NVK, Oss, NL
12-10-2017

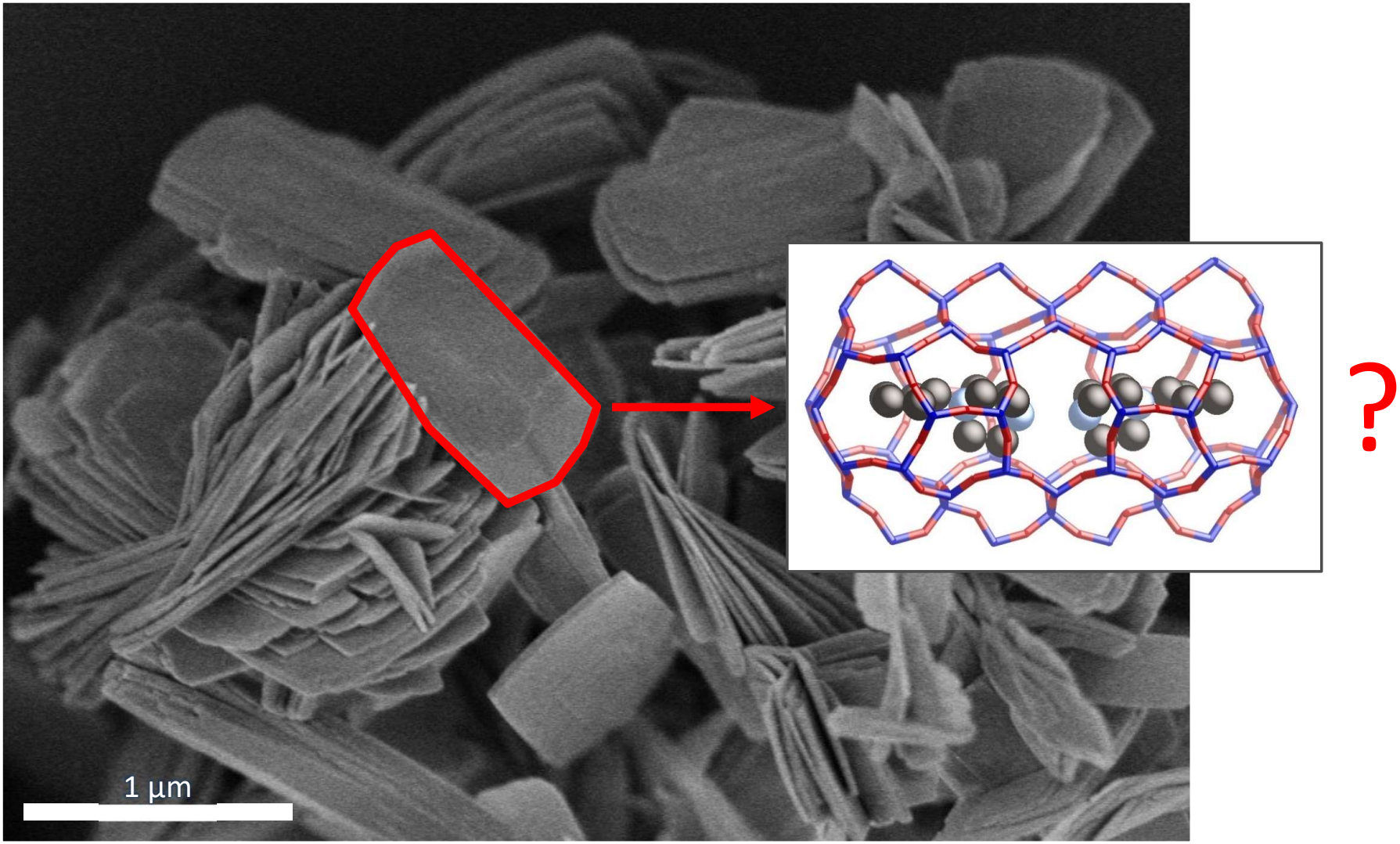
SWISS NATIONAL SCIENCE FOUNDATION

Stockholm University

Serial electron diffraction for structure determination and phase analysis of polycrystalline materials

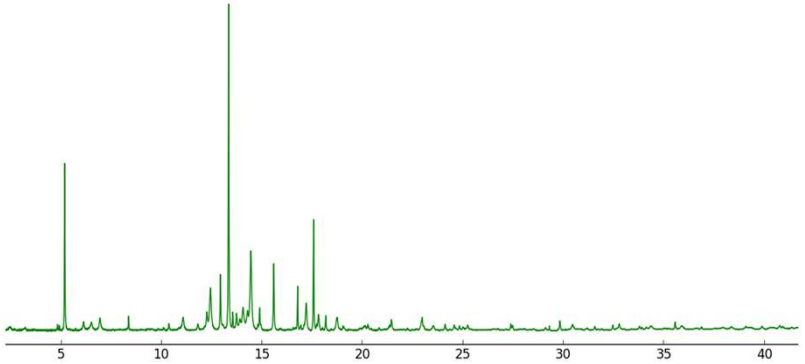
Stef Smeets

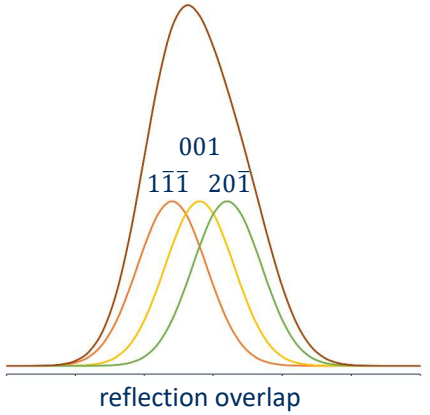
Stockholm University



zeolite SSZ-45

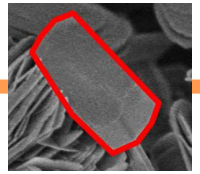
Bulk





X-ray powder diffraction

Crystal size



100 µm | 10 µm | 1 µm | 100 nm | 10 nm | 1 nm

X-ray diffraction

micro-diffraction

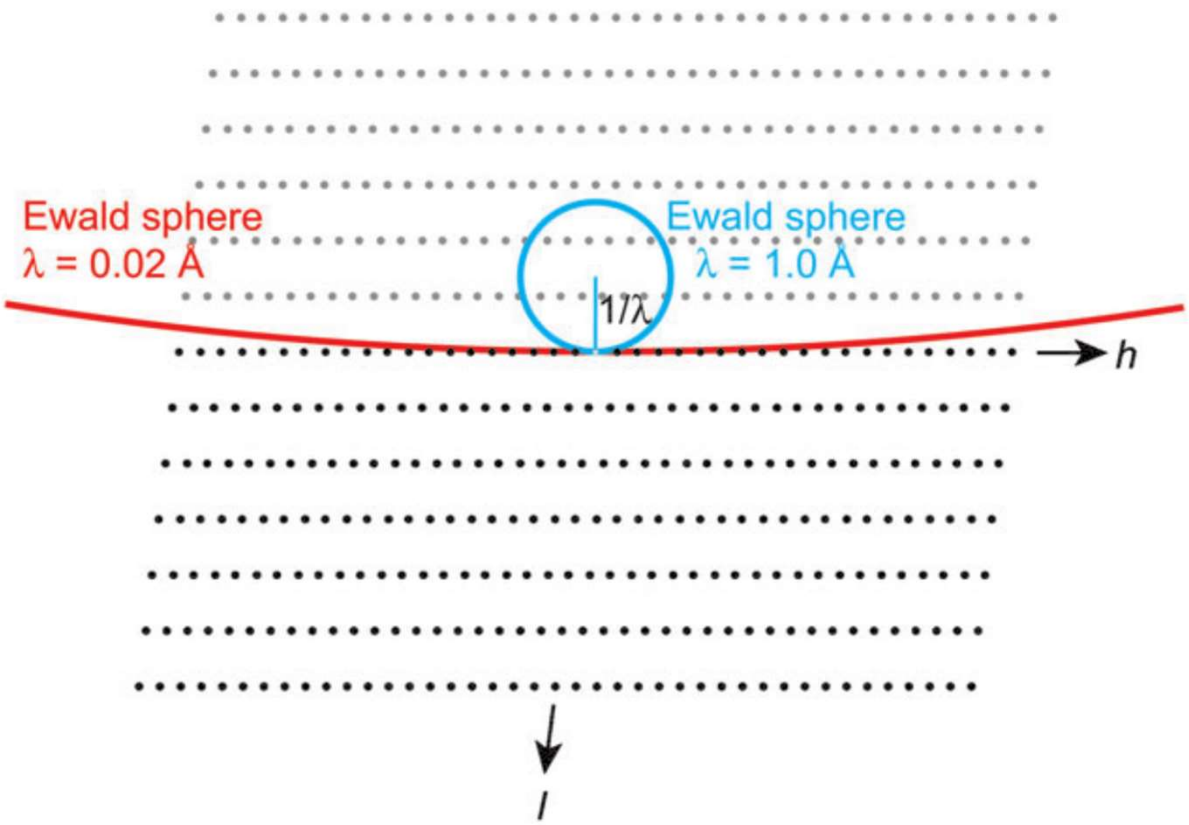
Electron diffraction

HRTEM imaging

Electron crystallography

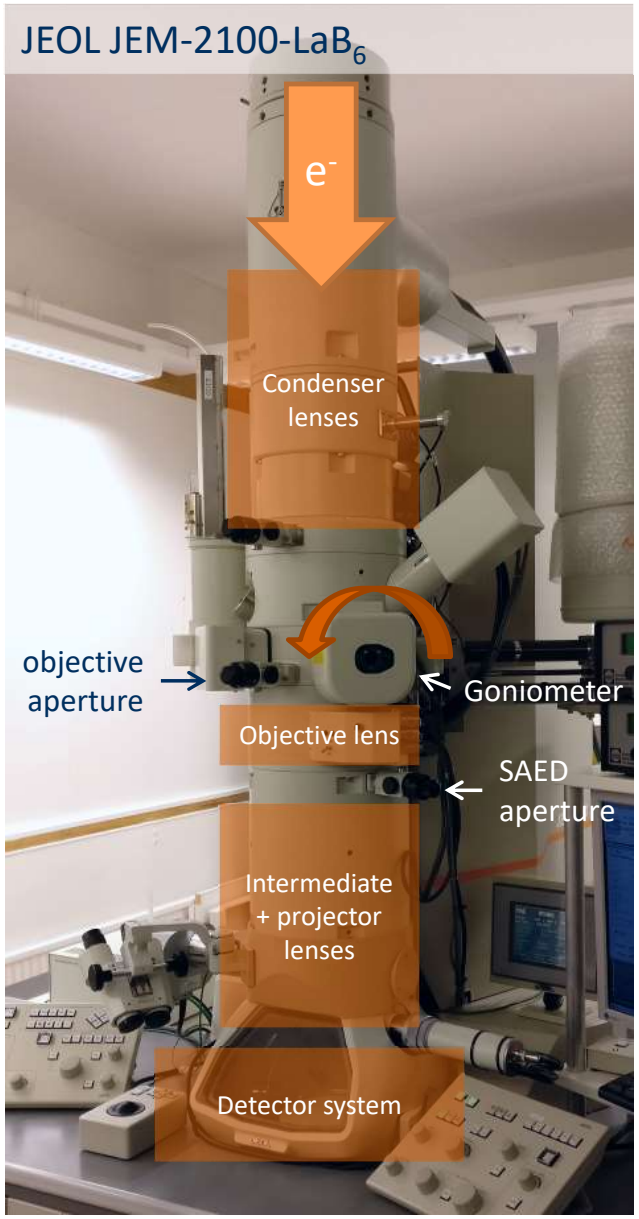
Single crystal

Electrons as a radiation source

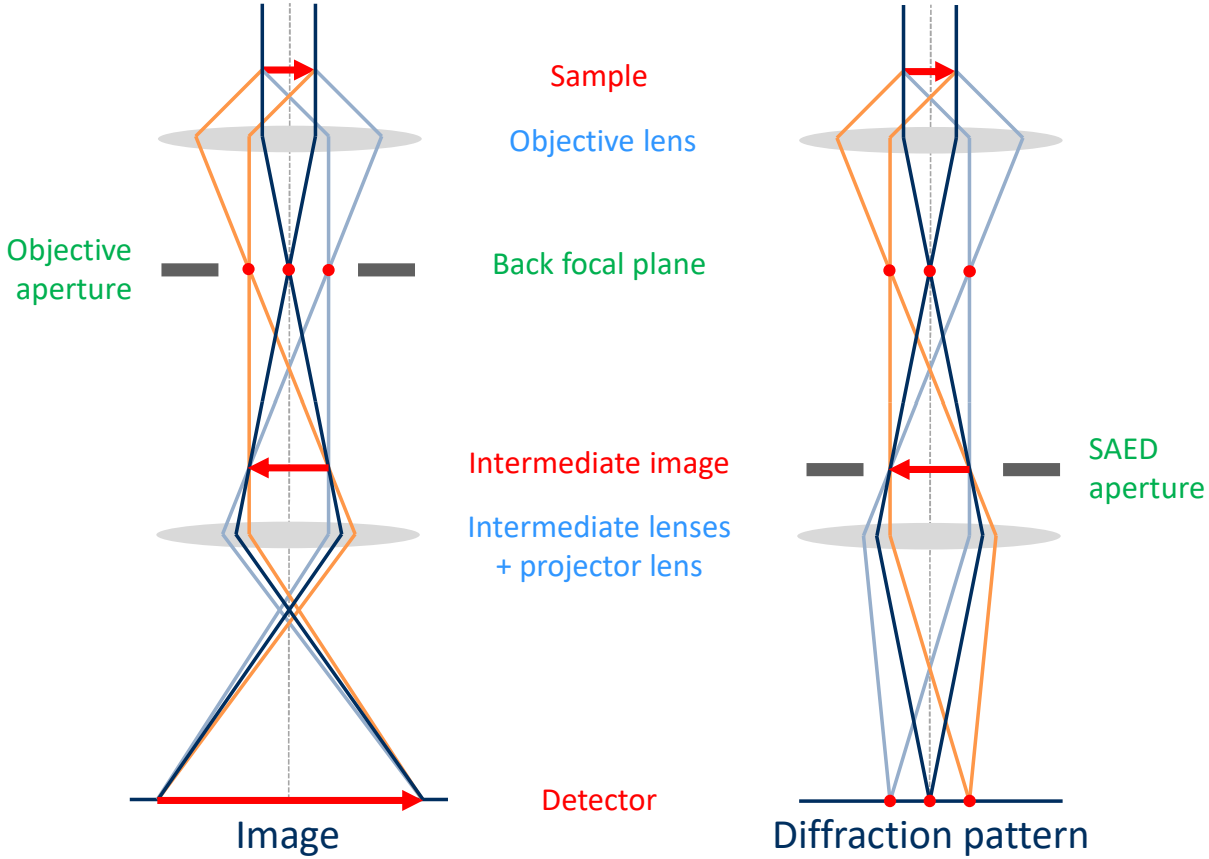


- Accelerating voltage: 100 to 300 keV
- Wavelength: 0.0251 Å @ 200 keV
- Probe electrostatic potential
- High vacuum (<10^{-3} mbar)
- Strong interaction (10^6 stronger than X-rays)
- Require small samples (< 1 µm)

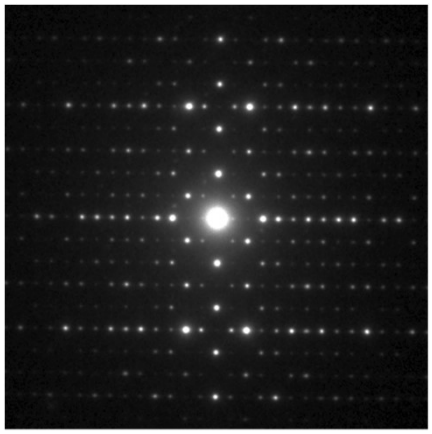
McCusker & Baerlocher, Chem. Commun., 2009, 1439–1451



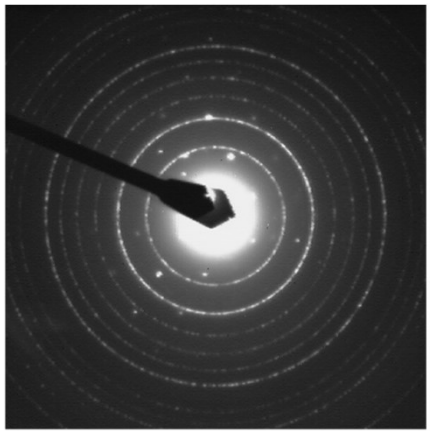
Electron 'diffractometer'



Diffraction



Selected area (SAED)

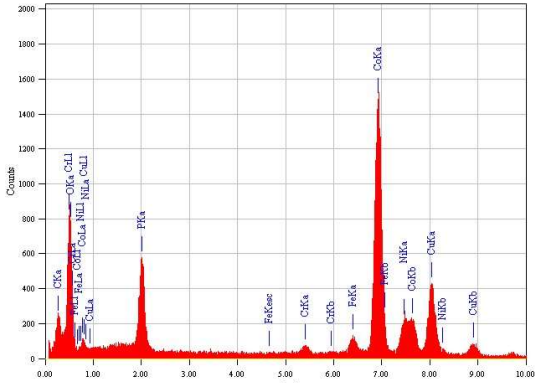


SAED powder

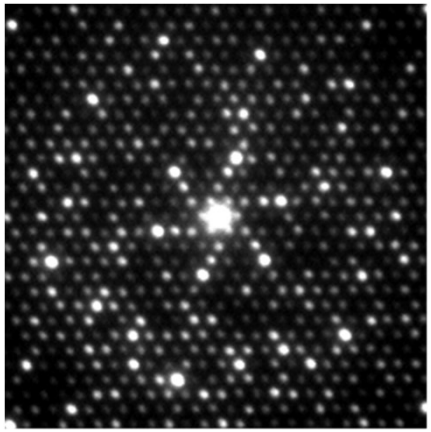
Imaging

High-resolution TEM

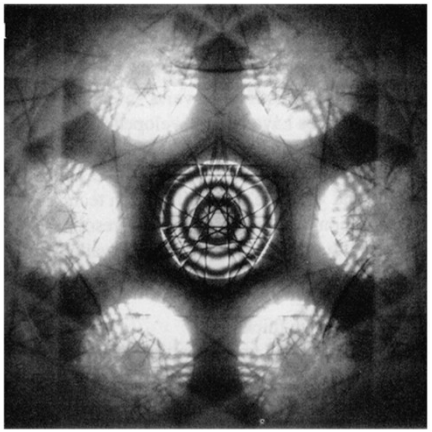
Spectroscopy



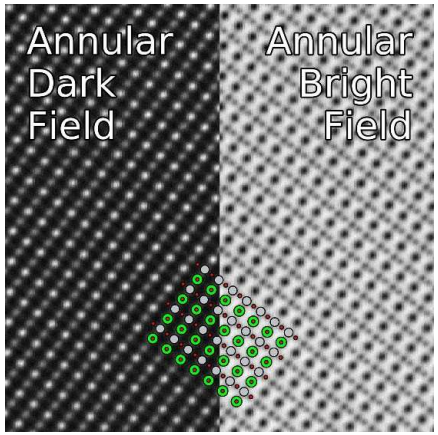
EDX



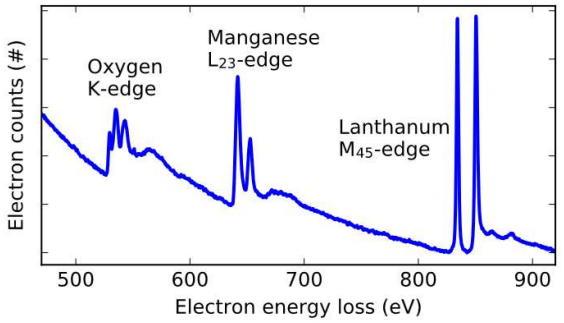
Nano-focused beam



Convergent beam (CBED)

