Powder Diffraction and Electron Microscopy

a powerful combination

Christian Baerlocher and Lynne B. McCusker
Laboratory of Crystallography, ETH Zurich

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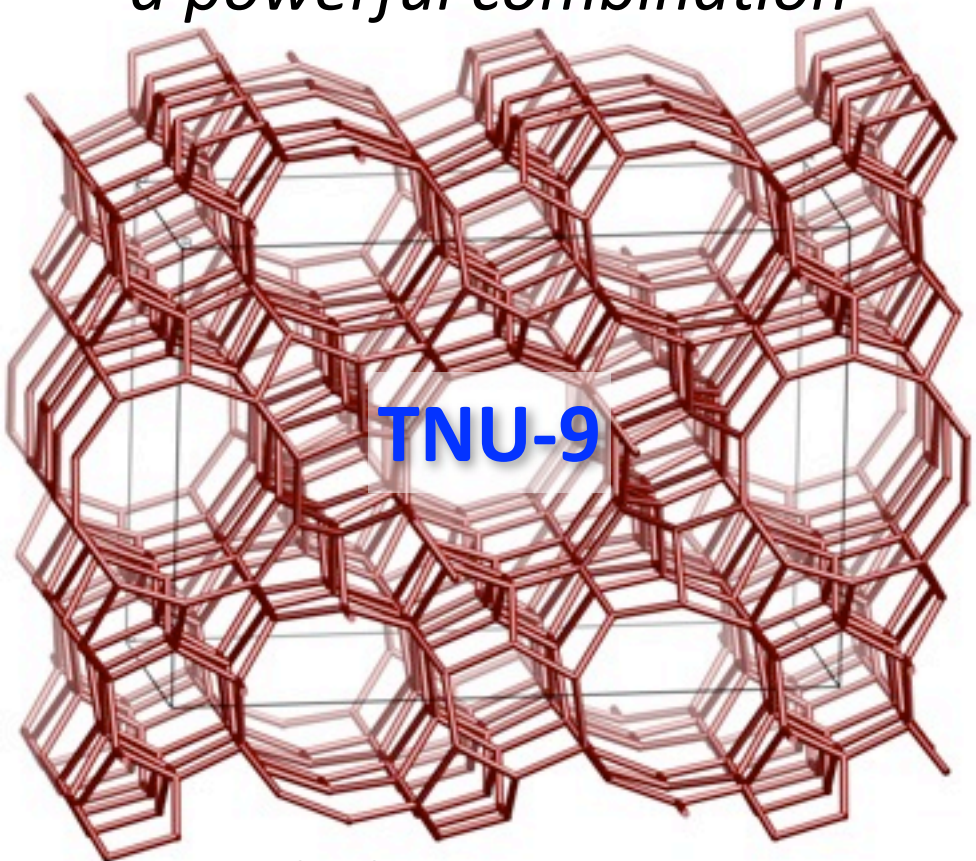

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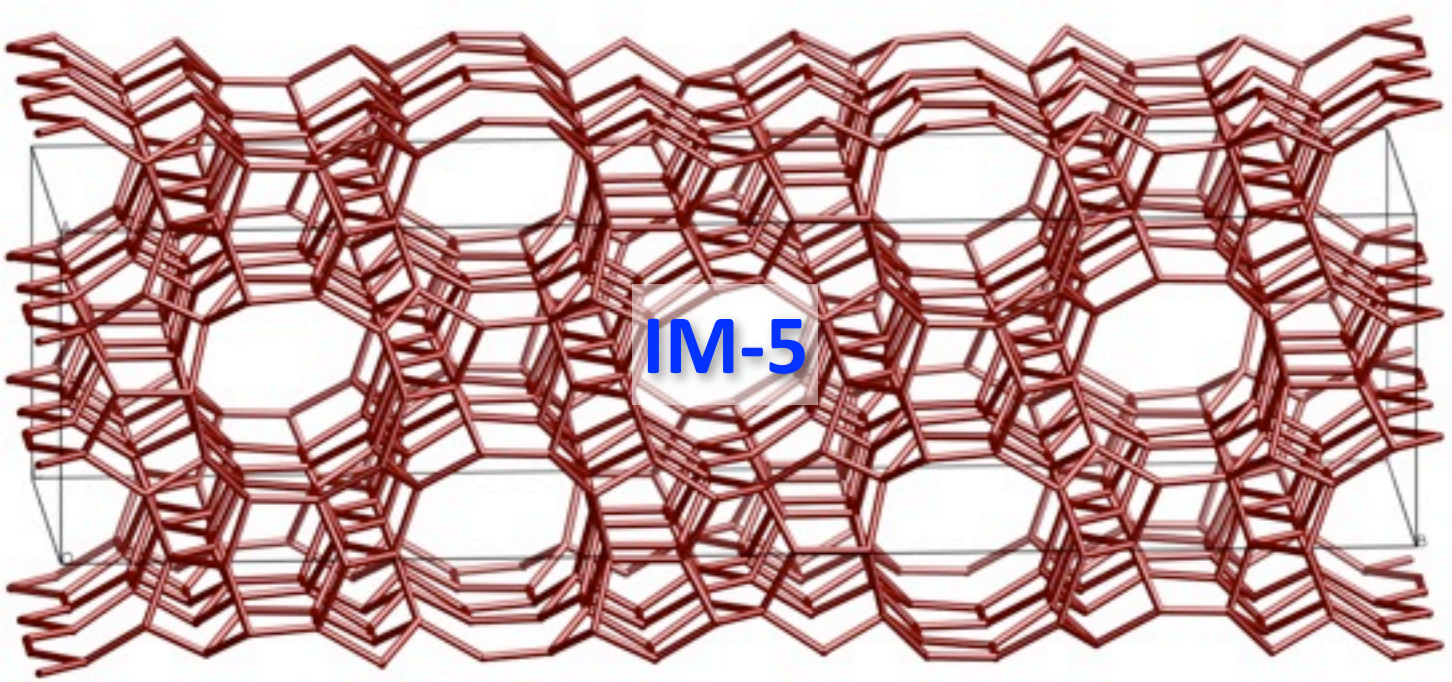

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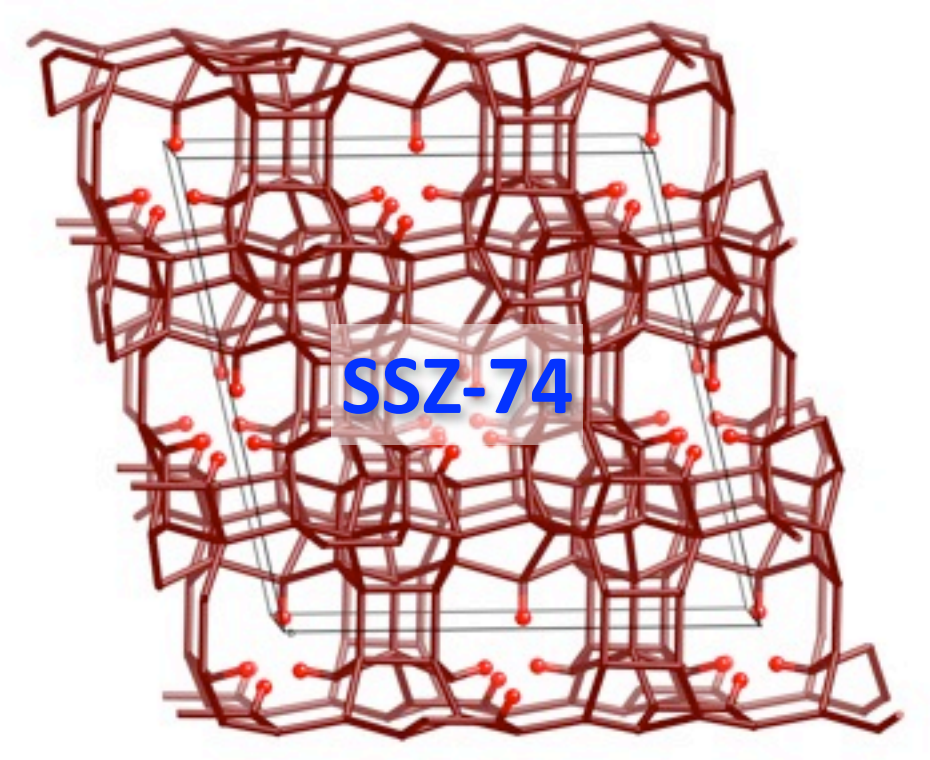

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Introduction

- powder diffraction and electron microscopy
- structure envelope

Combinations of XPD and electron microscopy

- TNU-9 (FOCUS + HRTEM)
- IM-5 (pCF + HRTEM)
- SSZ-74 (pCF + HRTEM)

Precession electron diffraction

- weak reflection elimination
- phase retrieval

FAKED electron diffraction data

- SSZ-82

Conclusions

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Powder Electron

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Combinations used are:

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1) to help in indexing powder pattern by
   - determine lattice parameters from SAED patterns
   - verifying indexed powder patterns
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Solving crystal structures by integrating the two data sets

Electron Microscopy

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High resolution transmission electron microscopy

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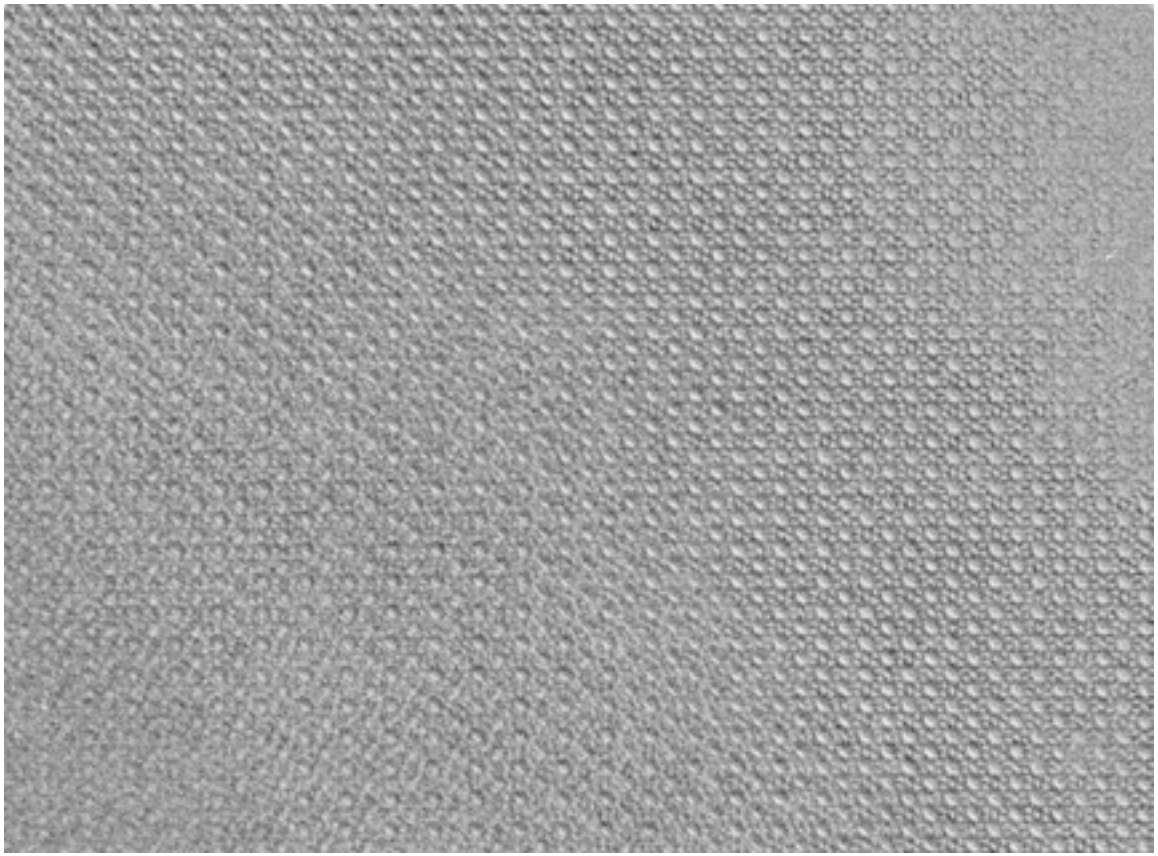
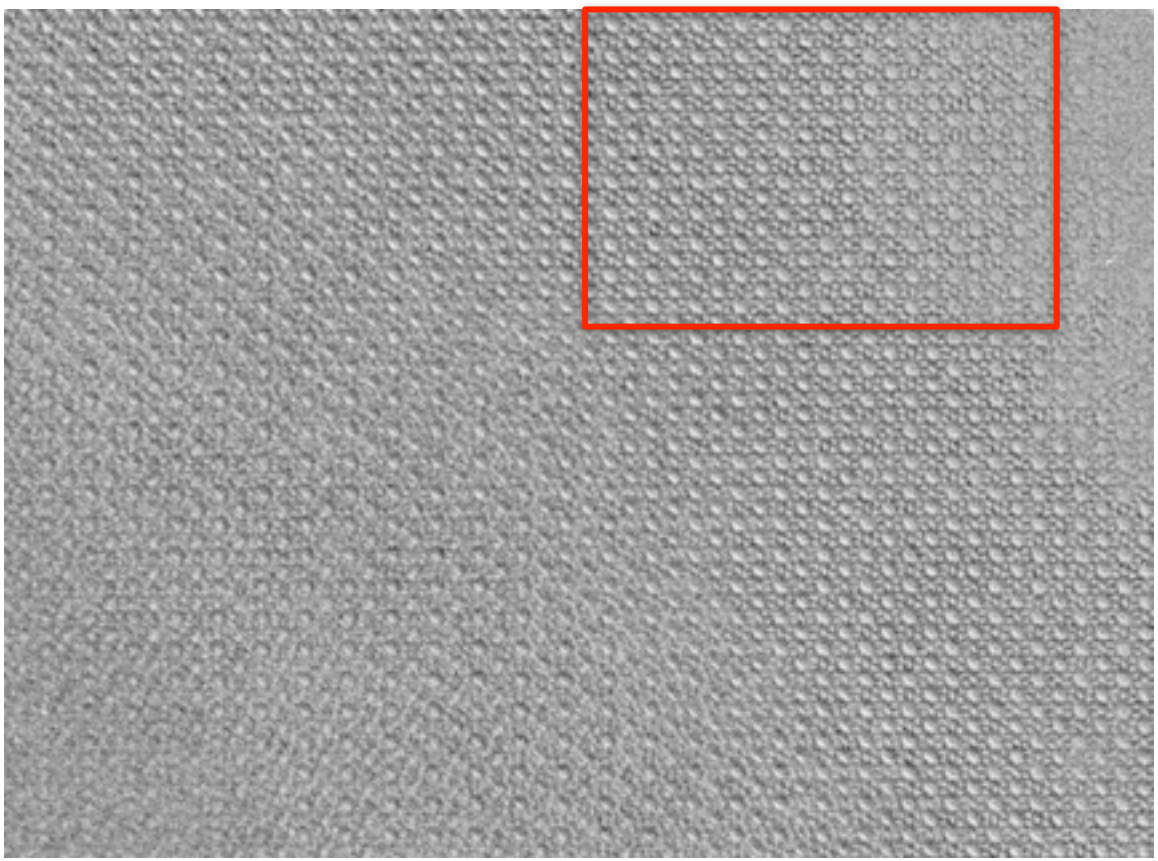
High resolution transmission electron microscopy



Electron Microscopy

High resolution transmission electron microscopy



Electron Microscopy

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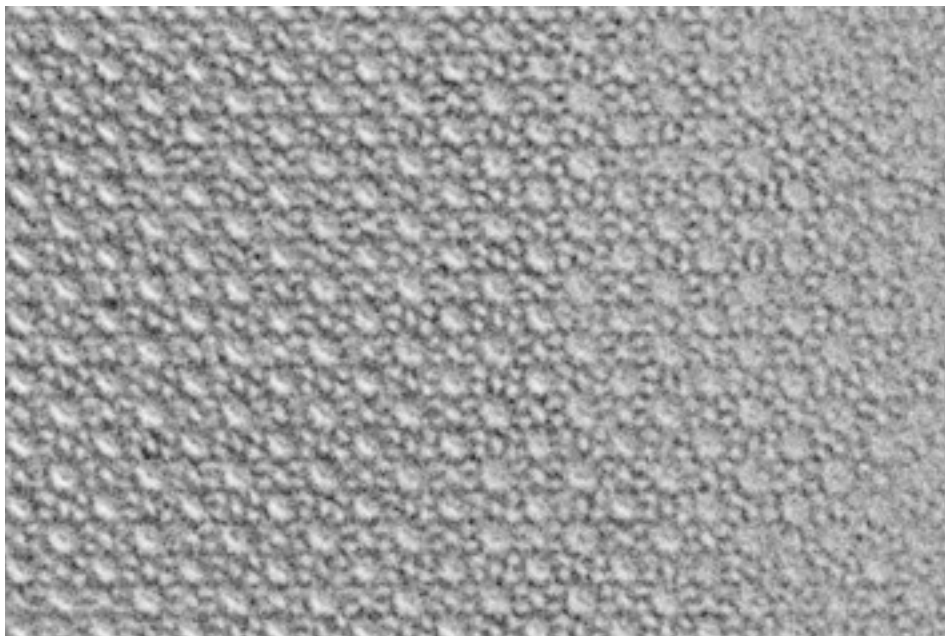

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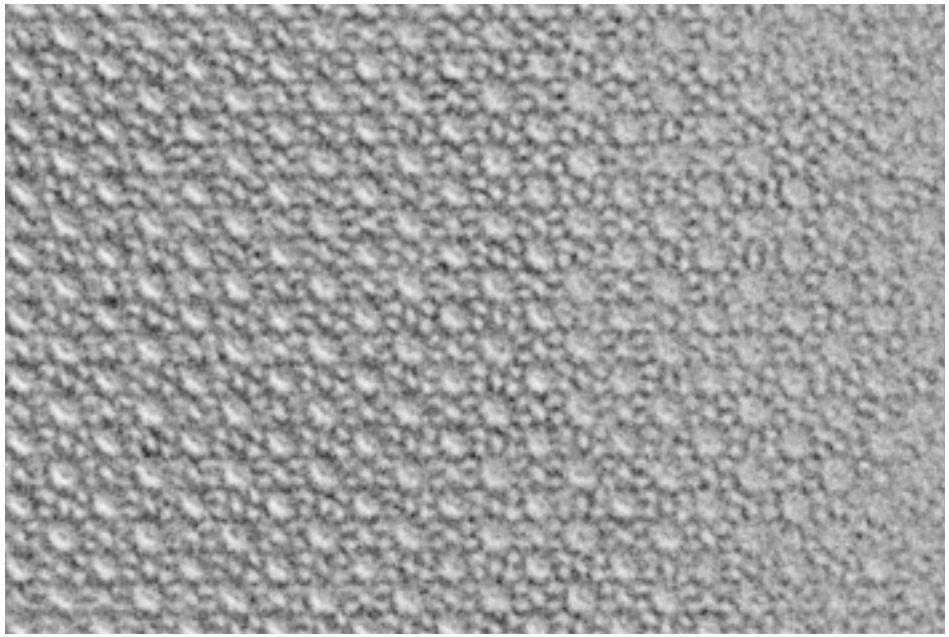
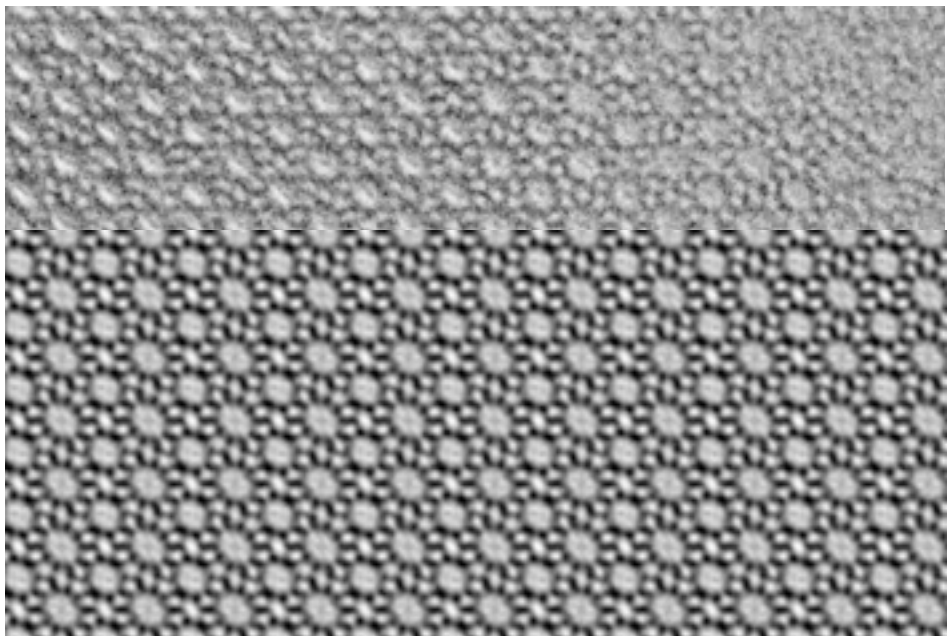


CTF corrected
symmetry averaged

Electron Microscopy

High resolution transmission electron microscopy



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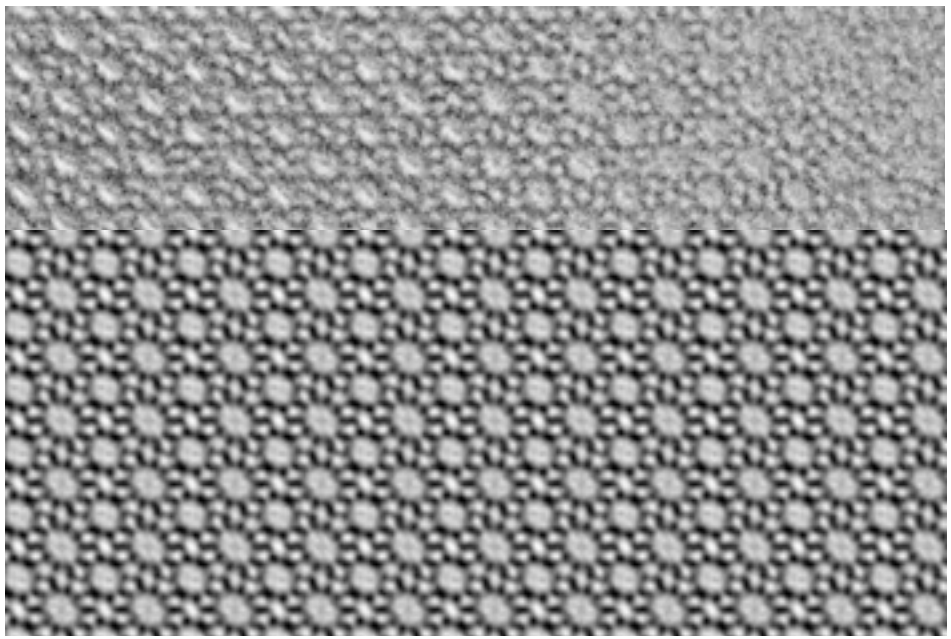

CTF corrected
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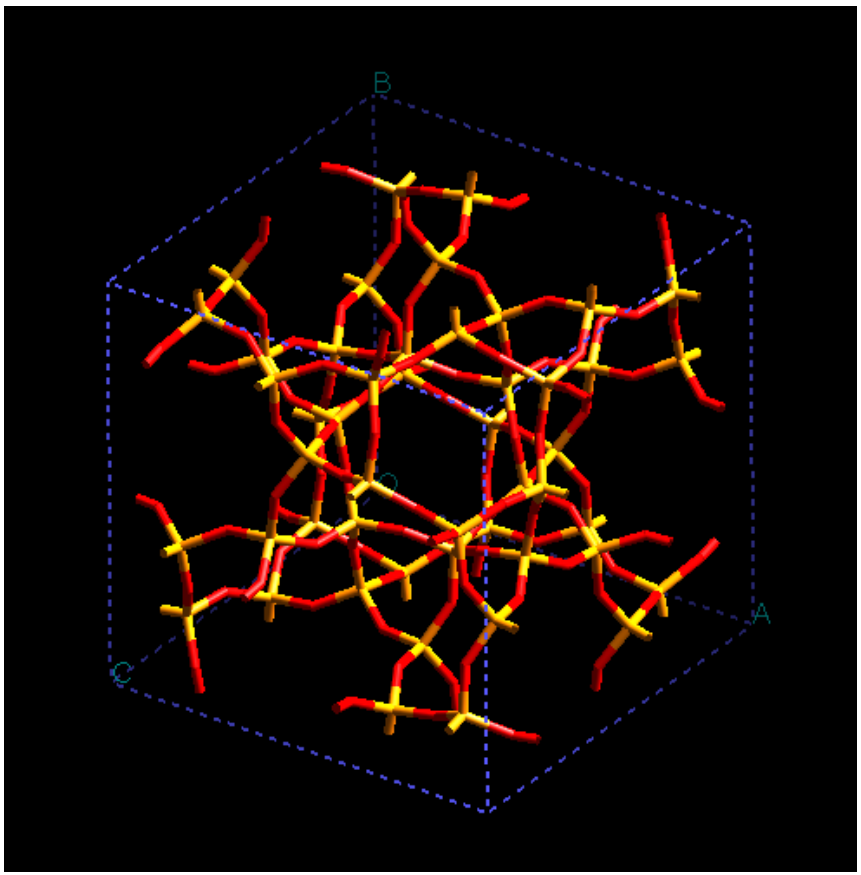
Fourier transform ➔ Structure factor amplitudes and phases

Structure Envelope

Zeolite Analcime



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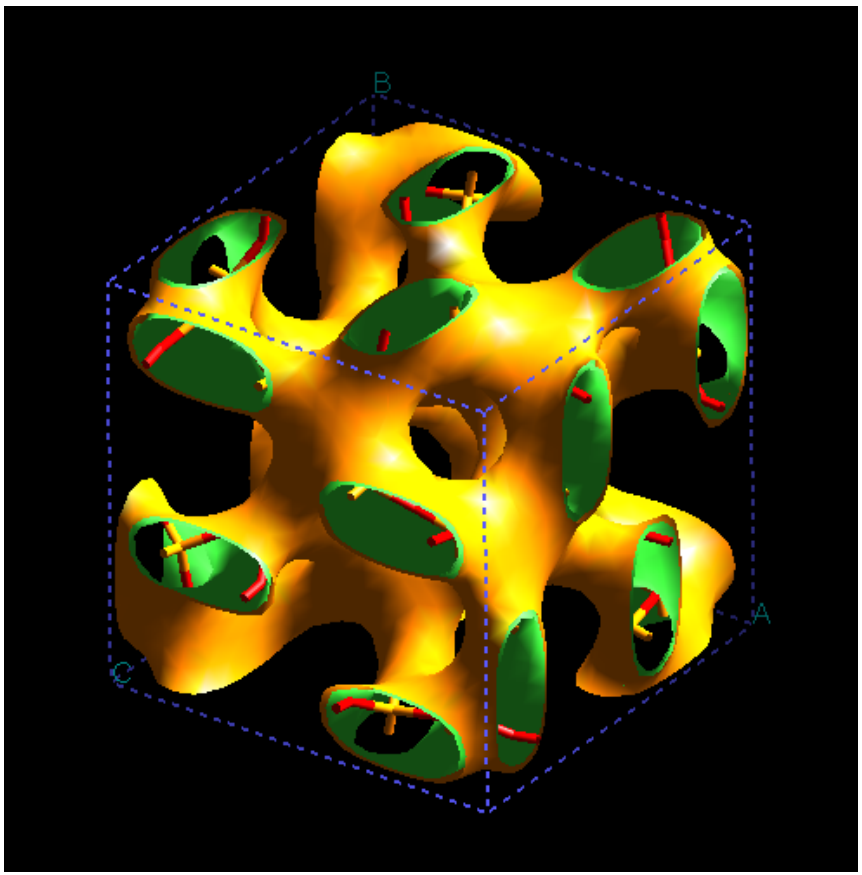
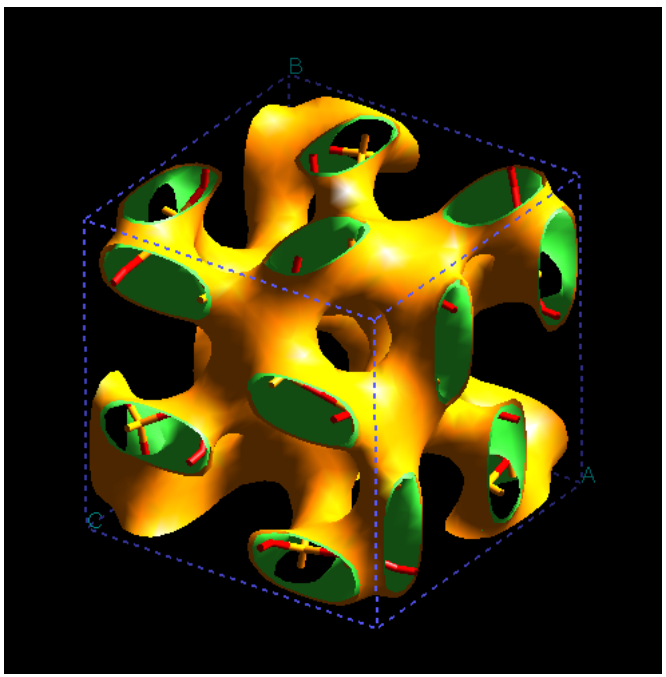


Structure Envelope

A structure envelope is a curved surface that separates regions of high electron density from those of low electron density



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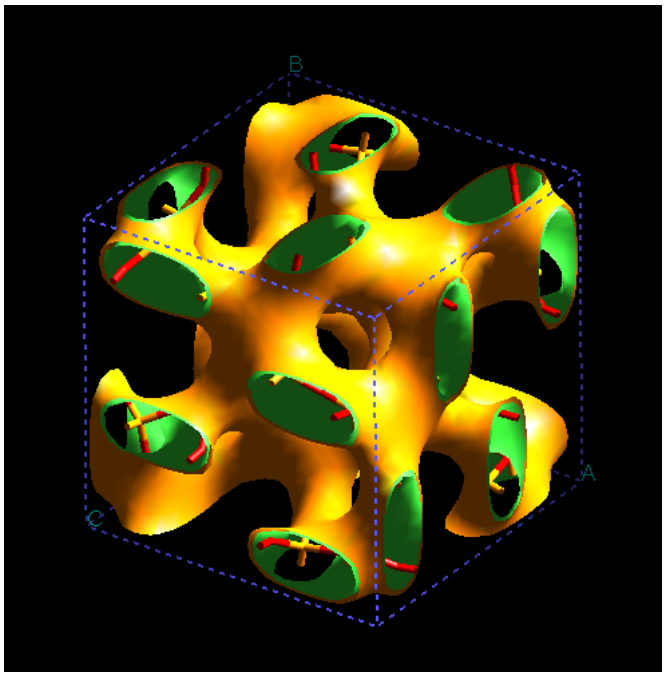
A structure envelope is a curved surface that separates regions of high electron density from those of low electron density

→ Isosurface of a low resolution electron density map



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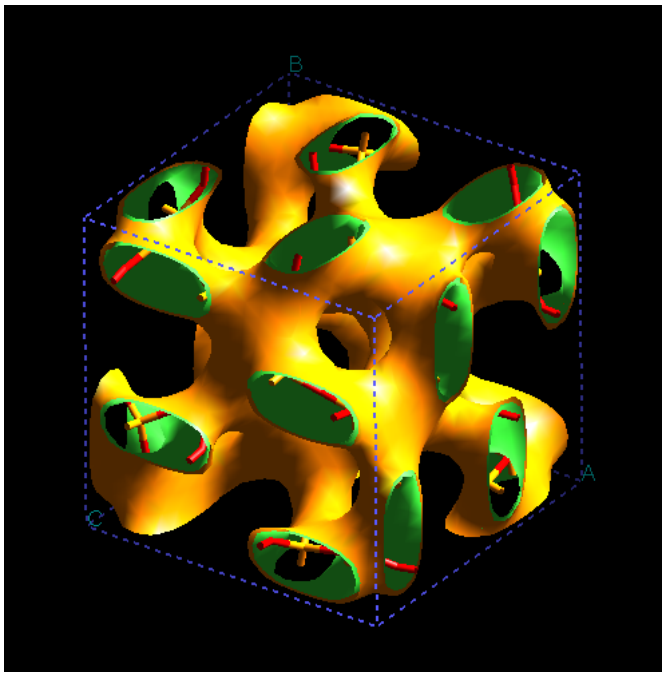

