Electron diffraction data: new perspectives

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Outline

- Electron diffraction
  - why and why not, when and when not?
- Oriented diffraction patterns
  - the beauty and the betrayal of symmetry
  - precession to the rescue!?
- Electron diffraction tomography
  - A weapon of mass structure production, finally! But...
- Dynamical refinement from (P)EDT
  - What God has joined together let not man separate (Mk 10:9)
- Outlook
  - Quo vadis, electron crystallography?

Electron vs. X-ray diffraction

X-rays

- ✓ weak interaction with crystal
- ✓ simple description of diffraction by kinematical theory
- ✓ little radiation damage
- ✓ possibility of diffraction in various environments (hp, gasses)
- × large crystals (>> 1 μm) or powder diffraction -> problems with mixtures and impurities

electrons

- × strong interaction with crystal
- × complicated description of diffraction by dynamical theory
- × radiation damage
- × experiment in vacuum
- ✓ small crystals down to X nm
- ✓ analysis of mixtures and impurities

Electron vs. X-ray diffraction

X-rays

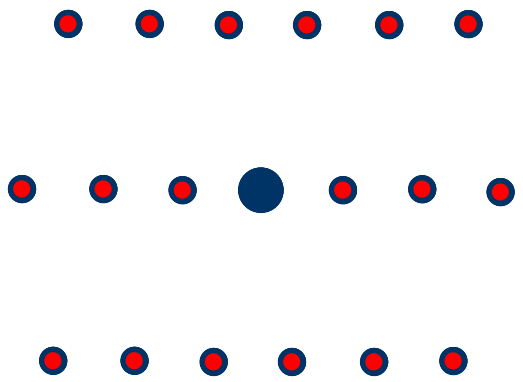
Diffraction mostly kinematical

$$F_{\mathbf{g}} = \sum_{i=1}^{q} f_i(g) \exp(2\pi i \mathbf{g} \cdot \mathbf{r}_i)$$

$$I_{\mathbf{g}_i} \propto \left| F_{\mathbf{g}_i} \right|^2$$

electrons

Diffraction strongly dynamical



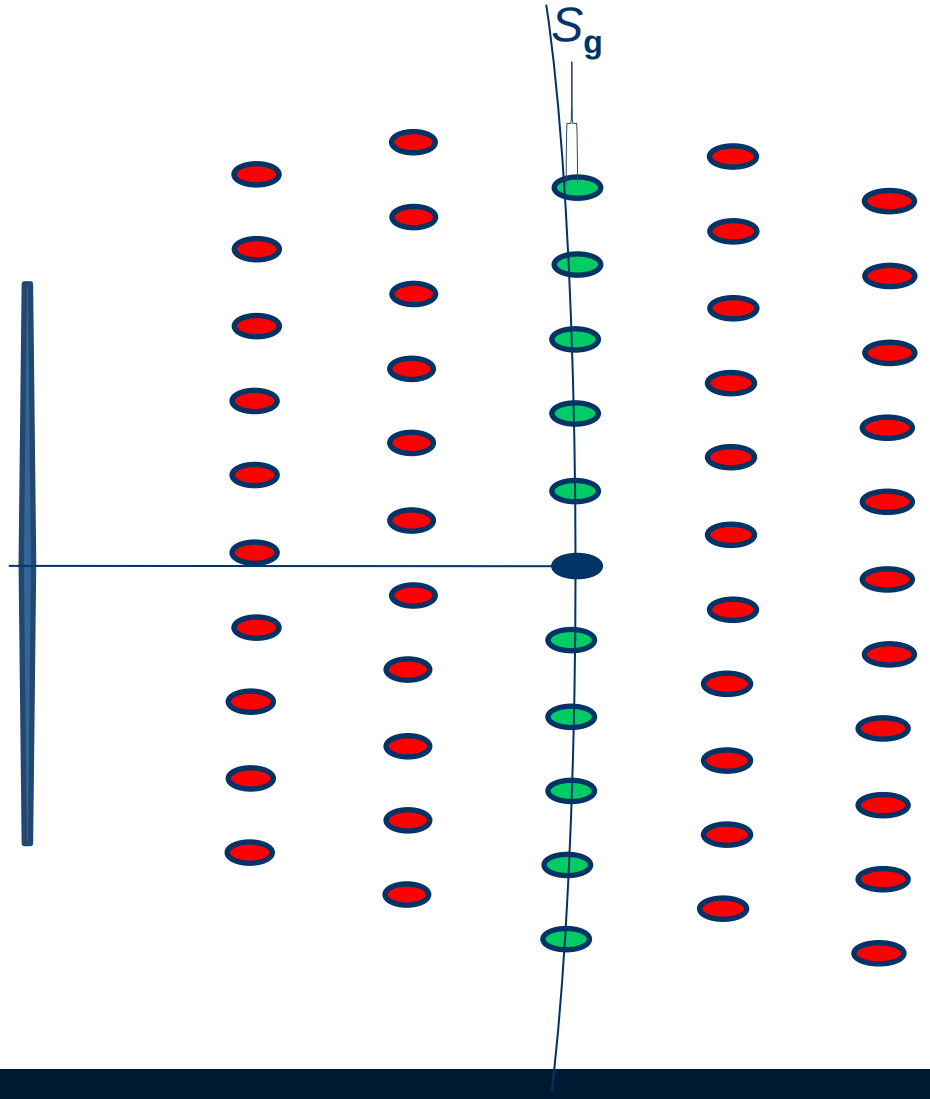
Dynamical diffraction – the Bloch-wave method

$$\mathbf{S} = \exp(2\pi i t \mathbf{A})$$

$$I_{\mathbf{g}_i} \propto |S_{i1}|^2$$

$$a_{ii} = 2K S_{\mathbf{g}_i}, i = 1, N_{beams}$$

$$a_{ij} = U_{\mathbf{g}_i - \mathbf{g}_j}, i, j = 1, N_{beams}; i \neq j$$



Dynamical diffraction – the Bloch-wave method

$$\mathbf{S} = \exp(2\pi i t \mathbf{A})$$

$$I_{\mathbf{g}_i} \propto |S_{i1}|^2$$

$$a_{ii} = 2KS_{\mathbf{g}_i}, i = 1, N_{beams}$$

$$a_{ij} = U_{\mathbf{g}_i - \mathbf{g}_j}, i, j = 1, N_{beams}; i \neq j$$

$$\begin{pmatrix} 0 & U_{-g_1} & U_{-g_2} & U_{-g_3} & U_{-g_4} \\ U_{g_1} & 2KS_{g_1} & U_{g_1-g_2} & U_{g_1-g_3} & U_{g_1-g_4} \\ U_{g_2} & U_{g_2-g_1} & 2KS_{g_2} & U_{g_2-g_3} & U_{g_2-g_4} \\ U_{g_3} & U_{g_3-g_1} & U_{g_3-g_2} & 2KS_{g_3} & U_{g_3-g_4} \\ U_{g_4} & U_{g_4-g_1} & U_{g_4-g_2} & U_{g_4-g_3} & 2KS_{g_4} \end{pmatrix}$$

Dynamical diffraction - multislice

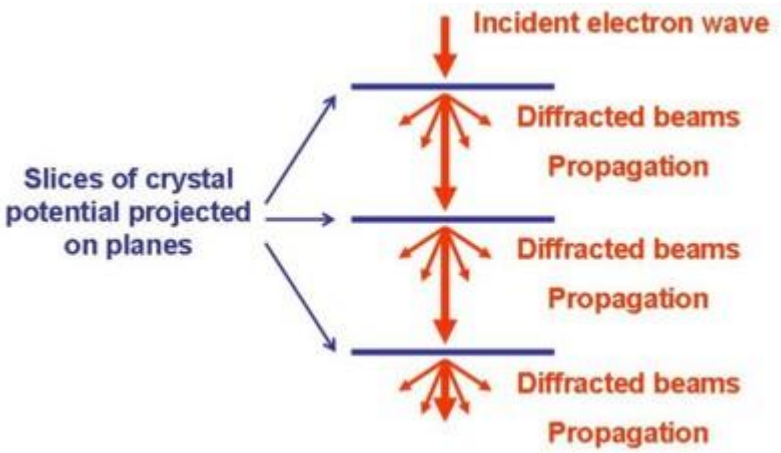


Image: http://www.microscopy.ethz.ch/simulation.htm

Scattering:

$$\psi'(x,y) = \psi(x,y)\exp(i\delta\varphi(x,y))$$

Propagation:

$$\psi''(x,y) = \psi'(x,y) \otimes \exp\left(\frac{\pi i(x^2+y^2)}{\lambda \Delta z}\right)$$

