Introduction to TEM and electron diffraction in the TEM

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Outline

- SEM/EPMA vs. TEM/STEM (AEM)
- CTEM modes of operation
- HTREM vs. Z-contrast imaging
- SAED vs. CBED
- Grain boundaries
- Nanocrystals
- Amorphous materials

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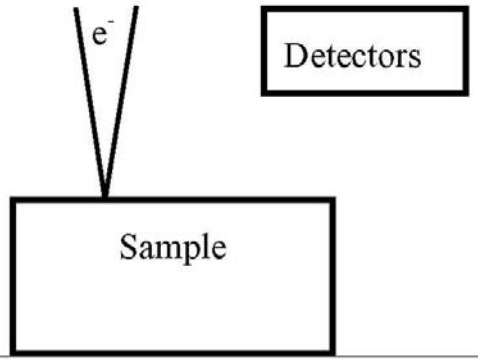
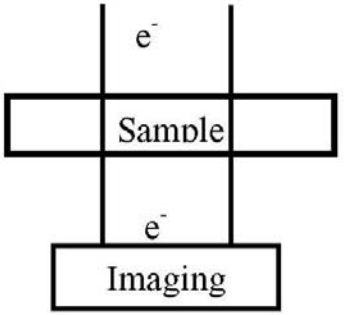
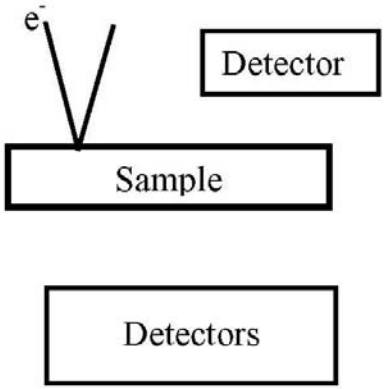
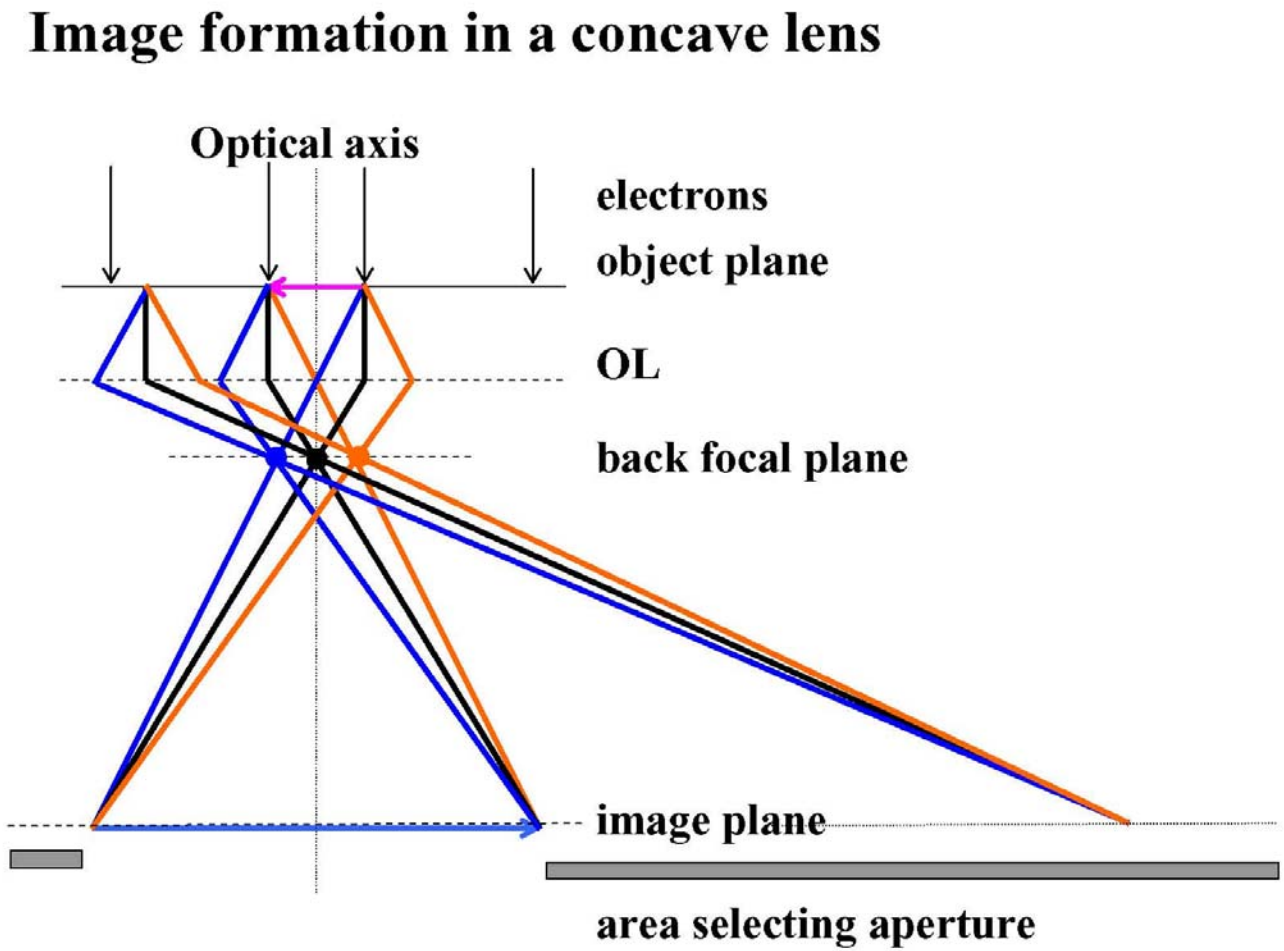
SEM	TEM	STEM (AEM)
Bulk sample	Thin sample	Thin sample
0.2-50 kV	80-1250 kV (typical 100-400 kV)	100-300 kV
Image formation is electronic (and NOT optical)	Image formation is based on optical principle (lenses after the sample)	Characterisctic imaging is electronic
Typical signals: SE, BE, AE, EBIC/EBIV, roentgen, EBSD	Typical signal: TE	Typical signal: TE, X-rays
Characteristic information: surface topography, average atomic number, potential, crystal orientation, composition	Characteristic information: grain structure, crystallography, defect structure	Characteristic information: average atomic number, composition, crystallography
		

Conventional TEM: Image formation of a concave lens



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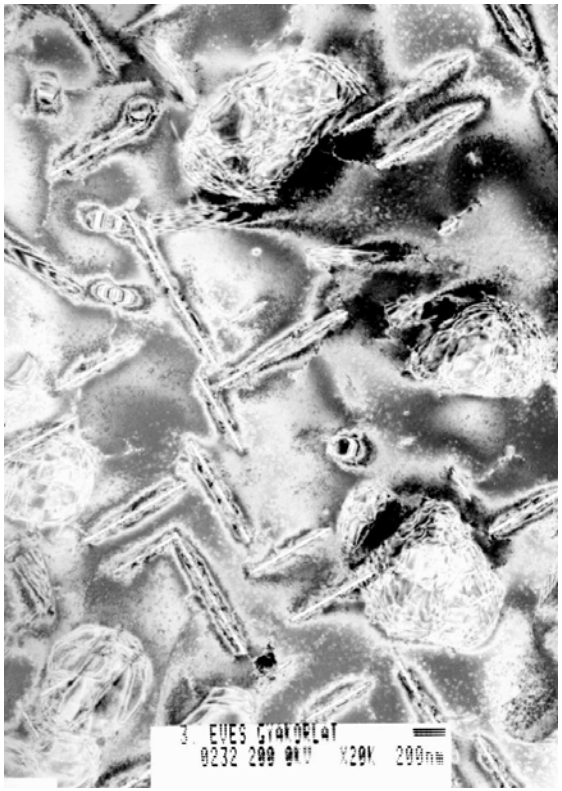
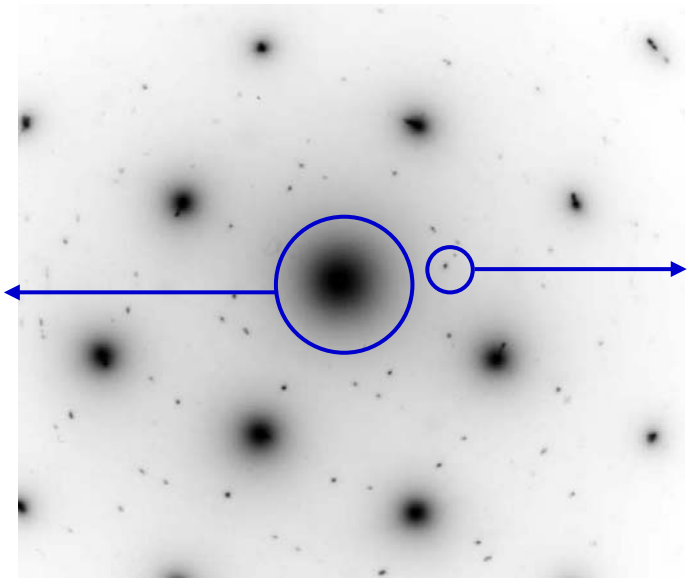
Conventional TEM: basic modes of operation: BF/DF, SAED



Bright-field image



Selected area electron diffraction

Dark-field image

BF / DF images are formed by amplitude-contrast (diffraction-contrast)

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Phase contrast

An ideal phase object imaged with perfect lenses would produce no contrast

$$\psi(x) = \psi_0 \cdot \exp\left(i\varphi(x)\right)$$

$$I = |\psi|^2 = |\psi_0|^2 = const$$

Obviously, it is the same for weak phase objects: no contrast to first order

$$\psi(x) = 1 + i\varphi(x)$$

Zernike phase-contrast for weak phase objects: shift the relative phase between diffracted beams and the central beam by 90°

$$\psi(x) = 1 + i \cdot i \cdot \varphi(x) = 1 - \varphi(x)$$

Then the intensity to first order is proportional to the phase shift with no loss of resolution.

