

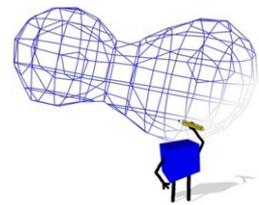
Introduction to the charge flipping for powder diffraction

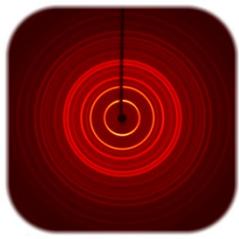
Jan Rohlíček

Institute of Physics, Department of Structure Analysis,
Academy of Science of the Czech Republic



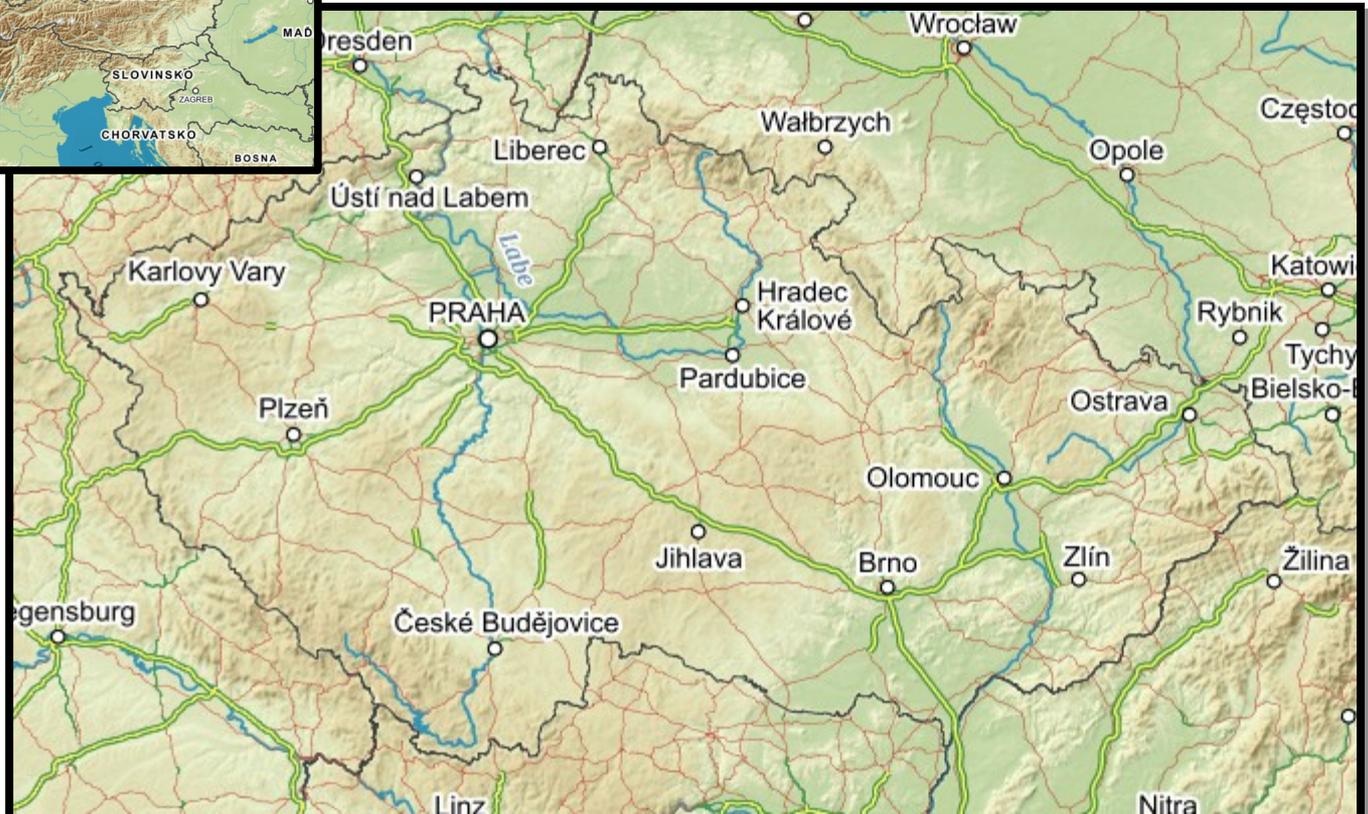
Superflip
amberlib

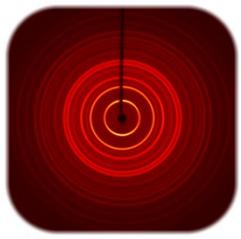




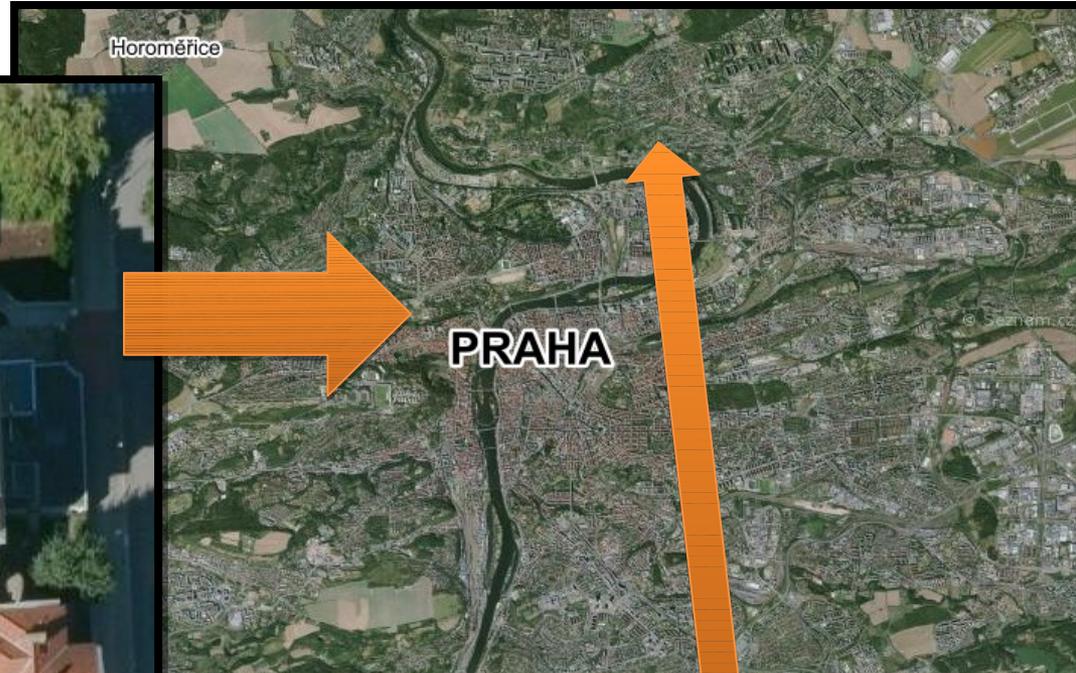
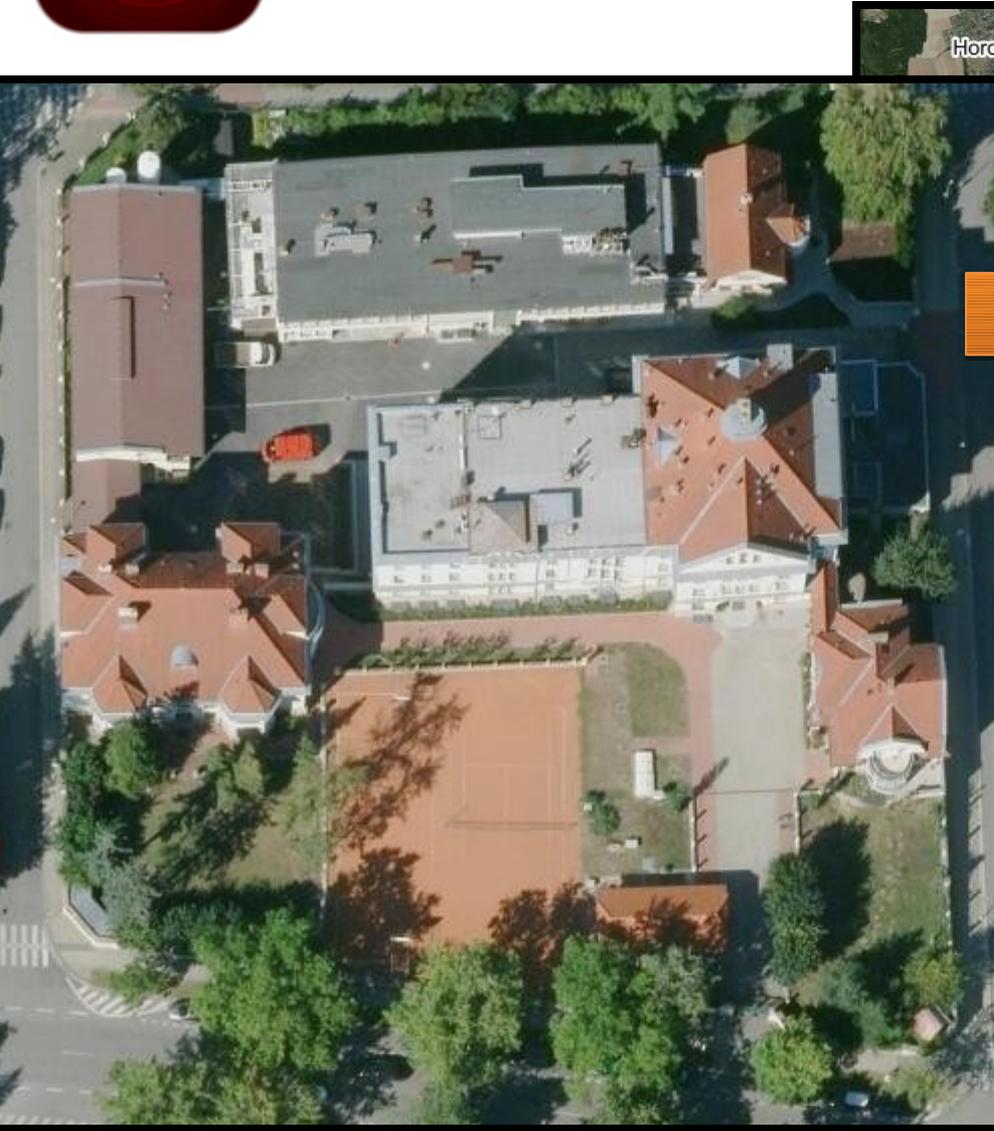
We are here

Approx. 800 km from here...

