Transmission Electron Microscopy

Part IIIb: Kinematic Electron Diffraction
(convergent beams + amorphous materials)

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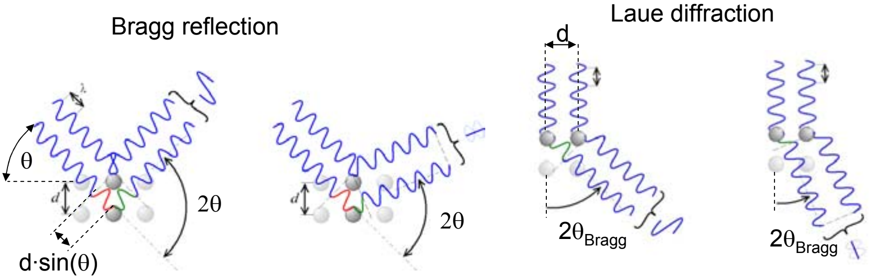
Bragg angle & deflection angle



Braggs law: $n\lambda = 2d\cdot\sin(\theta_{Bragg})$
$\approx d\cdot\sin(2\theta_{Bragg})$

Laue condition: $n\lambda = d\sin(2\theta_{Bragg})$
$\approx 2d\cdot\sin(\theta_{Bragg})$

Nomenclature: The **deflection angle** is usually denoted as 2x the **Bragg angle**!

$$\frac{n}{d} = 2\frac{\sin\left(\vartheta_{Bragg}\right)}{\lambda} = 2s \quad \Rightarrow q_t = k\cdot\sin(2\vartheta_{Bragg}) = 2s$$

Metric Tensor

Dot product of 2 vectors in cartesian coordinates **r**$_{1,2}$=(x,y,z):

$$\vec{r}_1 \cdot \vec{r}_2 = x_1 x_2 + y_1 y_2 + z_1 z_2$$

Dot product of 2 vectors in a general coordinate system (**e**$_1$,**e**$_2$,**e**$_3$):

$$\begin{aligned}\vec{r}_1 \cdot \vec{r}_2 &= x_1(\hat{e}_1 \cdot \hat{e}_1)x_2 + x_1(\hat{e}_1 \cdot \hat{e}_2)y_2 + x_1(\hat{e}_1 \cdot \hat{e}_3)z_2 \\ &\quad + y_1(\hat{e}_2 \cdot \hat{e}_1)x_2 + y_1(\hat{e}_2 \cdot \hat{e}_2)y_2 + y_1(\hat{e}_2 \cdot \hat{e}_3)z_2 \\ &\quad + z_1(\hat{e}_3 \cdot \hat{e}_1)x_2 + y_1(\hat{e}_3 \cdot \hat{e}_2)y_2 + z_1(\hat{e}_3 \cdot \hat{e}_3)z_2 \\ &= \begin{pmatrix} x_1 & y_1 & z_1 \end{pmatrix} \begin{pmatrix} \hat{e}_1 \cdot \hat{e}_1 & \hat{e}_1 \cdot \hat{e}_2 & \hat{e}_1 \cdot \hat{e}_3 \\ \hat{e}_2 \cdot \hat{e}_1 & \hat{e}_2 \cdot \hat{e}_2 & \hat{e}_2 \cdot \hat{e}_3 \\ \hat{e}_3 \cdot \hat{e}_1 & \hat{e}_3 \cdot \hat{e}_2 & \hat{e}_3 \cdot \hat{e}_3 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix}\end{aligned}$$

Metric Tensor G

Use of the Metric Tensor in reciprocal space

Length of a reciprocal lattice vector |**g**$_{hkl}$|=1/d$_{hkl}$:

$$|g_{hkl}| = \sqrt{\begin{pmatrix} h & k & l \end{pmatrix} \begin{pmatrix} \vec{a}^* \cdot \vec{a}^* & \vec{a}^* \cdot \vec{b}^* & \vec{a}^* \cdot \vec{c}^* \\ \vec{b}^* \cdot \vec{a}^* & \vec{b}^* \cdot \vec{b}^* & \vec{b}^* \cdot \vec{c}^* \\ \vec{c}^* \cdot \vec{a}^* & \vec{c}^* \cdot \vec{b}^* & \vec{c}^* \cdot \vec{c}^* \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}}$$

$$= \sqrt{g^{*t} G g^*}$$

$$g^* = \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

Angle γ between 2 reciprocal lattice vectors **g**$_1$ and **g**$_2$:

$$\cos(\gamma) = \frac{g_1^{*t} G g_2^*}{\sqrt{g_1^{*t} G g_1^*} \cdot \sqrt{g_2^{*t} G g_2^*}}$$

