Electron Microscopy I
Lecture 07

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Electron microscopy I

3.2 Kinematic diffraction theory

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Scattering on a crystal (<u>ordered</u> arrangement of atoms)

Scattering amplitude (general)

$$F_{(\theta)} = \sum_i f_{i(\theta)} \exp\left(2\pi i \left[\vec{k} - \vec{k}_o\right] \vec{r}_i\right)$$

For crystals: $\vec{g} = \vec{k} - \vec{k}_0$

$$F_{(\theta)} = \sum_i f_{i(\theta)} \exp\left(2\pi i \, \vec{g} \, \vec{r}_i\right)$$

Condition for constructive interference (maximum scattered intensity) :

$$\boxed{\vec{g}\vec{r}_i = integer}$$

Suitable definition of $\vec{g}$ for maximum scattering intensity

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Reciprocal lattice

Suitable definition of reciprocal lattice vectors for $\vec{g}_{hkl}$ constructive interference

$$\vec{g}_{hkl} = h\vec{a}_1^* + k\vec{a}_2^* + l\vec{a}_3^*$$

$\vec{g}_{hkl} = \vec{k} - \vec{k}_0$ Laue equation with $\vec{g}_{hkl}$ perpendicular to "reflective" lattice plane set (hkl)

$$\left|\vec{g}_{hkl}\right| = \frac{n}{d_{hkl}}$$

$2d \sin\theta_B = n\lambda$ Bragg condition equivalent to Laue equation

Constructive interference is independent of the arrangement of the atoms on the lattice plane

Ewald Konstruktion visualizes the Laue condition

$$\boxed{\vec{g} = \vec{k} - \vec{k}_0}$$

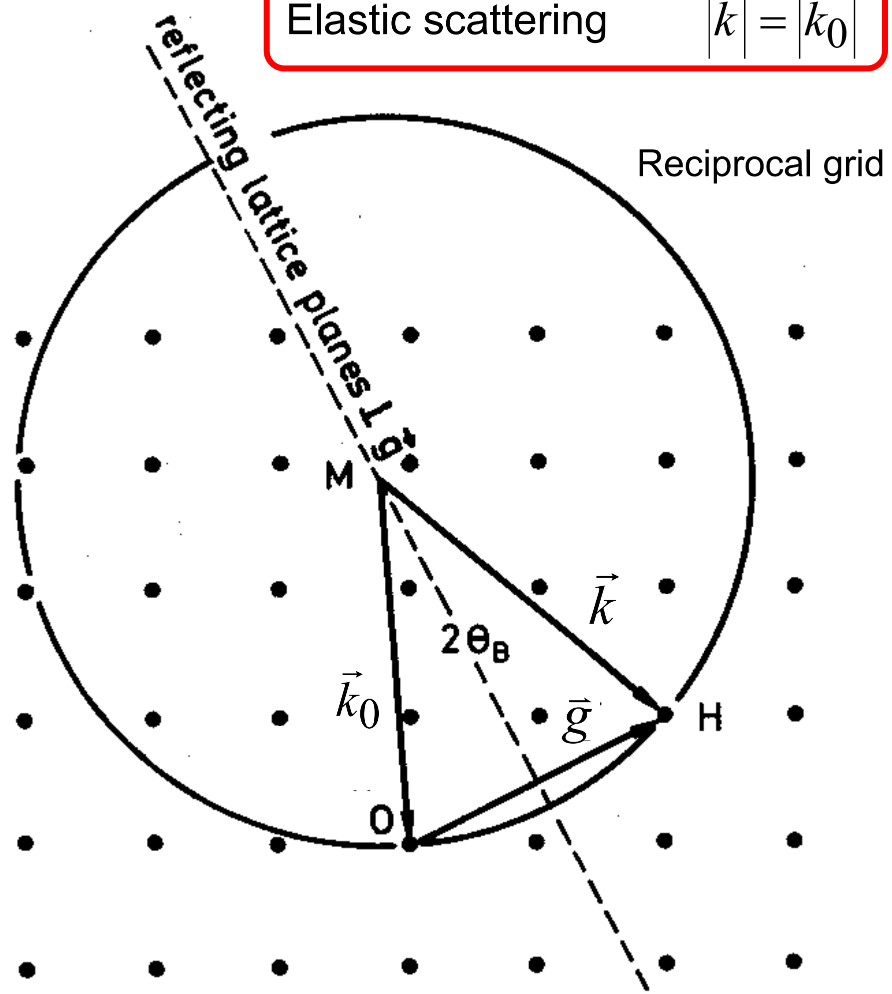
The equivalent of the Bragg condition is

$$\boxed{2d \sin\theta_B = n\lambda}$$

For reciprocal lattice points of planes with (hkl), which are cut by the Ewald Kugel, the Bragg condition is fulfilled

Determination of all directions with maximum scattering intensity, which belong to a specific angle of incidence

Elastic scattering $\left|\vec{k}\right| = \left|\vec{k}_0\right|$



L. Reimer; Transmission Electron Microscopy, Fig.7.8

Ewald construction in transmission electron microscopy

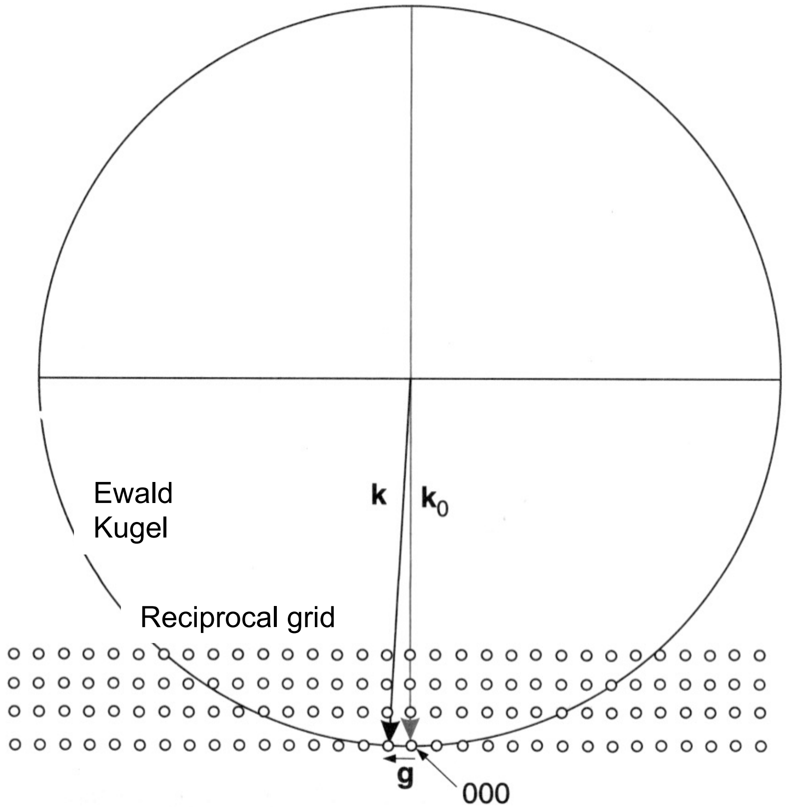
Radius of the Ewald sphere >> Distances between reciprocal grid points

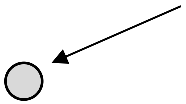
200 keV electrons: λ = 2.5 pm and |k| = 4 -10^{11} m $^{-1}$

$d_{Al,111}$ = 0.234 nm $g_{Al,111}$ = 4.3 -10^{9} m $^{-1}$

→ $|k| = |k_0| = 93\ |g_{Al,111}|$!