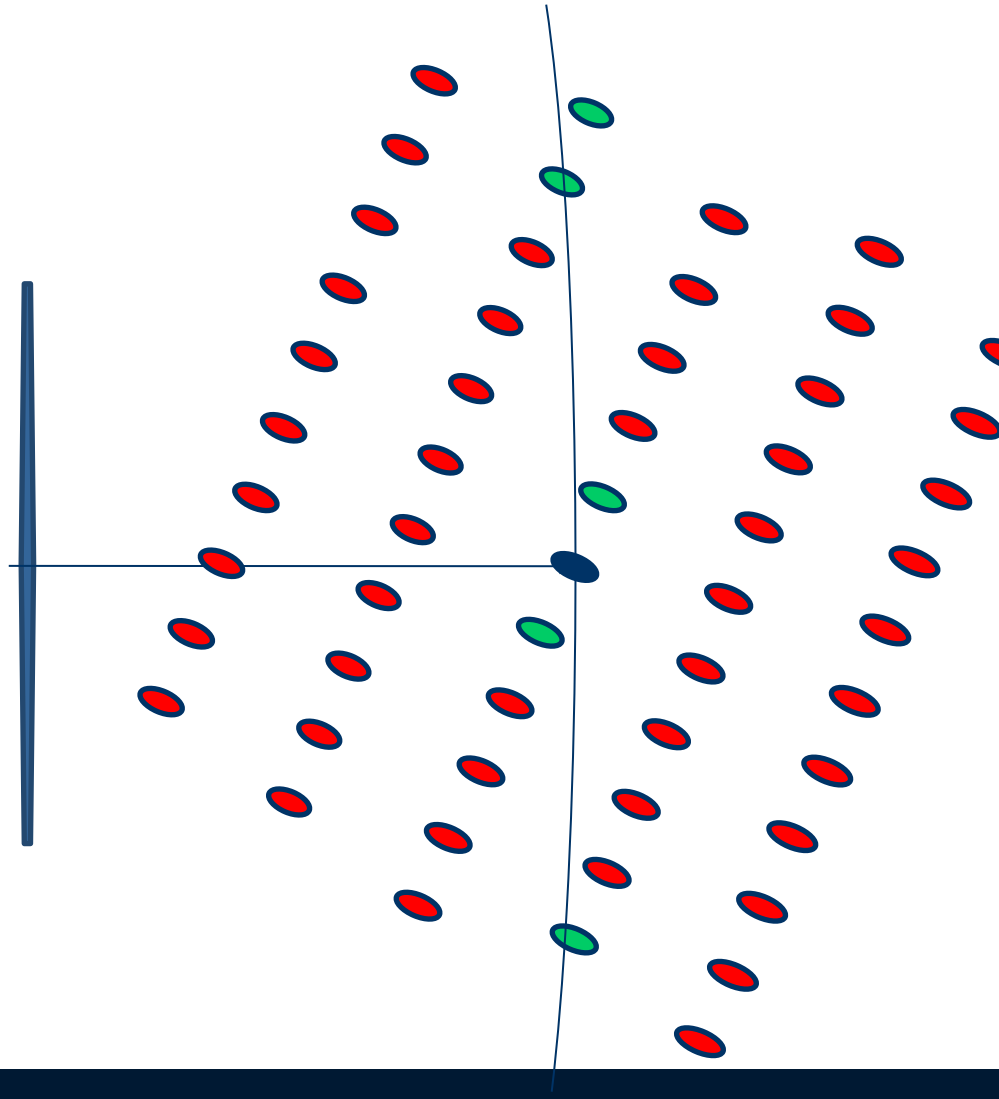
Dynamical diffraction

$$\mathbf{S} = \exp(2\pi i t \mathbf{A})$$

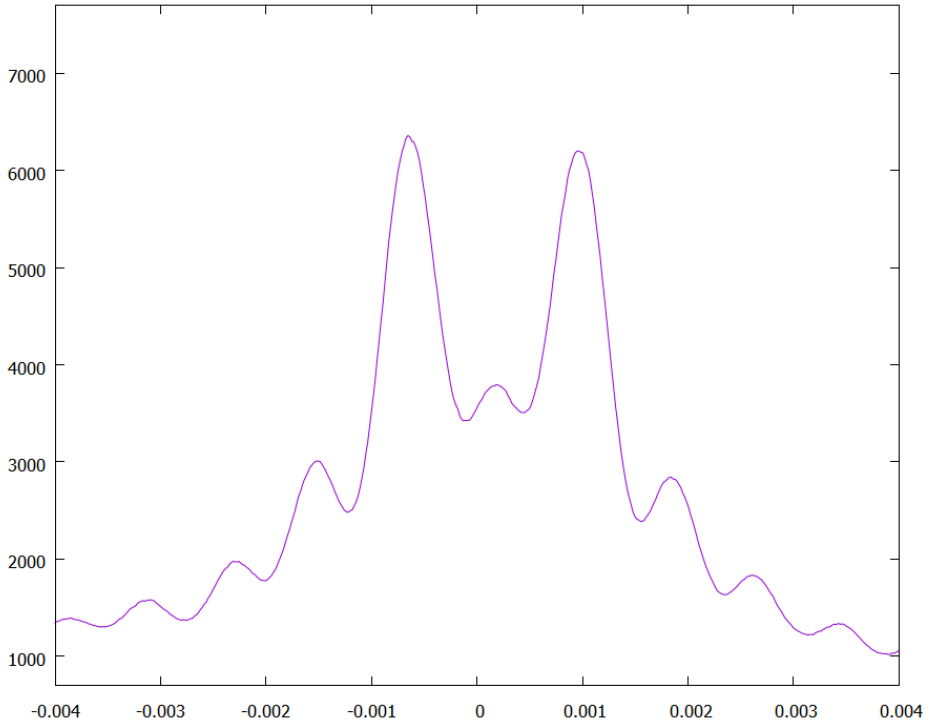
$$I_{\mathbf{g}_i} \propto |S_{i1}|^2$$

$$a_{ii} = 2K S_{\mathbf{g}_i}, i = 1, N_{beams}$$

$$a_{ij} = U_{\mathbf{g}_i - \mathbf{g}_j}, i, j = 1, N_{beams}; i \neq j$$



Dynamical diffraction

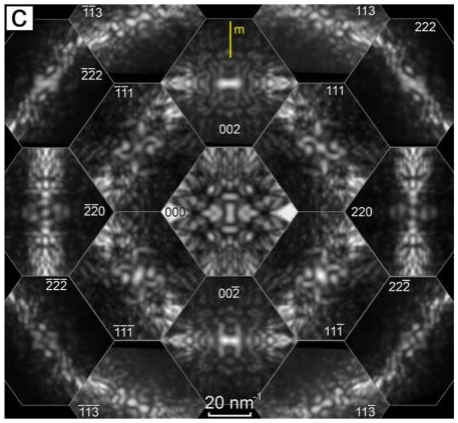


$$a_{ii} = 2KS_{\mathbf{g}_i}, i = 1, N_{beams}$$

$$a_{ij} = U_{\mathbf{g}_i - \mathbf{g}_j}, i, j = 1, N_{beams}; i \neq j$$

$$\mathbf{S} = \exp\left(\frac{2\pi i t \mathbf{A}}{2K_n}\right)$$

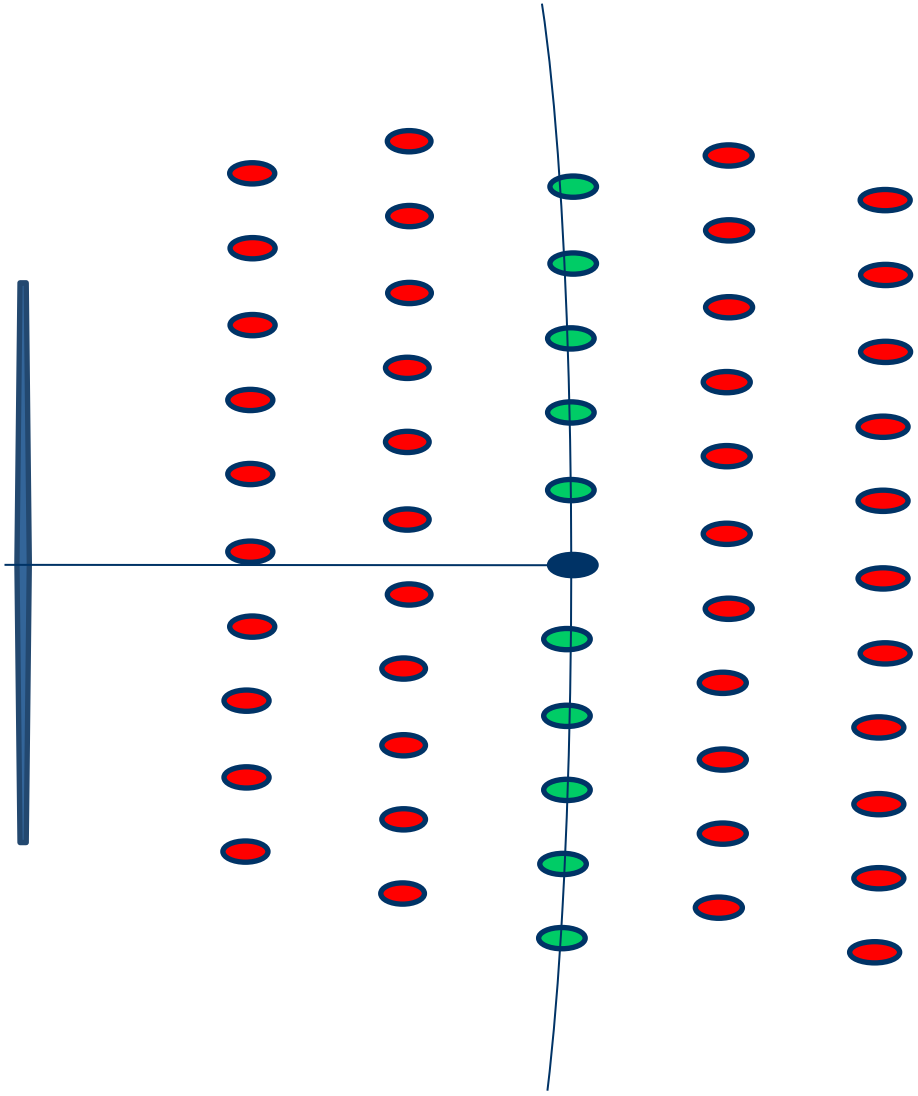
$$I_{\mathbf{h}_i} = |s_{i1}|^2$$



Each intensity is a function of:

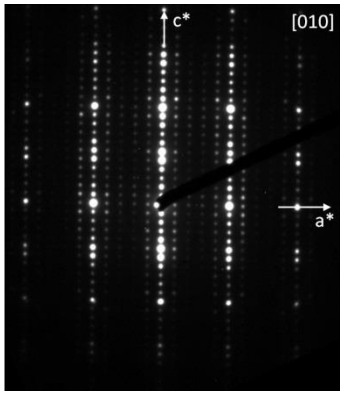
- Crystal thickness
- Crystal orientation
- Structure factors of all sufficiently excited beams

Oriented diffraction patterns

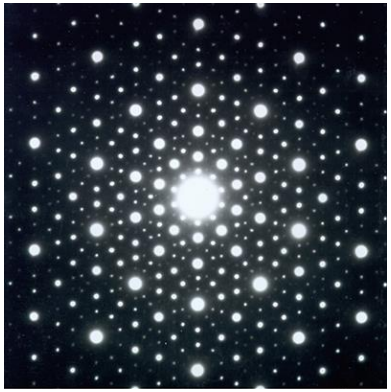


Oriented diffraction patterns

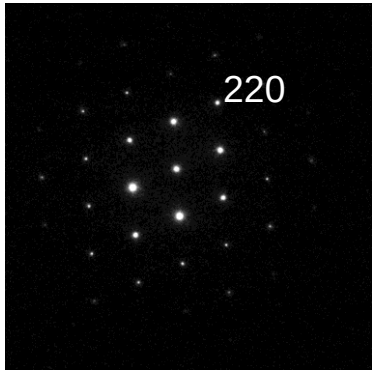
- ✓ very useful for determination of lattice parameters and symmetry
- ✓ beautiful spot patterns and CBED patterns
- ✓ computationally (more) easily tractable
- ✗ the strongest dynamical effects
- ✗ structure solution possible, but very cumbersome



