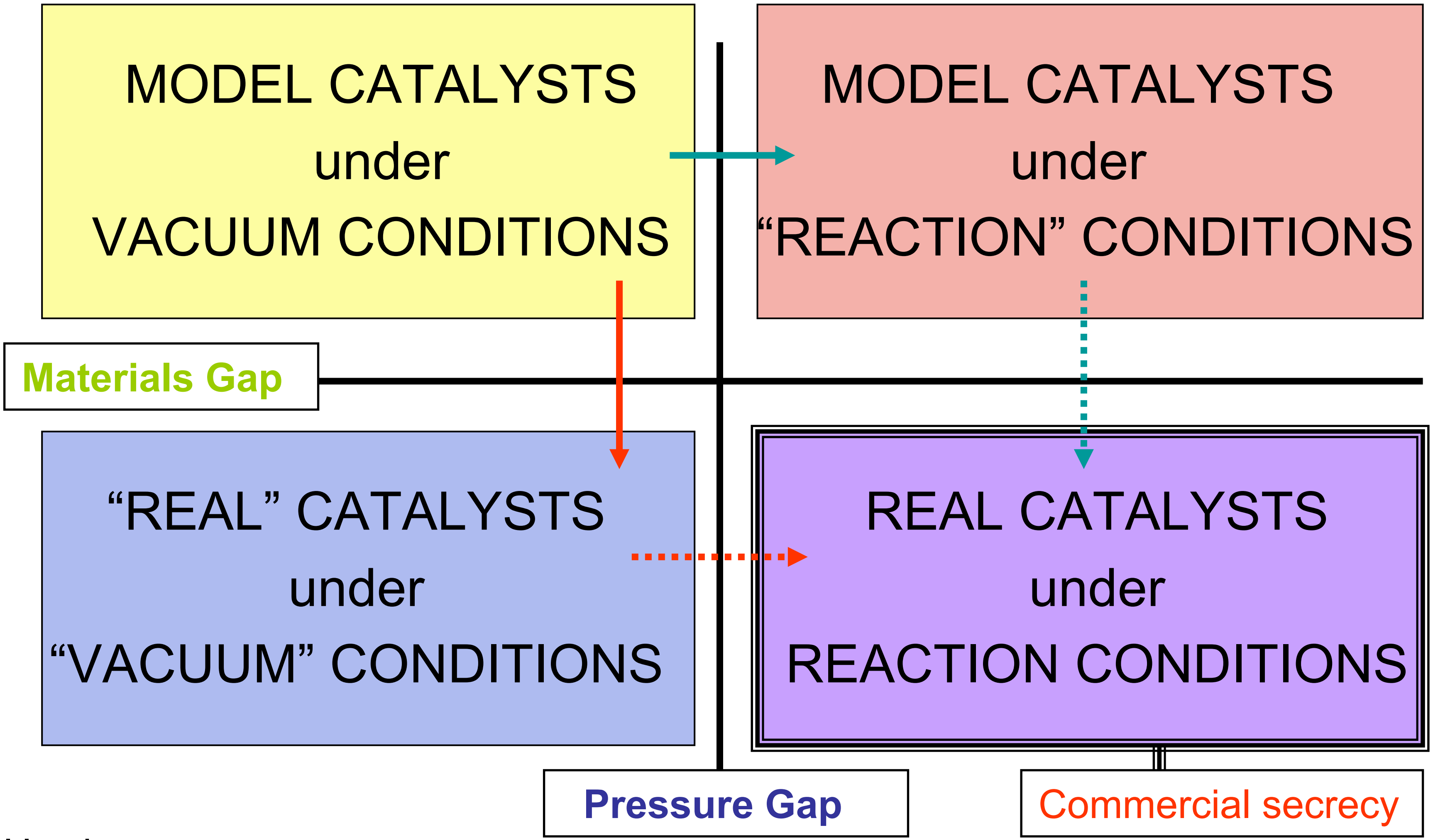
Electron Microscopy in Heterogeneous Catalysis Research

Dangsheng Su

Aims and Compromises for Catalyst Studies



A. Howie

Characterisation Methods for "Real" Catalysts under Vacuum Conditions

Auger electron spectroscopy

X-ray and UV photoelectron spectroscopy

Rutherford backscattering

Mass spectrometry with secondary ions or neutrals

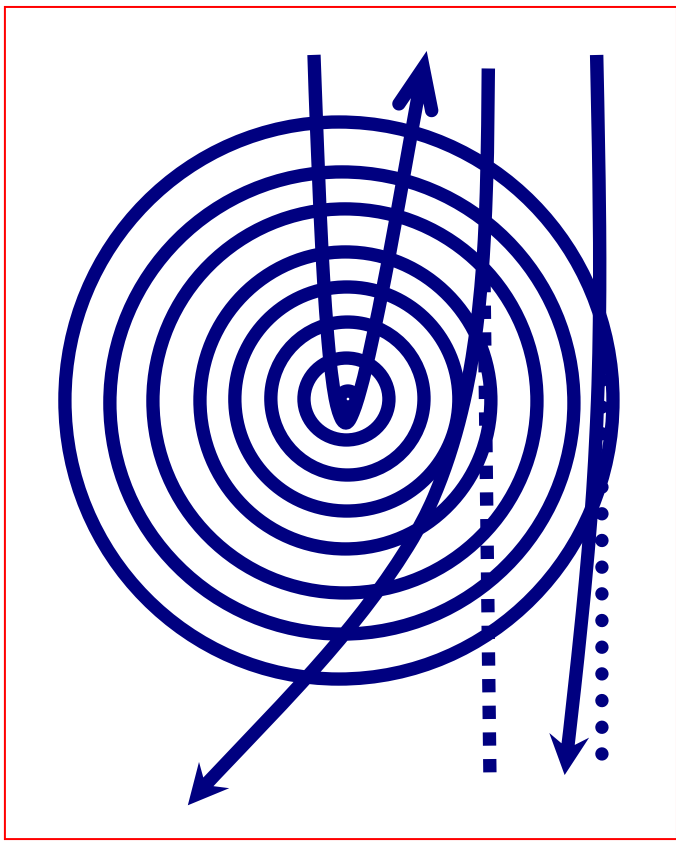
Scanning electron microscopy

TEM and STEM including EELS → ETEM

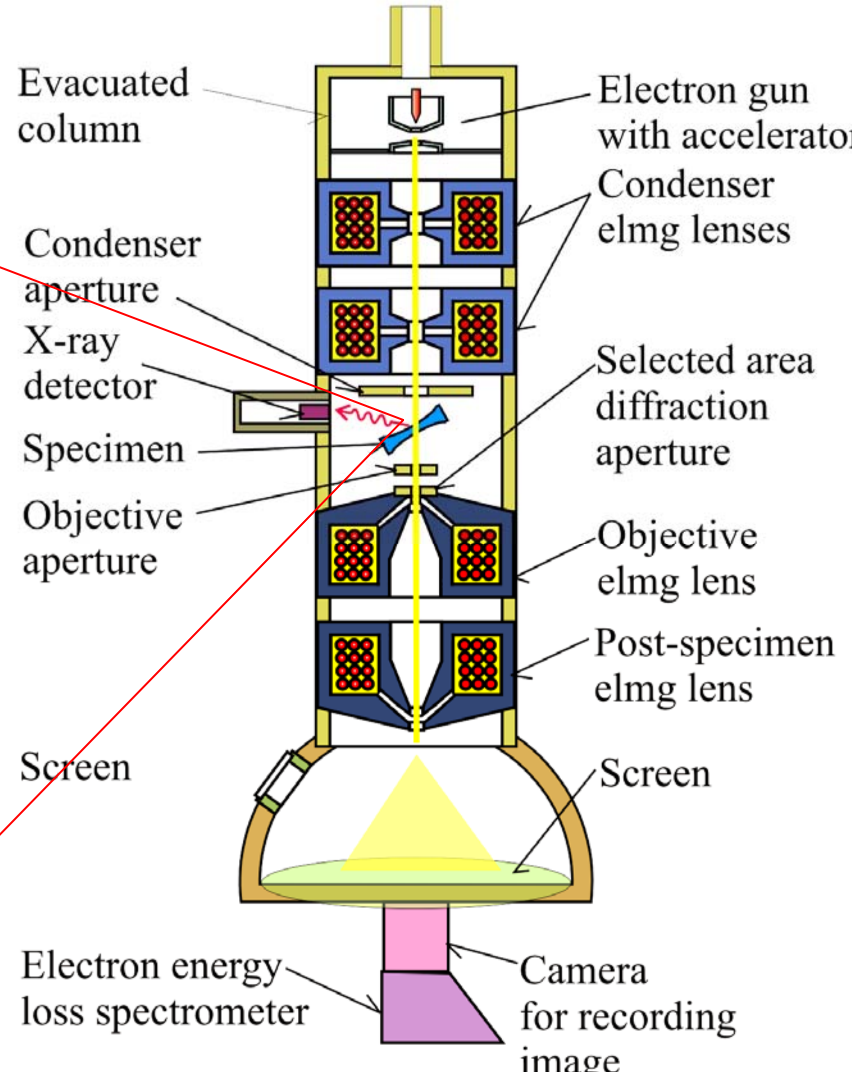
A. Howie

Transmission electron microscope

Interaction of electron with your samples



Electron scattering



Advanced TEM Techniques

Transmission Electron Microscopy

<u>Conventional TEM</u>

BF/DF/SAD

- Morphology
- Phase Distribution
- Defect Analysis
- *in situ*-Experiments
  - heating
  - cooling
  - deformation

<u>Spectroscopy and CBED</u>

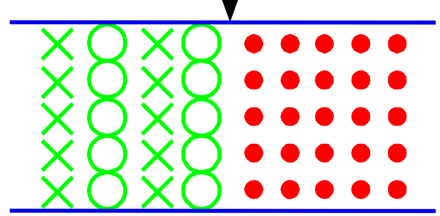
(high spatial resolution)

- EDS
  - compositions
  - gradients
- EELS
  (EXELFS, ELNES)
  -compositions
  -gradients
  -electronic states

<u>Lattice Imaging</u>

HREM

- Structure of materials
  -oxides
  -HT superconductors
- Structure of defects
  -interfaces
  -dislocations



Information on chemistry and bonding

Complicated evaluation:
lens aberration of HREM
scattering within specimen

Experimental studies
↔
Image simulations

Resolution < 1 Ǻ with Cs corrector

M. Rühle

Advanced EM in Catalysis

Why EM

Advanced electron microscopy techniques are the only ones that can provide Information on the individueal nanocomponents of heterogeneous catalysts

XRD, XAS, IR, NMR, XPS provide infromation averaged over millions to trillions of nanocomponets

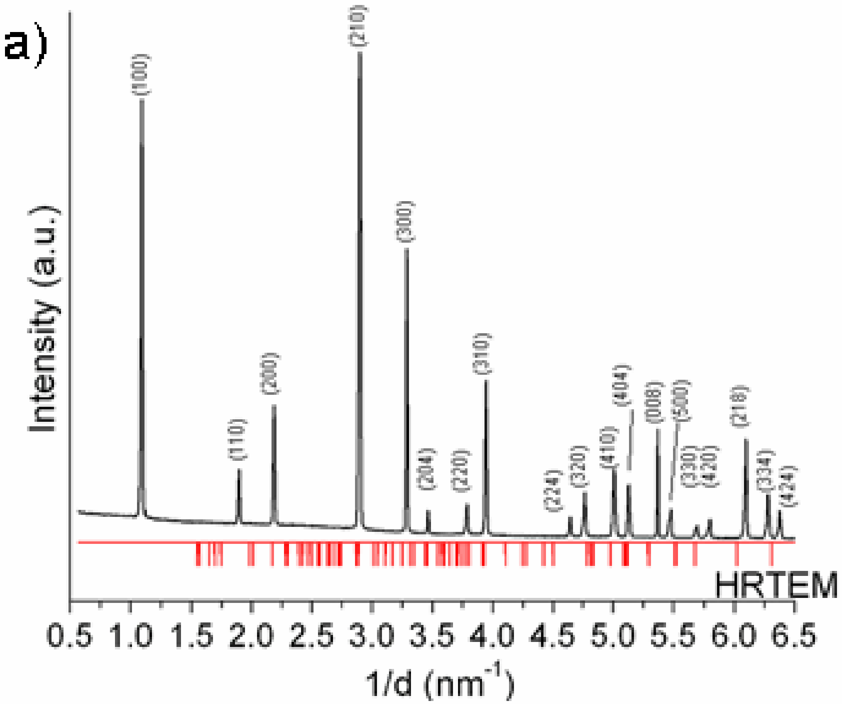
STM, AFM require stringent conditions on the samples to be examined

The versatility of a modern electron microscope

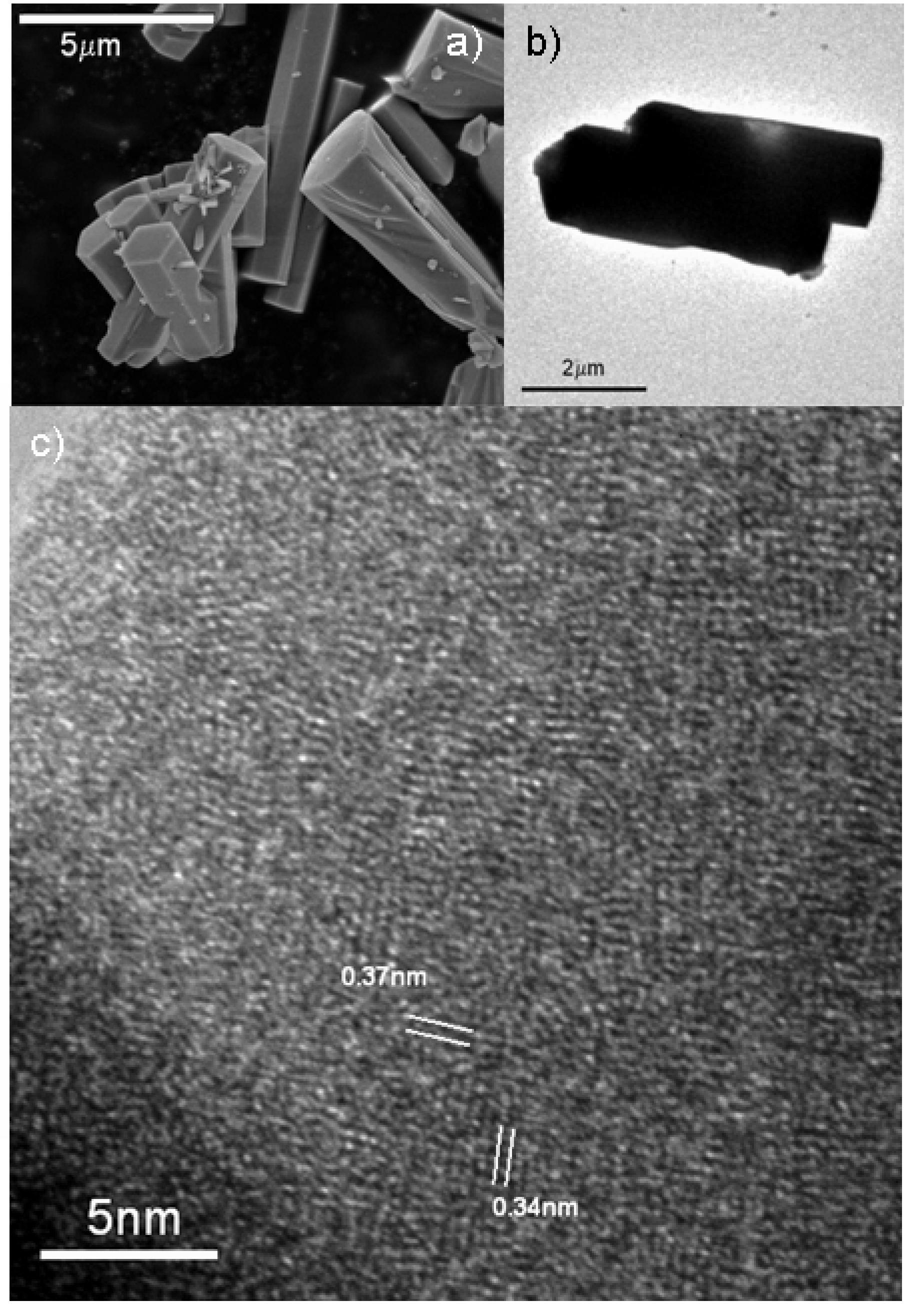
- Atomic resolution structural analysis
- Electron nanodffraction
- High-resolution nanoanalysis by X-ray Energy-Dispersive Specroscopy
- High-resolution nanoanalysis by Electron Energy-Loss Spectroscopy

either simultaneously or sequentially from the same region of the specimen !

TEM: an unique tool to characterize nanostructured materials



Nanostructured binary molybdenum oxide catalyst precursors for propene oxidation



EM in Catalysis

1. **Size, shape, and spatial distribution of the noble metal particles.**

2. **Chemical composition**

3. **Surface structure of the support**

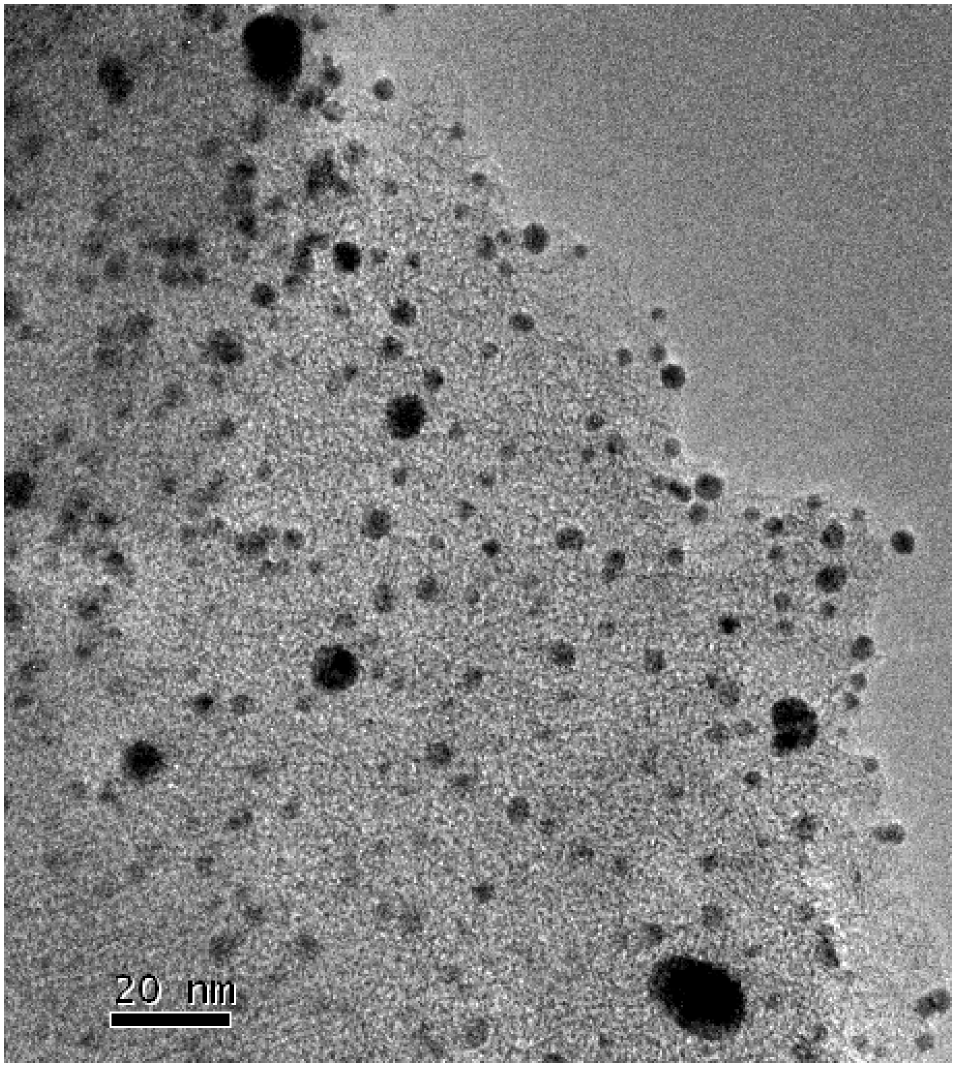
4. **Geometric relationship between metal particles and support**

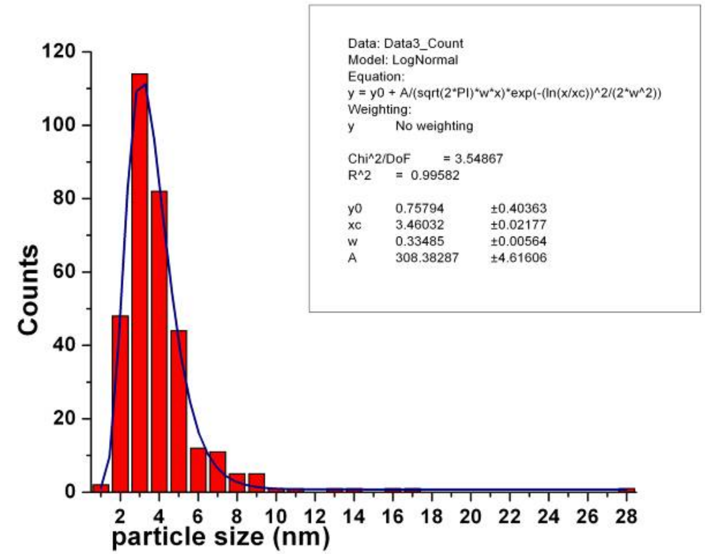
- Before and after reaction

EM in Catalysis

Size distribution and compositional analysis

EM in Catalysis: Size distribution of nanoparticles

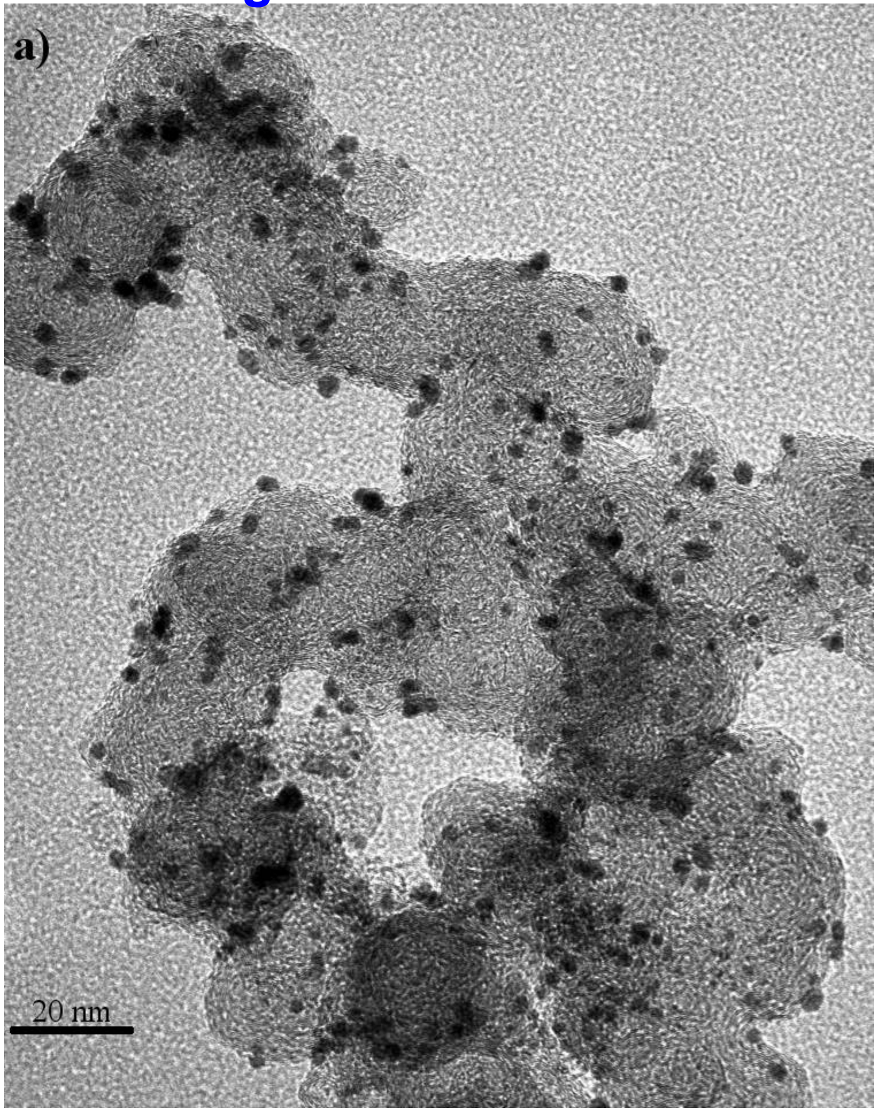




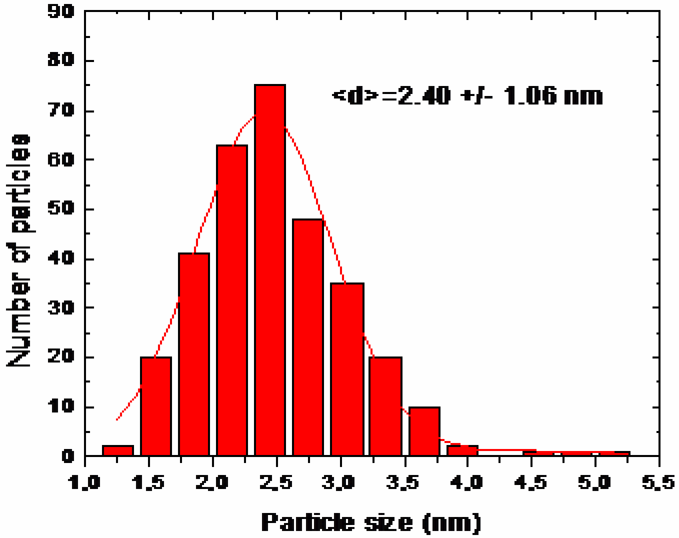
Wang et al, Chem. Commun., 2006, 1956–1958

High-dispersion

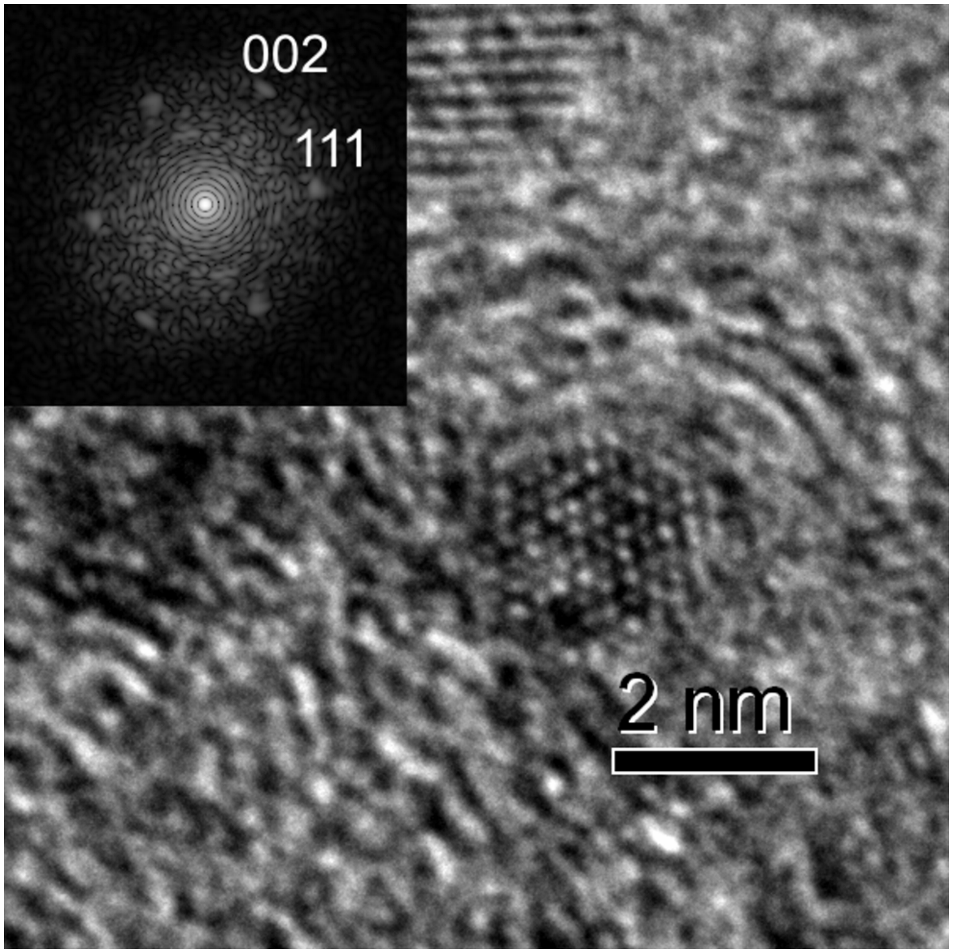
Increasing the tolerance towards methanol using nanoalloys