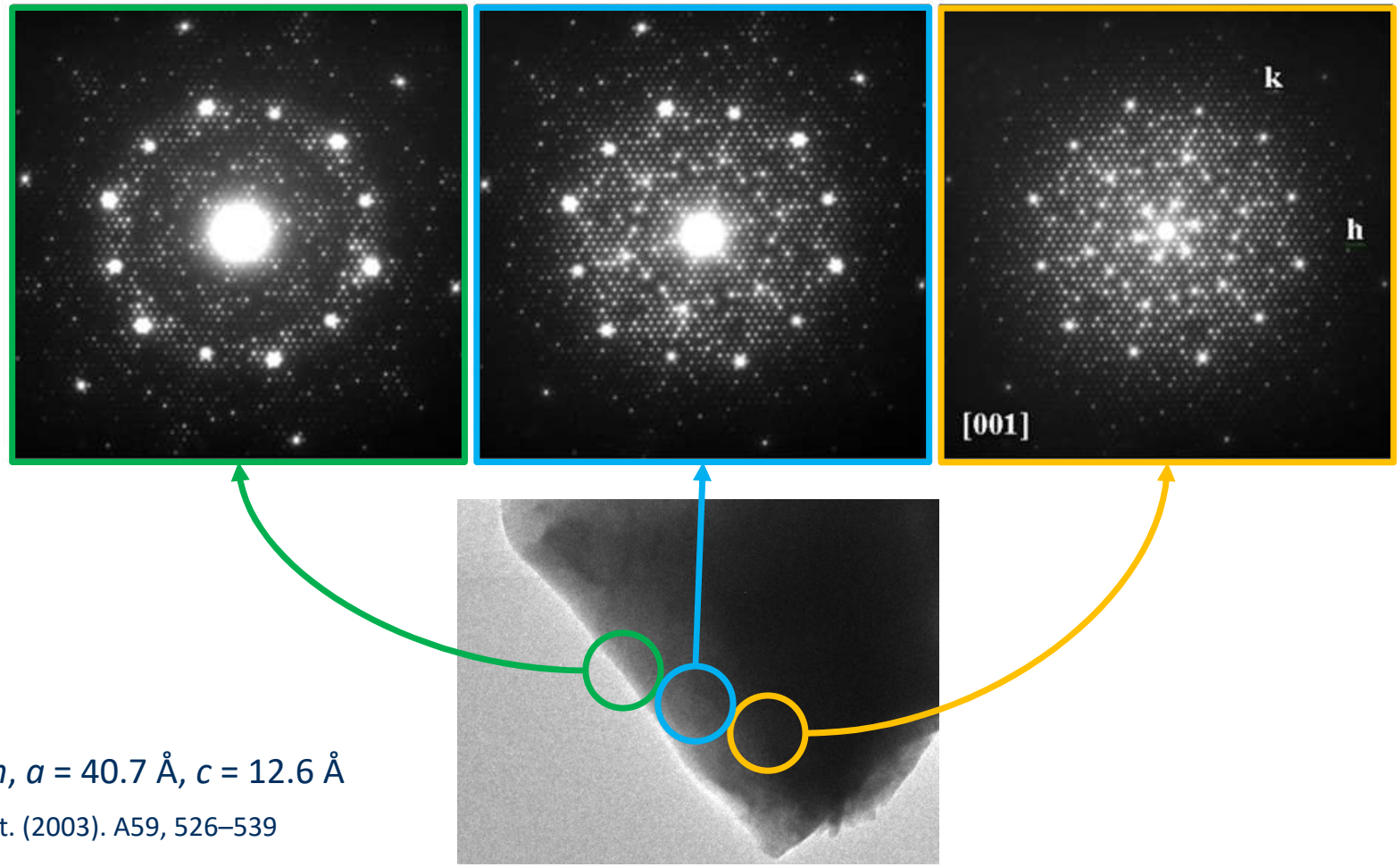


STM



EELS

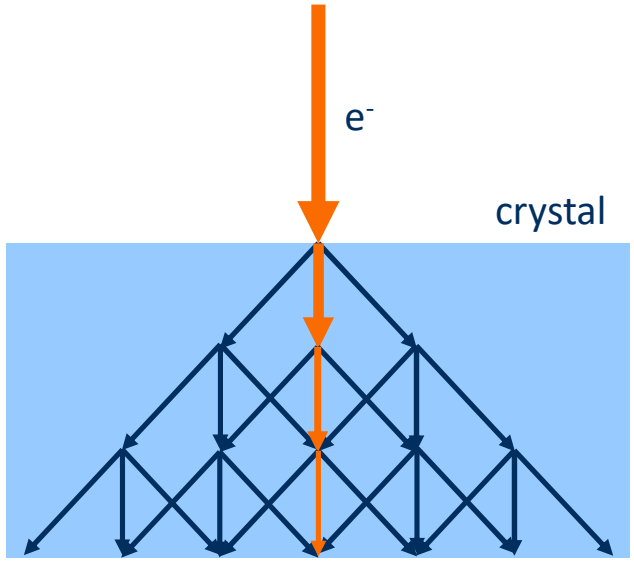
SAED with different sample thickness



v-AlFeCr: $P6_3/m$, a = 40.7 Å, c = 12.6 Å

Zou *et al.*, Acta Cryst. (2003). A59, 526–539

Dynamical effect



- Result of strong interaction with atoms
- Stronger with thicker or aligned crystals
- Forbidden reflections!

Average number of scattering events

$$\upsilon = \pi r^2 N t$$

thickness

Collision cross section

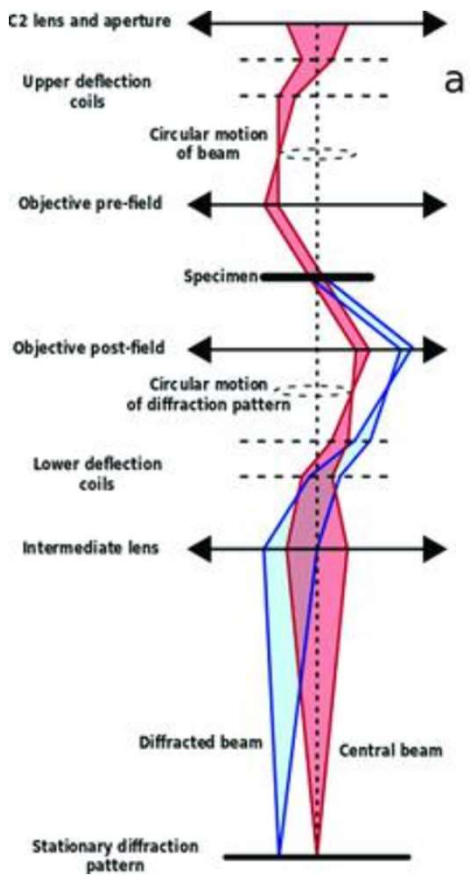
Density ($N_{scatterers} m^{-3}$)

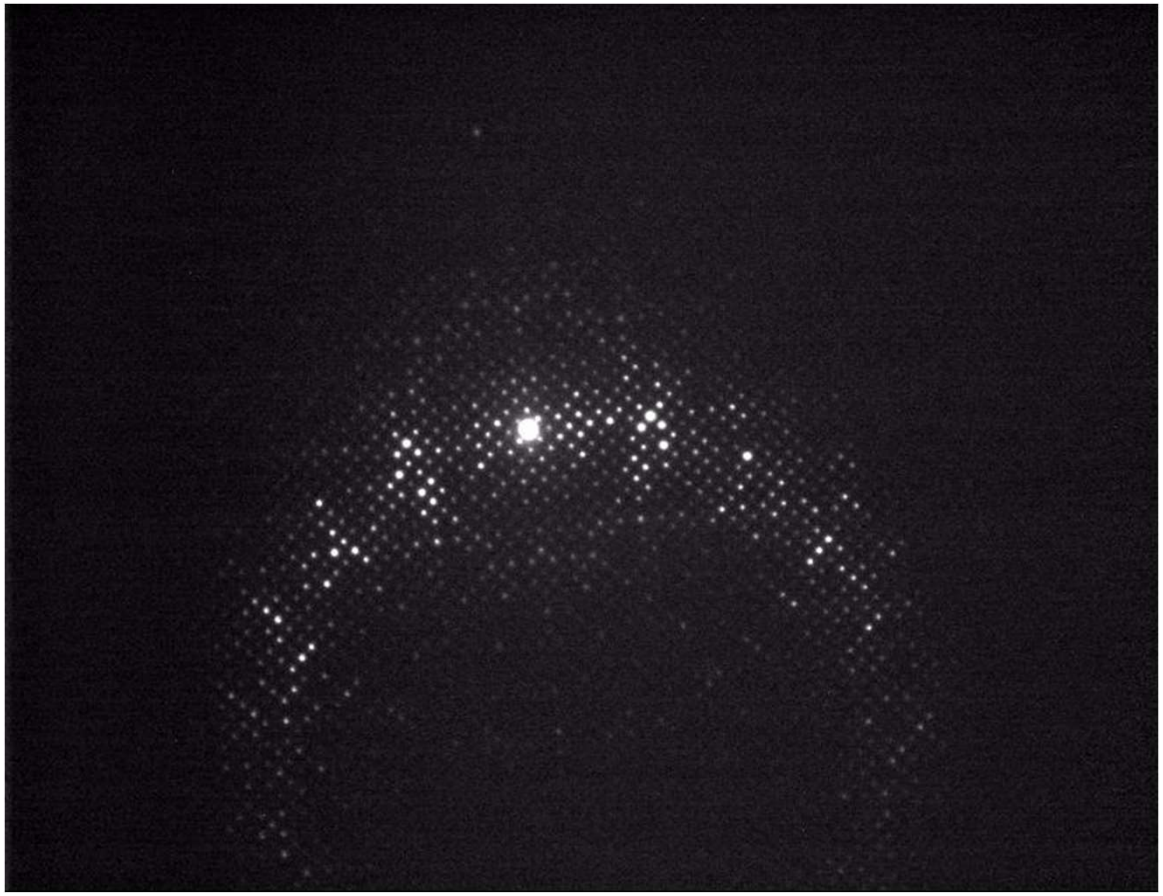
$$P(n) = e^{-\upsilon}\upsilon^n/n!$$

***t* (nm)**	***n*=0 (%)**	***n*=1 (%)**	***n*=2 (%)**	***n*=3 (%)**	***n*≥4 (%)**
10	95.1	4.7	0.1	0.0	0.0
50	77.9	19.4	2.4	0.2	0.0
100	60.6	30.3	7.6	1.3	0.2
200	36.8	36.8	18.4	6.1	1.9
500	8.2	20.5	25.6	21.4	20.7

silicon, πr^2:10^{-22} m^2, N: $5 \cdot 10^{-28}$

Precession electron diffraction (PED)

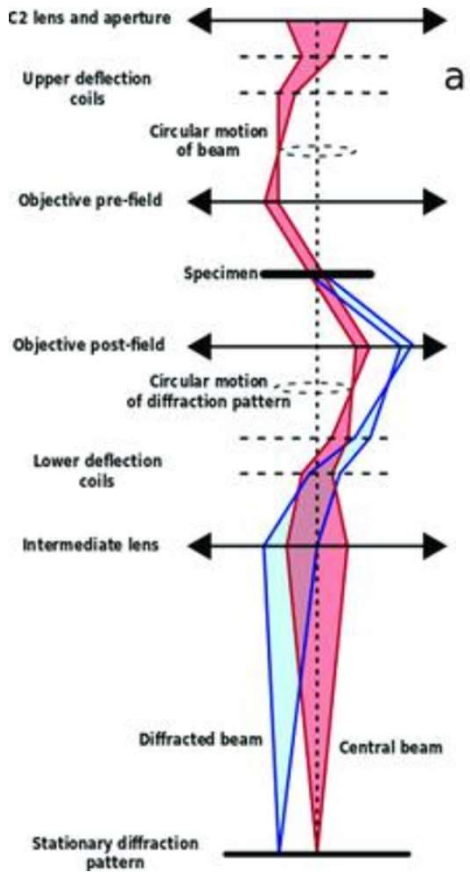


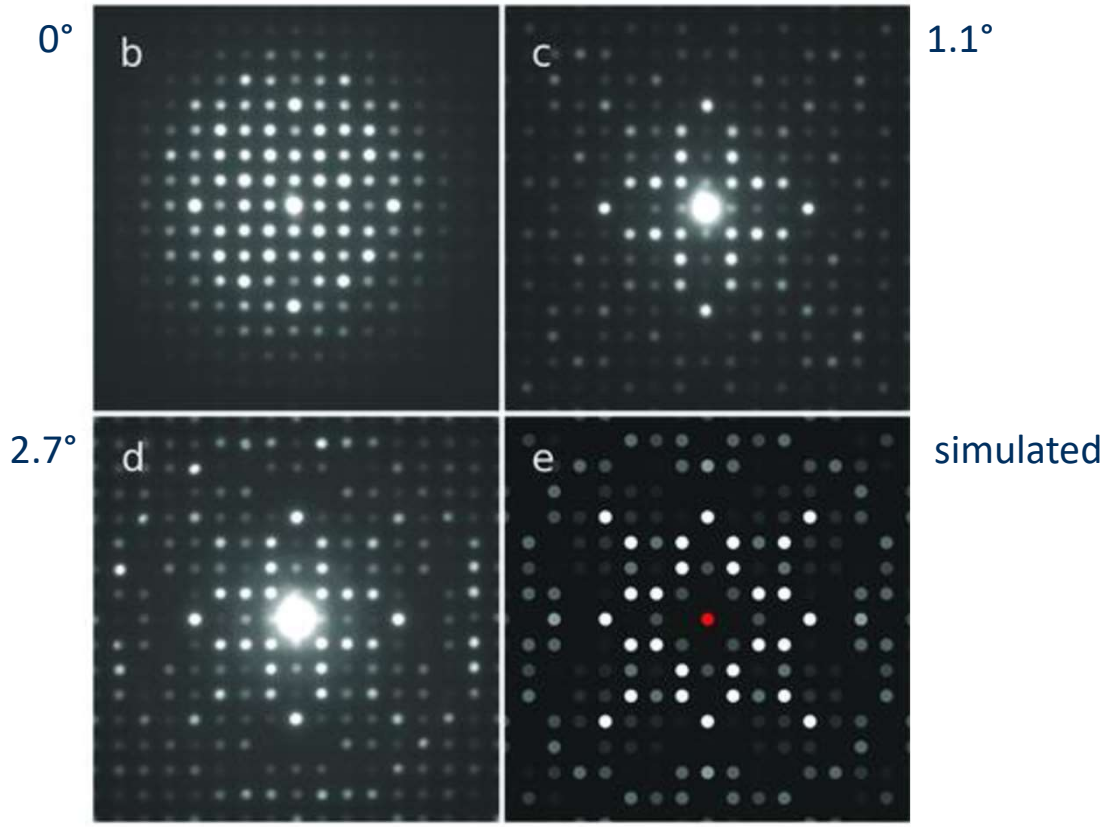


Vincent & Midgley, Ultramicroscopy 53 (1994) 271-282
Midgley & Eggeman, IUCrJ (2015), 2, 126-136

Zhang *et al.* Ultramicroscopy 111 (2010) 47–55

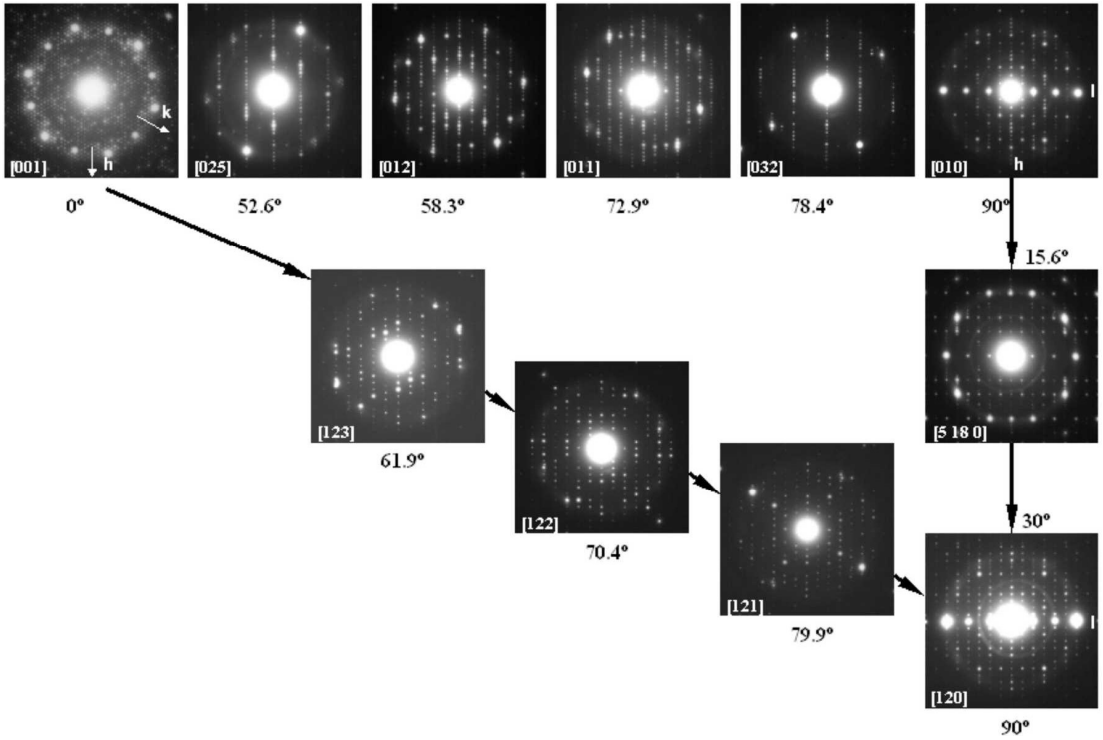
Precession electron diffraction (PED)

