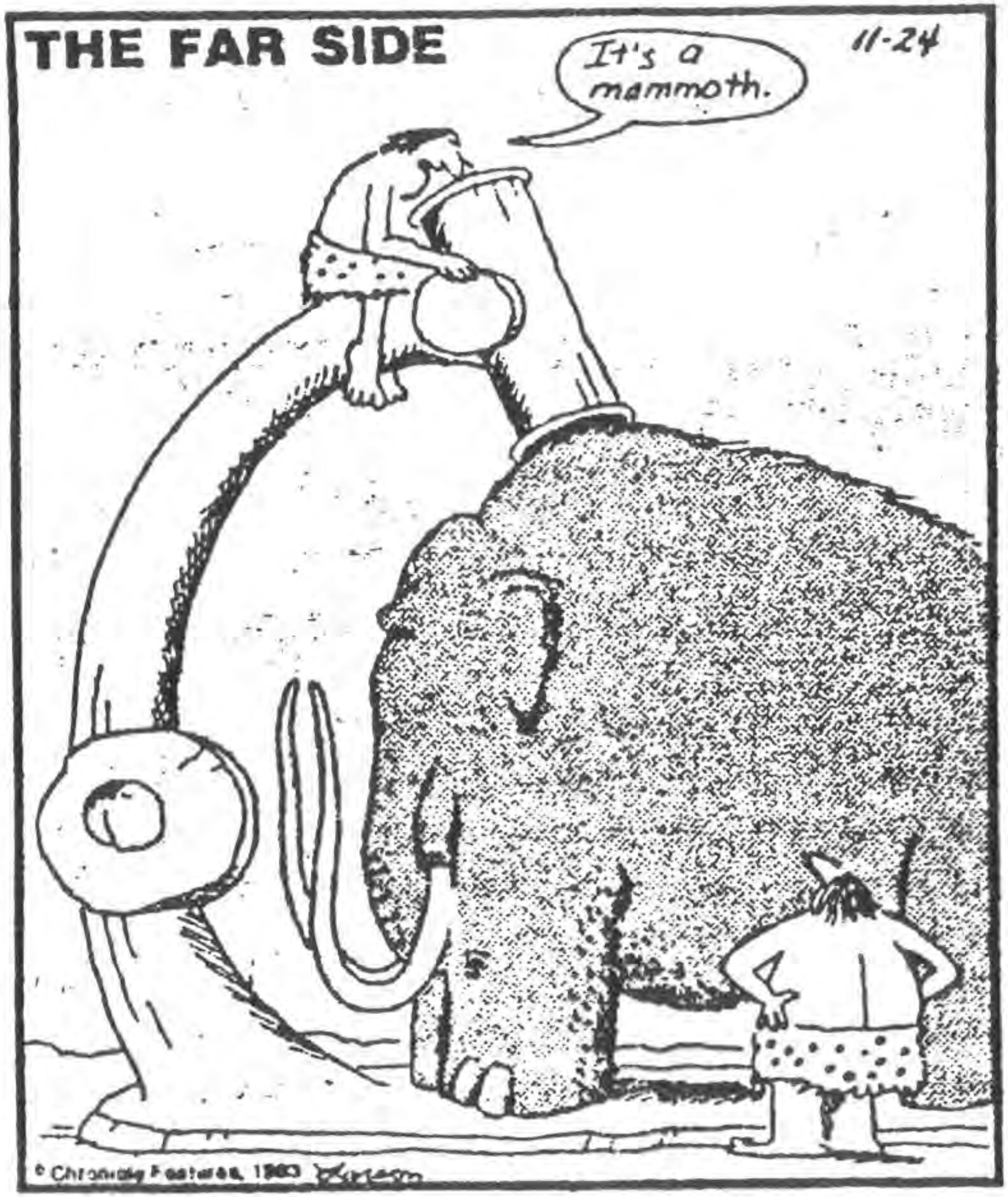
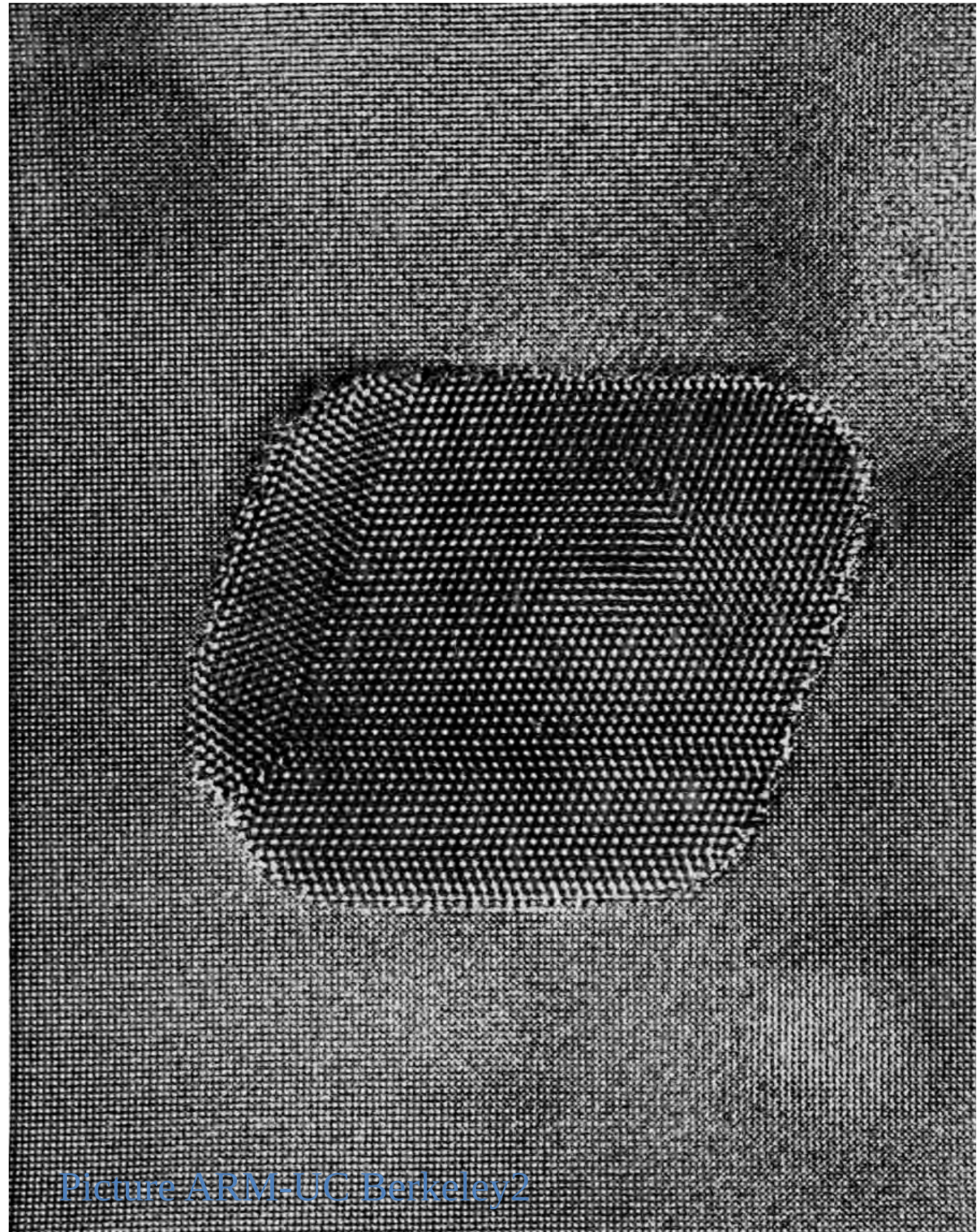
HREM



Early microscope.

Image close to visual interpretation

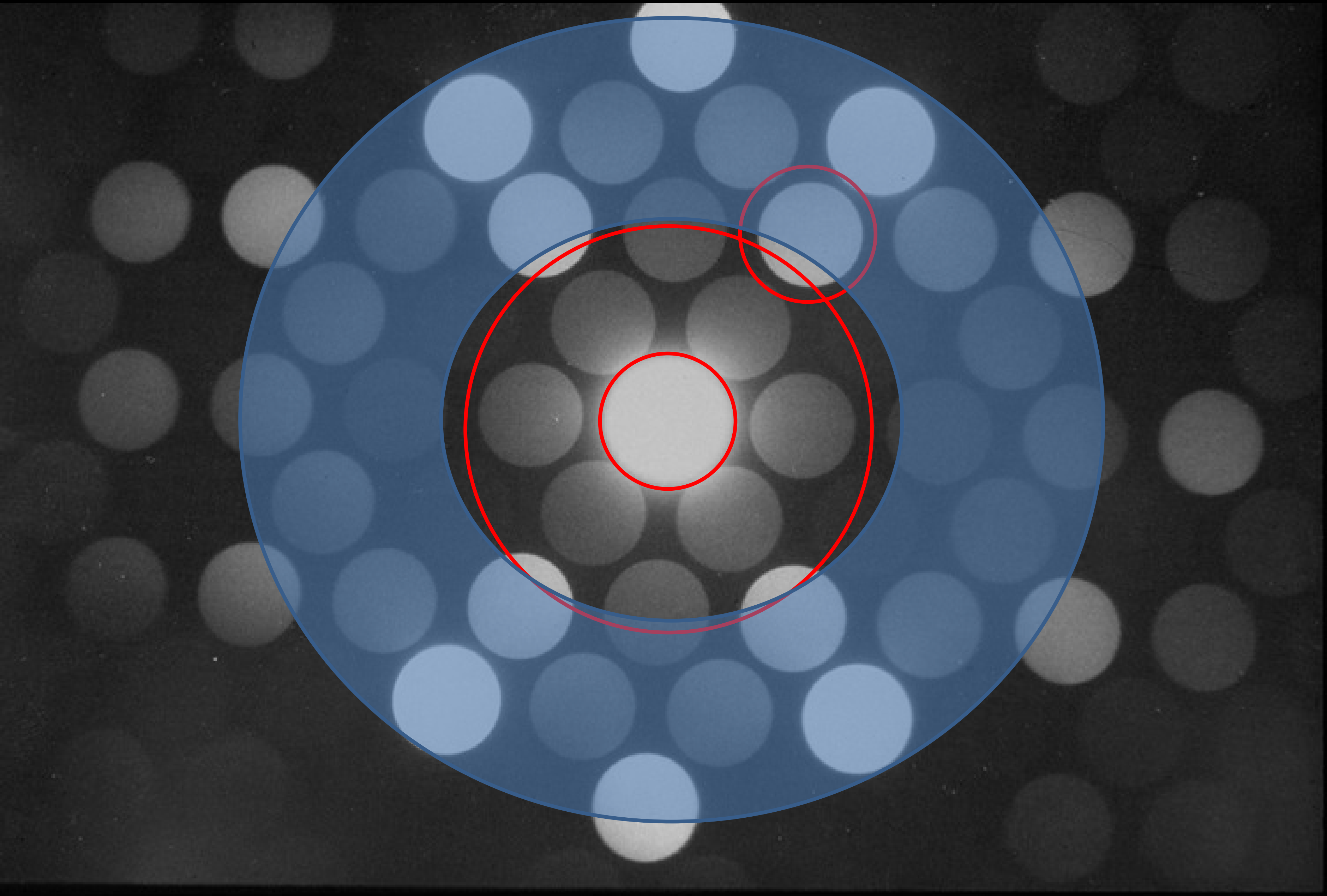


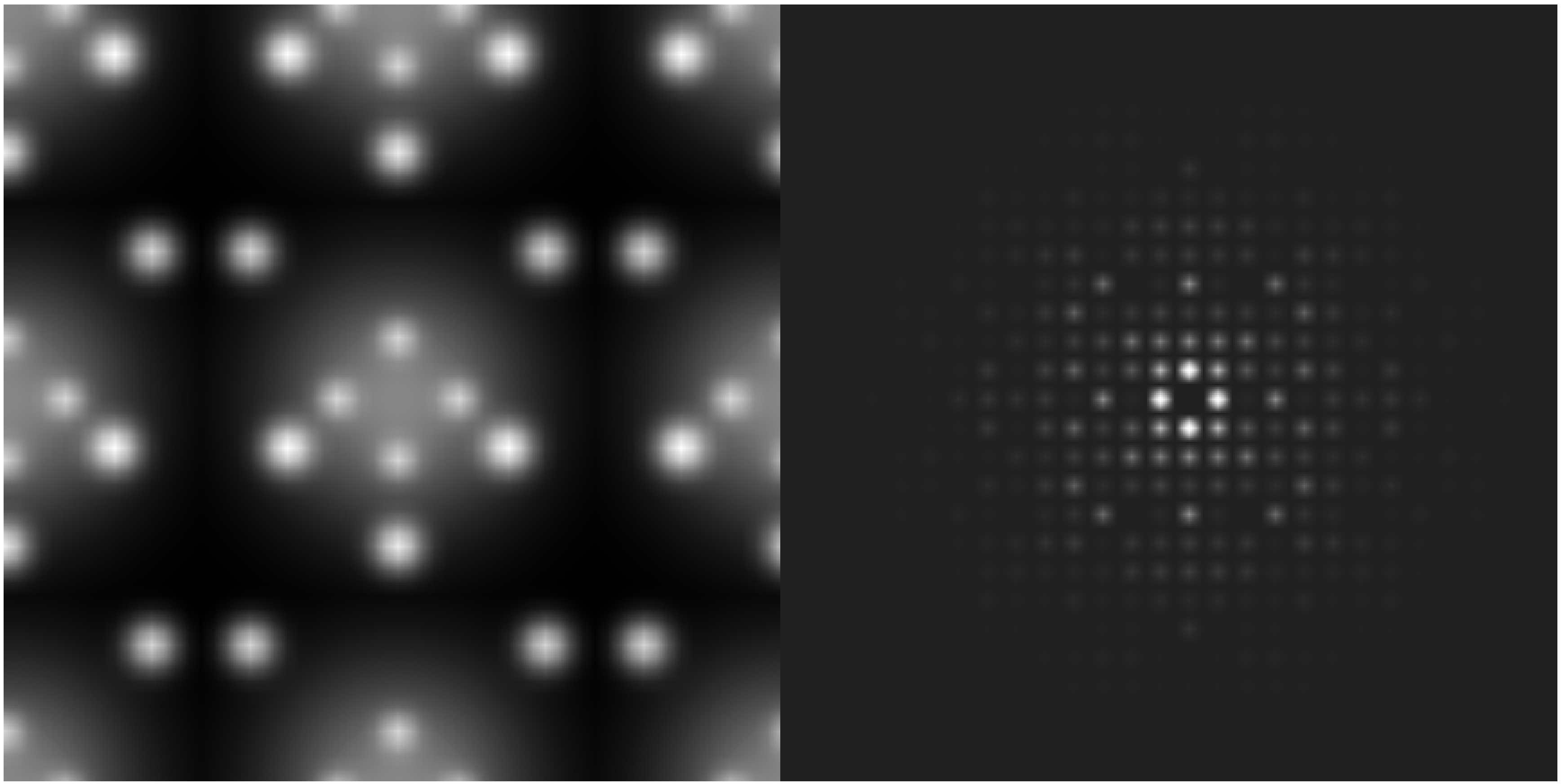
Curtesy S. Van Tenderloo

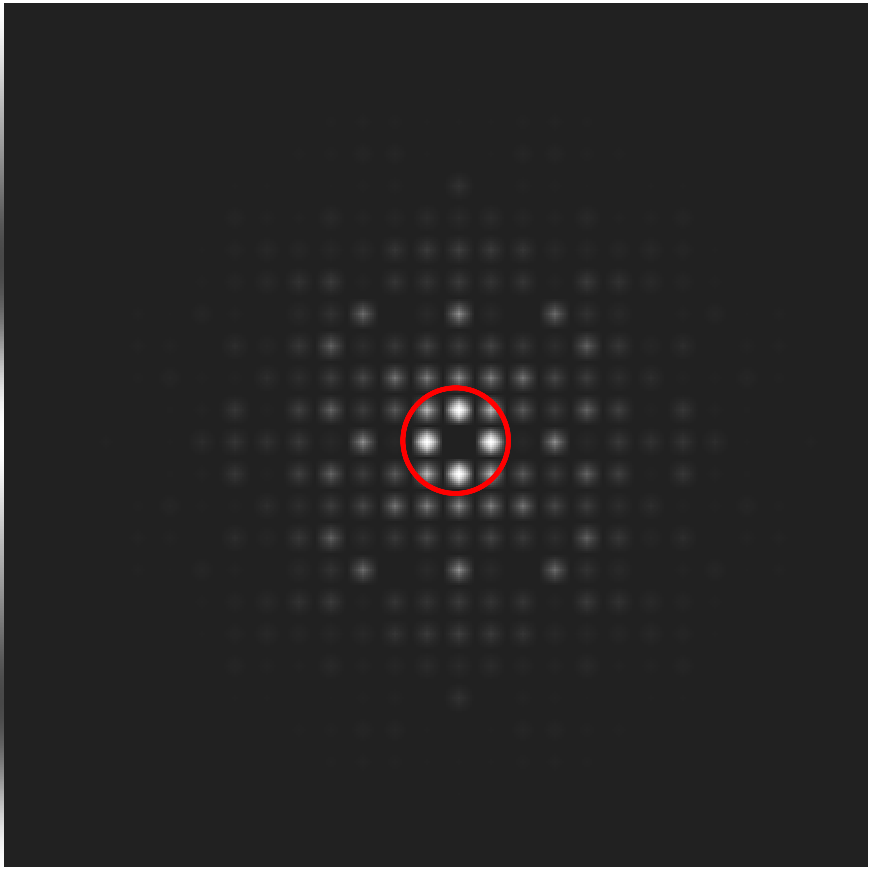
So what?

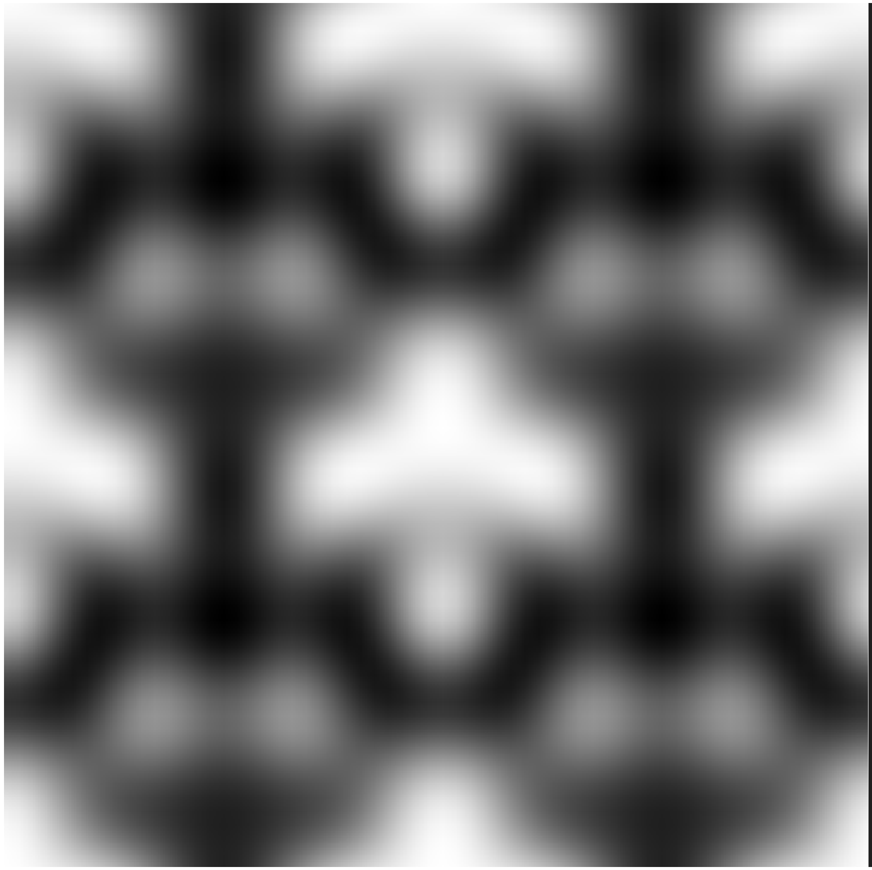
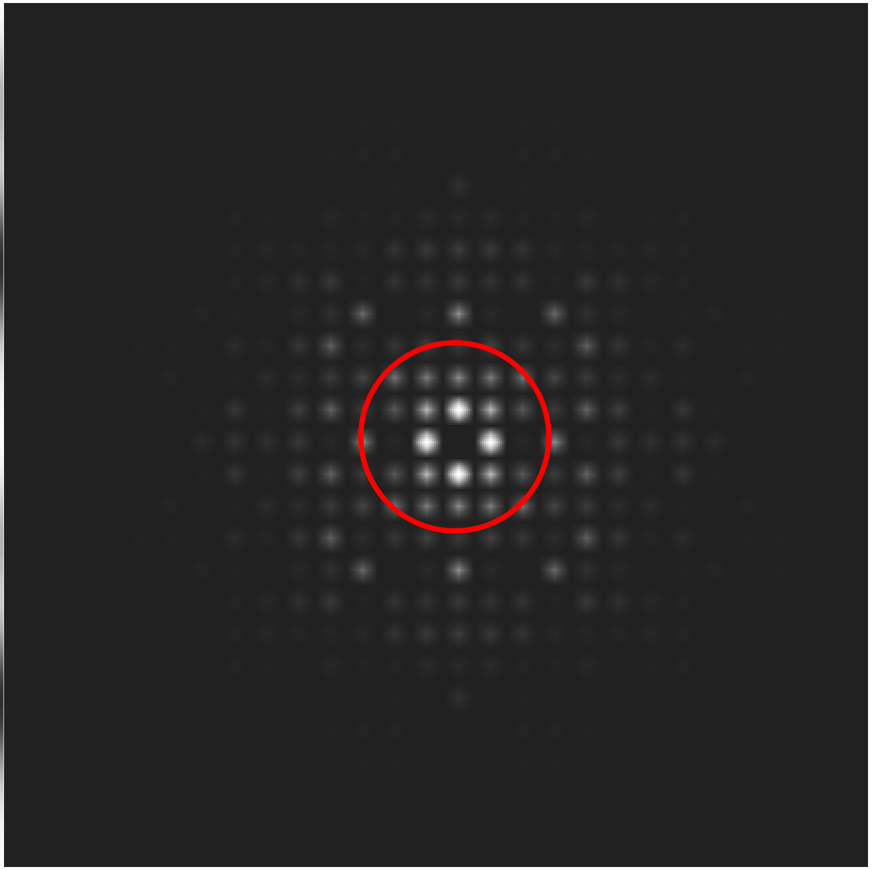
- Can obtain
  - Pretty picture for publication
  - Local structural information
  - Sometimes local chemical information
  - Precise structural information atomic column by atomic colum

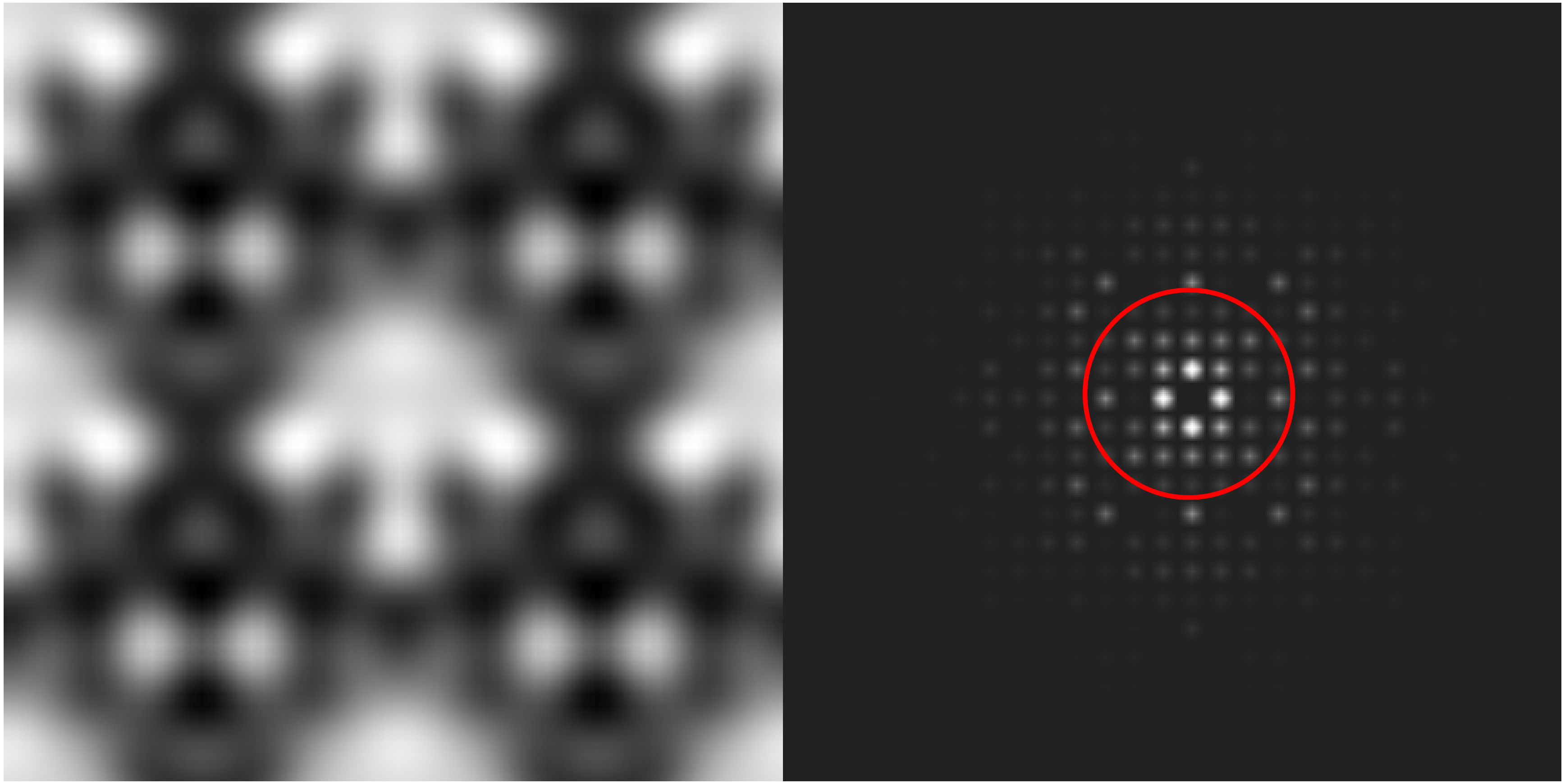
2-slit experiment; single electrons form interference statistically (Tonamura)