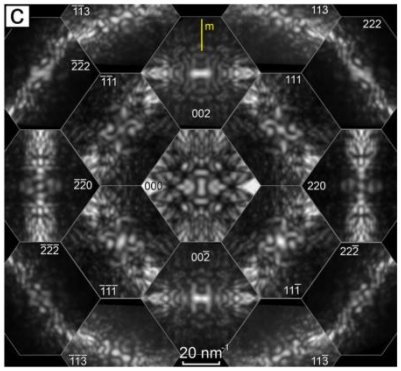
$Sr_{25}Fe_{30}O_{77}$;http://www.microscopy.cz/html/1450.html



Al-Cu-Fe quasicrystal; http://www.tohoku.ac.jp/en/research/research_highlights/research_highlight_07.html

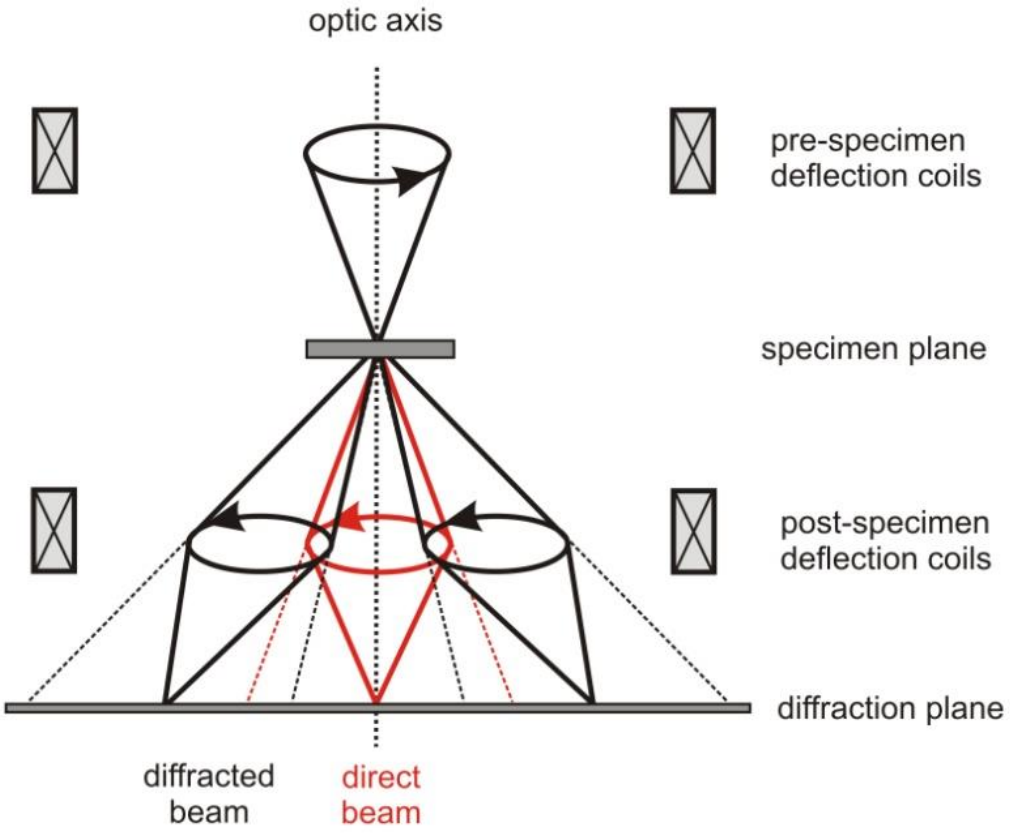


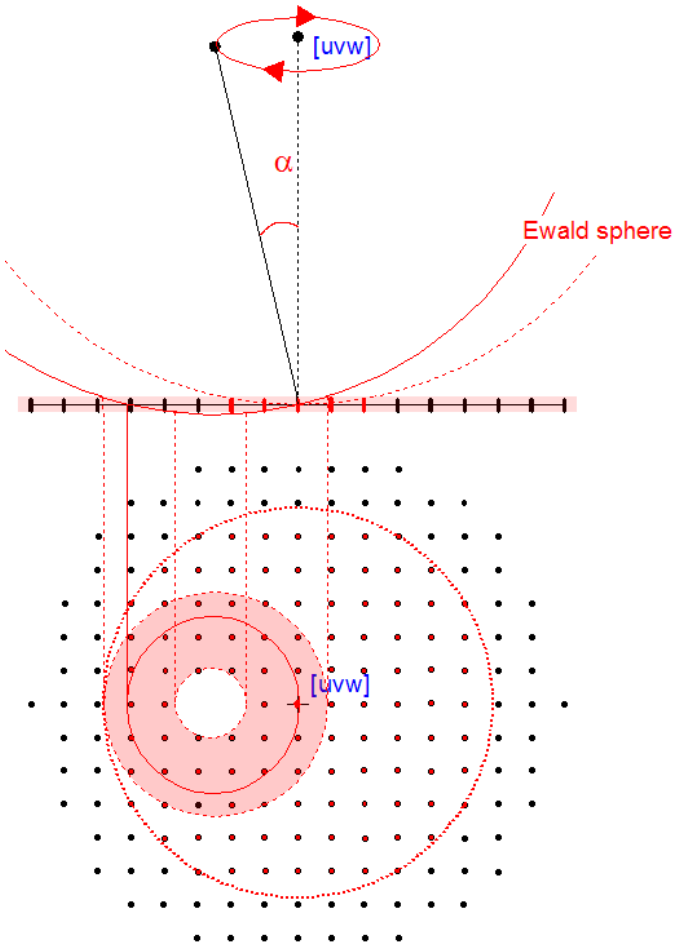
Silicon [110]



GaAs [1-10]; http://arxiv.org/ftp/arxiv/papers/1211/1211.6571.pdf

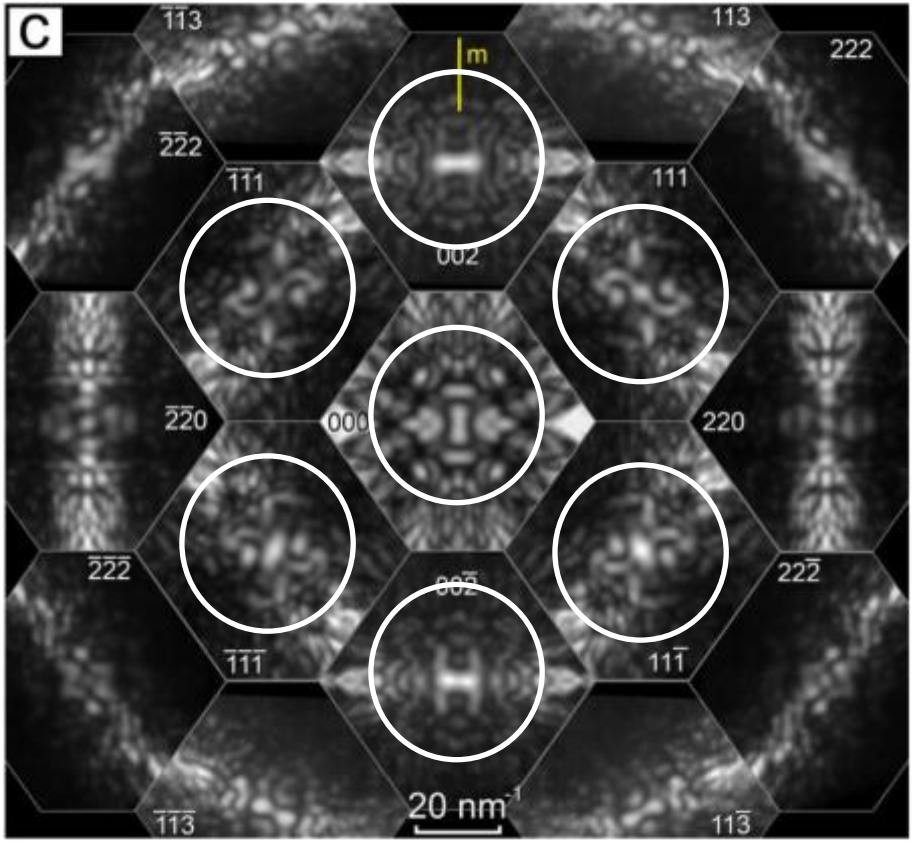
Precession electron diffraction





Vincent & Midgley, Ultramicrosocopy 53 (1994)

Precession electron diffraction



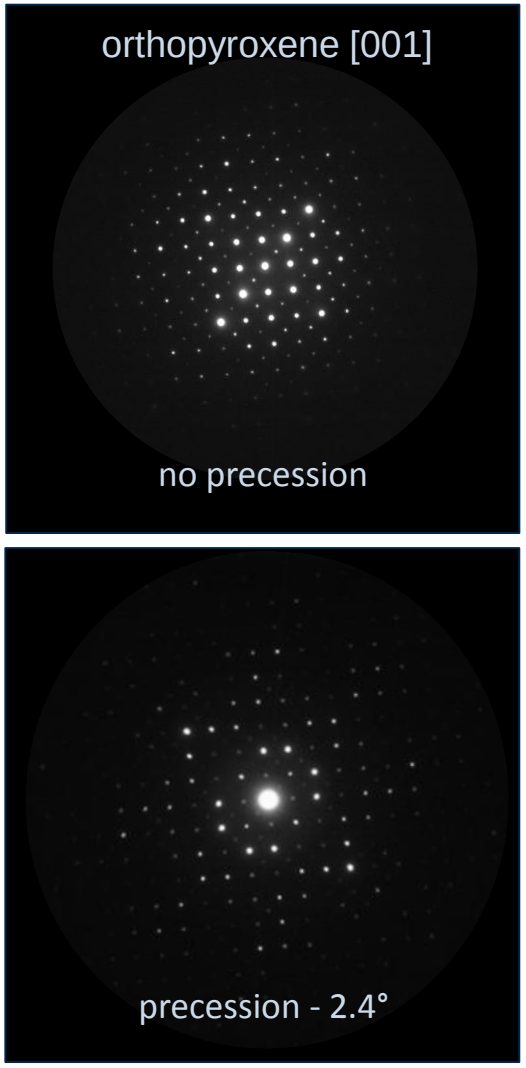
Precession electron diffraction

PED = integrating the diffracted intensities over many orientations of the incident beam around a circle

For symmetry determination: more reflections in one diffraction pattern, more obvious systematic absences, easier access to HOLZ lines, better symmetry

For structure solution: intensities are „more kinematical“ – more generally, the ordering of intensities is much closer to kinematical than non-precessed data.