Reflection 2 1 1

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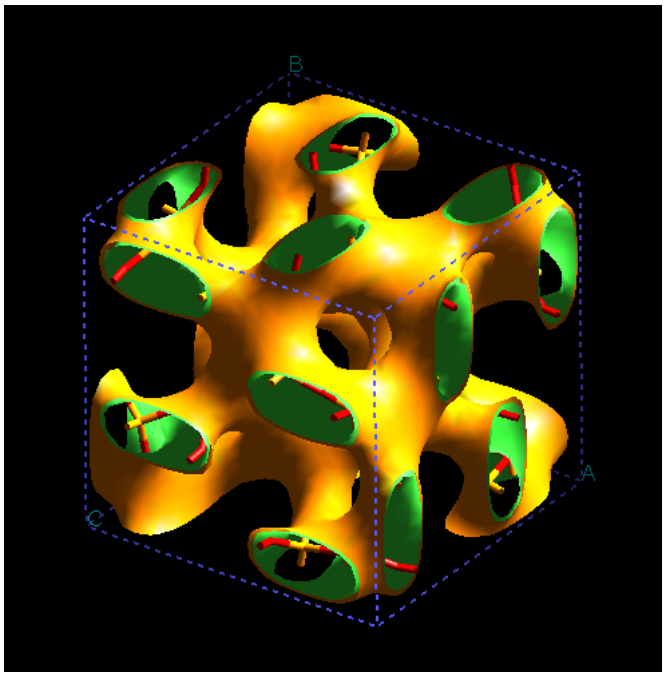

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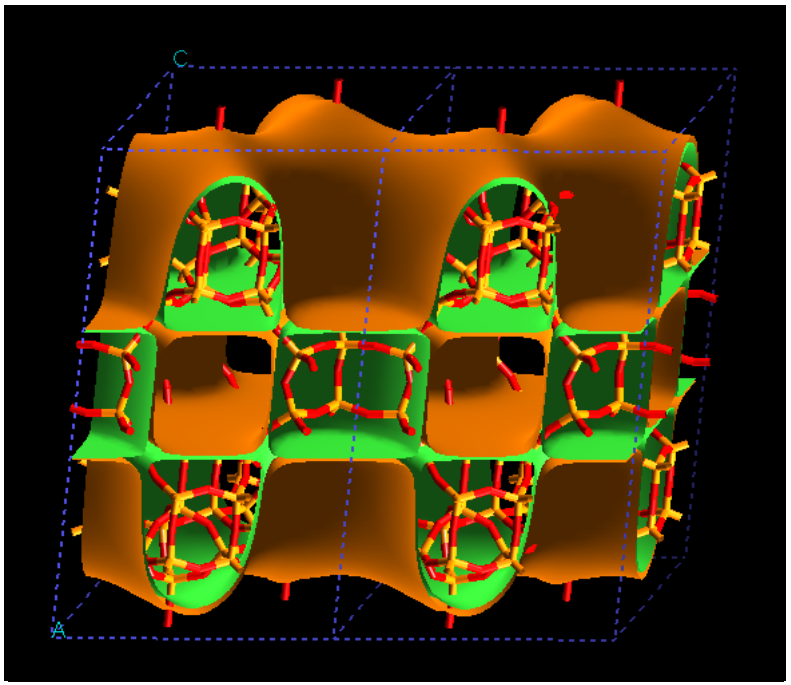

100, 101, 102, 002

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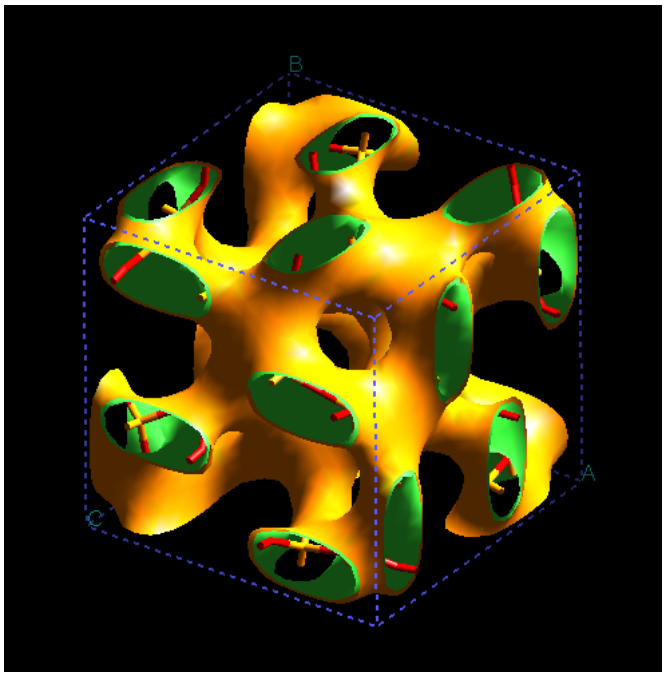

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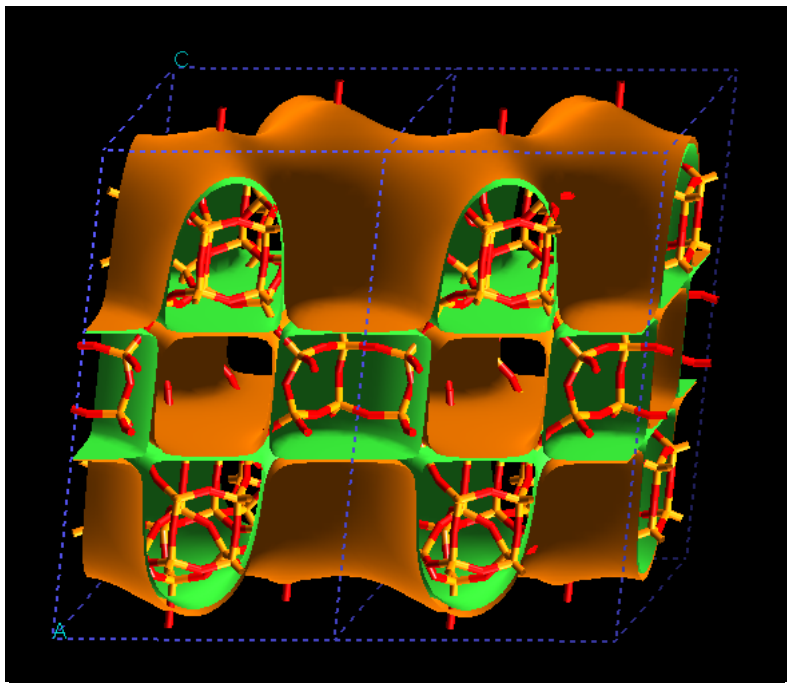

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phase can be fixed

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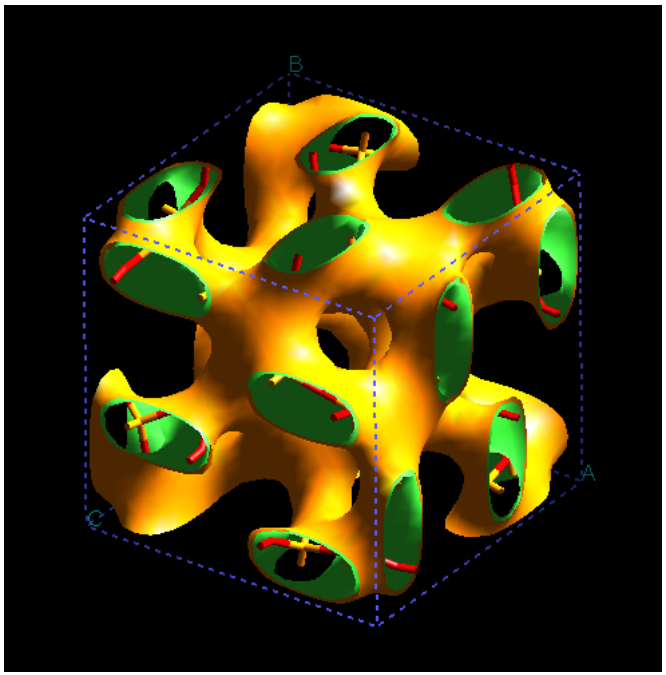

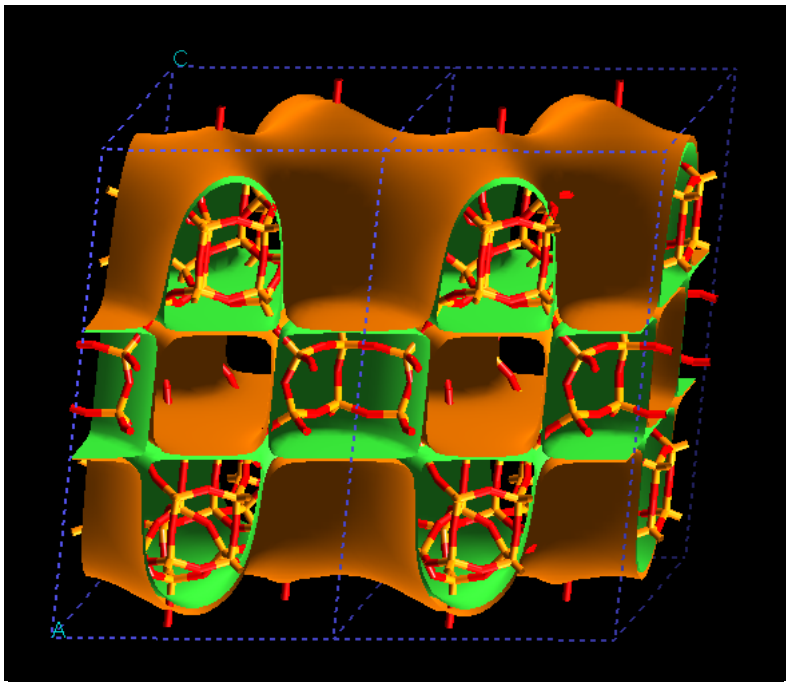

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Phases can be obtained from HRTEM images

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FOCUS

Zeolites

- 3-dimensional, 4-connected framework structure

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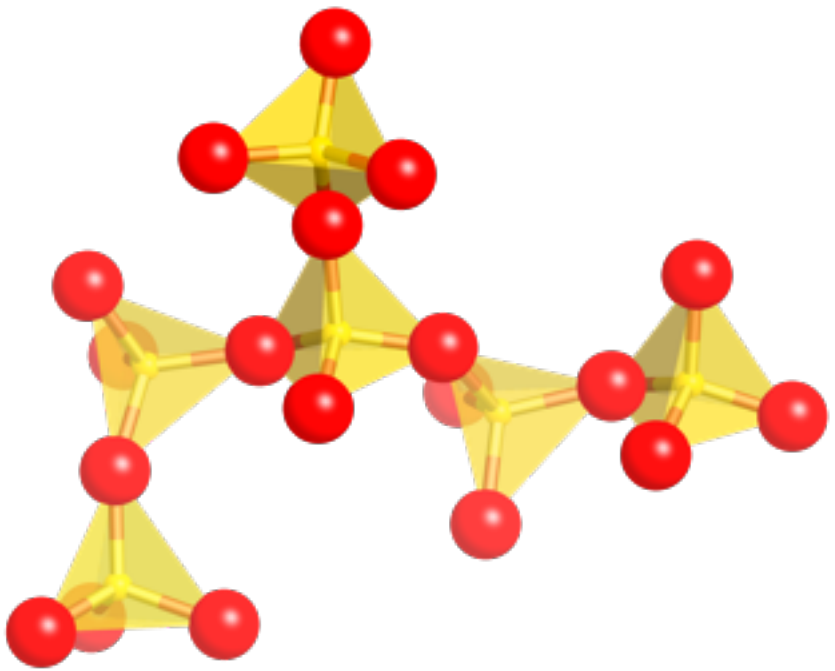

FOCUS

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- 3-dimensional, 4-connected framework structure
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- known T-O bond lengths, O-T-O angles and T-O-T angles

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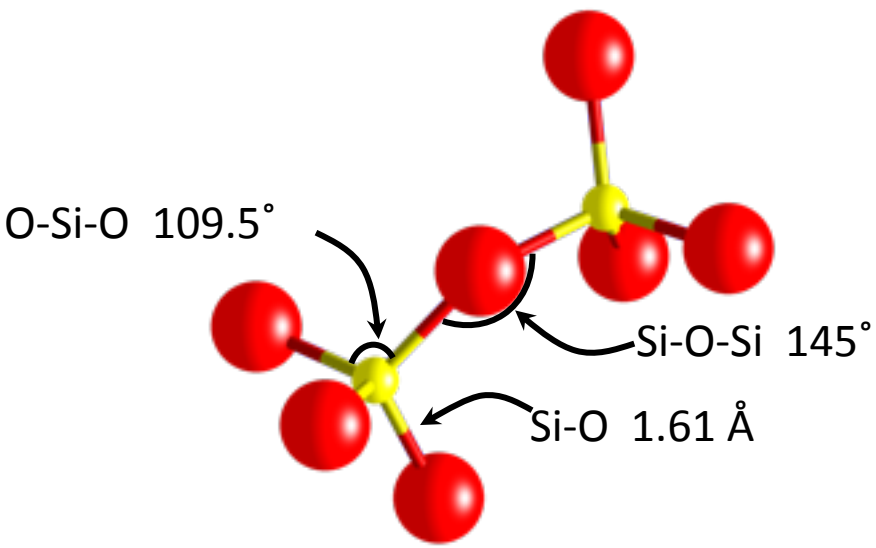

FOCUS

approximate unit cell contents
individual minimum distances
selected reflection intensities

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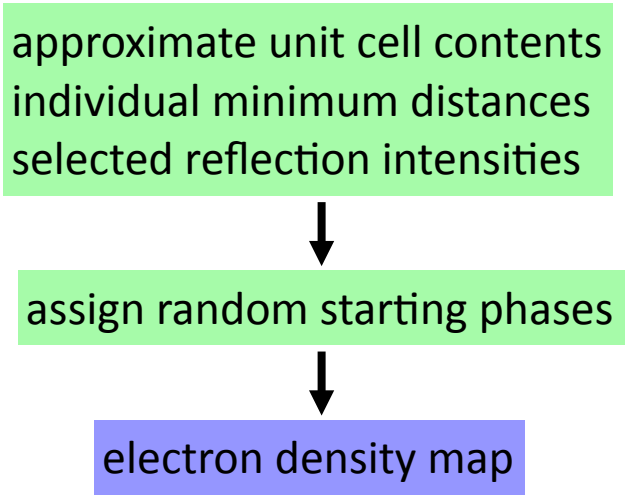
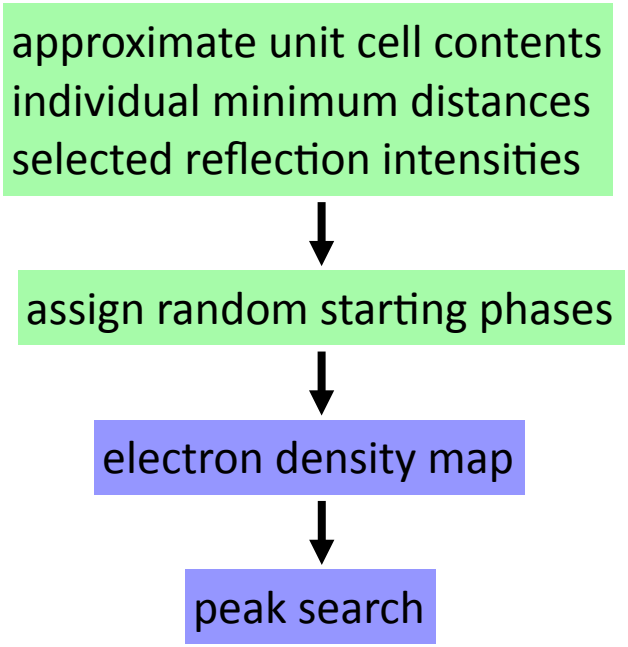
↓

assign random starting phases

FOCUS


approximate unit cell contents
individual minimum distances
selected reflection intensities
assign random starting phases
electron density map

FOCUS


approximate unit cell contents
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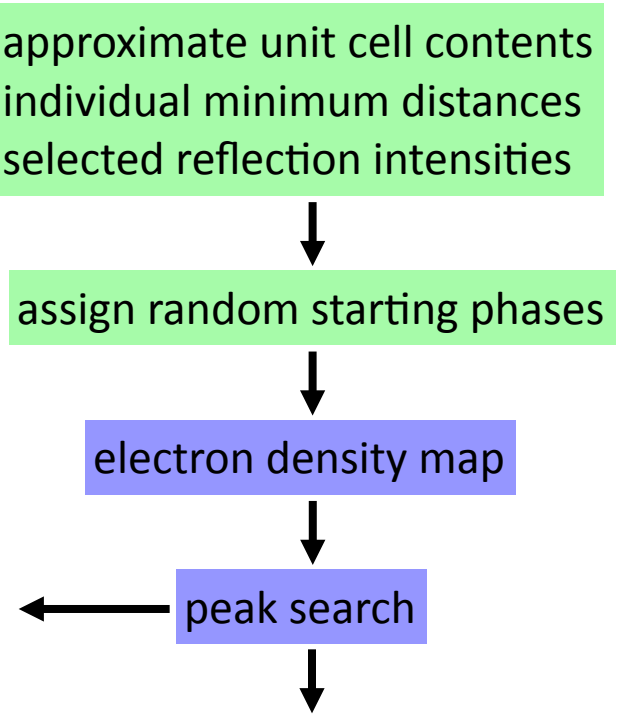
assign random starting phases
electron density map
peak search

FOCUS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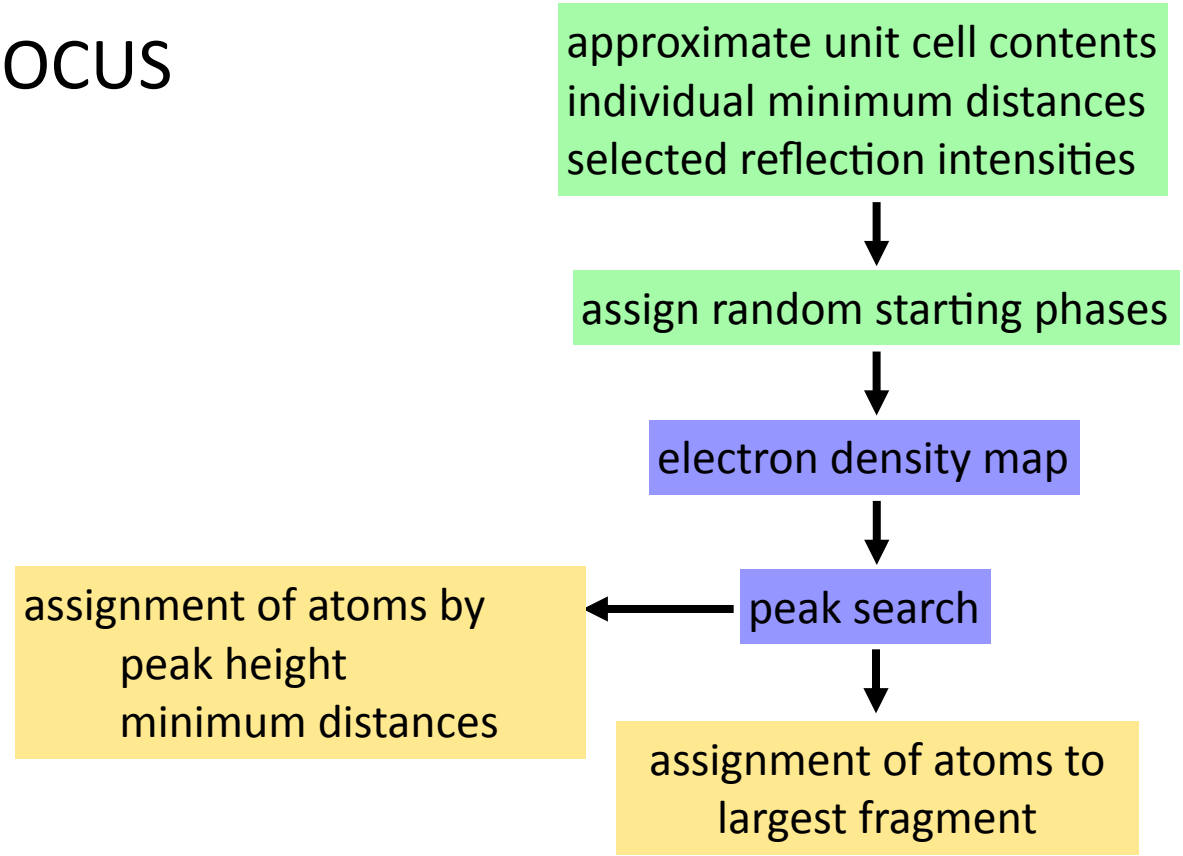
approximate unit cell contents
individual minimum distances
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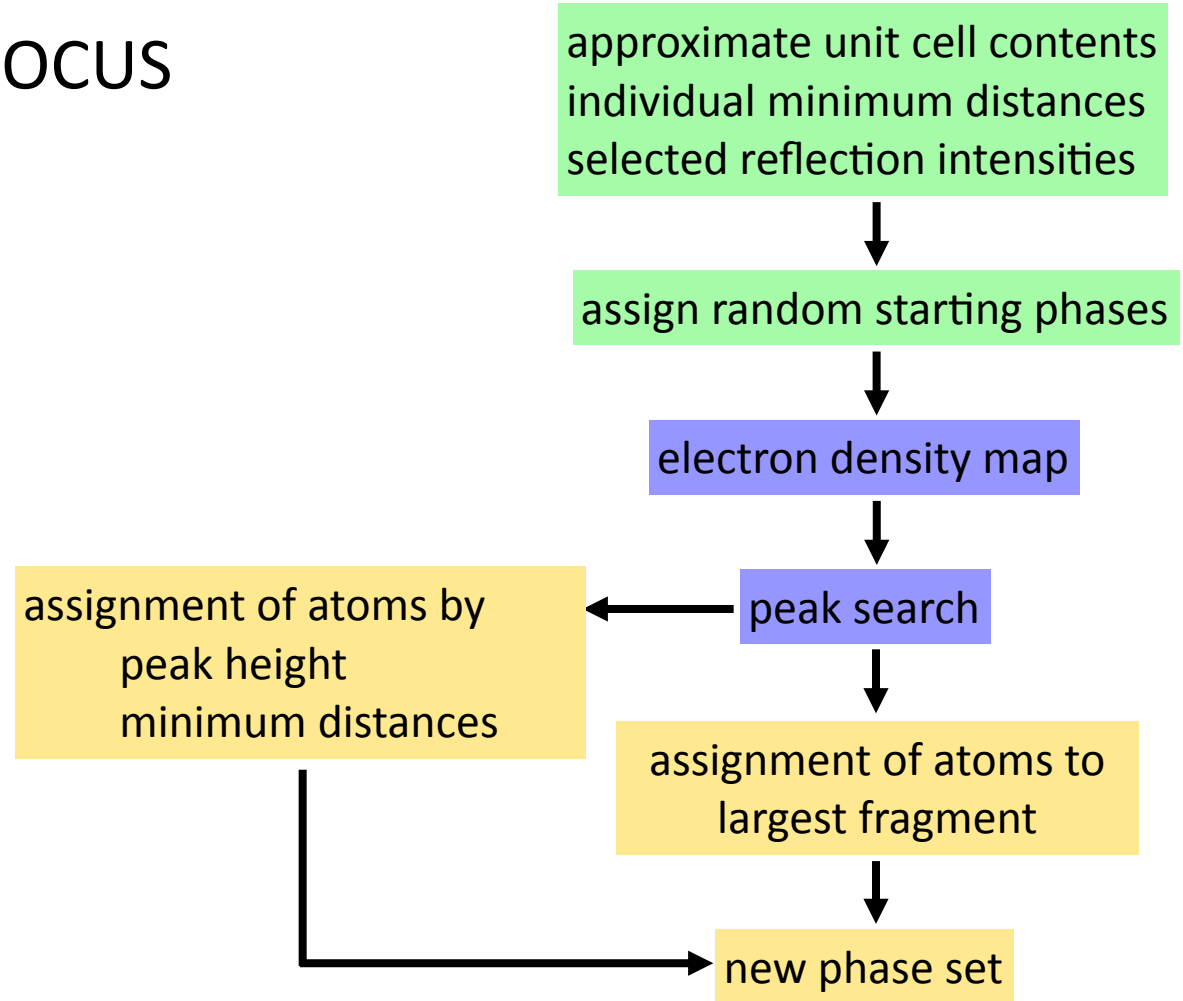
assign random starting phases
electron density map
peak search
assignment of atoms by
peak height
minimum distances
assignment of atoms to
largest fragment

FOCUS


approximate unit cell contents
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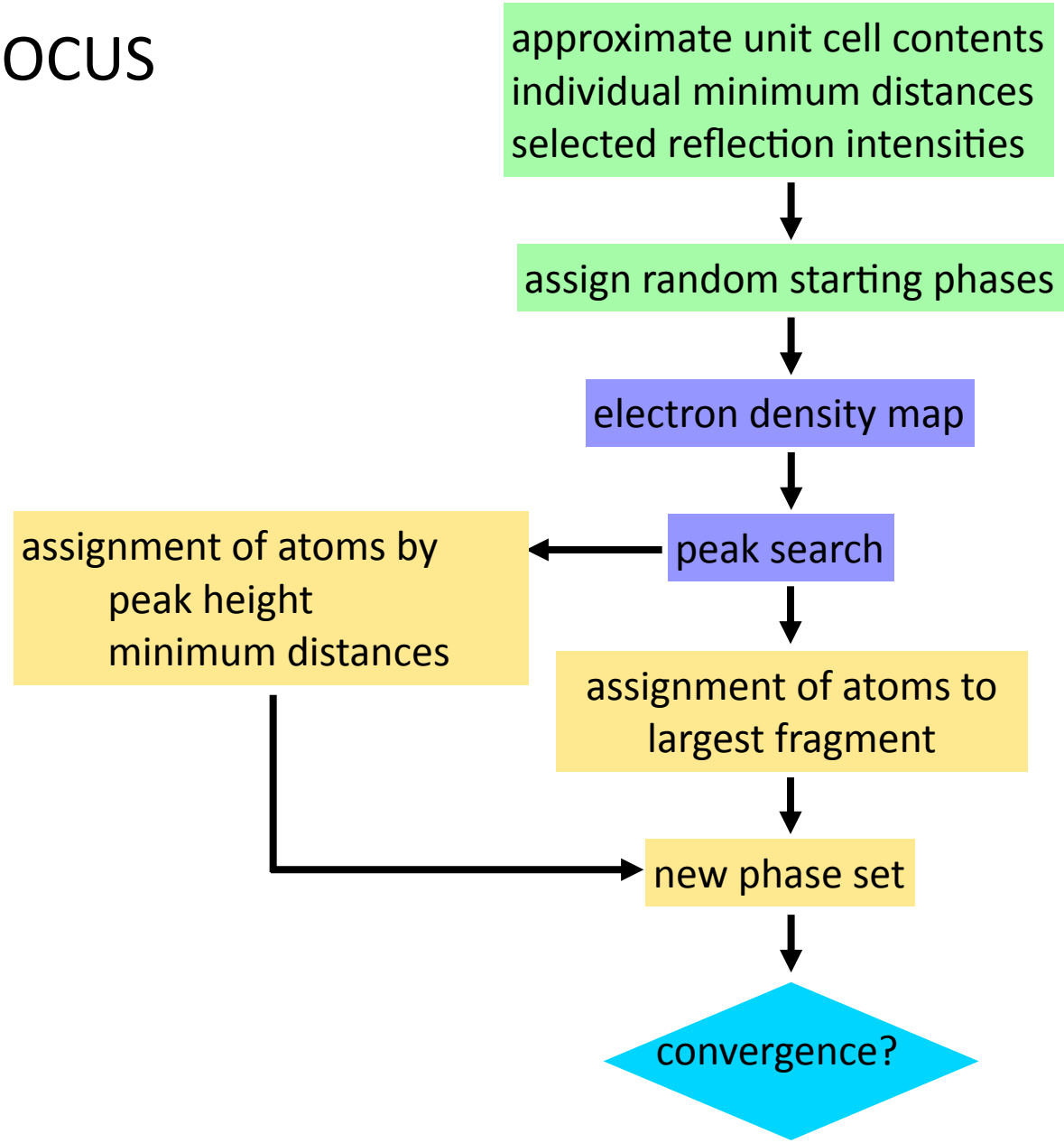
minimum distances
assignment of atoms to
largest fragment
new phase set

FOCUS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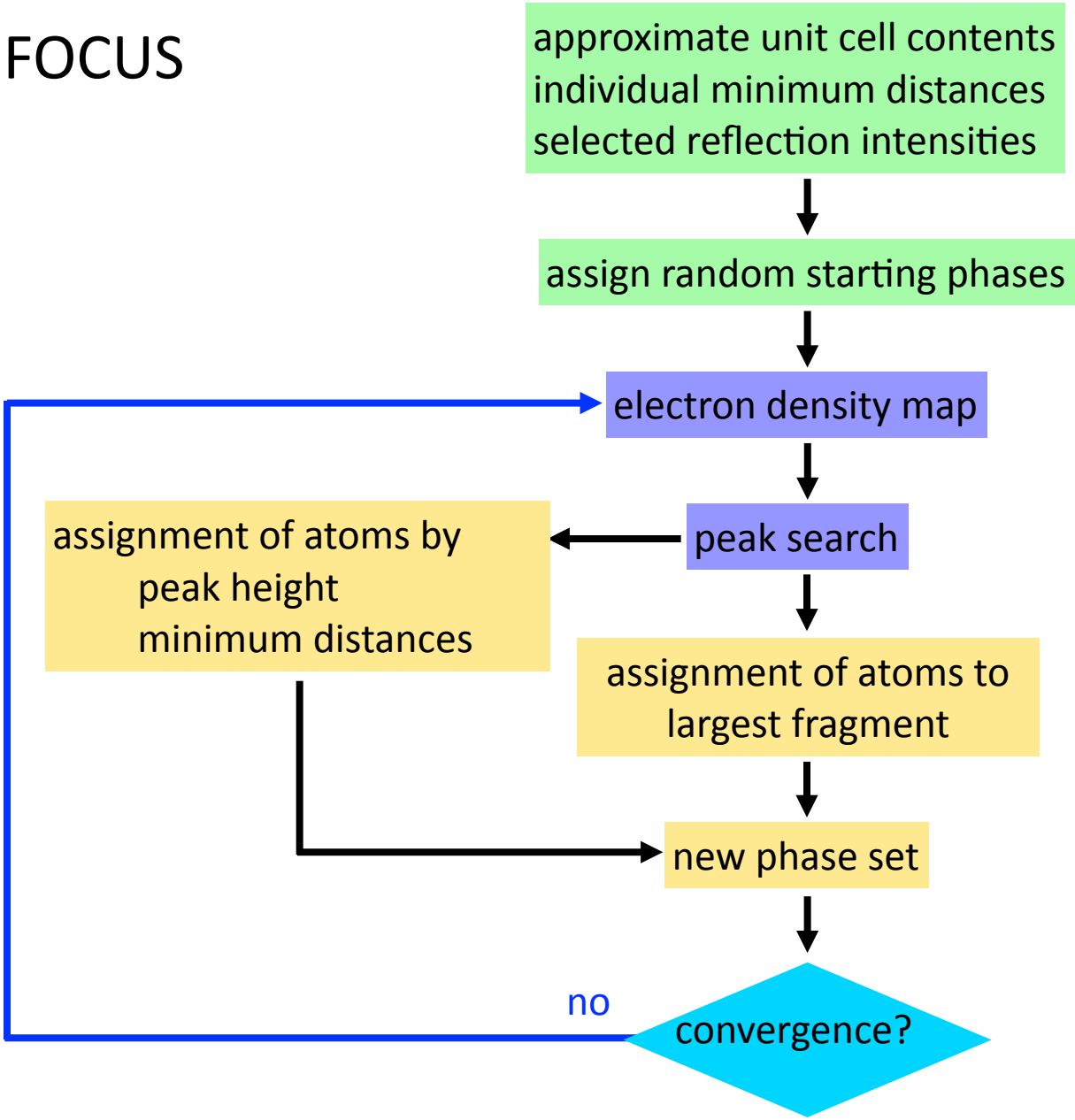
convergence?

