# Contrast Formation in (S)TEM

LECTURE SERIES
HETEROGENEOUS CATALYSIS

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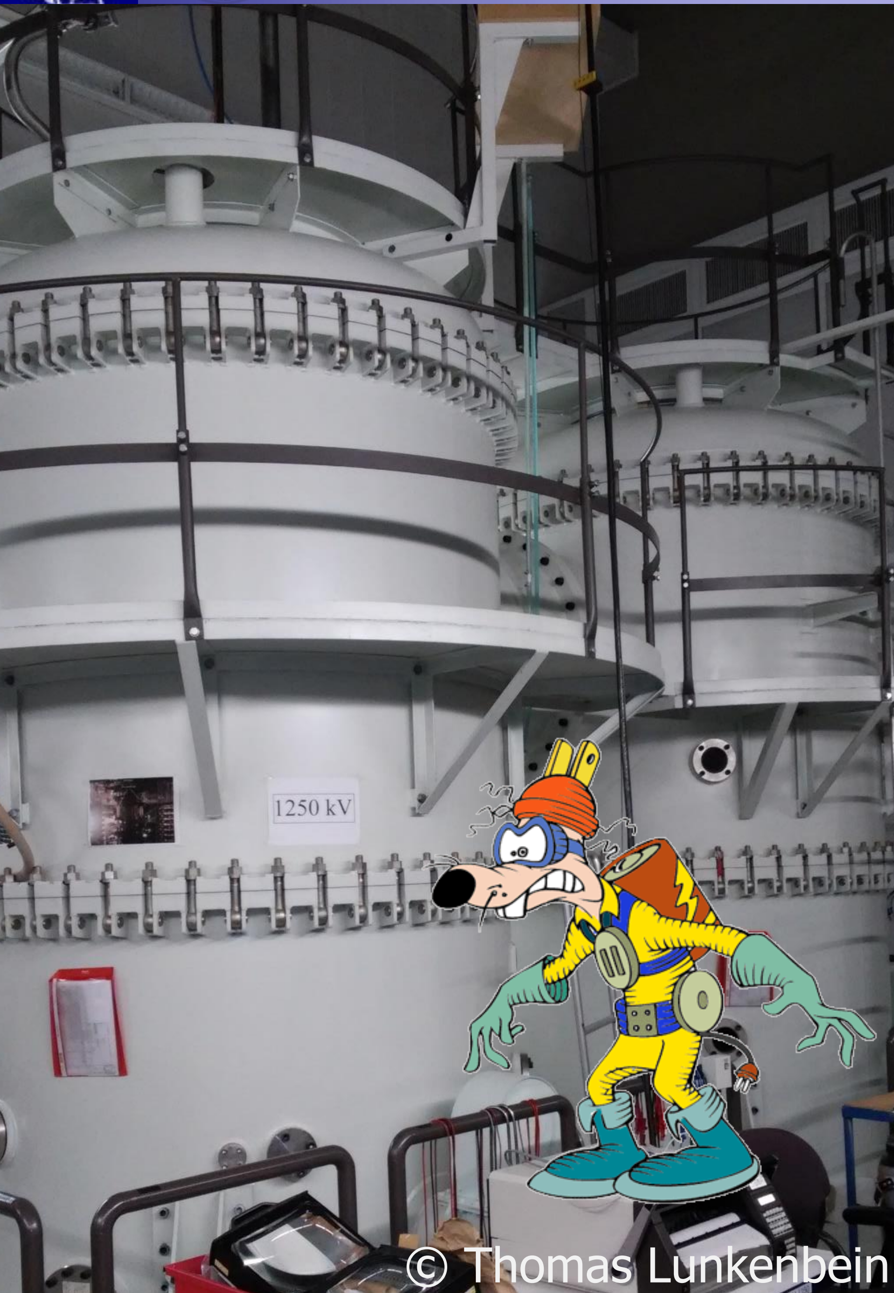
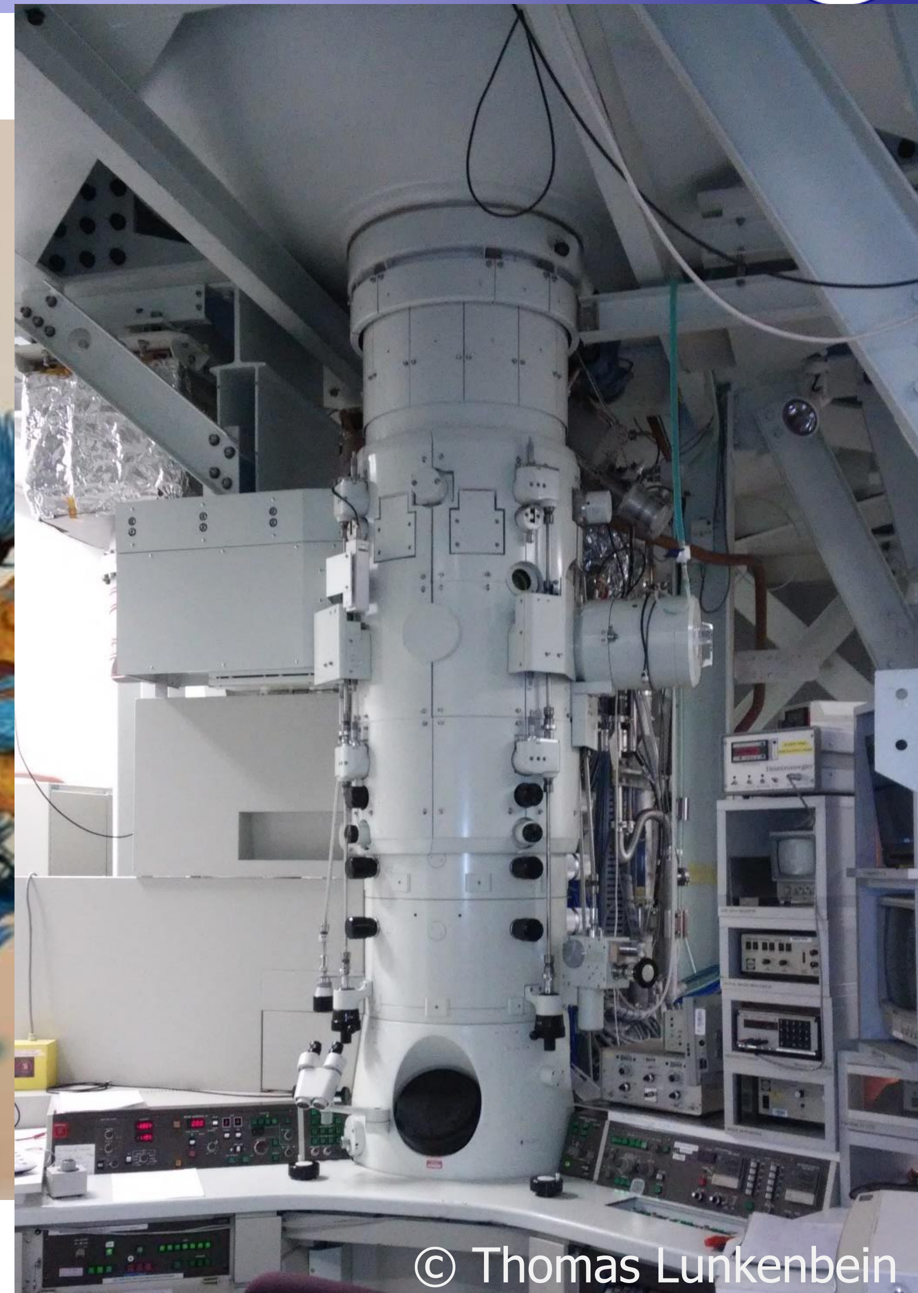
# TEM

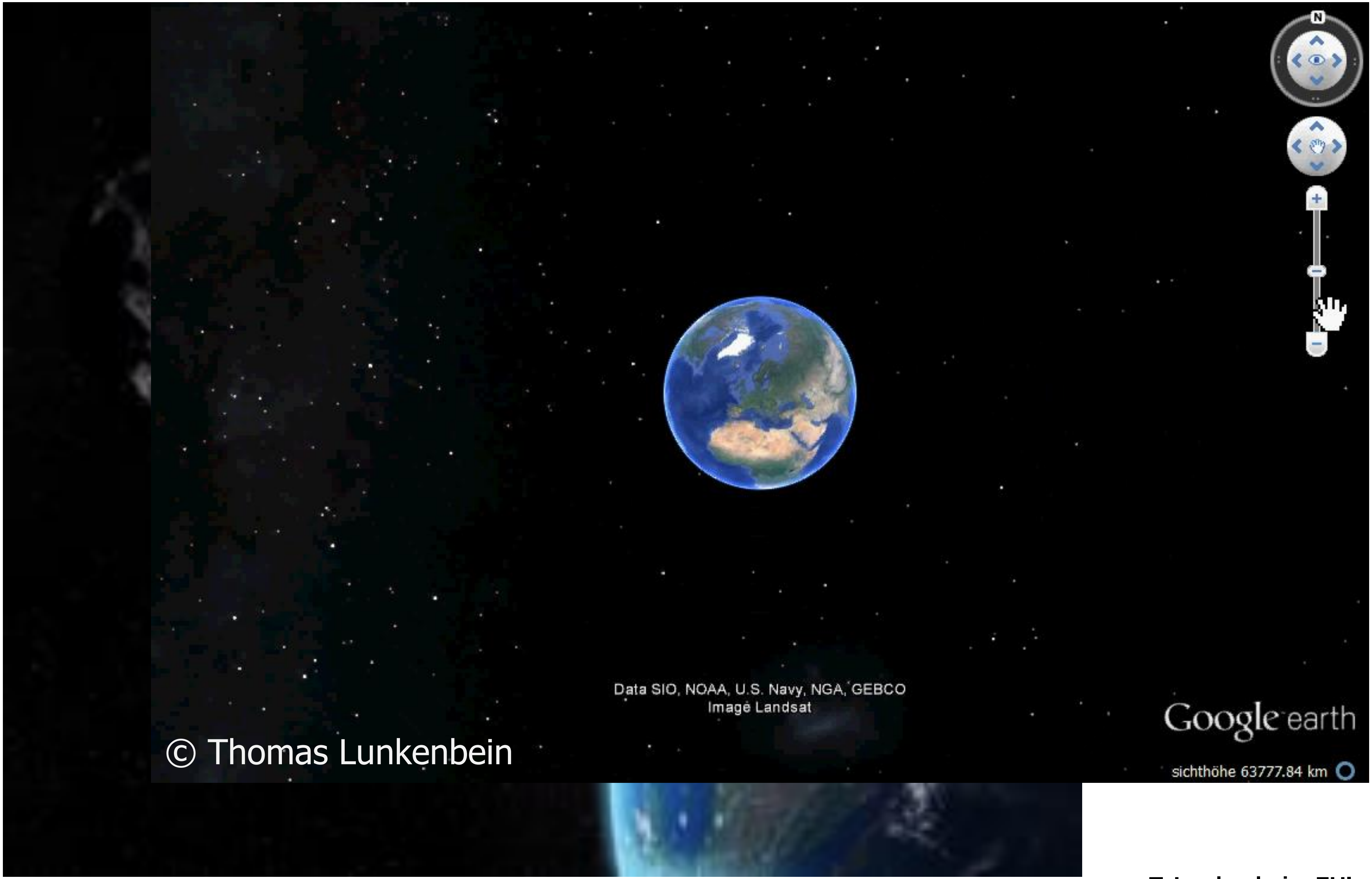

fei.com
jeol.com

# „The Monster“



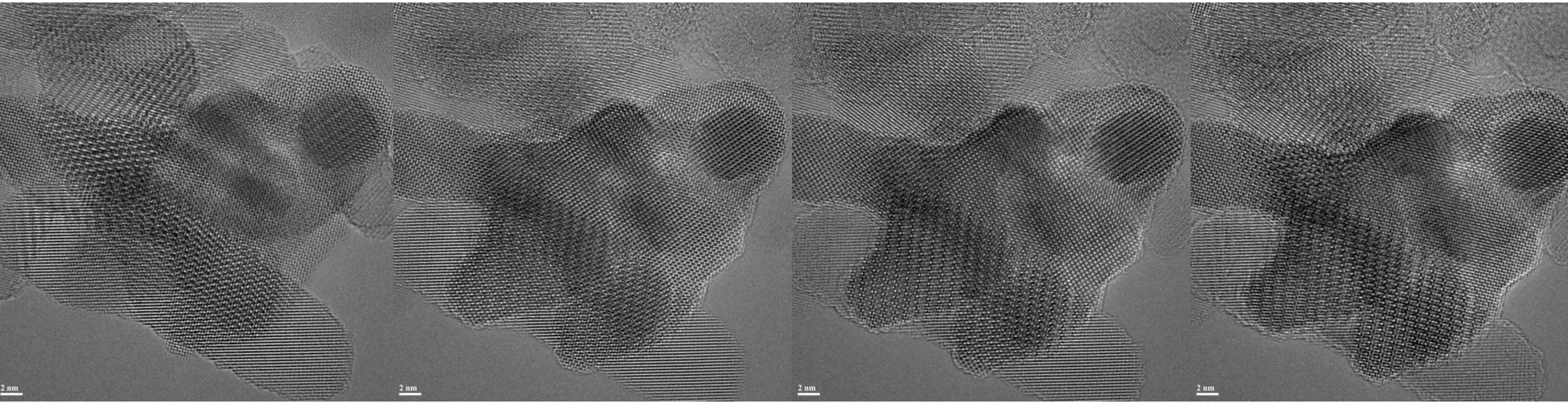



# Magnification



# What do TEM images tell us?






T. Lunkenbein, FHI

# Normally, it is easy…


# Outline

- Electron Scattering
- Amplitude contrast (mass-thickness contrast and diffraction contrast)
- Phase contrast