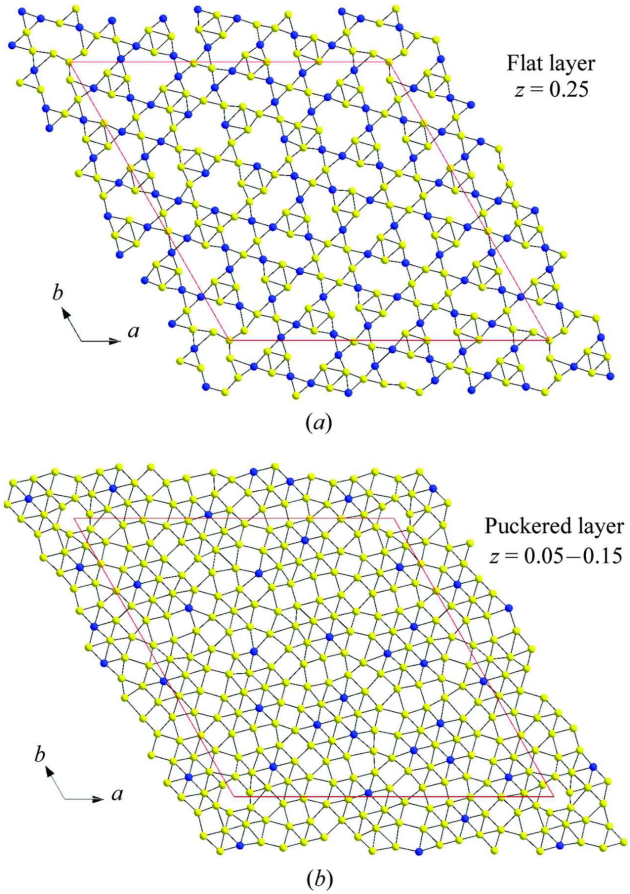




Vincent & Midgley, Ultramicroscopy 53 (1994) 271-282
Midgley & Eggeman, IUCrJ (2015), 2, 126-136

Structure determination from electron diffraction



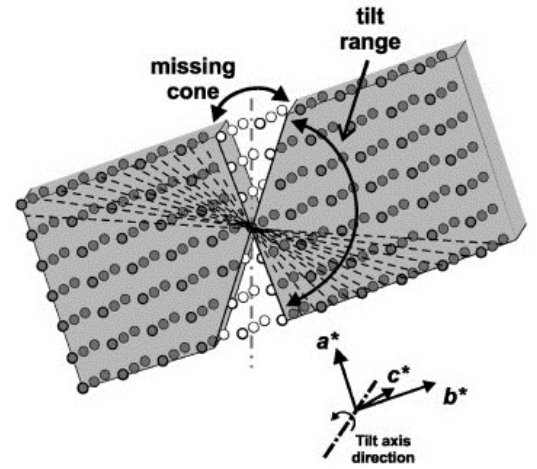


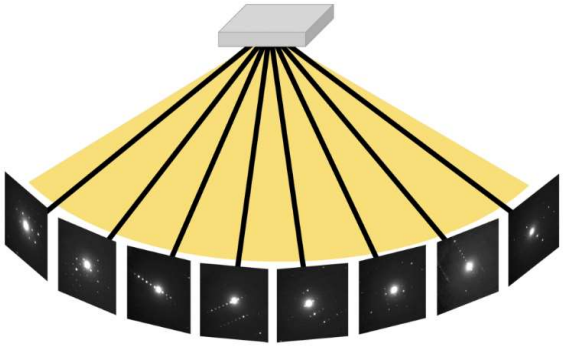
v-AlFeCr: $P6_3/m$, a = 40.7 Å, c = 12.6 Å

Zou *et al.*, Acta Cryst. (2003), A59, 526–539

Single crystal electron diffraction

- Automated diffraction tomorgraphy (ADT)
  - Kolb *et al.*, Ultramicroscopy (2007), 107:507
  - Kolb *et al.*, Ultramicroscopy (2008), 108:763
- Rotation electron diffraction (RED)
  - Zhang *et al.*, Z. Krist. (2010), 225:94
  - Wan *et al.*, J. Appl. Cryst. (2013), 46:1863
- MicroED (macro-molecules)
  - Shi *et al.*, eLife (2013), 2:e01345
- Electron diffraction tomography (EDT / PEDT)





- > 200 structures solved
  - Yun *et al.*, IUCrJ (2015), 2, 267

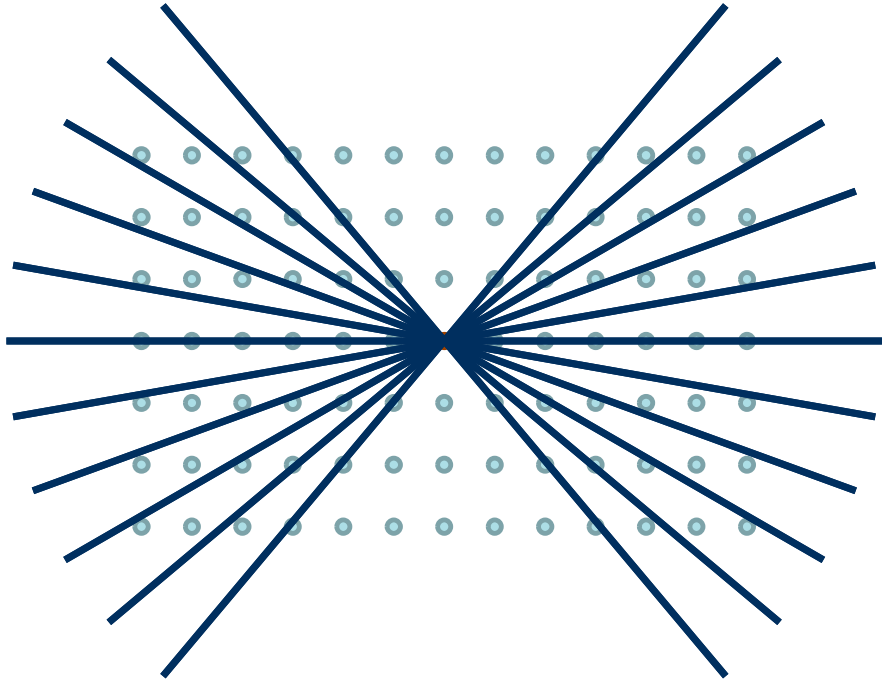
Single crystal electron diffraction

Limitations

- Dynamical scattering
- Beam damage
- Missing wedge
- Goniometer mechanics

- Filling the gaps:
  - Beam tilt (RED)
  - Precession (ADT)
  - Continuous rotation*

- Processing: standard crystallographic software

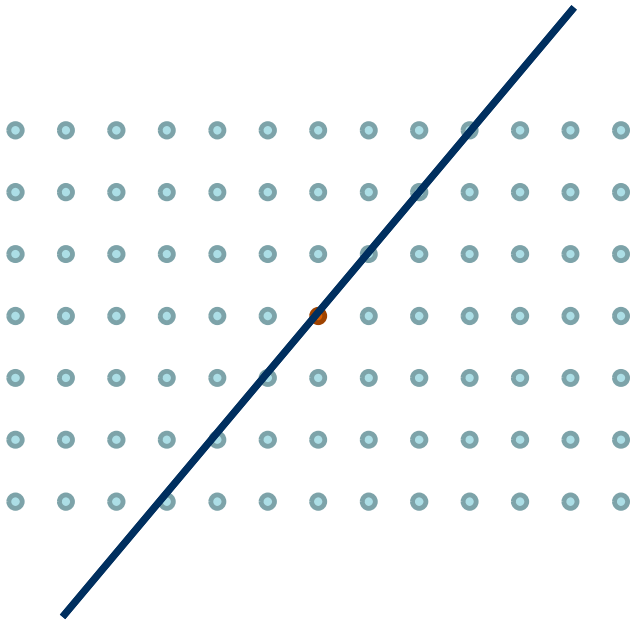


Tilt range: ±70°
Tilt step: ~1.0°
~30-60 minutes

Continuous rotation

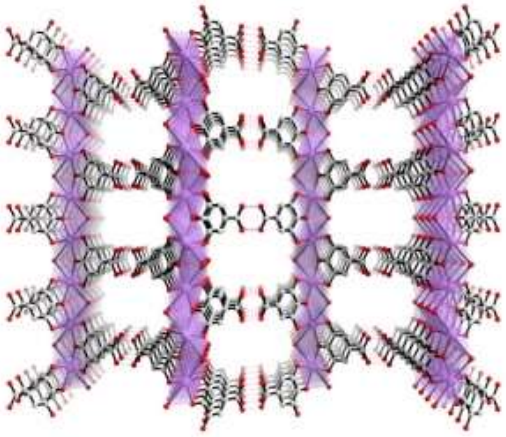
- microED
  - Nannenga *et al.*, Nat. Methods (2014), 11:927
- Fast EDT
  - Gemmi *et al.*, J. Appl. Cryst. (2015), 48:718
- Continuous RED (cRED)
  - Wang *et al.*, *Chem. Commun.*, (2017), 53:7018

- Advantages
  - Beam sensitive materials
  - Improved sampling
  - Integration of intensities

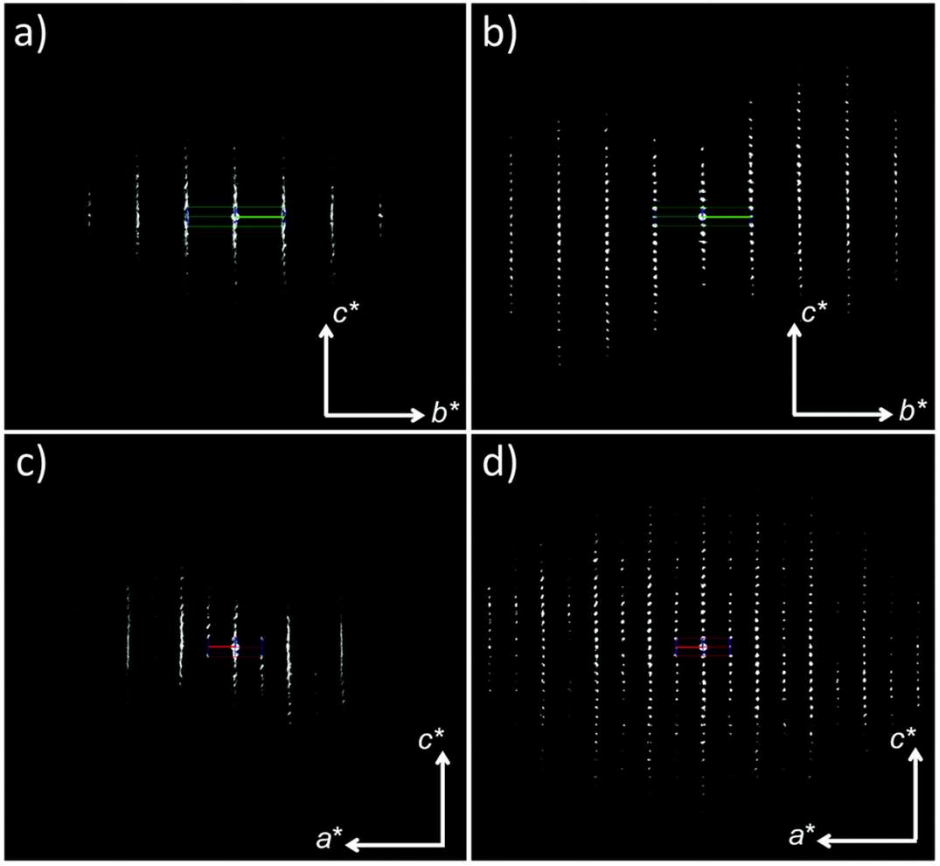


Tilt range: ±70°
Oscillation angle: 0.1-0.5°
1-5 minutes

RED
Discrete rotation steps
Orius CCD
Processed with REDp
Ambient temperature



Bismuth subgallate



Wang *et al.*, *Chem. Commun.*, 2017, 53:7018-7021

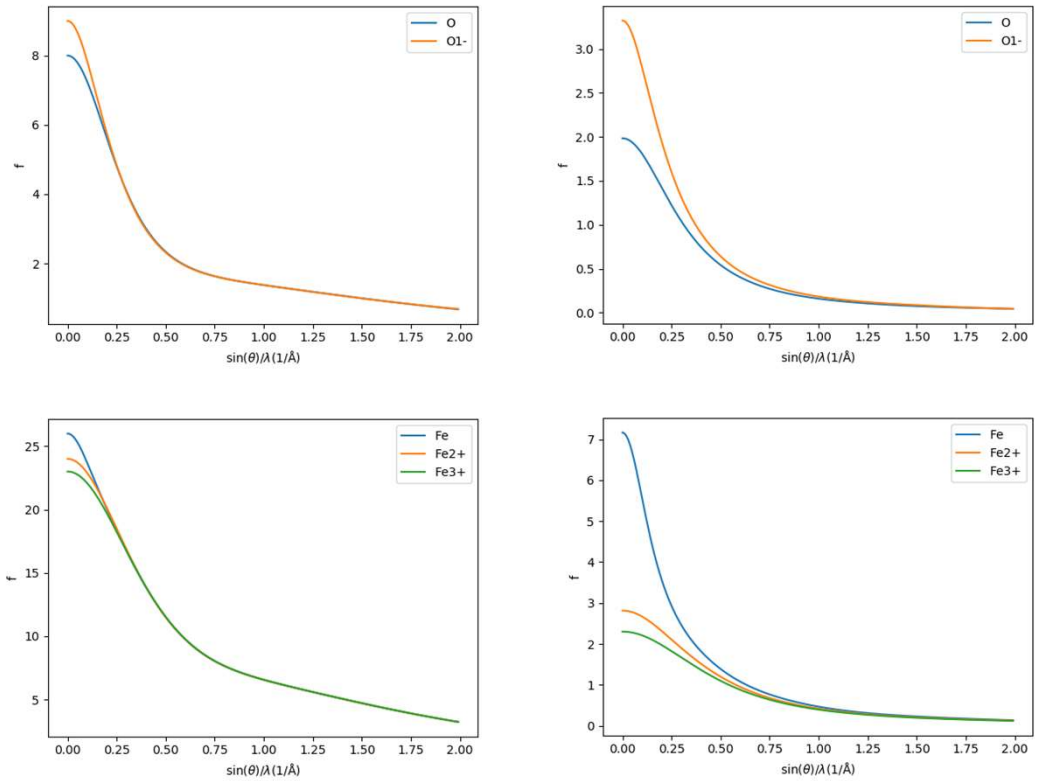
cRED
Continuous rotation
Timepix detector
Improved data reduction (XDS)
Cooling holder

ASI Timepix Camera

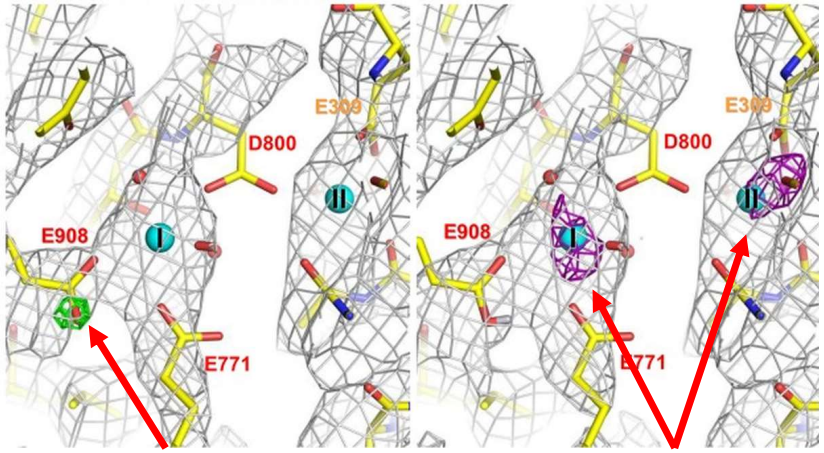
Determine charge states

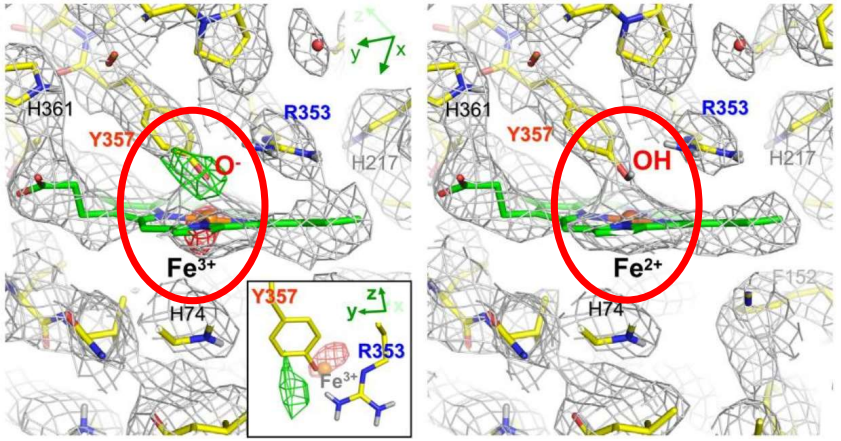
Enhanced constrast in scattering factors

X-rays → Electrons



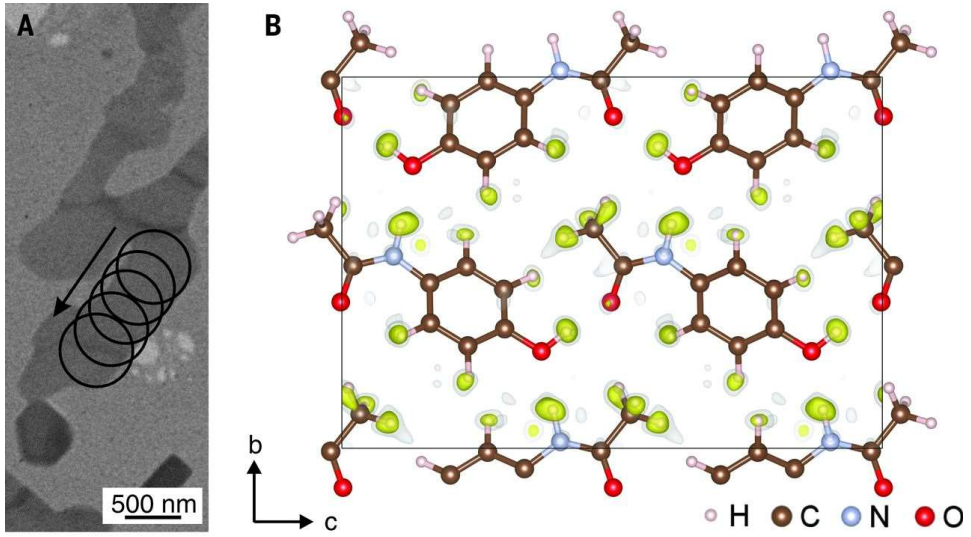
Yonekura *et al.*, PNAS (2015), 112(11):3368–3373