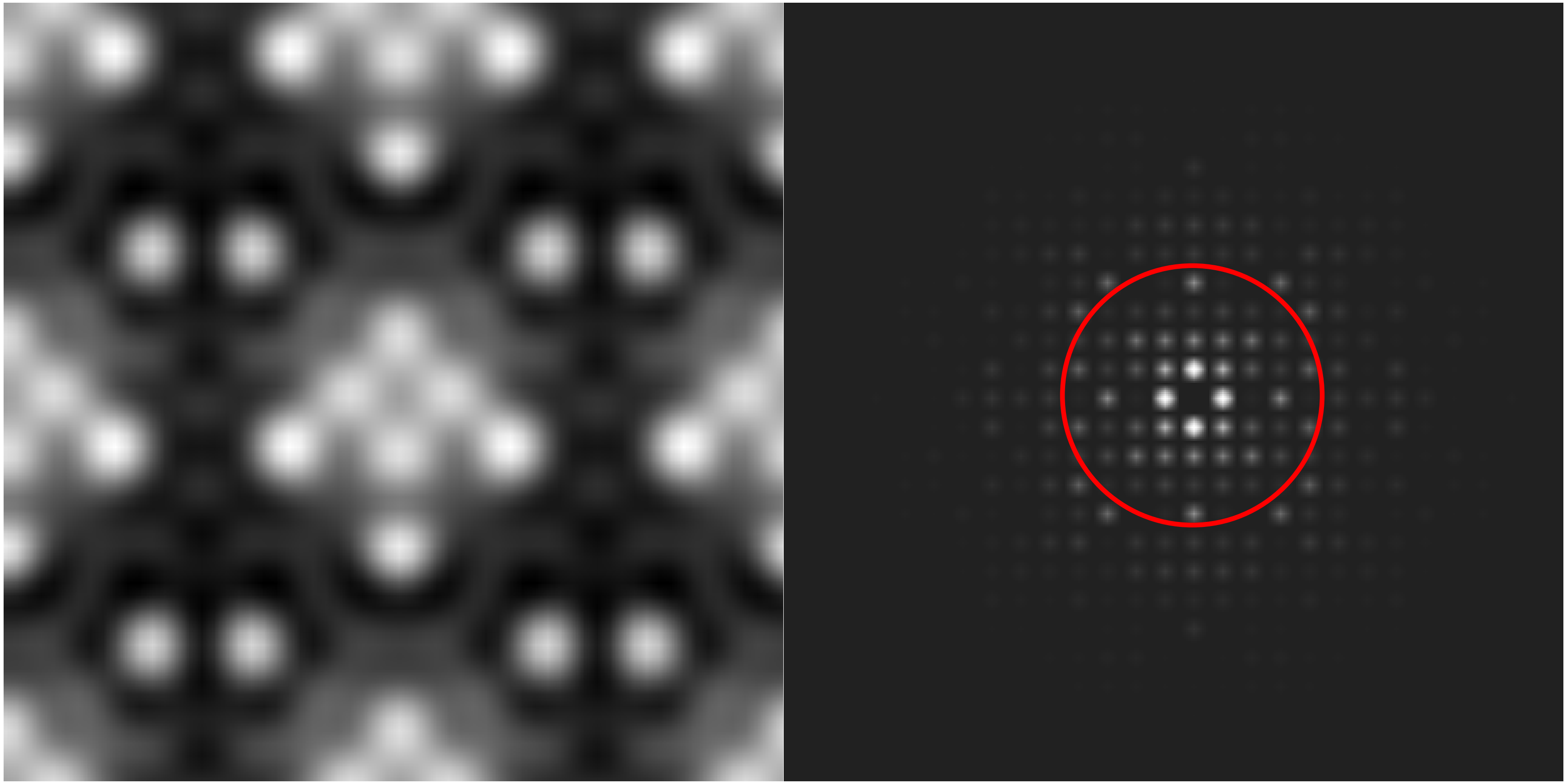


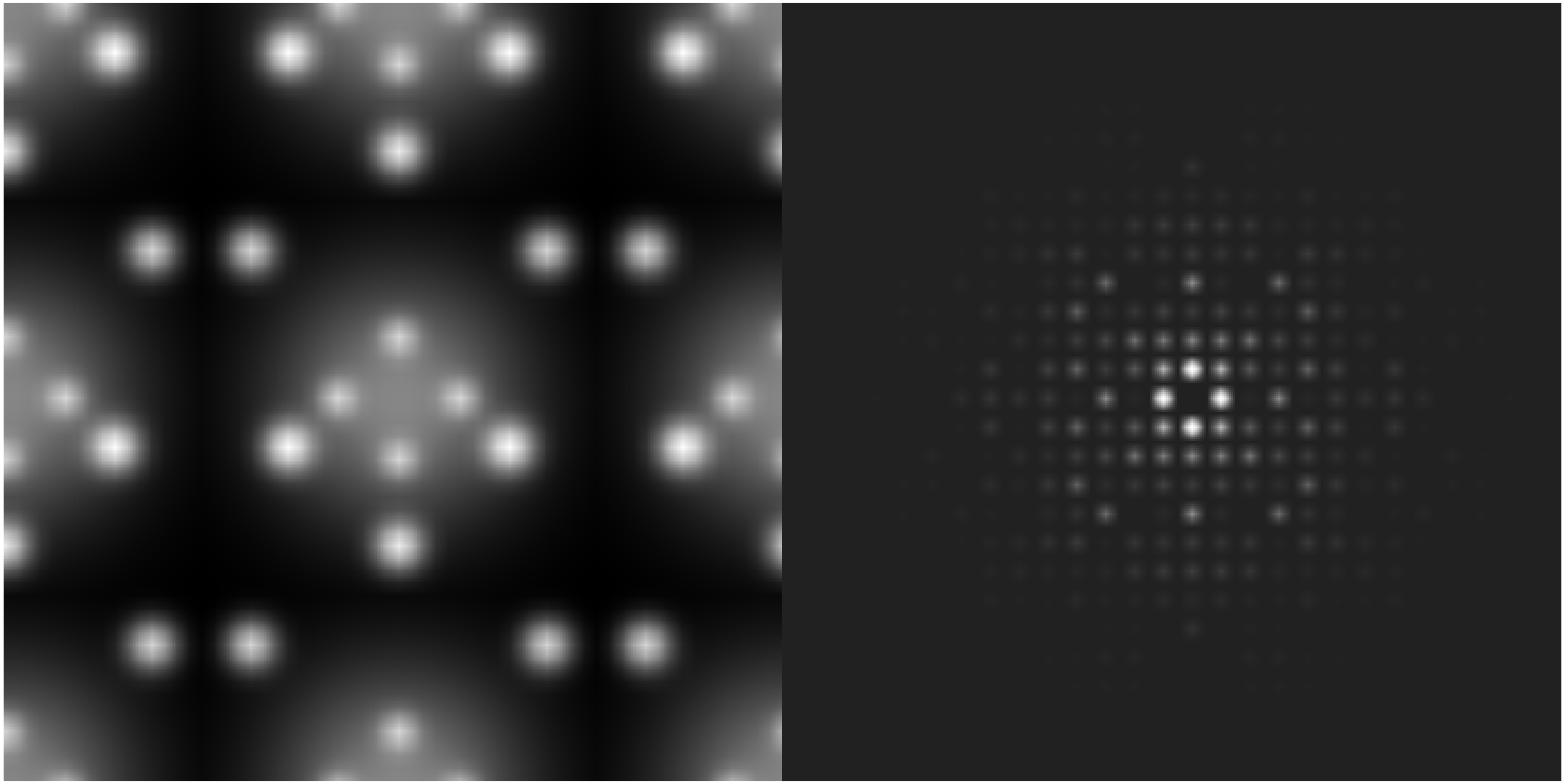


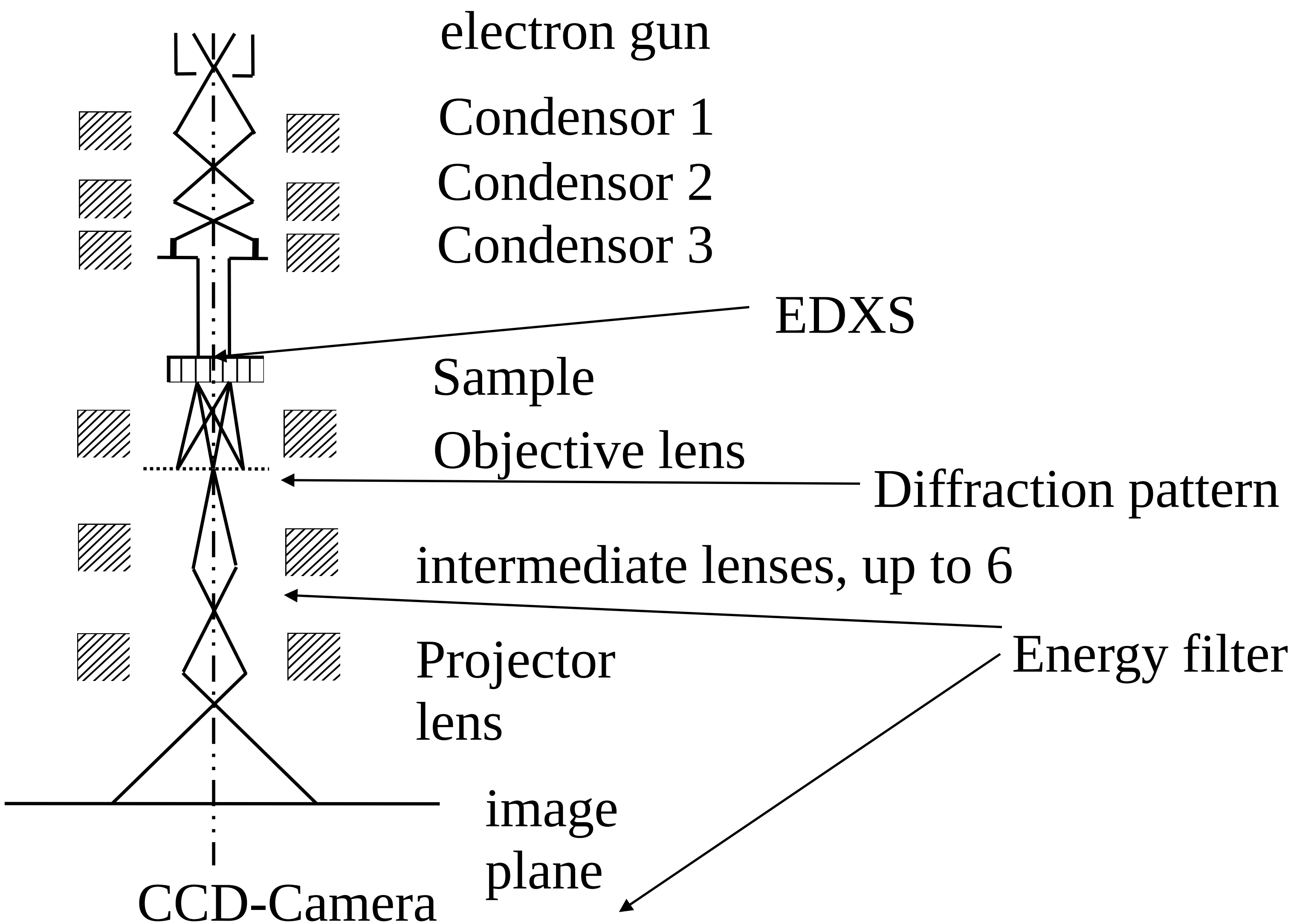
 







Ray Path

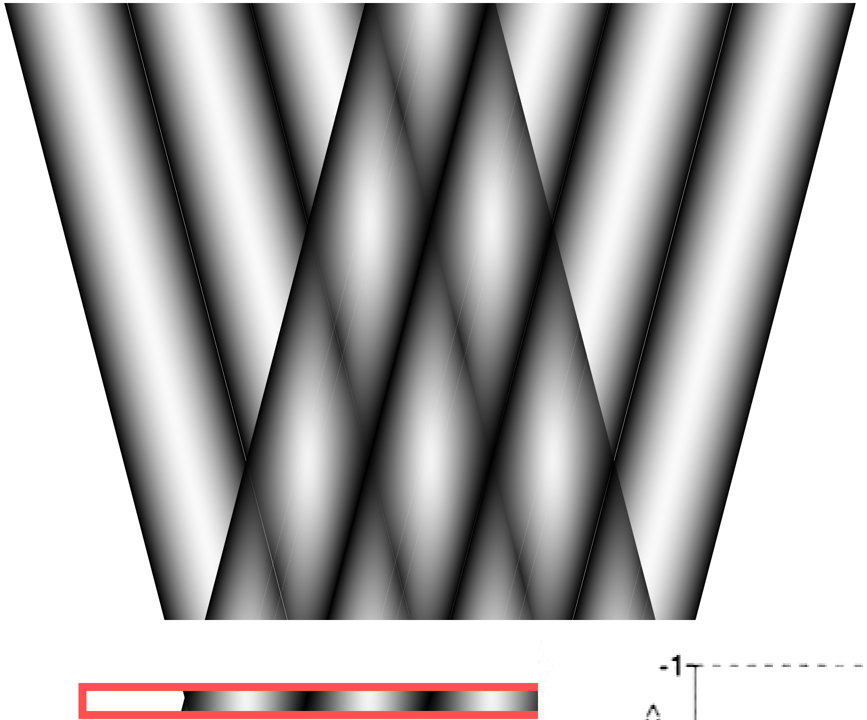


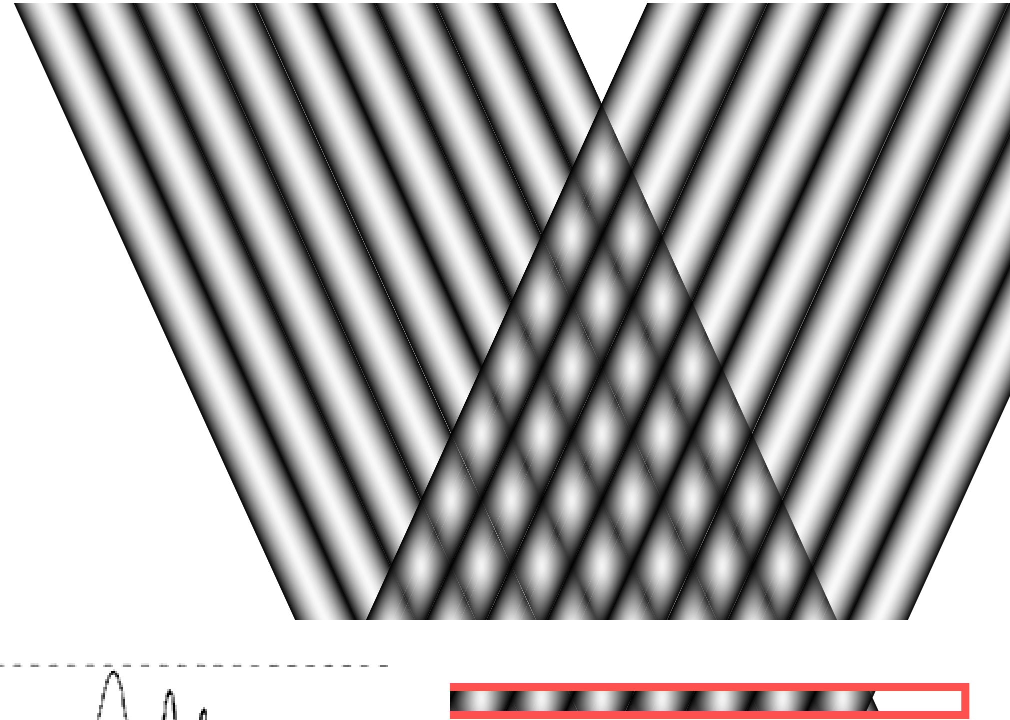
electron gun
Condensor 1
Condensor 2
Condensor 3
EDXS
Sample
Objective lens
Diffraction pattern
intermediate lenses, up to 6
Energy filter
Projector
lens
image
plane
CCD-Camera

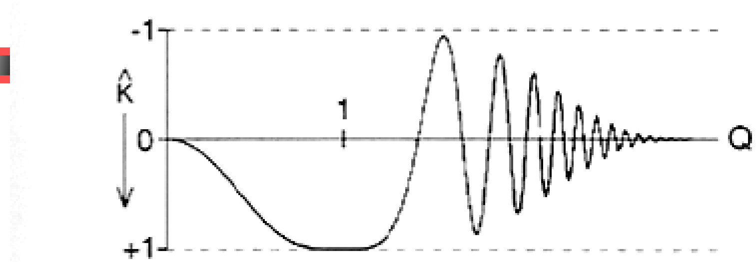
Aberrations

- Microscopes without correctors have lenses about as good as a milk bottle
  - Distortions
  - Some spacings show but should not
  - Some spacings should show but do not
  - Information is often not where it should be

Relation between defocus, contrast & spacing





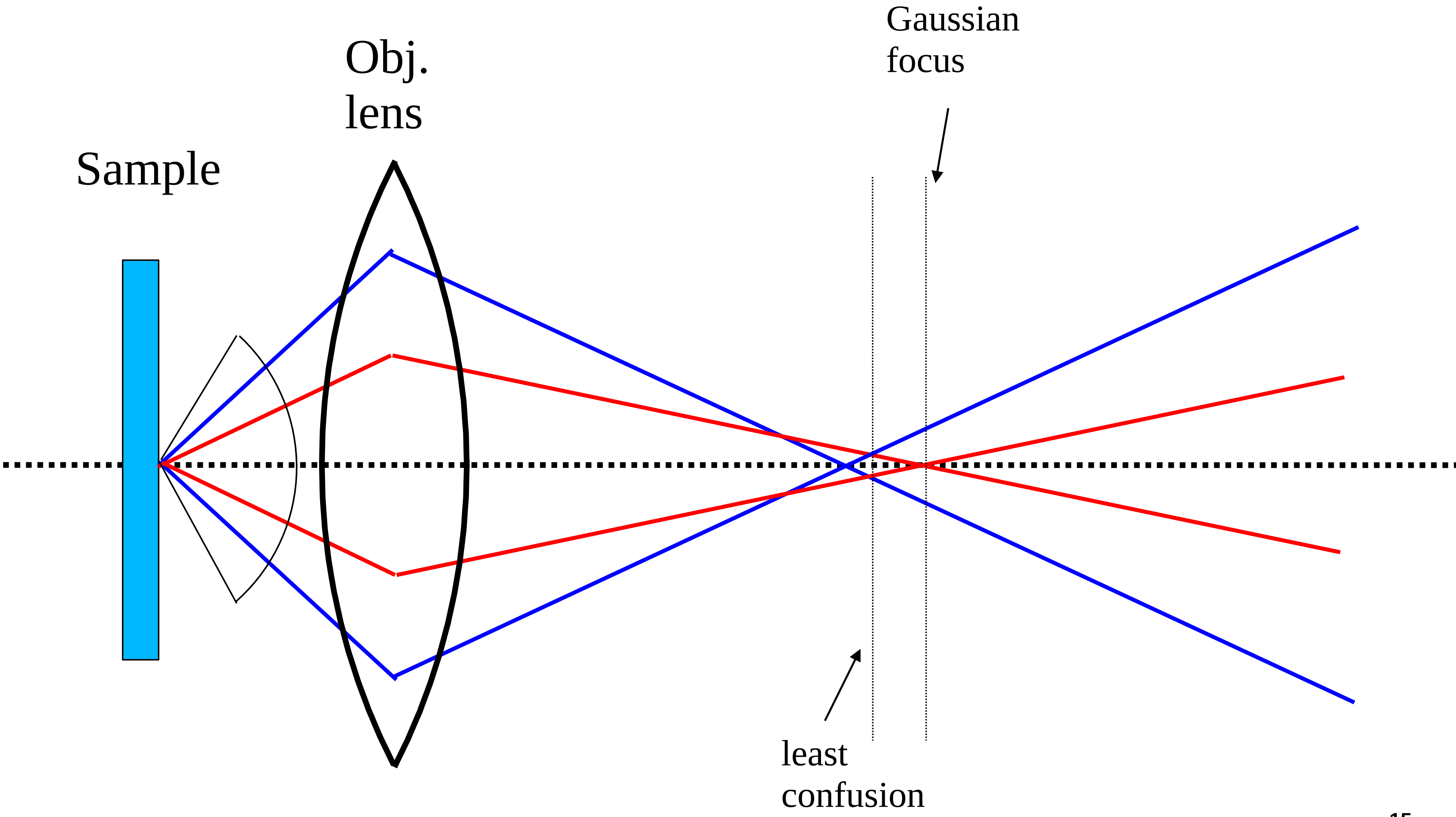


Contrast Transfer Function (CTF) establishes relationship

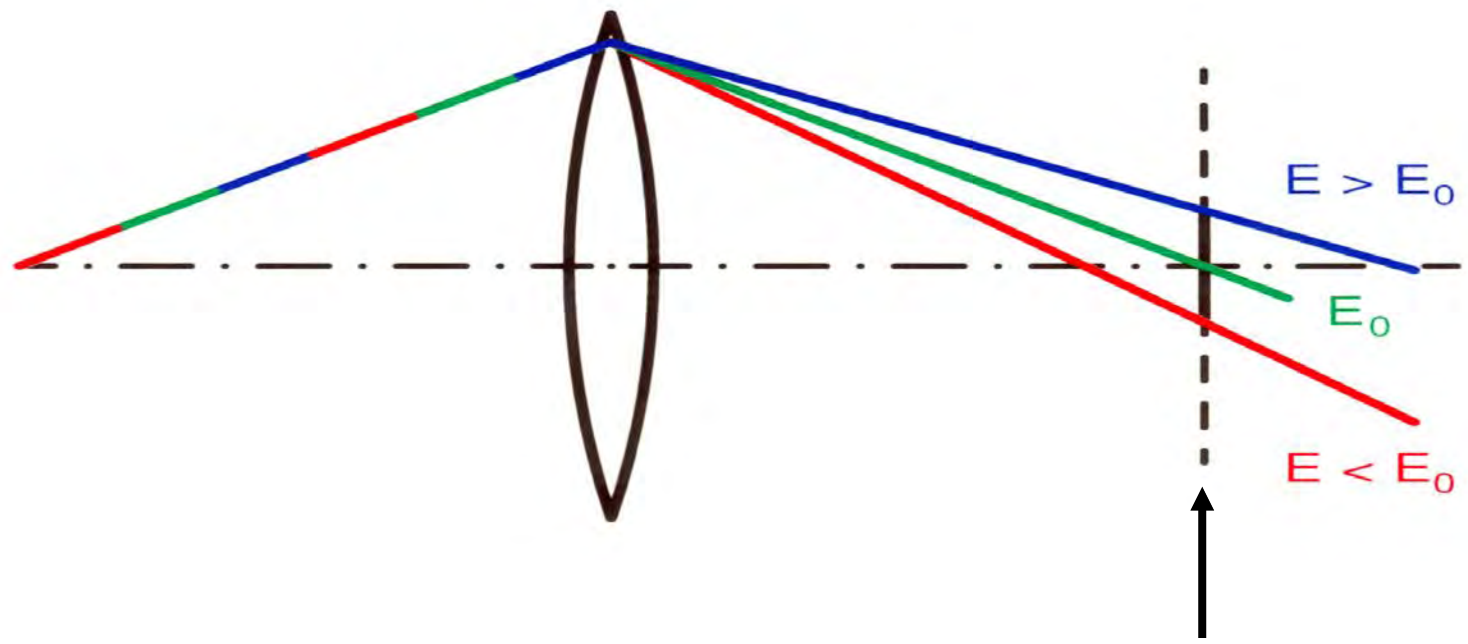
in reciprocal space between spacing (Q) and scale of

amplitude ($\hat{K}$, -1 to 1, dampened with resolution)

Spherical Aberration C_s



Chromatic Aberration.



Focal length of lens is dependent upon wavelength

Aberrations

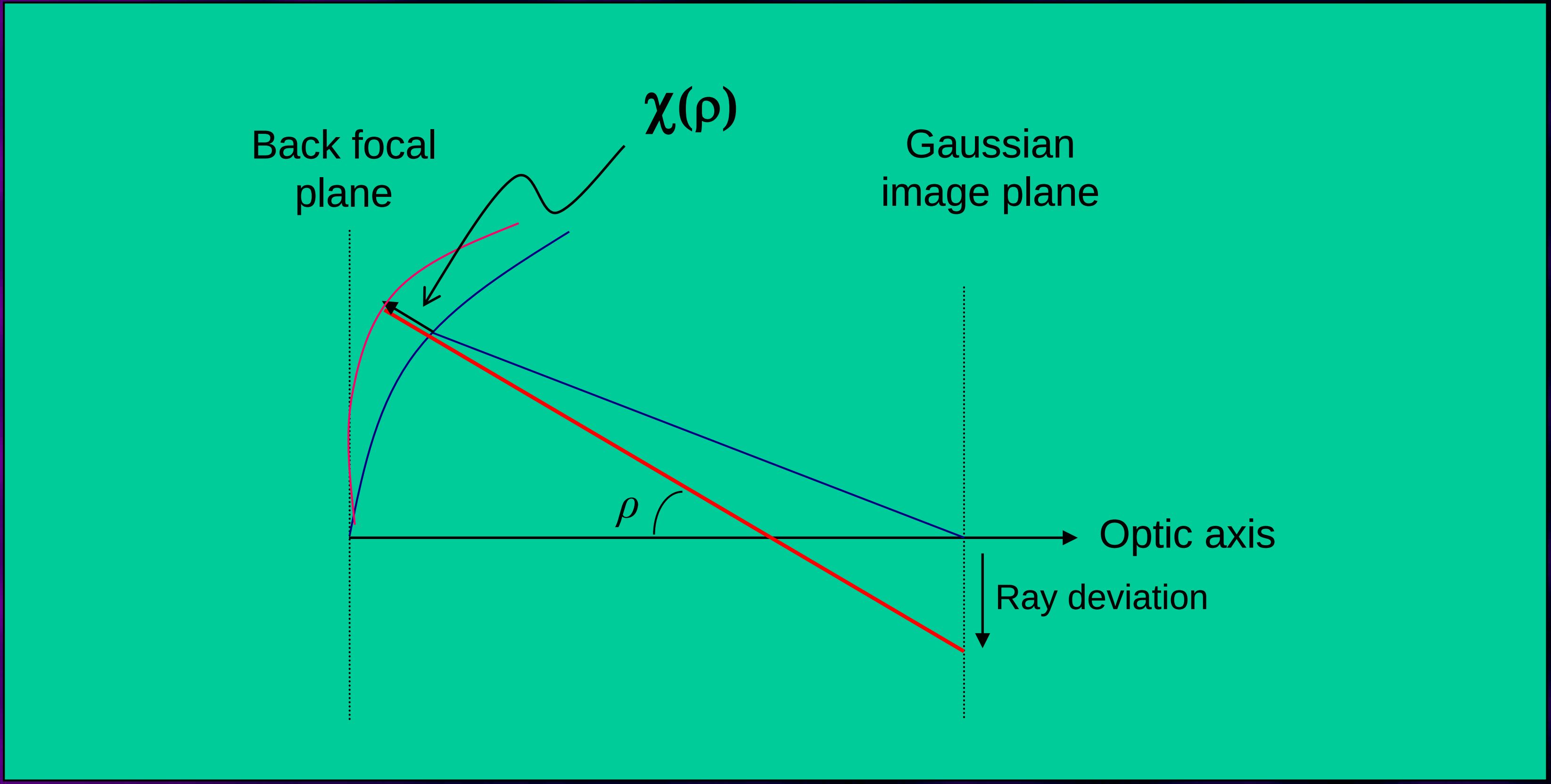
- Aberrations are a phase-shift in reciprocal space
- Multiply by $\exp(-i\chi(u))$
- Can expand as a Taylor series

$\chi(u) = A + Bu + Cu^2 + D(u.a) + \ldots$

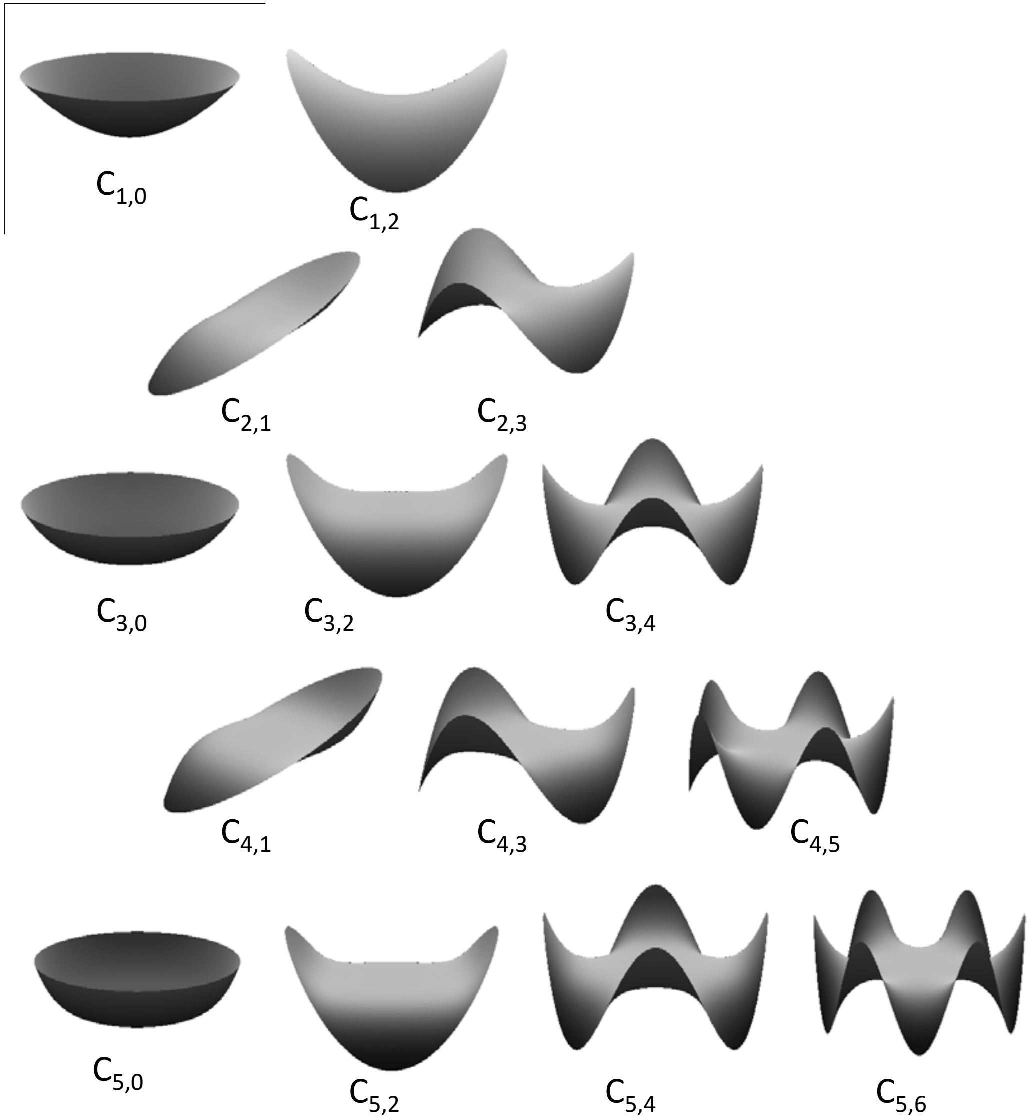
A,B don't matter

C is defocus, D is astigmatism, Cs has u^4

- The χ function can be expanded (as with any function) as a polynomial radially and harmonic function azimuthally



Aberrations



Basics of HREM (very incomplete)

Phase contrast transfer function:

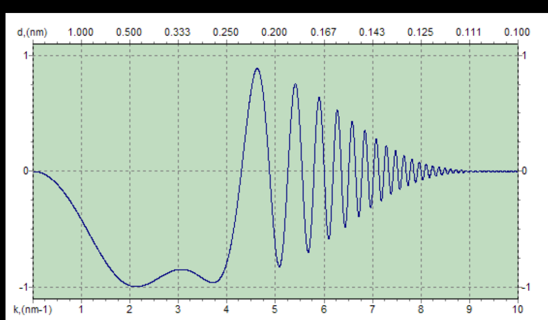
$T(u) \sim \sin(\pi C_s \lambda^3 u^4/2 + \pi \Delta z \lambda u^2)E(u)$.

Cs: Spherical aberration constant.

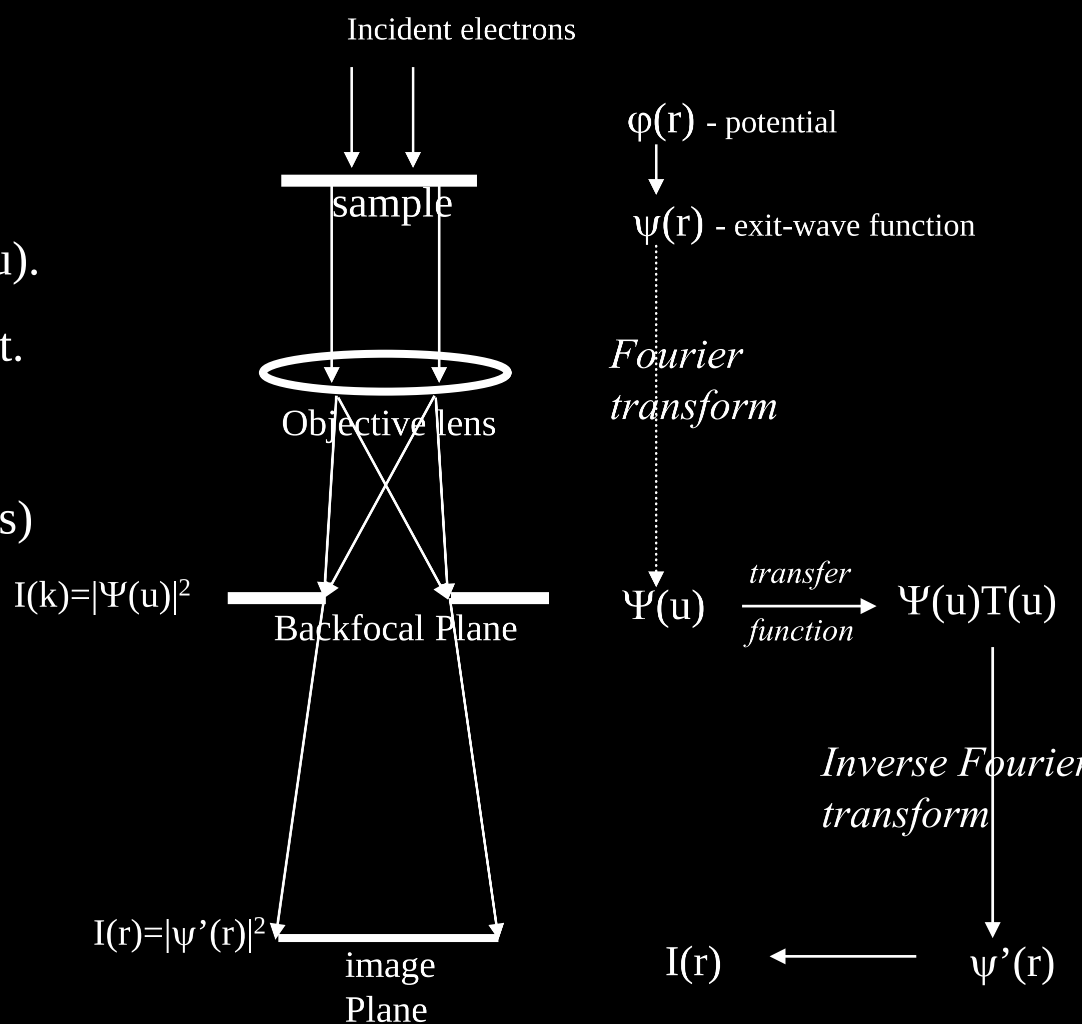
Δz: defocus value.

E(u): Envelope term (instabilities)

Only approximately right



Phase contrast transfer function calculated at Δf=-61 nm with Cs=1.0 mm.



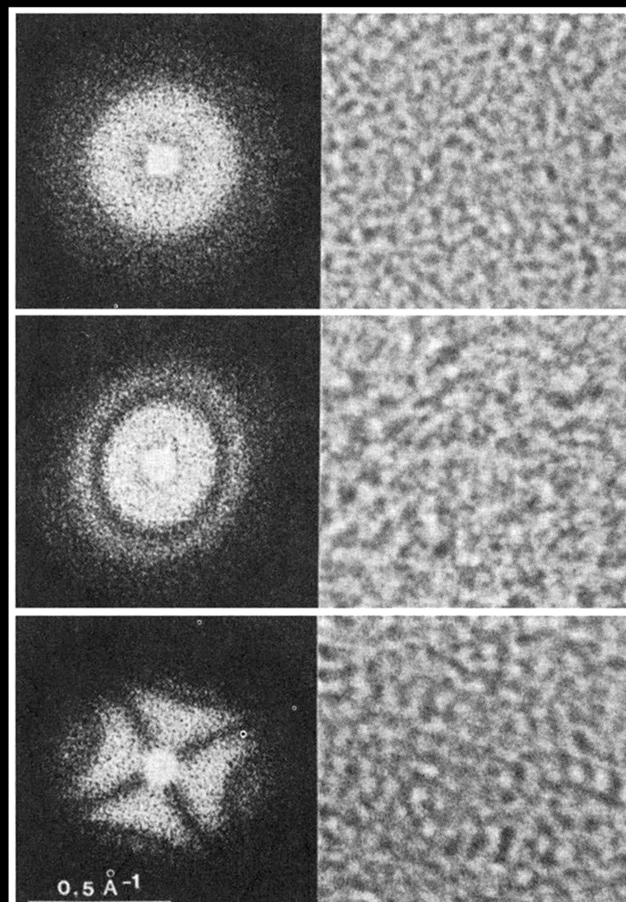
Astigmatism Correction

FFT pattern of amorphous area

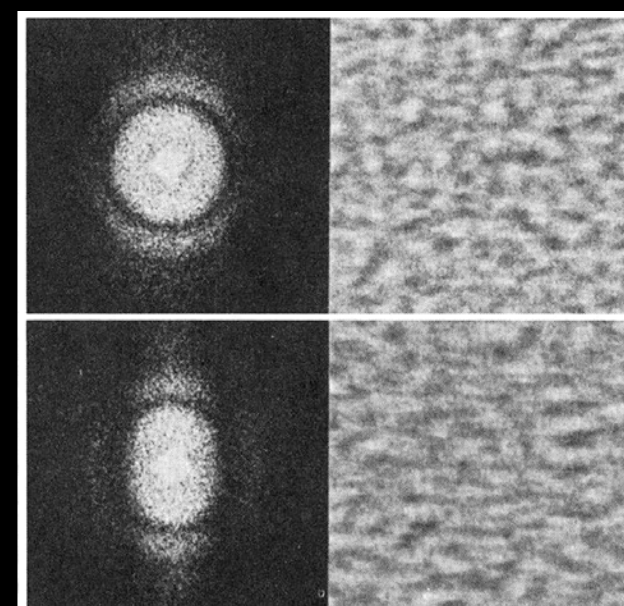
(Real-time processing

Well aligned

Misaligned

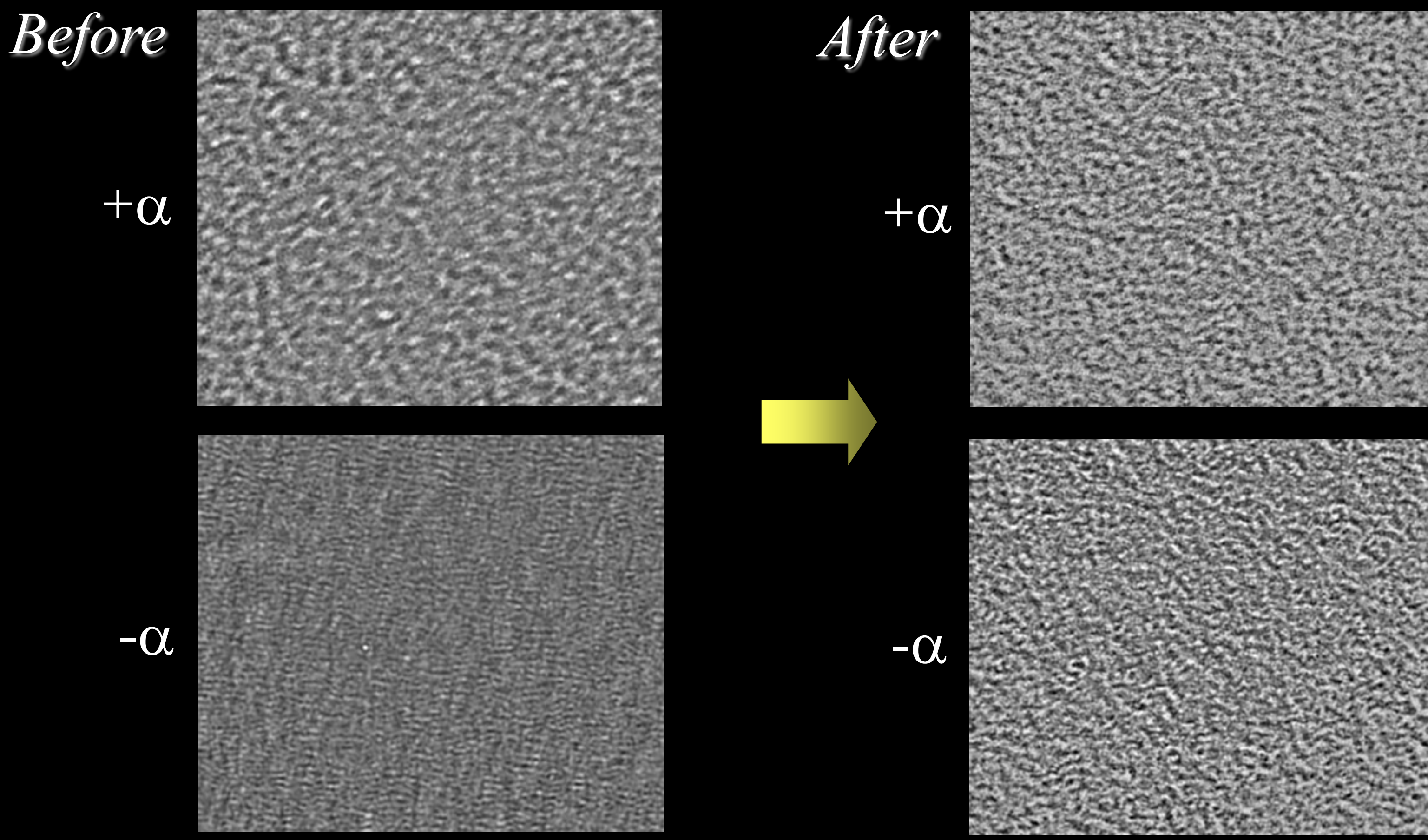


Drift

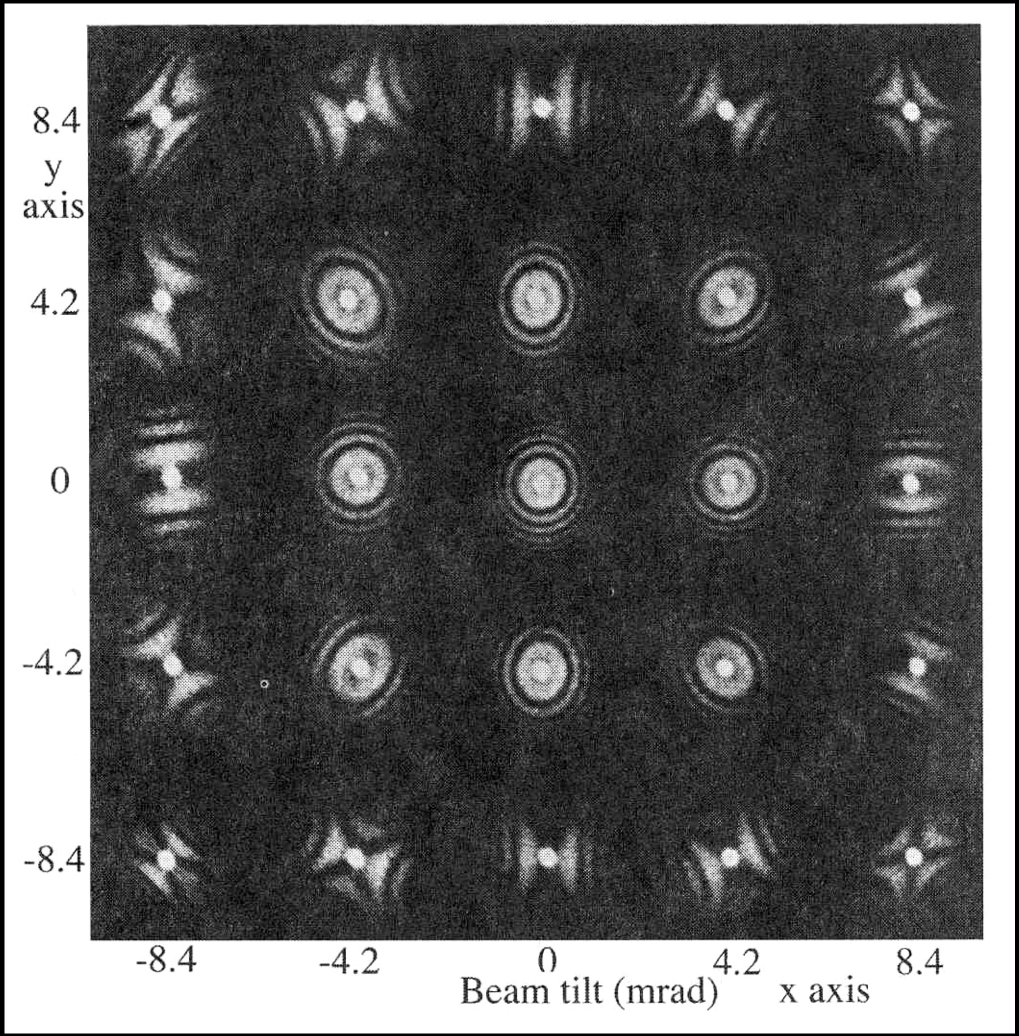


Coma-Free Alignment

Carbon foil images obtained at two different angles of the incident beam, before and after coma-free alignment.



