Precession Diffraction: The Philospher's Stone of Electron Crystallography?

Focus

- Many methods exist for obtaining diffraction information
  - Selected Area
  - Nanodiffraction and variants
  - CBED
- All are complicated to interpret
- Reciprocal space is right, but intensities depend upon thickness, tilt etc

What PED can do

- We would like a method where not just the positions of the spots, but also the intensities could be used.
- Not rigorously equivalent to simple kinematical diffraction, but has many similarities
  - If the structure factor is large → Intensity is large
  - Useful for fingerprinting structures
  - Often does not need calculations to interpret

History – Electron Precession (1993)

Double conical beam-rocking system for measurement of integrated electron diffraction intensities

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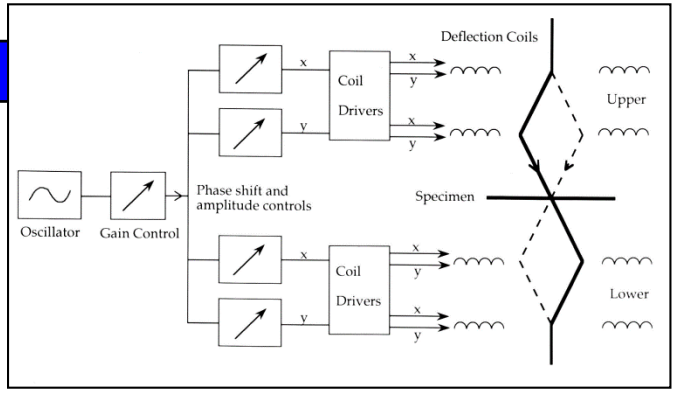
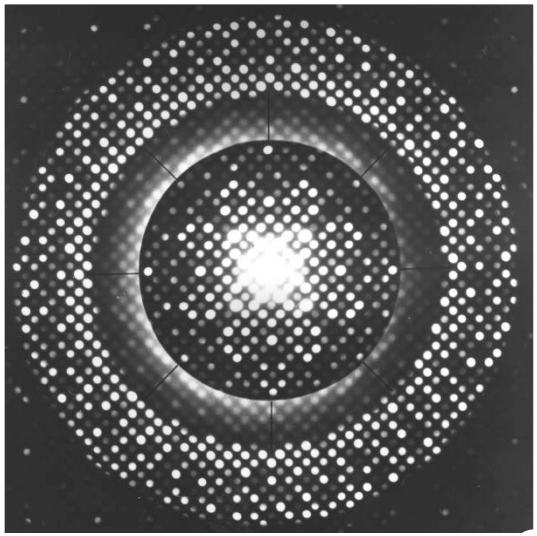
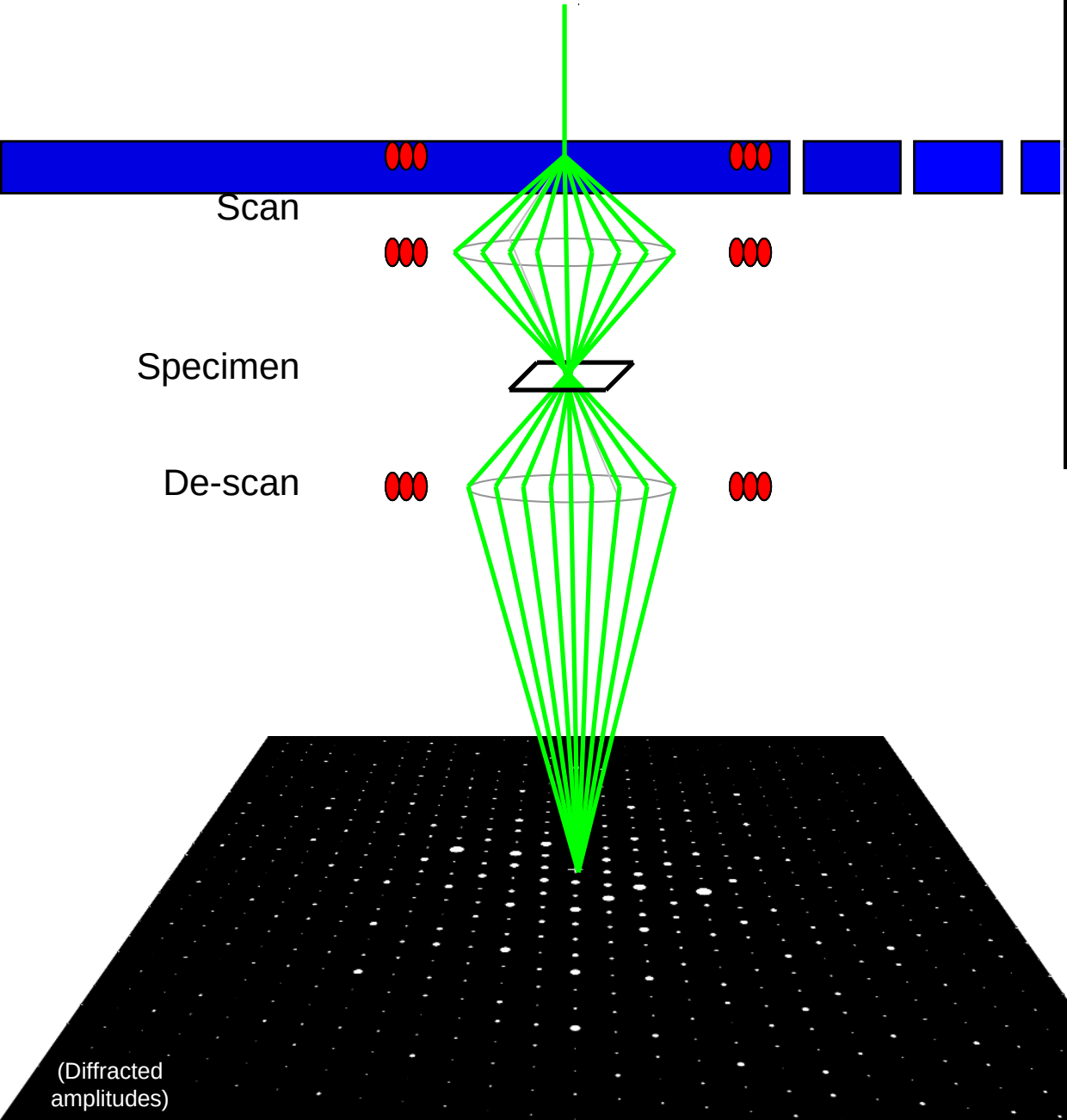
(Received 26 July 1993; in final form 4 October 1993)

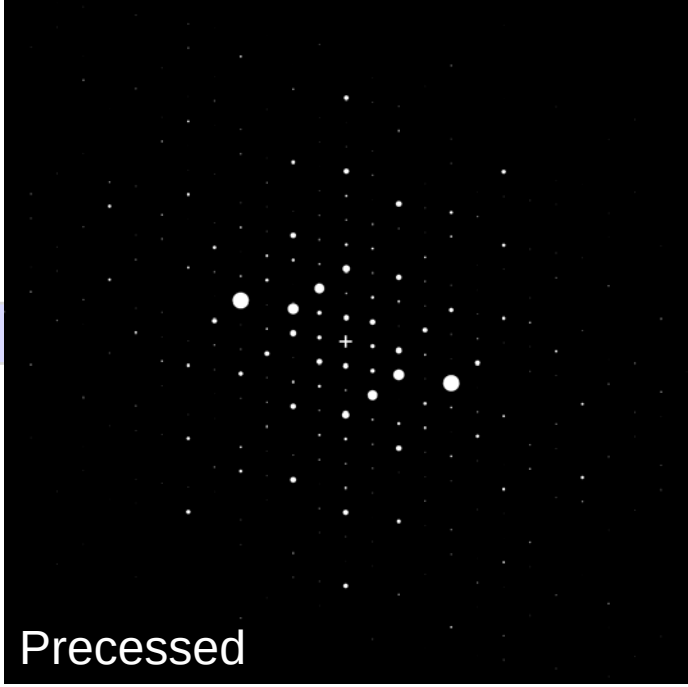


Advantages:

1. PRECESSION → MANY MORE REFLECTIONS INTERCEPTED BY EWALD SPHERE → LARGE DATA SET
2. DIFFRACTED INTENSITIES DETERMINED BY INTEGRATING THROUGH BRAGG CONDITION → NO BRANCH STRUCTURE
   ∴ $I_g \rightarrow |U_g|^2$ (NOT PARTIAL S.F.)
3. REDUCES NON-SYSTEMATIC DYNAMICAL EFFECTS
4. FOCUSSED PROBE → HIGH SPATIAL RESOLUTION (~0·1μm)







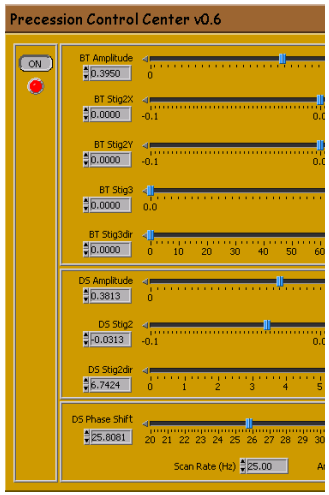
$(Ga,In)_2SnO_5$ Intensities

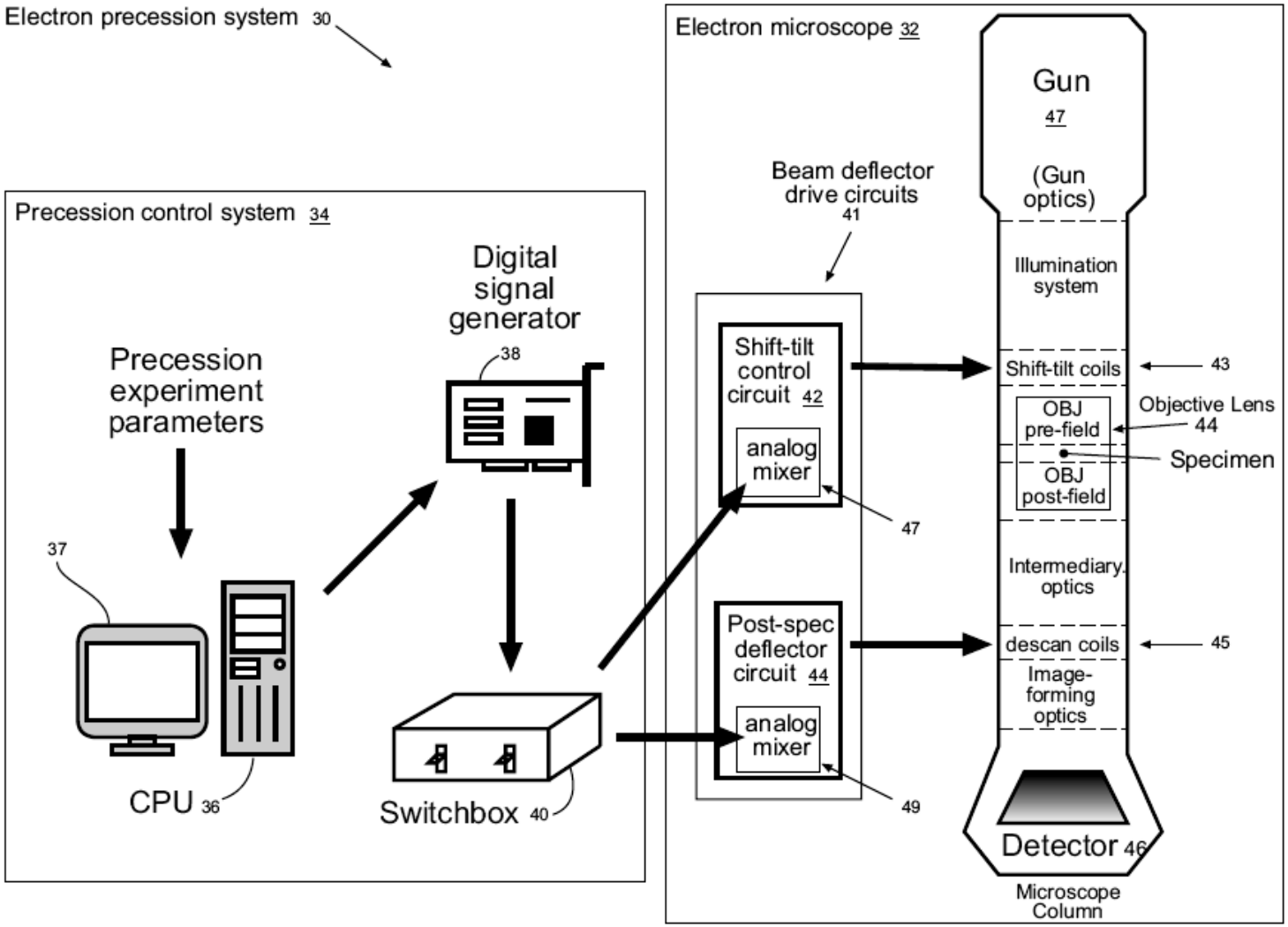
412Å crystal thickness

Conventional Precession Diffraction Pattern

Precession System

US patent application:
"A hollow-cone electron diffraction system".
Application serial number 60/531,641, Dec 2004.





SPINNING STAR : UNIVERSAL INTERFASE FOR PRECESSION ELECTRON DIFFRACTION FOR ANY TEM (120 -200 -300 KV)

- Can be easily retrofitable to any TEM 100- 300 KV
- **precession is possible for any beam size 300 - 50 nm**
- Precession is possible for a parallel or convergent beam
- **precession eliminates false spots to ED pattern that belong to dynamical contributions**
- precession angle can vary continuously (0°-3°) to observe true crystallographic symmetry variation
- **Software ELD for easy quantification of ED intensities and automatic symmetry (point, space group) research**

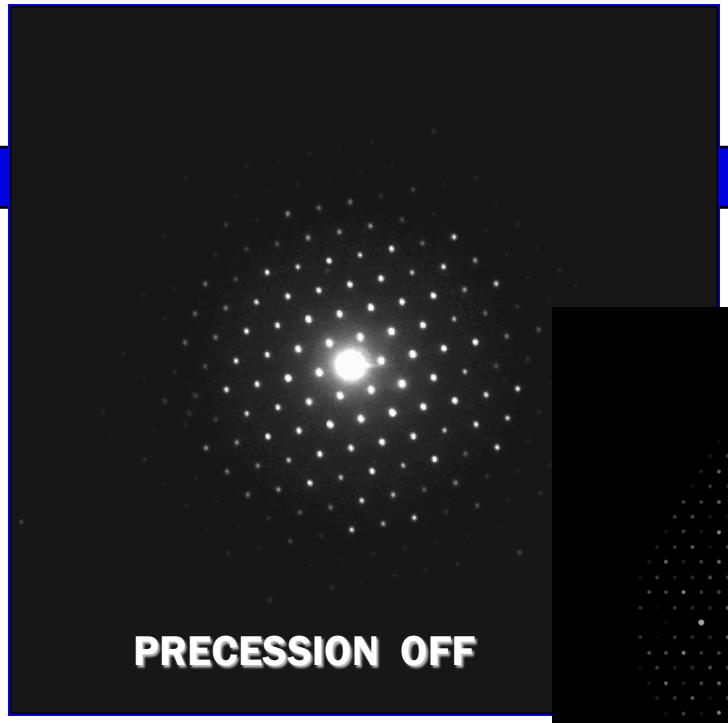
- Easily interfaced to electron diffractometer for automatic 3D structure determination

NanoMEGAS
Advanced Tools for electron diffraction

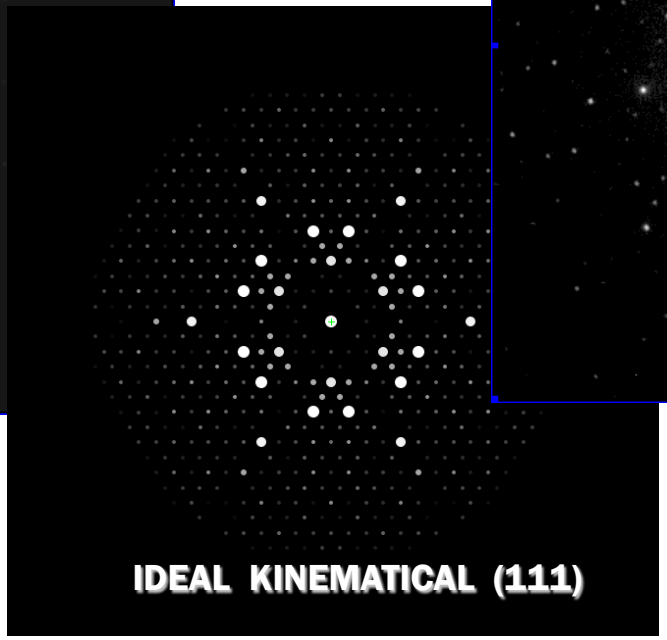
Examples:

- Complicated Structures
  - Hard to interpret SAED
  - Simple to interpret PED
- EDS
  - Elemental ratio’s depend upon orientation in standard mode
  - Weak to no dependence with PED

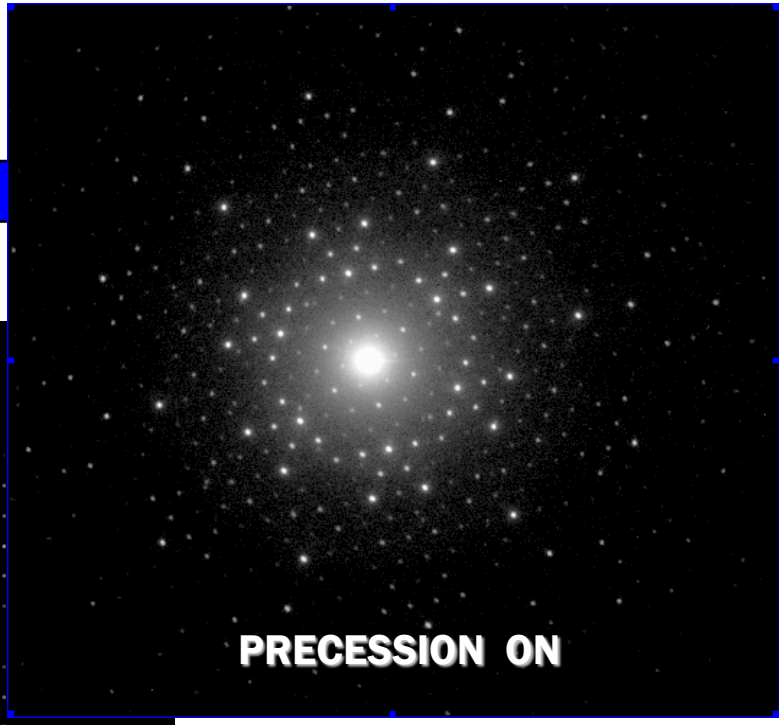
APPLICATION : FIND TRUE CRYSTAL SYMMETRY



PRECESSION OFF



IDEAL KINEMATICAL (111)



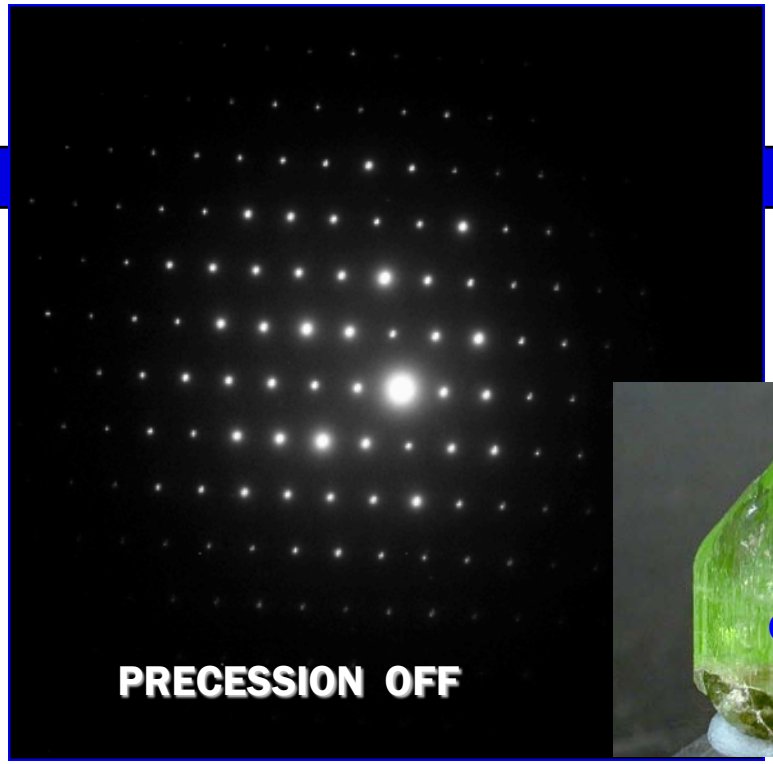
PRECESSION ON

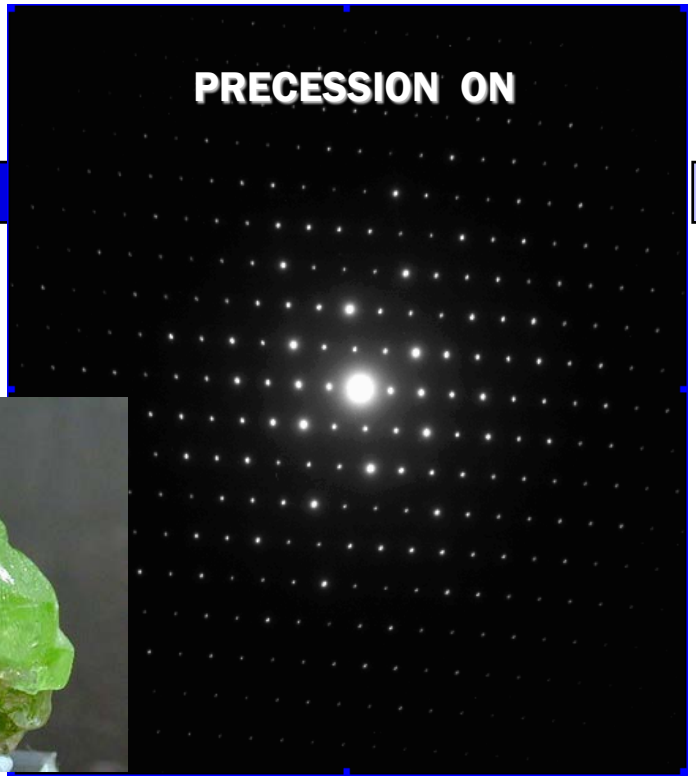
UVAROVITE (111)