FOCUS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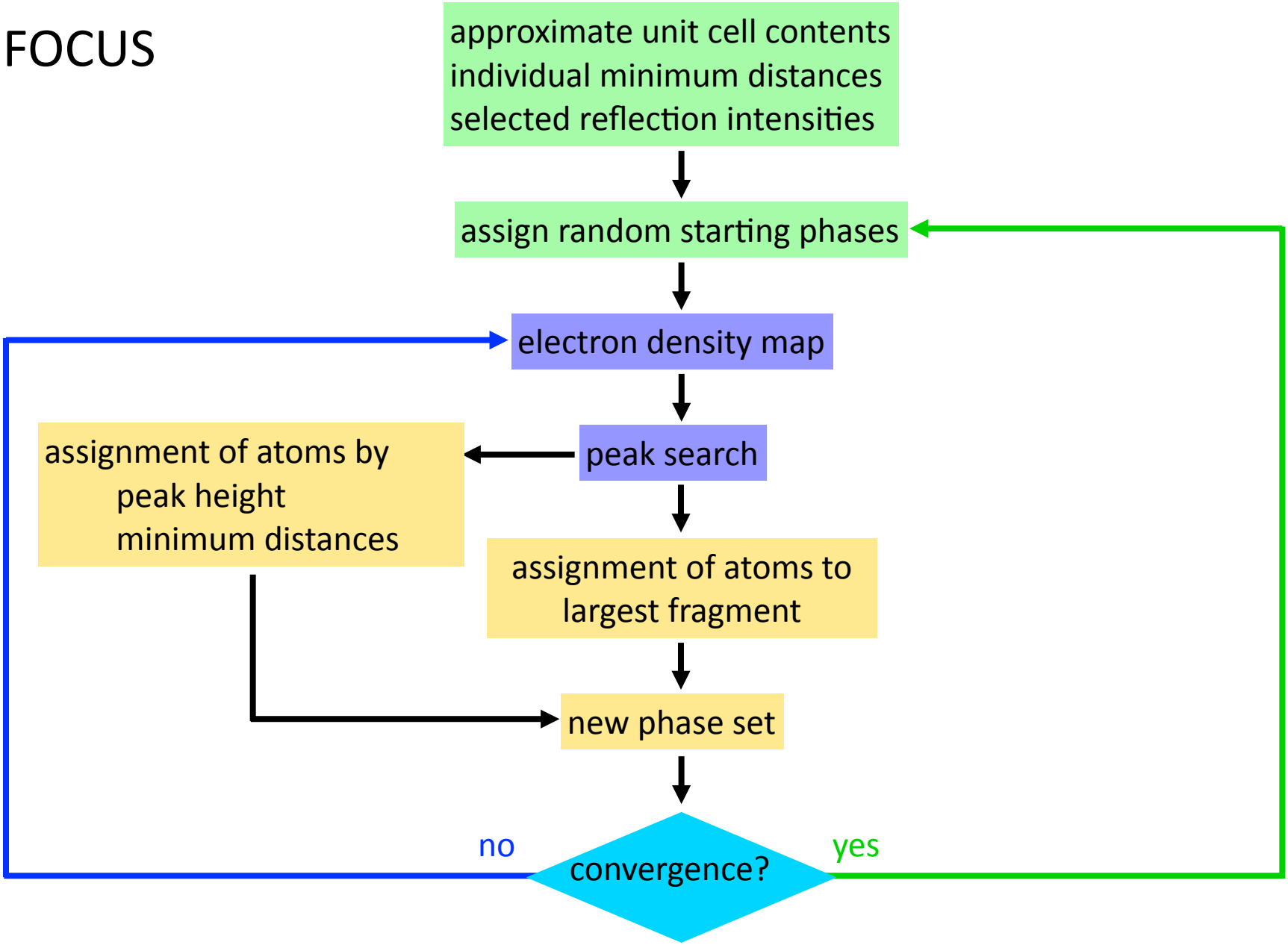
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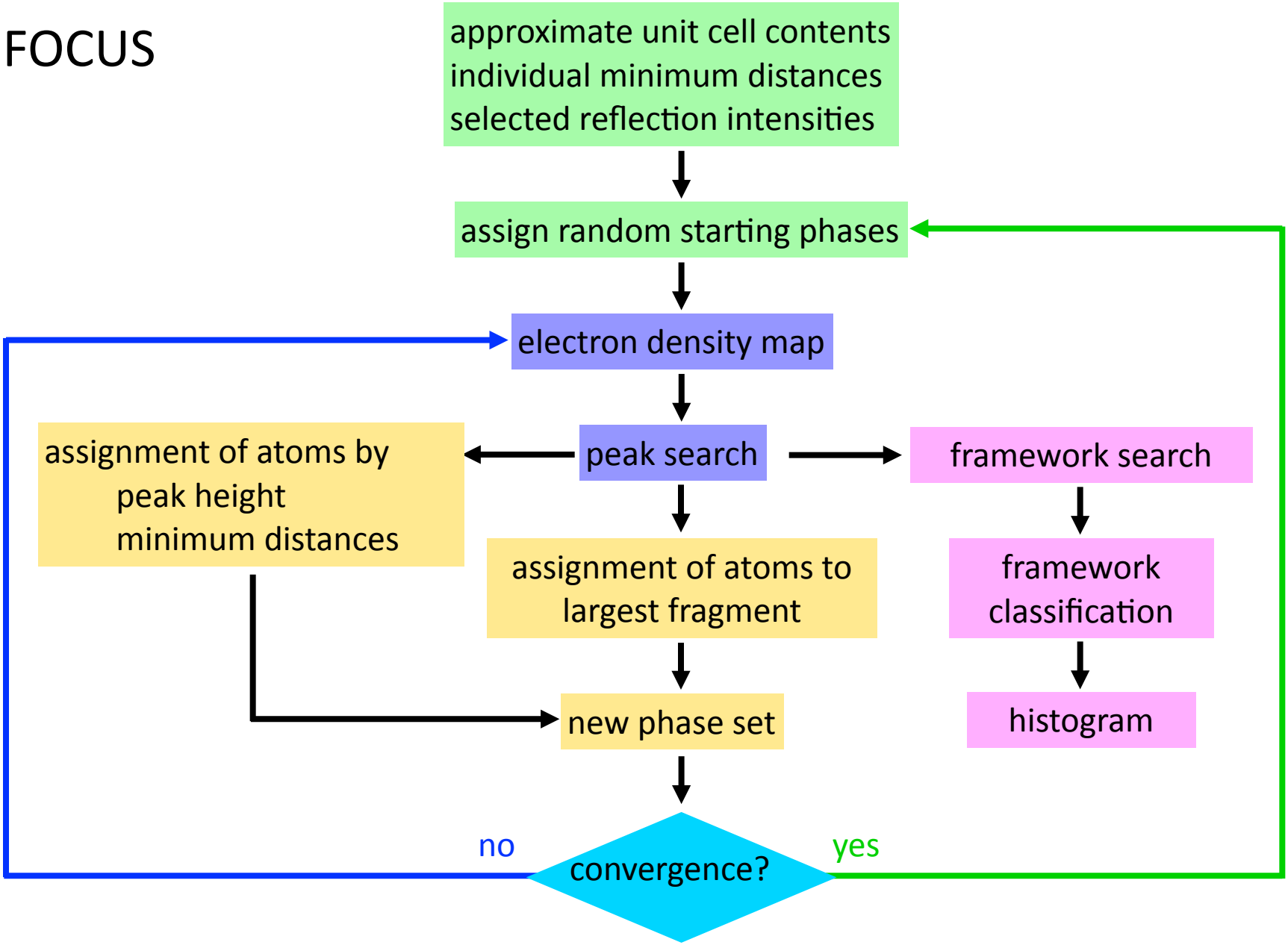
approximate unit cell contents
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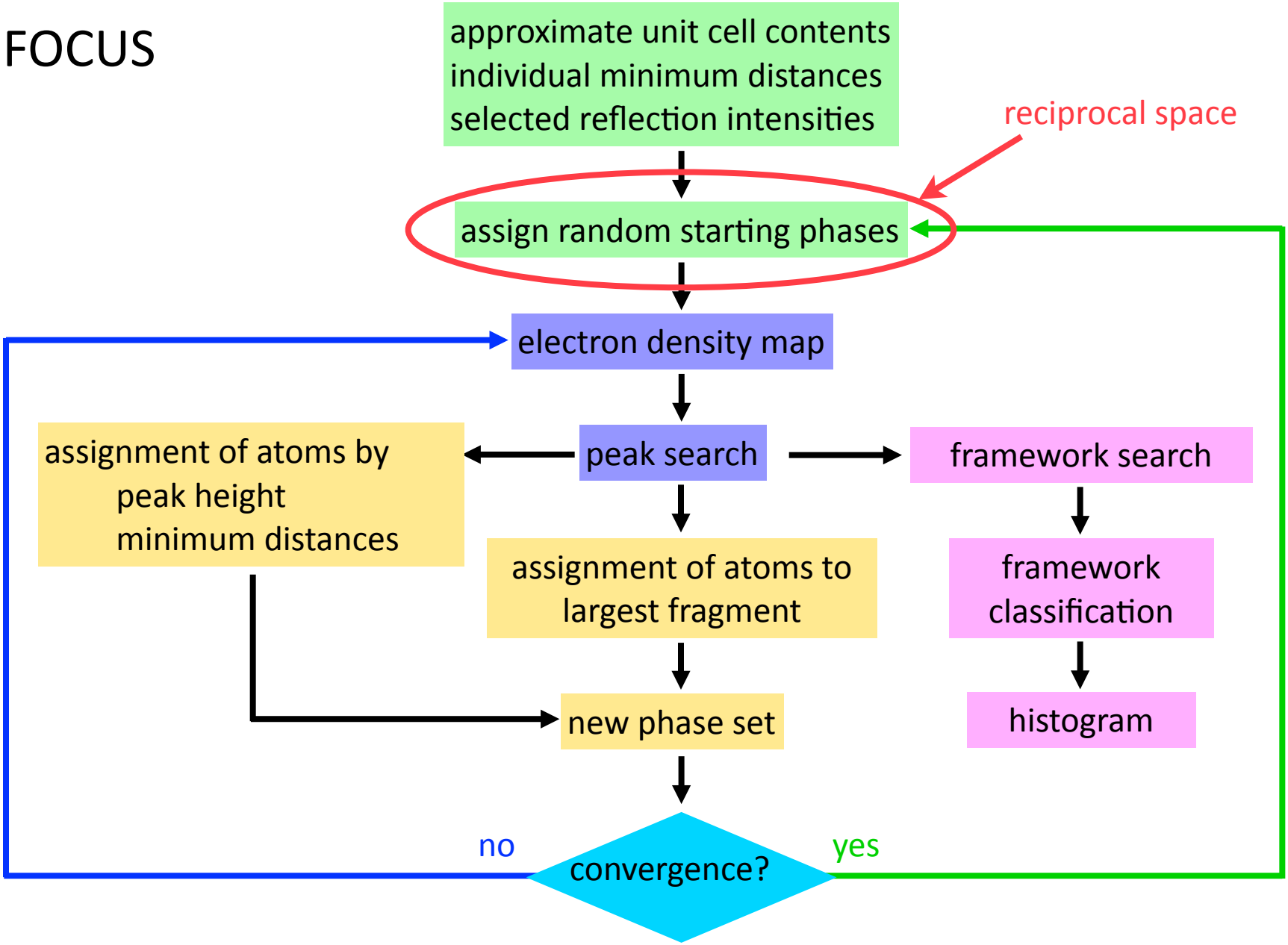
assign random starting phases
electron density map
peak search
assignment of atoms by
peak height
minimum distances
framework search
assignment of atoms to
largest fragment
framework
classification
new phase set
histogram
no
convergence?
yes

FOCUS


approximate unit cell contents
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selected reflection intensities
reciprocal space
assign random starting phases
electron density map
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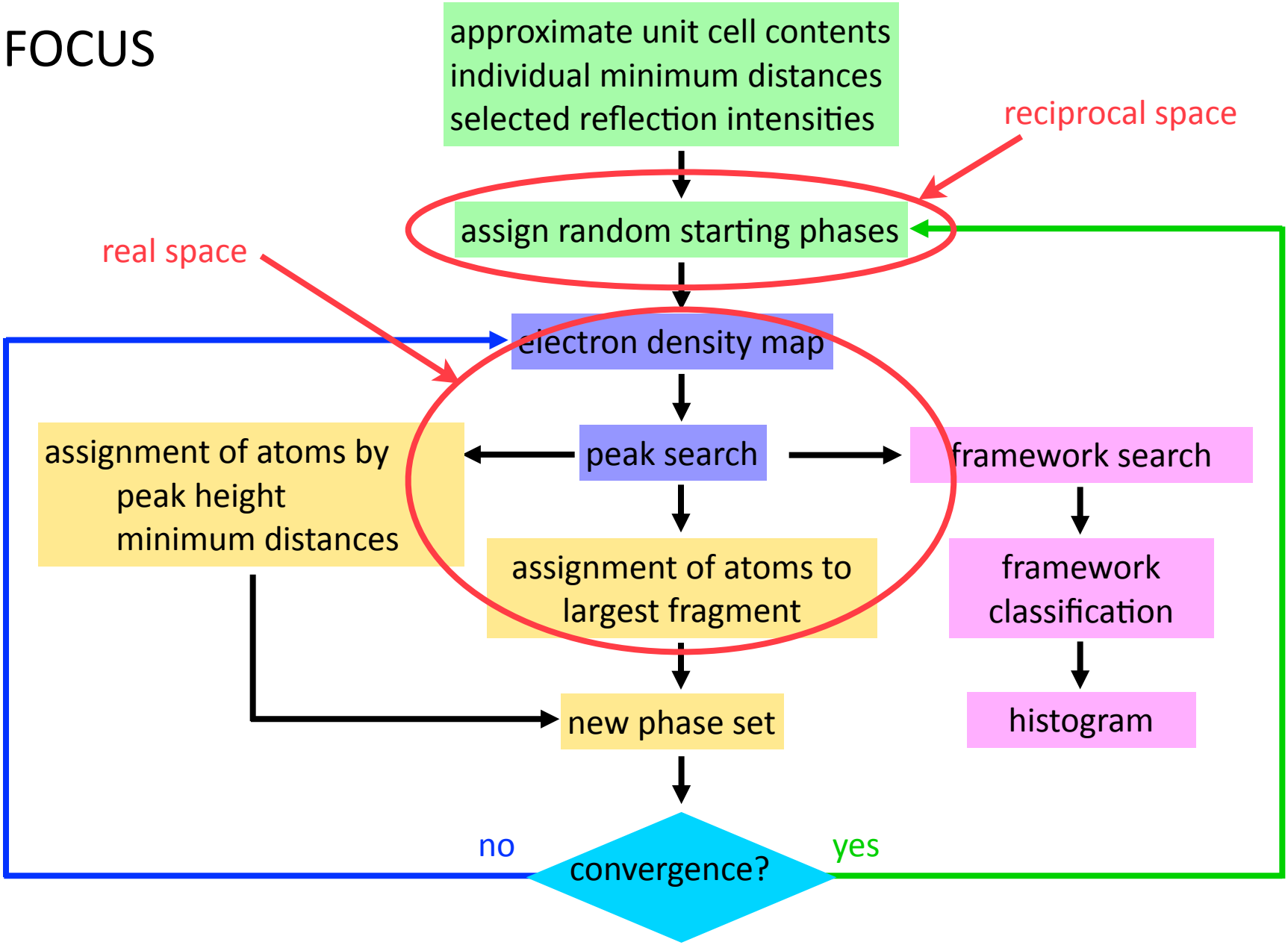
approximate unit cell contents
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reciprocal space
assign random starting phases
real space
electron density map
assignment of atoms by
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framework search
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new phase set
histogram
no
convergence?
yes

TNU-9

TNU-9

Unit Cell	
Space Group	*C*2/*m*
a	28.2219 Å
b	20.0123 Å
c	19.4926 Å
β	92.33˚
Reflections	
powder pattern (d_{min}=1.17Å)	3705
overlapping (0.3*FWHM)	3154
FOCUS	
reflections used (65% strongest)	1481

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85% overlap

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FOCUS

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→ no solution

TNU-9

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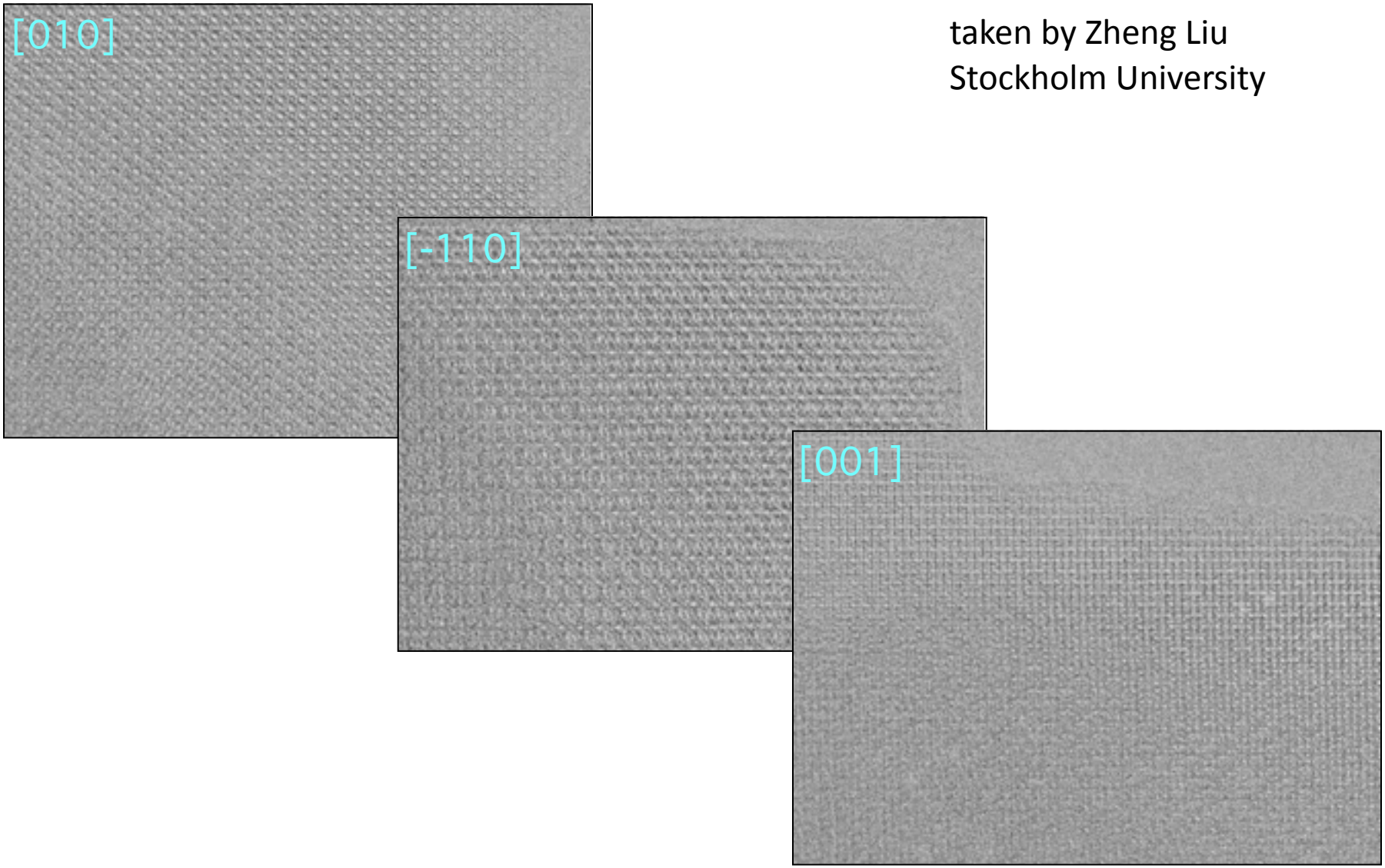
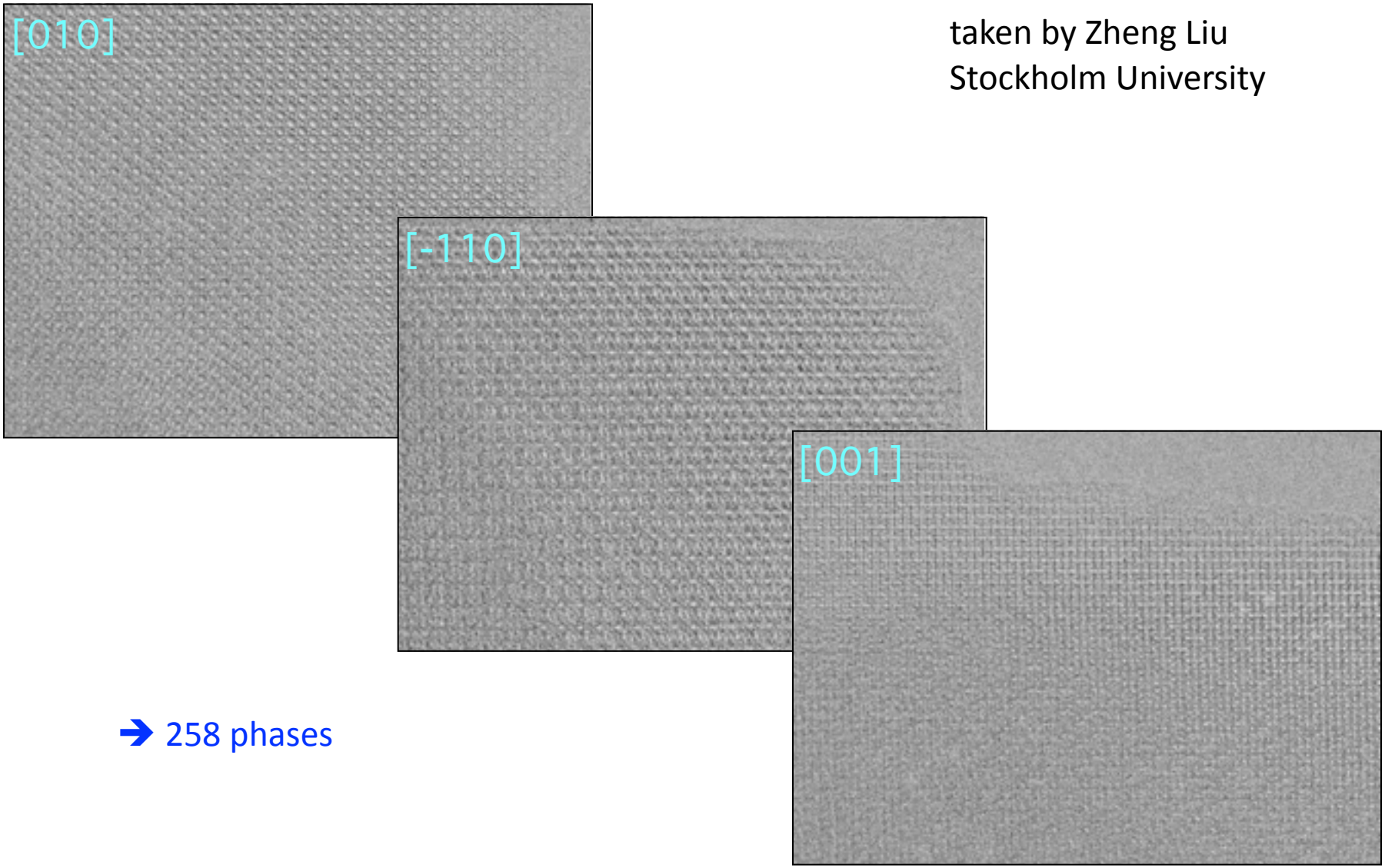


taken by Zheng Liu
Stockholm University

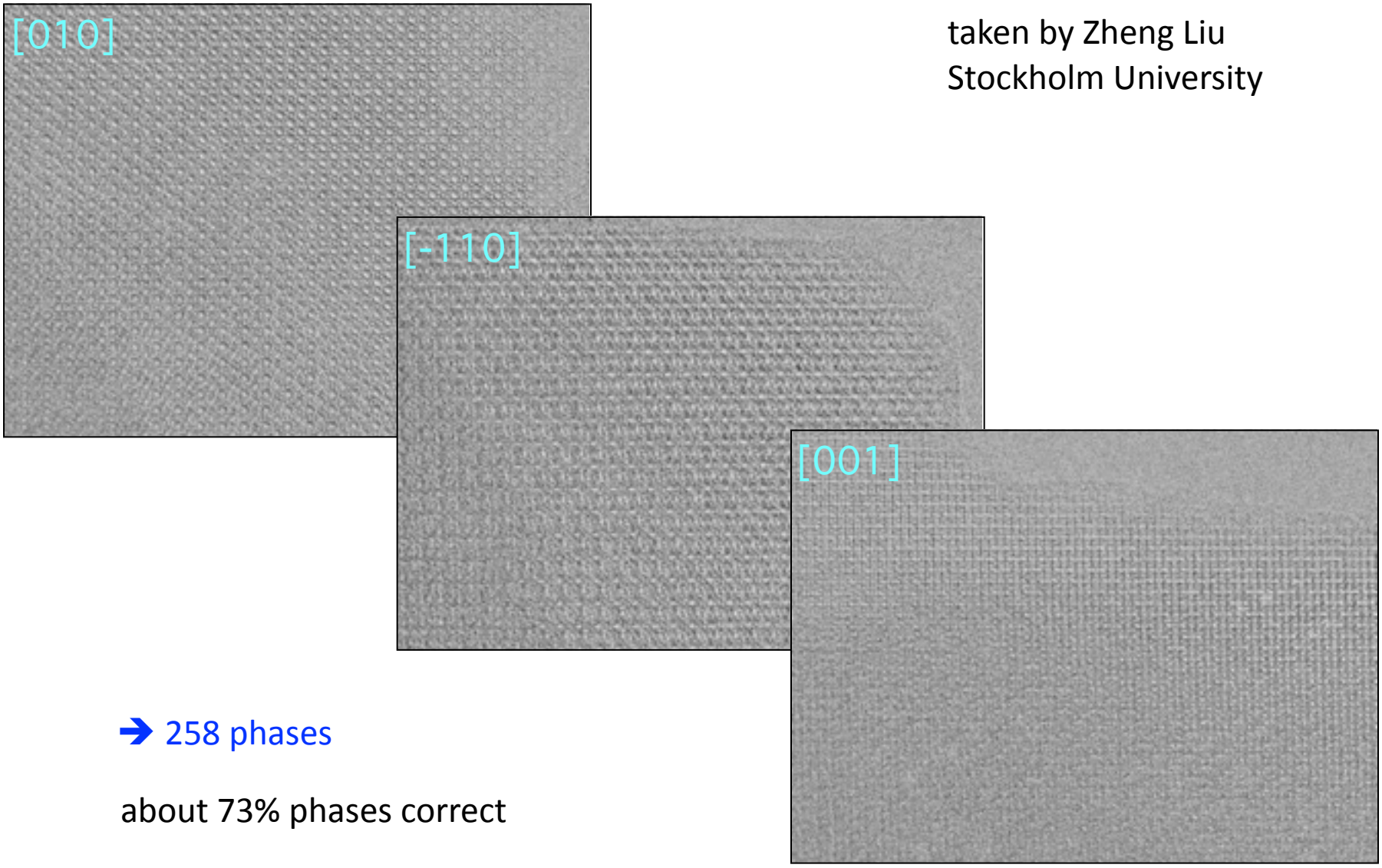
TNU-9



taken by Zheng Liu
Stockholm University

➔ 258 phases

TNU-9

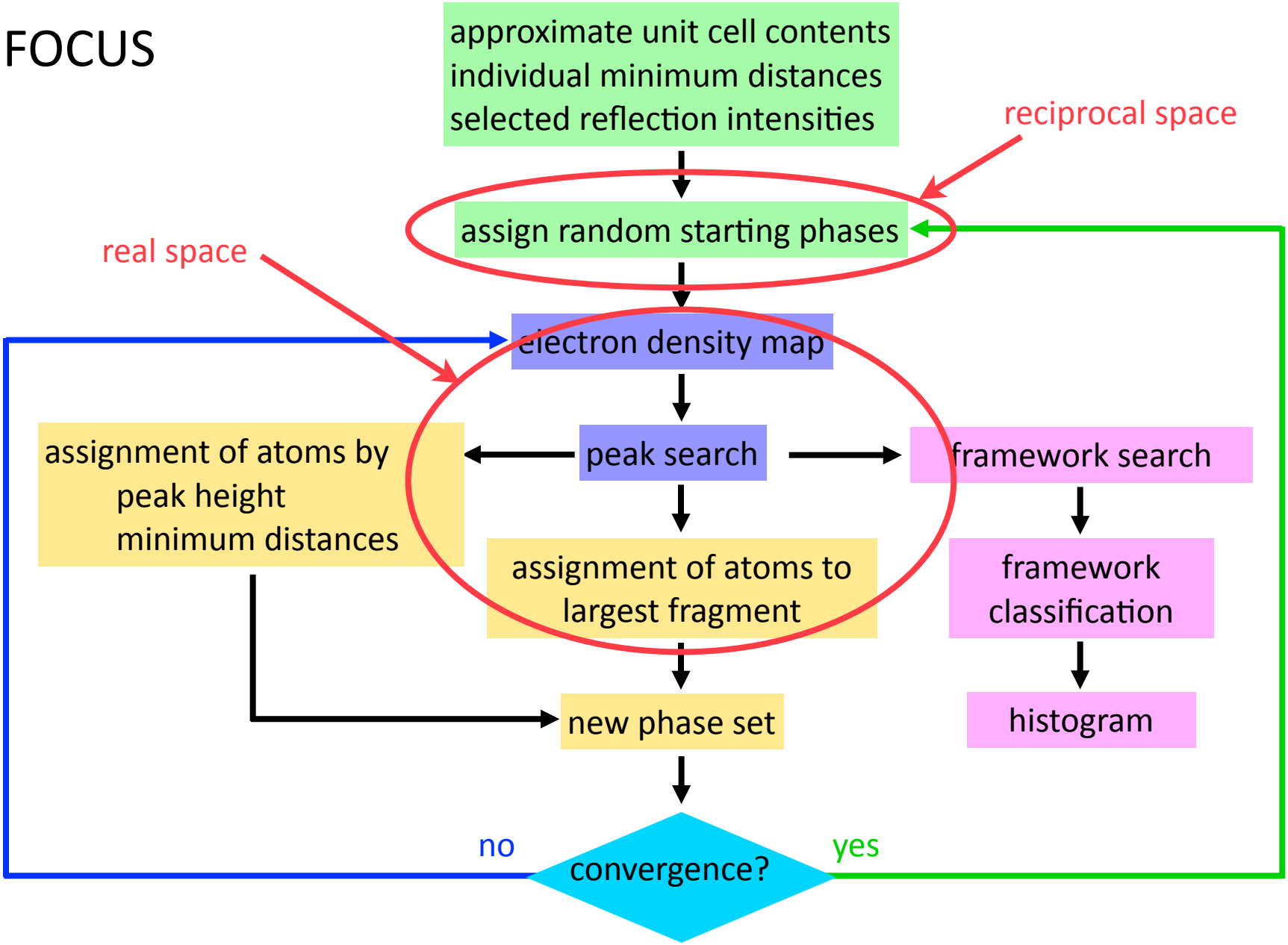


taken by Zheng Liu
Stockholm University

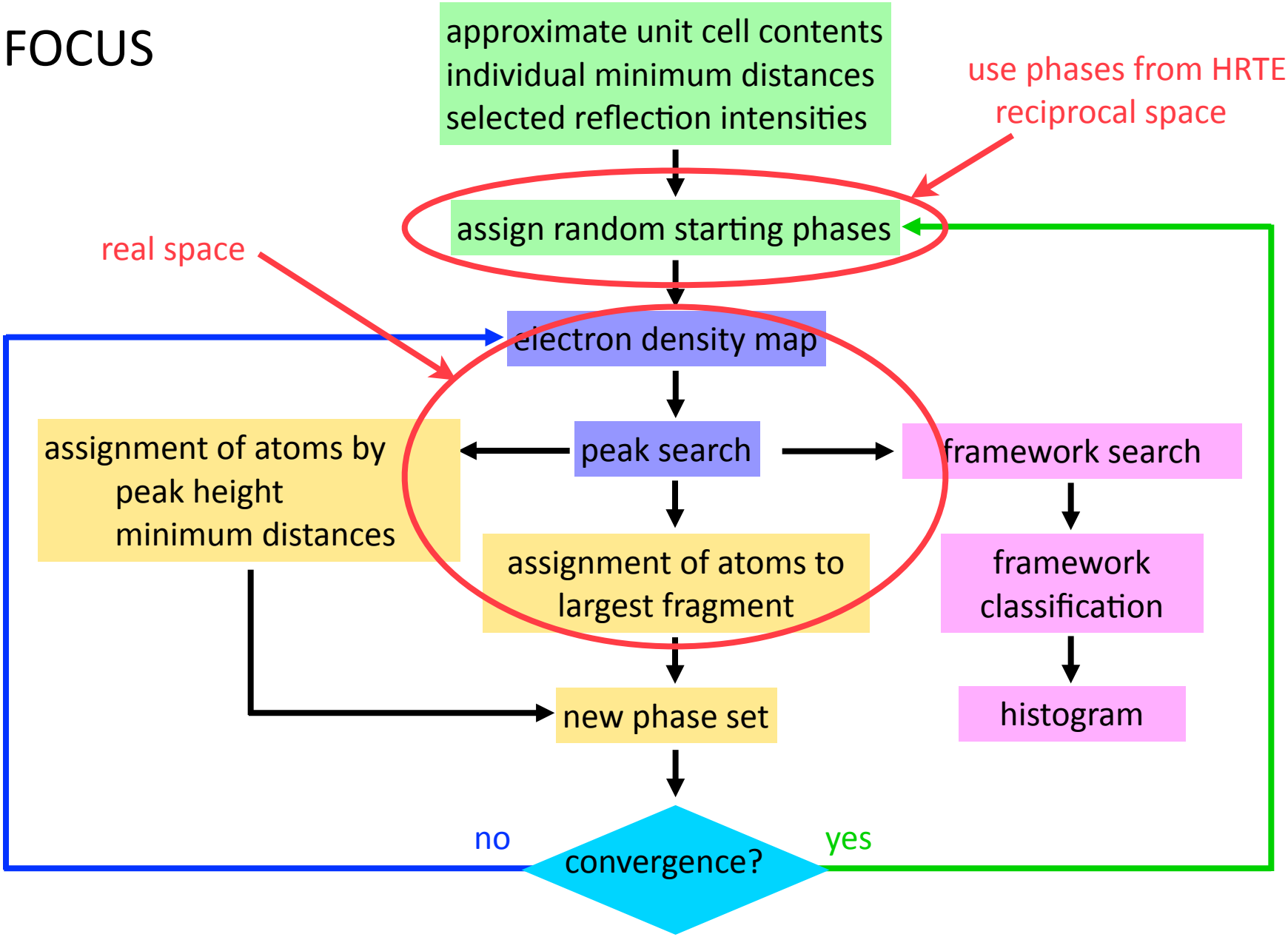
➔ 258 phases

about 73% phases correct

FOCUS


approximate unit cell contents
individual minimum distances
selected reflection intensities
reciprocal space
assign random starting phases
real space
electron density map
assignment of atoms by
peak height
minimum distances
peak search
framework search
assignment of atoms to
largest fragment
framework
classification
new phase set
histogram
no
convergence?
yes

