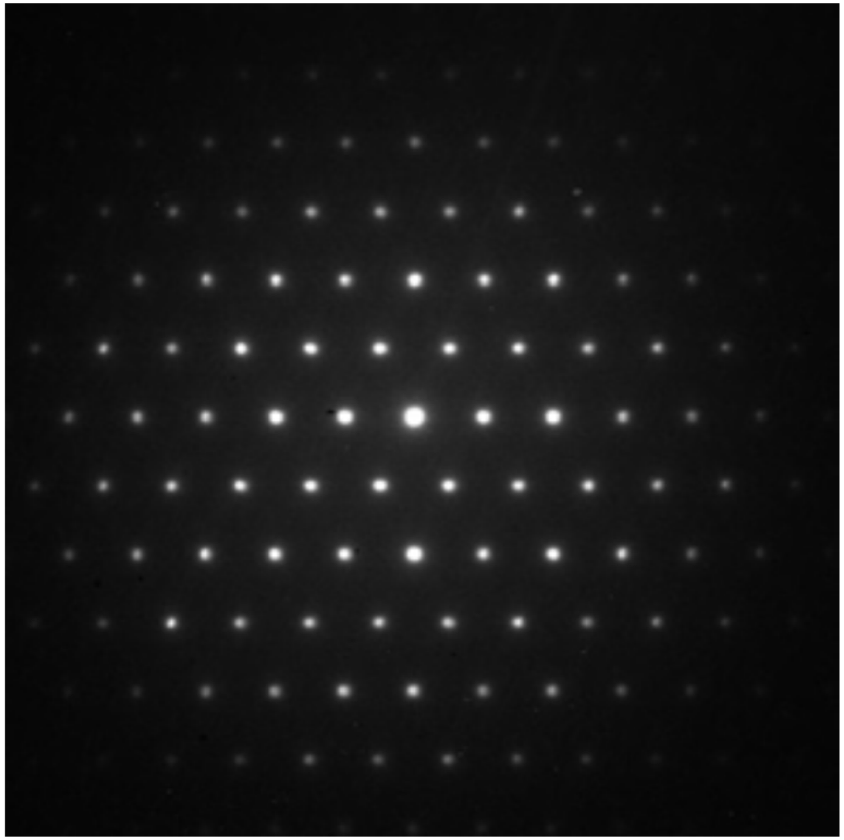


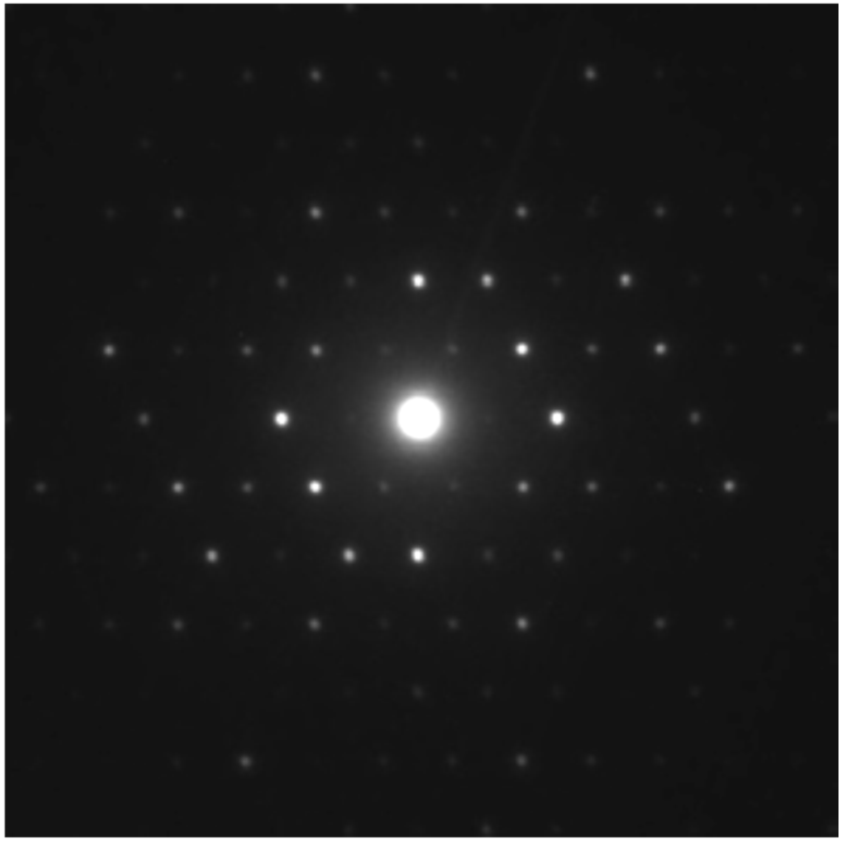
extra spots observed due to multiple scattering

affect all the diffracted intensities

SAED ►► **ZAP patterns have uniform intensities**

dynamical **vs.** **kinematical**



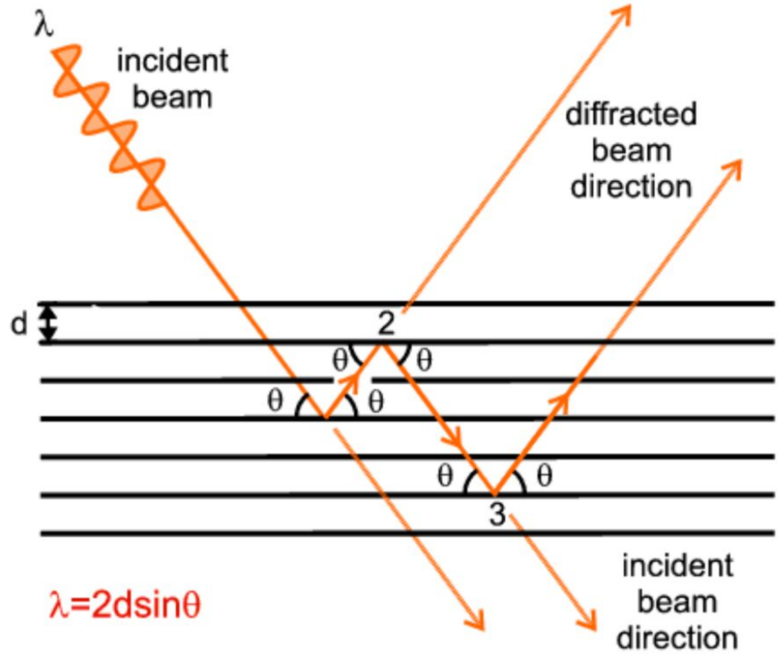


$I \propto |F|^2$ is not valid!

Crystallography using electron diffraction ?

e^- / matter : strong interactions **ED**

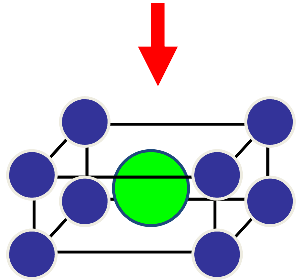
► dynamical scattering



multiple scattering

$I \propto |F|^2$ is not valid !

$$F_{hkl}(\vec{g}) = \sum_n f_n(\vec{g}) e^{i2\pi(h.x_n+k.y_n+l.z_n)}$$

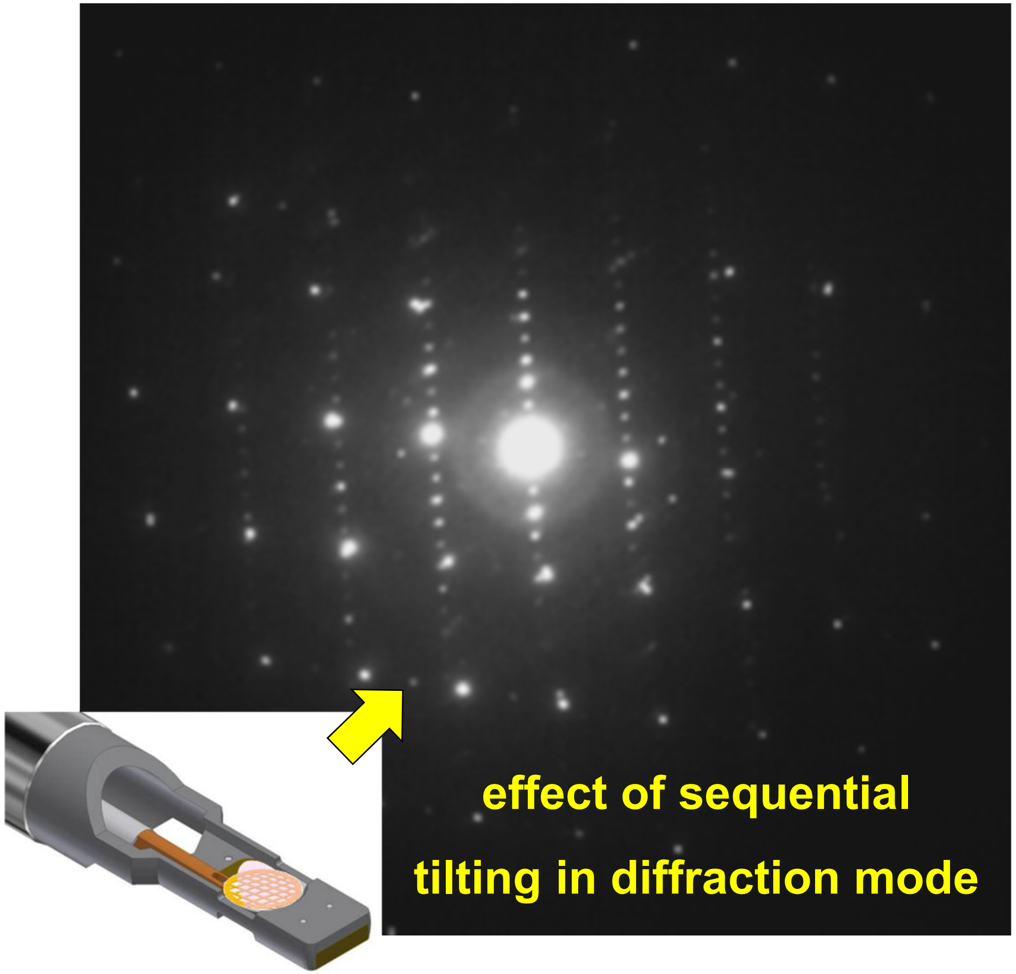


Electron Diffraction Tomography (EDT)

Avoid dense ZAP and increase data completeness

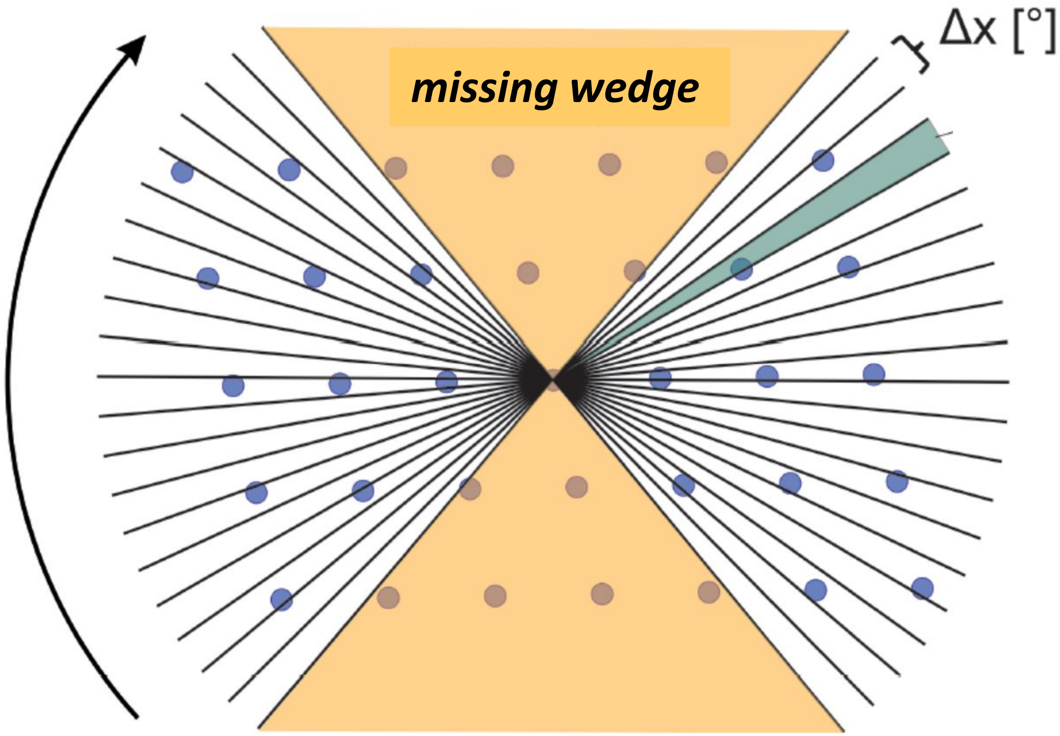
"phi-scan" data collection ► electron diffraction tomography (EDT or ADT*)

collection of a series of randomly oriented ED patterns at a fixed angular interval



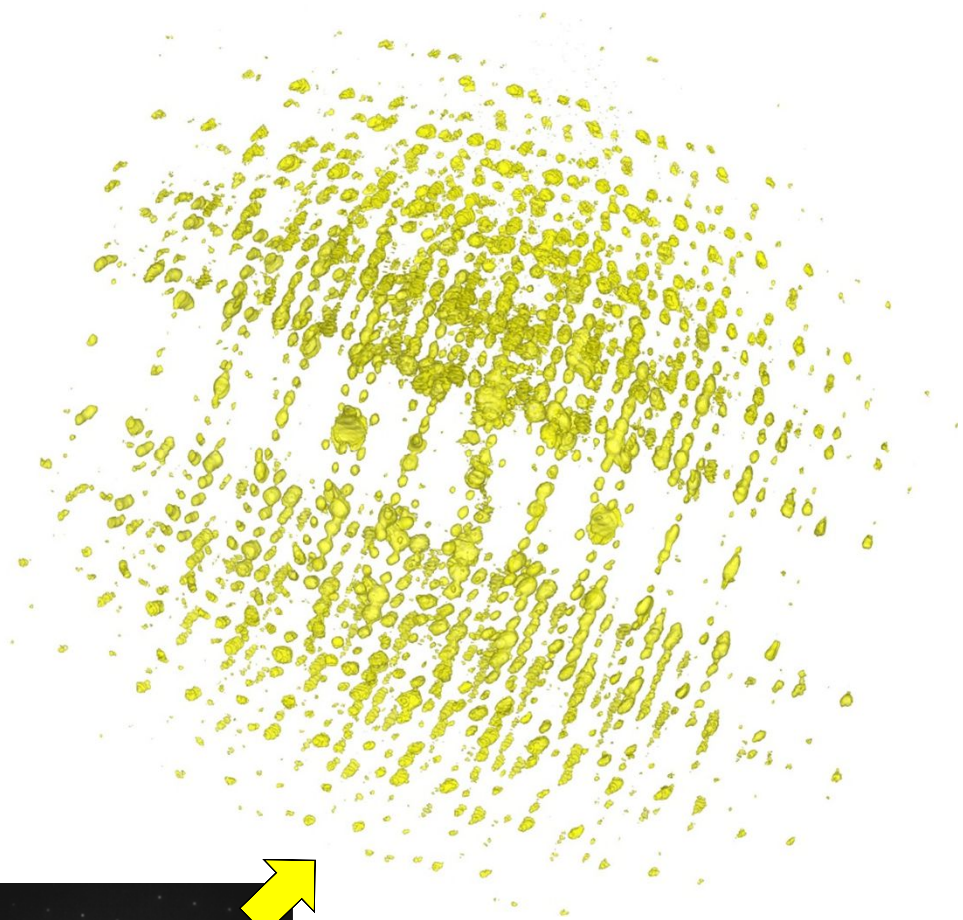
acquire numerous non-oriented electron diffraction patterns from one crystal

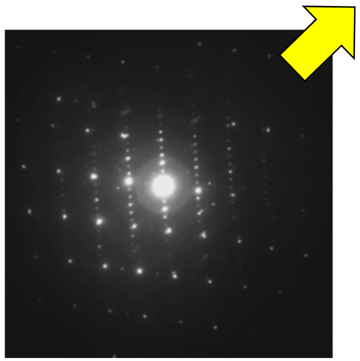
Tilt angle Δx (~1°) in EDT



* U. Kolb et al., Ultramicroscopy 107 (2007) 507

Precession Electron Diffraction Tomography (PEDT)





3D reconstruction of the reciprocal space

PETS (L. Palatinus)

1 > peak search

transmitted beam position, goniometer tilt, calibration, reflections size, …

n frames ► peaks list “2D” + center position

2 > peaks analysis

same reflection in several frames

peaks list “3D” (x,y,z) + clusters analysis

3 >

JANA2006 (V. Petricek)

indexing + orientation matrix + RS sections

lattice parameters

and symmetry determination

Electron Diffraction Tomography (EDT)

► **EDT datasets : go further and use intensities for <u>structure solution</u> ?**

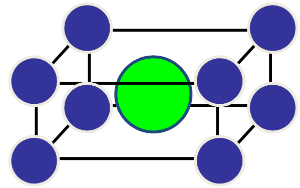
4 > data extraction

↓

hkl I σ(I) file

➡

structure ?



► **Electron crystallography : more complicated than XRD due to dynamical conditions**

e^- / matter : strong interactions **ED**

small diffracting volume → **thin films, nanosized sample**

dynamical scattering → **CBED**

can be seen as an advantage over X-ray diffraction

$I \propto |F|^2$ is not valid!

A very negative point for structural crystallography compared to X-ray diffraction

Electron Diffraction Tomography (EDT)

► **EDT datasets : go further and use intensities for <u>structure solution</u> ?** ***no precession***

EDT range ~ 55°

coverage 63% (0.9Å)

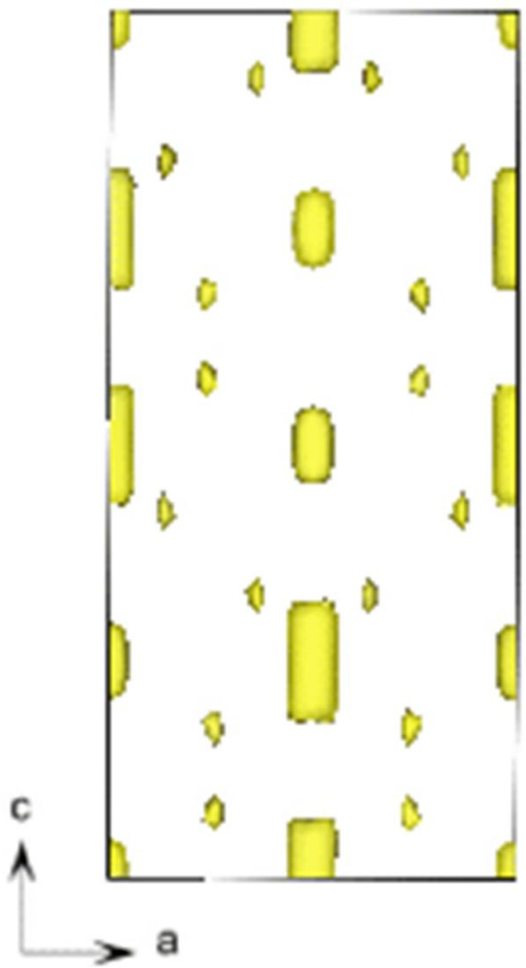
ab-initio structure

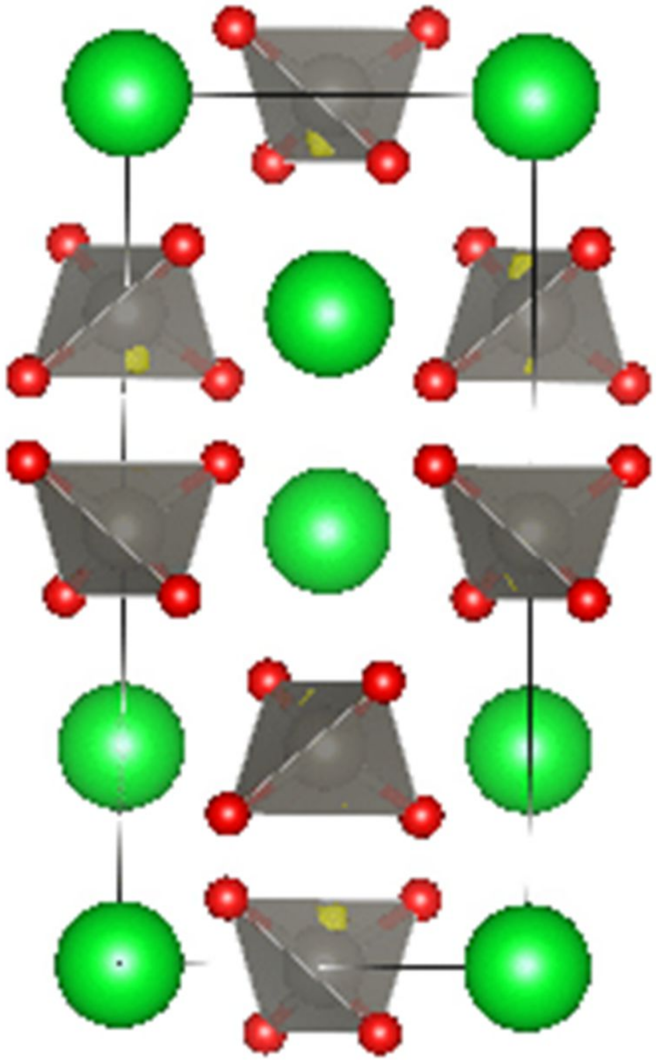
solution for $SrWO_4$

(SUPERFLIP)

Robs ~ 40%

but it works !