Courtesy M.Gemmi
Univ of Milano

NanoMEGAS
Advanced Tools for electron diffraction

APPLICATION : PERFECT CRYSTAL ORIENTATION

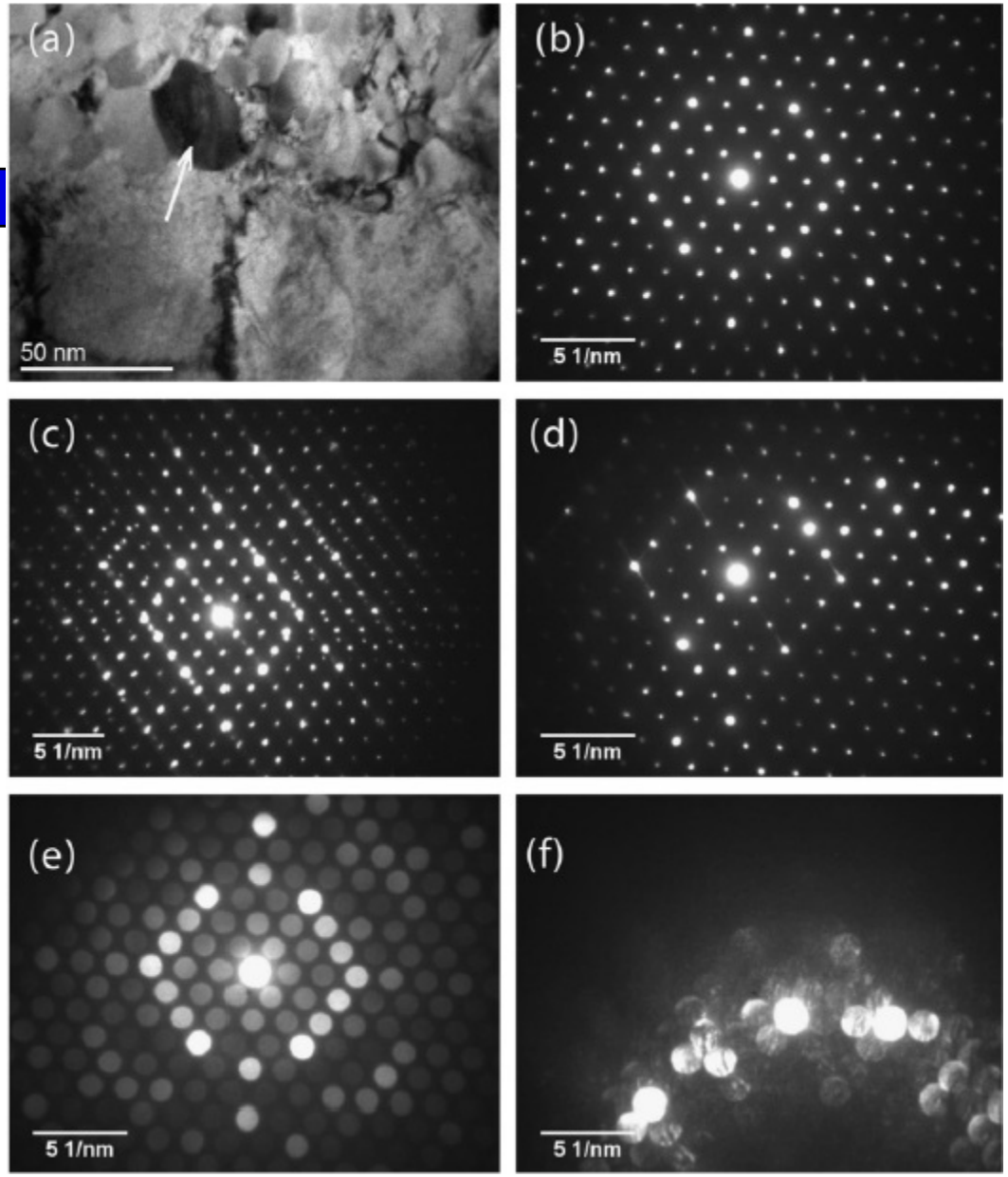




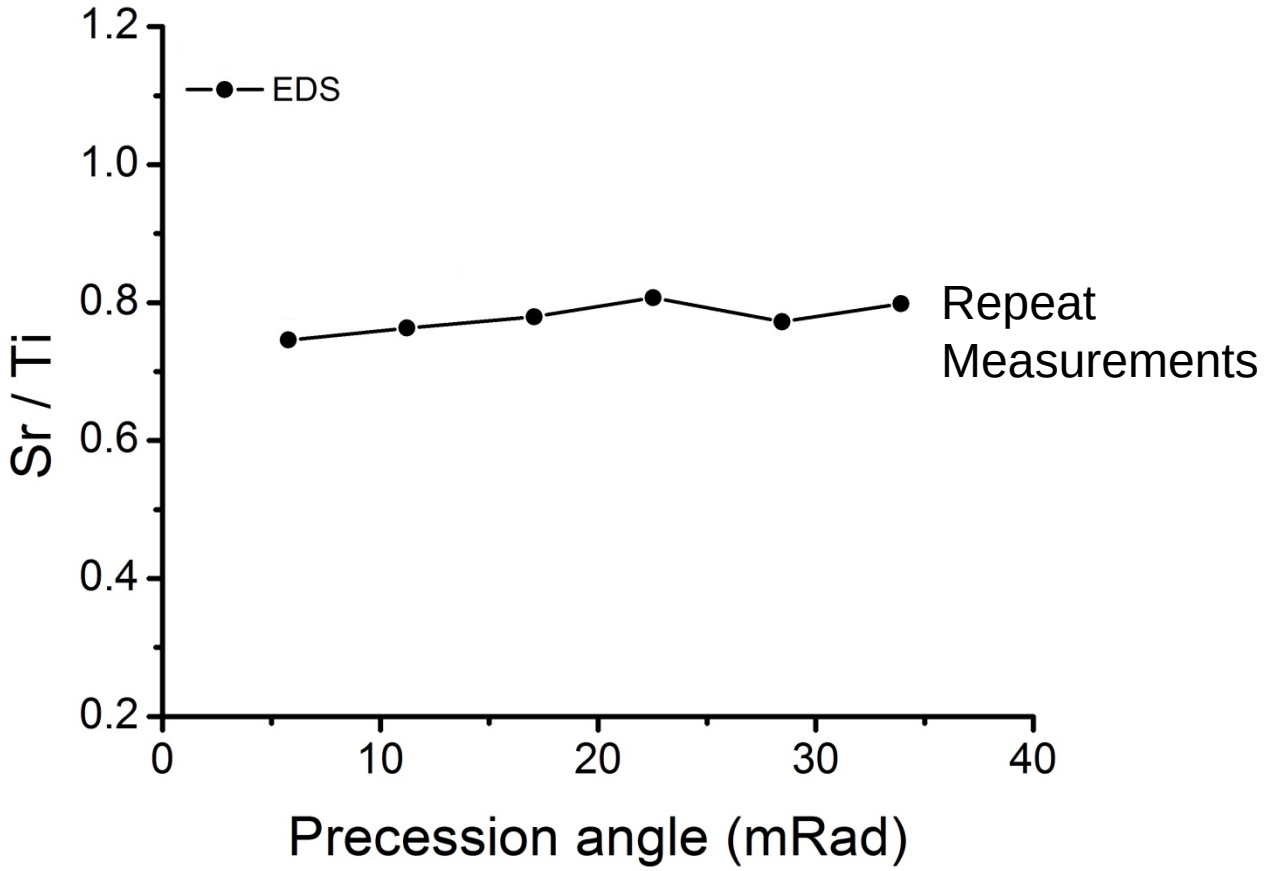
Crystals –specially minerals -usually grow in platelet or fiber shape and results dificult to orient perfectly in a particular zone axis; in this example olivine crystals are perfectly oriented after precession is on.

Courtesy X.Zou, S.Hovmoller Univ Stockholm

Carbide



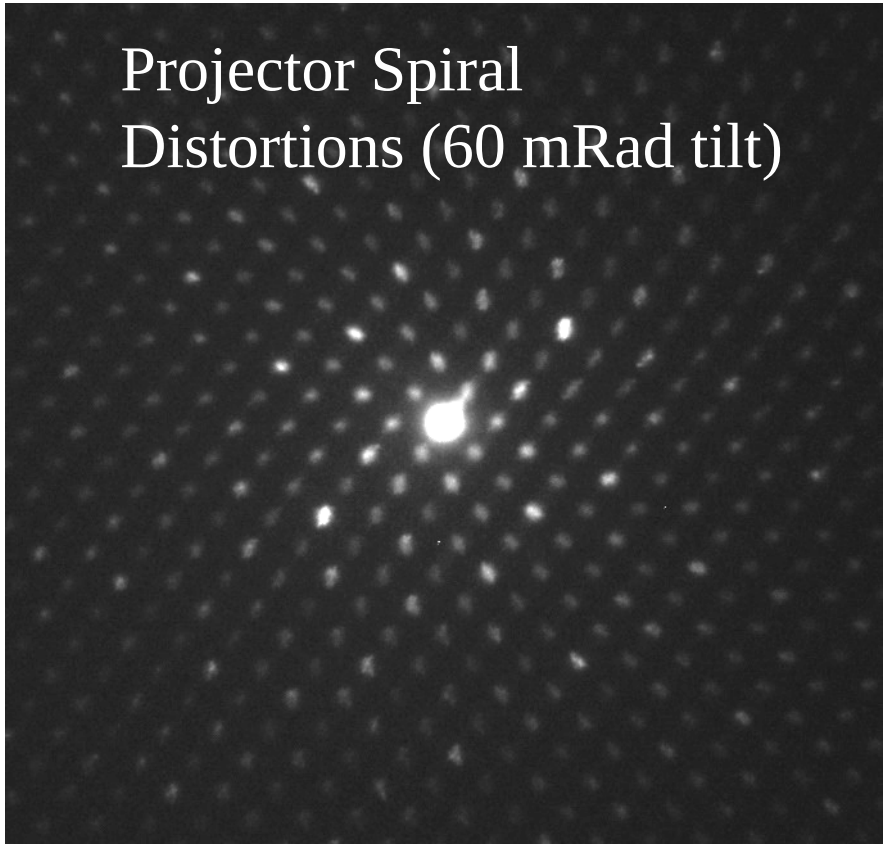
EDS, on zone ($SrTiO_3$)



Practical Use

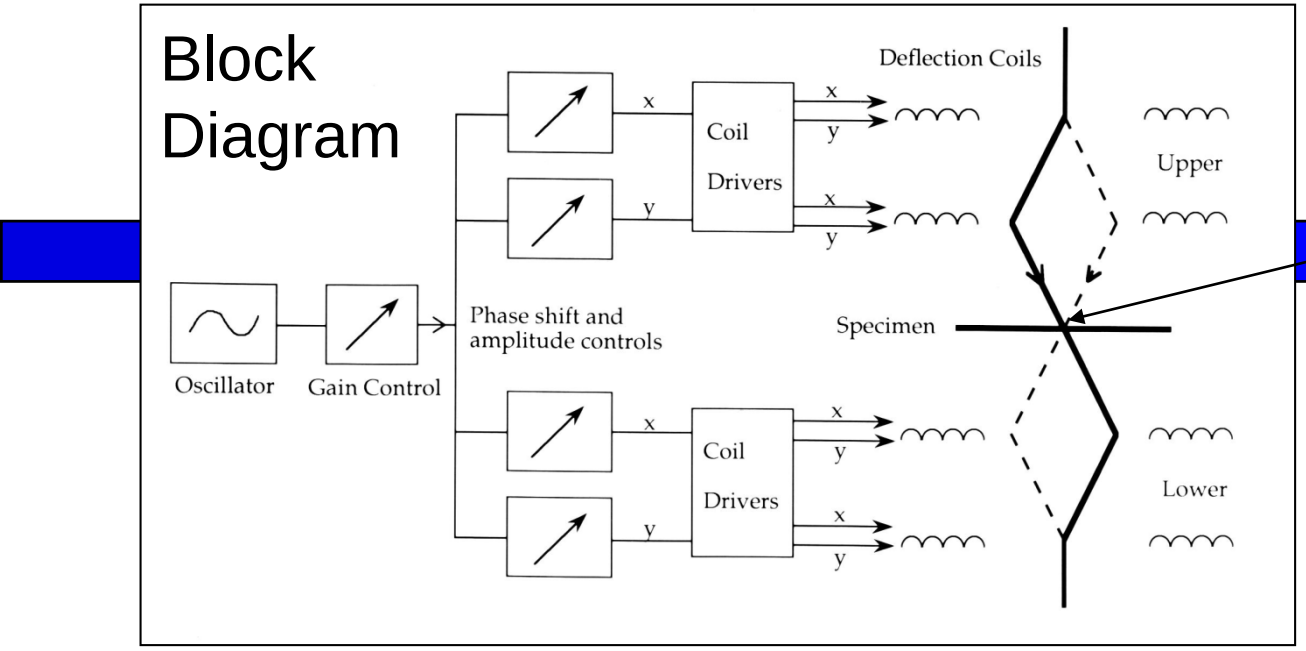
- Two commercial systems (one hardware, another software) are available
- Not complicated, and could probably be written in scripting language
- Alignment can be tricky – it always is
- Not rocket science to use

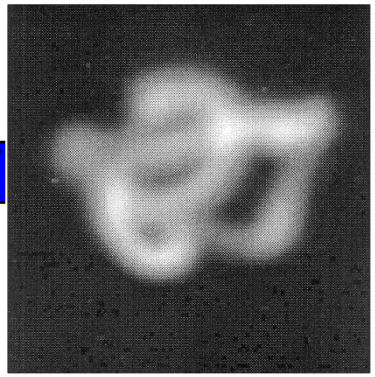
Some Practical Issues



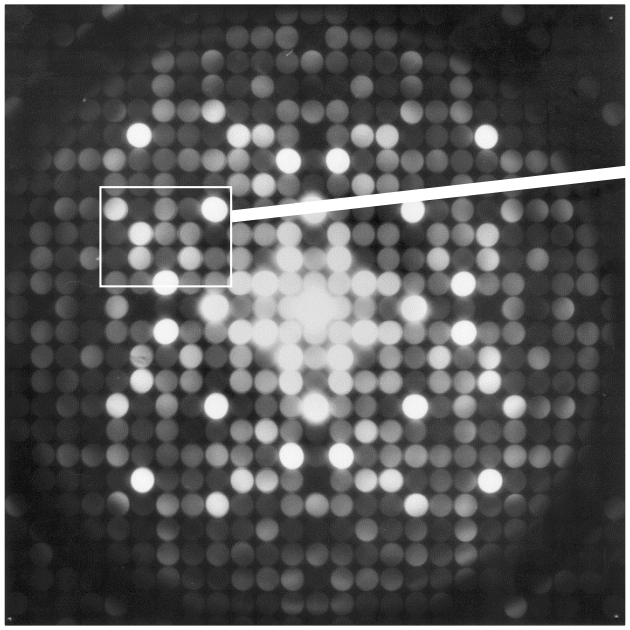
Bi-polar push-pull circuit
(H9000)

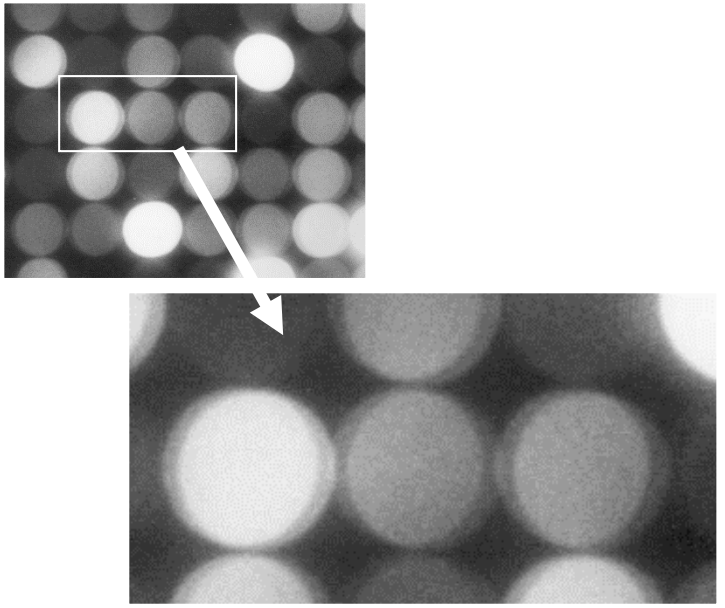
Block Diagram





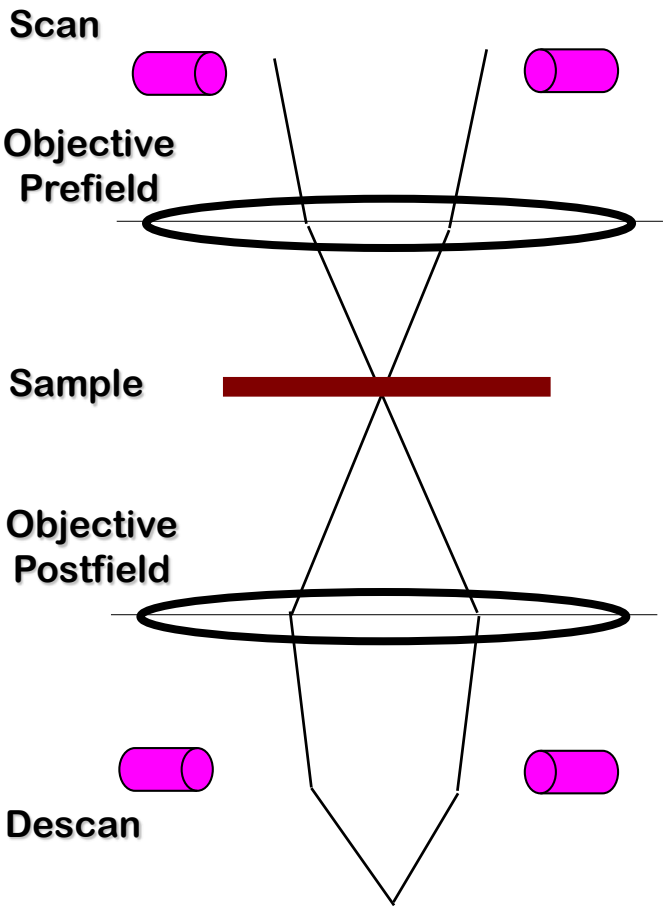
‘Aberrations’





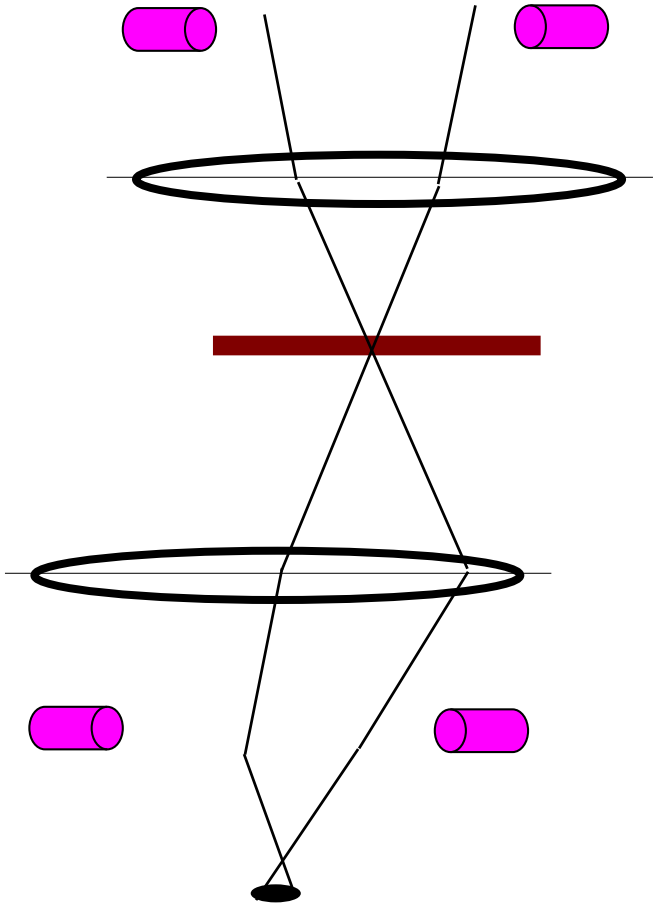
Optics

Idealized Diagram

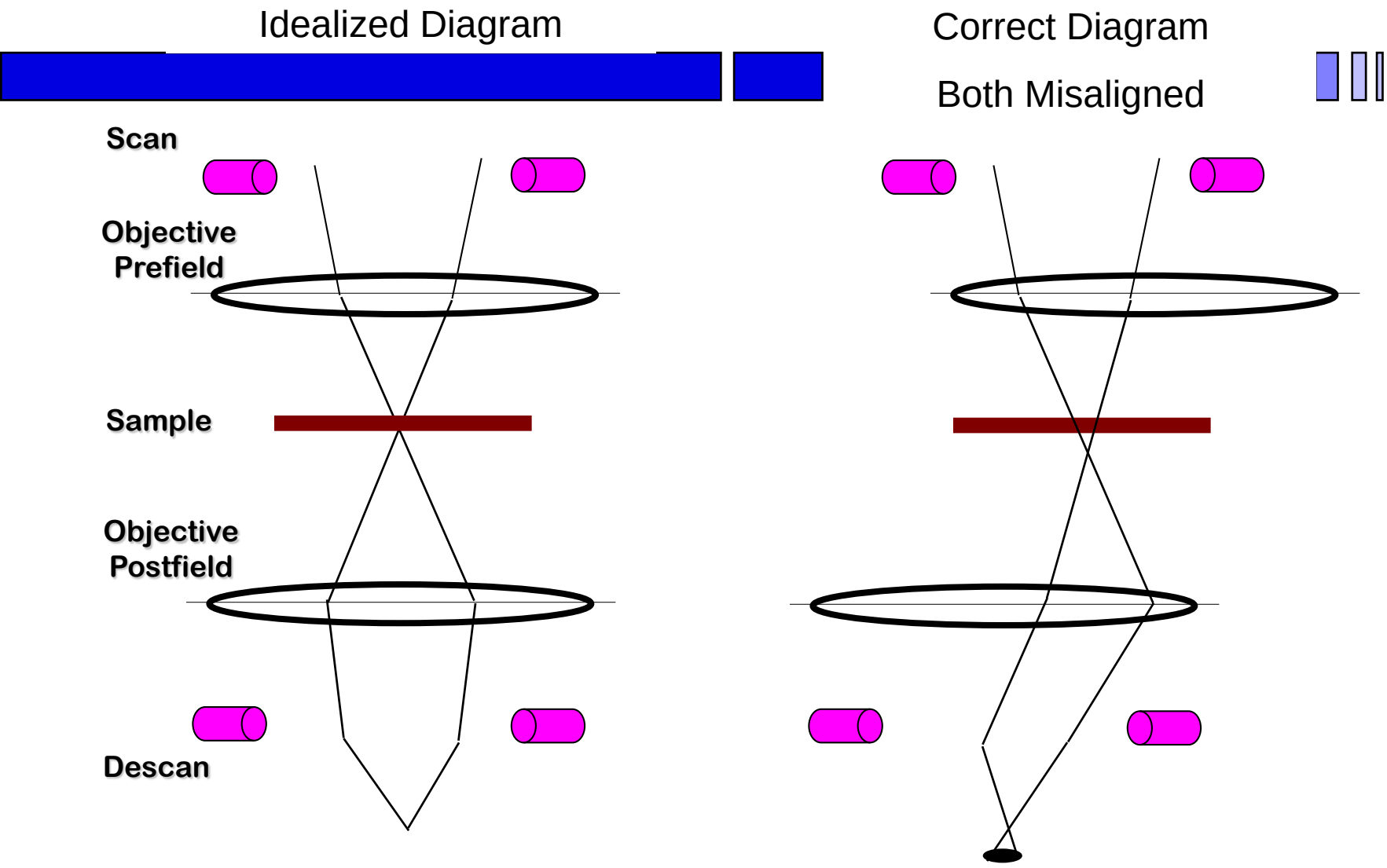


Better Diagram

Postfield Misaligned



Optics


Idealized Diagram
Correct Diagram
Both Misaligned
Scan
Objective
Prefield
Sample
Objective
Postfield
Descan

