Department of Inorganic Chemistry
Fritz-Haber-Institut der MPG

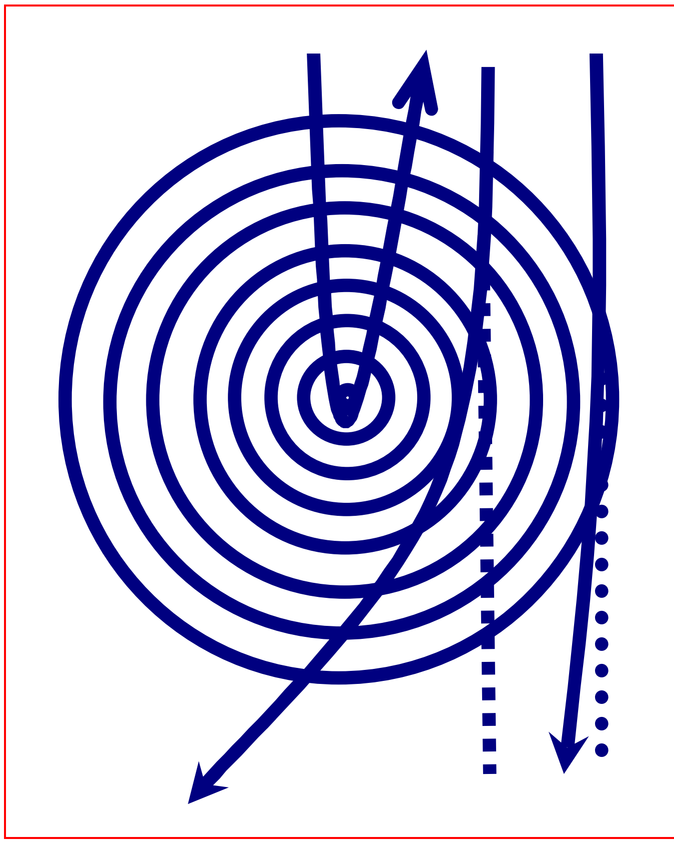
Electron Microscopy in Catalysis

Di Wang

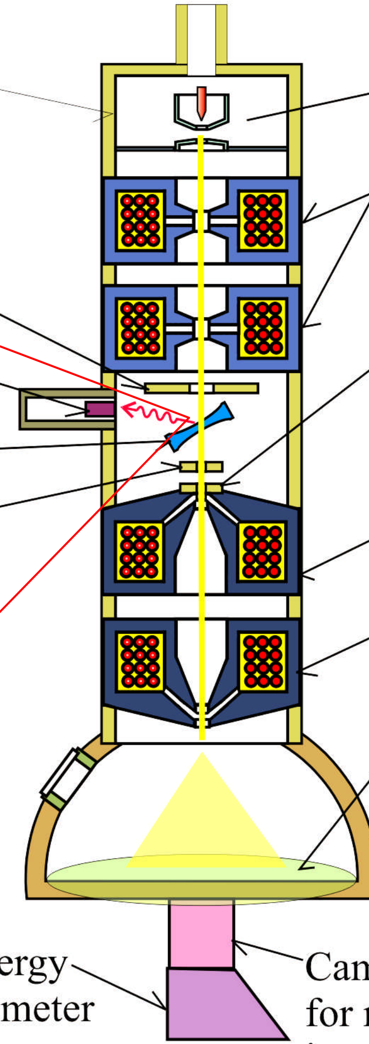

PHILIPS
PHILIPS
CM 200

Transmission electron microscope

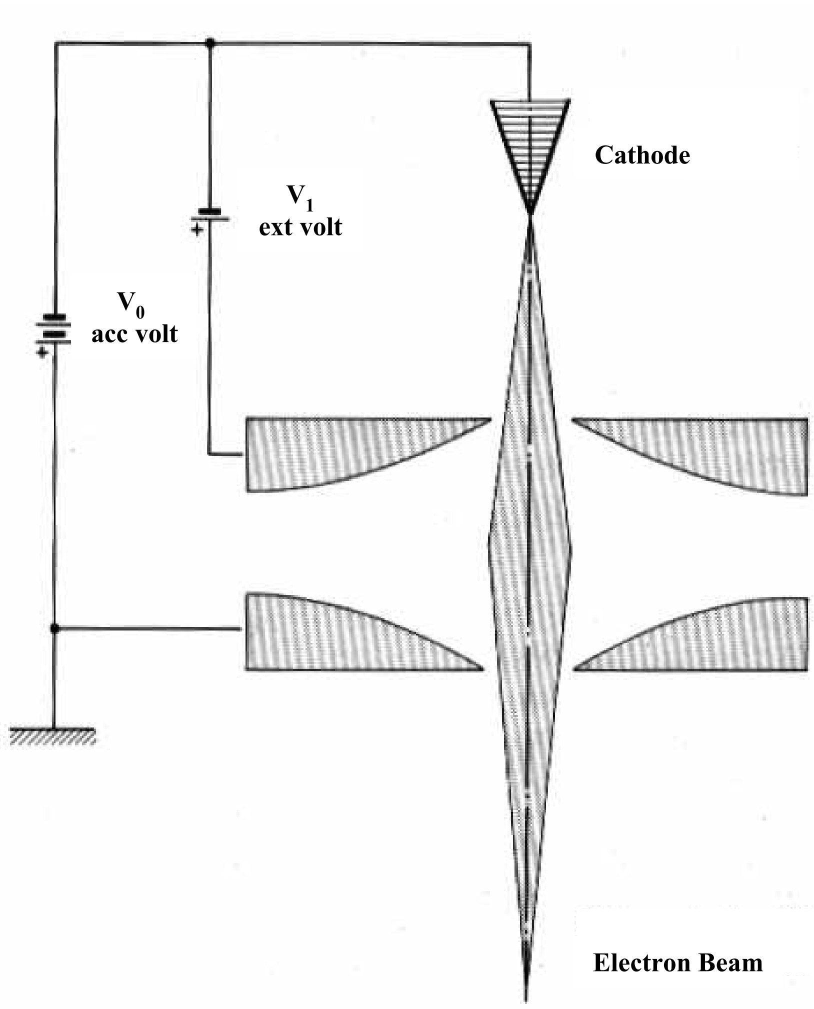
Interaction of electron with your samples

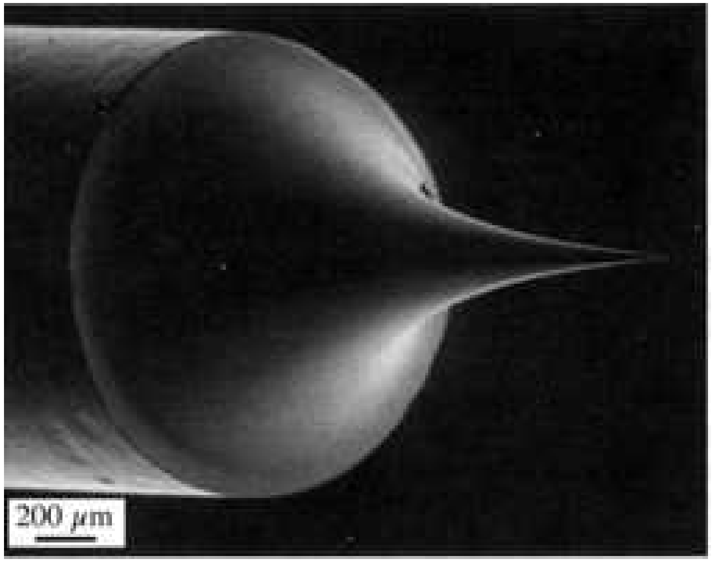


Electron scattering



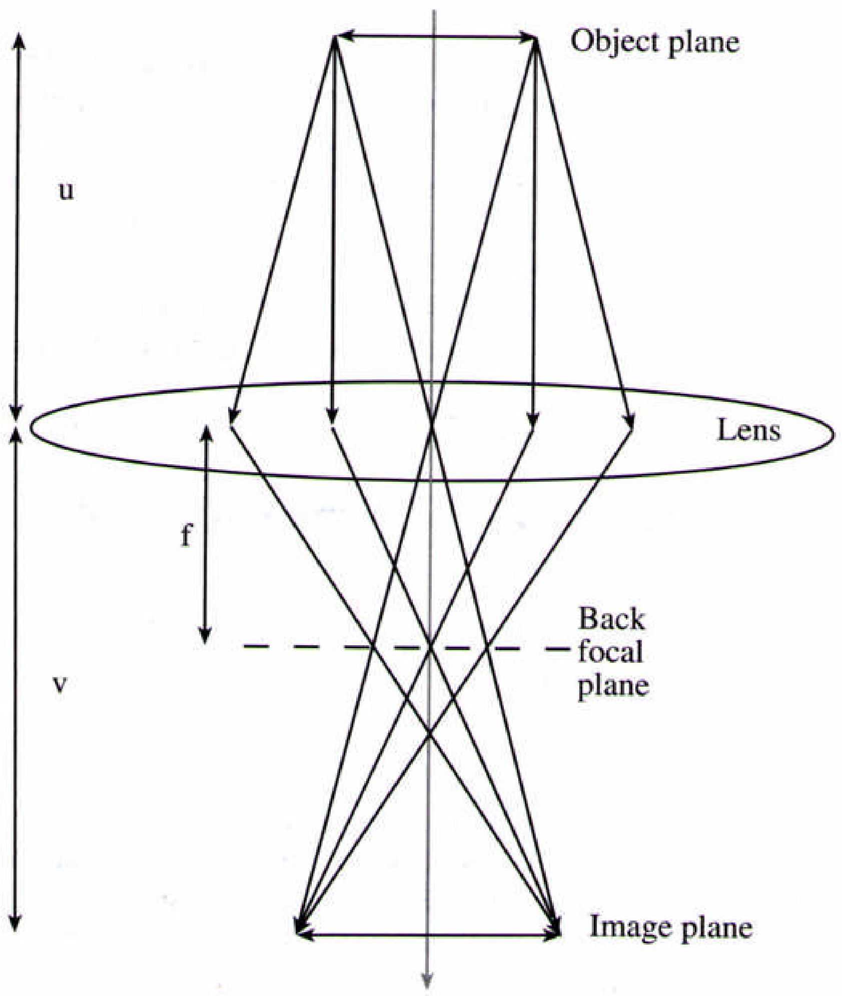
Field emission gun

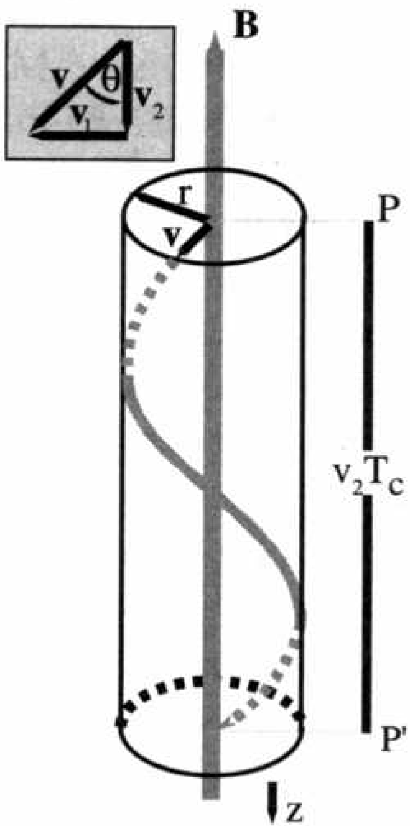




An FEG tip, showing the extraordinarily fine W needle

Lens


Object plane
u
Lens
f
Back
focal
plane
v
Image plane


B
v
θ
v₂
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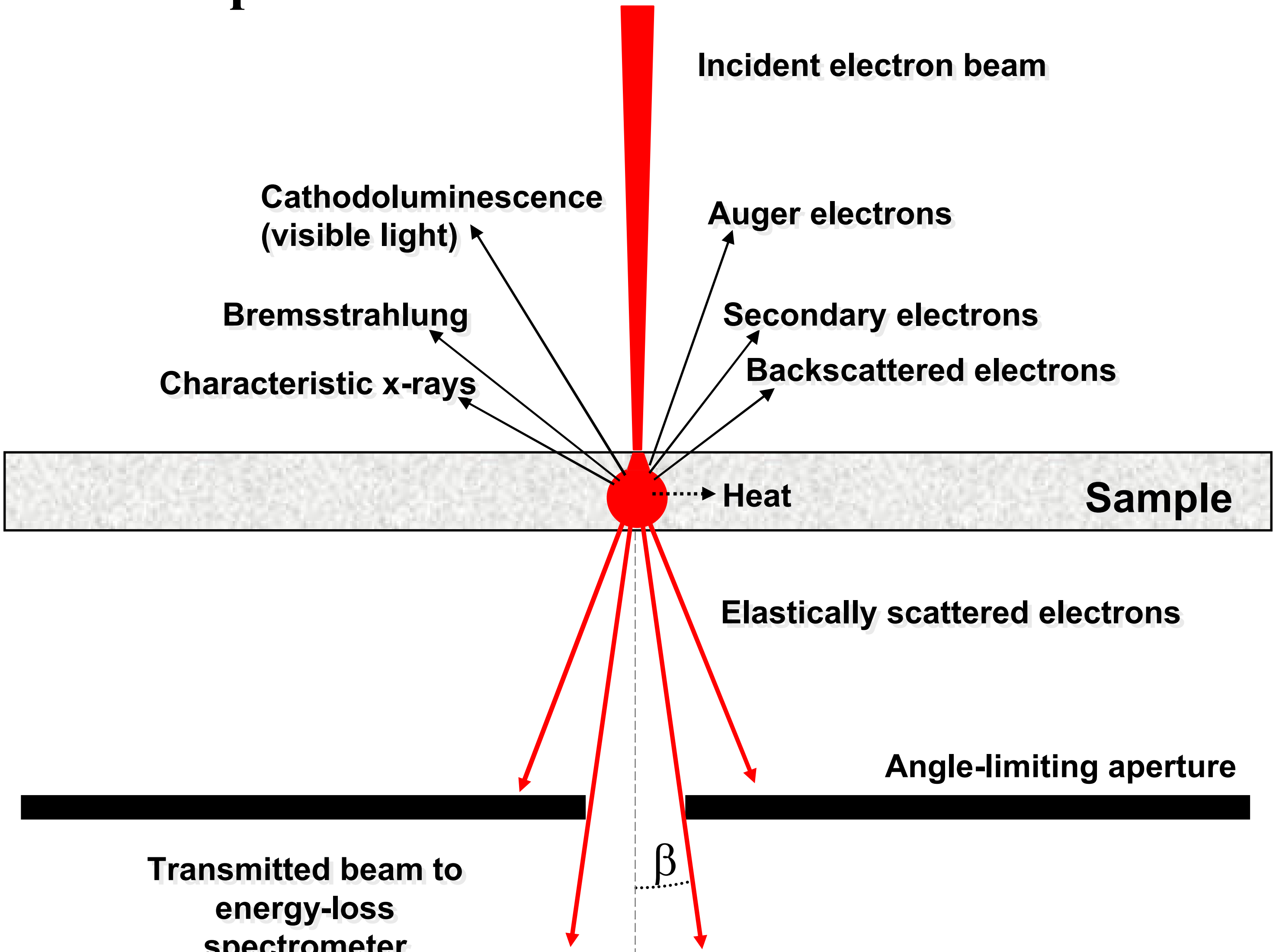
v
P
v₂Tc
P'
z

Electron-sample interactions



What can TEM do?

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)	Element analysis
Electron-energy loss spectroscopy (EELS)	Electronic structures
Energy-filtered TEM (EFTEM)	Imaging the distribution of elements and even chemical states
SEM	Morphology, surfaces
STEM	Morphology, Z-contrast

Image and diffraction mode

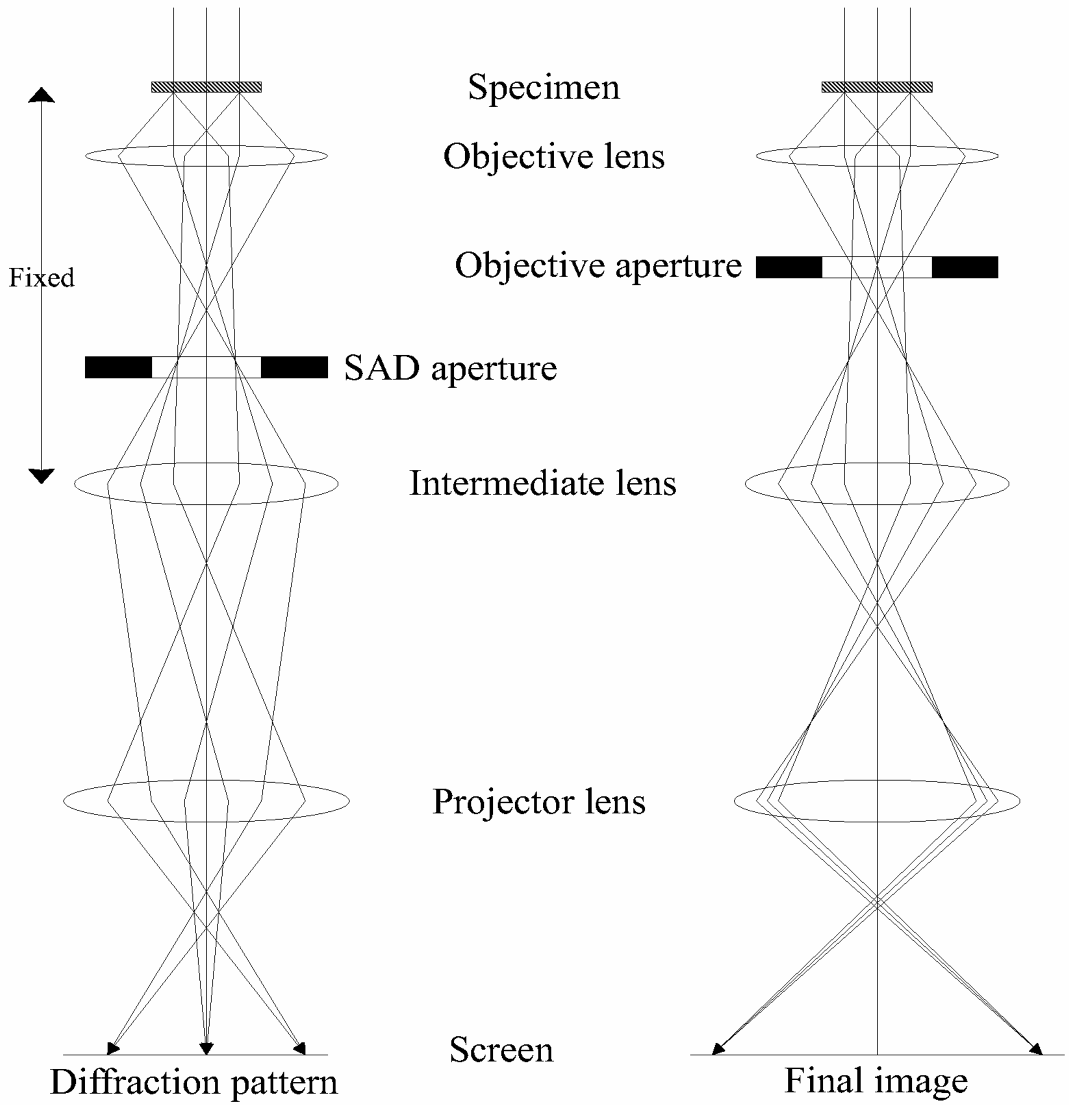
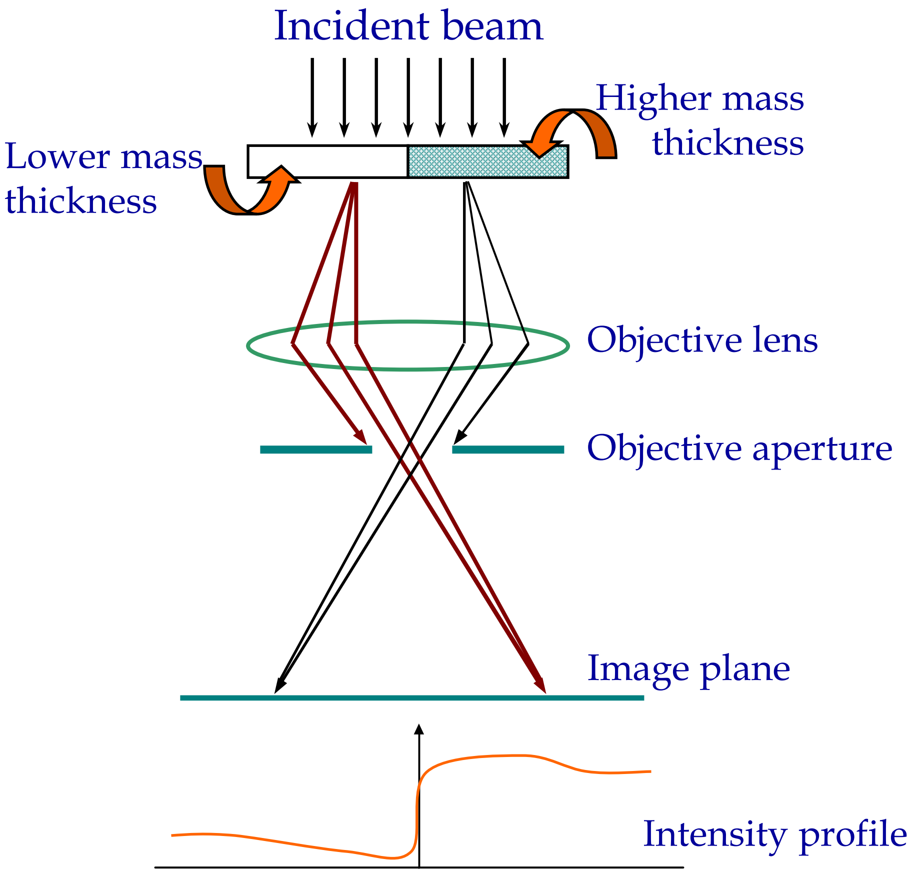