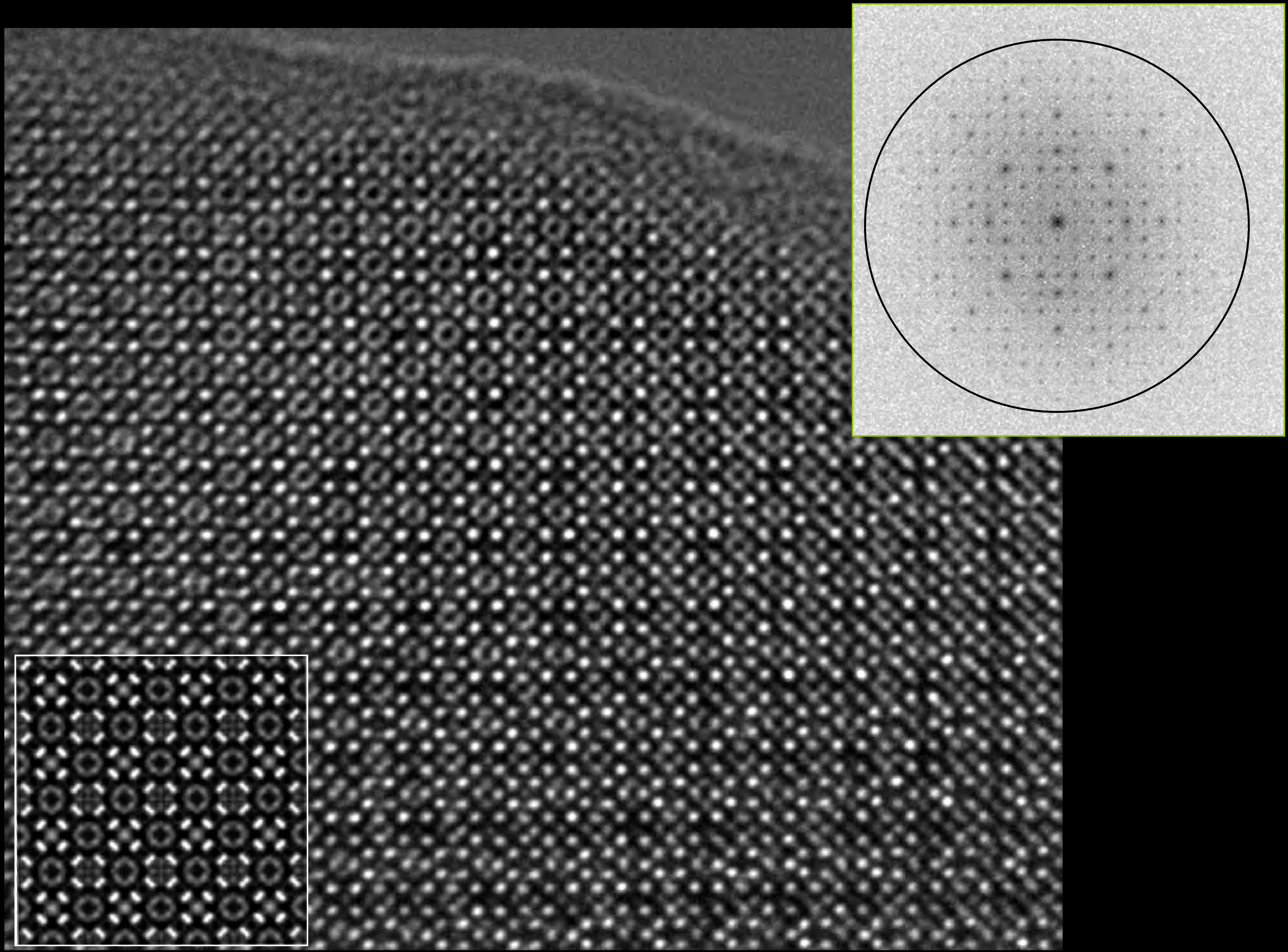
Effect of Beam Tilt on Diffractograms

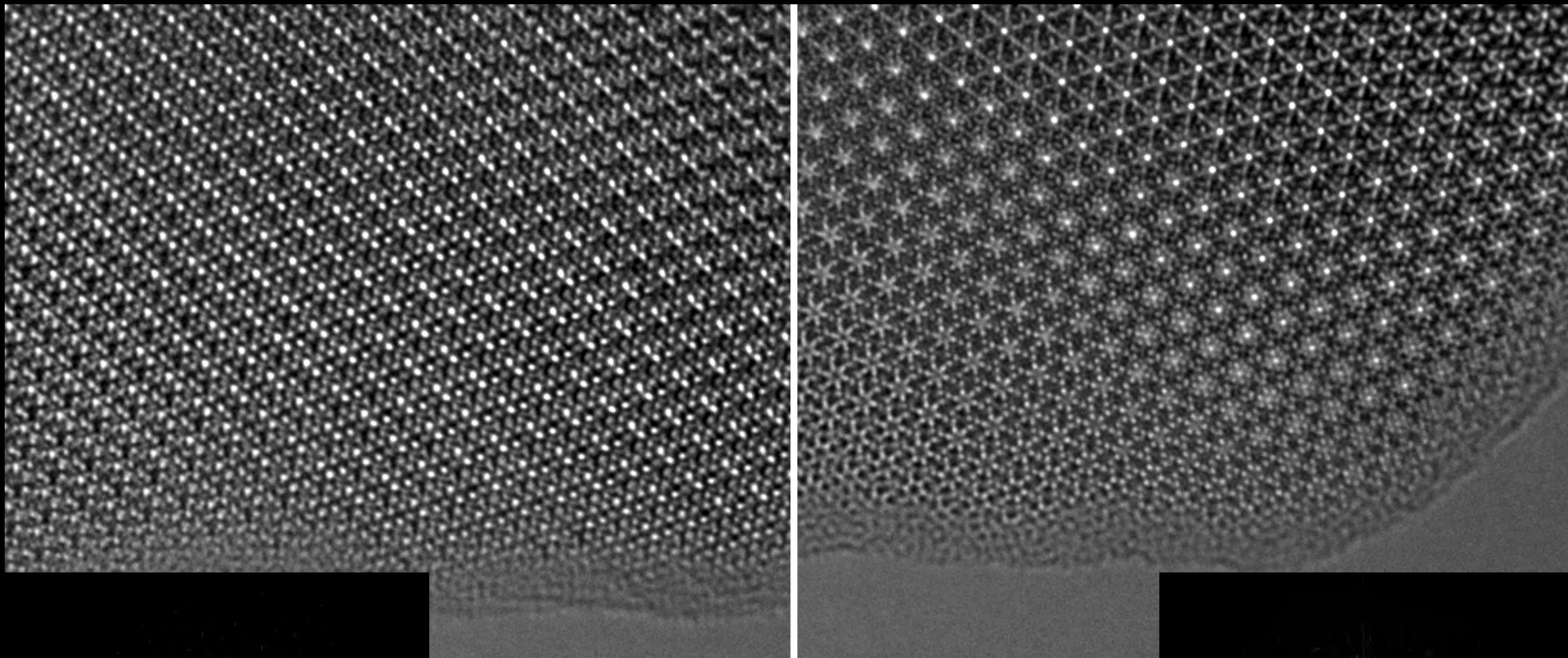


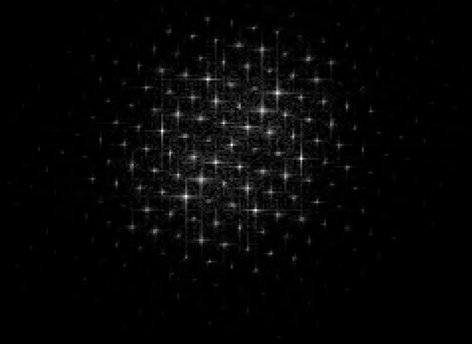
Diffractograms (FFT patterns of amorphous regions)

Similar to the effect of astigmatism

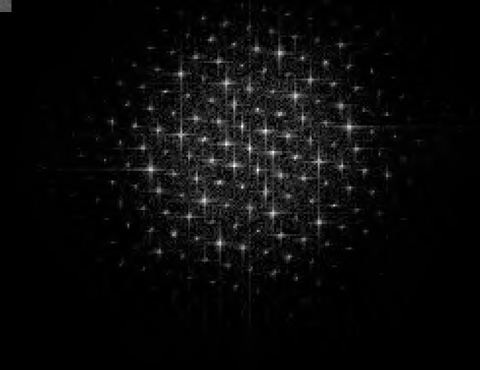
Astigmatism correction may be required after the alignment of beam tilt.



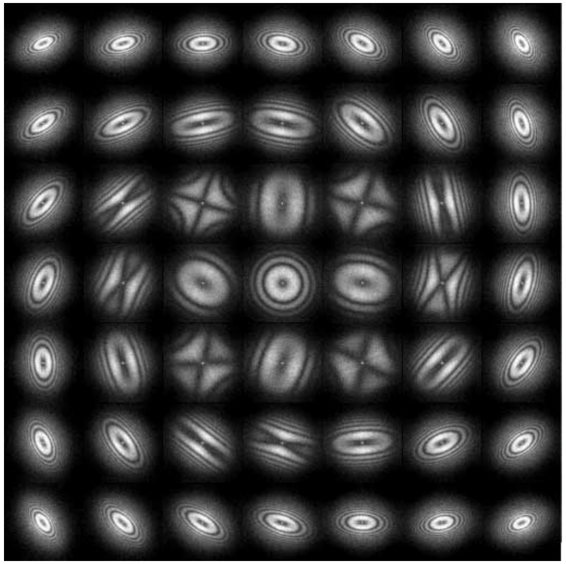


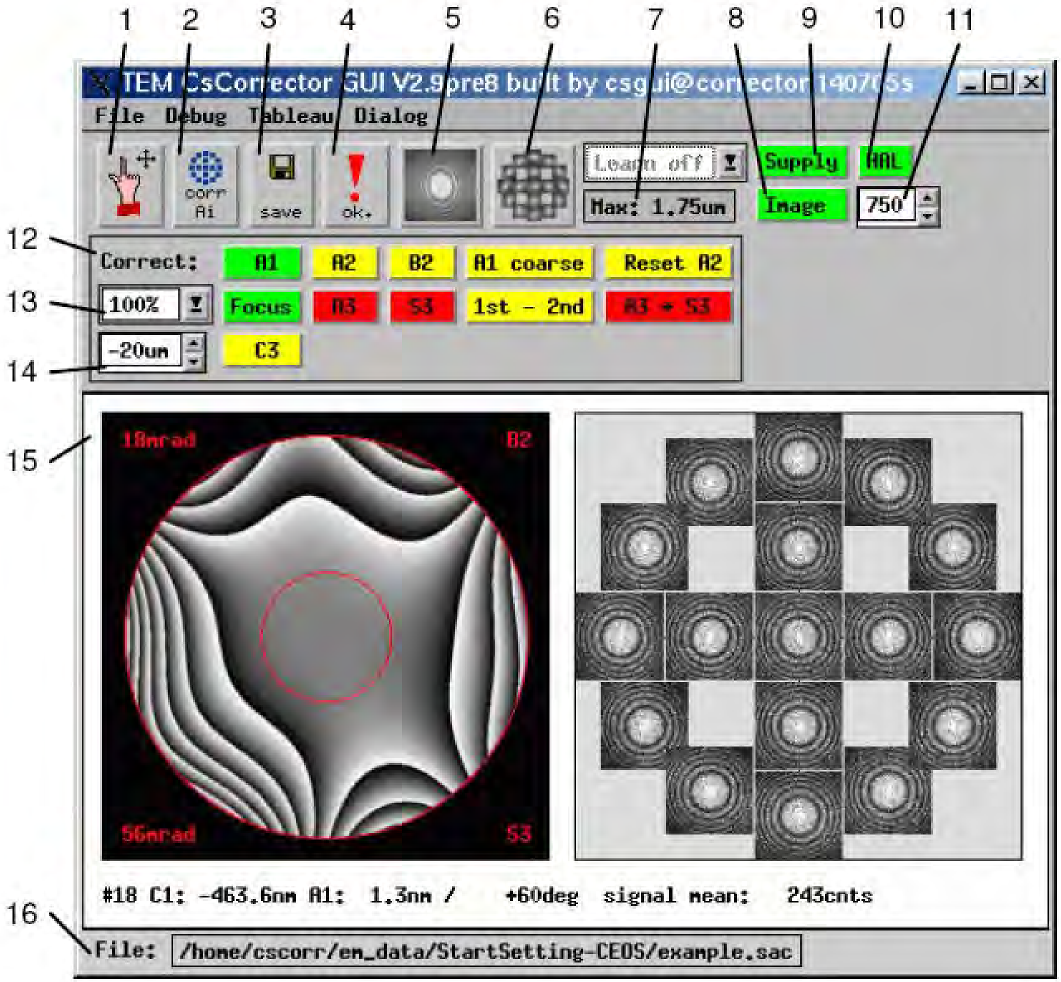


effect of slight
beam tilt

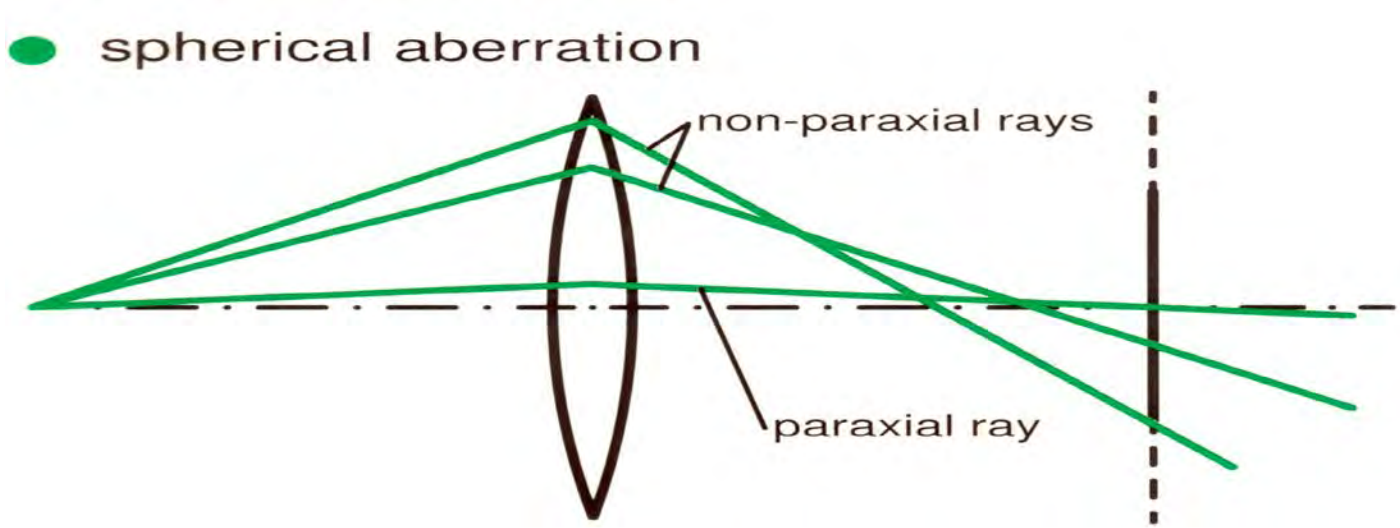


Computer Interface.





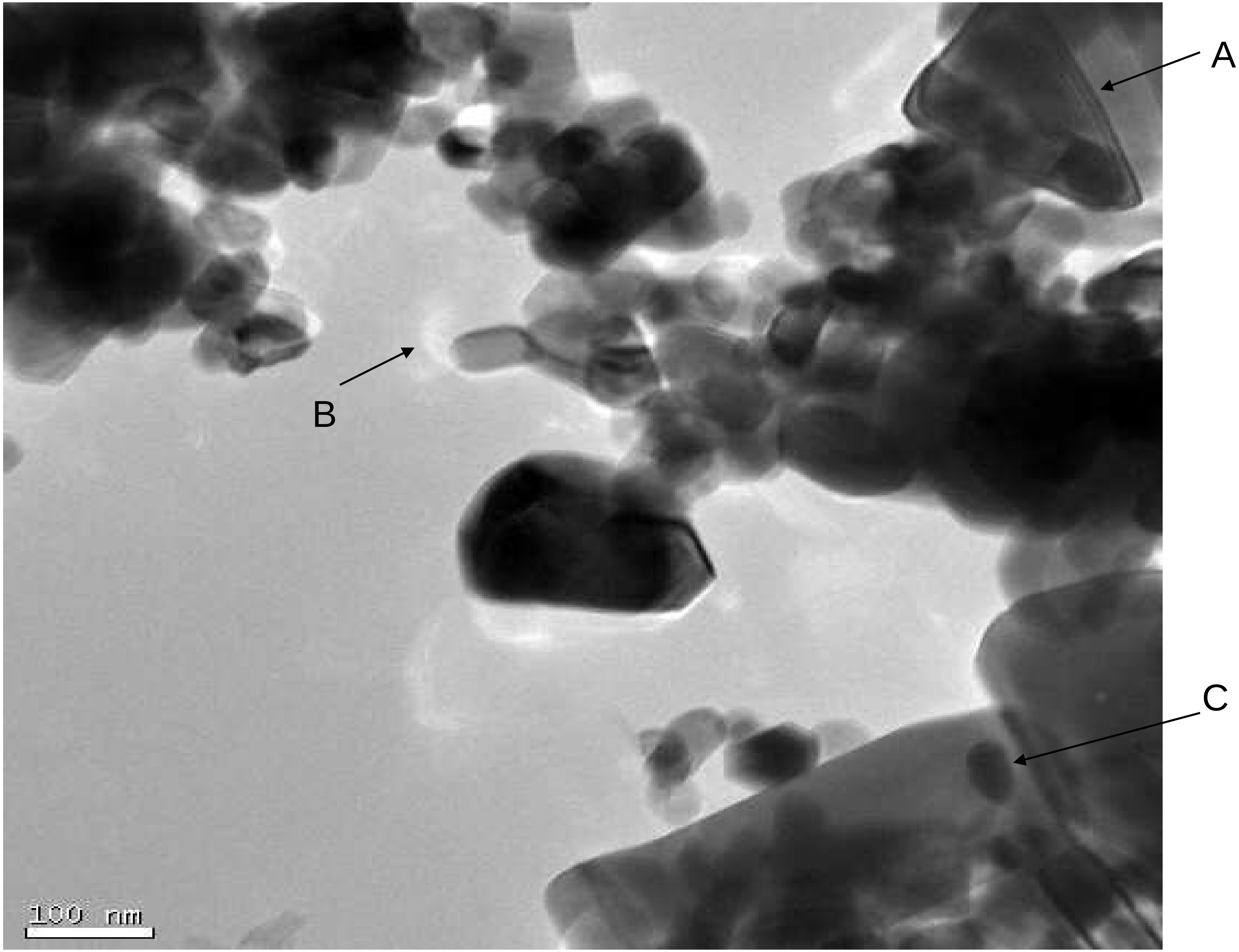
Positional Errors

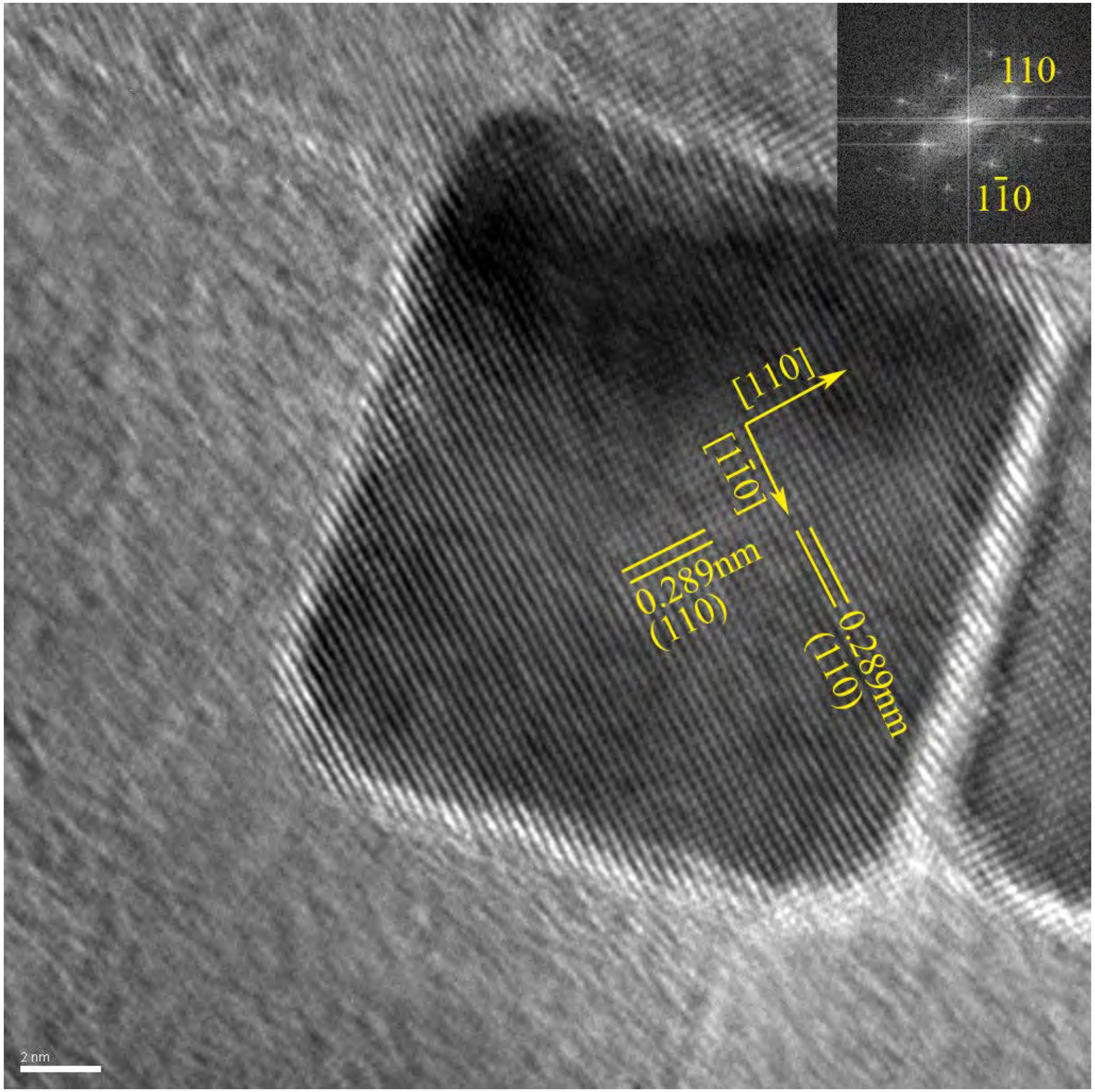


$\exp(-i\chi(u))$

$\chi(g+u) = \chi(g) + u.\nabla\chi(g) + \ldots$

Last term leads to a shift of $\nabla\chi(g)/2\pi$


A
B
C
100 nm

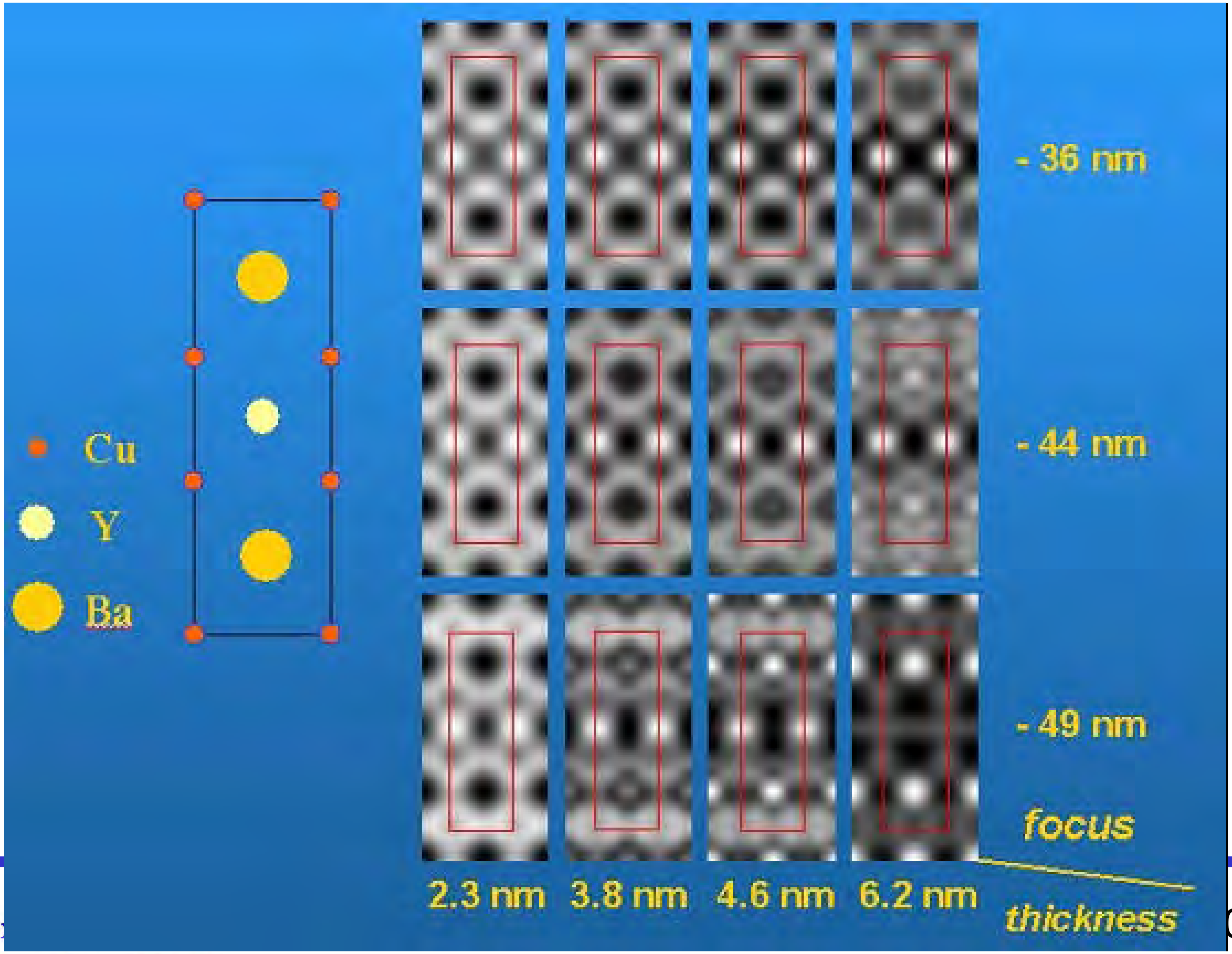


$Ba_{0.5}Sr_{0.5}TiO_3$ HRETM

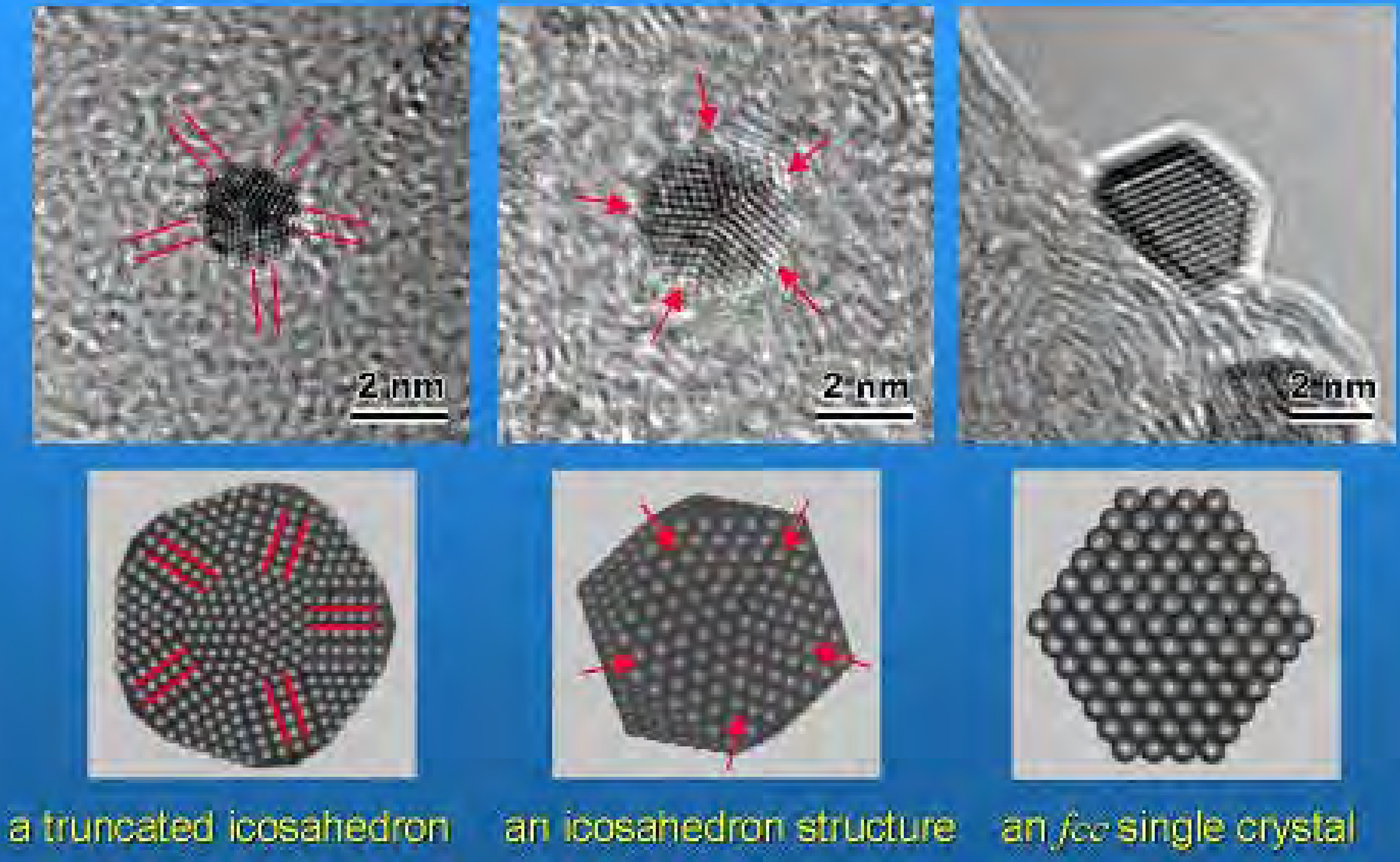
The surface lattice of $Ba_{0.5}Sr_{0.5}TiO_3$ is 0.289nm,which is consistent with that of $BaTiO_3$ (110), suggesting that it is possible core-shell structure.

