Introduction

"Electron Crystallography" part of International School on Fundamental Crystallography with applications to Electron Crystallography

Diffraction in general

Bragg law: \[ 2dsin\theta = n\lambda \]

When X-ray or electron waves diffract on a material we will get strong reflections at the positions where waves have constructive interference. In other positions, the intensity will be zero or very low. This is what is expressed by the Bragg law (for proof see basic crystallography texts). It means there will be a strong diffracted beam on the exit side of the crystal only if there is a set of planes oriented at an angle \( \theta \) that satisfies the above equation, relative to the incoming beam.
<table>
<thead>
<tr>
<th></th>
<th>X-rays</th>
<th>Neutrons</th>
<th>Electrons</th>
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<tbody>
<tr>
<td>λ≈1 Å</td>
<td>interact with electrons</td>
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<td></td>
<td>weak interaction with lighter elements</td>
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<td>penetrating</td>
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<tr>
<td>λ≈1 Å</td>
<td>interact with nucleons</td>
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<td></td>
<td>magnetic moment</td>
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<td></td>
<td>very penetrating</td>
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<tr>
<td>λ≈0.025 Å,</td>
<td>interacts on voltage</td>
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<td></td>
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<tr>
<td></td>
<td>stronger interaction</td>
<td></td>
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<tr>
<td></td>
<td>less penetrating</td>
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</tbody>
</table>

Electrons can be used on much smaller samples and for local investigations, compared to the bulk techniques of X-ray and neutron diffraction.

![Typical Electron Microscope](image-url)
Typical diffraction patterns

Electron diffraction  X ray powderdiffraction

X ray single crystal diffraction

very similar

Neutron powder diffraction

Goal of the Electron Crystallography part of this school

-learn how to interpret different electron diffraction patterns
-learn how to derive the correct symmetry from these patterns
-learn to connect the unit cell structure to these patterns
  on a basic level, in line with "Fundamental Crystallography" part of this school

Not

-go over all theoretical background
-learn how to do general TEM (spectroscopy, general imaging,...)
-work hands-on at the microscope
-very specific treatments valid for one particular type of material
In this course we will look at

Selected area electron diffraction
Convergent beam electron diffraction
Microdiffraction
Precession electron diffraction
Kikuchi Lines

All same basic relation with the reciprocal lattice of a structure

What do ED patterns look like and why?

Laue conditions

Alternative to Bragg Law: Laue conditions. Atoms O and L. Vector r from O (atom at origin) to atom at L. p₀ and p are incident and scattered wave (unit vectors). Scattered waves are in phase if POD = integral number of wavelengths, nλ.

→ PO = r.p₀, OD = r.p.
POD = r.(p-p₀) = r.P
PO = r.p₀ \iff POD = nλ

\begin{align*}
\vec{r} \cdot \vec{P} &= n\lambda \\
\vec{P} \cdot \vec{a} &= h\lambda \\
\vec{P} \cdot \vec{b} &= k\lambda \\
\vec{P} \cdot \vec{c} &= l\lambda
\end{align*}

(All vectors normalised by division by λ)
Laue conditions

\[ \vec{P} \cdot \vec{a} = h \lambda \]
\[ \vec{P} \cdot \vec{b} = k \lambda \]
\[ \vec{P} \cdot \vec{c} = l \lambda \]

⇒ \[ \vec{P} / \lambda = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \]

With \( \vec{a}^* \), \( \vec{b}^* \), \( \vec{c}^* \) defined such that
\( \vec{a} \cdot \vec{a}^* = \vec{b} \cdot \vec{b}^* = \vec{c} \cdot \vec{c}^* = 1 \)
\( \vec{a} \cdot \vec{b}^* = 0 \) etc

\( \vec{a}^* \), \( \vec{b}^* \), \( \vec{c}^* \) are the basis vectors of the reciprocal lattice

\[ \vec{g}_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \]

Relation of the reciprocal lattice to the planes of the structure is given above. Every node in the reciprocal lattice is a linear combination of the basis vectors \( \vec{a}^* \), \( \vec{b}^* \) and \( \vec{c}^* \).

The reciprocal lattice

Properties (not proven here):

The vector \( \vec{g}_{hkl} \) to the reciprocal lattice point hkl is normal to the plane (hkl) of the crystal lattice.

The magnitude of \( \vec{g}_{hkl} \) equals \( 1/d_{hkl} \), where \( d_{hkl} \) is the interplanar spacing of the family of (hkl) planes.
\[ \vec{F}/\lambda = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \]

\[ g_{hkl} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \]

\[ \vec{F}/\lambda = g_{hkl} \]

Small part of Ewald sphere with radius \( 1/\lambda \)

Expressions \( g \) and \( P/\lambda \) are equal. Allows to construct the figure on the right. Note that the length of the two vectors incident and diffracted is the same → they lie on a sphere with centre L, i.e. the Ewald sphere. Lattice nodes lying on the Ewald sphere are in Bragg condition/fulfill the Laue conditions → constructive interference at this position, reflection can be seen. E.g. 100 kV radius Ewald sphere ~50 times typical reciprocal lattice point spacing → almost flat → electron diffraction patterns considered as sections through reciprocal space.

Any type of electron diffraction pattern is a section of reciprocal space, going through 000, which is the central, undiffracted beam (here marked with a +).
The reflections are lying on a lattice. Here, for clarity, only $1/8$ of a lattice is depicted, with indices only between 0 and 2.

At the microscope, the user needs to look for the correct zone. This is done by tilting the crystal. This way you get different zone axis patterns which can give you different pieces of information. The currently indicated zone is [100].
When the crystal is rotated, the reciprocal lattice rotates along. This way one by one the different planes of the reciprocal lattice will coincide with the reflecting plane (where the Ewald sphere touches the reflections). Now the indicated zone is [-210].

Now the indicated zone is [-110].
Now the indicated zone is [1-20].

Now the indicated zone is [010]. By collecting the right zones, you can thus get information about the cell parameters, reflection conditions and symmetry, since this is basically the reciprocal lattice of the structure that you are sampling. The other way around, when you have a tilt series, you can reconstruct the three-dimensional reciprocal lattice by combining the patterns at the angles over which you tilted.
How to index Selected Area Electron Diffraction (SAED) patterns

Selected area electron diffraction is simplest to understand, because it resembles the reciprocal lattice closest. Therefore, we will treat this first, and use this background for the other types of diffraction patterns.

Suppose you have a set of SAED patterns (literature, experiment, collaborators, ...)

Do you know the cell parameters already? (literature, XRD, collaborators, ...)

- YES
  - This we do first, is simplest

- NO
  - More complicated → needs some extra steps

Start with the simplest case: you know the cell parameters, be it from another technique, from literature, or from collaborators.
Example: indexing the following simulated patterns with known cell parameters.

Next up: you try it yourself on real SAED patterns (guided step-by-step)

Example: MgSiO$_3$ (most abundant material on earth)

Assumed known:
Space group Pnma
a = 4.933 Å
b = 6.902 Å
c = 4.78 Å

*The example will use the structure of MgSiO$_3$, assuming we know the space group and cell parameters from an arbitrary source.*
This is the zone that we will index:

The scalebar can be given in different ways, depending on the manufacturer of the microscope.

You always need to extract a d-value ("interplanar spacing") in Å to match the length of the scalebar measured in, for example, mm. This d and R you then use in the formula \( R.d = \lambda L \). The constant is called the camera constant, also noted as \( \lambda L \) (wavelength e-beam x cameralongth). In the cases above, each time \( d=2.39 \) Å. The \( R \), and thus \( \lambda L \), depends on the size of your print of this page...
Once you know \( \lambda L \) you can use this same value to measure the distance from the central beam to a reflection (= \( R \) in mm) and calculate the interplanar spacing (\( d \)-value in Å) corresponding to each reflection.

\[
R.d = \lambda L \\
\downarrow \\
d = \frac{\lambda L}{R}
\]

Interplanar spacing for that reflection

Distance measured on diffraction pattern for that reflection

Calculate in this way the \( d \)-values for the reflections closest to the central beam. This pattern shows the \( d \)-values you would get in this way. All other indices can be obtained from any two indexed reflections not lying on one line through the central beam.
So we have three reflections, at 3.45 Å, 3.93 Å and 2.39 Å.

