Machine Learning in STEM 2023 Lecture 08

Lecture 8:Convergent Beam Electron Diffraction

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Outline

Fundamentals

Please note, that we assume strict incoherence in this chapter, we will discuss coherent CBED in Lecture 10.
For 4D-STEM relevance, we are talking about scanning "Nano-Diffraction". There, the diffraction disks do not or only slightly overlap.
In lecture 10, 4D-STEM, CBED and Z-contrast image simulation will be discussed in the coherent (overlapping disks) context.

Why CBED ?

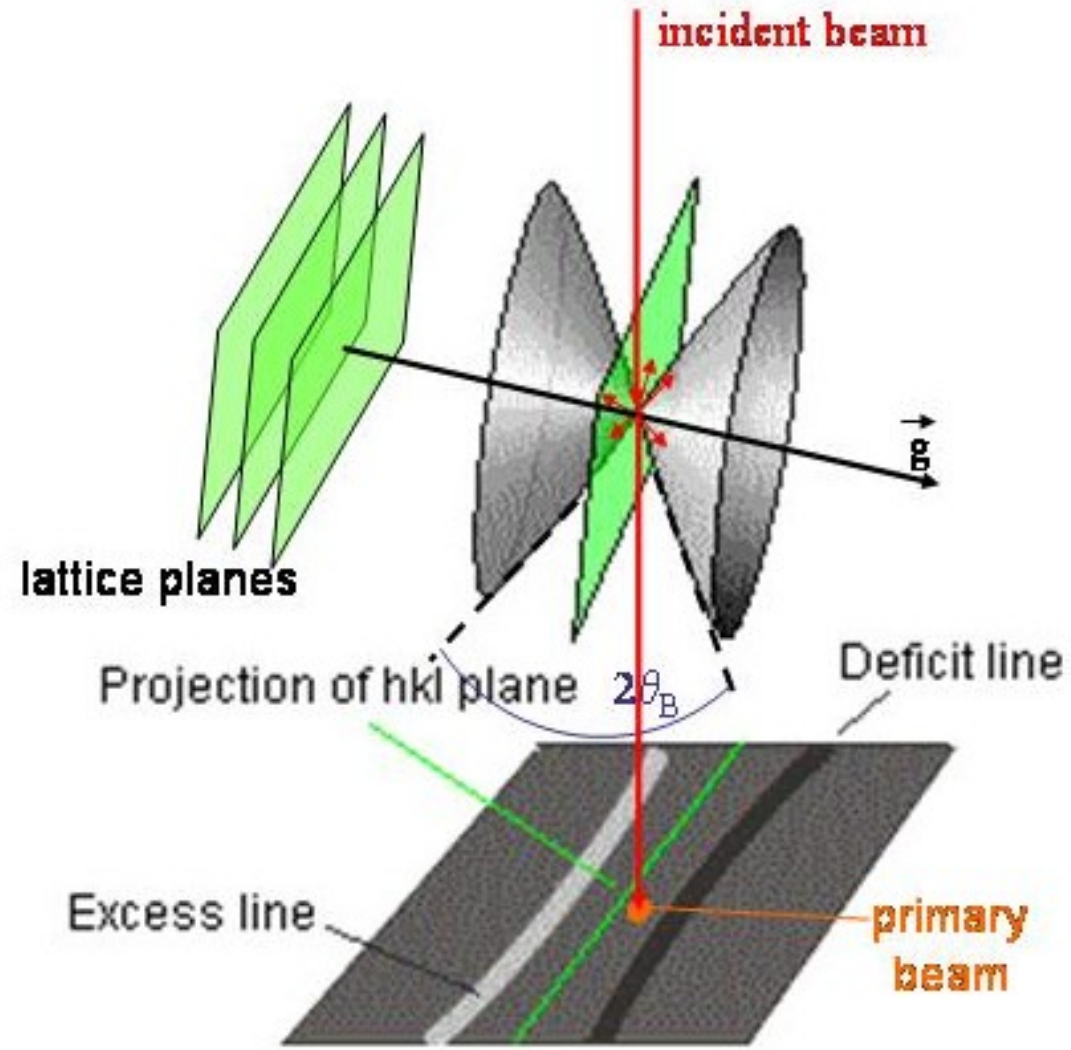
- Kikuchi lines are easier to see
- You can still measure distances of reflection spots
- The probed volume is very small and can almost always be considered single–crystalline.
- The probed volume is very small and the spatial resolution is very good (¡ 1 nm).
- Contains more symmetry information
- HOLZ rings and HOLZ lines are better visible

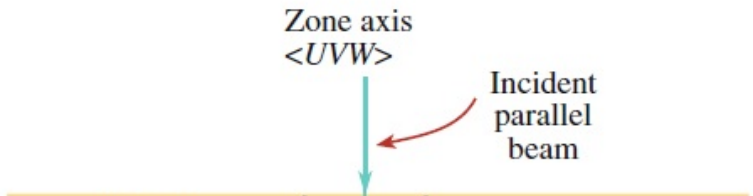
STEM is always in convergent beam mode!

When Not to Use CBED ?

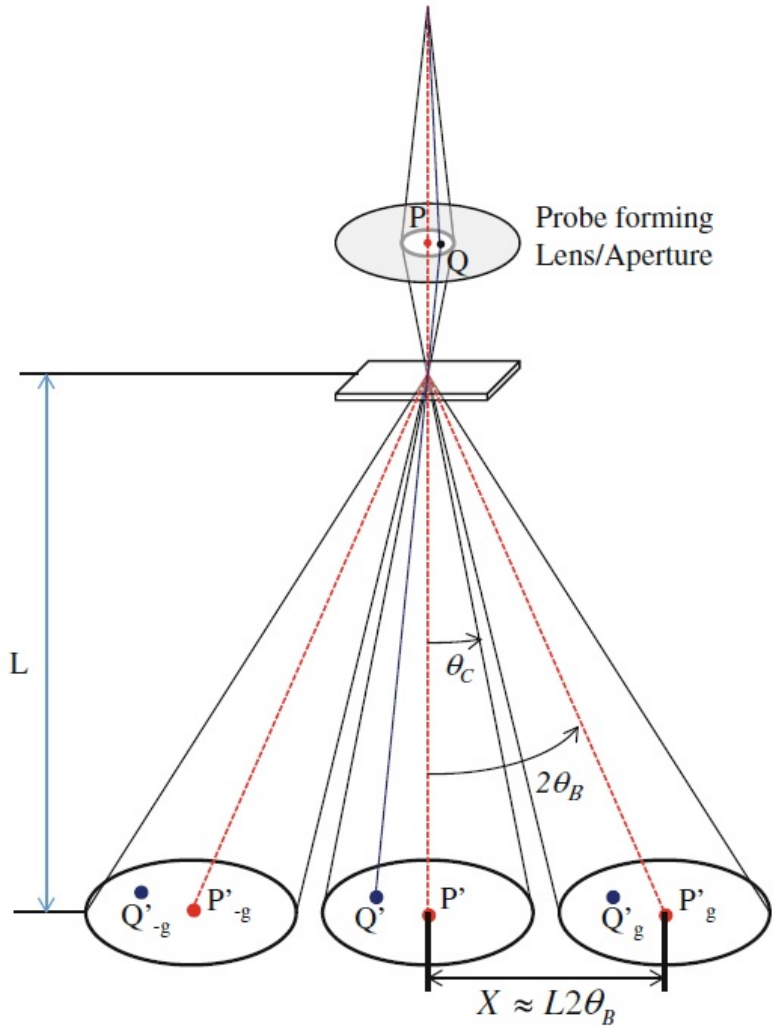
- If the grain size is very small
- If you want to characterize a poly–crystalline material as a whole (texture).