FOCUS


approximate unit cell contents
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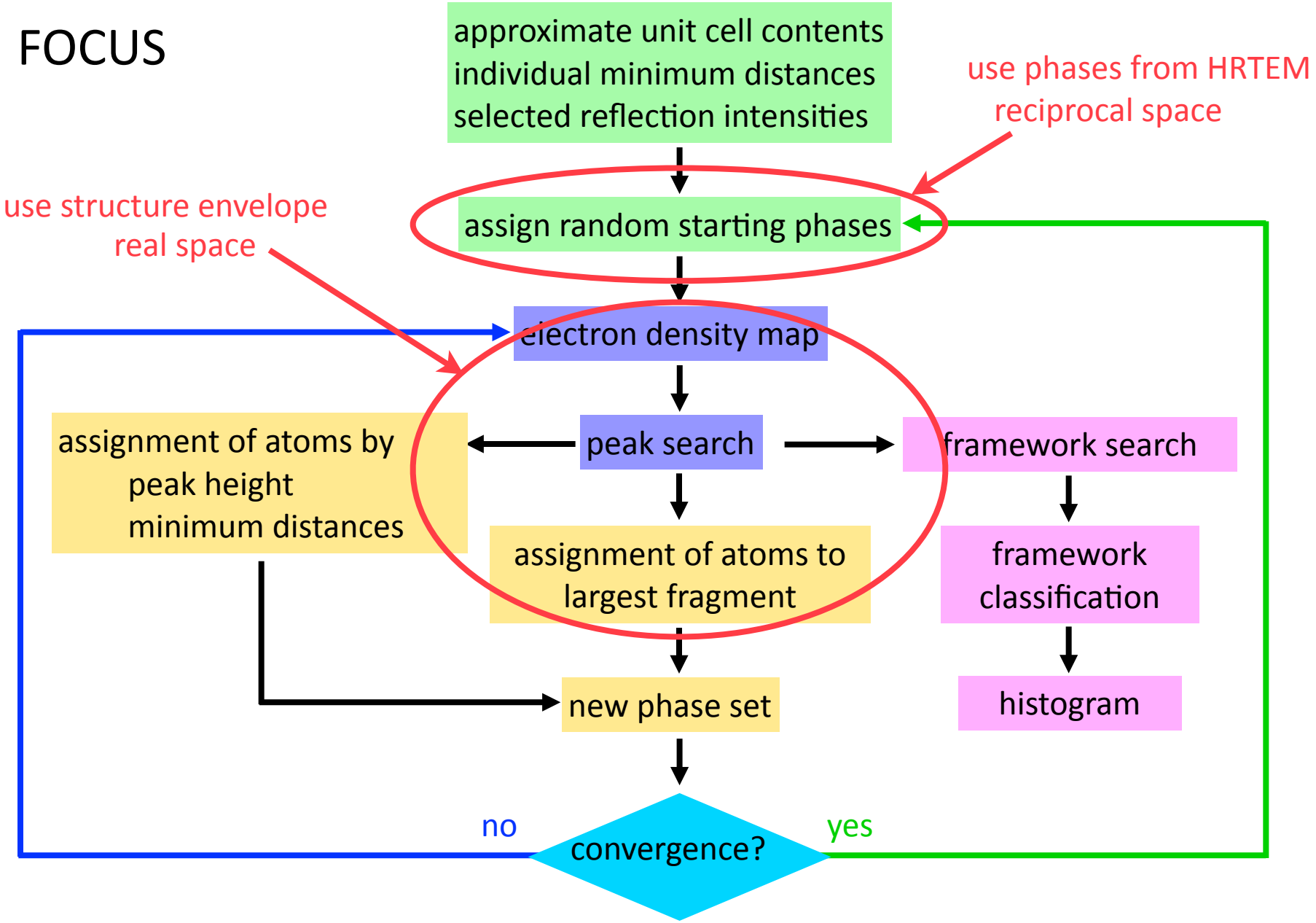
approximate unit cell contents
individual minimum distances
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use phases from HRTEM
reciprocal space
use structure envelope
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largest fragment
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classification
new phase set
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no
convergence?
yes

TNU-9

Unit Cell

Space Group	*C*2/*m*
a	28.2219 Å
b	20.0123 Å
c	19.4926 Å
β	92.33˚

Reflections

powder pattern (d_{min}=1.17Å)	3705
overlapping (0.3*FWHM)	3154

FOCUS

reflections used (65% strongest)	1481

TNU-9

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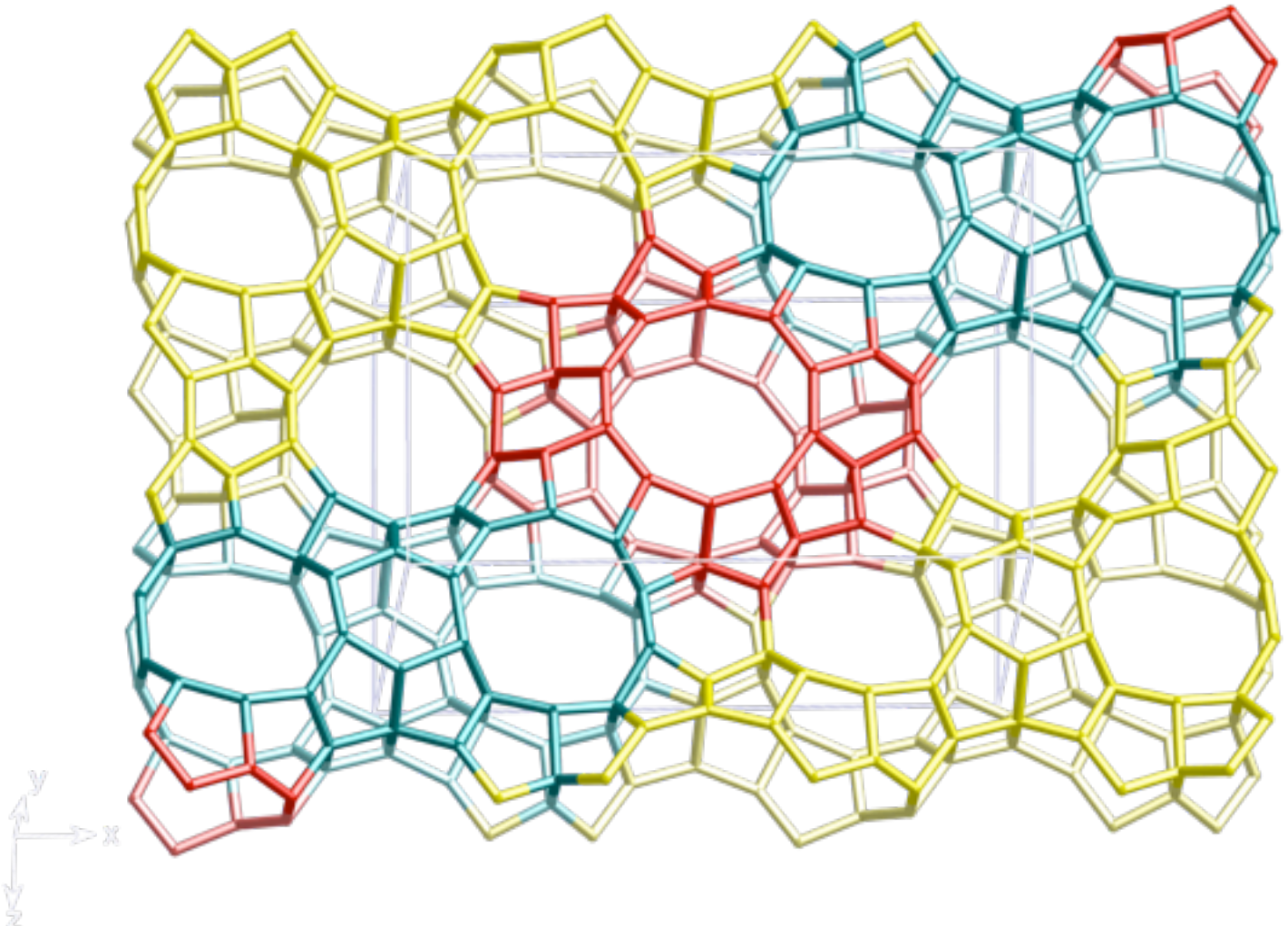
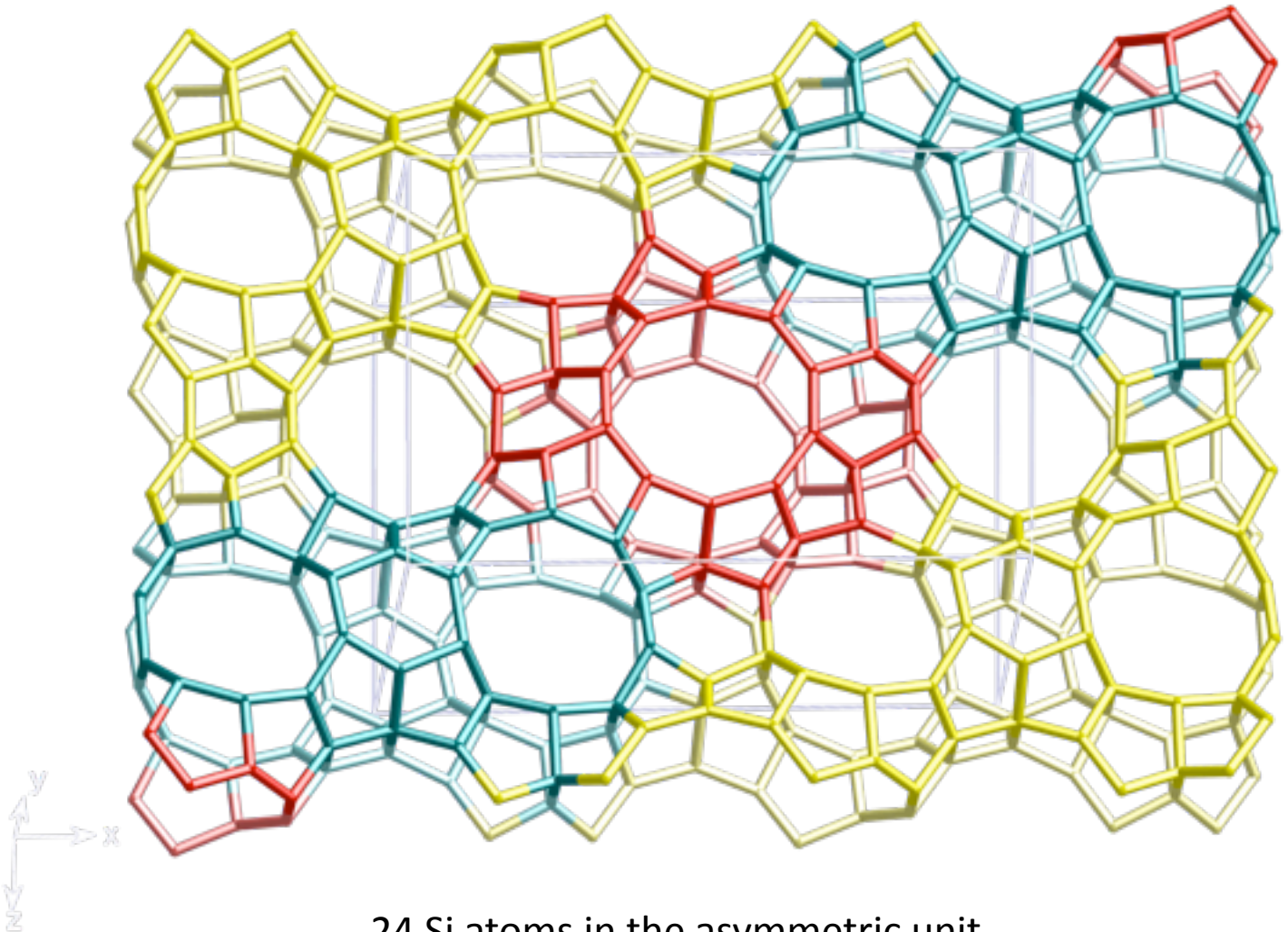
→ solution after 16 days

TNU-9

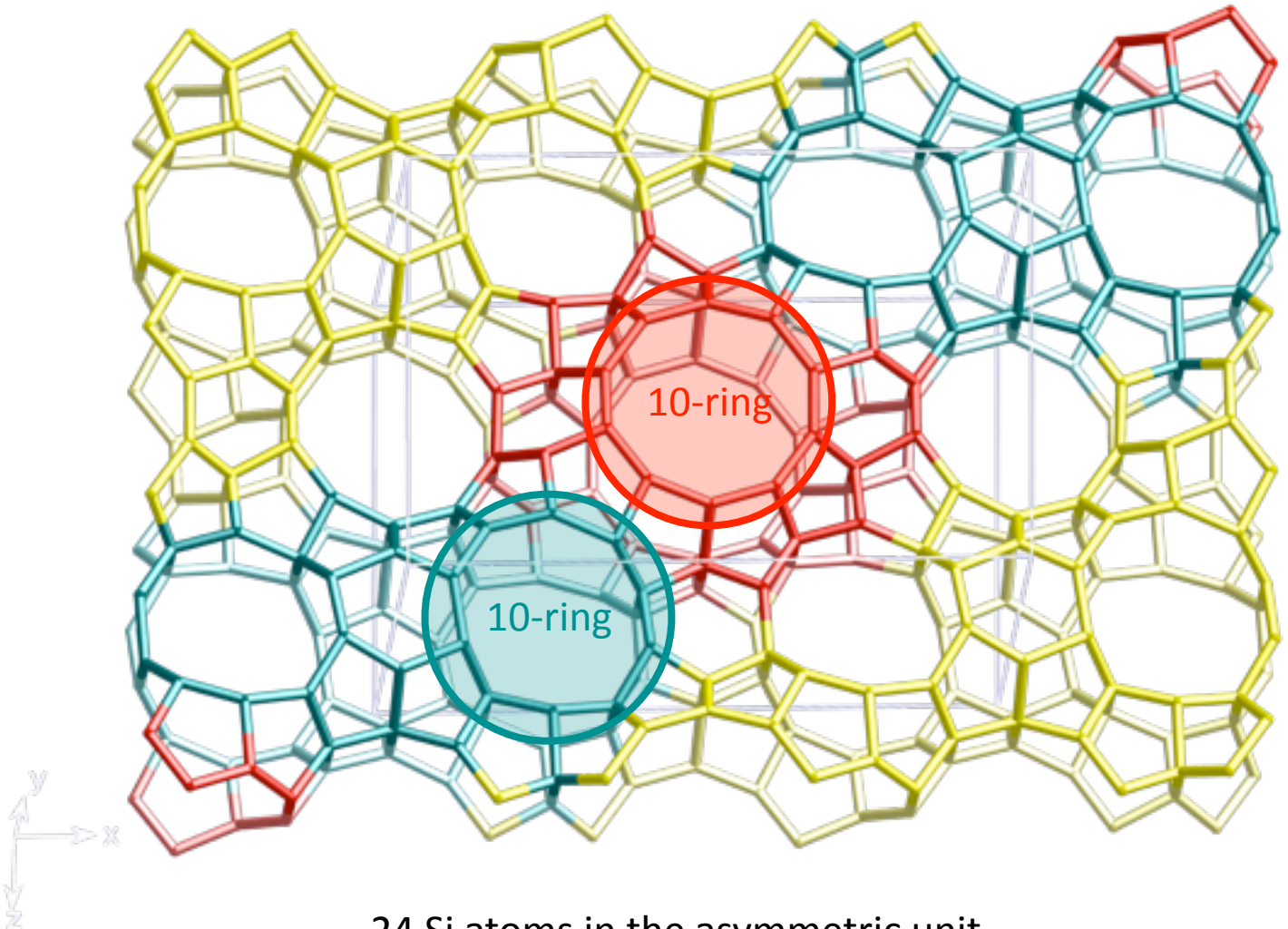


TNU-9



24 Si atoms in the asymmetric unit

TNU-9



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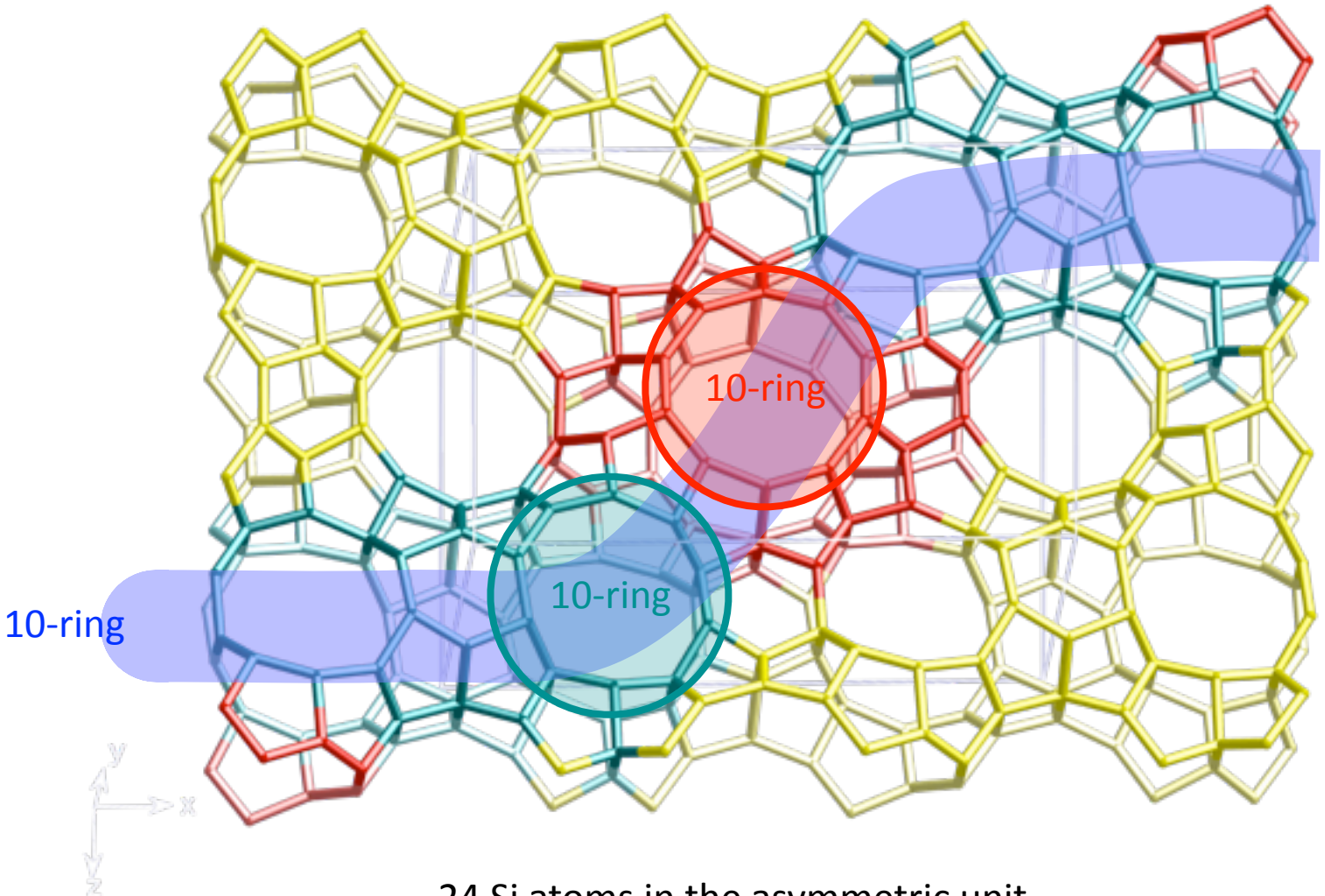


24 Si atoms in the asymmetric unit

Powder Diffraction and Electron Microscopy

a powerful combination

Introduction

- powder diffraction and electron microscopy
- structure envelope

Combinations of XPD and electron microscopy

- TNU-9 (FOCUS + HRTEM)
- IM-5 (pCF + HRTEM)
- SSZ-74 (pCF + HRTEM)

Precession electron diffraction

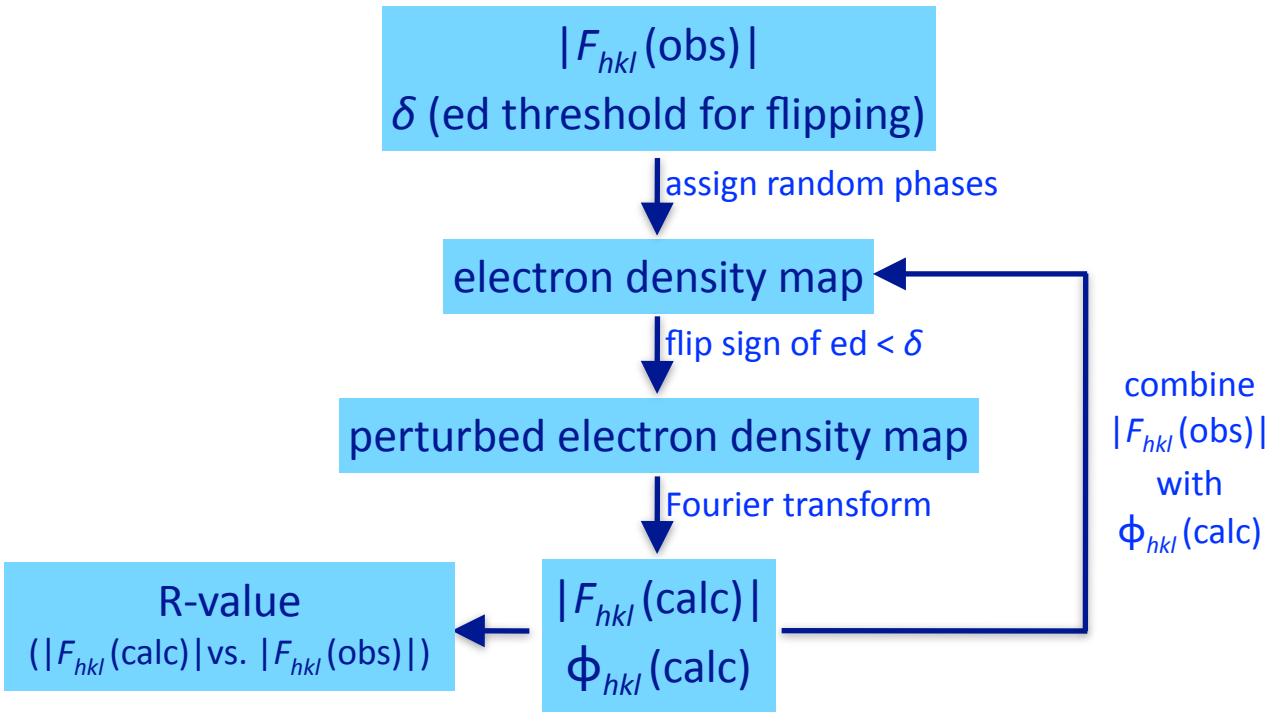
- weak reflection elimination
- phase retrieval

FAKED electron diffraction data

- SSZ-82

Conclusions

Charge flipping



G. Oszlányi and A. Sütő, *Acta Cryst*. **A60**, 134-141 (2004)

G. Oszlányi and A. Sütő, *Acta Cryst*. **A61**, 1347-1352 (2005)

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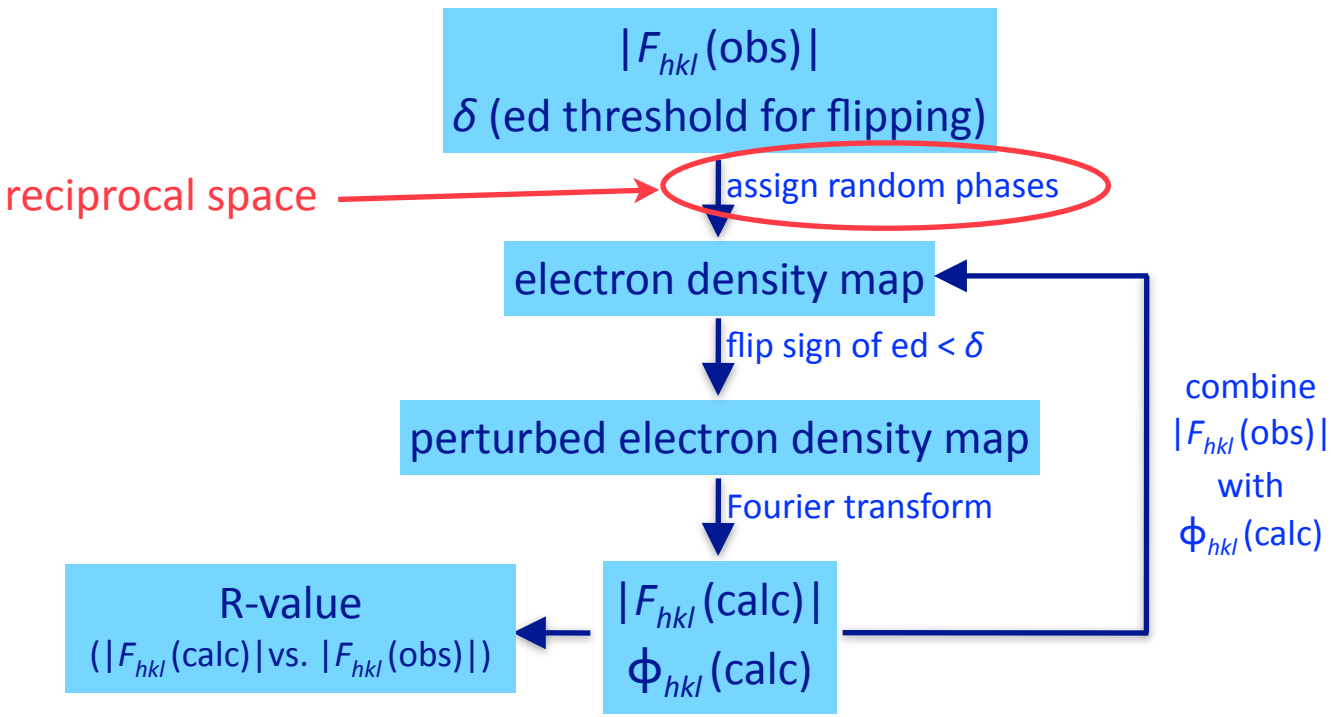

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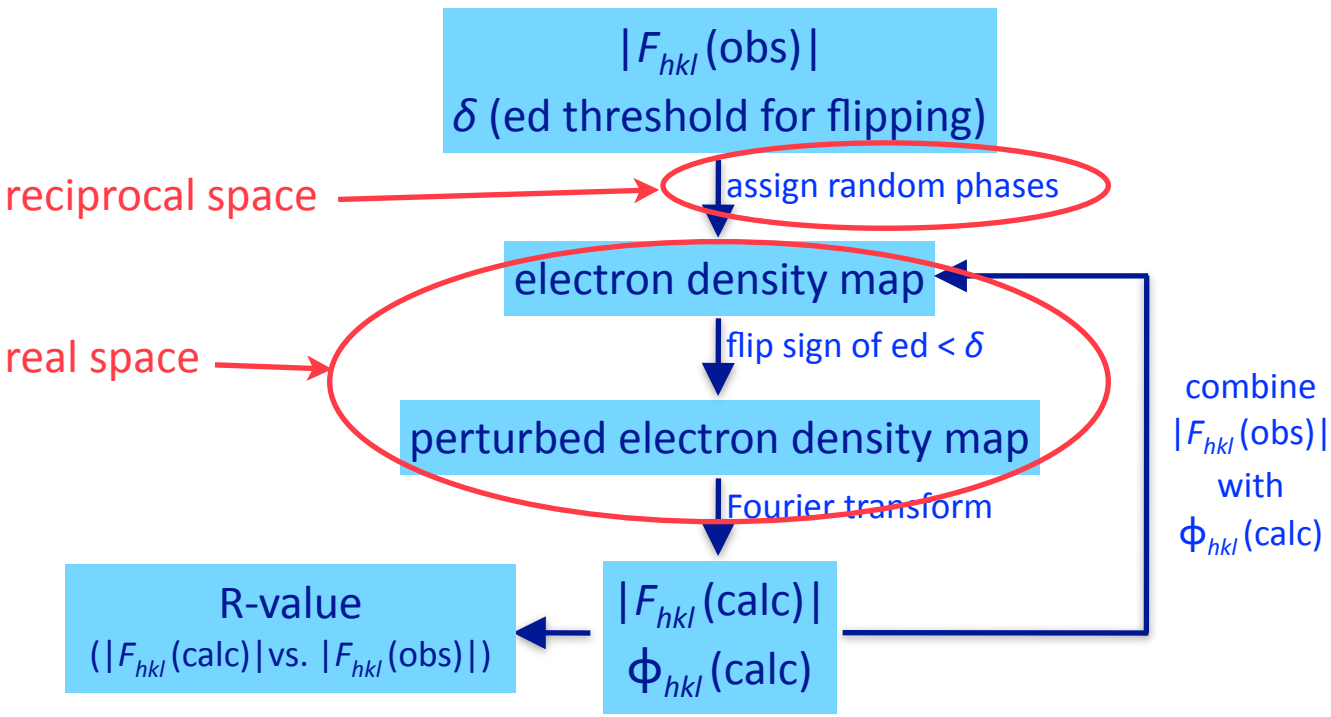