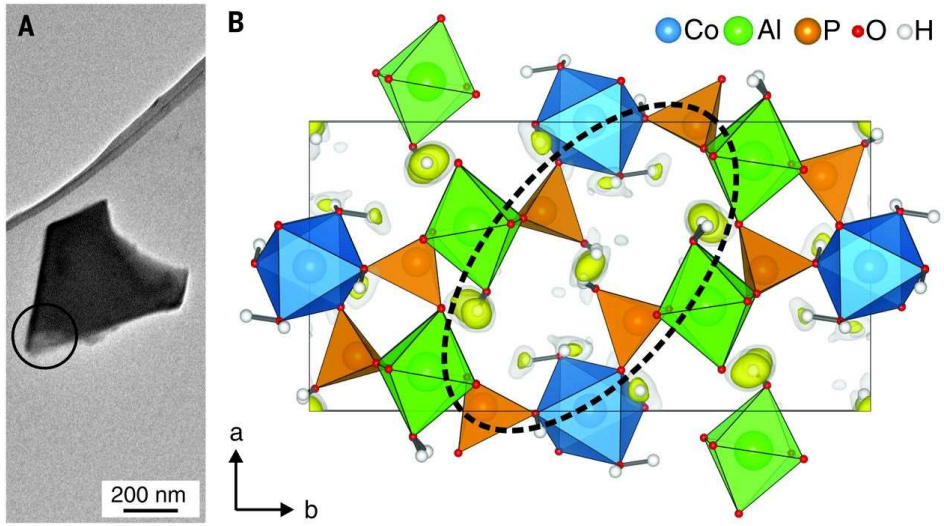


Catalase

Find light elements



Paracetamol II

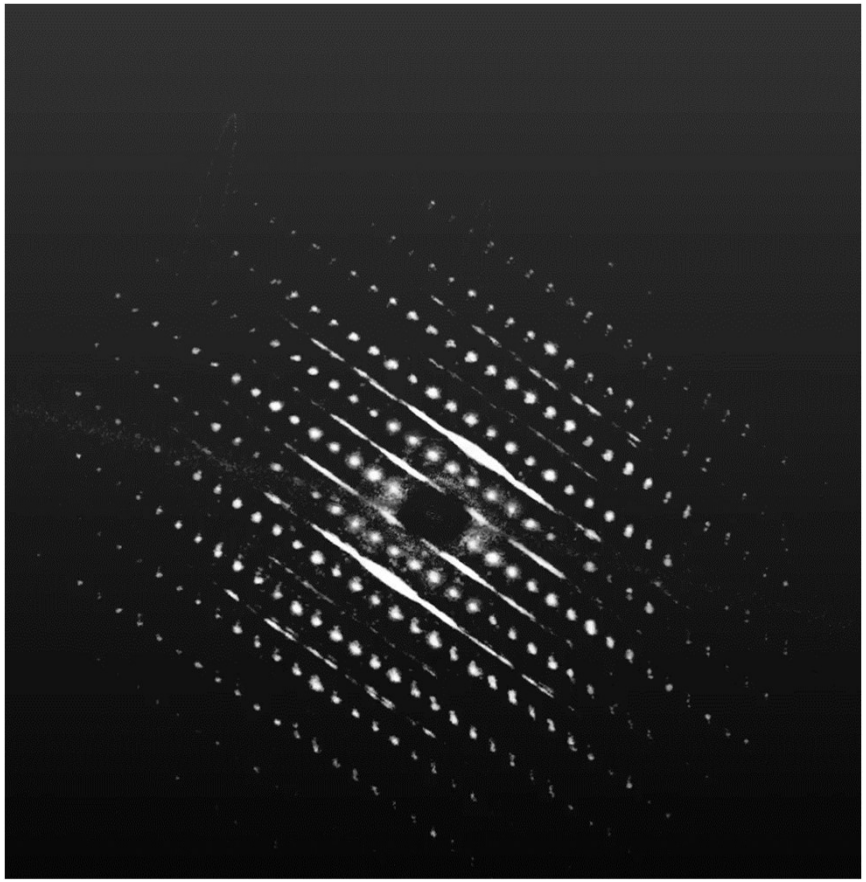


cobalt aluminophosphate

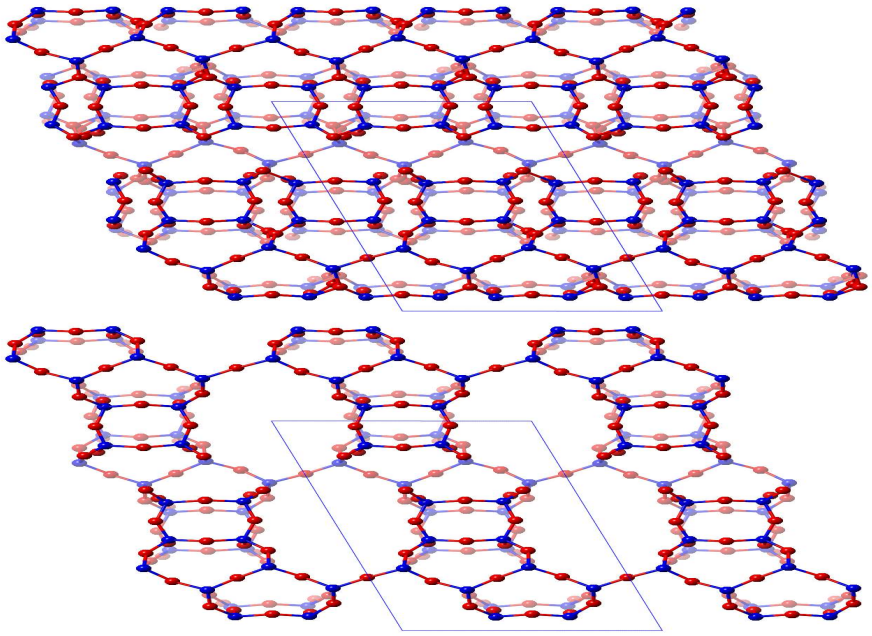
Dynamical refinement with JANA

Palatinus *et al.*, Science (2017), 355(6321):166-169

Example: Zeolite IM-18

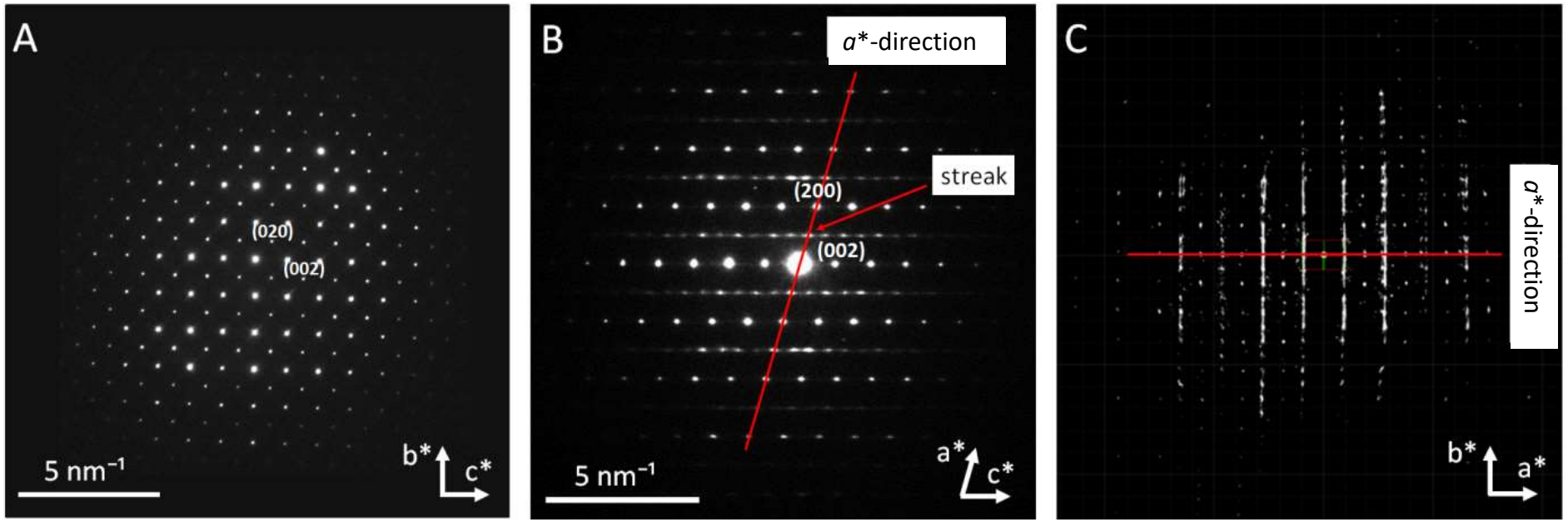


Tilt range (°)	119.46 (-66.83 to 52.63)
Tilt step (°)	0.2°
Exposure time/frame (s)	1
Total data collection time (min)	80
No. of frames	649
Crystal size (length x width) (µm)	0.66 x 0.74
Resolution (Å)	1.05
Completeness (%)	89.9
Detected reflections by RED	1265



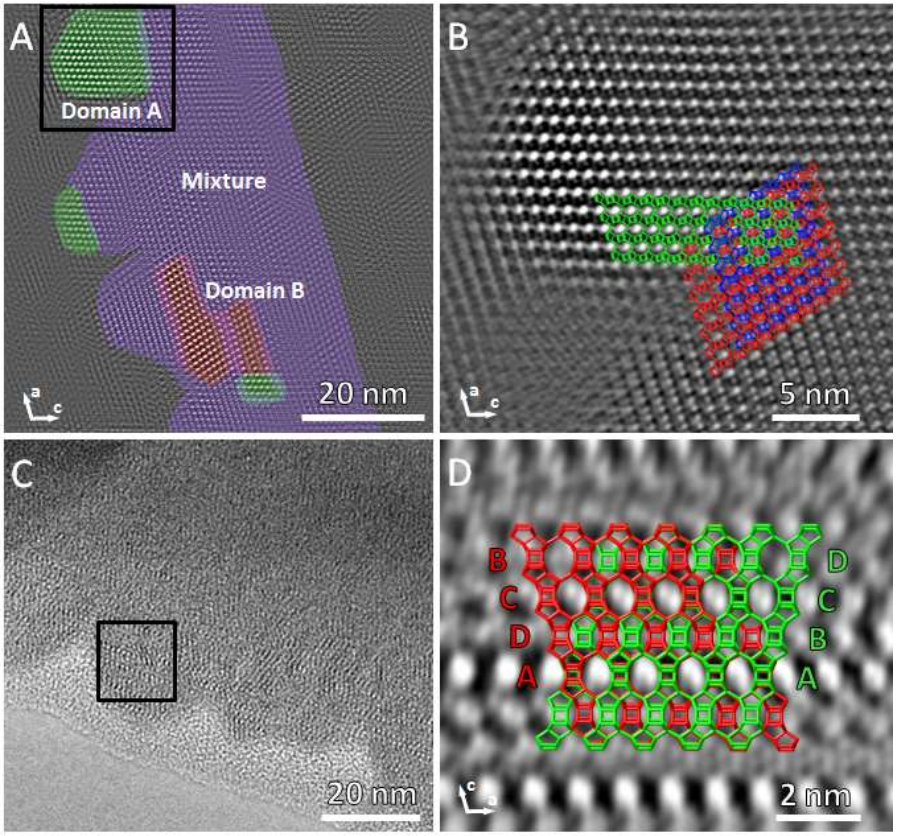
M. O. Cichocka, Stockholm University (in manuscript)

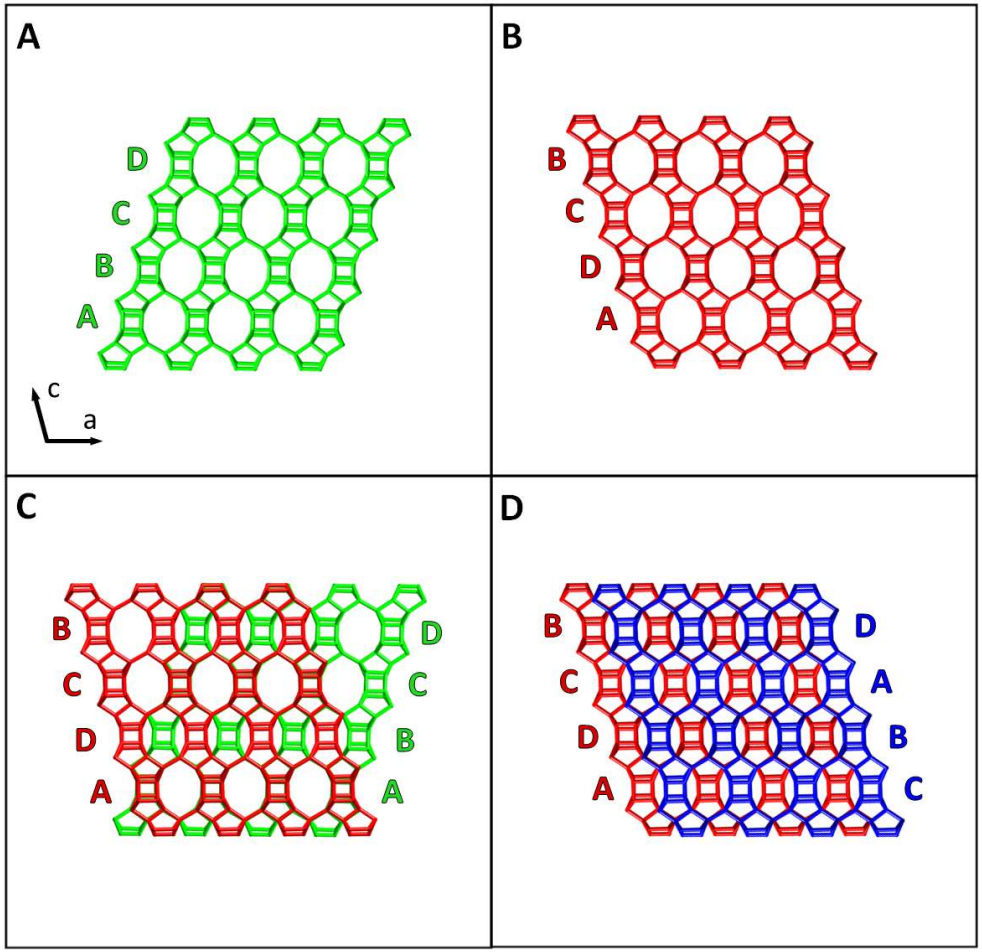
Zeolite IM-18: SAED



[100] [010] [001]

