Aberrations corrected (S)TEM, the end of HR(S)TEM image simulation?

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May 28, 2015

Introduction

At a time where axial aberrations of TEM or STEM are commonly corrected to order 4 or higher and image resolution close to 0.05 nm is it still necessary to calculate images in order to interpret the contrast of experimental images?

- HRTEM experimental images show contrast features that should ideally be correlated with the crystal projected potential.
- HRSTEM experimental images being acquired by mean of more specific signals are de facto simpler to interpret quantitatively.

The question is important since knowing the metric of the unit cell, the atoms position and atomic number, is in principle nowadays sufficient to calculate most of the properties of the solid (these "first-principles" calculations allow one to predict, rather than to model the solid[1]).

Moreover, computer codes being able to "discover" novel nano-materials with unrivalled properties, it seems important to be able to compare their structure with observations.

[1] Abinit, Medea, Quantum-Espresso, Wien2k, ...

It is shown that to avoid performing image simulation, several conditions must be realized in particular:

- Crystal thickness must be of the order of a few nanometers (to minimize dynamical scattering).
- Crystal misalignement should of the order of 1 mrad or less (to avoid phase shift).
- Aberrations correction should be stable during time periods of several minutes or larger.
- Beam damage should be minimized (crystal structure is perfect).
- ...

In practice, it is extremely difficult or impossible to satisfy all those conditions at the same time. As result, images are not perfect and the model - micrograph quantitative match is never perfect.

Important questions to achieve quantitative model - experiment match :

- Why should we still perform image simulation?
- How to perform image simulation?
- What can we learn from image simulation?

What effects must be included in the calculation $\rightarrow$ how long are you willing to wait for a calculation to terminate?

Why image simulation?

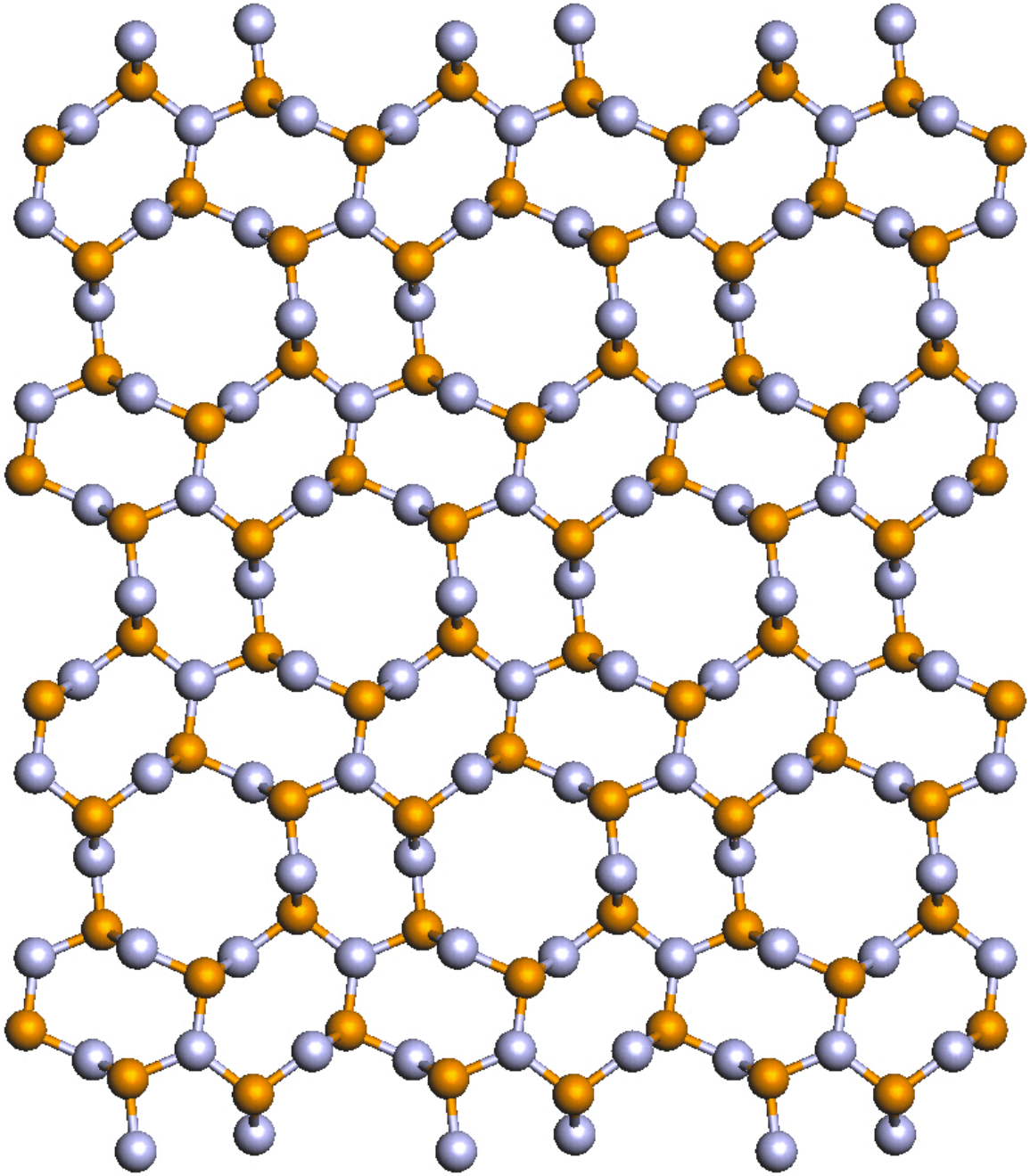
HR(S)TEM $\Longrightarrow$ to acquire knowledge on observed material (oriented in particular [uvw] directions):

- Specimen structure..
- Chemical composition.
- Functional properties.
- ...

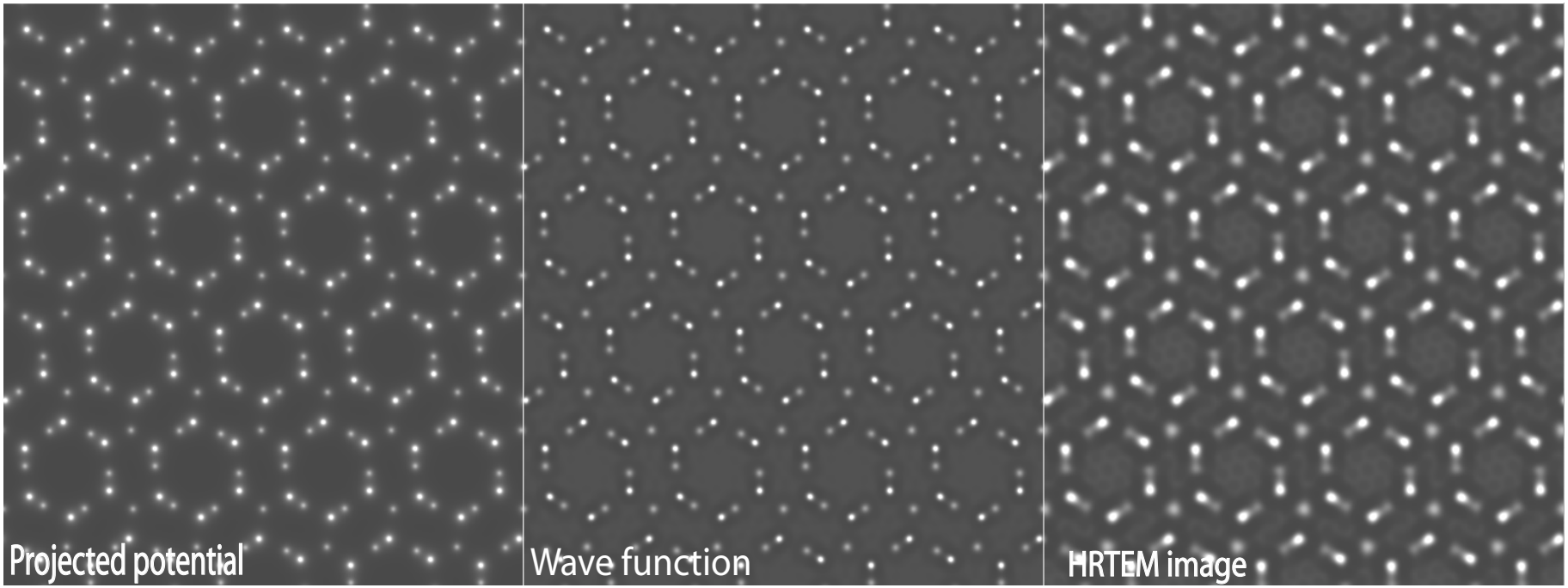
But HR(S)TEM images depend of several adjustable microscope parameters. Two examples:

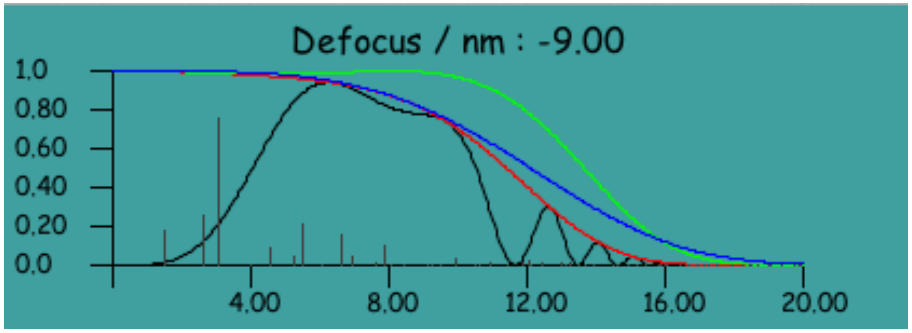
- object defocus affects strongly HRTEM images.
- AlN [111] (PICO Jülich, crystal thickness).

Example Si_3N_4 P 63: [001]



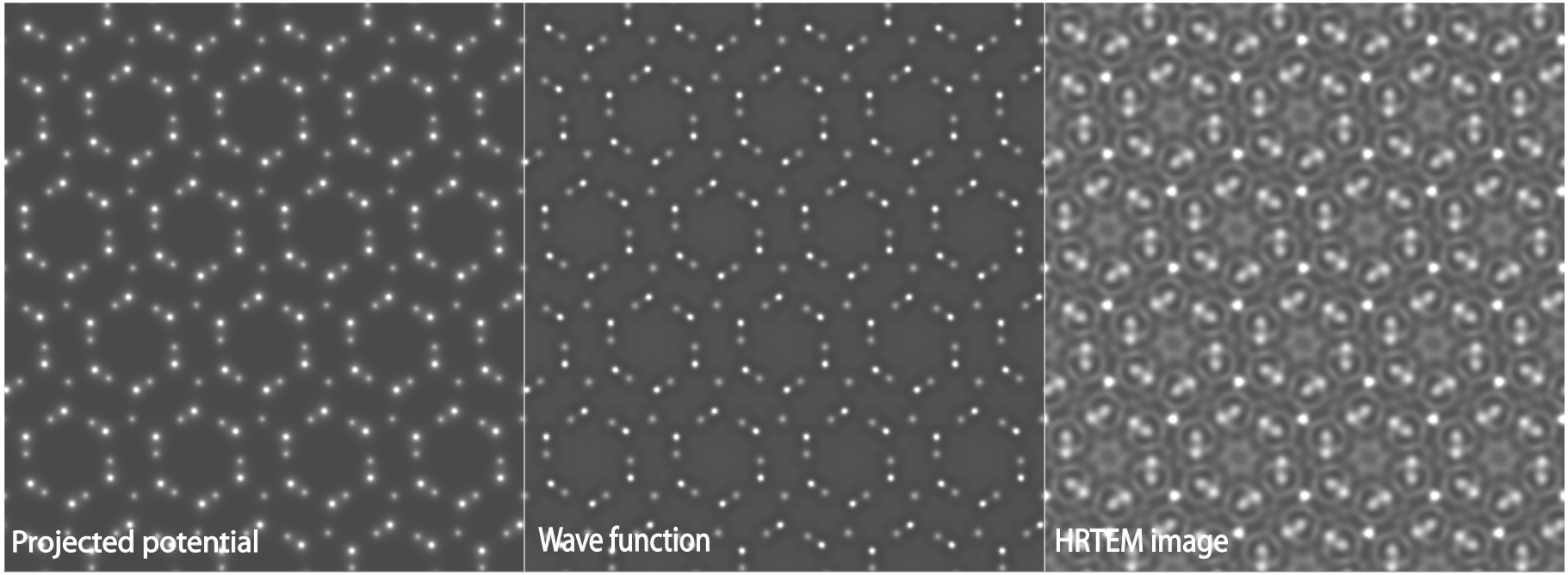
Si_3N_4 P 63: [001], 10 nm thick, -9 nm defocus

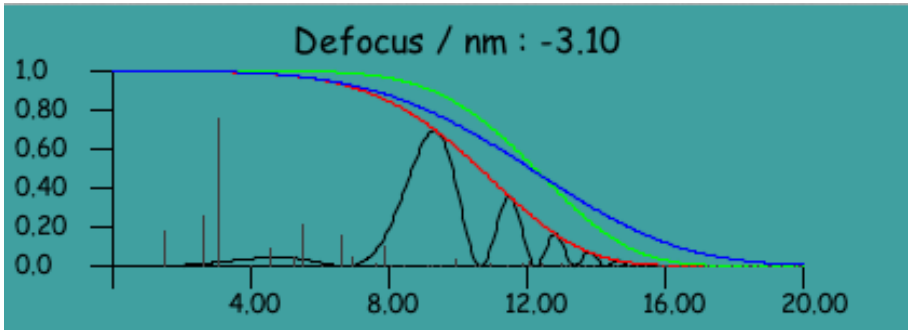




Imaging parameters: Titan 80-300 (300 kV), C_s -0.033 mm

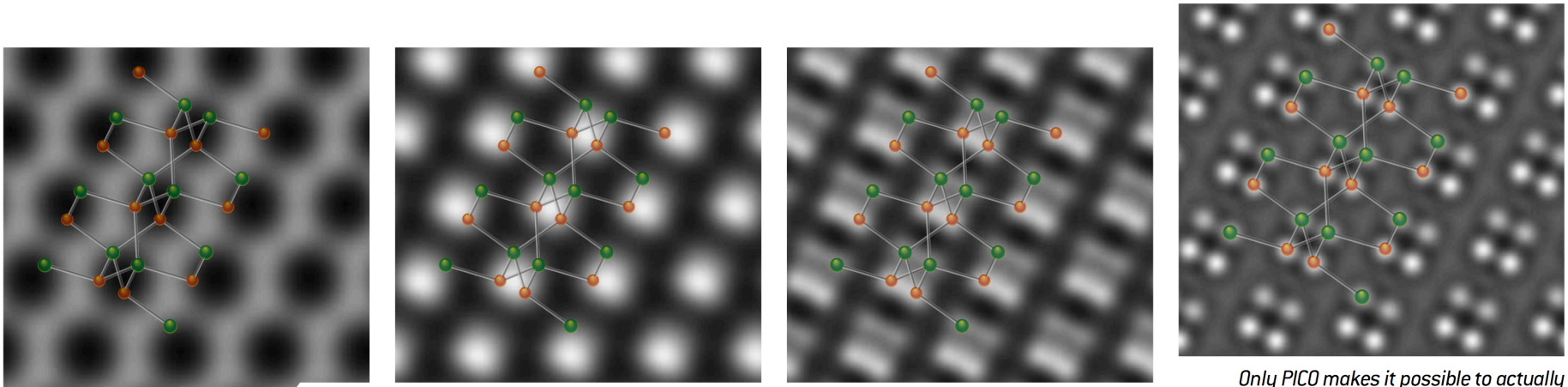
Si_3N_4 P 63: [001], 10 nm thick, -3 nm defocus





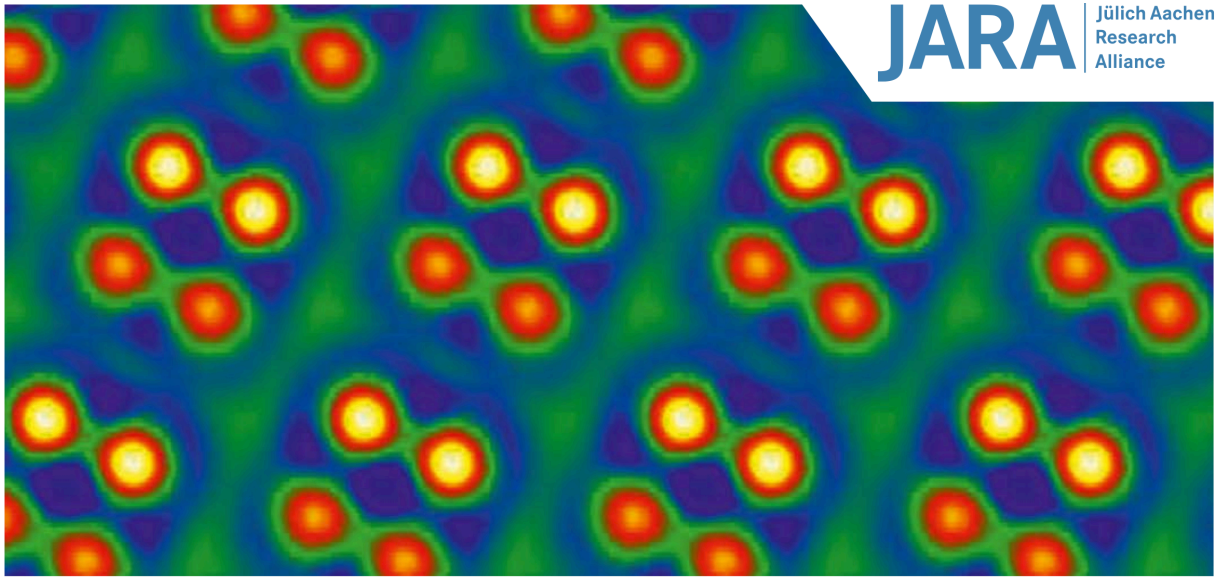
Imaging parameters: Titan 80-300 (300 kV), C_s -0.033 mm

From ER-C booklet[2].



