

Scanning TEM (STEM) part II

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EPFL-IPHYS-LSME

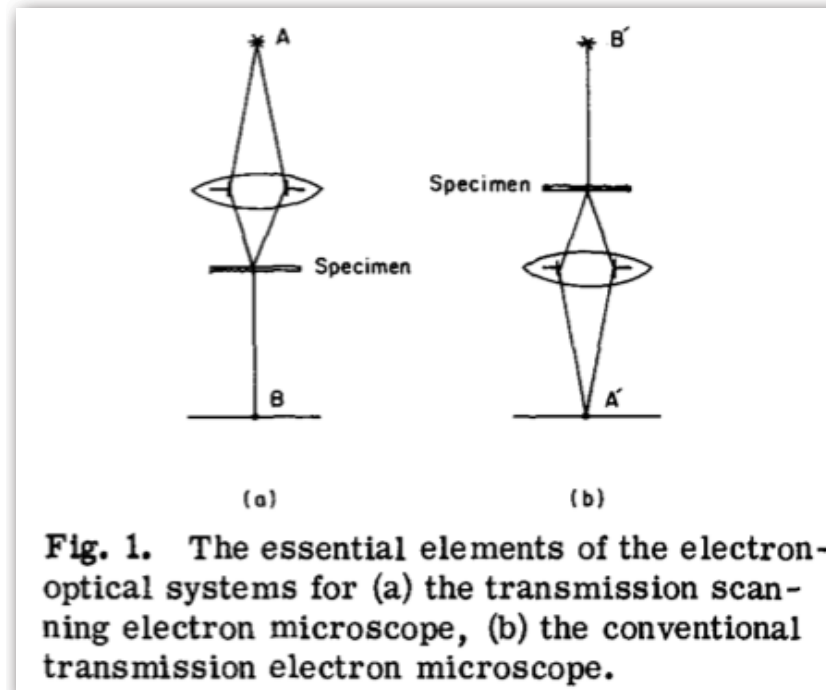
EPFL STEM II contents

- Reciprocity theorem and phase contrast BF STEM
- Incoherence in STEM imaging
- STEM focusing and electron Ronchigram (lens with C_s)
- C_s -aberration correction in STEM
- HAADF theory and simulation
- Phase contrast STEM for light atoms (ABF, iCOM/iDPC, electron ptychography)

EPFL Reciprocity Theorem

Reciprocity Theorem (from geometric optics): The amplitude of a wave at detector B due to an electron source at A (STEM) is equal to the amplitude at image place A' due to a source at B' (CTEM).

⇒ Optical equivalence of CTEM vs STEM imaging



J.M. Cowley *Applied Physics Letters* **15** (1969) 58

Quiz: for reciprocity with BF CTEM with a perfectly parallel incident beam, what collection angle do we need for the BF detector in STEM?

EPFL Phase contrast BF STEM imaging

- Following from the theory of reciprocity, with a sufficiently small probe a BF detector can produce an image equivalent to a HR-TEM image.
- This is conditional on having CBED discs overlapping on the BF detector.
- No overlap is like BF CTEM imaging with only the direct beam chosen, so will give no fringes

EPFL Phase contrast BF STEM imaging

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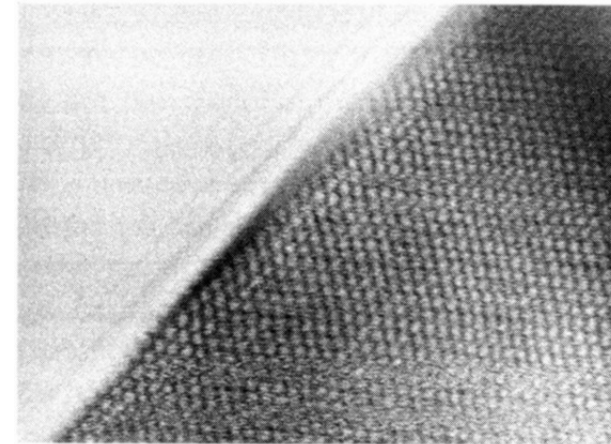
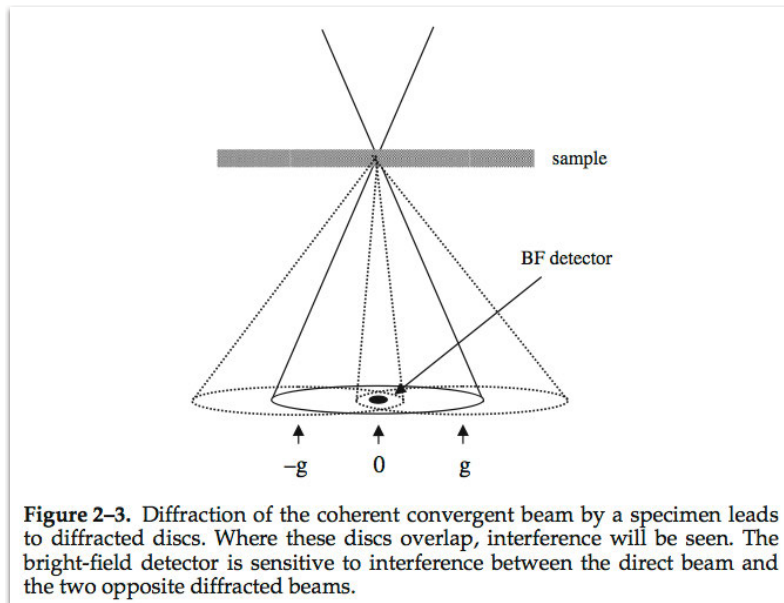


Figure 3. Bright-field STEM image of a small MgO crystal in $[1\ 1\ 0]$ orientation [95].

Quiz: for a particular lattice spacing, how can we increase disc overlap in the diffraction pattern?

Incoherence in STEM imaging

EPFL Coherent vs Incoherent imaging

- HR bright-field STEM image of a weak phase object has following intensity equation:

$$I_{\text{BF}}(\mathbf{R}) = |\varphi(\mathbf{R}) \otimes P(\mathbf{R})|^2$$

where $\mathbf{R}$ is a 2D position vector, $\varphi(\mathbf{R})$ is a phase shift and $P(\mathbf{R})$ is the probe amplitude distribution

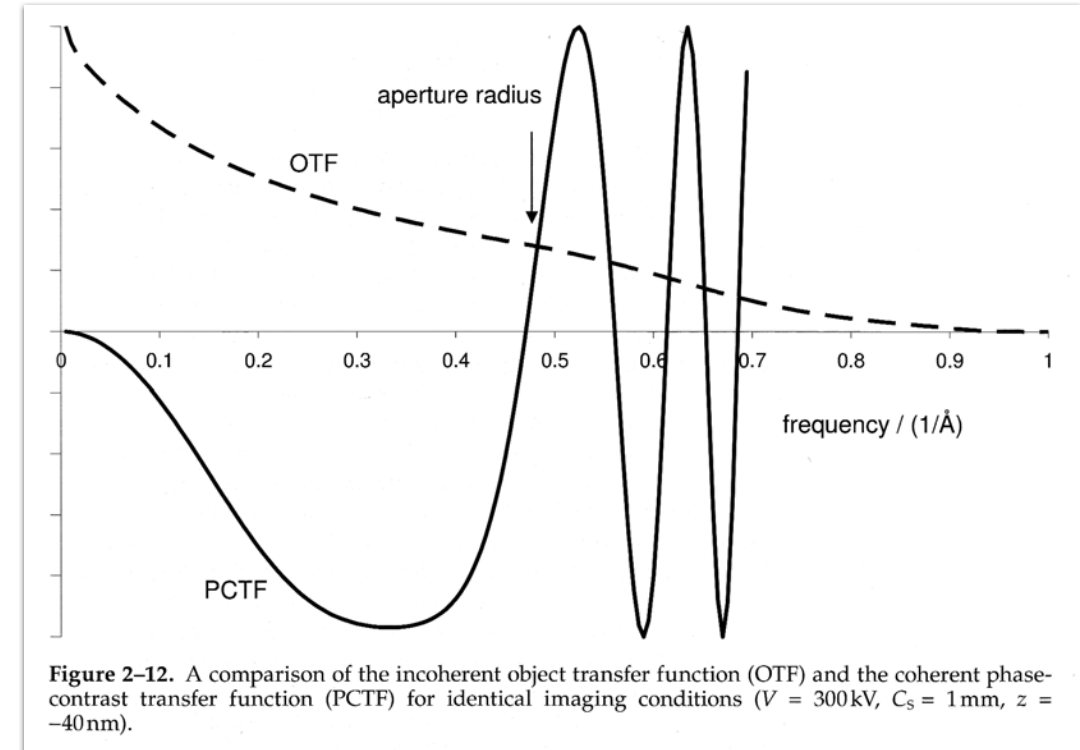
- Therefore can show positive or negative contrast depending on the phase of the transfer function
- If instead integrate *all* beams scattered onto an annular dark-field detector, obtain:

$$I(\mathbf{R}_0) = |\varphi(\mathbf{R}_0)|^2 \otimes |P(\mathbf{R}_0)|^2$$

where $\mathbf{R}_0$ is a scan coordinate that locates centre of the e⁻ probe

- This is a *convolution of intensities*

- A convolution of intensities corresponds to an *incoherent* imaging condition
- Compared to coherent – i.e. phase contrast – imaging, incoherent imaging has some specific (useful!) characteristics:
 - ➔ No image contrast inversion with defocus
 - ➔ “Camera-like characteristics”
 - ➔ Broad optical transfer function (OTF) instead of modulating PCTF
 - ➔ Improved point resolution for same optical characteristics



EPFL Resolution of incoherent imaging

- The above result means that an ADF STEM image has an improved spatial resolution (point resolution) compared to its BF counterpart
- Theory was originally developed by biologists
- However, strong diffraction from crystalline samples $\Rightarrow$ lower-angle ADF detector collects too much coherent diffraction signal to achieve such incoherency
- HAADF detector does achieve incoherent imaging criterion because uses *phonon-scattered* electrons that are fundamentally incoherent
 - i.e. the scattering mechanism destroys the phase relationship

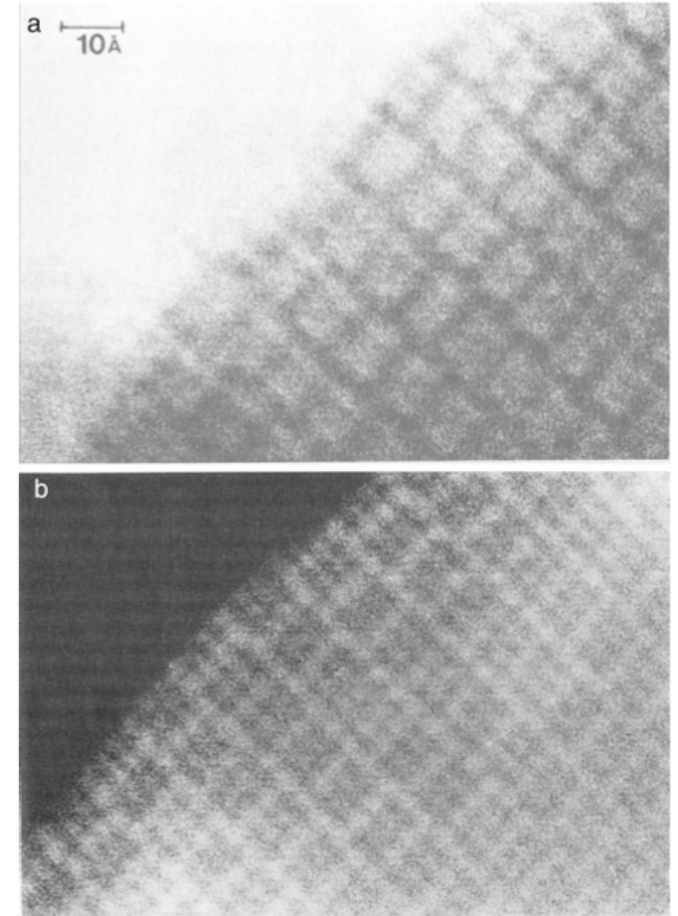


Figure 1-14. (a) Bright field and (b) ADF images of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ showing improved atomic resolution detail in the dark field image, reproduced from Cowley (1986b) with permission.