BaTiO3 d(110)=2.850A=0.285nm(PDF 31-0174)

High Resolution Electron Microscopy image simulation – influence of thickness of defocus



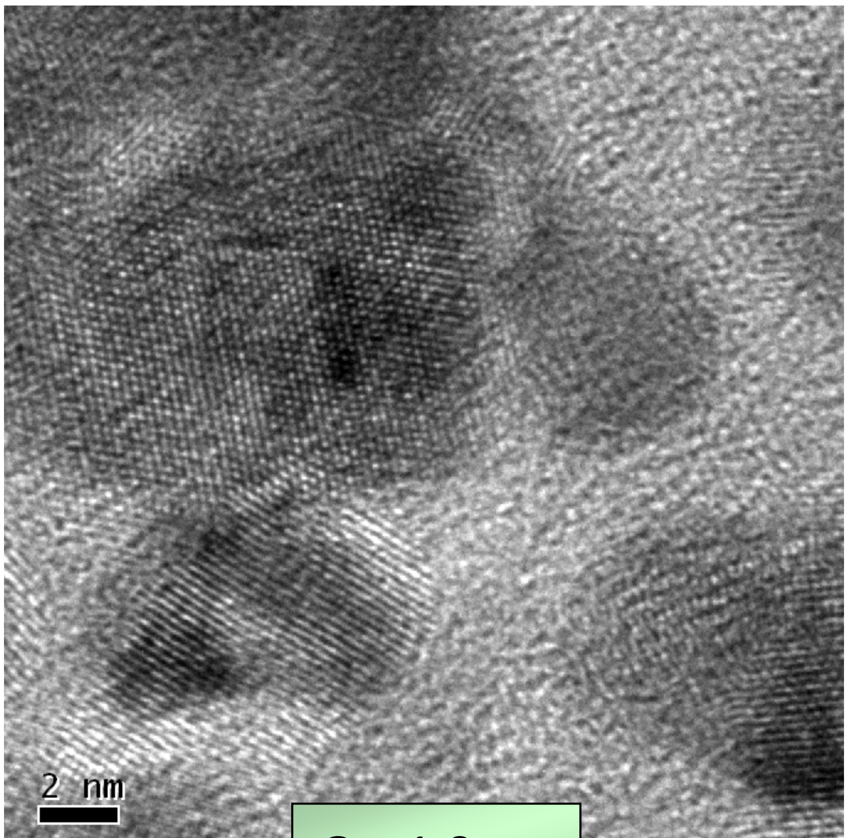
Shape Determination of Au Nanoparticles



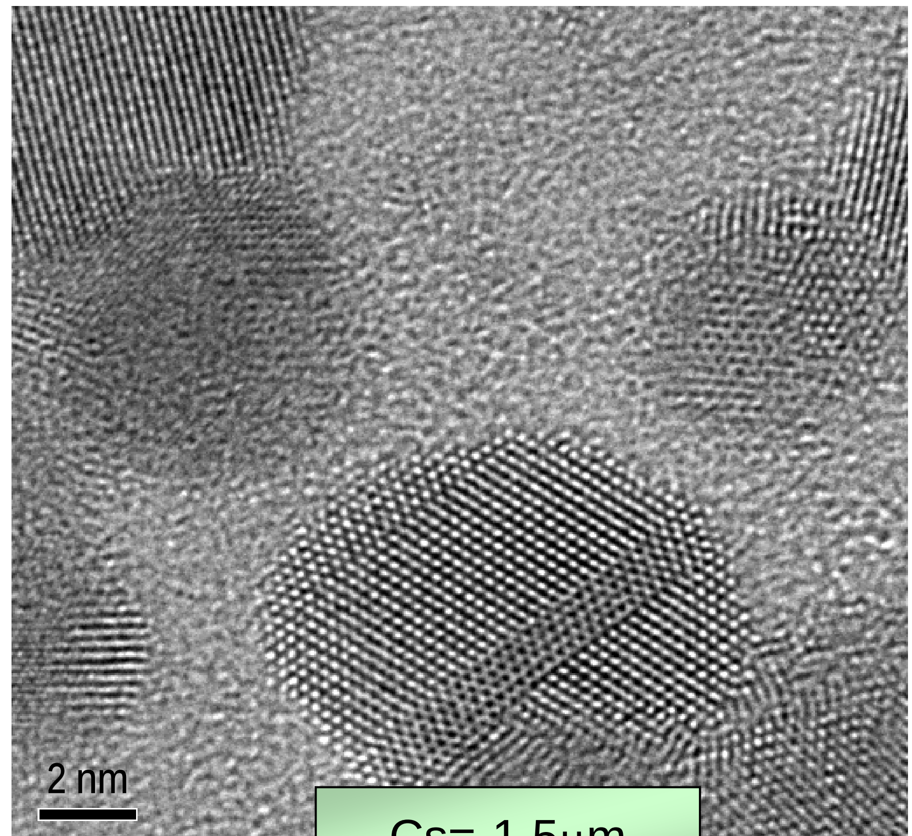
With/Without an imaging Cs-corrector

Gold nano-particles on carbon film

Not only the resolution is improved, but also the delocalization is minimized



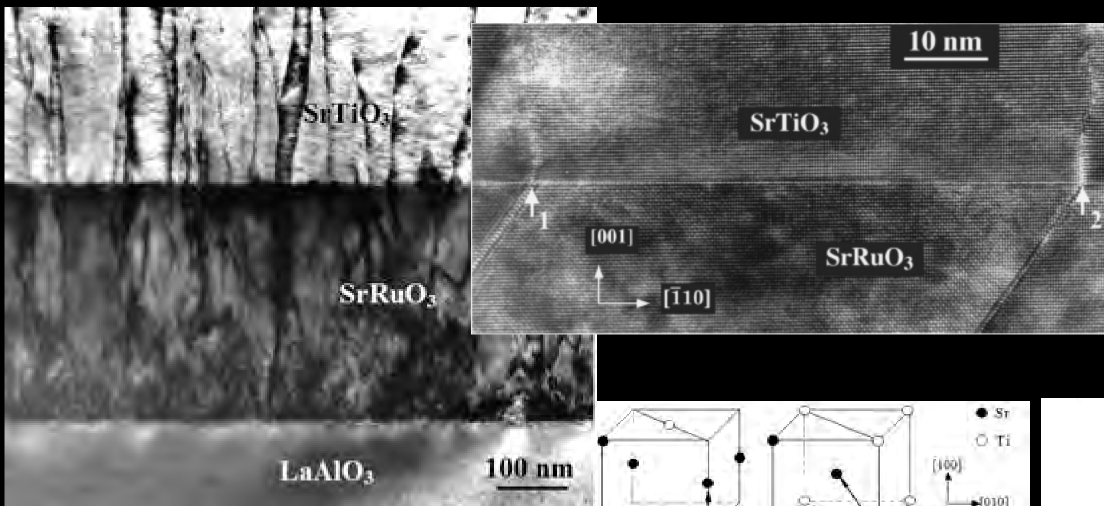
Cs=1.2mm

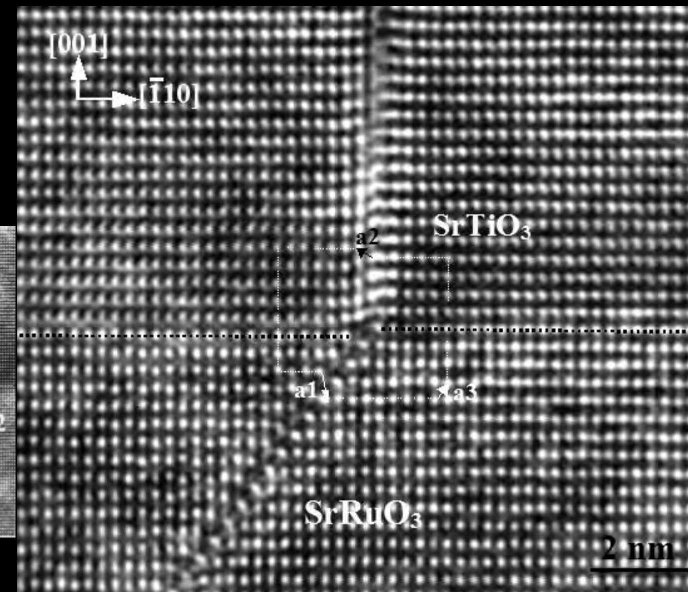


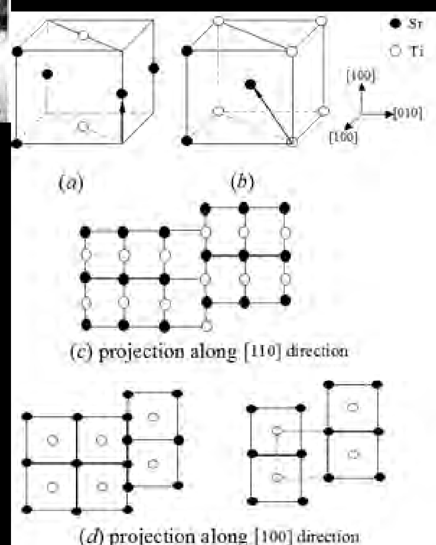
Cs=-1.5μm

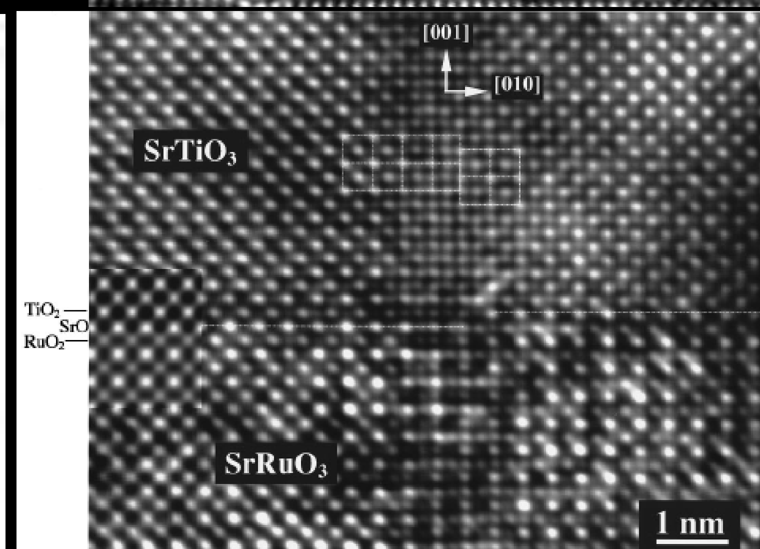
Examples

High-Resolution Electron Microscopy: Interfaces



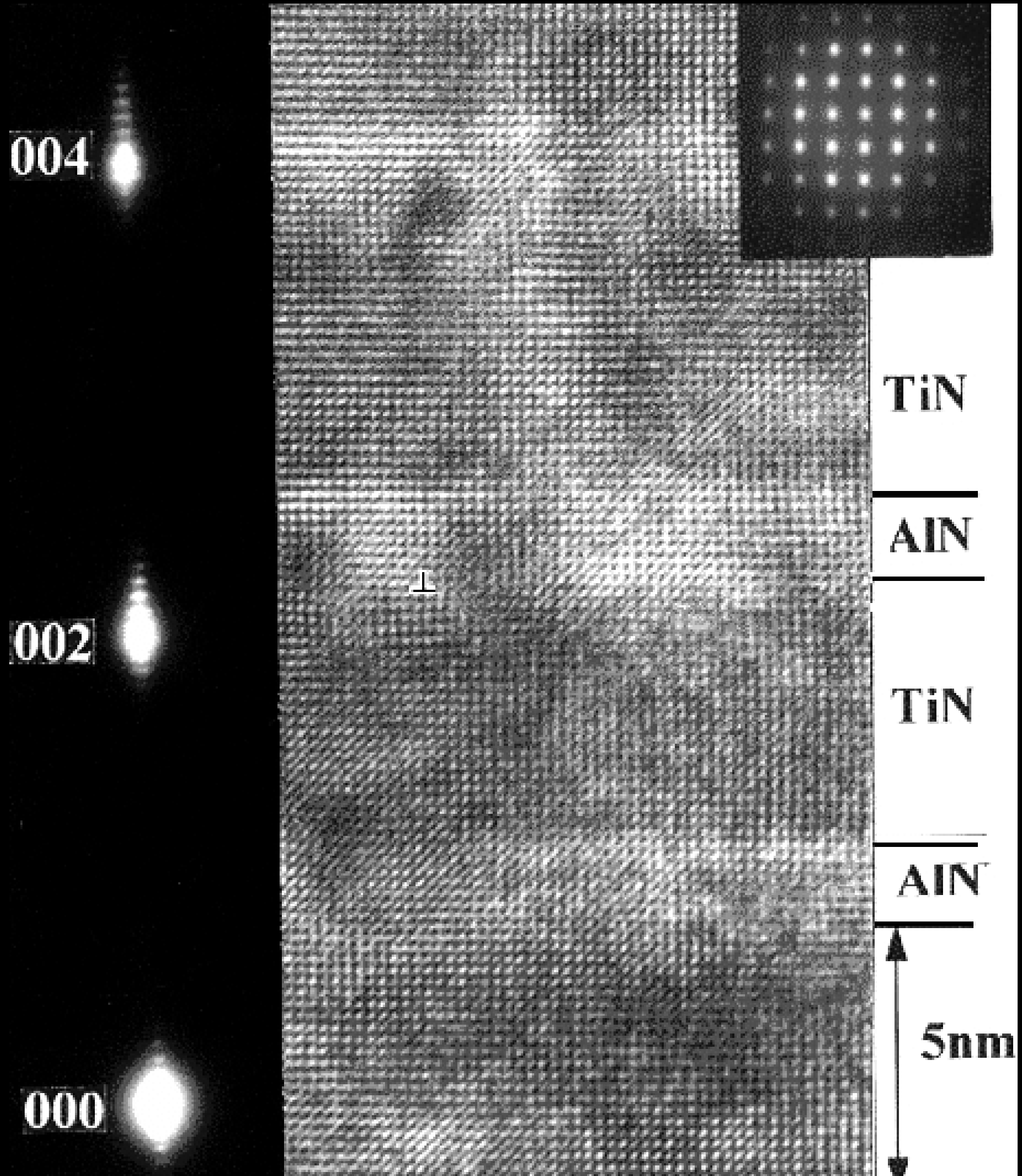


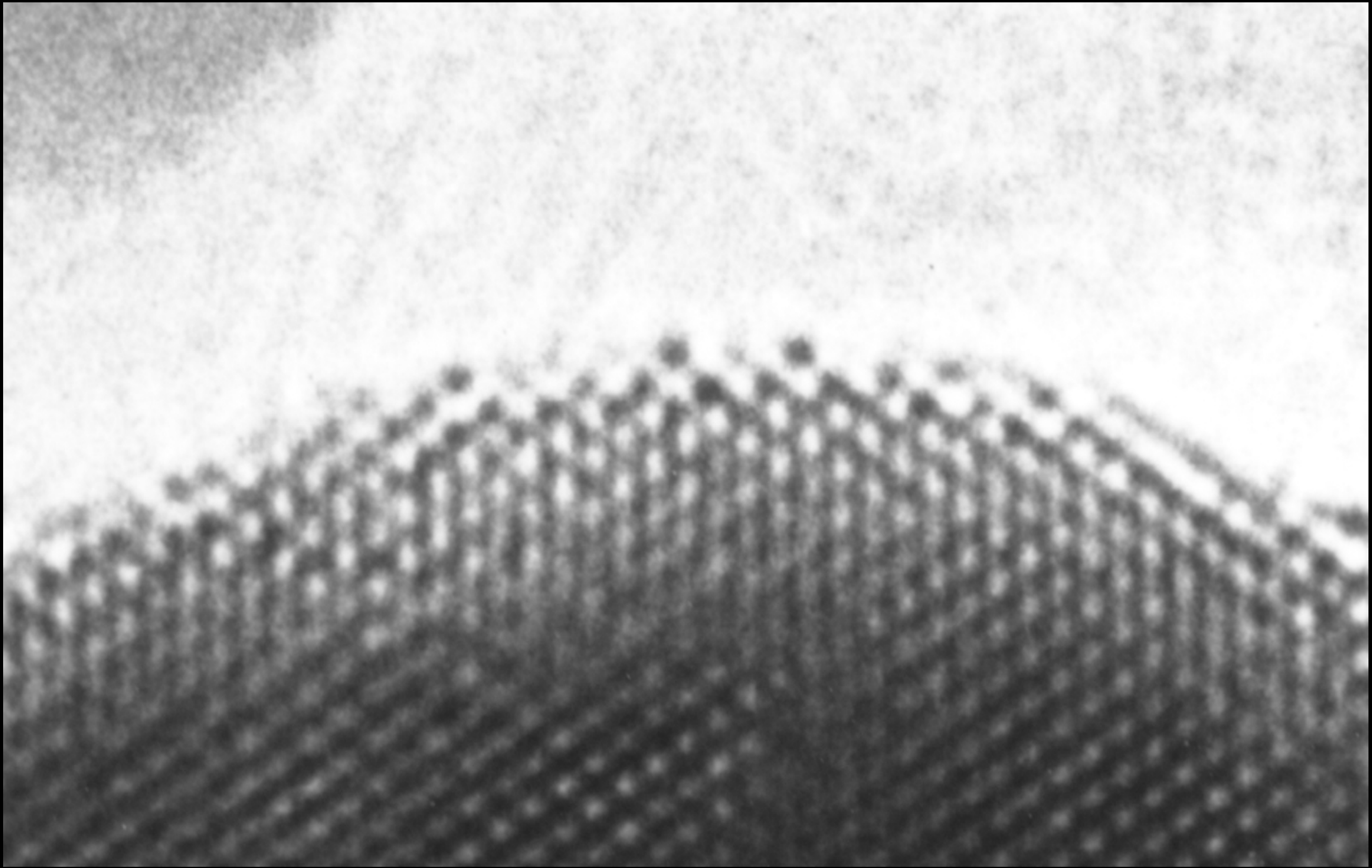


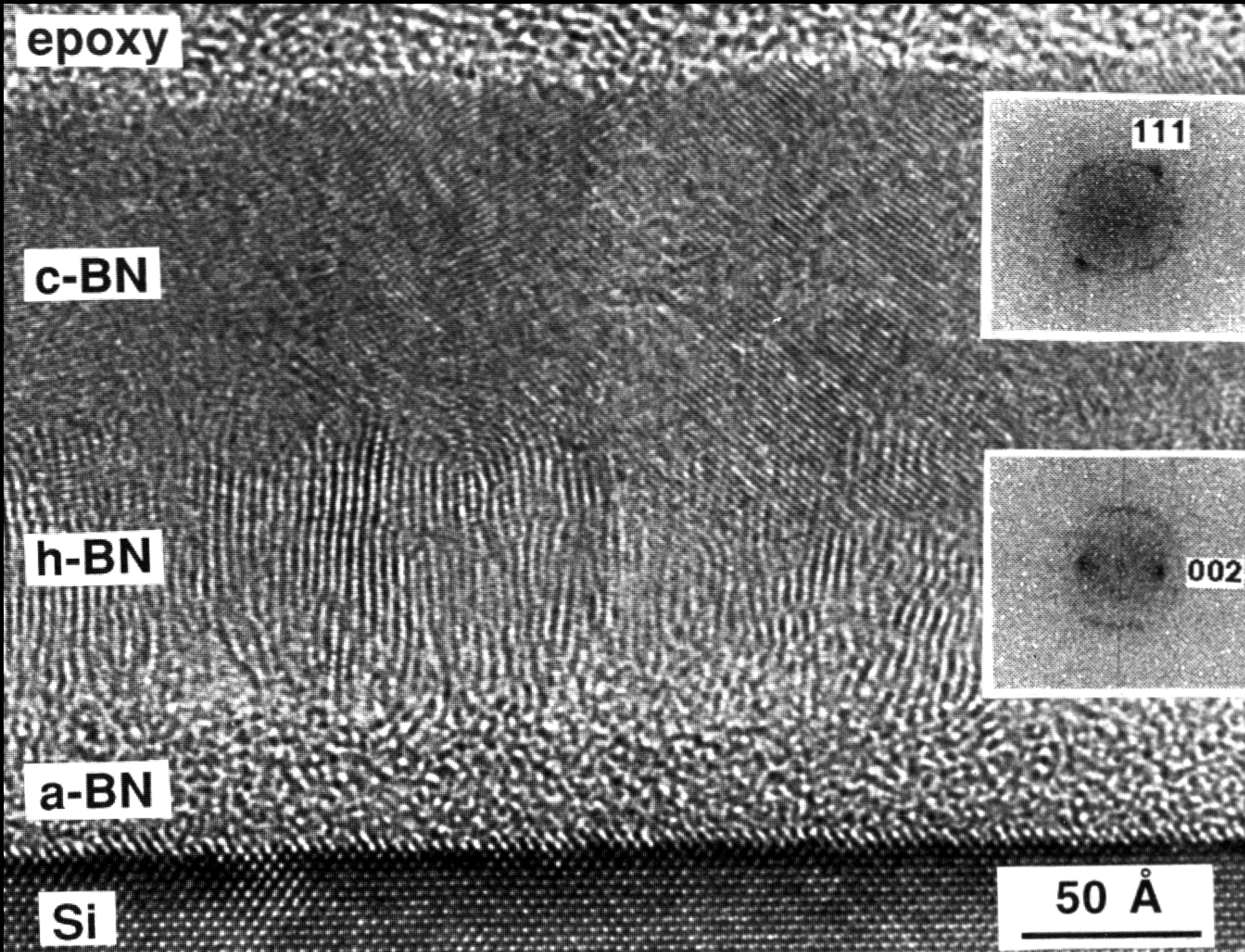


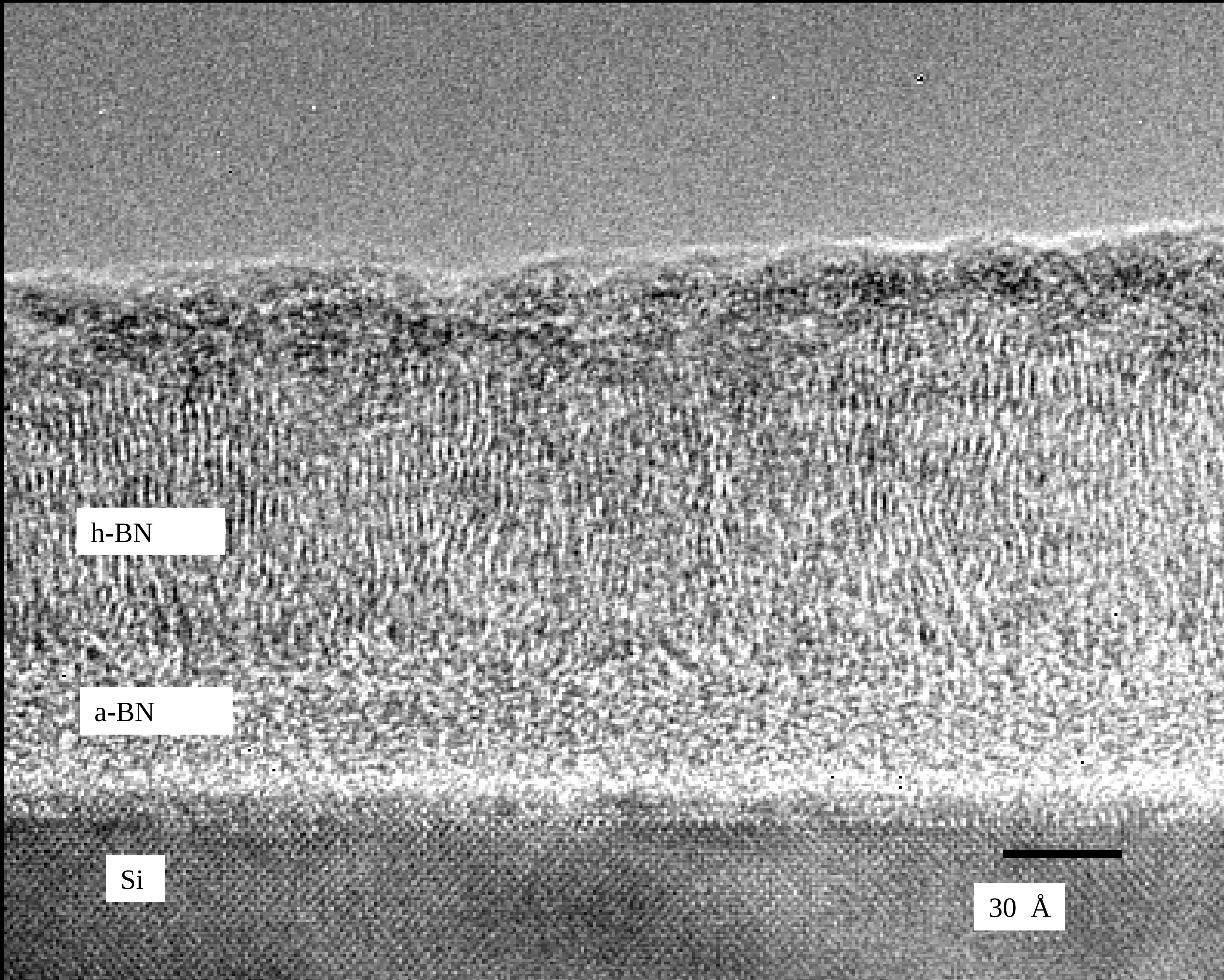
Columnar grain boundaries in SrTiO3 film are associated with {111} planar defects in the $SrRuO_3$ layer. Two atomic structural models of the antiphase boundaries in the (-110) plane, with a crystallographic shear vector ***R***=*a*/2[001] (a) and ***R***=*a*/2[-1-11] (b).

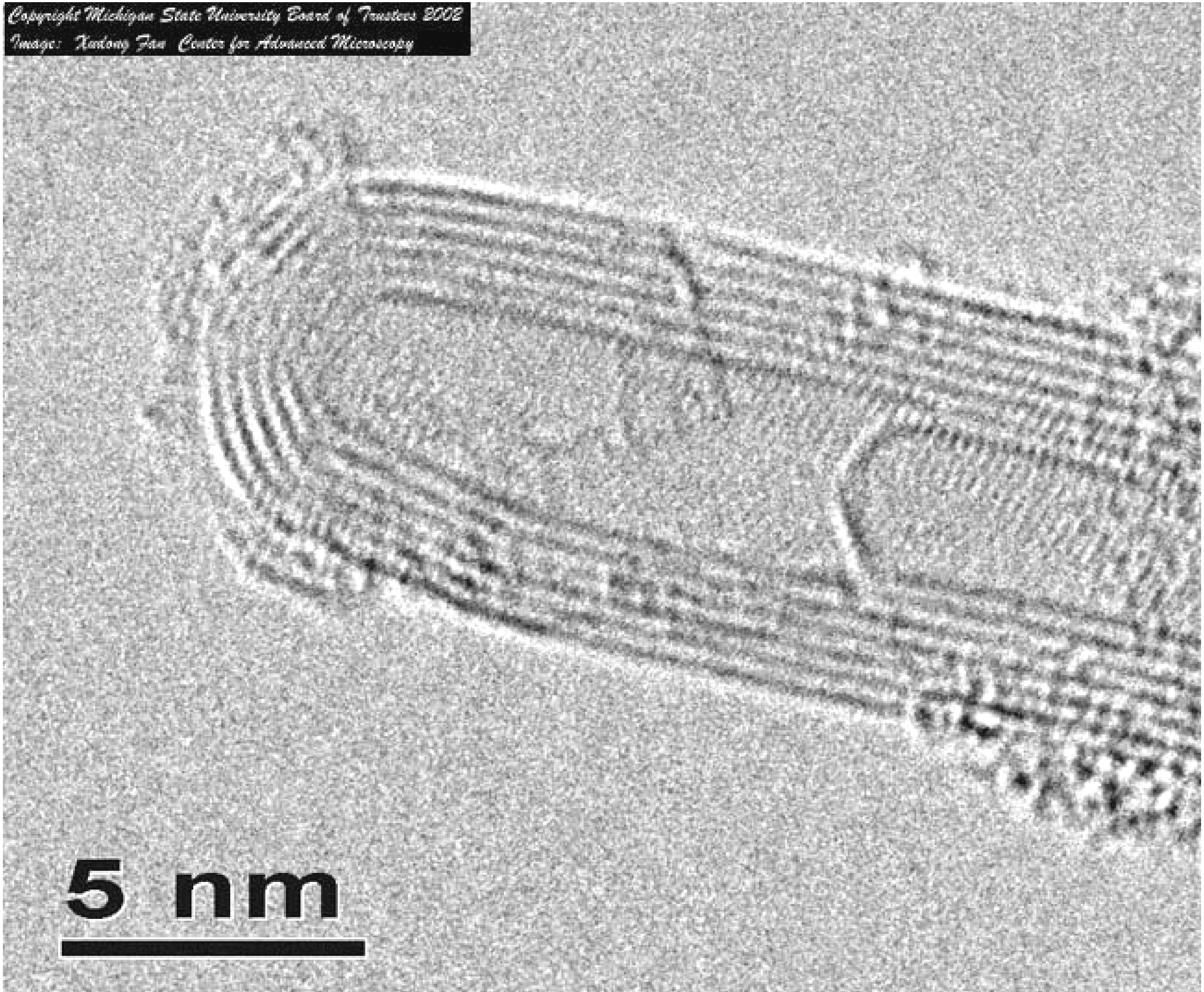
a/3[-112] → *a*/6[-221] + *a*/2[001]