These simulated images of aluminium nitride illustrate how much resolution has improved with each generation of electron microscopes from 1992, 1998 and 2005 up to the present day (from left to right).

Only PICO makes it possible to actually recognize the atoms in this material. The atoms are shown as green and red spheres as an aid to recognition.



[2] http://www.er-c.org/news/publications/er-c-booklet-english.pdf

HRTEM simulation (jems V4).

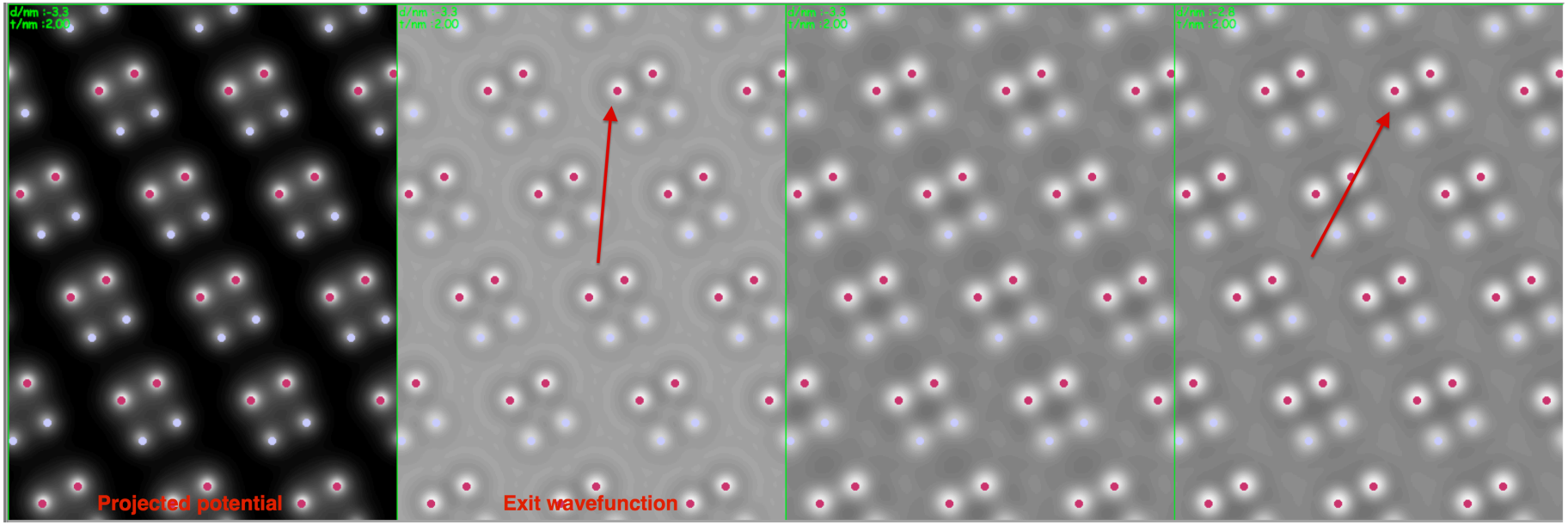


Figure: Note that electron channeling and depletion are observed in the images.

Question: do we have to take into account inelastic scattering when the crystal thickness of the order of 3-6 nm?

AlN [111], thickness series

HRTEM simulation (jems V4).

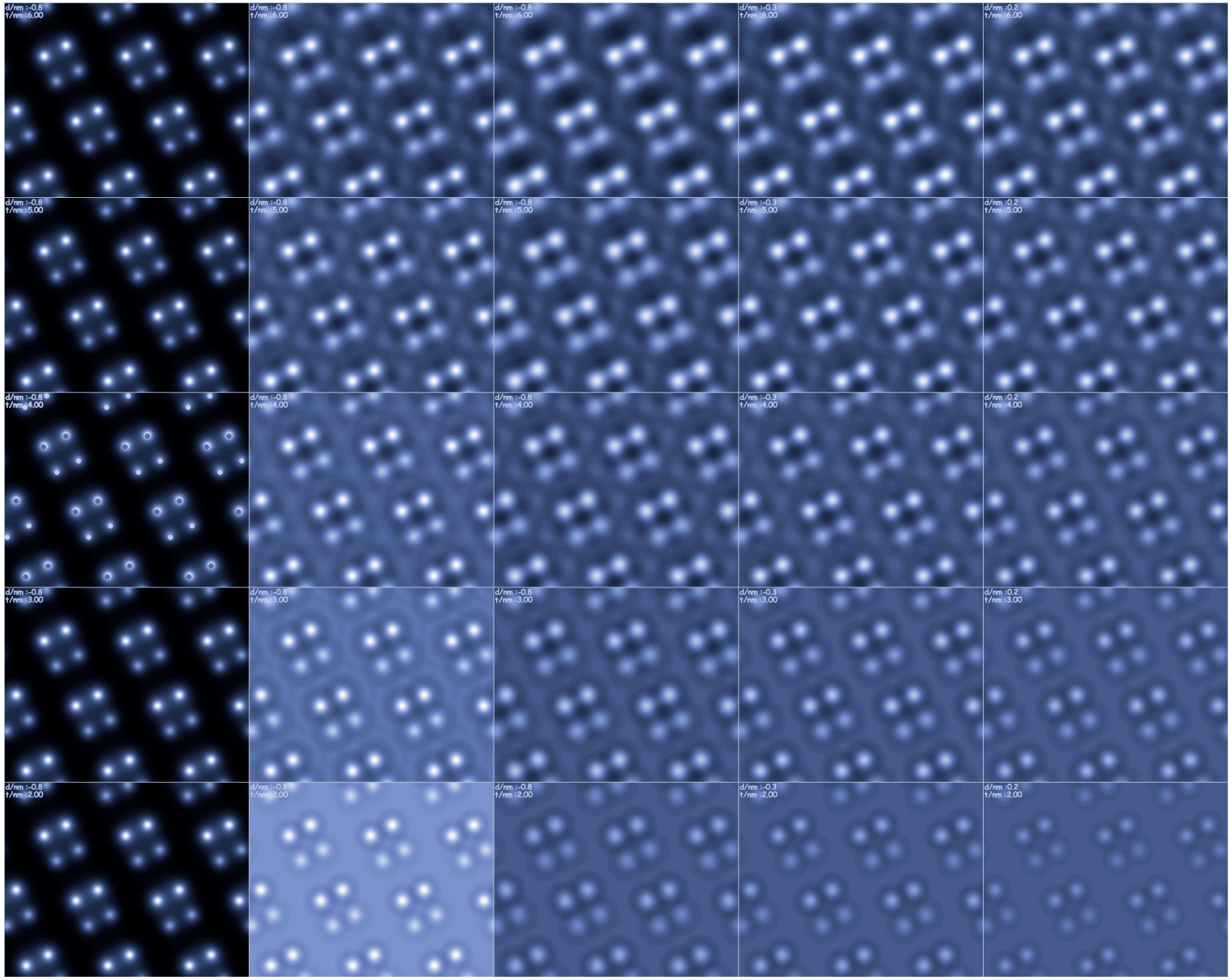


Image simulation can be used to assess crystal thickness (within +- 1 nm).

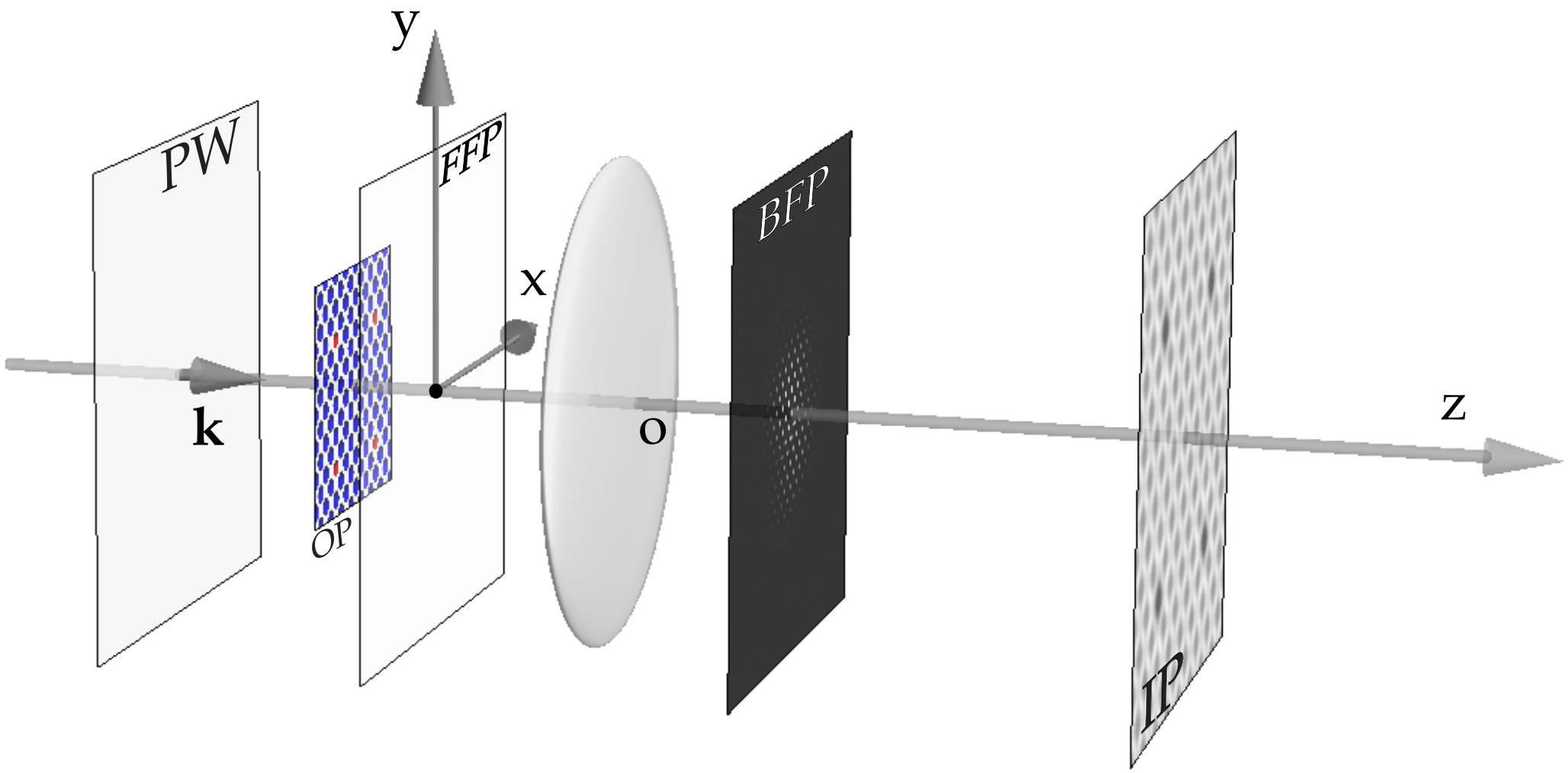
How to perform image simulation?

Formation of (Scanning) Transmission Electron Microscopy images involves complex physical processes. These processes are too complex to be fully taken into account.

$\rightarrow$ Approximations and models of these physical processes

are required in order to perform computer simulations.

TEM (very) simplified model



Modeling steps: Incident wave (PW), crystal (OP), electron-matter interaction, Fraunhofer approximation, image formation (Abbe theory), ...

Image formation modeling (HRTEM)

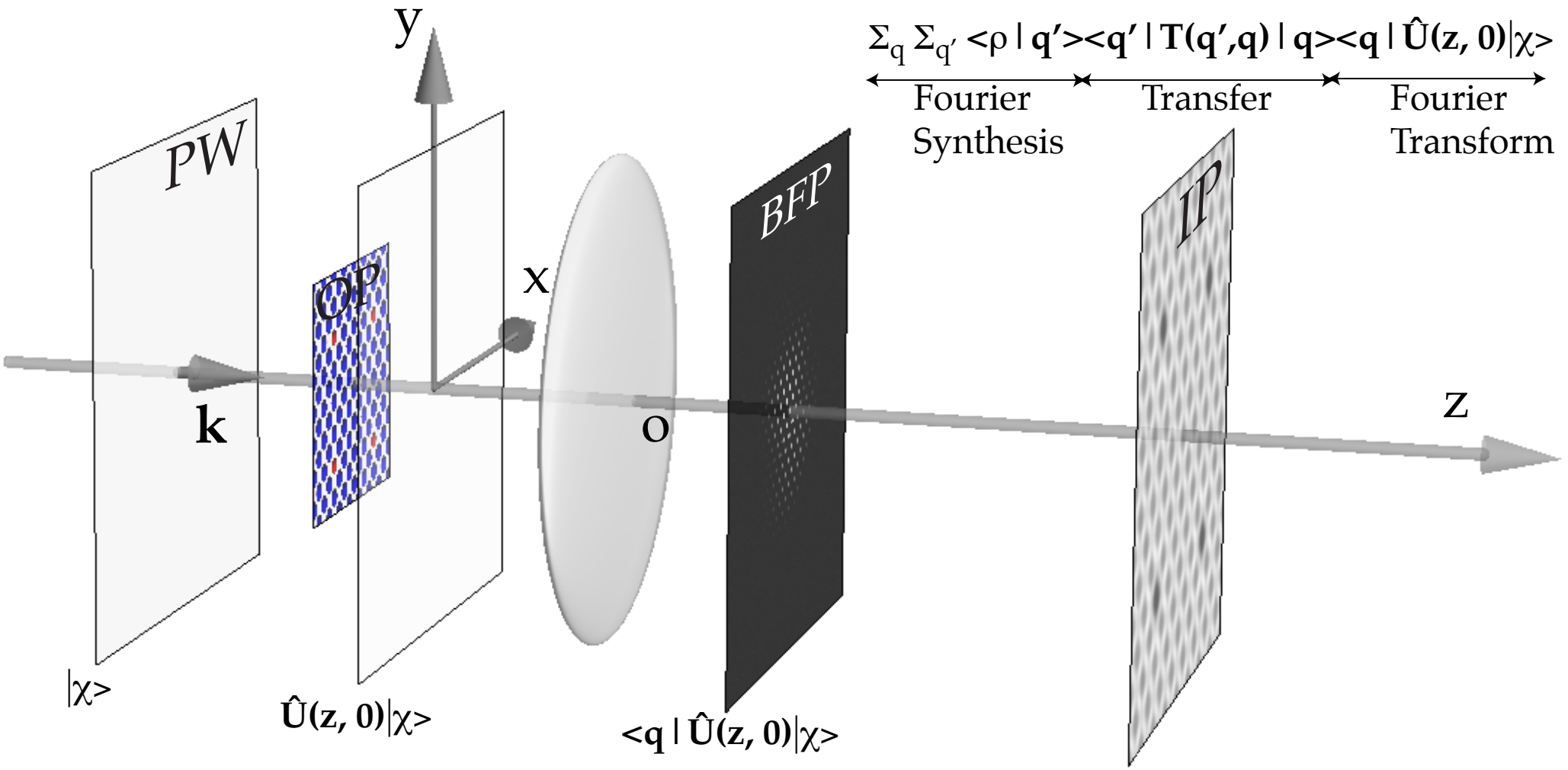


Image wave function: $|\Psi_i>$

$$|\chi> \implies \text{incident wave function}$$

$$|\Psi_i> = \underbrace{\sum^{q'} <\rho|q'>}_{\text{Fourier synthesis}} \underbrace{\sum^{q} <q'|T(q',q)|q>}_{\text{Objective lens transfer}} \underbrace{<q|U(z,0)|\chi>}_{\text{Fourier transform}}$$

Modeling steps

- Object.
- Scattering & diffraction.
- Image formation:
  - HRTEM.
  - HRSTEM.

