Structural Characterization of Nanoparticles

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Plan

1. Transmission Electron Microscopy

   - Selected Area Electron Diffraction
   - High Resolution Transmission Electron Microscopy
   - HRTEM Simulations

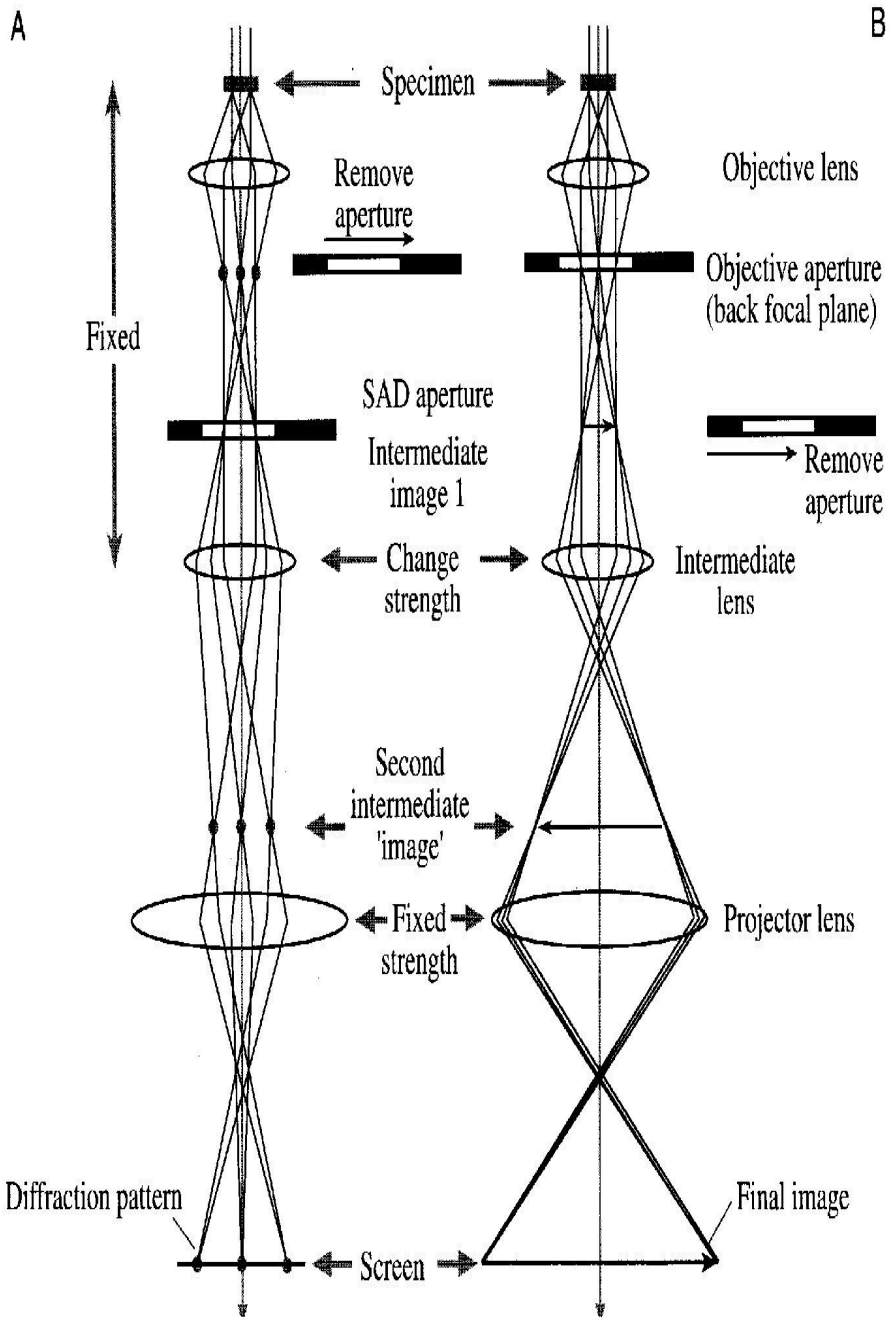
2. X-Ray Diffraction

   - Particle Size Broadening
   - Sherrer equation
   - Debye scattering equation

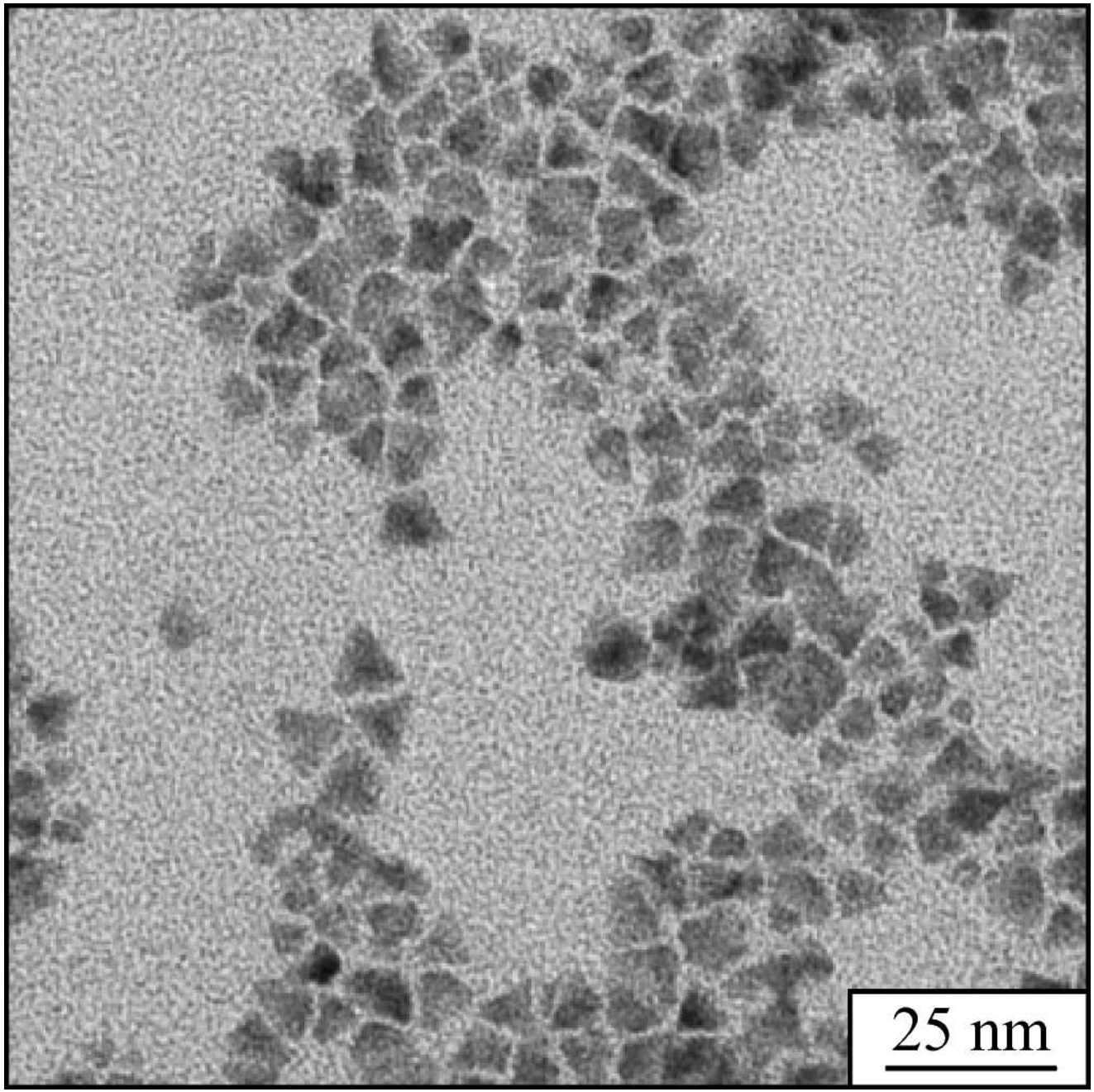
Transmission Electron Microscopy

Transmission Electron Microscopy

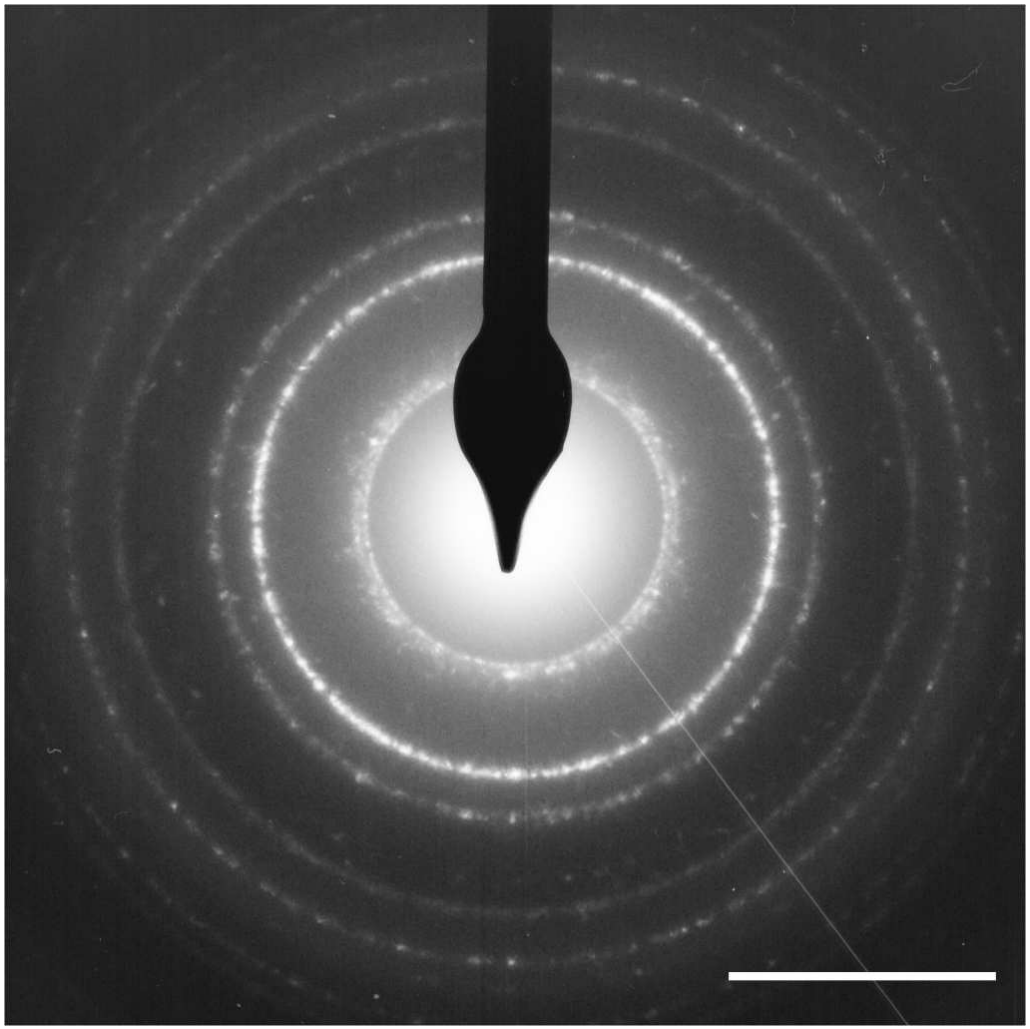
Transmission Electron Microscopy

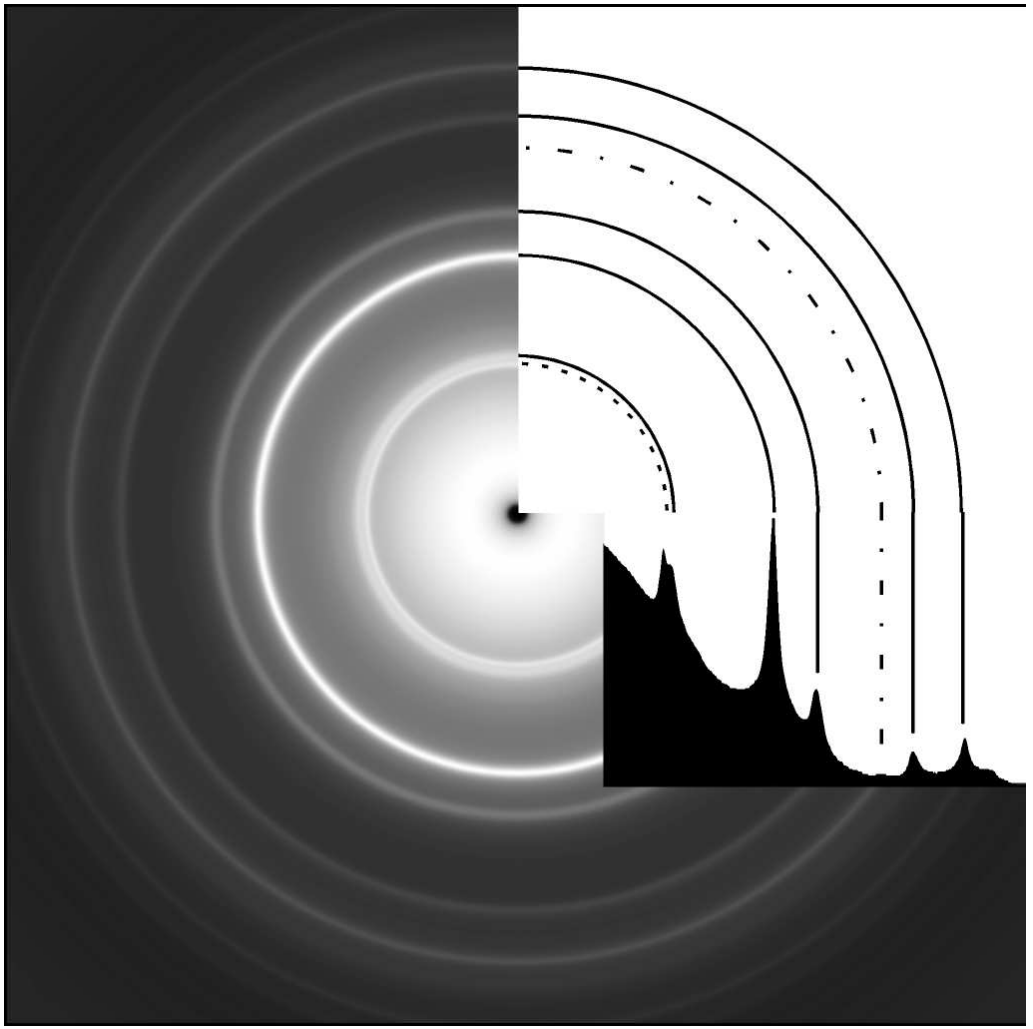


Assembly of Nanoparticles



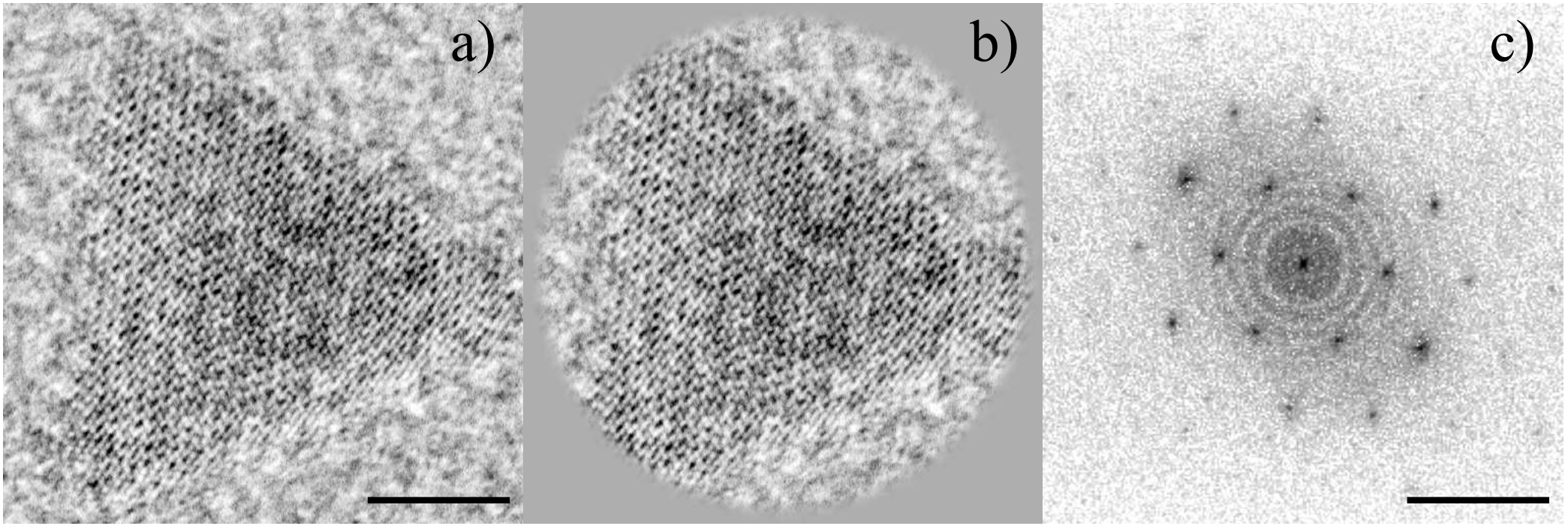
Electron Diffraction





HRTEM & Power Spectrum

$$d_{hlk} = \frac{N_{pix-image} * P_{size}}{N_{pix}} \quad (1)$$



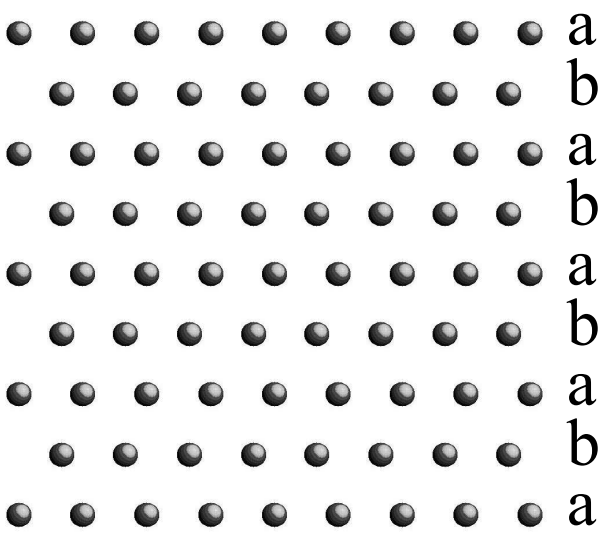
$N_{pix-image}$: N° of pixels along the quadratic frame (128, 256, 512 ...) of the image