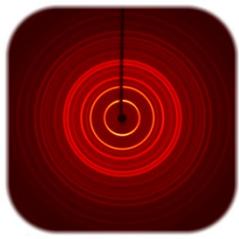




We are here

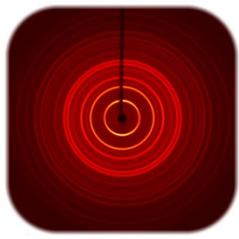


The main building of the institute is on the other side of Prague

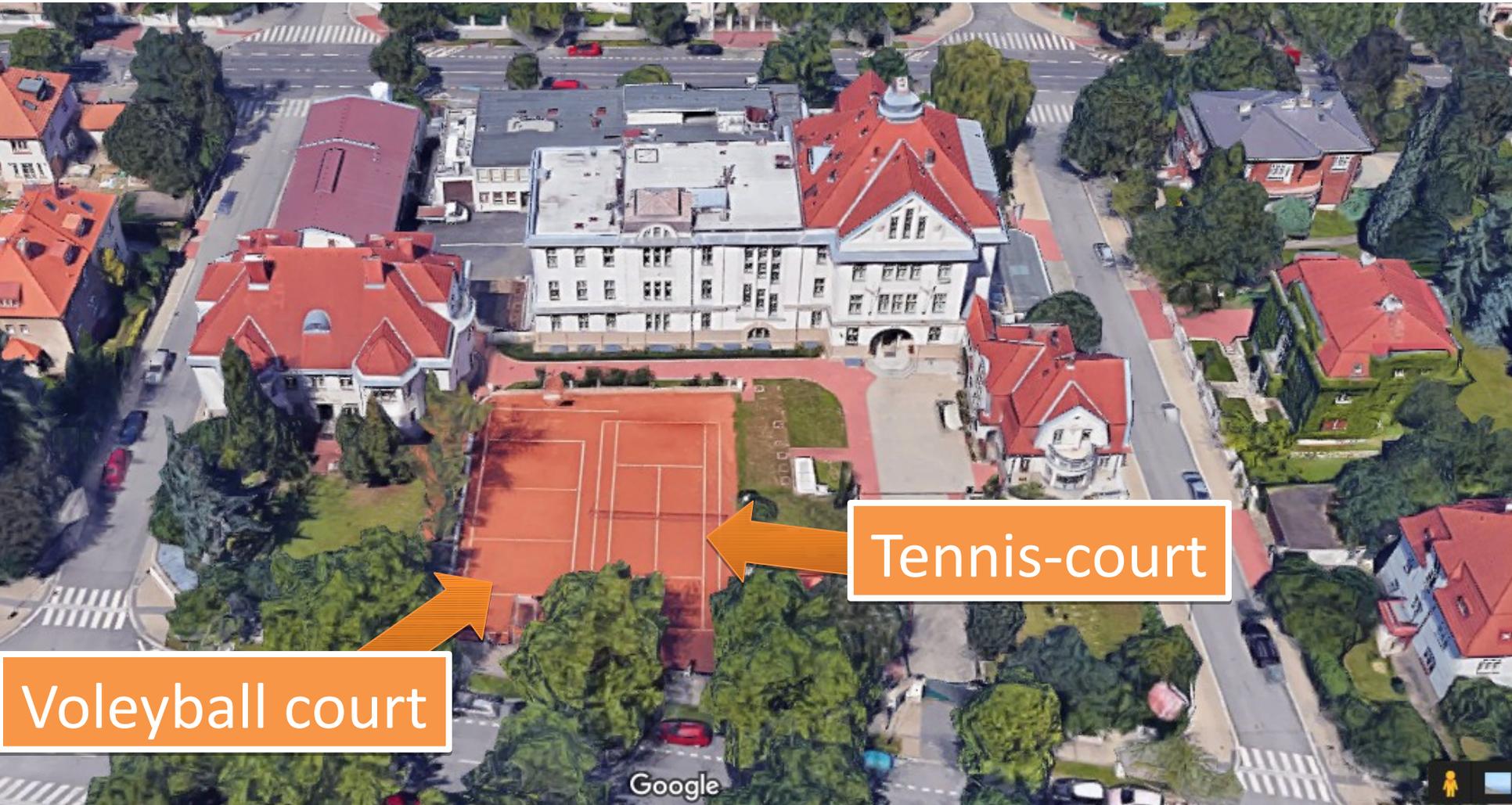


We are here





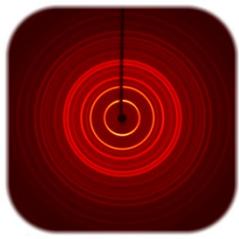
We are here



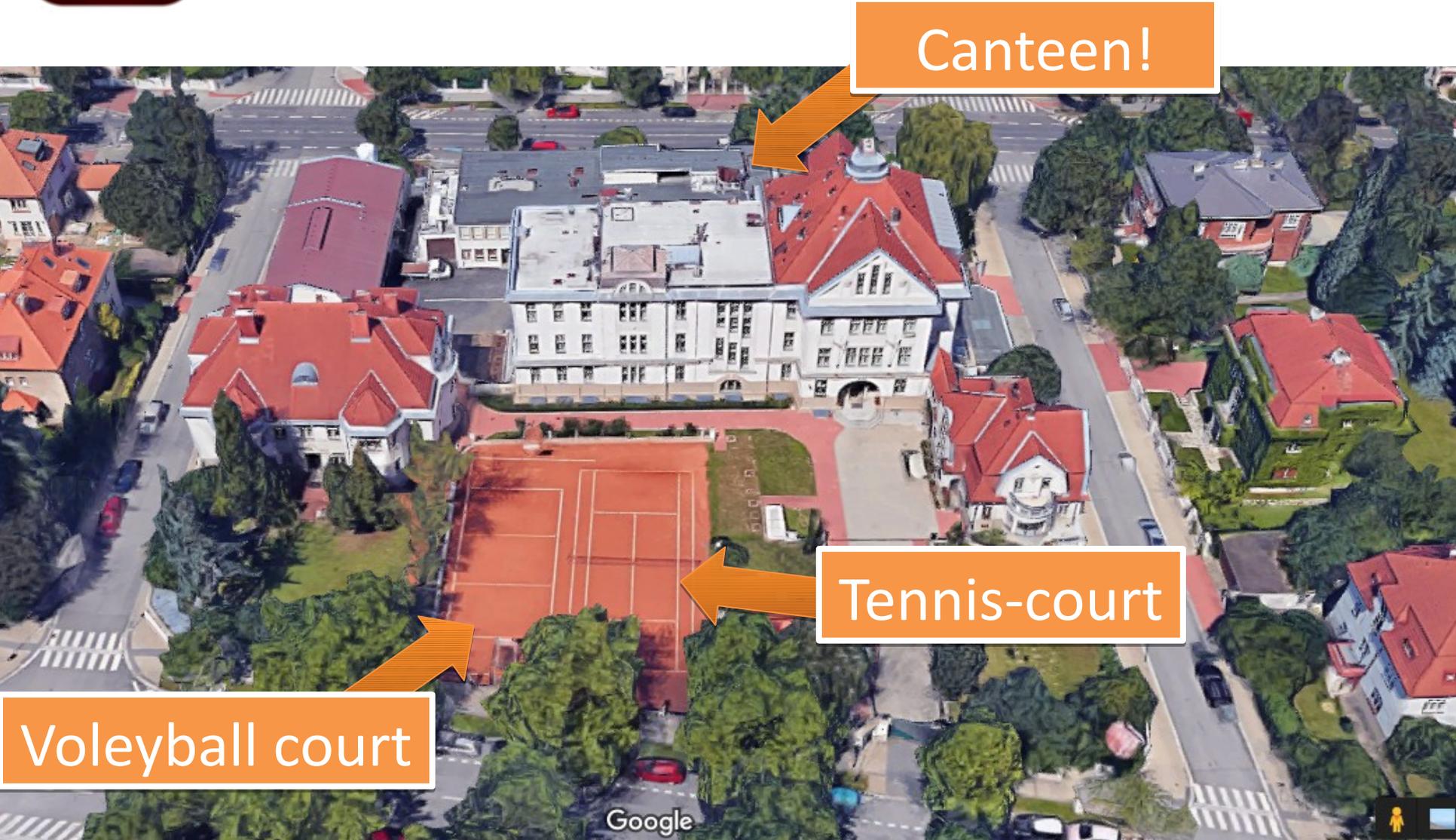
Tennis-court

Volleyball court

Google



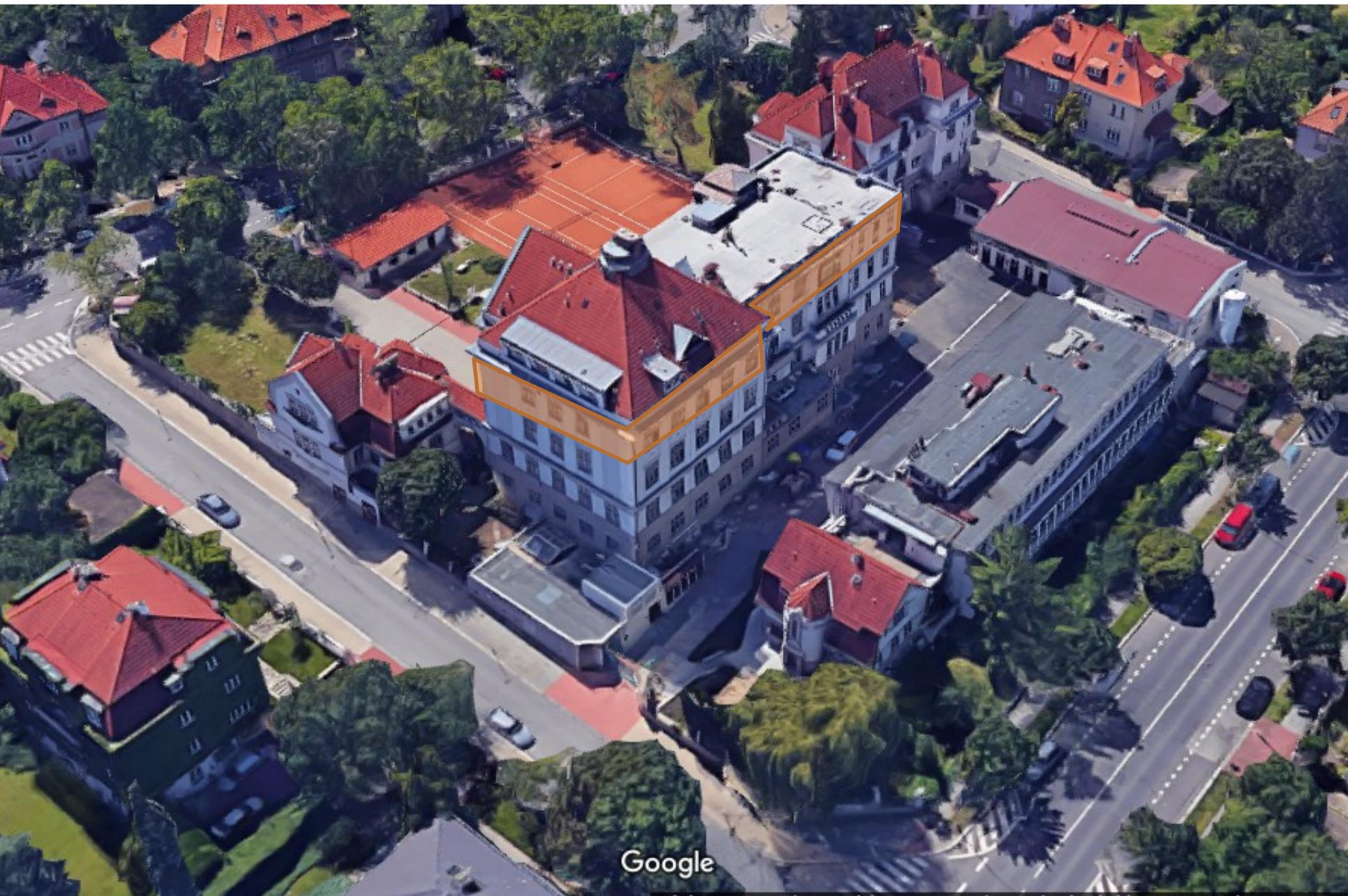
We are here



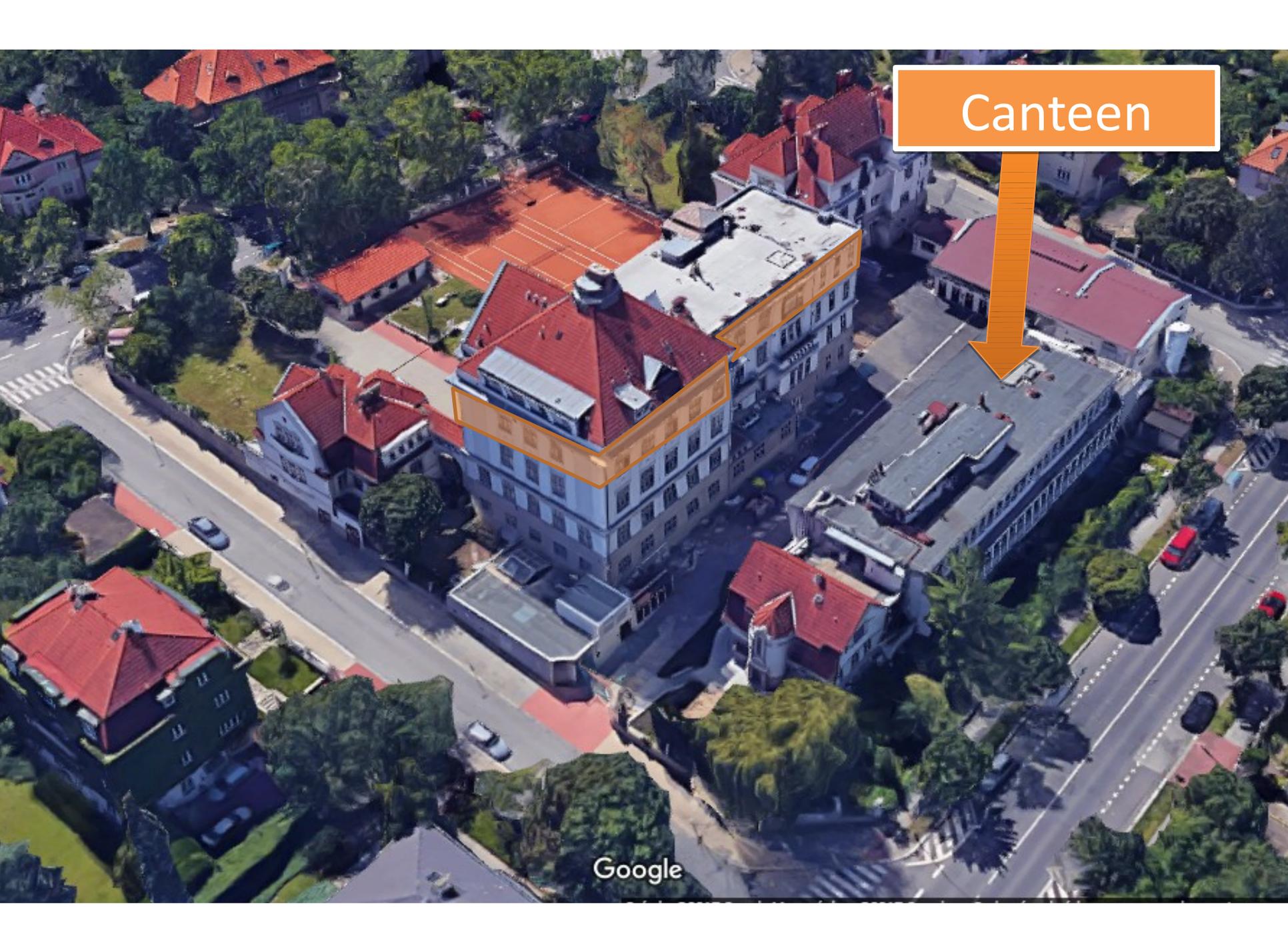
Canteen!

Tennis-court

Volleyball court

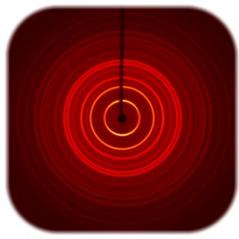


Google



Canteen

Google

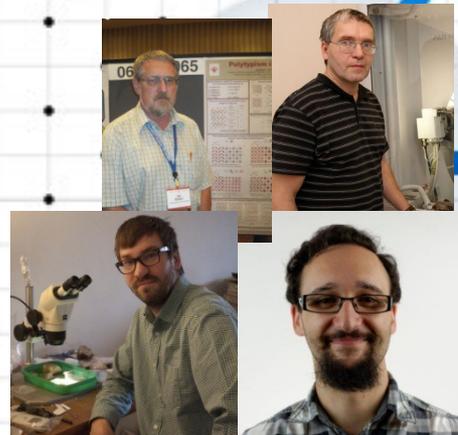


Department of structure analysis

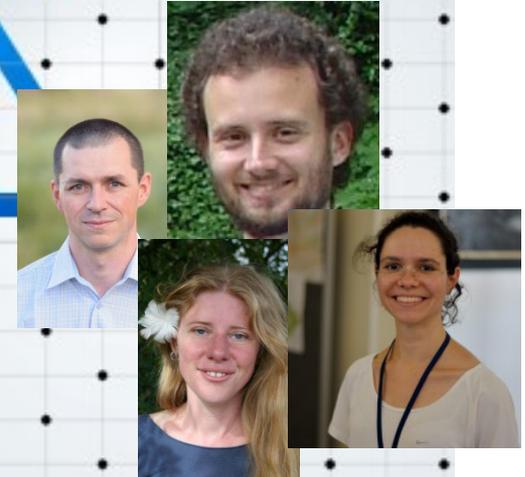
Powder diffraction

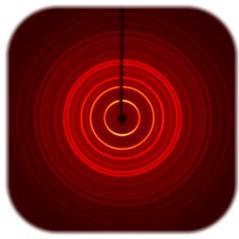


X-ray single crystal diffraction



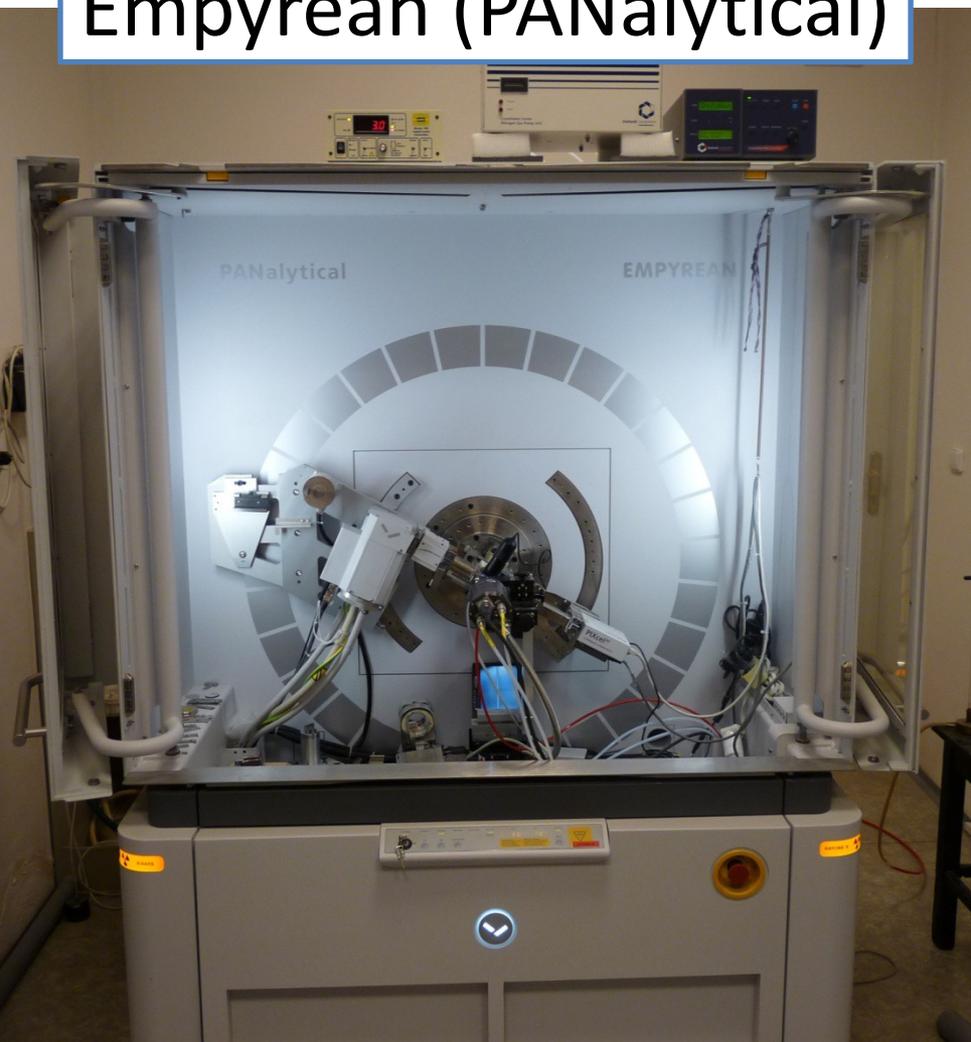
Electron precession diffraction





Powder diffractometers in our lab

Empyrean (PANalytical)



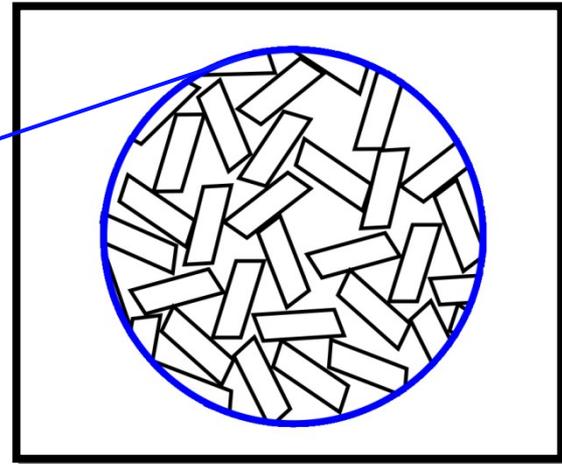
SmartLab (Rigaku)

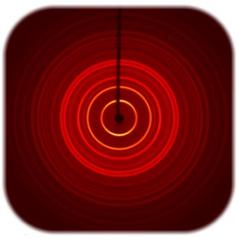




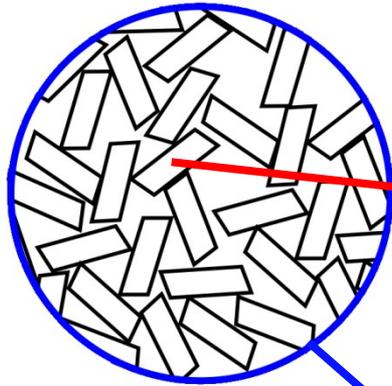
Powder sample

powder = polycrystalline material

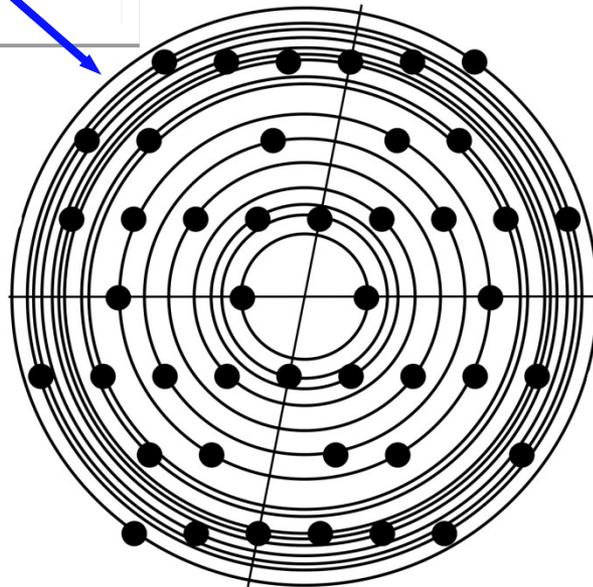
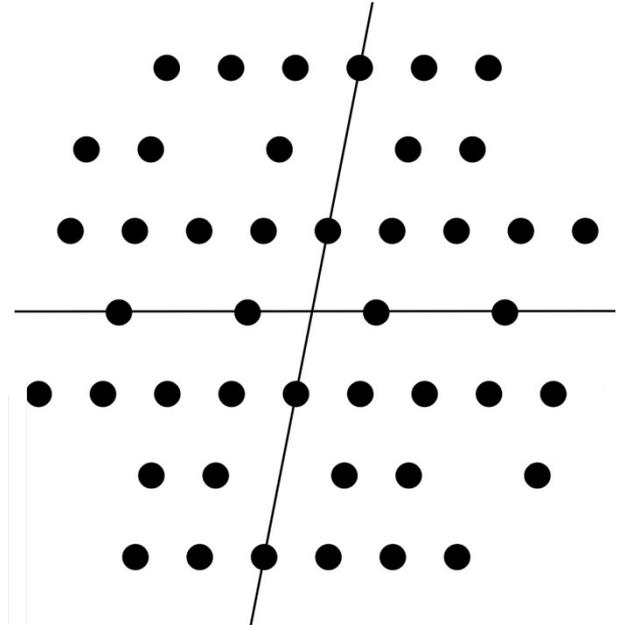




