Integrated intensities based on grain orientation distribution functions

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- and all project participants

Sixth Framework Programme

New and Emerging Science and Technology - Adventure

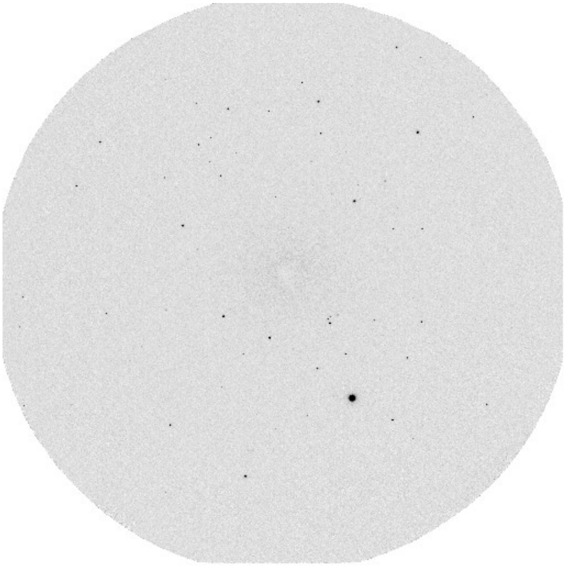
DANSCATT
X-RAYS & NEUTRONS

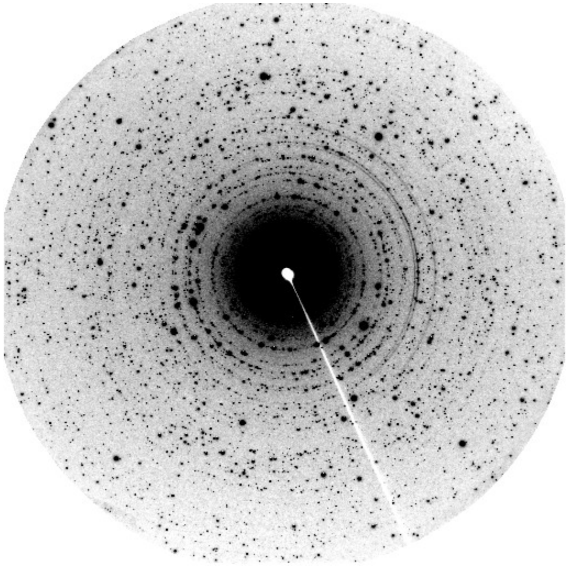
Peak overlap

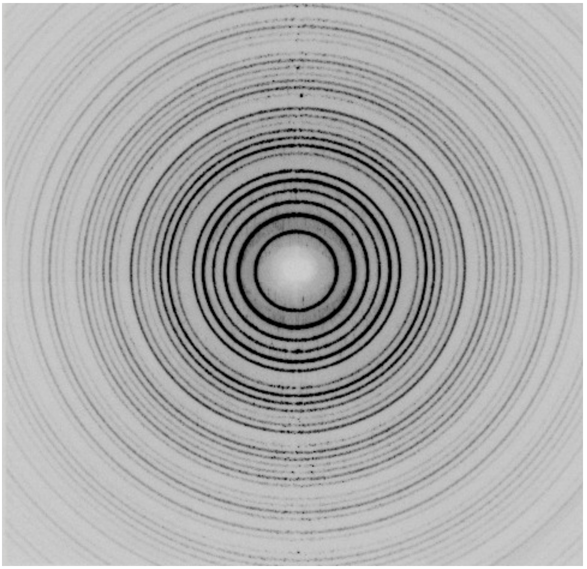
single crystal 

polycrystal

powder 





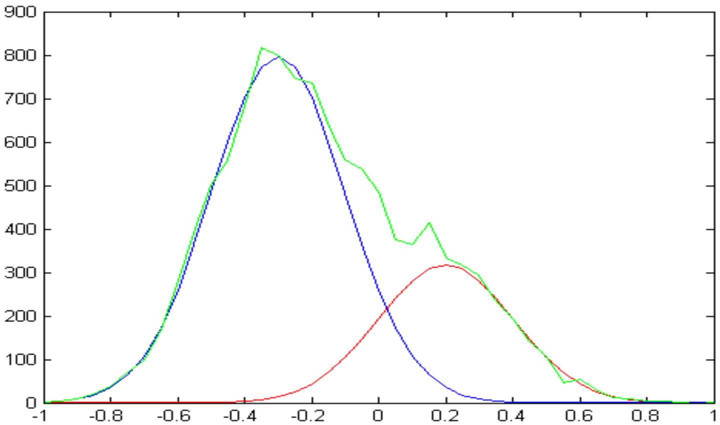


1 → ∞

No of irradiated grains

Intensity integration/separation

- Having known reflection profiles can help extracting the individual intensities
  - A simple fit can made of the intensities of the overlapping peak profiles
- Other integration programs do this, by “learning” the peak profile in different parts of detector space[1]
  - This is not a viable route with a high number of overlaps



[1] Kabsch, W. (1988) J. Appl. Cryst. **21**, 916.

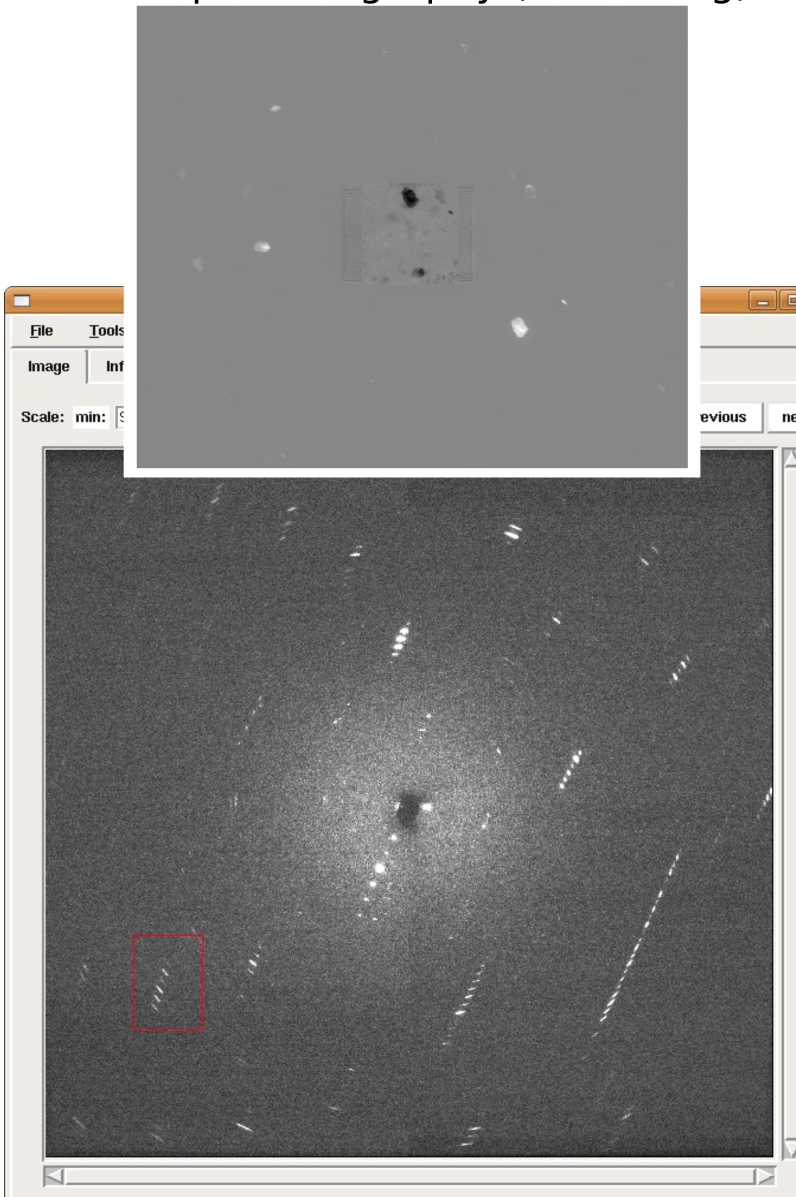
Peak profiles and shapes

A convolution of several factors

- <u>Some are related to the crystalline grains</u>
  - Morphology
  - Orientation distribution

- <u>Others are instrumental in nature</u>
  - beam divergence
  - beam profile
  - detector point spread
  - goniometer geometry

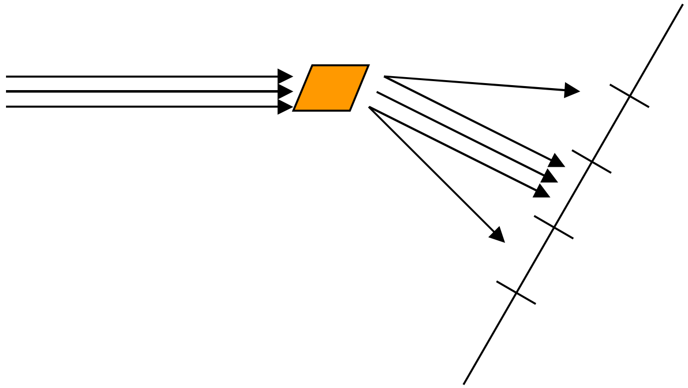
Topo-tomography (W. Ludwig)



Peak profiles and shapes

Grain properties

- Morphology
- Orientation distribution

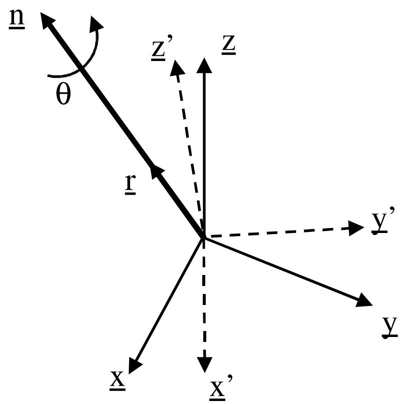


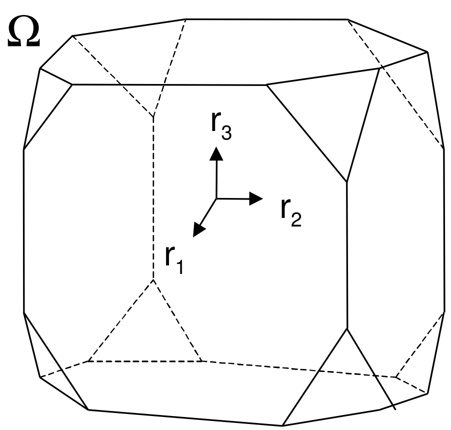
- If the grain size is *smaller* than the detector pixel size the crystal morphology does not contribute to the peak profile
- Hence the peak profile is determined mainly by the orientation spread of the grain
- The aim will then be calculate the grain orientation distribution from a few non-overlapping reflections.