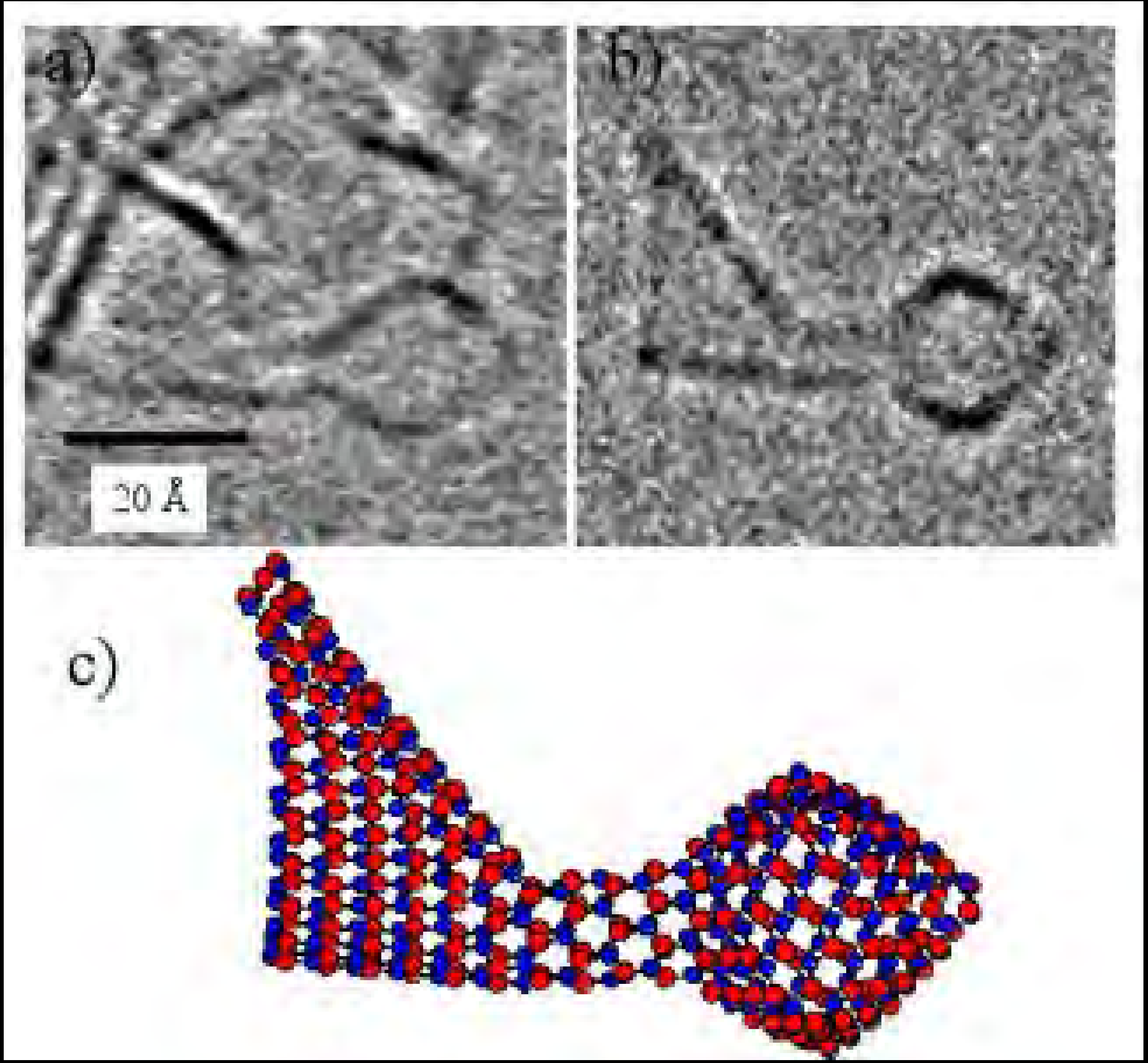

004
002
000
TiN
AlN
TiN
AlN
5nm

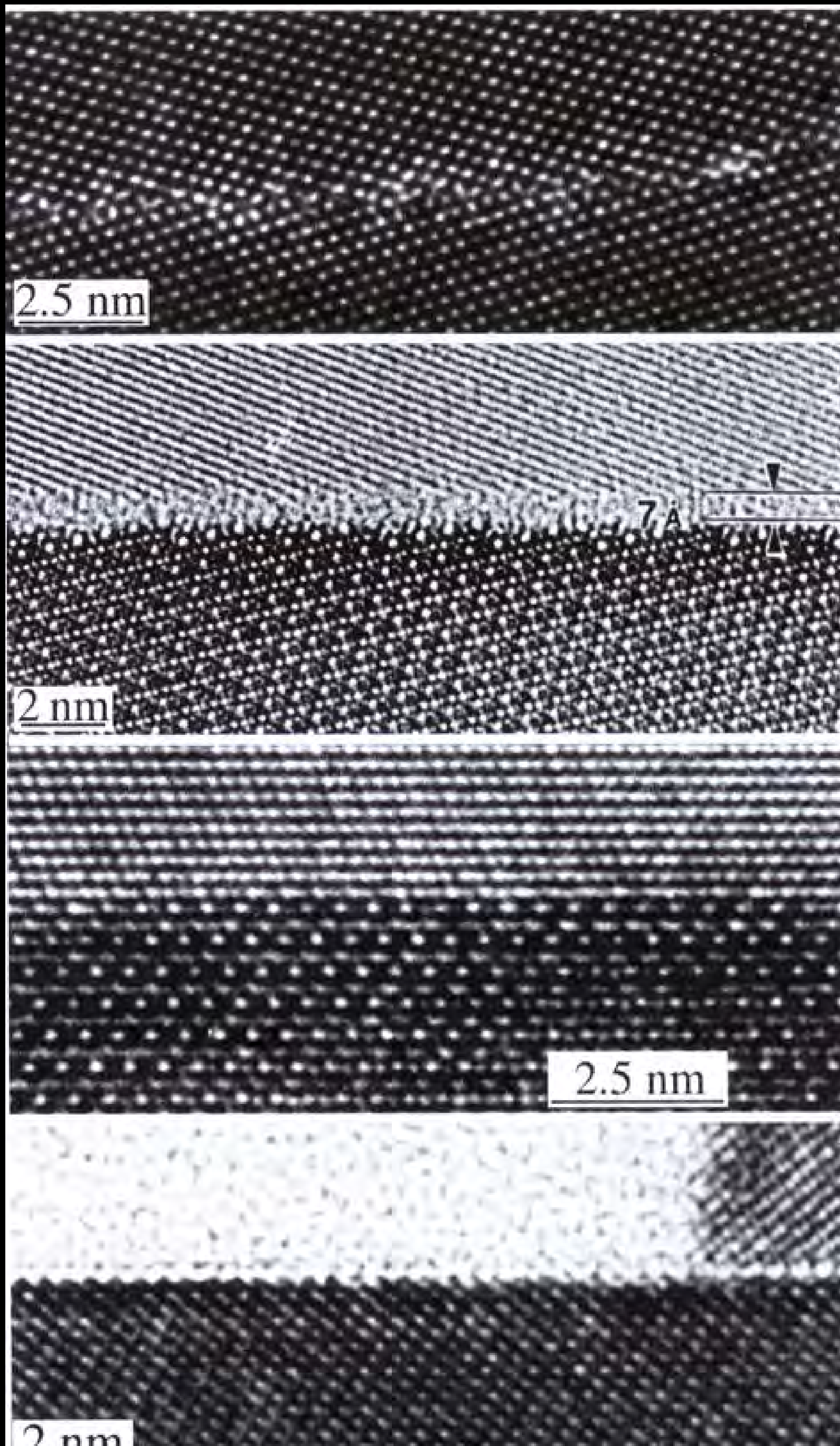



epoxy
c-BN
111
h-BN
002
a-BN
Si
50 Å

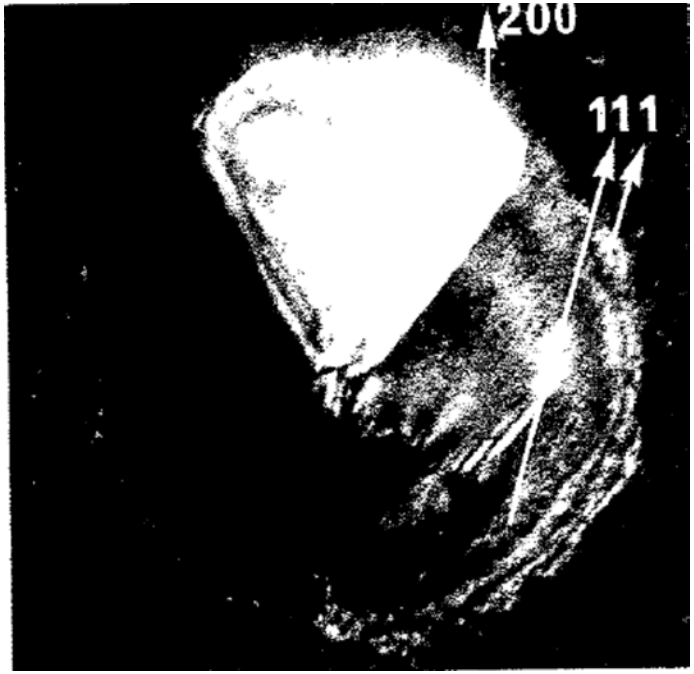

h-BN
a-BN
Si
30 Å

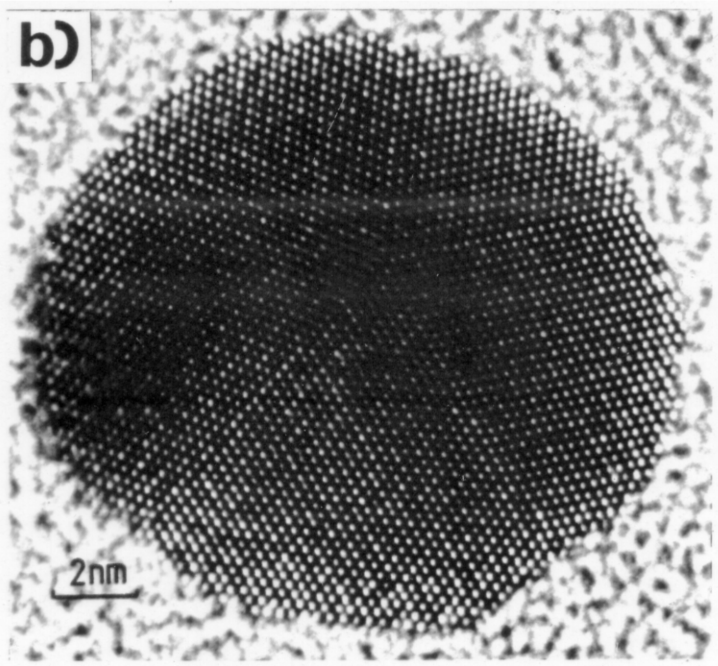

Copyright Michigan State University Board of Trustees 2002
Image: Xudong Fan Center for Advanced Microscopy
5 nm


a)
20 Å
b)
c)

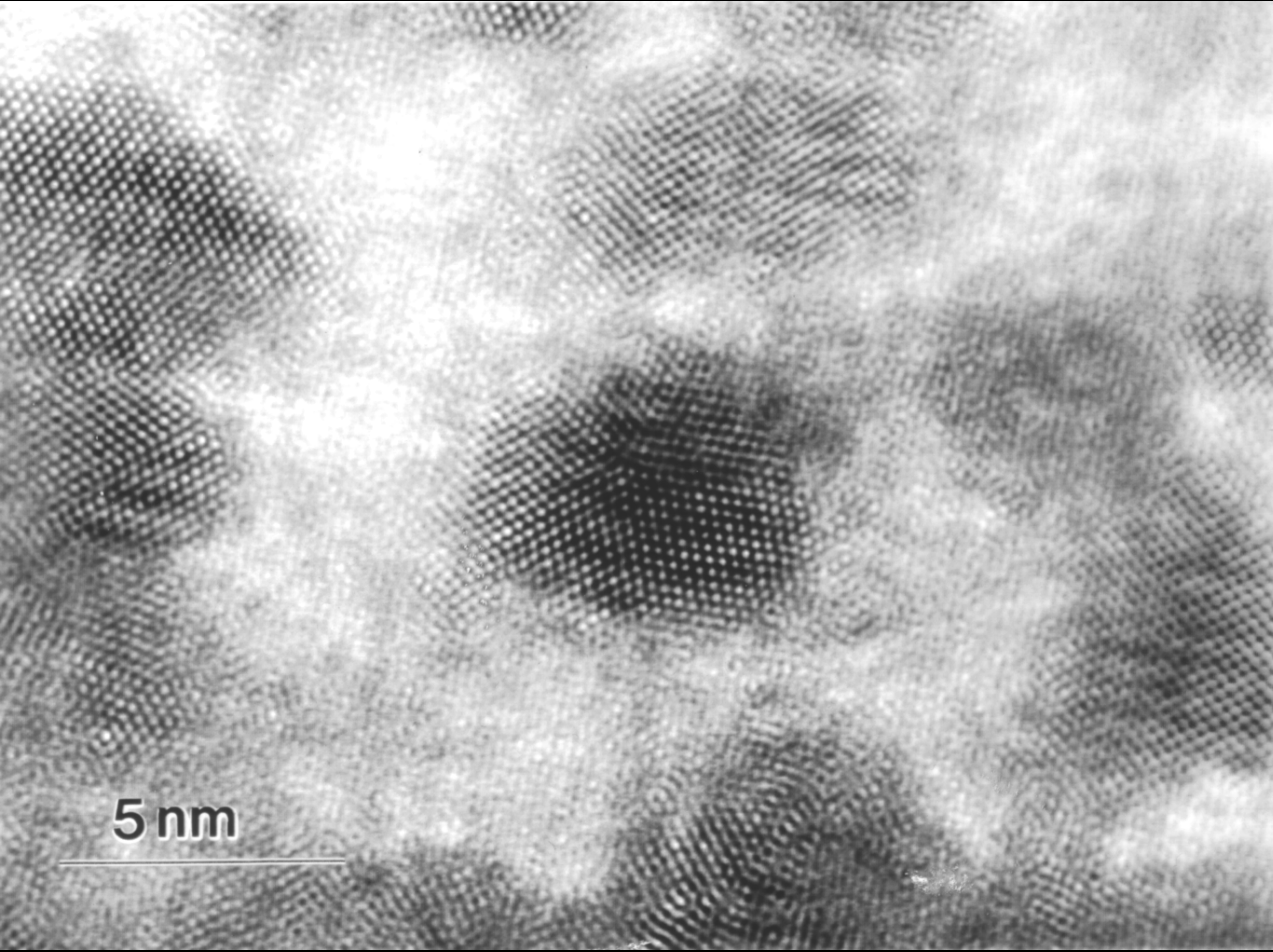

2.5 nm
7 Å
2 nm
2.5 nm
2 nm

Nanoparticles





L. D. Marks,. Philos. Mag. A. **49**, 81 (1984).


5 nm

Surfaces depend upon environment

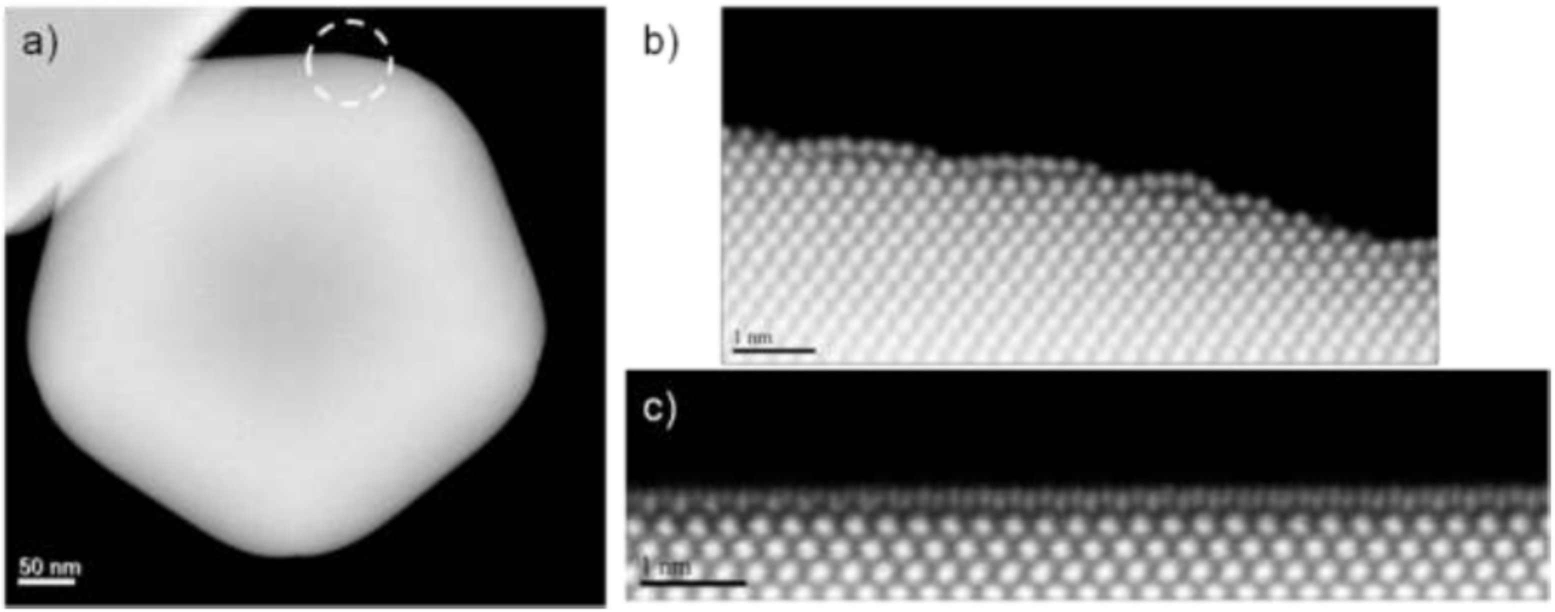


Fig. 20 a) Resulting decahedron after washing the solution. Area enclosed by the white circle is shown in b) and c). b) Dislocations observed on the (100) terraces. c) Surface reconstruction of the (100) surface.

“5x1” (001) reconstruction on Au Dh, Image courtesy of Gilberto Casillas-Garcia, UTSA

Structural Fluctuations (Iijima)

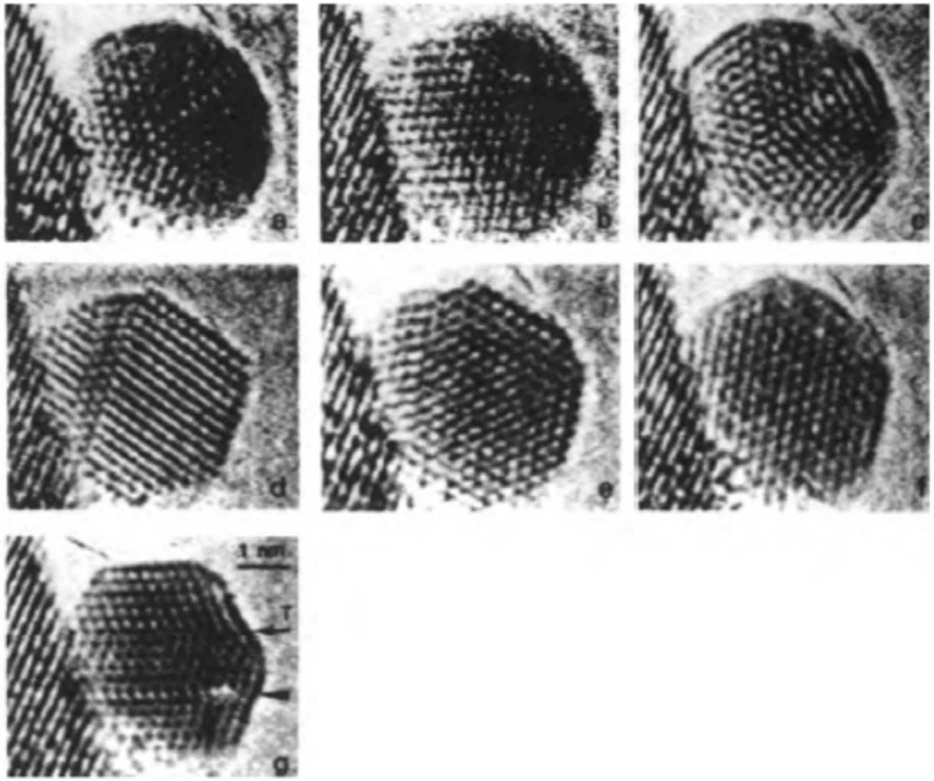
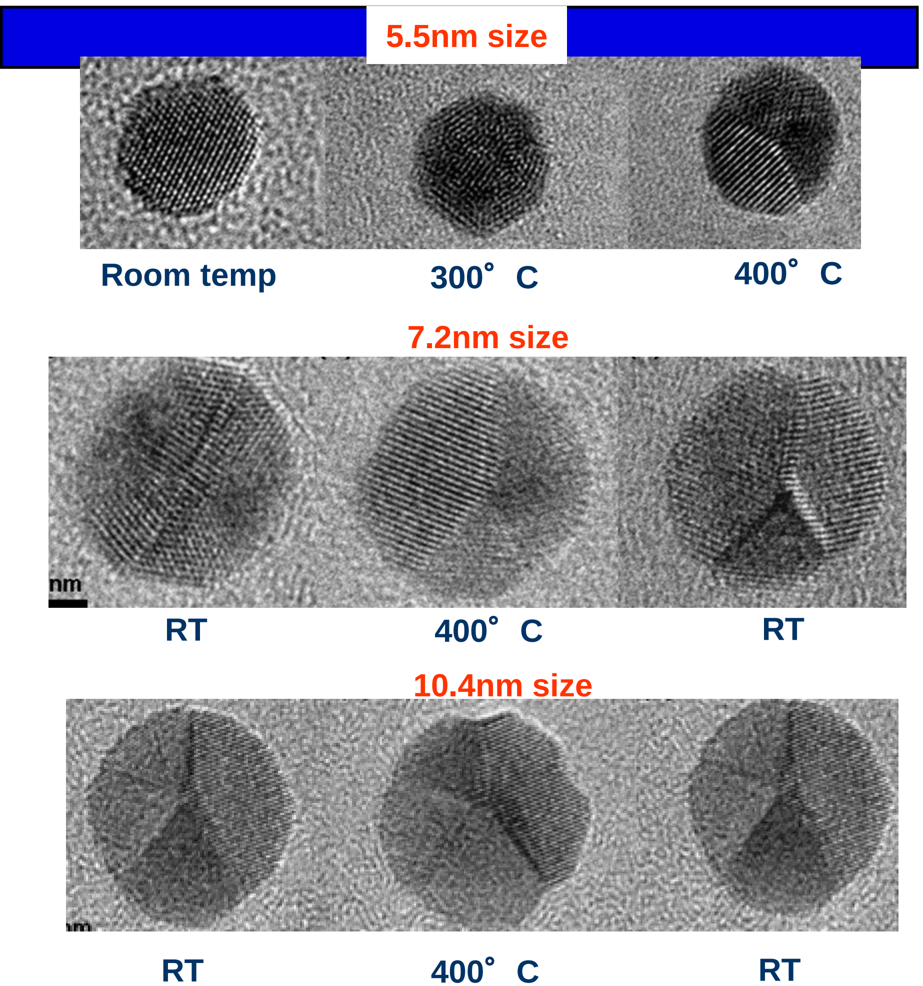
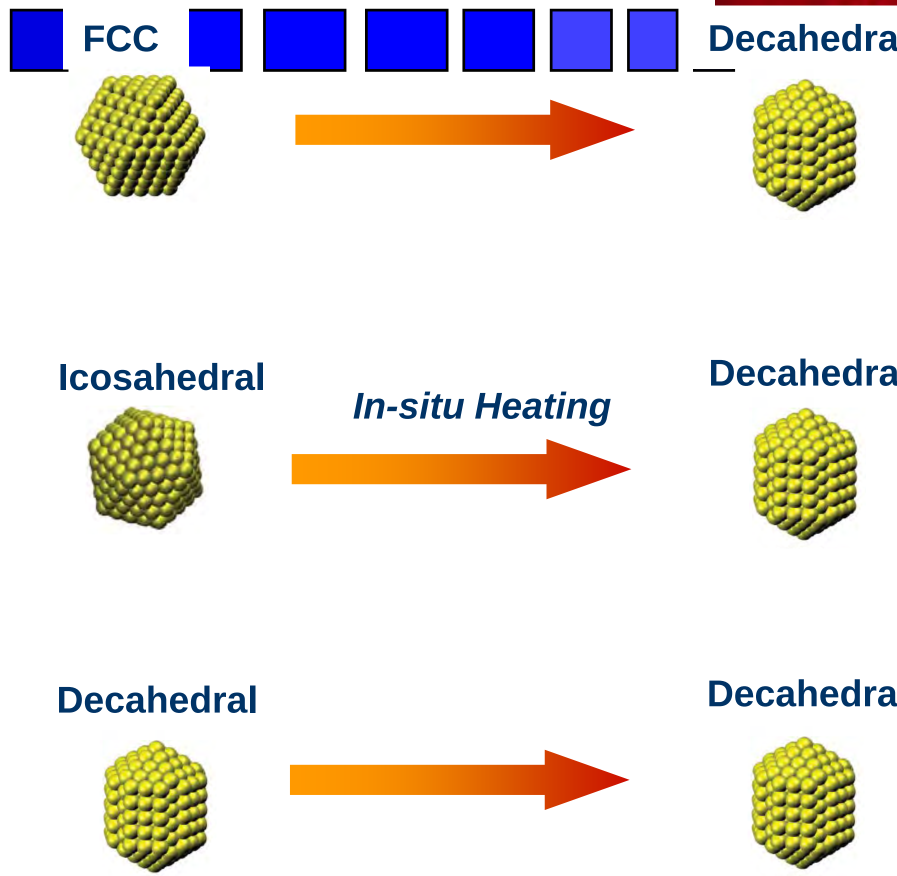


Figure 5 Shows the structural changes observed in a 3.5 nm gold crystal supported on amorphous silicon, as seen in single frame exposures from a real time video recording. The shapes change as follows: a) Icosahedral. b) Single crystal; 1.8 sec. c) Icosahedral; 4.2 sec. d) Stacking fault; 6.0 sec. e) Twin plane; 6.2 sec. f) Single crystal; 9.6 sec. g) Stacking fault (arrowed) and a twin plane, T; 20 seconds.

P. M. Ajayan, L. D. Marks,. 24-6, 229 (1990)

Morphological Transitions (Courtesy Angus Kirkland)





Ultramicroscopy, 110 (2010) 506

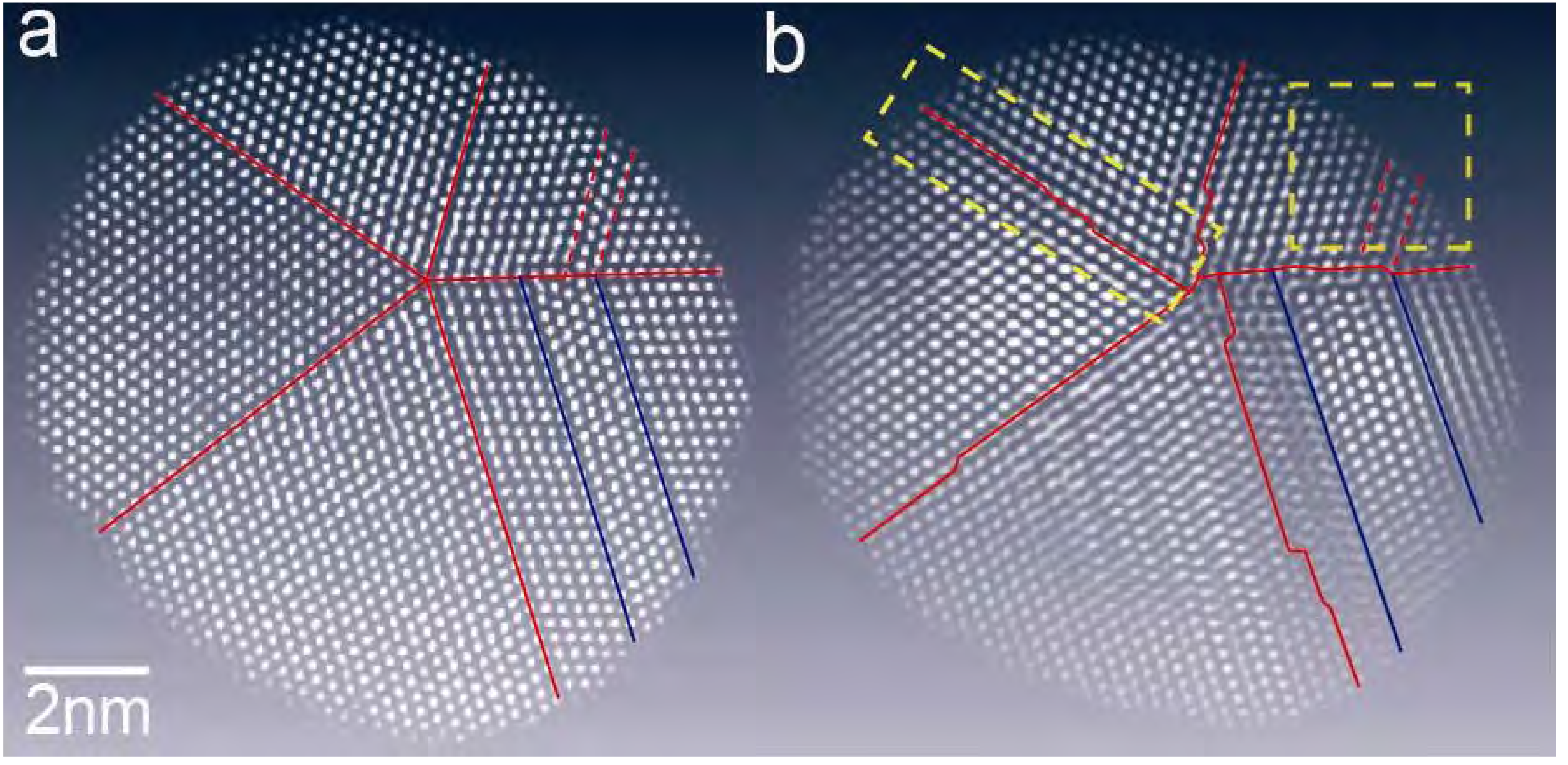
ACS Nano, 3 (2009) 1431

Solid – Solid Transition below T_m

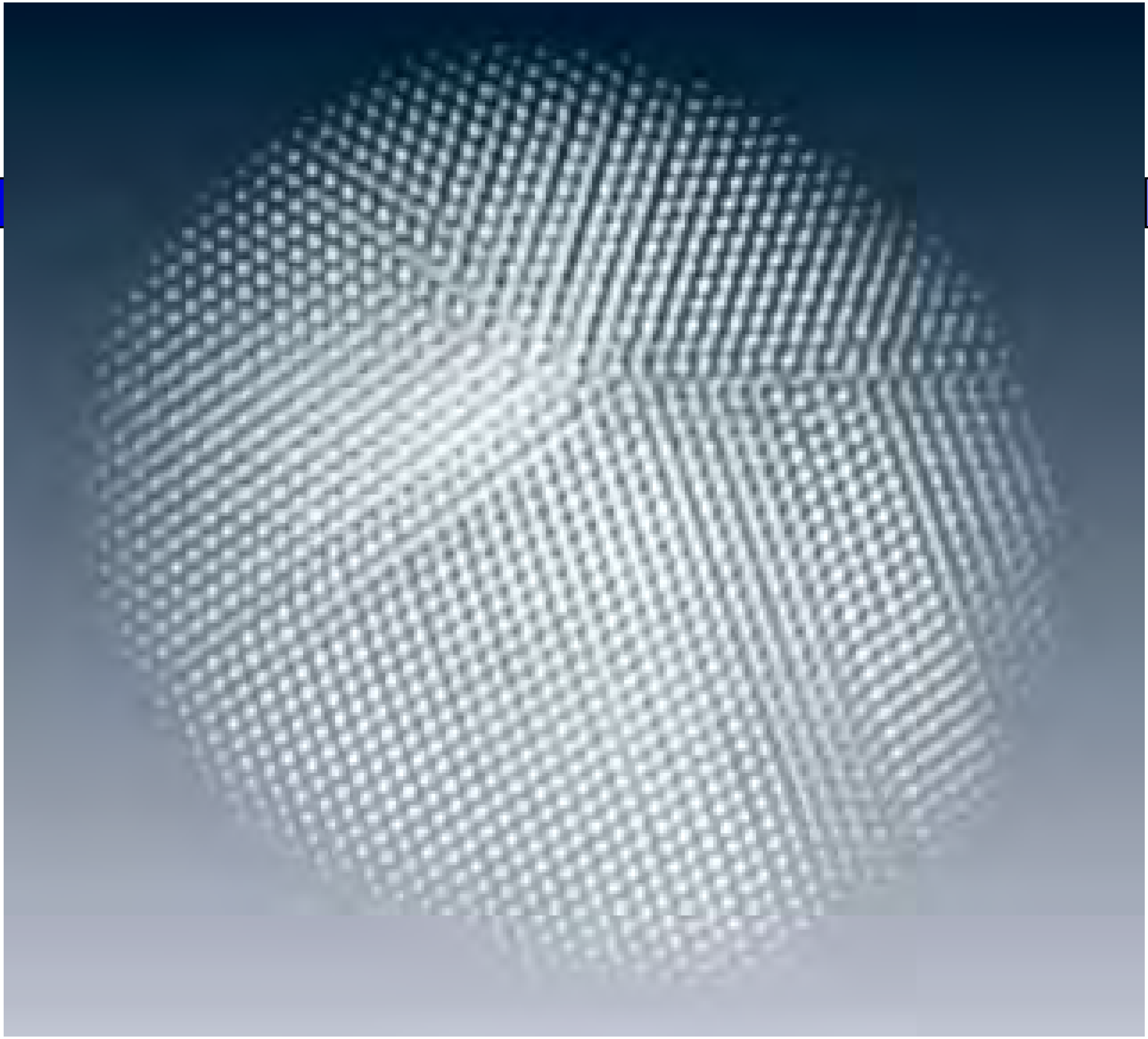
As Synthesised Particles not in Thermodynamic Ground State

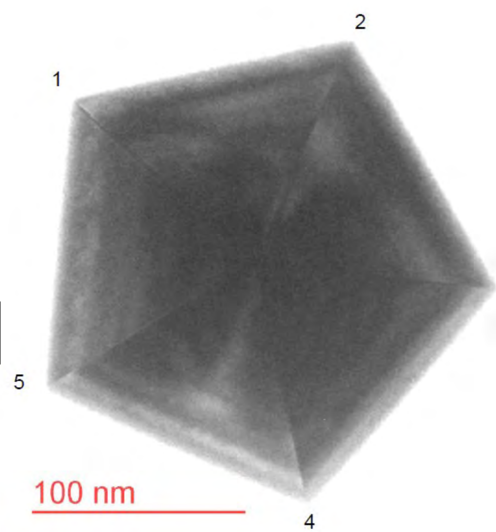
Nanoparticles are more complicated in 3D