Modeling the object

Evolution operator U (z, 0) defines object properties

1. Amorphous material or crystalline material.
2. Thin or thick.
3. Orientation (high or low symmetry [uvw]).

You might have to transform the unit cell in order to perform dynamical calculations[3].

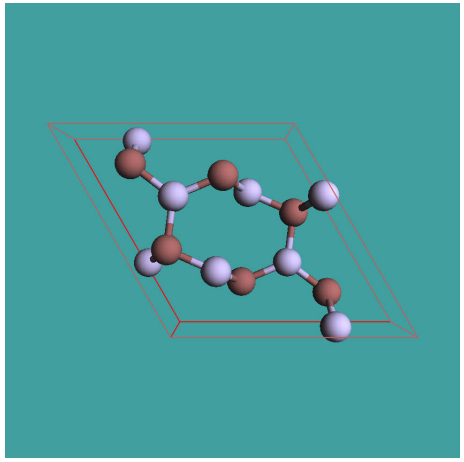


Figure: Si_3N_4 hexagonal lattice.

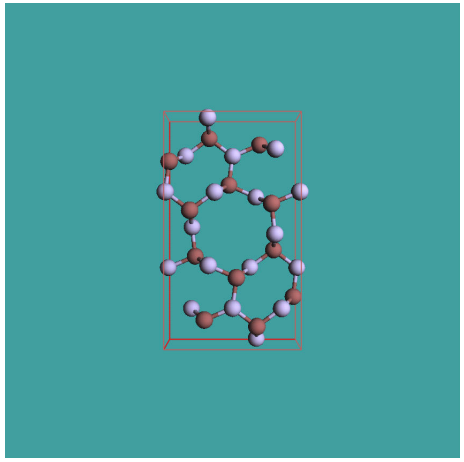


Figure: Si_3N_4 orthorhombic lattice.

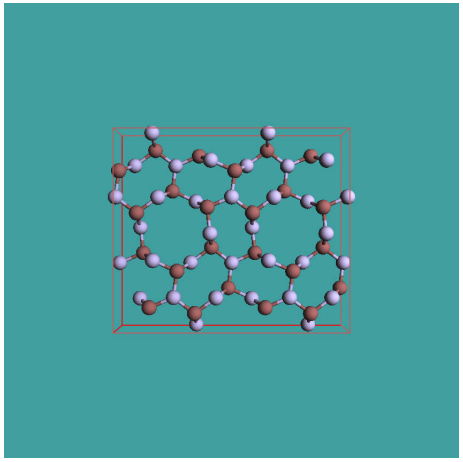


Figure: Si_3N_4 orthorhombic lattice x 2.

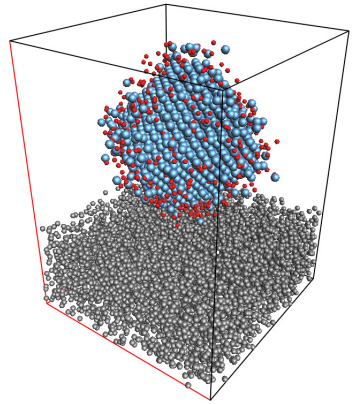


Figure: Pt catalyst on amorphous carbone film (9600 atoms).

Any model is considered a periodic unit cell independent of its complexity.

[3] See International Tables for Crystallography (1992) Vol. 1, Chapter 5.

Atomic form factors

Atomic form factors have been tabulated by many authors:

1. Doyle-Turner and Smith-Burge.
2. E.J. Kirkland.
3. Peng-Ren-Dudarev-Whelan.
4. ...

Take care ASA of heavy atoms aren't always tabulated properly.

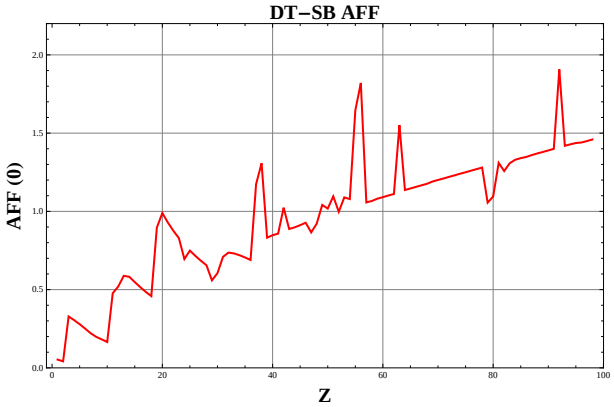


Figure: Doyle-Turner or Smith-Burger.

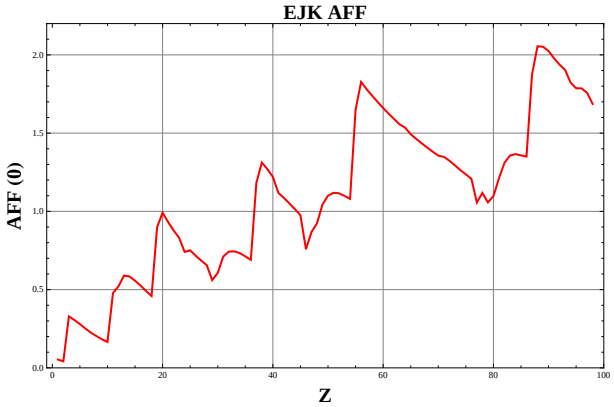


Figure: E. J. Kirkland.

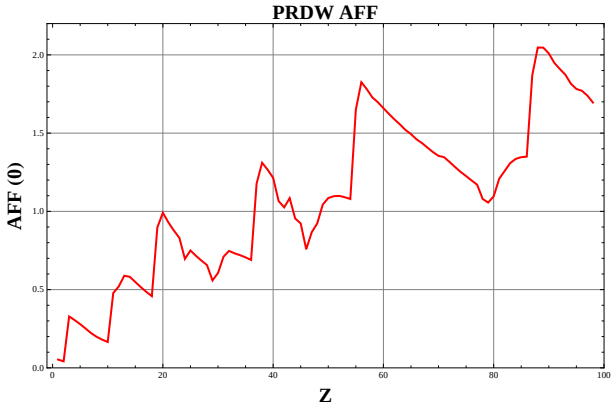


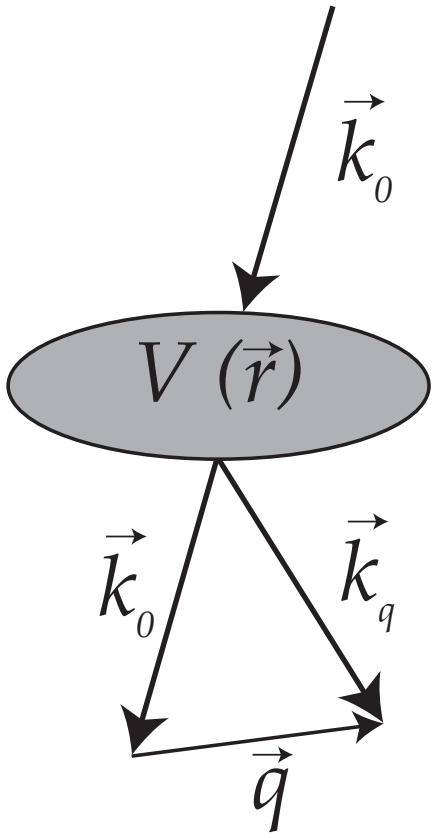
Figure: Peng-Ren-Dudarev-Whelan.

A extremely useful ASA tabulation including phonon and core loss absorption is due to Weickenmeier-Kohl[4].

[4] A. Weickenmeier, H. Kohl, Acta Cryst. A 47 (1991) 590.

Scattering & diffraction

Scattering: electron-matter interaction



An incident electron of wave vector $\vec{k}_0$ interacts with a solid of scalar potential $V(\vec{r})$. The wave vector of the scattered electron is $\vec{k}_q = \vec{k}_0 + \vec{q}$ where $\vec{q}$ is the momentum transfered by the solid[5].

$$\text{Elastic scattering} \longrightarrow ||\vec{k}_q|| = ||\vec{k}_0||.$$

[5] Magnetic and spin effects are ignored.

Diffraction: $< q|U(z,0)|\chi >$

$< q|U(z,0)|\chi > \implies$ Fourier transform of object wavefunction

Dynamical scattering (many approaches under small angle approximation and elastic scattering).

When V independent of z, $\widehat{H} = \frac{1}{2k_0}\left[-\Delta_{x,y} + V(x,y)\right]$

$$\widehat{U}(z,0) = e^{-i\widehat{H}z} = \sum_j e^{-i\gamma_j z}|j><j|$$

Gratias & Portier: small angle & elastic scattering approximations

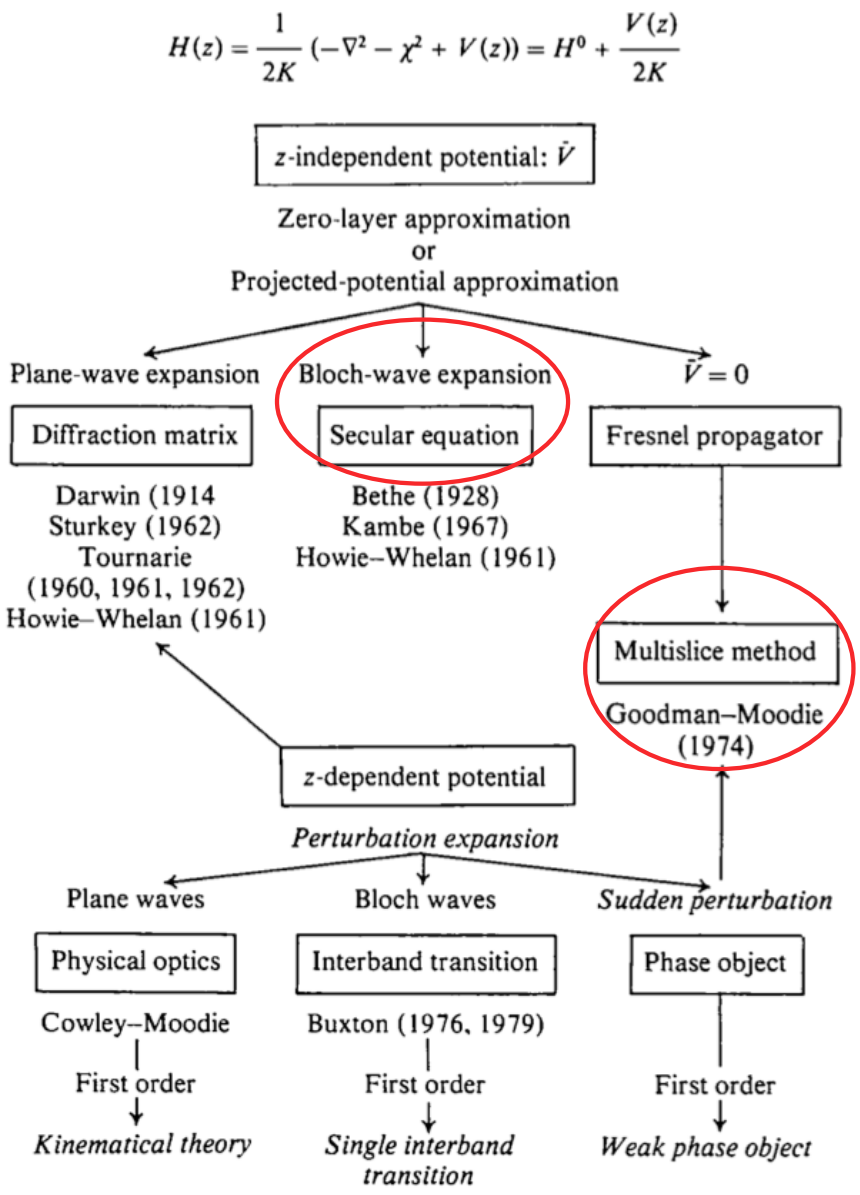
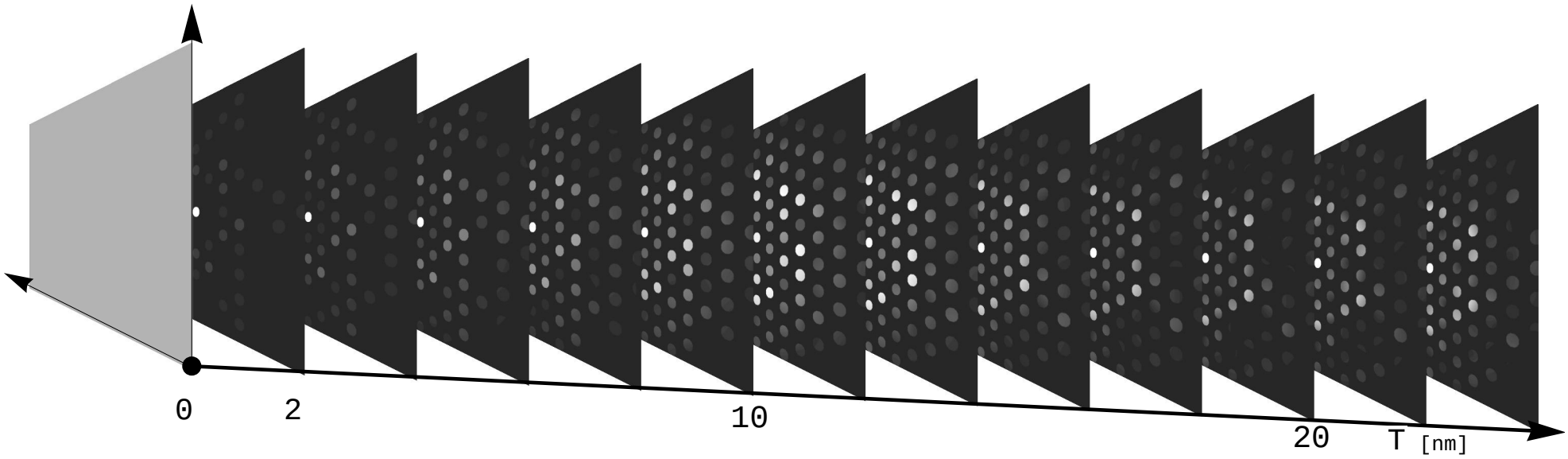


Figure: From Gratias and Portier [6]

[6] D. Gratias and R. Portier, Acta Cryst. **A39** (1983) 576.

Diffraction pattern & specimen thickness



In BFP diffraction pattern depends specimen thickness.

Goodness of dynamical diffraction theories?

Example: LACBED - Si [001]

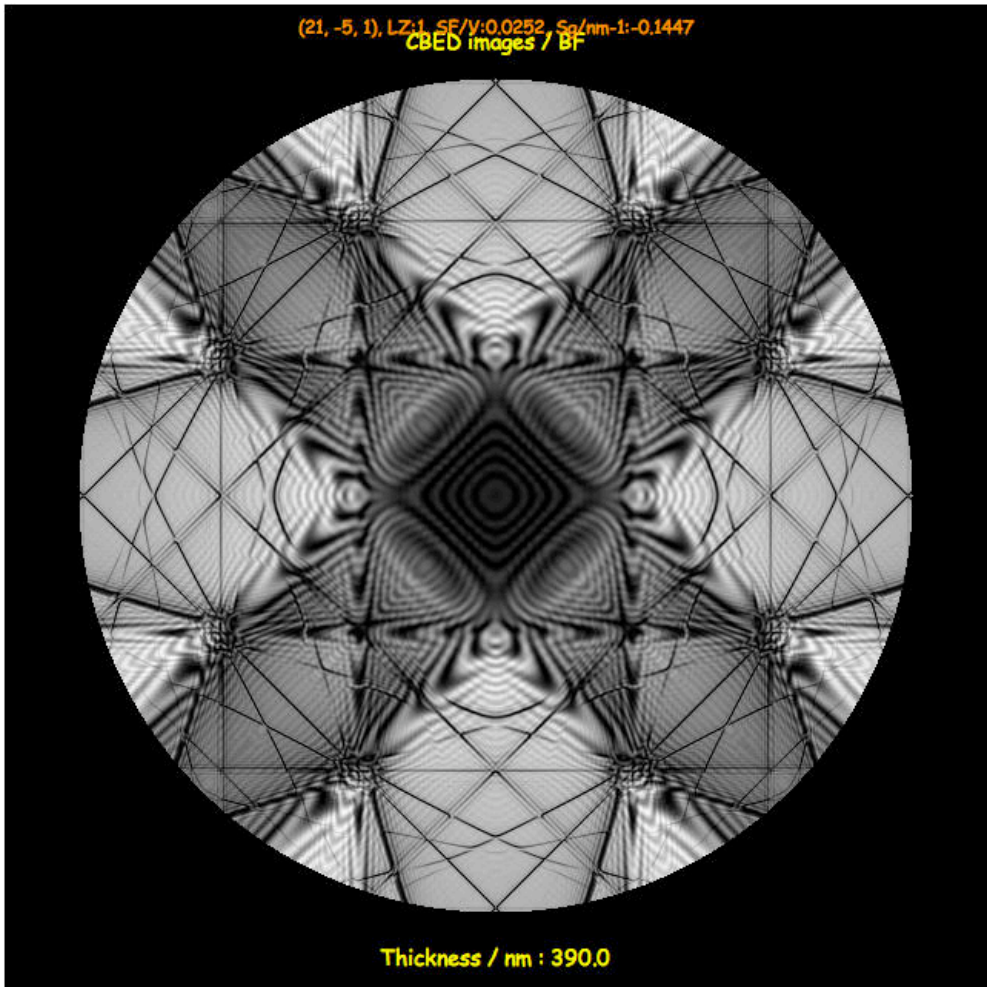


Figure: LACBED Si [001]: simulation.

