



**Methods in Chemistry III – Part 1**  
**Modul M.Che.1101 WS 2010/11 – 13**  
*Modern Methods of Inorganic Chemistry*

**Mi 10:15-12:00, Hörsaal II**

**George Sheldrick**

**[gsheldr@shelx.uni-ac.gwdg.de](mailto:gsheldr@shelx.uni-ac.gwdg.de)**

# Twinned crystals (of proteins!)



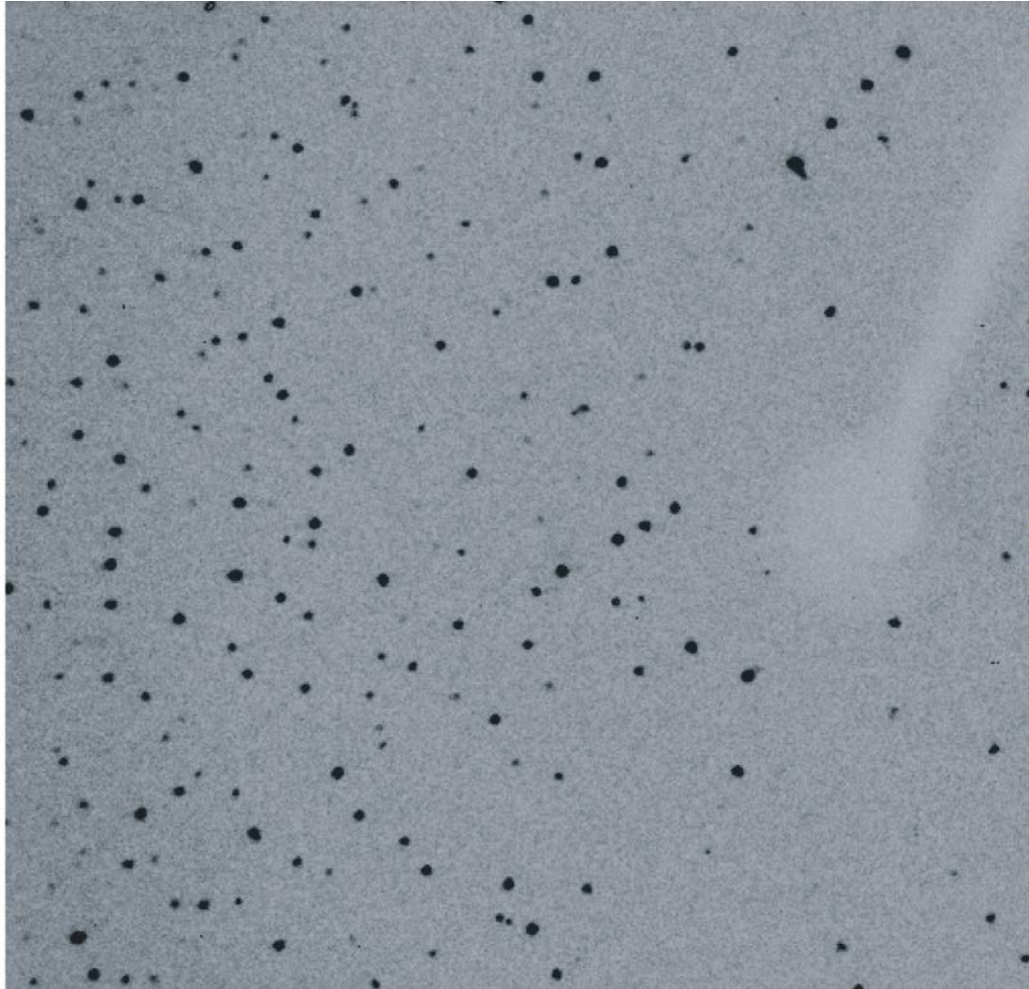
**Cubic insulin twin**



**Glucose isomerase 'drilling'**

**Two examples of non-merohedral twins**

# Diffraction pattern of a non-merohedral 'drilling'



Madhumati Sevvana

# Three types of twins

## Merohedral twins

The *twin law* is a symmetry operator of the crystal system, not of the Laue group. Merohedral twinning can only happen when the correct space group belongs to the lower tetragonal, trigonal, hexagonal or cubic Laue groups. The overlap of the reflections is perfect.