$$I(x) = |\psi(x)|^2 = 1 - 2\varphi(x)$$

In OM the 90° phase shift is done by the Zernike phase plate. In HRTEM, we approximate this phase shift by the phase shift, caused by the imperfect microscope.

$$\psi_i(x,y) = 1 - i \cdot \sigma \cdot \Phi_p(-x,-y) \otimes F\left\{A(u,v) \cdot \exp\left(i \cdot \chi[u,v]\right)\right\}$$

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Phase shift, contrast, resolution

OM: $\chi=\pi/2$

Zernike phase plate

TEM: no phase plate $\Rightarrow$

we use the phase shift caused by the spherical aberration and the de-focus

Requirements:

- $\chi=\pm\pi/2$ in broad band
- No oscillation at small u

$\Rightarrow$ Minimum of parabola

$$\chi(u,v) = i \cdot 2\pi \cdot \left(\Delta f \cdot \lambda \cdot \frac{u^2+v^2}{2} + c_s \cdot \lambda^3 \cdot \left\{ \frac{u^2+v^2}{2} \right\}^2 \right)$$

$C_s>0 \Rightarrow$ Solution:

Scherzer de-focus ($\chi=-\pi/2$):

$$-\ \Delta f = \left(\frac{3}{2} \cdot C_s \cdot \lambda \right)^{1/2}$$

„Black atom" contrast

Resolution:

$$d_p = 0.66 \cdot C_s^{1/4} \cdot \lambda^{3/4}$$

Consequences:

- Can be fulfilled for any $C_s \neq 0$
- Size of contrast is not affected if it is fulfilled at small C_s
- Better resolution for lower C_s
- $\Rightarrow$ C_s-corrected microscope
- For $C_s<0$ it can be fulfilled with $\Delta f>0 \Rightarrow$ $\chi=\pi/2 \Rightarrow$ „Bright atom" contrast $\Rightarrow$ Visibility of light atoms

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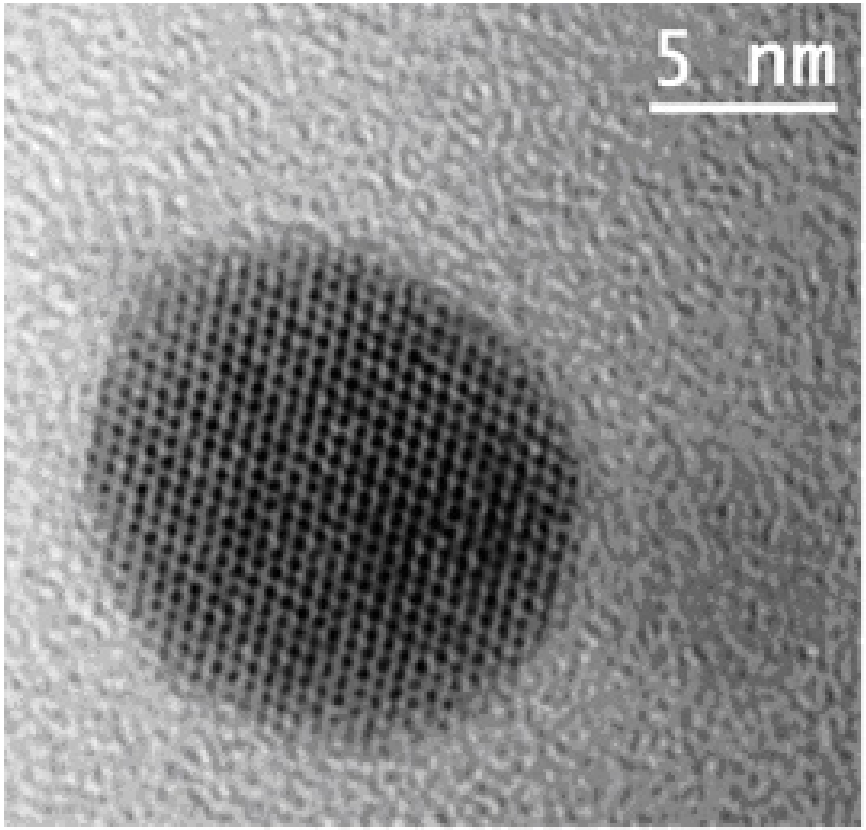
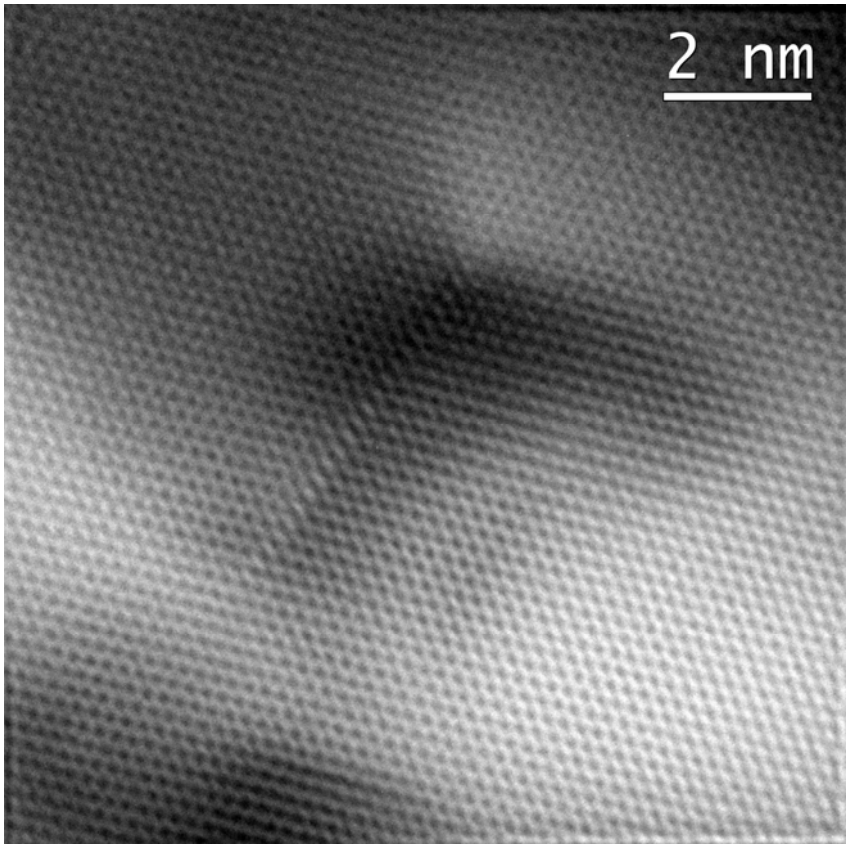
High resolution TEM (HRTEM): phase contrast Example



Magnetite nano-crystal on amorphous Carbon supporting film

$C_s>0$



Stacking fault in Ag

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Interpretation of phase contrast HRTEM images

Interpretation is based on ***assumptions***

- The sample is so thin that it is an ideal weak phase object
- The image was recorded at Scherzer focus. In that case the atomic columns are ***dark.***
- B/W contrast periodically reverses with both thickness and de-focus.

Interpretation is ***not intuitive*** in general case. A structure is generally assumed a priori and the images in a focal and thickness bi-series are calculated and ***compared*** to the experimental ones to prove that the assumed structure is in accordance with the measured one. If yes, it is declared to be the measured structure.

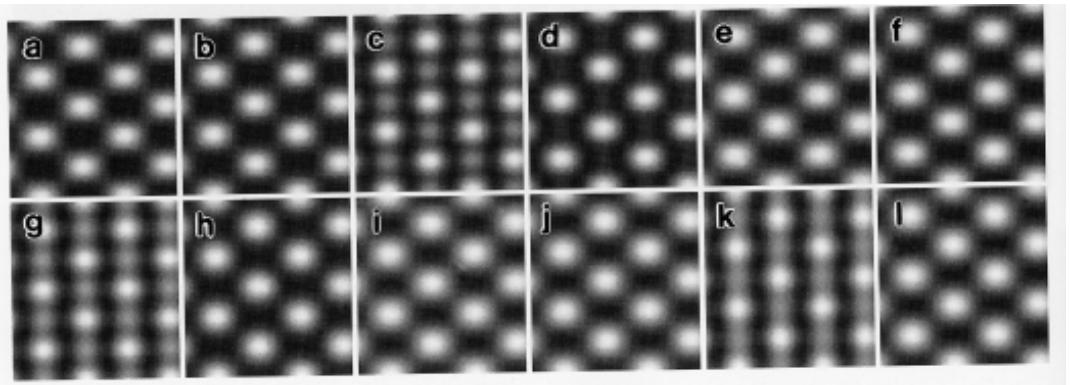

Fig. 2.6. Defocus dependency of lattice images of a Si crystal with incidence [0$\bar{1}$1]. Use of a 200 kV EM and a thickness of 6 nm are assumed. The defocus changes from −20 nm (overfocus) to 90 nm (underfocus) in steps of 10 nm