# TEM Techniques

Imaging

Diffraction

Spectroscopy

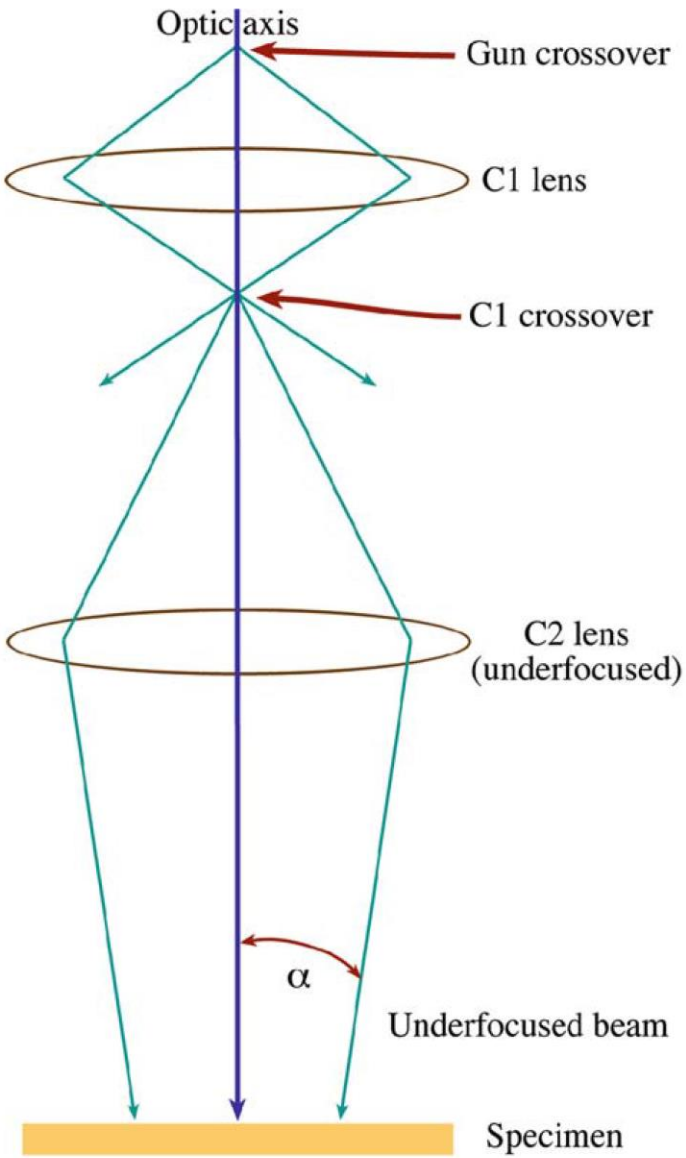
Amplitude Contrast

Phase contrast

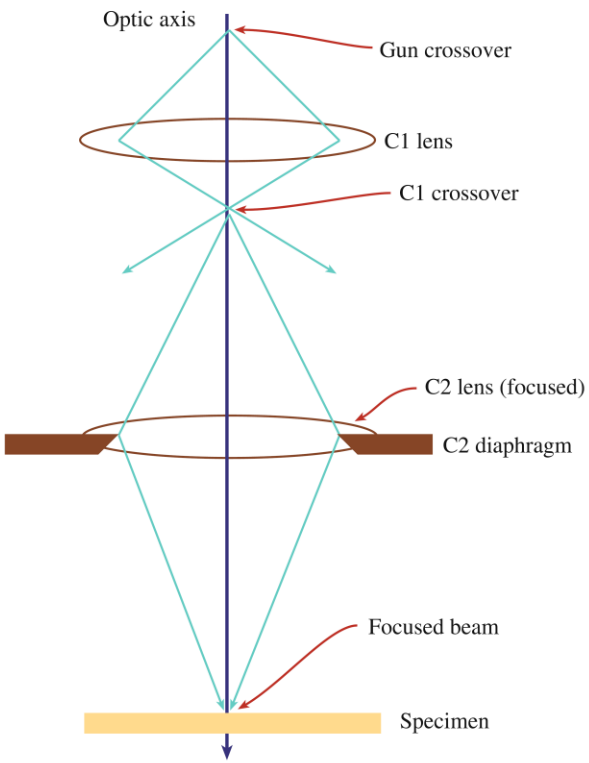
Selected Area Diffraction
Convergent beam diffraction
Micro-/nanodiffraction

Energy dispersive X-ray spectroscopy
Electron energy loss spectroscopy

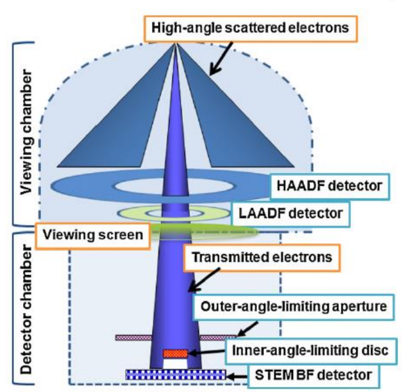
# TEM vs. STEM



Optic axis
Gun crossover
C1 lens
C1 crossover
C2 lens
(underfocused)
α
Underfocused beam
Specimen

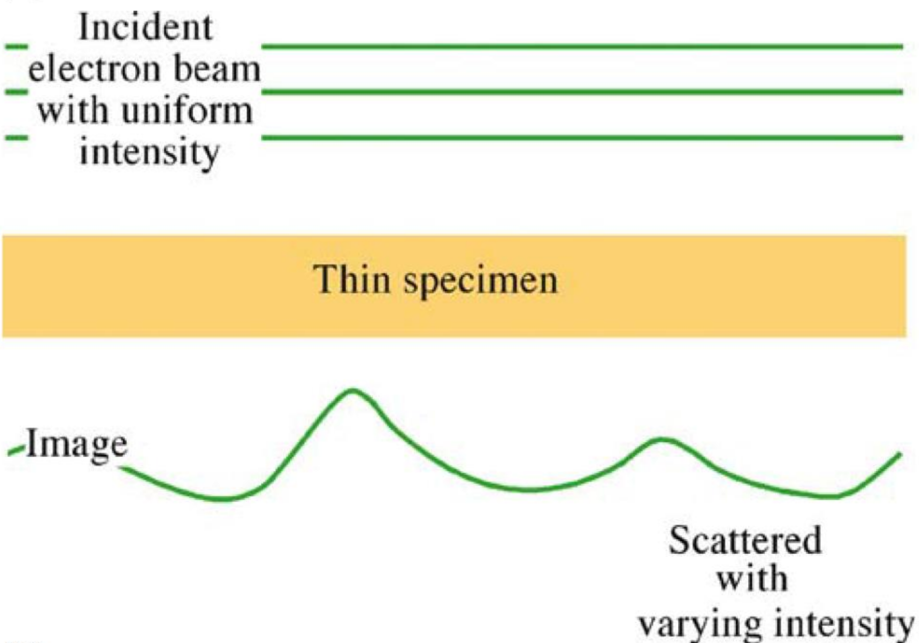
Optic axis
Gun crossover
C1 lens
C1 crossover
C2 lens (focused)
C2 diaphragm
Focused beam
Specimen

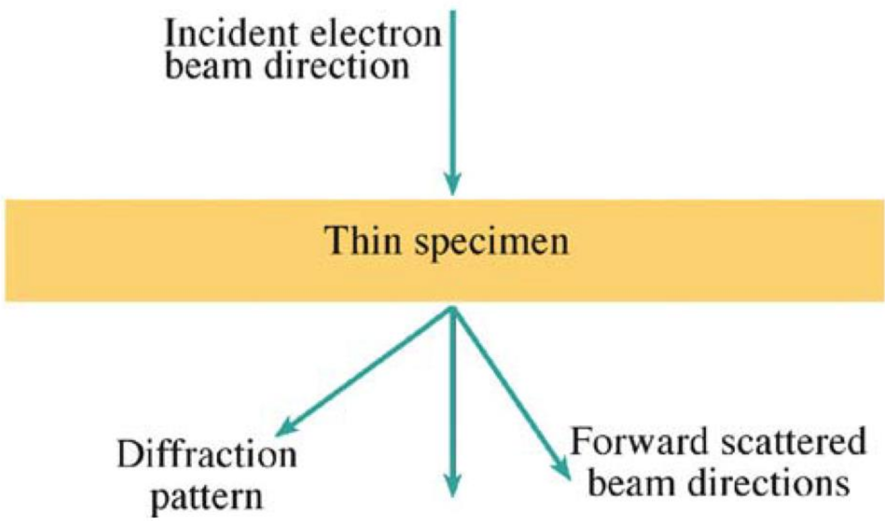
High-angle scattered electrons
Viewing chamber
HAADF detector
LAADF detector
Viewing screen
Transmitted electrons
Detector chamber
Outer-angle-limiting aperture
Inner-angle-limiting disc
STEM BF detector

# Electron Scattering

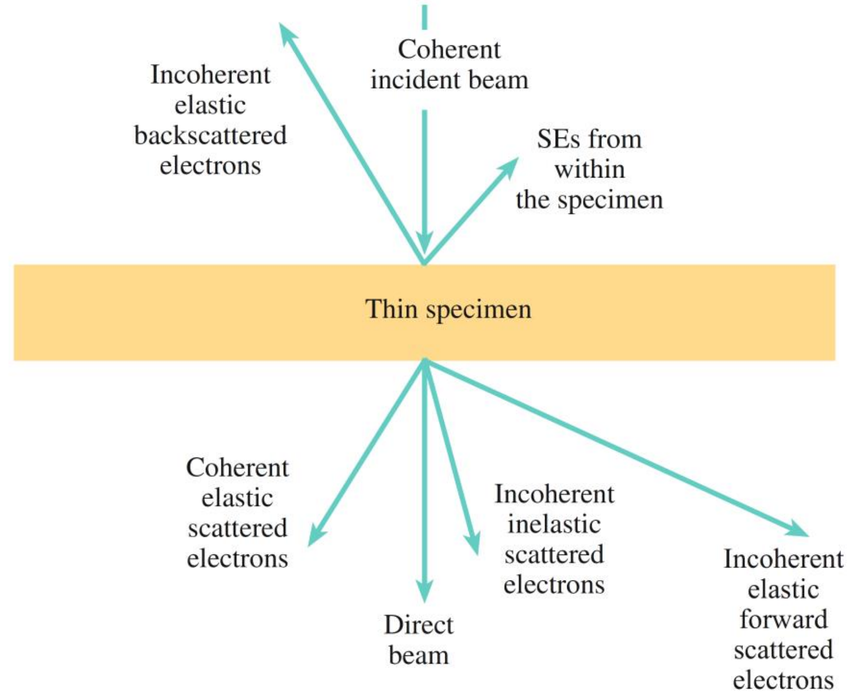
(A)



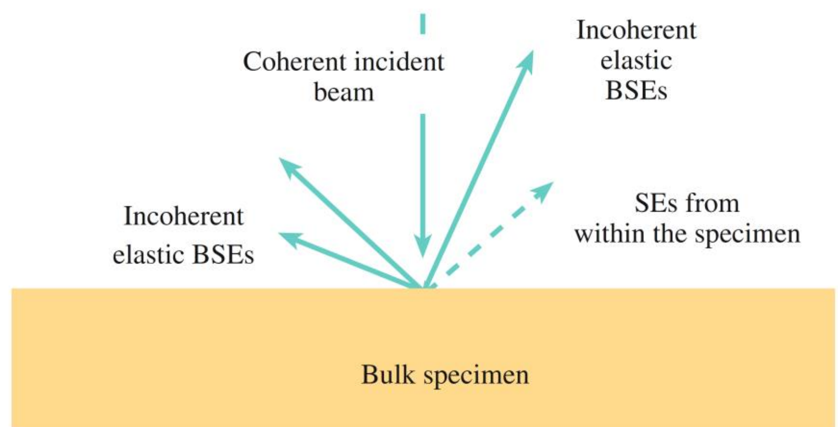

(B)




(A)



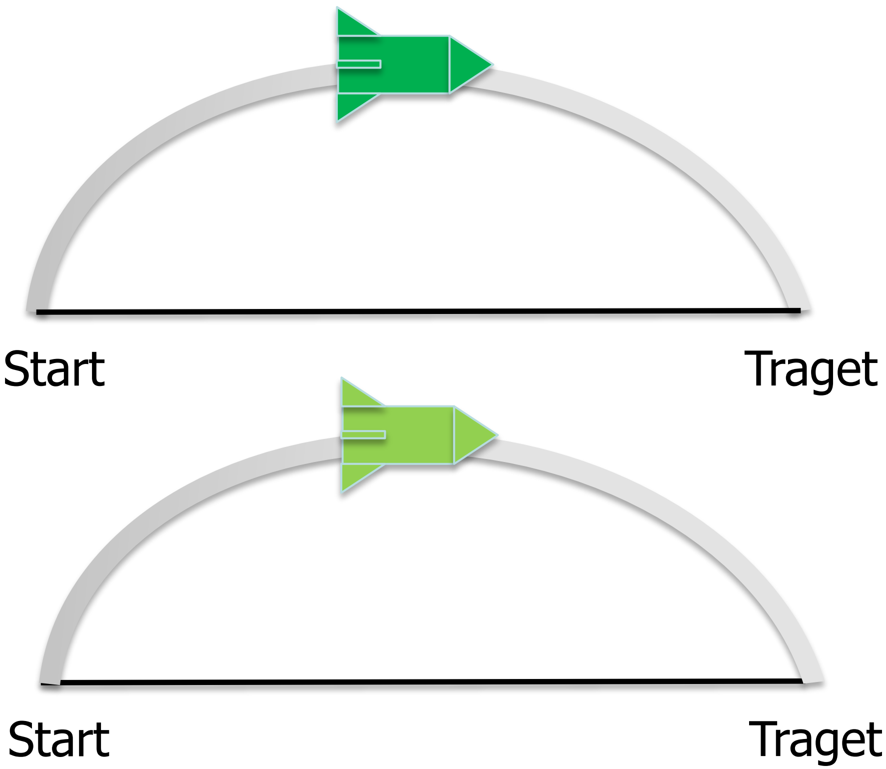

(B)



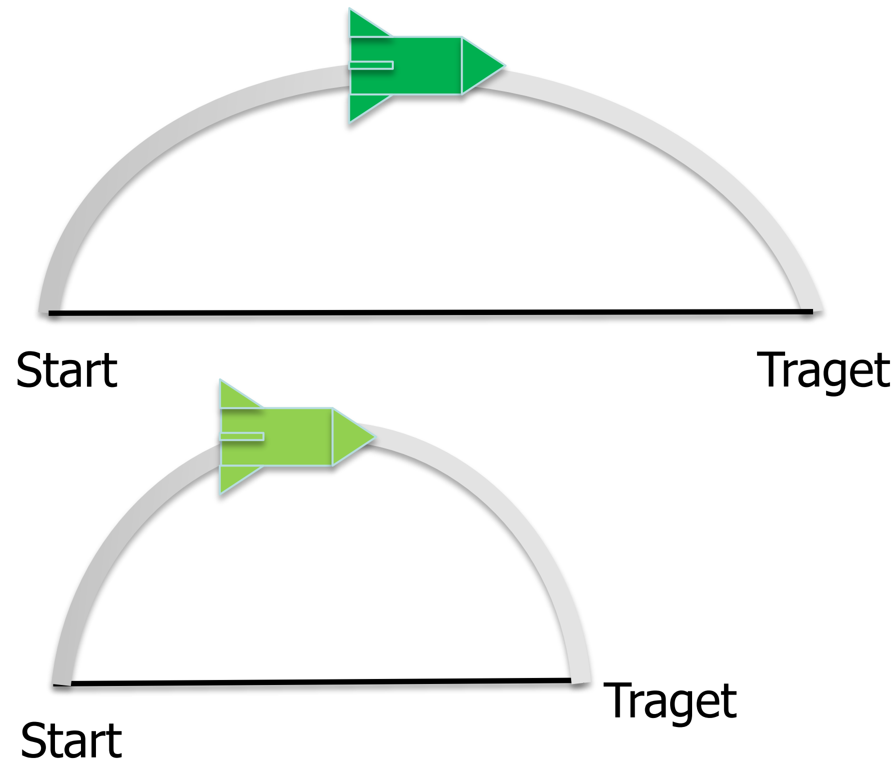
# Incoherent vs. Coherent Imaging

same start and end point
same departure and arrival time
same velocity

Same start point, but
Different velocity and
Different end point




Coherent




Incoherent

Shiojiri *J.Sci.* **2008**, 35, 495-520.

