

Electron-matter interactions: Elastic scattering (II)

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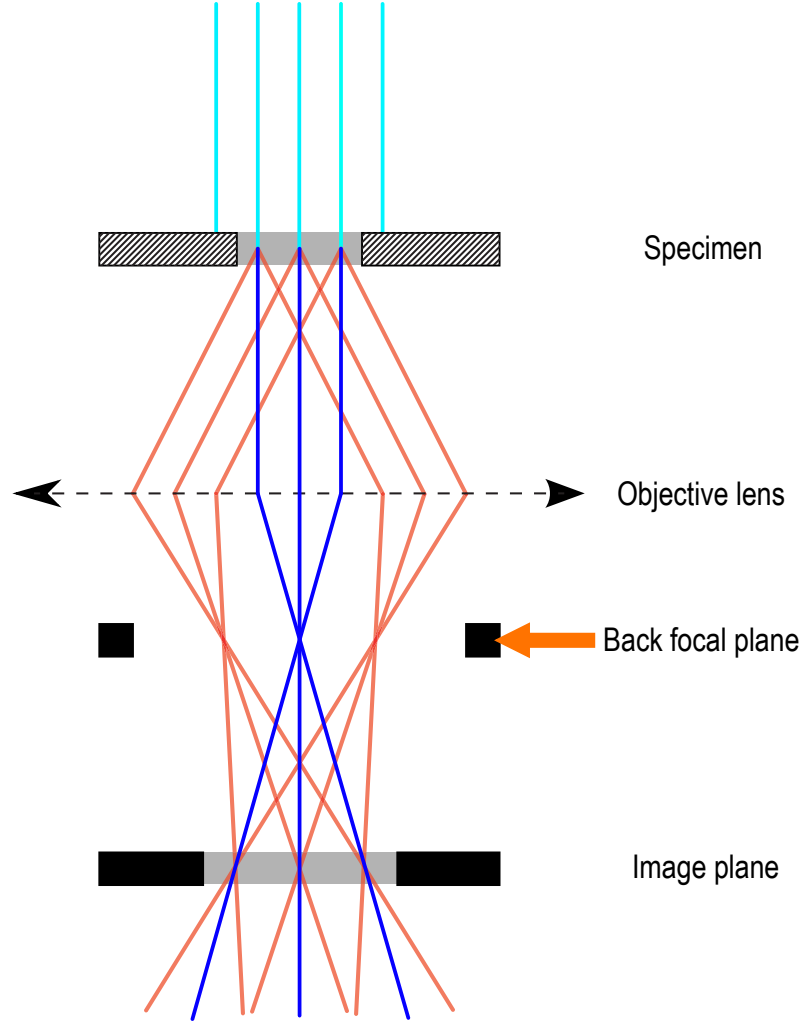
EPFL Contents

Part A: scattering from a crystal lattice – kinematical

- Scattering geometry: Bragg law, Laue condition, Ewald sphere/reciprocal lattice
- Scattering from a lattice (kinematical/first Born approximation)
- Kinematical curves of I_g vs s
- Introduction to convergent beam electron diffraction (CBED)
- Deficiencies of kinematical model

Part B: dynamical theory – Bloch wave approach

- Basic concepts
- Application with 2-beam approximation
- Dispersion surfaces
- Diffracted beam intensities



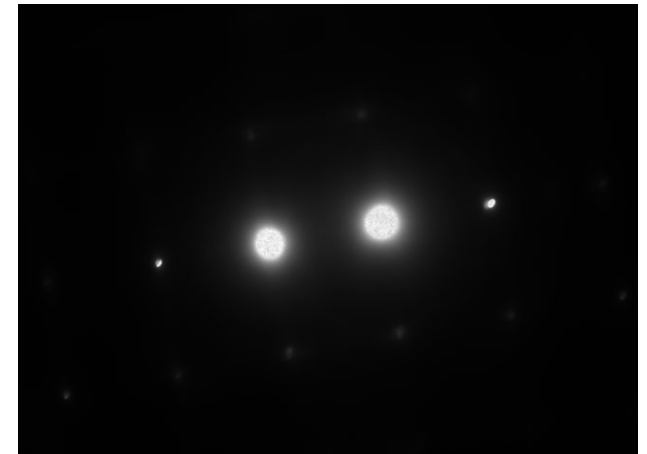
- Parallel rays focused to a point at back focal plane
- Equivalent to Fraunhofer far-field scattering

EPFL Bragg law

- Constructive interference for:

$$n\lambda = 2d_{hkl} \sin \theta \quad (1.36)$$

- Crystalline sample tilted such that one plane at Bragg angle θ_B relative to $k_0 \Rightarrow$ 2-beam diffraction pattern:



EPFL Laue condition

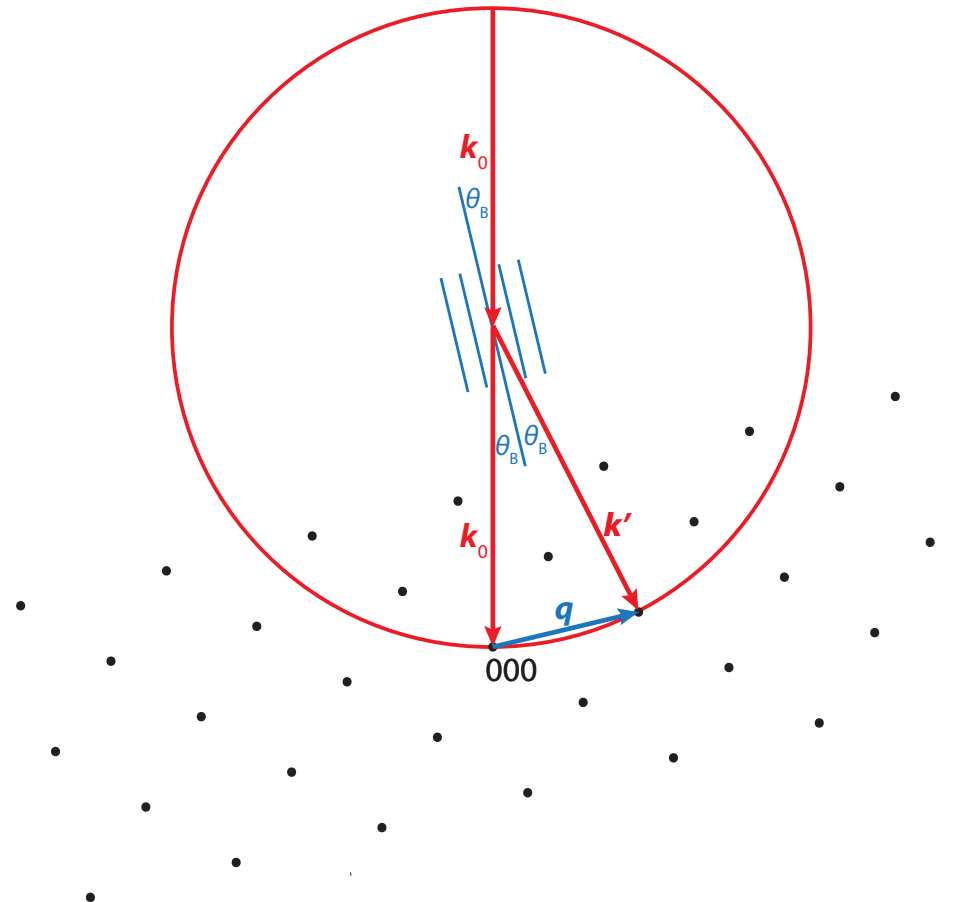
- TEM scattering geometry is that of Laue diffraction (not Bragg)

- Laue condition:
$$\vec{q} = \vec{k}' - \vec{k}_0 = \vec{g} \quad (1.37)$$

$$\vec{g} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \quad (1.38)$$

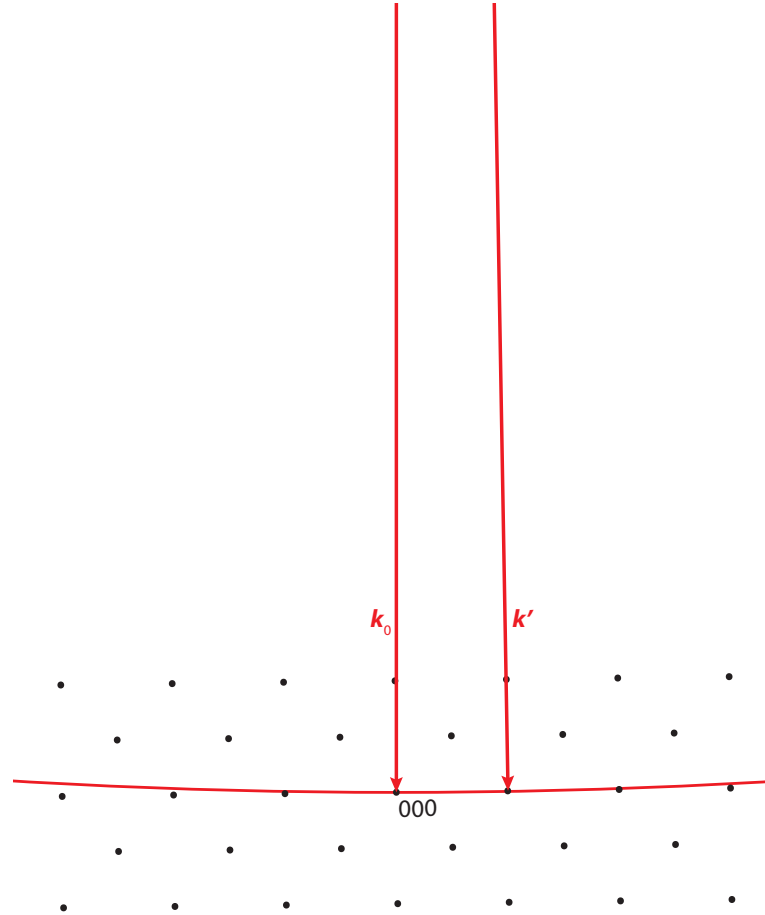
EPFL Ewald sphere/reciprocal lattice construction

- Ewald sphere/reciprocal lattice construction provides method to identify which plane(s) diffract under chosen incident beam/crystal geometry