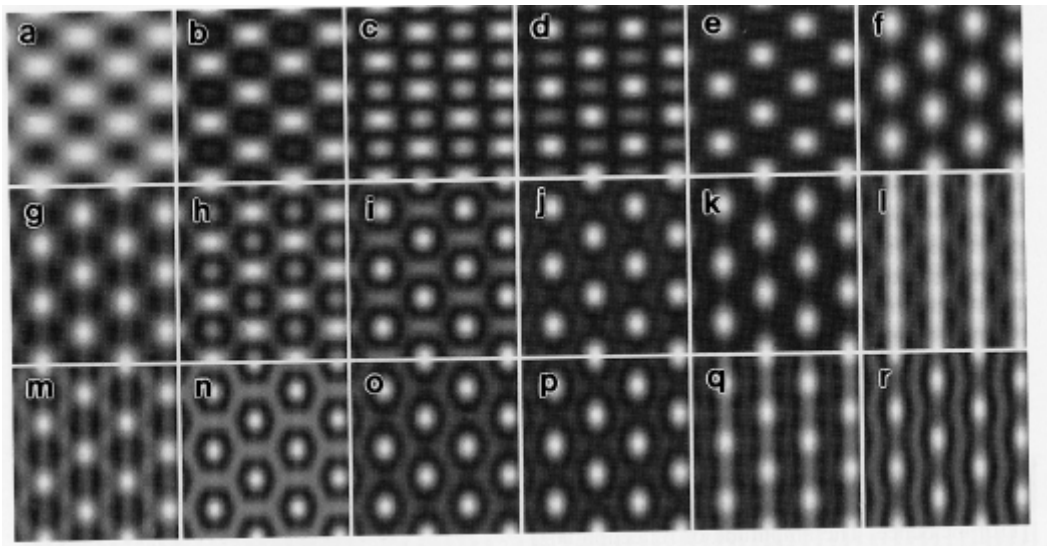

Fig. 2.5. Thickness dependency of lattice images of a Si crystal with incidence [0$\bar{1}$1]. Use of a 200 kV EM and a defocus value of 65 nm are assumed. The thickness changes from **a** 1 nm to **r** 86 nm in steps of 5 nm

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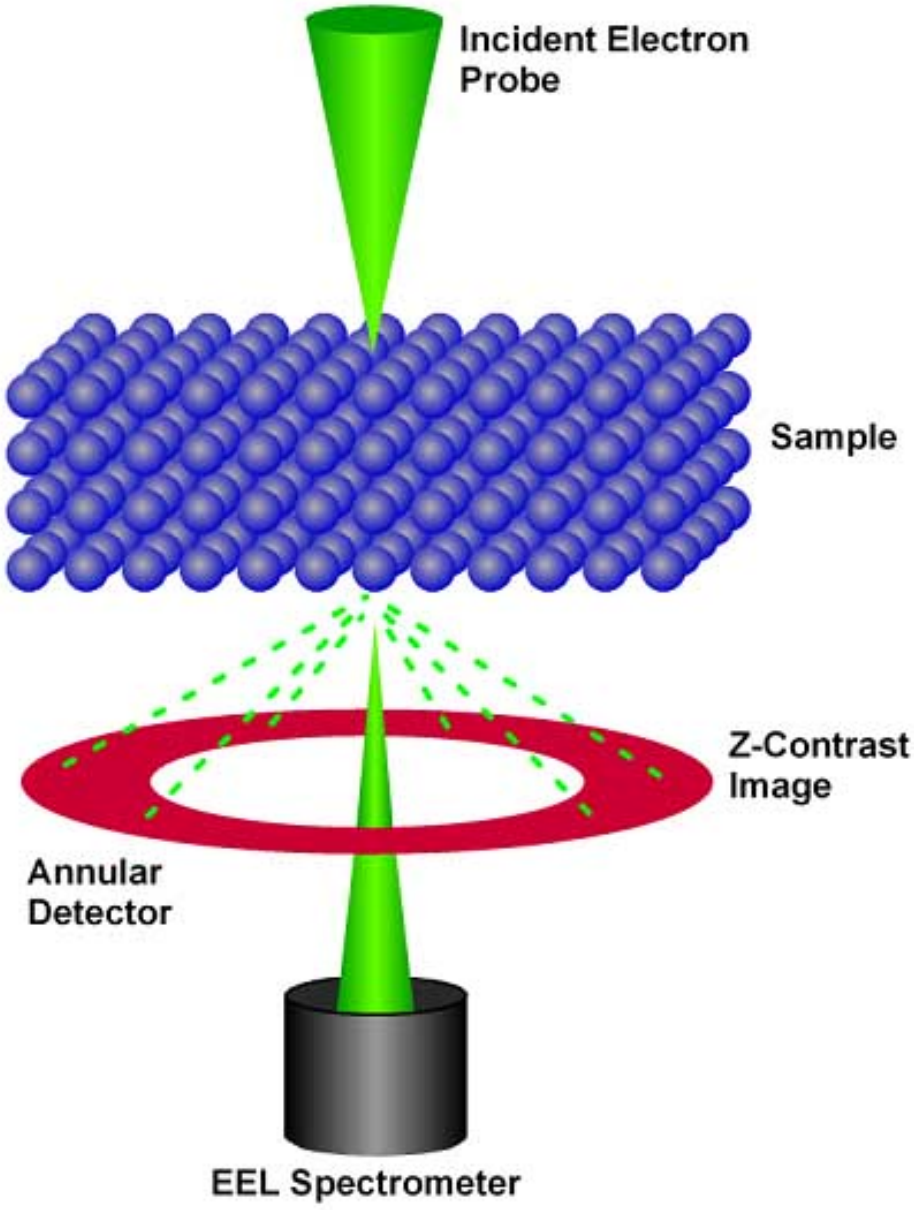

(D)STEM and Z-contrast imaging

Image is dominated by thermal diffuse scattering (TDS) ⇒ monotonic function of atomic number (Z).

No contrast reversal with sample thickness.

No contrast reversal with defocus.

⇒ Intuitive interpretation.

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STEM Z-contrast imaging: example

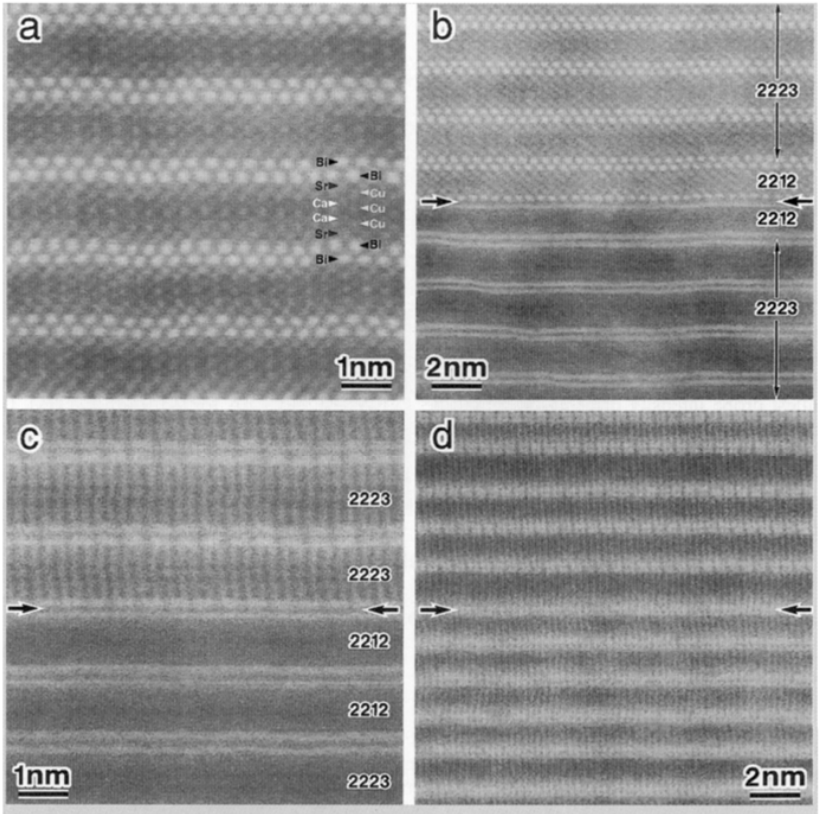

Fig.3. Z-contrast images of the BSCCO semiconductor: (a) the Bi-2223 phase in the [110] projection, (b, c) (001) twist boundaries at arbitrary misorientations and (d) a (001) twist boundary with a 90° twist angle. Positions of the grain boundaries are indicated by arrows.

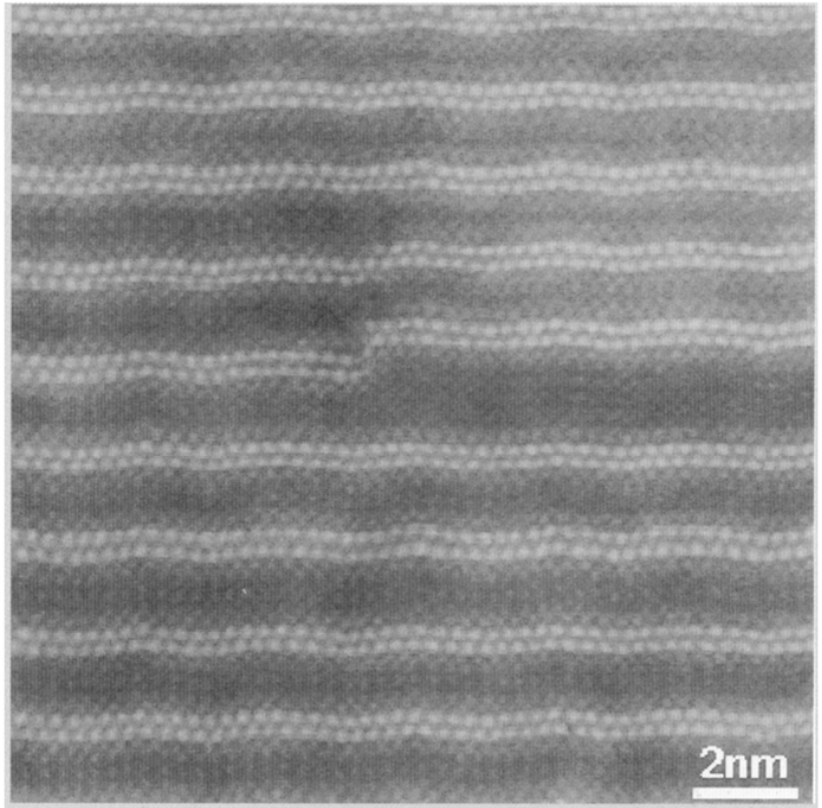

Fig.4. Z-contrast image of the BSCCO semiconductor in [110] projection. Departures from the Bi-2223 phase can be seen in the vicinity of the defect.