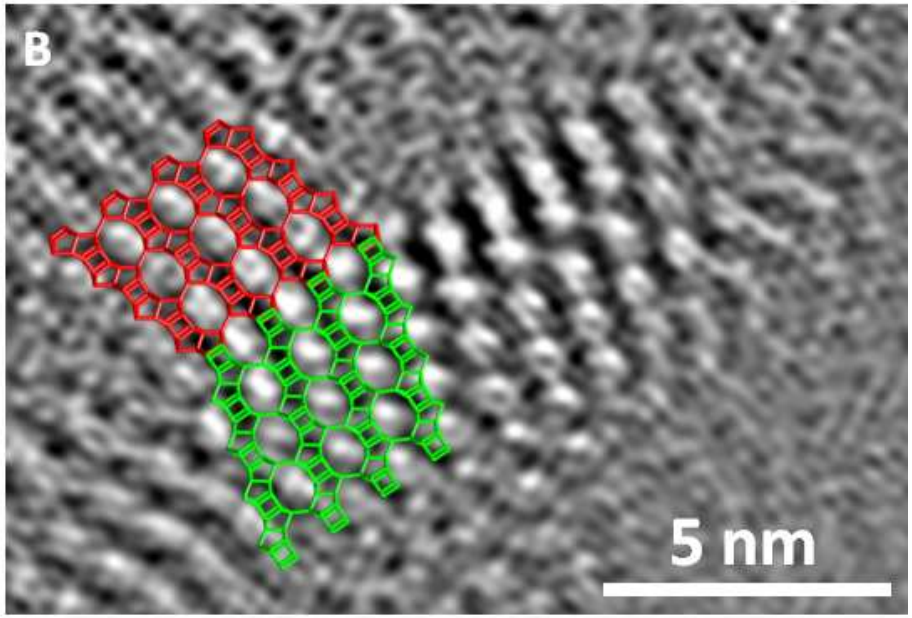
Zeolite IM-18: HRTEM

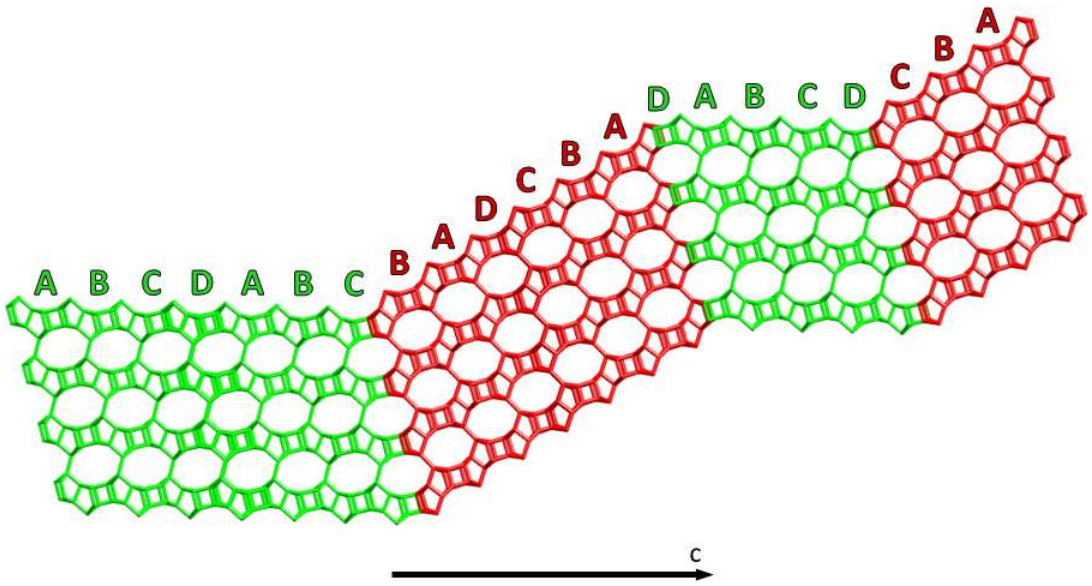




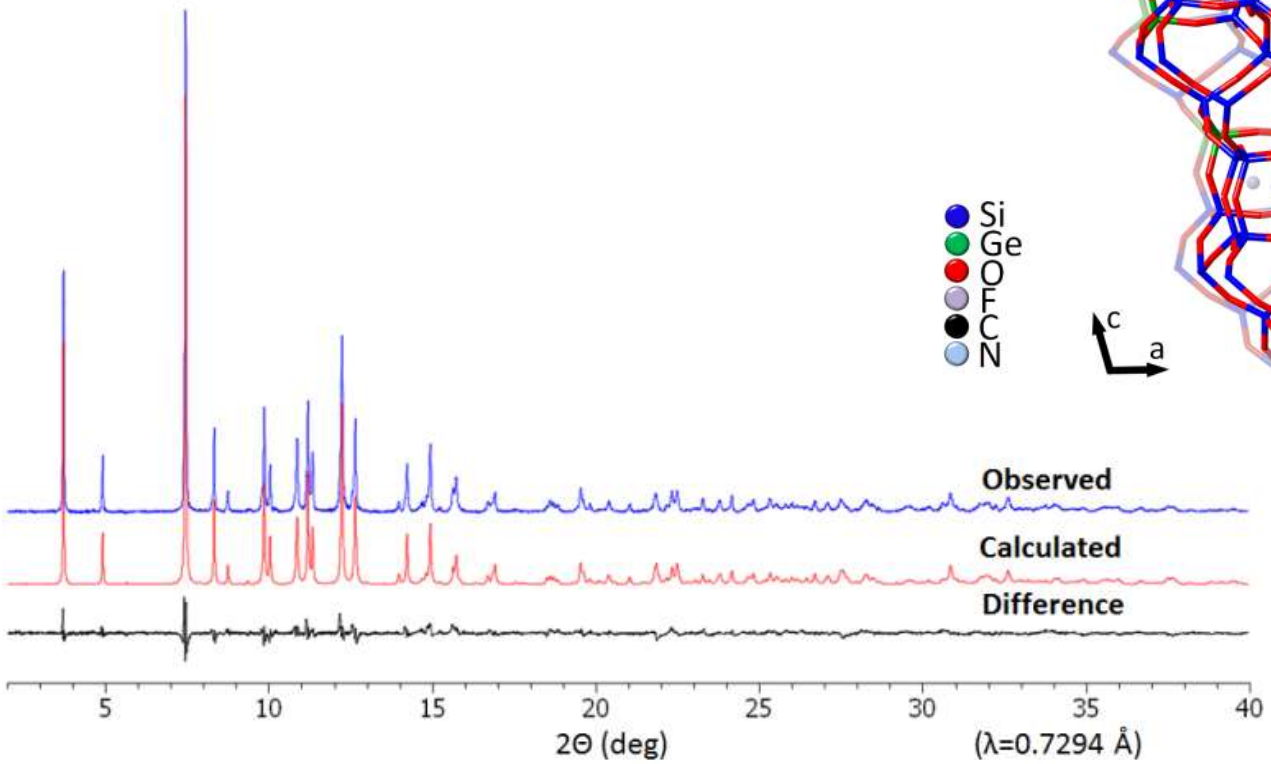
M. O. Cichocka, Stockholm University (in manuscript)

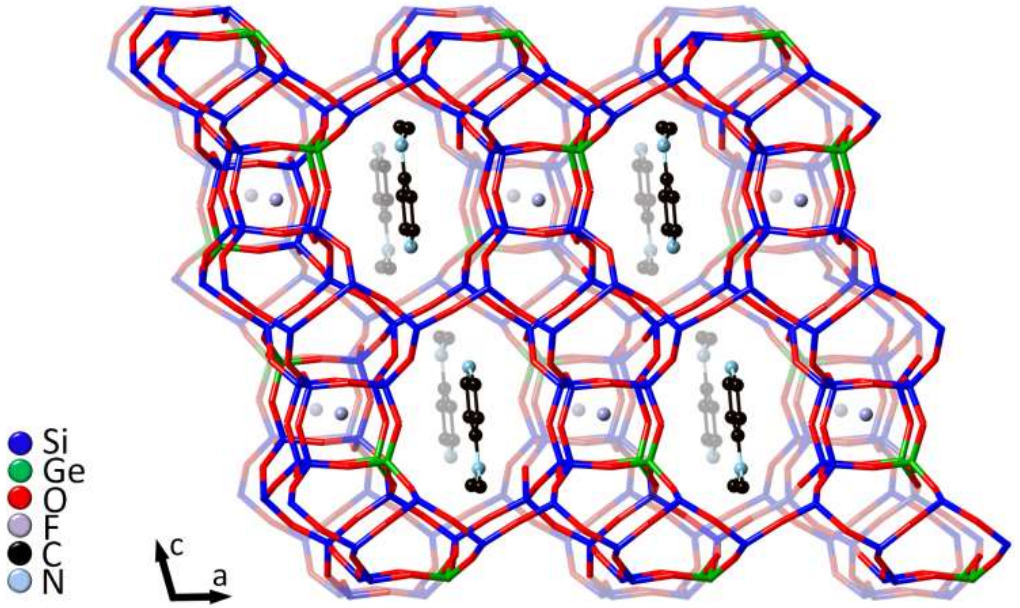
Zeolite IM-18: HRTEM





Zeolite IM-18: XRPD





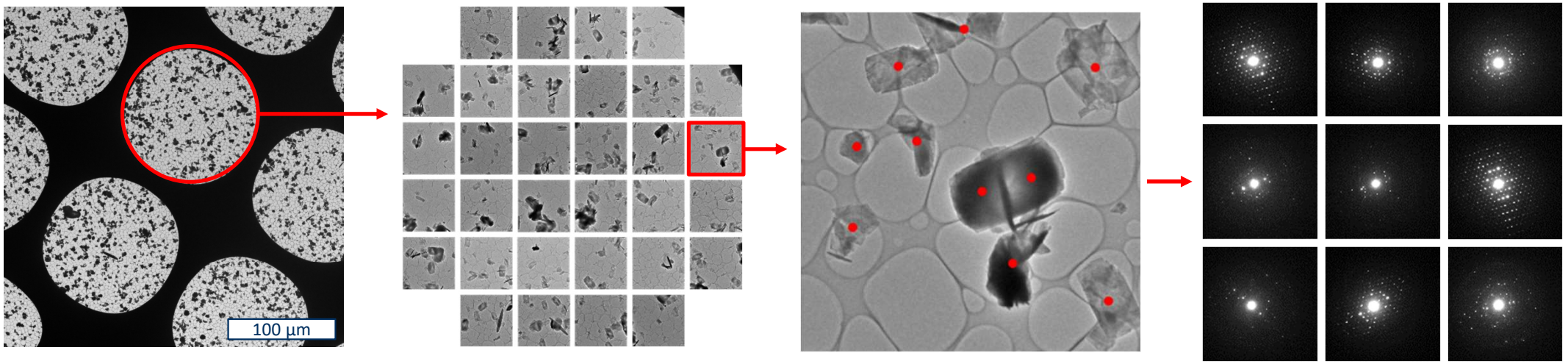
Space group	$P2_1/m$
a (Å)	10.5089(5)
b (Å)	14.9425(5)
c (Å)	17.7775(7)
β (deg)	107.323(4)

M. O. Cichocka, Stockholm University (in manuscript)

Serial electron crystallography

- Motivation:
  - *ED diffraction is not representative for bulk material*
  - *Do phase analysis of multi-phase materials*
  - *Structure determination of beam-sensitive materials*

Serial electron crystallography



Randomly oriented crystals

1 crystal = 1 diffraction pattern

Combine data from many crystals

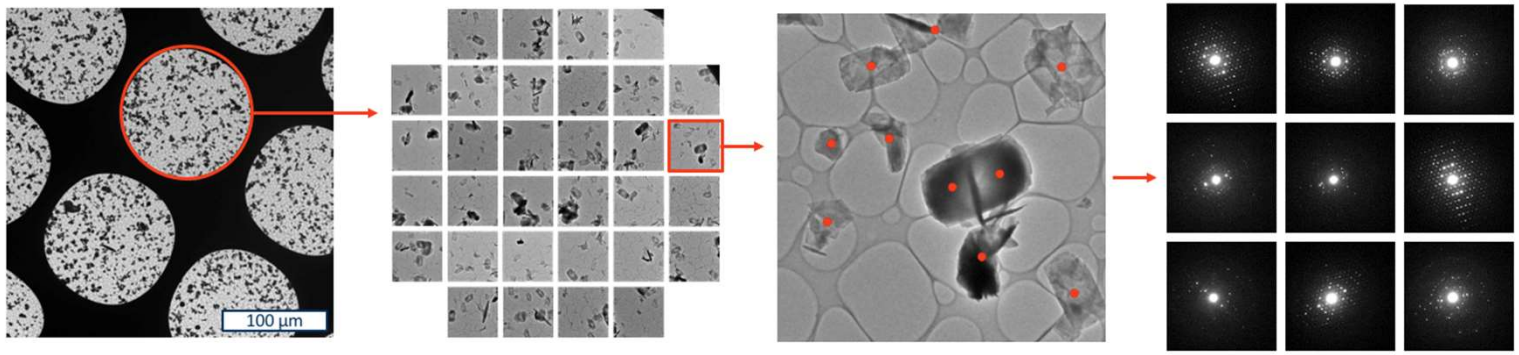
Serial electron crystallography

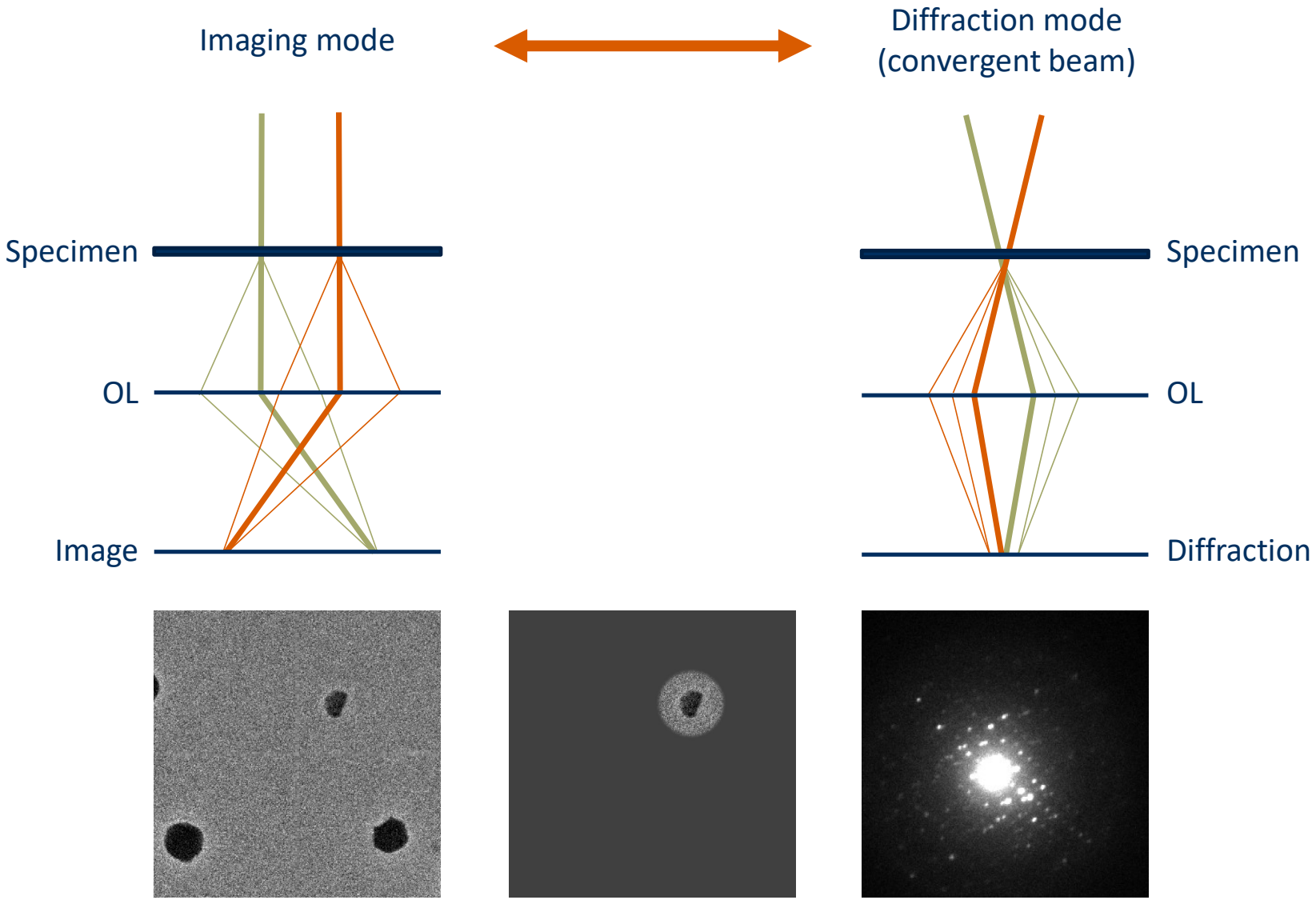
Why use a TEM?

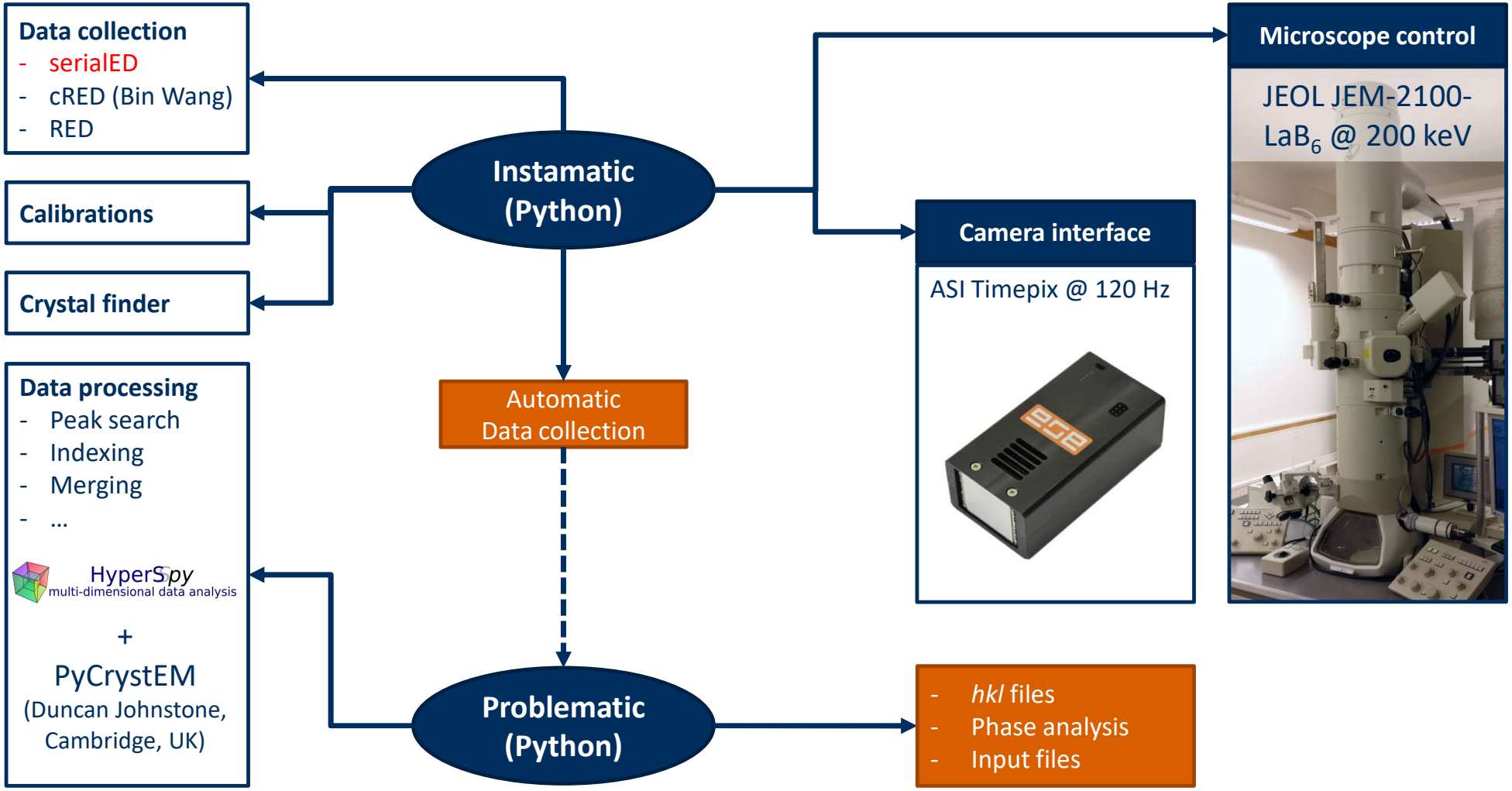
- Electron beam is very intense
- Crystals can be located from images
- TEMs can be programmed
- There is one in many labs

