ETH zürich

ScopeM

Electron Diffraction in TEM

Fabian Gramm, ETH Zürich

CCMX – ScopeM Course

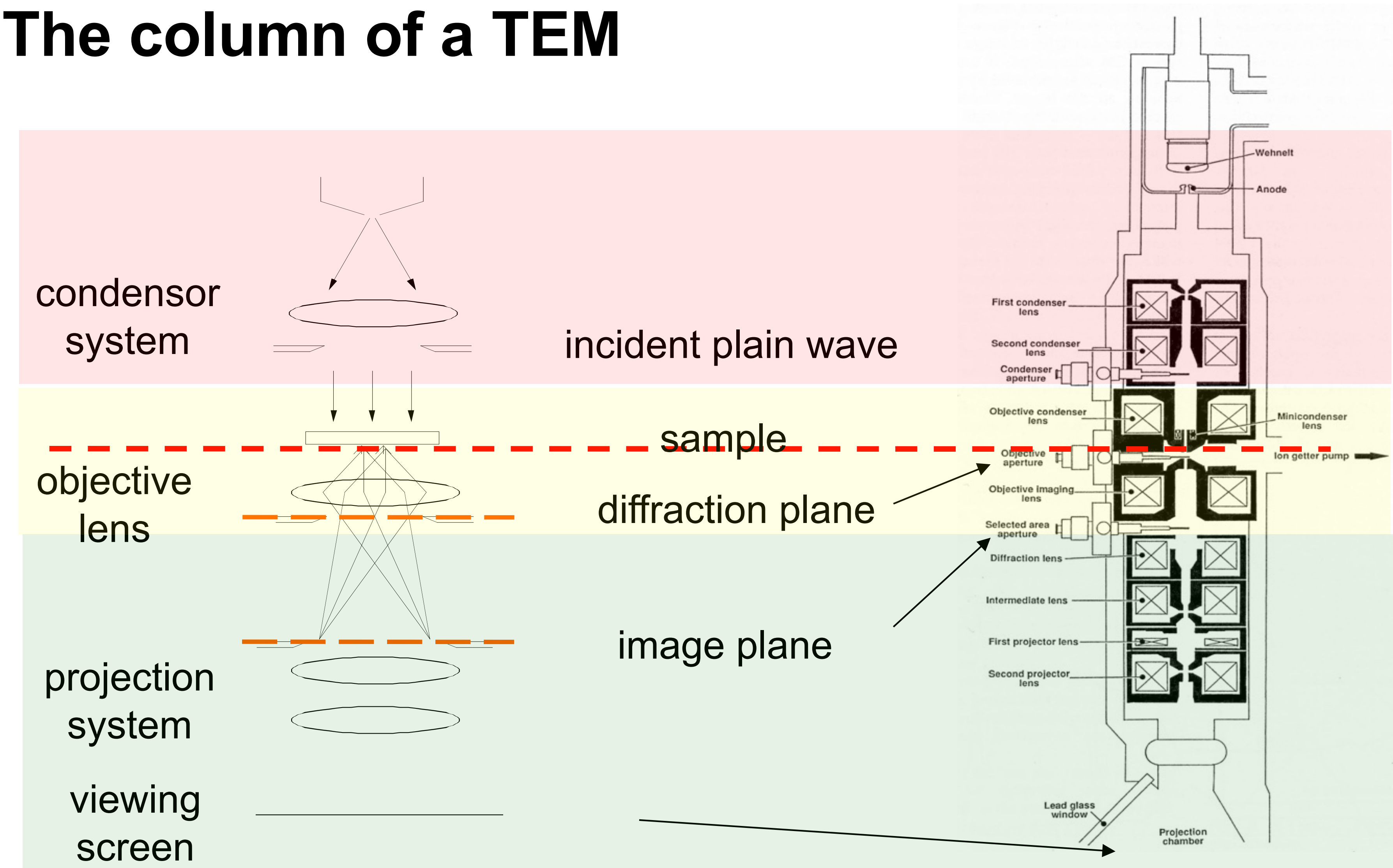
04th – 7th November 2024

Electron Diffraction Methods & Applications

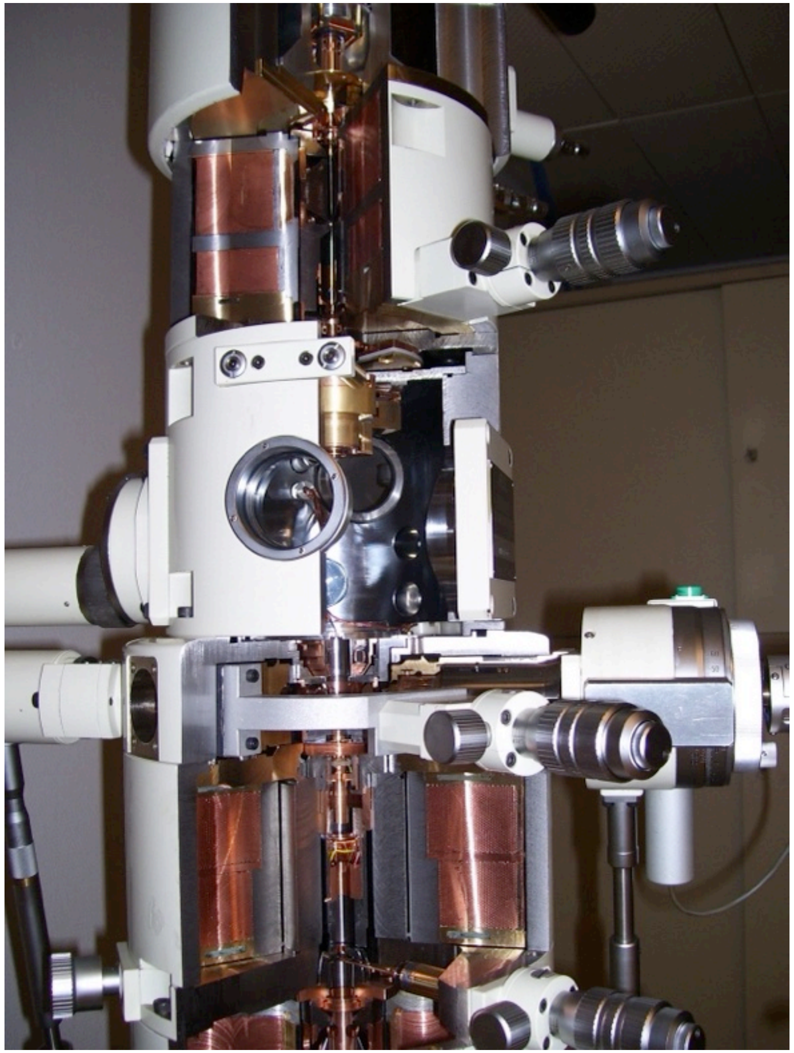
Outlook

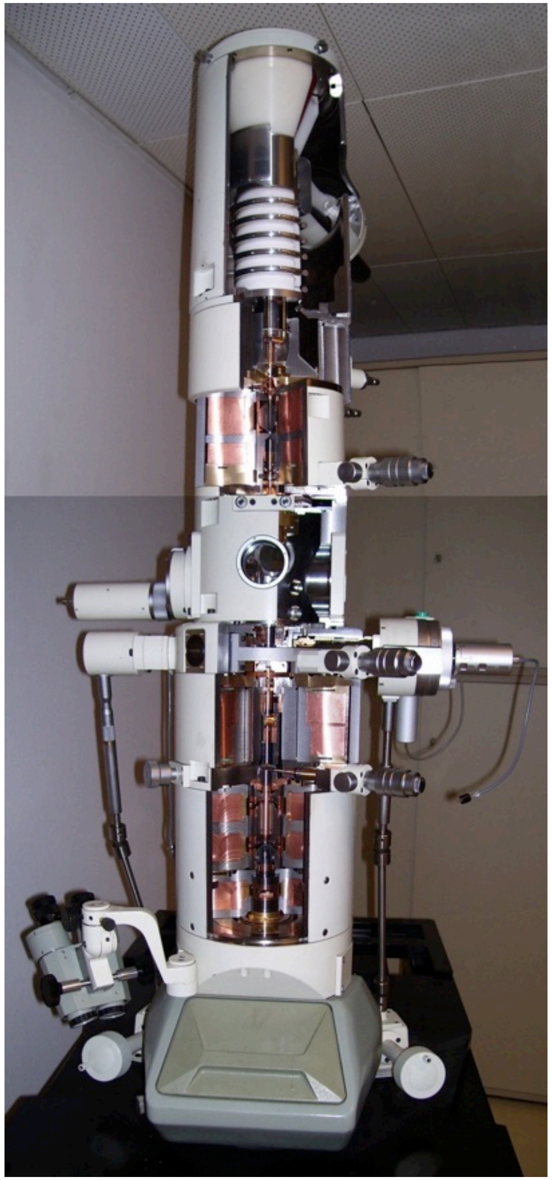
- **Imaging modes** in **TEM**
- Seeing **why** we use **electron diffraction**
- Quickly **looking at the basic concepts** to understand electron diffraction (ED)
- Give you an **overview of the main methods** of electron diffraction
- Show you **selected applications** using electron diffraction

The column of a TEM



TEM cross section

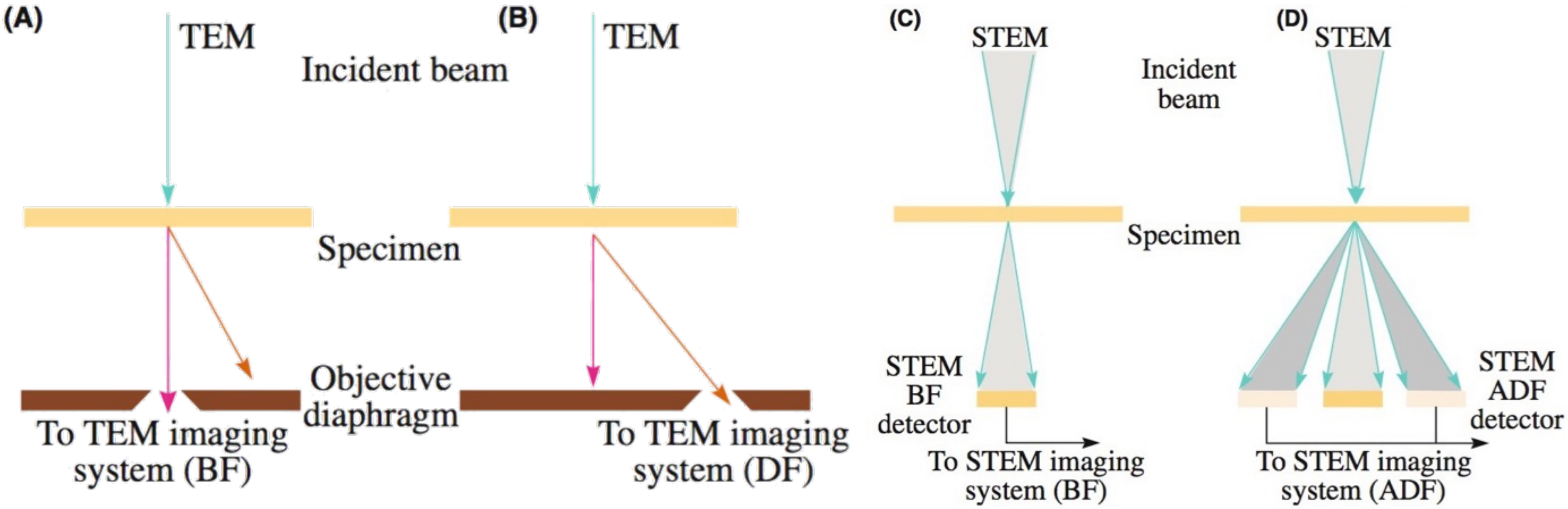




Operation modes in S(TEM)

Transmission Electron Microscopy
TEM

Scanning Transmission
Electron Microscopy
STEM

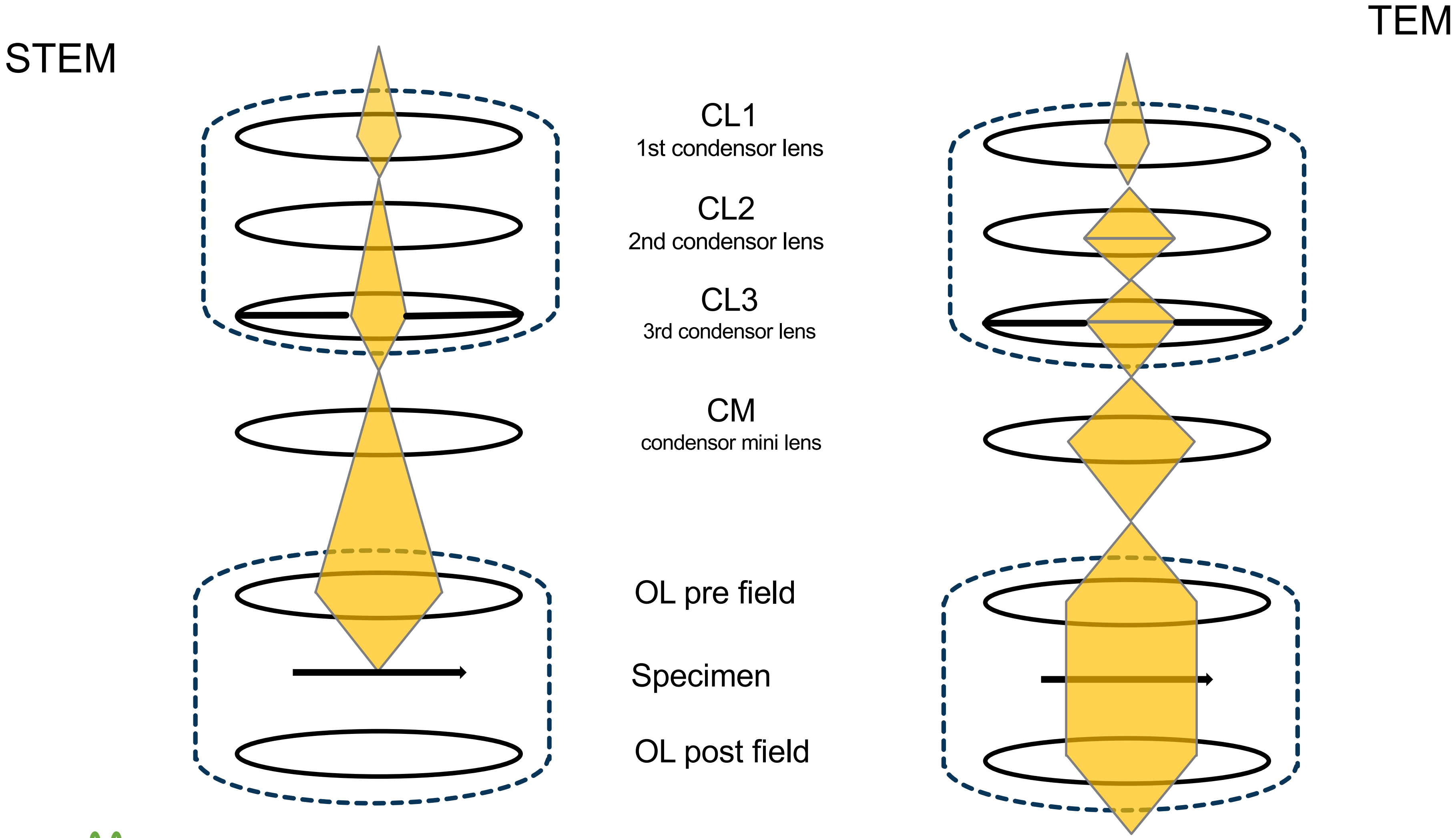


BF bright field

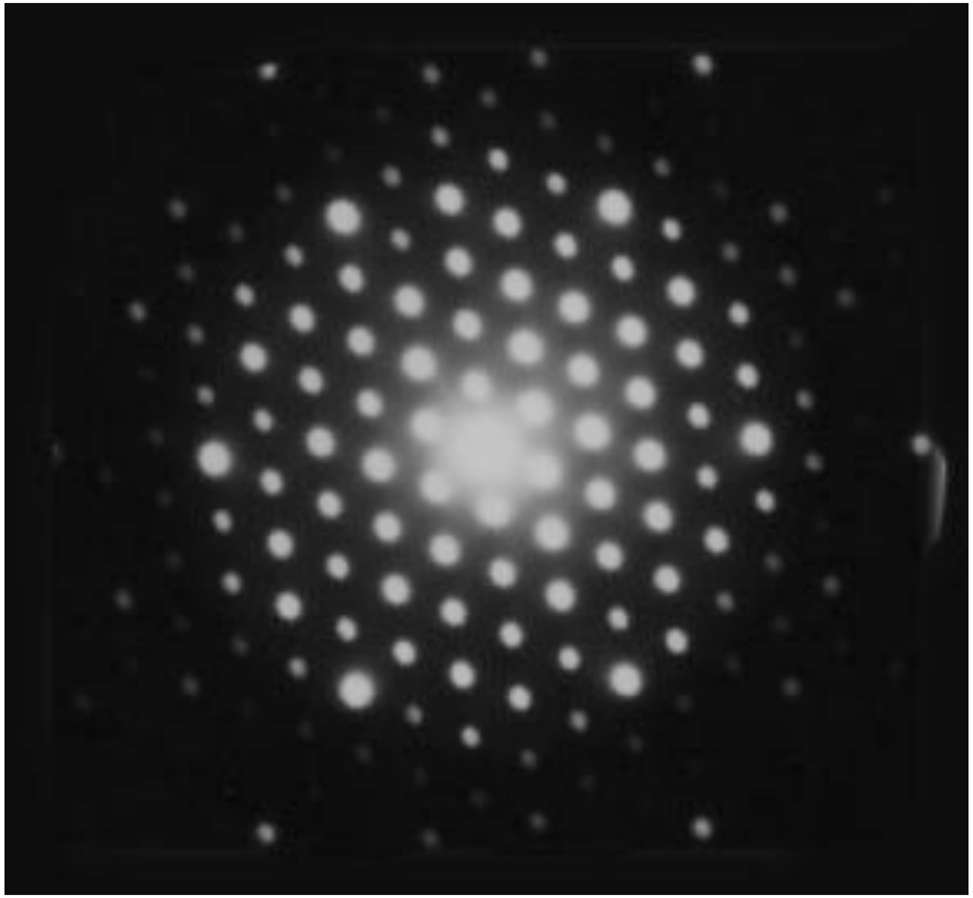
DF dark field

ADF annular dark field
HAADF High angle annular dark field

Electron Diffraction Methods & Applications



Why using electron diffraction?