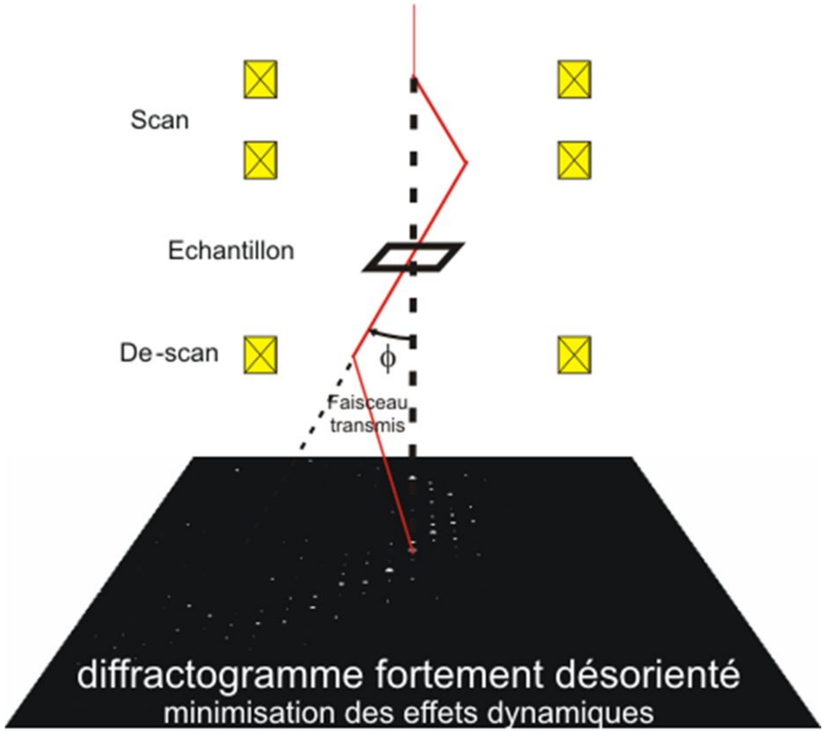


$SrWO_4$

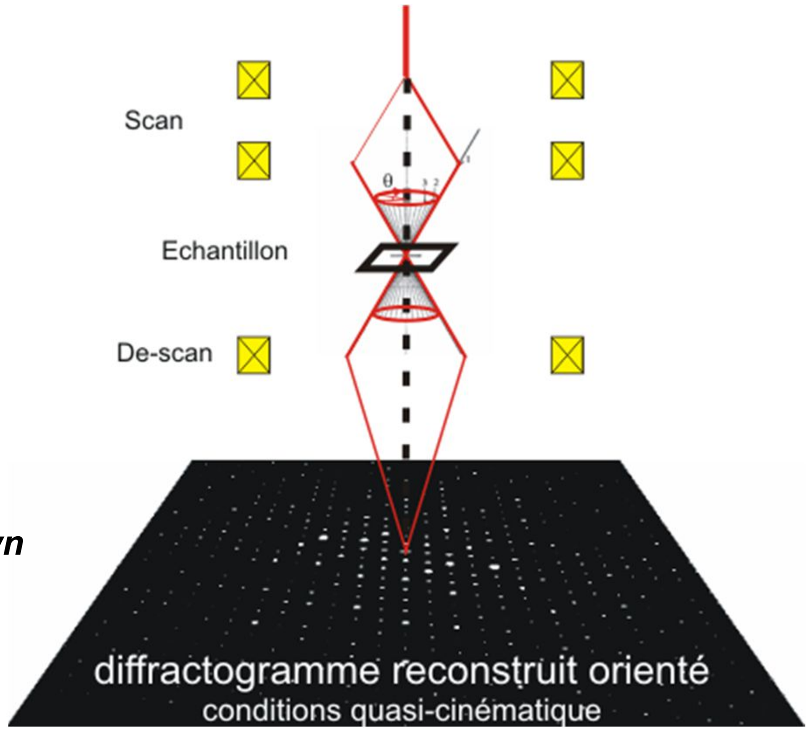
► **we should do better than that !**

Precession Electron Diffraction (PED)

Le faisceau électronique incident est fortement “incliné” et suit un cône avec un demi-angle ϕ autour de l’axe optique du microscope



After C.S. Own

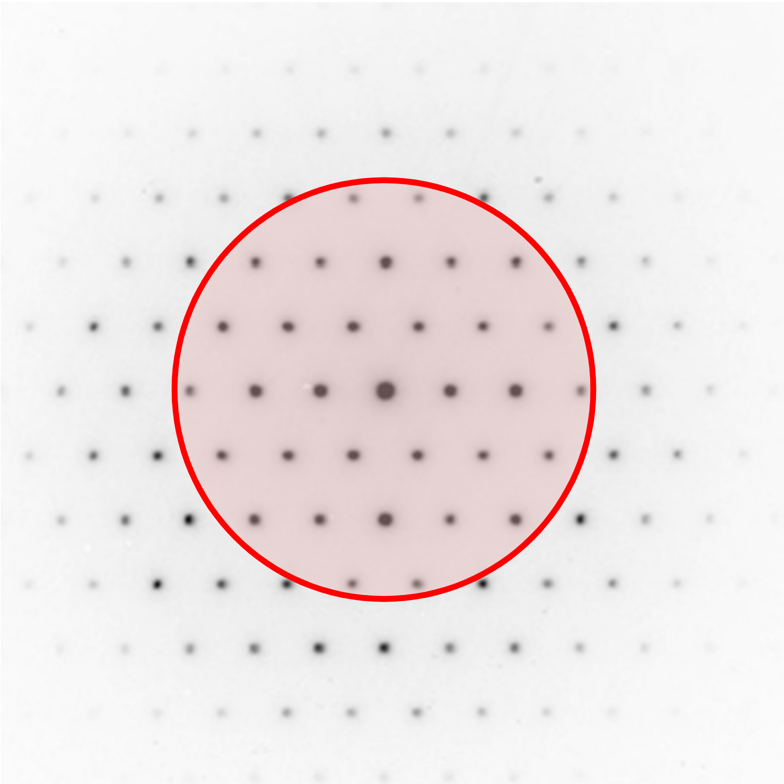


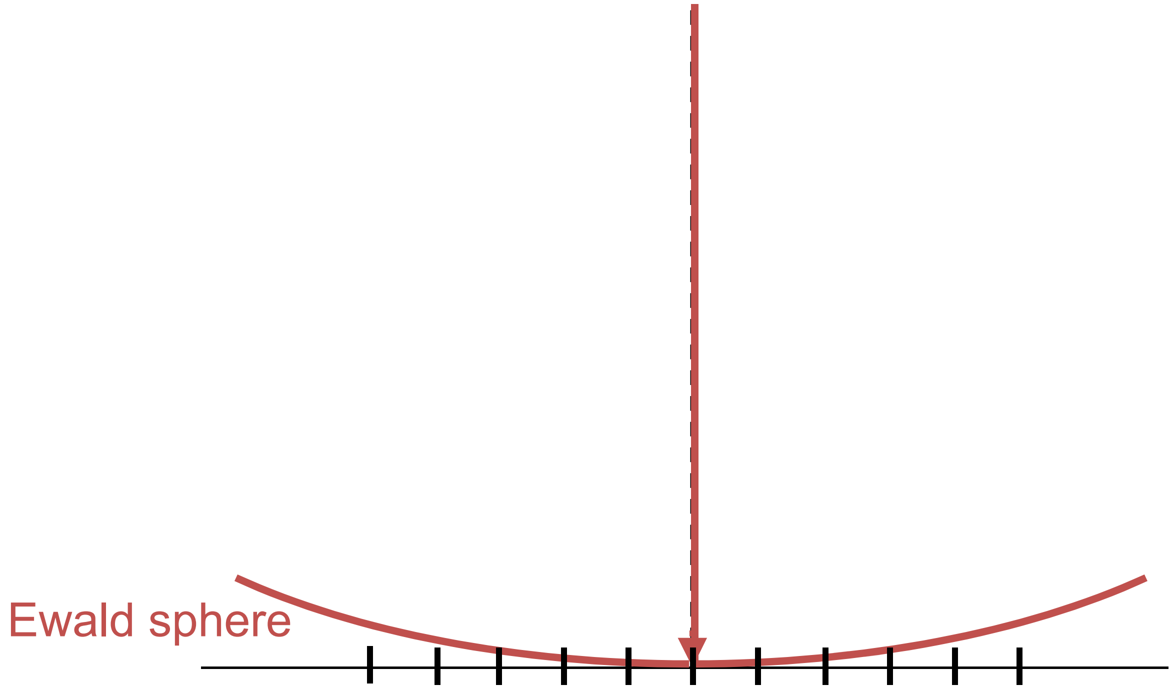
Intensités diffractées ⇨ série d’intensités enregistrées avec une forte désorientation par rapport à l’axe de zone ...

... qui sont sommées pour générer un diagramme de précession des électrons de l’axe de zone considéré.

R. Vincent and P.A. Midgley, *Ultramicroscopy* 53 (1994) 271

Faisceau d'électron suivant l'axe de zone [uvw]





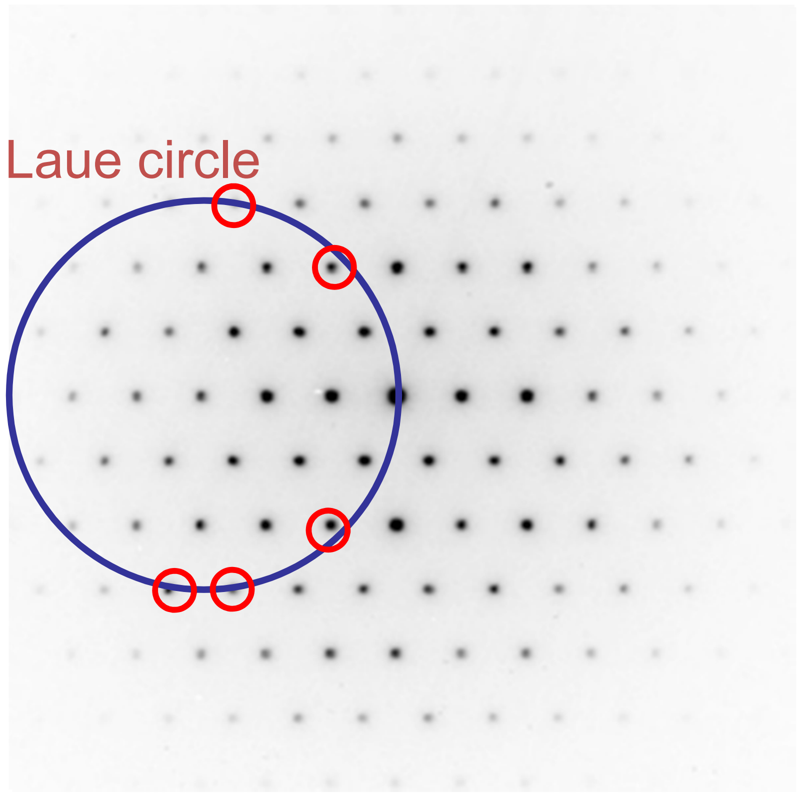
Faisceau fixe:

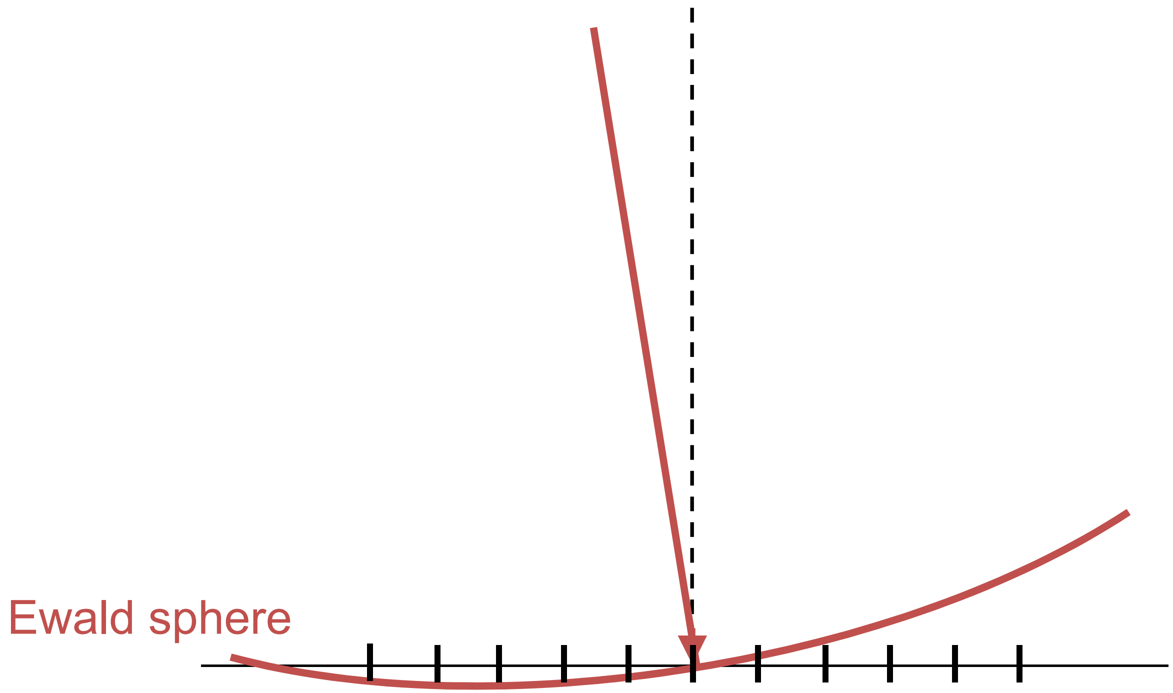
Interactions dynamiques fortes

Intensités très sensibles à l'orientation

from D. Jacob – UMET – Lille

Precession Electron Diffraction (PED)

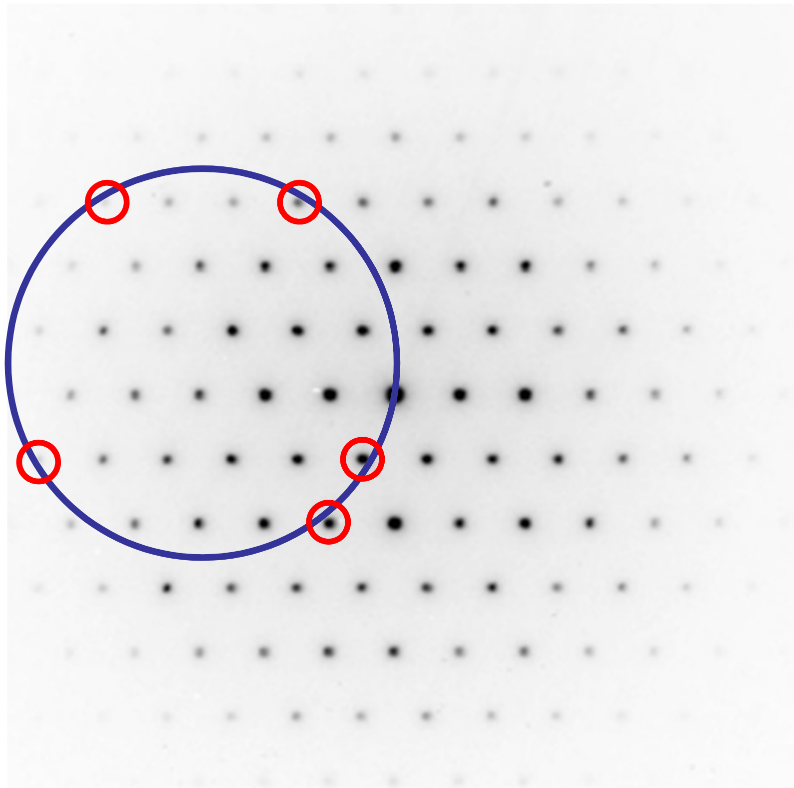


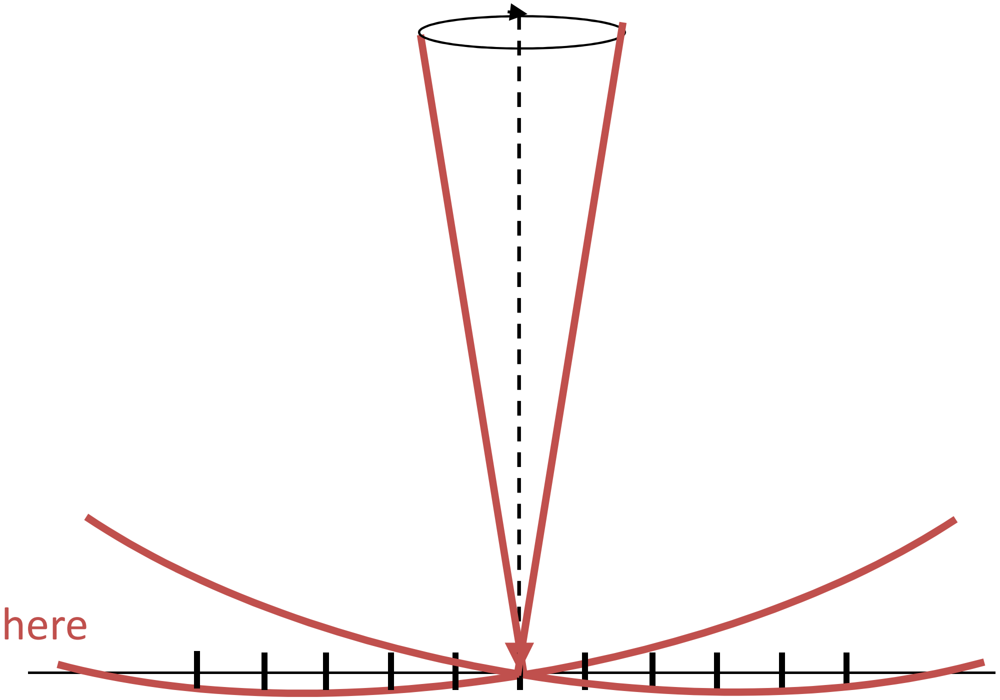


Faisceau incliné:

seules les reflexions situées sur la sphère d'Ewald interagissent

Precession Electron Diffraction (PED)



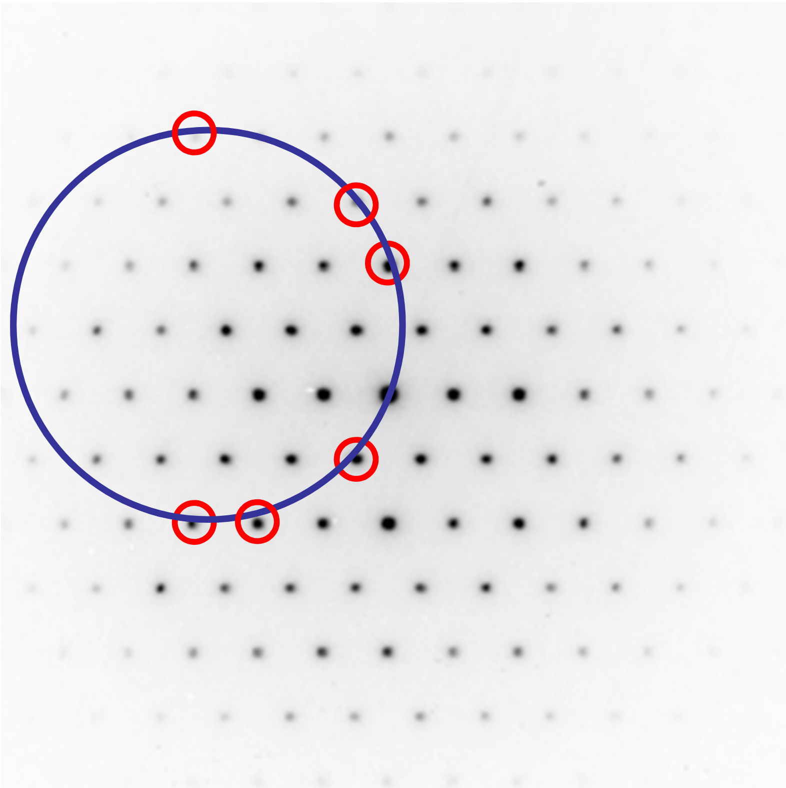


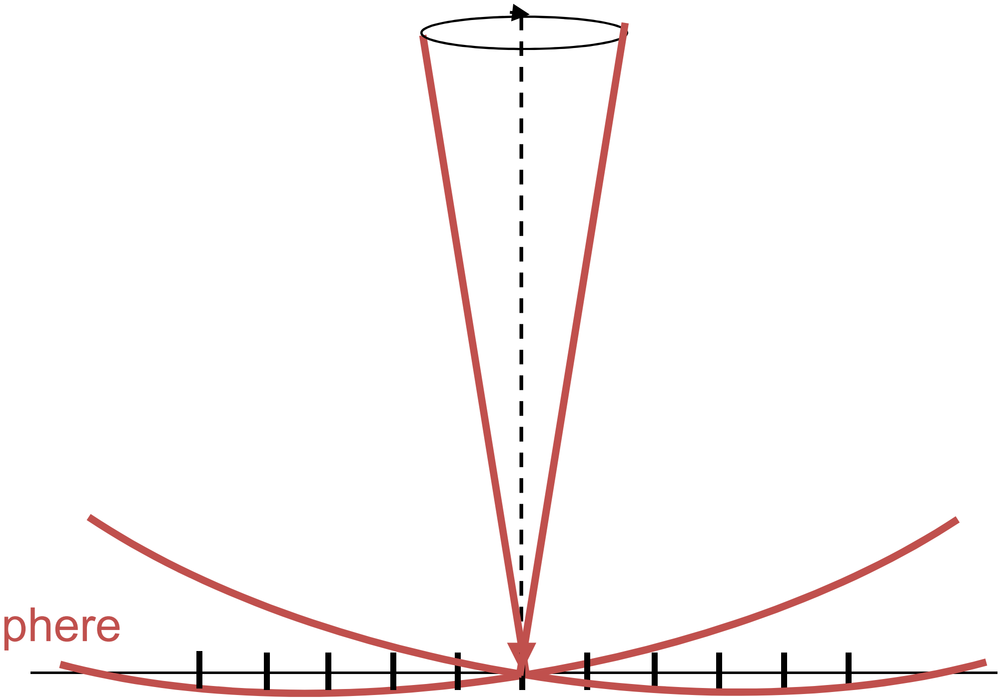
Faisceau tournant:

Le cliché de diffraction est reconstruit

de façon séquentielle

Precession Electron Diffraction (PED)



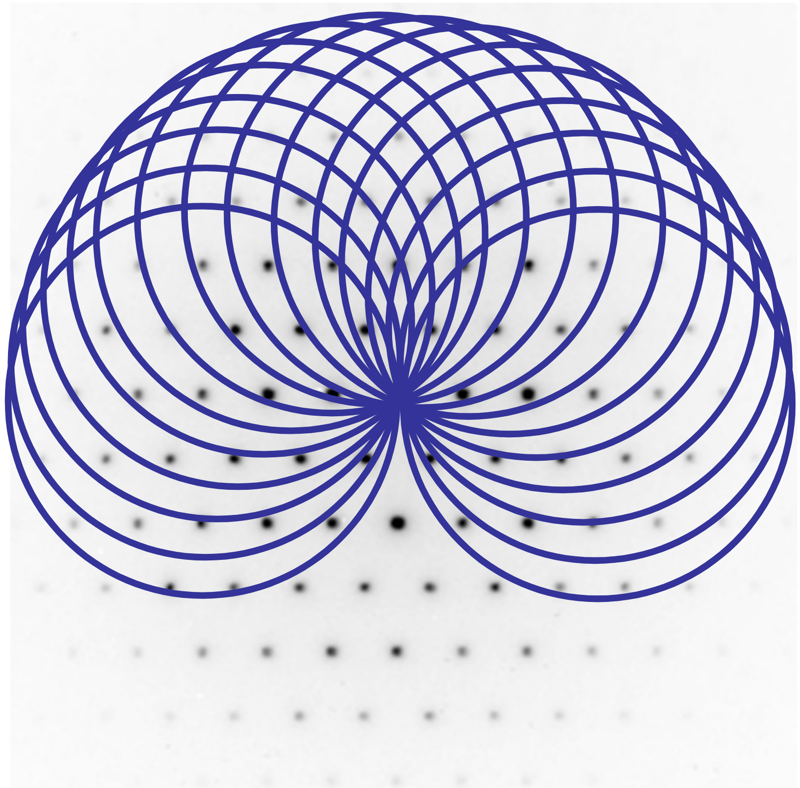


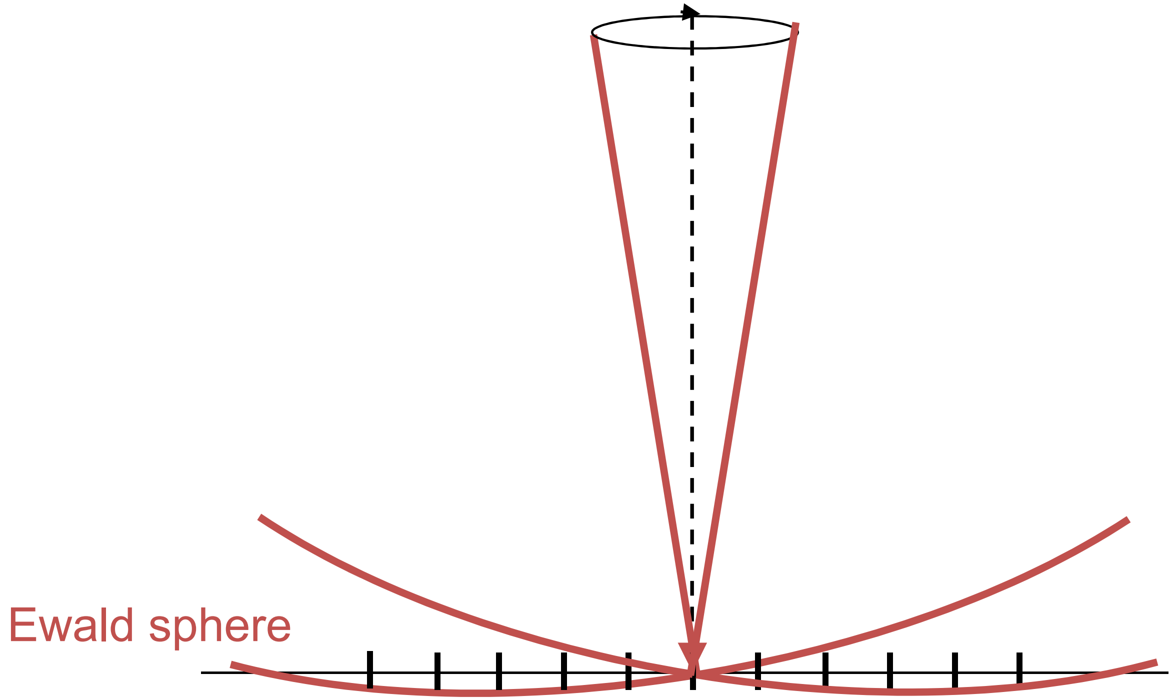
Faisceau tournant:

Le cliché de diffraction est reconstruit

de façon séquentielle

Precession Electron Diffraction (PED)





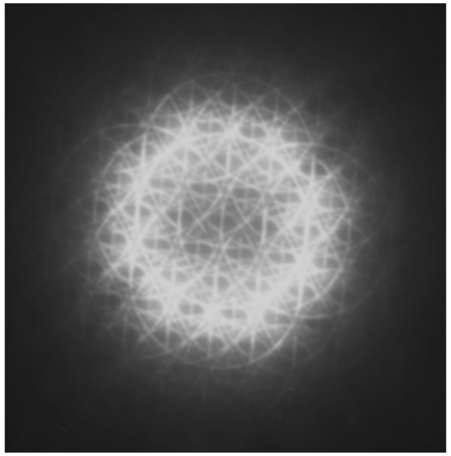
Faisceau tournant:

Le cliché de diffraction est reconstruit

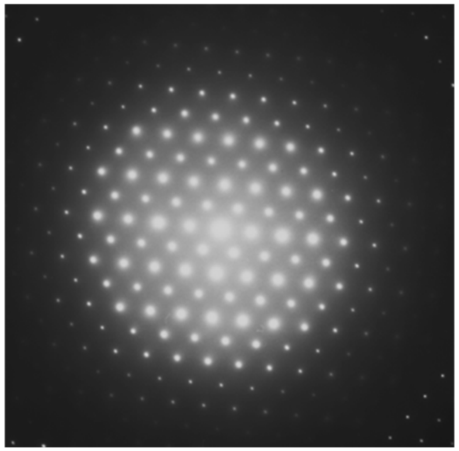
de façon séquentielle

Transmission Electron Microscope (TEM)

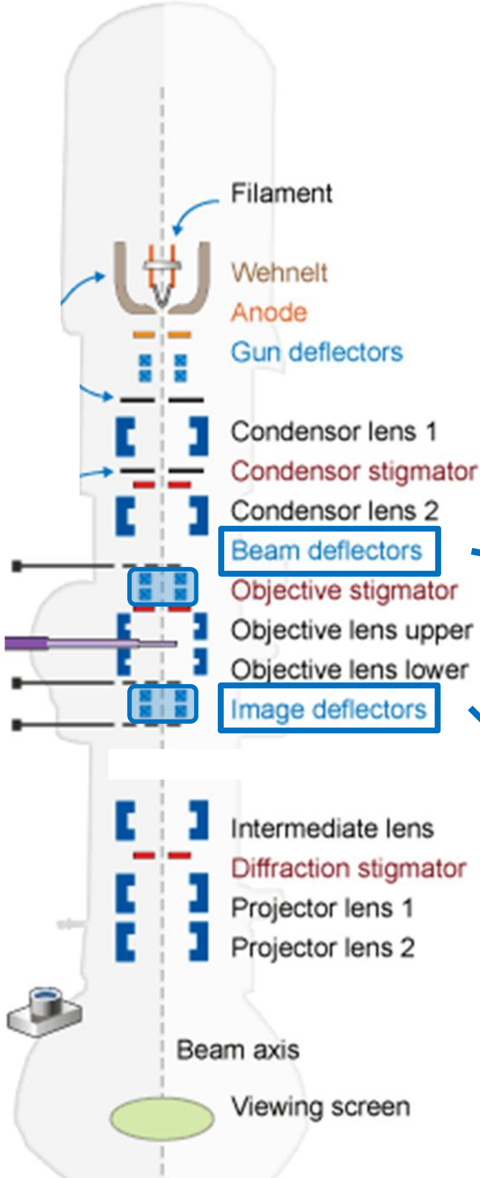
deflection coils ► precession



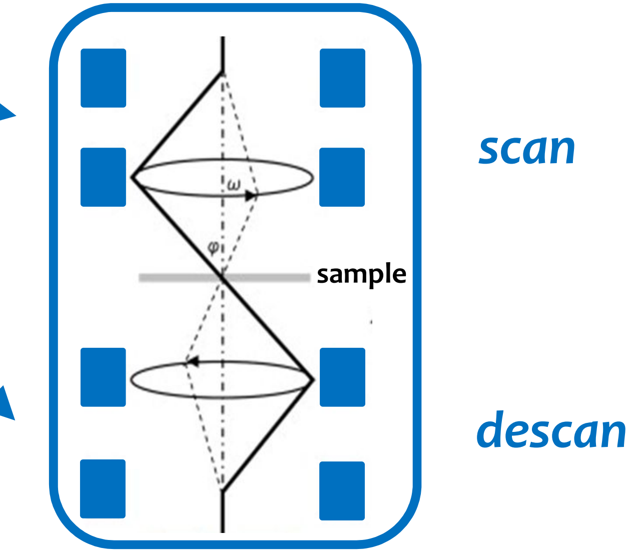
descan off



descan on

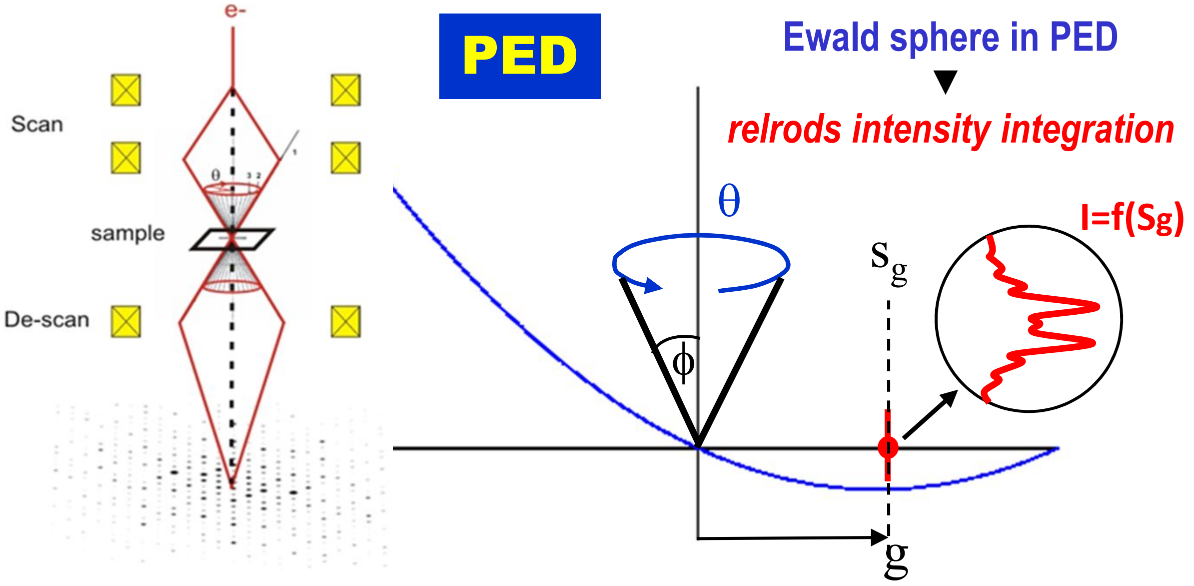


precession controller unit



Precession Electron Diffraction Tomography (PEDT)

Single-crystal electron diffraction ► PED + EDT ► PEDT

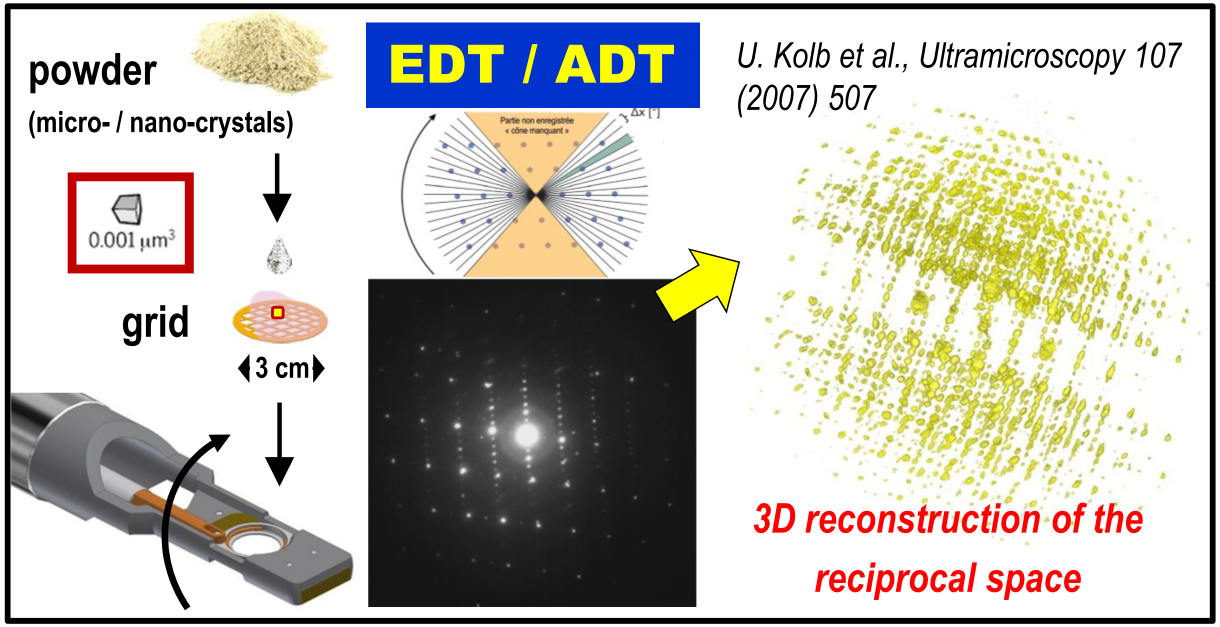


increase intensities quality

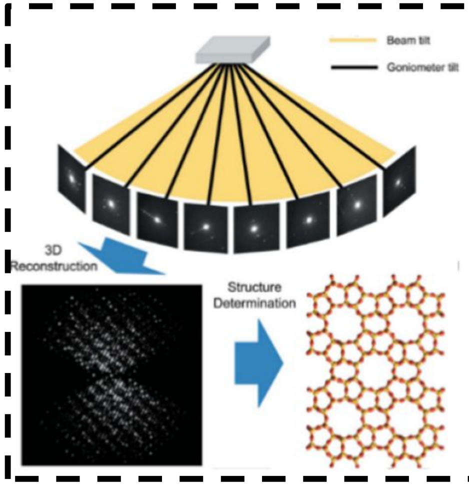
- limit the interactions between diffracted beams
- less sensitive to thickness variation
- increase the resolution limit
- integrated intensities

R. Vincent and P.A. Midgley, Ultramicroscopy 53 (1994) 271

system commercially available in 2005 (Nanomegas)



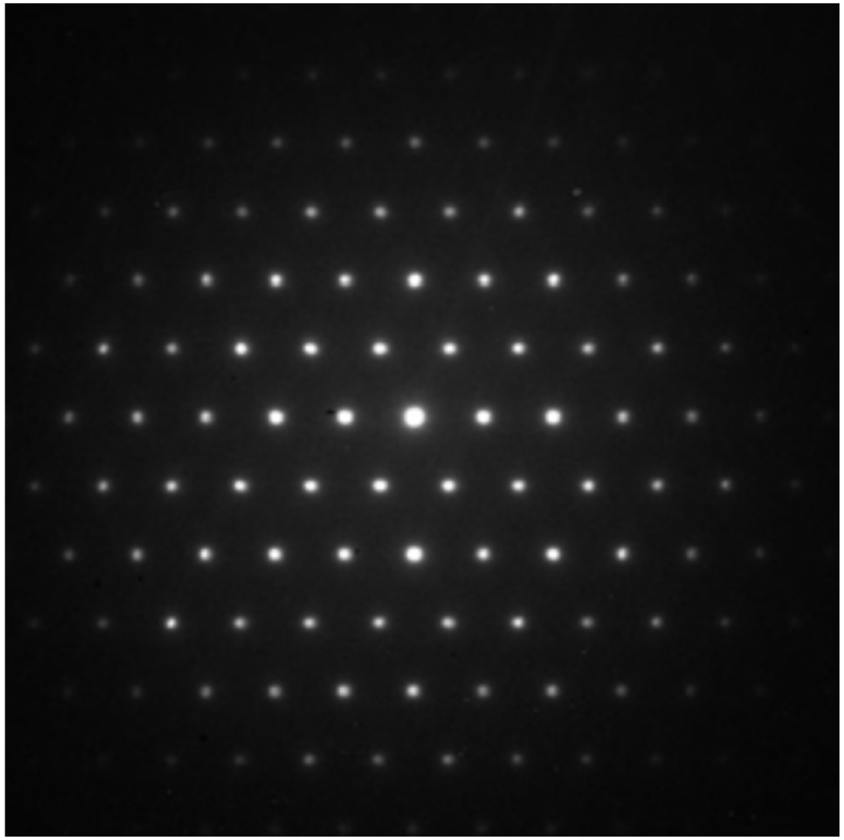
increase the data completeness



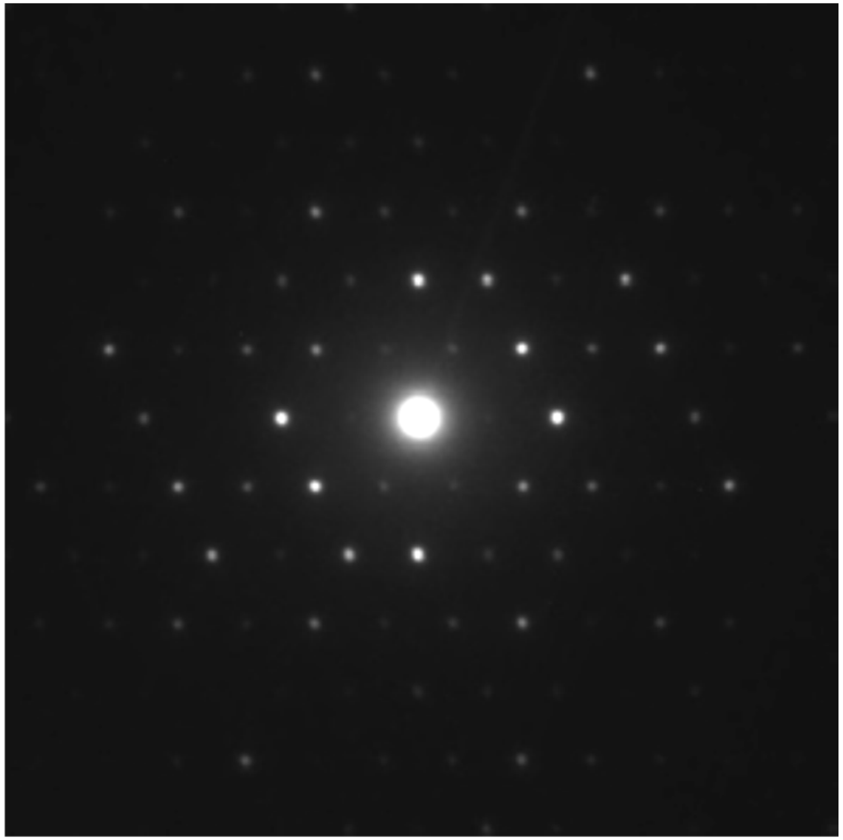
RED

W. Wan et al., Three-dimensional rotation electron diffraction: software RED for automated data collection and data processing, J. Appl. Crystallogr. 46 (2013) 1863.

dynamical vs. "kinematical"



SAED



PED

Precession Electron Diffraction Tomography (PEDT) ► kinematical

Solve structures when XRD fails ► no single crystals : complex structures

3300 ind. ref. $I > 3\sigma(I)$	**Incommensurate modulated structures**	630 ind. ref. $I > 3\sigma(I)$

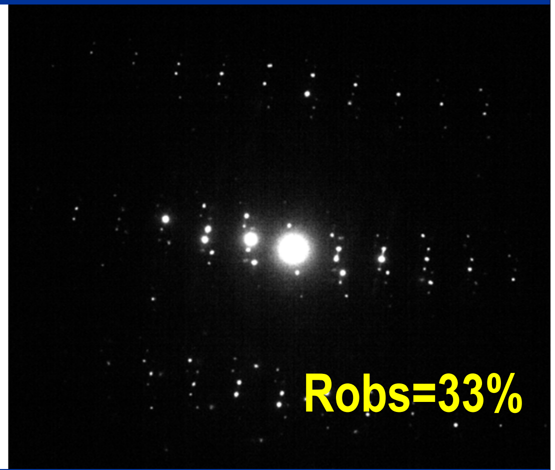
data analysis and reduction

▼

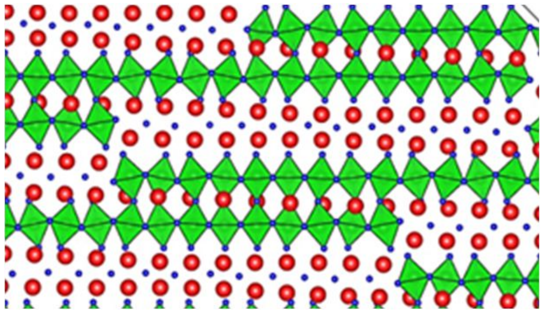
structure solution (kinematical approx.)

▼

refinement (kinematical approx.)



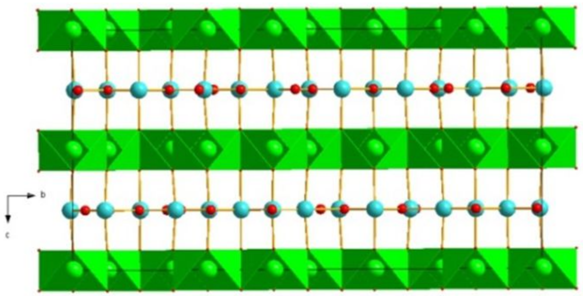
data collection : ~ 40 minutes / min. size : ~ 20 nm / T from -180°C to 800°C



◄ ***Solid State Chemistry*** ►

structure solution : PEDT

refinement : Neutron Powder Diffraction



"Unusual Relaxor Ferroelectric Behavior in Stairlike Aurivillius Phases"

G. Steciuk et al., *Inorg. Chem. 55 (2016) 8881*

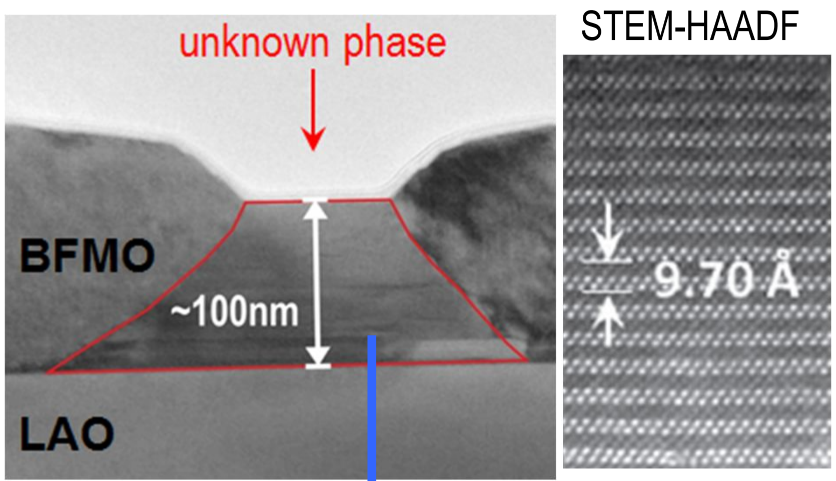
"A Rutile Chevron Modulation in Delafossite-like $Ga_{3-x}In_3Ti_xO_{9+x/2}$"

K. Rickert et al., *Inorg. Chem. 55 (2016) 4403*

coll. with K.R. Poeppelmeier (Northwestern Univ.)

Precession Electron Diffraction Tomography (PEDT) ► *kinematical*

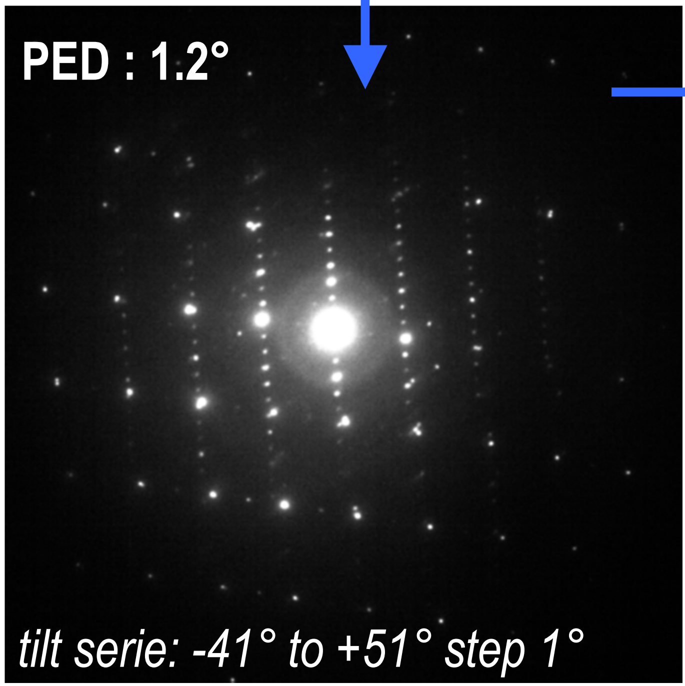
Solve structures when XRD fails ► small diffracting volume : thin films



"Two-Dimensional Layered Oxide Structures Tailored by Self-Assembled Layer Stacking via Interfacial Strain"

W. Zhang et al., *ACS Appl. Mater. Interfaces 8 (2016) 16845*

coll. with H. Wang (Texas A&M Univ.)



