Nanofront 2019, Courchevel, FR
22-03-2019

FNSNF
Swiss National Science Foundation

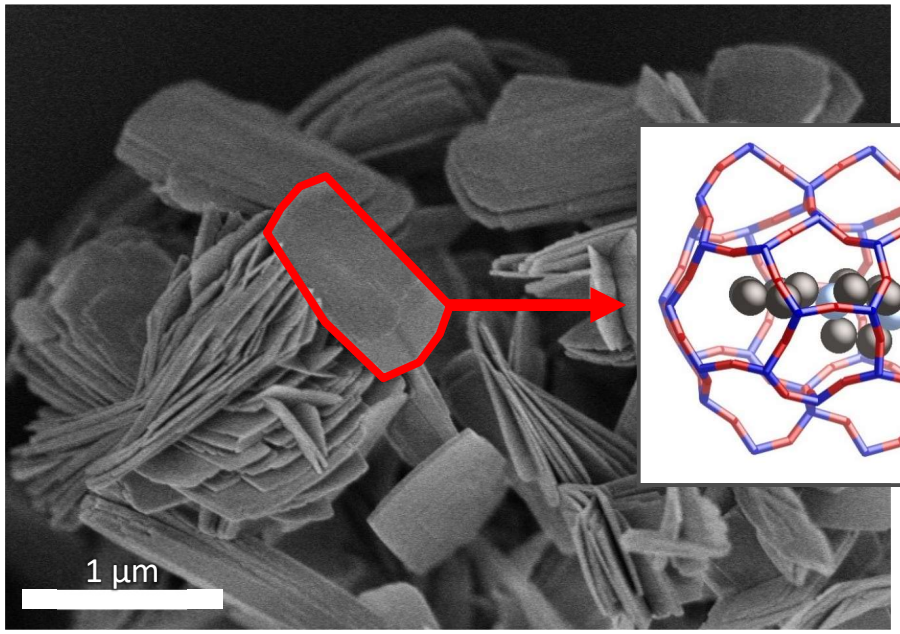
KAVLI INSTITUTE
of Nanoscience Delft

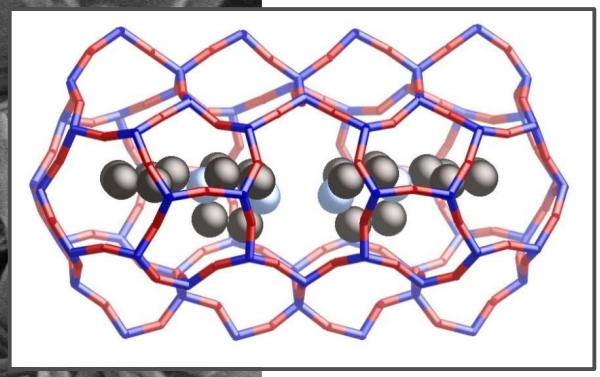
Structure determination of nanocrystalline materials using electron diffraction

Stef Smeets

Kavli Institute of Nanoscience Delft

TU Delft





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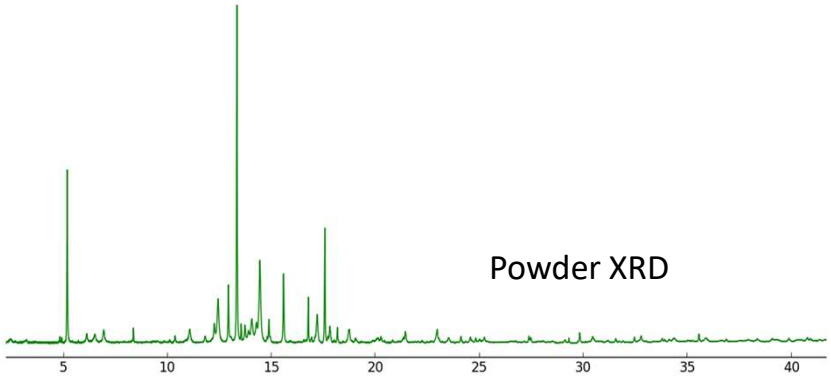
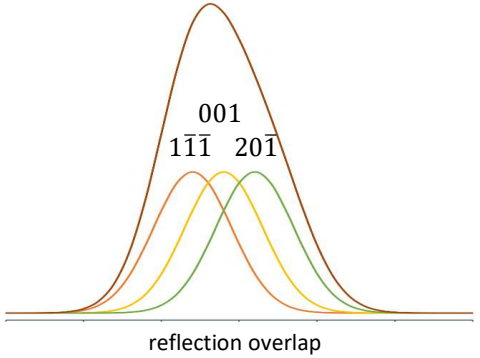
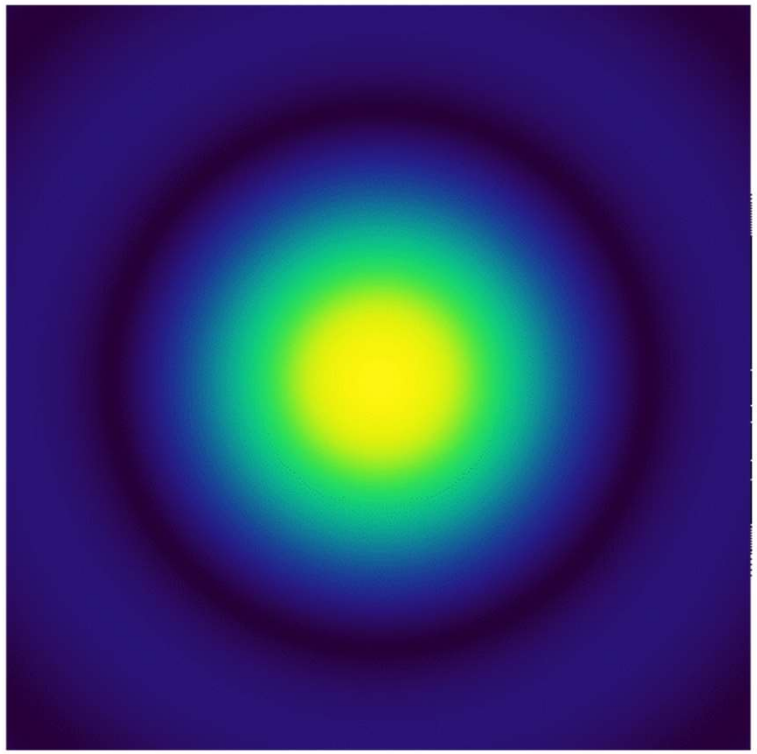


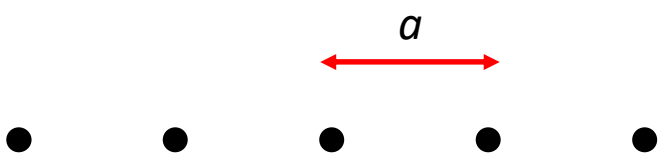
Powder XRD

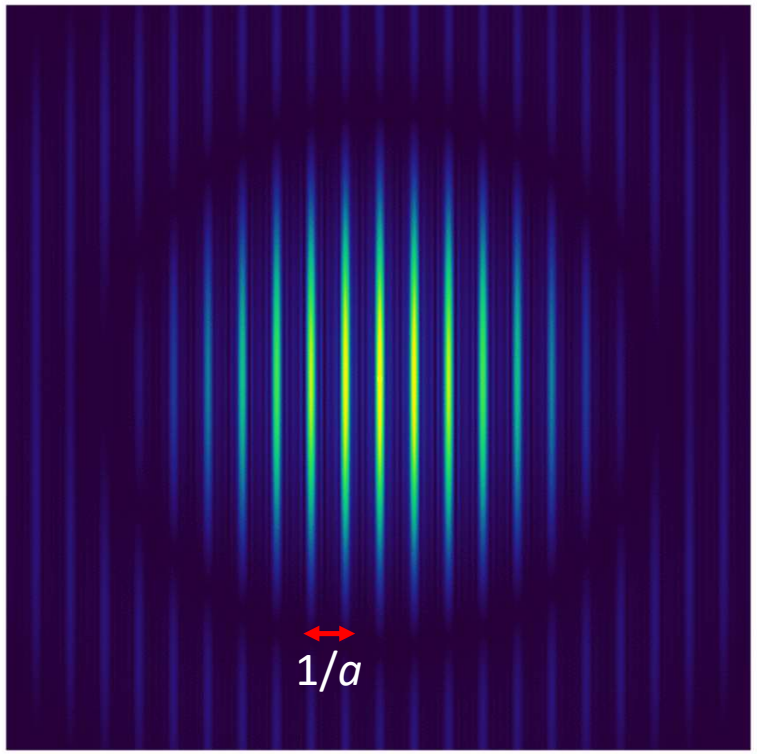


reflection overlap

Fourier Transform




a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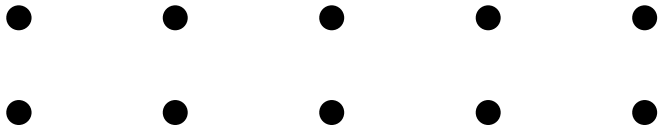
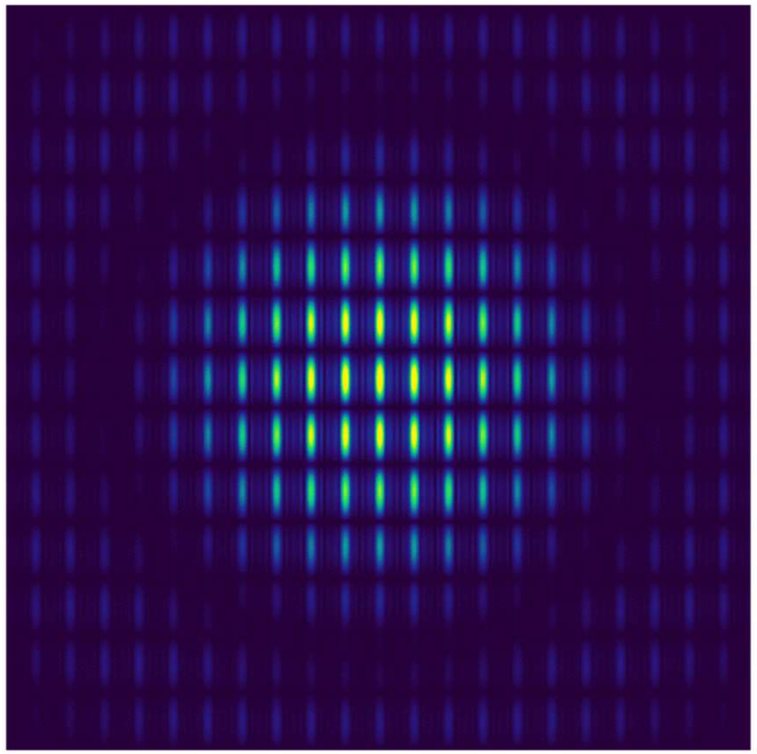
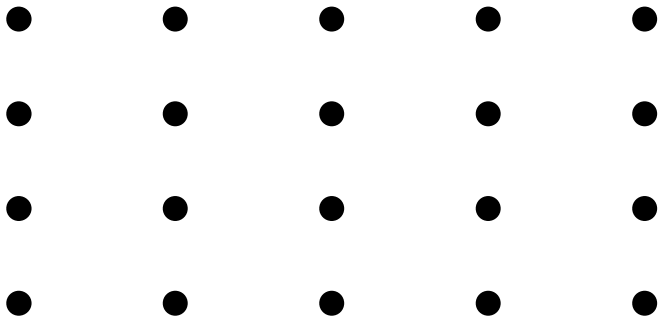
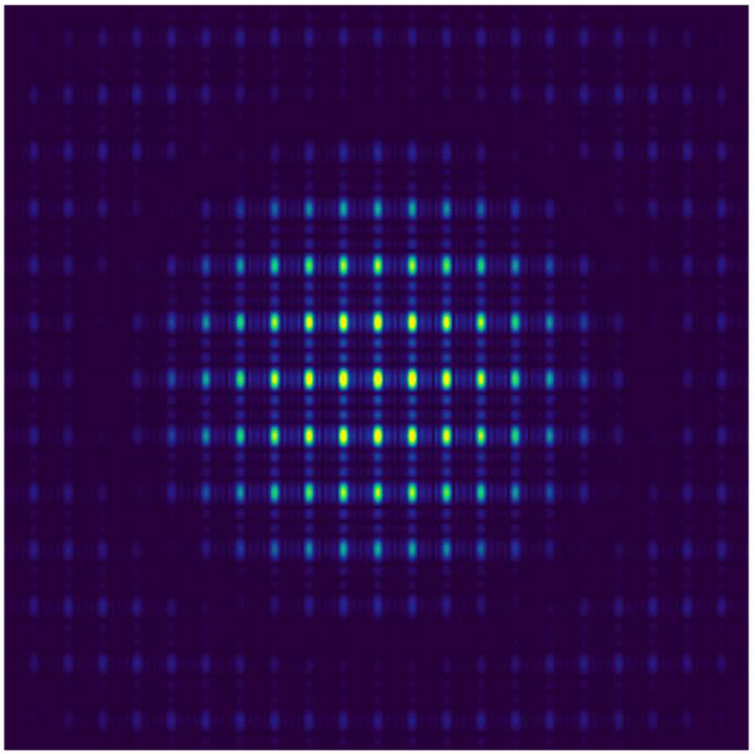
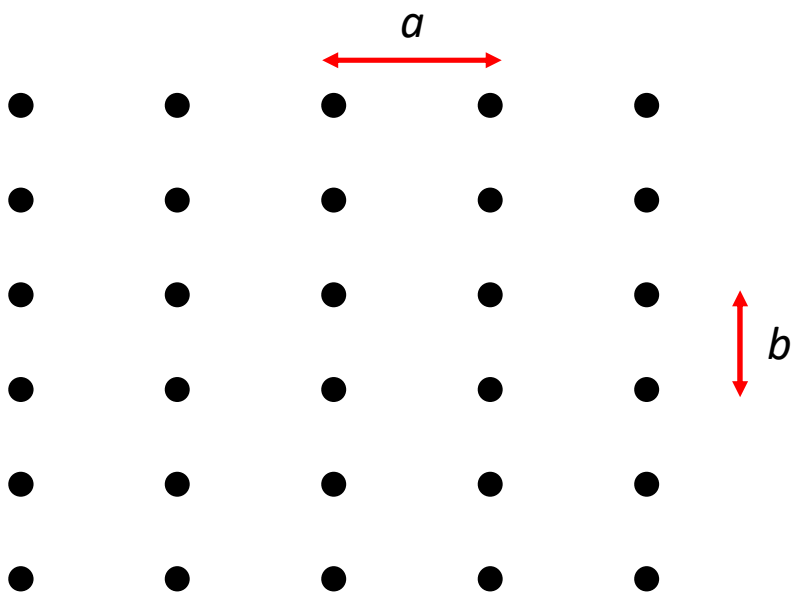
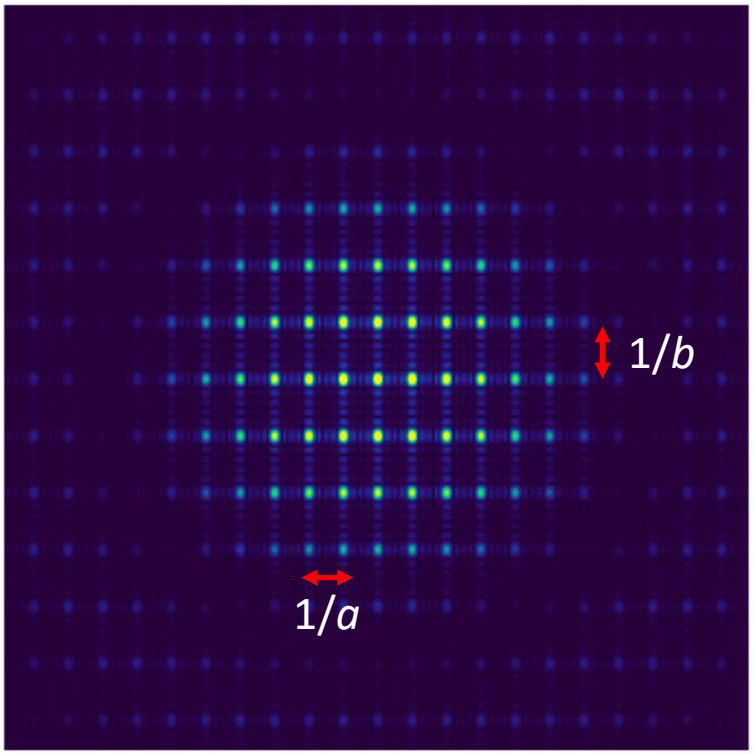