Why do we use Electron Diffraction in TEM

- Stronger interaction of the electrons with matter compared to X-rays

- Shorter wavelength than X-rays in the research lab

- Electron can easily be directed because this are charged particles

- Diffraction from small crystallites or grains
  -> local information

$$\mathbf{F} = Q_1 Q_2 / 4\pi\, \varepsilon_o\, r^2$$

(r : distance between the charges Q_1 and Q_2; ε_o : dielectric constant).

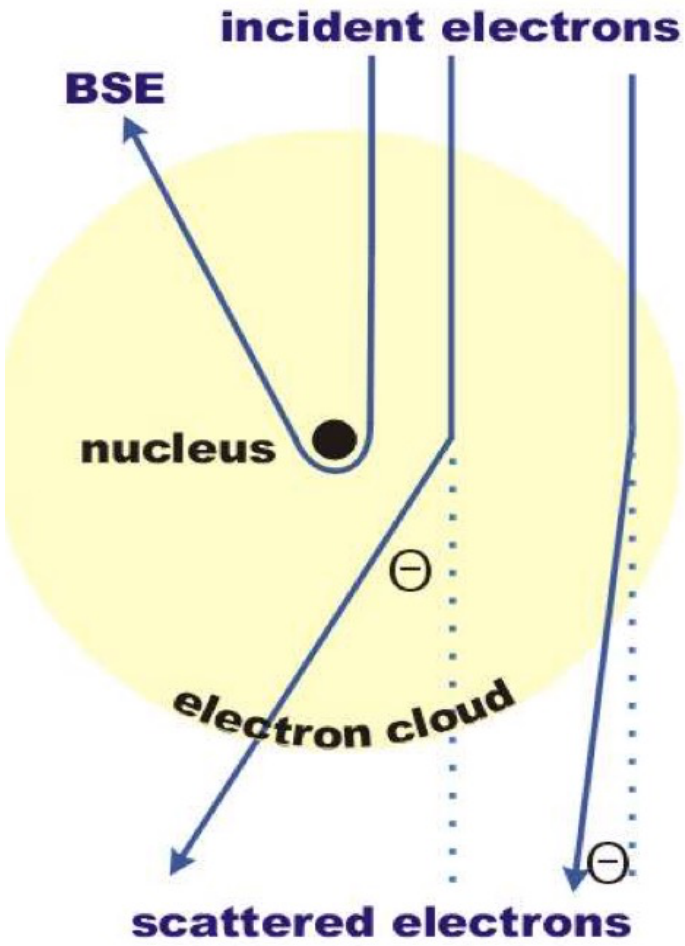


Image: www.microscopy.ethz.ch 11/04/2014

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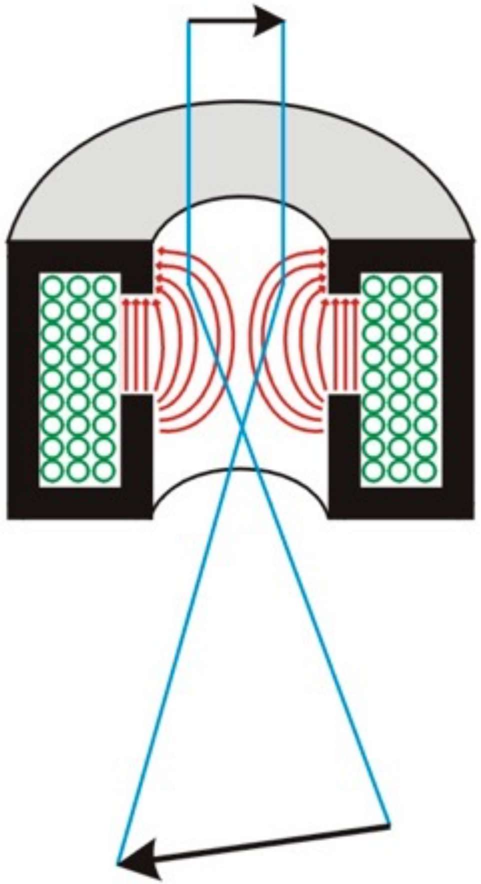

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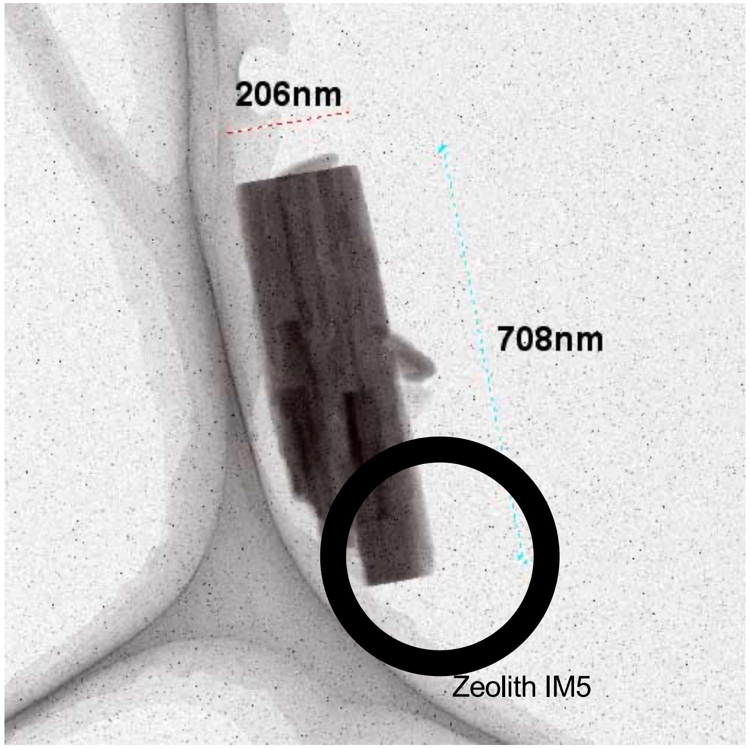


Image: www.microscopy.ethz.ch 11/04/2014

Common Questions adressed to Electron Diffraction

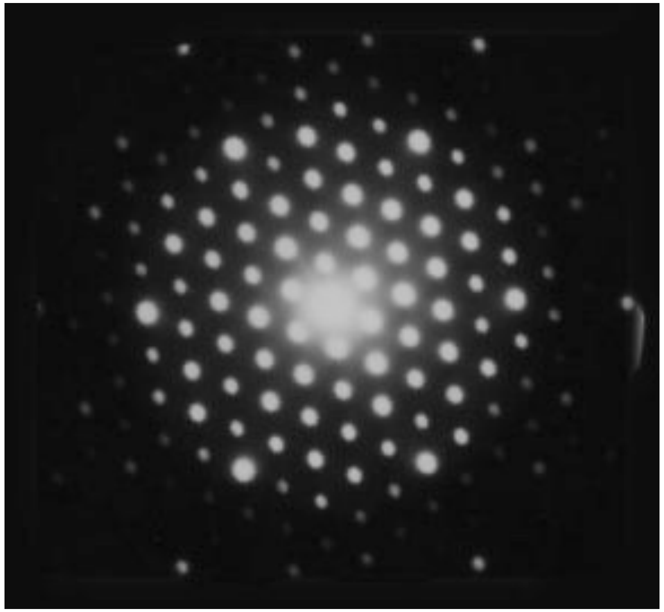
- Is the specimen
  … crystalline?
  … polycrystalline or single crystalline?
  … textured?

- Which phase(s) is/are present in the specimen?

- What is the orientation of the specimen or individual grains?

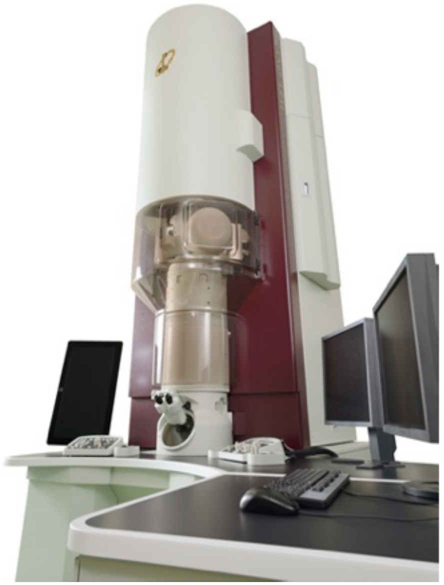
- Determine the unit cell of a crystalline structure?

- Solving crystal structures (ED often combined with other methods)



Instruments for Electron diffraction at ScopeM

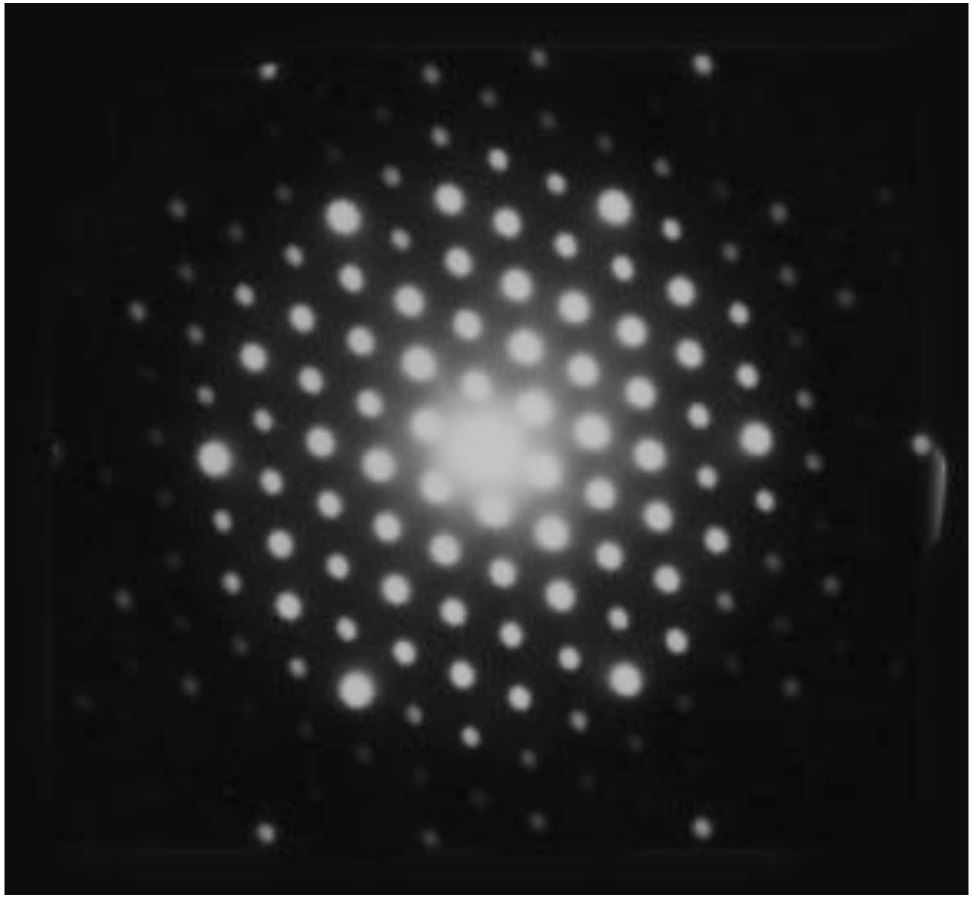
TFS Talos
F200X



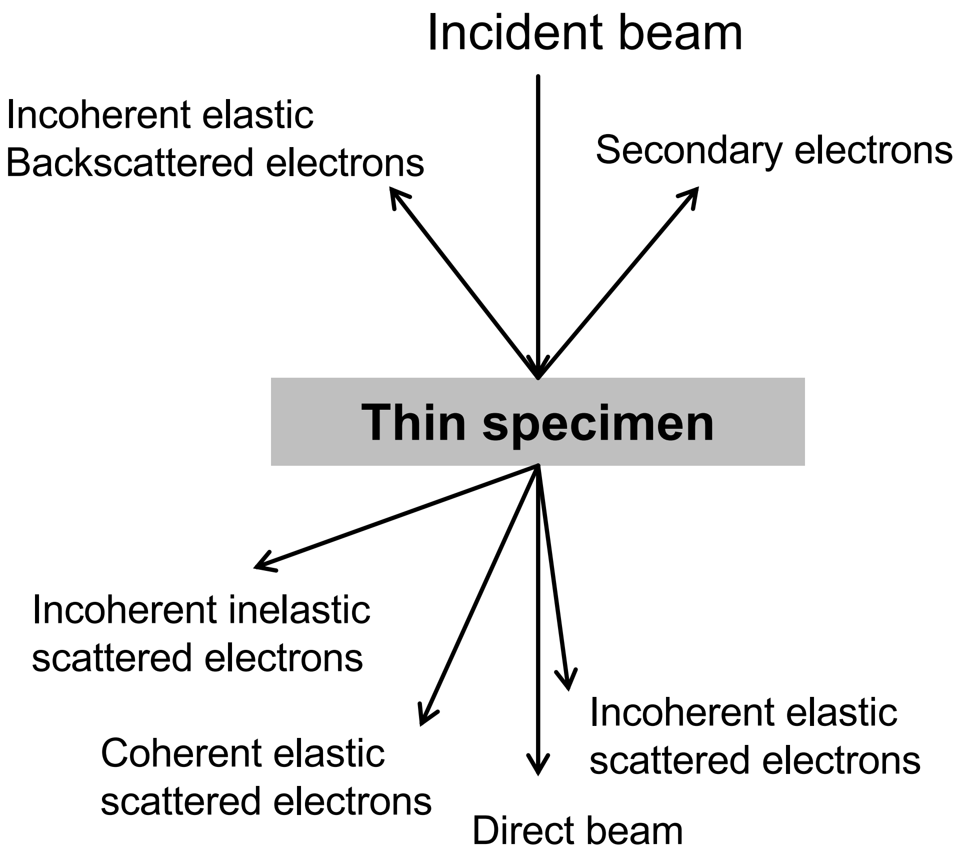
JEOL
GrandARM300F

JEOL
JEM F200

Basic concept in electron diffraction

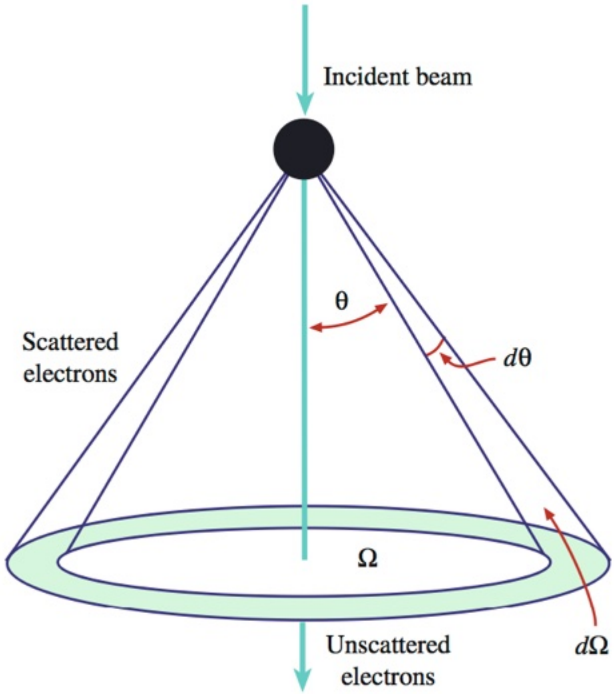


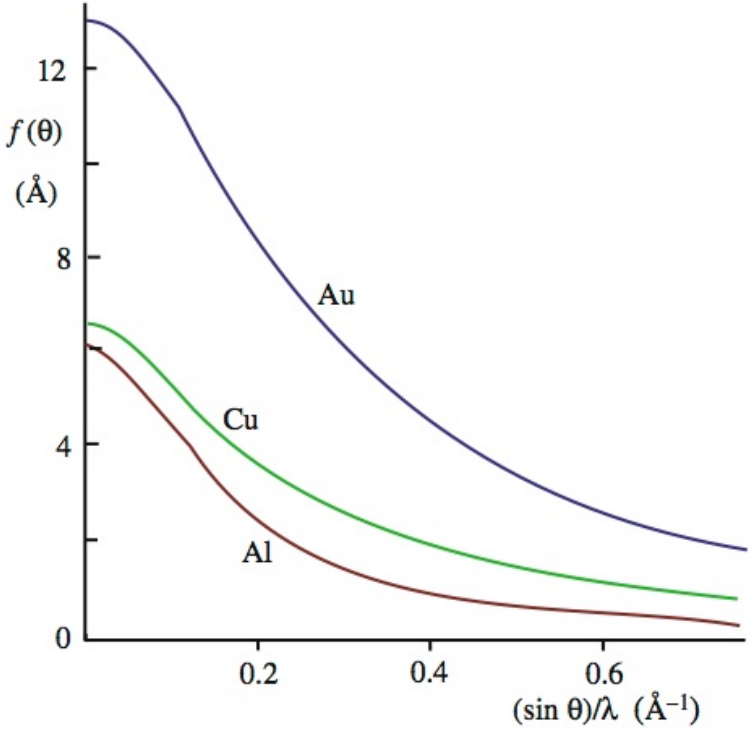
Interactions of electrons with matter



- **Elastic scattering** is **usually coherent**, if the specimen is thin and crystalline (think in terms of waves).
- **Elastic scattering** usually occurs **at relatively low angles (1–10°)**, i.e., it is strongly peaked in the forward direction (waves).
- At higher angles (> 10°) elastic scattering becomes more incoherent (now think of particles).
- **Inelastic scattering** is **almost always incoherent** and is very low angle (<18) scattering (think particles)
- As the specimen gets thicker, fewer electrons are forward scattered and more are backscattered. Incoherent, backscattered electrons are the only remnants of the incident beam that emerge from bulk, non-transparent specimens (think particles).