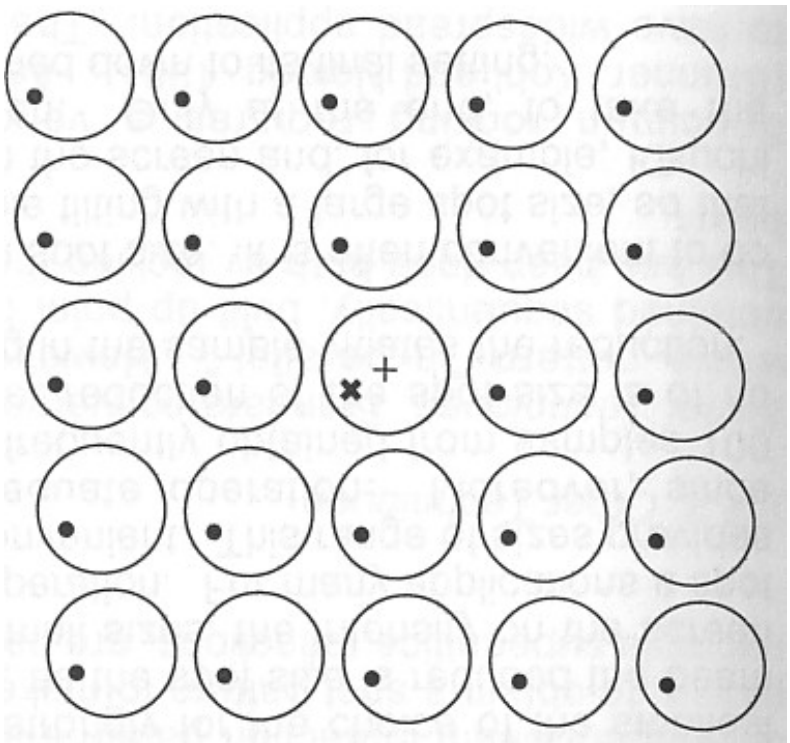
Fundamentals of Kikuchi





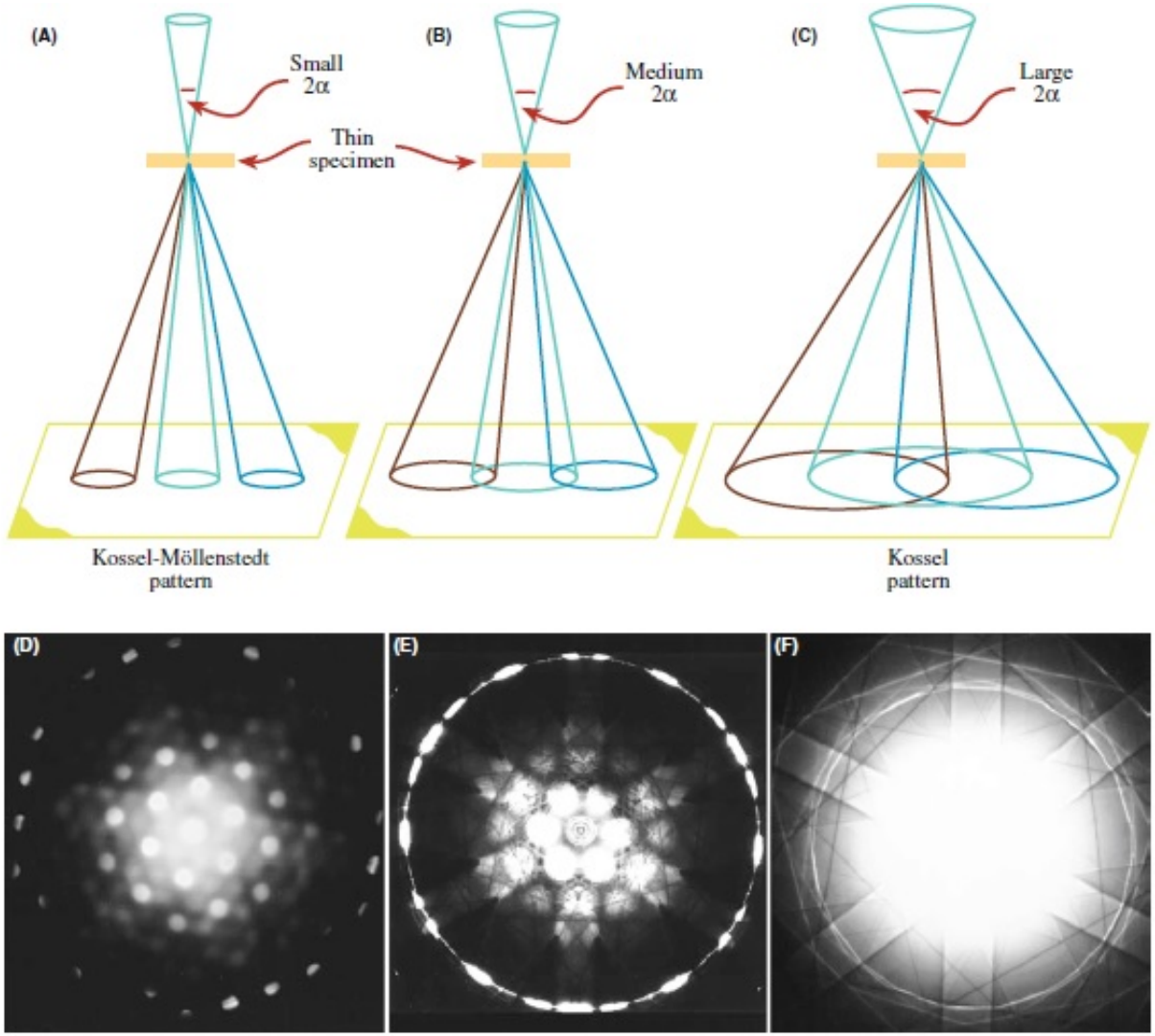
Fundamentals of CBED I





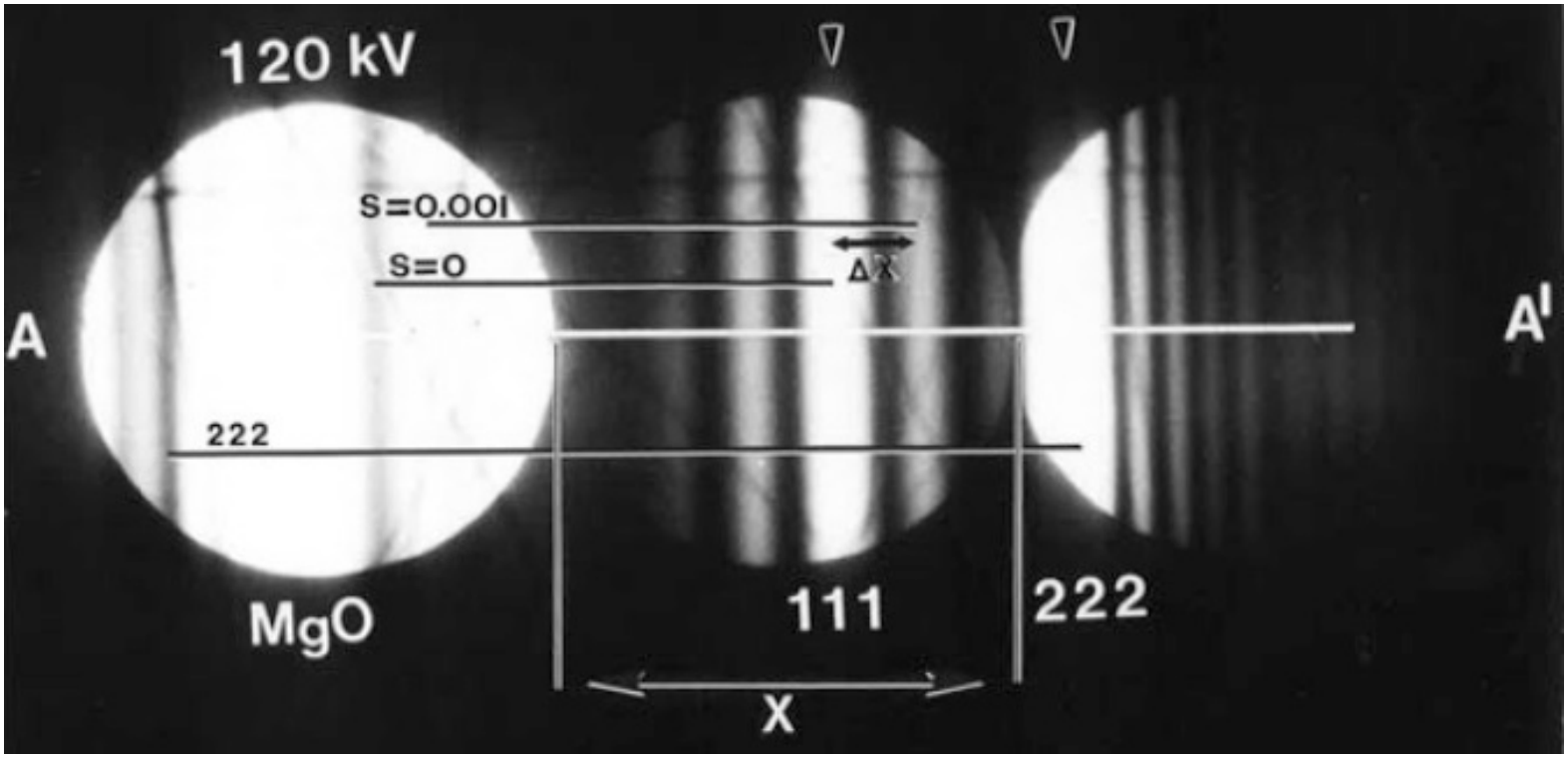