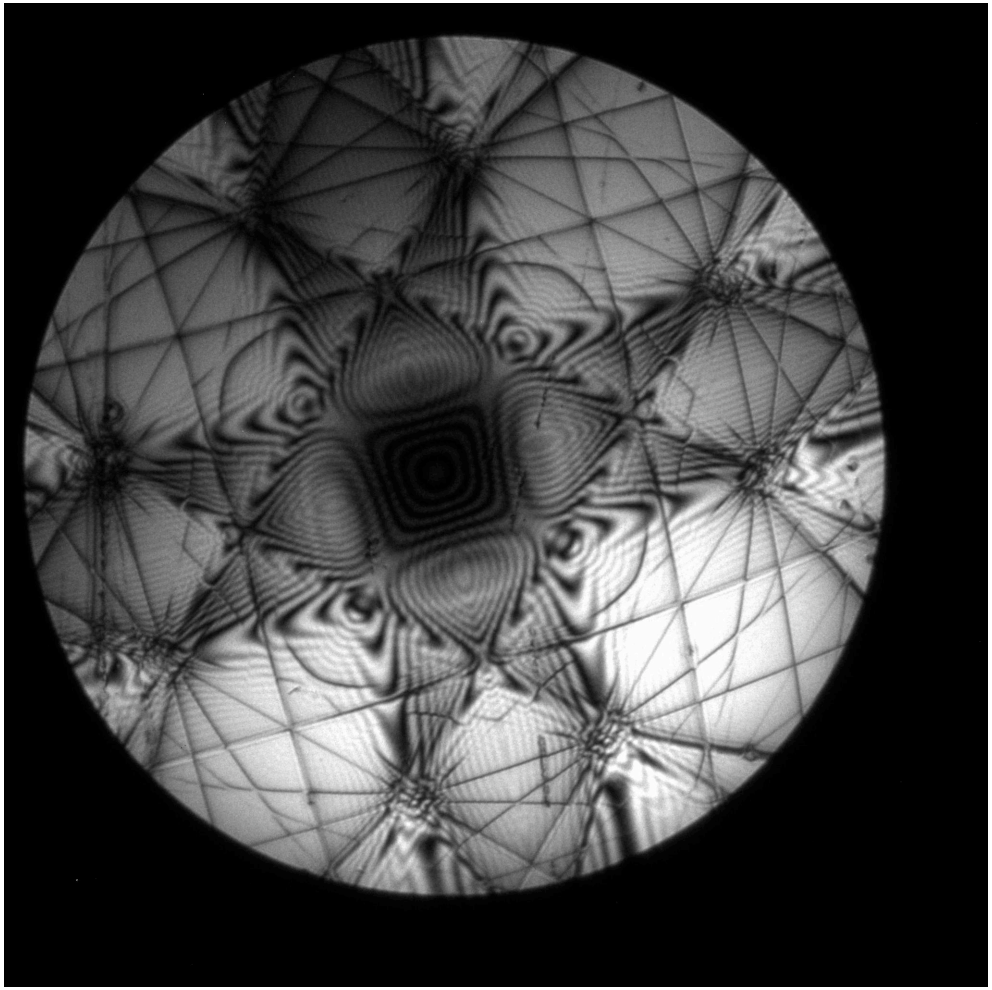


Figure: LACBED Si [001]: experimental (Web site EM centre - Monash university, J. Etheridge).

Note that the experimental LACBED pattern is blurred (inelastic scattering and/or MTF of CCD camera?).

Image formation

Transfer by objective lens: $< q' | T(q', q) | q >$

Image forming system has 2 properties (Abbe theory):

- Linear.
- Space invariant.

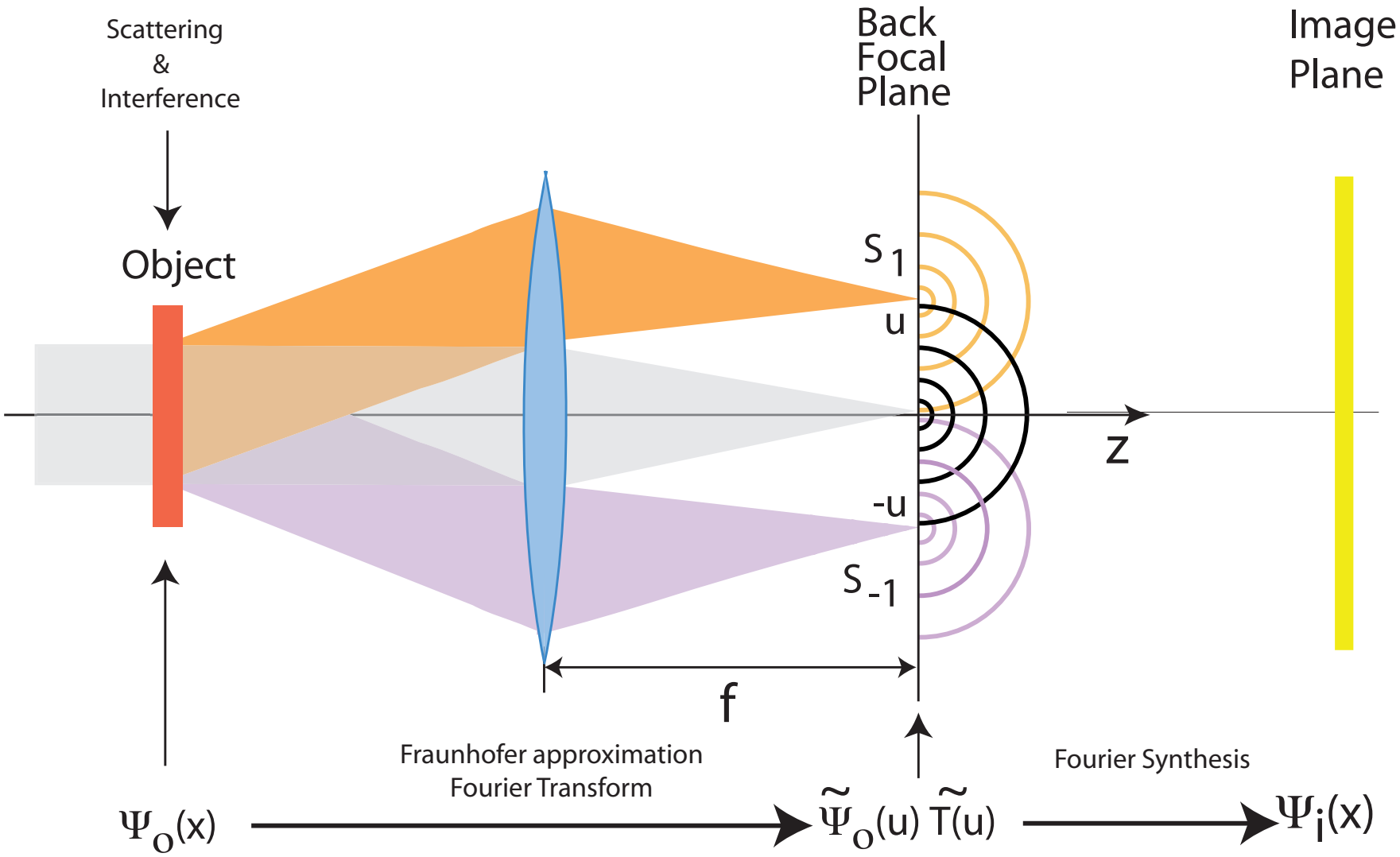
Coherence of illumination:

- Source size (spatial coherence).
- Energy spread (temporal coherence).

HRTEM: T (q', q) : transmission cross-coefficients $\Longrightarrow$ approximation by envelope functions is usually sufficient.

Microscope modeling: Abbe image formation theory

Objective lens is modeled as a thin lens that brings Fraunhofer diffraction pattern at finite distance (i.e. in its Back Focal Plane).



HRTEM image intensity: WPOA

In the Weak Phase Object Approximation under optimum transfer conditions the image intensity $I(\vec{x})$ is:

- positive C_s (black atomic columns)

$$I(\vec{x}) \sim 1 - 2\sigma V_p(\vec{x})$$

- negative C_s (white atomic columns)

$$I(\vec{x}) \sim \sigma V_p(\vec{x})$$

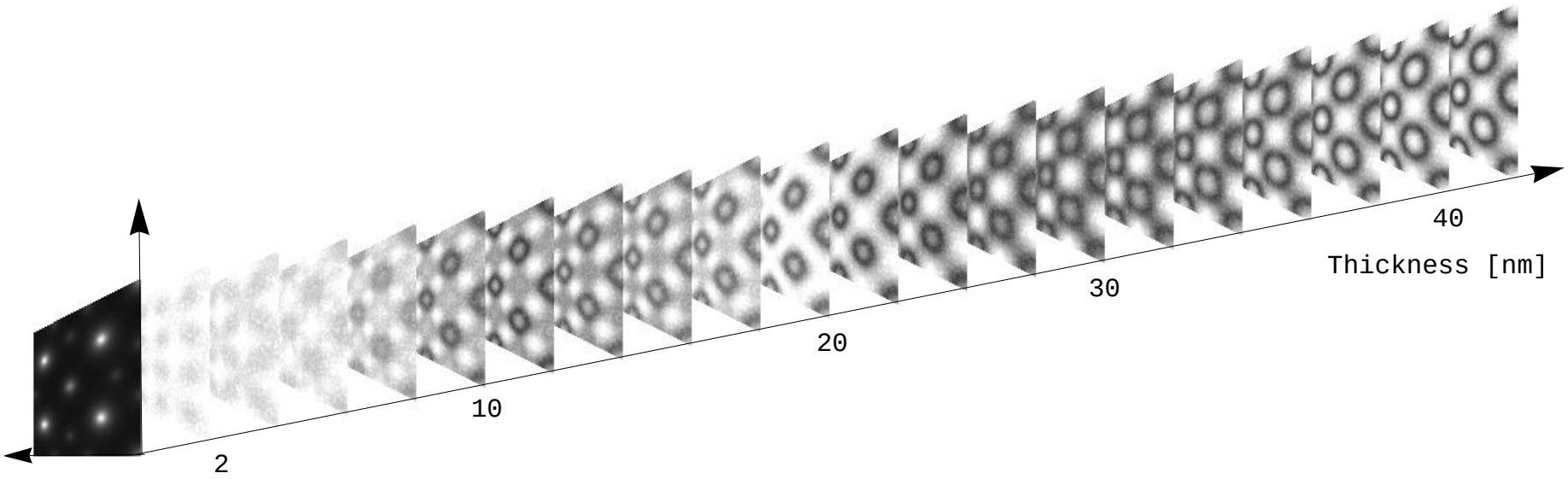
Where:

$$V_p(\vec{x}) : \text{projected potential}$$

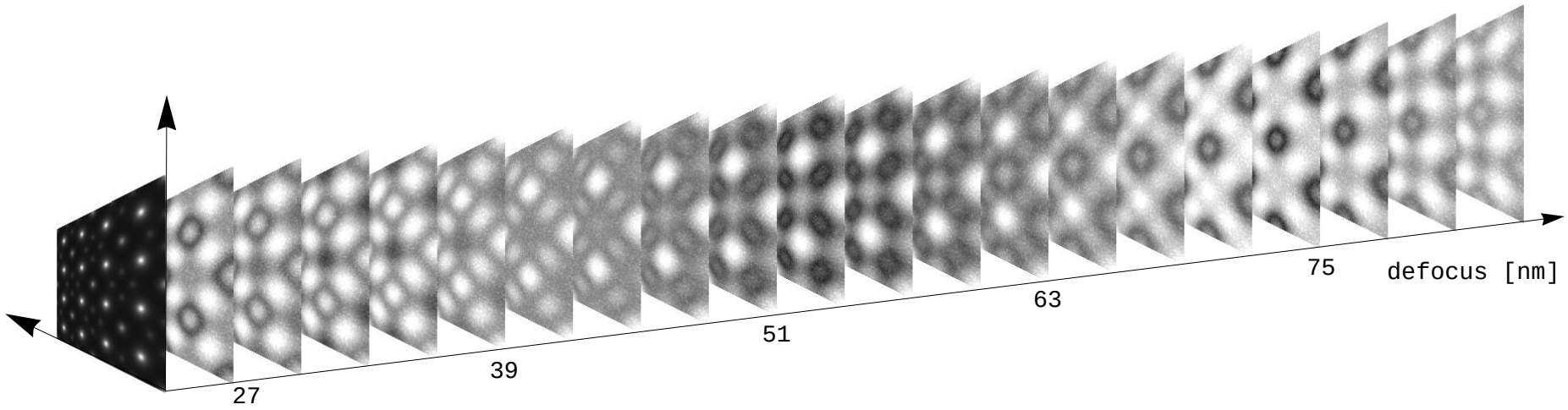
$$\sigma : \text{electron matter interaction constant}$$

HRTEM image depends on specimen thickness and object defocus

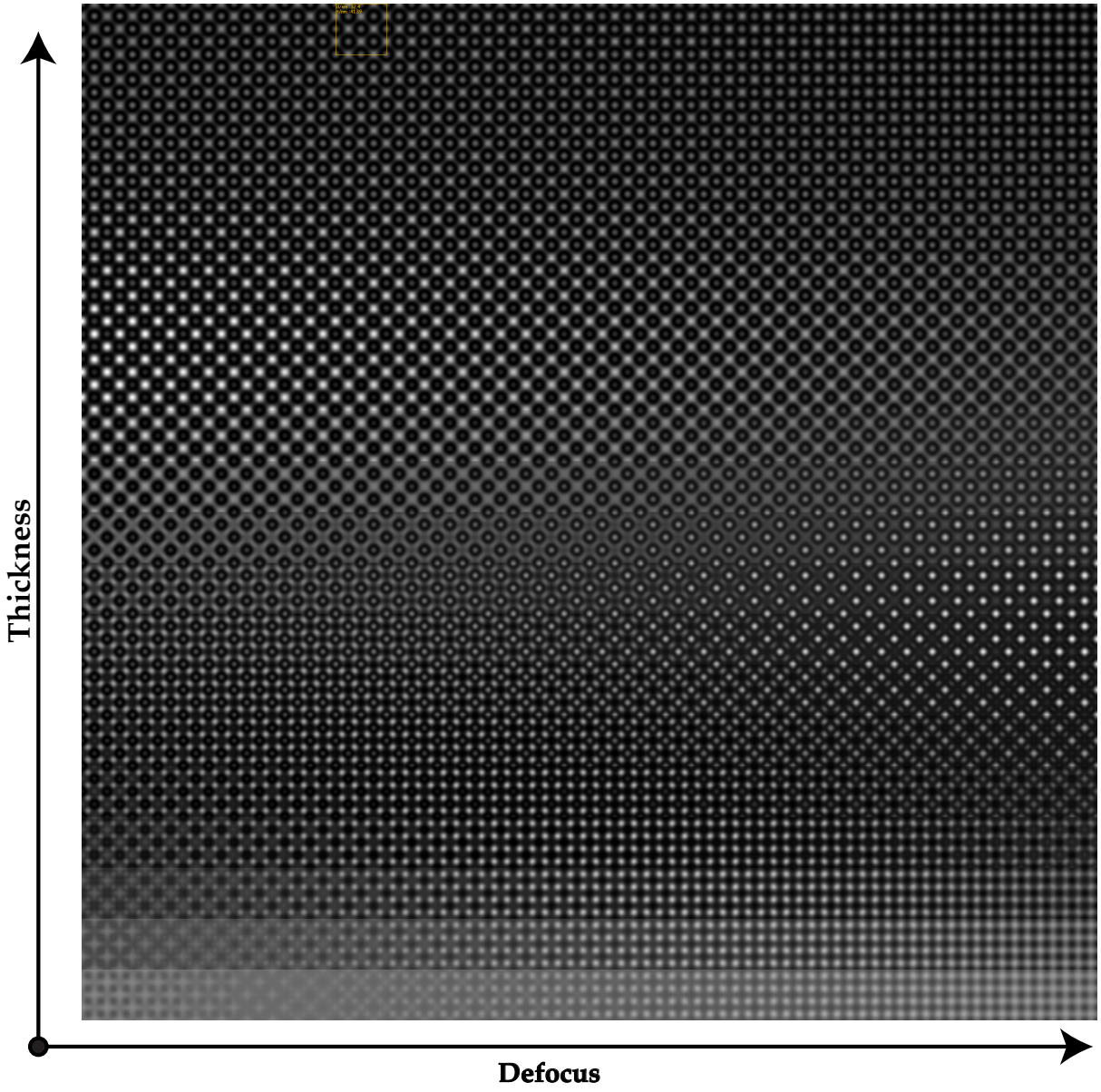
Thickness series



Defocus series



Si [001] images map: contrast dependence of defocus & thickness



HREM map does not include the Modulation Transfer Function (MTF) of the detector.