Projected Image | Single Planes from Tomography

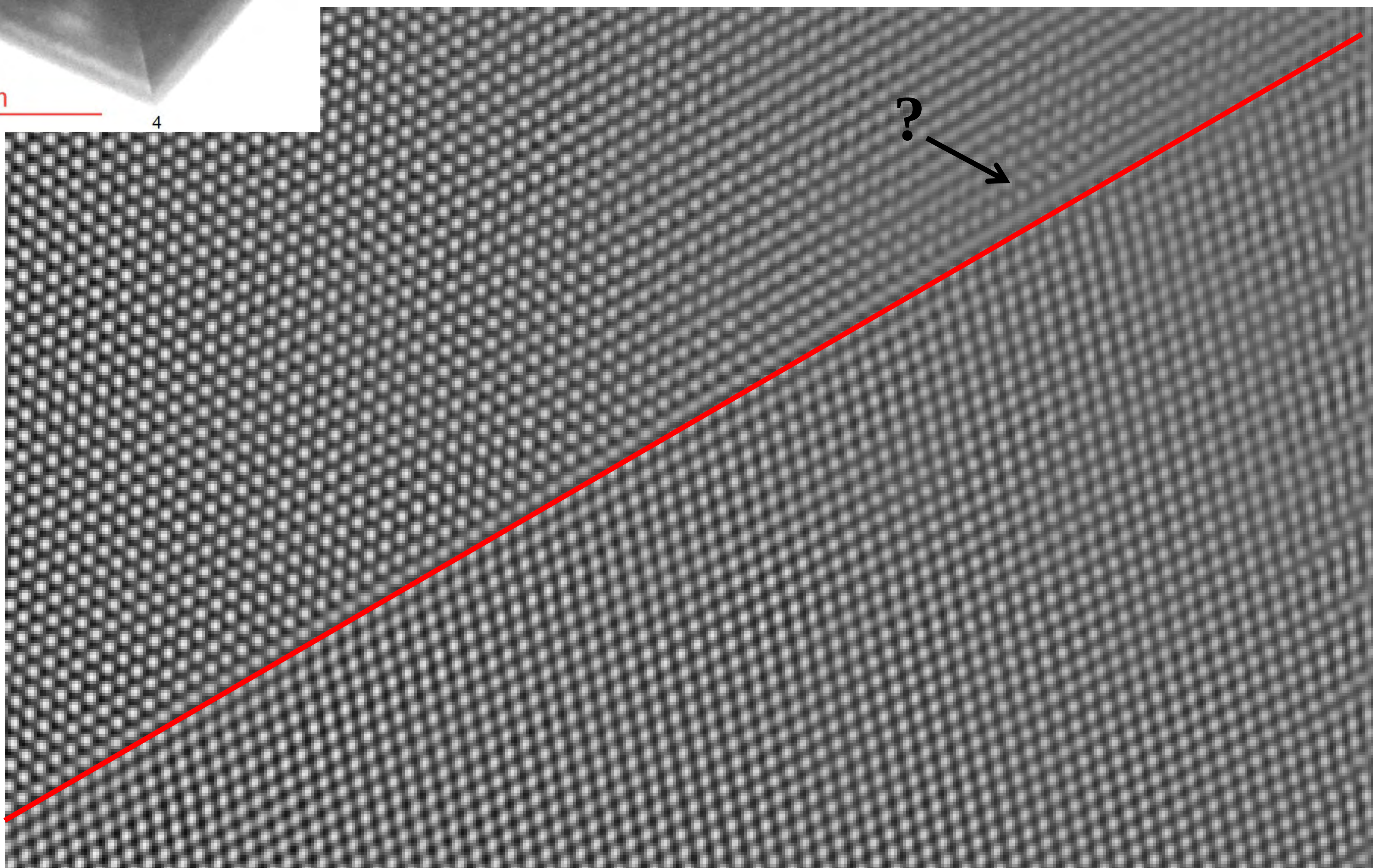


Steps at twin boundaries are a probable stress relief mechanism

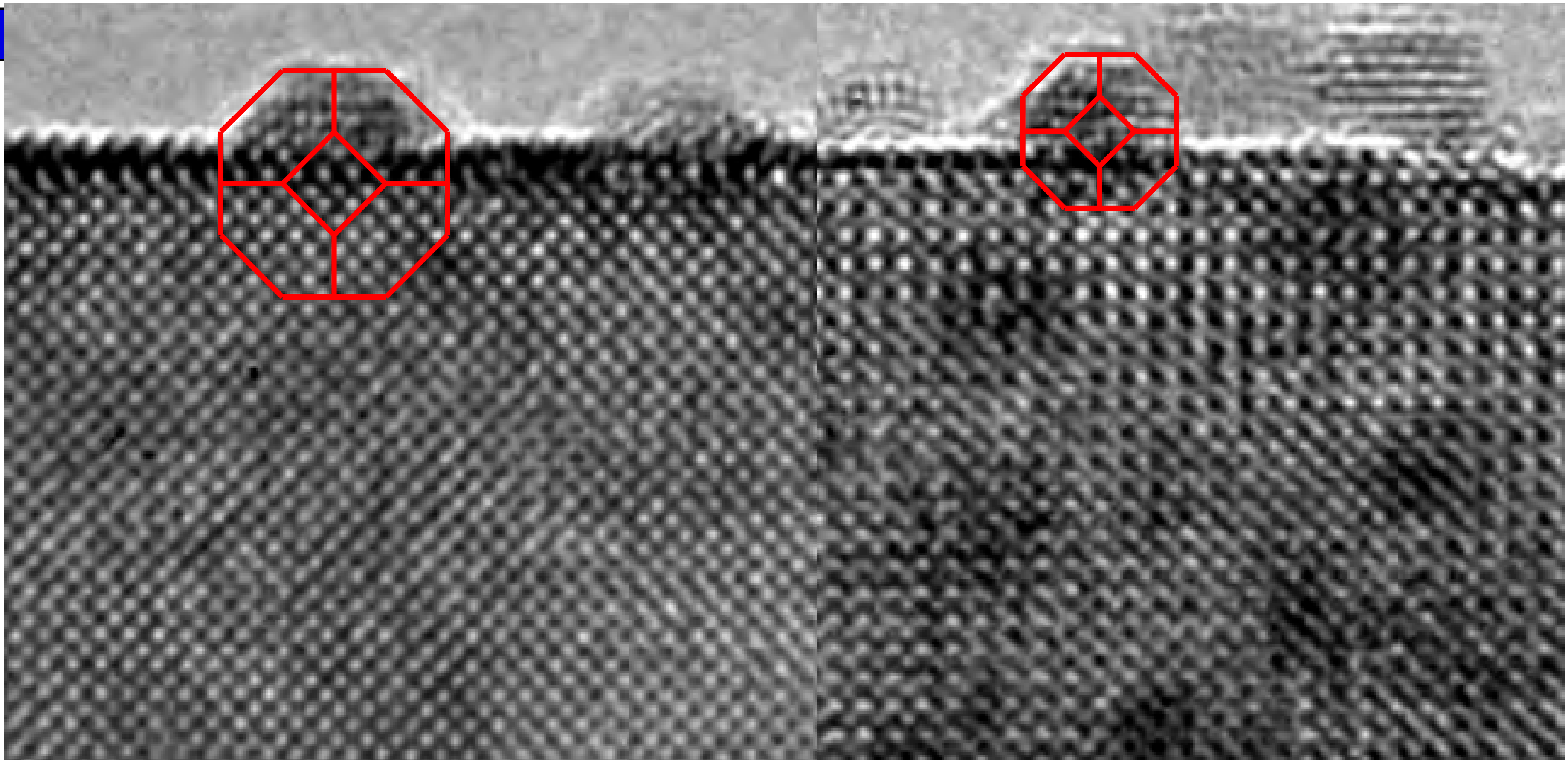




Consistent with HVEM data



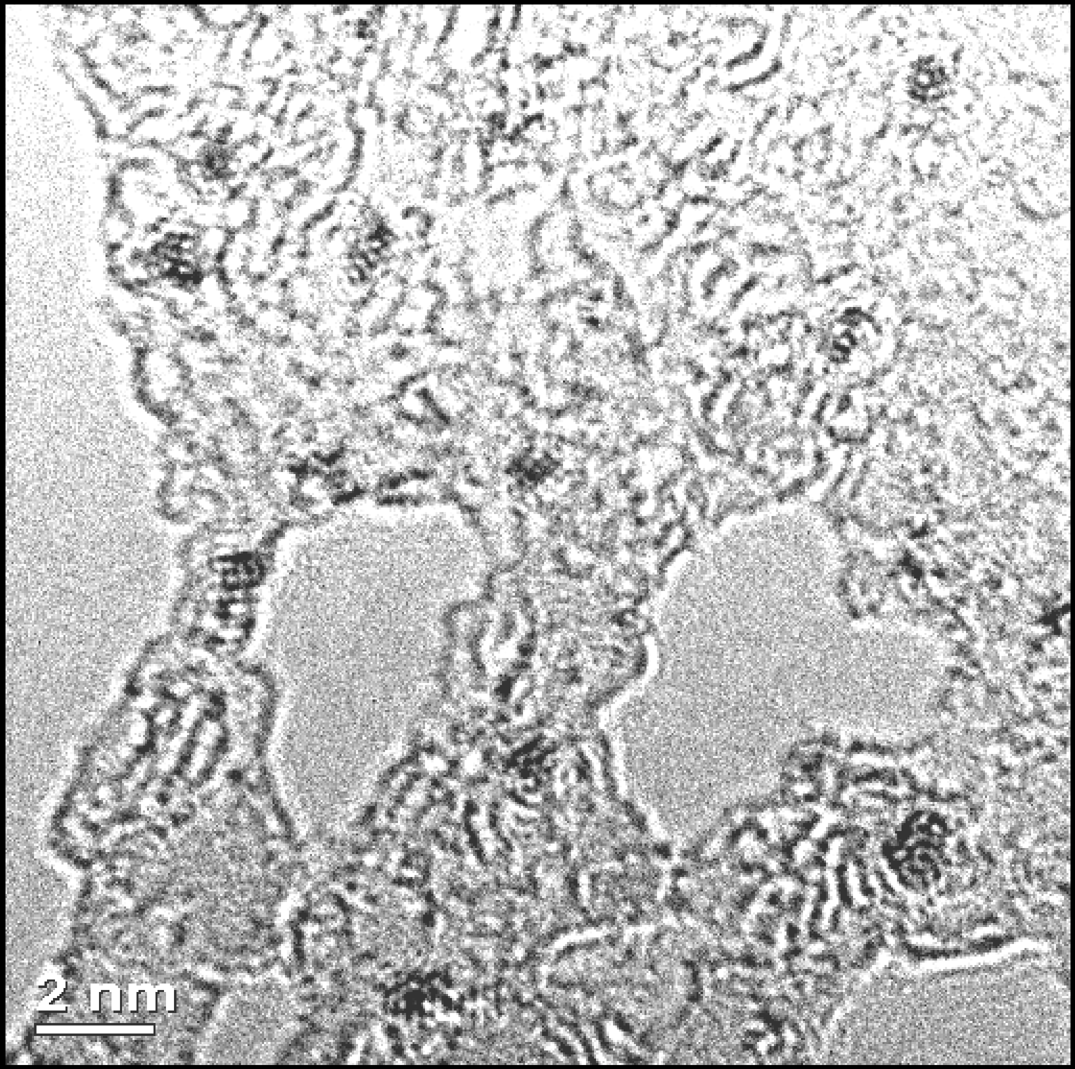
$Pt/Ba_{0.5}Sr_{0.5}TiO_3$

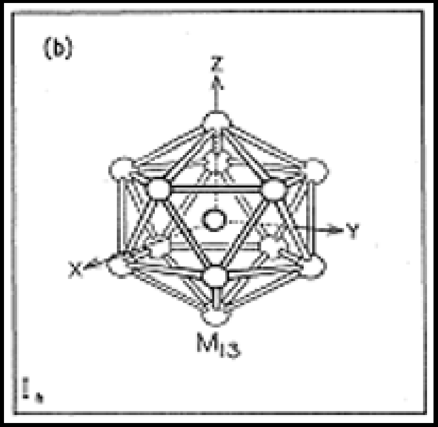


$Pt/SrTiO_3$

Preliminary

High-Resolution TEM: <1 nm





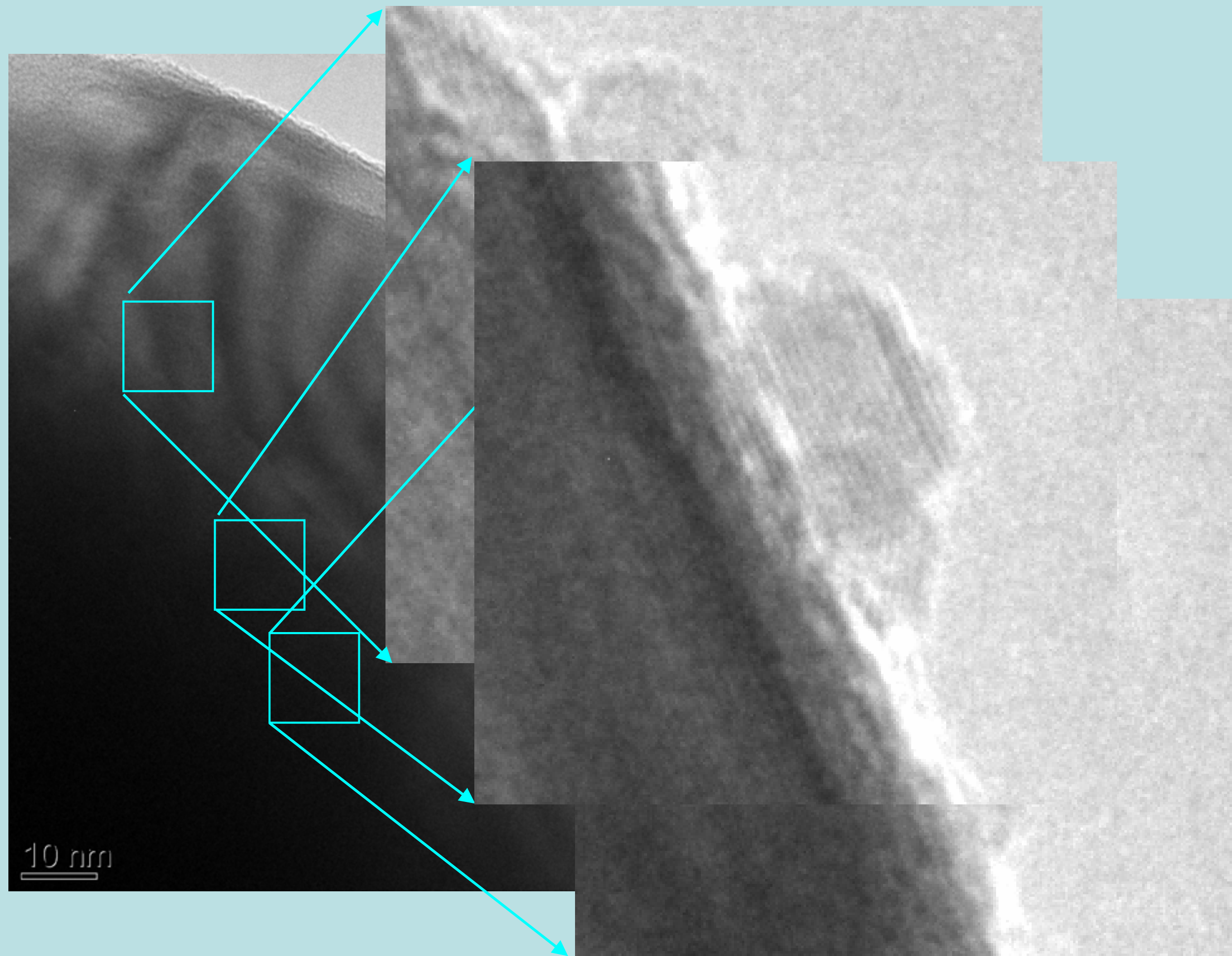
- Uniformity in size (<1nm) and spatial distribution
- High crystallinity evident from visible lattice fringes inside particles
- Lattice spacing = 2.39 ± 0.07(Å)
- Icosahedral shape based on trace analysis of particle edge

HREM image of $Au_{13}(PPh_3)_4(SC12)_4$

Huiping Xu, Ray Twesten

TEM -Identification of the Precipitates

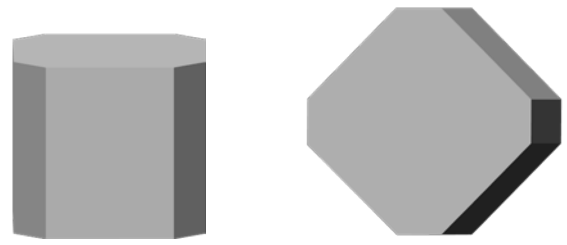
- Ru1steam

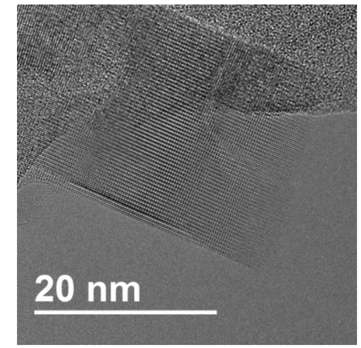


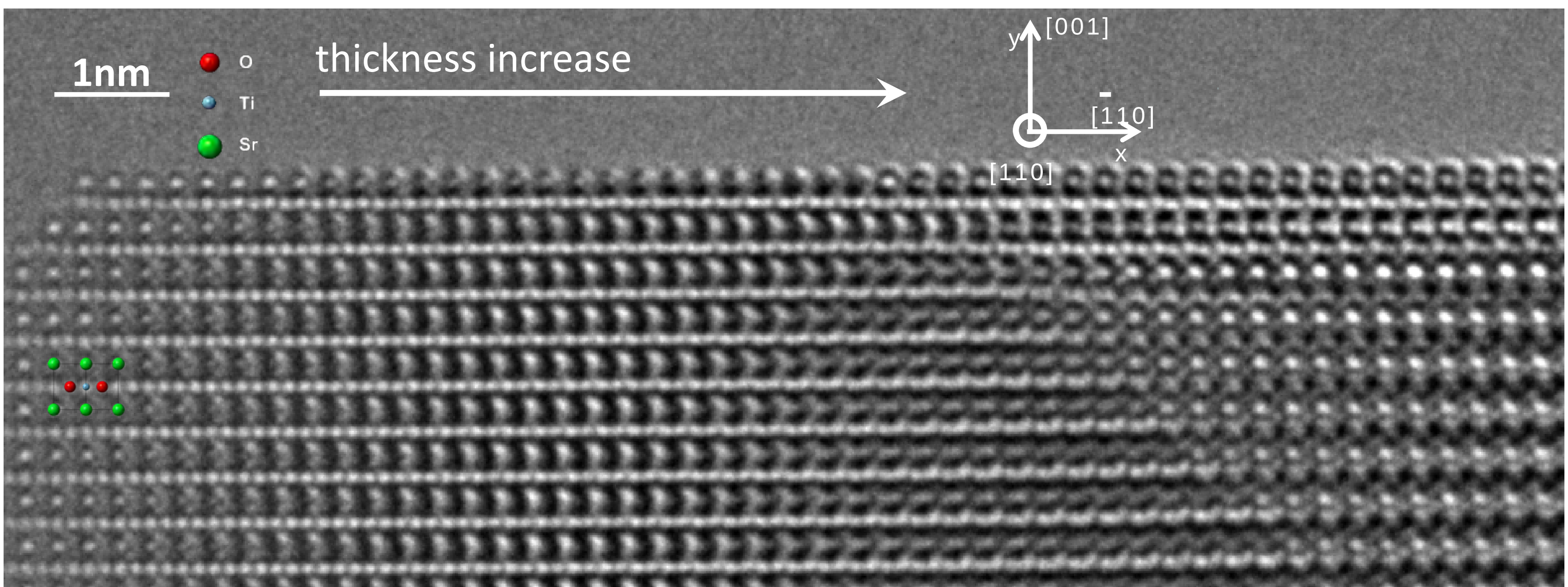
$SrTiO_3$ (001) surface

- Around 20 nm size
- Surface is flat in projection

[100] [110]

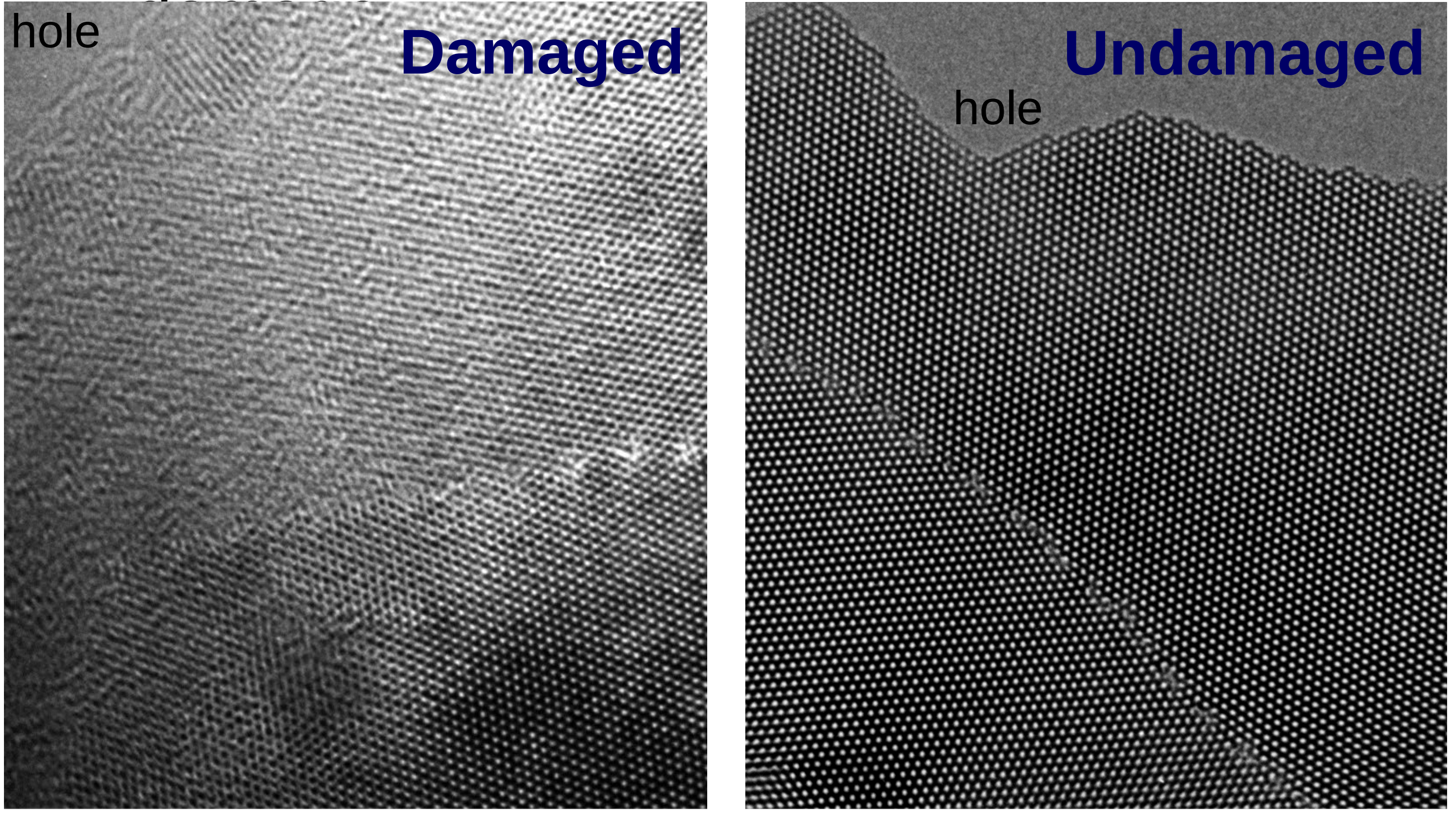






Thin Foil Specimen

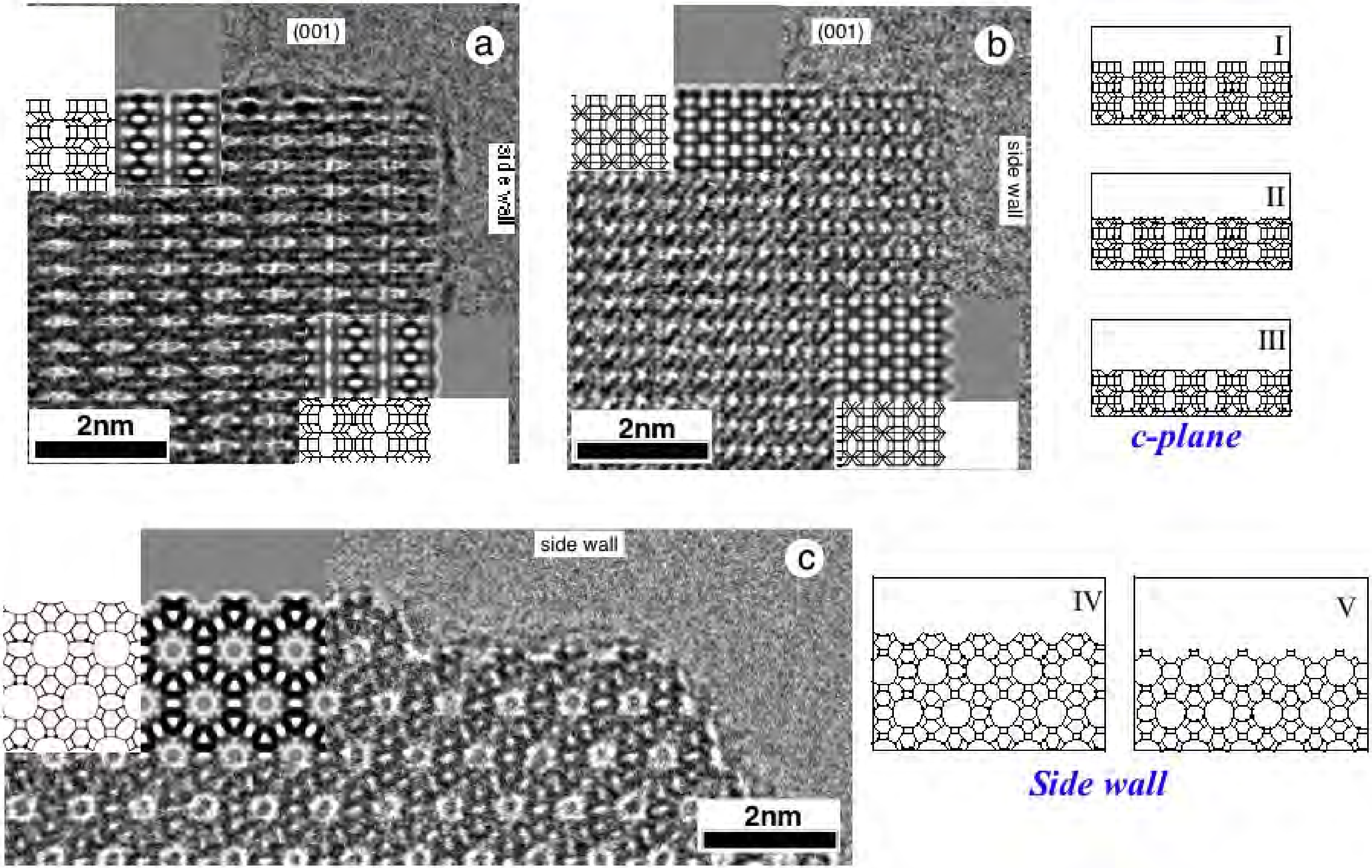
Make thin area with minimal ion-thinning damage



Finishing with low gun energy may be effective:

- PIPS: < 2.5keV
- DuoMill: < 3keV (+ liquid Nitrogen cooling stage)

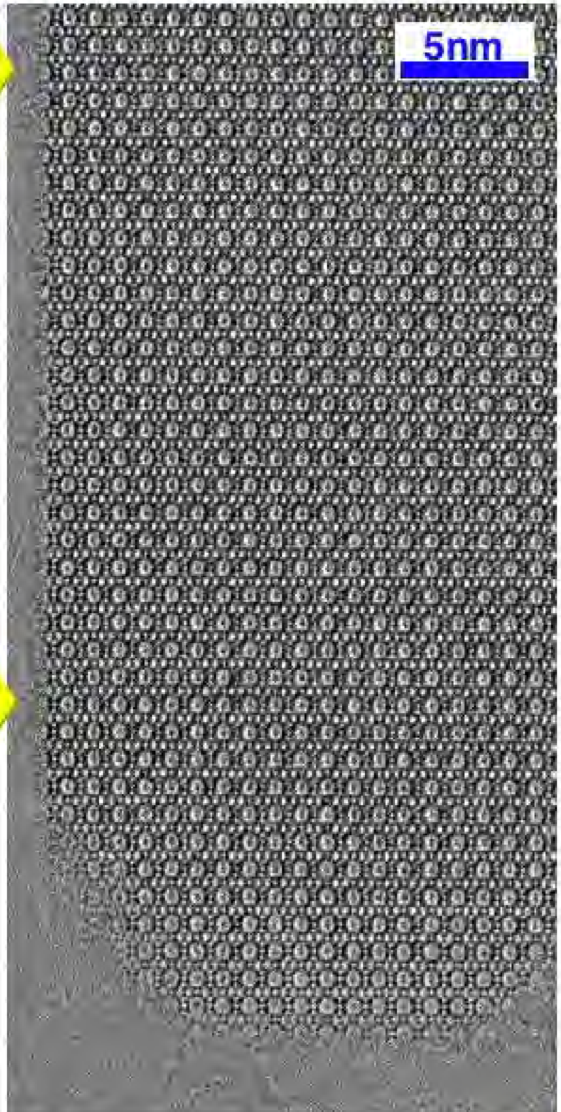
Surface Structures of LTL, c-plane and side wall



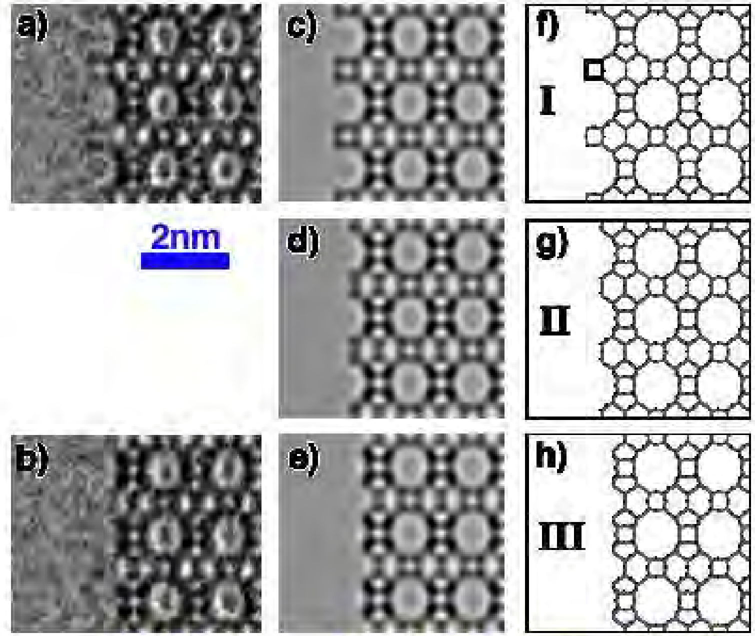
BEC (pure SiO_2)

(a)

(b)

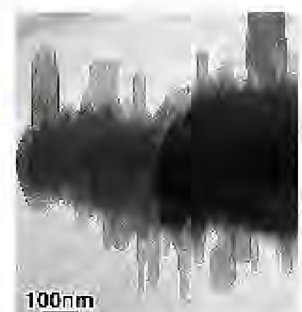


JEM-4000EX at 400kV

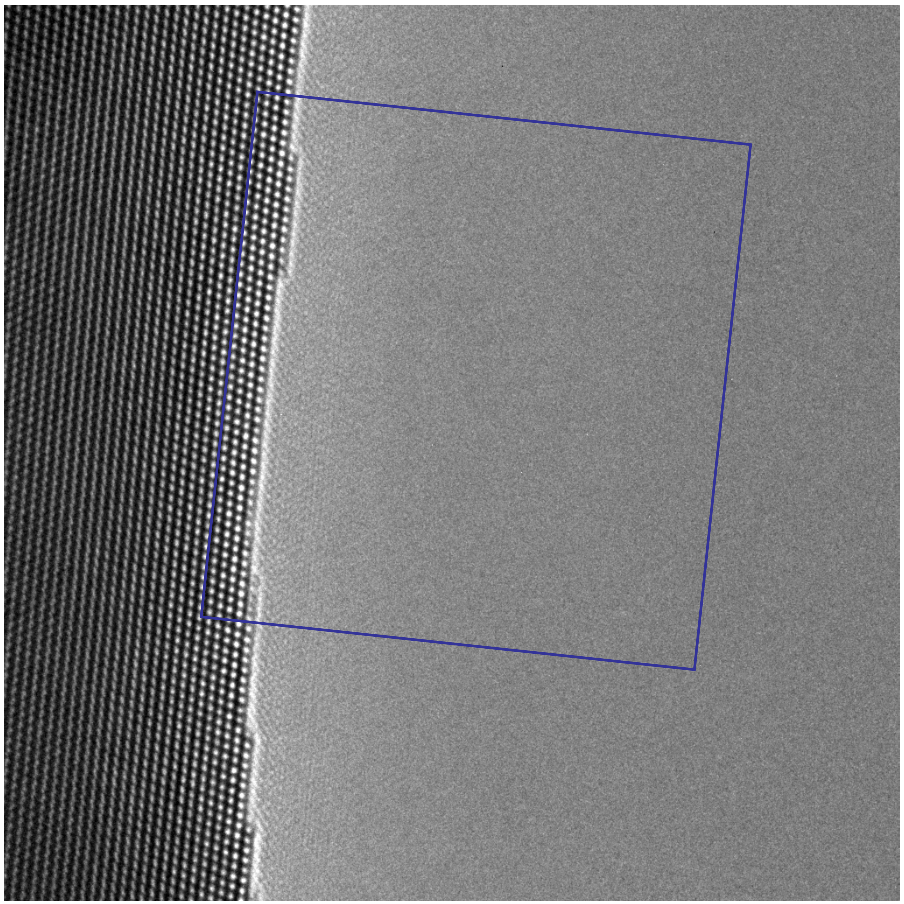


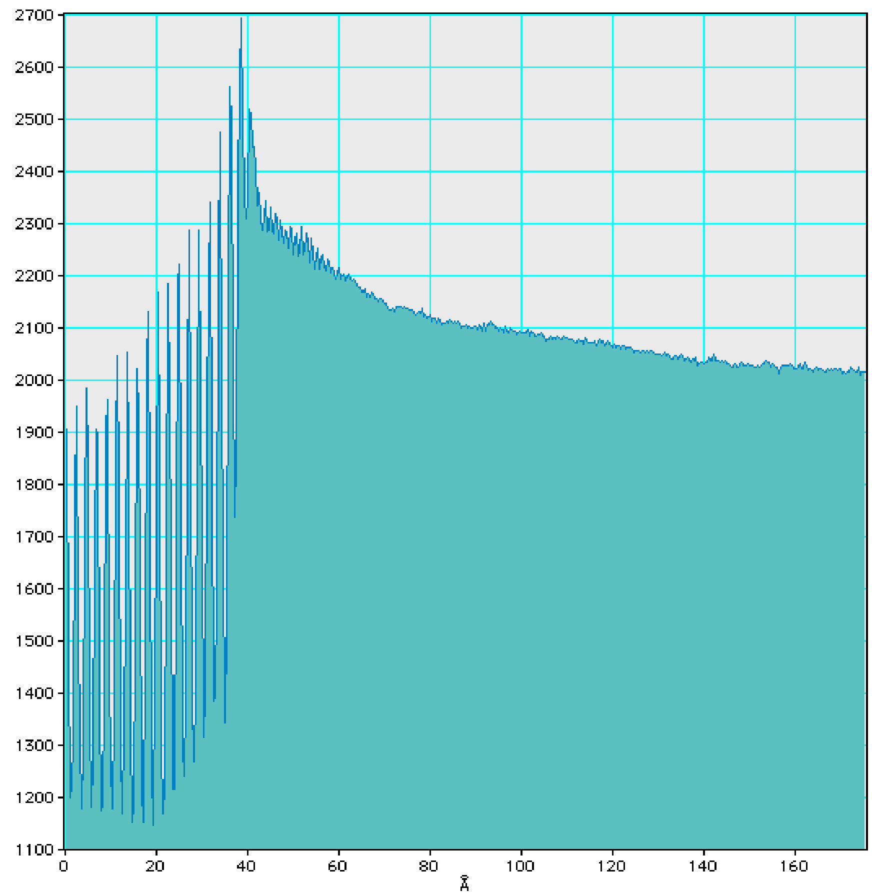
HREM Simulated Framework

Overgrowth on BEA



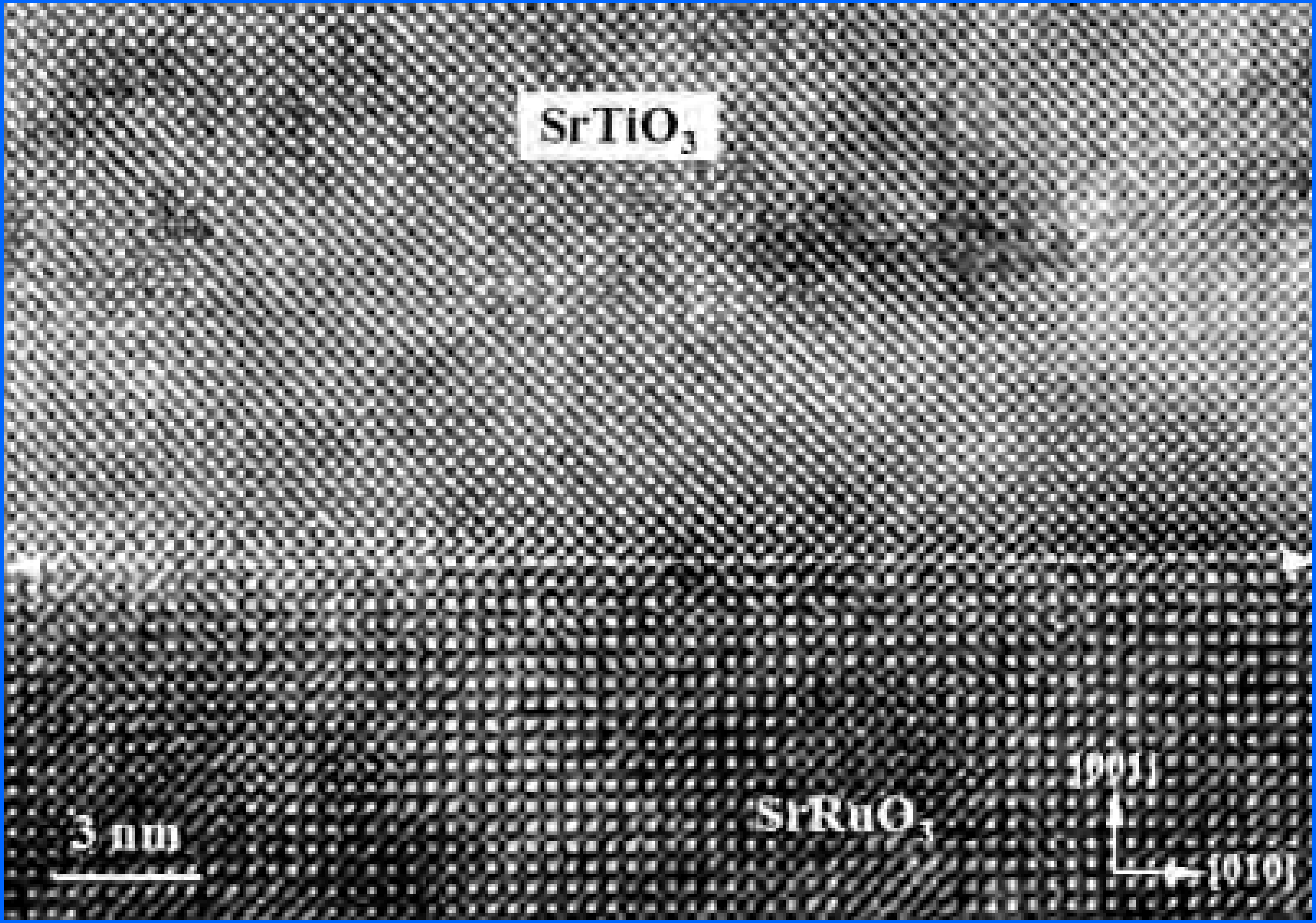
Au [110] – Vacuum wave





Courtesy C. Kisielowski, J.R. Jinschek (NCEM, Berkeley)