We know the cell parameters:
\[ a = 4.933 \text{ Å}, \quad b = 6.902 \text{ Å}, \quad c = 4.78 \text{ Å} \]

Calculate a table with \( d \)-values

- Manually
- Use software
  - Powdercell,... (free)
  - CrystalMaker, Carine,... (not free)

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We need to compare these \( d \)-values with the list of \( d \)-values appearing in this structure. You can calculate these manually (look for the formula in a crystallography course) or you can use any software available to you, e.g. Powdercell, freely available on the web.

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>( d \text{ (Å)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3.92963</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>0</td>
<td>3.45100</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1</td>
<td>3.43279</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3.07361</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>2.46650</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2.43376</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2.39000</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0</td>
<td>2.32265</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>2.19189</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>2</td>
<td>2.15086</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2.08908</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>1</td>
<td>2.07304</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2.05346</td>
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<tr>
<td>2</td>
<td>2</td>
<td>0</td>
<td>2.00666</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>2</td>
<td>1.96481</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1.91114</td>
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<tr>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1.85024</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1.82535</td>
</tr>
</tbody>
</table>

This is a short list corresponding to the given cell parameters and space group (SG) Pnma. The space group at this stage simply removes some reflections. If you do not know the SG, just use \( P1 \) for such list, the \( d \)-values are only dependent on the cell parameters.
<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1</td>
<td>3.92963</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
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<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1.82535</td>
</tr>
</tbody>
</table>

3.45 corresponds to 002 in the list, 3.93 to 011 and 2.39 to 002. Keep in mind that, depending on the space group, several reflections can be equivalent and thus have the same d-value and are not necessarily mentioned separately, such as in a cubic case 100, 010, 001, -100, 0-10 and 00-1. Choose the correct ones to make a consistent solution considering also other patterns in a tilt series if available.

Consistent solution needs a.o.:

1) vector addition gives correct indices

2) if available, other patterns in tilt series have the same indices for common reflections
In the current case (Pnma), 020 is equivalent to 0-20; 002 to 00-2; 011 to 0-11, 01-1 and 0-1-1 etc.

Same pattern in close-up. Check the vector addition. Fits here: 020 + 002 = 022, at half the distance you have 011.

By this vector addition you can find the indices of all other reflections also.
Finally, you have to determine the zone [see Fundamental crystallography]. Each reflection lies on the perpendicular to a plane, and the zone axis is the direction perpendicular to all planes in this zone. Therefore, the zone index is obtained by vector product of any two vectors in the pattern. The zone index of the pattern that is shown is [100].

But it is not that simple...

Note that the values for 121 and 210 are also close to the measured value 2.39 Å and that of 101 is close to 3.45 Å, in fact especially for the latter you will never be sure which one it is based on distances obtained from ED only, because ED is not very precise and depending on your measuring technique several might be possible. Also take into account possible distortions due to lens system or detector. How to make a conclusion? If you have only this pattern: use the need for a correct vector addition to decide (see next slide).
For 3.93 there is only one option: 011. This means it can be 011, 0-11, 01-1, 0-1-1. So the correct combination for 3.45 and 2.39 has to add up to twice this index.

Taking all possible sign changes into account, we can have 020+002=022, 101+121=022, -101+121=022, 10-1+12=022, -101+12=022. You can eliminate the last possibility by looking at the angle between these planes, which is 135°, clearly different from the 90° in the pattern. For all other combinations, the angle is either 90° or 88.72° (calculate using software (eg Carine or formulas in appendix). On ED patterns a deviation of 1.28° might not be noticeable in a conclusive manner. So we still have a lot of options left.
Calculate the zones. It comes down to [100] and zones equivalent (in Pnma) to [111]. You can see that <111> has an extinction, however, if you have only a pattern and you are not at the microscope, you cannot use this for a conclusion, because the extinction can be hidden by double diffraction.

To be able to decide which possibility is the correct one, you have to tilt to at least the nearest zones. They are different for [100] and [111].

Tilting over 13° over the row with shortest reciprocal distances gives from [100] a pattern with double the amount of reflections in all rows except the central one, compared to the pattern which you get when tilting over 13° from [111]. Thus you can decide. This example may seem very specific, but such ambiguity is very common and often overlooked. When the structure is derived from a high symmetry parent structure with only minor deviations away from the high symmetry, many zones will be very much alike.
Or another way to check, while you are at the microscope, would be to tilt around that axis for which in [111] you should have systematic absences. If the reflections disappear when you tilt around this axis, it is a <111> type zone.

Remarks:

there are systematic extinctions: all reflections with k+l≠2n

Suppose we found it was [100] after all. This means some reflections are extinct: all reflection for which k+l is odd. This fits with the space group Pnma, where the n means a glide plane perpendicular to the a axis, with a glide vector over ½(b+c), resulting in reflection condition 0kl:k+l=2n.
Important difference between calculated and real SAED patterns

Systematically extinct reflections can appear present due to double diffraction. The interaction of the material with the electrons is so strong that they diffract several times in their path through the material, this can cause positive intensities to occur at any place that is the addition of two reflections already present.

Examples.
Extinctions due to the Bravais lattice will never be hidden by double diffraction.

All possible paths are absent.

Very common: extinctions due to screw axes are often hidden by double diffraction.

Bravais lattice extinctions cannot be recreated by double diffraction, because the Bravais reflection condition makes all reflections extinct that could have recombined in the correct path of vector addition. The most common occurrence is that the extinctions along main axes, due to screw axes, are hidden. Therefore it is always wise to tilt around the main axes until all vector addition paths are destroyed (i.e. you have only the central row of reflections left) to check if the odd reflections remain present or not.

If you did not know the cell parameters

Determining the cell parameters from SAED patterns

Propose a realistic set of parameters

Try to index with these parameters

Adapt parameters if necessary
Tips for choosing first set of cell parameters

Look at all SAED patterns:

a) look for the ones with smallest interreflection spacing = largest d-spacing = often main zones containing basic vectors

b) look for patterns with high symmetry, such as 4-fold and 6-fold, they have more restricted indexing possibilities and are often low index zones

First try to find the best SAED patterns using the criteria above, then try for example first to index the vectors closest to the central beam as the basis vectors. This is a trial and error process.

Possibility to use software for this

Combine separate patterns into a 3D reconstruction, with the possibility to extract cell parameters:

PETS (free)

Trice (Calidris, not free)
Check your solution

Simulate patterns. Positions of all spots need to be reproduced with your choice of cell parameters

not free: CrystalMaker+SingleCrystal, CrystalKit, MacTempas, Jems,...
free: Jana, student version JEMS, GDIS, ...

The easiest way to check your solution is to simulate the patterns with one of the many software packages. The programs will ask you for the space group and coordinates, but you can already check just your cell parameters without these, because the positions of all reflections does not depend on your coordinates or space group, so for this you can use P1 and atoms at random positions.

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How to determine the diffraction symbol from electron diffraction patterns

For the lecture on how to use the positions of the reflections, go to “How to index SAED patterns”. This lecture is on how to use presence/absence of reflections. For information on how to use the intensities to get information on the symmetry, go to lecture "How the symmetry in real space reflects the amplitudes of the reflections"

Structure factor

\[ F_{hkl} = \sum_{j=1}^{\text{atoms}} f_j e^{2\pi i (hx_j + ky_j + lz_j)} \]

- \( f_j \) - scattering factor of atom \( j \)
- \( h, k, l \) - indices of the reflection
- \( x_j, y_j, z_j \) - coordinates of atom \( j \)

The intensities of the reflections are obtained from the structure factor. In this formula we take the sum over all atoms, with \( f_j \) the scattering factor of atom \( j \), \( hkl \) the indices of the reflection and \( x_j, y_j, z_j \) the coordinates of atom \( j \). This can be interpreted as if the scattering from all atoms creates an interference pattern. When there is destructive interference, the reflection is absent.
If there is only one type of atom A and it is a primitive cell, the structure factor is a constant $f_A$. This means that all reflections will have the same intensity. (There is a decrease in intensity as you go away from the central beam, independent of the structure.)