One Consequence

- Prefield/Postfield displacements of beam

$d^{Pre} = 1/(2\pi)\ \nabla\chi^{Pre}(s-t^{Pre});$ $\quad s$ = Scan

$d^{Post}=1/(2\pi)\ \nabla\chi^{Post}(s-t^{Post}) - s^{D}\theta$ $\quad s^{D}$ = DeScan

$\nabla\chi(u)/(2\pi) = \Delta z\theta+C_s\theta^3$

Total apparent displacement is the sum

$d^{Nett} = d^{Pre}+d^{Post}$

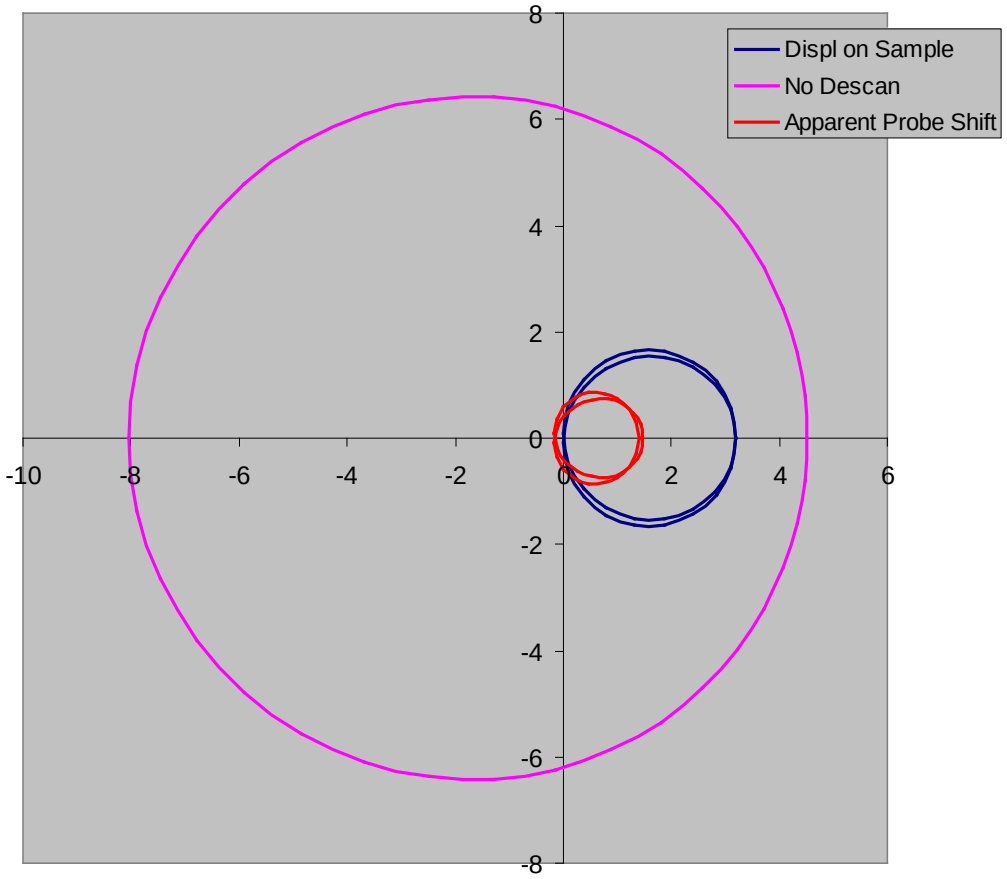
$= \Delta z^{Pre}(\theta-\theta^{Pre})+\Delta z^{Post}(\theta-\theta^{Post})$

$+ C_s{}^{Pre}(\theta-\theta^{Pre})^3+C_s{}^{Post}(\theta-\theta^{Post})^3$

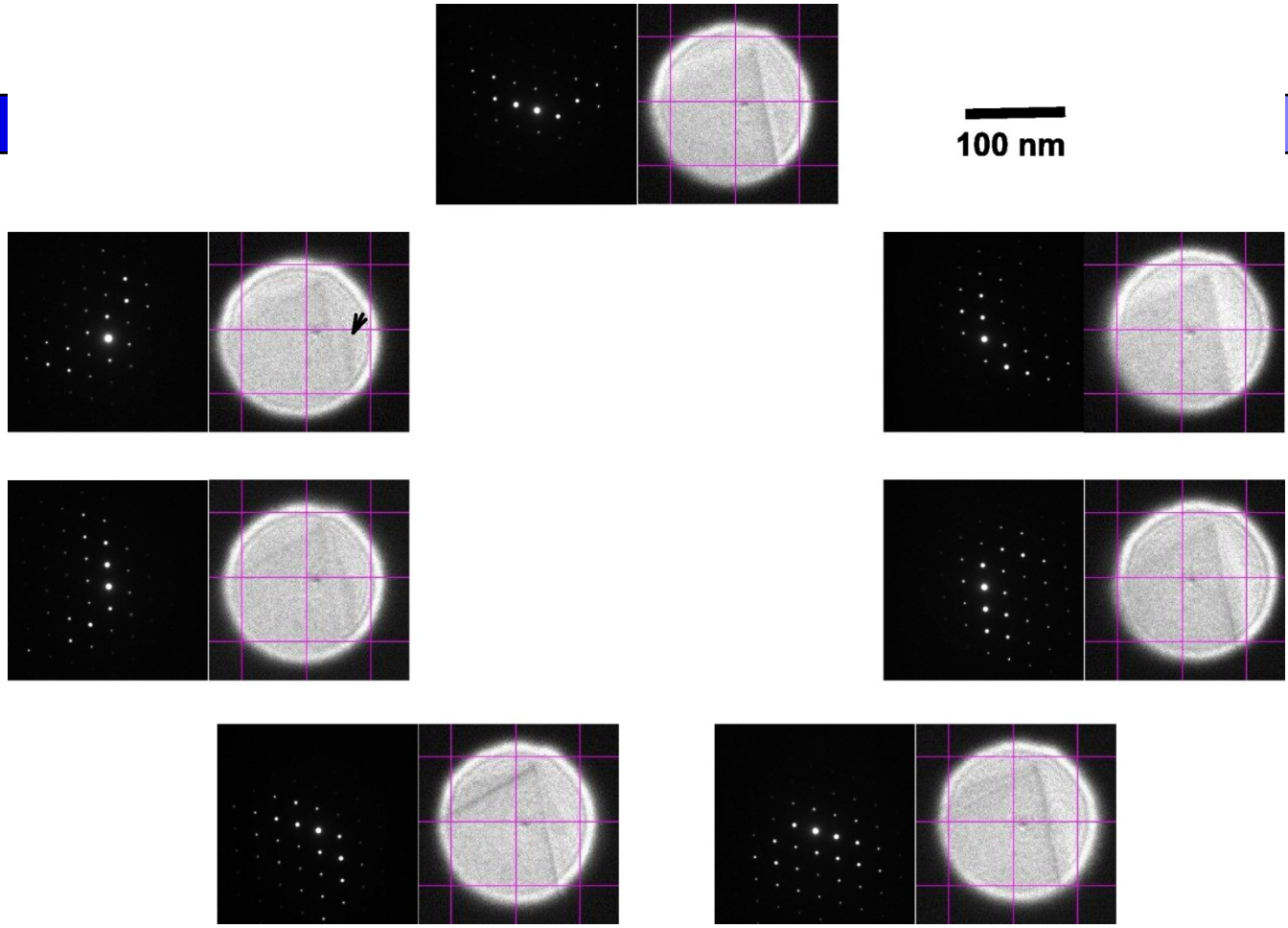
$-s^{D}\theta$

Probe and Displacements (nm)

Prefield misalignment 1 mRad; Postfield -1.0 mRad



Caveat: this ignores 3-fold astigmatism in pre/post field which is probably not appropriate, and any projector distortions


100 nm

Alignment can be tricky

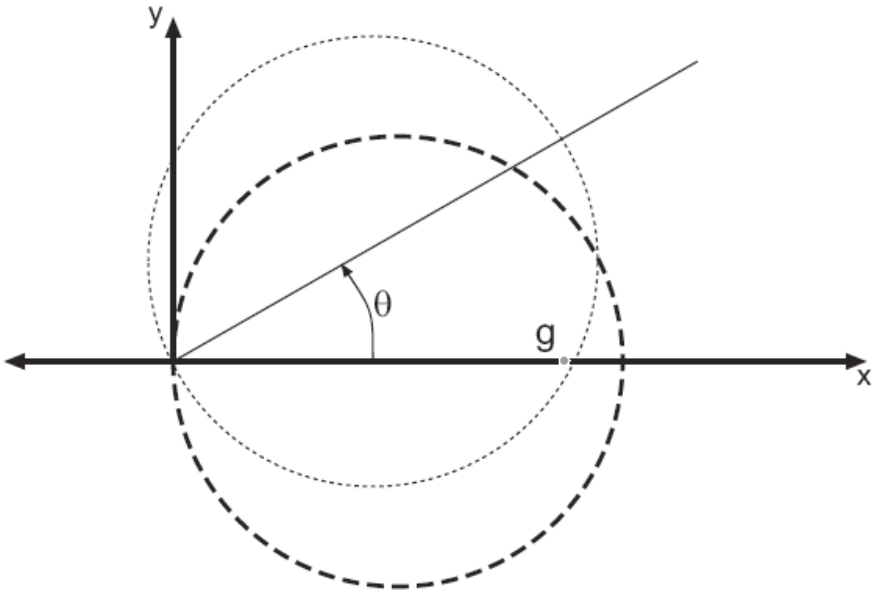
Why?

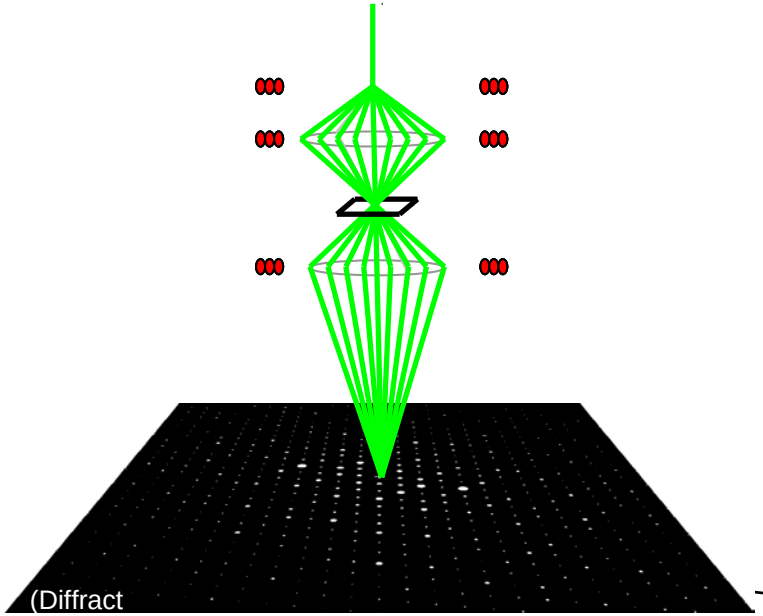
- Although PED has been around since 1992, and very actively used for ~10 years (mainly in Europe), there is *no* simple explanation (many have tried and failed)
- Explanation is a bit rocket science

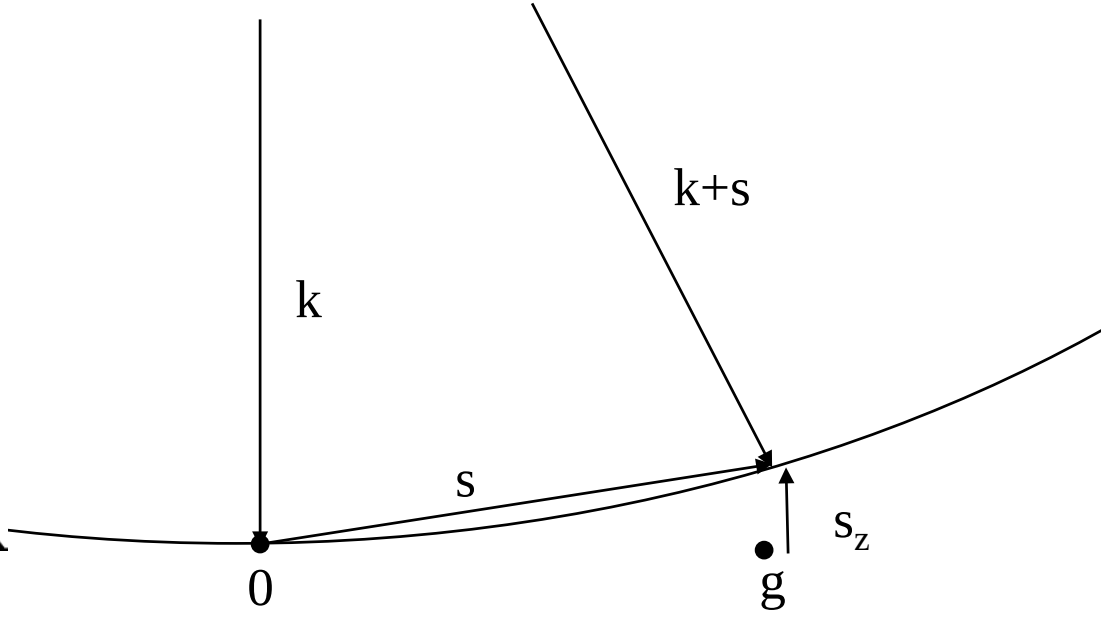
Why?

- What, if any generalizations can be made?
- Role of Precession Angle
  - Systematic Row Limit
- Importance of integration
  - Phase insensitivity
  - Important for which reflections are used
  - Fast Integration Options

Ewald Sphere Construction







Levels of theory

- Precession integrates each beam over s_z
- Full dynamical theory
  - All reciprocal lattice vectors are coupled and not seperable
- Partial dynamical theory (2-beam)
  - Consider each reciprocal lattice vector dynamically coupled to transmitted beam only
- Kinematical theory
  - Consider only role of s_z assuming weak scattering
- Bragg's Law
  - $I = |F(g)|^2$

Early Models

I_{obs} depends upon |F(g)|, g, ϕ (precession angle) which we "correct" to the true result

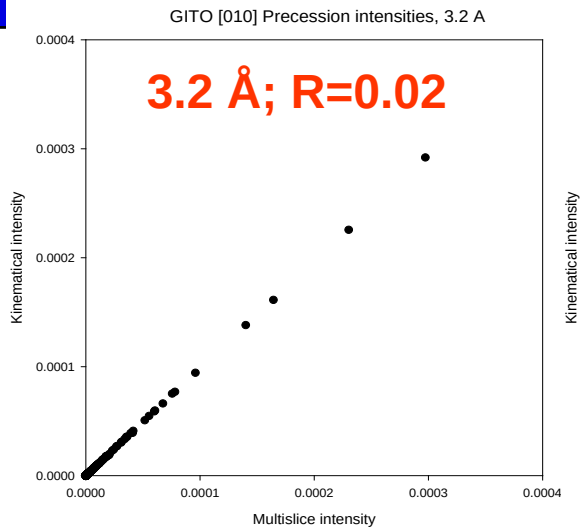
Options:

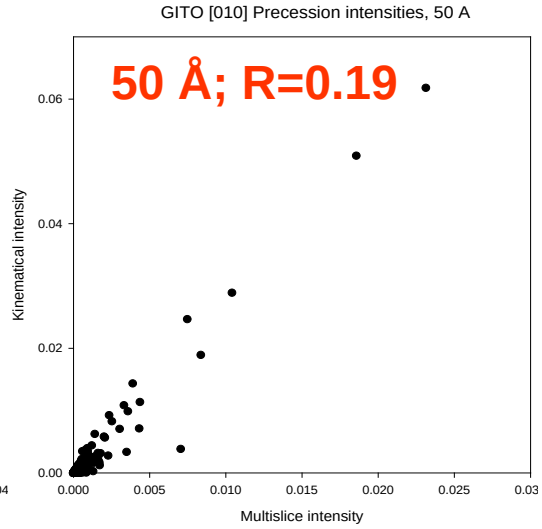
0) No correction at all, $I=|F(g)|^2$

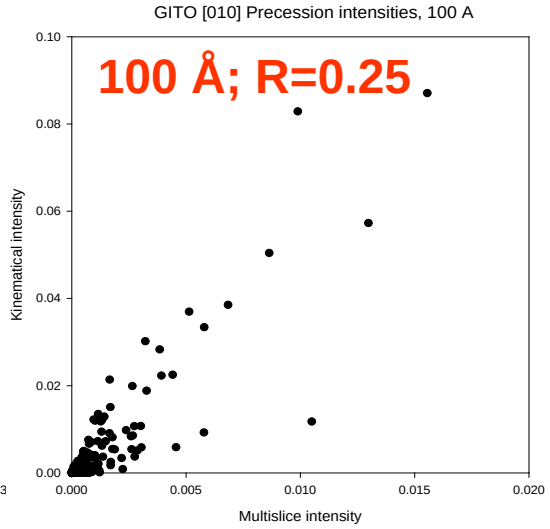
1) Geometry only (Lorentz, by analogy to x-ray diffraction) corresponds to angular integration

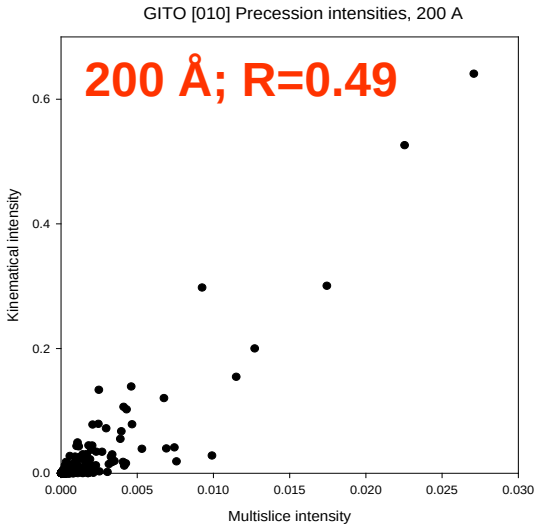
2) Geometry plus multiplicative term for |F(g)|

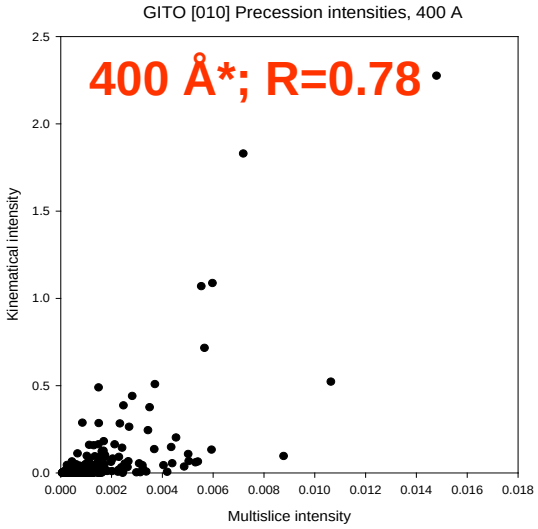
Bragg's Law fails badly $(Ga,In)_2SnO_5$

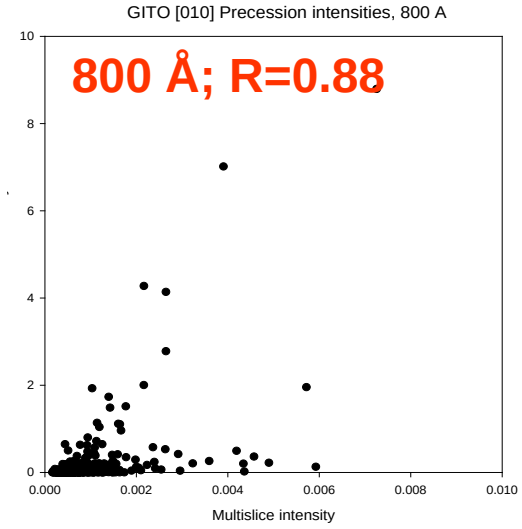












Kinematical Lorentz Correction

$I(g) = \int |F(g)\, \sin(\pi t s_z)/(\pi s_z)\,|^2\, ds_z$

s_z taken appropriately over the Precession Circuit

t is crystal thickness (column approximation)

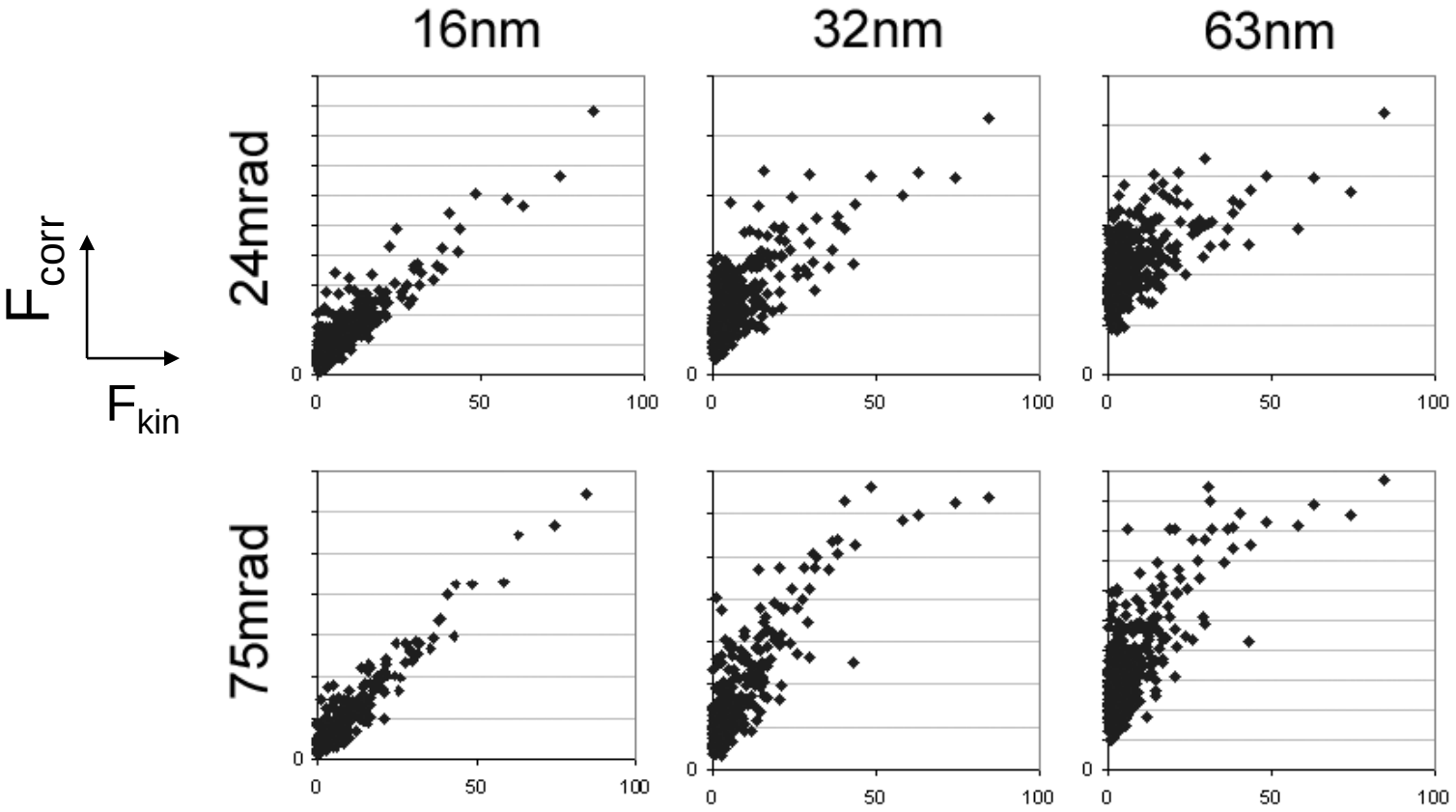
ϕ is total precession angle

$I(g) = |F(g)|^2 L(g,t,\phi)$ $\quad L(g,t,\phi) = g\sqrt{1-\left(\frac{g}{2R_0}\right)^2}$

K. Gjønnes, Ultramicroscopy, 1997.

Kinematical Lorentz correction:

Geometry information is insufficient



Need structure factors to apply the correction!