All the equivalent points in a CBED pattern, originate from one direction.

Fundamentals of CBED II



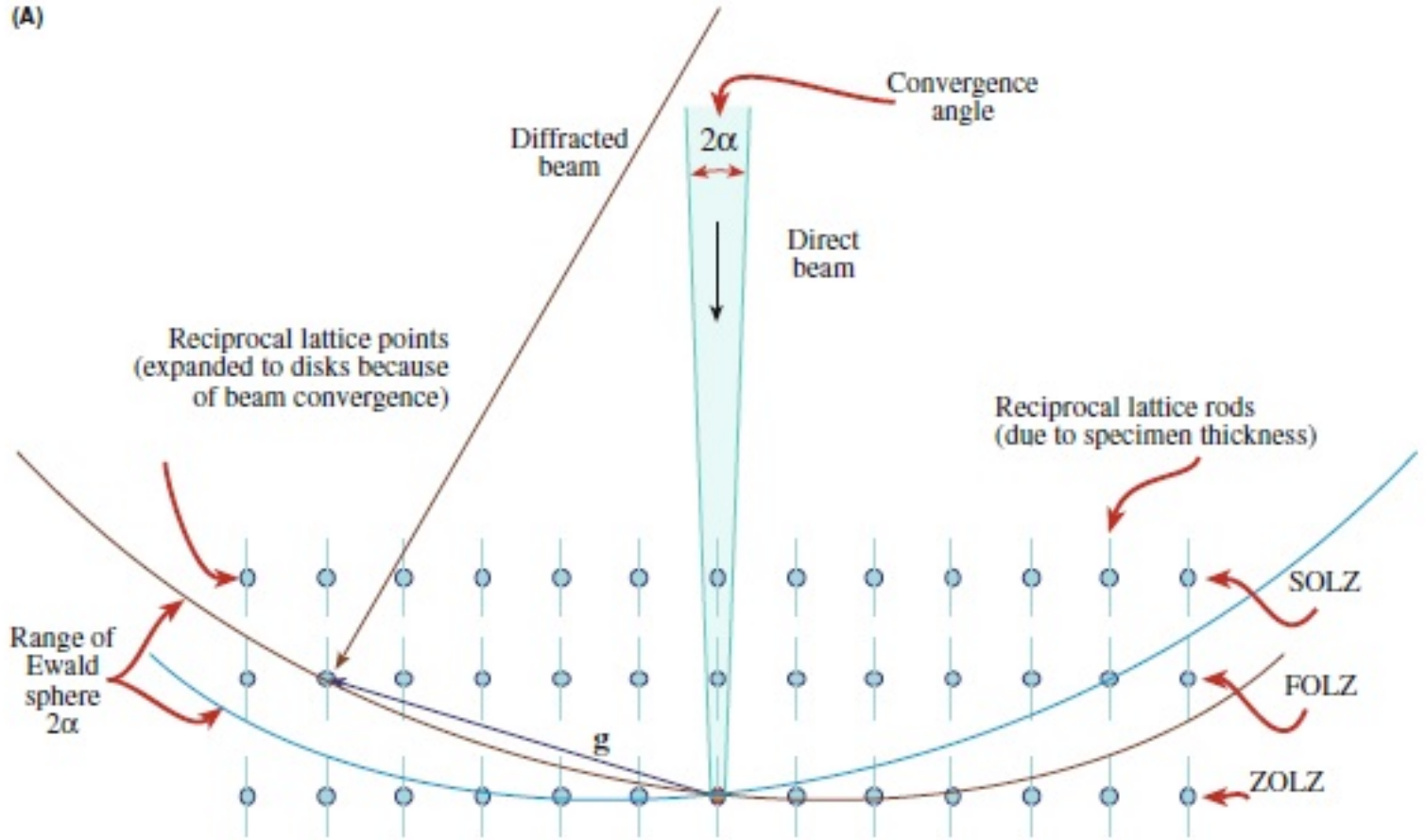
Differences in the convergence angles lead to different pattern.