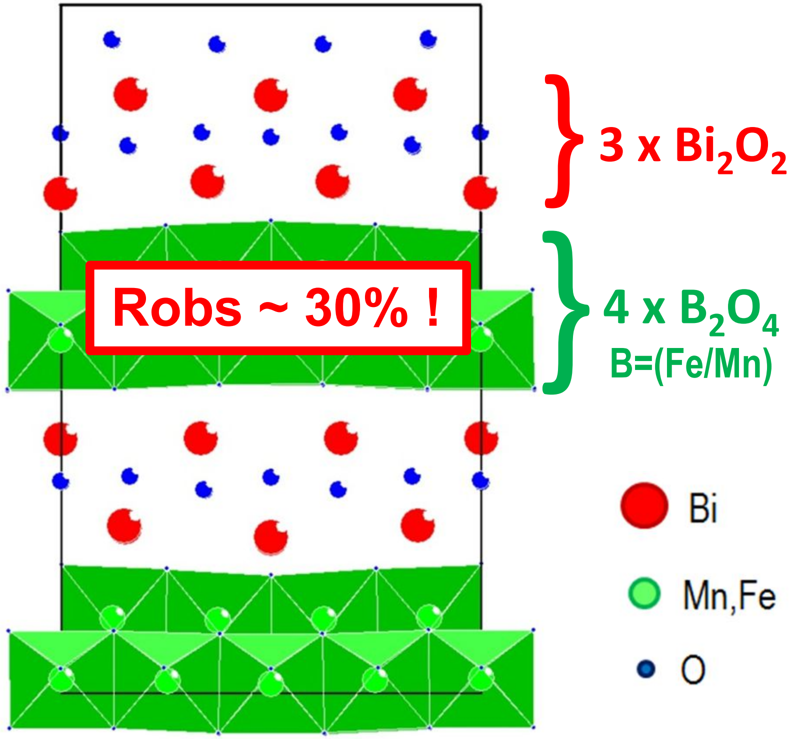
Intensity integration

Data analysis

(unit cell & symmetry)

Data reduction

Structure solution



Amm2 (SG n°38) a=3.96Å, b=11.78Å and c=19.37Å

La cristallographie aux électrons est en pleine évolution …

IUCrJ
ISSN 2052-2525
NEUTRON | SYNCHROTRON

Electron crystallography with the EIGER detector

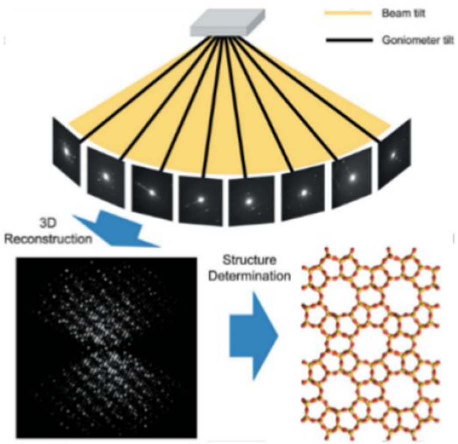
Gemma Tinti,[a]* Erik Fröjdh,[a] Eric van Genderen,[b] Tim Gruene,[b] Bernd Schmitt,[a] D. A. Matthijs de Winter,[c] Bert M. Weckhuysen[c] and Jan Pieter Abrahams[b,d]

[a]Swiss Light Source Detector Group, Paul Scherrer Institute, Villigen, Switzerland, [b]Laboratory of Biomolecular Research, Paul Scherrer Institute, Villigen, Switzerland, [c]Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht, The Netherlands, and [d]Center for Cellular Imaging and NanoAnalytics, University of Basel, Basel, Switzerland. *Correspondence e-mail: gemma.tinti@psi.ch

Received 9 October 2017
Accepted 15 January 2018

… PEDT et Rotation Electron Diffraction sont deux approches possibles …

collecte et réduction des données



RED

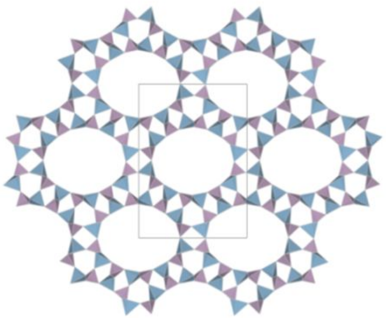
W. Wan et al., Three-dimensional rotation electron diffraction: software RED for automated data collection and data processing, J. Appl. Crystallogr. 46 (2013) 1863.

structure solution et affinement cinématique

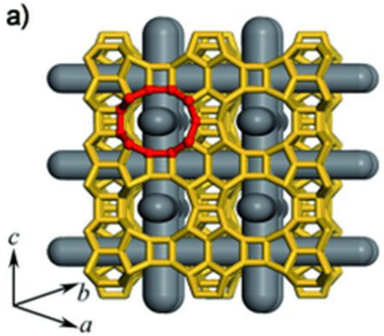
- ► *solution: SHELXT*
- ► *affinement: SHELXL* **R1 ~ 25%**
- ► *modélisation (?): SHELXLE*

… votre programme préféré peut être utilisé

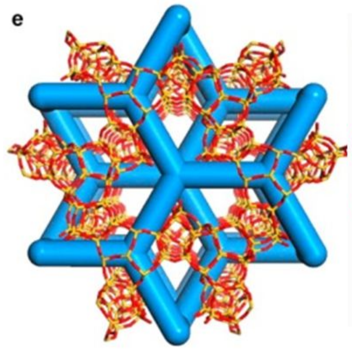
Cristallographie Structurale aux électrons ► approx. cinématique



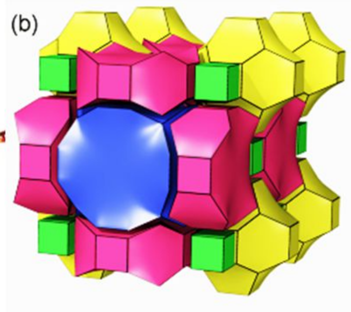
ITQ-51 (IFO)
PNAS
2013



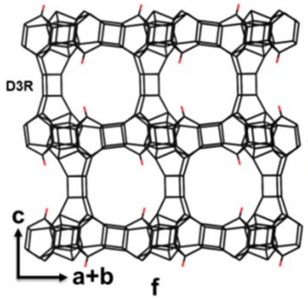
PKU-16 (POS)
Angew. Chem. Int. Ed.
2014



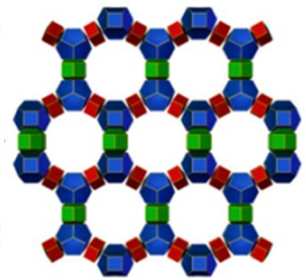
EMM-23 (-EWT)
JACS
2014



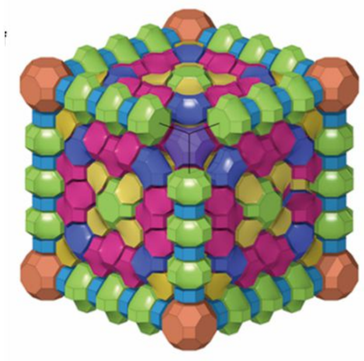
PKU-14
Chem. Eur. J.
2014



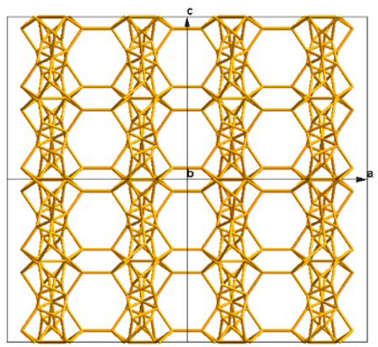
ITQ-53 (-IFT)
Chem. Commun.
2015



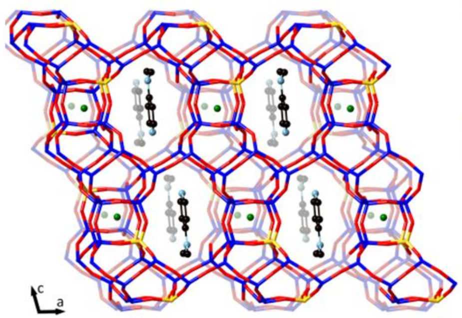
ITQ-54 (-IFU)
Chem. Sci.
2015



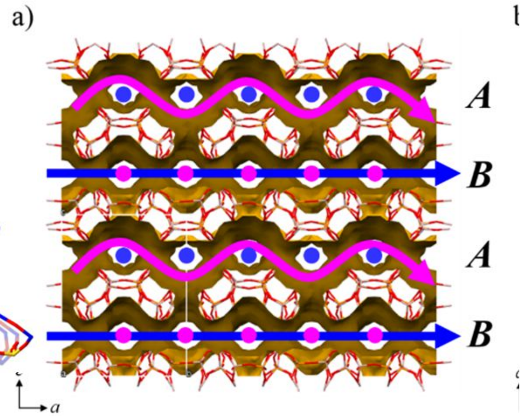
ZSM-25 (MWF)
Nature
2015



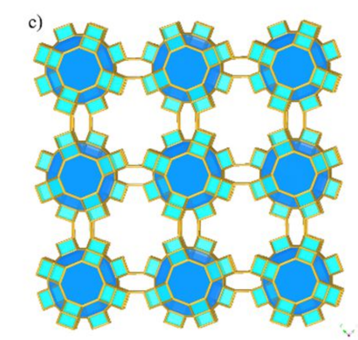
EMM-26 (EWS)
Inorg. Chem. Front.
2016



IM-18
Cryst. Growth Des.
2018



PST-14
Angew. Chem. Int. Ed.
2018



SYSU-3
Angew. Chem. Int. Ed.
2018

Zeolite structures solved by electron diffraction

from X. Zou – Stockholm University

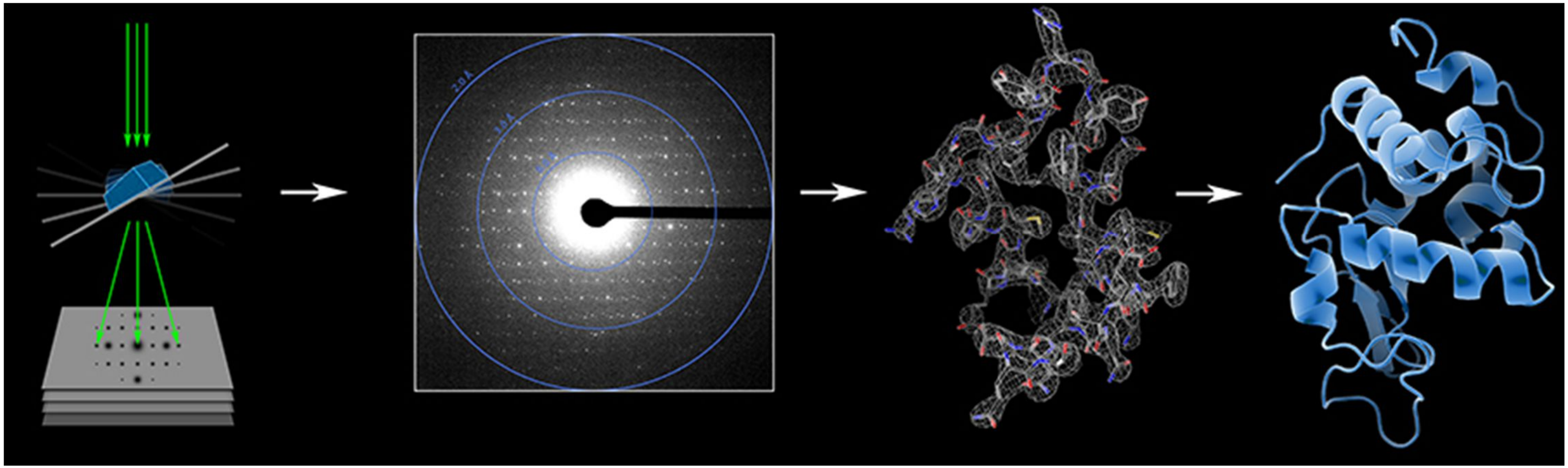
MicroED – Three dimensional electron diffraction in a CryoEM

Structure de protéines par diffraction des électrons

► ~ EDT avec ou sans rotation continue du cristal ...

► analyse des données : MOSFLM

► solution : molecular replacement



from https://cryoem.ucla.edu/pages/MicroED *T. Gonen Lab. – UCLA*

What is the problem with kinematical refinement ?

Currently the most widely used approach for PEDT data.

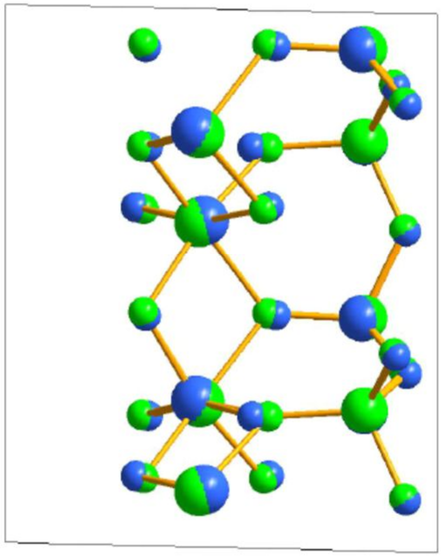
Yields "acceptable" structures but:

- High figures of merit
- Unreliable e.s.d.s
- Unknown accuracy

Issues to consider :

- symmetry is poorly defined (Rint)
- absent reflections may be present
- refinement quite insensitive to atomic numbers and occupancy
- R-values often high

Kaolinite - comparison of refined and reference structure



blue: refined structure
green: reference structure (Neder et al., Clays and Clay Minerals 29)

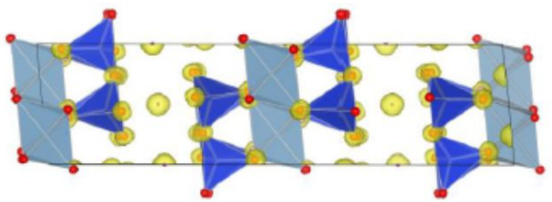
	kinematical
N refl (obs/all)	937/1057
N parameters	53
R(obs)	19.14%
GooF (obs/all)	8.74/9.27
ΔSi1	0.051
ΔSi2	0.037
ΔAl1	0.070
ΔAl2	0.084
ΔO1	0.136
ΔO2	0.110
ΔO3	0.270
ΔO4	0.061
ΔO5	0.041
ΔO6	0.111
ΔO7	0.060
ΔO8	0.141
ΔO9	0.101
mean Δ	0.098
max Δ	0.270

from L. Palatinus – CrystElec2018

What is the problem with kinematical refinement ?

Structure solution is so efficient that it works even with very poor quality data :

phengite



solution with Superflip

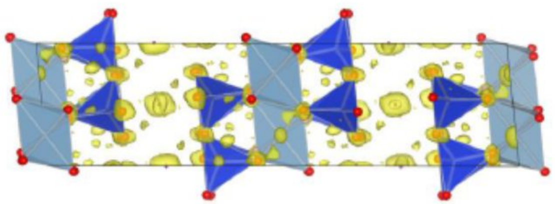
from L. Palatinus – CrystElec2018

2	0	0	1.
6	0	0	0.
-4	0	2	1.
0	0	2	0.
4	0	2	1.
-6	0	4	0.
-2	0	4	1.
2	0	4	0.

4	0	0	1.
-6	0	2	1.
-2	0	2	1.
2	0	2	1.
6	0	2	0.
-4	0	4	0.
0	0	4	0.
4	0	4	0.

from L. Palatinus

CrystElec2018



R-value
58.6%

refinement

with JANA

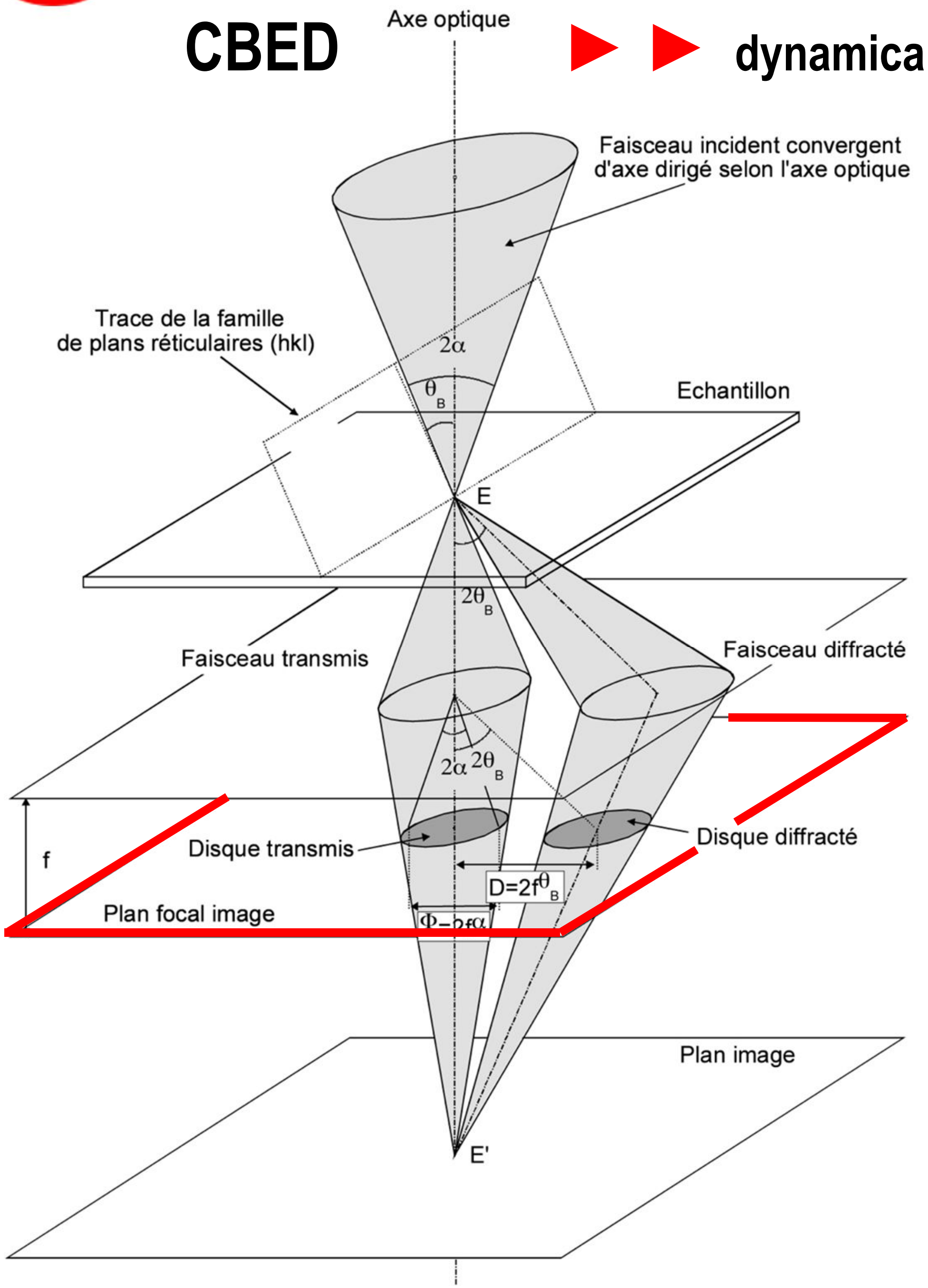
Kinematical approximation is not valid for electron diffraction including PEDT

- ► **good enough to provide a model : structure solution** ☑
- ► **need external validation (XRPD, …) : structure refinement** ☒

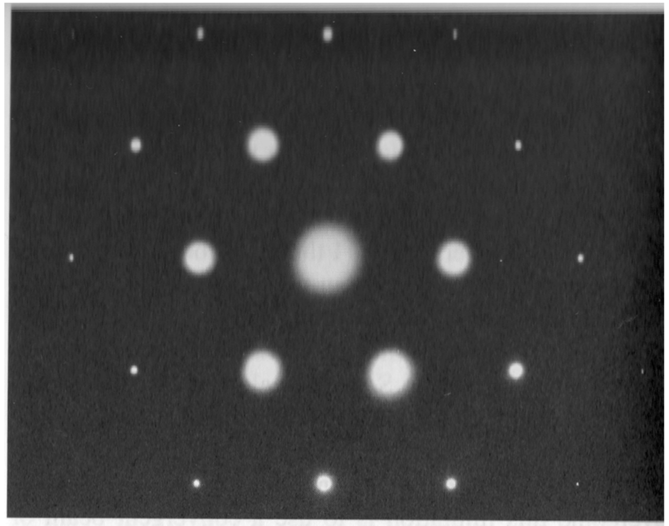
dynamical scattering effects even with PEDT (or RED)