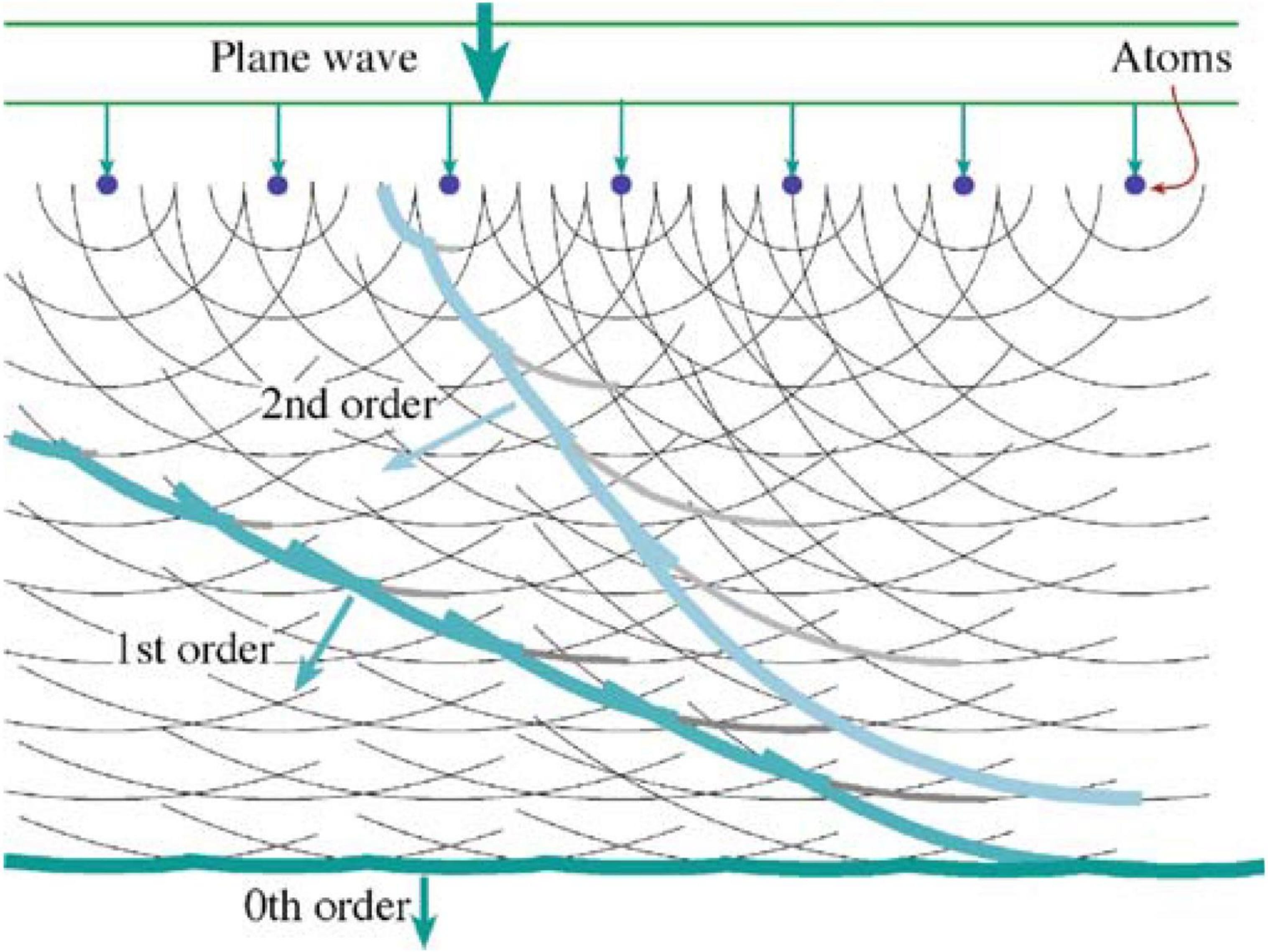
# Electron Scattering

- elastic, inelastic, coherent, incoherent, forward (<90° ), back (>90° ) scattering…
- Scattering (particles) vs. Diffraction (wave)

| |
|---|
| **Elastic scattering is usually coherent** |
| **Elastic scattering usually occurs at low angles (1-10°) and forward direction** |
| **At higher angles (>10°) elastic scattering becomes incoherent** |
| **Inelastic scattering is usually incoherent and occurs at very low angles (<1°)** |
| **The thicker the sample the less electrons are forward scattered.** |
| **Incoherent backscattered electrons are the only species that emerge from bulk, non-transparent samples** |

# Electron Scattering

Huygen´s principle



# Electron Scattering

Cross section for scattering at the nucleus (Rutherford):

$$\sigma_R(\theta) = \frac{e^4 Z^2}{16(4\pi\varepsilon_0 E_0)^2} \frac{d\Omega}{\sin^4 \frac{\theta}{2}}$$

After the scattering process

$$\psi_{sc} = \psi_0 f(\theta) \frac{e^{2\pi i k r}}{r}$$

Atomic scattering factor:

$$f(\theta) = \frac{\left(1 + \frac{E_0}{m_0 c^2}\right)}{8\pi^2 a_0} \left(\frac{\lambda}{\sin \frac{\theta}{2}}\right)^2 (Z - f_x)$$

$$\psi_{tot} = \psi + i\psi_{sc}$$

Incident beam:

$$\psi = \psi_0 e^{2\pi i k r}$$

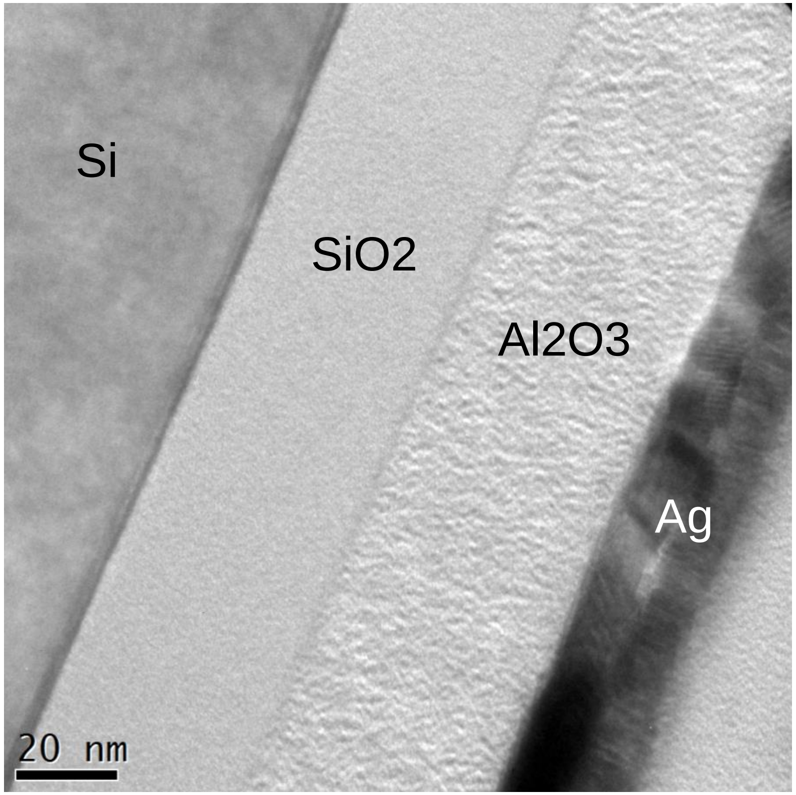
amplitude

phase

**New amplitude and phase**

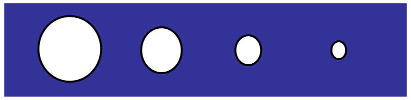
# Amplitude contrast and Phase-contrast images

The electron wave can change both its amplitude and phase as it traverses the specimen



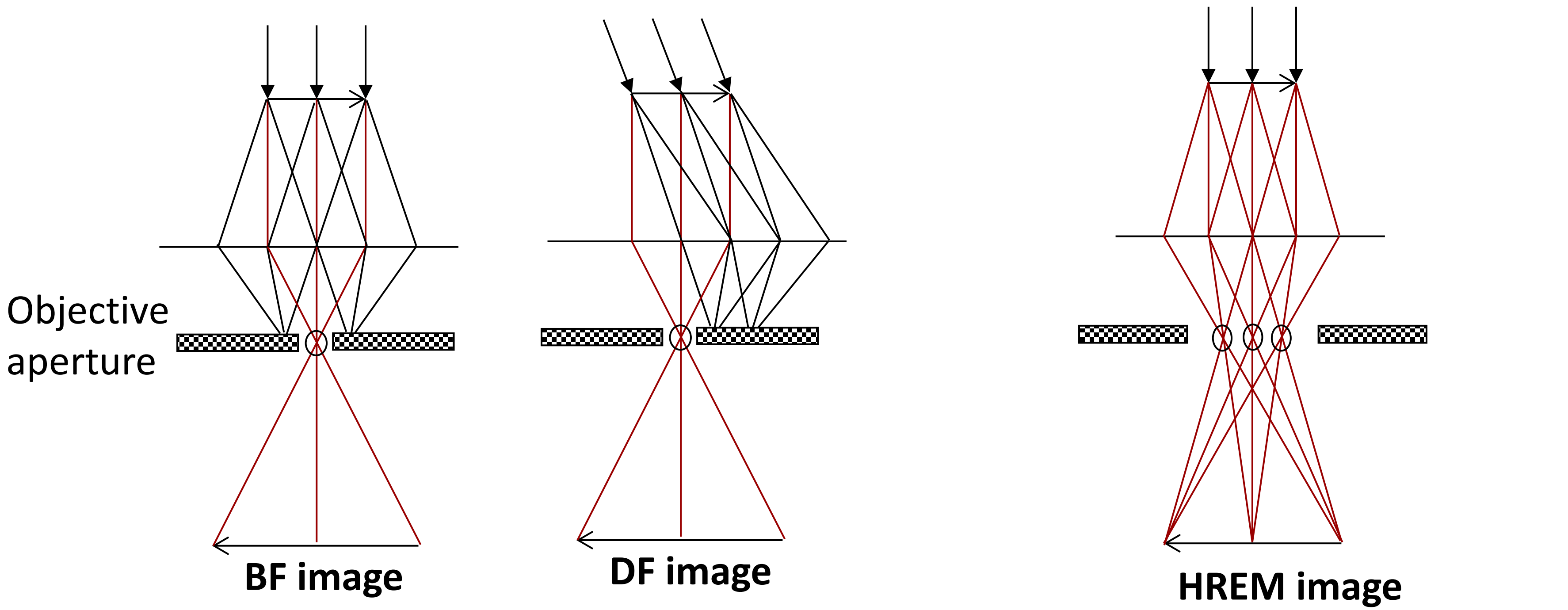

**Gives rise to contrast**

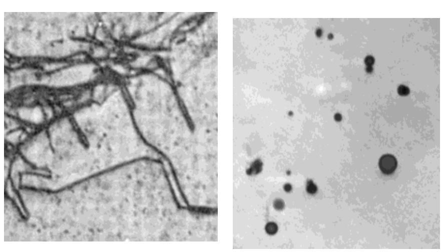
We select imaging conditions so that one of them dominates.

