Electron Microscopy in Catalysis Research

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Why TEM and Electron diffraction?

TEM Morphology

Bright field and dark field imaging Defects, Phases

High-resolution imaging Defects, Interfaces, Surfaces

Electron diffraction Structure

Convergent-beam diffraction Symmetry, Strain
Lattice parameter

Energy-dispersive X-ray spectroscopy (EDX)

Electron-energy loss spectroscopy (EELS)

Energy-filtered TEM (EFTEM)

Resolution of light microscopy

$$\delta = \frac{0.61\,\lambda}{\mu \sin \beta}$$

λ is the wavelength of the radiation

$\mu \sin \beta$ is approximately 1

For green light, λ is about 550 nm, so the resolution of a light microscope is 300 nm

For electrons, the wavelength is related their energy *E*,

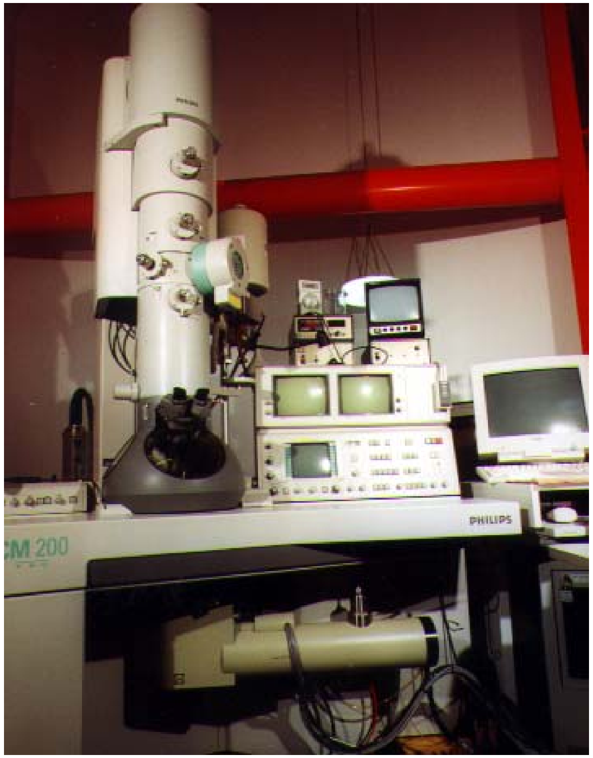
$$\lambda \sim 1.22\, E^{-1/2}$$

For a 100-keV electron, $\lambda \sim 0.004$ nm

Wavelength limit of resolution is not possible due to imperfect electron lenses !

The achievable resolution: < 0.15 nm

Electron Microscopes at FHI



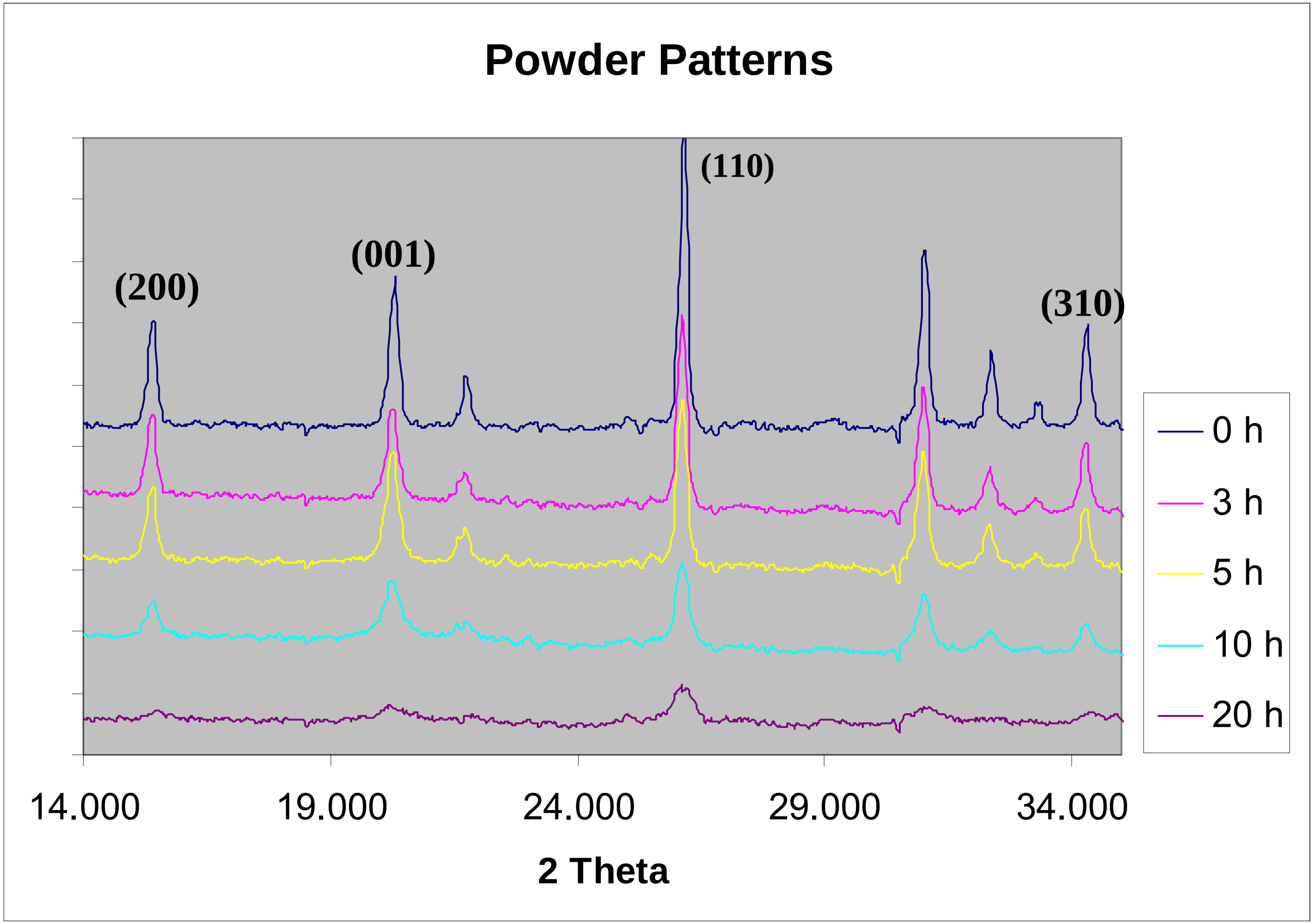
Two Philips TEMs

Hitachi SEM

…more to come…

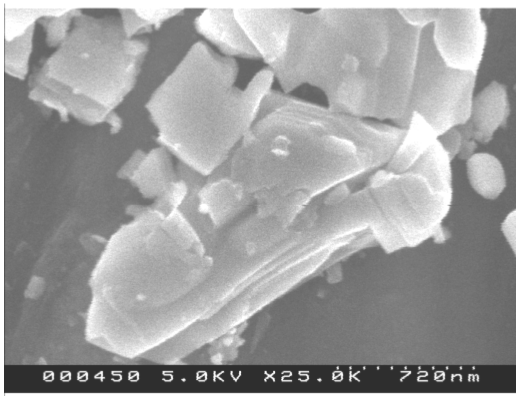
Why using electron microscopy - example

Tribomechanical activation of V_2O_5

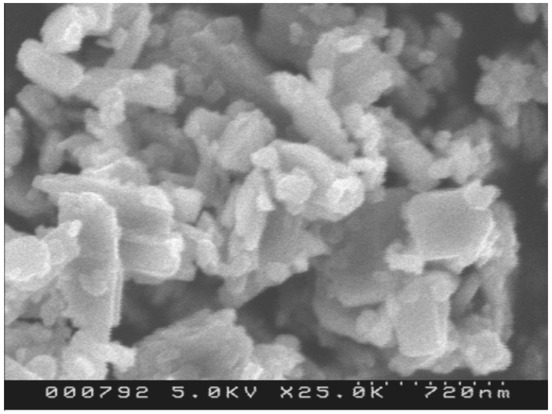


Why using electron microscopy - example

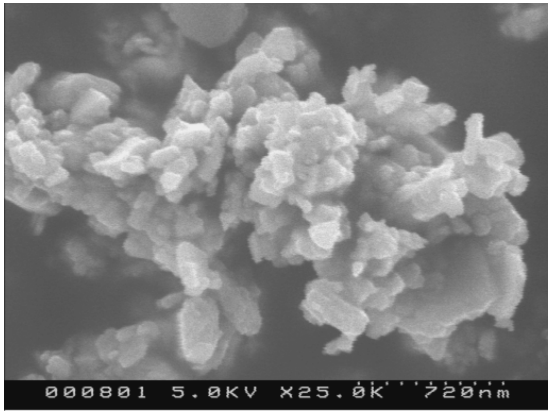
SEM



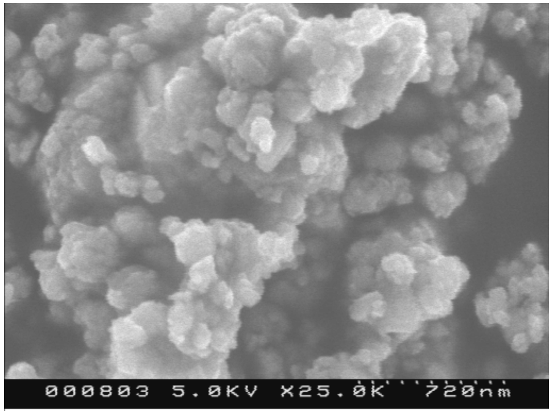
V_2O_5 precursor



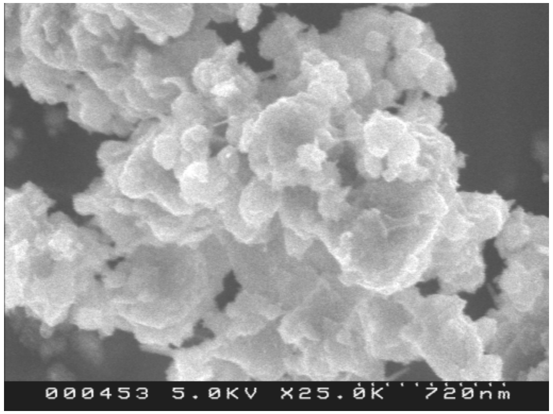
After 3 h milling



After 5 h milling



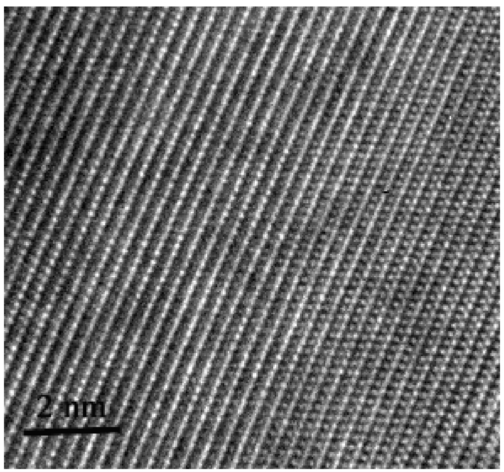
After 10 h milling



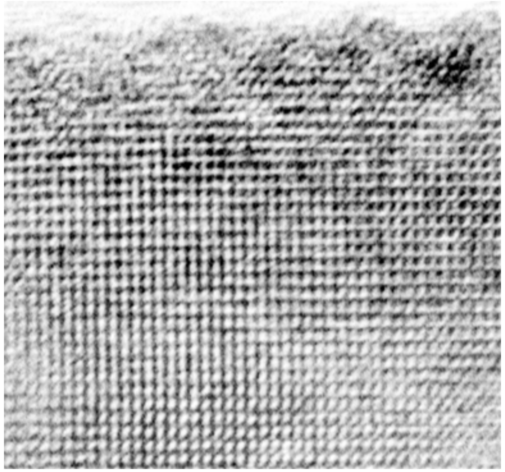
After 20 h milling

Why using electron microscopy - example

High-resolution TEM

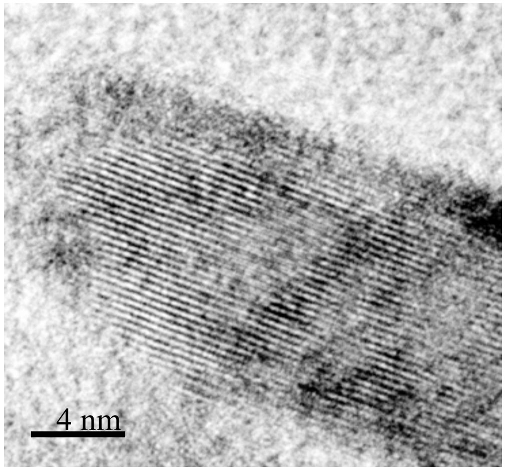


V_2O_5 precursor

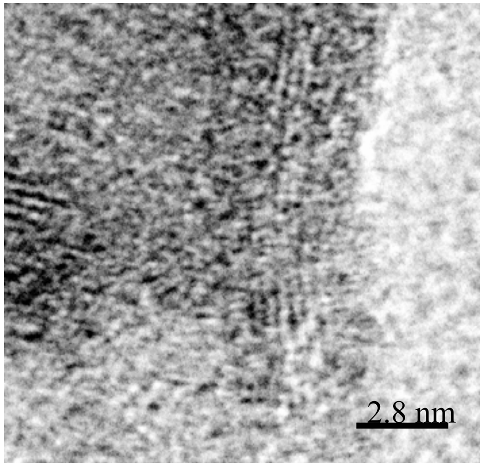


After 3 h milling

After 5 h milling



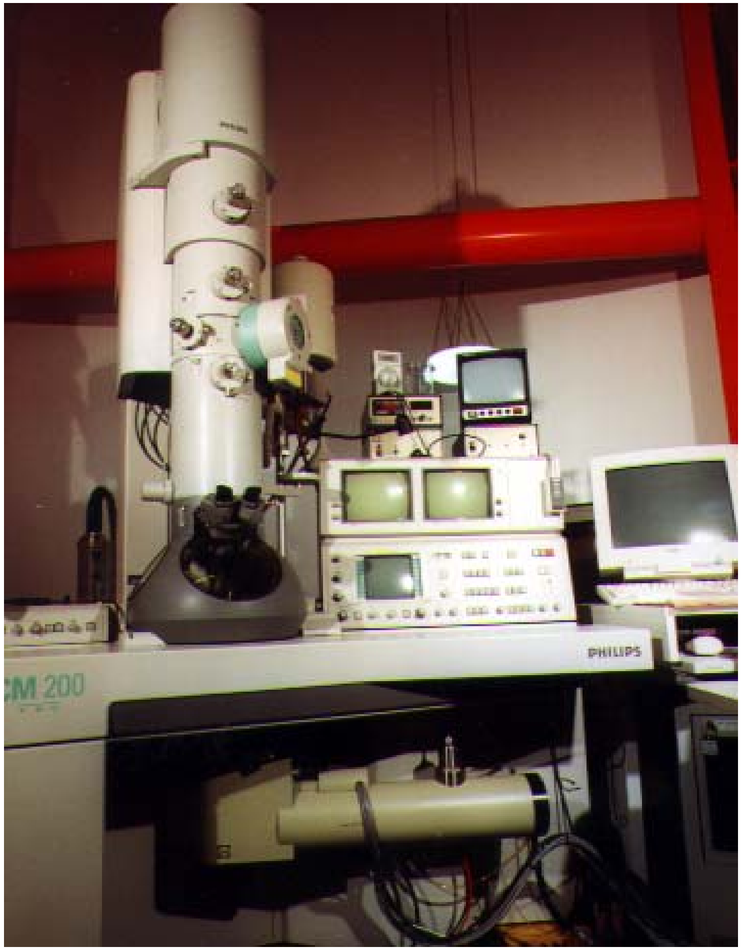
After 10 h milling



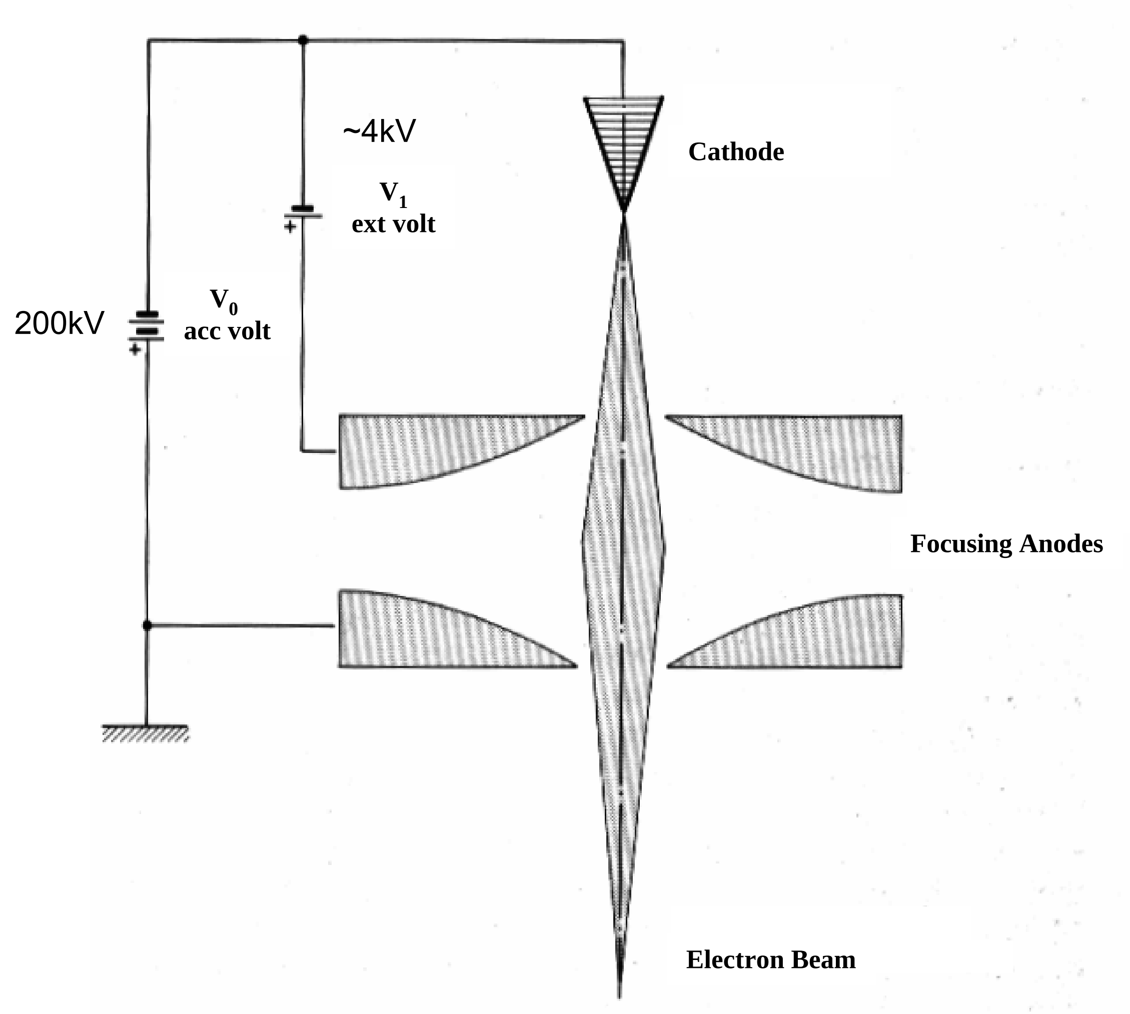
After 20 h milling

What makes an electron microscope

1. **Vacuum system**
2. **Electron guns**
3. **Electromagnetic lenses**
4. **Sample stages**
5. **Imaging recording system (digital or analog)**



Field Emission Gun (FEG)

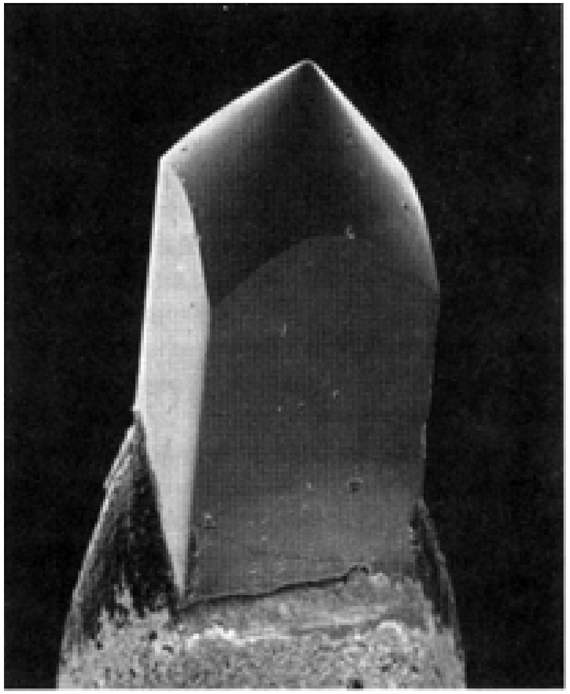


Probe diameter 2 nm

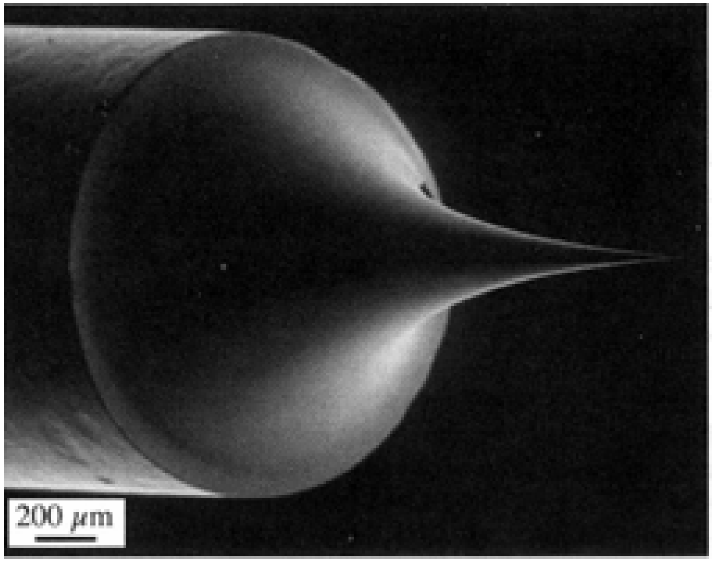
Brightness 10^9 A/cm^{2}ster

Vacuum required 10^{-8} Pa

Electron sources



An LaB_6 crystal



An FEG tip, showing the extraordinarily fine W needle

Illumination sources

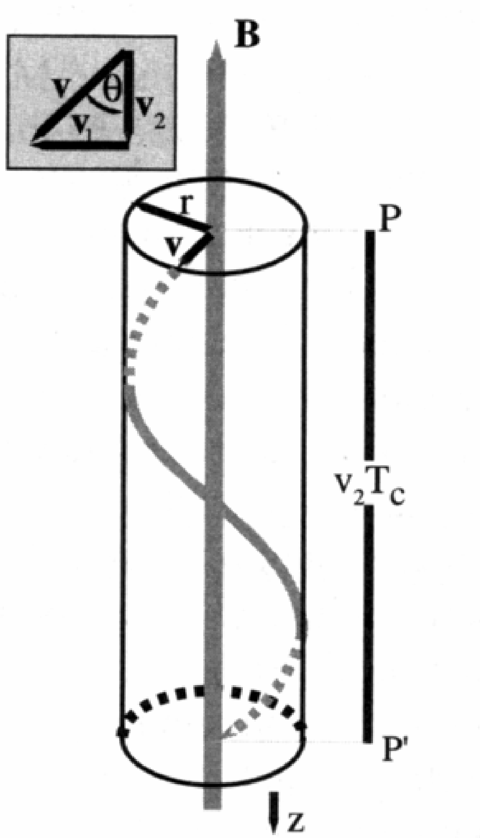
	Units	W	LaB_6	FEG
Work function, Φ	eV	4.5	2.4	4.5
Operating Temperature	K	2700	1700	300
Brightness	$A/m^2/sr$	10^9	$5\ 10^{10}$	10^{13}
Energy Spread	eV	3	1.5	0.3
Vacuum	Pa	10^{-2}	10^{-4}	10^{-8}
Lifetime	hr	100	500	>1000

Lorentz force and electromagnetic lenses

When an electron with charge q (= -e) enters a magnetic

field of strength **B**, it experience a force **F** (Lorentz force)

$$\mathbf{F} = q\,(\mathbf{E} + \mathbf{v} \times B) = -e\,(\mathbf{v} \times \mathbf{B})$$



Electron lenses are the magnetic equivalent
of the glass lenses in an optical microscopy,
And , to a large extent, we can draw comparisons
between the two.