reliability factors calculated based on kinematical intensities are biased

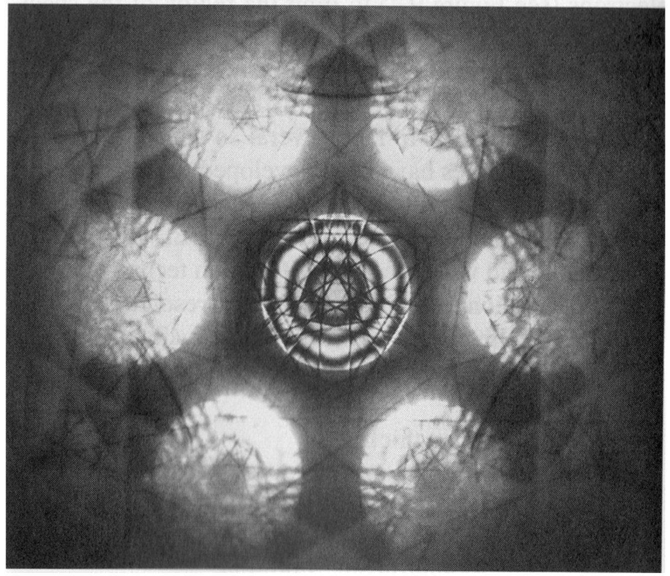
CBED ► ► dynamical scattering



[111] SAED diagramme du Si



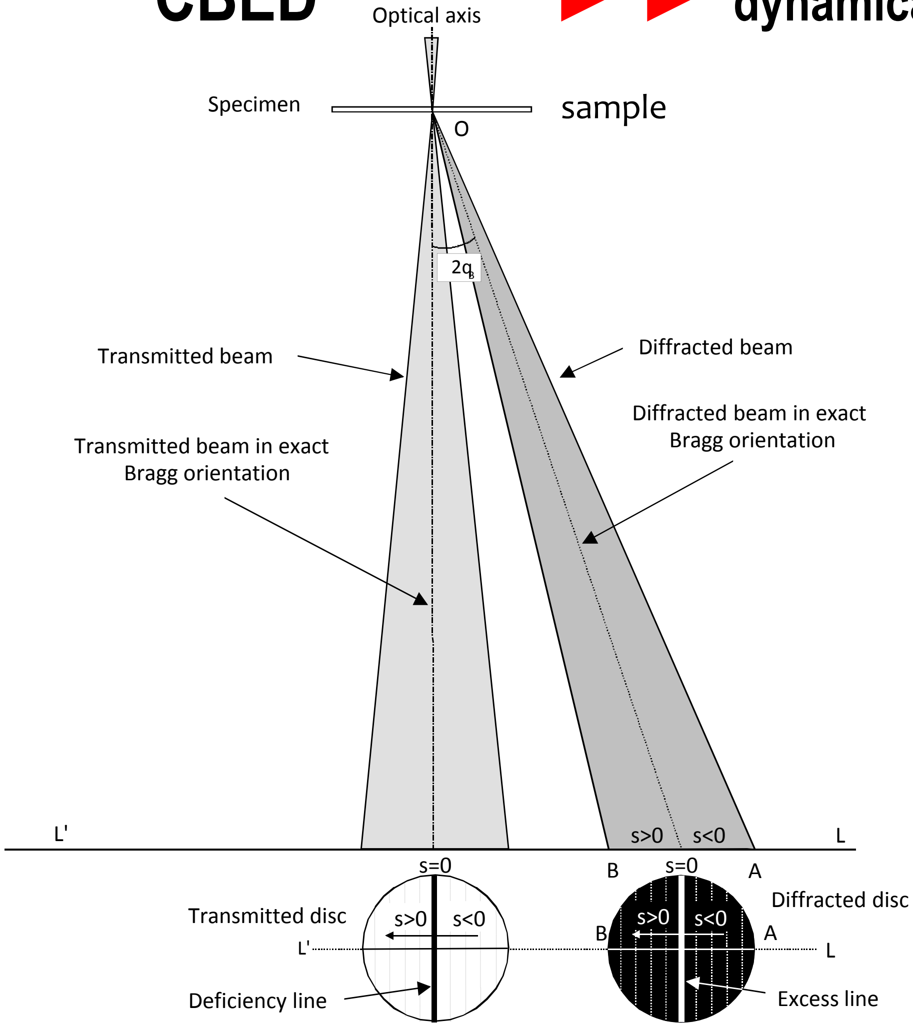
[111] CBED diagramme du Si

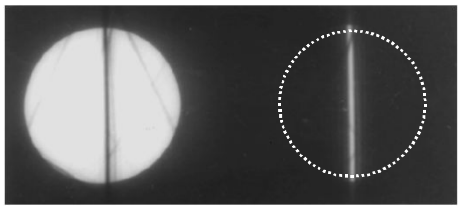


les disques présentent des contrastes liés au effets dynamiques

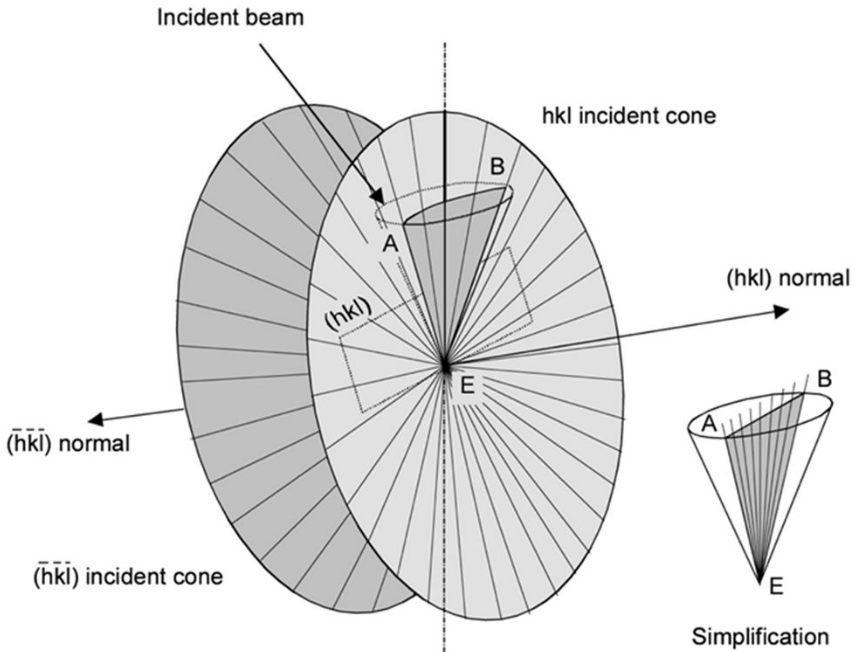
from D. Jacob - CrystElec2018

CBED ►► dynamical scattering – 2-beams





ligne de défaut hkl   ligne d'excès hkl

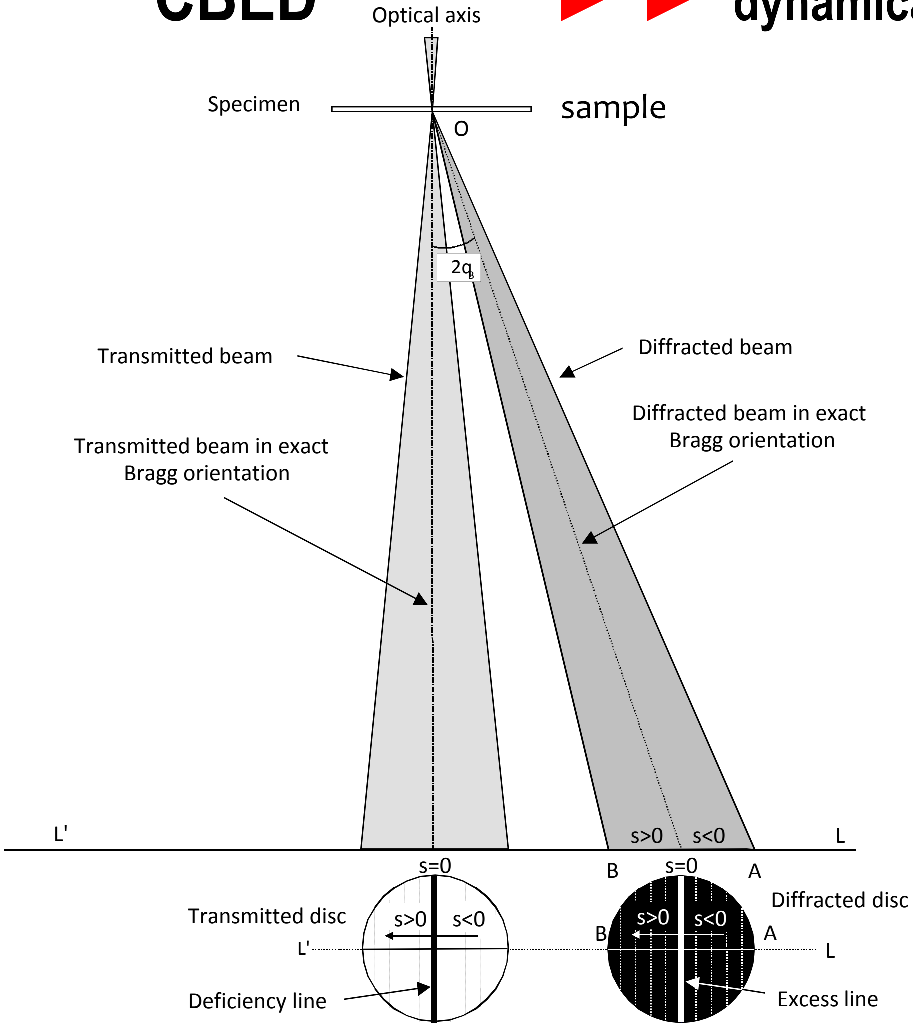


couplage entre le disque transmis et diffracté

from D. Jacob - CrystElec2018

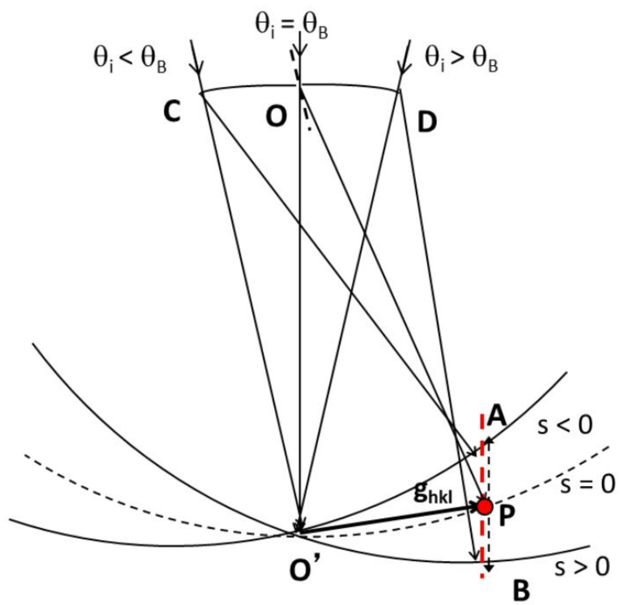
Electron Diffraction

CBED ►► dynamical scattering – 2-beams

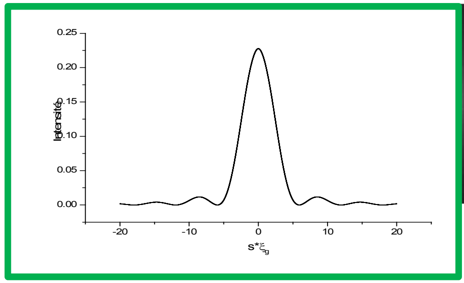


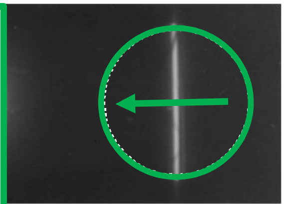
chaque point des disques correspond à une direction incidente particulière

▼



couplage entre le disque transmis et diffracté





I =f(s)

ligne d'excès hkl

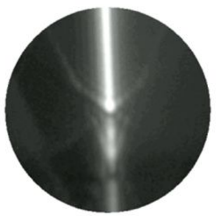
CBED ►► dynamical scattering – 2-beams

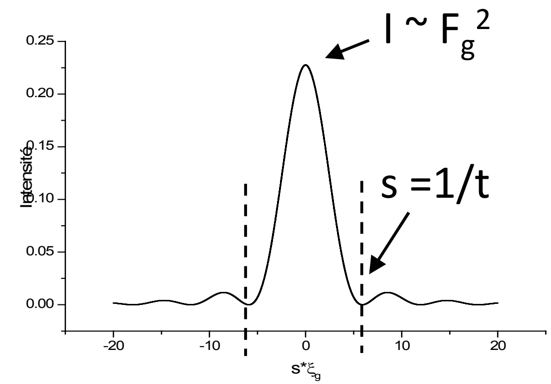
❖ Paramètre majeur : distance d'extinction $\xi_g = \dfrac{\pi V_c \cos\theta_B}{\lambda F_g}$

❖ $I_g = \left(\dfrac{\pi t}{\xi_g}\right)^2 \dfrac{\sin^2(\pi t s_{eff})}{(\pi t s_{eff})^2}$, avec $s_{eff} = \sqrt{s^2 + \dfrac{1}{\xi_g^{\,2}}}$ et t: épaisseur

❖ Cas « cinématique »: $\xi_g \geq 3t$

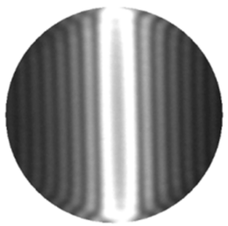
exemple: t= 100 nm, ξ_g = 600nm

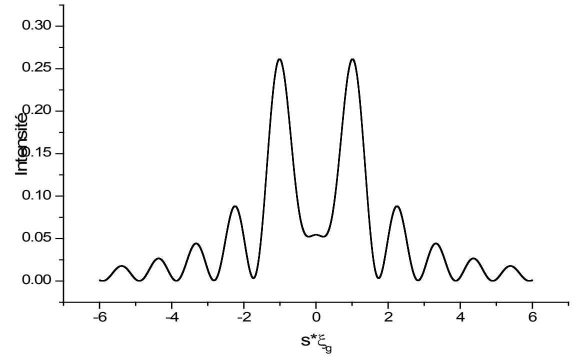




❖ Cas « dynamique » : distance d'extinction $\xi_g < 3t$

exemple: t= 200 nm, ξ_g = 200nm





from D. Jacob - CrystElec2018

Precession Electron Diffraction Tomography (PEDT)

dynamical scattering effects even with PEDT (or RED)

reliability factors calculated based on kinematical intensities are biased

structure refinement → **Use dynamical scattering theory** (MSLS *J. Jansen*, ASTRA *AP. Dudka et al.*, ...) — **Bloch wave formalism**

Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Structure refinement from precession electron diffraction data

Lukáš Palatinus,[a]* Damien Jacob,[b] Priscille Cuvillier,[b] Mariana Klementová,[a] Wharton Sinkler[c] and Laurence D. Marks[d]

Received 27 July 2012
Accepted 2 December 2012

ZAP : *Acta Cryst. A69 (2013) 171*

► **PEDT** : *Acta Cryst. A71 (2015) 235* ►

Acta Cryst. B71 (2015) 740

Acta Cryst B
STRUCTURAL SCIENCE
CRYSTAL ENGINEERING
MATERIALS
ISSN 2052-5206

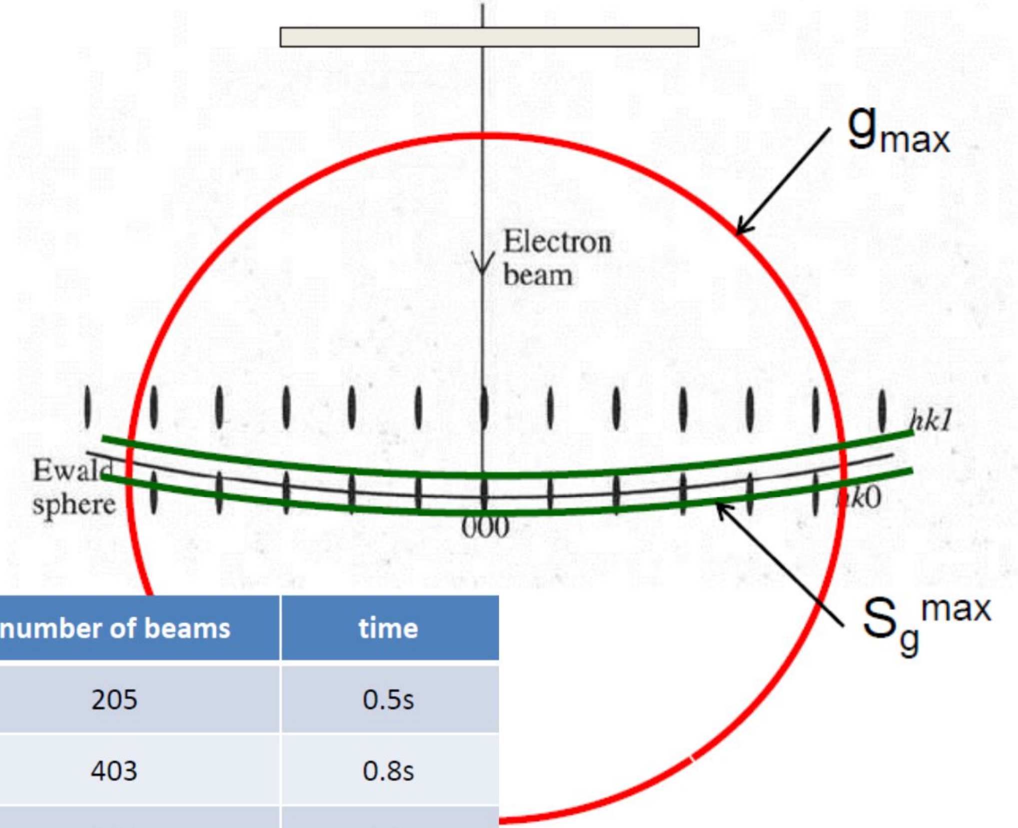
Structure refinement using precession electron diffraction tomography and dynamical diffraction: tests on experimental data

Lukáš Palatinus,[a]* Cinthia Antunes Corrêa,[a,b] Gwladys Steciuk,[c] Damien Jacob,[d] Pascal Roussel,[e] Philippe Boullay,[c] Mariana Klementová,[a] Mauro Gemmi,[f] Jaromír Kopeček,[a] M. Chiara Domeneghetti,[g] Fernando Cámara[h] and Václav Petříček[a]

Received 11 August 2015
Accepted 11 September 2015

Dynamical diffraction theory ►intensities calculation

1. Find all reflections that contribute to diffraction (► S_g^{max})

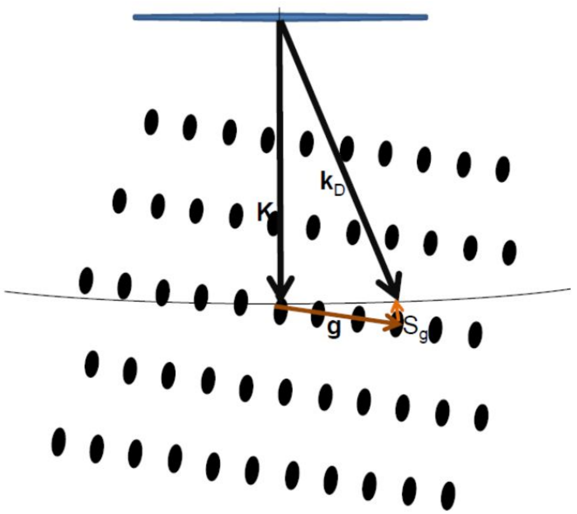


S_g^{max}	number of beams	time
0.005	205	0.5s
0.010	403	0.8s
0.020	817	4.6s
0.030	1215	12.8s
0.040	1623	31.4s

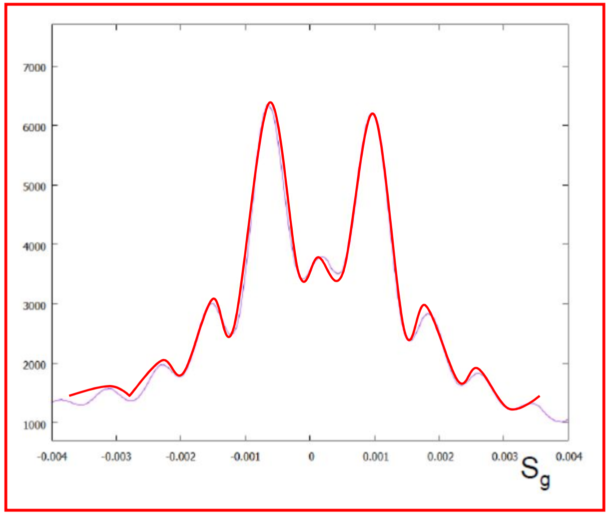
from L. Palatinus

CrystElec2018

Dynamical diffraction theory ► intensities calculation



$$2KS_g = K^2 - (\mathbf{K} + \mathbf{g})^2$$



1. Find all reflections that contribute to diffraction (► S_g^{max})
2. Build structure matrix A: for 3 beams:

$$a_{ii} = 2KS_{\mathbf{g}_i}, i = 1, N_{beams}$$

$$a_{ij} = U_{\mathbf{g}_i - \mathbf{g}_j}, i, j = 1, N_{beams}; i \neq j$$

$$A = \begin{pmatrix} 2K & U_{-g} & U_{-h} \\ U_g & 2KS_g & U_{g-h} \\ U_h & U_{h-g} & 2KS_h \end{pmatrix}$$

3. Calculate scattering matrix S: $S = exp\left(\frac{2\pi i t A}{2K_n}\right)$ t thickness

4. Calculate intensities from the 1st column of S ► $I_{\mathbf{h}_i} = |s_{i1}|^2$

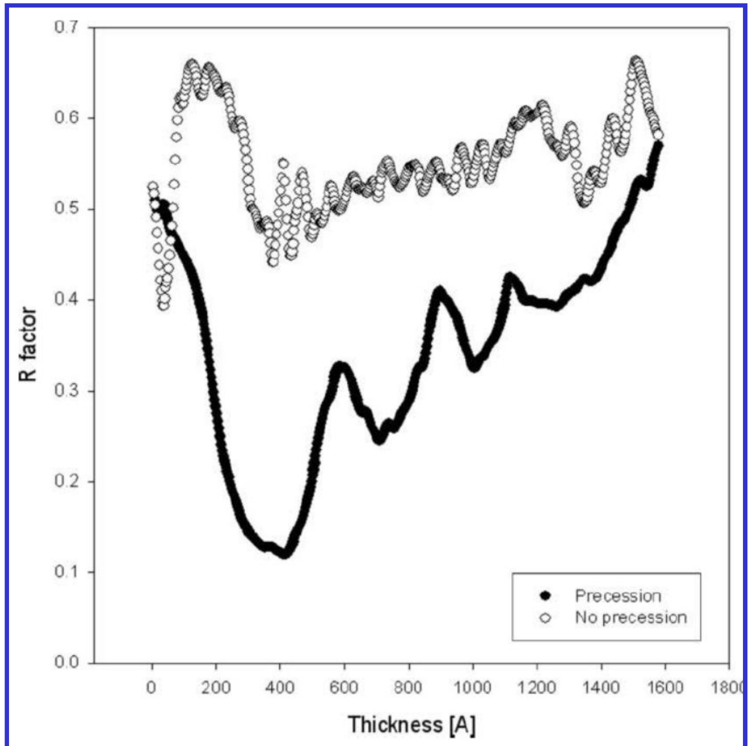
Each intensity is a function of:
- Crystal thickness
- Crystal orientation
- Structure factors of all sufficiently excited beams

Plus détails en français: Thèse de Gwladys Steciuk – 2016 – Caen

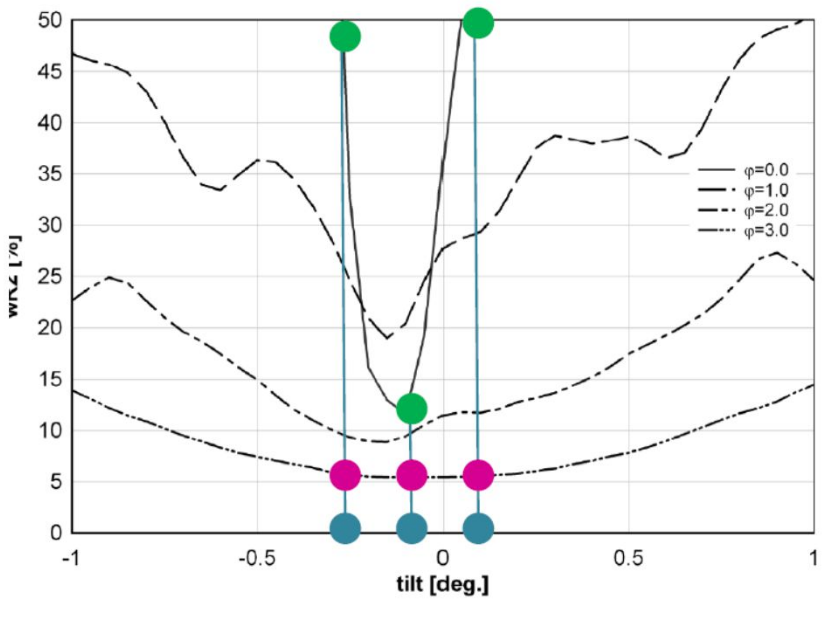
Dynamical diffraction theory ►intensities calculation

Calculated intensities ► high sensitivity to thickness and orientation

Experimental patterns without precession ► uniform distribution of intensities; difficulties to estimate the **thickness** and the **orientation**



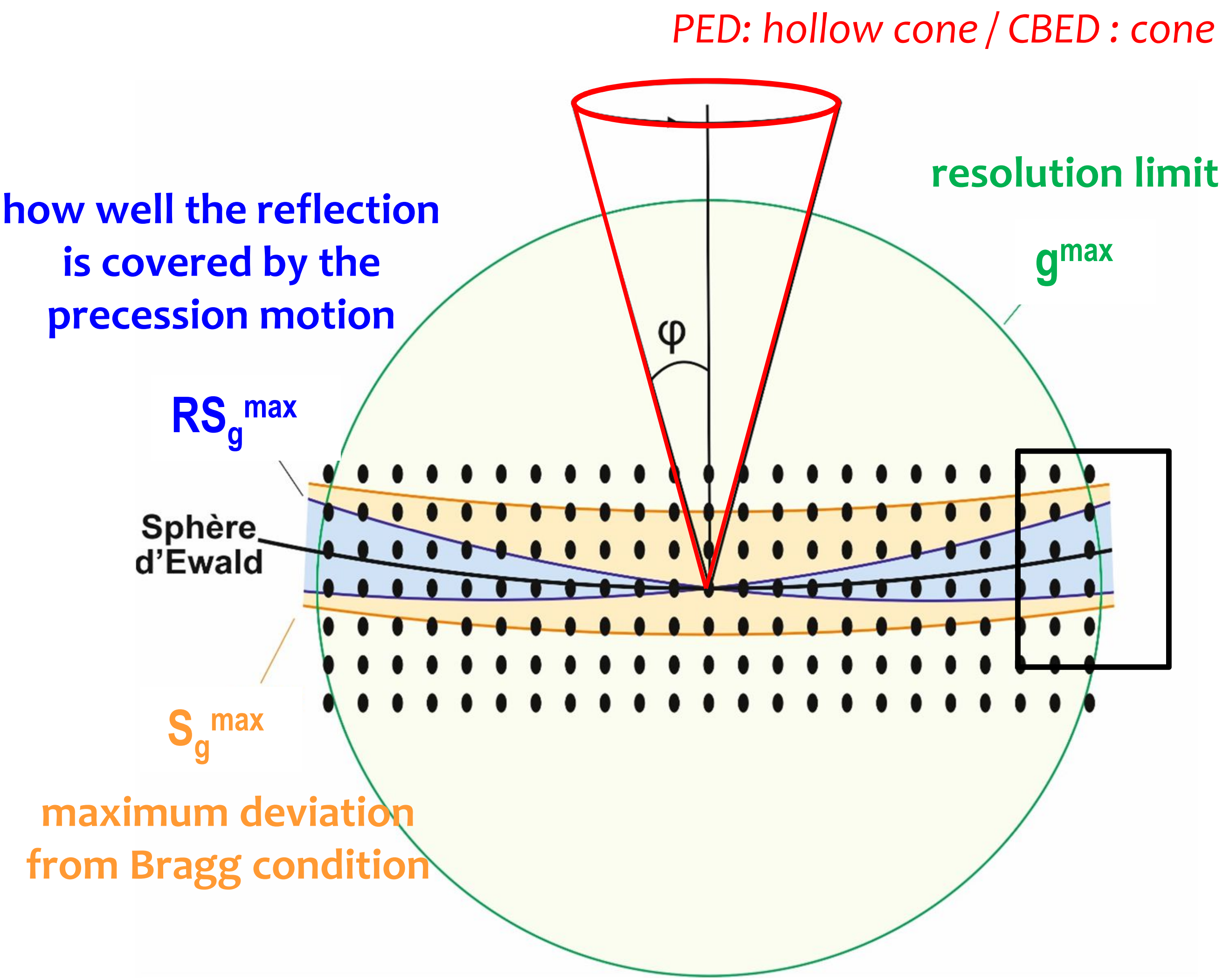
Own et al. (2006), Acta Cryst. A62

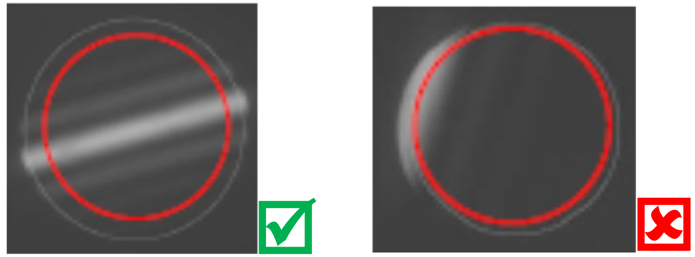


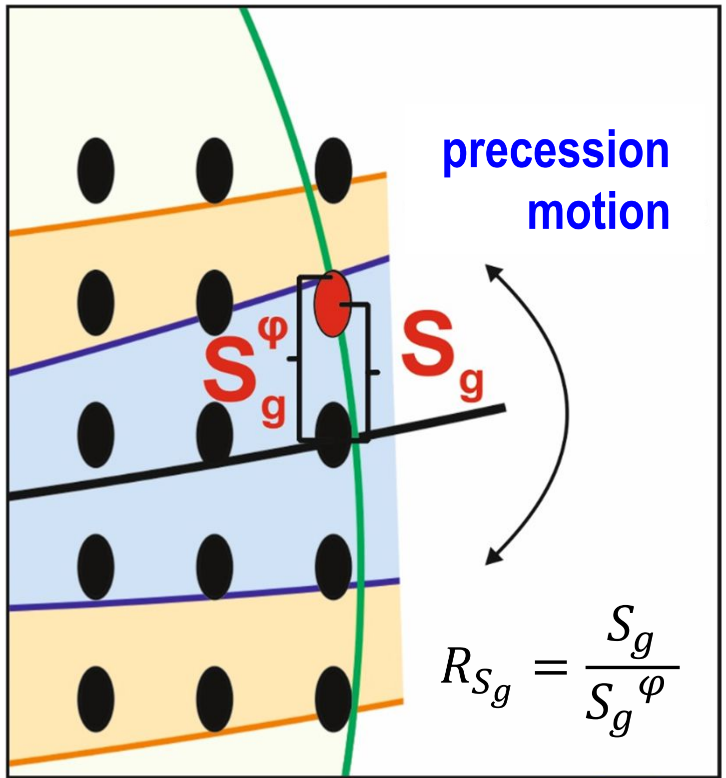
Palatinus et al (2013)., Acta Cryst. A69