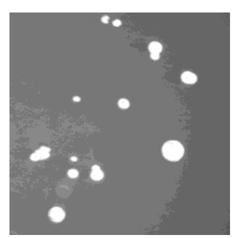


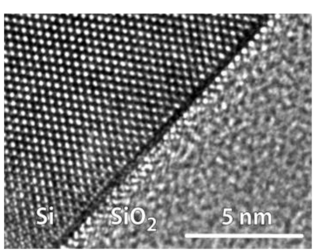
# objective aperture

**Bright Field (BF), Dark Field (DF) High Resolution EM (HREM)**



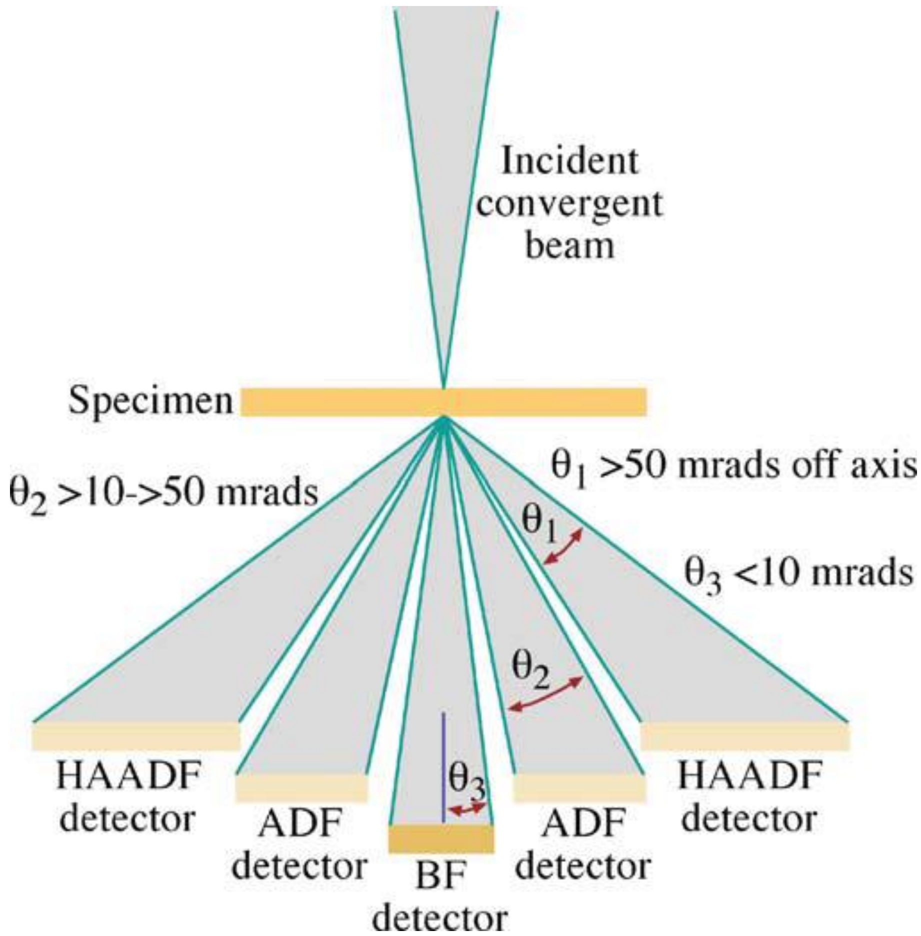


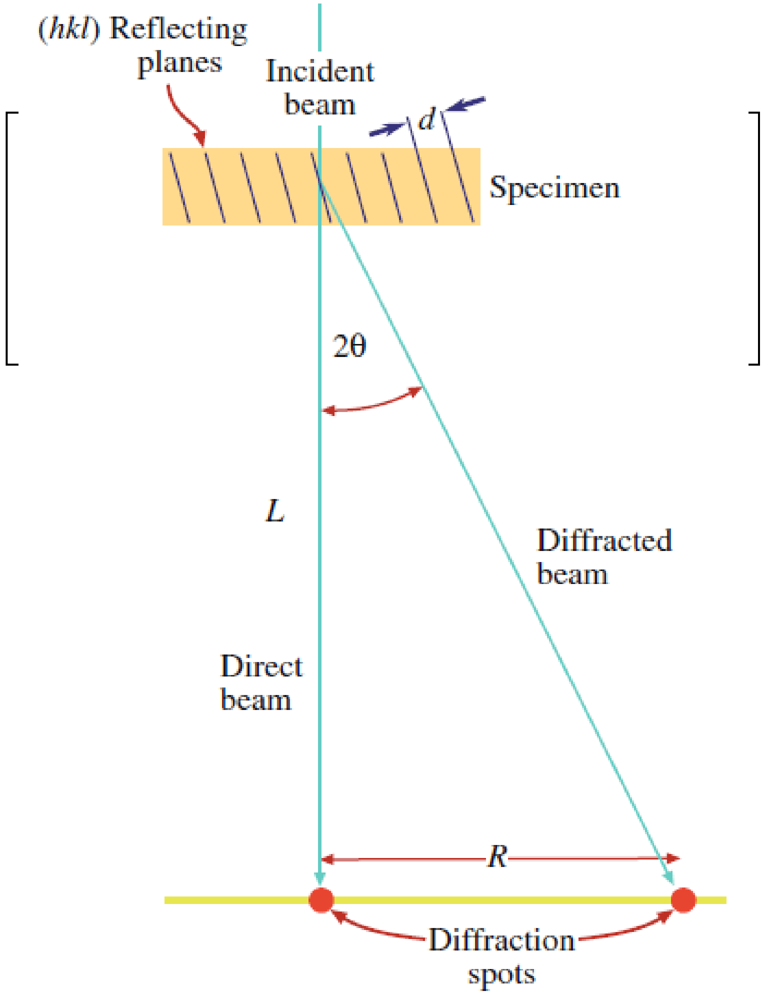



**Amplitude/Diffraction contrast**

**Phase contrast**

# BF-DF STEM


Incident convergent beam
Specimen
$\theta_1$ >50 mrads off axis
$\theta_2$ >10->50 mrads
$\theta_1$
$\theta_3$ <10 mrads
$\theta_2$
$\theta_3$
HAADF detector
ADF detector
BF detector
ADF detector
HAADF detector


(hkl) Reflecting planes
Incident beam
d
Specimen
2θ
L
Diffracted beam
Direct beam
R
Diffraction spots

# Contrast

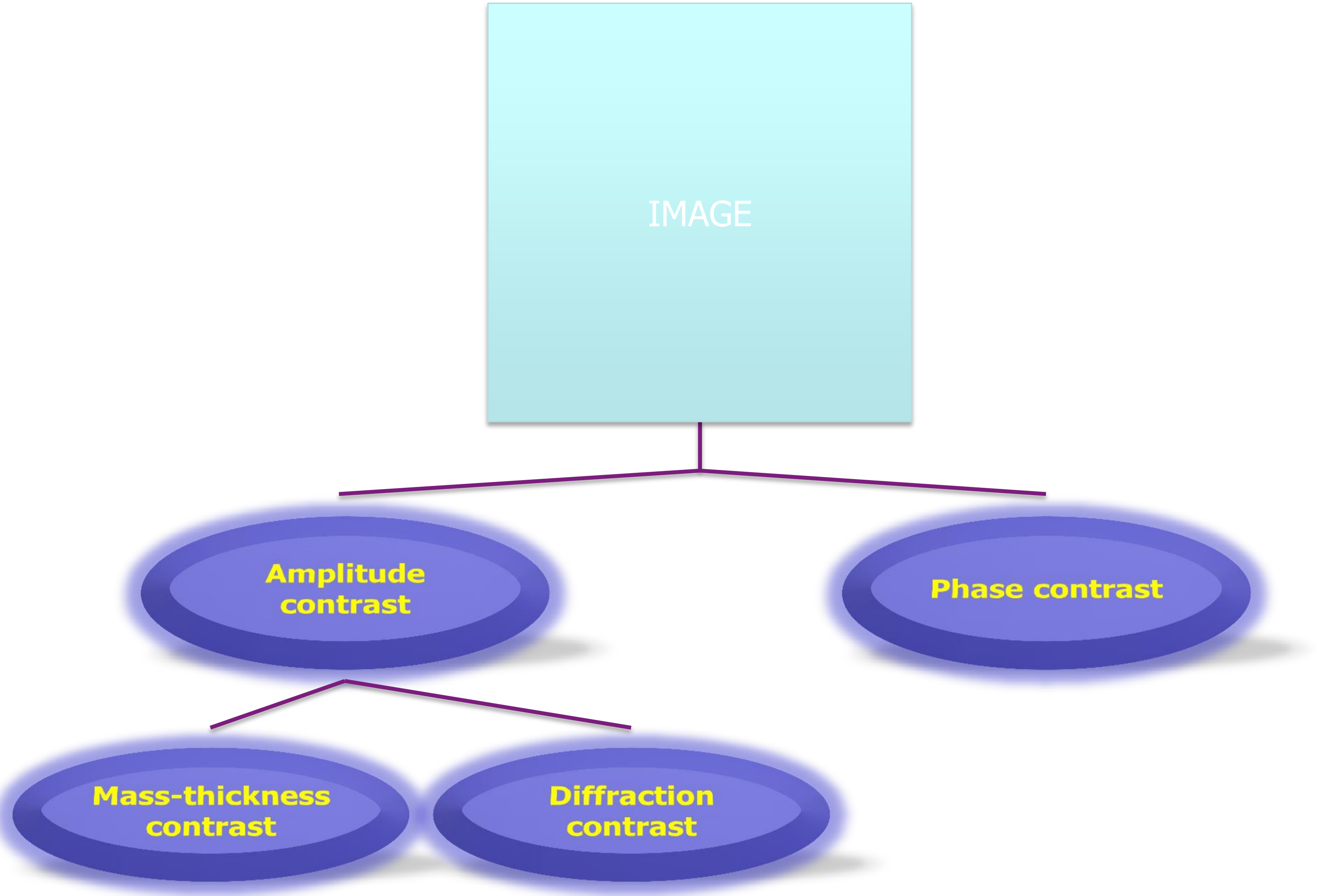
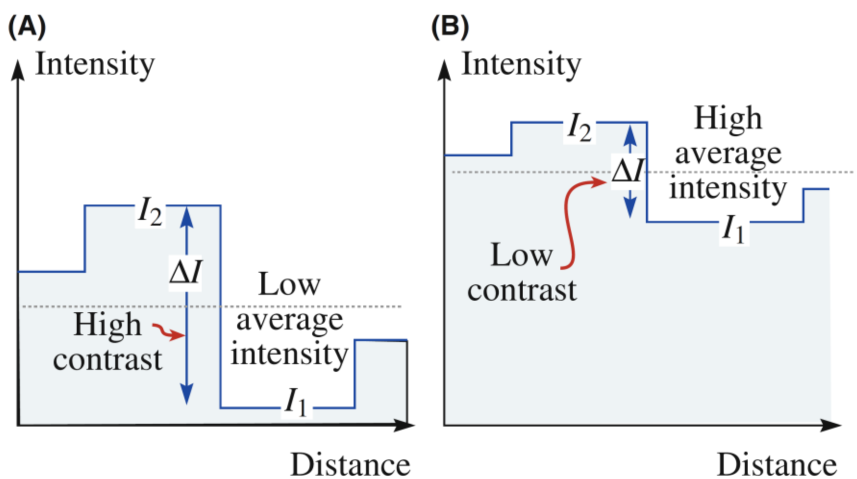


IMAGE
Amplitude contrast
Phase contrast
Mass-thickness contrast
Diffraction contrast

# Definition of Contrast

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




***Difference in intensity between two adjacent areas***

The eyes can only see intensity differences >5 – 10 %
In images: contrast enhancement digitally

# Mass-Thickness Contrast

Incoherent elastic Rutherford scattering

- **amorphous samples**

- **Crystalline samples → also: diffraction contrast**

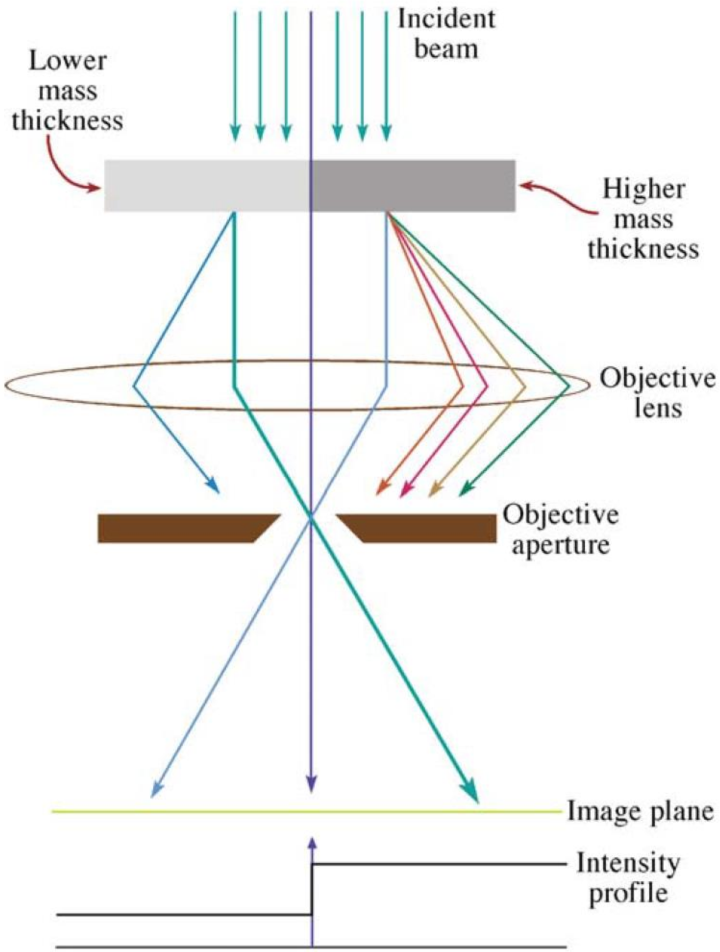
  - Peaked in the forward direction in thin samples

  - thickness and Z-dependent

$$\sigma_R(\theta) = \frac{e^4 Z^2}{16(4\pi\varepsilon_0 E_0)^2} \frac{d\Omega}{\sin^4 \frac{\theta}{2}}$$

1. **Cross-section for elastic scattering is a function of Z**
2. **As thickness increases, more elastic scattering**

# Mass-Thickness Contrast




$$\sigma_R(\theta) = \frac{e^4 Z^2}{16(4\pi\varepsilon_0 E_0)^2} \frac{d\Omega}{\sin^4 \frac{\theta}{2}}$$