P_{size} : Pixel size in the HR image

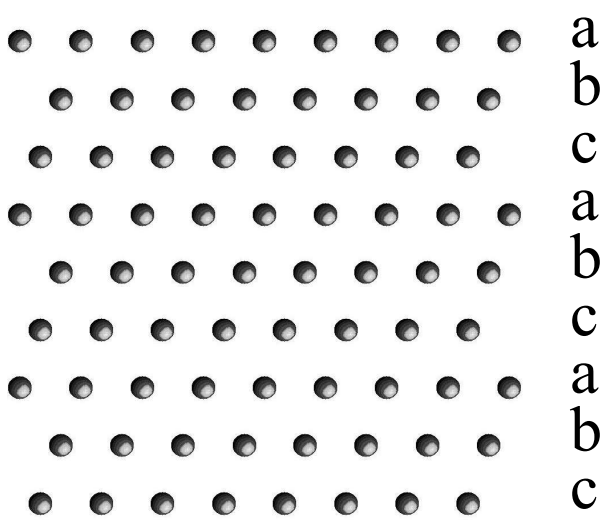
N_{pix} : N° of pixel between the origin and the reflection hkl studied

HCP - FCC structures*

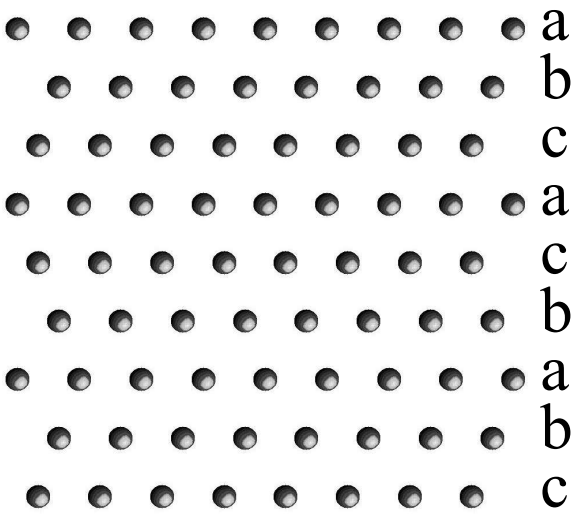
HCP



FCC



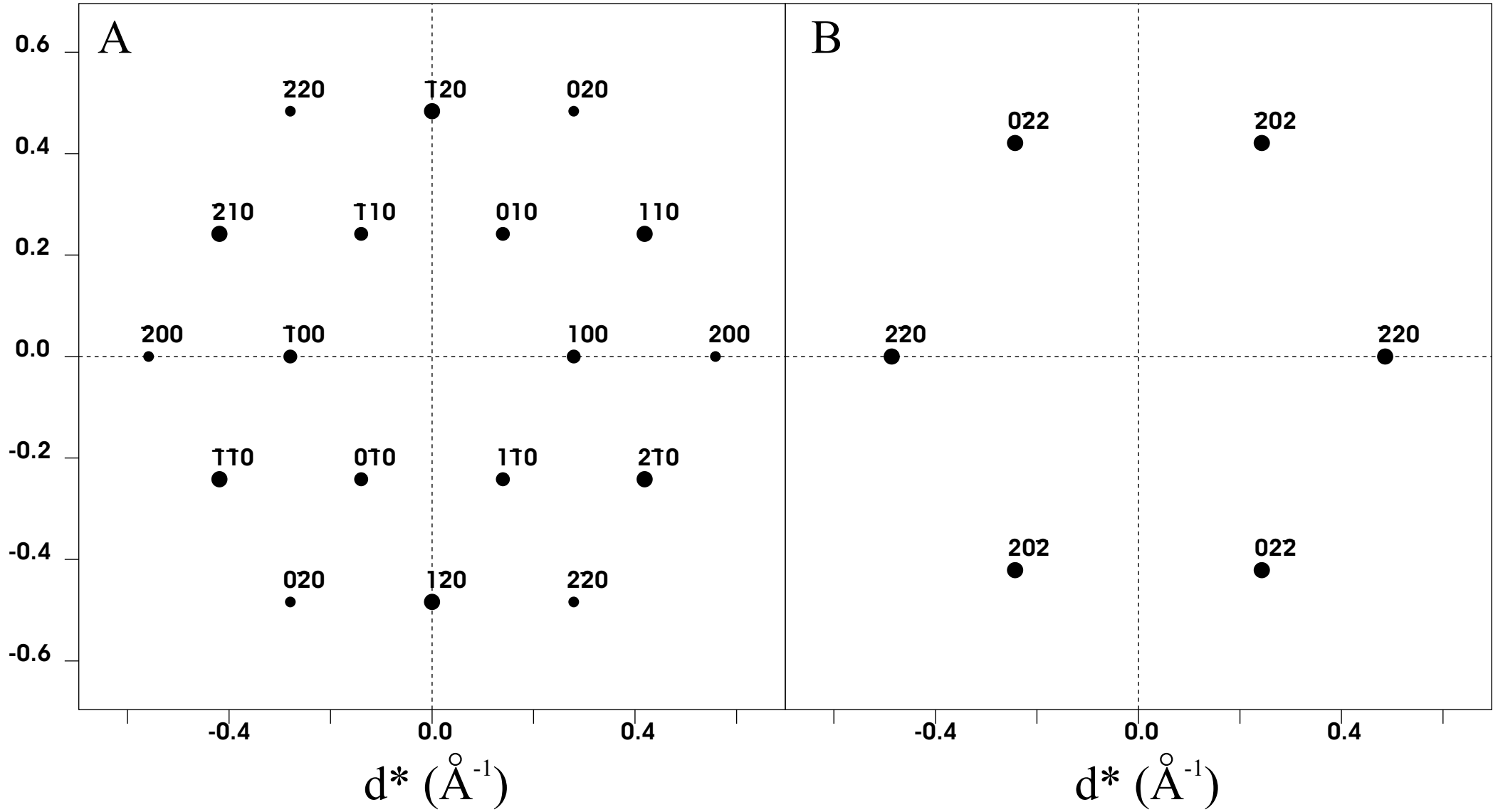
FCC + Twins



Crystals oriented along the [110] direction

*The wurtzite structure is composed by two hcp networks, one occupied by the sulfur and the other by the cadmium, shifted by $00\frac{1}{4}$. The zinc blende structure is composed by two fcc arrays, as for the hcp occupied by the sulfur and the zinc respectively, shifted by $\frac{1}{4}\frac{1}{4}\frac{1}{4}$.

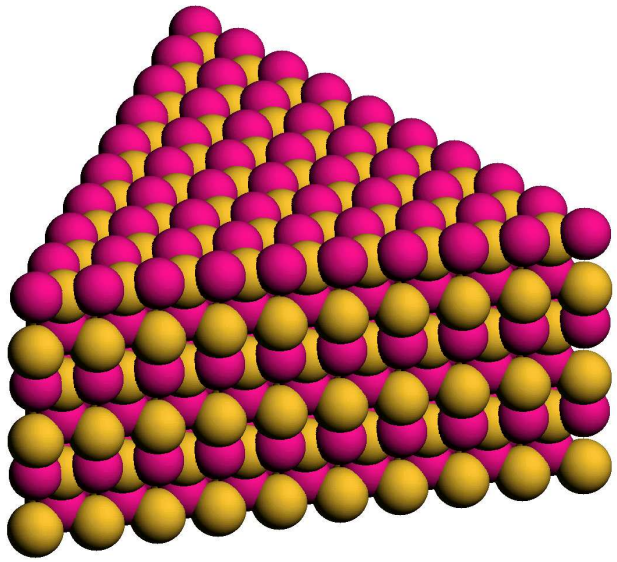
Single Crystal Diffraction



HRTEM Simulations

Computer simulation of the HRTEM images on the basis of the structure of model particles with the multislice technique:

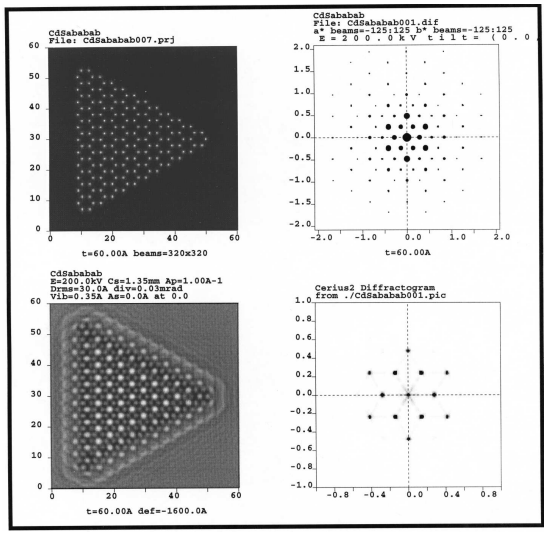
1. The construction of one or more atomic models of the nanocrystals
2. The calculation of the HRTEM image of these models
3. The calculation of the PS of the calculated HRTEM image
4. The comparison of the HRTEM images and the PS calculated with the data obtained from the experimental HRTEM



Multislice Technique*

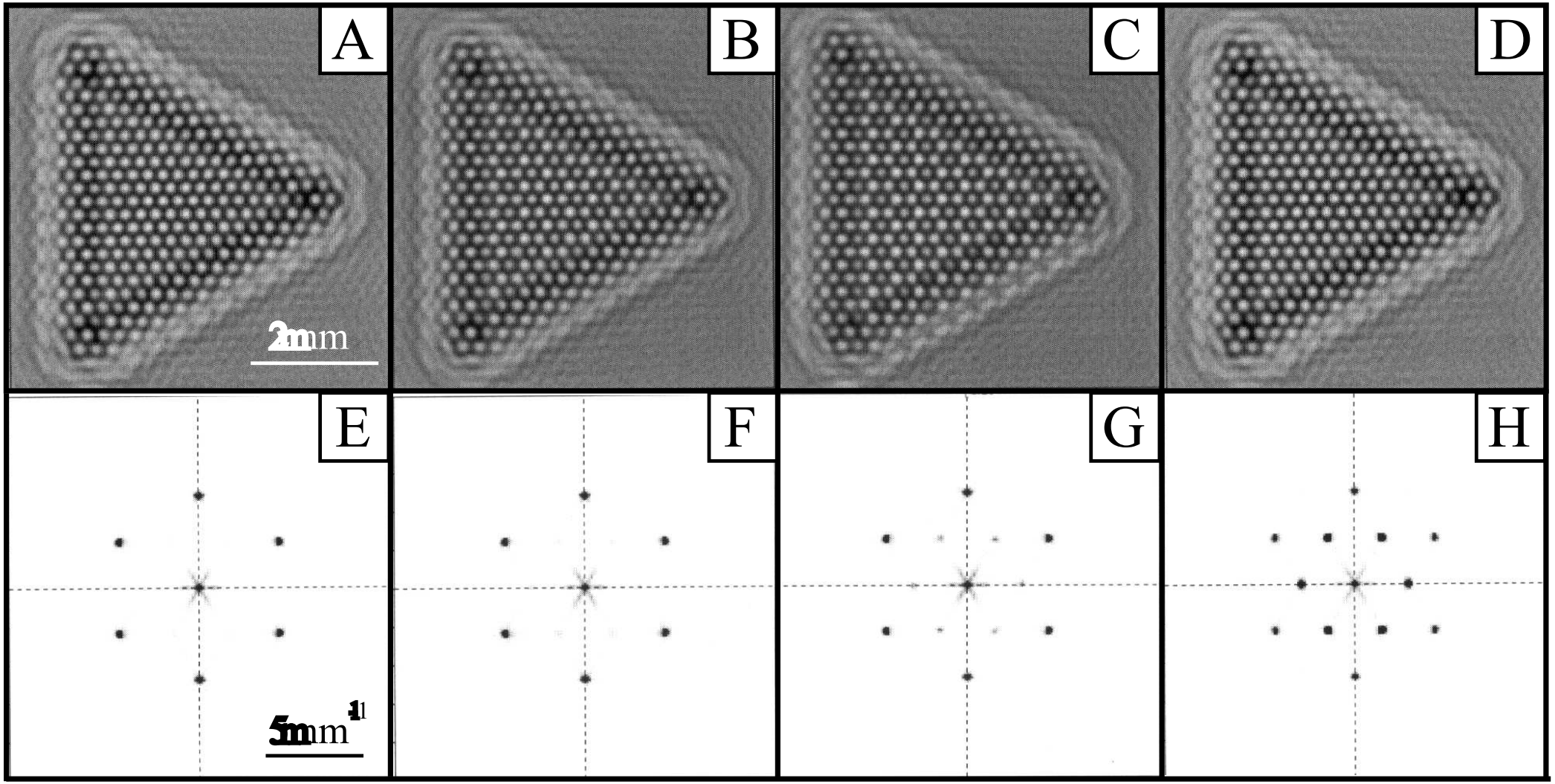
Electrons are assumed to scatter only in a forward direction with small diffraction angles. With this approximation the crystal can be divided in sub-slices with a thickness Δz perpendicular to the incident beam.

1. The crystal is divided in slices perpendicular to the electron beam
2. The electrostatic potential $V(x, y)$ with in-plane coordinates x,y of the sliced crystal or supercell is projected for each slice of the included atoms onto its exit surface
3. On the basis of $V_P(x, y)$ the amplitude of the electron wave function is calculated
4. Calculate the propagation of the electron wave throught all the slices