Image contrast in TEM

I. Mass-thickness contrast



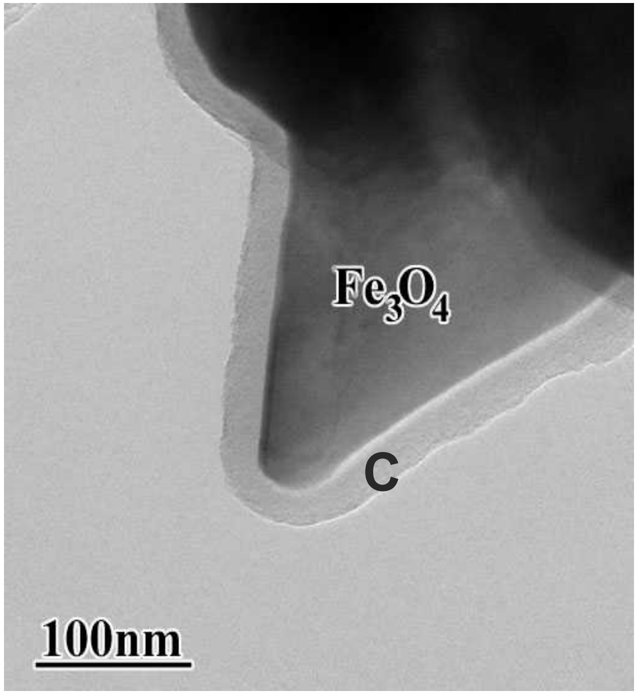
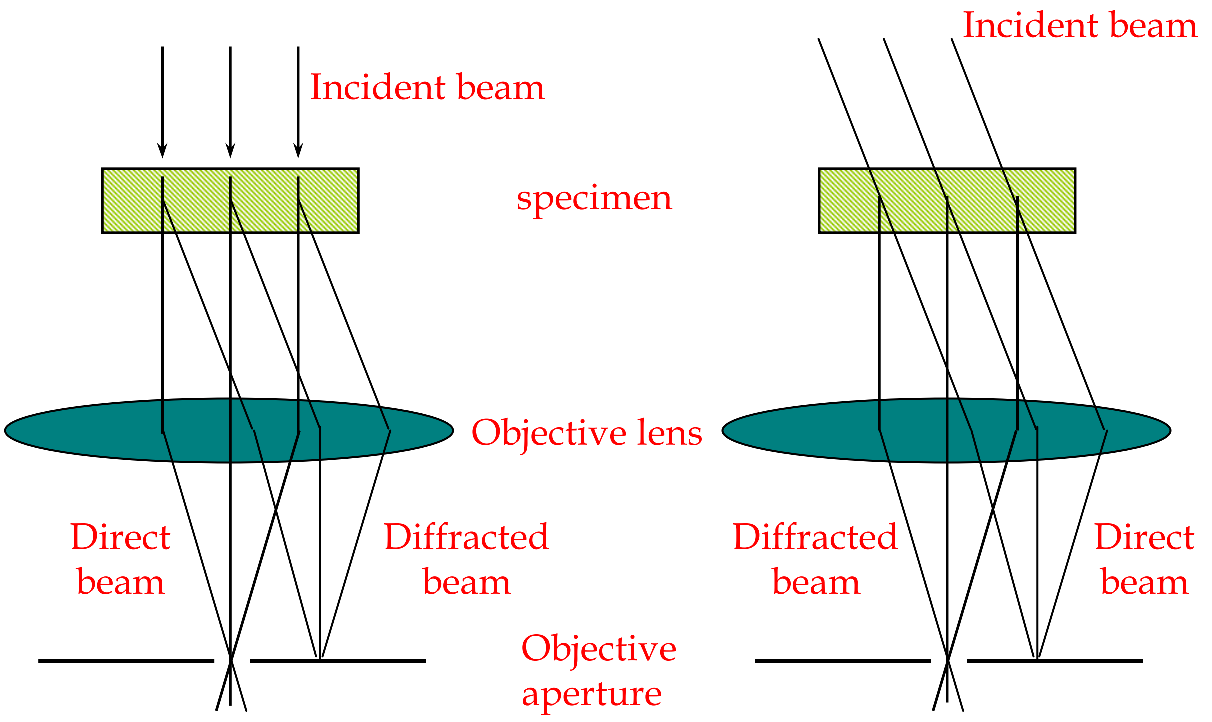


Image contrast in TEM

II. Diffraction contrast

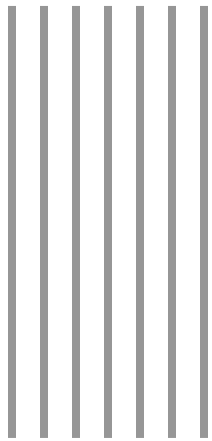


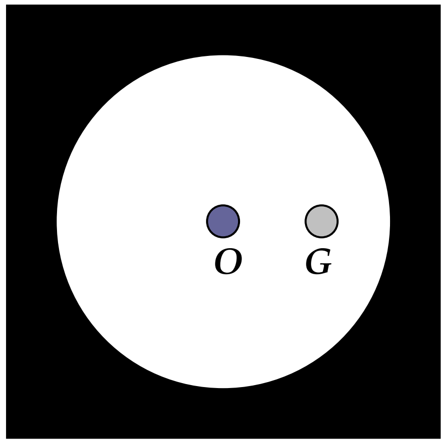
Bright field (BF)

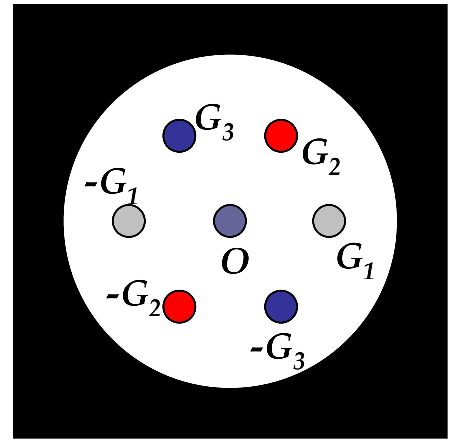
Dark field (DF)

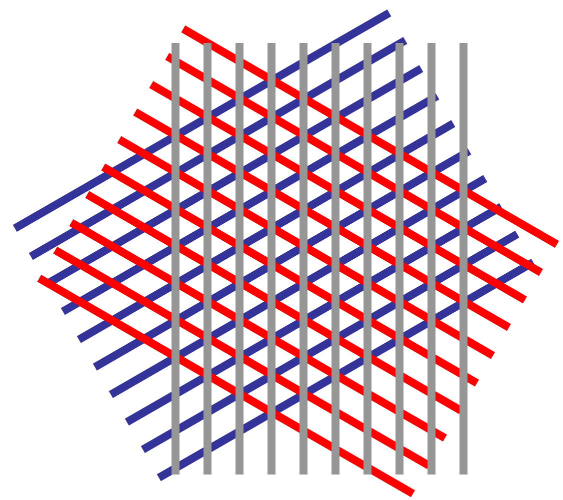
Image contrast in TEM

III. Lattice fringes in pictures

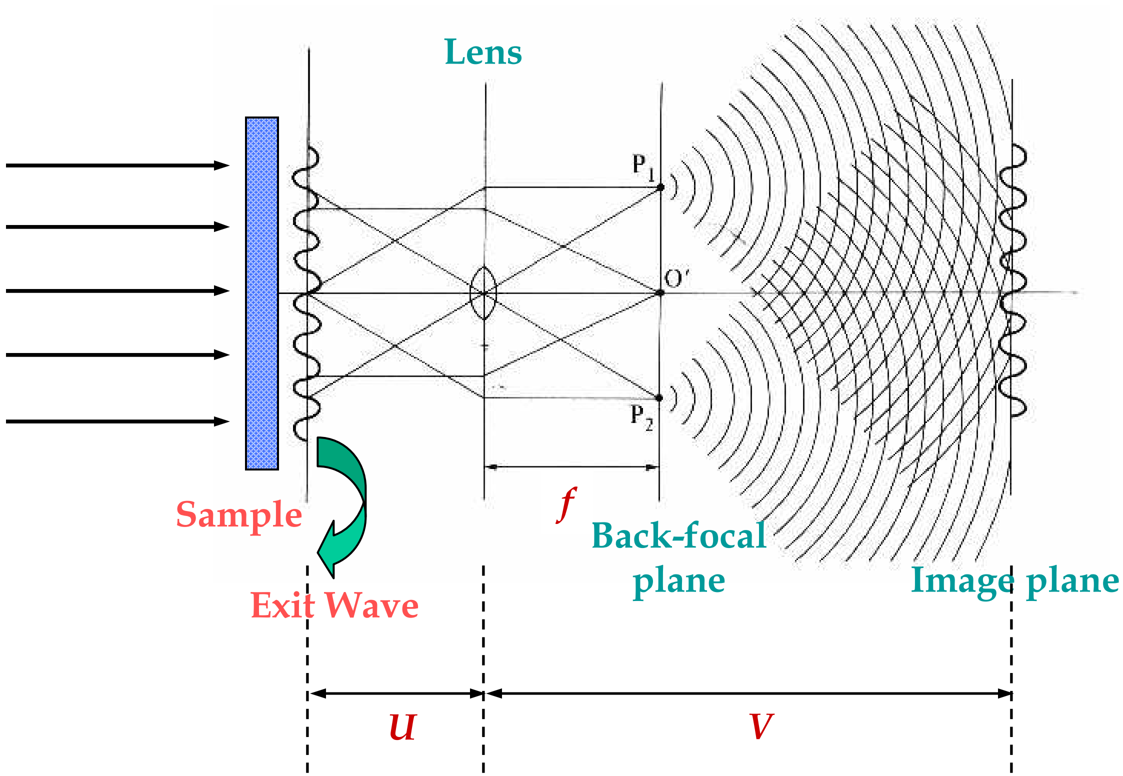






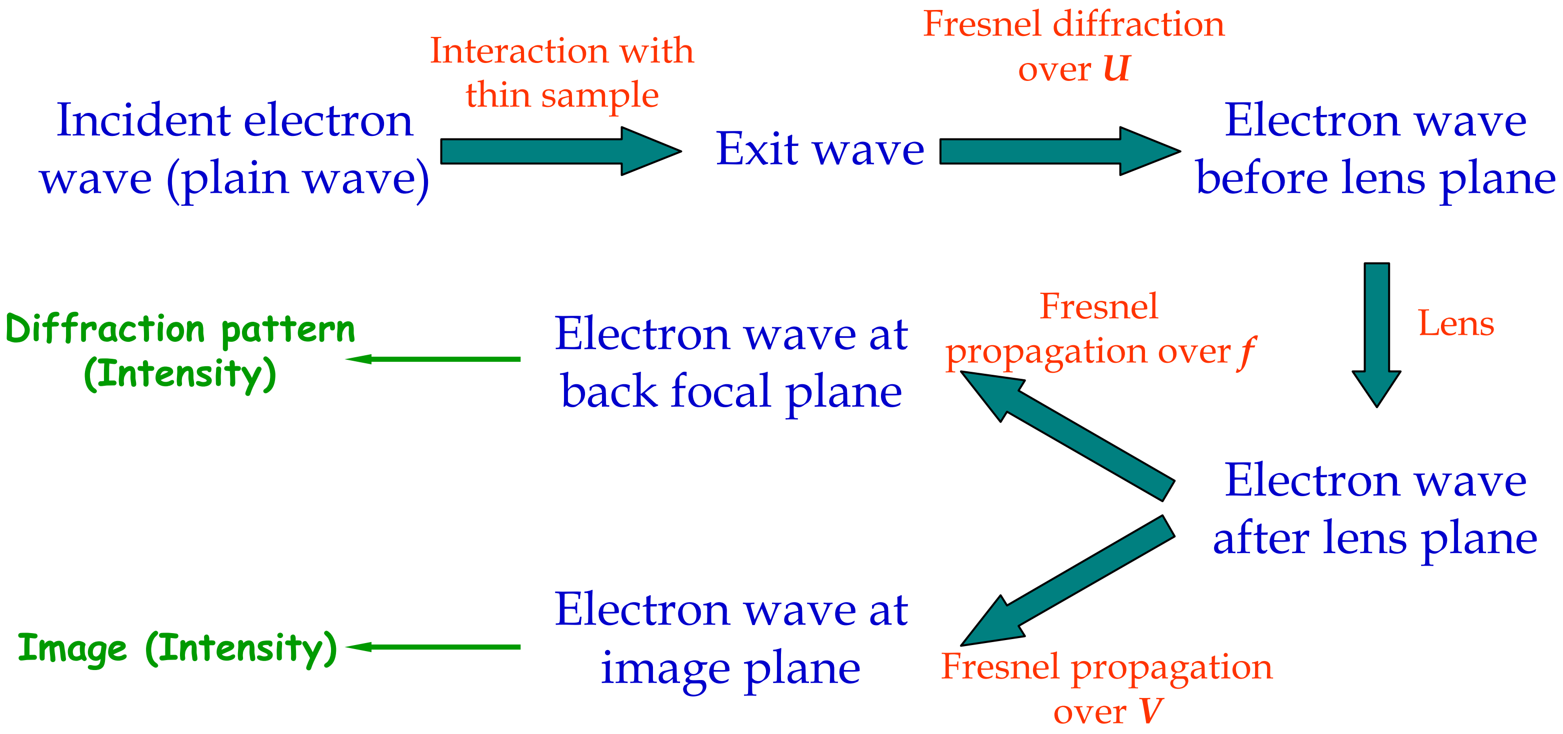


High-resolution imaging



Abbe Interpretation of imaging

Abbe Interpretation of imaging



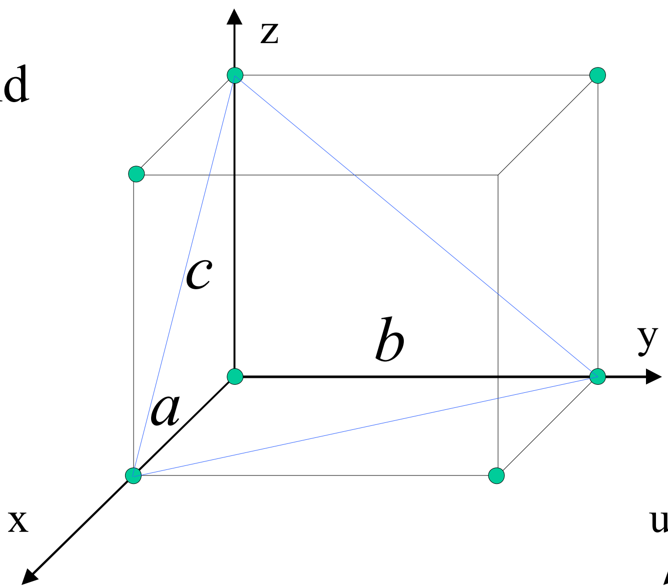
Fourier transform (FT)

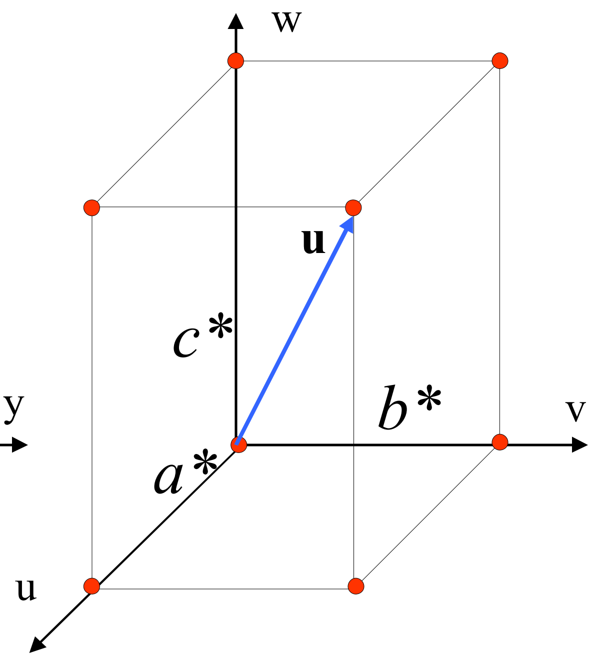
Real space ⟷ FT / Inverse FT ⟷ **Reciprocal space**

$$\mathbf{a}^* = \frac{\mathbf{b}\times\mathbf{c}}{V}, \mathbf{b}^* = \frac{\mathbf{c}\times\mathbf{a}}{V}, \mathbf{c}^* = \frac{\mathbf{a}\times\mathbf{b}}{V}$$