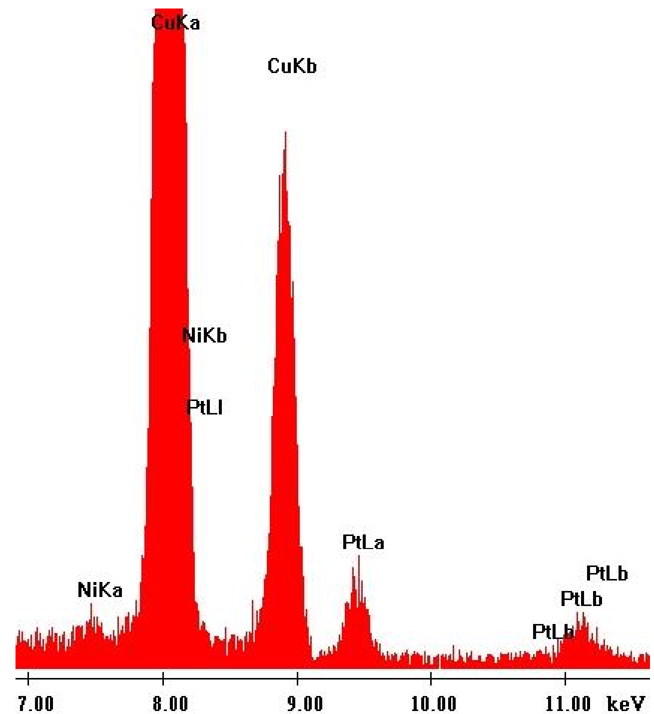
Pt-Co alloy cathode



EM in Catalysis: Size distribution of nanoparticles



Pt-Ni alloy cathode

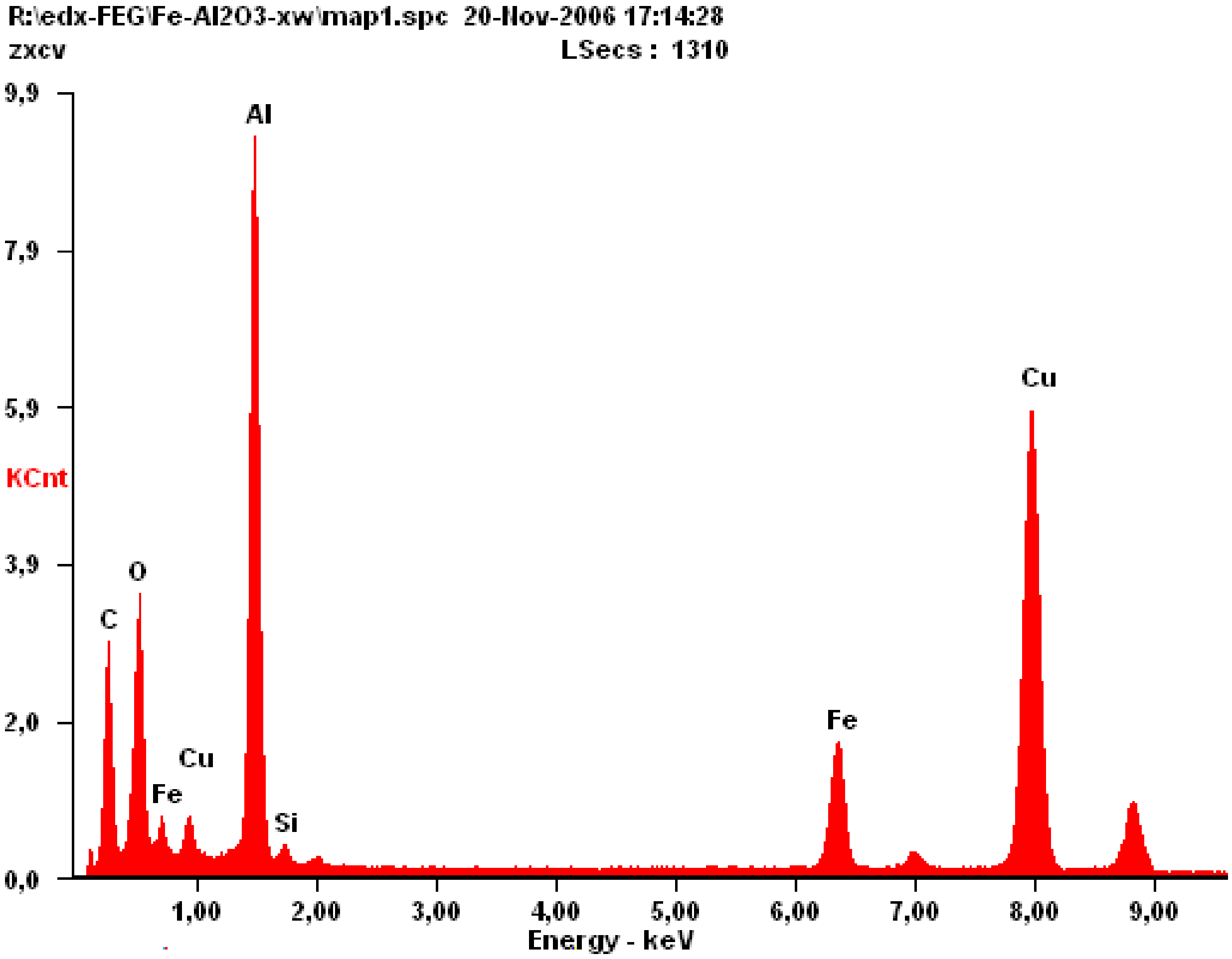


High-dispersion

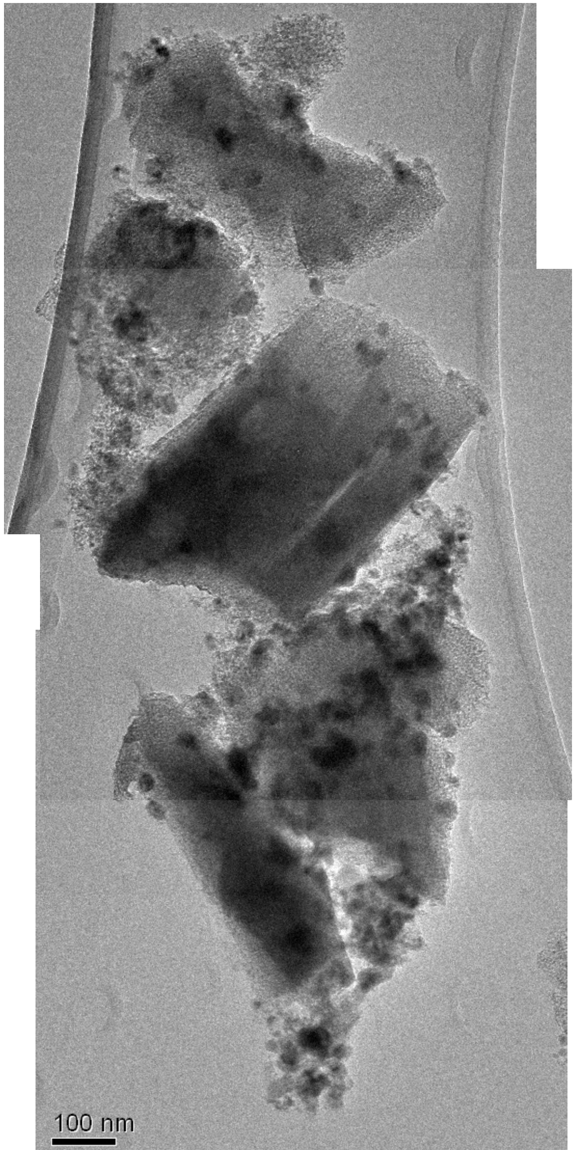
Increasing the tolerance towards methanol using nanoalloys

As-grown Fe/Al_2O_3 catalyst

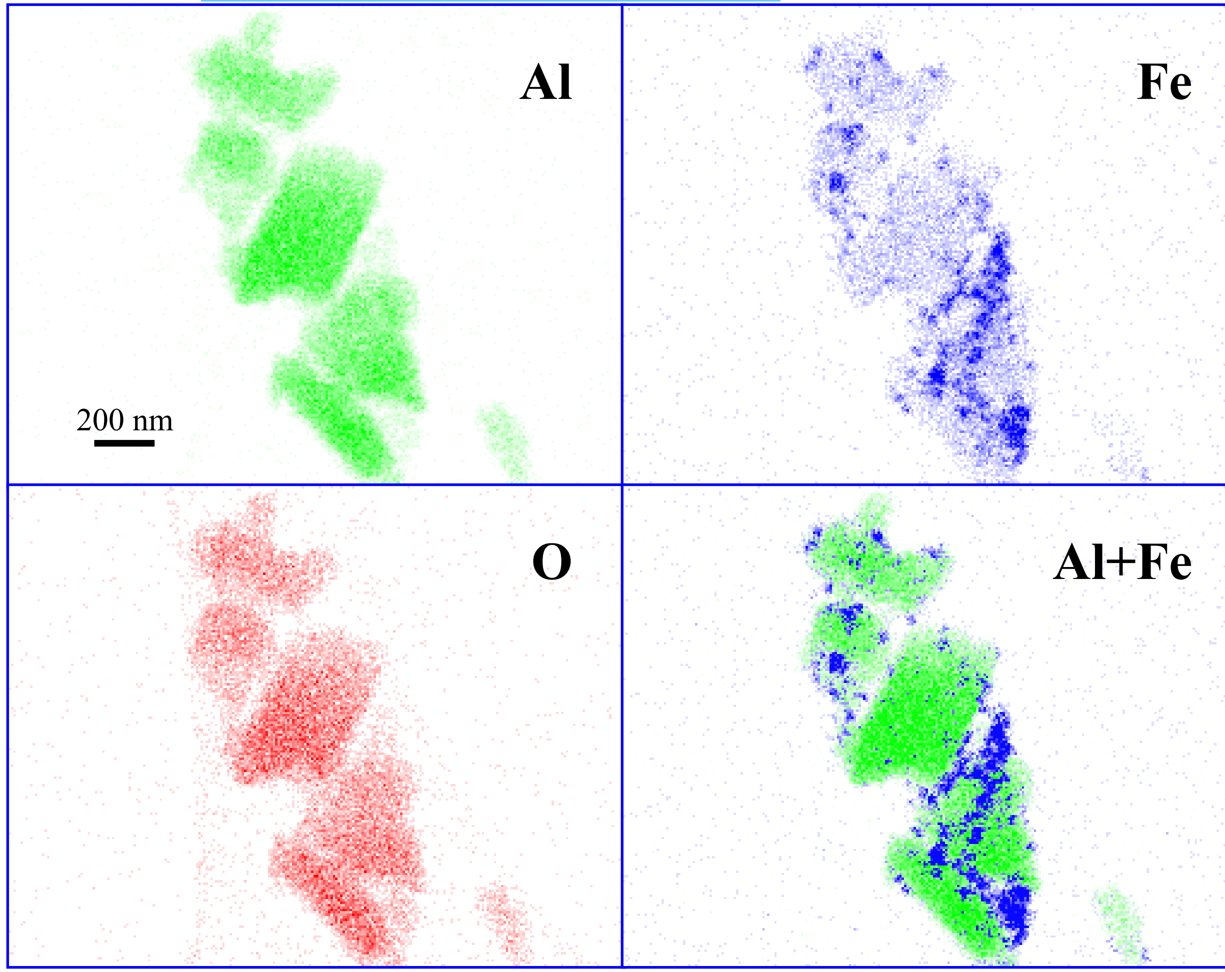
EDX



As-grown Fe/Al_2O_3 catalyst



TEM and X-ray mapping



5% $Fe\text{-}Al_2O_3$ particle size ~ 20 nm

EM in Catalysis

Imaging

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.

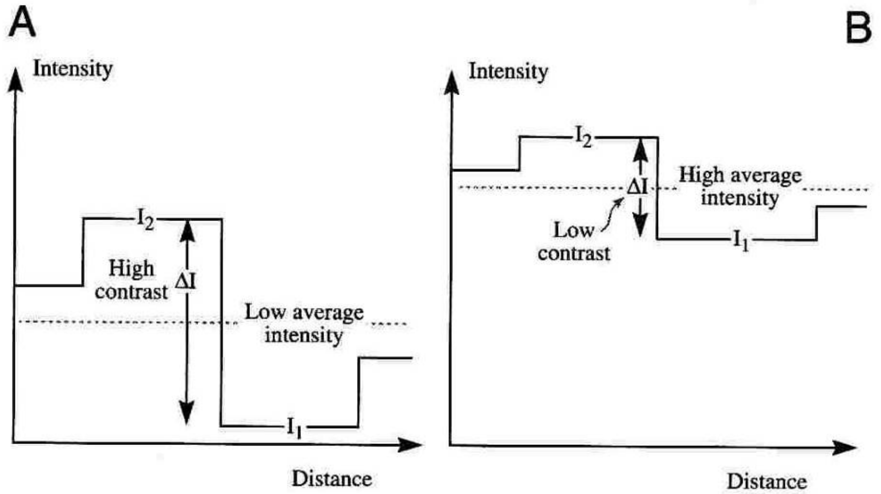


Figure 22.1. Schematic intensity profiles across an image showing (A) different intensity levels (I_1 and I_2) and the difference (ΔI) between them, which defines the contrast. Generally, in a TEM, if the overall intensity is increased (B) the contrast decreases.

What is image contrast

Do not confuse **intensity** with **contrast** when you describe your images. You can have ***strong*** or ***weak*** contrast but not ***bright*** or ***dark*** contrast.

The term ***bright*** and ***dark*** refer to density (number/unit area) of electrons hitting the screen/detector (and the subsequent light emission that you can see).

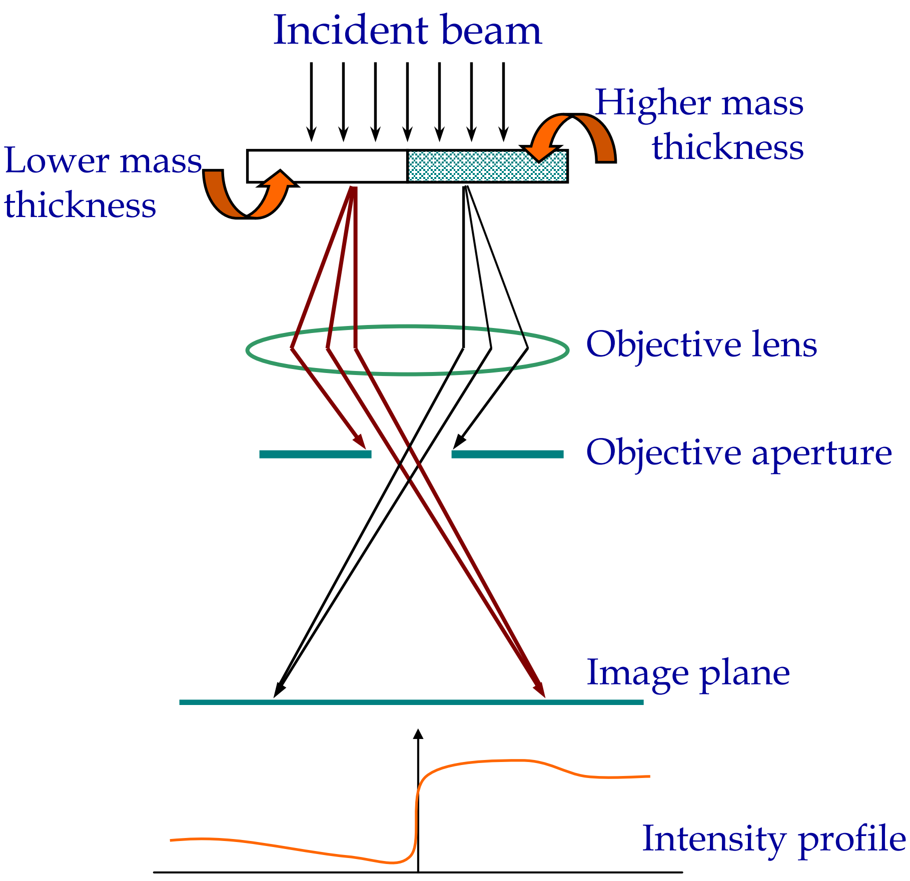
Lower the overall intensity → stronger contrast

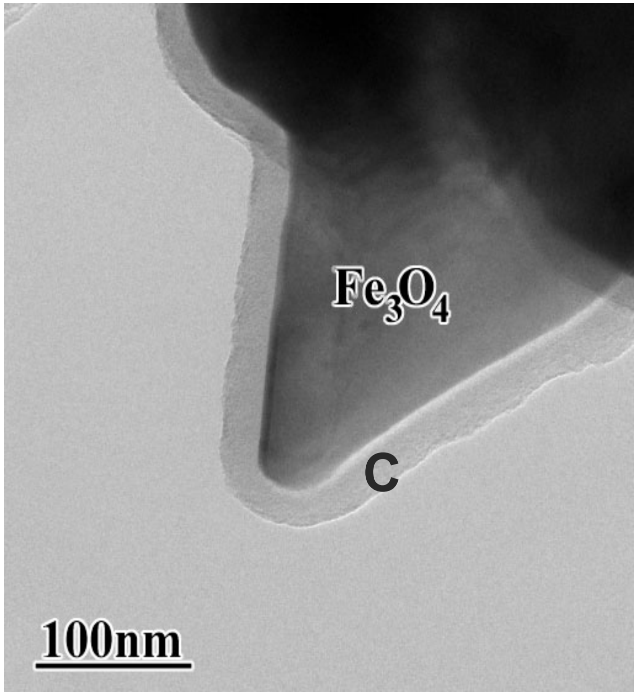
Condense the beam onto a small area → lower the image contrast

Image contrast in a TEM is obtained either by selecting specific electrons or excluding them from the imaging system. So you can form either bright field (BF) image or dark field (DF) image by selecting the direct or scattered electrons, respectively.

Image contrast in TEM

Mass-thickness contrast





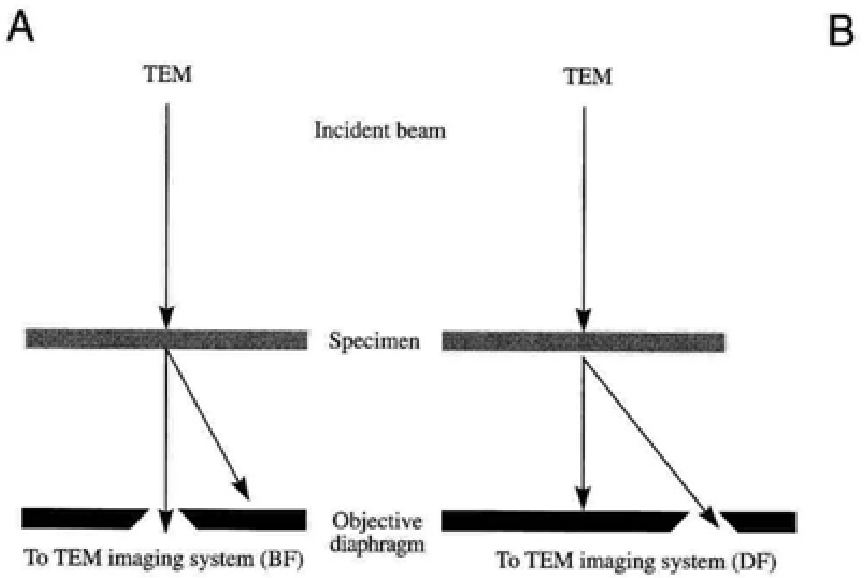
Mass-thickness contrast arises from incoherent (Rutherford) elastic scatter of electrons. The corss section for Rutherford scatter is a strong function of the atomic number *Z*, i.e., the mass or the density, as well as the thickness of the specimen.

Way to get a good image contrast

A right wag of imaging in TEM is:

first view the diffraction pattern, since this pattern tells you how your specimen is scattering.

Second select using objective aperture either direct beam or some diffricated beams to form BF or DF image respectively.



If you form an image without the aperture, the contrast will be poor because many beams then contribute to the image, and aberrations due to the off-axis electrons will make your image impossible to focus.
The aperture size govers which electrons contribute to the image and thus control the contrast.

Mass-thickness contrast

•The cross-section for elastic scattering is a function of *Z*.

•As the thickness of a specimen increases, there will be more elastic scattering because the mean-free path remains fixed

In a simple and qualatitive way, you can expect that

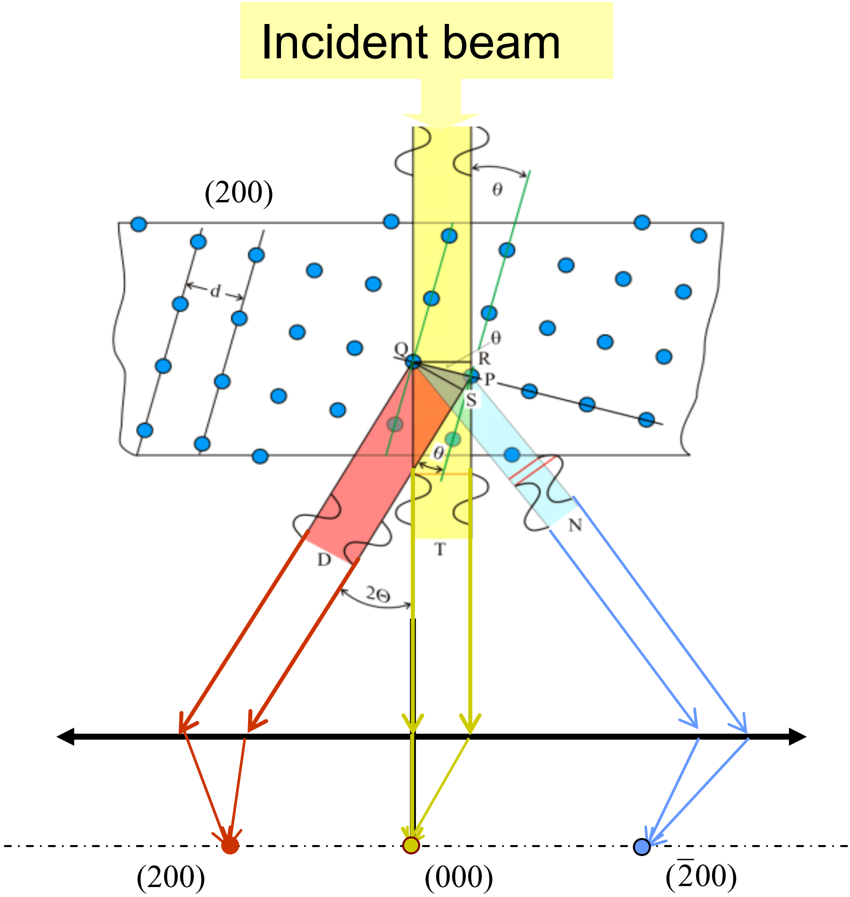
•High-*Z* (i.e. high-mass) region of a specimen can scatter more electrons than a low-Z region;
•Thick-region can scatter more electrons than a thin-region of the same average *Z* specimen.

Mass-thickness contrast is primarily contrast of amorphous specimen (polymers). But ususally any specimen can have mass-thickness contrast due to the change of thickness.

Image contrast in TEM: Diffraction contrast

Bragg diffraction is controlled by the crystal structure and orientation of the specimen.

You can use this diffraction to create contrast in a TEM image. Diffraction contrast is simply a special form of amplitude contrast since the scattering occures at a special (Bragg) angle.



Bright-Field and Dark-Field Imaging

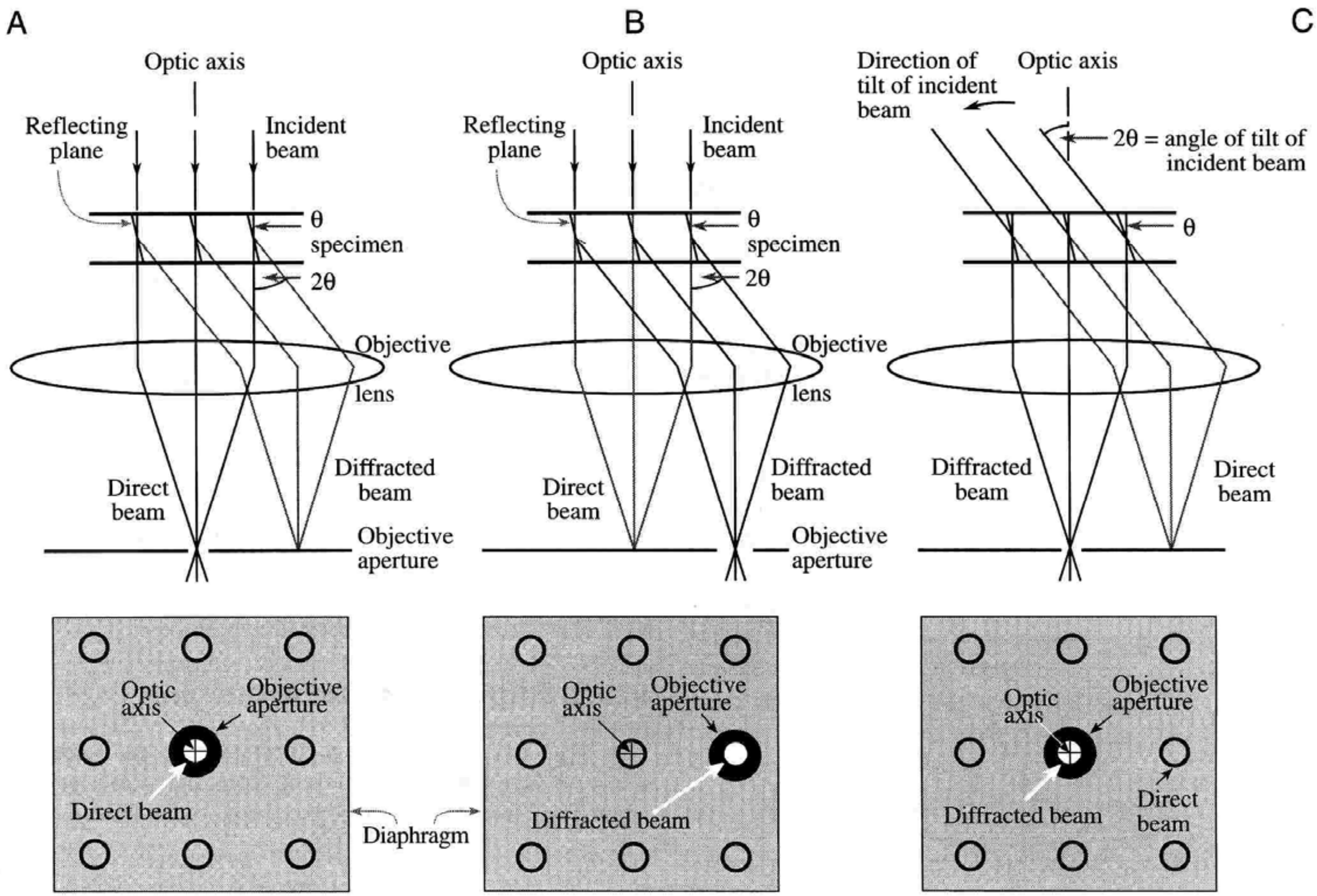
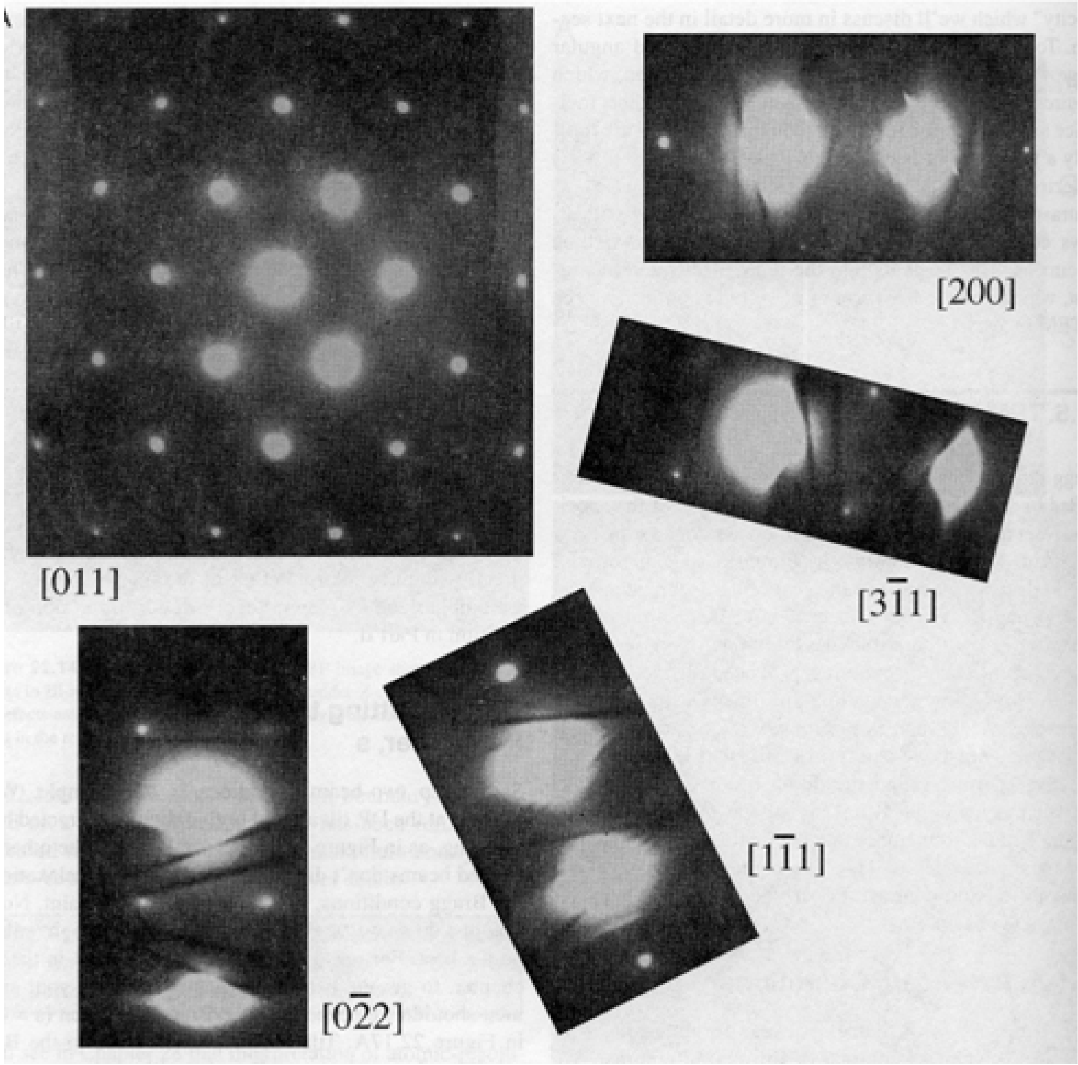


Figure 9.14. Ray diagrams showing how the objective lens/aperture are used in combination to produce (A) a BF image formed from the direct beam, (B) a displaced-aperture DF image formed with a specific off-axis scattered beam, and (C) a CDF image where the incident beam is tilted so that the scattered beam remains on axis. The area selected by the objective aperture, as seen on the viewing screen, is shown below each ray diagram.