Advantages

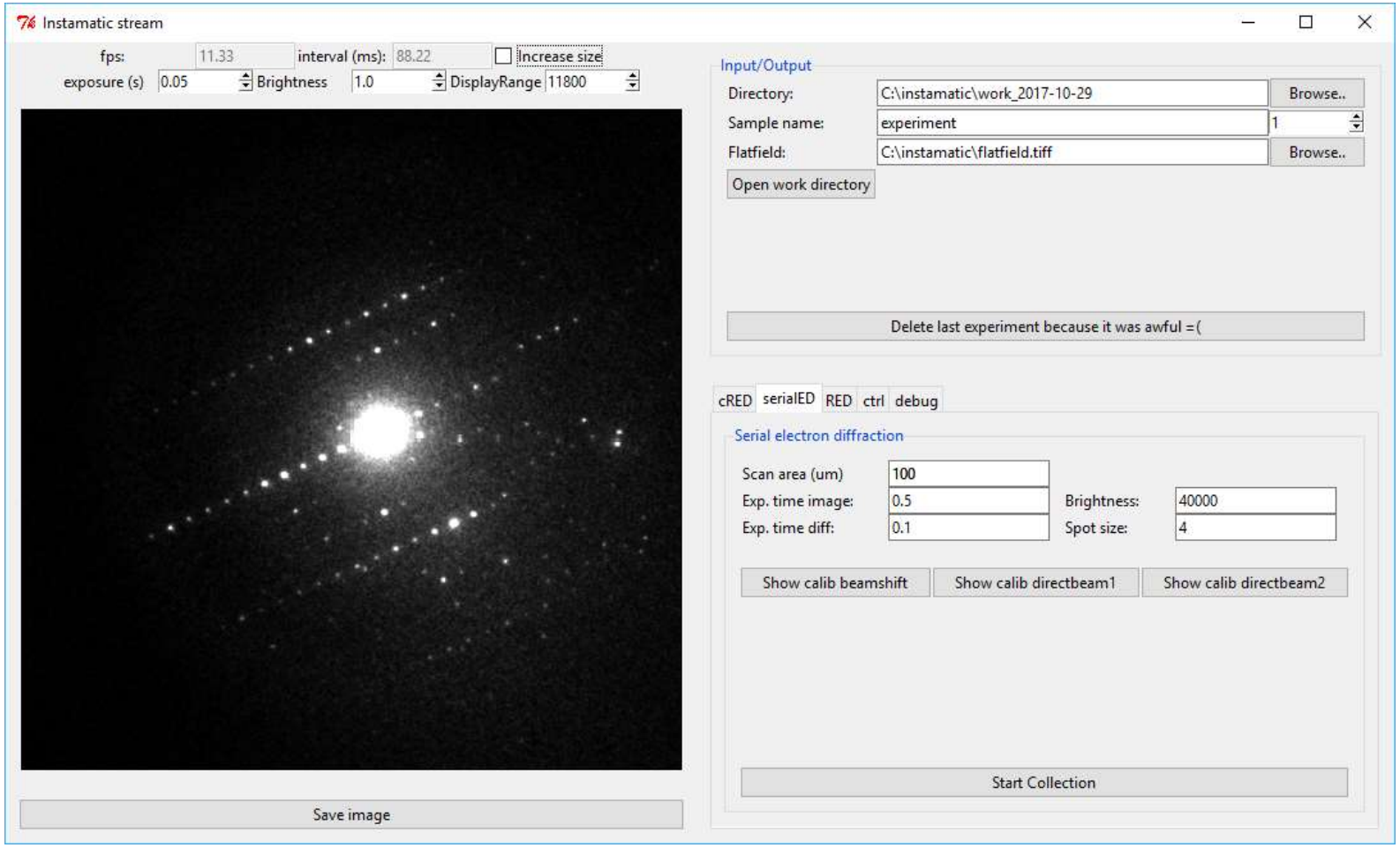
- Beam damage is avoided
- Simple alignment, no rotation
- Fully automatic data collection
- Obtain bulk information




Imaging mode
Diffraction mode
(convergent beam)
Specimen
OL
Image
Specimen
OL
Diffraction

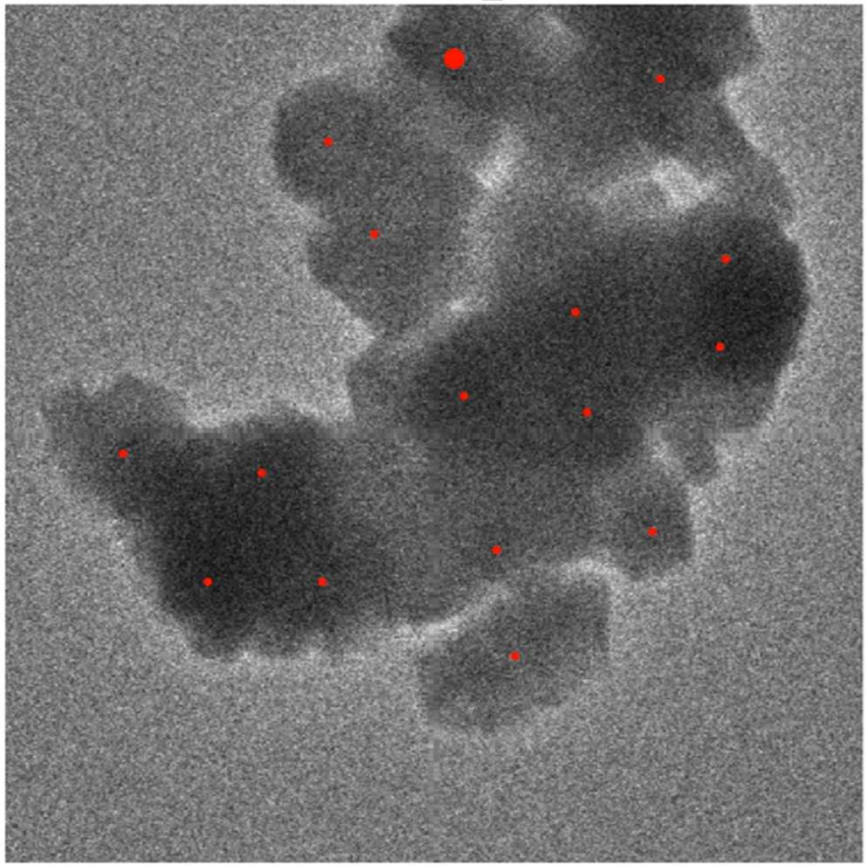

Data collection
- serialED
- cRED (Bin Wang)
- RED
Calibrations
Crystal finder
Data processing
- Peak search
- Indexing
- Merging
- …
HyperSpy
multi-dimensional data analysis
+
PyCrystEM
(Duncan Johnstone, Cambridge, UK)
Instamatic (Python)
Automatic Data collection
Problematic (Python)
Camera interface
ASI Timepix @ 120 Hz
Microscope control
JEOL JEM-2100-LaB6 @ 200 keV
- hkl files
- Phase analysis
- Input files

Data collection software

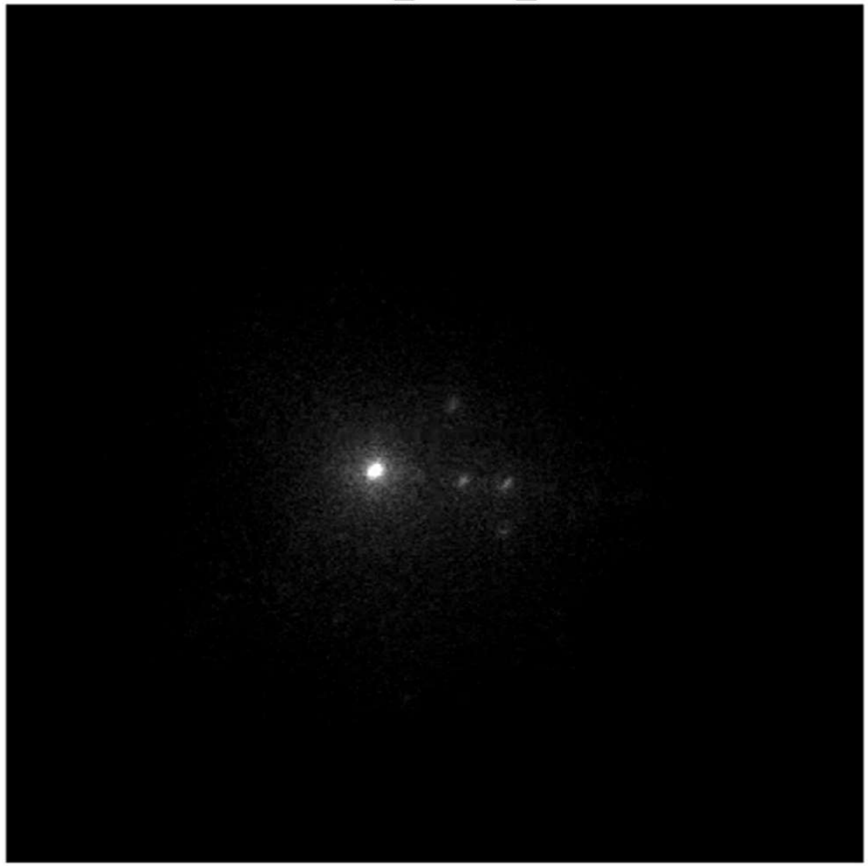


Data collection (Zeolite Y)

images\image_0000.h5

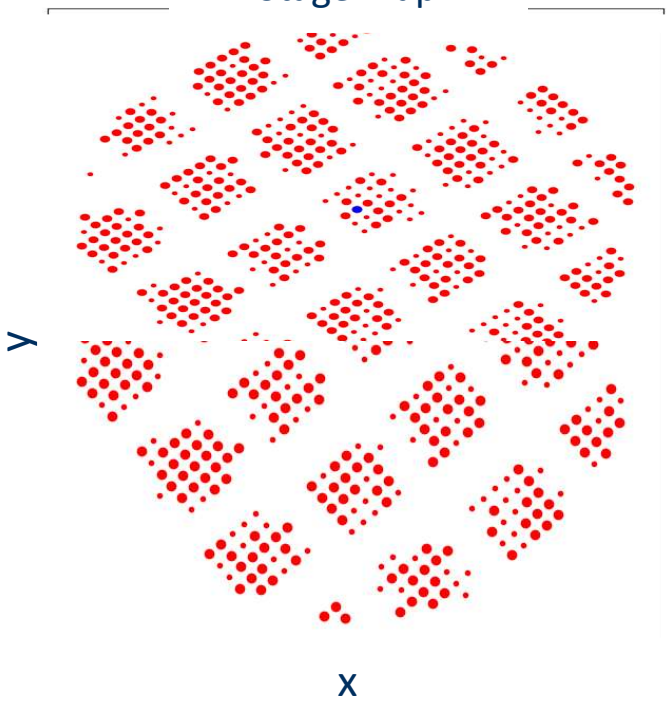


data\image_0000_0000.h5



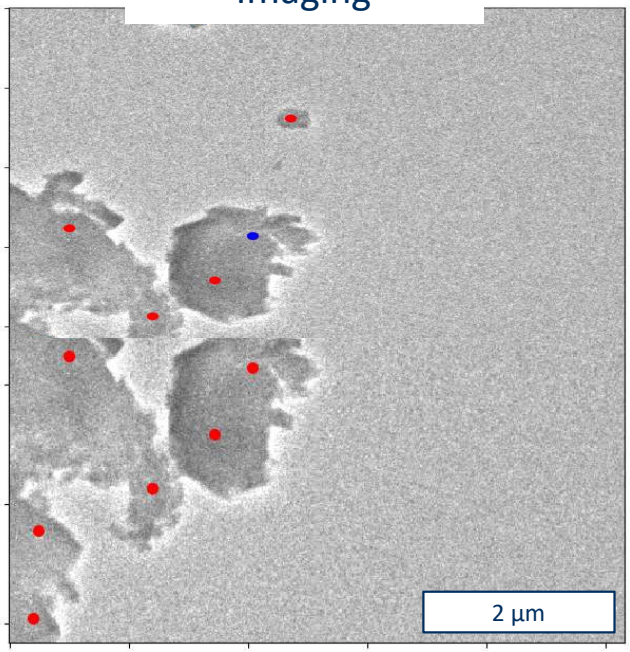
Data collection (zeolite A)