The physical basis of imaging and diffraction

Newton´s Lens Equation

$$\frac{1}{u} + \frac{1}{v} = \frac{1}{f}$$

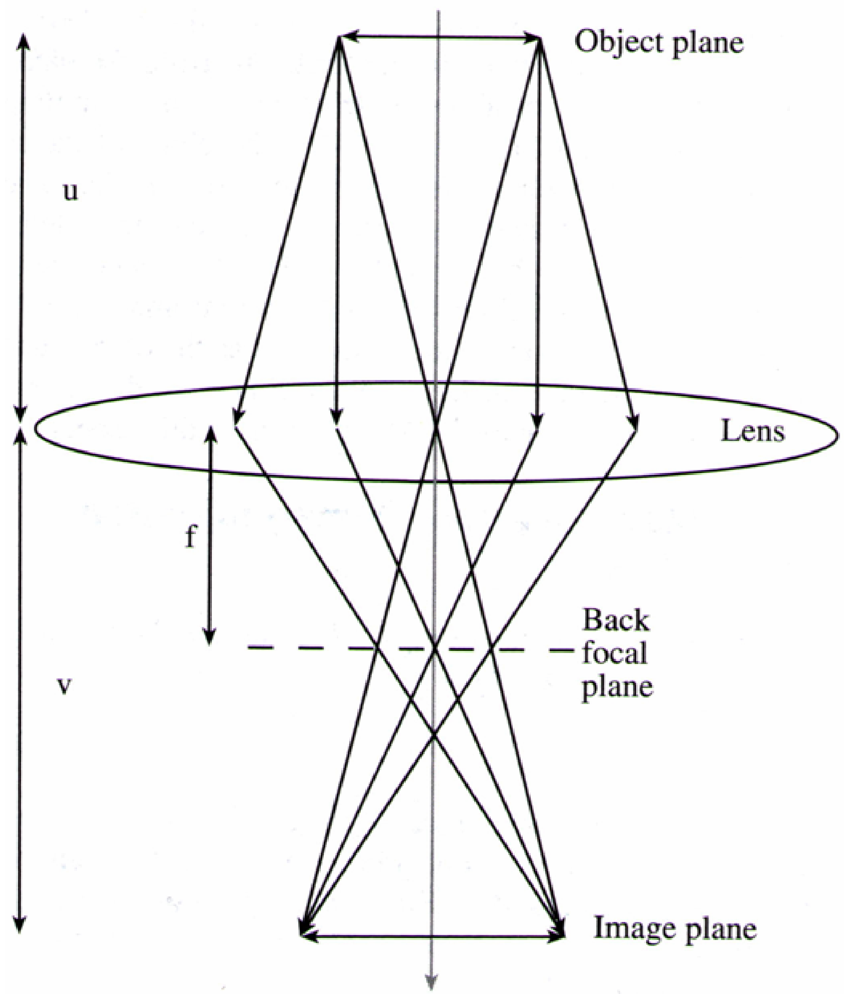
Magnification

$$M = \frac{v}{u}$$

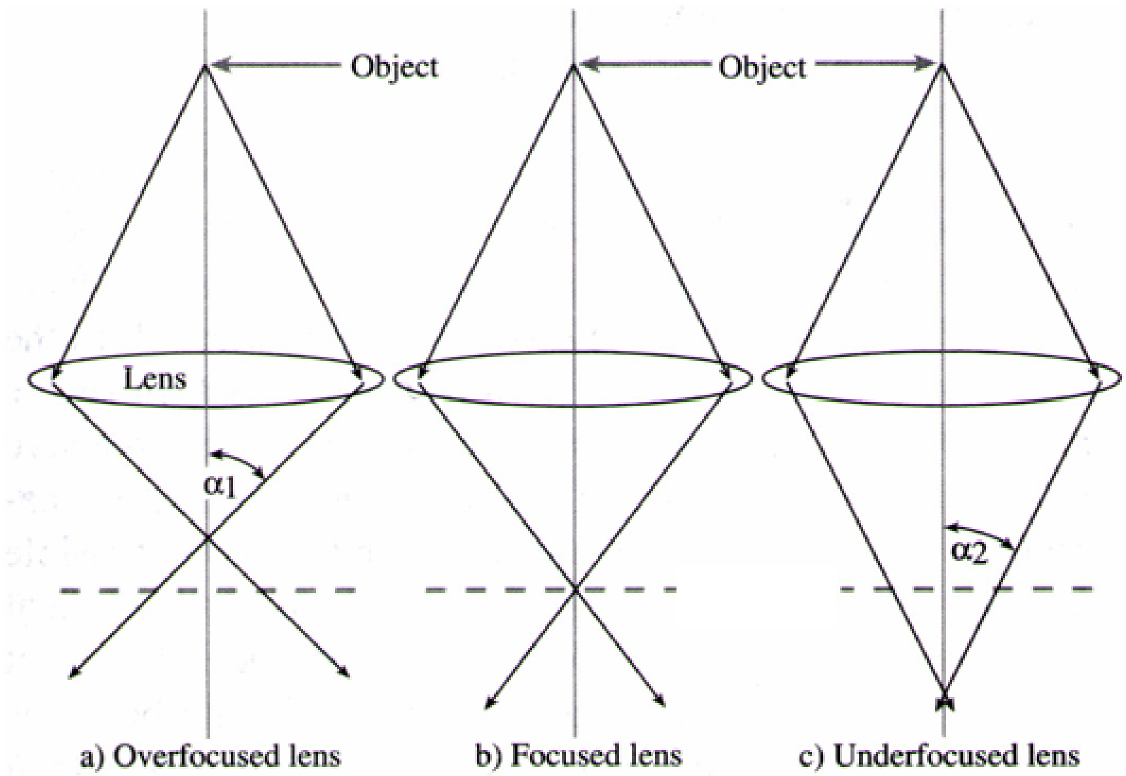
To resolve a lattice distance of 0.2 nm

a magnification of $5\ 10^6$ is needed,

assuming human eyes can resolve two points of 0.1 mm

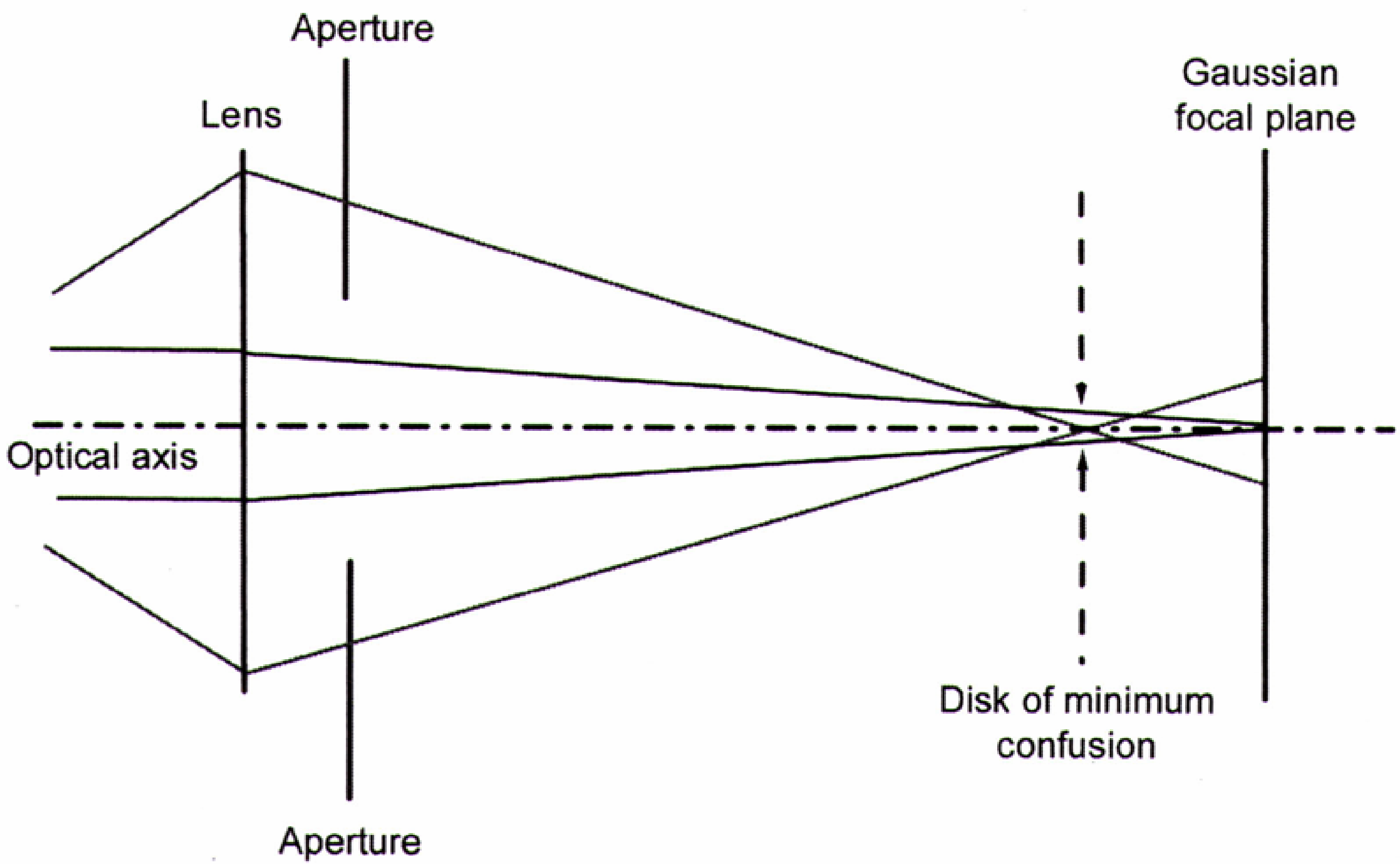


Exciting the lens strength - focus



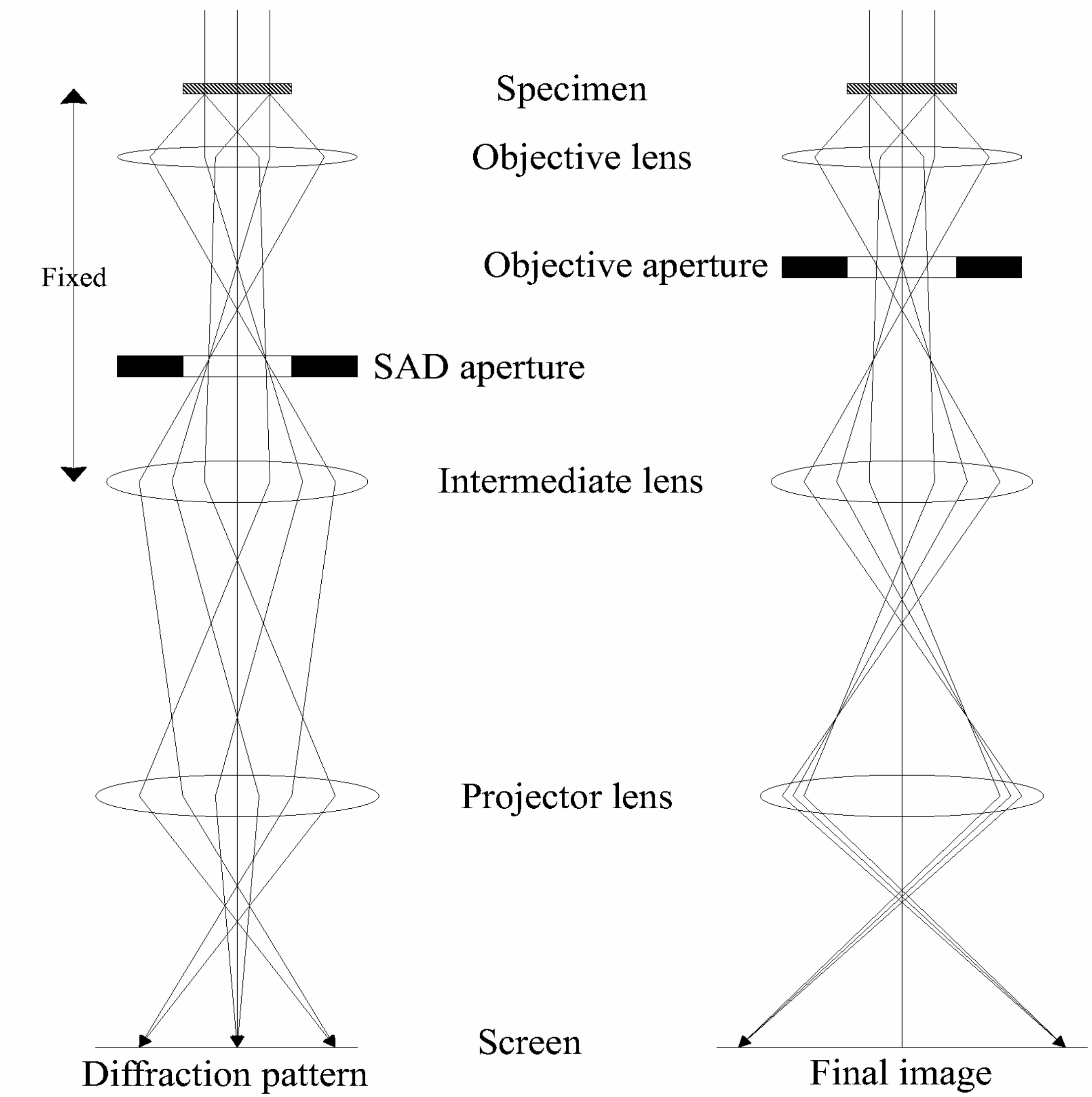
Lenses spatially fixed, but strength changeable

Aberrations of lenses



The electromagnetic lenses are not perfect

Ray paths in transmission electron microscope



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What is image contrast?

Contrast (C) as the difference in intensity (ΔI) between two adjacent areas

$$C = \frac{I_2 - I_1}{I_1} = \frac{\Delta I}{I_1}$$

Human eyes can´t detect intensity changes < 5%, even < 10% is difficult

Image contrast in TEM

I. Mass-thickness contrast

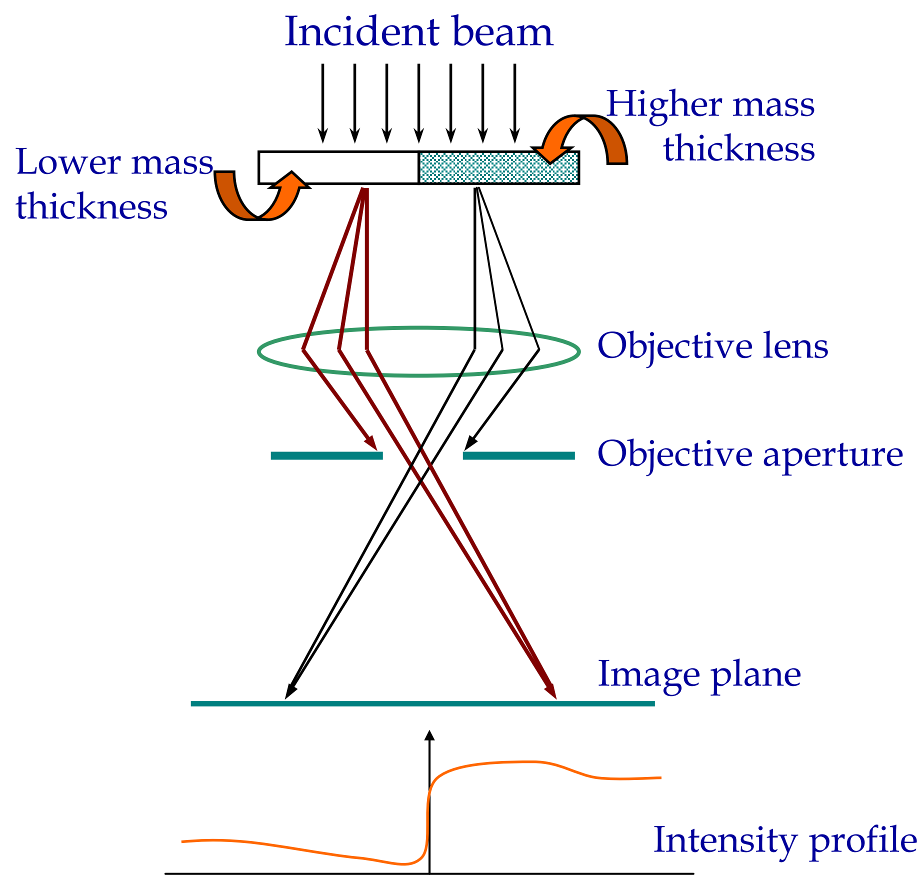
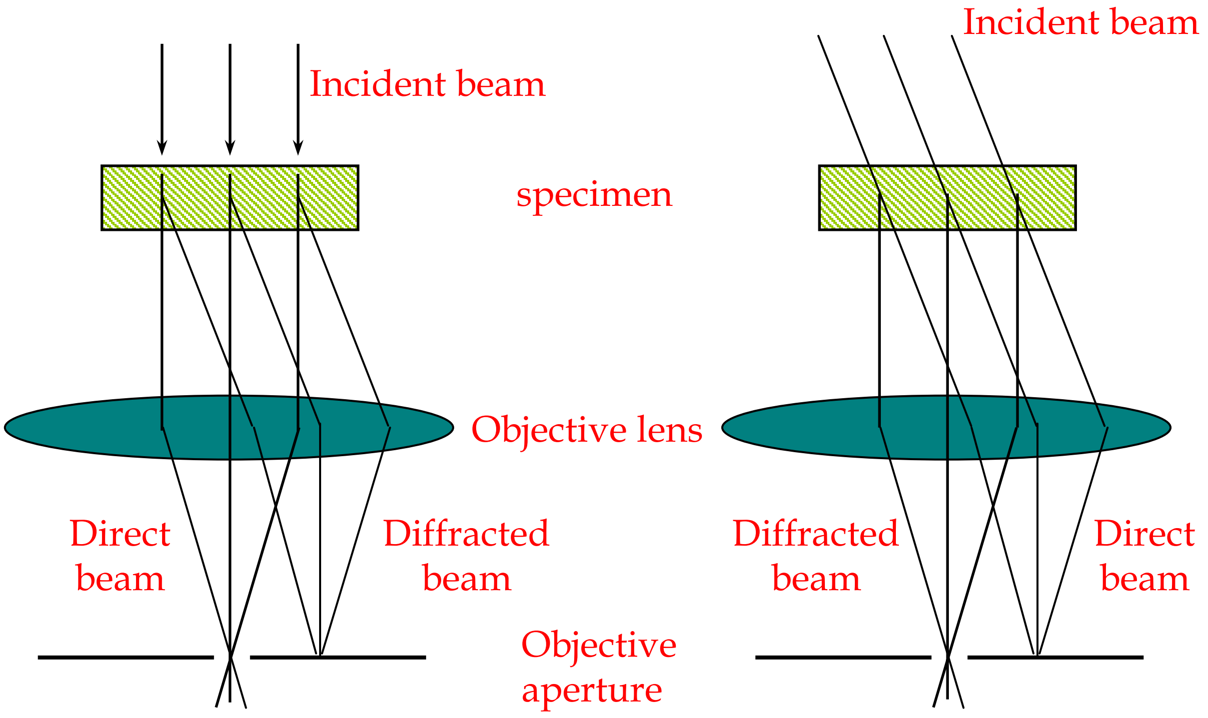


Image contrast in TEM

II. Diffraction contrast



Bright field (BF)

Dark field (DF)

III. Phase contrast – in pictures

The electron wave passing through the high potential has its wavelength reduced giving a phase advance

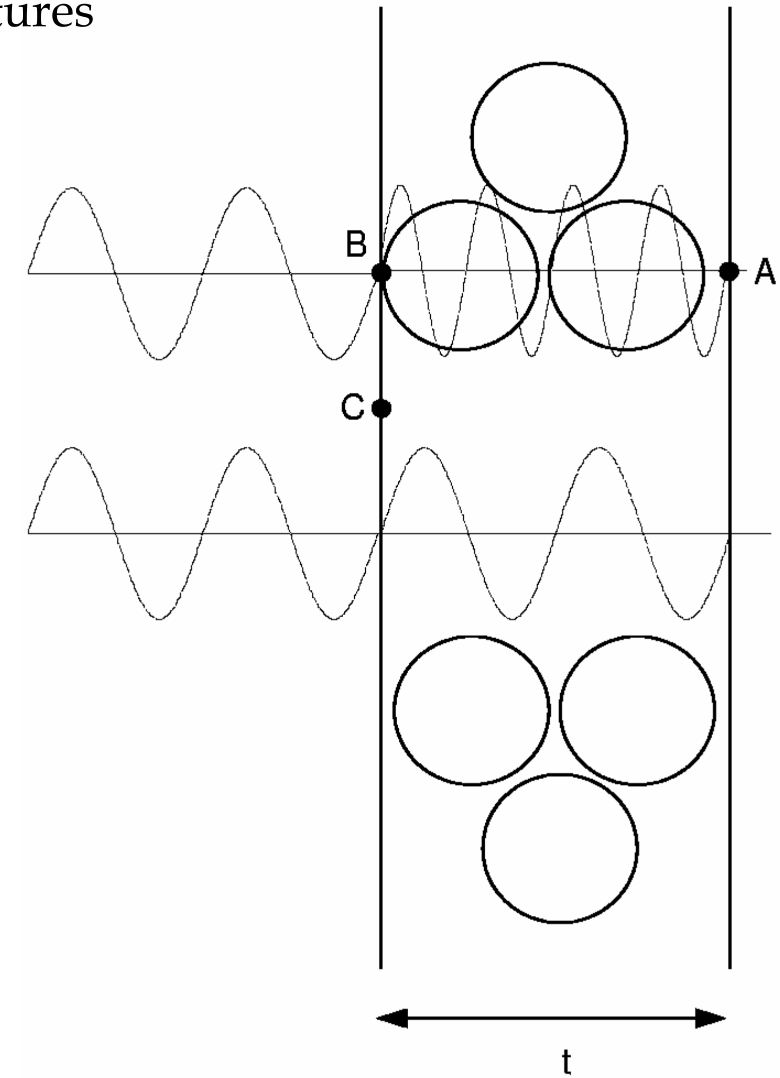


Image contrast in TEM

III. Phase contrast – in words and formulas

Incident wave: $\psi(\mathbf{r}) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$ Plane wave