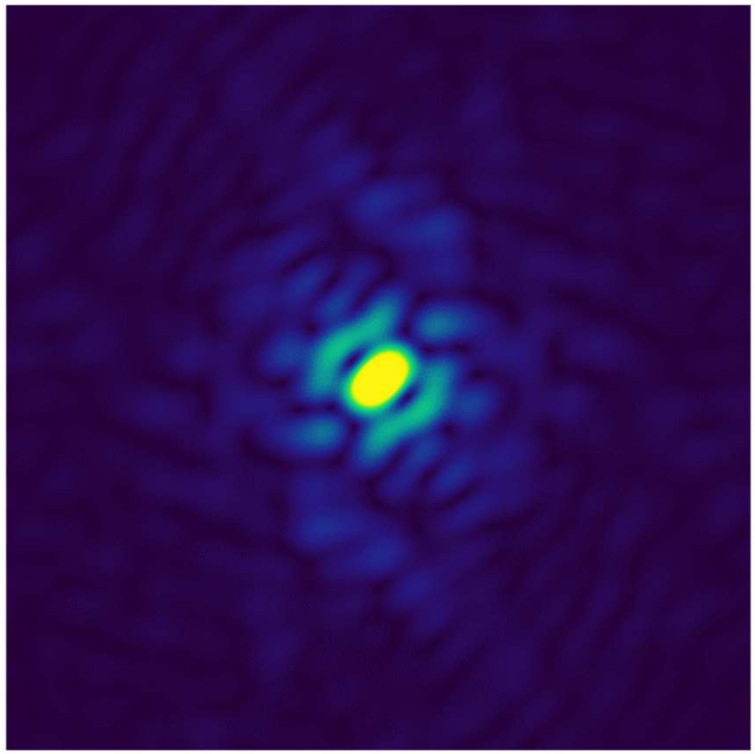




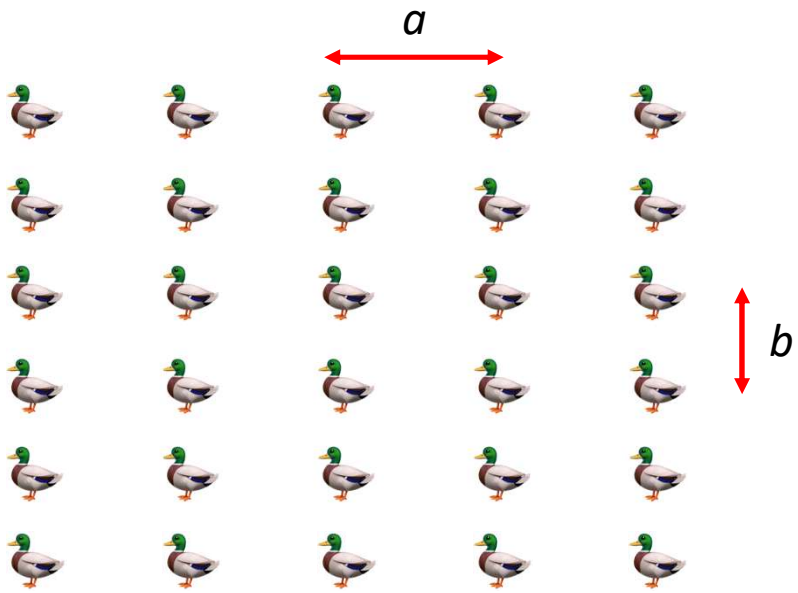



a
b


1/b
1/a



duck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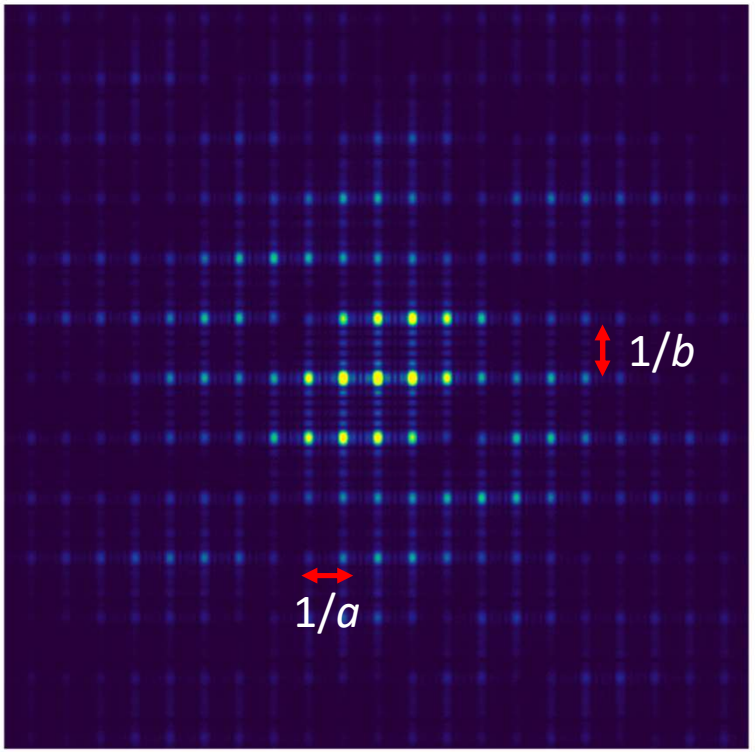
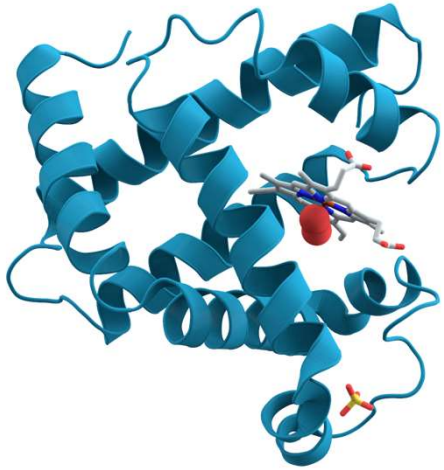
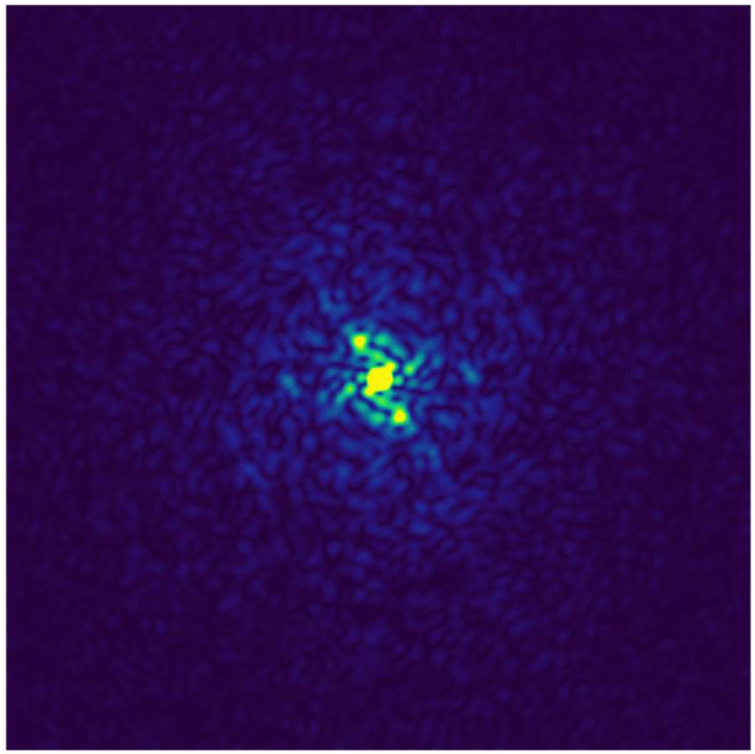
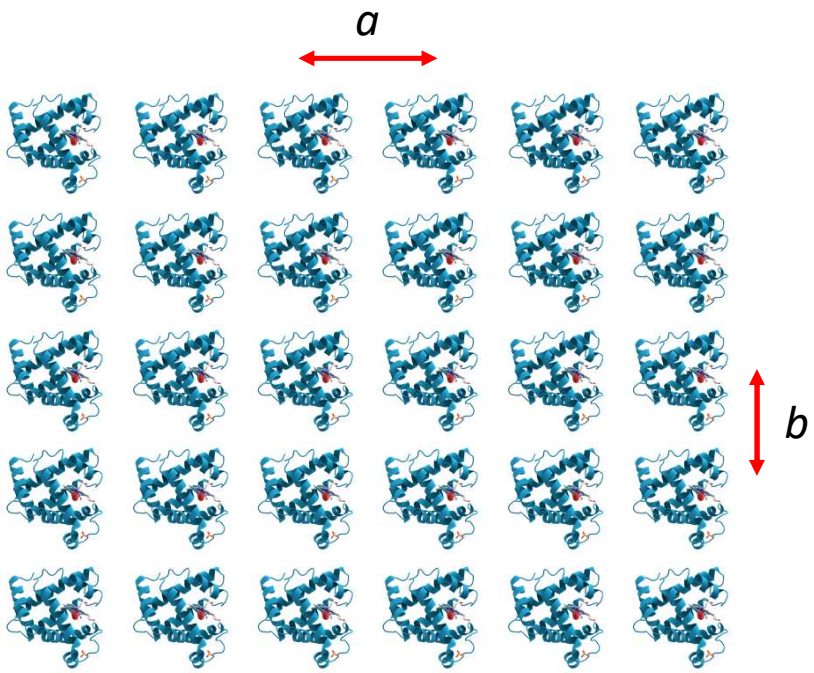
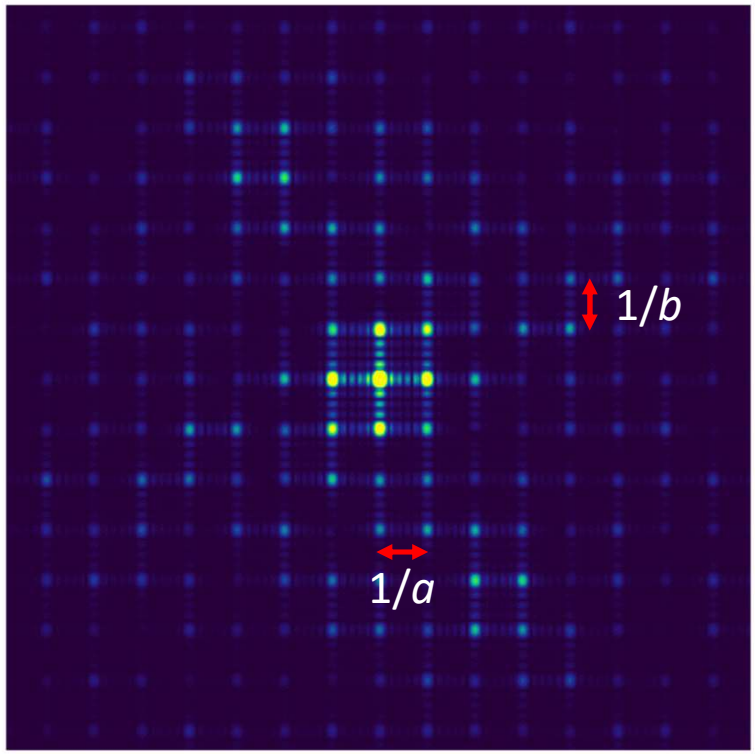

1/b
1/a

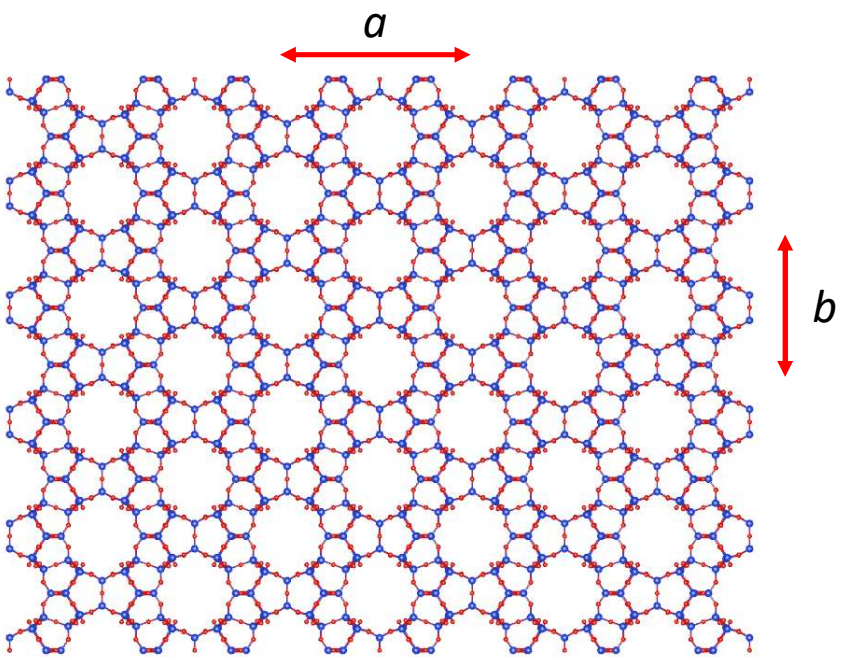


myoglobin

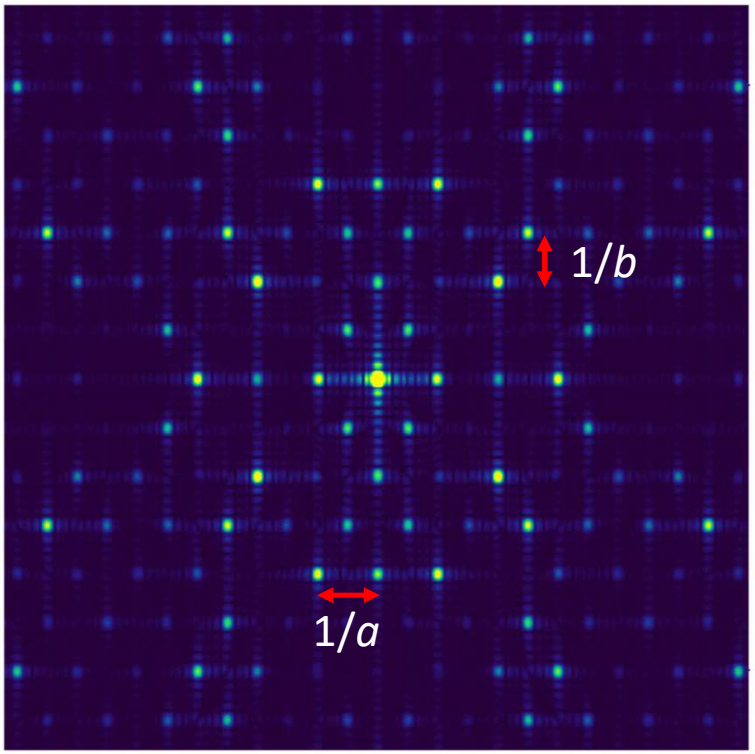



a
b

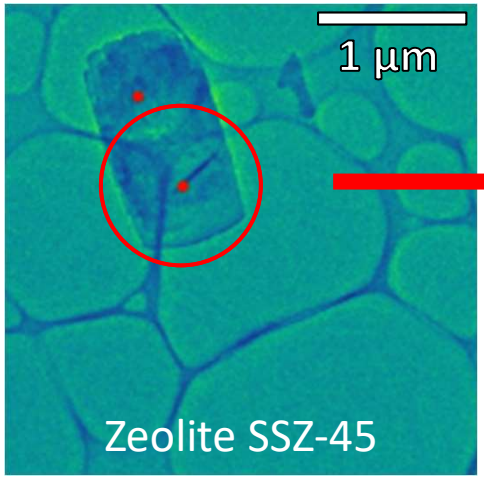

1/b
1/a

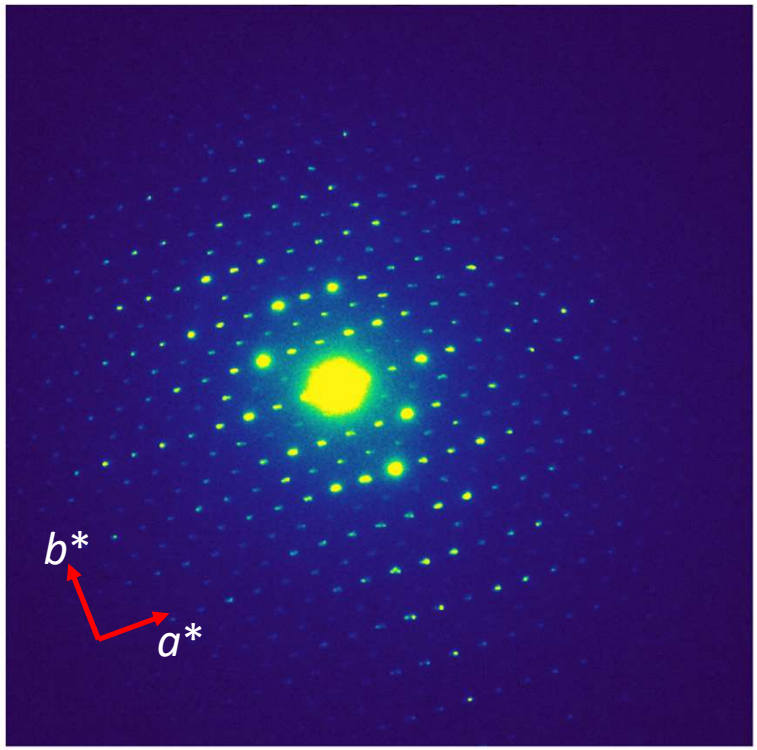


zeolite



Diffraction



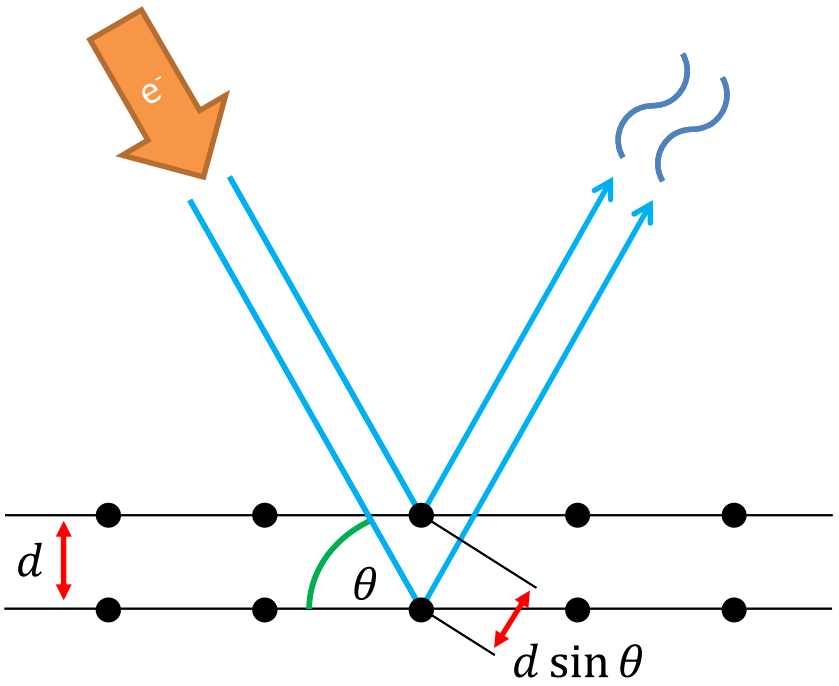


- Reflections
  - Positions → Unit cell
  - Intensities → Crystal structure
  - Shape → Microstructure (stress, strain)

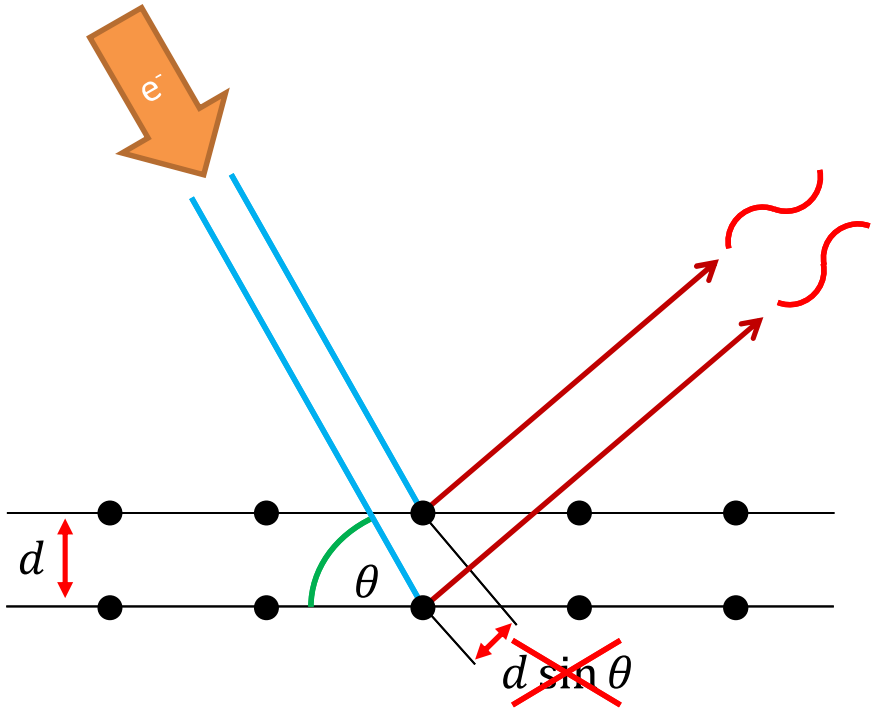
Diffraction

Bragg's law

$$n\lambda = 2d \sin\theta$$

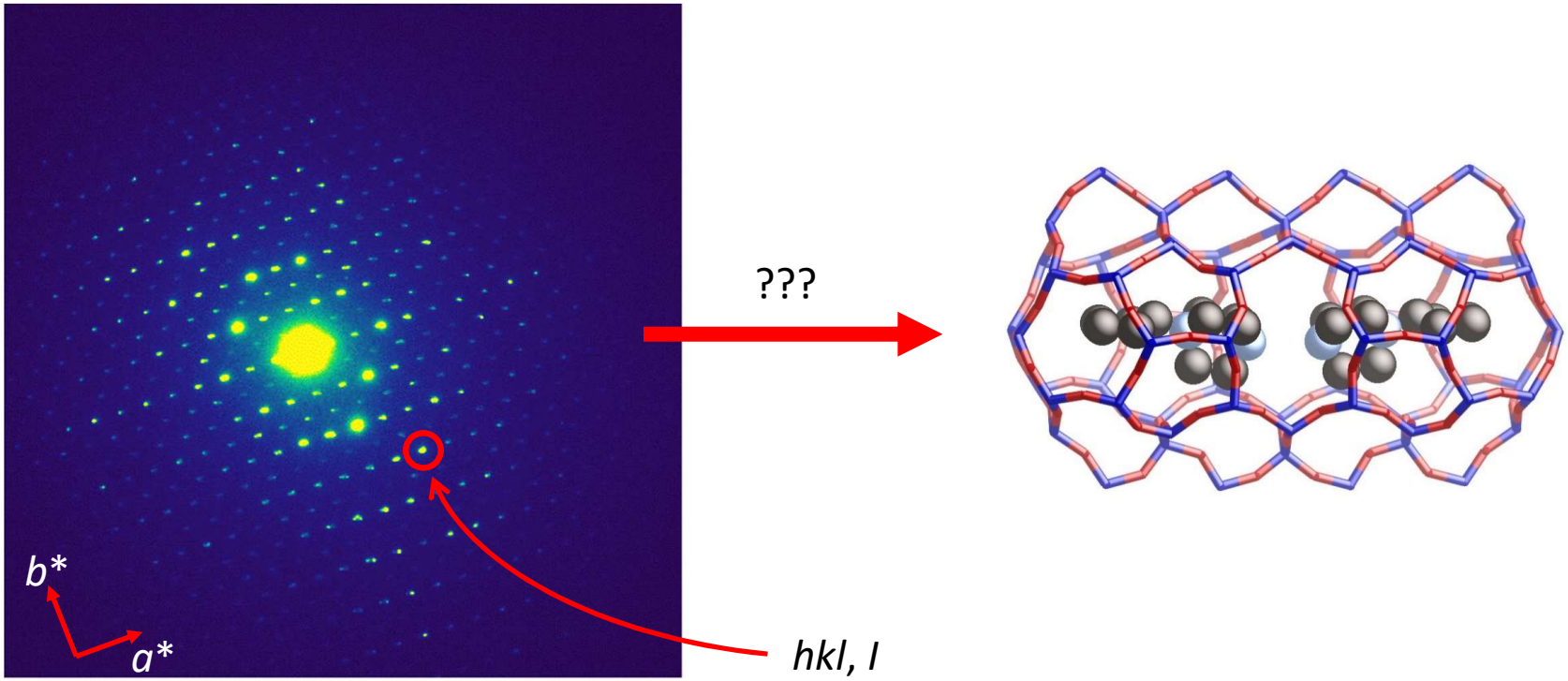


Constructive interference



Destructive interference

Crystallography



Crystallography

$$I_{hkl} \propto |F_{hkl}|^2$$

Structure factor

$$\rho(xyz) = \frac{1}{V}\sum_{hkl} |F_{hkl}| \cos(2\pi(hx + ky + lz) - \alpha_{hkl})$$