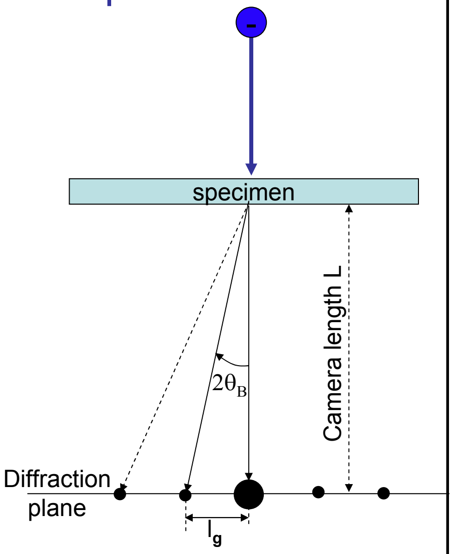
Metric Tensor in real space

The real-space metric tensor of a given lattice is just the inverse of the reciprocal-space metric tensor.

$$M = \begin{pmatrix} \vec{a}\cdot\vec{a} & \vec{a}\cdot\vec{b} & \vec{a}\cdot\vec{c} \\ \vec{b}\cdot\vec{a} & \vec{b}\cdot\vec{b} & \vec{b}\cdot\vec{c} \\ \vec{c}\cdot\vec{a} & \vec{c}\cdot\vec{b} & \vec{a}\cdot\vec{c} \end{pmatrix} = G^{-1}$$

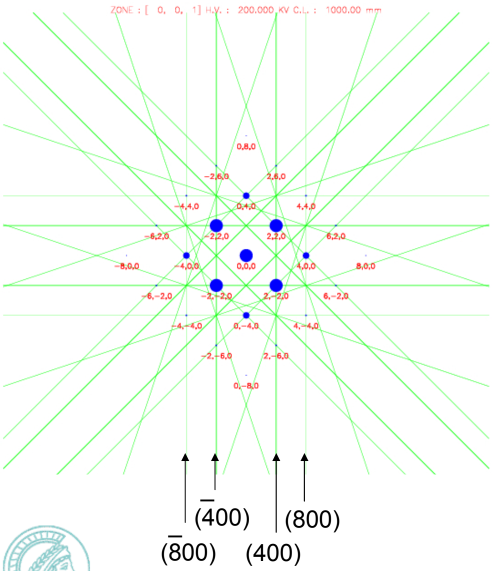
Indexing a diffraction pattern

1. Calibrate camera length using a specimen with known d-spacings (i.e. known **g**) according to: $L = l_g/\sin(2\theta_B[\mathbf{g}])$
2. Measure l_g for the unknown specimen.
3. Obtain d-spacing $d_{hkl}=L\lambda/l_g$
4. Look up the obtained d-spacing in a table of possible lattice plane spacings for the phase(s) in question.
   [The **metric tensor** helps to compute $|\mathbf{g}_{hkl}|$ very quickly for any (hkl)].
5. Repeat step 2-4 for at least 1 more (better more) diffraction spots.
6. Make sure that the identified phase and orientation agrees with the observed symmetry of the diffraction pattern.



$l_g = L\cdot\sin(2\theta_B) = L\lambda|\mathbf{g}|$

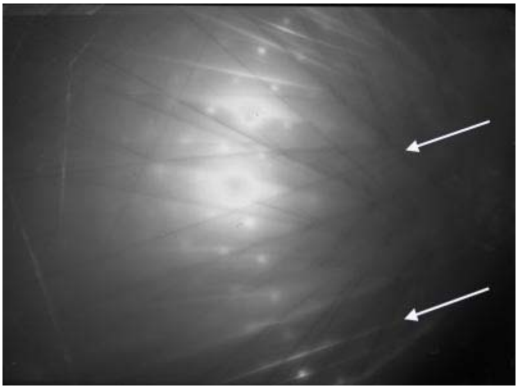
Indexing Kikuchi lines



Laue condition for diffraction spots: $n\lambda = d\sin(2\theta_{Bragg})$.

Kikuchi lines are **Bragg reflected** by lattice planes of the crystal. The angle between the reflected beams and the reflecting plane is therefore θ_{Bragg}. Kikuchi lines appear therefore at ½ the scattering angle of the corresponding diffraction spot.

