Dynamical Diffraction for Dummies
Channelling

- Reality: 3 nm of H_2 is dynamical, as is 1 atom of Au
- But…often dynamical effects do not appear to be critical
- Is dynamical theory wrong (no)
- Are kinematical strategies viable (often)
- Why?

Very basic

- Kinematical Model
  - $\Psi(k)=C\int V(r)\exp(2\pi ik.r)dr$
- Better, phase grating model
  - $\psi(r)=\exp(-i\sigma\int V(r)dz)= \exp(-i\sigma V_p(r))$

    $= 1- i\sigma V_p- ½(i\sigma V_p)^2-…$
- Alas….multiple scattering is strong, both are qualitatively right, quantitatively wrong

Standard Approaches

1. Multislice (fast numerical integration)
2. Bloch Waves: plane waves

   Expand $\psi(r)=\Sigma C_j \exp(2\pi i k_j.r)\Sigma \exp(2\pi i g.r)$

3. Channeling: 2D atomic orbitals

   Expand $\psi(r)=\Sigma C_{j,m} \exp(2\pi i k_j.r_n)\phi(r-r_m)$

4. Others exist, not in general use

Diffraction = Quantum Mechanics

Kinematical ~ 1st-order Perturbation Theory

Chemistry

Bloch Waves	Molecular Orbitals
Channeling Model	Atomic Orbitals (LCAO)

Physics

Bloch Waves	Plane Wave Expansion Matrix Diagonalization
Channeling Model	Tight Binding Model

Channeling: Real-Space model

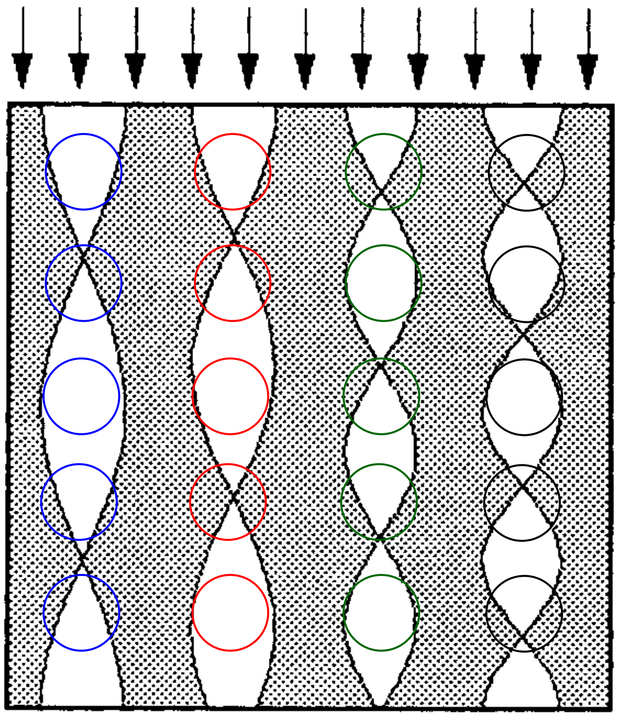
- Electron channeling approximation*:
  - 1) ignore all but ZOLZ interactions (high energy)
  - 2) assume sample orientation so that one has well separated atomic columns along z (in initial expansion only)

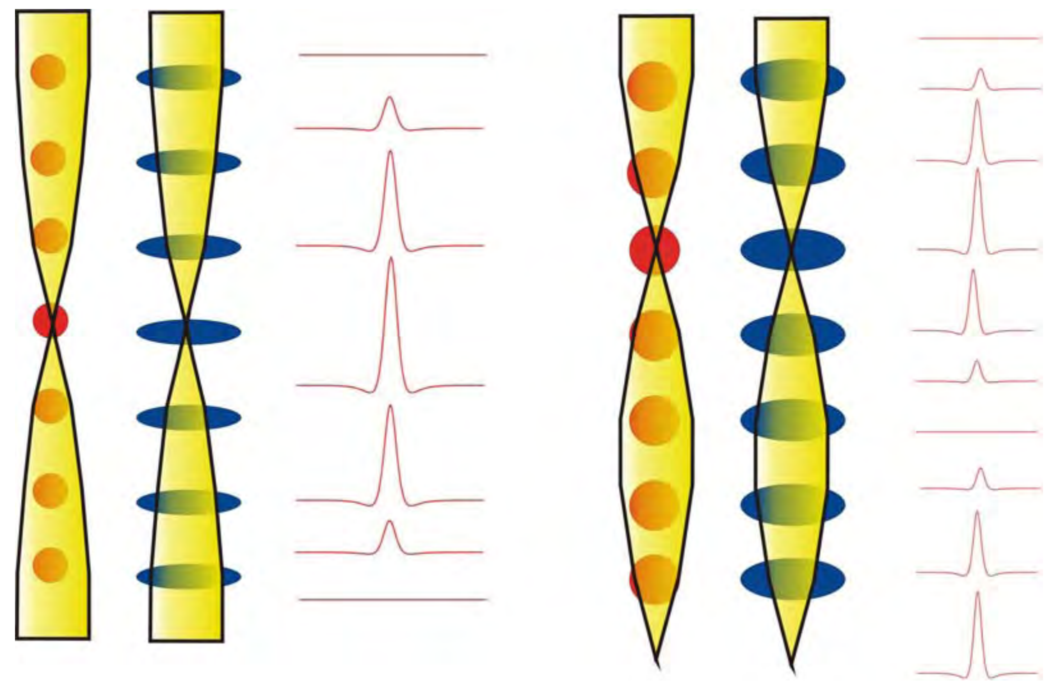
* Fujimoto, phys. stat. sol. (1978) + many others
Van Dyck and Op de Beeck, *Ultramicroscopy* (1996)

Zone axis orientation: channelling

- Atoms superimpose along beam direction
- Strong scattering
- Plane wave methods not appropriate
- Atom column as a new basis

Conceptual Picture



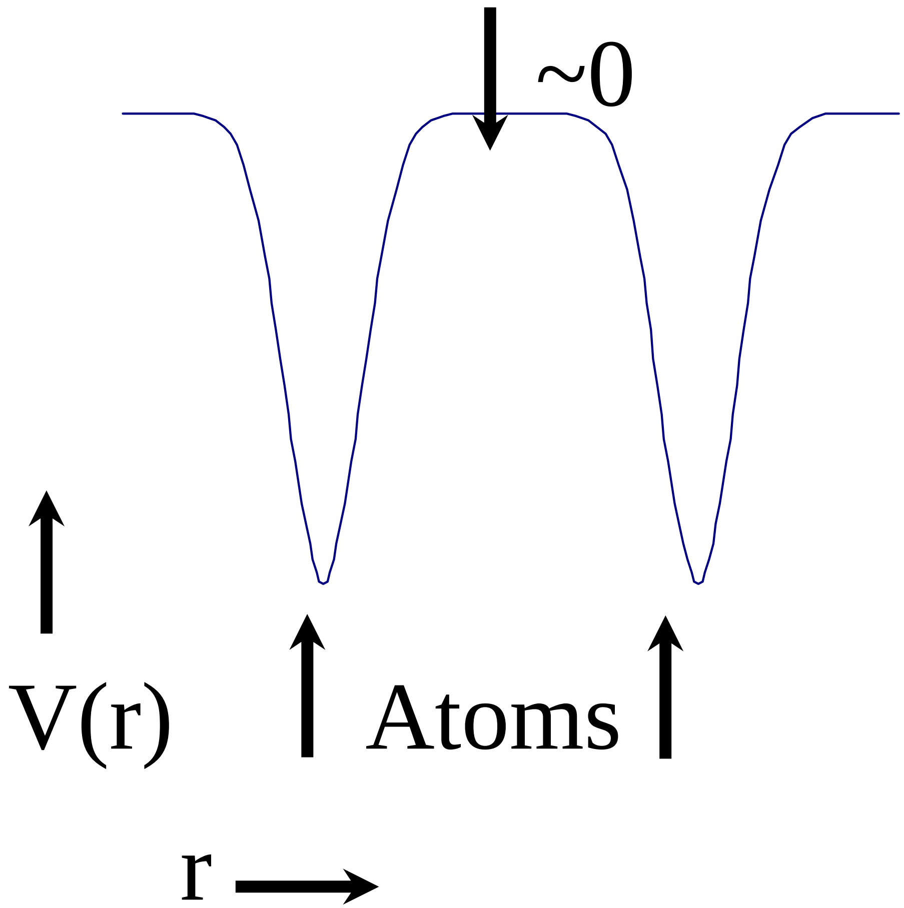


light atoms heavy atoms light atoms heavy atoms

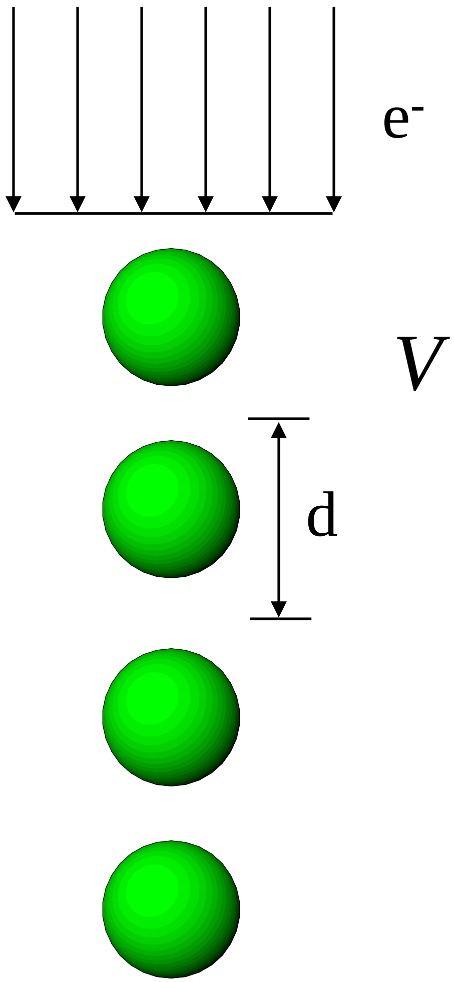
Curtesy D. Van Dyck

Channeling Concept

- For many zone axes, in projection atoms are well separated
- Potential large near columns
- Small between columns



Consider an isolated column: I



$$V(\underline{R}) = V(x,y) = \frac{1}{d}\int_{-d/2}^{d/2} V_0(\underline{R}, z)\,dz$$

Average potential

Consider an isolated column: II

- Problem reduces to 2-D Schrödinger's Eqn

$$\nabla^2_{\mathbf{R}}\Phi(\mathbf{R}) + \frac{8\pi^2 m}{h^2}\left[E + V(\mathbf{R})\right]\Phi(\mathbf{R}) = 0$$

- Solutions have form:

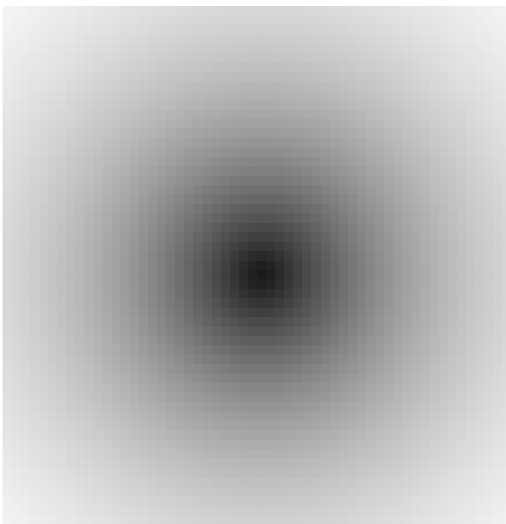
"Transverse Energy"

$$\psi(\mathbf{r}) = \sum_n C_n \Phi_n(\mathbf{R}) \exp\left\{-i\pi E_n z\right\}$$

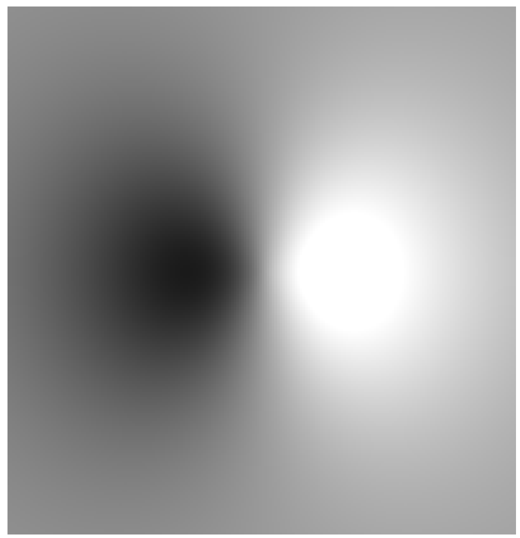
2D orbitals

Character of States

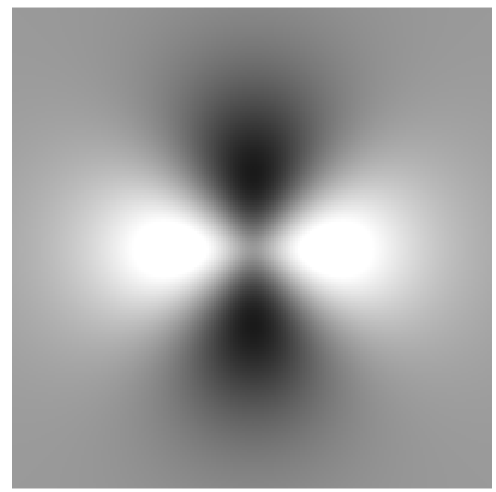
- 2D analogues of 3D atomic orbitals



1s



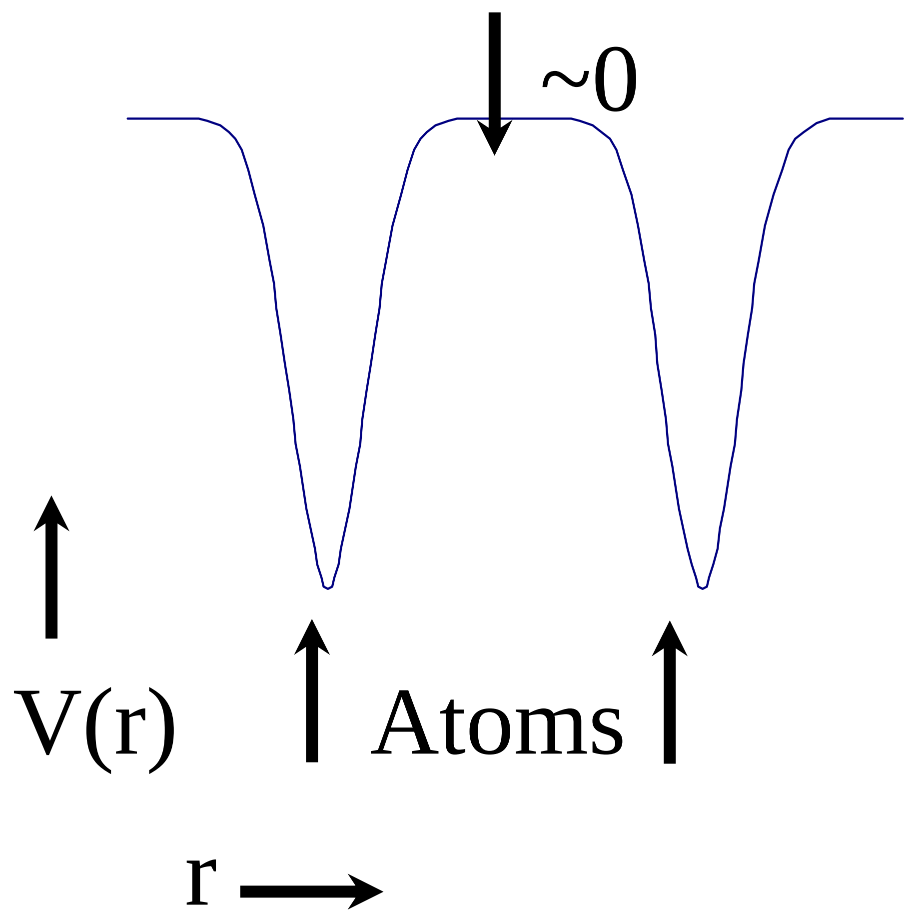
2p



3d

Channeling Concept

- For many zone axes, in projection atoms are well separated
- Potential large near columns
- Small between columns



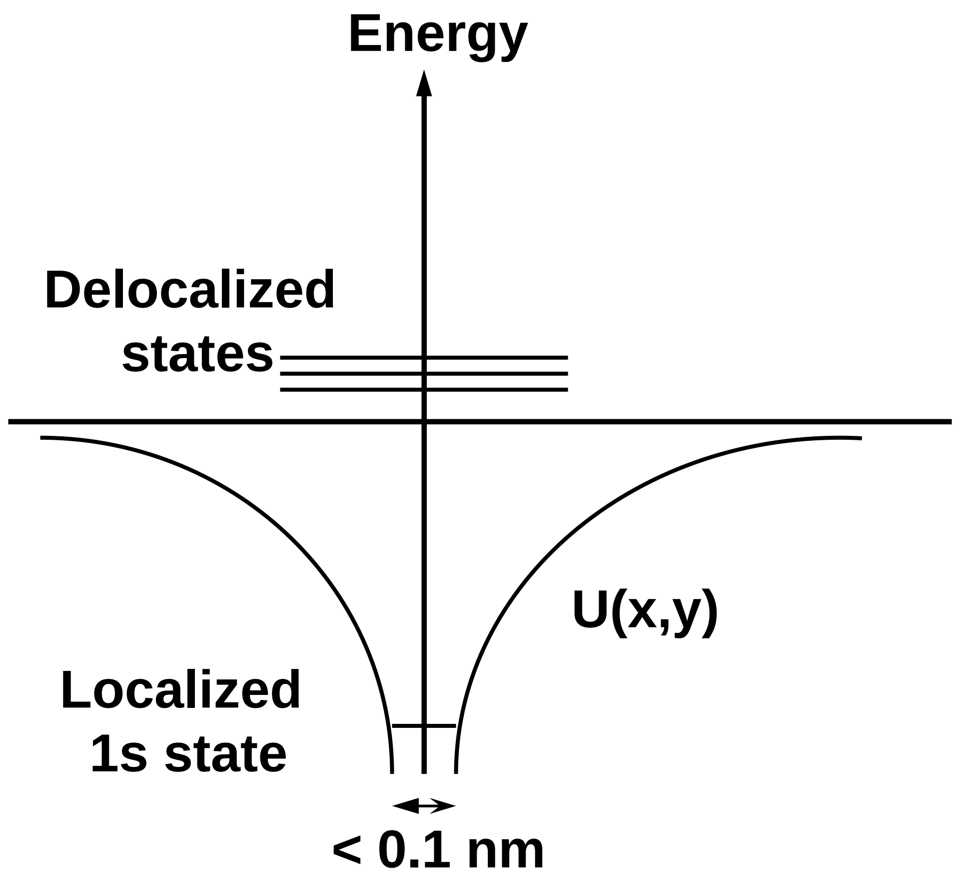
Dynamical Solutions: many columns

- General solution

$$\psi(\mathbf{R},z)-1\approx\sum_{i,j}C_i\Phi_i(\mathbf{R}-\mathbf{R}_j)\left(\exp(-i\pi E_n z)-1\right)$$