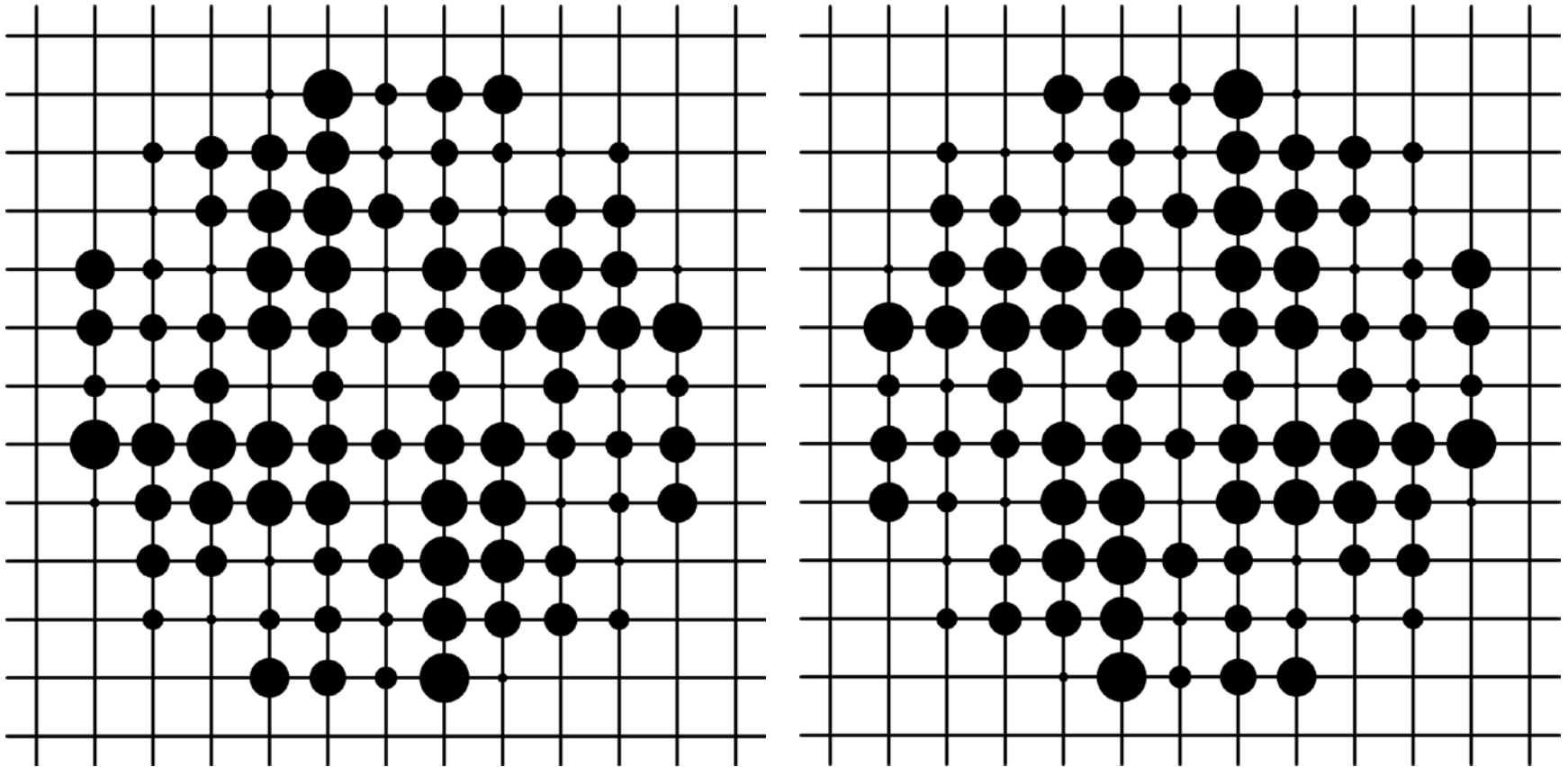
## Pseudo-merohedral twins

The metric symmetry appears to be higher than it really is, but the reflection overlap is not absolutely perfect.