If you have only one type of atom A, but you do not have a primitive cell, it could be that some reflections get a different intensity. You can see the equations for the structure factor in case of a body centered cell above for example. For all $h+k+l$ even you have a strong reflection with amplitude $2f_A$ while if $h+k+l$ is odd, the amplitude is zero, this means the reflection is absent.
This will result in the absence on the SAED patterns of all these reflections that have $F_{hkl}=0$. The left patterns, with a reflection at each node of the reciprocal lattice, will thus turn into the right side pattern.

$Lattice$ $centering$ $|$ $Reflection$ $condition$

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>no reflection condition</td>
</tr>
<tr>
<td>I</td>
<td>$hkl: h+k+l=2n$</td>
</tr>
<tr>
<td>A</td>
<td>$hkl: k+l=2n$</td>
</tr>
<tr>
<td>B</td>
<td>$hkl: h+l=2n$</td>
</tr>
<tr>
<td>C</td>
<td>$hkl: h+k=2n$</td>
</tr>
<tr>
<td>F</td>
<td>$hkl: h+k=2n, k+l=2n, h+l=2n$</td>
</tr>
</tbody>
</table>

This structure factor can be calculated for the different possible centerings, P, I, F, A, B, and C and will give you the different reflection conditions we will meet in the electron diffraction patterns of such structures.

\[
F_{hkl} = 2f_A \quad \text{if } h+k+l=\text{even} \\
F_{hkl} = 0 \quad \text{if } h+k+l=\text{odd}
\]
So the other way around, instead of calculating $F$ from a known structure, once you have indexed your electron diffraction patterns, you can derive from them which reflections are systematically absent and get from this information about the lattice centering and symmetry.

Systematic absences are caused by:

<table>
<thead>
<tr>
<th>Type</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>no reflection conditions</td>
</tr>
<tr>
<td>F</td>
<td>$h+k=2n$, $k+l=2n$, $h+l=2n$</td>
</tr>
<tr>
<td>I</td>
<td>$h+k+l=2n$</td>
</tr>
<tr>
<td>A/B/C</td>
<td>$k+l=2n/h+k=2n/h+k=2n$</td>
</tr>
</tbody>
</table>

Could be due to:

- glide plane perpendicular to $c$ with translation vector $(a+b)/2$ ($hk0: h+k=2n$)
- C centering ($hkl: h+k=2n \rightarrow hk0: h+k=2n$)

Necessary to collect all main zones before making a conclusion.

<table>
<thead>
<tr>
<th>Need</th>
<th>CBED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mirror planes</td>
<td></td>
</tr>
<tr>
<td>Inversion centre</td>
<td></td>
</tr>
<tr>
<td>Rotation(-inversion) axes</td>
<td></td>
</tr>
</tbody>
</table>

Not by

<table>
<thead>
<tr>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glide planes</td>
</tr>
<tr>
<td>Screw axes</td>
</tr>
</tbody>
</table>

SAED
Reflection conditions can be looked up in tables in *International Tables for Crystallography Vol. A*

(Click for image)

Or using freeware such as [Space Group Explorer](https://www.crystallography.info/sge/)

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Specific for electron diffraction:
Forbidden reflections can occur because of multiple diffraction → needs doublechecking

Because of the strong interaction of the electron beam with the material, a beam can be diffracted more than once on its passage through the material. This creates new “origins” for the lattice and can lead to reflections appearing at the positions of forbidden reflections. This is further explained on the following slides.
Maybe you see this: When reflection
conditions say you should see this:

```
 010
```

For example, above there is a reflection condition 0k0: k = 2n, however the pattern that we see is the one on the left, where we clearly see that 010 and 030 are present. The pattern should look like the one on the right. However, in the next slides it is shown how this right hand pattern can lead to the appearance of those forbidden reflections on the left side.

Because:

```
 010
```

If you have in the ED pattern two vectors that add up to the position of the forbidden reflection, the reflection can and usually will be present.

Above, vectors to reflections 100 and -110 add up to 010, and can lead to the appearance of a visible intensity at the 010 position. This is of if 100 (or -110) would be the new origin and from there you diffract over the vector -110 (resp. 010).
Destroy double diffraction paths by tilting.

If becomes

\[ \cdot \quad \bullet \quad \cdot \]\n
then extinct, was due to DD

If stays

\[ \cdot \quad \cdot \quad \cdot \quad \bullet \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \]\n
then not extinct.

This can be checked while still at the microscope: if you tilt around the row showing the reflections possibly due to double diffraction, until there are no two reflections left of which the vectors add up to this position (for example you only have that row left) then the reflections should disappear if they are forbidden.
How to determine the unit cell using higher order Laue zones

Sometimes a circle of reflections will be present around the central pattern. This is a higher order Laue zone. Its existence is explained on the next slide.
You should know the Ewald Sphere from general diffraction theory, if not: basically it represents the sphere on which all reflecting lattice nodes all lying. Since it is curved, at the sides it will cut higher lying planes of the reciprocal lattice. The reflections on the circle around the central pattern are those reflections. They are called higher order Laue zones.

\[ \frac{1}{H} = \frac{2(\lambda L)^2}{\lambda R^2} \]

1/H= perpendicular distance to the next reciprocal plane
\( \lambda L \) = camera constant
\( R \) = distance in mm to the circle of the first order Laue zone

Here: \( \frac{1}{H} = 5.46 \text{ Å} \)

\( c^* = H = 1/d_{001} \) so \( c = 5.46 \text{ Å} \)

Full calculation:

\[ R_{\text{scale}} \frac{d_{\text{scale}}}{\lambda_{\text{scale}}} = R_{\text{scale}} \frac{1}{20 \text{ nm}} = R_{\text{scale}} \frac{0.5 \text{ Å}}{\lambda} \]

(the \( R \)'s depend on the size of your print-out; ED taken at 200 kV \( \Rightarrow \lambda \) is 0.0251 Å)

\[ \frac{1}{H} = \frac{2(\lambda L)^2}{\lambda R_{\text{ring}}^2} = \frac{2(R_{\text{scale}} \frac{0.5 \text{ Å}}{0.0251 \text{ Å}})^2}{5.46 \text{ Å}} = \]

You can use them to get all three cell parameters from one pattern if that pattern is a main zone ([100], [010] or [001]). Example 1: CoF₂. The closest reflections in the central part are at 2.73 Å, \( H = 5.46 \text{ Å} \) (calculation on slide). If you would know nothing about how extinctions work, you would conclude \( a = b = 2.73 \text{ Å}, c = 5.46 \text{ Å} \). However, you have to consider possible extinctions. \( \Rightarrow \) see slides "How to use microdiffraction for determining diffraction symbol" \( \Rightarrow \) \( f \) centered and \( a = b = c = 5.46 \text{ Å} \)
Example 2: chalcopyrite. Again, if you do not know about extinctions, you would wrongly think $a=b=3.9\, \text{Å}$, $c=10.8\, \text{Å}$. The value for is correct, but this cell is I centered, so $a=b=5.51\, \text{Å}$. For this, check the slides on microdiffraction.

Remark: exact position HOLZ ring is often unclear.

Better to use Kikuchi (Kossel-Mollenstedt) patterns for this.
How to use microdiffraction for determining the space group

*Pnma has reflection conditions* \( hk0; h=2n \) and \( 0kl; k+l=2n \)

Systematic absences can (also) be determined using "whole patterns", i.e. patterns where you see the ZOLZ and at least one ring of FOLZ. Imagine looking at a cell with space group Pnma, along the [100] direction. As an example, we use again MgSO₄. The slide shows simulations of the consecutive \( 0kl \), \( 1kl \) and \( 2kl \) layers next to each other. The patterns are different because of the reflection conditions: \( hk0; h=2n \) and \( 0kl; k+l=2n \).
As mentioned in the lesson "How to determine the cell parameters using HOLZ", because of the curvature of the Ewald sphere, you will see the 0kl layer or "zero order Laue zone" (ZOLZ) at the center and a ring from 1kl and/or 2kl (first and second order Laue zones, FOLZ and SOLZ) as rings around this centre. Schematically, it would look approximately like on this slide for ZOLZ and FOLZ. We basically just overlapped the ZOLZ and FOLZ pattern of the previous slide, showing ZOLZ at the centre and FOLZ around it. This rough estimate is just for conceptual understanding. In reality the ring will be at a certain precise distance as seen in the lecture on using HOLZ for parameter determination, where the Ewald sphere cuts the layer.