AlN [111]: multislice calculations == Blochwave calculations

Multislice calculations give result identical to Blochwave calculations. It is only necessary to define an orthogonal unit with $[001]_{ortho}$ // to $AlN[111]_{hexa}$[7].

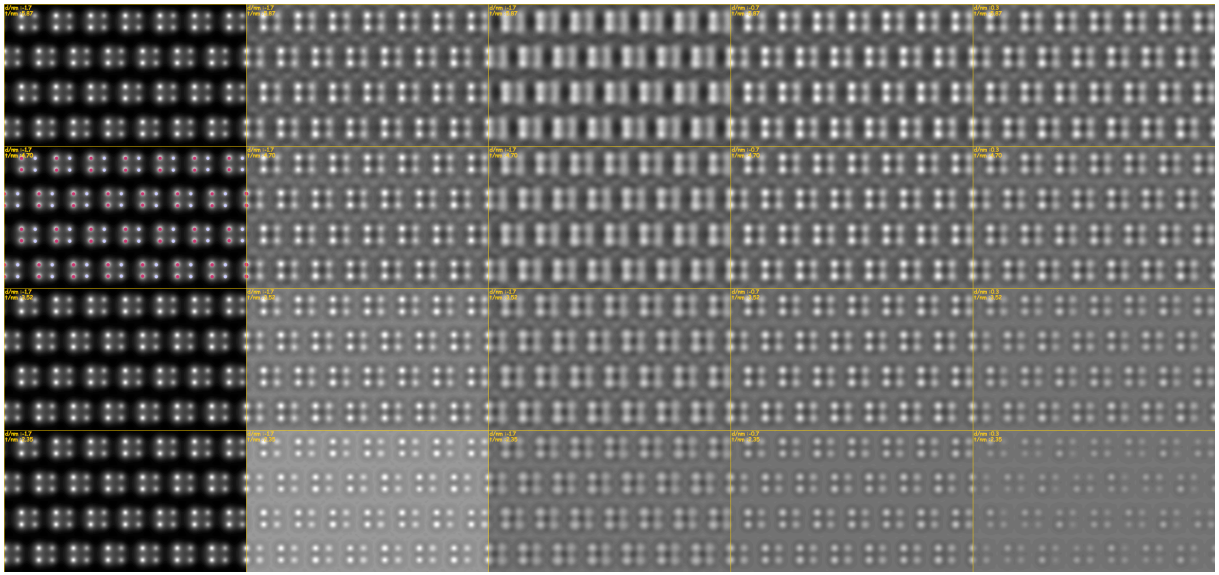


Figure: Multislice calculation AlN [111]

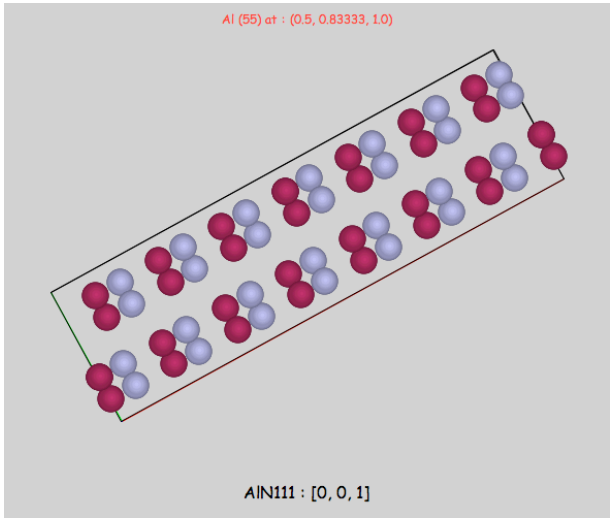


Figure: $AlN[001]_{Ortho}$ unit cell equivalent to $AlN[111]_{hexa}$ unit cell

[7] The new unit cell is adapted to ADF calculations, it only have to be duplicate in order to make it square.

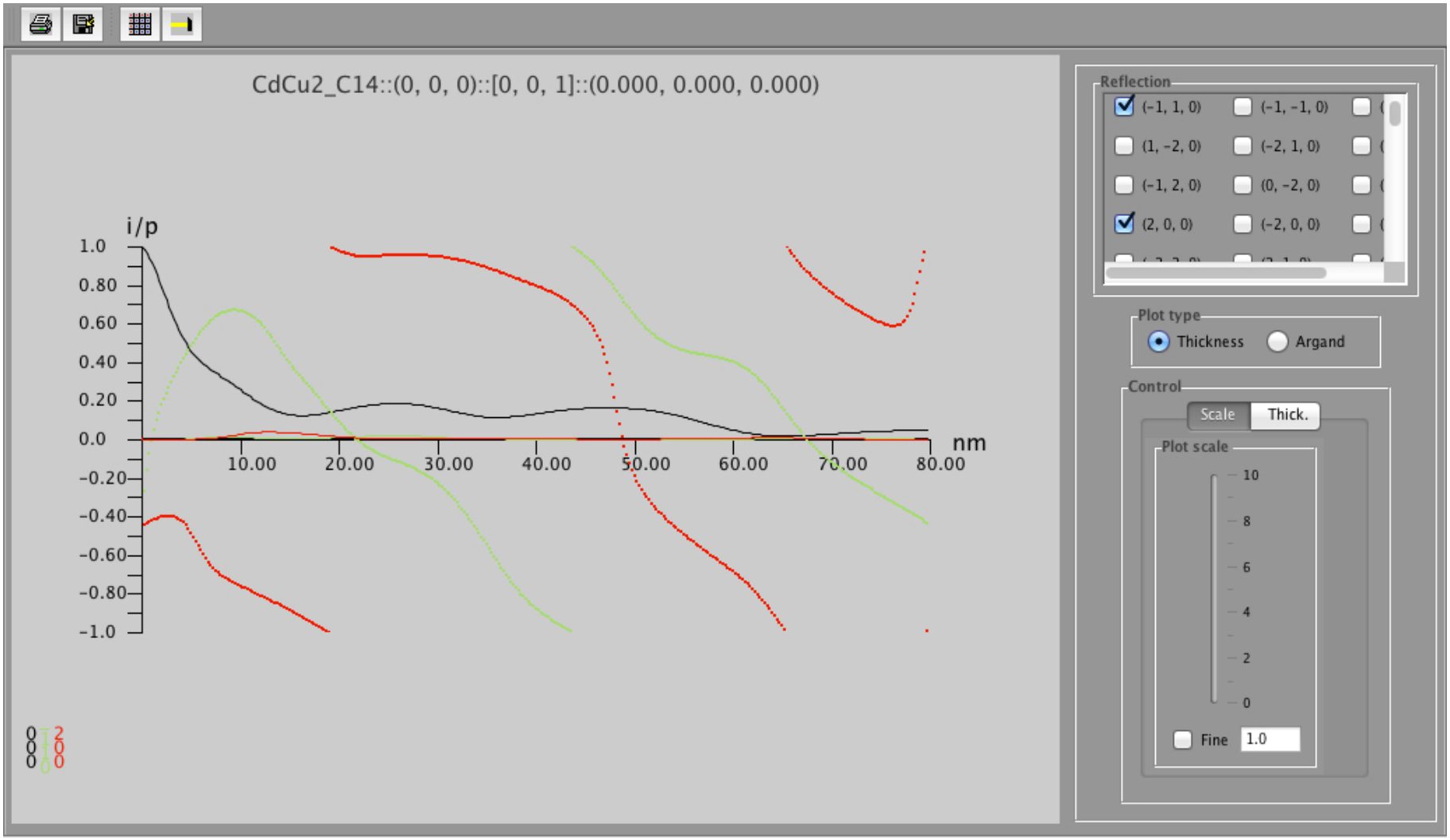
Problems

Problems...

- Object
  - → Atomic scattering amplitude below 50 kV?
  - → Potential by DFT calculation?
  - ...
- HRTEM → Phase of diffracted beams evolves with specimen thickness.
- HRTEM → MTF of image acquisition system (Stobbs factor?).
- HRTEM / HRSTEM → Electron channeling depends on atomic column content.
- HRTEM / HRSTEM → Aberrations of optical system.
- HRTEM → Inelastic scattering (J.M. Cowley, E.J. Kirkland, D. van Dyck, A. Rosenaurer, K. Ishizuka, Z.L. Wang, H. Rose, H. Mueller, L. Allen, ...).
- HRTEM / HRSTEM → Drift, vibration, Johnson-Nyquist noise[8], ...
- ...

[8] S. Uhlemann, H. Mueller, P. Hartel, J. Zach & M. Haider, Phys. Rev. Lett. **111** (2013) 046101.

HRTEM problem: amplitude and phase of diffracted beams



Note that phase of diffracted beam is $\frac{\pi}{2}$ out-of-phase with respect to transmitted beam.

HRTEM problem: CCD MTF (Gatan MSC 1K x 1K, 24 μm)

To make quantitative comparison with experimental HRTEM images the MTF of the detector must be introduced in the simulation.

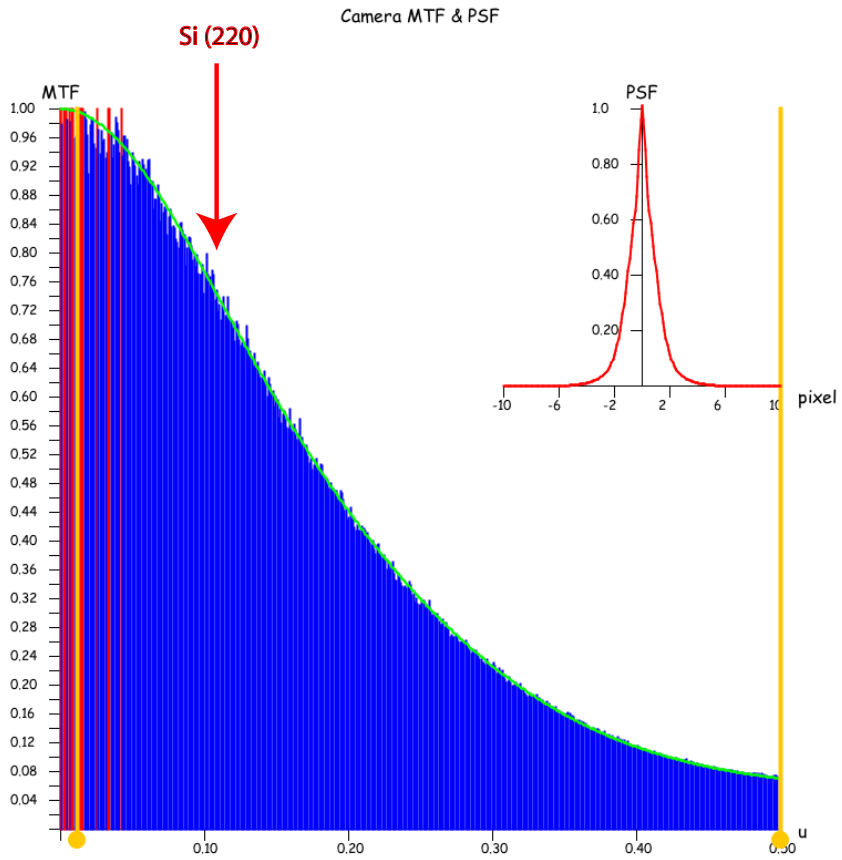


Figure: At high magnification Si (220) planes imaged with high contrast.

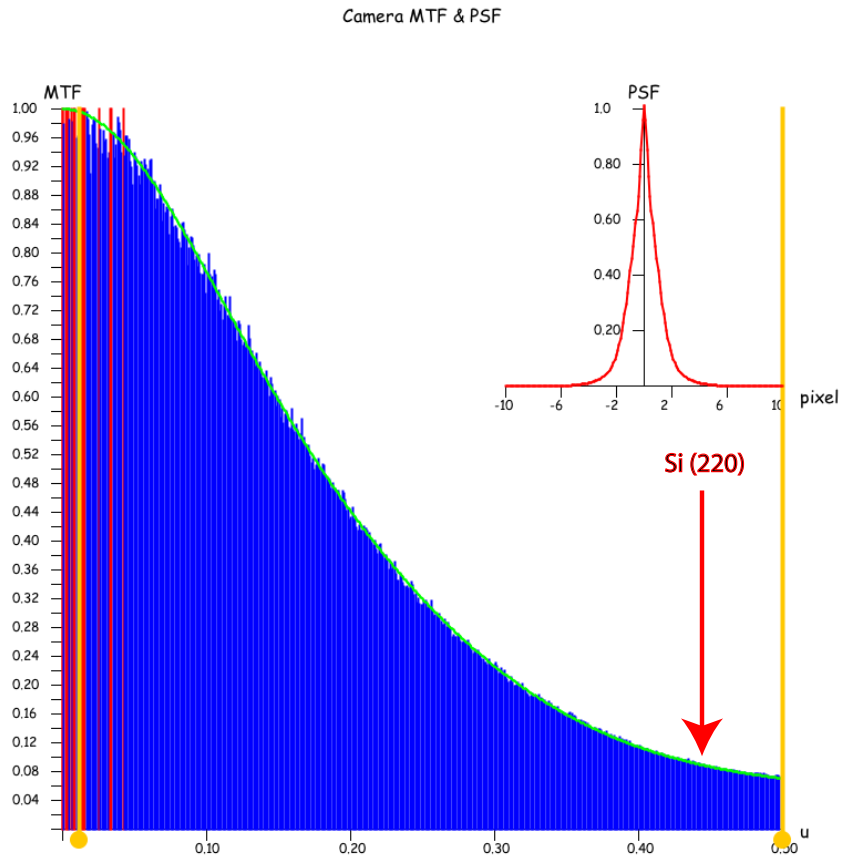


Figure: At low magnification Si (220) planes imaged with low contrast.

For quantitative comparison always use highest possible magnification (or include CCD MTF in simulations)!

CCD MTF: high magnification (900 kx)

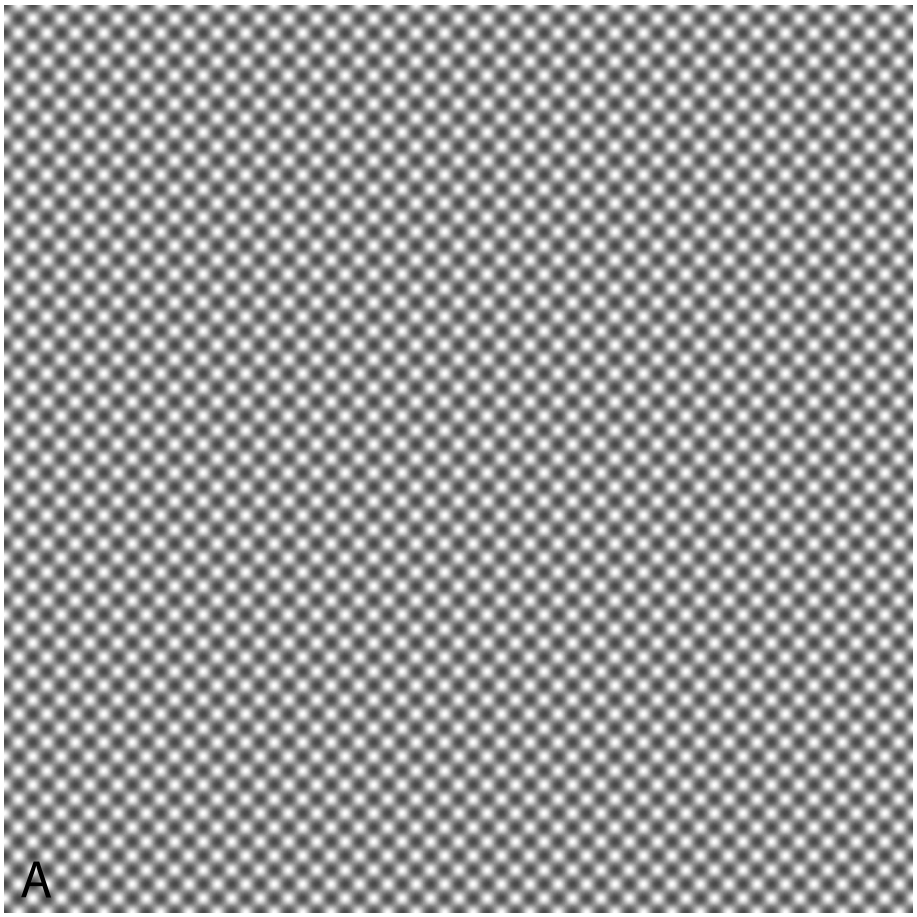


Figure: A: Si [001] simulation.