## Non-merohedral twins

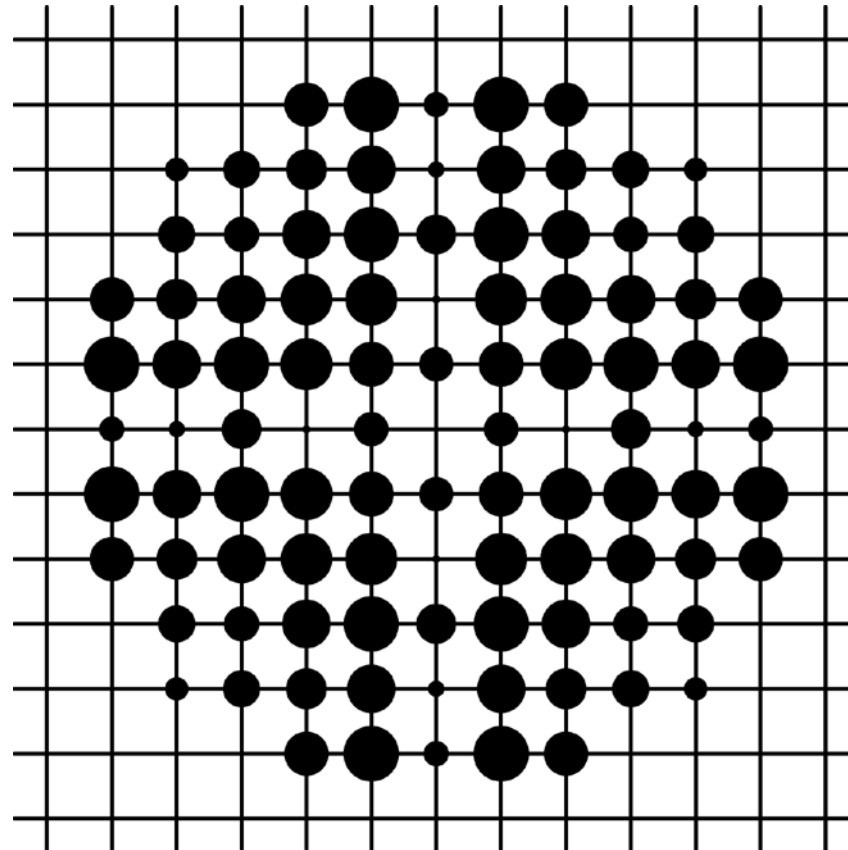
The reflection overlap is not perfect and the twin law (often a 180° rotation) is not a symmetry operation of the crystal system.

# Reciprocal lattice plot with $\ell = 0$



The two crystals that gave rise to these diffraction patterns are related by a symmetry operation that obeys the metric symmetry of the lattice ( $4/mmm$ ) but not the symmetry of the true Laue group ( $4/m$ ).

# Reciprocal lattice plot with $\ell = 0$



When two equally large crystals form a merohedral twin, there is an apparent increase in the Laue symmetry (in this case to 4/mmm) and the intensities become more equally distributed ( $\langle |E^2 - 1| \rangle$  is smaller).

# (Pseudo)merohedral twinning – the warning signs

- The Laue symmetry appears to be higher than the true Laue symmetry
- The agreement of the intensities of the reflections is only slightly worse for the higher (apparent) symmetry than for the lower (true) symmetry
- The mean value of  $|E^2-1|$  is smaller than expected (  $\ll 0.736$  )
- Trigonal or hexagonal space group
- Systematic absences not consistent with any space group
- No structure solution or  $R$ -value far too high

