Electron Matter Interactions in Transmission Electron Microscopy PHYS-637

Week 1- Introduction

Course Schedule

- **Week 1: Introduction (CH)**
- Week 2: The electron wave, elastic scattering by an atom, and crystal scattering geometry. (DA)
- Week 3: Diffraction from a crystal: kinematical and dynamical (Bloch wave) theories. (DA)
- Week 4: Week 4: Bloch wave theory: adaptations and observations; phonon scattering. (DA)
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- Week 6: Phase contrast, Lorentz TEM and other techniques. (TL)
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- Week 12: Low loss EELS: theoretical calculations and angular-resolved measurments. (CH)
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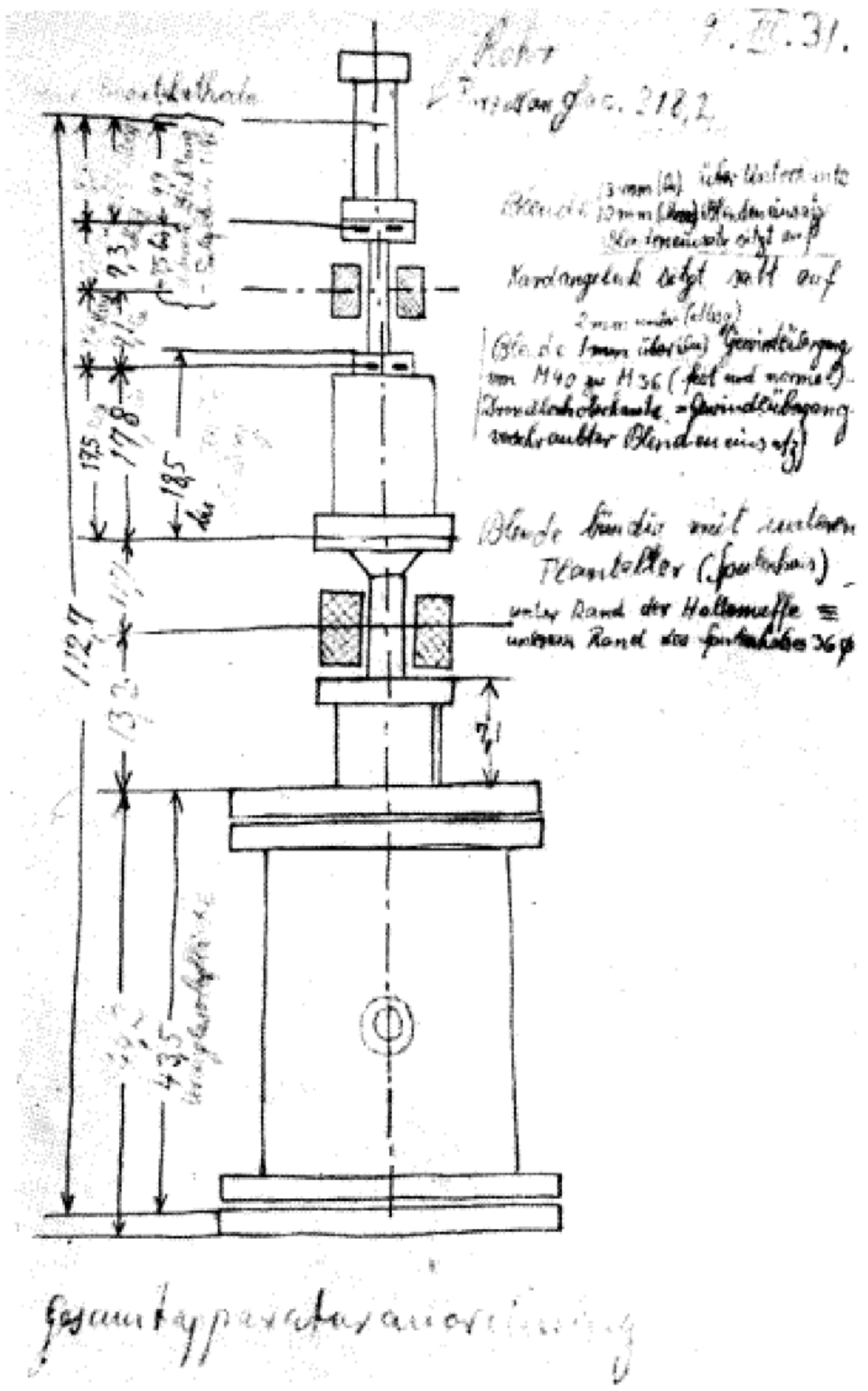
- Week 14: Vibrational spectroscopy (DA); Photon Induced Near-field Electron Microscopy (PINEM) (TL)

Week 1: Introduction

- A few words of history
- The Instrument
- Orders of magnitude
- Prerequisits: crystallography

History of TEM



E. Ruska

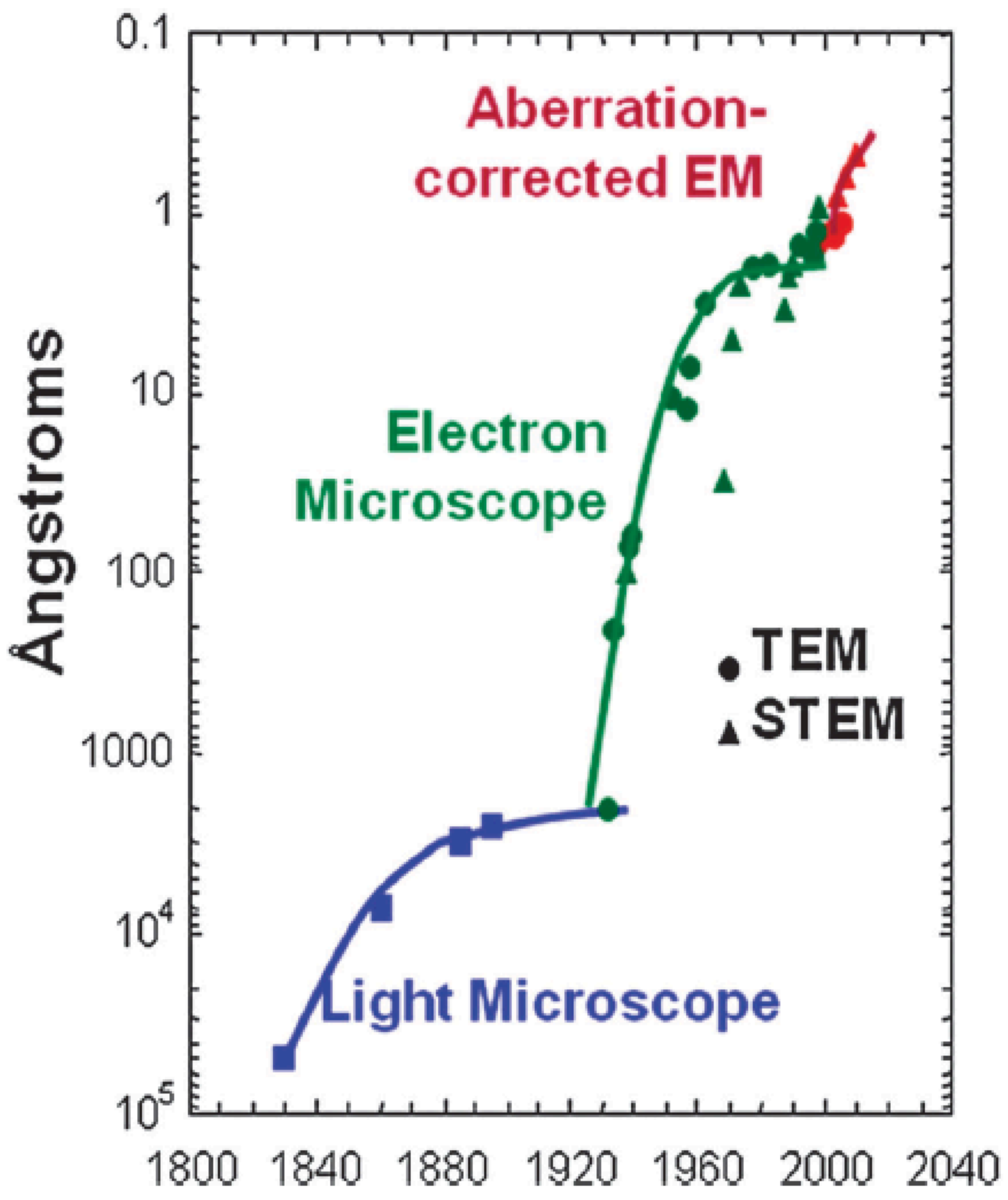
Sketch of first TEM by Ruska, 1931

- 1931: Knoll & Ruska build the first prototype
- 1933: The TEM surpasses the light microscope in resolution
- 1939: first commercial instrument

- 1986 E. Ruska is awarded the Nobel prize

From *Nobel Lectures*, *Physics 1981-1990*, Editor-in-Charge Tore Frängsmyr, Editor Gösta Ekspong, World Scientific Publishing Co., Singapore, 1993

History of TEM



- Abbe diffraction limit for the light microscope

$$d = \frac{\lambda}{2n\sin\theta}$$

- Equivalent for the electron microscope

$$d = \frac{1.2\lambda}{\sin\theta}$$

$$\lambda = 2.5\cdot 10^{-12}\,\mathrm{m}\ @\ 200\ \mathrm{kV};$$

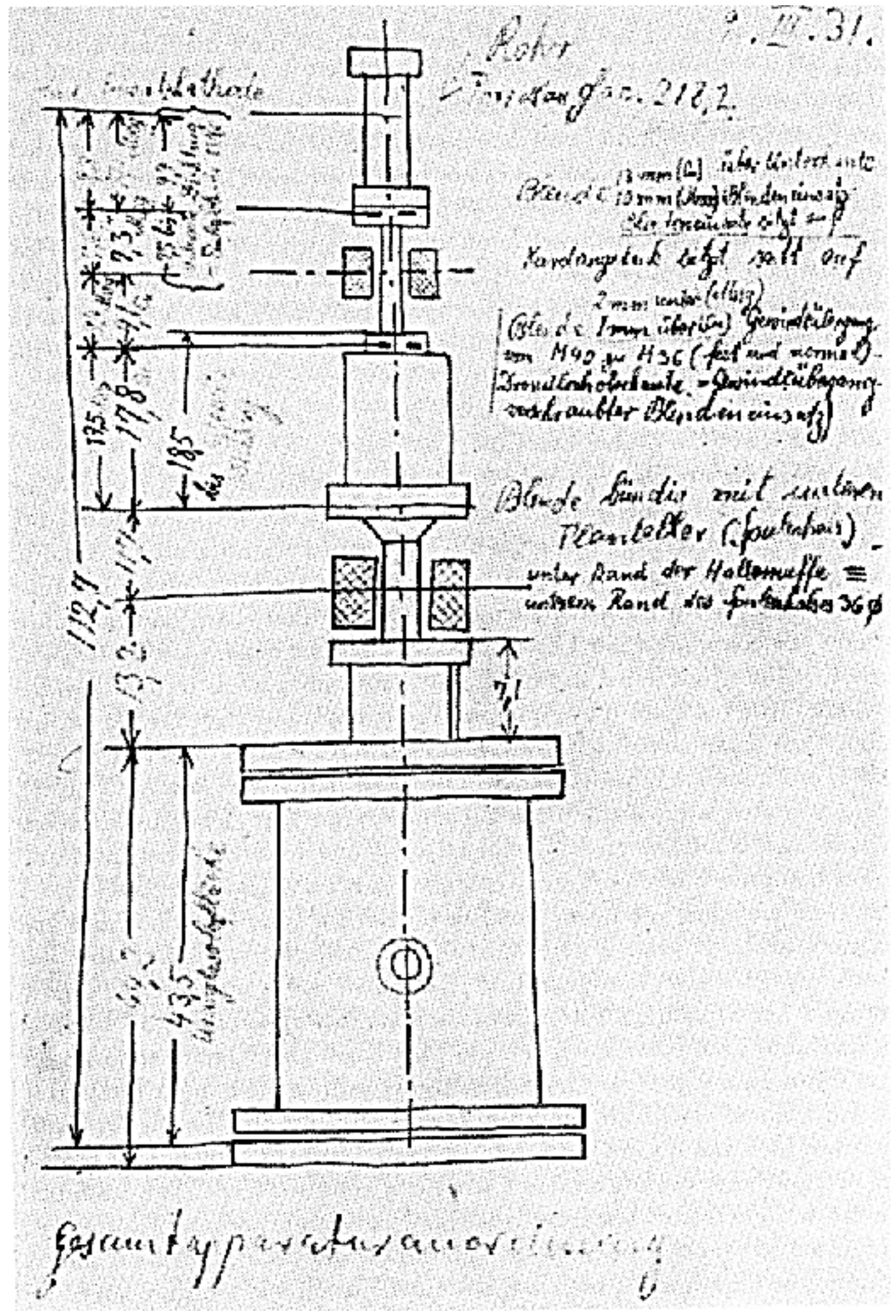
$$\theta \approx 10-20\ \mathrm{mrad}$$

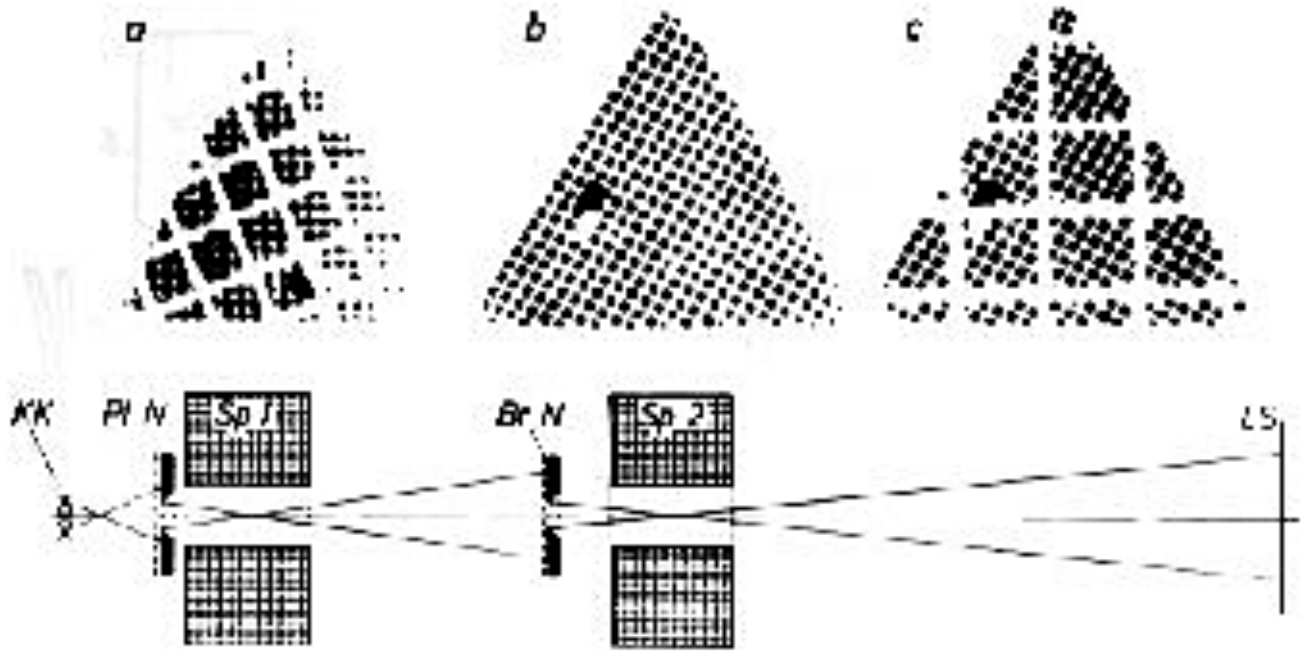
$$\Rightarrow\ d\ 1.5\ \mathrm{to}\ 3\ \text{Å}$$

S. J. Pennycook & al., in: The Oxford Handbook of Nanoscience and Nanotechnology, ed. A. V. Narlikar and Y. Y. Fu, Oxford University Press, Oxford, United Kingdom, 2010, p. 205.

History of (corrected) TEM

- 1931: Ernst Ruska & Max Knoll invent the TEM





Hope… and disappointment

- Wavelength of electrons at 200 kV: 2.5 pm

Über einige Fehler von Elektronenlinsen.

Von **O. Scherzer** in Darmstadt.

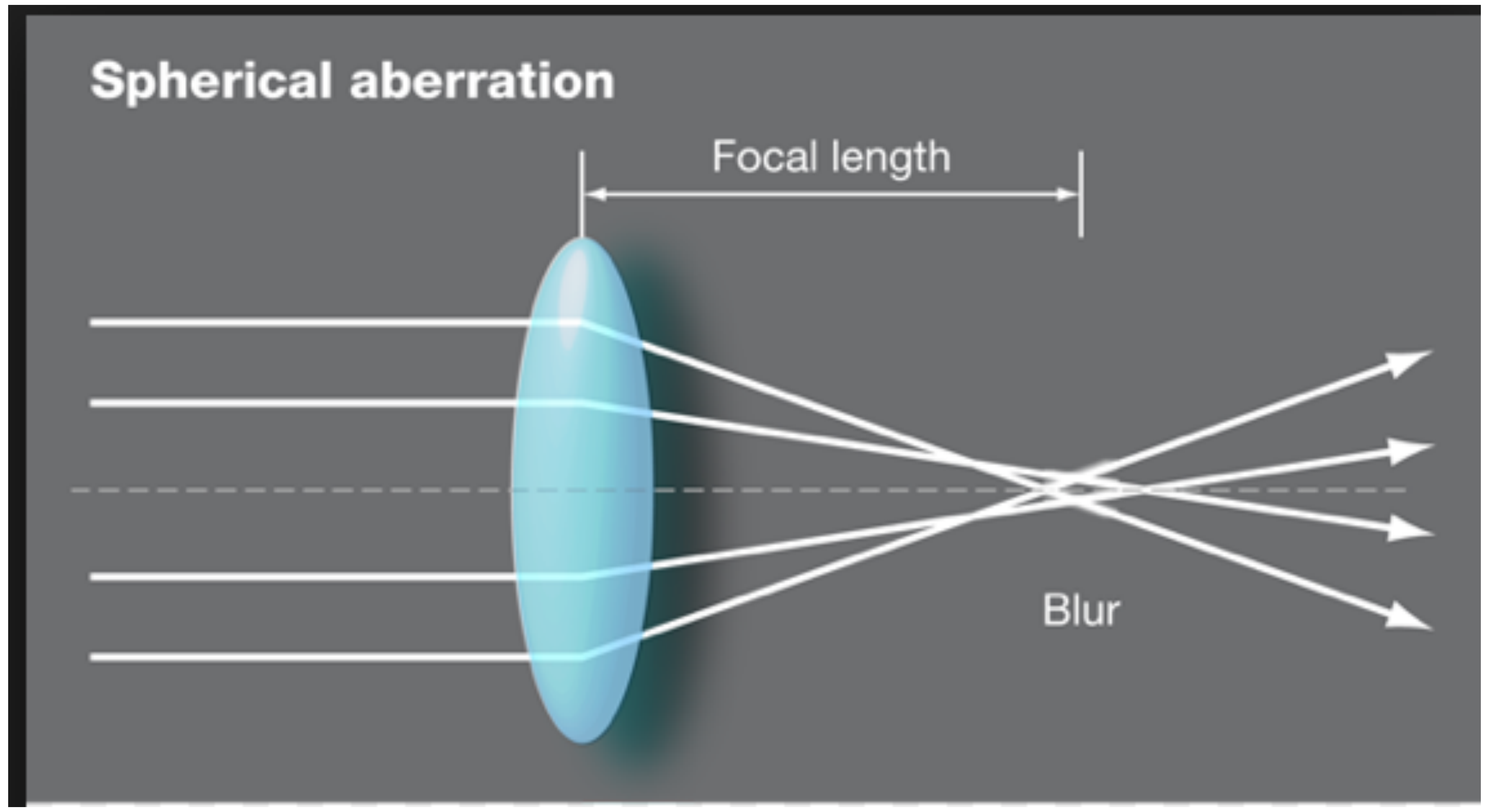
Mit 3 Abbildungen. (Eingegangen am 4. Juni 1936.)