Elastic scattering $|\vec{k}| = |\vec{k}_0|$

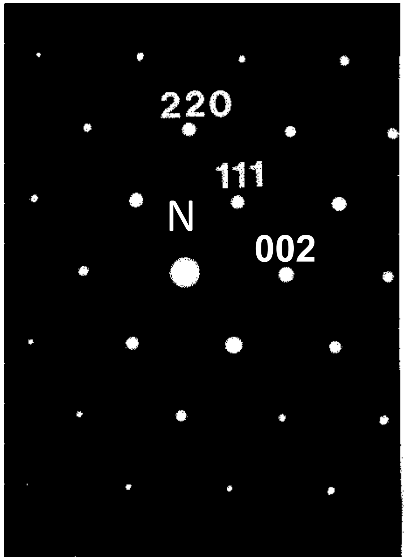




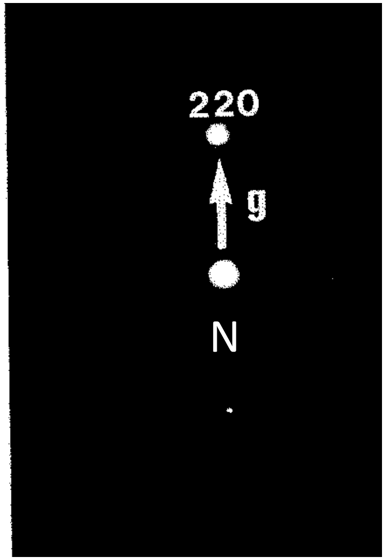
- Ewald sphere in TEM very large (very small λ)
- Almost straight cut through reciprocal grid
- TEM diffraction image usually shows many diffraction points.

Ewald construction in transmission electron microscopy

TEM diffraction pattern corresponds in good approximation to a plane section through the reciprocal lattice perpendicular to the direction of incidence!



GaAs diffraction pattern in $[1\bar{1}0]$ direction



(220) two-beam condition

- Occurrence of reflections in the diffraction image when Ewald sphere intersects with reciprocal lattice points
- Reciprocal lattice vectors points from the Zero beam N (origin of the reciprocal lattice) to the reflex

However:

- "too many" reflexes in highly symmetrical Radiation directions!
- "missing" reflexes (100), (110),...

Scattering amplitude: structure factor, lattice amplitude

$$F_{(\theta)} = \sum_{alle\ Atome\ i} f_{i(\theta)} \exp\left(2\pi i\, \vec{g}\, \vec{r}_i\right)$$

With $\vec{r}_i = \vec{r}_{pi} + \vec{r}_{ki}$ ← Atomic positions within of the unit cell

↑ Positions of the unit cell

$$F_{(\theta)} = \underbrace{\sum_{\substack{alle\ Atome \\ innerhalb\ der \\ Elementarzelle}} f_{i(\theta)} \exp\left(2\pi i\, \vec{g}\vec{r}_{ki}\right)}_{\text{Structure factor } F_S} \underbrace{\sum_{\substack{alle\ Elementar- \\ zellen}} \exp\left(2\pi i\, \vec{g}\vec{r}_{pi}\right)}_{\text{Lattice amplitude } G}$$

Reflex intensity ∞ F_S^2

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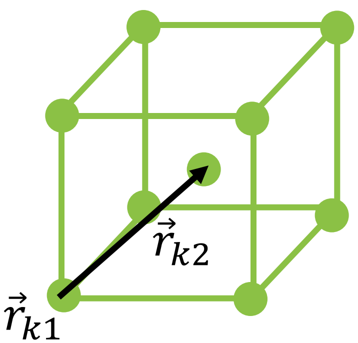
Structure factor for body-centered cubic (krz) lattice



all atoms equal: $f_i(\theta)=f(\theta)$

$$\vec{r}_{k2} = \frac{1}{2}\vec{a}_1 + \frac{1}{2}\vec{a}_2 + \frac{1}{2}\vec{a}_3 \qquad \vec{r}_{k1} = \vec{0}$$

$$F_{S(\theta)} = \sum_{2} f_{(\theta)} \exp\left(2\pi i\, \vec{g}\, \vec{r}_{ki}\right) \qquad F_S = f\left[1+\exp\left(2\pi i\, \vec{g}\left[\frac{1}{2}\vec{a}_1 + \frac{1}{2}\vec{a}_2 + \frac{1}{2}\vec{a}_3\right]\right)\right]$$

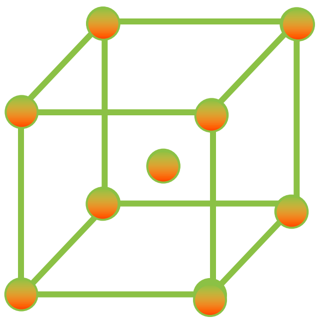
with $\vec{g} = h\vec{a}_1^{\,*} + k\vec{a}_2^{\,*} + l\vec{a}_3^{\,*}$ and $\vec{a}_i\vec{a}_j^{\,*} = \delta_{ij}$ $\quad$ δ_{ij} = 0 for i $\neq$ j, δ_{ij} = 1 for i = j

$$\longrightarrow \quad F_S = f\left[1+\exp\left(\pi i[h+k+l]\right)\right]$$

$F_S = 2f$ if h+k+l is an even number $\longrightarrow$ Allowed reflexes: (200), (220),...

$F_S = 0$ if h+k+l is odd $\longrightarrow$ *Kinematically forbidden* reflexes: (100), (111), ...

Structure factor for body-centered cubic (krz) lattice



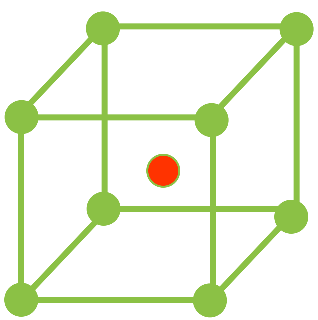
Alloy consisting of n different atoms with statistical Occupation of the grid spaces

$$\bar{f}(\theta) = \frac{1}{n}\sum_{n} f_n(\theta)$$

$F_S = 2\bar{f}$ for h+k+l even

$F_S = 0$ for h+k+l odd

Occurrence of reflexes unchanged, but with modified intensity



B2 Order structure with 2 types of atoms A/B

$F_S = f_A + f_B$ for h+k+l even

$F_S = f_A - f_B$ for h+k+l odd

$\longrightarrow$ Superstructure reflexes

For incomplete order with degree of order S < 1

$$F_S = S(f_A - f_B)$$

e.g. NiAl, FeAl,...

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Lattice amplitude G describes the "shape" of the reciprocal grid points

$$F_{(\theta)} = \sum_{\substack{\text{alle Atome}\\ \text{innerhalb der}\\ \text{Elementarzelle}}} f_{i(\theta)} \exp\left(2\pi i\, \vec{g}\, \vec{r}_{ki}\right) \underbrace{\sum_{\substack{\text{alle Elementar-}\\ \text{zellen}}} \exp\left(2\pi i\, \vec{g}\vec{r}_{pi}\right)}_{\text{Lattice amplitude G}}$$

replace $\vec{g}$ with $\vec{g} + \vec{s}$ $\qquad |\vec{s}| << |\vec{g}|$

$\vec{s}$ Excitation error

Assumption: Bragg condition is still fulfilled even for a small excitation error $\vec{s}$
(i.e. for a small deviation from the Bragg angle)

F_s remains unchanged to a good approximation

$$G = \sum_{\substack{\text{alle Elementar-}\\ \text{zellen}}} \exp\left(2\pi i \left(\vec{g} + \vec{s}\right)\vec{r}_{pi}\right)$$

$$G = \sum \underbrace{\exp\left(2\pi i\, \vec{g}\, \vec{r}_{pi}\right)} \exp\left(2\pi i\, \vec{s}\, \vec{r}_{pi}\right) \approx \frac{1}{V_e} \int_{\substack{\text{äußere}\\ \text{Probenabmessungen}}} \exp\left(2\pi i \left(s_x x + s_y y + s_z z\right)\right) dx\, dy\, dz$$