For structure refinement: less sensitive to crystal thickness and orientation, more sensitive to structural parameters



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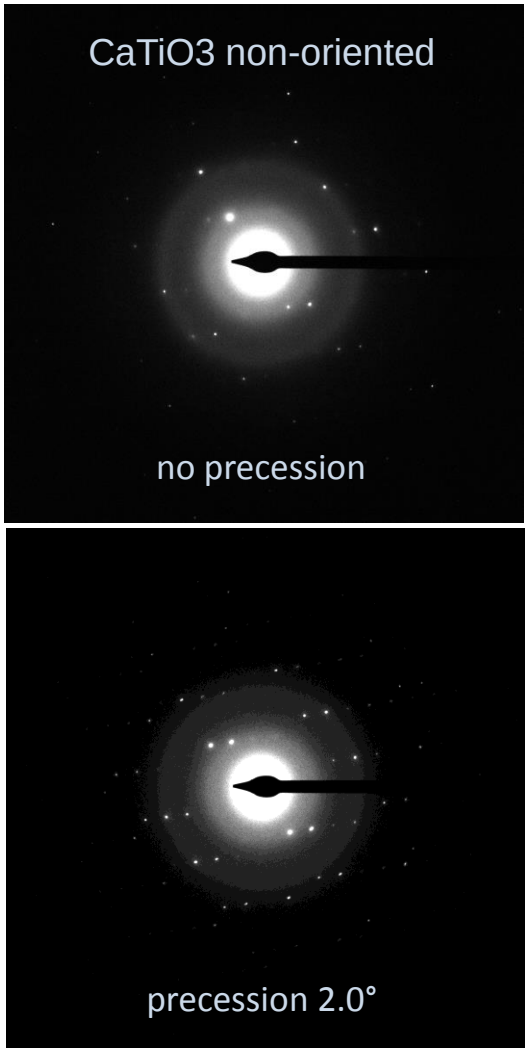
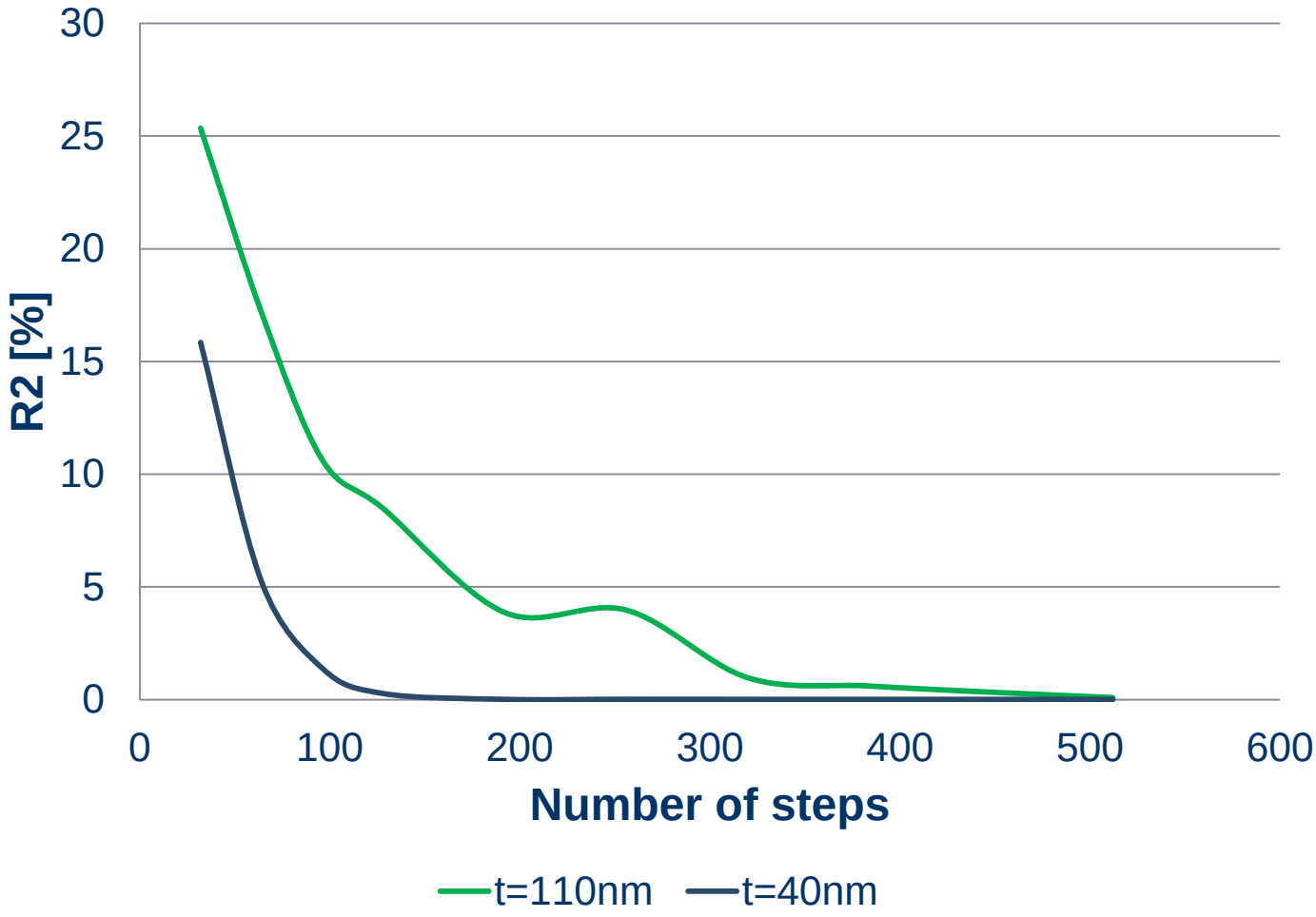


Precession electron diffraction



Structure solution from oriented patterns

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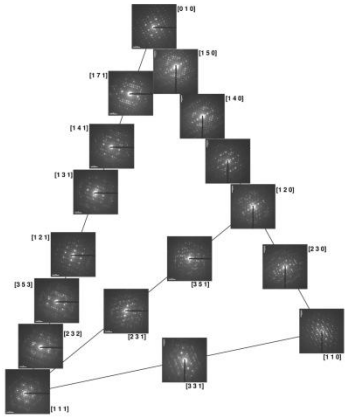
Precession electron diffraction of Mn_2O_3 and $PbMnO_{2.75}$: solving structures where X-rays fail

Holger Klein



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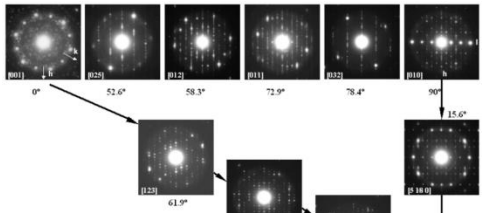
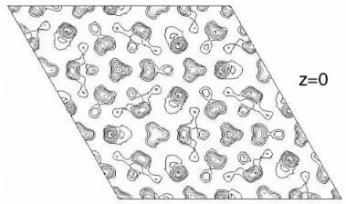
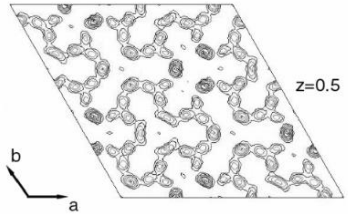
Structure of Ti_2P solved by three-dimensional electron diffraction data collected with the precession technique and high-resolution electron microscopy

Mauro Gemmi,[a]*† Xiaodong Zou,[a] Sven Hovmöller,[a] Andrea Migliori,[b] Marie Vennström[c] and Yvonne Andersson[c]







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Three-dimensional reconstruction of the ν-AlCrFe phase by electron crystallography

X. D. Zou,[a]* Z. M. Mo,[a]† S. Hovmöller,[a] X. Z. Li[b] and K. H. Kuo[c]

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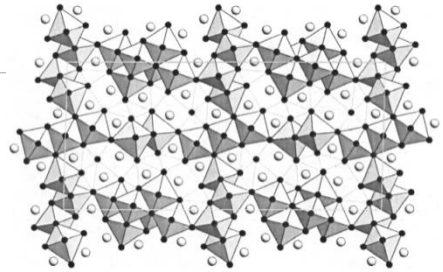
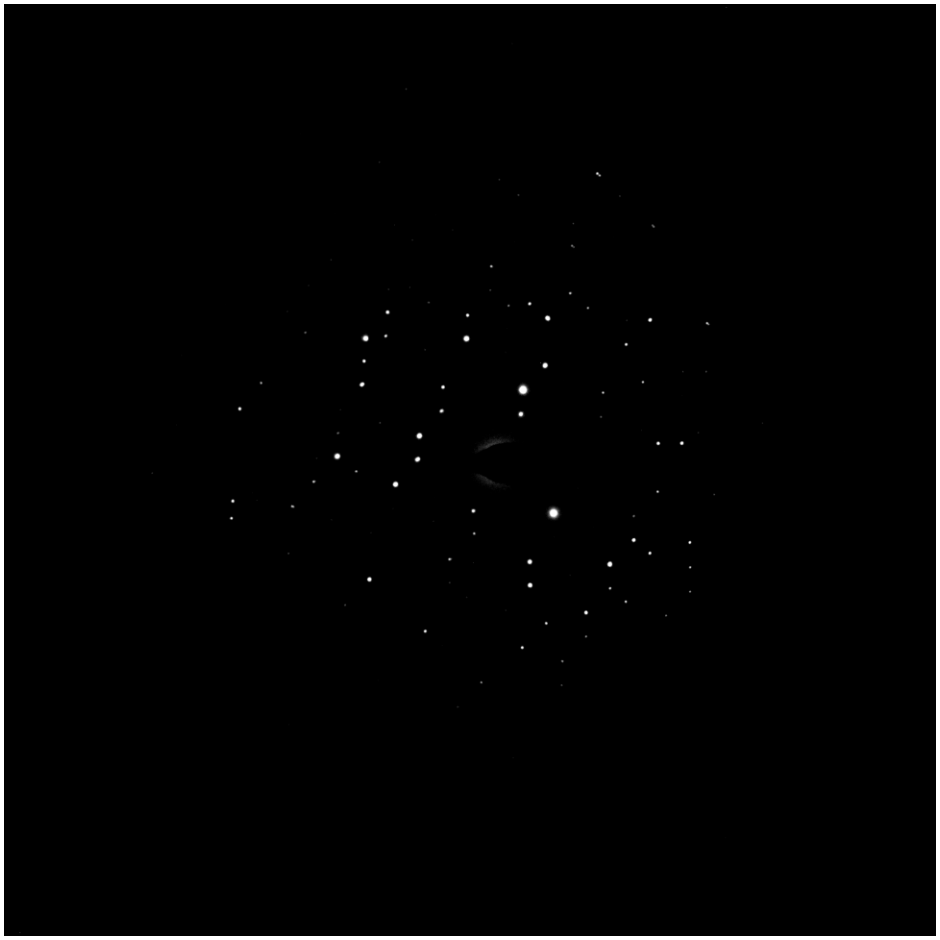
Electron crystallography without limits? Crystal structure of $Ti_{45}Se_{16}$ redetermined by electron diffraction structure analysis