For cubic, tetragonal and orthorhombic structure,

$\mathbf{a}^* = 1/a$, $\|$ $\mathbf{a}$
$\mathbf{b}^* = 1/b$, $\|$ $\mathbf{b}$
$\mathbf{c}^* = 1/c$, $\|$ $\mathbf{c}$

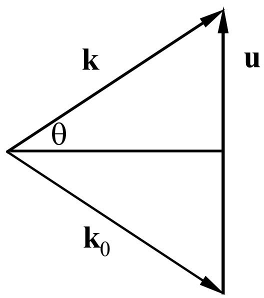




$\mathbf{u} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$
reciprocal vector

$$|\mathbf{u}| = \left|h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\right| = \frac{1}{d_{hkl}}$$

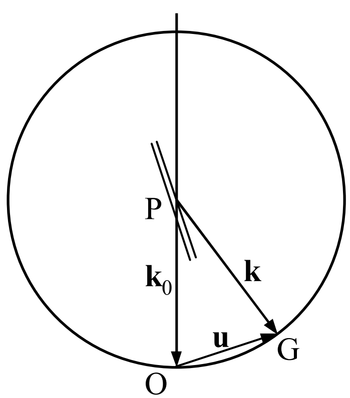
Bragg condition and Ewald sphere

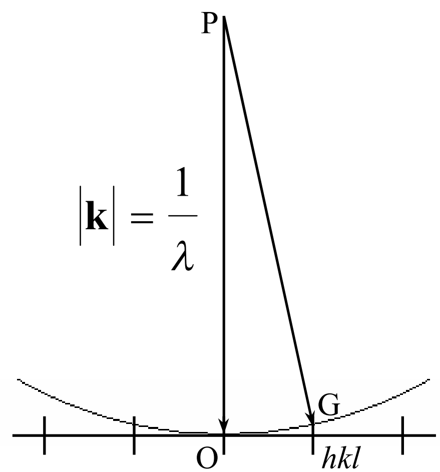


$$|\mathbf{u}| = 2|\mathbf{k}|\sin\theta = \frac{2\sin\theta}{\lambda}$$

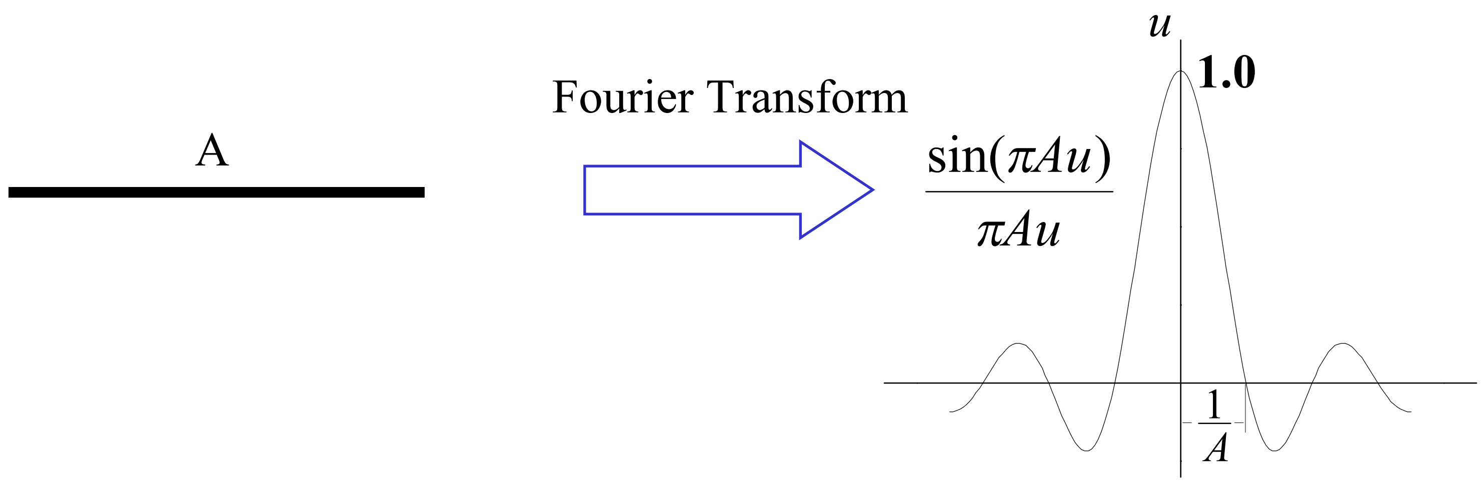
$$|\mathbf{u}| = \left|h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\right| = \frac{1}{d_{hkl}}$$

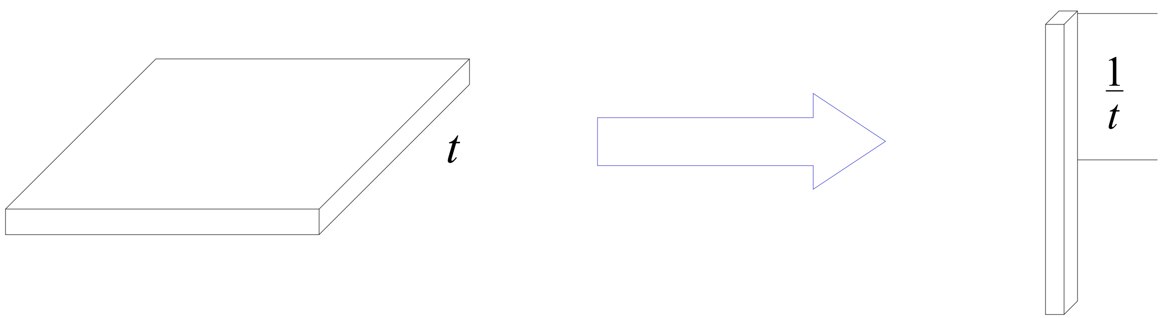
$$\Rightarrow \quad 2d_{hkl}\sin\theta_{hkl} = \lambda$$





Shape factor

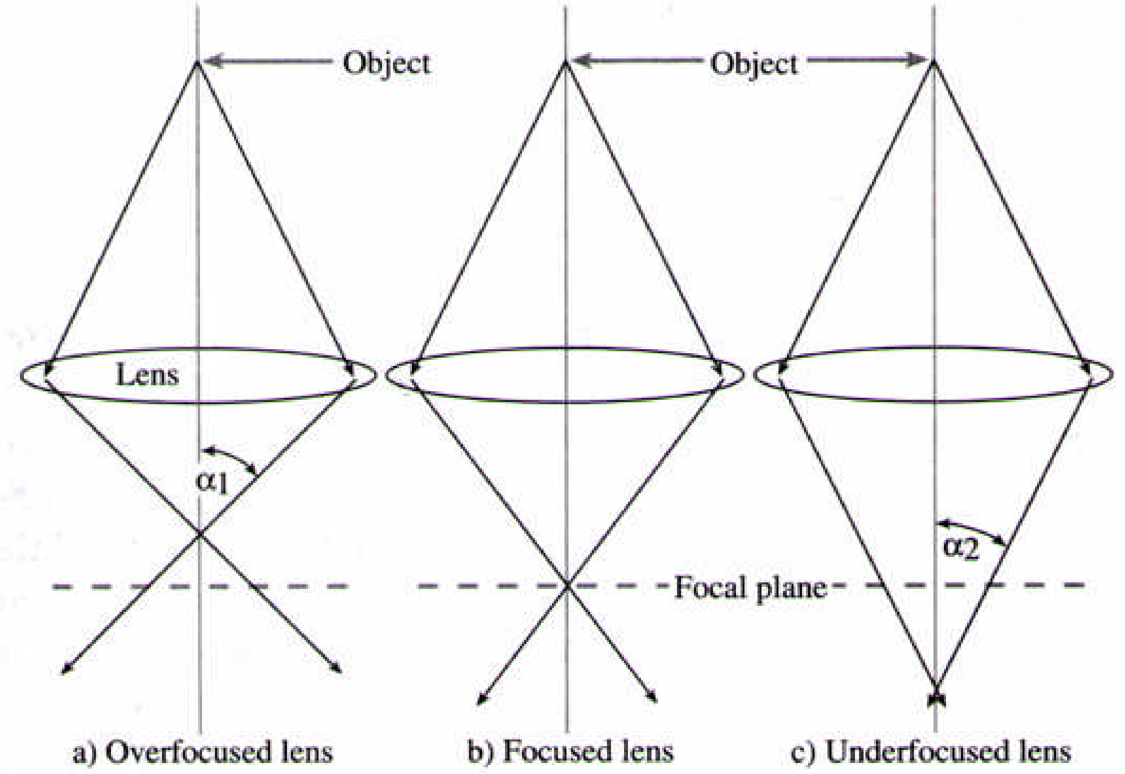




Sample shape

Shape of each reciprocal lattice point

Exciting the lens strength - focus



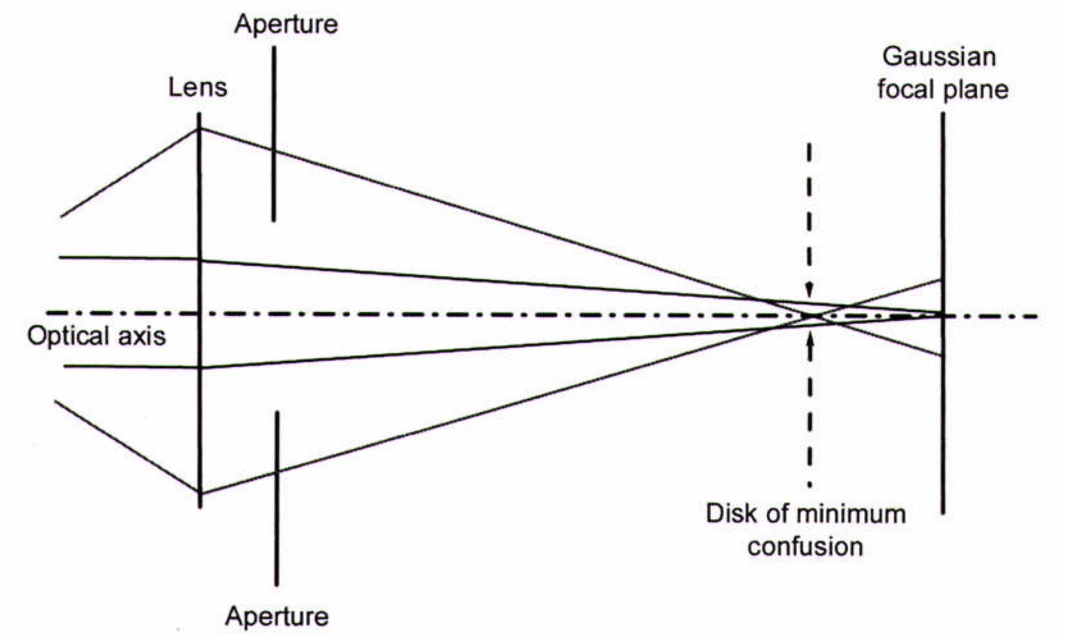
Lenses spatially fixed, but strength changeable

Phase shift factor in back focal plane

$$\exp\{i\pi\lambda\Delta f(u^2+v^2)\} = \exp(i\chi_1)$$

The electromagnetic lenses are not perfect

Spherical aberration of lenses



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

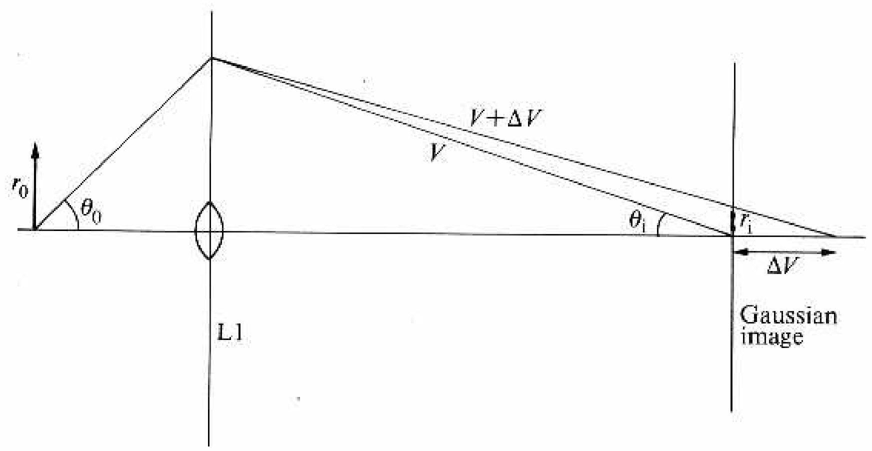
C_s : Spherical aberration coefficient

Phase shift in back focal plane
due to spherical aberration

$$\chi_2 = \frac{1}{2}\pi C_s \lambda^3 (u^2 + v^2)^2 = \exp(i\chi_2)$$

Chromatic aberration

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



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

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

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

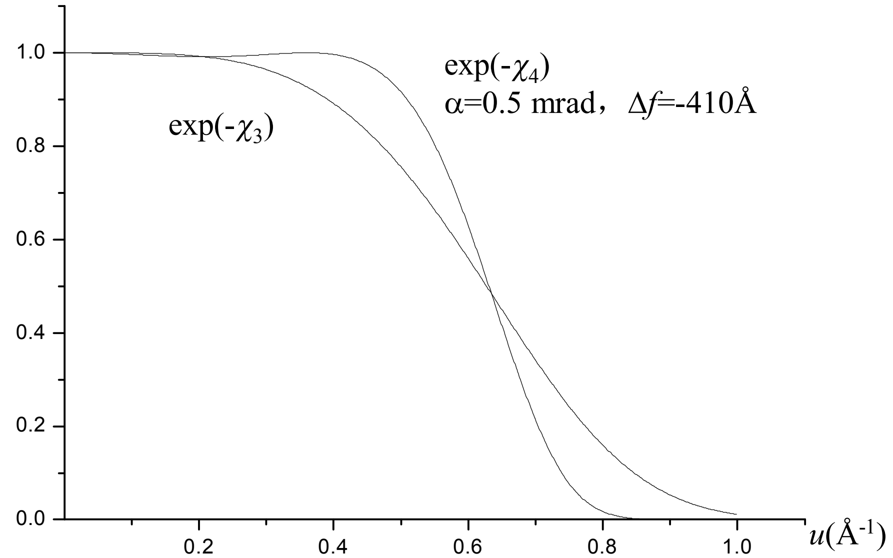
Beam divergence

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

Envelope in back focal plane

$$\exp(-\chi_4)$$

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



Transfer function $$W(\mathbf{H}) = \exp(i\chi_I)\exp(-\chi_{II})$$

Electron wave function and intensity in the image plane

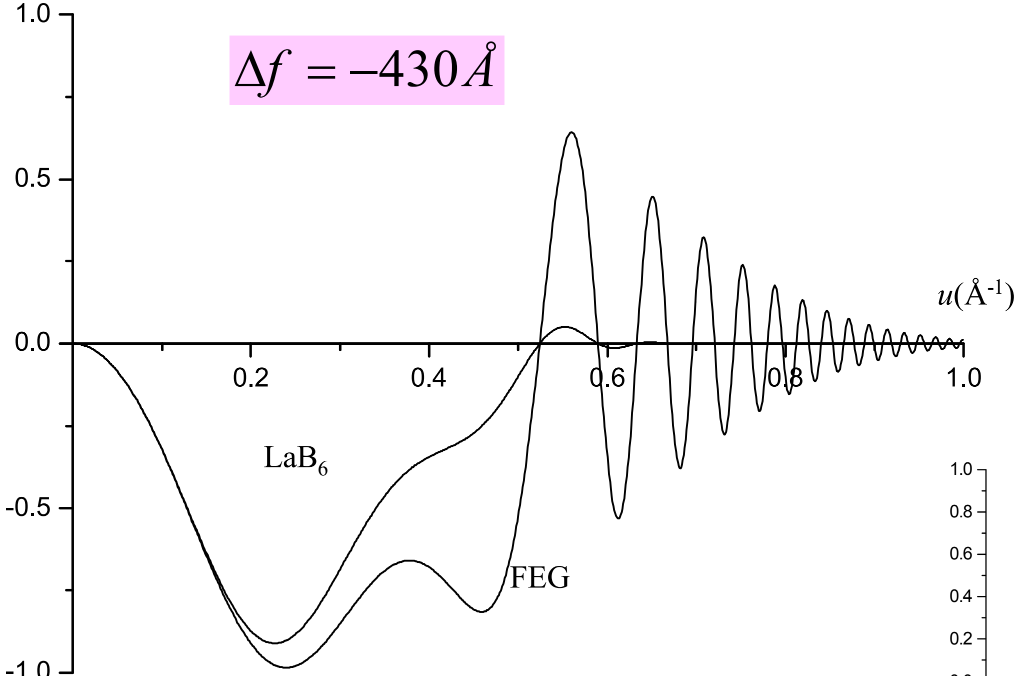
$$\psi_{image} = \mathcal{F}^{-1}\{\mathcal{F}[\psi_{exit}] \cdot W(\mathbf{H})\}$$

$$I = \psi_{image} \cdot \psi^*_{image}$$

Contrast Transfer Function (CTF)