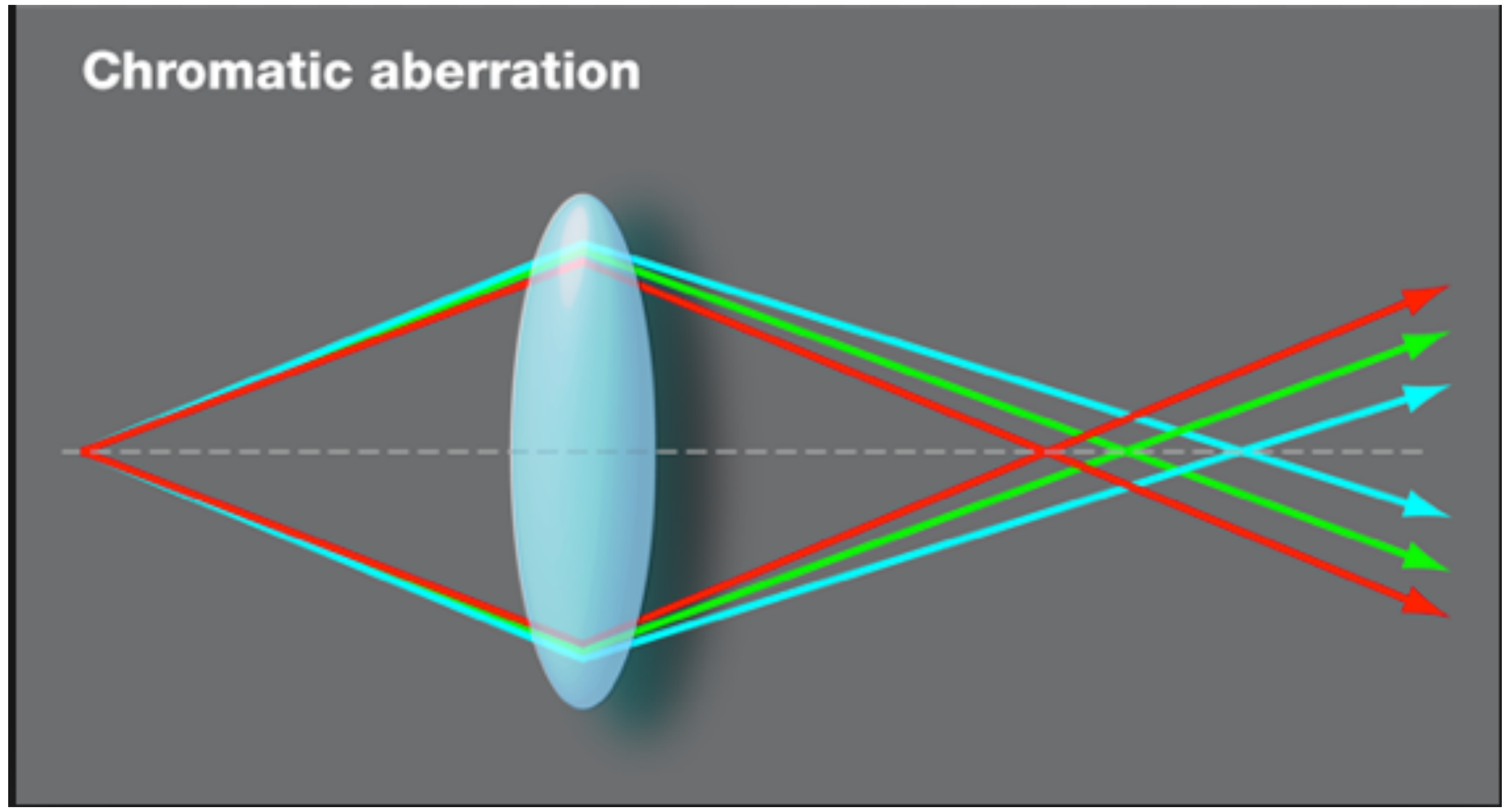
Unmöglichkeit des Achromaten. Die Bildfehler dritter Ordnung. Unvermeidbarkeit der sphärischen Aberration.

Zusammenfassung. Chromatische und sphärische Aberration sind unvermeidbare Fehler der raumladungsfreien Elektronenlinse. Verzeichnung (Zerdehnung wie Zerdrehung) und (alle Arten von) Koma lassen sich prinzipiell beseitigen. Durch die Unvermeidbarkeit der sphärischen Aberration ist eine praktische, nicht aber eine prinzipielle Schranke für das Auflösungsvermögen der Elektronenmikroskope gegeben.

Aberration are the limitation

- Electron lenses with a cylindrical symmetry have a positive Cs and Cc coefficient





- 2 options:
  - 1 Correct the aberration of the TEM
  - 2 Design lenses with the smallest possible aberration & “correct the images”

2- design lenses with small Cs and Cc

- Small pole piece gap
- High tension
- "Straightforward" and successful route to HRTEM from 1931 to (very) late 90s
- Correct the image, not the TEM (image simulation; exit wave reconstruction)

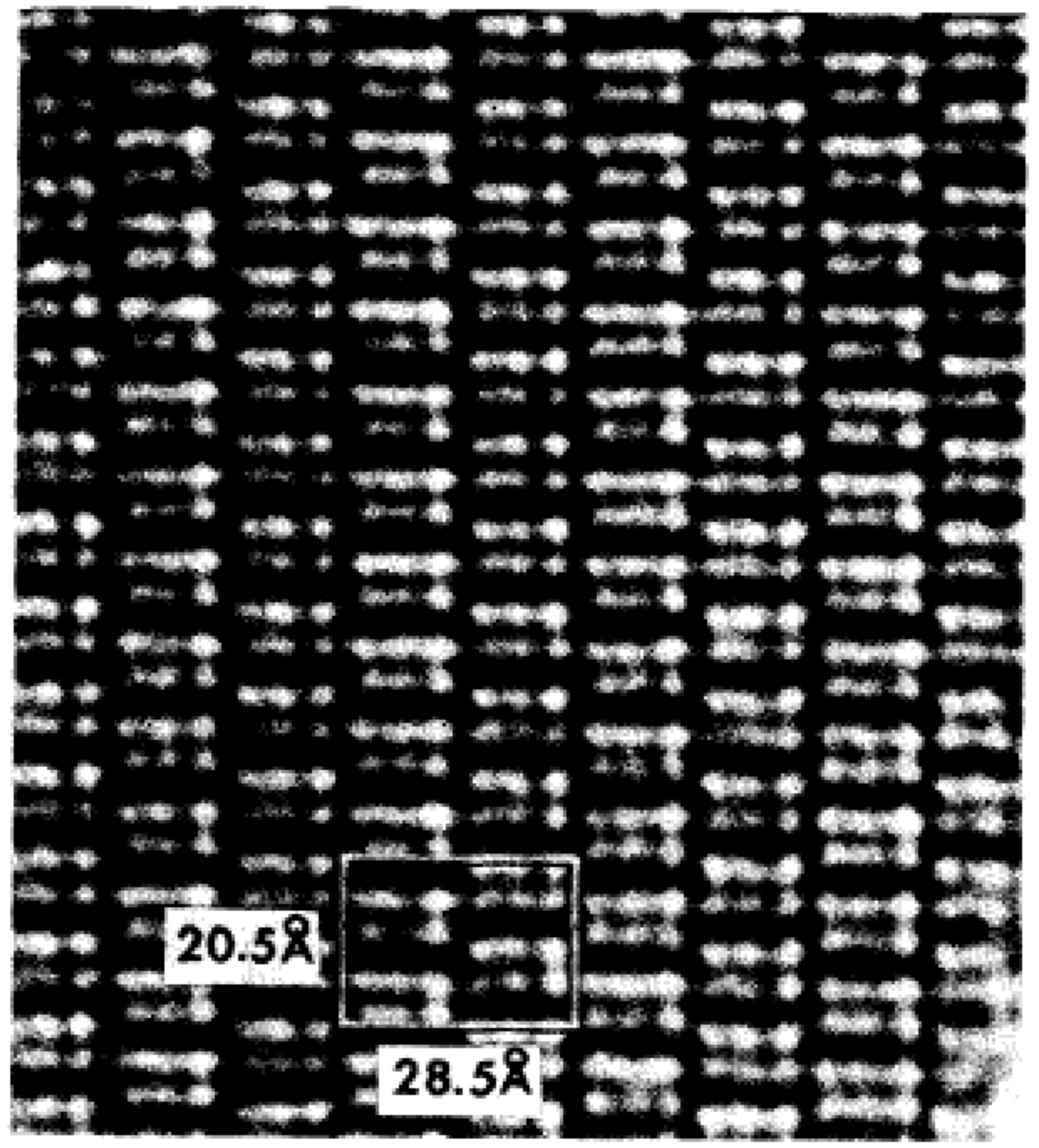
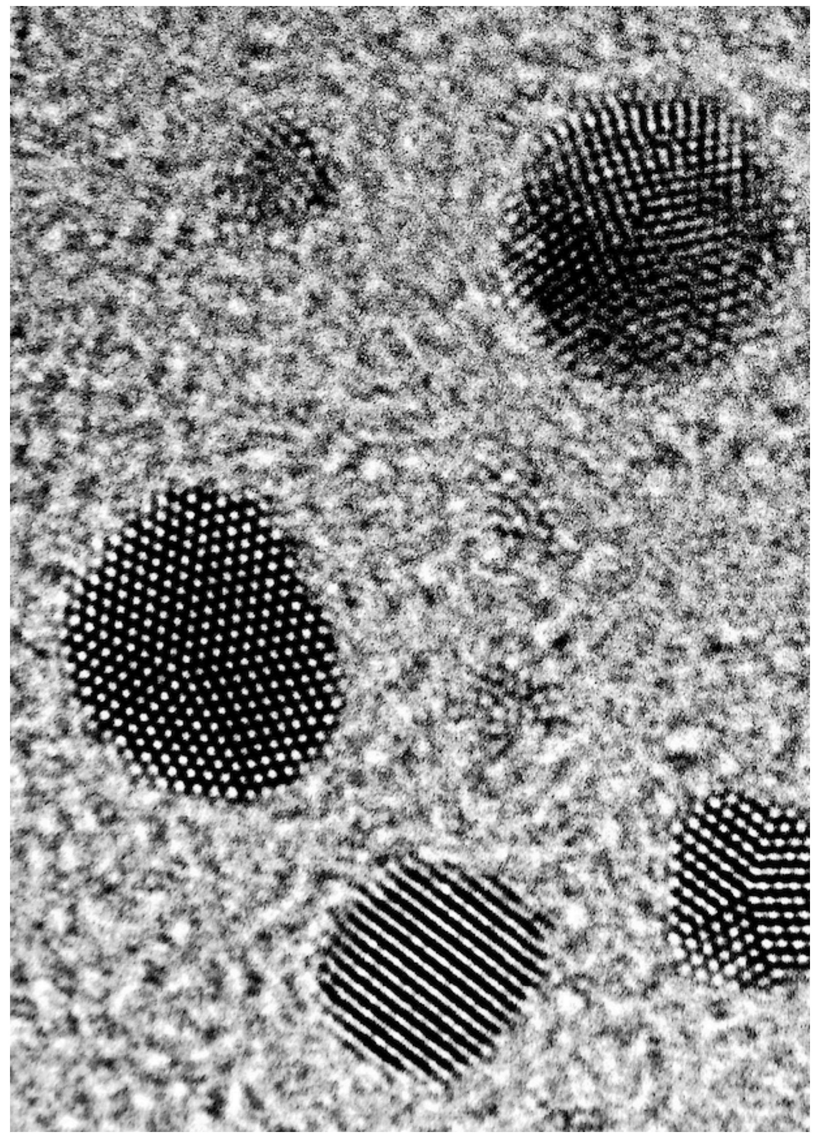
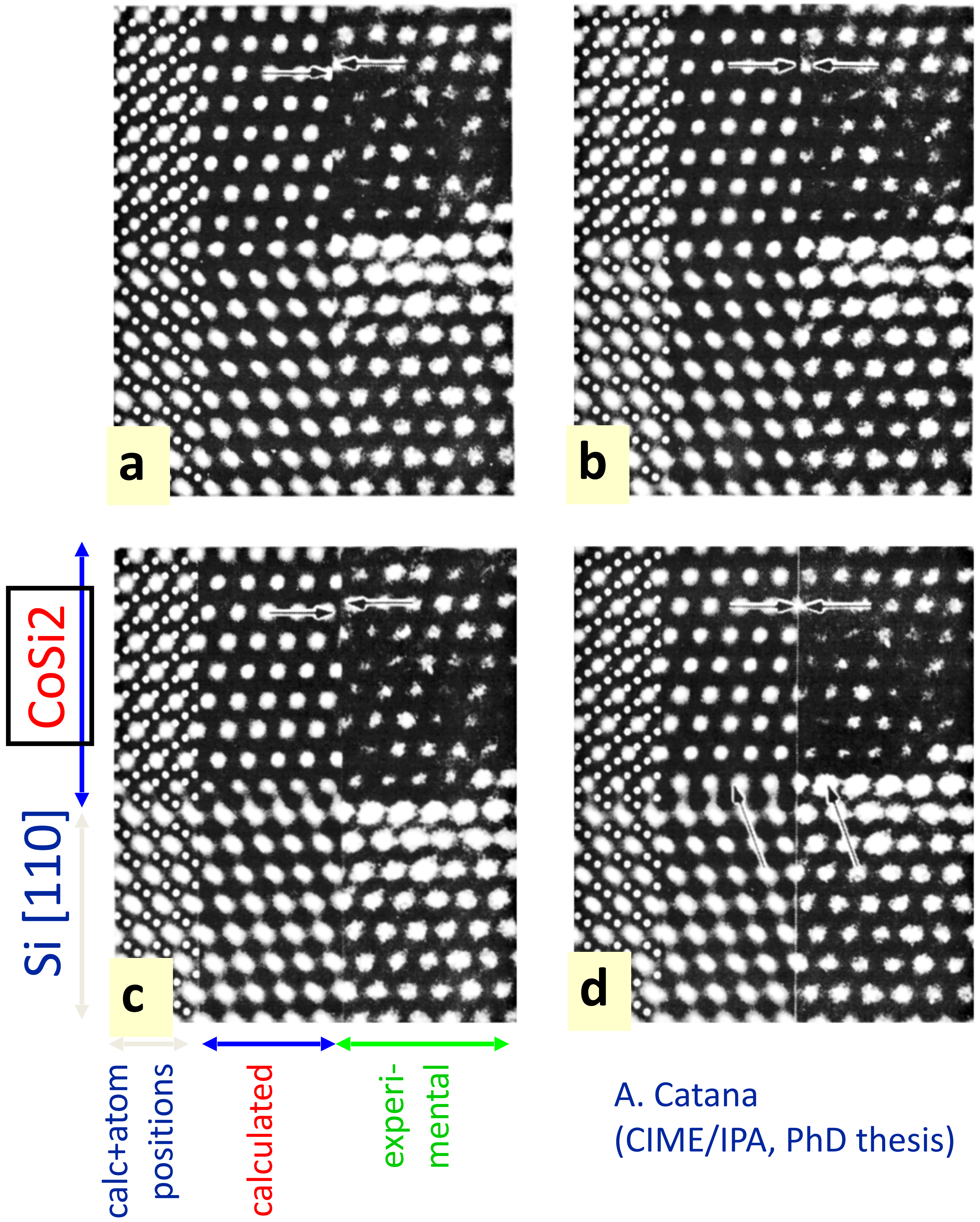


FIG. 1. Two-dimensional lattice image of orthorhombic $Ti_2Nb_{10}O_{29}$ obtained with electron beam incident parallel to the *b* axis. The unit cell projection is shown by white lines ($a = 28.5$ Å, $c = 20.5$ Å).

S. Iijima, APL, 1971



EM430@CIME: Au NPs, Flueli



A. Catana (CIME/IPA, PhD thesis)

1- correct lens aberrations

Sphärische und chromatische Korrektur von Elektronen-Linsen.

Von O. Scherzer, z. Zt. USA.

(Aus den Süddeutschen Laboratorien in Mosbach.)

(Mit 7 Textabbildungen.)

Die Brauchbarkeit des Elektronenmikroskops bei hohen Vergrößerungen wird durch den Öffnungsfehler und die chromatische Aberration beeinträchtigt. Beide Fehler sind unvermeidlich, solange die abbildenden Felder rotations-symmetrisch, ladungsfrei und zeitlich konstant sind. Die vorliegende Untersuchung soll zeigen, daß die Aufhebung irgendeiner dieser drei Einschränkungen genügt, um den Weg zur sphärischen und chromatischen Korrektur und damit zu einer erheblichen Steigerung des Auflösungsvermögens freizugeben.

Solange nicht klar zu sehen ist, welche Art Linsen das beste Mikroskop ergibt, müssen alle sich bietenden Wege verfolgt werden. Es scheint daher angebracht, etwas ausführlicher auf die verschiedenen Arten korrigierter Linsen einzugehen.

Optik, 1947

One "just" need to relax one of the following constraint: cylindrical symmetry of the lens, permanent fields, no space charge.

1- correct lens aberrations

Aberration correction past and present

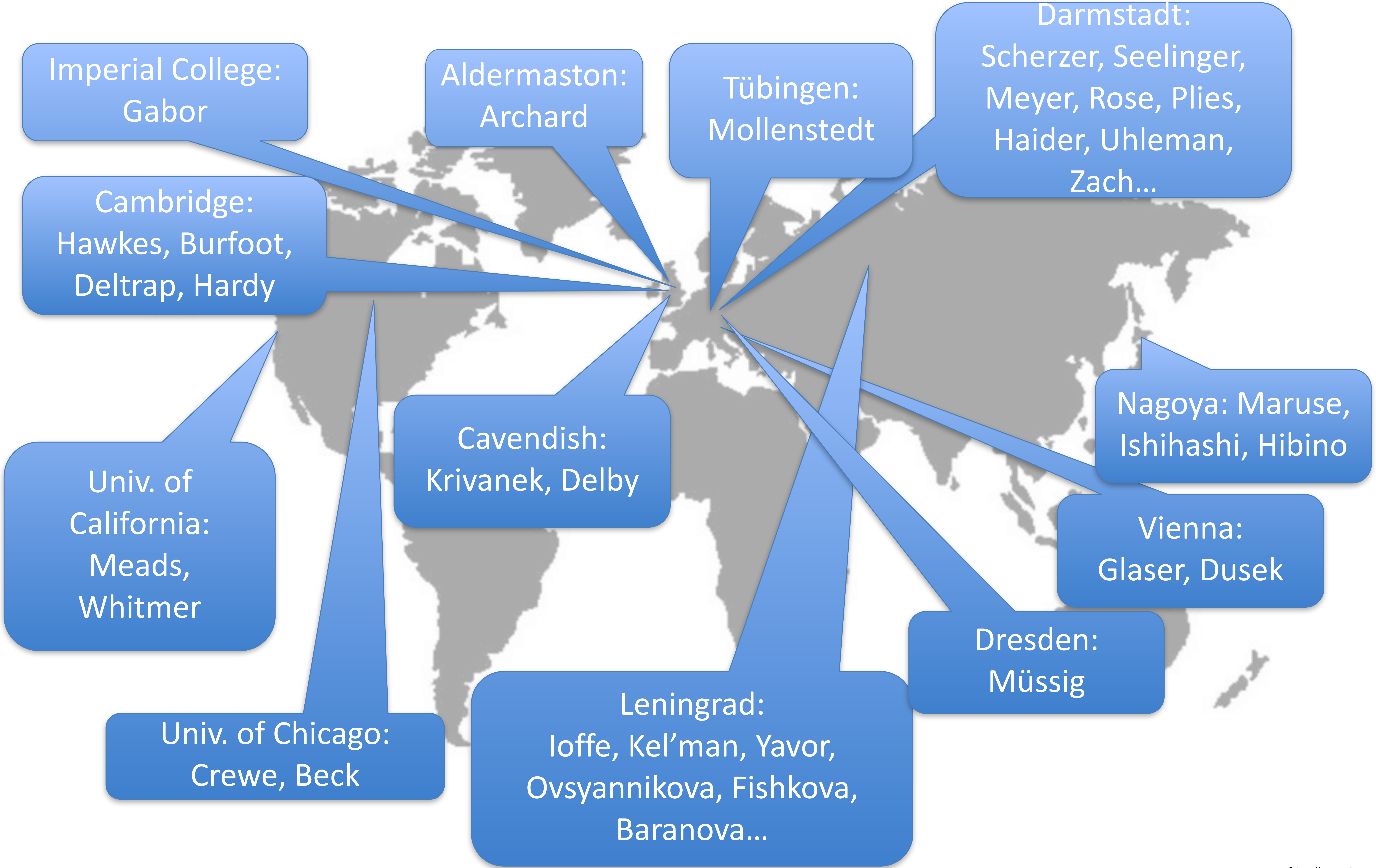
P. W. Hawkes

Phil. Trans. R. Soc. A 2009 **367**, doi: 10.1098/rsta.2009.0004, published 17 August 2009