Electrostatic potential

Phases

Atomic model

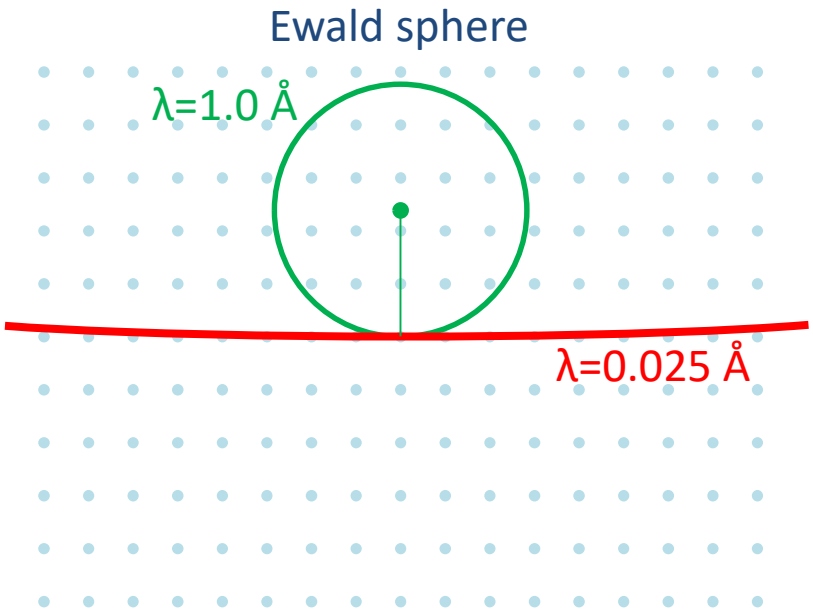
$$F_{hkl} = \sum_{j=1}^{N} f_j e^{i2\pi(hx_j + ky_j + lz_j)}$$

"The Phase problem"

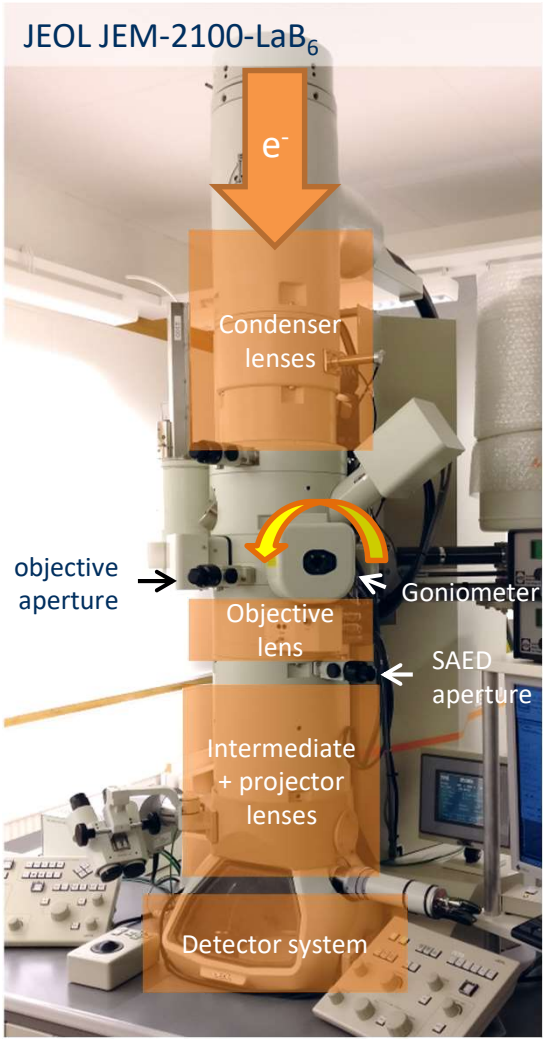
Structure determination

- Molecular replacement
- Direct methods
- Charge flipping
- …

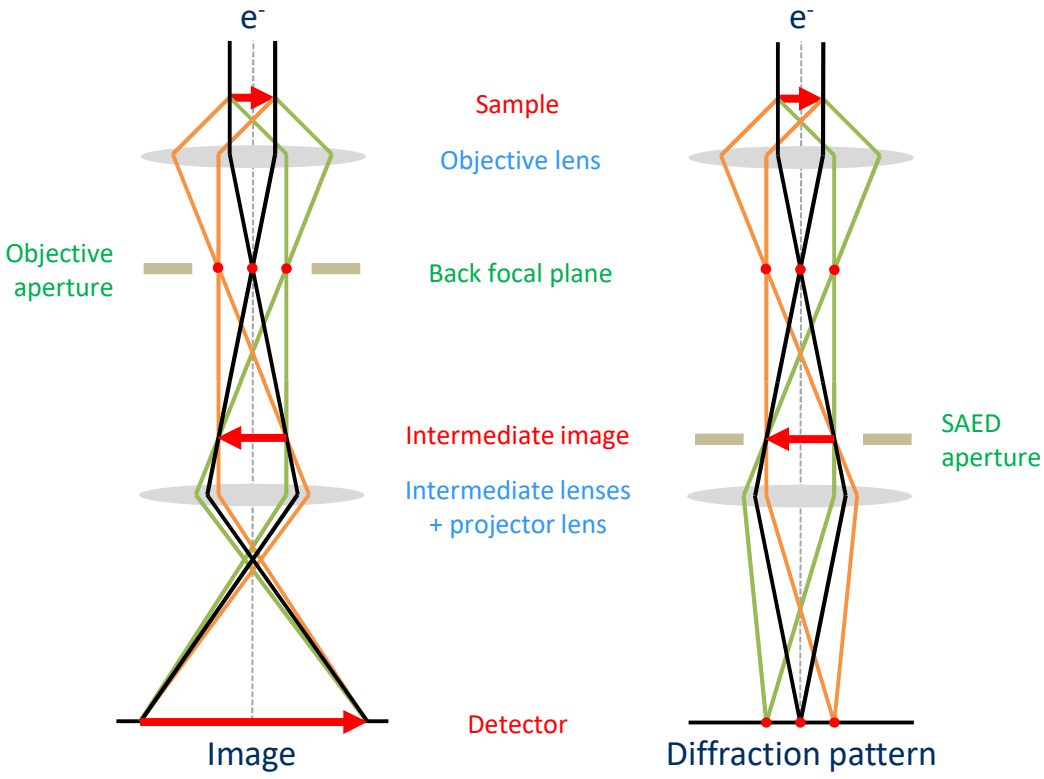
Electrons as a radiation source



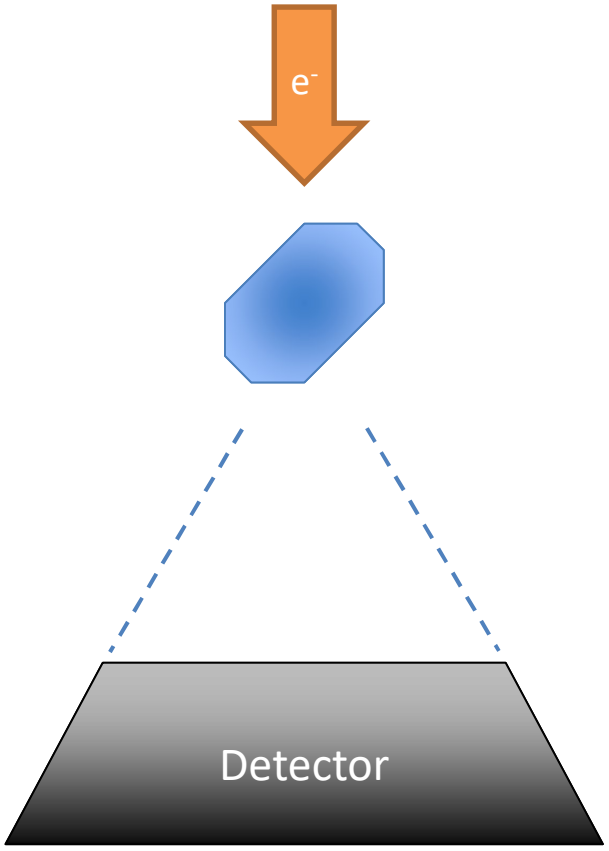
- Accelerating voltage: 100 to 300 keV
- Wavelength: 0.0251 Å @ 200 keV
- Probe electrostatic potential
- Strong interaction (10^6 stronger than X-rays)
- Require small samples (< 1 µm)
- High vacuum (<10^{-3} mbar)



Electron ‘diffractometer’

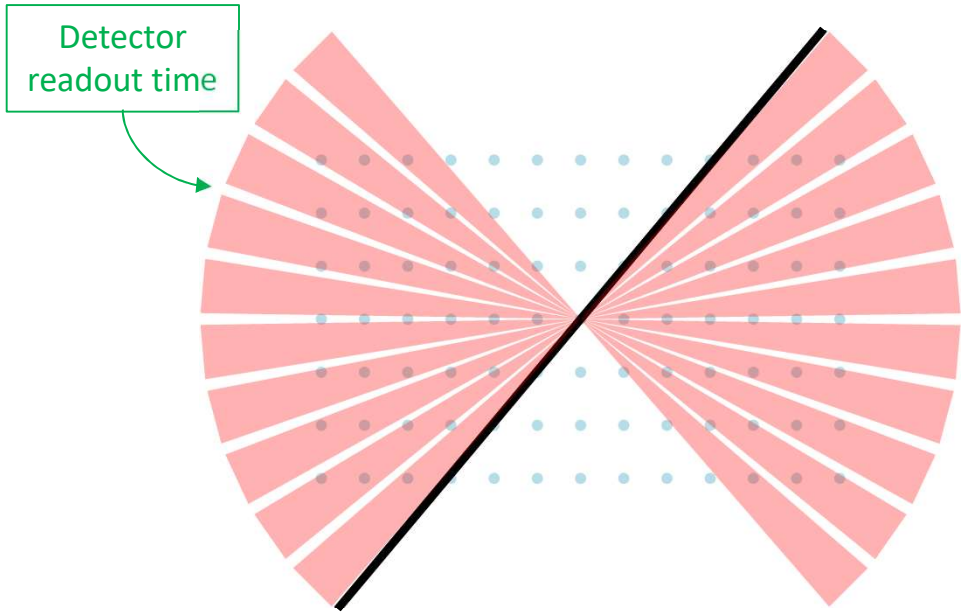


3D Electron diffraction



Continuous rotation method

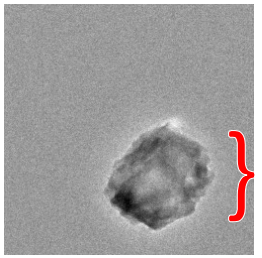
Nederlof *et al.*, Acta Cryst. D (2013), 69:1223
Nannenga *et al.*, Nat. Methods (2014), 11:927
Gemmi *et al.*, J. Appl. Cryst. (2015), 48:718
Cichocka *et al.*, J. Appl. Cryst. (2018), 51:1652

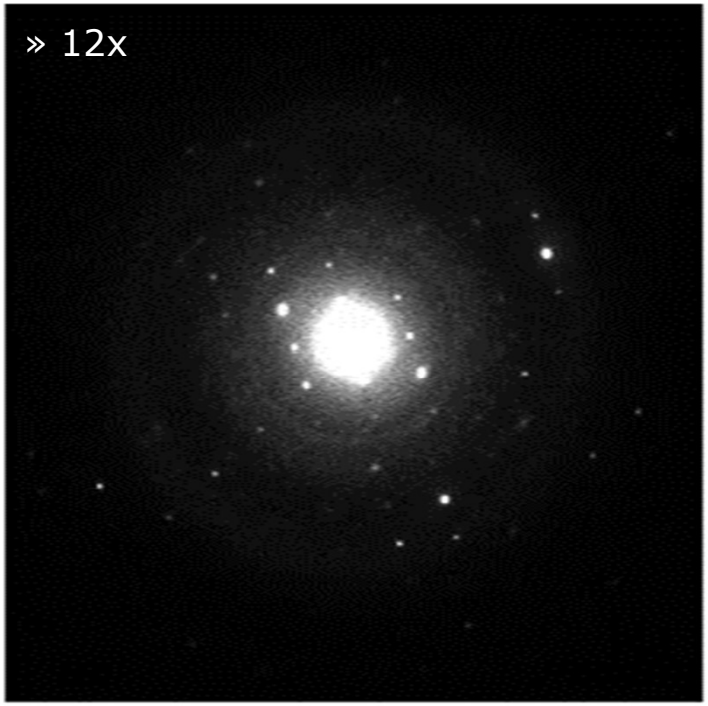


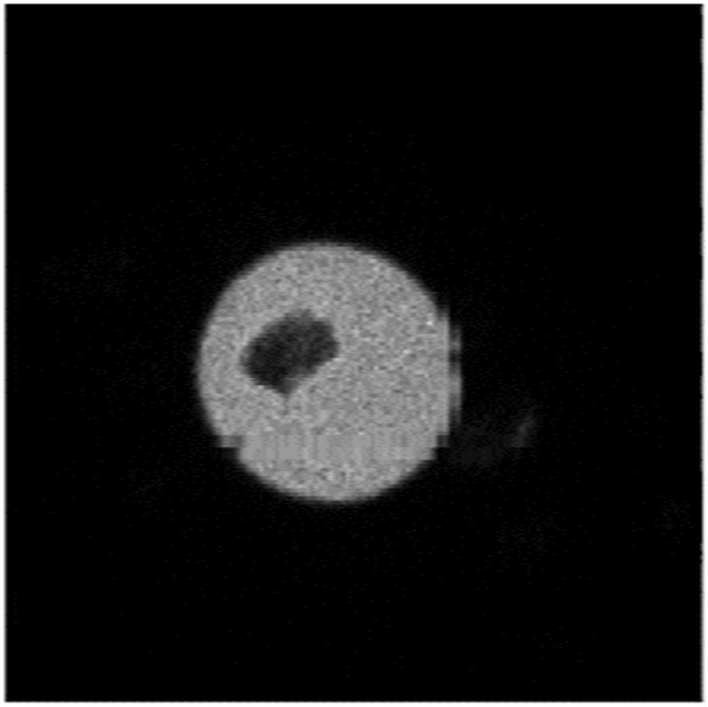
Tilt range: up to 150°
Oscillation angle: 0.1-0.5°
Rotation speed: 0.5-2.0°/s
<5 minutes

Zeolite mordenite

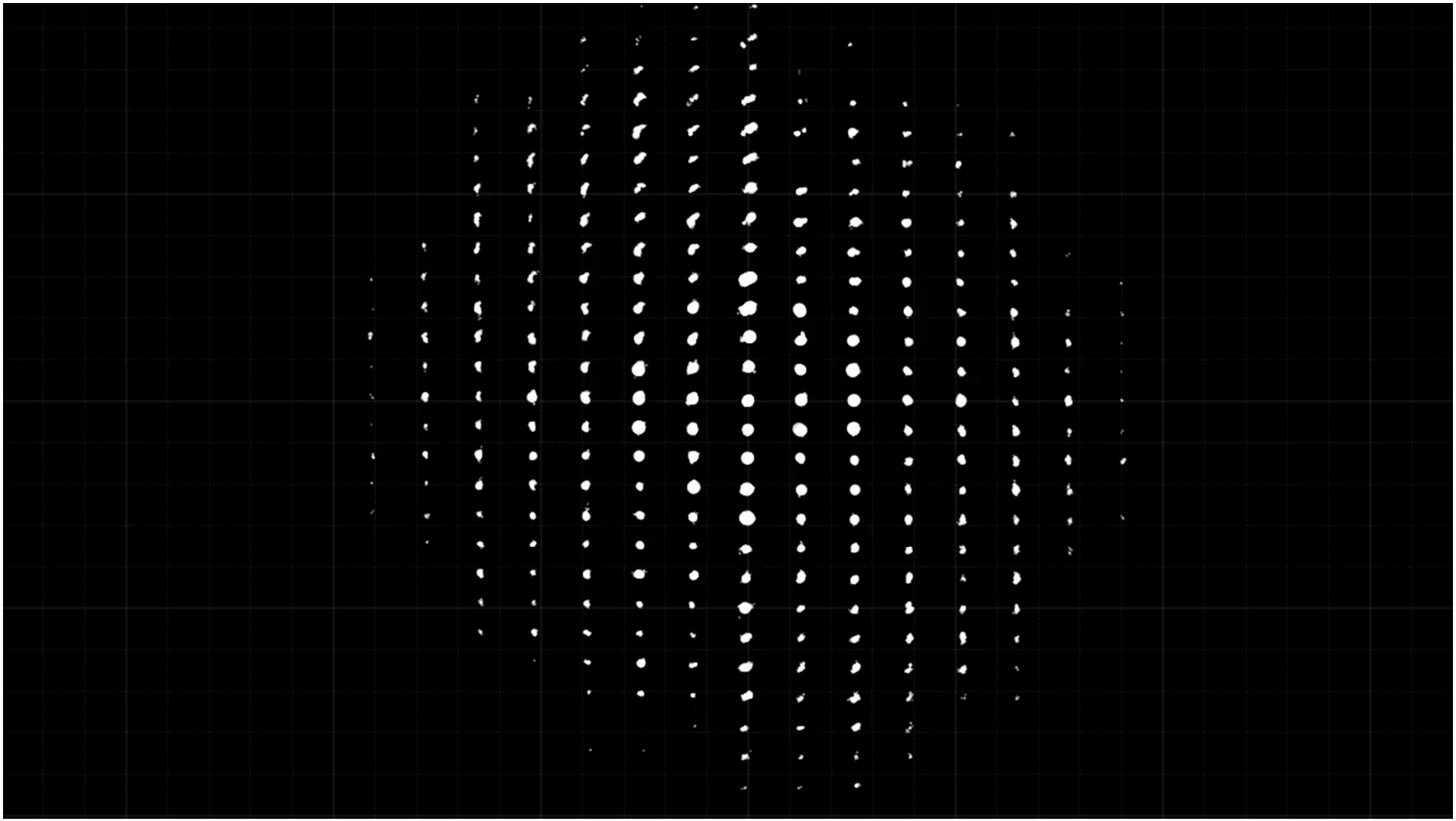
Rotate: -43.90° to 58.65° @ 0.45°/s (102.55°)
Exposure: 0.5 s, oscillation angle: 0.23°