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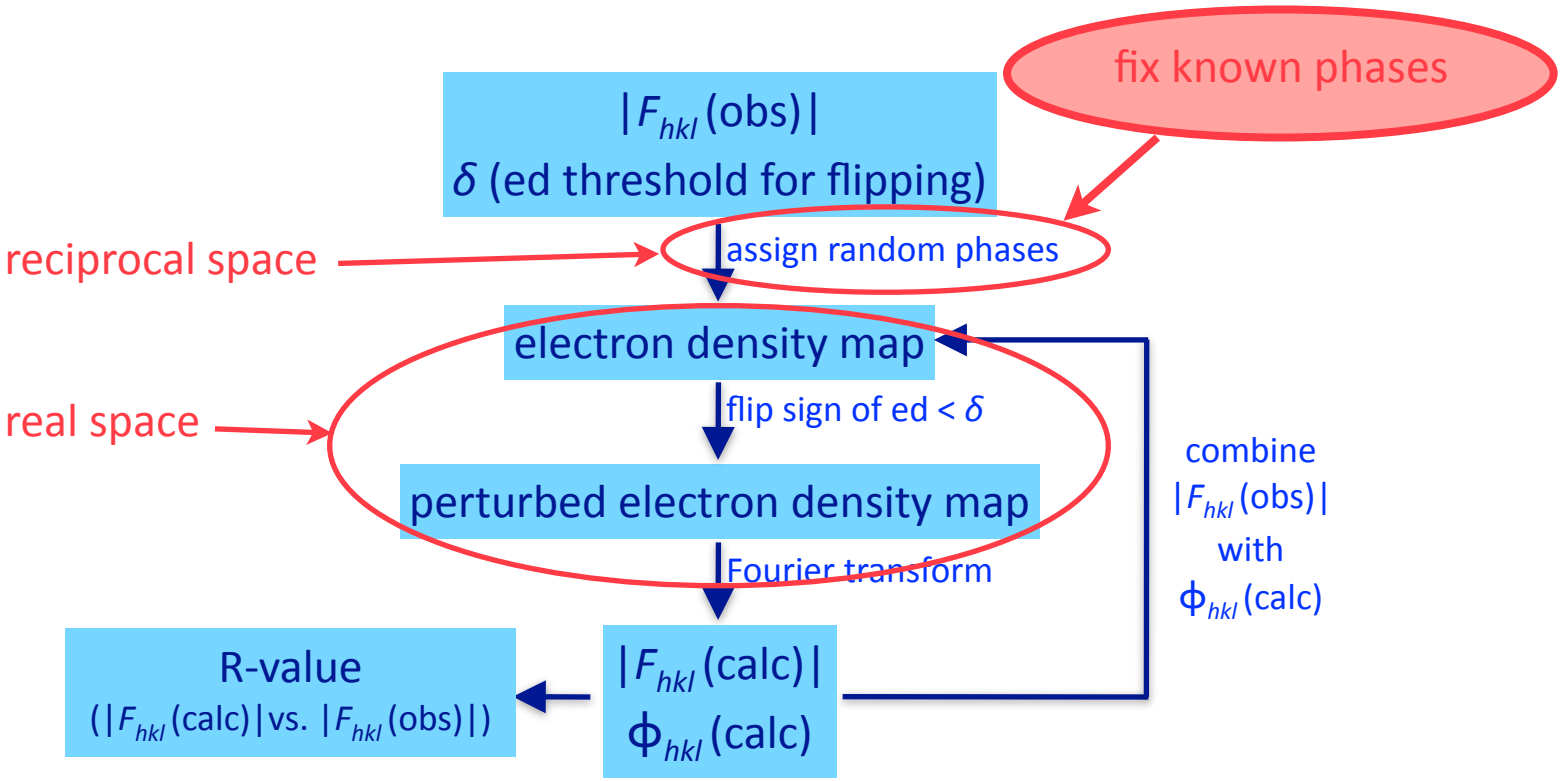

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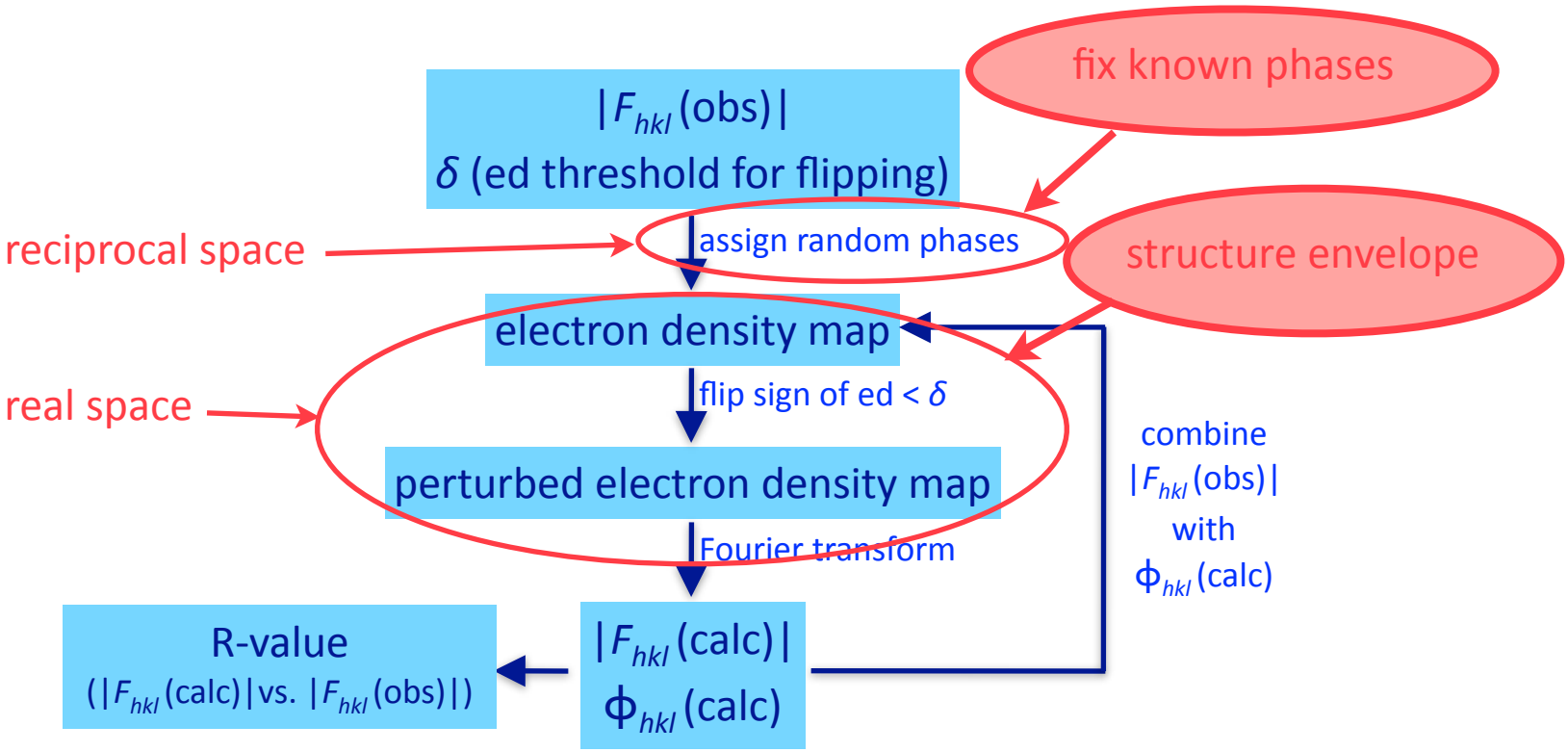

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IM-5

Unit Cell

Space Group	*Cmcm*
a	14.2088 Å
b	57.2368 Å
c	19.9940 Å

Reflections

powder pattern (d_{min} =1.05 Å)	4120
overlapping (0.3*FWHM)	3499

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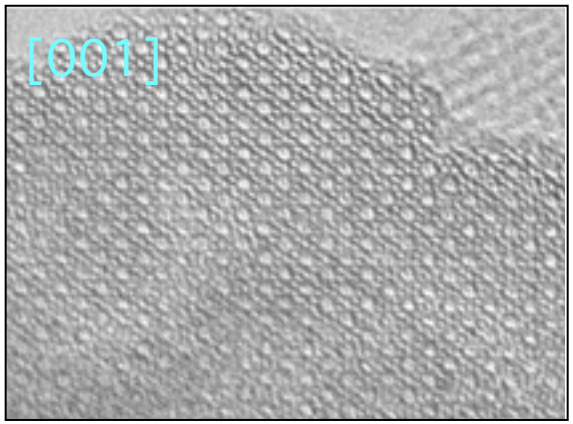
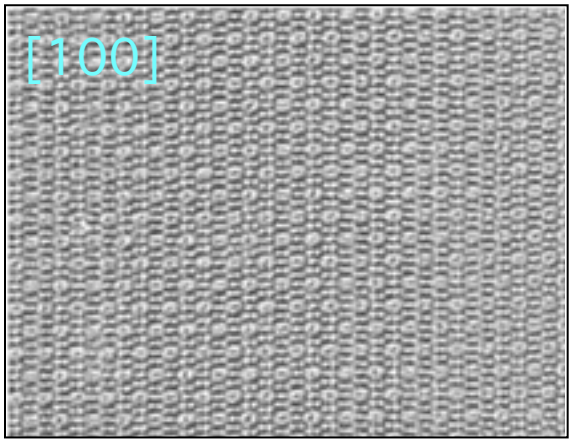
85% overlap

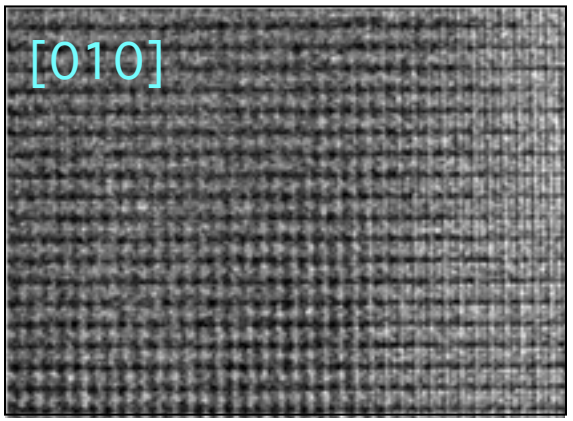
Superflip

no phases	promising, but...

IM-5

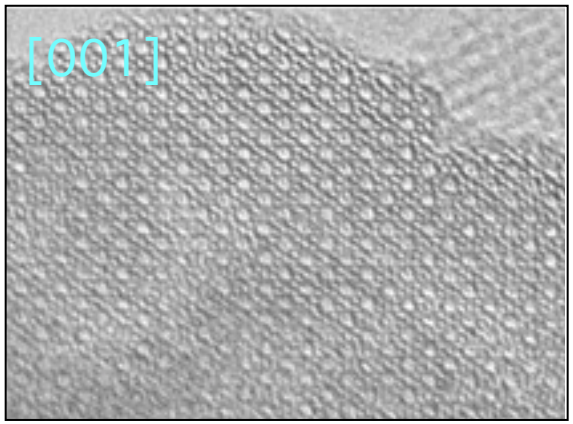


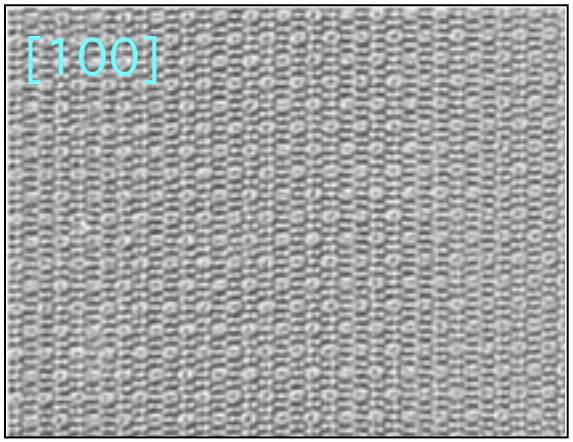


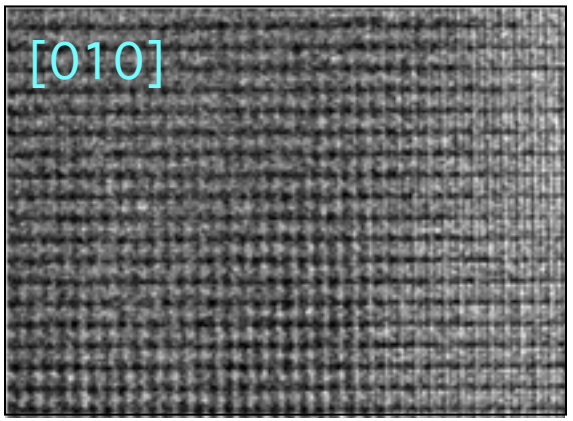


taken by Zhanbing He
Stockholm University

IM-5







taken by Zhanbing He
Stockholm University

➔ 95 phases

IM-5

introduced in Superflip → still no good solutions

IM-5

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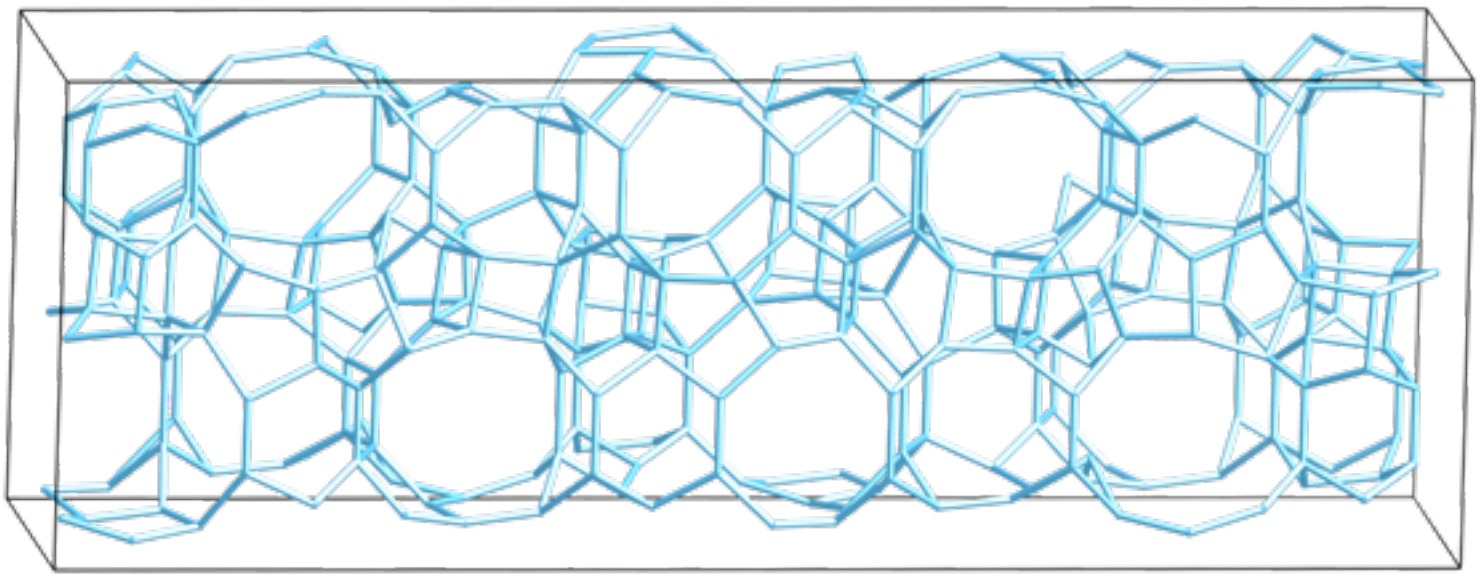
approximated model derived from HRTEM data in *C*2*cm*

IM-5

introduced in Superflip → still no good solutions

approximated model derived from HRTEM data in *C*2*cm*

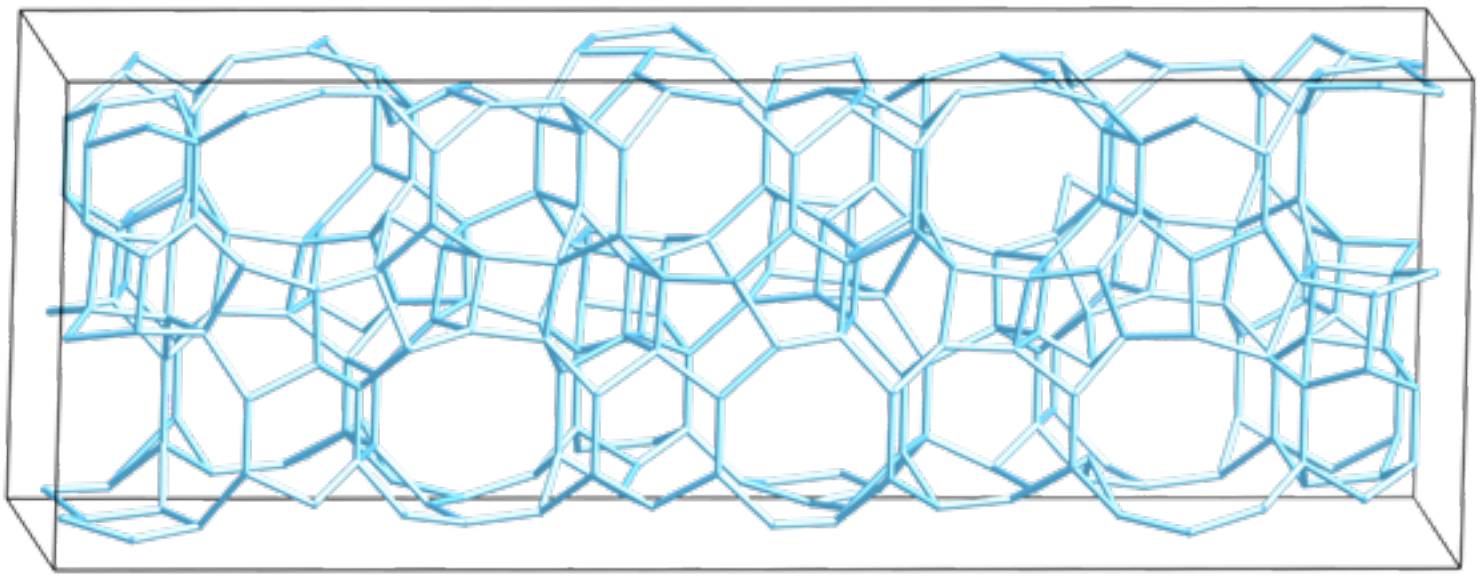


36 Si atoms

IM-5

introduced in Superflip → still no good solutions

approximated model derived from HRTEM data in *C*2*cm*



36 Si atoms

geometry strained

IM-5

introduced in Superflip → still no good solutions

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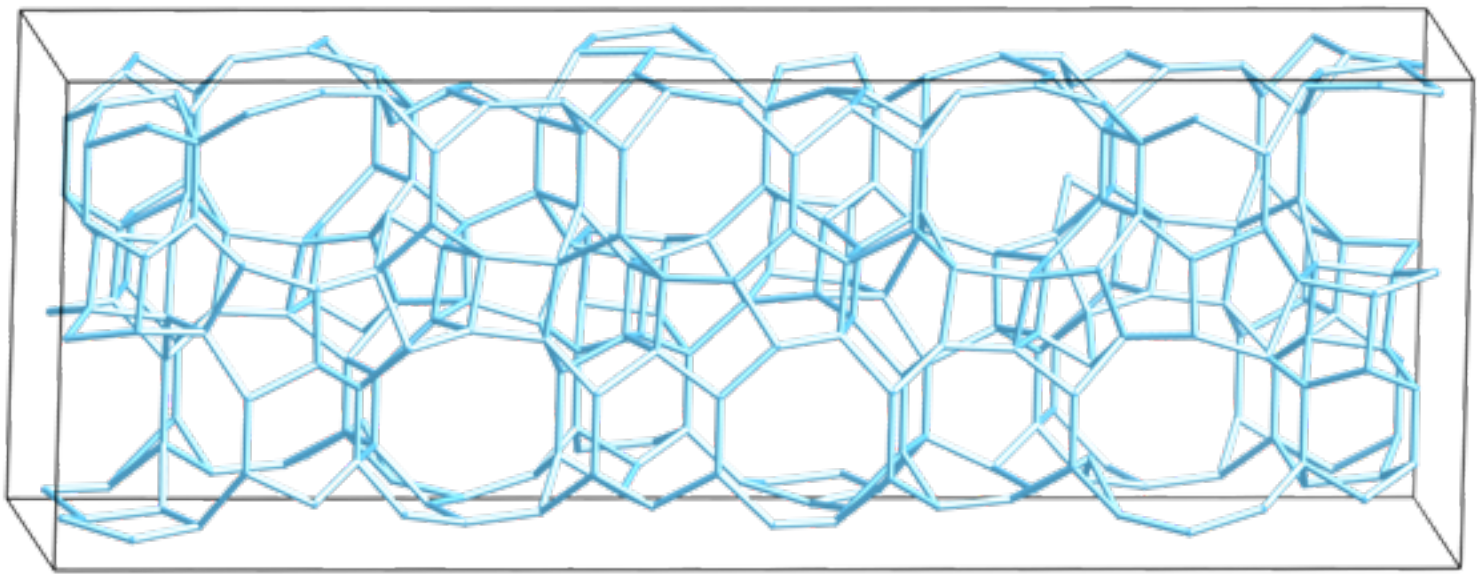

36 Si atoms

geometry strained
calculated powder diffraction pattern does not fit measured one

IM-5

IM-5

Superflip run with

IM-5

Superflip run with

1000 starting phase sets generated from HRTEM model

(each ϕ_{hkl} allowed to vary by up to 25%)

IM-5

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structure envelope used to enforce channel system

IM-5

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Five best electron density maps averaged

*C*2*cm* symmetry imposed

IM-5

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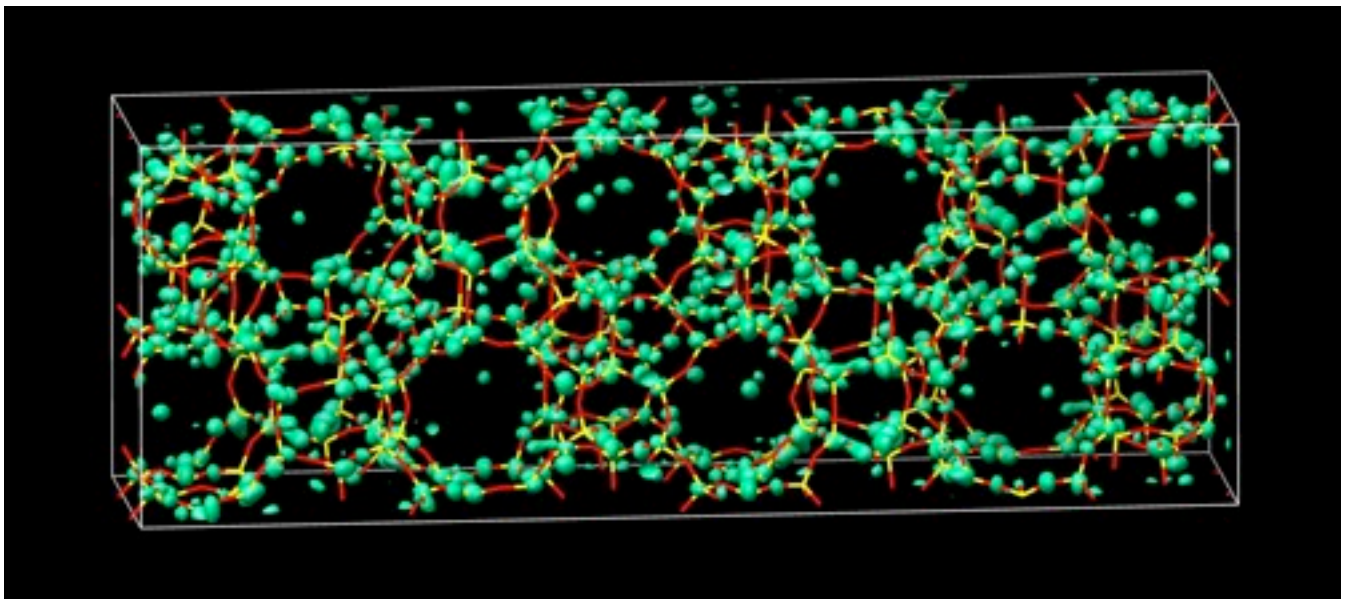

IM-5

Superflip run with

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Five best electron density maps averaged

*C*2*cm* symmetry imposed

Peaks interpreted in *C*2*cm*

geometry not strained

IM-5

Superflip run with

1000 starting phase sets generated from HRTEM model

(each ϕ_{hkl} allowed to vary by up to 25%)

structure envelope used to enforce channel system

Five best electron density maps averaged

*C*2*cm* symmetry imposed

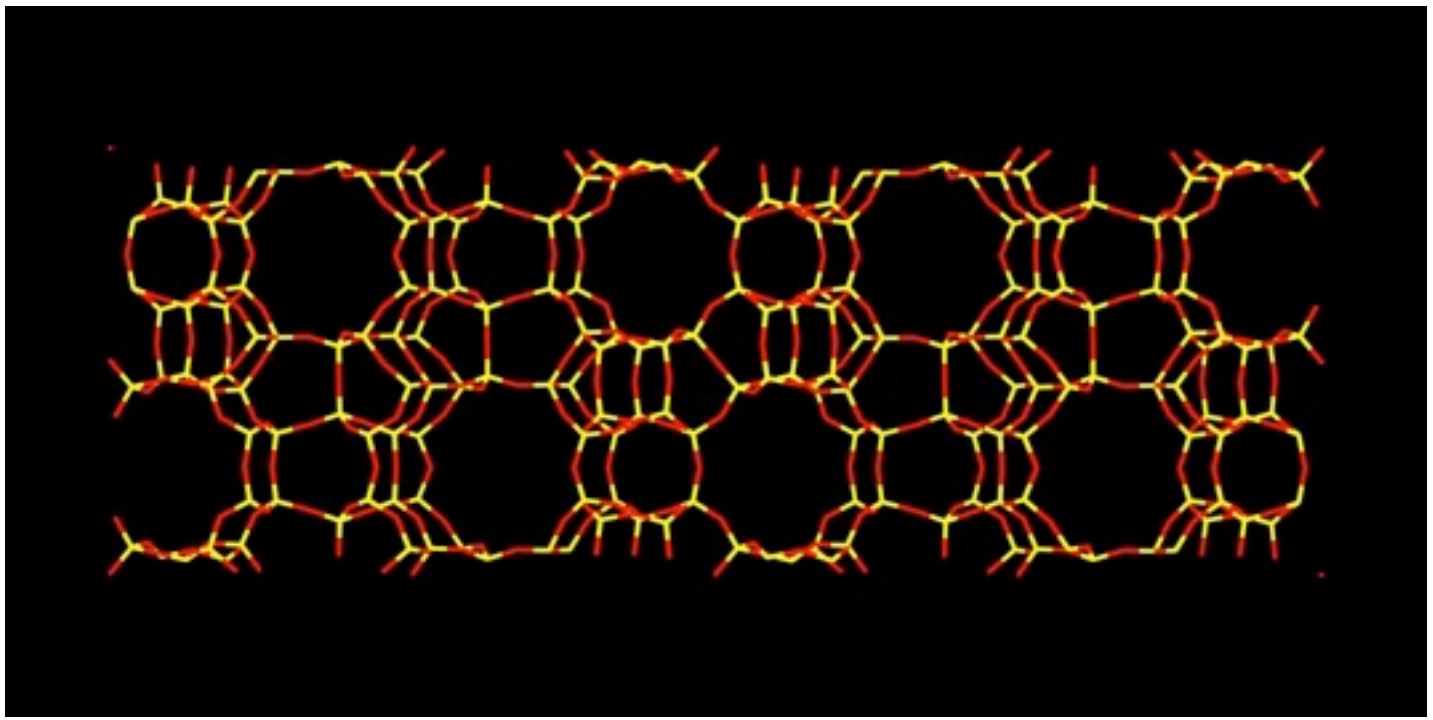
Peaks interpreted in *C*2*cm*

geometry not strained

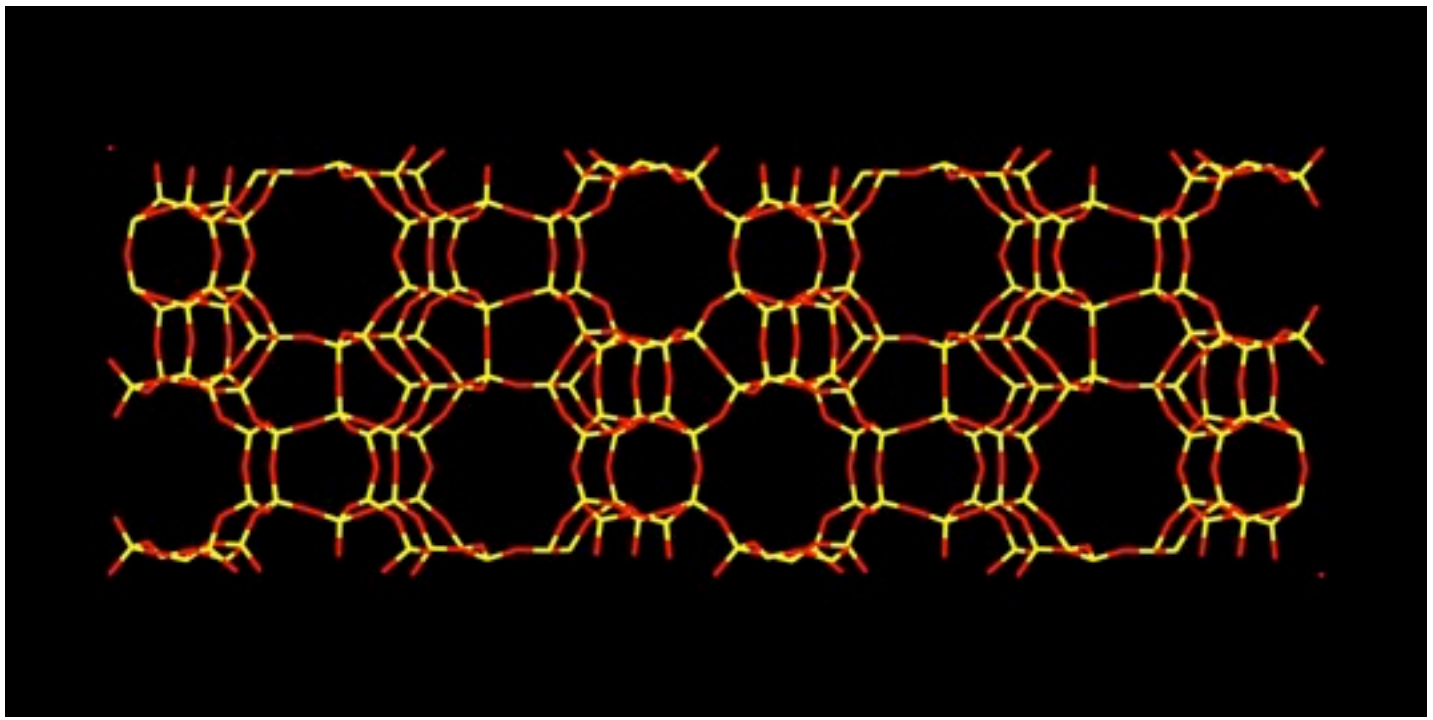
main features of powder pattern reproduced