Integer according to the definition of $\vec{g}$

V_e : Volume of the unit cell

Lattice amplitude G

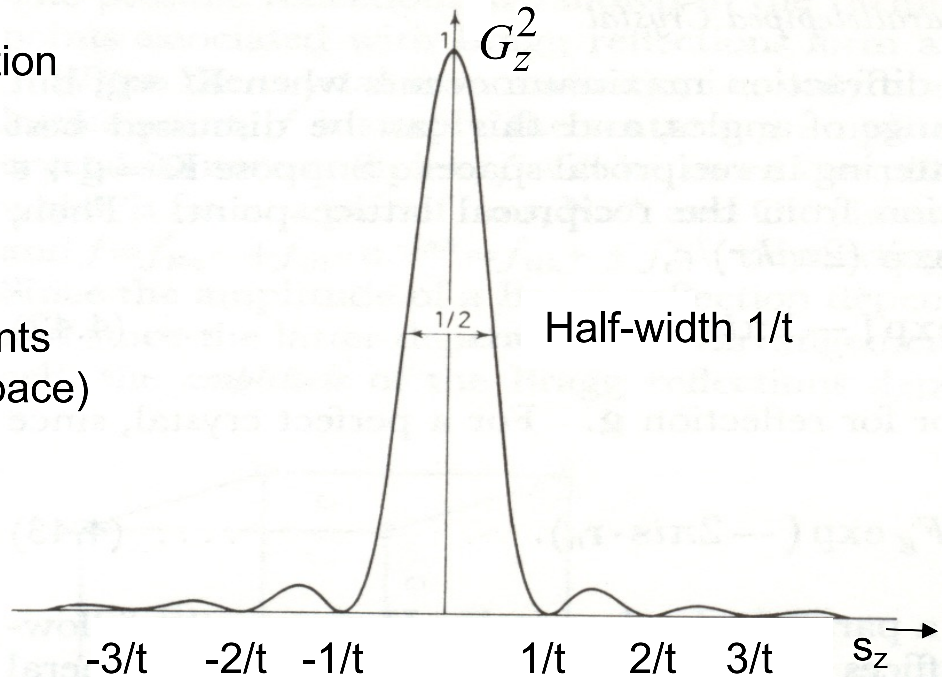
For TEM specimen: lateral dimensions along x, y >> specimen thickness t (z-coordinate)

Consideration of the contribution of the z-component to G

$$G_z = \frac{1}{a_z} \int_{-t/2}^{t/2} \exp(2\pi i \, s_z z) dz \longrightarrow G_z = \frac{\sin \pi \, s_z t}{\pi \, a_z \, s_z}$$

a_z : Elementary cell size in z-direction

For small object dimensions
in the real space:
Widening of the reciprocal grid points
(i.e. Bragg reflexes in reciprocal space)



P. Hirsch et al, Electron Microscopy of Thin Crystals, Fig.4.11a

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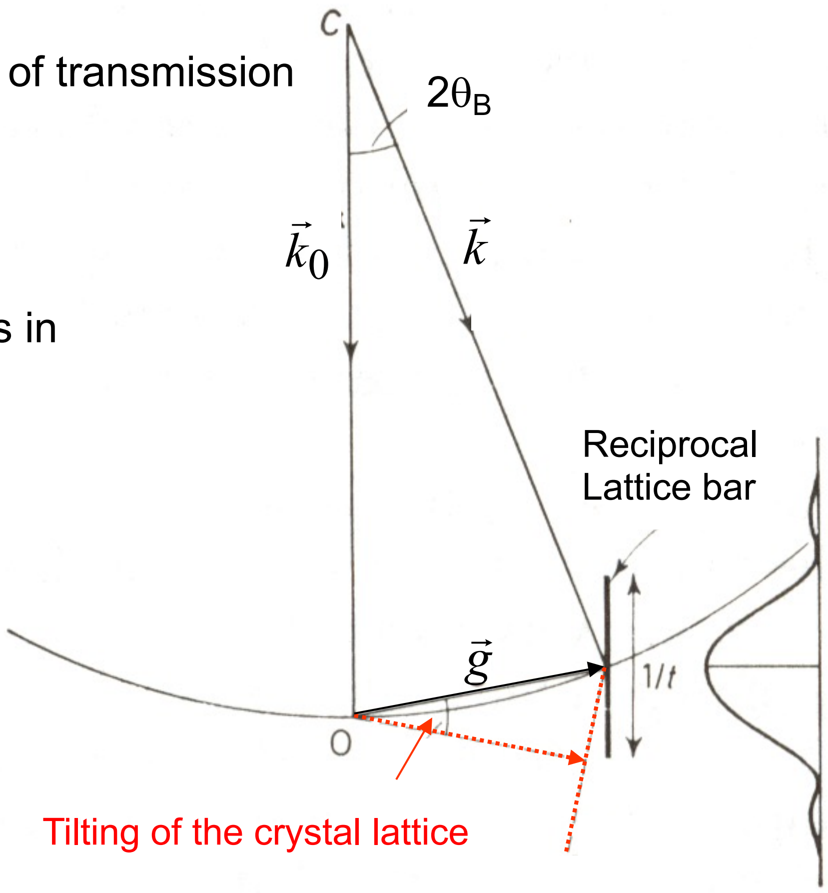
Reciprocal lattice "*rods*" (instead of reciprocal lattice *points*) for thin TEM samples

Low sample thickness in the direction of transmission

Expansion of the reciprocal grid points in Reciprocal "bars" with a length ≅ 2/t

Occurrence of Bragg reflexes, also if Bragg condition is not exactly is fulfilled



P. Hirsch et al, Electron Microscopy of Thin Crystals, Fig.4.11(c)

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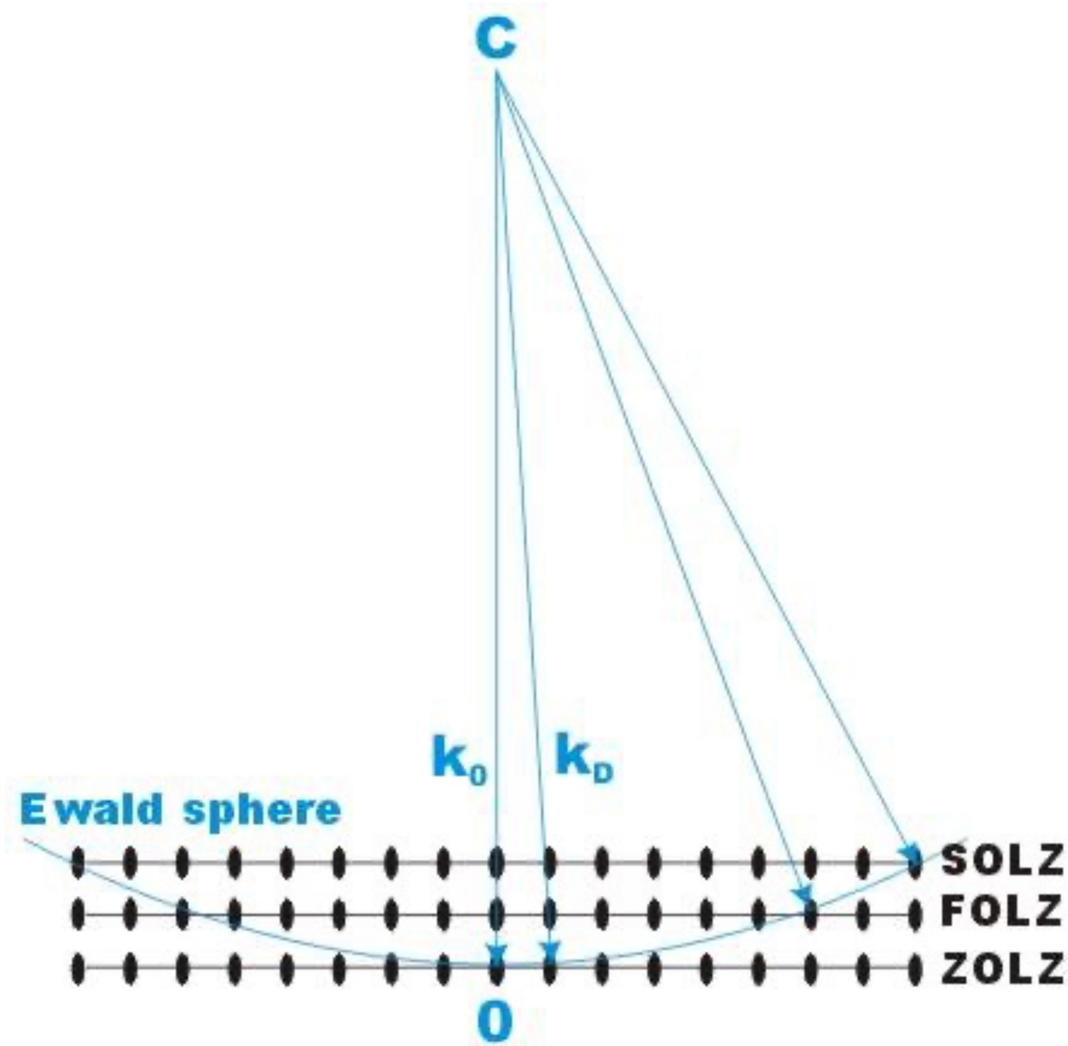