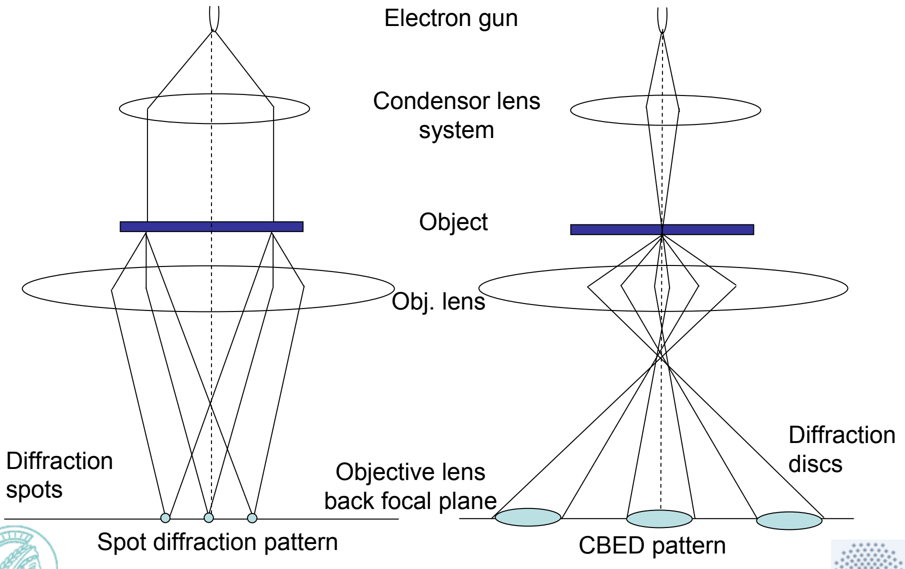
Indexing Kikuchi lines



Angle between excess and deficiancy line: $2\theta_{Bragg}$

Kikuchi lines in a spot pattern

Parallel vs. convergent beam electron diffraction



Electron gun

Condensor lens
system

Object

Obj. lens

Diffraction
spots

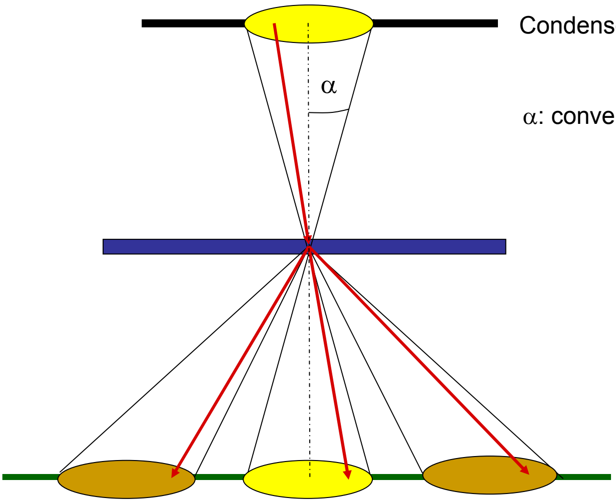
Objective lens
back focal plane

Diffraction
discs

Spot diffraction pattern

CBED pattern

Convergent beam electron diffraction (CBED)

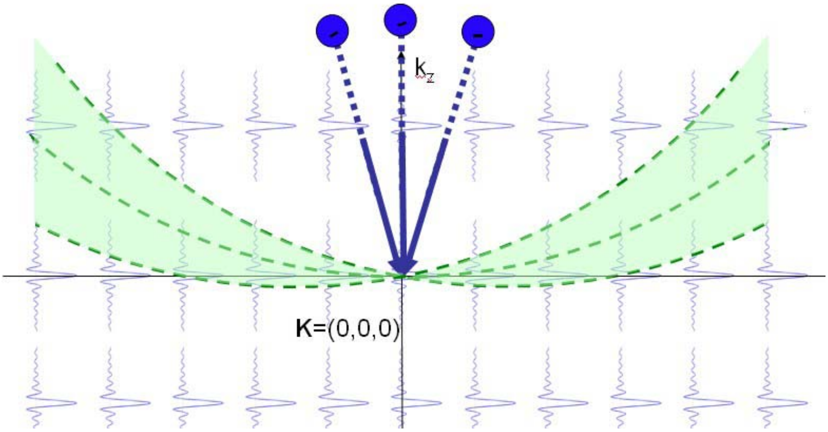


Condensor aperture

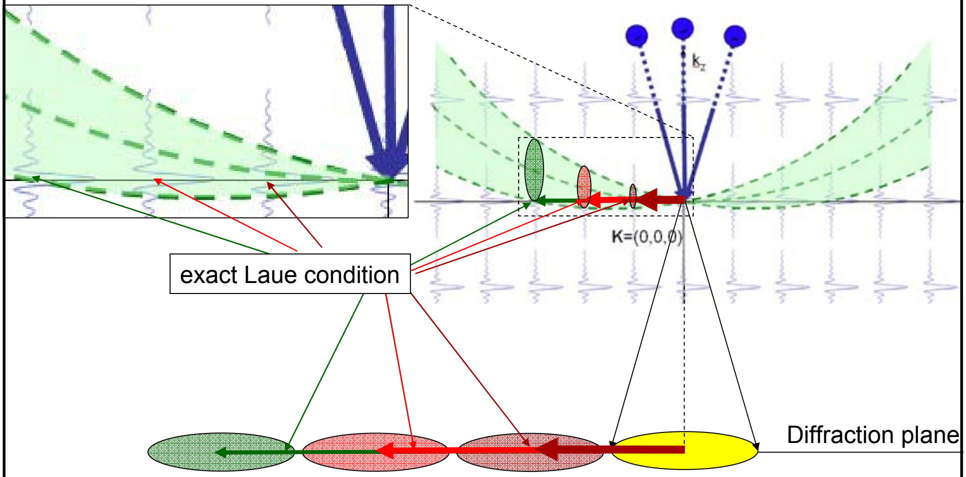
α: convergence semi-angle

Each point in the diffraction pattern is a separate diffraction experiment,
but they may all recorded simultaneously.