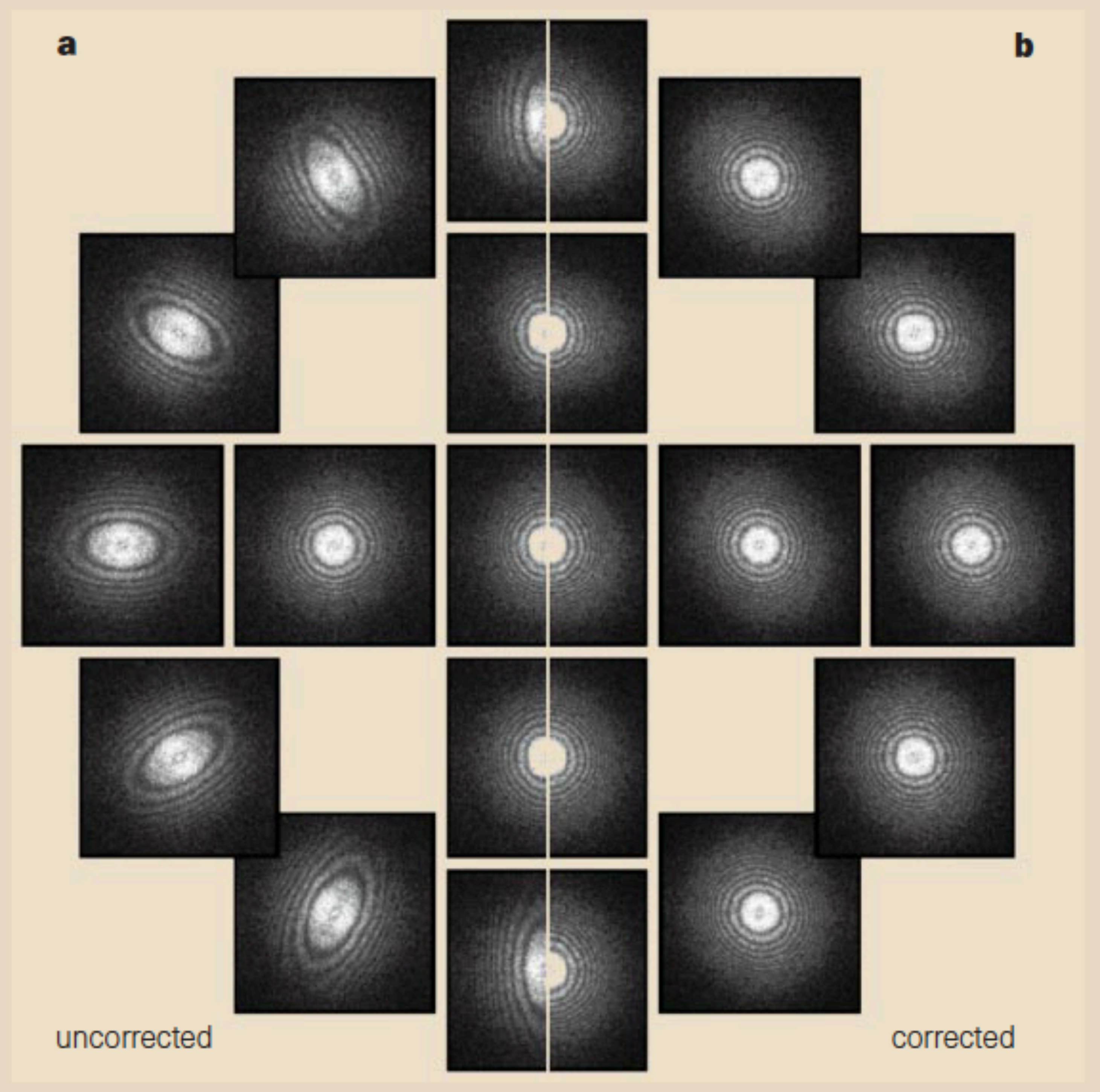
2. Forty disappointing years

During the next four decades, all of the four major families of correction methods attracted considerable attention. Here, we can only provide a representative selection; some other projects and the corresponding references are to be found in earlier surveys (Hawkes 1980, 2007, 2008; Hawkes & Kasper 1989, ch. 41; Rose 2008*a*,*b*).

“40 disappointing years”

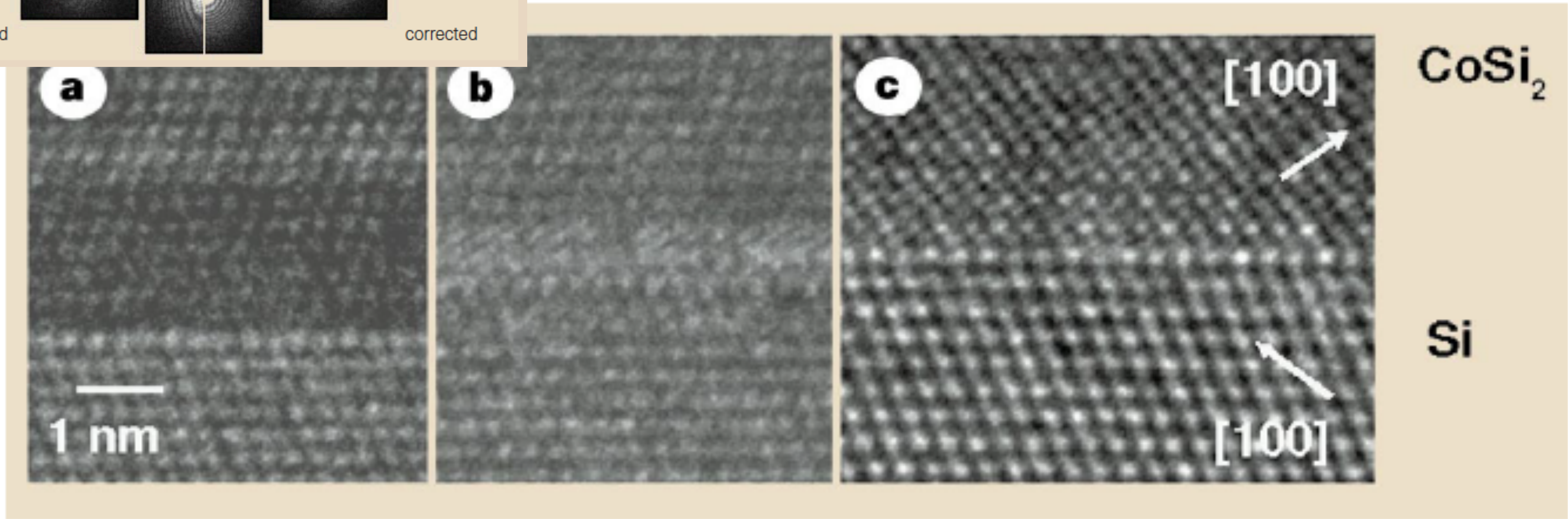


1997: Success



Haider, Uhlemann, Schwan, Rose, Kabius, Urban
Nature, 392 (1998), p. 268

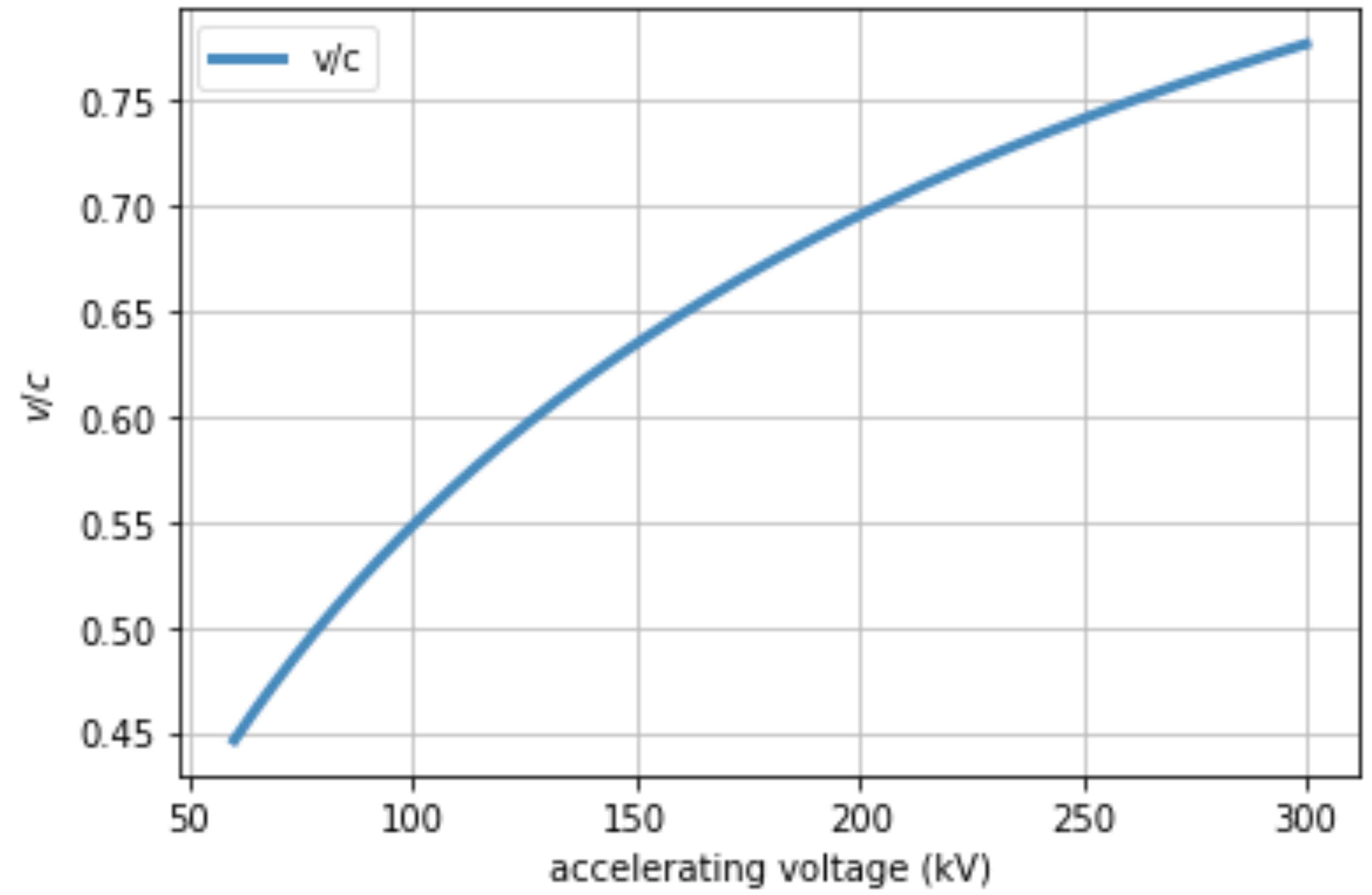
Project funded by the Volkswagen Foundation

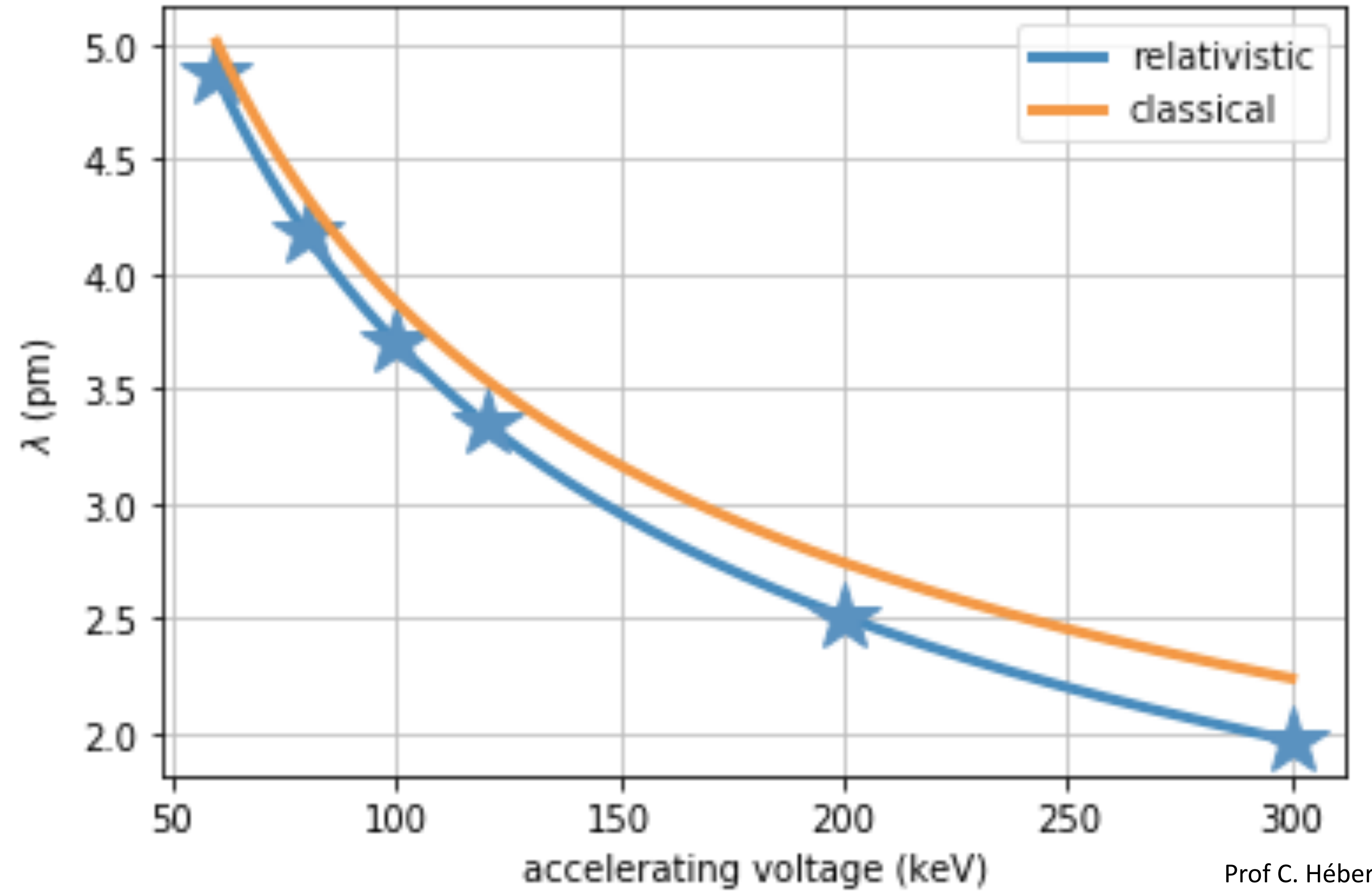


Presentation of the instrument

The electron source

Typical high tensions: 60-300 kV





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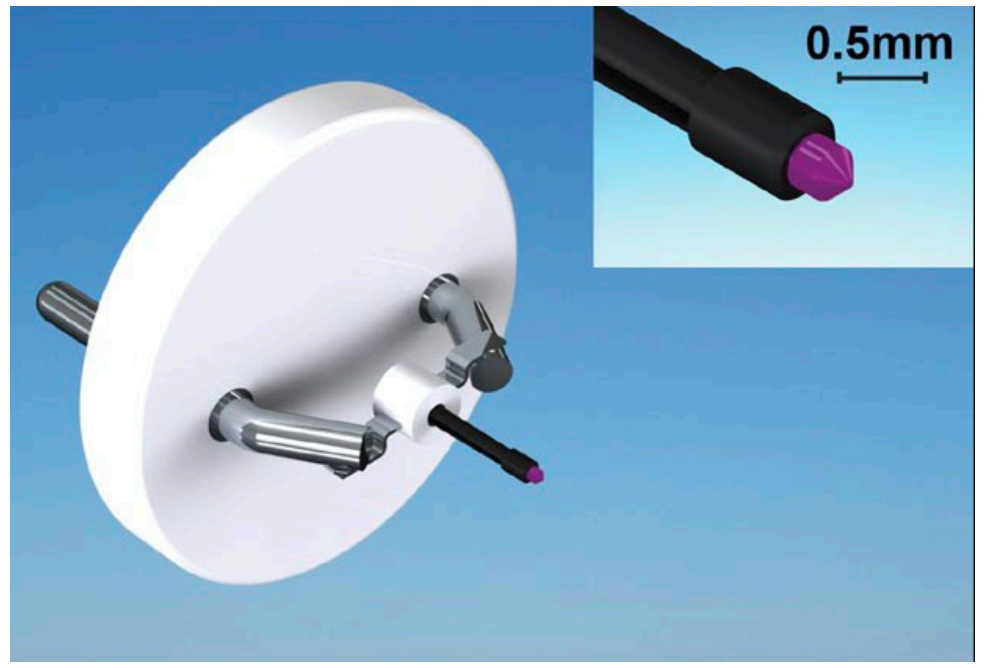
The electron source

Type of sources
Coherence; energy spread



	W	LaB_6	Schottky	cold field emission
work function [eV]	4.5	2.7	2.5	4.5
emiss. current [μ A]	100	20-50	<100	20
temperature[^{0} C]	2500	<1800	<1500	20
brightness [A m^{-2} sr^{-1}]	10^9	$<5\cdot10^{10}$	$<10^{13}$	$5\cdot10^{12}$
crossover [μm]	50	10	0.02-0.05	¡ 0.01
energy width[eV]	1-3	0.5-2	0.3-0.8	0.2-0.7