$$\sin(\chi_I)\exp(-\chi_{II})$$

$\Delta f = -430 \mathring{A}$



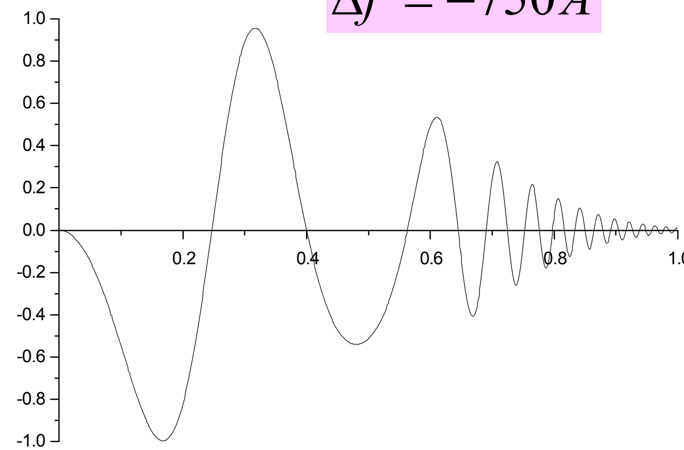
$U = 200kV$

$C_s = 0.5mm$

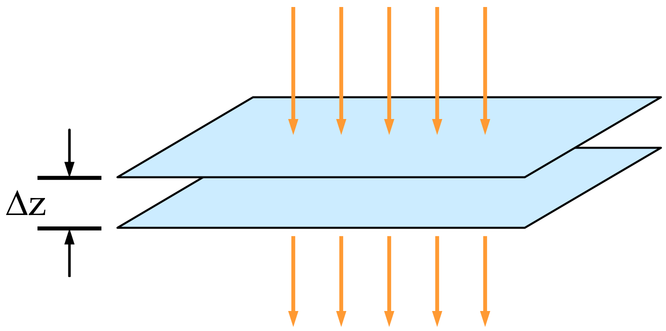
$D_{FEG} = 38\mathring{A}$

$D_{LaB_6} = 100\mathring{A}$

$\Delta f = -750\mathring{A}$



Phase contrast in TEM



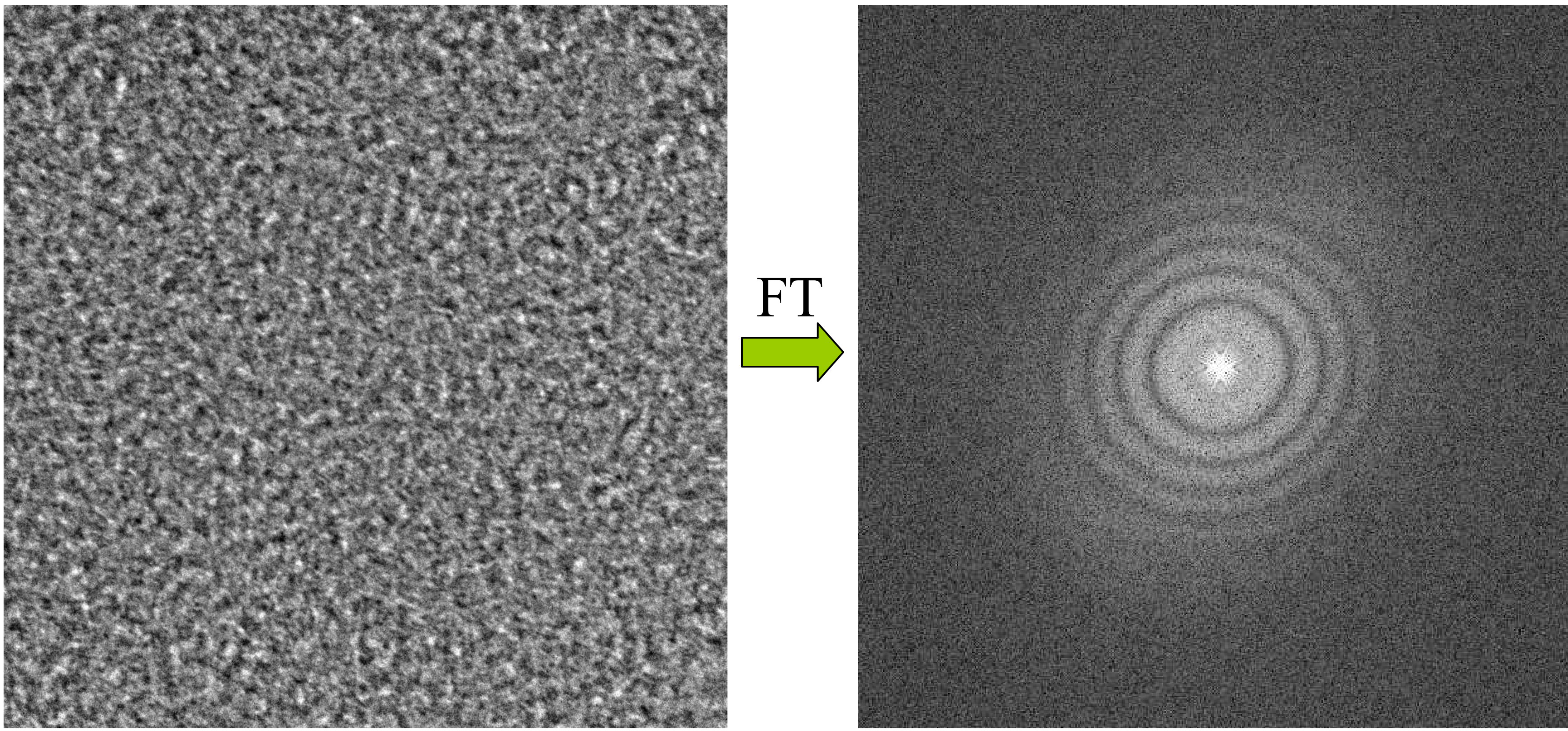
Exit wave: $$\psi_e(\mathbf{r}) = e^{-i\sigma V_p(\mathbf{r})} \approx 1 - i\sigma V_p(\mathbf{r})$$

Assuming weak-phase object approximation
V_p : scattering potential

Final intensity: $$I(\mathbf{r}) \approx 1 + 2\sigma V_p(\mathbf{r}) * \mathcal{F}^{-1}\{CTF\}$$

Picturing the Contrast Transfer Function

Amorphous Thin Carbon Film

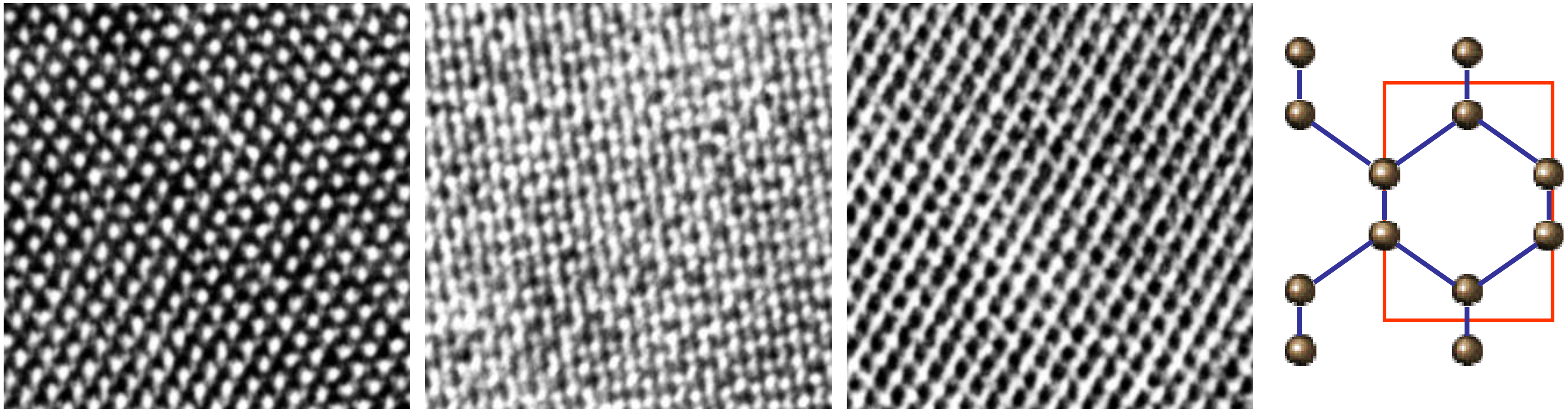


Real Space $I(\mathbf{r}) \approx 1 + 2\sigma V_p(\mathbf{r}) * \mathcal{F}^{-1}\{CTF\}$

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. !

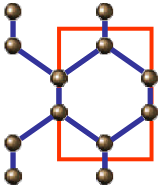


Si [110] image with different defocus values

Simulated HRTEM images

Thickness(Å): 23.04 | 46.08 | 69.12 | 92.16 | 115.20 | 138.24

Defocus(Å): -100, -300, -500, -700



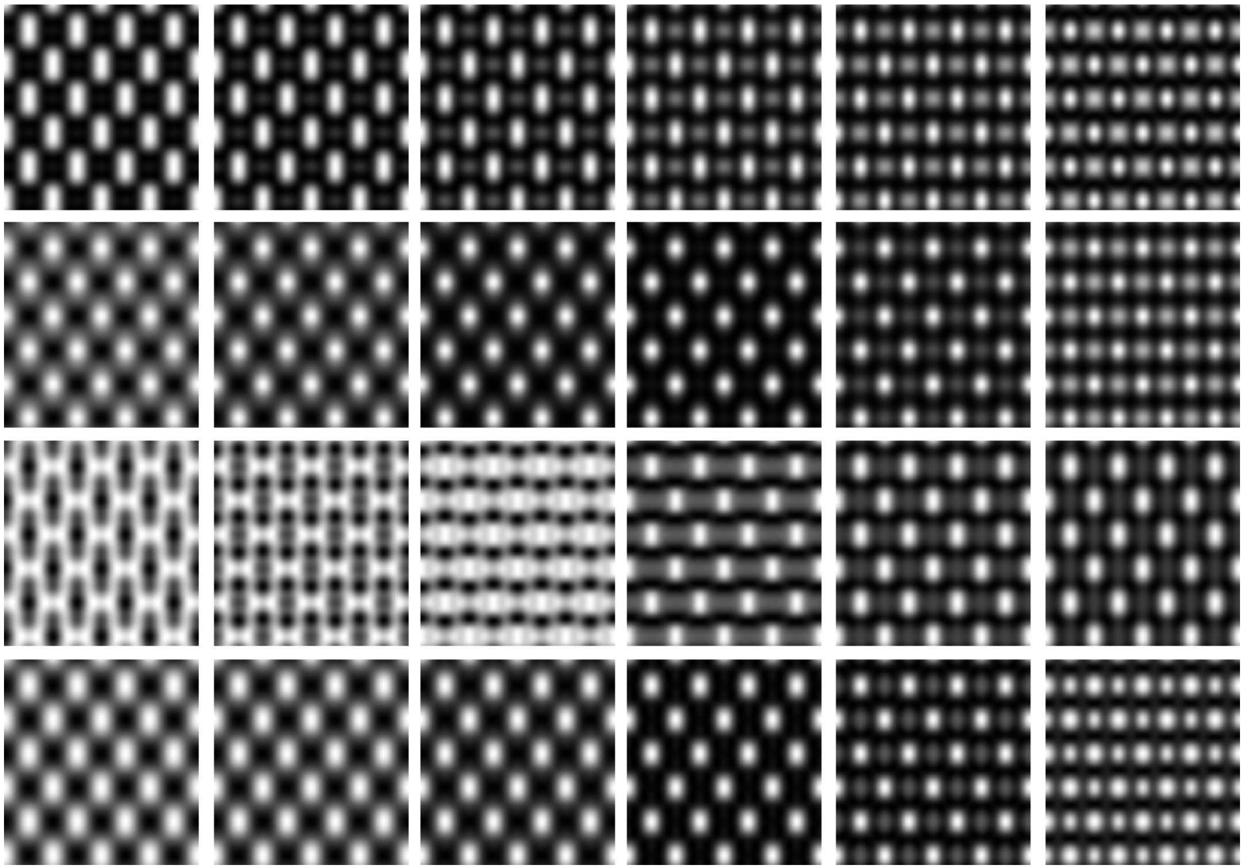
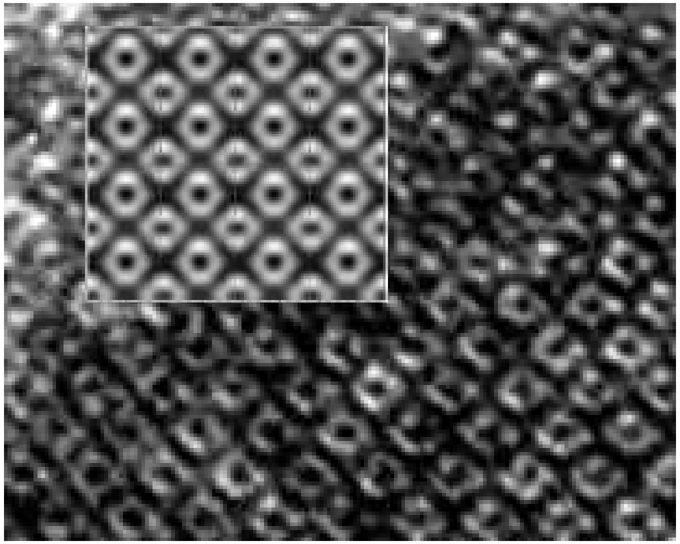
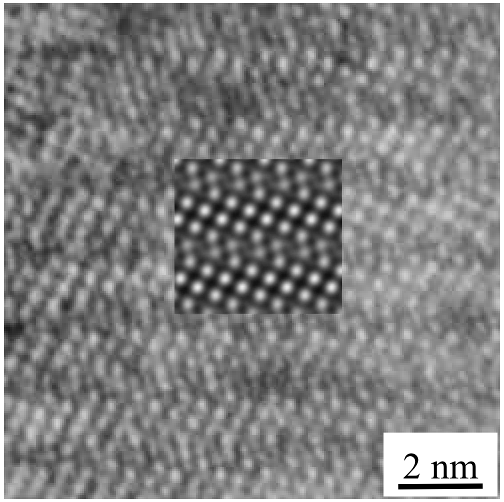