PEDT allows feasibility of the dynamical refinements

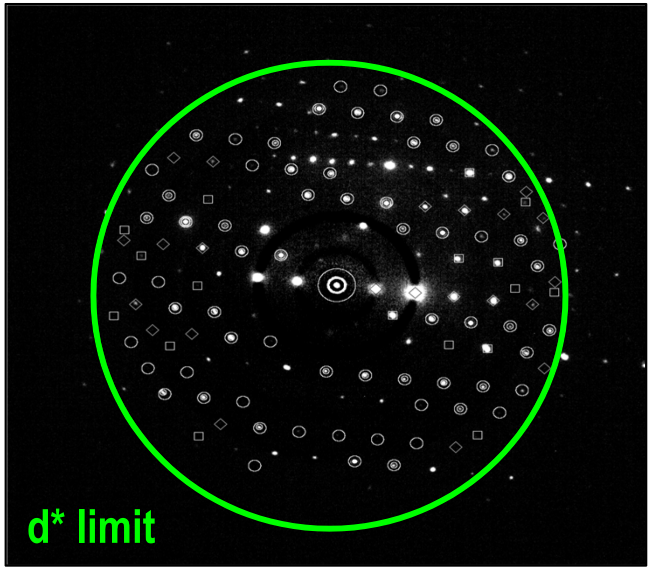
Dynamical refinement ► selection of reflections







Precession Electron Diffraction Tomography (PEDT) ► dynamical



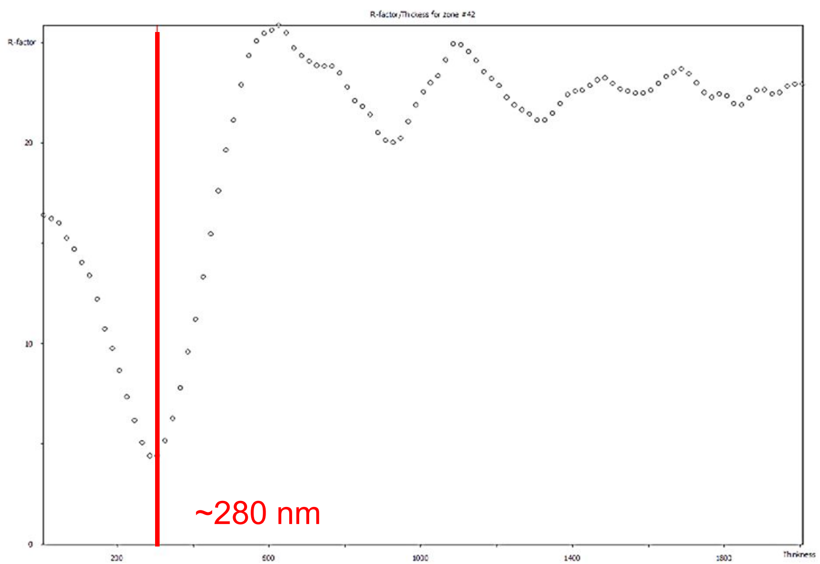
► **Dedicated integration procedure of intensities** **PETS**

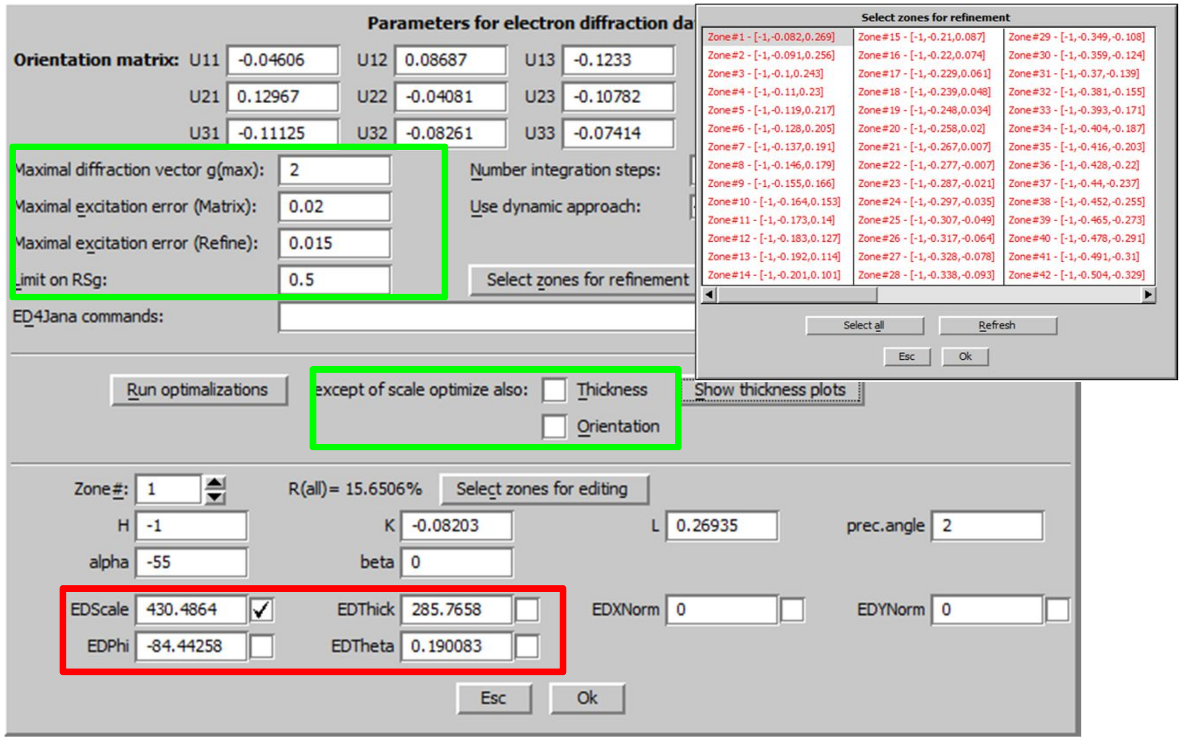
for each frame : list of reflections, hkl , intensity,

scale and estimated standard deviation σ(I) **► n hkl I σ(I) files !**

► **Parameters optimization** **JANA2006**

Thickness optimization

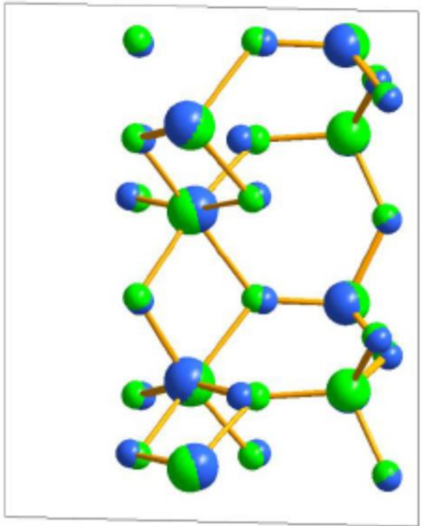




orientation optimization

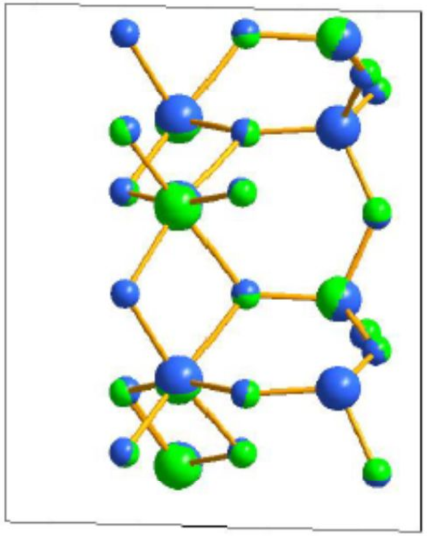
Precession Electron Diffraction Tomography (PEDT) ► dynamical

Kaolinite - comparison of refined and reference structure



kinematical

dynamical



	kinematical	Dynamical
N refl (obs/all)	**941/1062**	**1650/2177**
N parameters	**53**	**153**
R(obs)	**19.15%**	**5.61%**
GooF (obs/all)	**8.74/9.27**	**1.92/2.14**
ΔSi1	0.031	0.005
ΔSi2	0.052	0.021
ΔAl1	0.083	0.011
ΔAl2	0.074	0.024
ΔO1	**0.266**	0.009
ΔO2	0.130	0.021
ΔO3	0.034	0.033
ΔO4	0.055	**0.050**
ΔO5	0.053	0.024
ΔO6	0.106	0.013
ΔO7	0.093	0.012
ΔO8	0.148	0.013
ΔO9	0.104	0.045
mean Δ	**0.095**	**0.022**
max Δ	**0.266**	**0.050**

blue: refined structure
green: reference structure (Neder et al., Clays and Clay Minerals 29)

from L. Palatinus – CrystElec2018

Precession Electron Diffraction Tomography (PEDT) ► dynamical

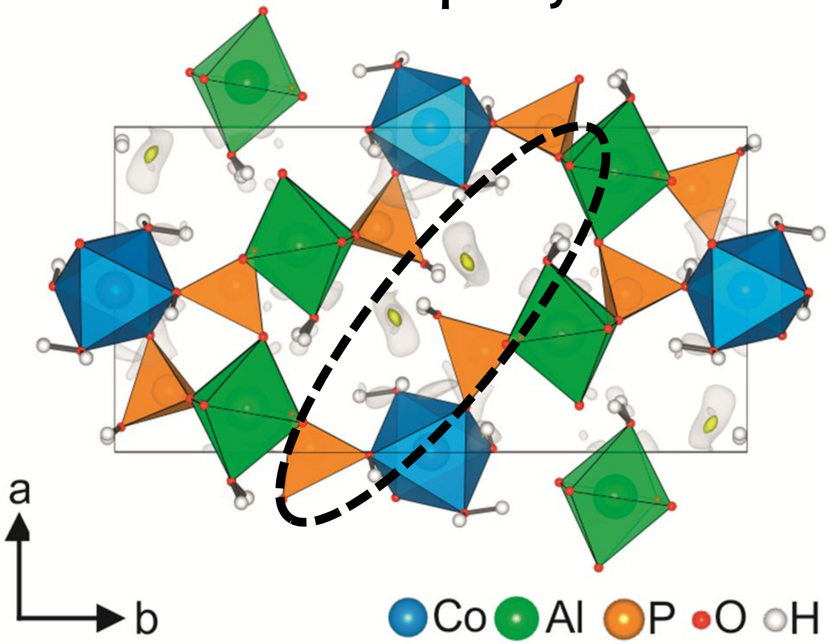
	orthopyroxene	kaolinite	mayenite	Ni_3Si_2	$PrVO_3$
Composition	$(Fe,Mg)_2Si_2O_6$	$Al_2Si_2O_5(OH)_4$	$Ca_{12}Al_{14}O_{33}$	Ni_3Si_2	$PrVO_3$
Space group, cell vol. [Å^3]	Pbca, 867.6	C1, 329.9	I-43d, 1718.9	Cmcm, 970.0	Pbnm, 240.6
No. of indep. atoms/parameters	10/42	13/52	5/12	10/59	4/11
Tilt range/tilt step [°]	-45→45,1	-50→50,1	-50→54, 1	-52→50,1	-56→59,1
Precession angle[°]	1.2	1	2	2	1.5
N(refl)/R(obs) (kinematical)	2558/24.98	1062/19.15	420/17.56	571/17.12	296/31.62
N(refl)/R(obs) (dynamical)	17991/7.48	1650/5.77	11062/8.63	8250/8.45	2741/14.61
Mean/max difference to reference structure [Å] (dynamical)	0.010/0.019	0.022/0.050	0.012/0.033	0.016/0.048	0.017/0.024
Mean/max difference to reference structure (kinematical)	0.049/0.081	0.095/0.266	0.027/0.039	0.006/0.014	0.082/0.135
Remark	Occupancy of mixed sites determined with accuracy of < 2%	Absolute structure could be determined. R(obs) of inverted structure 8.14%. Mean BVS difference 0.04.	Partially occupied oxygen (occupancy 0.25) detected in the difference Fourier map		The tilt angles of the VO_6 octahedron determined to the accuracy of < 0.3°

L. Palatinus et al., Acta Cryst. B71 (2015) 740-751

Co-AlPO : PEDT kinematical vs. dynamical refinement

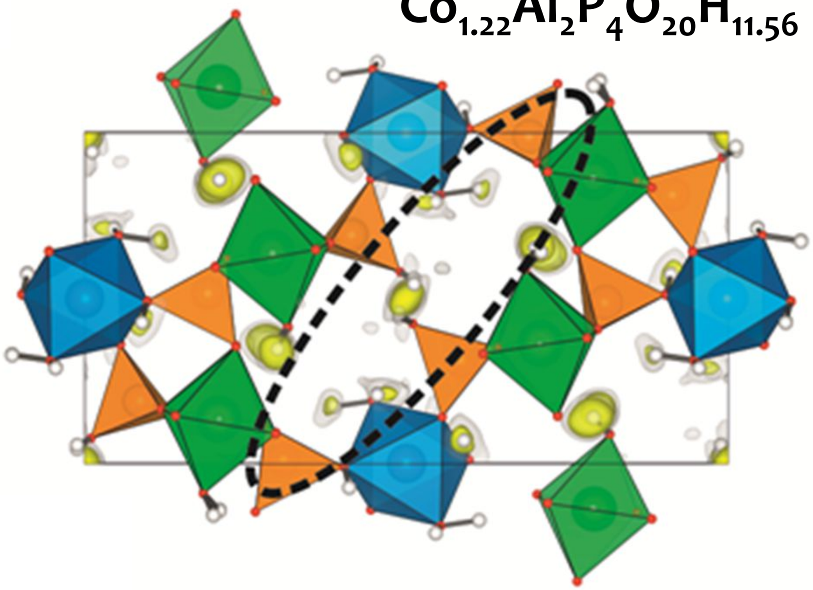
Isosurface levels are 2σ[ΔV(**r**)] (light gray) and <u>3σ[ΔV(**r**)] (yellow)</u>

Co-AlPO ► Co occupancy ? H ?



►

$Co_{1.22}Al_2P_4O_{20}H_{11.56}$



H positions are clearly above noise level

PEDT kinematical : R(obs) = 24.3%

PEDT dynamical : R(obs) = 10.7%

Hydrogen positions in single nanocrystals revealed by electron diffraction

L. Palatinus, P. Brázda, P. Boullay, O. Perez, M. Klementová, S. Petit, V. Eigner, M. Zaarour and S. Mintova

Science 355 (2017) 166-169

Capture de molecules dans les zéolithes

► congélation du composé sur PO de transfert

► localisation de petites molecules et/ou de templates dans les cages

CryoEM, cellules liquide,

electrochimique, gaz, pression …

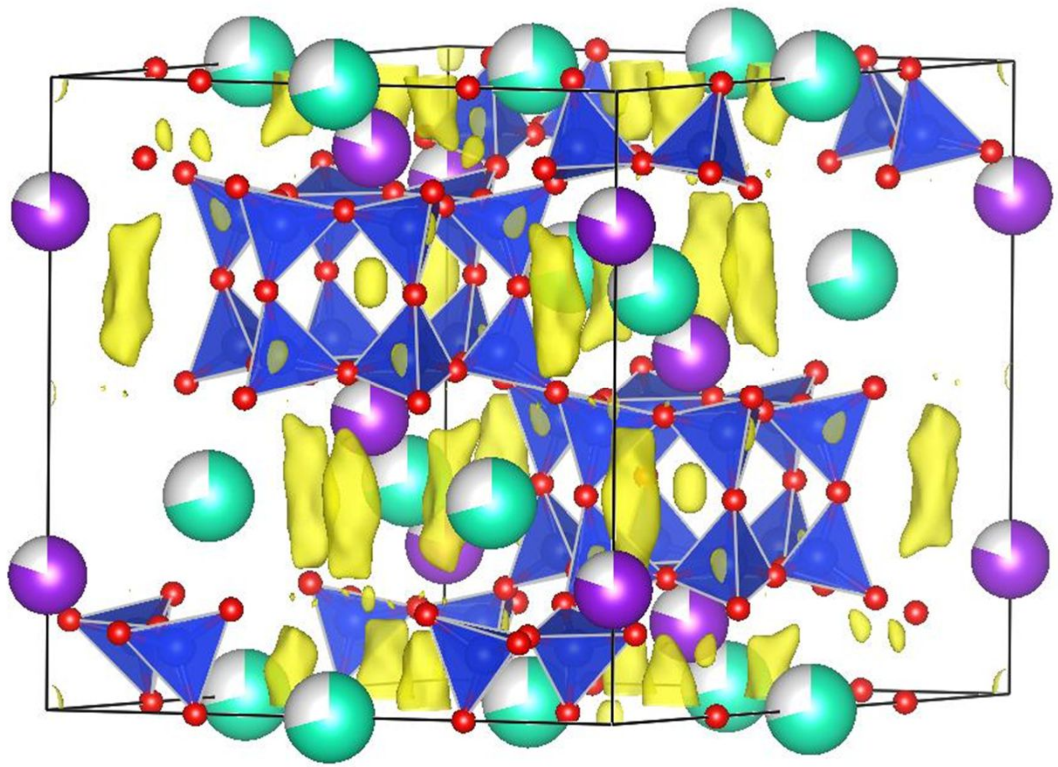
autant de possibilités de diffraction

sous conditions « extrêmes »

…

peu utilisées pour faire de la

cristallographie structurale à ce jour.



1. Institute of Physics, Prague, Czech Republic
2. CRISMAT, ENSICAEN, CNRS, Caen, France
3. LCS, ENSICAEN, CNRS, Caen, France

limit the dynamical effects **PED**

use dynamical scattering theory **JANA**

Data Analysis ▶ 1 hkl I σ(I) file

- limit the interactions between the diffracted beams
- less sensitive to thickness variation
- increase the resolution limit
- integrated intensities

increase the data completeness **EDT**

Frame by frame fit ▶ n hkl I σ(I) files

- Bloch-wave formalism
- models for thickness variation
- orientation optimization for each frame
- max. deviation from exact Bragg condition (S_g^0)
- PED: S_g^{min} and S_g^{max} where $S_g^{min/max} = S_g^0 \pm |\mathbf{g}|\varphi$
- …

Precession Electron Diffraction Tomography

structure solution
kinematical approximation

structure refinement
dynamical approach

Accès possible via le réseau national de plateformes en Microscopie Électronique et Sonde Atomique

cnrs cea metsa

2 appels à expérience par an (mai et novembre)
http://metsa.prod.lamp.cnrs.fr/

Traitement et outils pour l'analyse des données PEDT

Intégration et réduction des données: ***PETS ▶ Process Electron Tilt Series***

PETS ▶ **PETS 2** 2018 http://pets.fzu.cz/download/pets2.zip

documentation: http://pets.fzu.cz/download/pets2_manual.pdf

▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼

cinématique

1 fichier hkl intensité sigma

1 fichier *.cif_pets

▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼ ▼

dynamique

1 fichier contenant hkl intensité sigma par cliché

1 fichier *_dyn.cif_pets

Résolution structurale: Superflip, SIR, …

Affinement cinématique: JANA, *possiblement autres …*

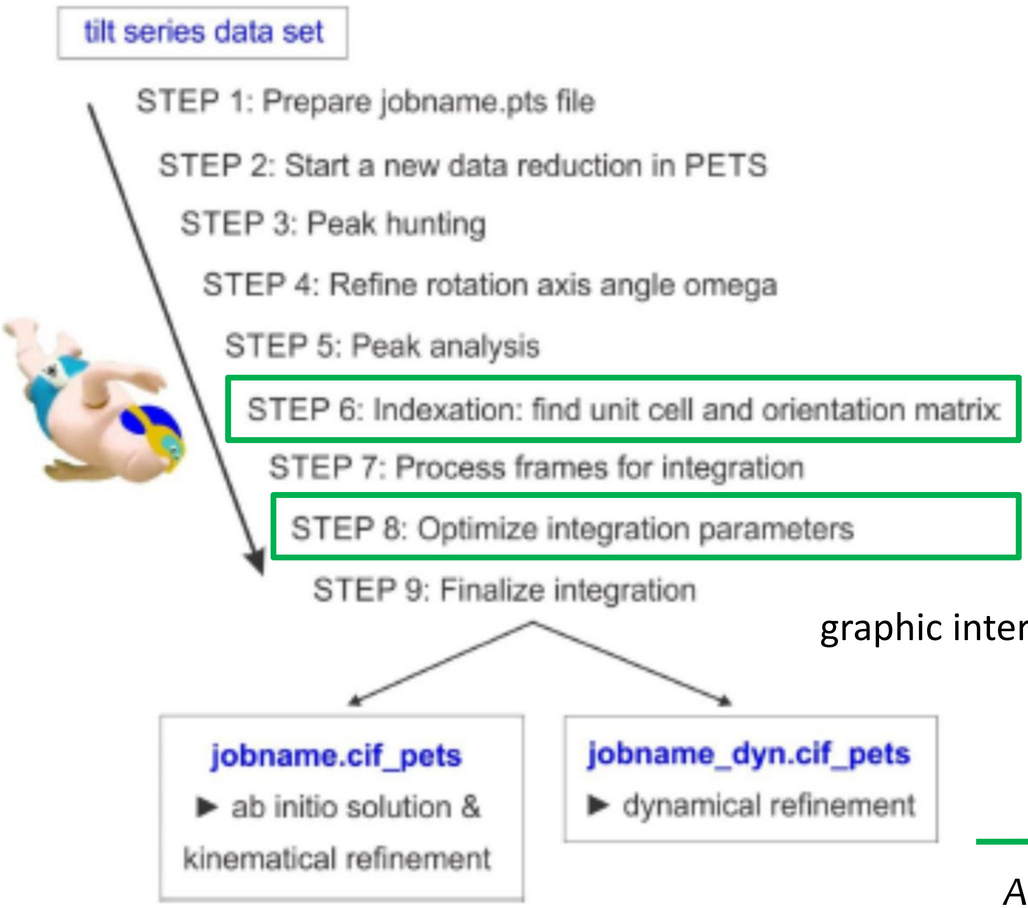
JANA2006 Affinement dynamique: JANA http://jana.fzu.cz

Traitement et outils pour l'analyse des données PEDT

Intégration et réduction des données: ***PETS* ► *Process Electron Tilt Series***

PETS ► **PETS 2** 2018 http://pets.fzu.cz/download/pets2.zip

documentation: http://pets.fzu.cz/download/pets2_manual.pdf



	PETS ►	PETS 2
STEP 1	☑	☑
STEP 2	☑	☑
STEP 3	☑	☑
STEP 4	☑	☑
STEP 5	☑	☑
STEP 6	☒ JANA	☑
STEP 7	☑	☑
STEP 8	☒	☑
graphic interface	☒	☑