**Parameters that improve mass-thickness contrast**

**Small** objective aperture size (large -- bad).

**low** high tension of the TEM (small -- good)

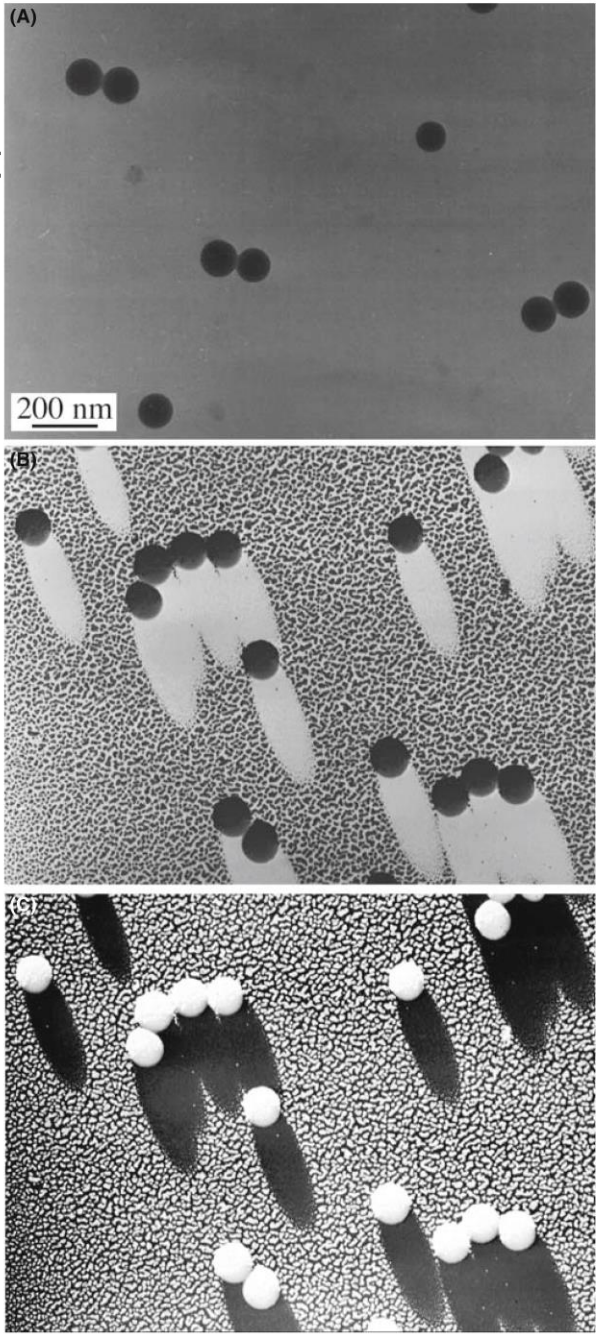
# Mass-Thickness Contrast

examples

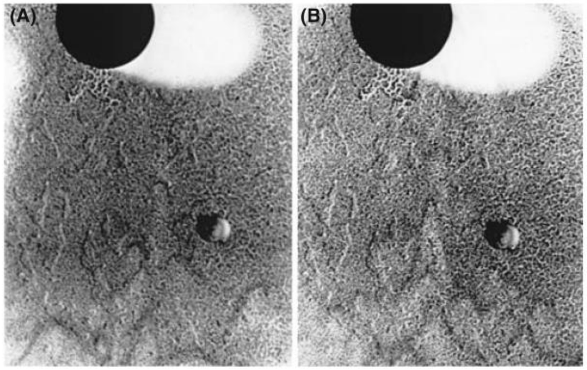
Latex on Amorphous carbon
Contrast is thickness dependent

What is the shape?

Solution: Metal shadowing




The effect of different apertures




d=70 µm d=10 µm

Similar effect as reducing the HT of the microscope

# Mass-thickness imaging

Imaging electron scattering at:

1. Low angles (<~5º) : - Mass-thickness contrast + Bragg diffraction

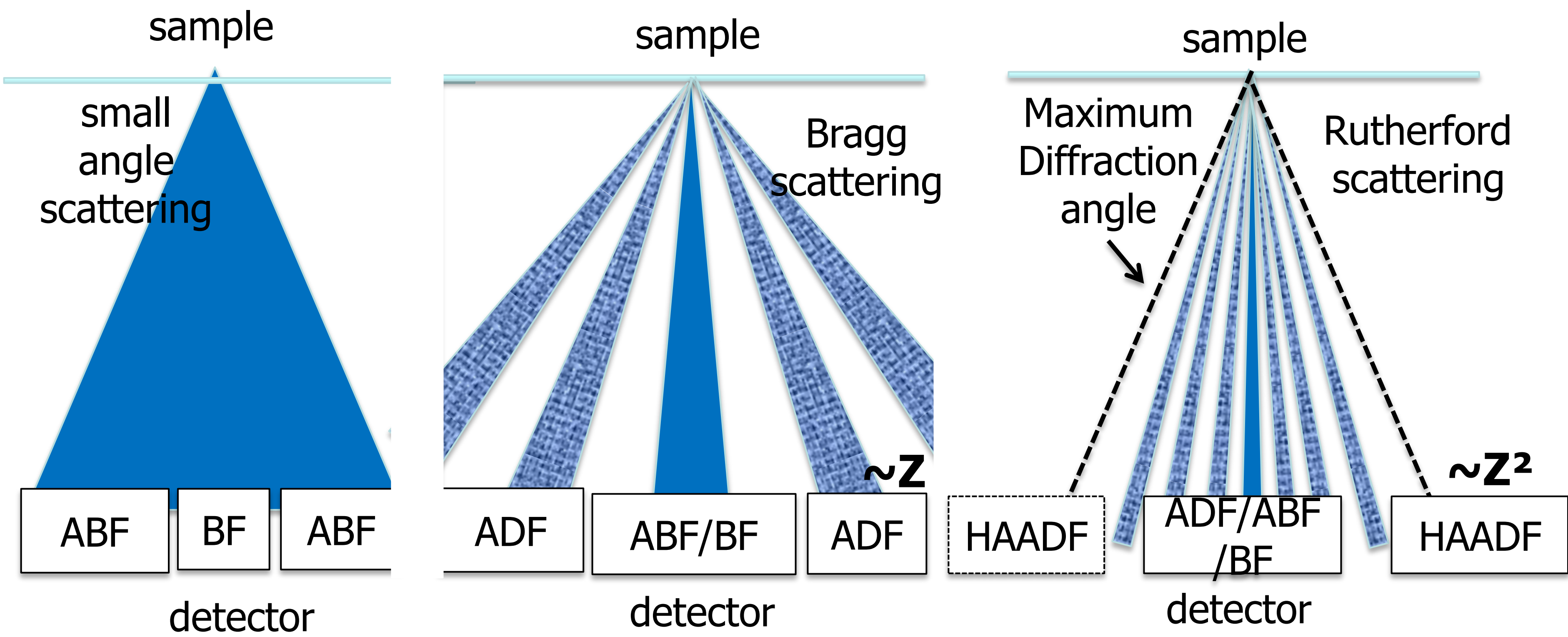
2. Higher angles: - Only mass-thickness contrast (low intensity scattered beams)
   - Intensity only depends on Z (and on thickness)

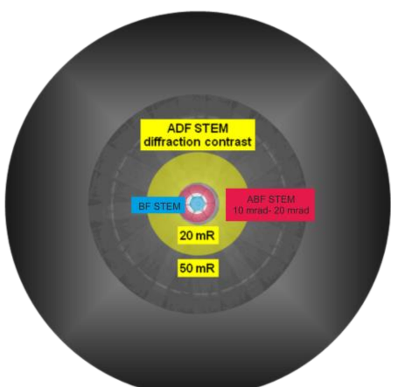
➡ Only mass-thickness contrast:

A) Amorphous samples: All contrast is mass contrast

B) Crystalline samples: ADF/HAADF mode

# Mass-thickness imaging



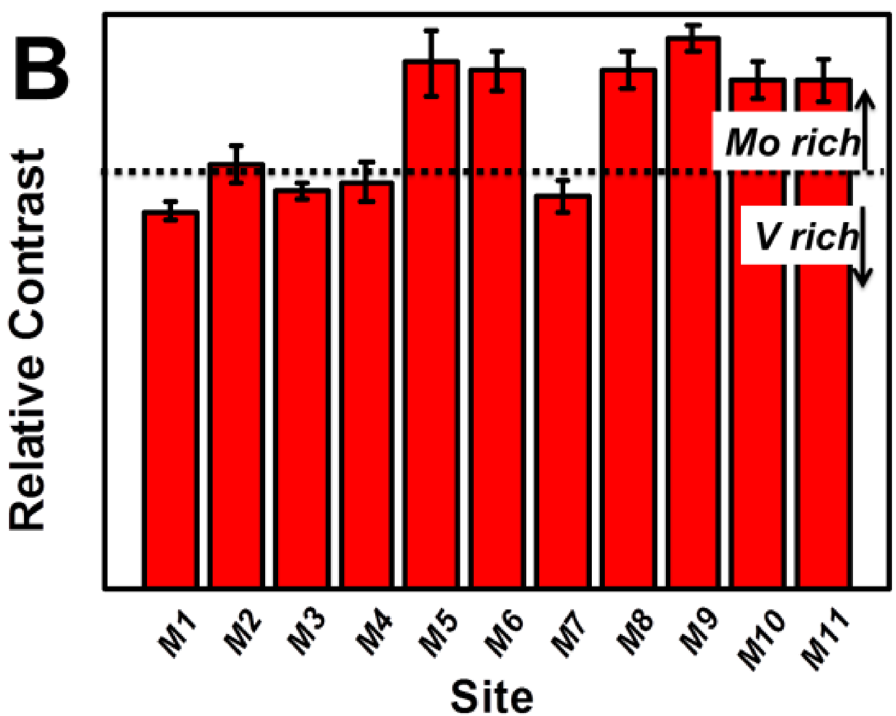

Batson, P.E. *Nature Materials* **2011**, *10*, 270.
Otten - *Journal of Electron Microscopy Technique* **1991**, 17, 221.

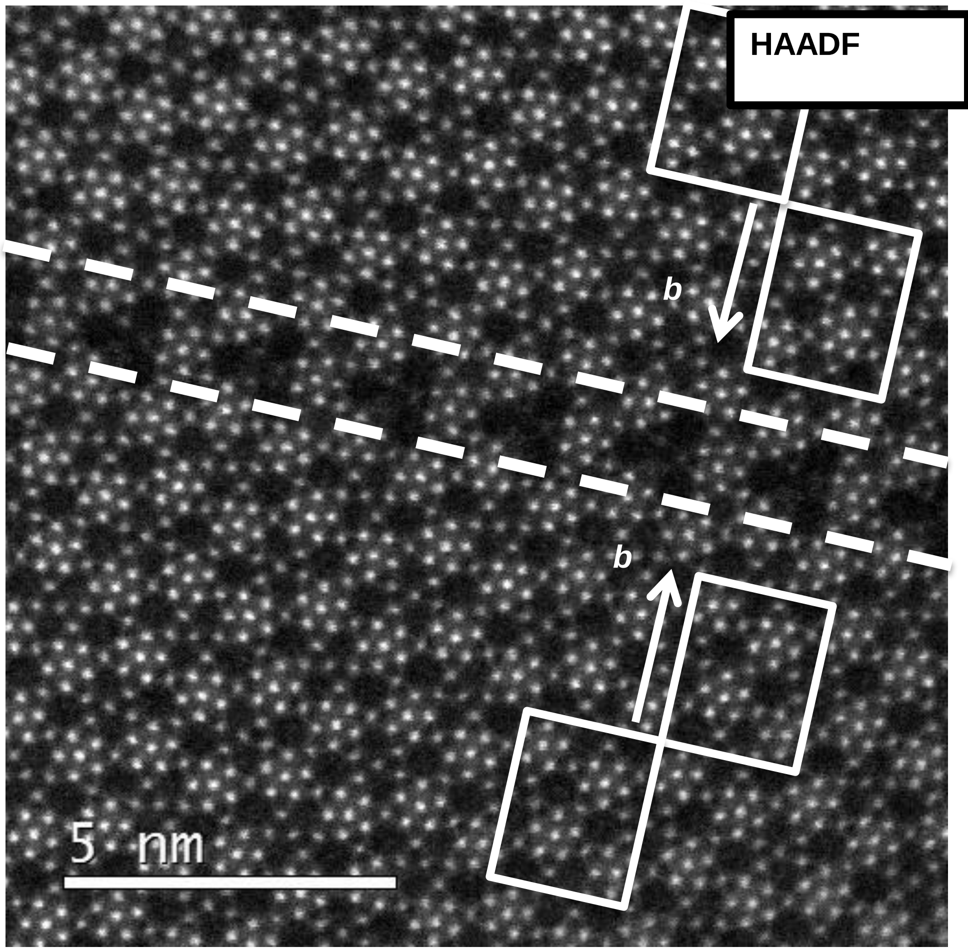
# Mass-Thickness Contrast

**Z-contrast (STEM)**

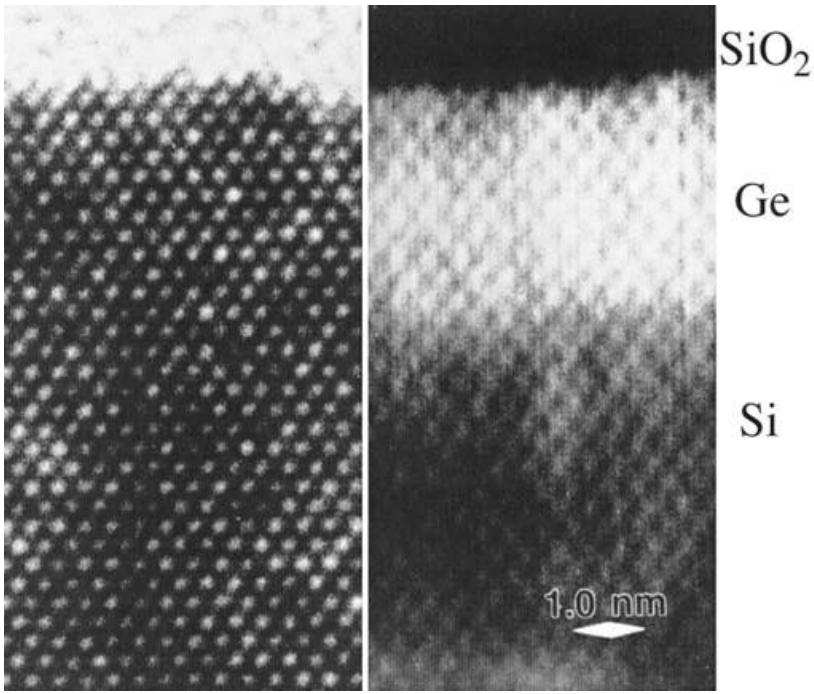
- Less noisy than DF-TEM: gathers all scattered electrons, not just electrons scattered from one atomic plane
- No lenses are used to make the image → less chromatic aberration
- More contrast than DF-TEM: Adjust L to optimize the ratio of the number of scattered electrons hitting the detector

# Mass-Thickness Contrast



# Example of HR Z-contrast with the HAADF detector




HREM-TEM    HR Z-contrast STEM

Atomic structures are visible in both HREM and HAADF images.