# Non-merohedral twinning – the warning signs

- **Some reflections are sharp, others appear split**
- **Problems with the unit-cell determination**
- **Unusually long cell edges**
- **No consistent space group**
- **Many outliers with  $|F_o| \gg |F_c|$  after structure refinement, particularly for reflections with small  $|F_c|$**
- **Curious residual electron density that cannot be interpreted as disorder or solvent molecules**



# Determination of absolute configuration (1)

Friedel's law  $|F_{hke}|^2 = |F_{-h-k-e}|^2$  is only rigorously true for centrosymmetric structures. For non-centrosymmetric structures, there are small deviations when the imaginary component of the scattering factor is significant:

$$f = f_0 + f' + if''$$

$f''$  is in general larger for heavy atoms, especially close to an absorption edge. In favorable cases the absolute structure (in the case of chiral molecules the absolute configuration) can be determined from accurate measurements of  $|F_{hke}|^2$  and  $|F_{-h-k-e}|^2$ .

When  $f'' \neq 0$  and the wrong absolute structure is refined, systematic errors are introduced into the bond lengths etc.

## Determination of the absolute configuration (2)

Flack [*Acta Cryst.* A39, 876 (1983)] suggested that all non-centrosymmetric structures could be treated as *racemic twins*. The Flack Parameter  $x$  is defined as the volume fraction of the inverted structure. After the refinement,  $x = 0$  means that the absolute structure is correct and  $x = 1$  means that the structure should be inverted.  $x$  is refined by least-squares to minimize  $\sum_{hke} w(|F_o|^2 - |G|^2)^2$ , where

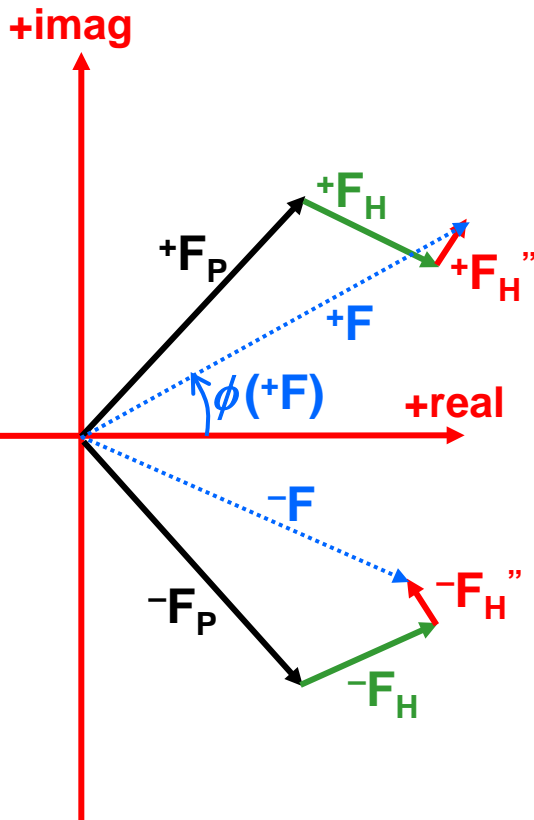
$$|G|^2_{hke} = (1-x) |F_c|^2_{hke} + x |F_c|^2_{-h-k-e}$$

The most important aspect of this procedure is that it produces a statistically sound *estimated standard deviation (esd)* for  $x$ . With this, one can see immediately how reliable the absolute structure determination is.

E.g.  $x = 0.5$  with an esd of 0.1 or less means that it is either a racemic twin, or the wrong space group, or wrong  $f''$ -values. On the other hand  $x = 0.5$  with a standard deviation of 1.0 means that the absolute structure cannot be determined (data too inaccurate or  $f''$  too small).

# Anomalous diffraction as a vector diagram

In this Argand diagram,  $F_{hkl}$  is represented as  $+F$  and  $F_{-h-k-l}$  as  $-F$ .  $F_H$  is the structure factor of the heavy atoms with an anomalous component  $F_H''$  (from  $f''$ ).  $F_H''$  is proportional to  $F_H$  and rotated by  $+90^\circ$  (i.e. to the left). The remaining (normal) atoms make a contribution  $F_P$  to the total  $F$ .