Fundamentals of CBED II



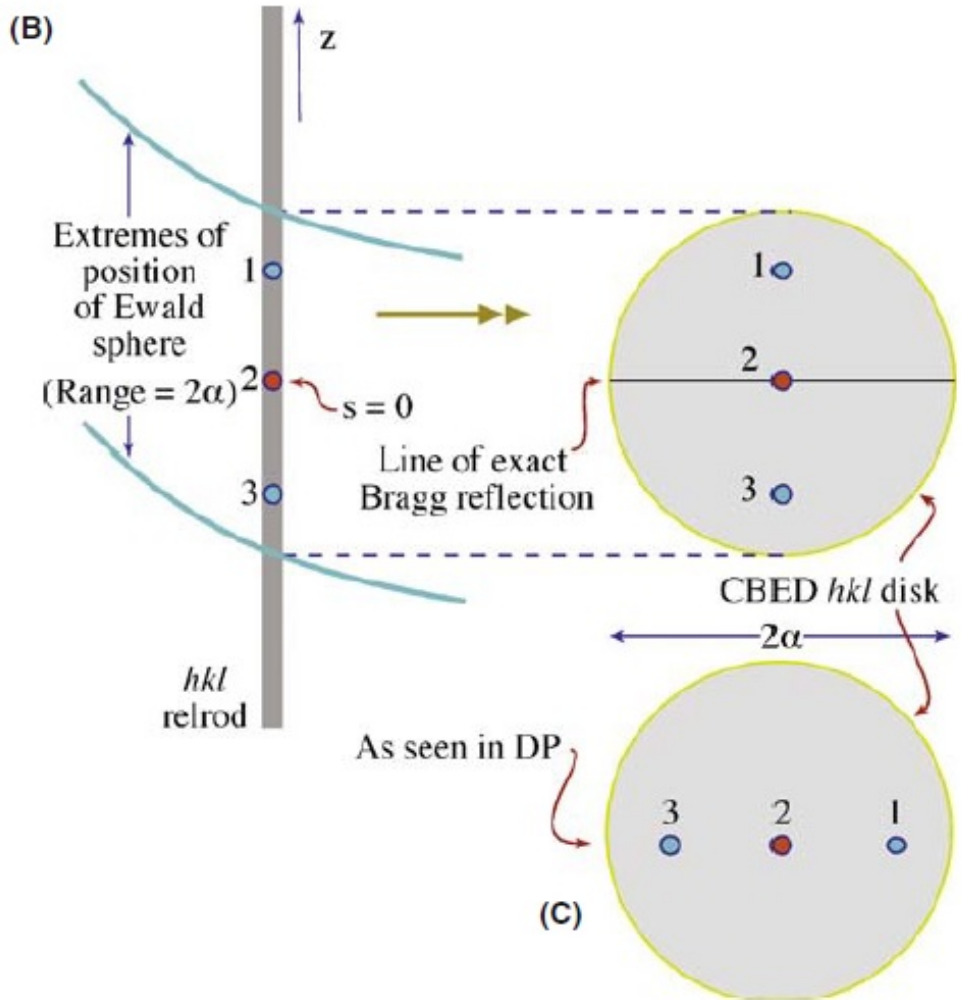
Distances can be measured from center to center or a rim to rim of a diffraction disk. Inside the disk the Bragg condition only changes in terms of excitation error.

Fundamentals of CBED II



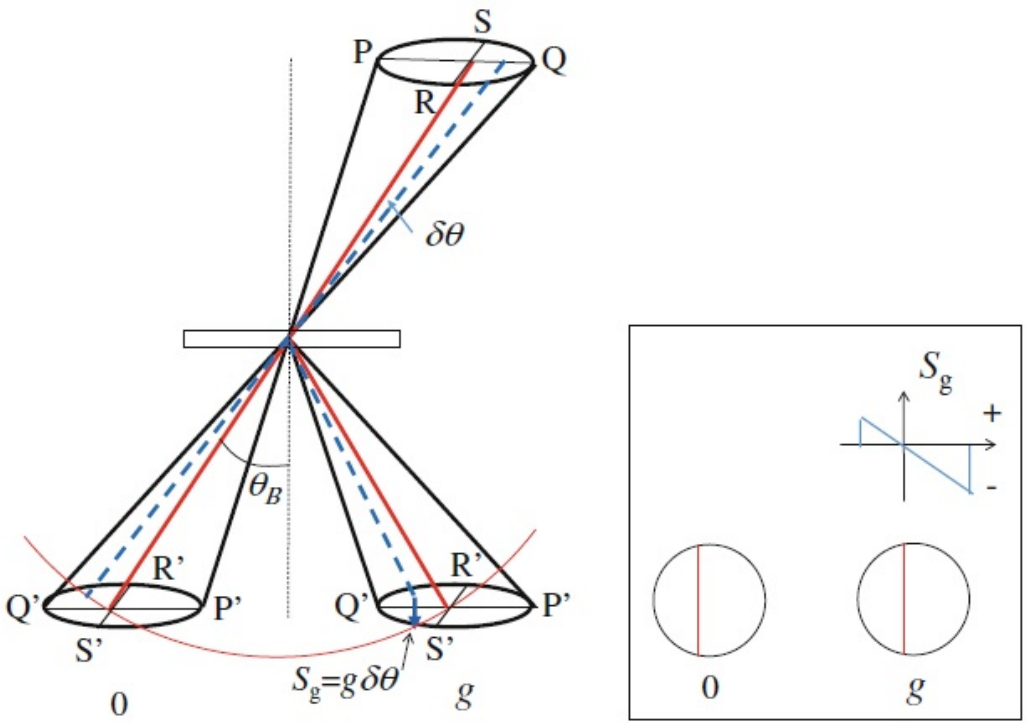
Ewald spheres construction for the CEBD pattern