Orientation Distribution Function (ODF)

The ODF will be discretized in Rodrigues space

$$\boldsymbol{r} = \tan(\theta/2)\,\boldsymbol{n}$$





Properties:

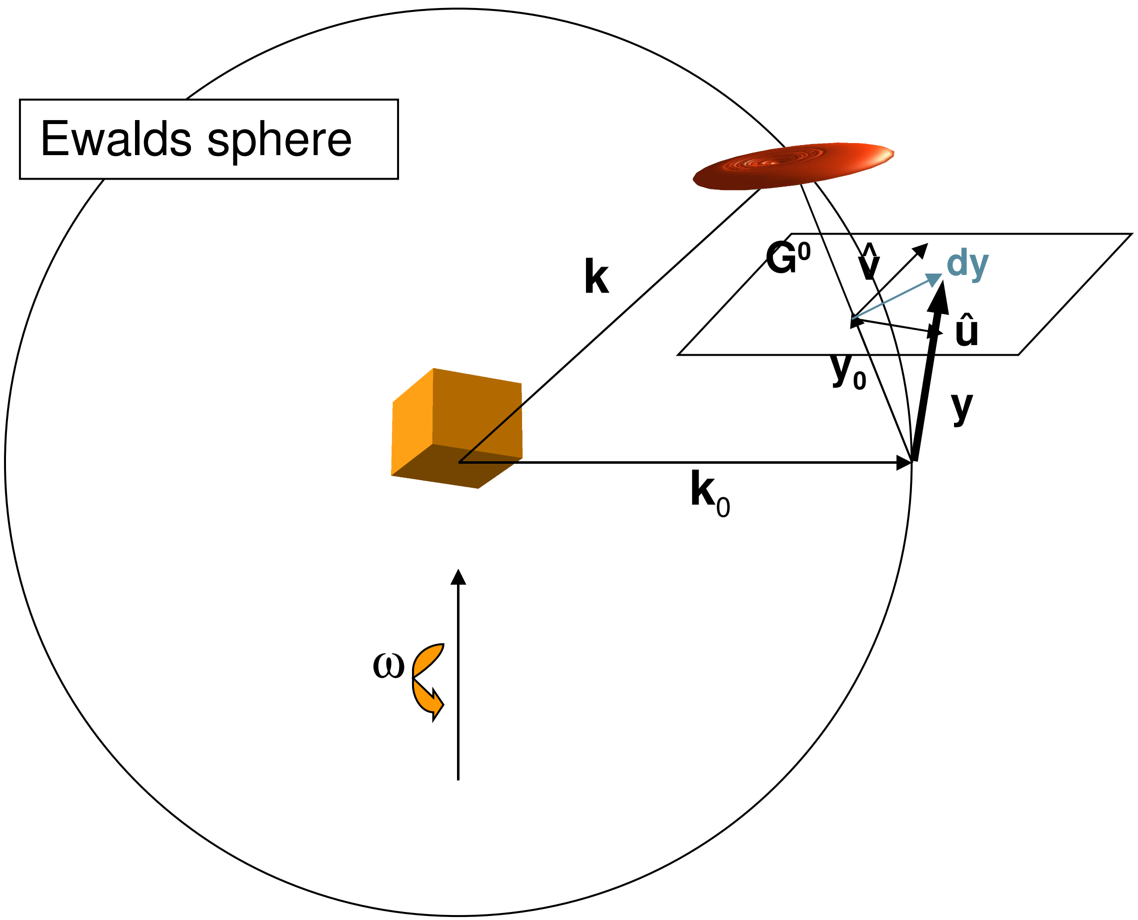
Perfect single-crystal => single point in Ω

Mosaic crystal => a distribution function in Ω

Pro: Euclidian at small angles ϕ

Con: For many space groups Ω extents to infinity

From data to the ODF



$y = y_0 + dy$,

dy is parameterized in

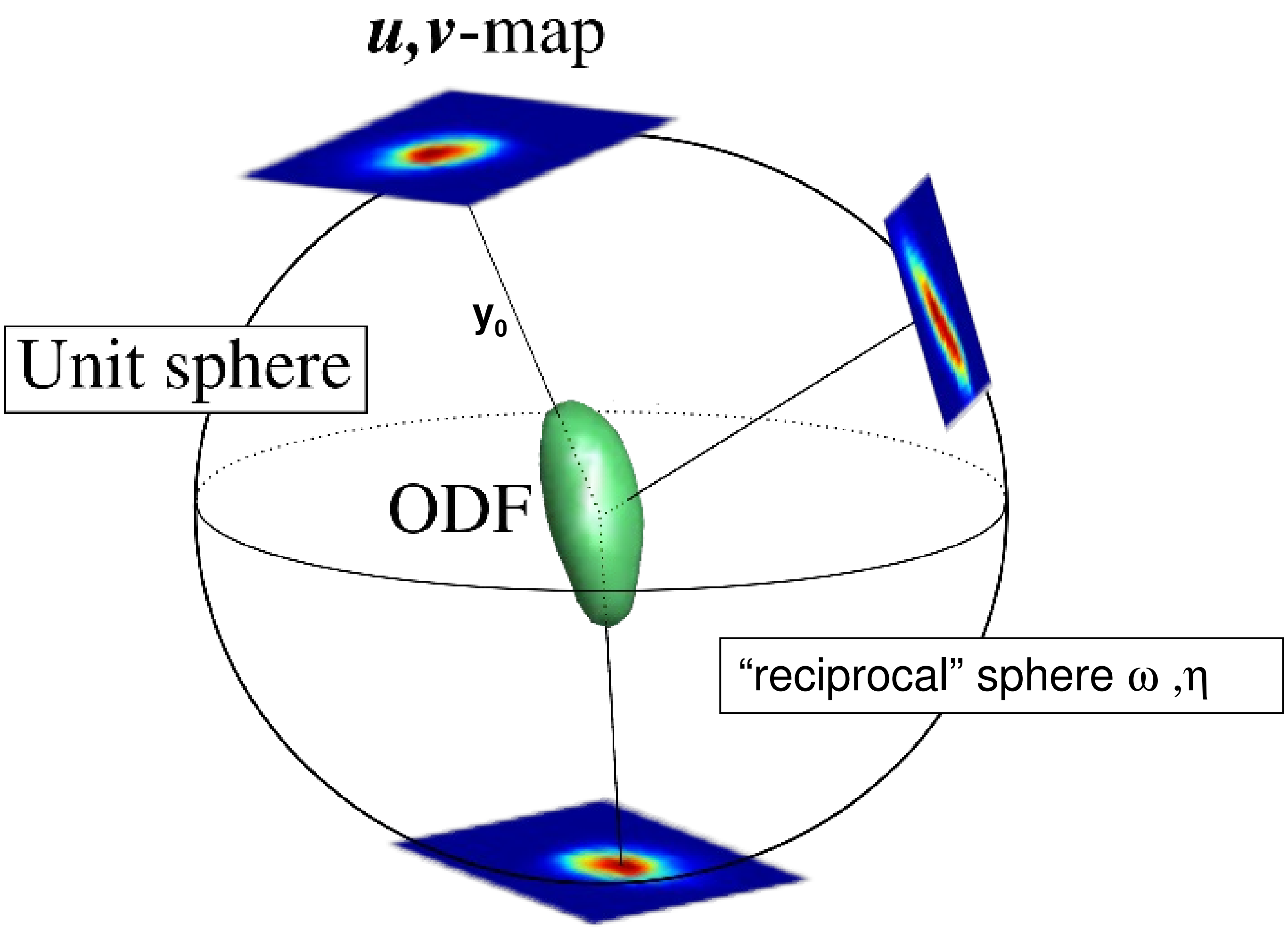
u,v coordinates

$$\hat{u} = \frac{\vec{y}_0 \times \hat{z}}{|\vec{y}_0 \times \hat{z}|}$$

$$\hat{v} = \hat{u} \times \vec{y}_0$$

Poulsen, H.F. (2005) MST, **21**, 1397

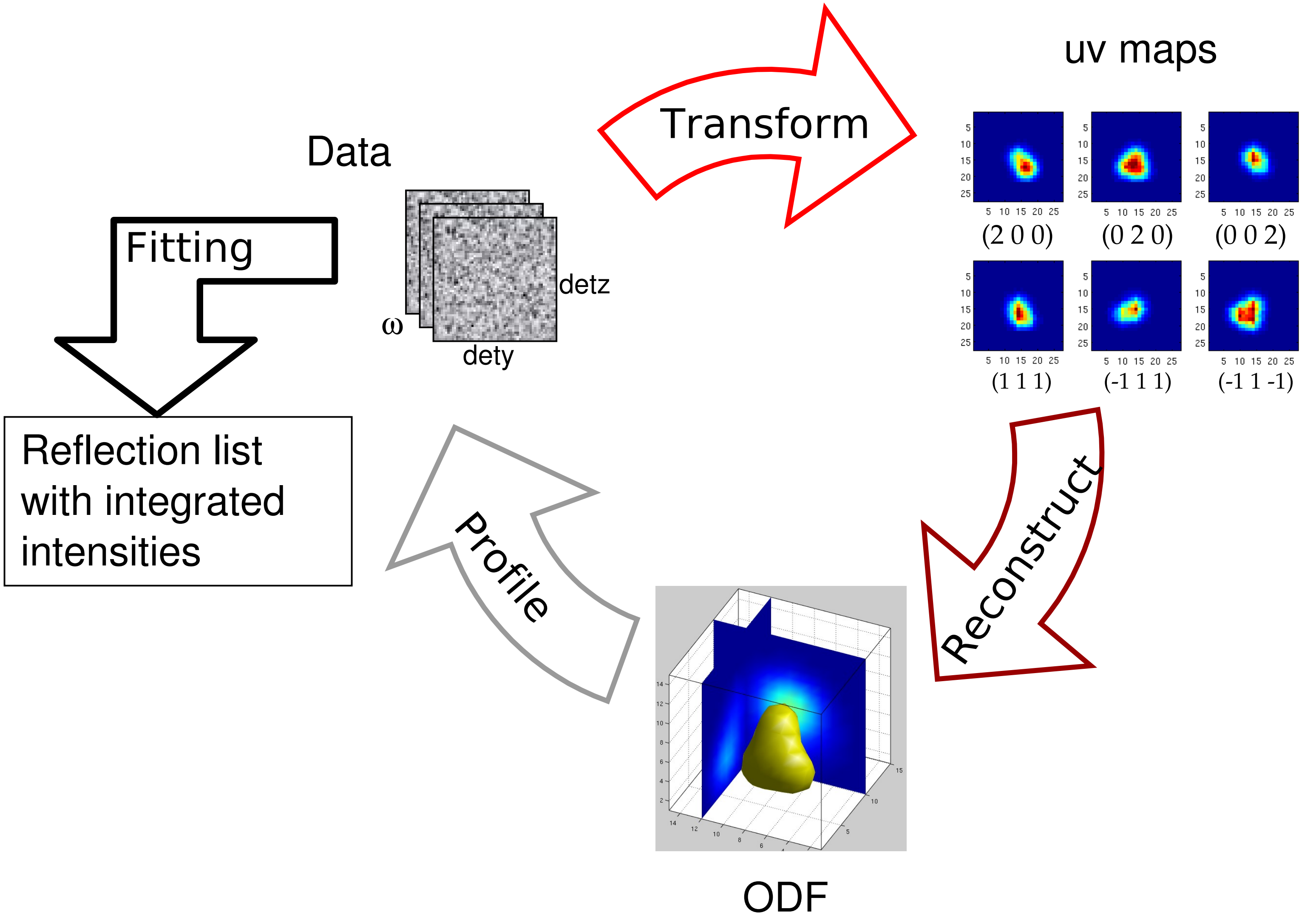
From data to the ODF



Relation between ODF and "data" is: $\mathbf{dy} = 2(\mathbf{r} \times \mathbf{y}_0)$

