

**Methods in Chemistry III – Part 1**  
**Modul M.Che.1101 WS 2010/11 – 12**  
*Modern Methods of Inorganic Chemistry*

**Mi 10:15-12:00, Hörsaal II**

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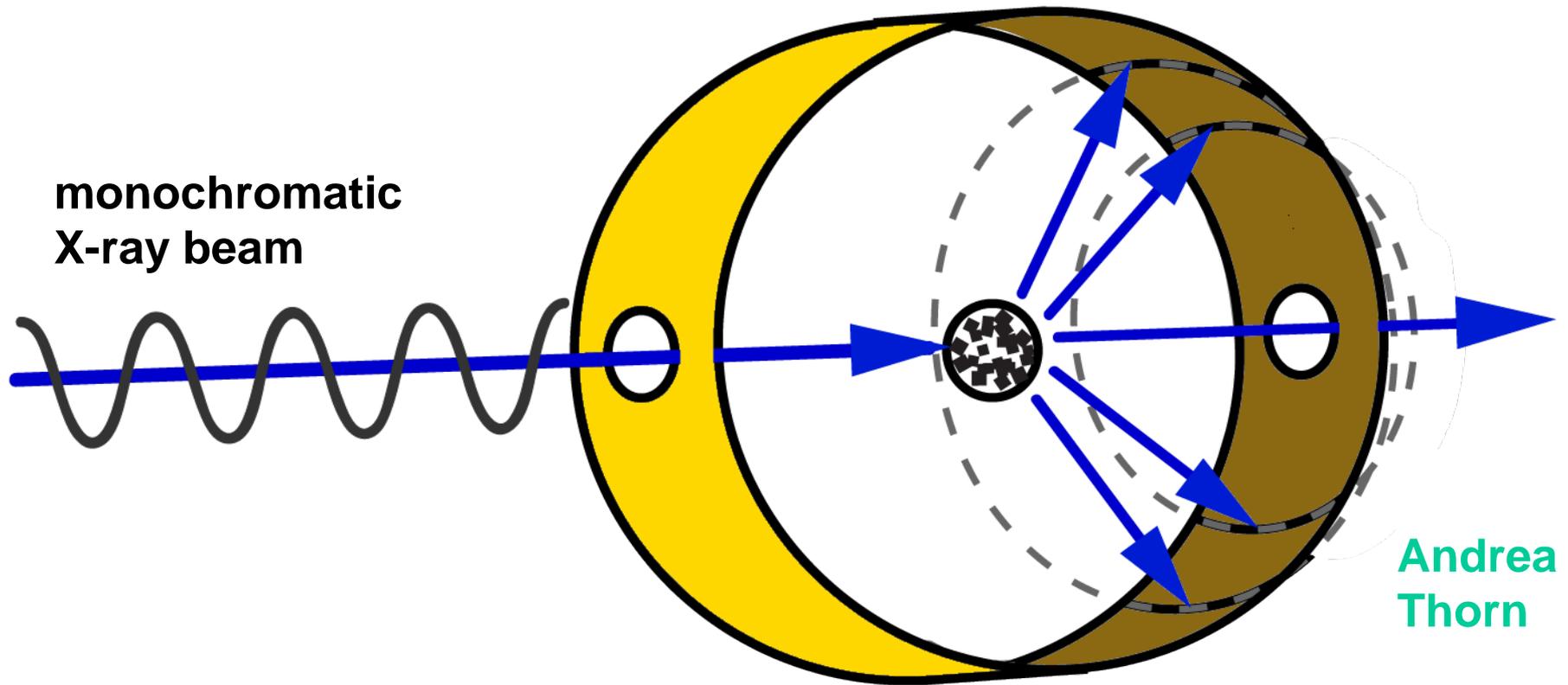
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# Powder X-ray diffraction (XRD)

It is not always possible to grow crystals, especially of insoluble compounds. Such samples are often microcrystalline and give X-ray diffraction patterns that are characteristic for a particular phase. The complete 3D reciprocal space is squashed into a single dimension. Except when the cell is small and the symmetry high, many reflections then overlap one another. In spite of this, X-ray diffraction of powders finds many applications, especially in industry, e.g.

