

Electron-matter interactions: Elastic scattering (II)

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EPFL-IPHYS-LSME

EPFL Contents

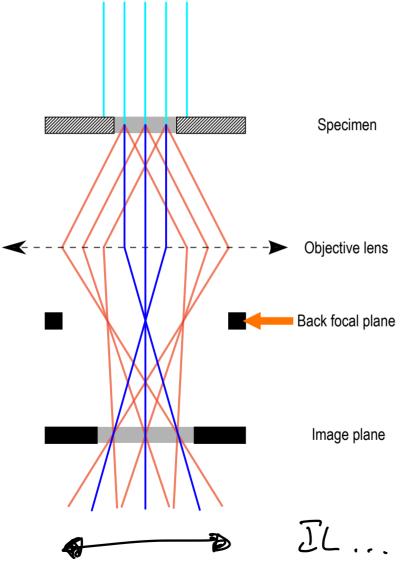
Part A: scattering from a crystal lattice – kinematical

- 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

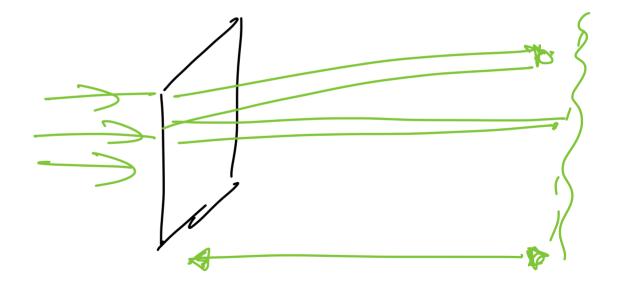
Part B: dynamical theory – Bloch wave approach

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

EPFL Diffraction pattern formation



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



EPFL Bragg law

• Constructive interference for:

$$n\lambda = 2d_{hkl}\sin\theta$$

(1.36)

Plano spacing with a day

Pall di Norme: 2d44,5,20 For constructive interleunce = a A $\lambda = 2d_{nhahal} \sin \theta$

=> A = 2dsinds

TEM: 12 2dos

• Crystalline sample tilted such that one plane at Bragg angle $\theta_{\rm B}$ relative to $k_0 \Longrightarrow$ 2-beam diffraction pattern:

het: (200) (400) (600) (800)



EPFL Laue condition

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

Laue condition:

$$\vec{\boldsymbol{q}} = \vec{\boldsymbol{k}}' - \vec{\boldsymbol{k}}_0 = \vec{\boldsymbol{g}}$$

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

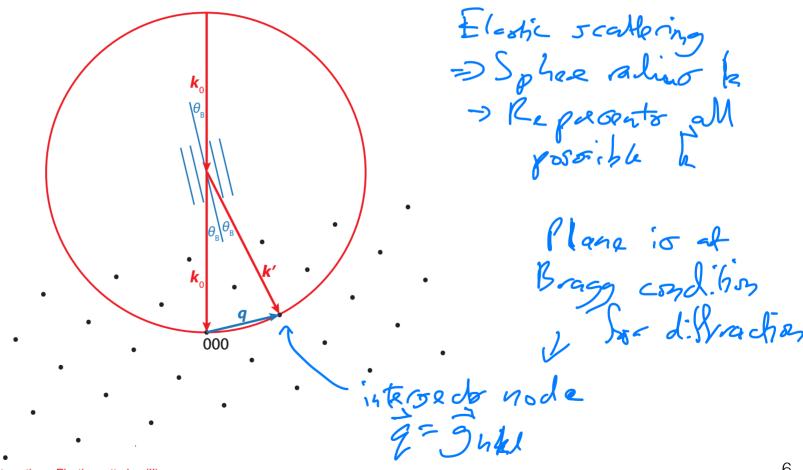
"Reciprocal lative vector for plana (hkl)

$$\frac{1}{3} = \frac{1}{3} = \frac{1}$$

(1.37)