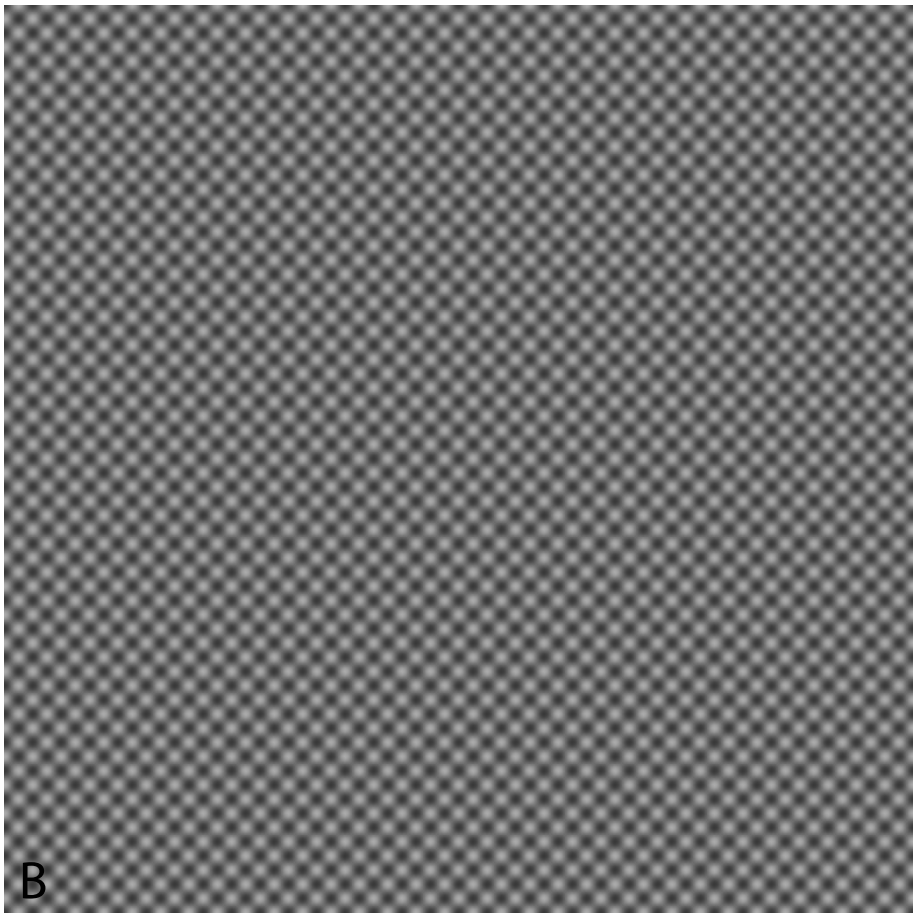


Figure: B: Si [001], simulation + CCD MTF.

CCD MTF: low magnification (225 kx)

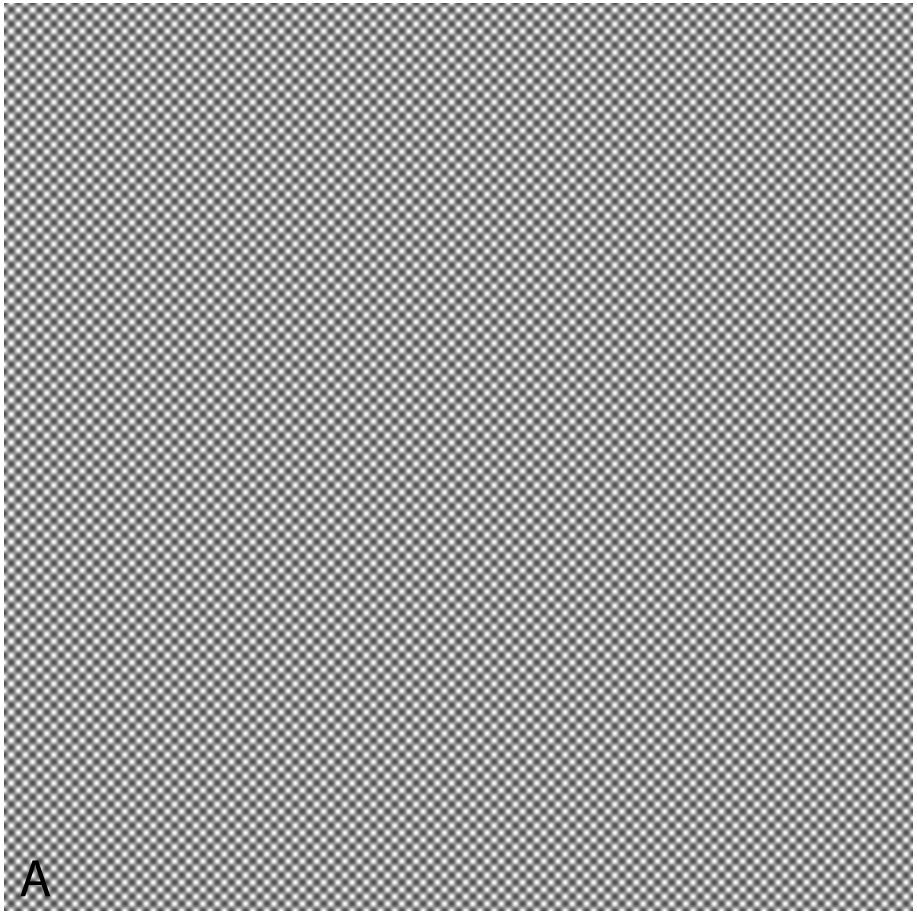


Figure: A: Si [001] simulation.

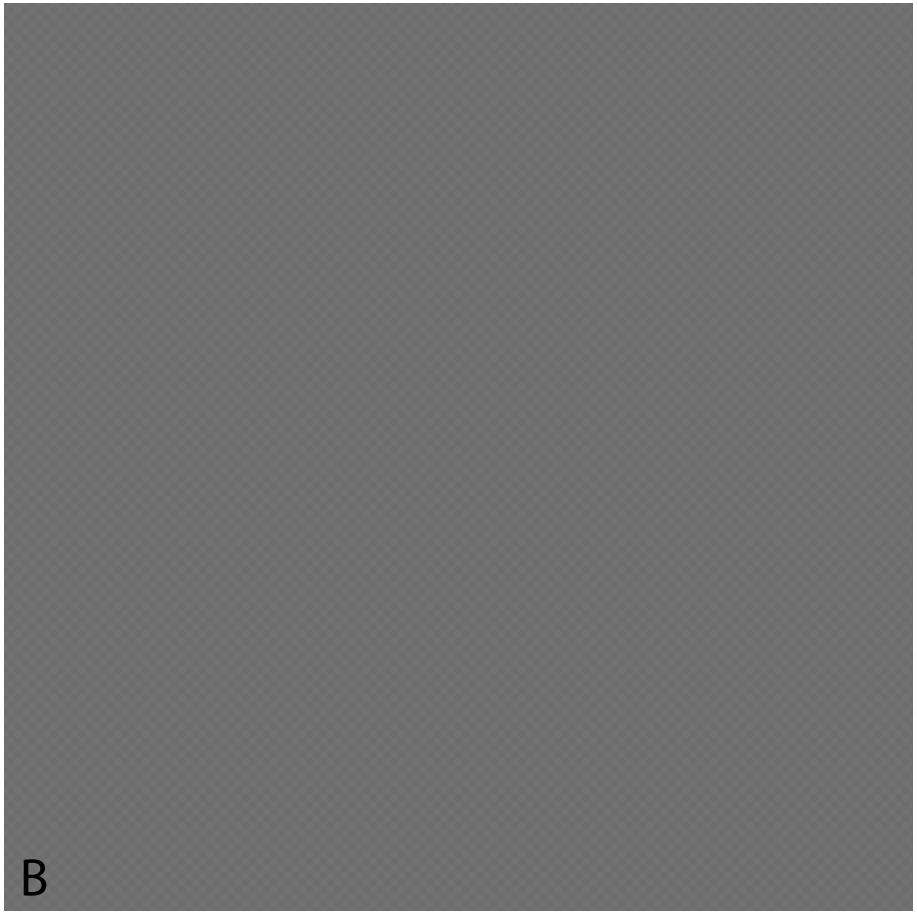


Figure: B: Si [001], simulation + CCD MTF.

HRTEM / HRSTEM problem: electron channeling (ZnTe [110])

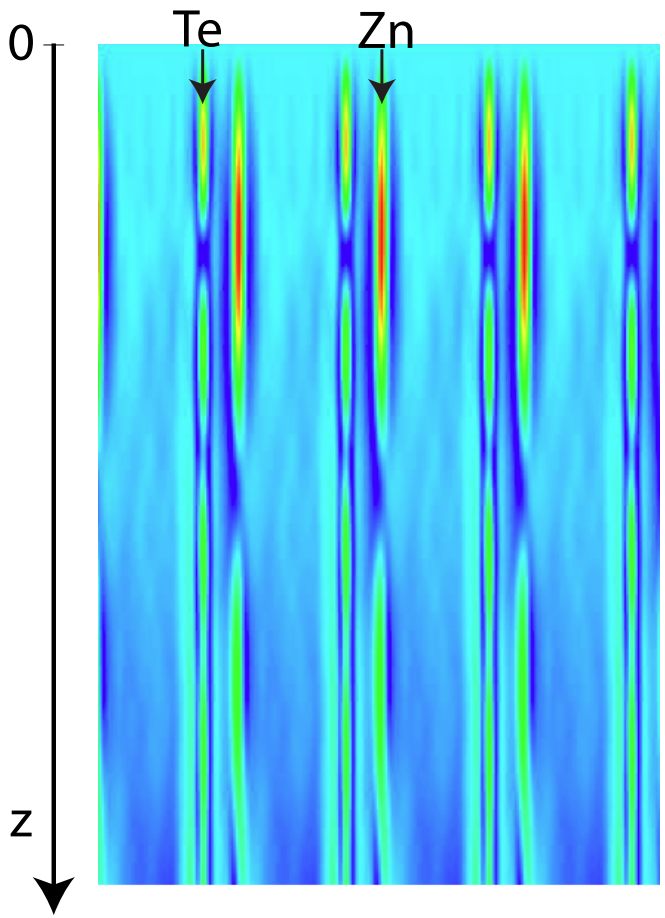
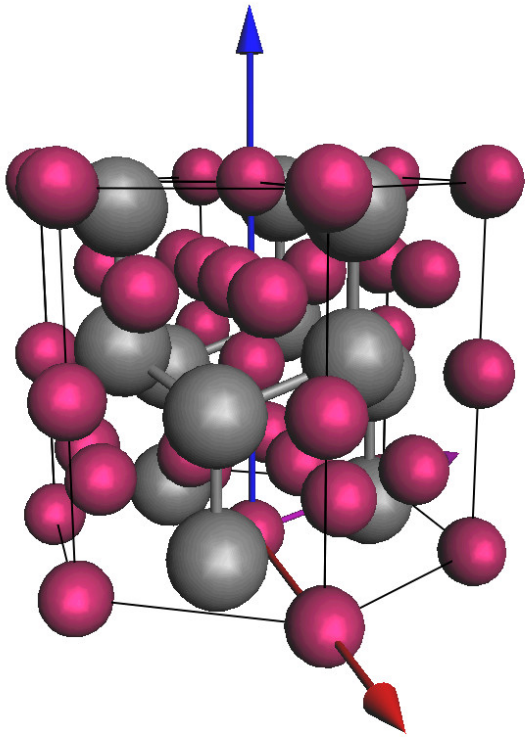


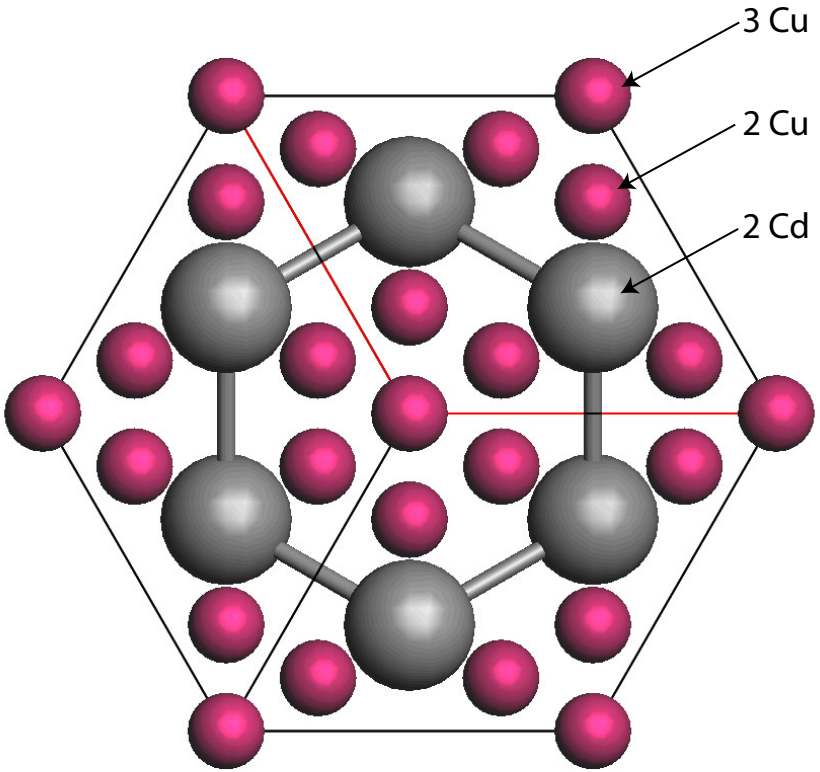
Figure: ZnTe [110] wave function intensity.

Channeling explains several features of HRTEM and STEM images (i.e. appearance / disappearance of contrast of impurities).

Does C_s and C_c correction solves all imaging problems?

Example: CdCu_2, visibility of the 3 Cu atomic columns.