Scattering of electrons on a single atom

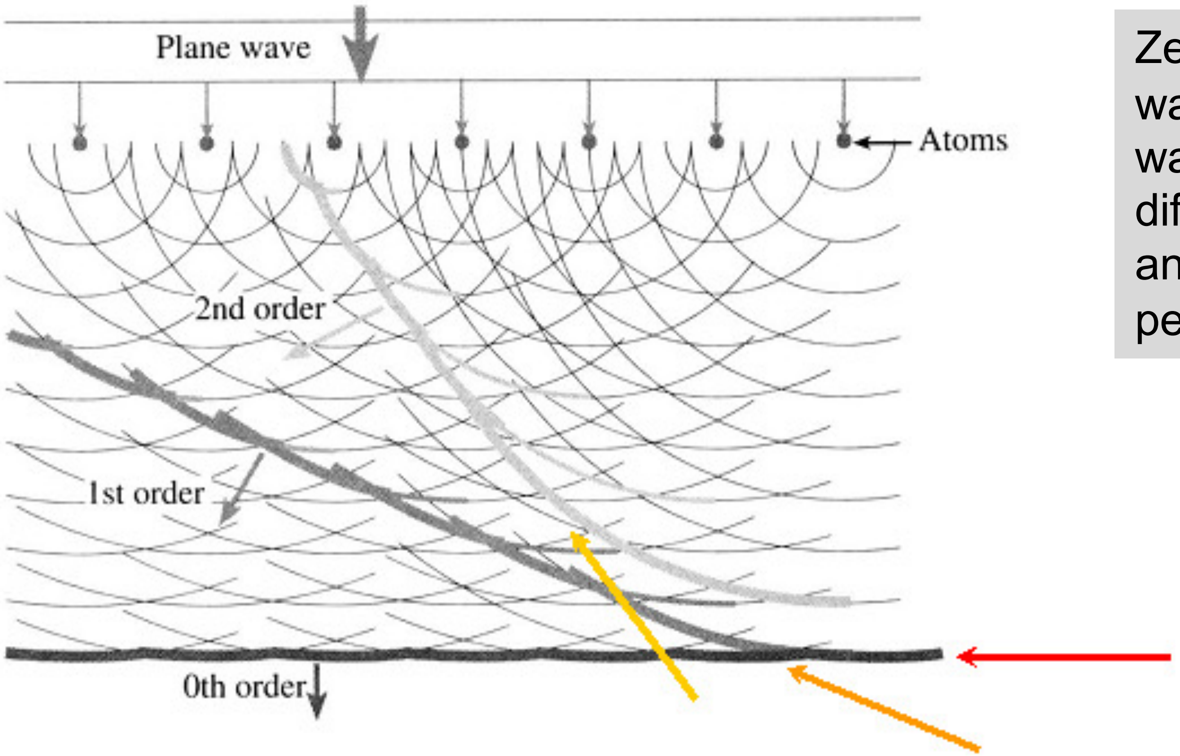




The atomic scattering factor f(θ) is a measure of the scattering power of an individual atom. It is increasing with the Z-number of the atom and it changes with the angle θ, decreasing for high scattering angles (=angles away from incident beam).

Williams D.B., Carter C.B (2004), Transmission Electron Microscopy

Scattering of a plane wave at a periodic structure



Zero-, first- and second order wave fronts of a scattered plane wave marked with arrows of different colors. The scattering angle is dependent on the periodicity of the structure.

Bragg‘s law of diffraction

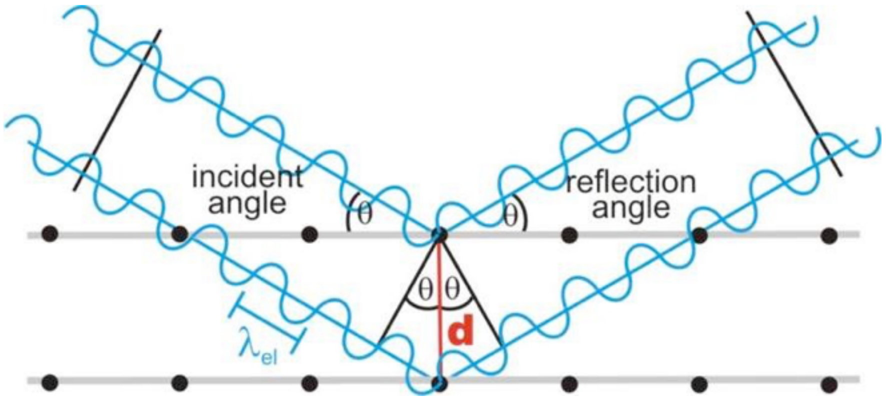
The first beam is reflected by first atomic layer. The second beam continues to the next atomic layer where it is reflected. This result in a longer traveling distance for the second beam.

Additional traveling distance 2^{nd} beam: $= 2d * \sin \theta_B$

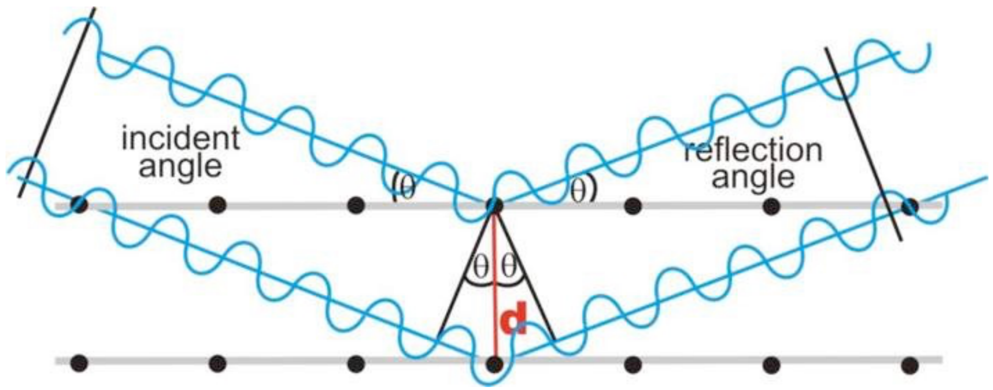
Constructive interference of 1^{st} and 2^{nd} beam if the additional travelling distance is equal to $n\lambda$

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

The scattering angle θ_B is in fact a semi-angle, not a total angle of scattering.



In Bragg condition.



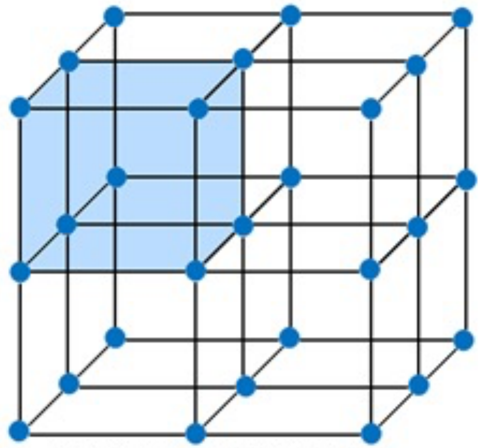
No Bragg condition.

Crystal

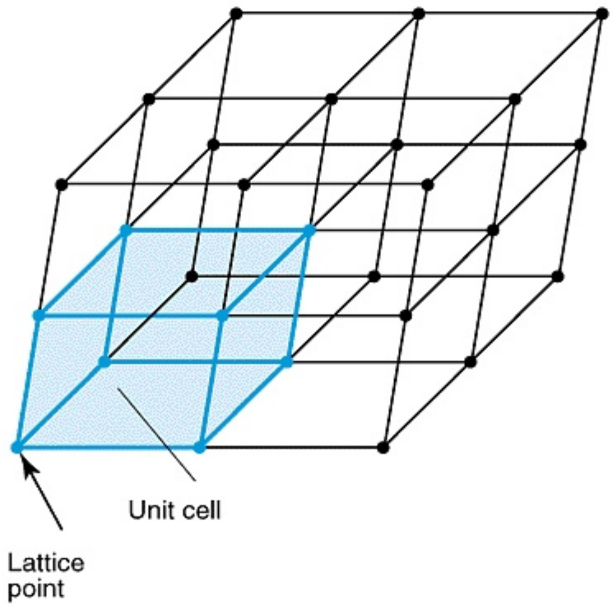
a substance in which the constituent atoms, molecules, or ions are packed in a regularly ordered, **repeating three-dimensional pattern**, forming a crystal lattice. Most crystals are solids.

Unit cell

The unit cell is the smallest repeating unit which describes the crystal lattice.



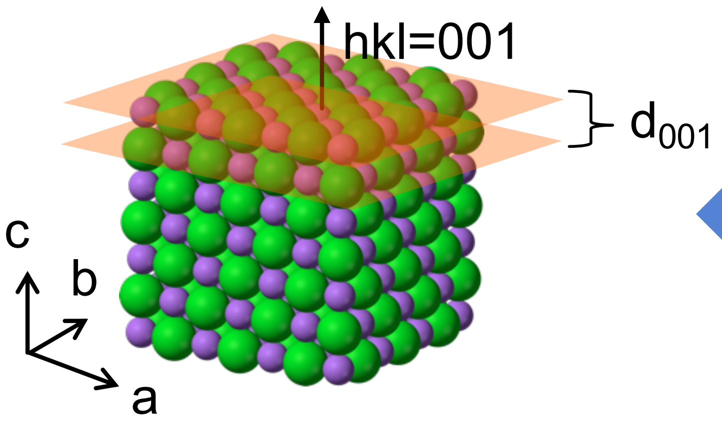
A Portion of three dimentional cubic lattice and its unit cell



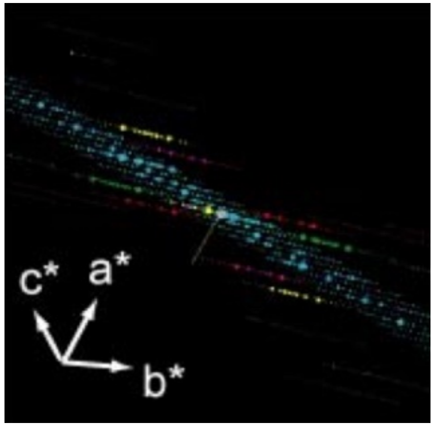
Images: http://www.excellup.com/

The Reciprocal Space

crystal lattice



reciprocal lattice



$$a^* = \frac{b \times c}{V_c}$$

⇨ a* in reciprocal space is perpendicular on b and c direction of direct space

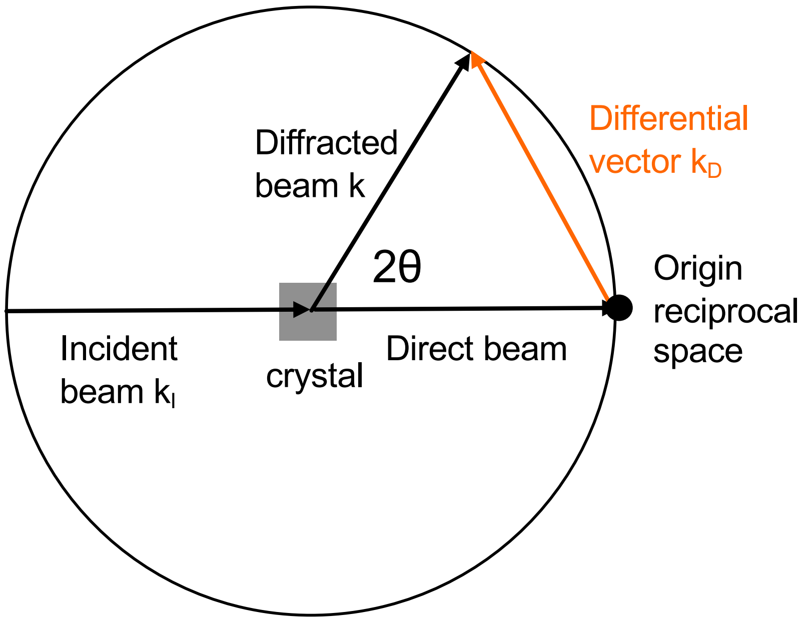
$$a^* \cdot a = 1;\; b^* \cdot b = 1;\; c^* \cdot c = 1$$

⇨ Long distances in real space are short in reciprocal space

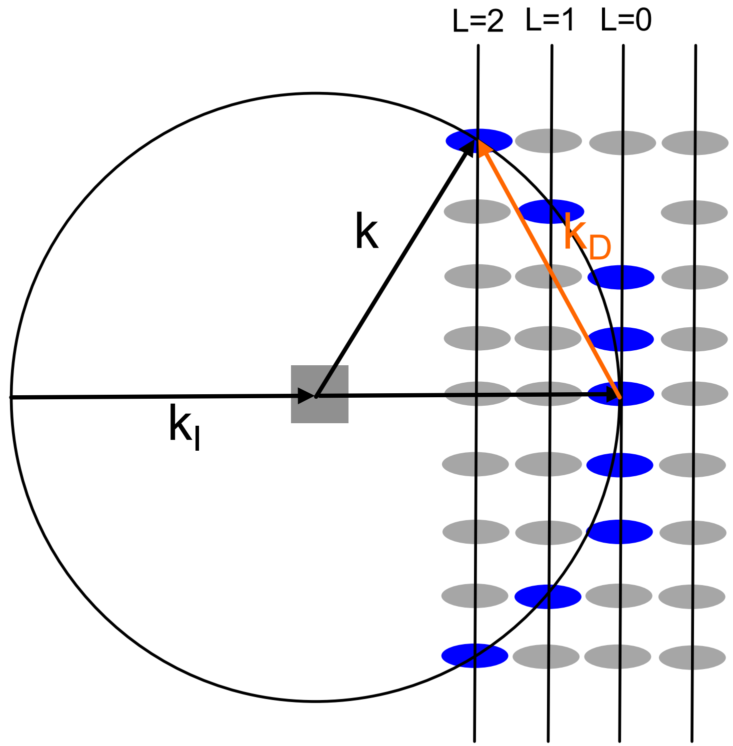
for the cubic system

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The Ewald Sphere



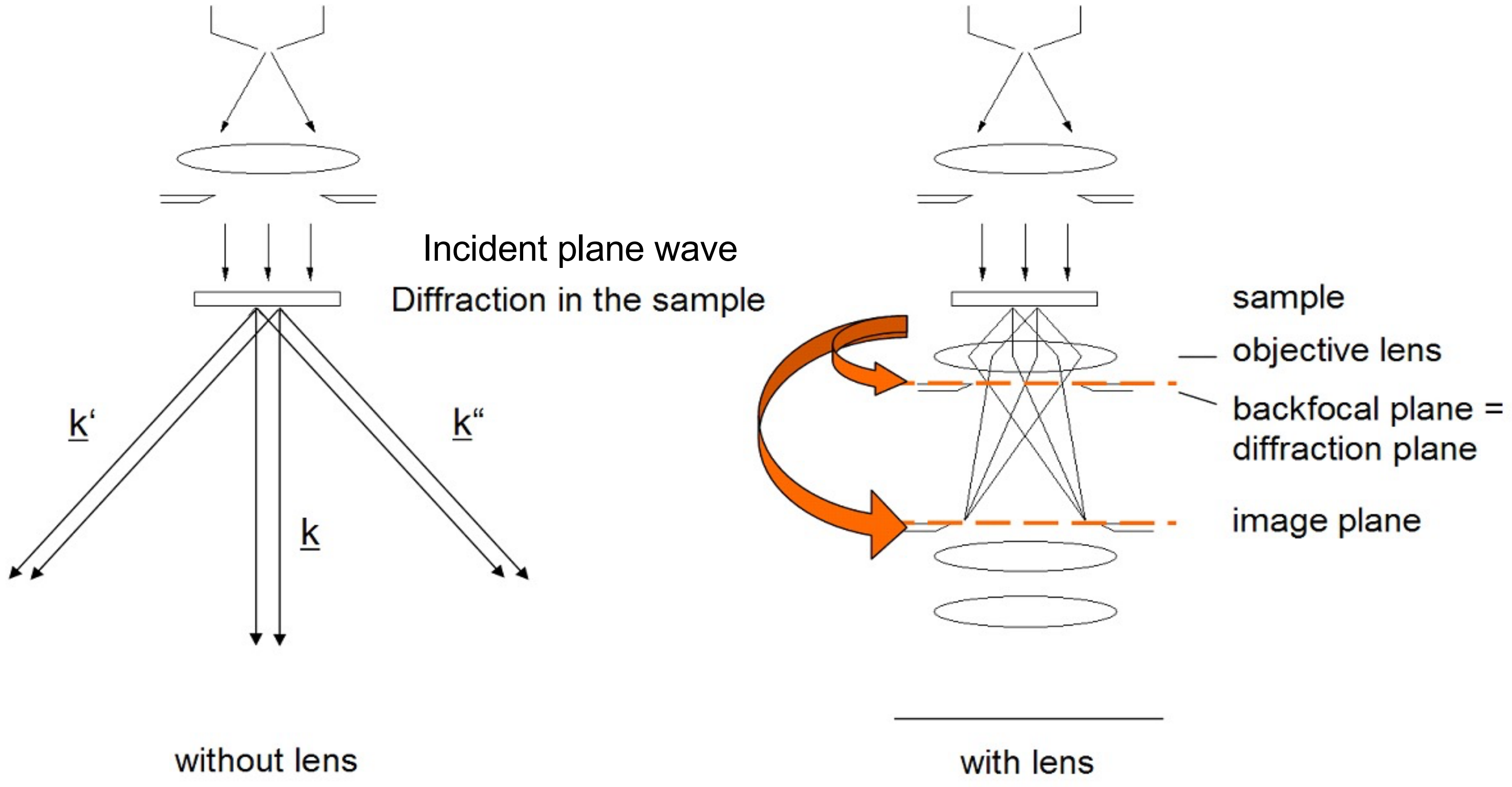
Reciprocal lattice



The Ewald sphere is a geometrical representation of Bragg's law of diffraction: $n\lambda = 2d \sin \theta_B$