EPFL Ewald sphere/reciprocal lattice construction

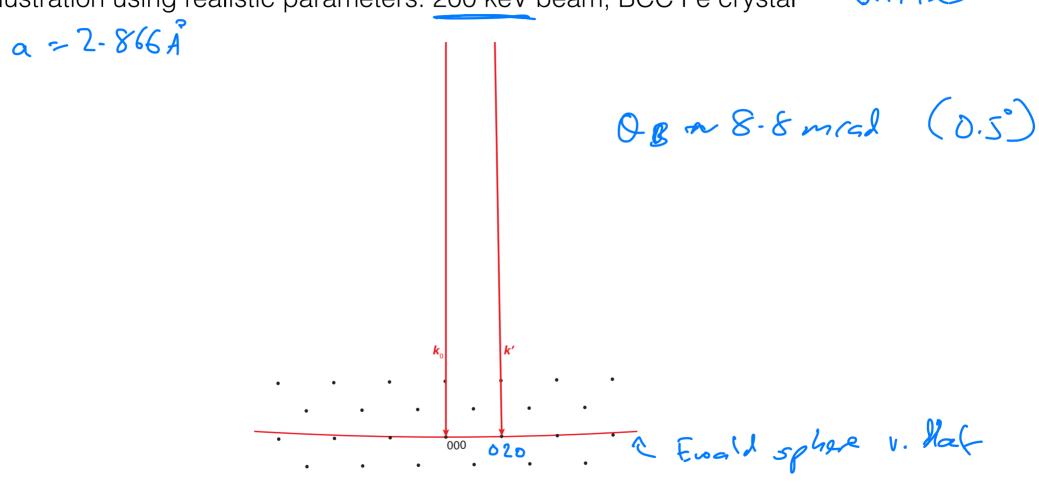
 Ewald sphere/reciprocal lattice construction provides method to identify which plane(s) diffract under chosen incident beam/crystal geometry



EPFL Ewald sphere/reciprocal lattice construction

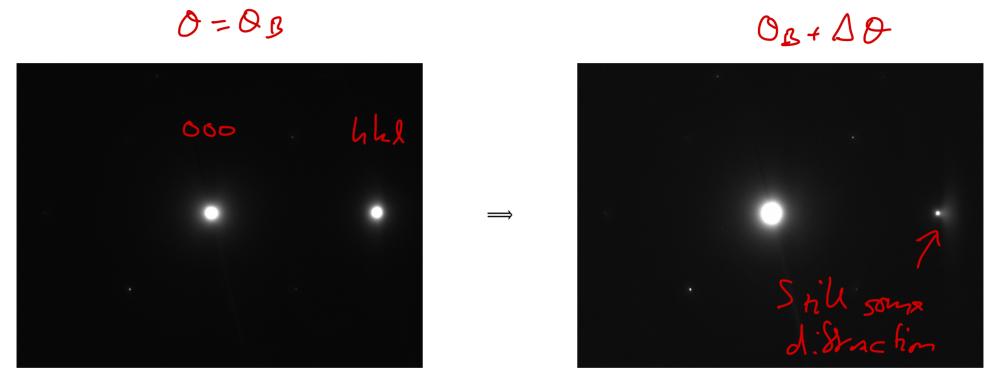
Illustration using realistic parameters: 200 keV beam, BCC Fe crystal

Gerrite)



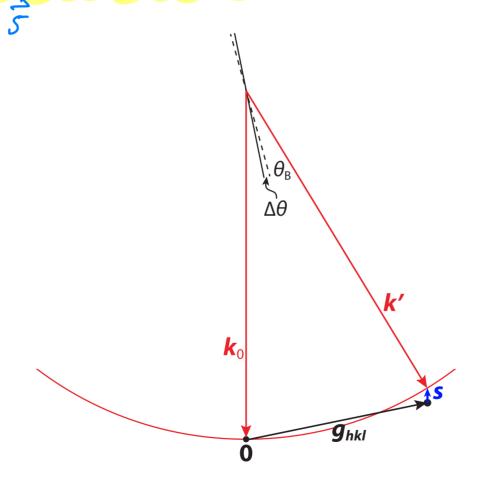
EPFL Diffraction away from exact Bragg condition

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



EPFL Deviation parameter

Introduce deviation parameter vector to describe deviation from Bragg:



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

The property deviations from parted Bragg

Conditions

 \vec{s} : outside Ewooldsphee

-ve

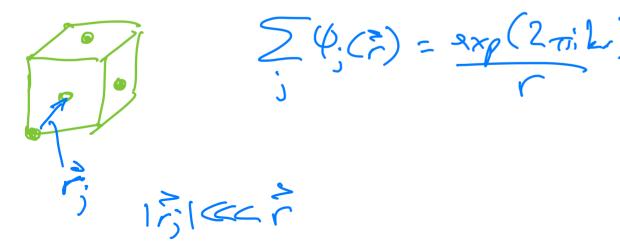
: in side: +ve

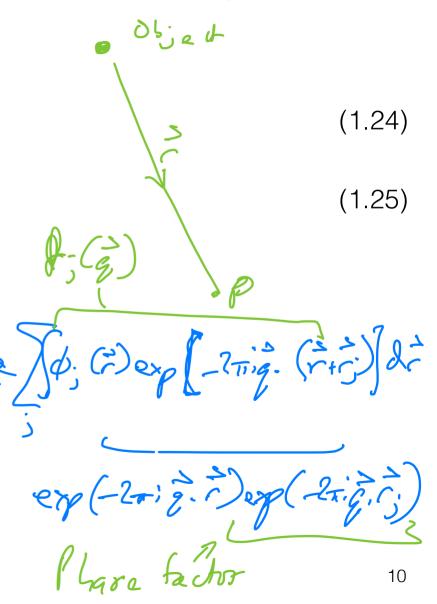
• From last week, scattering amplitude for one atom:

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

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

Consider assembly of atoms into a unit cell:



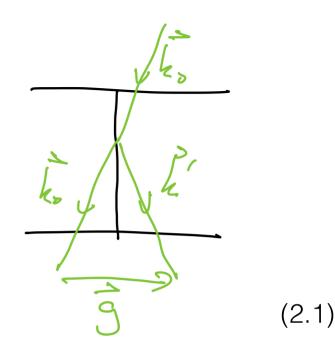


EPFL Scattering from a unit cell

Total scattered wave from unit cell is:

$$\psi_{s}(\vec{r}) = \frac{\exp\{2\pi i k r\}}{r} \sum_{j} f_{j} \exp(-2\pi i \vec{q} \cdot \vec{r}_{j})$$

$$= \frac{\exp\{2\pi i k r\}}{r} F(\vec{q})$$



• Defines the structure amplitude $F(\bar{q})$ for the unit cell

Scalleing amplihde for atoms accanged in anit cell

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

$$\vec{q} = \vec{g} + \vec{s} \tag{2.2}$$

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

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

$$a.b = 0$$
 (2.3)

$$\vec{r}_n = n_x \vec{a} + n_y \vec{b} + n_z \vec{c}$$

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

$$\psi_{s}(\vec{r}) = \frac{\exp\{2\pi i kr\}}{r} \sum_{n_{x}} \sum_{n_{y}} \sum_{n_{z}} F(\vec{q}) \exp\left[-2\pi i \left(n_{x} a s_{x} + n_{y} b s_{y} + n_{z} c s_{z}\right)\right]$$
(2.5)

$$a = (a)$$

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

$$\sum_{A} \exp(-2\pi i A \alpha s_{\alpha}) = \frac{\sin(\pi A \alpha s_{\alpha})}{\sin(\pi \alpha s_{\alpha})}$$
 (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:

$$\psi_{s}(\vec{r}) = \frac{\exp\{2\pi i kr\}}{r} F(\vec{q}) \left[\frac{\sin(\pi N_{x} as_{x})}{\sin(\pi as_{x})} \right] \left[\frac{\sin(\pi N_{y} bs_{y})}{\sin(\pi bs_{y})} \right] \left[\frac{\sin(\pi N_{z} cs_{z})}{\sin(\pi cs_{z})} \right]$$

$$(2.7)$$

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

t: Hickory

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

$$I_{s}(\vec{r}) = \left[\frac{\left|\exp\{2\pi i kr\}\right|}{r} \frac{F(\vec{q})}{V_{c}}\right]^{2} \times D_{x} \delta(s_{x}) D_{y} \delta(s_{y}) \times \left[\frac{\sin(\pi N_{z} c s_{z})}{\pi s_{z}}\right]^{2}$$

$$(2.8)$$

- 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:

$$d\Omega = \frac{ds_x ds_y}{k^2 \cos \theta}$$



• From eq. 2.8:
$$I_{s}(\vec{r}) = D_{x}D_{y} \left[\frac{F(\vec{q})}{rV_{c}} | \exp\{2\pi i kr\}| \right]^{2} \left[\frac{\sin(\pi N_{z}cs_{z})}{\pi s_{z}} \right]^{2} \underline{\delta(s_{x})\delta(s_{y})}$$

• The intensity scattered in direction near \vec{g} with deviation parameter s_z is:

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

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

Scallers was
$$I_{g} = \left[\frac{F_{g}}{\pi k V_{c} \cos \theta_{B}} \frac{\sin(\pi t s_{z})}{s_{z}}\right]^{2}$$

$$\text{ (Huygen's principle)}$$
 where F_{g} is $|F(\bar{g})|$ for the reflection \bar{g}



(2.9)



EPFL Fourier transform equivalence

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

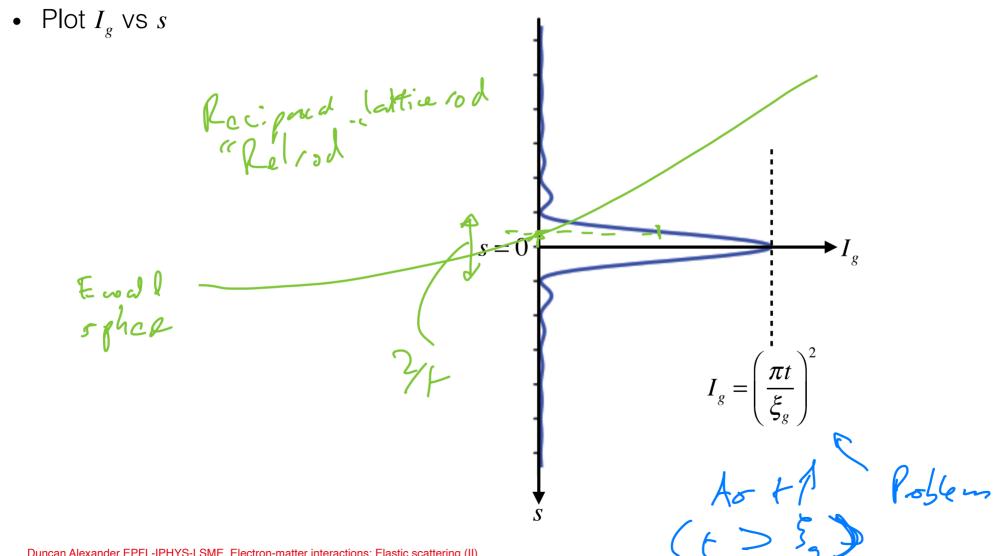
$$\psi_{s}(\vec{r}) = \frac{\exp\{2\pi i kr\}}{r} \int \frac{F(\vec{q})}{V_{c}} \exp(-2\pi i \vec{s} \cdot \vec{r}') d\vec{r}'$$