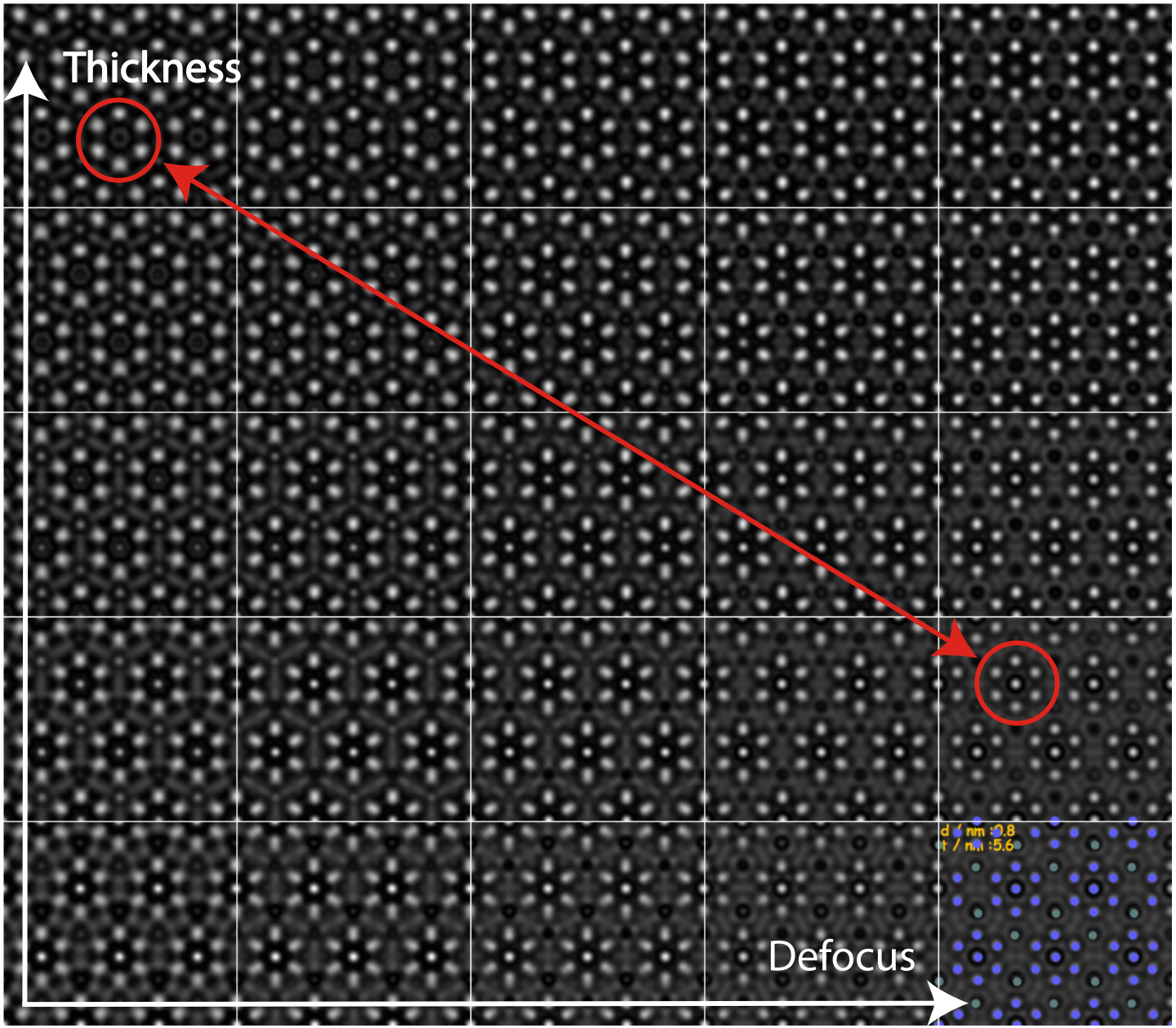


HRTEM image simulation conditions

Acc. [kV]	$C_s[mm]$	$C_5[mm]$	$C_c[mm]$	$\Delta E[eV]$	Z [nm]	$\Delta z[nm]$
300	-0.008	30	0.5	0.6	-4.9	1
300	-0.008	30	0.1	0.2	-2.0	1

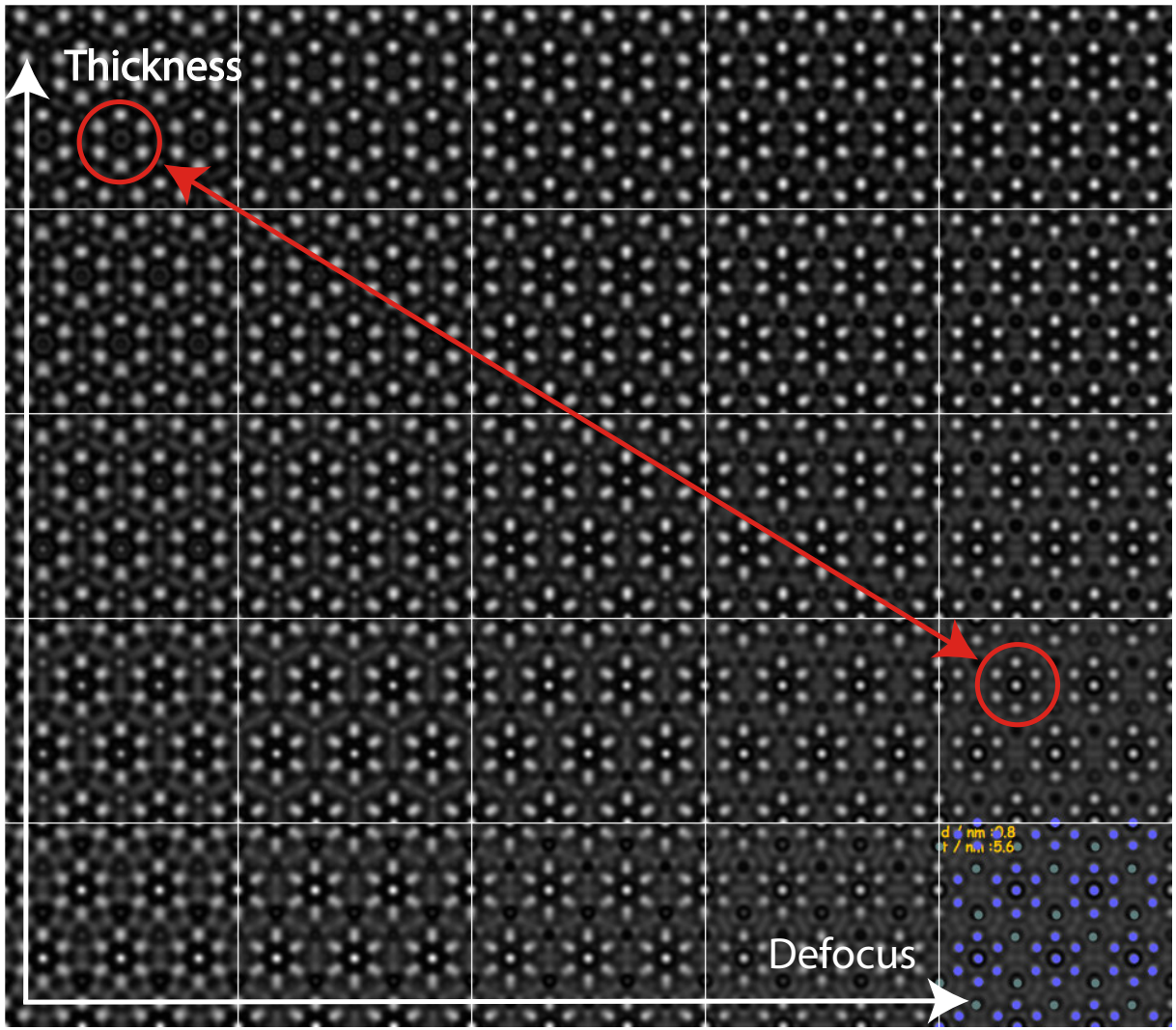
Dynamical scattering effects are not affected by C_s and/or C_c corrected TEM!

$CdCu_2[001]$: imaging parameters set 1



Visibility of 3 Cu atomic columns depends on specimen thickness and defocus.

$CdCu_2[001]$: imaging parameters set 2



Improving C_c and ΔE does not affect the visibility of 3 the Cu atomic columns. It depends on specimen thickness (and defocus indeed). Visibility of the 3 Cu atomic columns is always affected by dynamical scattering. Only extremely thin specimen ($\leq$ 10 nm) will allow faithful imaging of crystal projected potential.

STEM HAADF imaging

High Angle Annular Dark Field (HAADF): inelastically scattered electrons.

When simulation is necessary how to simulate images?

Numerous approximations:

- Simple projected + convolution with probe intensity: no channeling effect (Weak Object Approximation).
- Multislice calculation: channeling + inelastic scattering (absorption potential) + convolution with probe intensity.
- Frozen lattice (phonon) approximation: atoms of super-cell displaced out of equilibrium position, probe scanned on imaged area, intensity collected by annular detector.
- Pennycook, Nellist, Ishizuka, Shiojiri, Allen, Wang, Rosenauer, van Dyck, ...

Except the first 2 methods, simulation is (too) time expensive (luxury?). Approximations (necessity) may suffice...

HRTEM / HRSTEM problem: aberrations of optical system

Reaching 0.05 nm resolution sets very strong conditions on aberrations correction.

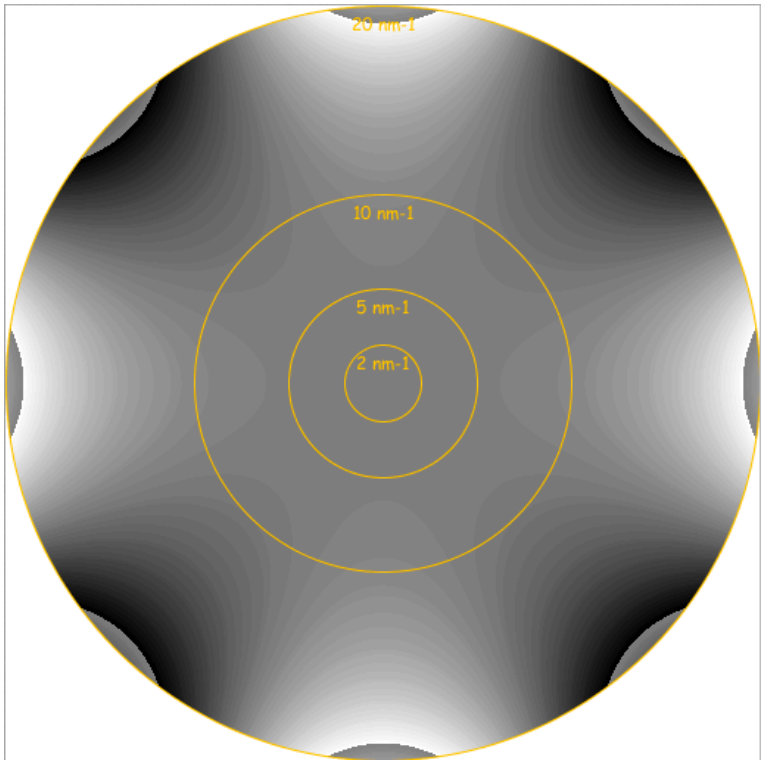


Figure: Aberration figure of $C_{34}(0.5\mu\text{m})$, phase jump at $\frac{\pi}{4}$.

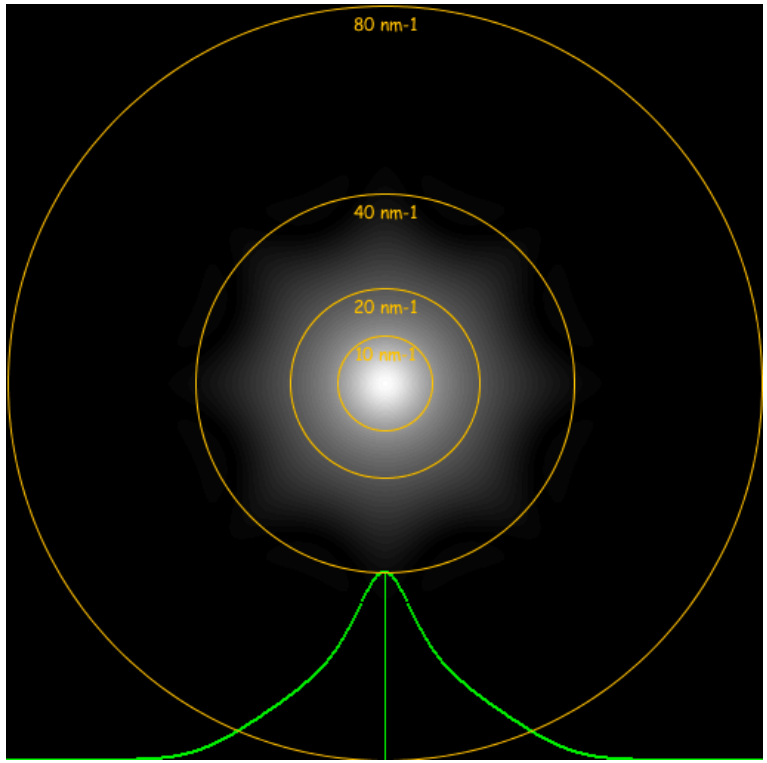


Figure: Optical Transfer Function.

Note that Optical Transfer Function (HRSTEM) transfers higher spatial frequencies than Ccoherent Transfer Function (HRTEM).

HAADF: graphene

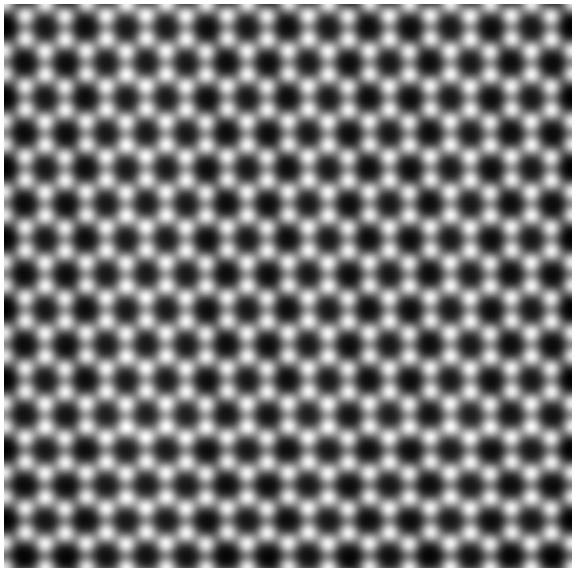


Figure: Proj. pot. approx.

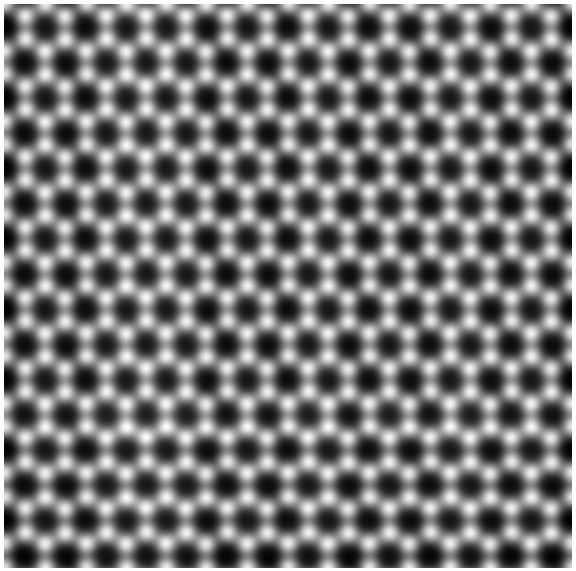


Figure: Channeling calculation.

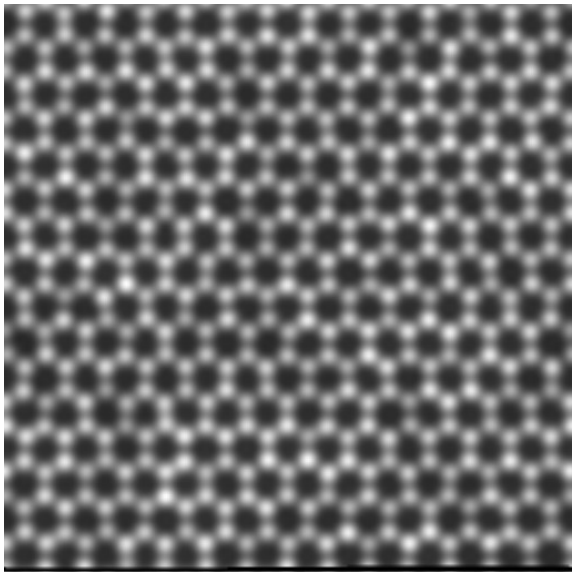


Figure: Frozen lattice 5 conf.

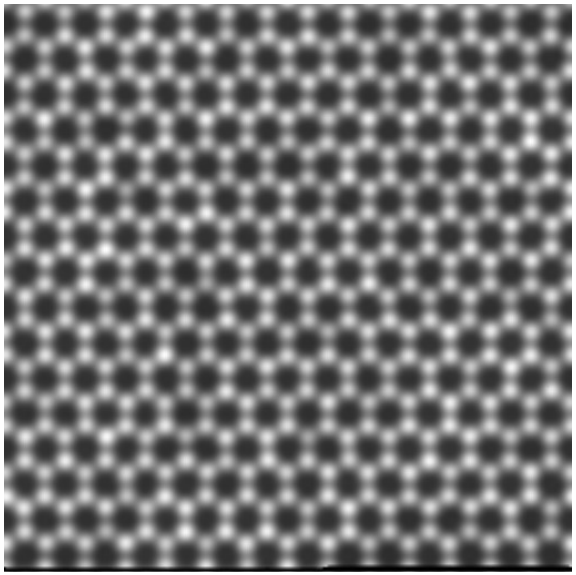


Figure: Frozen lattice 10 conf.