- Due to the thin TEM sample the lattice point in the reciprocal lattice are elongated -> rods
- Where the reciprocal lattice intersects the Ewald sphere a diffraction spot is visible in the diffraction pattern

Diffraction in the Transmission Electron Microscope (TEM)



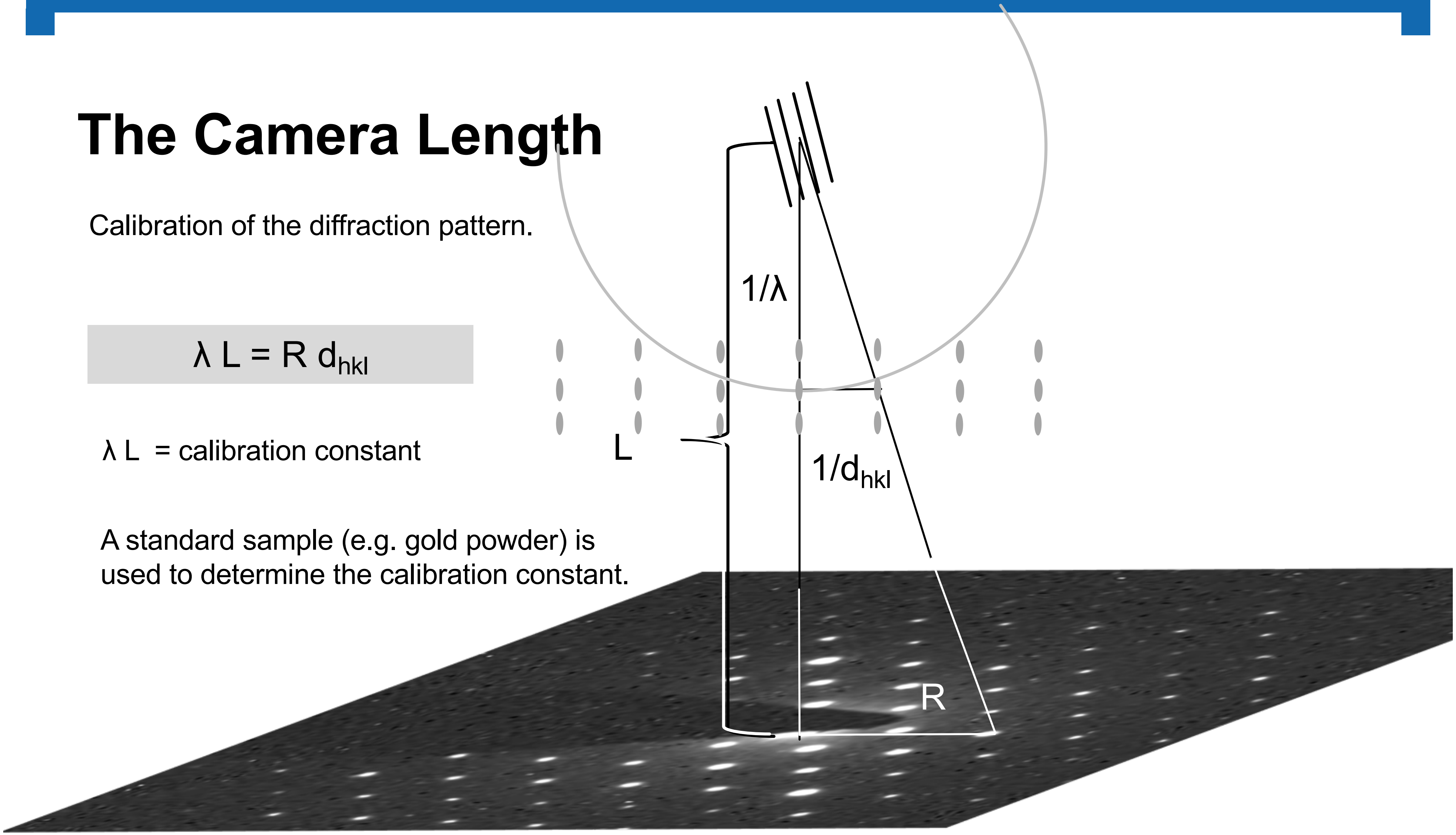
The Camera Length

Calibration of the diffraction pattern.

$$\lambda L = R\, d_{hkl}$$

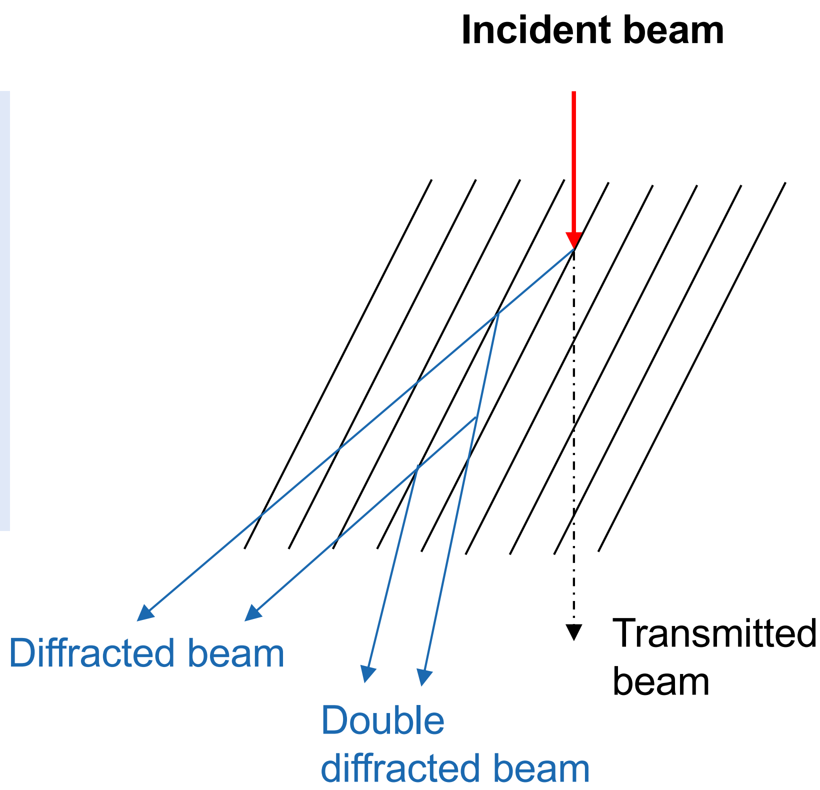
λL = calibration constant

A standard sample (e.g. gold powder) is used to determine the calibration constant.

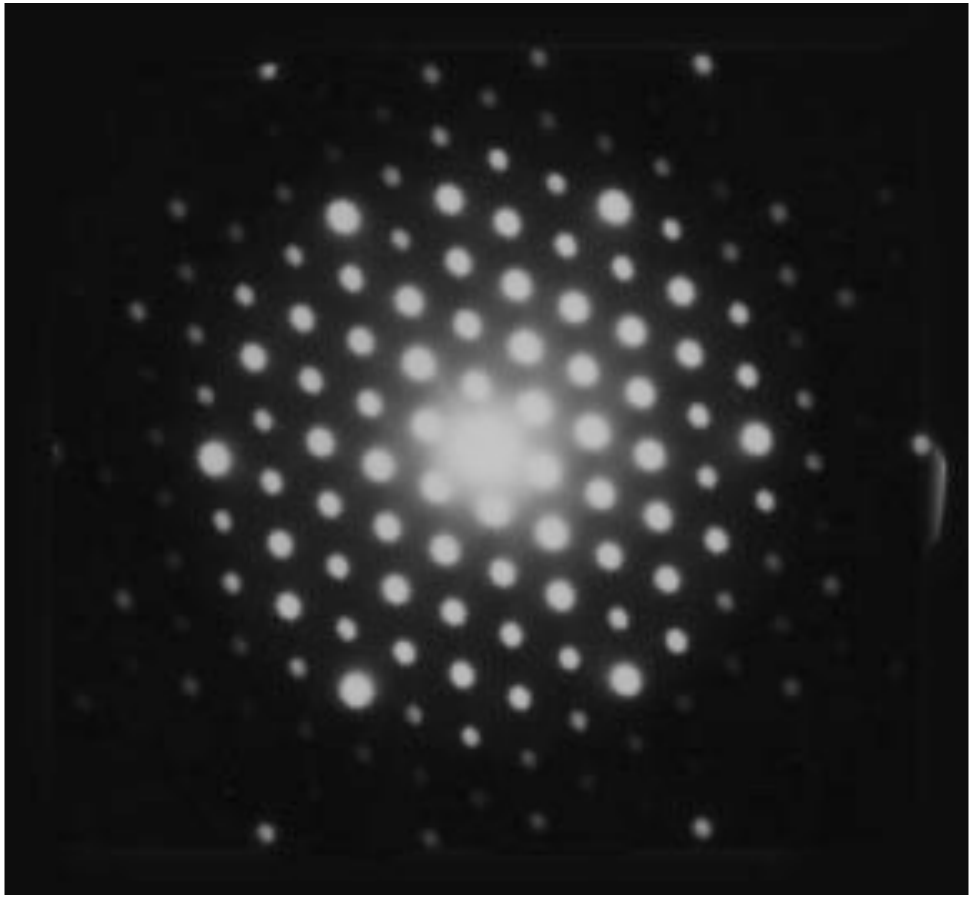


Double diffraction

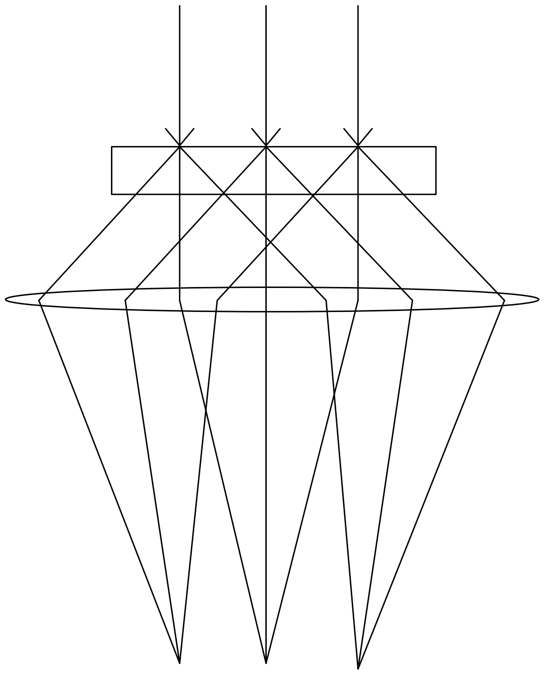
- **Double diffraction in ED** leads to oscillations in the diffracted intensities with increasing thickness of the sample.
  - Forbidden reflection may be observed in ED
  - Non kinematical intensities in ED
  - No double diffraction with XRD, kinematical intensities



Methods of electron diffraction

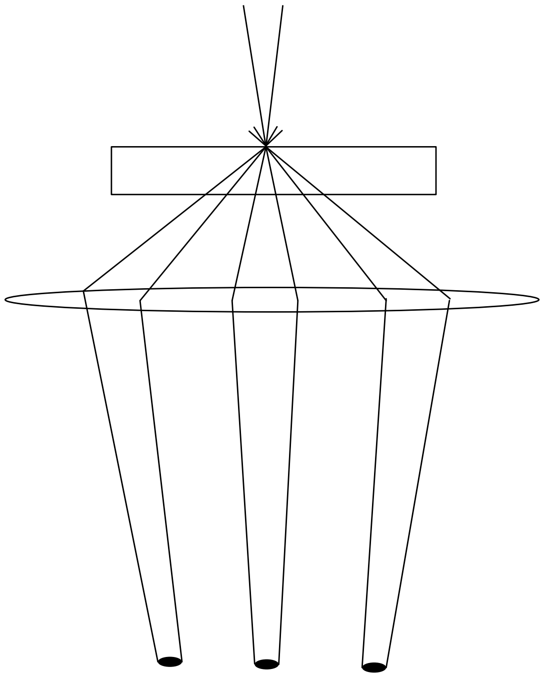


Different diffraction methods

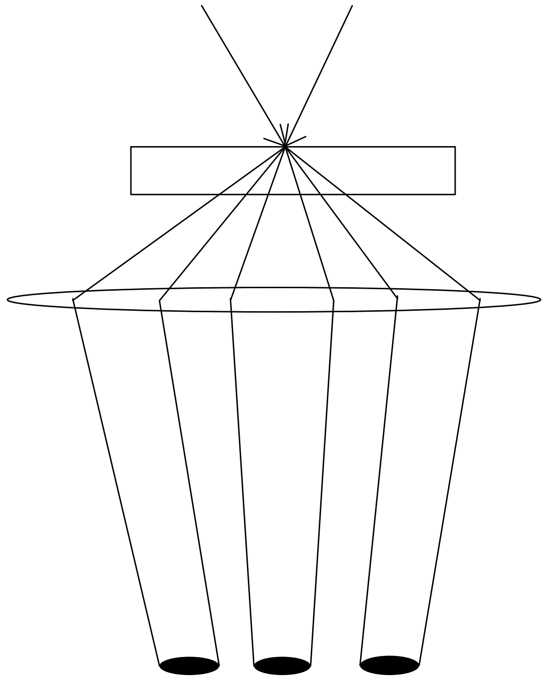


SAED

Selected Area
Electron Diffraction



Nanodiffraction

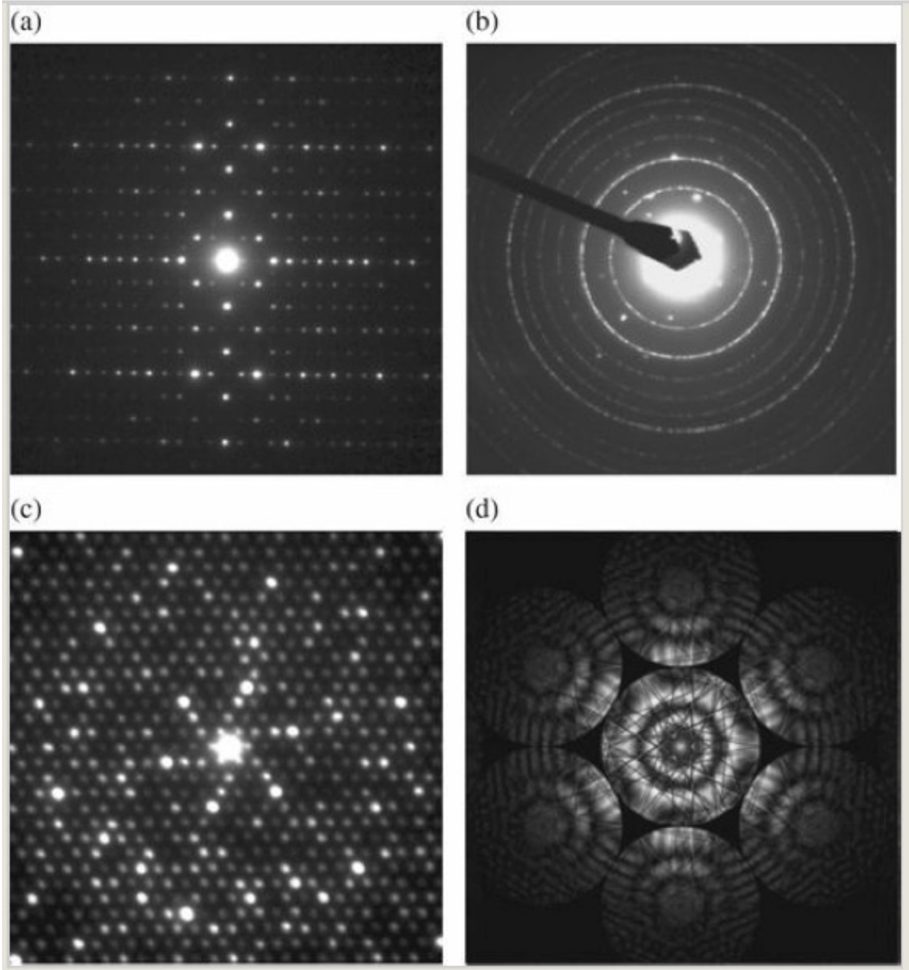


CBED

Convergent Beam
Electron Diffraction

Methods in Electron Diffraction

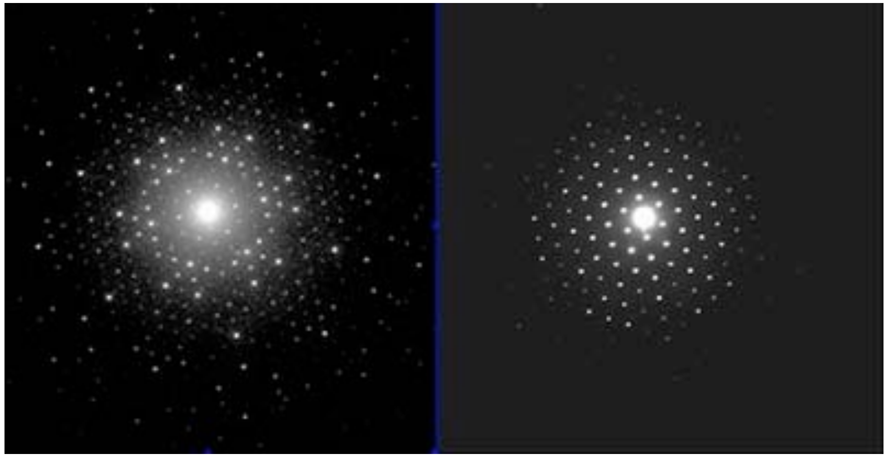
- **SAED**
  - single crystal (a)
  - powder sample (b)
- **CBED** (d)
- **Micro-/Nanodiffraction** (c)