High-Resolution Electron Microscopy: Interfaces

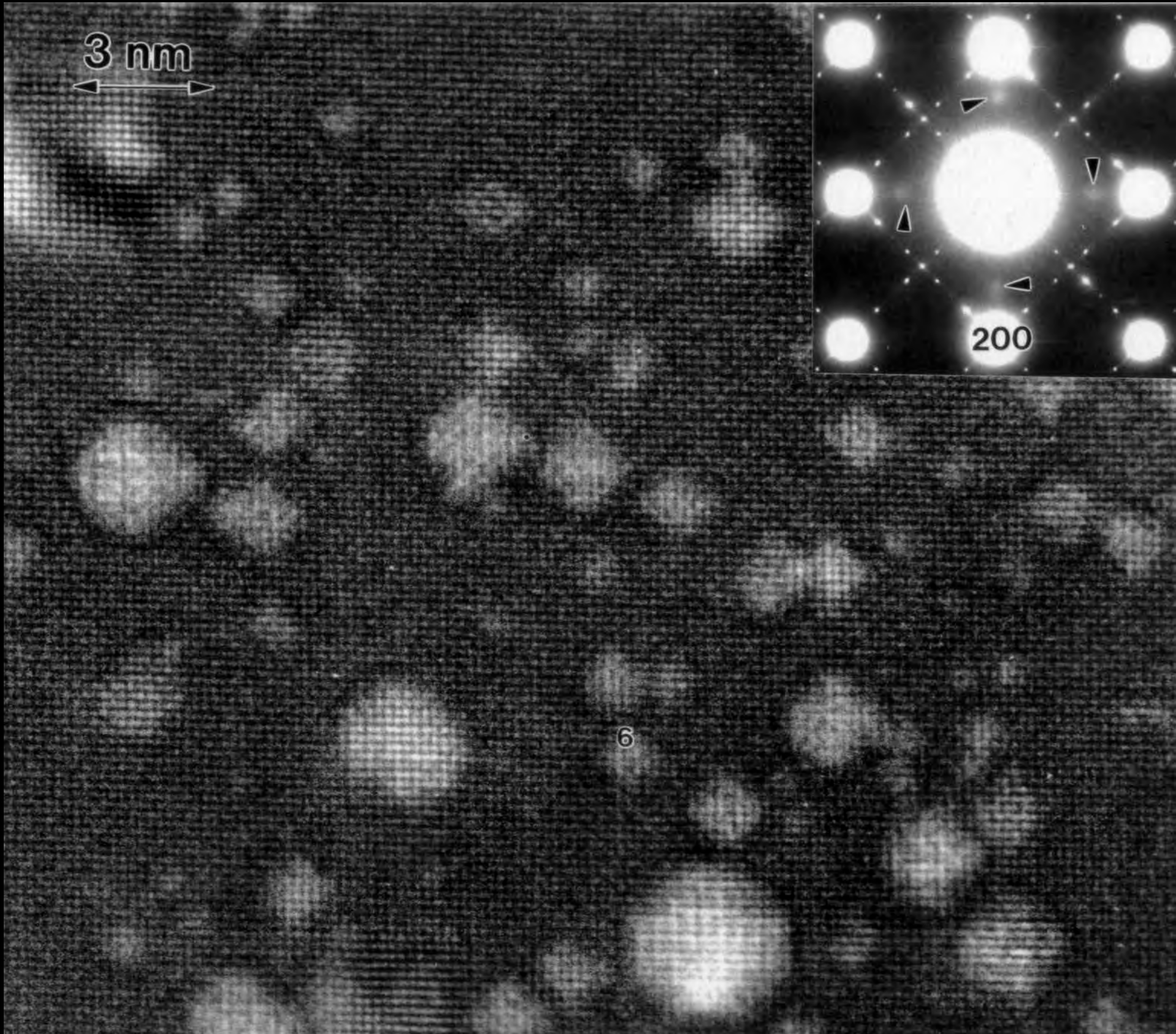


a=0.3905 nm

Misfit=0.64%

a=0.3982 nm

HREM image of coherent $SrTiO_3/SrRuO_3$ interface.



3 nm
200
6

Resolution Limiting Factors.

Incoherent Aberrations

(Source Size, Energy Spread

HT stability, lens stability

Chromatic Aberration).

Coherent Aberrations

(Objective lens

Spherical Aberration)

Detectors

(Phosphor coupled CCD)

Resolution Limiting Factors.

Incoherent Aberrations

(Source Size, Energy Spread

HT stability; lens stability

Chromatic Aberration).

(Monochromation, Novel Sources, improved stabilities, C_c correction)

Coherent Aberrations

(Objective lens

Spherical Aberration)

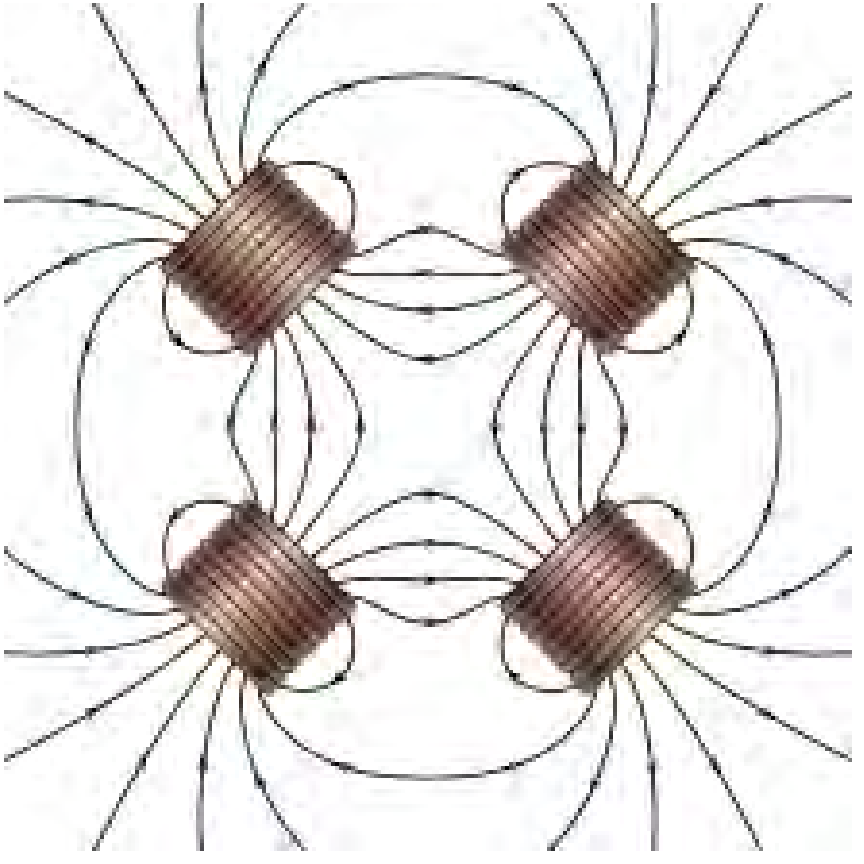
(Spherical Aberration Correctors)

Detectors

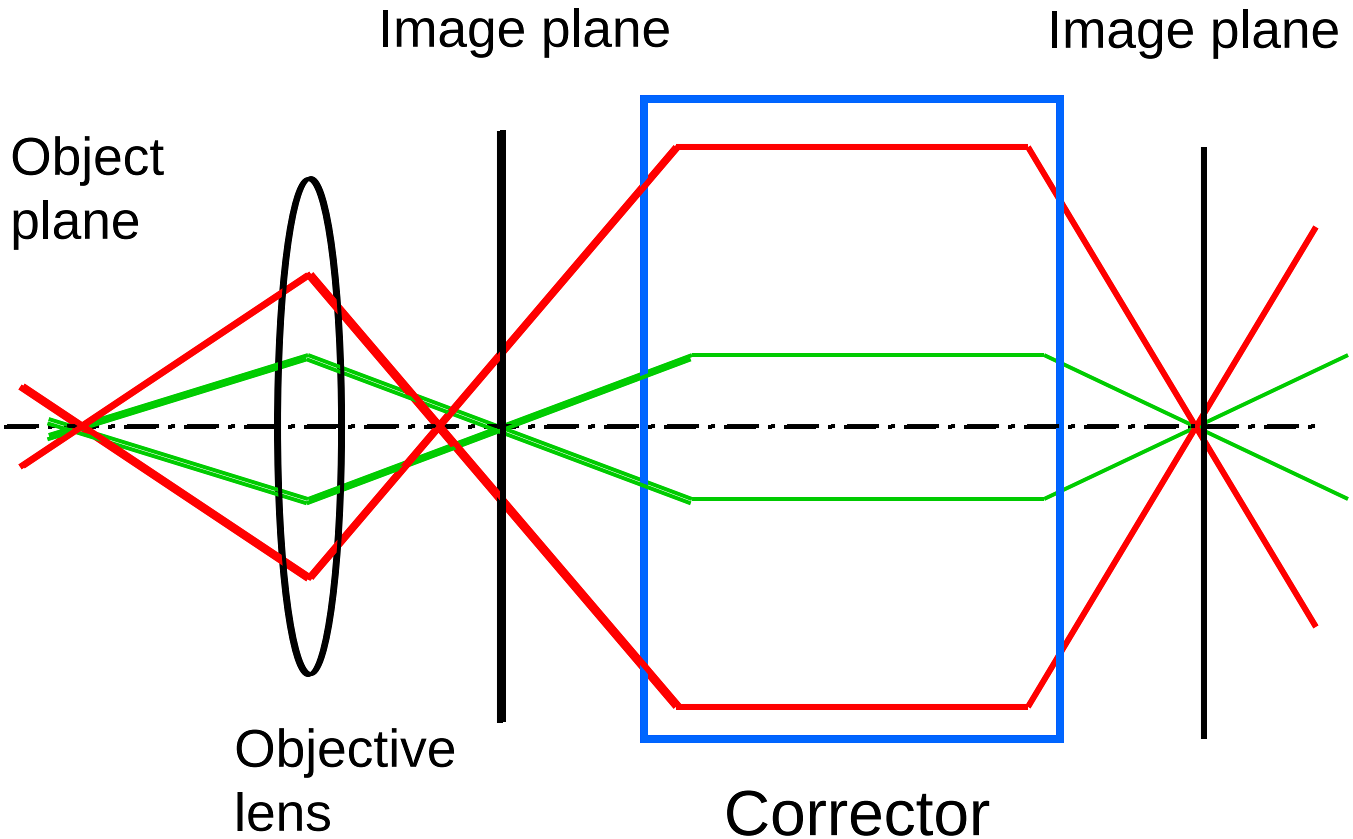
(Phosphor coupled CCD)

(Direct Electron Detectors)

Multipole Lenses



Correction of Spherical Aberration.



Need to have non-spherical elements

Aberrations

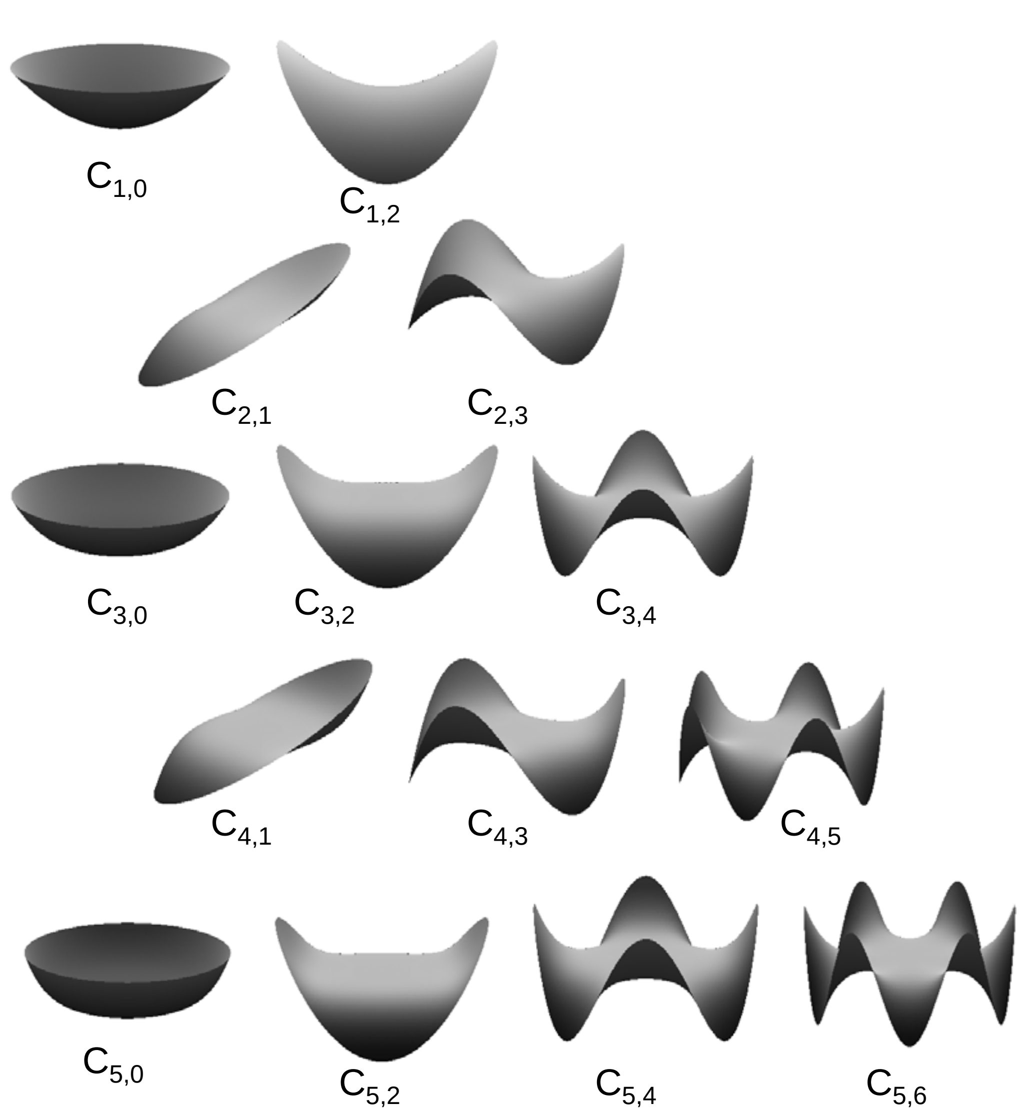
- Aberrations are a phase-shift in reciprocal space
- Multiply by $\exp(-i\chi(u))$
- Can expand as a Taylor series

$\chi(u) = A + Bu + Cu^2 + D(u.a) + \ldots$

A,B don't matter

C is defocus, D is astigmatism, Cs has u^4

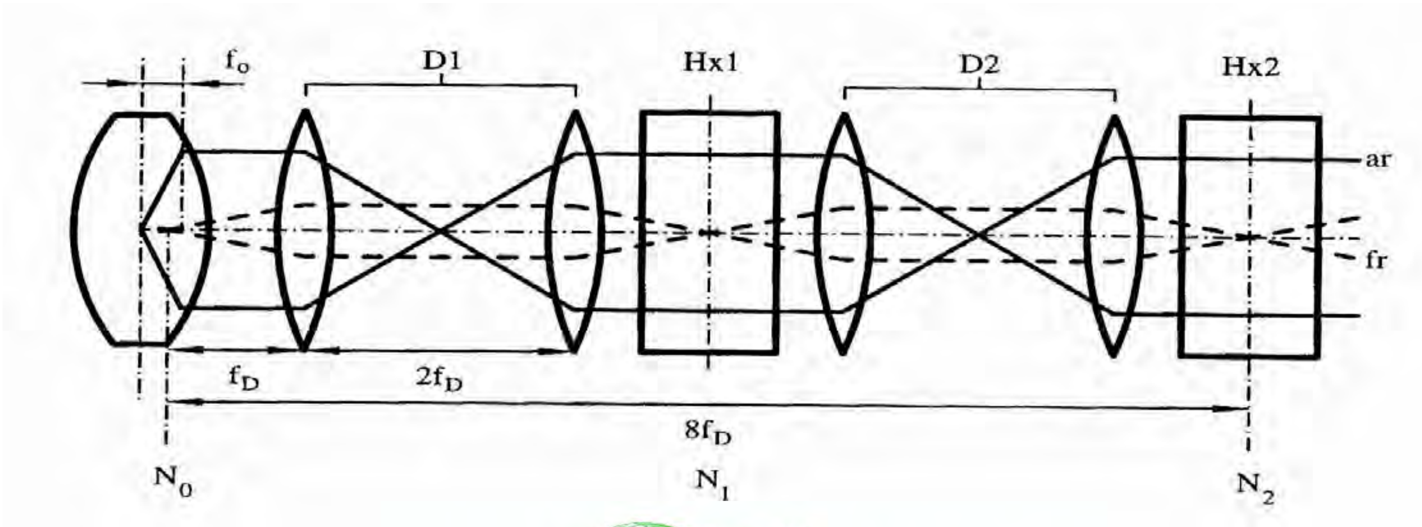
Aberrations

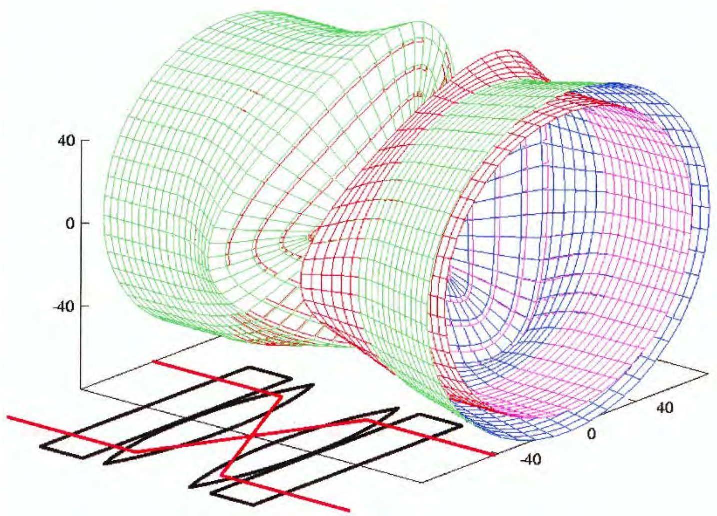


Basic concept

- One cannot correct with a spherical lens, i.e. one with only even u terms
- One can, however, generate –ve 4^{th} order terms by breaking symmetry
  - – Use hexapoles, which introduce terms with 3-fold symmetry
  - – Octapoles, 4-fold symmetry
  - – Arrange to cancel out most of the 3-fold or 4-fold aberrations

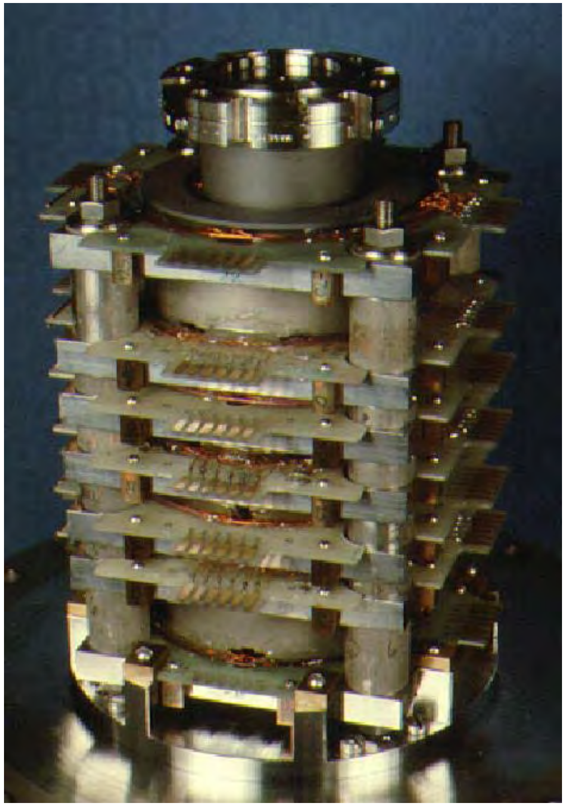
Corrector Optics.



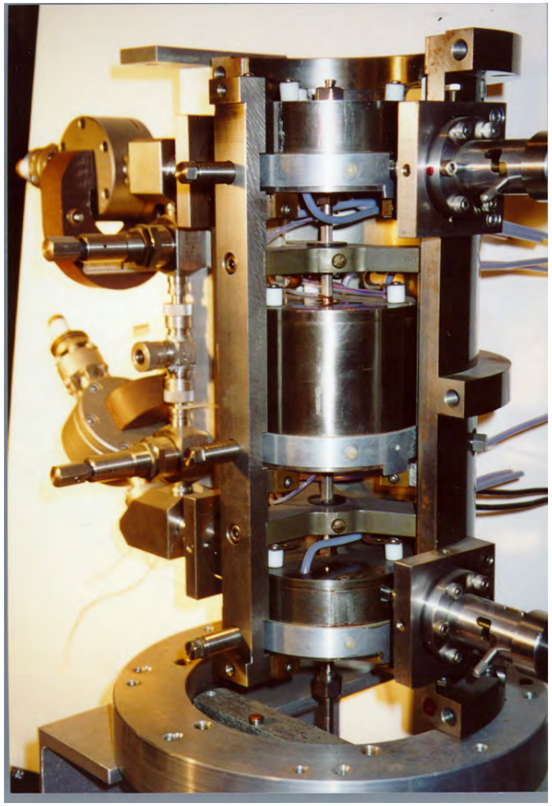


Dr Peter Hartel, CEOS

Two early aberration correctors



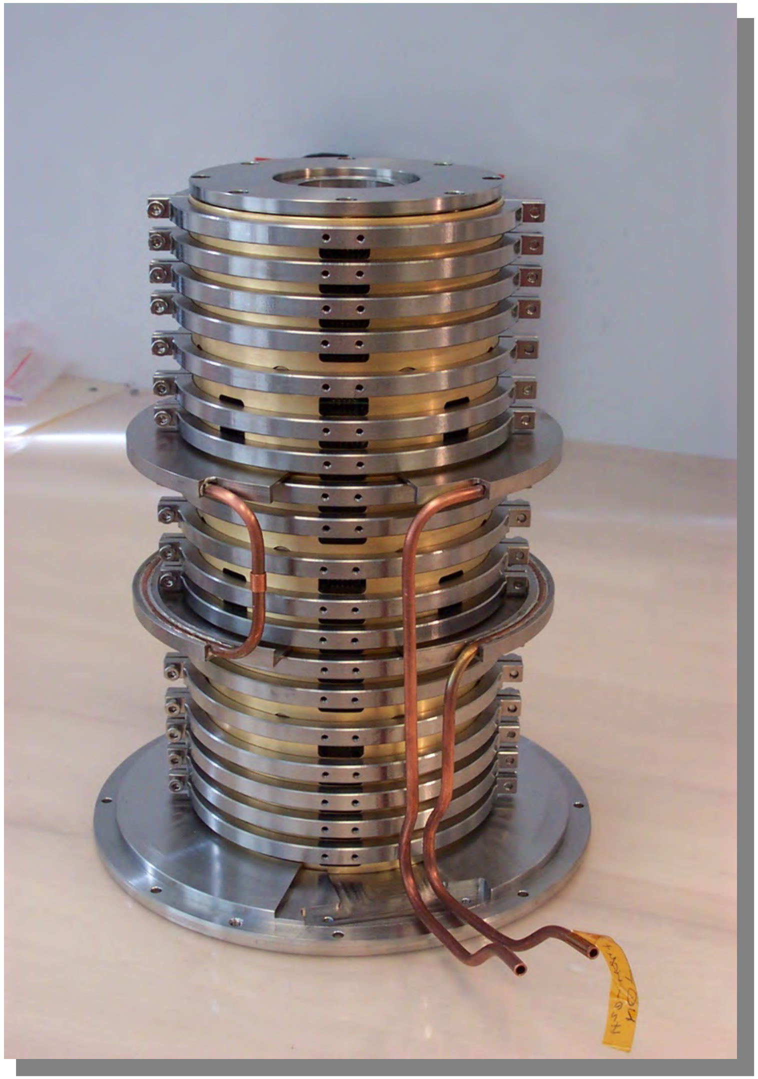
Quadrupole-octupole corrector (~1975)
(grandfather to Nion's corrector)

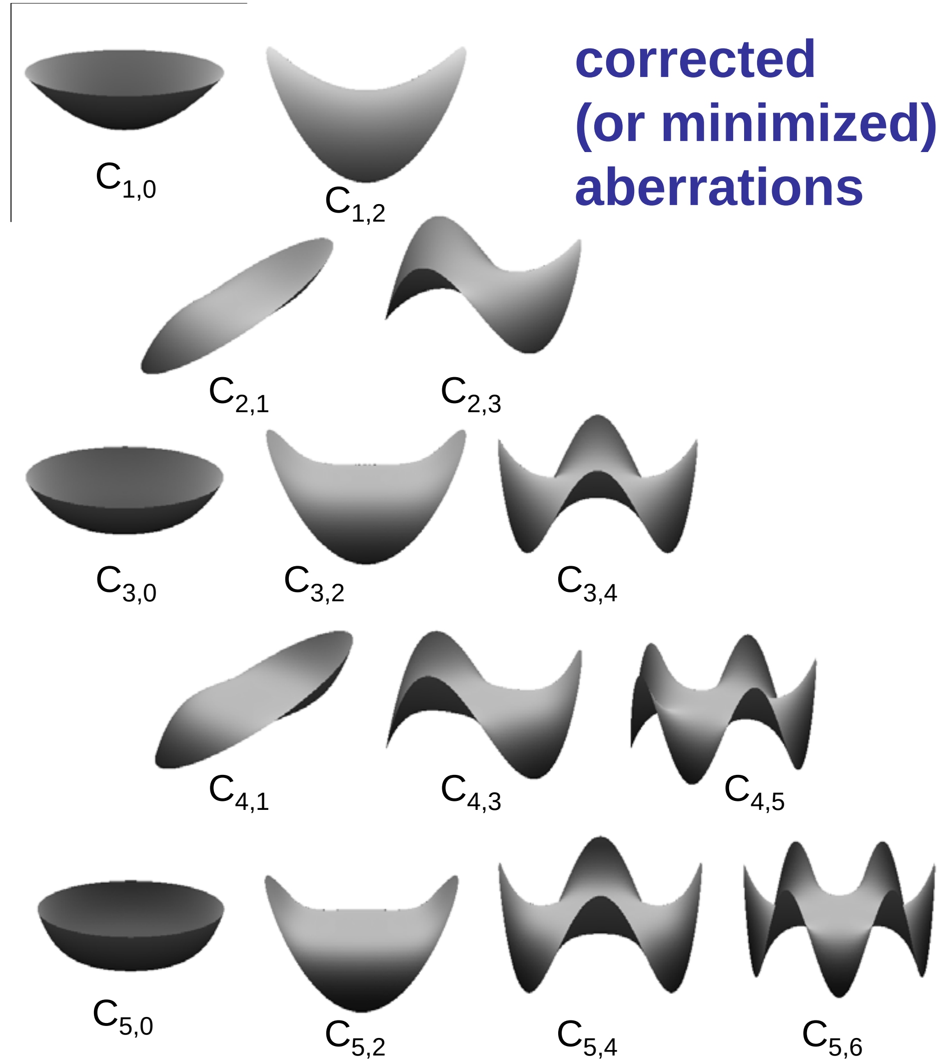


Sextupole - round lens - sextupole corr. (~1980)
(grandfather to CEOS's corrector)

Neither corrector ever worked properly, most likely because parasitic aberrations were neither quantified nor accurately compensated.