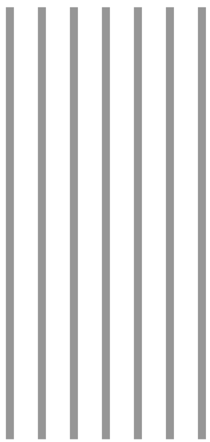
Exit wave: $\psi_e(\mathbf{r}) = e^{-i\sigma V_p(\mathbf{r})} \approx 1 - i\sigma V_p(\mathbf{r})$

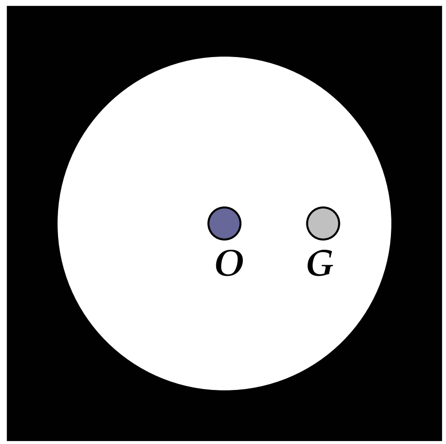
Assuming weak-phase object approximation
V_p : scattering potential

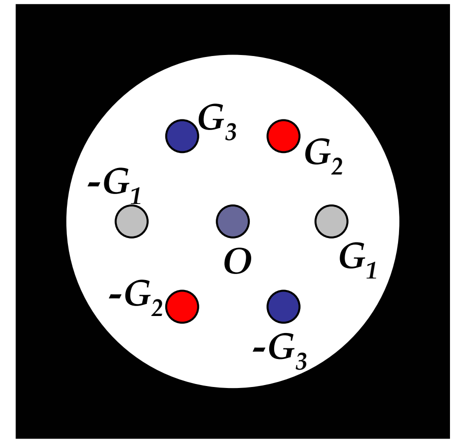
Final intensity: $I(\mathbf{r}) = \psi_e(\mathbf{r})\psi_e^*(\mathbf{r}) \approx 1 + 2\sigma V_p(\mathbf{r})$

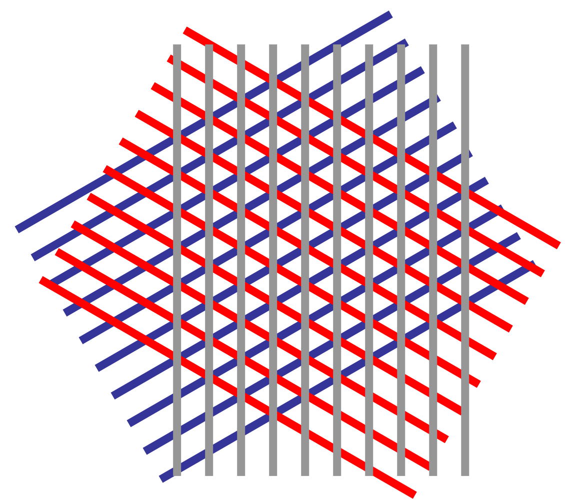
Image contrast in TEM

III. Lattice fringes in pictures

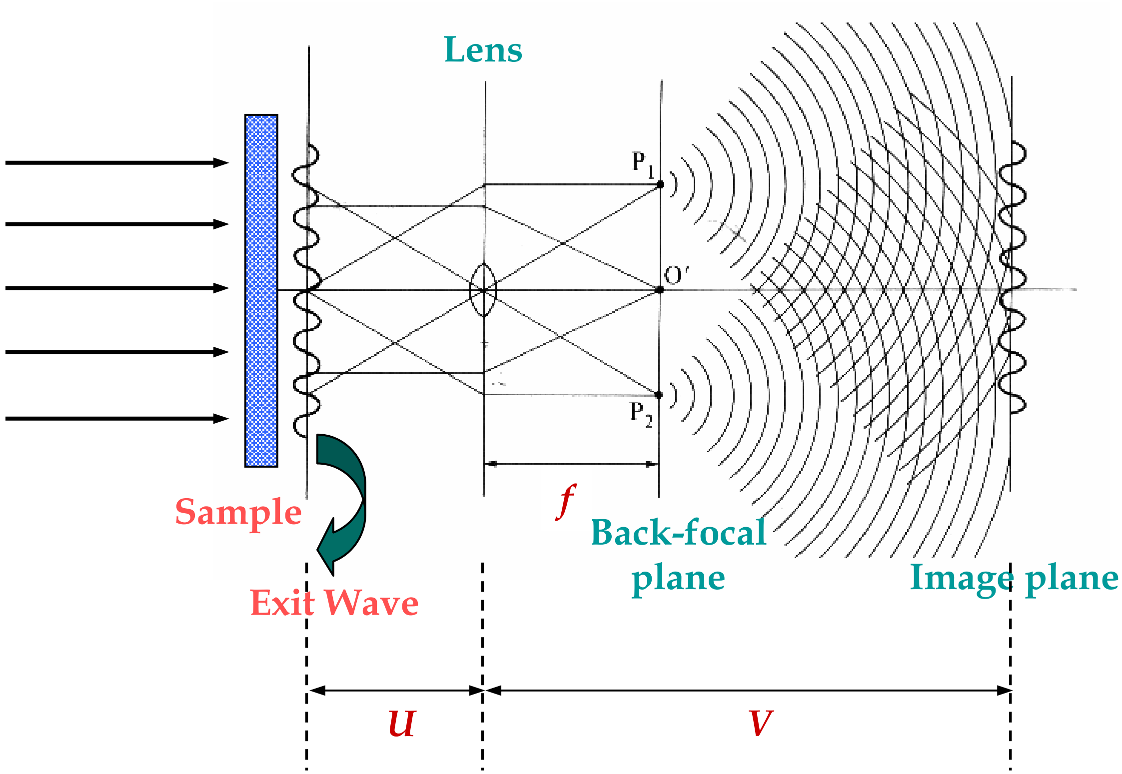






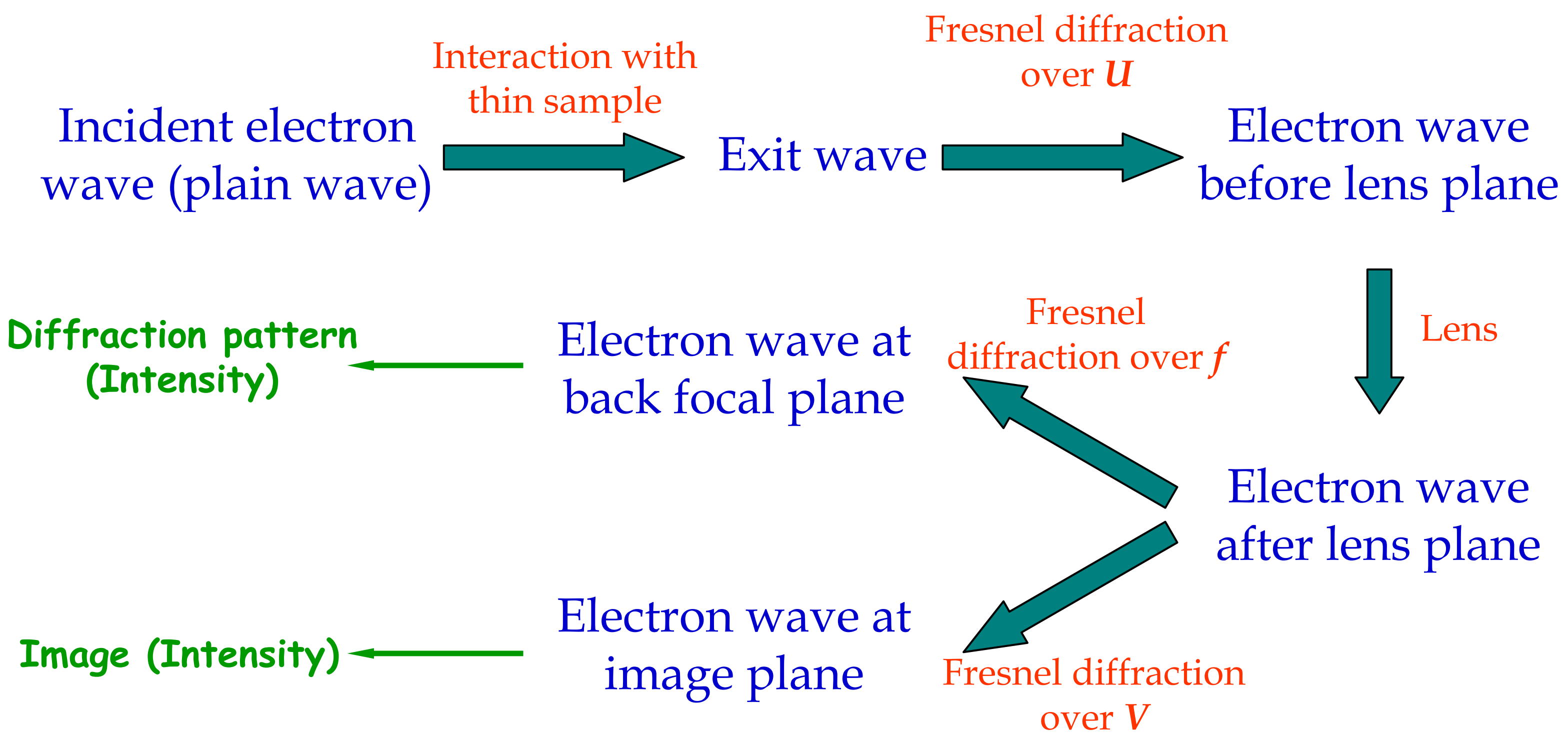


High-resolution imaging



Abbe Interpretation of imaging

Abbe interpretation of imaging



MAX-PLANCK-GESELLSCHAFT

Some mathematics…

FT and IFT

$$F(u) = \mathcal{F}\{f(x)\} = \int_{-\infty}^{+\infty} f(x)\exp(2\pi ixu)\,dx$$

$$f(x) = \mathcal{F}^{-1}\{F(u)\} = \int_{-\infty}^{+\infty} F(u)\exp(-2\pi ixu)\,du$$

Function of space	FT → / ← IFT	Distribution of spatial frequency
Function of time		Distribution of frequency

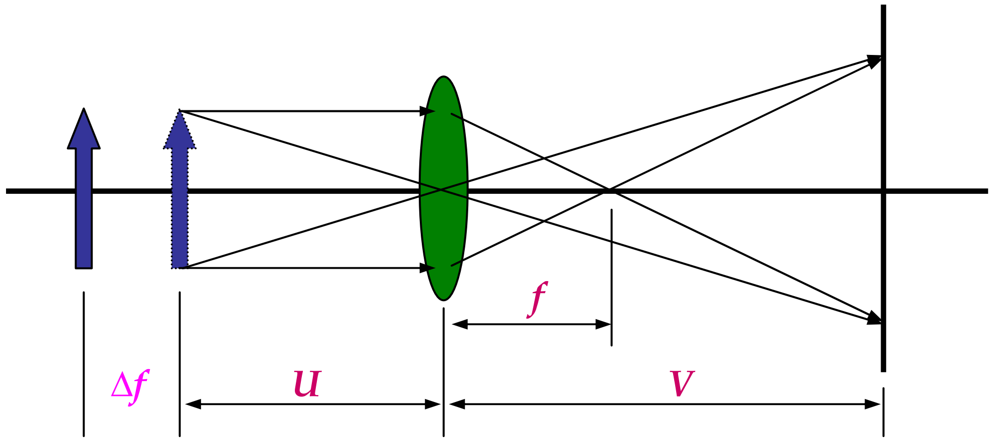
Convolution

$$f(x) * g(x) = \int_{-\infty}^{+\infty} f(X)g(x-X)\,dX$$

$$\mathcal{F}\{f(x) * g(x)\} = \mathcal{F}\{f(x)\}\cdot\mathcal{F}\{g(x)\} = F(u)\cdot G(u)$$

Defocus and aberrations

I. Defocus



Propagation factor
$p_{\Delta f}(x,y)$

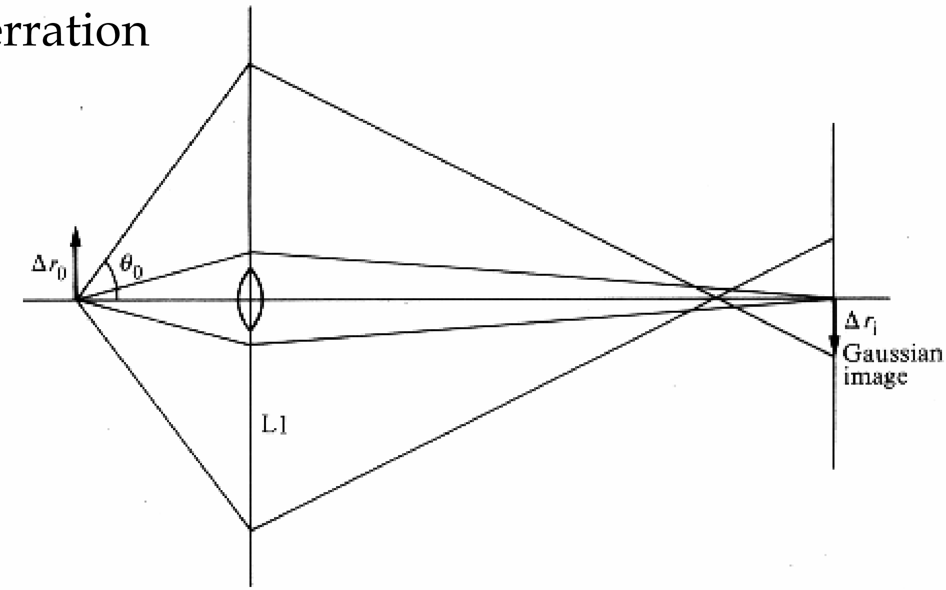
$$\psi_{object}(x,y) = \psi_{exit}(x,y) * \exp\left(\frac{-i\pi(x^2+y^2)}{\lambda\Delta f}\right)$$

$$\psi_{back\_focal}(u,v) = \mathcal{F}\{\psi_{exit}(x,y)\}\mathcal{F}\left\{\exp\left(\frac{-i\pi(x^2+y^2)}{\lambda\Delta f}\right)\right\}$$

$$\mathcal{F}\left\{\exp\left(\frac{-i\pi(x^2+y^2)}{\lambda\Delta f}\right)\right\} = \exp\{i\pi\lambda\Delta f(u^2+v^2)\} = \exp\{i\pi\lambda\Delta f\mathbf{H}^2\} = \exp(i\chi_1)$$

Defocus and aberrations

II Spherical aberration



$$\Delta r_0 = C_s \theta_0^{\,3}$$

C_s : Spherical aberration coefficient

Phase shift in back focal plane due to spherical aberration

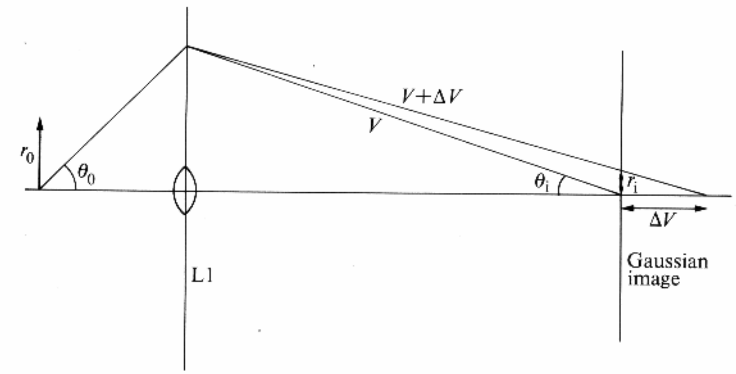
$$\chi_2 = \frac{1}{2}\pi C_s \lambda^3 (u^2 + v^2)^2 = \frac{1}{2}\pi C_s \lambda^3 \mathbf{H}^4$$

Factor $\exp(i\chi_2)$

Defocus and aberrations

III Chromatic aberration

Faster electrons are brought to a focus beyond the Gaussian image plane.



- ♦ **Fluctuations of the acceleration voltage**
- ♦ **Fluctuation of lens current**

→ **Spread of focal length**

$$\Delta f = C_c\left(\frac{\Delta V_0}{V_0} - \frac{2\Delta I}{I}\right)$$

D: Standard deviation of Gaussian distribution due to the chromatic aberration

Envelope in back focal plane $\exp(-\chi_3)$

$$\chi_3 = \frac{1}{2}\pi^2\lambda^2 D^2 \mathbf{H}^2$$

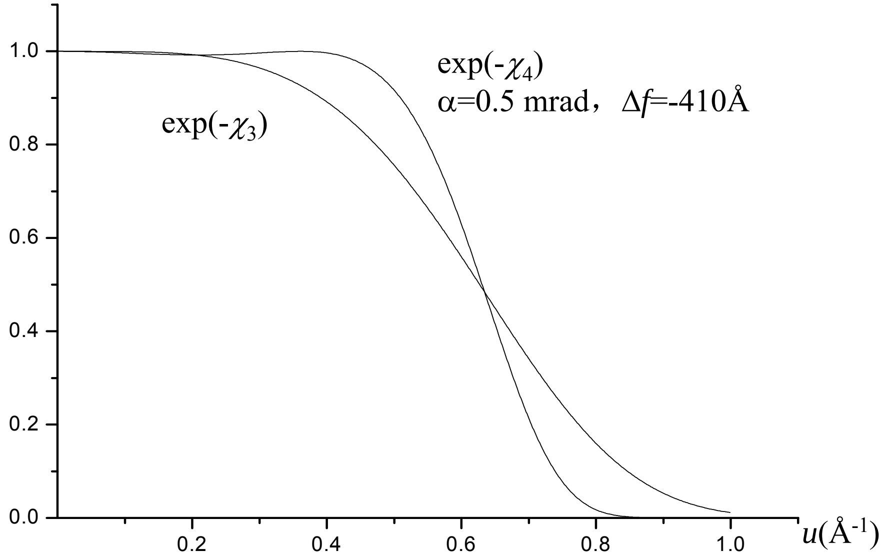
IV Beam divergence

Paralell incident beam (ideal condition)
Divergence angle α~ 0.5 mrad (real condition)

Envelope in back focal plane

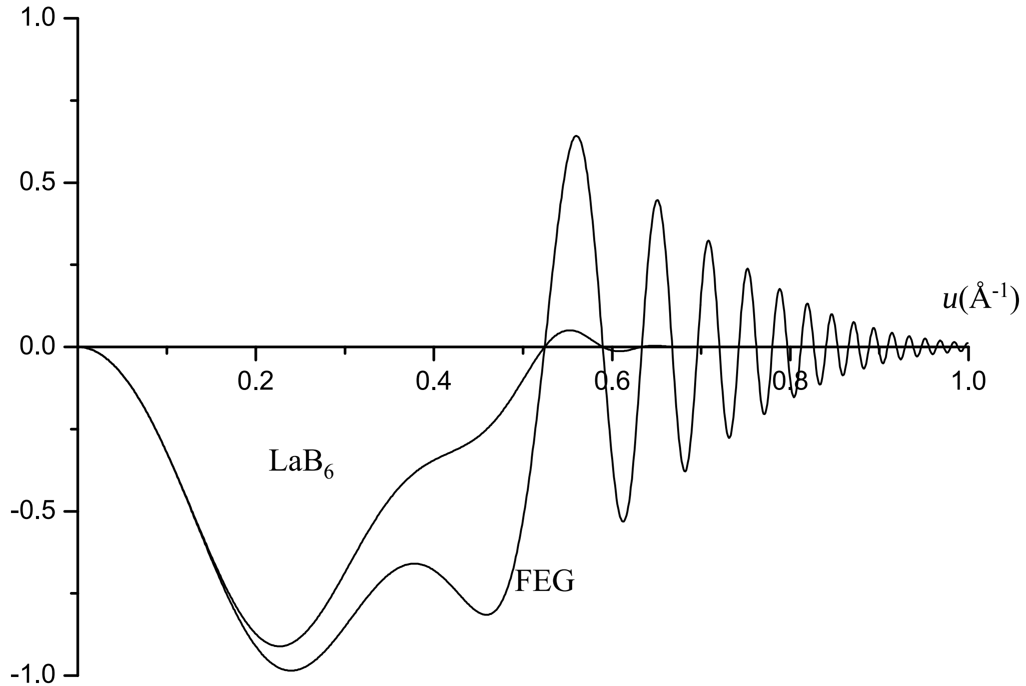
$$\exp(-\chi_4)$$

$$\chi_4 = \pi^2 \alpha^2 \mathbf{H}^2 (C_s \lambda^2 \mathbf{H}^2 + \Delta f)^2$$

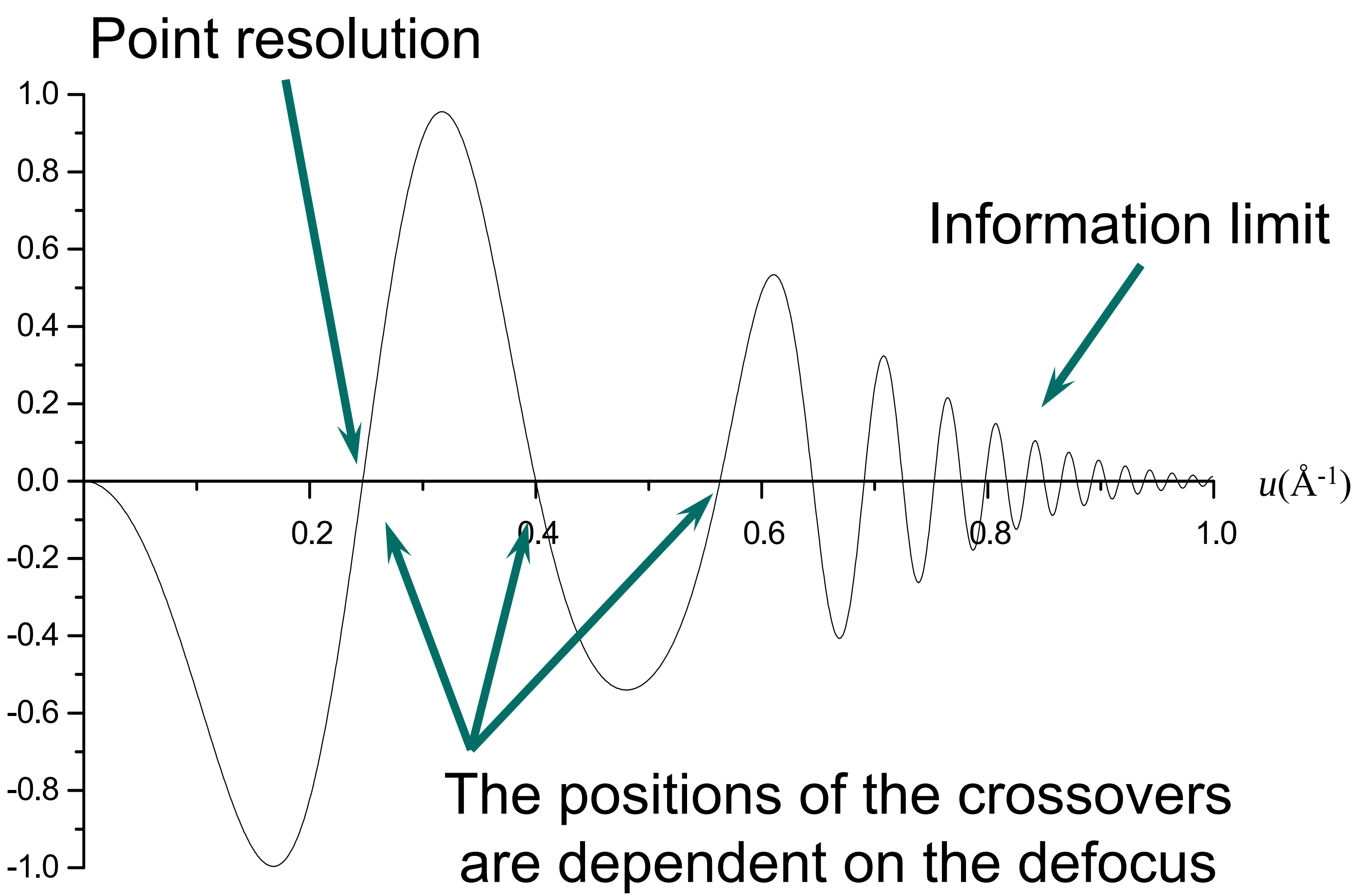


Contrast Transfer Function (CTF)