Incoherent ⇒ Unambiguous contrast ⇒ ***Intuitive interpretation*** ⇒ Determination of unexpected structures

Determining factor: beam diameter must be comparable to the atomic distances

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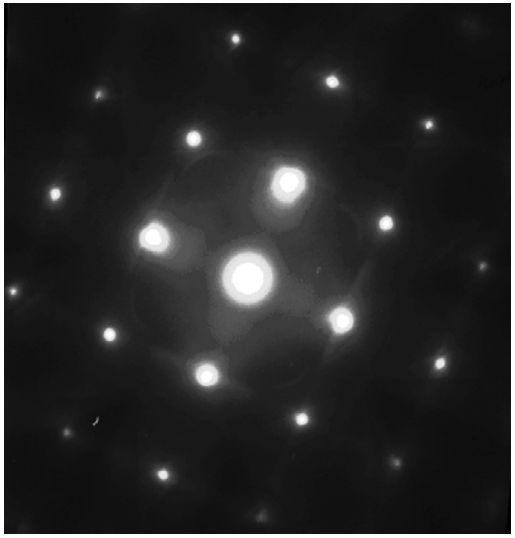
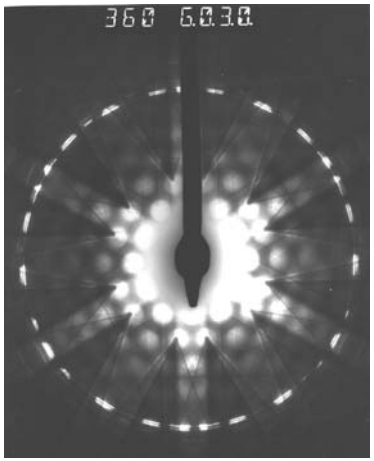
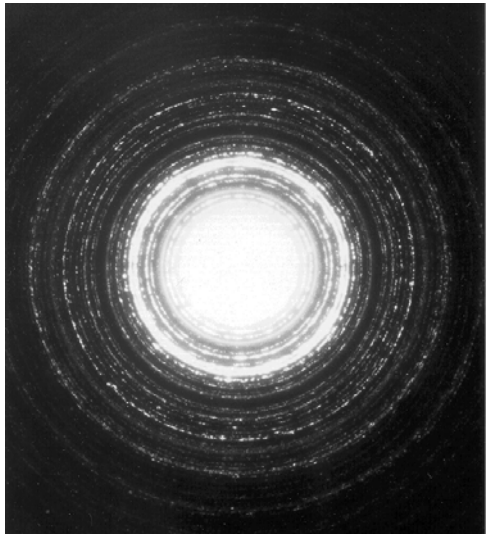
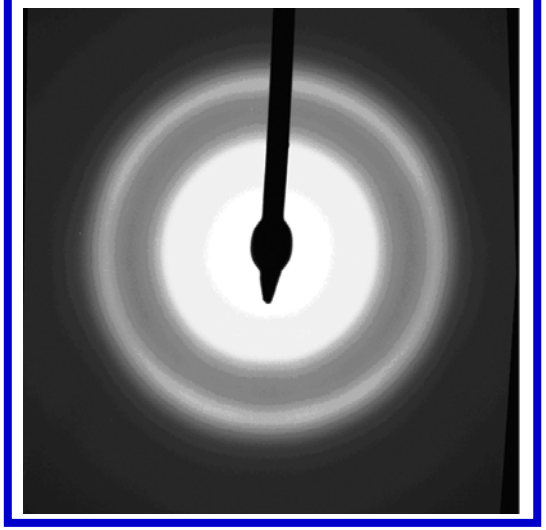
Basic types of ED patterns in the TEM

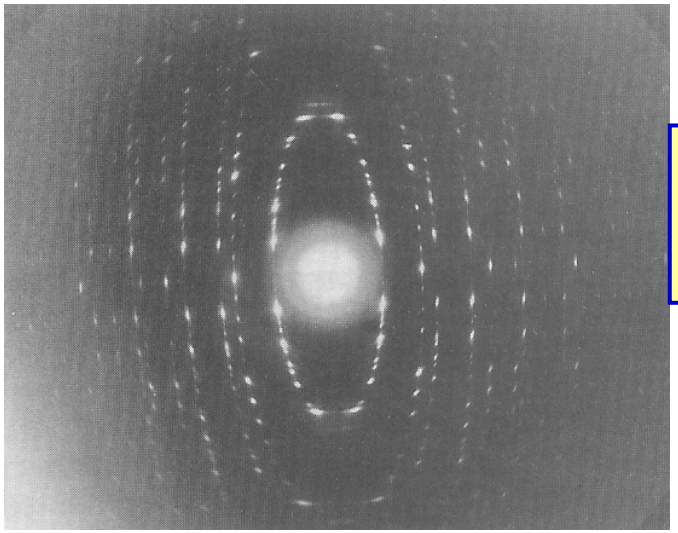


Convergent beam









Randomly oriented nanocrystals

Fiber textured set of nanocrystals, seen from the texture axis

Both produce concentric rings

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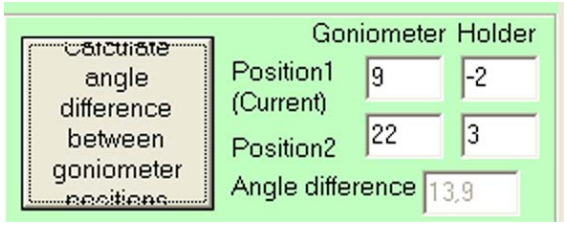
Indexing **single crystals** from a tilt series

24 Symmetry equivalent solutions

1. Angle [-1 -5 8] & [0 -1 1] = 14,3°

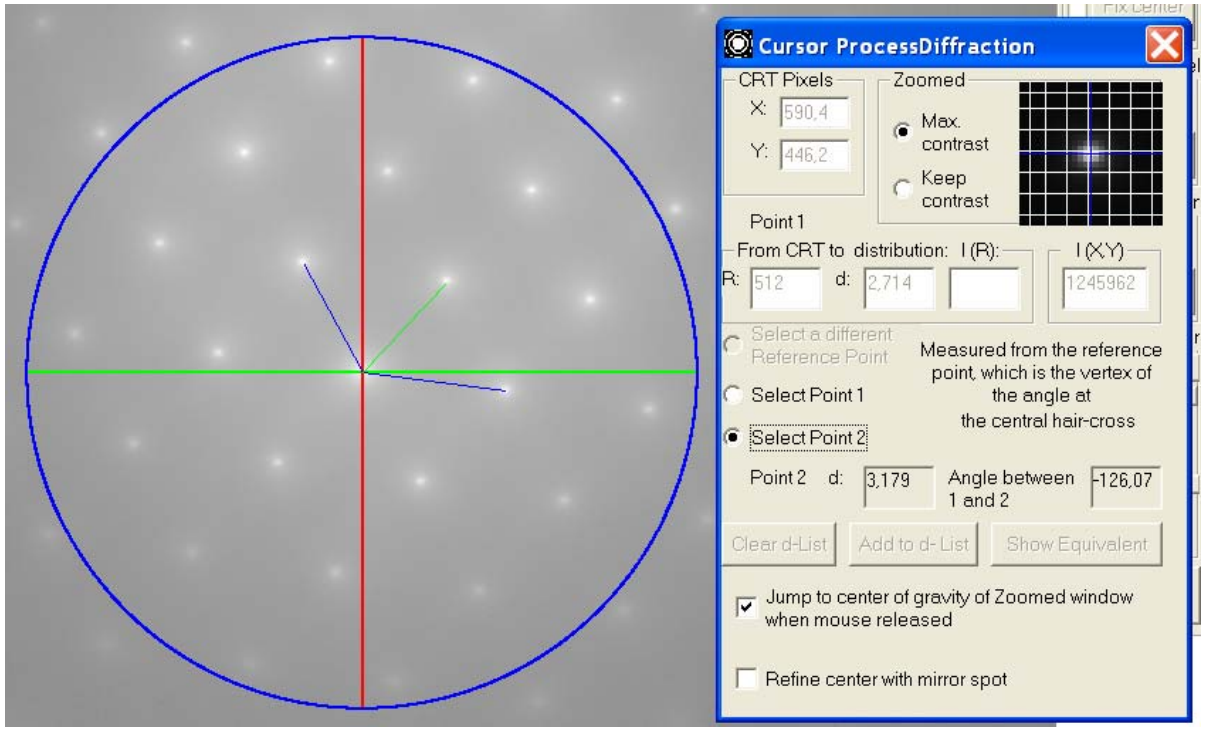
...