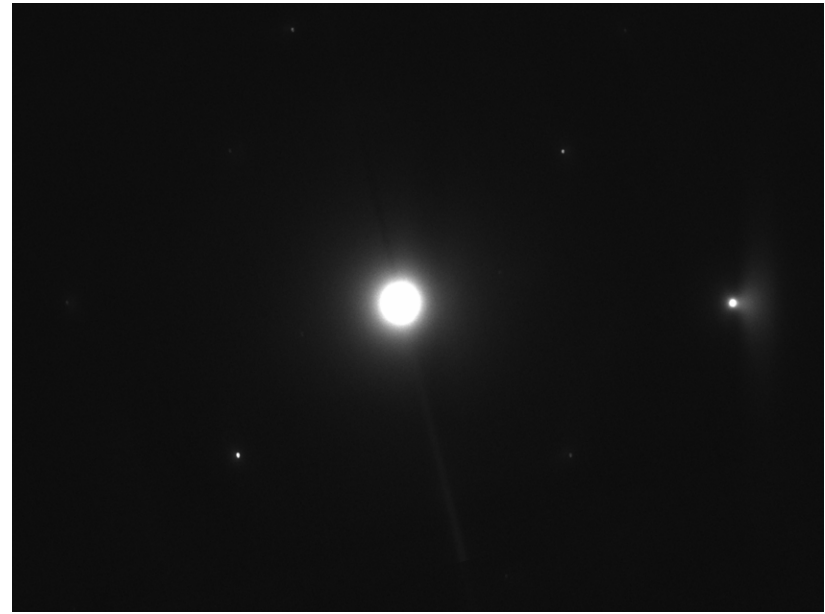
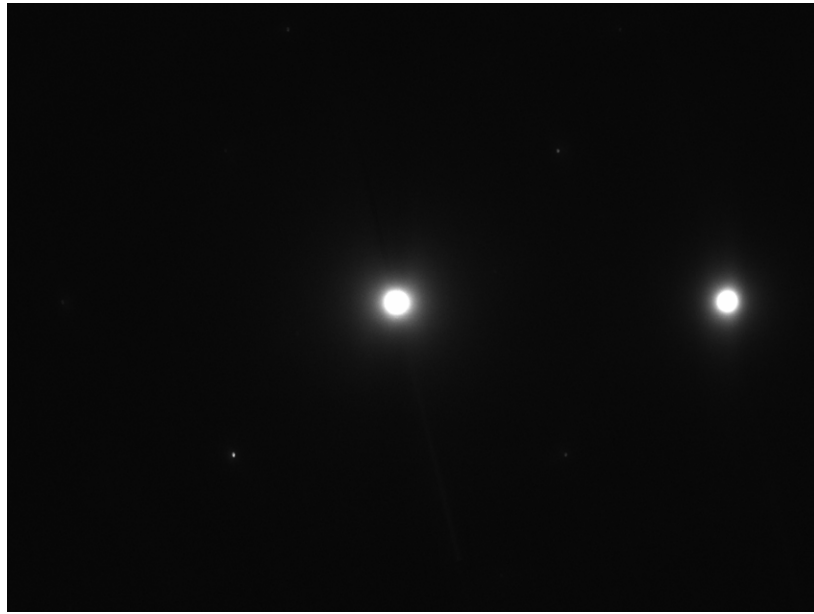
EPFL Ewald sphere/reciprocal lattice construction

- Illustration using realistic parameters: 200 keV beam, BCC Fe crystal



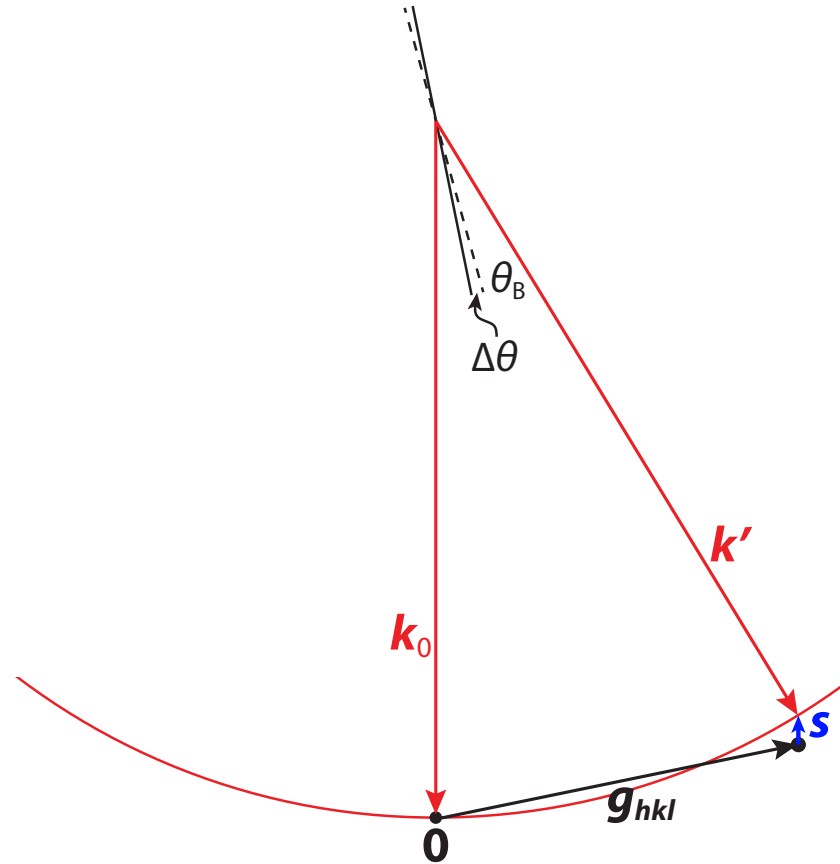
EPFL Diffraction away from exact Bragg condition

- Tilt crystal away from exact Bragg condition – plane still diffracts:



EPFL Deviation parameter

- Introduce deviation parameter vector to describe deviation from Bragg:



$$\vec{k}' = \vec{k}_0 + \vec{g} + \vec{s} \quad (1.39)$$

EPFL Scattering from a lattice (kinematical)

- From last week, scattering amplitude for one atom:

$$\psi_1(\vec{r}) = \frac{\exp\{2\pi i \vec{k} \cdot \vec{r}\}}{r} f(\vec{q}) \quad (1.24)$$

$$f(\vec{q}) = \frac{2\pi m e}{h^2} \int_{-\infty}^{\infty} \phi(\vec{r}) \exp\{-2\pi i \vec{q} \cdot \vec{r}\} d\vec{r} \quad (1.25)$$

- Consider assembly of atoms into a unit cell:

EPFL Scattering from a unit cell

- Total scattered wave from unit cell is:

$$\begin{aligned}\psi_s(\vec{r}) &= \frac{\exp\{2\pi i k r\}}{r} \sum_j f_j \exp(-2\pi i \vec{q} \cdot \vec{r}_j) \\ &= \frac{\exp\{2\pi i k r\}}{r} F(\vec{q})\end{aligned}\tag{2.1}$$

- Defines the structure amplitude $F(\vec{q})$ for the unit cell

EPFL Scattering from a lattice (kinematical)

- Unit cell therefore scatters spherical wave (if viewed at large r) modulated as function of scattering angle according to value of $F(\vec{q})$
- Now consider $N_x \times N_y \times N_z$ assembly of identical unit cells
- Reprising from eqs 1.37 and 1.39:

$$\vec{q} = \vec{g} + \vec{s} \quad (2.2)$$

EPFL Scattering from a lattice (kinematical)

- Separate $\vec{q}$ and position of n^{th} unit cell $\vec{r}_n$ into their components:

$$\vec{q} = \vec{g} + \vec{s} = \vec{g} + s_x \vec{a}^* + s_y \vec{b}^* + s_z \vec{c}^* \quad (2.3)$$

$$\vec{r}_n = n_x \vec{a} + n_y \vec{b} + n_z \vec{c} \quad (2.4)$$

- By definition $\vec{g} \cdot \vec{r}_n$ is necessarily an integer. Therefore:

$$\psi_s(\vec{r}) = \frac{\exp\{2\pi i k r\}}{r} \sum_{n_x} \sum_{n_y} \sum_{n_z} F(\vec{q}) \exp\left[-2\pi i (n_x a s_x + n_y b s_y + n_z c s_z)\right] \quad (2.5)$$

EPFL Scattering from a lattice (kinematical)

- The three summations in eq. 2.5 are geometric progressions of type:

$$\sum_A \exp(-2\pi i A \alpha s_\alpha) = \frac{\sin(\pi A \alpha s_\alpha)}{\sin(\pi \alpha s_\alpha)} \quad (2.6)$$

- Letting the size of the sample be: $D_x \times D_y \times t = N_x a \times N_y b \times N_z c$
we obtain:

$$\psi_s(\vec{r}) = \frac{\exp\{2\pi i k r\}}{r} F(\vec{q}) \left[\frac{\sin(\pi N_x a s_x)}{\sin(\pi a s_x)} \right] \left[\frac{\sin(\pi N_y b s_y)}{\sin(\pi b s_y)} \right] \left[\frac{\sin(\pi N_z c s_z)}{\sin(\pi c s_z)} \right] \quad (2.7)$$

- $\vec{s}$ is small, therefore: $\sin(\pi a s_x) \approx \pi a s_x$ etc.
- Take volume of unit cell as: $V_c = abc$

EPFL Scattering from a lattice (kinematical)

- For TEM specimen, N_x and $N_y \gg N_z$
- When calculate scattering intensity $I_s = |\psi_s|^2$ eq. 2.7 becomes:

$$I_s(\vec{r}) = \left[\frac{|\exp\{2\pi i k r\}|}{r} \frac{F(\vec{q})}{V_c} \right]^2 \times D_x \delta(s_x) D_y \delta(s_y) \times \left[\frac{\sin(\pi N_z c s_z)}{\pi s_z} \right]^2 \quad (2.8)$$

- To find total scattered intensity need to integrate over sphere at distance r from sample
- Element of surface area of sphere is: $dS = r^2 d\Omega$
- In reciprocal space: $d\Omega = \frac{ds_x ds_y}{k^2 \cos \theta}$