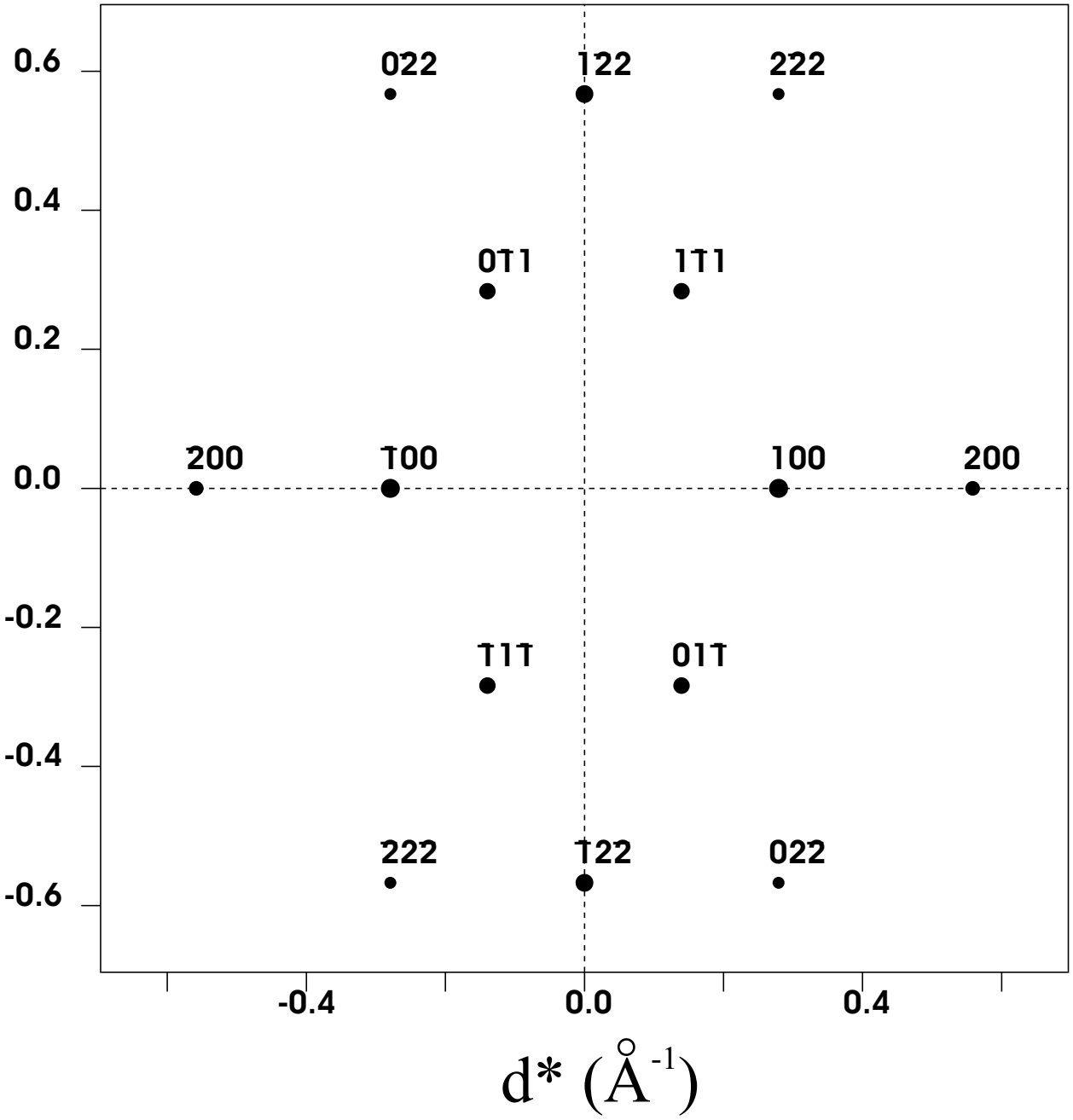


*J.W. Cowley, A.F. Moodie, Acta Cryst. 10, 609, 1957

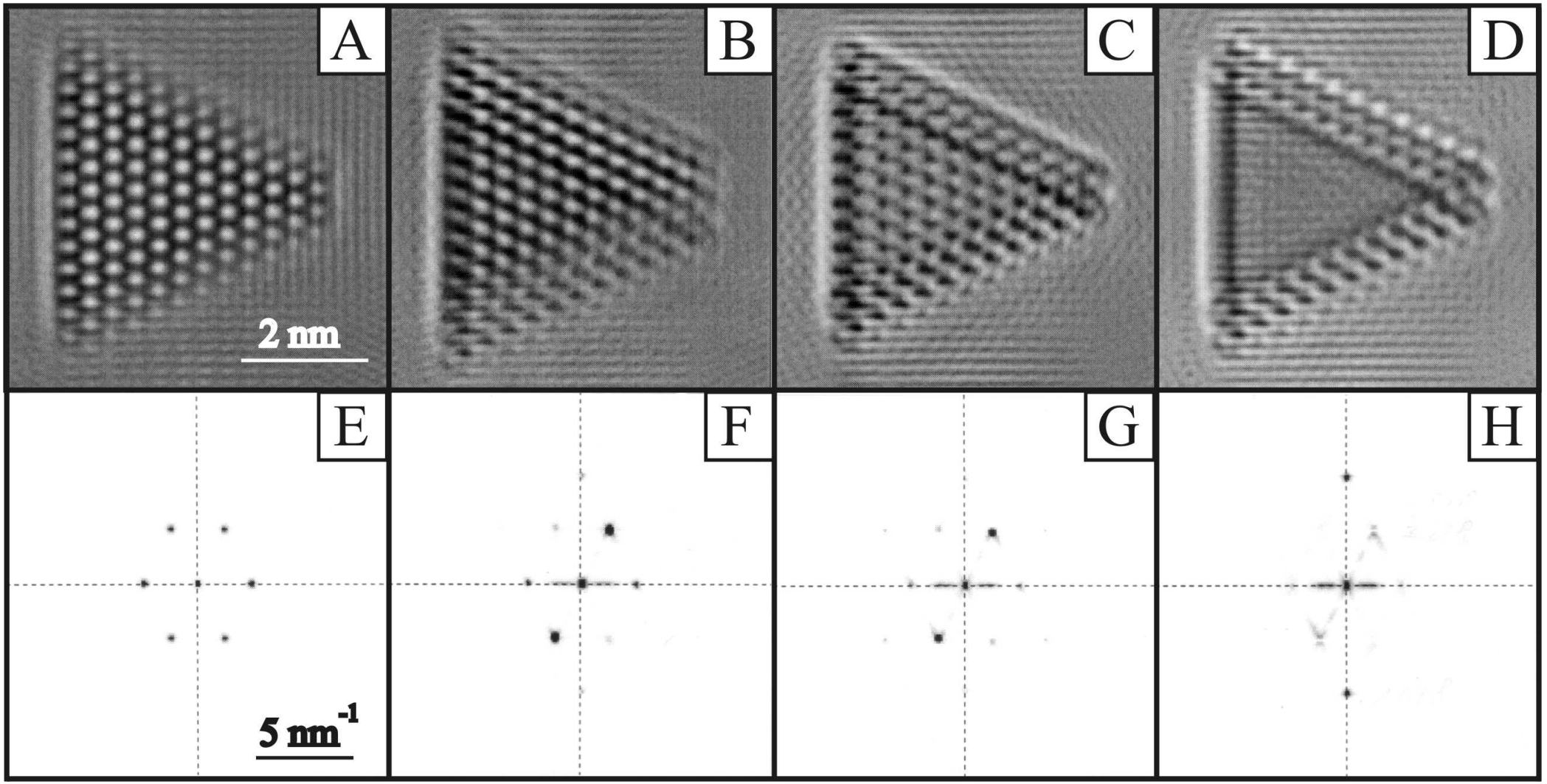
HRTEM Simulations



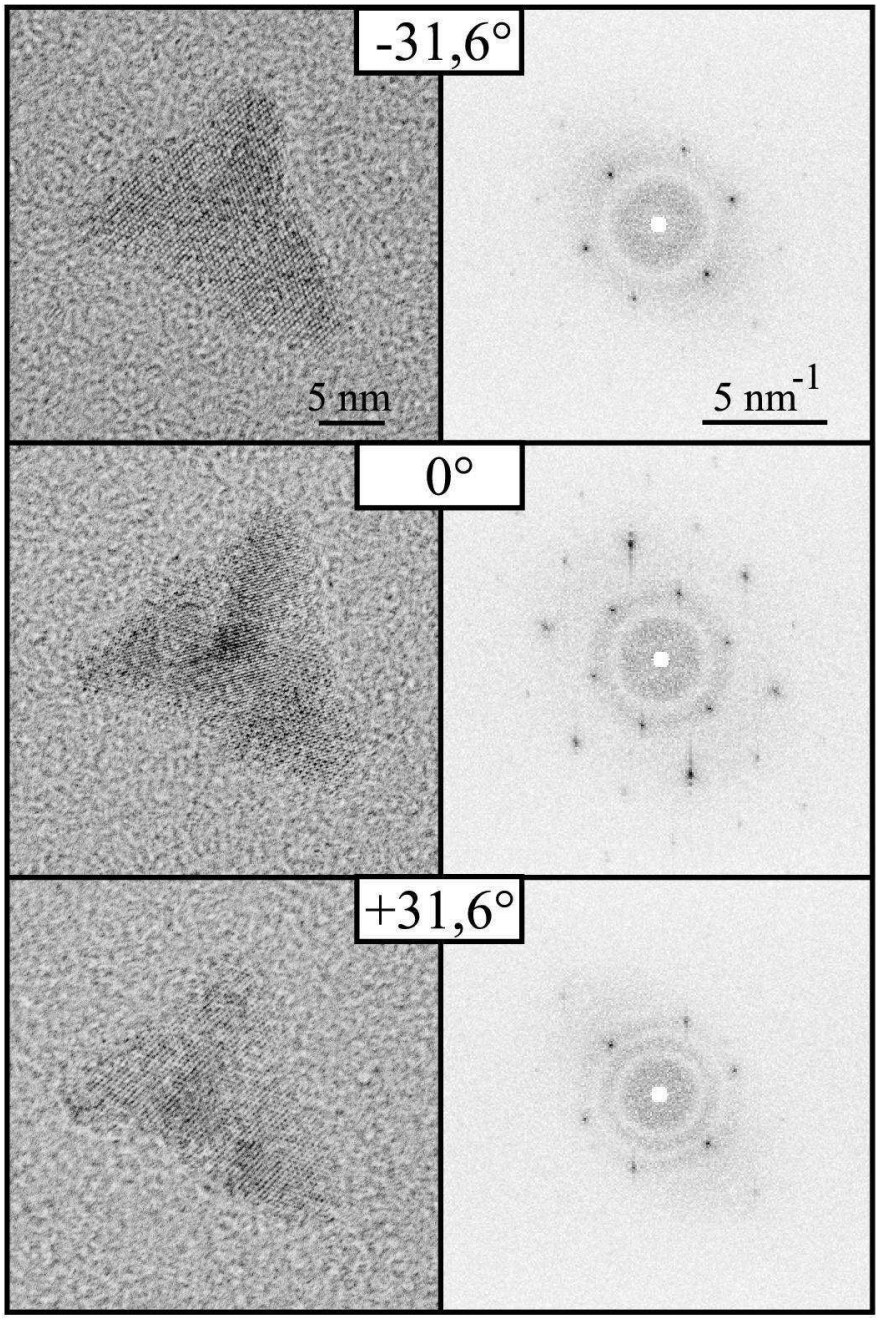
HRTEM Simulations

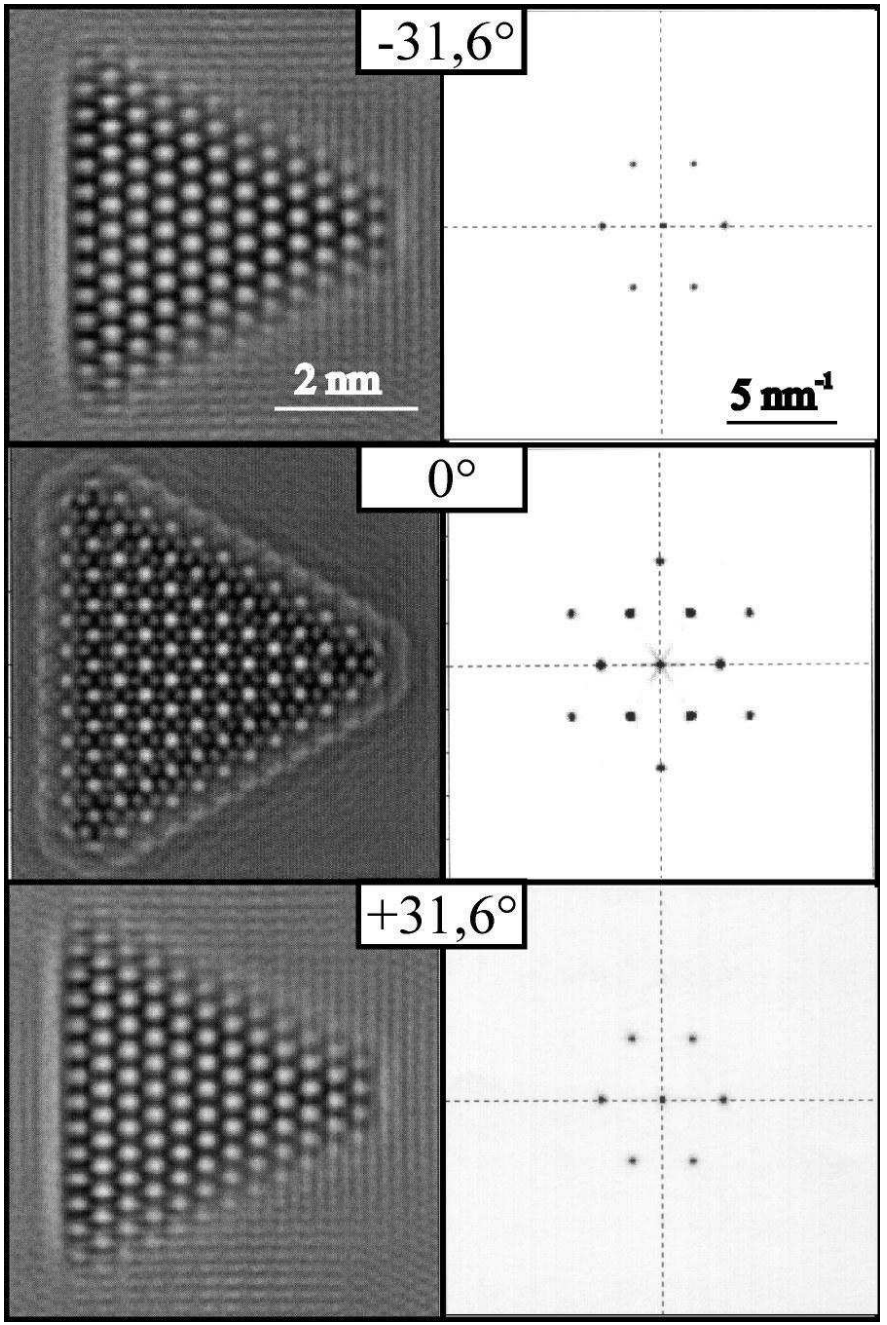


HRTEM Simulations

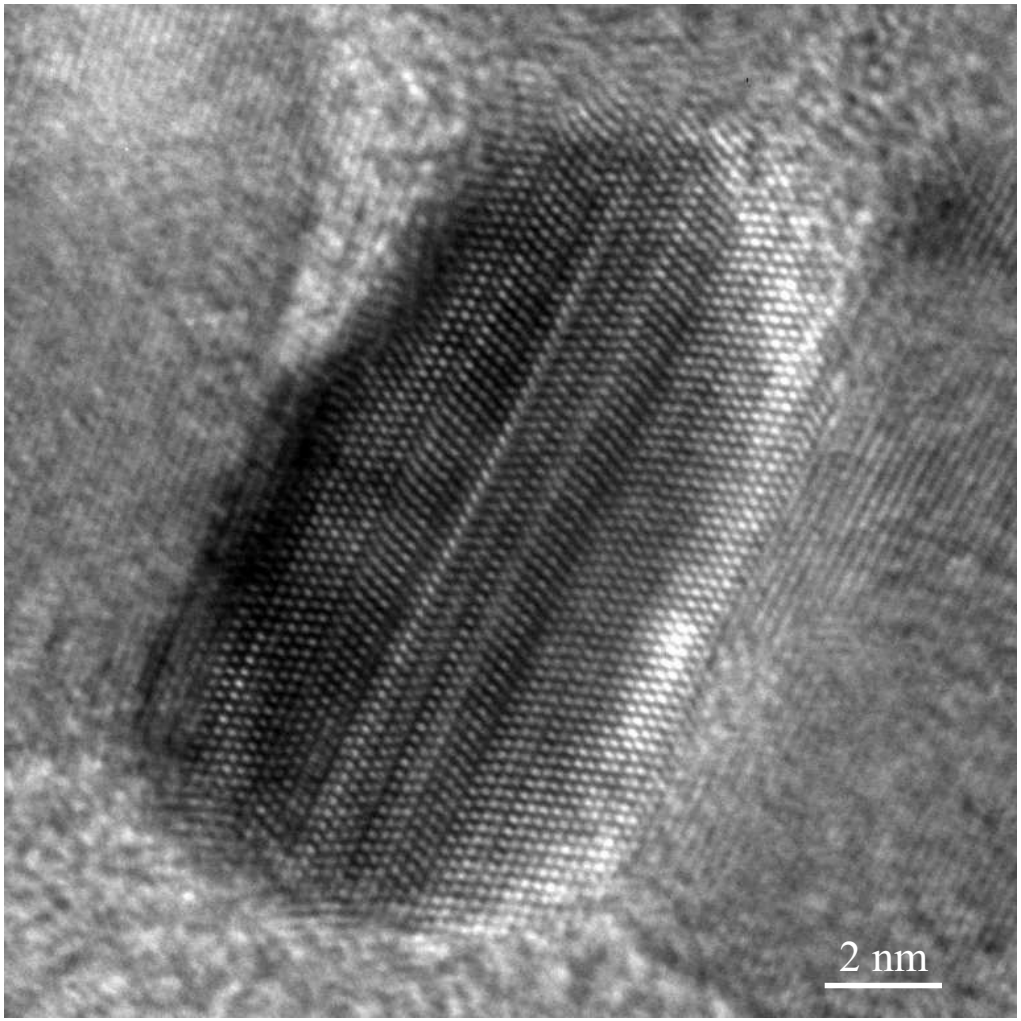


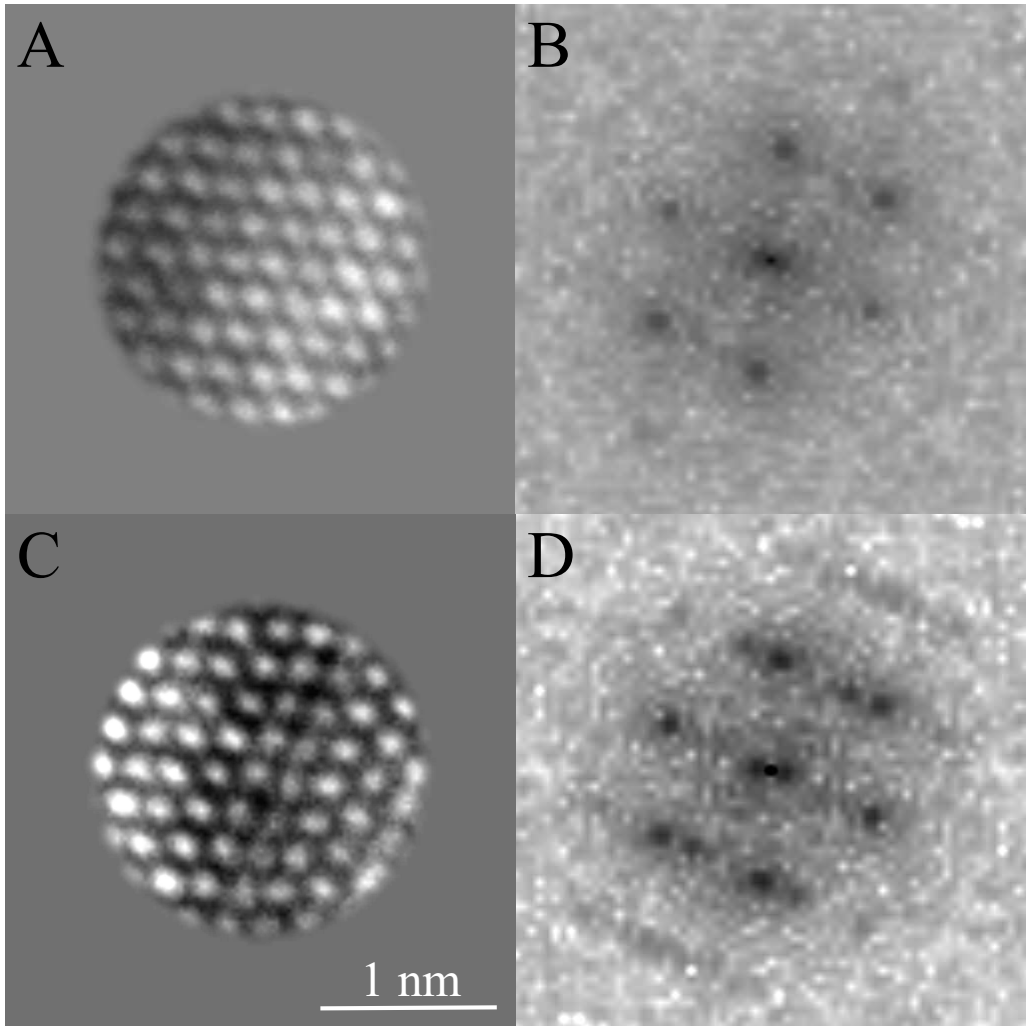
HRTEM Simulations