The CTF is the collection of effects due to defocus and aberrations:



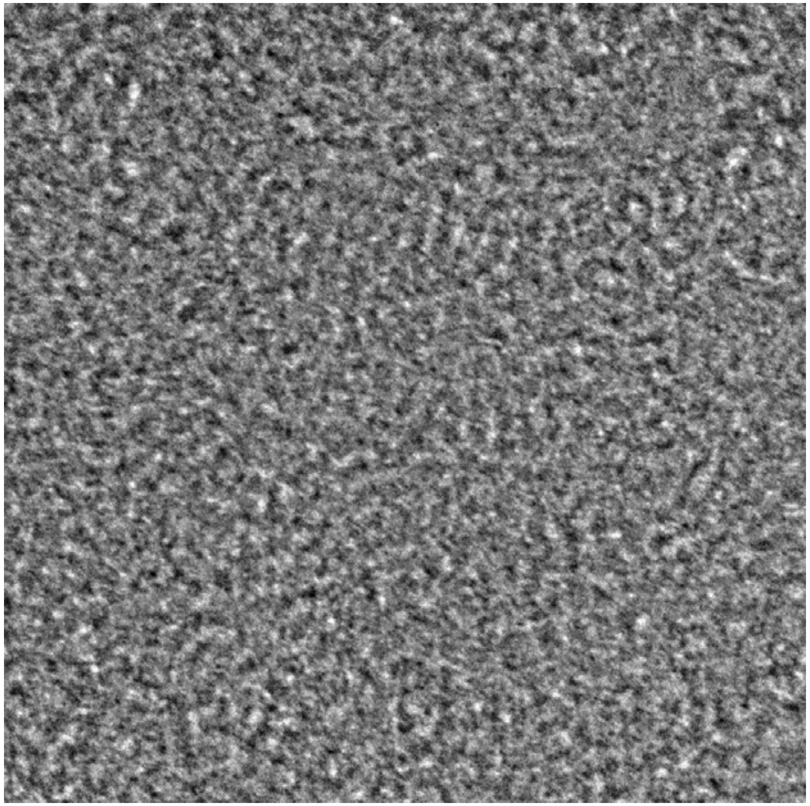
CTF Terms



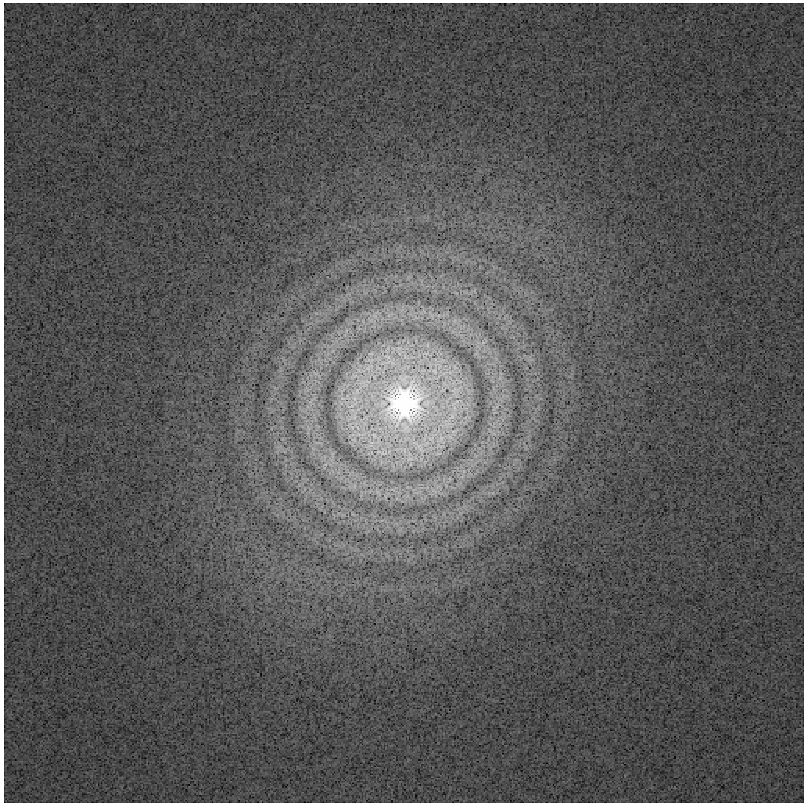
Point resolution
Information limit
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
0.2
0.4
0.6
0.8
1.0
u(Å-1)
The positions of the crossovers
are dependent on the defocus

Picturing the Contrast Transfer Function

Amorphous Thin Carbon Film



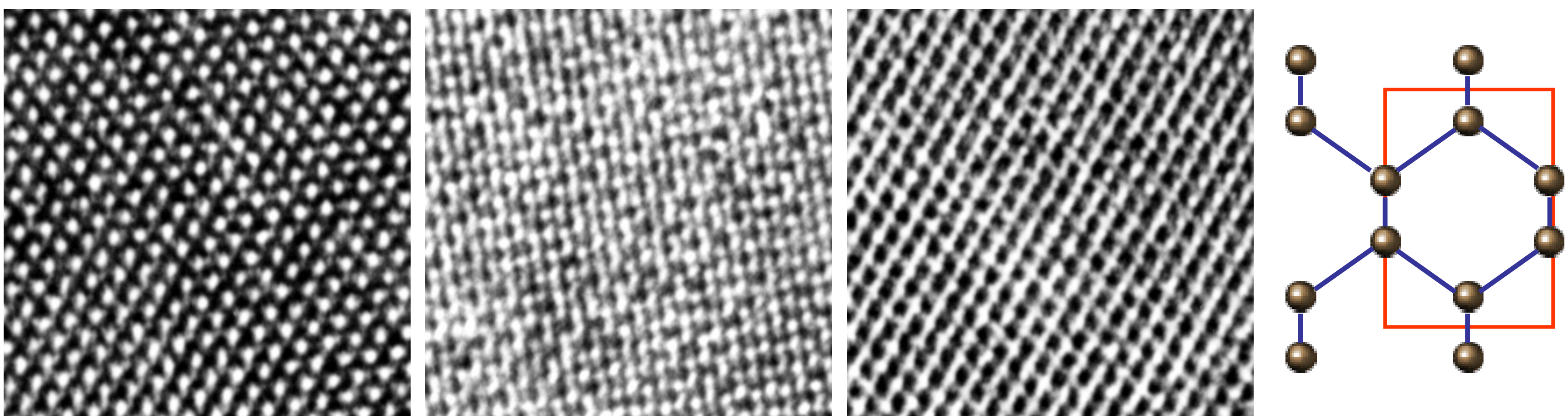
Real Space



Reciprocal Space

Image interpretation

! Only for thin crystal (WPOA) and the focus value close to Scherzer focus, the contrast of HREM image can be interprated as crystal structure up to point resolution.
In general, the black or white dots in HREM image DO NOT correspond to atoms or atom groups. !



Si [110] image by JEM-2010 FEG electron microscope with different defocus values

Structure determination

- Go back from image(s) to structure

Through-focus images → Exit wave → Structure

Deconvolution method → Projected potential $\varphi(x,y)$

Thin crystal and defocus value can be obtained

- Image simulation and matching

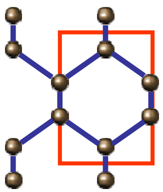
Initial model

Experimental image

Image simulation

Modified model

Simulated HRTEM images



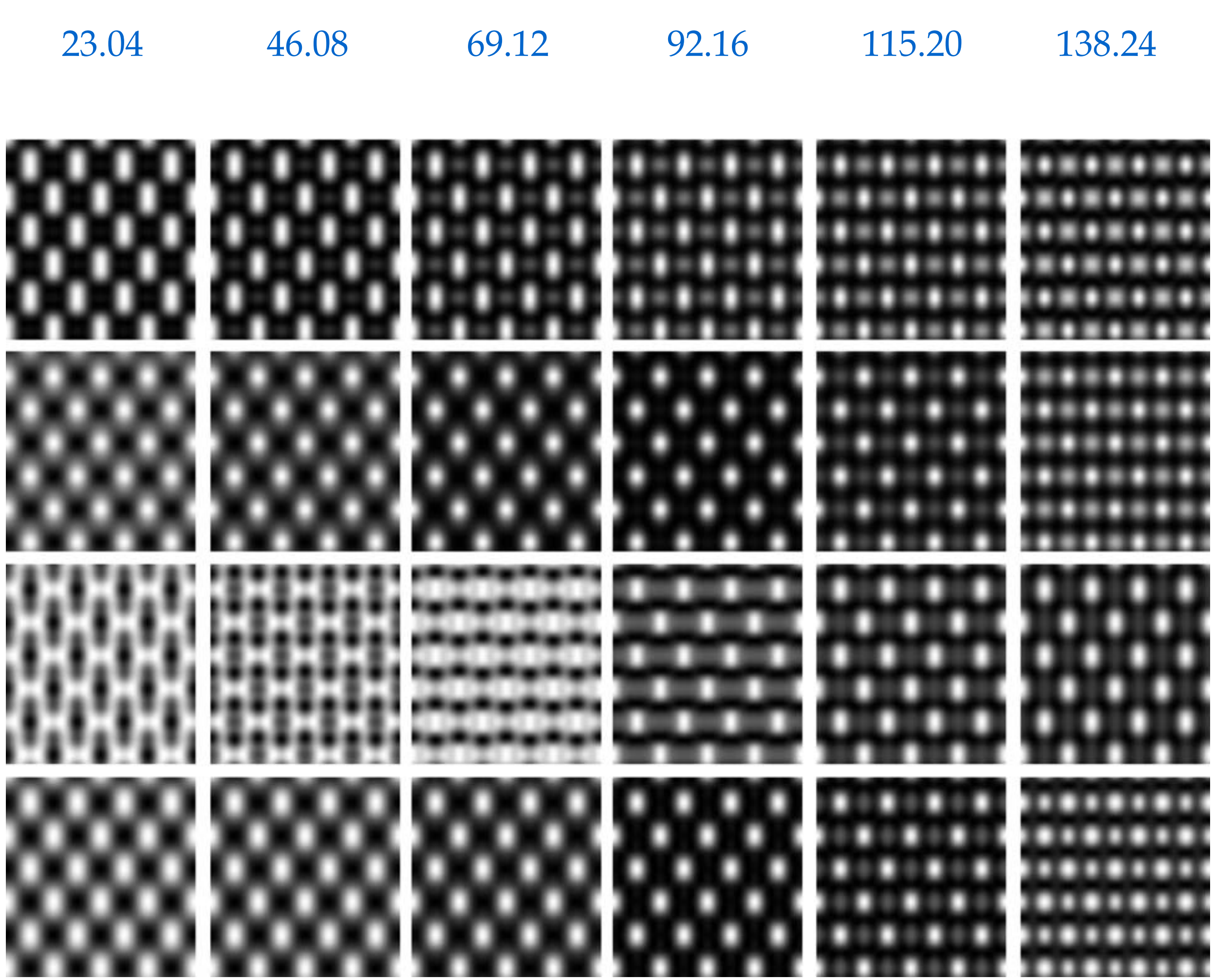


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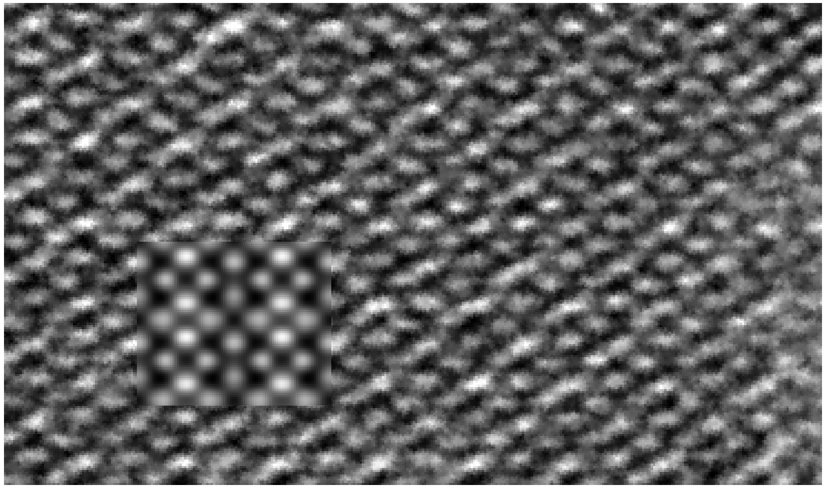
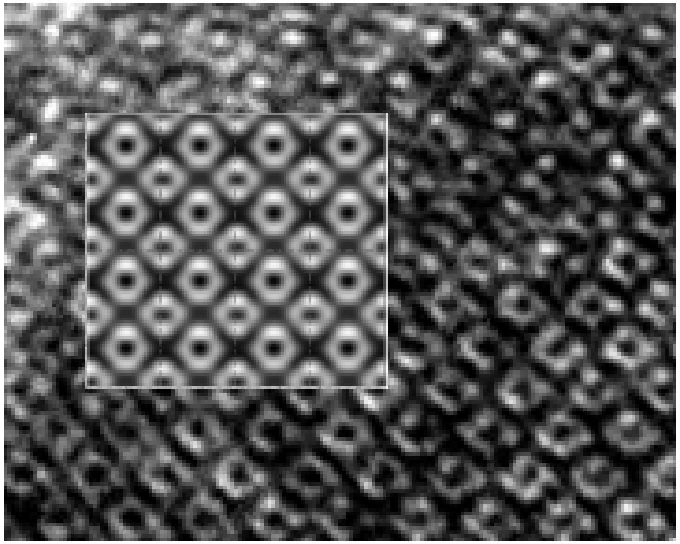
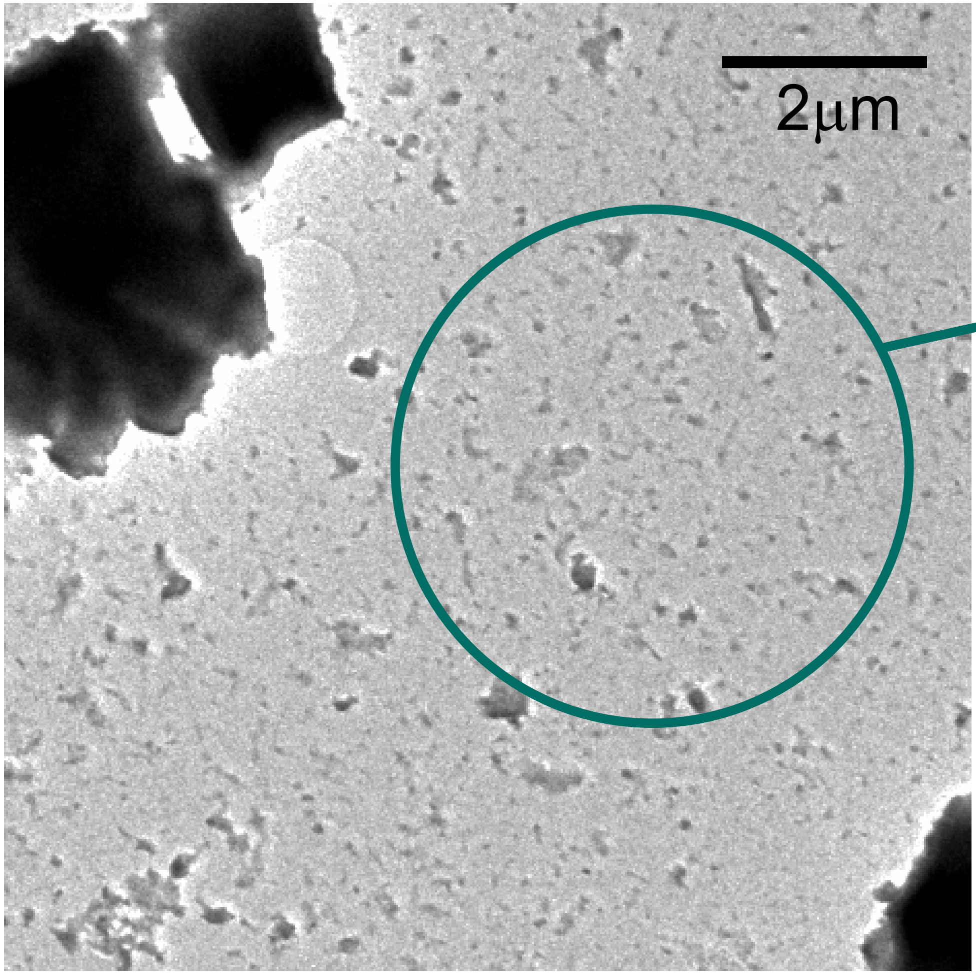
Image contrast matching