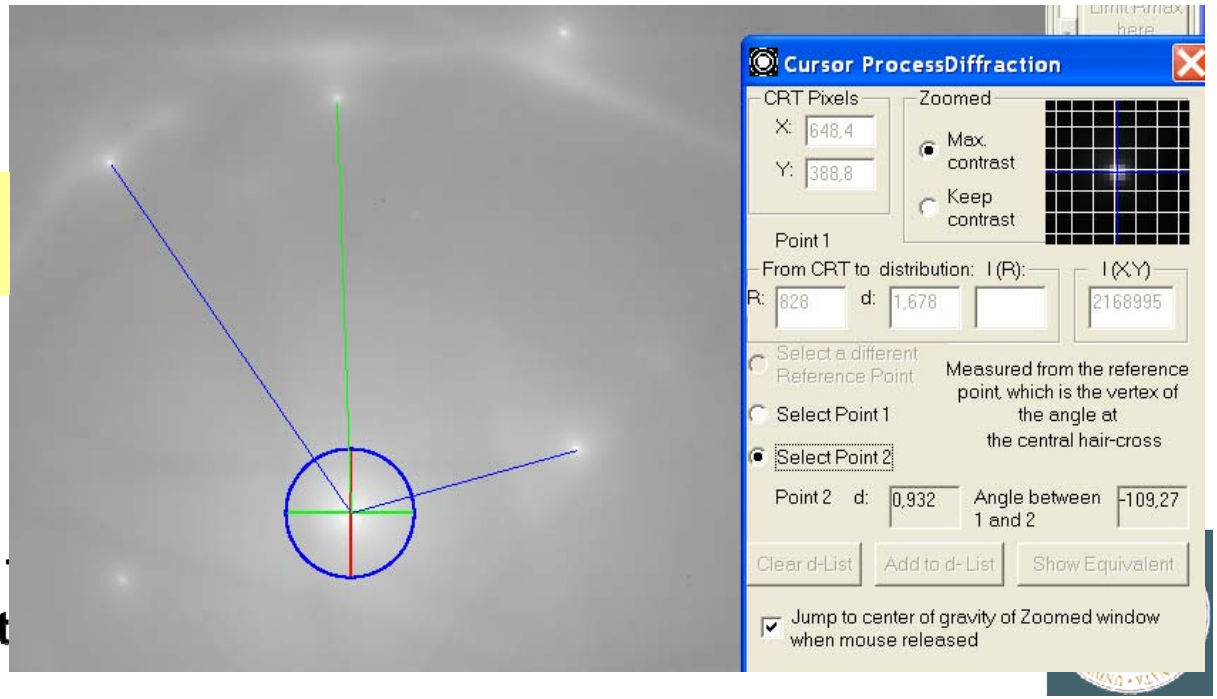


Exp. angle between GoniPos : 13.9°

Three zones along an angular triangle can be processed together.

Phase identification orientation determination





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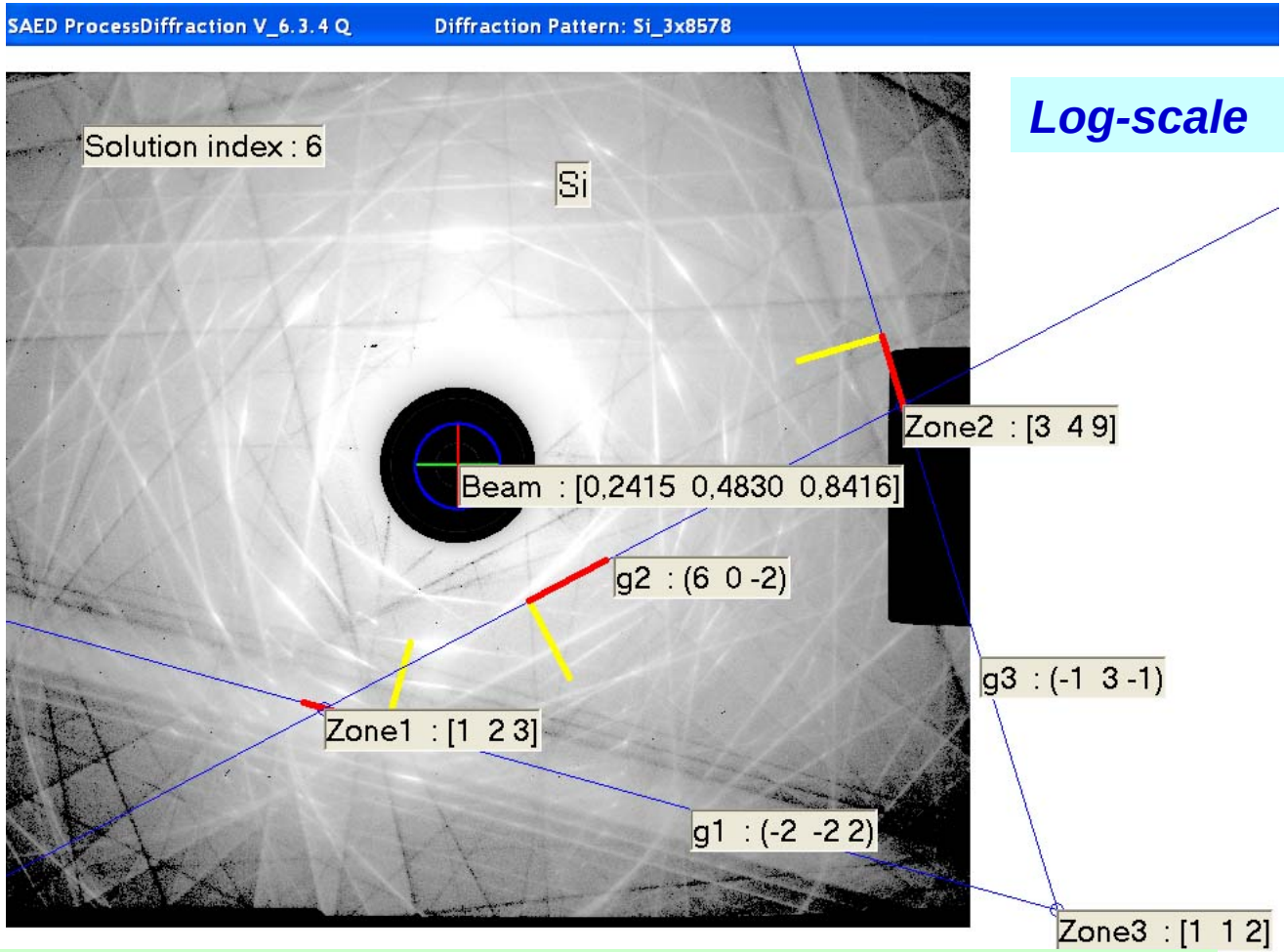
Orientation of **single crystals** from CBED

- Non-linear BKG correction for visibility
- Indexed triangle
  - d-value
  - plane-angle
  - zone-angle
  - handedness
- Indexed zone can be slightly outside of the measured range
- Beam position (PC)
- Transformation to Photo coordinate system



One, out of the 24 symmetry equivalent solutions is shown

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Orientation / Misorientation → $\underline{\underline{M}} = \underline{\underline{O}}_2 * \underline{\underline{O}}_1^{-1}$

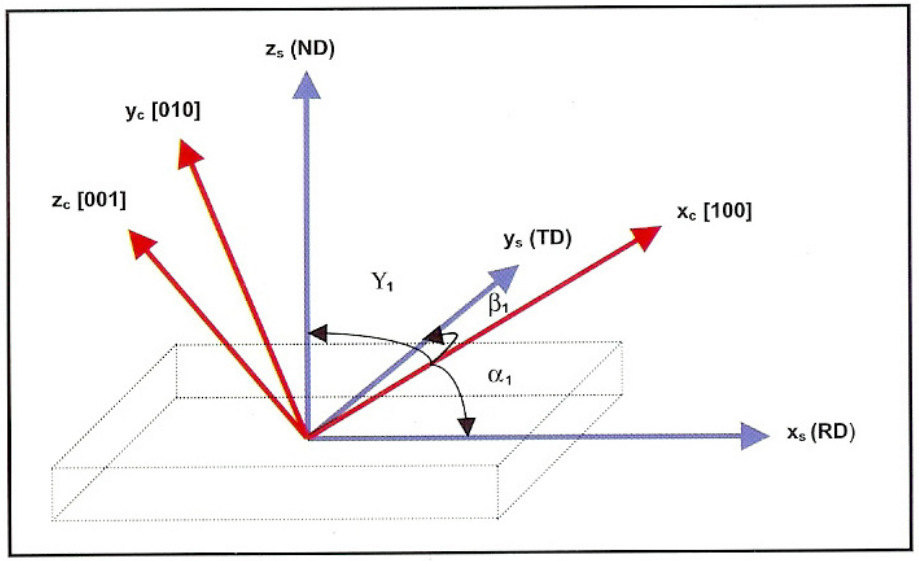


Figure 36: Relationship between crystal and sample coordinate systems. α_1, β_1 and γ_1 are the angles between the crystal direction [100] and RD, TD and ND respectively.

$$O = \begin{pmatrix} \cos\alpha_1 & \cos\beta_1 & \cos\gamma_1 \\ \cos\alpha_2 & \cos\beta_2 & \cos\gamma_2 \\ \cos\alpha_3 & \cos\beta_3 & \cos\gamma_3 \end{pmatrix}$$

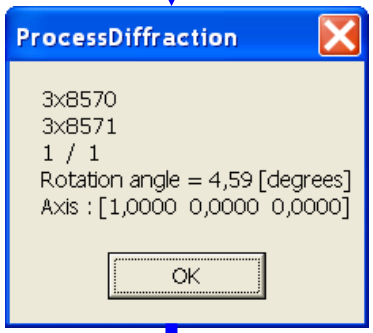
The orientation can also be related to the photo coordinate system.

Calculate symmetry related equivalent solutions from stored Orientation matrices.

Disorientation is picked.