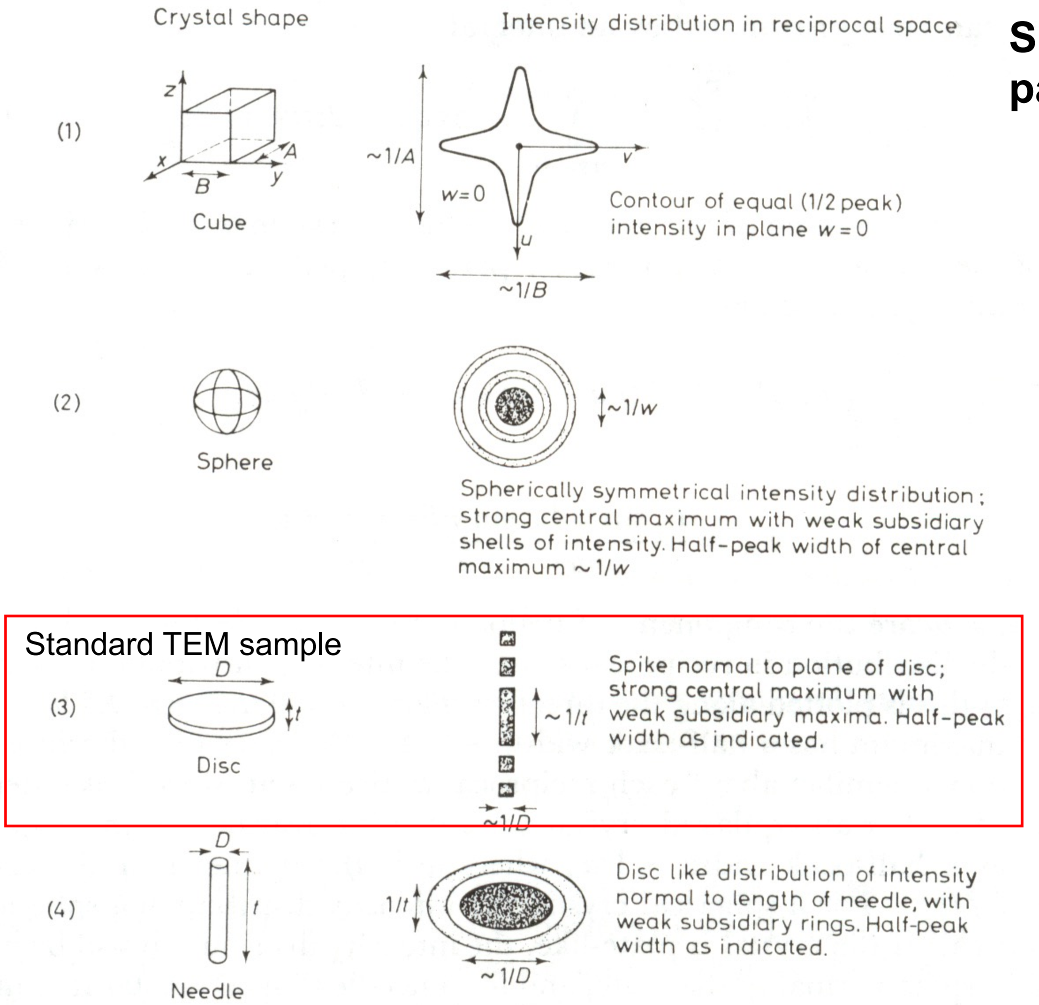


Figure 4.11. (b) Intensity distributions (schematic) for various crystal shapes: (1) cube shape; plot of contour of equal intensity in u, v plane (w = 0); (2) spherical shape; (3) disc shape; (4) needle shape

Shape of the reflexes in the diffraction pattern

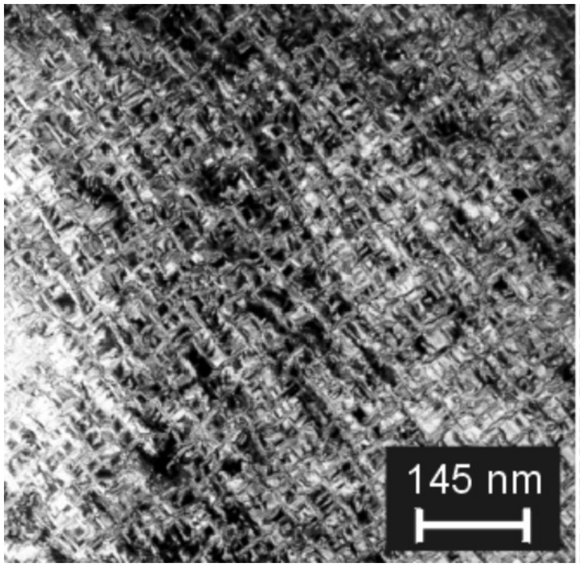
Shape and size of an object in real space

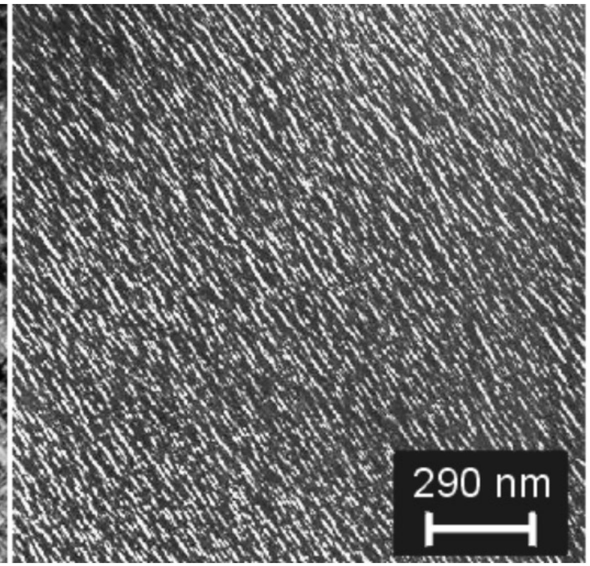
Reverse extension of reflexes proportional to dimensions of the object in real area

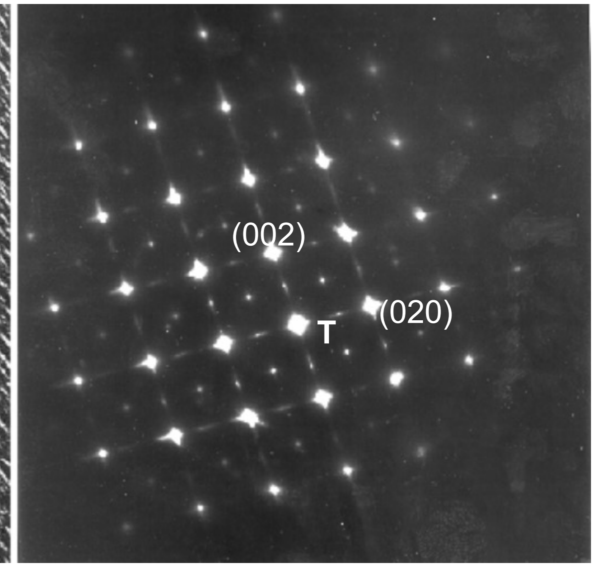
P. Hirsch et al, Electron Microscopy of Thin Crystals, Fig.4.11(b)

Microstructure of an AuAgCu dental alloy Stabilor G (vehicle structure)

Electron beam direction parallel to [100] direction







Kasanicka et al, Sonderbände der Praktischen Metallographie Vol.35, Fortschritte in der Metallographie, ed. G. Petzow and P. Portella, Materials Information Society, 2004, pp. 451-456

Superstructure reflexes?