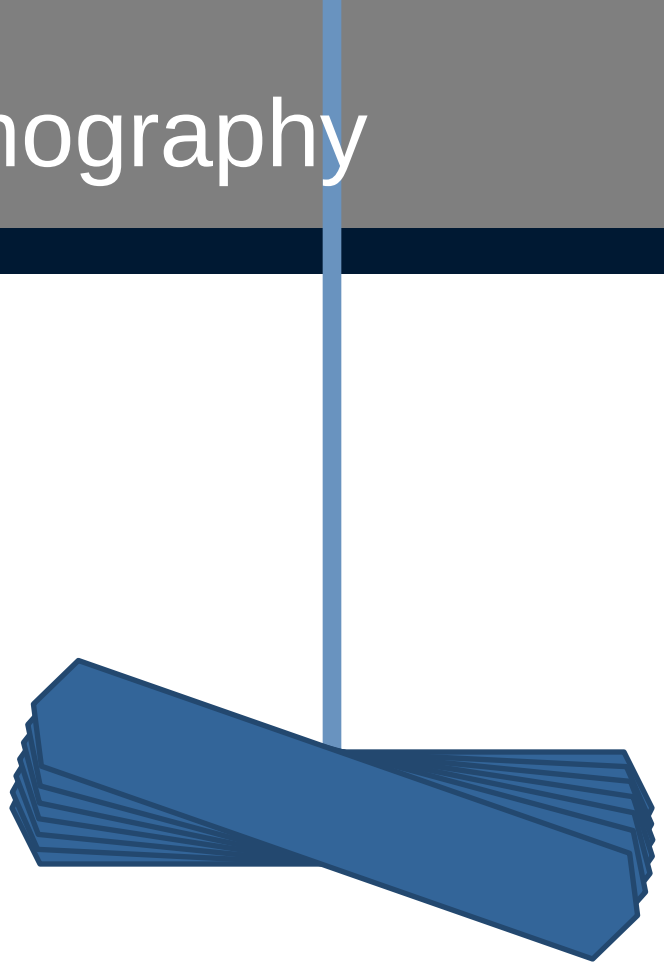
Thomas E. Weirich†



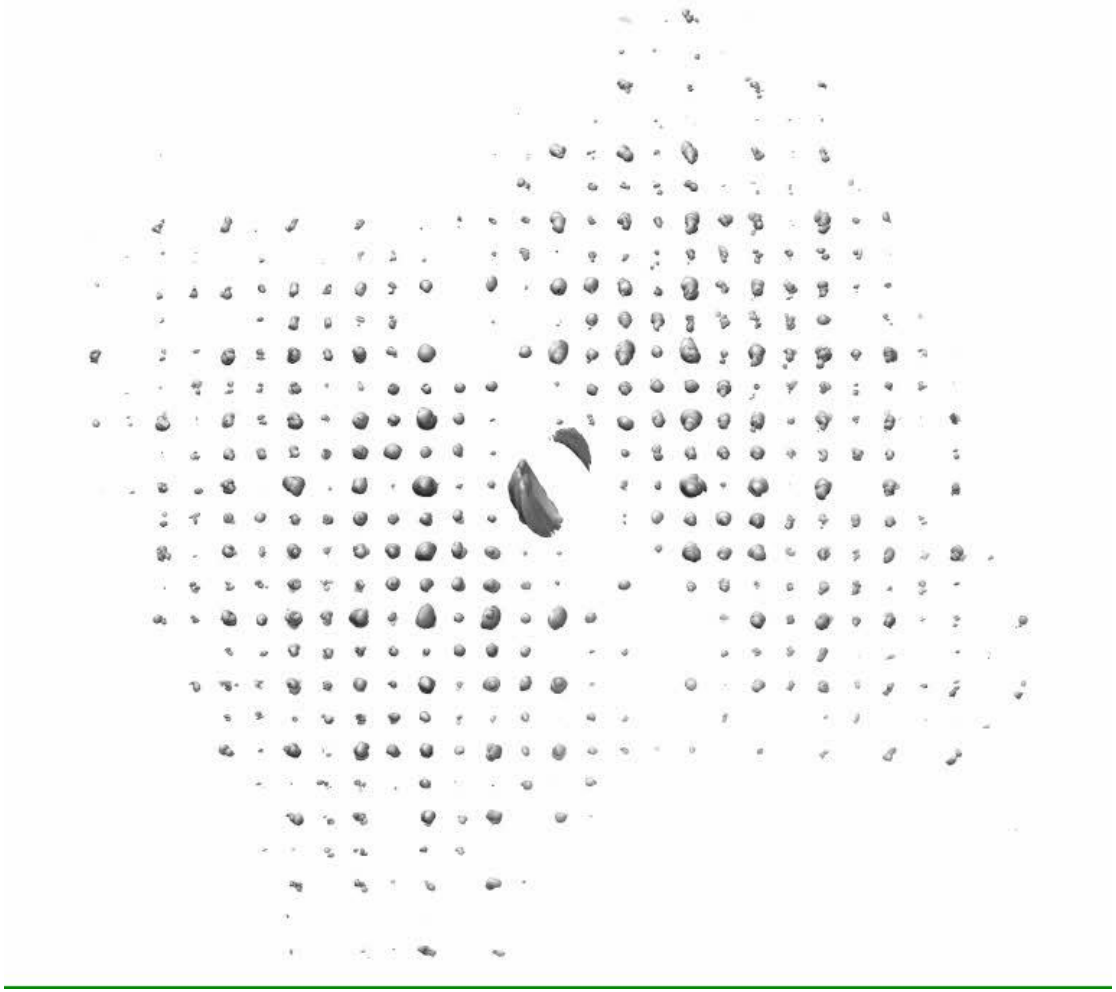
Problems: low coverage, tedious data collection, strong dynamical effects even with precession

Electron diffraction tomography

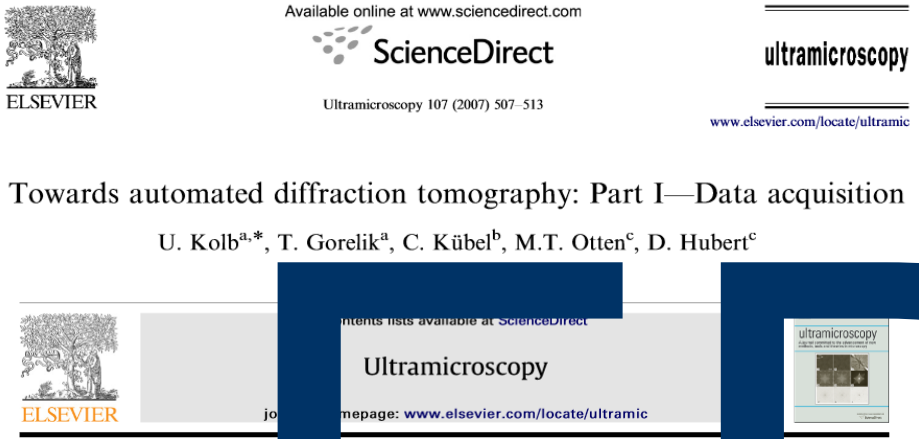




Electron diffraction tomography



Electron diffraction tomography



ADT – „Mainz school"

RED – „Stockholm school"