Error reduction by using *redundant* data in misorientation matrix:

- **Diagonal** elements
- **Off-diagonal** elements



Geometrical characterization of **grain boundaries**

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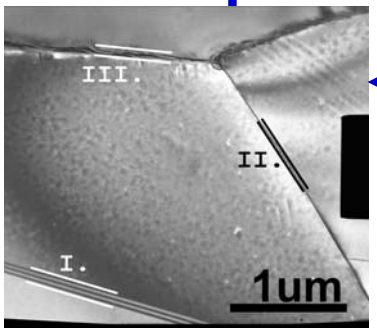
Measurement of the orientation of the GB plane: **Advantage over EBSD**

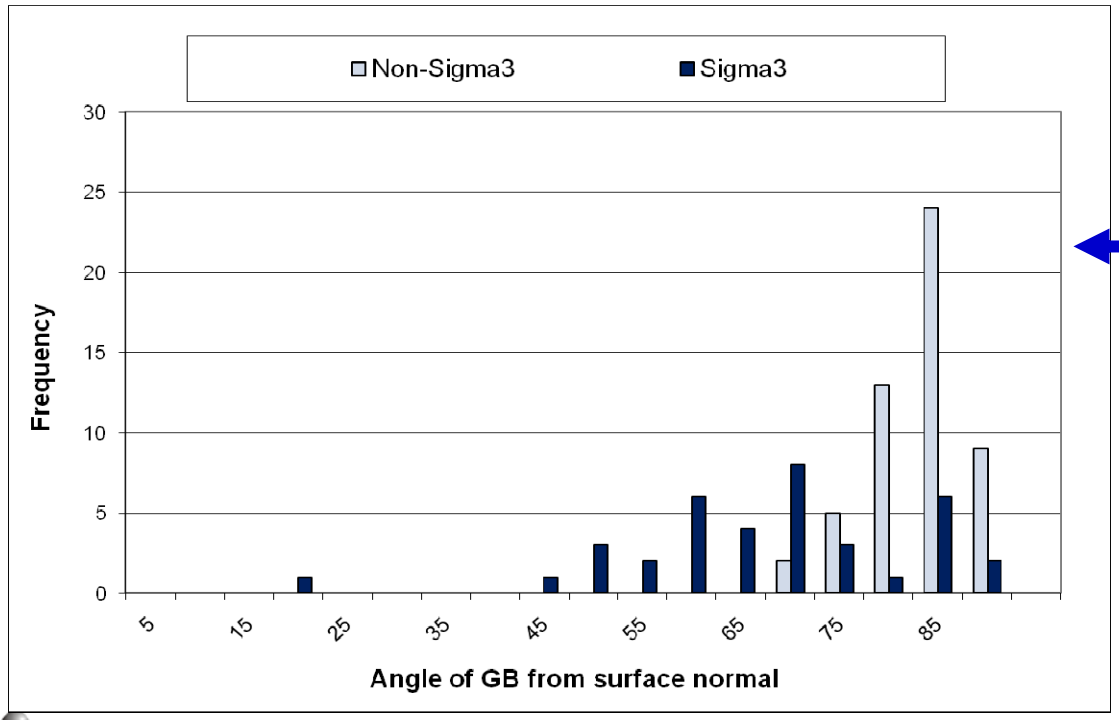


Example of projections of different GB planes.

Width of projection is measured.

Projections are measured at two distinct goniometer settings.

Local thickness is determined from two-beam CBED.



Example: GB characterization by ***combining*** diffraction and imaging (=misorientation and plane orientation)

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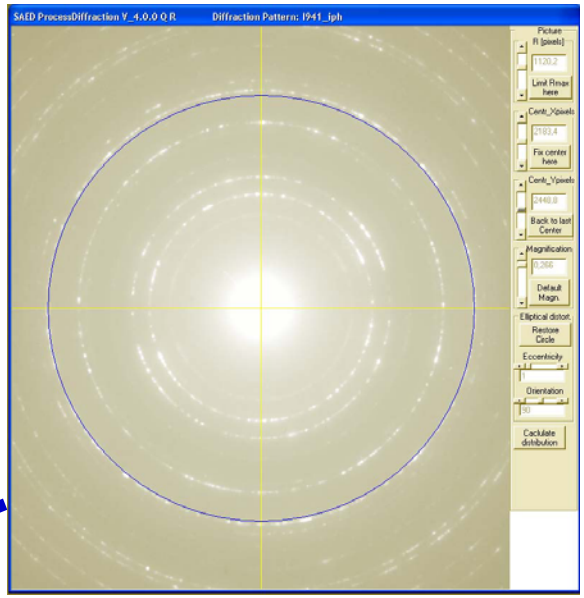
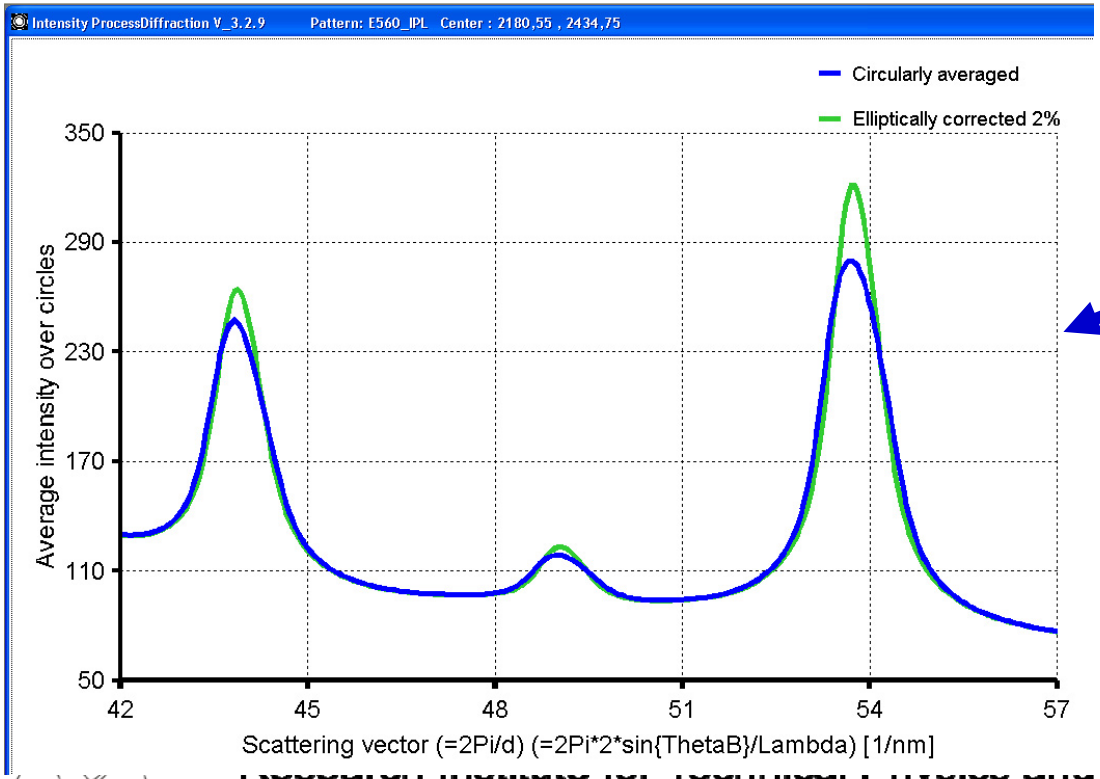
Identification of phases in ***nanocrystalline*** thin films (SAED …)

- Conversion of 2D patterns into 1D distributions
- Correction for elliptical distortion
- Extension of dynamic range





- Units of x-axis (pixel, Q, 2θ),
- peak search
- Average above average (Beam-stop, etc.)
- Background, net, …