HAADF image:
noisier but Z-contrast.

Relate the intensity differences to an absolute measure of the Si concentration:

Contrast

Cross-section for elastic scattered by matrix A

Fraction of the alloying element that sub. For matrix atoms

$$C = \left( \frac{\sigma_A}{\sigma_B} - F_B \right) c_B \qquad (22.10)$$

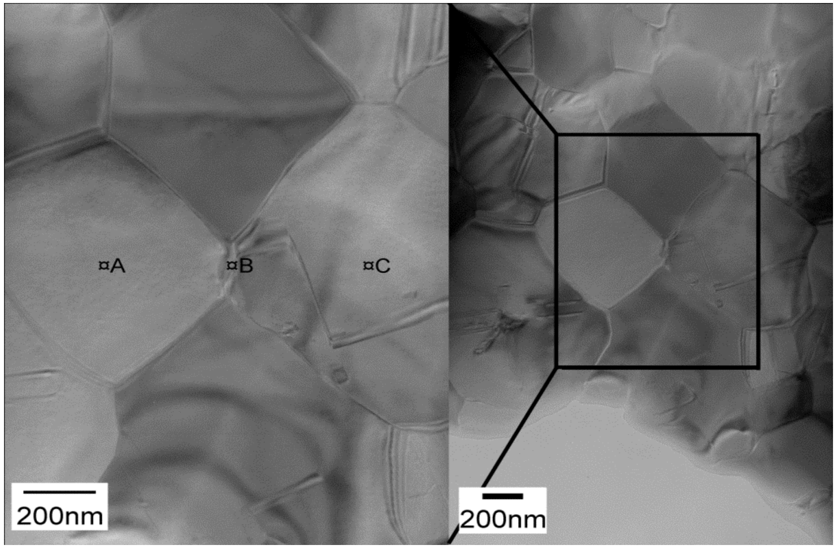
Alloying/dopant B

Atomic concentration of alloying element

# Diffraction Contrast

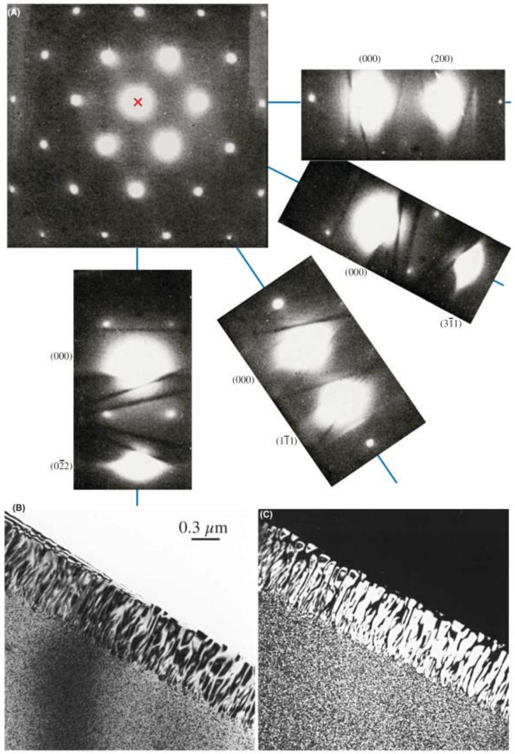
Bragg diffraction contrast

- Controlled by crystal structure and orientation of the sample
- Scattering at special angles
- Elastic coherent scattering
- Contrast can be enhanced by two beam conditions



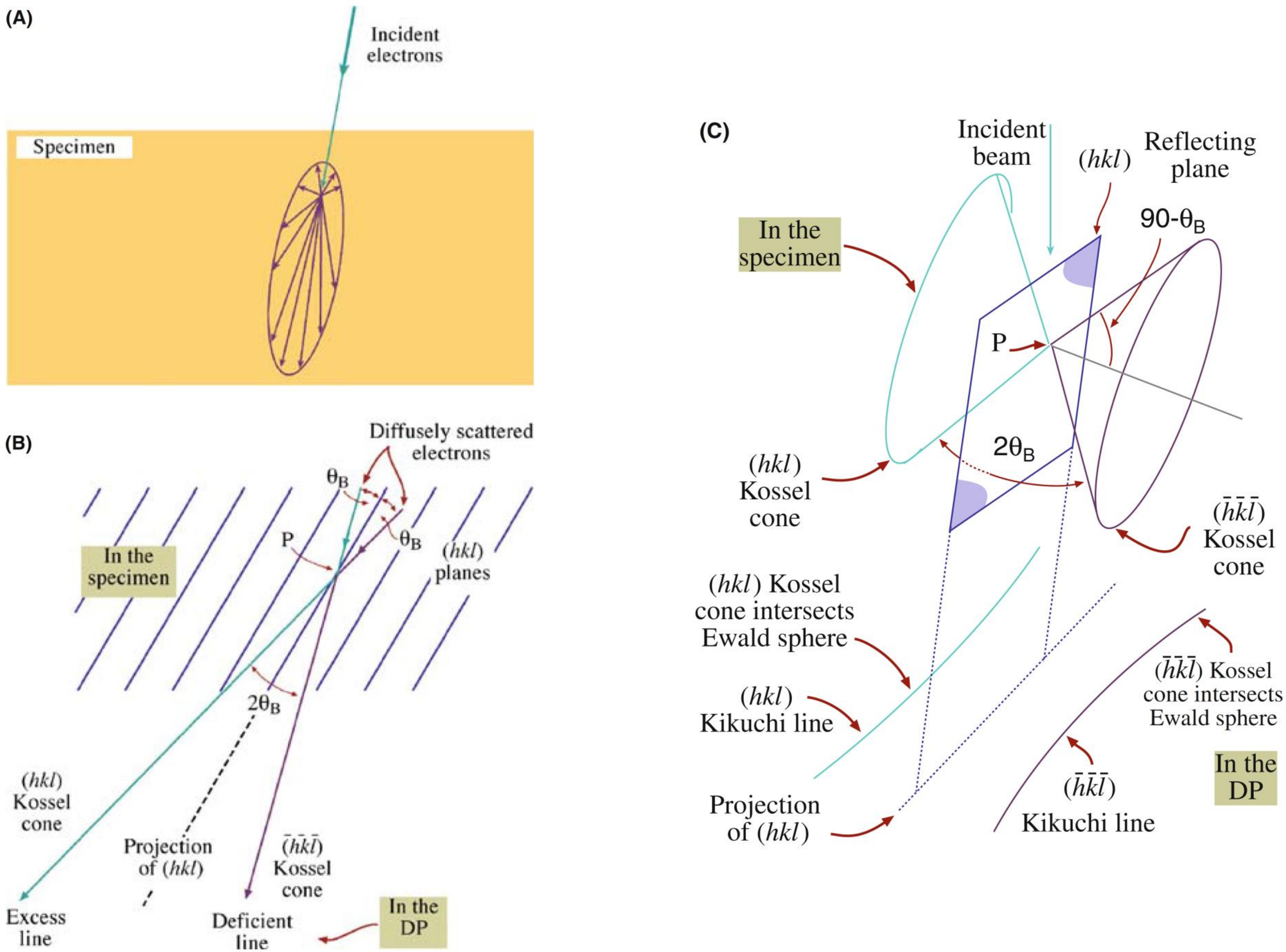
# Two beam conditions

- Strong diffraction contrast in BF and DF images
- →one diffracted beam is strong
- +direct beam
- Deviation parameter (s>0)




BF DF

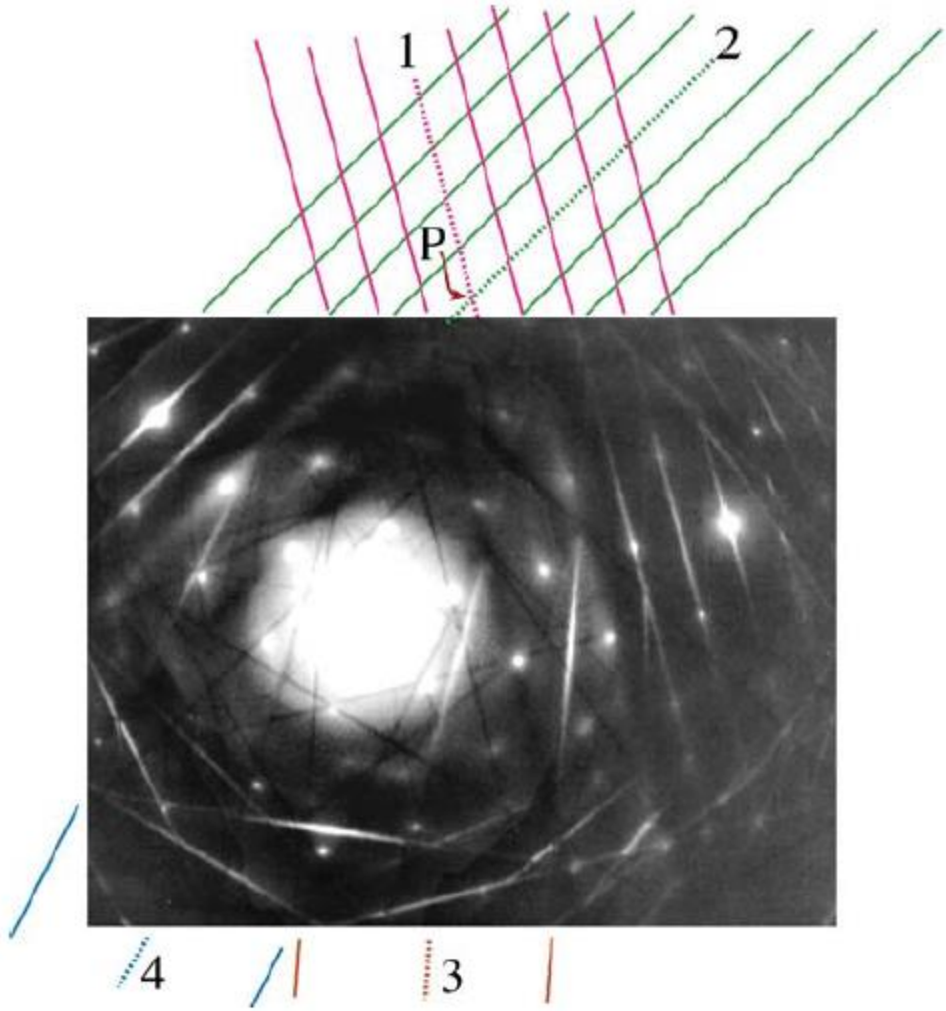
# Diffraction Contrast – Kikuchi lines



# Two-beam condition

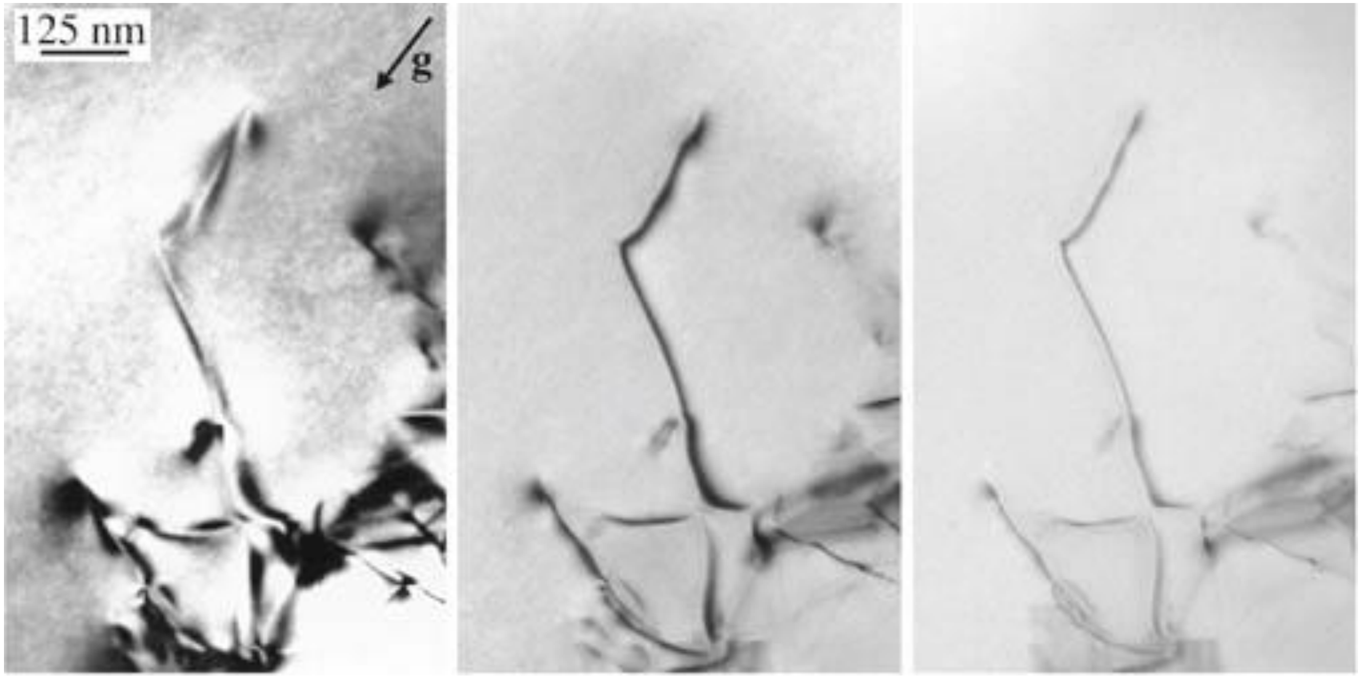
S: small and positive

The excess (bright) hkl Kikuchi line, just outside the hkl spot;



# Diffraction Contrast

Variation in the diffraction contrast when s is varied from




zero small + larger +

**TEM always shows better contrast than STEM images**

# Thickness and bending effects

- TEM specimens are thin but their thickness

Invariably changes

→ elastic bending, i.e physical rotation of lattice

Planes

Planes also bend when lattice defects are introduced

→Diffraction contrast due to thickness or diffraction conditions variations

# Summary amplitude contrast

**Mass-thickness contrast**
-Areas of greater Z and or t scatter more strongly
-TEM images are better quality (lower noise and higher resolution) than STEM images, but digital STEM images can be processed to show higher contrast than analog TEM images.
-STEM mass-thickness contrast images are most useful for thick and/or beam-sensitive specimens.
-Z-contrast (HAADF) images can show atomic-level resolution.