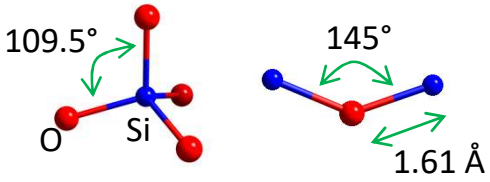


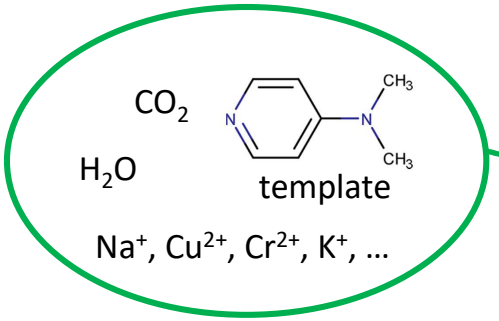
Cichocka *et al.*, *J. Appl. Crystallogr.* 51 (2018): 1652–61

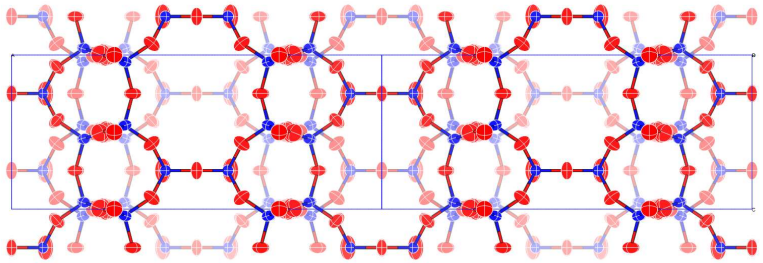


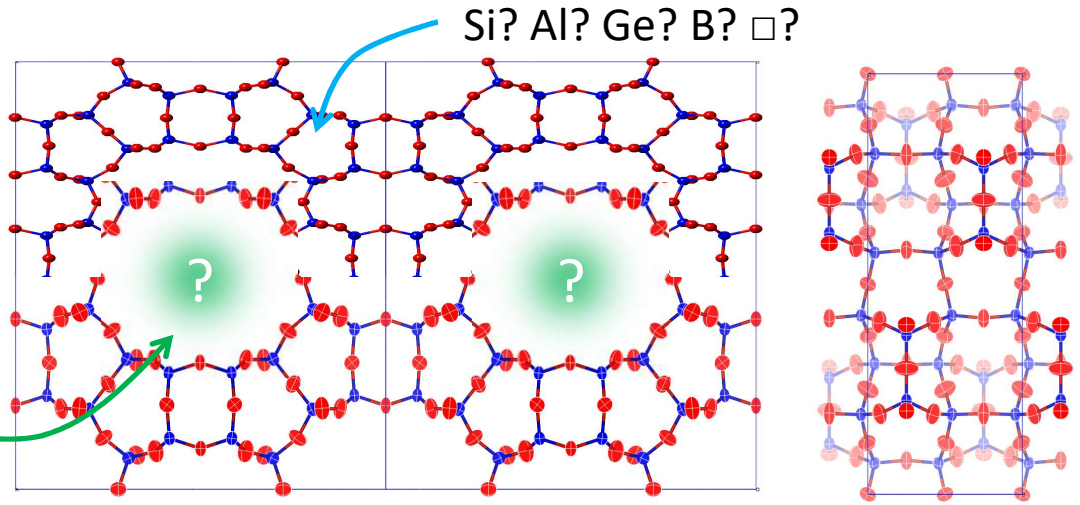
Framework structure

Si—O	1.614 ± 0.012 Å
Si—O—Si	109.5 ± 1.9°
O—Si—O	153.3 ± 12.0°





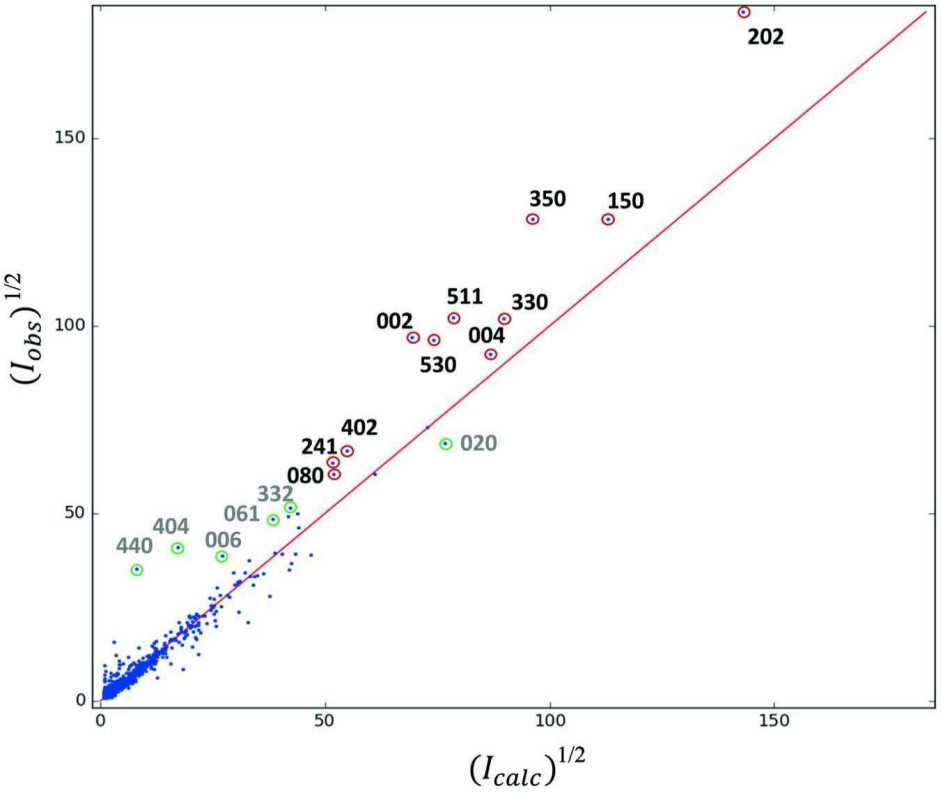




*R*1=0.160 (0.80 Å)

Cichocka *et al.*, *J. Appl. Crystallogr.* 51 (2018): 1652–61

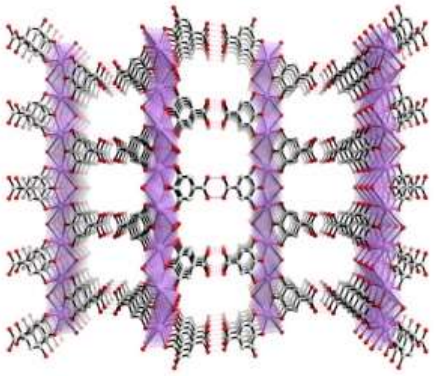
Refinement



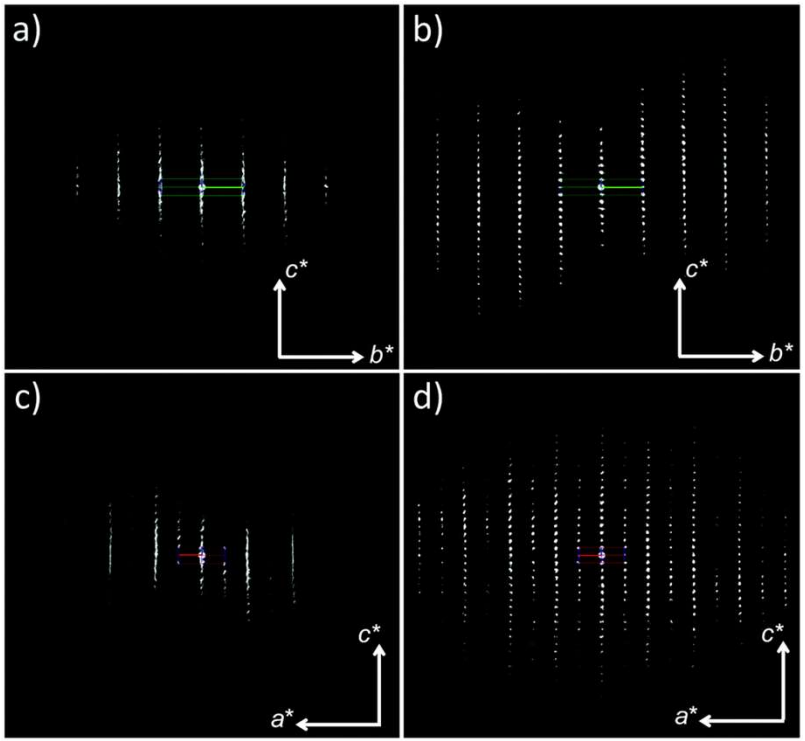
Chemical formula (refined)	$Si_{48}O_{96}$
Space group	*Cmcm* (63)
a (Å)	18.110
b (Å)	20.530
c (Å)	7.528
Resolution (Å)	0.80
No. of total reflections	5244
No. of unique reflections (all)	1585
No. of unique reflections [$F_o > 4\sigma(F_o)$]	1140
Refined parameters	96
Restraints	0
R_{int}	0.0878
*R*1 for $F_o > 4\sigma(F_o)$	0.1602
*R*1 for all data	0.1769
Goodness of fit	1.610

Improved data collection

Discrete rotation steps
CCD camera
Ambient temperature
Custom processing scripts



Bismuth subgallate



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

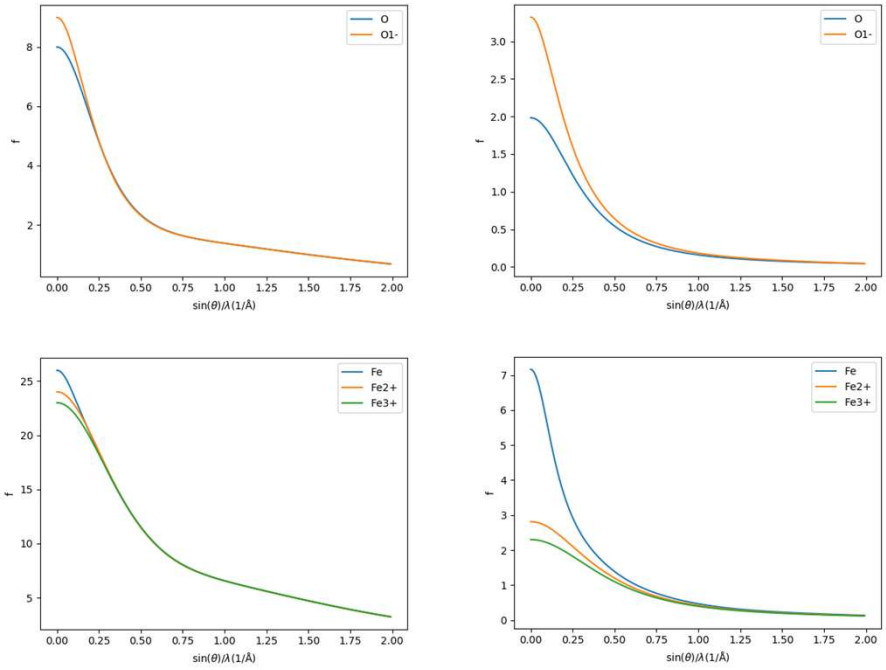
Continuous rotation
Hybrid pixel detectors
Sample cooling
Data reduction by standard crystallographic software

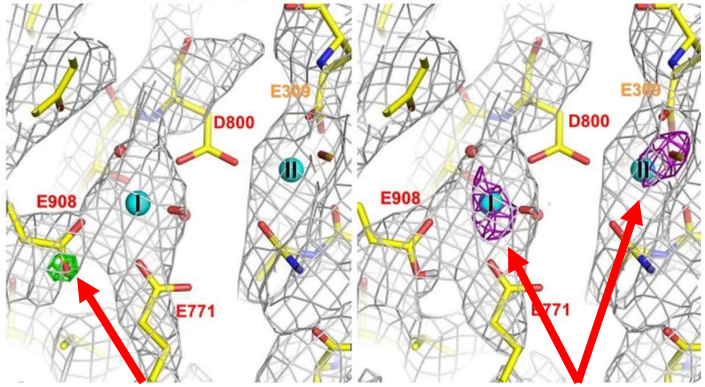
ASI Timepix Camera

Determine charge states

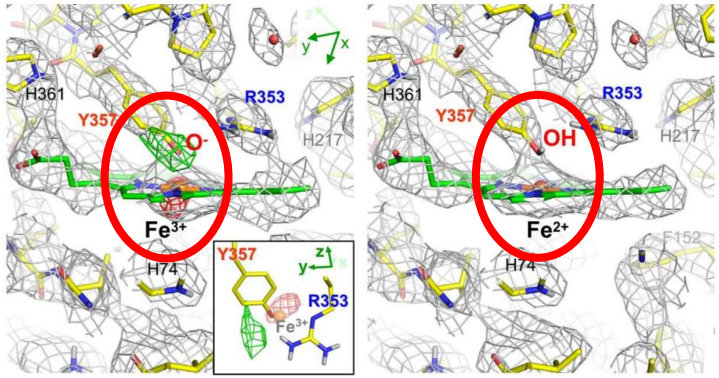
Enhanced constrast in scattering factors

X-rays → Electrons





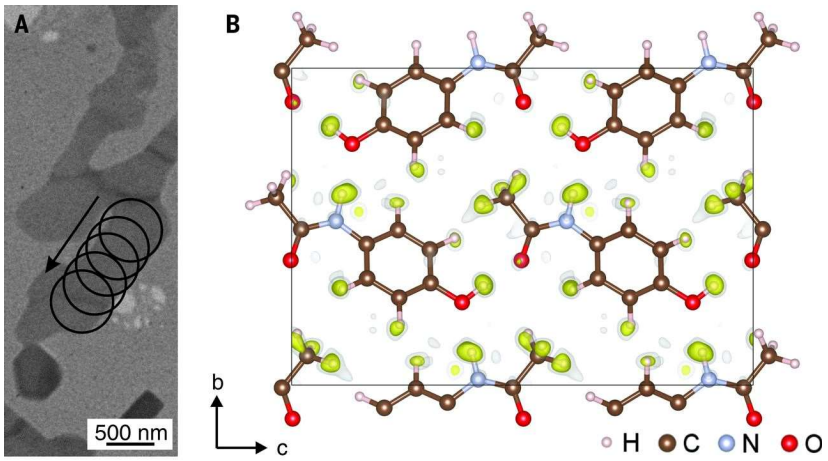
H^+ ATPase Ca^{2+}



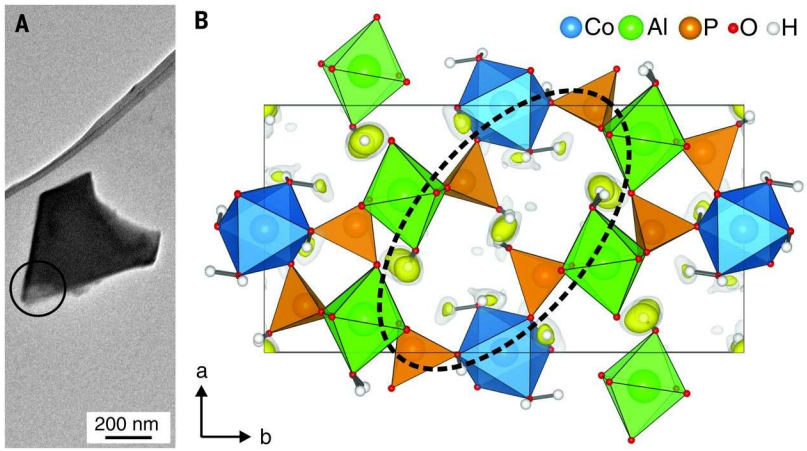
Catalase

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

Find light elements



Paracetamol II



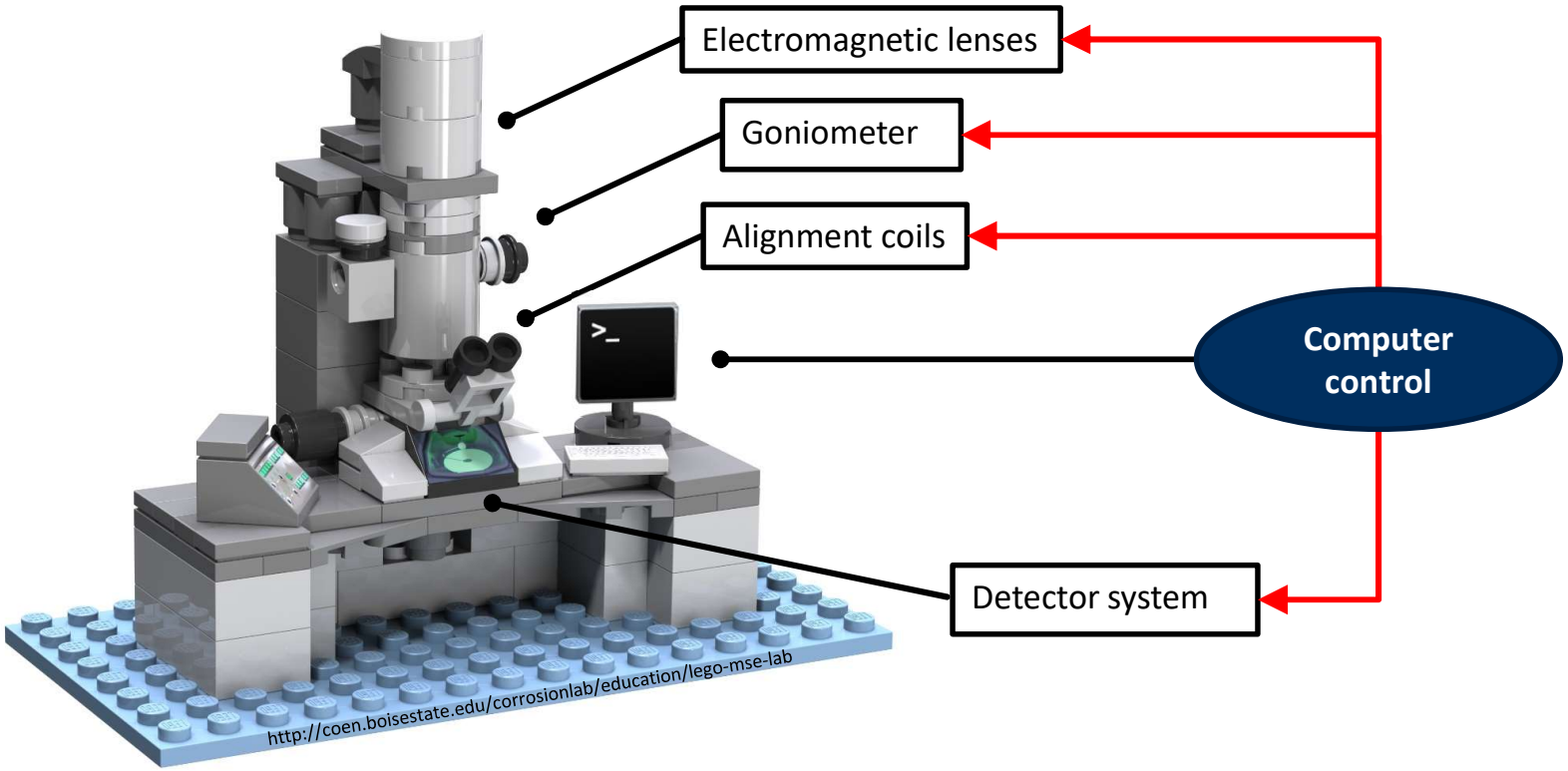
cobalt aluminophosphate

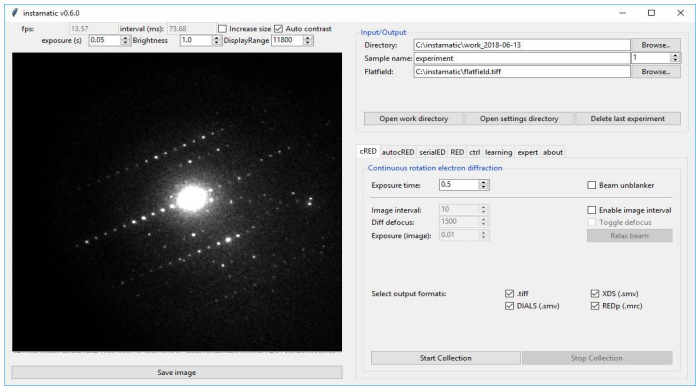
Dynamical refinement with JANA

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

Serial electron diffraction

The electron microscope as a giant toy





- Modular GUI
- Crystal finder
- Crystal tracking
- Neural network
- Calibrations