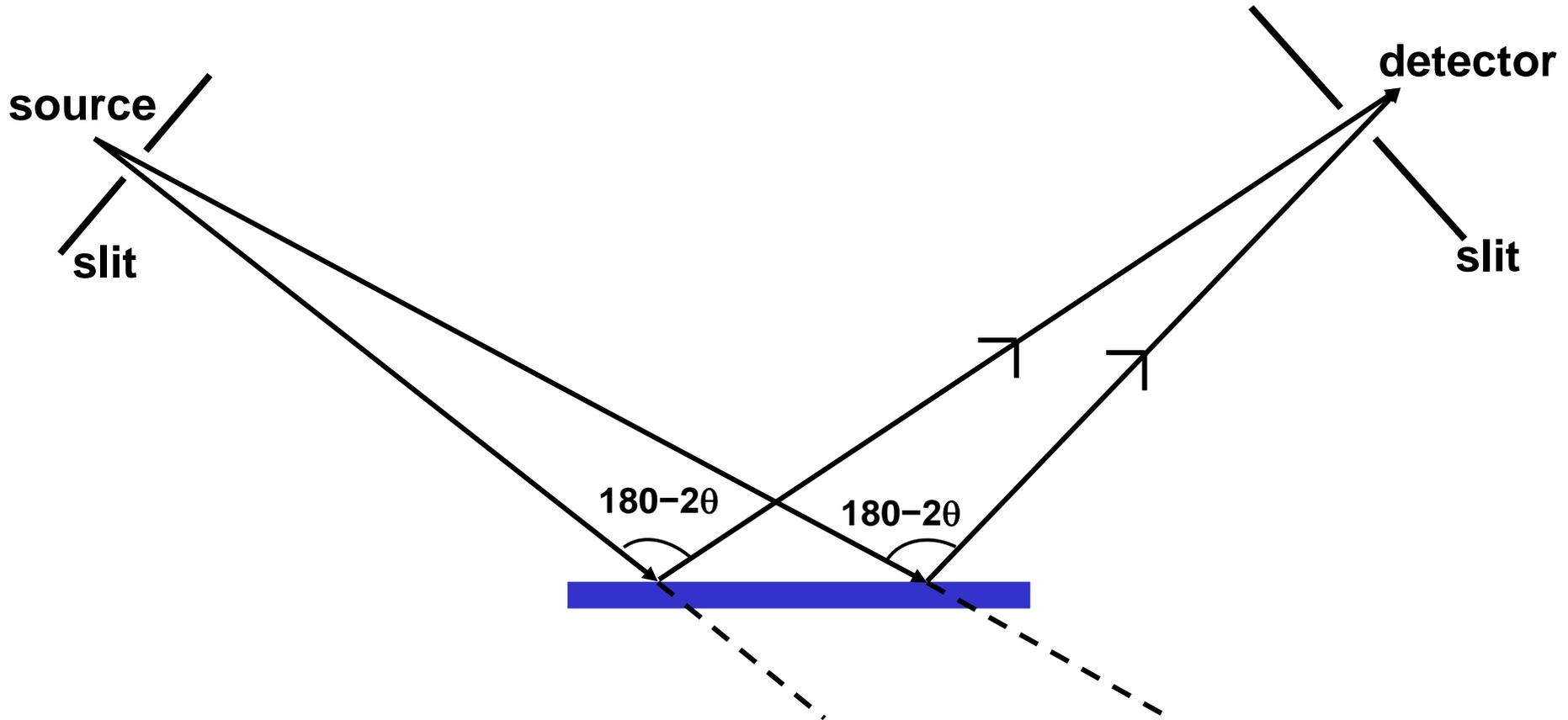
- 1. Identification of compounds and polymorphs with the help of a database of powder diffraction patterns**
- 2. Semiquantitative analysis of mixtures**
- 3. Investigation of phase transitions as a function of temperature and pressure**
- 4. Clarification of the question as to whether a single crystal structure is typical of the complete sample**

# The Debye-Scherrer method (Göttingen, 1915)



Since the microcrystals are in all possible orientations, the diffraction pattern consists of concentric cones with diffraction angles  $2\theta$ . These can be recorded with a cylindrical film or area detector. The intensities are measured as a function of  $\theta$ .

# Bragg-Brentano geometry



The diffraction angles are only exactly equal when the plane of the sample lies on a circle that goes through the source and detector. This circle varies with  $2\theta$ . Despite this, Bragg-Brentano geometry enables a relatively extended flat sample to be used.

# A modern X-ray powder diffractometer



In this diffractometer with Bragg-Brentano geometry, the sample is stationary, and the counter and X-ray source are moved so that they make the same angle with the plane of the sample.

The monochromator is positioned between the sample and detector so that as little fluorescence is recorded as possible.

This arrangement is particularly suitable for flat or immobile samples.