- On a zone (symmetry), s-type orbitals dominate
- Not so simple if the zone axis is complicated – not a solved problem

S-state model



S-state

$$\Psi(\rho, z) \simeq 1 + 2c_{00} \sin\left(\pi \frac{-E_{00}}{E_0} \frac{k_z}{2} z\right) \psi_{00}(\rho) \exp\left\{-i\pi \left(\frac{E_{00}}{E_0} \frac{k_z}{2} z - \frac{1}{2}\right)\right\}$$

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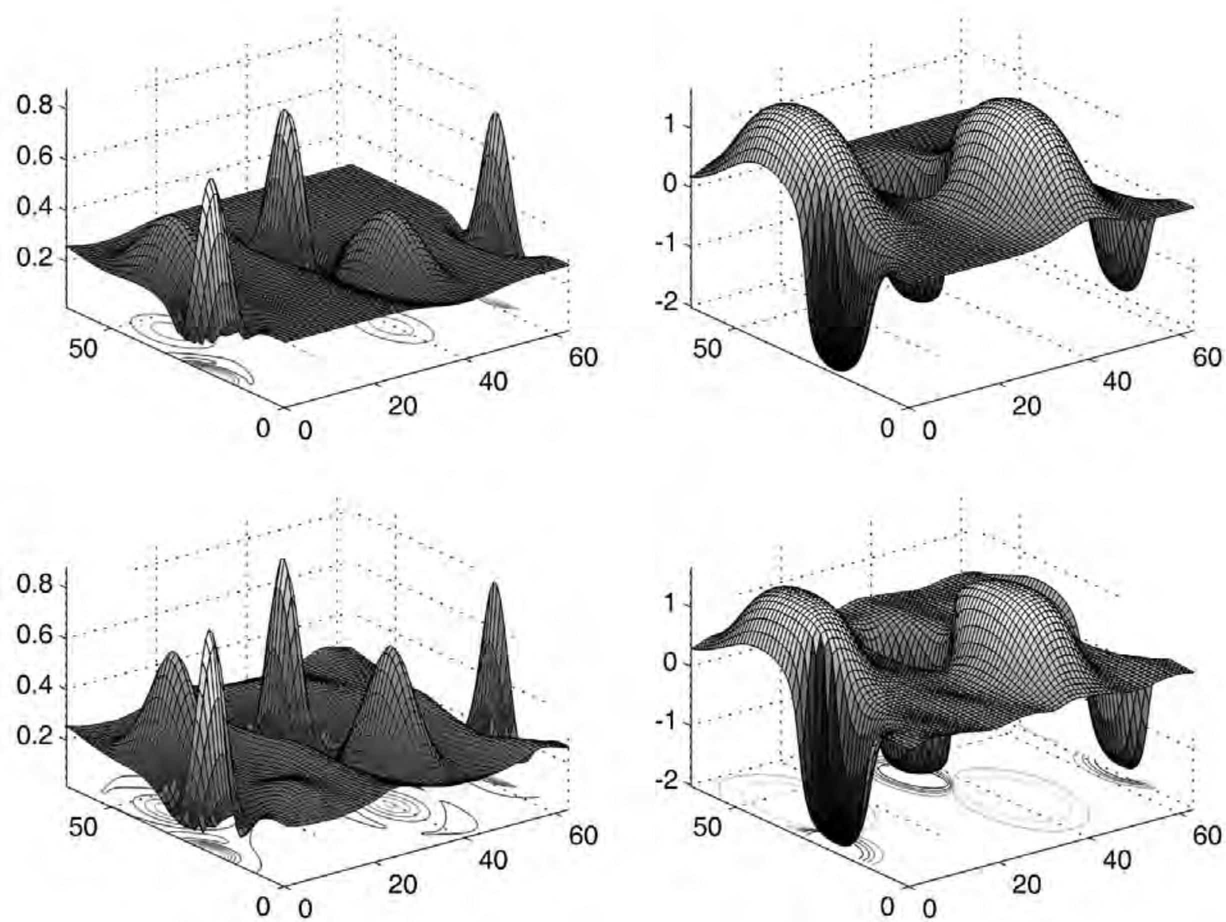

GaN [110] thickness 8 nm 300 keV

S-state model

multislice

amplitude

phase

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Dynamical Solutions: many columns

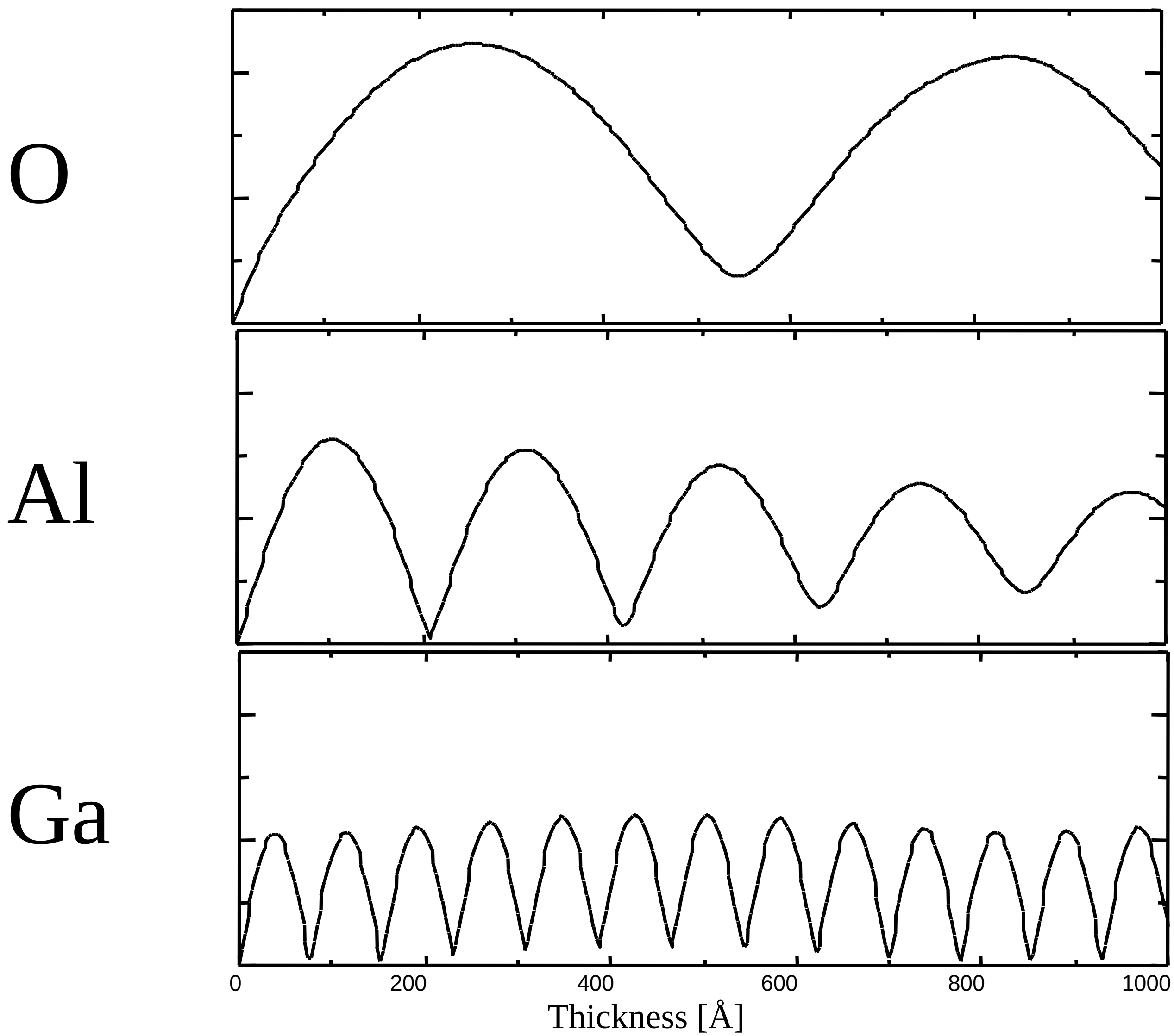
$$\psi(\mathbf{R},z)-1\approx\sum_{i,j}C_i\Phi_i(\mathbf{R}-\mathbf{R}_j)\left(\exp(-i\pi E_n z)-1\right)$$

$$|\psi(\mathbf{R},z)-1|$$

Peaked atom-like term, localized at columns in projection

Depth dependence by atom type

$|1-\psi(r)|$
at atom



Why?

$$\psi(\mathbf{R}, z) - 1 \approx \sum_{i,j} C_i \Phi_i(\mathbf{R} - \mathbf{R}_j)\left(\exp(-i\pi E_n z) - 1\right)$$

z small

$$\psi(\mathbf{R}, z) - 1 \approx \sum_{i,j} C_i \Phi_i(\mathbf{R} - \mathbf{R}_j)\left(-i\pi E_n z\right)$$

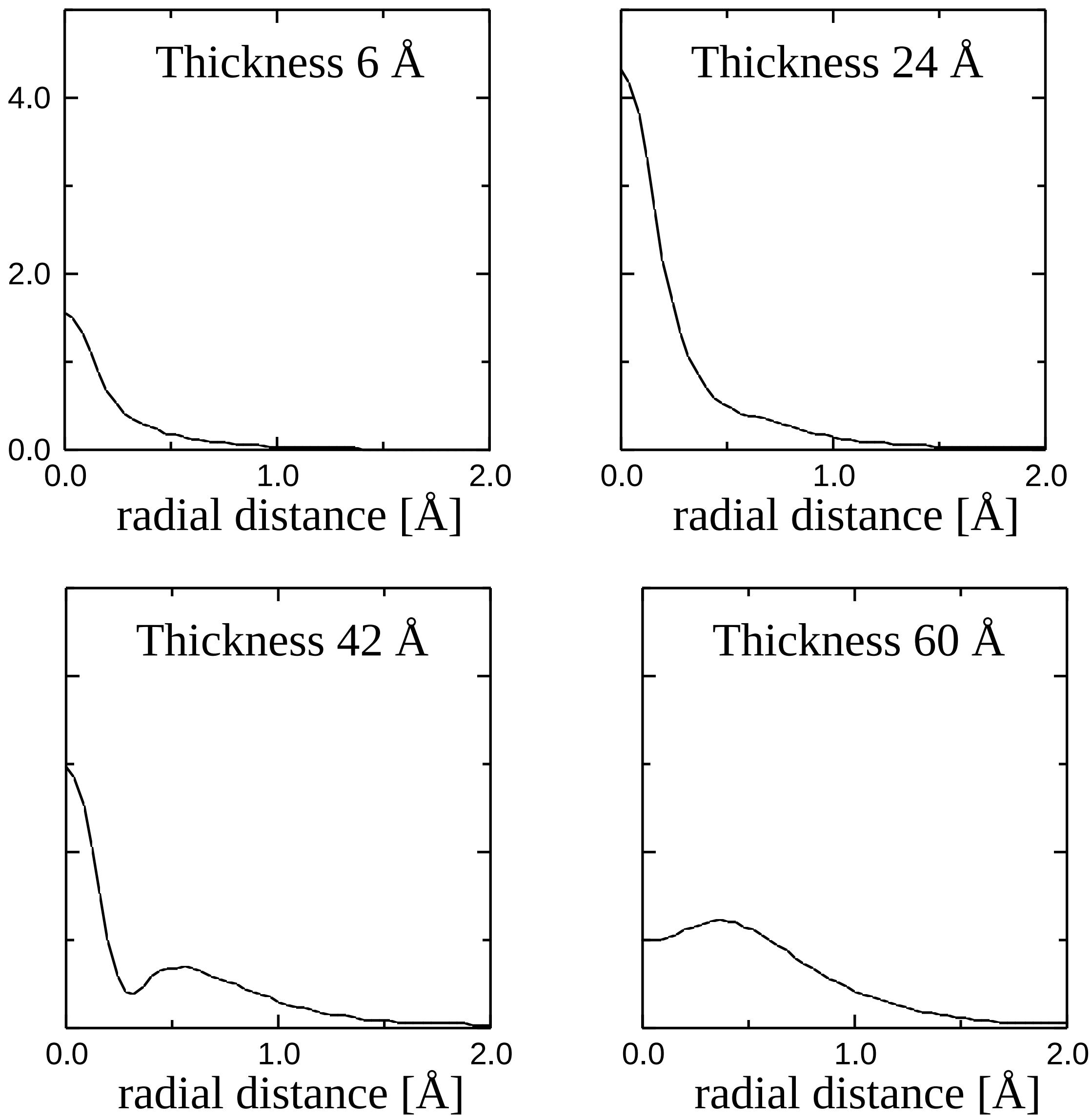
Phase grating approximation

$$\psi(\mathbf{R}, z) - 1 \approx i\sigma z V(\mathbf{R} - \mathbf{R}_j)$$

$$C \approx \sigma / E_n$$

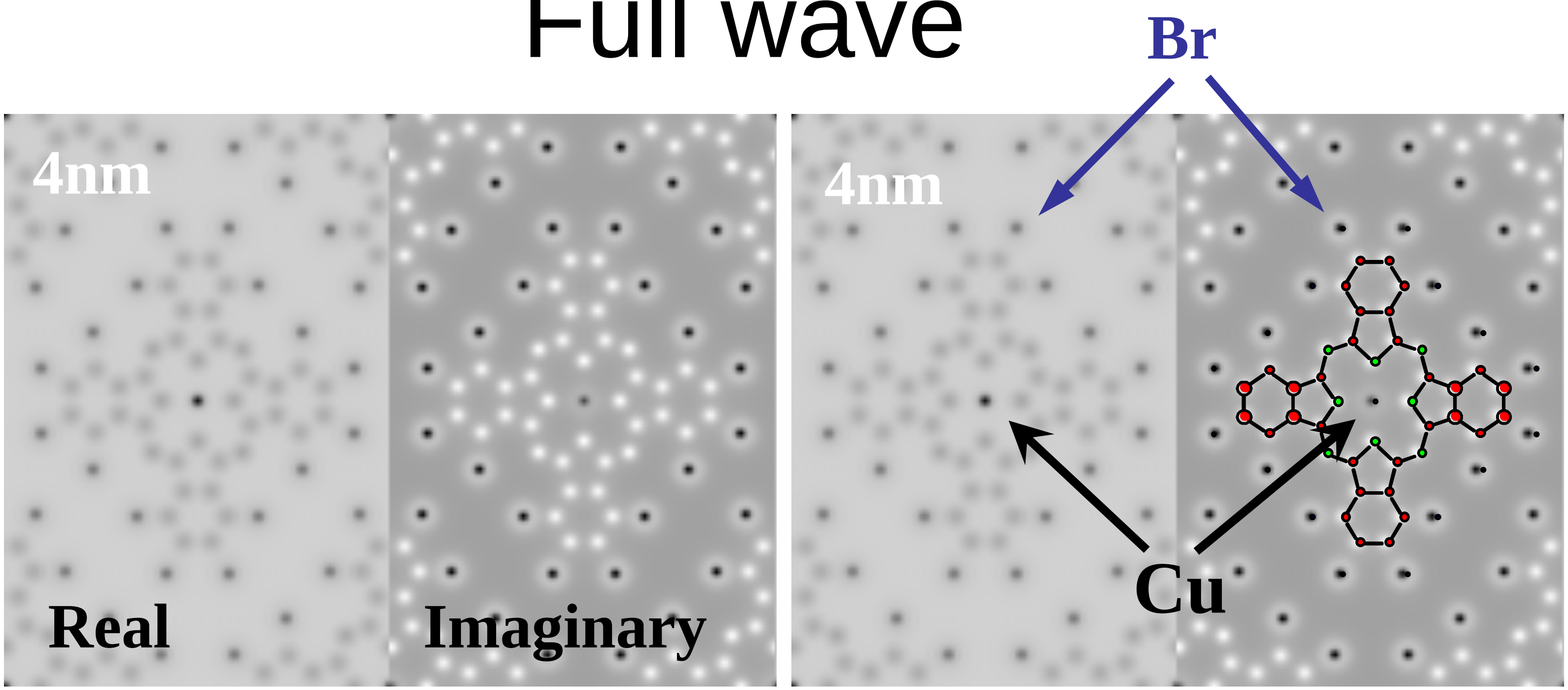
E_n is larger for heavier atom

Mo Solutions (1s & 2s)