Diffraction of the powder sample



Single crystal diffraction

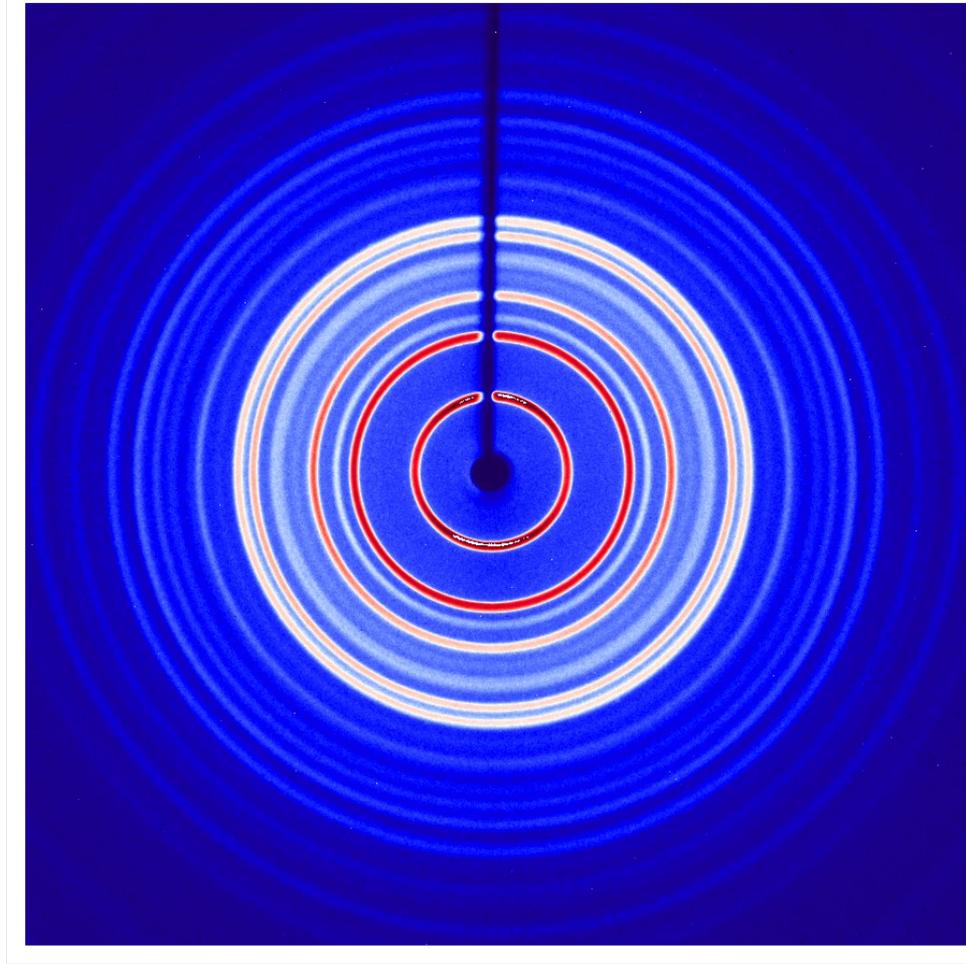


Powder diffraction pattern is a combination of a large number of the single crystal diffraction patterns

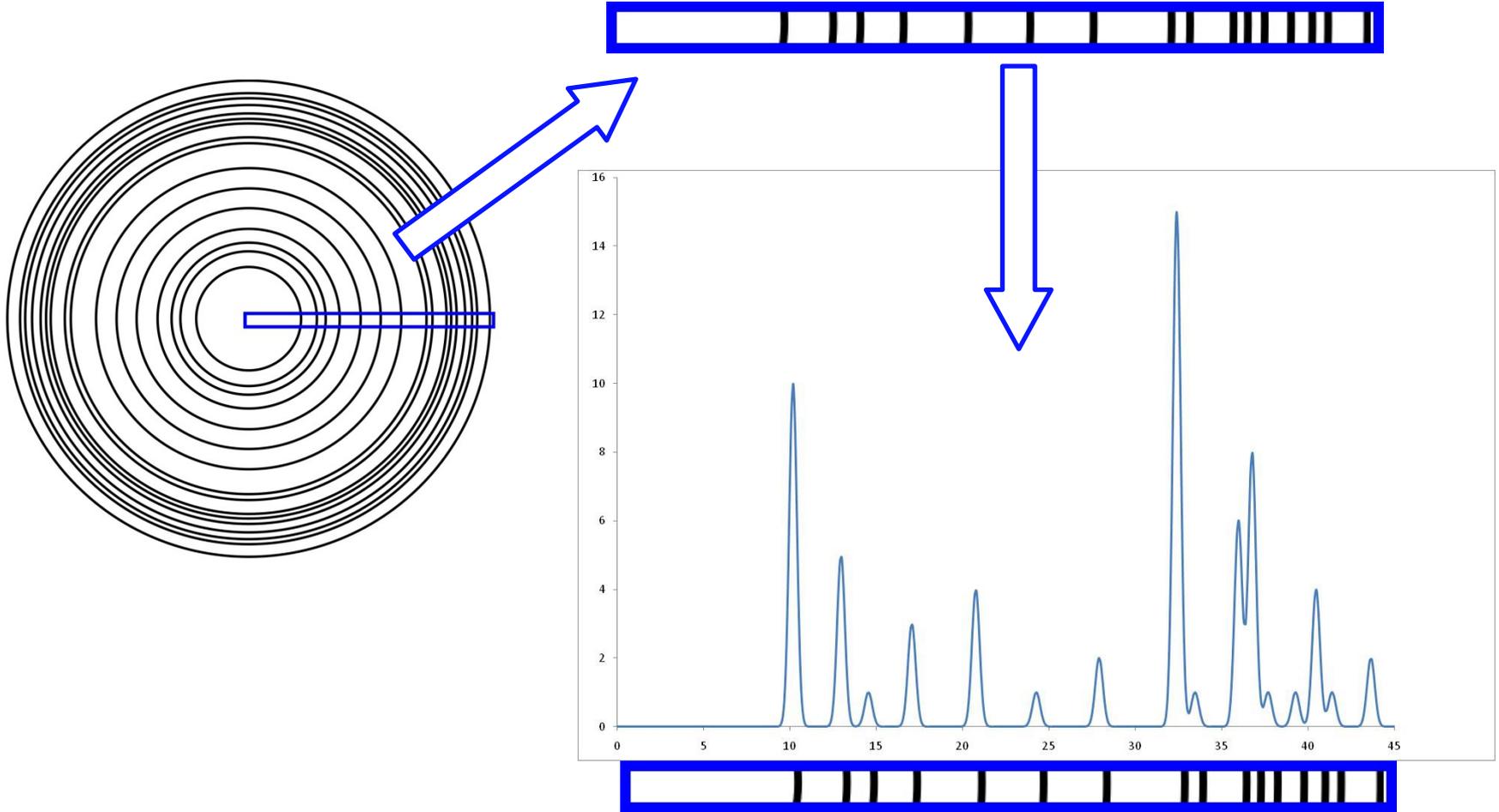
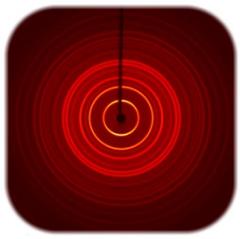


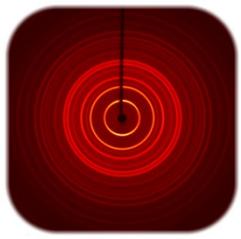
Diffraction pattern

Powder diffraction pattern of alaptide powder on the area detector



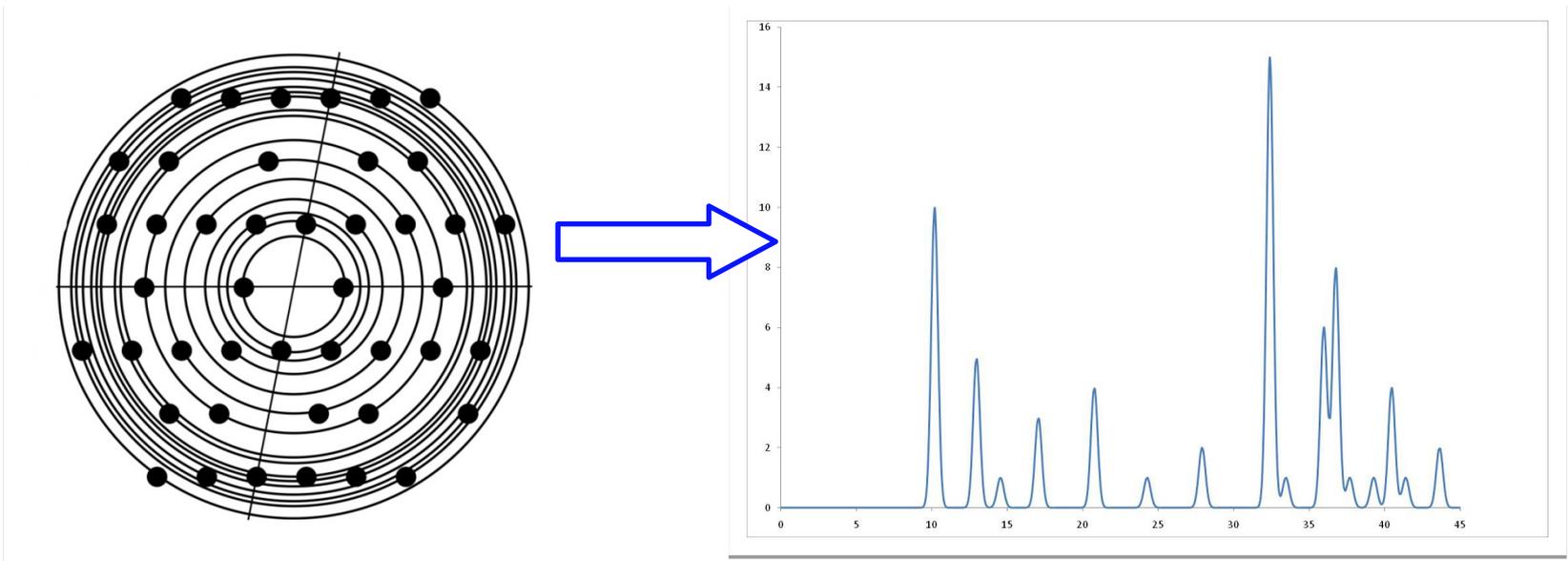
Diffracted pattern

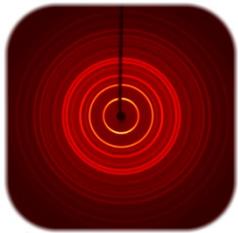




Problems and limitations

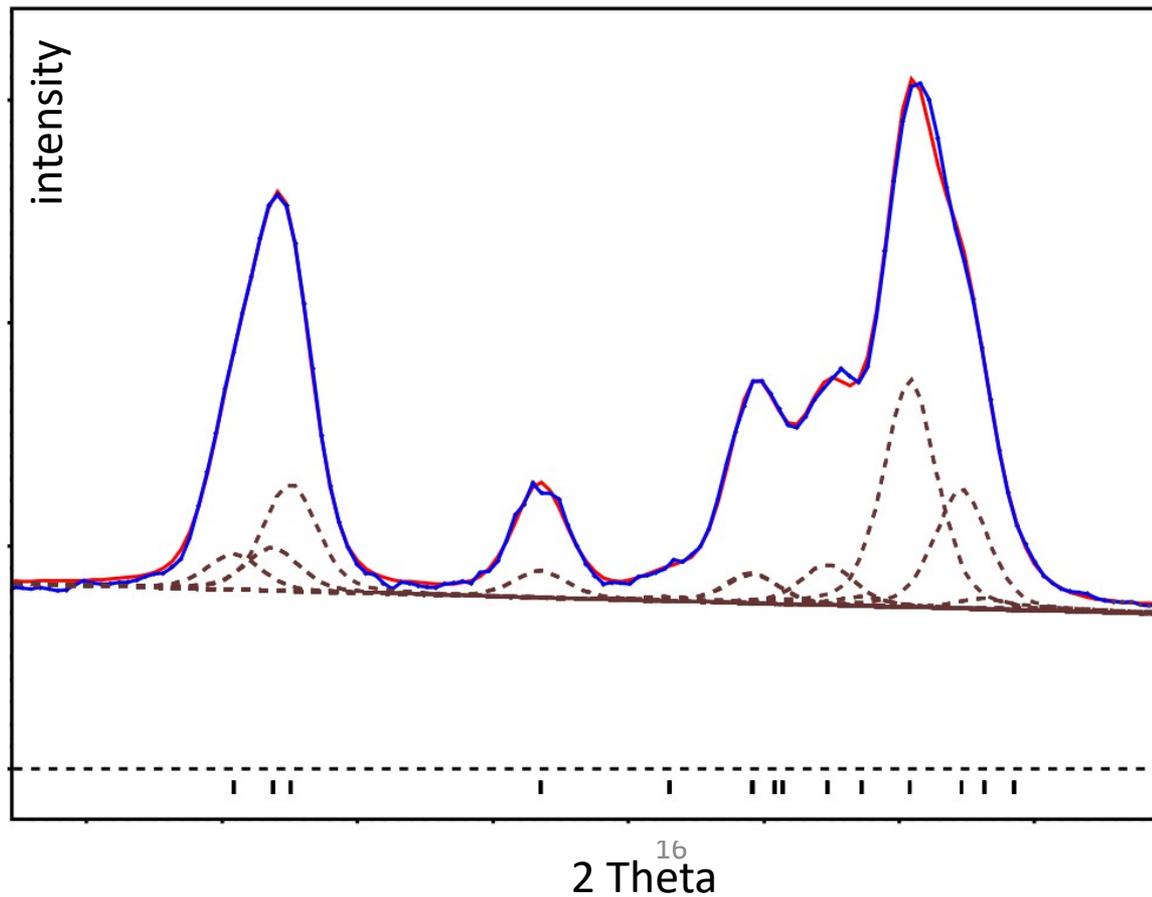
- **Information loss** – data are projection of a 3D diffraction pattern to 1D





Problems and limitations

- **Peak overlap** – extraction of intensities.

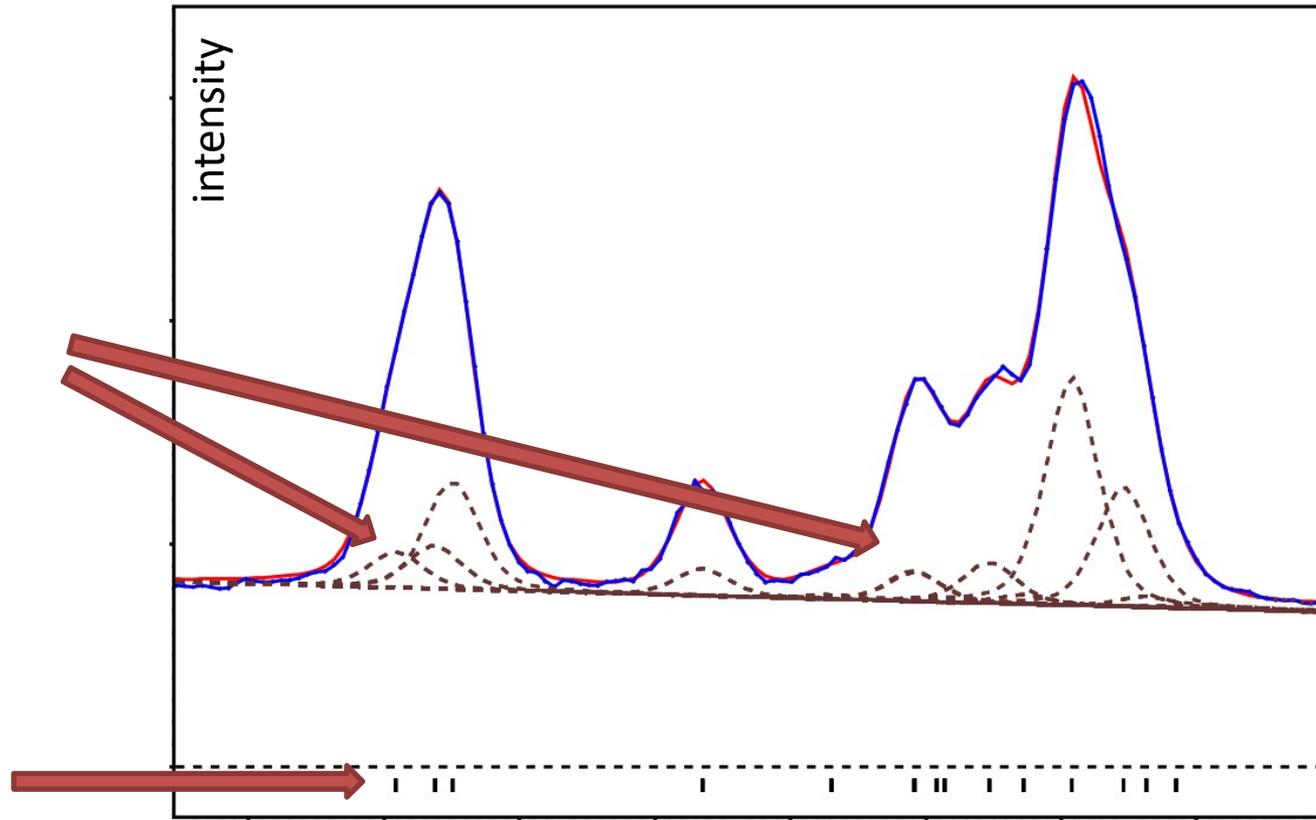




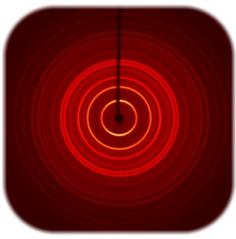
Problems and limitations

- **Peak overlap** – extraction of intensities.