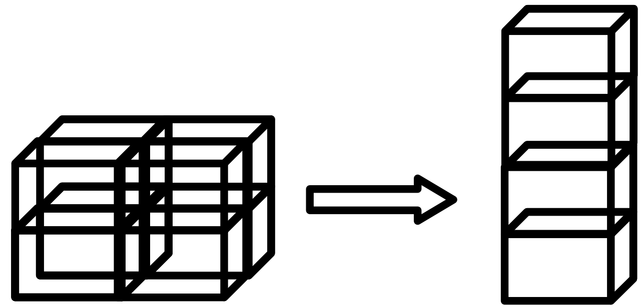
Poulsen, H.F. (2005) MST, **21**, 1397

Data integration route



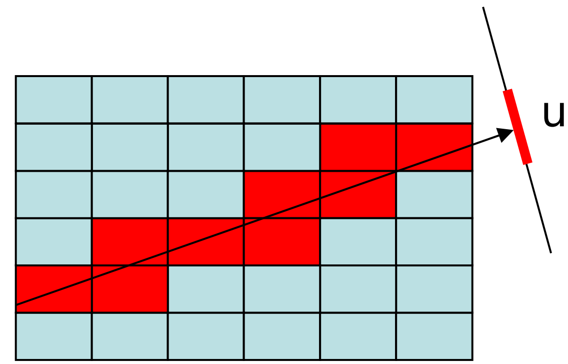
Projection method

- ODF voxels can be listed in 1D array, **x**



- The transformed intensities in the uv map is listed as 1D array, **b**
- **A** describes the geometrical relation between *uv-maps* (**b**) and ODF (**x**)

$$\mathbf{Ax = b}$$



ODF voxel grid (x)

- Fast voxel traversal algorithm (3D-DDA) – Amanatides in *Eurographics '87,*(Elsevier)

Solve: Ax = b

We want to solve **Ax = b,** but **A** is ill-conditioned and **b** is noisy, hence

$$\mathbf{Ax} = \mathbf{Ax}_{exact} + \mathbf{e}, \qquad \mathbf{e} \text{ being noise}$$

It follows that

$$\mathbf{x}_{naive} = \mathbf{A}^{-1}\mathbf{b} = \mathbf{x}_{exact} + \mathbf{A}^{-1}\mathbf{e}\ , \quad \text{where} \quad ||\ \mathbf{A}^{-1}\mathbf{e}|| >> |\mathbf{x}_{exact}|$$

Not very useful results will be obtained

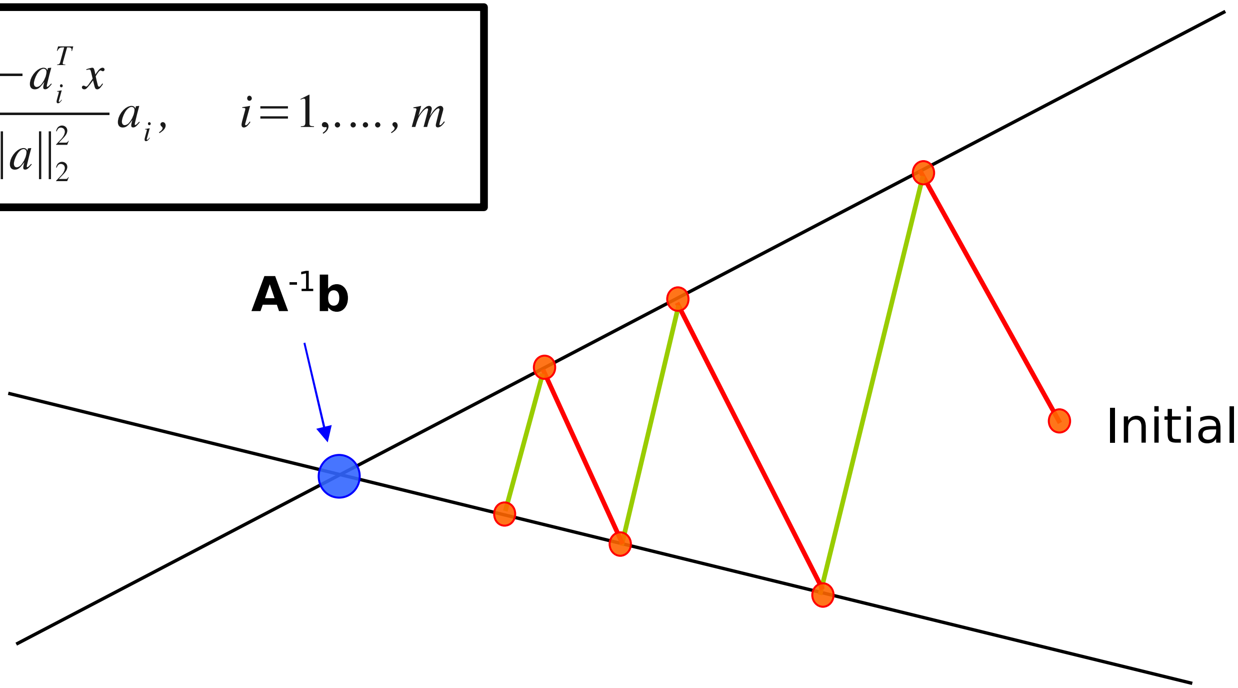
Aim: Find a solution for which $||Ax - b||$ is small (good fit) and $\mathbf{x} \sim \mathbf{x}_{exact}$

- To be solved by iterative methods as ART, CGLS etc.

Algebraic Reconstruction Technique

One approach to compute an approximate soulution to Ax = b
ART does (by projections on hyperplanes):

$$x <- x - \frac{b_i - a_i^T x}{\|a\|_2^2} a_i, \qquad i = 1, \ldots, m$$



During the initial iterations the convergence is fast
Later the convergence slows down
Good method if only few iterations can be afforded

CGLS algorithm

Krylov subspace $\mathcal{K}_k \equiv \text{span}\{A^T b, A^T A\, A^T b, \ldots, (A^T A)^{k-1} A^T b\}$, that is:

$$x^{(k)} = \text{argmin}_x \|A\,x - b\|_2 \quad \text{subject to} \quad x \in \mathcal{K}_k.$$

$x^{(0)} = 0,\ r^{(0)} = b,\ d^{(0)} = A^T r^{(0)}$

for $k = 1, 2, \ldots$

$\bar{\alpha}_k = \|A^T r^{(k-1)}\|_2^2 / \|A\,d^{(k-1)}\|_2^2$

$x^{(k)} = x^{(k-1)} + \bar{\alpha}_k\, d^{(k-1)}$

$r^{(k)} = r^{(k-1)} - \bar{\alpha}_k\, A\, d^{(k-1)}$

$\bar{\beta}_k = \|A^T r^{(k)}\|_2^2 / \|A^T r^{(k-1)}\|_2^2$

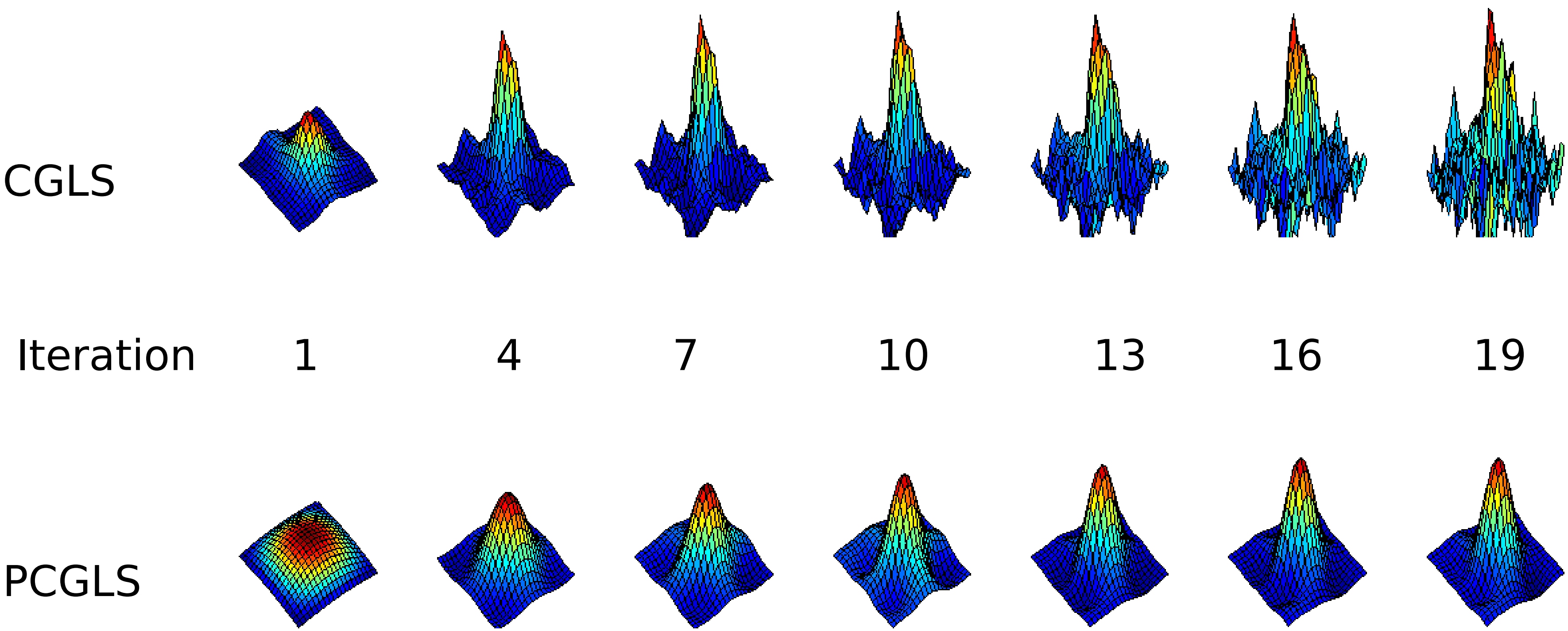
$d^{(k)} = A^T r^{(k)} + \bar{\beta}_k\, d^{(k-1)}$

end

preconditioned reconstructions

Since the border pixels generally are transversed by less rays than more central this can lead to ripples at the border