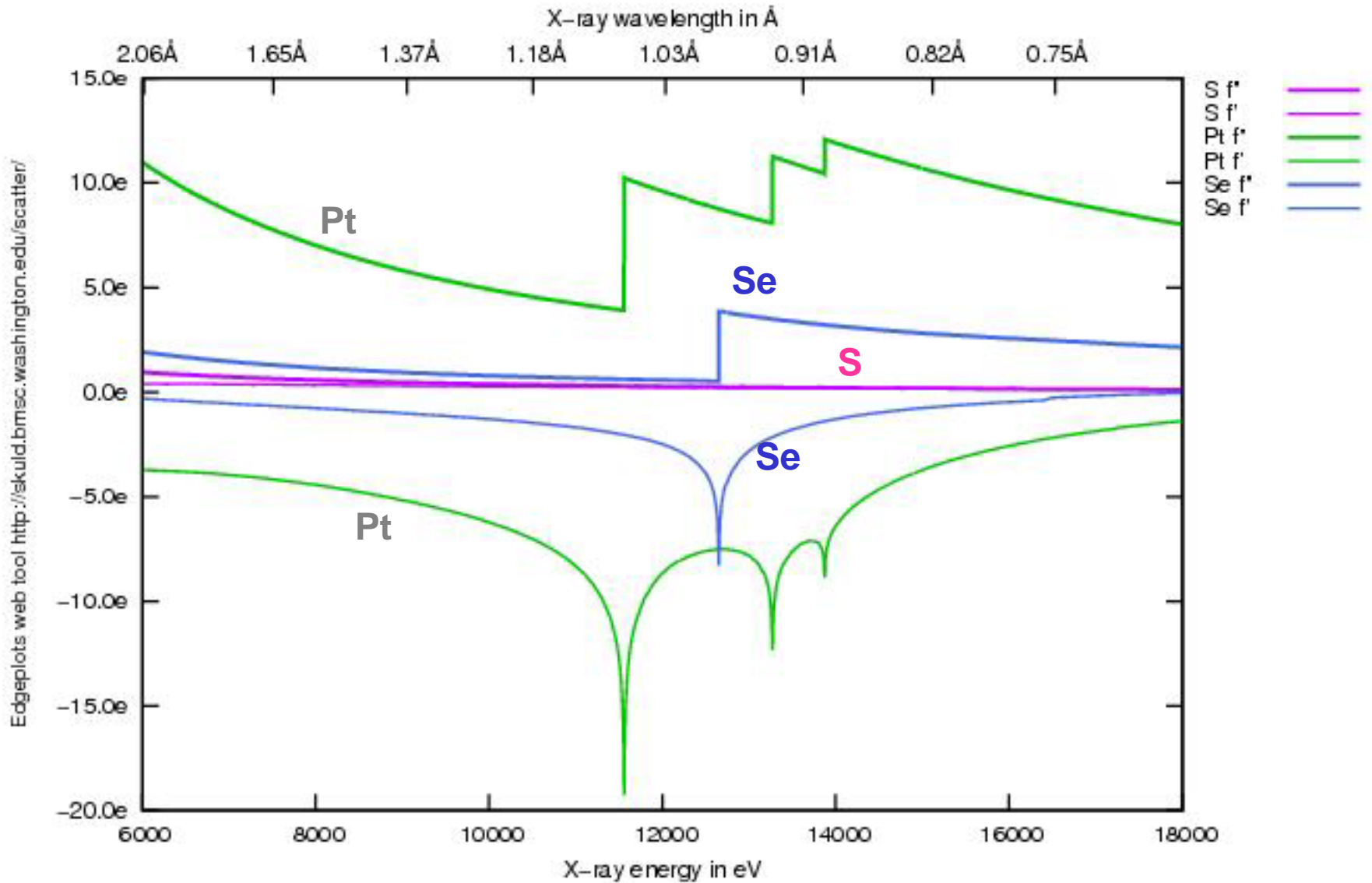
If  $f''$  and thus  $\pm F''$  are zero,  $|+F| = |-F|$  and  $\phi(+F) = -\phi(-F)$  (Friedel's law).