Line-like expansion of the reflexes?

Information from dark field imaging with superstructure reflex?

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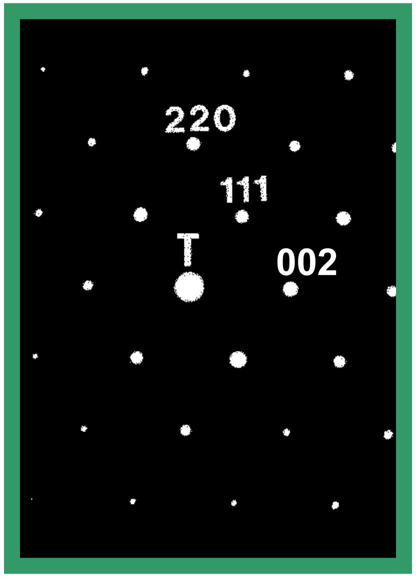
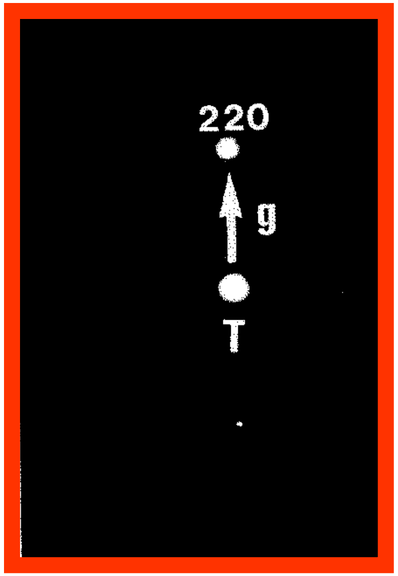
Validity of the kinematic diffraction theory

$$I = I_o + \sum I_g = 1$$

I: Overall intensity
I_0 : Intensity of the zero beam
I_g : Intensity of the Bragg reflexes

Kinematic theory required: $\sum I_g << I_0$





Two-beam condition

Particularly simple case: dual-beam conditions (only one reflex Excited with I_g)

$$\boxed{I_o = 1 - I_g}$$

- Increase of I_g with the sample thickness ⟶ Maximum sample thickness for which kinematic theory is applicable
- Maximum sample thickness depends on the atomic number of the sample material, electron energy, Bragg reflex - maximum in the order of 10 nm (!)
- Extension of the applicability of the kinematic theory by setting a Excitation error $\vec{s}$

Extension of the specimen thickness range for the validity of the kinematic Diffraction theory by setting an excitation error s_z in the direction of incidence

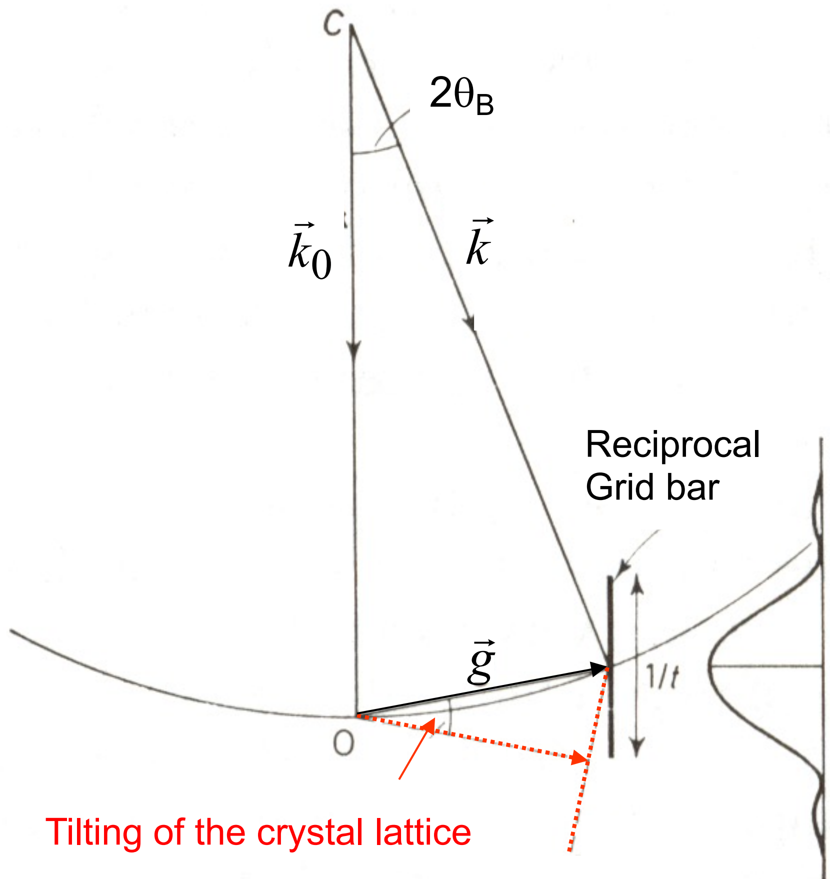
Decrease in reflex intensity due to cutting of the Ewald sphere in the outer area of the reciprocal Lattice bar