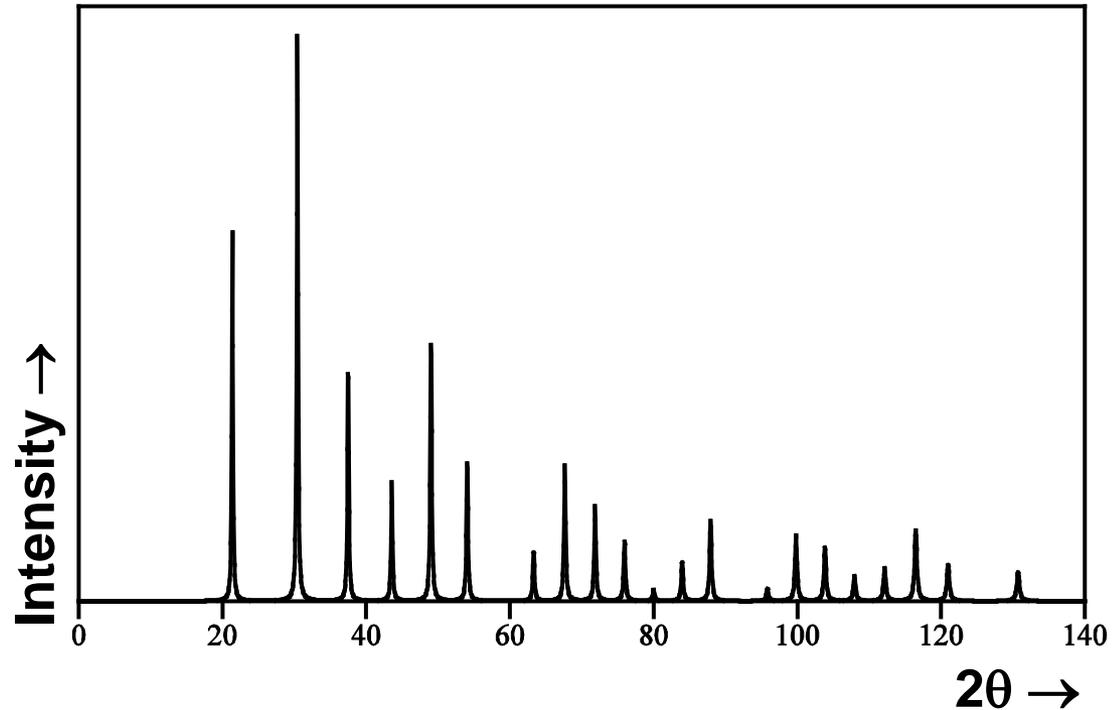
# X-ray powder diffraction

The diffraction angles are calculated from the reciprocal cell:

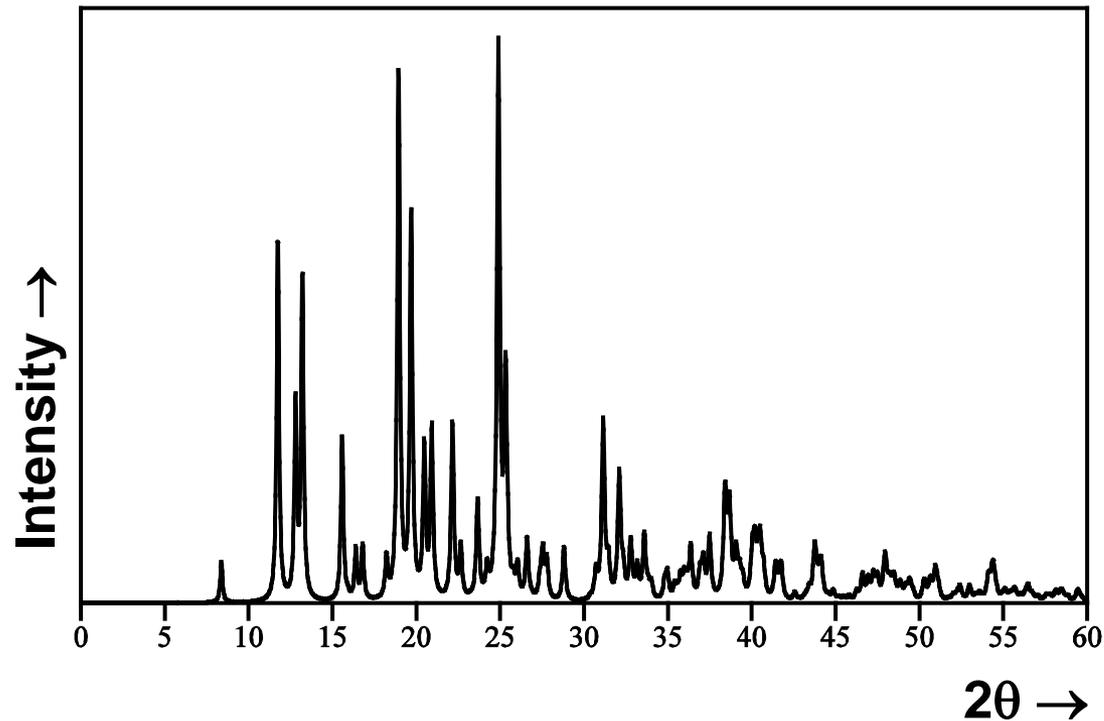
$$\sin^2\theta = (\lambda^2/4)\{h^2a^{*2}+k^2b^{*2}+\ell^2c^{*2}+2k\ell b^*c^*\cos\alpha^*+2h\ell a^*c^*\cos\beta^*+2hka^*b^*\cos\gamma^*\}$$