If the structure is centrosymmetric, both  $\pm F_P$  and  $\pm F_H$  lie along the real axis, with the result that  $|+F| = |-F|$ .

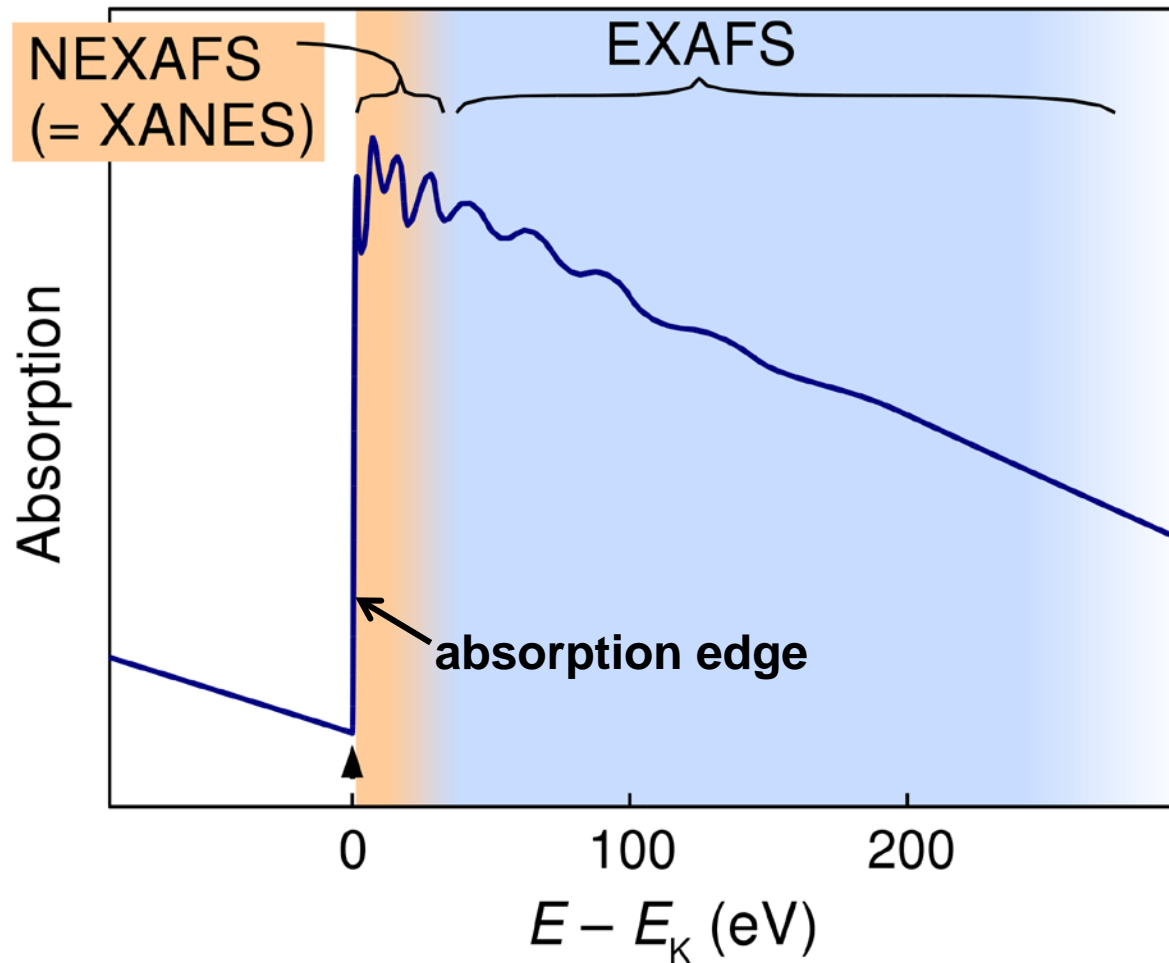
If  $\pm F_P$  are zero, because only atoms of the same element are present,  $|+F|$  and  $|-F|$  are again equal; the absolute structure cannot be determined (e.g.  $\alpha$ -Se in  $P3_221$  or  $P3_121$ ).