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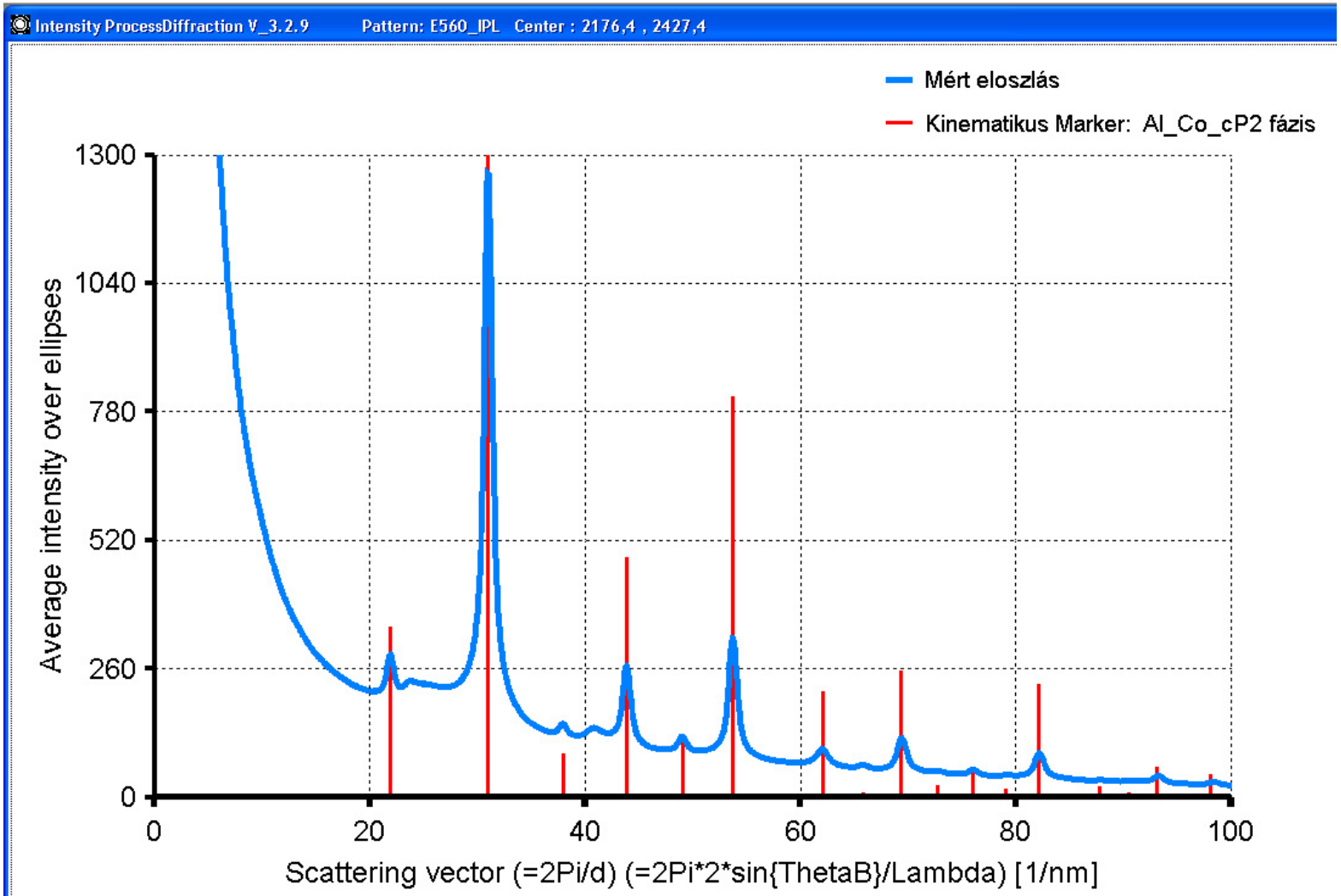
Qualitative phase analysis (identification of phases): Visual comparison to ***Markers***



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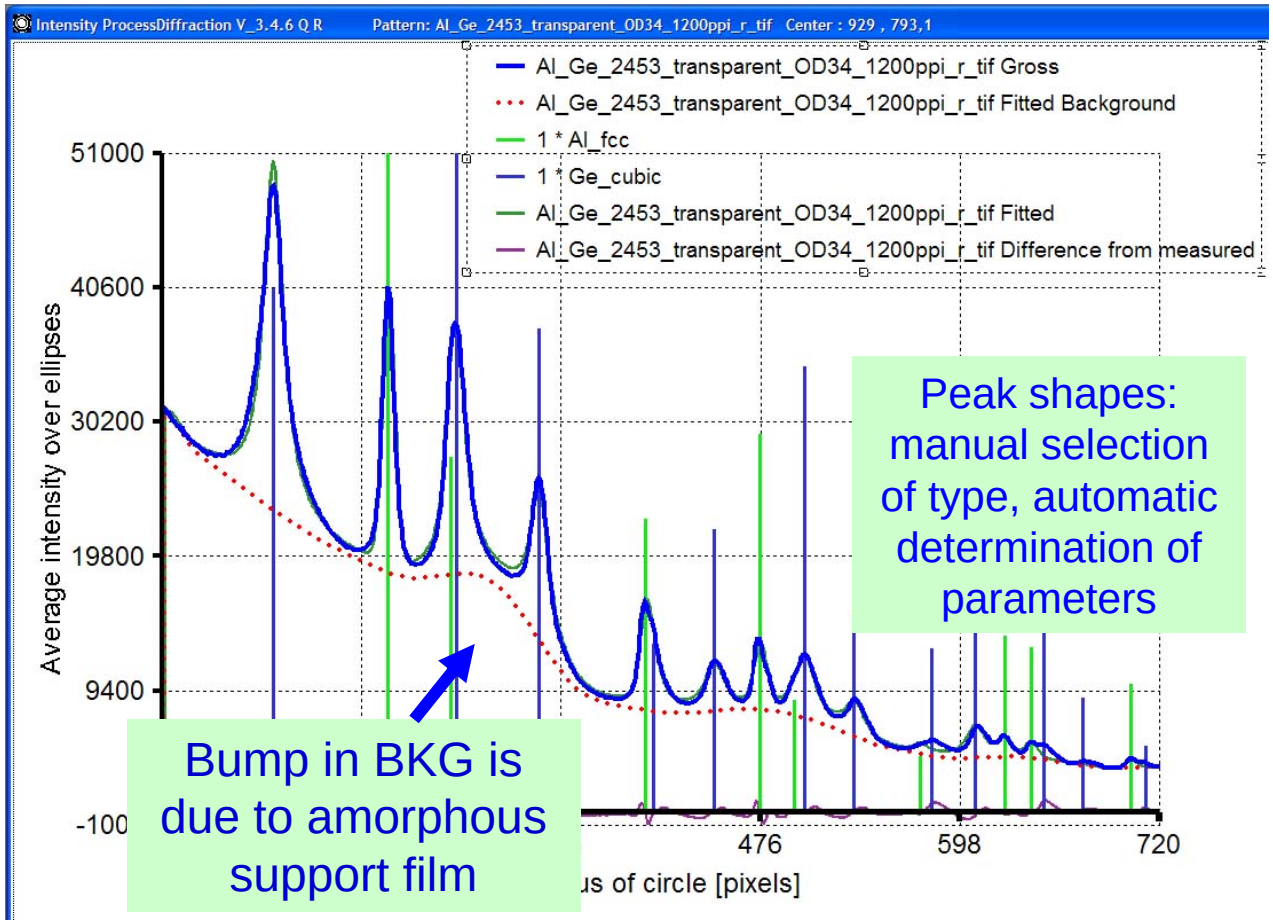
Modeling / fitting the measured intensity distribution

- Background
  - Normal, log-Normal
  - Polynomial, Spline
- Peak shapes
  - Gaussian, Lorentzian
  - Pseudo-Voigt
- Global minimum
  - Downhill SIMPLEX
  - Manual control
  - ⇒ ***parameters*** (camera length, peak-width, Gaussian-fraction, …)
- **Example**: Al + Ge: SAED on C-film
  - Large crystal Al: Gaussian
  - Small crystal Ge: Lorentzian



Different peak-shapes are observed for the two phases of the same sample

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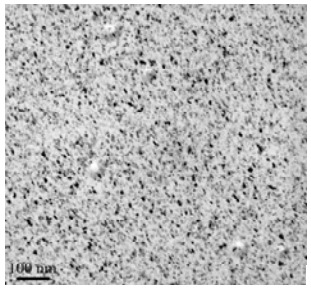
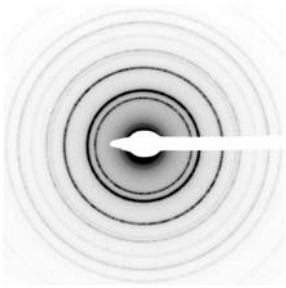
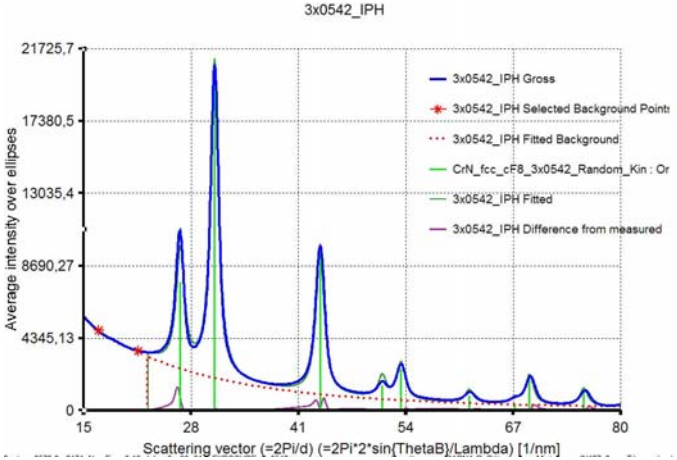
Example: Measuring change in lattice parameter

Camera length can be reproduced with 0.3% precision with our ***experimental protocol***. Absolute changes in lattice parameter can only be determined if they significantly exceed this level. Smaller relative change can be determined in comparison to an other (unchanged) phase of the same sample.

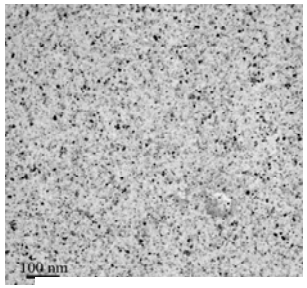


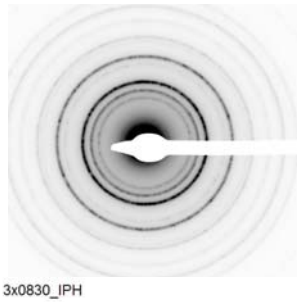


3x0542_IPH

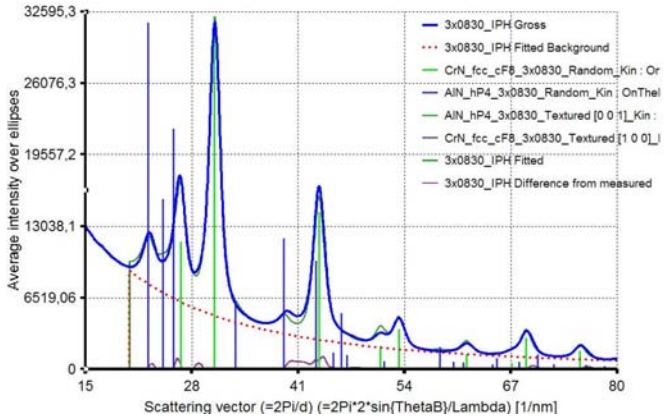


fcc-CrN with 70% AlN dissolved (**a=4.14 ⇒ 4.07Å**).