2-Beam (Blackman) form

$$I_{Blackman}(t) = \int_0^{A_g} J_0(2x)dx;\ \ A_g(k) \propto tF(k)$$

Limits:

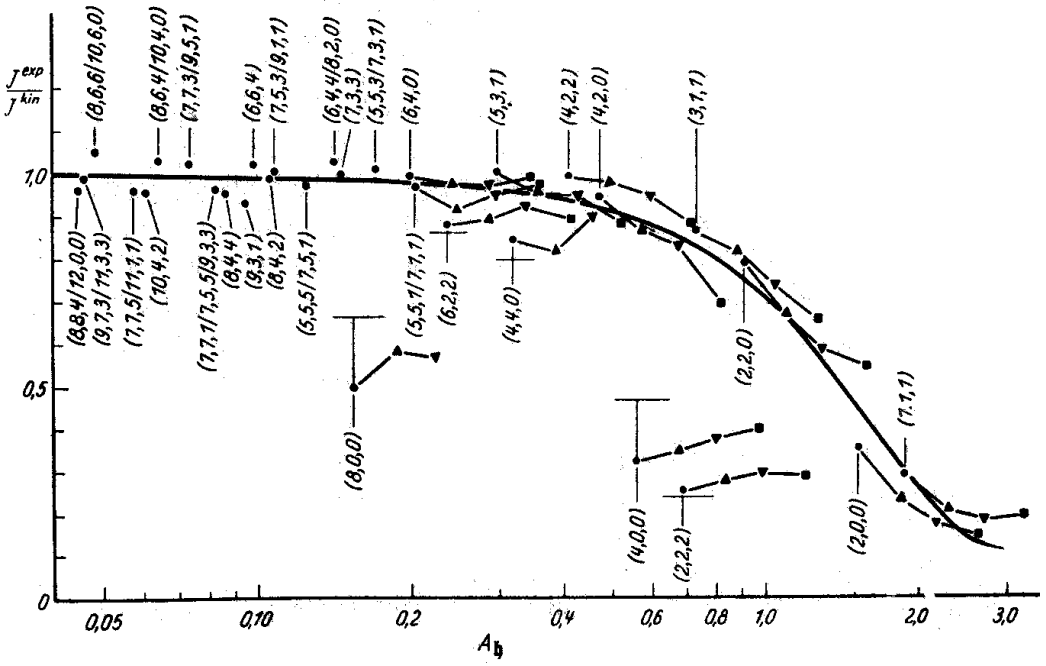
A_g small; $I_{dyn}(k) \propto I_{kin}(k)$

A_g large; $I_{dyn}(k) \propto \sqrt{I_{kin}(k)} = |F_{kin}(k)|$

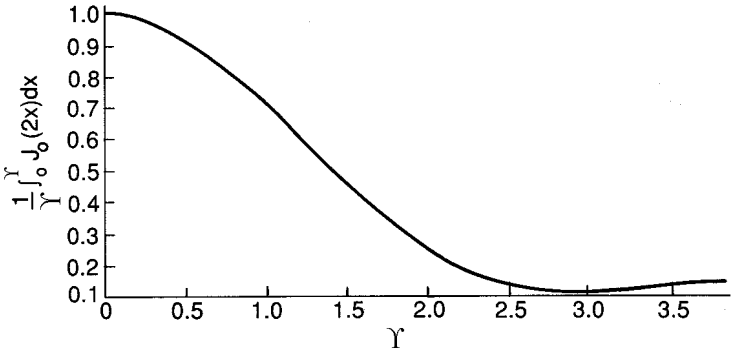
But…

This assumes integration over all angles, which is not correct for precession (correct for powder diffraction)

Blackman Form



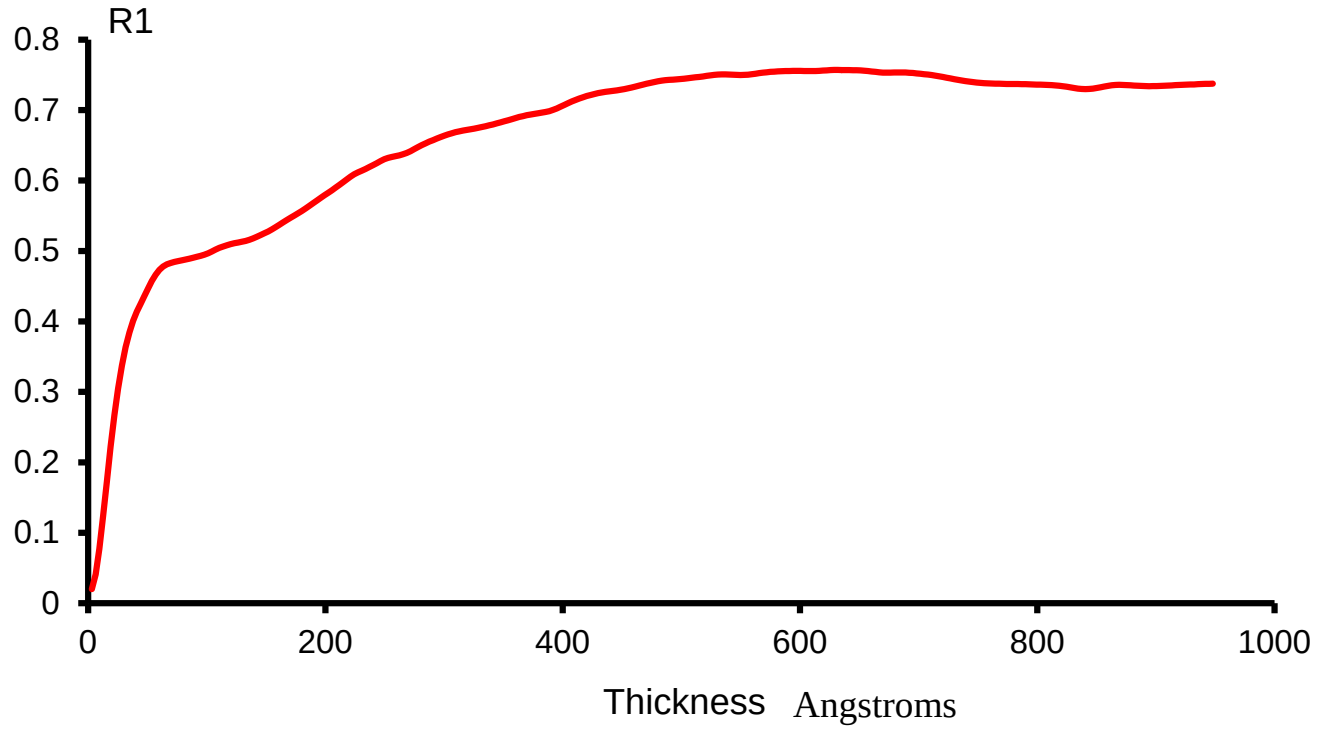
The Blackman curve (Blackman [1939]) for the ratio of dynamical to kinematical intensities for a ring pattern as a function of $A = \sigma H \Phi_h$. The experimental points are those obtained by Horstmann and Meyer [1965], from measurements on ring patterns from aluminum films at various voltages. The short horizontal lines indicate values calculated using the Bethe potentials, equation (12). (After Horstmann and Meyer [1965].)



"Blackman curve" used for "two-beams corrections"

Blackman+Lorentz

Comparison with full calculation, 24 mRad



Alas, little better than kinematical

Two-Beam Form

$I(g) = \int | F(g) \sin(\pi t s^{eff}_z)/(\pi s^{eff}_z) |^2 \, ds_z$

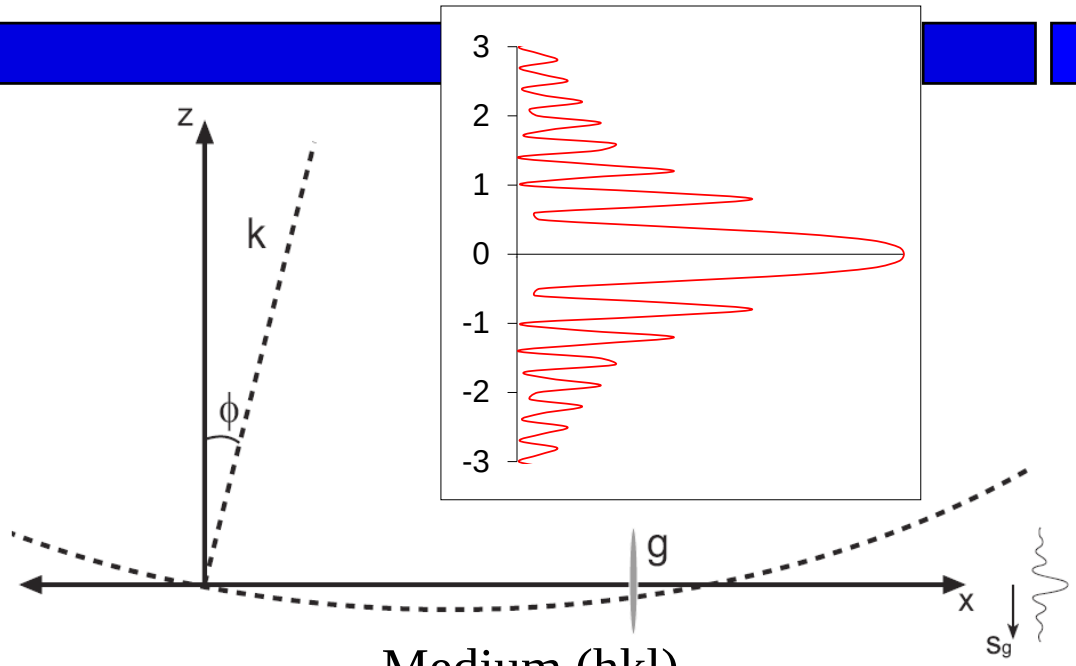
s_z taken appropriately over the Precession Circuit

$s_z^{eff} = (s_z^2 + 1/\xi_g^2)^{1/2}$

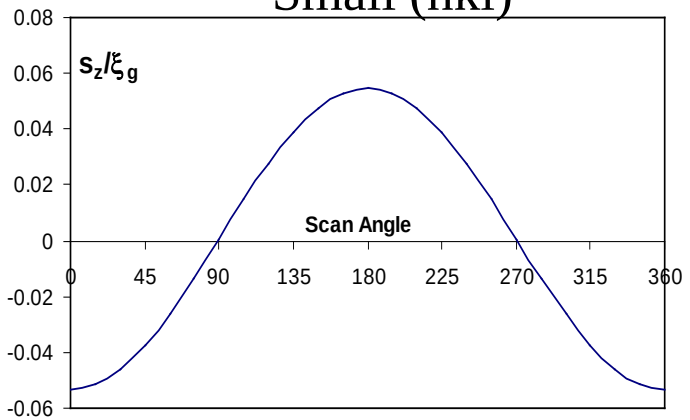
$$\xi_g = \frac{\pi V_c \cos\theta_B}{\lambda F_g}$$

Do the proper integration over s_z

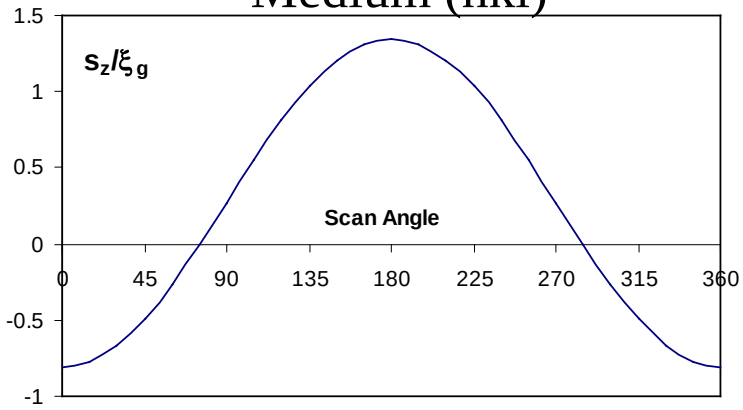
Two-Beam Integration: Ewald Sphere



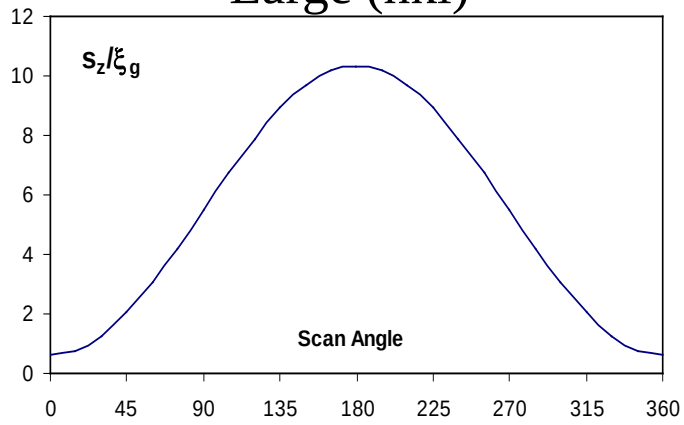
Small (hkl)



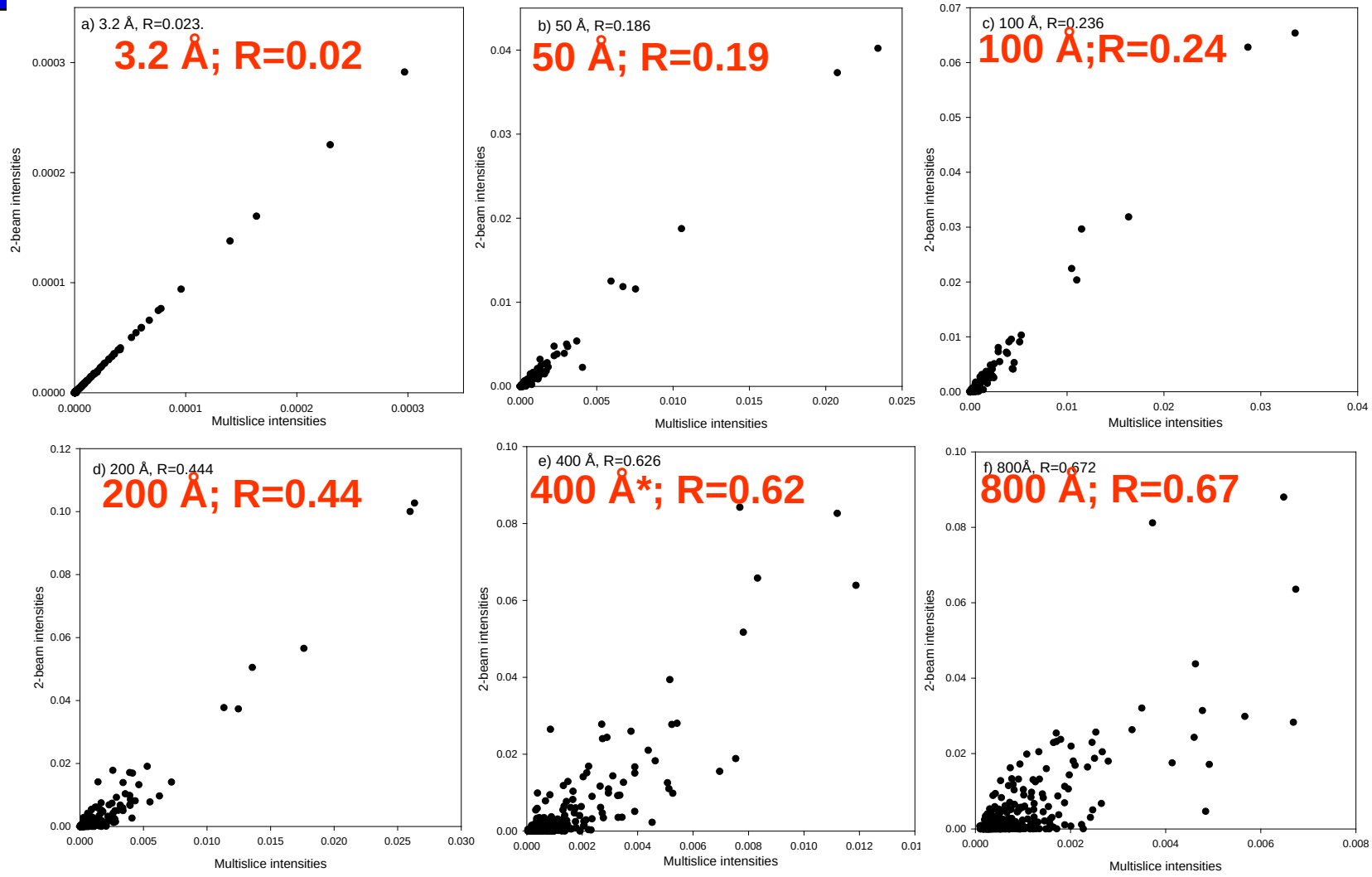
Medium (hkl)



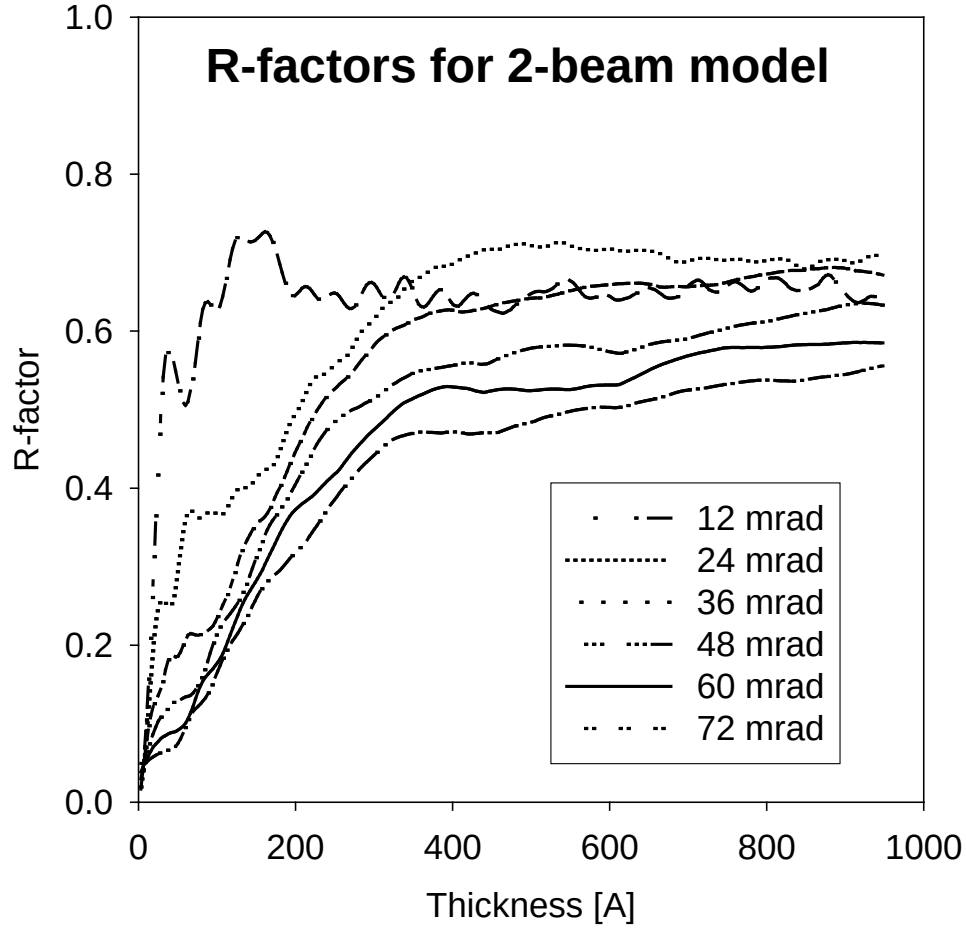
Large (hkl)