Instamatic **(Python3.6)**

Microscope control

JEOL JEM-2100-LaB_6 @ 200 keV

Camera interface

ASI Timepix @ 120 Hz

Continuous rotation electron diffraction

Serial electron diffraction

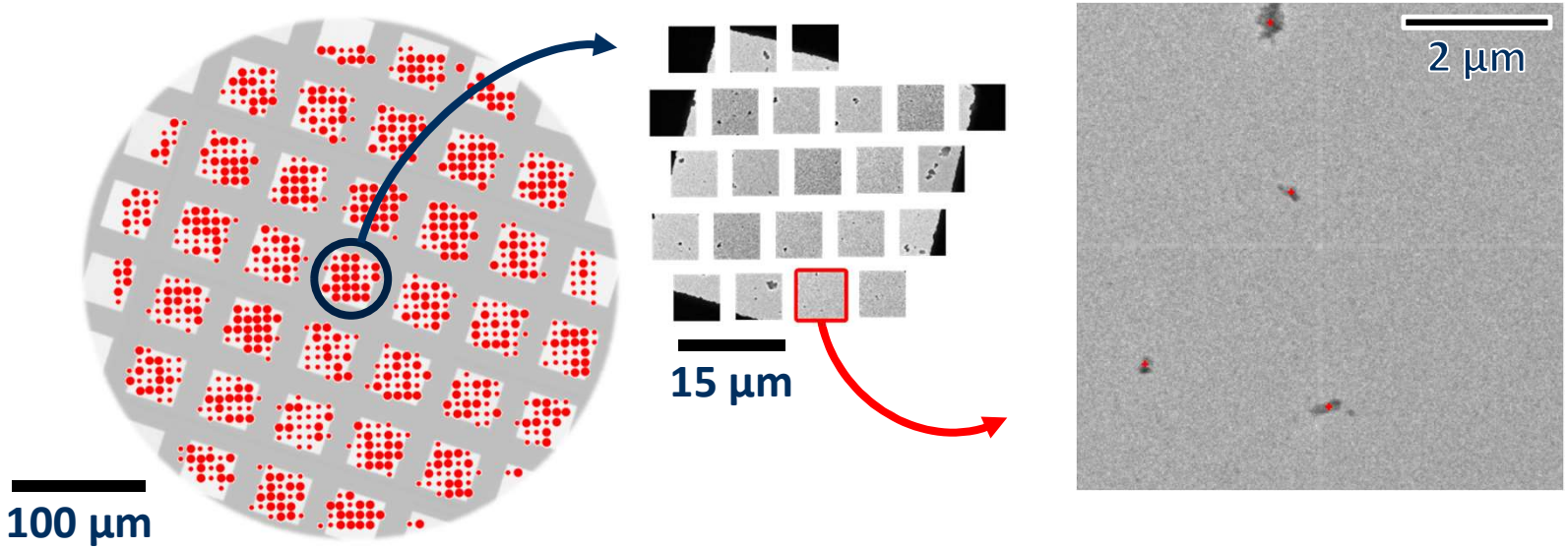
Data reduction server

- .tiff (patterns + images)
- *REDp* (.ed3d, .mrc)
- *XDS* (XDS.INP, .smv)
- DIALS (.bat files)

- .hkl files
- Phase analysis
- Input files

Source code:
http://github.com/stefsmeets/instamatic

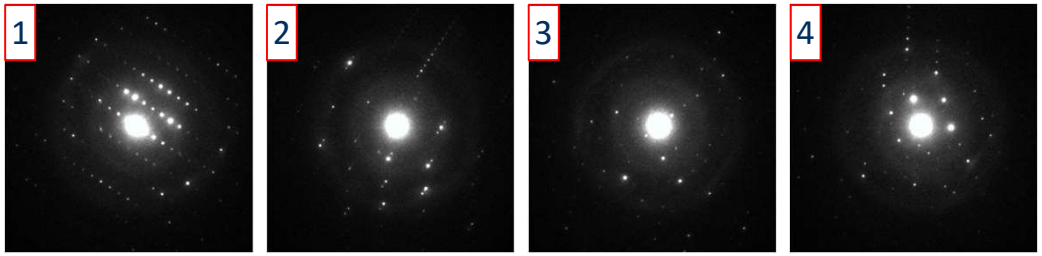
Serial electron diffraction



Screen up to 4000 crystals per hour

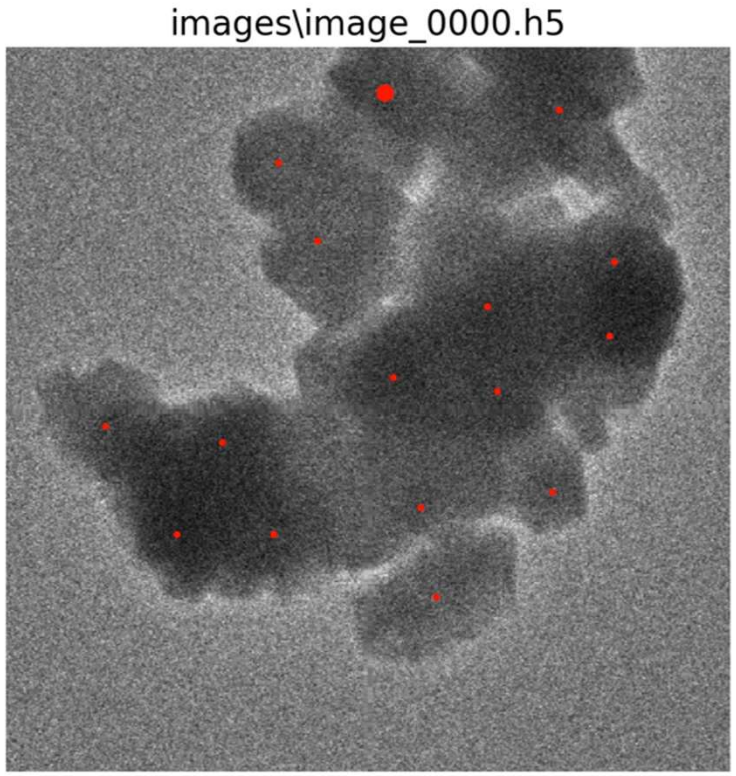
1 crystal = 1 diffraction pattern

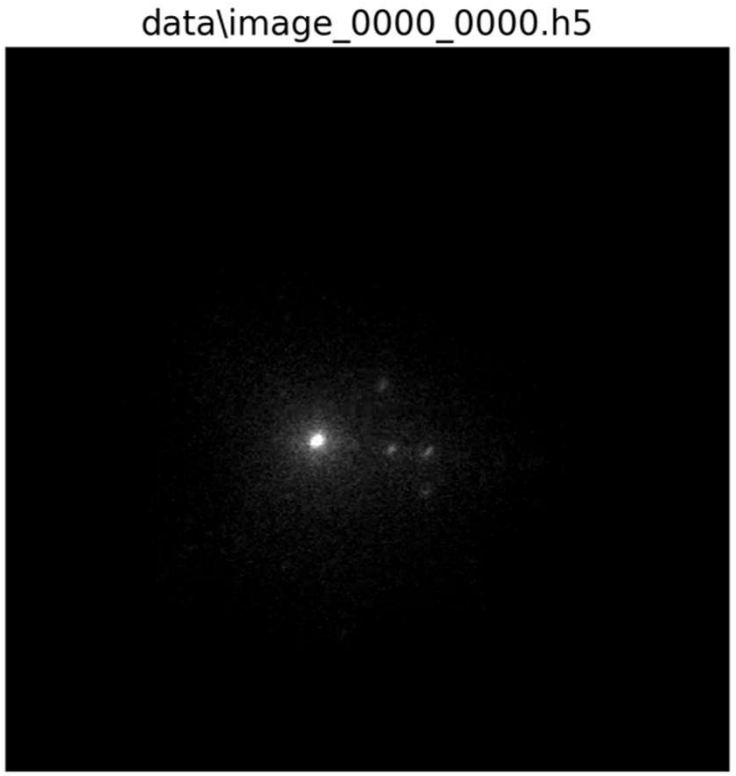
Obtain data from 1000s of crystals



Smeets *et al.*, *J. Appl. Cryst.*, 2018, 51:1262

Data collection (zeolite Y)

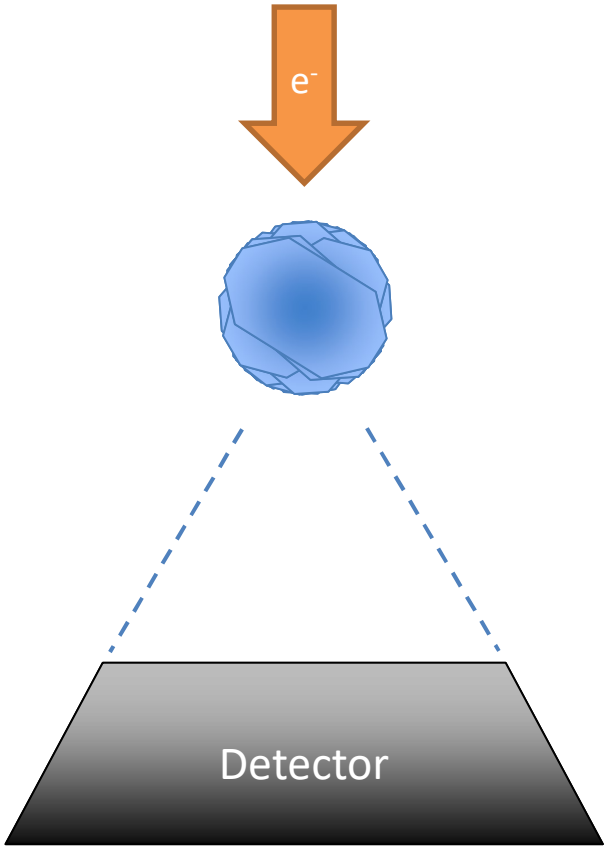


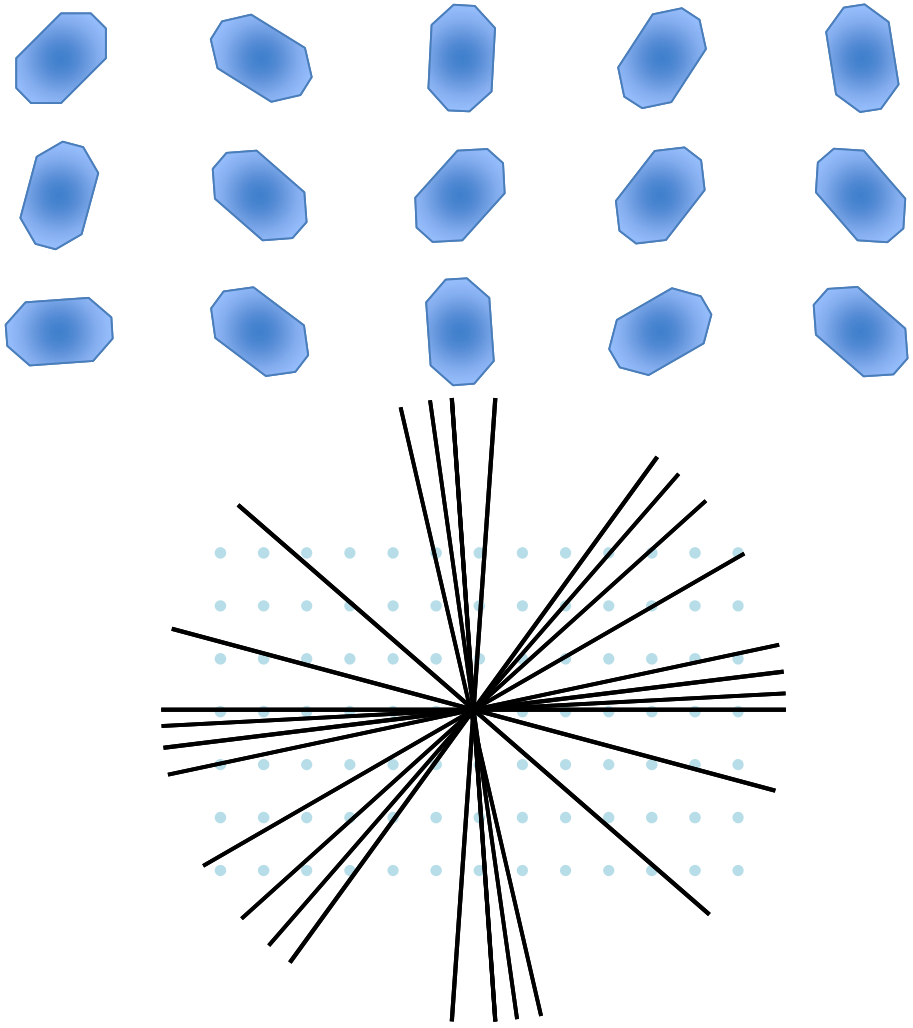


Serial electron diffraction

- Structure determination?
- Phase analysis?
- Screening?

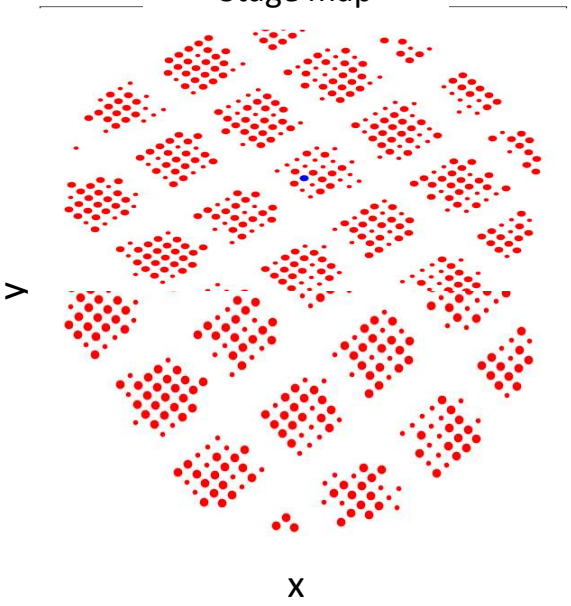
Random orientations





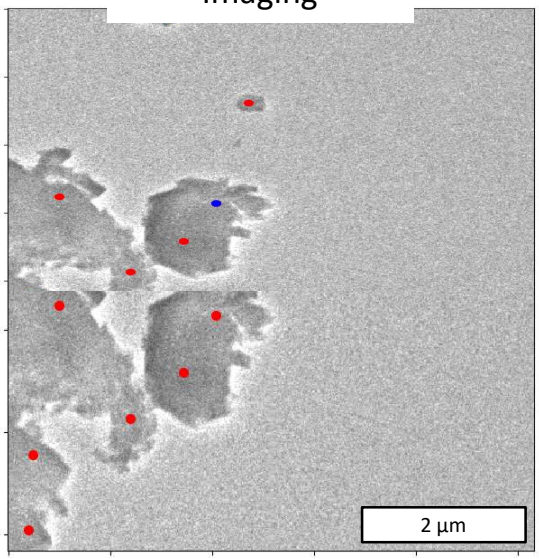
Data collection (zeolite A)

Stage map



200 x 200 µm
484 images
35 minutes

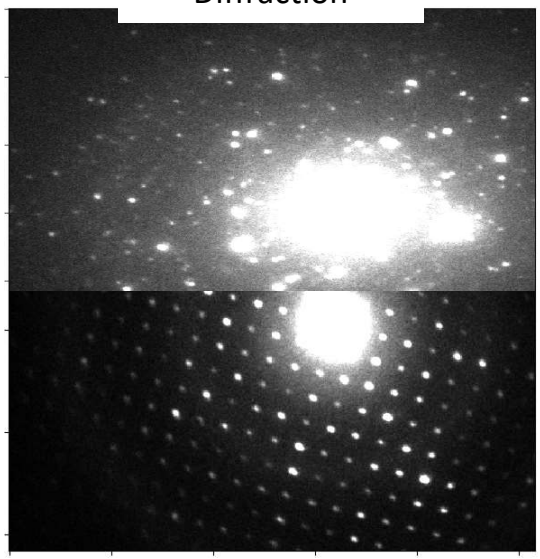
Imaging



Locate crystals

Probe size ~500 nm

Diffraction

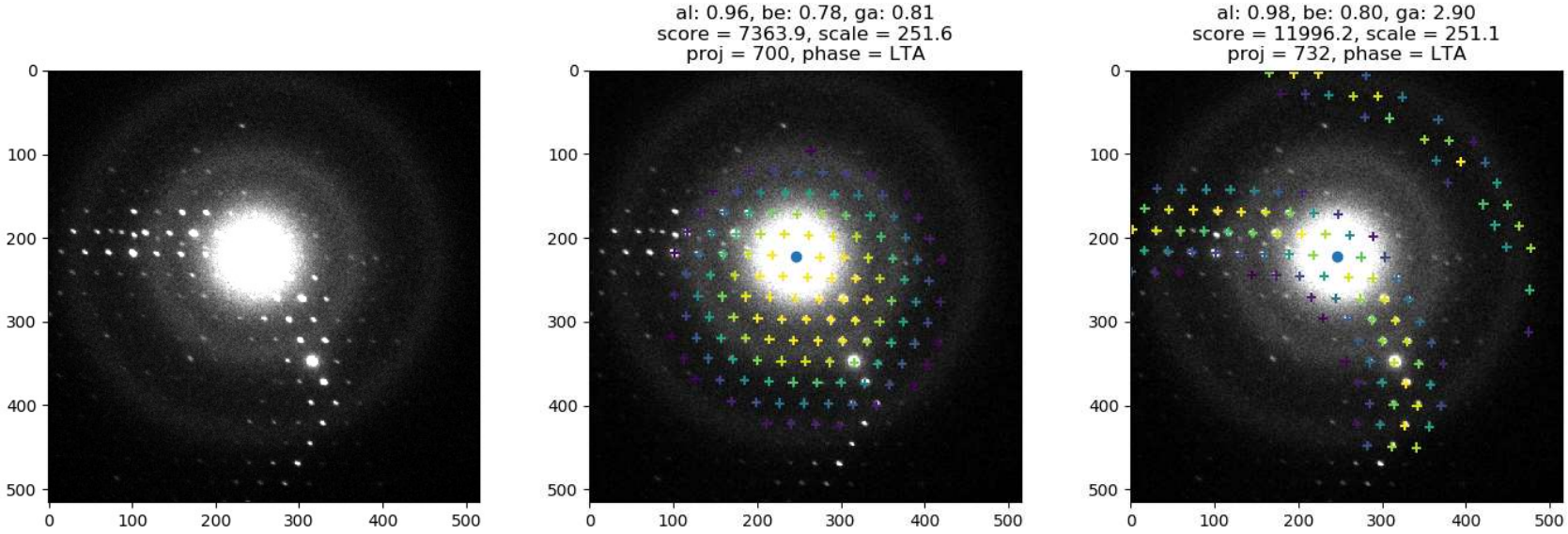


Collect data

Total: 1107 patterns

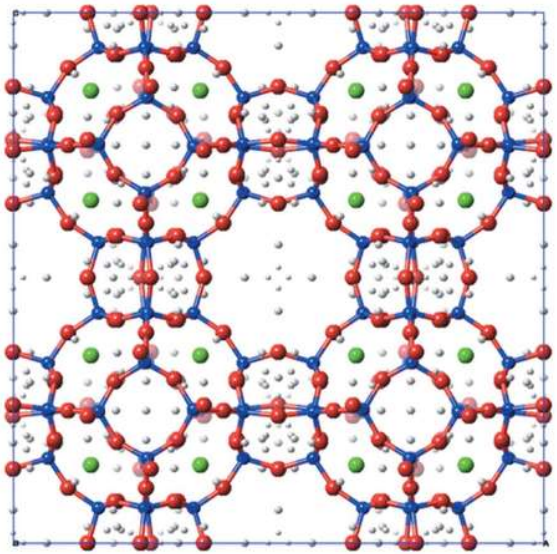
Orientation finding

- Forward projection model using known lattice parameters
- Generate pattern library of all possible orientations (~1.5M in $P1$)
- Match best orientation and index data