CBED: many independent diffraction experiments

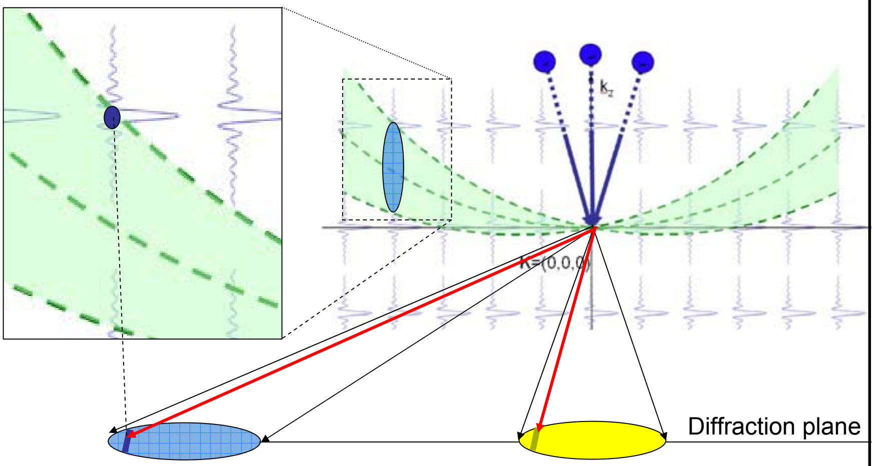


Exact Lause condition within CBED disks



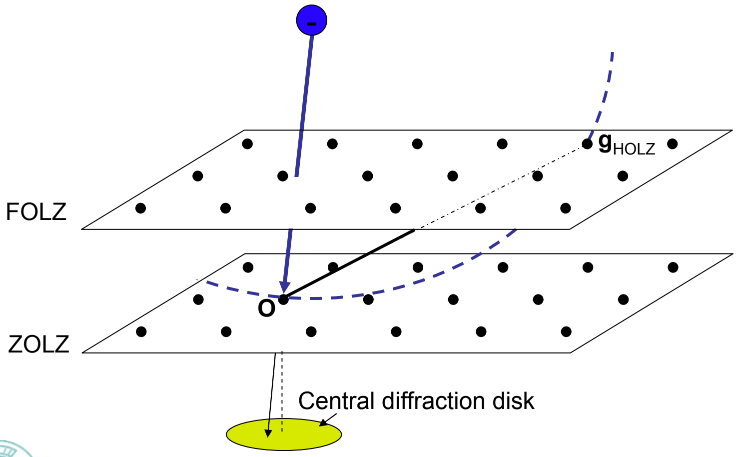
The exact Laue (or Bragg) condition is satisfied only for a single line within each diffraction disk. This line is at different positions in different disks.

HOLZ lines within CBED disks



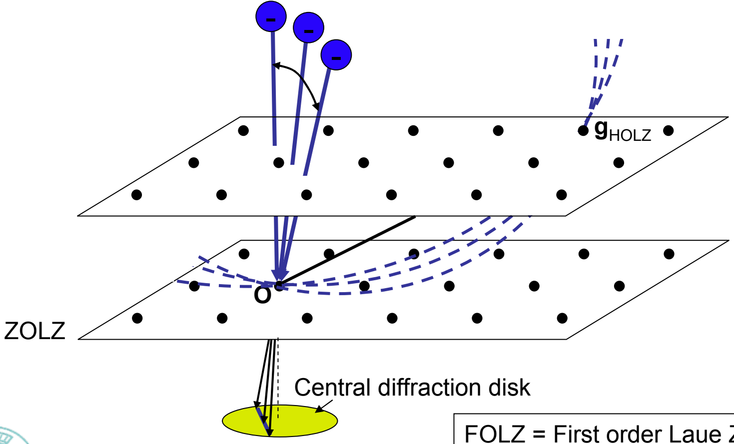
Inside HOLZ disks the Laue condition is satisfied only in a thin line, because of the steep angle at which the Ewald sphere intersects the HOLZ. The electrons that have scattered into this line are missing in the central disk at exactly the same diffraction angle.