Fundamentals of CBED II



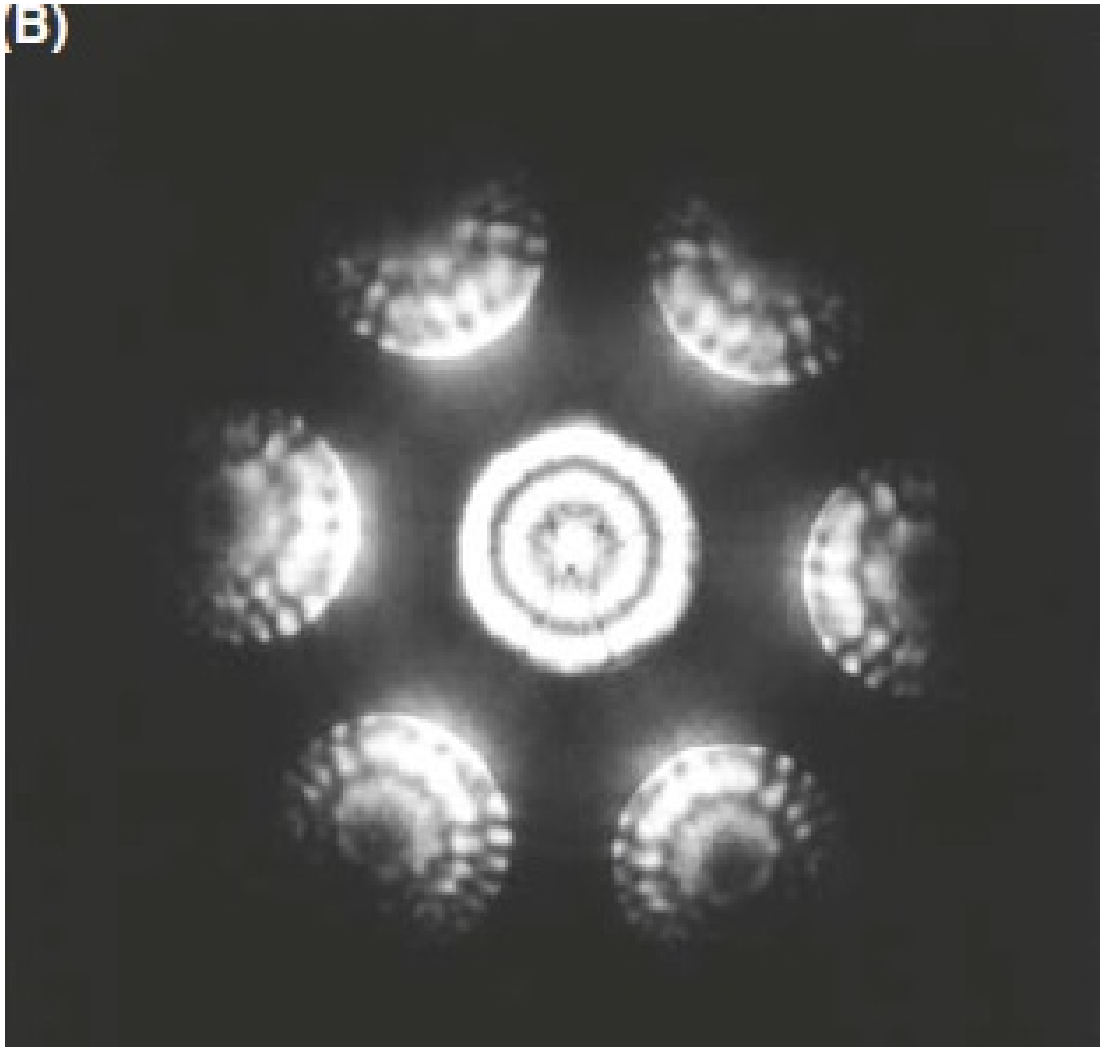
The Ewald spheres for different incident angles cut the relrod at different excitation errors.

Fundamentals of CBED II



The excitation error is consistent in all diffraction disks.

Thickness Determination



ZOLZ-CBED shows a black and bright pattern. These rings come from the relrod of the excitation error and can be used to determine the thickness.

Thickness Determination

- The accurate thickness of the sample is an important but hard to obtain parameter, but it influences the contrast in all imaging modes.
- Be aware that with different techniques you perform different thickness measurement. In any high resolution image and diffraction experiment, you always look at the thickness of the crystalline part of the sample, omitting the contribution of contamination and amorphous surface layer (from sample preparation).
- In the Analytic Section of this class we learn how to the thickness from the whole sample.

Thickness Determination

- Choose a convergence angle α so that $\alpha < \theta_B$, to avoid overlapping of disks in the ZOLZ.
- The 000 disk usually contains concentric diffuse fringes, the Kossel-Möllenstedt fringes
- If you move the specimen, then you will see that the number of this fringes changes. In fact the number of each fringes increases by one every time the thickness increases by one extinction length.
- The foil thickness can be measured precisely at the point where you do your other analysis.

Please be aware that dynamic effects also occur for the HOLZ lines in a CBED pattern.

Thickness Determination

- In practice to simplify the interpretation, we don't use zone axis conditions, but tilt to two–beam conditions with only one strongly excited Bragg beam.
- The CBED disks contain then parallel rather than concentric intensity oscillations as shown in the earlier figure.
- In fact, this intensity oscillations are equivalent to the rocking curve intensity oscillations discussed earlier.
- It helps, of you use an energy filter for this method.

Thickness Determination

- Because the oscillations are symmetric in the hkl disk we concentrate the analysis on this disk.
- The middle of the hkl disk is bright and originates from the exact Bragg condition ($\vec{s} = 0$).
- We measure the distance between the midle (bright fringe) of the *hkl* disk and the dark lines.

You obtain a deviation s_i for each fringe from the equation:

$$s_i = \lambda \frac{\Delta\theta_i}{e\theta_B d^2} \tag{1}$$

The Bragg angle θ_B is known from the separation of two disks and the lattice spacing d is known from the sample or can be calculated through the camera length.

Thickness Determination

If the extinction distance ξ_g is known you can calculate the foil thickness t with:

$$\frac{1}{t^2} = \frac{s_1^2}{n_k^2} + \frac{1}{\xi_g^2 n_k^2} \tag{2}$$

where n_k is an integer.