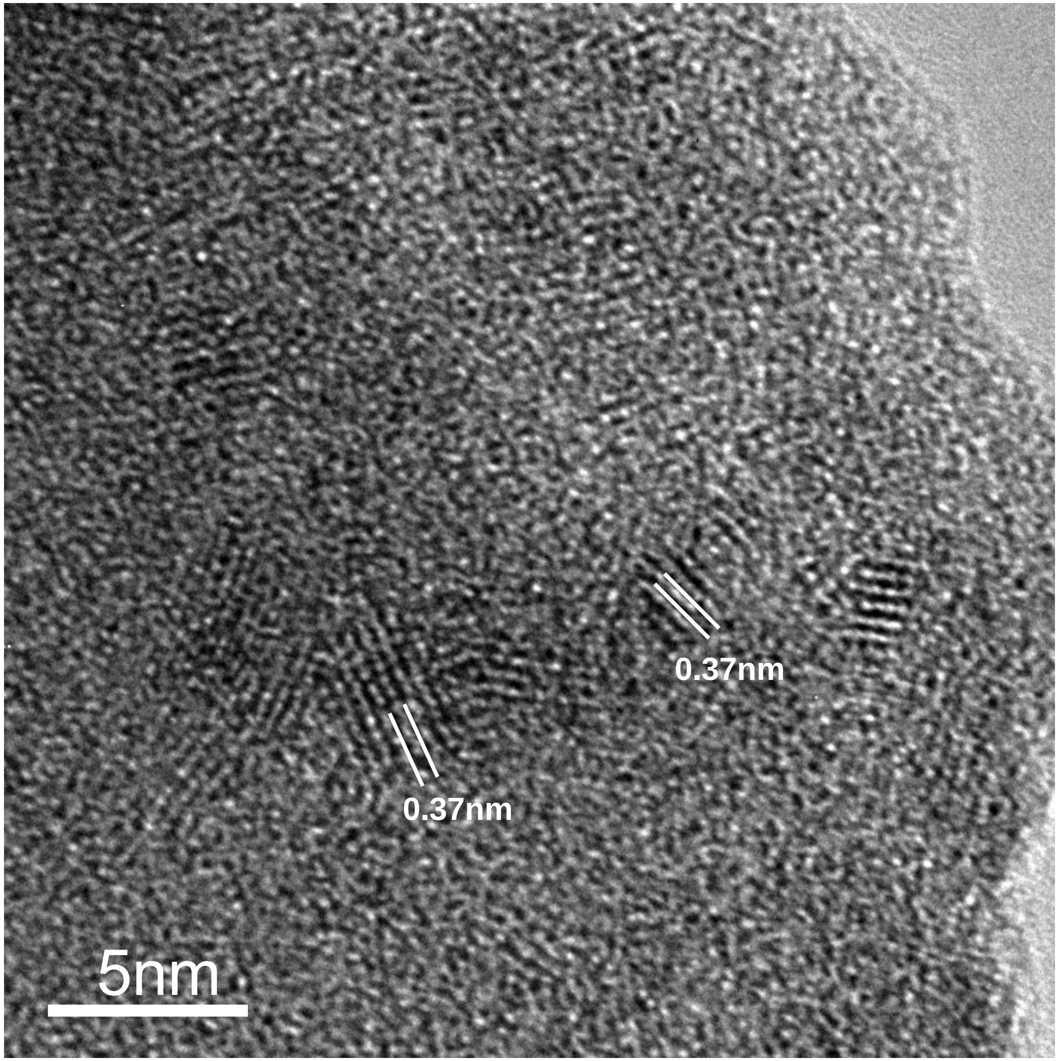
Imaging the catalyst



Mo oxide

Suitable size/thickness for lattice fringe imaging

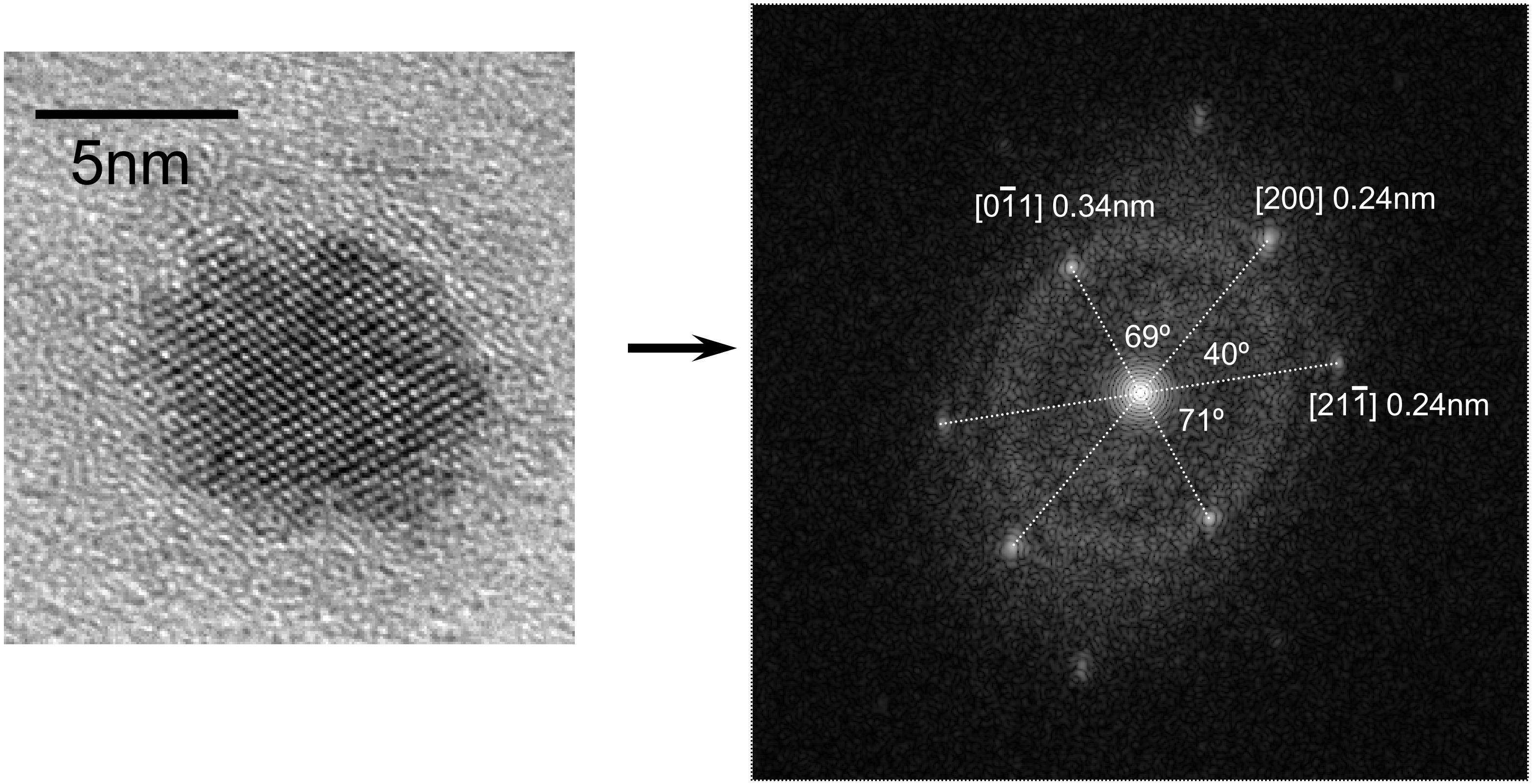
Imaging the catalyst



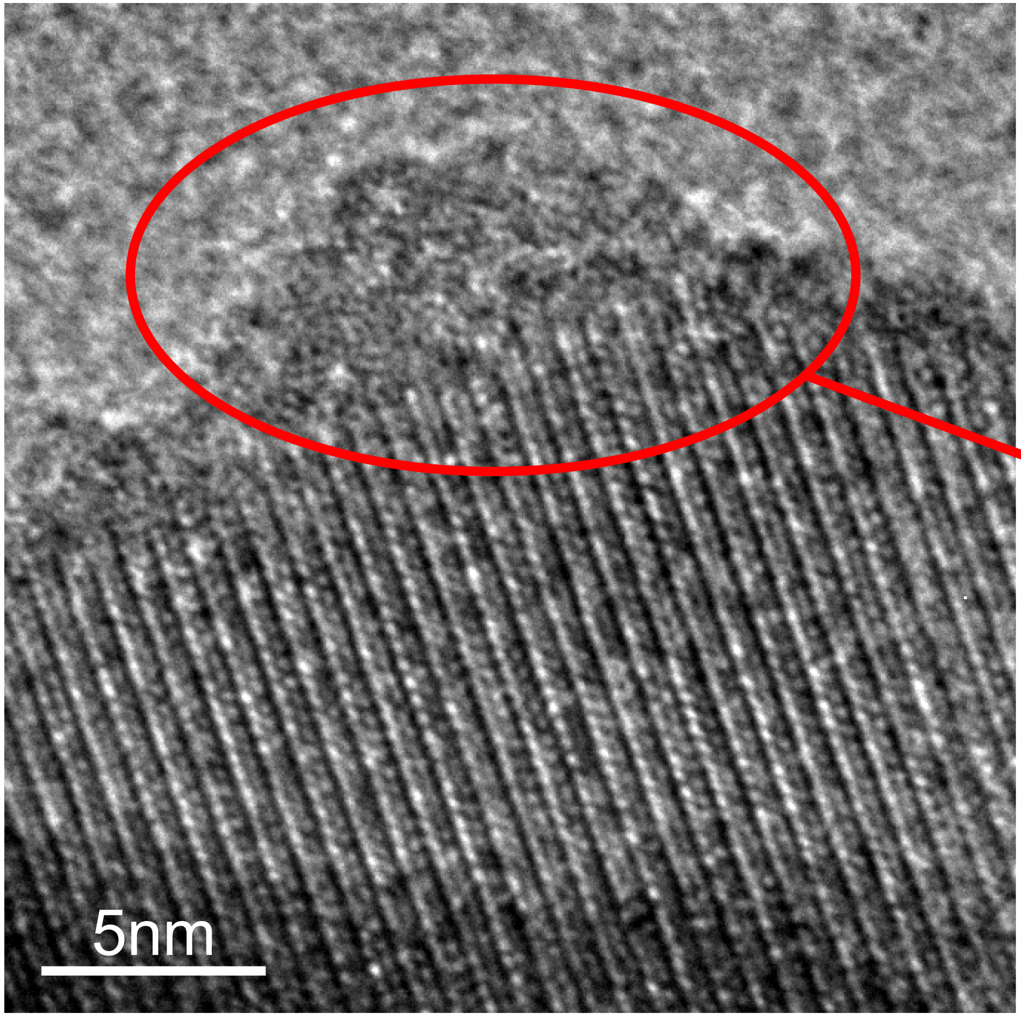
- Crystals embedded in non-crystalline material
- Lattice plane spacing are in general not equal to atom distance

Imaging the catalyst

MoO_2 [011]

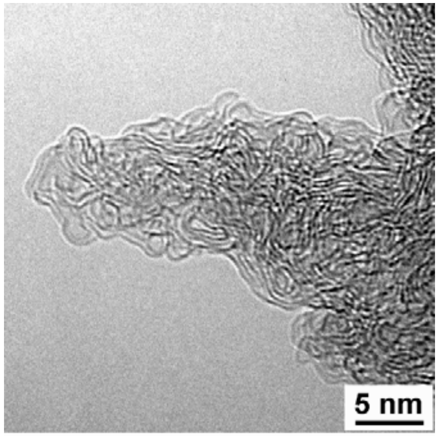


Imaging the catalyst

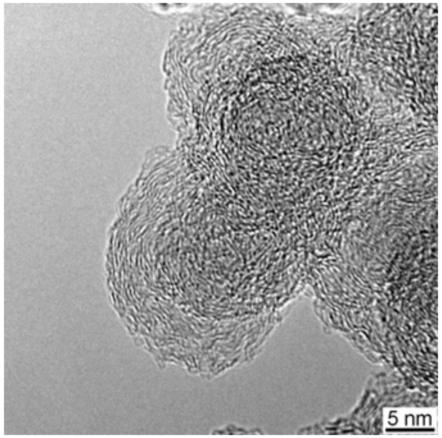


Surface decoration

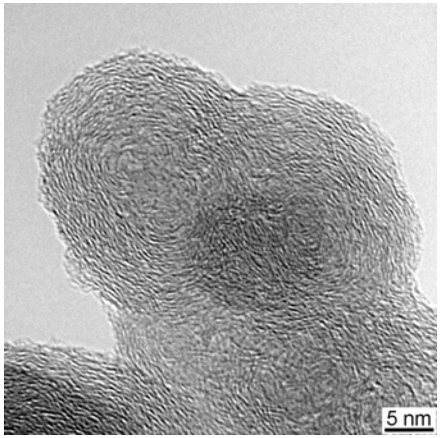
Imaging…



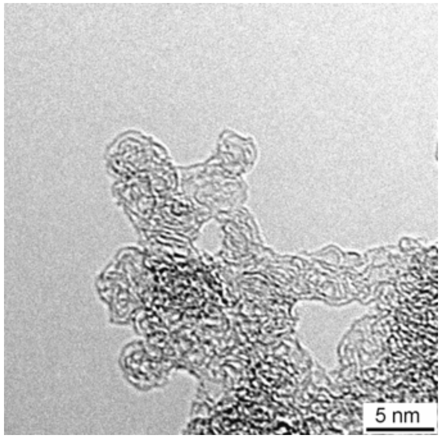
Synthesized Graphene Ribbons



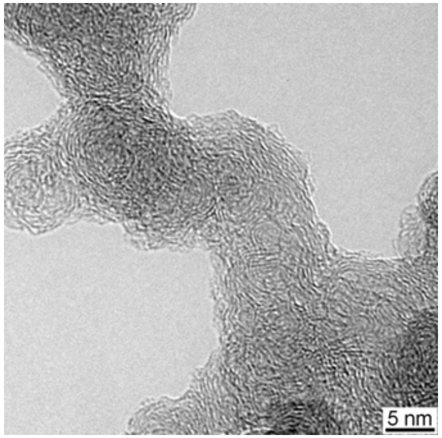
Furnace Soot

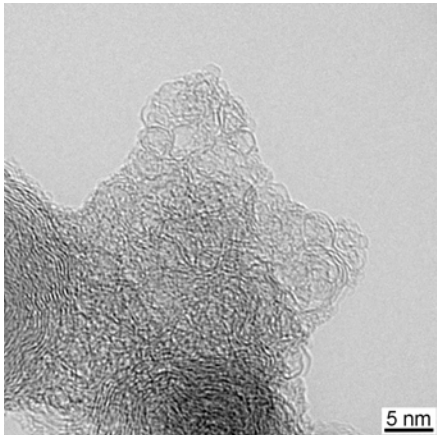


Black Smoke



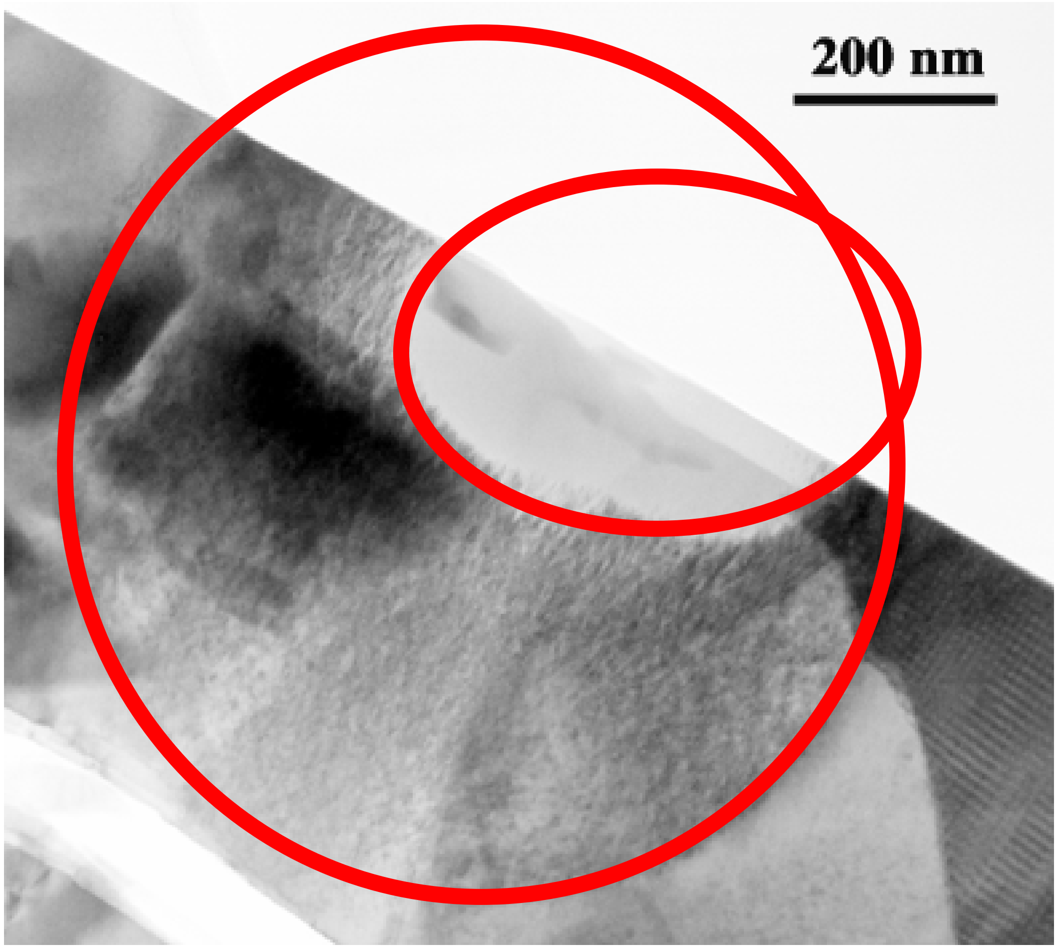
Sparc Discharge Soot





Euro IV Soot from Heavy Duty Diesel Engine

Radiation damage



Jakob B. Wagner, Microstructure, Dept. AC, Fritz-Haber-Institute (MPG), Berlin, Germany

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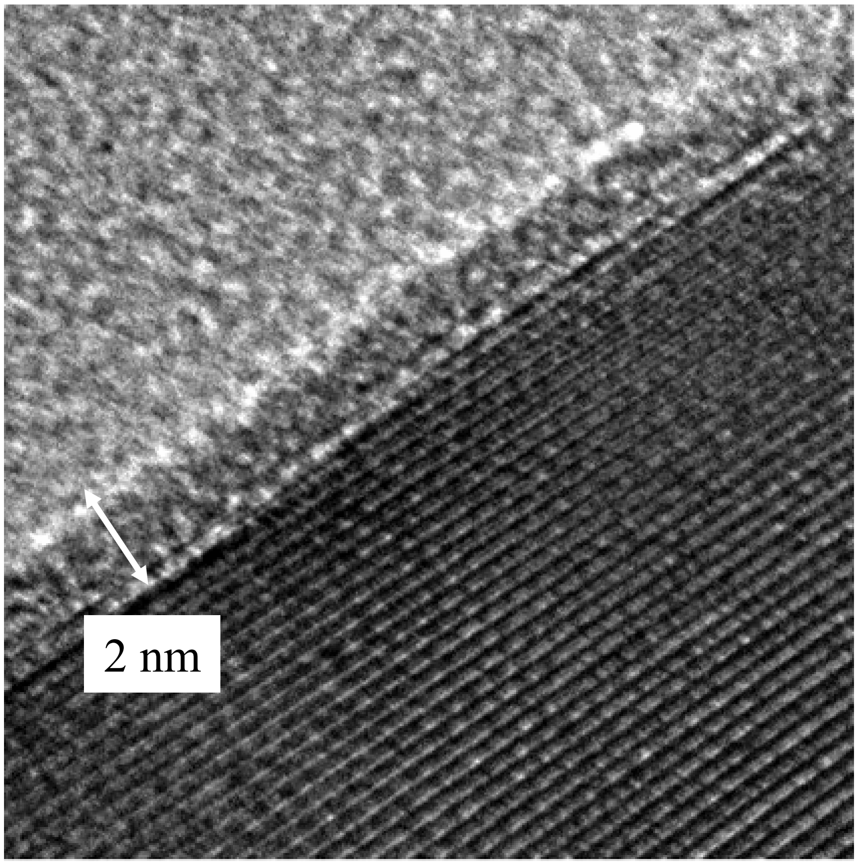
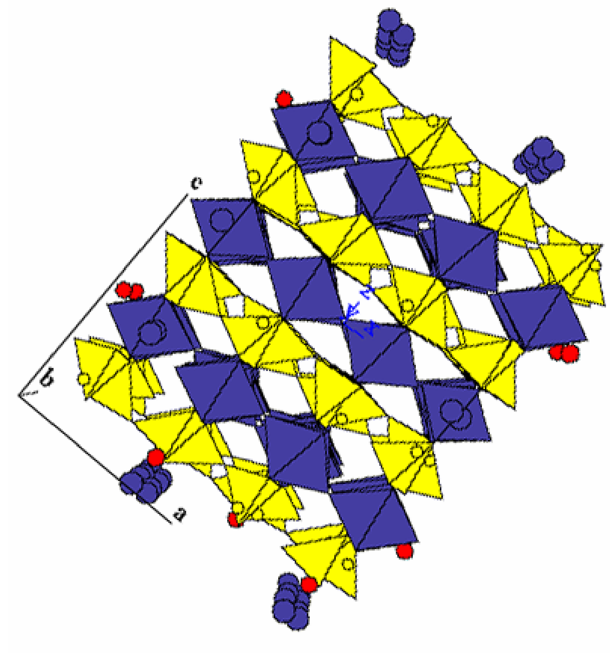
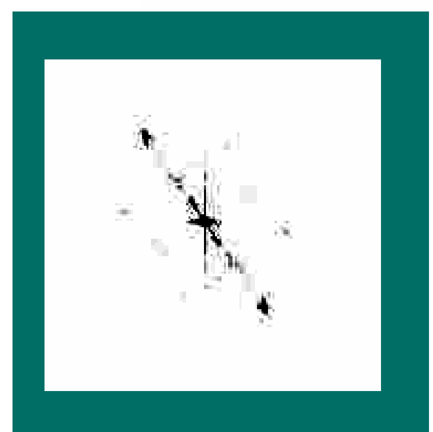
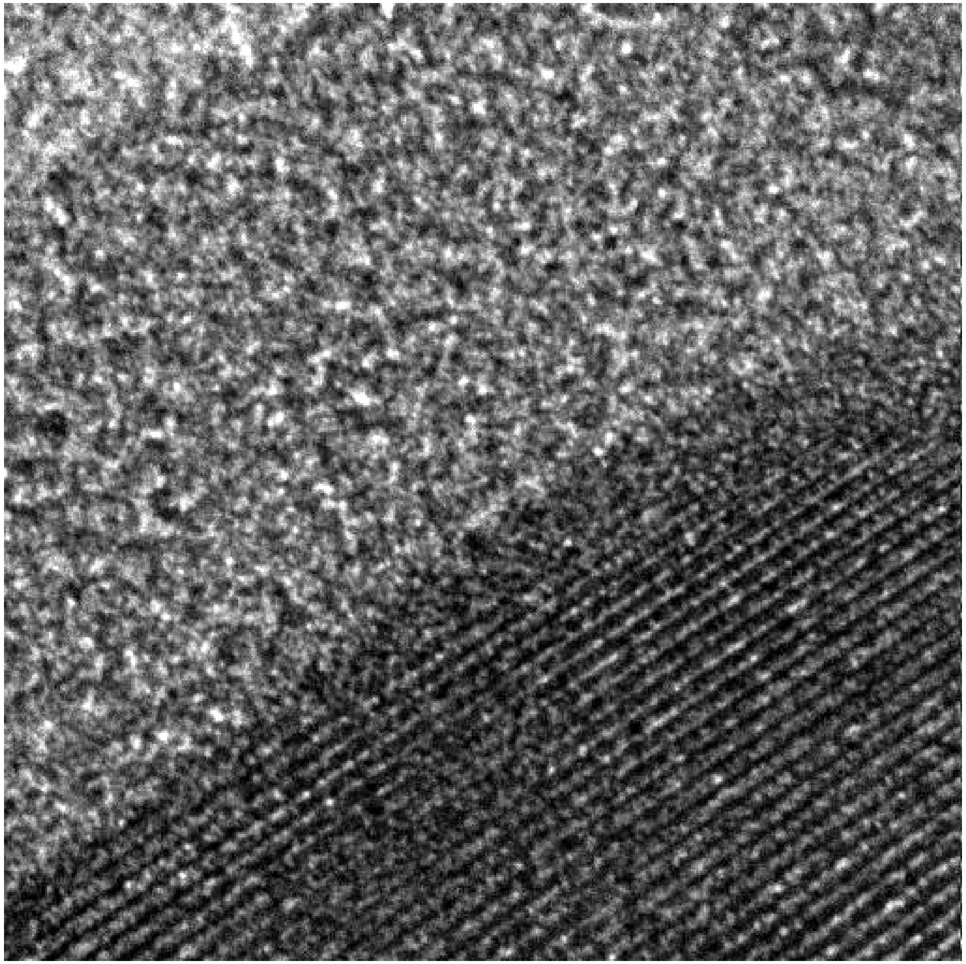






Radiation damage



Duration: 93 s

Why TEM and Electron diffraction?

TEM Morphology

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High-resolution imaging Defects, Interfaces, Surfaces

Electron diffraction Structure

Convergent-beam diffraction Symmetry, Strain
Lattice parameter

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For a 100-keV electron, $\lambda \sim 0.004$ nm

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Possible due to imperfect electron lenses !

The achievable resolution: < 0.15 nm

Electron diffraction

What can be extracted from electron diffraction?