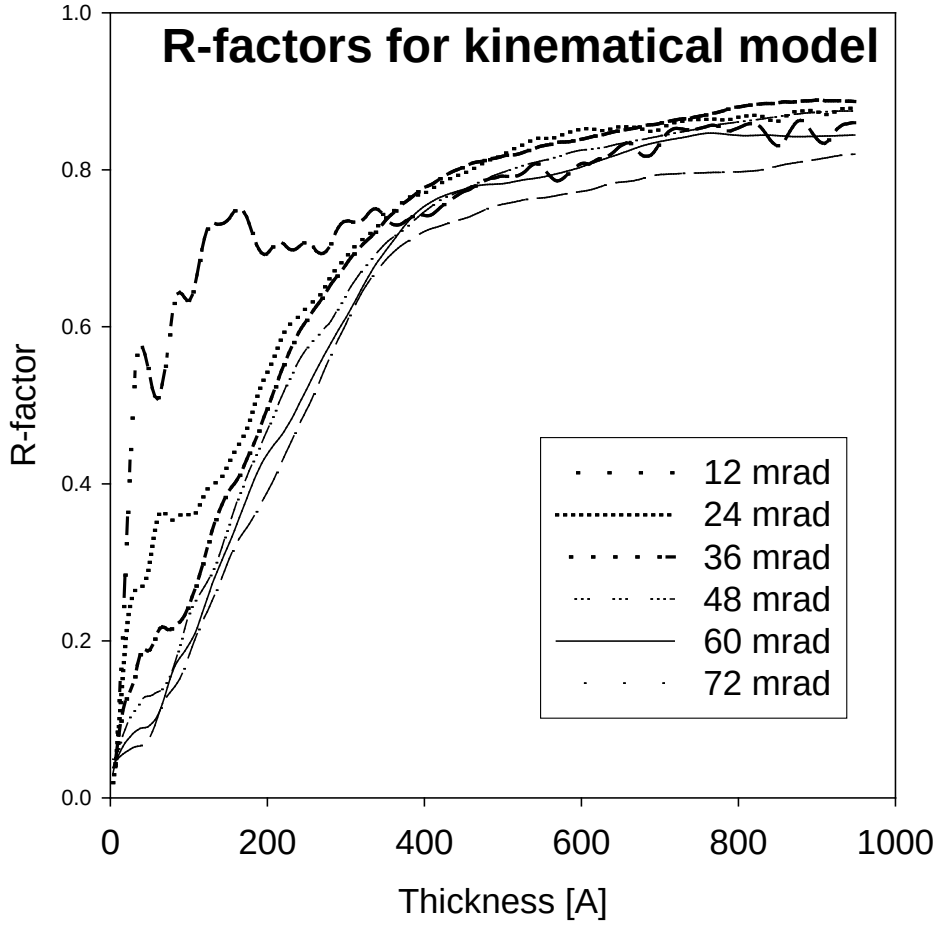


2-Beam Integration better



Some numbers

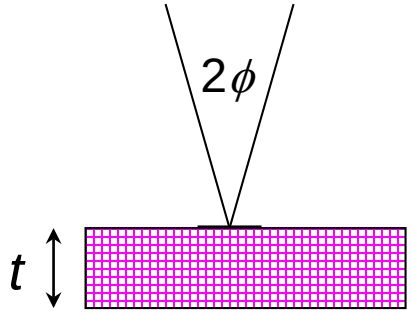


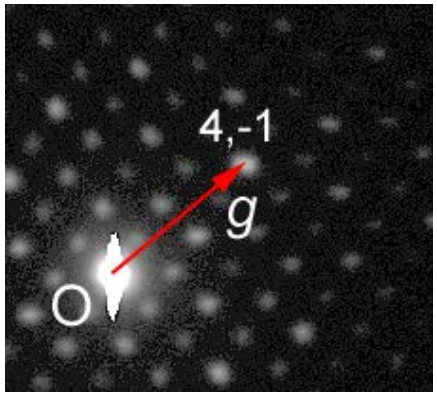


See Sinkler, Own and Marks, Ultramic. 107 (2007)

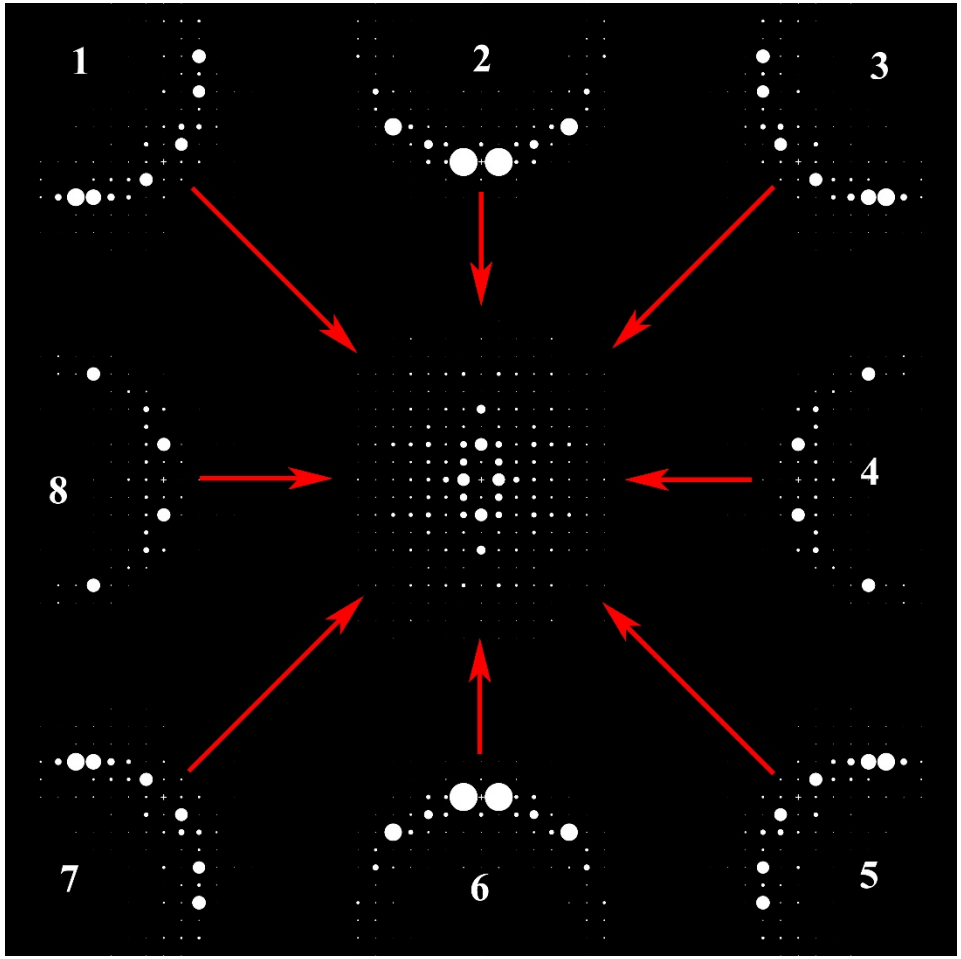
Fully Dynamical: Multislice

- "Conventional" multislice (NUMIS code, on cvs)
- Integrate over different incident directions
  100-1000 tilts
- ϕ = cone semi-angle
  - 0 – 50 mrad typical
- t = thickness
  - ~20 – 50 nm typical
  - Explore: 4 – 150 nm
- $\boldsymbol{g}$ = reflection vector
  - $|g|$ = 0.25 – 1 Å^{-1} are structure-defining





Multislice Simulation



Multislice simulations carried out using 1000 discrete tilts (8 shown) incoherently summed to produce the precession pattern[1]

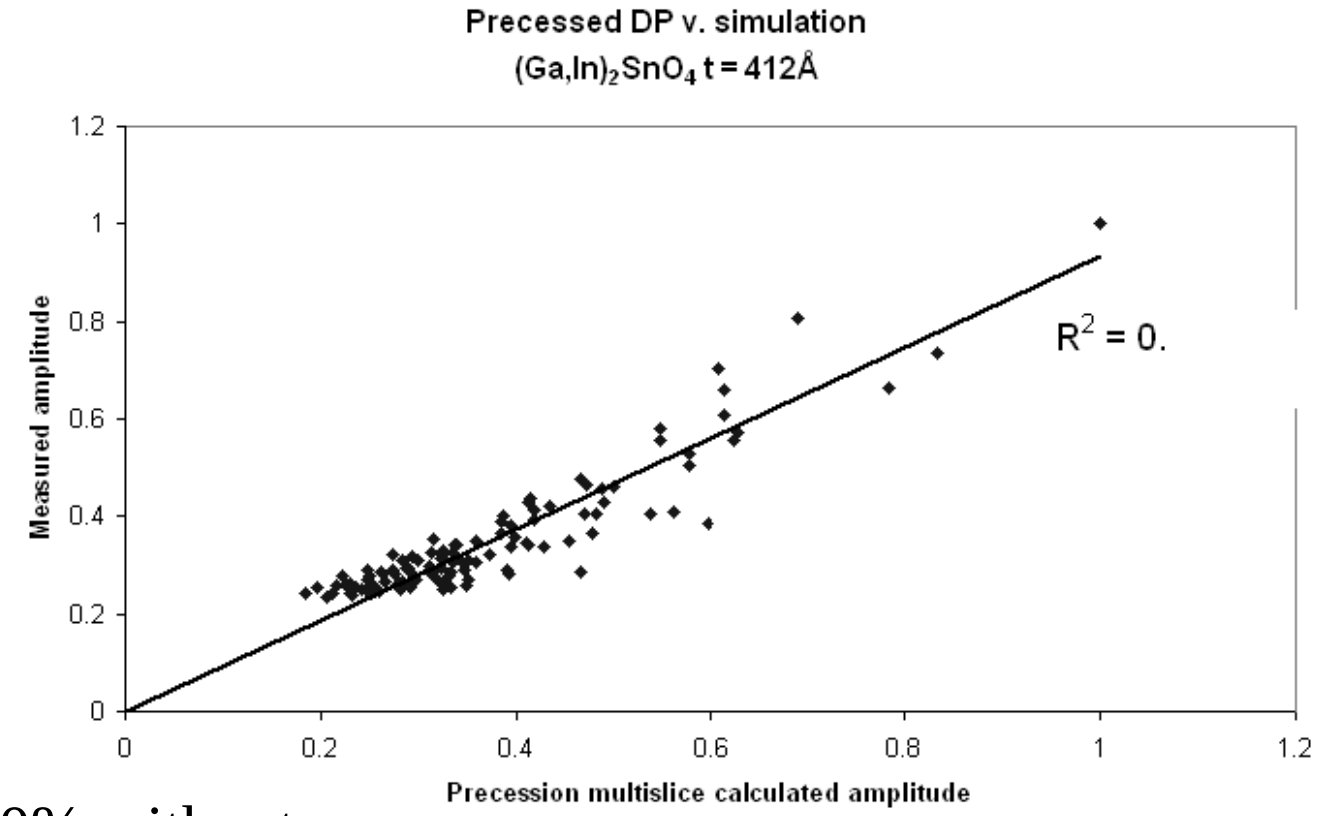
How to treat scattering?

1) Doyle-Turner (atomistic)

2) Full charge density string potential -- later

[1] C.S. Own, W. Sinkler, L.D. Marks Acta Cryst A62 434 (2006)

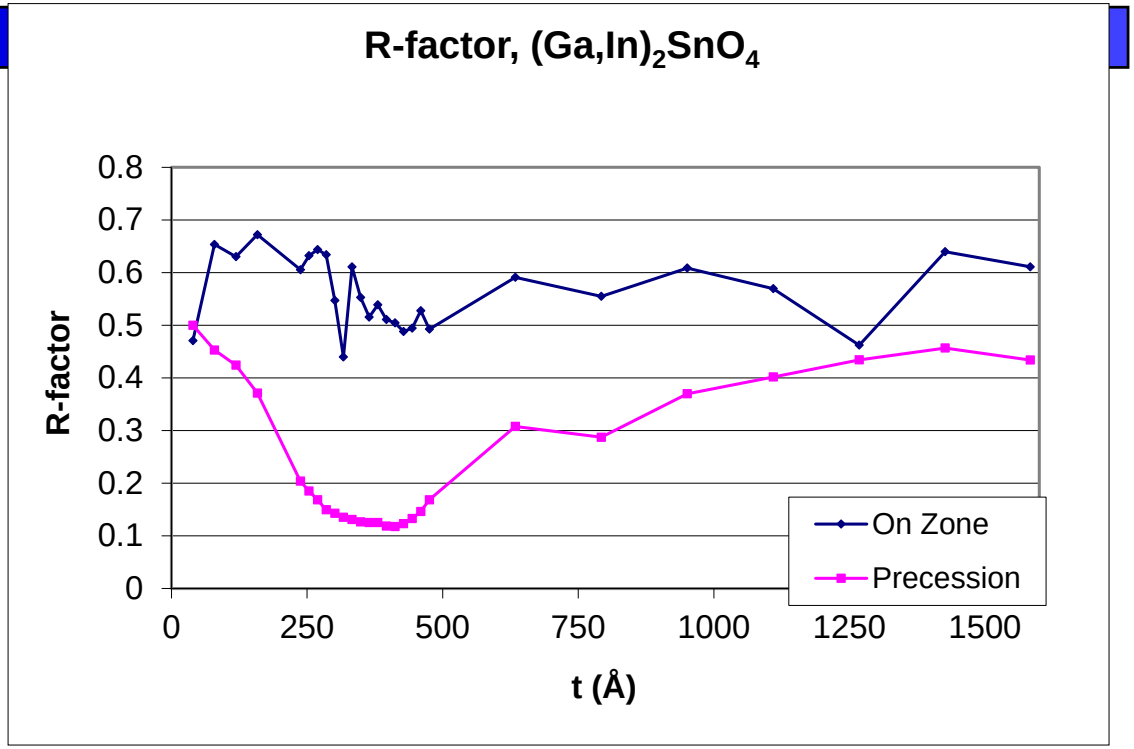
Multislice Simulation: works (of course)



R1 ~10% without refinement of anything

Global error metric: R_1

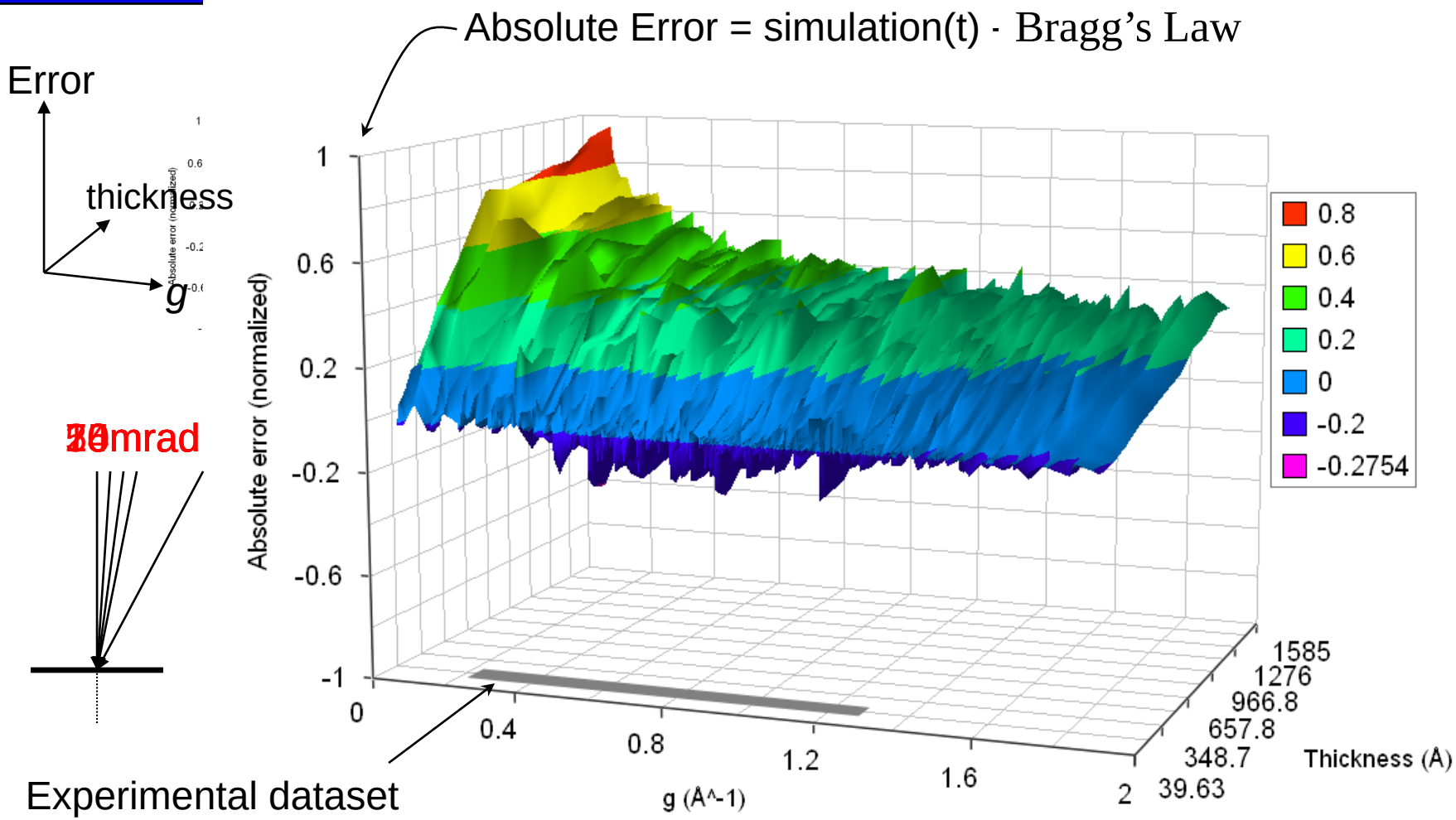
$$R_1 = \frac{\sum \left| F_{\exp} - F_{sim} \right|}{\sum F_{\exp}}$$



- Broad clear global minimum – atom positions fixed
- R-factor = 11.8% (experiment matches simulated known structure)
  - Compared to >30% from previous precession studies
- Accurate thickness determination:
  - **Average *t* ~ 41nm** (very thick crystal for studying this material)

(Own, Sinkler, & Marks, in preparation.)

Quantitative Benchmark: Multislice Simulation



(Own, Sinkler, & Marks, in preparation.)

Partial Conclusions

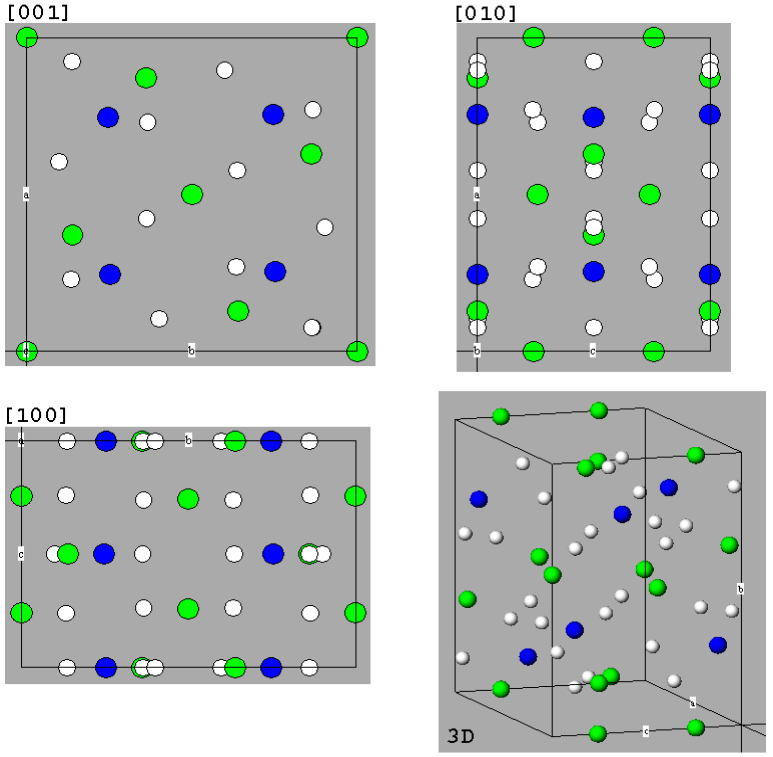
- Separable corrections fail; doing nothing is normally better
- Two-beam correction is not bad (not wonderful)
- Only correct model is full dynamical one (alas)
- N.B., Other models, e.g. channelling, so far fail badly – the “right” approximation has not been found

Overview

- What, if any generalizations can be made?
- Role of Precession Angle
  - Systematic Row Limit
- Importance of integration
  - Phase insensitivity
  - Important for which reflections are used

Role of Angle: Andalusite

- Natural Mineral
  - Al_2SiO_5
  - Orthorhombic (Pnnm)
    - a=7.7942
    - b=7.8985
    - c=5.559
  - 32 atoms/unit cell
- Sample Prep
  - Crushm Disperse on holey carbon film
  - Random Orientation



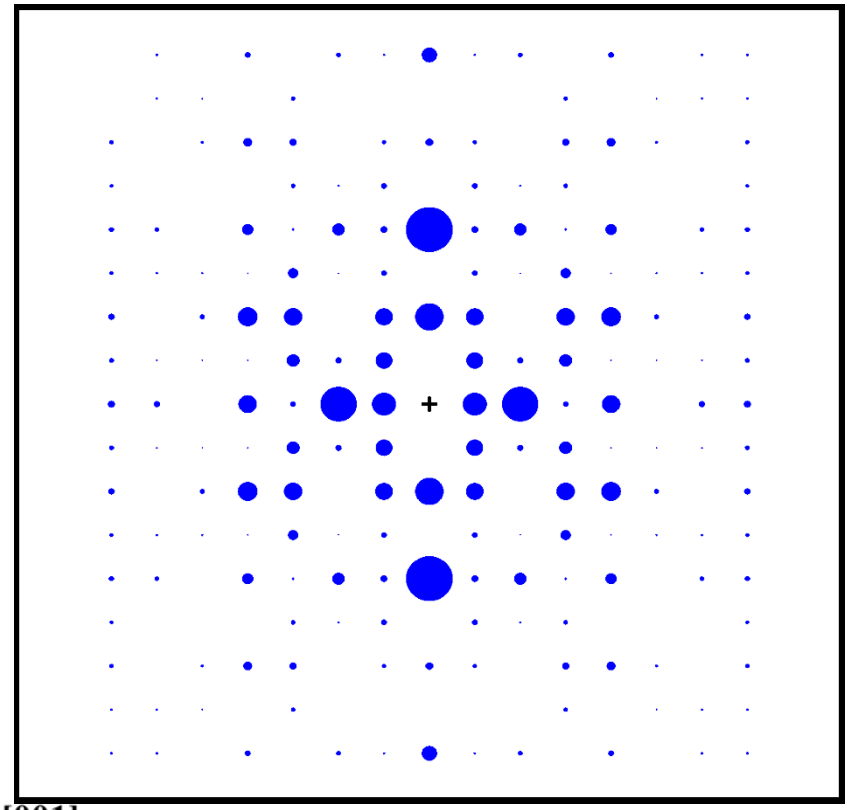
2 C.W.Burnham, Z. Krystall. 115, 269-290, 1961

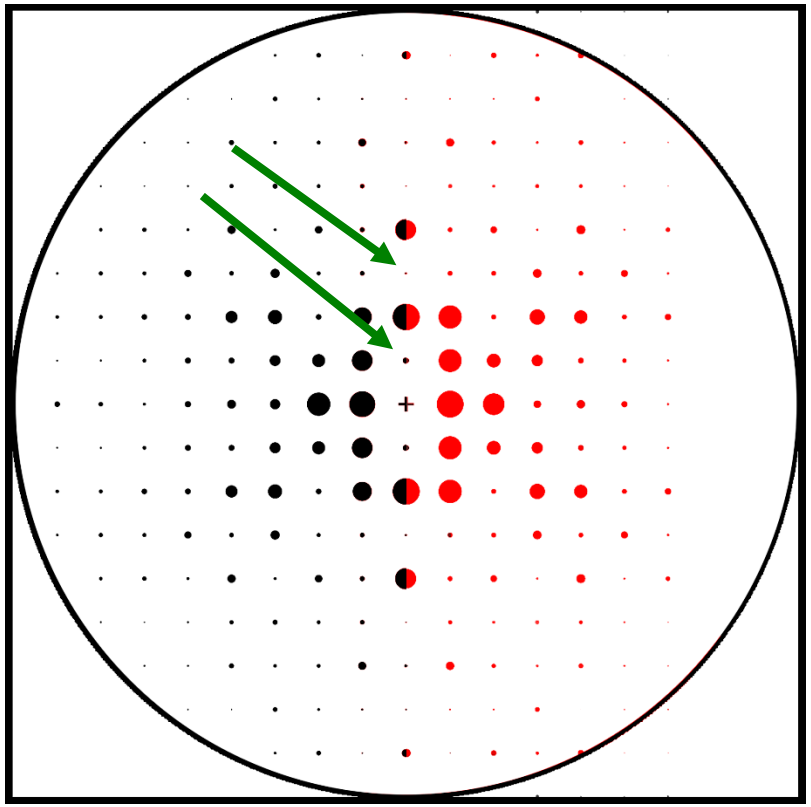
Measured and Simulated Precession patterns