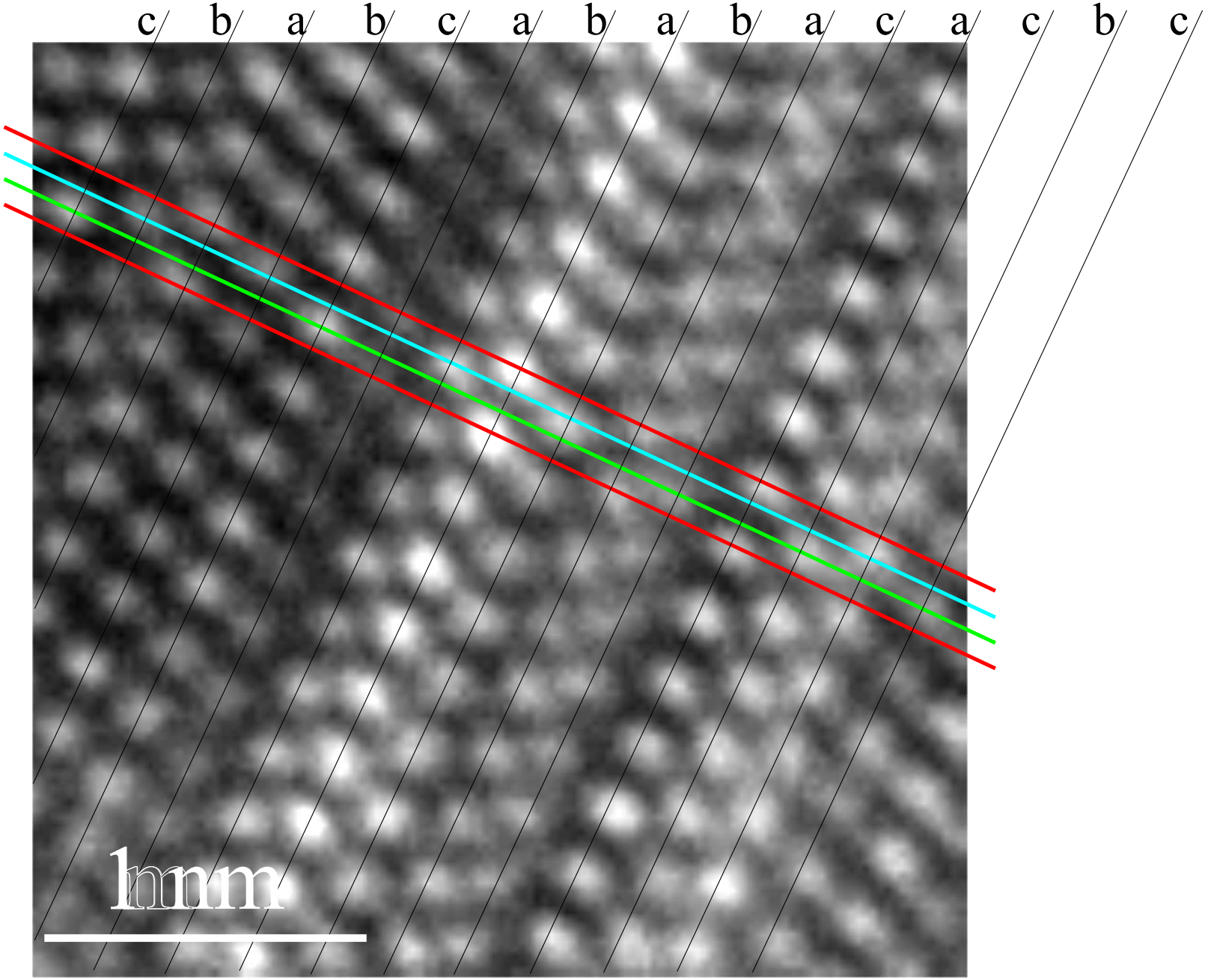


Copper Nanoparticles





Copper Nanoparticles



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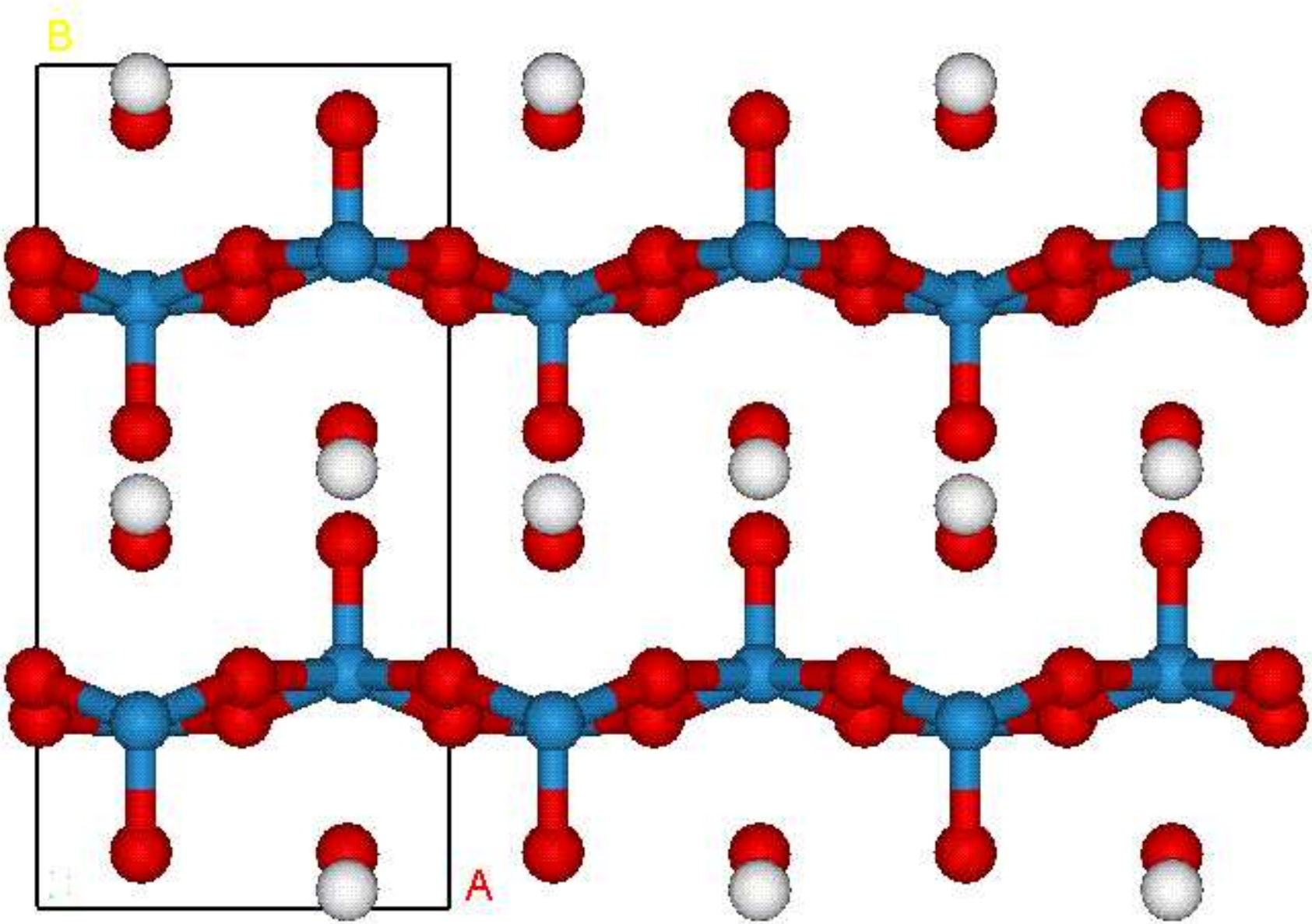

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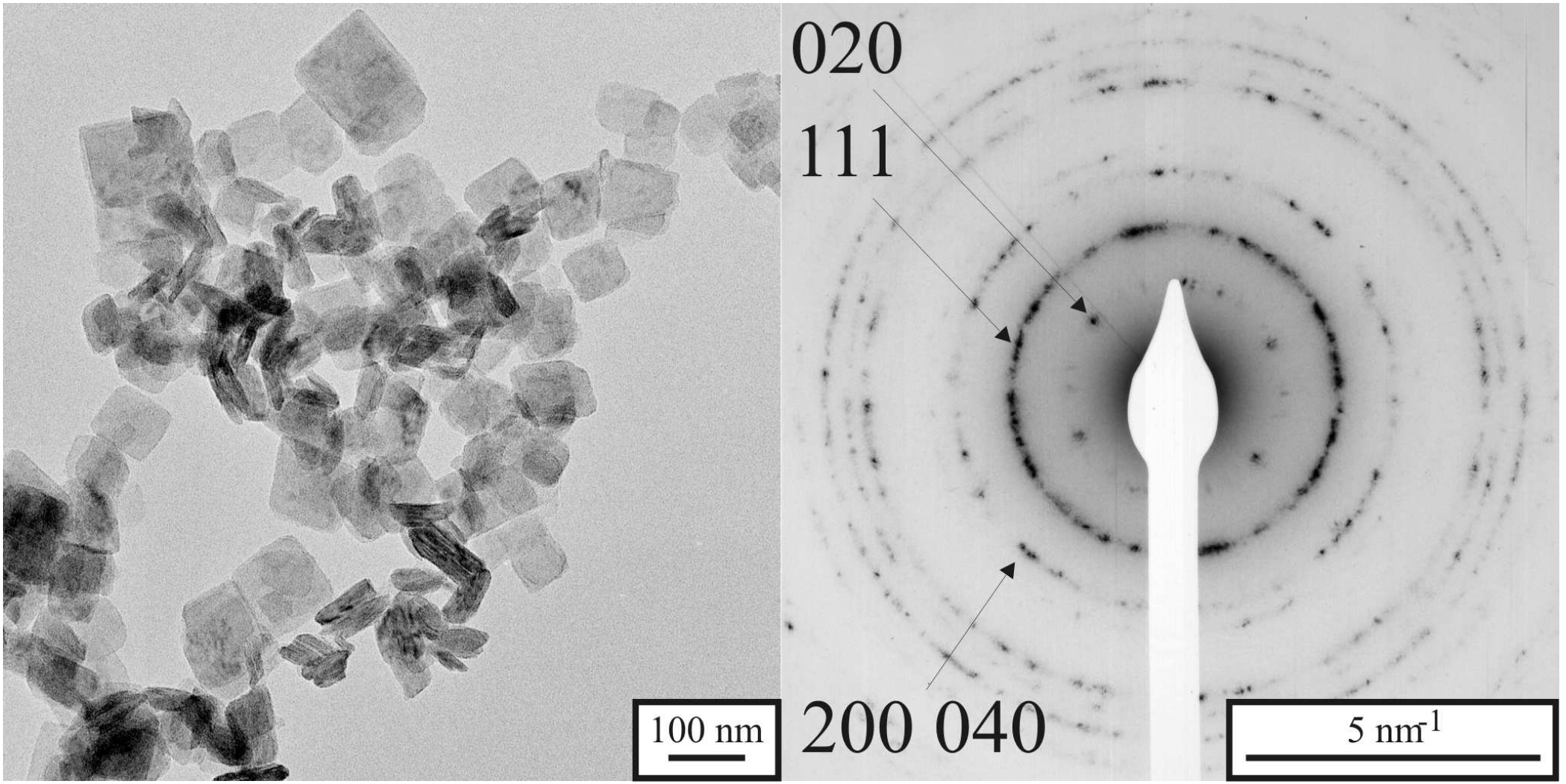

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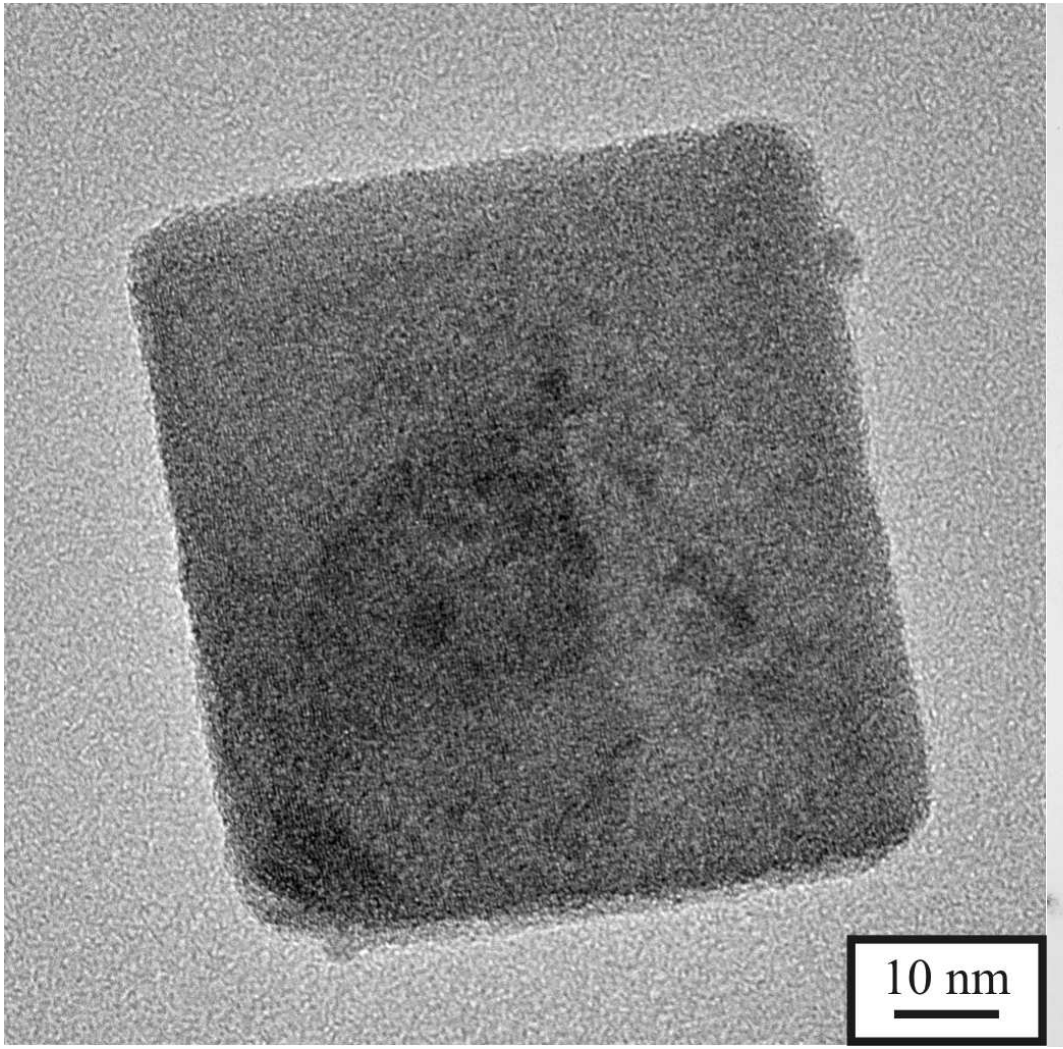