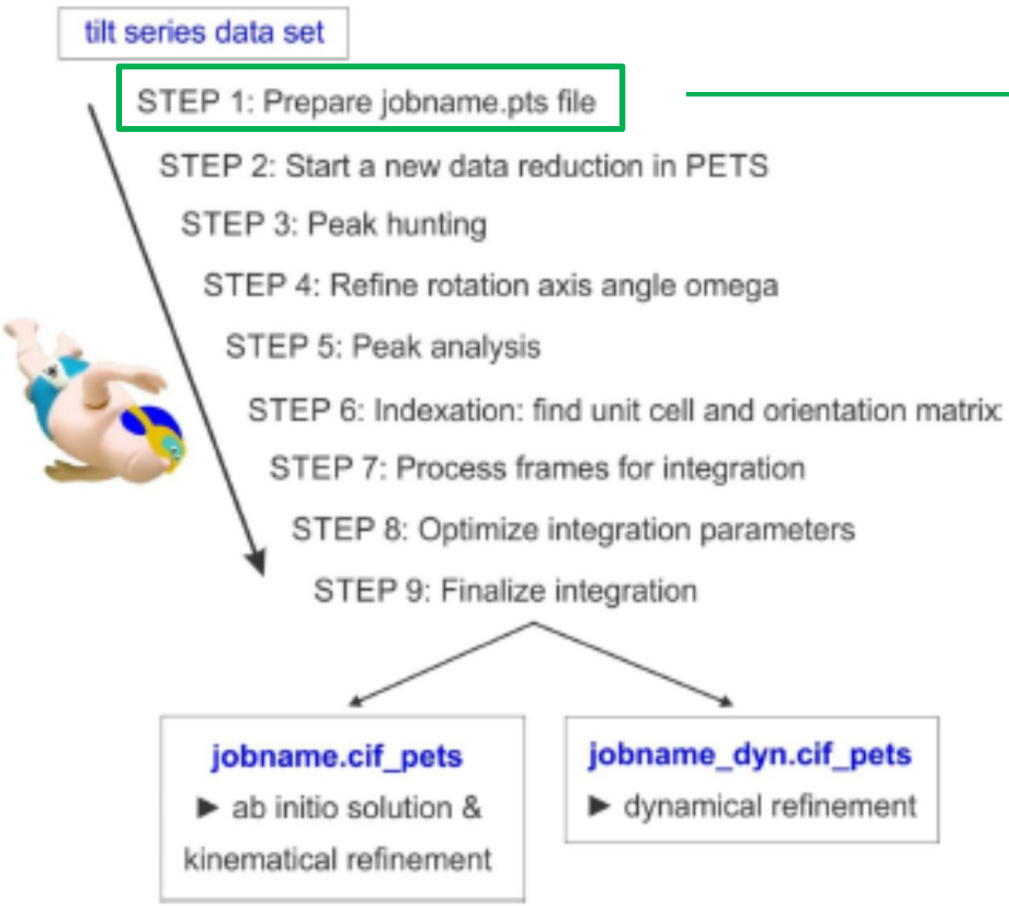
DOS-shell
Image J

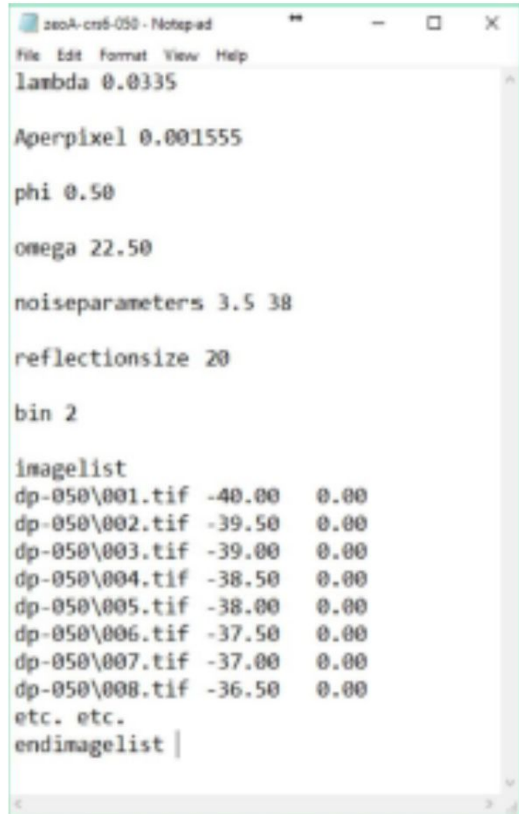
Traitement et outils pour l'analyse des données PEDT

Intégration et réduction des données: ***PETS ▶ Process Electron Tilt Series***

PETS ▶ **PETS 2** 2018 http://pets.fzu.cz/download/pets2.zip

documentation: http://pets.fzu.cz/download/pets2_manual.pdf





```
lambda 0.0335

Aperpixel 0.001555

phi 0.50

omega 22.50

noiseparameters 3.5 38

reflectionsize 20

bin 2

imagelist
dp-050\001.tif -40.00   0.00
dp-050\002.tif -39.50   0.00
dp-050\003.tif -39.00   0.00
dp-050\004.tif -38.50   0.00
dp-050\005.tif -38.00   0.00
dp-050\006.tif -37.50   0.00
dp-050\007.tif -37.00   0.00
dp-050\008.tif -36.50   0.00
etc. etc.
endimagelist
```

Traitement et outils pour l'analyse des données PEDT

Intégration et réduction des données: ***PETS ▶ Process Electron Tilt Series***

PETS ▶ **PETS 2** 2018 http://pets.fzu.cz/download/pets2.zip

documentation: http://pets.fzu.cz/download/pets2_manual.pdf

lambda: *relativistic wavelength of the incident electrons in Angstroms (100kV=0.0370A, 120kV=0.0335A, 200kV=0.0251A, 300kV=0.0197A)*

Aperpixel: *Scale of the images given as the size of one pixel in reciprocal angstroms*

phi: *Precession angle in degrees used during the data collection. Can be zero, of course.*

omega: *orientation of the tilt axis of the sample holder with respect to the positive horizontal axis of the image. Must be estimated either by calibration, or by visual inspection of the series of images. Should be close to the correct value within +/-20 deg. Can be refined later in PETS.*

bin: *Binning of the images prior to any treatment. Saves time, makes nicer pictures, and seems to make the whole analysis somewhat more robust. bin 2 is a good choice from my experience for most data sets. Important: All parameters in the input file that are given in pixels refer to the original, unbinned images. This concerns Aperpixel, center, reflectionsize, mask.*

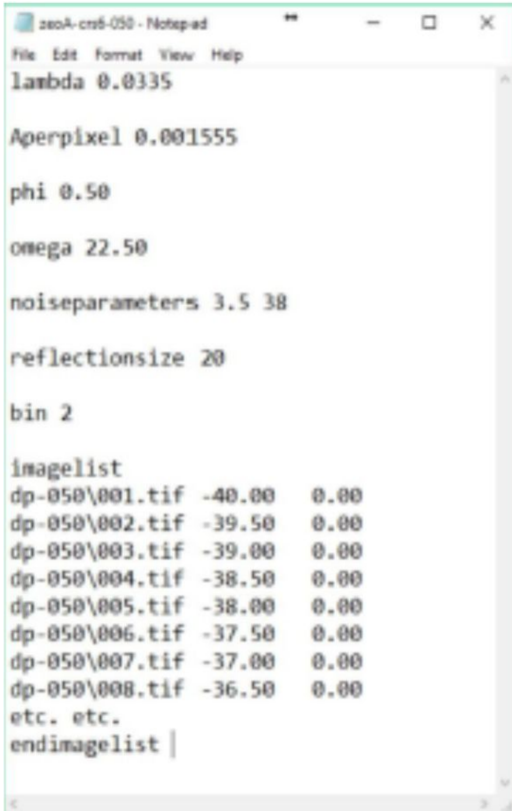
reflectionsize: *Diameter of the spots on the images in pixels. Used for peak search and integration, should be large enough to encompass also the strong spots, but small enough to avoid overlaps of neighboring spots.*

noiseparameters: *two parameters for the determination of σ(I). The first value is Gγ, the second is ψ. The uncertainty on each pixel γ is then calculated as:*

σ2(p)=Gγp+ψ

For more information see Waterman, D. & Evans, G. (2010). J. Appl. Cryst. 43, 1356-1371.

imagelist – endimagelist: *Multiline keyword. Each line contains one image. The format is: name alpha beta. Name is the file name of the image (including possible relative or absolute path), alpha is the tilt angle, and beta is the possible second tilt value of the double tilt holder.*

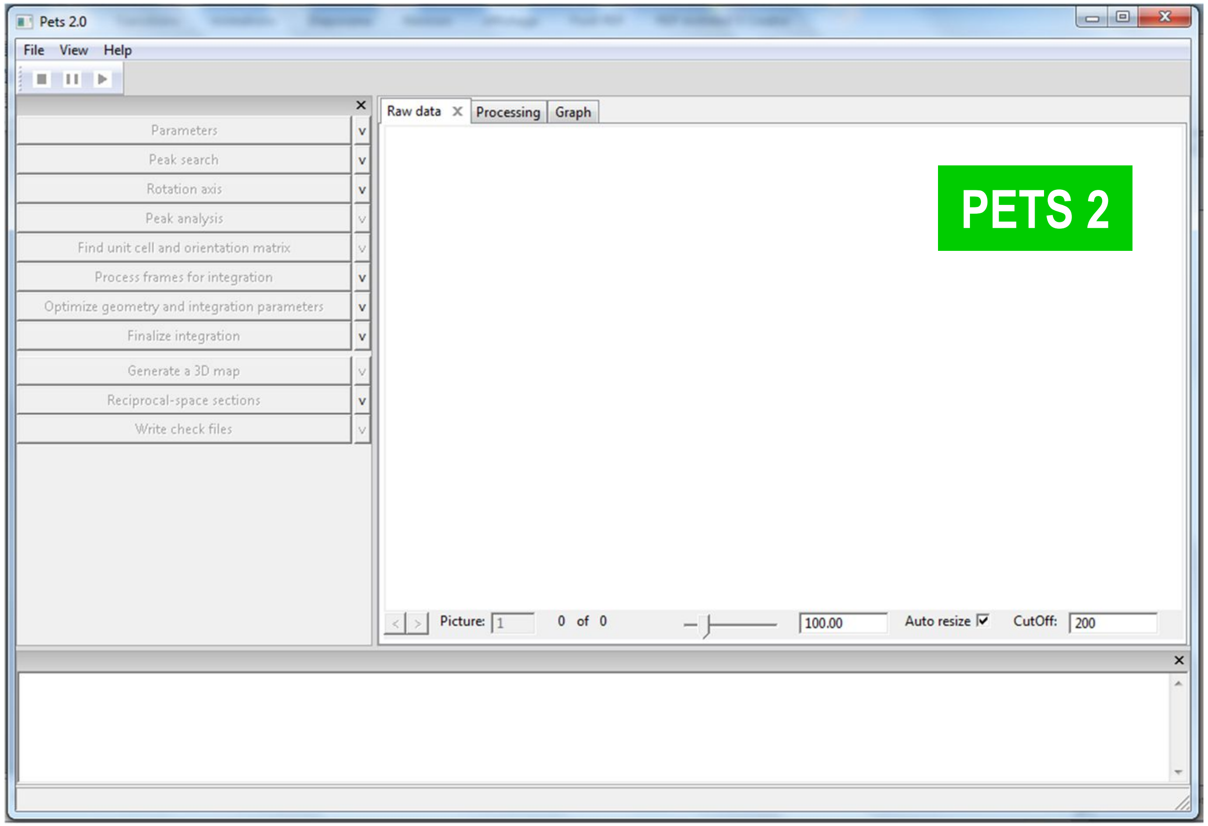

```
lambda 0.0335

Aperpixel 0.001555

phi 0.50

omega 22.50

noiseparameters 3.5 38

reflectionsize 20

bin 2

imagelist
dp-050\001.tif -40.00    0.00
dp-050\002.tif -39.50    0.00
dp-050\003.tif -39.00    0.00
dp-050\004.tif -38.50    0.00
dp-050\005.tif -38.00    0.00
dp-050\006.tif -37.50    0.00
dp-050\007.tif -37.00    0.00
dp-050\008.tif -36.50    0.00
etc. etc.
endimagelist
```

Traitement et outils pour l'analyse des données PEDT

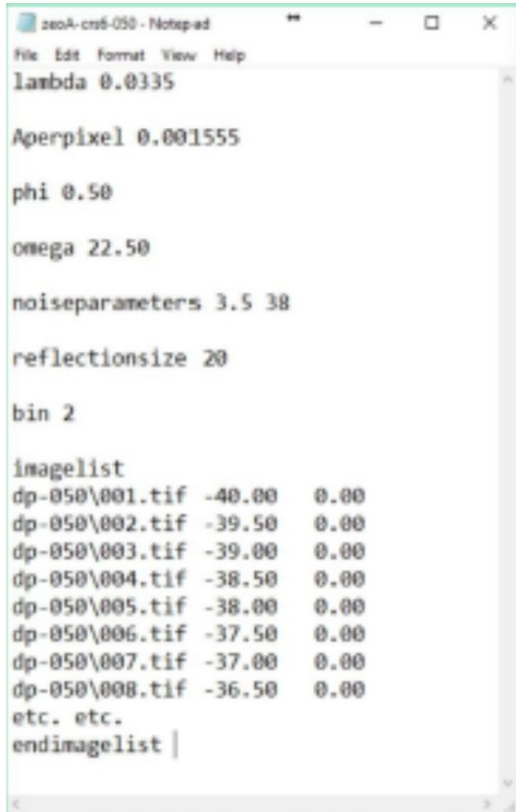
Intégration et réduction des données: ***PETS ▶ Process Electron Tilt Series***

PETS ▶ **PETS 2** 2018 http://pets.fzu.cz/download/pets2.zip

documentation: http://pets.fzu.cz/download/pets2_manual.pdf



◀



Traitement et outils pour l'analyse des données PEDT

Intégration et réduction des données: *PETS ▶ Process Electron Tilt Series*

PETS ▶ PETS 2 2018 http://pets.fzu.cz/download/pets2.zip

documentation: http://pets.fzu.cz/download/pets2_manual.pdf

JANA2006 Affinement cinématique puis dynamique http://jana.fzu.cz

Example: CAP

Solution of CAP (cobalt aluminium phosphate) from PEDT (precession electron diffraction tomography) data. Complete procedure from data reduction to structure refinement using the dynamical approach.

Revised: May 2018

Chemical formula: $Co_{1.13}Al_2P_4O_{20}H_{11.74}$

Data and tutorial for CAP including

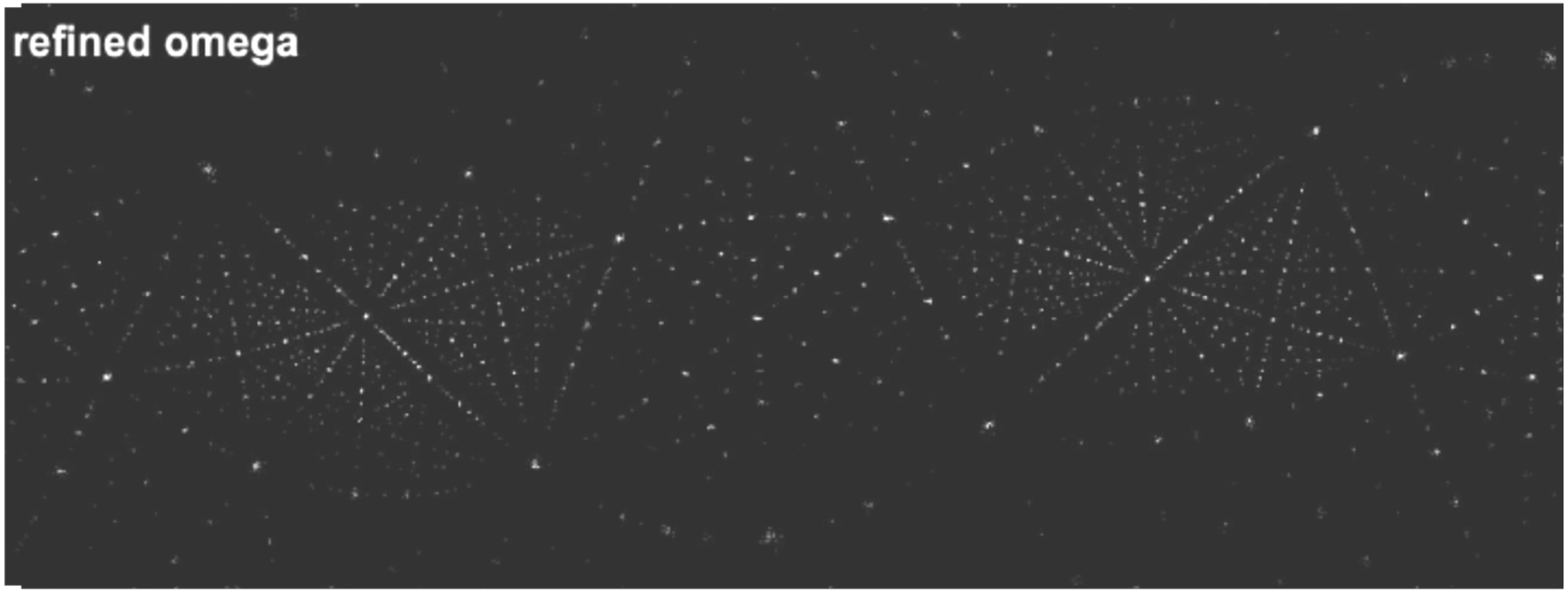
1. Data treatment in PETS 2
2. Structure solution and kinematical refinement in Jana2006
3. Dynamical refinement in Jana2006

http://pets.fzu.cz/download/Workshop_PETS+Jana.zip

Intégration et réduction des données: *PETS ▶ Process Electron Tilt Series*

STEP 4: Refine rotation axis angle omega

The angle omega (angle between the projection of the tilt axis on the image and the horizontal axis) depends on the camera length and on the exact focusing conditions. Therefore it cannot be exactly calibrated, and must be refined for each data set. One can access the quality of the data and accuracy of the parameters by looking at the cylindrical projection of the peak positions that is shown by PETS during the refinement.



Intégration et réduction des données: ***PETS ▶ Process Electron Tilt Series***

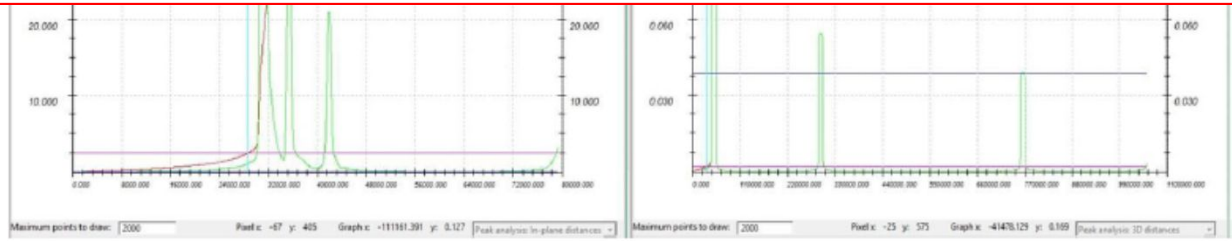
STEP 5: Peak analysis

The raw peak list is usually too noisy to be used for indexing directly ▶ PETS

1. All reflections measured on subsequent frames are clustered, and the centers of the clusters are used instead of individual peak positions. The program shows a plot of inter-peak distances sorted from the shortest to the longest

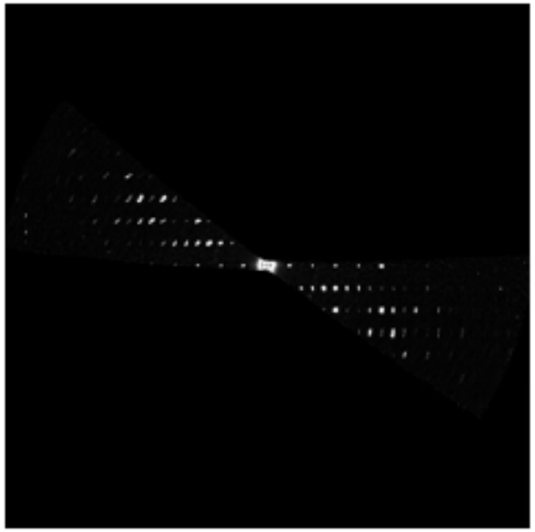
2. PETS calculates difference vectors between the peaks. Then the same clustering procedure is applied to the group of difference vectors, and again a plot of distances is shown for checking the correctness of the choice.

At the end of this procedure three files are produced: jobname.xyz contains the "cleaned" peak list, where individual peaks are replaced by the cluster centers. jobname.diff contains the difference vectors, and jobname.clust contains the list of cluster centers from the difference vectors.

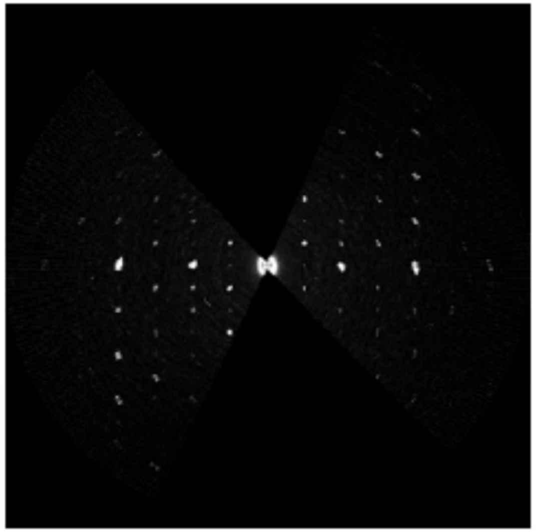


Traitement et outils pour l'analyse des données PEDT

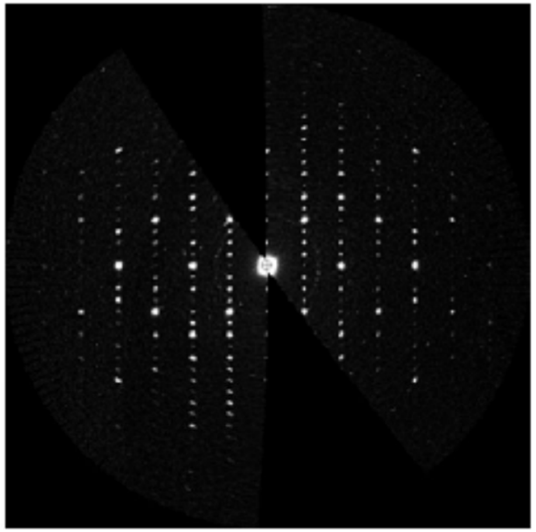
Intégration et réduction des données: *PETS ▶ Process Electron Tilt Series*