$$(2.13)$$

- 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": $\xi_g = \frac{\pi k V_c \cos \theta_B}{F_g}$ (2.11)
- Then: $I_g = \left[\frac{\sin(\pi t s_z)}{\xi_g s_z}\right]^2 \tag{2.12}$

- 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

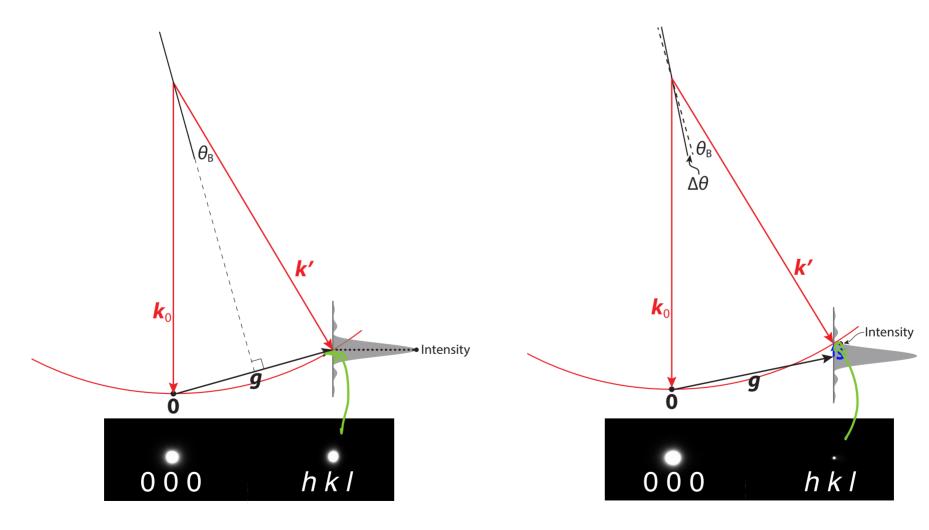
EPFL I_g vs excitation error s



EPFL Interaction with Ewald sphere

Exact Bragg condition

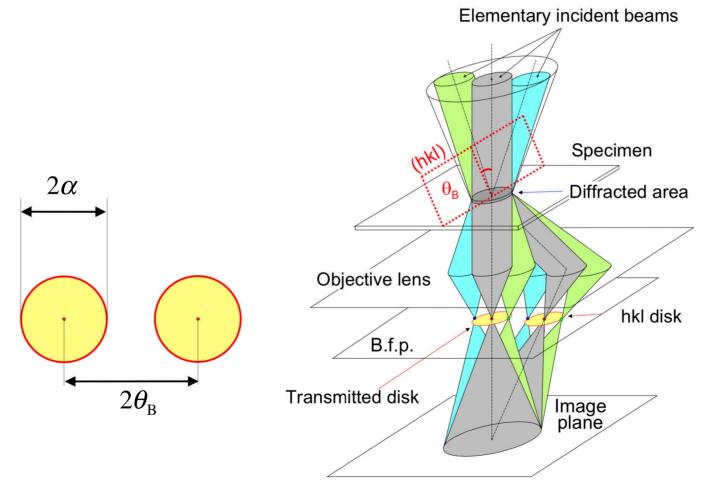
Near Bragg condition



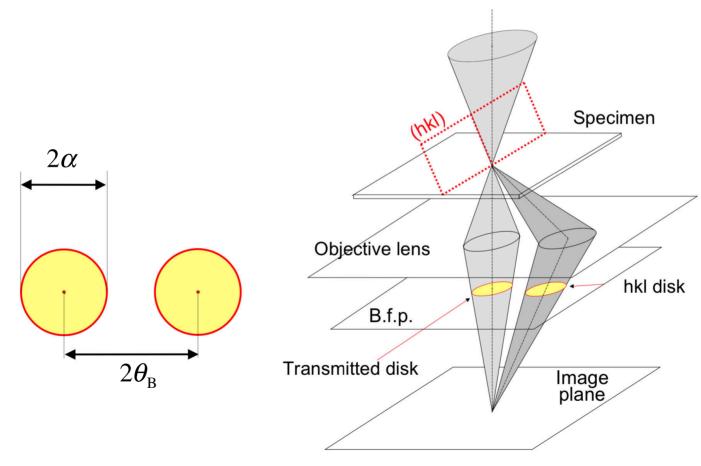
EPFL Methods for measuring I_g vs s

• How could we measure I_g vs s experimentally?