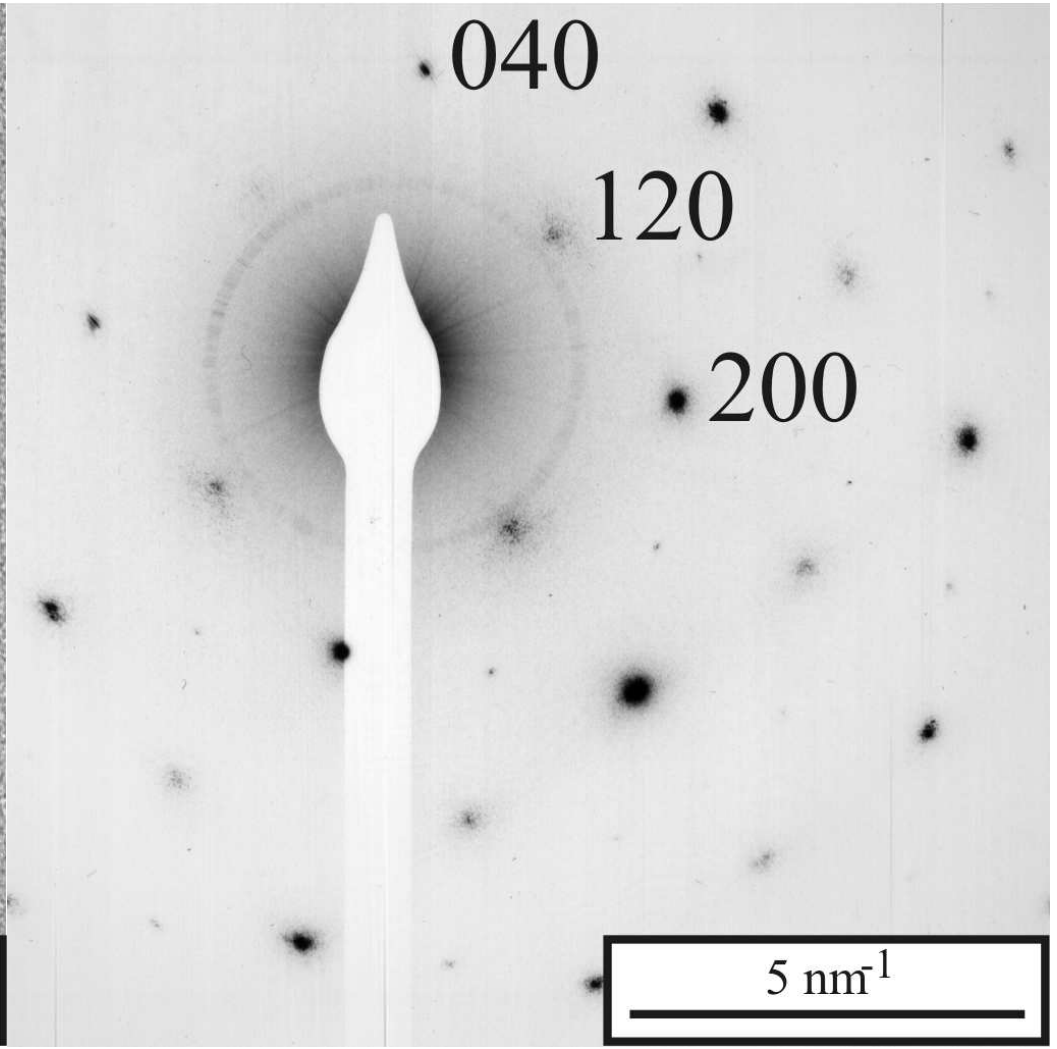

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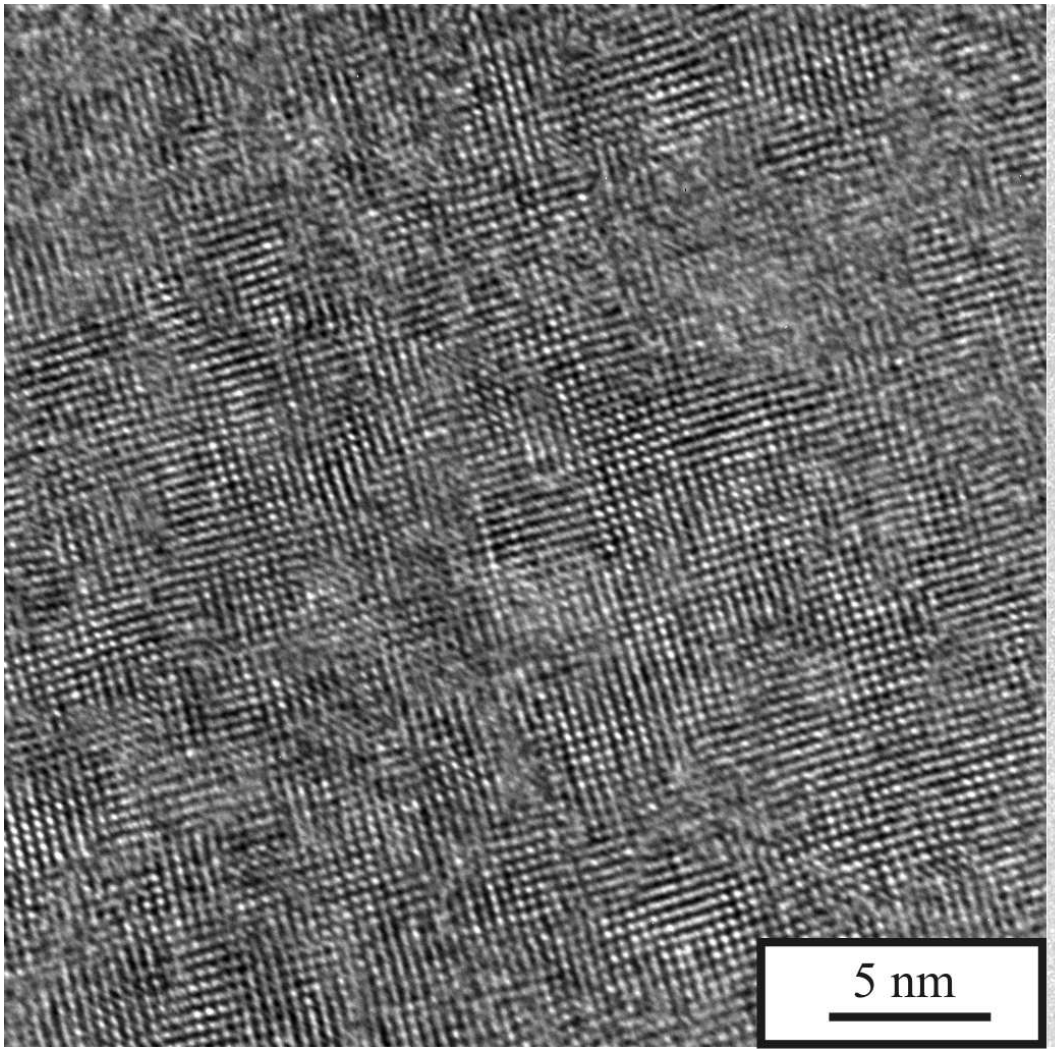

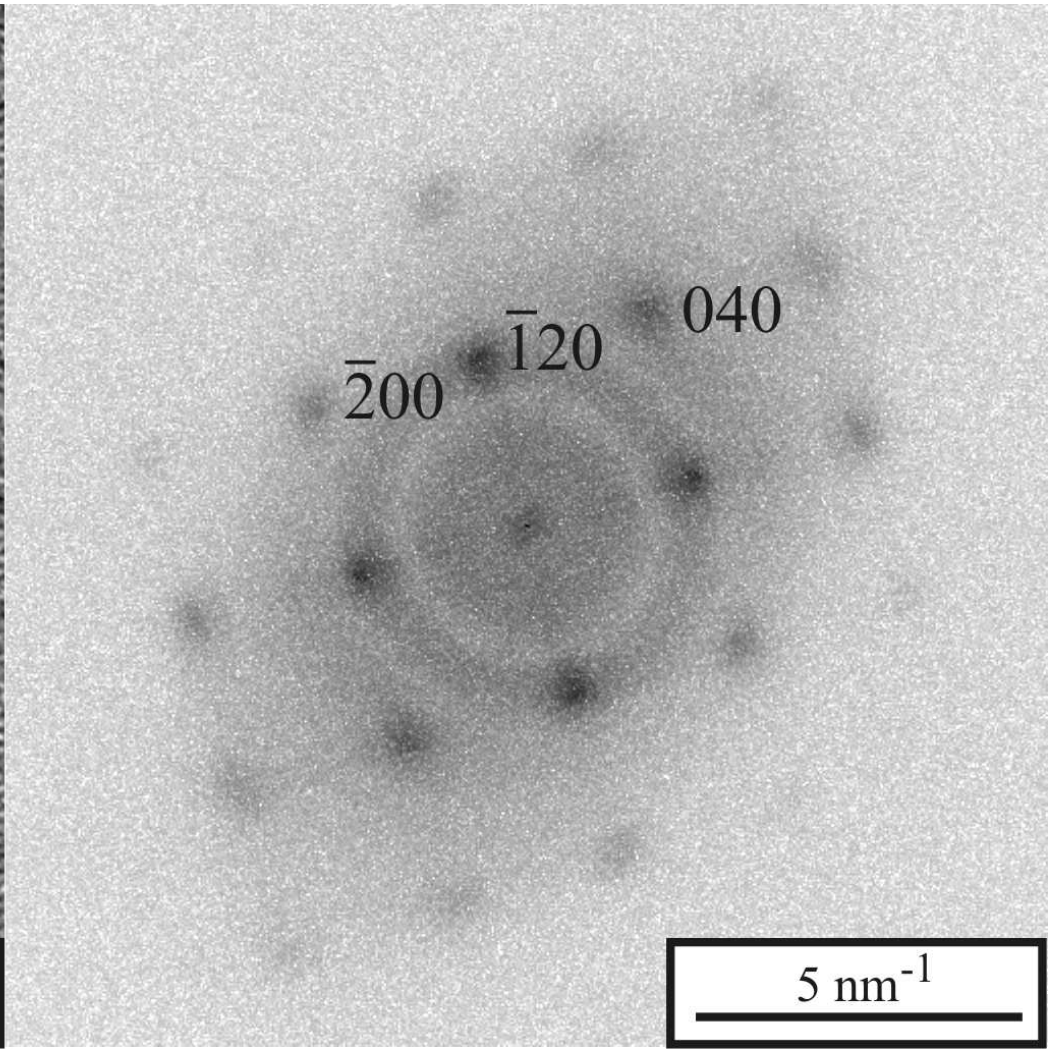

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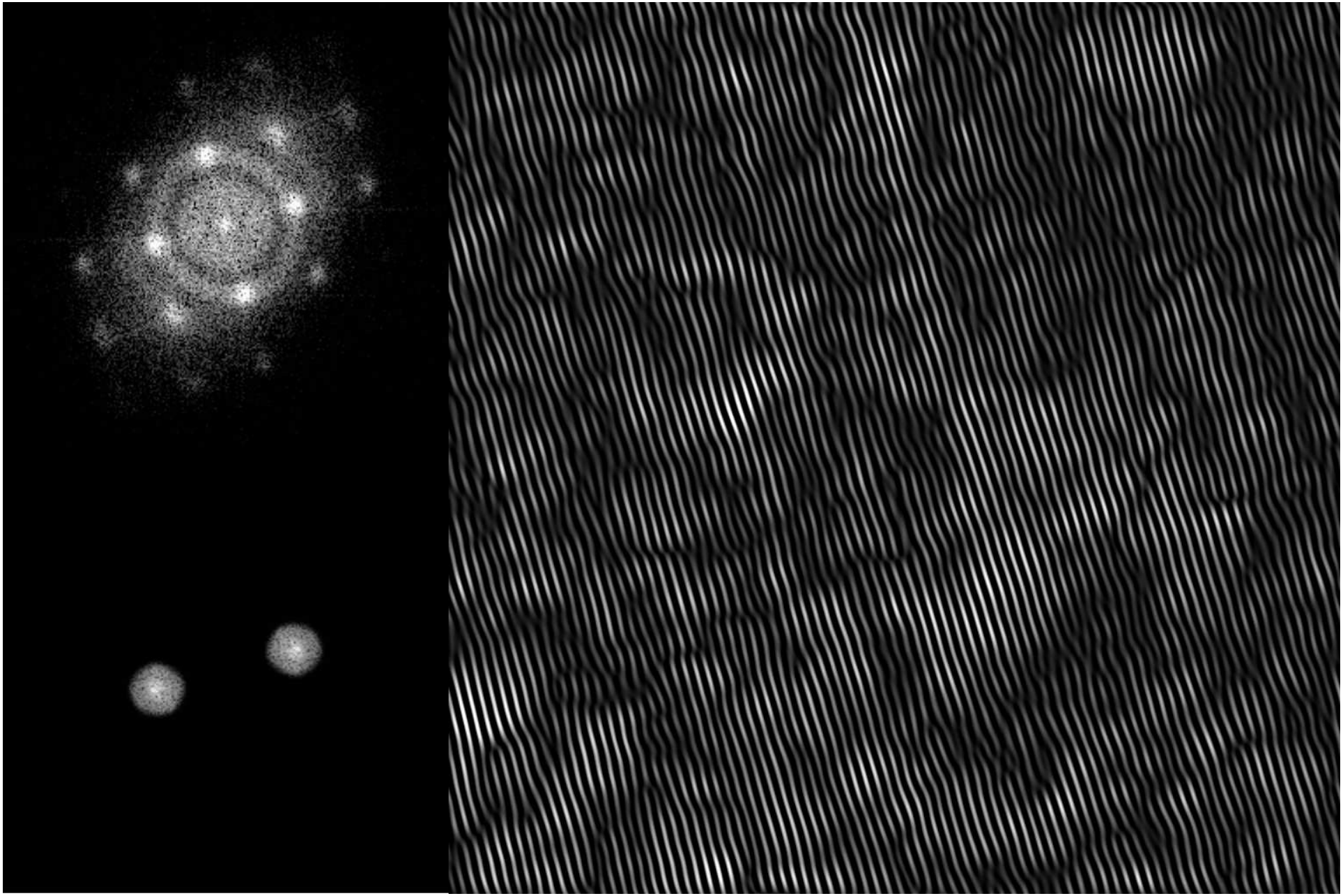
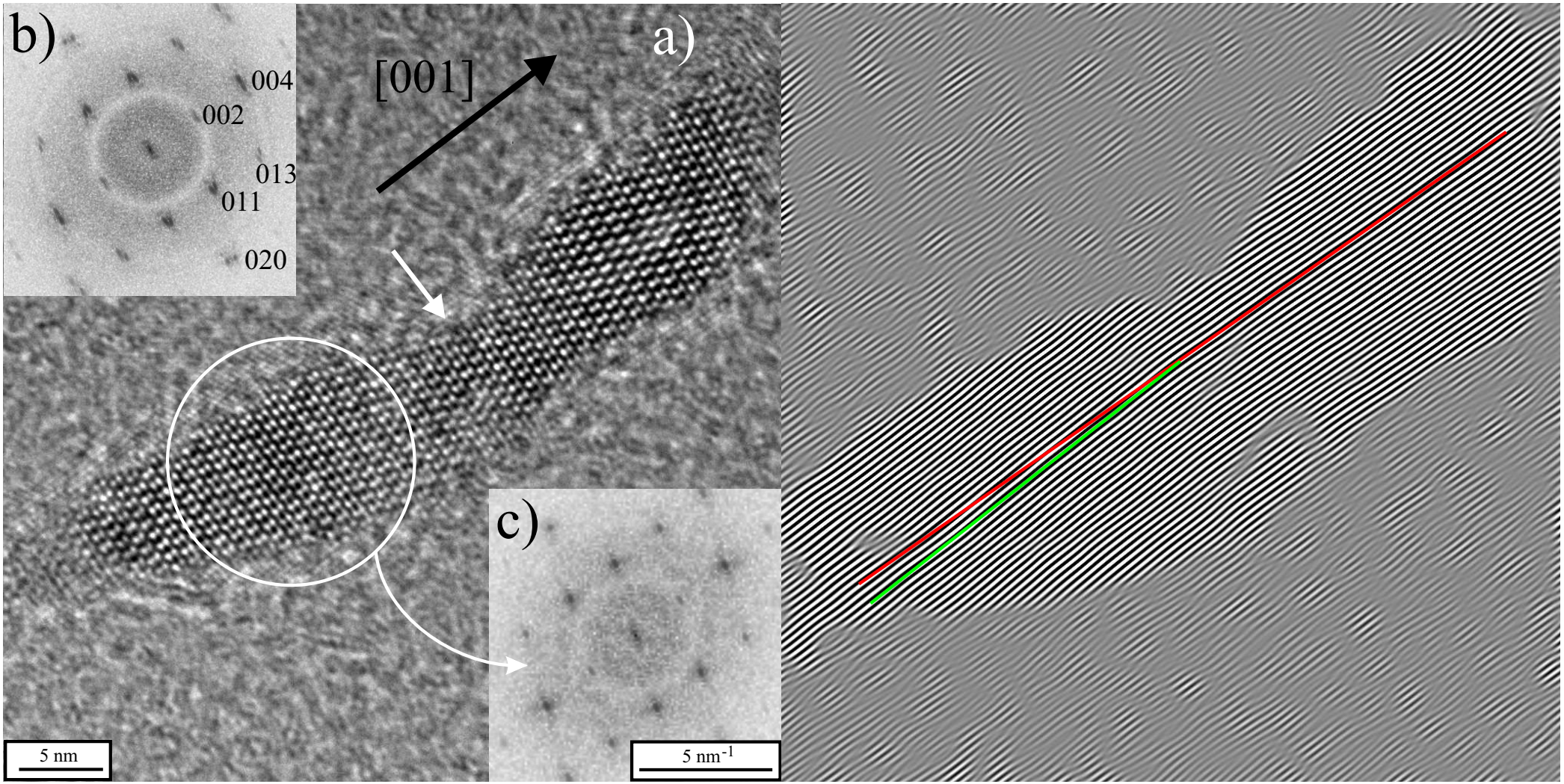


Oriented Attachement

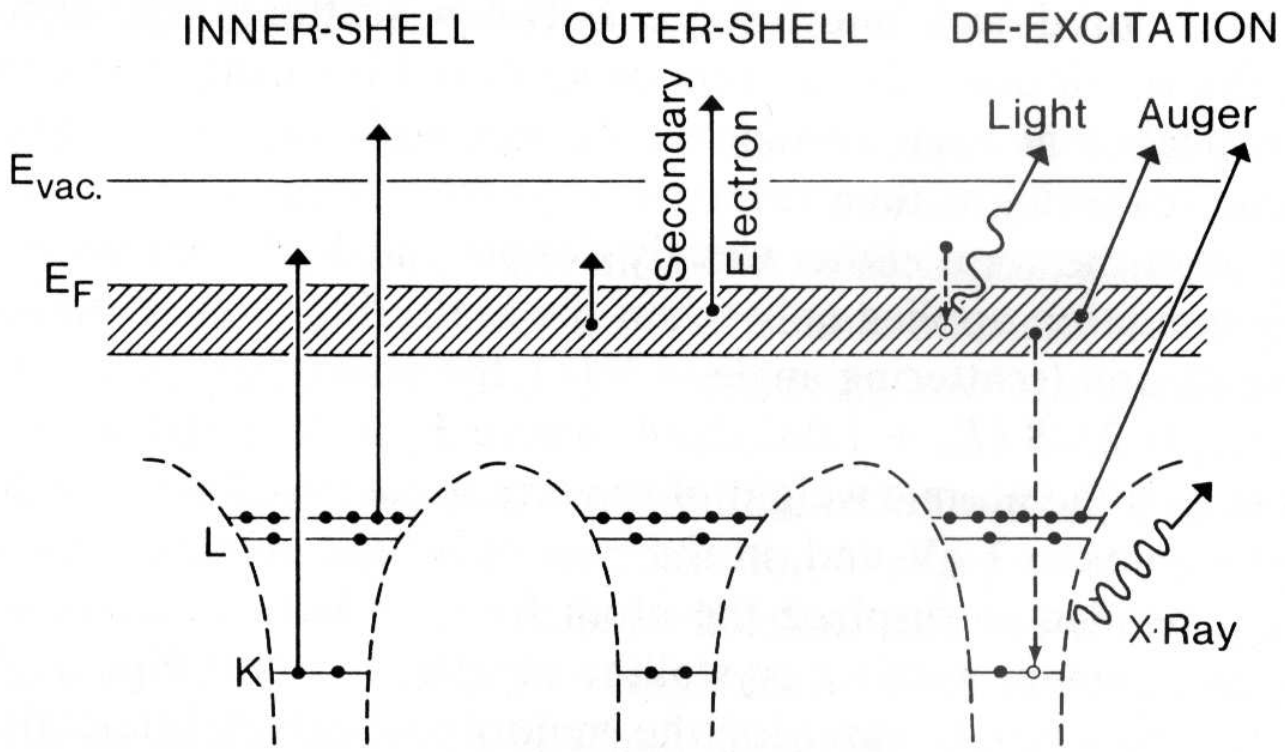


J. Polleux, N. Pinna, M. Antonietti, M. Niederberger, Adv. Mat. 2004, 16, 436

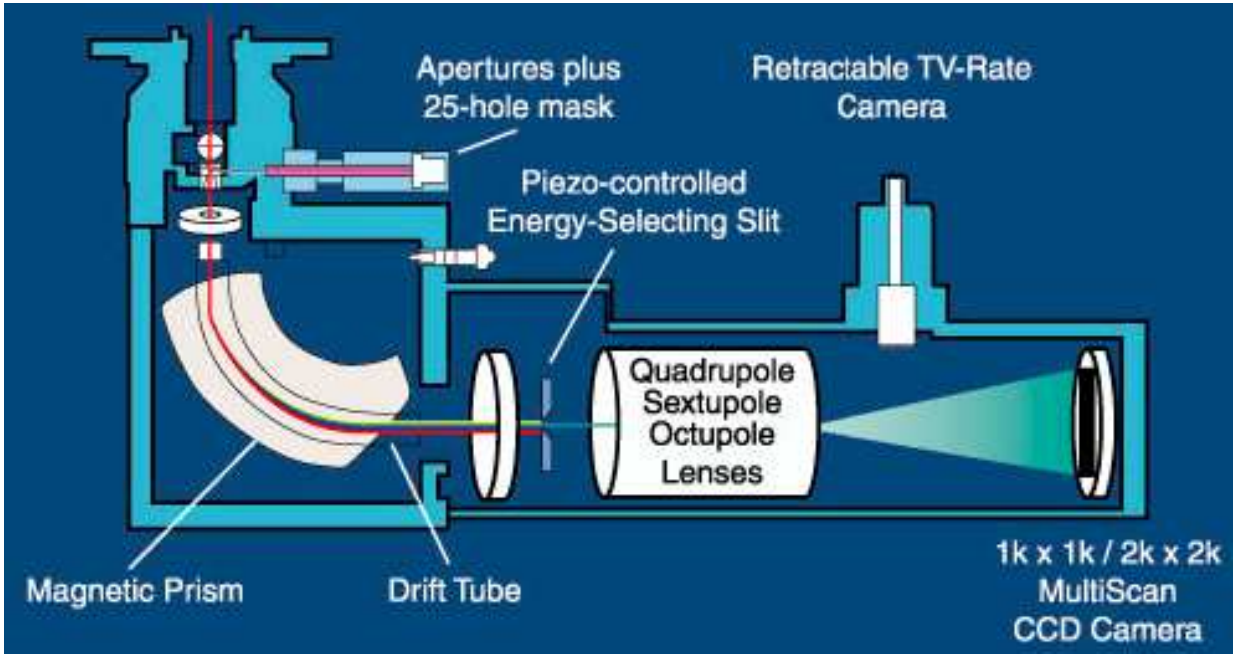
Electron Energy Loss Spectroscopy

Inelastic scattering of an electron of the incident beam and the atomic electrons of the solid.