EPFL Scattering from a lattice (kinematical)

- From eq. 2.8: $I_s(\vec{r}) = D_x D_y \left[\frac{F(\vec{q})}{r V_c} \exp\{2\pi i k r\} \right]^2 \left[\frac{\sin(\pi N_z c s_z)}{\pi s_z} \right]^2 \delta(s_x) \delta(s_y)$
- The intensity scattered in direction near $\vec{g}$ with deviation parameter s_z is:

$$I_g = \int I dS = \frac{D_x D_y}{\cos \theta} \left[\frac{F(\vec{q})}{k V_c} \frac{\sin(\pi t s_z)}{\pi s_z} \right]^2 \int \delta(s_x) ds_x \int \delta(s_y) ds_y \quad (2.9)$$

- $D_x D_y \cos \theta$ is area of crystal projected along $\vec{k}'$
Therefore intensity per unit area of diffracted beam is:

$$I_g = \left[\frac{F_g}{\pi k V_c \cos \theta_B} \frac{\sin(\pi t s_z)}{s_z} \right]^2 \quad (2.10)$$

where F_g is $|F(\vec{g})|$ for the reflection $\vec{g}$

EPFL Fourier transform equivalence

- Consider again eq. 2.5: $\psi_s(\vec{r}) = \frac{\exp\{2\pi i k r\}}{r} \sum_{n_x} \sum_{n_y} \sum_{n_z} F(\vec{q}) \exp\left[-2\pi i (n_x a s_x + n_y b s_y + n_z c s_z)\right]$
- Summation term originating from $\vec{q} \cdot \vec{r}_n = \vec{s} \cdot \vec{r}_n$ is slowly varying between the cells.
- Therefore can argue to replace summation by integral:

$$\psi_s(\vec{r}) = \frac{\exp\{2\pi i k r\}}{r} \int \frac{F(\vec{q})}{V_c} \exp(-2\pi i \vec{s} \cdot \vec{r}') d\vec{r}' \quad (2.13)$$

EPFL Scattering from a lattice (kinematical)

- Going back to eq. 2.10:
$$I_g = \left[\frac{F_g}{\pi k V_c \cos \theta_B} \frac{\sin(\pi t s_z)}{s_z} \right]^2$$

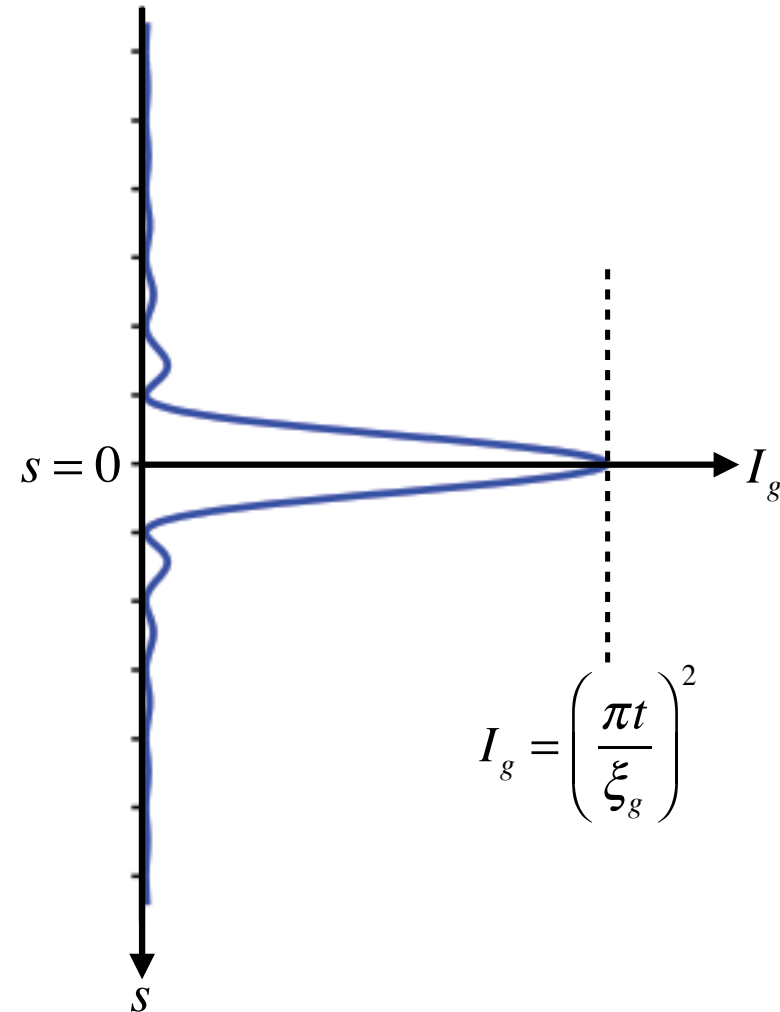
- Define “extinction distance”:
$$\xi_g = \frac{\pi k V_c \cos \theta_B}{F_g} \quad (2.11)$$

- Then:
$$I_g = \left[\frac{\sin(\pi t s_z)}{\xi_g s_z} \right]^2 \quad (2.12)$$

- Call z component of deviation parameter vector $\vec{s}$ the excitation error where: $s = s_z$
- Intensity of diffracted beam I_g modulates with t and s

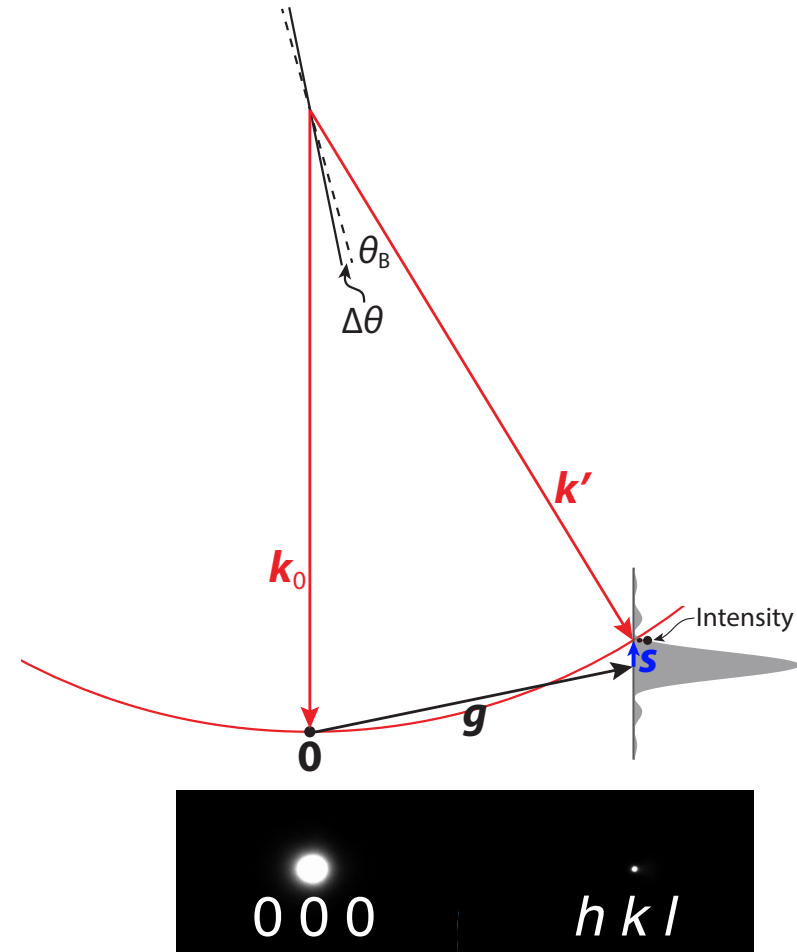
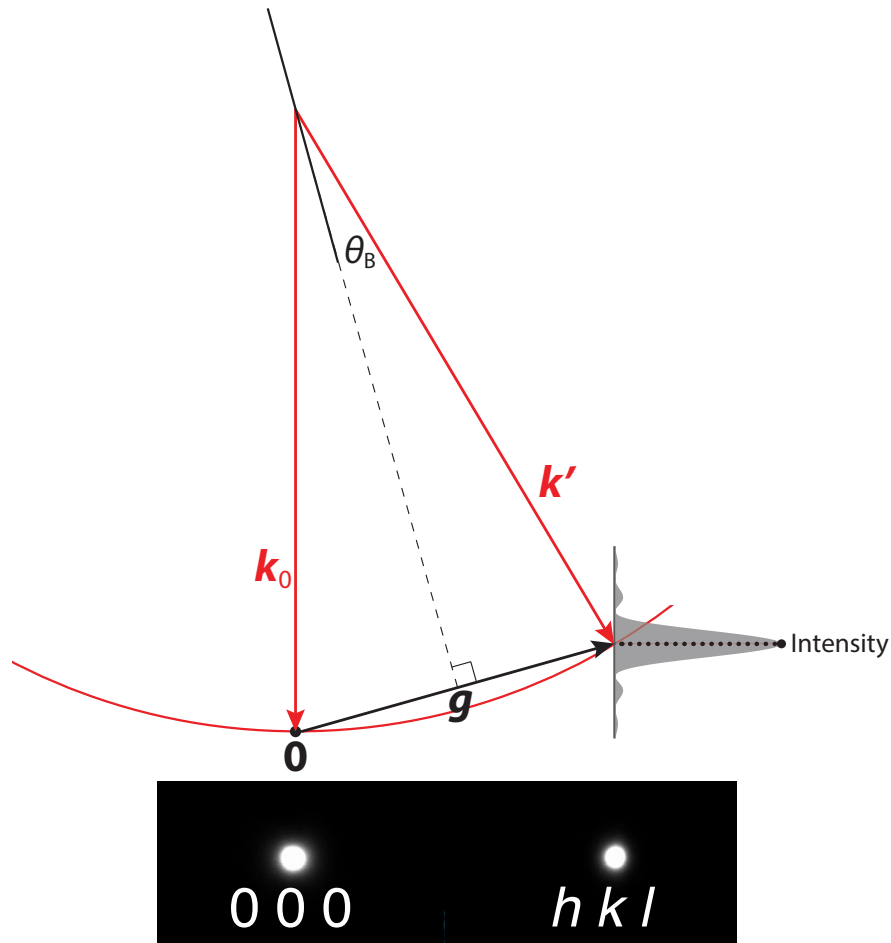
EPFL I_g vs excitation error s