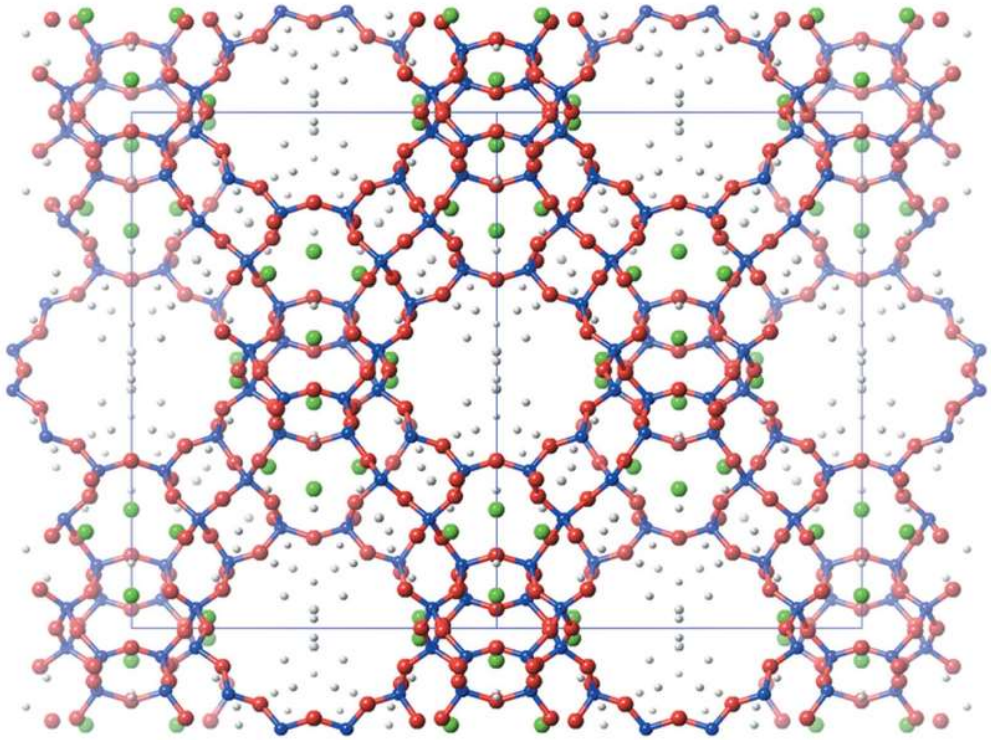


Smeets *et al.*, *J. Appl. Cryst.,* 2018, 51:1262

Structure determination



Zeolite A
(using 200 / 1107 frames)



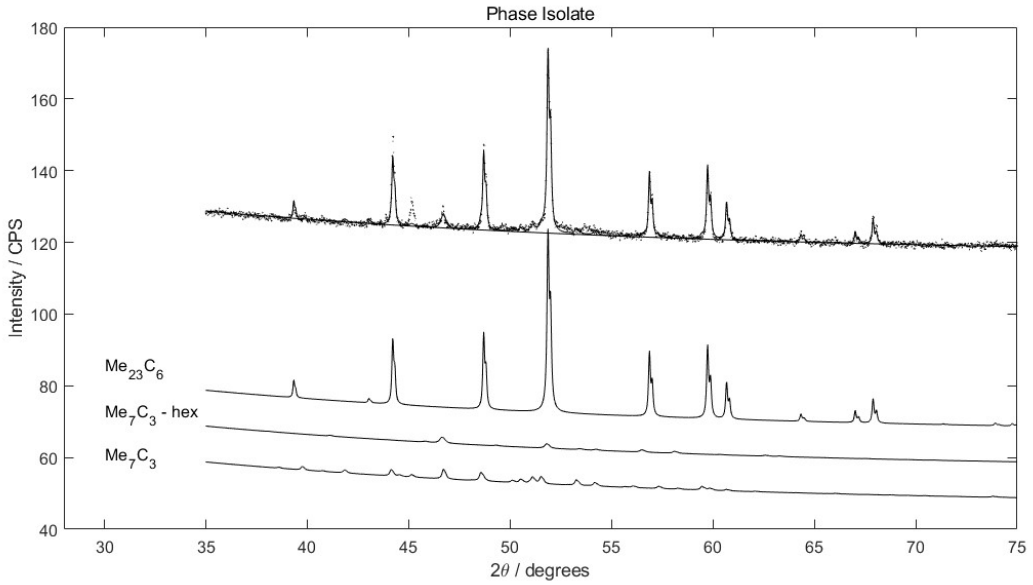
Zeolite Y
(using 99 / 2506 frames)

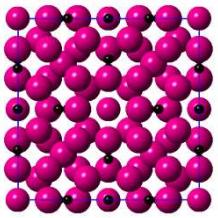
Serial electron diffraction

- Structure determination?
- ➡ Phase analysis?
- Screening?

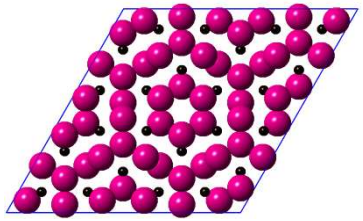
Carbide quantitative phase analysis

X-ray powder diffraction

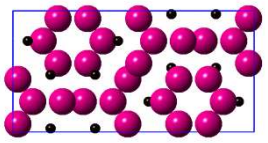




$M_{23}C_6$



M_7C_3 (hex)

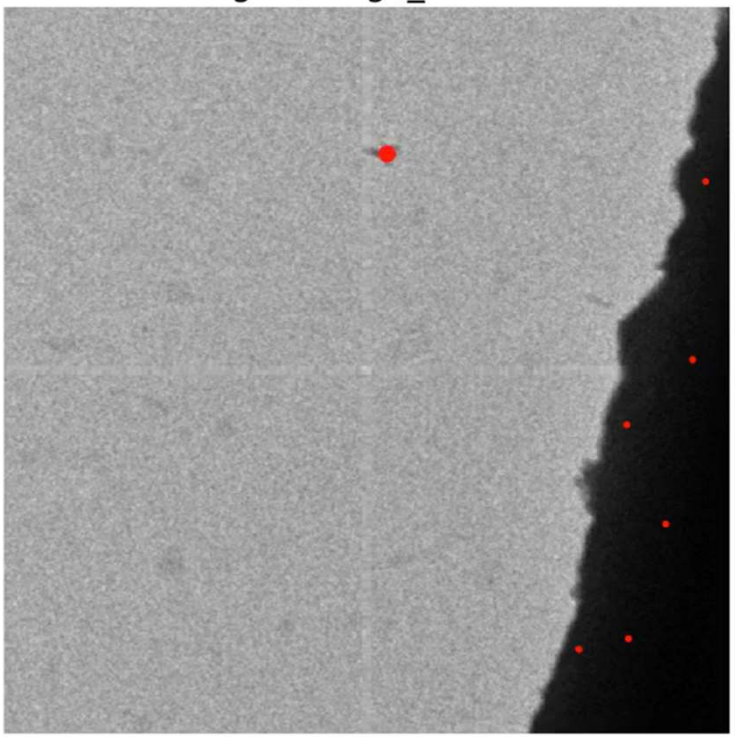


M_7C_3 (ortho)

With Claes Olsson (Sandvik Materials Technology)
Smeets et al., *Steel Res. Int.* 90 (2019), 1800300

Automated ED data collection on Cr carbides

images\image_0449.h5



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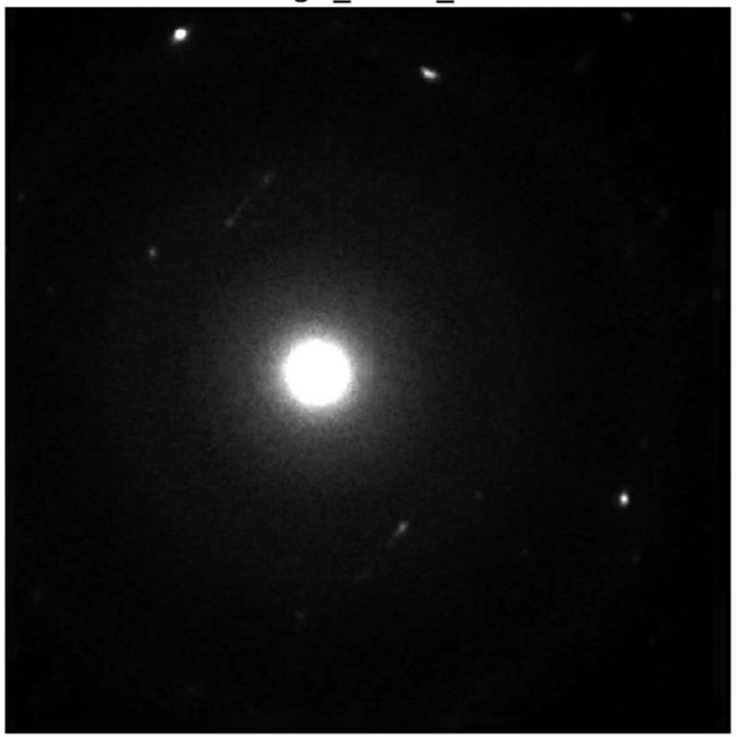
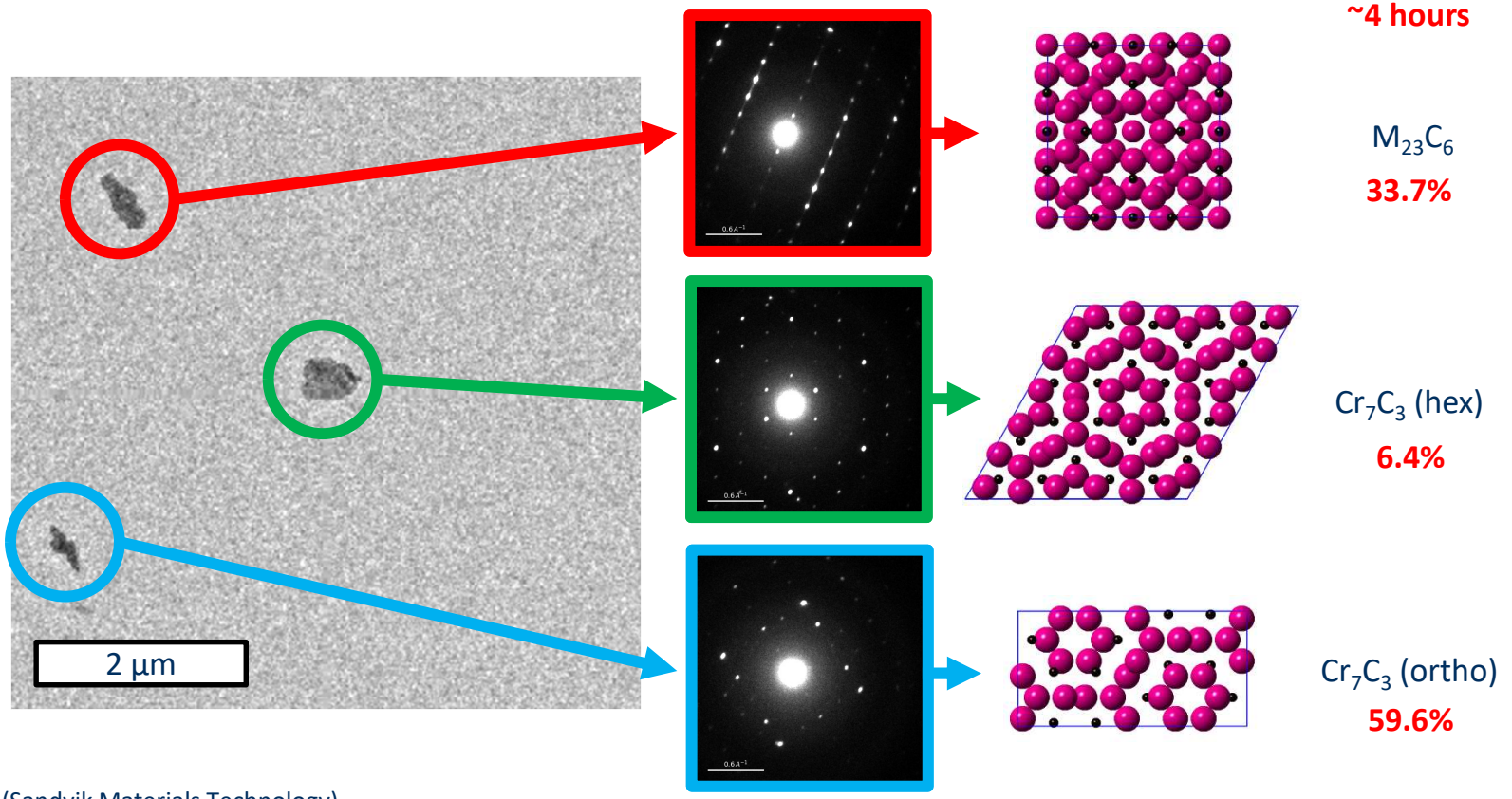


Quantitative phase analysis

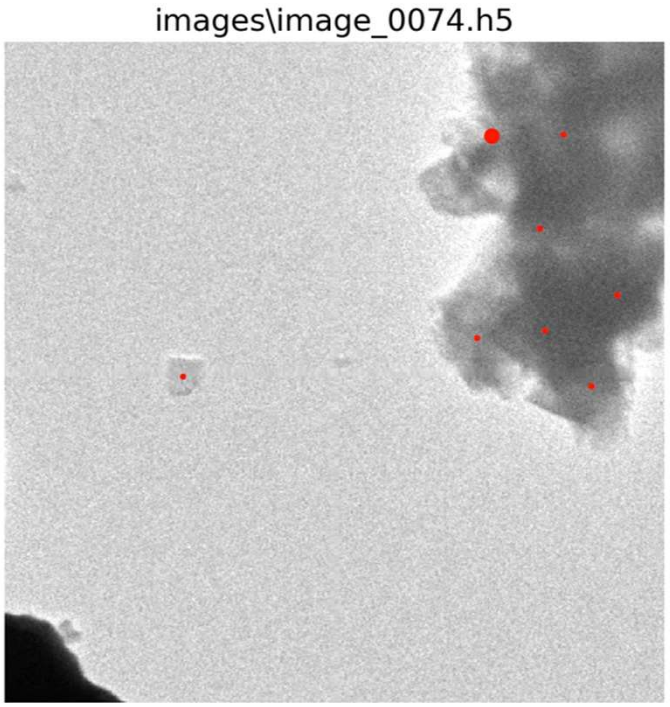


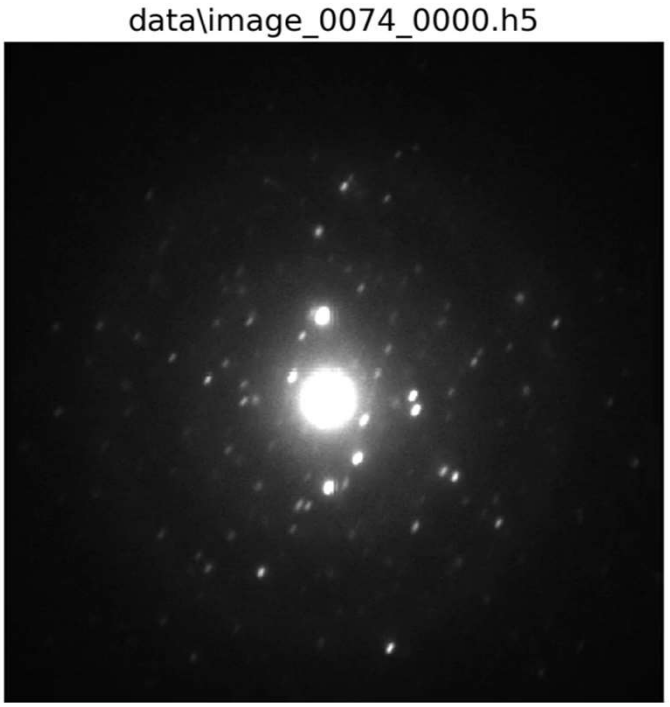
With Claes Olsson (Sandvik Materials Technology)
Smeets et al., *Steel Res. Int.* 90 (2019), 1800300

Serial electron diffraction

- Structure determination?
- Phase analysis?
- ➡ Screening?