Image contrast in TEM

Diffraction contrast



Two-Beam Conditions

Bright- and dark-field images of 5-15 nm Pd grains

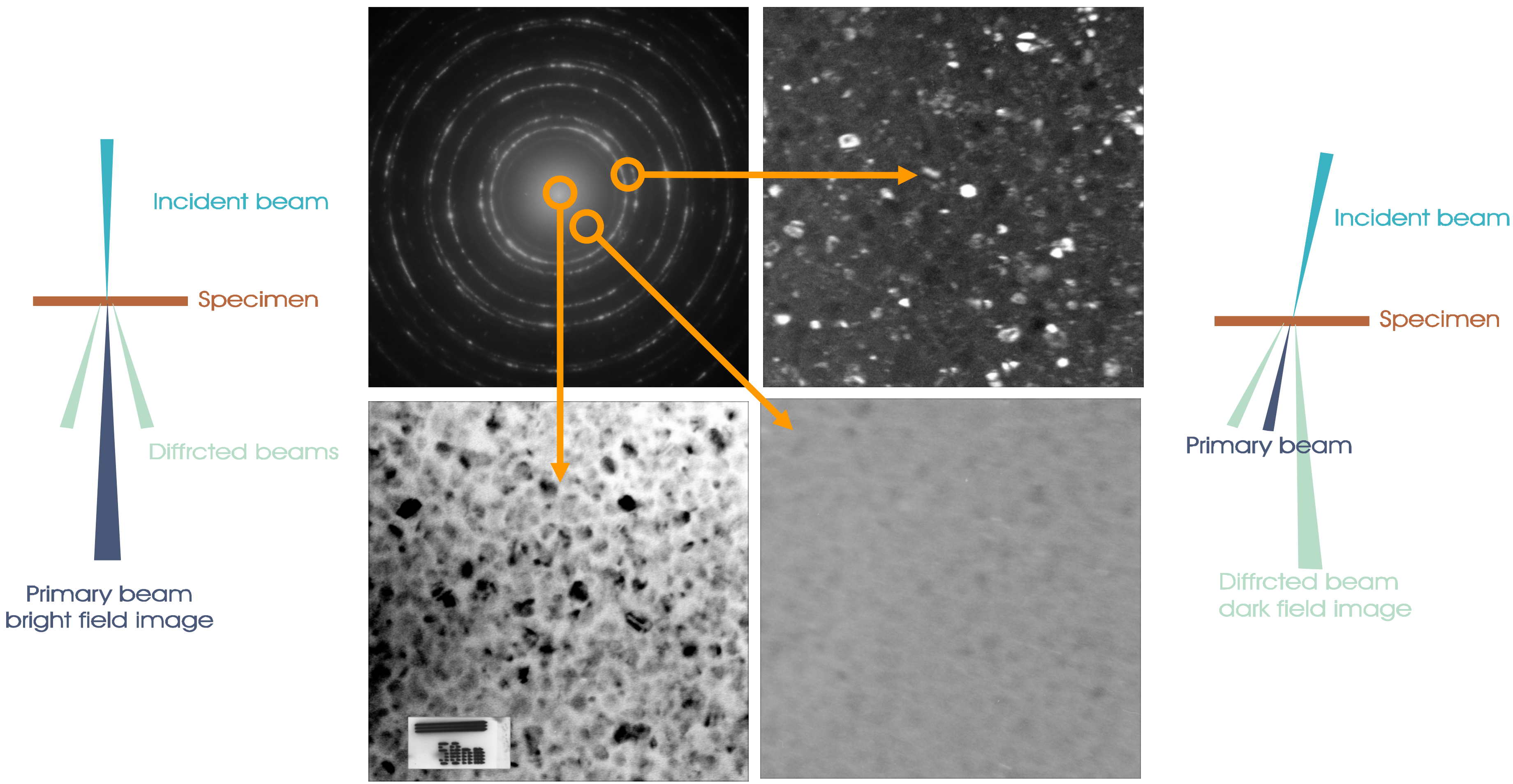


Image contrast in TEM

Phase contrast

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

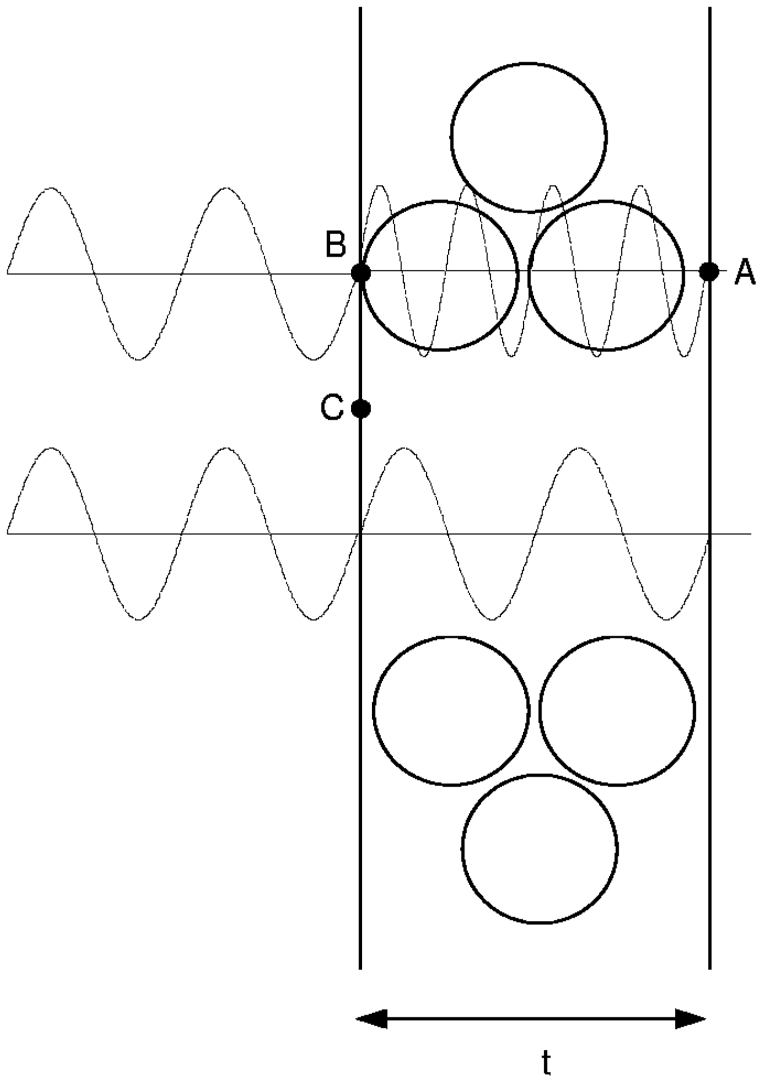


Image Contrast in TEM: Phase Contrast

High-resolution TEM can be obtained if you work with phase-contrast

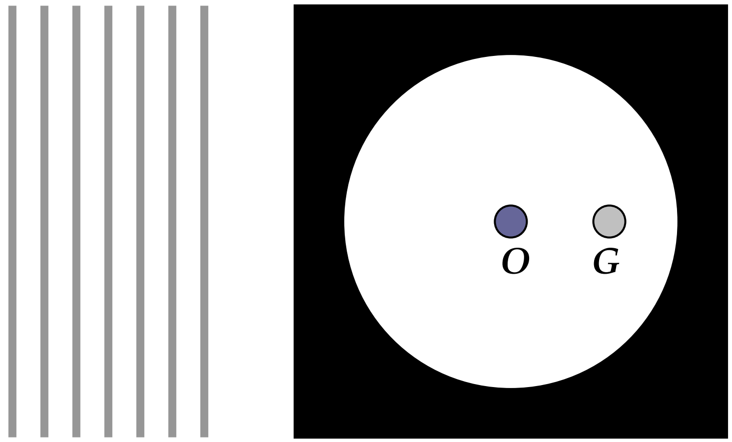
The phase contrast arises due to the differences in the phase of the electron waves scattered through a thin specimen.

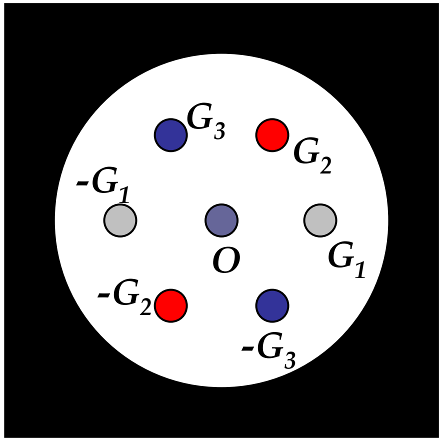
Phase contrast can be exploited to image the atomic structure of thin specimens if the TEM has sufficient resolution to deteced contrast variations at atomic dimensions.

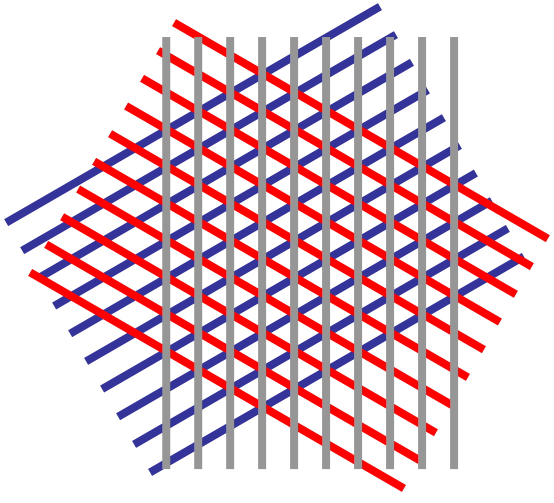
The procedures can be straightforward, but phase-contrast is very sensitive to small changes in the thickness, orientation, to the variation in focus or astigmatism of the objective lens.

Image Contrast in TEM: Phase Contrast

The origin of lattice fringes



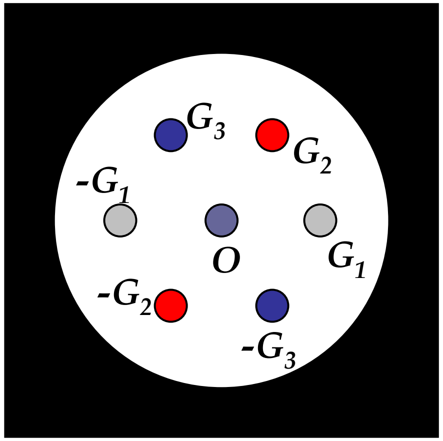




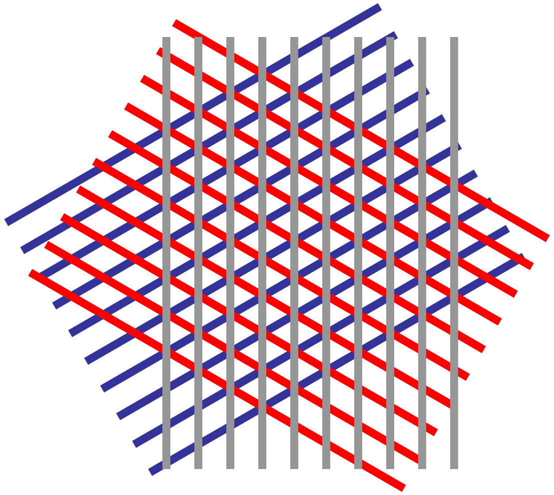
If more than 1 diffraction sopts are included in the objective aperture, the diffractions will interfere with each other and in image plane interference fringes can be formed

Image Contrast in TEM: Phase Contrast

The origin of lattice fringes

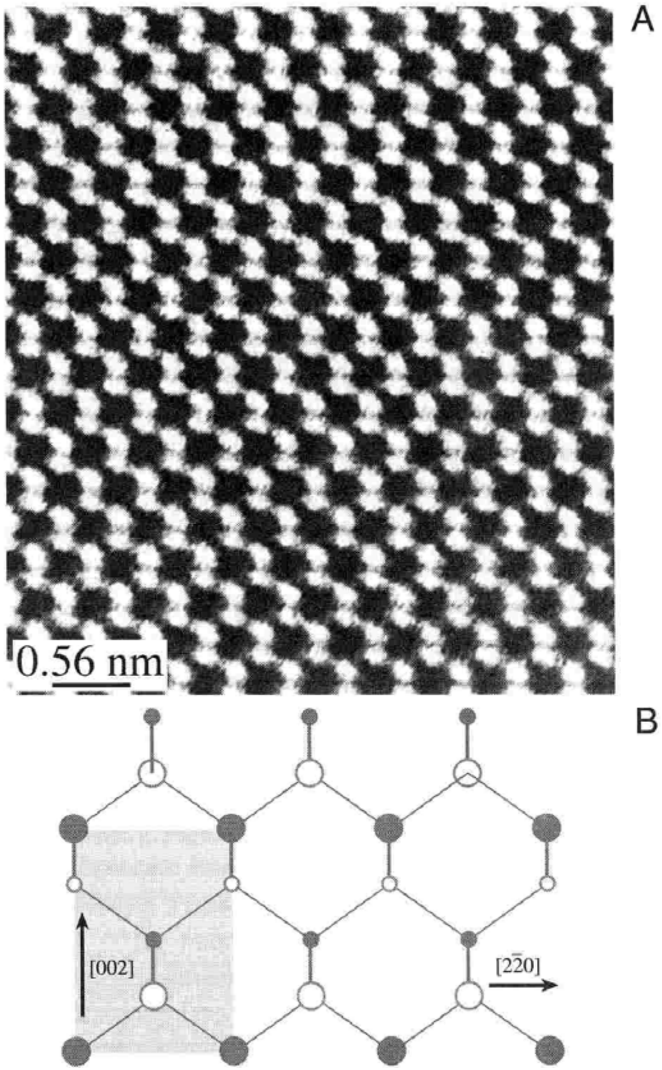


High resolution lattice fringes arise from interference of *direct* beam and diffracted beams.



Phase-contrast imaging differs from other forms of TEM imaging in the number of beams collected by the objective aperture. A BF or DF image requires a *single* beam. a phase-contrast image requires the selection of *more than one* beam.

Image Contrast in TEM: Phase Contrast



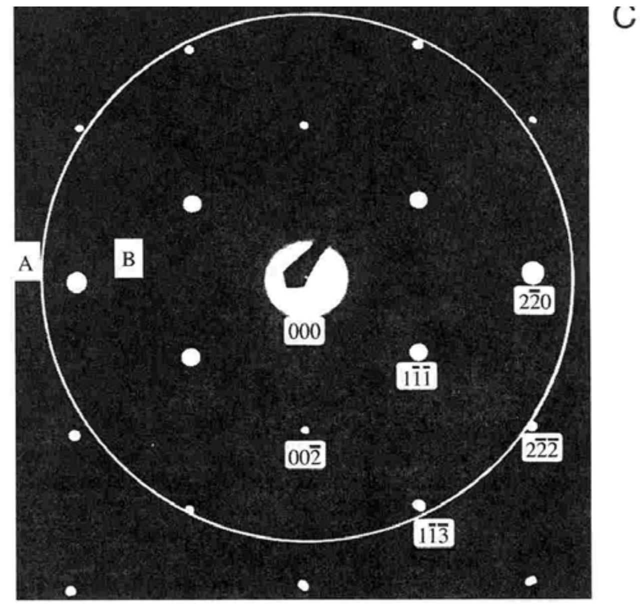
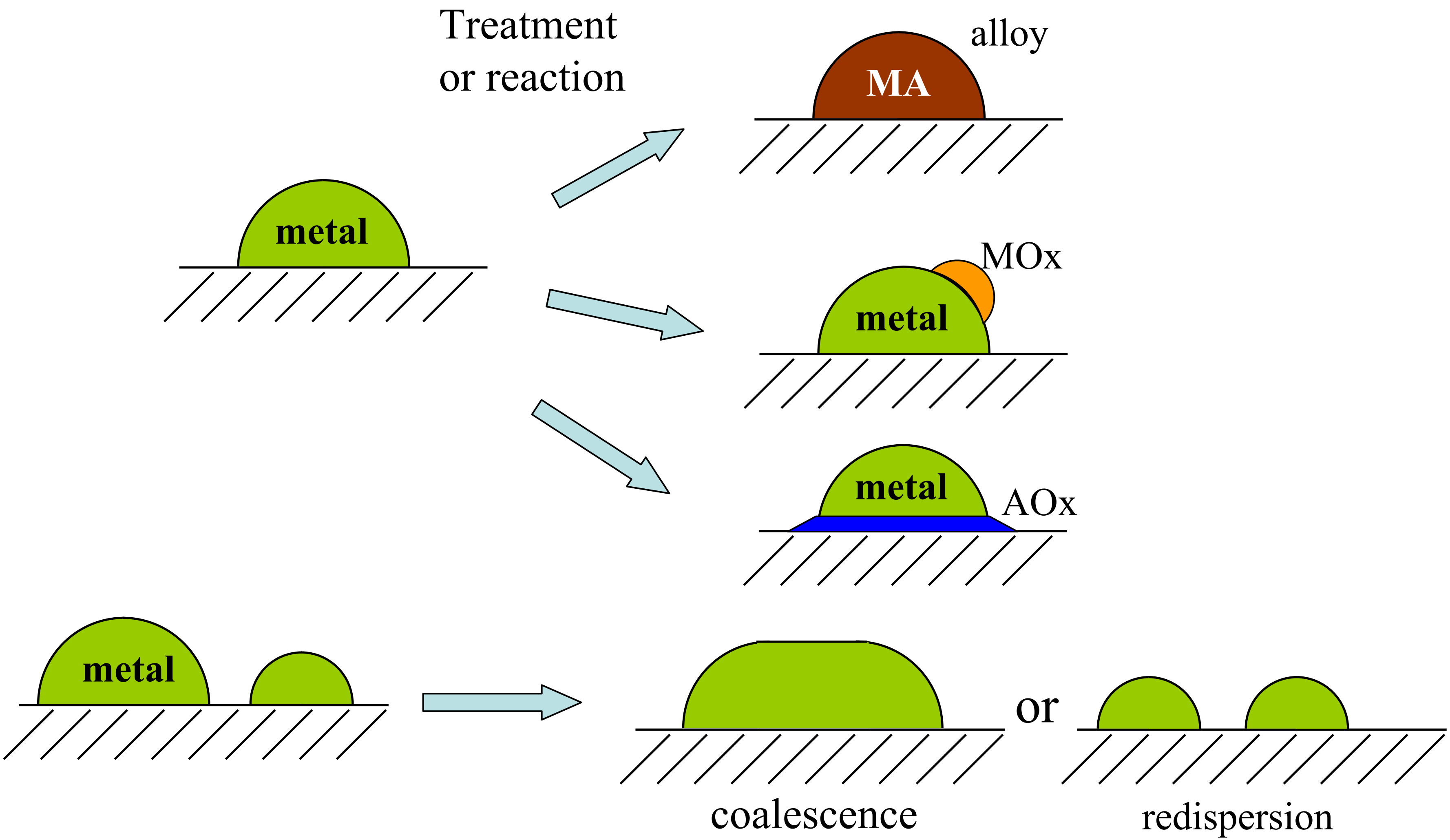


Figure 27.3. (A) On-axis image of a perfect Si crystal; (B) the projected structure; (C) the diffraction pattern showing the 13 spots used to form the image inside the aperture (ring). The Si dumbbells do not correspond to the closely spaced pairs of spots in the image.

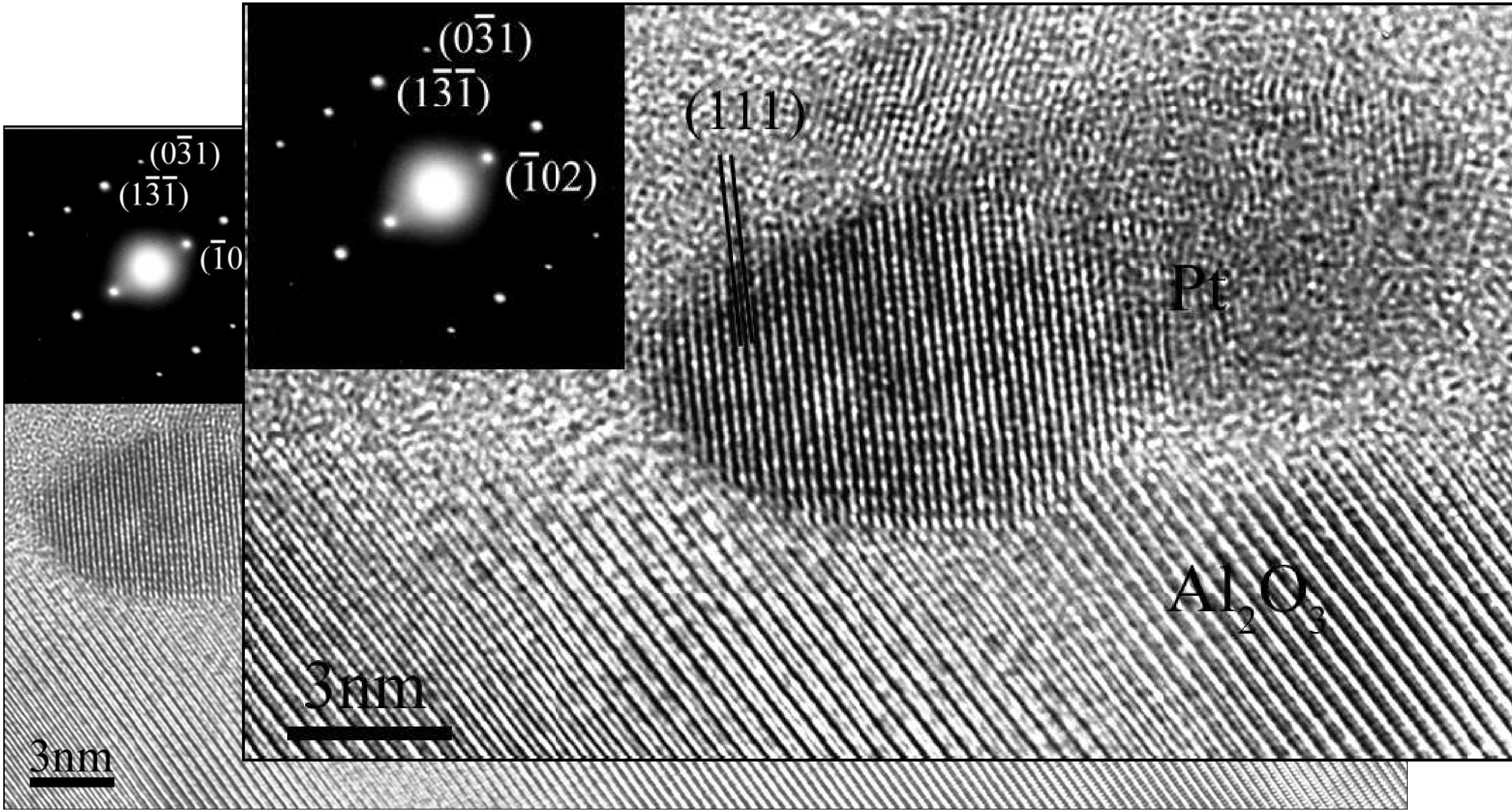
Application

Metal-support interaction



Metal-support interaction

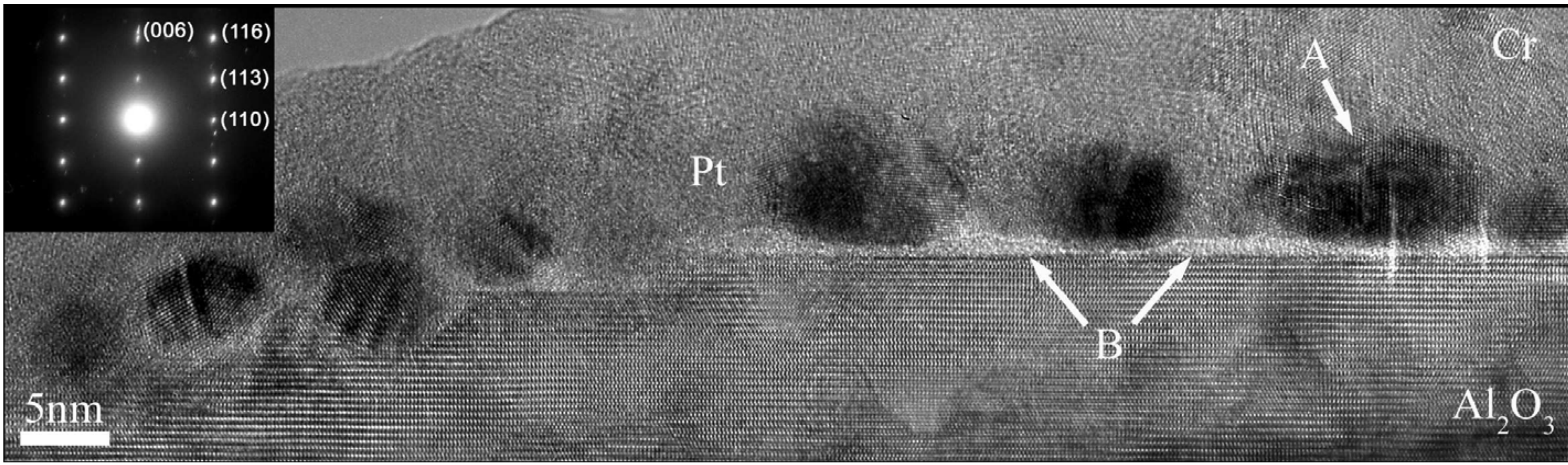
Pt/Al_2O_3: as prepared



Zhong et al, J. Catal. 2005, 236:9.

Metal-support interaction

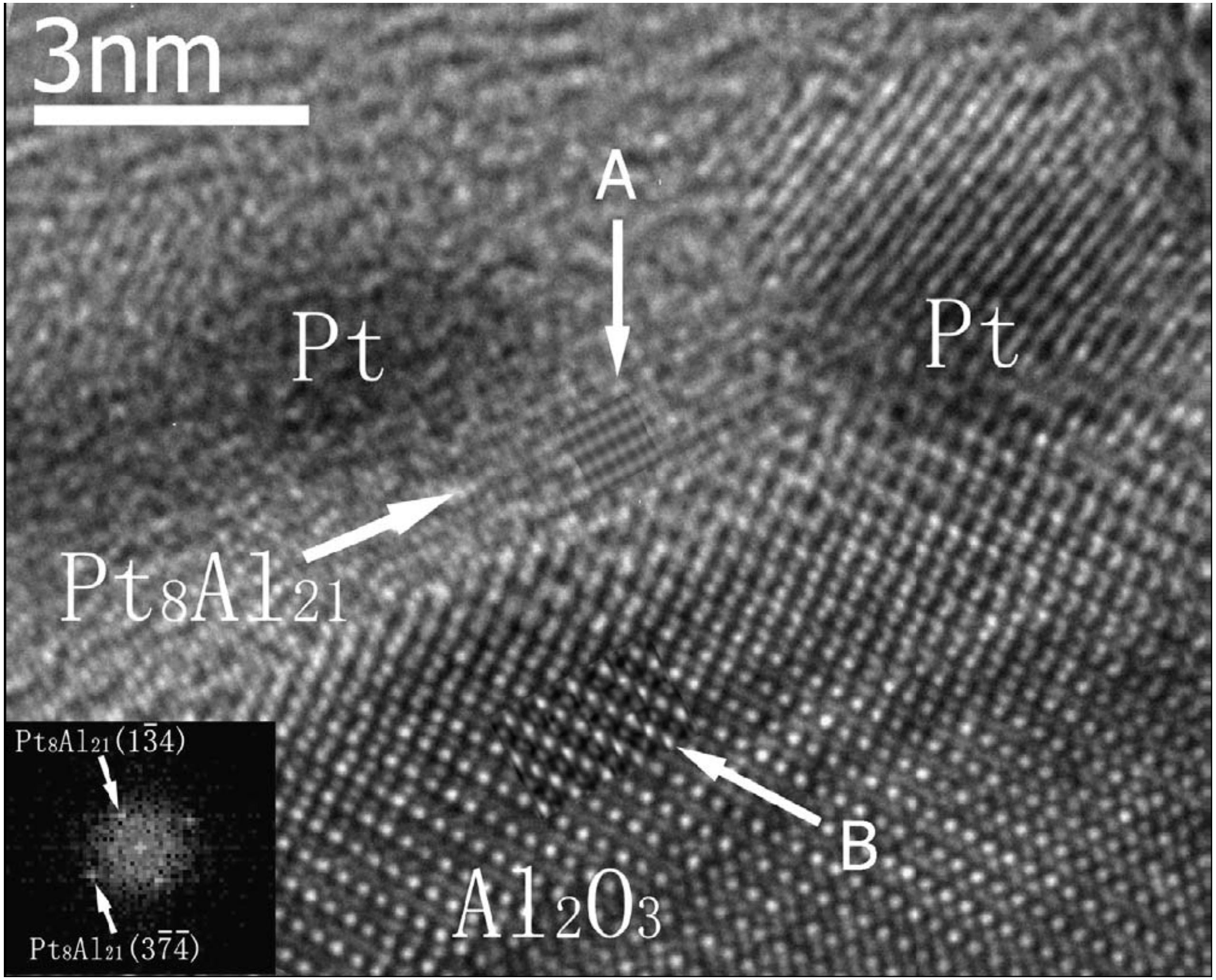
Pt/Al_2O_3: after reduction



Cross-section HRTEM of Pt/Al_2O_3 catalyst after reduction in H_2 at 1072 K. SAED of [-110] zone axis is insert.

Zhong et al, J. Catal. 2005, 236:9.