By “constraining” the solution to go towards zero at the border these types of effects can be suppressed



Preconditioning

- Further smoothing and assert zero boundary conditions
- Can be done by introducing a derivative operator **D**

Variable transformation of Ax=b

$$\xi = Dx$$

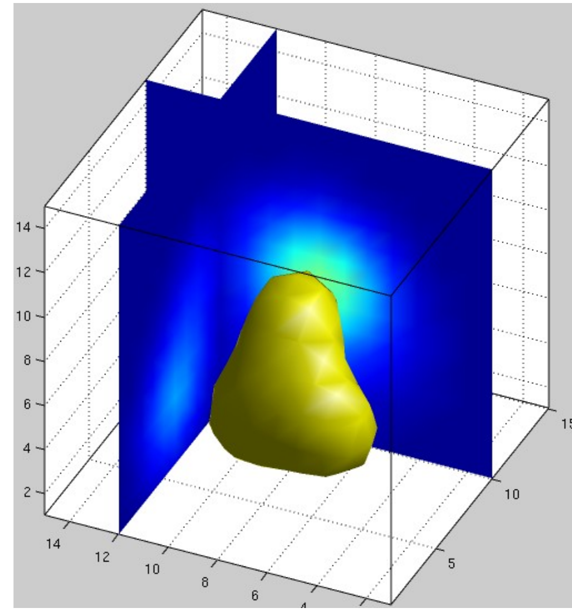
minimize

$$\min_x \| (AD^{-1})\xi - b \|_2$$

back transform

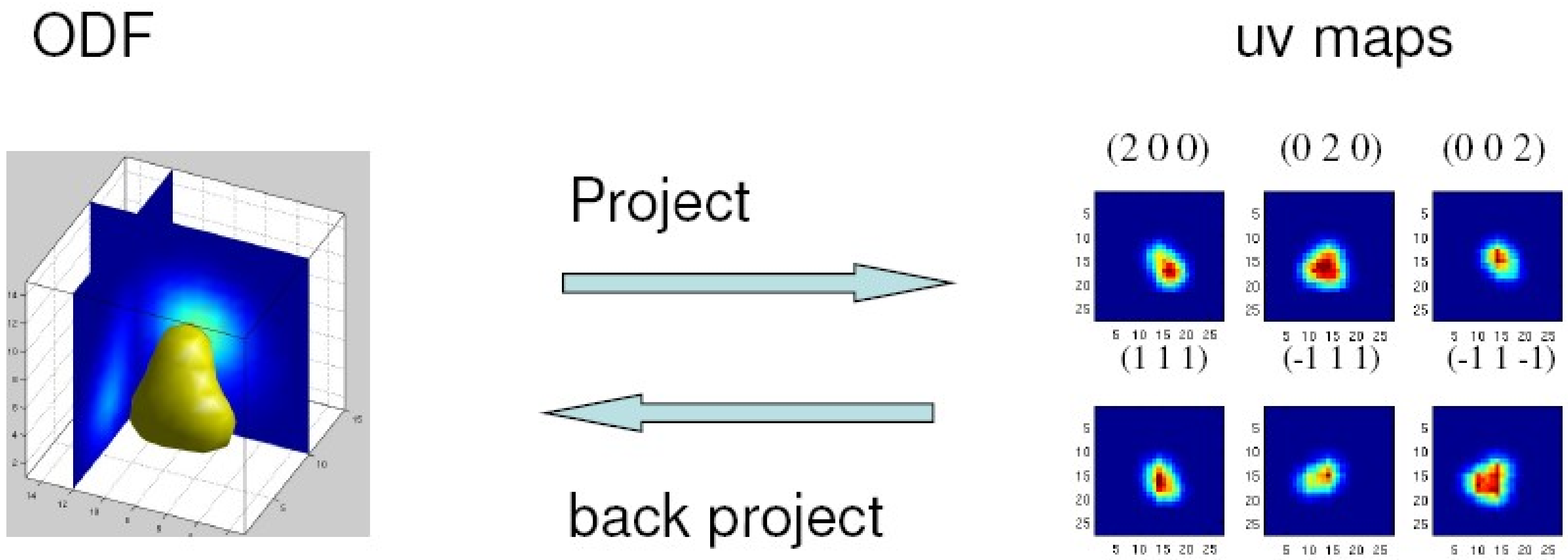
$$x = D^{-1}\xi$$

Investigate quality of reconstruction methods by simulation

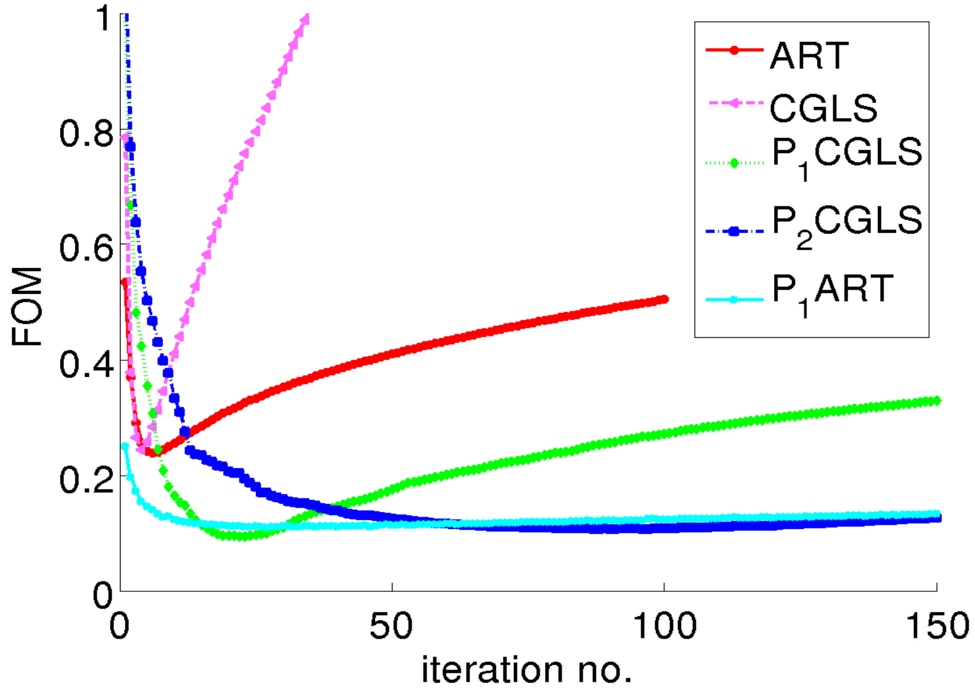


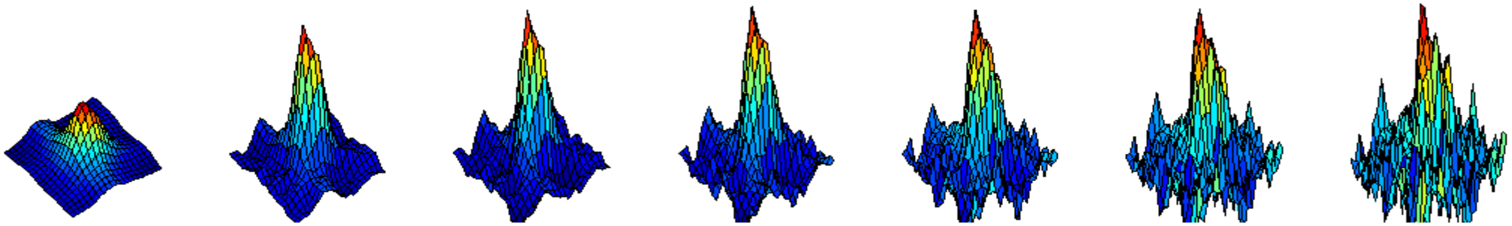
- 5 reconstruction methods
  - ART
  - CGLS
  - P_1ART
  - P_1CGLS
  - P_2CGLS
- Alu grain ODF simulated by 3 Gaussians
- uv maps calculated out $\sin\theta / \lambda = 0.45$ Å^{-1} (29 reflections)
- Added Poissonian noise (6 SNR levels)
- 3 to 18 reflections used in reconstruction – randomly chosen
- All calculations repeated 10 times

Simulations with ”inverse crime”



Error histories of the iterative methods





Iteration 1 4 7 10 13 16 19

Stopping Criterion:

Stop the iterations when $x^{(k)}$ captures the desired information

How do we measure this?

- No way to measure if $x^{(k)}$ is close to $\mathbf{x}_{\text{exact}}$
- Fit to noise level: $||\mathbf{A}\ \ \mathbf{x}_{\text{exact}}\ ||_2 \sim ||\mathbf{e}||_2$
- Information criterion: residual behaves statistically like **e**

Fit to noise level can sensitive to the estimate of $||\mathbf{e}||_2$

If **e** is white noise, then the *normalized cumulative periodogram* can be used to measure the ”white-ness” of the residual.