Setting an *excitation error s_z* by Tilting the sample by Dθ $_B$

$$s_z = |\vec{g}| \tan\Delta\theta_B \approx |\vec{g}|\,\Delta\theta_B$$

$$|\vec{g}| = \frac{2\sin\theta_B}{\lambda n}$$

$$\boxed{s_z = \frac{2\sin\theta_B}{\lambda n}\Delta\theta_B}$$



P. Hirsch et al, Electron Microscopy of Thin Crystals, Fig.4.11(c)

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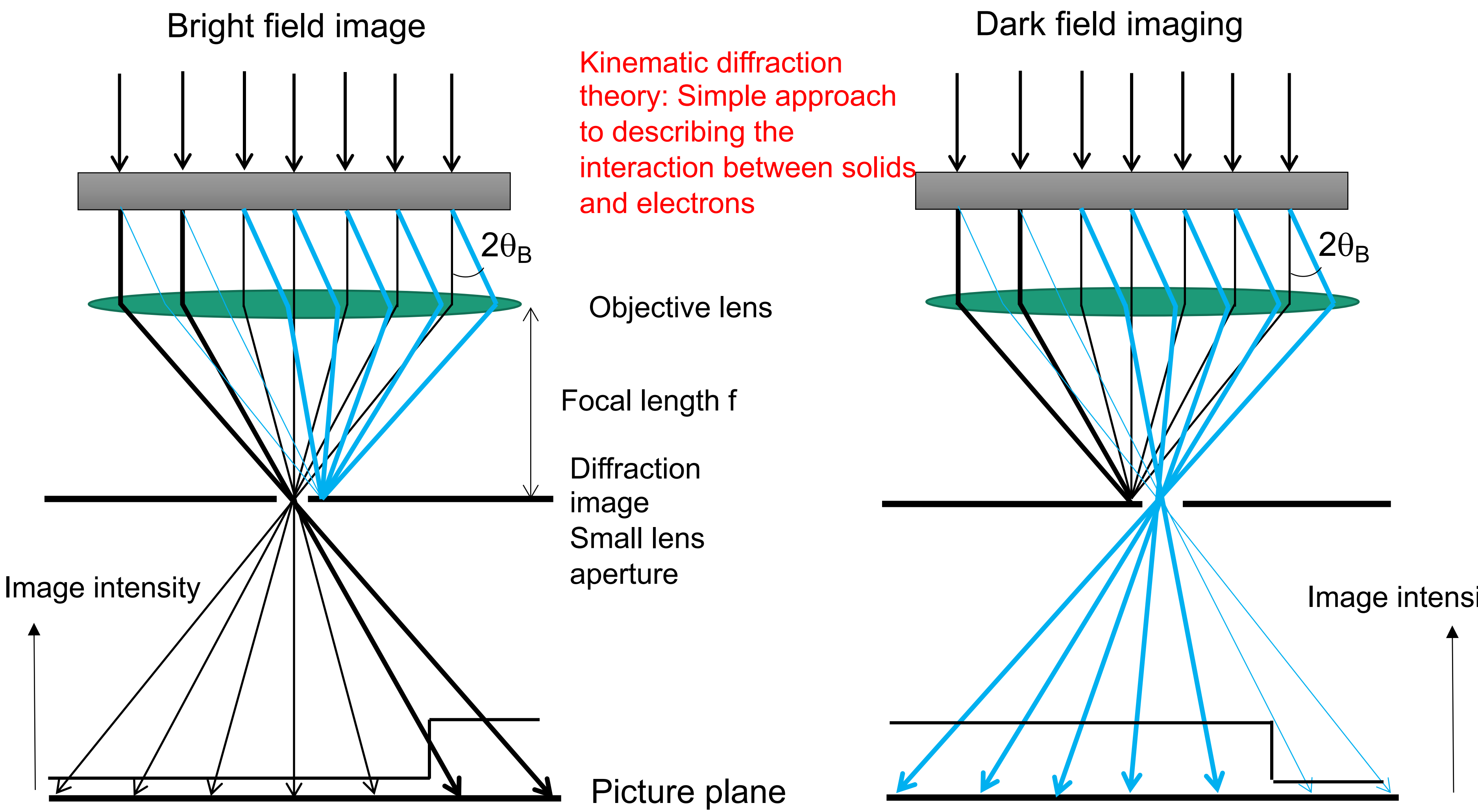
Summary: kinematic diffraction theory

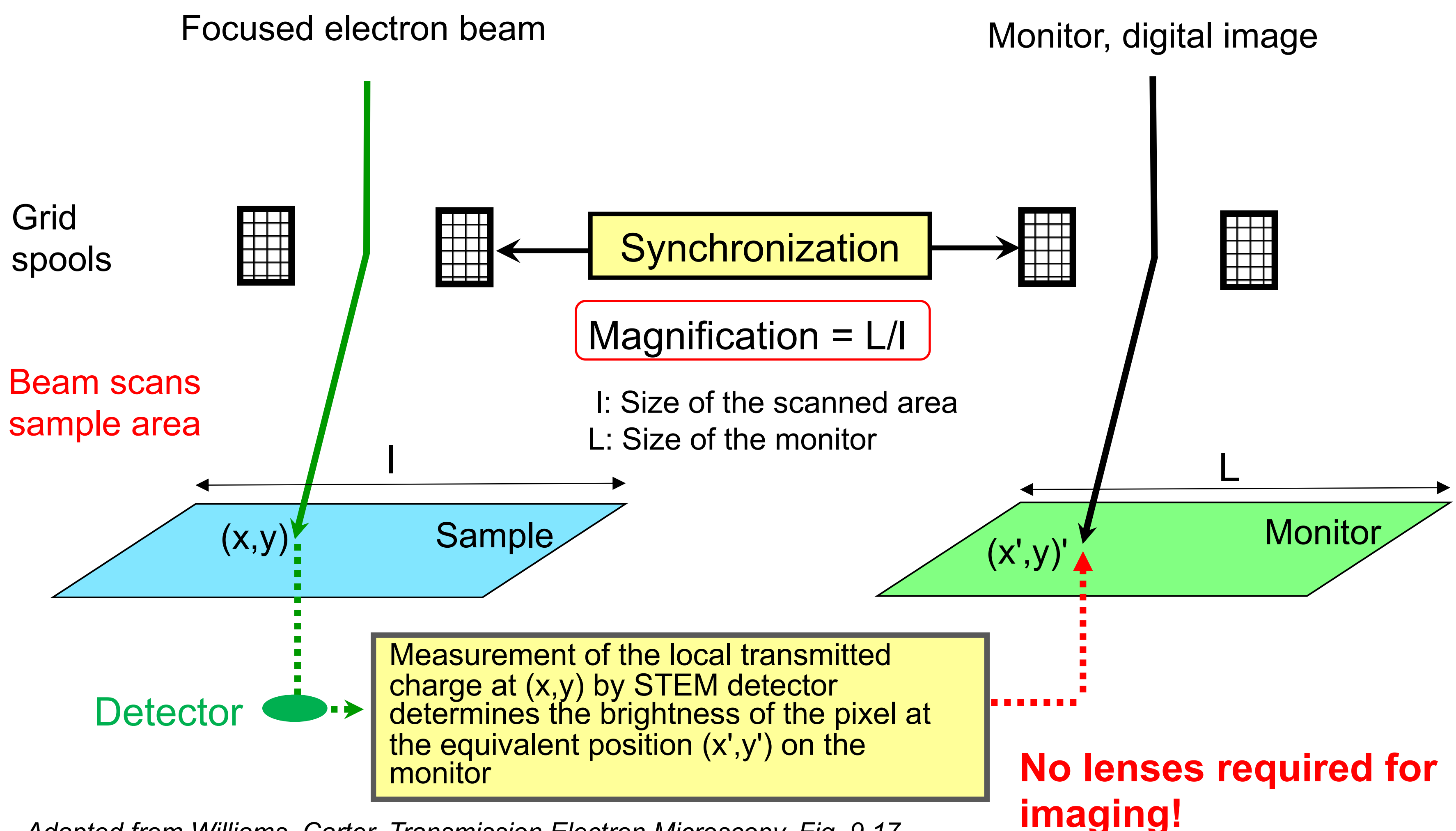
- Spherical waves emanate from atoms (Huygens-Fresnel principle) with a scattering angle-dependent amplitude f(θ) with maximum amplitude in the forward direction.
- For a group of atoms, the resulting scattered wave results from the phase-correct superposition of the spherical waves, taking into account the atomic arrangement.
- For a crystal (ordered arrangement of atoms with a large number of atoms) you get Intensity maxima in certain directions, which are characterized by the Bragg condition (Ewald construction).
- The intensity of the intensity maxima (reflexes in the diffraction pattern) is proportional to the Magnitude squared of the scattering amplitude F, which contains the *structure factor* and the *lattice amplitude.*
- The size and symmetry of the elementary cell (crystal structure) determines the position of the reflexes in the diffraction pattern.
- The structure factor F_s (atomic arrangement in the elementary cell) describes the occurrence and intensity of reflexes under kinematic conditions.
- The lattice amplitude G describes the shape of the reflections (reciprocal lattice points) as a function of the external dimensions and the shape of the sample (or small particles in the sample).
- TEM samples that are thin in the direction of transmission generate reciprocal lattice bars $\longrightarrow$ large number of reflections in TEM diffraction images with zone axis irradiation
- Validity of the kinematic theory when the intensity of the Bragg reflexes is small compared to the to the zero beam intensity.