Bragg's Law Simulation

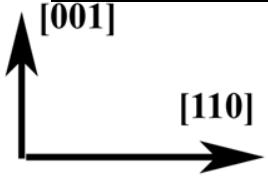
Experimental

Multislice





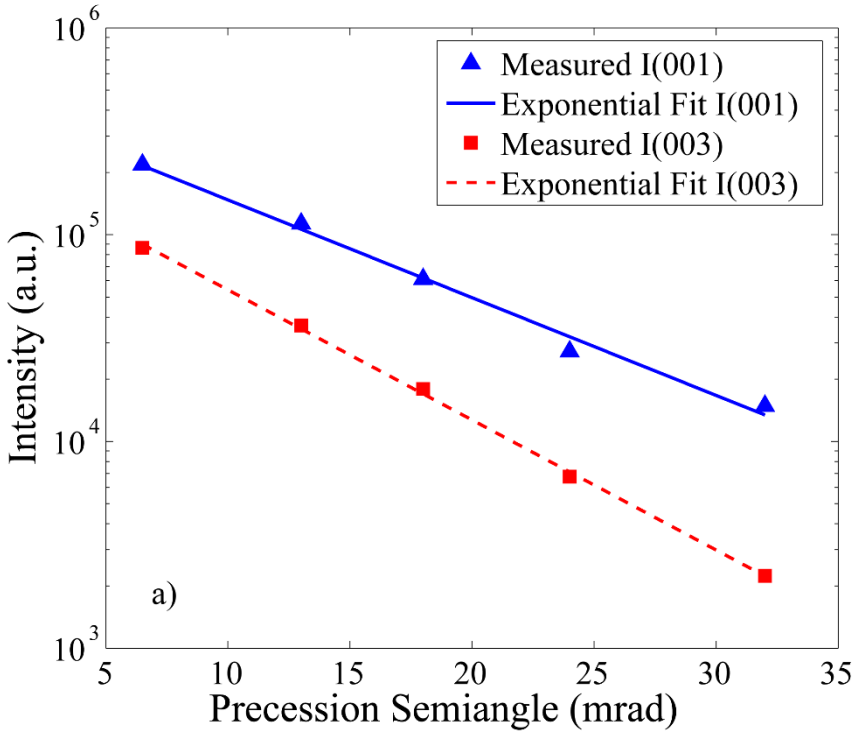
32 mrad



Decay of Forbidden Reflections

- Decay with increasing precession angle is exponential
  - The non-forbidden (002) reflections decays linearly

$$I = A\exp(-D\phi)$$

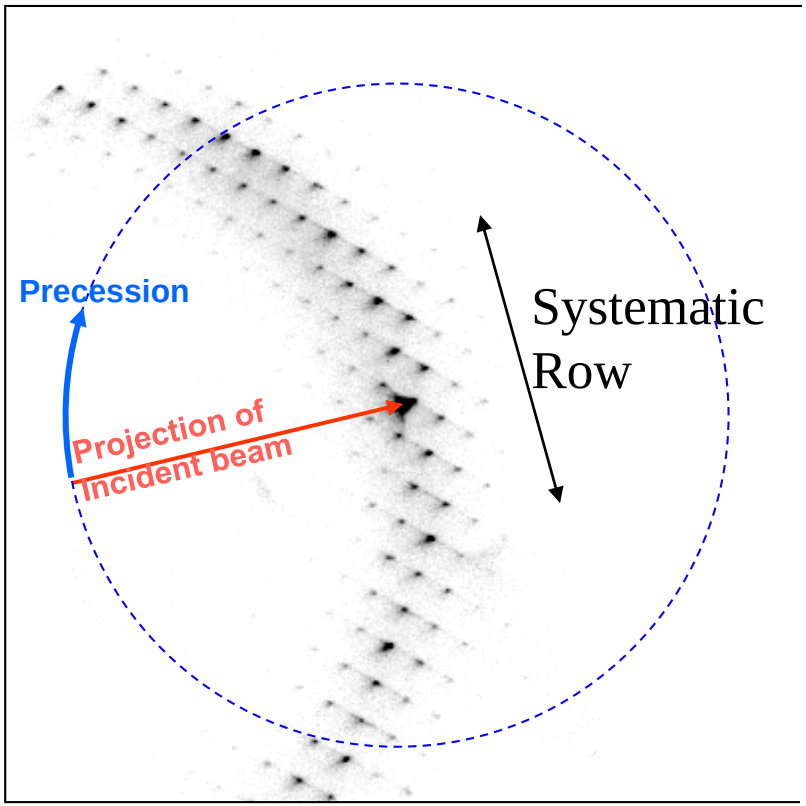


	D(001)	D(003)
Experimental	0.109 R^2=0.991	0.145 R^2=0.999
Simulated (102nm)	0.112 R^2=0.986	0.139 R^2=0.963
Simulated 28-126 nm	0.112±0.012	0.164±0.015

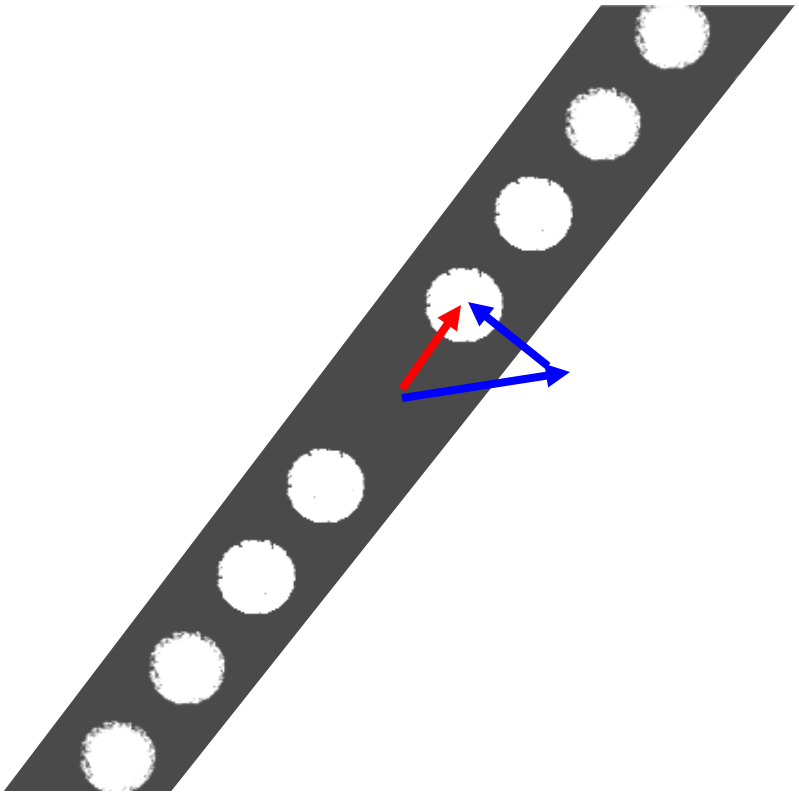
Rate of decay is relatively invariant of the crystal thickness

Slightly different from Jean-Paul's & Paul's – different case

Quasi-systematic row

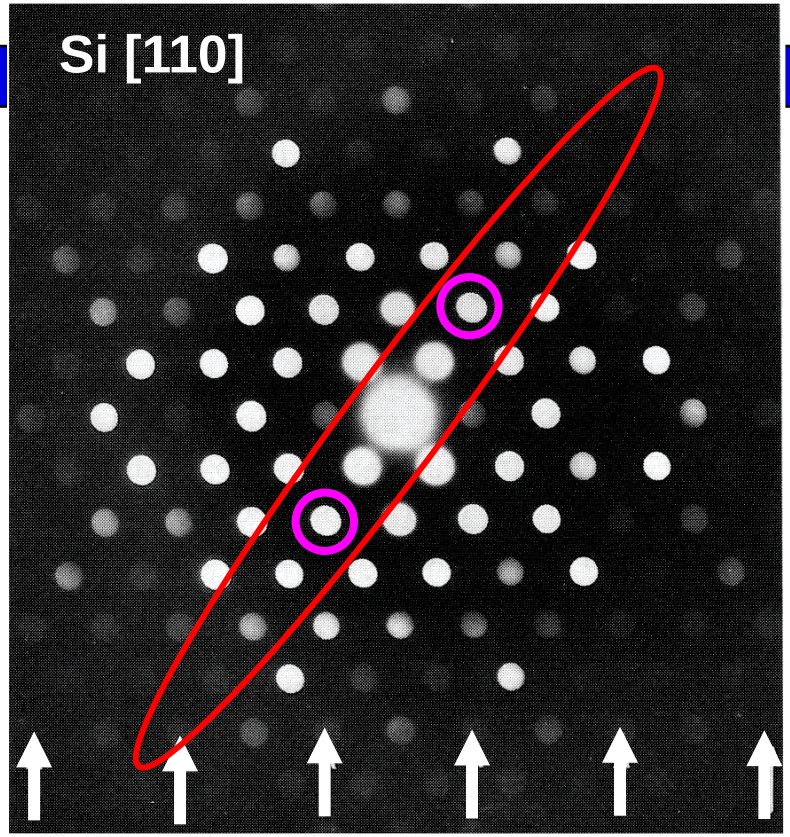


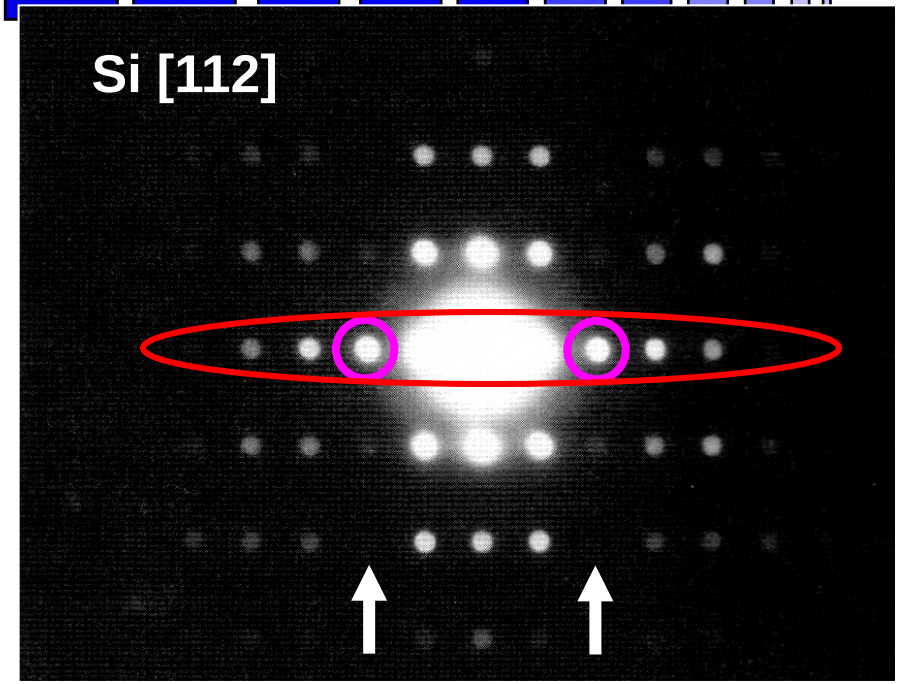
Precessed



Forbidden, Allowed by Double Diffraction

Evidence: 2g allowed





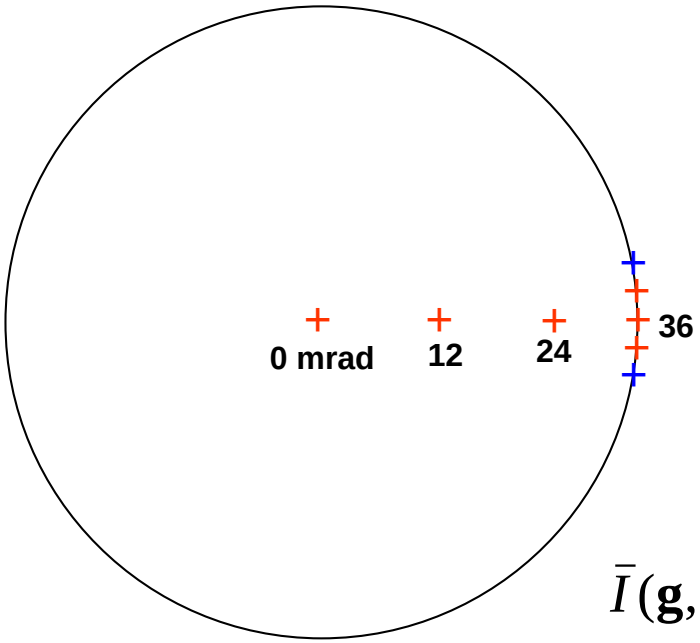
Rows of reflections arrowed should be absent (F_{hkl} = 0)

Reflections still present along strong systematic rows

Known breakdown of Blackman model

Phase and Averaging

For each of the incident condition generate 50 random phase sets {f} and calculate patterns:



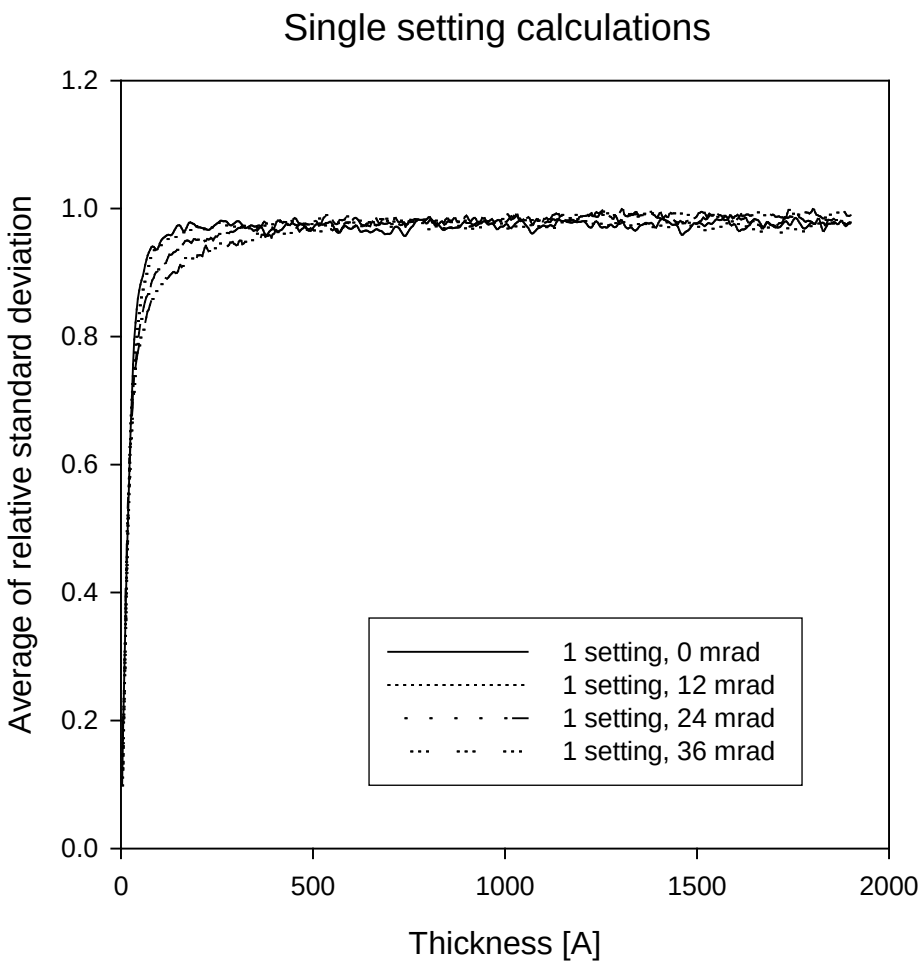
Single settings at 0, 12, 24 and 36 mrad (along arbitrary tilt direction).

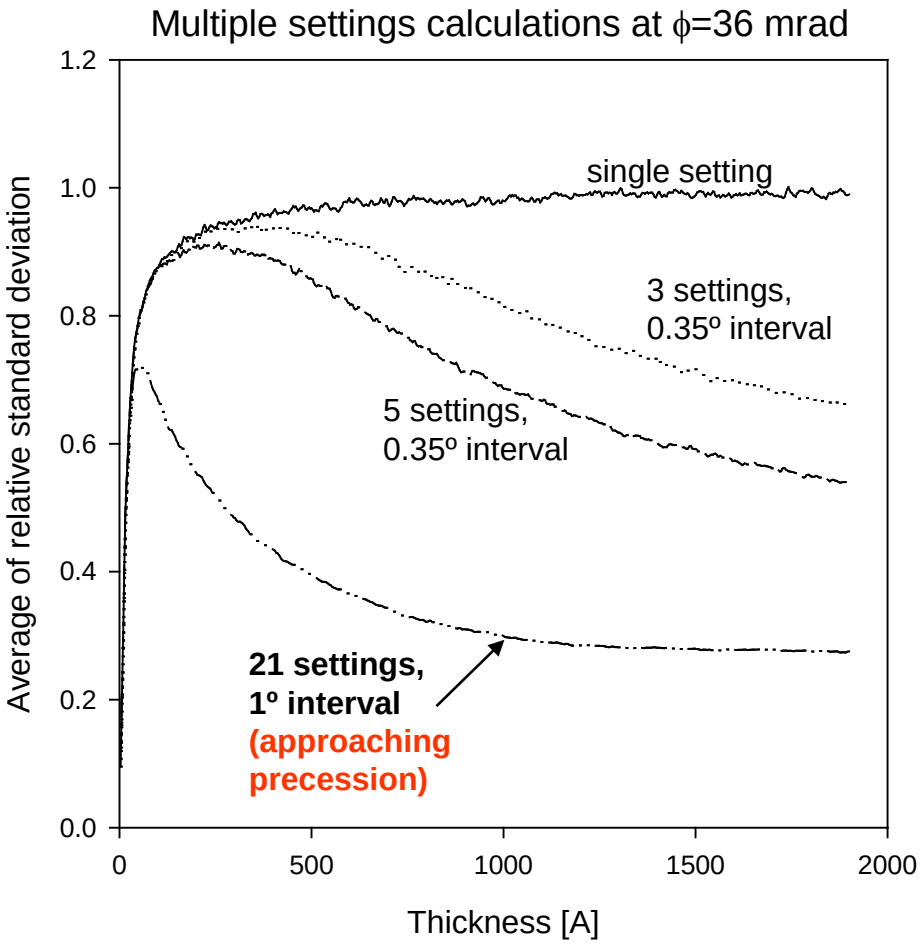
At fixed semi-angle (36 mrad) average over range of a as follows:
3 settings at intervals of 0.35º
5 settings at intervals of 0.35º
21 settings at intervals of 1º

For each **g** and thickness compute avg., stdev:

$$\bar{I}(\mathbf{g},t)=\frac{1}{50}\sum_{\{\varphi\}}I(\mathbf{g},t) \quad \sigma(\mathbf{g},t)=\left[\frac{1}{50}\sum_{\{\varphi\}}I(\mathbf{g},t)^2-\bar{I}(\mathbf{g},t)^2\right]^{1/2}$$

Phase independence when averaged





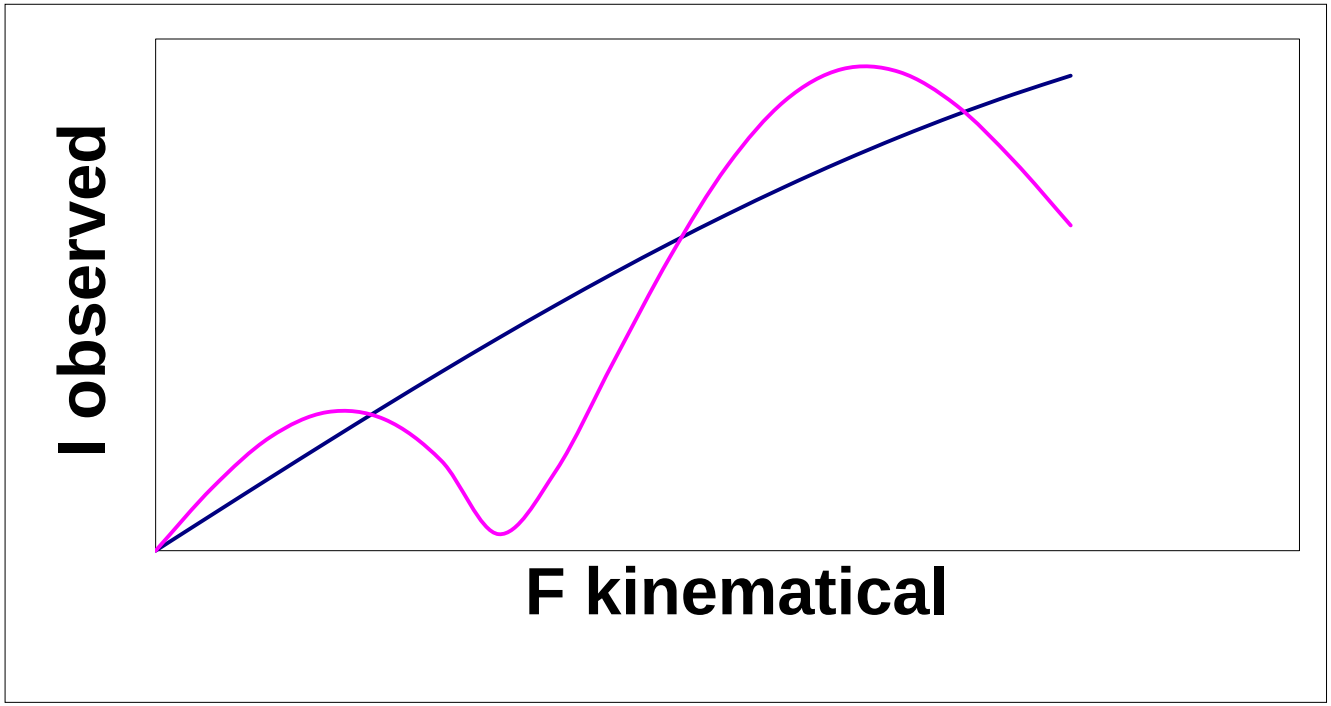
Sinkler & Marks, 2009

Why does it work?