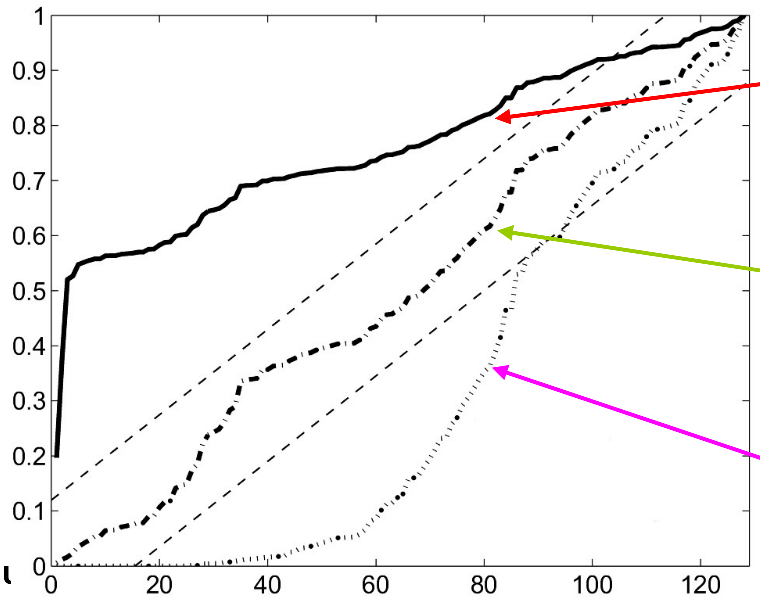
NCP = Normalized Cum. Periodogram

The NCP measures the frequency content in a signal s.
Let the power spectrum of s (of length *n*) be given by p = |dft(s)|^2
then the NCP is a plot of the vector c with elements

$$c_l = \frac{\sum_{i-1}^{l} p_i}{\sum_{i-1}^{q} p_i}, \quad i = 1, 2, \ldots\ldots, q, \quad q = [n/2]$$

The closer c is to a straight line, the ”whiter” the signal s

Examples with *n* = 256 and *q* = 128



Dominated by low frequencies

Quite white

Dominated by high frequencies

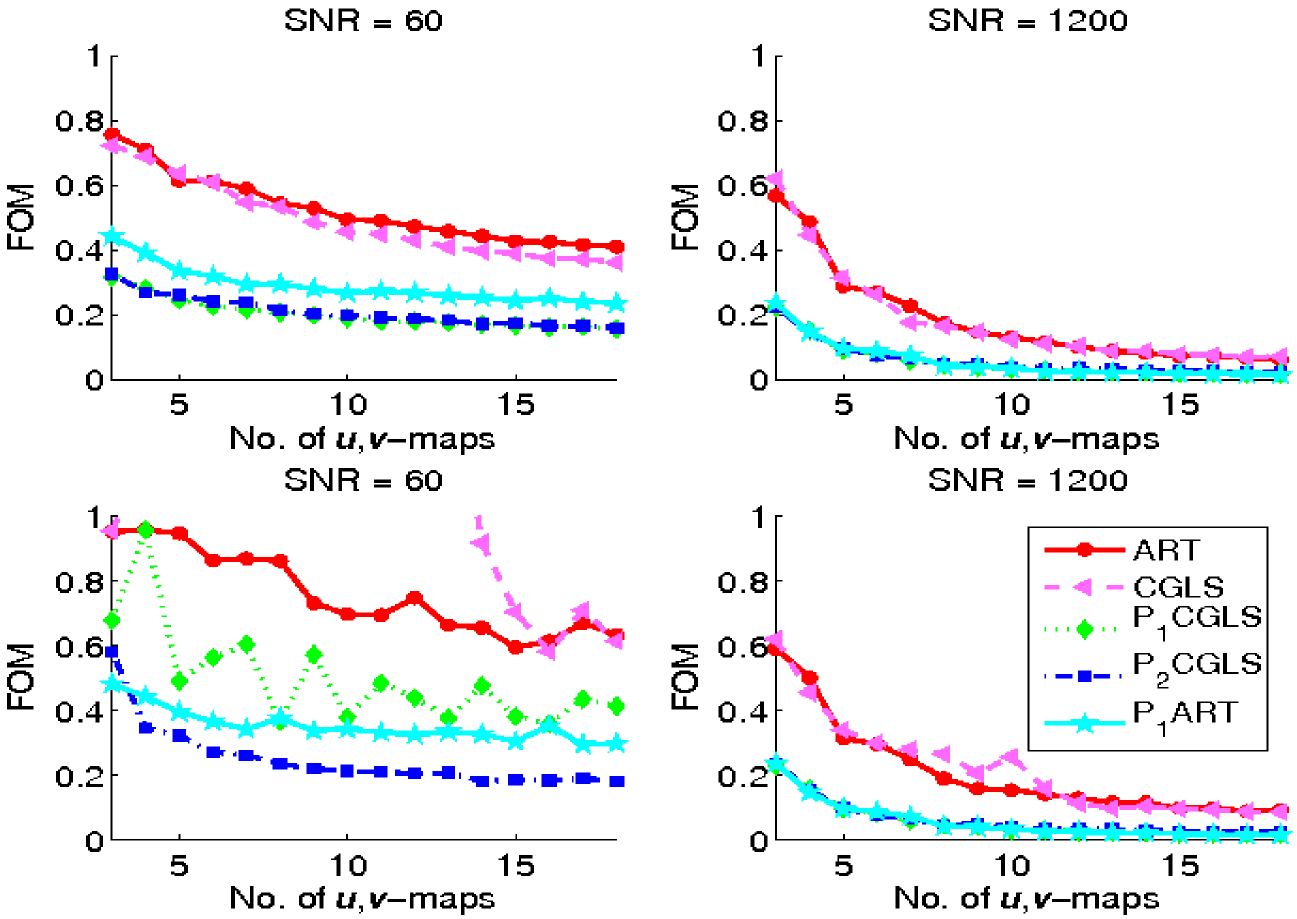
Use of the NCP stopping criteria

- For each *uv*-map ($i = 1,2,3,....,N_{uv}$)
  - For each iteration step *k*
    - Compute the NCP
  - Return the iteration step giving the optimal NCP
- Choose the iteration step *k* as

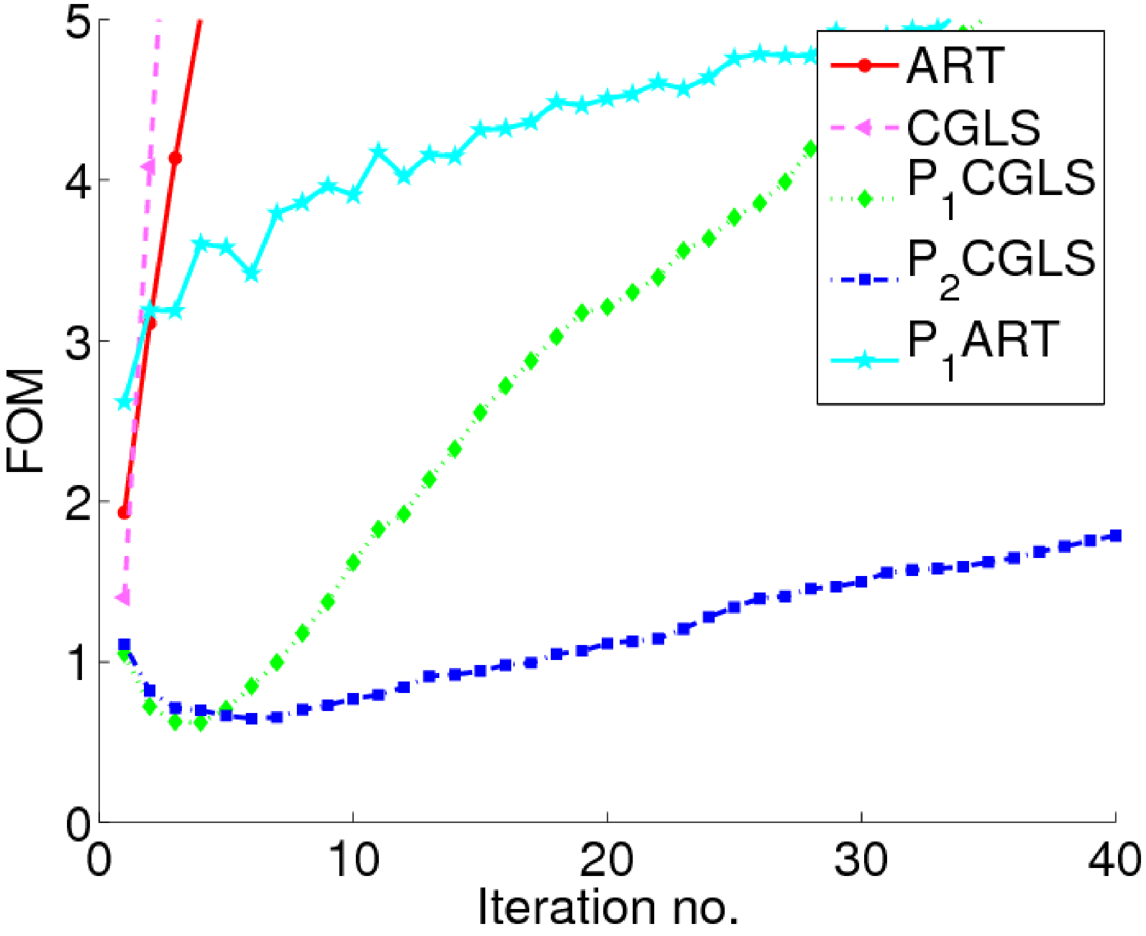
$$k_{opt} = \text{median}\,(k_1, k_2, k_3, ..., k_{Nuv})$$

The median was choosen to minize the influence of outlier *uv*-maps

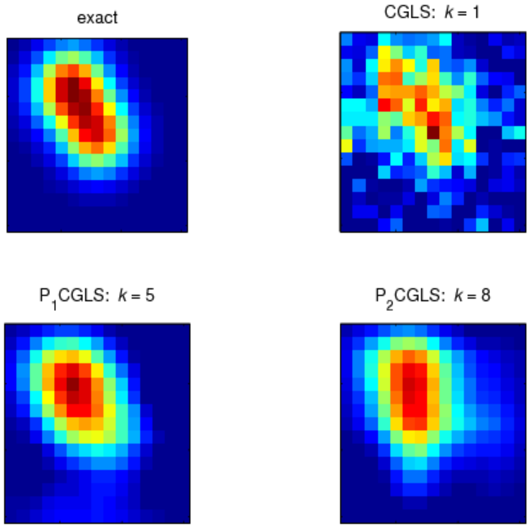
Quality of reconstructed ODF as a func. of projections