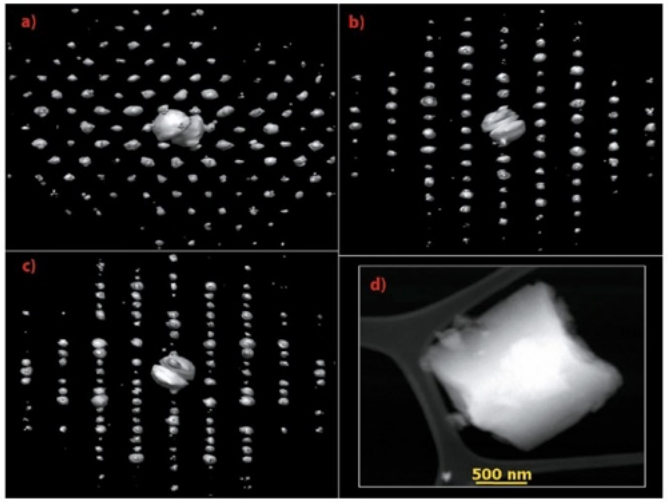
Xiaodong Zou, Sven Hovmöller, and Peter Oleynikov (2011), Electron Crystallography

More Methods based on Electron Diffraction

- **PED**
  Precession electron diffraction

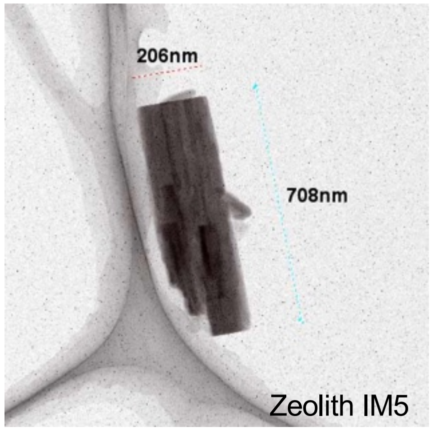


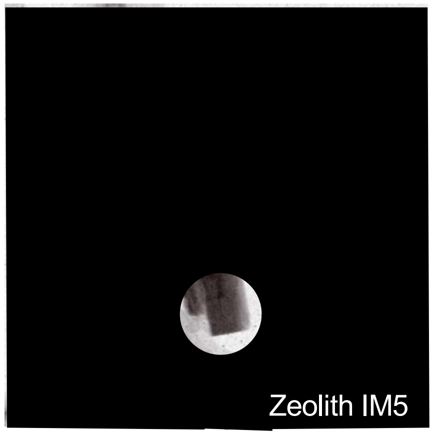
- **ADT**
  Automated Electron diffraction tomography



Xiaodong Zou, Sven Hovmöller, and Peter Oleynikov (2011), Electron Crystallography

Selected Area Electron Diffraction SAED



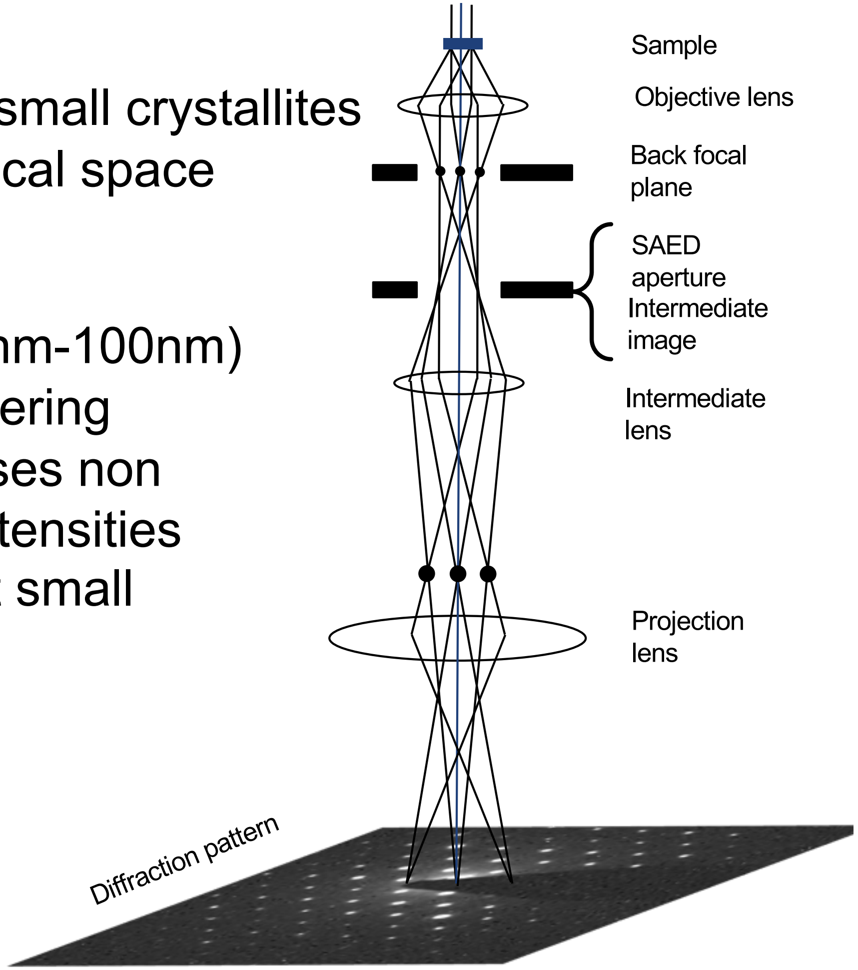


Advantages

- single crystal data from small crystallites
- reconstruction of reciprocal space

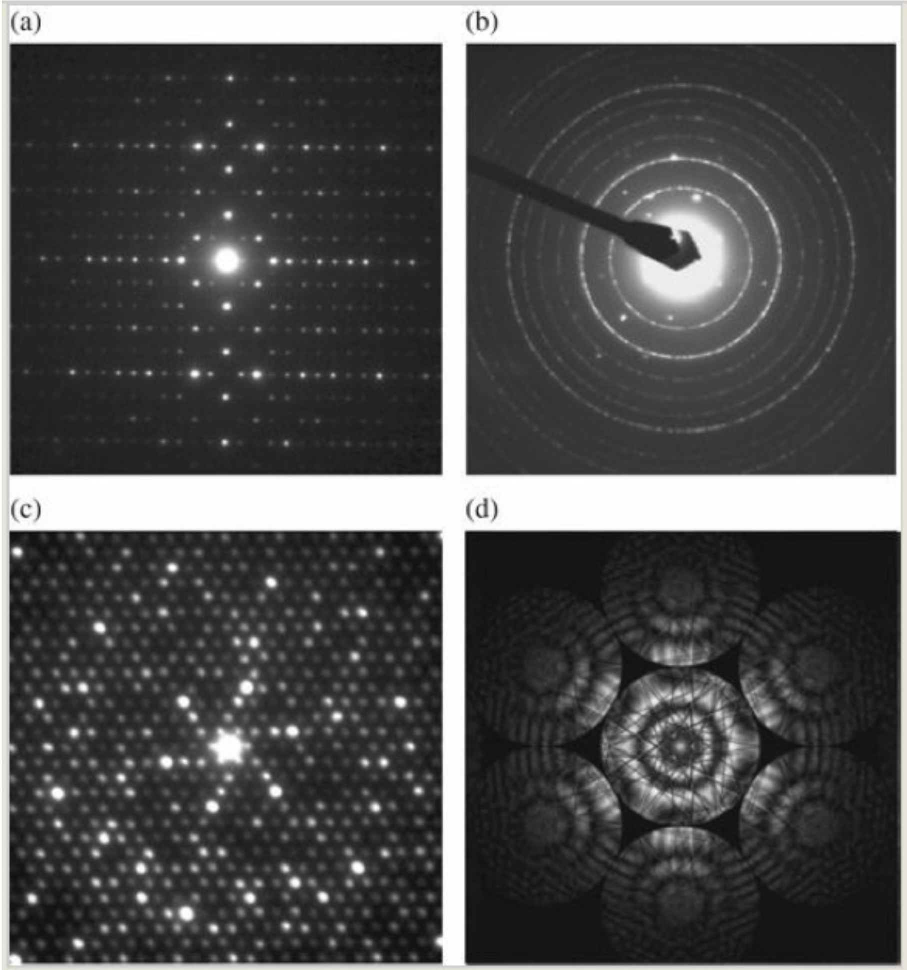
Disadvantage

- Sample thickness (<60nm-100nm)
- Double or multiple scattering
- Inelastic scattering causes non kinematical reflection intensities
- It could be tedious to tilt small particles



Methods in Electron Diffraction

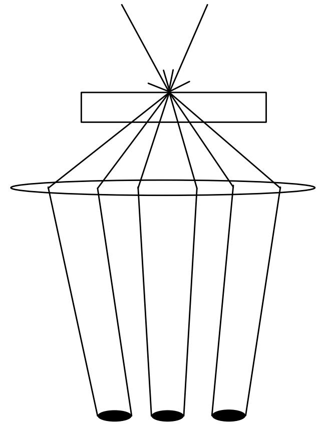
- **SAED**
  - single crystal (a)
  - powder sample (b)
- **CBED** (d)
- **Nanodiffraction** (c)



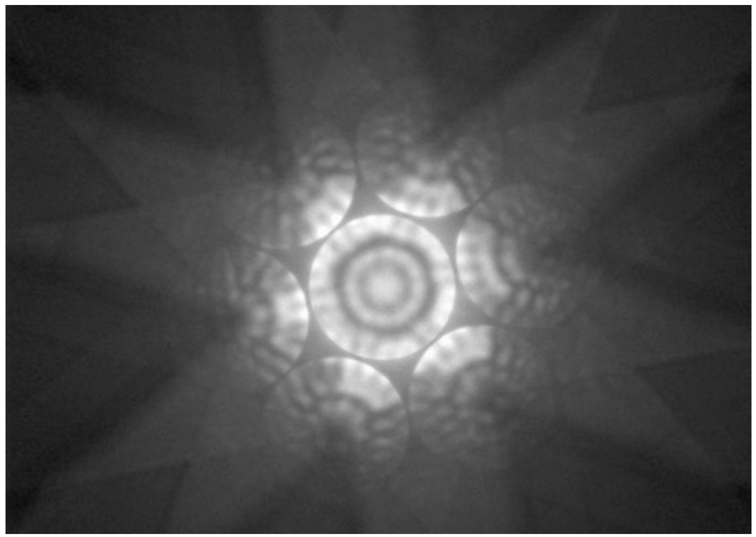
Xiaodong Zou, Sven Hovmöller, and Peter Oleynikov (2011), Electron Crystallography

Convergent Beam Electron Diffraction

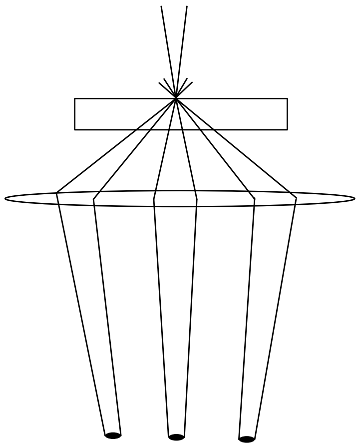
- Convergence angle 0.1°-1°



- Why use CBED?
  - Contains more information about symmetry than SAED.
  - Extinctions due to screw axes or glide plane symmetry in the crystal unit cell can be determined
  - Probe small areas (some 10th of nm)
  - Strain measuerments



Nano- / Microdiffraction

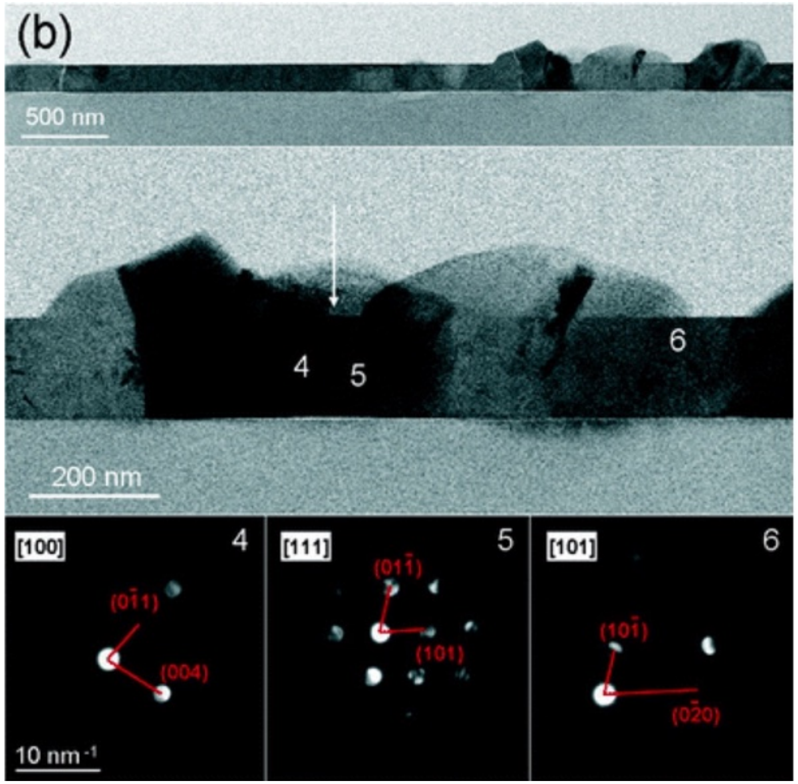


Probing the sample with a small beam.

Beam diameter is typically between sub nanometer range to some 10th of nanometers.

Probe size also depends on the thickness of the sample. Only for thinnest samples the smallest beam diameter is useful.

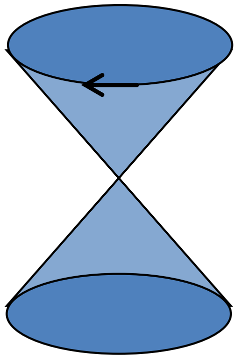
The STEM beam coils allow to **place the beam** on different positions on the sample.

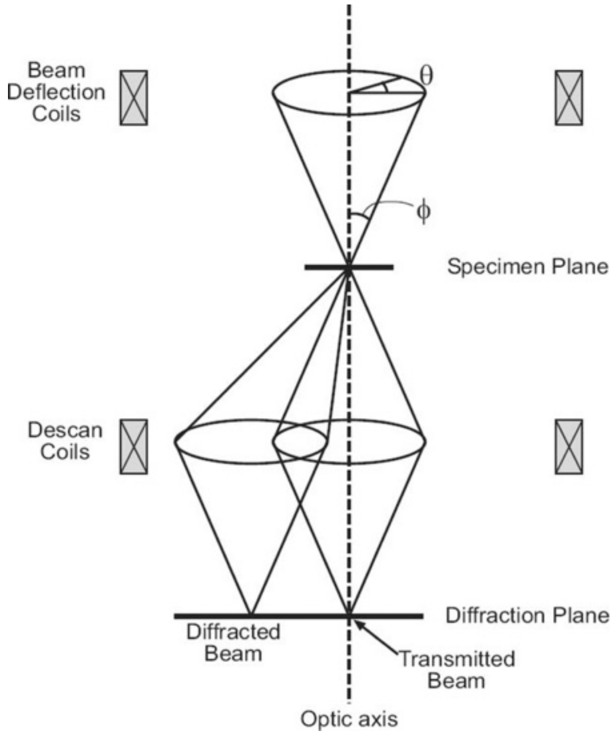


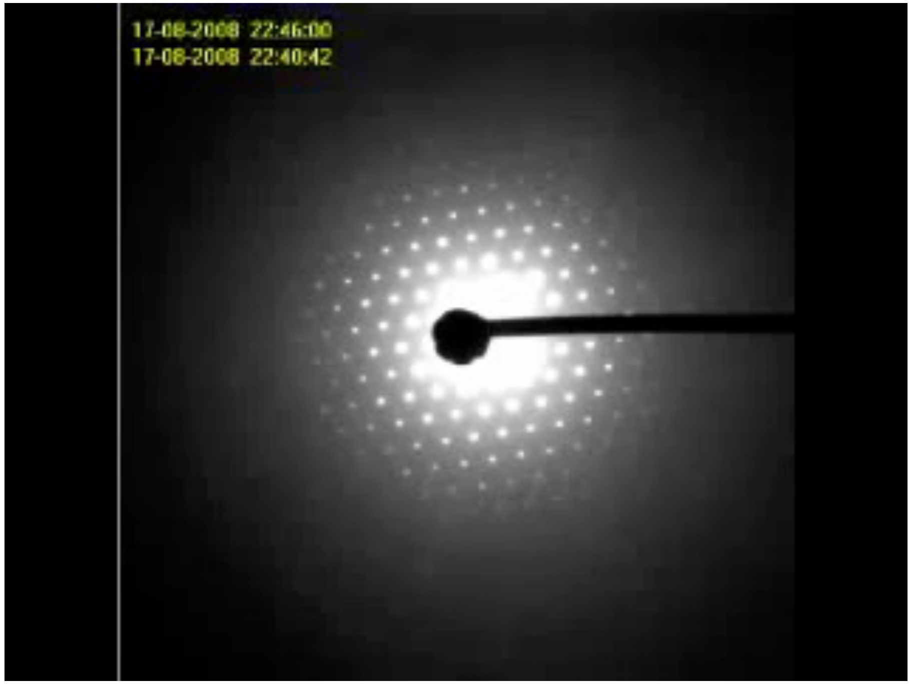
TiO2 films grown on Si at 200 °C, annealed at 200 °C for 3 hours. The bottom images show nano diffraction patterns taken from areas 3 depicted in the upper image.