- Transition from an inner-shell (K, L M ...) to an unoccupied energy level (i.e. above the Fermi level)
- Transition of a valence electron across the energy gap (insulator, semiconductor) or excitation of a plasma resonance (mostly in metals metals).

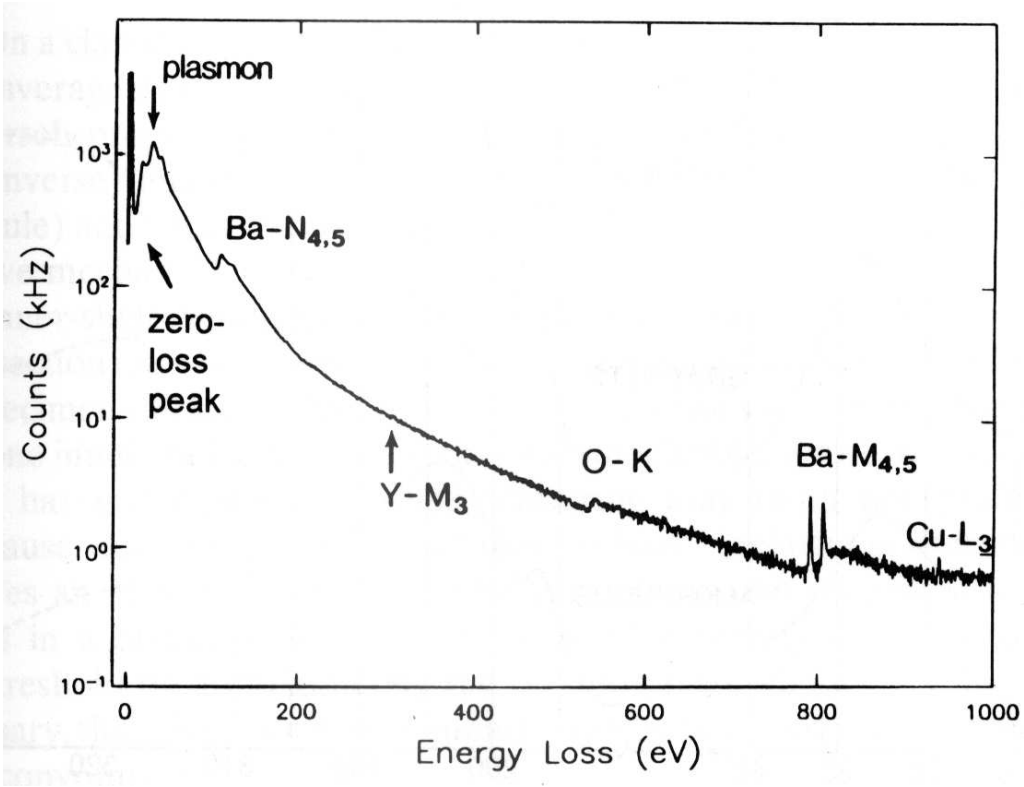


Electron Energy Loss Spectroscopy

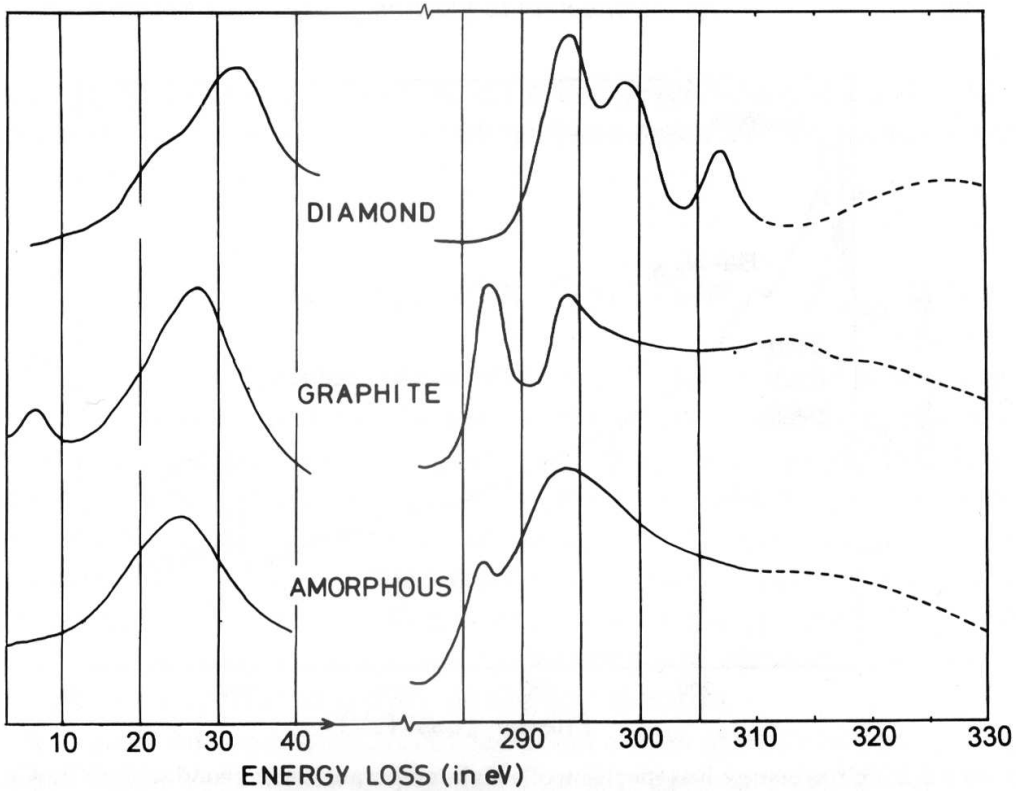


Electron Energy Loss Spectroscopy

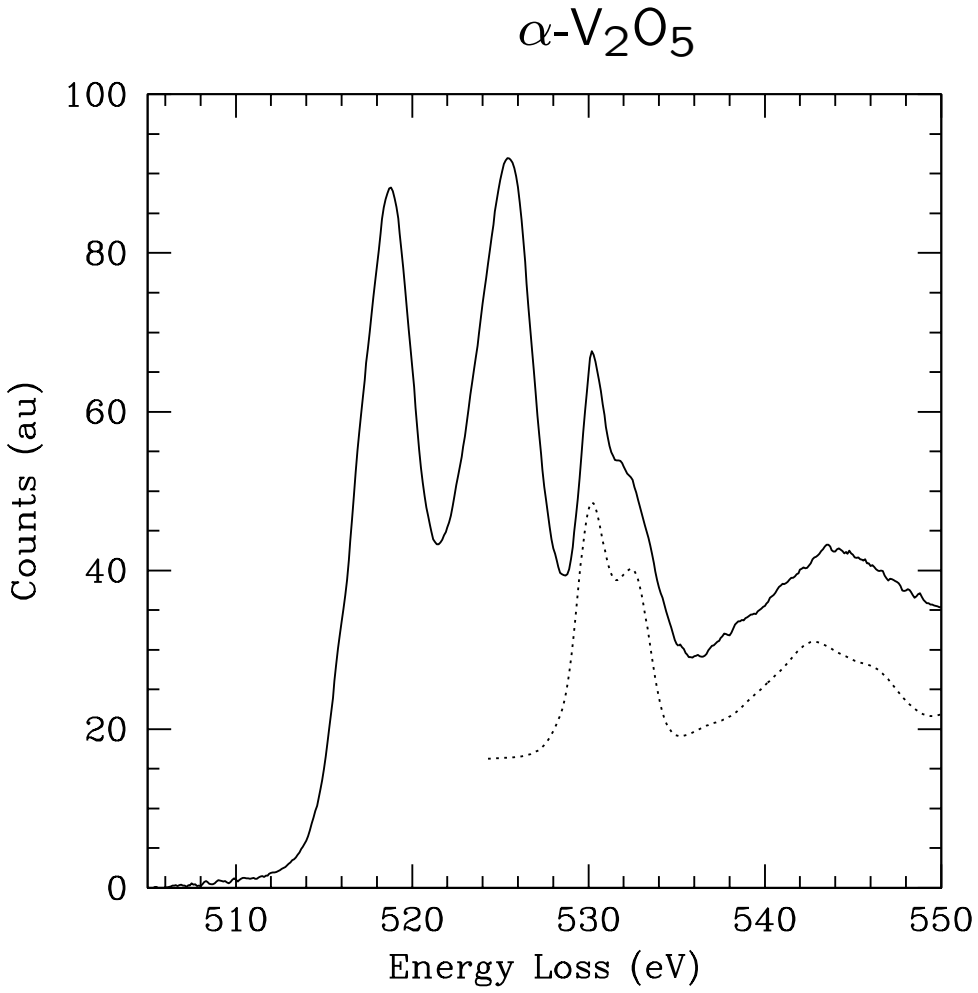
$YBa_2CU_3O_7$

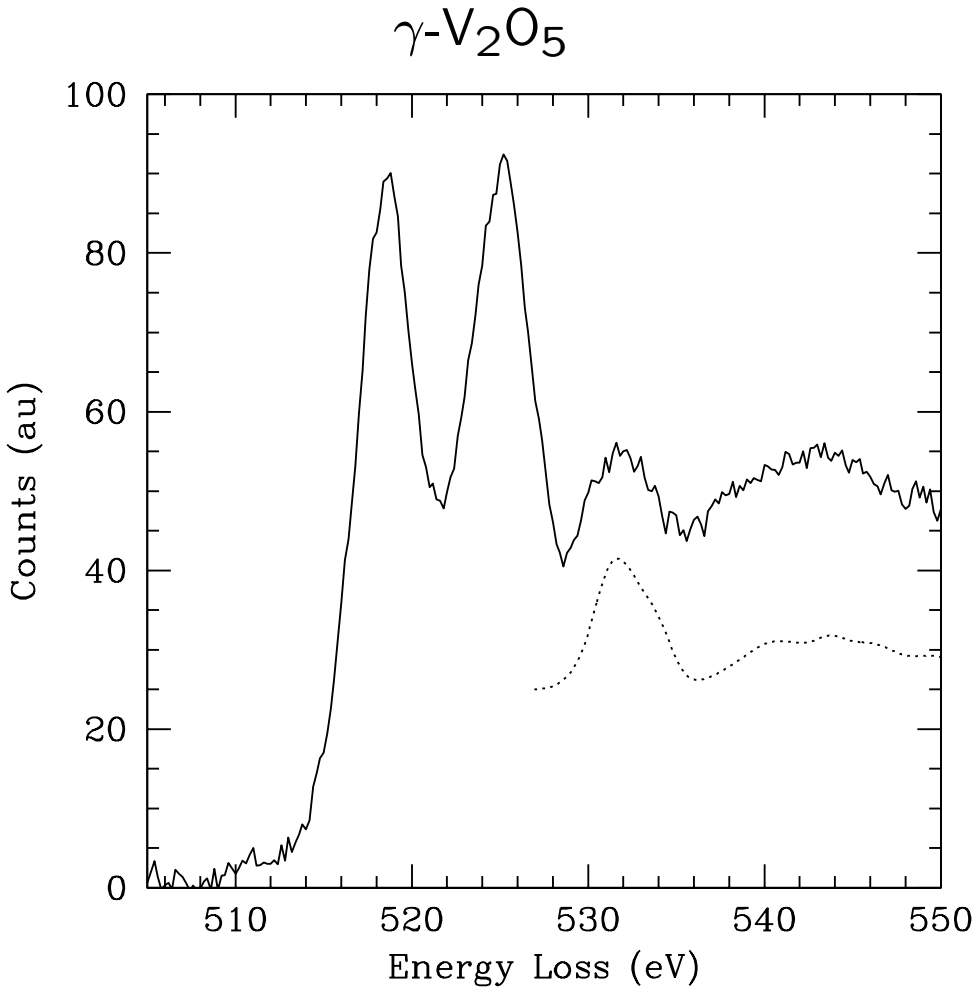


Carbon allotropes

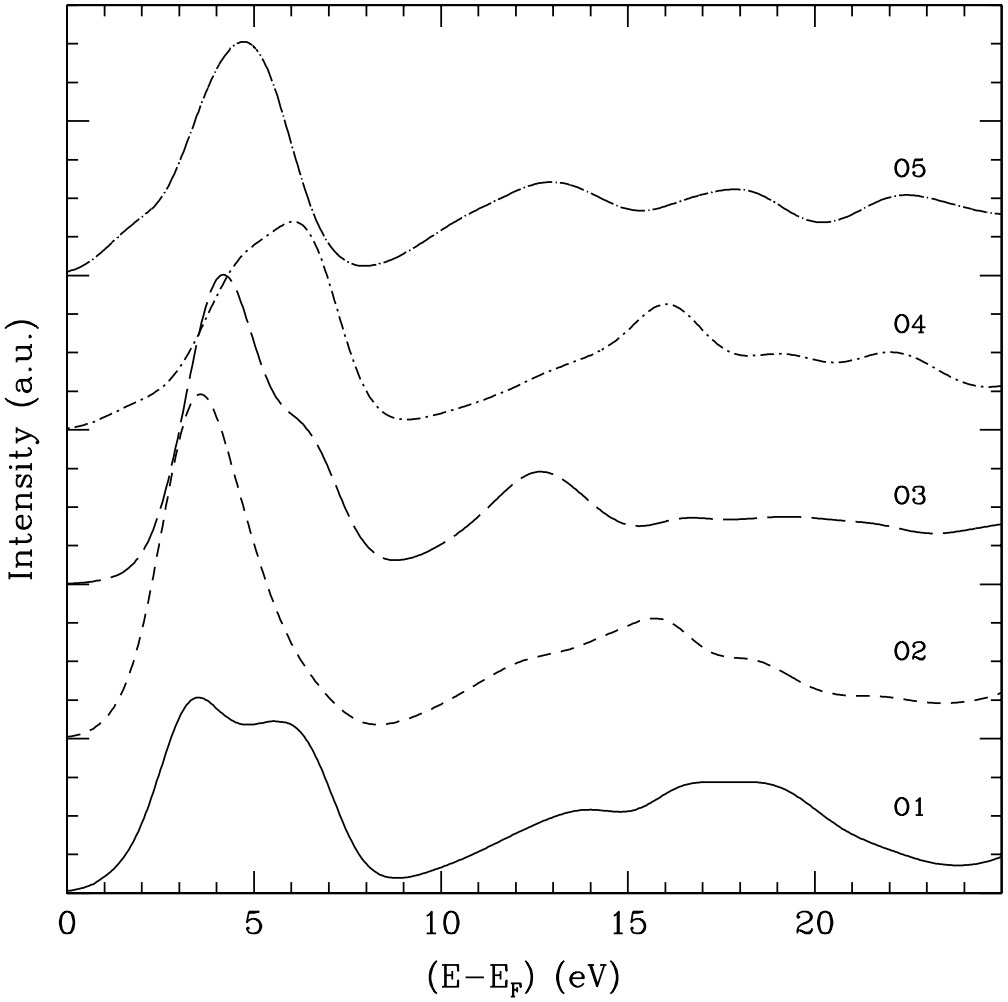


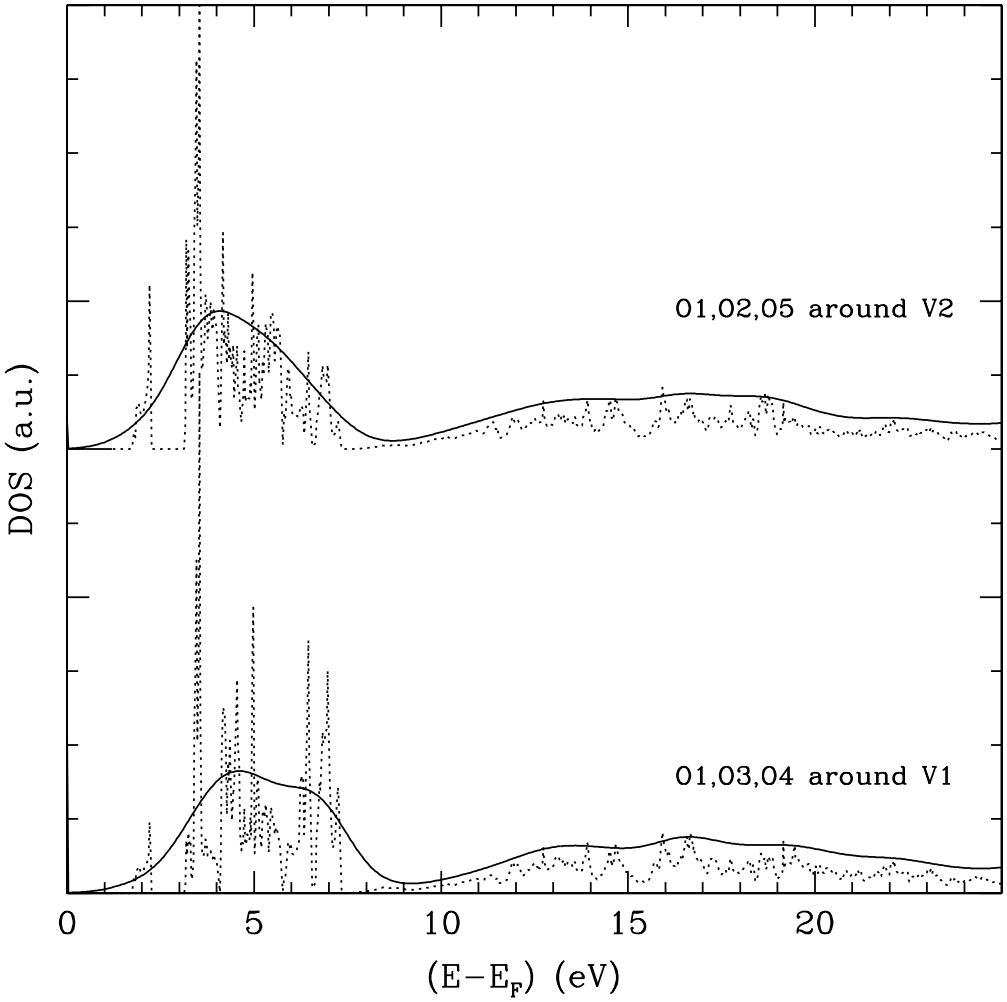
Electron Energy Loss Spectrometry





Electron Energy Loss Spectrometry





Conclusion

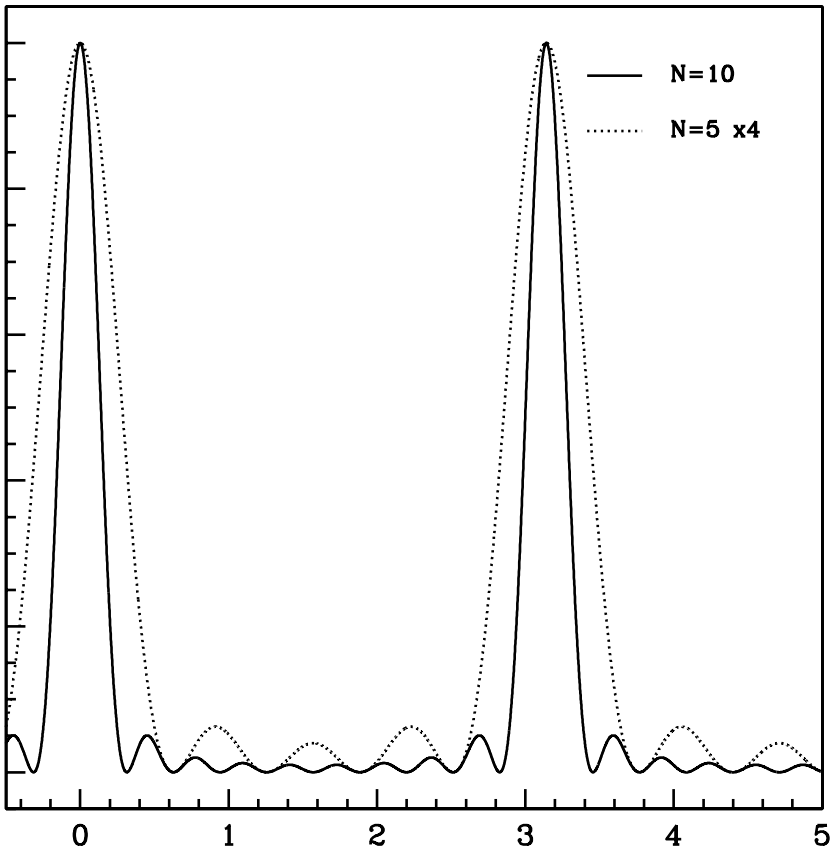
- TEM permits the structural characterization of a collection or isolated nanoparticles
- Electron Diffraction $\longrightarrow$ structure of single or many particles
- HRTEM $\longrightarrow$ structure, orientation, crystallinity, defaults
- Image processing: fondamental tool for structural studies in electron microscopy
- Spectroscopy: EELS, EDX $\longrightarrow$ local structure, band structure, composition
- Do not permit to study structural properties of the whole sample $\longrightarrow$ Necessity to compare the results with other techniques

Particle Size Broadening

$$I = I_e F^2 * \frac{sin^2(\pi/\lambda)(\mathbf{s}-\mathbf{s_0})N_1\mathbf{a_1}}{sin^2(\pi/\lambda)(\mathbf{s}-\mathbf{s_0})\mathbf{a_1}} * \frac{\cdots N_2\mathbf{a_2}}{\cdots \mathbf{a_2}} * \frac{\cdots N_3\mathbf{a_3}}{\cdots \mathbf{a_3}} \quad (2)$$

N_1, N_2, N_3 Number of the unit cells along the $\mathbf{a_1}, \mathbf{a_2}, \mathbf{a_3}$ directions