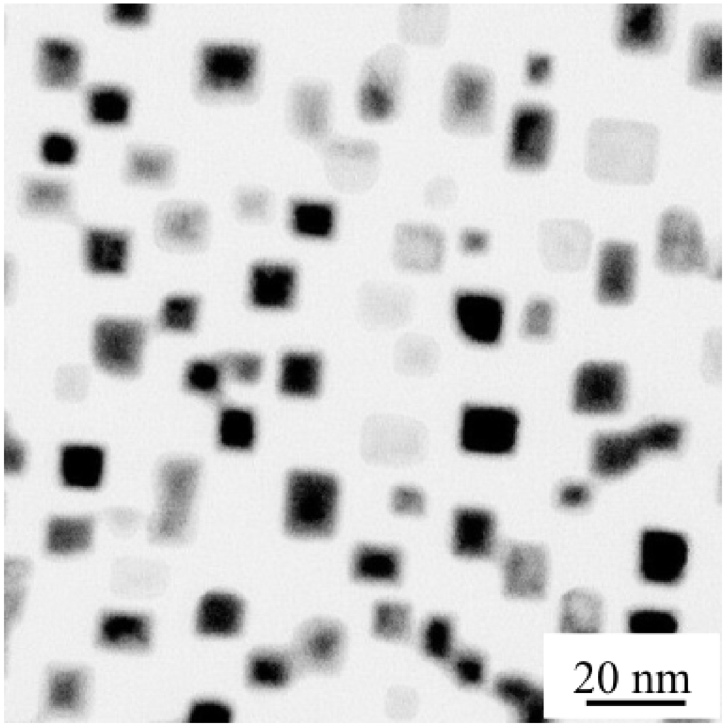
Metal-support interaction: Pd/Al_2O_3

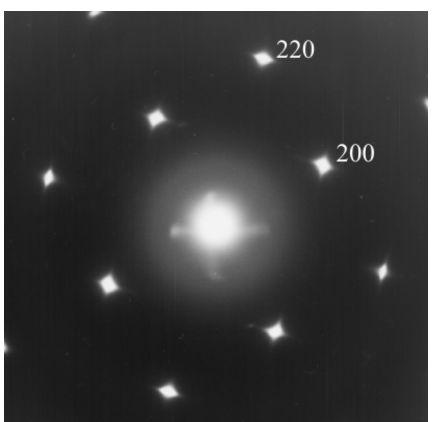


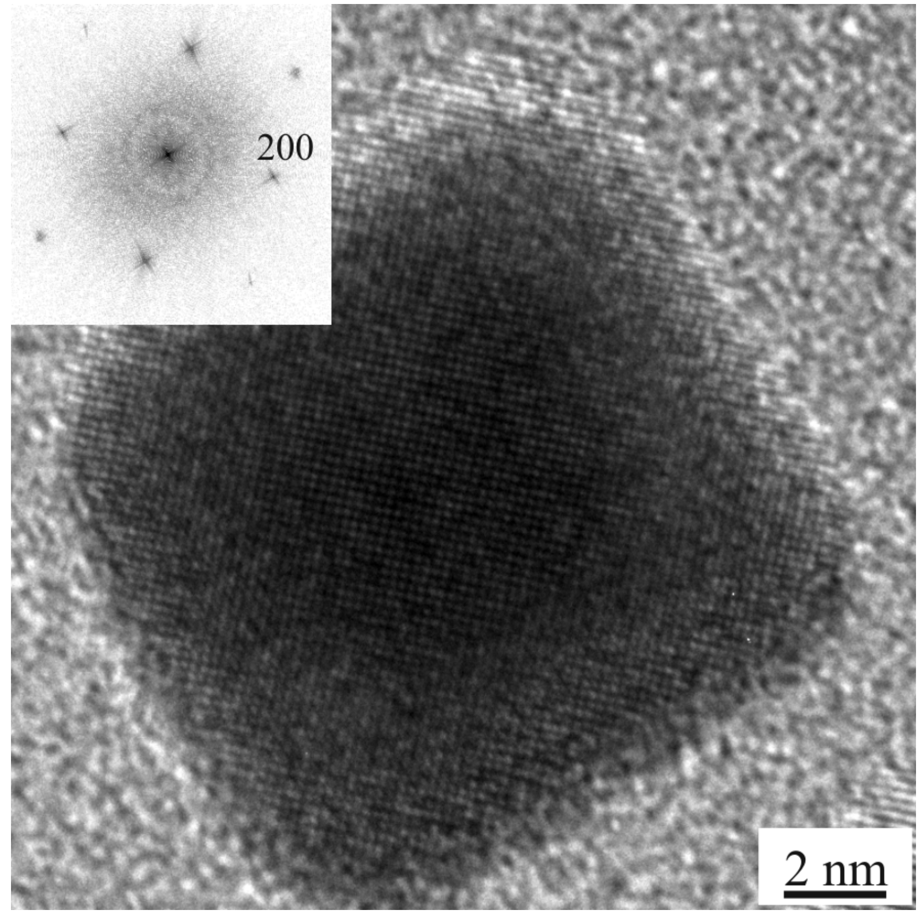
Atomic resolution TEM image of a cross-section sample of a Pt/Al_2O_3 model catalyst clearly shows the Pt nanoparticles, the structure of the alumina substrate, and the interfacial structures. The sample was reduced in H2/N2 mixture for 1 h at 1073 K. Simulated HRTEM images of the interfacial phase Pt_8Al_{21} oriented along the [20 8 1] zone axis and the α-Al_2O_3 substrate oriented along the [010] zone axis were shown in the insets indicated by the letters A and B, respectively.

Metal-support interaction: Pt/SiO_2

As-prepared sample



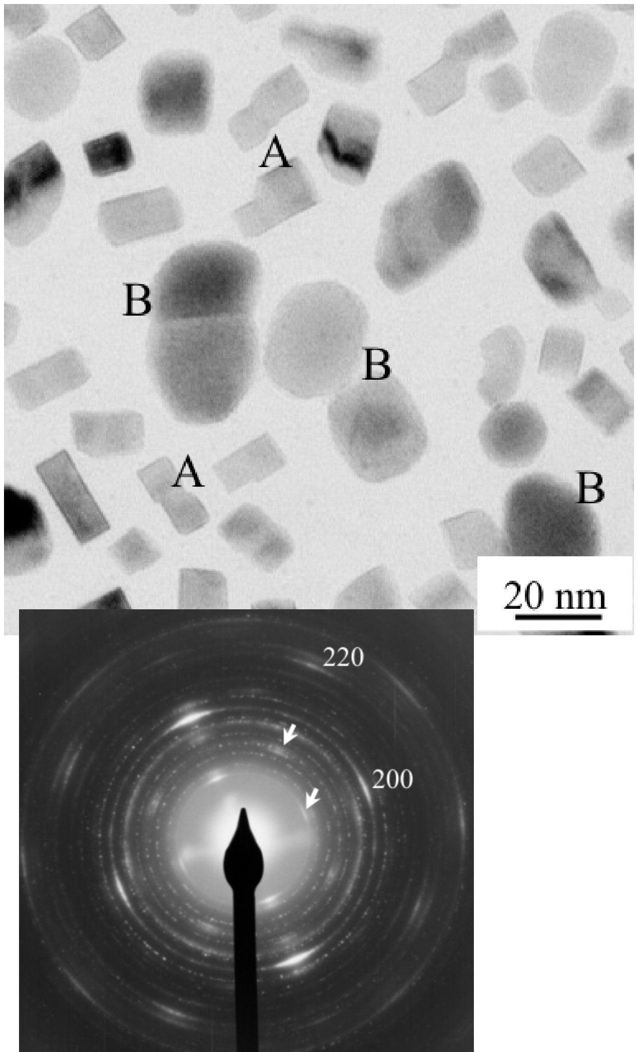


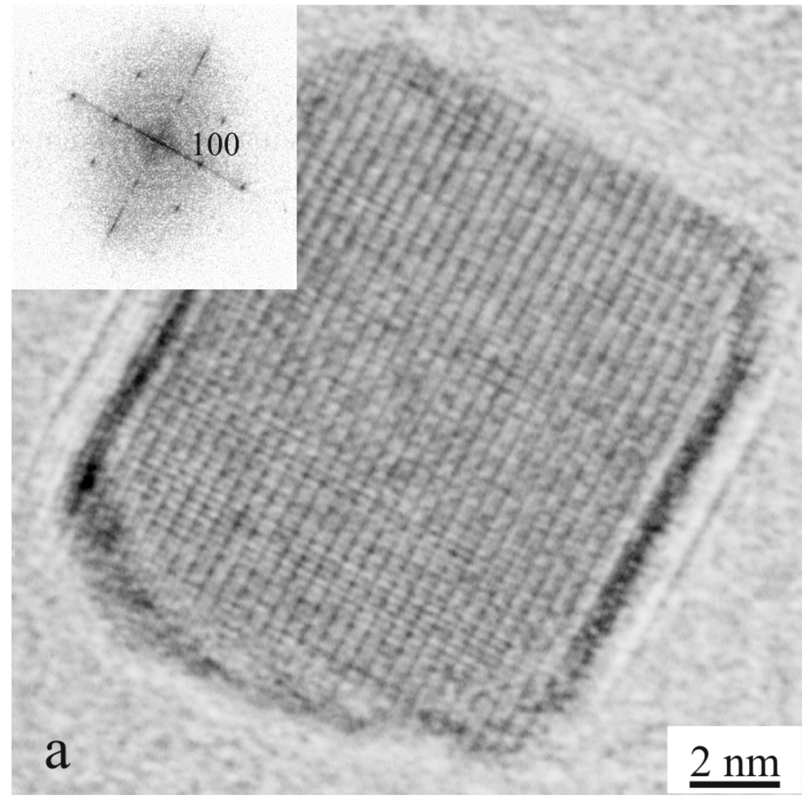


Wang et al. J. Catalysis, 219 (2003) 434

Metal-support interaction: Pt/SiO_2

After reduction in H2 at 800°C

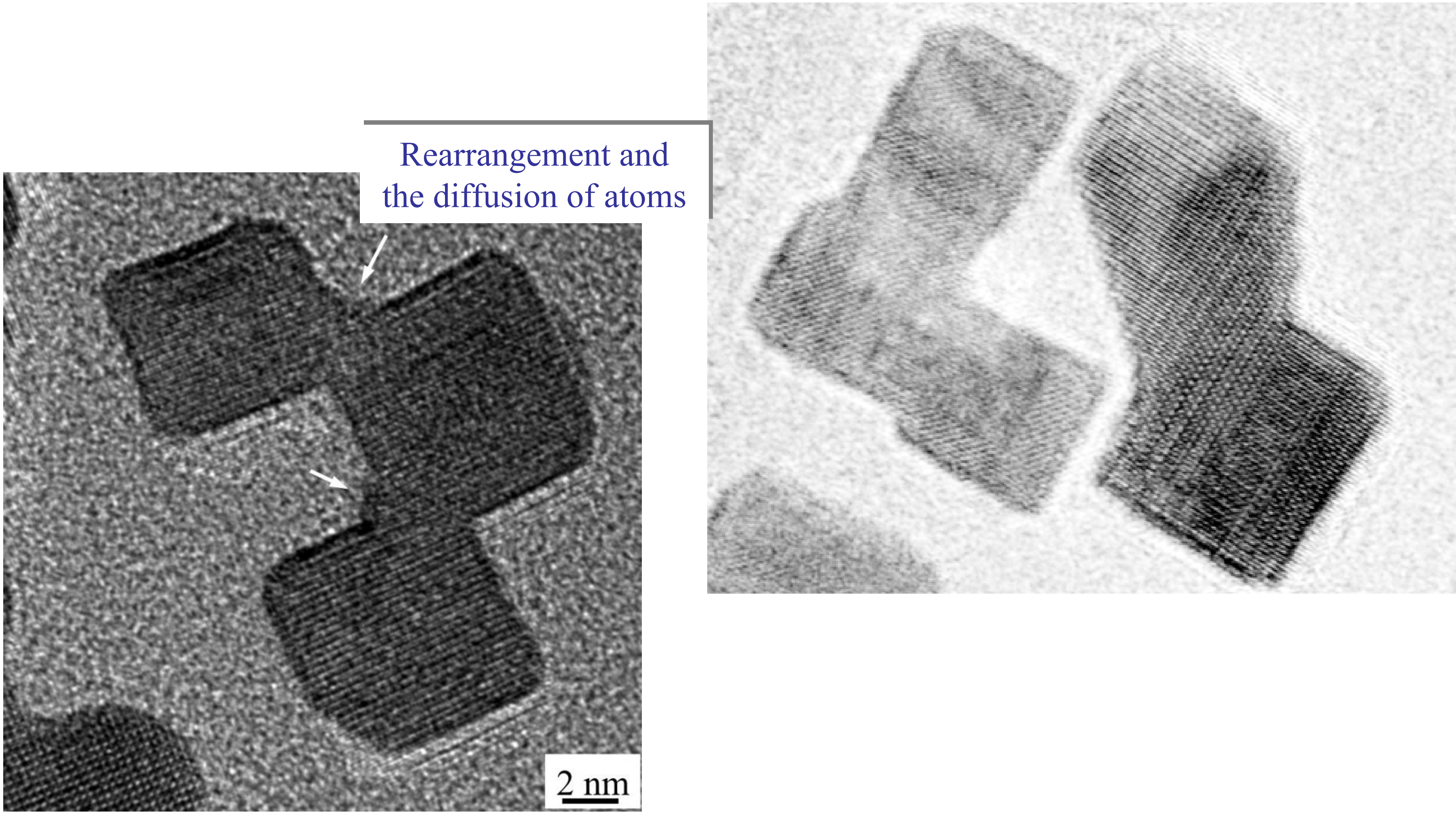




Pt_3Si particle

Wang et al. J. Catalysis, 219 (2003) 434

Metal-support interaction: Pt/SiO_2

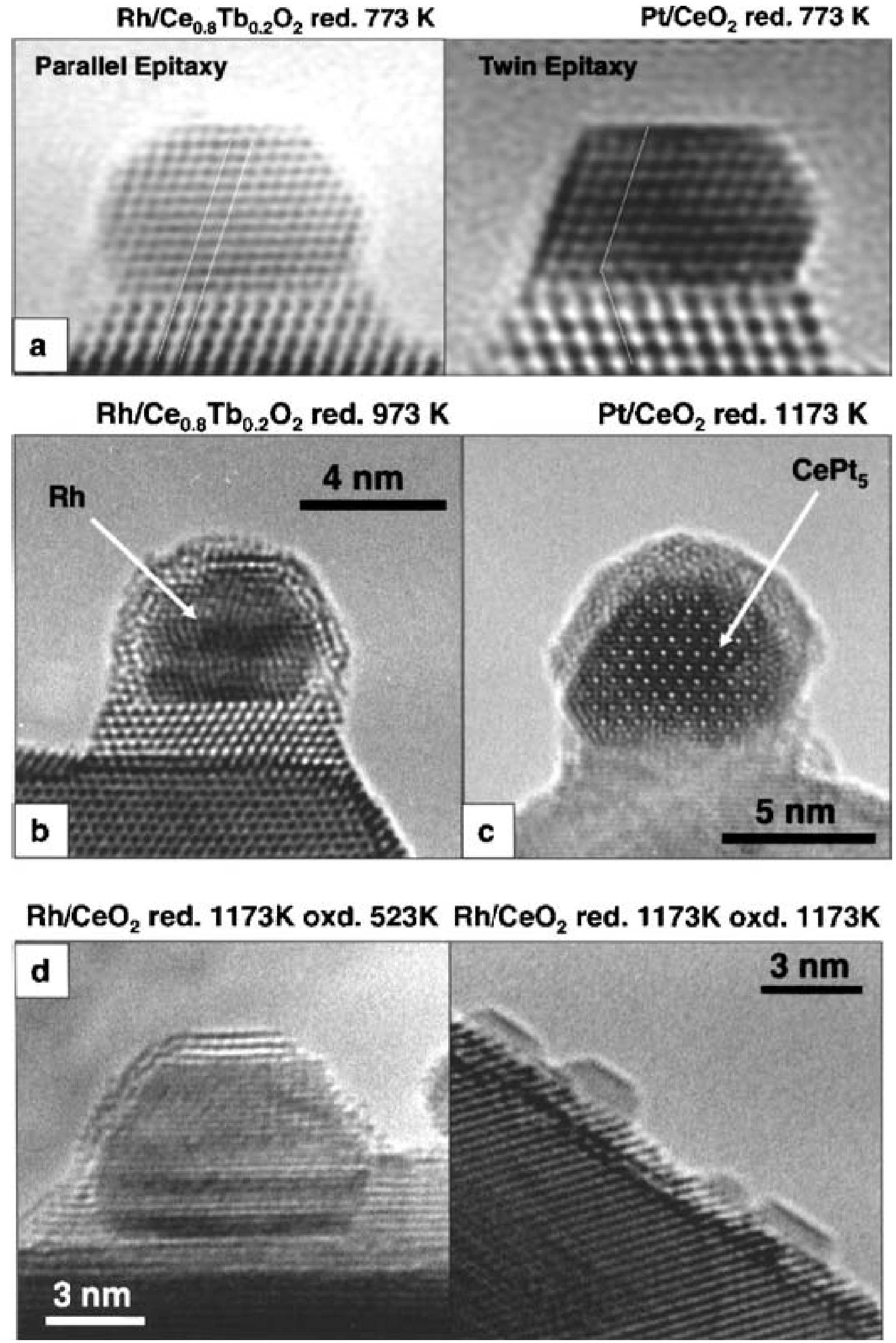


The beginning stages of a coalescence process of three particles with platelet shape.

Wang et al. J. Catalysis, 219 (2003) 434

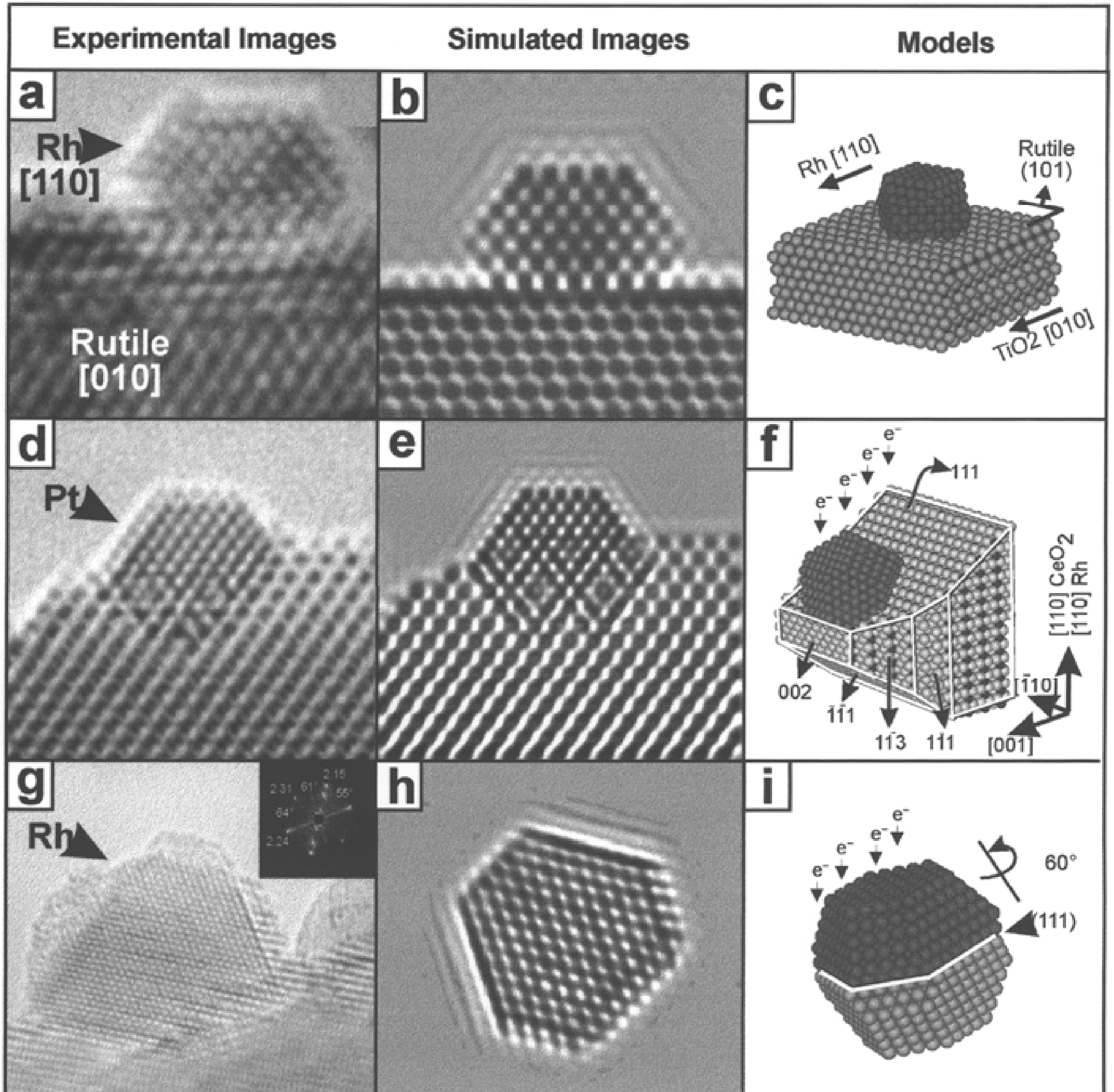
EM in Catalysis

Evaluation of metal-support interacton effects



A: Metal-support epitaxy
B: Decoration of metal particles
C: Pt-Ce alloying
D: Reversibility of metal-support decoration effects (left).
Redispersion of Rh into small, surface-clean particles after oxidation at a high temperature of 1173 k (right).
Gai et al, Annu. Rev. Mater. Res 2005, 36, 456

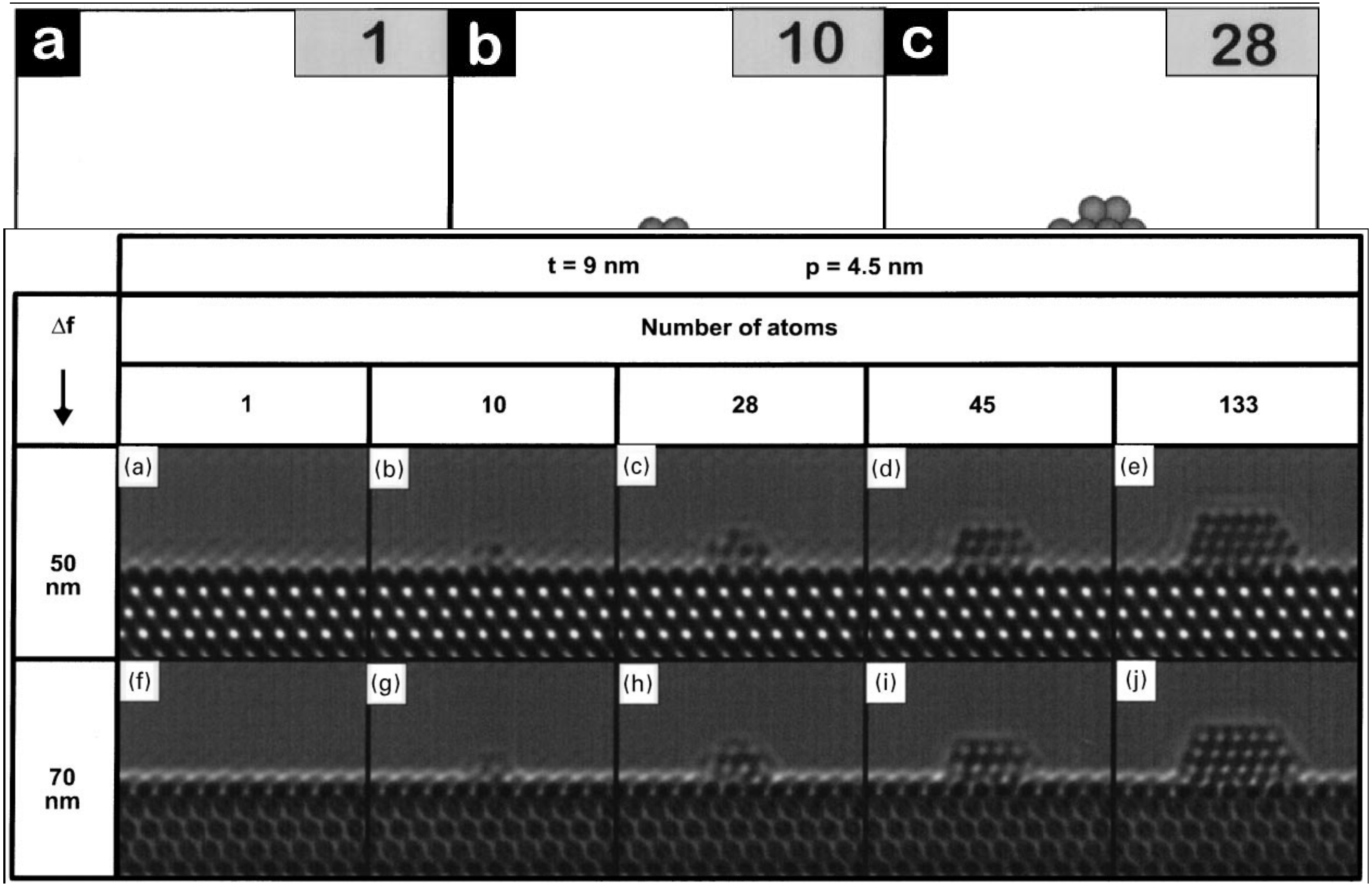
EM in Catalysis: Challenges and Opportunities



Bernal et al
Surf. Interface Anal. **29**, 411 (2000)

Interpretation of image contrast: image simulation

Supported catalyst: How small can a particle be imaged ?



S. Bernal et al. / Ultramicroscopy 72 (1998) 135

EM in Catalysis

Catalytic reaction occurs on the surface of a catalyst

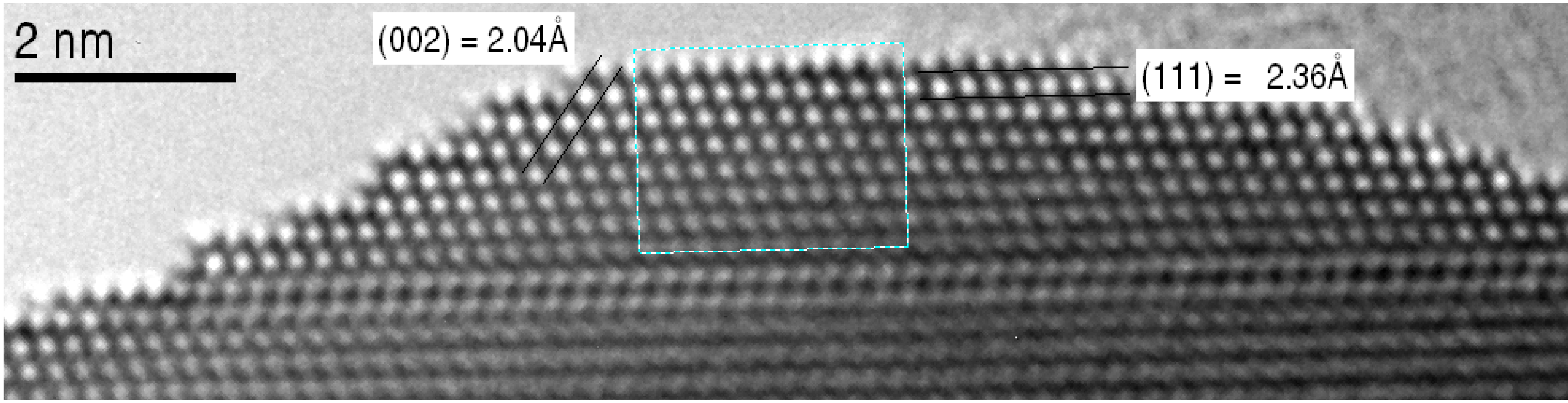
Can TEM provide information about surface structure of a real catalyst ?

Ag Catalyst: Ag/SiO2 IW

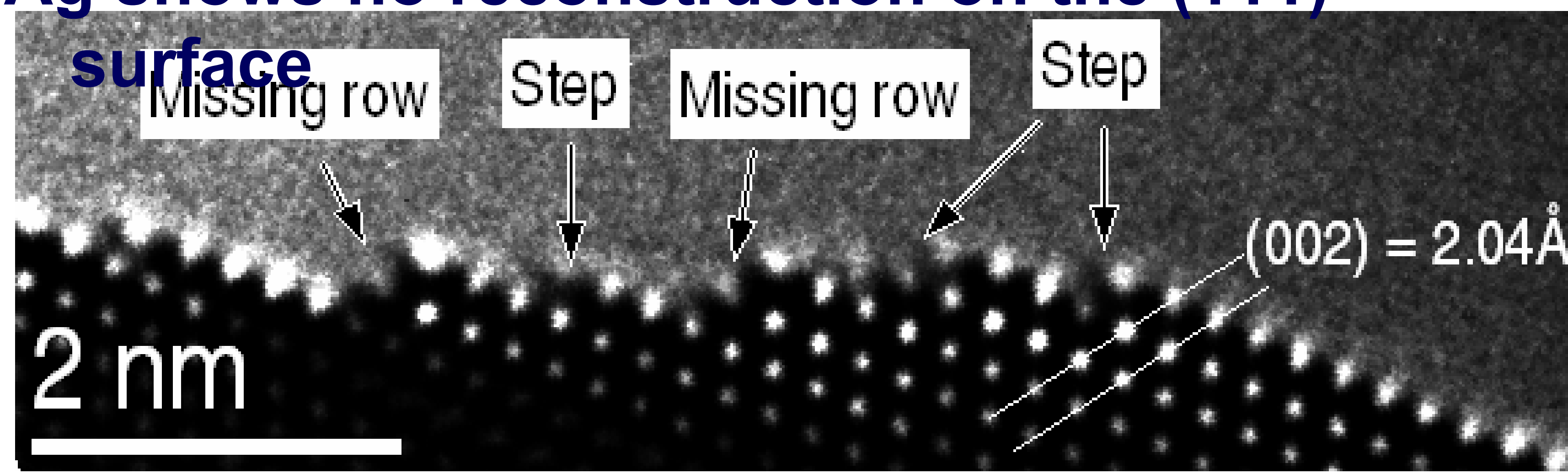
Surface Structure

- The formation of allyl alcohol is bound to active sites
- Atoms at kinks and edges favor the formation of AyOH

Ag Catalyst: Ag/SiO2 IW: Surface Structure



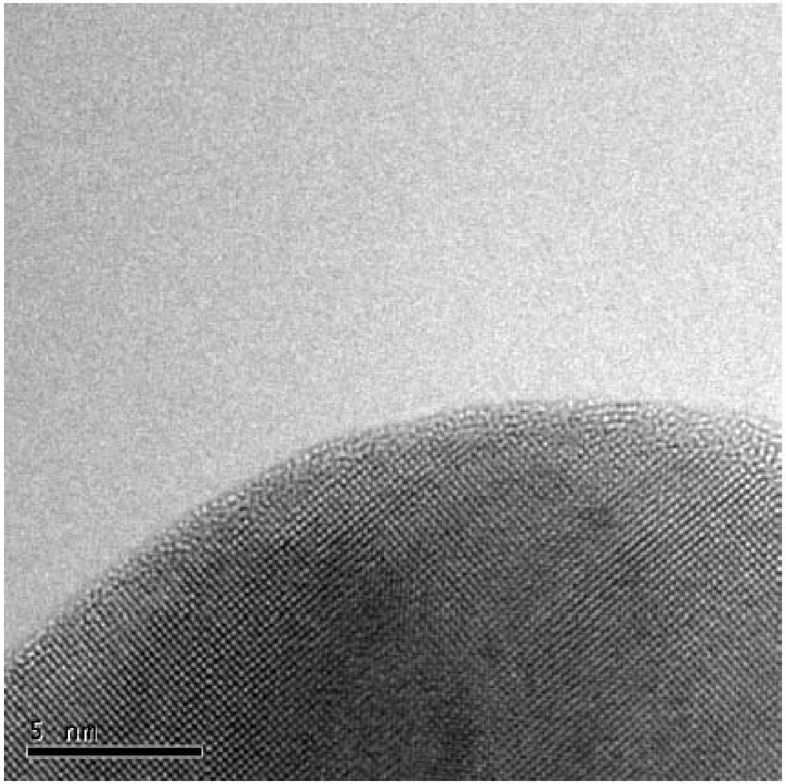
Ag shows no reconstruction on the (111) surface