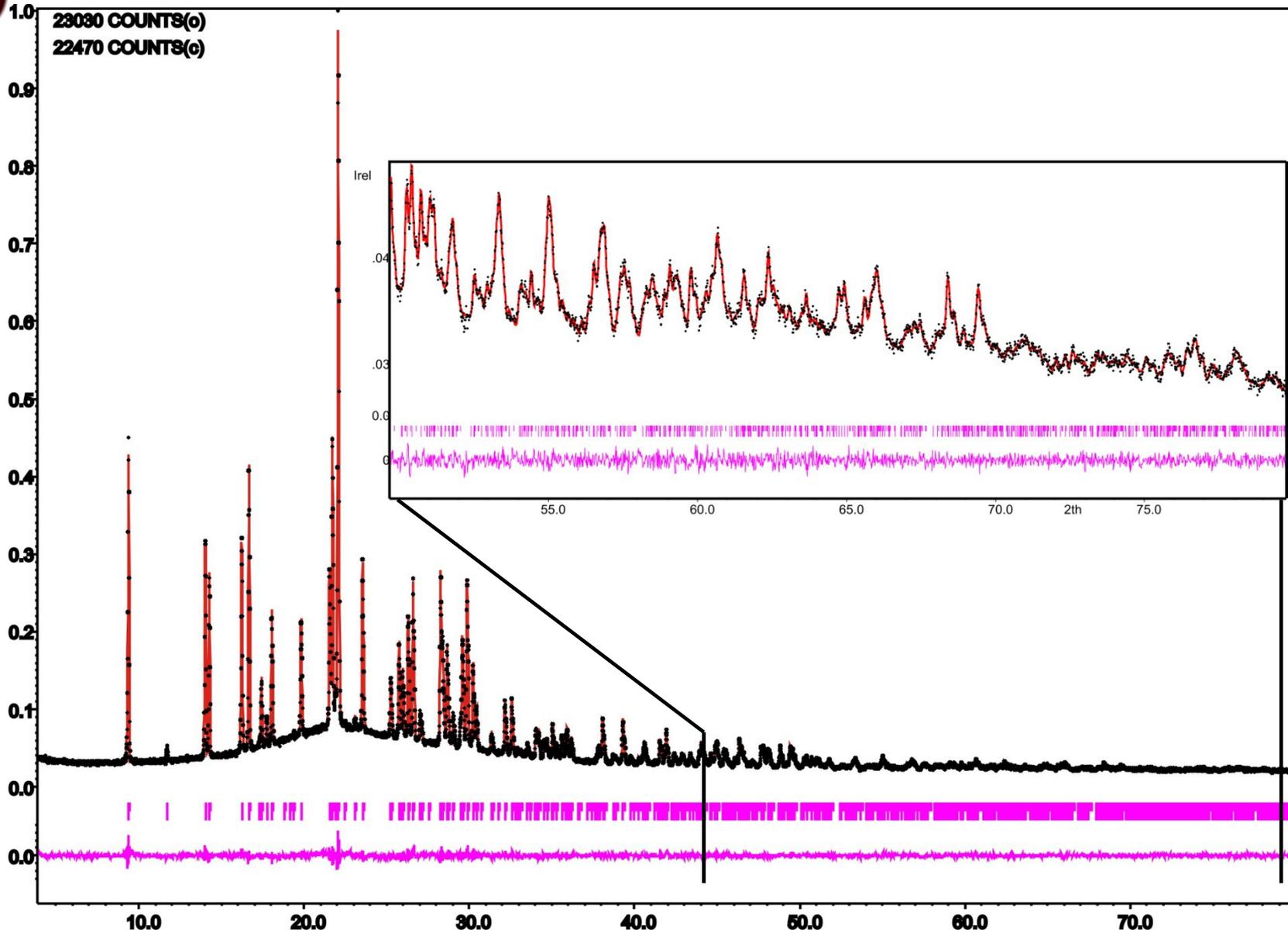
What is the intensity of these reflections?

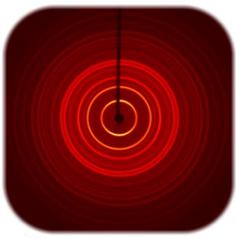


Positions of reflections

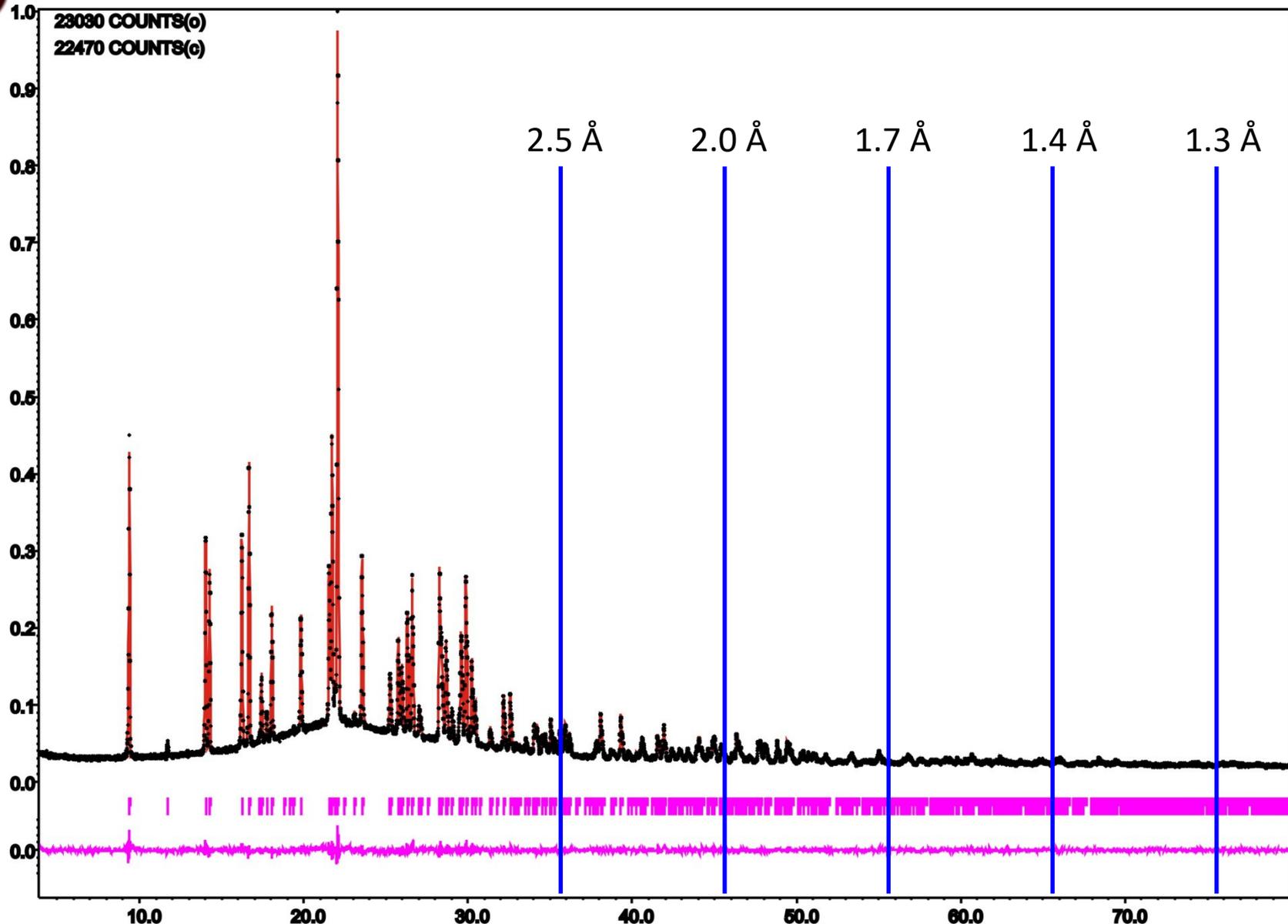


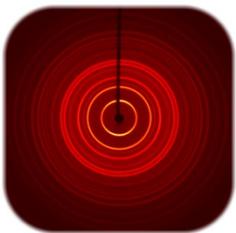
Peak overlap





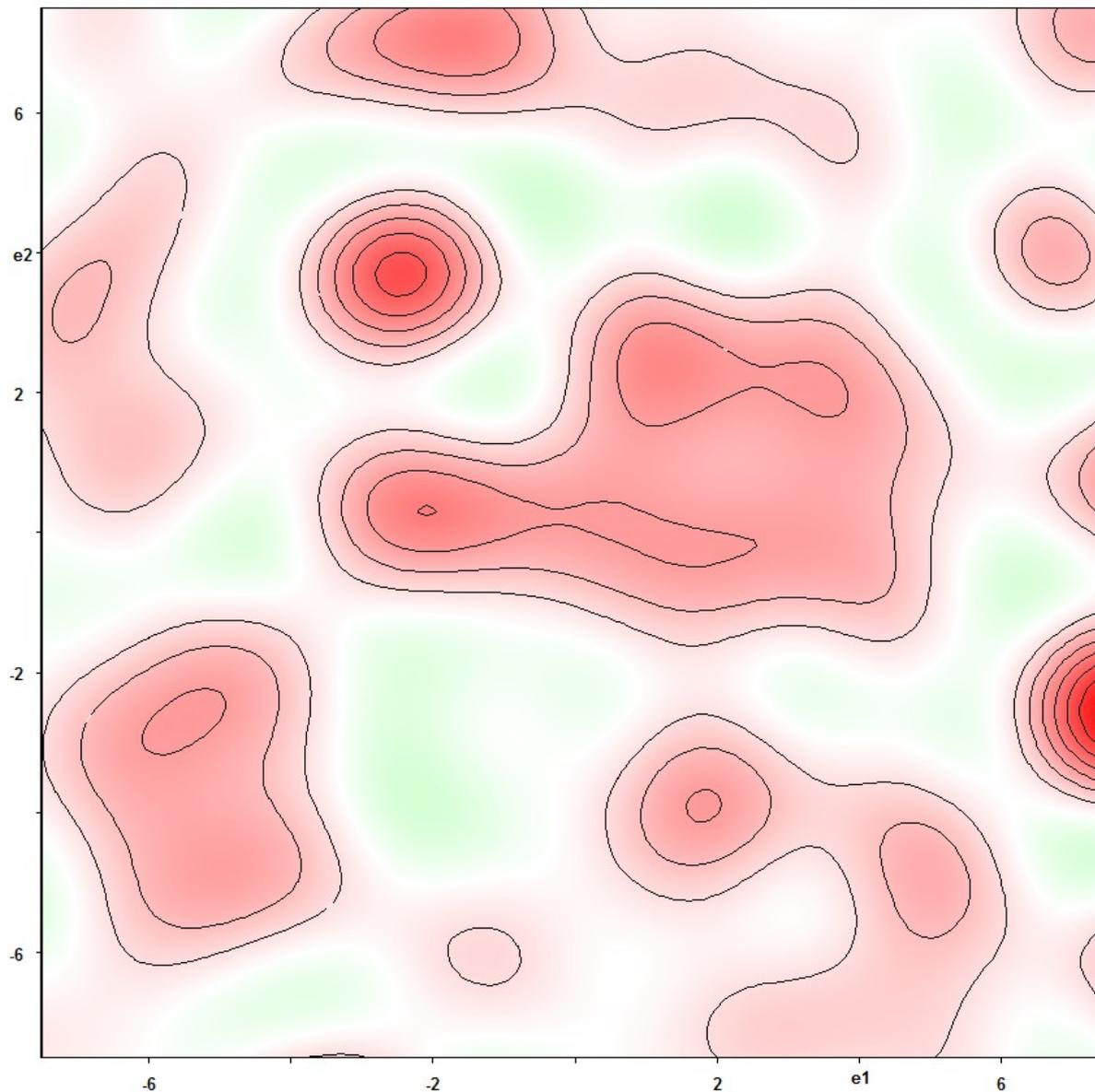
Peak overlap





El. density – F_{calc} Fourier

e3=0.000

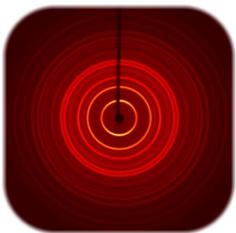


$$\sin \Theta / \lambda = 0.2$$

$$\lambda = 1.5418 \text{ \AA}$$

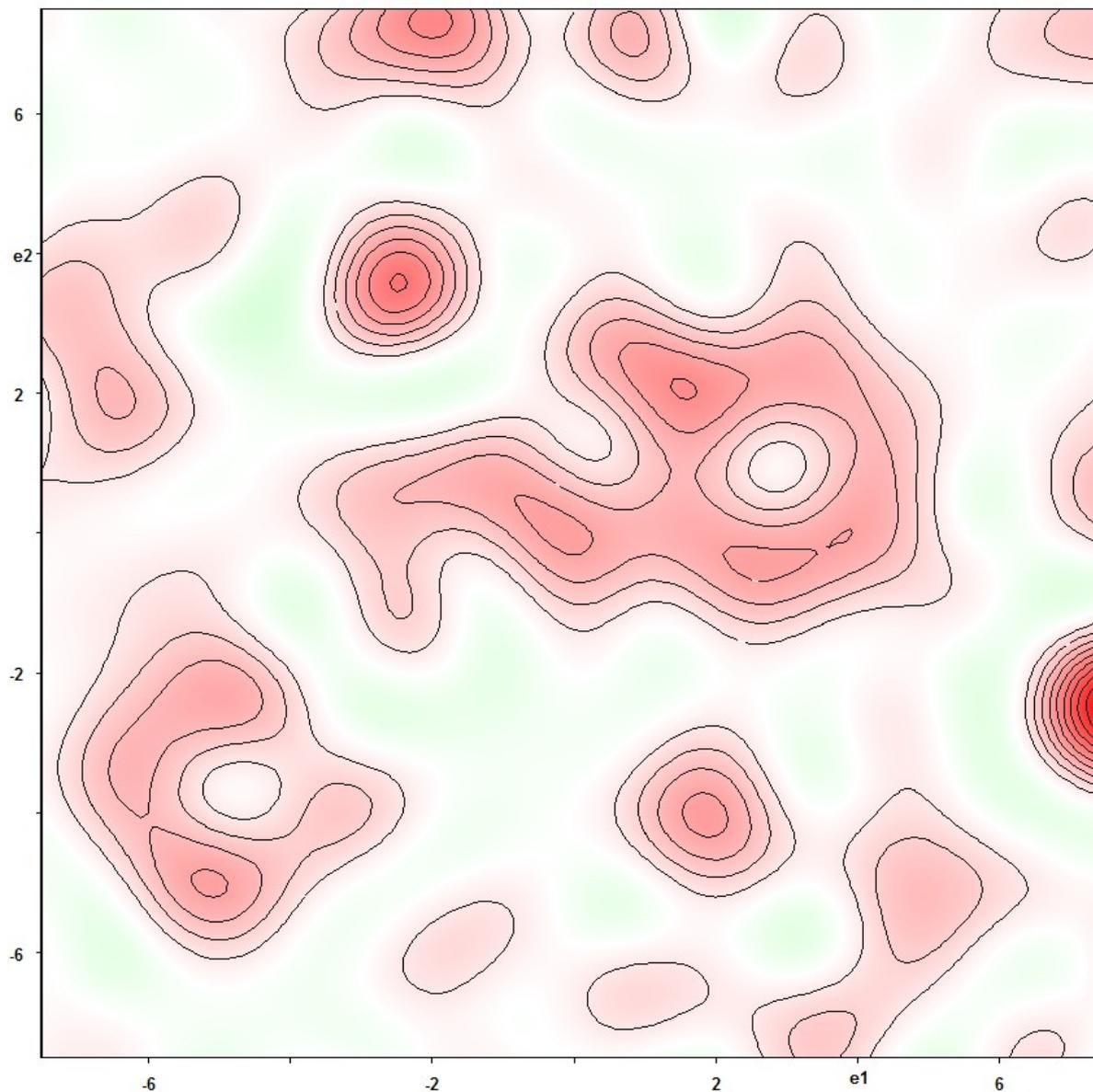
$$\text{max} = 36^\circ 2\Theta$$

$$\text{dmax} = 2.5 \text{ \AA}$$



Rozlišení ELD

e3=0.000

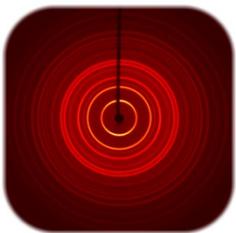


$$\sin \Theta / \lambda = 0.25$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\max = 45^\circ 2\Theta$$