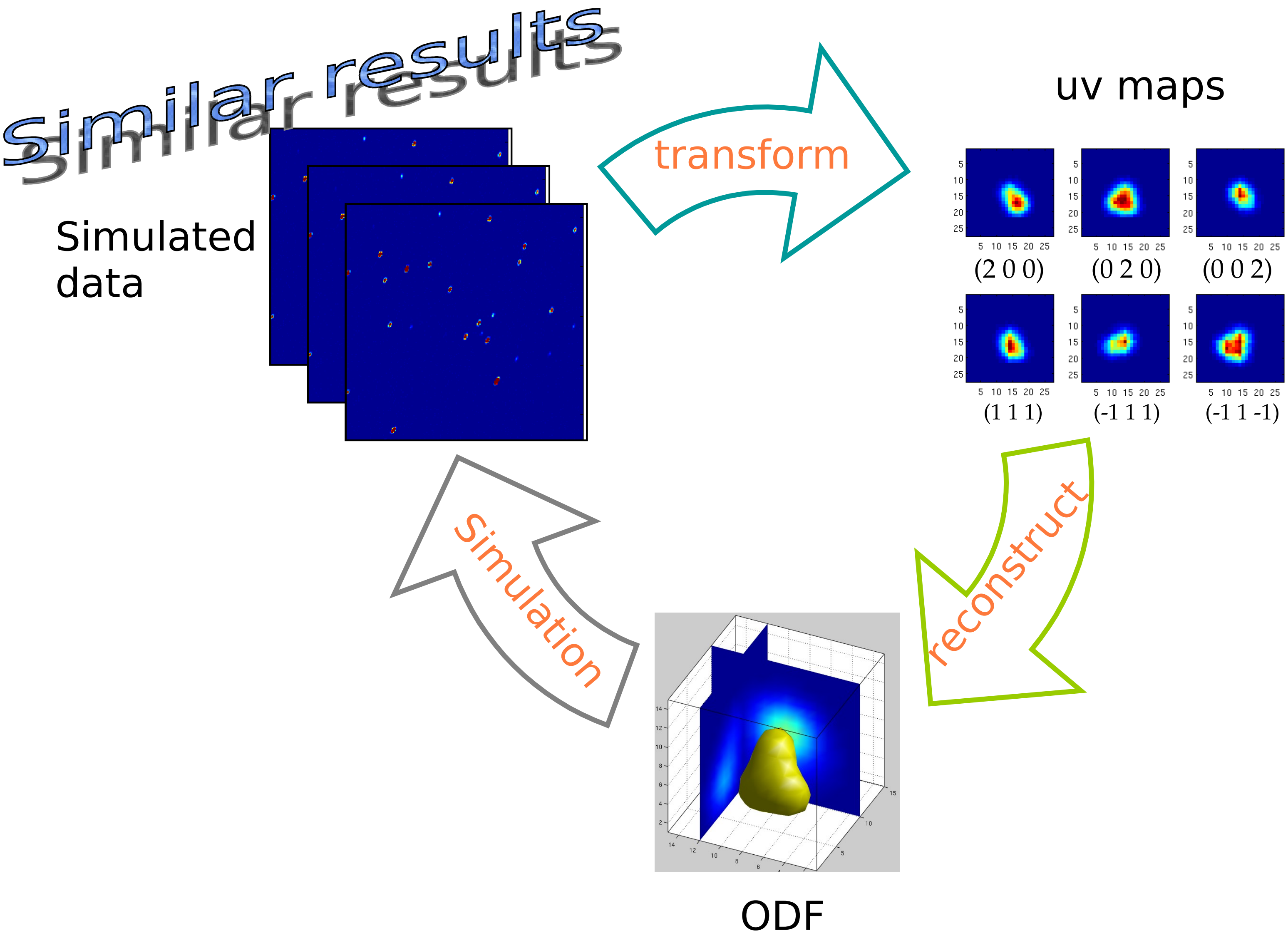
Extremely noisy data



Slice through ODF

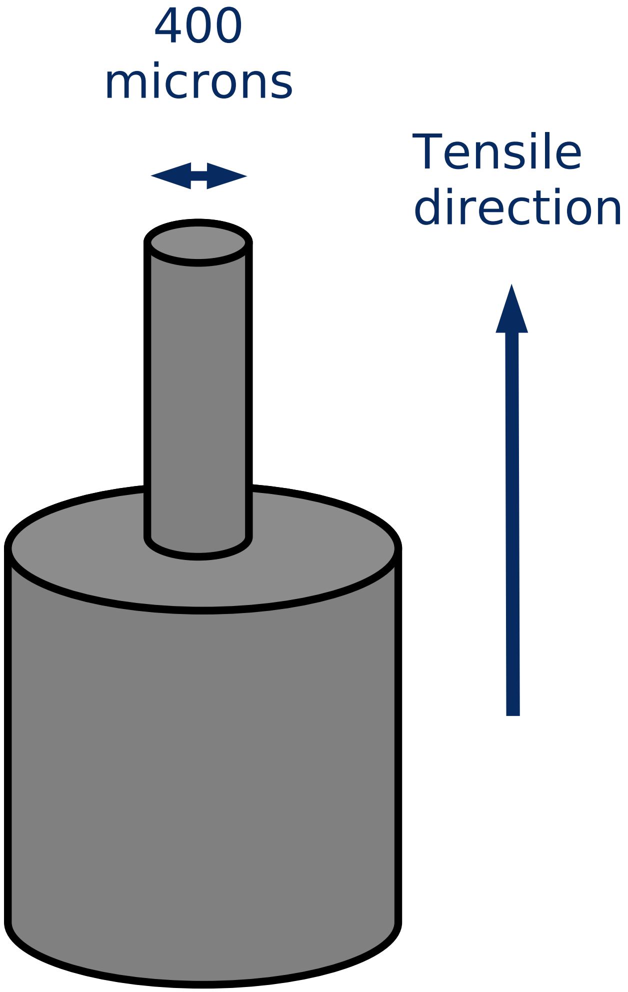


Simulations without ”inverse crime”

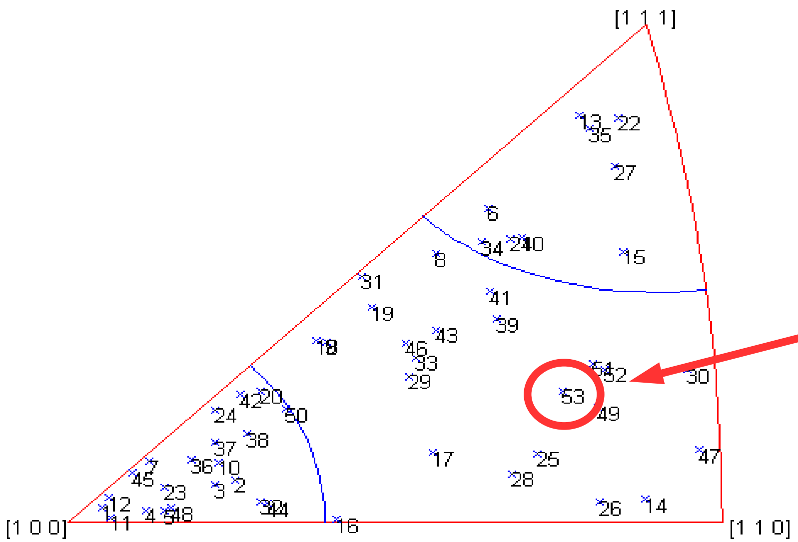


Strained Al samples

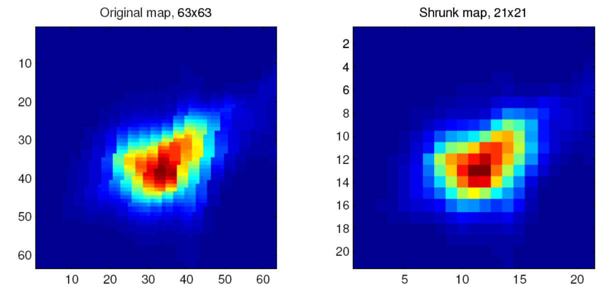
- For a test sample we have used pre-strained Al 1050 samples
- Mean grain size 75 microns
- Strained to 2, 4, **<u>6</u>**, 8 and 10 %
- Beam energy 25.514 keV
- Beam vertical 100 microns