- Orientation relationships
- Diffraction from small volumes
- Specimen thickness determination (however, only from 100nm and >)
- Symmetry determination
- Lattice parameters determination
- Structure factor determination

Selective area diffraction
Micro-diffraction
Convergent beam electron diffraction

The real space lattice

•The content of unit cell can be translated:

$\mathbf{r}_n = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$

n_i - integers

•A direction is given

$\mathbf{r}_{hkl} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c}$

•symmetry related directions

<hkl>

[001], [100], [010] = <100> etc (or <010>)

The reciprocal lattice

$\mathbf{a} \bullet \mathbf{b}^* = \mathbf{a} \bullet \mathbf{c}^* = \mathbf{b} \bullet \mathbf{a}^* = \mathbf{b} \bullet \mathbf{c}^* = \ldots = 0$

$\mathbf{a} \bullet \mathbf{a}^* = \mathbf{b} \bullet \mathbf{b}^* = \mathbf{c} \bullet \mathbf{c}^* = 1$

$|\mathbf{g}_{hkl}| = g_{hkl} = 1/d_{hkl}$

$\mathbf{g}_{hkl} \perp$ (hkl) planes

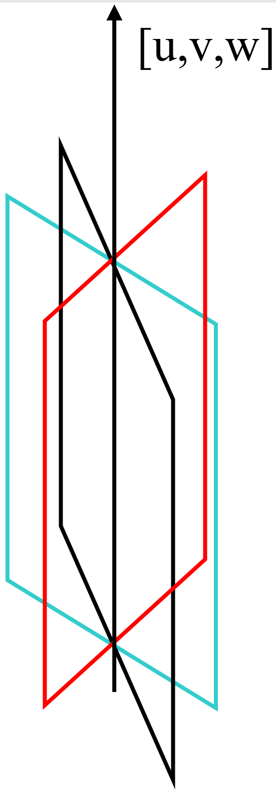
$$\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a}(\mathbf{b} \times \mathbf{c})} \qquad \mathbf{b}^* = \ldots$$

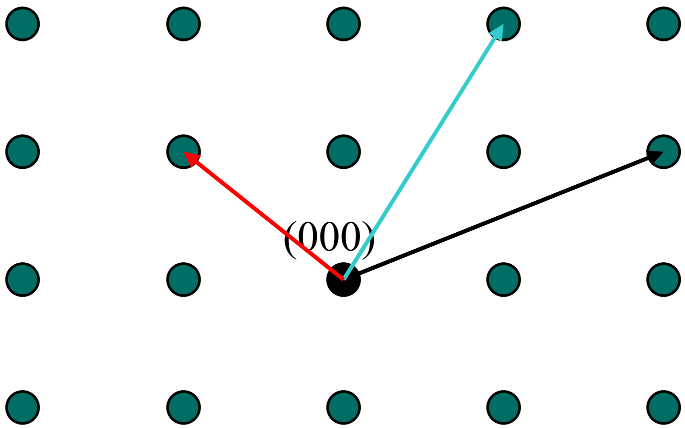
$$\mathbf{g}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$$

The reciprocal space is a standard coordinate system, just as real space

$$\mathbf{r}_{hkl} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c}$$

Zone axis

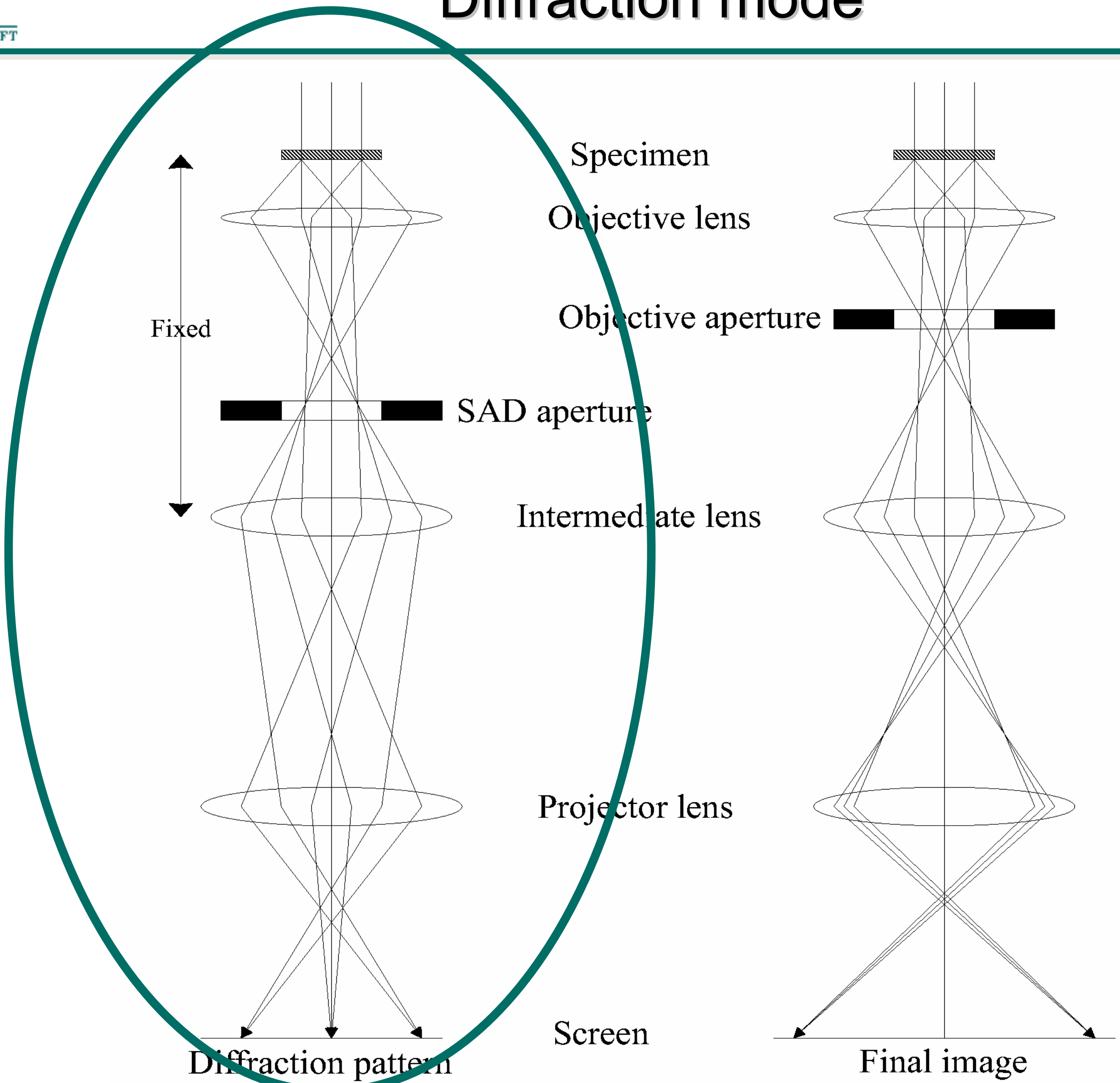




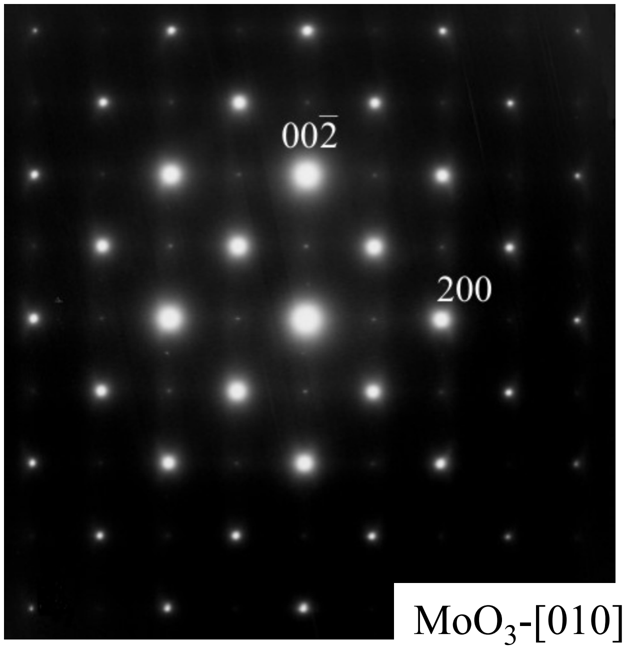
$$[u,v,w] \perp (h,k,l)$$

Example: cubic structure, (100), (110), (120), (340)…… planes belong to [001] zone axis

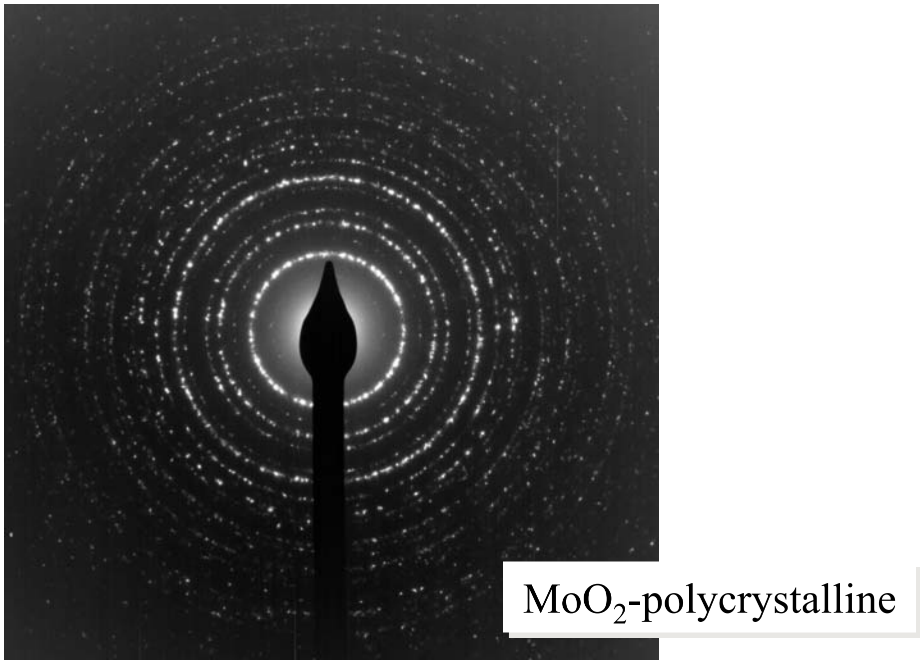
Diffraction mode



Diffraction patterns



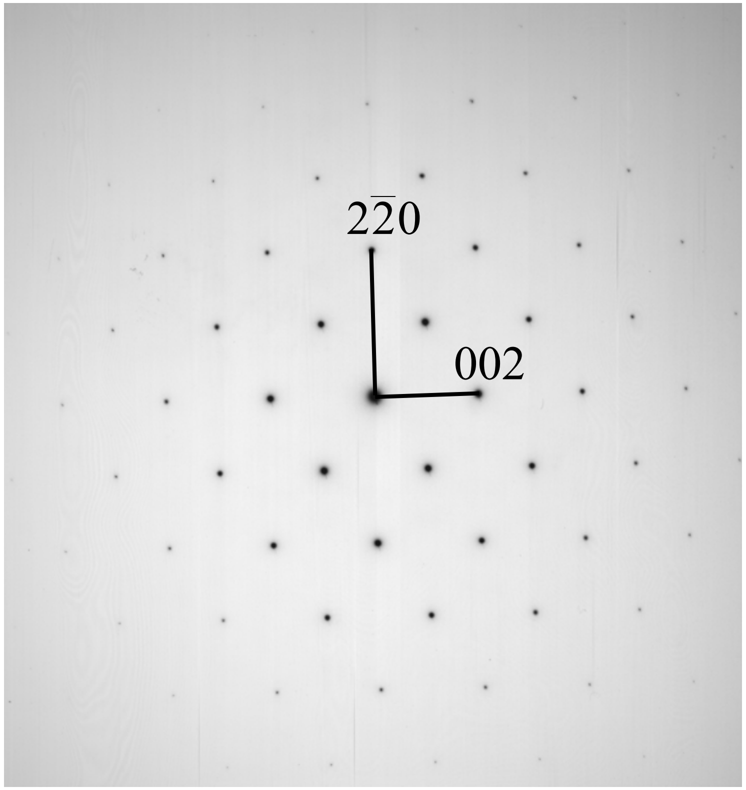
Single crystal



Polycrystalline material

Indexing of diffraction pattern

Single crystal pattern

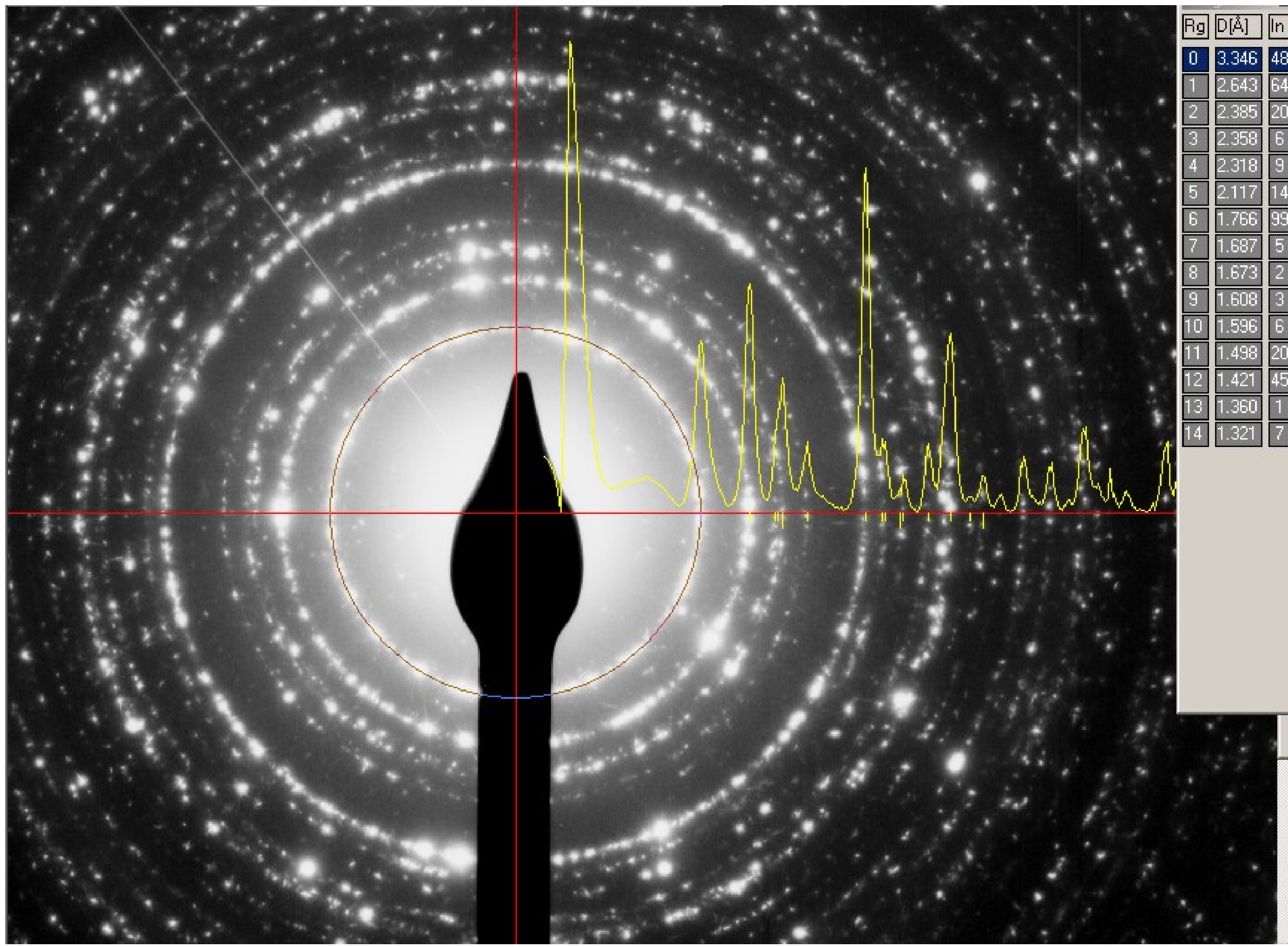


- Two sets of lattice planes and the angle in between
- Using extinction rules
- Using diffraction pattern on other zone axis
- Simulation

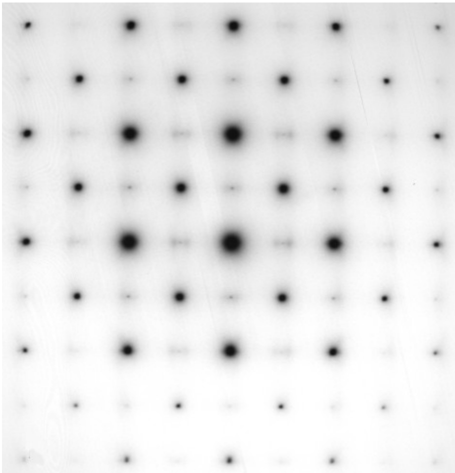
Cubic ZrO_2 (fluorite structure) on [110] projection

Indexing of diffraction pattern

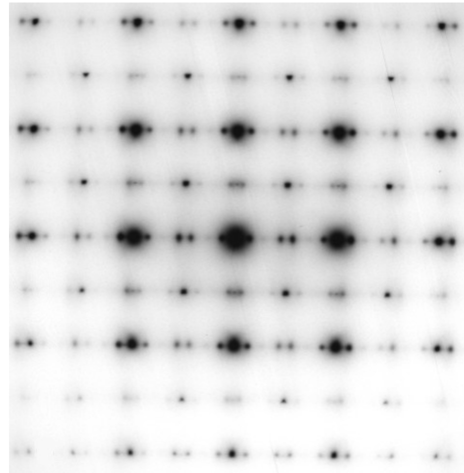
Ring pattern



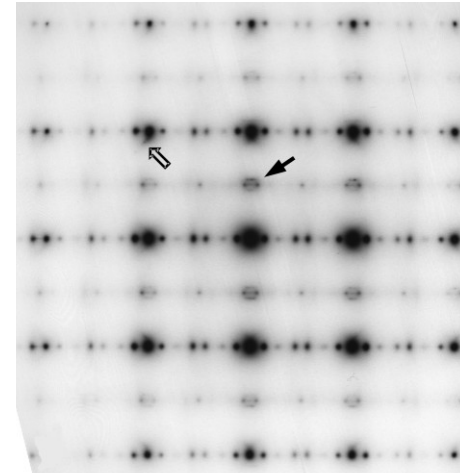
Structure development



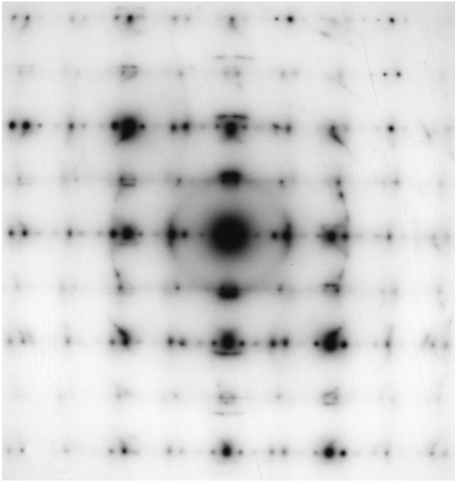
After irradiation of 10 min



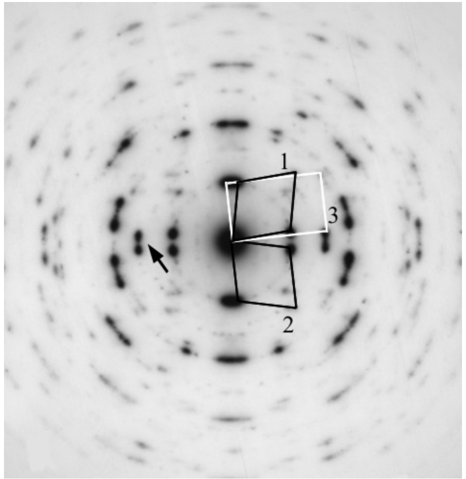
60 min



120 min



200 min



360 min

Frame 1 and 2: diffractions can be attributed to MoO_2 on [-111] projection.
Frame3: Diffractions can be attributed to MoO_2 on [-122] projection.

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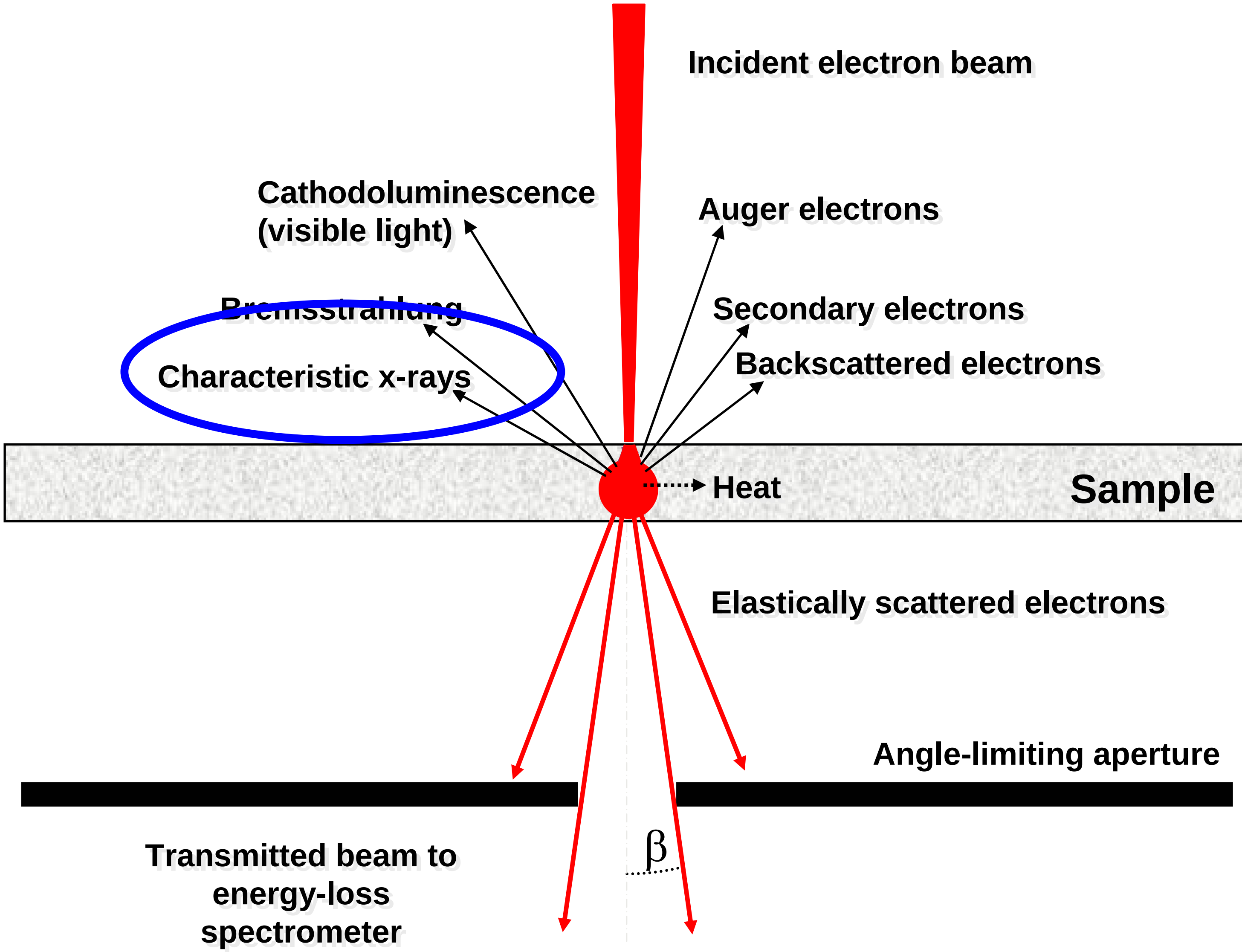
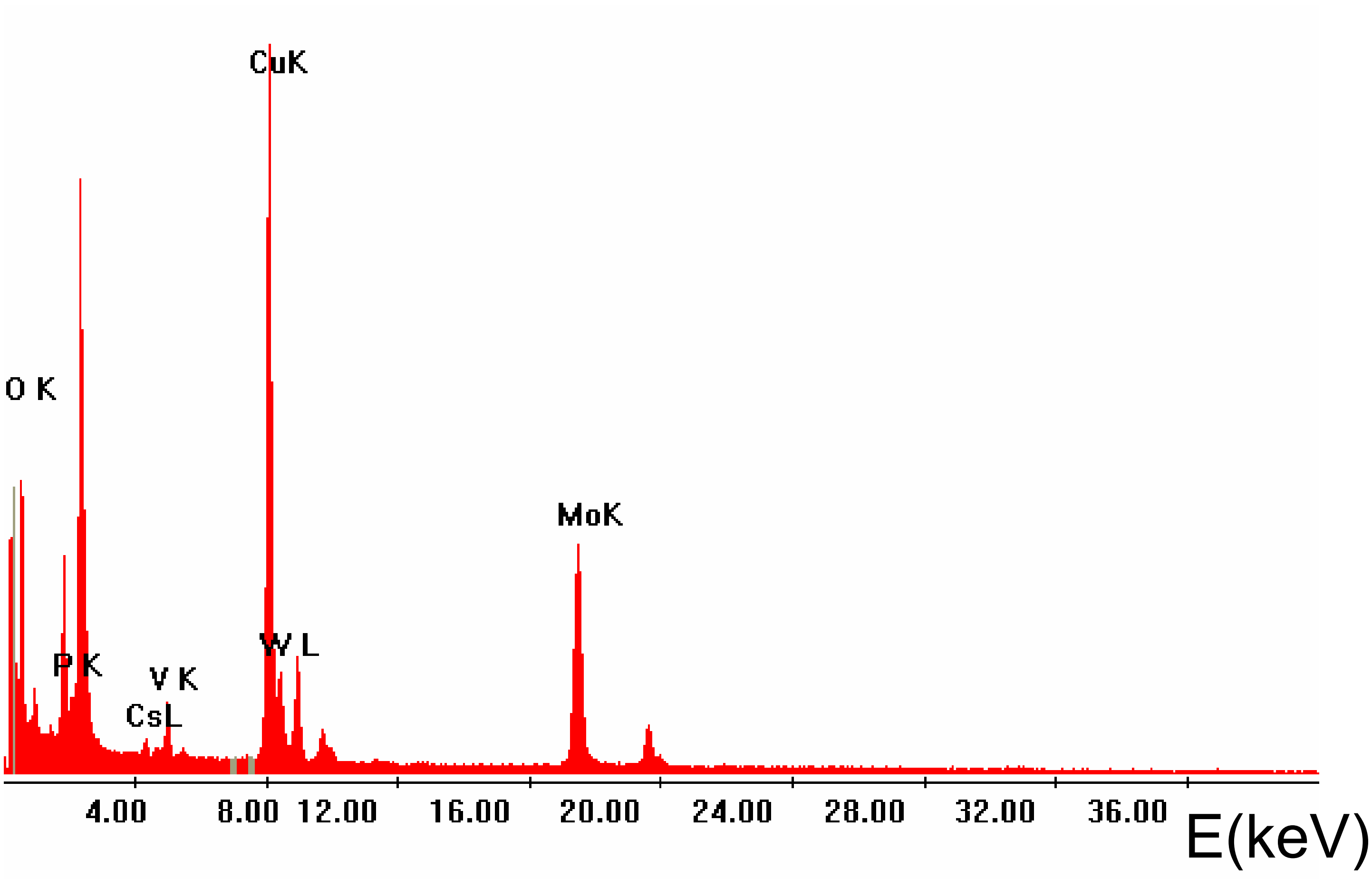
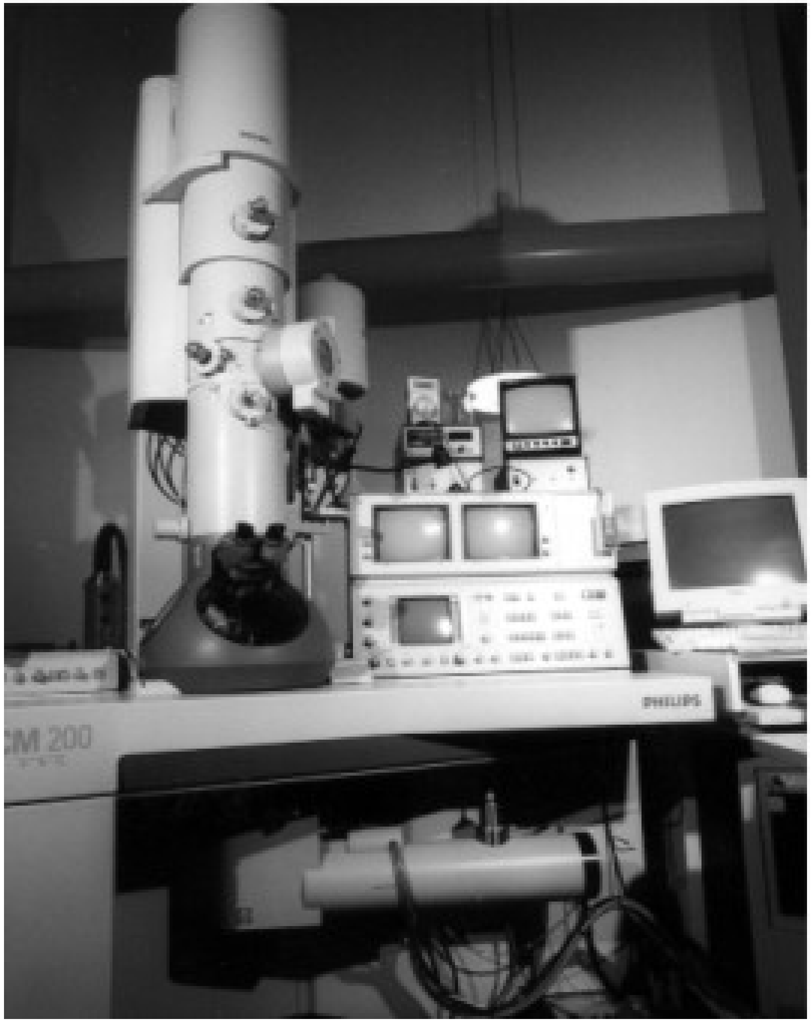
Electron-sample interactions