Image contrast matching

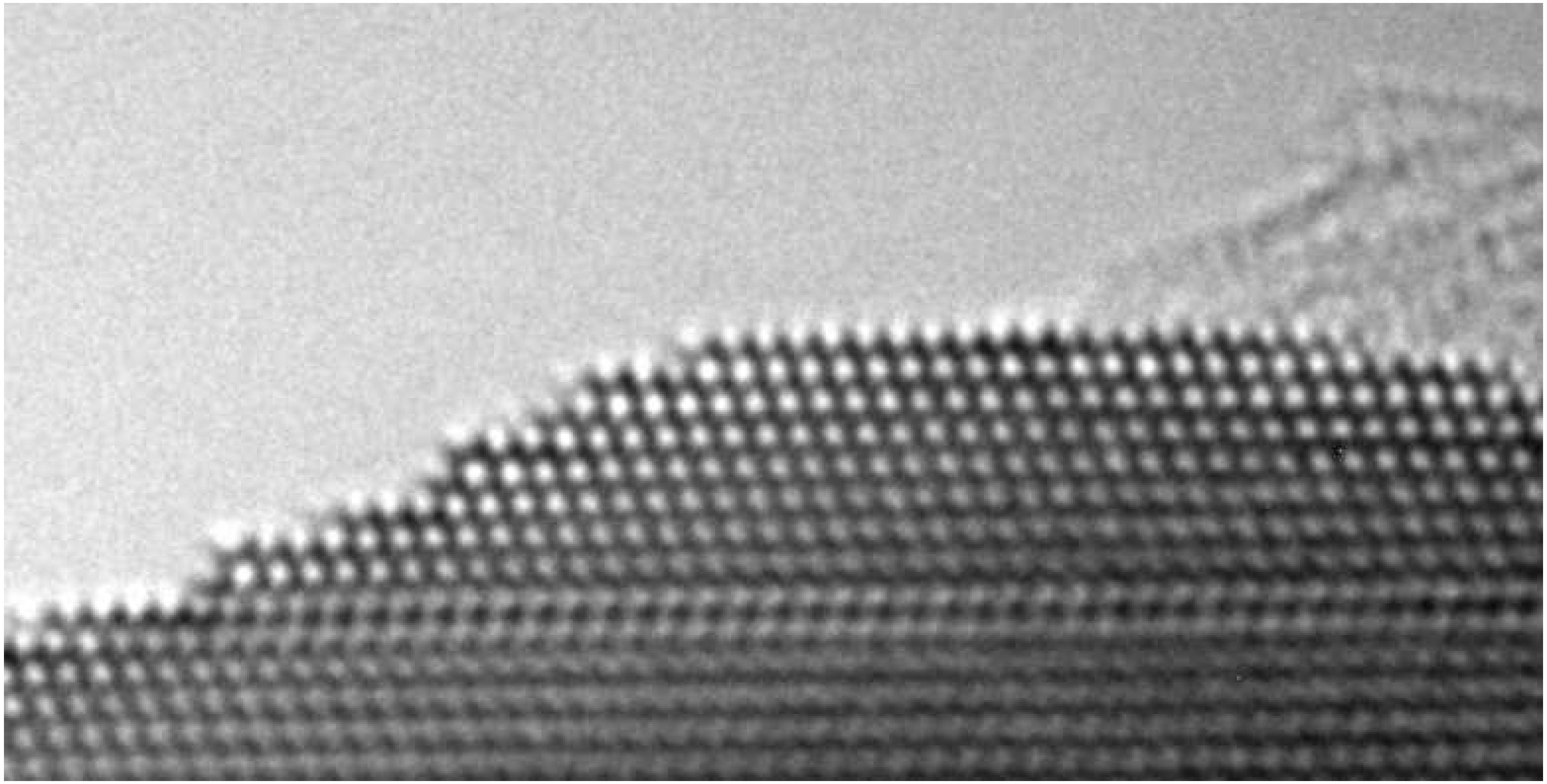
$(VO)_2P_2O_7$



Mo_8O_{23}

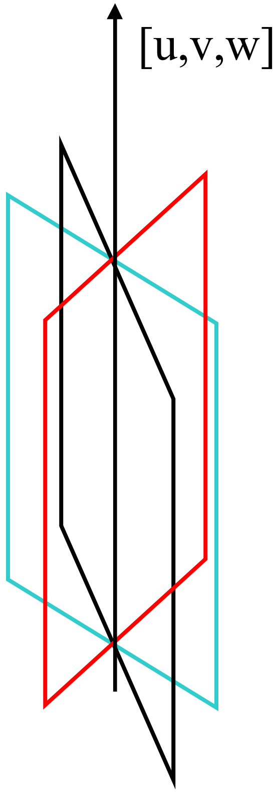


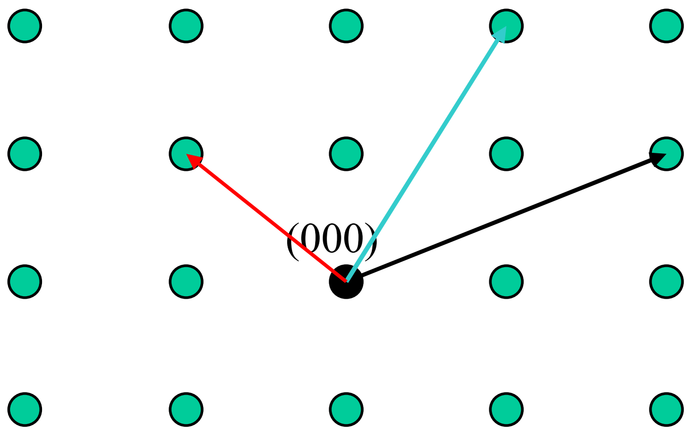
HRTEM-profile imaging



Electron diffraction

Zone axis



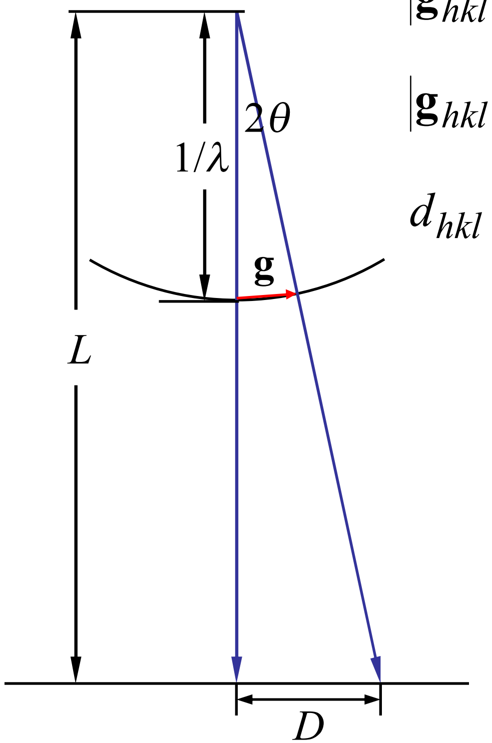


$$[u, v, w] \perp (h, k, l)$$

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

Electron diffraction

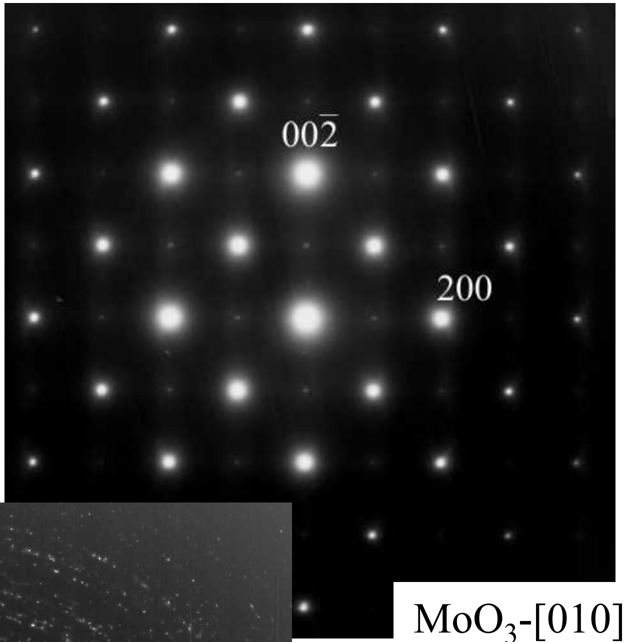
Camera length



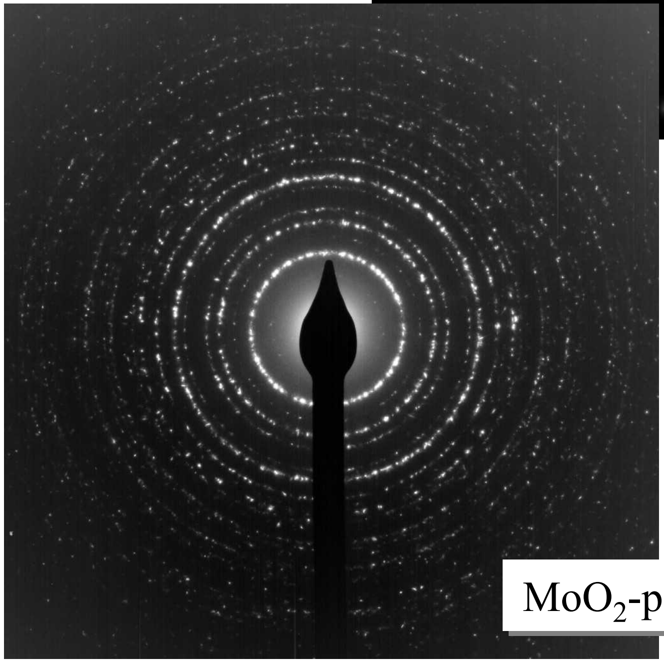
$$|\mathbf{g}_{hkl}|\lambda = D/L$$

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

$$d_{hkl} = \lambda L/D$$



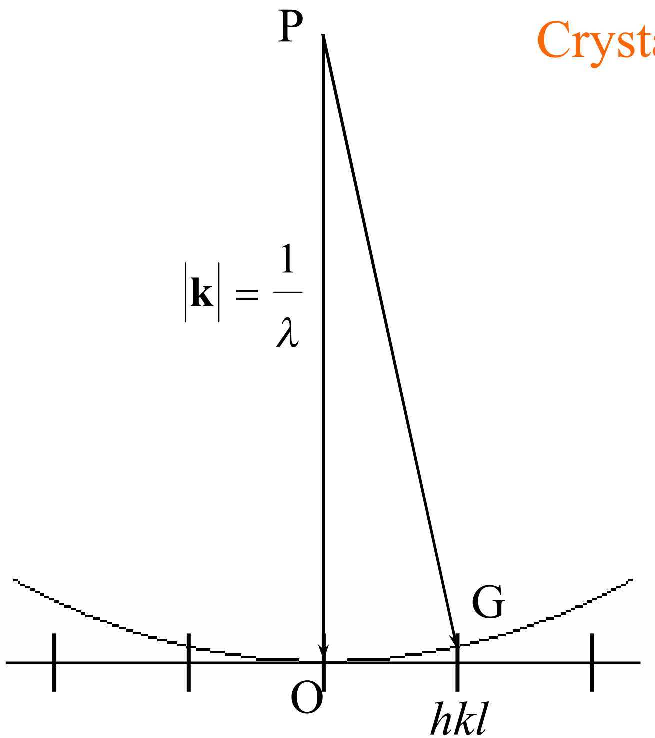
MoO_3-[010]

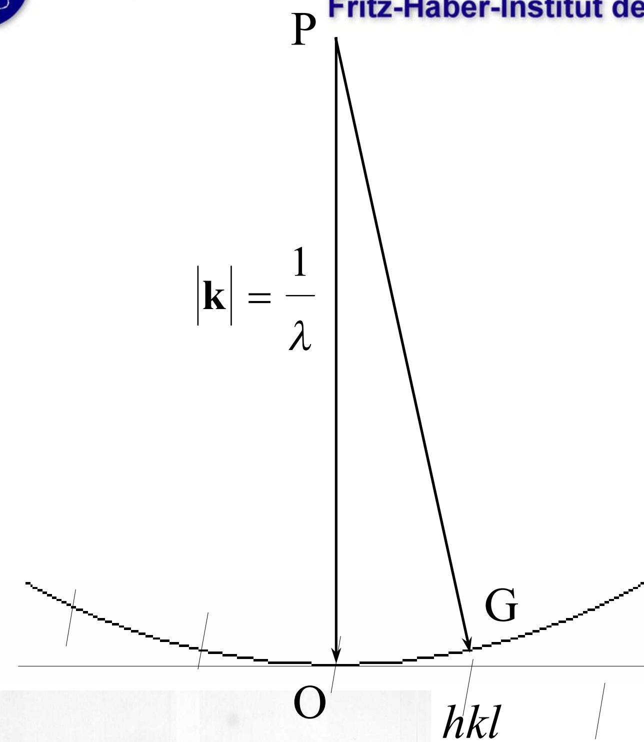


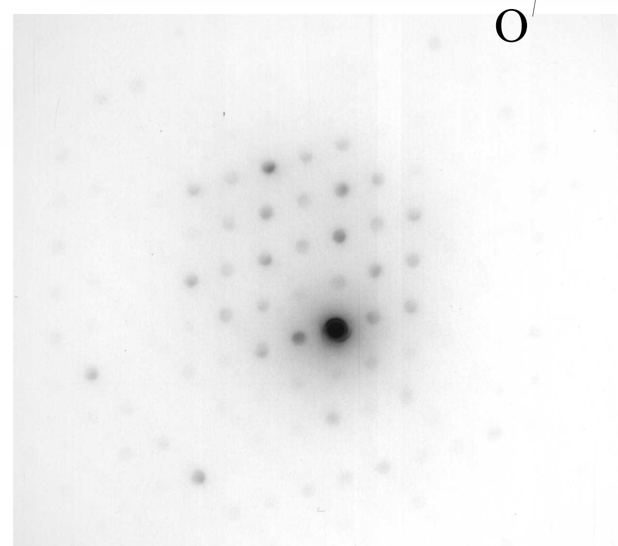
MoO_2-polycrystalline

Electron diffraction

Crystal tilt

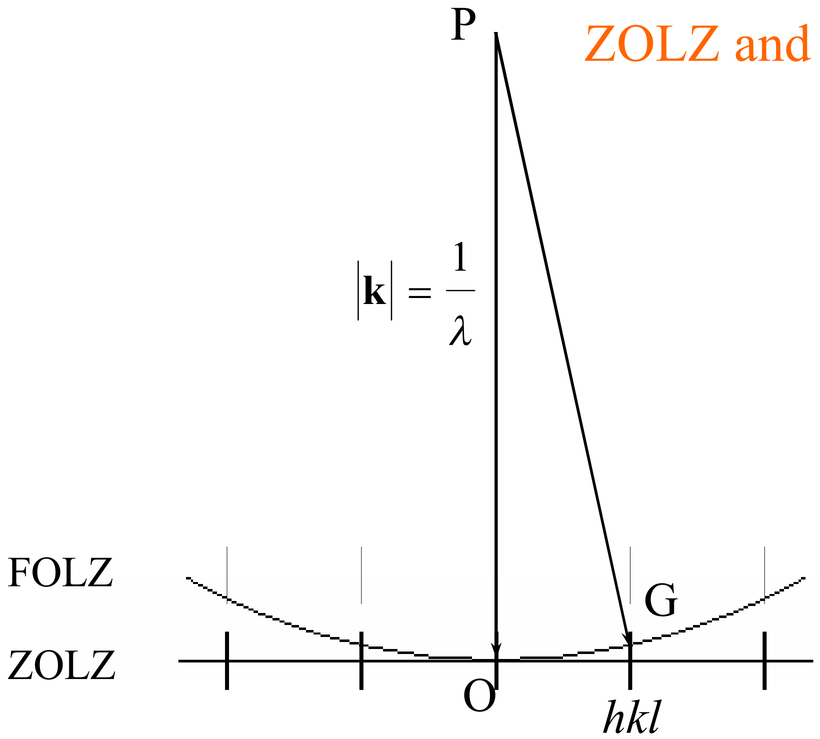


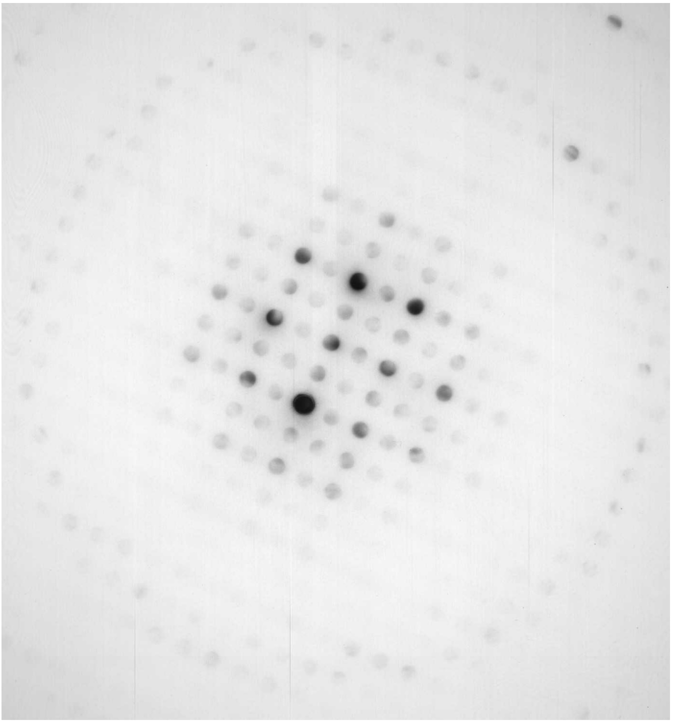




Electron diffraction

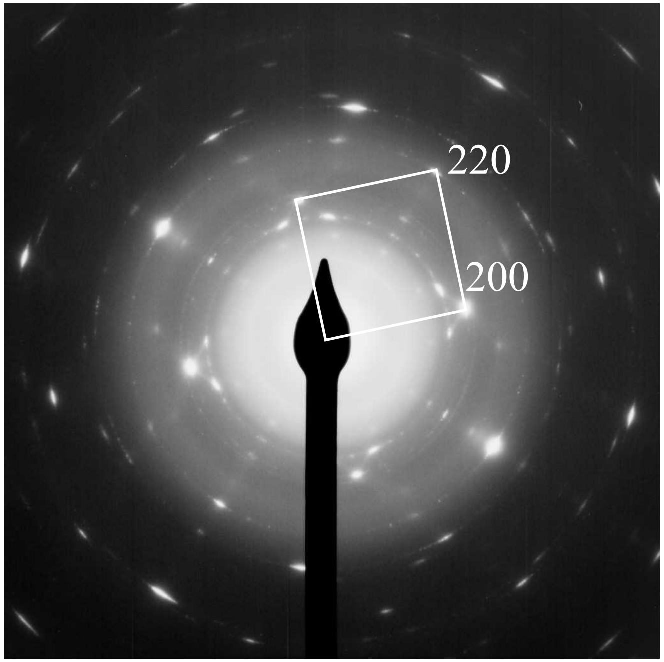
ZOLZ and HOLZ





Electron diffraction

Calibration by a known structure

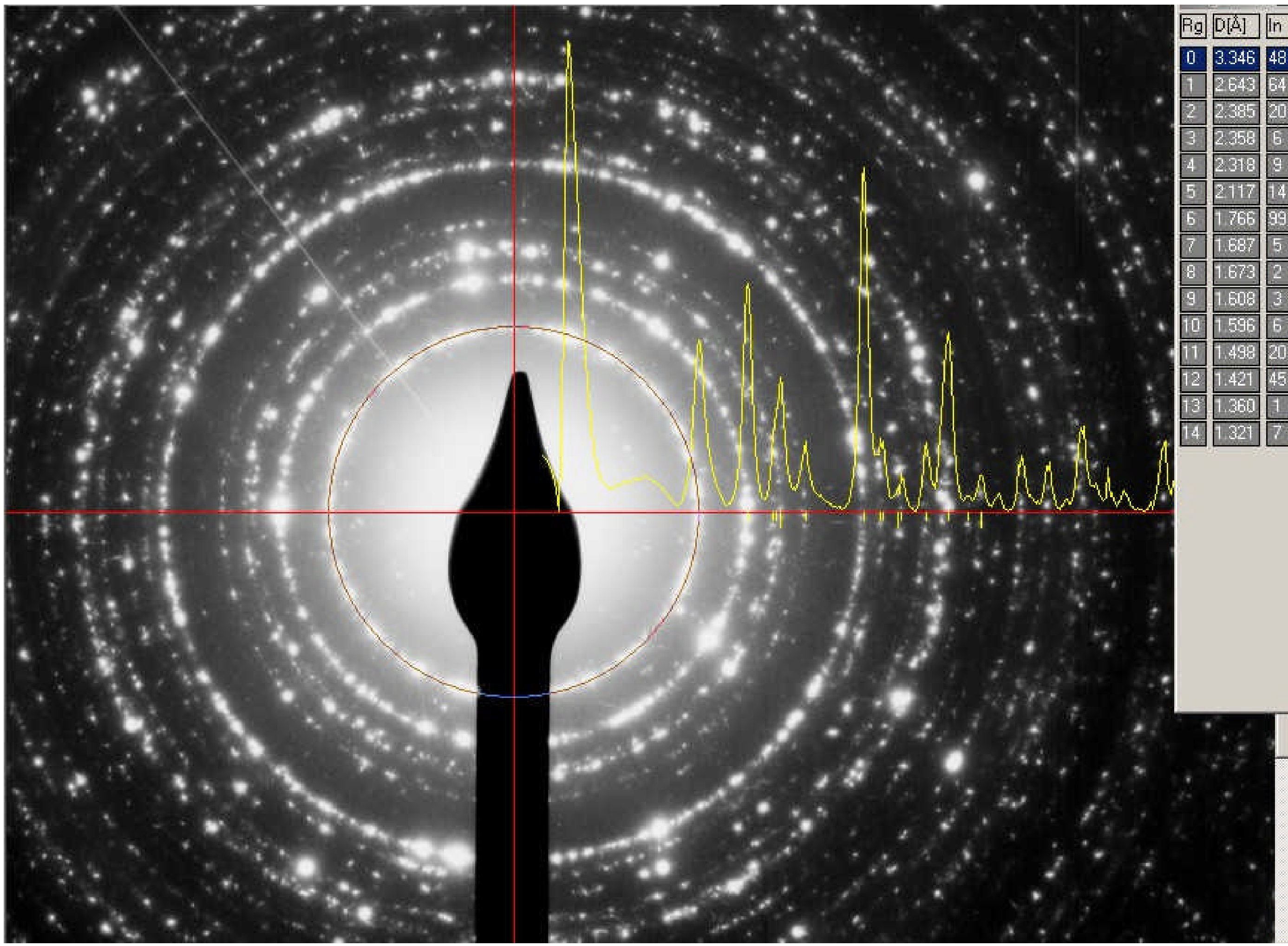


If a $h_0k_0l_0$ diffraction from a known structure can be determined in a diffraction pattern and its distance to the center is measured as u_0, for any other diffraction with distance u to the center, the lattice spacing d is given by:

$d = u_0 d_{h0k0l0}/u$

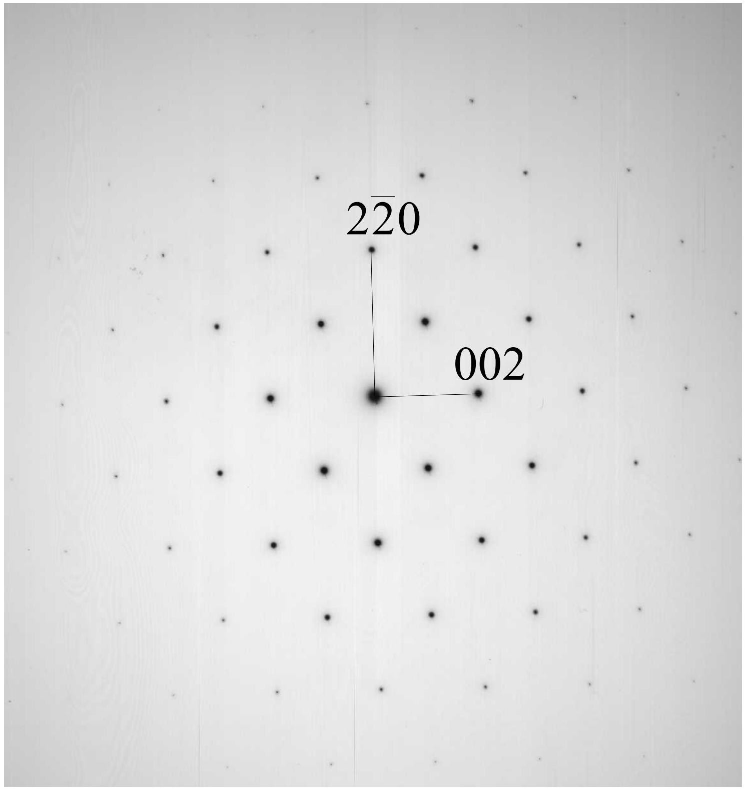
Electron diffraction

Indexing of a ring pattern



Electron diffraction

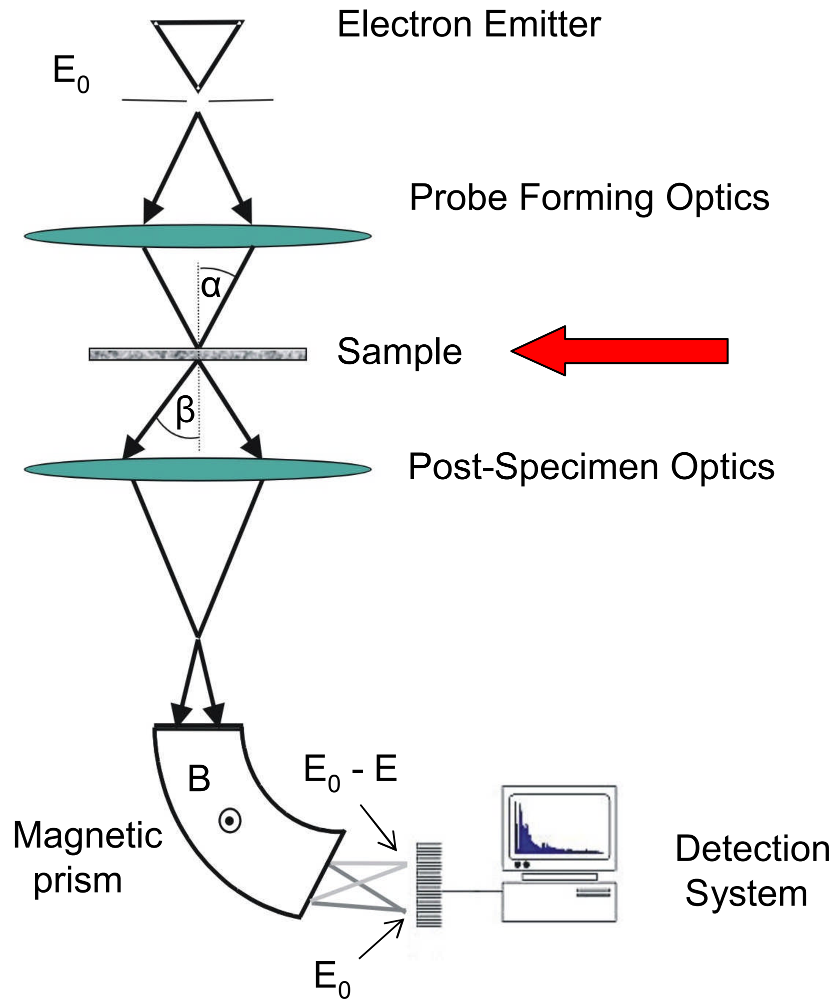
Indexing of a single crystal pattern



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

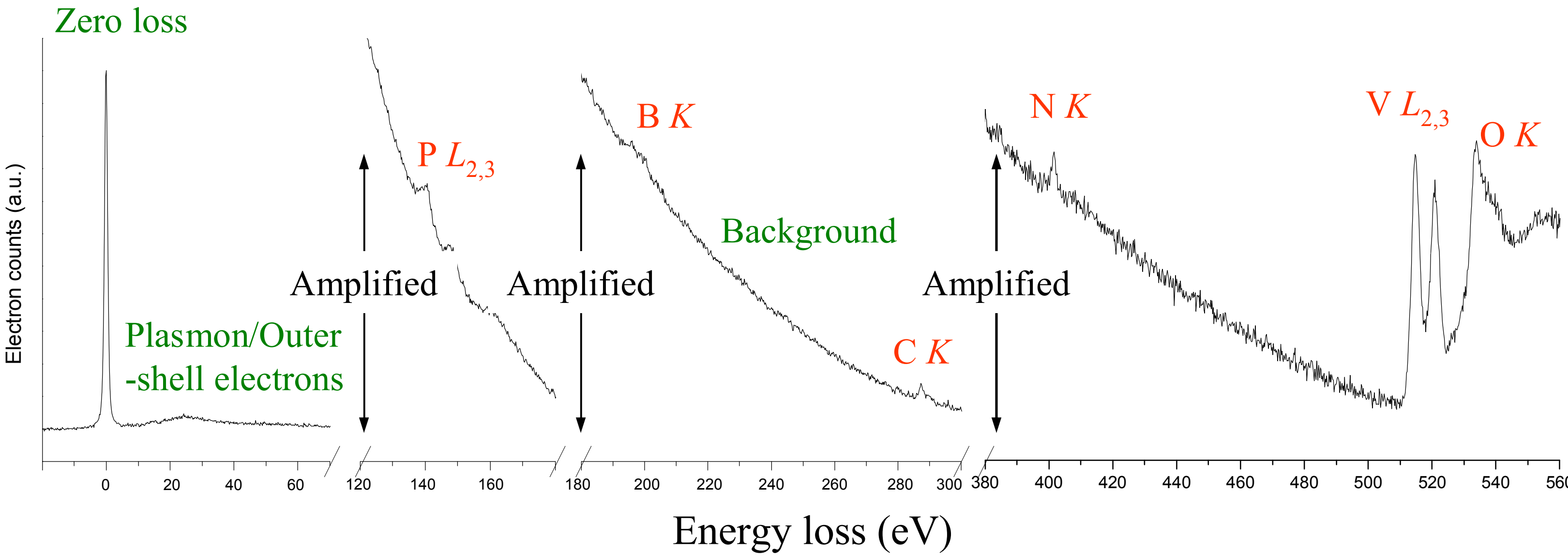
Cubic ZrO_2 (fluorite structure) on [110] projection

Electron Energy Loss Spectroscopy (EELS)



EELS

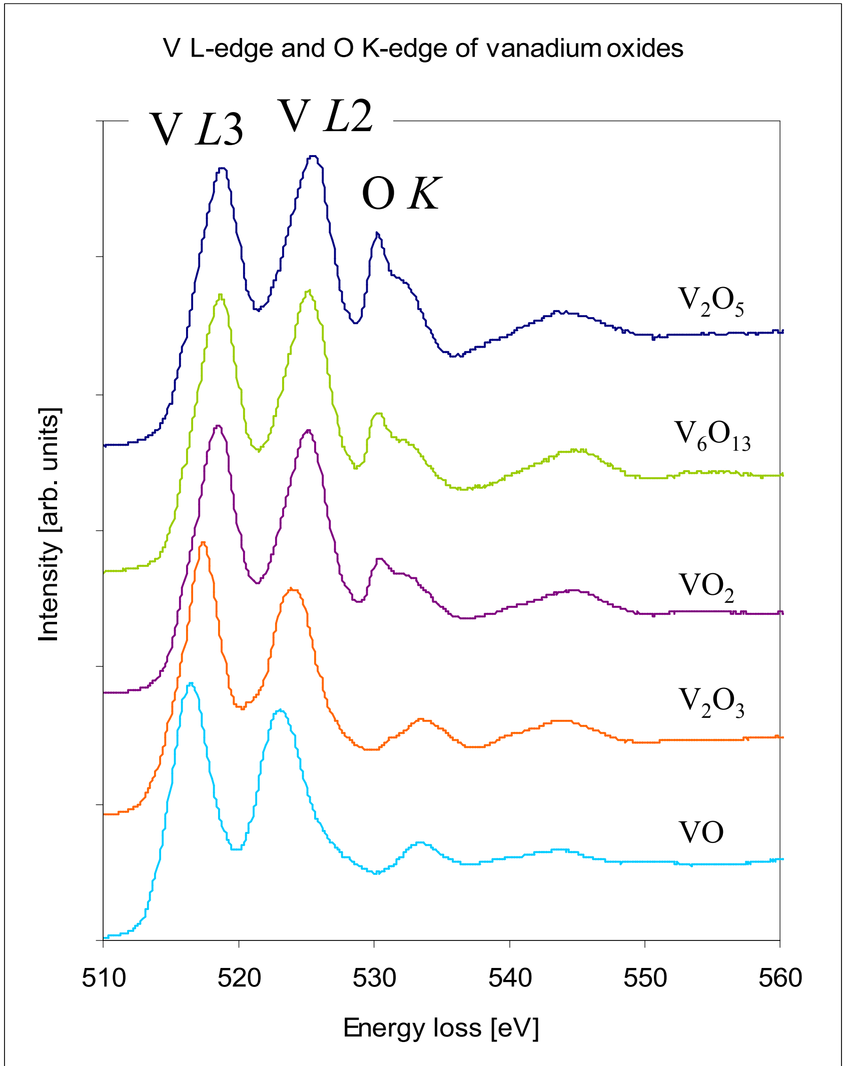
EELS



- -zero-loss peak
- -plasmon peak
- -Inner-shell ionization edges, low intensity
- -Near edge structure on top of edges
- -background
- -Plural scattering

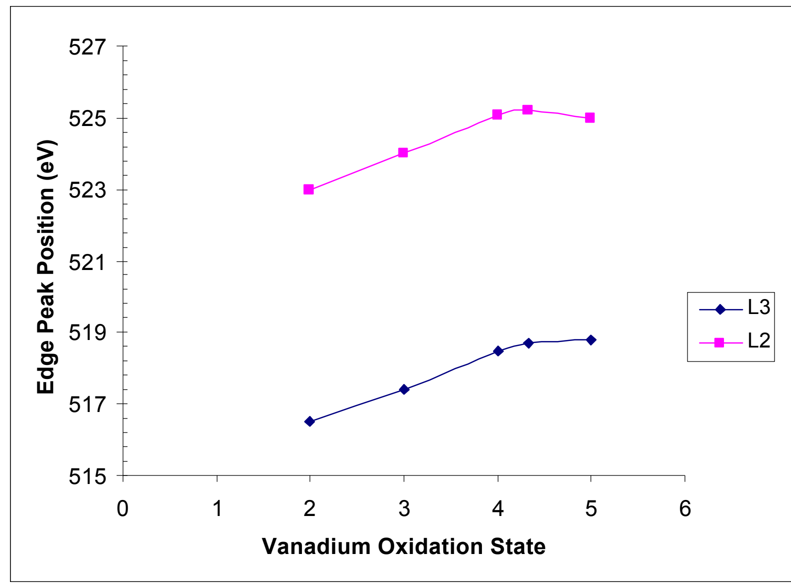
EELS

ELNES as "fingerprints"



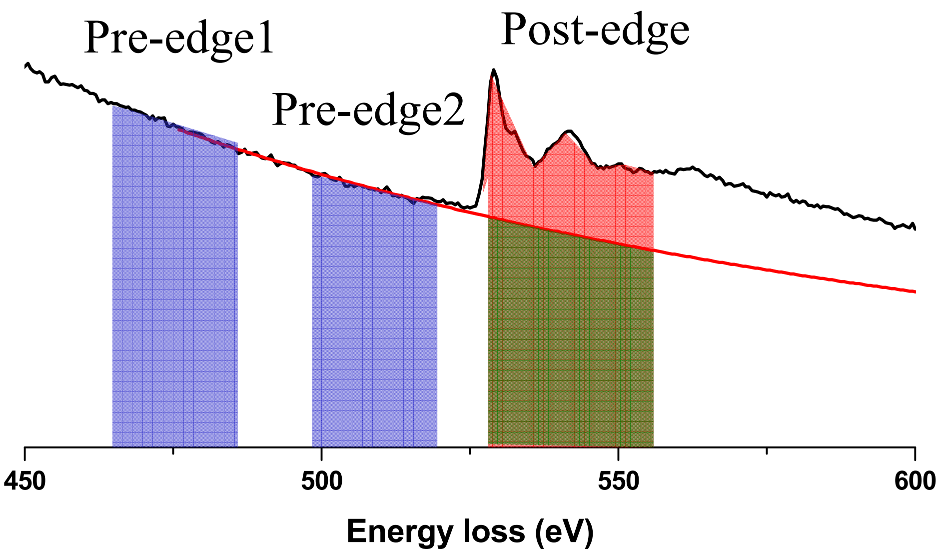
ELNES of Vanadium Oxides

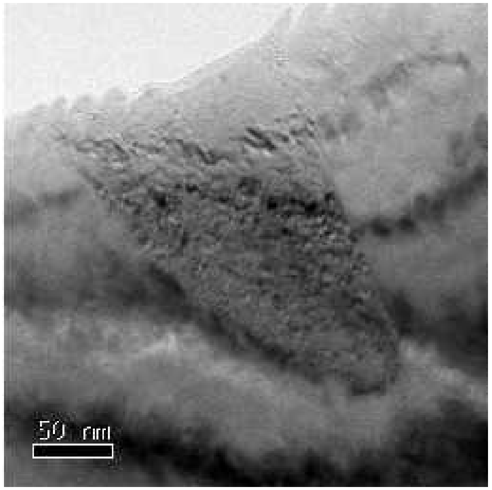
Correlation of peak positions of the vanadium L-edges with the oxidation sates of vanadium atoms in various vanadium oxides



EELS

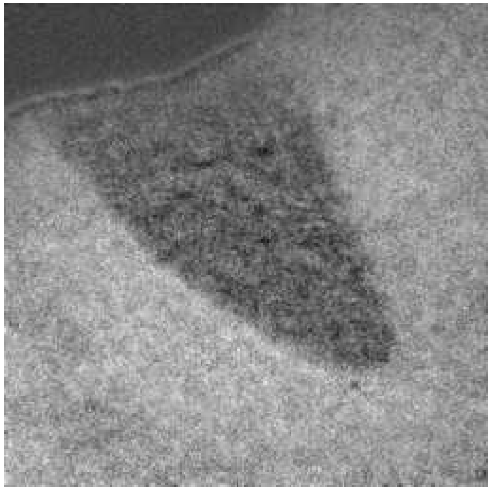
Element mapping



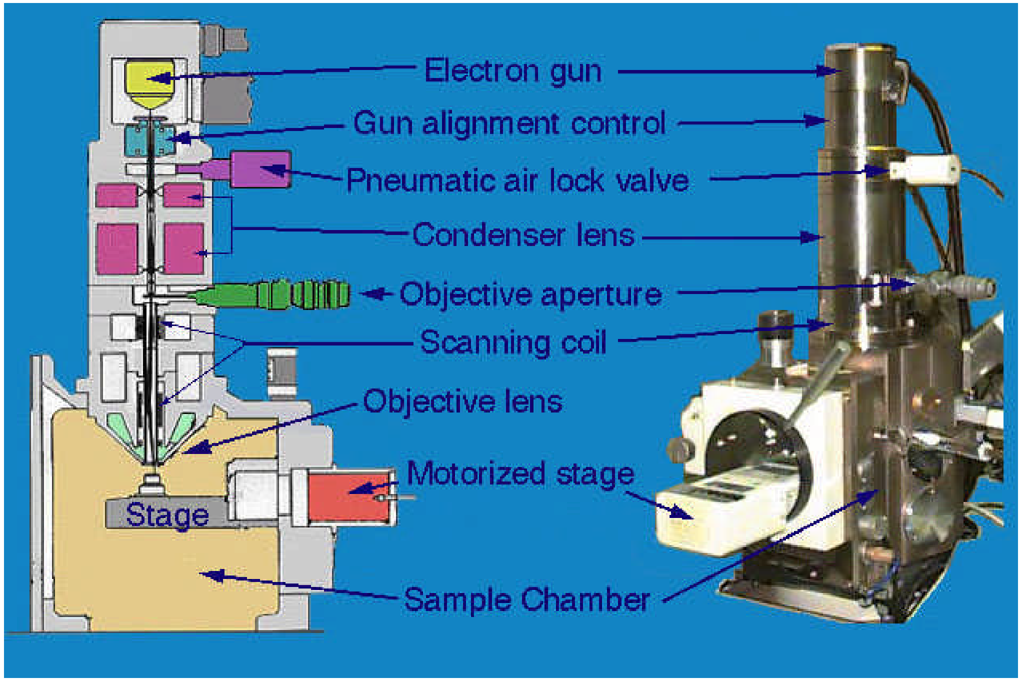


TEM image of ZrN/ZrO_2

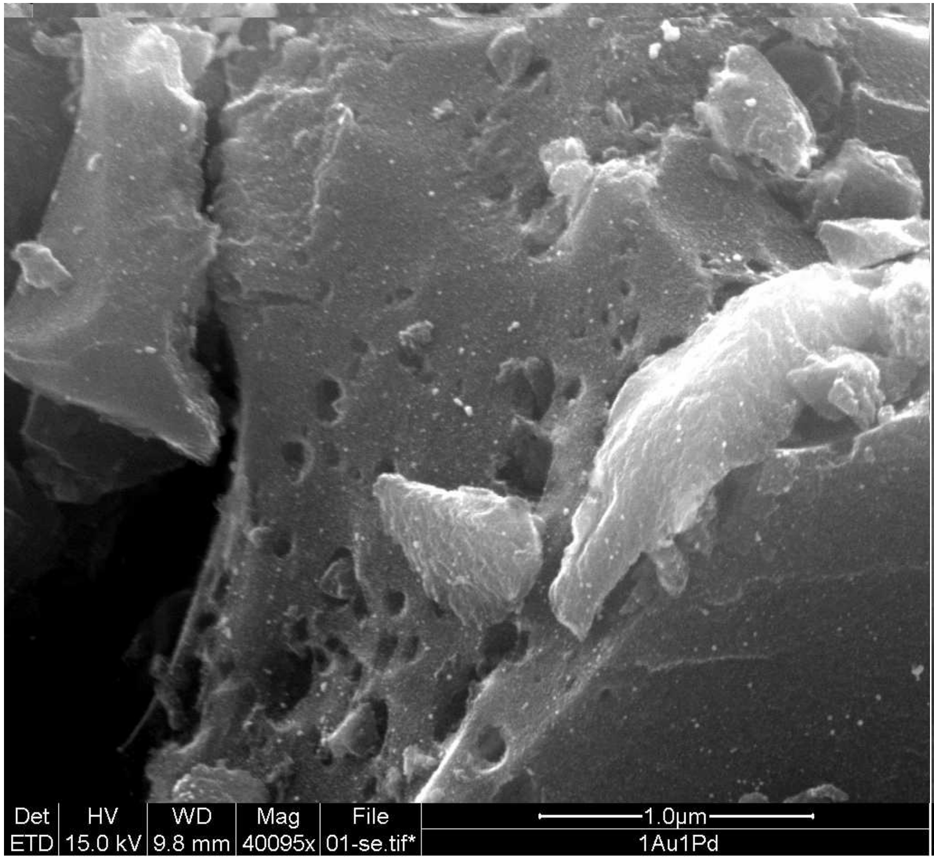
Oxygen map



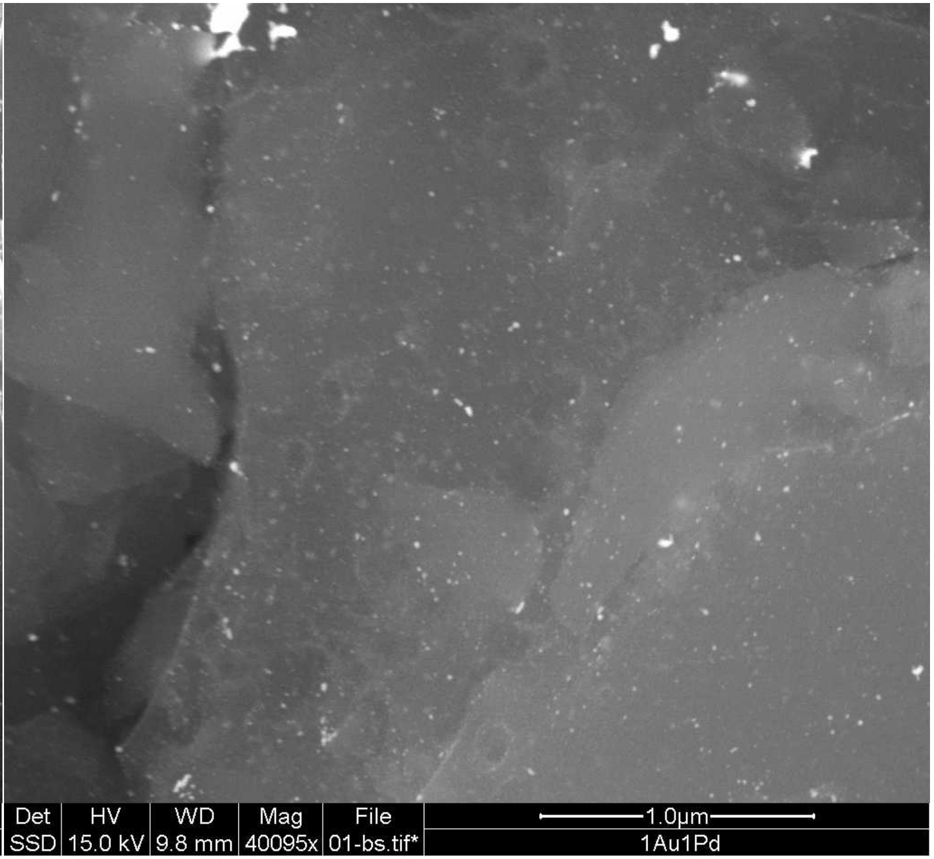
SEM


Electron gun
Gun alignment control
Pneumatic air lock valve
Condenser lens
Objective aperture
Scanning coil
Objective lens
Motorized stage
Stage
Sample Chamber