Stage map



200 x 200 µm
484 images
35 minutes

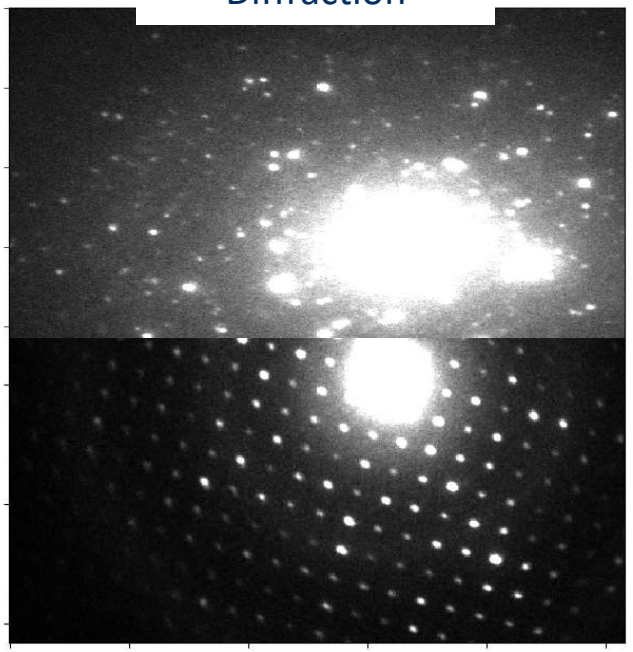
Imaging



Locate crystals

Probe size ~500 nm

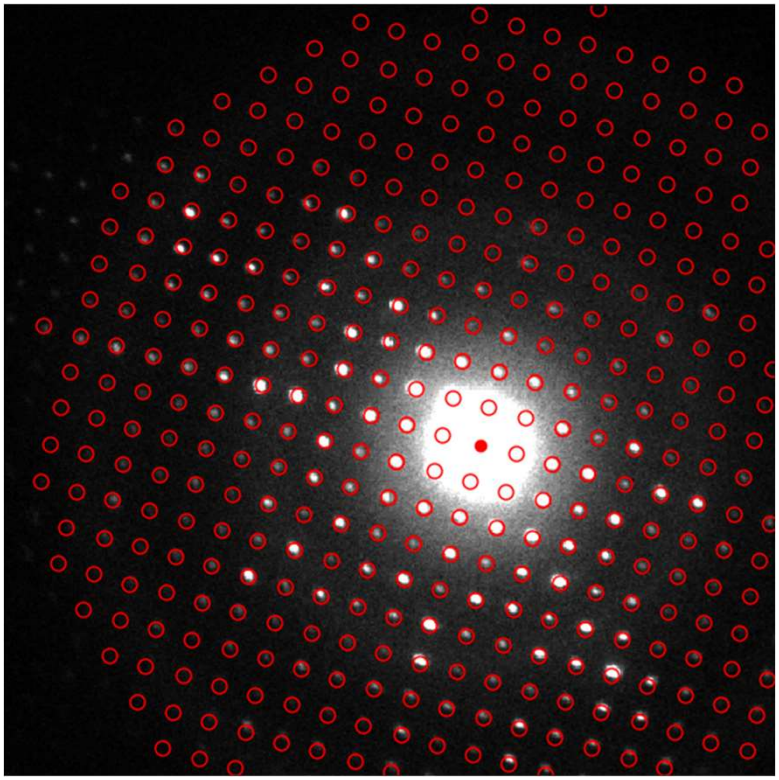
Diffraction

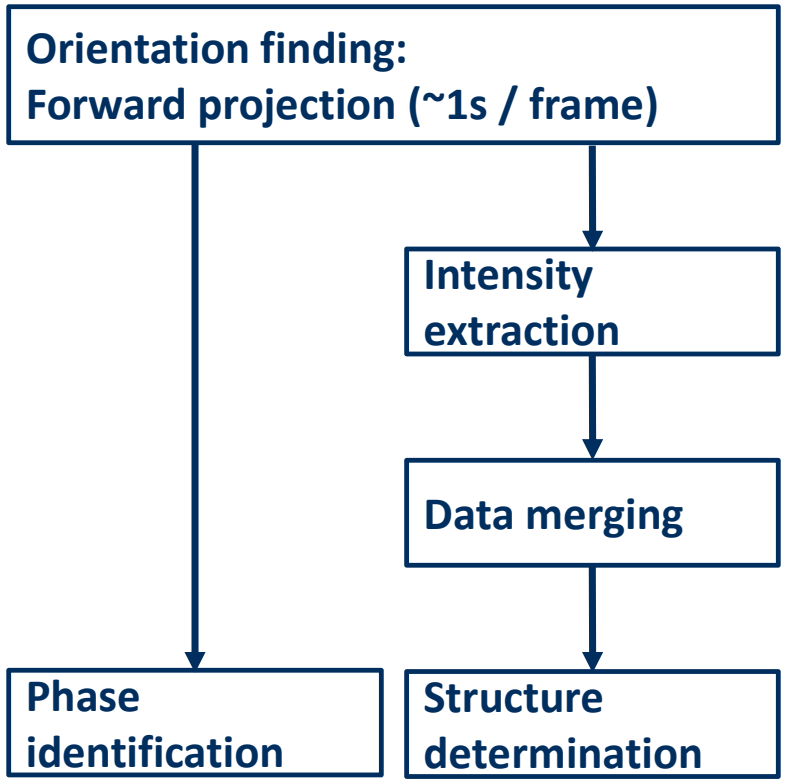


Collect data

Total: 1107 patterns

Data processing





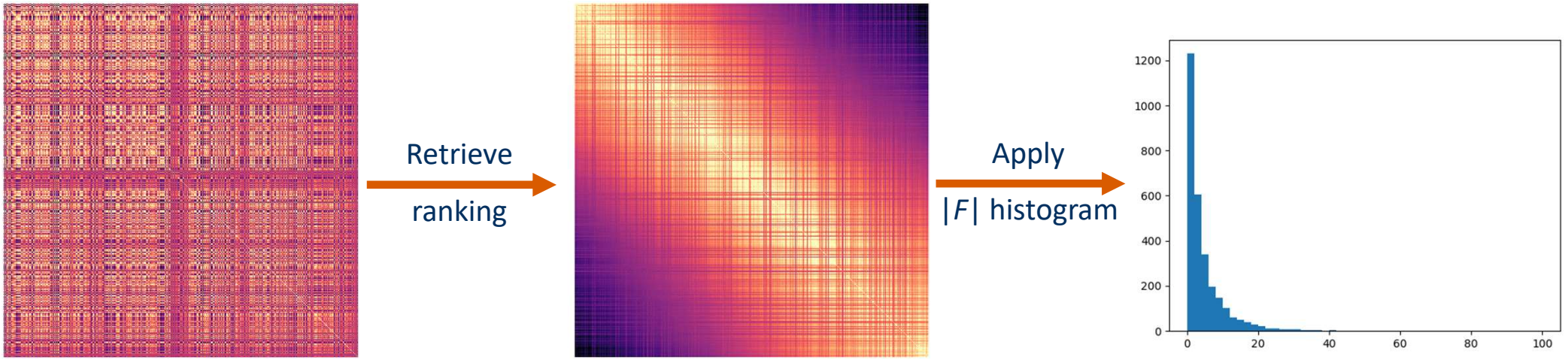
Data Merging

Challenges

- Scaling
- Dynamical effects
- Reflection partiality

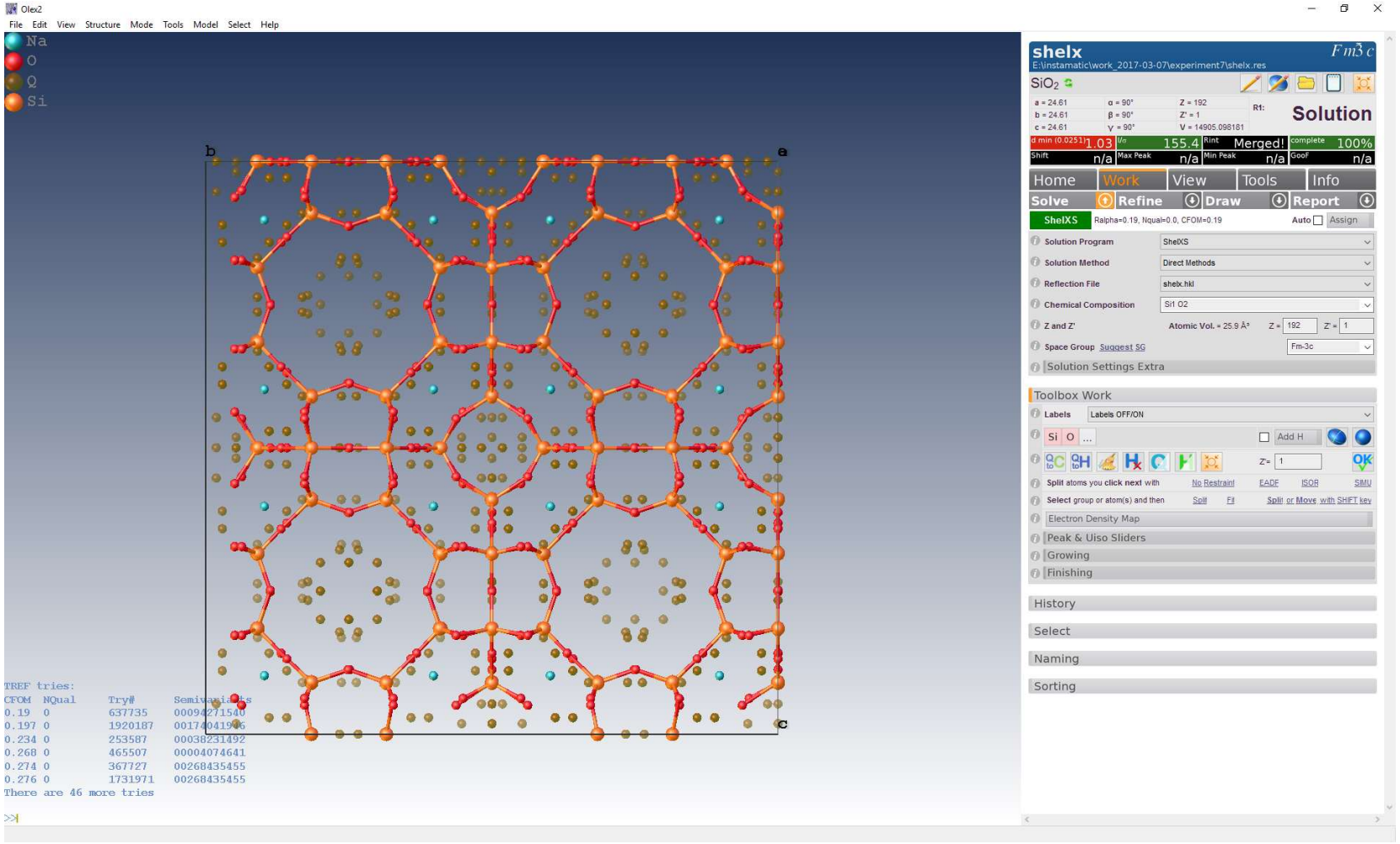
SerialMerge – rank-based merging

- Avoid scaling
- Avoid modelling intensities
- Robust with low quality data



S. Smeets & W. Wan, *J. Appl. Cryst.* (2017). **50**, 885-892
www.github.com/stefsmeets/serialmerge

Structure determination



Zeolite A

$Fm\bar{3}c$

$a = 24.61$ Å

$Si_{96}Al_{96}O_{384}$

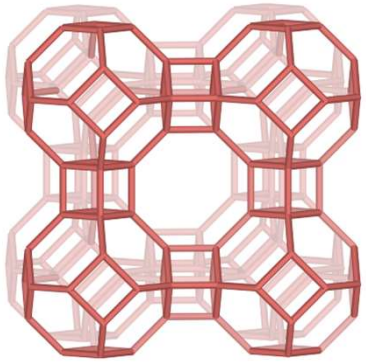
$Z = 192$

200 frames

Reflections

Total:	19804
Unique:	227
d_{min}:	1.03 Å
Compl.:	100%

Structures solved



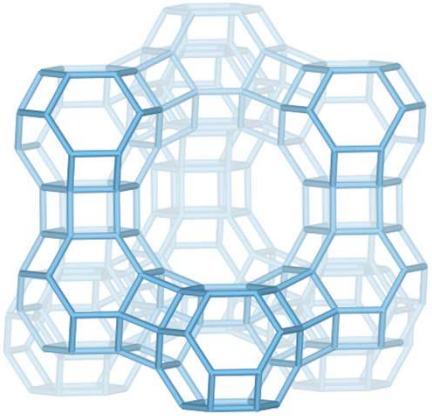
Zeolite A

$Fm\bar{3}c$

$a = 24.61$ Å

$Si_{96}Al_{96}O_{384}$

$Z = 192$



Zeolite Y

$Fd\bar{3}m$

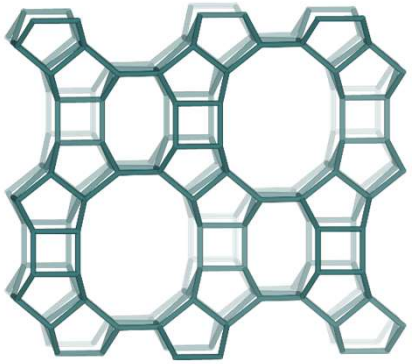
$a = 24.74$ Å

$Si_{192}O_{384}$

$Z = 192$

Direct methods

ShelXS



Mordenite

$Cmcm$

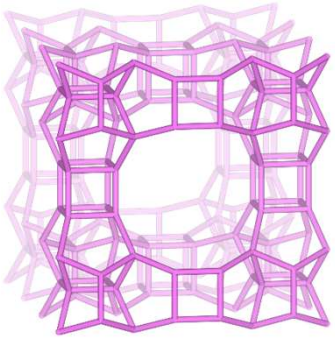
$a = 18.11$ Å

$b = 20.53$ Å

$c = 7.53$ Å

$Si_{40}Al_8O_{96}$

$Z = 16$



Ge-BEC

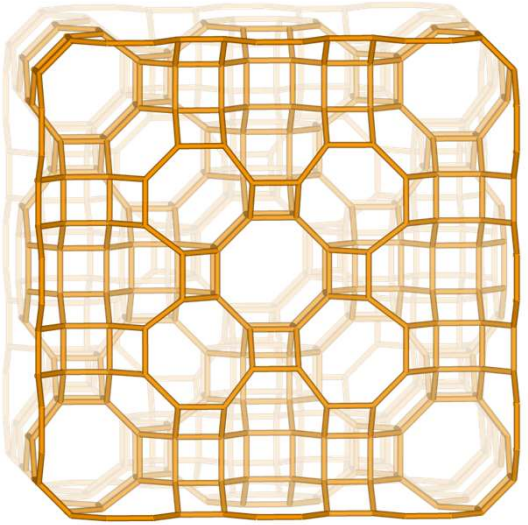
$P4_2/mmc$

$a = 12.82$ Å

$c = 13.35$ Å

$Si/Ge_{32}O_{64}$

$Z = 16$



Paulingite

$Im\bar{3}m$

$a = 35.08$ Å

$Si_{672}O_{1344}$

$Z = 96$

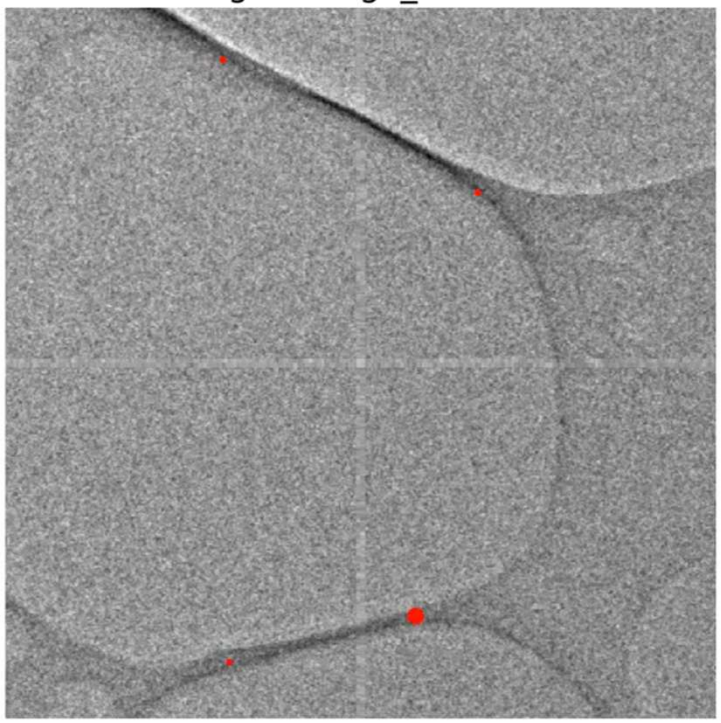
Dual-space methods

FOCUS

Phase analysis

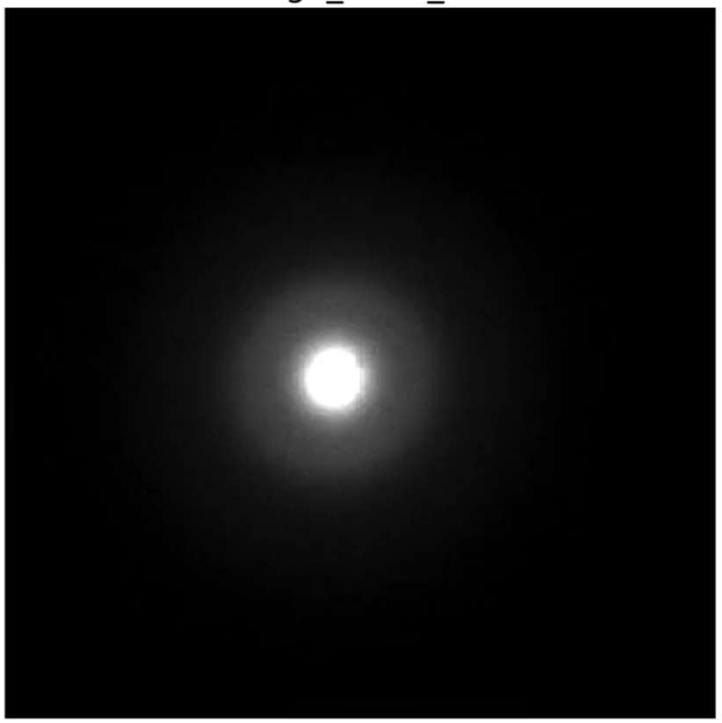
Serial ED data collection on Co-CAU-36

images\image_0342.h5



200 x 200 µm
30 minutes

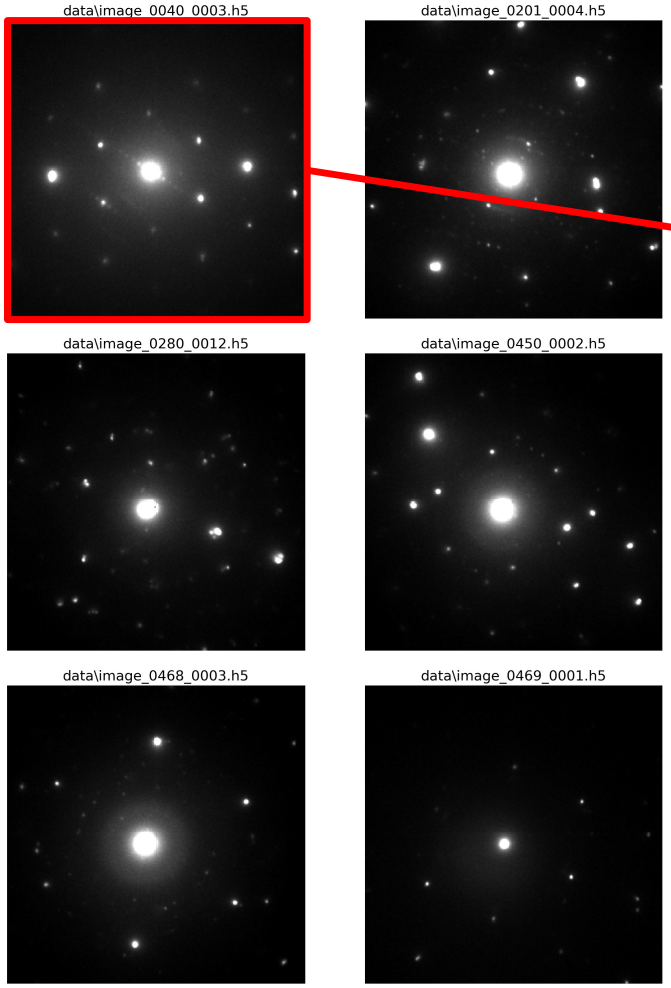
data\image_0342_0002.h5

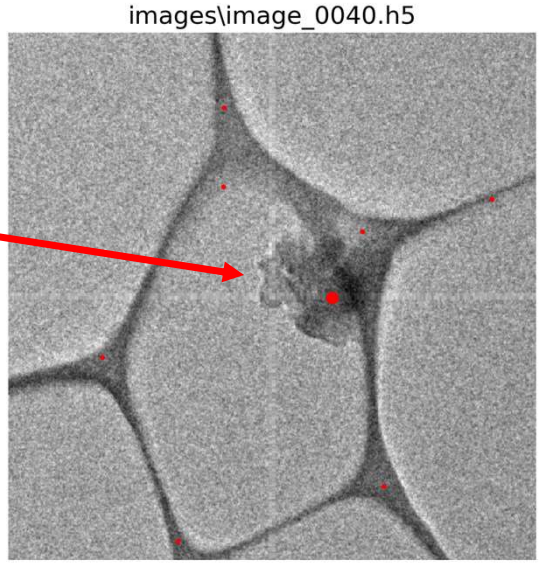


309 images
1202 patterns

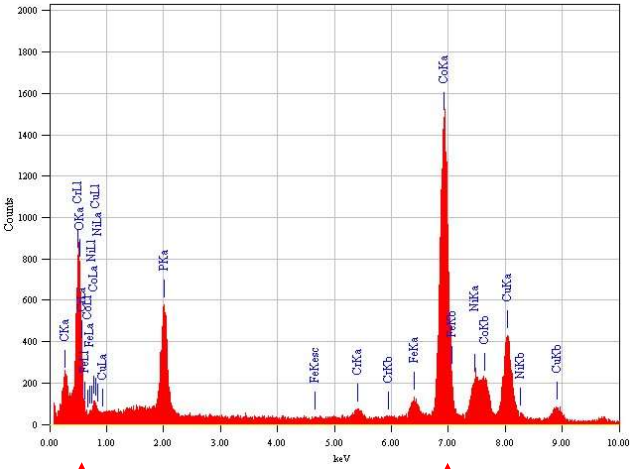
With Bin Wang & Ken Inge (Stockholm University)

Serial ED data collection on Co-CAU-36



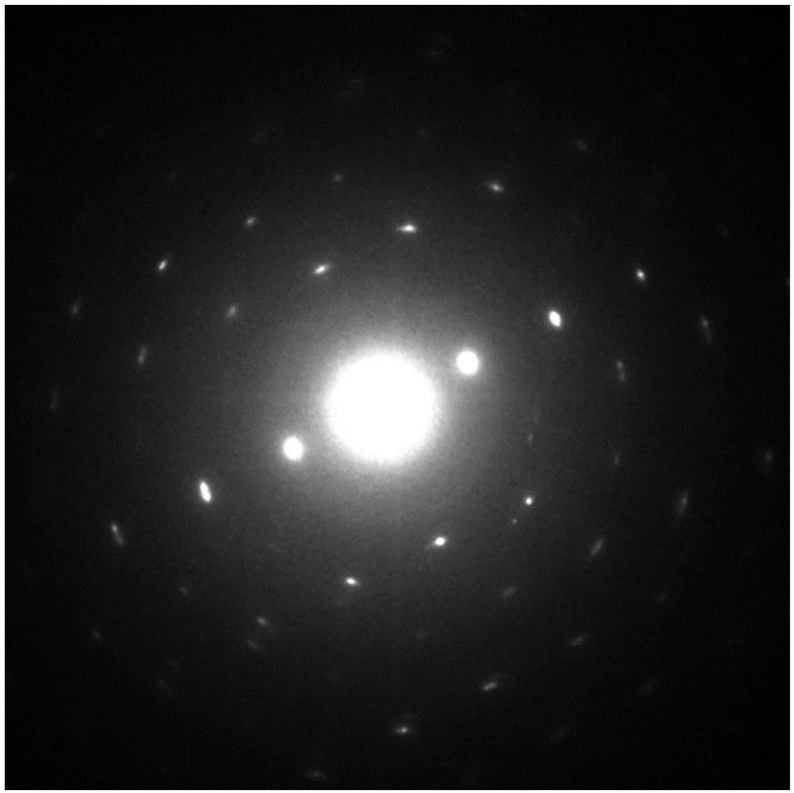


EDS



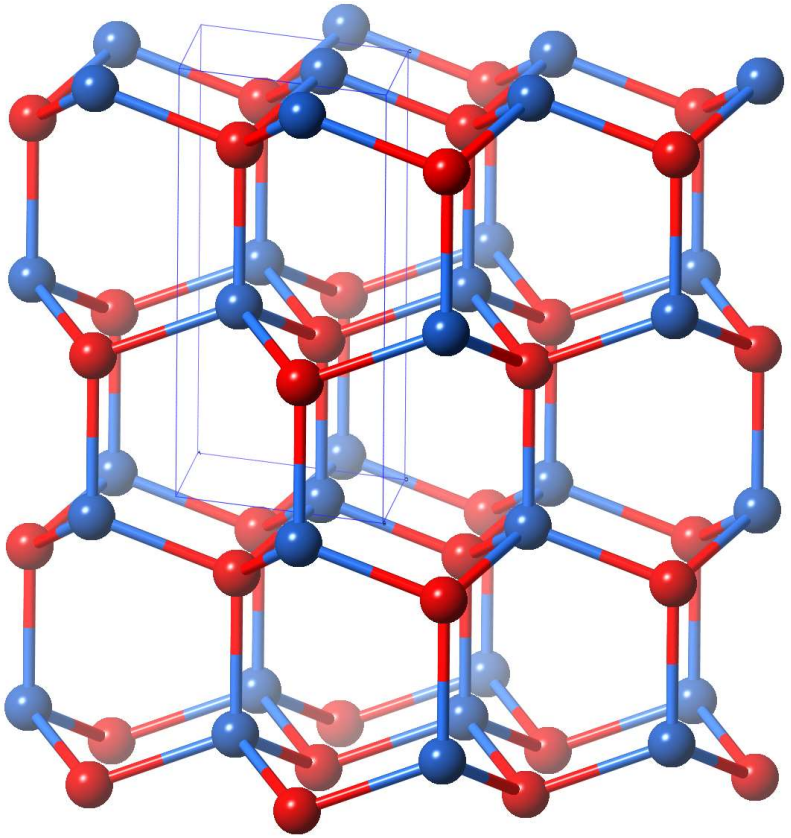
500 diffraction patterns
6 impurity crystals