For an orthorhombic structure,  $\cos\alpha^* = \cos\beta^* = \cos\gamma^* = 0$  and  $a^* = 1/a$  etc. For cubic samples, the expression is further simplified to  $\sin^2\theta = N\lambda^2/4a^2$ , where  $N = h^2 + k^2 + \ell^2$ . Depending on the lattice type, not all integers  $N$  are possible. In this way it is possible to distinguish cubic  $P$ ,  $I$  and  $F$  lattices.

The picture shows the powder X-ray diffraction pattern of  $\text{LaB}_6$ , space group  $\text{Pm}\bar{3}\text{m}$ ,  $\lambda = 1.54178 \text{ \AA}$



# Powder X-ray diffraction pattern of sugar



Many X-ray powder diffraction patterns are difficult to index, as in the case of sucrose, space group  $P2_1$ . However, even in such cases the reflections can often be indexed and so the unit-cell dimensions determined. The determination of the space group and the crystal structure is much more difficult.

# Further complications for powder samples

Although the use as a 'fingerprint method' does not cause significant technical problems, the quantitative applications of powder diffraction are much more demanding. Amongst others, the following effects that are not so problematic for single crystals need to be taken into account:

1. Preferred orientation (texture)
2. Background
3.  $K_{\alpha 1}/K_{\alpha 2}$  splitting
4. Line shape
5. Contamination by other compounds or phases

In addition, in the Laue groups  $\bar{3}$ ,  $\bar{3}m1$ ,  $\bar{3}1m$ ,  $4/m$ ,  $6/m$  and  $m\bar{3}$  non-equivalent reflections inevitably overlap one another.

# The phase problem for powders

Although the phase problem is probably unsolvable in a mathematical sense, small molecule structures are often solved using single crystal diffraction data in seconds by direct methods. For powders the phase problem is still a real challenge, mainly because the effective data to parameter ratio is so much worse.

A possible way of solving structures from powder data is fragment search. One or more rigid molecules with known structures are moved around the cell, until for example the correlation coefficient between observed and calculated intensities reaches a maximum. Then the space group is deduced from the positions of the atoms in the cell. Once the unit-cell has been established, this search can be performed directly against the experimental intensities measured as a function of the diffraction angle  $\theta$ .

# Rietveld structure refinement

In the Rietveld method the structure is refined directly against the measured intensities as a function of  $\theta$ , without first decomposing the powder diffraction pattern into a list of indexed reflections. The same parameters are refined as with single crystal data, with extra parameters to describe the background and line shape. The unit-cell dimensions are also refined. For mixtures it is even possible to refine several crystal structures simultaneously!

**This method is very popular, but should not be pushed too far. There are well-documented cases where a completely wrong structure was refined – with enough parameters one can fit an elephant! The estimated standard deviations are often suspect, because correlations between neighboring data-points cannot adequately be taken into account.**

# Neutron diffraction with powders

Neutron diffraction with a *spallation source* and *time-of-flight* data recording is particularly suitable for powder samples. It is easier to obtain large powder samples than large single crystals!

In the case of (ferro-)magnetic samples the magnetic diffraction of the neutrons must also be taken into account. This can cause for example a doubling of cell dimensions or a change of space group.

In the 1651 'black-and-white' (magnetic) space groups the atoms are considered to be small magnets that can be aligned either parallel or antiparallel.

With single crystals and even better with polarized neutrons it is possible to determine the *unpaired* electron density.

# Exercises

1. For a cubic crystal  $\sin^2\theta = N\lambda^2/4a^2$  with  $N = h^2+k^2+\ell^2$ . Which  $N$ -values up to  $N = 20$  inclusive are allowed for (a) a  $P$ -lattice, (b) an  $I$ -lattice ( $h+k+\ell=2n$ ) and (c) a  $F$ -lattice ( $h, k$  and  $\ell$  either all even or all odd)?
2. How can one distinguish between  $P$ ,  $I$  and  $F$ -lattices using the powder diffraction pattern of a cubic compound?
3. With  $\lambda = 1.54178 \text{ \AA}$  the following powder lines were observed for powdered copper:  $\theta = 21.68, 25.25, 37.10, 45.00, 47.63, 58.53, 68.27$  and  $72.50^\circ$ . Attempt to index these lines and deduce the unit-cell dimension  $a$ .
4. Suggest a simple structure that would be consistent with these results. How long is the shortest Cu-Cu-distance in the metal?