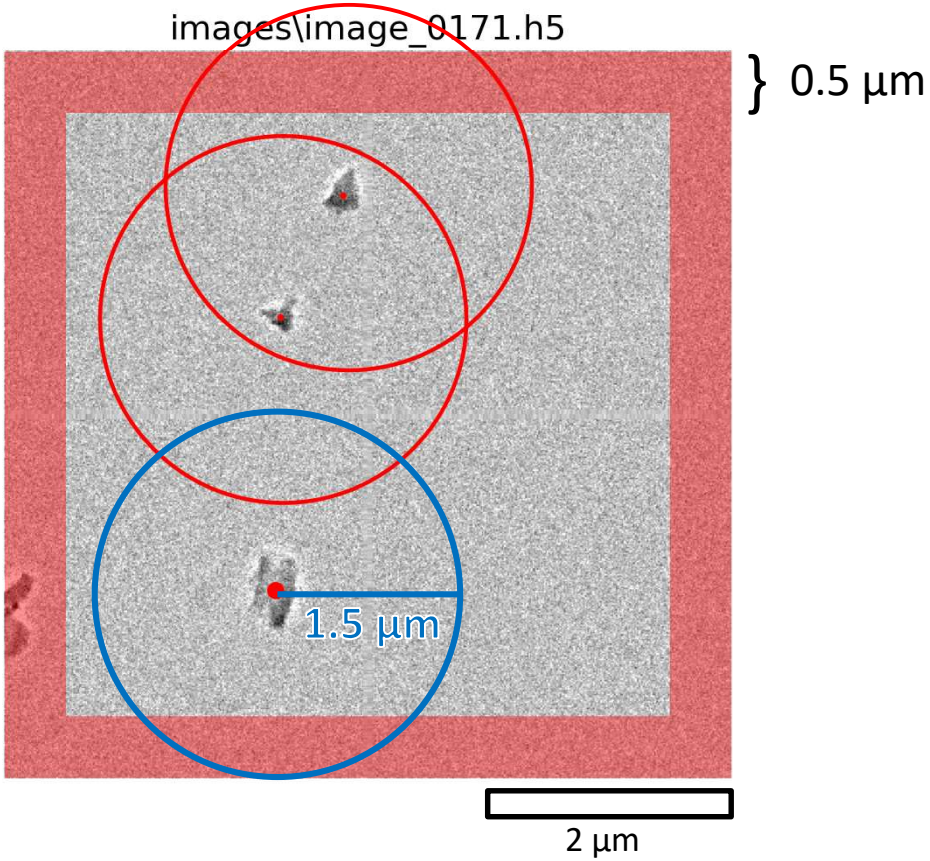
Screening: Mordenite





Scan 200 x 200 µm in 24 minutes
836 diffraction patterns (2090 / hour)

Screening: Crystal selection



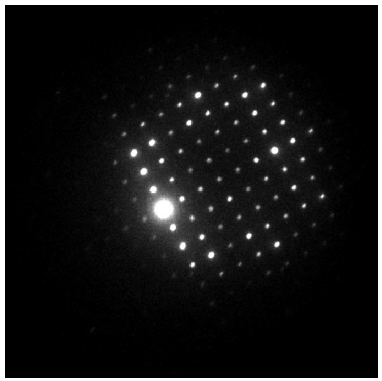
Crystal selection

1. Find isolated crystals
   - Must be 0.5 µm away from edge
   - No crystals in 1.5 µm radius

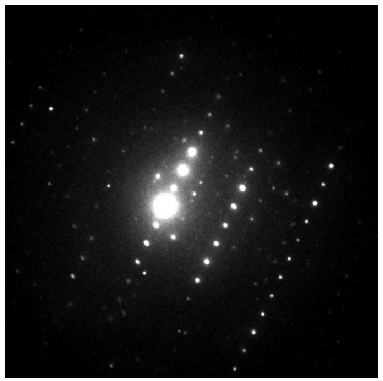
2. Select most suitable crystals
   - Machine learning (CNN)

Screening: Machine learning

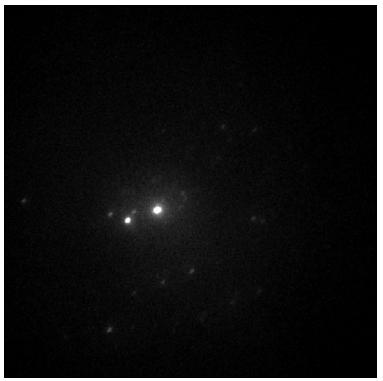
- A deep convoluted neural network trained on ~78.000 diffraction patterns predicts which crystals are suitable for collecting ED data



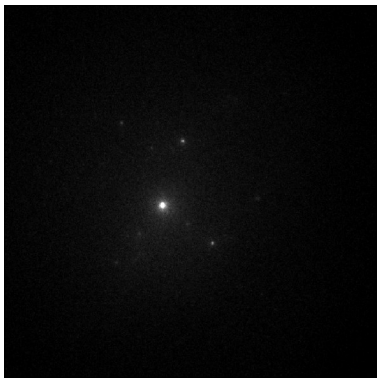
Prediction: 1.0



Prediction: 1.0



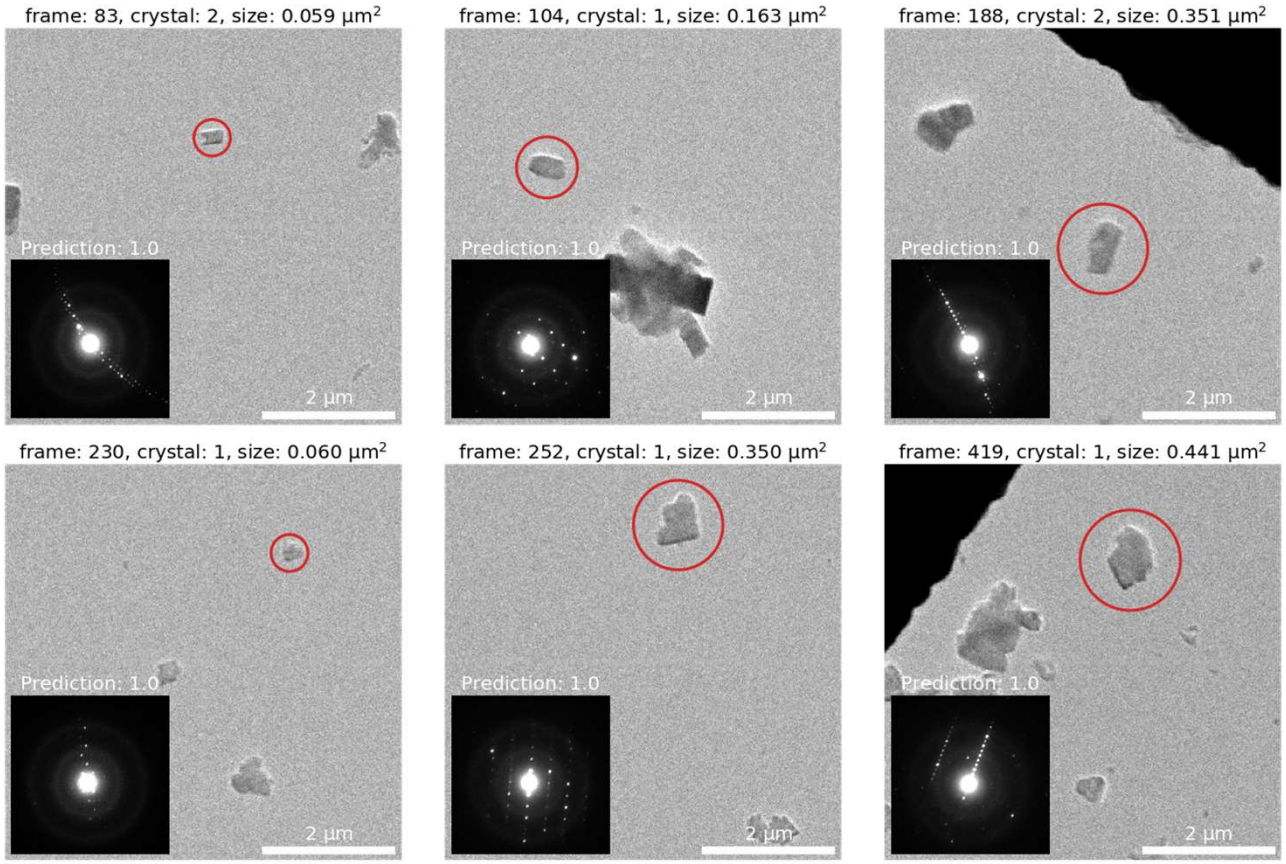
Prediction: 0.26



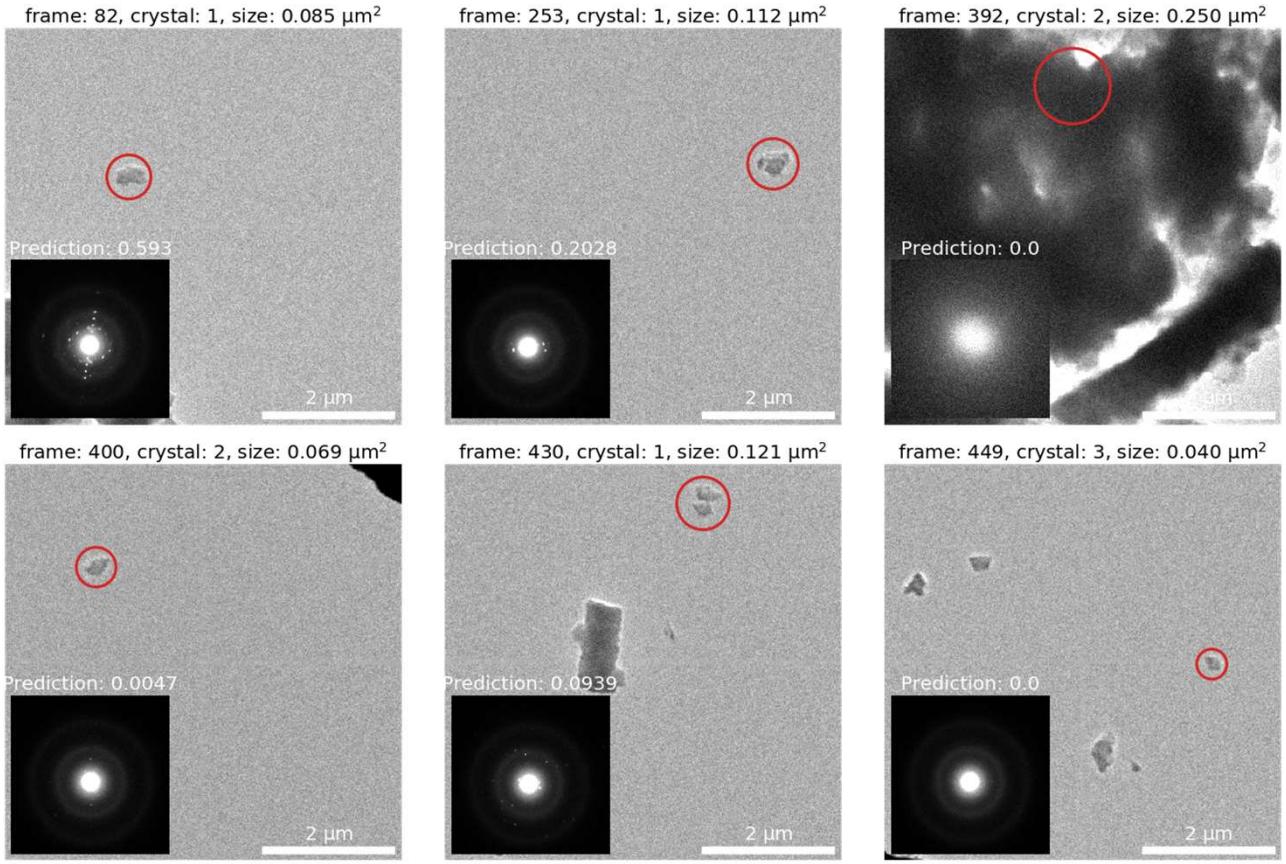
Prediction: 0.25

Jonas Ångström (Stockholm University)

Screening: 6 of the ‘best’ crystals (53)

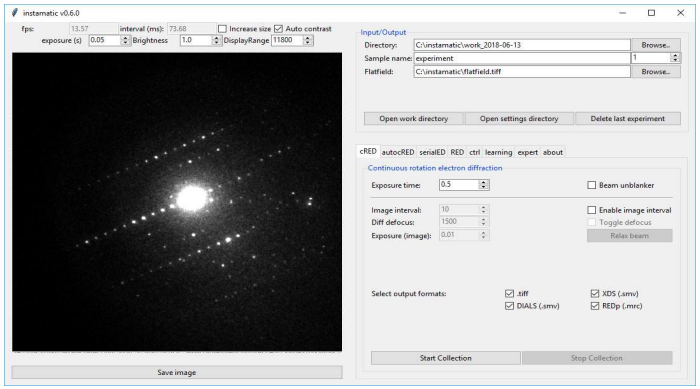


Screening: 6 of the ‘worst’ crystals (53)



Serial rotation electron diffraction

- Structure determination?
- Phase analysis?
- Screening?



- Modular GUI
- Crystal finder
- Crystal tracking
- Neural network
- Calibrations

Instamatic **(Python3.6)**

Microscope control

JEOL JEM-2100-LaB_6 @ 200 keV

Camera interface

ASI Timepix @ 120 Hz

Continuous rotation electron diffraction

Serial electron diffraction

Data reduction server

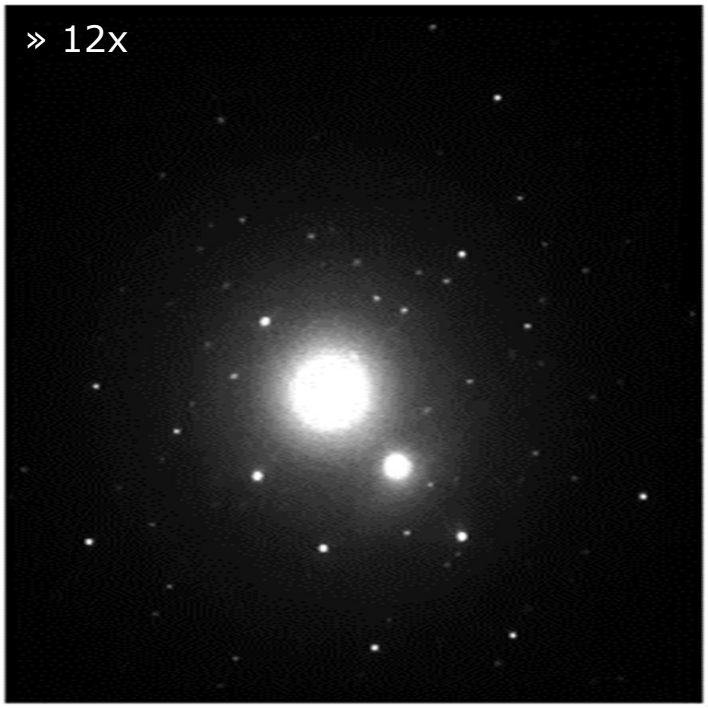
- .tiff (patterns + images)
- *REDp* (.ed3d, .mrc)
- *XDS* (XDS.INP, .smv)
- DIALS (.bat files)

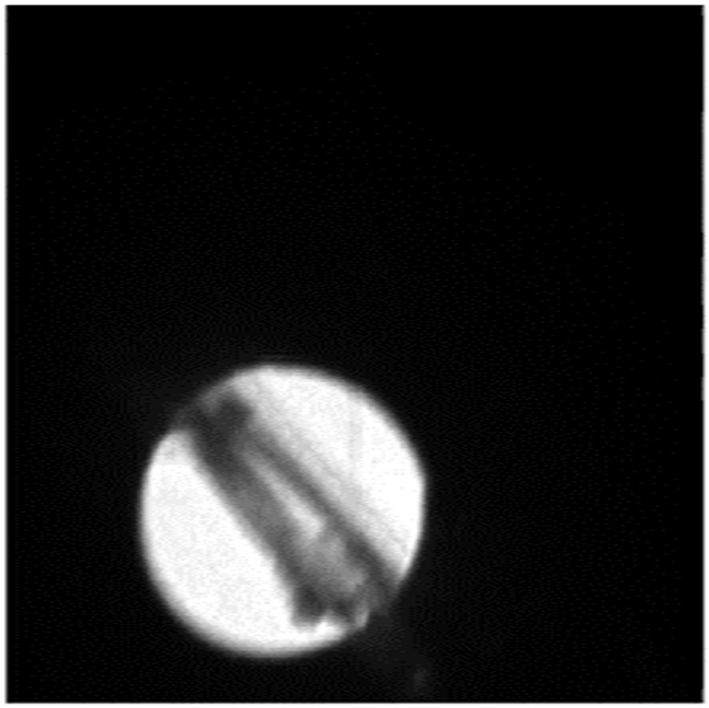
- .hkl files
- Phase analysis
- Input files

Source code:
http://github.com/stefsmeets/instamatic

Automated data collection

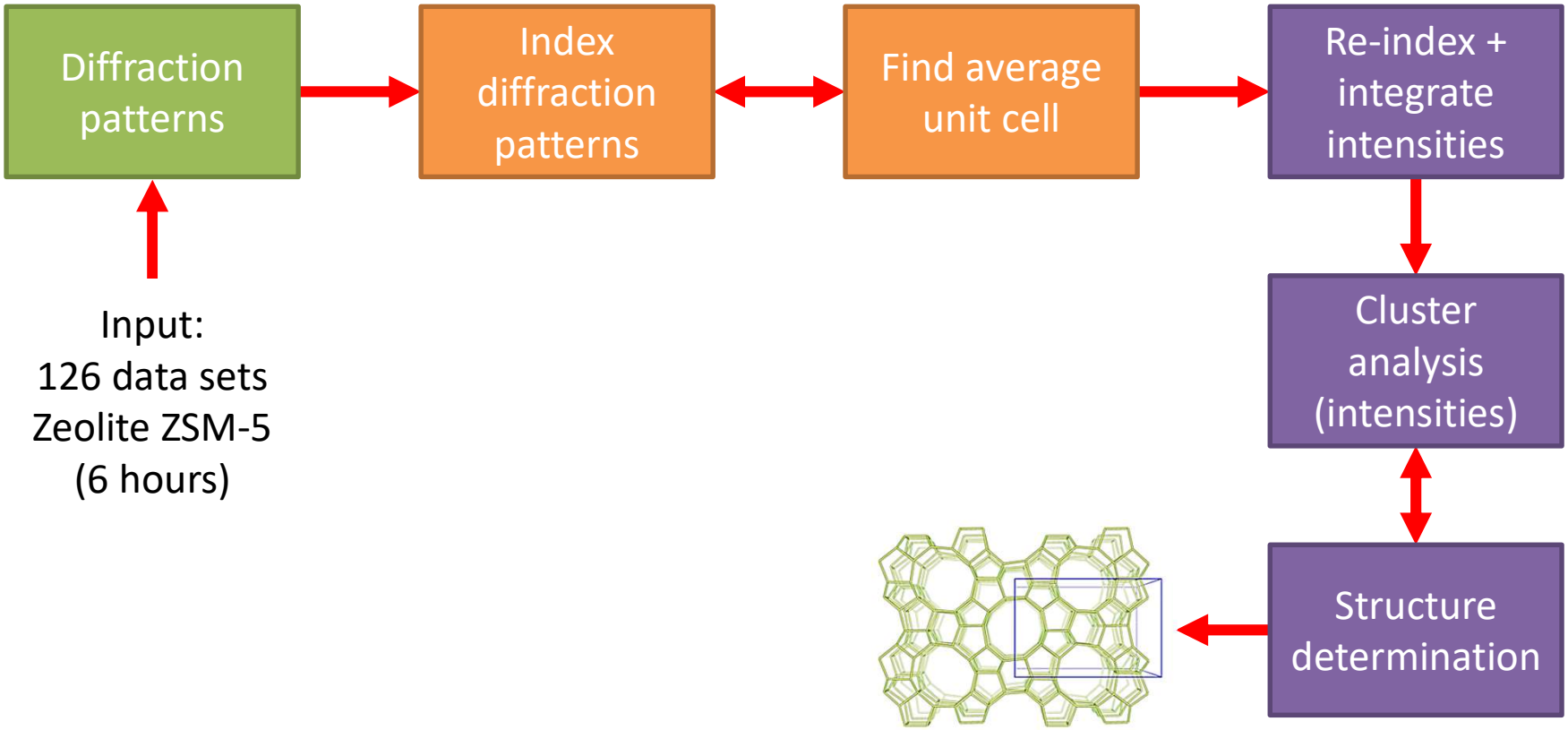
Rotation: -44.0 to 47.4° @ 0.76°/s (91.4°)
Exposure: 0.5 s, oscillation angle: 0.39°