HRSTEM - HRTEM comparison: graphene with add atoms

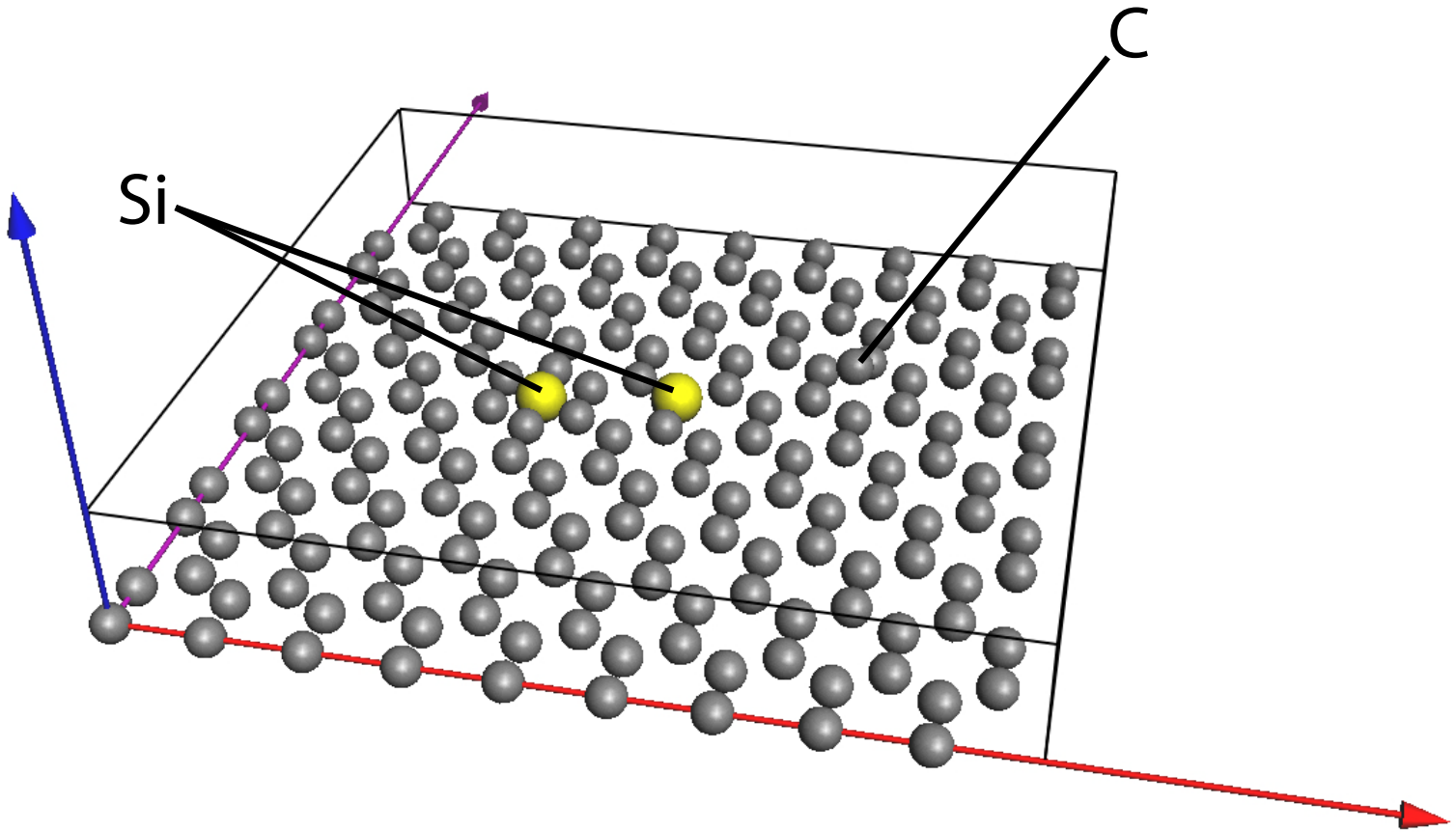


Figure: Graphene with Si in 6 C ring, Si substitutional and 2 C column.

Graphene HAADF (100 kV, 70 -150 mrad)

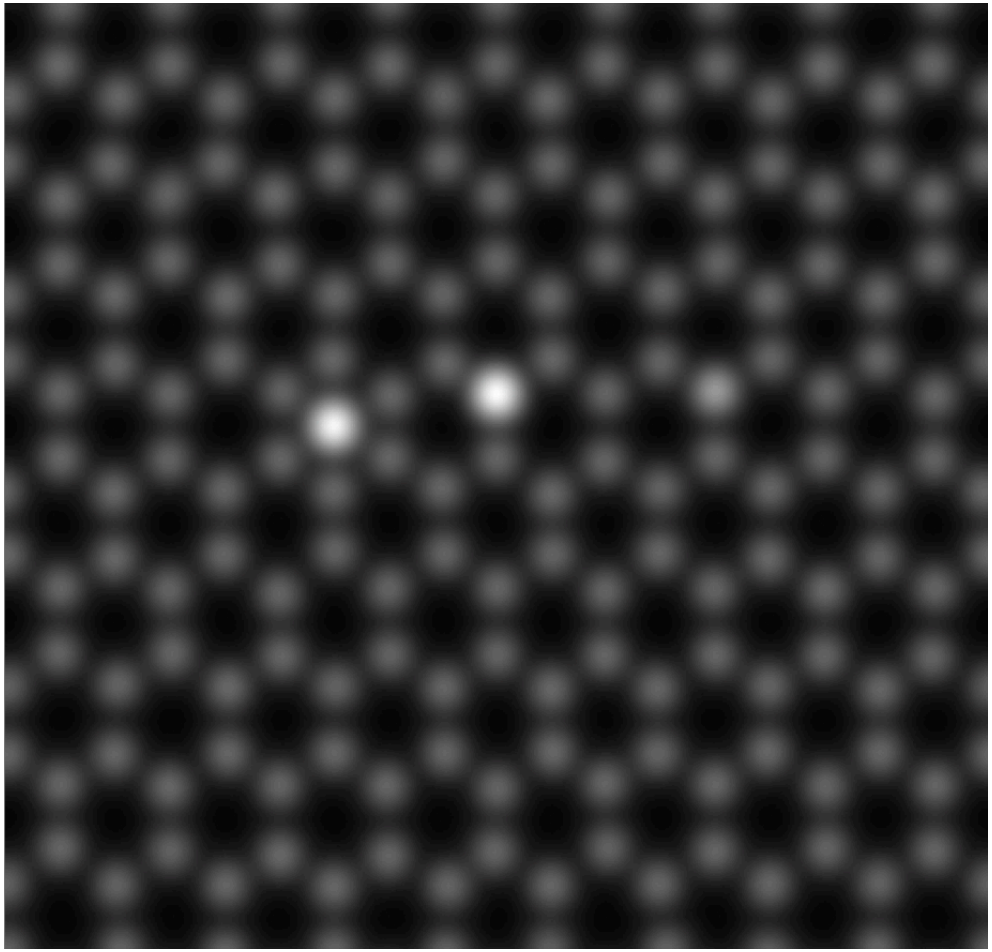


Figure: Frozen lattice (∼400 s).

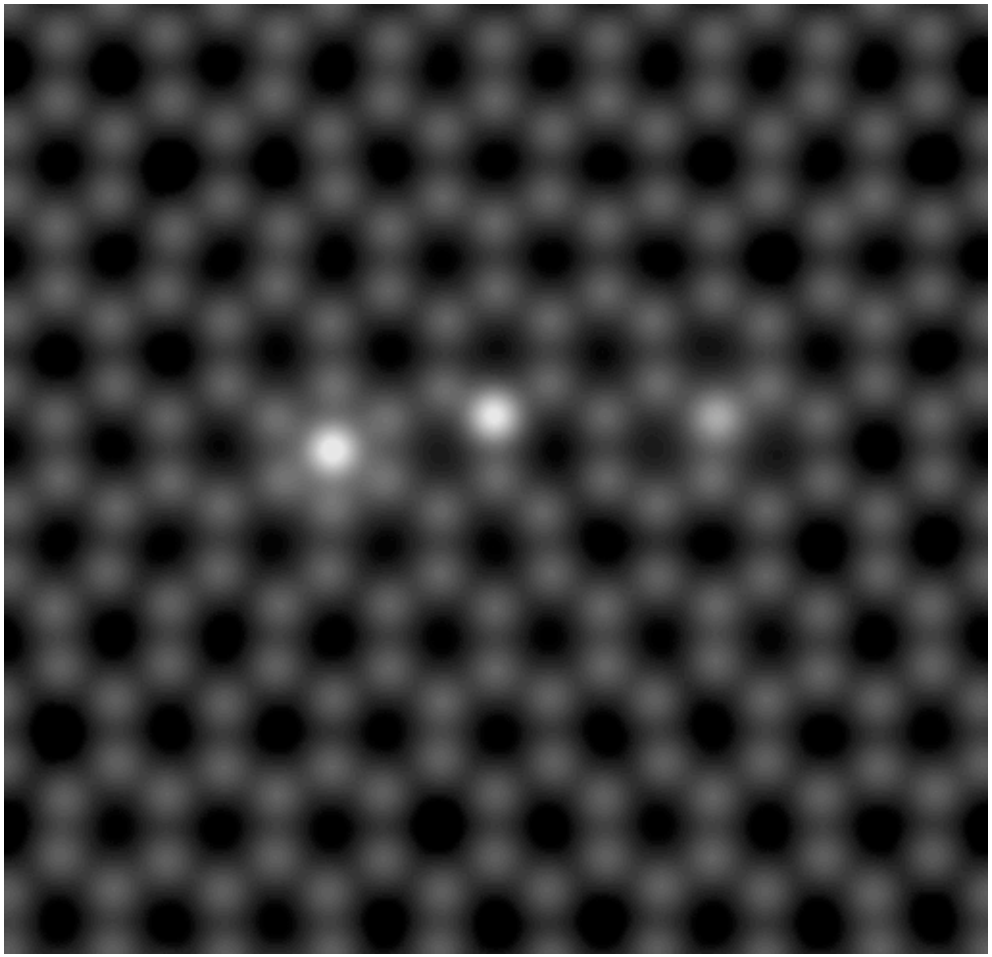


Figure: Channeling (∼2 s).

One Si shows more contrast than 2 C atoms ($i \sim Z^2$) : 14^2 compared to $\sim 2 \times 6^2$.

Graphene HRTEM (100 kV, $C_s - 0.033mm$)

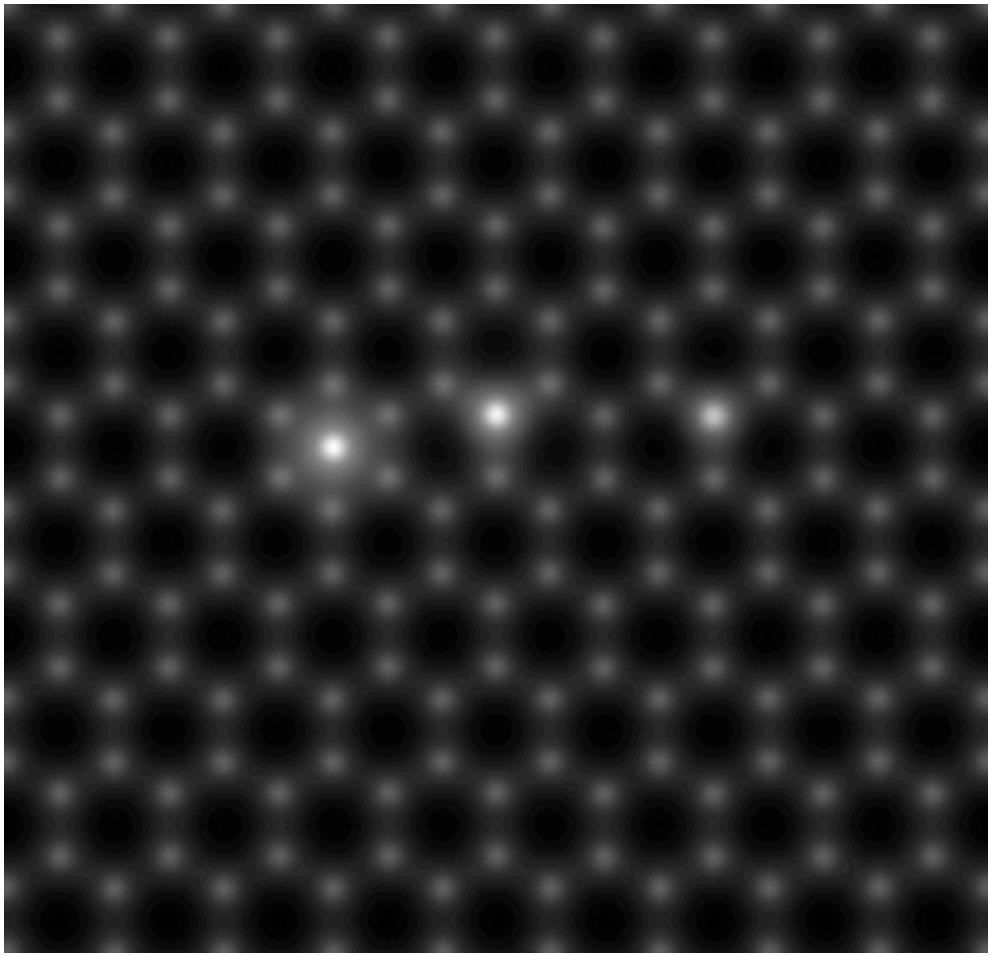


Figure: Weak phase object app., $C_c = 0.5mm$

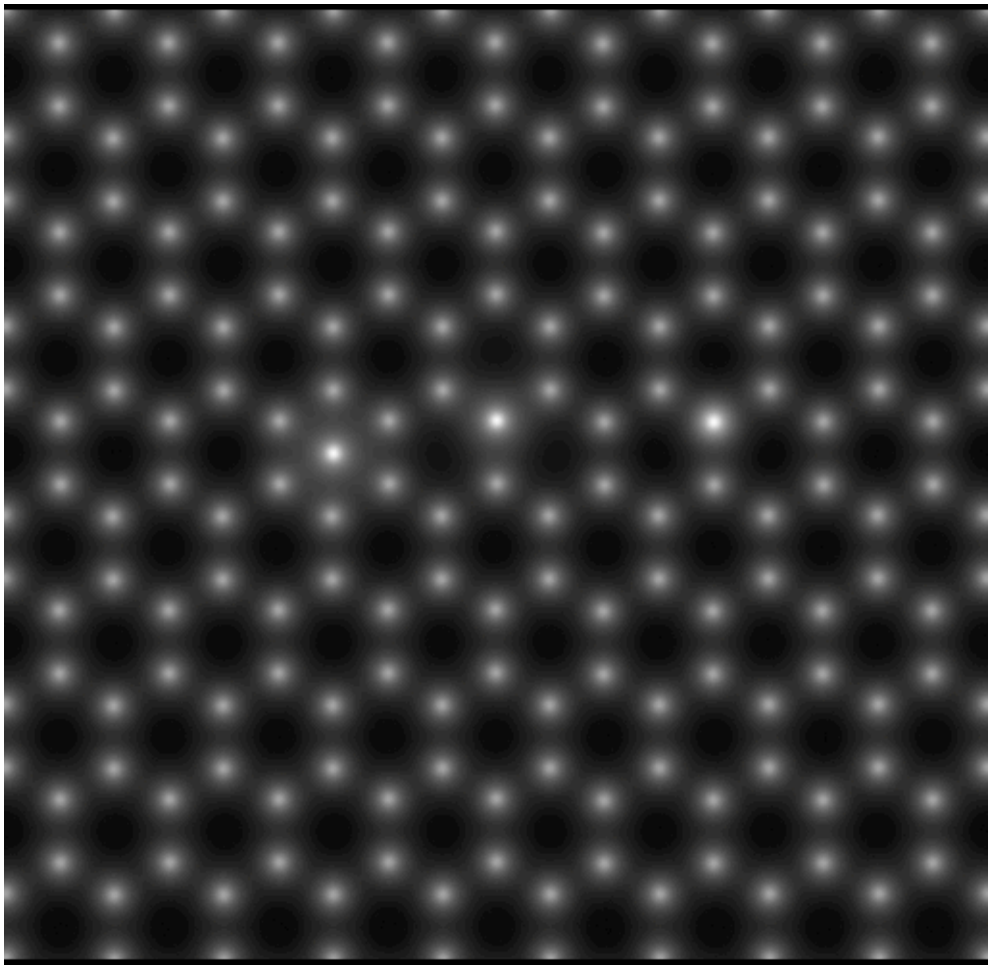


Figure: Multislice, $C_s = -0.033mm$, $C_c = 0$, no thermal magnetic noise.

HRTEM does not display the strong contrast difference between one Si and two C as given by HAADF.

Quantitative HR(S)TEM

No doubt that **image simulation** is necessary for quantitative work[9].

Combined with:

- Exit wave function recovery using focal series reconstruction.
- Transport of intensity equation.

makes accessible structural information necessary to model and develop new functional materials.

But...can also be used for teaching or planing HR(S)TEM observations.
It requires:

- Simple and reliable models describing the physical processes.
- Interactive calculations allowing to adjust the many parameters in real time.
- Easy access to the simulations (tablet computer $\rightarrow$ Surface Pro 3, GPU - OpenCL).

[9] K. W. Urban, Science **321** (2008) 506.

Thank you for attention!