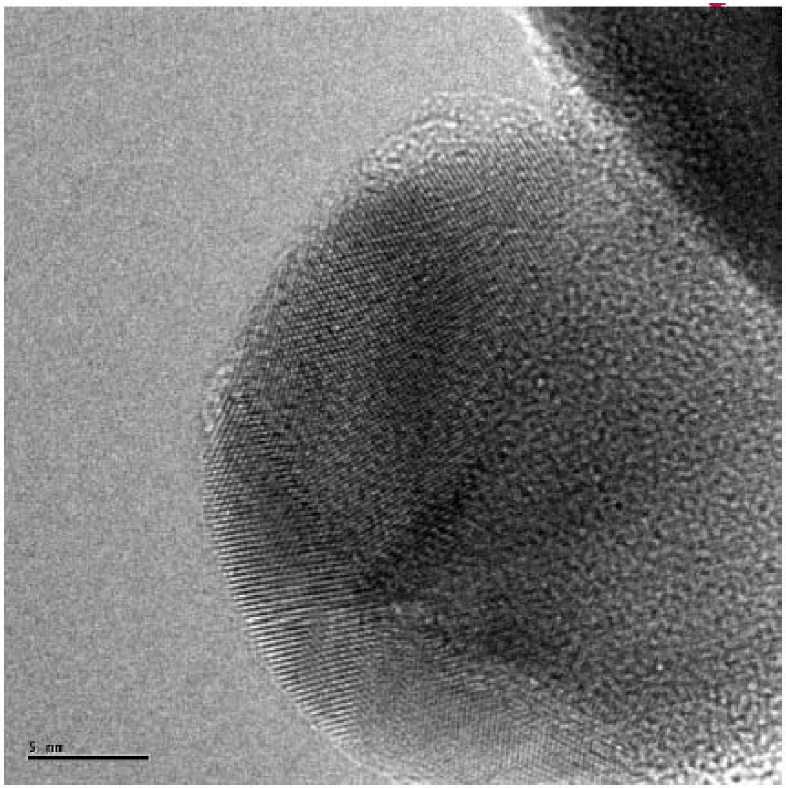


The (110) surface of Ag shows steps and missing rows, but in ordered fashion

Ag Catalyst: $9Ag/SiO_2$ P(NaOH)

Surface Structure



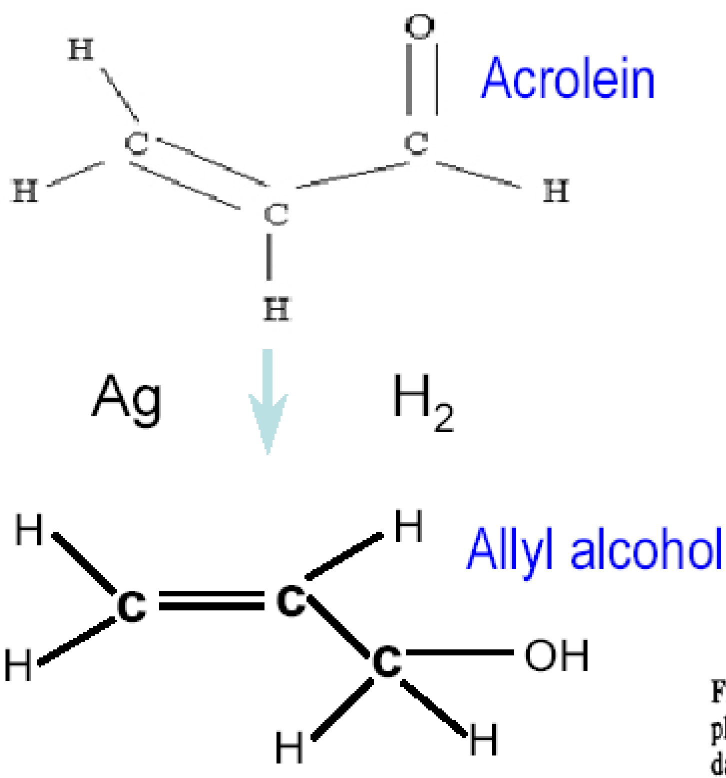


Highly disordered surface, which looses the crystalline symmetry

Hardly any kinks and sharp edges

Hydrogenation of acrolein over silver catalysts

Chemical reaction



Change in selectivity of ~ 5%

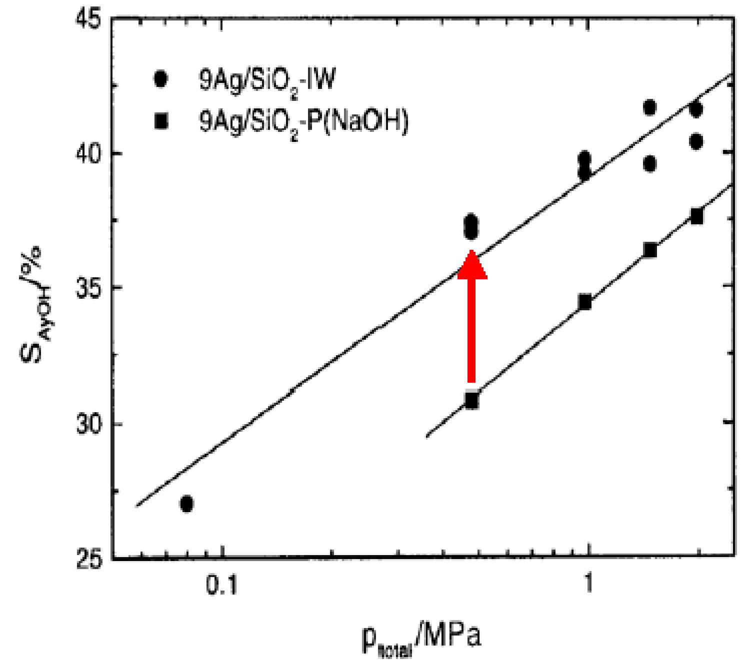
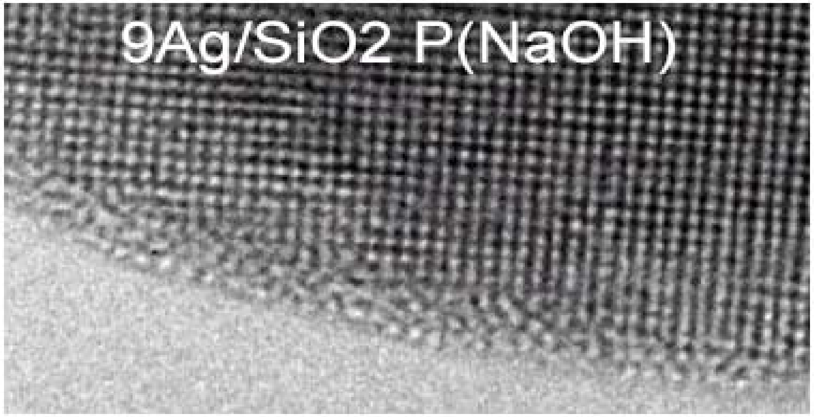
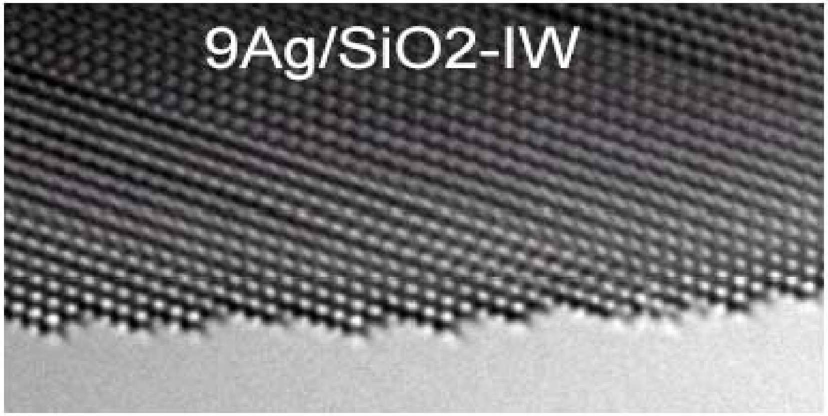


Fig. 2. Dependence of the selectivity towards allyl alcohol on the total pressure in the gas phase hydrogenation of acrolein over two different Ag/SiO$_2$ catalysts. Conversion for all data points was *ca.* 25%, reaction temperature was 250 °C.

M. Bron, et al, Z. Phys. Chem, 218 (2004) 405

Ag Catalyst: Comparison of Surface Structure



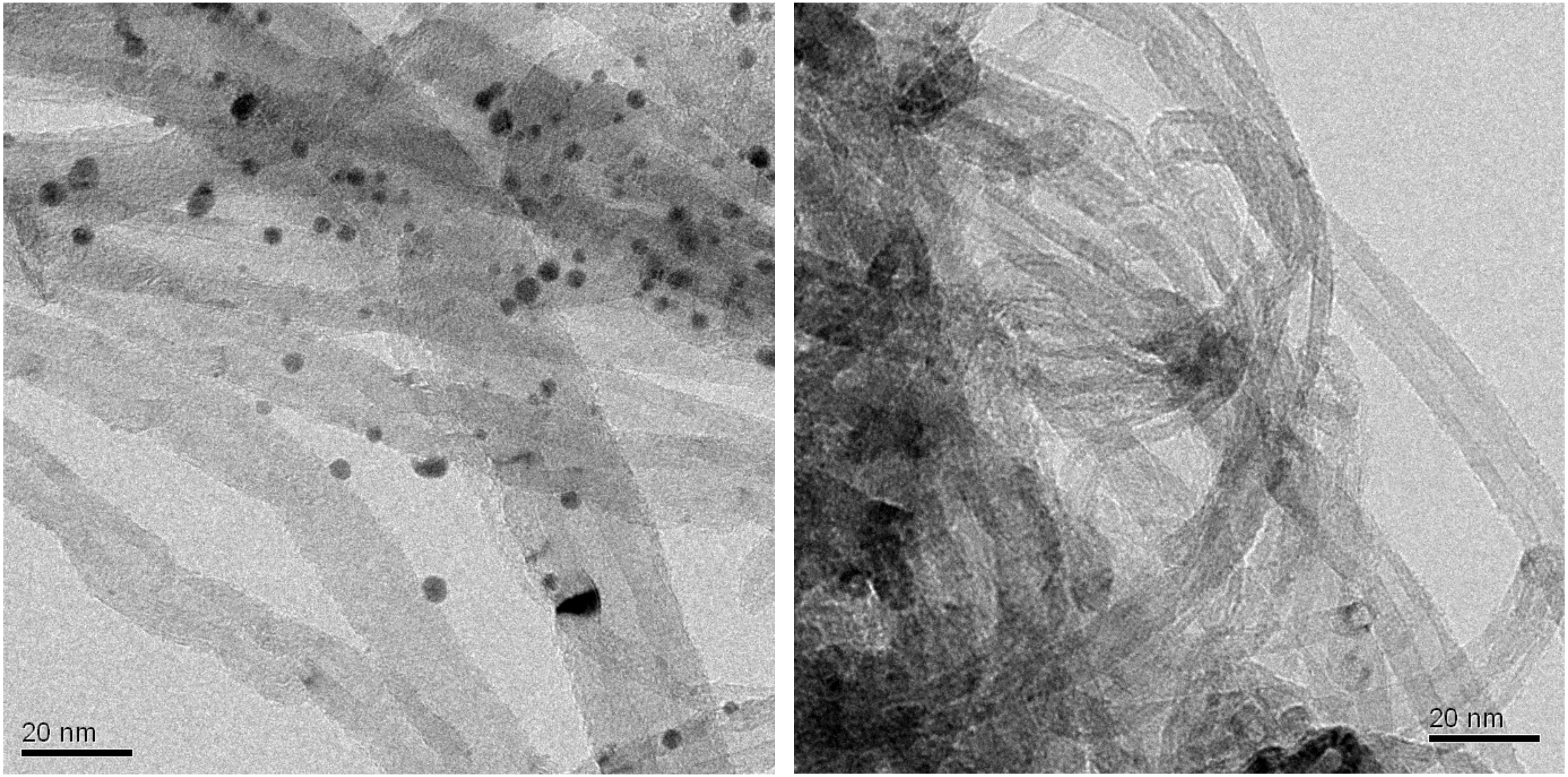


- Surface of particles prepared via incipient wetness (IW) show more kinks and edges than particles prepared via precipitation (P) technique

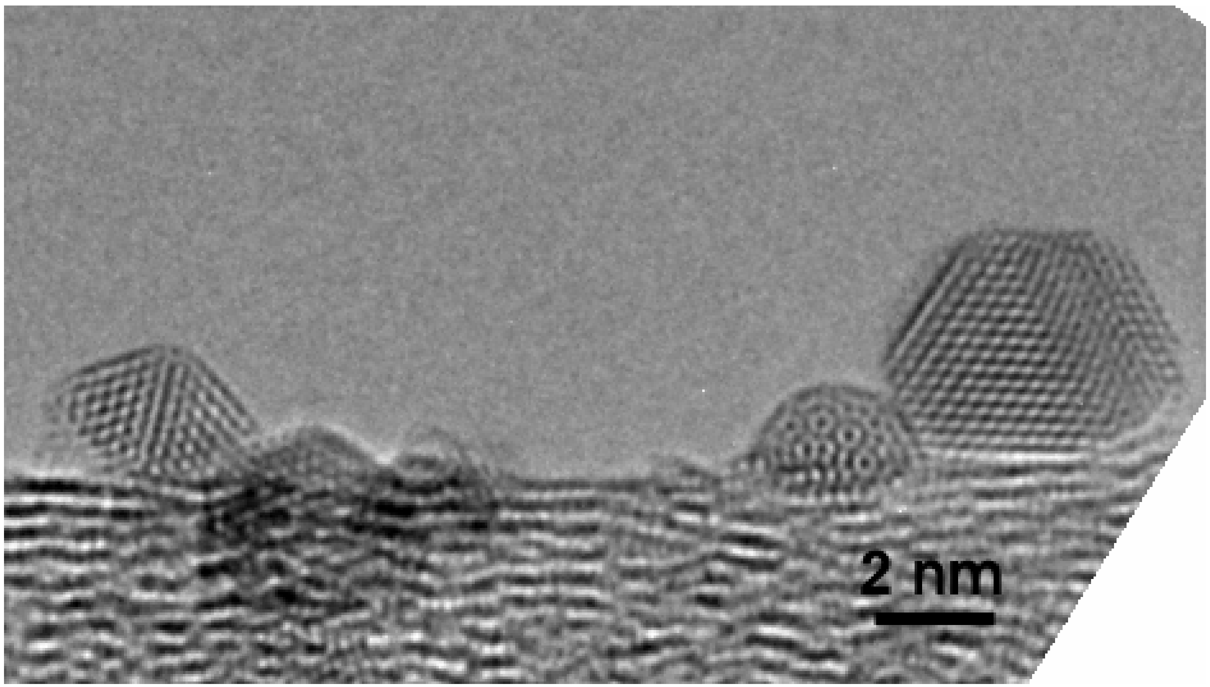
- Atoms at kinks and edges favour the formation of AyOH, this explains the higher selectivity of sample 9Ag/SiO2-IW

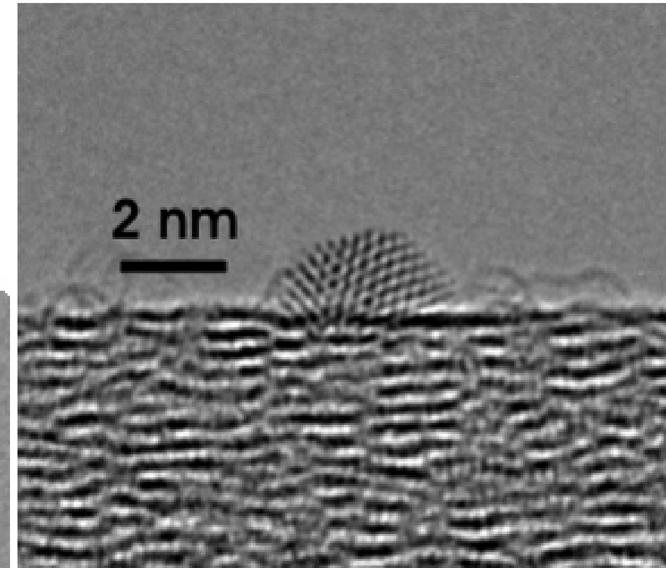
- HR-TEM images of the surfaces clearly reveal the difference in the active sites of both samples

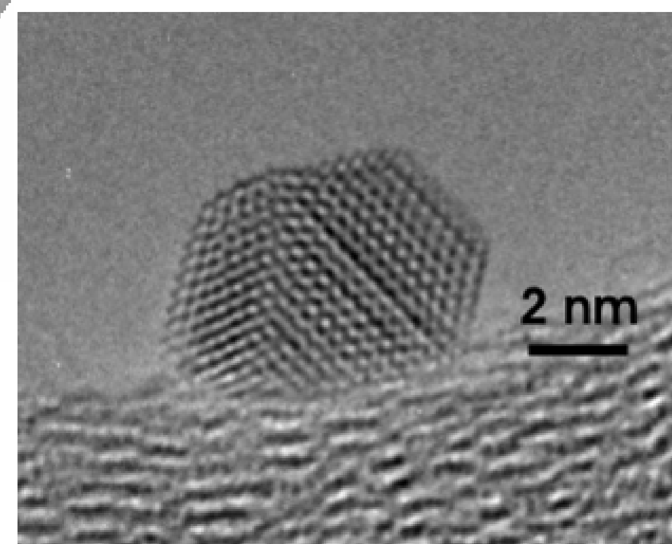
Overview of Au/CNTs



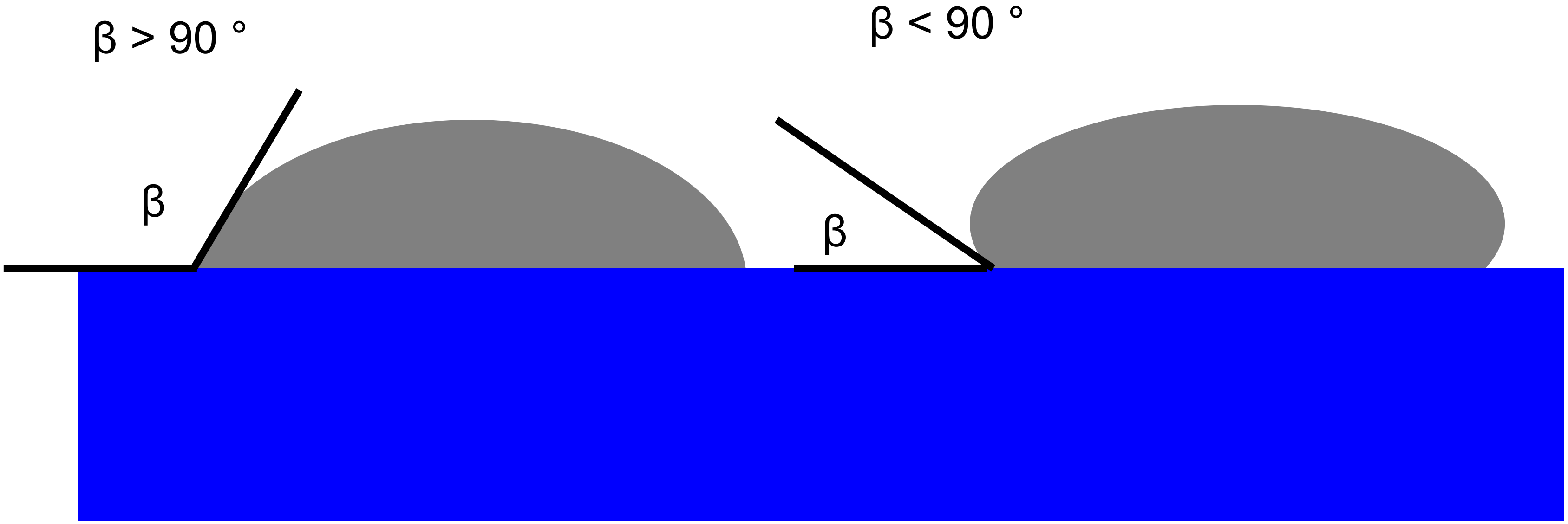
Au/CNT







Can the contact area and contact angle play a role ? Wetting condition



EM in Catalysis

Diffraction

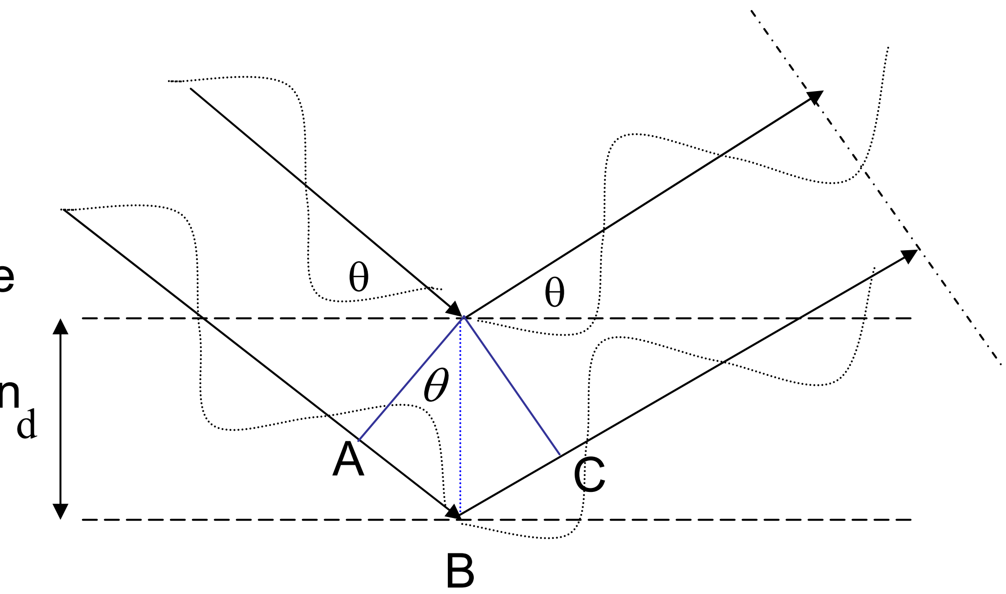
Interaction of electrons with specimen

Diffraction equations

Bragg equation

The electron waves behave as if they were reflected off atomic planes

The reflected wave remains in phase
If the path difference AB + BC
(2 d sin θ) follows the Bragg equation



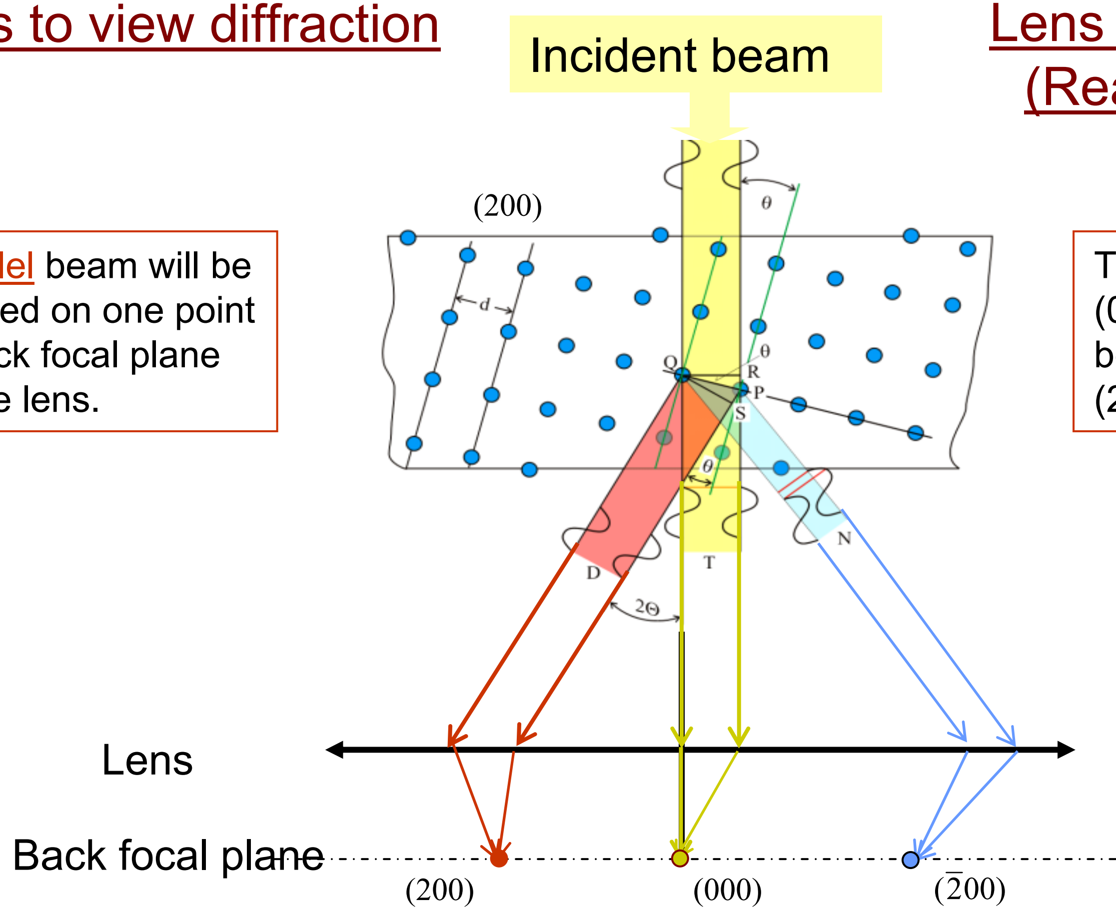
$$n\,\lambda = 2\,d\,\sin\theta$$

Thinking in reciprocal space

Using lens to view diffraction pattern

Lens = Fourier transform (Real ⟺ Reciprocal)

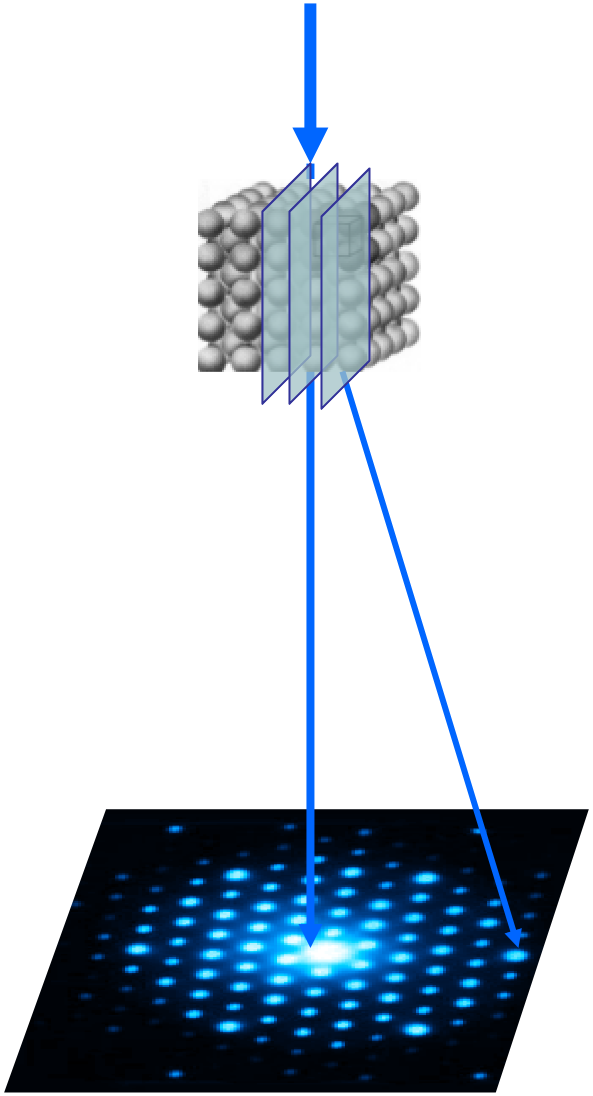
Parallel beam will be focused on one point at back focal plane by the lens.

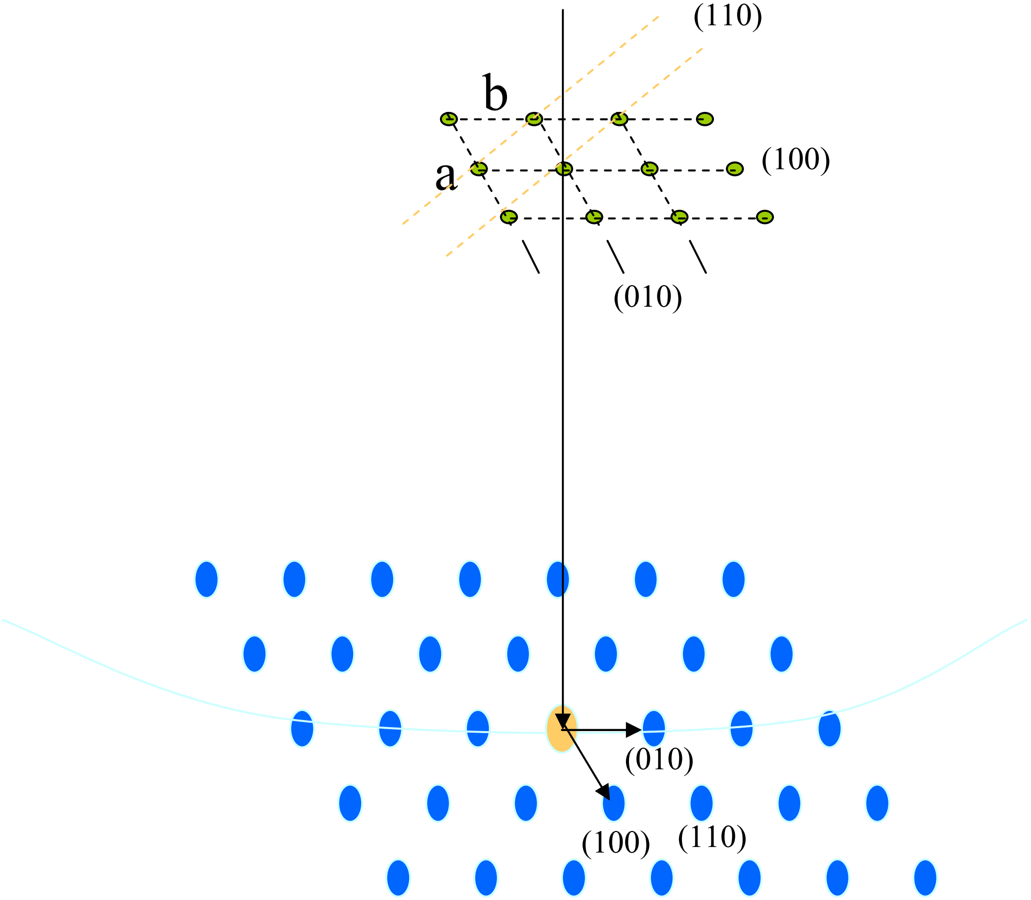


Transmitted beam gives (000) spot, and diffracted beam by (200) plane gives (200) diffraction spot.