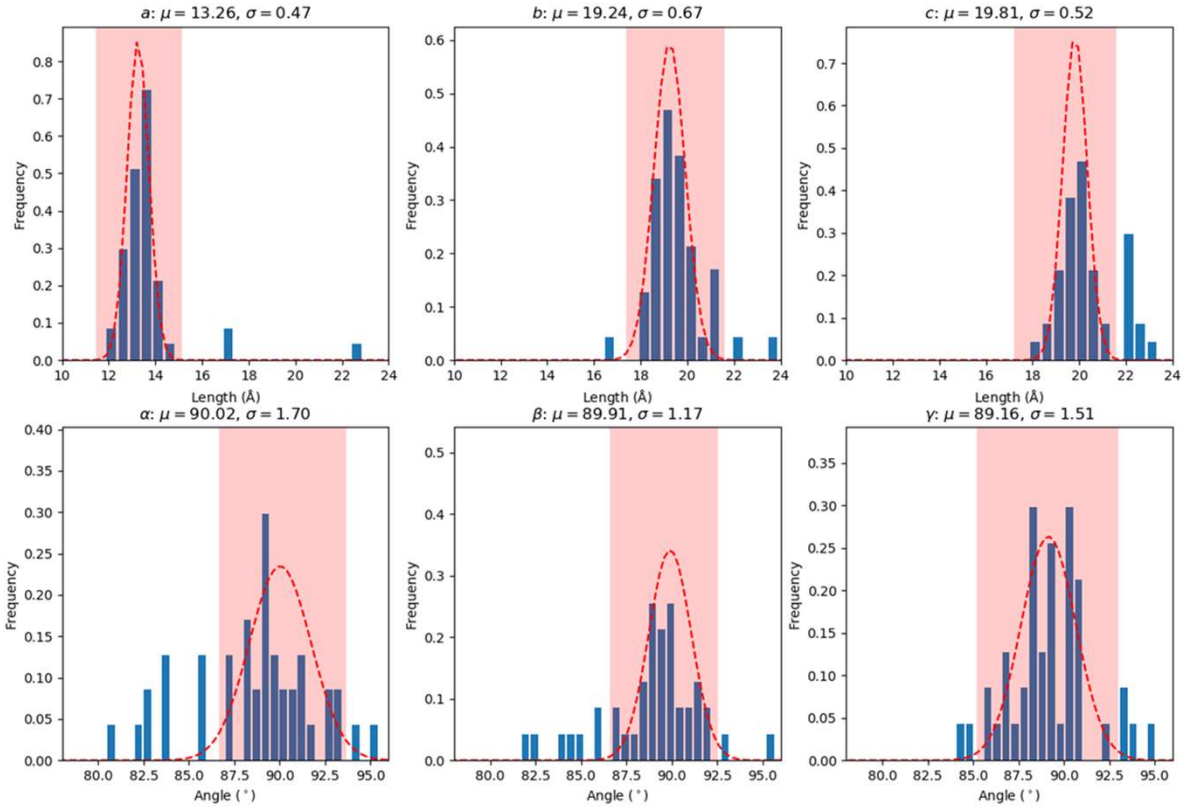


Bin Wang (Stockholm University)

Data processing pipeline



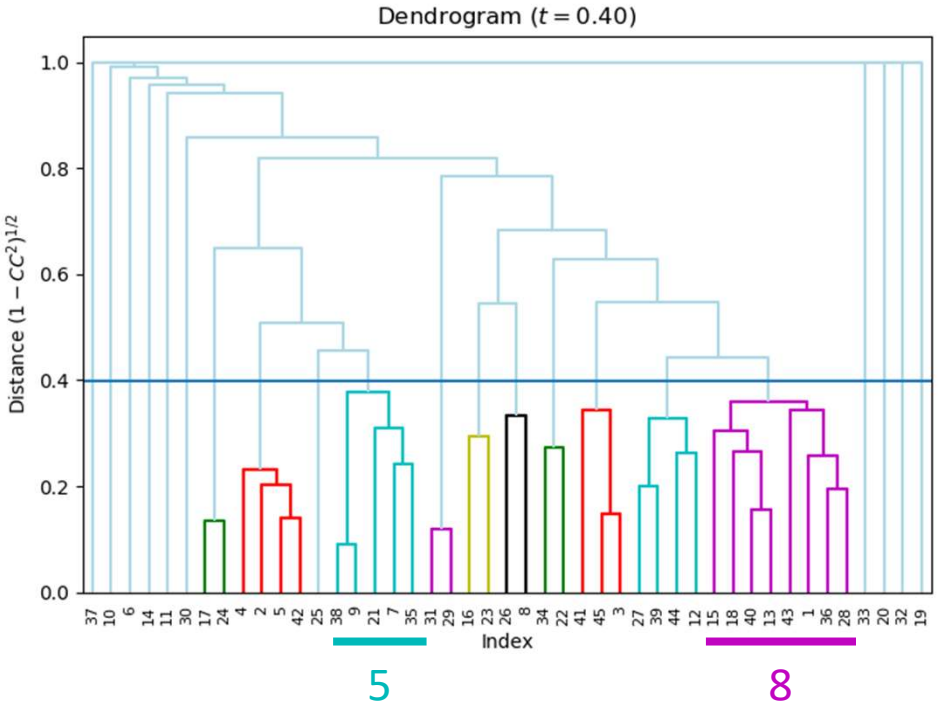
Find average unit cell

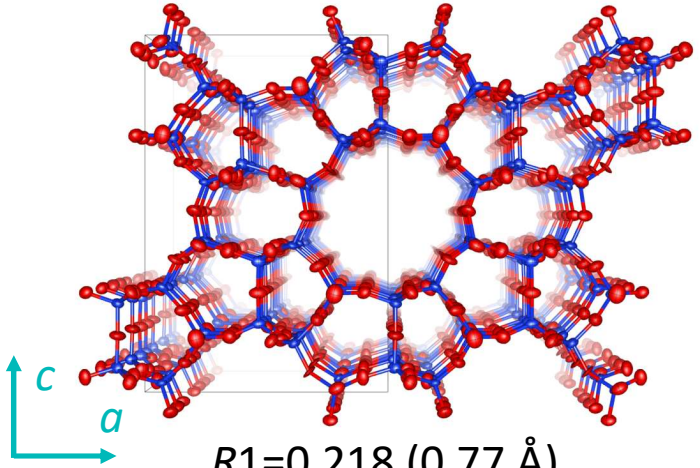


a=13.3(5) Å
b=19.2(7) Å
c=19.8(5) Å
α=90.0(1.7)°
β=89.9(1.2)°
γ=89.16(1.5)°

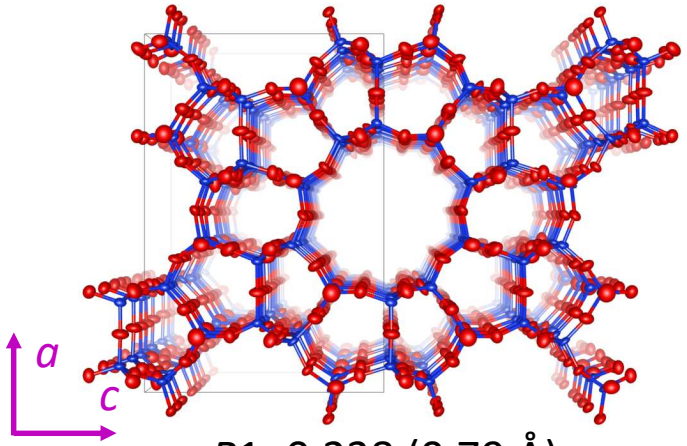
Orthorhombic
C-centered

Cluster analysis (intensities)



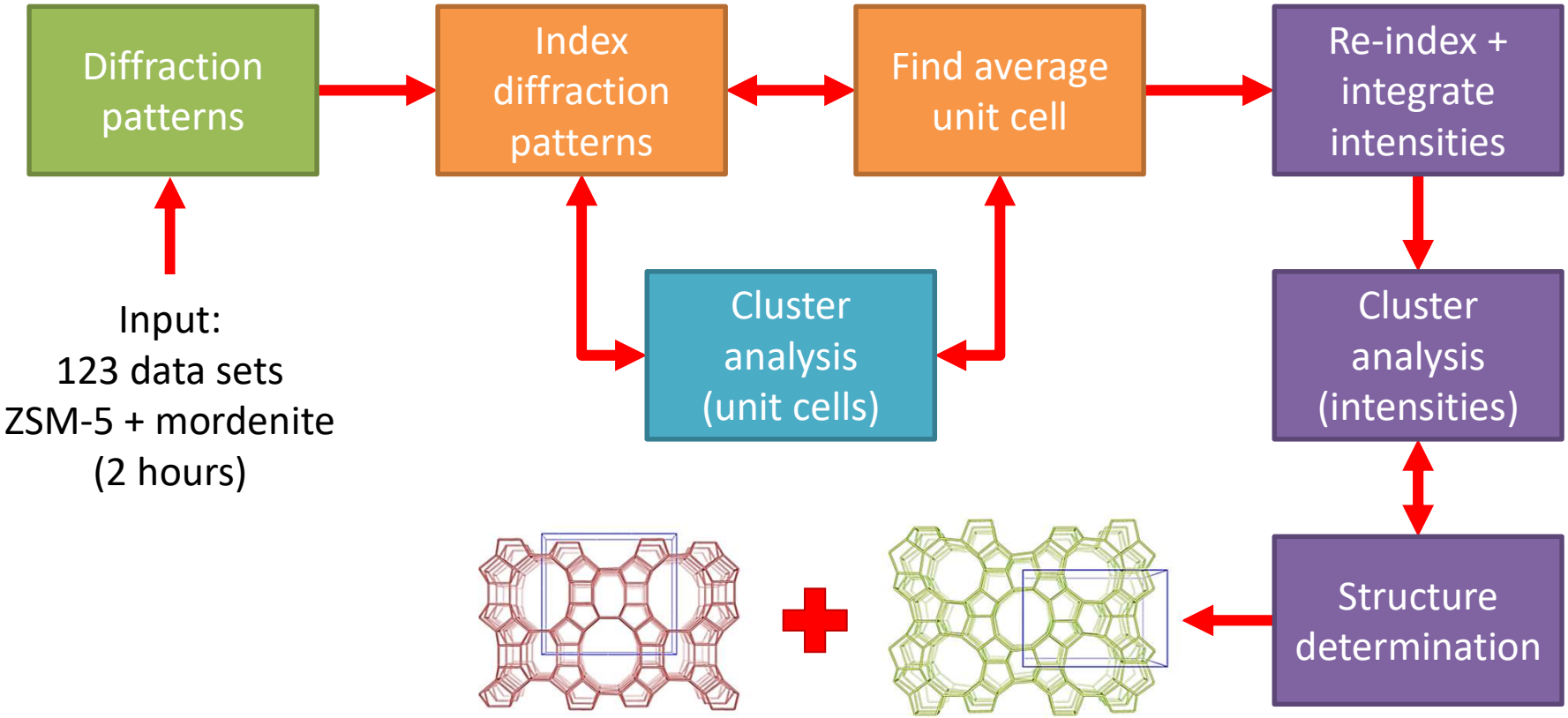


$R1$=0.218 (0.77 Å)

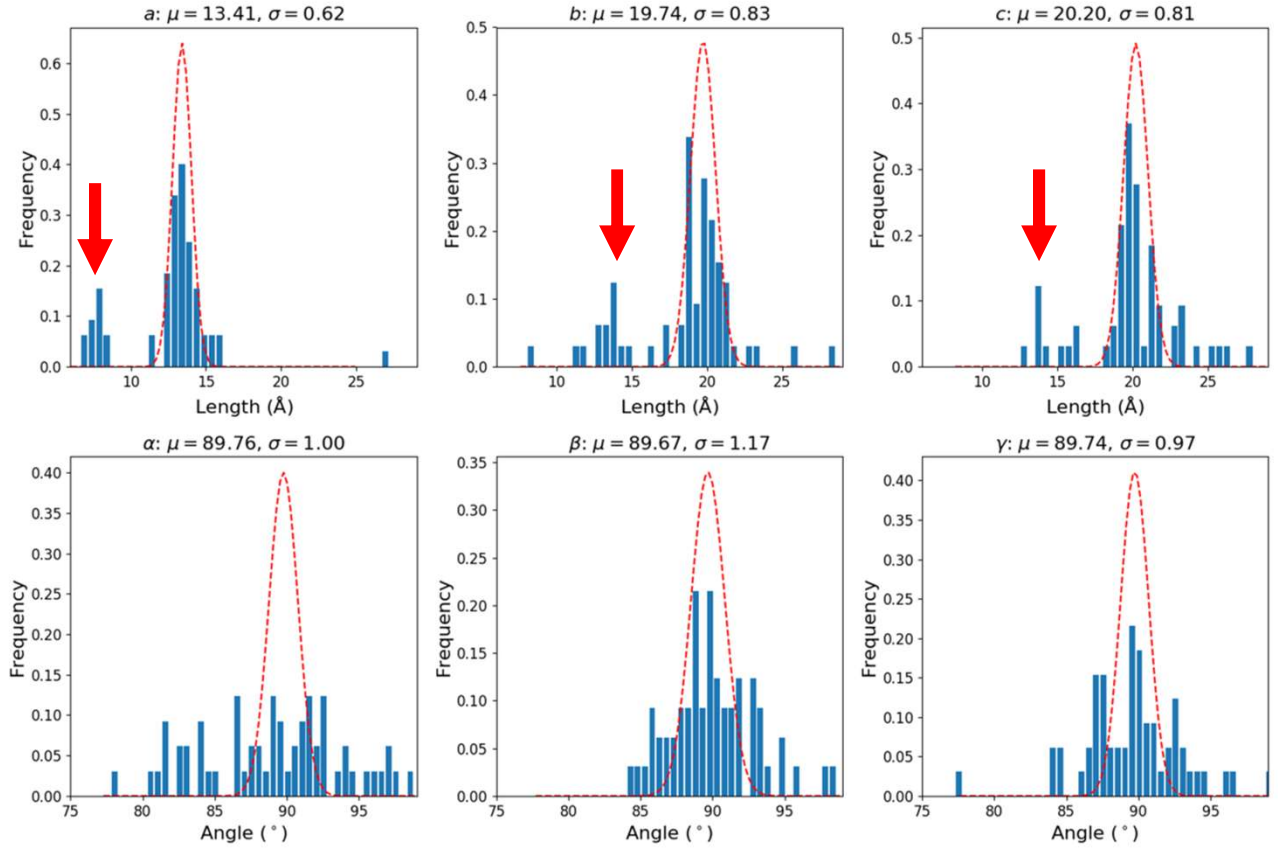


$R1$=0.238 (0.79 Å)

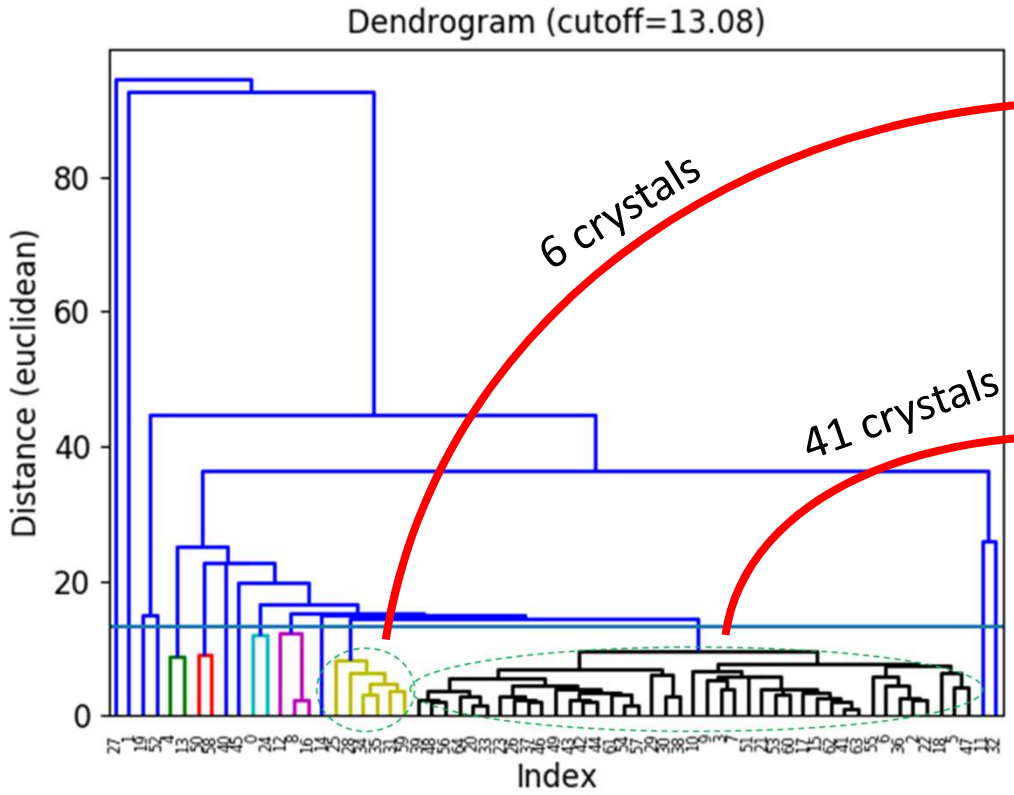
Data processing pipeline (phase mixture)



Cell parameters



Cluster analysis (unit cells)

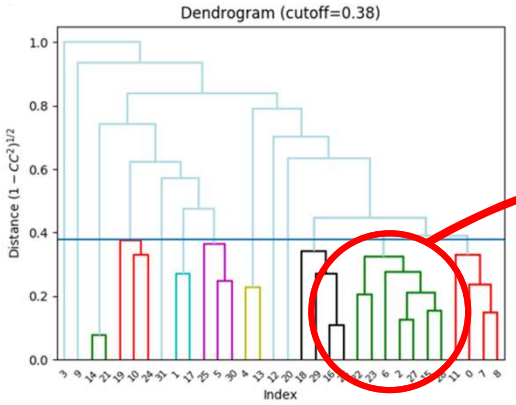


Orthorhombic (C)
a=18.1(3) Å
b=20.0(1) Å
c=7.7(4) Å

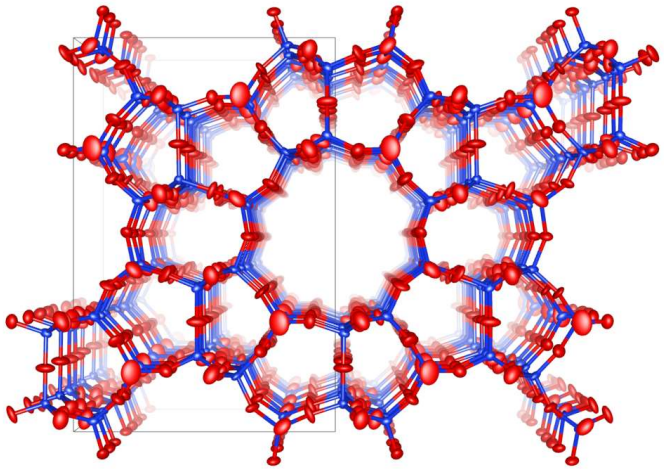
Orthorhombic (C)
a=20.4(6) Å
b=20.1(8) Å
c=13.6(4) Å

Cluster analysis (intensities)

ZSM-5

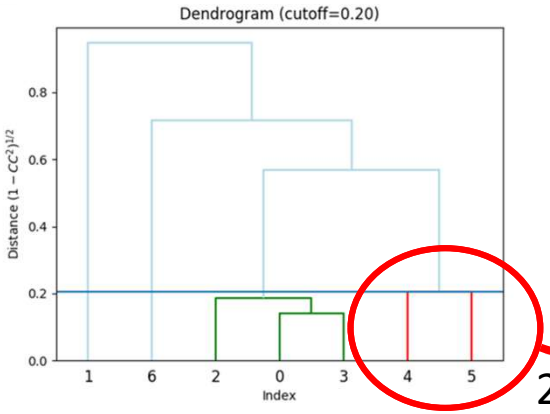


7 crystals

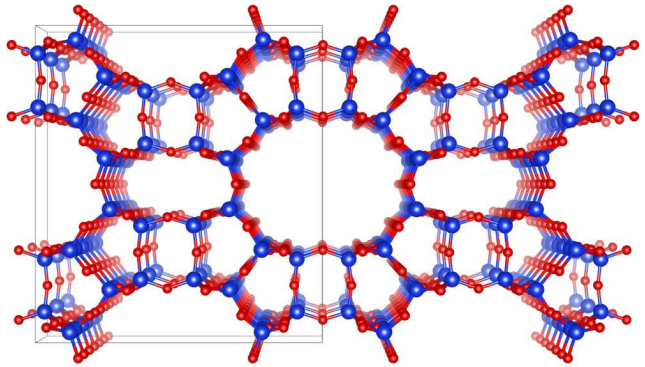


*R*1=0.196 (0.76 Å)

Mordenite



2 crystals



*R*1=0.291 (0.79 Å)

What's next?

- Electrons are very well suited for structure analysis
  - Reliable structures can be obtained routinely
- Small, but growing community
- Data collection (and processing!) protocols are under active development
  - Automation is key
- Equally useful for structural biology / materials science applications