By analysing the differences between the ZOLZ and FOLZ (SOLZ) in such type of pattern, you can thus oppositely derive the extinction symbol (using more than one zone). This has been clearly tabulated by Morniroli and Steeds (Ultramicroscopy 45 (1992) 219-239), plus there is an "atlas" of all this made by JP Morniroli on this link.
A real example of a microdiffraction pattern (Journal of Solid State Chemistry 175 (2003) 188–196)

If you do not see a FOLZ/SOLZ ring (distance between reciprocal layers is too large):

tilt until you see a section of the ring
How the symmetry in real space affects the amplitudes of reflections.

Symmetry-relation in real space
\[ \vec{r}' = R \cdot \vec{r} + \vec{t} \]
R = rotation matrix
t = translation vector

Symmetry-relation amplitudes in reciprocal space
\[ (h'k'l') = (hkl).R \]

We can only see the amplitudes of the reflections in electron diffraction patterns, not the phases, therefore the only symmetry present in the patterns is the point group symmetry, i.e. the symmetry given by R (rotation, inversion, mirror plane) and by the 32 point groups.
Within one point group, there are the same equivalences between the reflections.

For example, have the same equivalent reflections:

\[ P4 \quad P4_1 \quad P4_2 \quad P4_3 \quad I4 \quad I4_1 \]

But not

\[ P\bar{4} \quad I\bar{4} \]

(although they again have the same among themselves)

Therefore the first row of space groups above, all have the same relations between the amplitudes of the reflections, since they all belong to the same point group, i.e. 4. The second row belongs to point group 4 and has different relations from the first row.

---

**Example:** Imaginary UC (5Å x 1.3Å) with one basis atom Au at 0.1, 0.2, 0.3 and space group difference only.

This allows you for example to decide between several leftover possible point groups if the difference is really clear. Caution: dependence on perfect orientation, sometimes difference too small, if you have the pattern on the right, you can definitely exclude P4/mmm and any other space group belonging to 4/mmm, however, if you have the pattern on the left, it could be 4. It is not because you see 4/mmm in a spot pattern, that it is 4/mmm. Differences might be too small to see, or clouded by dynamical diffraction for example. The absence of a symmetry can also not be decided if the orientation of your pattern is not perfectly in-zone.
If you want to use the intensities of the reflections for symmetry determination, it is best to use precession electron diffraction patterns if possible. As you can see, the SAED pattern often has a much more flat distribution of intensities, plus the precession process corrects minor deviations from the correct orientation.

Where do you get the equivalences?

-Use simulation software (CrystalMaker-SingleCrystal, Jems, CrystalKit,eMap,...)
-Calculate manually using the rotation matrices
-Use International Tables of Crystallography volume B, p.150-161

<table>
<thead>
<tr>
<th>ITB example:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Point group: 4 Tetragonal</strong></td>
</tr>
<tr>
<td><strong>Space group: 4ma</strong></td>
</tr>
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<td>1.h:6  2.h:0  3.0:0  4.e:0</td>
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</tr>
<tr>
<td>1.h:6  2.h:0  3.0:0  4.e:0</td>
</tr>
</tbody>
</table>
How to use CBED to determine the point group

(the Eades way)

For example,
in "How to determine de diffraction symbol from SAED":
CaF$_2$ has F - - -

This still leaves 5 possible space groups

F23  Fm3  F432  F43m  Fm3m

→ need Convergent Beam Electron Diffraction (CBED)

After deriving the diffraction symbol from SAED, you often still have several possible space groups left, with as only difference between them the presence or absence of rotation axes, mirror planes and inversion centres. These elements do not result in extinctions and thus cannot be derived from the diffraction symbol. You need a technique that can differentiate between the point groups, i.e. convergent beam electron diffraction. CBED cannot differentiate between rotation axes and screw axes, or between mirror planes and glide planes. SAED and CBED are thus nicely complementary.
For CBED you need sufficiently thick crystals:

CBED patterns obtained by focusing your beam onto your crystal instead of using a parallel beam and aperture as for SAED. This will result in discs instead of spot patterns. The diameter of the disc depends on the condenser aperture that you use. If you use a very small condenser aperture you get (quasi) spots again and this is more commonly called microdiffraction patterns. For CBED you need to have dynamical diffraction, therefore crystals that are too thin will not give you nice CBED patterns. In the slide you see the difference in the CBED patterns upon changing thickness only. The exact thickness needed depends of course on your material.

Easiest* : Eades method

1) Obtain CBED patterns of high symmetry zones, preferably showing HOLZ
2) Derive "diffraction group" of each zone
3) Look for the point group that can have all the diffraction groups you found for the different zones
   → You need two tables:
     - relation symmetries - diffraction groups
     - which point groups contain which diffraction groups
     (both included in these slides)

* purely personal opinion

There are several CBED methods, in this school we will pick the Eades method, as it is the easiest to implement on the microscope*. 
This is the table connecting the symmetry in the CBED patterns to a certain "diffraction group". Each zone has its own diffraction group. Knowing that certain diffraction groups exist for a material, you can eliminate the not-matching point groups using a next table. To work with this, we first need to define what is meant in this table with the projection symmetry, the bright field and the whole pattern.

### Table 7.1: Diffraction Groups

<table>
<thead>
<tr>
<th>diffraction group</th>
<th>bright field</th>
<th>whole pattern</th>
<th>projection symmetry</th>
<th>diffraction group</th>
<th>bright field</th>
<th>whole pattern</th>
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### Table 7.2: Projections

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### Whole pattern, 3D symmetry

*aka "whole pattern symmetry"

- **3D WP**
  - **Whole pattern, 3D symmetry**
  - **Bright field, 3D symmetry**
  - **no HOLZ lines? 2D BF = BF projection symm**

### Whole pattern, 2D symmetry

*aka "whole pattern projection symmetry"

- **2D WP**
  - **Whole pattern, 2D symmetry**
  - **Bright field, 2D symmetry**
  - **no HOLZ lines? 2D BF = BF projection symm**

The different symmetries are indicated in this slide. The BF (proj) symmetry is often hard to get, so our examples will use only WP symmetries (=basics, if you want more advanced ➔ J.A. Eades, Convergent beam diffraction, in: Electron Diffraction Techniques, volume 1, ed. J. Cowley, Oxford University Press, 1992) Also the HOLZ ring cannot always be seen, as e.g. in our example on the next slides. However, the treatment of the WP is the same as of the WP projection symmetry, using simply the other side of the table.
We will take the experimentally easiest route to explain the concept: using only whole pattern projection symmetries, i.e. we need only ZOLZ CBED patterns. If you have also HOLZ, treatment is analogous, and leaves less options (so better, but applicable for less materials). Suppose we found the two patterns (WP projection) shown above for the CaF₂ compound. (These are calculated images for clarity of the example, calculated using Jems.)
Symmetry is 4mm.

**Whole pattern projection symmetry**

Determine the symmetry of the pattern, which can only be 1, 2, m, 2mm, 3, 3m, 4, 4mm, 6 or 6mm. The symmetry of the pattern above is 4mm, i.e. a fourfold axis a mirror plane perpendicular to \( \langle a \rangle \) and a mirror plane perpendicular to \( \langle 110 \rangle \) (as you learnt in the first part of this school).

Symmetry is 6mm.

**Whole pattern projection symmetry**

Determine the symmetry of the other pattern. The symmetry of the pattern above is 6mm, i.e. a sixfold axis a mirror plane perpendicular to \( \langle a \rangle \) and a mirror plane perpendicular to \( \langle 210 \rangle \).
Using only ZOLZ CBED patterns, we first need the part of the table containing the projection symmetries (indicated) first, i.e. the right hand side. The first pattern had WP proj symm 4mm, the second one 6mm. Thus we can derive the projection diffraction groups for each zone, as shown in the next slides.

Table from: J.A. Eades,
Convergent beam diffraction, in:
Electron Diffraction Techniques,
volume 1, ed. J. Cowley, Oxford University Press, 1992

<table>
<thead>
<tr>
<th>Diffraction Group</th>
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</table>

The first zone has projection diffraction group 4mm1m, which leaves as diffraction groups 4m, 4mm, 4m1m and 4mm1m.
The second zone has projection diffraction group $6mm_{1R}$, which leaves as diffraction groups $6mm_{m}, 6mm, 6_{2}mm_{m}, 6mm_{1R}$.