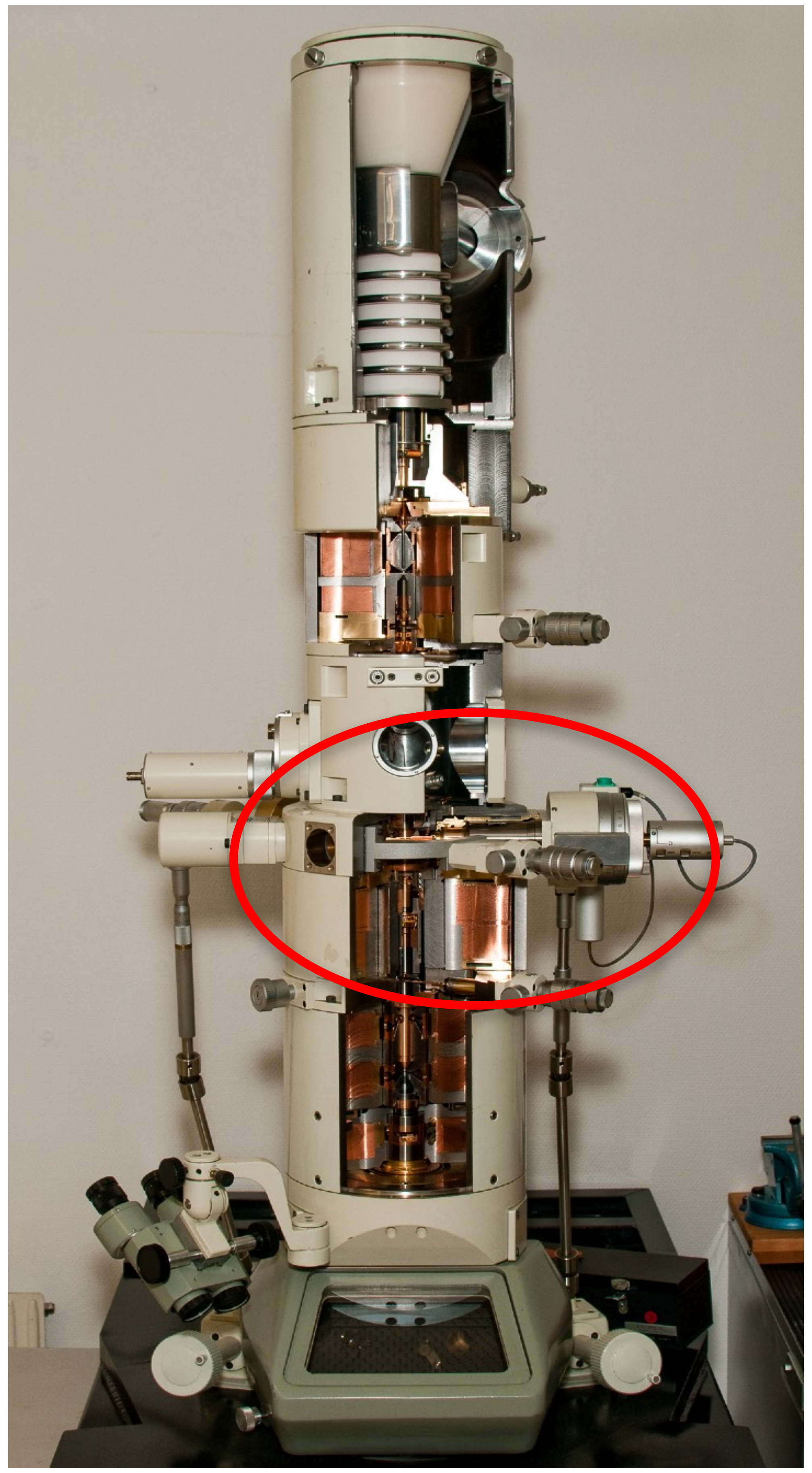
The objective lens

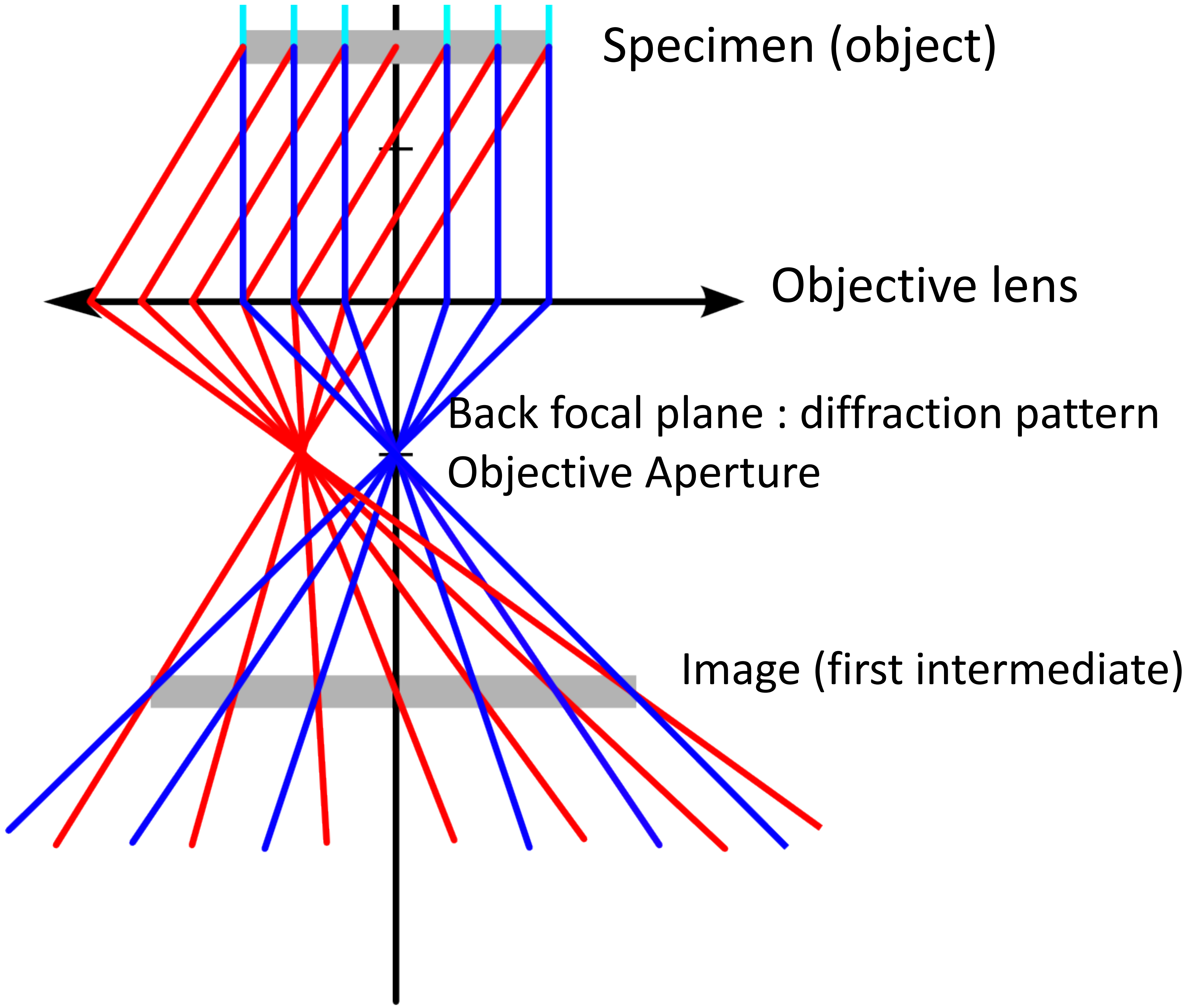
- Aberration
- Contrast transfer function
- magnification

The intermediate and projector lenses

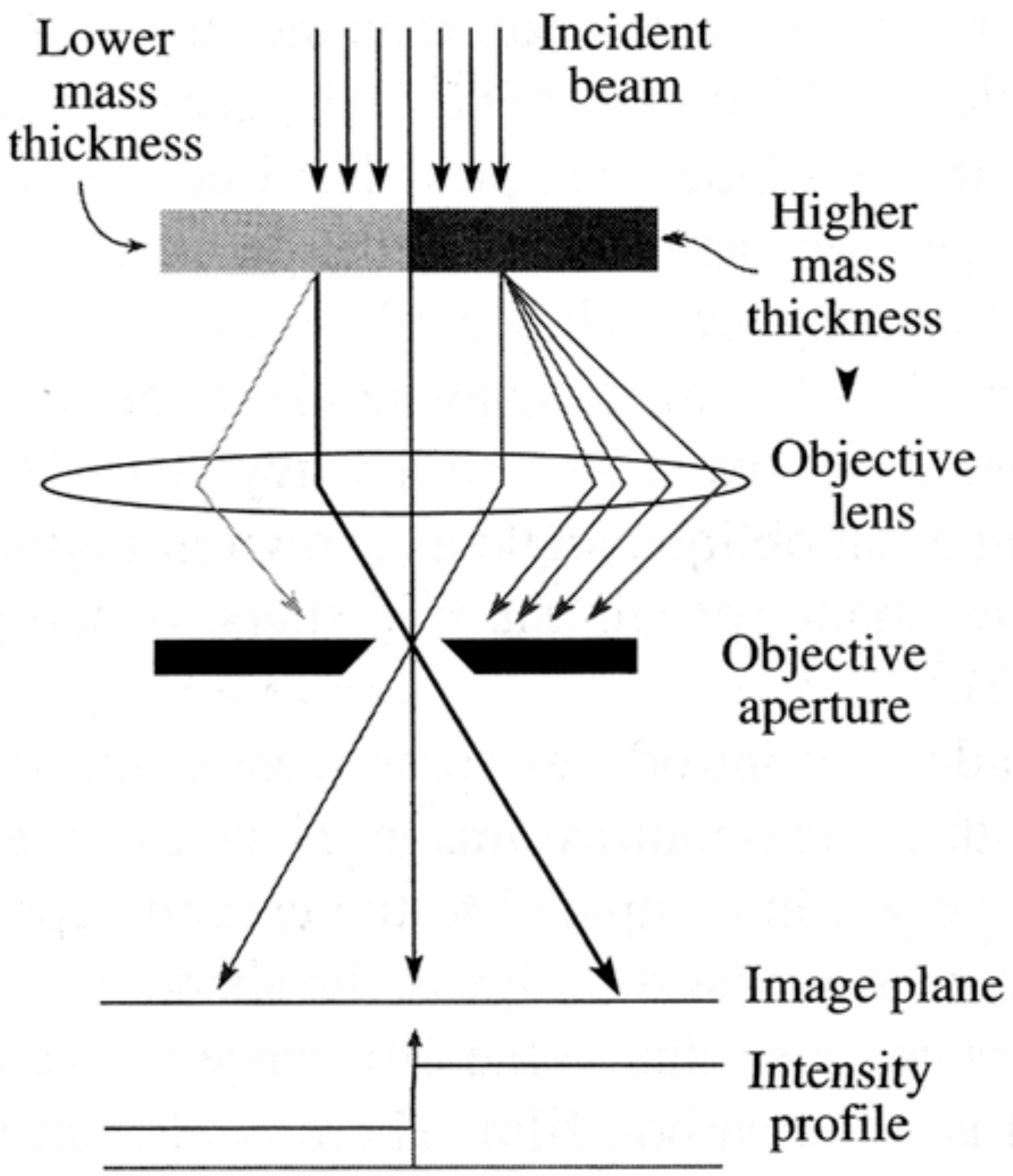
- Further magnification
- Switch between imaging and diffraction

The type of contrasts

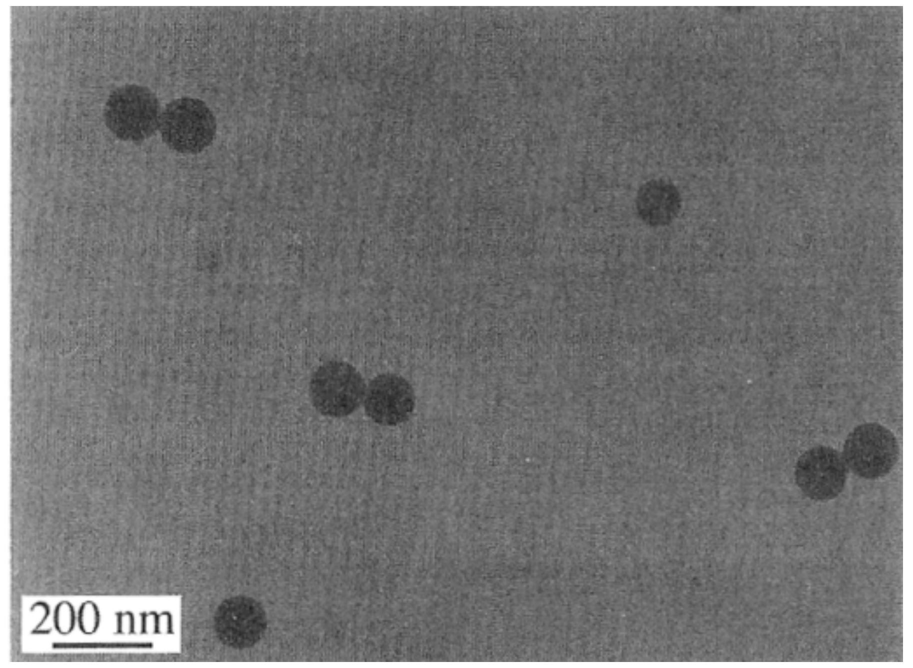




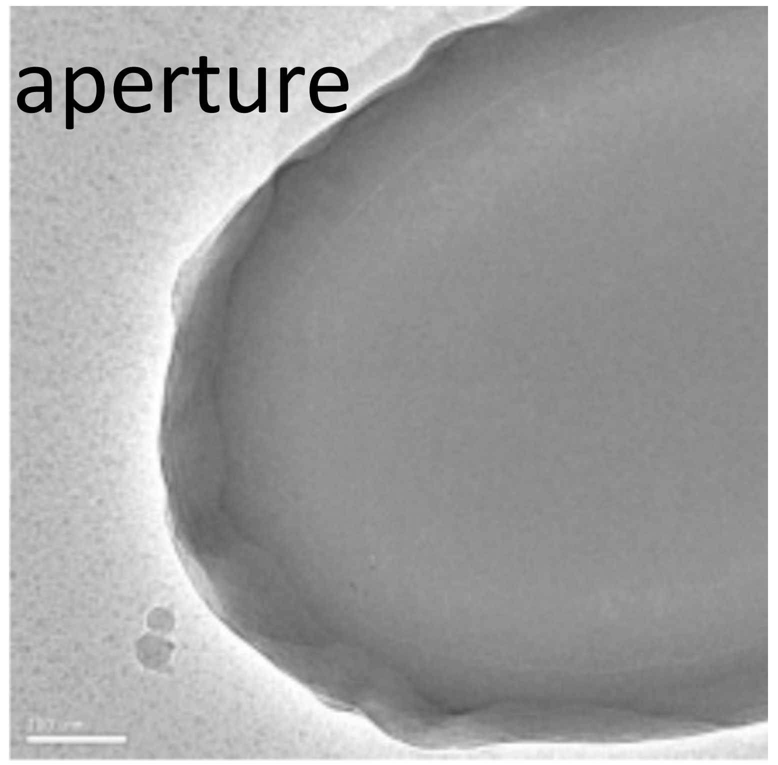
TEM mass-thickness contrast



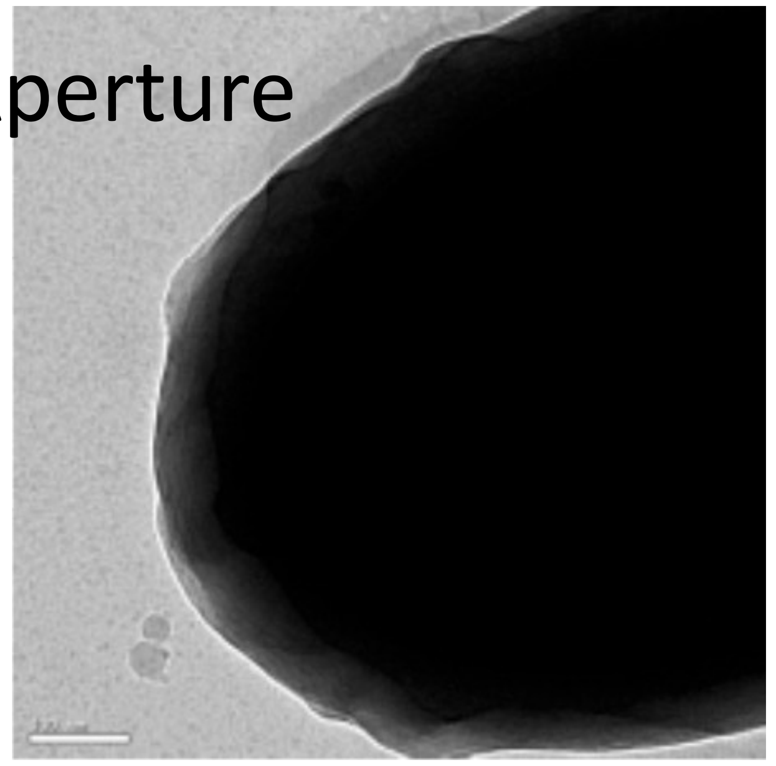
- Areas of higher mass thickness scatter electrons more than others
- Electrons are captured by the aperture and lost from the beam path
- Areas of higher mass thickness will therefore appear dark in the image
- This is known as
  - **mass thickness contrast**,
  - **scattering contrast**,
  - **aperture contrast** or
  - **amplitude contrast**!