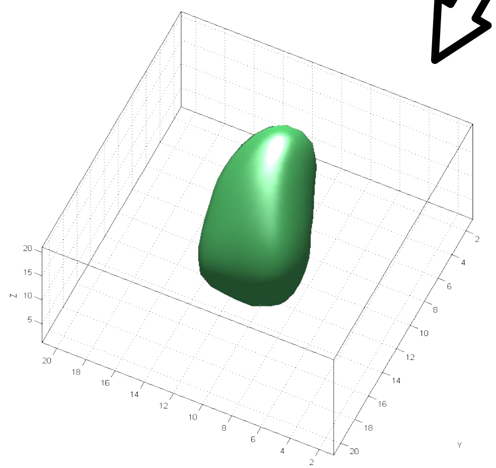


Al sample - strain 6%



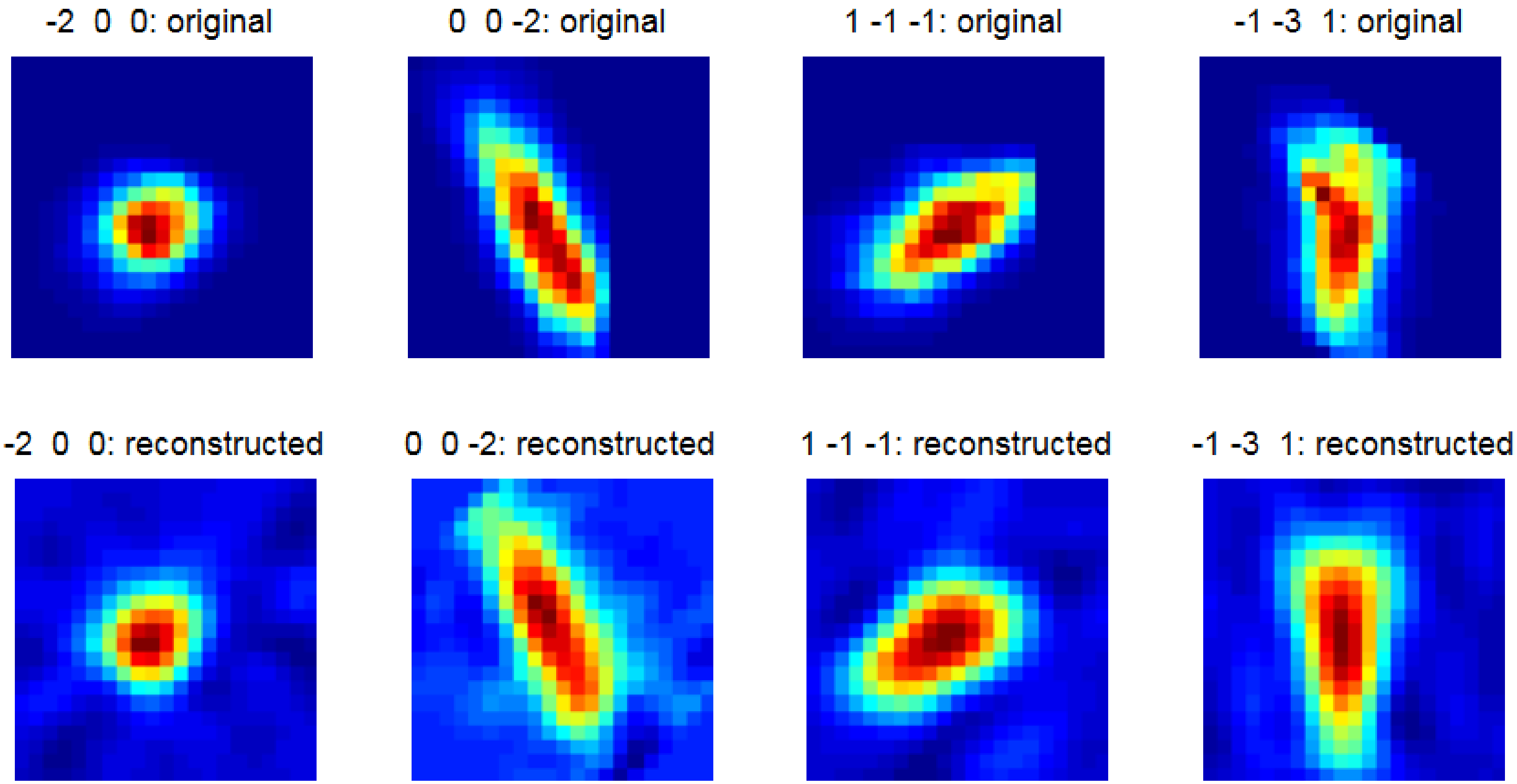
uv-map



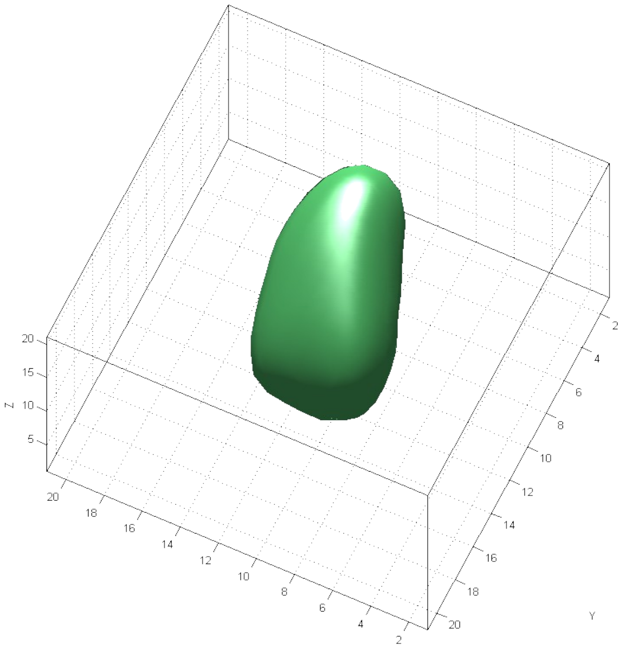


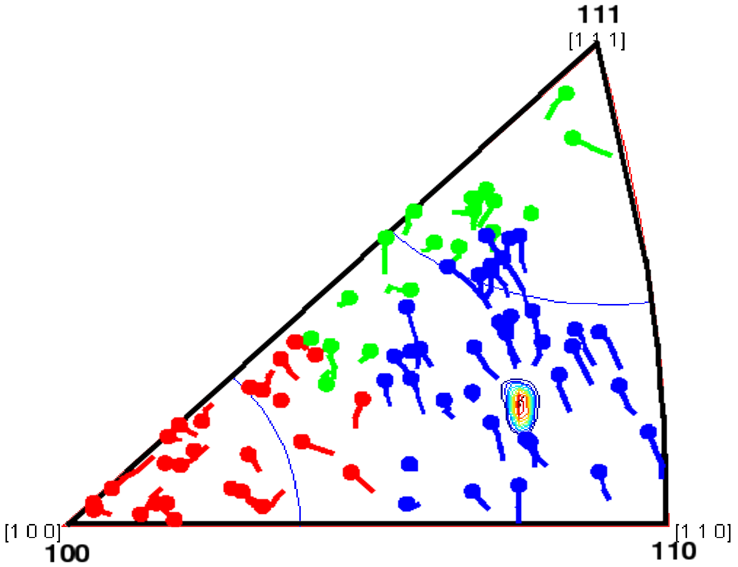
ODF

Compare experimental and reconstructed maps



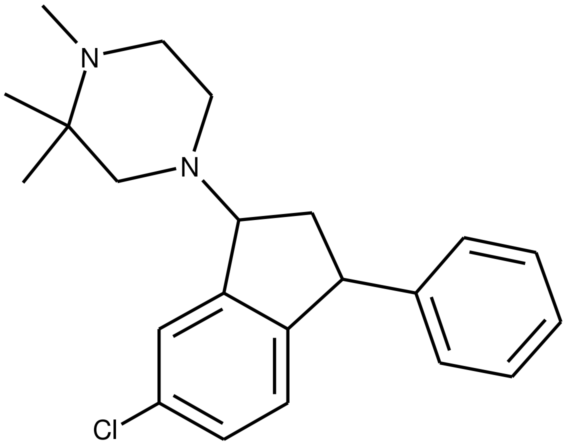
Al sample - strain 6%





Winther et al. Acta Mater. (2004), **51**, 2863

Test on an organic compound



HLU1 kindly provided by H. Lundbeck A/S

Narrow (a few microns in height) and wide beam (>1 mm) to optimize flux for small crystals

High energy 46.837 keV (λ = 0.2647 Å)

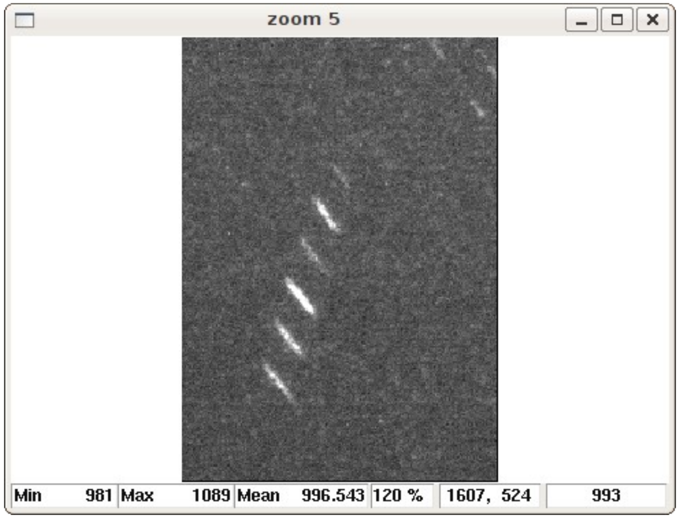
Frelon4m detector (2k by 2k)

Mounted samples on cryoloops

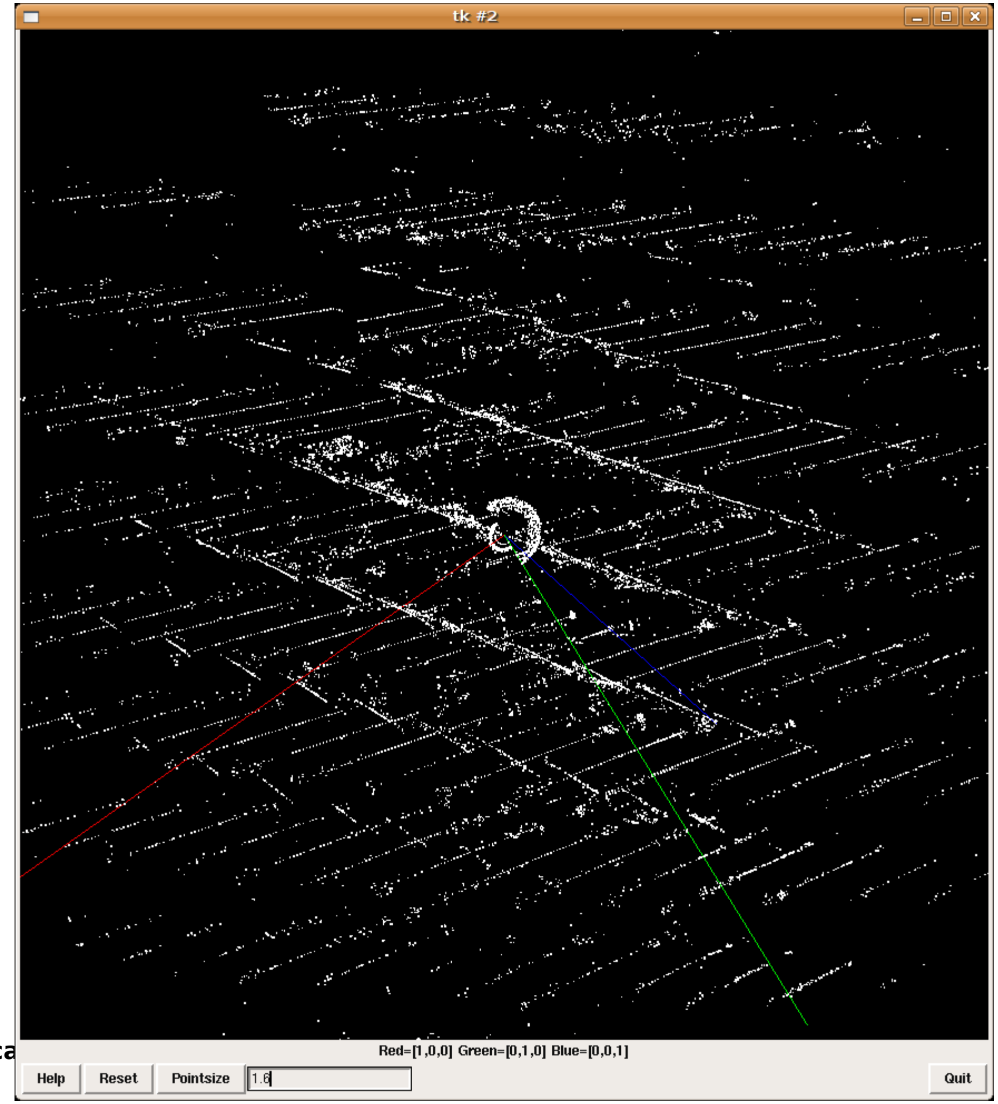
Temperature ~122 K

Omega rotation 180 degress in 0.3 deg. steps

Orientation spread



HLU1 - Not quite single crystal



Indexing

First grain indexed

(fft_index.py, J. Wright)