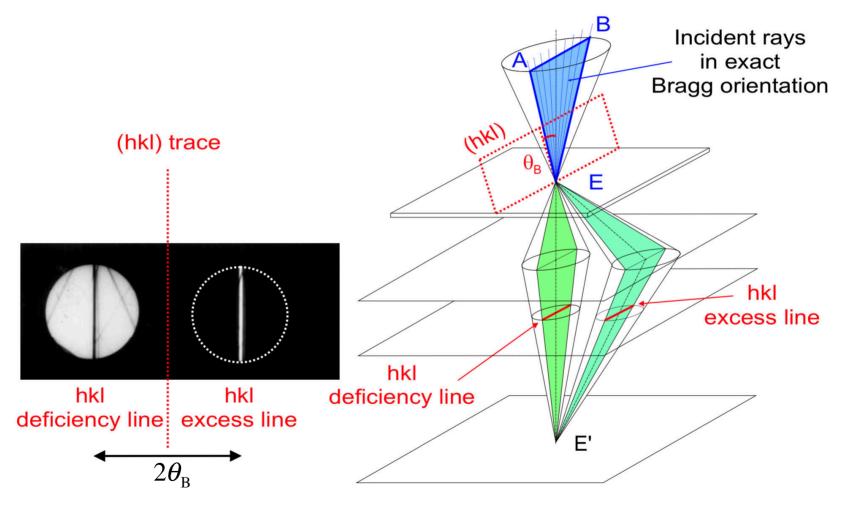
• 2-beam illustration with semi-focused beam (from J.-P. Morniroli)



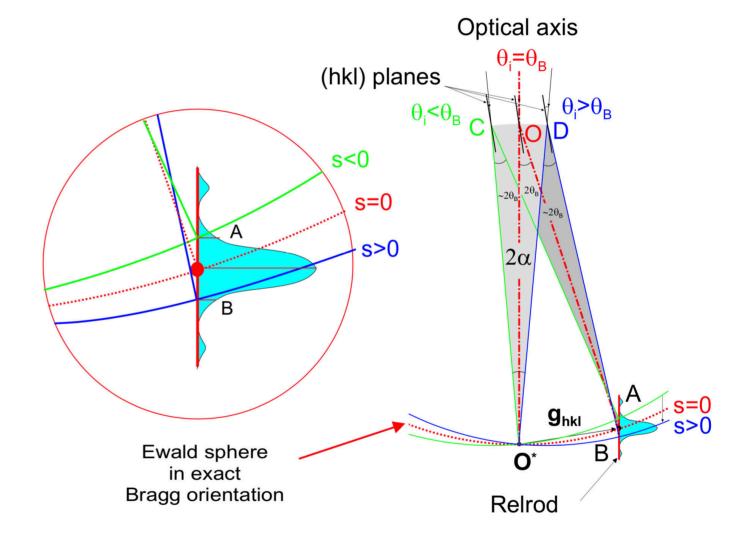
• 2-beam illustration with fully-focused beam (from J.-P. Morniroli)



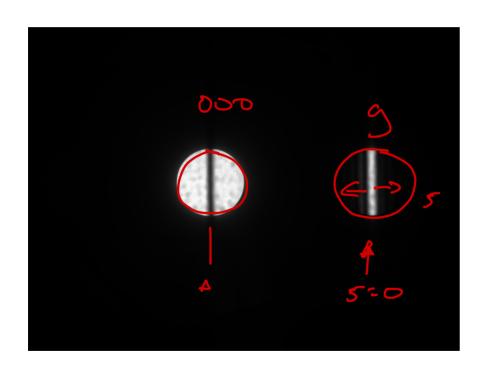
• 2-beam illustration with fully-focused beam (from J.-P. Morniroli)

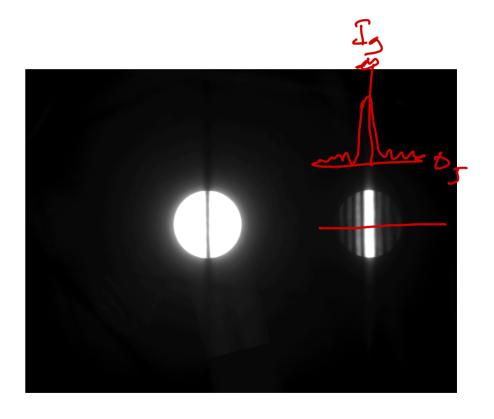


- Diffracted beam CBED disc contains different ray paths that have sampled different excitation errors s
- Illustrate with Ewald sphere construction (diagram from J.-P. Morniroli)