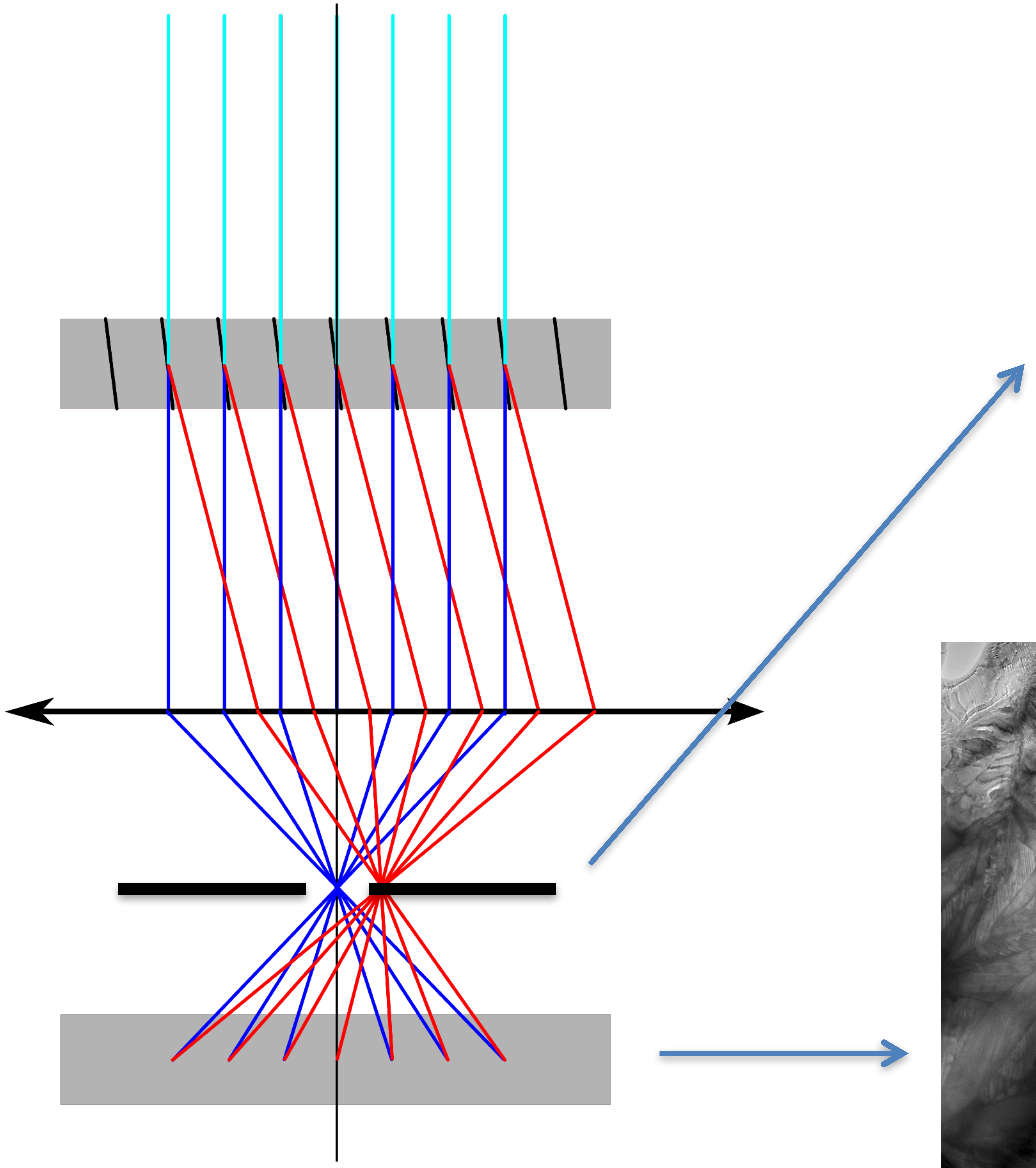
No aperture



Aperture

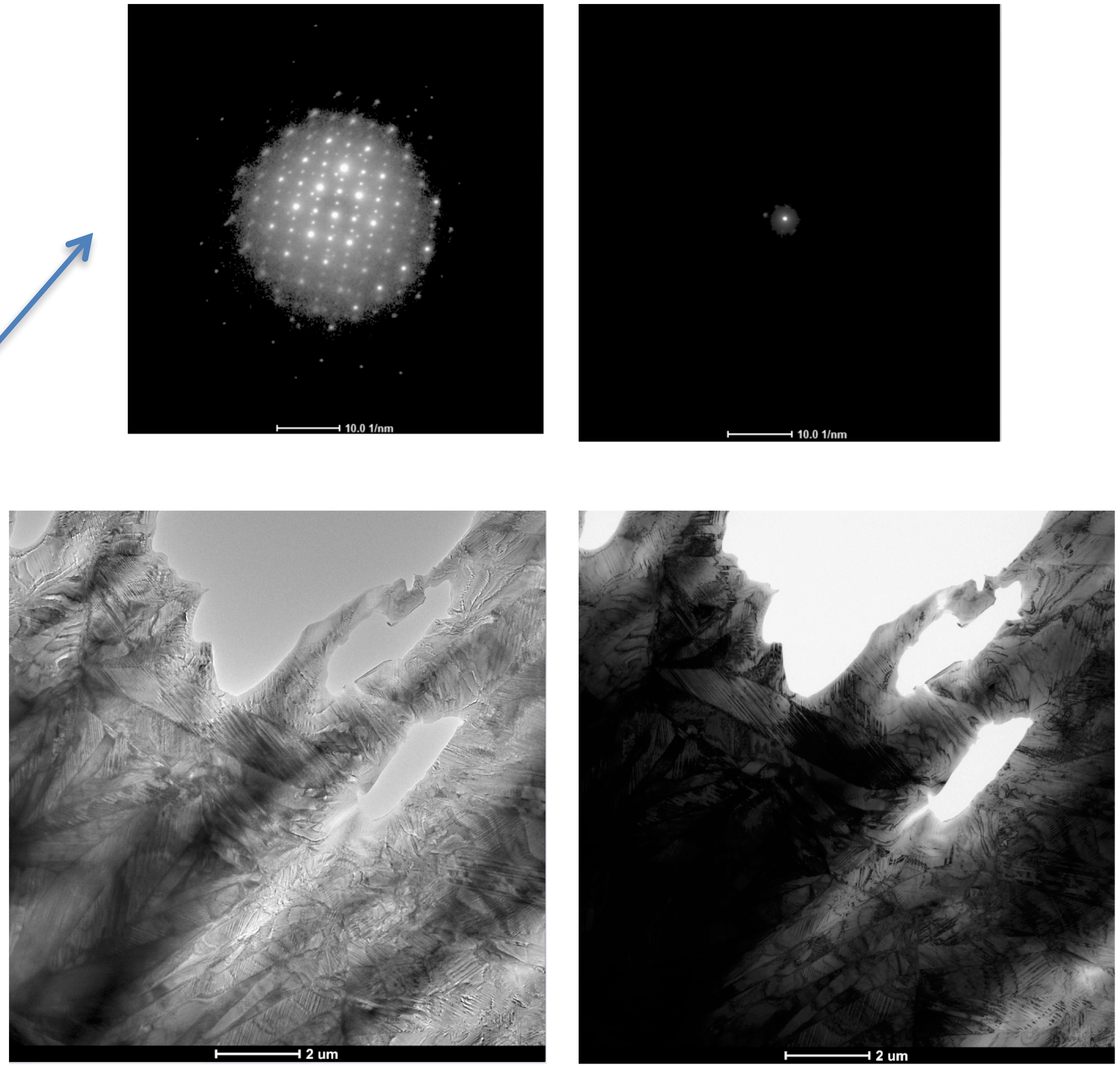


Diffraction contrast



No aperture

Objective aperture



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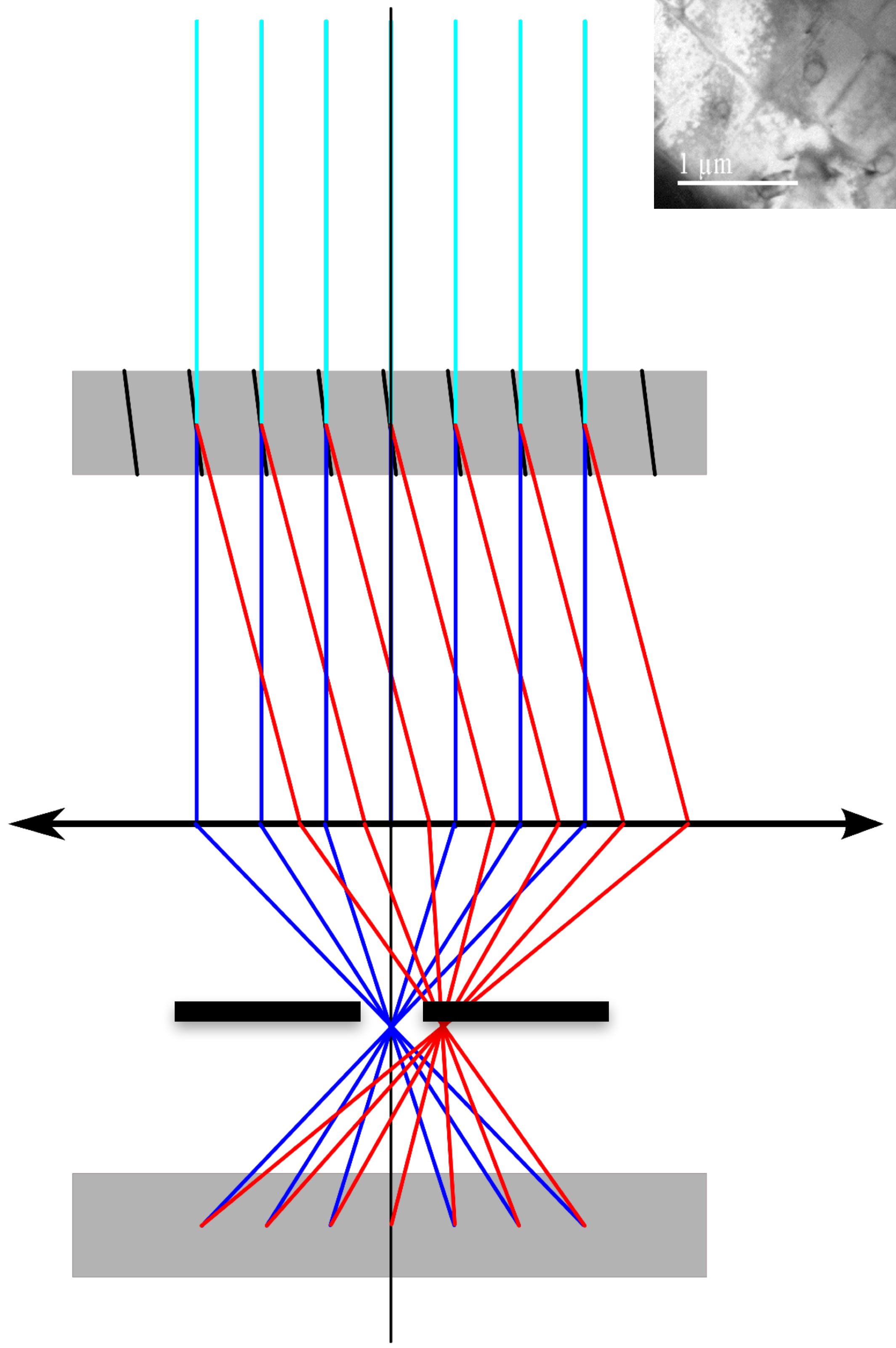
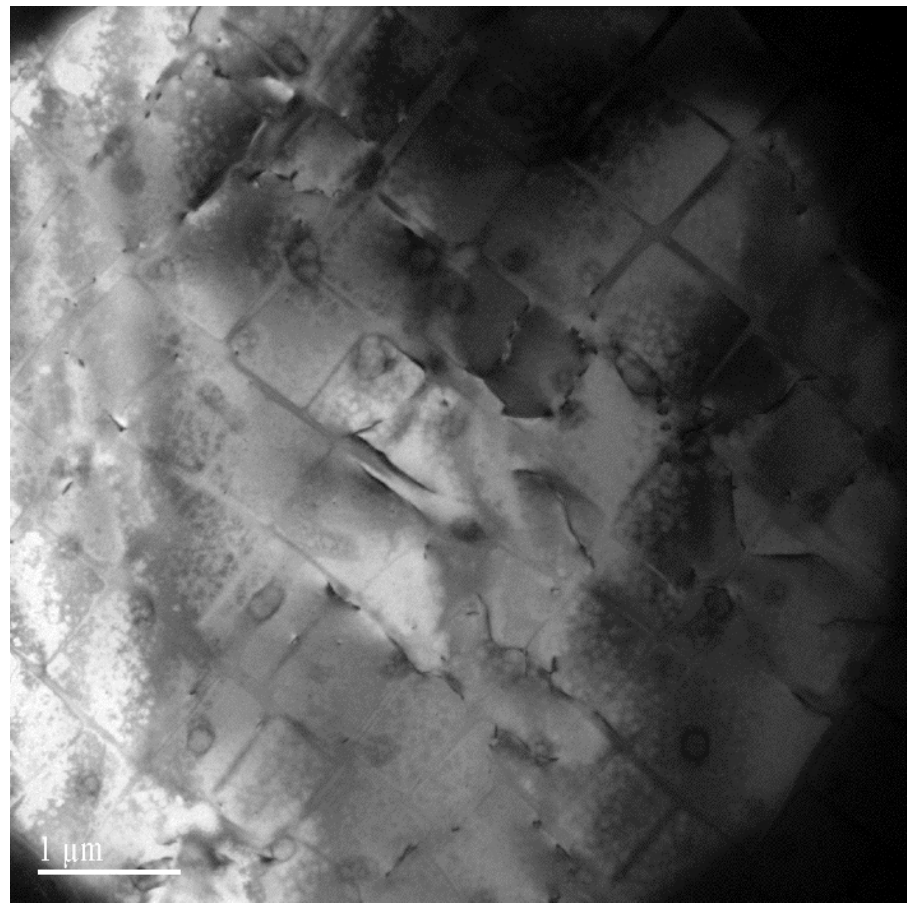
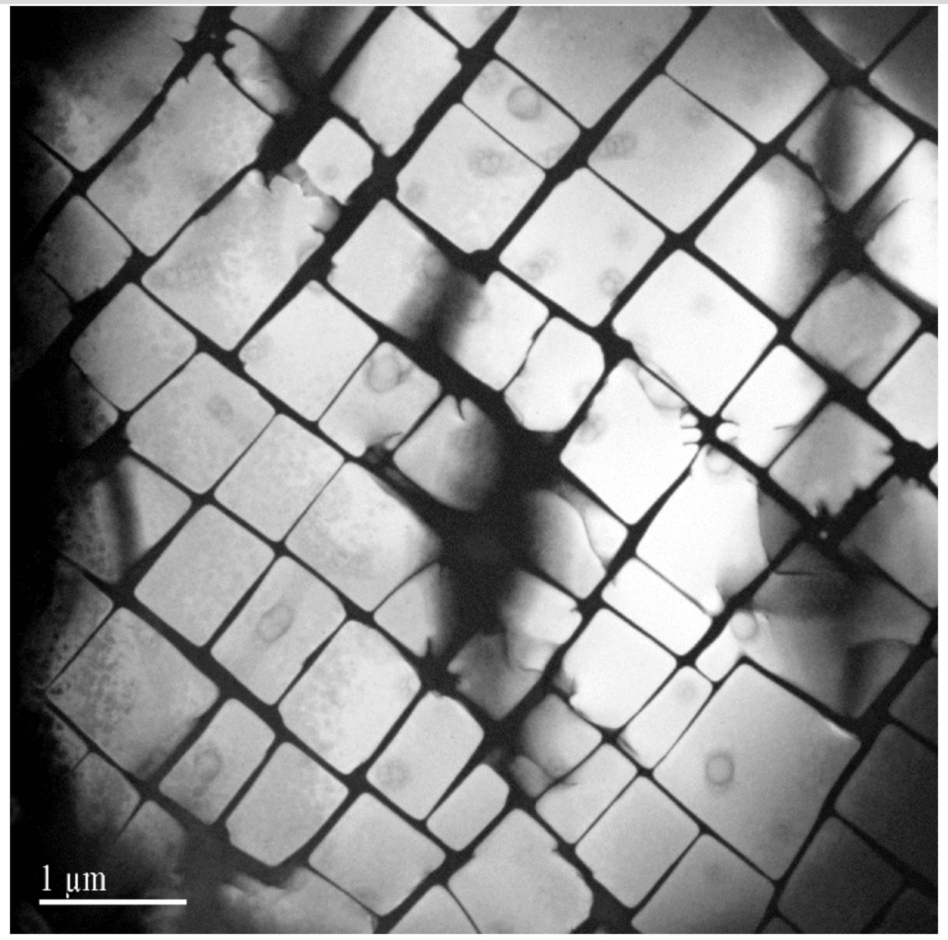
Bright-field/dark-field imaging

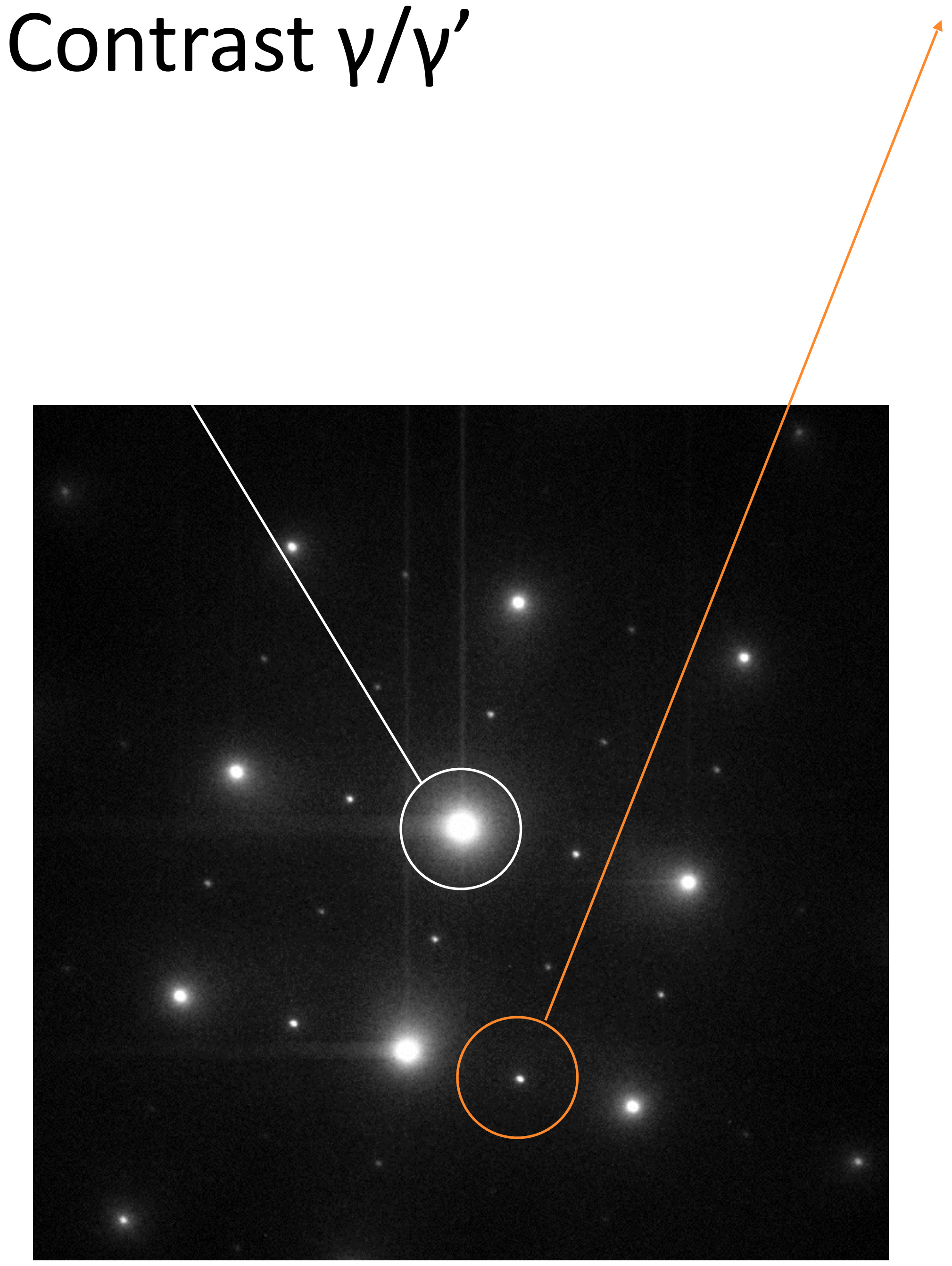


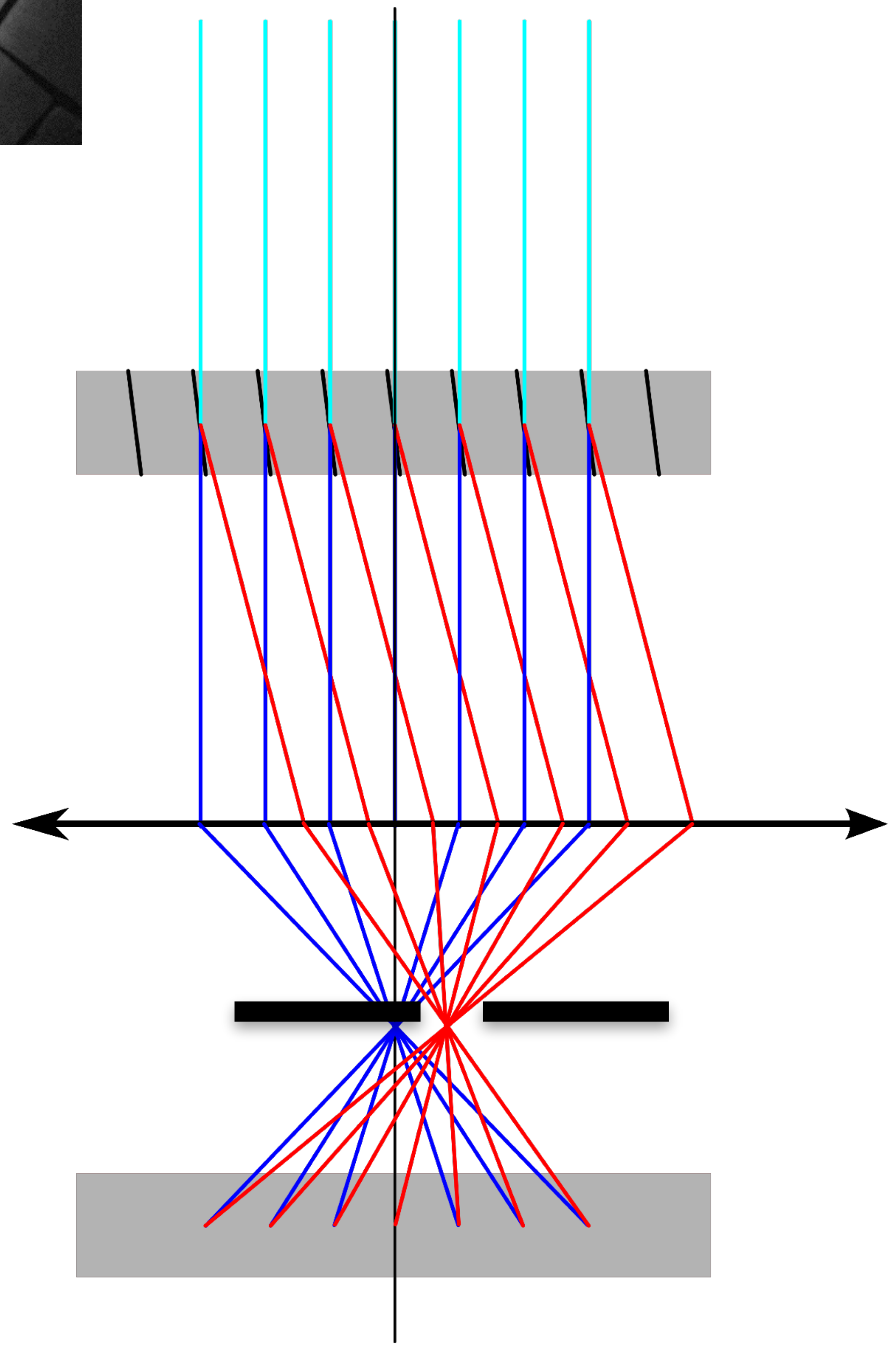


Nickel based superalloys

Contrast γ/γ'







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Diffraction in this lecture

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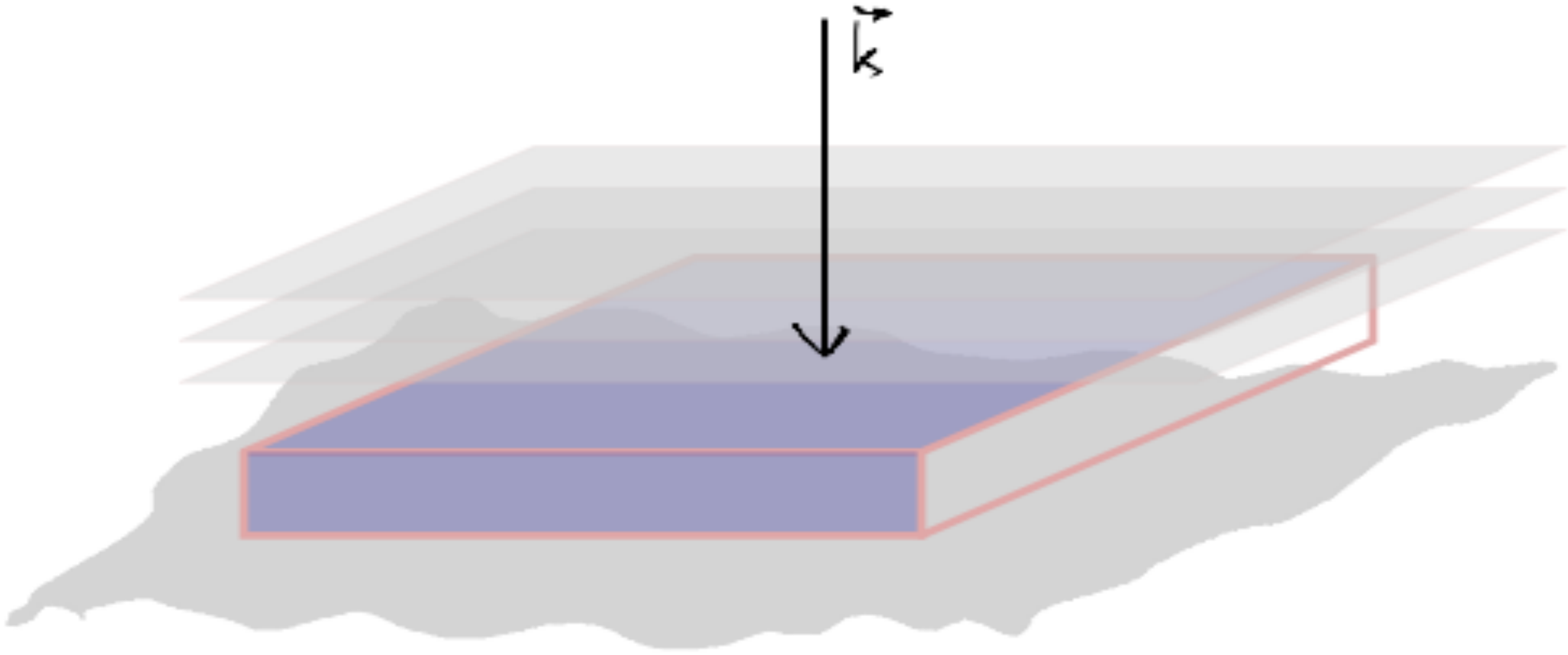
Phase contrast