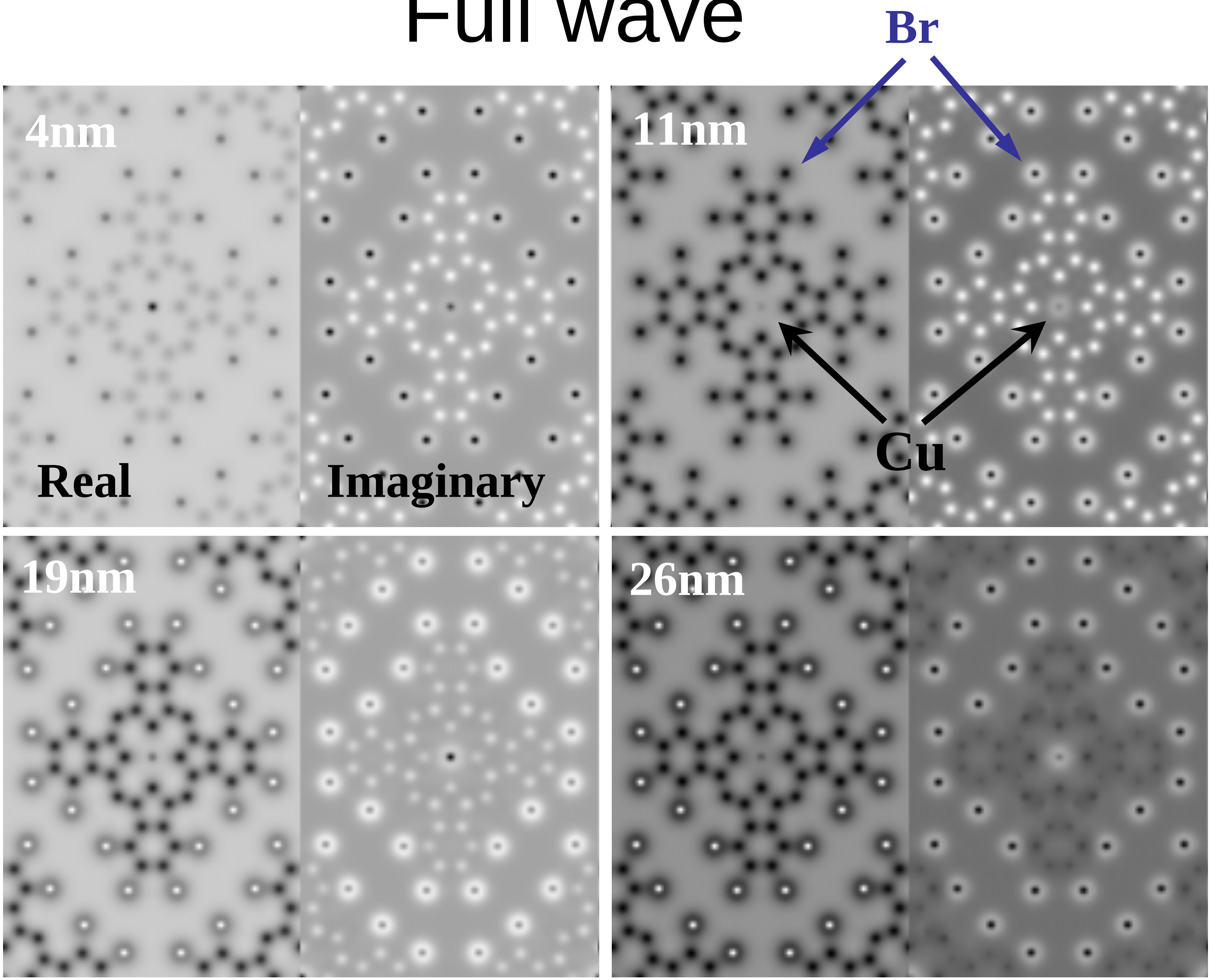


1s solutions dominate for thin crystals, then 2s etc

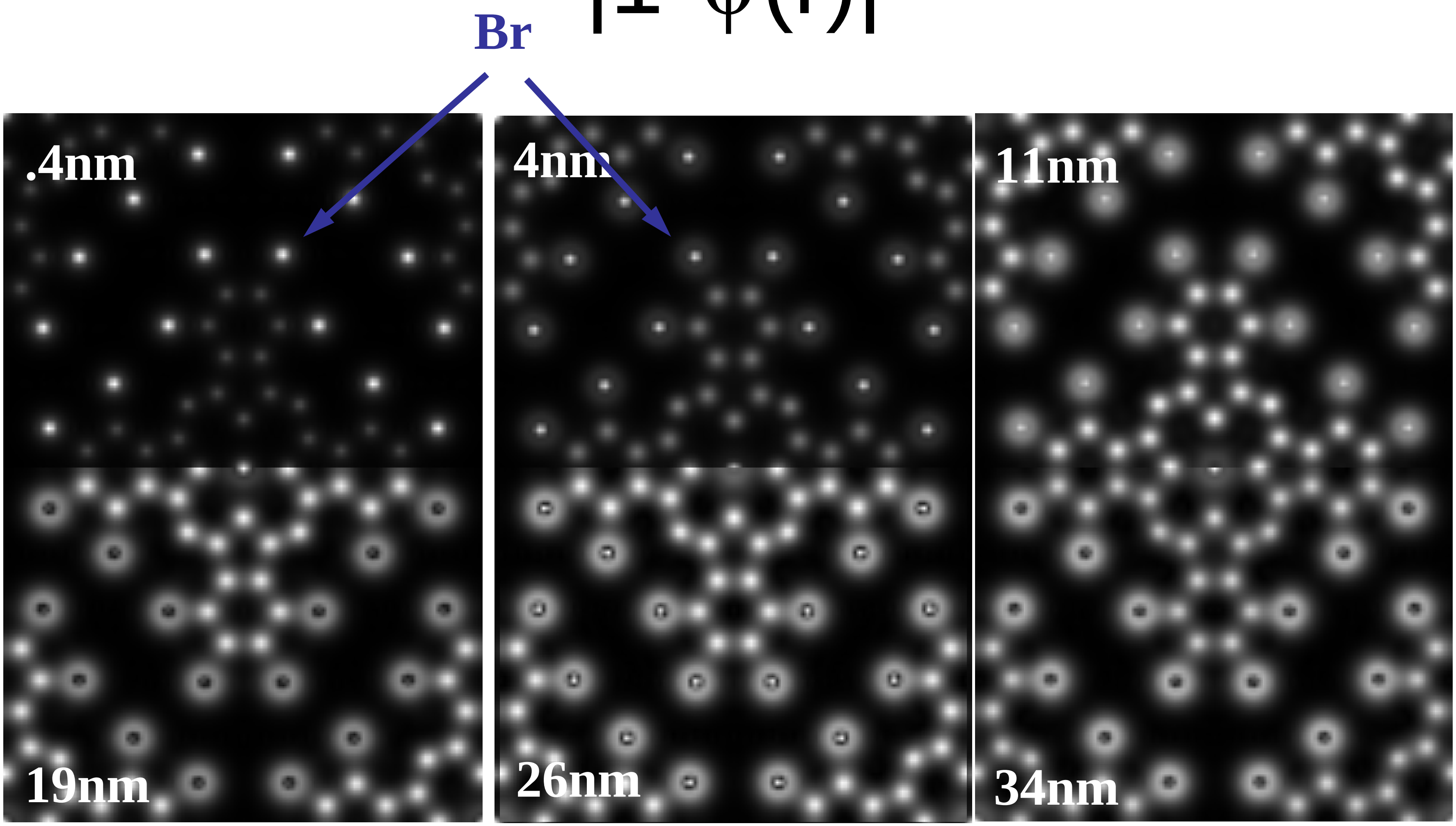
Full wave



Full wave

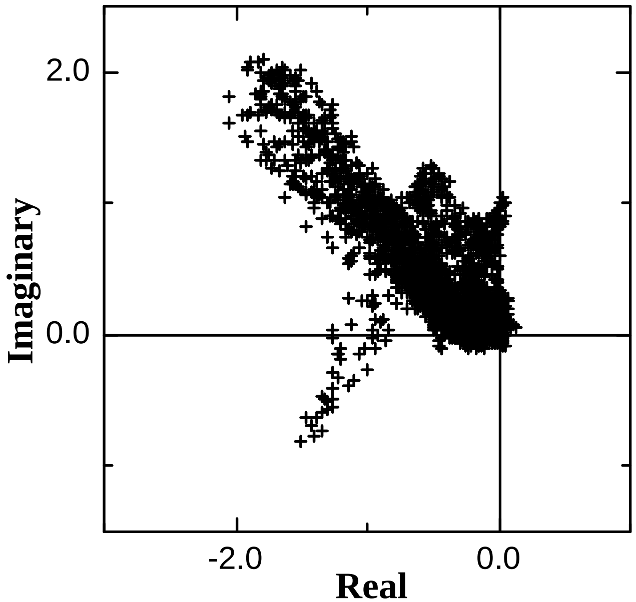


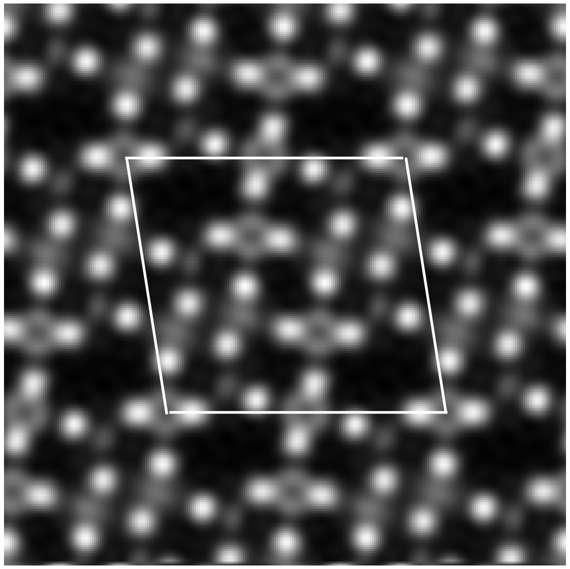
$$|1-\psi(r)|$$

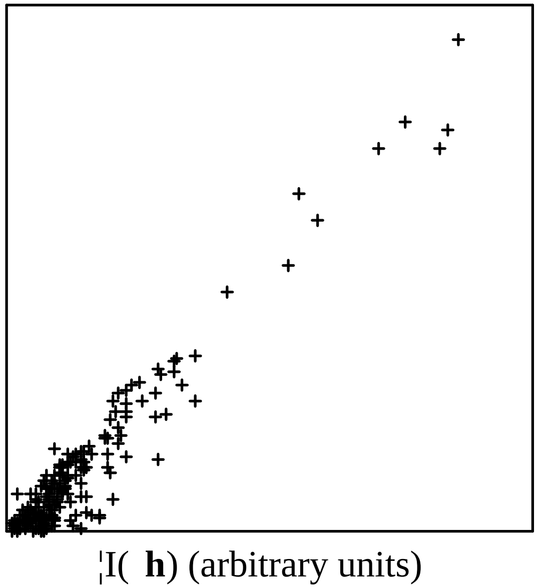


Carbon is more important than Bromine for ~ 10nm

Scatter, |1-ψ(r)| and F.T.







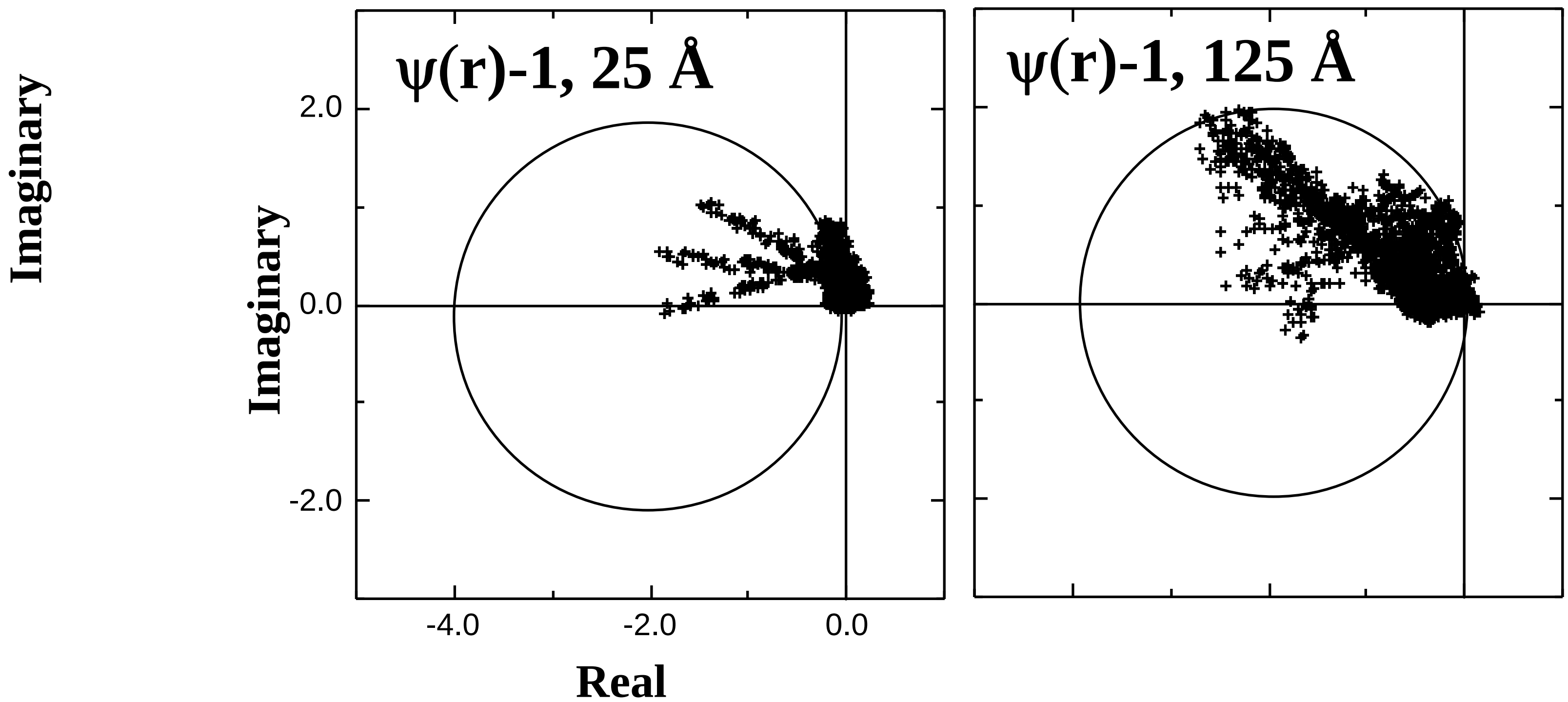
ψ(r) at every point

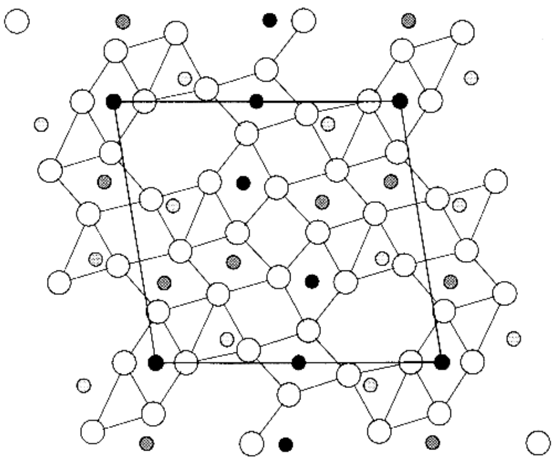
|1−ψ(r)| at every point

F.T. |1−ψ(r)| versus |Ψ(k)|

Sinkler Plots: Quasi-Kinematical

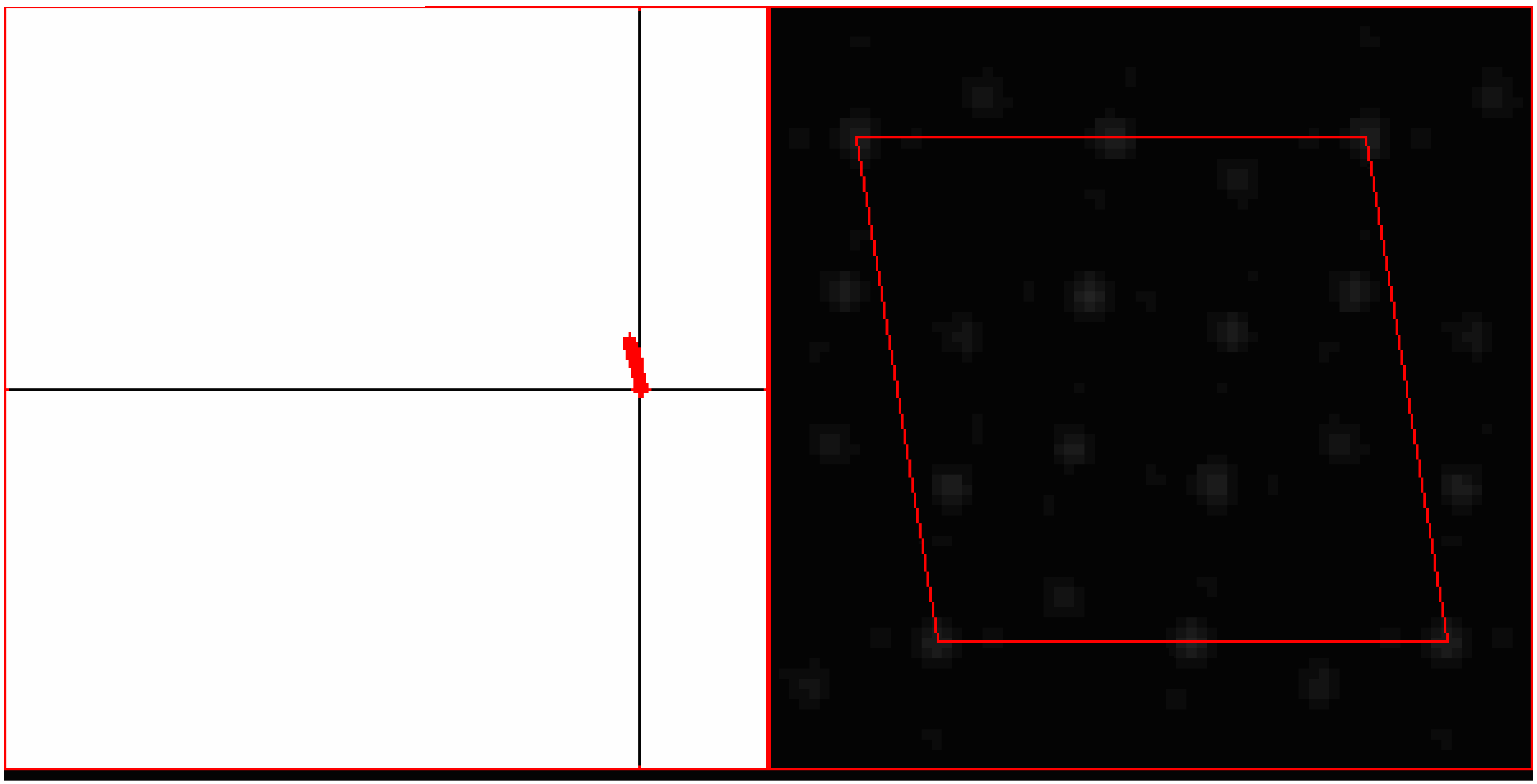
ψ(r)-1 has atom-like peaks with species-dependent oscillation