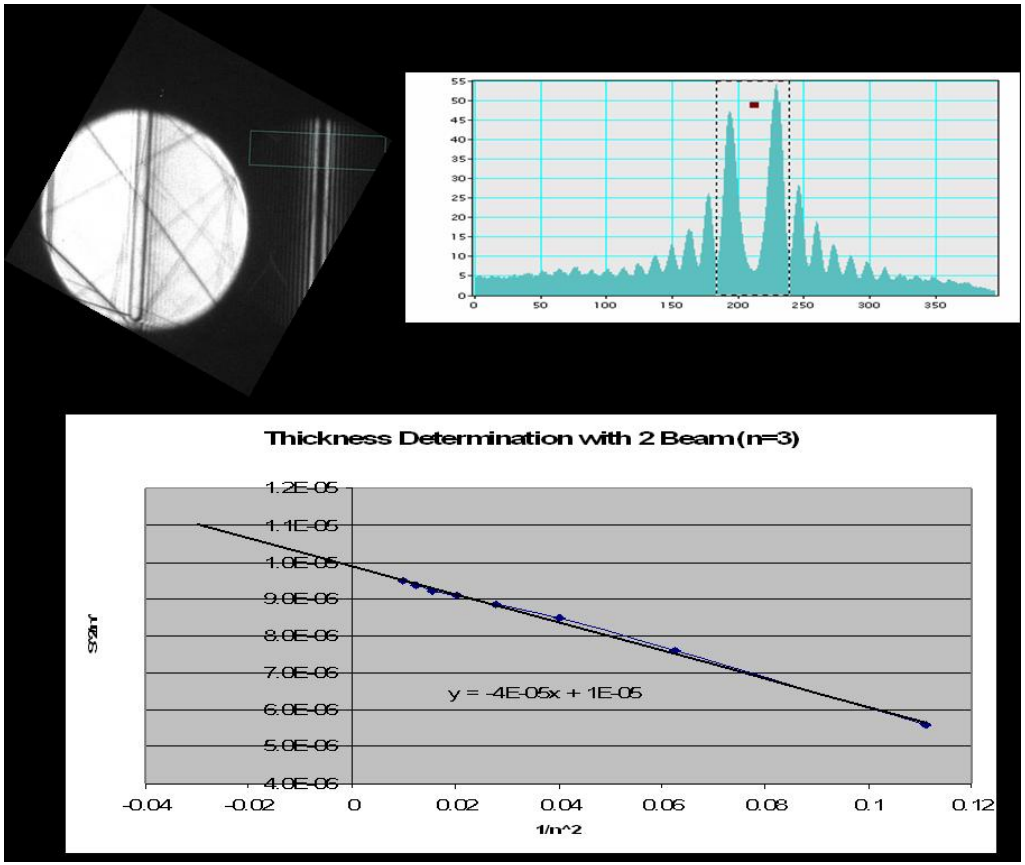
Thickness Determination

If you don't know the extinction distance, you can solve it graphically with following method.

- assign $n = 1$ to the first fringe s_1
- assign $n = 2$ to the second fringe s_2
- and so on for all other fringes
- plot $(s_1/n_k)^2$ versus $(1/n_k)^2$.
- if you get a straight line, then you are finished and you have $k = i + j$, where j is the largest integer $< (t/\xi_g)$.
- if not repeat the same thing with $n = 2$ for s_1, $n = 3$ for s_2, etc.
- repeat this increase by one till you get a straight line
- the slope of the line is $1/\xi_g^2$
- the extrapolated value for $1/n_k^2$ is $1/t^2$.

Thickness Determination

The whole procedure is shown in the figure below:



Acquire a CBED pattern in two beam condition. Plot the intensity linescan of the deficient part (top right). Evaluate the distances using above procedure. Please note that the slope in the graph (bottom) must be negative.

Unit-Cell Determination

- The HOLZ rings will give the lattice repeat vector (reciprocal vector parallel to the zone axis).
- So tilting in [001] zone axis, the ZOLZ pattern will give you the [100] and [010] distance
- and the HOLZ ring radius the [001] distance.

This is the determination of the lattice parameter of a unit cell.

Thus, we see that one can determine 3D information from a single two dimensional pattern. It might be necessary to use other low order zone axes.

Unit-Cell Determination

- Record HOLZ and ZOLZ patterns, if possible in one picture (use double illumination with different exposure times to enhance dynamic range), but with different convergence angles.
- If the angle of the ring is too large then your measurments may suffer from lens distortions.
- If the HOLZ ring is split measure the inner one.
- A Kossel pattern allows easier measurment of the HOLZ rings, while Kossel-Möllenstedt patterns allow the measurements of the ZOLZ disks.

Unit-Cell Determination

If H is the distance between the reciprocal-lattice planes parallel to the beam and G_n is the projected radius of the HOLZ ring, then

$$G_1 = \left(\frac{2H}{\lambda}\right)^{1/2} \tag{3}$$

$$G_2 = 2\left(\frac{H}{\lambda}\right)^{1/2} \tag{4}$$

for FOLZ and SOLZ. Similar expressions can be developed for higher order HOLZ rings. In real space you get for example for FOLZ:

$$\frac{1}{H} = \frac{2}{\lambda G_1^2} = \frac{2}{\lambda}\left(\frac{\lambda L}{r}\right)^2 \tag{5}$$

Unit-Cell Determination

If you did use a zone axis which is not 100, then you have to compare your result to calculated values.
Assuming you are looking down $[UVW]$ then we know:

$$\frac{1}{H} = |[UVW]| \tag{6}$$

Unit-Cell Determination

Now we have to calculate this $|[UVW]|$ for different structures:

for fcc:

$$\frac{1}{H} = \frac{a_0}{p(U^2 + V^2 + W^2)} \tag{7}$$

with a_0 is the lattice parameter and $p = 1$ for $U + V + W$ is odd; $p = 2$ for $U + V + W$ is even.

for bcc:

the same relationship is true but p is different: $p = 2$ for U, V, and W are all odd; $p = 1$ otherwise.

Look up other crystal systems.
If a ring is forbidden: you have to multiply your measurement $1/H_m$ with an integer n to obtain the distance of the crystal.