Normally N_1, N_2, N_3 are large numbers $\rightarrow$ the three quotients differs from zero only if the three Laue equations are closely satisfied. If N_1, N_2, N_3 are small, the quotients broaden.



B.E. Warren, X-Ray Diffraction, Dover

Sherrer Equation

Approximations:

1) Cubic crystal $N_1, N_2, N_3 = N$

2) Crystal free from strains and faulting $\rightarrow$ peak broadening is only due to the small crystallite size

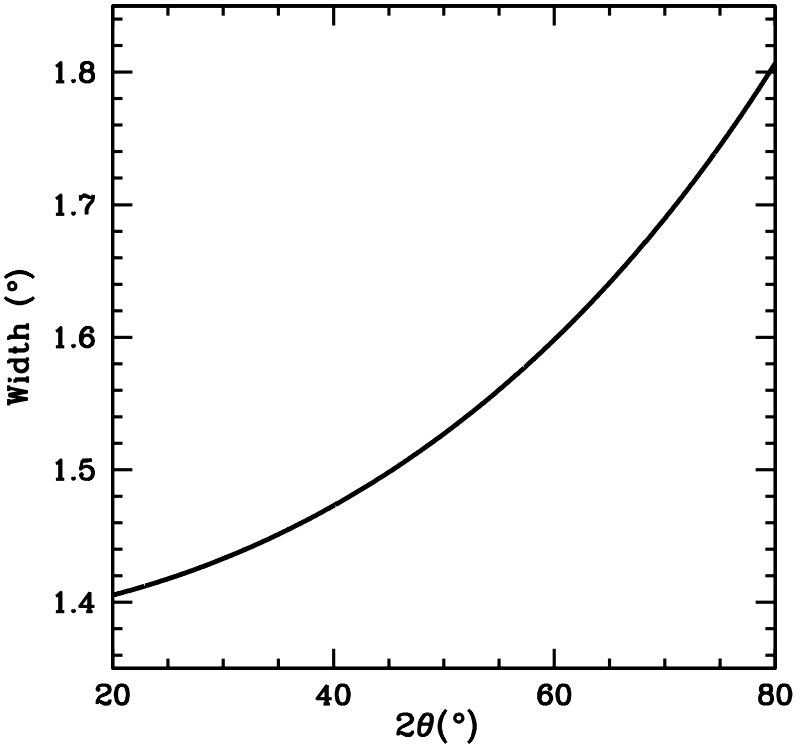
3) Each of the three quotients of equation 2 by a Gaussian function

$$B(2\theta) = \frac{2\,[(ln2)/\pi]^{1/2}\,\lambda}{N\;a\;cos\theta} = \frac{0.94\;\lambda}{L\;cos\theta} \qquad (3)$$

$B(2\theta)$: full width in radians at half maximum intensity of the powder pattern peak.

L: cube edge dimension

Normally valid for cubic crystal but often applied to non-cubic materials. It is not a bad approximation if for each hkl-reflection the L value is iterpreted as an average crystal dimension perpendicular to the reflecting plane.



Debye Scattering Equation

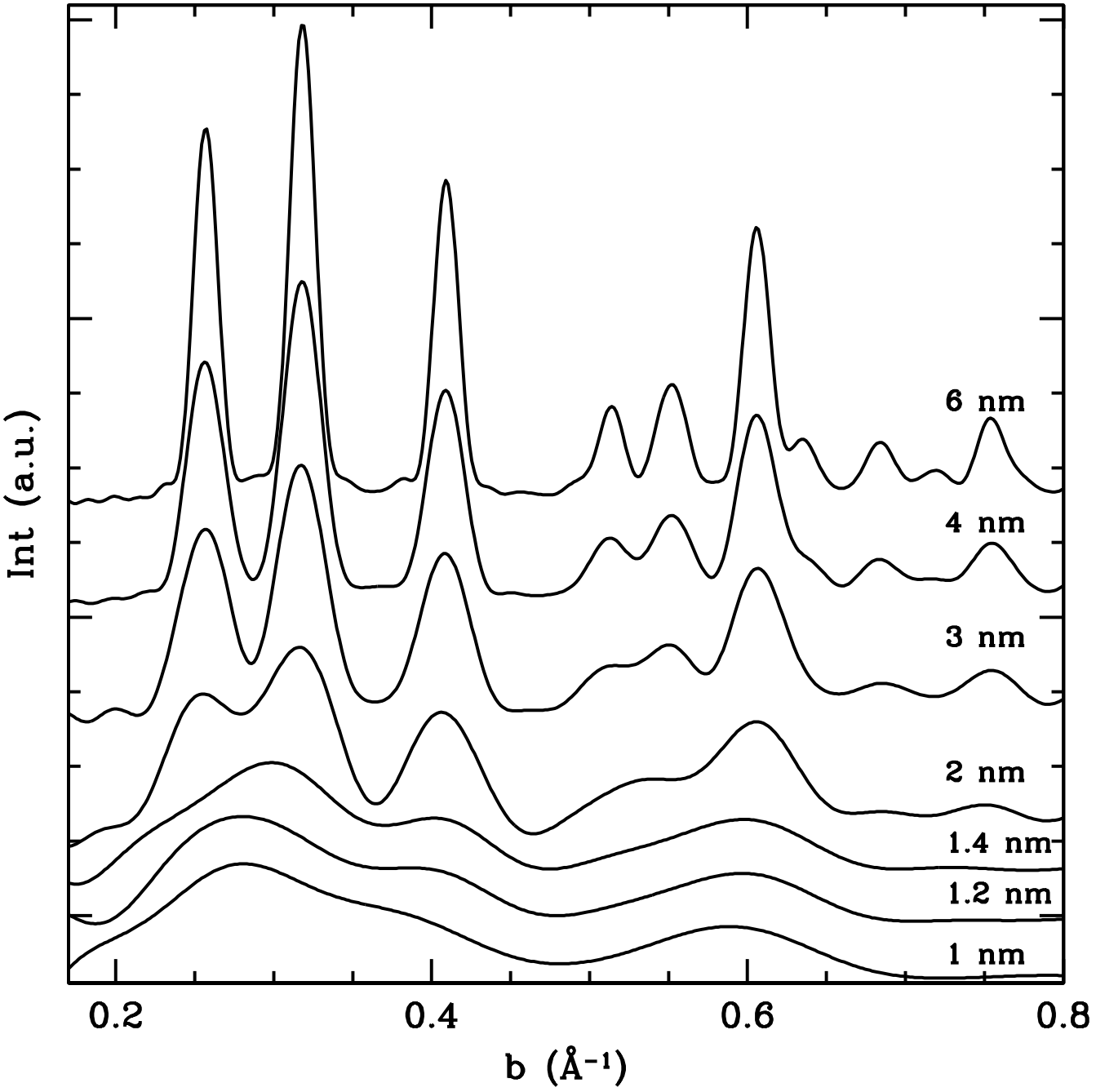
The intensity distribution spherical averaged over the reciprocal space is descibed by the Debye formula:

$$I_N(b) = \sum_{n,m \neq n}^{N} f_n f_m \frac{sin(2\pi b r_{nm})}{2\pi b r_{nm}} \tag{4}$$

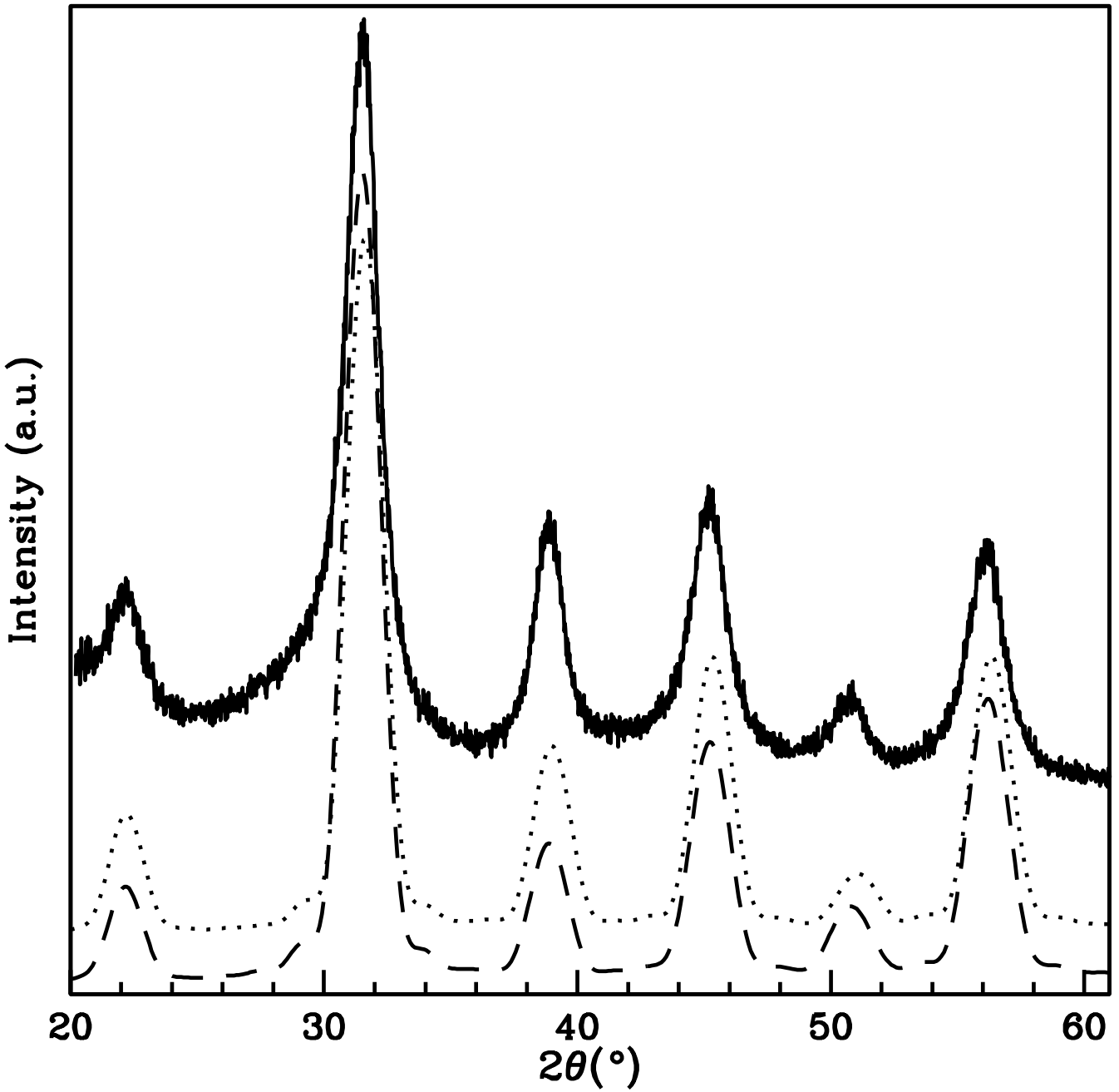
$b = \frac{1}{d} = \frac{2sin\theta}{\lambda}$
r_{nm} distance between atom n, m
f_n, f_m atomic scattering factors

- General equation valid for any form of matter in which there is a random orientation: gases, liquids, amorphous solids, and crystalline powders.
- No limitation on the number of different kinds of atoms in the sample.
- The number of terms increases proportional to the sixth order!