STEM focusing and the electron Ronchigram

EPFL STEM focusing

- Consider probe-forming (objective) lens with C_s . Ideally want to form e- probe from rays which have the same phase.
- Approximate using criterion that phase shift $\chi(\vec{q})$ must not depart more than $\pi/4$ from 0. It is found that for a given C_s and λ optimal defocus is:

$$z = -0.71\lambda^{1/2}C_s^{1/2}$$

- Condition allows probe-forming aperture with radius of:

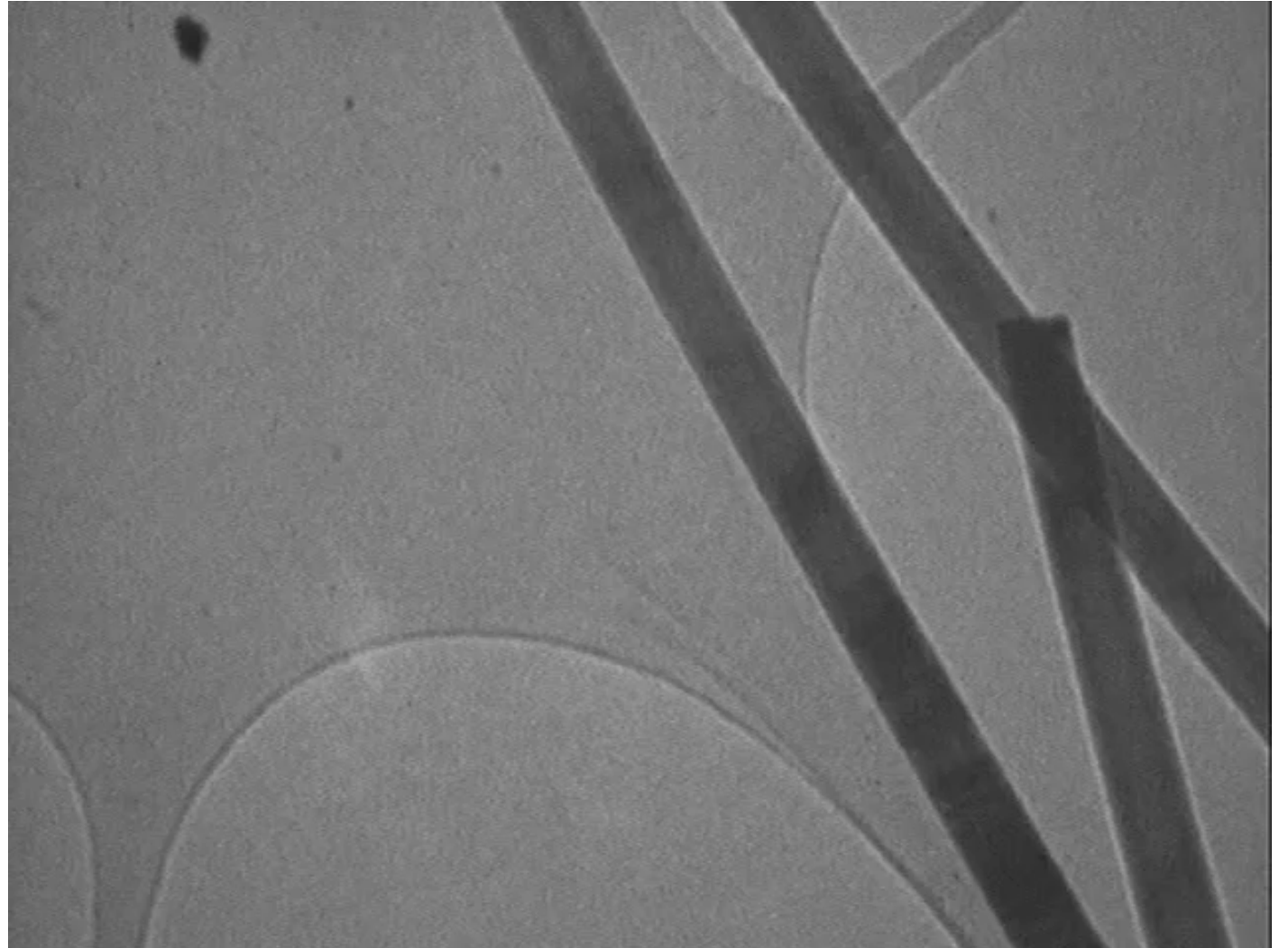
$$\alpha = 1.3\lambda^{1/4}C_s^{-1/4}$$

- Using this optimum defocus and aperture size, the probe FWHM is given by:

$$d = 0.4\lambda^{3/4}C_s^{1/4}$$

EPFL The electron Ronchigram

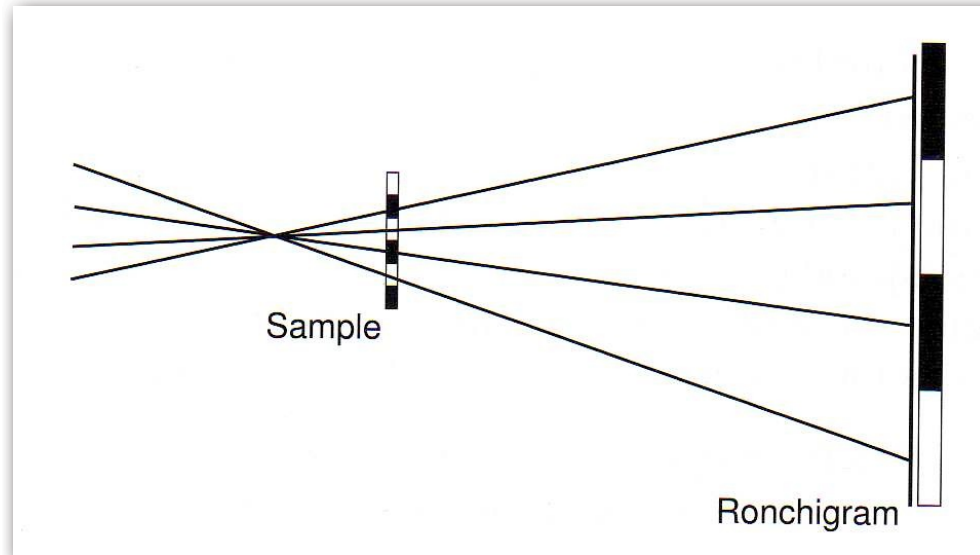
- STEM mode; fix the probe; large/no aperture in probe-forming lens
- Record 2-D image of intensity in diffraction (i.e. STEM detector) plane
- See “shadow image” of sample in the direct beam diffraction disc



EPFL Basics of shadow image formation

EPFL Basics of shadow image formation

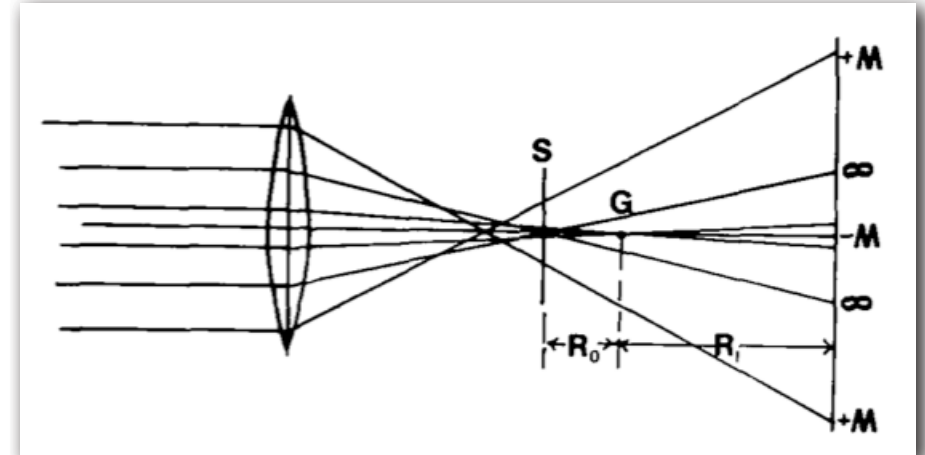
- Assuming perfect optics:



- Ronchigram is similar to defocused TEM diffraction pattern, blending image information with scattering angles
- At overfocus the STEM detector plane is a shadow image of the sample
magnification $M = d_{\text{probe-detector}} / d_{\text{probe-sample}}$
- At underfocus the image will be magnified, but also inverted

EPFL Shadow image formation with C_s

- For lens with positive C_s , focal point of rays depends on their angle
- Consider sample S in underfocus for paraxial rays:
- Paraxial rays with Gaussian focus G have magnification $M = -R_1/R_0$
- Rays that cross at S have infinite magnification



- Ronchigram focal series:
- When sample at Gaussian focal point or in overfocus for paraxial rays: direct image of sample, with magnification decreasing smoothly for larger angles

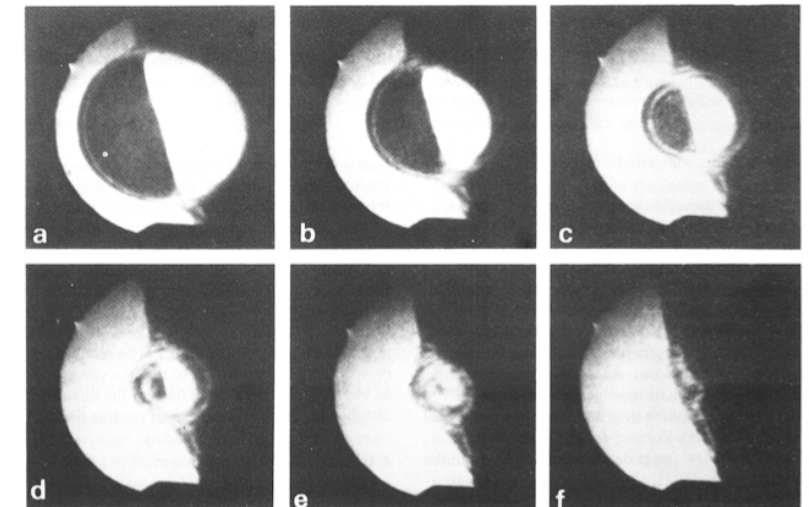
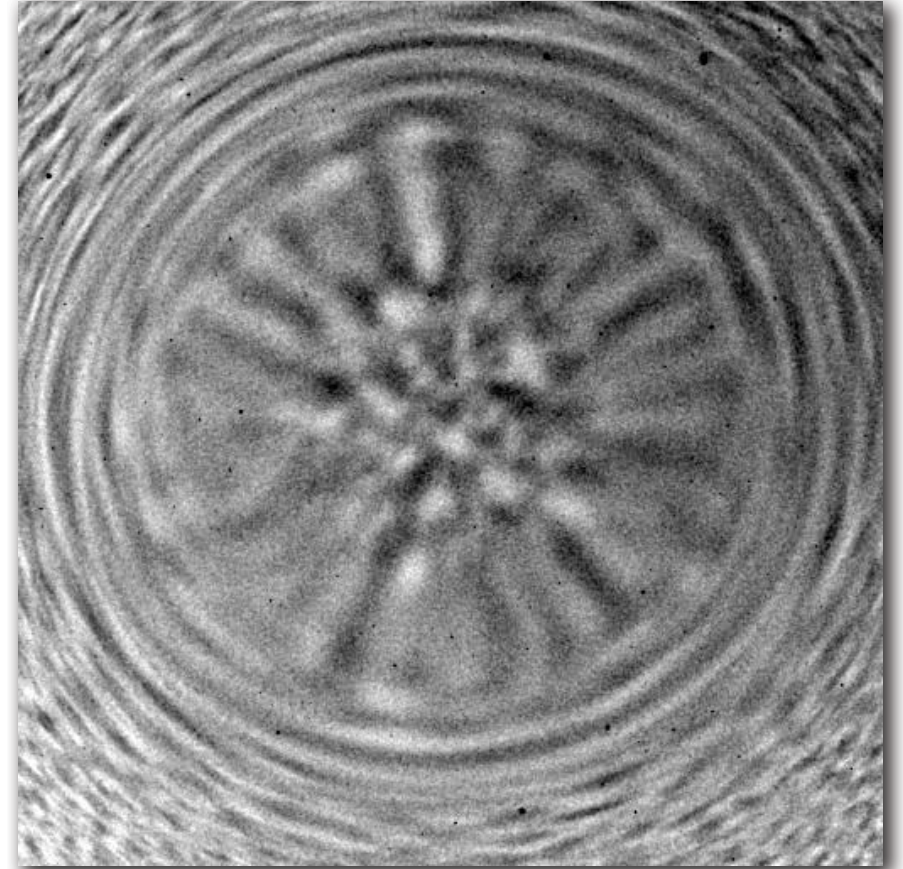


Fig. 3. Through-focus series of shadow images of the edge of a thick crystal. An asymmetry of the scanning in the display system gives the infinite-magnification circles a slightly elliptical shape. Approximate defocus values: (a) $-1.2 \mu\text{m}$, (b) $-0.7 \mu\text{m}$, (c) $-0.5 \mu\text{m}$, (d) $-0.25 \mu\text{m}$, (e) $0 \mu\text{m}$, (f) $+0.25 \mu\text{m}$.

EPFL Radii & azimuths of infinite magnification

- The under focus Ronchigram shows infinite magnification at more than one scattering angle
- There are radii (radial spokes) and tangential azimuths (rings) of infinite magnification
- Why is this?



EPFL Radii & azimuths of infinite magnification

- Phase shift due to aberration in *Front Focal Plane* of objective (probe-forming) lens:

$$\chi(\vec{q}) = \left(\pi z \lambda |\vec{q}|^2 + \frac{1}{2} \pi C_s \lambda^3 |\vec{q}|^4 \right) \text{ for defocus } z \text{ and wave vector } \vec{q} \text{ where } |\vec{q}| = \theta / \lambda$$

- Cowley derived that, in a 1-D optical system:
$$M' = \frac{M}{1 + C_s \lambda^2 |\vec{q}|^2 / z}$$