0kl

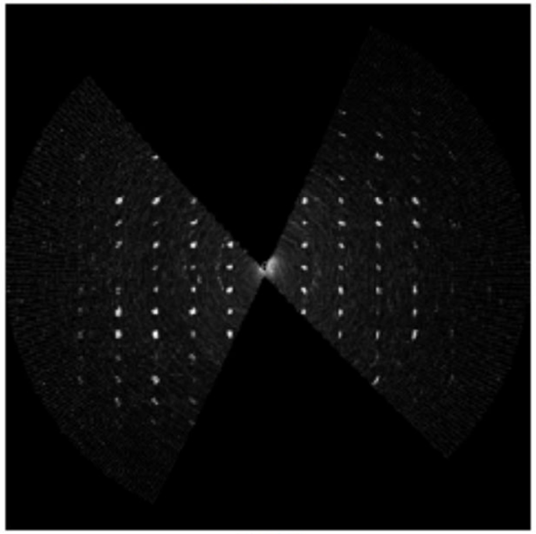


h0l

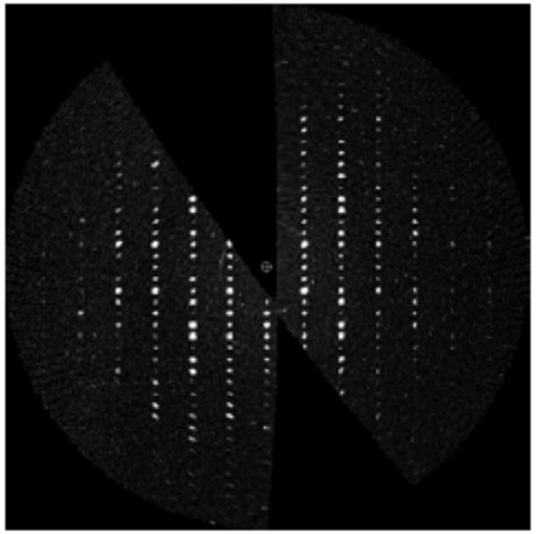


hk0

1kl



h1l



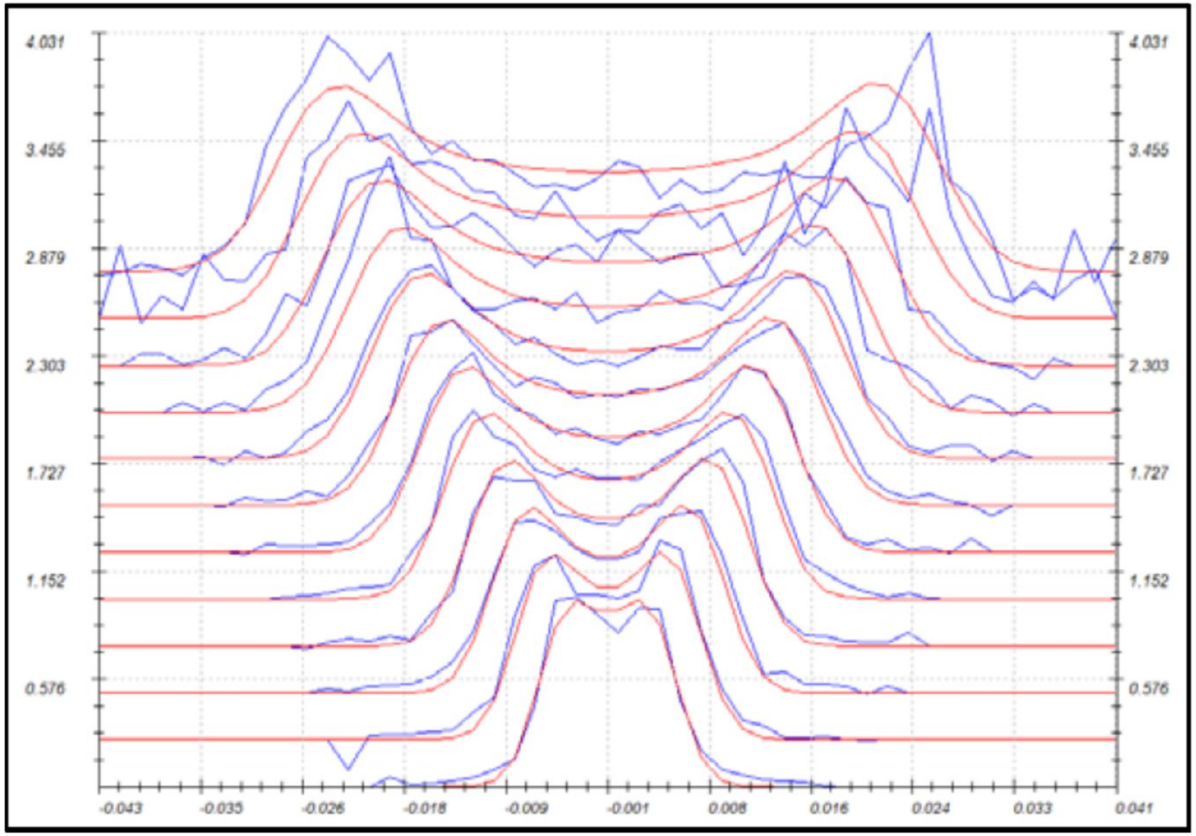
hk1

$P2_1/n$

Intégration et réduction des données: *PETS ► Process Electron Tilt Series*

STEP 8: Optimize integration parameters

Rocking curve (RC) **I=f(s_g)** for PEDT data is a two-peaked curve with the separation of the peaks depending on the precession angle ►camel plot



average rocking curve of reflections in one resolution shell

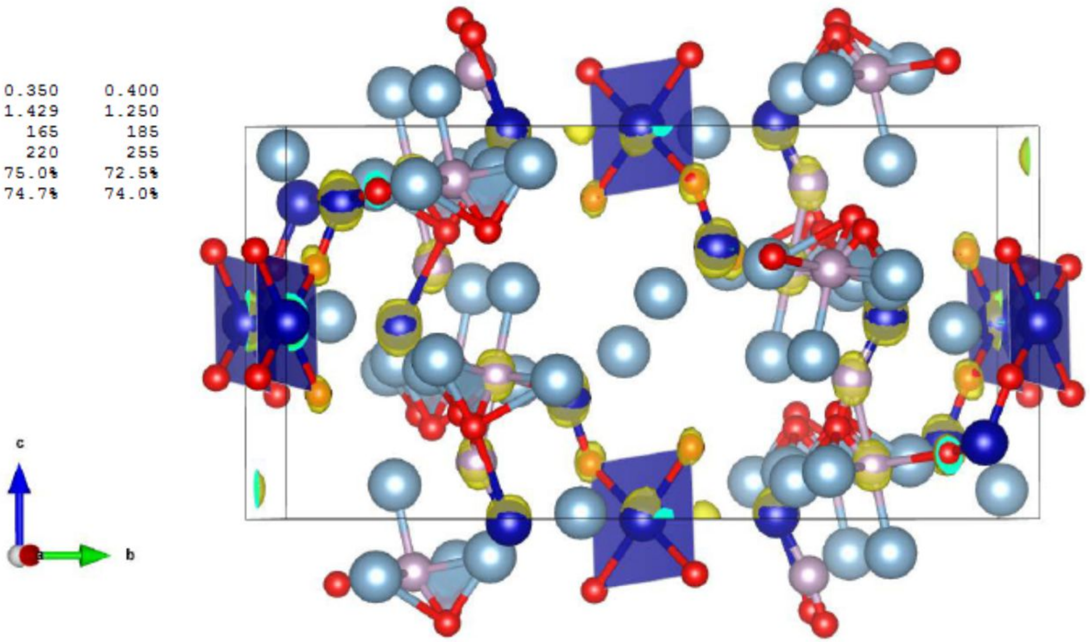
↑ step 0.1 Å^{-1}

start 0.2 - 0.3 Å^{-1}

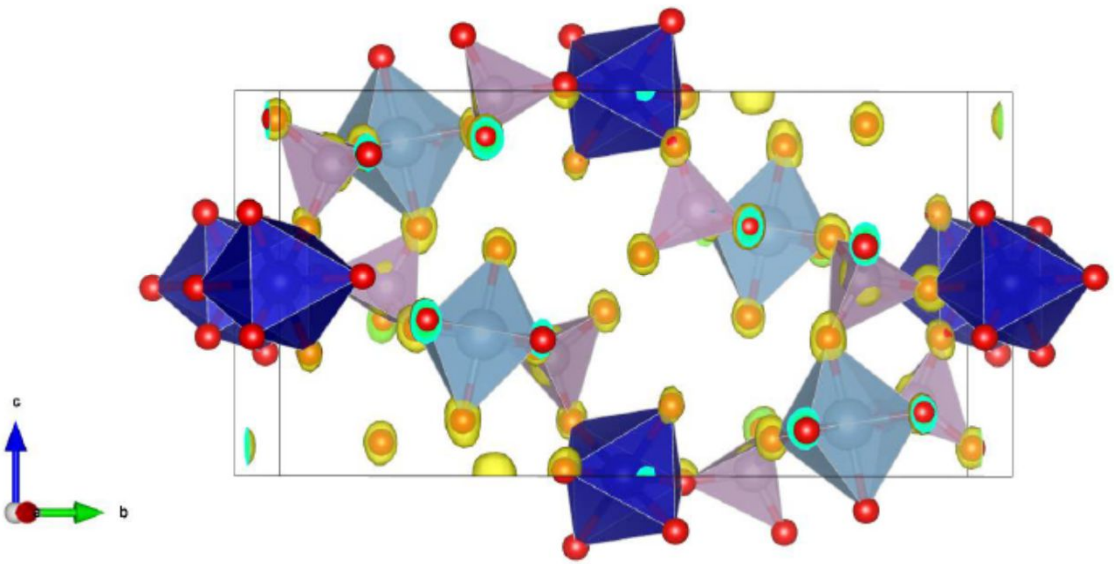
Traitement et outils pour l'analyse des données PEDT

JANA2006 Solution : Superflip in JANA2006 http://jana.fzu.cz

```
------------------------------------------------------------
Coverage statistics of the expanded reflections by shells:
------------------------------------------------------------
Resolution (sin(th)/l):    0.050   0.100   0.150   0.200   0.250   0.300   0.350   0.400
Resolution (d_min):       10.000   5.000   3.333   2.500   2.000   1.667   1.429   1.250
Obs. refl. in shell:           0       2      30      43      85     100     165     185
Total refl. in shell:          0      10      40      59     112     128     220     255
Coverage in shell:          0.0%   20.0%   75.0%   72.9%   75.9%   78.1%   75.0%   72.5%
Commulative coverage:       0.0%   20.0%   64.0%   68.8%   72.4%   74.5%   74.7%   74.0%

Resolution (sin(th)/l):    0.450   0.500   0.550   0.600   0.650   0.700
Resolution (d_min):        1.111   1.000   0.909   0.833   0.769   0.714
Obs. refl. in shell:         277     304     406     457     574     650
Total refl. in shell:        366     400     526     591     742     844
Coverage in shell:         75.7%   76.0%   77.2%   77.3%   77.4%   77.0%
Commulative coverage:      74.5%   74.9%   75.5%   75.9%   76.2%   76.4%


 Current FOM is the best until now. Saving the density.
 Properties of the saved density:
   Run  Rvalue   Peaks  Symm.    Der.SG
    8   42.04    2.10   14.65     P21/n
 Electron density written to file CAP_reference_Superflip.m81.
```



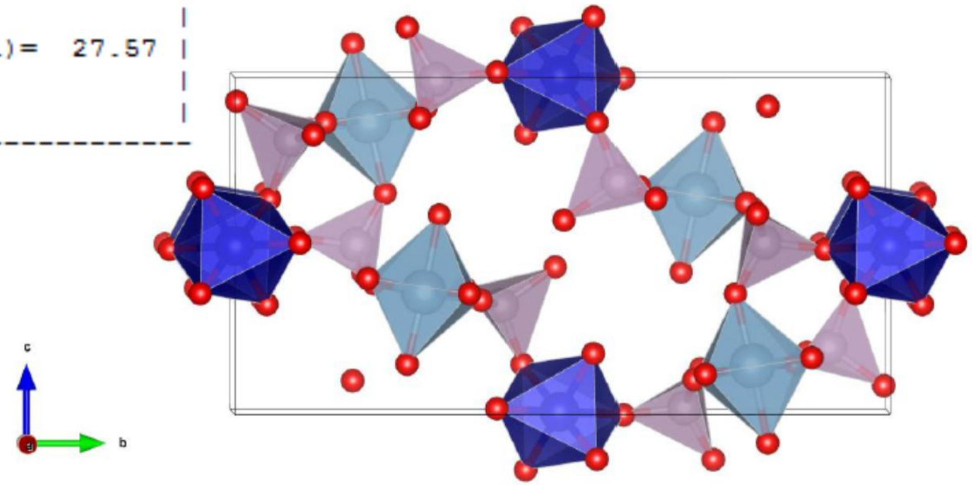
brute



après interprétation

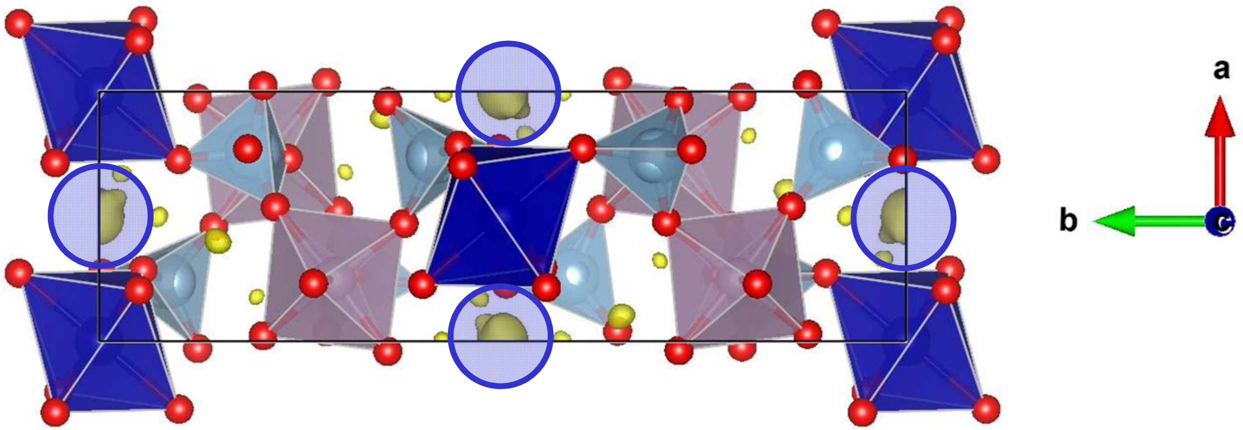
JANA2006 Affinement cinématique : JANA http://jana.fzu.cz

```
--------------------------------------------------------------------------
|R factors : [1577=1209+368/54],     Damping factor:    1.0000            |
|GOF(obs)= 13.81     GOF(all)= 12.07                                      |
|R(obs)=  25.34    wR(obs)=  27.48    R(all)=   28.86    wR(all)=  27.57 |
|Last wR(all): 37.26 28.87 27.70 27.57 27.57 27.57                        |
|Maximum change/s.u.  :     0.0051 for Uiso[Al2]                          |
--------------------------------------------------------------------------
```



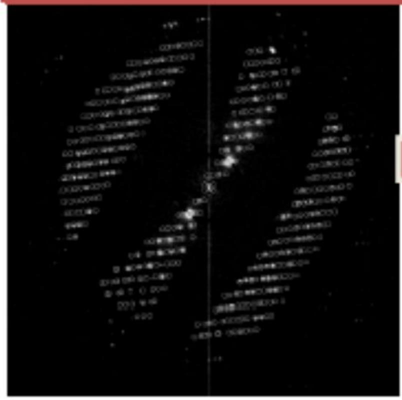
carte de Fourier différence

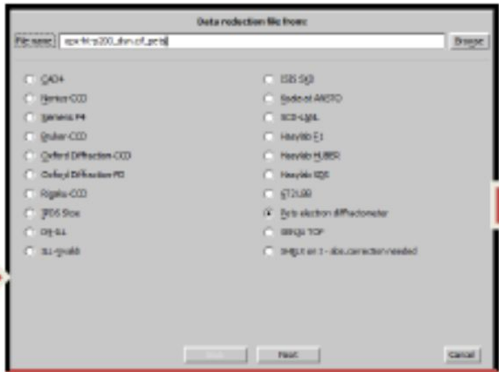
Co occup. partielle



JANA2006 Affinement dynamique: JANA http://jana.fzu.cz

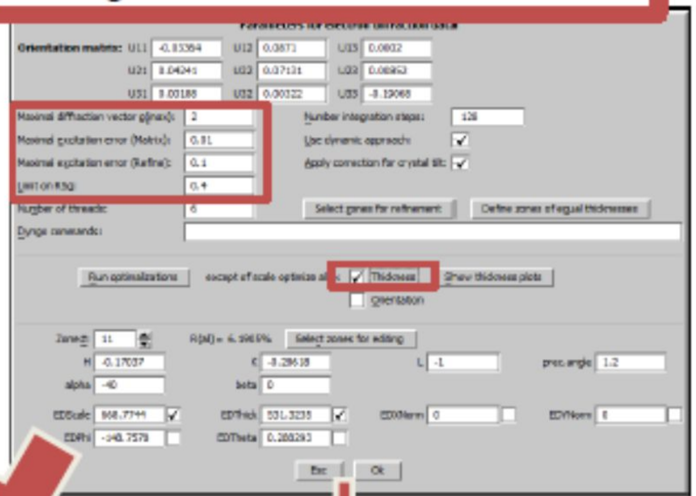
Analyze data and extract intensities

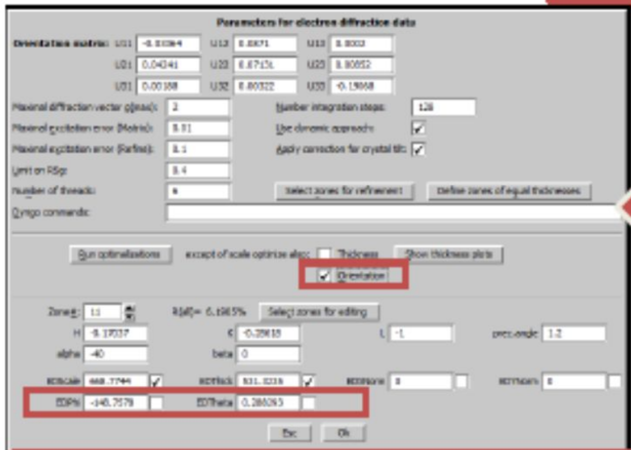




Import the data to Jana. All information is stored in CIF format and imported automatically

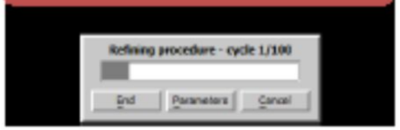
Set up the parameters of refinement, calculate thickness plots to indentify starting thickness

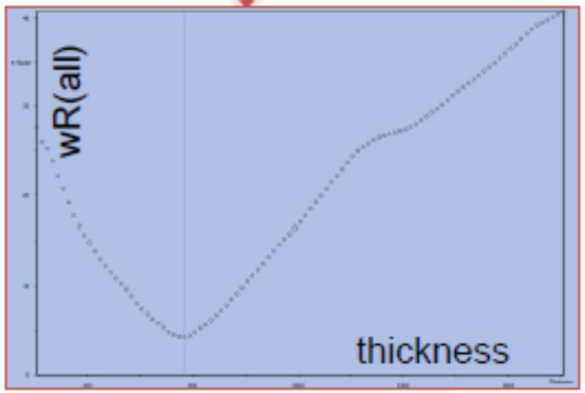




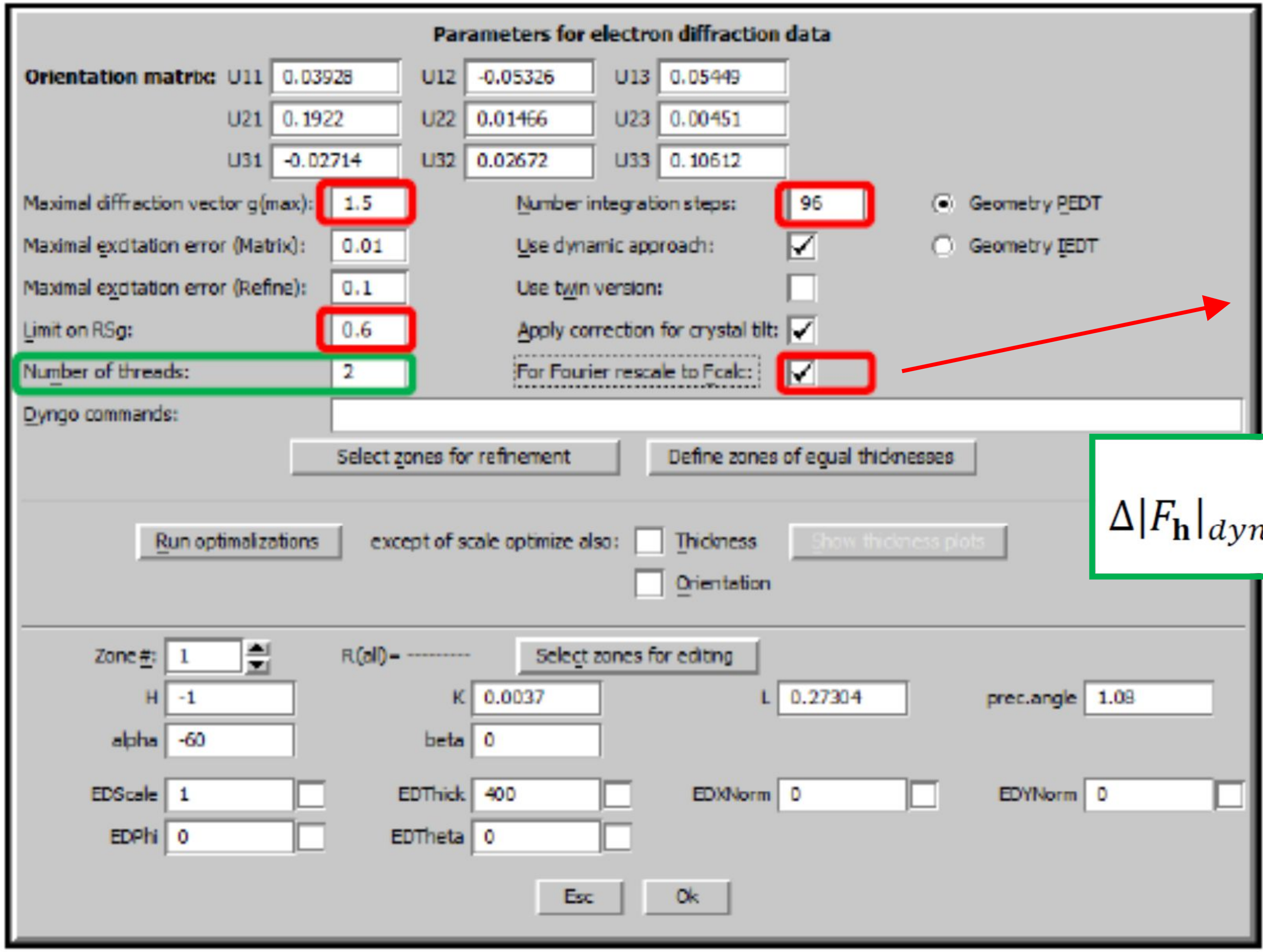
Fine-tune the orientation of individual patterns

Run standard least-squares refinement. Refine structure parameters, sample thickness, scales of individual patterns.





JANA2006 Affinement dynamique: JANA http://jana.fzu.cz



$\Delta|F_{\mathbf{h}}|_{kin}$

$$\Delta|F_{\mathbf{h}}|_{kin} = sA_{\mathbf{h}}^{exp} - \left|F_{\mathbf{h}}^{model}\right|$$

$$e^{-}\ (\mathrm{kin}):\ sA_{\mathbf{h}}^{exp} \neq \left|F_{\mathbf{h}}^{exp}\right|$$

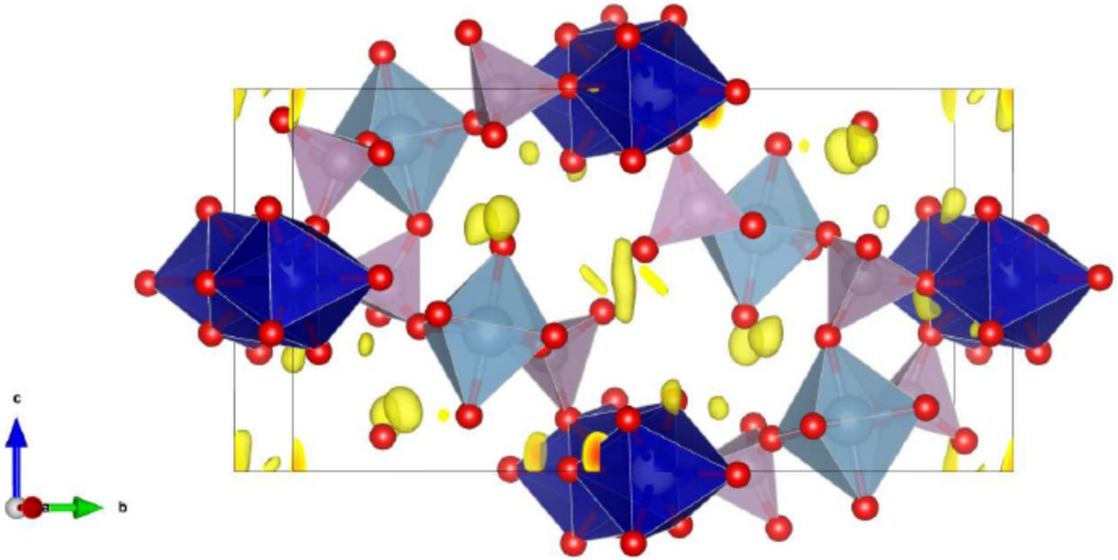
$$\Delta|F_{\mathbf{h}}|_{dyn} = \left(sA_{\mathbf{h}}^{exp} - A_{\mathbf{h}}^{model}\right)\frac{\left|F_{\mathbf{h}}^{model}\right|}{A_{\mathbf{h}}^{model}}$$

meilleure approximation

JANA2006 Affinement dynamique: JANA http://jana.fzu.cz

► CAP_dyn4_all

refinement without hydrogens



► CAP_dyn5_final

refinement with hydrogens and orientation