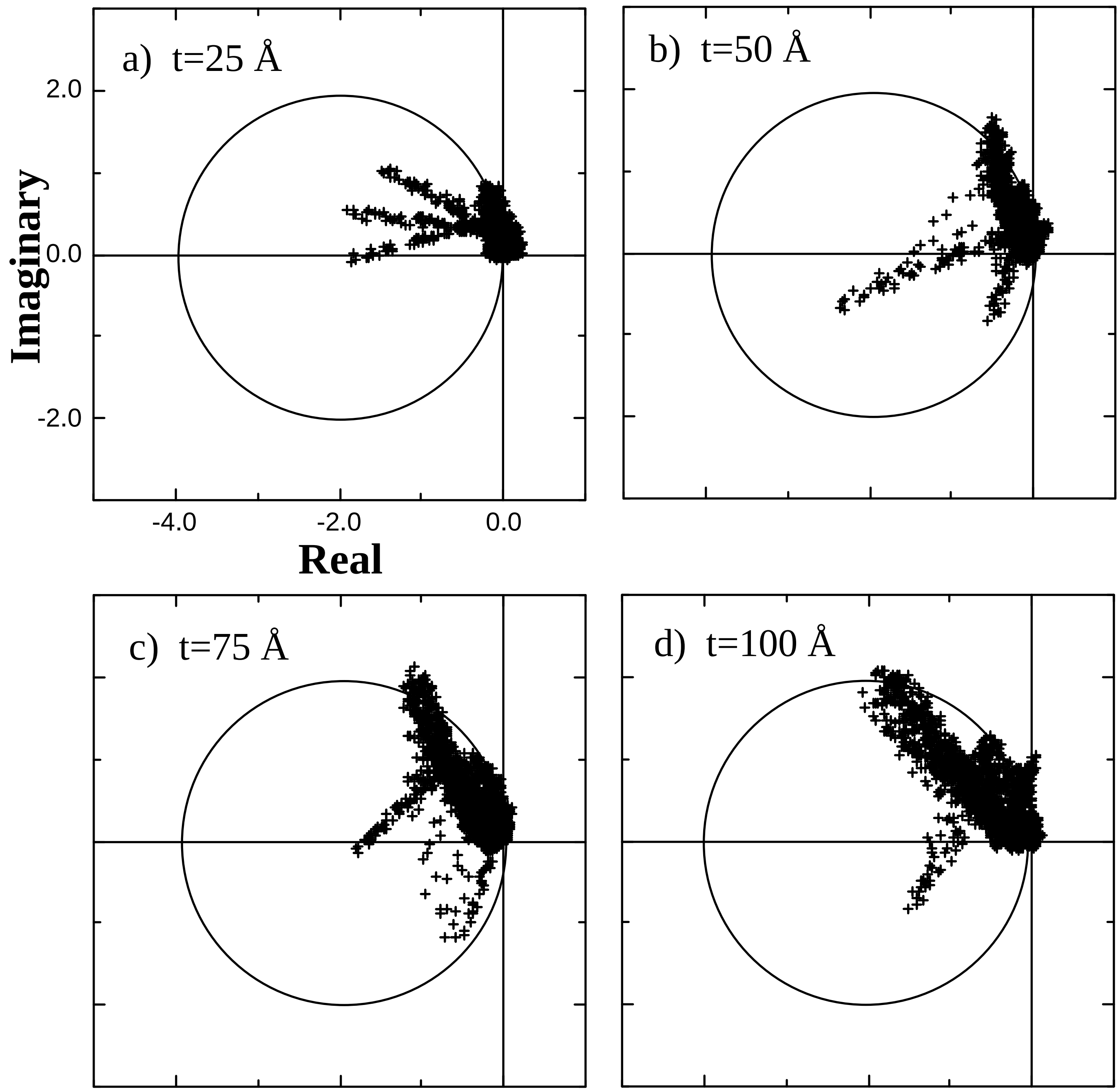


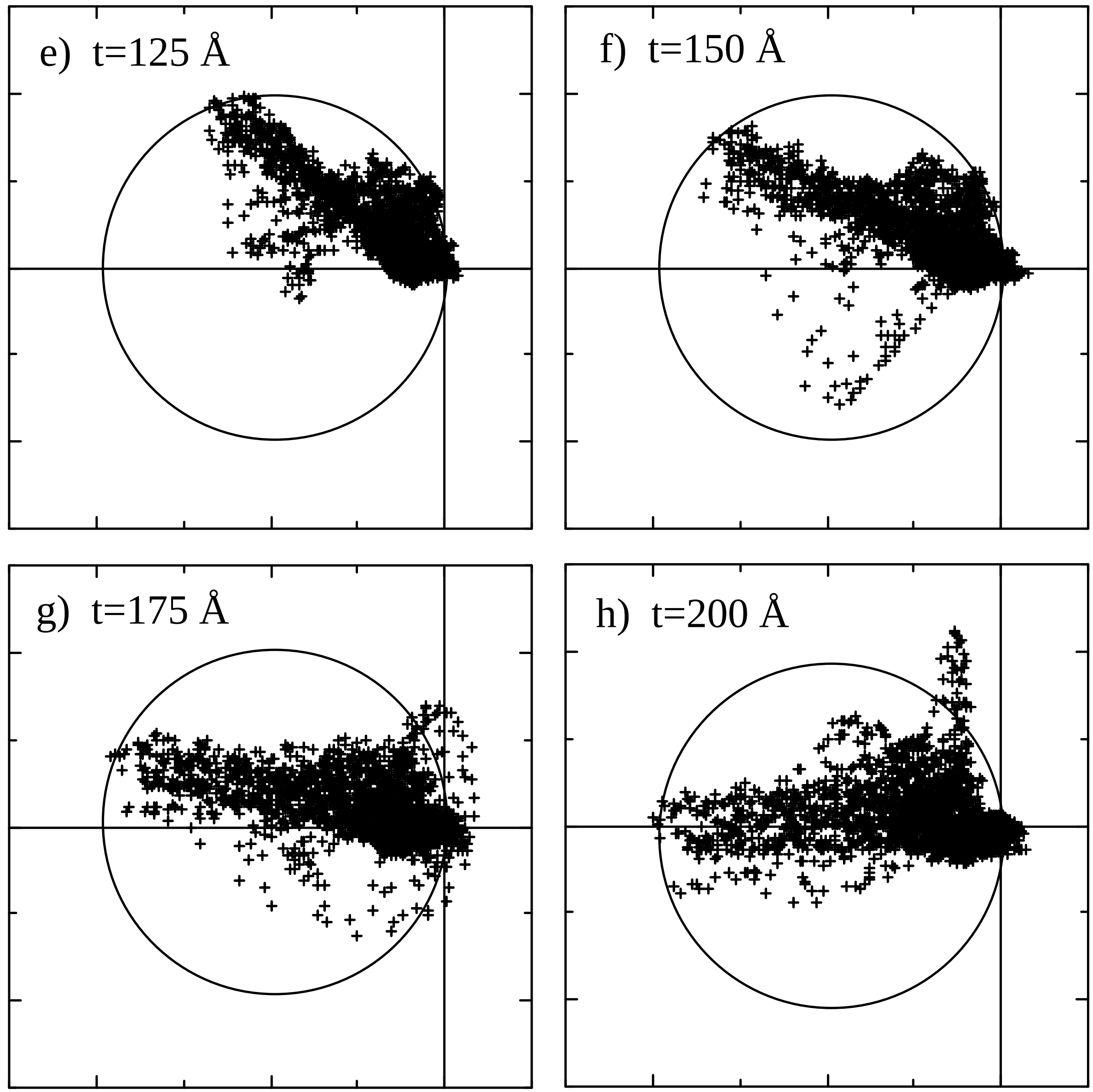


The Movie

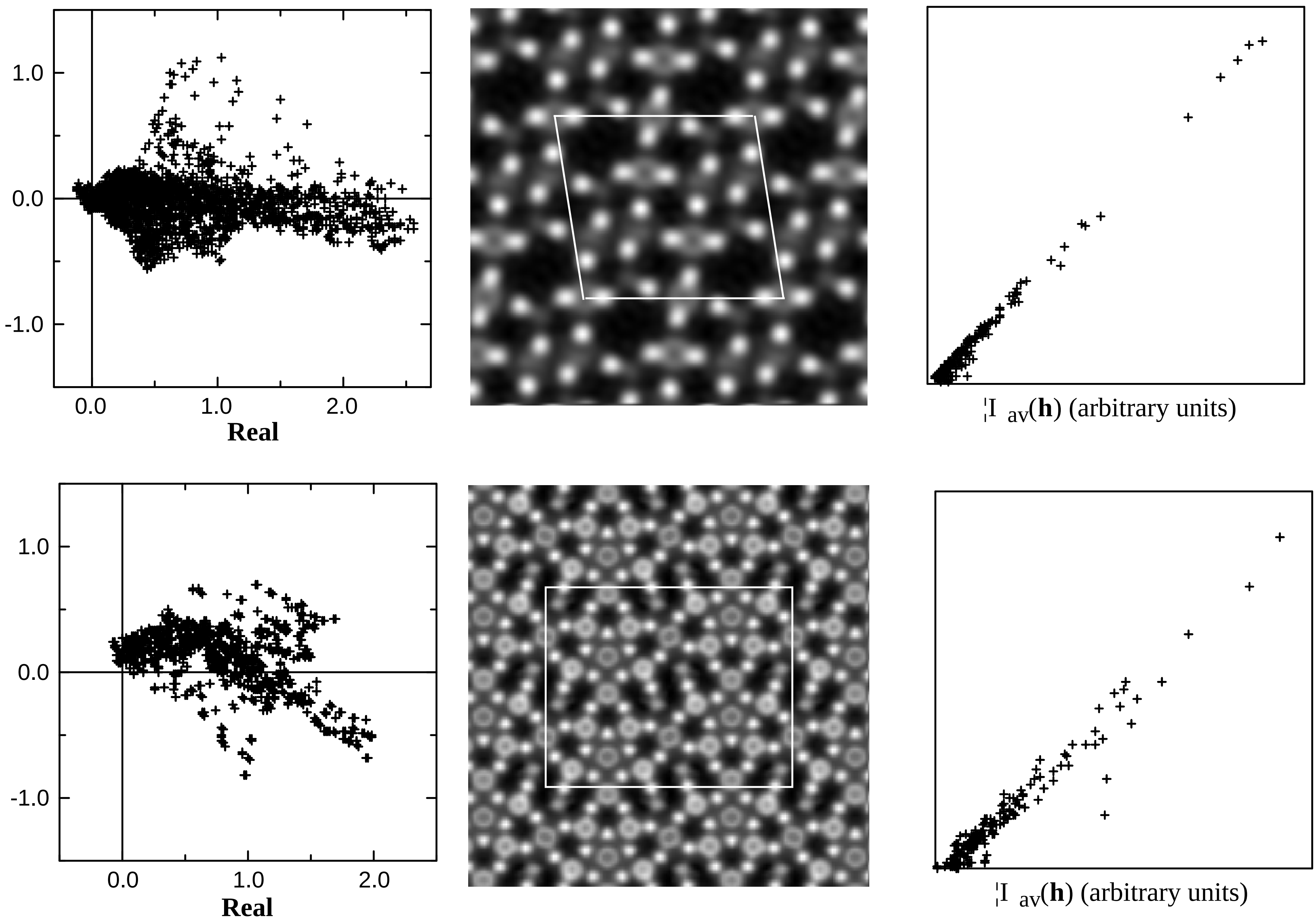
oxygen　tin
gallium　indium/gallium



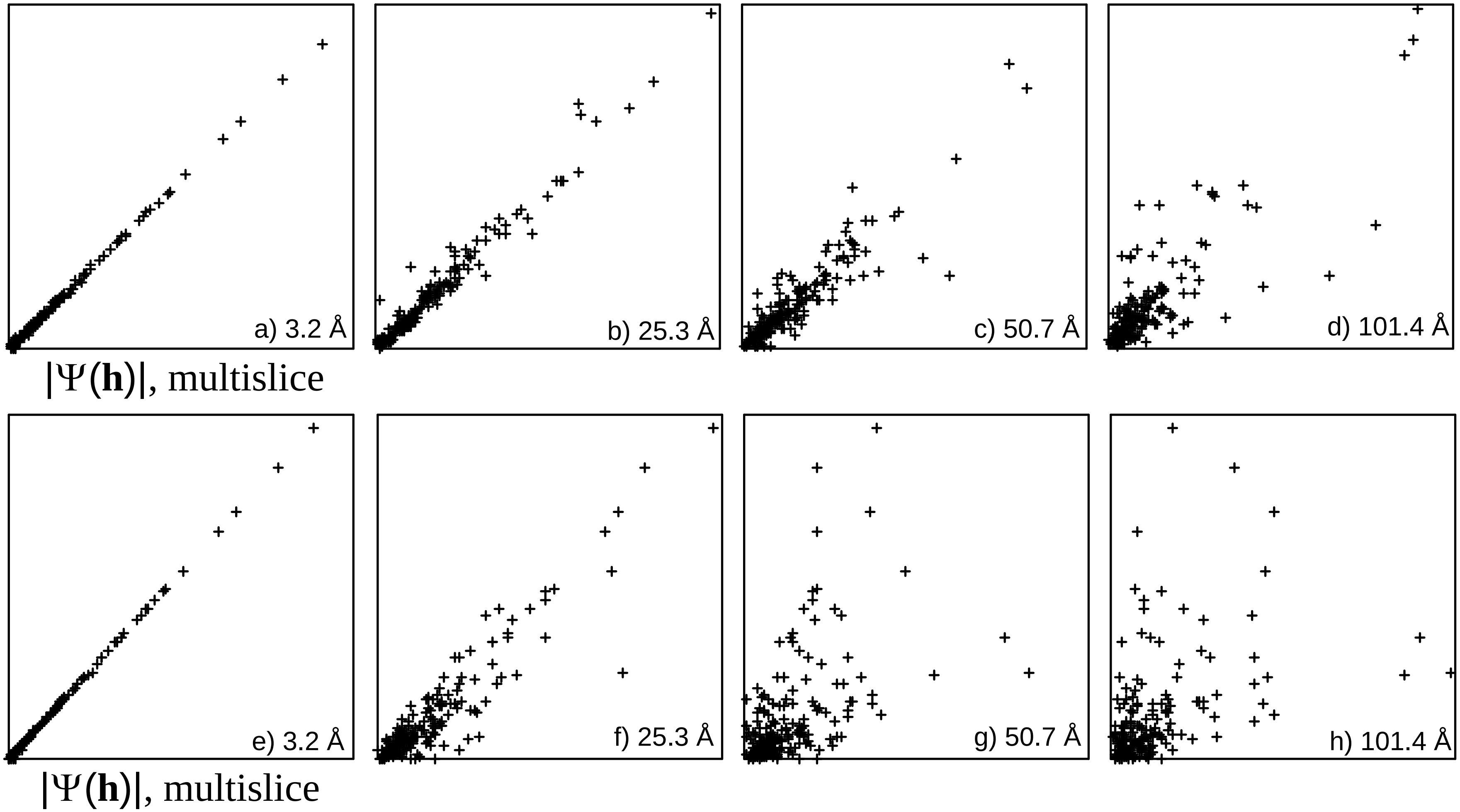

a) t=25 Å
b) t=50 Å
c) t=75 Å
d) t=100 Å
Imaginary
Real
2.0
0.0
-2.0
-4.0
-2.0
0.0



e) t=125 Å
f) t=150 Å
g) t=175 Å
h) t=200 Å

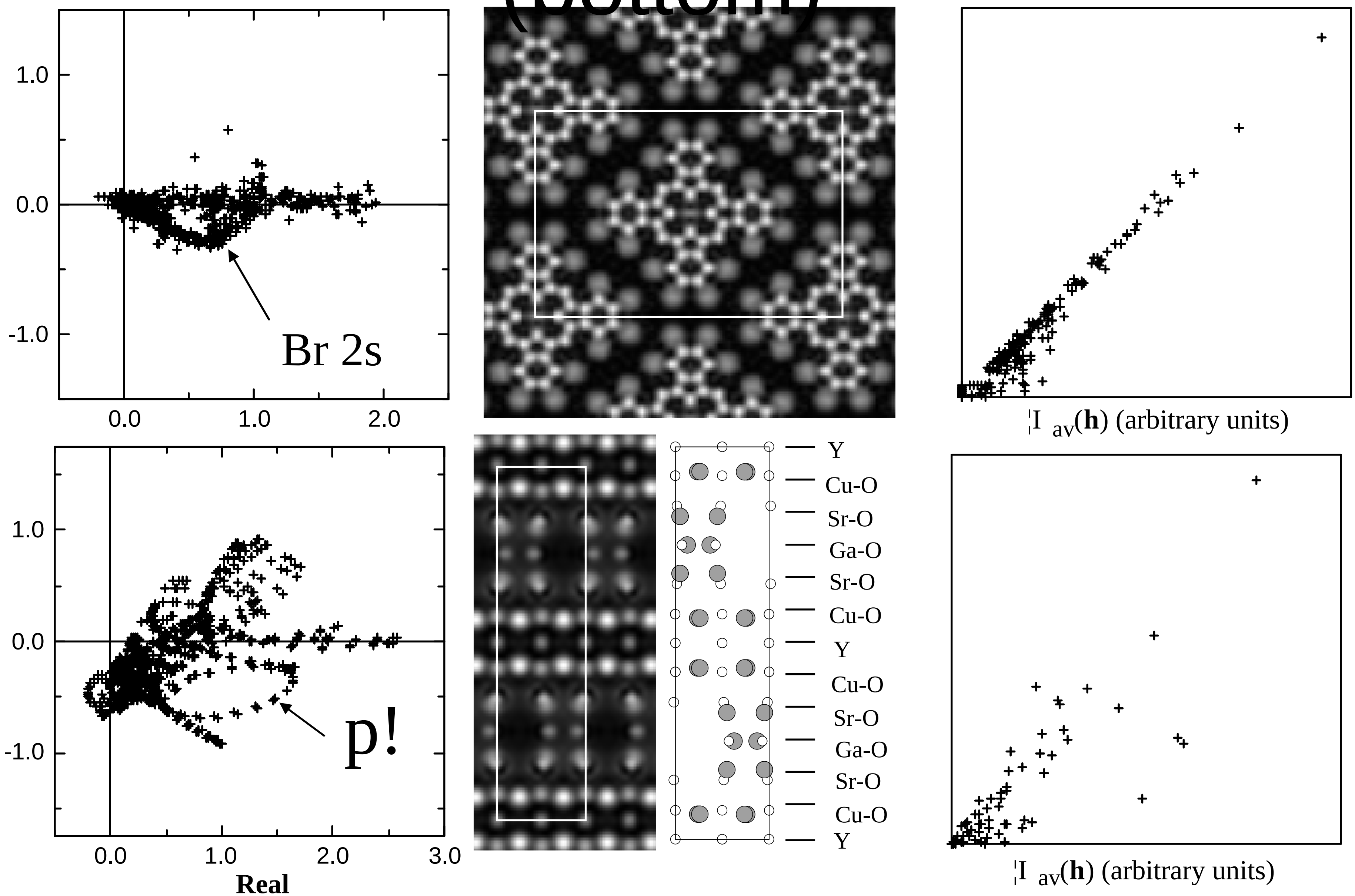

1.0
0.0
-1.0
0.0
1.0
2.0
Real
¦I av(h) (arbitrary units)
1.0
0.0
-1.0
0.0
1.0
2.0
Real
¦I av(h) (arbitrary units)

F.T.{|1-ψ(r)|} & |Ψ(k)| (Top)



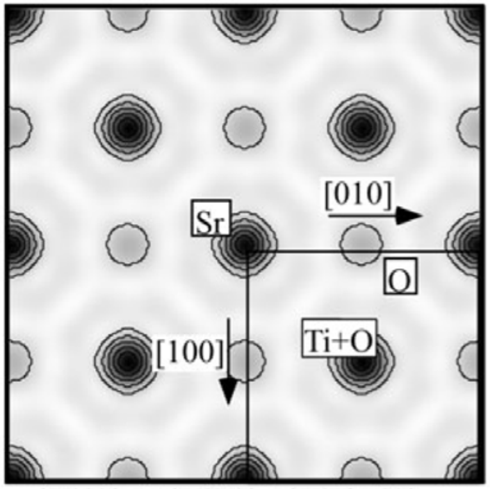
Kinematical & |Ψ(k)| (Bottom)

Perbromo (top) and 123 (bottom)