Ref: Grzegorz Luka et al CrystEngComm, 2013, **15**

PED - Precession Electron Diffraction



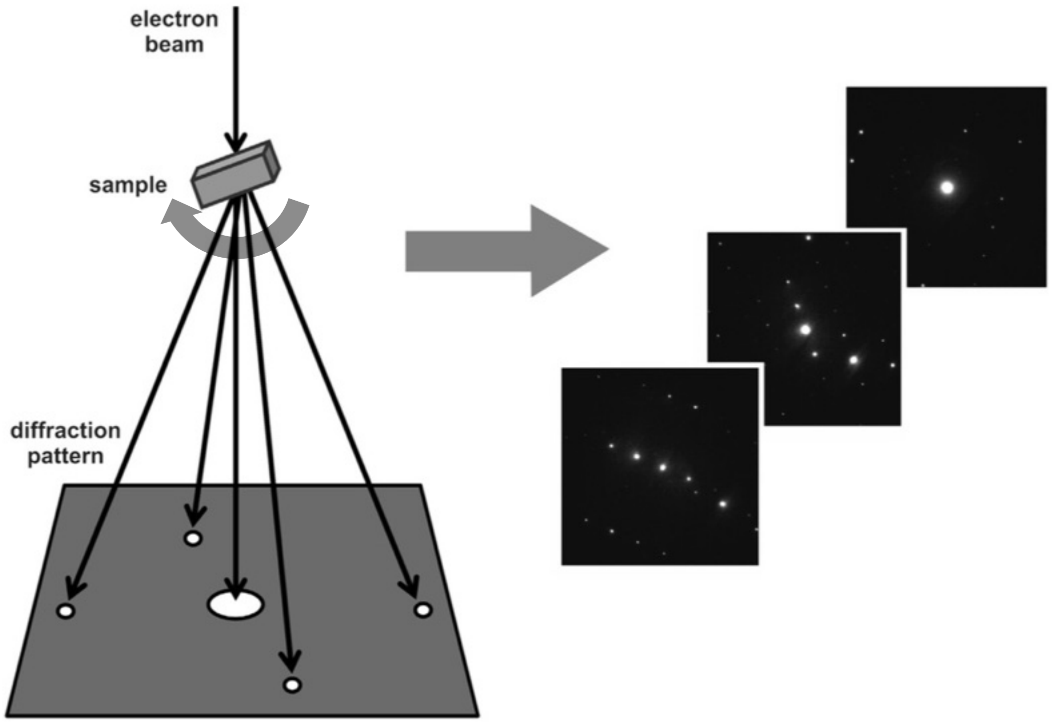




- More high angle reflections observable
- Reflection intensities are "more" kinematical

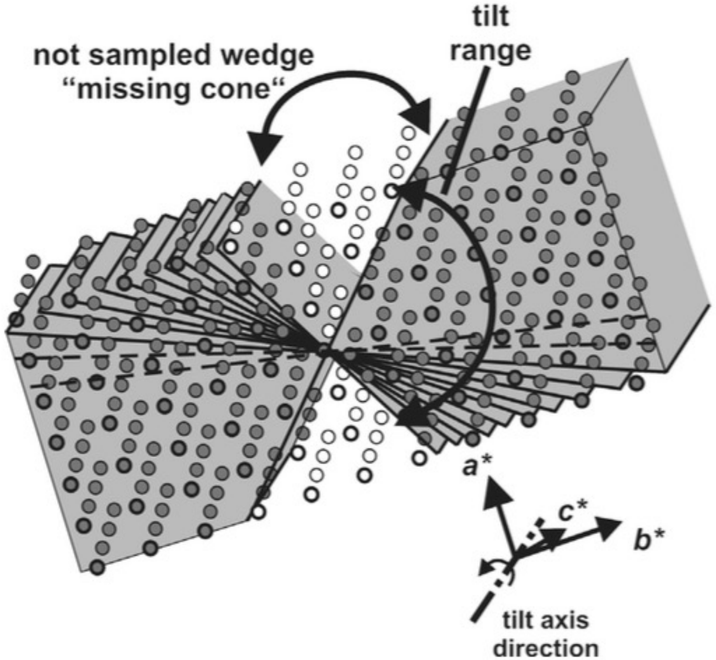
Own C. et al. (2006), Acta. Cryst, Vol. 62
Nanomegas, www.nanomegas.com, 10/23/2014

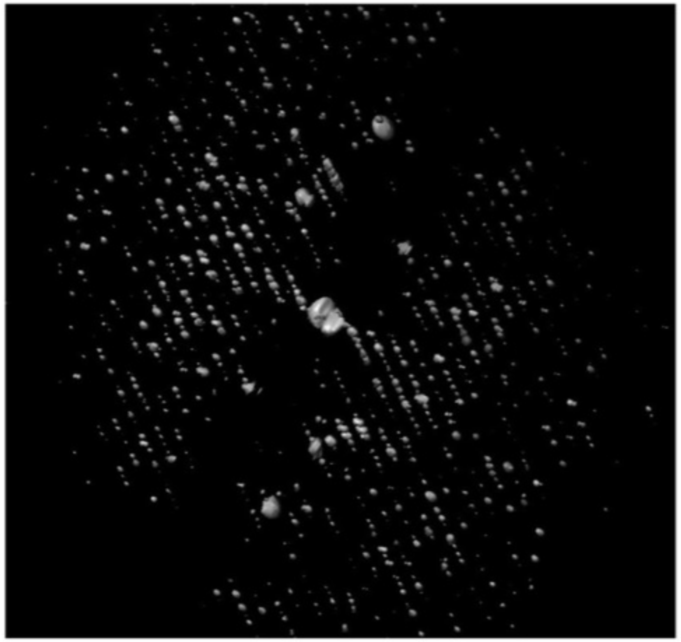
Automated electron diffraction tomography (ADT)



ADT data acquisition: scheme showing the sequential collection of electron diffraction patterns by tilting the crystal resulting in three exemplary off-zone diffraction patterns of one crystal.

Reconstructing the collected data in reciprocal space with ADT data

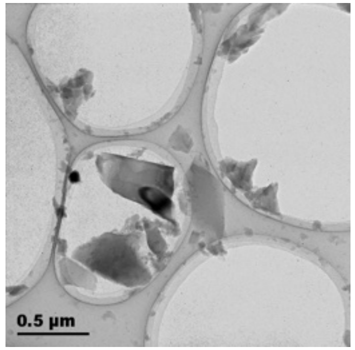




Collection scheme showing the reconstruction of the three-dimensional diffraction volume and the missing cone volume (left), A typical tilt step is about 1°; Reconstructed diffraction space (right).

E. Mugnaioli, U. Kolb / Microporous and Mesoporous Materials 189 (2014) 107–114

ADT



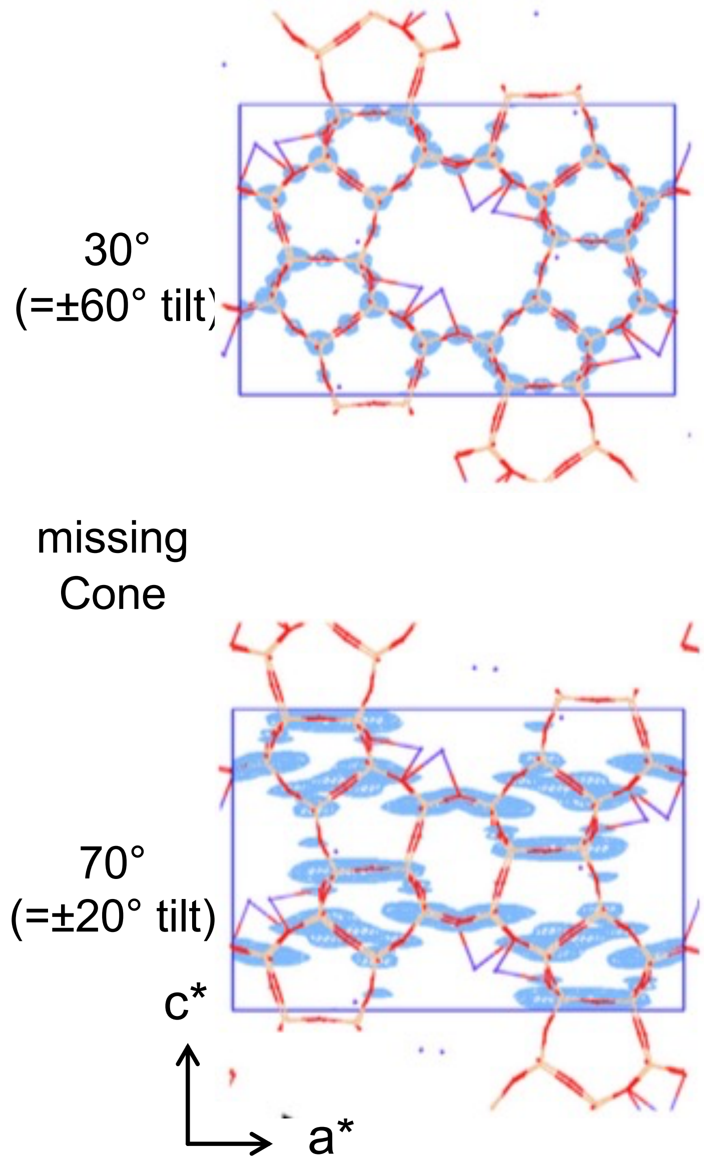
- **Acquiring diffraction pattern off-zone** -> significant reduction of dynamical effects -> quasi kinematical data
- **No pre-orientation** of the crystal is necessary
- Now a days **automated acquisition** is possible in a few minutes
- Additionally precession electron diffraction (**PED**) can be applied (improved reflection quality)
- Data collection in SAED or in nanodiffraction mode is possible
- **Missing cone** is a problem especially for platelets (e.g. ZSM-5)
- **Combination of datasets** collected on different crystal orientations possible (e.g. with tilt rotation holder)

ADT results

Example:
Data collection in nano electron diffraction mode for zeolite ZSM-5:

- platelet in h00 orientation
- tilting ±60°
- recording the data up to 1Å resolution
- using SIR 2011 for solving the structure

found all 12 silicon positions,
while only 24 of 26 oxygen positions were found.



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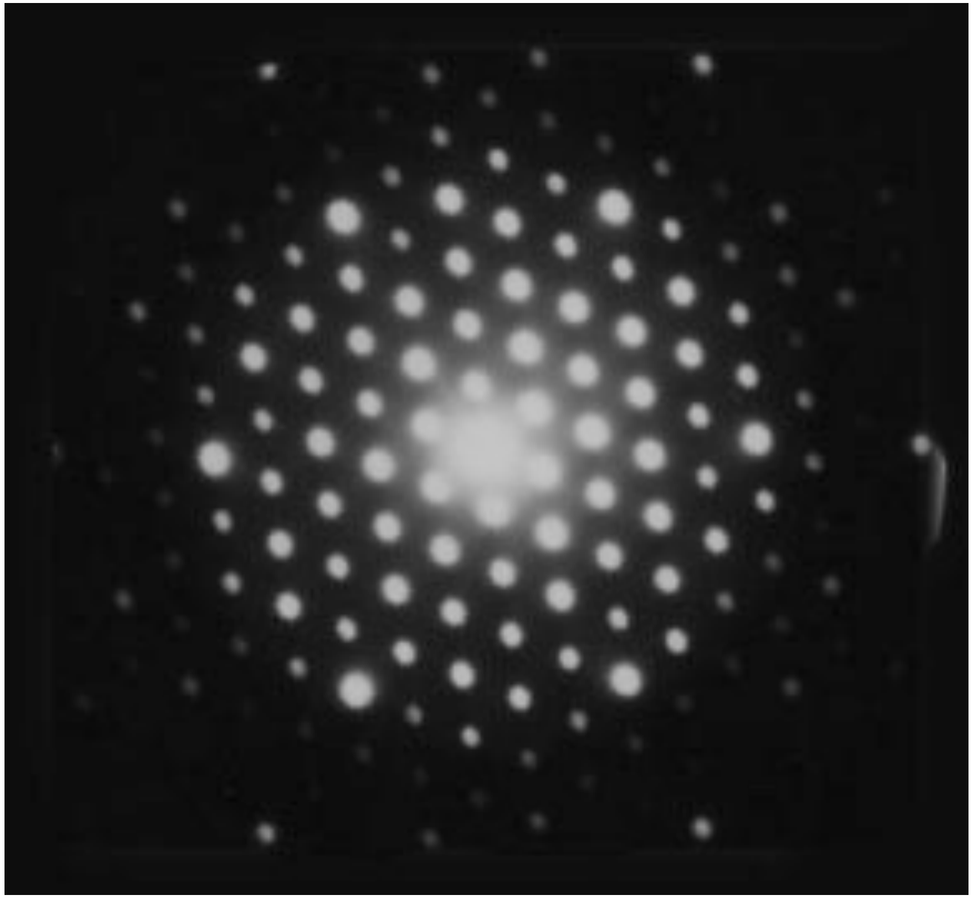
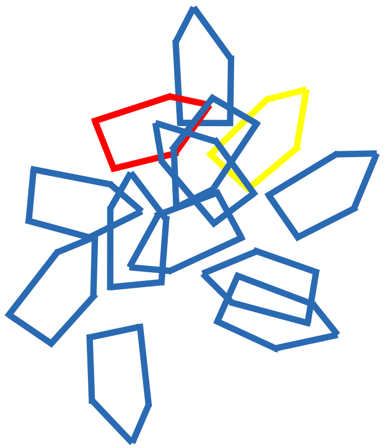
Selected applications in electron diffraction?



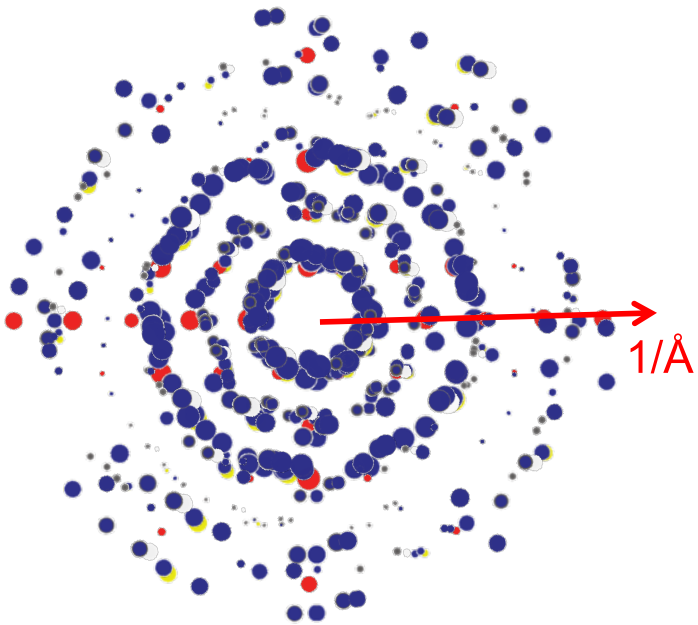
Applications for Electron Diffraction

- Crystallinity of the sample
- Orientation of a crystal
- Phase analysis
- Unit Cell Determination
- Solving crystal structures