M : magnification for ideal $C_s = 0$; M' : actual magnification

- Infinite magnification at:
$$|\vec{q}|^2 = \frac{-z}{C_s \lambda^2}$$

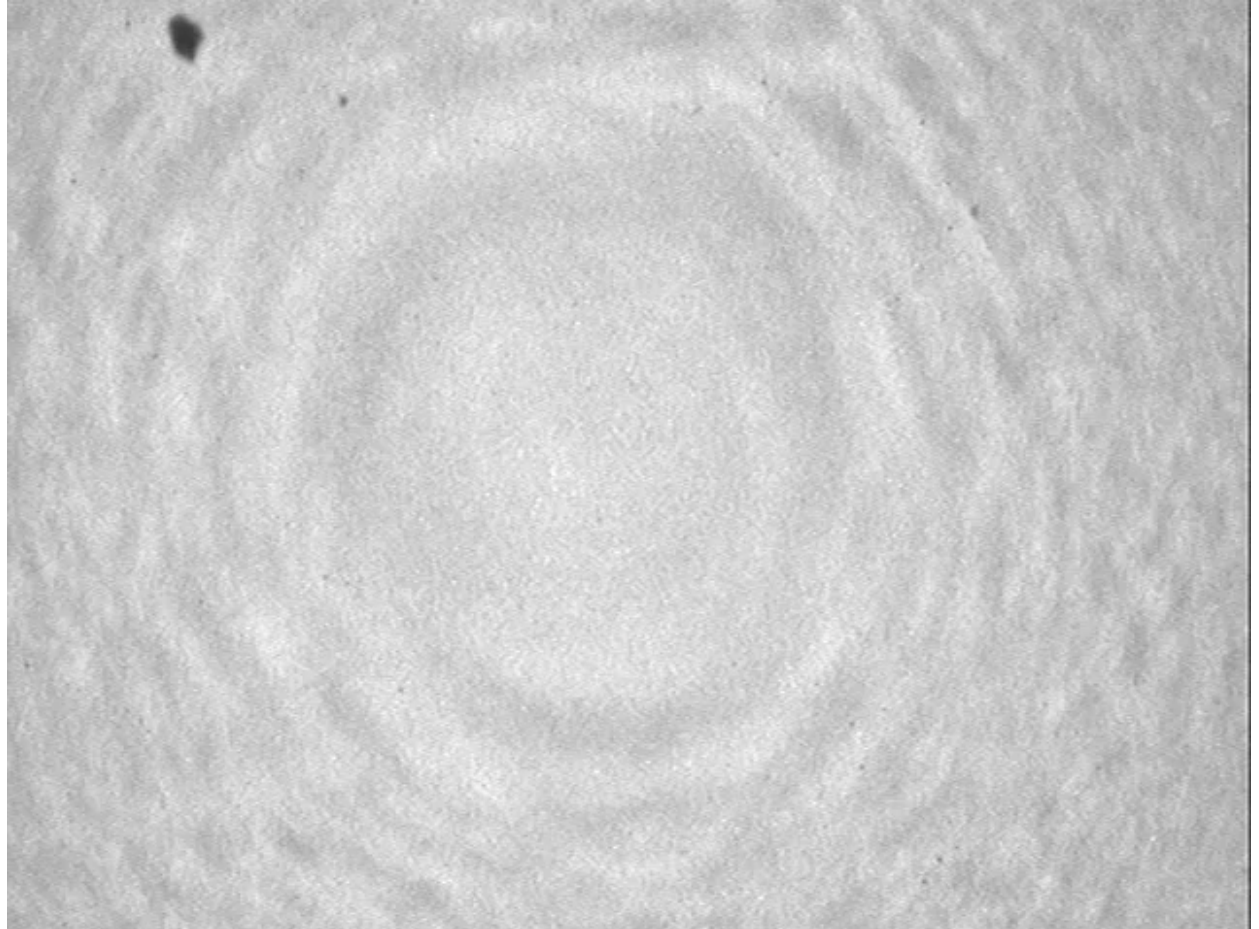
- In a 2-D optical system there are **two** critical angles:

➔ Radial magnification is infinite for:
$$|\vec{q}|^2 = \frac{-z}{3C_s \lambda^2}$$

➔ Circumferential magnification is infinite for:
$$|\vec{q}|^2 = \frac{-z}{C_s \lambda^2}$$

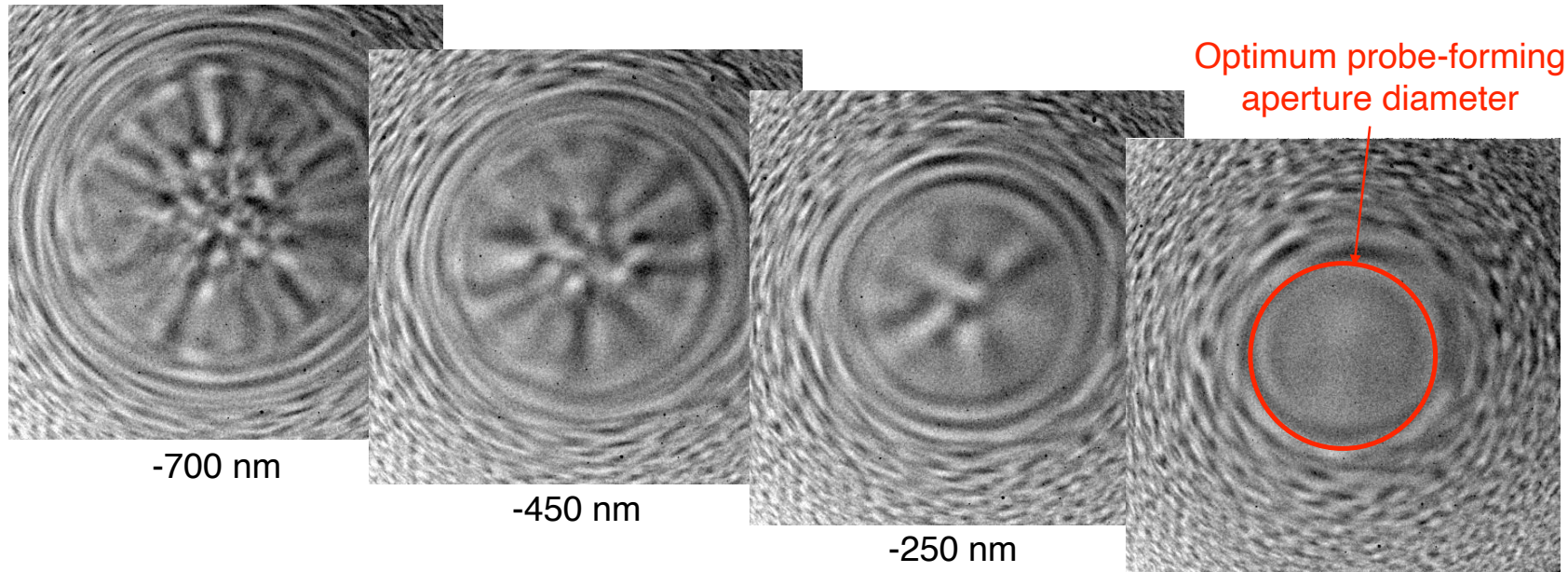
EPFL Aligning STEM mode

- The Ronchigram of amorphous carbon is to STEM as the FFT of amorphous carbon is to CTEM: use it to correct objective lens astigmatism and tune defocus
- Example: tuning astigmatism:



EPFL Aligning STEM mode

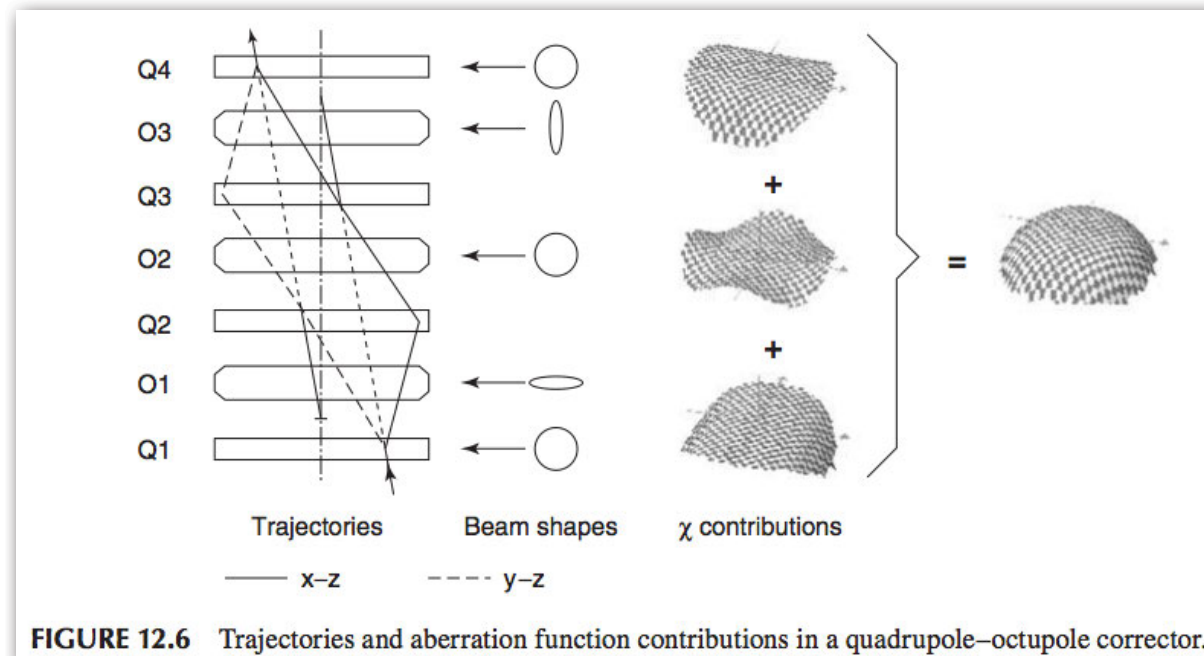
- The Ronchigram of amorphous carbon is to STEM as the FFT of amorphous carbon is to CTEM: use it to correct objective lens astigmatism and tune defocus
- Focusing with Ronchigram:
 - ▶ Reduce under-focus until infinite-magnification rings are of minimum diameter $\Rightarrow$ optimum defocus (c.f. Scherzer defocus in HR-TEM)



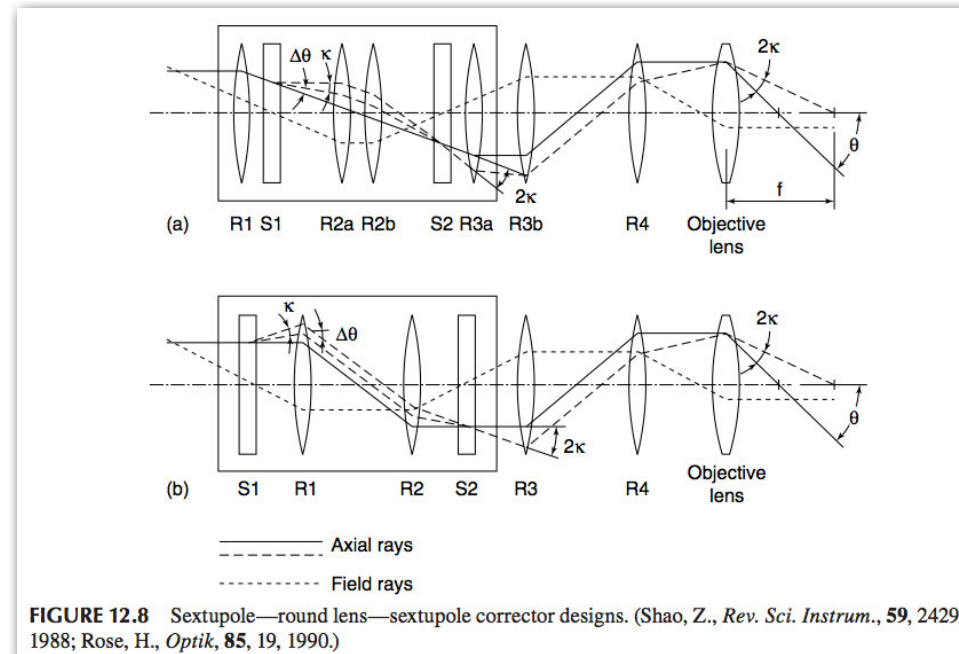
- ▶ Fit probe-forming aperture to the “sweet spot” or “blow up” region of constant phase within this diameter

C_s -aberration correction in STEM

- Correcting the C_s of the probe-forming lens overcomes above limits
- Correction realised by coupling radially-symmetric, convergent EM lenses with positive C_s with non-symmetric lenses which are divergent and so have negative C_s
- Pioneering STEM corrector: quadrupole–octupole design by NION (Krivanek):



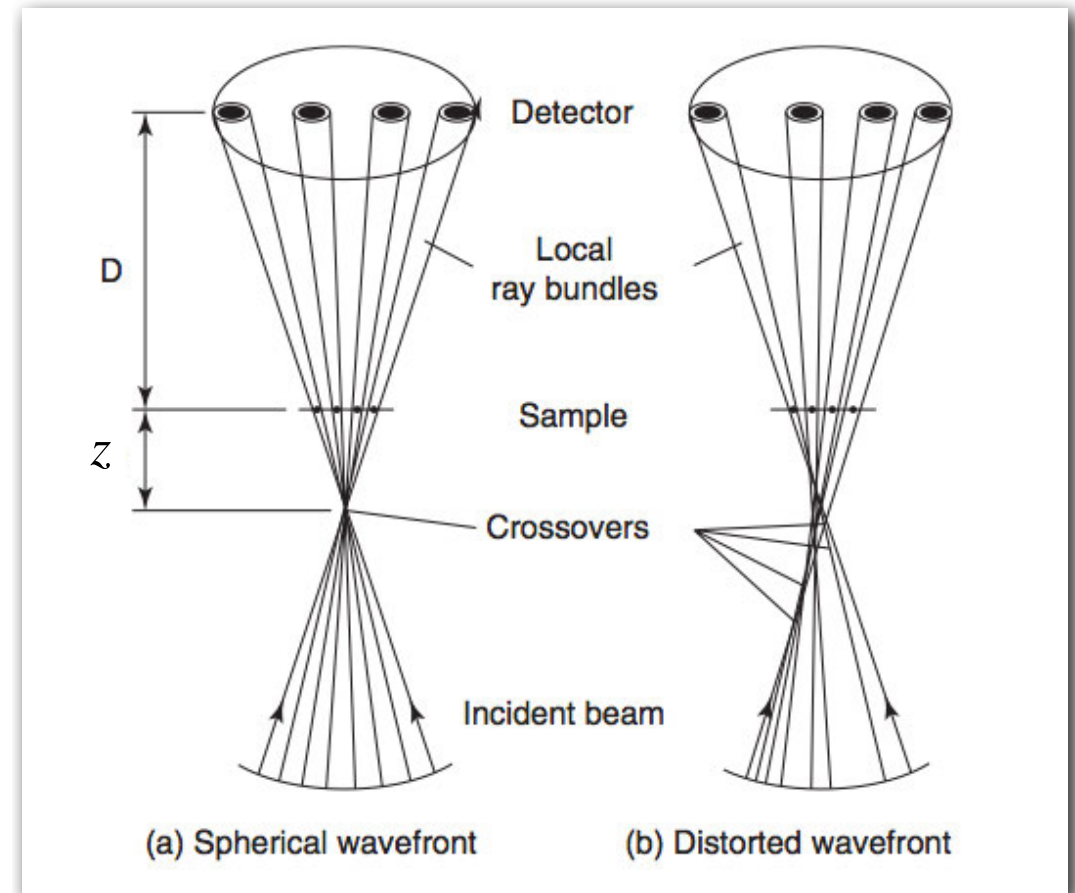
- Correcting the C_s of the probe-forming lens overcomes above limits
- Correction realised by coupling radially-symmetric, convergent EM lenses with positive C_s with non-symmetric lenses which are divergent and so have negative C_s
- Most common STEM corrector: hexapole-round lens-hexapole by CEOS:



DCOR version on
CIME's FEI Titan Themis:
< 0.7 Å resolution at 300 kV
~1 Å resolution at 80 kV

EPFL Measuring aberrations

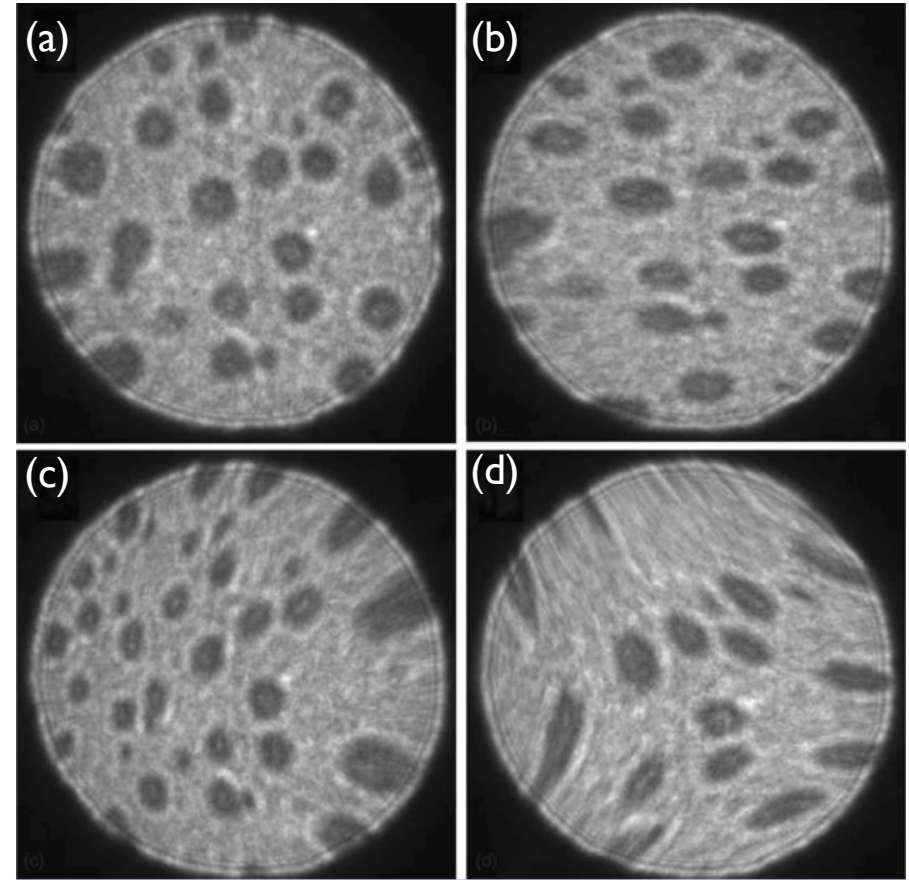
- With the sample at a defocus z and an incident wavefront that is not spherical local ray bundles go through cross-overs at different heights in the column
- The magnification of the shadow image becomes position-dependent, and different in different directions
- C.f. FFT of amorphous material for measuring aberrations in HR-TEM



EPFL Measuring aberrations

- Quiz: which shadow image of Au nano particles on amorphous carbon film, taken at defocus of -600 nm, shows which type of aberration?

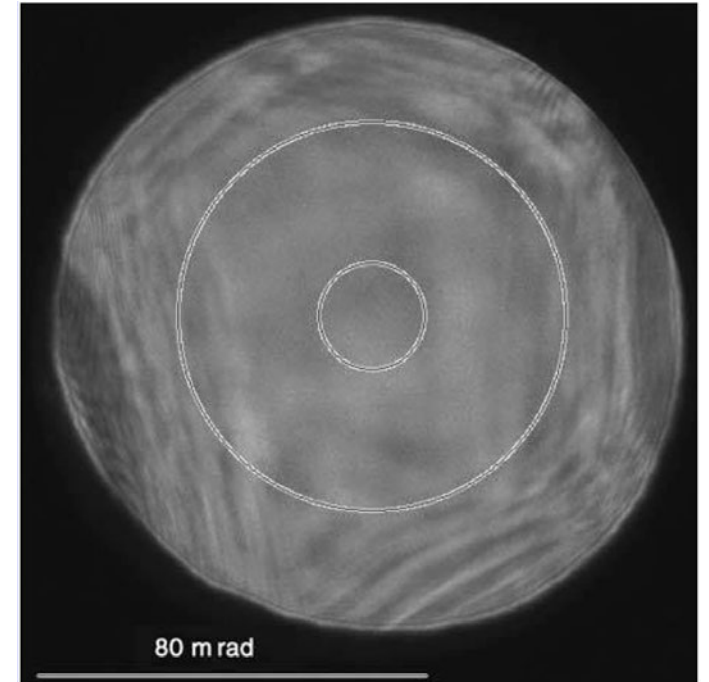
- ➔ *Coma – i.e. incident beam tilt*
- ➔ *Astigmatism*
- ➔ *3-fold astigmatism*
- ➔ *no aberration?*



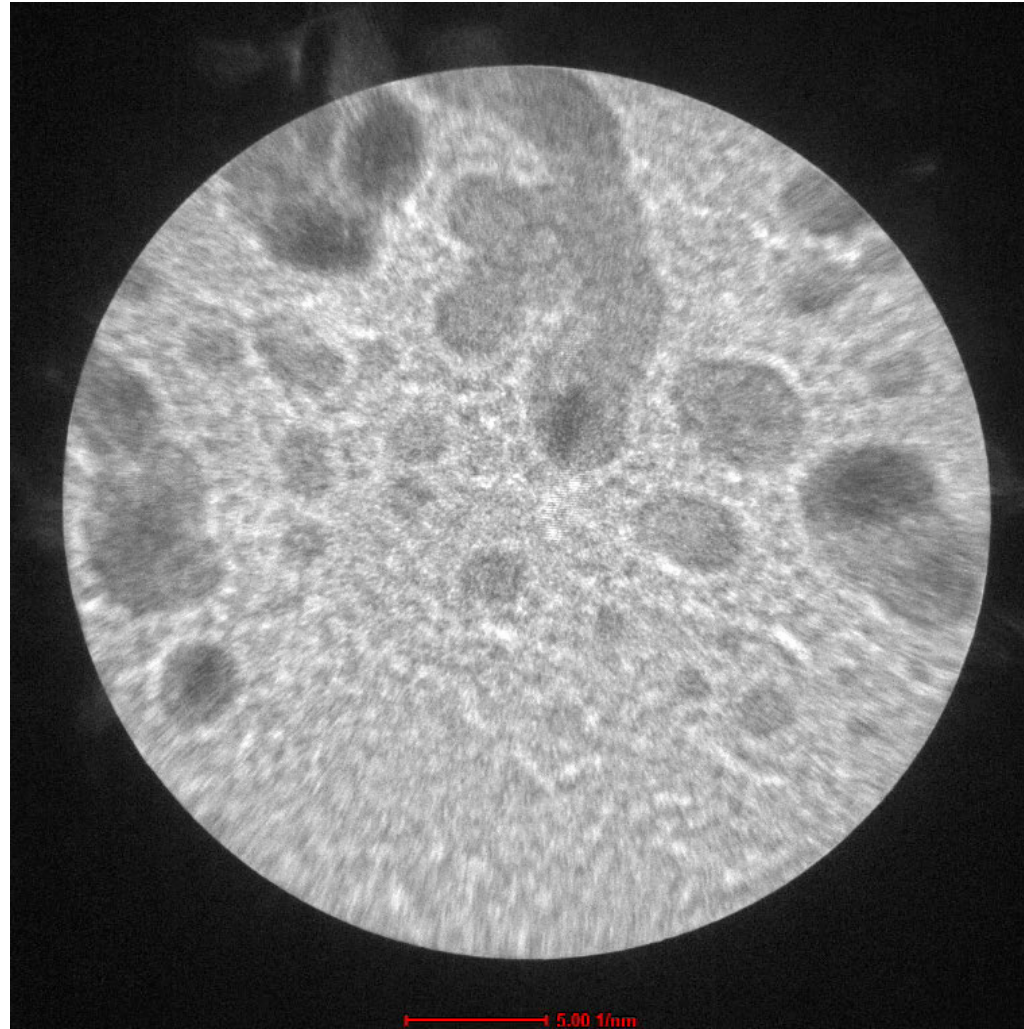
- Note: CEOS corrector alignment software instead estimates probe size and shape, by taking under-, in-, and over-focus STEM images of Au nanoparticles and performing a deconvolution. Probe shapes are measured for different incident beam tilts to measure lens aberrations.

EPFL C_s -corrected Ronchigram

- At optimum defocus aberration correction produces a sweet spot (region of flat phase) with much greater diameter
- E.g. for HT 100 kV, $C_s = 1.0$ mm, sweet spot has:
With no correction $\alpha_{\max} = 1.5\lambda^{1/4}C_s^{-1/4} = 11.6$ mrad
With C_s / C_5 correction (as shown) $\alpha_{\max} = 40$ mrad $\rightarrow$
- Demagnification of virtual source size by the objective (probe-forming) lens increases in proportion with illumination angle (assuming this does not exceed sweet spot diameter) $\Rightarrow$ Probe size decreases as $(\alpha_{\max})^{-1}$
- Using larger probe-forming aperture also improves resolution slightly because diffraction limit reduced

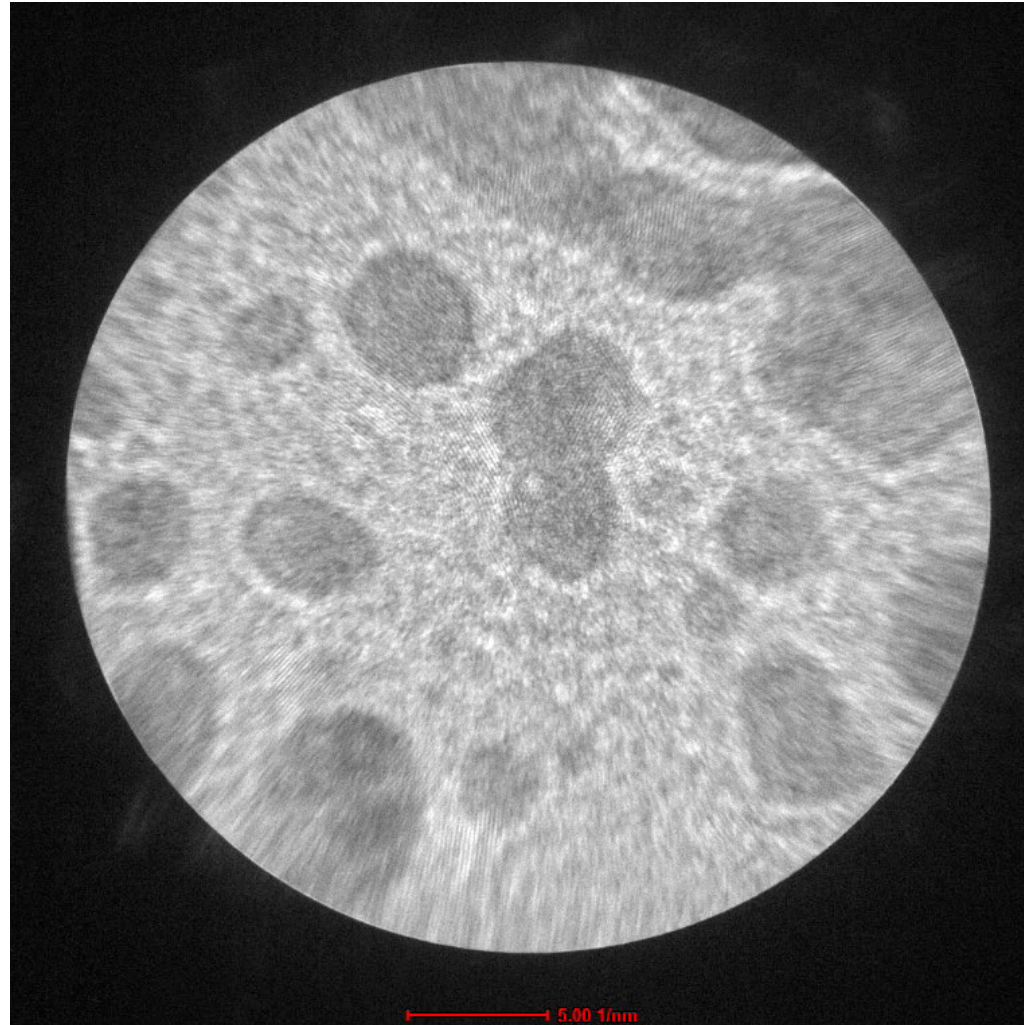


EPFL C_s -corrected Ronchigram movie



Recorded from FEI Titan Themis at CIME

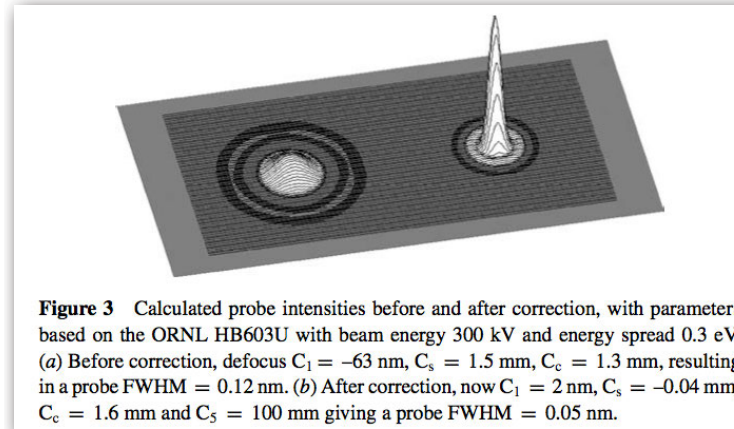
EPFL C_s -corrected Ronchigram movie



Recorded from FEI Titan Themis at CIME

EPFL Aberration-corrected examples

- Effect of C_s -correction on e^- probe intensity distribution:

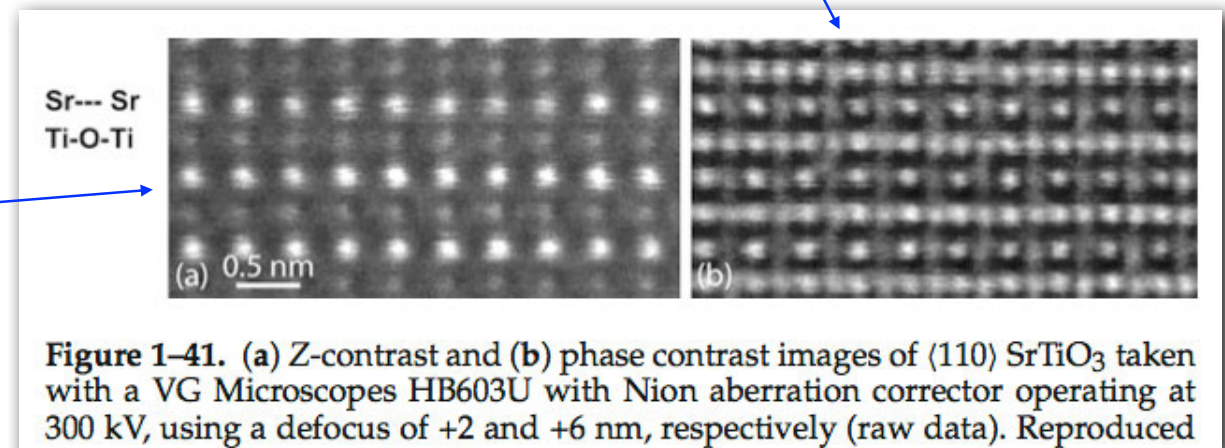


Varela et al. Annu. Rev. Mater. Res. 2005 **35** 539–569

- C_s -corrected imaging example:

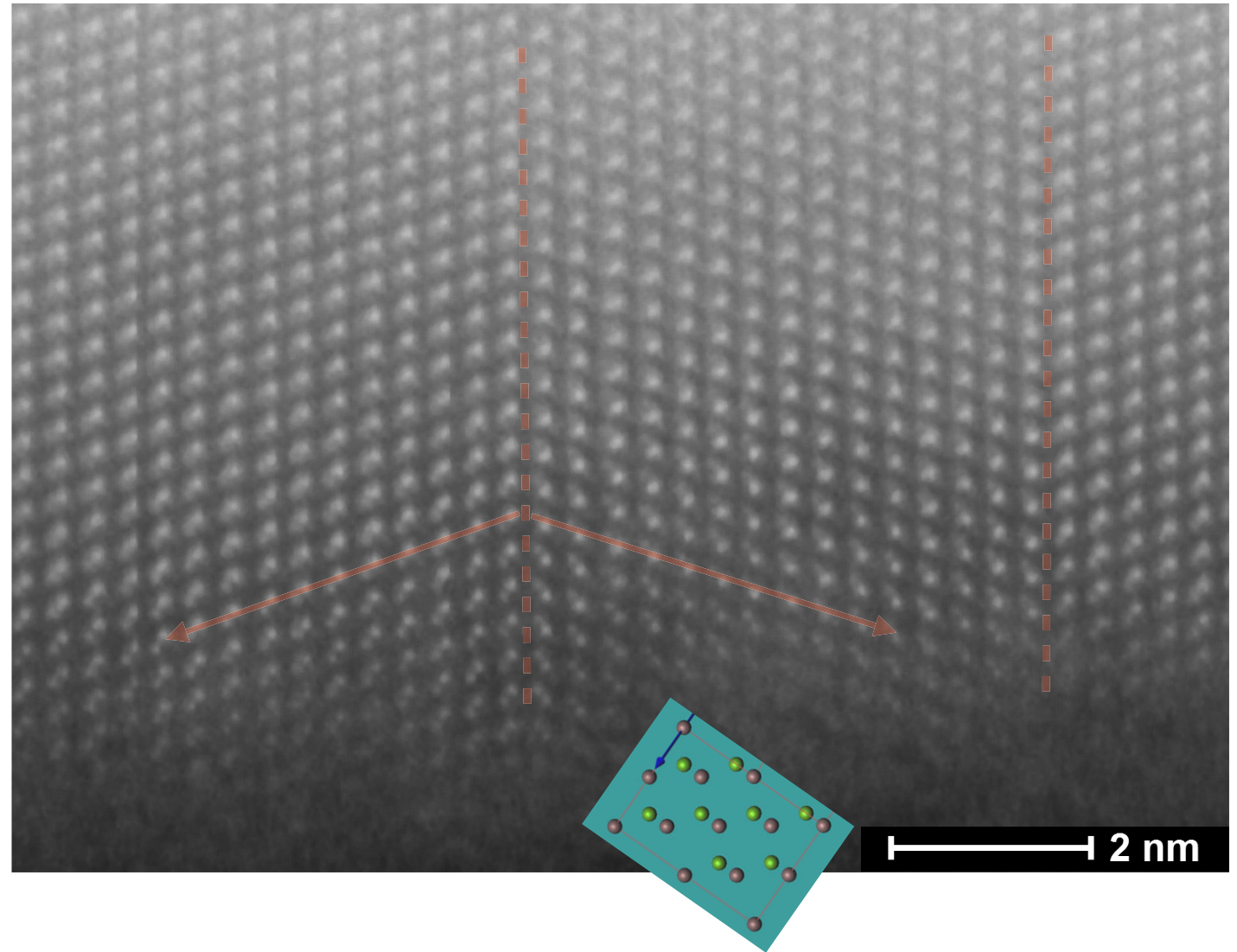
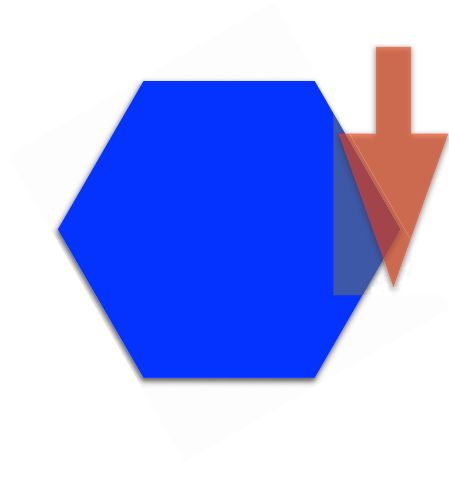
Z-contrast image: “direct” interpretation, but light O columns not visible.

BF detector gives simultaneous phase contrast image equivalent to HR-TEM image; O columns visible but similar problems to interpret as HR-TEM image



EPFL Aberration-corrected examples – HAADF

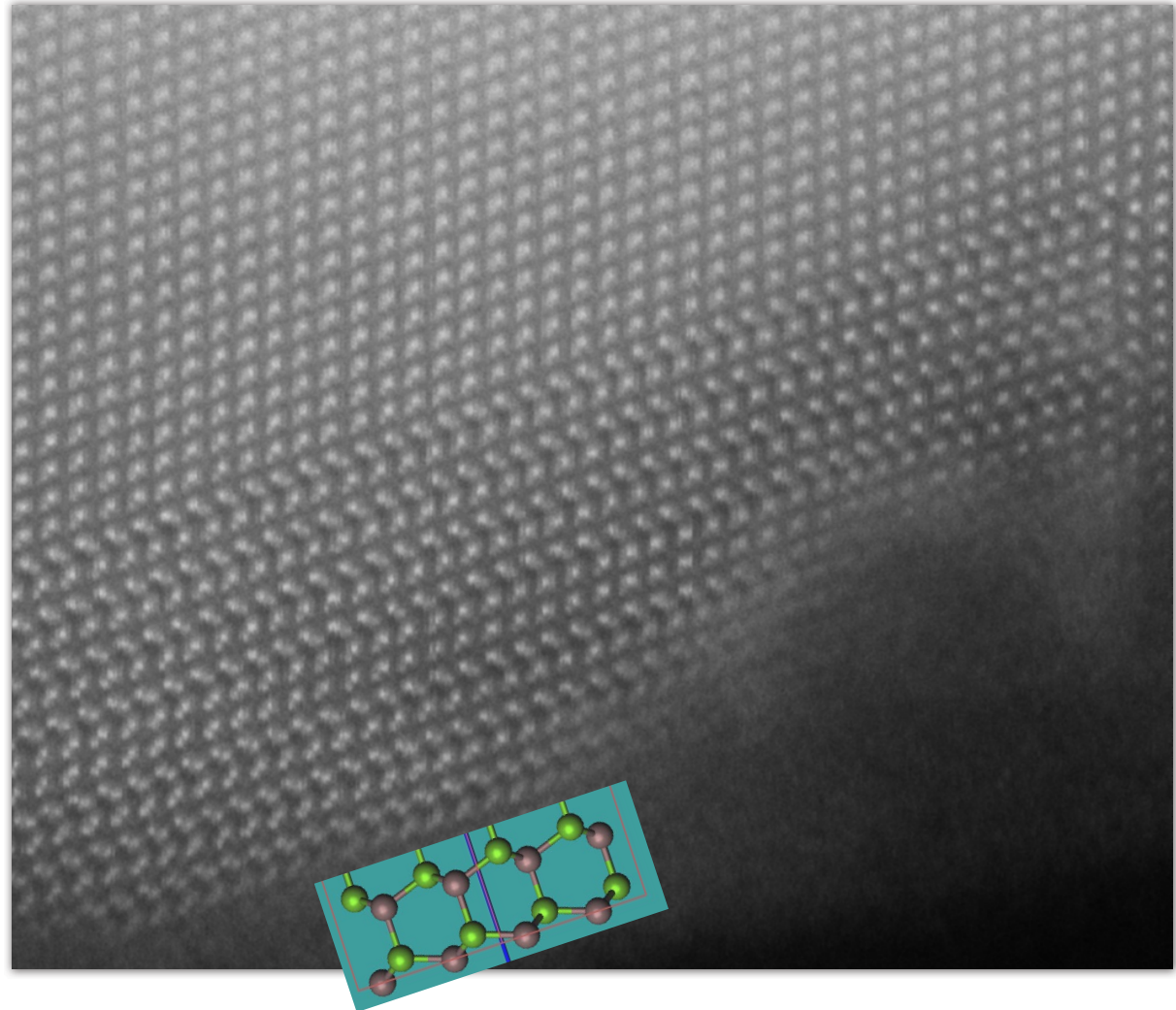
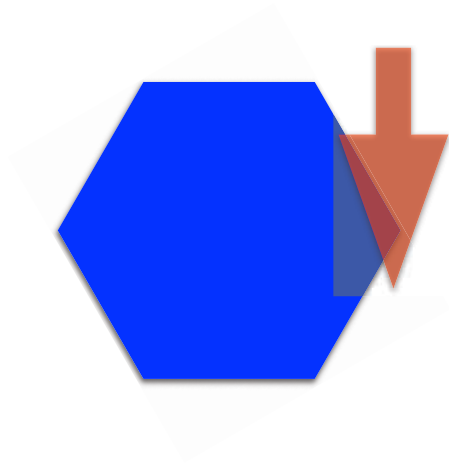
- $(\text{Al}_x\text{Ga}_{1-x})\text{As}$ nanowire



Sample courtesy of Yannick Fontana, Anna Fontcuberta-i-Morral, LMSC

EPFL Aberration-corrected examples – HAADF

- $(\text{Al}_x\text{Ga}_{1-x})\text{As}$ nanowire



Sample courtesy of Yannick Fontana, Anna Fontcuberta-i-Morral, LMSC

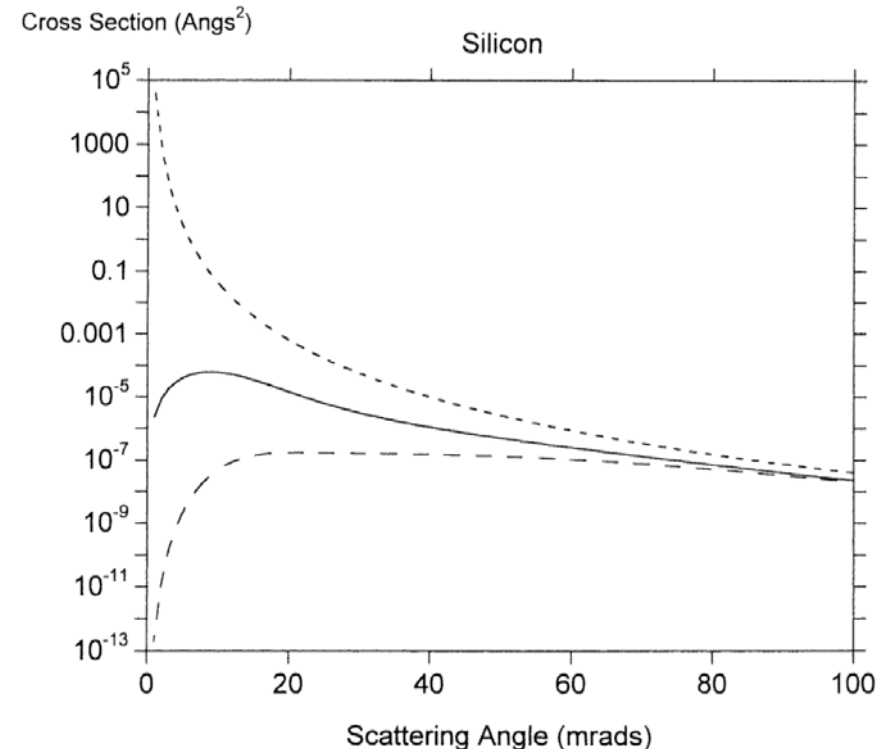
Atomic resolution HAADF theory and simulation