SEM

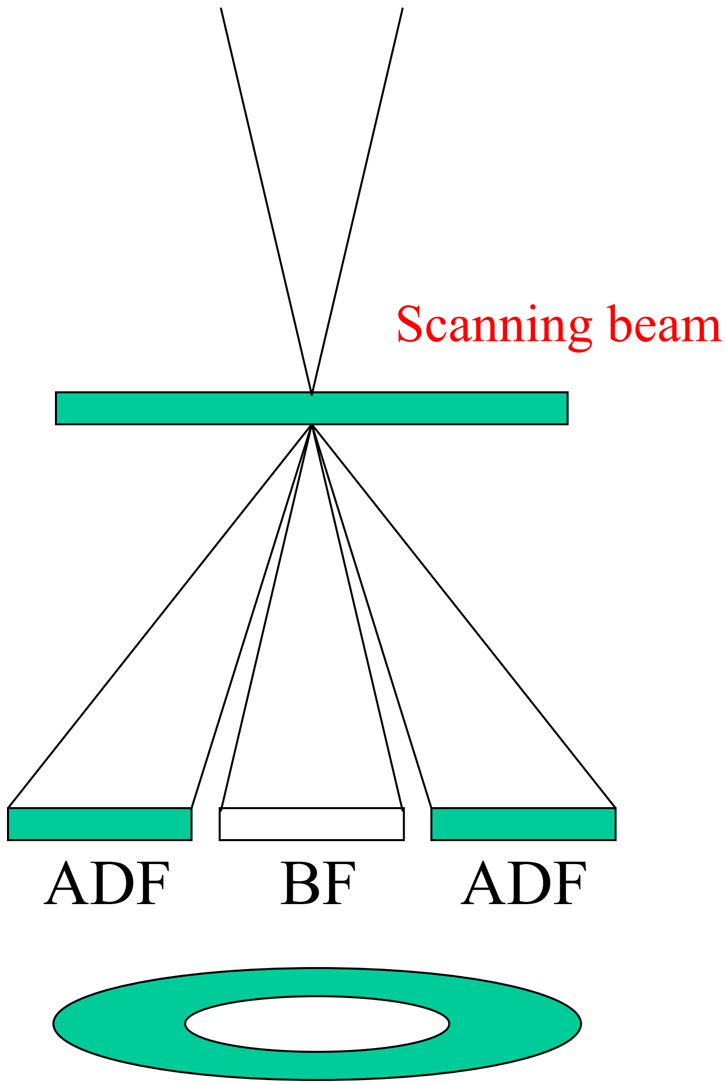


Secondary electron

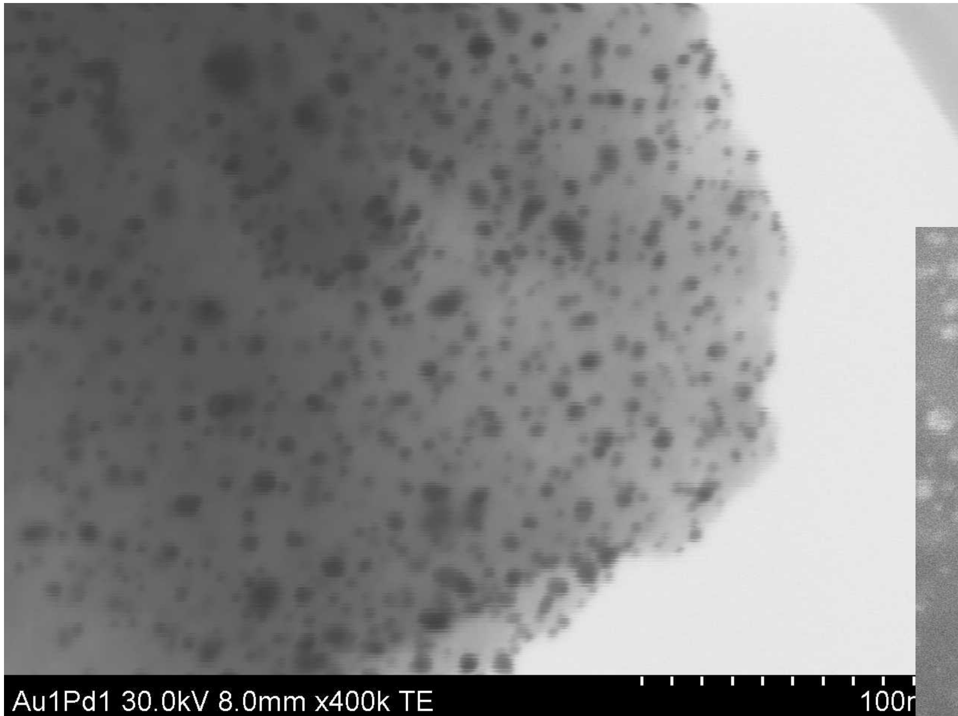


Back scattered electron

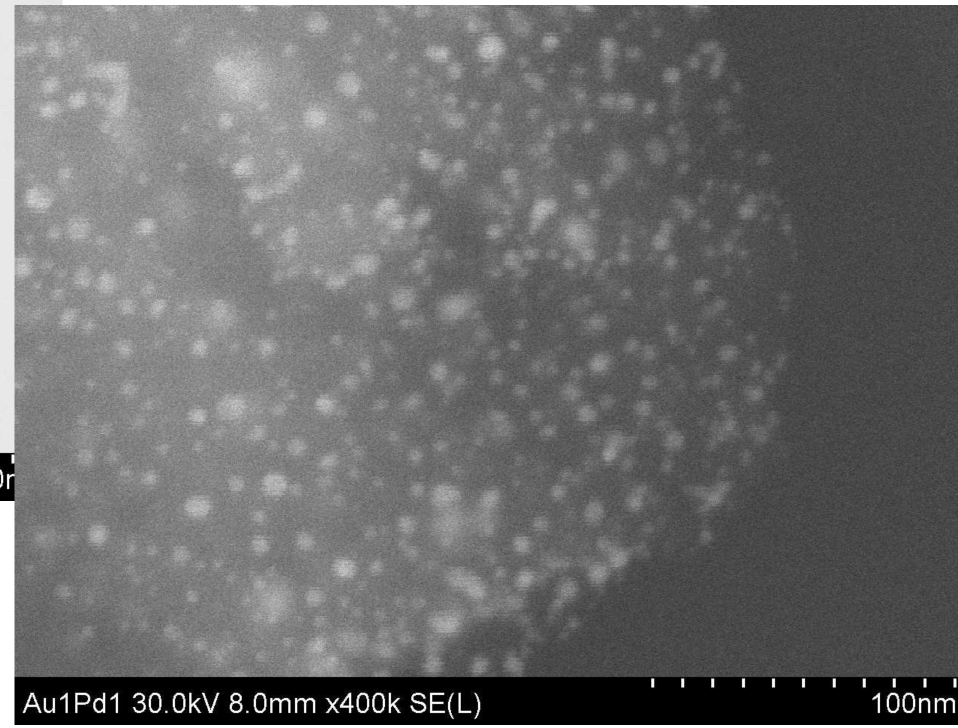
STEM



STEM

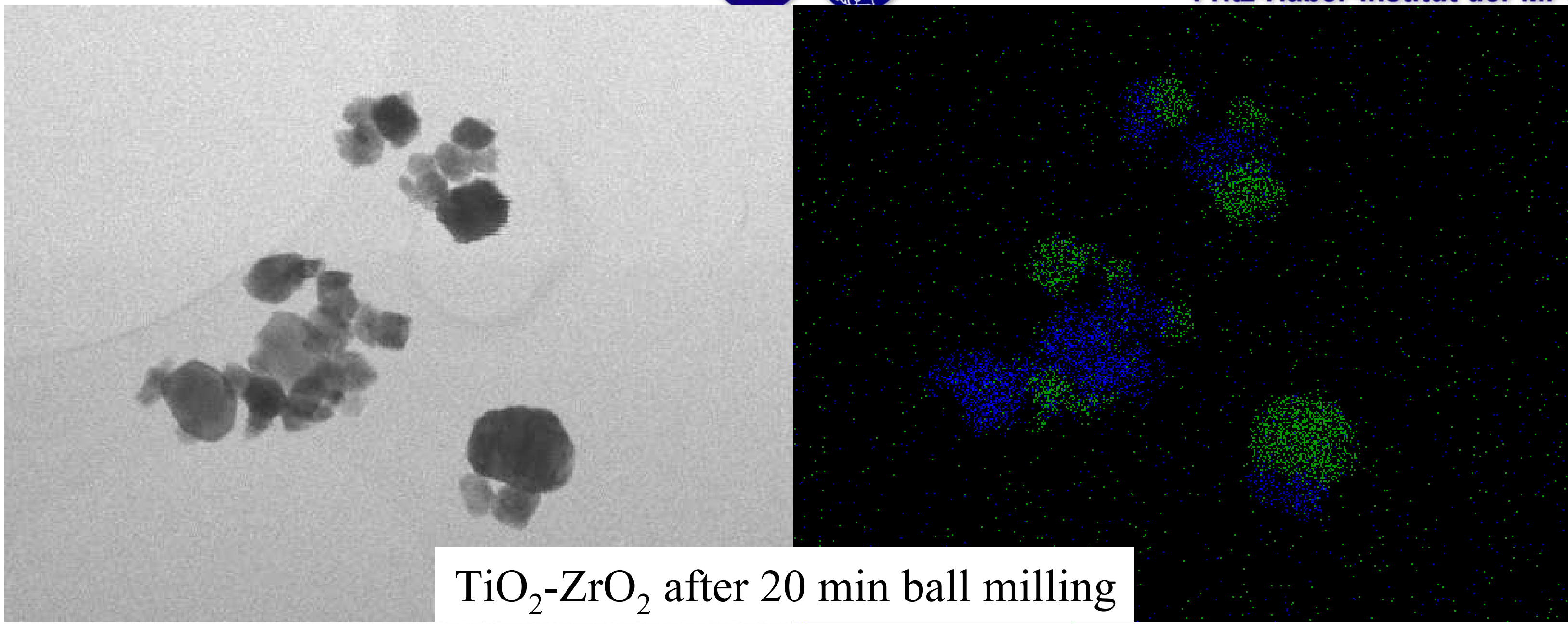

Au1Pd1 30.0kV 8.0mm x400k TE
100n

BF

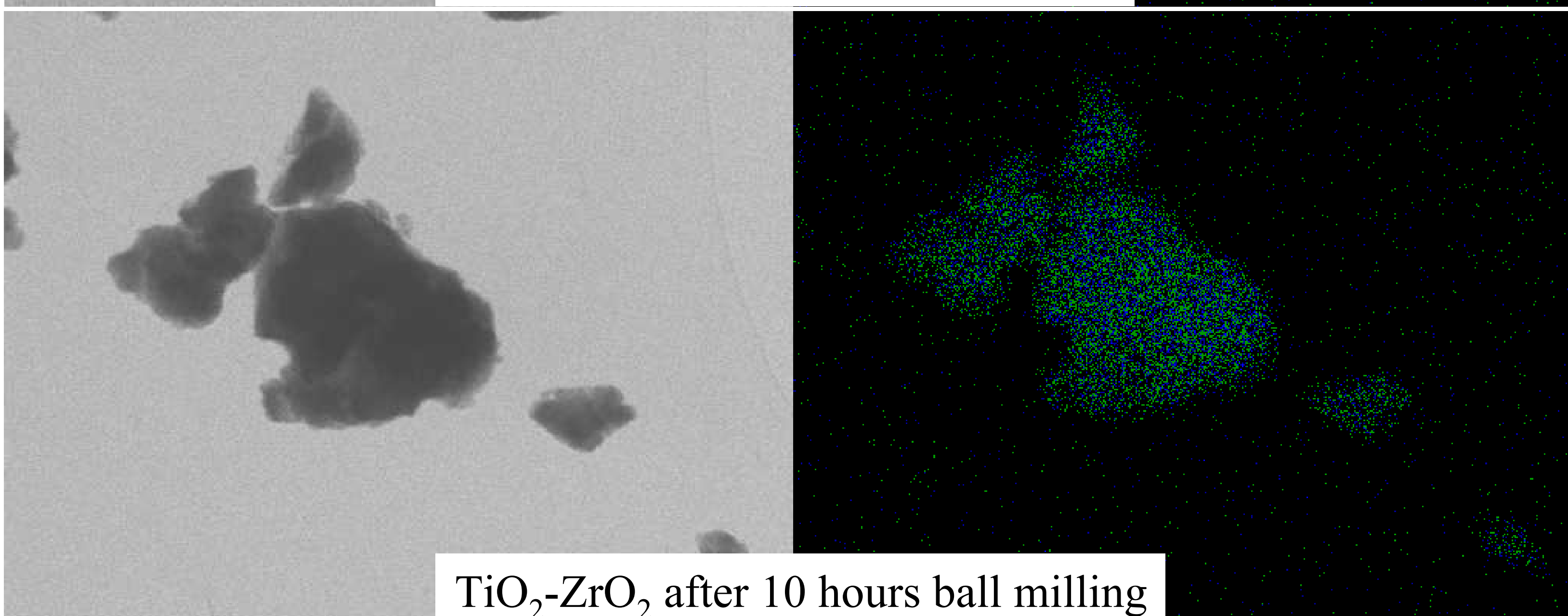

Au1Pd1 30.0kV 8.0mm x400k SE(L)
100nm

DF

STEM+EDX



TiO_2-ZrO_2 after 20 min ball milling



TiO_2-ZrO_2 after 10 hours ball milling

Application in catalytic systems

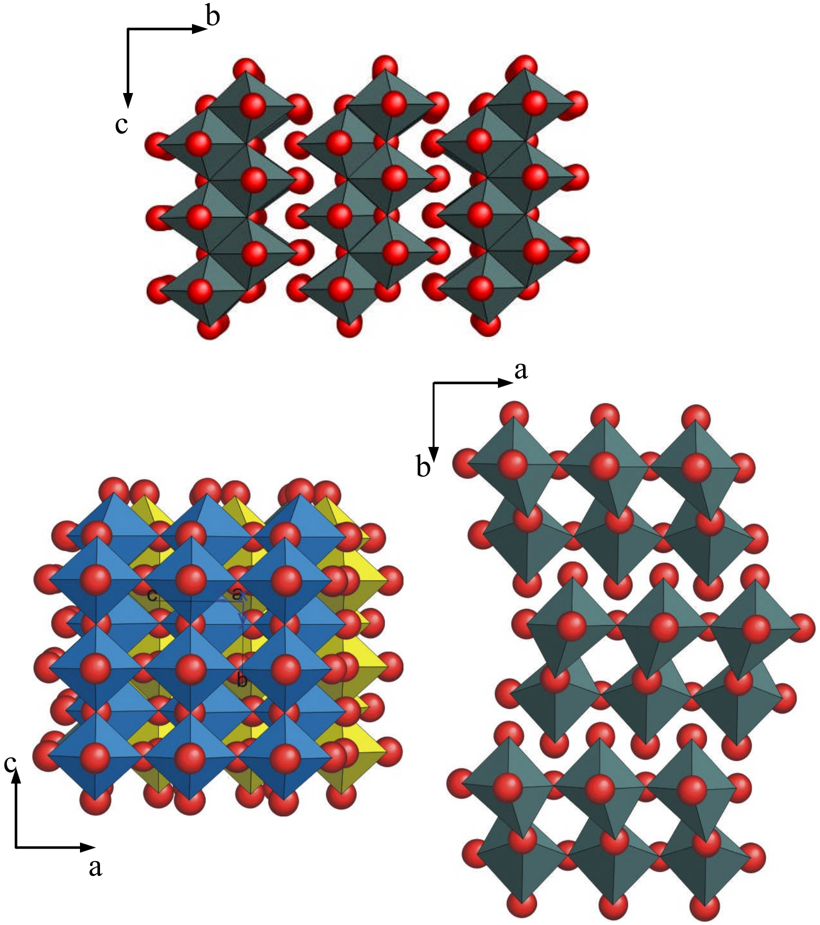
Important heterogeneous catalysts	Information of interests
Supported metal	particle size effects; metal-substrate interaction; structural change under chemical treatments
Transition metal oxide	reduction behavior; defects structures
Zeolites (porous structure)	3D structure; intergrowth of different zeolitic structures; guest species inside a zeolitic host
Carbon nanofibers as support	structure and growing mechanisms

Application in catalytic systems

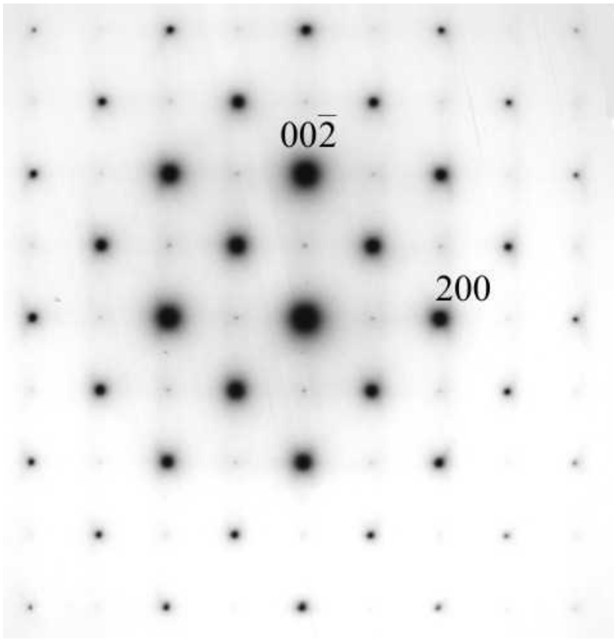
Reduction of MoO_3 induced by electron beam irradiation