EDT

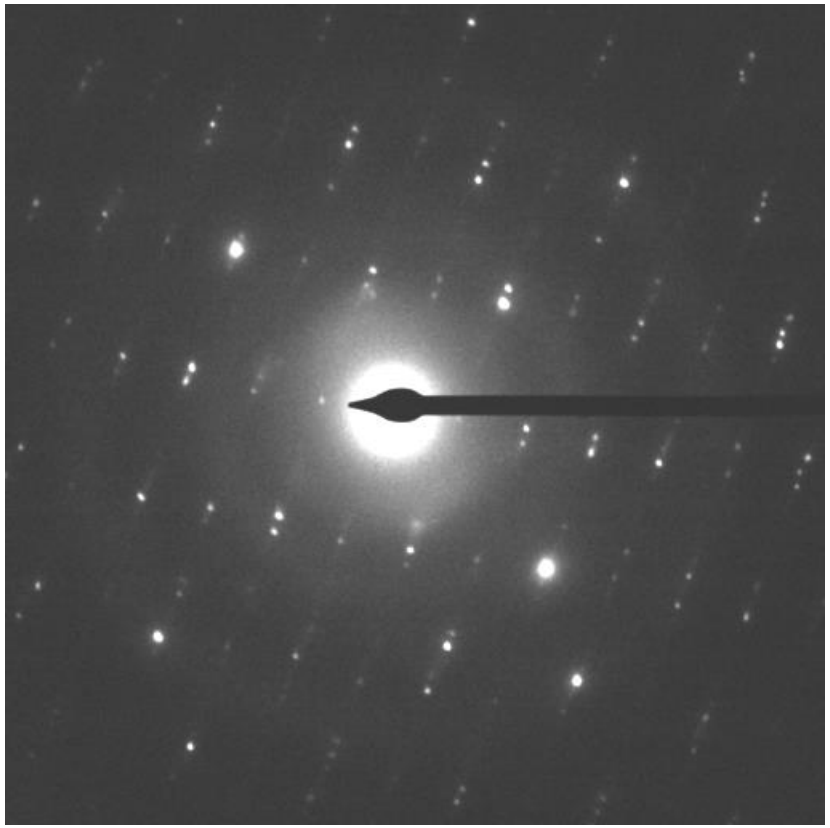
IEDT

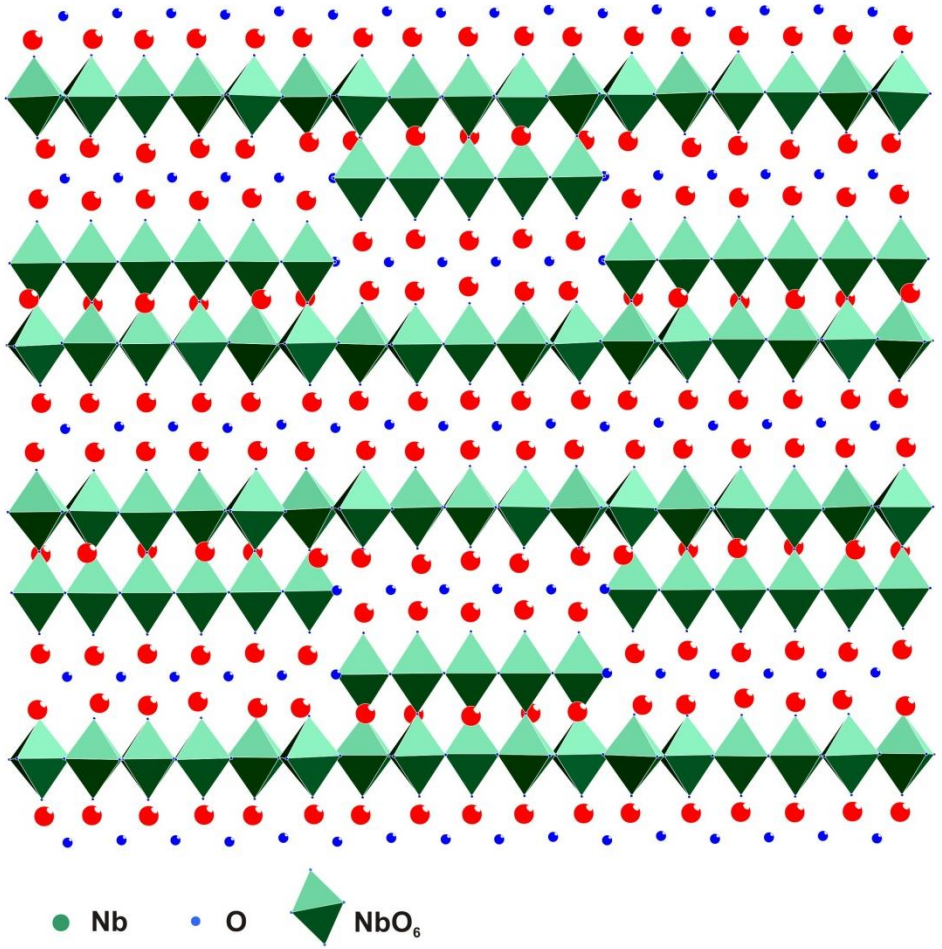
MDT

MicroED

rotating crystal method

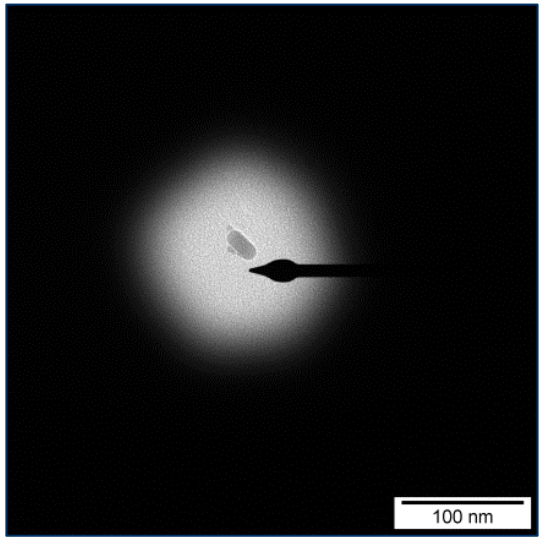
EDT – examples

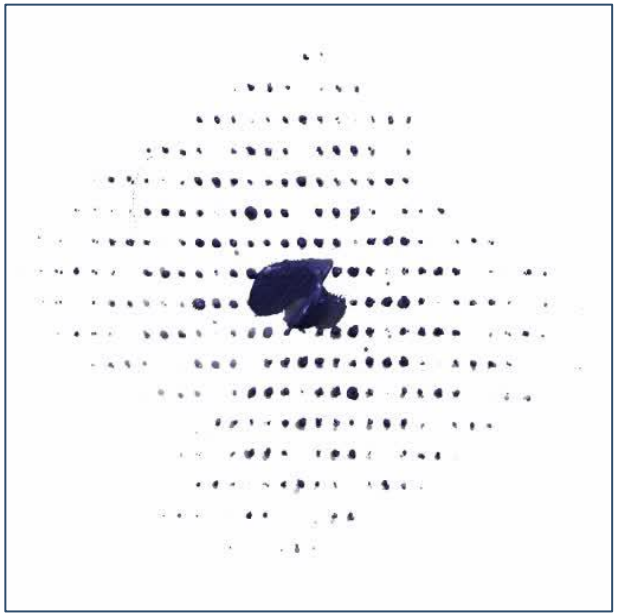


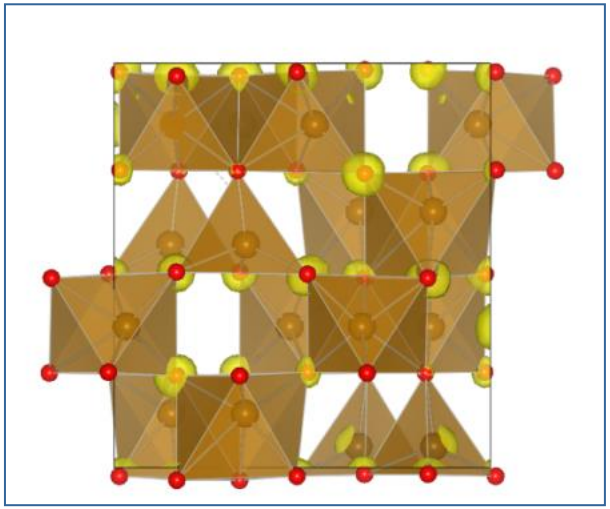


P. Boullay, N. Barrier and L. Palatinus, Inorg. Chem. 52 (2013) 6127–6135

EDT – examples







Electron diffraction tomography

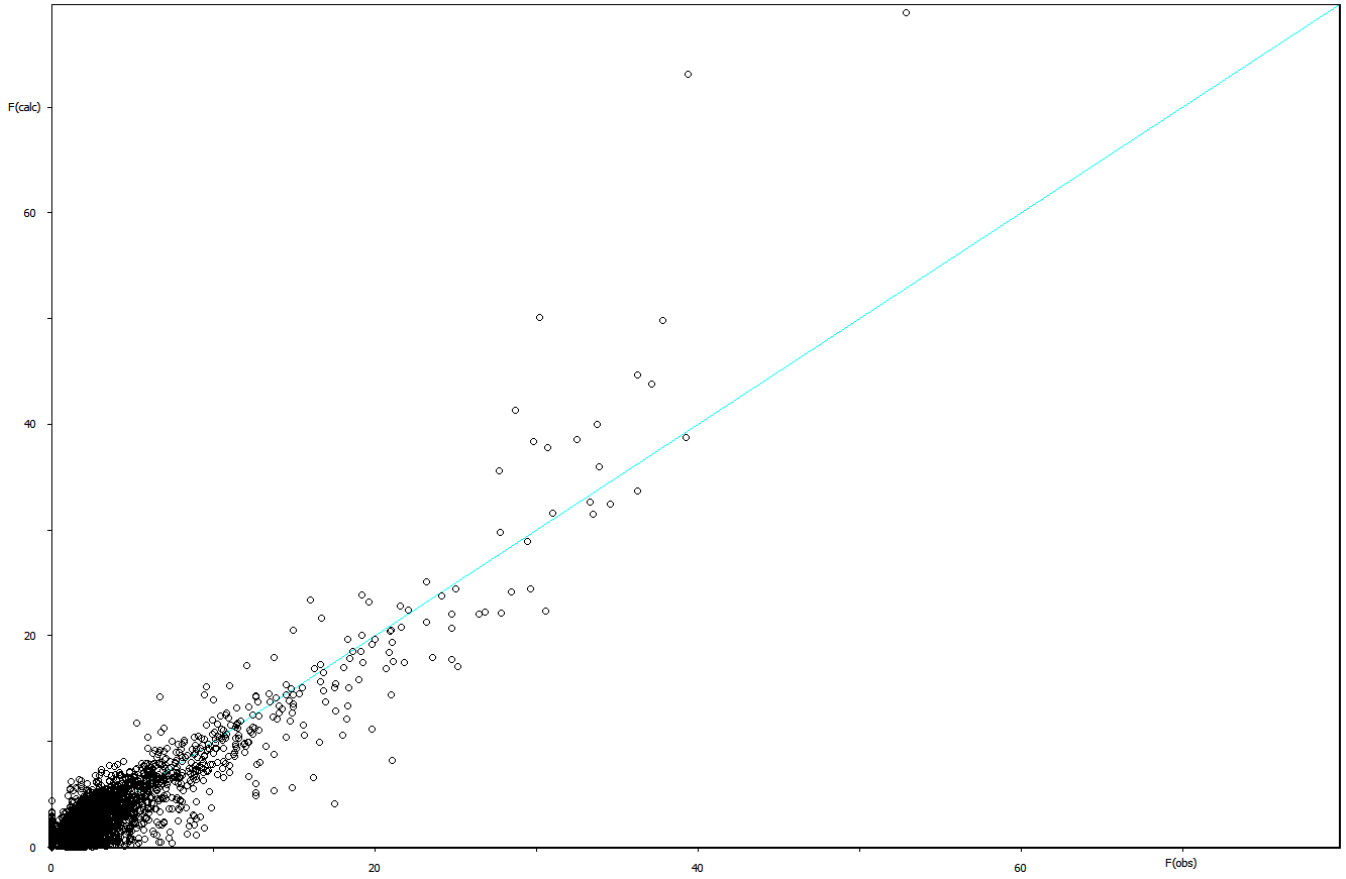
- ✓ **complete or almost complete diffraction data**
- ✓ **conceptually simple, fast and potentially fully automatic experiment**
- ✓ **easy solution of structures by *ab initio* methods**
- × **Poor figures of merit, unreliable atomic positions, unreliable e.s.d.s**

structure	R_{obs} [%]	average Δ [Å]	max Δ [Å]
barite	27	0.1	0.3
$Li_4Ti_8Ni_3O_{21}$	35	0.23	0.4
$Zn_5Cl_4(BTDD)_3$	32	?	0.2 (rigid bodies and soft constr.)
natrolite	20	0.1	0.183
charoite	17	---	---
$Na_2Ti_6O_{13}$	29	0.152	0.454