- Plot I_g vs s



Interaction with Ewald sphere

- Exact Bragg condition
- Near Bragg condition

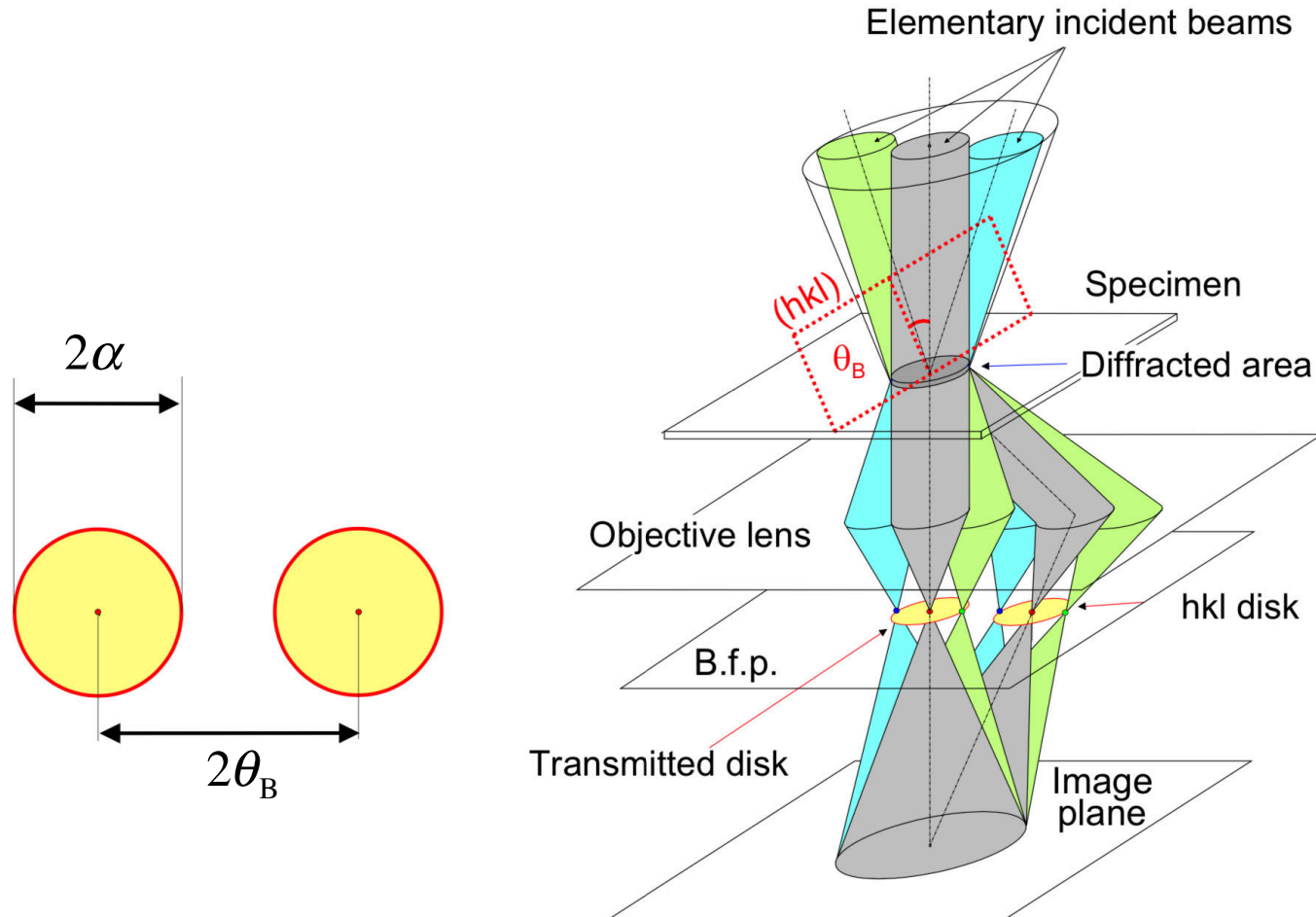


EPFL Methods for measuring I_g vs s

- How could we measure I_g vs s experimentally?

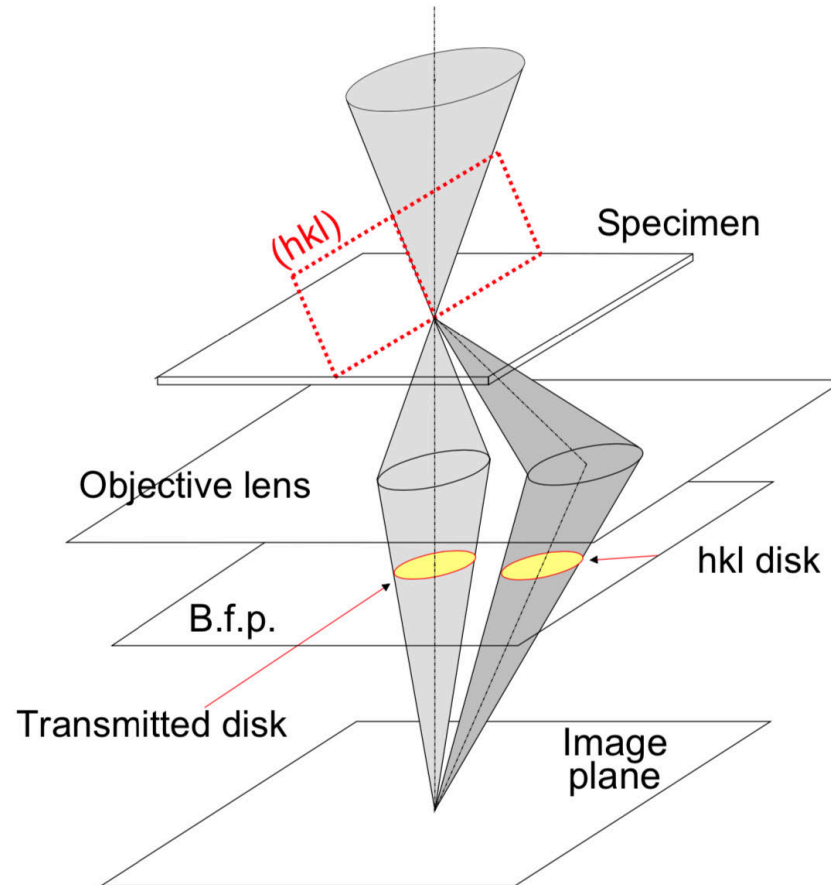
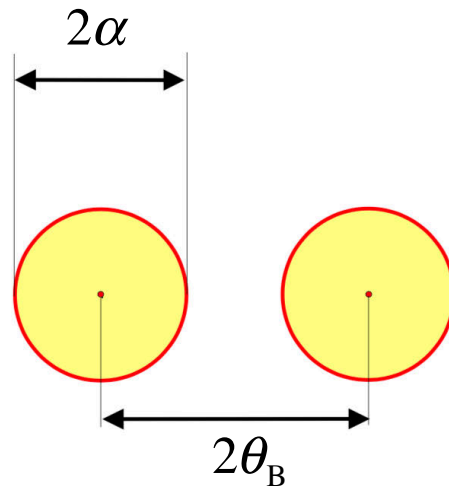
EPFL Convergent beam electron diffraction

- 2-beam illustration with semi-focused beam (from J.-P. Morniroli)

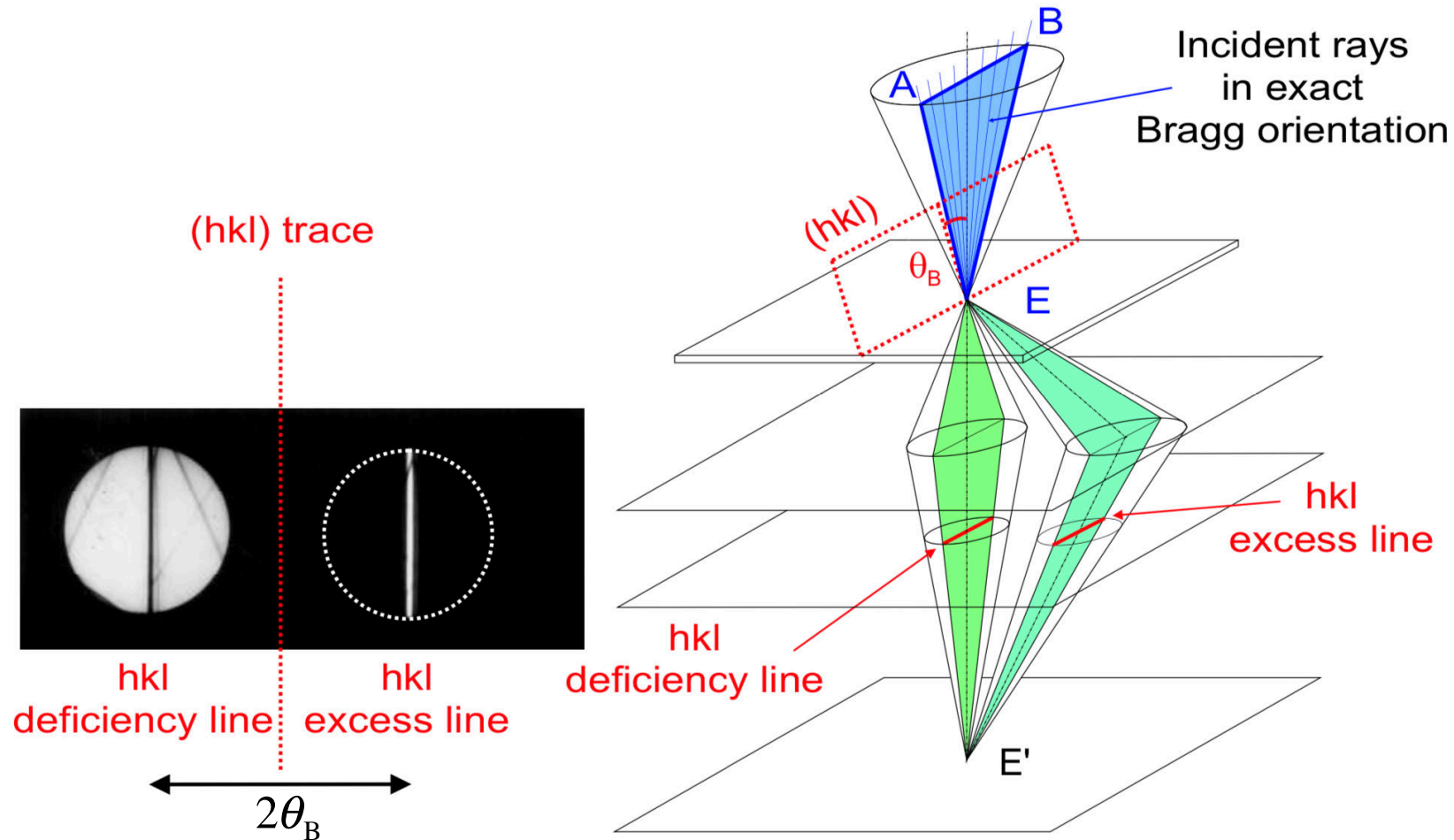


EPFL Convergent beam electron diffraction

- 2-beam illustration with fully-focused beam (from J.-P. Morniroli)