Reduction of MoO_3 by electron beam irradiation

Department of Inorganic Chemistry
Fritz-Haber-Institut der MPG



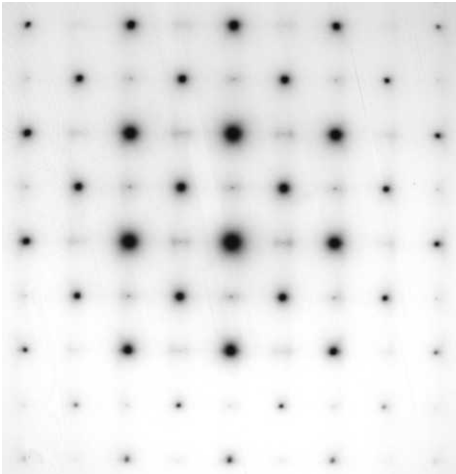
Structure of MoO_3



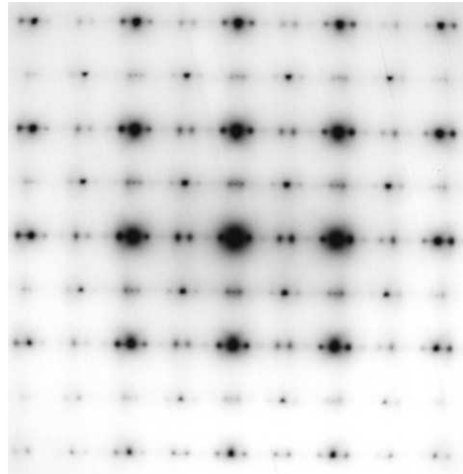
Diffraction of MoO_3 on [010] projection

Low electron current density

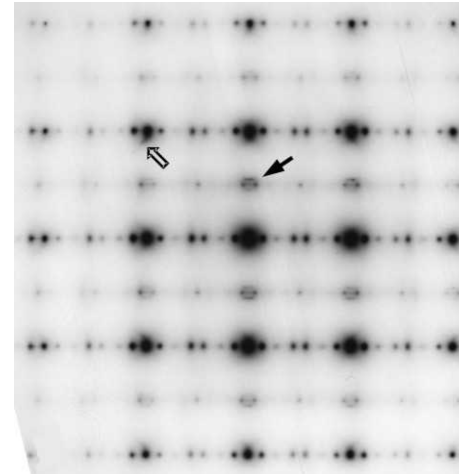
Department of Inorganic Chemistry
Fritz-Haber-Institut der MPG



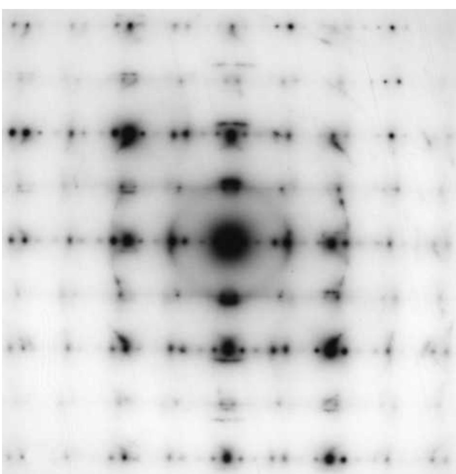
After irradiation of 10 min



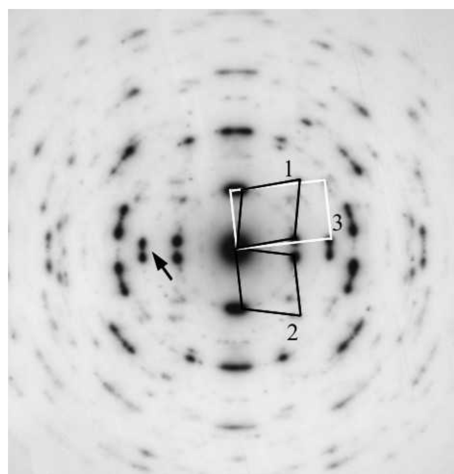
60 min



120 min



200 min

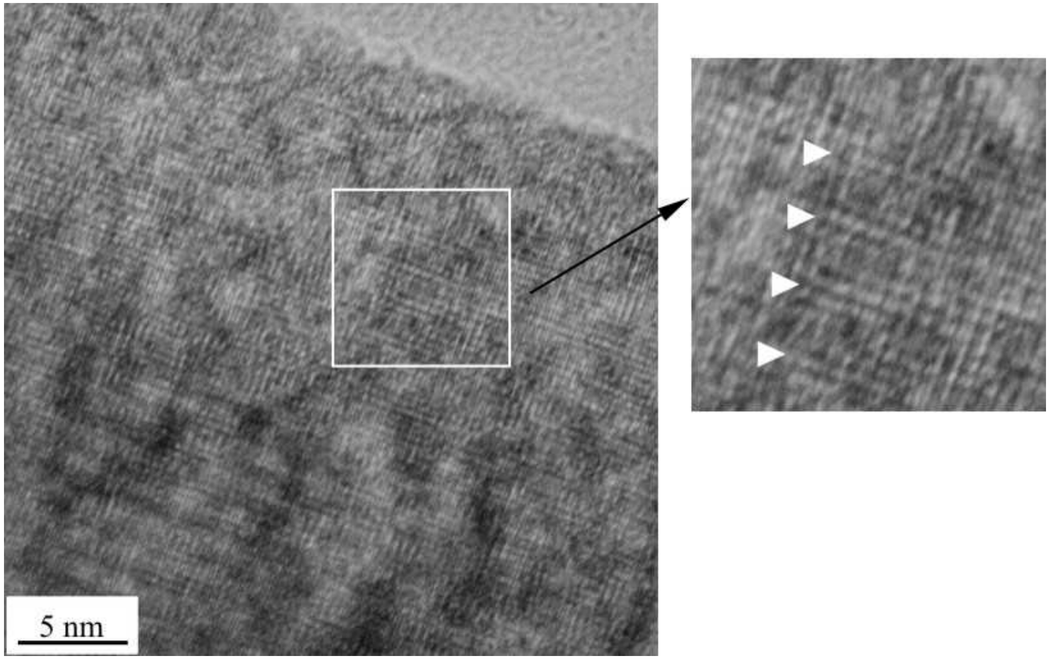


360 min

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.

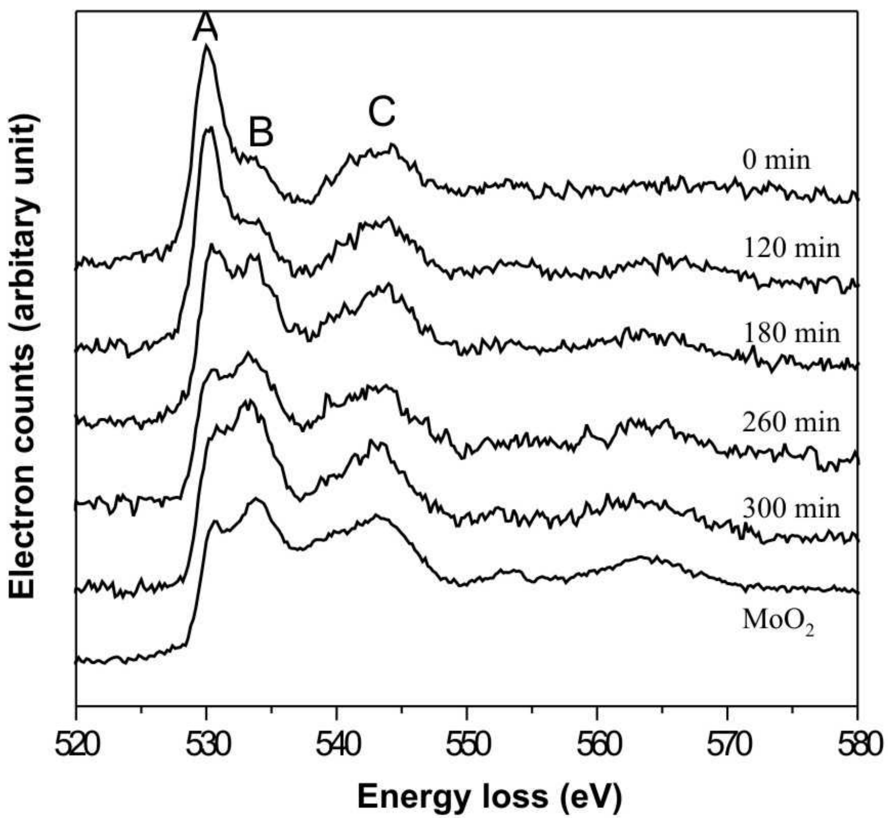
Low electron current density

HRTEM image showing contrast from CS structure, formed at the early stage of reduction.



Low electron current density

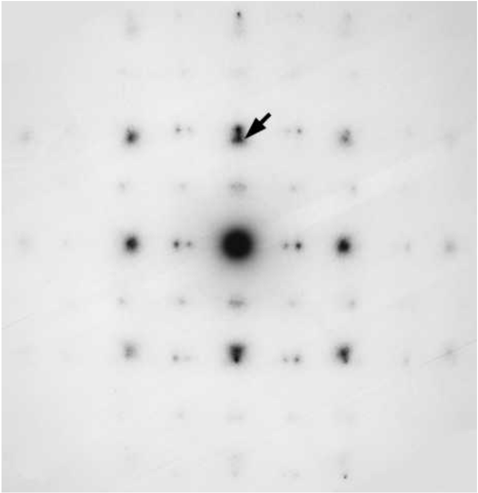
ELNES on O *K*-edge



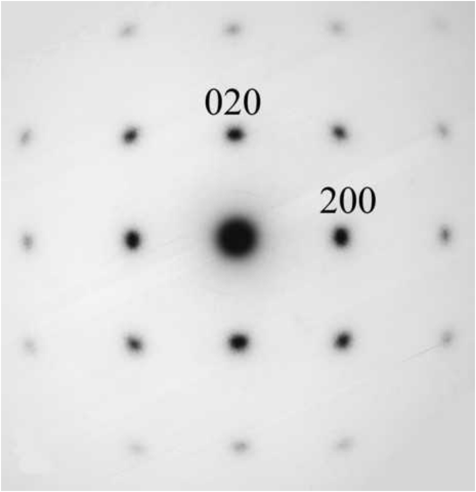
MoO_3: $(MoO_6)^{6-}$ octahedral configuration

MoO_2: $(MoO_6)^{8-}$ octahedral configuration
t_{2g} anti-bonding orbitals are partially filled by ***two*** electrons.

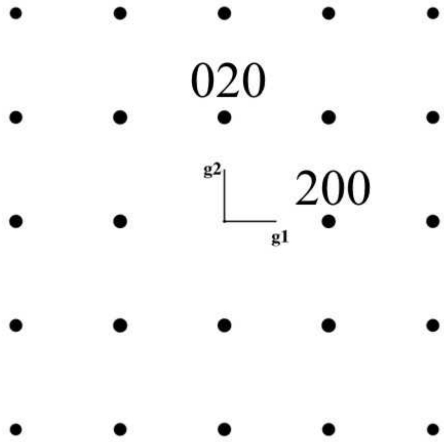
High electron current density



After irradiation of 10 min

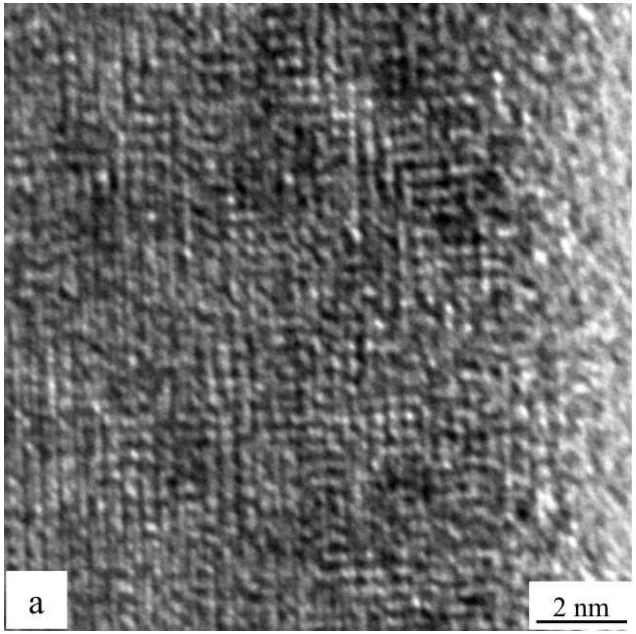


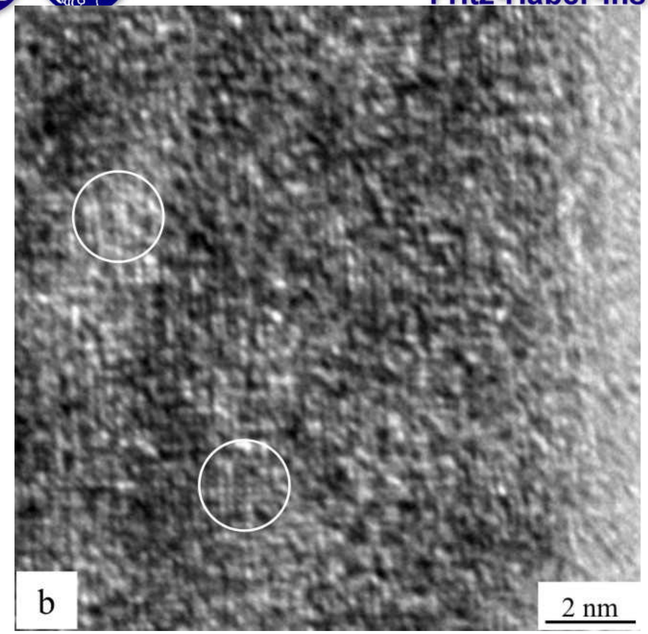
40 min



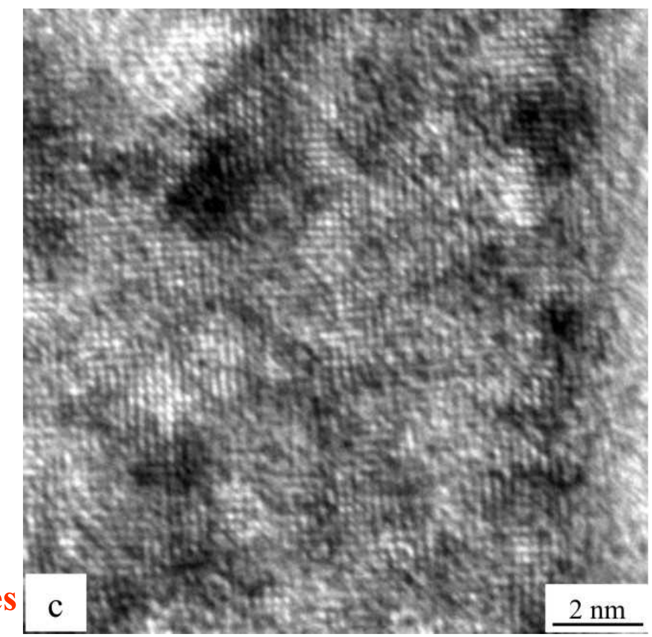
MoO (a = b = c = 4.08 Å) with NaCl structure? → Simulation

High electron current density



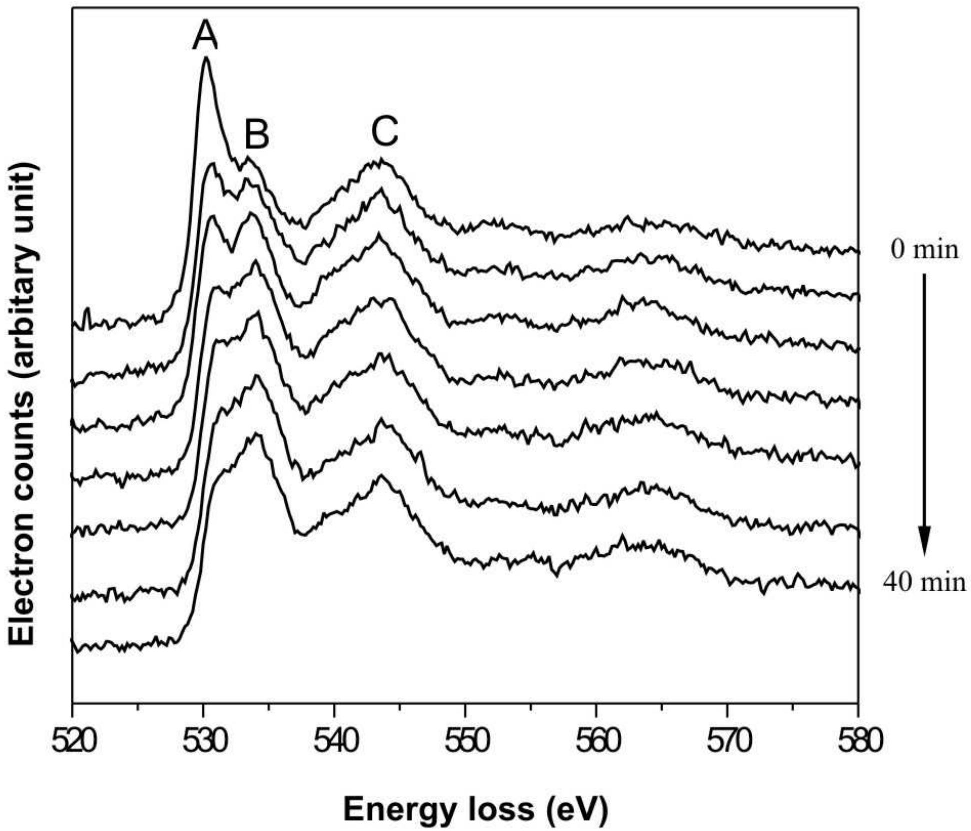


HRTEM images for evolution of Mo oxide under electron irradiation



High electron current density

ELNES on O *K*-edge



MoO_3: $(MoO_6)^{6-}$ octahedral configuration

MoO: $(MoO_6)^{10-}$ octahedral configuration t_{2g} anti-bonding orbitals are partially filled by ***four*** electrons.

Summary

- **Importance of model catalyst — simplifying complex system; facilitating analytic techniques; aware of the gap between the TEM environment and the "real" condition.**

- **Be sure that TEM observation on the *local* structure is representative to the whole catalyst.**

- **Distinguish electron induced effect from intrinsic features of catalyst**

Literature

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Transmission electron microscopy : physics of image formation and microanalysis

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