- If the experimental Patterson Map is similar to the Bragg's Law Patterson Map, the structure is solvable – Doug Dorset
- If the deviations from Bragg's Law are statistical and "small enough" the structure is solvable – LDM

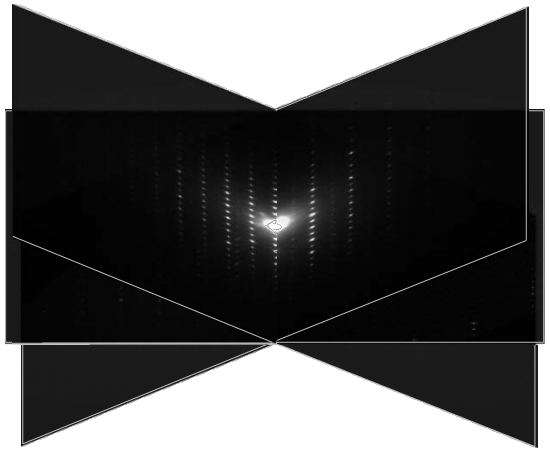
Why is works - Intensity mapping

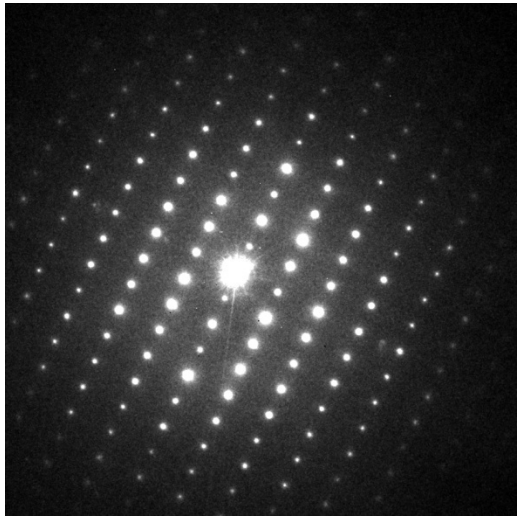
- Iff $I_{obs}(k_1) > I_{obs}(k_2)$ when $F_{kin}(k_1) > F_{kin}(k_2)$
  - Structure should be invertible (symbolic logic, triplets, flipping…)

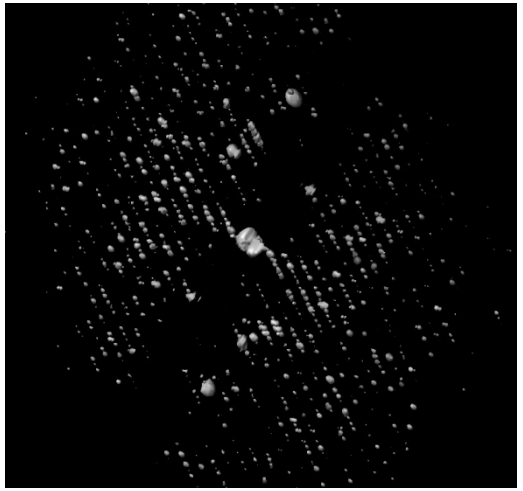


Automated Diffraction Tomography (ADT)

Most electron diffraction use TEM on-zone (oriented) patterns

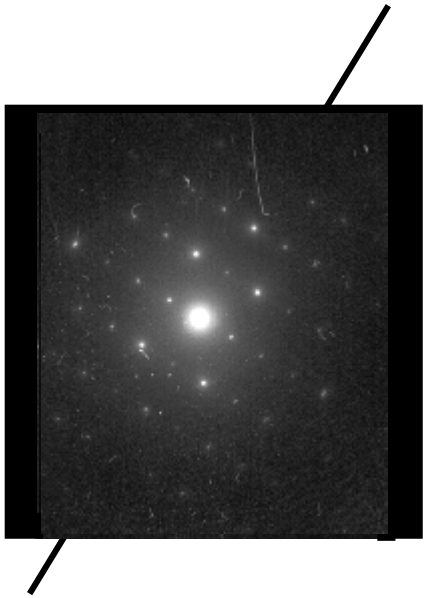


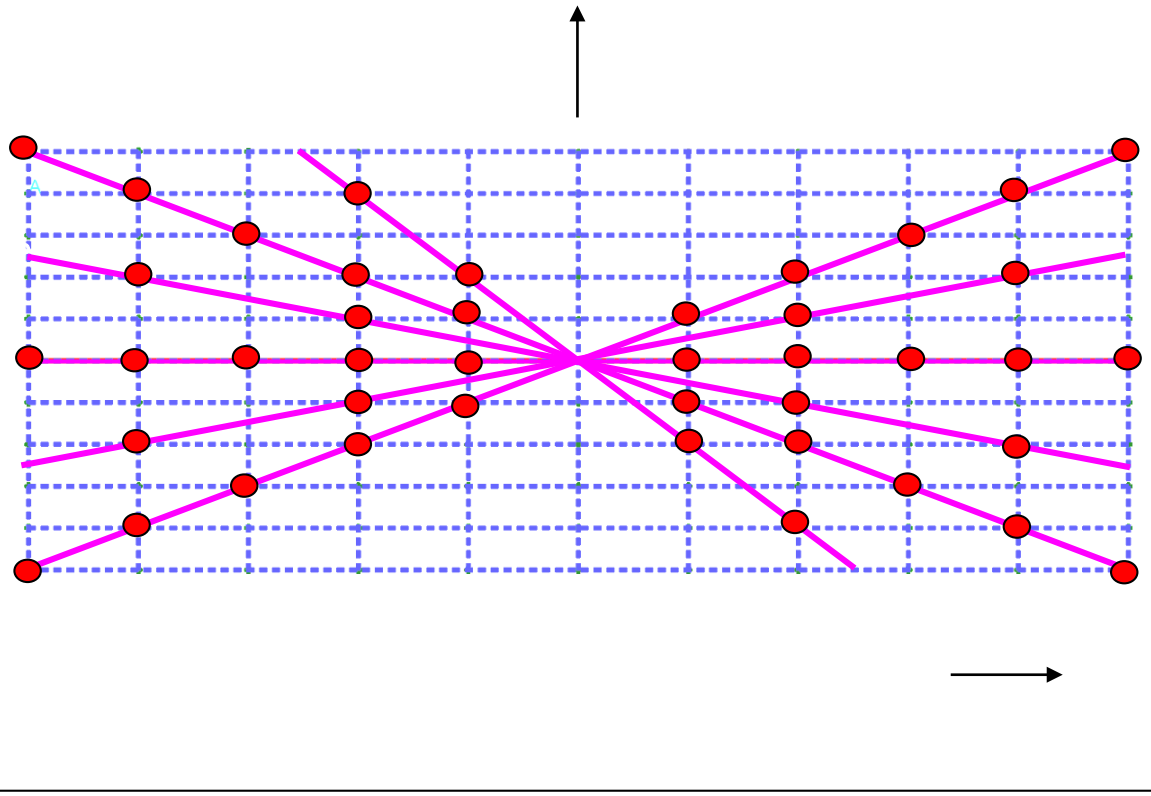




ADT approach: collection of full 3D reciprocal space starting from not oriented patterns

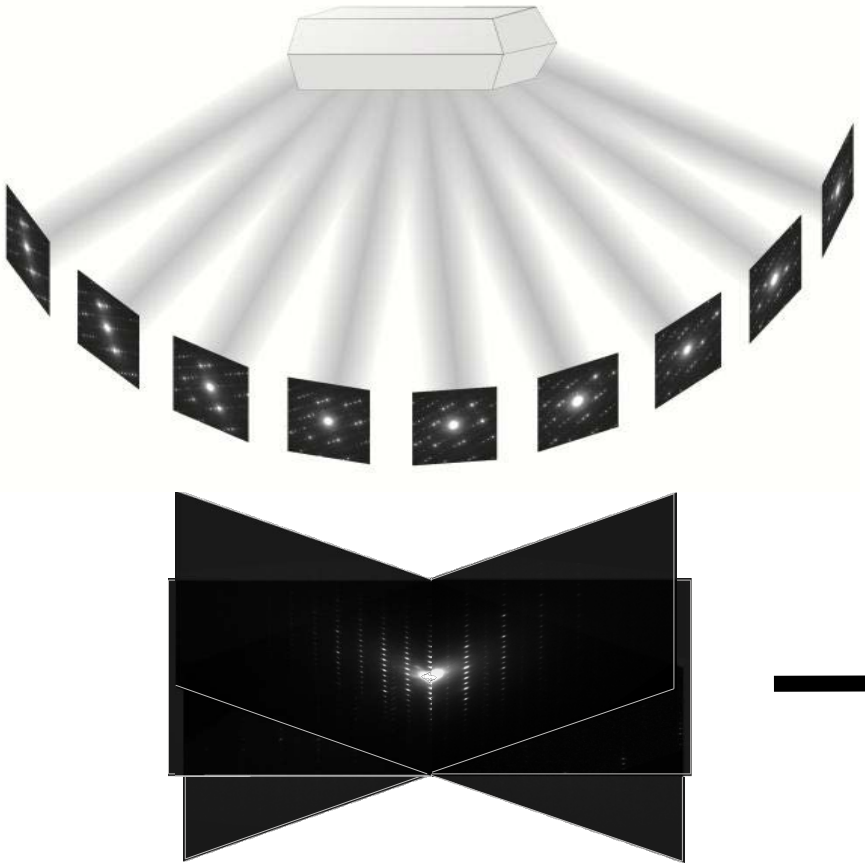
Zone Axis Data



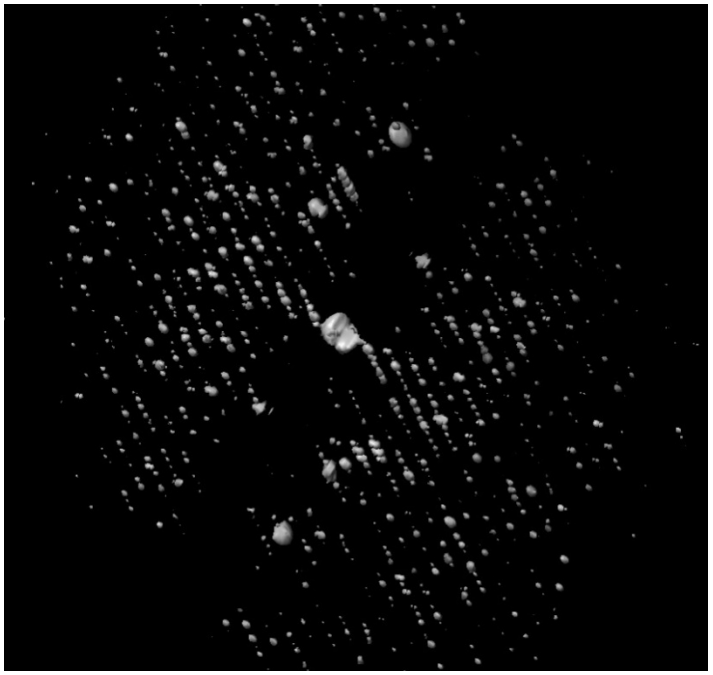


Courtesy : Prof. U Kolb UMainz

ADT concept



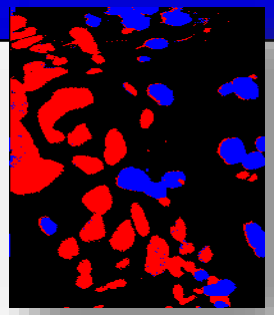
Data analysis by ADT3D
3D reconstrucution of diffraction space

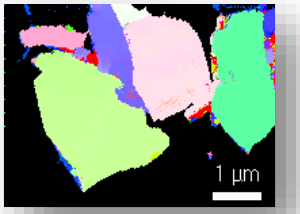


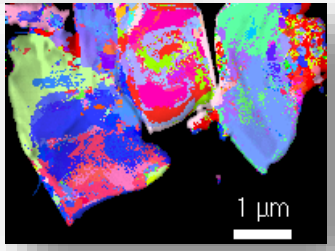
diffraction tomography. Part II – Cell parameter determination. U. Kolb, T. Gorelik and M.T. Otten, *Ultramicroscopy*, **108**, 763-772 (2008).

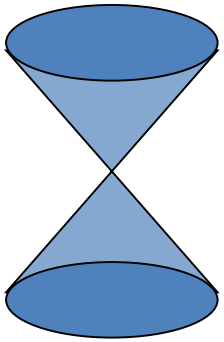
ASTAR (EBSD-TEM like)

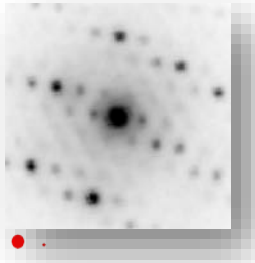
Automatic Crystal Orientation/Phase mapping for TEM

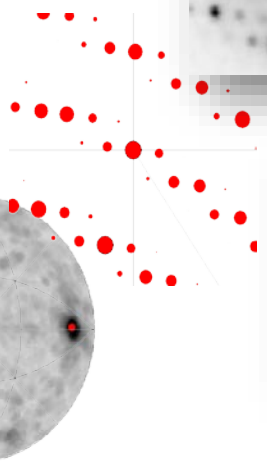


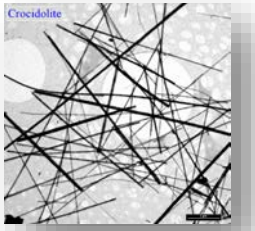








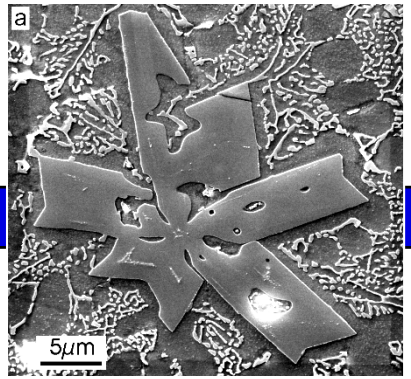


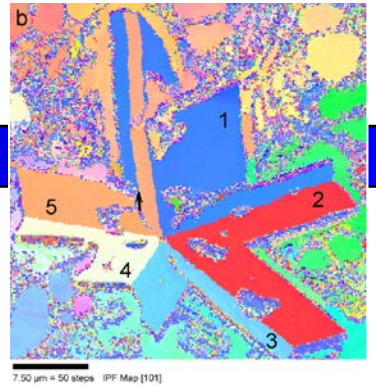


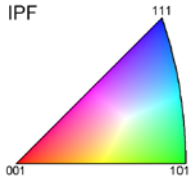
Grenoble INP

NanoMEGAS
Advanced Tools for electron diffraction

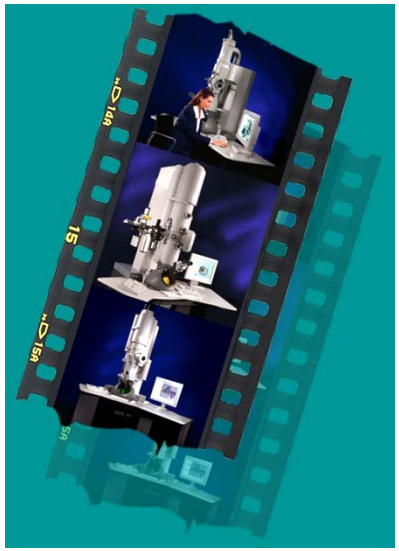
www.nanomegas.com

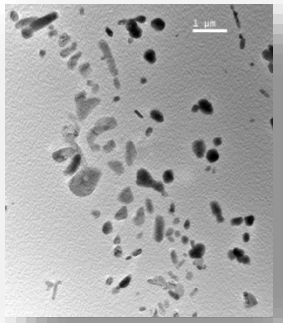


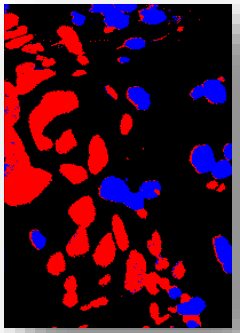


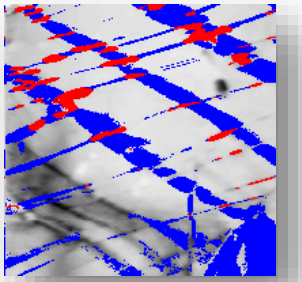


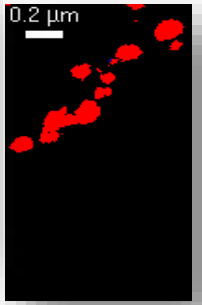
NEW precession application "EBSD" – TEM







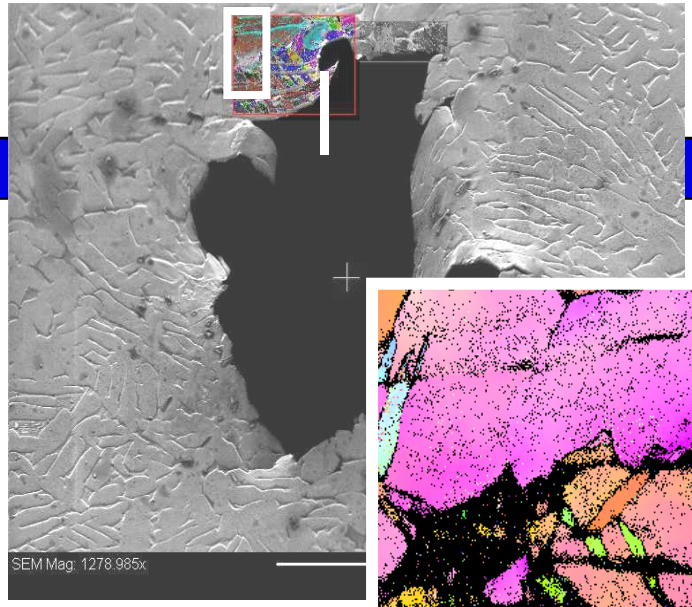




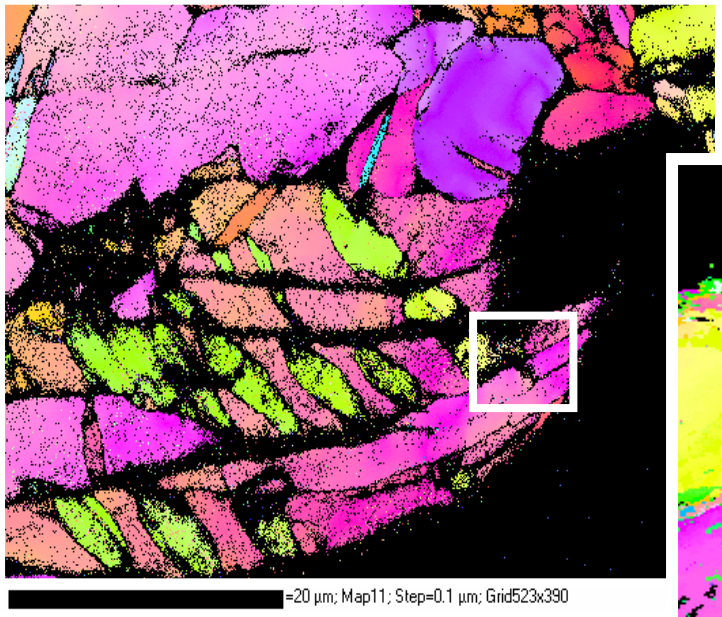
EBSD-TEM : beam is scanned over the sample (eg. 10 μ x 10 μ)

- spot electron diffraction patterns are collected (NOT sensitive to stress/ strain or surface sample preparation like in EBSD-SEM)
- Beam scanning performed by “spinning star” unit / no STEM need
- Thousands of experimental spot ED patterns are acquired by a very fast optical CCD camera attached to TEM screen (180 patterns/sec)
- Slow scan CCD can also be used (but slow : 20-30 patterns/sec)
- Thousands of theoretical ED patterns are generated (templates) from .cif files or commercial databases for all known phases in a sample
- Template matching is used (by cross-correlation of all experimental ED patterns with all templates) to generate most probable orientation of every scanned position in the sample.