Aberrations

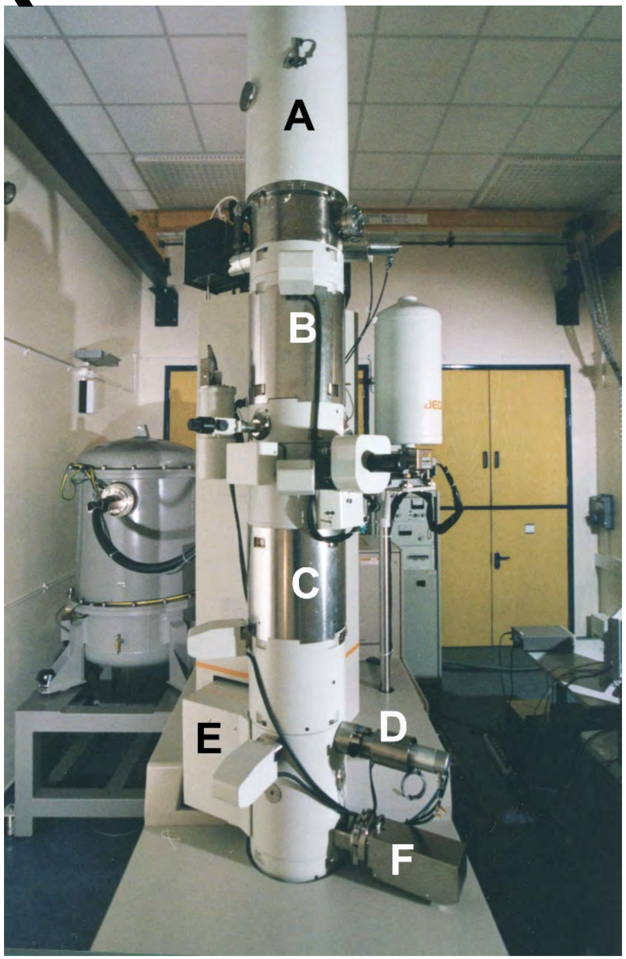




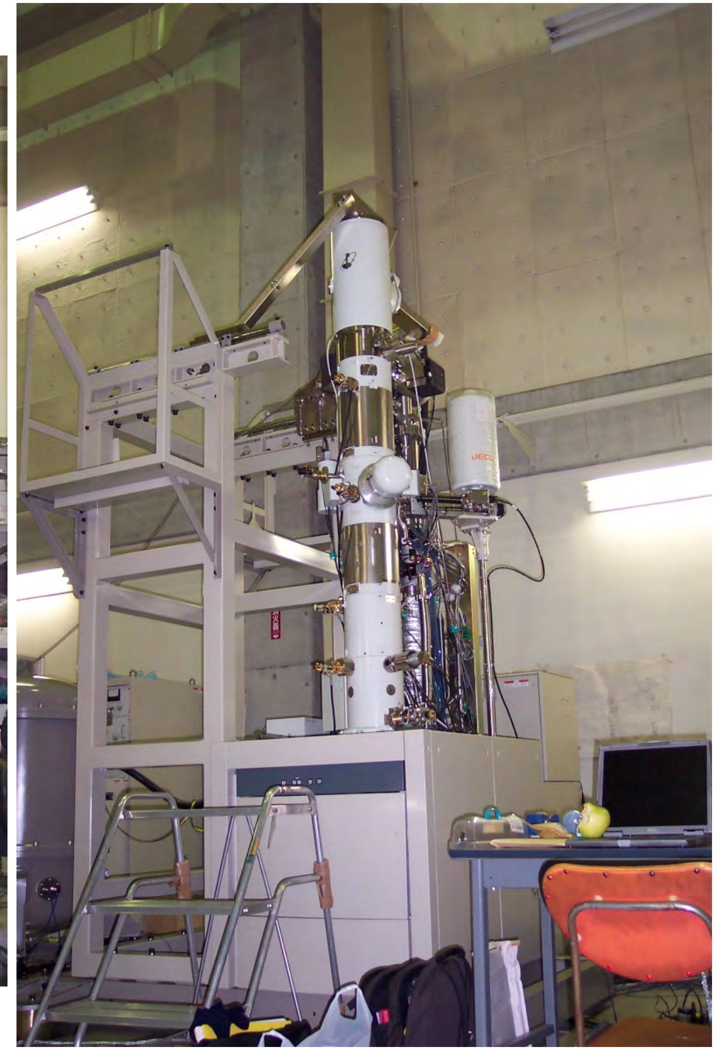
Coherent Aberration Resolution Limits.

	TEM	HAADF-STEM
200kV Interpretable Limit		
Uncorrected	0.19nm	0.13nm
C_3 corrected	0.08nm	0.05nm
C_5 corrected	0.05nm	0.03nm

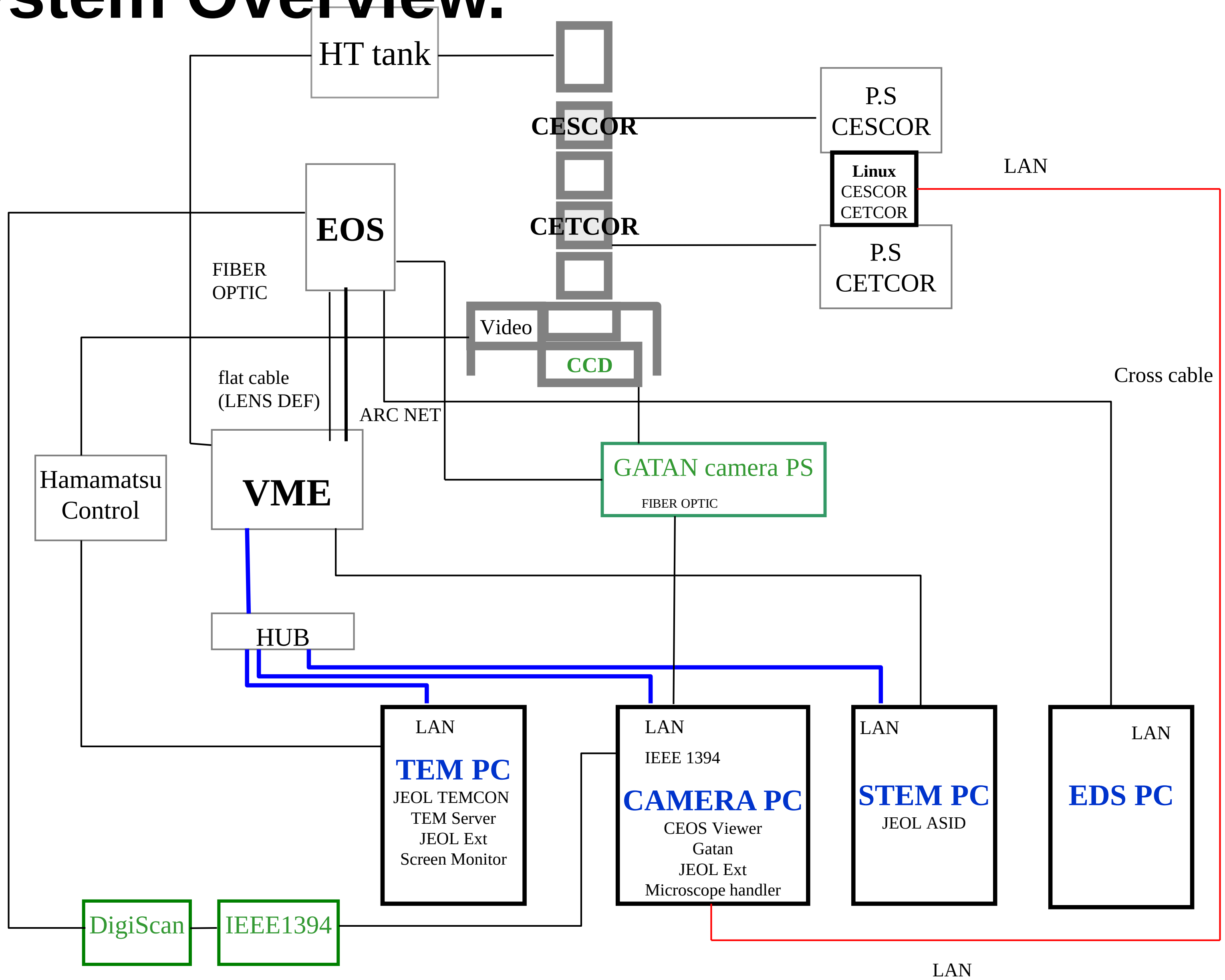
Instrumentation – Mark 1 (JEOL 2200FS).

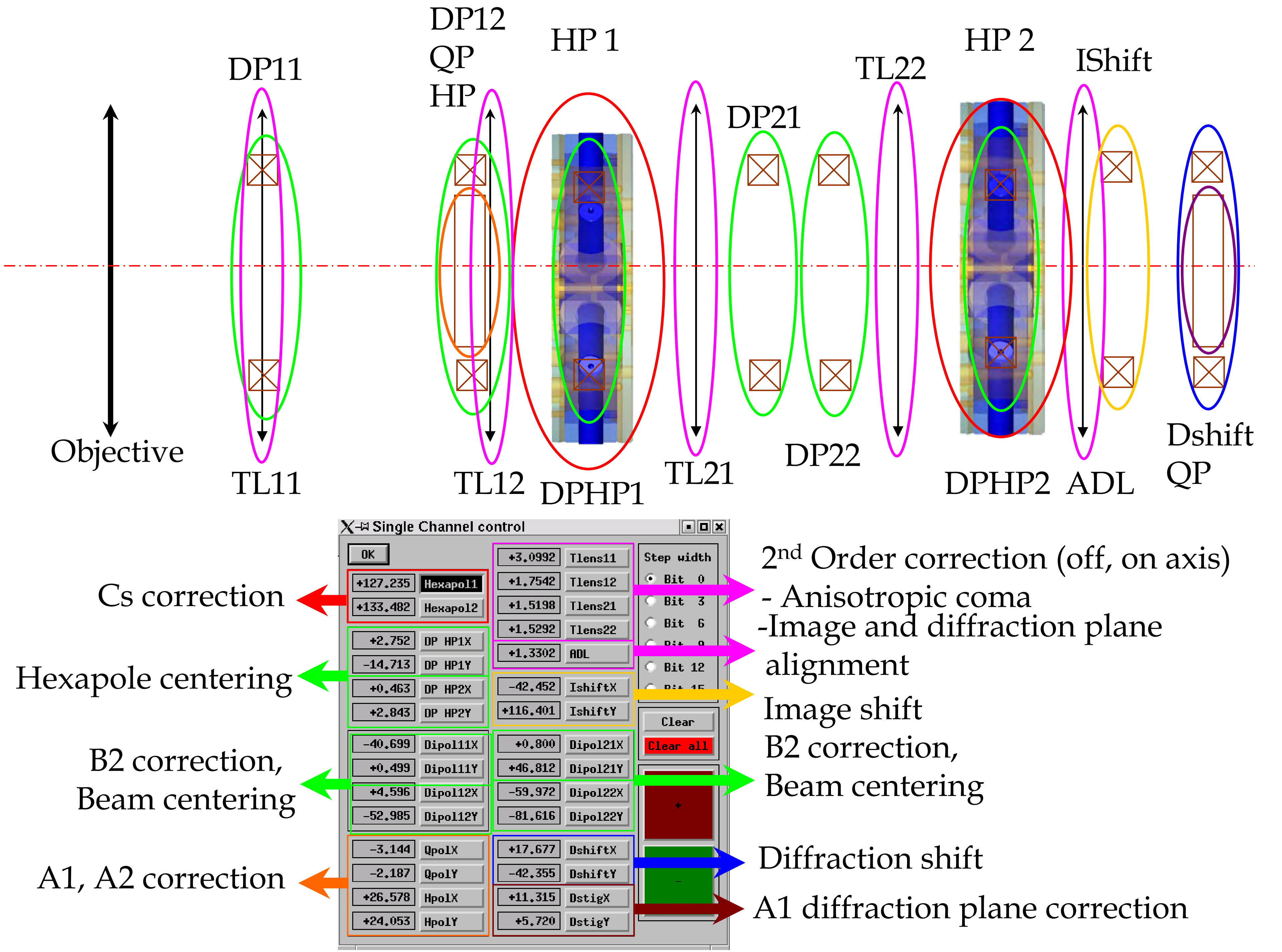


Instrumentation – Version 2 (JEOL 2200 MCO).

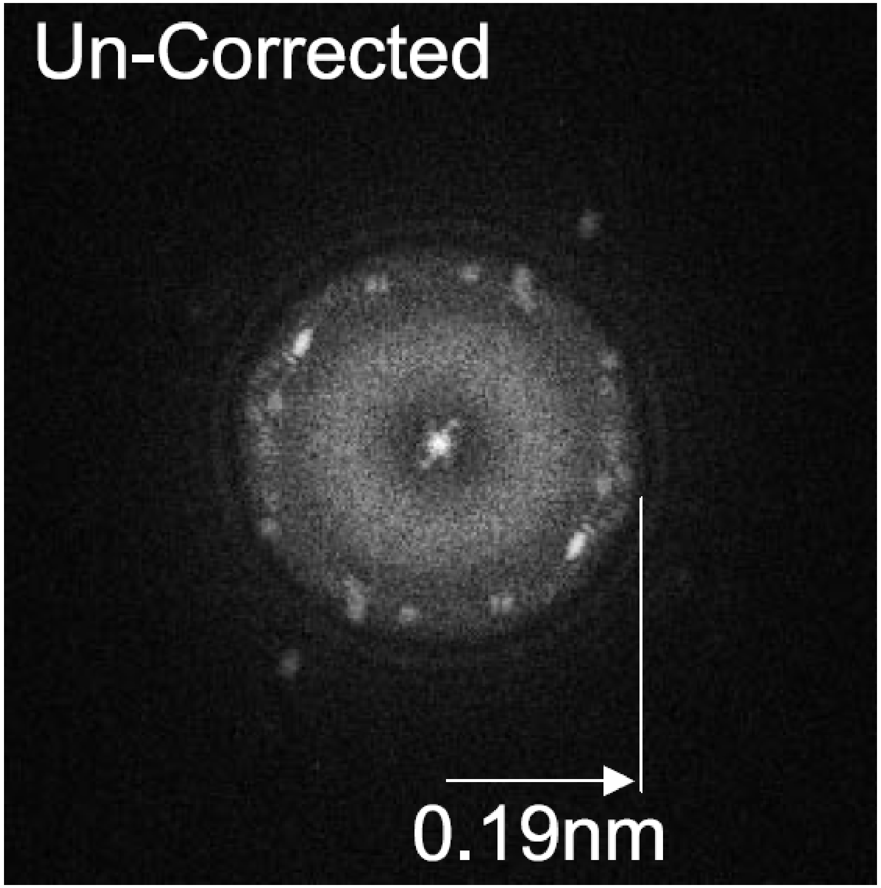


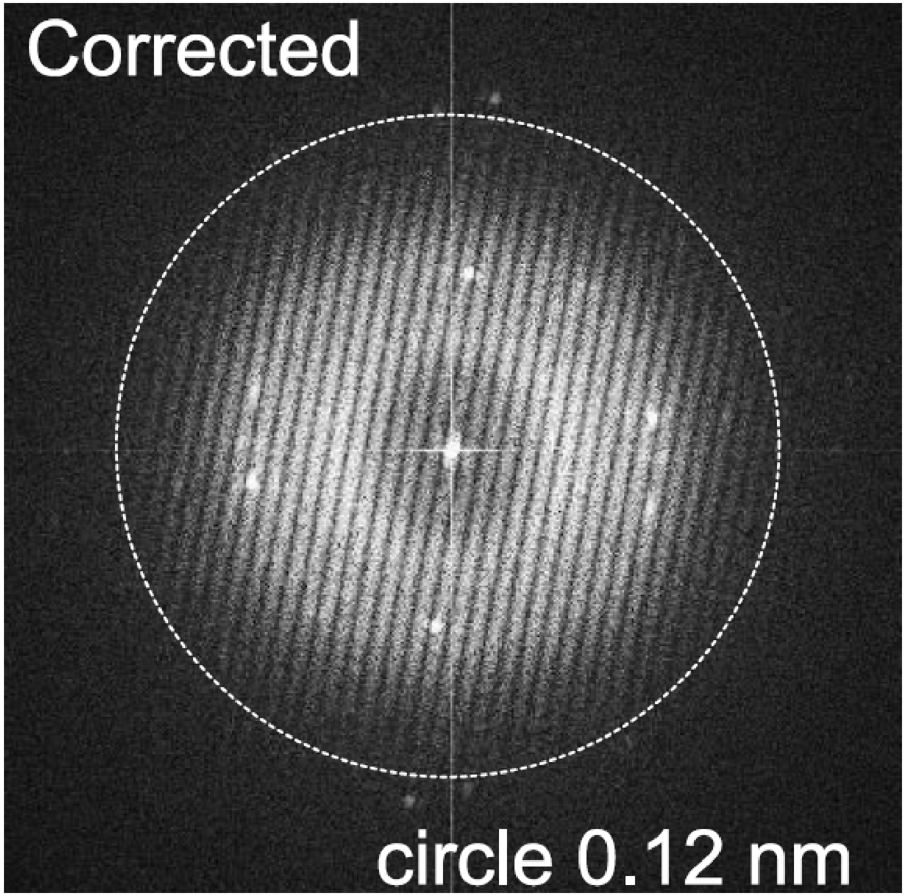
System Overview.





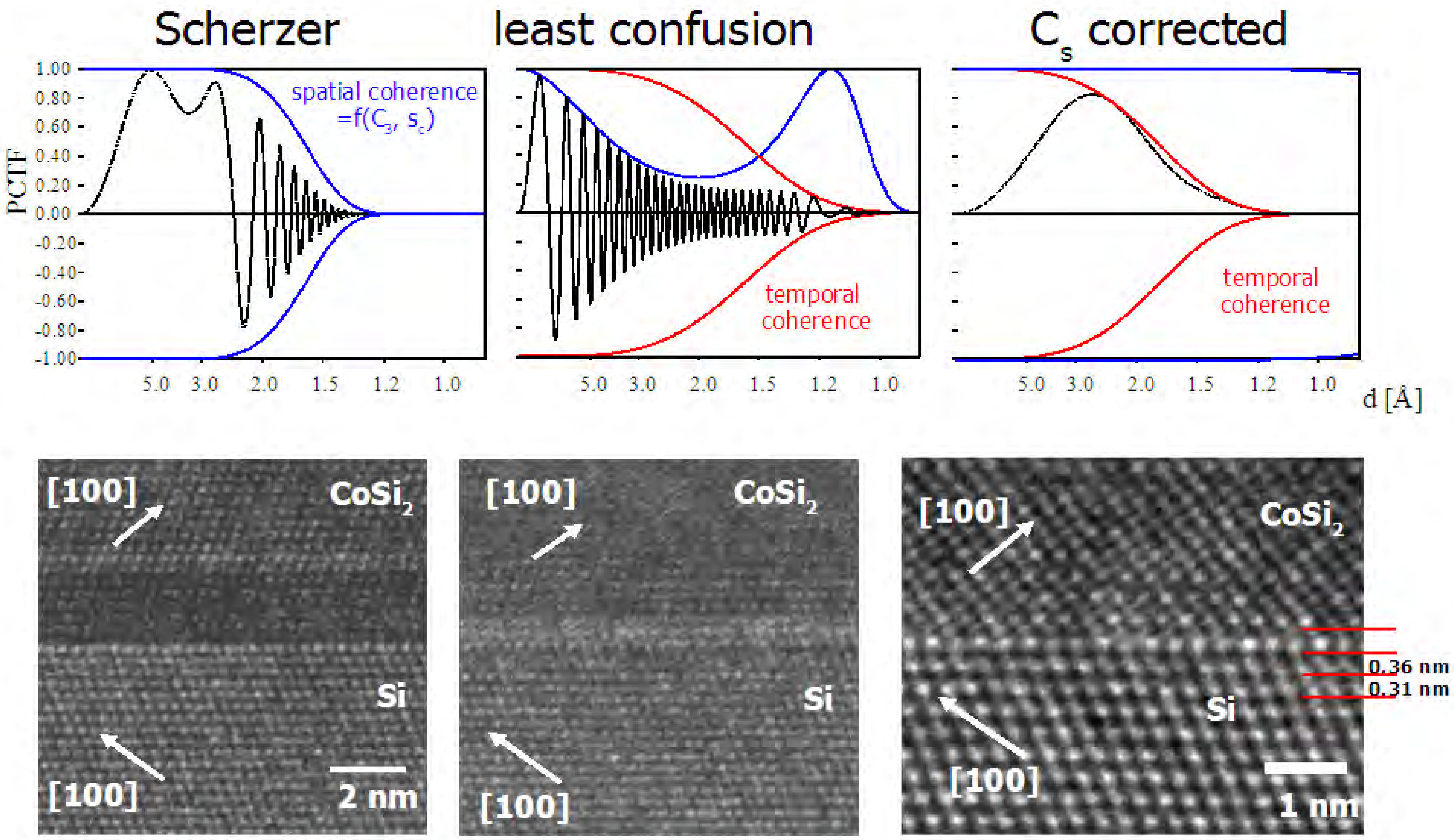
DP11
DP12
QP
HP
HP 1
TL22
HP 2
IShift
DP21
Objective
TL11
TL12
DPHP1
TL21
DP22
DPHP2
ADL
Dshift
QP
Single Channel control
OK
+127.235 Hexapol1
+133.482 Hexapol2
+2.752 DP HP1X
-14.713 DP HP1Y
+0.463 DP HP2X
+2.843 DP HP2Y
-40.699 Dipol11X
+0.499 Dipol11Y
+4.596 Dipol12X
-52.985 Dipol12Y
-3.144 QpolX
-2.187 QpolY
+26.578 HpolX
+24.053 HpolY
+3.0992 Tlens11
+1.7542 Tlens12
+1.5198 Tlens21
+1.5292 Tlens22
+1.3302 ADL
-42.452 IshiftX
+116.401 IshiftY
+0.800 Dipol21X
+46.812 Dipol21Y
-59.972 Dipol22X
-81.616 Dipol22Y
+17.677 DshiftX
-42.355 DshiftY
+11.315 DstigX
+5.720 DstigY
Step width
Bit 0
Bit 3
Bit 6
Bit 12
Clear
Clear all
Cs correction
Hexapole centering
B2 correction,
Beam centering
A1, A2 correction
2nd Order correction (off, on axis)
- Anisotropic coma
-Image and diffraction plane
alignment
Image shift
B2 correction,
Beam centering
Diffraction shift
A1 diffraction plane correction





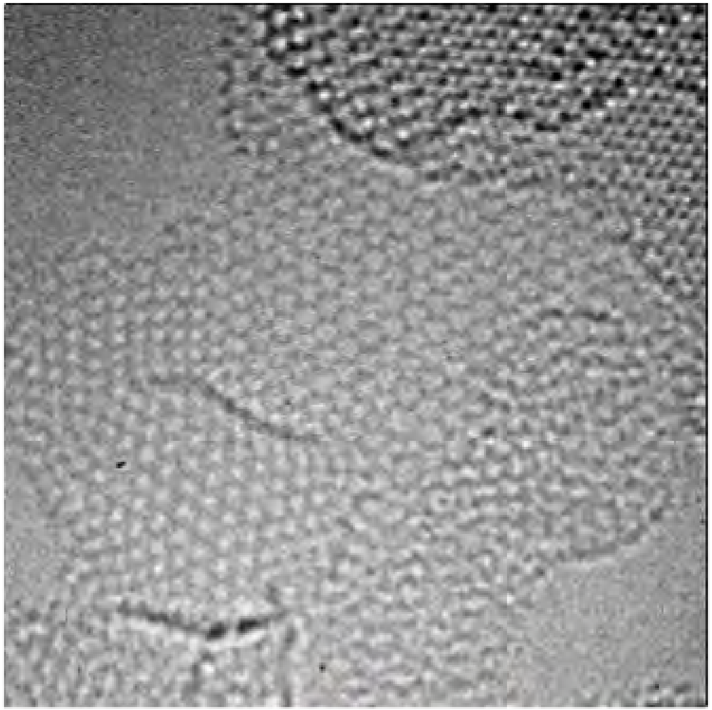
Sawada, H. et al. Experimental
evaluation of a spherical aberration corrected TEM and STEM, Journal of Electron Microscopy, 2005, 52, 2, 120,

C_s correction

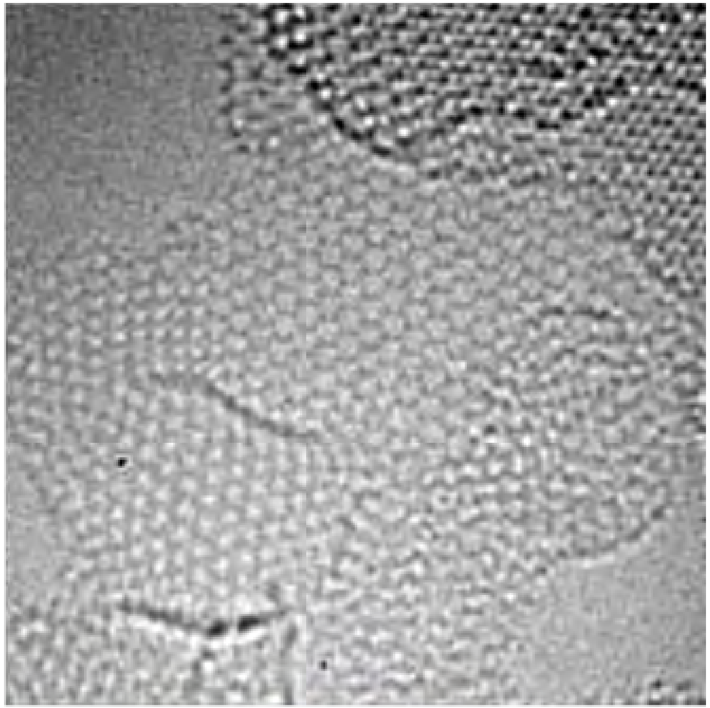


M.Haider, S.Uhlemann, E.Schwan, H.Rose, B.Kabius, K.Urban, Nature, 392 (1998) 768

TEM of Graphene at 80 kV



Raw



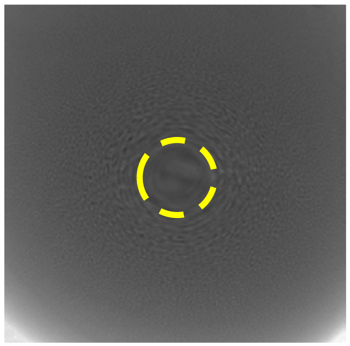
Filtered

$\Delta E = 0.3$ eV, $\Delta f = -2.2$ nm

Aberration Correction in JEM-2200FS

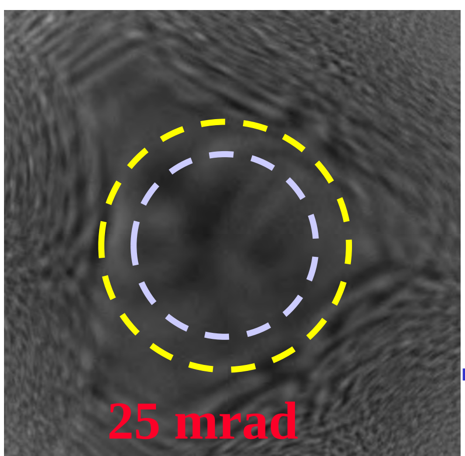
Ronchigram

Hexapole off



11 mrad

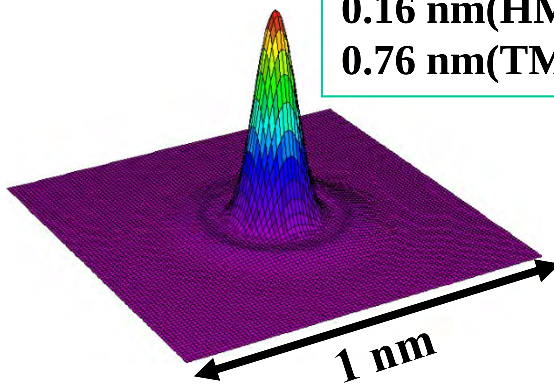
Hexapole on



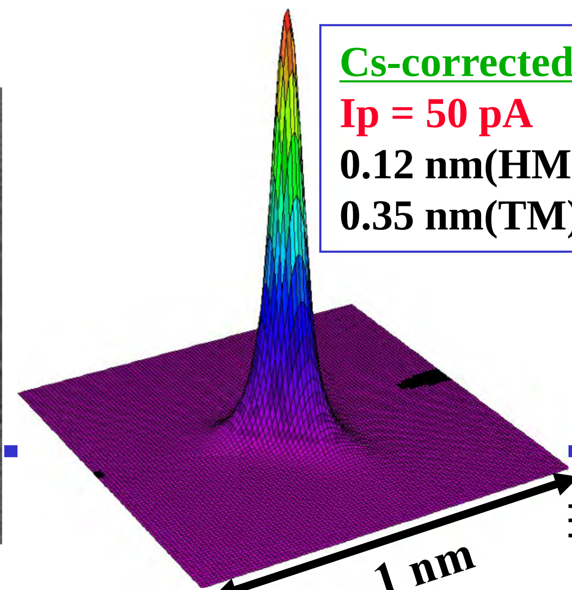
34 mrad

Simulated probe

Conventional
Ip = 10 pA
0.16 nm(HM)
0.76 nm(TM)

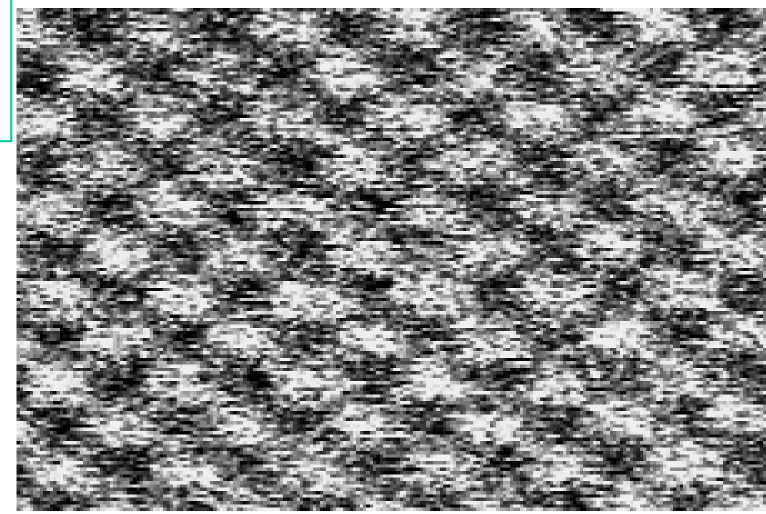


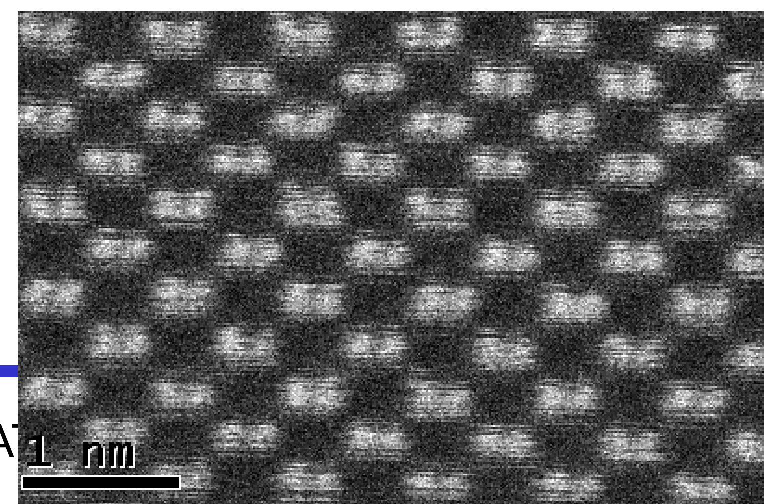
Cs-corrected
Ip = 50 pA
0.12 nm(HM)
0.35 nm(TM)



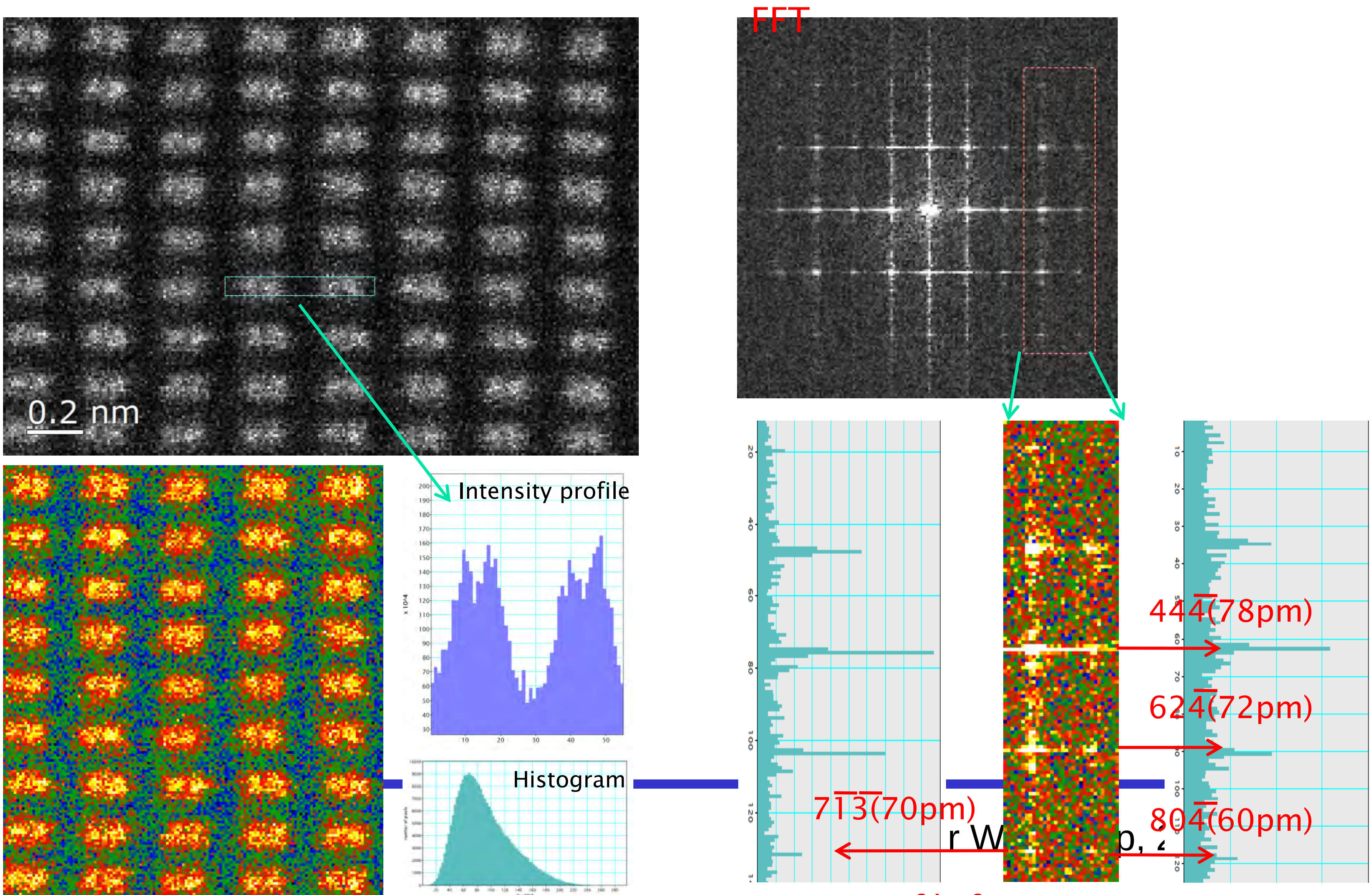
HAADF-STEM image

Si(110)





Si(112) 78 pm dumbbell image



Intensity profile from FFT spot

Beware!

- All you get with advanced instruments is easier/quicker alignment and better signal/images
- Many people sell the advantages of their instrument/technique (42, Douglas Adams)
- It is easier for a novice to get a “good” image, but that does not make it correct or representative
- There is no “dynamical diffraction” corrector
- Nothing will correct for a bad sample
- Nothing will correct for a bad interpretation