Conventional brightfield and darkfield imaging

Kinematic diffraction theory: Simple approach to describing the interaction between solids and electrons



Scanning transmission electron microscopy (STEM) in the transmission electron microscope: Principle of image formation



Adapted from Williams, Carter, Transmission Electron Microscopy, Fig. 9.17

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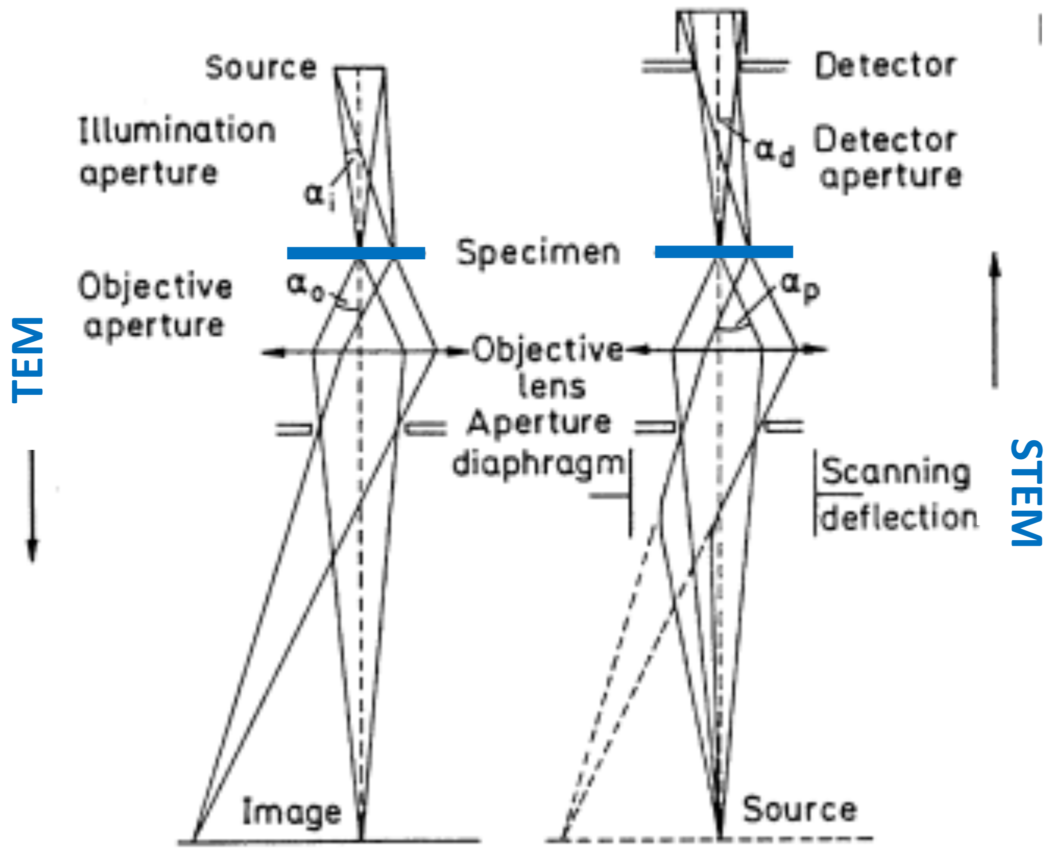
The reciprocity theorem describes conditions under which STEM and TEM Illustrations show identical contrast



L. Reimer, H. Kohl, Transmission Electron Microscopy, Fig. 4.20

TEM:
Illumination of the sample with small Beam convergence angle α_i (0.1 - 1 mrad)
Figure: Lens aperture α_o > 3 mrad significantly larger as α_i

STEM:
Illumination of the sample with a focused beam (large beam convergence angle α)$_p$
Figure: Detection by bright field detector with small detection angle range α_d

Equal contrast of brightfield TEM and brightfield STEM images when

$$\alpha_i = \alpha_d \text{ and } \ll \alpha_0 = \alpha_p$$

Extension to dark field (S)TEM and high resolution resolving phase contrast images possible

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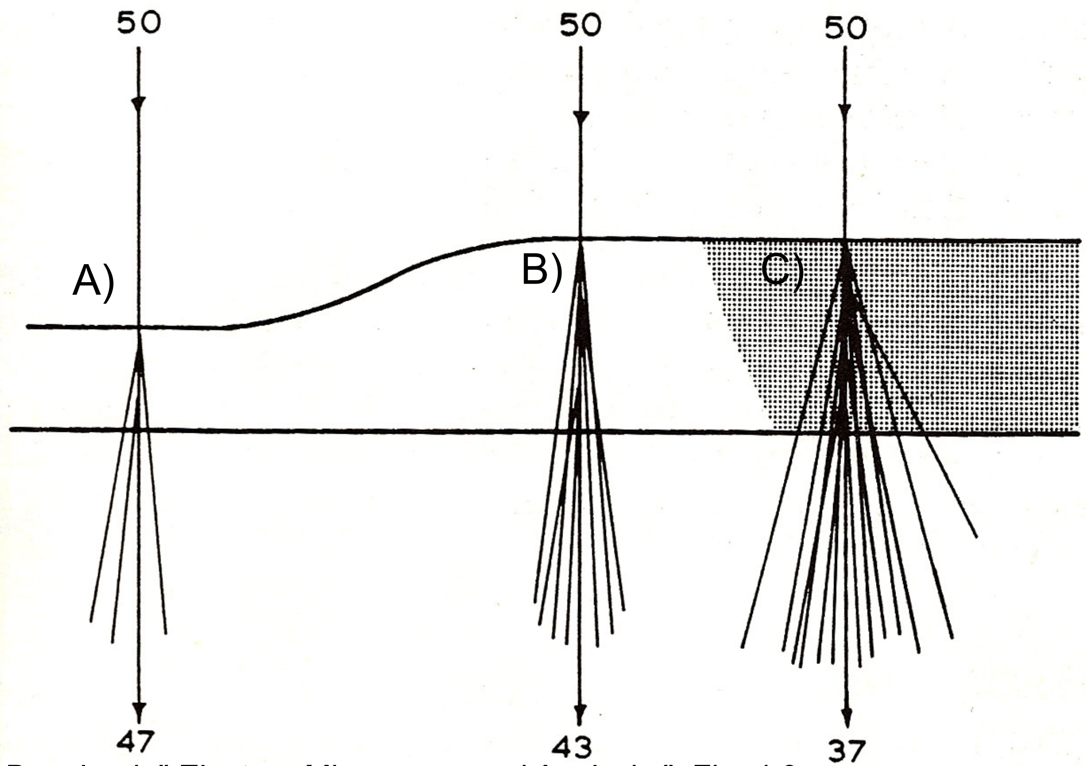
Mass thickness contrast in objects with amorphous structure and crystalline objects without strongly excited Bragg reflexes ("kinematic diffraction conditions")