Geometry of HOLZ lines



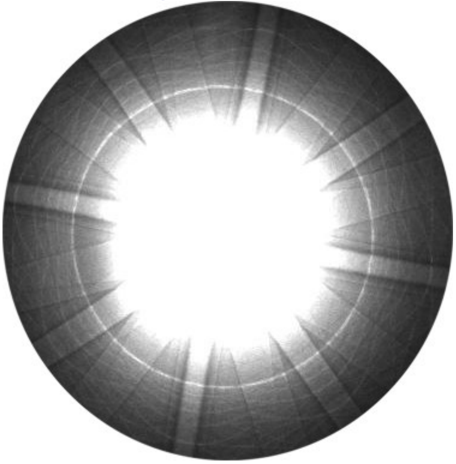
Geometry of HOLZ lines

The condition of keeping the HOLZ reflection ($\mathbf{g}_{\text{HOLZ}}$) and the reciprocal space lattice origin (**O**) on the Ewald sphere leaves one degree of freedom, a tilt about the rotation axis $\overline{\mathbf{Og}}_{\text{HOLZ}}$. This one-dimensional rocking curve appears as line in the diffraction pattern (bright excess line in HOLZ ring and **dark deficiency HOLZ line** in central disk).



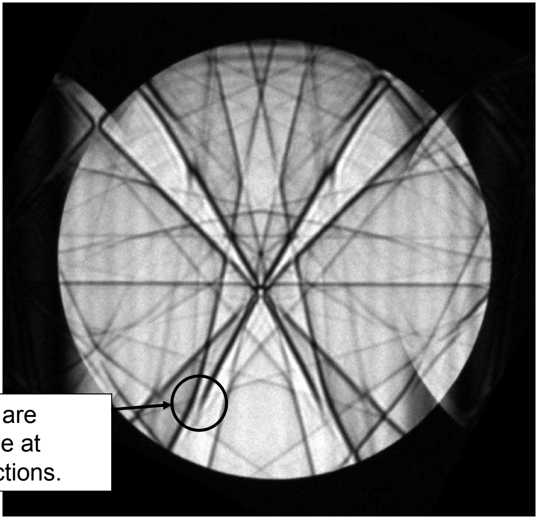
FOLZ = First order Laue Zone
ZOLZ = Zero Order Laue Zone

HOLZ rings = Excess Lines



Under convergent illumination the intersection of the Ewald sphere with the HOLZs produces a ring. This ring consists of short line segments. At very high scattering angles HOLZ rings are only visible if the specimen is kept at very low temperatures (e.g. liq. N_2)

HOLZ lines = Deficiency Lines



Dynamical effects are especially noticable at HOLZ line intersections.

Electrons that have scattered into the HOLZ ring are missing in the central disc, producing dark HOLZ lines. HOLZ lines carry therefore 3-dimensional information about the crystal structure.

Applications using HOLZ lines

HOLZ lines are produced by very long reciprocal lattice vectors $\mathbf{g}_{HOLZ}$. Their position is therefore extremely sensitive to changes in **lattice parameters** and /or the electron **wavelength** and thus the high voltage.

A few applications:

1. **Very precise sample orientation**: HOLZ line patterns are very sensitive to tilt.
2. **Determination of 3D lattice parameters** from a single CBED pattern.
3. **Strain mapping**: CBED patterns are recorded as a fine beam rasters across the sample. Strain (local changes in lattice constants) is determined by relative shifts of the HOLZ lines.
4. **Calibration of the high voltage of the microscope**: The relative position of HOLZ lines depends on the radius of the Ewald sphere and thus the accelerating voltage of the microscope (can be determined to <1V accuracy).
5. **Determination of 3D symmetry**: ZOLZ diffraction data shows the symmetry of the projected structure, HOLZ lines carry 3D information.
6. **Analysis of defects** … (to be discussed later)

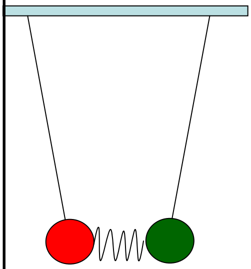
Note: Dynamical scattering (multiple eleastic scattering) may shift HOLZ line positions. The usage of dynamical diffraction theory (e.g. Bloch wave method) is therefore necessary for quantitative HOLZ line analysis.

Indexing HOLZ lines

- The position of a HOLZ line depends on the excitation error at the HOLZ reflection ($\mathbf{g}_{HOLZ}$ must be excactly in diffracting condition).
- Its orientation is always perpendicular to $\mathbf{g}_{HOLZ}$ as well as to the projection of $\mathbf{g}_{HOLZ}$ in the Zero Order Laue Zone (ZOLZ)

2-Beam Diffraction Theory

In dynamical (multiple) diffraction theory the beams will feed on each other, shifting intensity back-and forth, in the same fashion, the 2 masses in a coupled pendulum share the available kinetic energy.
If only the central beam and the reflection **g** are strongly excited, the solution is analytic and agrees with the solution of a pendulum of 2 equal masses ($\xi_{\mathbf{g}} = \xi_{-\mathbf{g}}$).