• Experimental 2-beam CBED pattern:

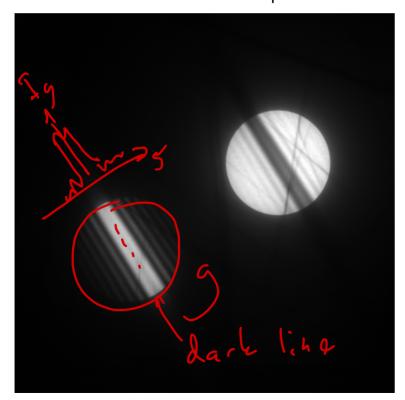


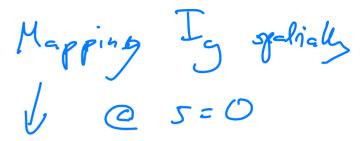


EPFL Deficiencies of kinematical model

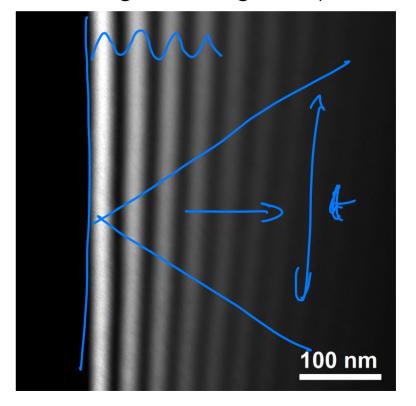
- As sample thickness t increases for s = 0, $I_g > 1$
- Cannot explain experimental data e.g.:

2-beam CBED pattern



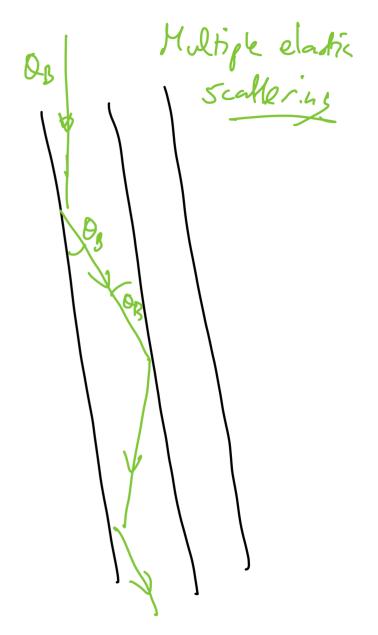


Dark-field image of wedge-shaped sample



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



- 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:

$$\nabla^{2}\psi(\bar{\mathbf{r}}) + \frac{8\pi^{2}me}{h^{2}} \left[E_{0} + \phi(\bar{\mathbf{r}})\right]\psi(\bar{\mathbf{r}}) = 0$$
(2.14)

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

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

$$V_g = \frac{F_g}{V_g} \tag{2.16}$$

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

$$\Psi(\bar{\mathbf{r}}) = \sum_{i} \alpha^{(j)} \psi^{(j)}(\bar{\mathbf{r}})$$
 (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:

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

where $u_{\scriptscriptstyle k}(ar{m{r}})$ has periodicity of the lattice

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

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

- ullet C_g are the Bloch wave coefficients
- Collect coefficients together by defining "modified potential" $U(\bar{r})$ with Fourier coefficients: $U_g = \frac{2me}{h^2} V_g$

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

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

(c.f. equations 1.17) 4

(2.20)

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

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

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

$$\left[\kappa^{2} - (\bar{\mathbf{k}} + \bar{\mathbf{g}})^{2}\right] C_{g} + \sum_{h \neq g} U_{g-h} C_{h} = 0$$

$$n \quad \text{reductions on a partition of } n \quad \text{Block wave solution}$$

$$n \quad \text{determines accuracy of solution}$$

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{g}
- Eq. 2.19 terminated after two terms:

$$\psi(\vec{r}) = C_0 \exp(2\pi i \vec{k} \cdot \vec{r}) + C_g \exp\left[2\pi i (\vec{k} + \vec{g}) \cdot \vec{r}\right]$$
• Eq. 2.23 gives two equations:
$$(2.24)$$

$$\left[\kappa^{2} - \vec{k}^{2}\right]C_{0} + U_{-g}C_{g} = 0$$

$$\left[\kappa^{2} - \left(\vec{k} + \vec{g}\right)^{2}\right]C_{g} + U_{g}C_{0} = 0$$
(2.25)

EPFL Bloch wave: 2-beam approximation

Rewrite these two equations in matrix form:

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

Solution if determinant of the coefficients is equal to zero:

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

EPFL Bloch wave: 2-beam approximation

Make high energy approximation:

$$\kappa^{2} - k^{2} = 2\kappa(\kappa - k)$$

$$\approx 2\kappa$$

$$\kappa^{2} - (\bar{k} + \bar{g})^{2} = 2\kappa(\kappa - |\bar{k} + \bar{g}|)$$

$$\kappa^{2} - (\bar{k} + \bar{g})^{2} = 2\kappa(\kappa - |\bar{k} + \bar{g}|)$$

$$\kappa^{2} - (\bar{k} + \bar{g})^{2} = 2\kappa(\kappa - |\bar{k} + \bar{g}|)$$
(2.28)

• Eq. 2.27 becomes:

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

• 2 values of wave vector $\vec{\pmb{k}}^{(1)}$ and $\vec{\pmb{k}}^{(2)}$ 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 ∇Ψ 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:

$$\begin{pmatrix} \kappa^2 - \left(k^{(j)}\right)^2 & U_{-g} \\ U_g & \kappa^2 - \left(\vec{\boldsymbol{k}}^{(j)} + \vec{\boldsymbol{g}}\right)^2 \end{pmatrix} \begin{pmatrix} C_0^{(j)} \\ C_g^{(j)} \end{pmatrix} = 0$$
 (2.30)

Further high energy approximations yield:

$$\kappa^{2} - \left(k^{(j)}\right)^{2} \approx 2\kappa \left(\kappa - k_{z}^{(j)}\right) - k_{t}^{2}$$

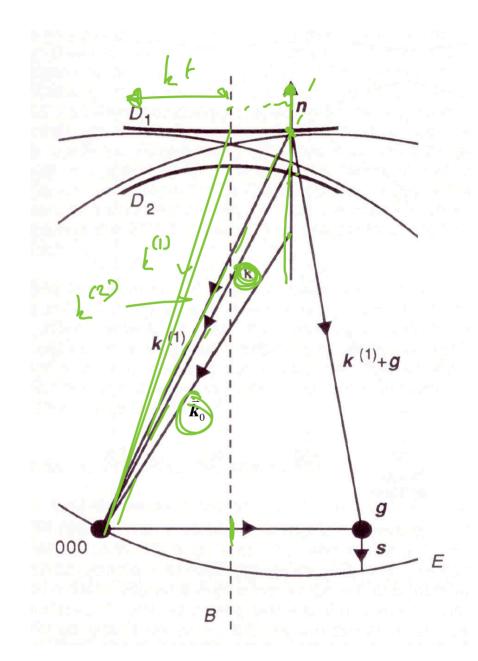
$$\kappa^{2} - \left(\vec{k}^{(j)} + \vec{g}\right)^{2} \approx 2\kappa \left(\kappa - k_{z}^{(j)}\right) - \left(k_{t} + g\right)^{2}$$
(2.31)

Together yielding:

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

EPFL Dispersion surfaces

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



From eqs 2.17 and 2.1 total wave function is:

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

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

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

Intensity in diffracted beam is then:

$$I_{g}(t) = \left| \sum_{j} C_{0}^{(j)*} C_{g}^{(j)} \exp(2\pi i k_{z}^{(j)} t) \right|^{2}$$
(2.35)

• Further at exact Bragg $k_t = -0.5g$:

$$k_z^{(1)} - k_z^{(2)} = \frac{U_g}{\kappa \cos \theta_{\rm B}}$$

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

• Extinction distance:

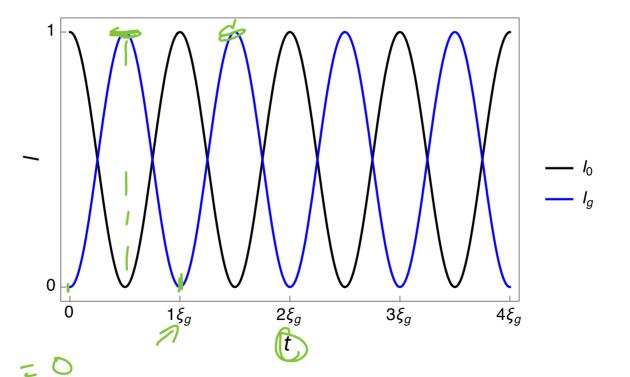
$$\xi_g = \frac{1}{k_z^{(1)} - k_z^{(2)}} = \frac{\kappa \cos \theta_{\rm B}}{U_g}$$

(2.38)

(2.36)

• From eqs 2.35–2.38, at exact Bragg condition:

$$I_{g}(t) = \sin^{2}\left(\frac{\pi t}{\xi_{g}}\right) \qquad I_{0}(t) = 1 - I_{g}(t) = \cos^{2}\left(\frac{\pi t}{\xi_{g}}\right)$$