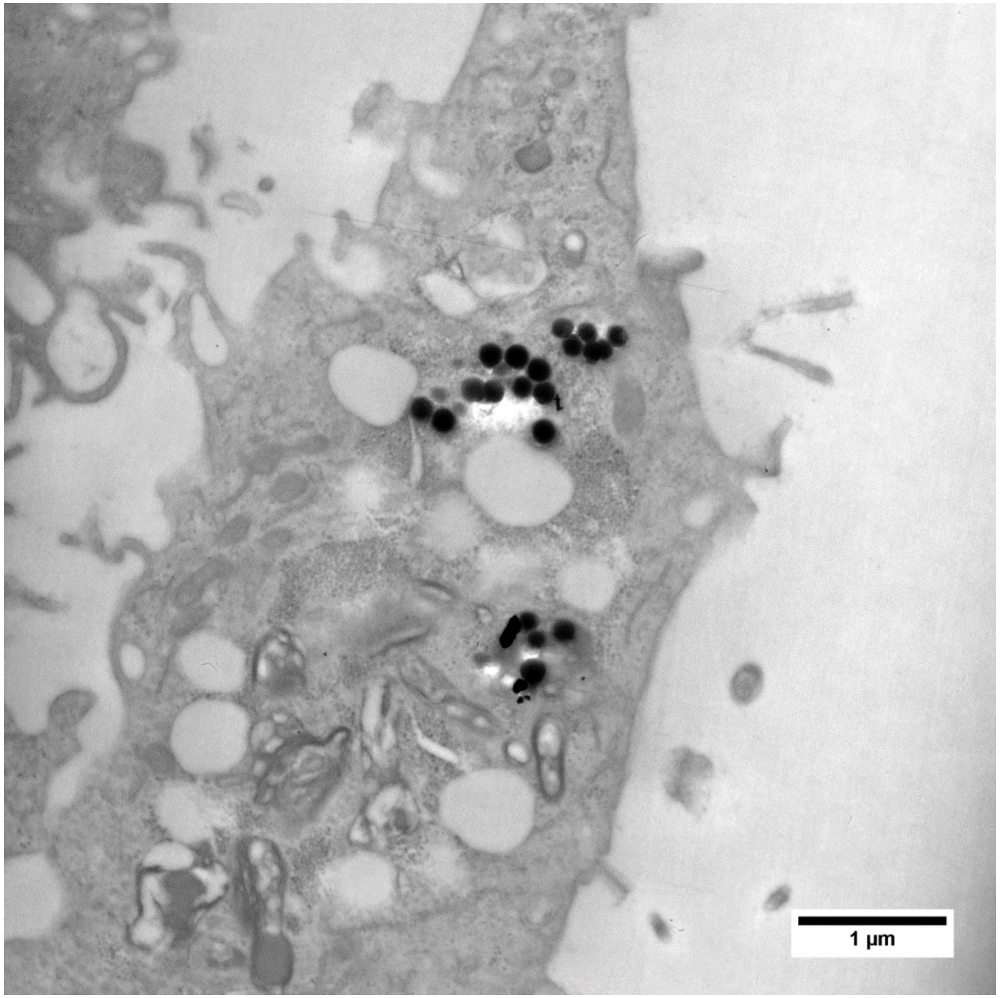
Goodhew, Humphreys, Beanland, " Electron Microscopy and Analysis ", Fig. 4.9

Electron scattering in different areas of a thin sample

A) Scattering of a few electrons in thin sample areas
B) scattering of a larger number of electrons with increasing sample thickness
C) in the range of the same thickness but higher density, the scattering is even greater

4.1 Mass thickness contrast

Mass thickness contrast in biological objects with amorphous structure



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HT29 Intestinal carcinoma cell with SiO_2 - and Pt nanoparticles: TEM bright field image of a Thin section with *homogeneous* thickness → Image brightness determined by local material density

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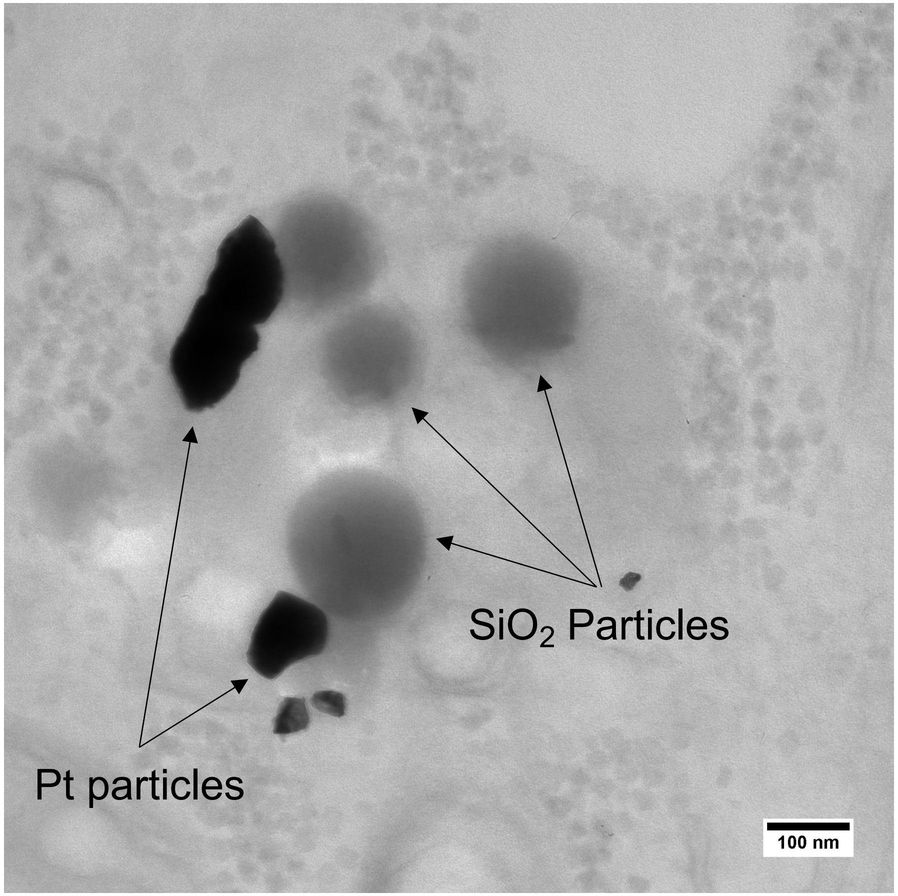
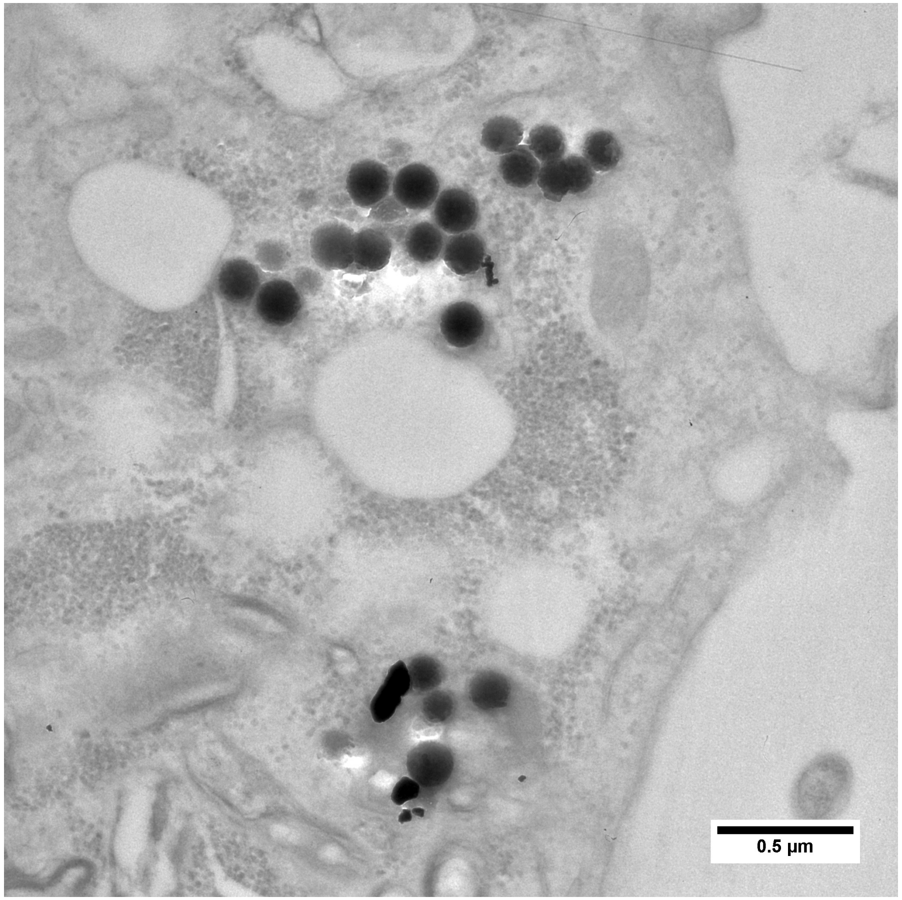
Mass thickness contrast in biological objects with amorphous structure





HT29 Intestinal carcinoma cell with SiO_2 - and Pt nanoparticles:
TEM bright field image

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