Diffracted intensity:

$$I_g = \lambda^2 |U_g|^2 \frac{\sin^2\left(\pi t \sqrt{s_g^2 + \lambda^2 |U_g|^2}\right)}{s_g^2 + \lambda^2 |U_g|^2} = \frac{1}{\xi_g^2} \frac{\sin^2\left(\pi t \sqrt{s_g^2 + \xi_g^{-2}}\right)}{s_g^2 + \xi_g^{-2}}$$

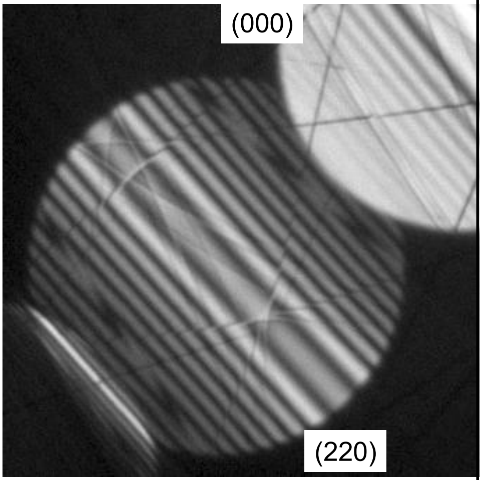
Intensity in central beam: $I_0 = 1 - I_g$

Extinction distance:

$$\xi_g = \frac{|\vec{k}|}{|U_g|} = \frac{1}{\lambda |U_g|}$$

Thickness determination from CBED disks

$$I_g = \frac{1}{\xi_g^2}\frac{\sin^2\left(\pi t\sqrt{s_{2g}^2+\xi_g^{-2}}\right)}{s_g^2+\xi_g^{-2}}$$



The diffracted intensity is a sinusoidal function of the excitation error s_g.
Fringe minima must therefore occur when

$$t\sqrt{s_{2\bar{2}0}^2+\xi_{2\bar{2}0}^{-2}} = n_i$$

Where n_i is an integer.
Maxima must then be located where

$$t\sqrt{s_{2\bar{2}0}^2+\xi_{2\bar{2}0}^{-2}} = n_i + \frac{1}{2}$$

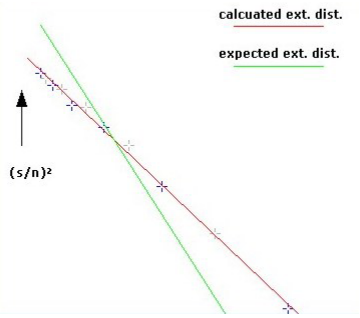
Excitation error in 2-beam condition: $s_g = -\frac{g \cdot k_t}{2}$

Procedure for thickness determination

1. Calibrate the diffraction pattern using the known distance |**g**| of the disc centers.
2. Measure k_t for a few of the minima around the diffracted disk center and compute s_i for each one of them. Index the minima with increasing distance from the center of symmetry within the disk.
   (Remember: In the center of the diffracted disk s = |**g**|·k_t=0).
3. Given the correct indices n_i, the thickness may now be determined from the known extinction distance and
   $$t = n_i / \sqrt{(s_i^2 + 1/\zeta_g^2)}$$
4. Vary the index n_1 of the first minimum (and the other indices accordingly) until the thickness determined from the different minima positions are roughly the same.

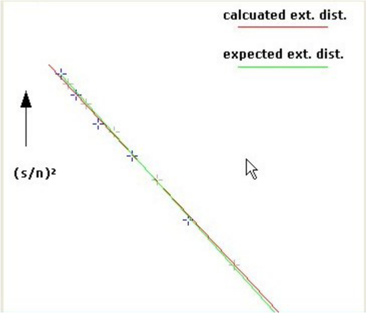
Finding the correct index

ξ_{220}(expected) = 960Å



n$_1$=3: wrong

ξ_g(fitted) = 1234Å

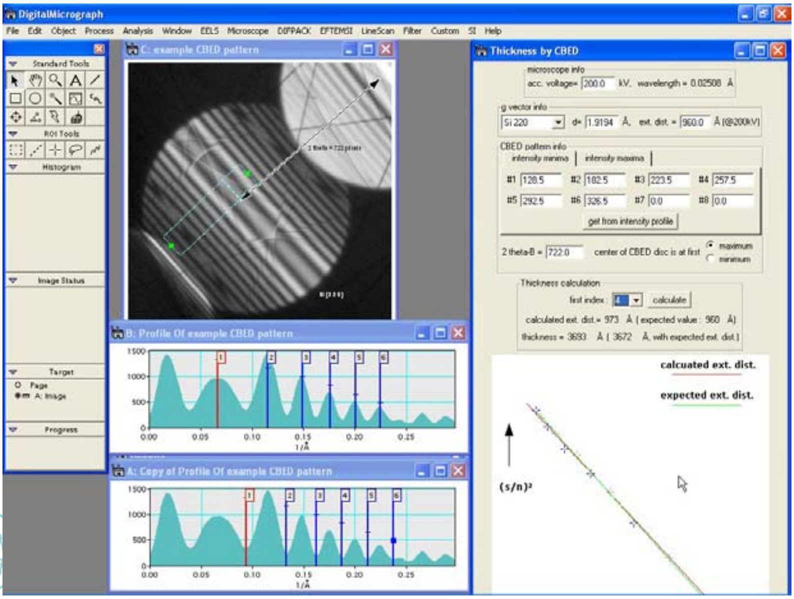


n$_1$=4: correct

ξ_g(fitted) = 973Å

Digitalmicrograph: Thickness Measurement GUI

http://felmpc14.tu-graz.ac.at/dm_scripts/freeware/programs/Thickness_by_CBED.htm



microscope info
acc. voltage= 200.0 kV, wavelength = 0.02508 Å

g vector info
Si 220 d= 1.9194 Å, ext. dist. = 960.0 Å (@200kV)