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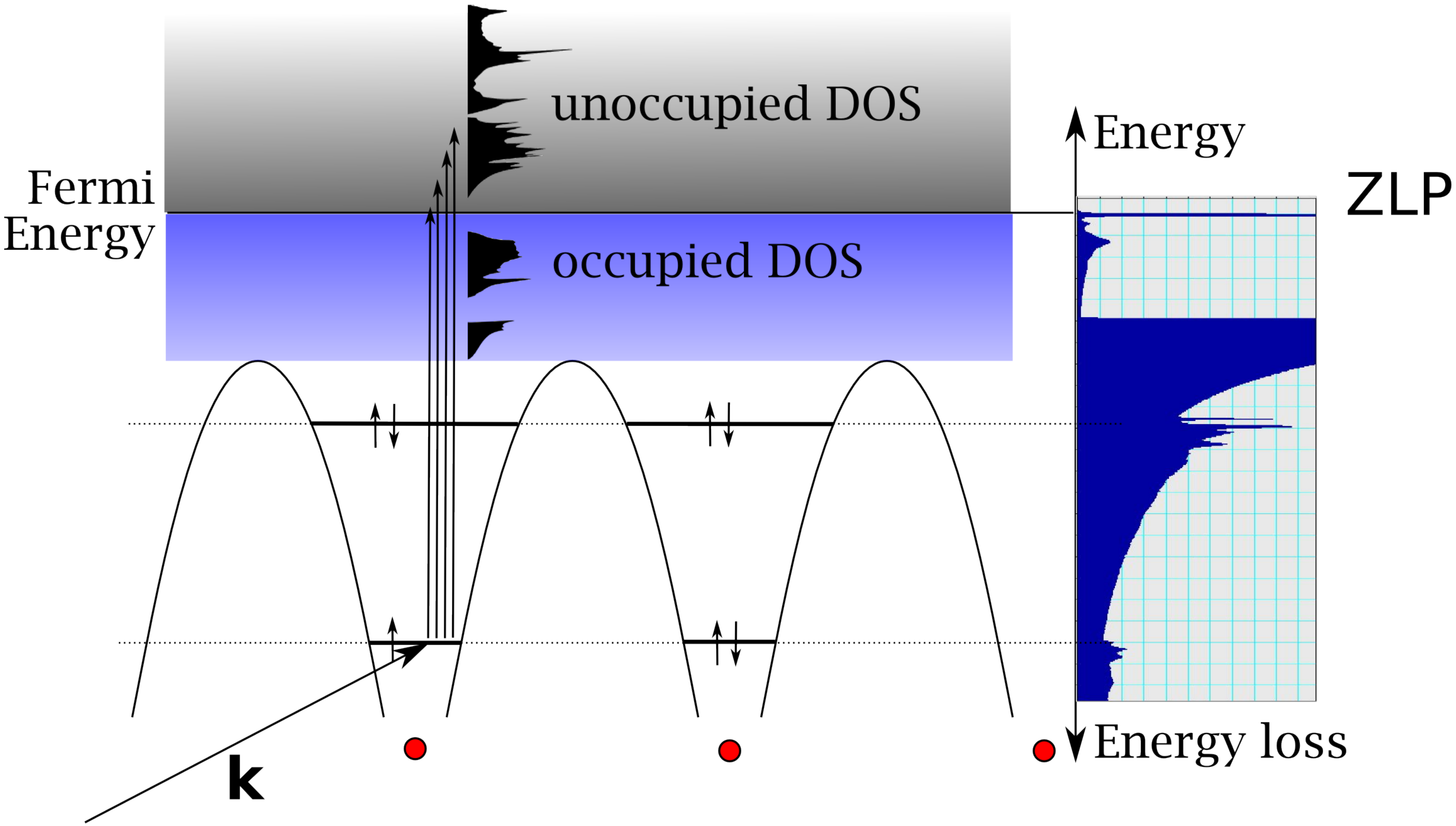
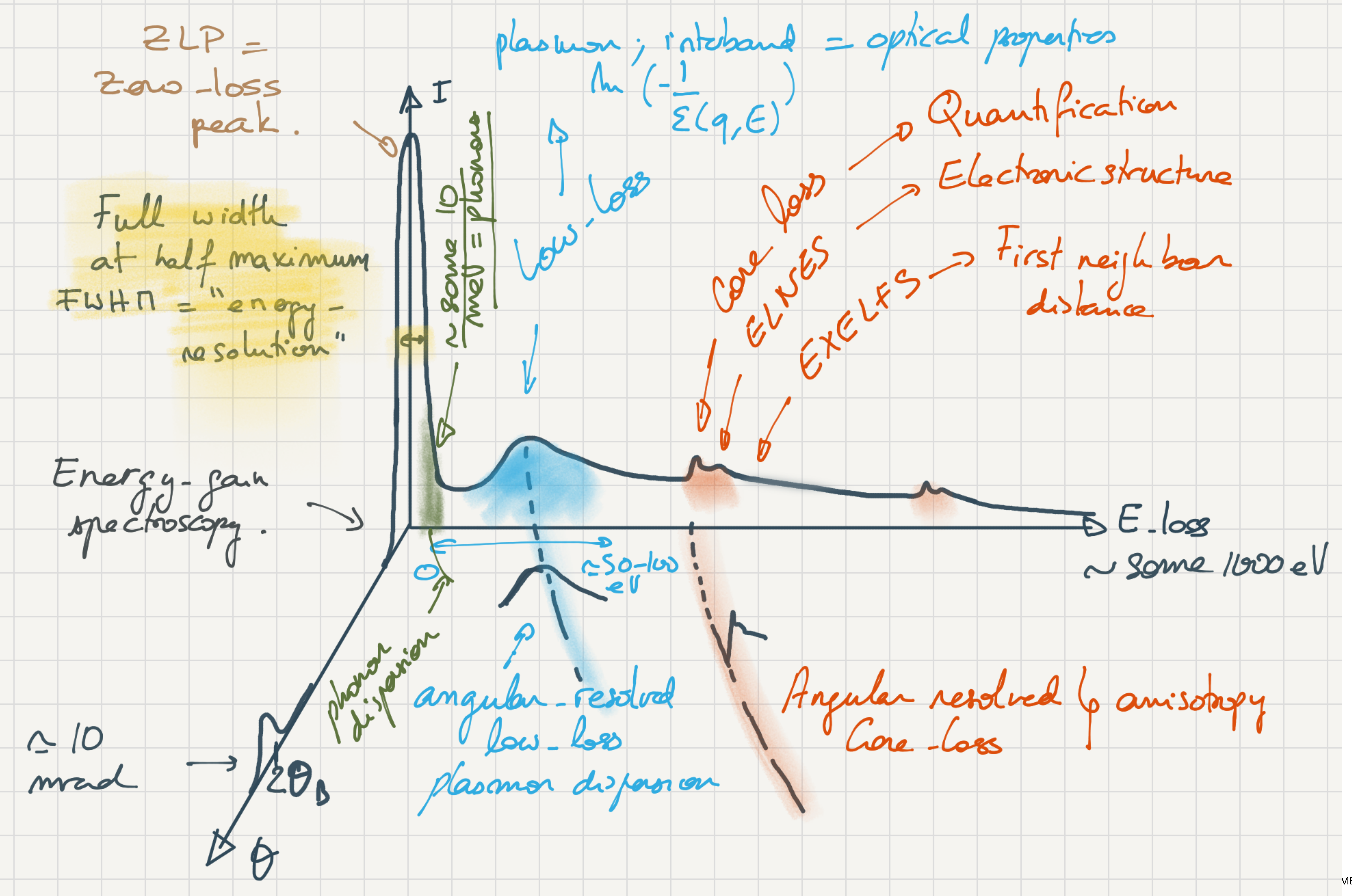
EELS :Excitation process



EELS: accessible information



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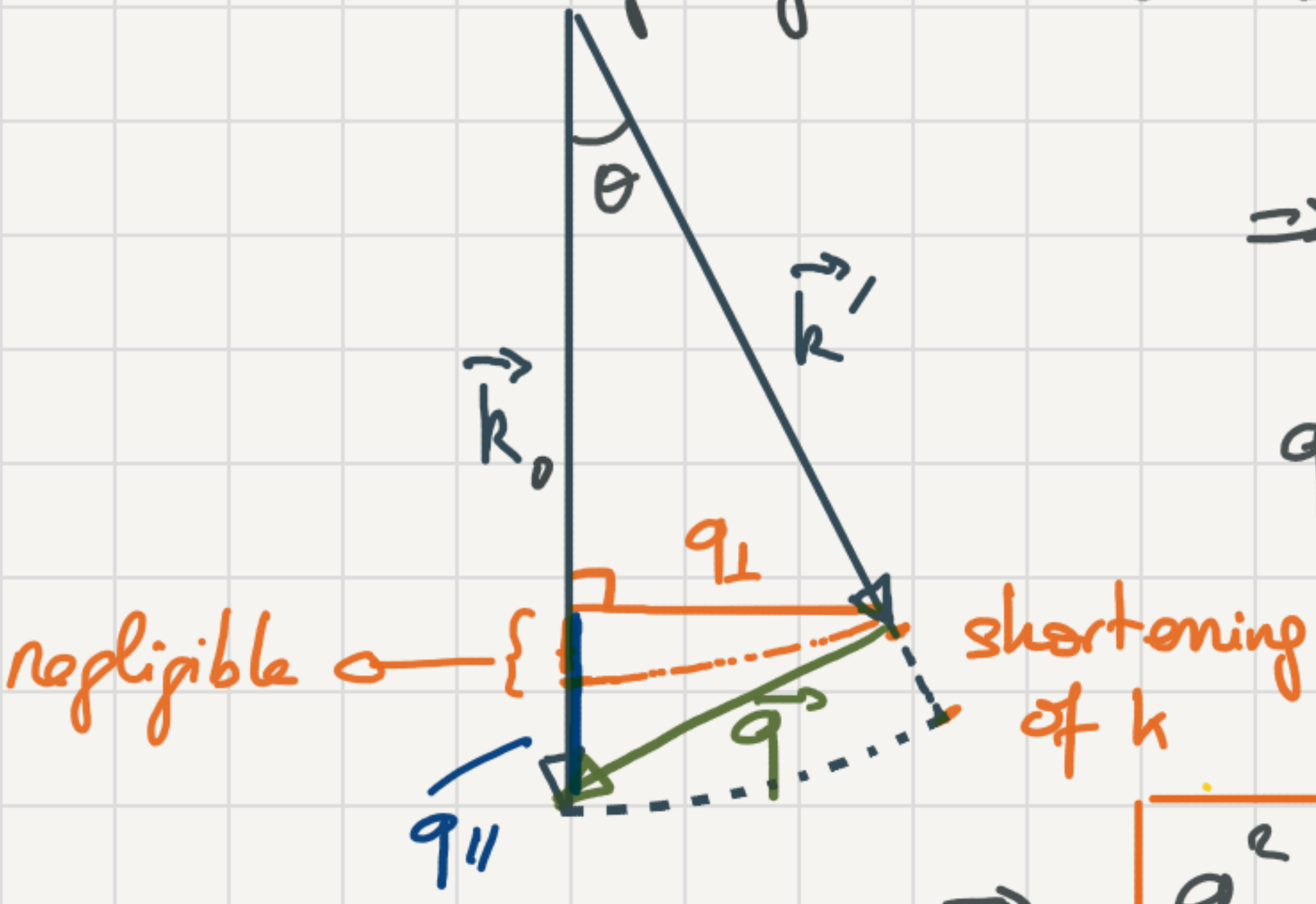
EELS: geometry

θ: scattering angle

$\theta \ll 1$ & $k' \simeq k_0$



$$\Rightarrow q^2 \simeq q_\parallel^2 + q_\perp^2$$

$$q_\perp^2 = k_0^2 \theta^2$$

$$q_\parallel^2 = k_0^2 \theta_E^2 \ (\text{def})$$

θ & $\theta_E \ll 1$

$$\Rightarrow \boxed{q^2 \simeq k_0^2 (\theta^2 + \theta_E^2)}$$

$$\theta_E = \frac{E\, m_0 \gamma}{\hbar^2 k_0^2} \simeq \frac{E}{2 E_0}$$

E: Energy loss

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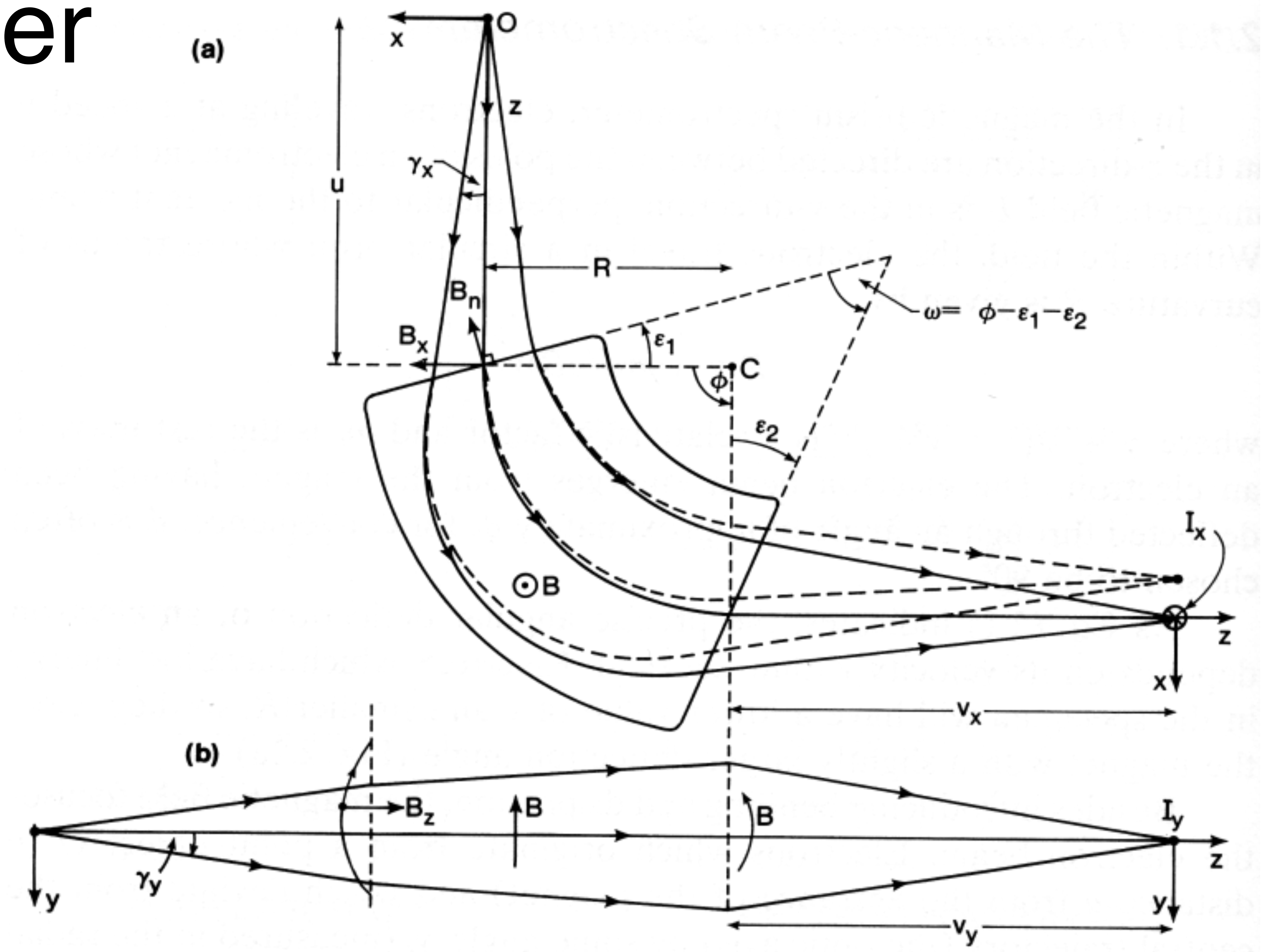
Instrumentation for EELS

Spectrometer



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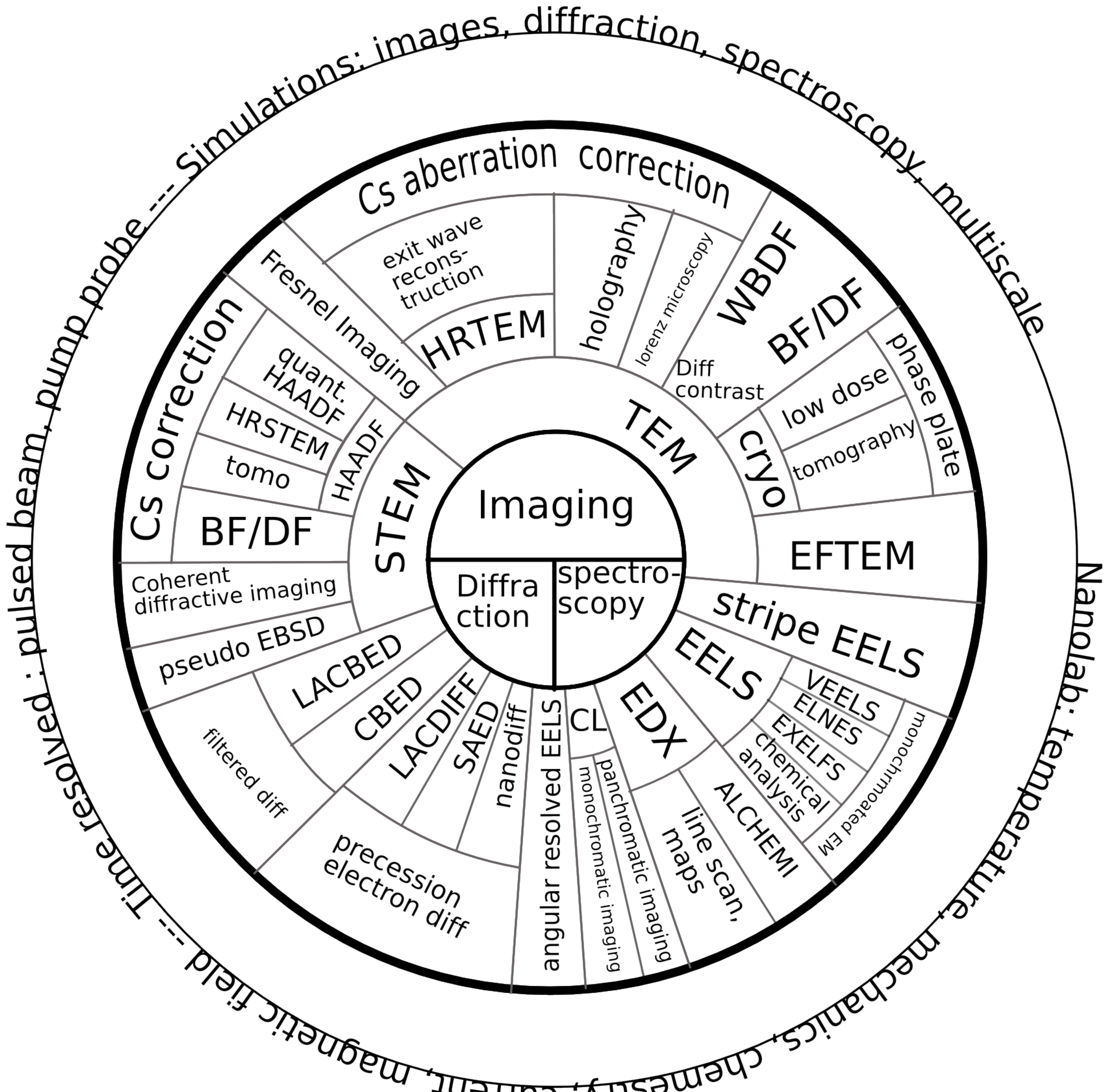
Techniques in Microscopy



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The (crystalline) specimen

A large part of the investigated specimens are crystals (even sometimes in biology: e.g proteins can be crystallised!)