EPFL Phonon scattering ↔ Mott scattering

- For scattering from *single atom*, Rez derived the phonon-scattering cross-section as:

$$I(\vec{\mathbf{K}}) = \frac{d\sigma}{d\Omega} = \frac{\gamma^2}{4\pi^4 a_0^2} \frac{[Z - f_x(\vec{\mathbf{K}})]^2}{K^4} \left[1 - \exp\left(-\frac{MK^2}{2\pi^2}\right) \right]$$

- Plot of scattering cross-sections vs scattering angle (log scale for σ) →
 - Short dashed line: Rutherford cross-section
 - Solid line: Mott scattering
 - Long dashed line: multiple-phonon scattering – often called “*thermal diffuse scattering*” (TDS)



- 3-dimensional calculations of probe shape show that it is only well focused over very limited depth of field
- Simulation for 300 keV beam, $C_s = -149$ nm
- However, for well-aligned atomic columns, electrons are focused by electric field of atoms, and beam *channels* down the column

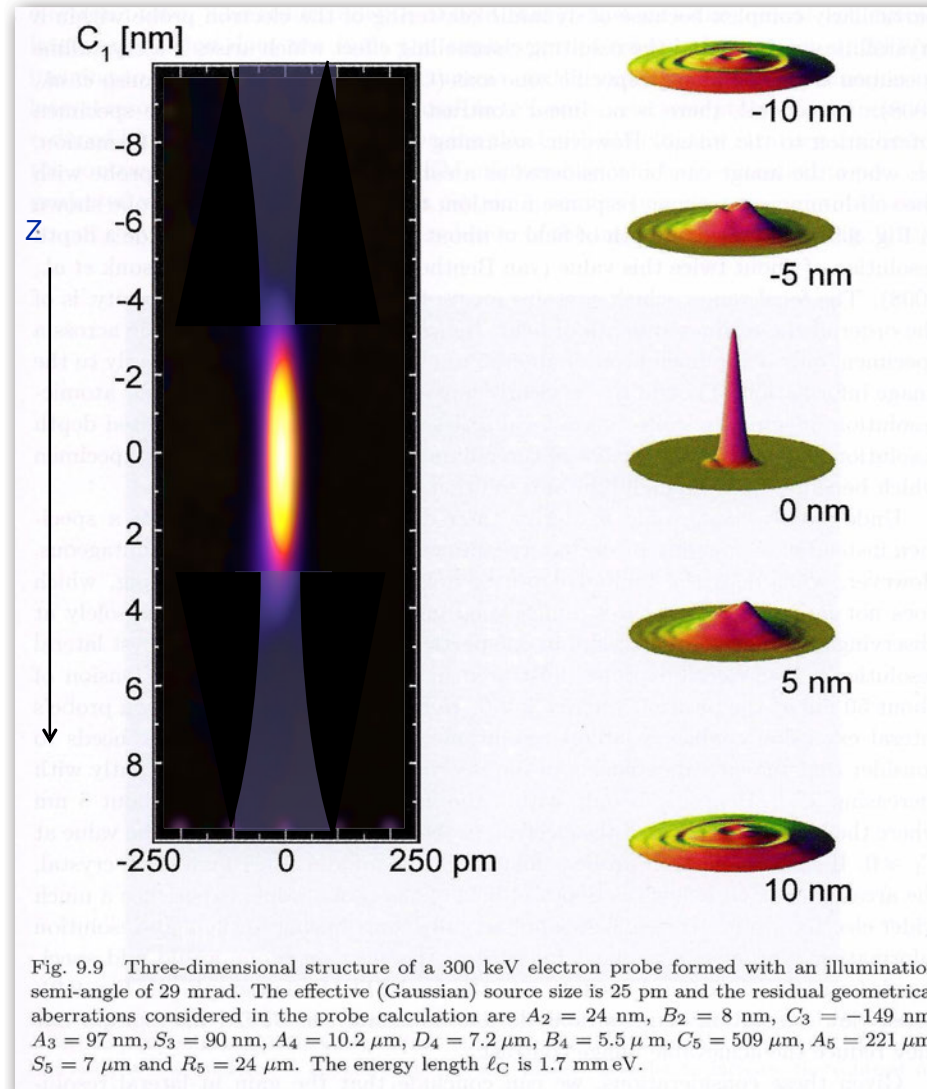
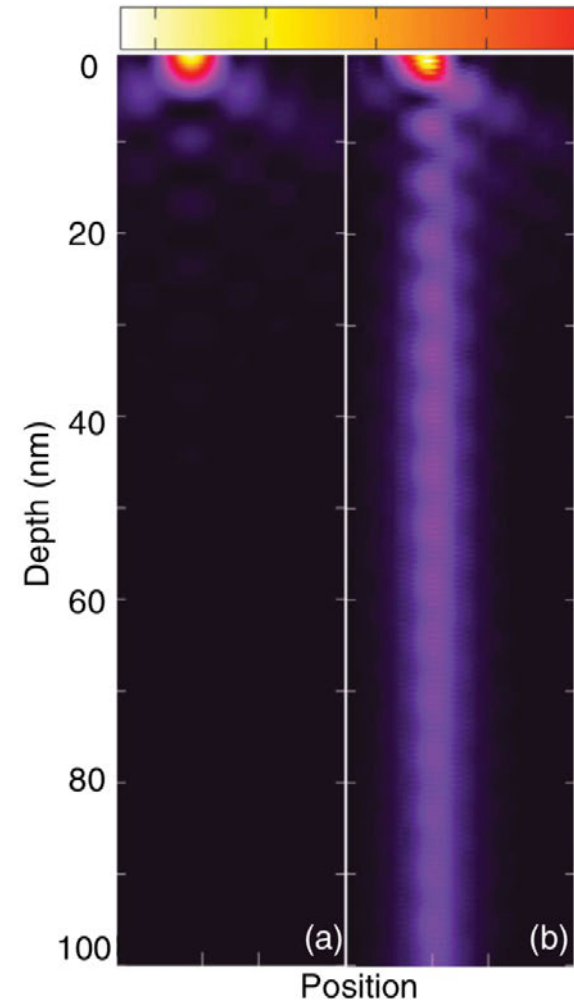


Figure from: R. Erni, Aberration-Corrected Imaging in Transmission Electron Microscopy

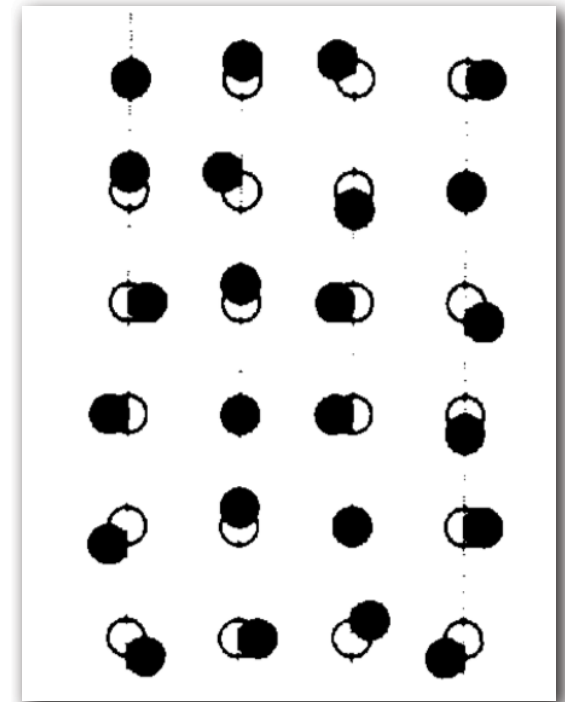
EPFL Electron channeling

- When a (sub-)Å convergent probe focused on the top surface of a well aligned and spaced atomic column, the electron density is channeled down the column by the atomic nuclei
- This is often associated with a Bloch wave known as the 1s Bloch state, by analogy to 1s orbital of an atom
- At first approximation, high angle annular dark-field (HAADF) and annular bright field (ABF) images are consequence of the scattering of this 1s-state to their respective detectors
- HAADF image: channeling couples with thermal diffuse scattering



EPFL “Thermal diffuse scattering”

- “*Thermal diffuse scattering*” (TDS) is name given to incoherent scattering caused by thermal vibrations in the crystal lattice – i.e. phonons
- The small, random displacements of atoms/atomic nuclei caused by these vibrations are considered to scatter the electron beam/wave function incoherently
- This incoherent scattering, coupled to coherent elastic scattering, is responsible for formation of Kikuchi lines
- Conceptualised into a “frozen phonon” which is often used as the basis for a simulation methodology



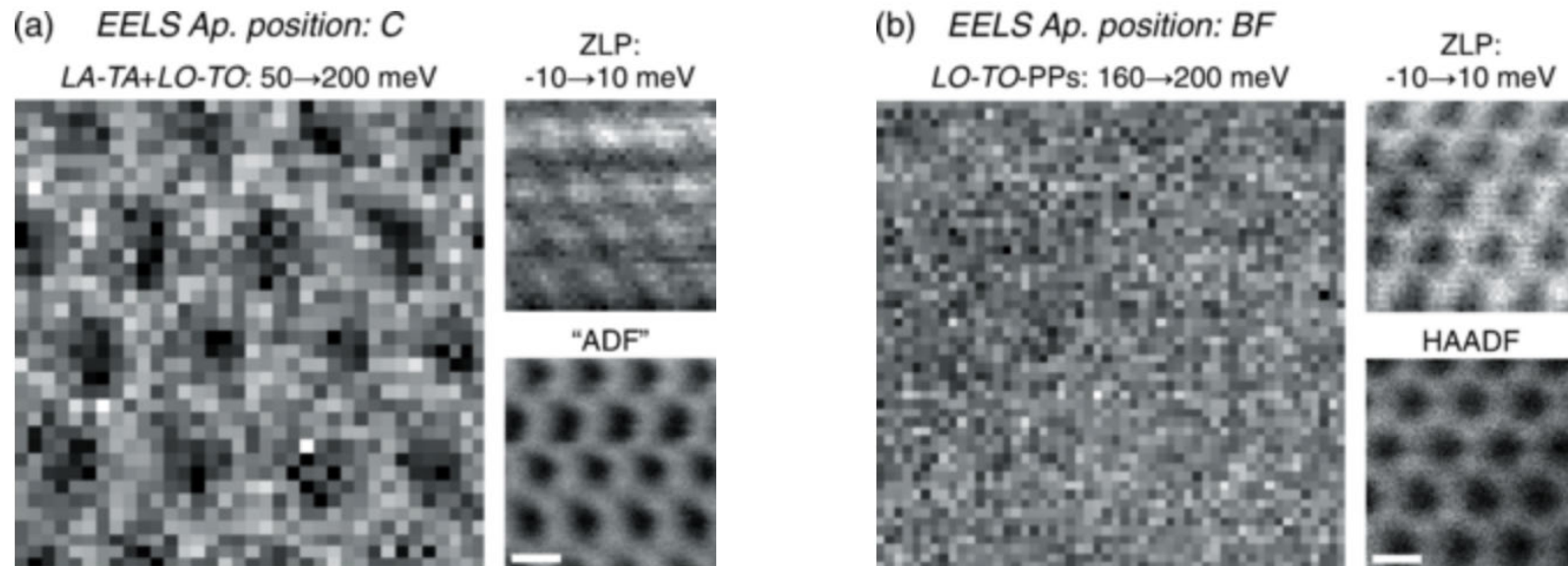
Loane and Silcox
*Acta Cryst. A***47** (1991) 267–278

EPFL Atomic resolution HAADF theory

- Phonon scattering is an *inelastic* process. Transmitted electron suffers an energy loss of $\sim 10\text{--}200$ meV. Scattering nature is incoherent.
- Scattering involves the exchange of a phonon; e.g. the scattered e^- excites a phonon mode of a certain energy in the crystal lattice, and loses a corresponding amount of energy.
- Unlike plasmon and ionisation excitations (see coming lectures by C.H.), this scattering has high probability of giving a large momentum change to the transmitted e^- , scattering it to high angles
- Excitation of atomic nuclei – therefore strong scattering of 1s-state Bloch wave of e^- density channeling down the nuclei.
- HAADF detector collects these phonon-scattered electrons, allowing formation of image of atomic columns from this incoherent signal