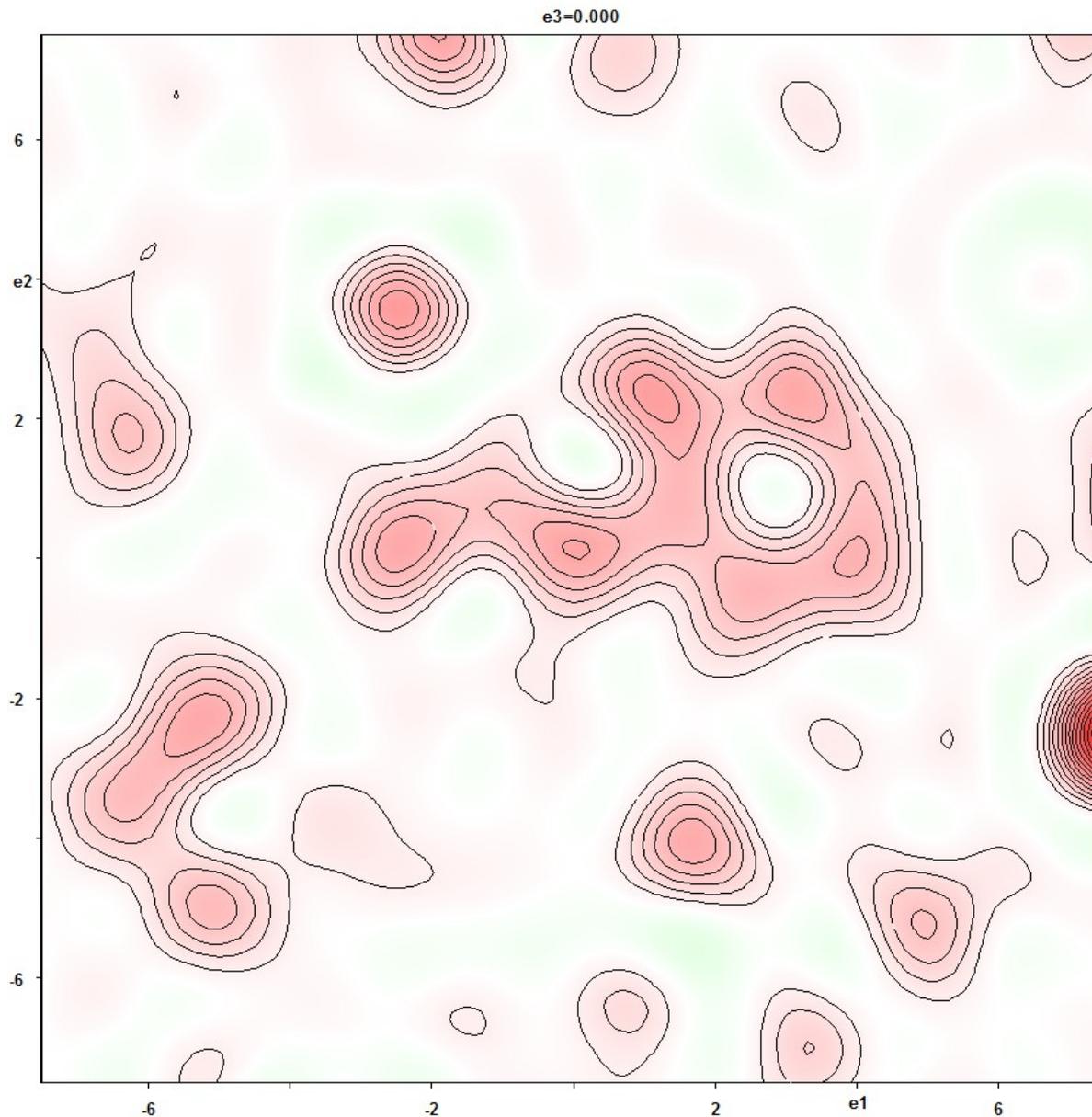
$$d_{\max} = 2.0 \text{ \AA}$$

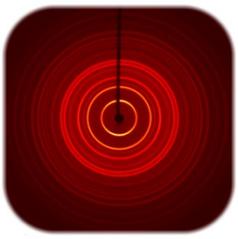


Rozlišení ELD

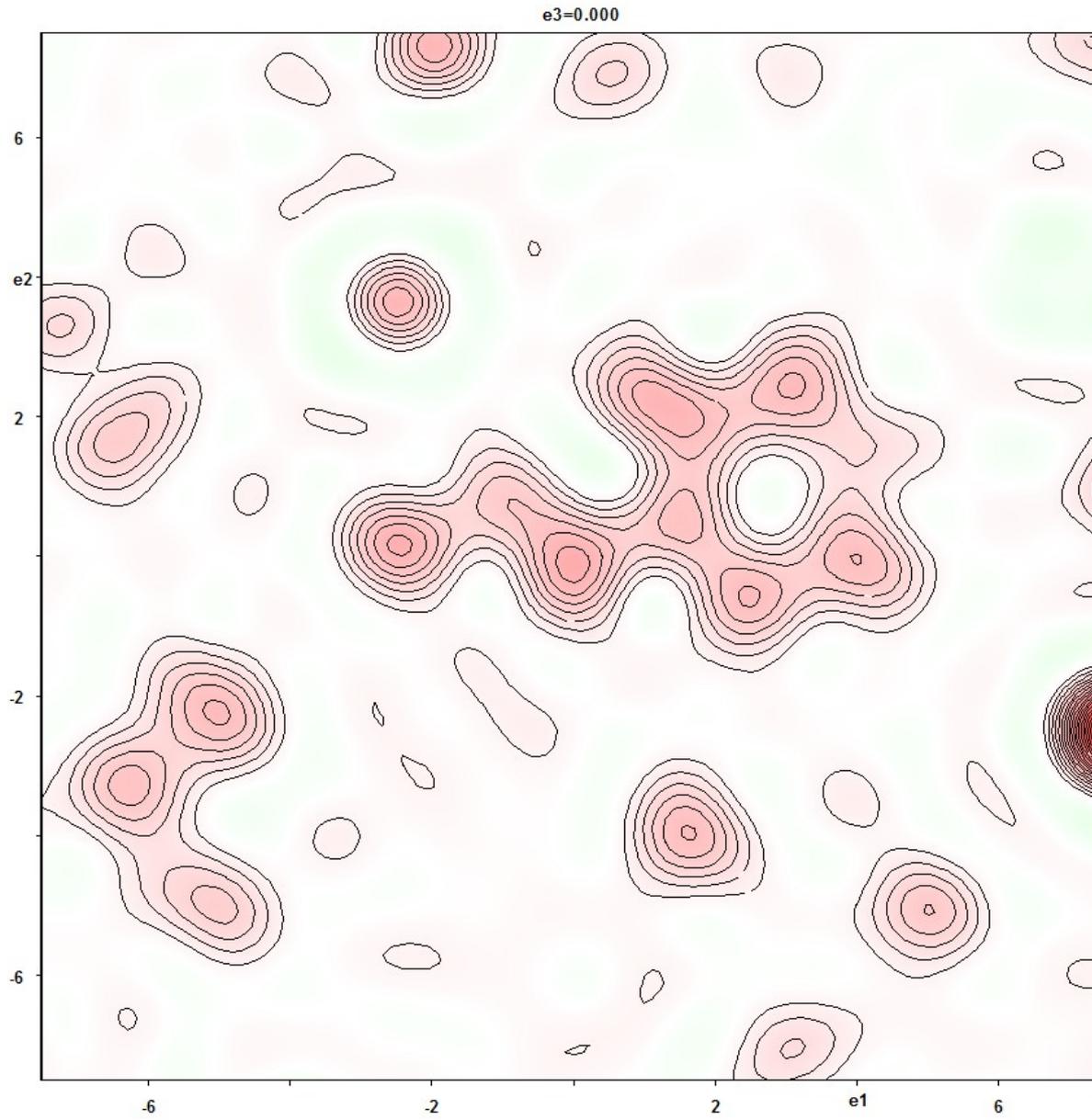
$$\sin \Theta / \lambda = 0.3$$

$$\lambda = 1.5418 \text{ \AA}$$
$$\max = 55^\circ 2\Theta$$
$$d_{\max} = 1.7 \text{ \AA}$$





Rozlišení ELD

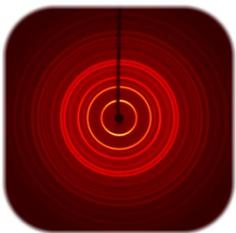


$$\sin \Theta / \lambda = 0.35$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\max = 65^\circ 2\Theta$$

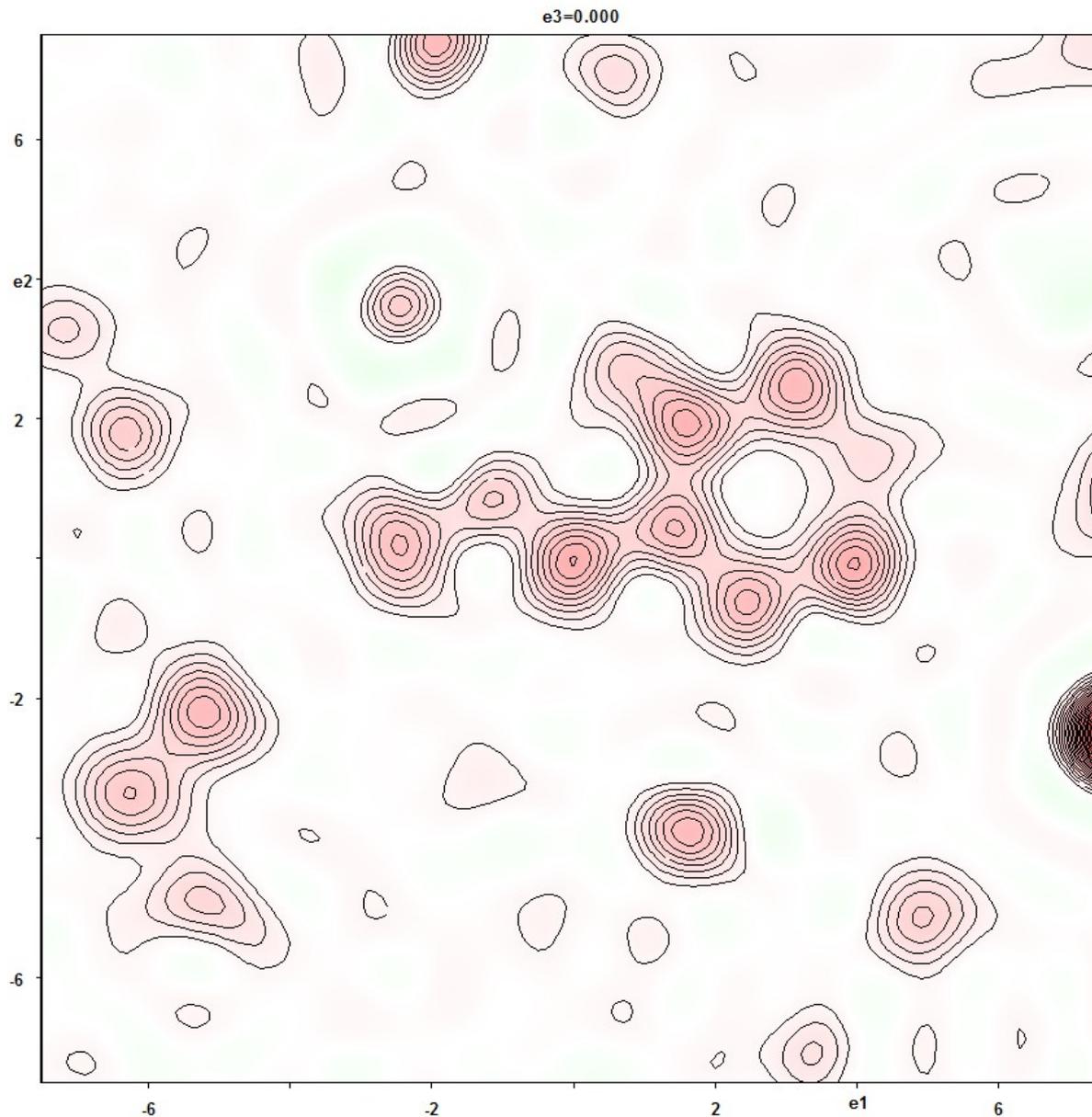
$$d_{\max} = 1.4 \text{ \AA}$$

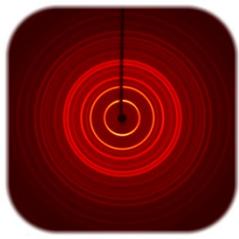


Rozlišení ELD

$$\sin \Theta / \lambda = 0.4$$

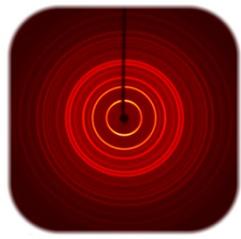
$$\lambda = 1.5418 \text{ \AA}$$
$$\max = 76^\circ 2\Theta$$
$$d_{\max} = 1.3 \text{ \AA}$$





Effect of the peak overlap

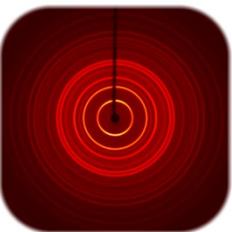
- Dual space methods and **direct methods** need:
 - High resolution data ($\sim 1.2\text{\AA}$ and better)
 - Low peak overlap
 - charge flipping combined with histogram matching may solve the „peak overlap“ issue
- **Direct Space methods**
 - Starting model
 - Time consuming process



What is charge flipping?

Charge flipping is a method for *ab initio* determination of an approximate scattering density from the set of structure-factor amplitudes

- Published by Oszlányi & Sütő (2004), Acta Cryst A
- The output is an **approximate scattering density** of the structure sampled on a discrete grid
- Requires only **lattice parameters** and **reflection intensities**
- No use of atomicity, only of the “sparseness” of the electron density
- **No use of symmetry apart from the input intensities**



Charge flipping

The direct-space constraint must restrict the scattering densities to a physically meaningful subset.

Typical requirements are positivity, sparseness and atomicity.

$|F_{hkl}(\text{obs})|$
 δ (ed threshold for flipping)

assign random phases

electron density map

flip sign of ed $< \delta$

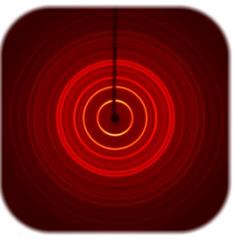
perturbed electron density map

back transform

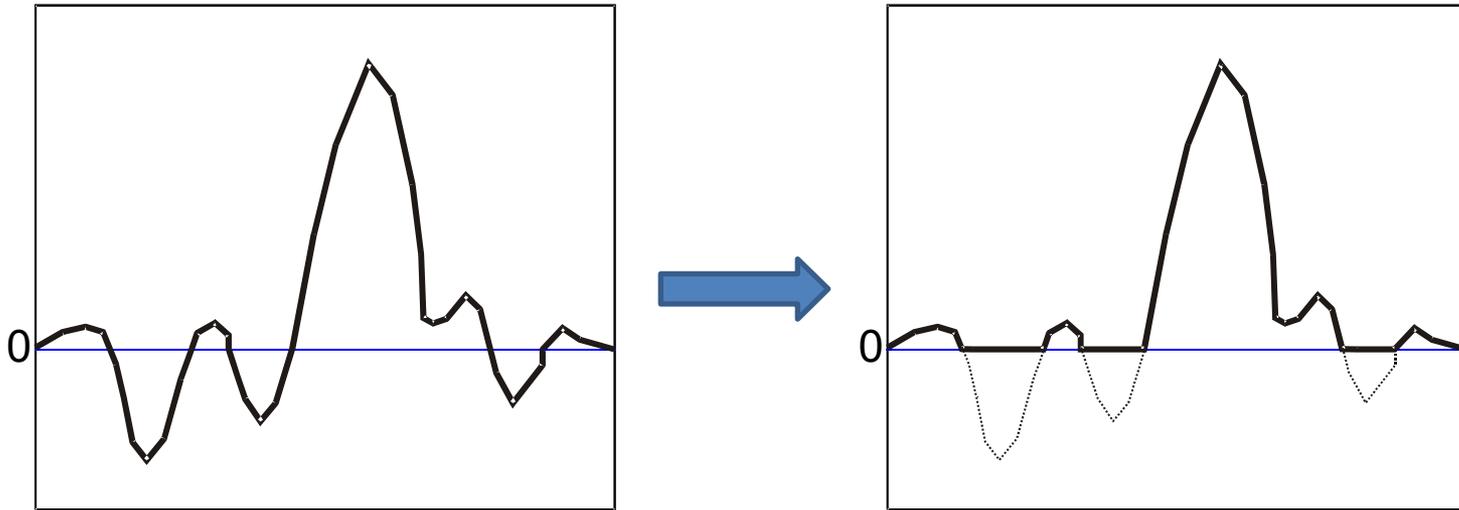
R-value

$|F_{hkl}(\text{calc})|$
 $\phi_{hkl}(\text{calc})$

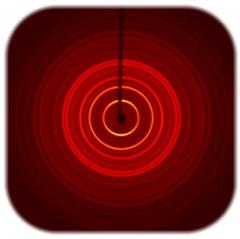
combine
 $|F_{hkl}(\text{obs})|$
with
 $\phi_{hkl}(\text{calc})$