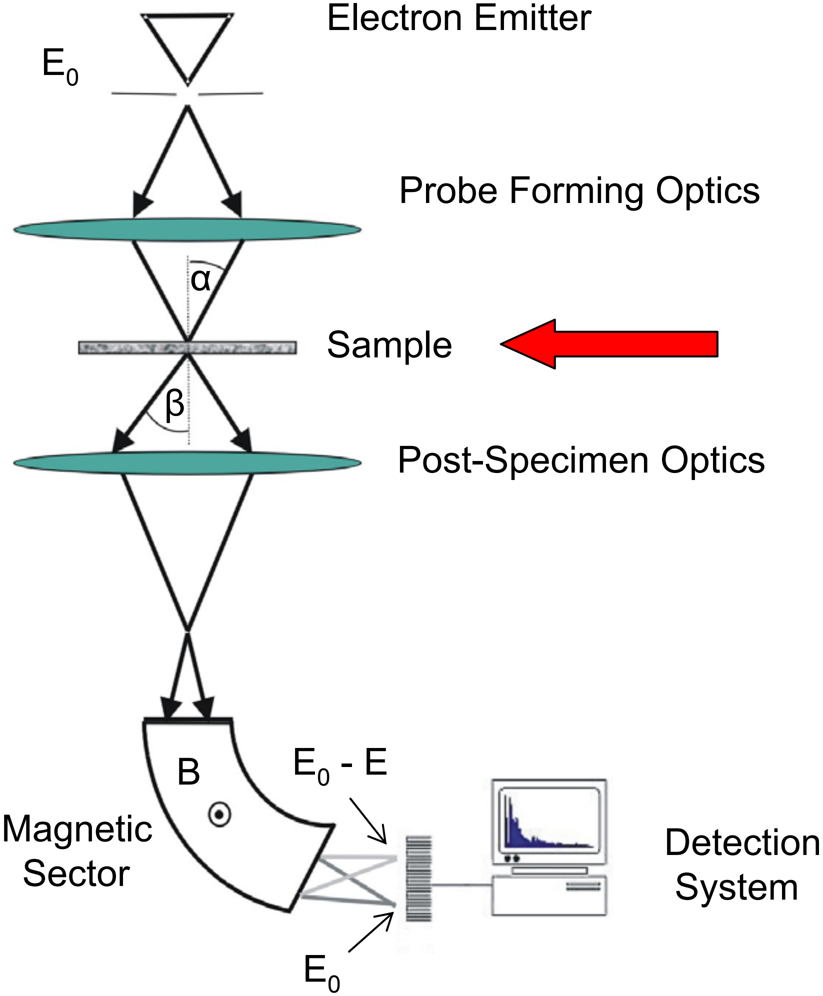


EDX – Energy-dispersive X-ray spectrometry



Electron Energy Loss Spectroscopy



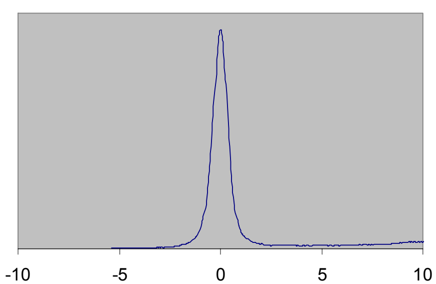


The energy loss spectrum

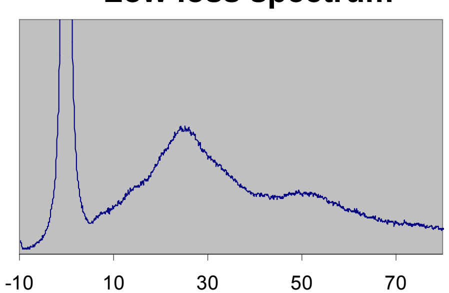
The EELS spectrum corresponds to the probability of an interaction over energy loss.
EELS measures the **double differential cross section** for inelastic scattering :

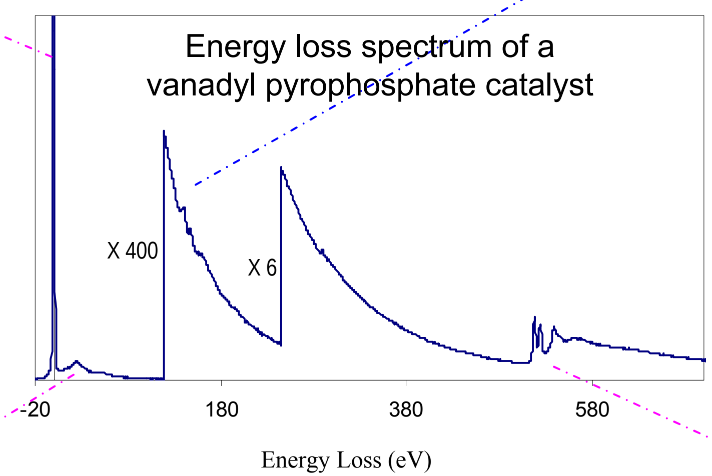
$$\frac{\partial^2 \sigma}{\partial E \partial \Omega}$$

Zero loss peak

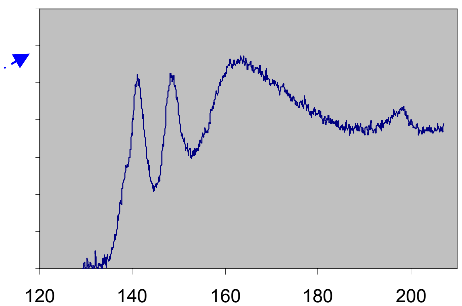


Low loss spectrum



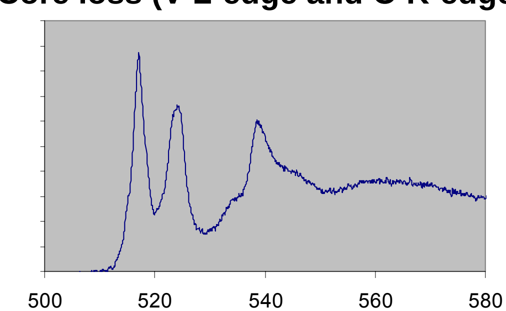


Core loss spectrum (L -edge)

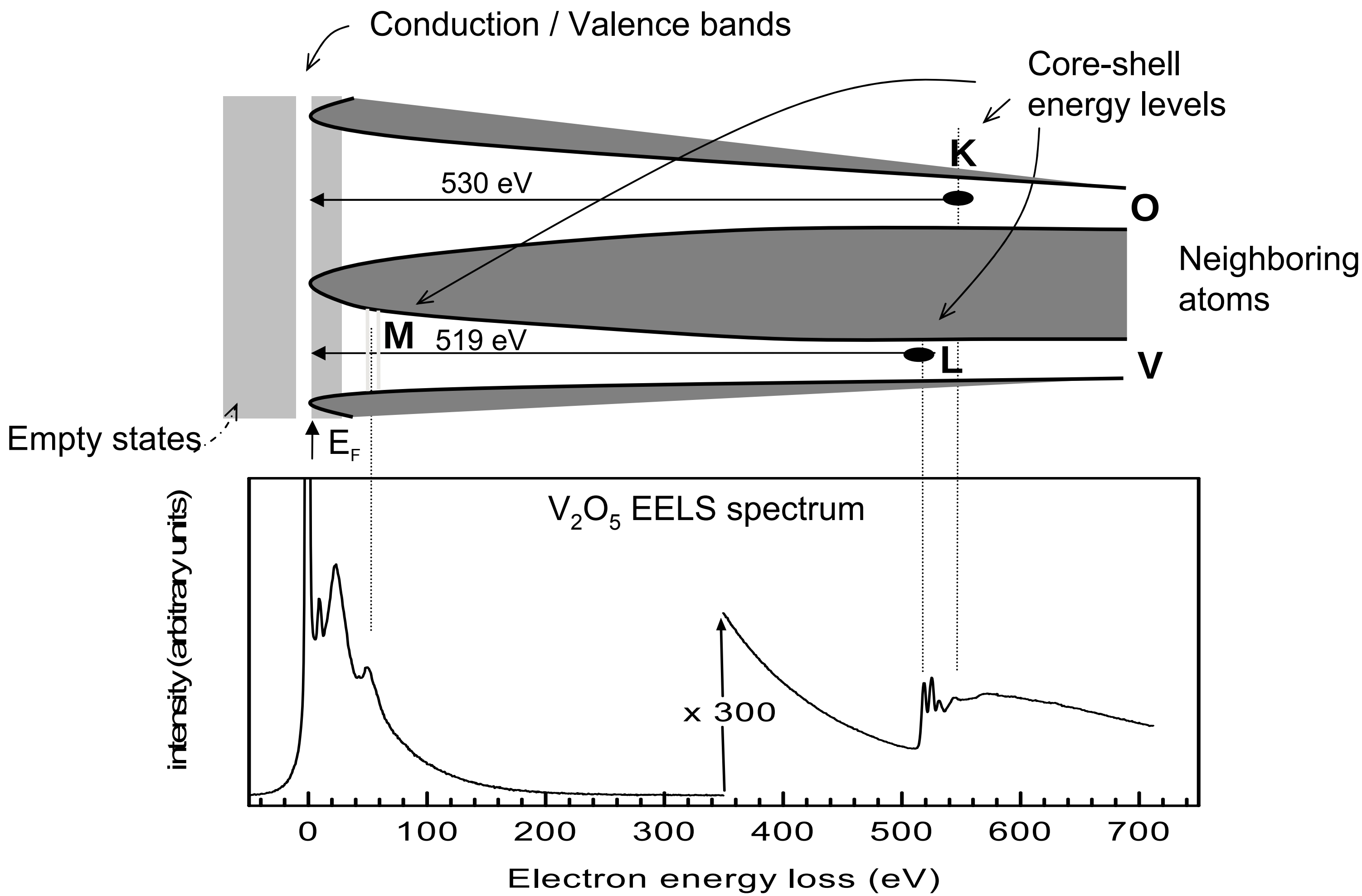


After spectrum processing

Core loss (V L-edge and O K-edge)

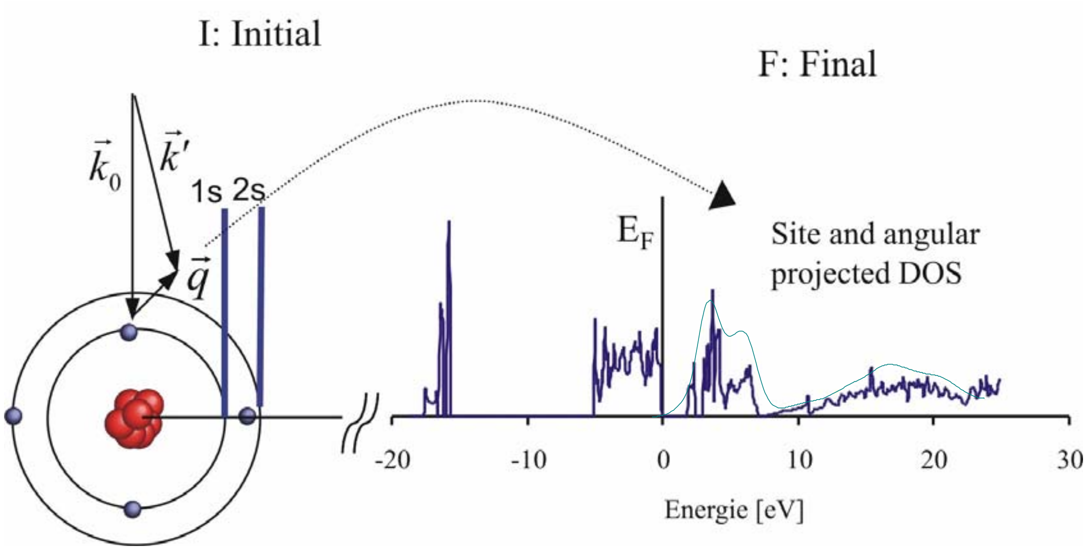


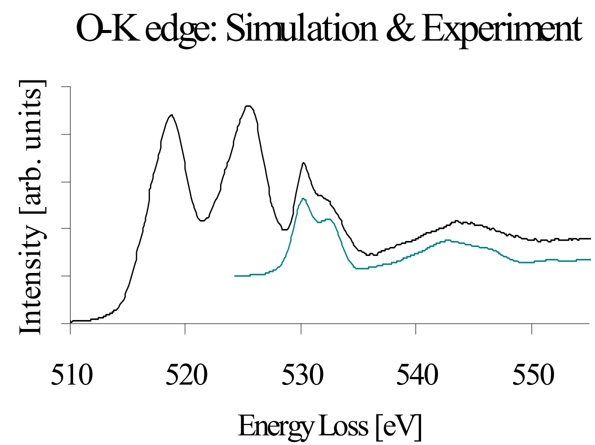
The energy loss spectrum



Energy Loss Near Edge Structure

Information about the Density of States





$$\frac{\partial^2 \sigma}{\partial \Omega \, \partial E} \propto \frac{1}{\vec{q}^{\,4}} \sum_F \sum_I \left| \left\langle I \left| e^{i\vec{q}\vec{R}_j} \right| F \right\rangle \right|^2 \delta\left(E - \left(E_F - E_I\right)\right)$$

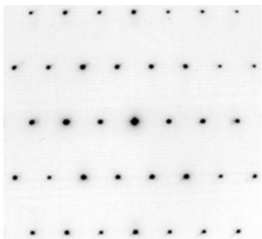
Matrix element term & density of states term (DOS)

Dipole Approximation &

Orthogonality of $|i\rangle, |f\rangle$: $\left\langle f \left| e^{i\vec{q}\vec{R}} \right| i \right\rangle \Rightarrow \left\langle f \left| i\vec{q}\vec{R} \right| i \right\rangle$