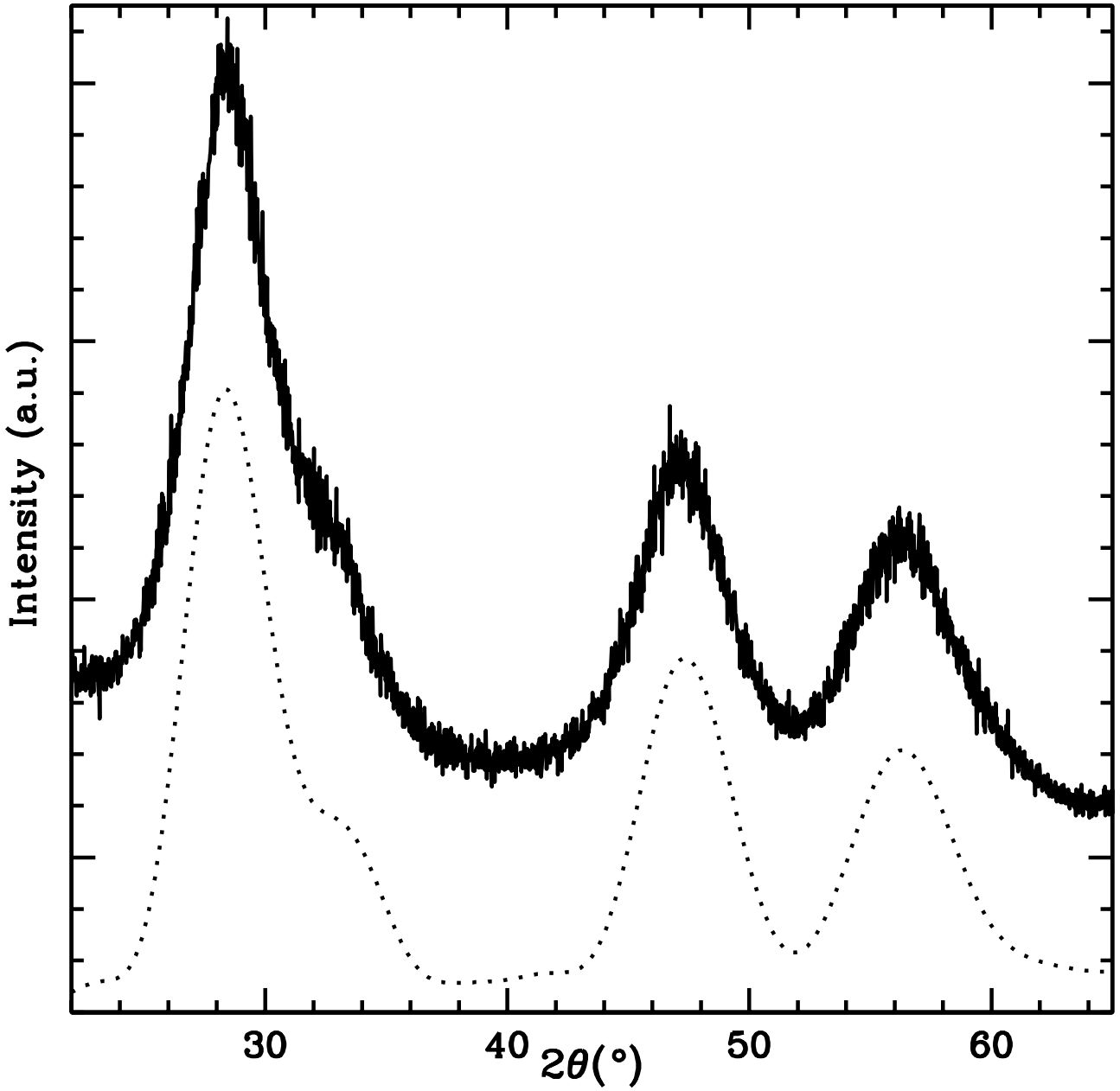
Ta_2O_5

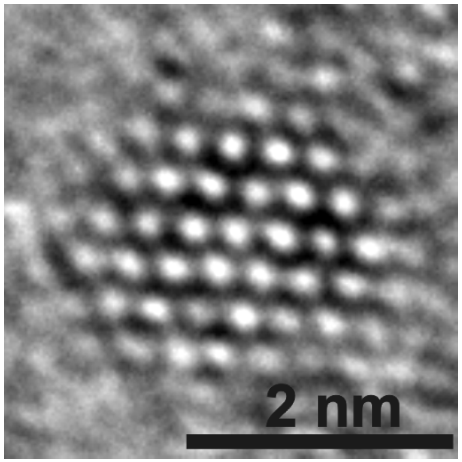


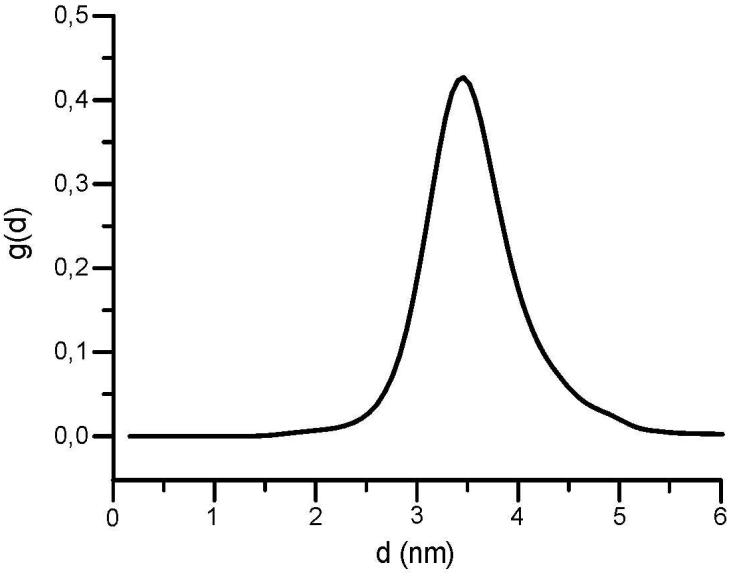
$BaTiO_3$ 6 nm



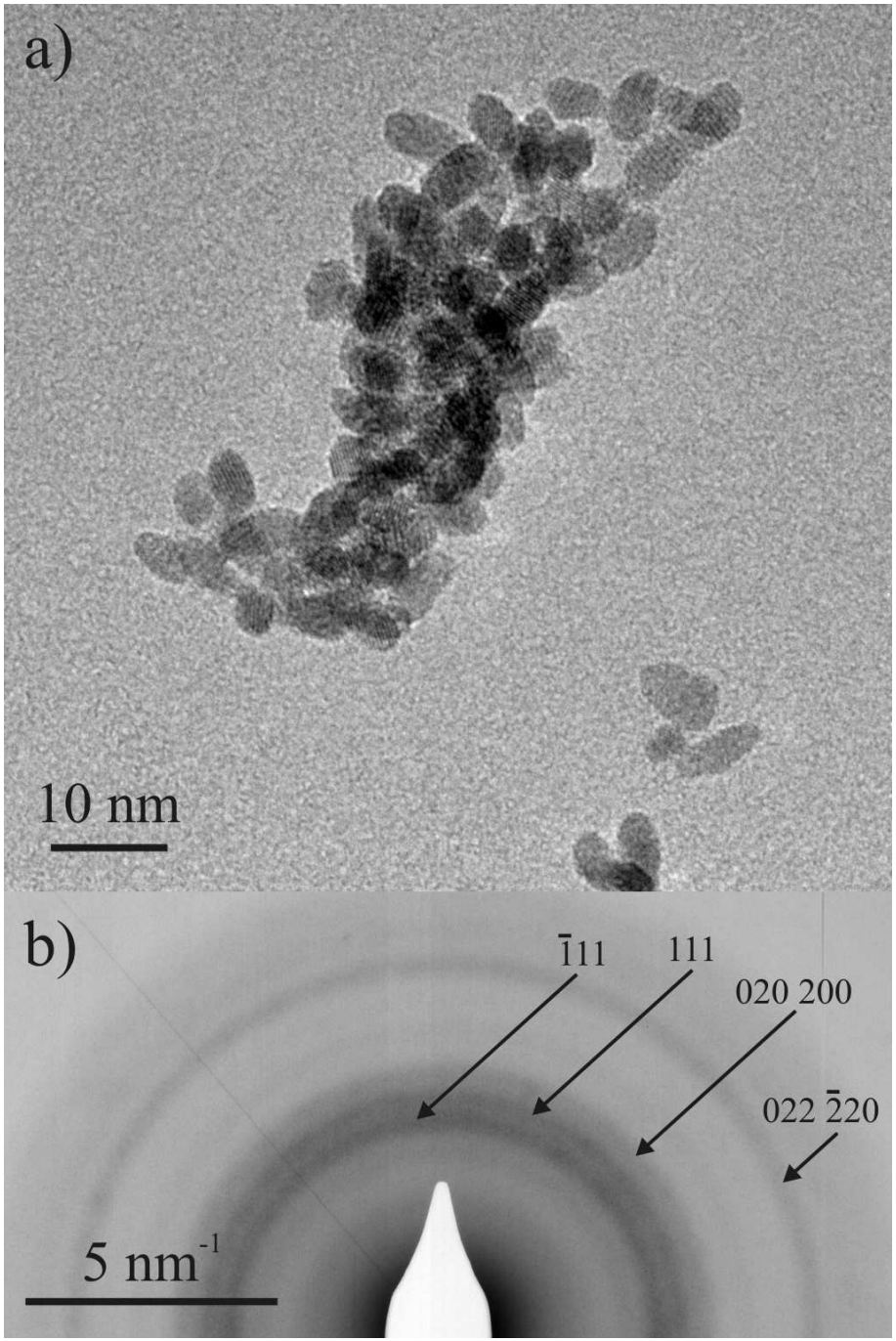
CeO_2 2.5 nm







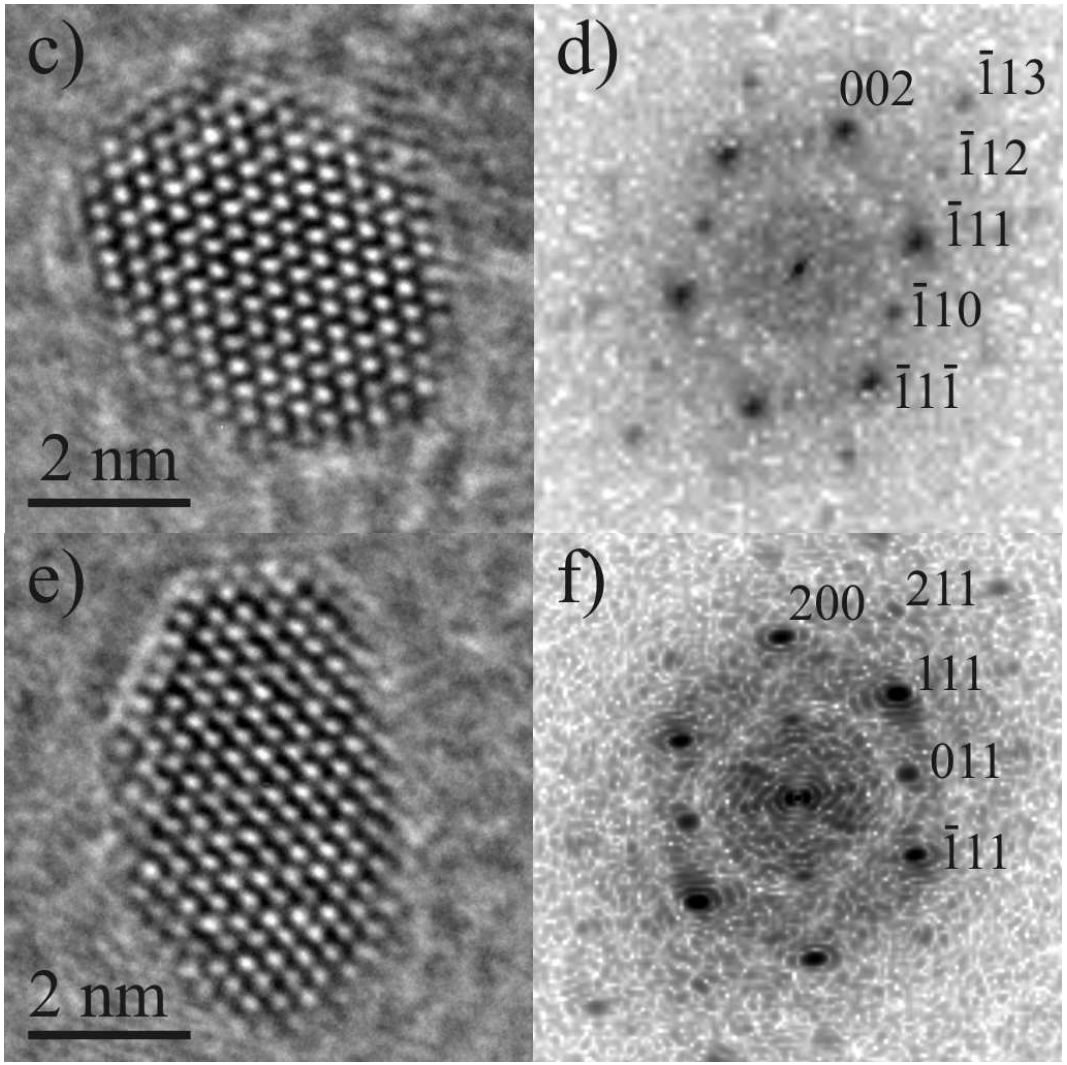
Final Example: HfO_2



Monoclinic Structure:

$a = 5.12$ Å $b = 5.18$ Å $c = 5.25$ Å

$\beta = 98°$



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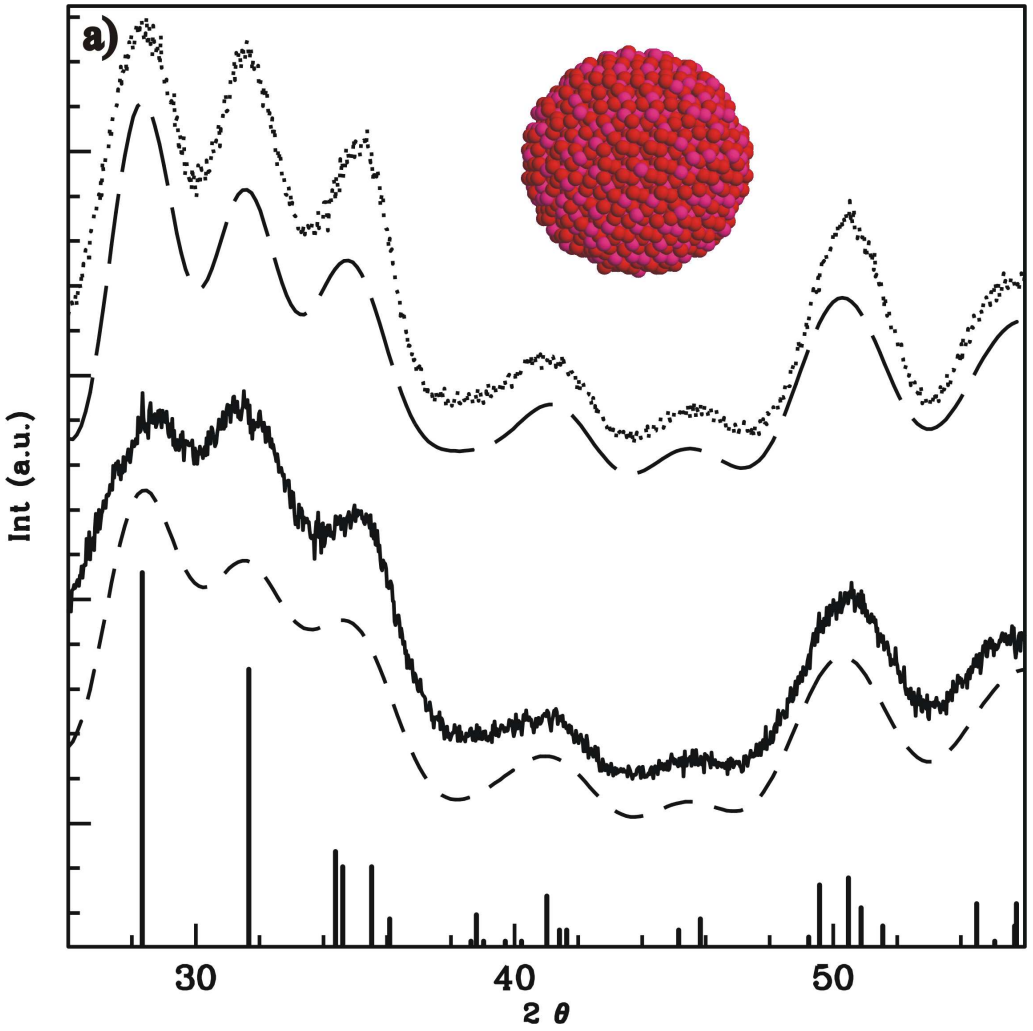

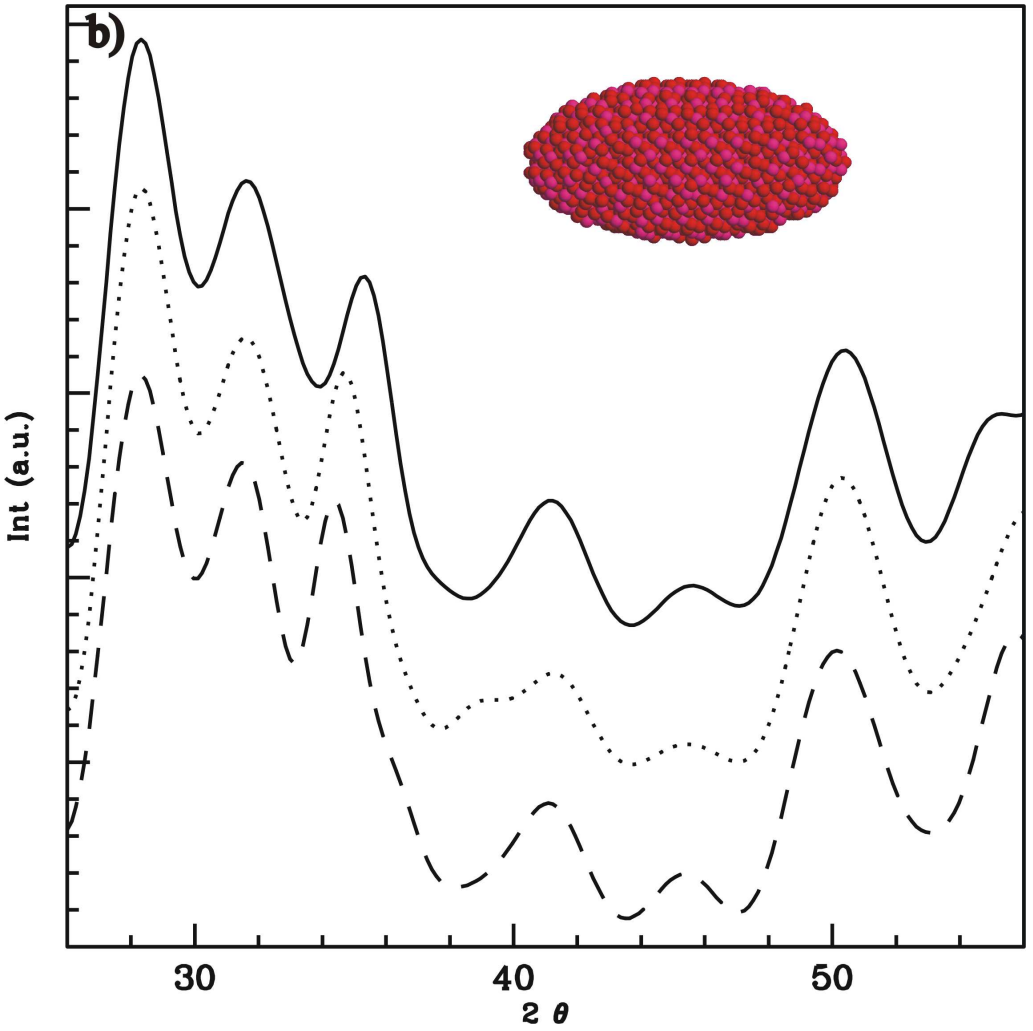

Conclusion

X-Ray diffraction associated to calculations is a powerfull tool to study the:

- Structure
- Crystallinity
- Particle size and size distribution
- Particle shape
- Homogeneity of the whole sample

It is the perfect tool to be associated with transmission electron microscopy study