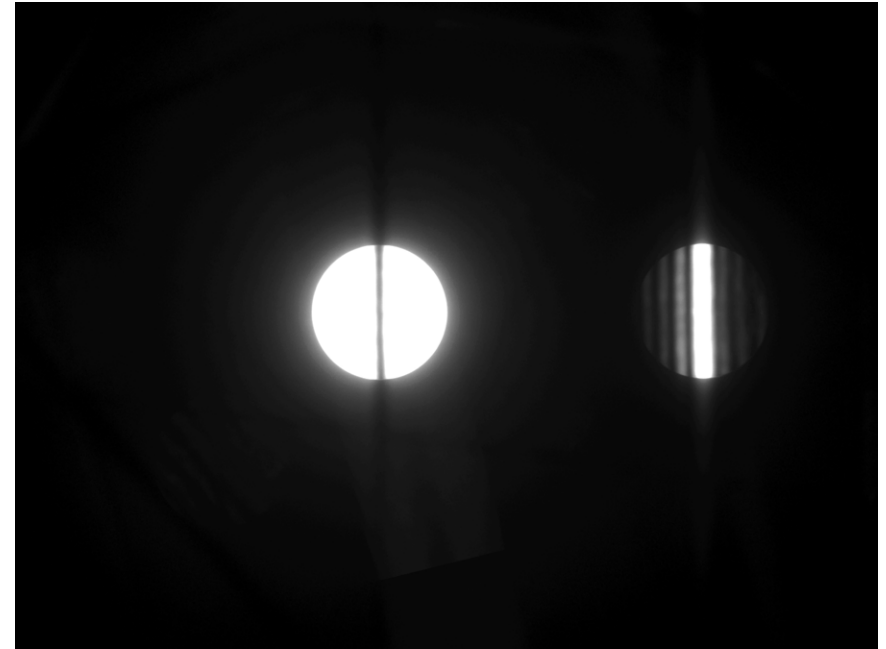
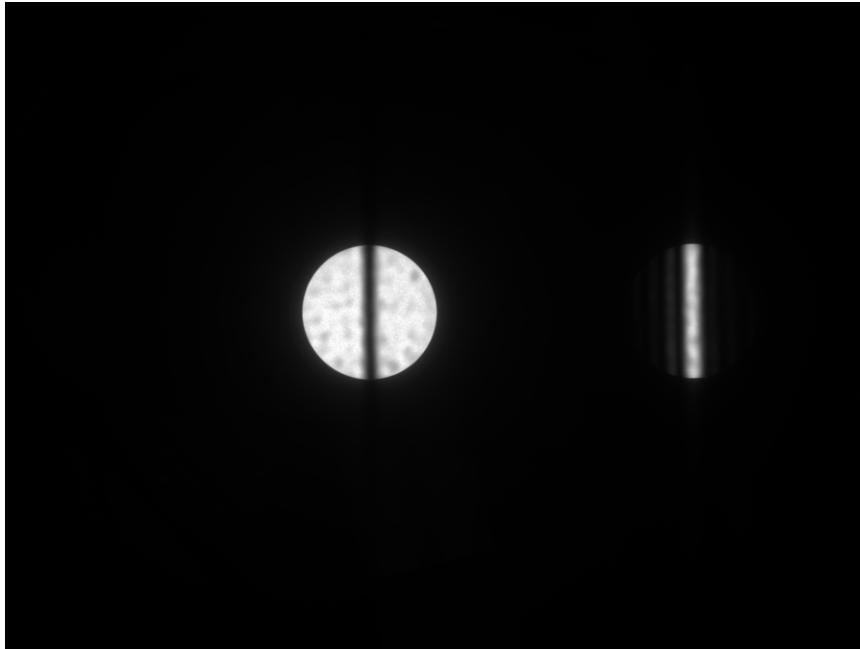
- 2-beam illustration with fully-focused beam (from J.-P. Morniroli)



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- Figure 1 consists of two diagrams illustrating the optical axis in different orientations.
- The left diagram, labeled "Ewald sphere in exact Bragg orientation", shows a red circle representing the Ewald sphere. A red dot is at the center. A vertical red line passes through the center. A blue line and a green line intersect at the center. A cyan shaded region is on the right side of the sphere. Points A and B are marked on the sphere's surface. Labels $s < 0$ (green), $s = 0$ (red), and $s > 0$ (blue) are placed near the center.
- The right diagram, labeled "Relrod", shows a 3D view of the optical axis. A red dashed line represents the optical axis. A green line and a blue line intersect at a point O. A cyan shaded region is on the right side. Points A and B are marked on the surface. Labels $\theta_i = \theta_B$, $\theta_i < \theta_B$, and $\theta_i > \theta_B$ are placed near the top. Angles $2\theta_B$ and 2α are indicated. A vector $\mathbf{g}_{hkl}$ is shown. Labels $s = 0$ (red) and $s > 0$ (blue) are placed near the bottom right.

EPFL Convergent beam electron diffraction

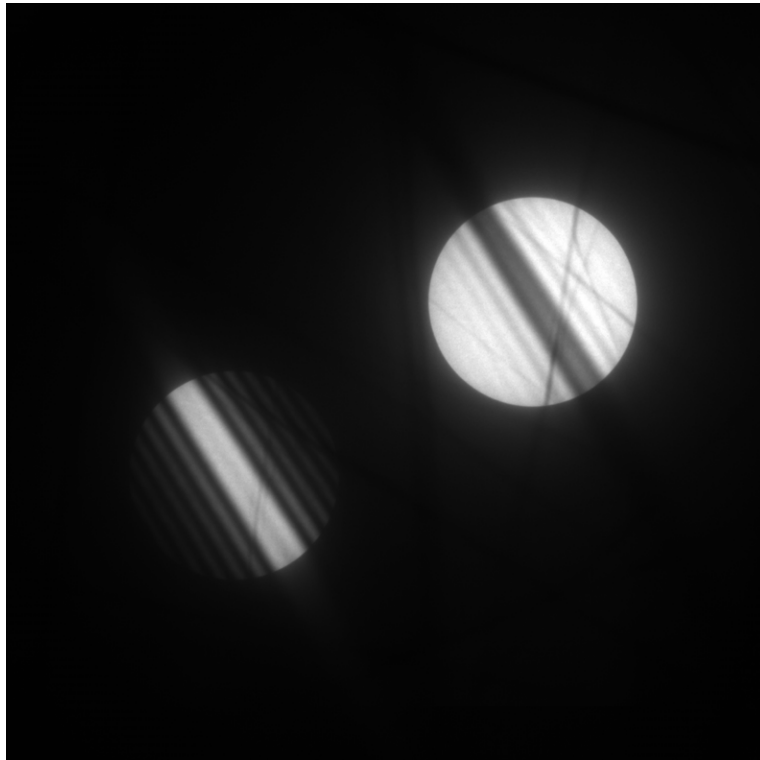
- Experimental 2-beam CBED pattern:



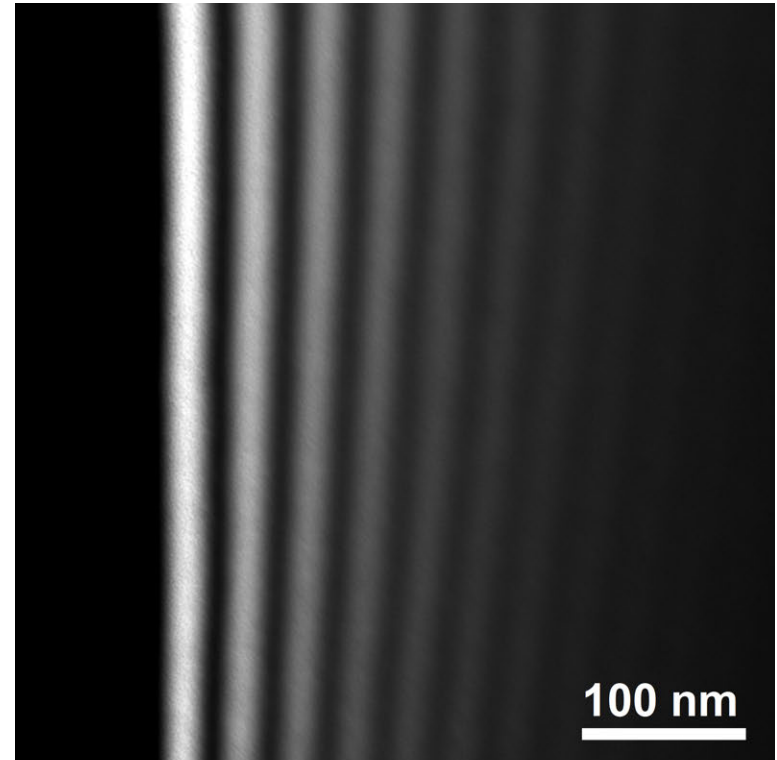
EPFL Deficiencies of kinematical model

- As sample thickness t increases for $s = 0$, $I_g > 1$
- Cannot explain experimental data e.g.:

2-beam CBED pattern



Dark-field image of wedge-shaped sample



EPFL Dynamical scattering

- Kinematical model very successful for predicting geometry of diffraction data.
- *However does not predict intensities well.* Because electrons are strongly scattered by atoms!
- On propagation of electron beam through crystal lattice this leads to multiple elastic scattering: called *dynamical scattering*
- The first Born approximation does not apply, except for very thin and weakly scattering objects!
- Introduce Bloch wave theory as generally-applicable approach for treating dynamical scattering

EPFL Dynamical theory: Bloch wave approach

- Aim: solve Schrödinger equation for wave function of fast electrons within crystal lattice
- Take eq. 1.16, but now define $\phi(\vec{r})$ as crystal potential:

$$\nabla^2 \psi(\vec{r}) + \frac{8\pi^2 me}{h^2} [E_0 + \phi(\vec{r})] \psi(\vec{r}) = 0 \quad (2.14)$$

- Expand periodic potential of lattice as a Fourier series based on the reciprocal lattice:

$$\phi(\vec{r}) = \sum_{-\infty}^{\infty} V_g \exp(2\pi i \vec{g} \cdot \vec{r}) \quad (2.15)$$

$$V_g = \frac{F_g}{V_c} \quad (2.16)$$

EPFL Dynamical theory: Bloch wave approach

- Full solution of eq. 2.14 written as linear superposition of Bloch waves $\psi(\vec{r})$:

$$\Psi(\vec{r}) = \sum_j \alpha^{(j)} \psi^{(j)}(\vec{r}) \quad (2.17)$$

- Each Bloch wave is an eigen solution of eq. 2.14
- Amplitudes $\alpha^{(j)}$ are determined by boundary conditions
- Being inside a periodic crystal lattice, each Bloch wave can be represented by:

$$\psi(\vec{r}) = u_k(\vec{r}) \exp(2\pi i \vec{k} \cdot \vec{r}) \quad (2.18)$$

where $u_k(\vec{r})$ has periodicity of the lattice

EPFL Dynamical theory: Bloch wave approach

- Wave function can then be expanded as a Fourier series based on the reciprocal lattice to give:

$$\psi(\vec{r}) = \sum_g C_g \exp\left[2\pi i(\vec{k} + \vec{g}) \cdot \vec{r}\right] \quad (2.19)$$

- C_g are the Bloch wave coefficients
- Collect coefficients together by defining “modified potential” $U(\vec{r})$ with Fourier coefficients:

$$U_g = \frac{2me}{h^2} V_g \quad (2.20)$$

- Define κ as the mean electron wave vector in the crystal after allowing for mean crystal potential ϕ_0

$$\kappa^2 = \frac{2me}{h^2} (E_0 + \phi_0) \quad (2.21)$$

(c.f. equations 1.17)

EPFL Dynamical theory: Bloch wave approach

- Substitute eqs 2.19–2.21 in the Schrödinger equation 2.14:

$$\sum_g \left\{ \left[\kappa^2 - (\vec{k} + \vec{g})^2 \right] C_g + \sum_{h \neq g} U_{g-h} C_h \right\} \exp \left[2\pi i (\vec{k} + \vec{g}) \cdot \vec{r} \right] = 0 \quad (2.22)$$

- This equation holds for all points $\vec{r}$ in crystal. Therefore coefficient of each exponential term must be equal to zero:

$$\left[\kappa^2 - (\vec{k} + \vec{g})^2 \right] C_g + \sum_{h \neq g} U_{g-h} C_h = 0 \quad (2.23)$$

EPFL Bloch wave: 2-beam approximation

- Consider 2-beam case with strong scattering from only one plane
– i.e. diffraction pattern with direct beam and one diffracted beam $\bar{\mathbf{g}}$
- Eq. 2.19 terminated after two terms:

$$\psi(\bar{\mathbf{r}}) = C_0 \exp(2\pi i \bar{\mathbf{k}} \cdot \bar{\mathbf{r}}) + C_g \exp[2\pi i (\bar{\mathbf{k}} + \bar{\mathbf{g}}) \cdot \bar{\mathbf{r}}] \quad (2.24)$$

- Eq. 2.23 gives two equations:

$$\begin{aligned} [\kappa^2 - \bar{\mathbf{k}}^2] C_0 + U_{-g} C_g &= 0 \\ [\kappa^2 - (\bar{\mathbf{k}} + \bar{\mathbf{g}})^2] C_g + U_g C_0 &= 0 \end{aligned} \quad (2.25)$$

EPFL Bloch wave: 2-beam approximation

- Rewrite these two equations in matrix form:

$$\begin{pmatrix} \kappa^2 - k^2 & U_{-g} \\ U_g & \kappa^2 - (\bar{\mathbf{k}} + \bar{\mathbf{g}})^2 \end{pmatrix} \begin{pmatrix} C_0 \\ C_g \end{pmatrix} = 0 \quad (2.26)$$

- Solution if determinant of the coefficients is equal to zero:

$$\begin{vmatrix} \kappa^2 - k^2 & U_{-g} \\ U_g & \kappa^2 - (\bar{\mathbf{k}} + \bar{\mathbf{g}})^2 \end{vmatrix} = 0 \quad (2.27)$$

EPFL Bloch wave: 2-beam approximation

- Make high energy approximation:

$$\begin{aligned}\kappa^2 - k^2 &= 2\kappa(\kappa - k) \\ \kappa^2 - (\bar{\mathbf{k}} + \bar{\mathbf{g}})^2 &= 2\kappa(\kappa - |\bar{\mathbf{k}} + \bar{\mathbf{g}}|)\end{aligned}\tag{2.28}$$

- Eq. 2.27 becomes:

$$(\kappa - k)(\kappa - |\bar{\mathbf{k}} + \bar{\mathbf{g}}|) = \frac{U_g U_{-g}}{4\kappa^2}\tag{2.29}$$

- 2 values of wave vector $\bar{\mathbf{k}}^{(1)}$ and $\bar{\mathbf{k}}^{(2)}$ inside the crystal, one for each Bloch wave

EPFL Meaning of 2 (or more) Bloch waves

- Incident beam partitioned into Bloch waves in crystal. Each Bloch wave propagates with different wave vector $\vec{k}^{(j)}$ so they become out of phase with each other.
- Leads to interference: crystal acts as interferometer.
- Entrance surface: need to match incident wave with total wave in crystal. Ψ and $\nabla\Psi$ must be continuous.
- Define z as downward normal to crystal surface. Let $k_z^{(j)}$ and $k_t^{(j)}$ be components of $\vec{k}^{(j)}$ in z direction and plane of surface.
- For symmetrical Laue case – $\vec{g}$ parallel to surface – tangential $k_t^{(j)}$ components must be equal and equal to tangential component of $\vec{k}_0$. Therefore set $k_t^{(j)} = k_t$
- Also: $\alpha^{(j)} = C_0^{*(j)}$

EPFL Dispersion surfaces

- Considering a general case, eq. 2.26 becomes:

$$\begin{pmatrix} \kappa^2 - (k^{(j)})^2 & U_{-g} \\ U_g & \kappa^2 - (\bar{\mathbf{k}}^{(j)} + \bar{\mathbf{g}})^2 \end{pmatrix} \begin{pmatrix} C_0^{(j)} \\ C_g^{(j)} \end{pmatrix} = 0 \quad (2.30)$$

- Further high energy approximations yield:

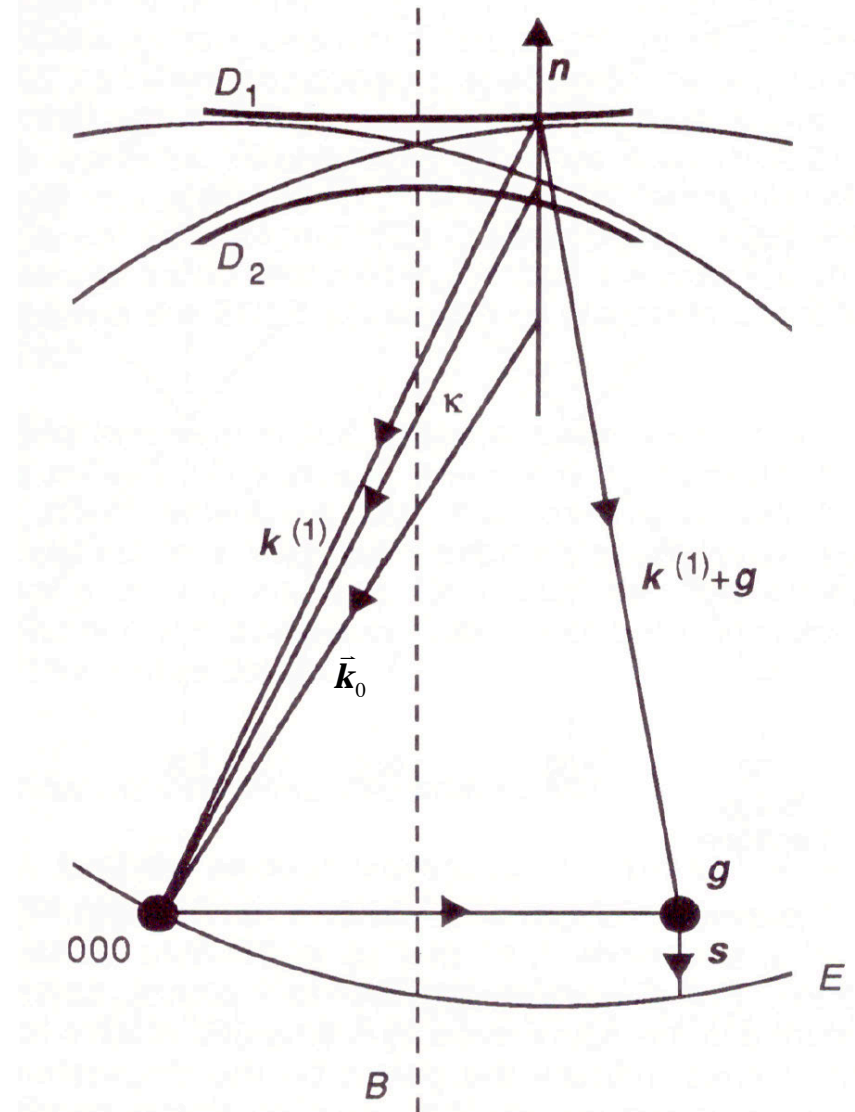
$$\begin{aligned} \kappa^2 - (k^{(j)})^2 &\approx 2\kappa(\kappa - k_z^{(j)}) - k_t^2 \\ \kappa^2 - (\bar{\mathbf{k}}^{(j)} + \bar{\mathbf{g}})^2 &\approx 2\kappa(\kappa - k_z^{(j)}) - (k_t + g)^2 \end{aligned} \quad (2.31)$$