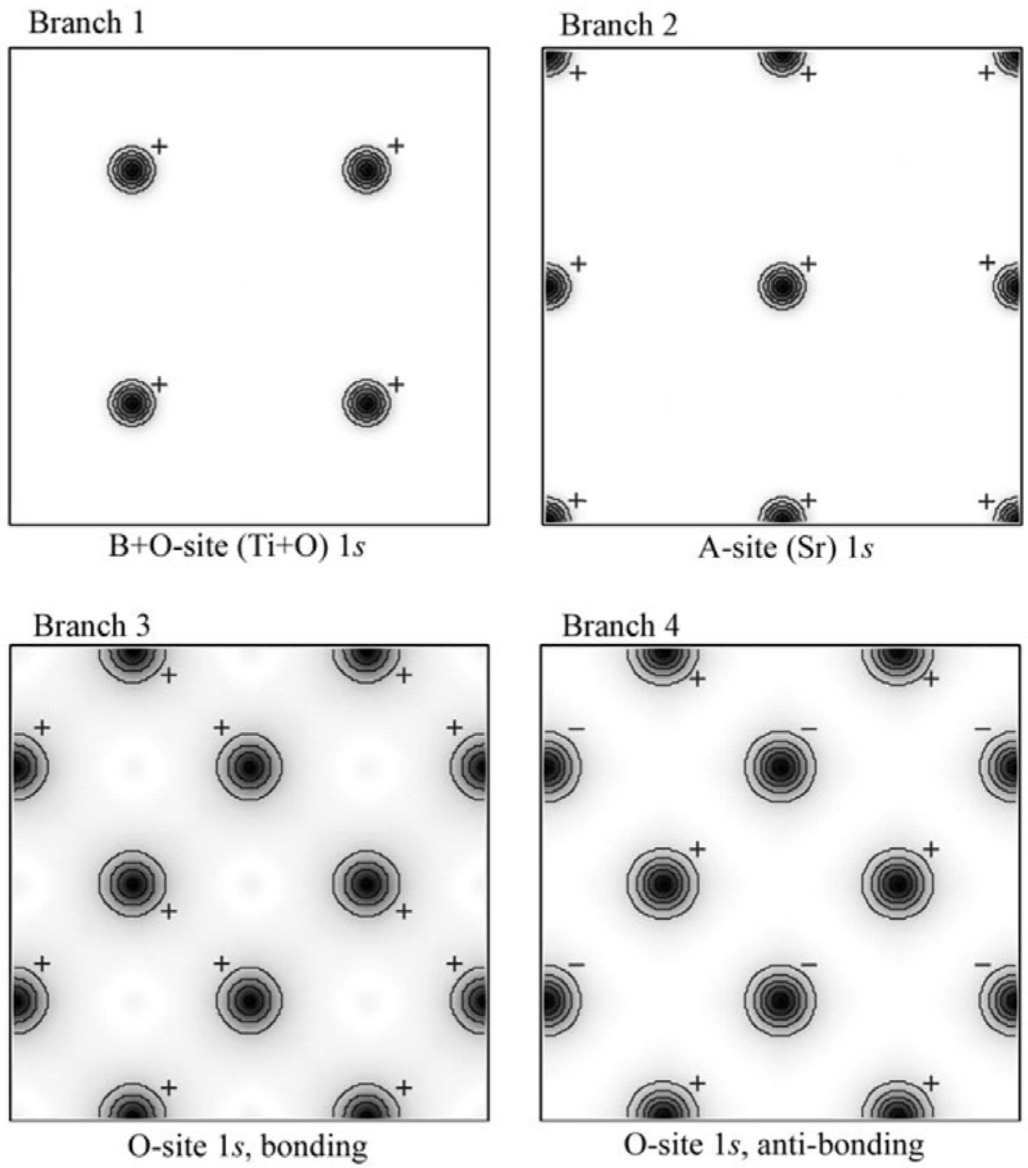
Simulations of Bloch states : $SrTiO_3$ [001]

100kV



|*V*(O)| << |*V*(Sr)| < |*V*(Ti+O)|

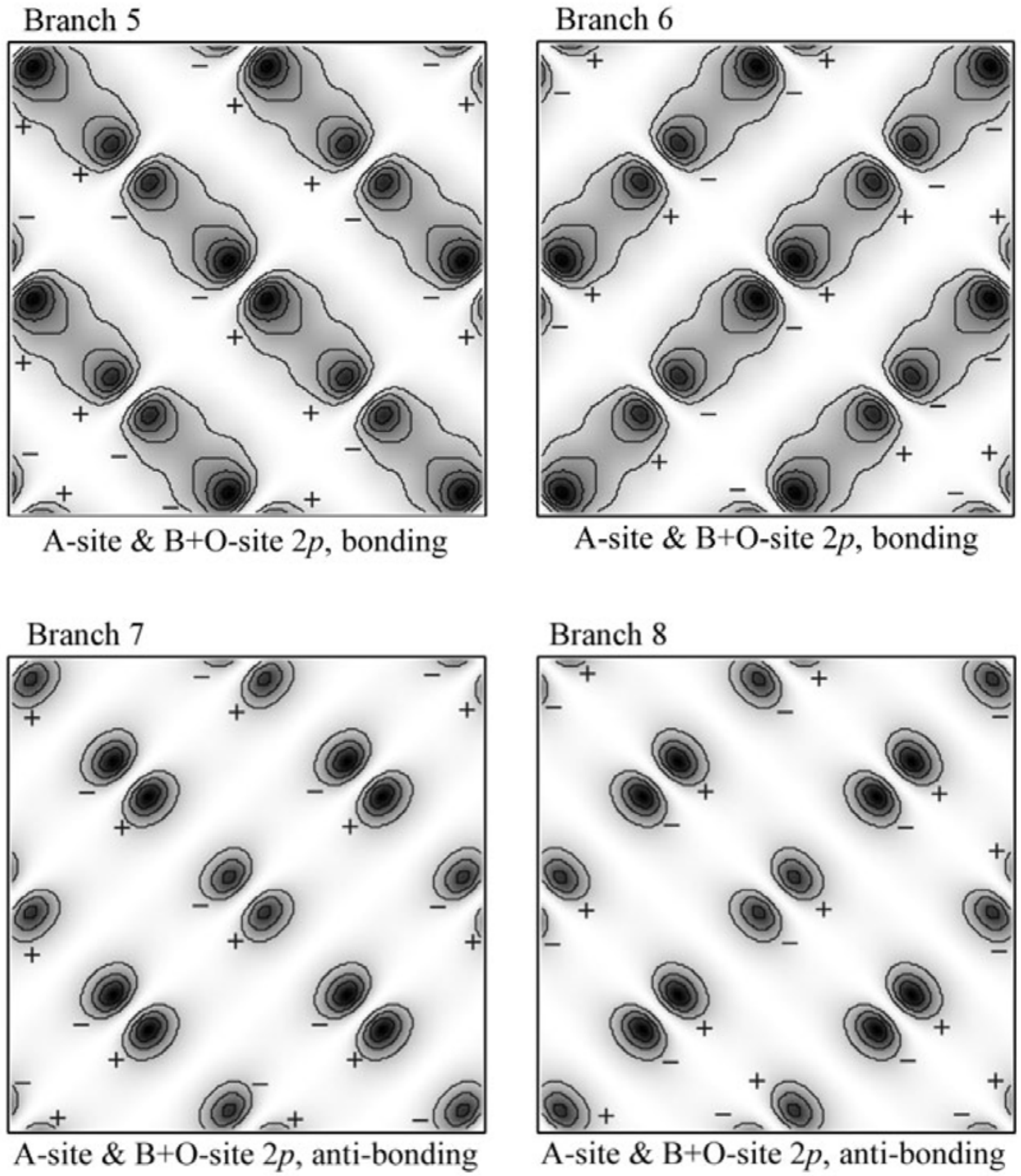
Potential (projected)



(Kenji Tsuda)

Electron distributions of Bloch states (branches 1-4)

Simulations of Bloch states : $SrTiO_3$ [001]



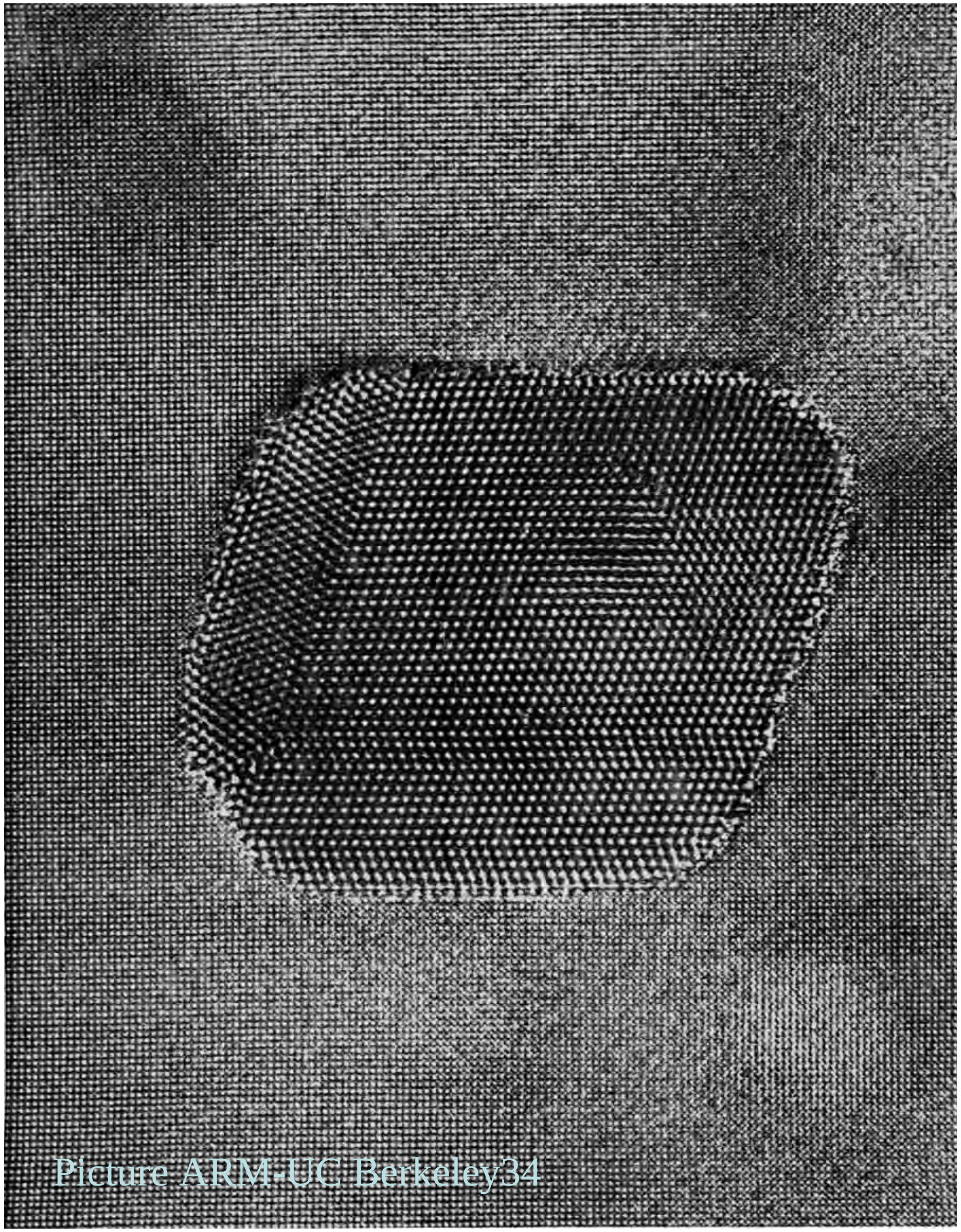
(Kenji Tsuda)

Electron distributions of Bloch states (branches 5-8)

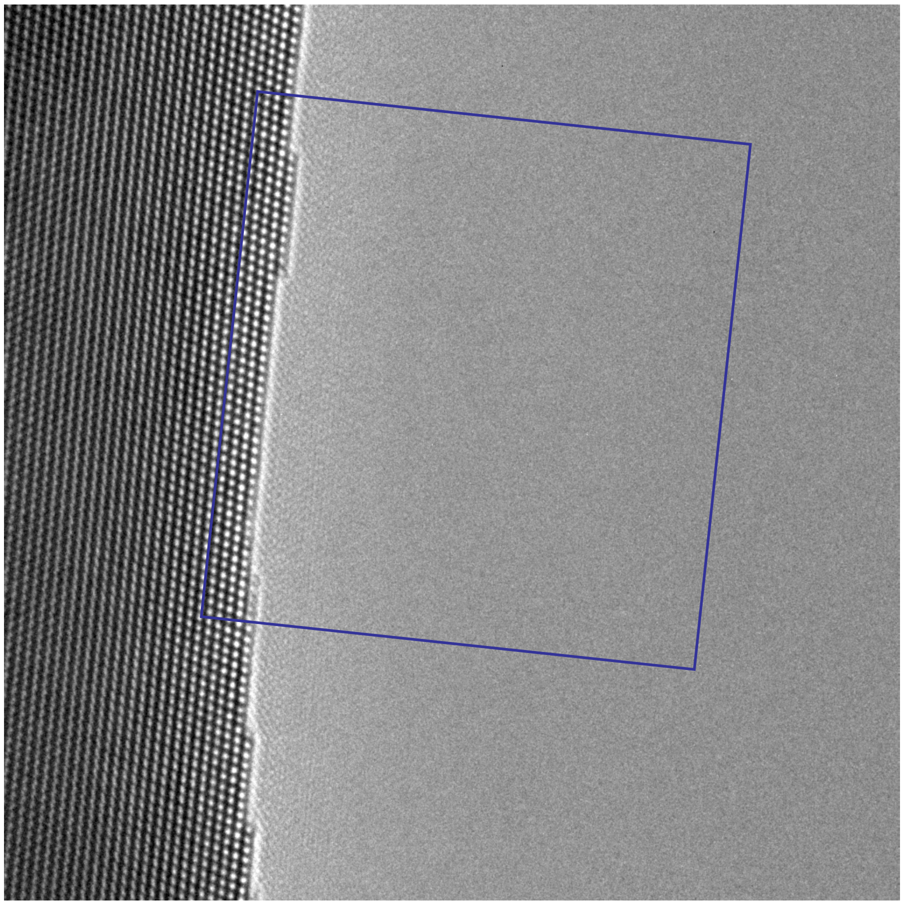
Examples

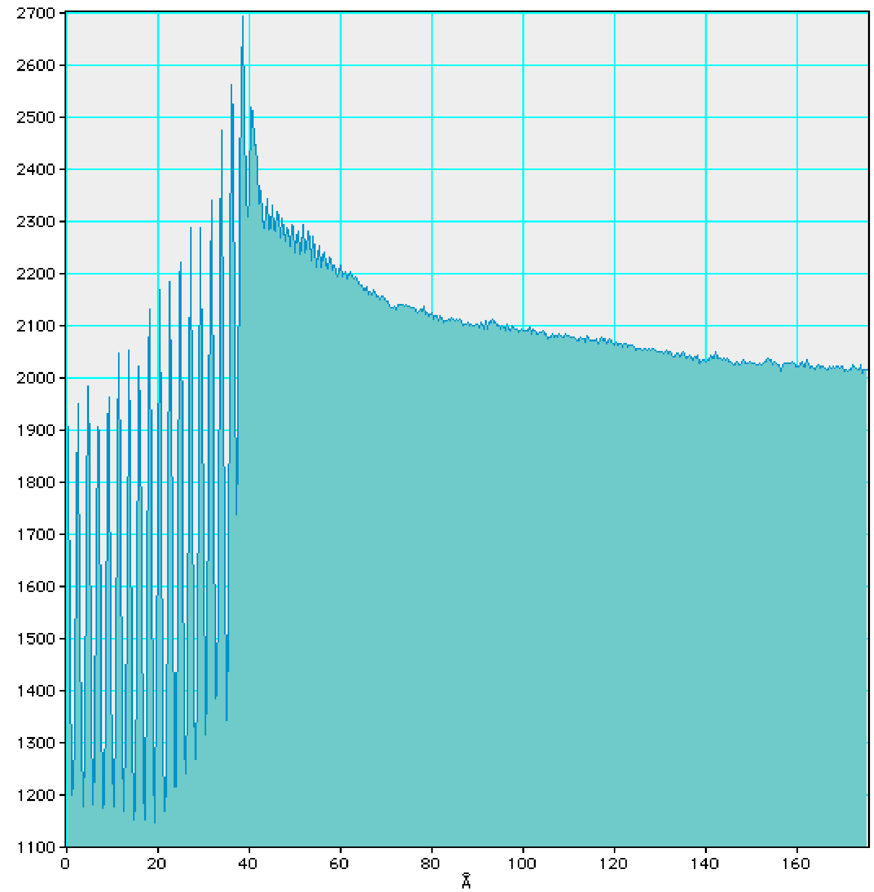
Image close to visual interpretation

Curtesy S. Van Tenderloo



Au [110] – Vacuum wave

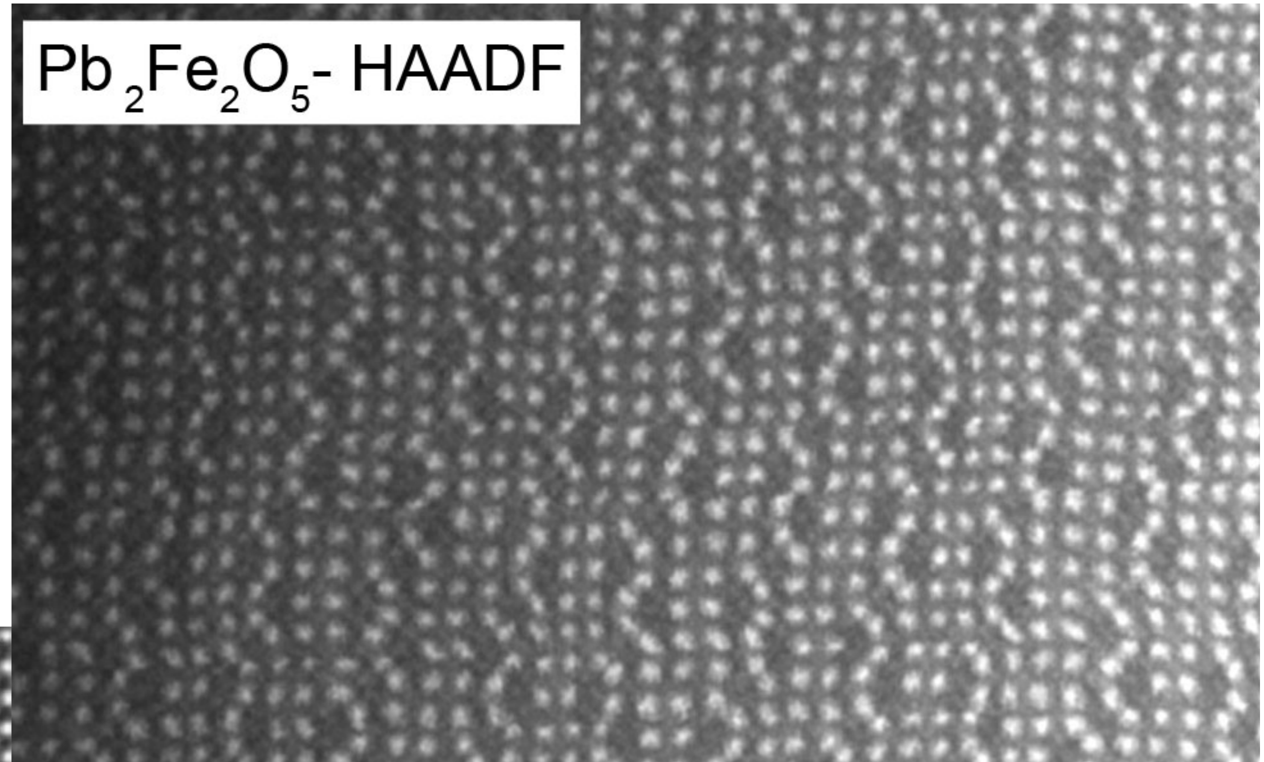


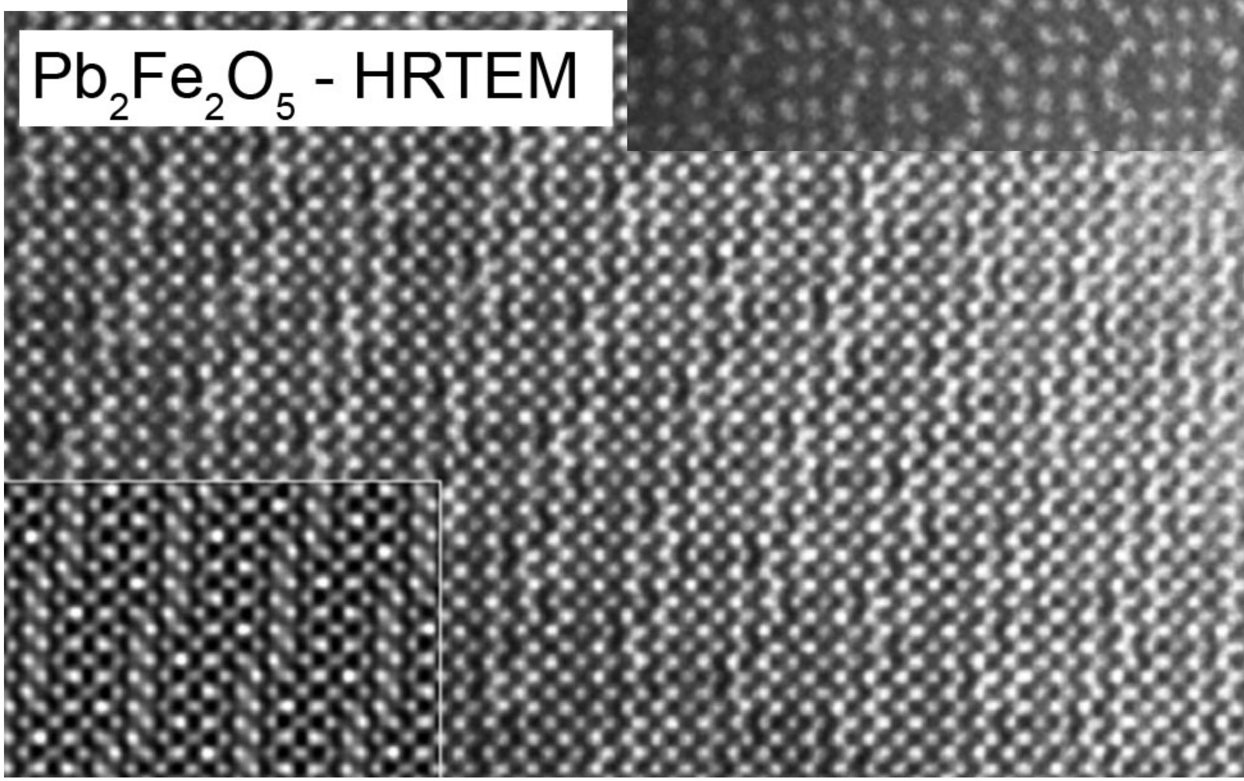


Courtesy C. Kisielowski, J.R. Jinschek (NCEM, Berkeley)