Otherwise  $|+F|$  and  $|-F|$  differ and the absolute structure can be determined.

# X-ray absorption edges



# EXAFS



**XANES: X-ray Absorption Near-Edge Structure**

**EXAFS: Extended X-ray Absorption Fine Structure**

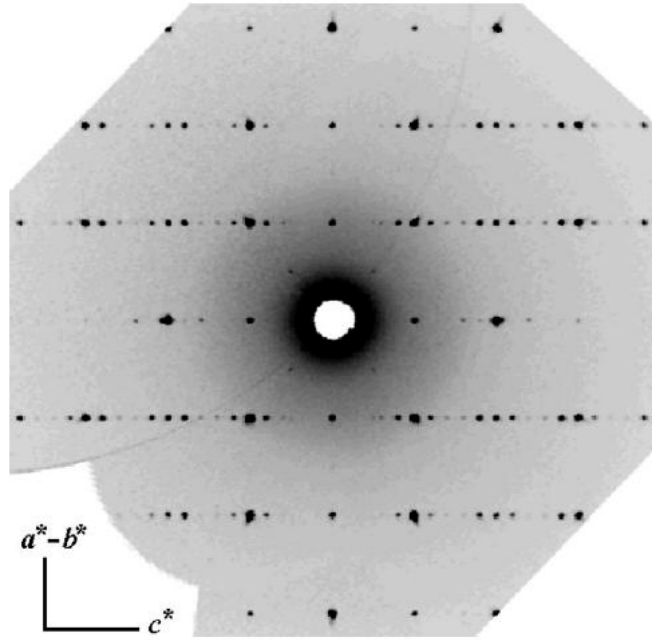
# EXAFS and XANES

At the absorption edge, an X-ray photon possesses just enough energy to eject an electron from an inner shell. The electron is reflected back by the neighboring atoms. Depending on the wavelength of the electron and the distances between the atoms, either constructive or destructive interference occurs and thus there is a change in the X-ray absorption as a function of the energy of the incident X-ray photon. By analyzing the absorption in the range  $20 < E - E_K < 500$  eV, it is possible to draw conclusions about the number and distances of the neighboring atoms.

EXAFS is also suitable for amorphous and liquid samples and is element-specific. Compounds with a metal atom in the molecule are particularly suitable (e.g. enzymes).

The analysis of XANES is more difficult because the electrons, that have less energy than for EXAFS, can be reflected repeatedly. XANES-spectra can still be used as a fingerprint method, because they can be characteristic of coordination geometry and oxidation state.

# Modulated structures



CaAlSi superconductor, *Acta Cryst. B* 62, 710 (2006)

It can happen that a reciprocal lattice of strong reflections is accompanied by weak satellites. When the distance between satellites is a rational fraction of a reciprocal cell distance, the diffraction pattern can be indexed with a large cell. The structure is then *commensurably modulated* and the deviations of the atoms from idealized positions can often be described by a sine wave.

*Incommensurate modulations* happen when the periodicity of the modulation does not fit the main cell. Such structures can be elegantly described and refined in higher dimensional space. Unfortunately the number of possible space groups increases rapidly with the number of dimensions, e.g. in 4 dimensions there are 4753 and in 6 dimensions exactly 28927922!

# Crystal structure databases [as of 5.2.2011]

**ICSD – Inorganic structures [135468]**

**CSD – Organic and organometallic structures [541748]**

**ICDD – X-ray powder patterns (PDF-4+) [301282]**

**CRYSTMET – Metals and alloys [139058]**

**PDB – Proteins, RNA, DNA, etc., also NMR- and EM-structures [70947]**

**NDB – Only DNA and RNA structures [5066]**

**The CSD search software is particularly powerful. Many programs use the PDB, which is a cornerstone of the subject called bioinformatics. Only the PDB and NDB are accessible free in the Internet. See <http://www.rcsb.org>, e.g. ‘Molecule of the month’.**