- Together yielding:

$$\frac{1}{2\kappa} \begin{pmatrix} -k_t^2 & U_{-g} \\ U_g & -(k_t + g)^2 \end{pmatrix} \begin{pmatrix} C_0^{(j)} \\ C_g^{(j)} \end{pmatrix} = (k_z^{(j)} - \kappa) \begin{pmatrix} C_0^{(j)} \\ C_g^{(j)} \end{pmatrix} \quad (2.32)$$

EPFL Dispersion surfaces

- Dispersion surface:
plot of permitted values of $k_z^{(j)}$ against k_t
- Calculated by solving eq. 2.32
- $\bar{\mathbf{k}}^{(j)}$ values found by plotting normal to end of incident wave vector $\bar{\mathbf{k}}_0$ and identifying its intersection with the branches



EPFL Diffracted beam intensities

- From eqs 2.17 and 2.1 total wave function is:

$$\Psi(\vec{r}) = \sum_j \alpha^{(j)} \psi^{(j)}(\vec{r}) = \sum_j \alpha^{(j)} \sum_g C_g^{(j)} \exp\left[2\pi i (\vec{k}^{(j)} + \vec{g}) \cdot \vec{r}\right] \quad (2.33)$$

- At bottom of crystal thickness t the Bloch waves decouple into their plane wave components.

For zero order Laue zone ($g_z = 0$) amplitude in diffracted beam direction $(\vec{k} + \vec{g})$ is:

$$\varphi_g(t) = \sum_j \alpha^{(j)} \sum_g C_g^{(j)} \exp(2\pi i k_z^{(j)} t) \quad (2.34)$$

where $\alpha^{(j)} = C_0^{*(j)}$

EPFL Diffracted beam intensities

- Intensity in diffracted beam is then:

$$I_g(t) = \left| \sum_j C_0^{(j)*} C_g^{(j)} \exp(2\pi i k_z^{(j)} t) \right|^2 \quad (2.35)$$

- Further at exact Bragg $k_t = -0.5g$: $k_z^{(1)} - k_z^{(2)} = \frac{U_g}{\kappa \cos \theta_B}$ (2.36)

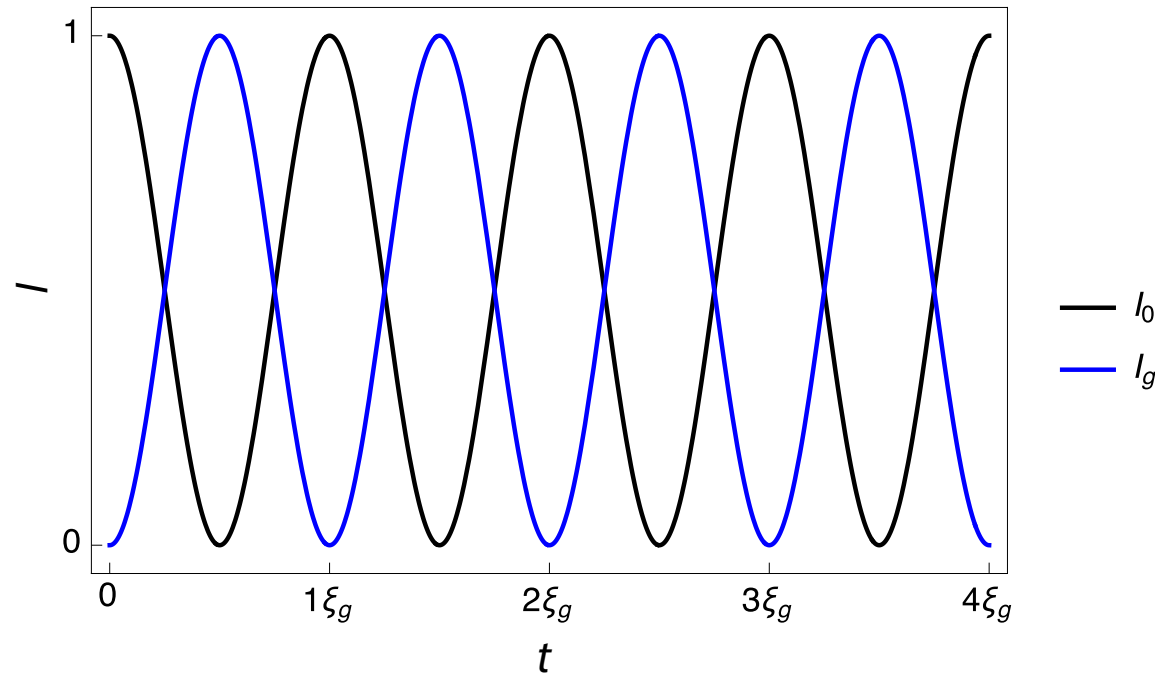
$$C_0^{(1)} = C_0^{(2)} = C_g^{(1)} = -C_g^{(2)} = \frac{1}{\sqrt{2}} \quad (2.37)$$

- Extinction distance: $\xi_g = \frac{1}{k_z^{(1)} - k_z^{(2)}} = \frac{\kappa \cos \theta_B}{U_g}$ (2.38)

EPFL Diffracted beam intensities

- From eqs 2.35–2.38, *at exact Bragg condition*:

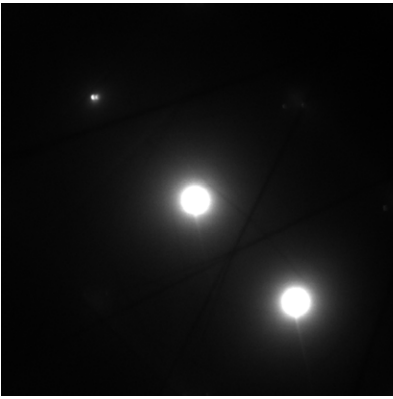
$$I_g(t) = \sin^2\left(\frac{\pi t}{\xi_g}\right) \quad I_0(t) = 1 - I_g(t) = \cos^2\left(\frac{\pi t}{\xi_g}\right) \quad (2.39)$$