Diffraction pattern

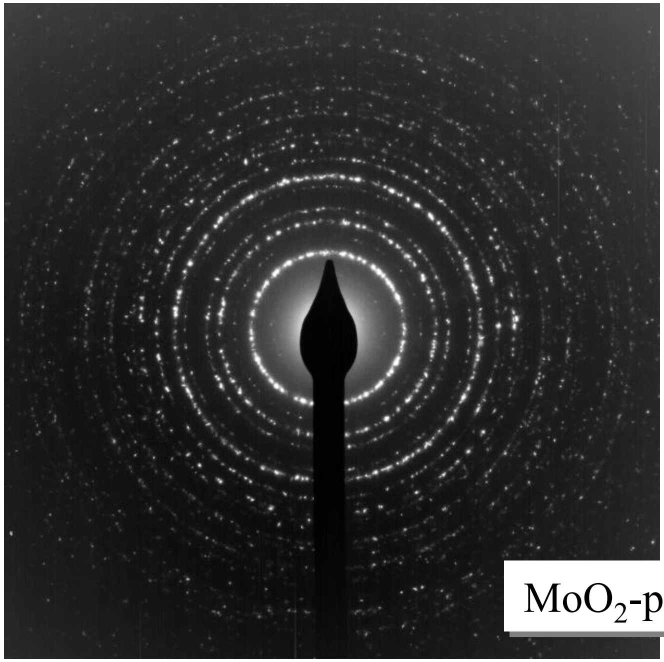
Electron Diffraction Pattern from a Single Crystal



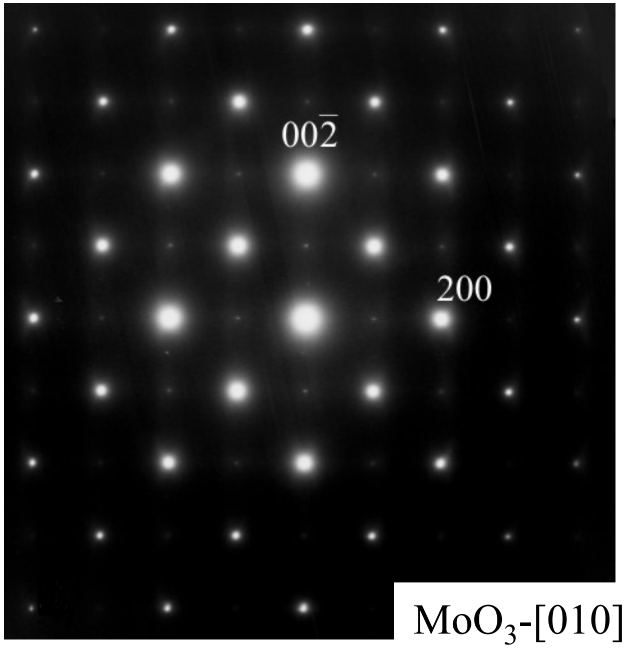


Selected-Area Diffraction (SAD)

Use select area aperture to include many crystallites and single crystallite

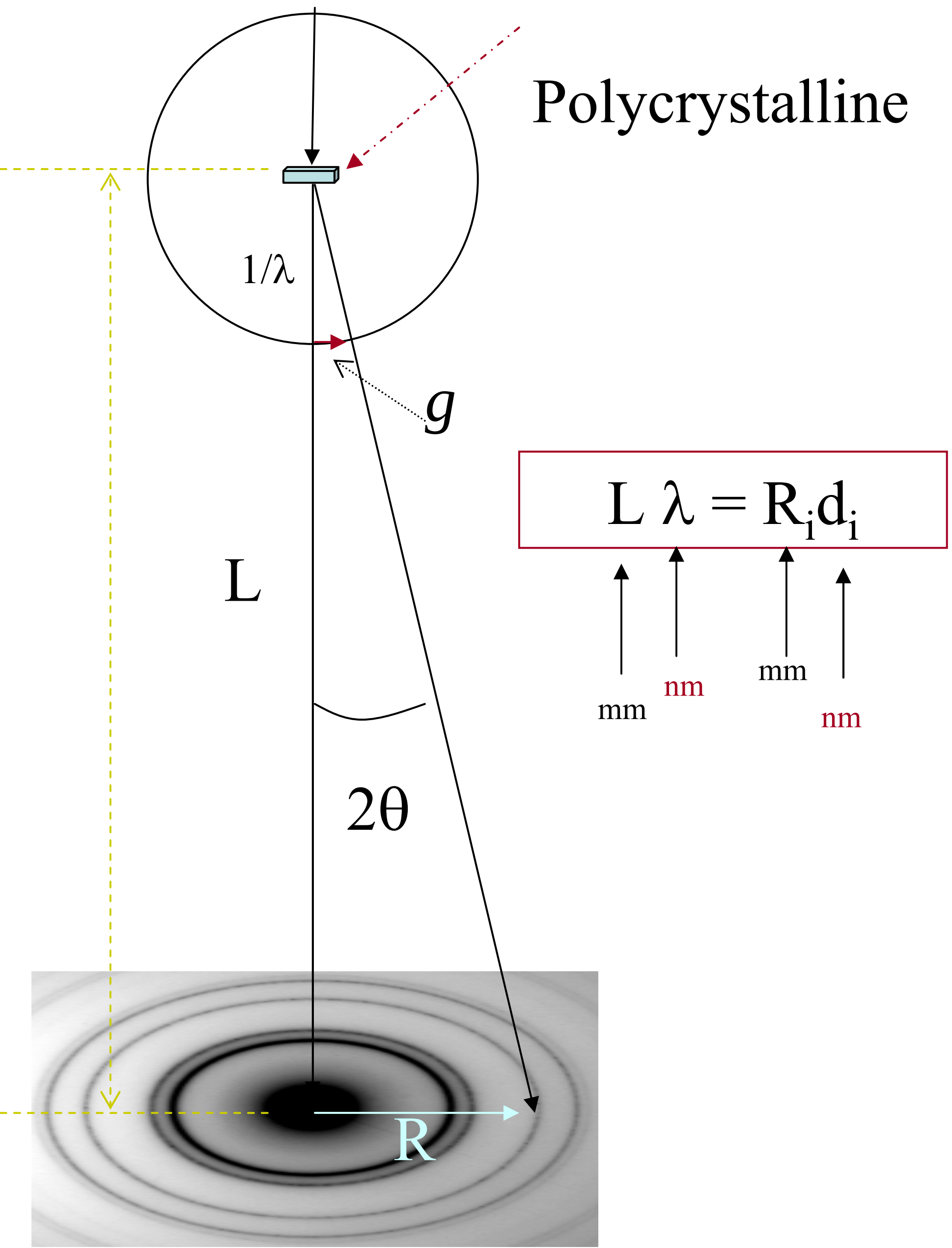


MoO_2-polycrystalline



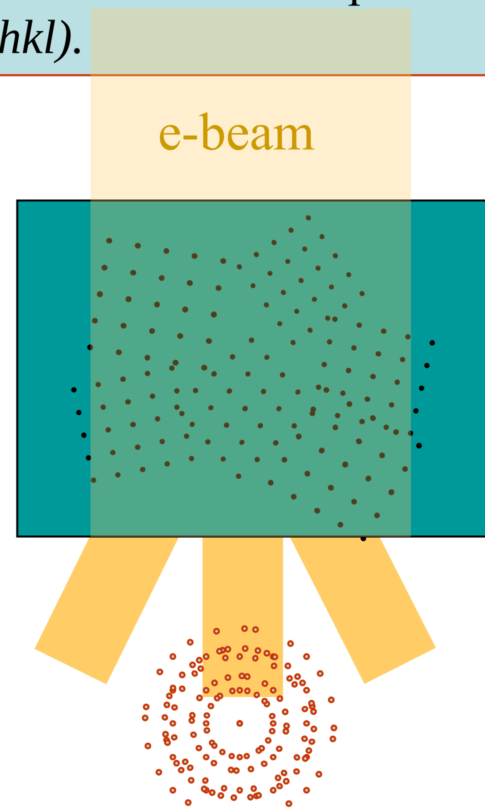
MoO_3-[010]

Electron Diffraction Pattern from a Polycrystalline

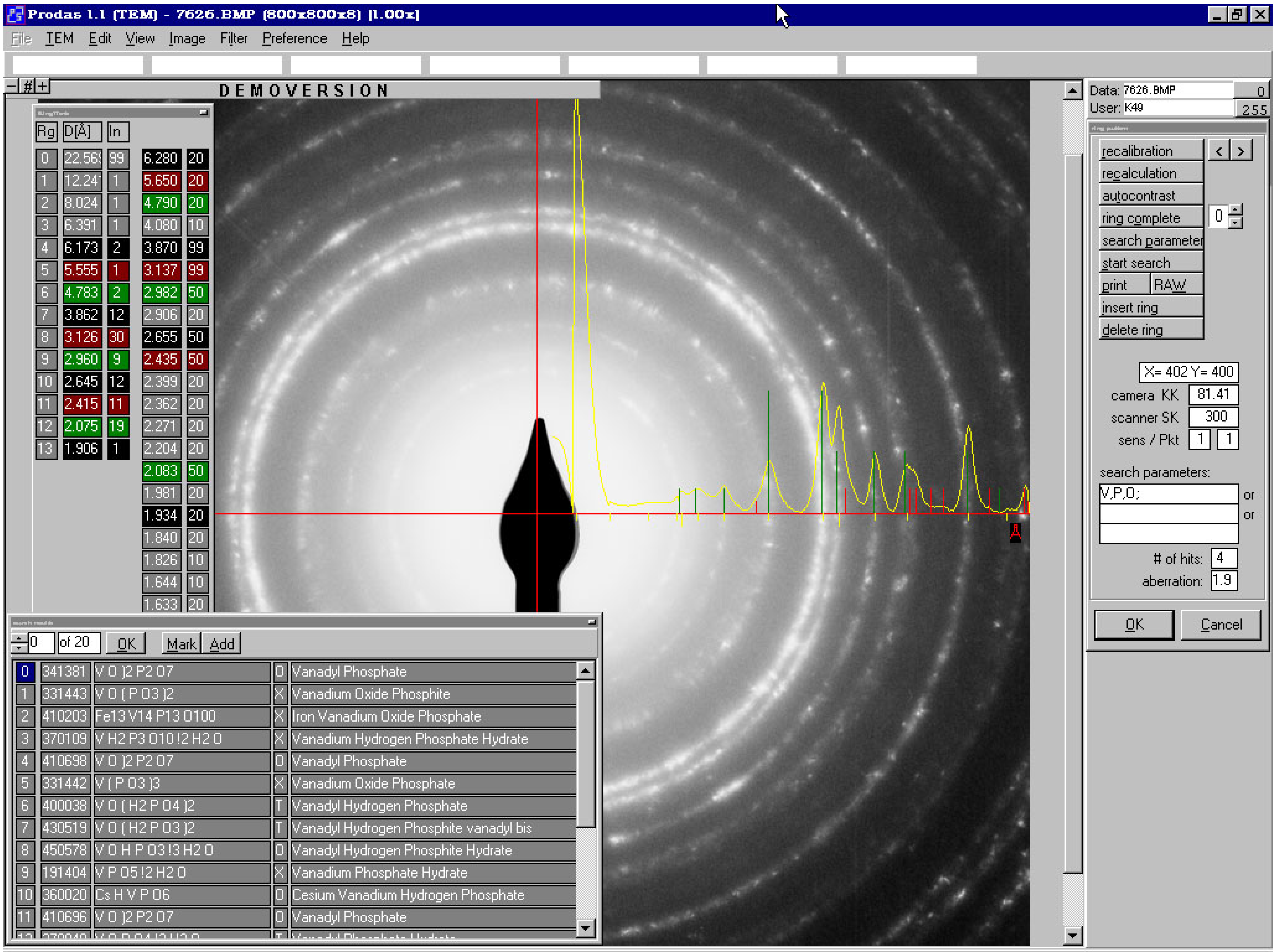


$$L\,\lambda = R_i d_i$$

Poly-crystals consist of different orientated single crystals. Their diffraction patterns come from these single crystal diffraction patterns superposed to each other. One diffraction ring is generated by superposing all spots of the single crystalline diffraction patterns with the same *(hkl)*.



Electron Diffraction Pattern



Classification of space lattices by crystal system

Cubic:

$a = b = c$

$\alpha = \beta = \gamma = 90^o$

Tetragonal:

$a = b \neq c$

$\alpha = \beta = \gamma = 90^o$

Hexagonal:

$a = b \neq c$

$\alpha = \beta = 90^o$

$\gamma = 120^o$

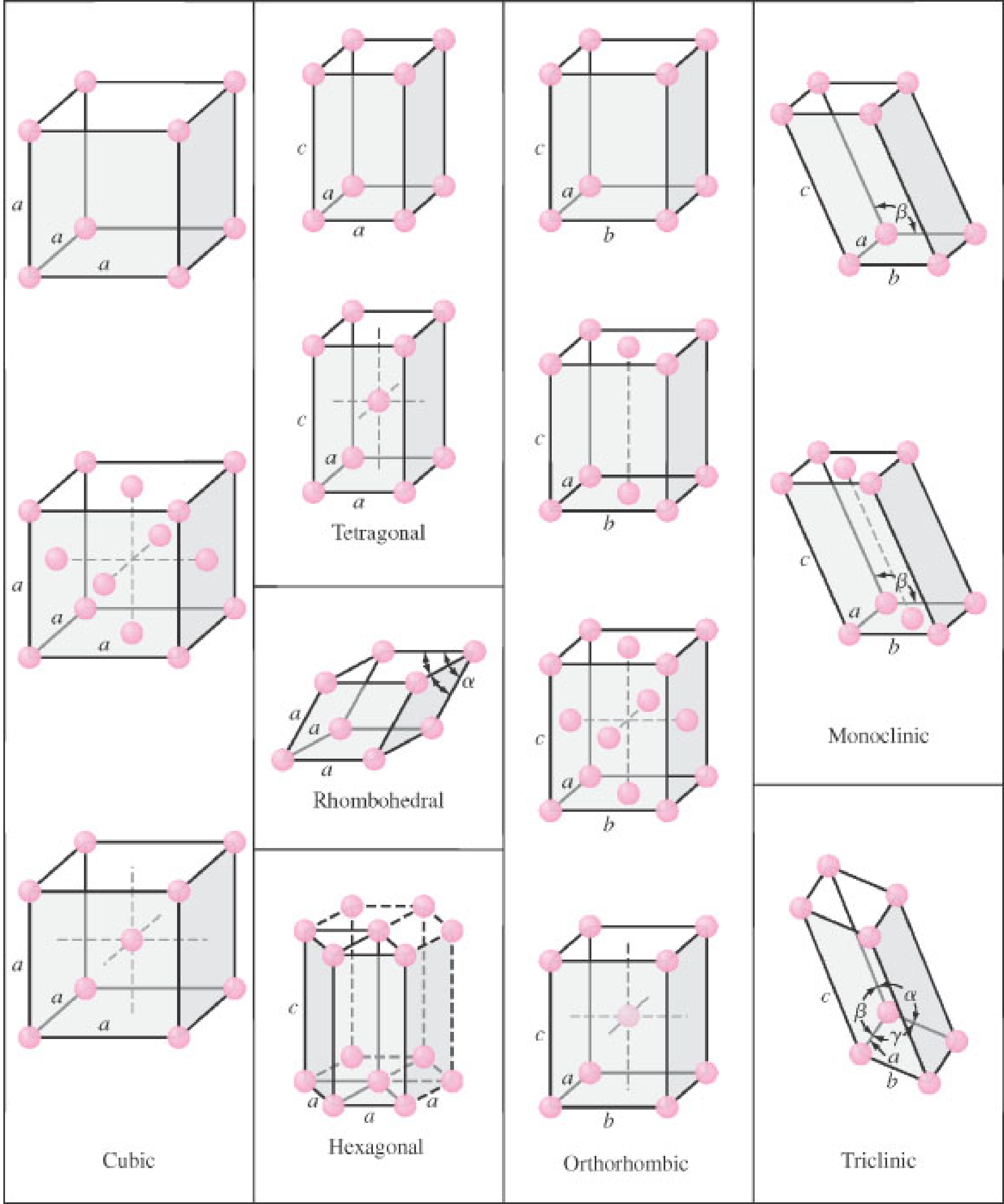


Image Interpretation

Image interpretation and analysis can be even more difficult than taking an image

TEM gives only a 2D projection !

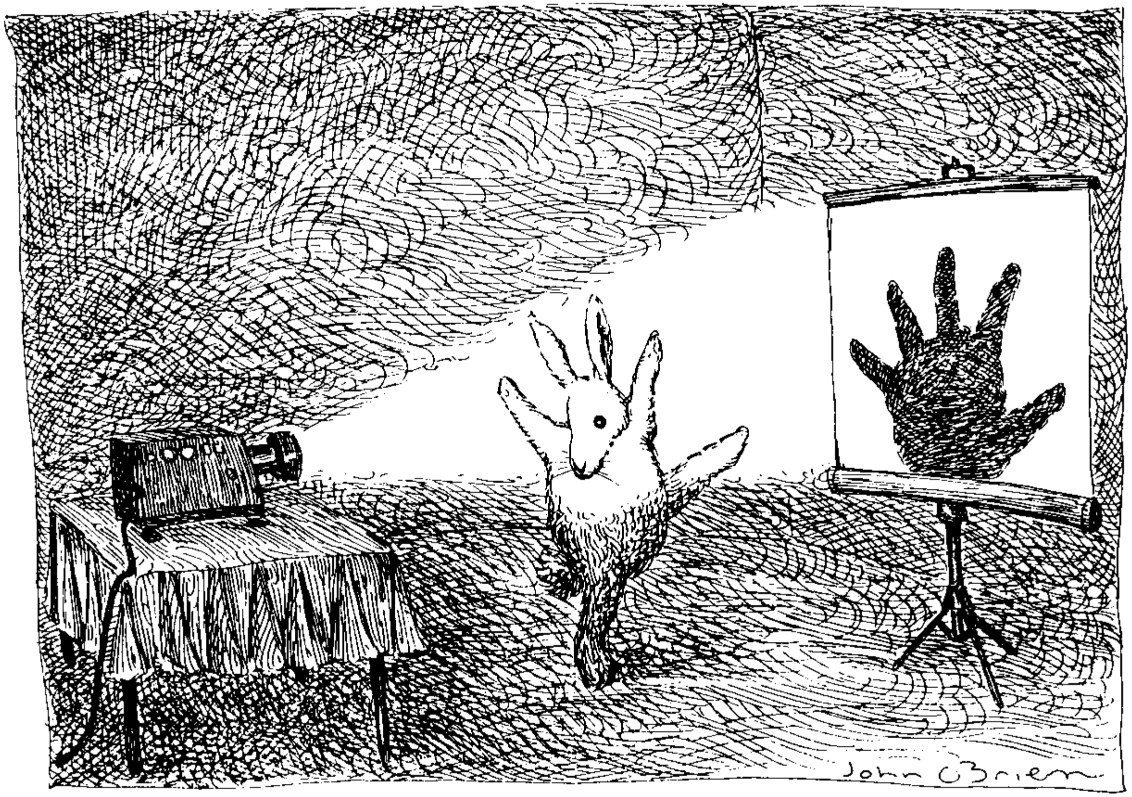
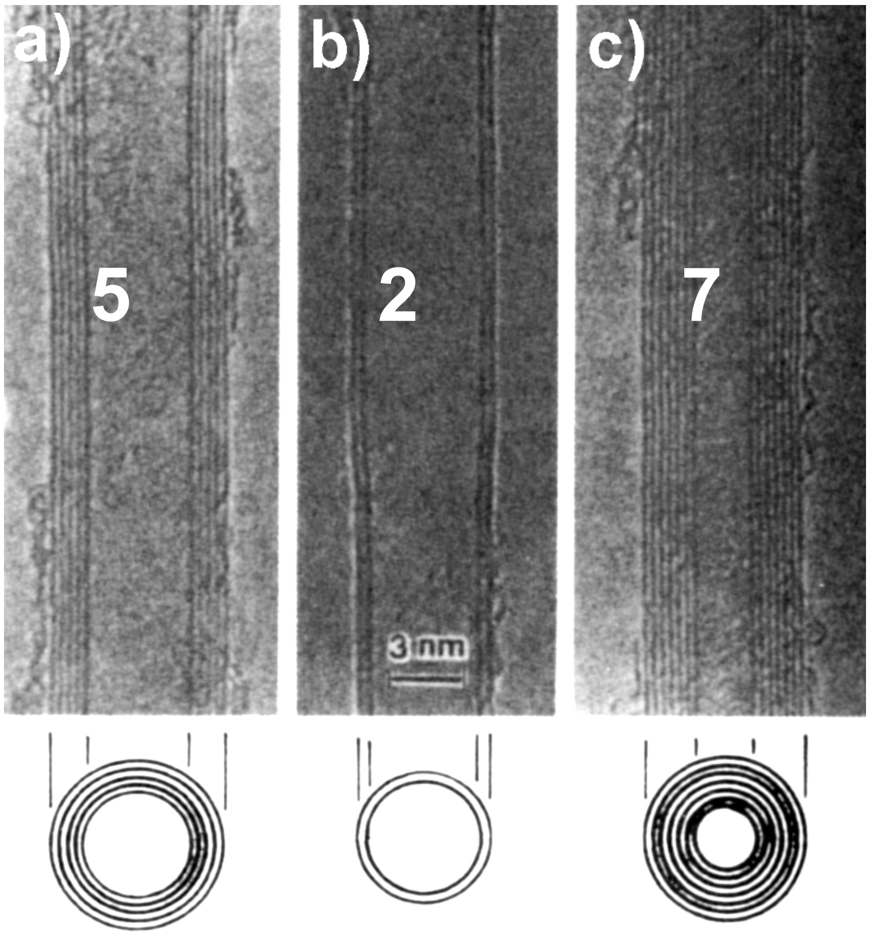


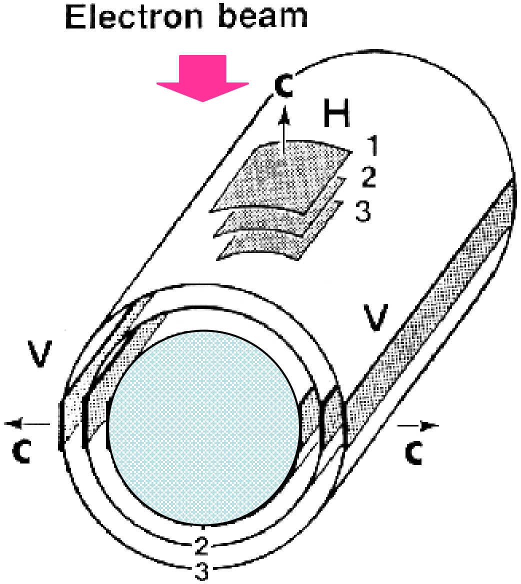
Fig. 5.1. A single projection image is plainly insufficient to infer the structure of an object. Drawing by John O'Brien; © 1991 The New Yorker Magazine.

By looking only in projection we can be fooled !

Multiwall Carbon Nanotube (MWCNT)

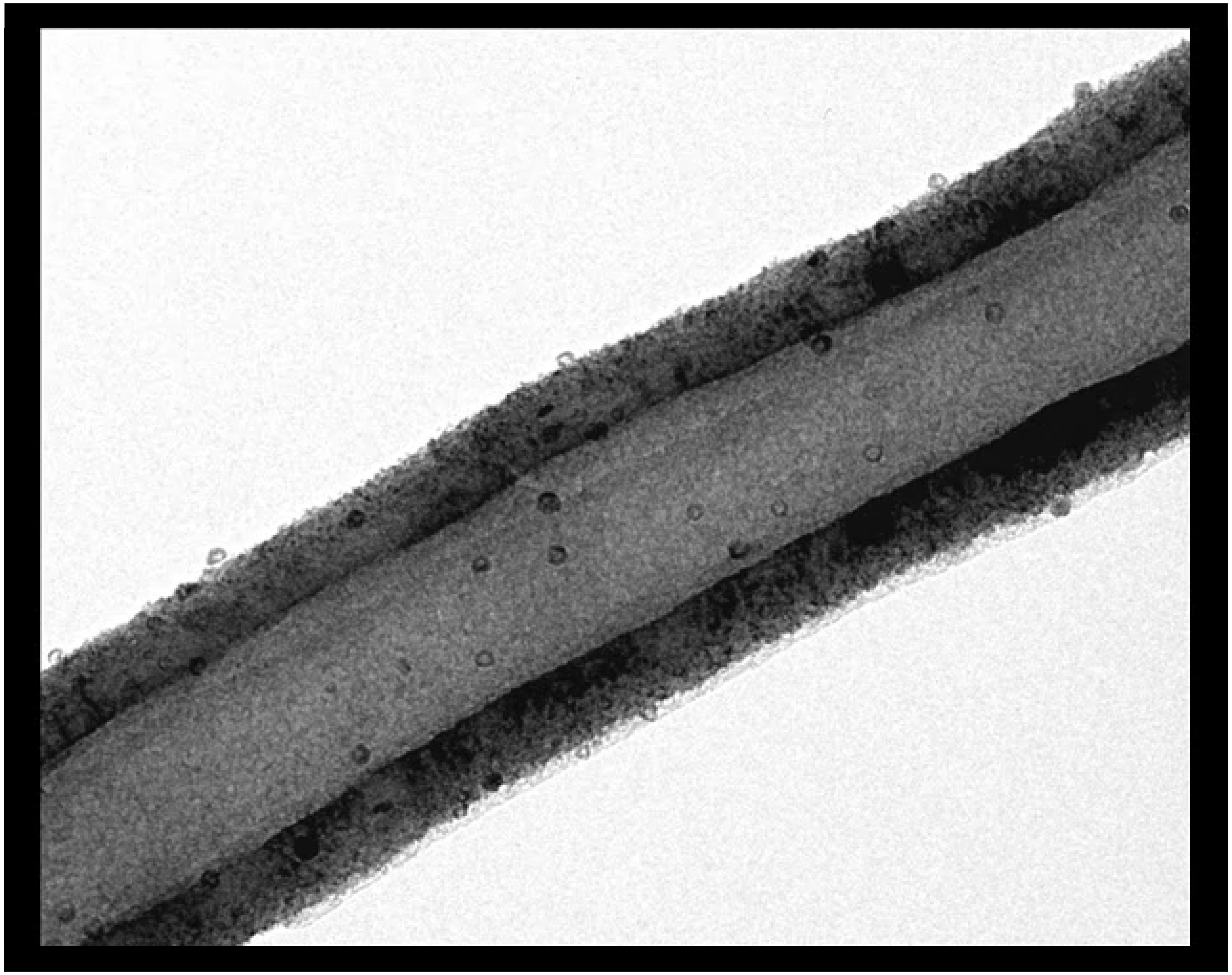


Iijima, Nature 354, 56-58 (1991)

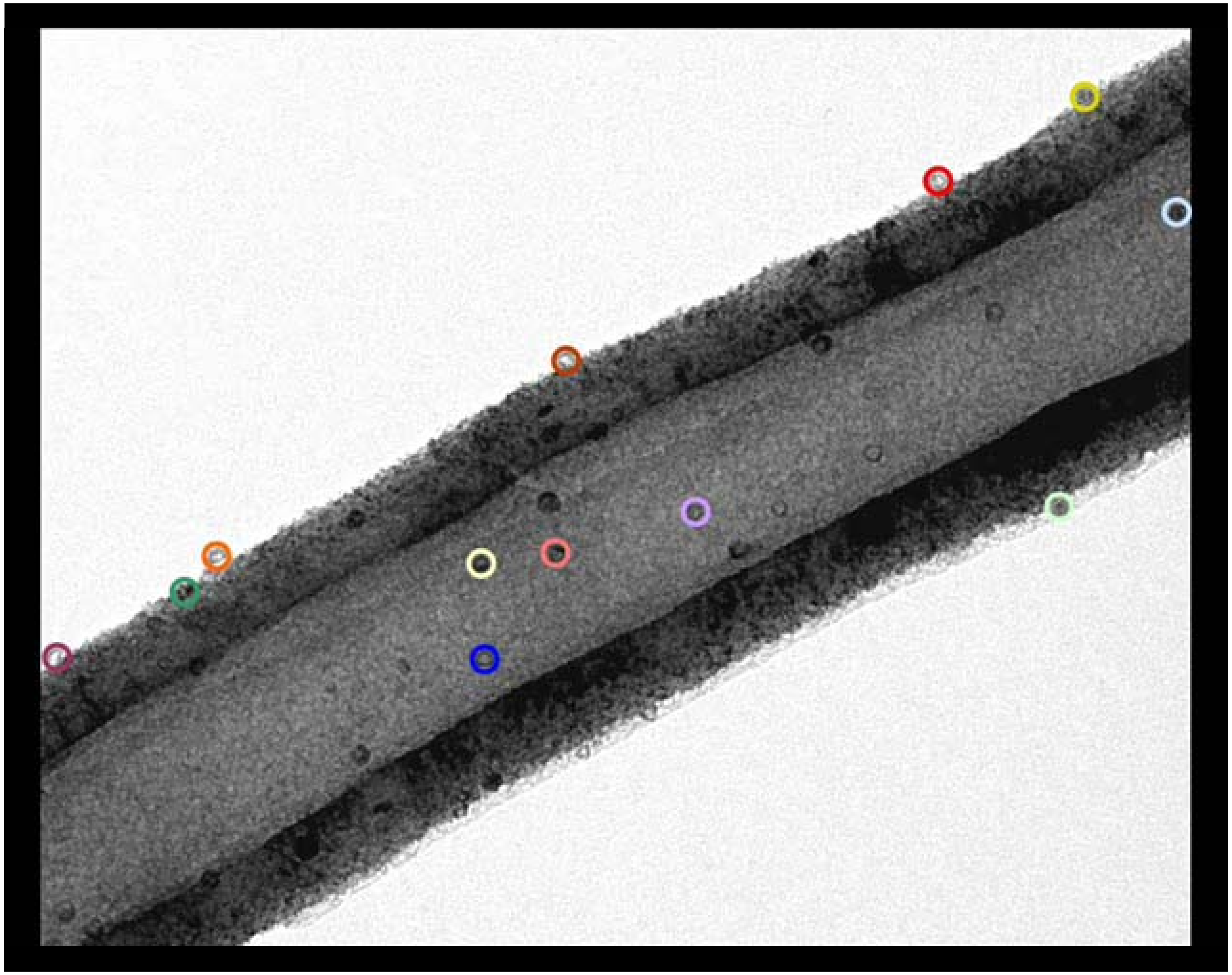


Geometry of transmission electron microscopy in plan-view

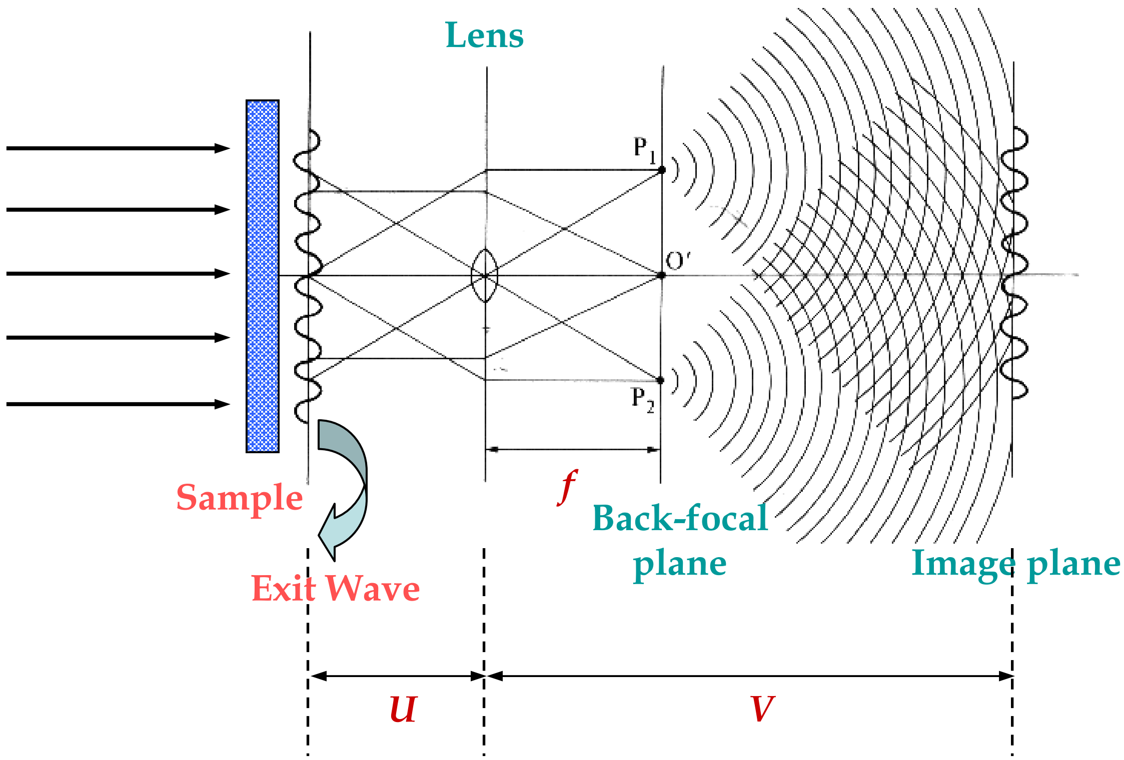
2D Projection: Are the Particles inside or outside of the CNT ?