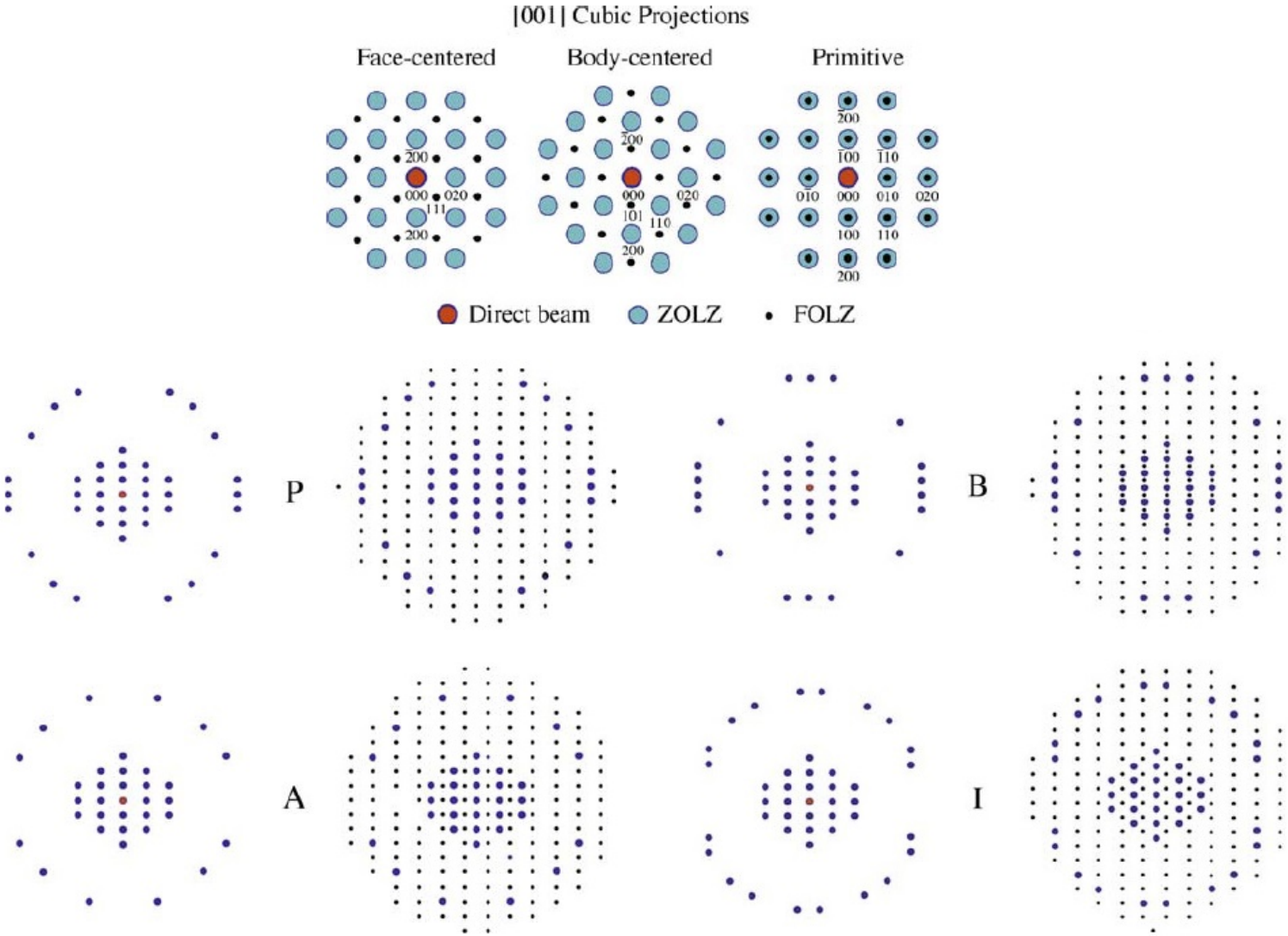
Lattice Centering

When you have measured H^{-1} the next thing is to compare ZOLZ and FOLZ patterns in the Kossel-Möllenstedt pattern.

Use the ZOLZ disk/points and extend it out into the FOLZ region.

Only in the primitive crystal system there are no extinctions (forbidden reflections) and all FOLZ lay on the grid given by the ZOLZ pattern.

Lattice Centering



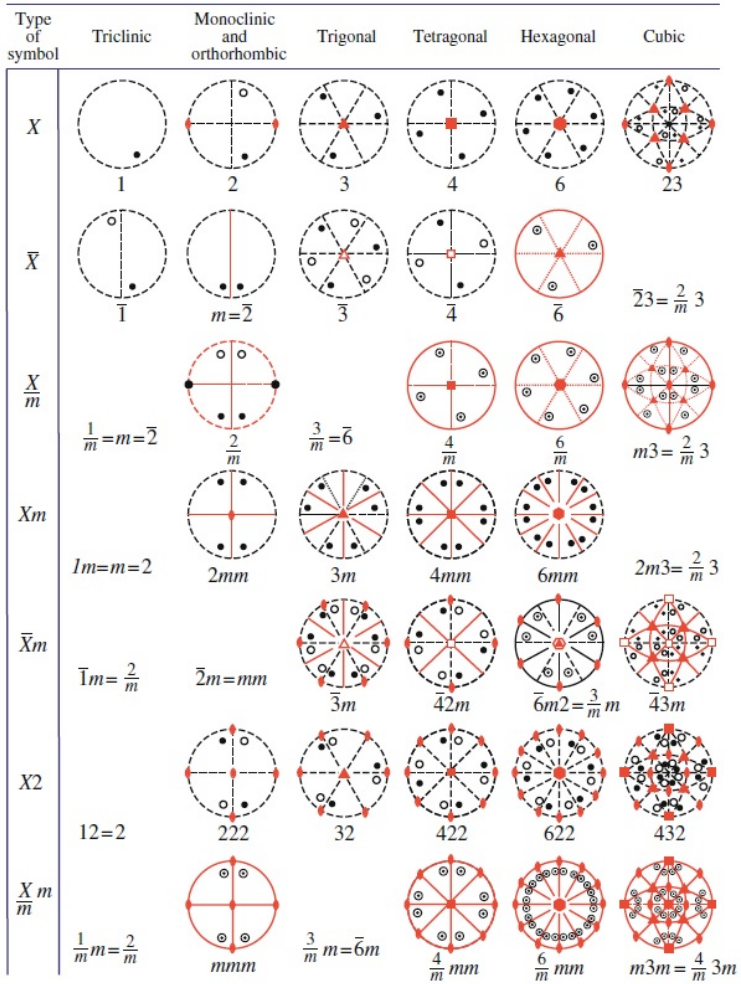
Extend the pattern for the ZOLZ into the HOLZ ring and look for

Symmetry Determination

Before we start with symmetry determination, I want to make sure you know all the terms. Let's remember it by looking at table 1 where all the 32 point groups are summarized.

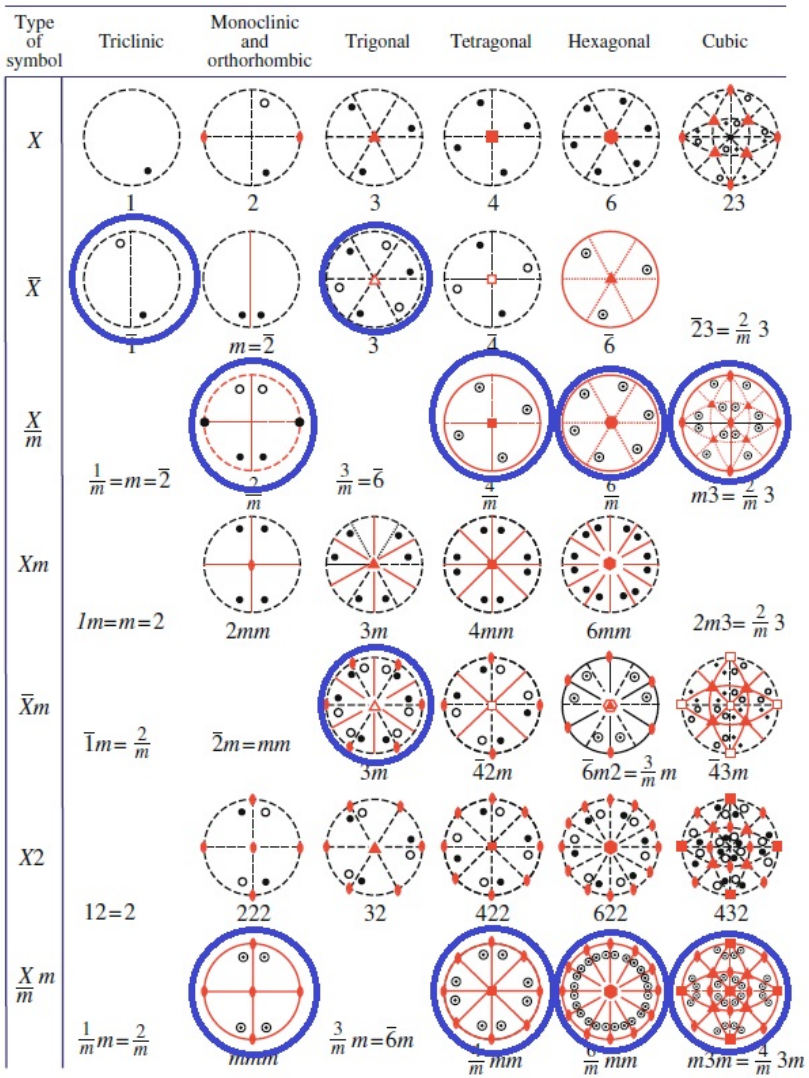
Symmetry Determination

Table: The 32 point groups with schematic of their symmetry.