A lot of possibilities left, but next we combine it with the possible space groups and we will see there is only one match.

<table>
<thead>
<tr>
<th>Diffraction group</th>
<th>Bright field</th>
<th>Whole pattern</th>
<th>Projection group</th>
<th>Bright field</th>
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Diffraction groups vs. Point groups

These are the point groups between which we need to make a conclusive decision for the case of CaF₂ (since we already have the diffraction symbol).


### Conclusion: the point group of CaF$_2$ = m3m

If not conclusive:

-need more zones

and/or

-need more types of symmetry (e.g. WP symmetry is taken&treaten same way, just smaller magnification at TEM)

and/or

-combine with knowledge on indexation (more restrictions on which point group can have which diffraction group if you know the zone of the CBED pattern, see *Atlas of Electron Diffraction* p.25-27)
To complete the CaF$_2$ example: now we can combine the diffraction symbol we obtained from SAED...

[Table of reflection conditions and extinction symbols]

---

...with the point group we obtained from CBED. (This table can be found in the International Tables for Crystallography volume A)
We can then pinpoint the space group Fm-3m. (note that m3m and m-3m are different notations for the same space group)

Note of Caution:

the absence of a symmetry element can also be due to imperfect orientation by the microscopist!
Symmetry from images

HRTEM & HAADF-STEM = Projections → 17 plane groups

Since images are 2D projections of the 3D structure, they only show the plane groups as symmetry groups (see first part about Fundamental Crystallography, or see International Tables for Crystallography A).

For example, if the structure has space group P4/mnm, under "symmetry of special projections" in the ITA, you can find that [001] zone has symmetry p4gm, a plane group. Plane groups are also listed in the ITA and you can compare the symmetry to that in your experimental image.
Example:
SAED: tetragonal, absence of systematic extinctions for this sample: \( P - - - \)

**8 possible space groups!**
P4, P-4, P4/m, P422, P4mm, P-42m, P-4m2, P4/mmm

ITA: plane group along [001]?
P-4, P4, P4/m: \( p4 \)
P422, P4mm, P-42m, P-4m2, P4/mmm: \( p4mm \)

Allows to eliminate already 5/8 SG

---

Crystallographic image processing: phases can also be used (e.g. software CRISP (not free))

Amplitudes symmetry related reflections always equal
Phases of symmetry related reflections equal if no translation component in symmetry operation, may be different if translation component present in symm. op.

But XR/E diffraction cannot measure phases
Phases present in HRTEM images versus

Work with Fourier transforms of HRTEM images

\[
\varphi_{res} = \frac{\sum_{hk} w(hk) |\varphi_{obs}(hk) - \varphi_{sym}(hk)|}{\sum_{hk} w(hk)}
\]

---

According to Hovmoller [Ultramicroscopy 41 (1992) 121-138], phases can also be extracted to aid in finding the correct matching plane group. For this, image processing needs to be done, for example using CRISP. The process uses the Fourier transform of the image and calculates the average phase error of symmetry related reflections for that plane group. The plane group with the lowest residual phase should be the correct one. If several exist with very similar residual phase, usually the one with higher symmetry should be the best choice.
Example above: HRTEM cut from the paper [Ultramicroscopy 110 (2010) 881–890]. (1) HRTEM image as input, (2) Fourier transform is made and lattice is located, (3) lattice is indexed, (4) phase residuals are calculated. Among the tetragonal groups, $p4$ has the lowest phase residual and thus matches best. This agrees with the visual conclusion before that $p4$ was the correct plane group.

Also, Fourier transforms of images can help to figure out the reflection conditions when you have domains, since FTs can be taken from smaller areas than ED patterns can. FTs of HRTEM images can thus give single domain views of the corresponding reciprocal space section, but are further also subject to double diffraction effects, misorientation effects, etc like SAED patterns.
FT’s of HAADF-STEM can also be used, however, when there are columns with only light elements in the projected structure, the result might be misleading. An example is shown on the slide: in this structure, there are columns of oxygen in the projection. The [100] pattern could not be obtained by SAED because the domains were too small. However, the SAED pattern should look like the calculated pattern on the left. There are systematic absences in the FT that are not in the calculated patterns (neither kin. nor any thickness of dyn.). When calculating the pattern without oxygen in the structure, you get the exact same pattern as in the FT of the HAADF-STEM image.

Note of Caution

Orientation and alignment influence the symmetry in the image: both need to be as perfect as possible!
How to use kikuchi lines for orienting your crystal

If the specimen is thick enough, but not so thick that inelastic scattering dominates, many electrons will be incoherently scattered in all directions (diffusely scattered) (Figure A). The ones travelling at an angle \( \theta \) fit for Bragg scattering can then be Bragg diffracted by the crystal planes (Figure B).
Since the incoming electrons come from all directions, there will be a cone of such electrons and the diffracted beams will form two cones. In the diffraction pattern we will see the intersection of these cones with the screen. For small regions close to the optic axis, as in an electron diffraction pattern, these intersections will look like two parallel lines. One is a bright line (excess) and one a dark (deficient) line. The cones behaves as if fixed to the hkl plane. A line halfway between the two kikuchi lines represents the trace of the hkl plane.

Real example of a pattern showing both the Kikuchi lines and the spot pattern.
Patterns created using eMap

For one particular zone, you can draw the kikuchi lines by drawing the perpendicular bisectors of every g-vector in the ZOLZ. The distance between each pair of lines hkl is $g_{hkl}$.

Software that can do this for you is for example JEMS, eMap, ElectronDiffraction (same sit as Atlas of Electron Diffraction).

If you construct these for several zones, using common reflections, you will obtain the kikuchi lines that lead from one zone to the next. If you often work with the same material or same structure type, it might be worthwhile to add experimental images of the different nodes to the kikuchi map. Also, if you want to have a precise orientation, positioning yourself in the node of kikuchi lines is much more precise than orienting on the relative intensities in SAED patterns.
Some possible origins of extra reflections

Before trying to index all reflections with one unit cell, best check whether all reflections are due to the same defectless crystalline structure. Some, but far from all, possible origins for extra reflections are shown in this lecture.

Double diffraction on multiple phases

Double diffraction has also been explained in the lecture on indexing SAED patterns, for single phase single orientation patterns. However, it can also occur in the case of multiphase crystals where it combines the diffraction off of both phases. For example if both phases occur on top of each other along the direction of the incident beam, the strongly diffracted beams of the first crystal become the incident beams for the second crystal. This results in an SAED that is the superposition of the patterns of both phases separately, with the strong reflections of the first crystal as origins for the patterns of the second crystal.
Twinning

A twin is one part of the crystal oriented relative to another part according to a symmetry operation. This results in extra reflections in the SAED, compared to a non-twinned pattern. The example above shows the simple case of a mirror plane, but also rotation operations are possible. The mirror shown above will give double spots for all except the reflections corresponding to the mirror plane itself. The splitting will increase when moving further away from the central beam.

Example in real space, twin in LaFeO₃, images using HAADF-STEM.
An experimental example of such case

Example in reciprocal space from Journal of Physics and Chemistry of Solids 65 (2004) 87–93, the compound is $Y_{0.8}Sr_{2.2}Mn_2GaO_8$.

Another simple example involves a twin by a 90° rotation around the c-axis, with the c-axis lying in the electron diffraction pattern plane with the other two lattice parameters a and b slightly differing in length, such as in a slight orthorhombic deviation from a tetragonal unit cell. This will give increasing spotsplitting when moving away from the central beam. This helps to detect small deviations from seemingly equal cell parameters and lowering of the symmetry.
If long range order occurs, this can lead to superstructure reflections, if the order results in a superstructure (comensurate case) or to satellites, if the order results in an incommensurate modulation. Both cases will be discussed in detail in day 3 in dedicated lecture "How to analyse ED patterns of superstructures and modulated structures"

Regular arrays of defects like antiphase boundaries will also give extra reflections in the direction perpendicular to the defect plane with an interspacing that is the inverse of the spacing between the defects.

Spinodal decomposition

Example LaCaCuGa(O,F)_5; amount F varies sinusoidally
Hadermann et al., Int.J.In.Mat.2, 2000, 493

Spinodal decomposition = composition fluctuations in the elastically soft directions in the crystal. Satellites are produced in the direction of the fluctuation. The spacing between the satellites depends on the period of the modulation.
Solving and refining a structure from electron diffraction data (very concisely)

These slides very concisely give the concepts of solving/refining a structure from electron diffraction data, as a longer presentation will be given right after by Nanomegas.