Structure successfully refined in *Cmcm*

IM-5

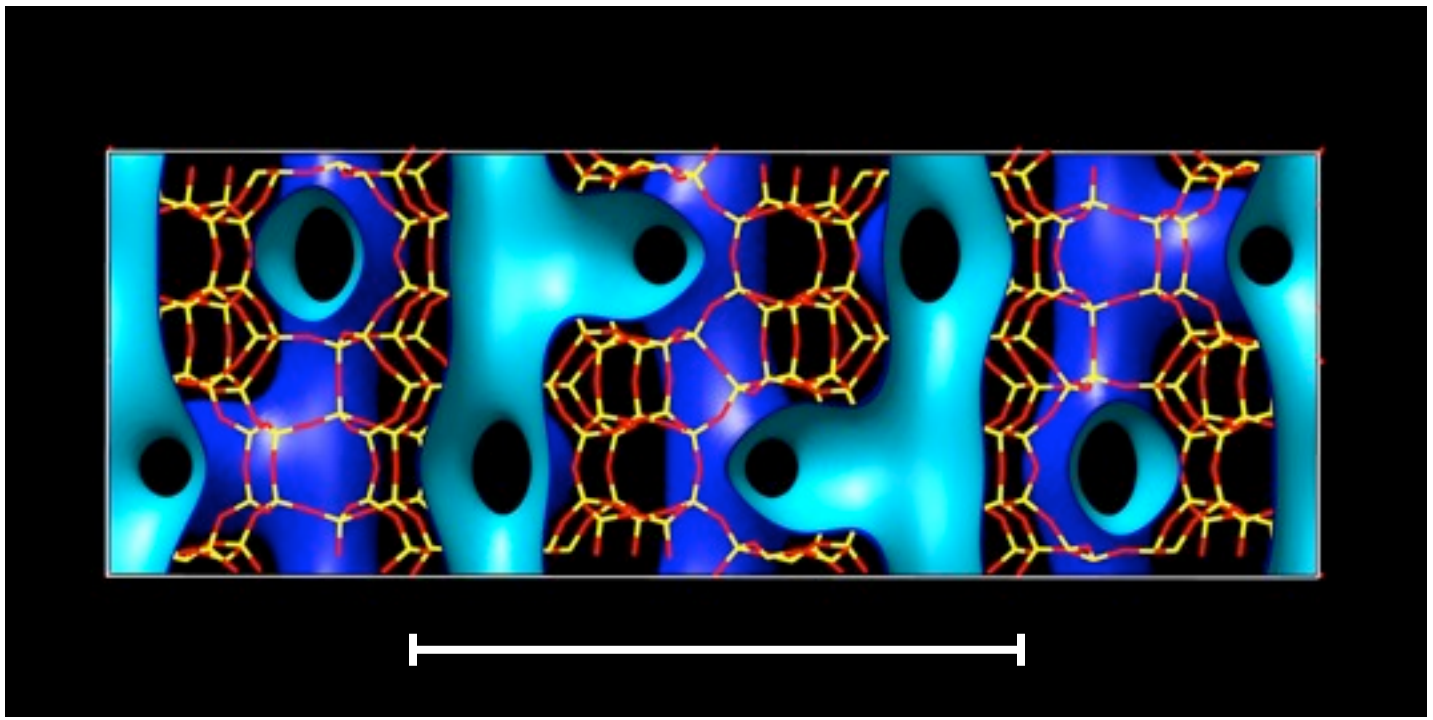


IM-5



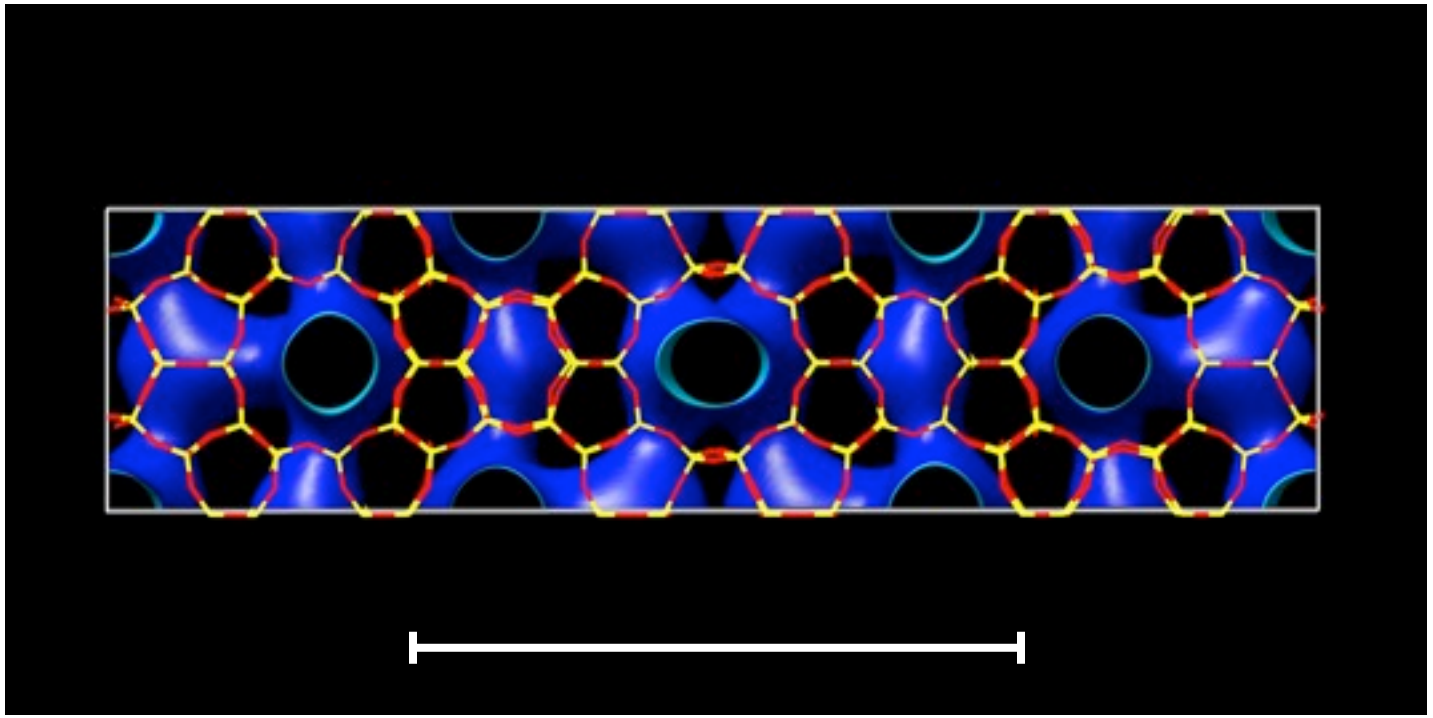
24 Si-atoms in the asymmetric unit

IM-5



24 Si-atoms in the asymmetric unit
unusual 2-dimensional 10-ring channel system

IM-5



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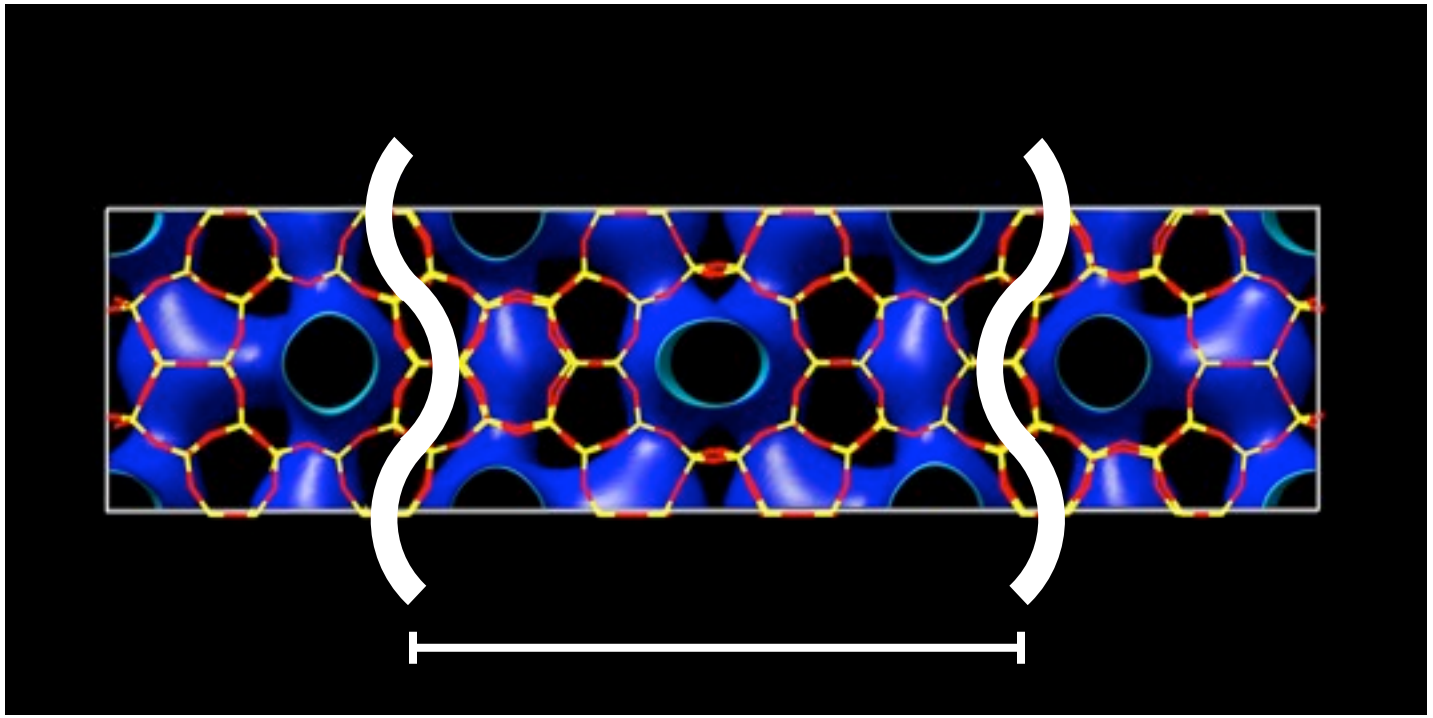

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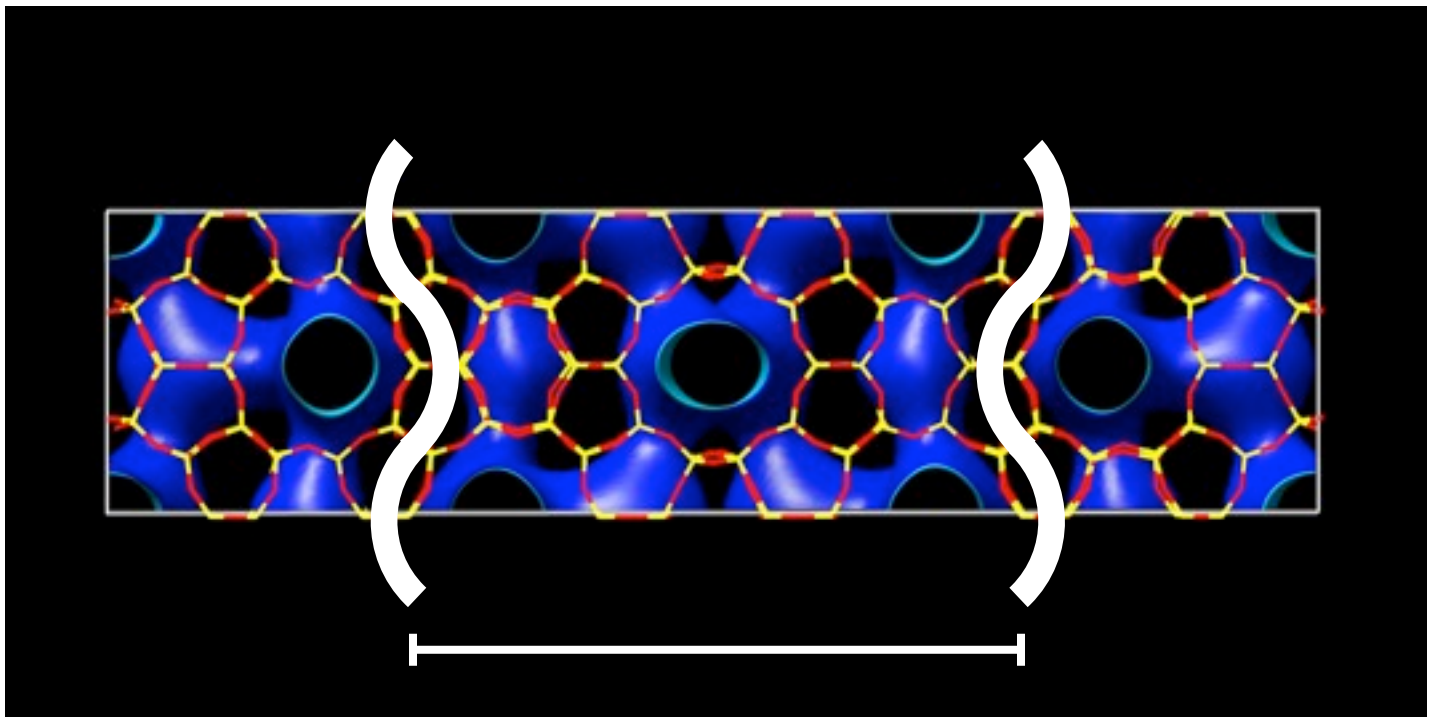

24 Si-atoms in the asymmetric unit
unusual 2-dimensional 10-ring channel system
288 Si and 576 O = 864 atoms in the unit cell

SSZ-74

Unit Cell	
Space Group	*C*2/*c* or *Cc*
a	20.507 Å
b	13.394Å
c	20.099 Å
β	102.2˚
Reflections	
powder pattern (d_{min} = 0.95 Å)	3258
overlapping (0.3*FWHM)	2717

SSZ-74

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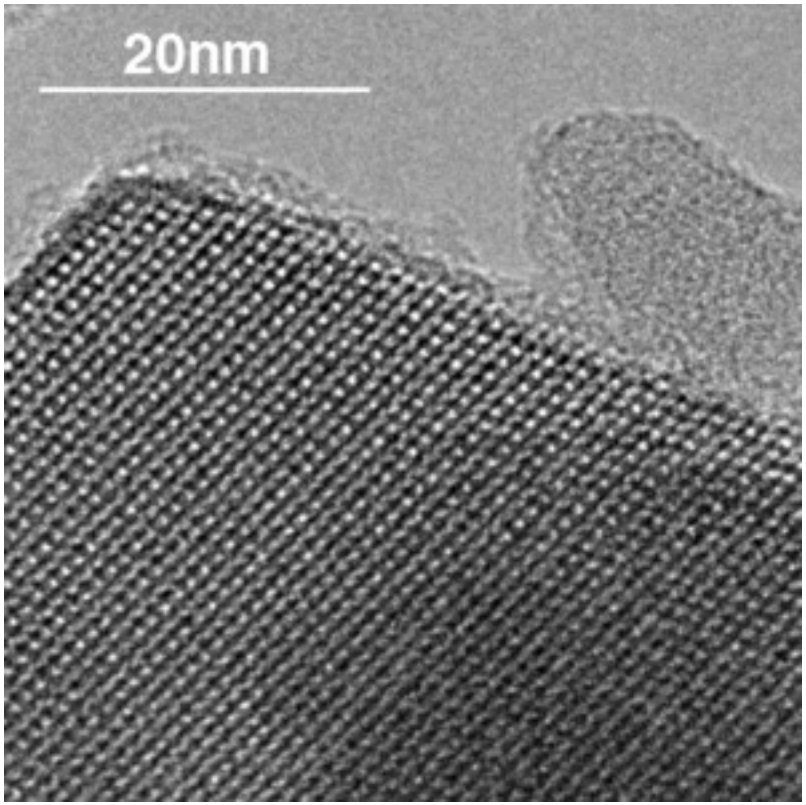
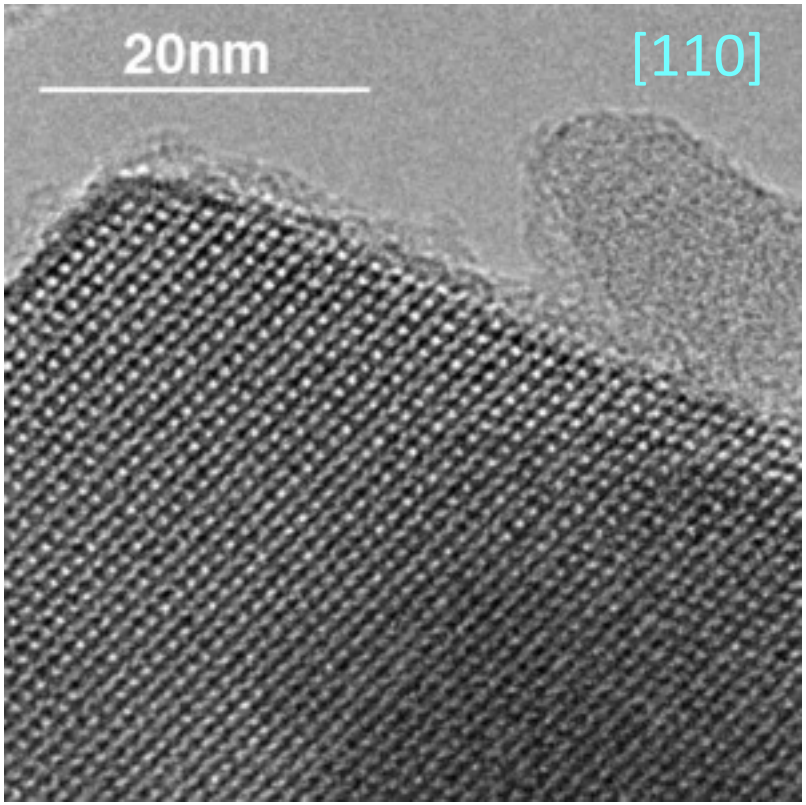
overlapping (0.3*FWHM)	2717

83% overlap

SSZ-74

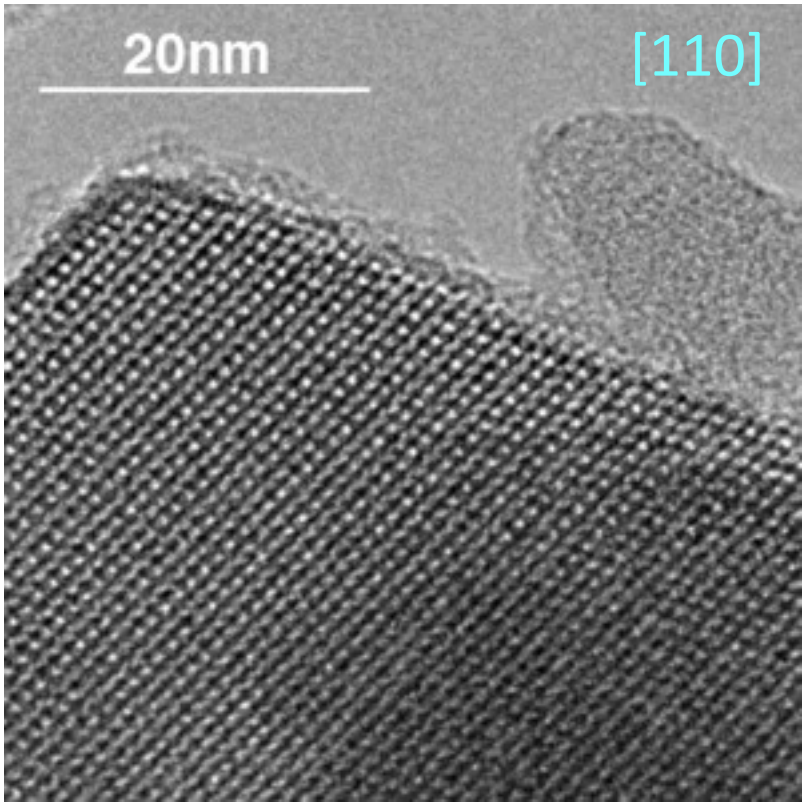


SSZ-74



HRTEM

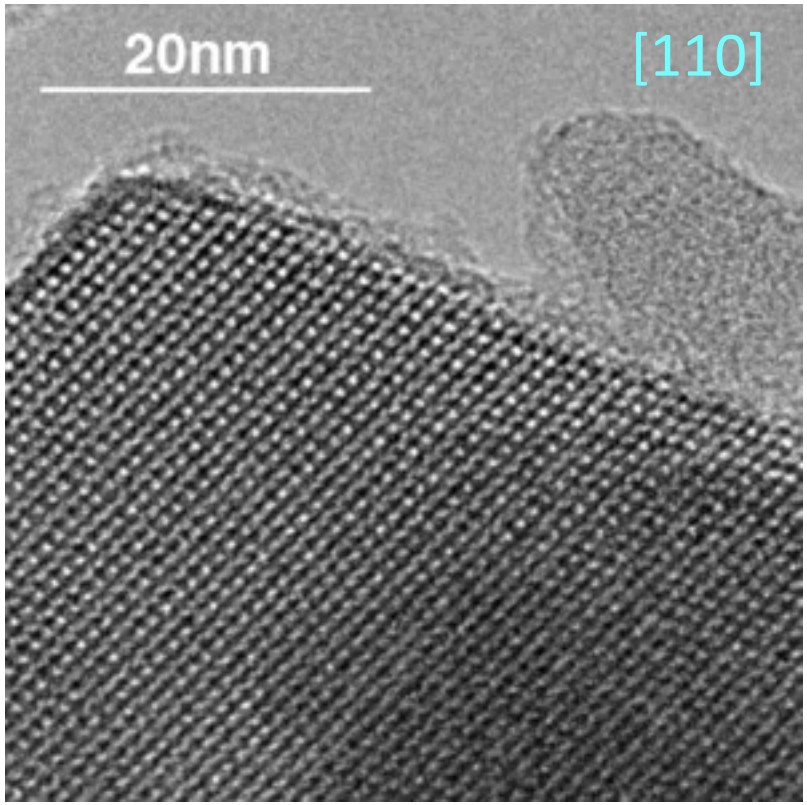
SSZ-74

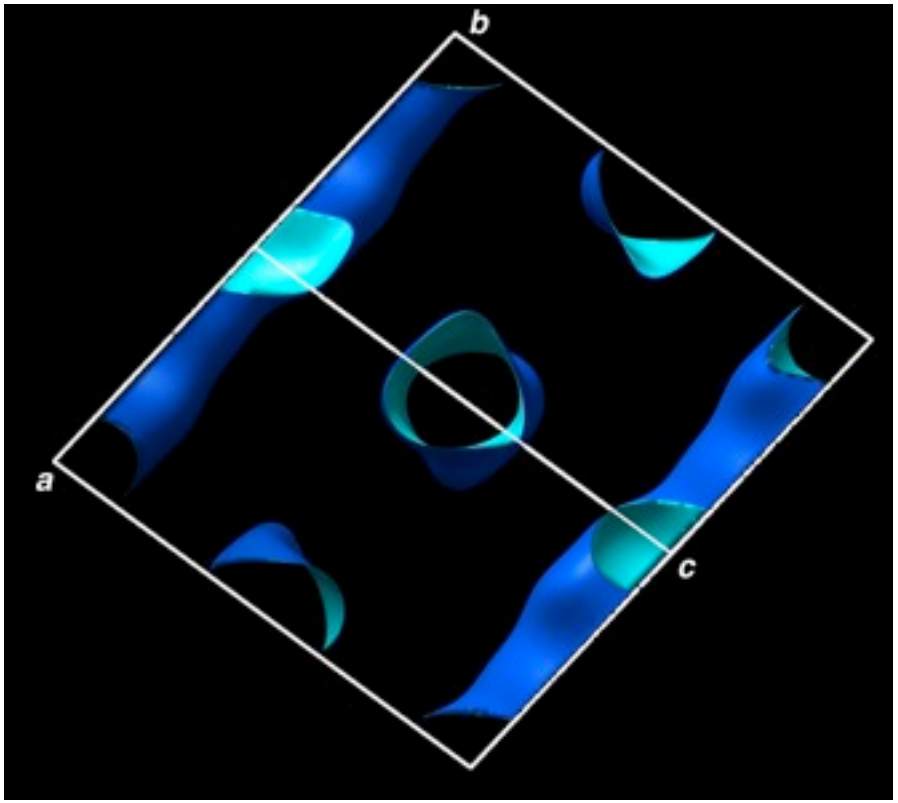


HRTEM

29 reflections

SSZ-74

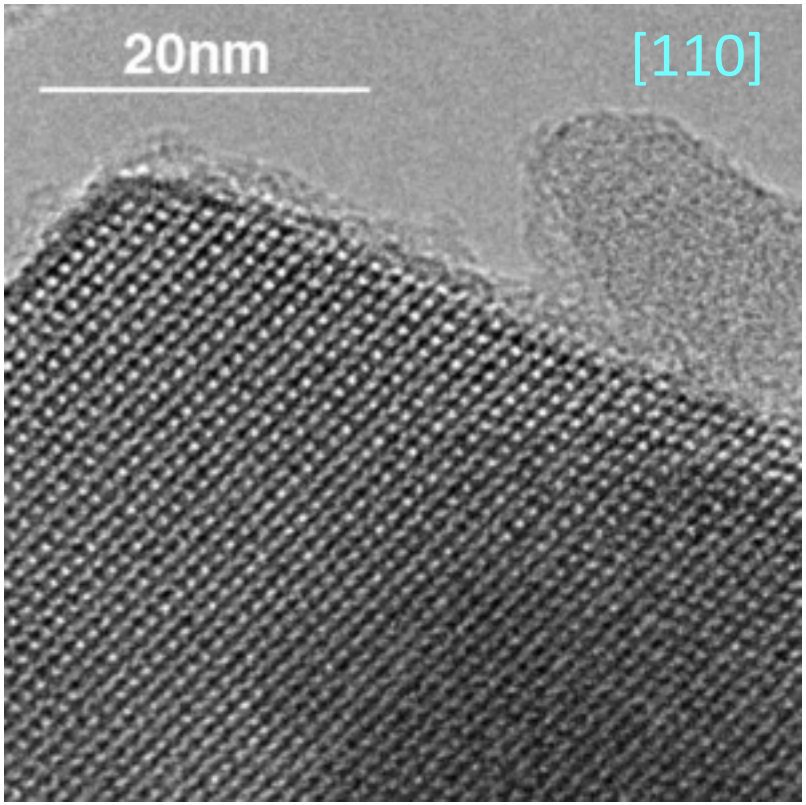


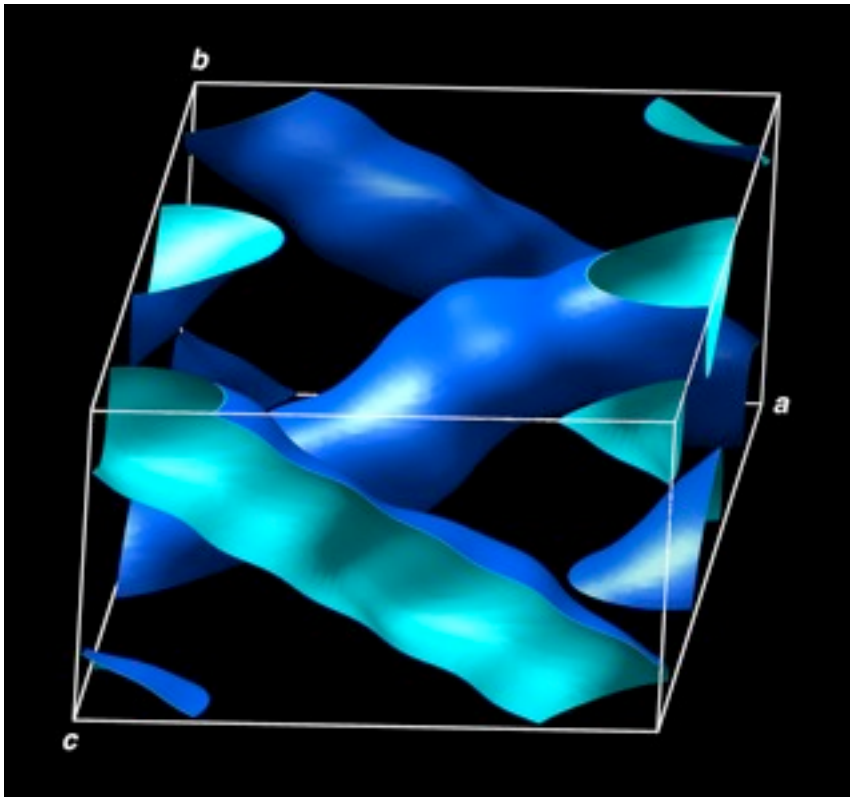


HRTEM

29 reflections → structure envelope

SSZ-74





HRTEM

29 reflections → structure envelope

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Superflip	
with structure envelope	partial solution

SSZ-74

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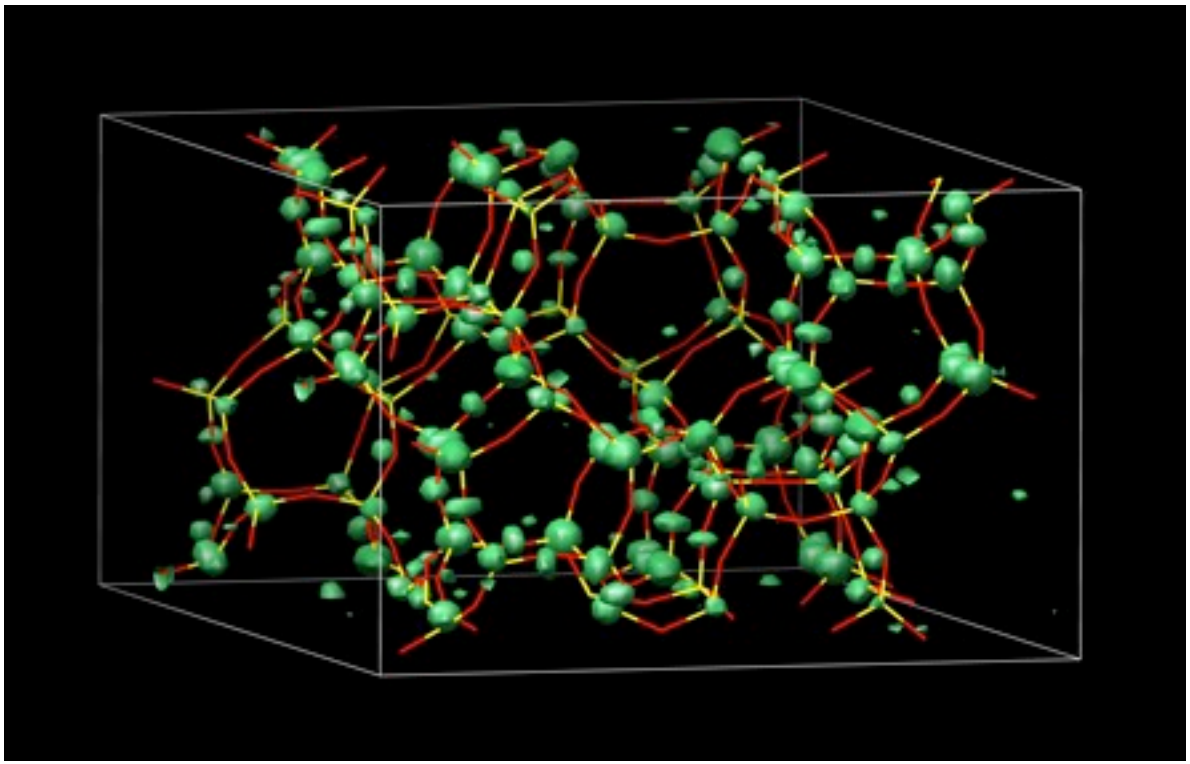
overlapping (0.3*FWHM)	2717
Superflip	
with structure envelope	partial solution
above used as seed for 100 phase sets	

SSZ-74

Superflip



SSZ-74

Superflip

SSZ-74

Superflip

symmetry ambiguous, *C*2/*c* assumed

SSZ-74

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Structure solution gave the right answer!