Examples from Kolb *et al.*, Cryst. Res. Technol. 46

Electron diffraction tomography

Why is the refinement so poor?
Because of the dynamical difraction



Dynamical refinement

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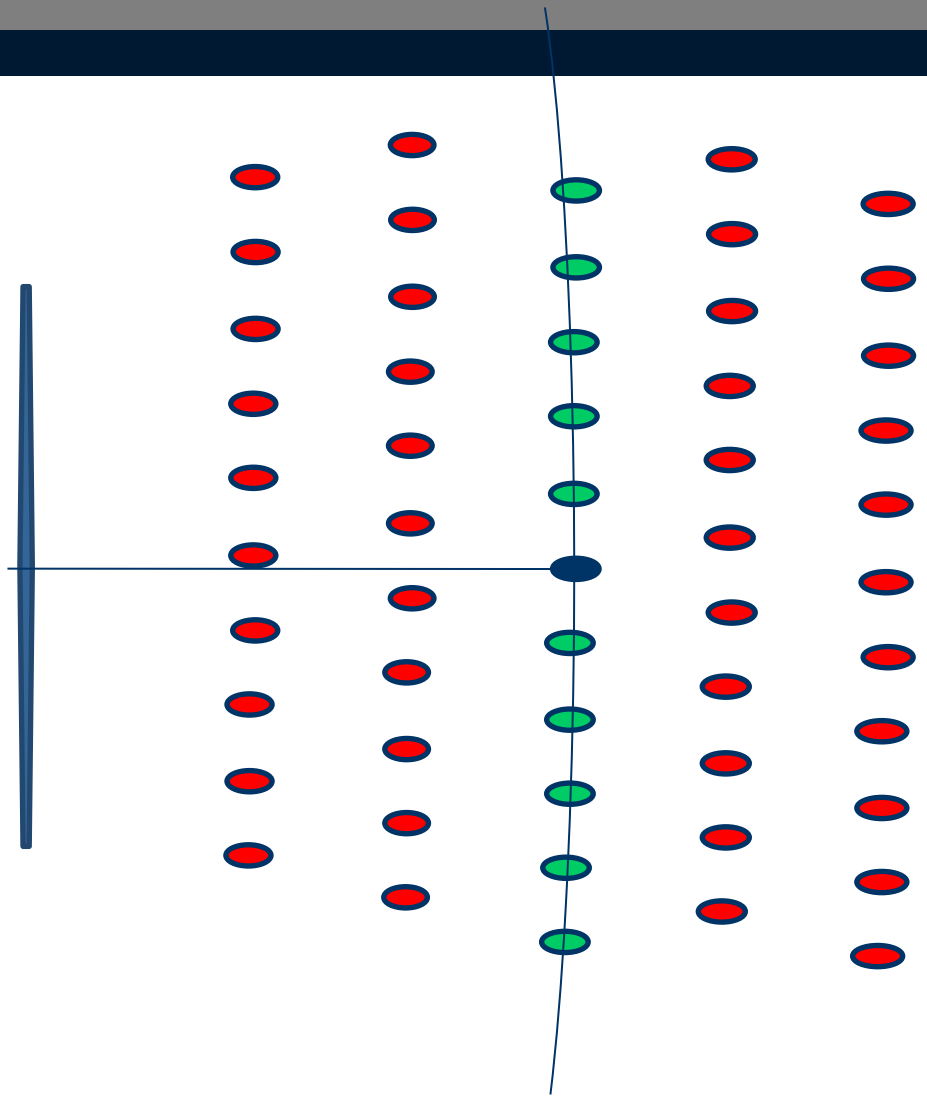


Dynamical refinement = least-squares refinement with I_{calc} calculated with the dynamical diffraction theory

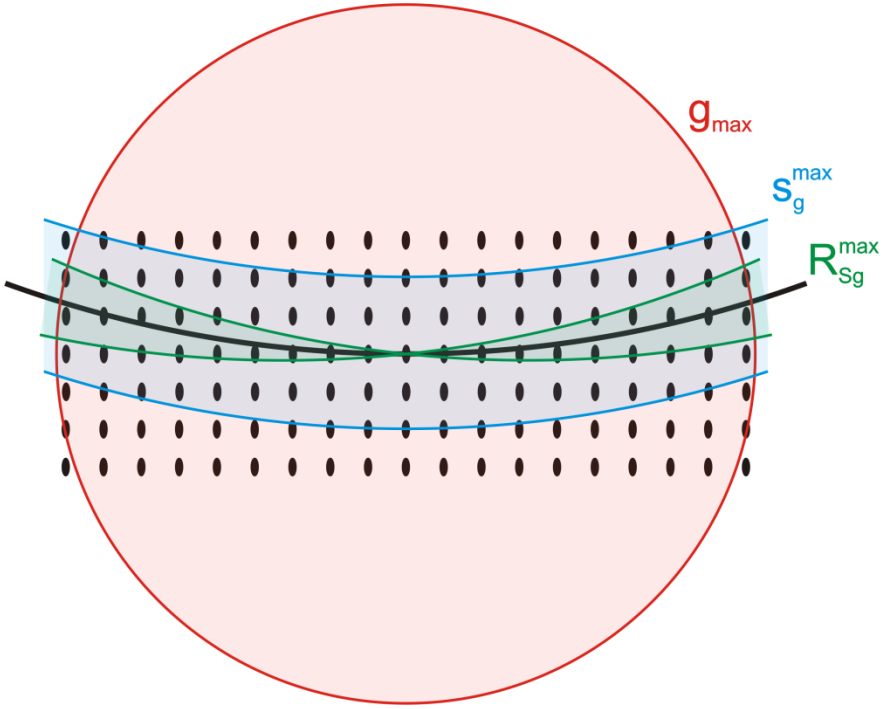
Dynamical refinement - specifics

data selection – a key to success:

$g_{\max}$: the maximum resolution of the experimetal data (typically 1.4 Å^{-1})

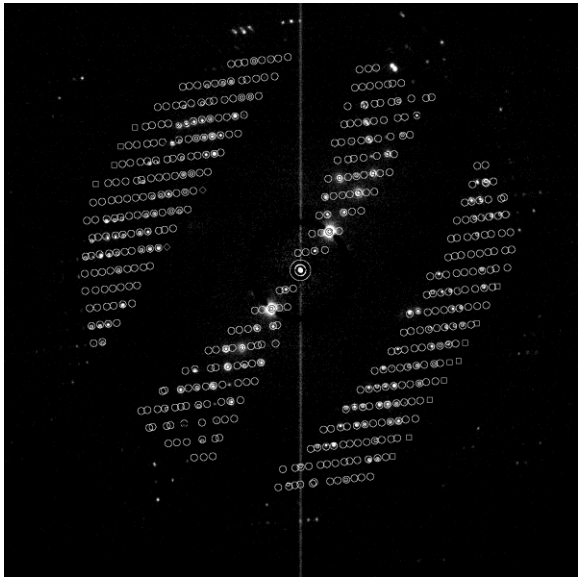
$S_g{}^{\max}$: maximum excitation error of the experimental data

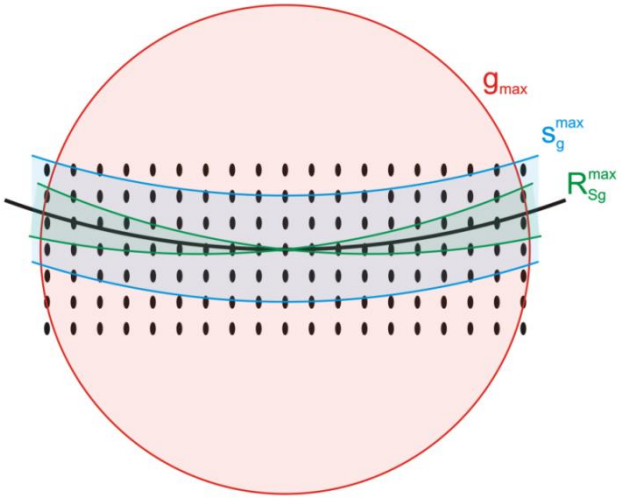
$R_{Sg}{}^{\max}$: The ratio between S_g and the amplitude of the precesion motion at ***g***



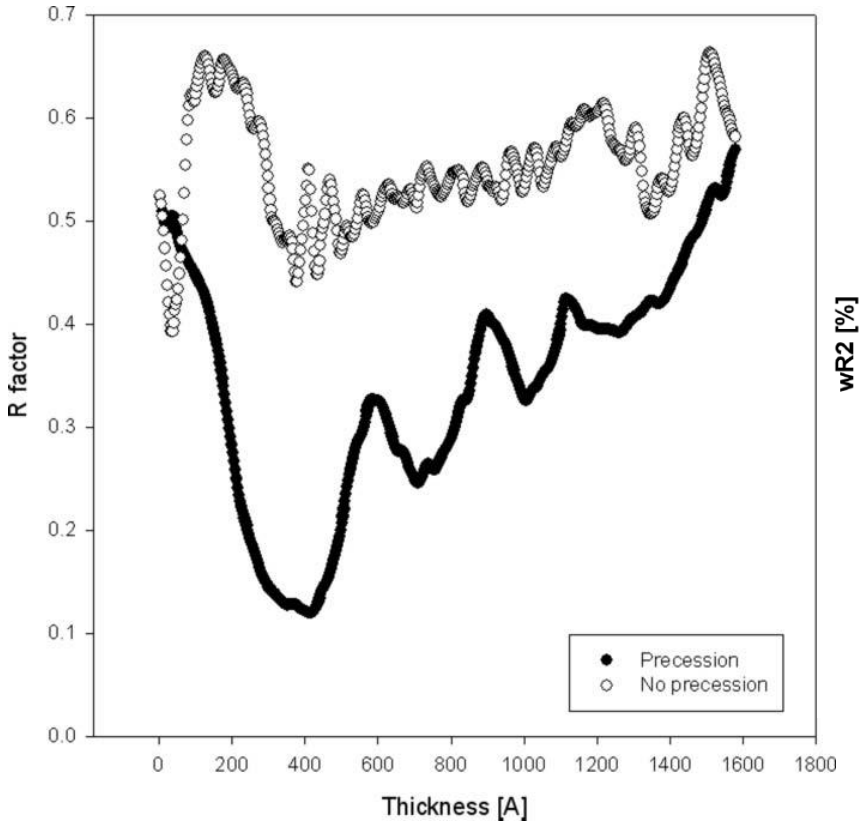
Dynamical refinement - specifics

- Each experimental frame is treated separately. Reflections are not merged accross frames
- Symmetry-equivalent reflections are not merged
- Each frame has a separate scale factor
- Crystal thickness is refined
- Exact orientation of the crystal w.r.t. incident beam for each frame is important and must be known
- Data selection procedure is important!