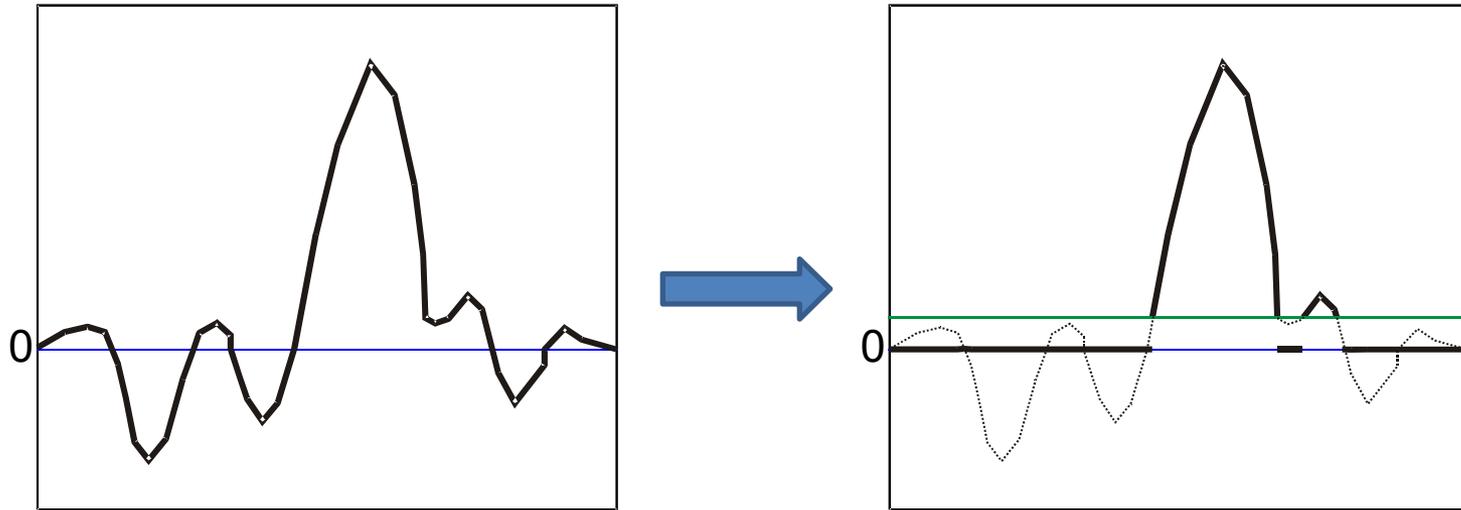
Constraints and projections



Positivity projection



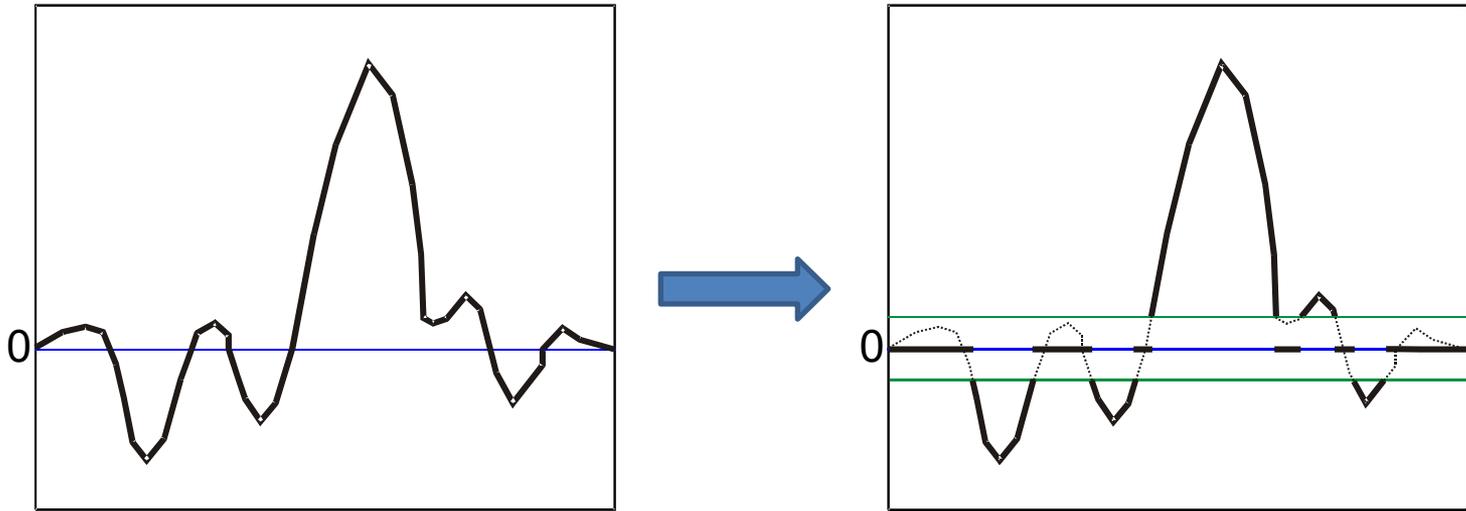
Constraints and projections



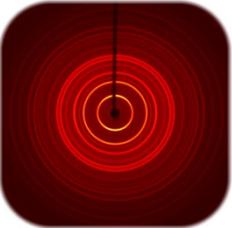
Significance + positivity projection (dynamic support with positivity)



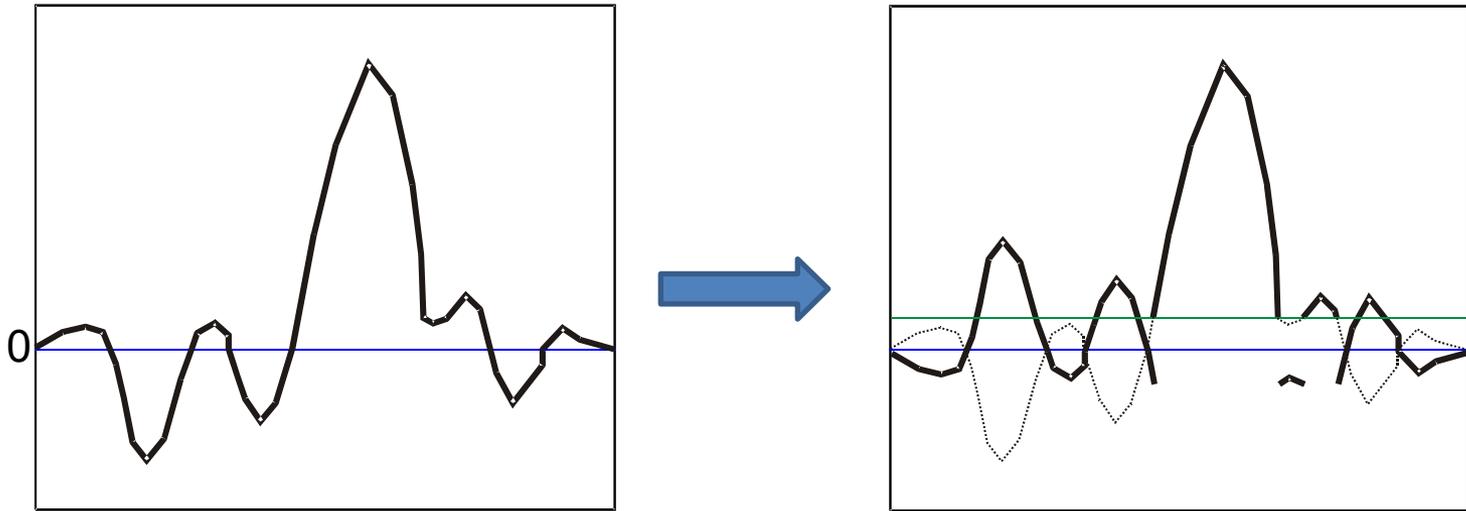
Constraints and projections



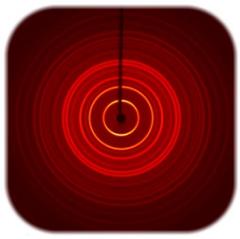
Significance projection (dynamic support without positivity)



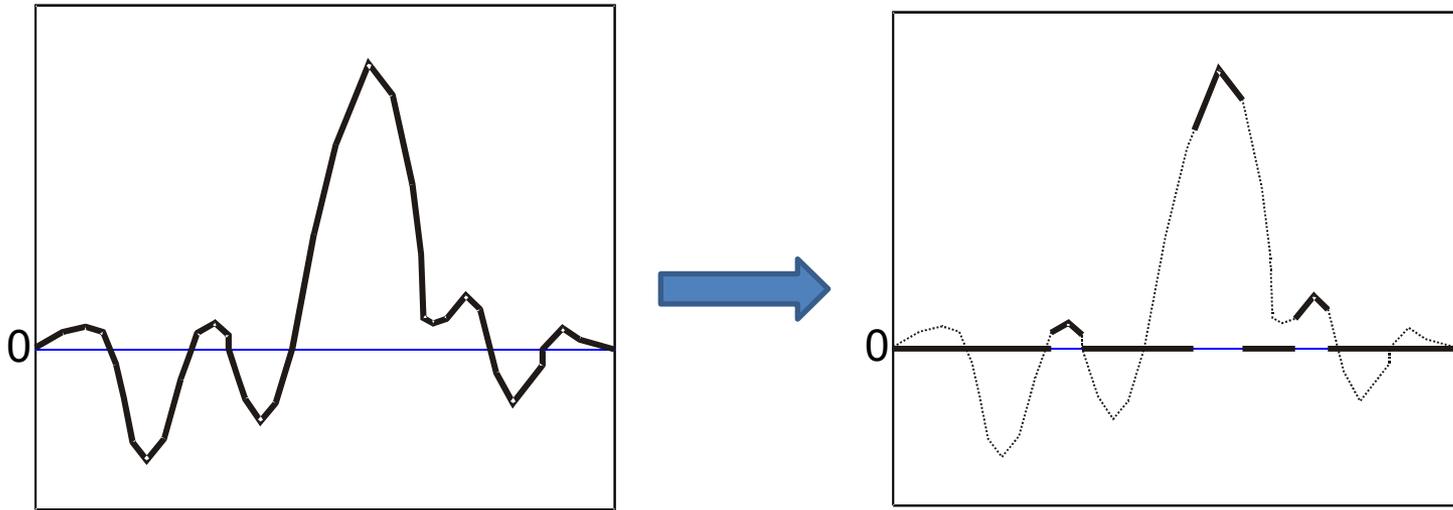
Constraints and projections



Reflector of the significance + positivity projection – the charge flipping operation



Constraints and projections



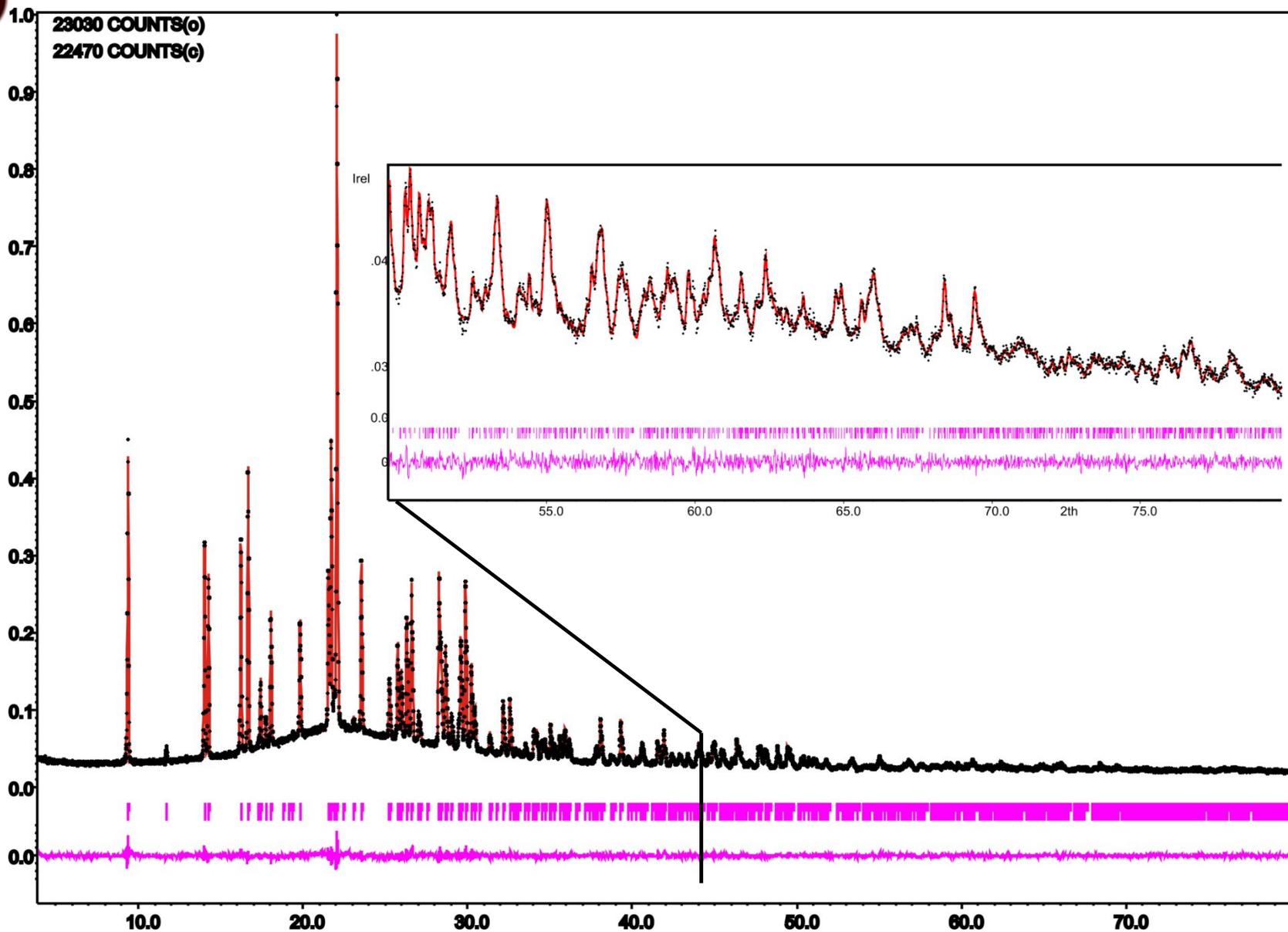
Constraint on the number of maxima in the density

Charge flipping - applet

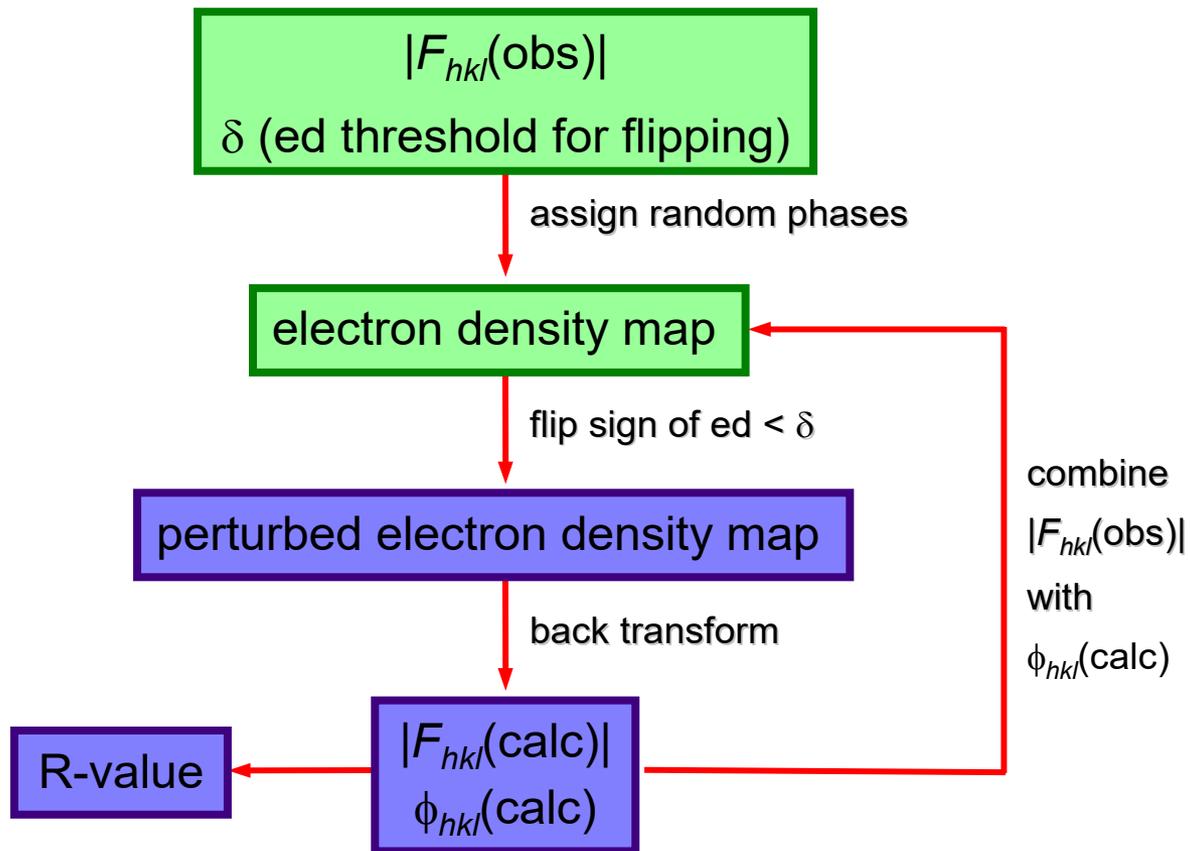
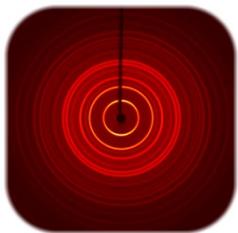
The applet interface is titled "Charge Flipping" and is divided into several sections:

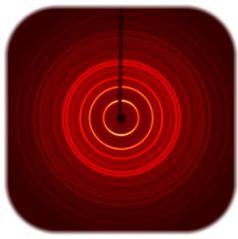
- Original structure:** A grid showing a pattern of black dots representing the original structure.
- Reconstructed structure:** A large empty white box for the reconstructed structure.
- Flowchart:** A central diagram illustrating the process:
 - "Draw a Structure" (orange button) leads to a sphere labeled ρ .
 - An arrow labeled "Flip charges ($\rho < \delta$)" points from ρ to a sphere labeled g .
 - An arrow labeled "FFT" points from ρ down to a sphere labeled F .
 - An arrow labeled "Random Phases" points from F to ρ .
 - An arrow labeled "FFT-1" points from F up to ρ .
 - An arrow labeled "Restore amplitudes" points from a sphere labeled G to F .
 - An arrow labeled "FFT" points from G down to ρ .
- Help:** A button located below the flowchart.
- Graph:** A plot area with a y-axis from 0% to 100%. A legend indicates:
 - Red line: Total Charge $G(0)$
 - Blue line: R factor
- Control Panels:**
 - Drawing:** Includes a pen size slider (set to 10), a darkness slider (set to 100), a position field (116 78), and a "Clear" button.
 - Run:** Includes "FFT", "Do one cycle", "Loop", and "Reset" buttons.
 - Parameters:** Includes a "Mask Radius" checkbox and slider, a "Delta" field (0.0032), a "Dynamic" checkbox and slider (10%), a "Weak reflections" field (0%), and a "Default" button. Below these, it shows "Re=0.0 Im=0.0 A=0.0 $\phi=0^\circ$ ".
 - Image:** Includes "Zoom" and "Contrast" sliders, and a "Rotate 180°" button.
 - Show:** Includes radio buttons for "Complex" (selected), "Real part", "Imaginary part", "Magnitude²", and "Phase".
 - Color ref:** A color wheel for reference.