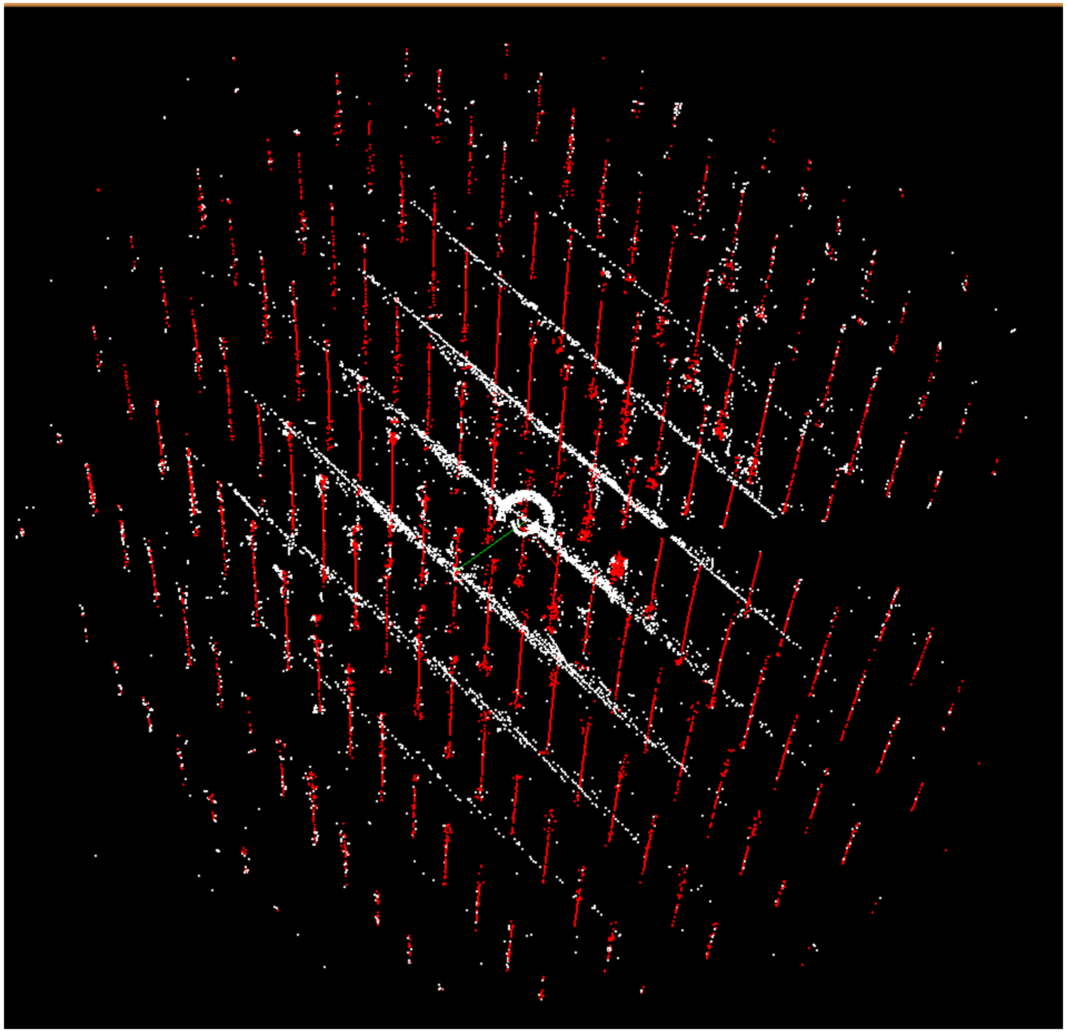
- Unit cell

  a = 9.076 Å

  b = 6.050 Å

  c = 43.922 Å

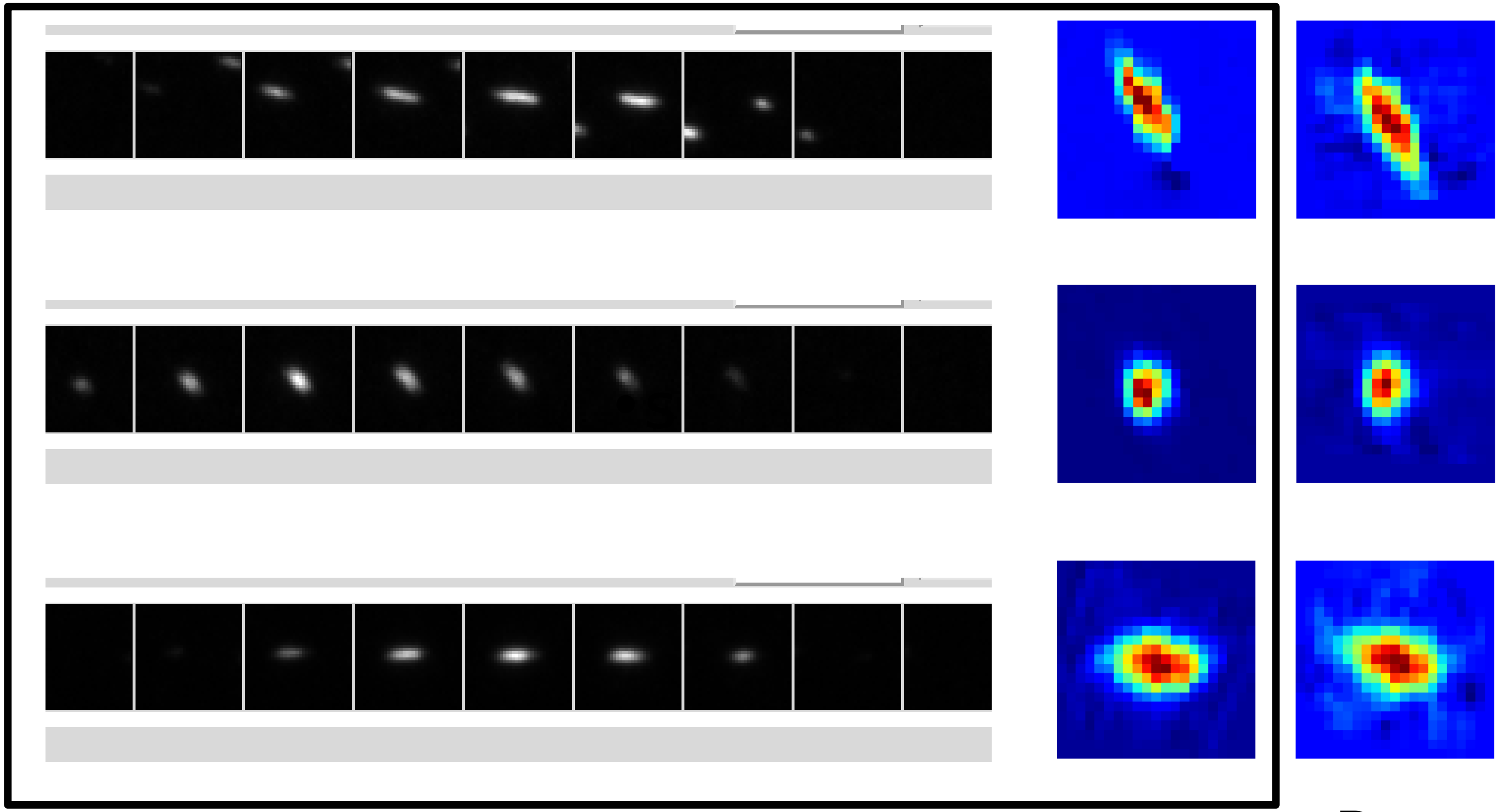
- Space gr. *?*



Comparison of exp. and recontructed uv-maps

Reflections on detector

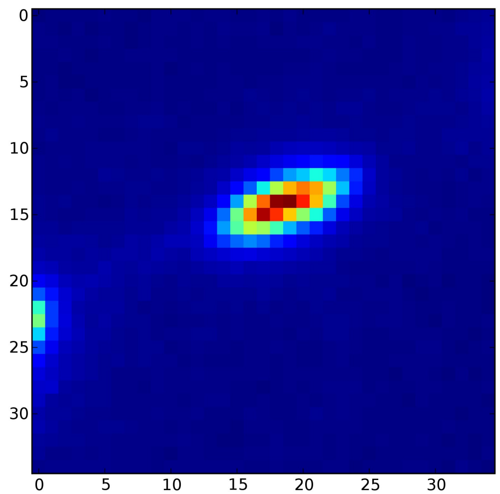
uv-maps

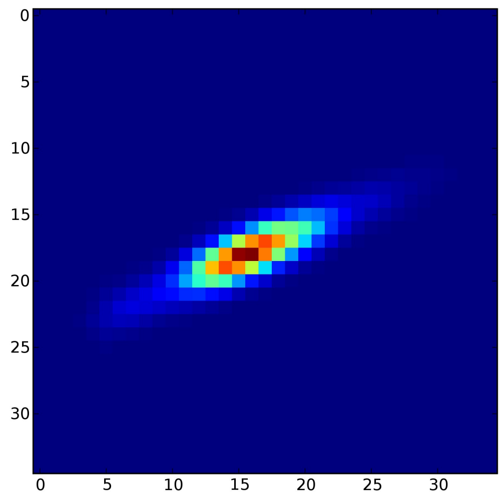


Reconstructed maps

Integration by fitting the profile

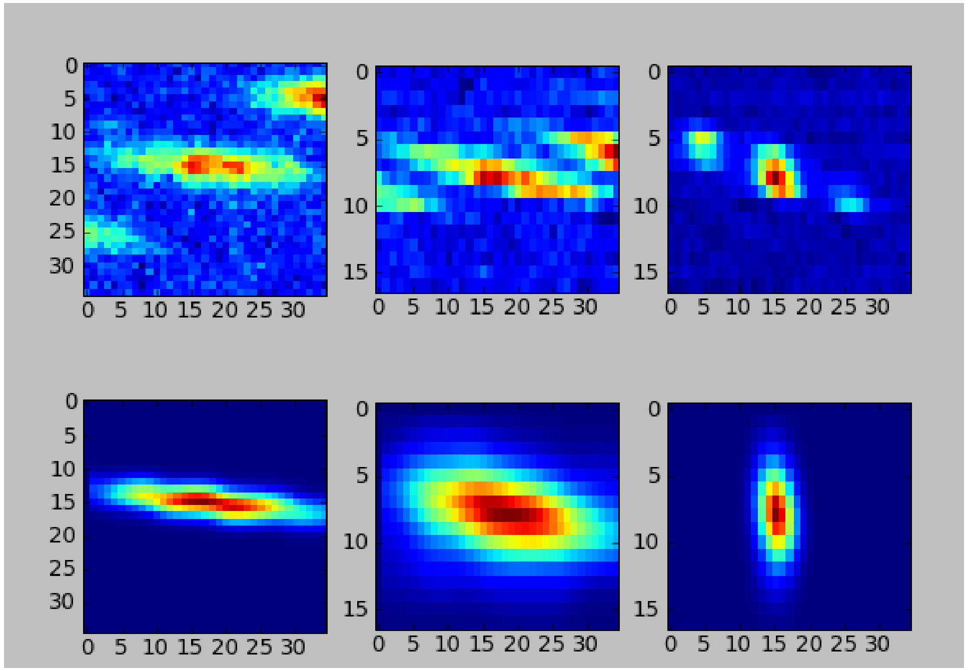
- Reflection profiles calculated from ODF + point-spread function





- calculate CMS and maximum for both reflection box and profile
- compare their positions
  - If far apart make initial fit a center
  - If not move profile grid to have same CMS as peak for intial fit
- Calculate residual moving profile 1 grid point in all directions (26)
  - if **not** move center to position with lowest residual and do another round
  - If residuals all higher – stay
    - Decrease steps to ¼ grid points and do the same analysis until minimum residual found

Integration by fitting the profile



3084 Unique reflections, of which 2886 observed (5982 Reflections read)

R_{int} = 0.1055

No structure yet .....

Summery

- Developed a method to reconstruct orientation-distribution functions of single grains.
- Applied this in a procedure for extraction of integrated intensities.

The python program **Fabric (not in GUI yet)** is made to reconstruct ODF's and do intensity integration.