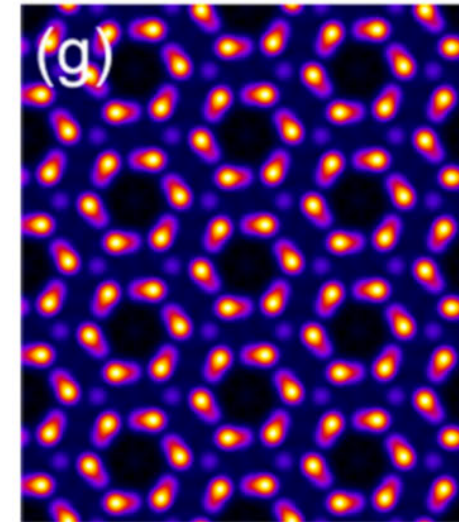
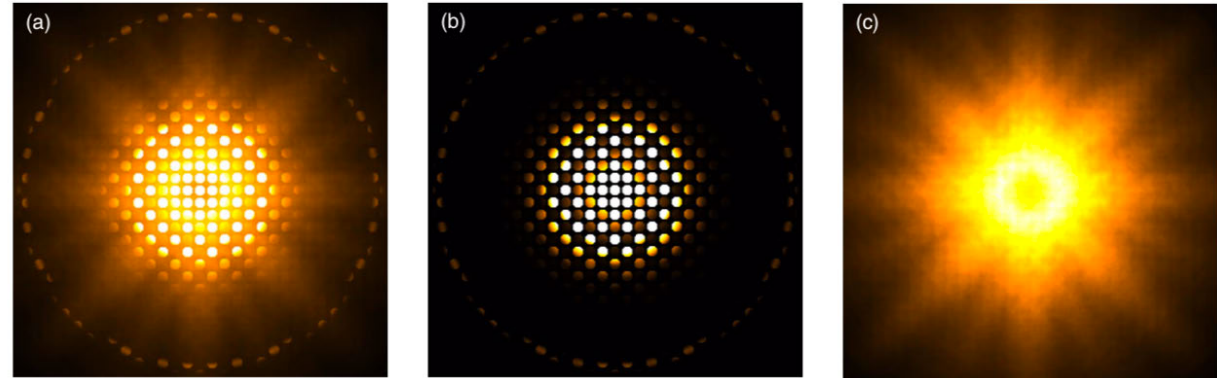
EPFL Atomic resolution HAADF theory

- Inelastic nature of TDS/phonon scattering was experimentally confirmed by Hage et al.
- Using ultra high energy resolution electron energy-loss spectroscopy show that only the high angle scattered electrons which have 50–200 meV give the spatial intensity distribution of a HAADF image



- This inelastic, quantum mechanical exchange is incorporated into a simulation code based on a many-body quantum-mechanical model for phonon scattering introduced by Forbes et al. with Les Allen.
- Allows separation of incoherent, phonon-scattered intensity from coherent, elastically-scattered intensity.

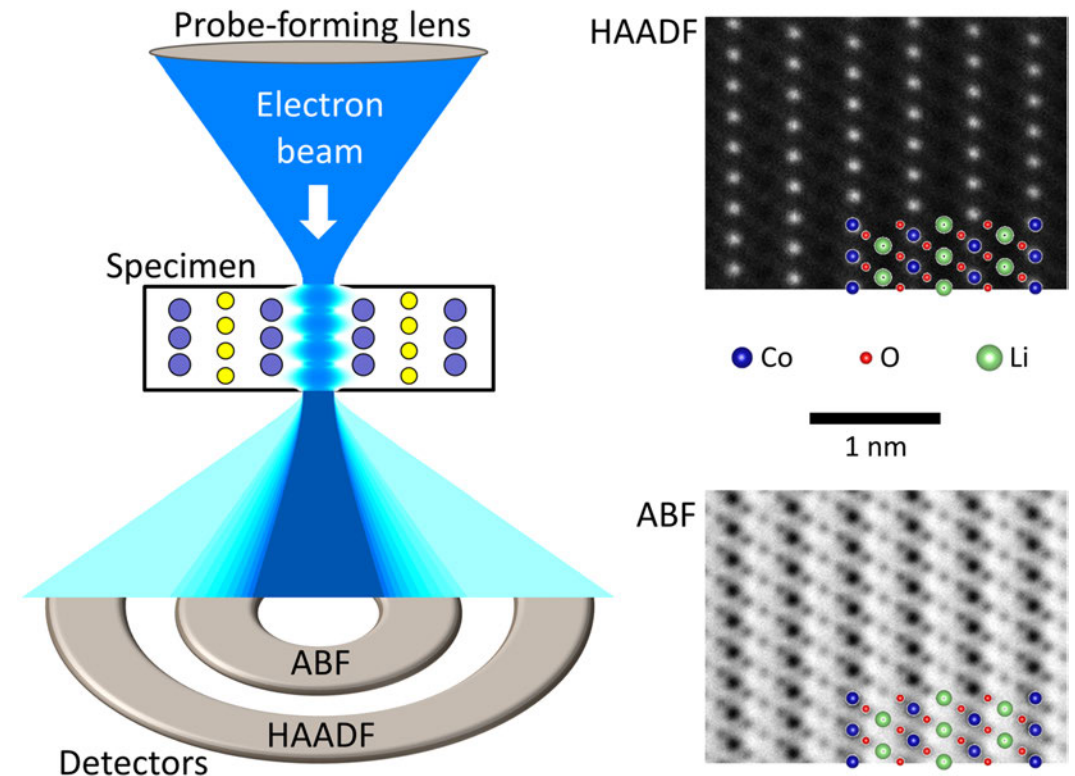
CBED simulation

HAADF STEM
simulation

Phase contrast STEM imaging for atomic resolution of light atoms

EPFL Annular bright-field (ABF)

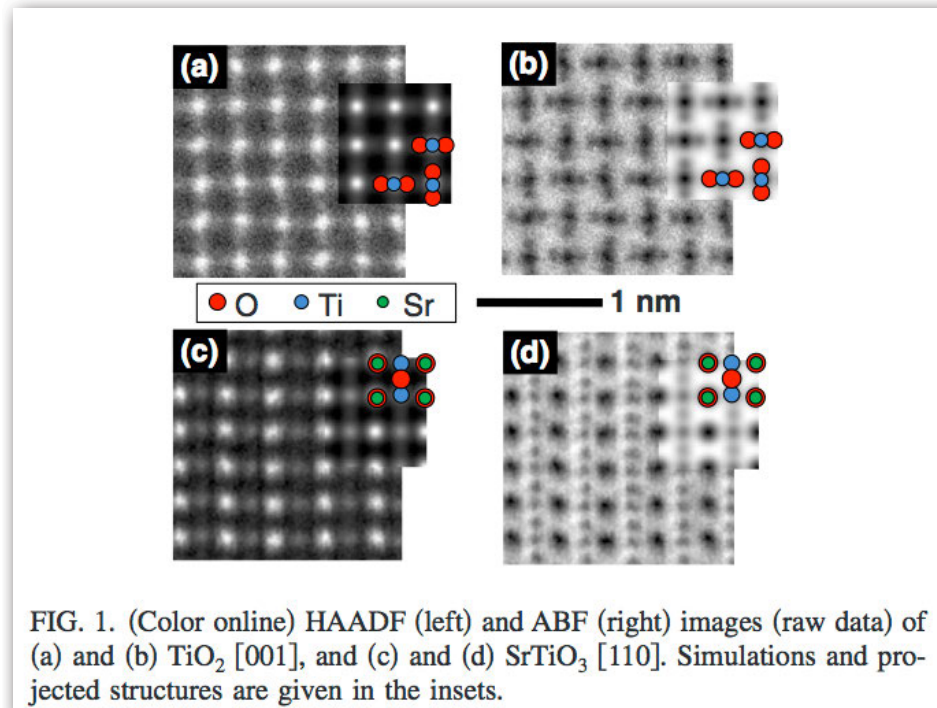
- HAADF not useful for imaging light atoms in a sample with heavy atoms because contrast so strongly dependent on atomic number
- BF imaging has same disadvantages for imaging light atom columns as phase-contrast HR-TEM imaging
- Annular bright-field imaging (with aberration correction), where central part of BF detector is obscured, arguably solves these problems.
- For instance, for $\alpha = 22$ mrad, use $\beta = 11$ – 22 mrad.



Li visualised in LiCoO₂ using ABF
Findlay et al. Microscopy **66** (2017) 3–14

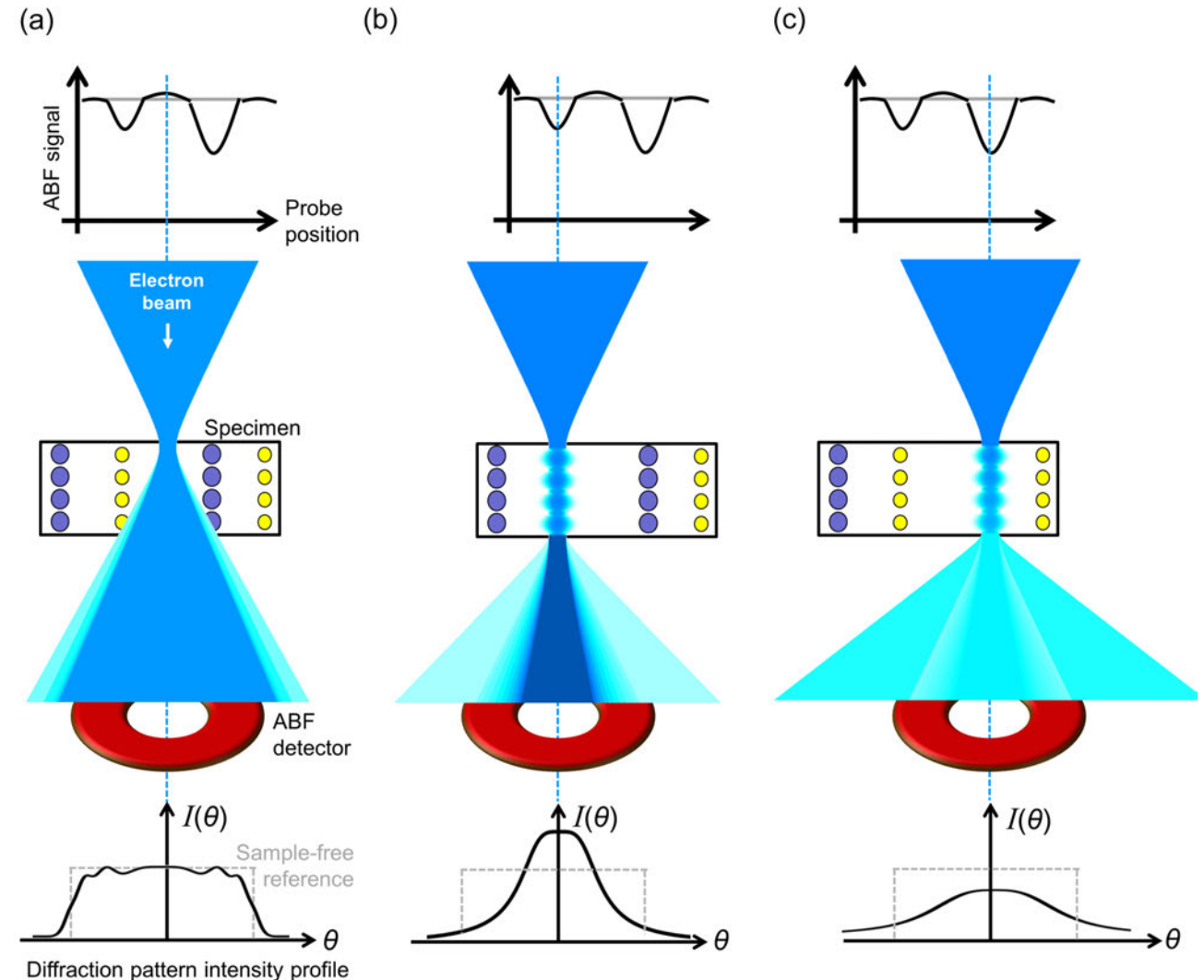
EPFL Annular bright-field (ABF)

- Simulations show the ABF detector produces an “absorption” image in which light and heavy columns are visible and interpretable over a wide thickness range. Even H columns have been imaged.
- Optimal focal range very small (like HAADF) but slightly different optimum defocus to HAADF.



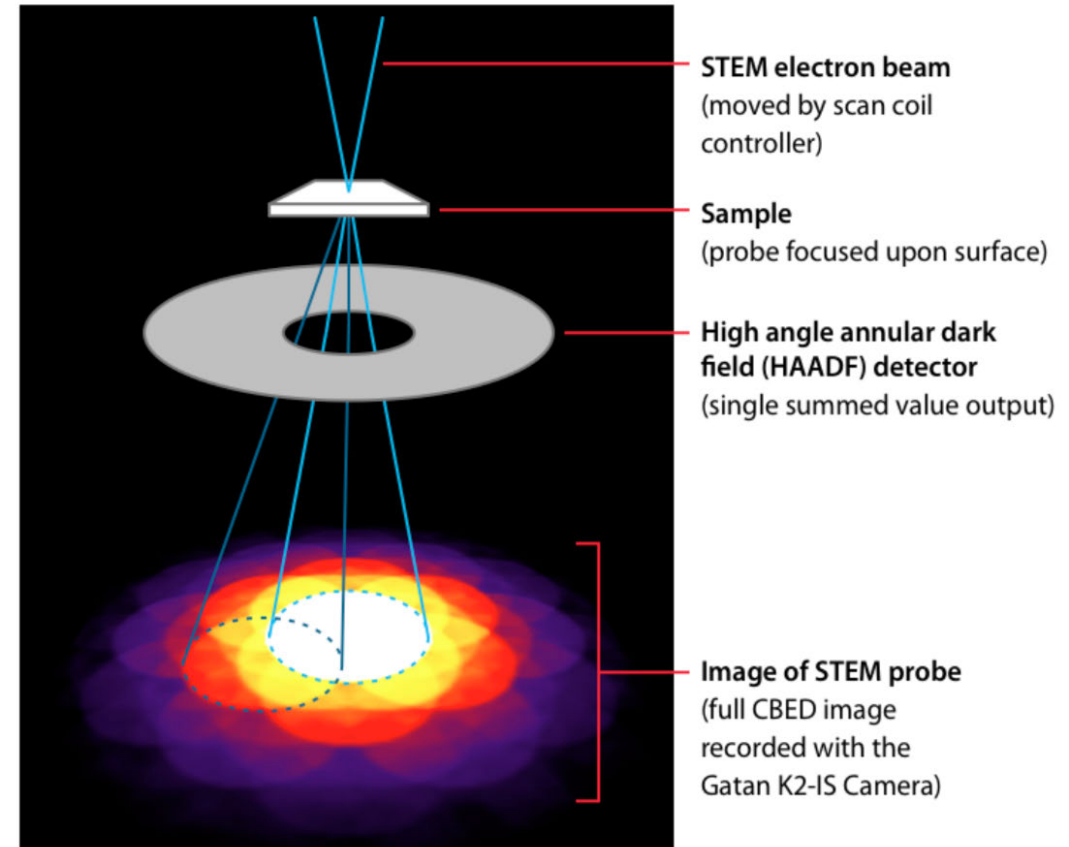
EPFL Annular bright-field (ABF)

- Simplified theory:
 - channelled e⁻ scattered mostly into centre of BF detector by light columns giving some dark ABF contrast (b)
 - e⁻ scattered more strongly to diffracted beams by heavy columns give darker ABF contrast (c)
 - between columns little scattering so brighter ABF contrast (a).