Powder Diffraction and Electron Microscopy

a powerful combination

Introduction

- powder diffraction and electron microscopy
- structure envelope

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- TNU-9 (FOCUS + HRTEM)
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➡ Precession electron diffraction

- weak reflection elimination
- phase retrieval

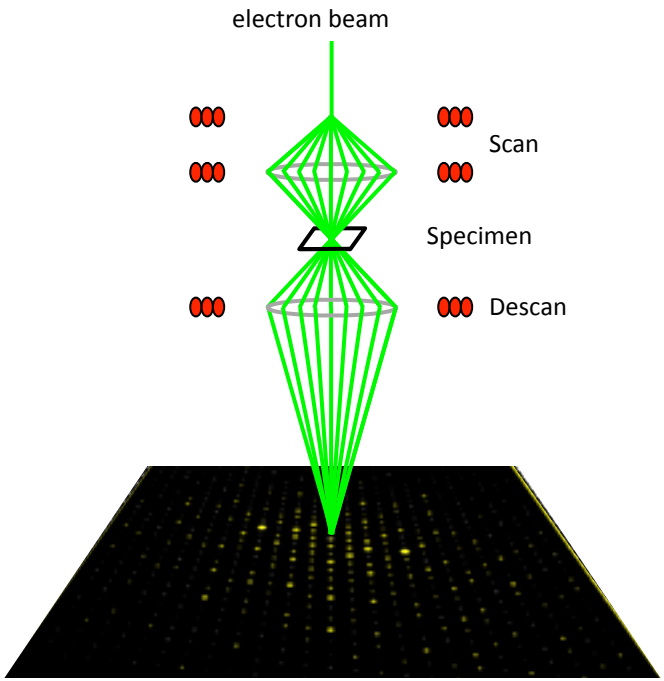
FAKED electron diffraction data

- SSZ-82

Conclusions

Electron Diffraction

Precession electron diffraction



R. Vincent and P. Midgley, Ultramicroscopy 53, 271-281 (1994)

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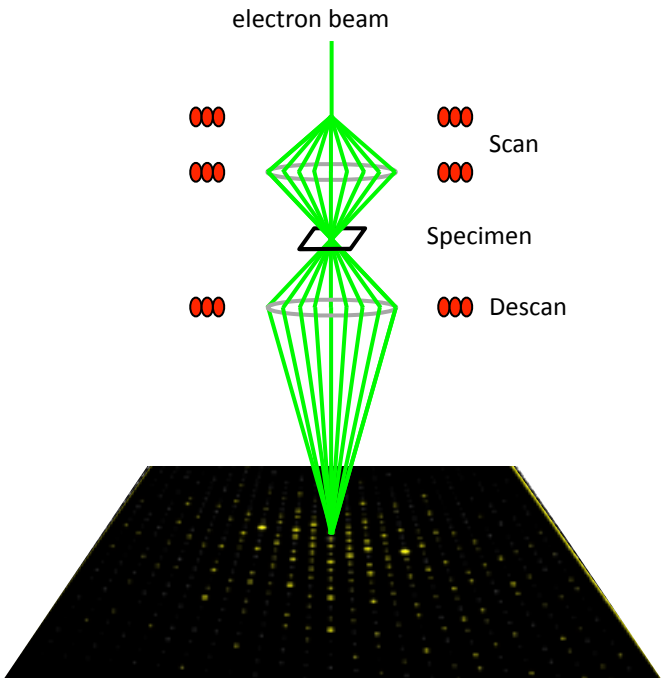

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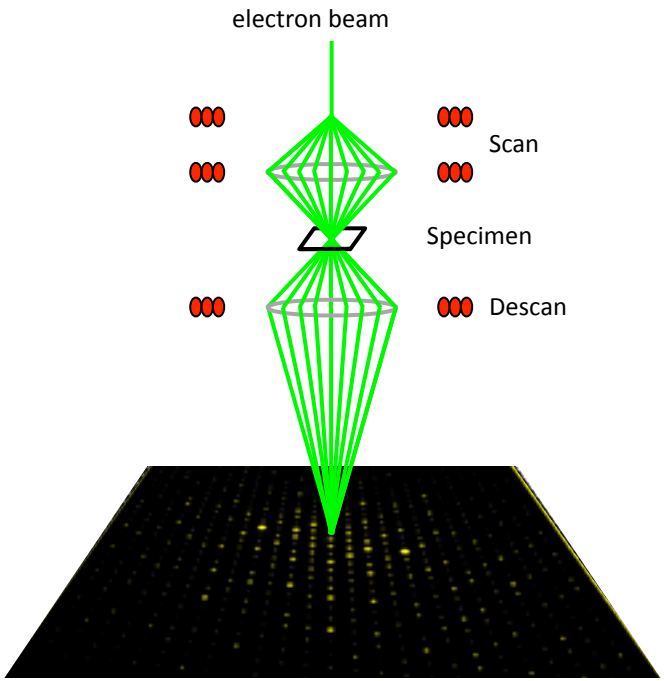

R. Vincent and P. Midgley, Ultramicroscopy 53, 271-281 (1994)

reduced multiple scattering
➔ intensities more reliable

X-ray Powder and Electron Diffraction

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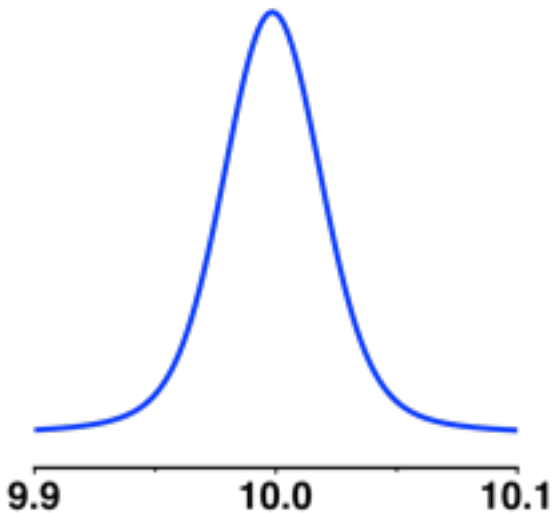

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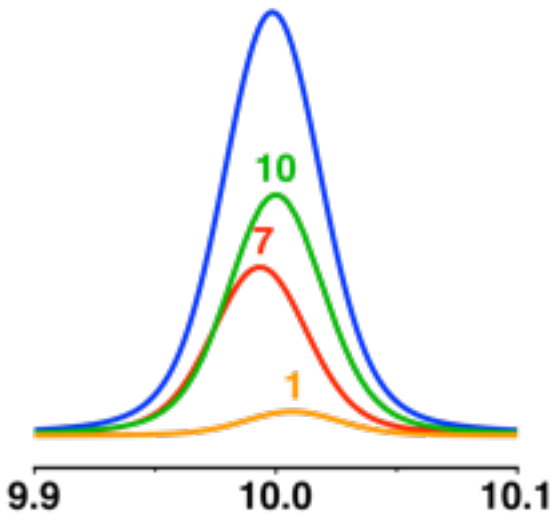

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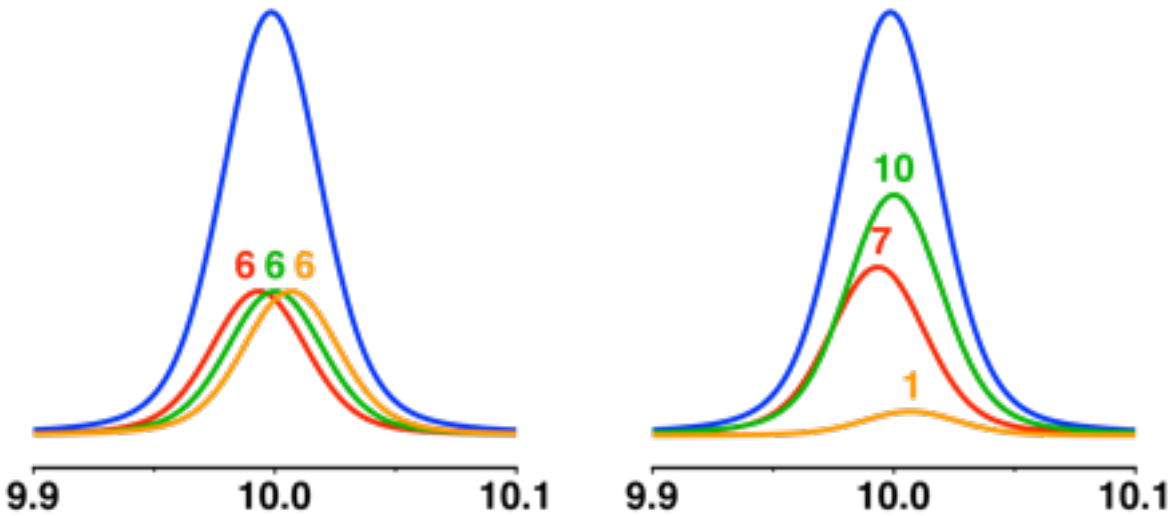

Equipartitioned

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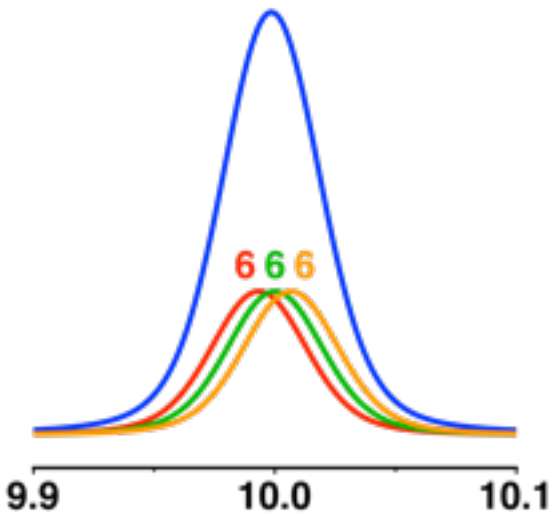

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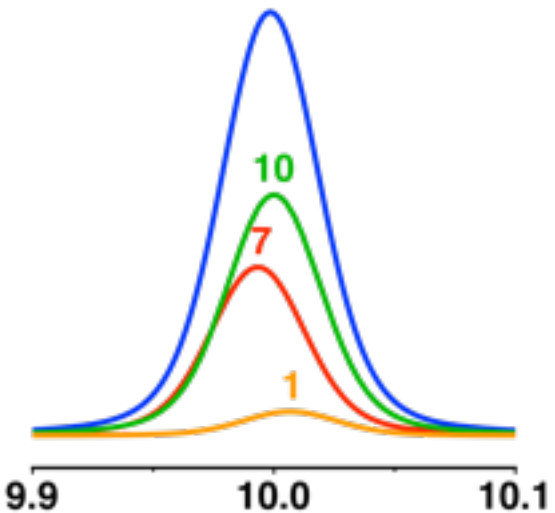

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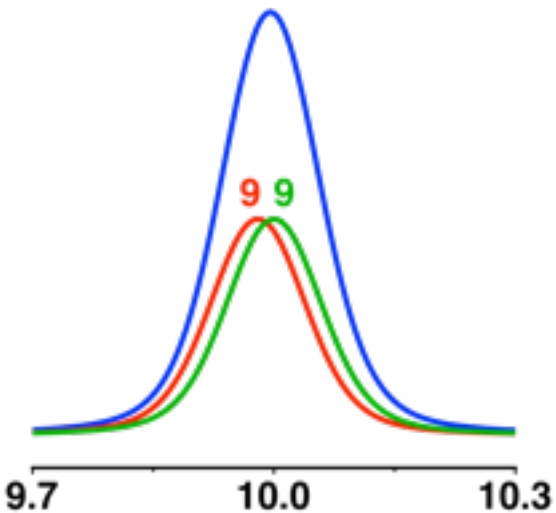

WRE

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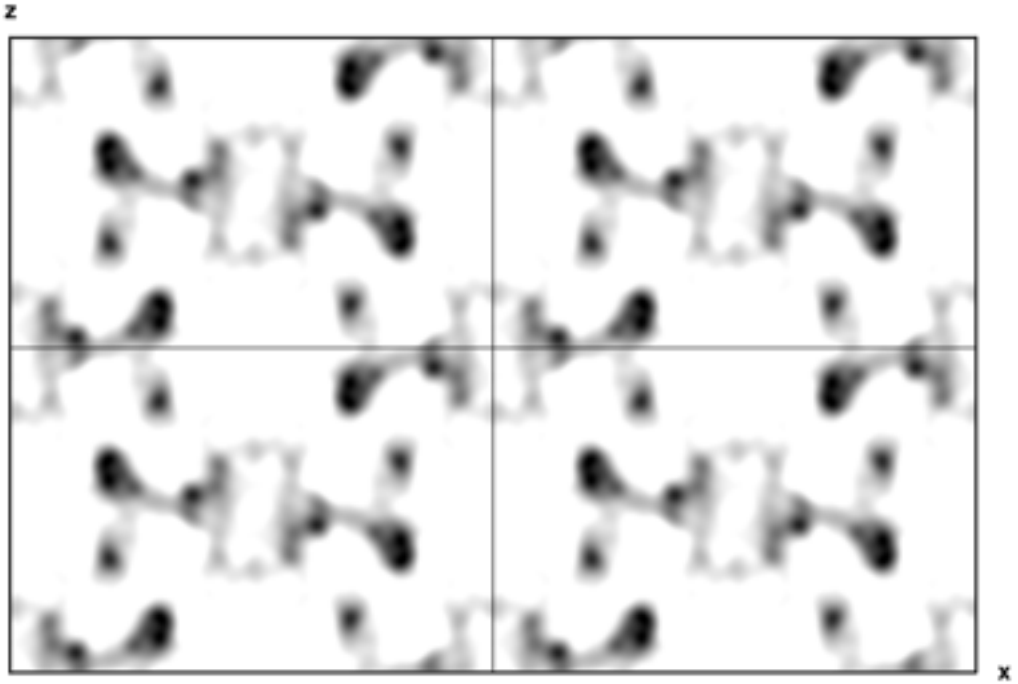

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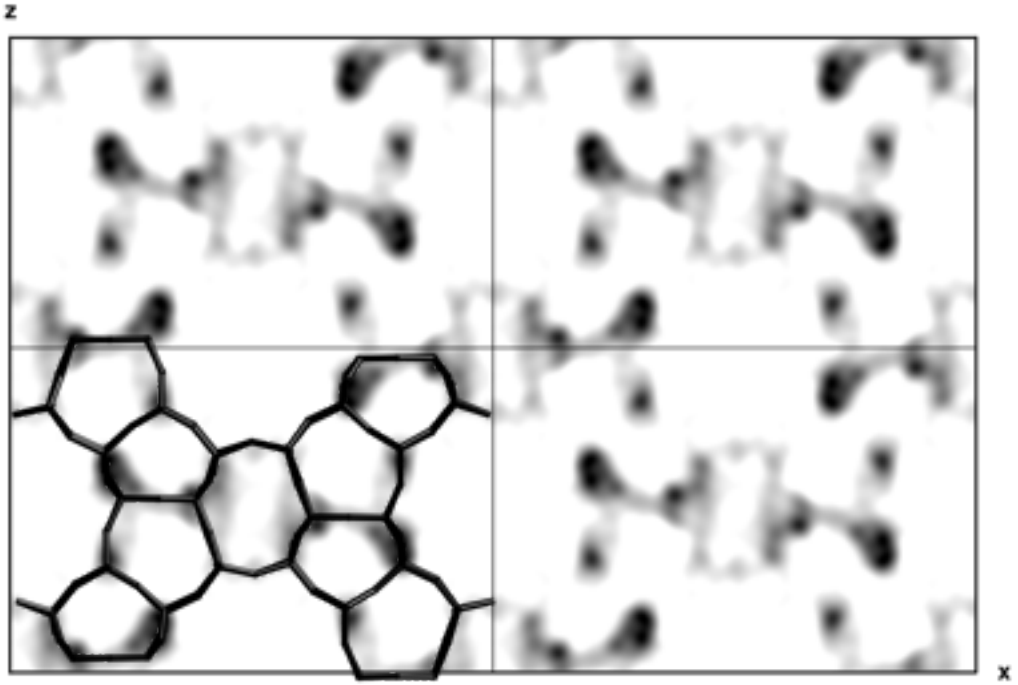

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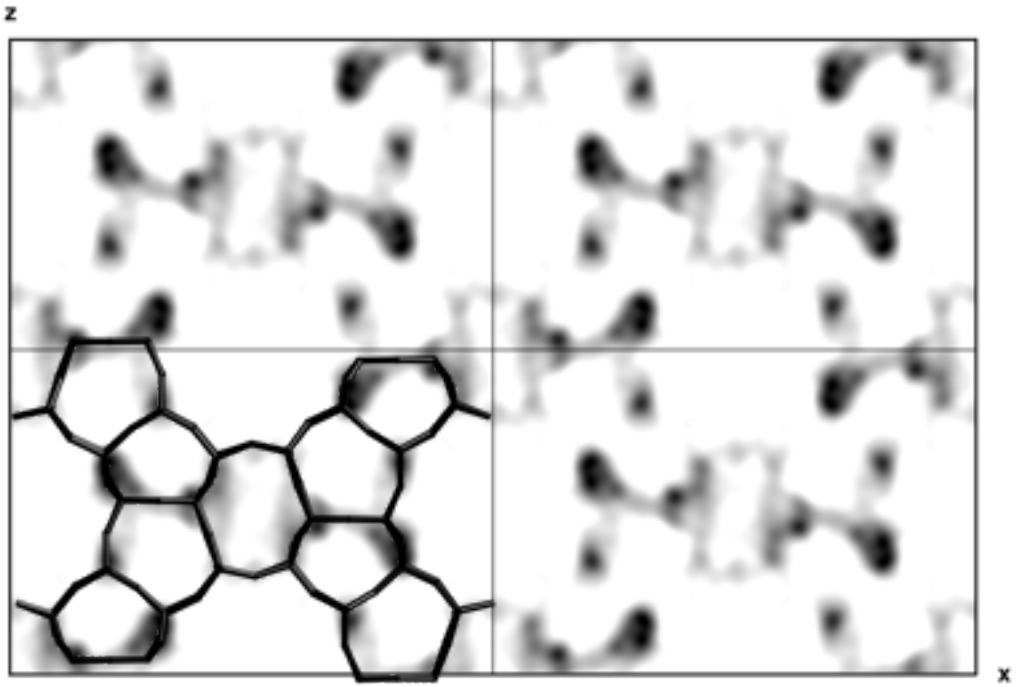

PED amplitudes
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Phases are almost as good as those from HRTEM, but easier to obtain

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FAKED electron diffraction

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2D-XPD

2D-XPD: Zeolite TNU-9

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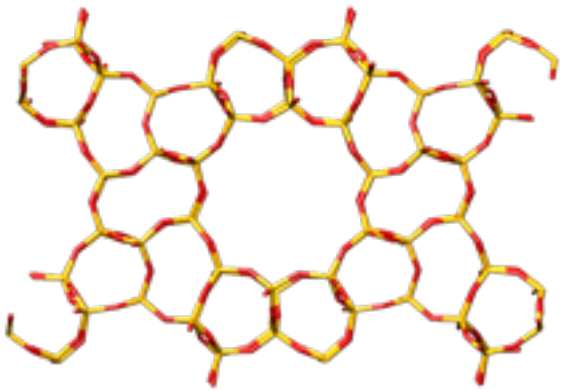

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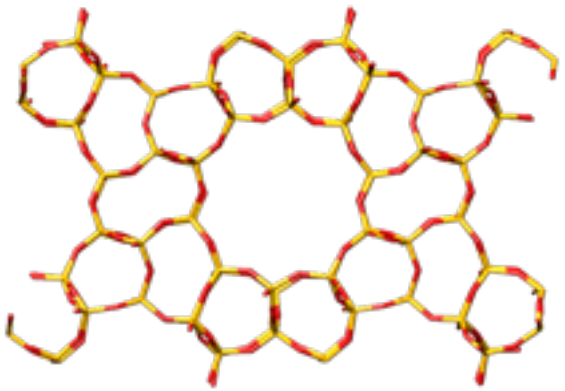

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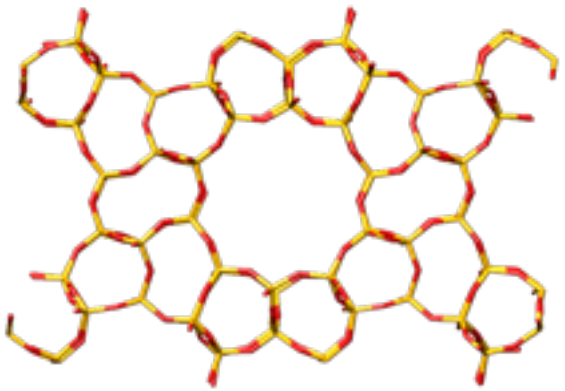

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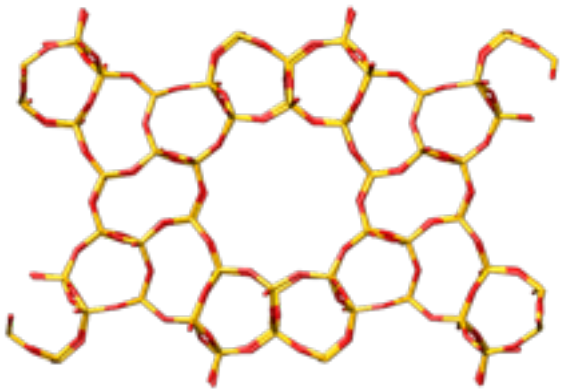

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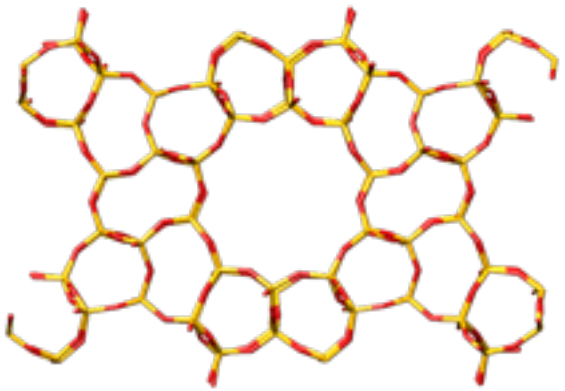

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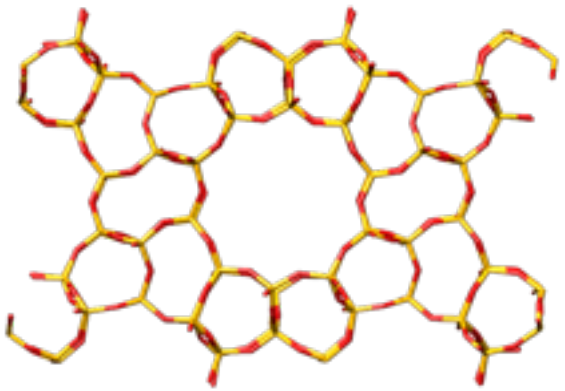

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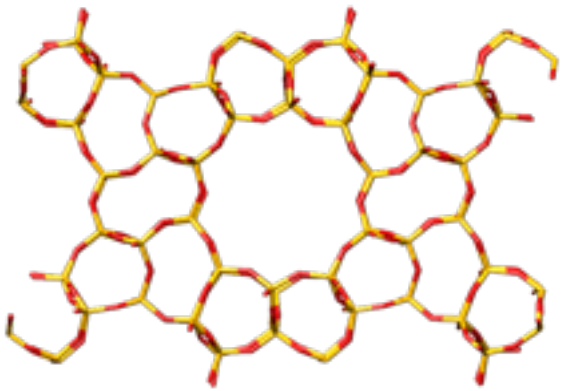

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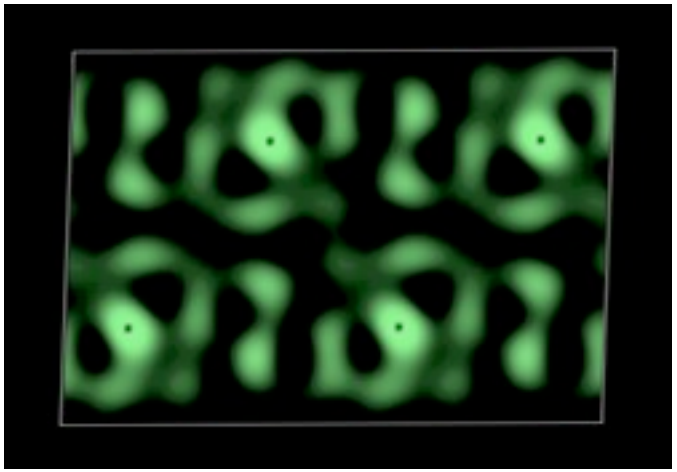

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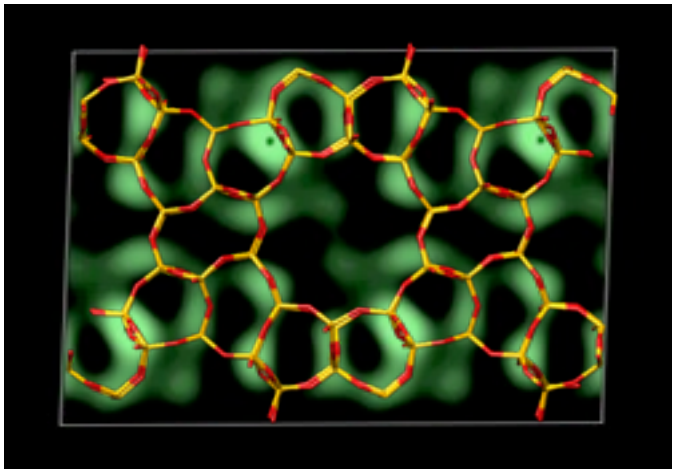

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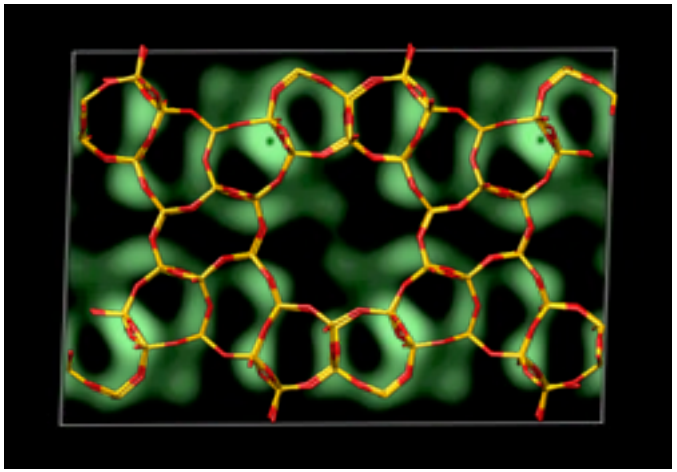
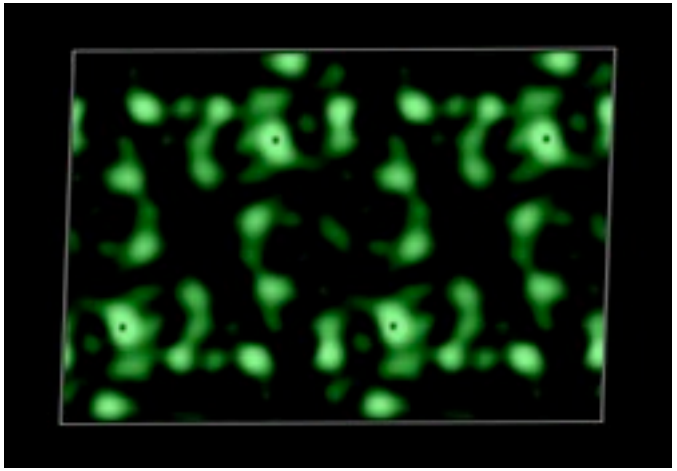


1.5Å



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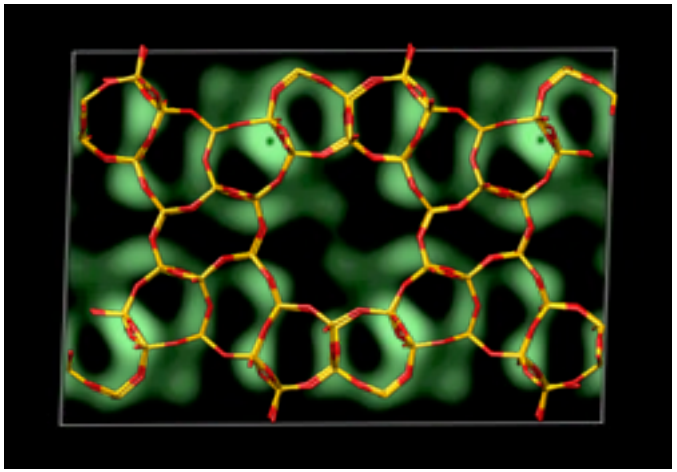

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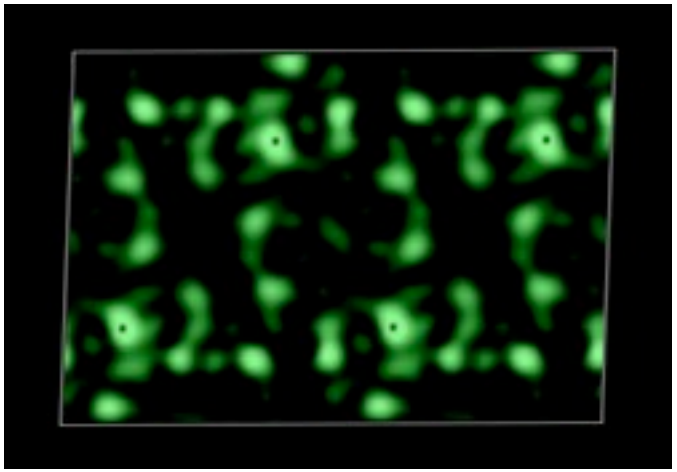

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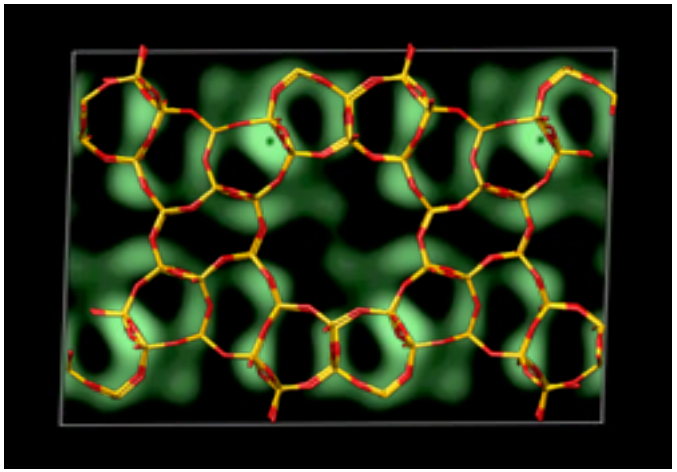

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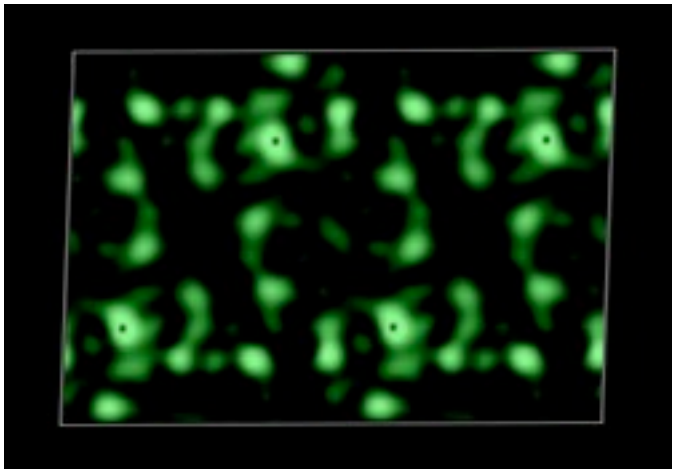

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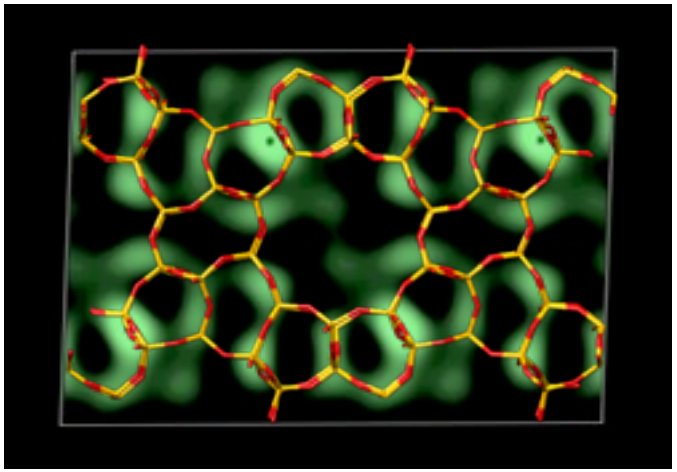

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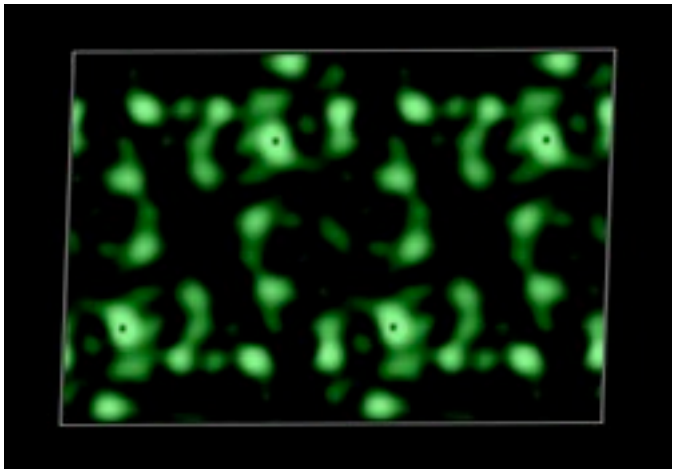