You have as experimental data:
- electron diffraction patterns
- targeted composition

You get:
- a model for the structure

Trouble: dynamical diffraction

Intensities of reflections on electron diffraction patterns can be used quantitatively to solve structures using algorithms as for XRD. The strong interaction of the electrons with matter causes multiple diffraction to occur, complicating the relation between the structure and the intensities, as a function of the thickness. Refinement can be done taking thickness into account, for solution no algorithm exists yet that allows this.
Possible ways around dynamical diffraction:

- Precession electron diffraction (PED)
- Electron diffraction tomography (EDT)

To be able to solve structures from ED data, we need to reduce the effects of dynamical diffraction as much as possible. Precession electron diffraction and electron diffraction tomography are two ways to do this, as shown in further slides.
PED technique:
R. Vincent, P. Midgley,
Ultramicroscopy, 1994, 53, 271

In precession electron diffraction the beam is pivoted around its contactpoint with the specimen, and by consequence you get a series of out-of-zone-patterns, centered around the correct in-zone orientation. This animation is not completely technically correct, but it shows the concept more clearly. In each of these out-of-zone patterns, the dynamical diffraction is much less, and all these patterns then combined in one pattern to replace the normal in-zone pattern.

This slide shows the effect of PED on the diffraction patterns of a typical crystal of SnO$_2$. The intensity distribution changes to one that is closer to kinematical intensities (intensities in case of single diffraction events as in XRD), reflections that should be systematically absent decrease in intensity, sometimes even disappear.
In the PED method, as many in-zone patterns as possible need to be acquired for extraction of the intensities.
Extract the intensities using

**EDM** (free)

**EXTRAX** (free)

**PETS** (free)

**CRISP-EDT** (not free)

...
Treat the data of the individual patterns:

- Lorentz factor could be applied (no consensus whether necessary)

\[ I' = I \cdot g \sqrt{1 - \left(\frac{g}{2R}\right)^2} \quad (R=\text{radius Laue circle}) \]

- could symmetrize = replace reflections by average of equivalent reflections (also gives \( R_{\text{sym}} \))

- ...

The data can be improved (or not) using several additional optional steps, such as applying a geometrical correction [Gemmi, M. et al. Ultramicroscopy 2007, 107, 483.] or using the intensity averaged over all equivalent reflections, if you know the space group (do it manually in excel, use CRISP, ...). Symmetrizing also gives you an idea of the quality of the pattern, by showing how much the intensities deviate from the average.

Merge separate lists into one list
Scale factor based on common reflections

Possible pitfalls in merging:
- (wrong?) ratio of small amount of reflections is imposed on all reflections
- merging is done in series, errors accumulate
- typical tilt series around main axis, but main axes often stronger deviations by themselves
- should a weighing be used?
- ...

Finally you merge all lists that you find reliable together to one long list of hkl and intensities to use in the structure solution software. At the end you have one list with hkl and intensities, which you will feed into the structure solution or refinement software (discussed after slides on also EDT).
Electron diffraction tomography uses the fact that out-of-zone patterns have less influence of dynamical diffraction. It uses a tilt over a regular interval of degrees, around one holder axis, preferably avoiding all zones. The first link in the slide shows a typical experimental result, the second link the reconstructed reciprocal lattice from such an experiment.

Manually + treatment of patterns with PETS (free)

Automated in ADT (not free)

You obtain a list of hkl and intensities

Direct methods, or optimisation methods made for single crystal data

SIR2011 (free)
Fox (free)
Endeavour (not free)
Superflip (free)
...
Same concerning refinement e.g. Jana (free)

Right structure càn come out (GIGO).

For both PED and EDT, the next step is now to solve the structure using this one list of hkl and intensities. For this you can use different methods/software, such as simulated annealing (Endeavour, FOX), charge flipping (Superflip), direct methods (SIR),... Detailed explanations of each procedure do not fit within the time allocated in this course, plus are more suitable for dedicated workshops. (see for example http://jana.fzu.cz/#workshops1). Each of these programs also has a good manual or even tutorial on its website.
How to analyse ED patterns of superstructures and modulated structures with reference to a known subcell structure

In a modulated structure there is an underlying average structure, but from one average cell to the next there are changes, e.g. substitution or shifts of certain atoms, resp. compositional and displacement modulation. If the periodicity of this modulation is a whole number of times the periodicity of the average pattern, it is called commensurate. If the periodicity of the average cell does not fit an integer number of times in the periodicity of the modulation, it is called incommensurate.
Suppose you have a very simple structure, consisting from a stacking of the planes shown here. The a and b axes are lying in the plane as shown, the c-axis is perpendicular to the plane. The ED pattern will look like shown at the right side. Throughout this lecture the axes a and b will keep referring to that simple cell with all blue atoms, which we call the average cell. New axes for the modulated structure will be a’ and b’. The purple indices are the indices using the parameters of this first simple structure with only A atoms, the average structure.

\[
F_I = f_A e^{2\pi i (0h+0k+0l)} = f_A
\]

You have only one atom A, at 000, so all reflections have the same structure factor, thus the same intensity.
Alternation A and B atoms

If you now replace each second atom along the b-direction by another atom of type B, you will have a periodicity along the b-direction that is twice larger, thus you will get electron diffraction patterns where the reflections along the \( b^* \) axis are twice closer to each other. \( G \) = all vectors to reflections of the average cell, \( g \) = all reflections in the complete modulated cell. The extra reflections at a half \( b^* \) off from each basic reflection are called the satellites, or also the superstructure reflections if commensurate.

Consider the new structure as being a modulated version of that first average structure which had only A atoms. Supercell treatment ok for commensurate cases, modulation vector treatment needed for incommensurate cases. Sometimes modulation vector treatment is used for commensurate cases when for example it is an advantage to keep a clear relation of a whole group of structures to one and the same average cell.
Supercell treatment

Supercell treatment: you choose new axes $a', b'$ that allow to index all reflections. In the example above, the indices for the reflections will change: original 010 will now be 020. The indices in the supercell will be put in green throughout this lecture.

Modulation vector treatment

Modulation vector treatment: keep the cell parameters of the basic cell, and describe the extra reflections you have relative to that cell with a modulation vector $q$ using 4 indices instead of 3 (see further in this lecture)
Supercell treatment

\[ F_{II} = f_A e^{2\pi i (0h + 0k + 0l)} + f_B e^{2\pi i (0h + \frac{1}{2}k + 0l)} \]

\[ F_{II} = f_A + f_B e^{\pi ik} \]

\[ F_{II} = f_A + f_B \text{ if } k = 2n \]
\[ F_{II} = f_A - f_B \text{ if } k = 2n + 1 \]

Usually extra reflections are weaker than reflections from the average structure. Reason shown above with structure factor: atom A at 000 and an atom B at 0 ½ 0 \( \rightarrow \) structure factor = sum \( f_A \) and \( f_B \) for all reflections with \( k \) even = reflections average cell, structure factor = difference \( f_A \) and \( f_B \) for all reflections with \( k \) odd = superstructure \( \rightarrow \) superstructure reflections are weaker.
If the periodicity of the modulation in direct space is \( nb \):

Extra ref.: \[ \vec{g} = \vec{G} \pm \frac{m}{n} \vec{b}^* \]

Can use supercell:

\[ b' = nb \quad b'^* = \frac{1}{n} b^* \]

So for the simple case where the modulation is along one of the main axes, you can use a supercell where the length of that axis is multiplied by \( n \) in direct space and you will have a corresponding reciprocal axis that is \( n \) times shorter to be able to index all reflections.

Extra reflections

\[ \vec{g} = \vec{G} \pm \frac{m}{2} \vec{b}^* \]

\[ b' = 2b \]

\[ b'^* = \frac{1}{2} b^* \]

For the example with alternating atoms A and B along the B-axis, you multiply \( b \) by 2, in reciprocal space \( b^* \) is two times shorter.
Extra reflections \[ \vec{g} = \vec{G} \pm \frac{m}{3} \vec{b}^* \]

If you have one other atom every three atoms, you will have extra reflections at \( \frac{1}{3} \) of the original spacing between the reflections. In direct space your \( b' \) parameter is \( b \) multiplied by 3, the reciprocal \( b'^* \) basic vector is three times shorter than \( b^* \), allowing you to again index all extra reflections.