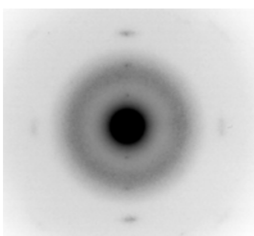
Matrix element equal to XAS

ELNES fingerprinting – vanadium oxides

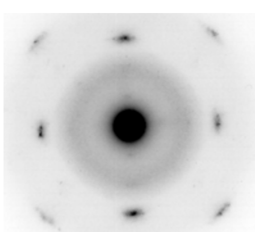


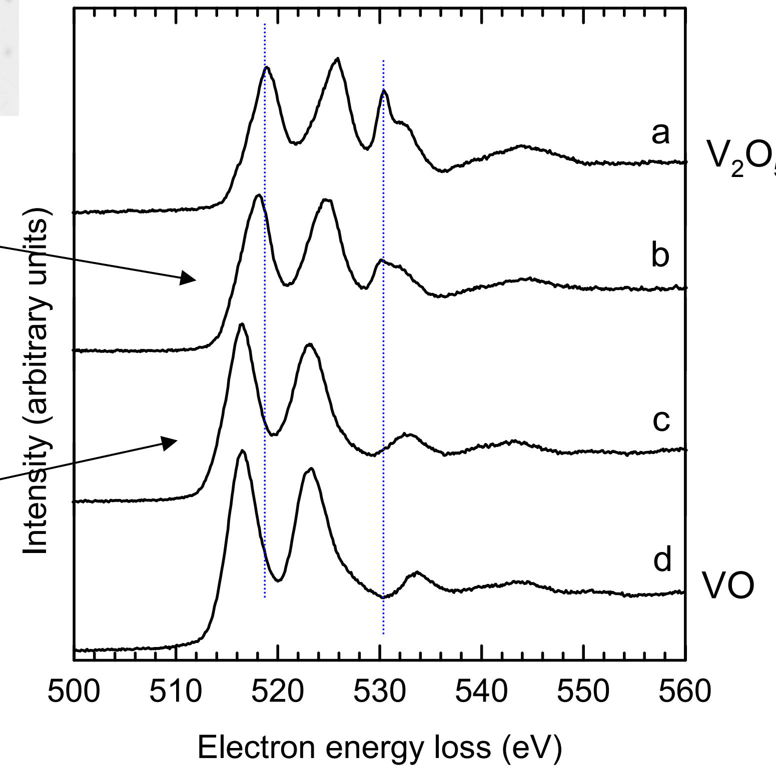
20 min irradiation
at room temperature

20 min irradiation
at 4 K

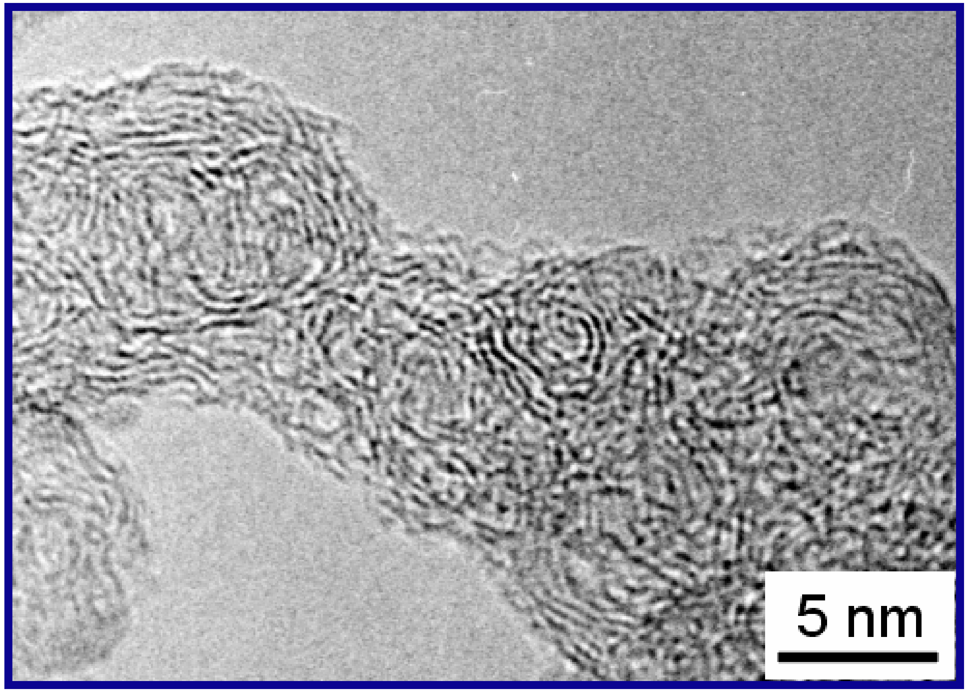


10 min irradiation
at room temperature

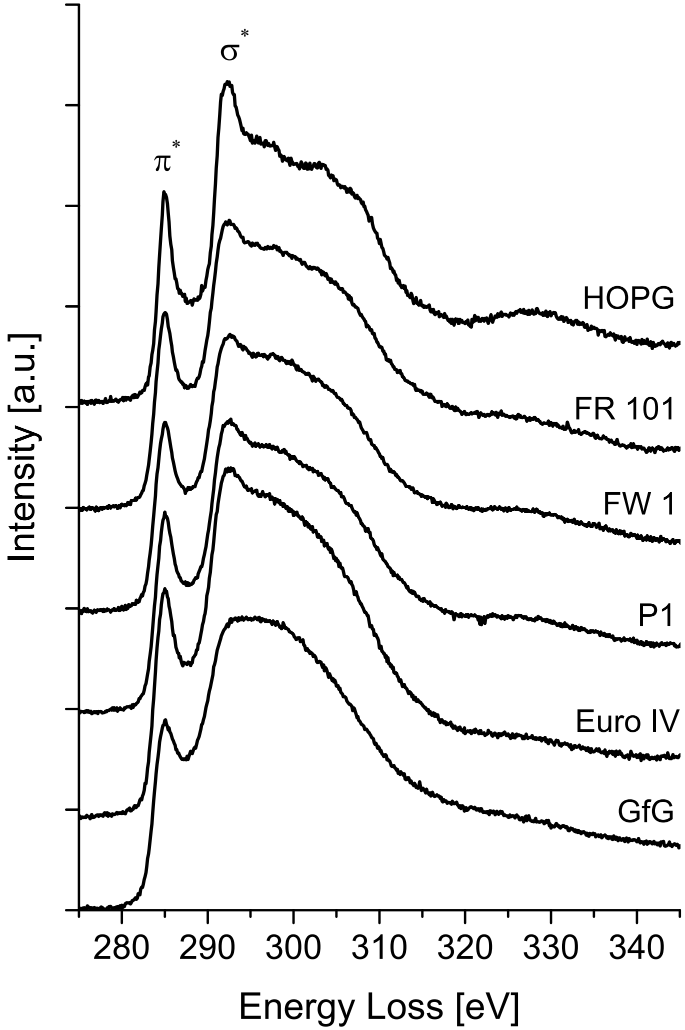




ELNES fingerprinting – soot, carbon black



Euro IV Diesel Engine Soot



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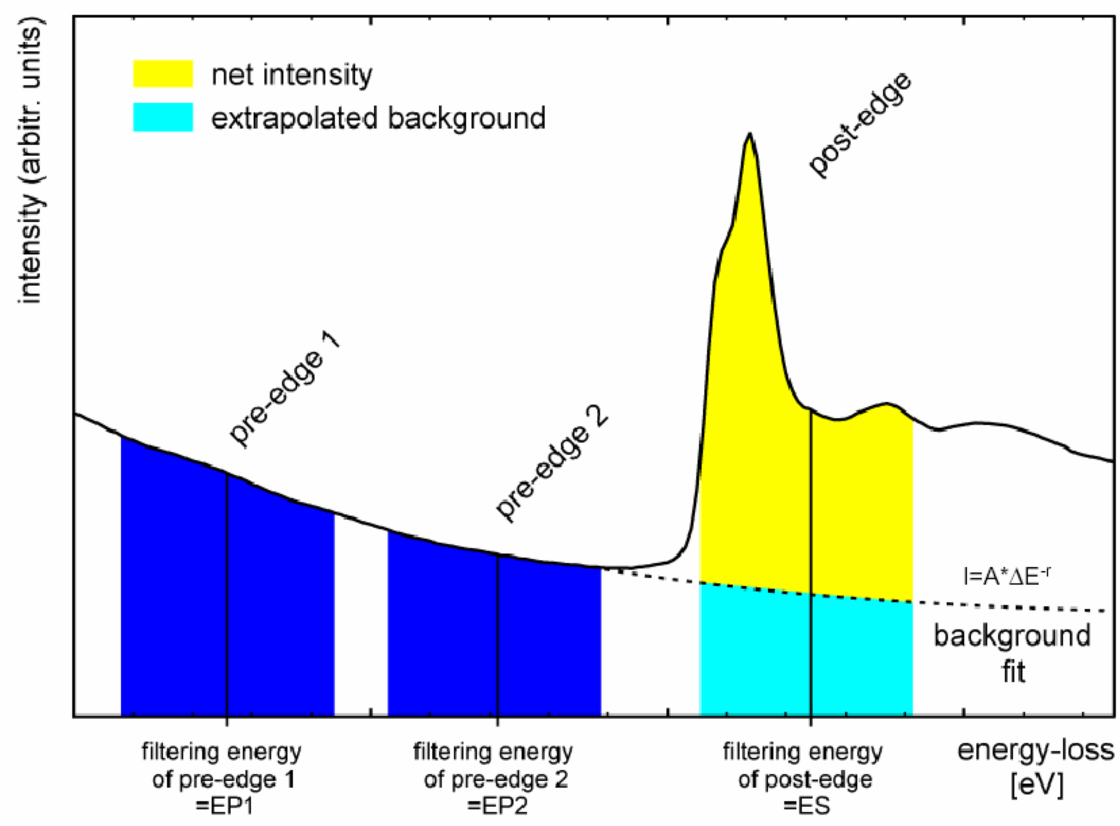
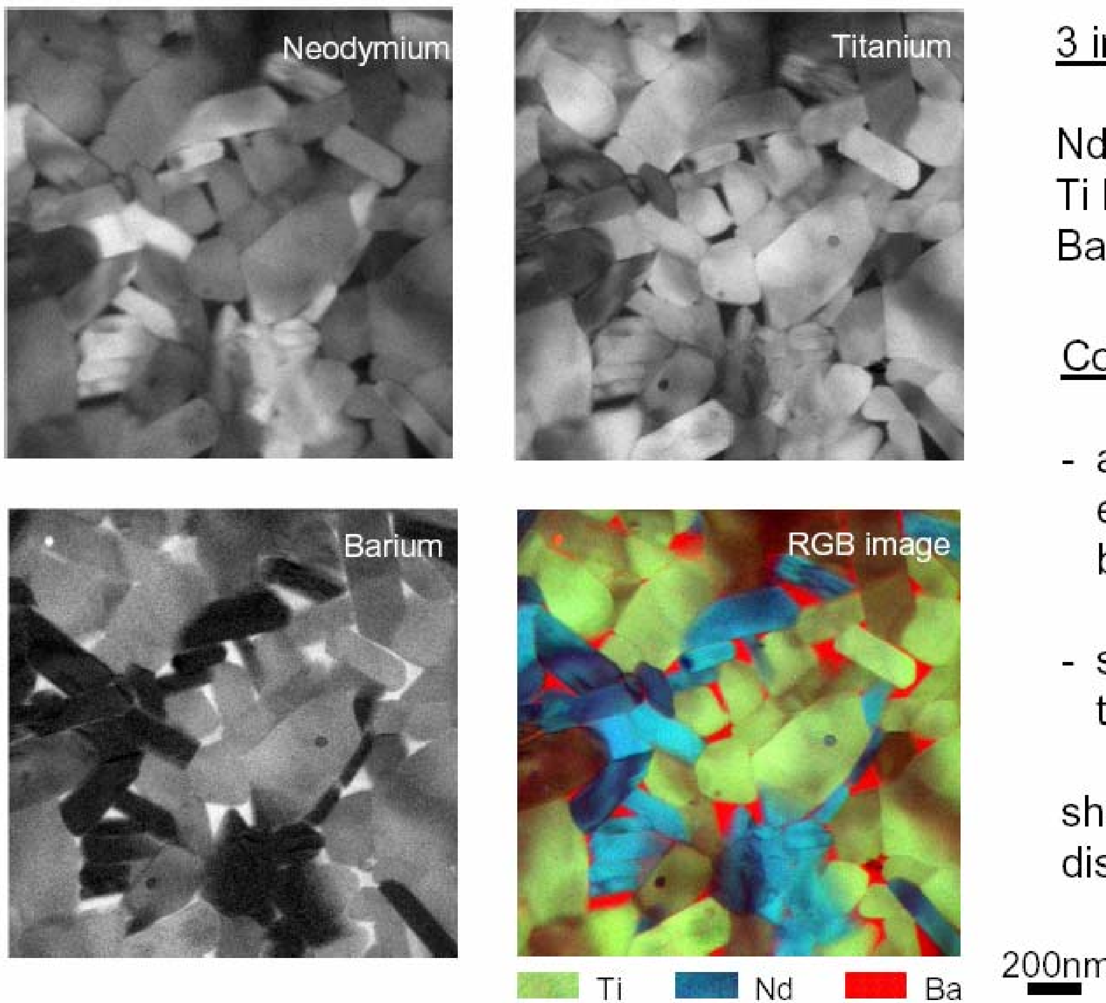
Using energy loss electrons for imaging



EFTEM – an example



<u>3 images/element using:</u>

Nd M_{45} edge:	@ 978 eV
Ti L_{23} edge:	@ 455 eV
Ba M_{45} edge:	@ 781 eV

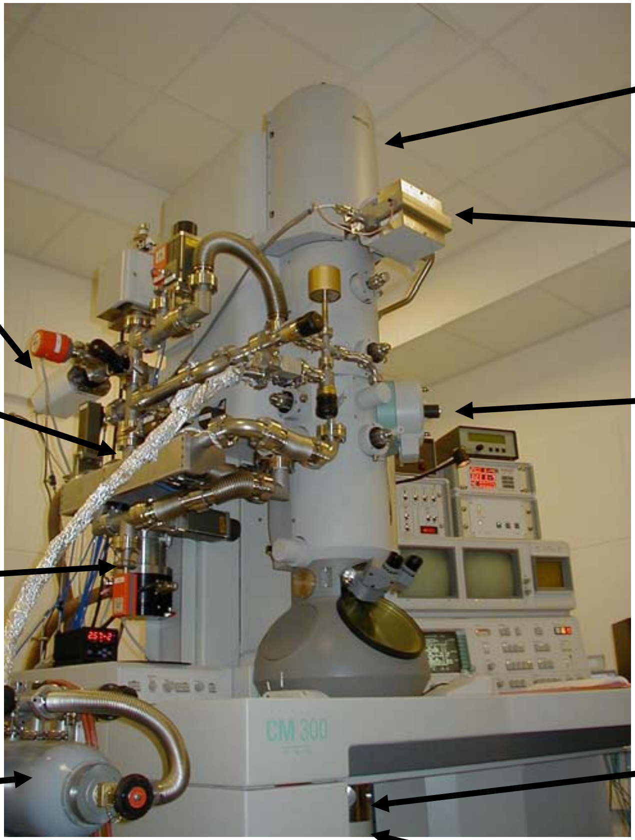
<u>Color overlays,RGB images:</u>

- assign a color to each elemental map: Ti green, Nd blue and Ba red
- superimpose three color layers to form RGB composite

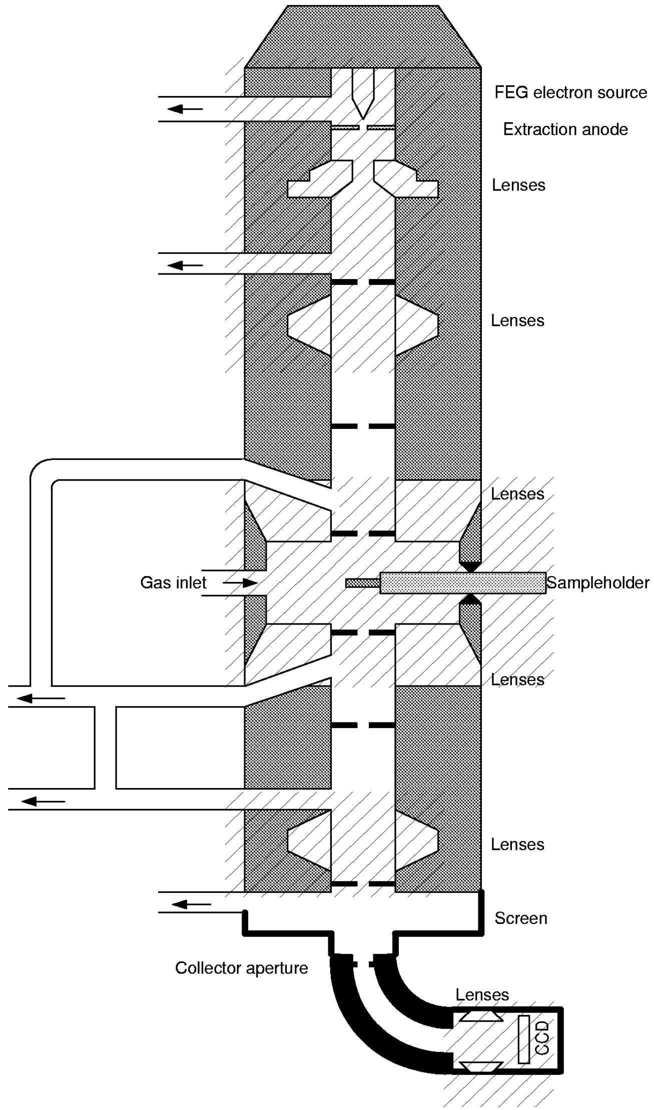
shows chemical phase distribution qualitatively only

In situ electron microscopy

Placed at Haldor Topsøe A/S, Lyngby, Denmark

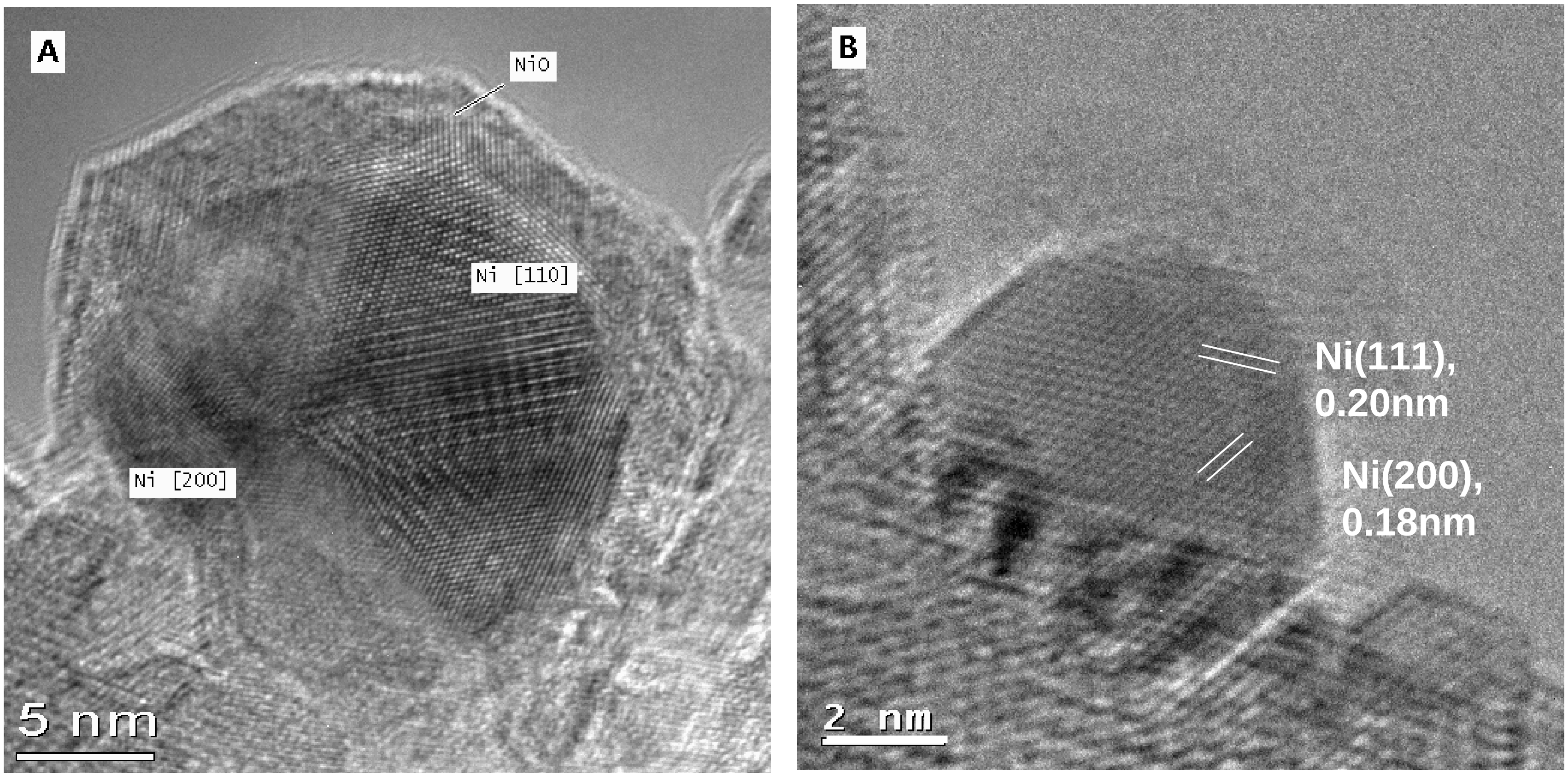


In situ electron microscope



In situ HRTEM – does it matter?

Passivated sample | **Reduced in 3.5 mbar H_2 at 450 °C**

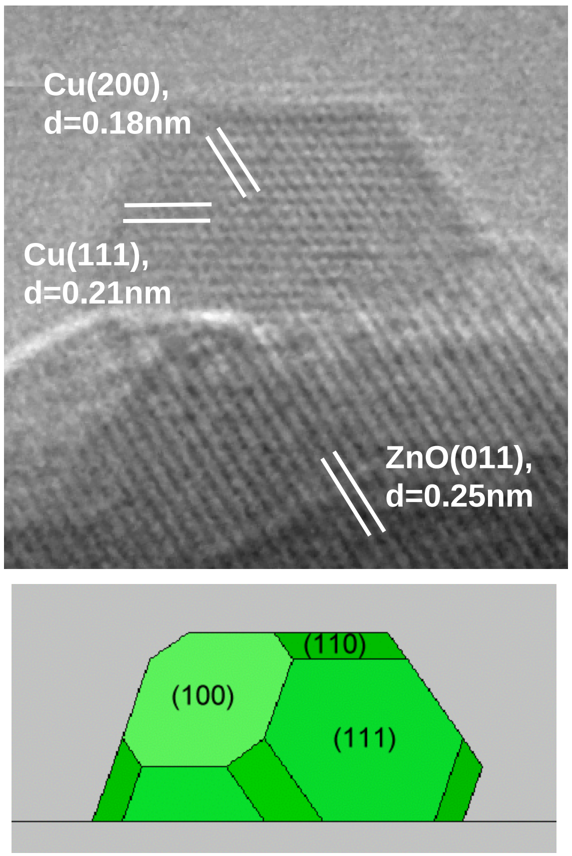


$Ni/MgAl_2O_4$ steam reforming catalyst

Jakob B. Wagner, Microstructure, Dept. AC, Fritz-Haber-Institute (MPG), Berlin, Germany

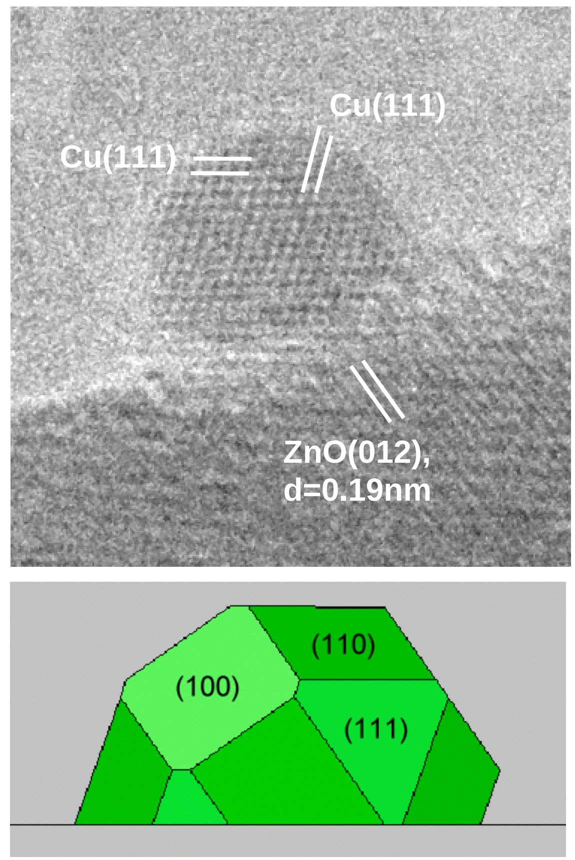
Equilibrium shapes versus gas composition

H_2



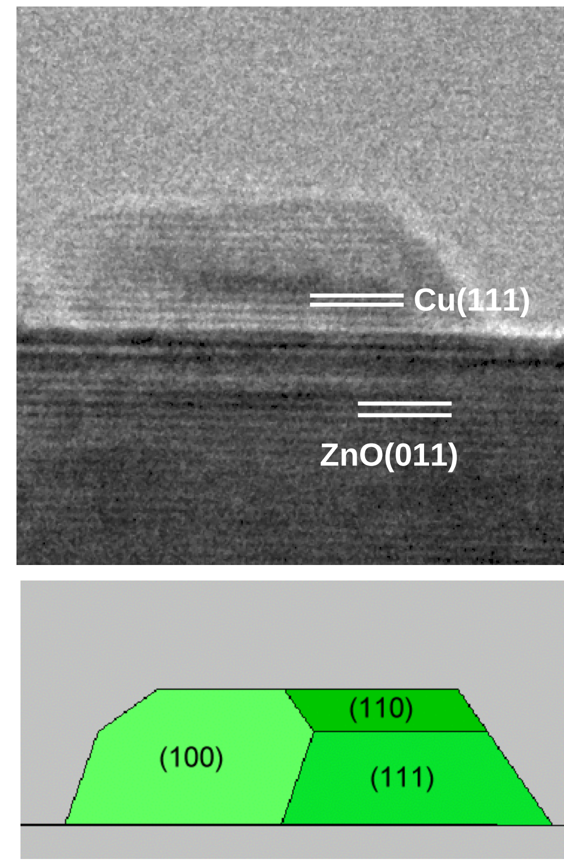
1.5mbar, 220°C

H_2/H_2O



1.5mbar, H_2/H_2O=3/1, 220°C

H_2/CO



1.5mbar, H_2/CO=95/5, 220°C

For your information!

Doing (electron) microscopy is a 100% occupation
-no operator = no outcome

-And then the interpretation and analysis as well…

Literature

Reimer, Ludwig; Pfefferkorn, Gerhard.
Scanning Electron Microscopy

Reimer, Ludwig;
Transmission electron microscopy : physics of image formation and microanalysis

Williams, David B. Carter, C. Barry
Transmission electron microscopy : a textbook for materials science

Egerton, R. F.
Electron energy-loss spectroscopy in the electron microscope

Spence, John C. H.
Experimental high-resolution electron microscopy

Spence, John C. H.; Zuo, J. M.
Electron microdiffraction