EPFL 4D-STEM

- 2D grid detector records whole STEM CBED pattern (see last week's STEM intro)
- Also known as “pixelated STEM”
- Currently very active area of EM research, with new applications being developed
- Very rich (and large!) data sets, see this for some applications:
<https://www.youtube.com/watch?v=-KpxeNDoB5I>



Schematic by Colin Ophus, Molecular Foundry

EPFL iCOM: integrated center of mass imaging

- Project STEM-CBED direct beam disc onto 4D-STEM detector
- As STEM probe moves, intensity distribution in disc varies
- In thin sample (i.e. weak phase approximation): displacement of center of mass (COM) of direct beam disc is proportional to gradient of phase shift of transmitted e^- wave $\rightarrow$

image intensity: $I^{(\text{COM})}(\vec{r}_p)$

- Taking integral of COM displacement vector gives phase shift and hence image intensity proportional to projected potential:

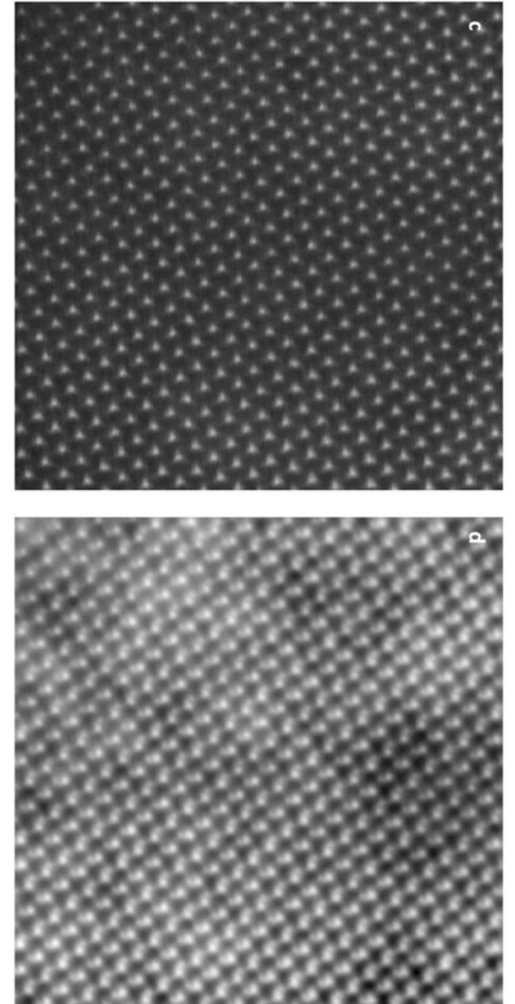
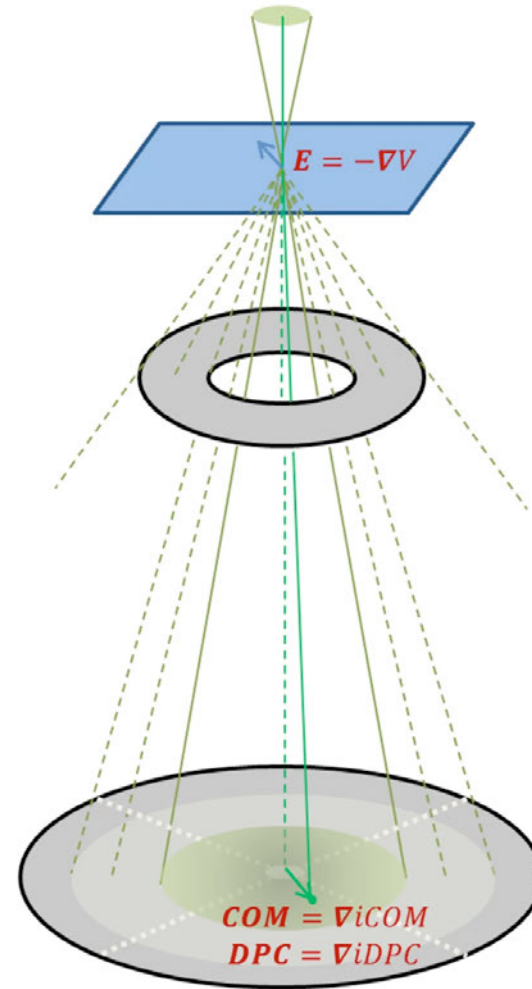
$$I^{(\text{iCOM})}(\vec{r}_p) \propto V_t(\vec{r})$$

- Therefore should obtain atomic image with intensity proportional to atomic number Z



EPFL iDPC: integrated differential phase contrast

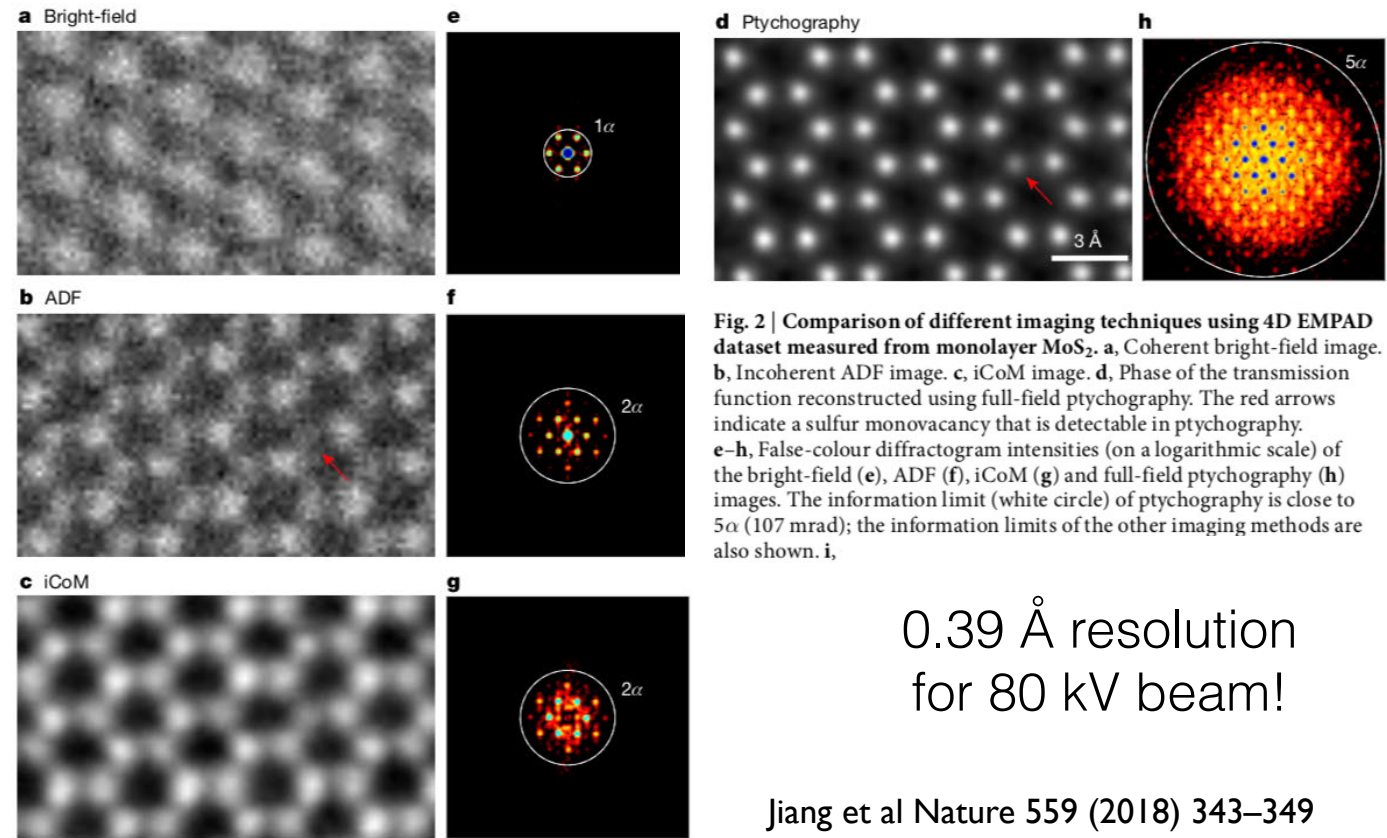
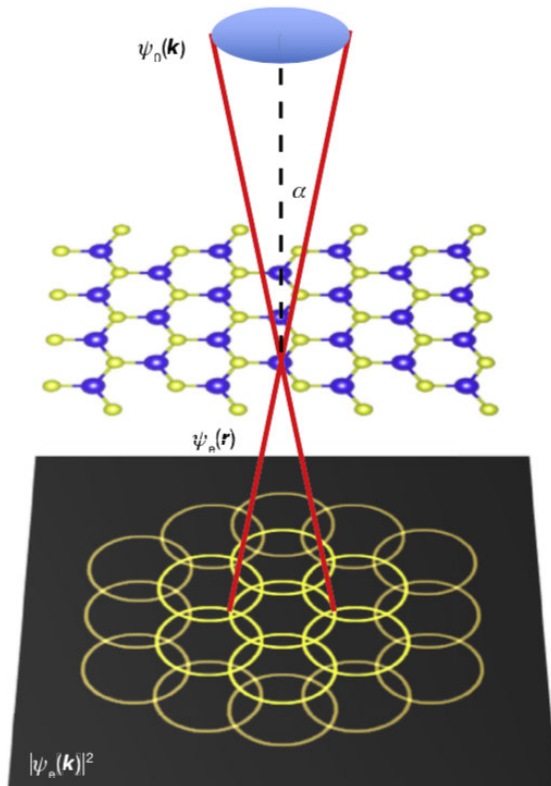
- Like iCOM but use a simpler and faster detector
- Project direct beam disc on 4 quadrant segmented detector, calculate iDPC
- DPC: differential phase contrast: image intensity of one quadrant minus opposite quadrant
- Still can work well for imaging light and heavy atoms when sample is much thicker than weak phase object



EPFL Electron ptychography (single slice)

- *Ptychography*: uses 4D STEM data to retrieve phase differences from interference patterns of overlapped diffracted beams
⇒ Go beyond diffraction limit for “super resolution”!

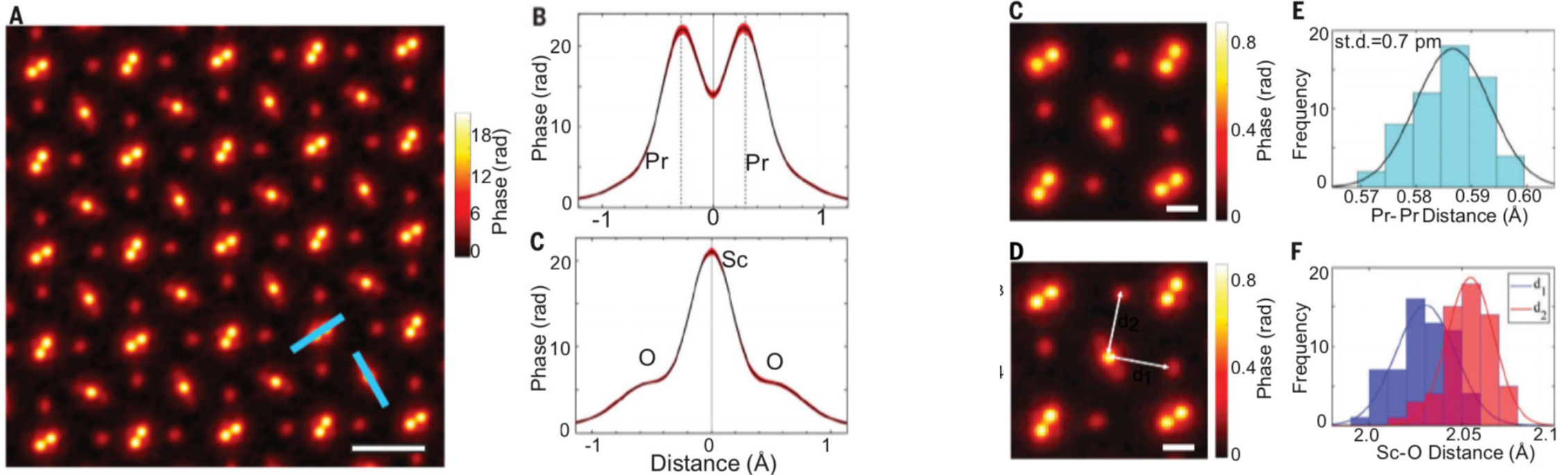
Imaging monolayer MoS₂



0.39 Å resolution
for 80 kV beam!

EPFL Electron ptychography (multislice)

- “Inverse” multislice ptychographic reconstruction for “thick” samples (15–30 nm)
- PrScO_3 on [001] with 59 pm spaced Pr dumbbells:



- “The measured widths of atomic columns are limited by thermal fluctuations of the atoms” – instrumental blurring of < 20 pm!