Extra reflections \[ \vec{g} = \vec{G} \pm \frac{m}{4} \vec{b}^* \]

Same, if you have a fourfold supercell, you will have extra reflection at \( \frac{1}{4} \) of the spacing of your basic cell. In direct space you have a new \( b' \) parameter that is 4 times \( b \) and in reciprocal space your basic vector \( b'^* \) is 4 times shorter than \( b^* \).
Modulation not along main axis of basic structure

Next example: the modulation is not lying along one of the basis vectors.

Modulation not along main axis of basic structure

In this example, the blue atoms are lying on the planes (110). The d-spacing between equivalent planes has become three times larger for this orientation of the planes.
Since the reflections corresponding to a certain set of planes lie along the perpendicular to that set of planes, and have a distance that is the inverse of the d-spacing between the planes, you will now get extra reflections at 1/3 of the distance to the 110 reflection. So in terms of the diffraction vectors, you have reflections at all positions of the basic reflections, given by \( \mathbf{G} \), plus extra reflections at \( m \times \frac{1}{3} \frac{1}{3} 0 \), in which \( m \) is an integer.

If you would index these extra reflections using the cell parameters of the basic cell, that would give you 1/3 1/3 0 and 2/3 2/3 0 etc. Since all indices have to have whole numbers, this is not acceptable. You can thus go to a supercell.
If you simply multiply all cell parameters by 3, you will get the green indices. This allows to index all reflections, but there will be a lot of extinctions.

What you should do instead in general: choose the shortest reciprocal vectors and assign to those the indices 100 and 010 and from another pattern 001. Calculate the cell parameters from that choice, then try to index with those cell parameters all other reflections. The shortest vectors could be lying in another zone! You have to be able to index also all other zones you might have of the same material with this same choice. You have to collect enough different zones to be able to get a 3D view of the whole reciprocal lattice. So this is in fact the same as when you have no parent cell. The difference comes next.
When you have found the new basis vectors, write down their relation to the basis vectors of the basic cell. The general relations are given on the slide, plus the specific relation for this example and the transformation matrix resulting from this relation. Using the way as on the slide, the $P^{-1}$ matrix actually consists of the indices of your new 100, 010, 001 relative to your old axes. With this same matrix you can easily convert all reflections of your parent cell to the new cell, to make sure you index it consistently. The matrix $P$ you will need for converting the parent cell to the new cell in direct space.

$$ \begin{pmatrix} a' \ b' \ c' \end{pmatrix} = \begin{pmatrix} a \ b \ c \end{pmatrix} P $$

This example:

$$ a'^* = \frac{1}{3} a^* + \frac{1}{3} b^* $$

$$ b'^* = \frac{1}{3} a^* + \frac{2}{3} b^* $$

$$ P^{-1} = \begin{pmatrix} 1/3 & 1/3 & 0 \\ -1/3 & 2/3 & 0 \\ 0 & 0 & 1 \end{pmatrix} \Rightarrow P = \begin{pmatrix} 2 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} $$

Indices superstructure reflections in new cell parameters:

$$ \begin{array}{ccc} h'_1 & k'_1 & l'_1 \\ h'_2 & k'_2 & l'_2 \\ h'_3 & k'_3 & l'_3 \\ \vdots \\ h'_m & k'_m & l'_m \\ h'_n & k'_n & l'_n \end{array} = \begin{pmatrix} h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \\ h_3 & k_3 & l_3 \\ \vdots \\ h_m & k_m & l_m \\ h_n & k_n & l_n \end{pmatrix} P^{-1} $$

All integers, if not, supercell choice is wrong

Indices superstructure reflections in old cell parameters:

Not necessarily all integers

(For more advantages of using the transformation matrix, see International Tables Volume A, section 5.)
This example:

\[
\begin{pmatrix}
\vec{a}^* \\
\vec{b}^* \\
\vec{c}^*
\end{pmatrix}
= P^{-1}
\begin{pmatrix}
\vec{a}^* \\
\vec{b}^* \\
\vec{c}^*
\end{pmatrix}
\]

\[
P
= \begin{pmatrix}
2 & -1 & 0 \\
1 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
\begin{pmatrix}
\vec{a}' \\
\vec{b}' \\
\vec{c}'
\end{pmatrix}
= \begin{pmatrix}
\vec{a} \\
\vec{b} \\
\vec{c}
\end{pmatrix}P
\]

\[
\begin{align*}
\vec{a}' &= 2\vec{a} + \vec{b} \\
\vec{b}' &= -\vec{a} + \vec{b} \\
\vec{c}' &= \vec{c}
\end{align*}
\]

Sidenote, you can also do it in opposite manner, as on this slide.

This transformation matrix \(P\) will then immediately also give you the relation in direct space between the average or parent cell and the supercell. You then can easily calculate the average coordinates of all atoms in the supercell, because you know those in the average cell and you have the transformation matrix.

Afterwards you still have to add a proposal for the modulation and either confirm it with direct space images or with quantitative electron diffraction or a non-TEM technique.
\[ \vec{g} = \vec{G} + m \{ \alpha, \beta, \gamma \} \]

\( \alpha, \beta, \gamma = p/n \)  
Can take supercell, e.g. \( n \times \) basic cell parameter

However, e.g.: \( \vec{g} = \vec{G} + m \cdot 0.458 \vec{b} \)  
\( 0.458 = 229/500 \)

Use approximation?  
\( 5/9 = 0.444, 4/11 = 0.455, 6/13 = 0.462, \ldots \)
Different cells, space groups, inadequate for refinements,

\[ \Rightarrow \]  
Might be better to work with modulation vector description.

---

Even in commensurate cases, sometimes it will be better to work with a modulation vector; for example, if you would have to take a very large supercell, or if you want to retain the relation between several different structures derived from the same parent cell,...
The q-vector approach

All reflections

\[ g = ha^* + kb^* + lc^* + mq \]

\[ q = \alpha a^* + \beta b^* + \gamma c^* \]

Basic structure reflections

\[ \vec{G} = ha^* + kb^* + lc^* + 0q \]

Use the cell parameters of the average cell, \( a^*, b^* \) and \( c^* \) (purple indices in following slides) + a vector to one of the extra reflections as a fourth reciprocal basis vector to index all reflections = modulation vector \( q \). \( q \) is a linear combination of the three basic vectors, with components alpha, beta and gamma.

The basic reflections have \( 0q \), so \( hkl0 \), all satellites are given by \( hklm \) with \( m \) different from \( 0 \).

Same example as before. The diffraction pattern is indexed using the cell parameters of the average cell. You see extra reflections at \( \frac{1}{2} b^* \) away from the basic reflections. You could take this as the modulation vector \( q \), as written explicitly on the slide.
\[ q = \frac{1}{2} \]

The indices using this modulation vector are in brown colour.

\[ \mathbf{g} = \mathbf{G} + m \cdot 0.458 \mathbf{b}^* \]
\[ \mathbf{q} = 0.458 \mathbf{b}^* \]

For the case where the extra reflections were at 0.458b* off of the basic reflections, the modulation vector is 0.458b*. The average cells the same as for the previous example/slide. Compared to the commensurate case, the vectors 0001 and 010-1 do not overlap anymore (nor do any of the similar couples of vectors).
With this approach many structures with different periodicities of the modulations are described with the same unit cell, the same space group, which we will call a superspace group in case of more than 3 indices, and the only parameter that changes from one structure to the other is the modulation vector.

\[ g = G + m \left[ \frac{1}{3}, \frac{1}{3}, 0 \right] \]

\[ q = \frac{1}{3} a^* + \frac{1}{3} b^* + 0c^* \]
Advantages of the q-vector method:

- subcell remains the same
- precise, no approximations necessary
- also applicable to incommensurate modulations

Incommensurately modulated materials

Loss of translation symmetry

Shown are two simple cases of incommensurately modulated structures: an occupationally modulated incommensurate structure and a displacively modulated one. There is no translation symmetry, the pattern does not repeat itself, i.e. the period is infinite. These modulations do give sharp extra reflections, so that are not random or defects, they are periodical in higher than three dimensions (see some slides furtheron).
Example of a compositional modulation

LaCaCuGa(O,F)₅: amount F varies sinusoidally

Hadermann et al., Int.J.In.Mat.2, 2000, 493

Real example of a compositionally modulated structure.