3x0830_IPH



hP4-AlN with dissolved 25% fcc-CrN (**a=3.11 ⇒ 3.20Å; c=4.98 ⇒ 5.13Å**).

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Example: phase and texture analysis for very small grains ⇒ Kinematic

Simultaneously evaporated Cu and Ag.

EDS: 34 Vol % Ag

66 Vol % Cu

Measured relative amount of the phases:

Ag_fcc_Random : 3.9 Vol %

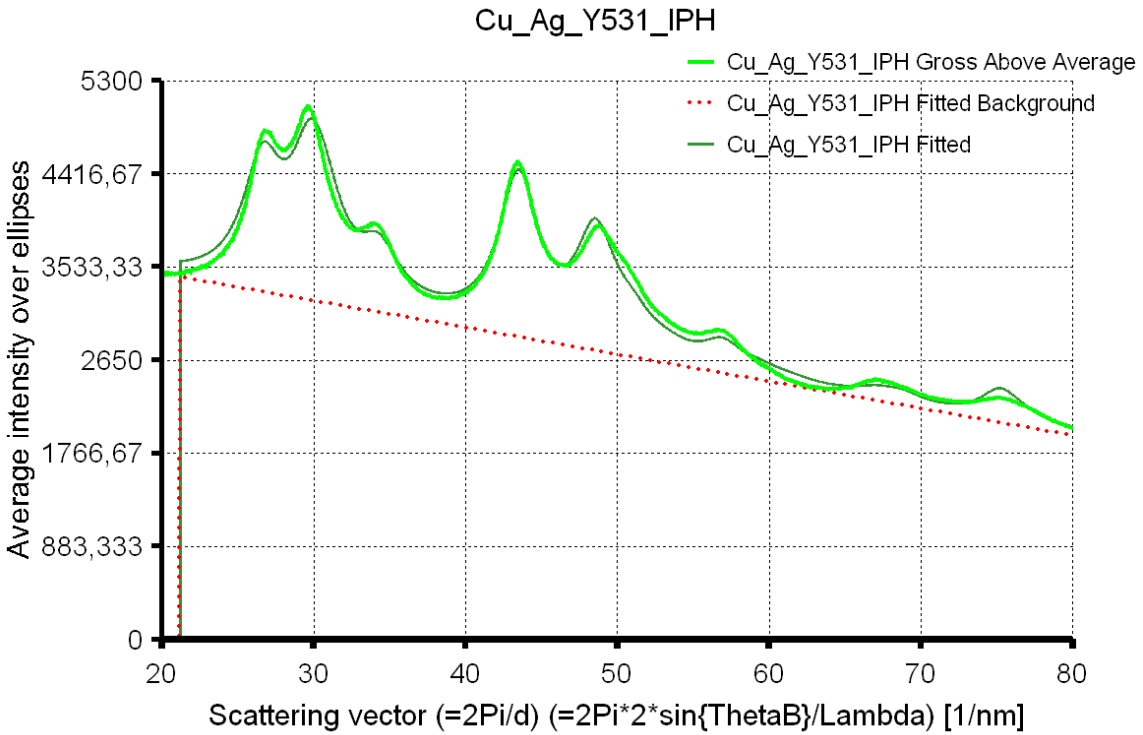
Ag_fcc_**Textured** [1 1 1]: 28.7 Vol %

Total Ag: 32.6 Vol %

Cu_fcc_Random : 10.6 Vol %

Cu_fcc_**Textured** [1 1 1] : 56.7 Vol %

Total Cu: 67.3 Vol %



Agreement with EDS is good in spite of the presence of high background and broad peaks.

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Determination of the Short Range Order in **amorphous** samples

I(Q)	⇒	Q*I(Q)	⇒	G(r)	⇒	g(r) [,RDF(r), ρ(r), …]
Measured		Normalized		Fourier-transformed		

Assumptions:

- Homogeneous, izotropic material
- Elastic scattering only
- Single (kinematic) scattering
- Composition of the sample is known
- Illumination is parallel

Empirical corrections are needed because of:

- Inelastic scattering
- Multiple scattering
- Black level from stray radiation, noise, etc.

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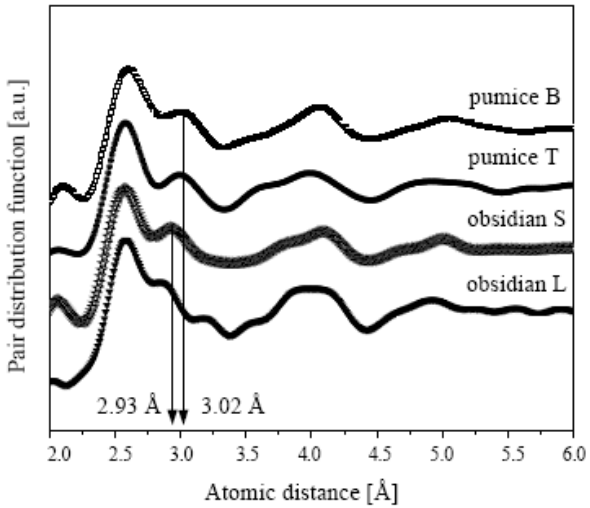
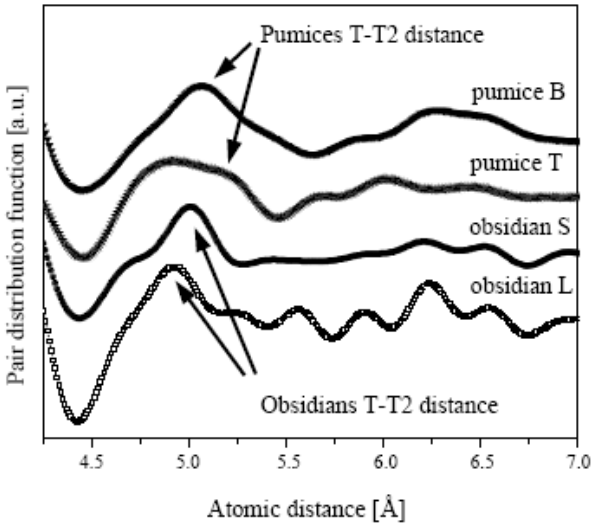
Determination of the SRO of amorphous samples: examples

Amorphous SiO_2 minerals

- obsidian
- pumice



- Building block: SiO_4 tetrahedron
- The ordering of the SiO_4 tetrahedra is different in the two amorphous minerals
- Structure in both amorphous materials already resembles the SRO in the respective crystalline forms



V Kovács Kis, I Dódony, JL Lábár, Eur. J. Miner. 18. 745-752. (2006)

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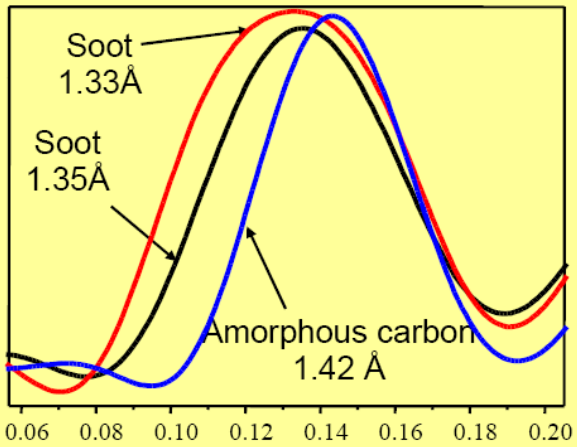
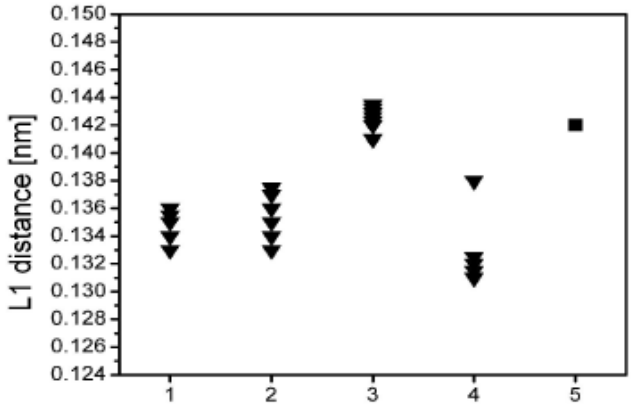
Determination of the SRO of amorphous samples: examples

Structure of soot from aerosols



V Kovács Kis, M Pósfai, JL Lábár
Atmospheric Environment
40 (2006) 5533–5542

First nearest neighbour atomic distances in carbonaceous materials



1 – soot 1 from Central Europe
2 – soot 2 from South Africa
3 – magnetron sputtered amorphous carbon (H/C = 0)
4 – kerogen with 95 at% total carbon (H/C = 0.61)
5 – graphite (not measured)

Conclusions:

1. Atomic distances are similar in soot both from Central European Troposphere and a savanna fire in South Africa
2. First peaks in PDF results from the superposition of C-C and C-H distances
3. H/C ratio is lower in soot than in kerogen (0.61)

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Thank you for your attention

Further reading:

- JL Lábár, *Ultramicroscopy*, **103** (2005) 237-249
- JL Lábár, *Microsc. Microanal*. **14** (2008) 287-295
- JL Lábár, *Microsc. Microanal*. **15** (2009) 20-29
- JL Lábár et al., *Microsc. Microanal*. **18** (2012) 406-420

The ProcessDiffraction program can be downloaded free from
http://www.mfa.kfki.hu/~labar/ProcDif.htm

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