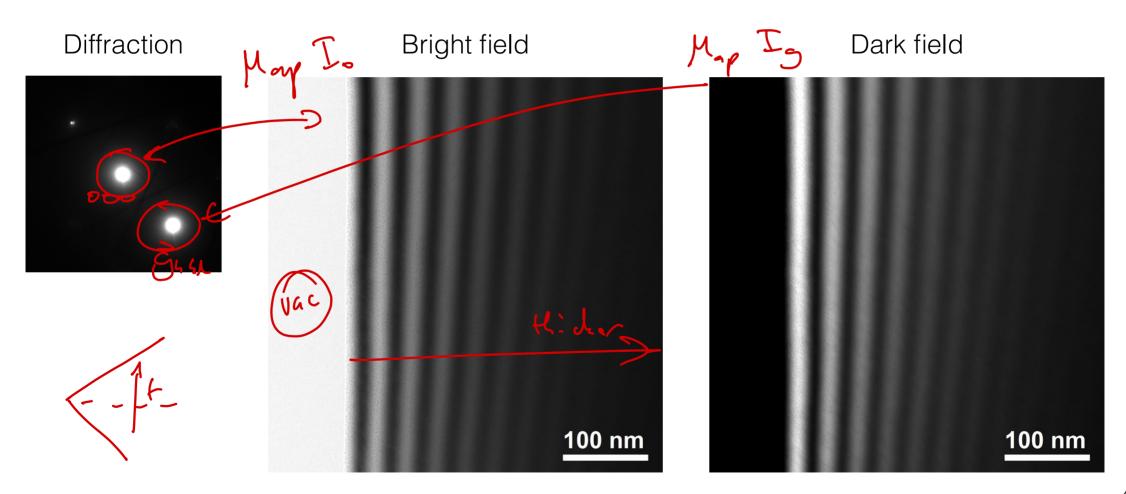


(2.39)

EPFL Thickness fringes

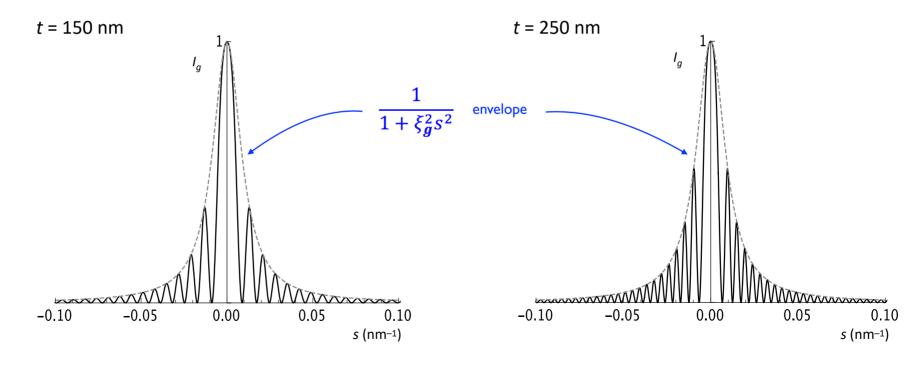
Selections become

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



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

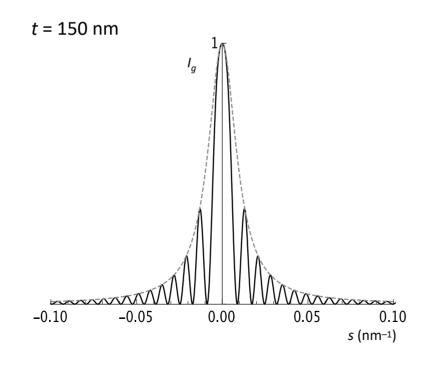
• Model I_g vs s for $\xi_g = 100$ nm

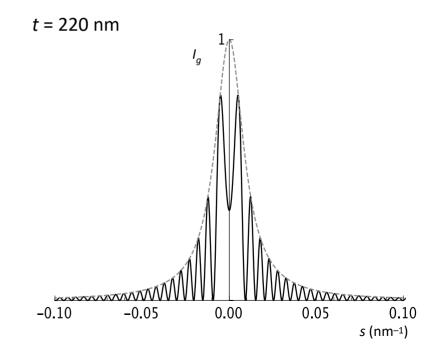


• More generally:
$$I_g(t) = \frac{1}{1 + \xi_g^2 s^2} \sin^2\left(\pi t \sqrt{\frac{1}{\xi_g^2} + s^2}\right)$$
 $I_0(t) = \frac{1}{1 + \xi_g^2 s^2} \sin^2\left(\pi t \sqrt{\frac{1}{\xi_g^2} + s^2}\right)$

$$I_0(t) = 1 - I_g(t)$$
 (2.40)

• Model I_g vs s for $\xi_g = 100$ nm





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

$$I_0(t) = 1 - I_g(t)$$
 (2.40)

• Model I_g vs s for $\xi_g = 100$ nm