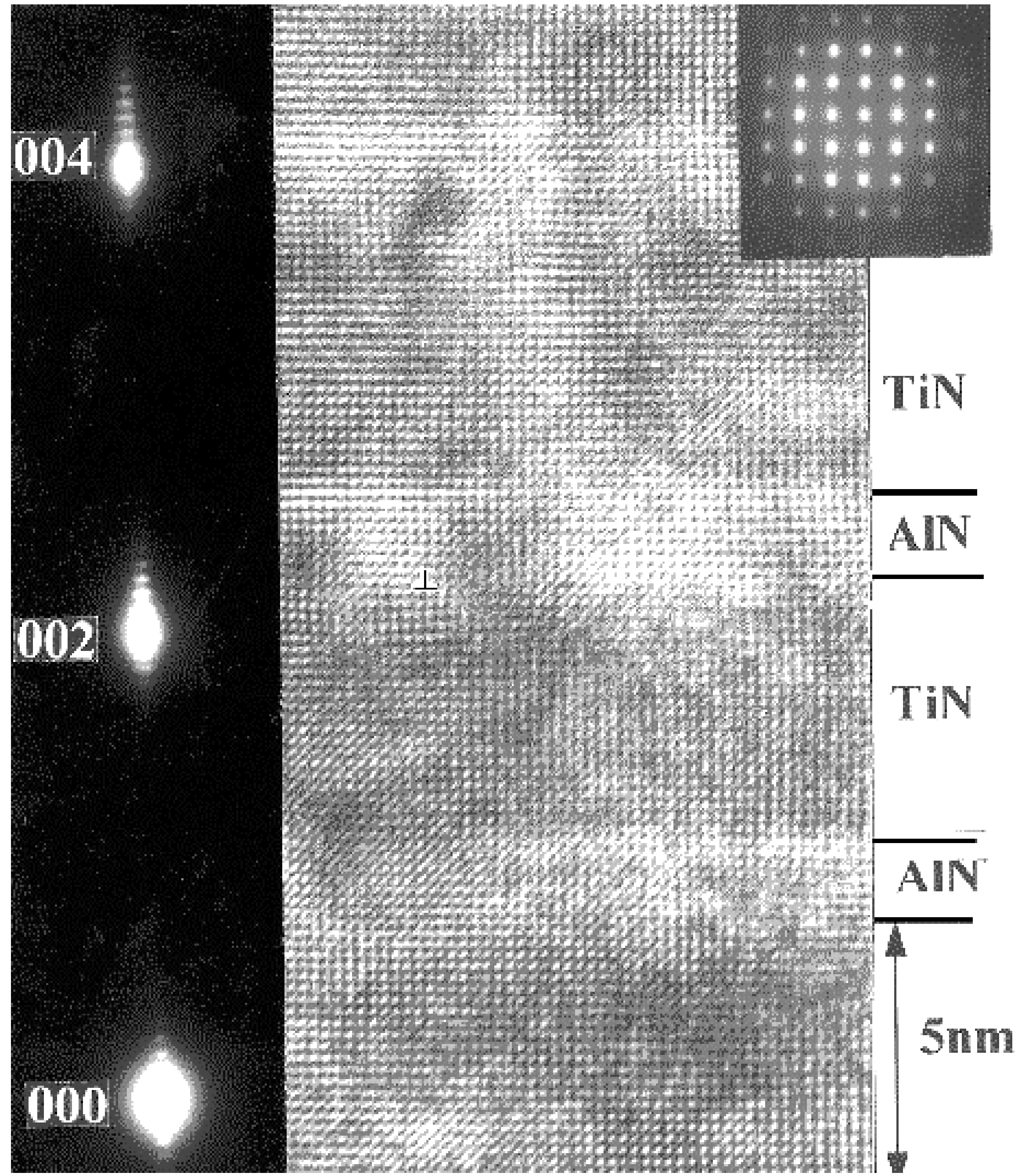
$I = ß Z^n$

$Z_O = 8$
$Z_{Fe} = 26$
$Z_{Pb} = 82$





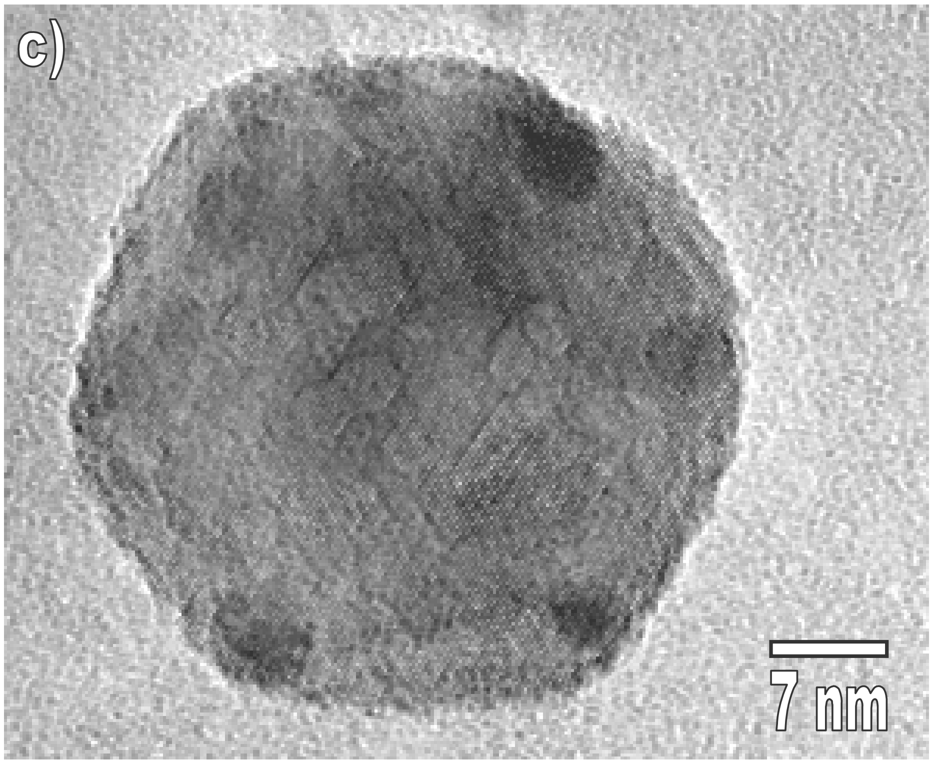
Abakumov et al.
Angewandte Chemie (2006)



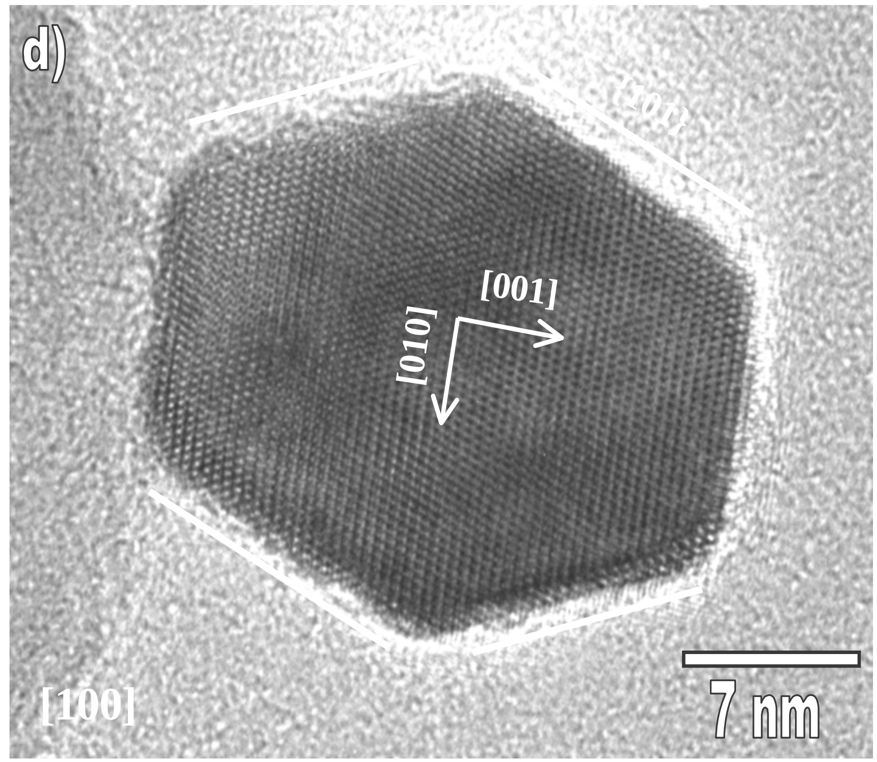
004
002
000
TiN
AlN
TiN
AlN
5nm

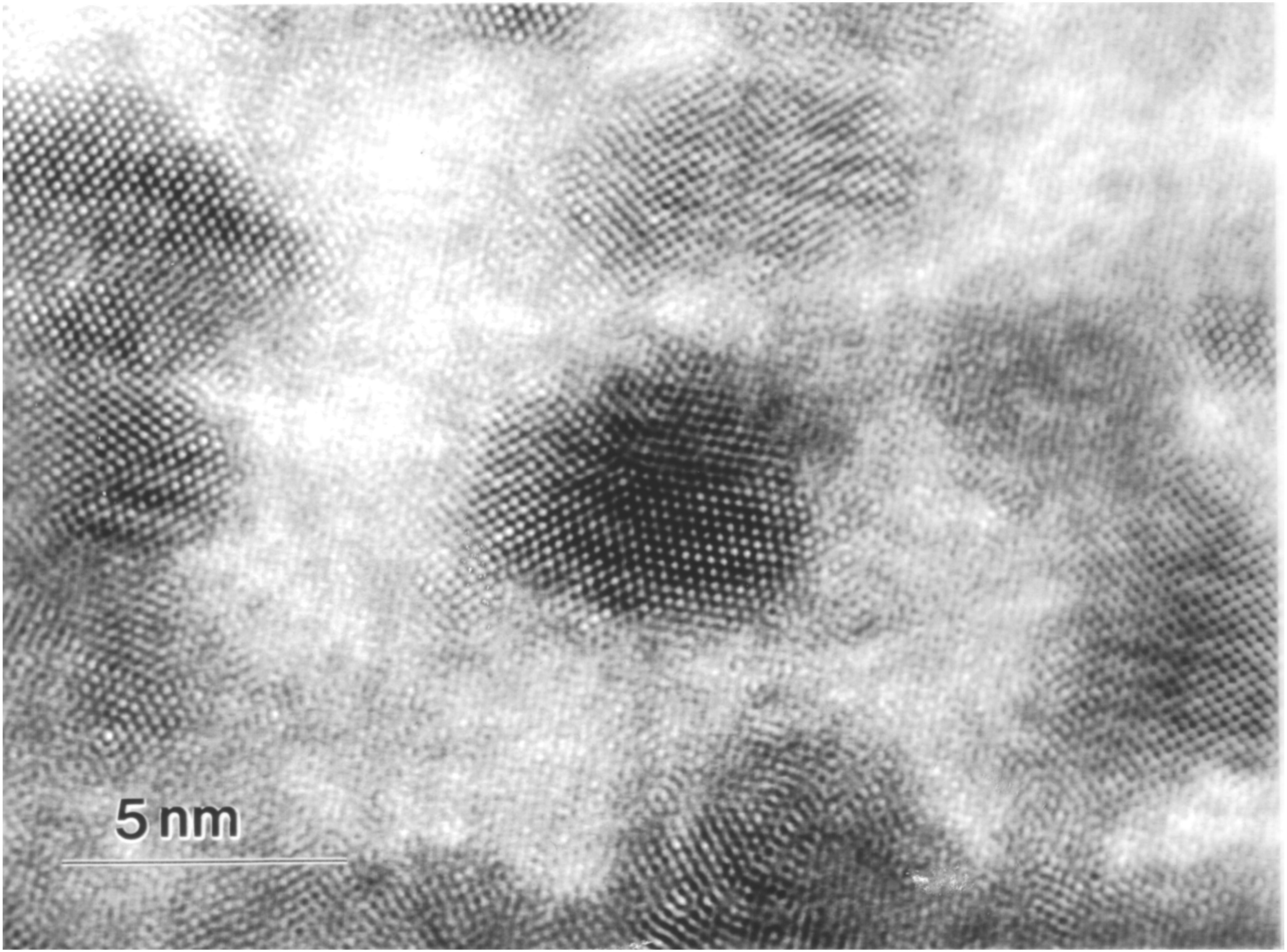
HR-TEM of TiO_2 (anatase) Nanoparticles (P. Ahonen, 2001)

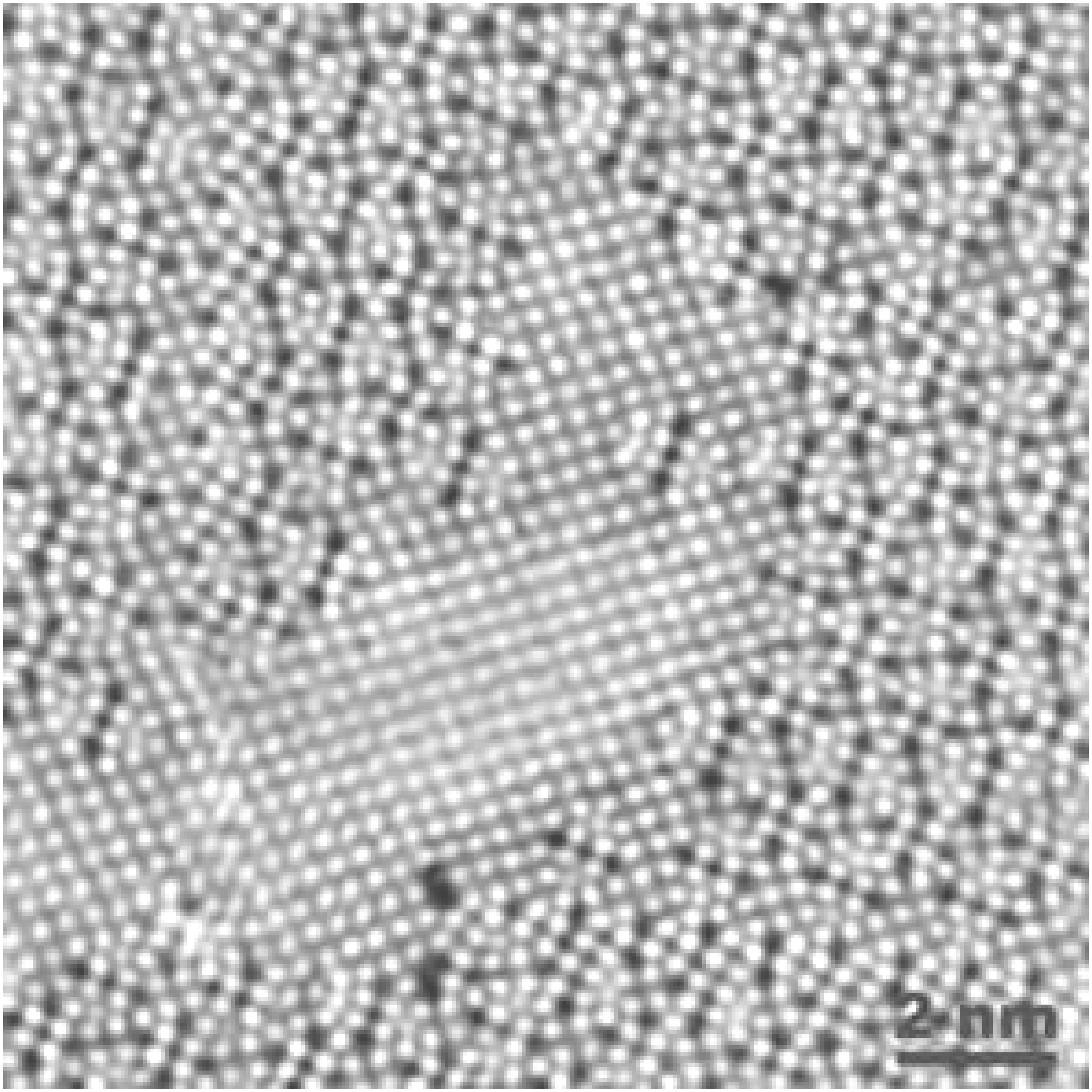
900°C
(unfaceted)



1200°C
(faceted)