From single crystals to powder diffraction

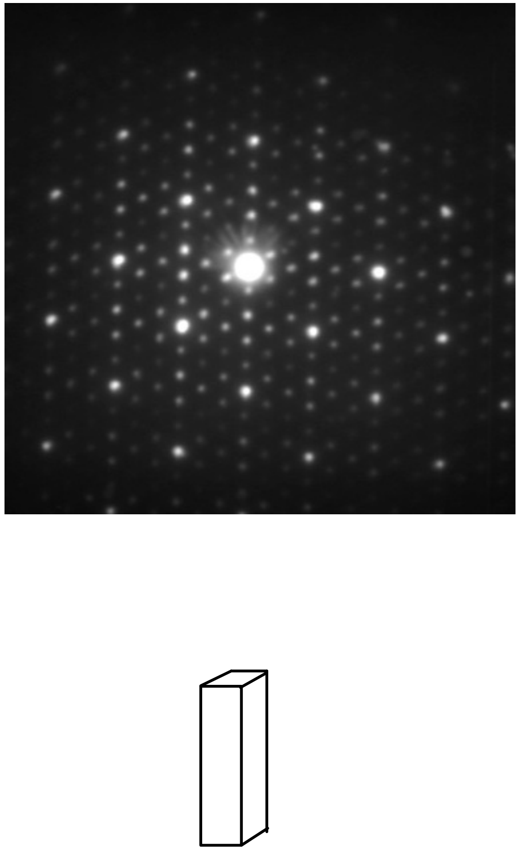


Crystal arrangement

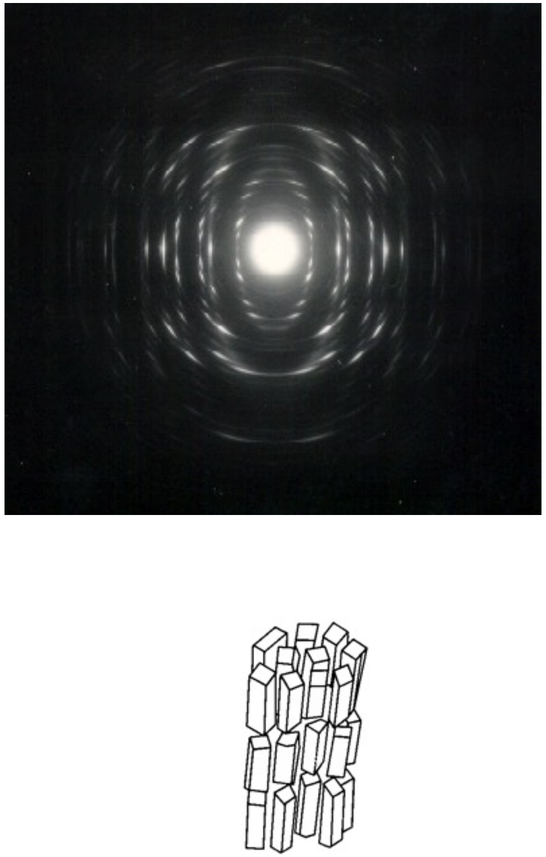


Ring diffraction pattern
from many crystals

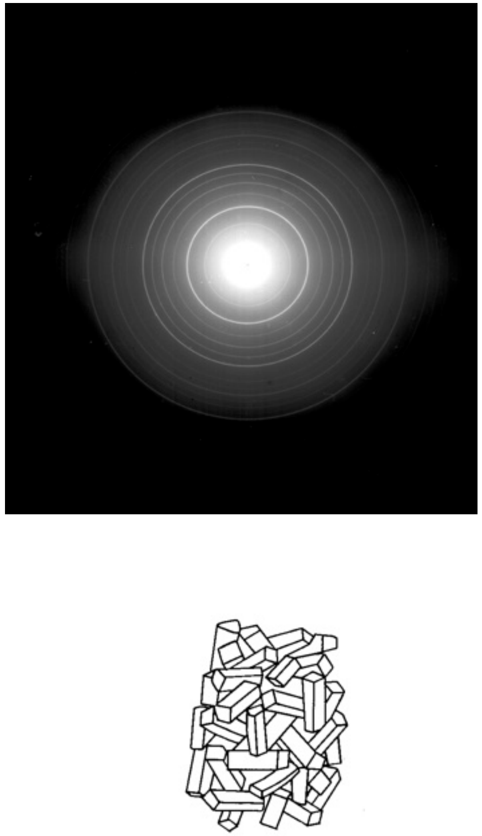
Crystallinity and texture of the sample



SINGLE CRYSTAL



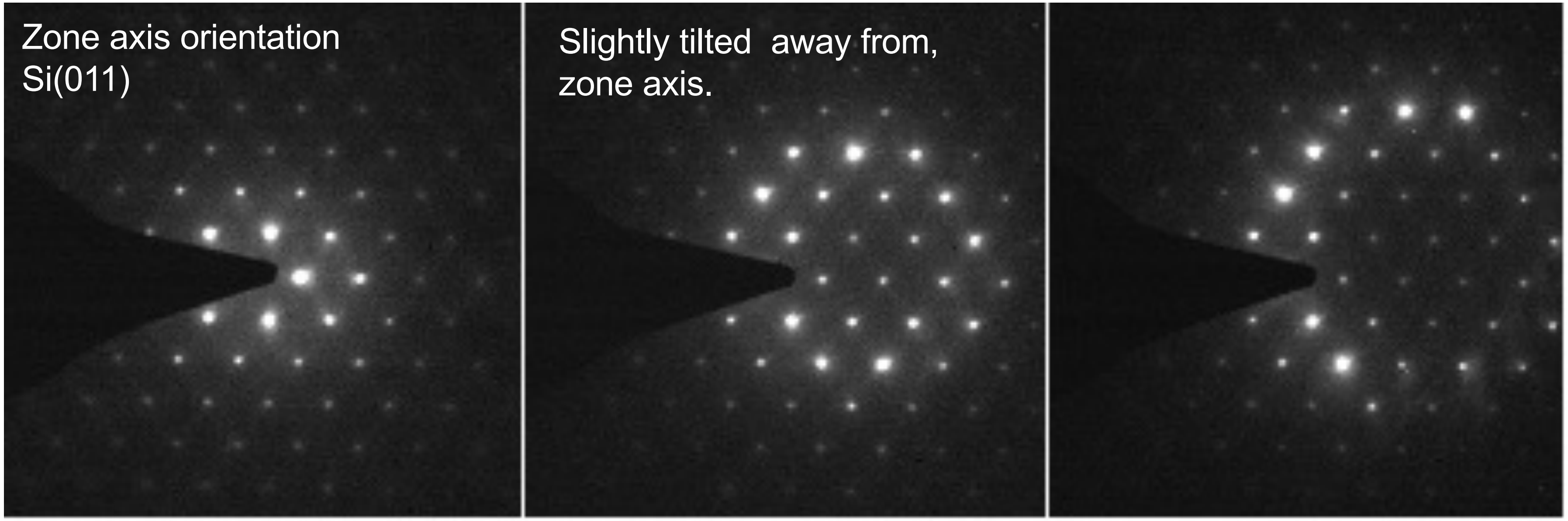
PLATELIKE TEXTURE



POLYCRYSTAL

Images: University of Georgia: caur.uga.edu/ppt/EleDiffWu.ppt 10/23/2014

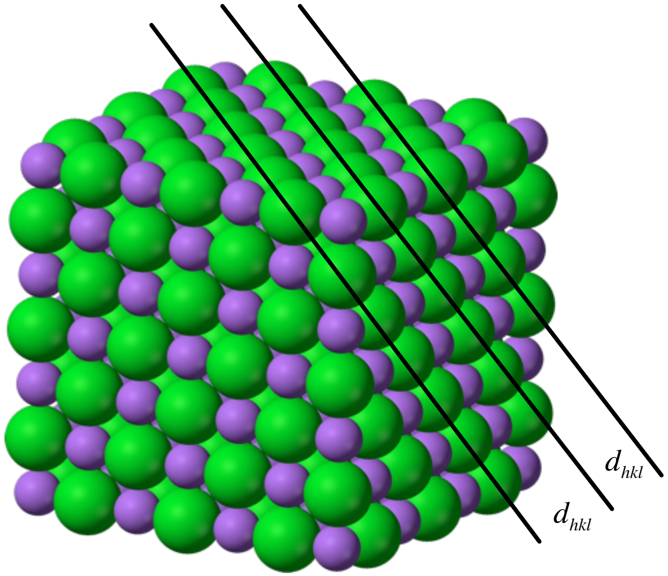
Orientation of a crystal using SAED

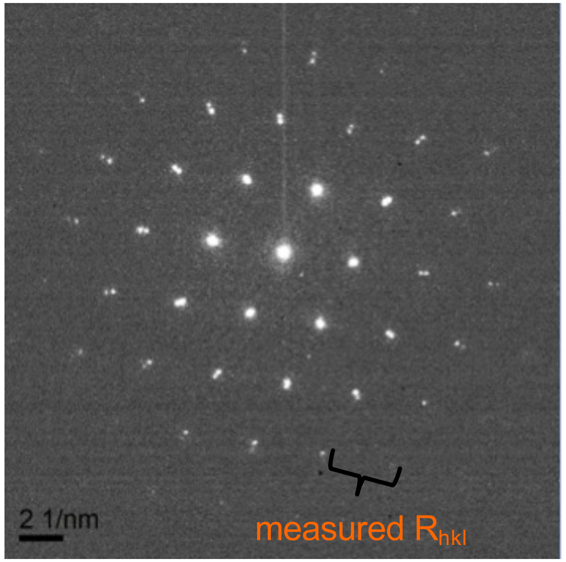


Effect of crystal tilt onto the diffraction pattern: the left image shows the diffraction pattern, where the incident beam is oriented almost exactly along a zone axis – Si(011) – while the other two images show diffraction patterns of the same crystal with increasing deviation from zone-axis orientation.

Phase Analysis

Verification of a known Phase:
Comparing calculated (from structure model) d-values with experimental ones from diffraction pattern (SAED) to confirm the presence of a phase.

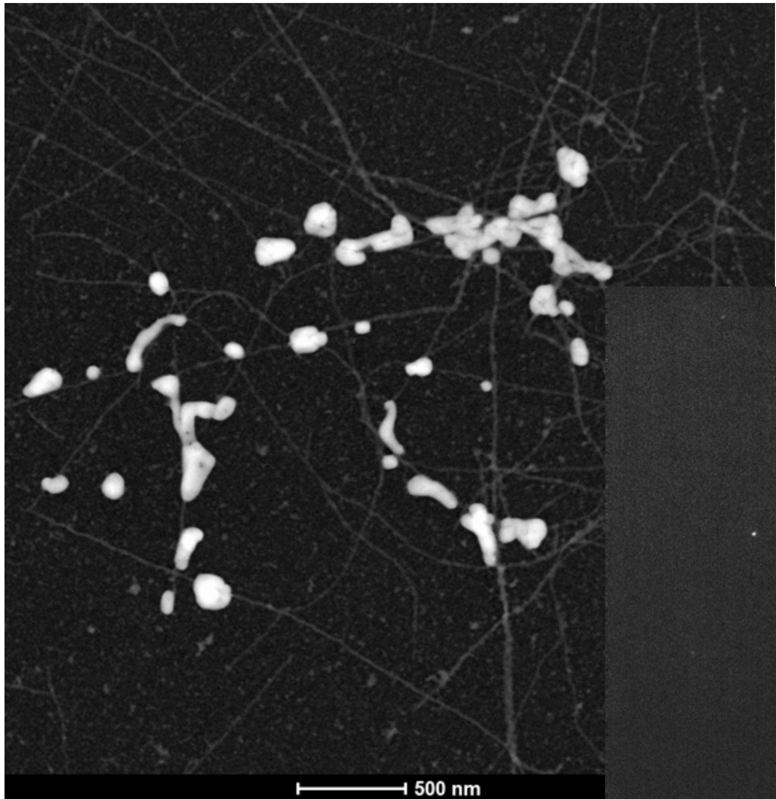




Inter planar spacing in cubic system:

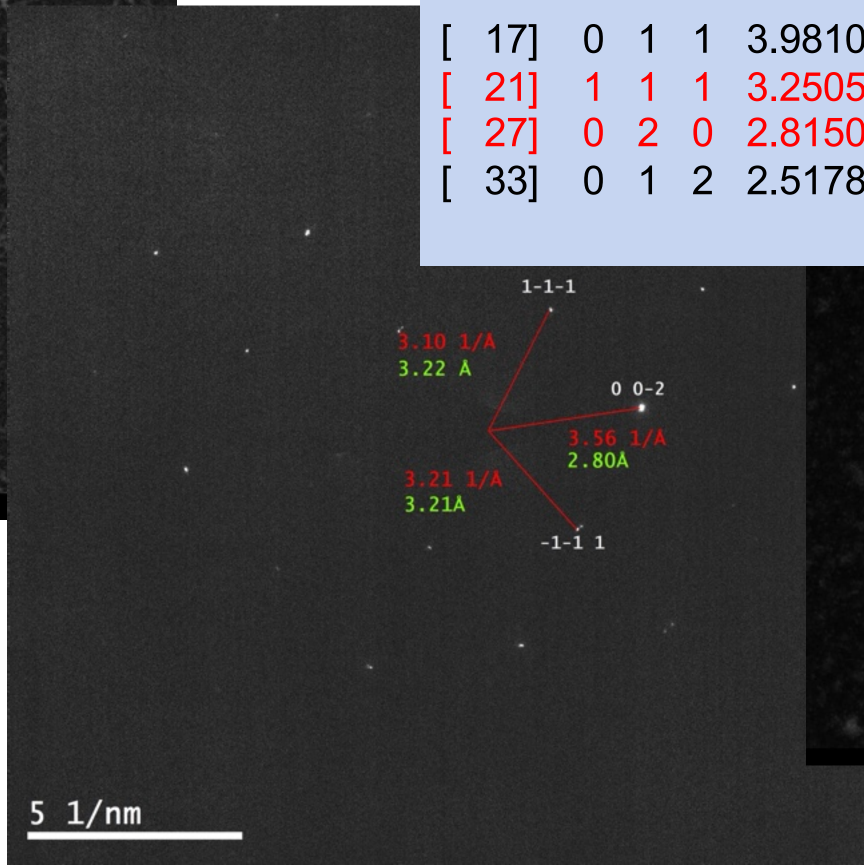
$$d_{hkl}^{calc} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \longleftrightarrow d_{hkl}^{exp} = \frac{\lambda L}{R_{hkl}}$$

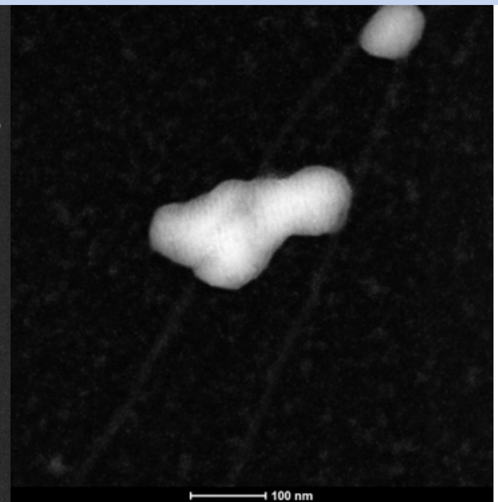
Fe-Nanoparticles on betalactoglobulin fibers?



Calculated d_{hkl} of NaCl:

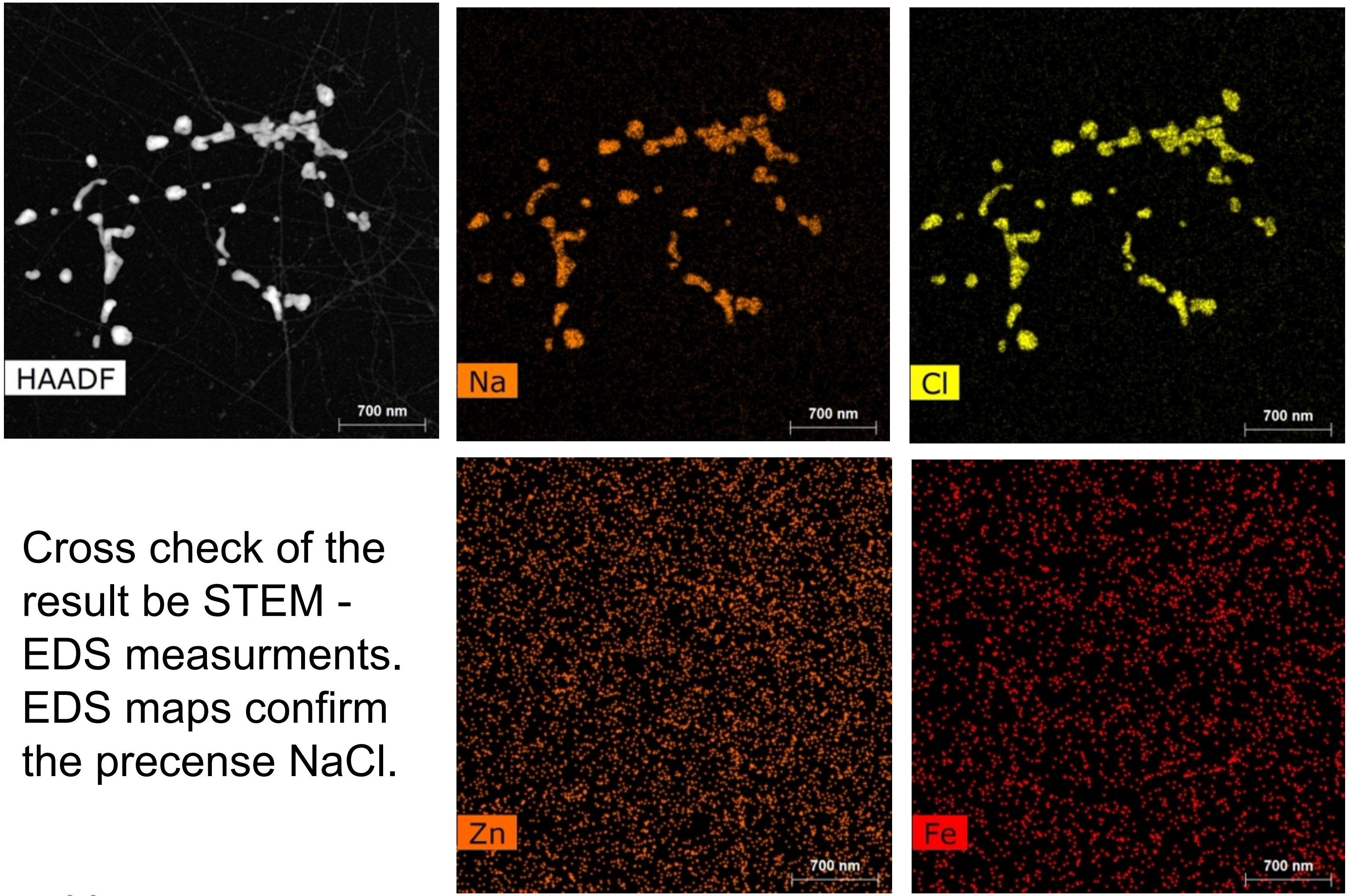
ref no.	h	k	l	d calc [A]	d obs	d* [1/A]
[17]	0	1	1	3.9810		0.25119
[21]	1	1	1	3.2505	3.22	0.30765
[27]	0	2	0	2.8150	3.56	0.35524
[33]	0	1	2	2.5178		0.39717





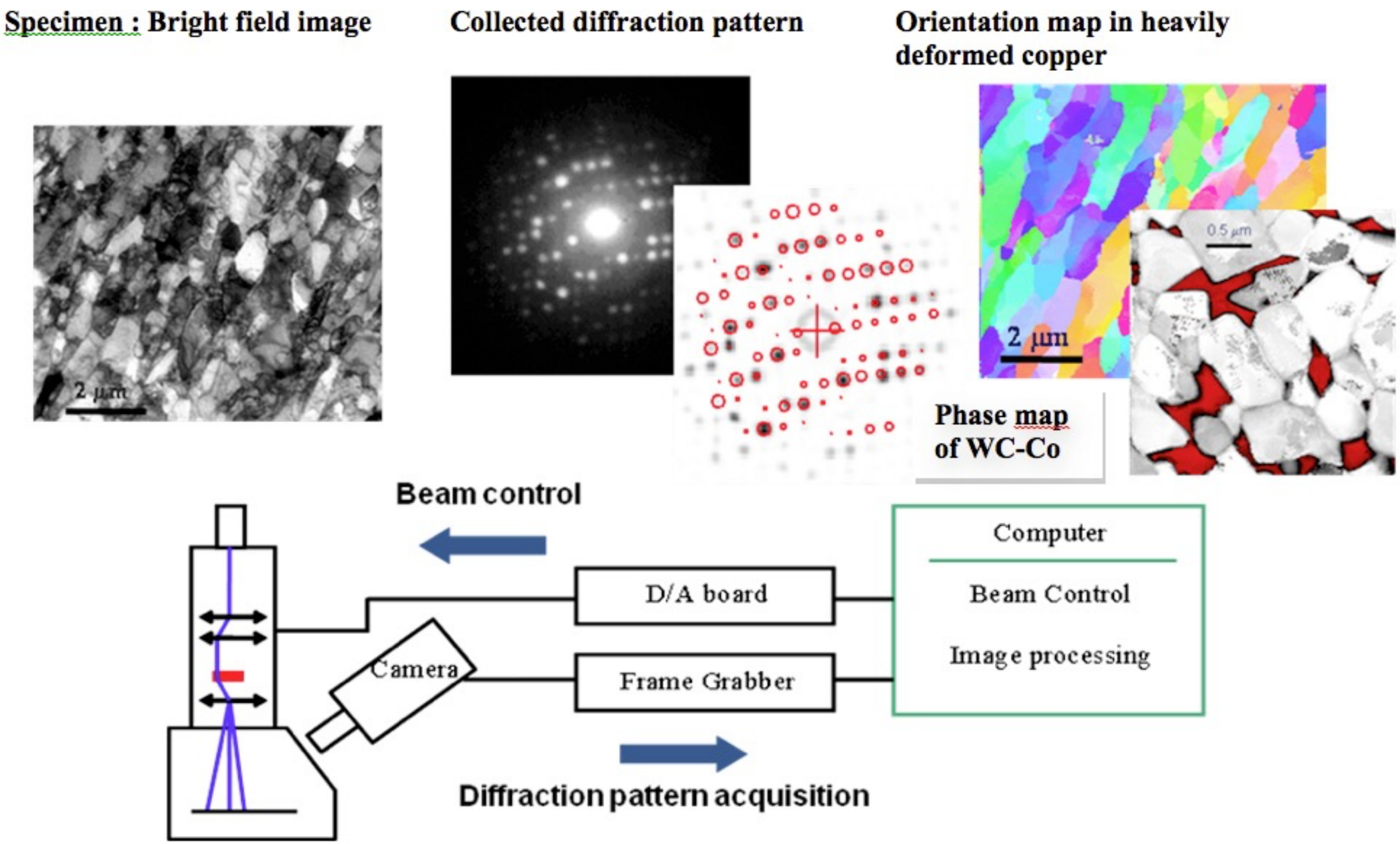
SAED patterns from the particles show reflections with d-values that fit to NaCl

ZnFe-Nanoparticles on betalactoglobulin fibers?