Many imaging techniques make use of the interaction of the beam with the crystal: High resolution, diffraction, dark field, weak beam, convergent beam diffraction, large angle convergent beam diffraction…

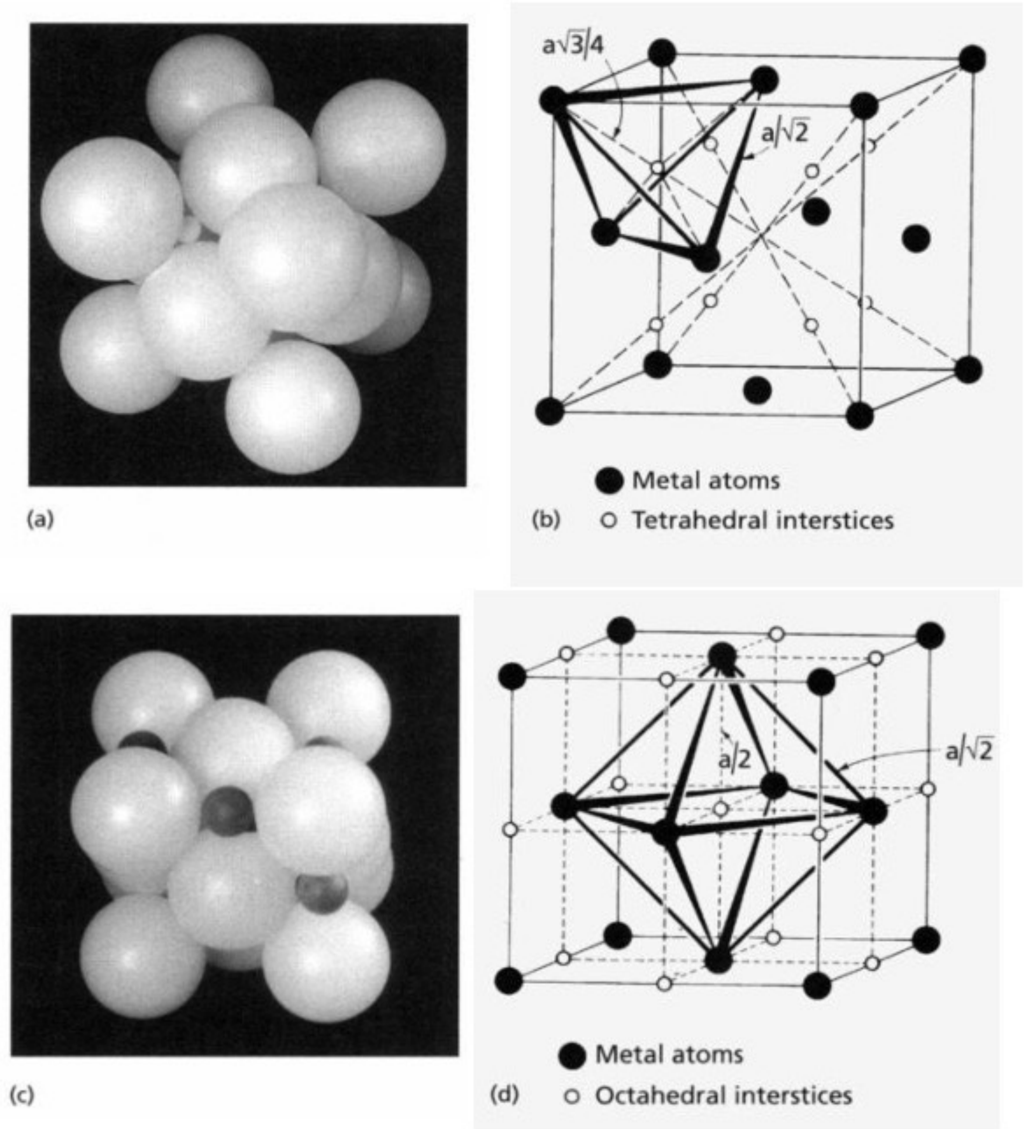
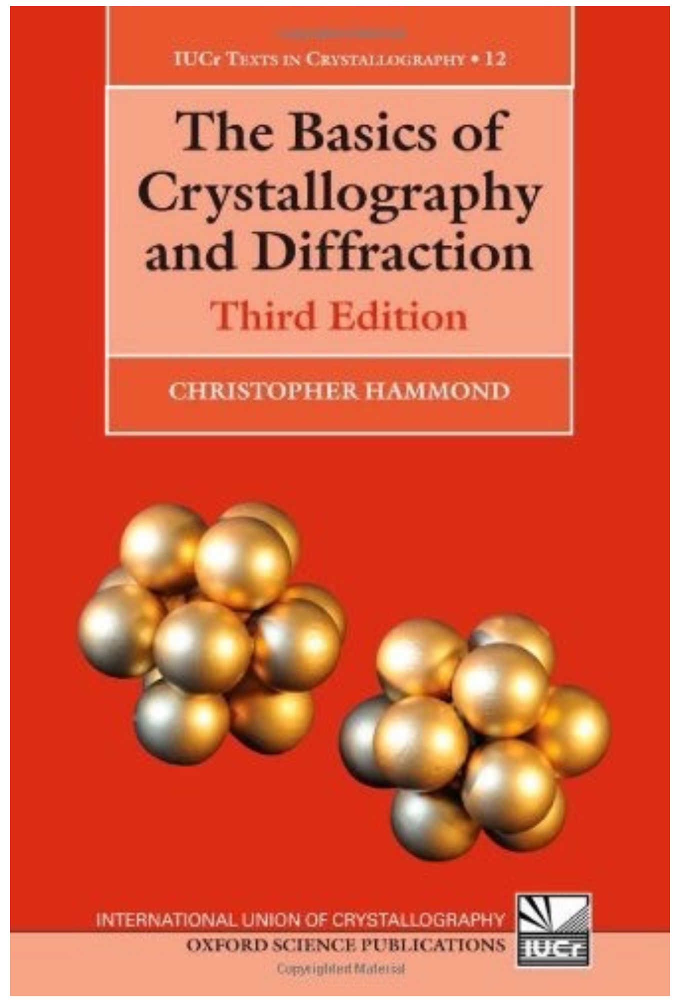
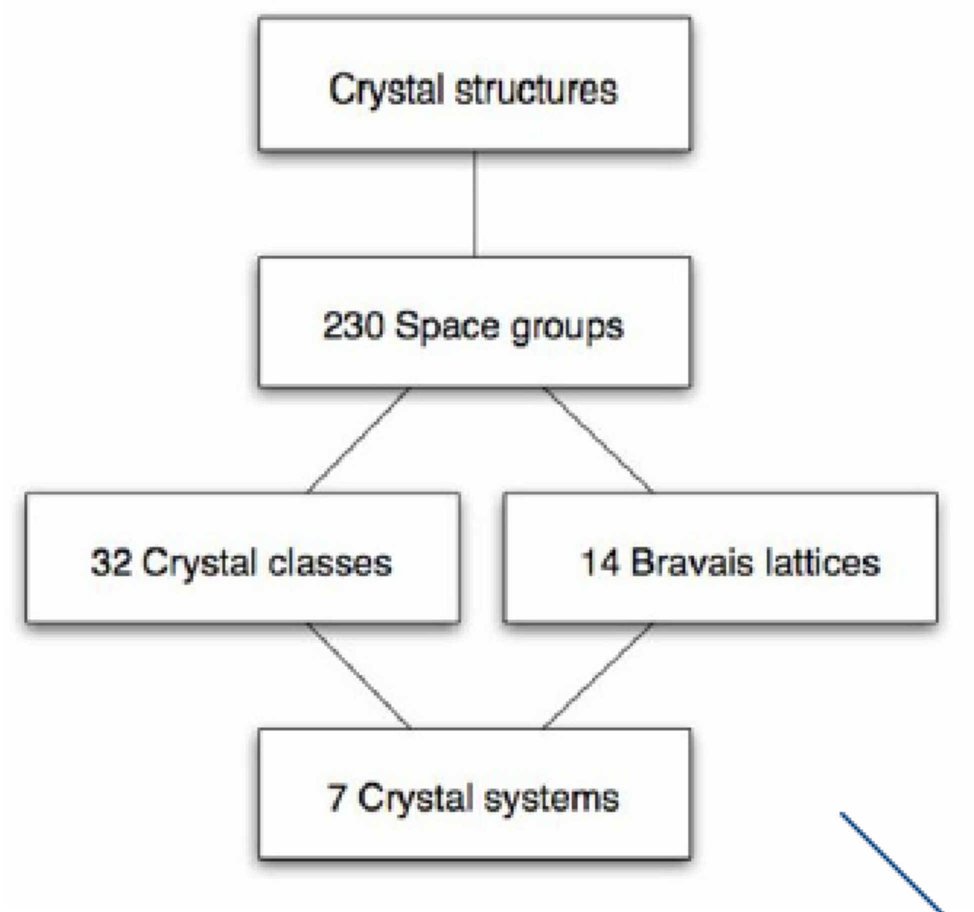
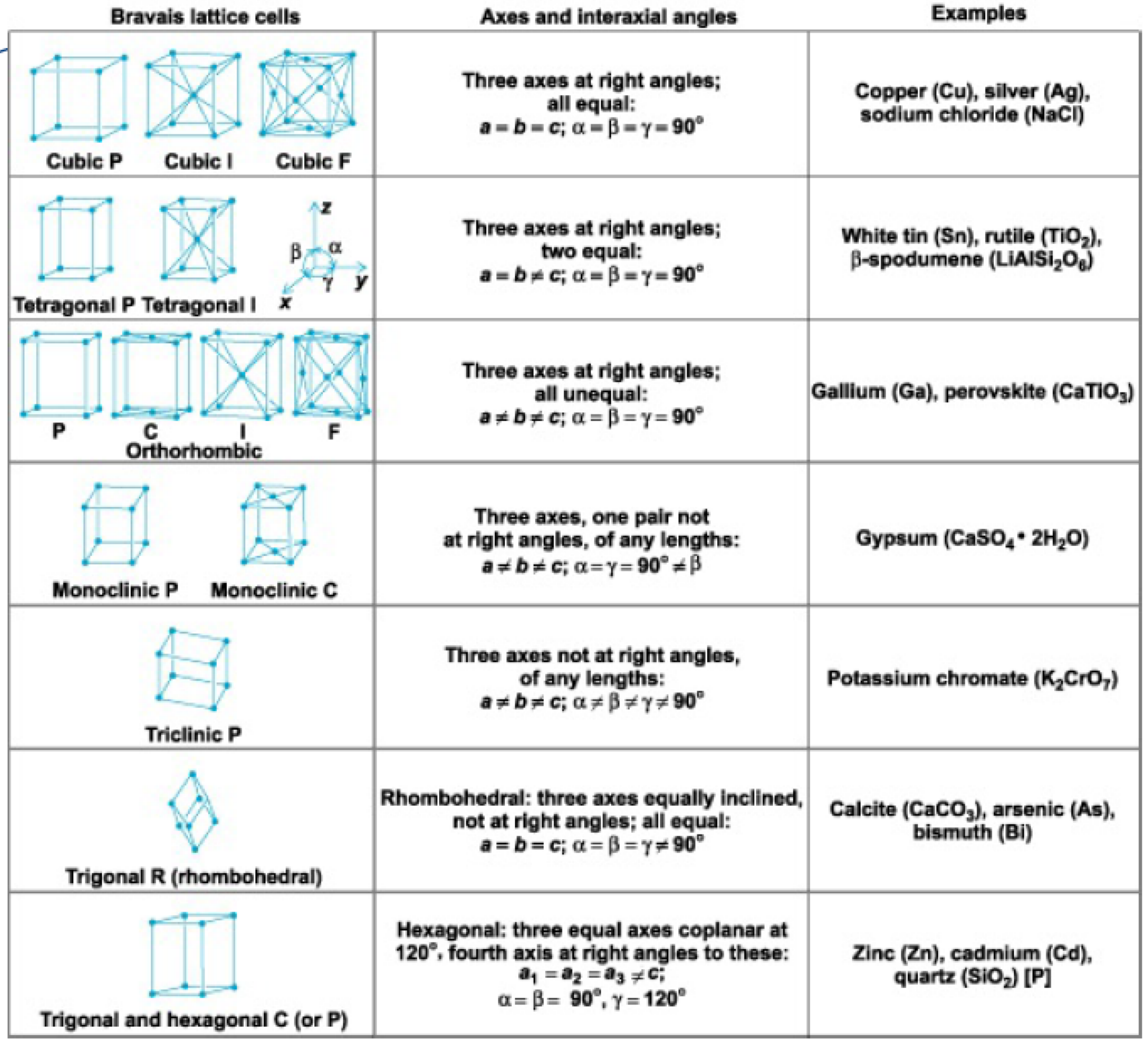


Fig. 1.10. (a) An atom in a tetrahedral interstitial site, $r_X/r_A = 0.225$ within the ccp unit cell and (b) geometry of a tetrahedral site, showing the dimensions of the tetrahedron in terms of the unit cell edge length a. (c) Atoms or ions in some of the octahedral interstitial sites, $r_X/r_A = 0.414$ within the ccp unit cell and (d) geometry of an octahedral site, showing the dimensions of the octahedron in terms of the unit cell edge length a. (From *The Structure of Metals*, 3rd edn, by C. S. Barrett and T. B. Massalski, Pergamon, 1980.)



The (crystalline) specimen





Bravais lattice cells	Axes and interaxial angles	Examples
Cubic P, Cubic I, Cubic F	Three axes at right angles; all equal: $a = b = c$; $\alpha = \beta = \gamma = 90°$	Copper (Cu), silver (Ag), sodium chloride (NaCl)
Tetragonal P, Tetragonal I	Three axes at right angles; two equal: $a = b \neq c$; $\alpha = \beta = \gamma = 90°$	White tin (Sn), rutile (TiO_2), β-spodumene ($LiAlSi_2O_6$)
Orthorhombic P, C, I, F	Three axes at right angles; all unequal: $a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	Gallium (Ga), perovskite ($CaTiO_3$)
Monoclinic P, Monoclinic C	Three axes, one pair not at right angles, of any lengths: $a \neq b \neq c$; $\alpha = \gamma = 90° \neq \beta$	Gypsum ($CaSO_4 \cdot 2H_2O$)
Triclinic P	Three axes not at right angles, of any lengths: $a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$	Potassium chromate (K_2CrO_7)
Trigonal R (rhombohedral)	Rhombohedral: three axes equally inclined, not at right angles; all equal: $a = b = c$; $\alpha = \beta = \gamma \neq 90°$	Calcite ($CaCO_3$), arsenic (As), bismuth (Bi)
Trigonal and hexagonal C (or P)	Hexagonal: three equal axes coplanar at 120°, fourth axis at right angles to these: $a_1 = a_2 = a_3 \neq c$; $\alpha = \beta = 90°, \gamma = 120°$	Zinc (Zn), cadmium (Cd), quartz (SiO_2) [P]

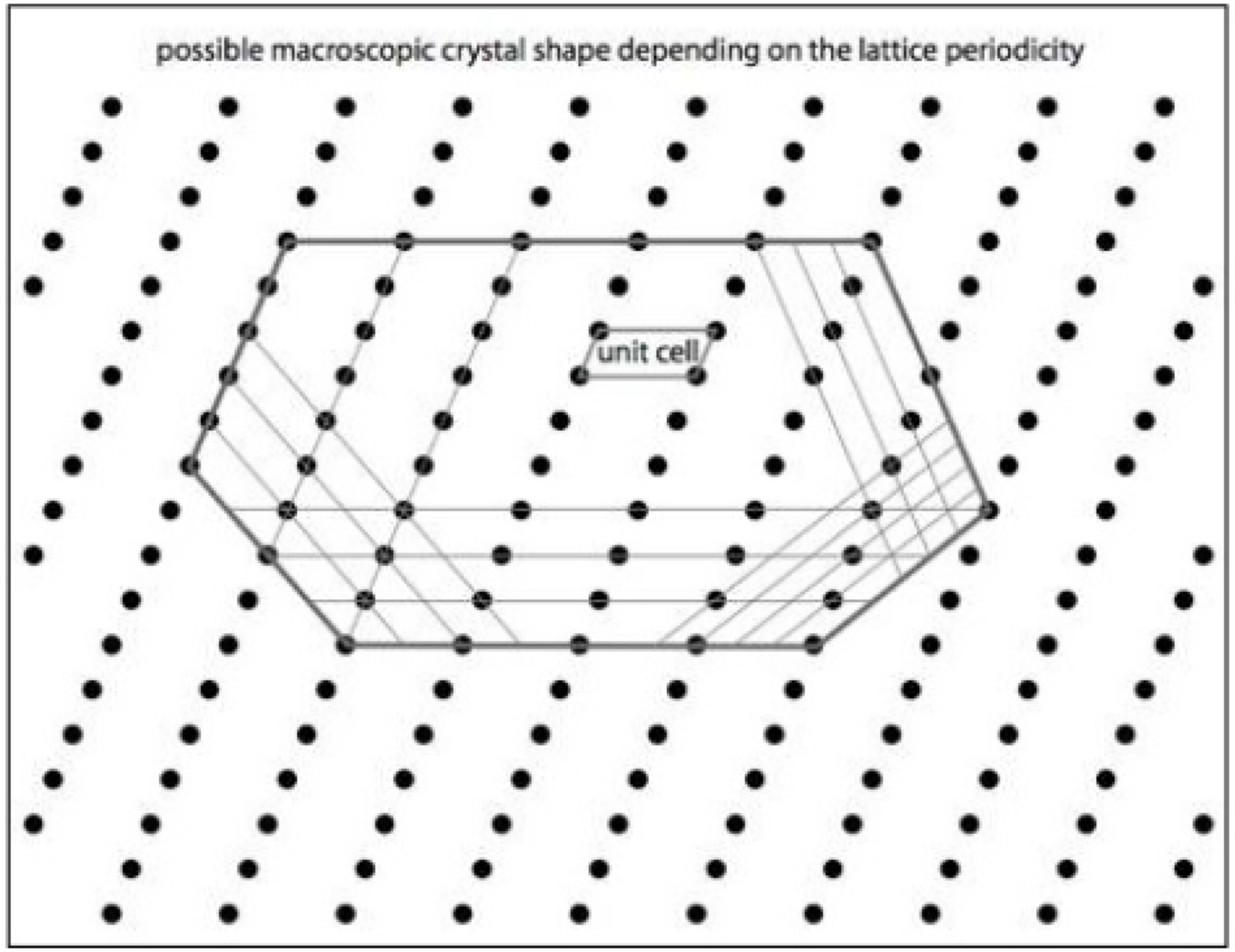
There are :

- the cubics
- the others…

The (crystalline) specimen

Planes, directions and families of those. Miller indices.

- Electrons are waves … and articles



In 2D, we can draw families of lines parallel to each other, containing the same linear arrangement of atoms. In 3D these are **planes.**

They are called lattice planes

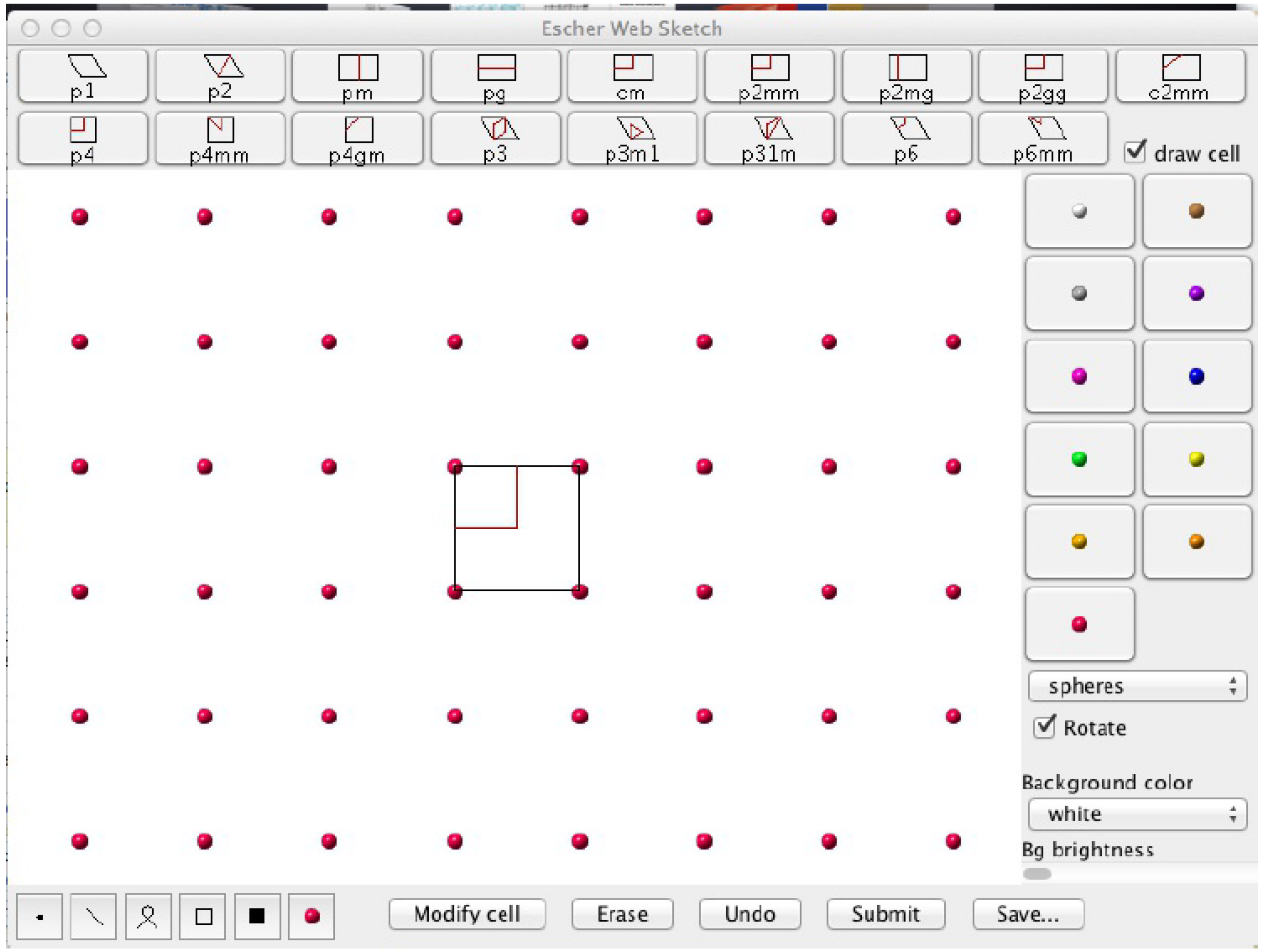
We can also look at vectorial directions with respect to the unit cell.