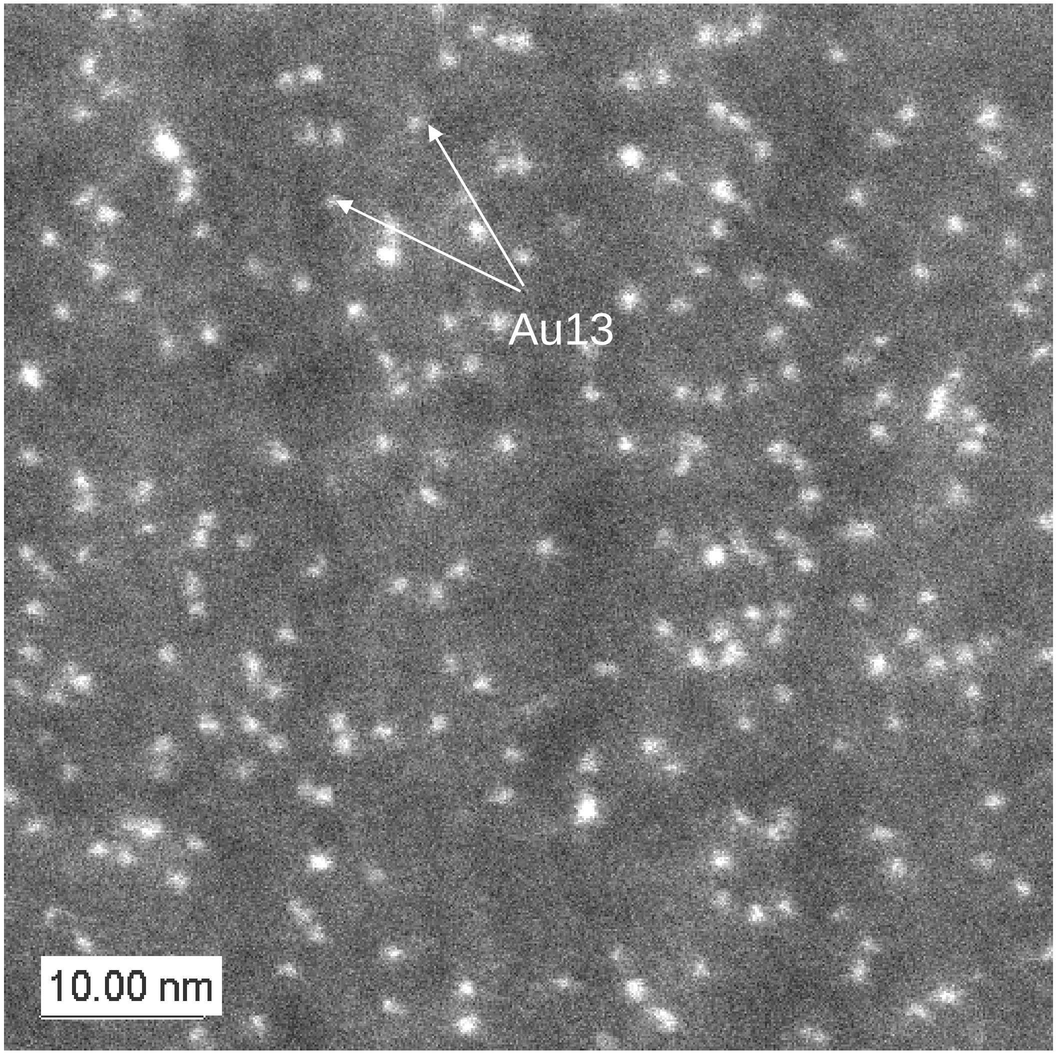



5 nm


2 nm

HAADF-STEM

High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy



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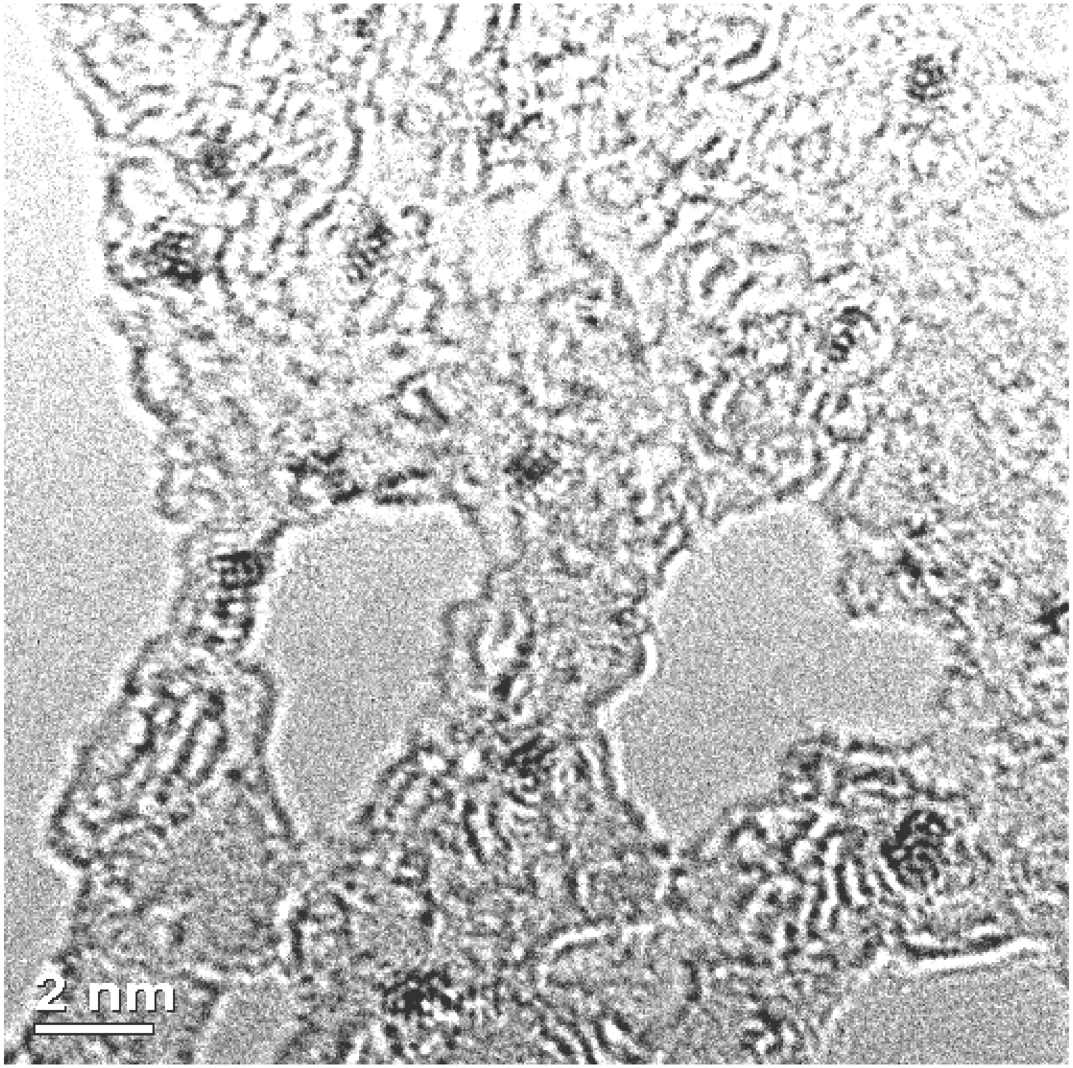
A representative STEM-HAADF image (HB 501, 100kv, inner angle: 96mgrad) of sample $Au_{13}(PPh_3)_4(SC12)_4$

High-Resolution TEM: <1 nm



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

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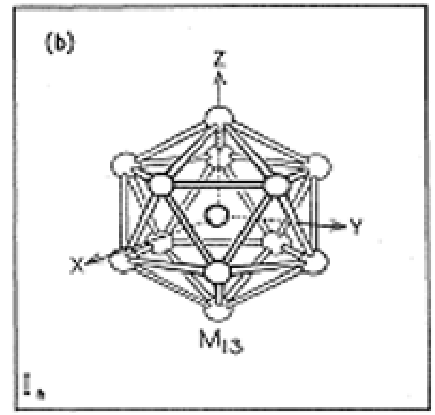
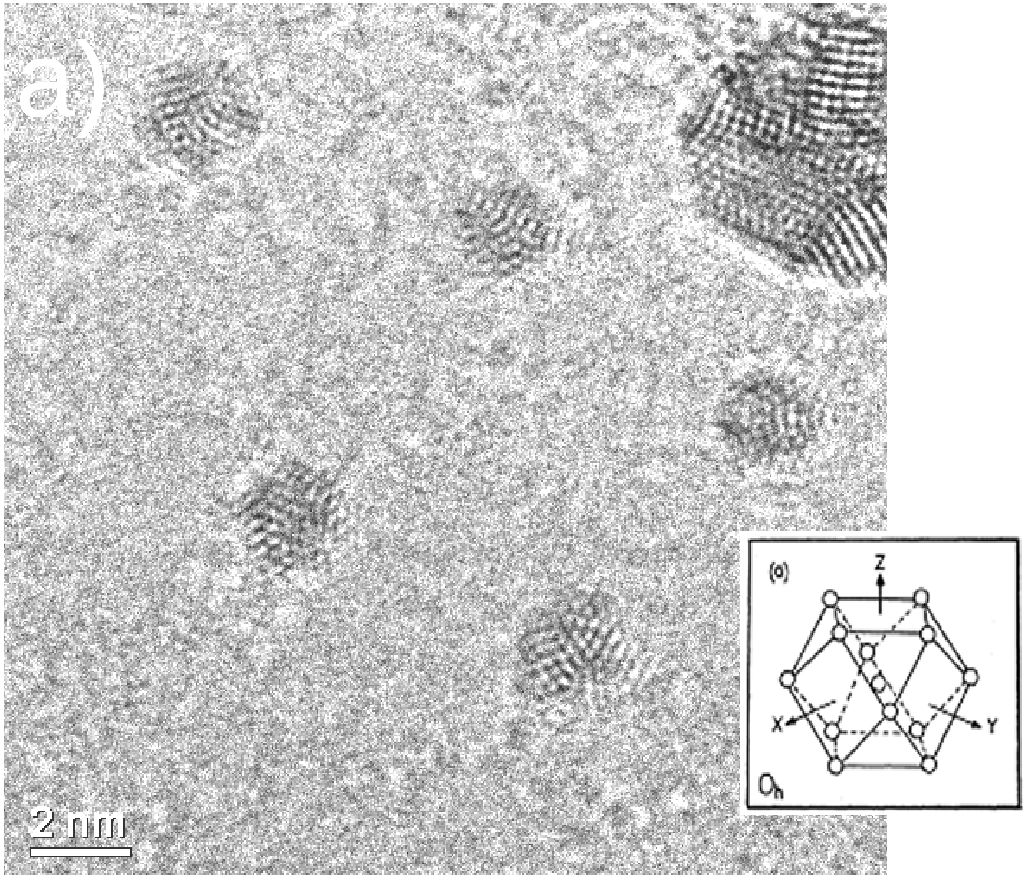
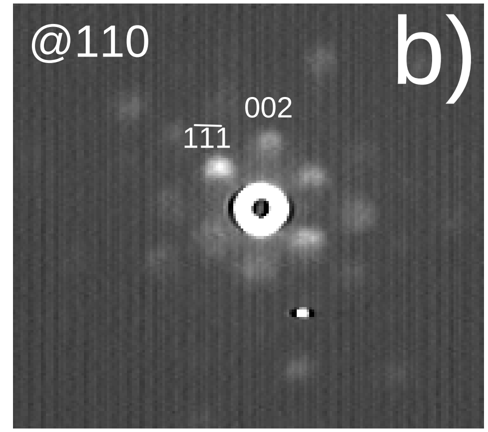
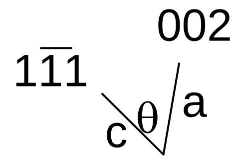


- Uniformity in size (<1nm) and spatial distribution
- High crystallinity evident from visible lattice fringes inside particles
- Lattice spacing = 2.39 ± 0.07(Å)
- Icosahedral shape based on trace analysis of particle edge

HREM – Larger Clusters







c/a = 1.1 ± 0.1
(FCC:1.155)
θ = 56° ± 1°
(FCC:54.74°)

FCC, a=4.0±0.2 (Å).

Cuboctahedra Au clusters

(a) A HREM image (Jeol 2010F) of large Au clusters in the sample of $Au_{11}(PPh_3)_4(SC12)_2Cl_2$. (b) Microdiffraction taken from the individual cluster with size of ~2nm. It is noted that Au-Au NN distance: a/square root (2) =2.8±0.1(Å), which is close to the value of bulk gold (2.885 Å).