Example of a displacive modulation

Bi-2201

Picture from JSSC 156, 2001, 445

Real example of a displacively modulated structure.
Consider an example in one dimension. The two biggest black dots represent the subcell reflections. The smaller black dots are the satellites. The periodicity between the satellites does not fit an integer number of times into the periodicity of the basic reflections.

Define a unit vector for an extra dimension as perpendicular to all existing reciprocal basis vectors. In the one dimensional example this means that unit vector $e_2$ is perpendicular to vector $a_1^*$. Reciprocal basis vector $a_2^*$ is the vector sum of this unit vector $e_2$ and the modulation vector $q$. 
Construct the reciprocal lattice using these two reciprocal basis vectors $a_1^*$ and $a_2^*$. Aperiodic diffraction pattern in 1D is the projection of the periodic reciprocal lattice in 2D onto this 1D space. For 3D instead of 1D, the concept is exactly the same.

Basis vectors of the reciprocal lattice

\[
\begin{align*}
\vec{a}_1^* &= \vec{a}^* \\
\vec{a}_2^* &= \vec{b}^* \\
\vec{a}_3^* &= \vec{c}^* \\
\vec{a}_4^* &= \vec{e}_4 + \vec{q} \\
\vec{q} &= \alpha \vec{a}^* + \beta \vec{b}^* + \gamma \vec{c}^*
\end{align*}
\]
Basis vectors of the (3+1)D direct lattice

\[ \mathbf{a}_1 = \mathbf{a} - \alpha \mathbf{e}_4 \]
\[ \mathbf{a}_2 = \mathbf{b} - \beta \mathbf{e}_4 \]
\[ \mathbf{a}_3 = \mathbf{c} - \gamma \mathbf{e}_4 \]
\[ \mathbf{a}_4 = \mathbf{e}_4 \]

\[ \mathbf{a}_i \cdot \mathbf{a}_j = \delta_{ij} \]

Example: \(q = \gamma \mathbf{c}^*\) (Displacive modulation along \(c\))

We finally need the relation between the basis vectors in reciprocal space, the basis vectors in real space and the modulation vector in order to derive the structure. Example: displacive modulation with displacement along the c-axis. Suppose you are looking at two neighbouring unit cells of the basic structure. In the first cell a certain atom has a displacement out of the average position over such a distance along the c-axis as indicated by the bottom fat black line. In the neighbouring cell that atom has a displacement out of the average position, given by the top fat black line. So in 3D there is no translation symmetry between the two cells.
Example: $q = \gamma \mathbf{c}^*$ (Displacive modulation along c)

The unit vector for the extra dimension lies perpendicular to the other three original basis vectors, this is $\mathbf{e}_4$ and it is immediately also basis vector $\mathbf{a}_4$.

$\mathbf{a}_3 = \mathbf{c} - \gamma \mathbf{e}_4$

Construct the other new basis vectors in direct space by subtracting from the original basis vectors the corresponding component times $\gamma$. In the current example there is only a displacement along c, so $\gamma$ component.
The unit cell is defined by the basis vectors.

The displacements in the neighbouring cells can be projected back to the first unit cell.
Example: \( q = \gamma c^* \) (Displacive modulation along \( c \))

\[ a_3 = c - \gamma e_4 \]

This will correspond to a function, which is called the modulation function. This function now represents the atom, instead of three coordinates representing the position of the atom. This function is the same in each 3+1 dimensional unit cell, restoring the translation symmetry.

Superspace groups: position and phase

\[ (\vec{r}, t) \rightarrow (R\vec{r} + v, \varepsilon t + \Delta) \]

\( \{R|v\} \) is an element of the space group of the basic structure
\( \Delta \) is a phase shift and \( \varepsilon \) is \( \pm 1 \)

Example

Pnma(01/2\( \gamma \))s00

\( \{R|v\} \) is an element of the space group of the basic structure
\( \Delta \) is a phase shift and \( \varepsilon \) is \( \pm 1 \)

Symmetry-operators for the phase

Since you now have more than three basis vectors, you can no longer use the normal three dimensional space groups, but need to use the superspace groups. They consist of point group \( R \) and translation parts, plus an extra part which contains the symmetry of the phase of the modulation function. In this part of the symmetry delta is a phase shift and epsilon is plus or minus one. Example superspace group shown: Pnma is the space group of the average structure, (0 1/2 \( \gamma \)) are the components of the modulation vector, s00 is the symmetry of the phase where specific letters stand for specific translations.
Separate the basic reflections \((m=0)\) from the satellites \((m\neq 0)\)

Basic reflections often brighter.

Should form a regular 3D lattice

Example: first separate the basic reflections from the satellites. Almost always you can do this on sight, as the satellites are usually weaker. Above example: reflections circled in purple are the basic reflections. The basic reflections should still form a regular 3D lattice and if you have several choices, go for the one with the highest symmetry and lowest volume.

Separate the basic reflections \((m=0)\) from the satellites \((m\neq 0)\)

Hint from changes vs. composition, temperature,…

Possible help in recognizing the satellites: sometimes they change position as a function of composition or temperature while the basic reflections do not.
Select the modulation vector

$$\mathbf{q} = \mathbf{q}_i + \mathbf{q}_r$$

Possibly multiple solutions

Find a modulation vector which allows you to index all satellites. There are often several possibilities. You can split them in an irrational and a rational part.

The slide shows two different possible modulation vectors for this case and the corresponding indexation. Each will lead to its own set of reflection conditions and thus corresponding superspace group.
Conditions for the basic cell and modulation vector

\[ R : \mathbf{G} (m = 0) \rightarrow \mathbf{G}' (m = 0) \]

\[ R : \mathbf{g} (m \neq 0) \rightarrow \mathbf{g}' (m \neq 0) \]

\[ (q_x, q_y) \] in correspondence with chosen crystal system & centering basic cell

The choice of modulation vector is not completely free. It can be proven that only specific modulation vectors can be combined with certain choices of space groups for the basic structure. This is a consequence of the condition that the point group of the subcell should transform basic reflections into basic reflections and satellites into satellites.

Possible irrational components in the different crystal systems

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>( q_i )</th>
<th>Crystal system</th>
<th>( q_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>(( \alpha, \beta, \gamma ))</td>
<td>Tetragonal</td>
<td>(0,0,( \gamma ))</td>
</tr>
<tr>
<td>Monoclinic ((\gamma\text{-setting}))</td>
<td>(( \alpha, \beta, 0 ))</td>
<td>Trigonal</td>
<td>(0,0,( \gamma ))</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>(0,0,( \gamma ))</td>
<td>Hexagonal</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(( \alpha, 0, 0 ))</td>
<td>Cubic</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>(0,( \beta ))</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(0,0,( \gamma ))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

This condition leads to the following combinations. The possible irrational components have to correspond with the chosen crystal class, for example if you have an \( \alpha \) and a \( \beta \), you cannot have orthorhombic, but at the most monoclinic (case for a one-dimensionally modulated structure, i.e. \( 3+1d \)).
Compatibility of rational components with centering types

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>q</th>
<th>Crystal system</th>
<th>q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>no rational component</td>
<td>Orthorhombic-P</td>
<td>(0, 1/2, γ)</td>
</tr>
<tr>
<td>Monoclinic-P</td>
<td>(α, β, 1/2)</td>
<td>Orthorhombic-C</td>
<td>(1/2, 1/2, γ)</td>
</tr>
<tr>
<td>Monoclinic-B</td>
<td>(1/2, 0, γ)</td>
<td>Orthorhombic-A</td>
<td>(1, 0, γ)</td>
</tr>
<tr>
<td>(γ-setting)</td>
<td>(0, 1/2, γ)</td>
<td>Orthorhombic-F</td>
<td>(1/2, 0, γ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tetragonal-P</td>
<td>(1/2, 1/2, γ)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Trigonal-P</td>
<td>(1/3, 1/3, γ)</td>
</tr>
</tbody>
</table>

The rational component needs to correspond with the centering.
In total you get the possibilities listed above for modulations vectors per crystal class.
In this course we do not go further into detail, this is for dedicated courses.