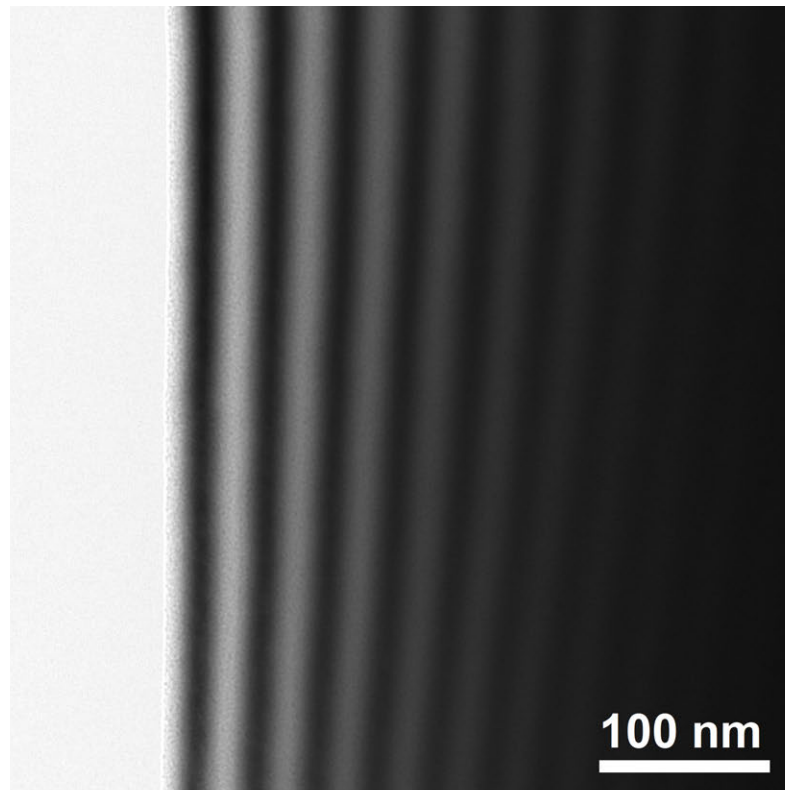
EPFL Thickness fringes

- Bright-field and dark-field imaging of Si cleaved wedge at 2-beam condition

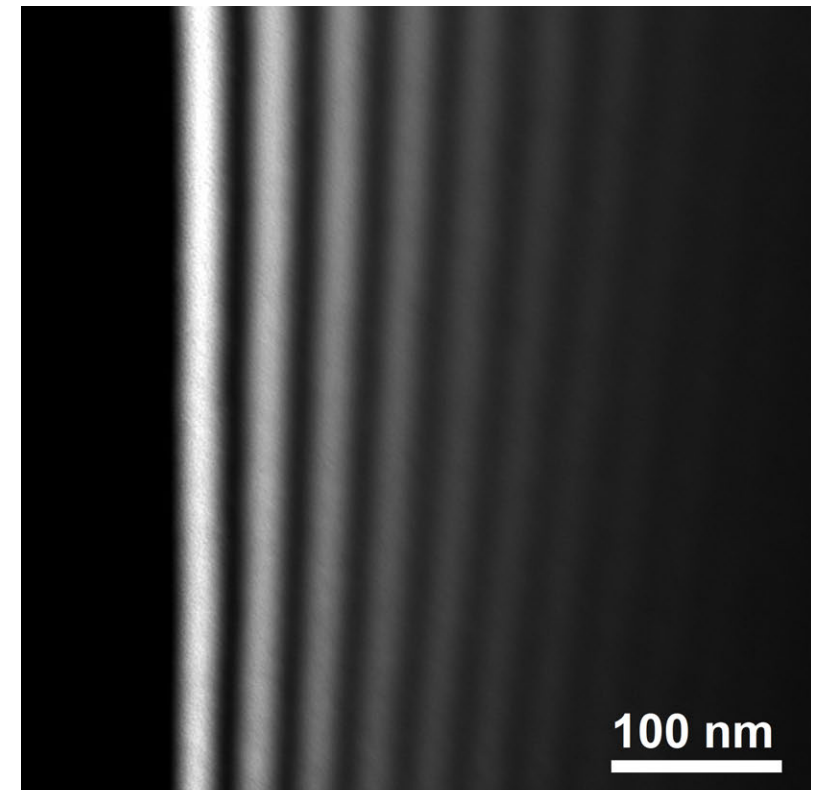
Diffraction



Bright field



Dark field

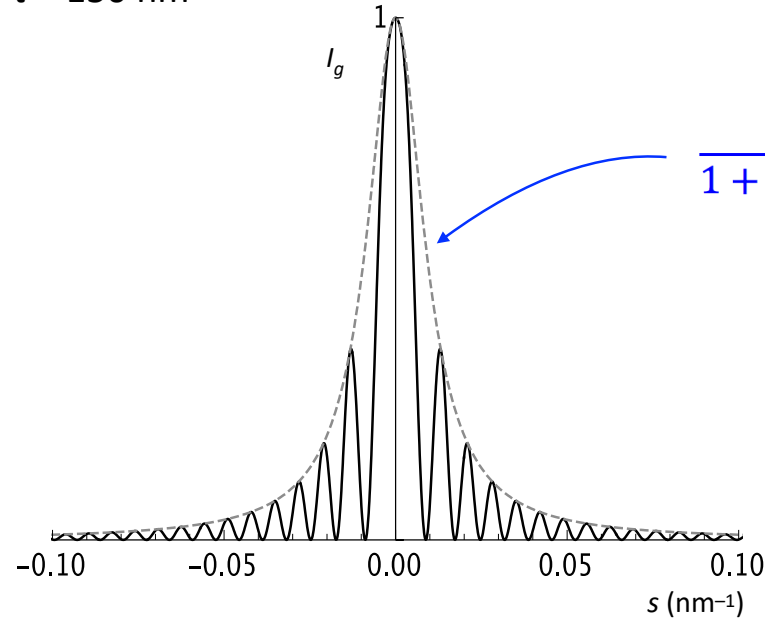


EPFL Diffracted beam intensities

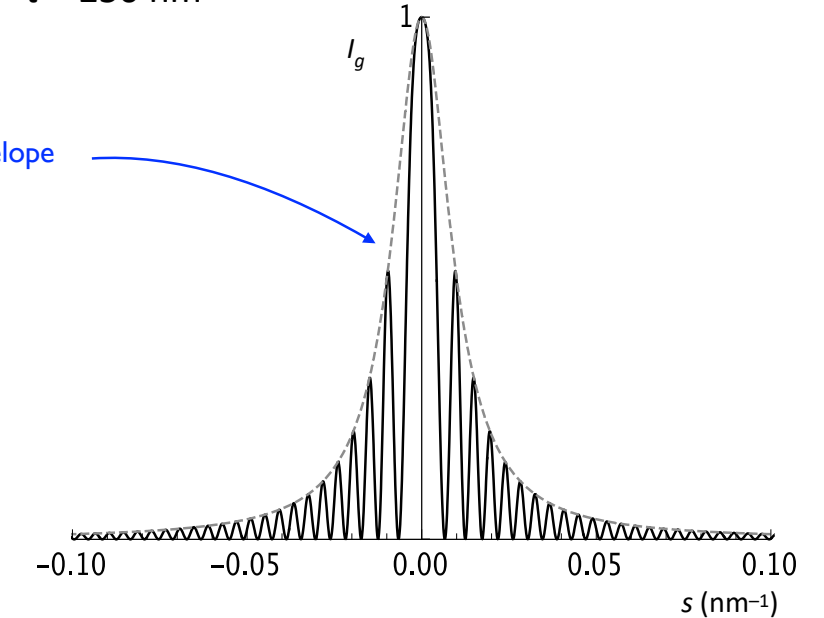
- More generally:
$$I_g(t) = \frac{1}{1 + \xi_g^2 s^2} \sin^2 \left(\pi t \sqrt{\frac{1}{\xi_g^2} + s^2} \right) \quad I_0(t) = 1 - I_g(t) \quad (2.40)$$

- Model I_g vs s for $\xi_g = 100$ nm

$t = 150$ nm



$t = 250$ nm

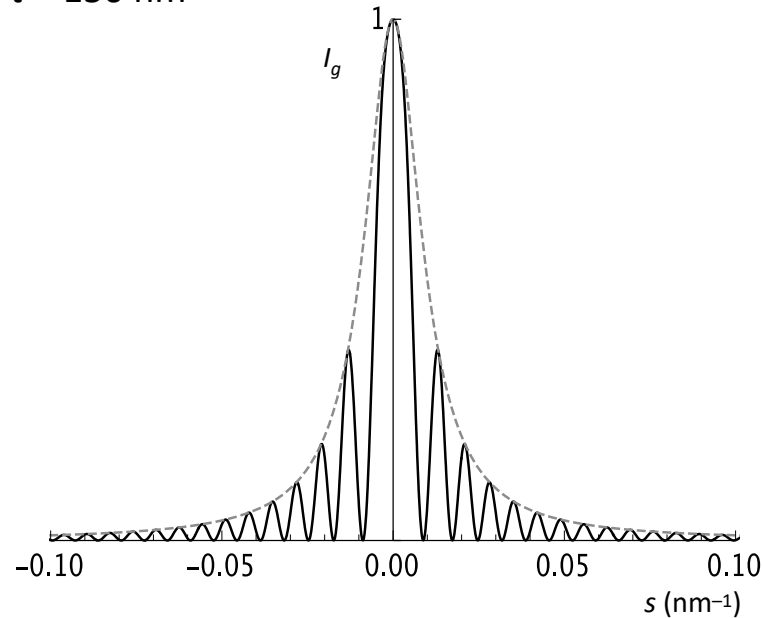


$\frac{1}{1 + \xi_g^2 s^2}$ envelope

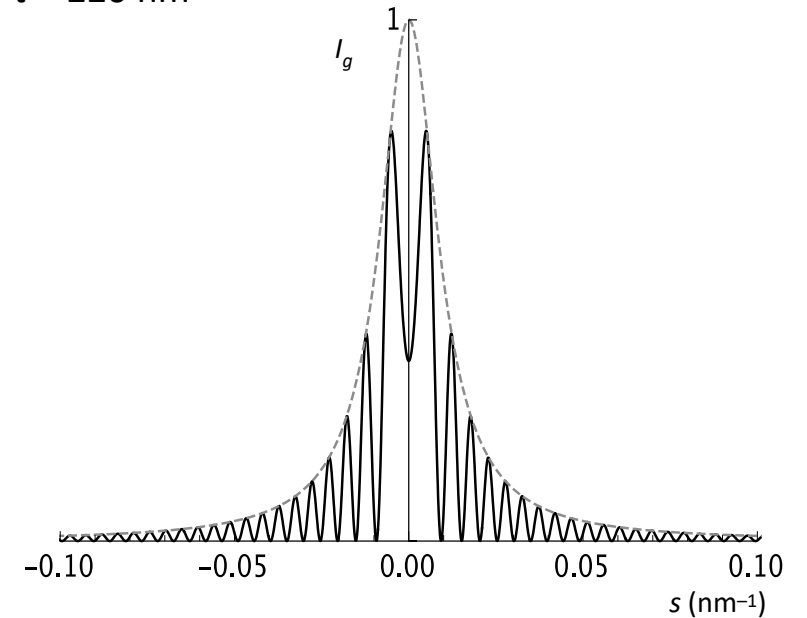
EPFL Diffracted beam intensities

- More generally:
$$I_g(t) = \frac{1}{1 + \xi_g^2 s^2} \sin^2 \left(\pi t \sqrt{\frac{1}{\xi_g^2} + s^2} \right) \quad I_0(t) = 1 - I_g(t) \quad (2.40)$$
- Model I_g vs s for $\xi_g = 100$ nm

$t = 150$ nm



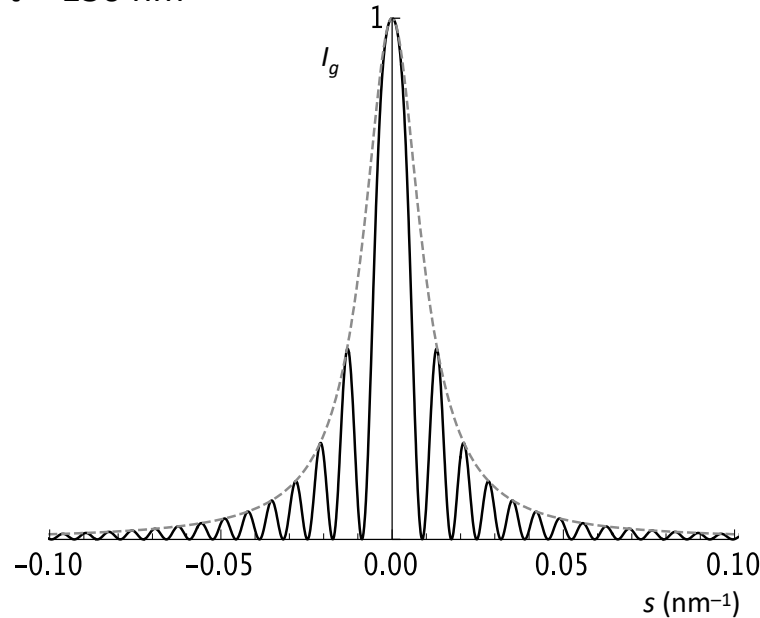
$t = 220$ nm



EPFL Diffracted beam intensities

- More generally:
$$I_g(t) = \frac{1}{1 + \xi_g^2 s^2} \sin^2 \left(\pi t \sqrt{\frac{1}{\xi_g^2} + s^2} \right) \quad I_0(t) = 1 - I_g(t) \quad (2.40)$$
- Model I_g vs s for $\xi_g = 100$ nm

$t = 150$ nm



$t = 200$ nm