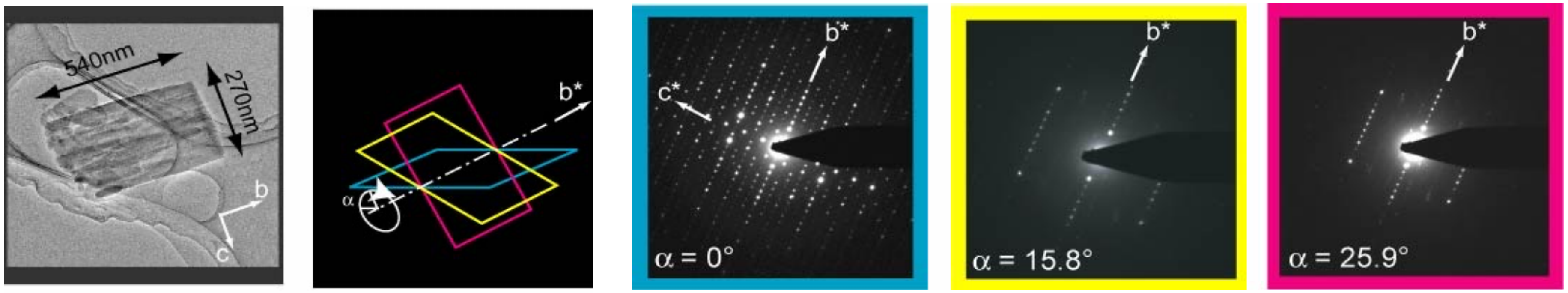


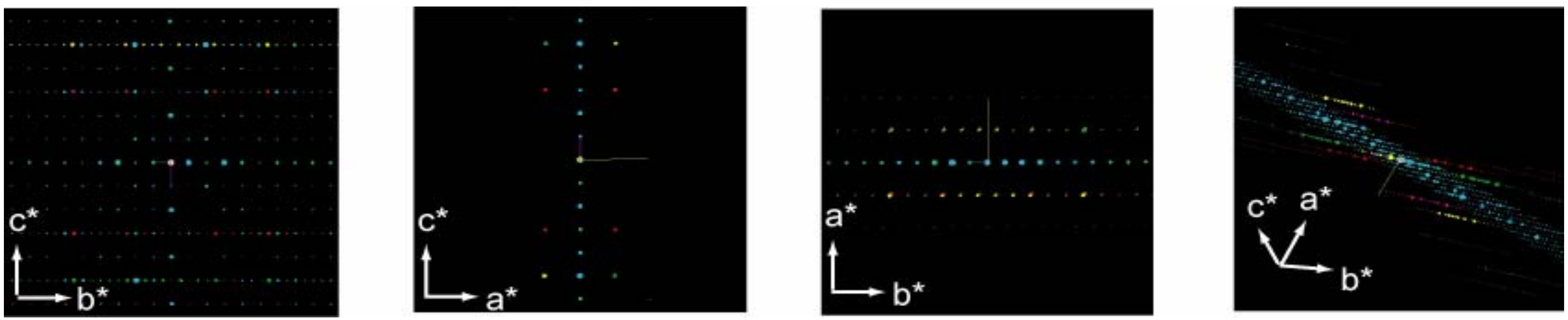
Cross check of the result be STEM - EDS measurments. EDS maps confirm the precense NaCl.

Orientation Mapping using PED



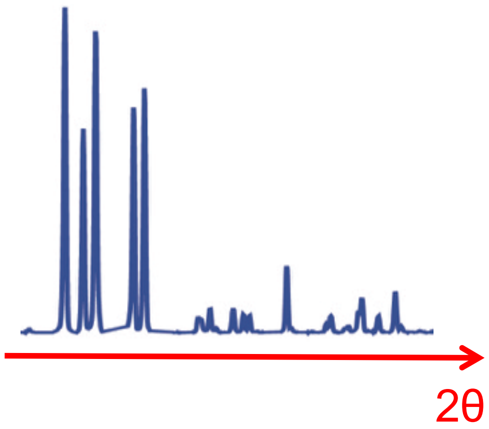
Tilt series to determine the unit cell of a crystal with SAED tilt series





A tilt series of diffraction patterns allows to partly reconstruct the reciprocal space. Possible unit cells of an unknown crystal can be found in the reciprocal lattice.

The phase problem



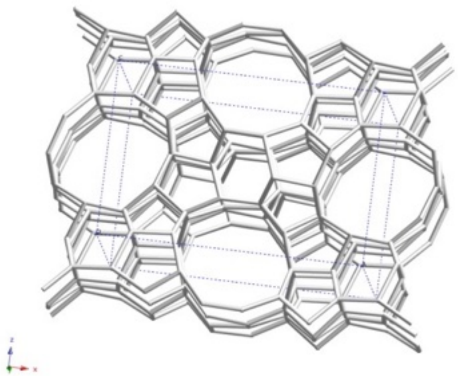
Intensity — Structure factor

$$I \propto \left|F_{hkl}\right|^2$$

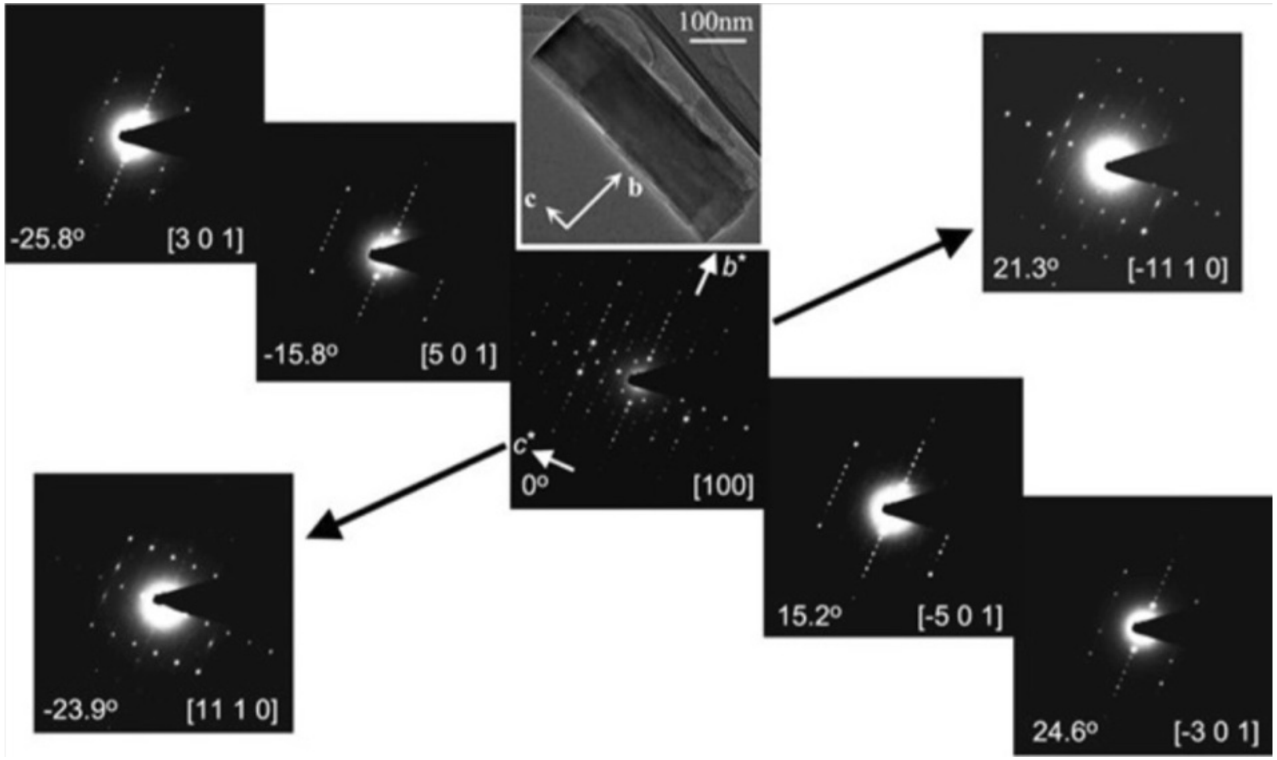
?

$$\rho_{xyz} = \frac{1}{V}\sum_{hkl}\left|F_{hkl}\right|\cdot e^{-i\Phi_{hkl}}$$

Electron density — Phase



Solving structure of zeolite IM-5 from electron diffraction and HRTEM



The unit-cell parameters were determined from the tilt series and the SAED patterns were then indexed.

=> Unit cell volume
14.33 × 56.9 × 20.32Å
= 16 568 Å^3

⇒ Space group: Cmcm

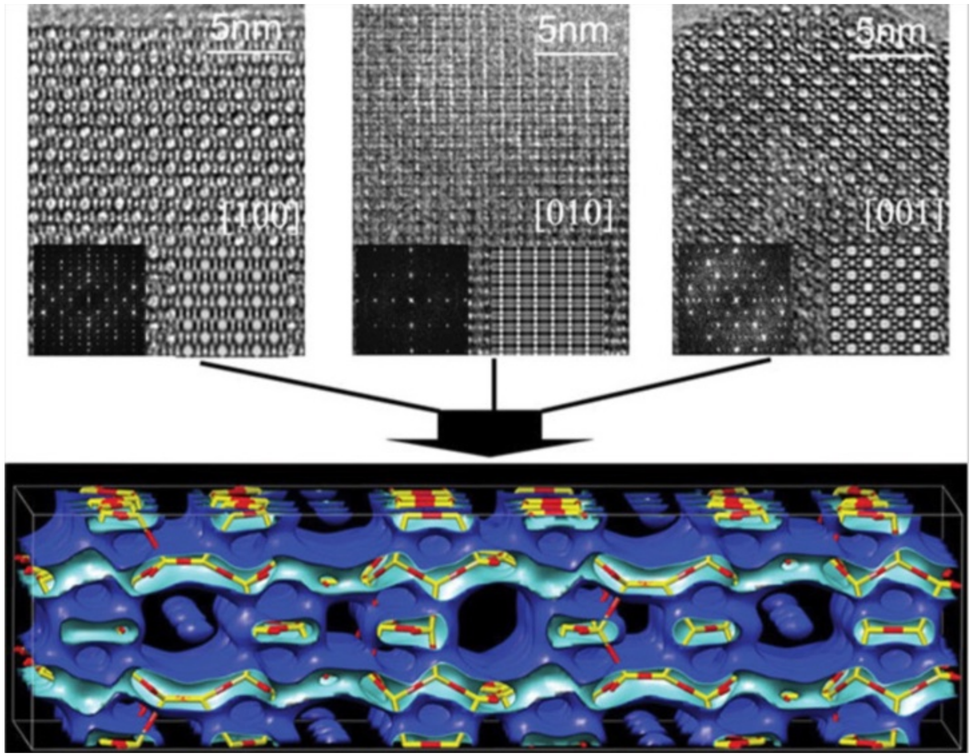
⇒ max. 920 atoms expected

Similarly, the SAED patterns along the [1 0 0], [11 1 0] and [−11 1 0] directions all have the mirror-symmetry perpendicular to the **c***-axis

SAED patterns along the [5 0 1], [−5 0 1], [3 0 1] and [−3 0 1] directions show a mirror- symmetry perpendicular to the **b***-axis.

Sun et. al., Z. Kristallogr. 225 (2010) 77–85

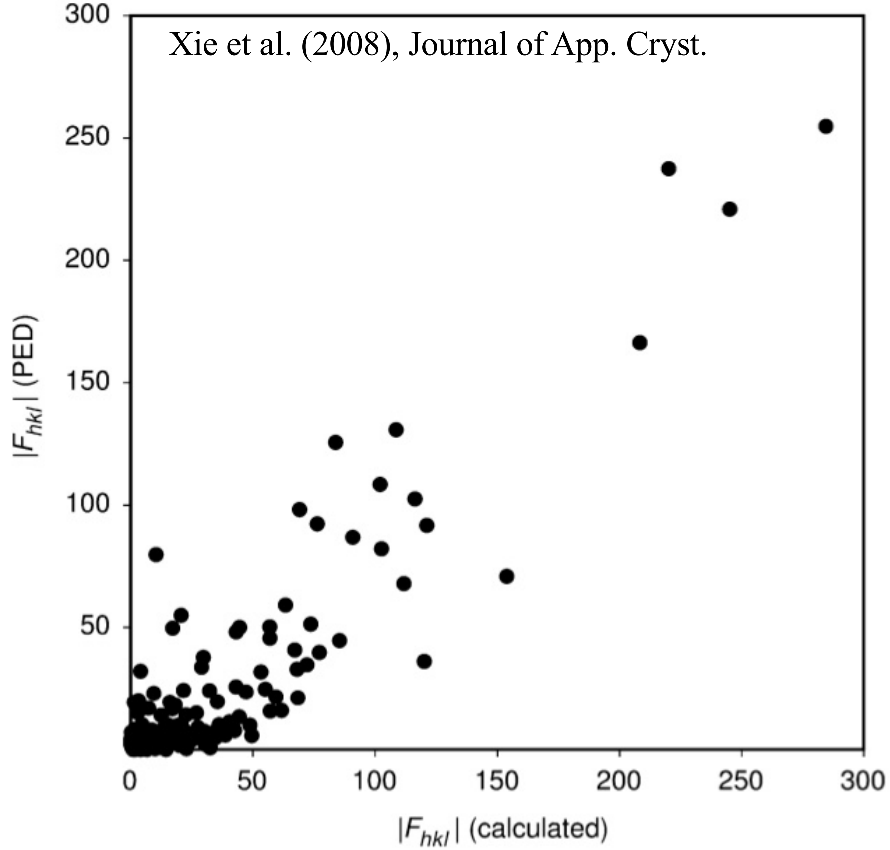
Electrostatic potential map calculated from 3 HRTEM images



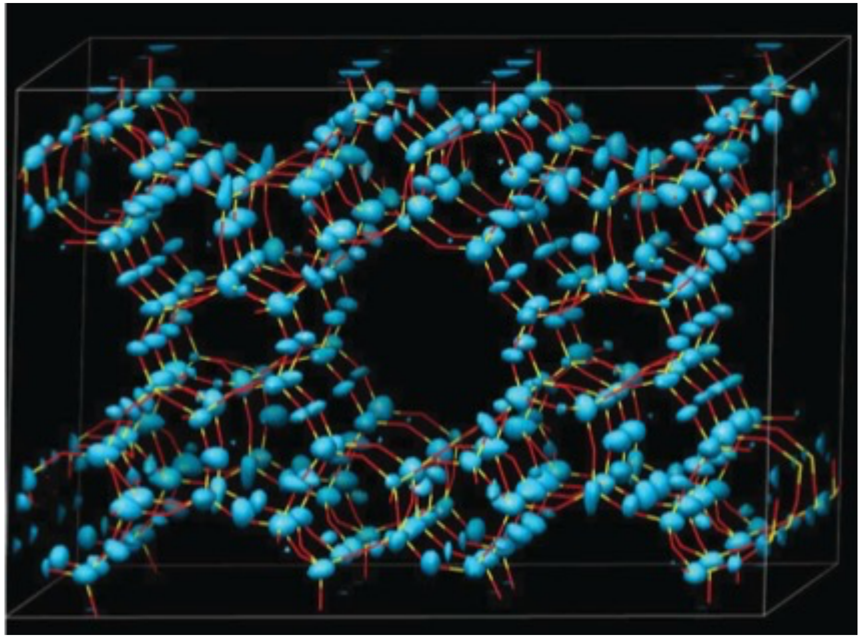
HRTEM images of the zeolite IM-5, taken along the three main crystallographic axes. The inserts show their corresponding Fourier transforms and images after imposing the Cmcm symmetry.

The 3D electrostatic potential map generated from HRTEM images given above. From the three projections 128 reflection were obtained in total. All **24 unique Si atomic** positions could be **located** from the 3D potential map. From Sun et al (2010)

Solving crystal structures with precession electron diffraction data



Comparison between experimental (PED) and calculated structure-factor amplitudes for the [010] projection of ZSM-5.



Charge flipping density map of zeolite TNU-9: One of the two most complex known zeolites solved by Xie et al. (2008), demonstrated that this structure can be solved using **5 PED patterns** combined with a **charge flipping** algorithm to retrieve the phase information and **weak reflection elimination based on the PED** pattern, combined with a X-ray powder diffraction dataset.

Summary

Electron diffraction is **very useful technique** to get many structural information's of the sample on a nano or atomic scale:

- **crystallinity**
- **crystallographic information (e.g. unit cell, space group)**
- **phase analysis**
- **crystal structures**
- strain measurement
- thickness determination

etc.

Compared to X-ray diffraction **electron diffraction** provides more local information on the nano scale, but it is usually less precise than X-ray diffraction.

Thank you for your attention !