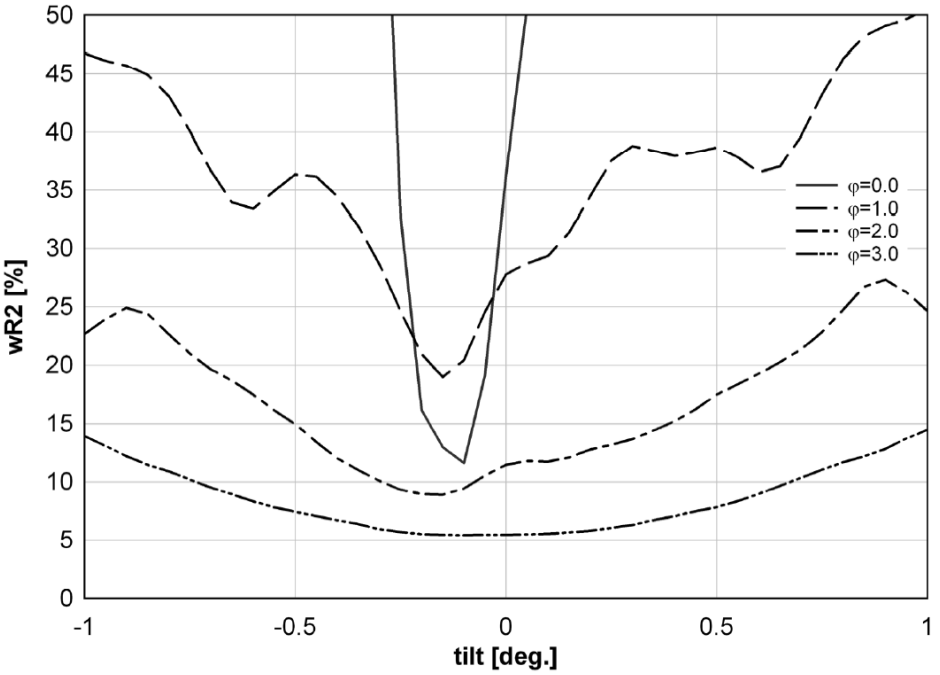




Dynamical refinement and PED – why bother?



Own et al. (2006), Acta Cryst. A62

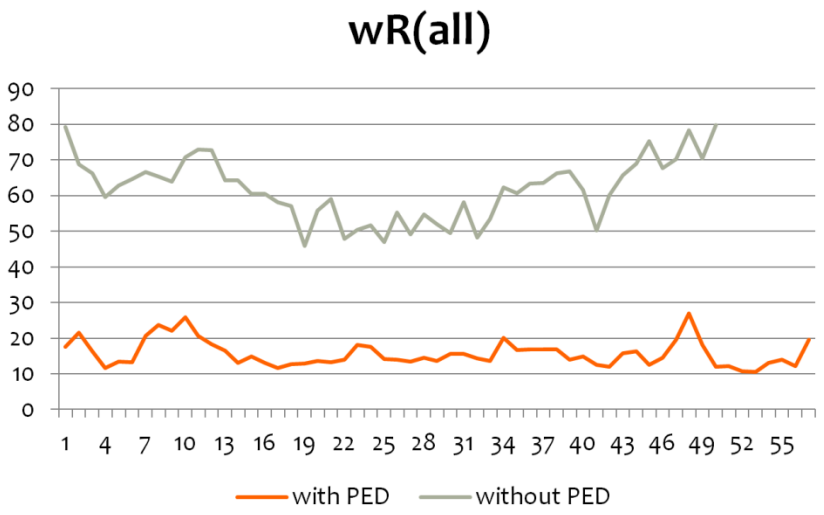


Palatinus et al. (2013), Acta Cryst. A69

Price to pay: much longer computing times!

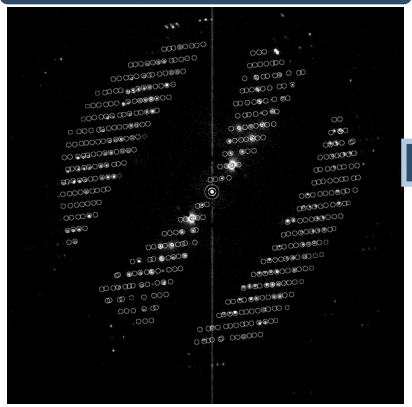
Dynamical refinement and PED – why bother?

Paracetamol form II – two data sets		
	Data set I	Data set II
precession angle	1.5°	0.0°
tilt step	1.5°	1.5°
tilt range	85°	74.5°
R_{obs}	9%	35%

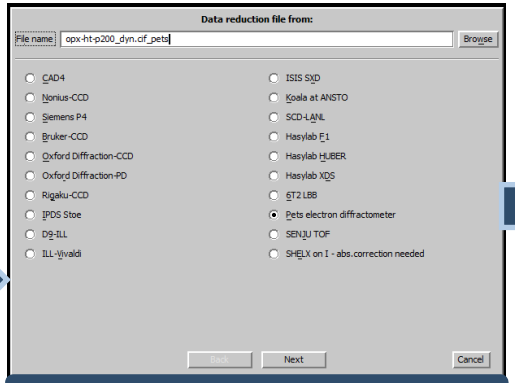


Dynamical refinement – practical procedure

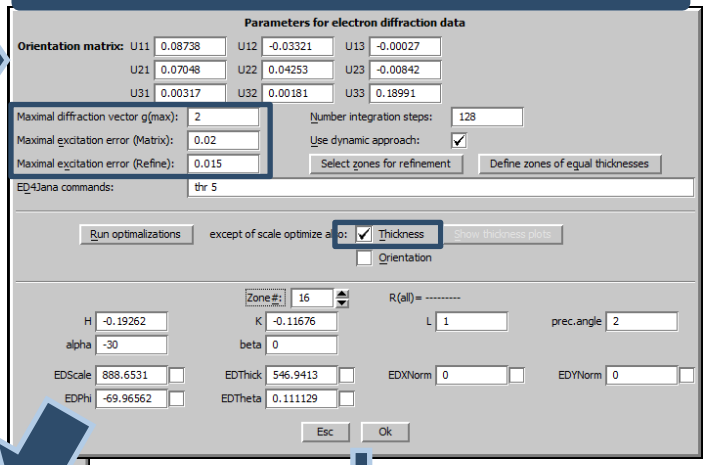
Analyze data and extract intensities

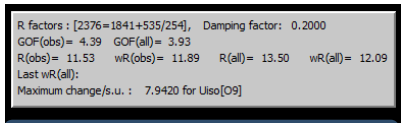


Import the data to Jana. All information is stored in CIF format and imported automatically

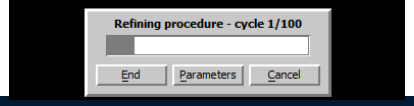


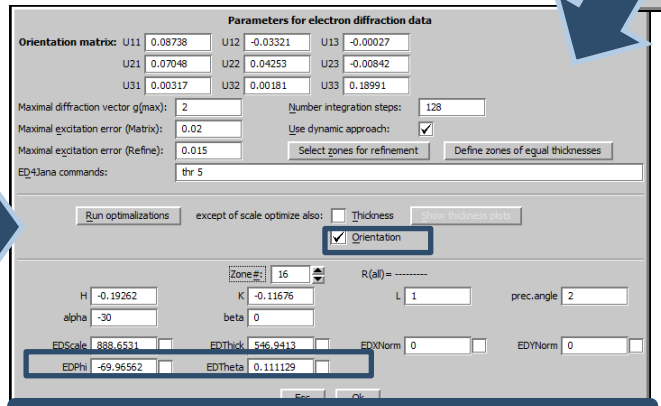
Set up the parameters of refinement, calculate thickness plots to indentify starting thickness



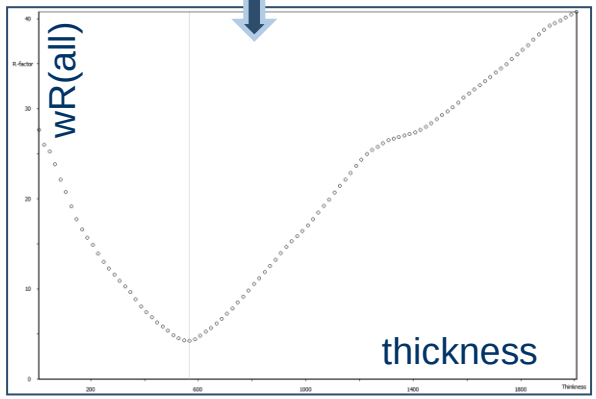


Run standard least-squares refinement. Refine structure parameters, sample thickness, scales of individual patterns.





Fine-tune the orientation of individual patterns



Palatinus et al. (2015), Acta Cryst. A69

Dynamical refinement – test results

material	kinematical		dynamical		computing time per cycle (desktop PC)	Remark
	ADRA / MDRA	R1	ADRA / MDRA	R1		
kaolinite	0.0946 / 0.2660	19.15	0.0216 / 0.0504	5.77	2 m 24 s	inverted structure R1=8.19
Ni_2Si	0.0206 / 0.0240	11.07	0.0076 / 0.0110	7.28	54 s	15 nm nanowire
Ni_3Si_2	0.0163 / 0.0482	17.95	0.0065 / 0.0139	8.45	5m 27s	35 nm nanowire
$PrVO_3$	0.1549 / 0.2395	21.52	0.0174 / 0.0298	9.11	1 m 52 s	
mayenite	0.0270 / 0.0392	17.56	0.0121 / 0.0334	8.63	16 m 20 s	partially occupied O visible in the difference Fourier
orthopyroxene	0.0492 / 0.0814	24.98	0.0104 / 0.0236	7.06	38 m	partial occupancies of Fe/Mg refined to accuracy better than 2%

Palatinus et al., Acta Cryst. B 2015a,b; Correa et al., J. Alloys Comp. 2016

Current challenges

- ✓ Can we still improve the fit to get to the typical x-ray levels of accuracy and figures of merit?
- ✓ Can we find data collection protocols that do not require PED and still can be well refined?
- ✓ Can we port the dynamical refinement strategy to macromolecules and is it necessary?
- ✓ Develop random diffraction tomography for the solution of *really* unstable crystals
- ✓ We need an appropriate instrument!

Future of electron crystallography

- ✓ Presentation of the method, more widespread use
- ✓ Use of special cameras with improved signal-to-noise ratio
- ✓ Random diffraction tomography, combination of diffraction from many crystals