CBED pattern info
intensity minima | intensity maxima

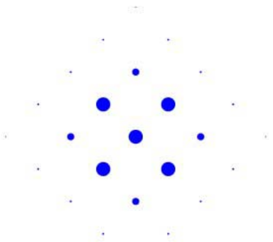
#1 128.5 #2 182.5 #3 223.5 #4 257.5
#5 292.5 #6 326.5 #7 0.0 #8 0.0

get from intensity profile

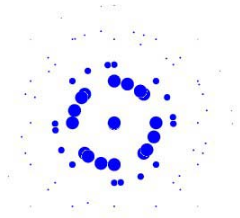
2 theta-B = 722.0 center of CBED disc is at first ● maximum ○ minimum

Thickness calculation
first index : 4 calculate
calculated ext. dist.= 973 Å (expected value : 960 Å)
thickness = 3693 Å (3672 Å, with expected ext. dist.)

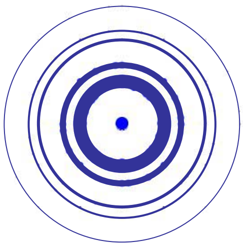
Diffraction from polycrystalline specimen



Single grain

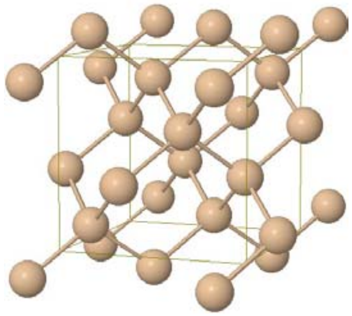


Few grains

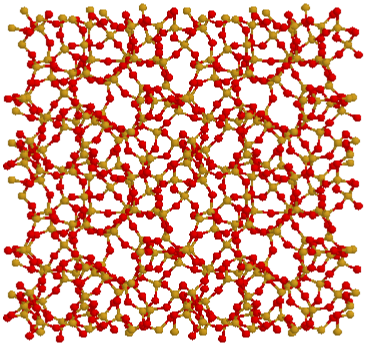


Many grains

Crystal vs. Glass

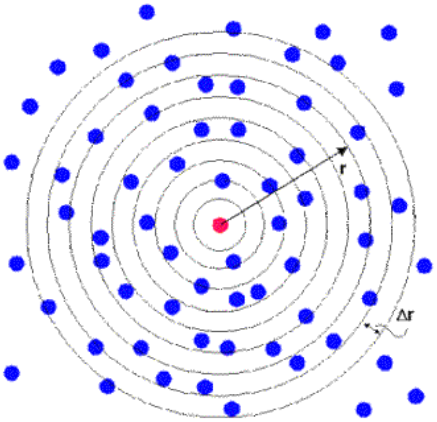


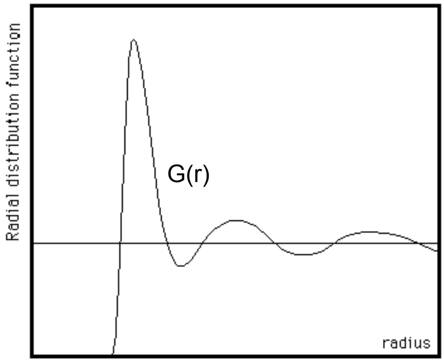
Crystal (Si)
very well defined (sharp) d-spacings



Glass (SiO_2)
Certain ranges of preferred distances
Between neighboring atoms.

Radial distribution function G(r)





distance-dependent density

$$G(r) = 4\pi r\left[\rho^R(r) - \rho_0\right]$$

mean density

RDF from diffraction pattern

Structure factor: $$F(\vec{q}) = \sum_{j=1}^{N_{atom}} f_j(|\vec{q}|)\exp\left[2\pi i\vec{q}\cdot\vec{r}_j\right]$$

Kin. diffr. pattern: $$I(\vec{q}) = |F(\vec{q})|^2 = \sum_{j=1}^{N_{atom}} f_j(q)^2 + \sum_{j=1}^{N_{atom}}\sum_{l\neq j} f_j(q)f_l(q)\exp\left[2\pi i\vec{q}\cdot\vec{r}_{jl}\right]$$