**Diffraction contrast**
-Arises when the electrons are Bragg scattered.
-In TEM, the objective aperture selects one Bragg scattered beam.
-Often, the STEM detectors gather several Bragg beams which reduce diffraction contrast.
-TEM always shows better contrast than STEM images (noisier and almost never used)
- Contrast improvement by setting the two beam conditions

# Contrast

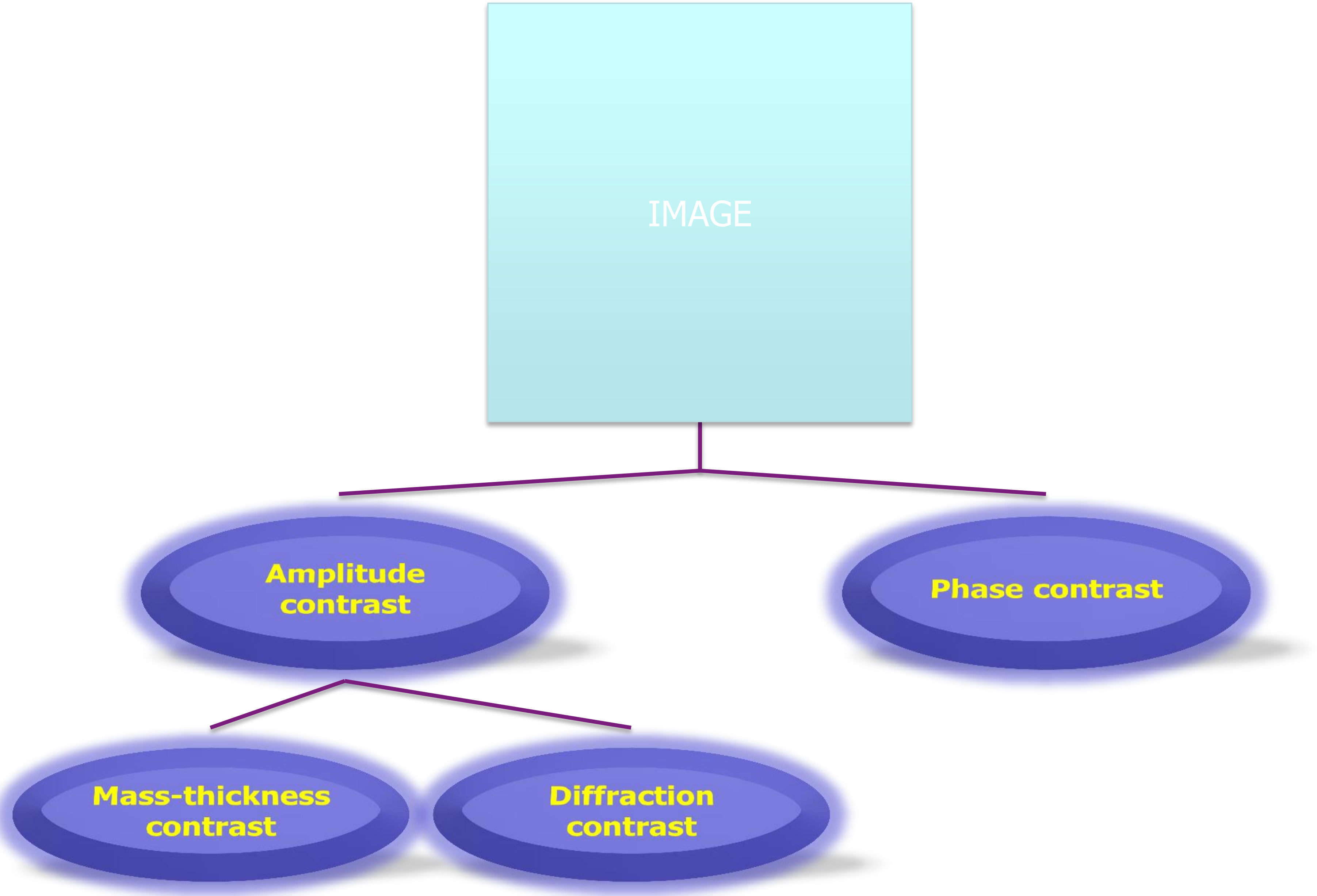
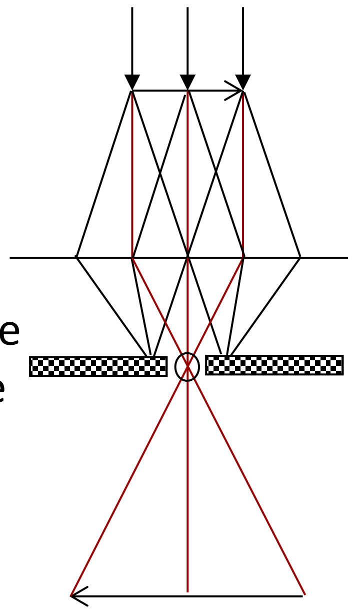


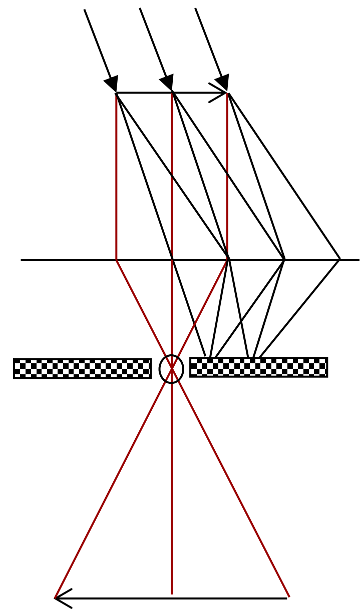
IMAGE
Amplitude contrast
Phase contrast
Mass-thickness contrast
Diffraction contrast

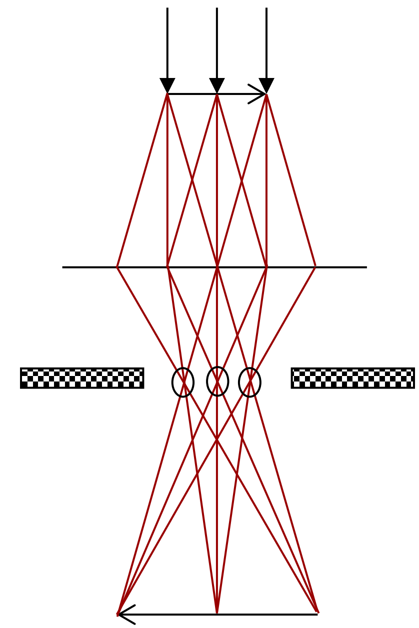
# objective aperture

**Bright Field (BF), Dark Field (DF) High Resolution EM (HREM)**

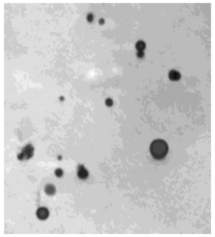
Objective aperture



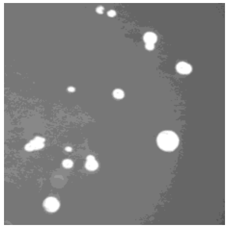




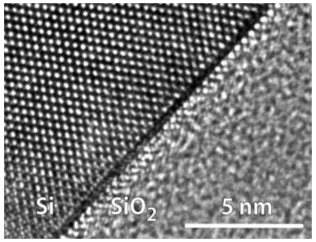
**BF image**



**DF image**



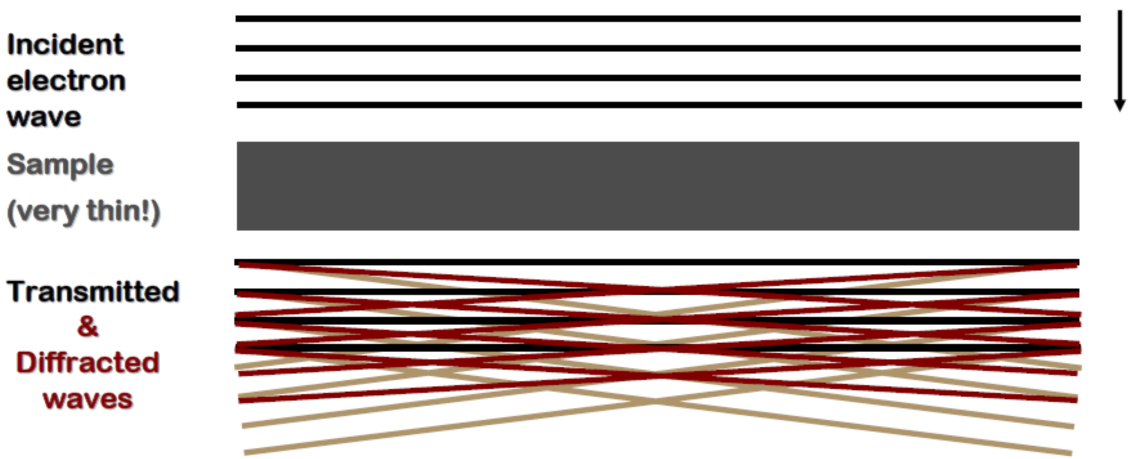
**HREM image**




## Amplitude/Diffraction contrast

## Phase contrast

# Phase Contrast Imaging

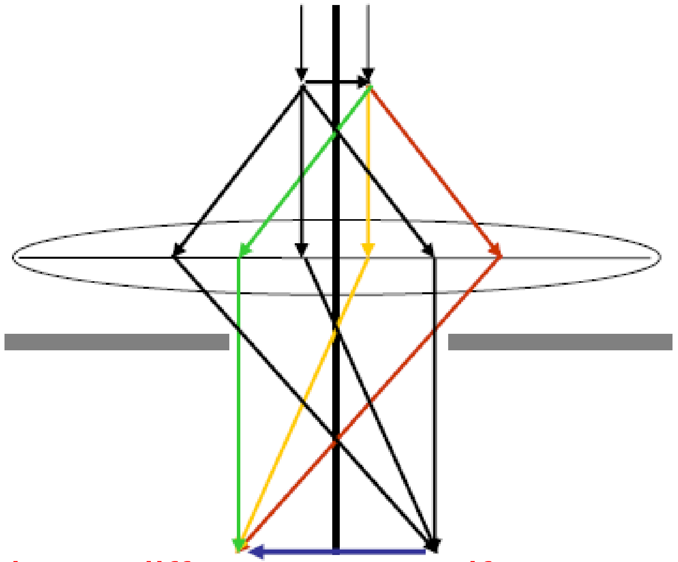



**Transmitted & diffracted waves each have a different phase**

**Result is an interference pattern - our 'phase contrast' or HREM image**

# Why different phases?

- Transmitted and diffracted waves travel through different distances in the crystal
- Each diffracted wave will have its own phase
- Each diffracted wave represents a different solution to the Schrödinger equation



When several waves are allowed to interact, the phase differences manifest themselves in the 2-D interference pattern in the image plane
--- Phase contrast image

Factors that contribute to the phase shift:
Thickness, orientation, scattering factor, focus and astigmatism.

→ Be careful when interpreting them

# Be careful when interpreting the images

Not even this "simple"

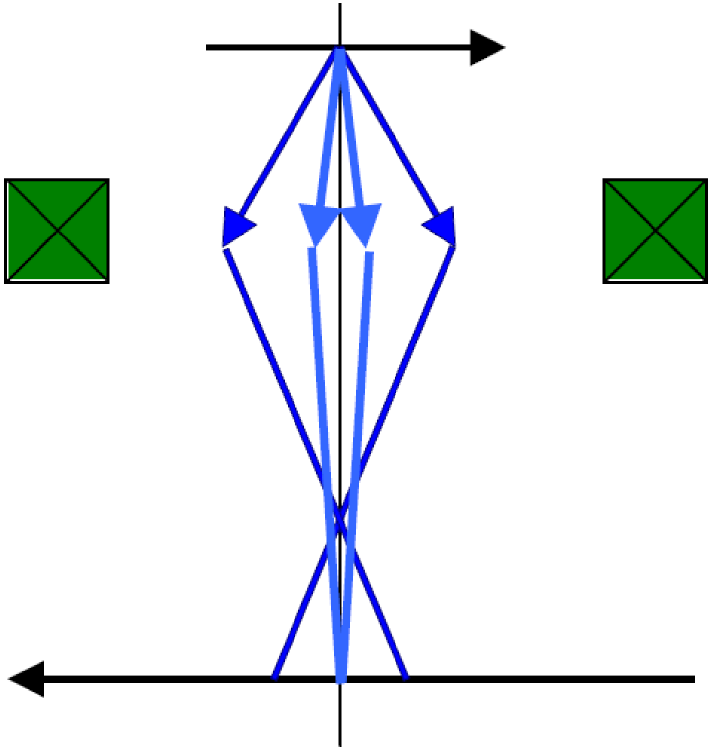
The TEM has very poor lenses

- Spherical aberration in particular

This aberration causes diffracted waves to be 'phase shifted' by the objective lens

- Complex dependence on wavelength, $C_s$, diffraction vector and defocus
- Magnitude of phase shift varies with distance from optic axis
  - And thus diffraction angle
  - Thus each diffracted wave undergoes a different phase shift

Complicates image interpretation



Spherical aberration

# Phase Contrast

- Imaging of atomic structures (proper control of instrument parameters).