2D Projection: Are the Particles inside or outside of the CNT ?

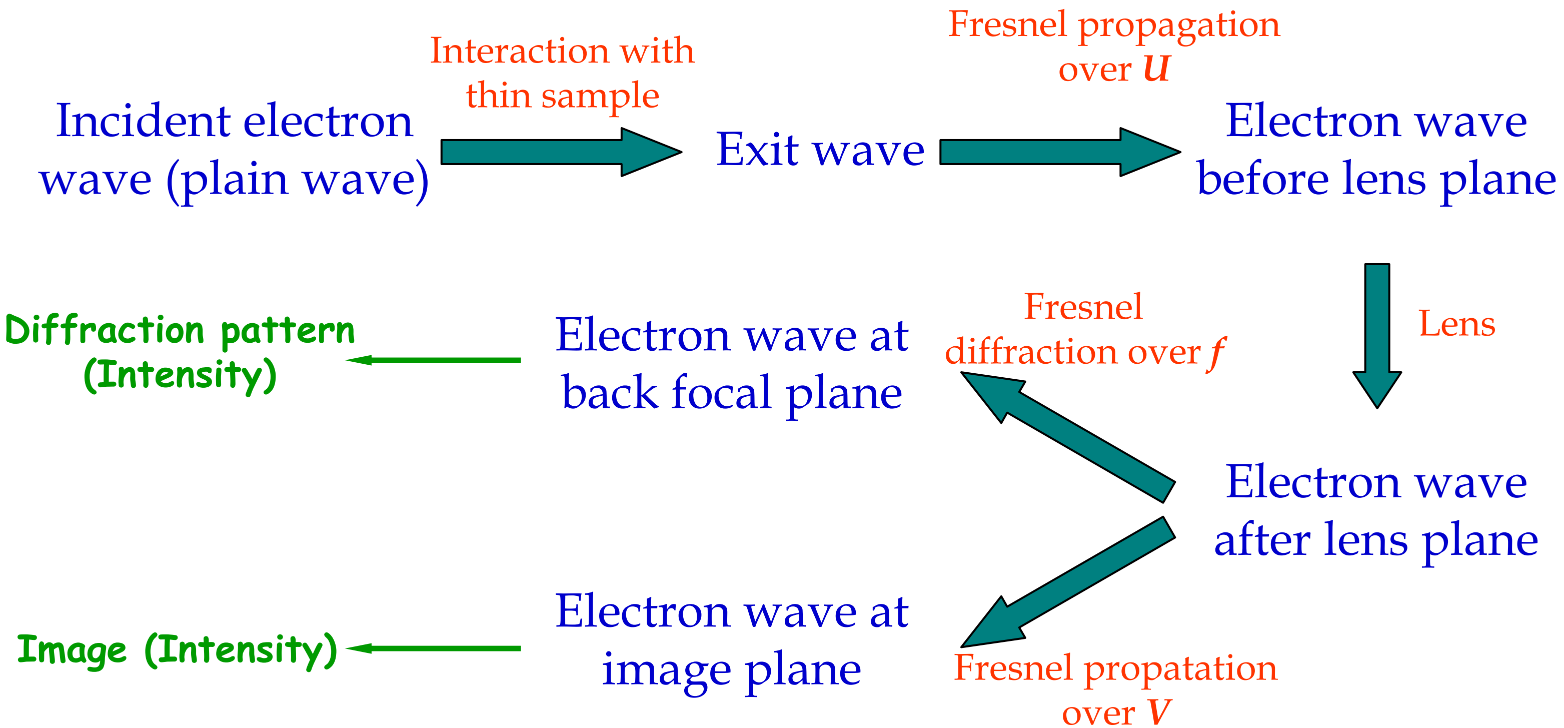


High-resolution imaging



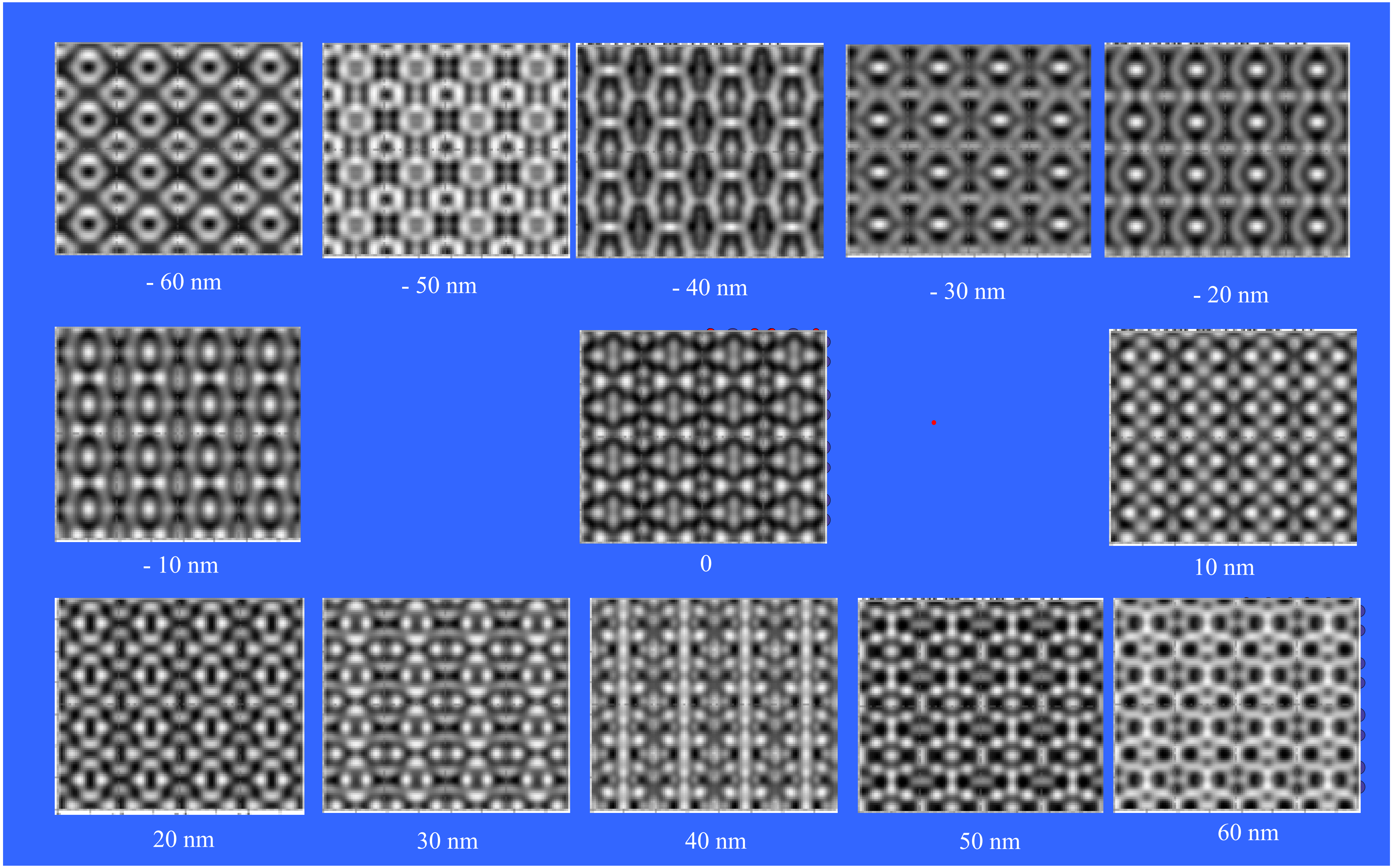
Abbe Interpretation of imaging

Abbe Interpretation of imaging



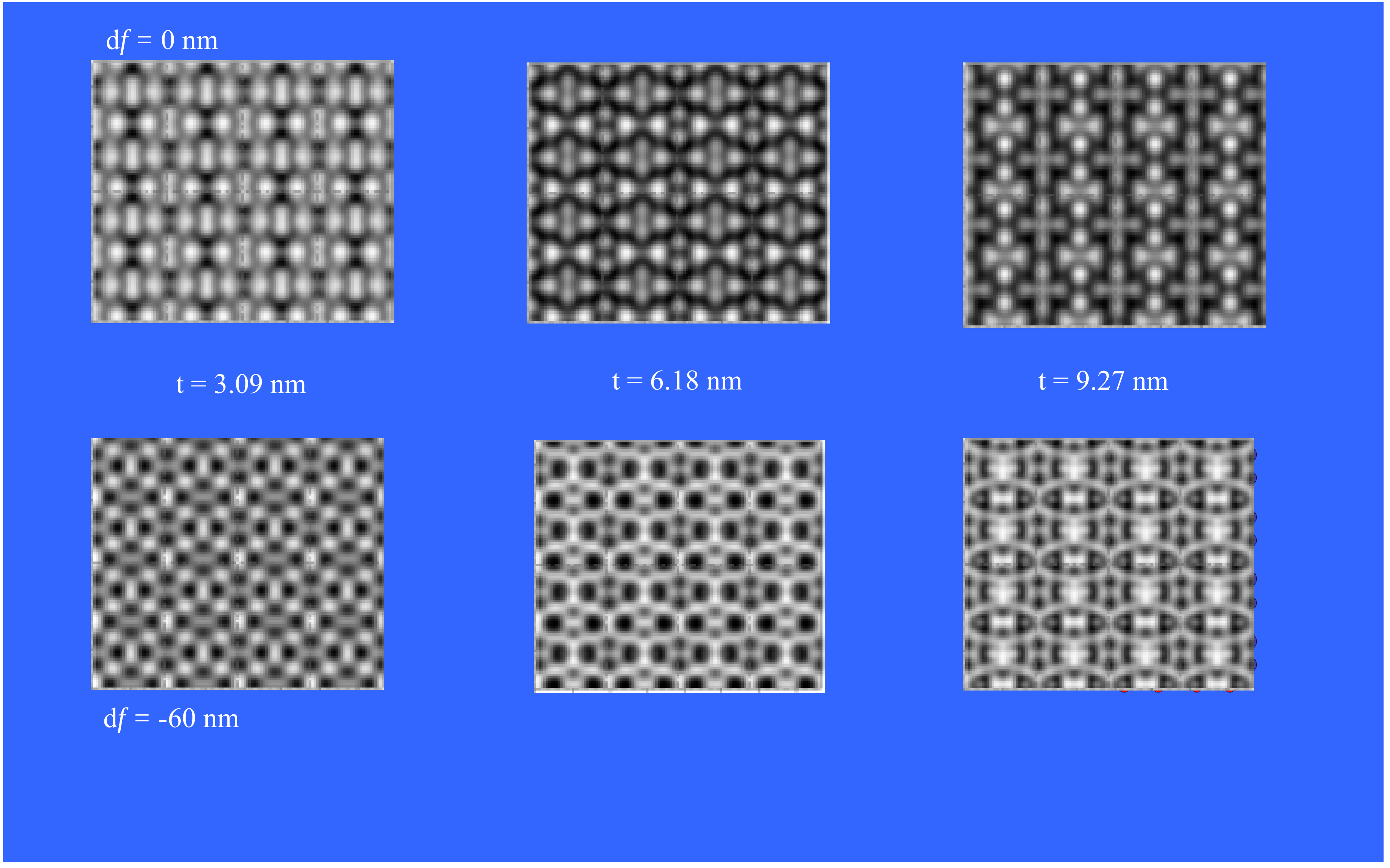
High resolution image: influence of focus

$(VO)_2P_2O_7$



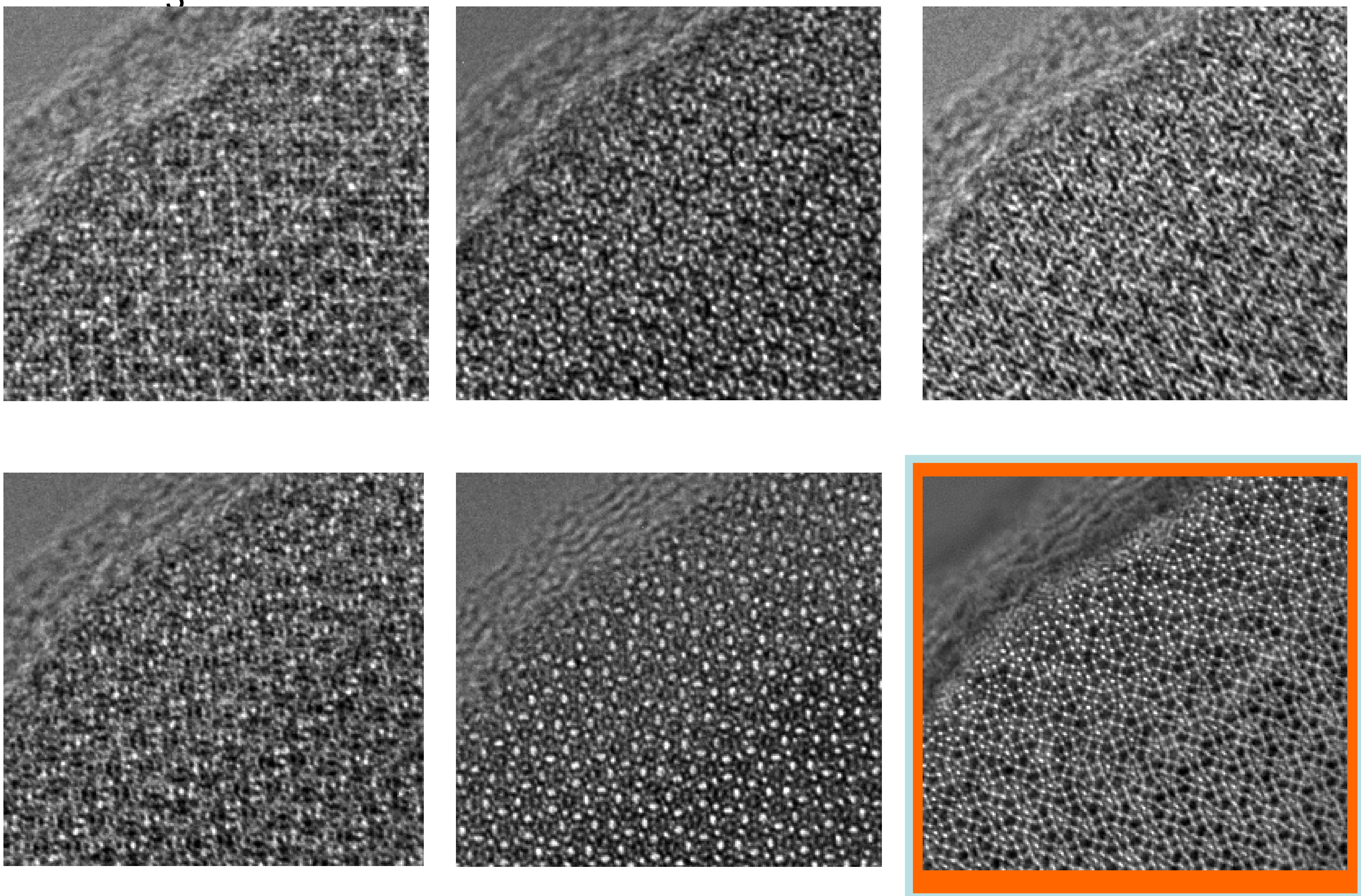
High resolution image: influence of thickness

$(VO)_2P_2O_7$



High-resolution Image: experiment

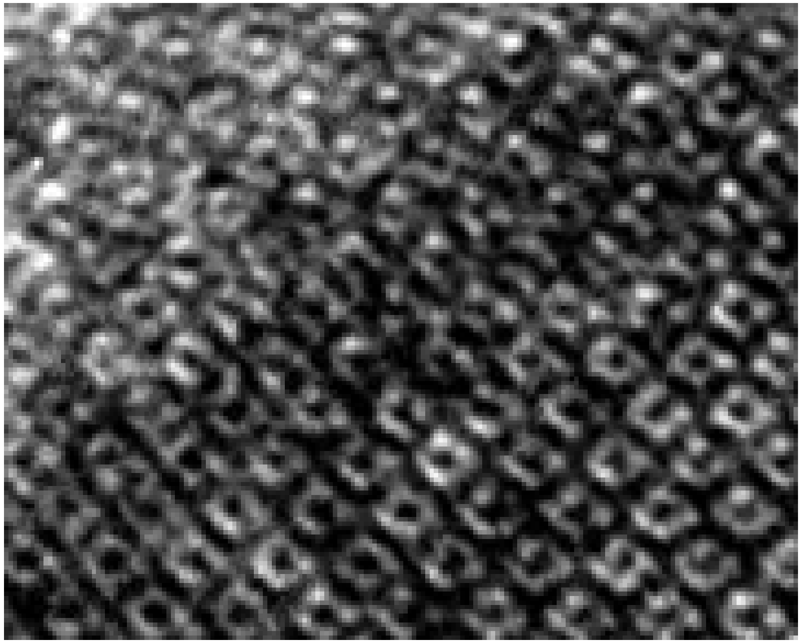
$NbMoO_3$ HRTEM at various defocus

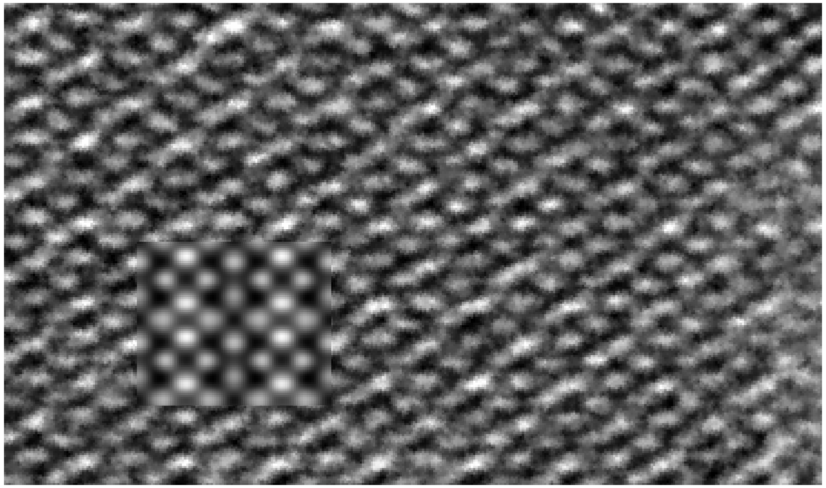


Prof. A. Kirkland, University of Cambridge

Contrast matching: experimental and simulation

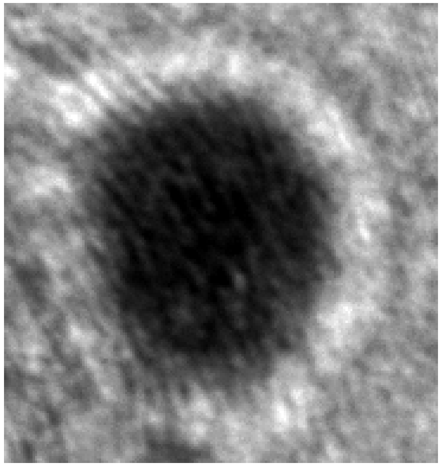
$(VO)_2P_2O_7$

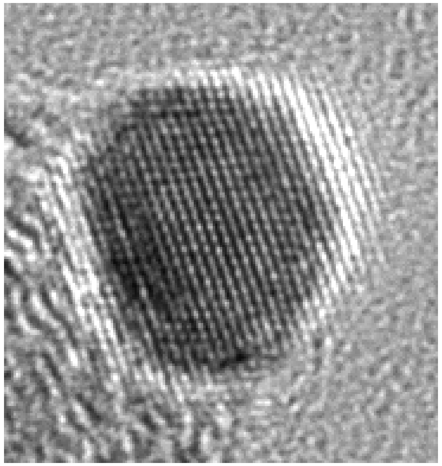


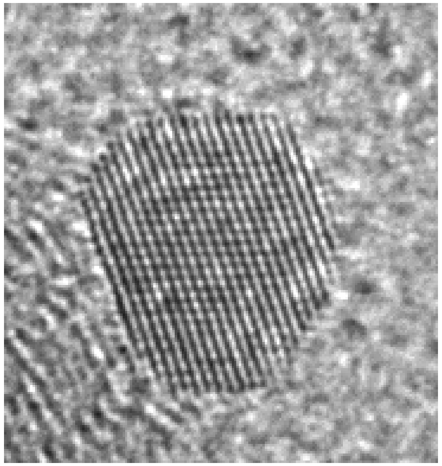


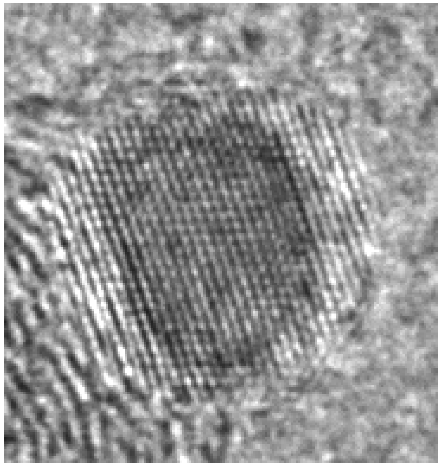
Delocalization effect in high-resolution image

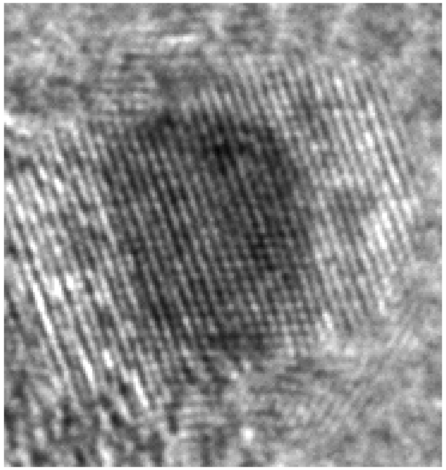
High resolution images of an Au nanoparticle