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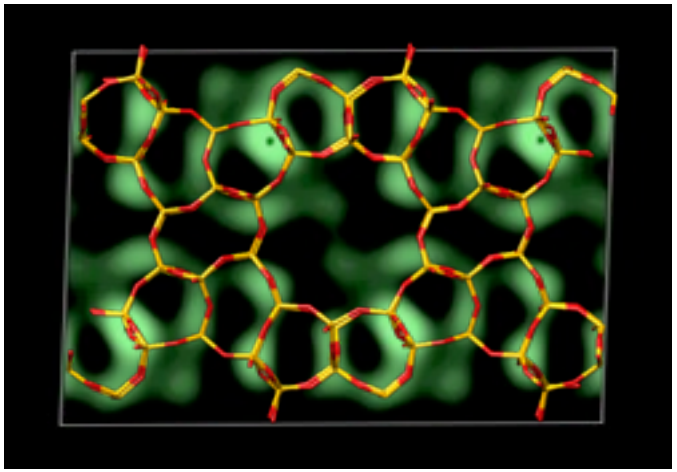

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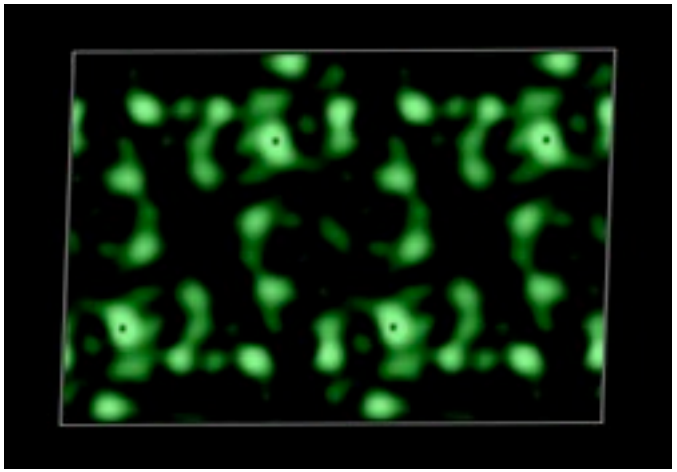

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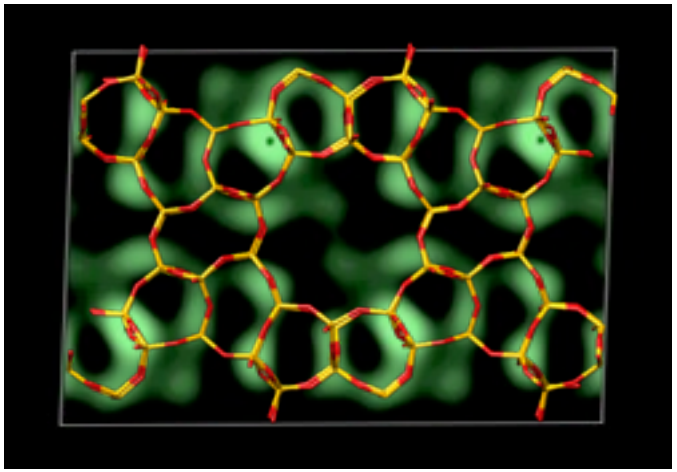

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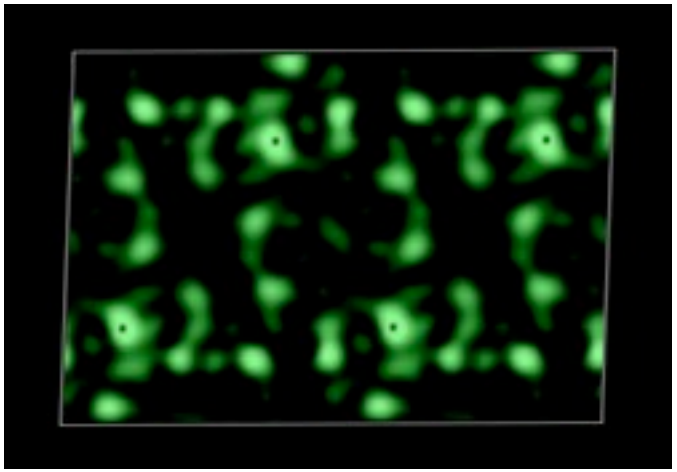
  (47 reflections, 30% overlapped)
- Run superflip with delta = 0.0
- Use some more tricks
- Add similar maps

1.5Å

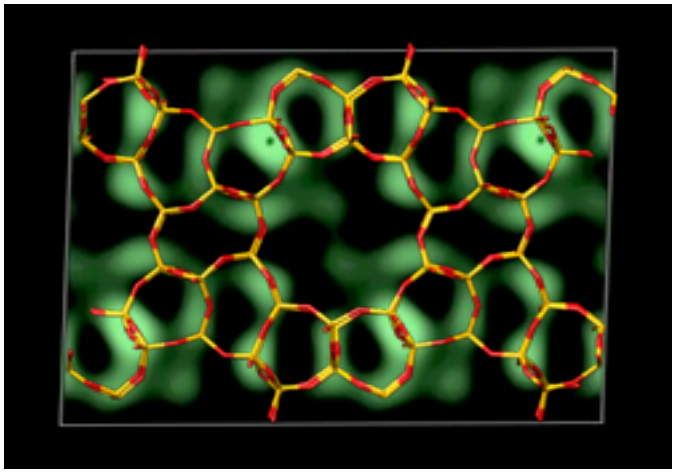


- Select reflections of zone [010] with d_{min}=1.5Å
- start with phases from previous phase set
- Run superflip with delta = 0.0
- Align maps with previous map
- Add similar maps

2D-XPD: Zeolite TNU-9

[010] Projection with “empty” regions

3.0Å



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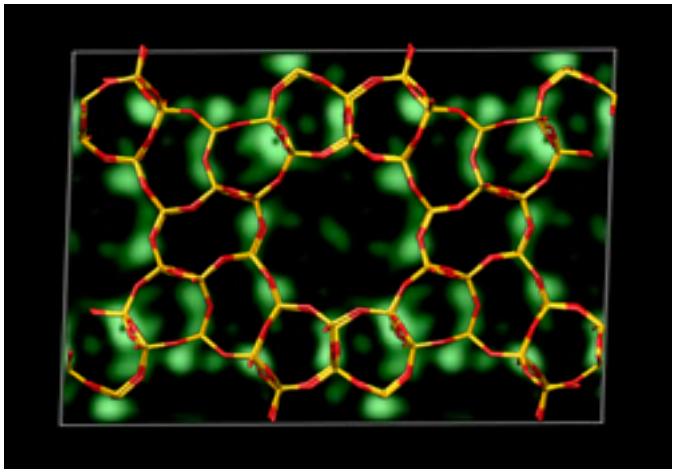

- Select reflections of zone [010] with d_{min}=1.5Å
- start with phases from previous phase set
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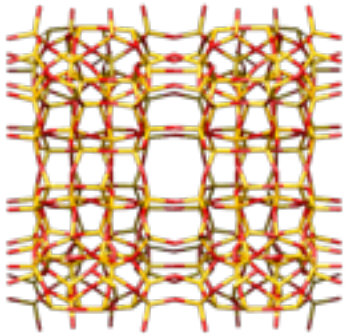
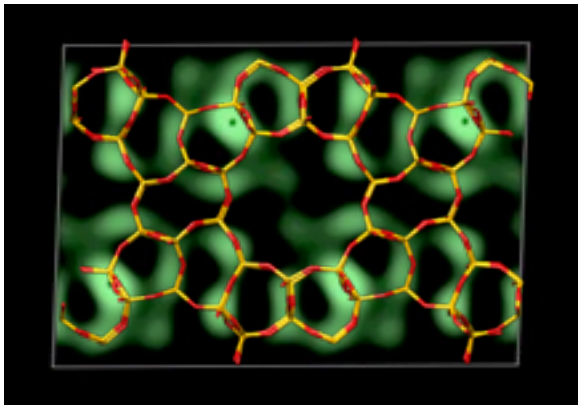
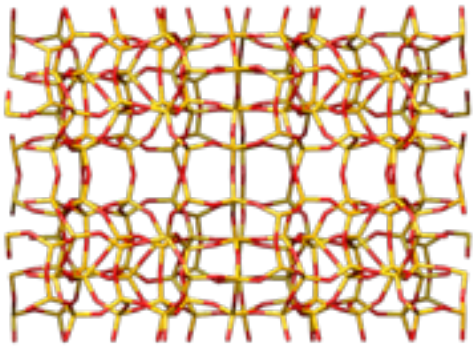
TNU-9

3.0A [100] [010] [001]

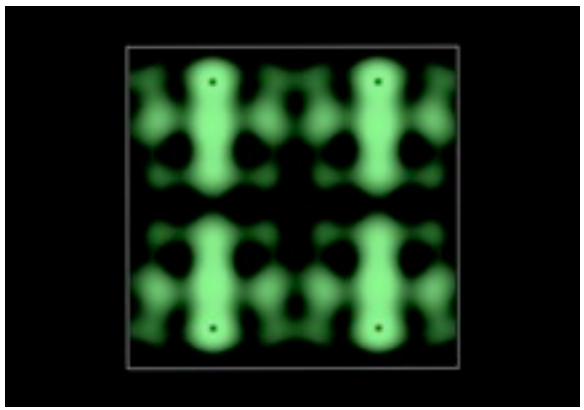


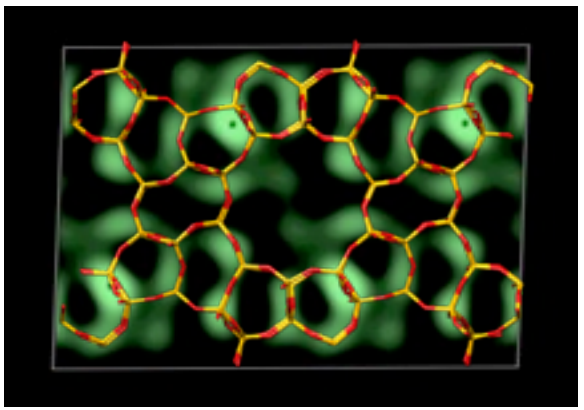


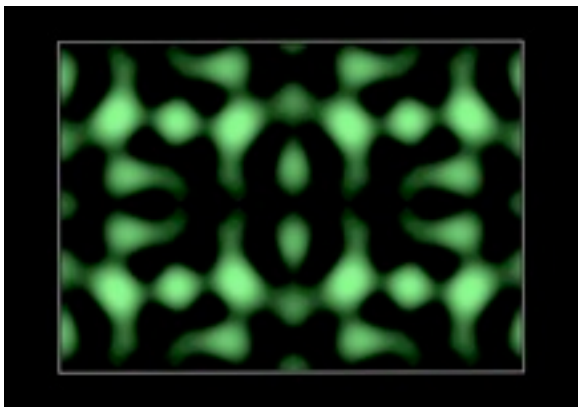


TNU-9

3.0A [100] [010] [001]

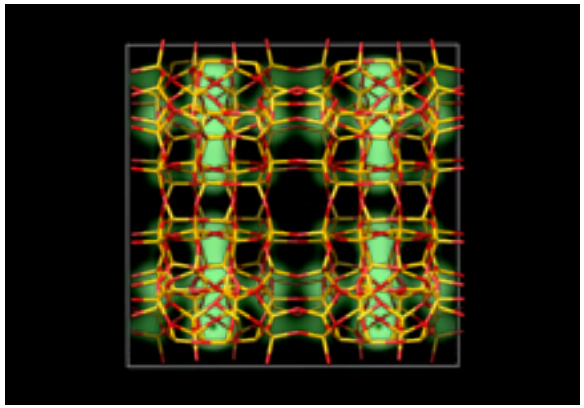






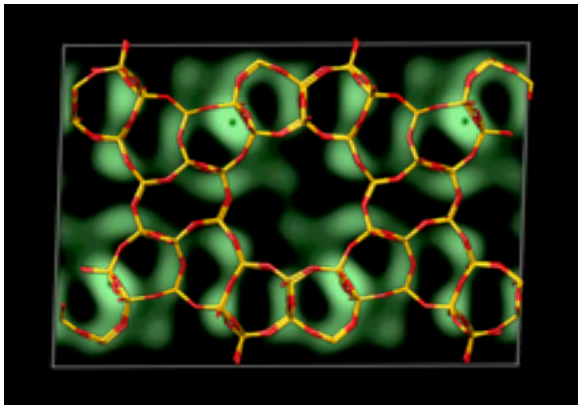
TNU-9

3.0A [100]



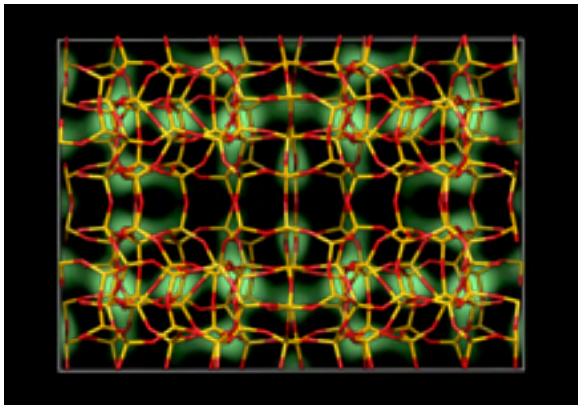
22 reflections, 83% correct

[010]



47 reflections, 72% correct

[001]



28 reflections, 85% correct

TNU-9

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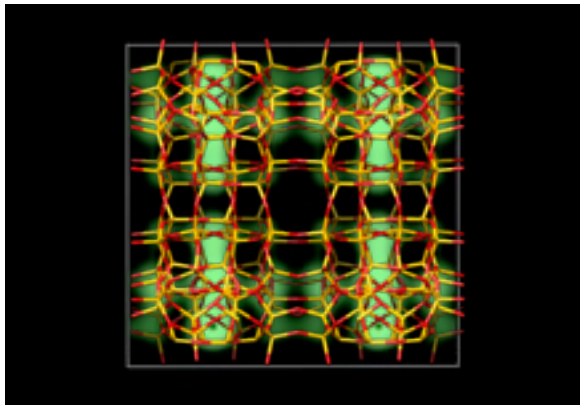

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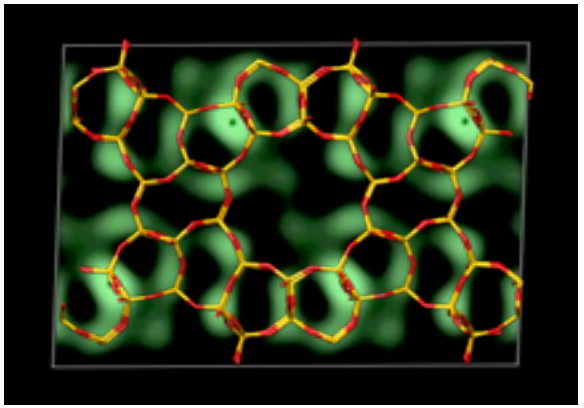

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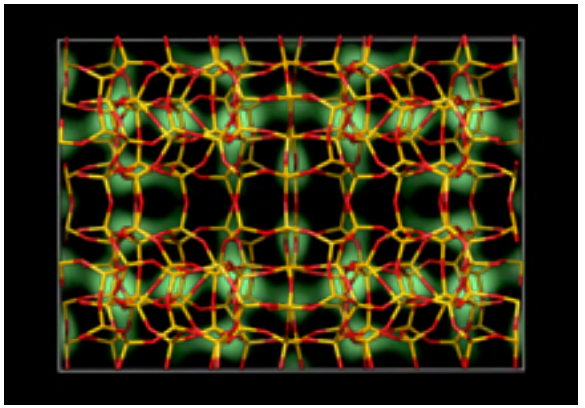
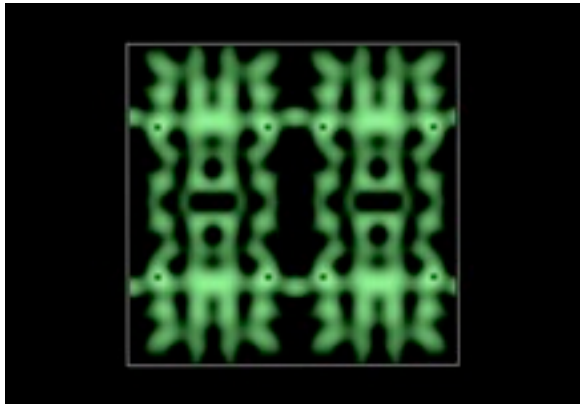
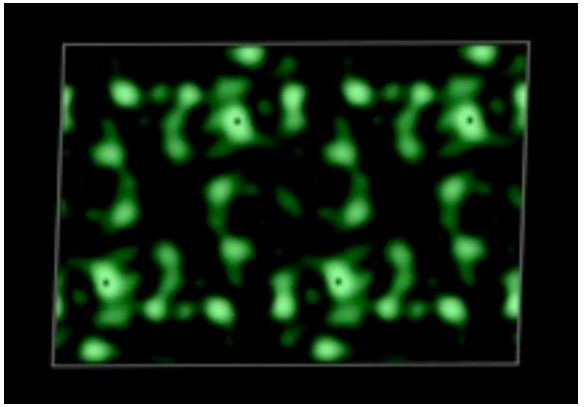
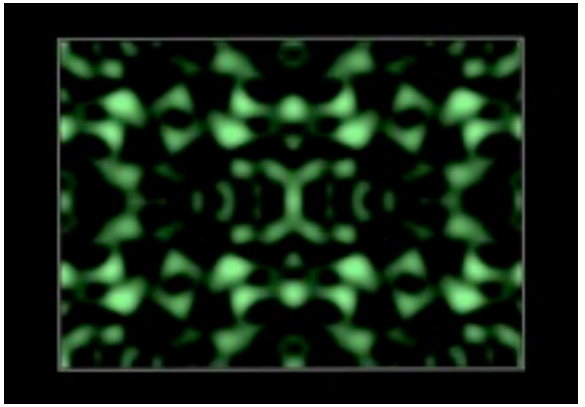


28 reflections, 85% correct

1.5A







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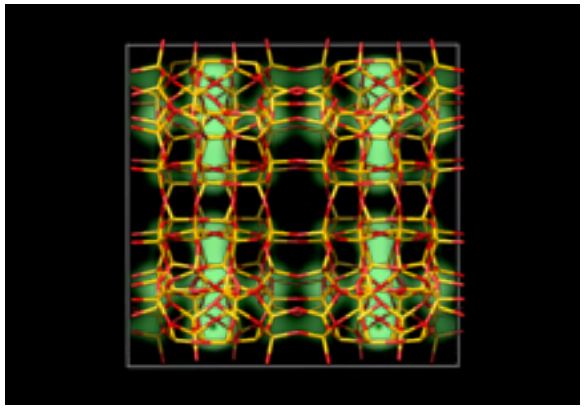

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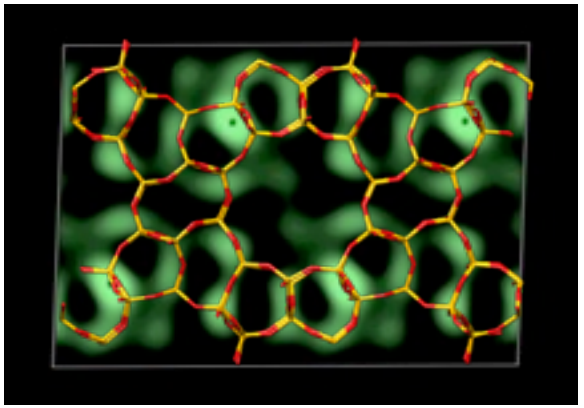

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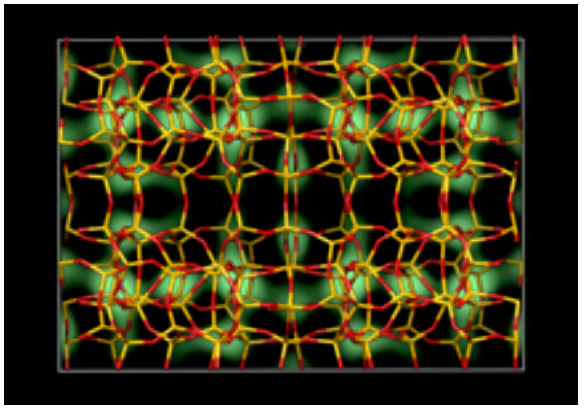

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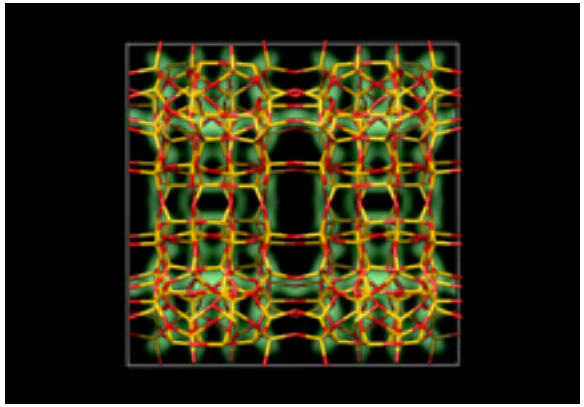
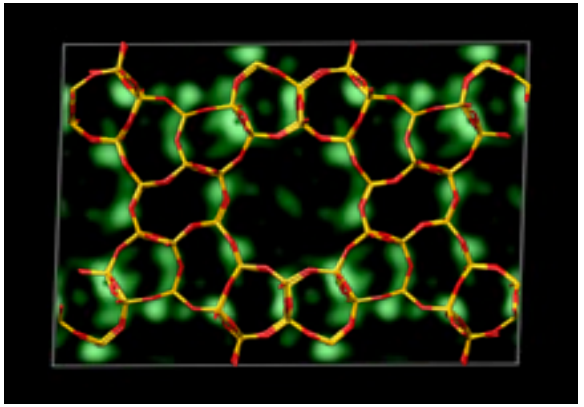
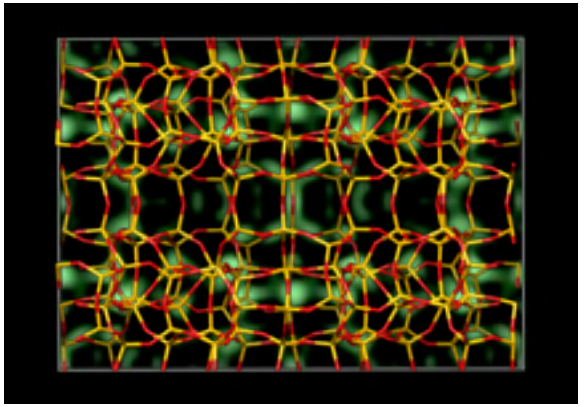
1.5A



76 reflections, 79% correct



192reflections, 68% correct



106 reflections, 85% correct

Zeolite SSZ-82

Unit Cell	
Space Group	*Pmmn*
a	24.278 Å
b	11.466 Å
c	14.113 Å
Reflections	
powder pattern (d_{min} = 0.95 Å)	3116
overlapping (0.25*FWHM)	2783
d_{min}	0.9 Å

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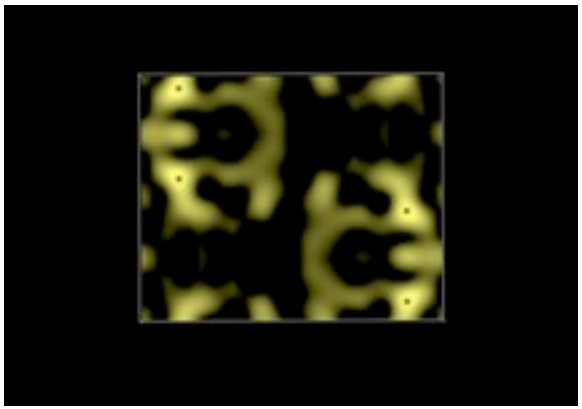
Zeolite SSZ-82

2D-XPD fourier maps

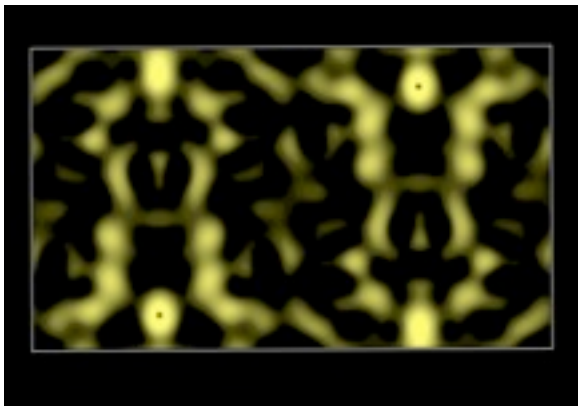
1.5Å

[100]



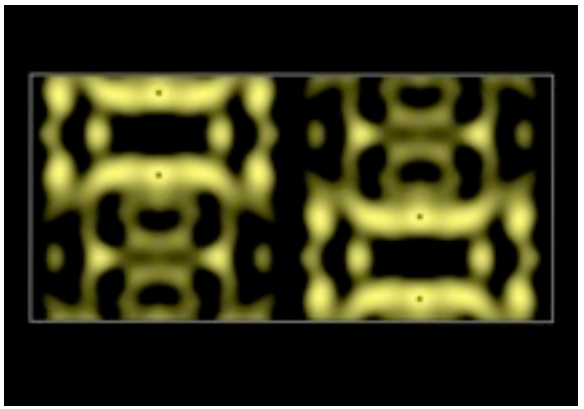
61 Reflections

[010]



124 Reflections

[001]



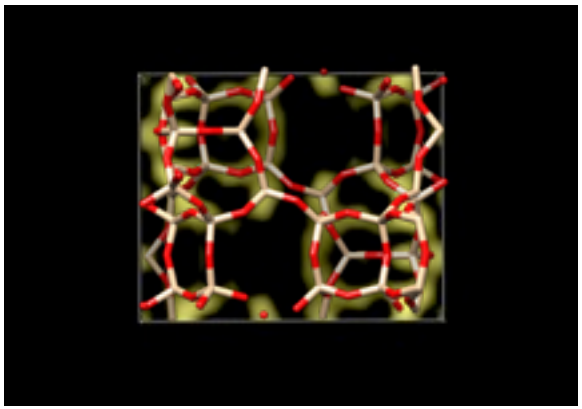
53 Reflections

Zeolite SSZ-82

2D-XPD fourier maps

1.5Å

[100]



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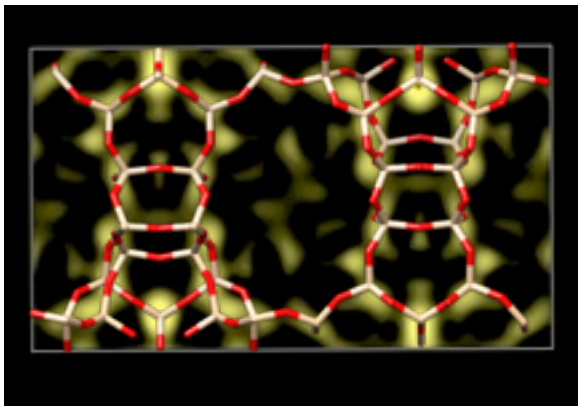
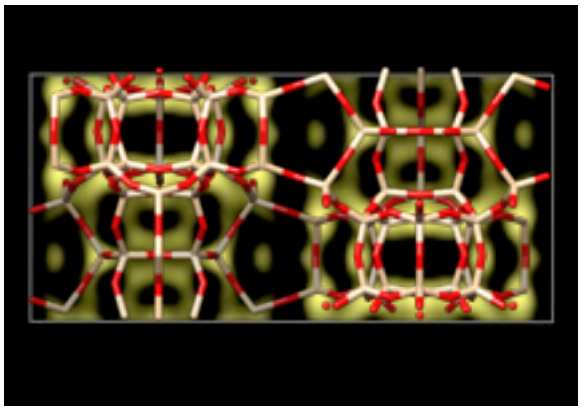
[010]



124 Reflections

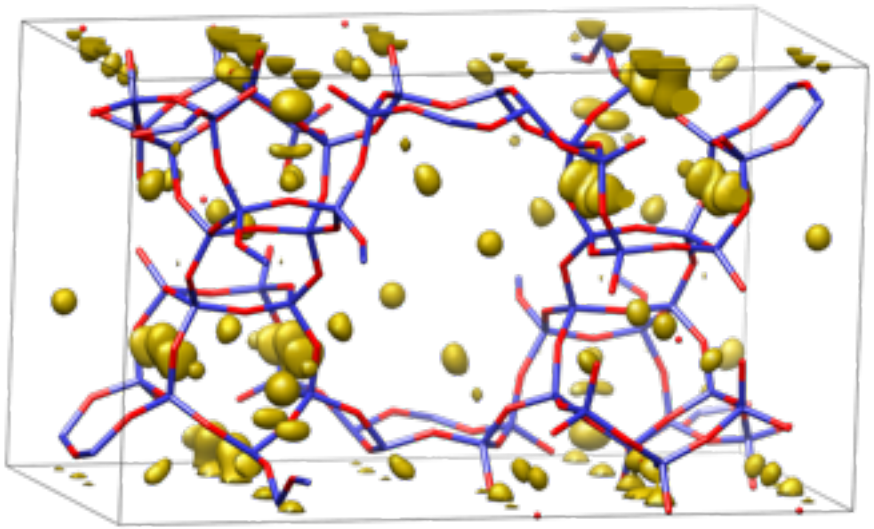
[001]



53 Reflections

Zeolite SSZ-82

best “superflip” solutions



normal run

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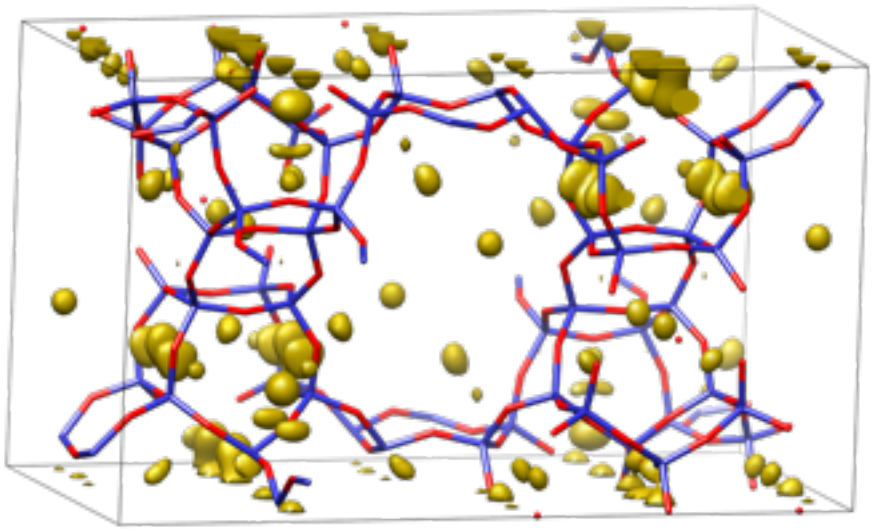

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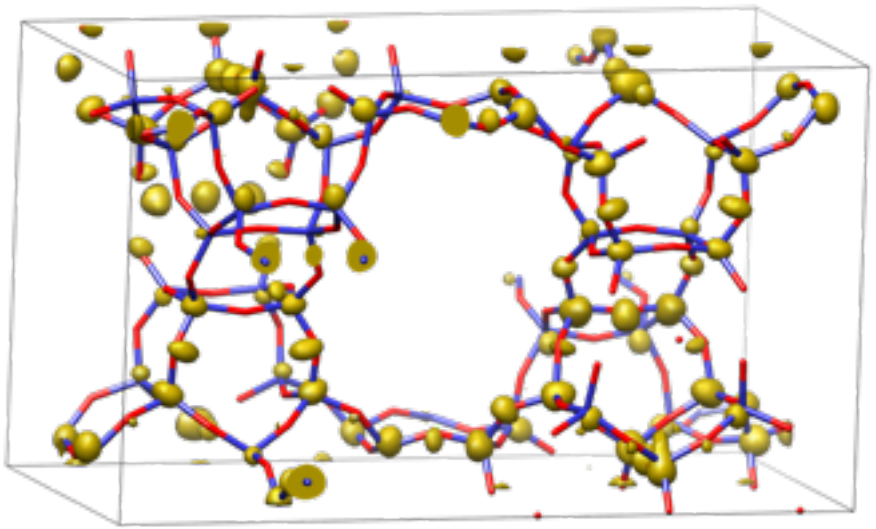

using phases from 2D-XPD

Conclusions

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Electron microscopy is a valuable complement to powder diffraction

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The framework structures of three complex polycrystalline zeolites

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2D-X-ray powder diffraction data

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2D-X-ray powder diffraction data

- can be phased with charge flipping
- used successfully in the structure determination of SSZ-82

Acknowledgments

Acknowledgments

TNU-9

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Bada Han
Suk Bong Hong
Zheng Liu
Tetsu Ohsuna
Osamu Terasaki
Fabian Gramm

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All of the above: *Lynne McCusker*