Charge flipping for powders

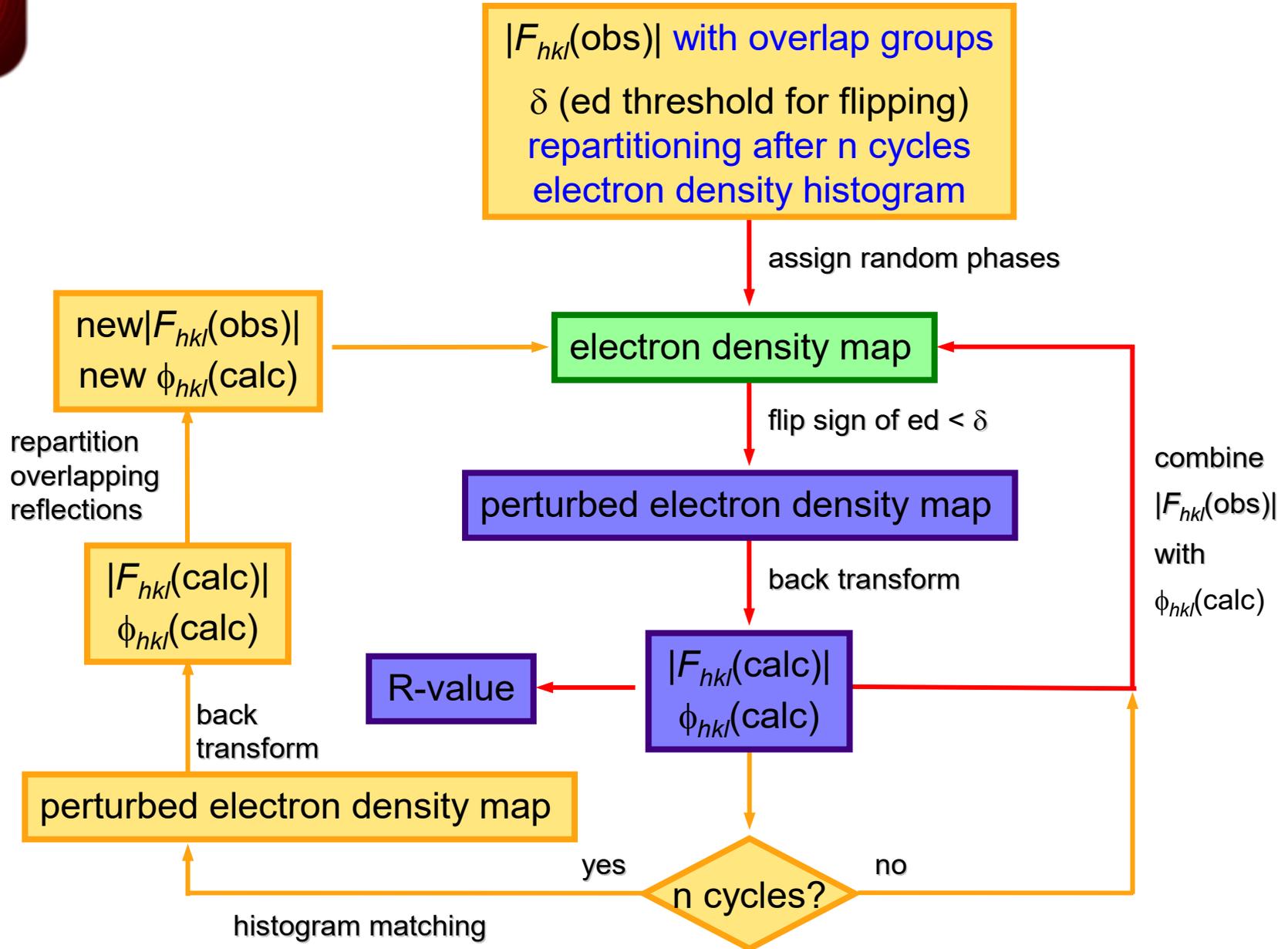


Charge flipping

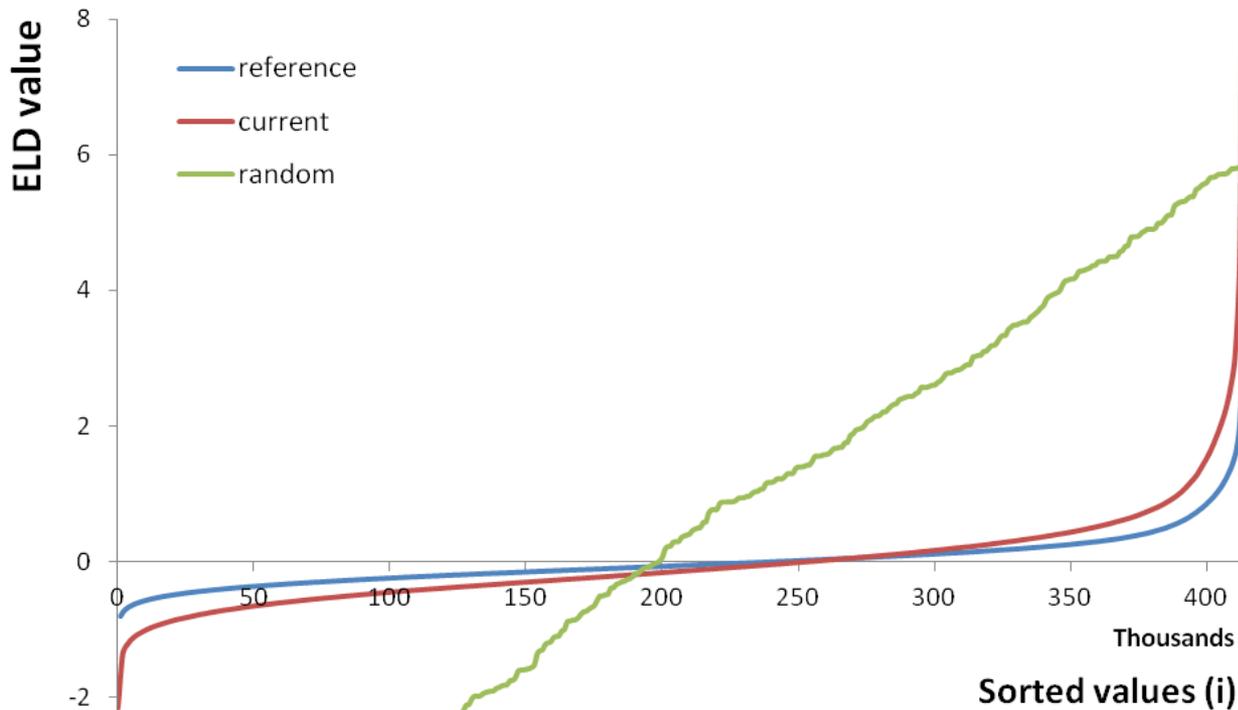




Charge flipping for powders

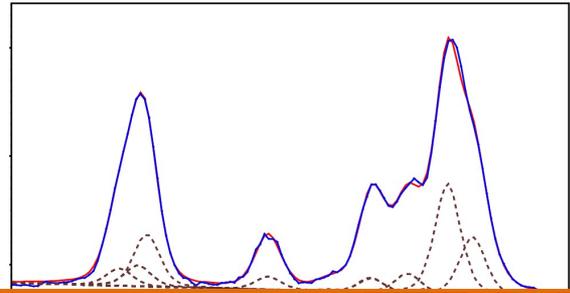
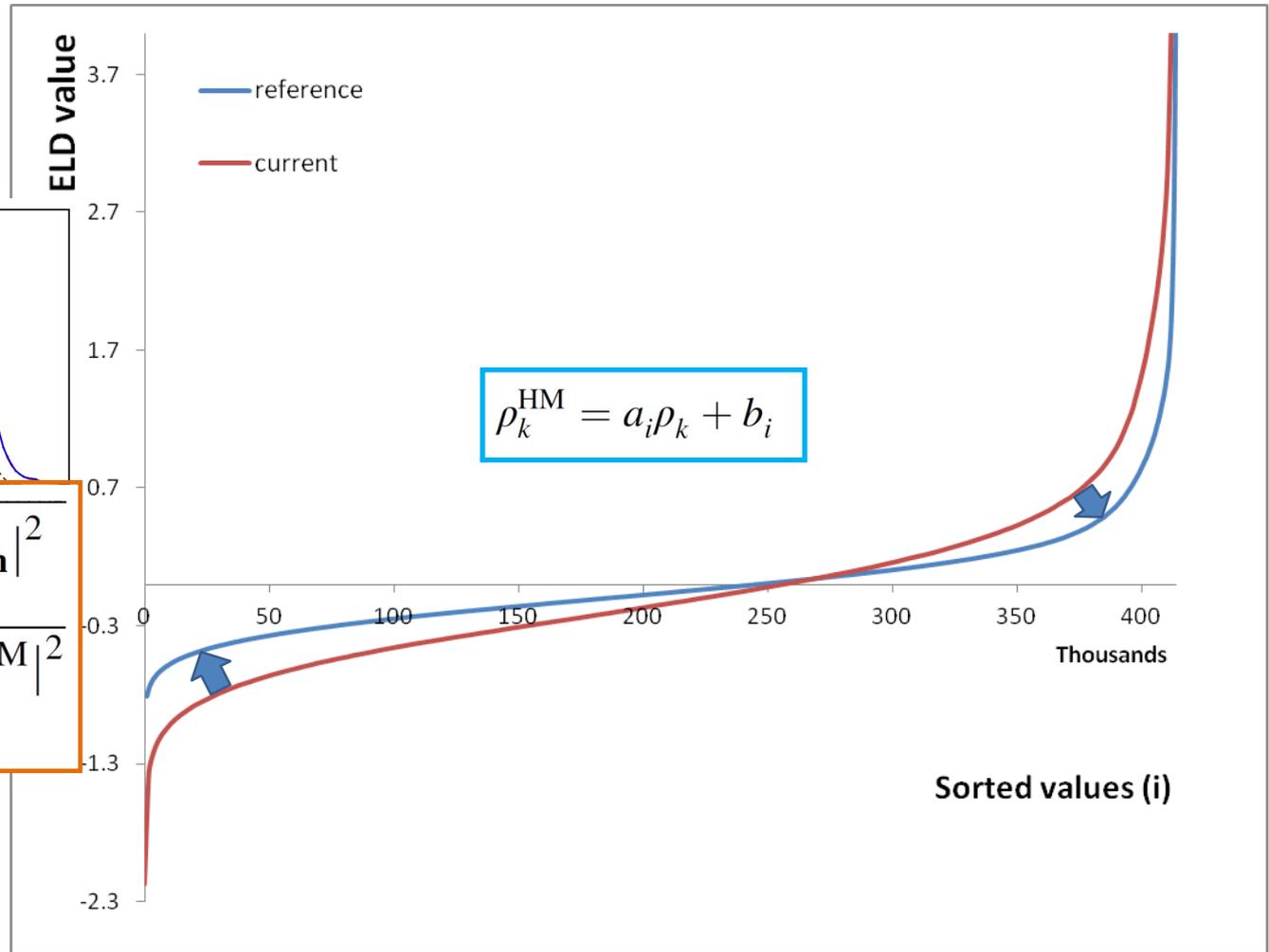
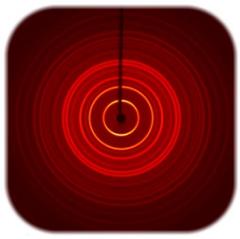


Electron density histograms



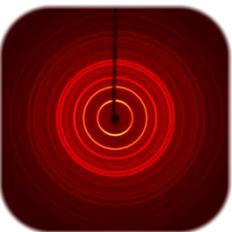
Original idea: Zhang & Main, Acta Cryst A46, 1990 – used to improve phases, not intensities

Electron density histograms



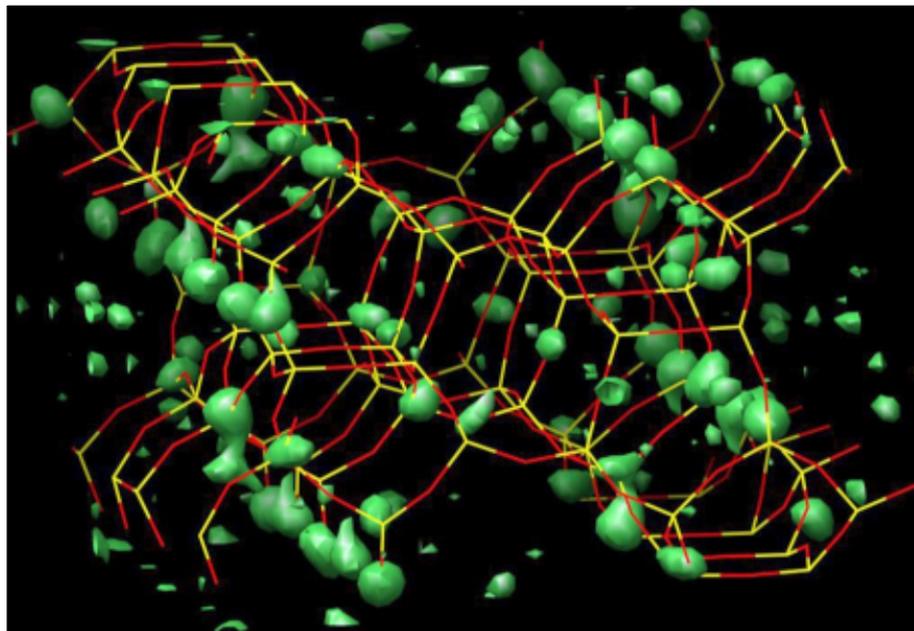
$$F_{\mathbf{h}}^{\text{new}} = F_{\mathbf{h}}^{\text{HM}} \sqrt{\frac{\sum \Gamma_k |F_{\mathbf{h}}|^2}{\sum \Gamma_k |F_{\mathbf{h}}^{\text{HM}}|^2}}$$

Original idea: Zhang & Main, Acta Cryst A46, 1990 – used to improve phases, not intensities

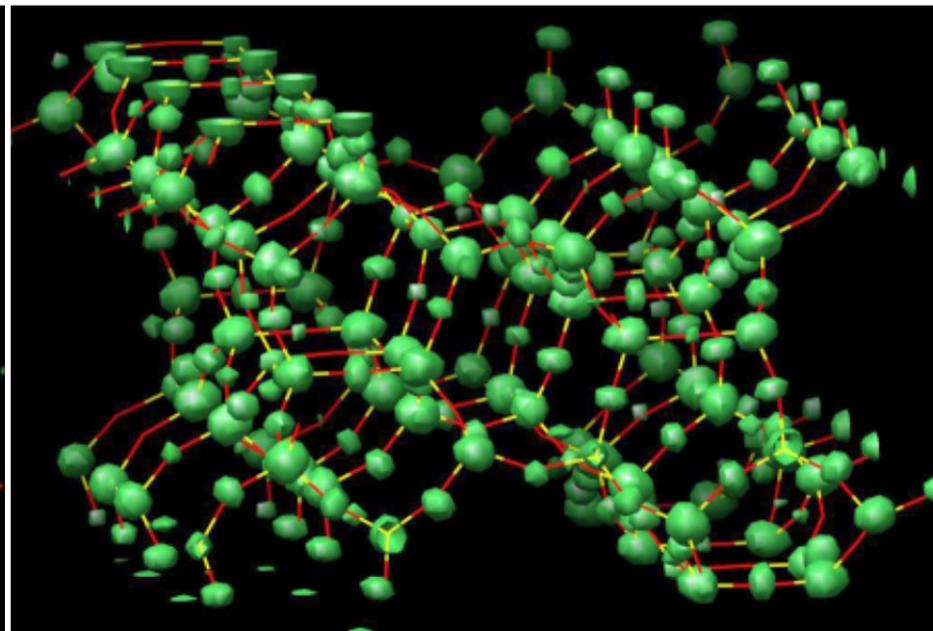


Charge flipping for powders

Zeolite ZSM-5, $\text{Si}_{96}\text{O}_{192}$

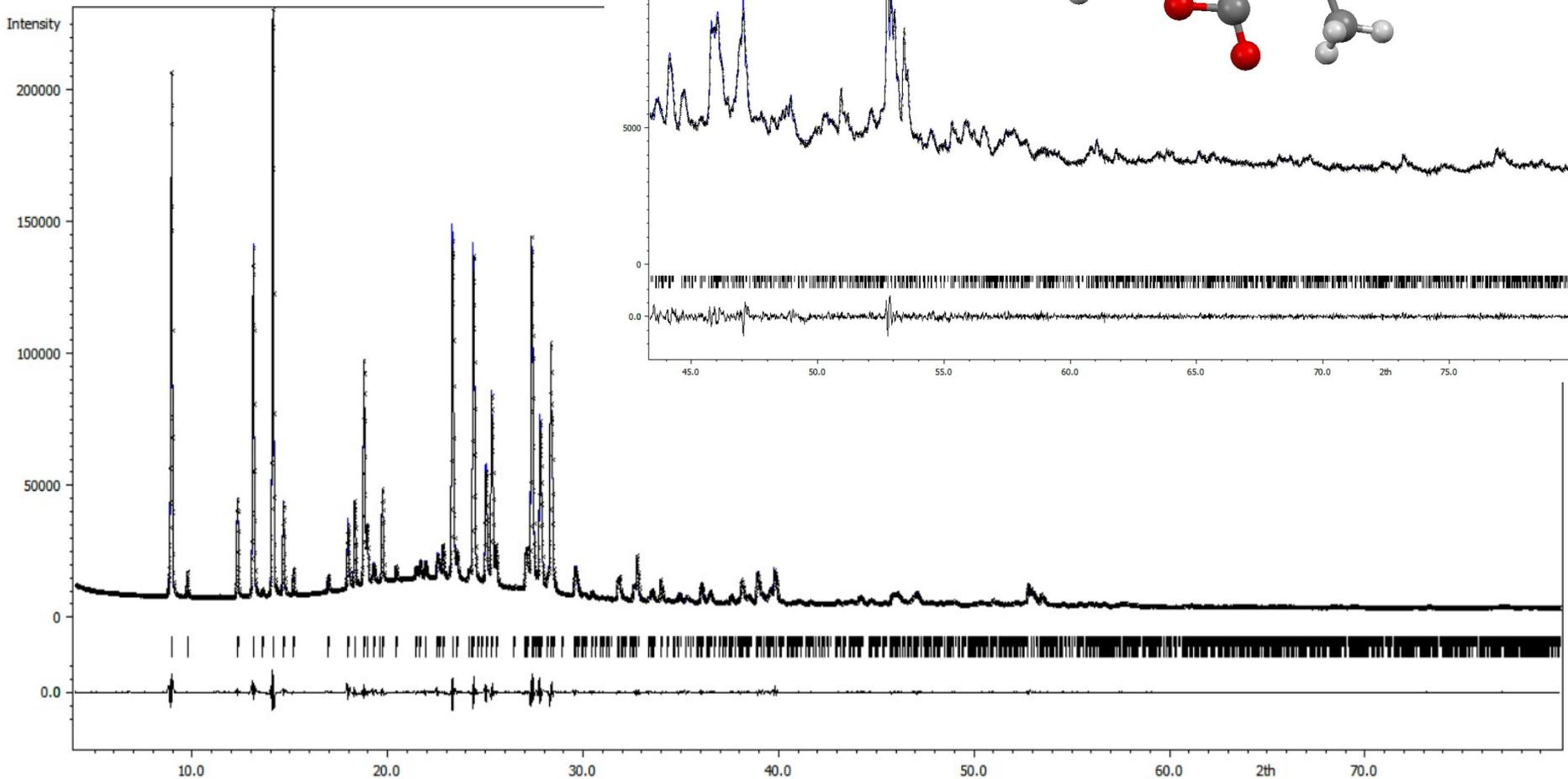
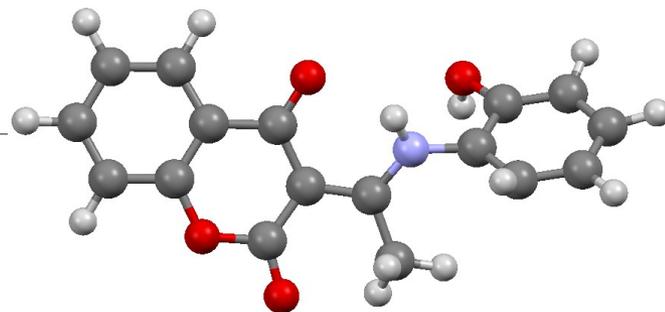
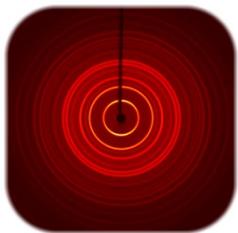