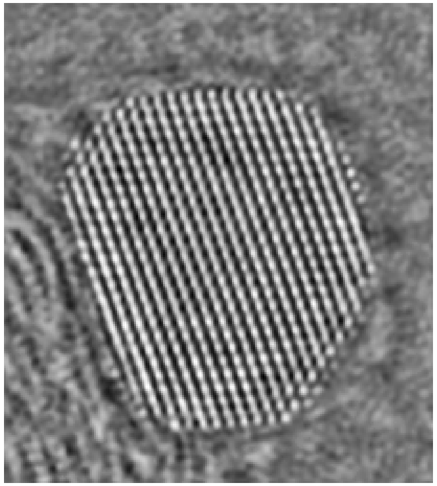




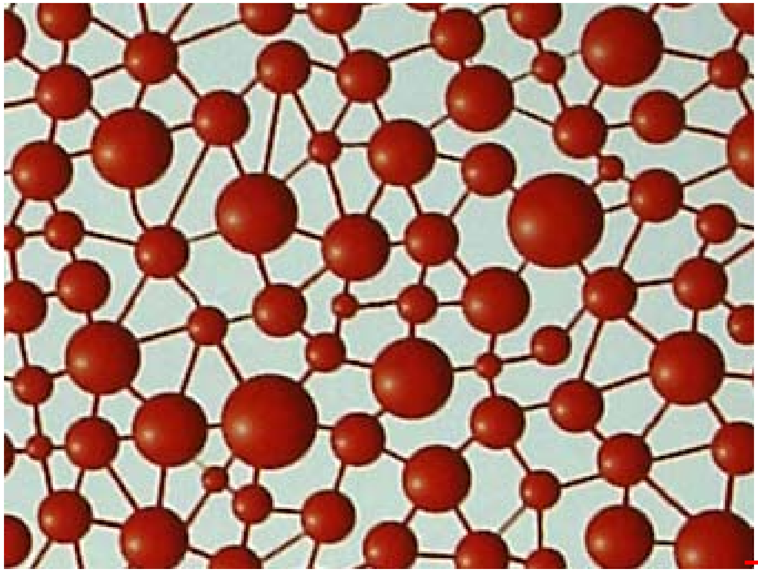


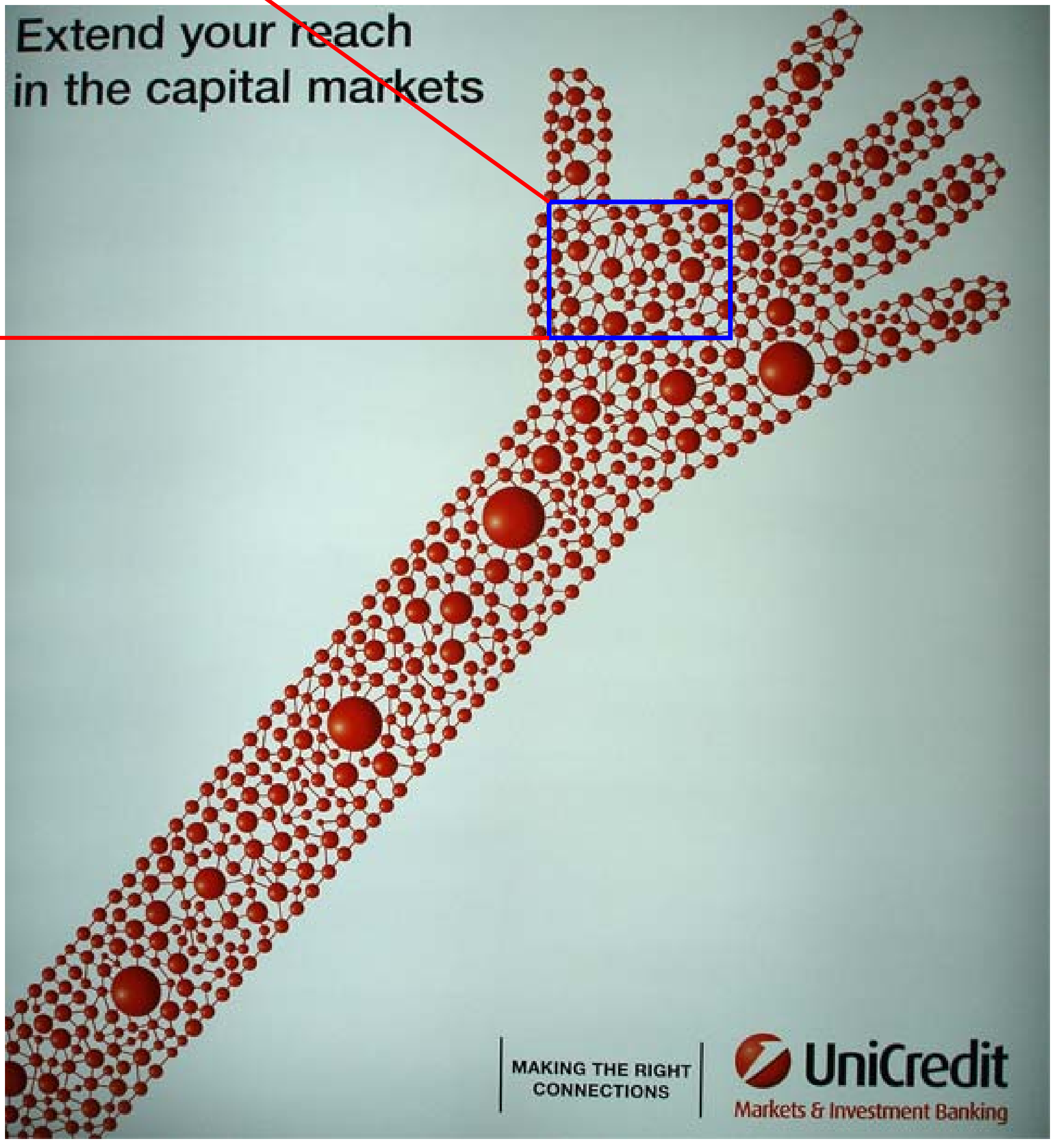






Reconstructed phase contrast

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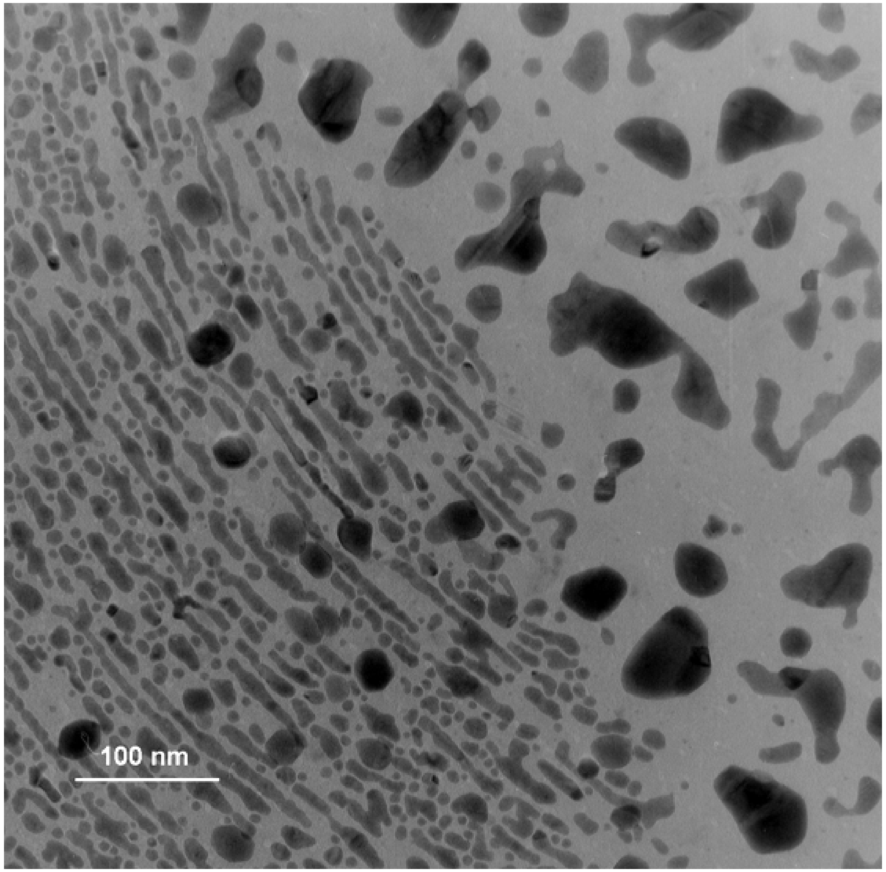
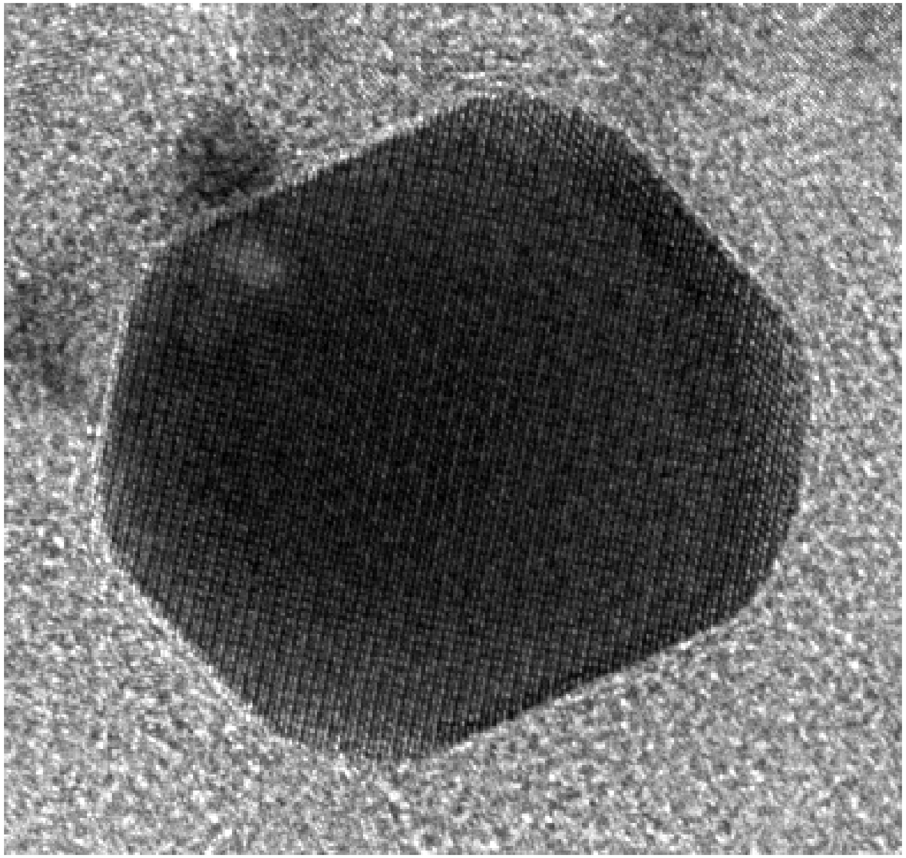
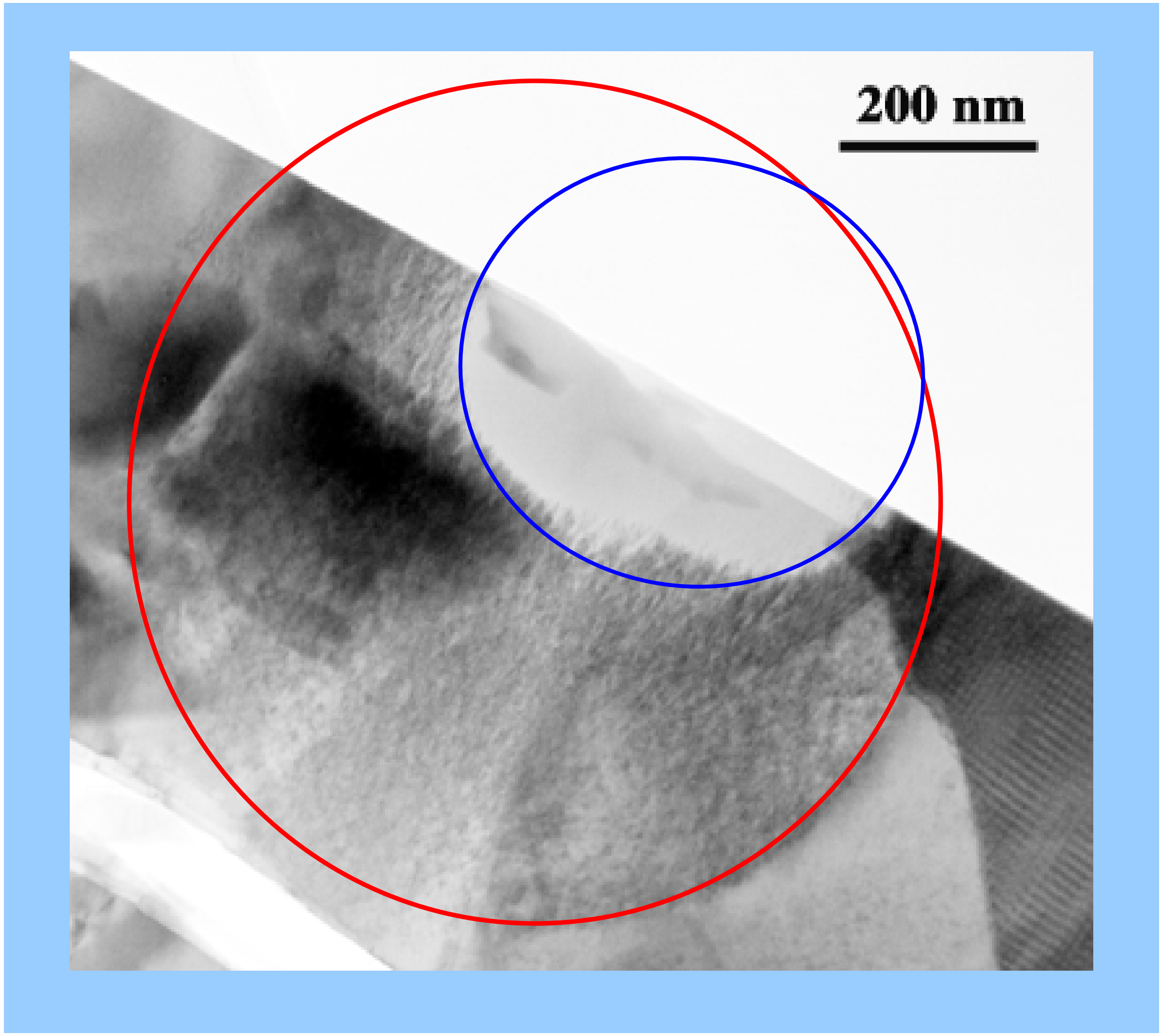




Di Wang

Electron-Matter interaction and radiation damage !

Electron-Matter interaction and radiation damage !



Electron-Matter interaction and radiation damage !

The processes responsible for radiation damage are the same processes that provide diffraction and chemical information in electron microscope:

Electron-nucleus (elastic) collisions

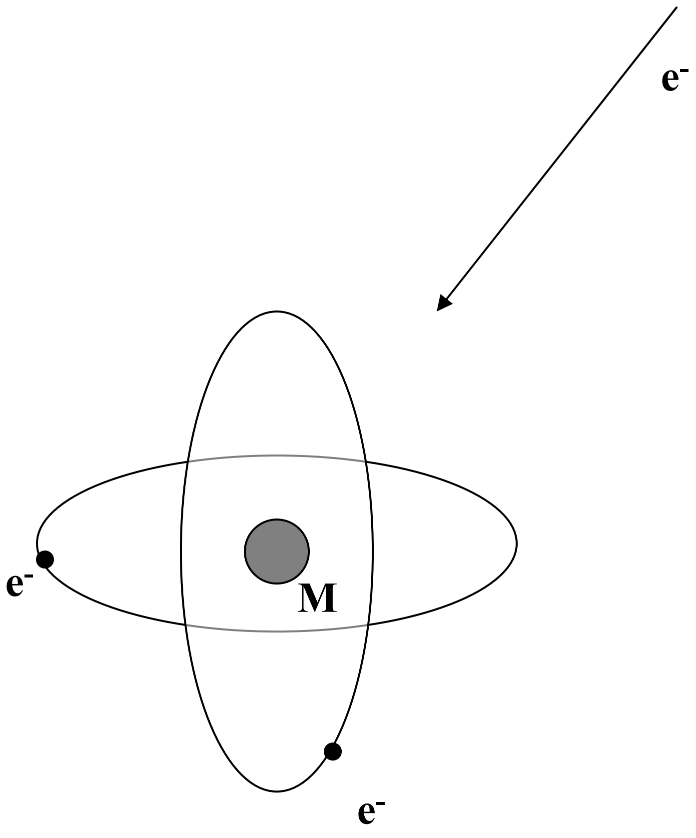
↓

Knock-on displacement

Electron-electron (inelastic) collisions

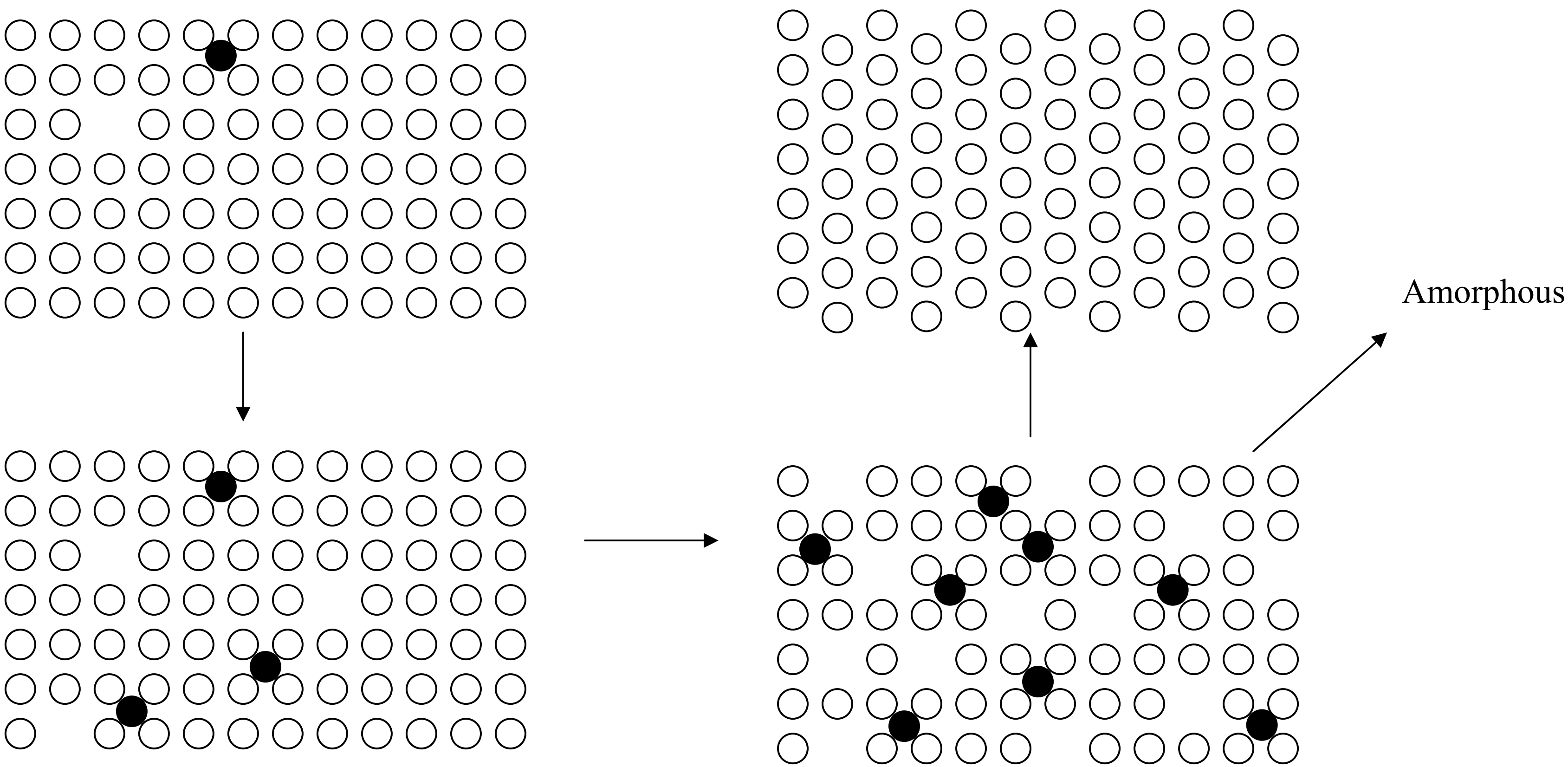
↓

Radiolysis processes



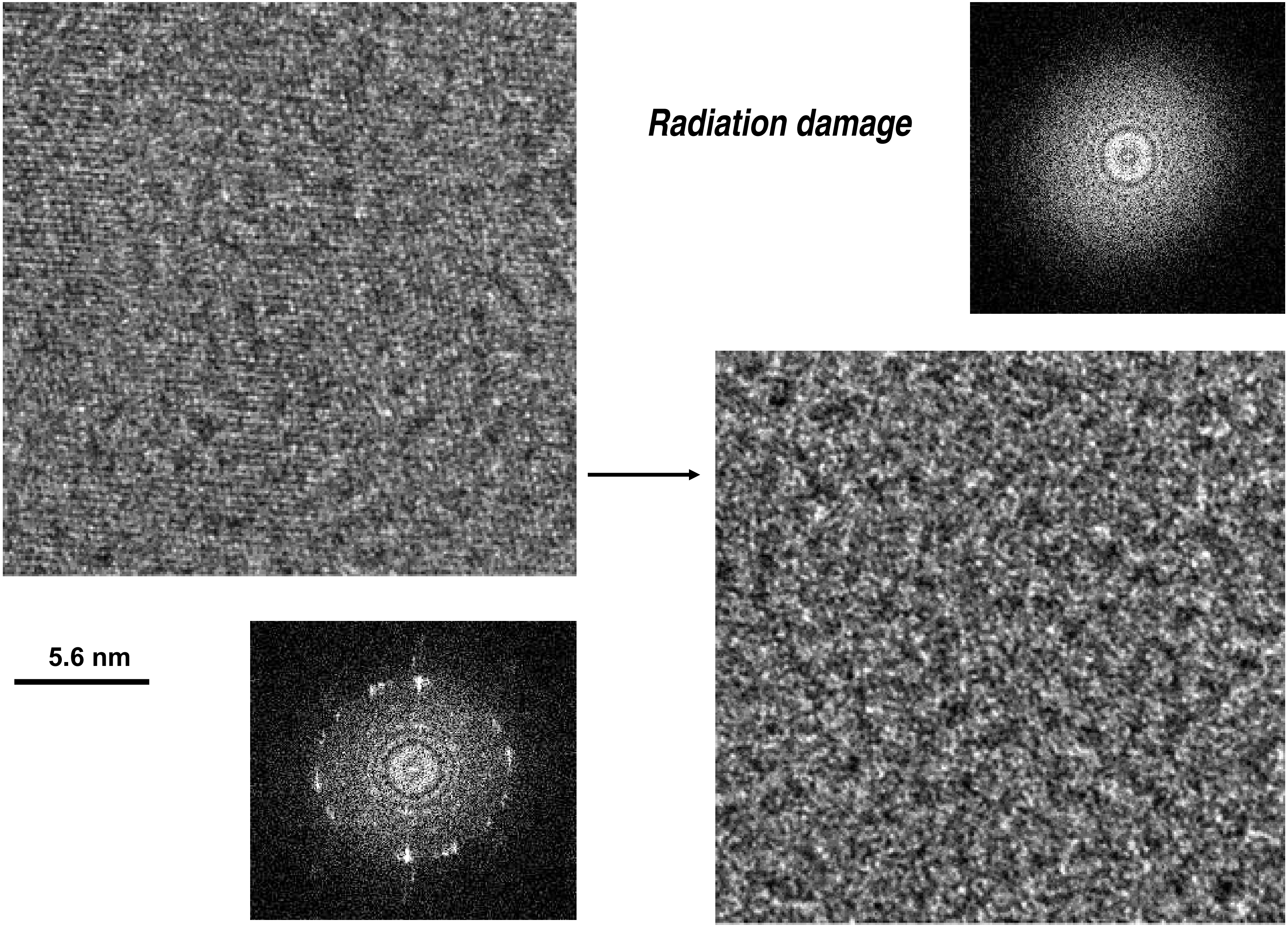
Electron-Matter interaction and radiation damage !

The fundamental unit of damage is an atom displaced to an interstitial site and its attendant vacancy, called collectively as a Frenkel defect

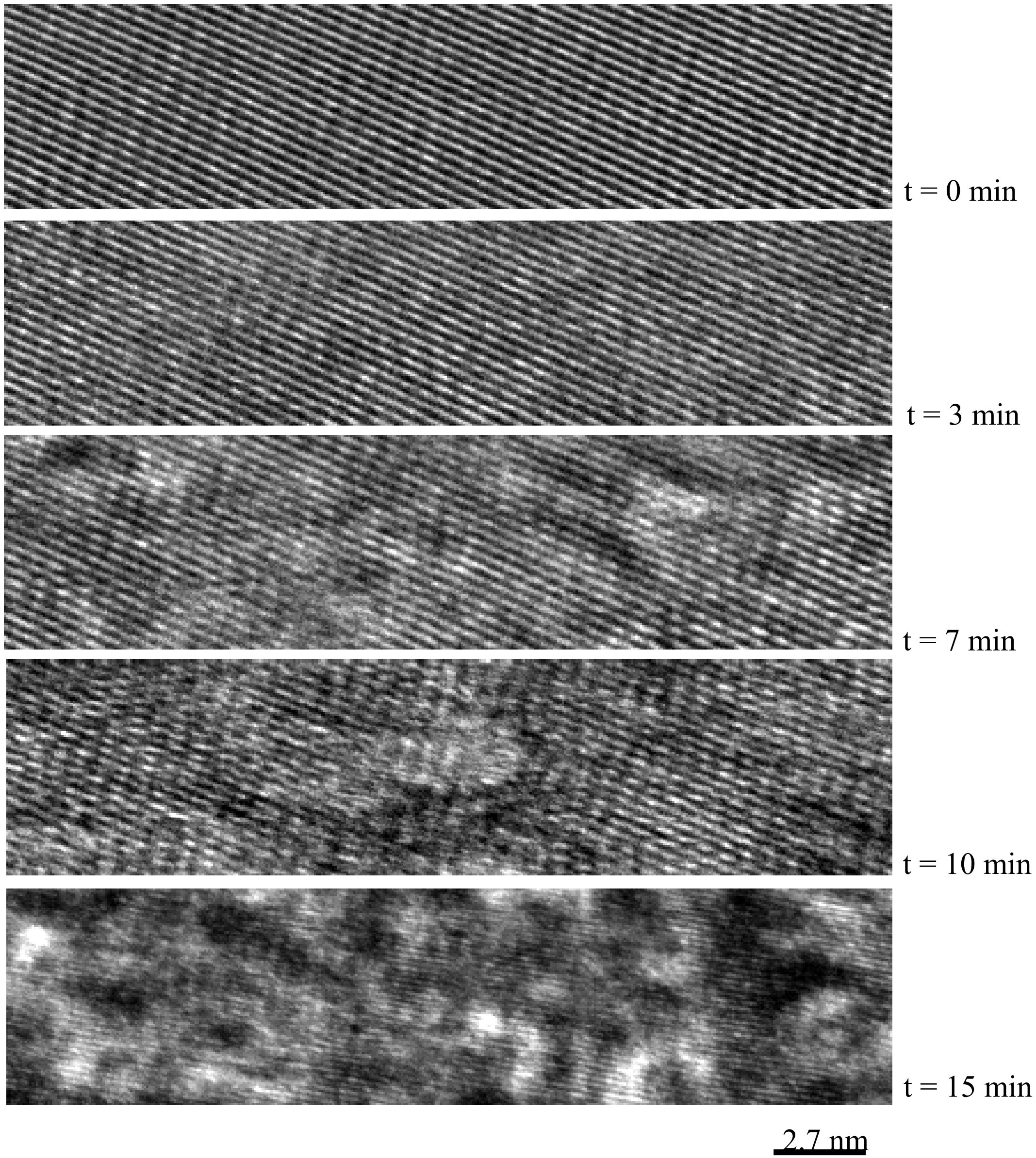


Sample is damaged (point defects), but the structure does not change

High density of Frenkel defects; the long range order of sample is seriously perturbed


Radiation damage
5.6 nm

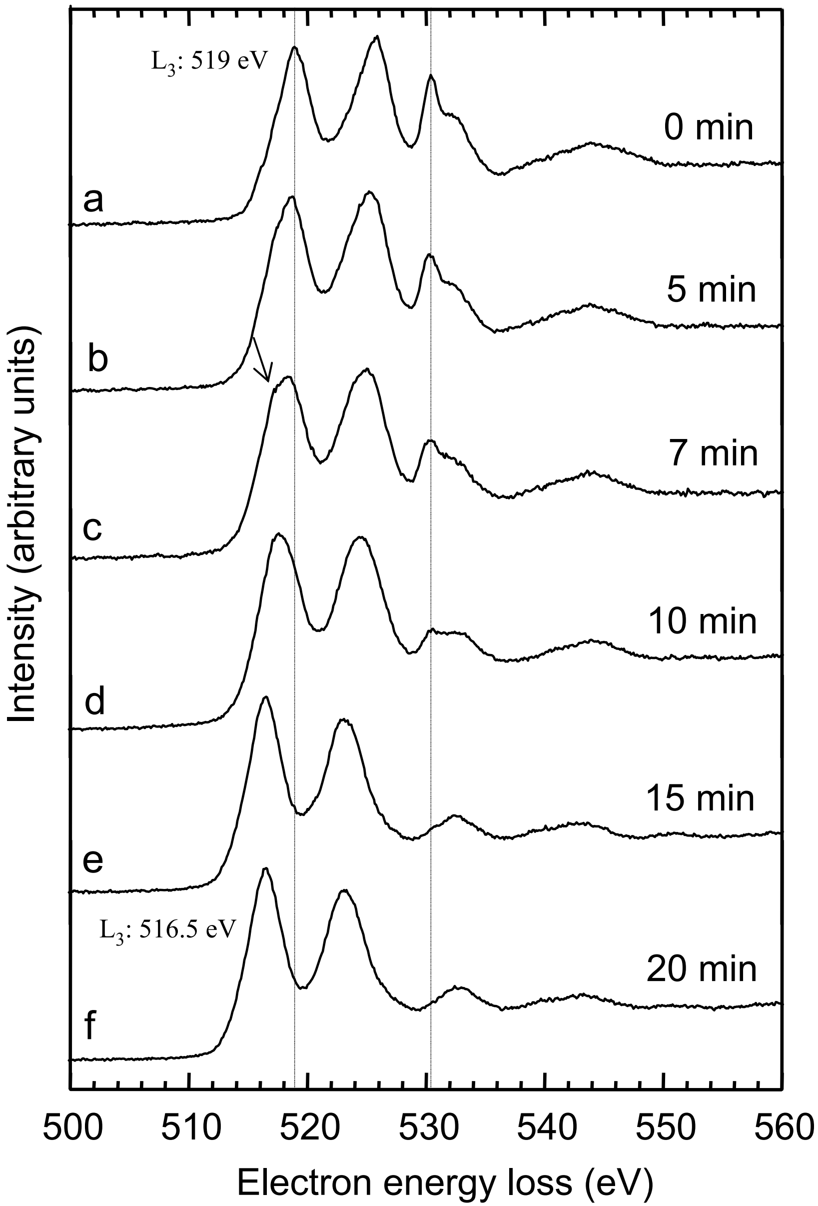
Electron-Matter interaction and radiation damage !



HREM-series at different irradiation time. Specimen is nearly [001] oriented. The 110- and 100-lattice fringes of V_2O_5 and VO are clearly recorded. The electron current density is 0.5 A/cm^2

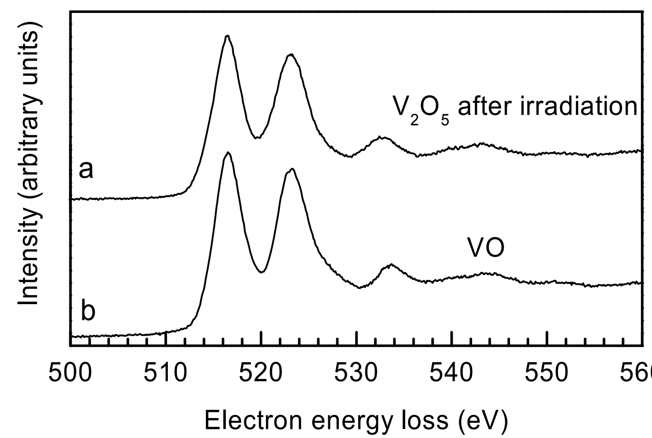
D. Su, et al, *Catal. Lett*. 2001

Electron-Matter interaction and radiation damage !

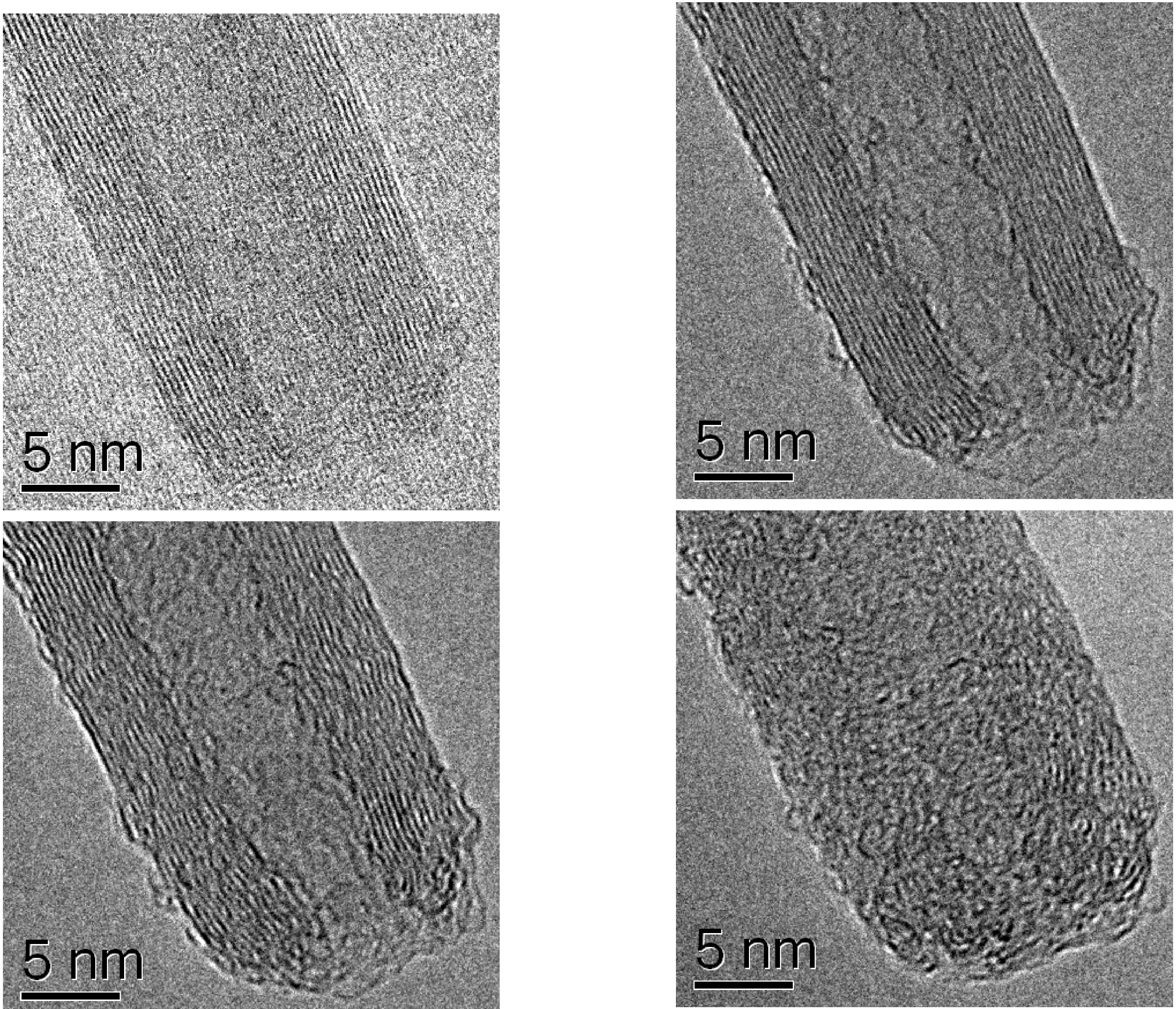


V 2p and O 1s ELNES as a function of irradiation time.

The electron current density is 0.5 A/cm^2



D. Su, et al, *Catal. Lett*. 2001


5 nm
5 nm
5 nm
5 nm

Acknowledgment

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