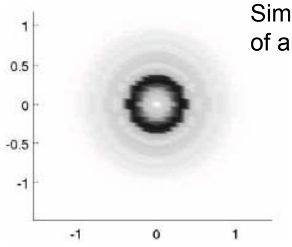
2D RDF (g(r)): $$g(\vec{r}) = \mathrm{FT}^{-1}\left\{\left[I(\vec{q}) - \sum_{i=1}^{N_{atom}} f_i(q)^2\right]/\tilde{f}(q)^2\right\}$$

1D RDF (G(r)): $$G(r) = \int_0^{2\pi} g(\vec{r})r\,d\phi$$

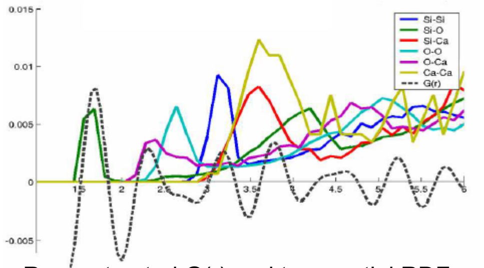
$$\vec{r}_{jl} = \vec{r}_j - \vec{r}_l$$

$$\tilde{f}(q)^2 = \frac{1}{N_{atom}^2 - N_{atom}}\sum_{j=1}^{N_{atom}}\sum_{l\neq j} f_j(q)f_l(q)$$

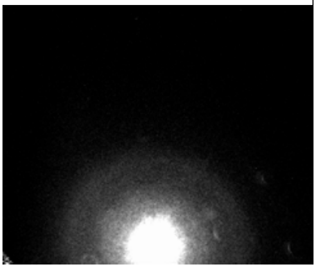
RDF of amorphous materials



Simulated diffraction pattern of an amorphous structure.

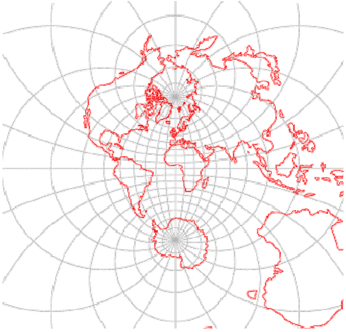


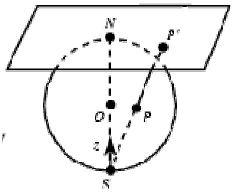
Reconstructed G(r) and true partial RDFs obtained directly from a Si-O-Ca glass model.



Experimental diffraction pattern of an amorphous specimen

Homework: Stereographic projection

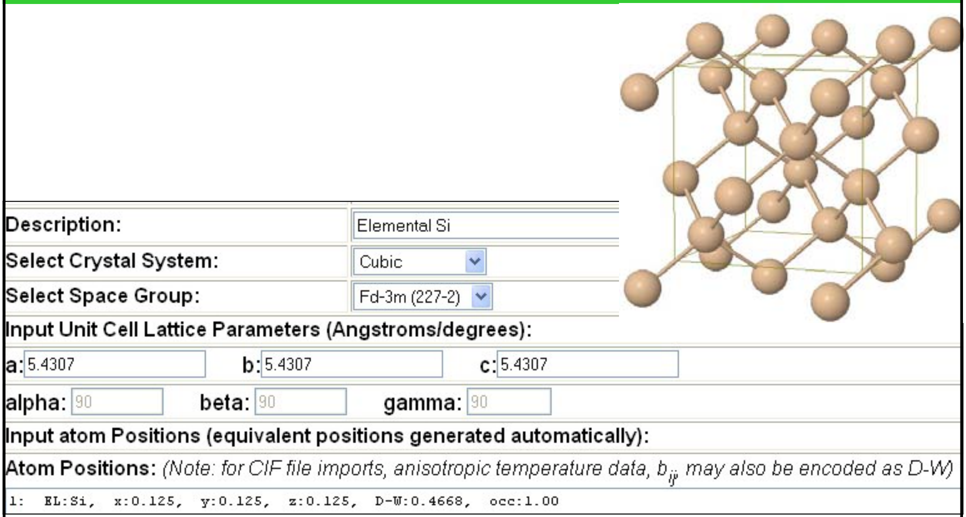




$$P' = \frac{2r}{z} P$$

The plane of projection is tangential to the equator of the globe.
The axis of rotation of the earth lies horizontal in the projection diagram shown to the right.

Homework: Space Group 227 (diamond structure)



Description: Elemental Si

Select Crystal System: Cubic

Select Space Group: Fd-3m (227-2)

Input Unit Cell Lattice Parameters (Angstroms/degrees):

a: 5.4307 **b:** 5.4307 **c:** 5.4307

alpha: 90 **beta:** 90 **gamma:** 90

Input atom Positions (equivalent positions generated automatically):

Atom Positions: *(Note: for CIF file imports, anisotropic temperature data,* b_{ij}*, may also be encoded as D-W)*

```
1:  EL:Si,  x:0.125,  y:0.125,  z:0.125,  D-W:0.4668,  occ:1.00
```

Screenshot from WEBEMAPS (http://emaps.mrl.uiuc.edu/emaps.asp)