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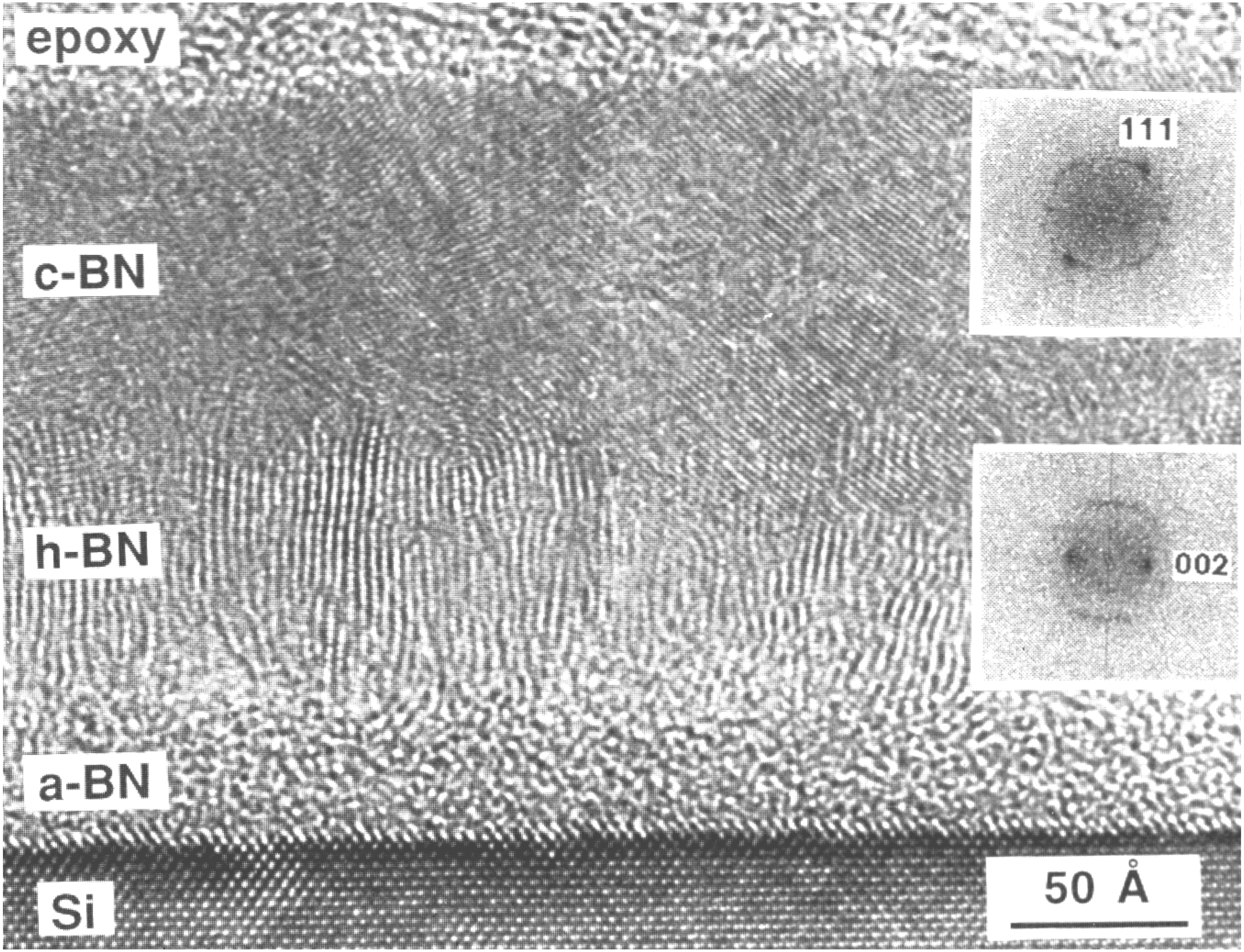
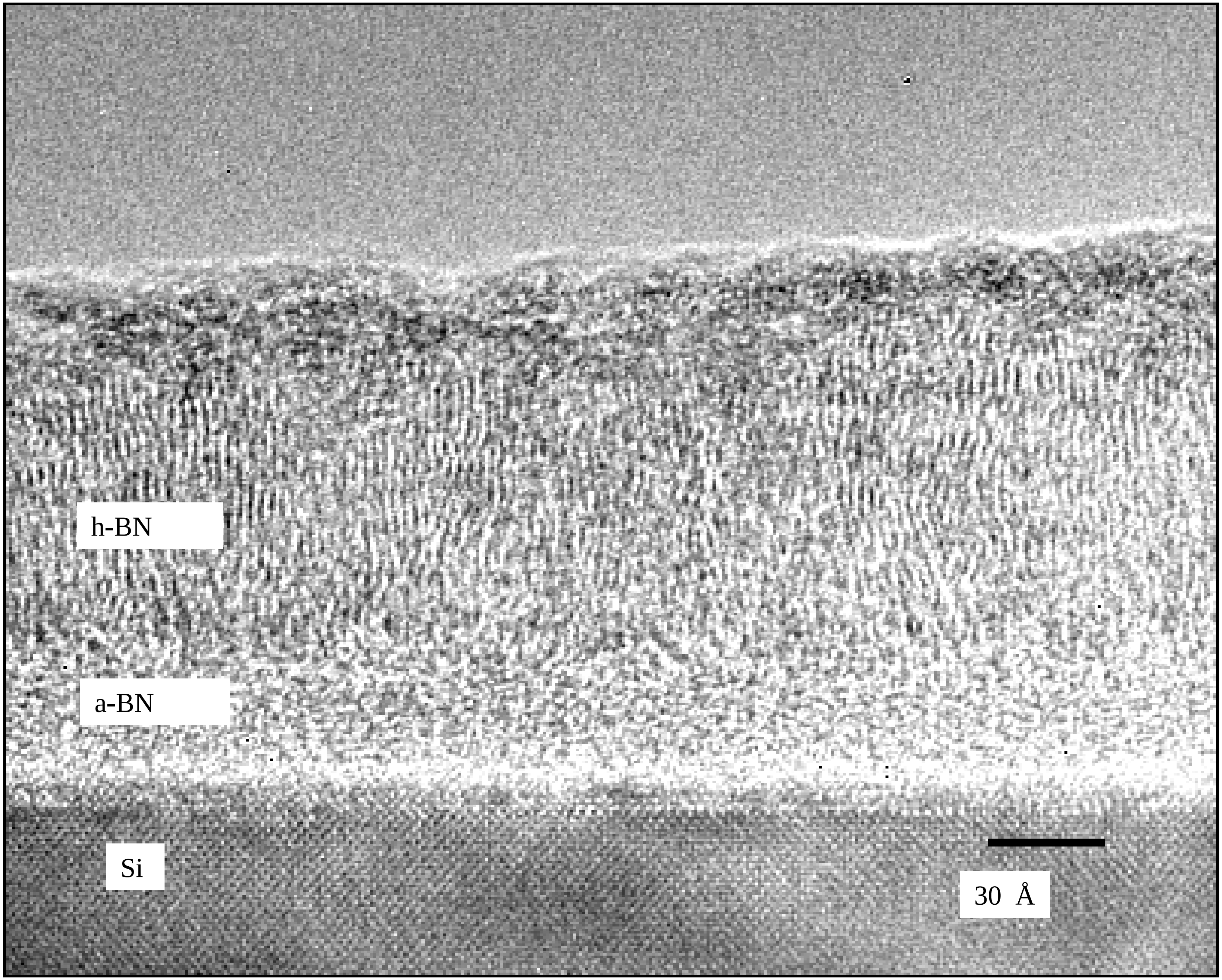
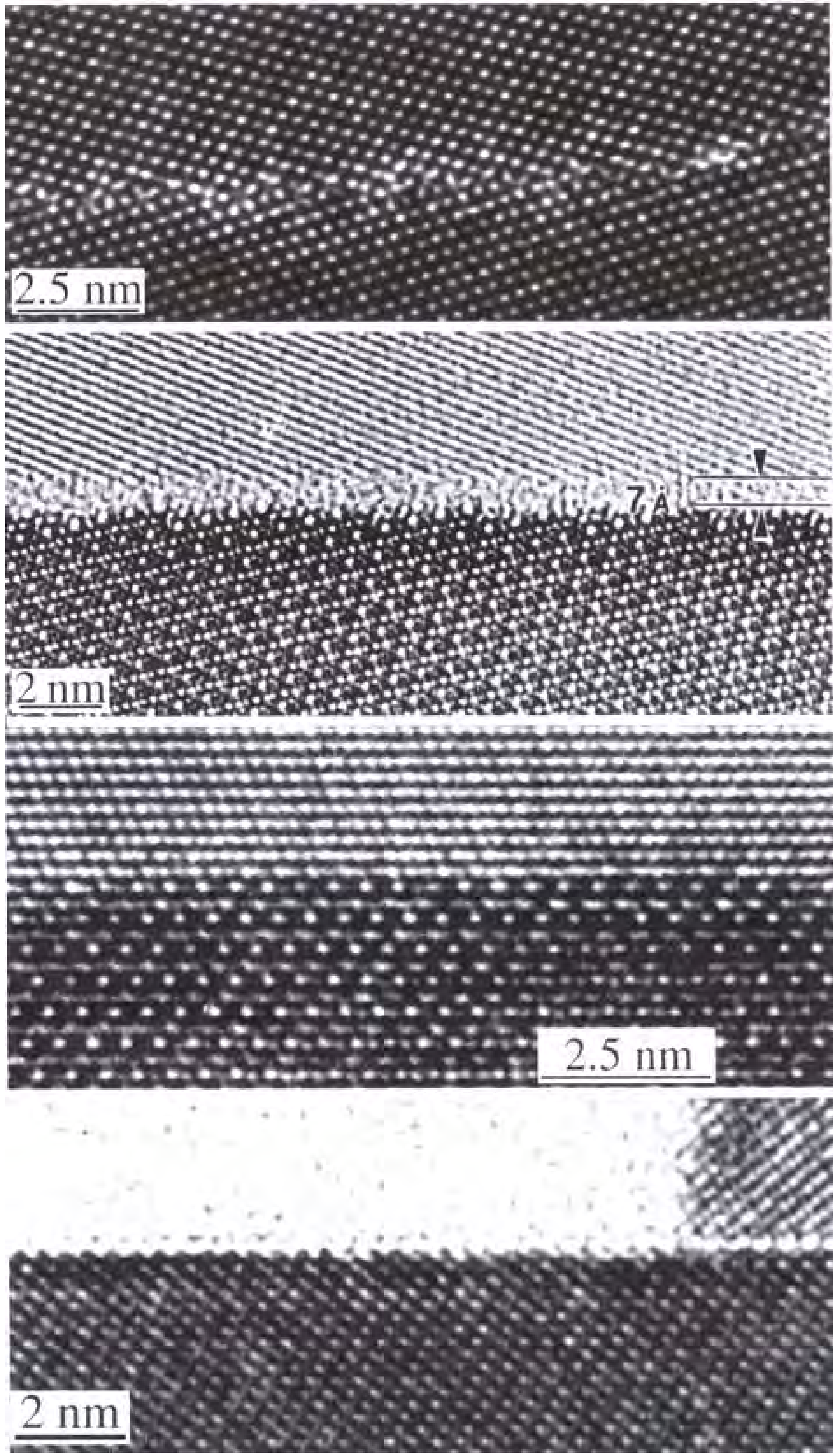
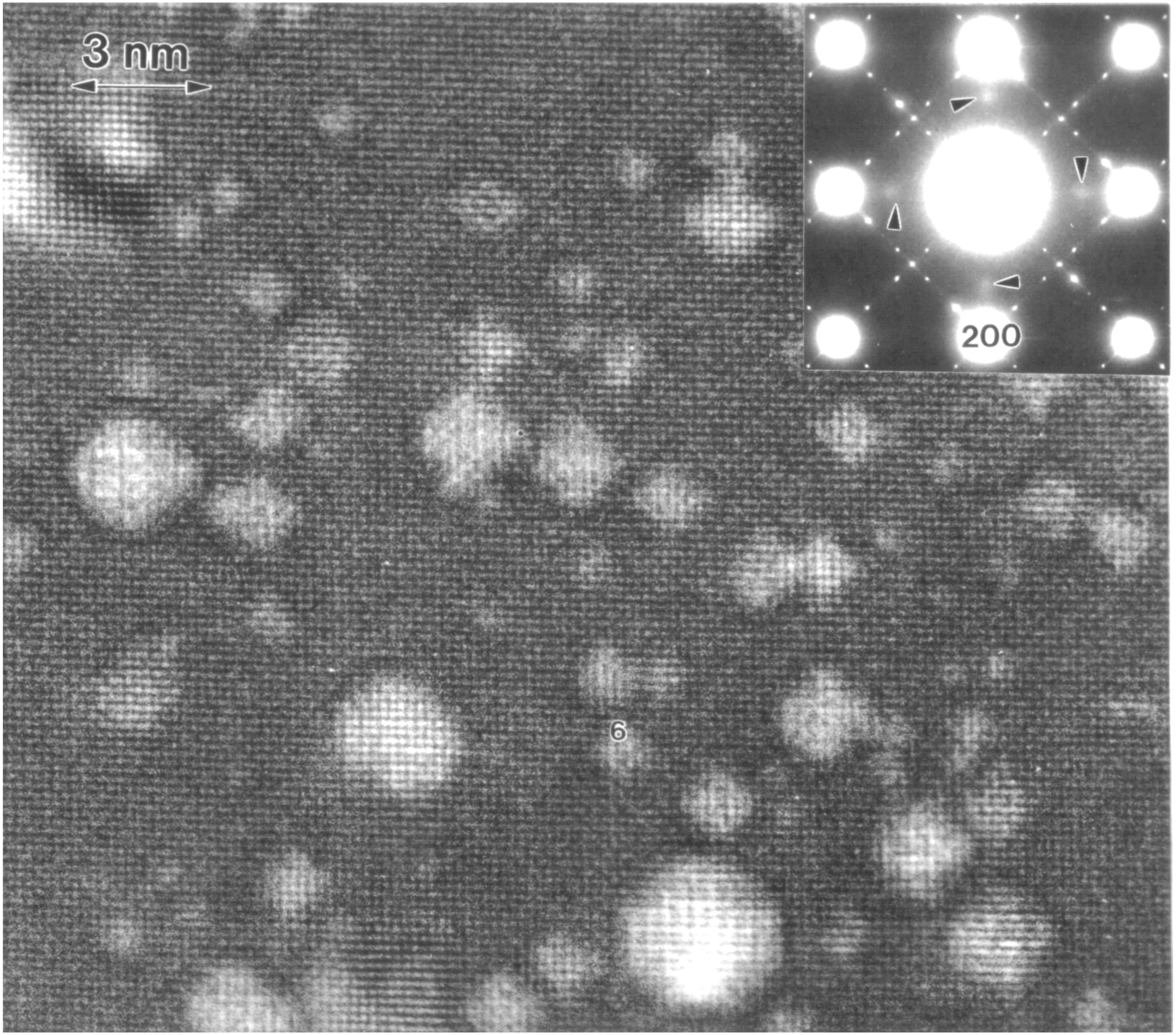
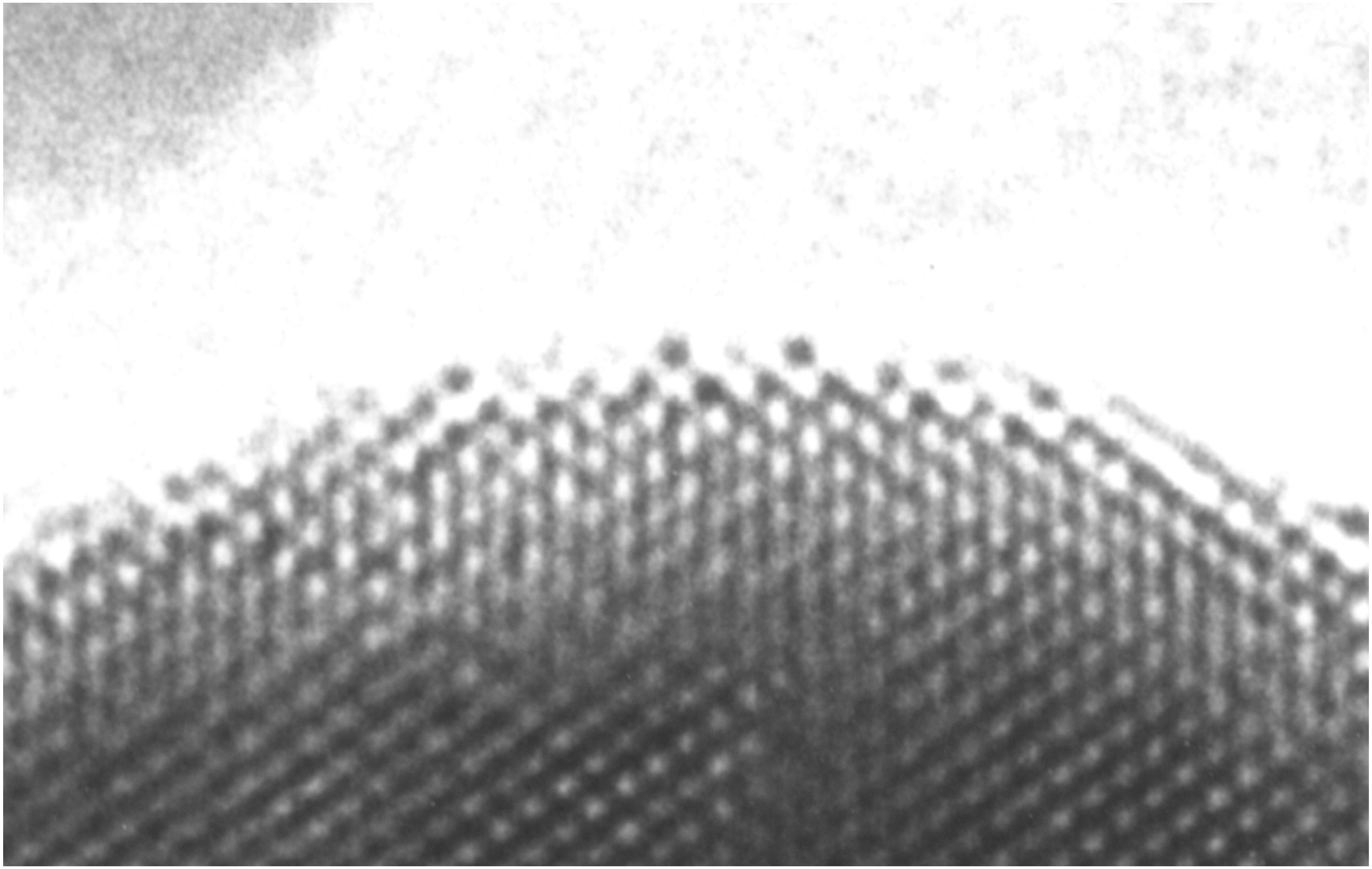
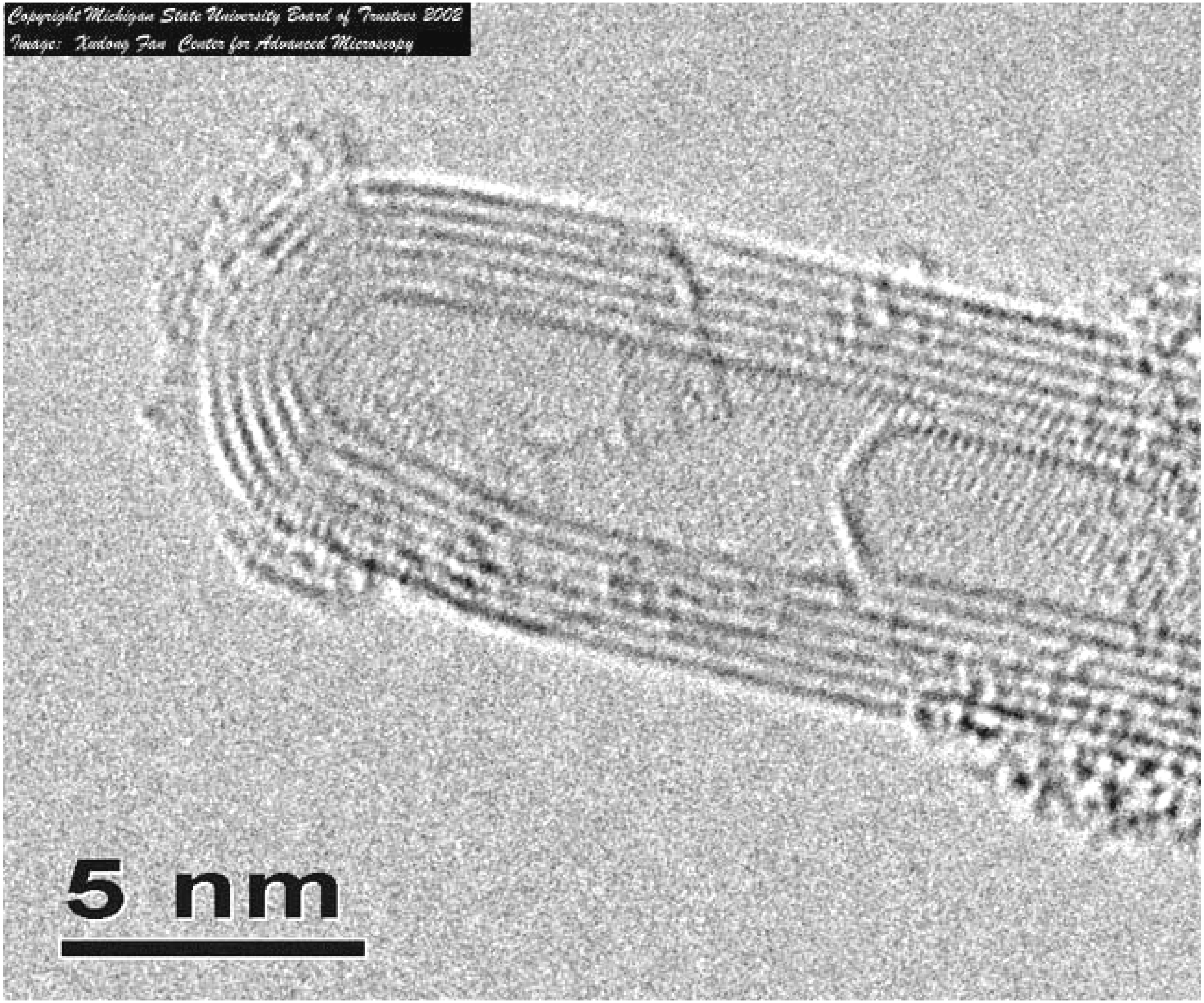

epoxy
c-BN
h-BN
a-BN
Si
111
002
50 Å

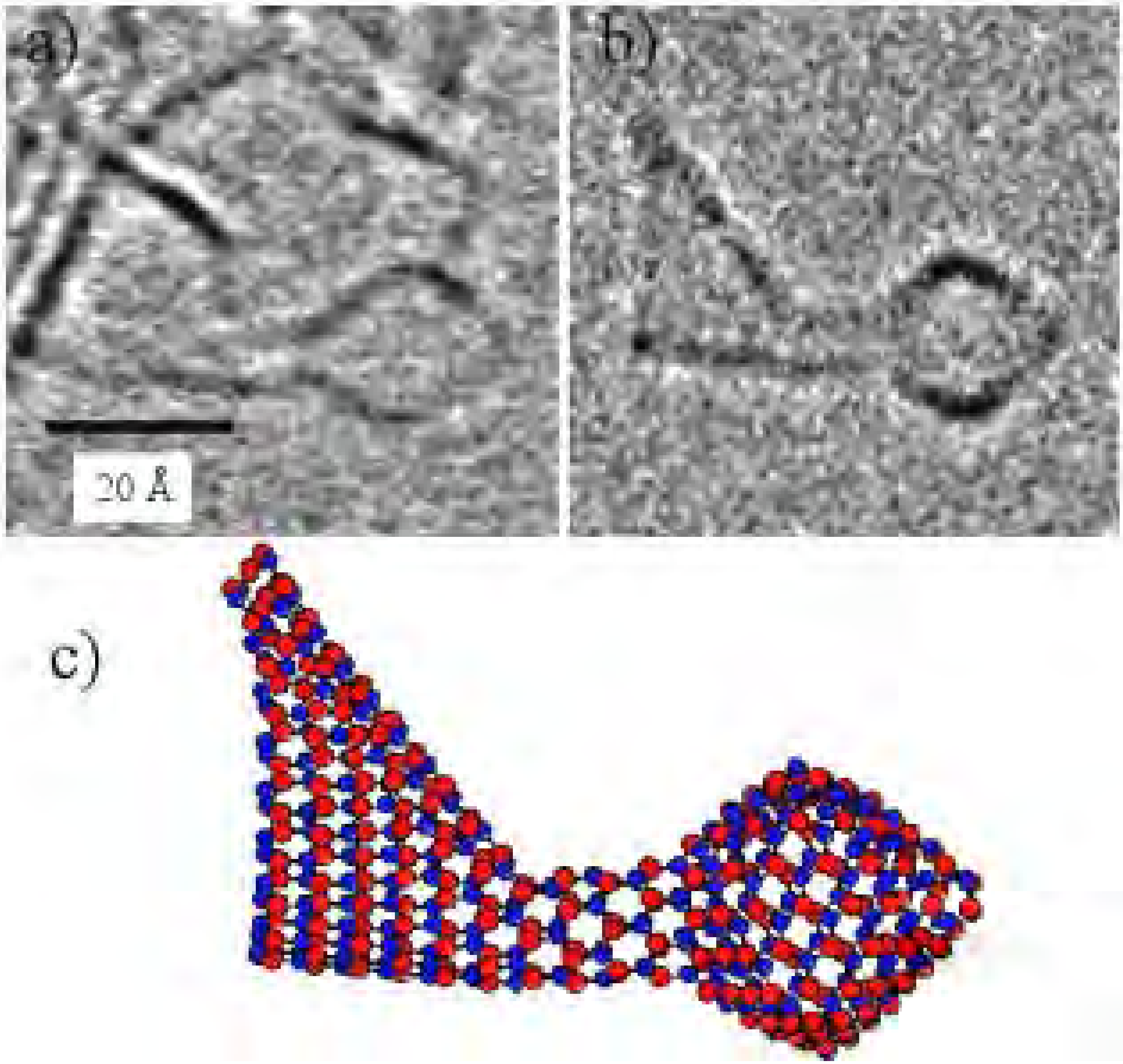

h-BN
a-BN
Si
30 Å


2.5 nm
7 Å
2 nm
2.5 nm
2 nm


3 nm
200
6




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


a)
20 Å
b)
c)