Collect cRED data



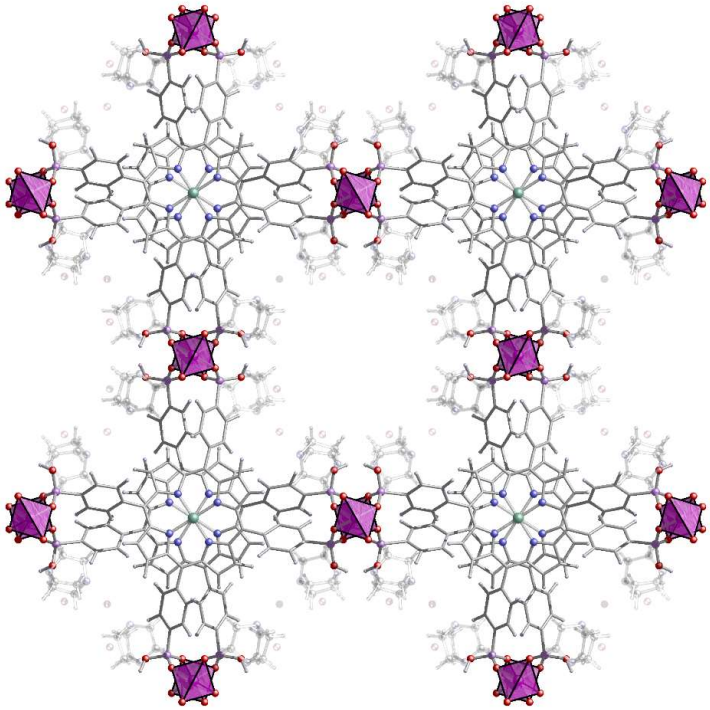
34.45 to -13.79°
Oscillation angle: 0.23°
1.5 min data collection

XDS

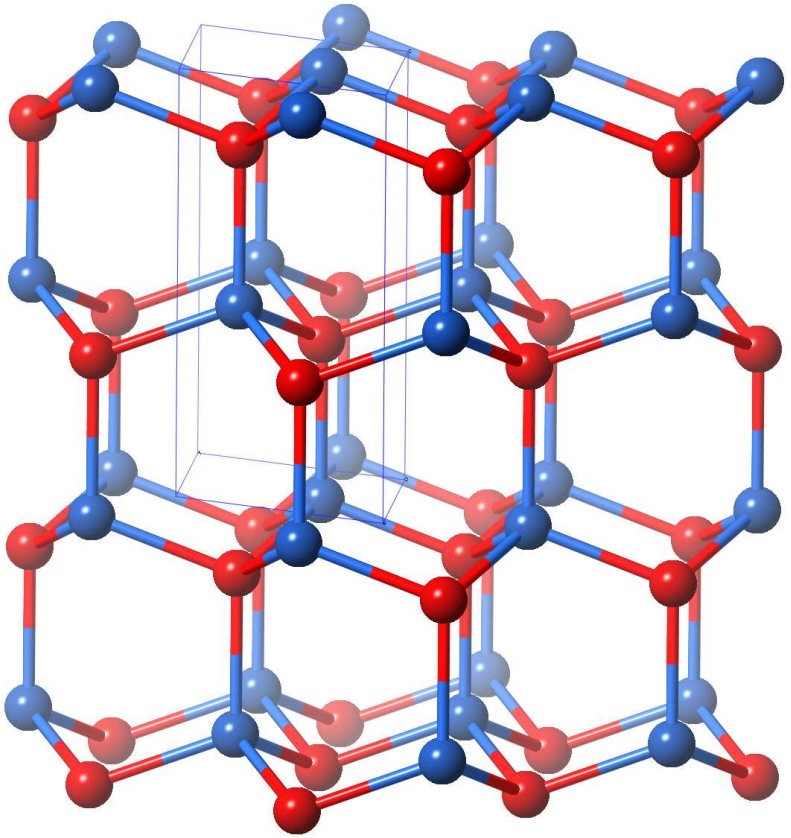


$P6_3mc$
a = 3.10 Å, b = 5.45 Å
Wurtzite structure (CoO)

‘Quantitative’ phase analysis

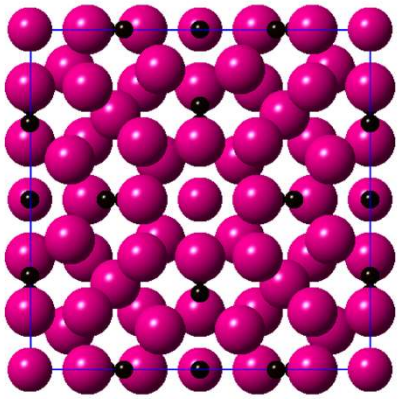


Co-CAU-36: ~99%

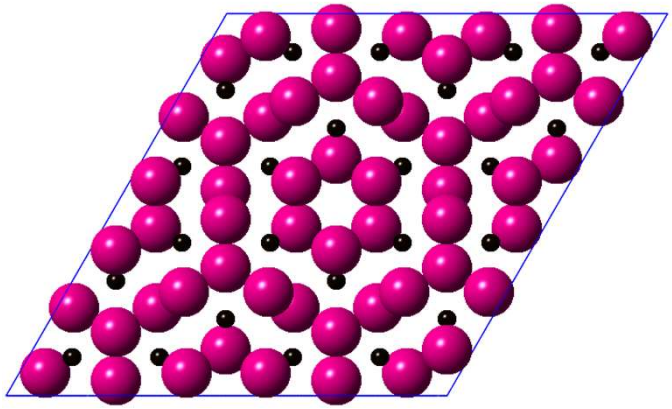


CoO: ~1%

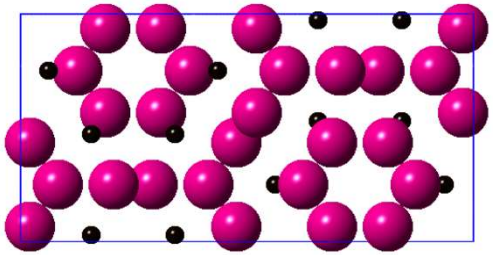
Study on Cr carbides



1



2

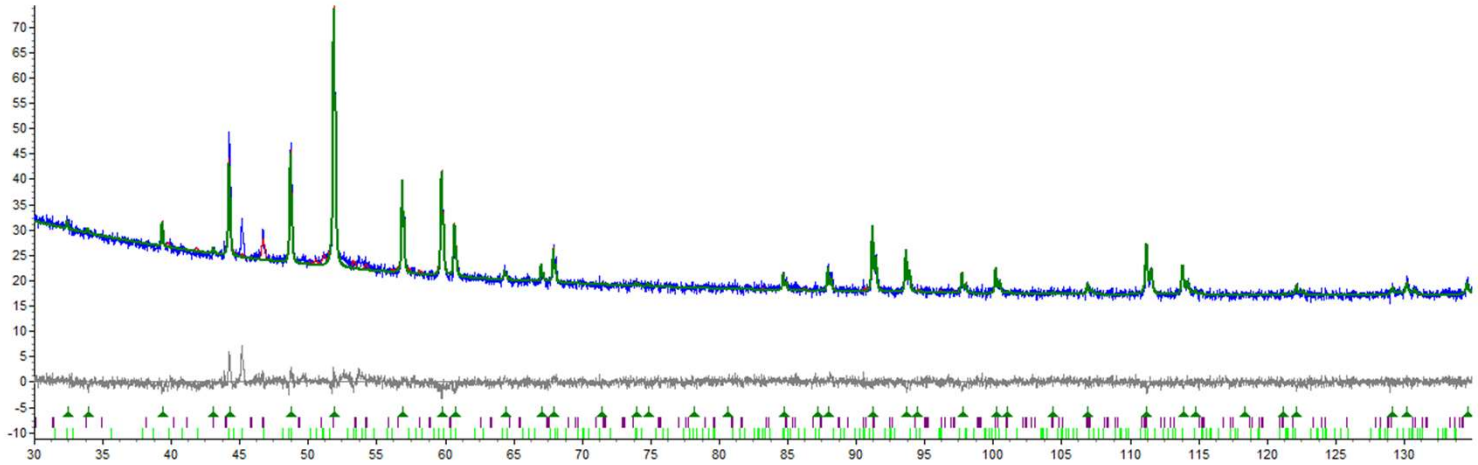


3

	Space group	a / Å	b / Å	c / Å
Phase 1	$Fm\bar{3}m$	10.62	=*a*	=*a*
Phase 2	$P6_3mc$	13.77	=*a*	4.88
Phase 3	$Pnma$	4.39	7.08	14.16

Samples from C. Olsson, Sandviken (SE)

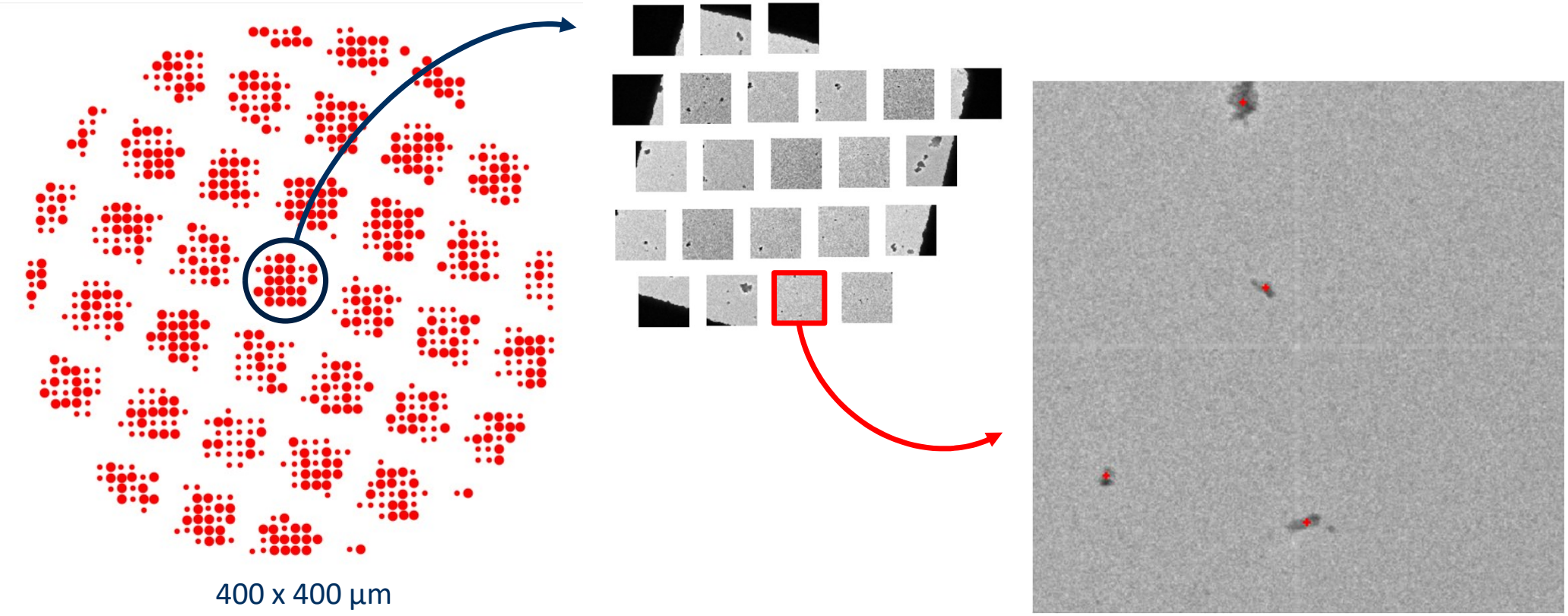
XRPD quantitative phase analysis (Cr carbides)



	Space group	a / Å	b / Å	c / Å	composition
Phase 1	$Fm\bar{3}m$	10.62	=*a*	=*a*	84.49 %
Phase 2	$P6_3mc$	13.77	=*a*	4.88	3.09 %
Phase 3	$Pnma$	4.39	7.08	14.16	12.42 %

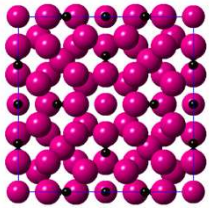
Samples from C. Olsson, Sandviken (SE)

SerialED data collection on Cr carbides

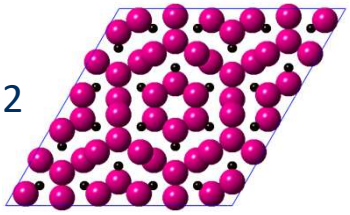


400 x 400 µm
836 images
1019 patterns
~80 minutes

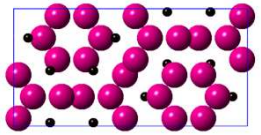
Quantitative phase analysis

1 

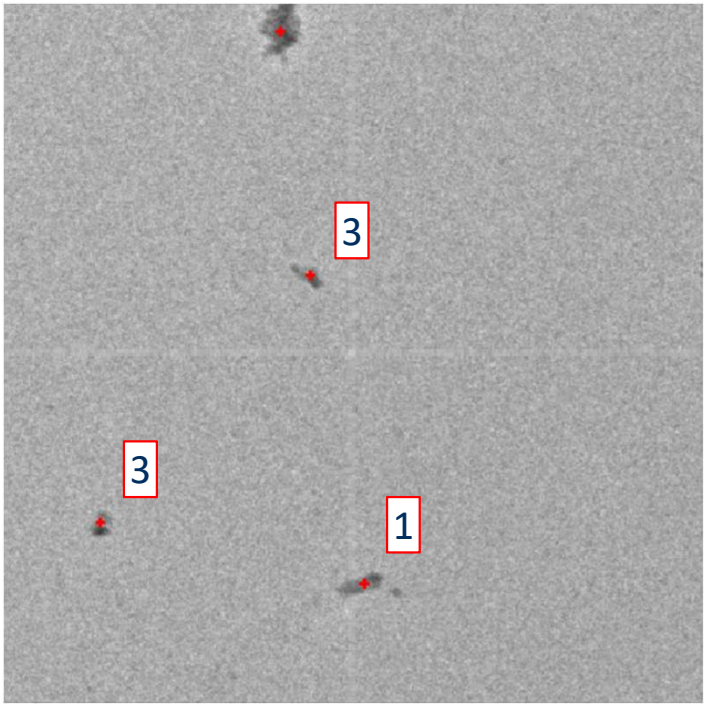
136 – 171 (67.9 – 94.4 %) 84.49 %

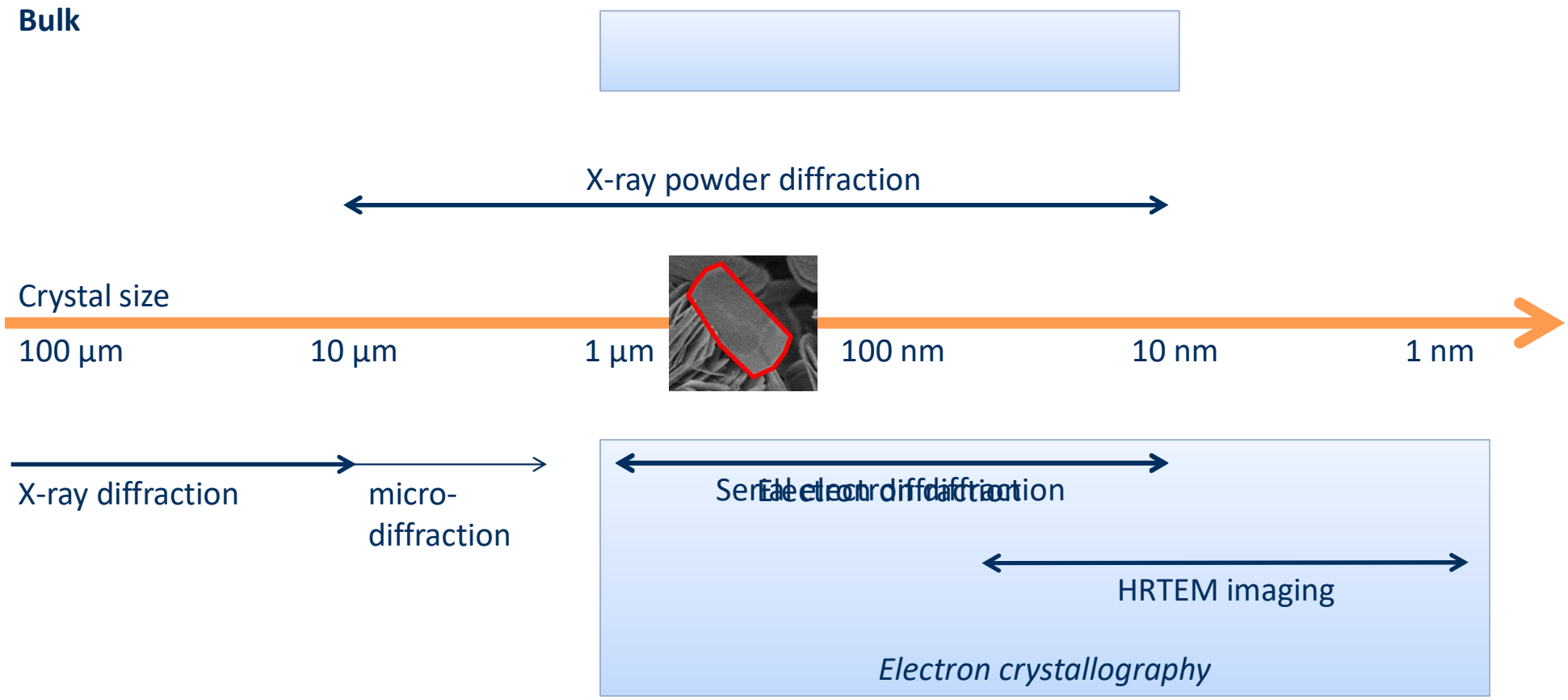
2 

1 – 14 (0.7 – 5.6%) 3.09 %

3 

7 – 67 (4.9 – 26.6%) 12.42 %




Bulk
X-ray powder diffraction
Crystal size
100 µm
10 µm
1 µm
100 nm
10 nm
1 nm
X-ray diffraction
micro-
diffraction
Serial electron diffraction
Tilt electron diffraction
HRTEM imaging
Electron crystallography
Single crystal

Conclusions

- Electrons are well suited for structure analysis of nanocrystalline materials

SerialED

- Data can be collected routinely & automatically
- 100-200 patterns are enough for structure determination
- Applications
  - Structure determination (of beam-sensitive materials)
  - Crystal identification (screening, polymorphism)
  - Phase analysis