Symmetry Determination

Table: Experimentally we can only identify the 11 Laue groups X-ray diffraction or SAED.



Symmetry Determination

- We look at the rotation, inversion and mirror symmetry. For the space groups, we also have to consider translation symmetries (later).
- I mentioned already that we CBED is more convenient than X-ray diffraction to determine the point group and that we can even determine the space group.
- X-ray diffraction experiments can rely on Fridel's law, because kinematical condition is fulfilled.
- The intensity of some reflections hkl is equal to the intensity in its opposite reflection $\bar{h}, \bar{k}, \bar{l}$.

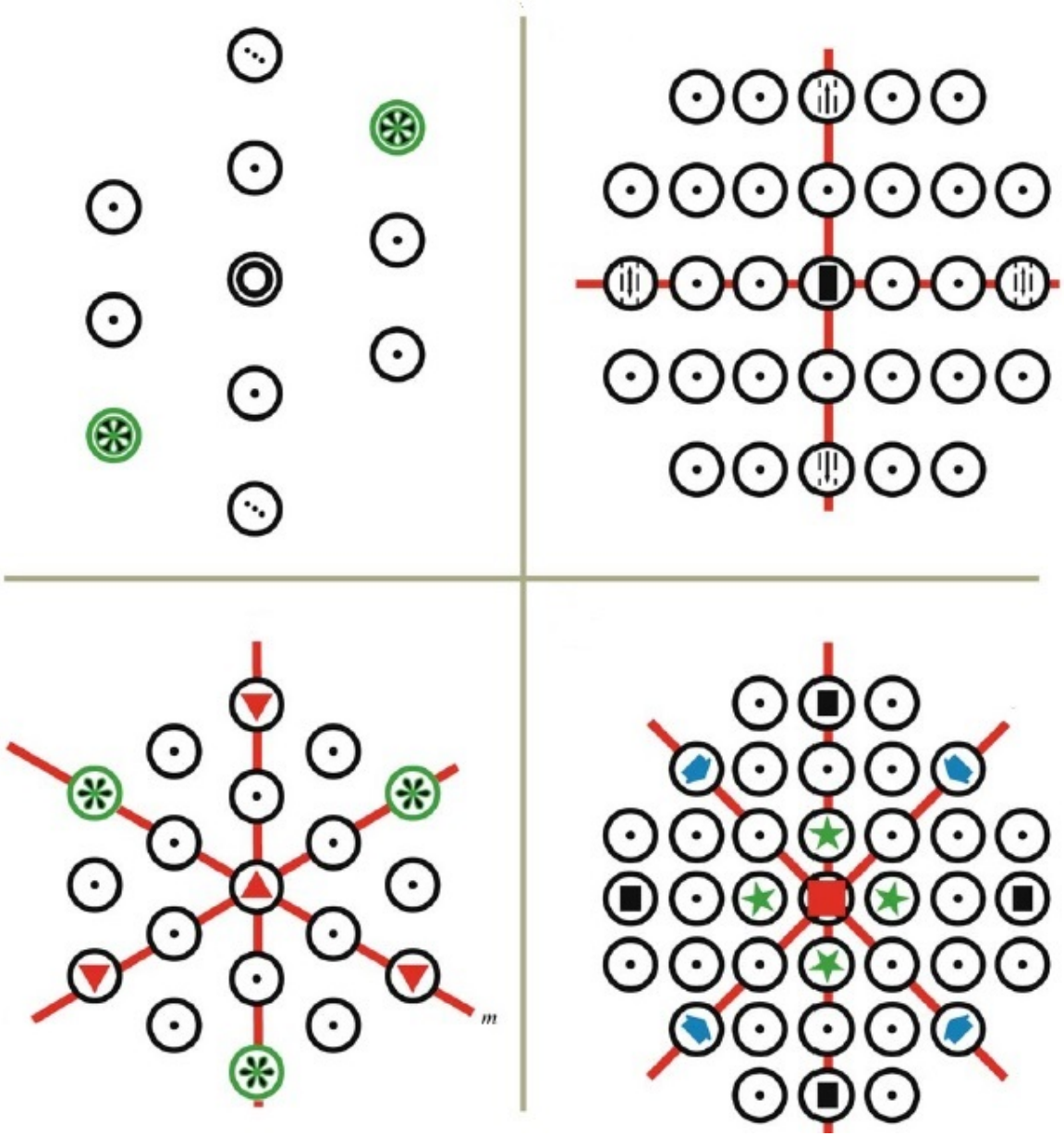
Symmetry Determination

In X-ray diffraction and SAD experiments

- we cannot distinguish a twofold rotational axis from a mirror plane;
- we cannot distinguish a m from a 2 point group.
- we cannot distinguish 4 and mm (a fourfold symmetry and a two perpendicular mirror planes).

Please see fin the next figure if you think that there is no difference between a 180^{o} rotation and mirroring.

Point Group Determination



Point Group Determination

All the diffraction patterns in X-ray are centro–symmetric.

In summation, with X-ray diffraction pattern you can only distinguish between 11 point groups, the Laue groups. Only under anomalous scattering conditions, you can access the full symmetry with X-ray scattering.

Friedel's law can be broken under dynamical conditions,

which is easily done in the TEM, we just use thicker areas. The disks have now an intensity distribution, which allows to access all the 32 point groups.

Point Group Determination

We look for symmetries now:

- We use X for the number of rotation axes and m for mirror planes parallel to the rotation axis and a second m for a any independent mirror plane.
- Inversion symmetry $\bar{X}$ and a mirror plane normal to the incident beam X/mcannot be discerned.
- By simply looking at a single CBED pattern, we can discriminate 10 point groups $1, 2, m, 2mm, 3, 3m, 4, 4mm, 6, 6mm$. These are the symmetries, which leave the direction of the zone axis unchanged.

Point Group Determination

- You can look at the symmetry of the whole pattern or look at the symmetry of the 000 disk (bright field symmetry).
- With the 000 disk, we can access the third dimension, which we need to get the 32 point groups.
- If you omit the HOLZ lines and look at the diffuse scattering diffraction contribution only, that is called projection symmetry, but, if possible, we analyze the HOLZ lines as well as any other feature in the bright field or whole pattern.

The HOLZ lines just add to the complexity and, therefore, the symmetry information in the CBED pattern.

Point Group Determination

- Again, do not let the disks overlap, modern microscopes have a coherent enough source to screw up any symmetry (especially FEG-TEMs).
- Ultimately, you want to determine a crystal's space group, which completely characterizes the crystal's symmetry.
- The space group is a combination of the point group, the Bravais lattice, the glide planes and the screw axes.
- The point group gives the whole symmetry information, while the space group determines which of the axes is a screw axis and which of the planes is a glide plane.

Under normal condition the point group is sufficient to characterize the sample.
However, with some tilting and crystallography, the space group can be determined from CBED as well.