How do we label those ?

The (crystalline) specimen

We use miller indices for planes and directions for the vectors.

They are taken in the referential system of the unit cell. For a cubic system, it is an orthonormal one. For any other system, it is not. Be careful, some « intuitive evidences » will be WRONG!



Direction: end point of the vector.

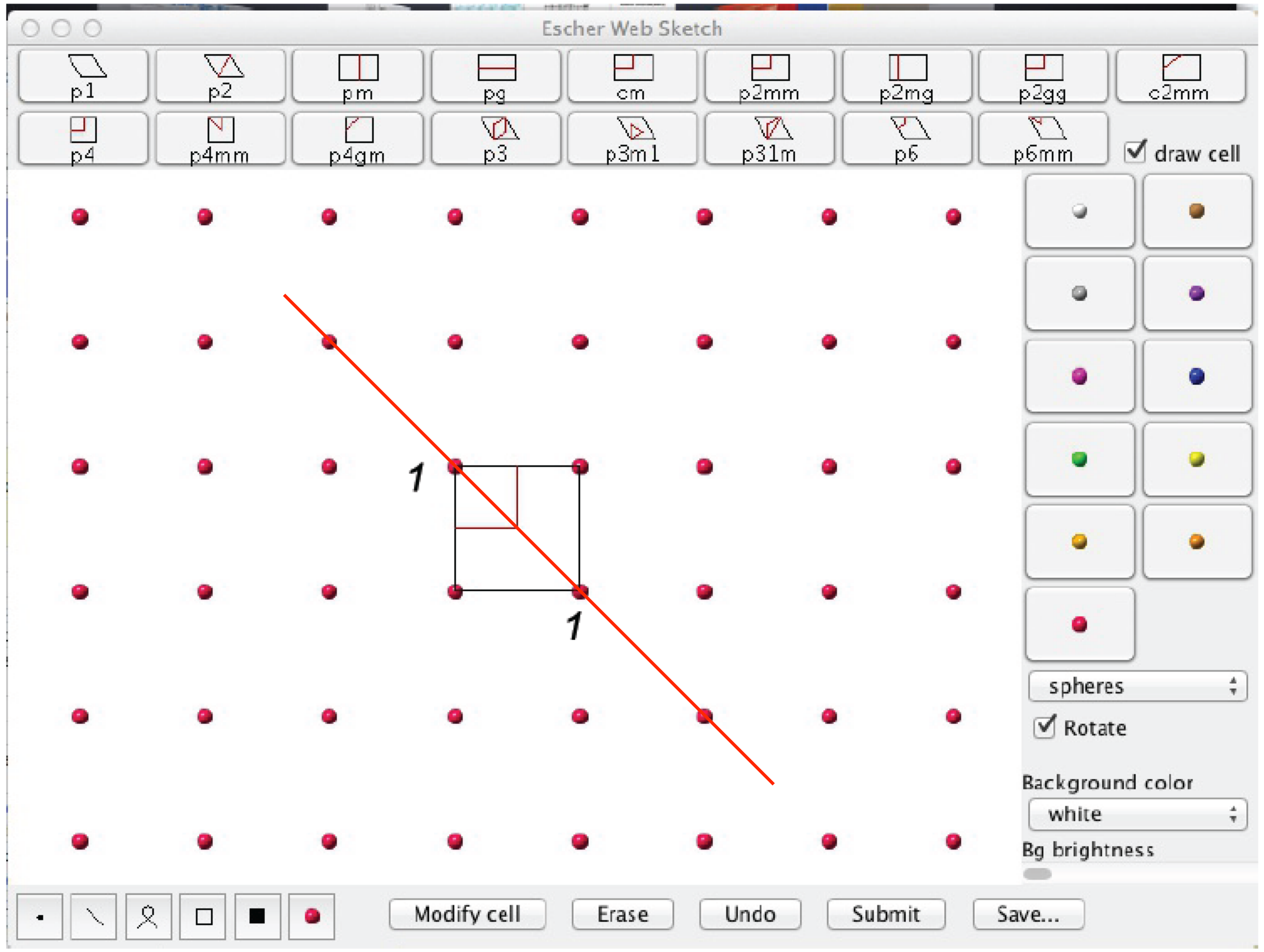
e.g. :

- // to a: 1,0
- on the diagonal: 1,1
- it can point down: 1,-1

Directions are given in squared brackets
in 3D they are labelled
u,v,w
[u,v,w]

The (crystalline) specimen

Lines (planes) are given by the miller indices h,k (l).
The line (plane) intercepts the crystal at a/h,b/k,(c/l)



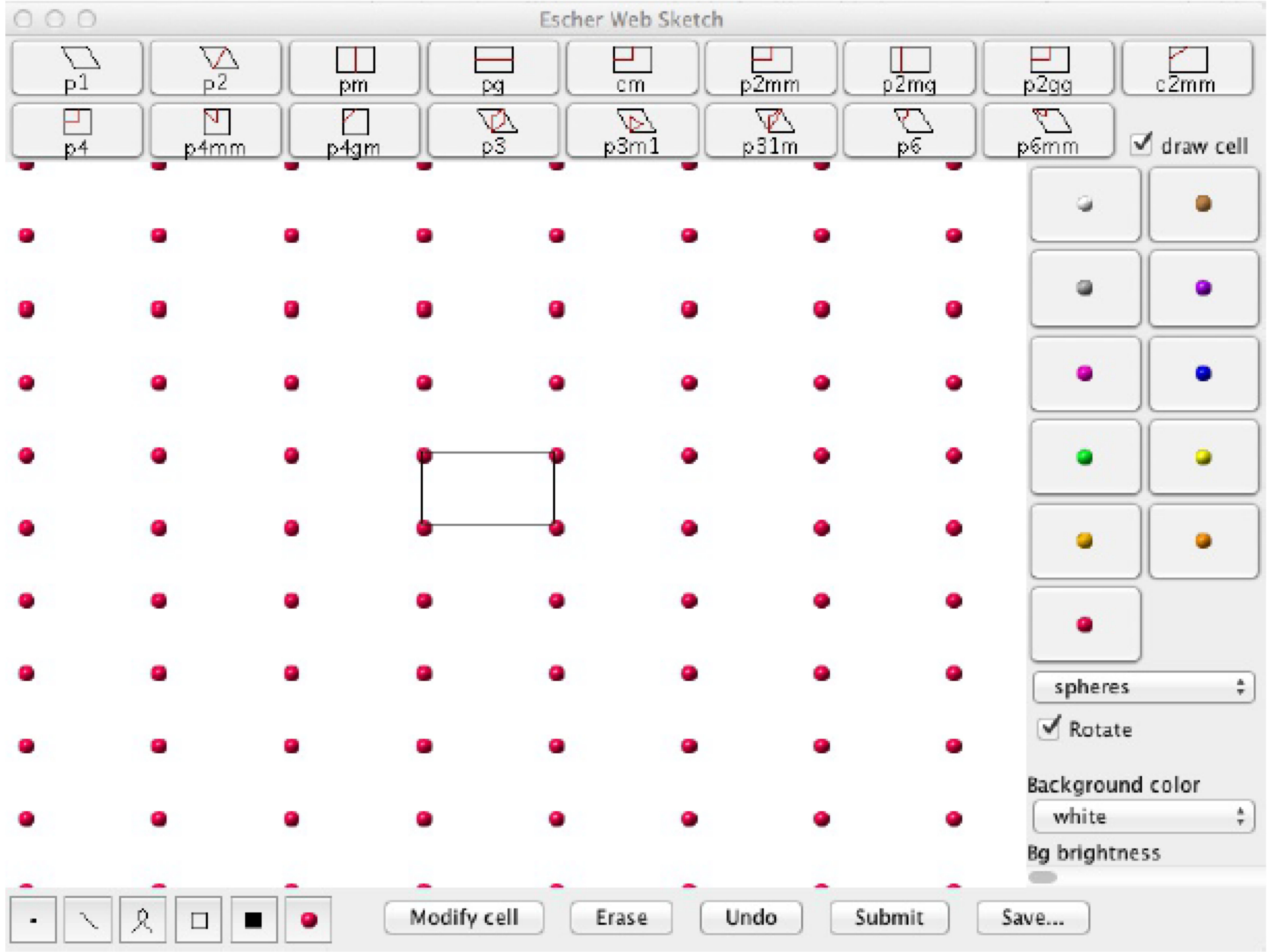
Here, we have the 1,1 line

Planes are given in round brackets (h,k,l)

Families of planes are given in curled brackets {h,k,l}

The (crystalline) specimen

Draw the (2,1) line and the [2,1] direction



The (crystalline) specimen

Zone and zone axis

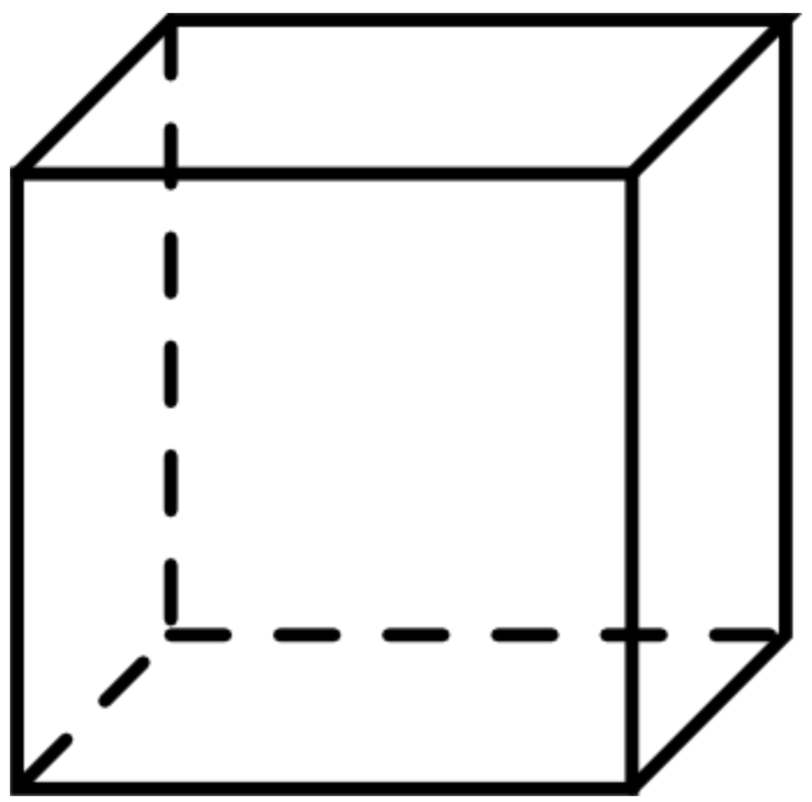
A **zone** is a set of plane whose intersections in a crystal are parallels.

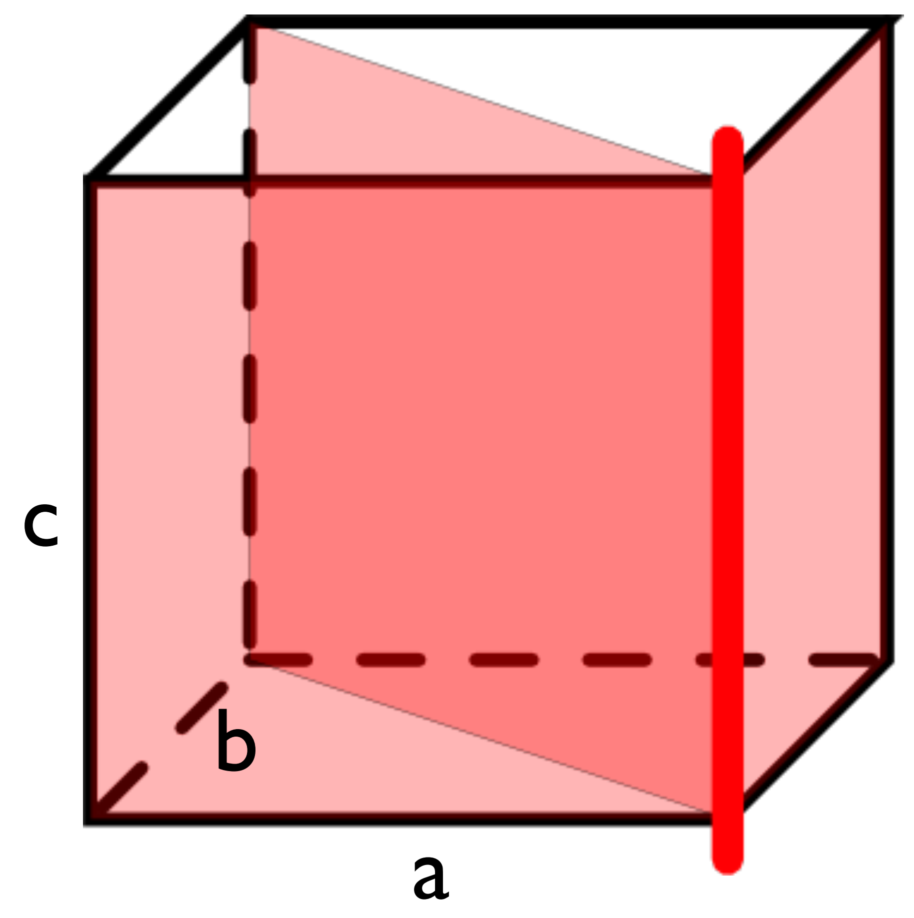
The **zone axis** is the direction of those intersections

Therefore zone and directions are equivalent.
Zone and zone axis are then noted in squared brackets [u,v,w]

In TEM, you will commonly read « The crystal is oriented in the [u,v,w] zone axis.
This means the optical axis of the microscope is // to this zone axis

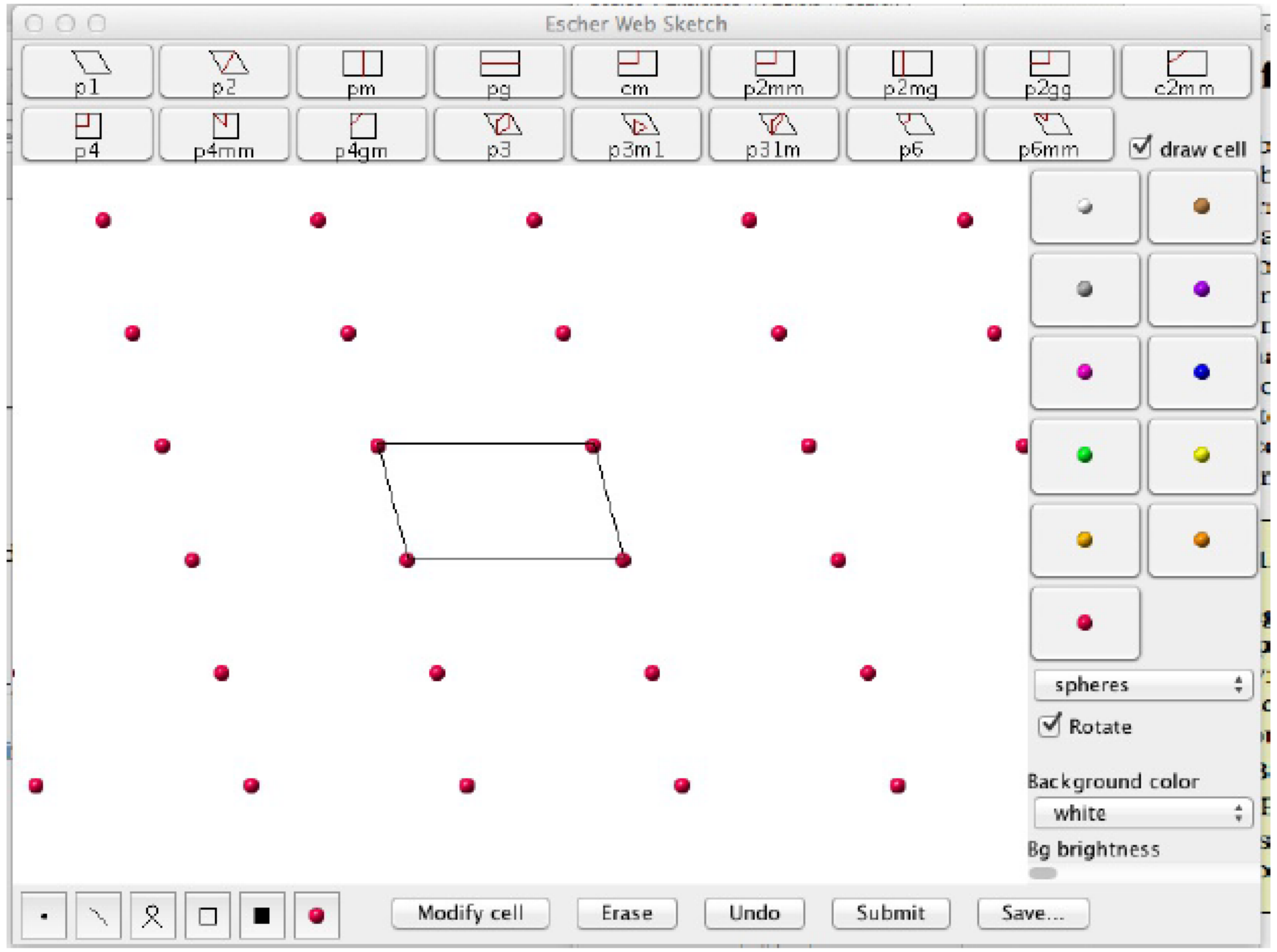
Zone law or Weiss zone law:
if a plane (hkl) lies in a zone [uvw] hu+kv+lw=0





The (crystalline) specimen

Reciprocal space



a* is perpendicular to b and c
b* is perpendicular to a and c
c* is perpendicular to a and b

a*.a = b*.b = c*.c = 1

similarly to real space, the reciprocal vectors define the reciprocal unit cell.

thus we have directions in reciprocal space. They are identified by h k and l
An hkl direction in reciprocal space is perpendicular to the (hkl) plane in real space.

a reciprocal space vector $\mathbf{d}^*_{hkl}=ha^*+kb^*+lc^*$ has a length d^*_{hkl} $d^*_{hkl}=1/d_{hkl}$
with d_{hkl} the interplane distance of planes (hkl)

The reciprocal space vector's length gives the **spacial frequency** of the planes (hkl)

Draw the a* and b* reciprocal unit vectors; draw the 11 reciprocal direction and the (11) line

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The (crystalline) specimen

2 pi or not 2 pi ?

A word of caution: investigated volume

One TEM sample : ⟷ 1 µm ; 100 nm $(10^{-6})^2 \cdot 10^{-7} = 10^{-19}\ m^3$

Average TEM-day : 5 samples
Average day / year 200
} 1000 samples / y

$10^{-16}\ m^3$ / year & TEM

EPFL 5 TEM 10'000 students   TU Graz 16'000
4 TEM
EMAT 6 TEM 20'000 students   ...

Take 5 TEM per 20'000 students

$\sim 200 \cdot 10^6$ students worldwide → 10'000 TEM worldwide

⇒ $10^{-12}\ m^3$ matter / year   ~ 80 y   linear increase ⇒ ~ 50 y

$5 \cdot 10^{-11}\ m^3$ matter   **0,05 mm³**

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