- Normally: BF or DF image → selection of a single beam
- Phase contrast: more than one beam (the more beams collected, the higher the resolution)

$$\Psi = \phi_0(z)e^{2\pi i(\mathbf{k}_I\cdot\mathbf{r})} + \phi_{\mathbf{g}}(z)e^{2\pi i(\mathbf{k}_D\cdot\mathbf{r})}$$

$$\phi_0(z) = A \qquad B = \frac{\pi t}{\xi_{\mathbf{g}}}\cdot\frac{\sin \pi t s_{eff}}{\pi s_{eff}}$$

$$\phi_{\mathbf{g}}(z) = Be^{i\delta} \qquad \delta = \frac{\pi}{2} - \pi t s_{eff}$$

some substitutions

$$\Psi = e^{2\pi i(\mathbf{k}_I\cdot\mathbf{r})}A + Be^{i(2\pi\mathbf{g}'\cdot\mathbf{r}+\delta)}$$

# *The intensity in the image:* $I = \psi^*\psi$

$$I = A^2 + B^2 + AB\left[e^{i(2\pi\mathbf{g}'\cdot\mathbf{r}+\delta)} + e^{-i(2\pi\mathbf{g}'\cdot\mathbf{r}+\delta)}\right]$$

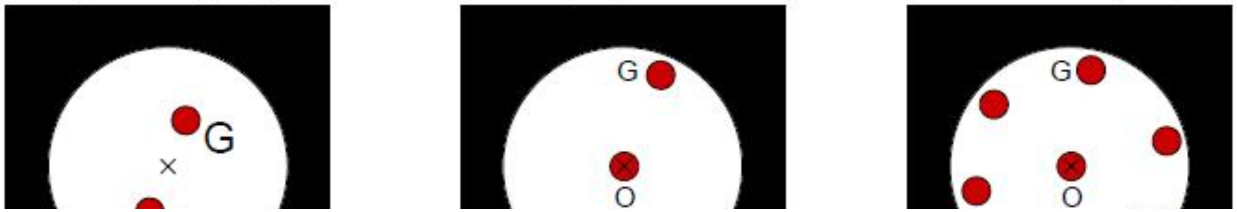
Now $g_0$ is effectively perpendicular to the beam so we'll set it parallel to x and replace d giving

$$I = A^2 + B^2 + 2AB\cos(2\pi\mathbf{g}'\cdot\mathbf{r} + \delta)$$

take g to be parallel to x

$$I = A^2 + B^2 - 2AB\sin(2\pi g' x + \pi s t)$$

Therefore, the intensity is a sinusoidal oscillation (this is the lattice fringe!) normal to **g**', with a periodicity that depends on excitation error (*s*) and thickness (*t*) off-axis lattice fringe imaging | on-axis 3-beam imaging | on-axis many-beam imaging



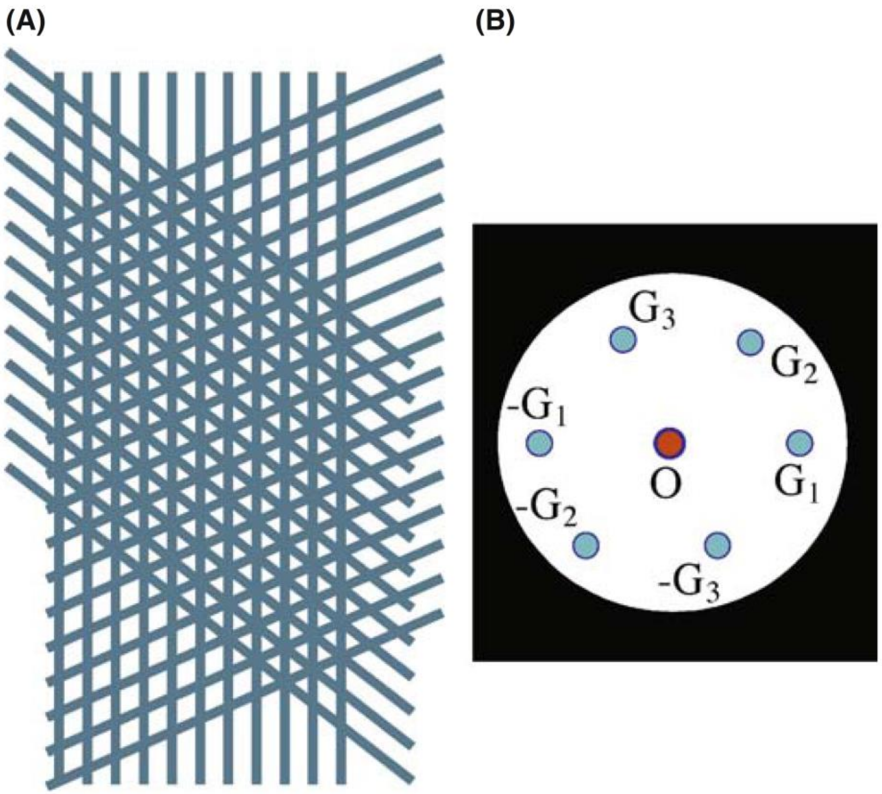

**FRINGES NOT PLANES**

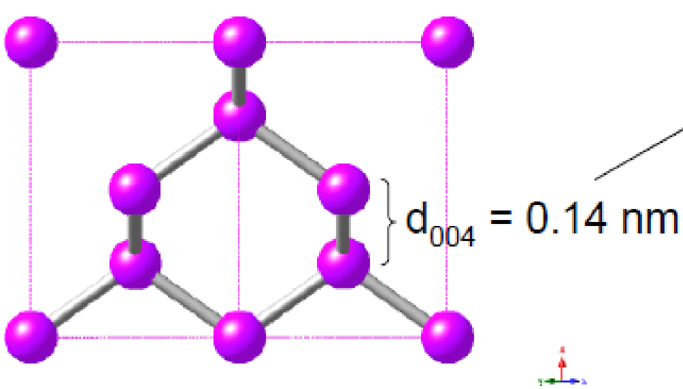
So lattice fringes are not direct images of the structure, but just give you information on lattice spacing and orientation.

Resist the temptation of interpreting the spots in the image as atoms!

All this is a some of the individual fringes. Proof on the next slide.

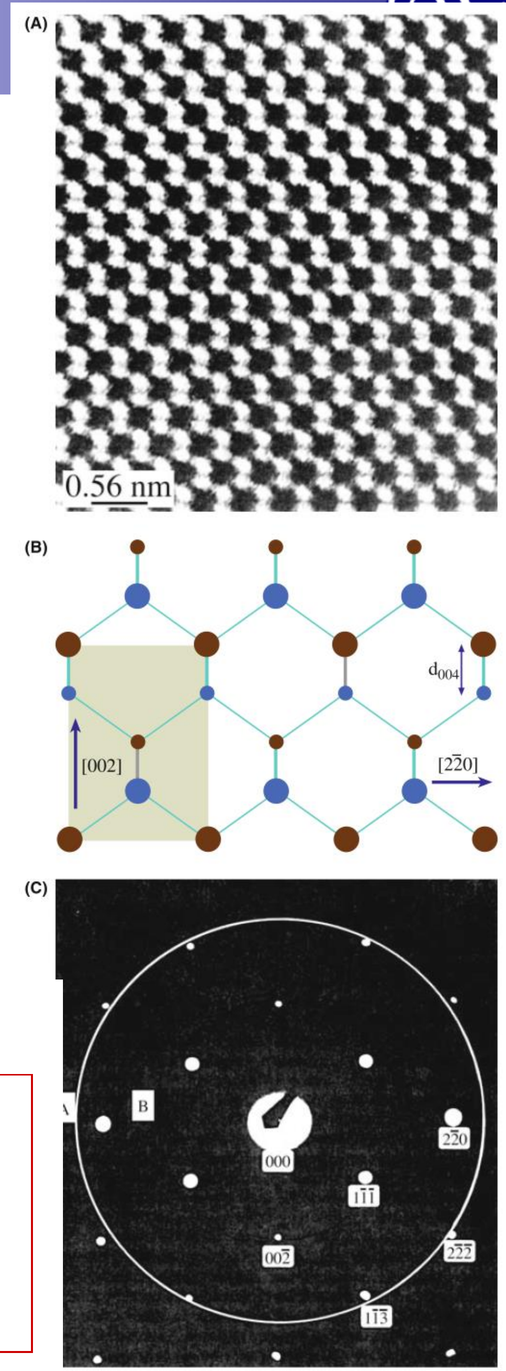
# Phase Contrast




0.13 nm fringe spacing in a 0.25 nm resolution TEM?

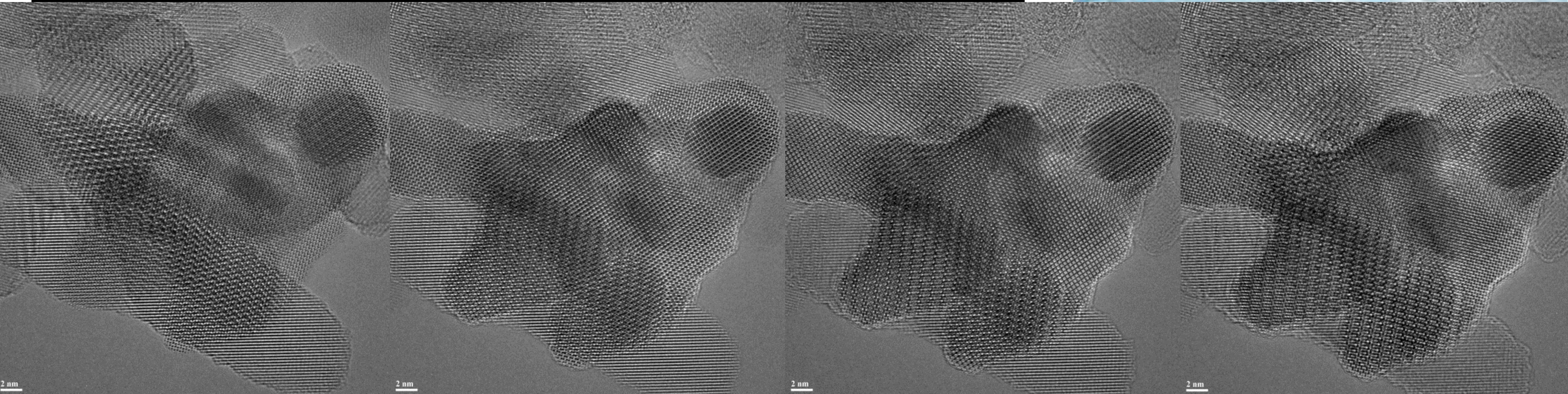
generated by interference of 113 fringes



# Computing in Electron Microscopy

| | |
|---|---|
| Image simulation | - Interpreting the image<br>- Easy change of instrumental parameters (e.g. high voltage, focus...)<br>- Two methods: Bloch wave eigenstates or multi-slice methods |
| Image processing | -Improve interpretability<br>-Recover additional information<br>(image restoration deconvolve transfer function of the instrument from a single image vs.<br>image reconstruction combination of several images into one image) |
| Instrument design | Broad research field |
| On-line control | Record the data and to control the instrument |
| Data archiving | Digital storage vs. Photographs (degrading time) |





# Contrast

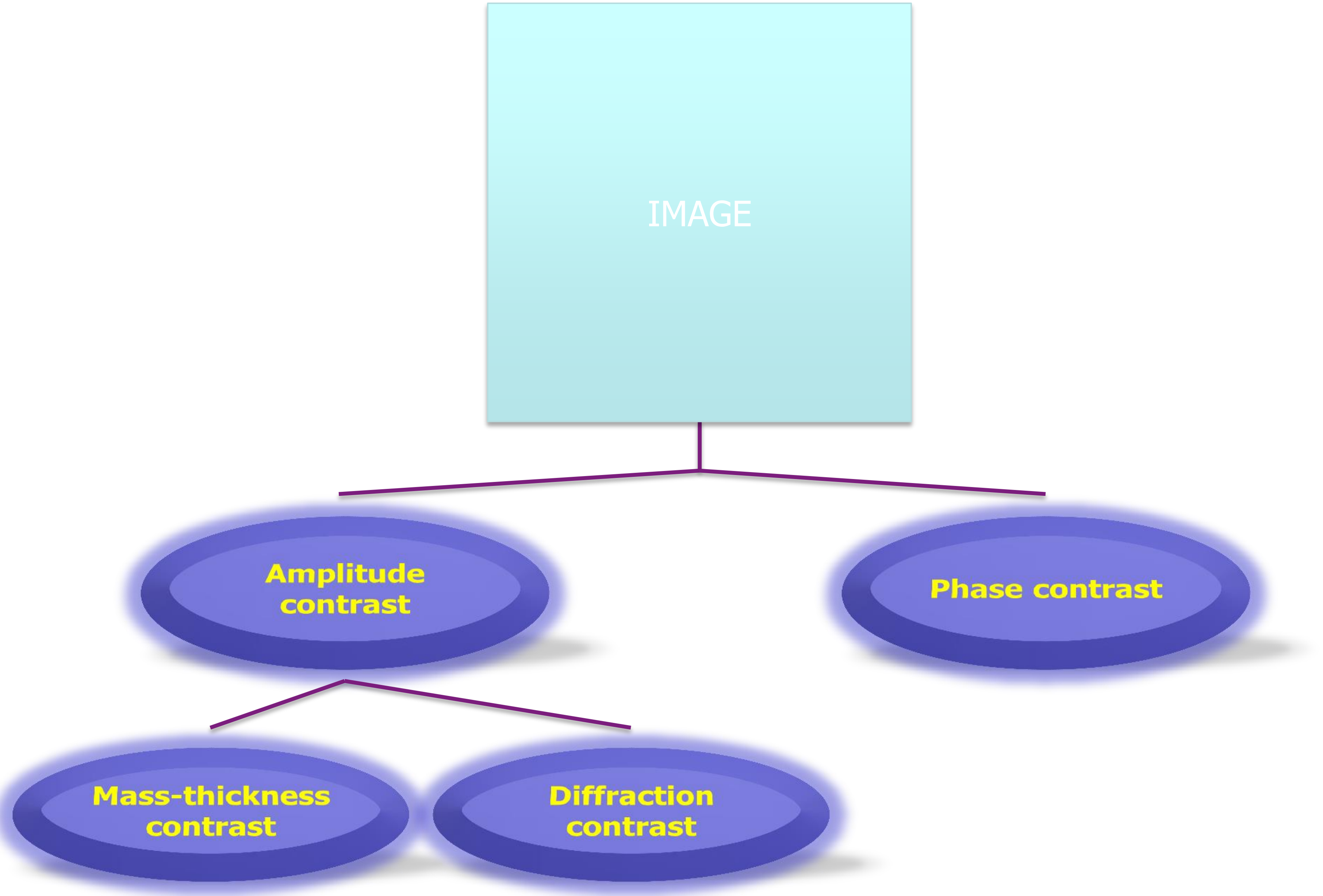


IMAGE
Amplitude contrast
Phase contrast
Mass-thickness contrast
Diffraction contrast