without histogram matching

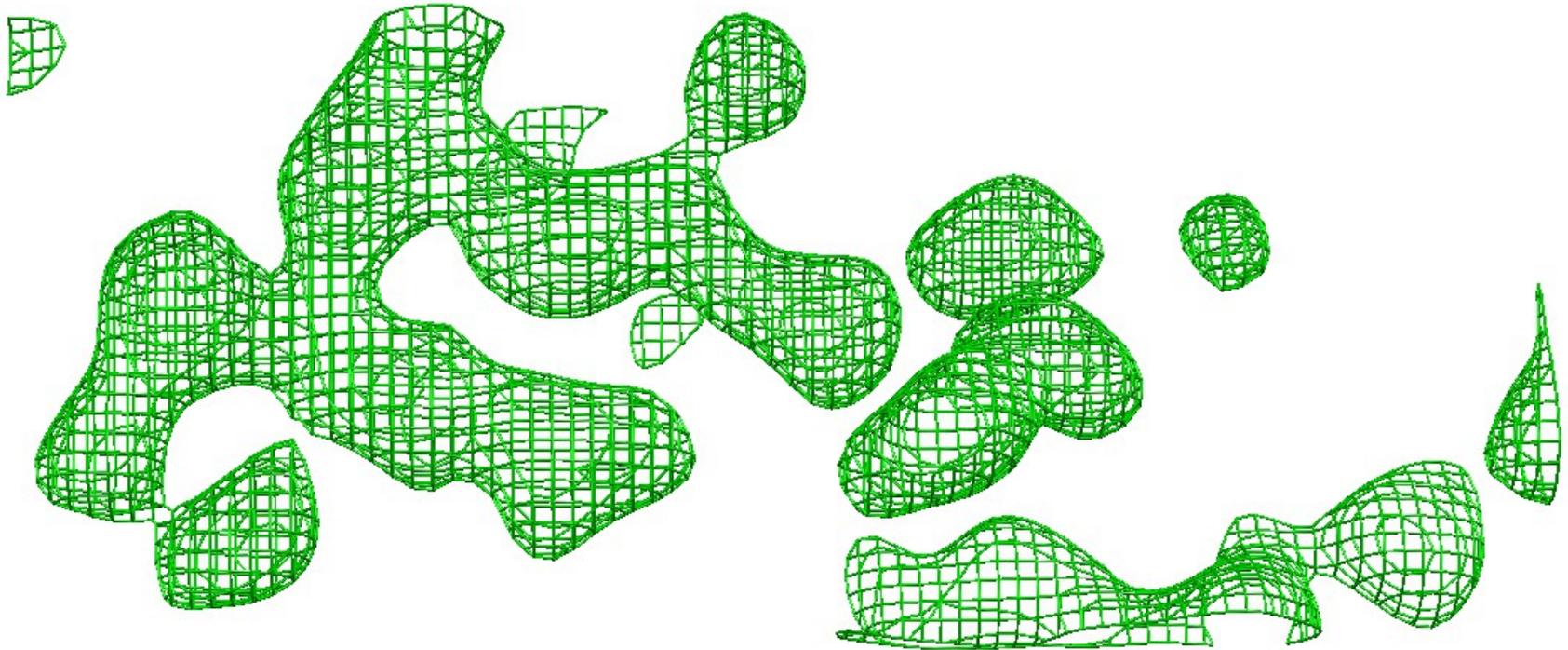
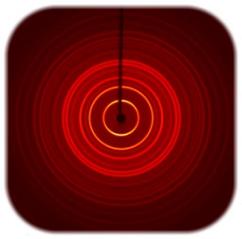


with histogram matching

Charge flipping for powders

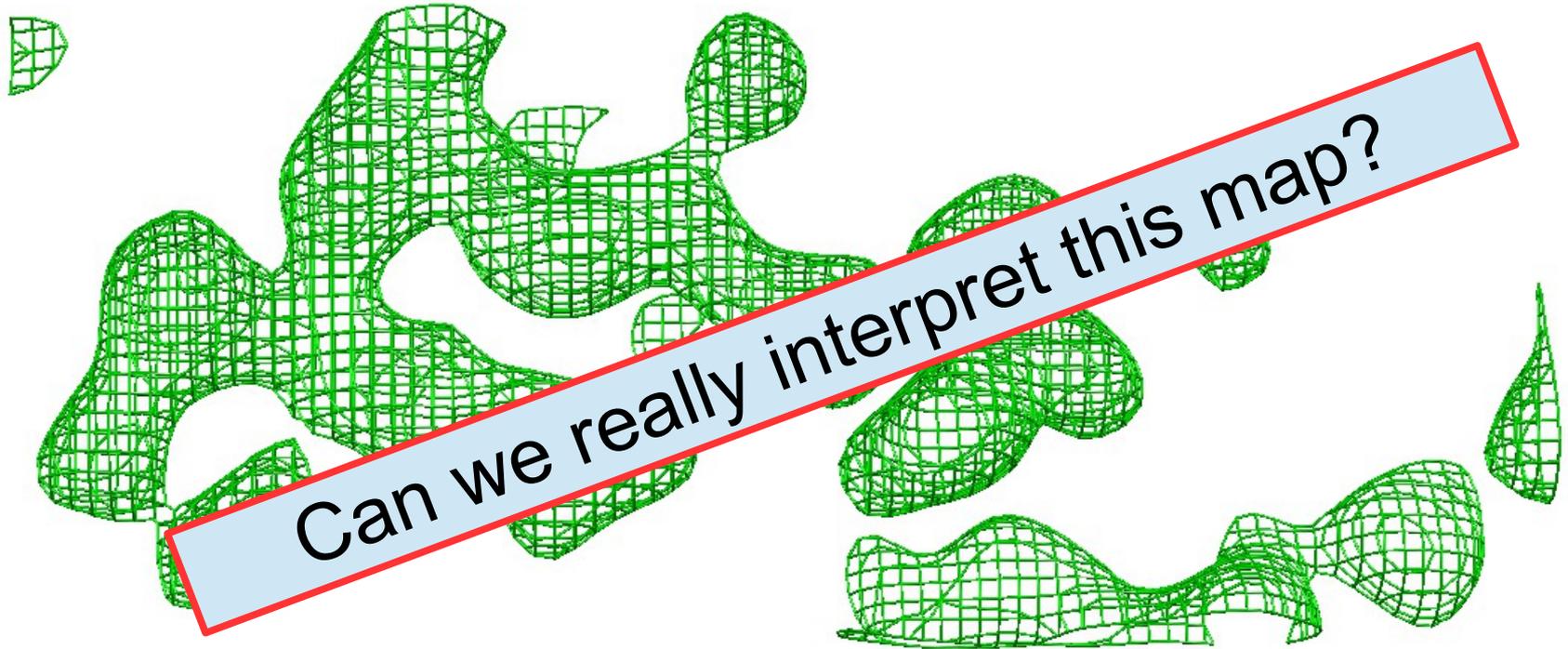


Charge flipping for powders



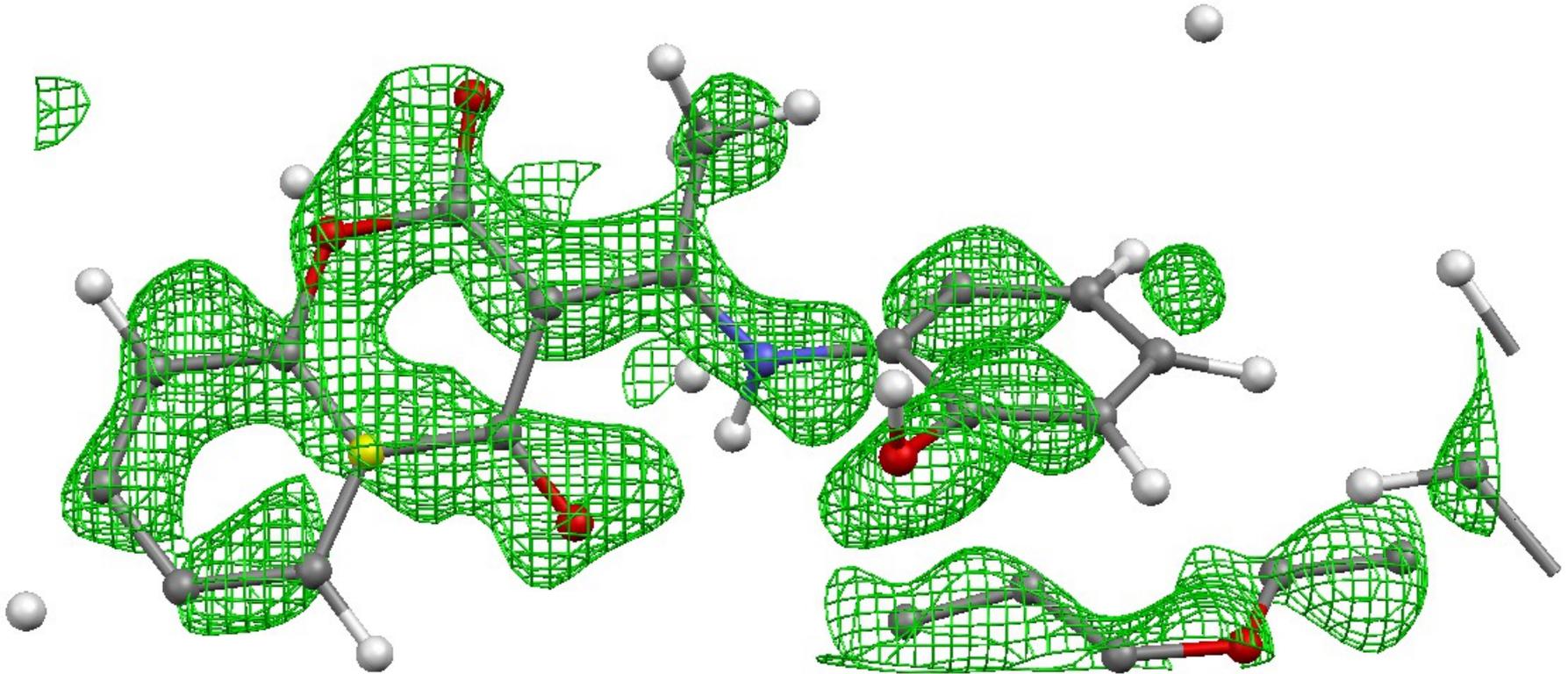


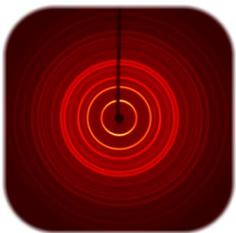
Charge flipping for powders



Can we really interpret this map?

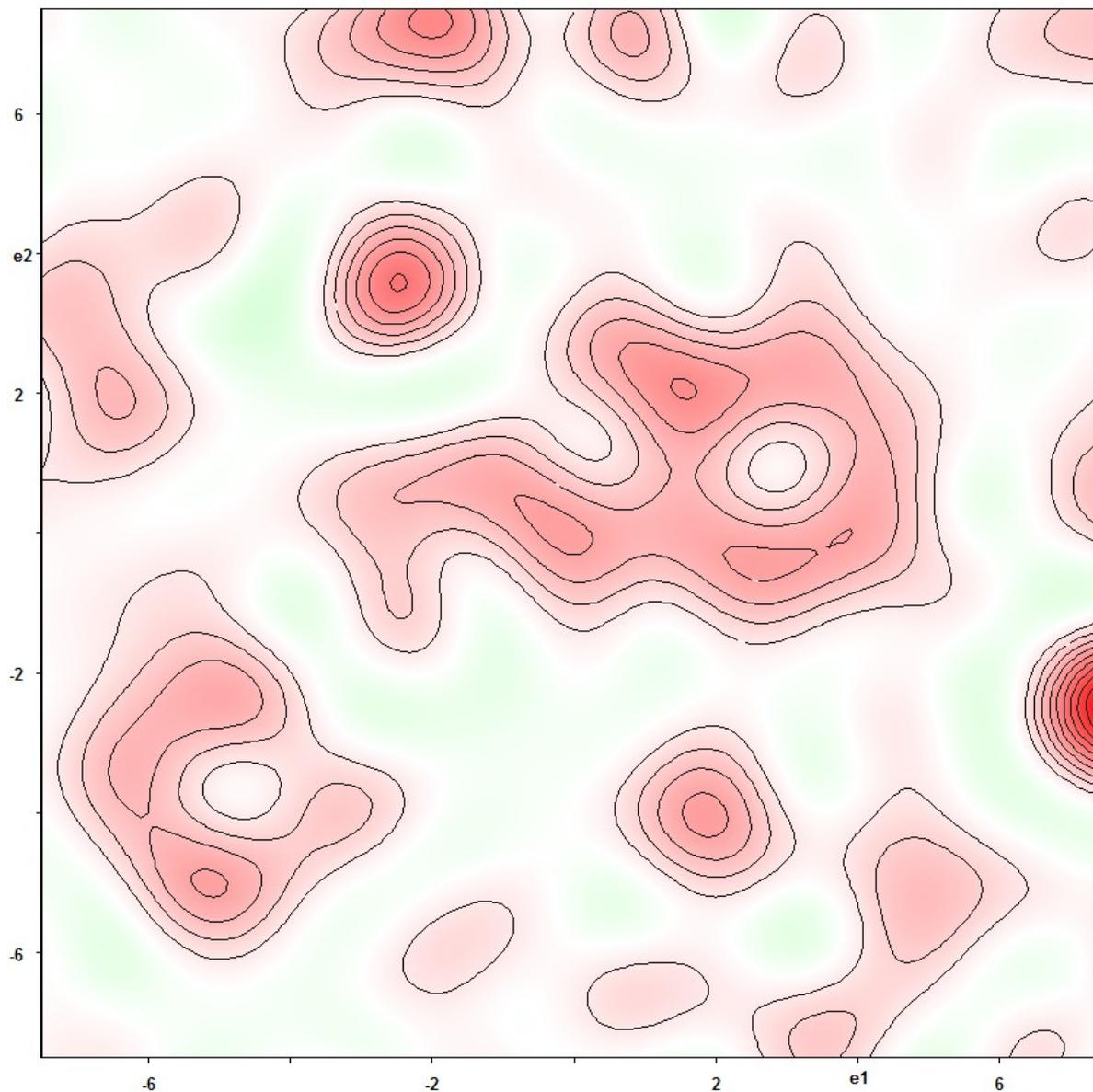
Charge flipping for powders





Rozlišení ELD

e3=0.000

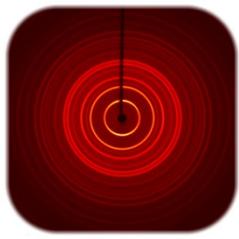


$$\sin \Theta / \lambda = 0.25$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\max = 45^\circ 2\Theta$$

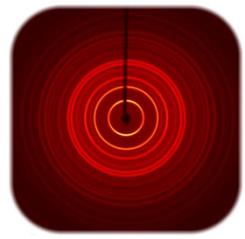
$$d_{\max} = 2.0 \text{ \AA}$$



Advantages and disadvantages

- + **Minimum assumptions** and approximations involved
- + No explicit use of **chemical composition** and form factors
- + No explicit use of **space group** symmetry
- + **Obtaining symmetry** with solution
- + Applicable to x-ray, neutron, electron diffraction

- **Requires atomic resolution** ($d < 1.3\text{\AA}$ for light atoms, much more relaxed for heavier atoms)
- **Peak overlap** should not be so high



End

Thank you !