Comparison SEM-(EBSD) vs TEM spatial resolution

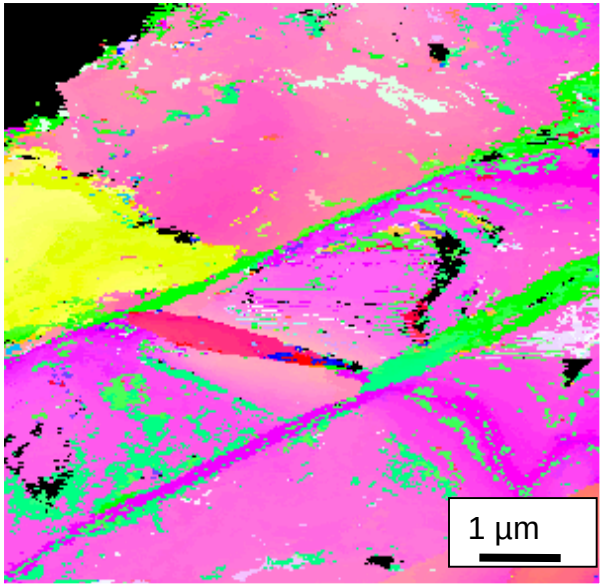


SEM orientation map
deformed Ta6V alloy

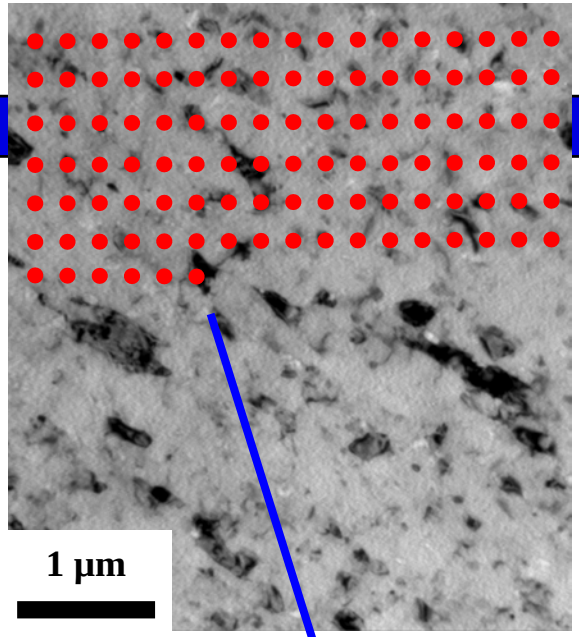


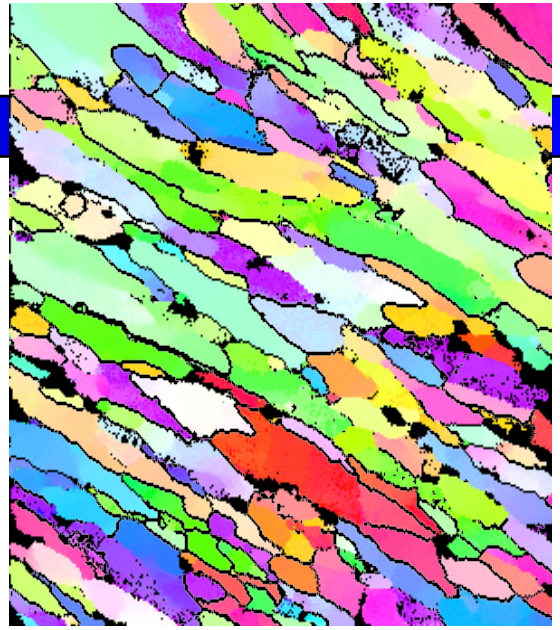
EBSD map (100 nm stepsize)

TEM orientation map
(25 nm stepsize)

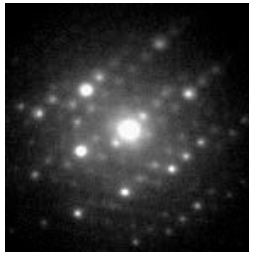


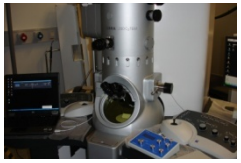
ASTAR : diffraction pattern adquisition





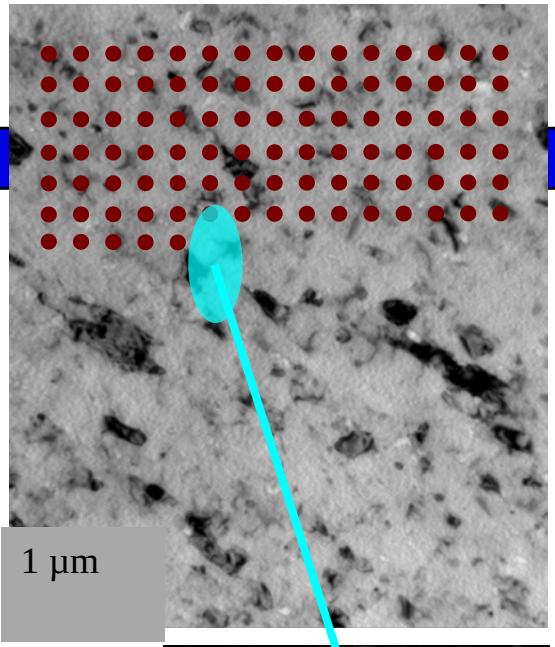
Example :Severely deformed 7075 Aluminium Alloy



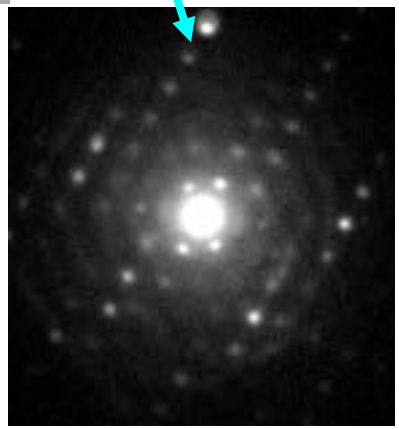


Any TEM –FEG/LaB6 may work with ASTAR

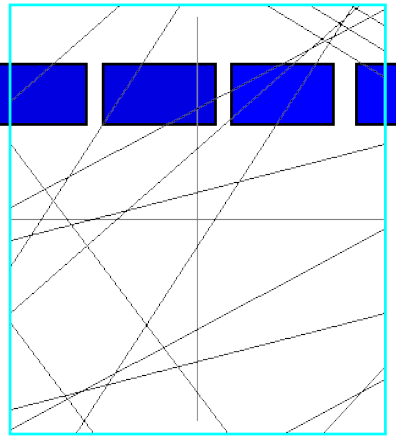
EBSD-TEM : Automated Crystal Orientation Mapping

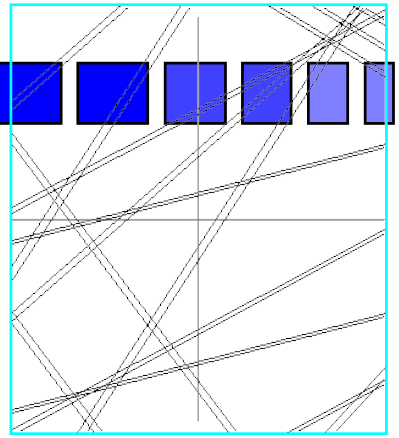


Severely deformed 7075 Al. Alloy



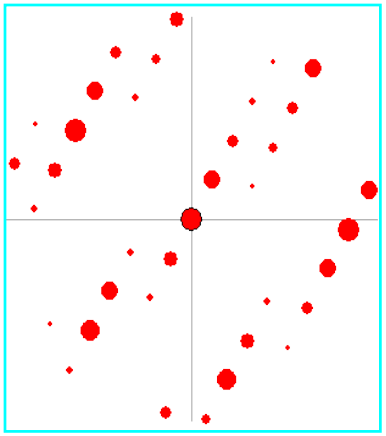
Kikuchi pattern

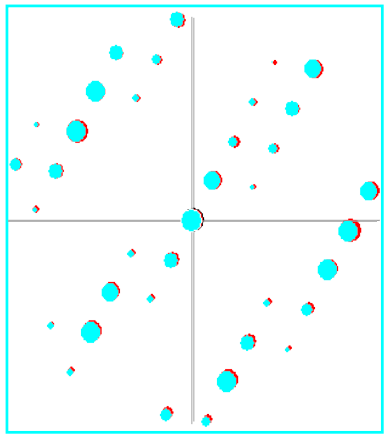




Orientation Ω

Orientation Ω + Ω'(= Ω +0.1°)





Bragg Spot pattern

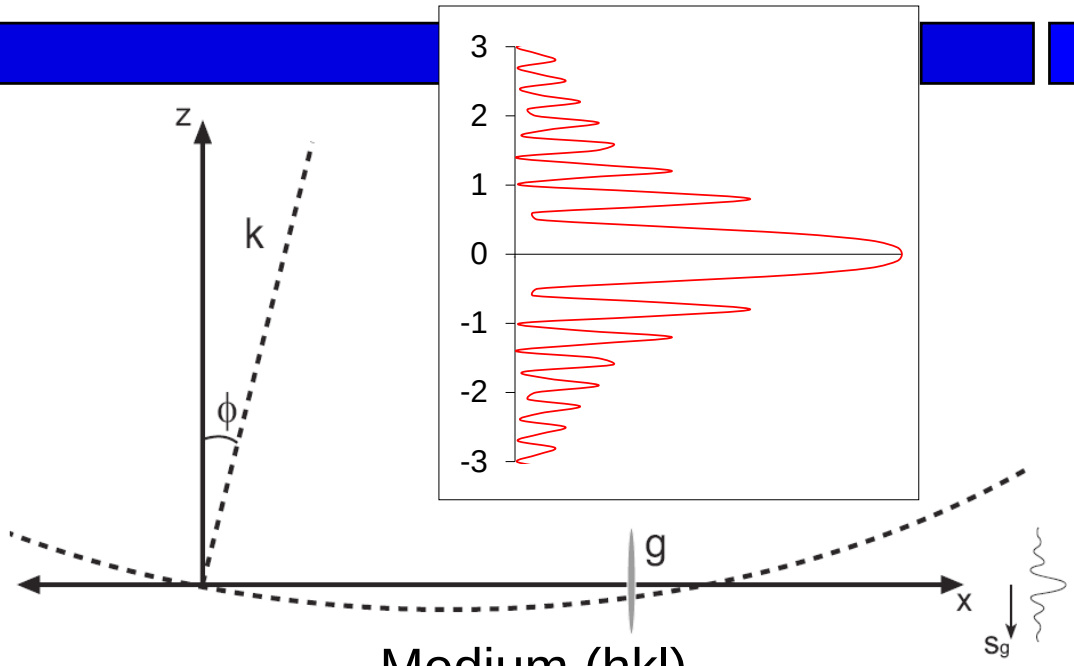
Summary

- PED is
  - Approximately Invertable
  - Pseudo Bragg's Law
  - Approximately 2-beam, but not great
  - Properly Explained by Dynamical Theory
- PED is not
  - Pseudo-Kinematical (this is different!)
  - Fully Understood by Dummies, yet
- Important offshoots – ADT and OIM

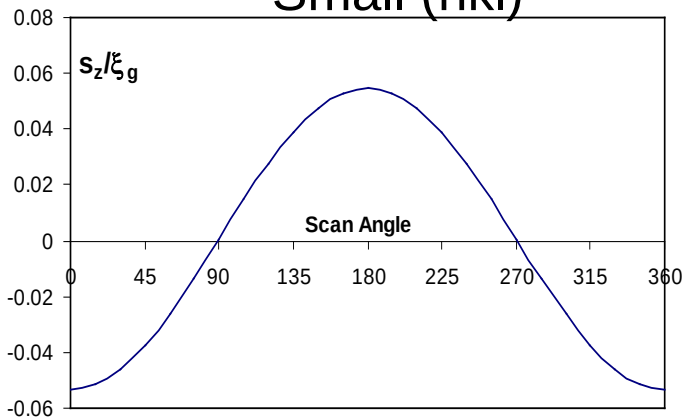
Speculation…Full Method

- Generate initial structure estimate
  - Intial Bragg's Law Analysis or part of data

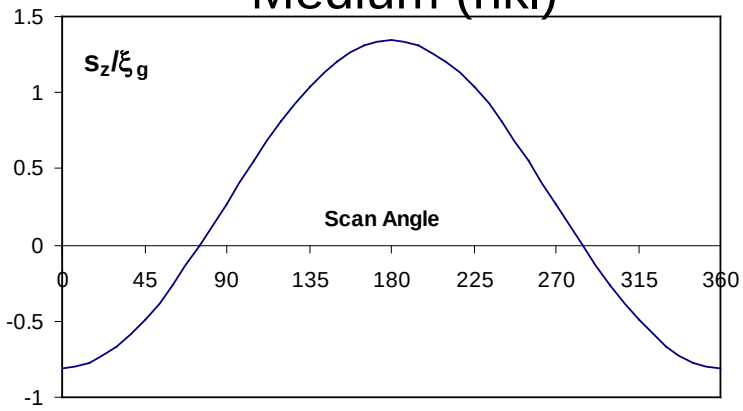
Two-Beam Integration: Ewald Sphere



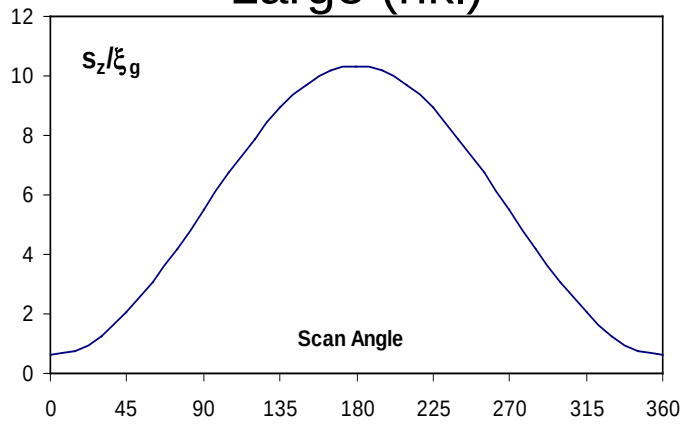
Small (hkl)



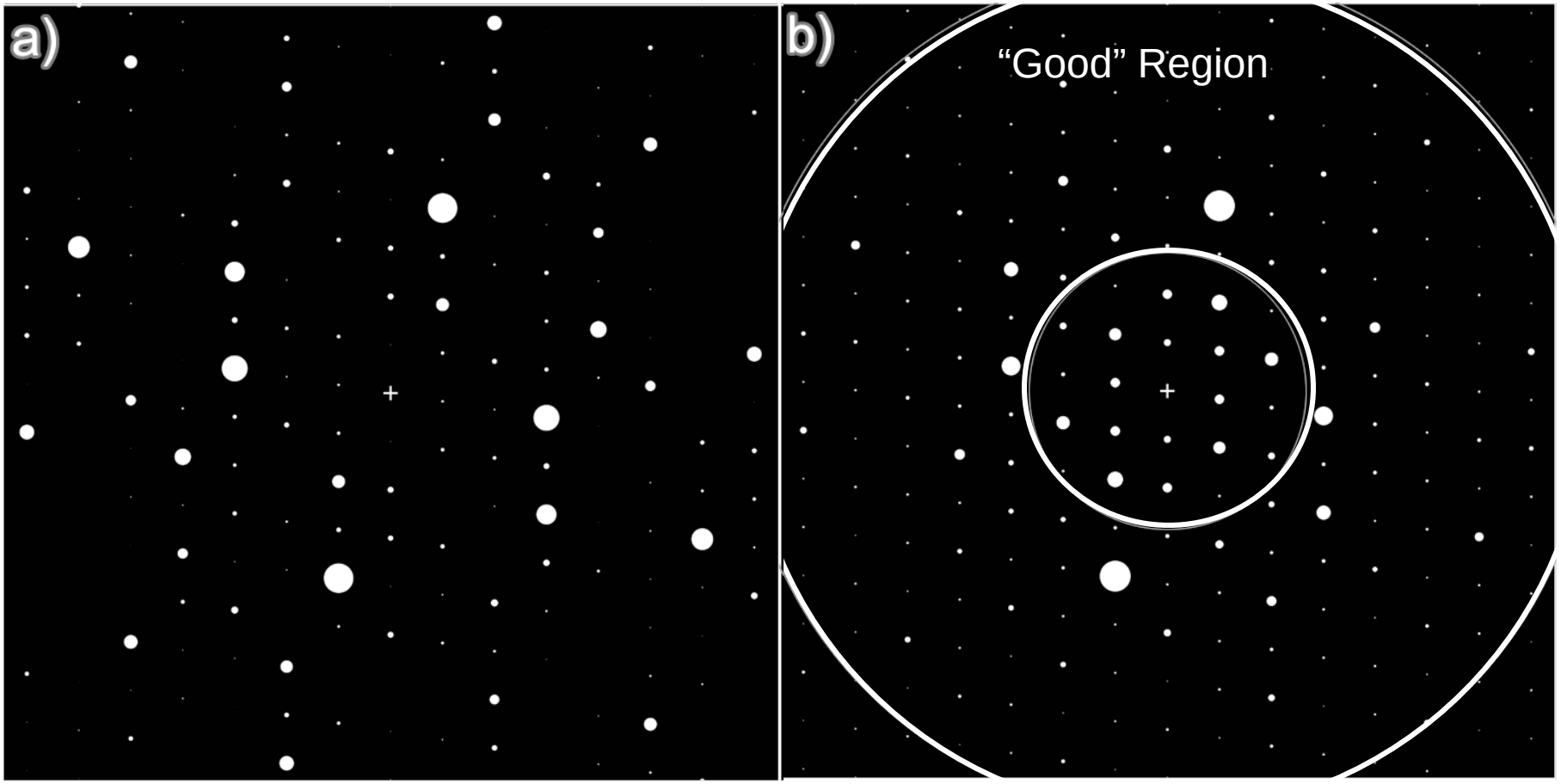
Medium (hkl)



Large (hkl)



Preprocess?



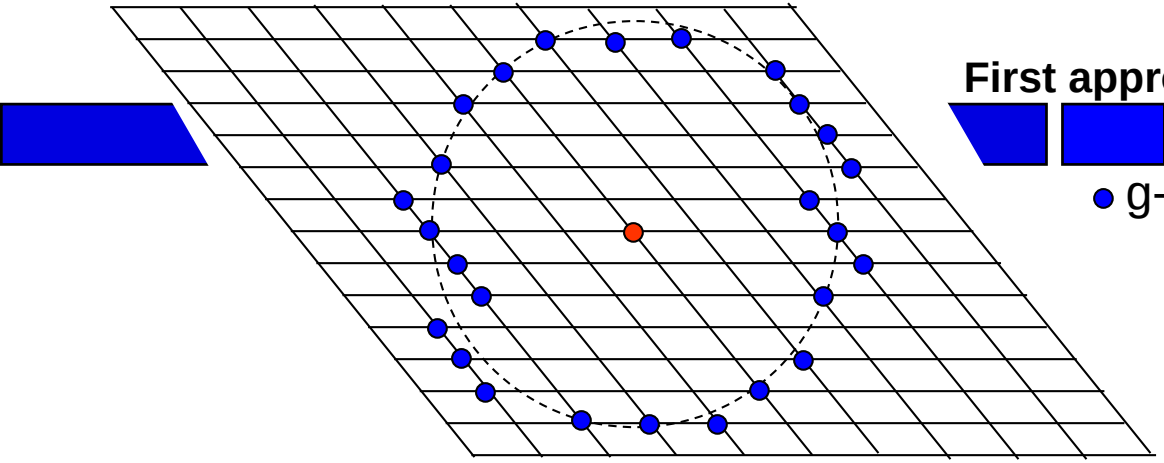
Bragg’s Law (reference)

Precession pattern (experiment)
ϕ = 24mrad

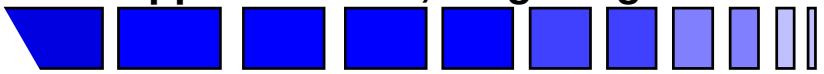
Speculation…Full Method

- Generate initial structure estimate
  - Intial Bragg's Law Analysis or part of data
  - Use 2-beam approximation to invert/correct
  - Partial refinement, using 1/2 kpoint Bloch-Wave method

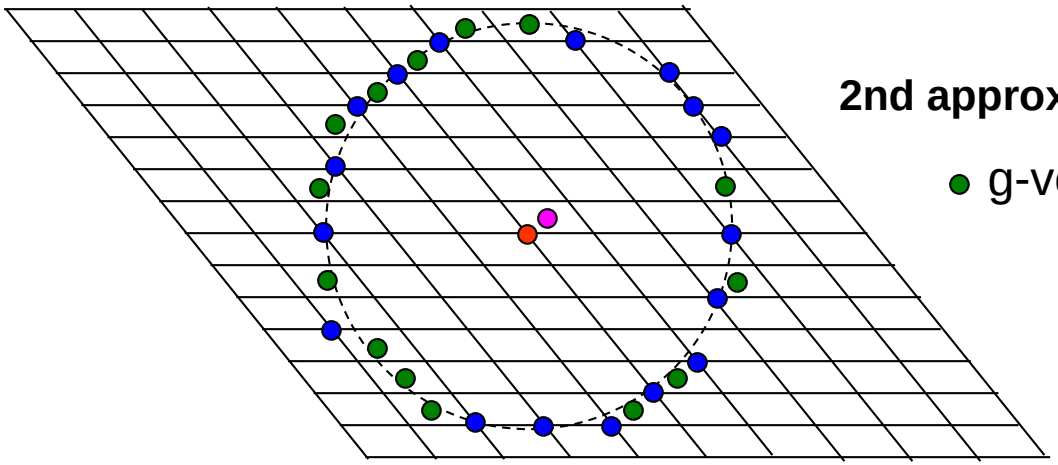
Approximation of precession circuit by series of g-vector tilts:



First approximation; single eigen-solution



g-vector tilts obtained from

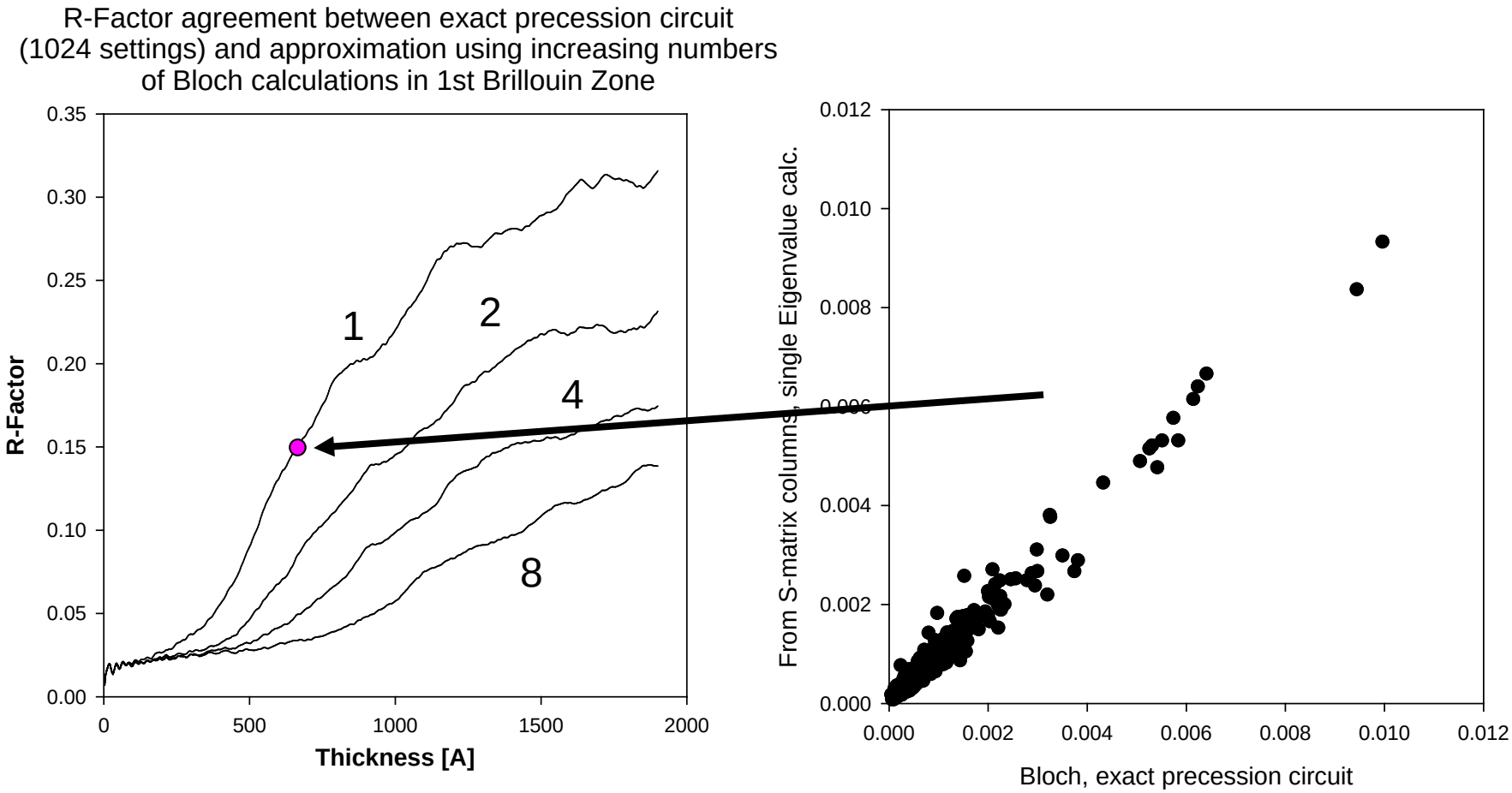


2nd approximation; two eigen-solutions

g-vector tilts obtained from

=> increasingly accurate precession calculation

Precession calculations for $(Ga,In)_2SnO_5$, 36 mrad semi-angle, increasing numbers of eigensolutions.



Speculation…Full Method

- Generate initial structure estimate
  - Intial Bragg's Law Analysis or part of data
  - Use 2-beam approximation to invert/correct
  - Partial refinement, using 1/2 kpoint Bloch-Wave method
  - Final full refinement using 25-100 beam BW (+Bethe terms, e.g. Stadleman or NUMIS + dmnf, large residual code)

Hypothesis: Thickness ranges

HREM

Bragg's Law

Dynamical (not so easy)

PED (pseudo-Bragg's Law)

Questions ?