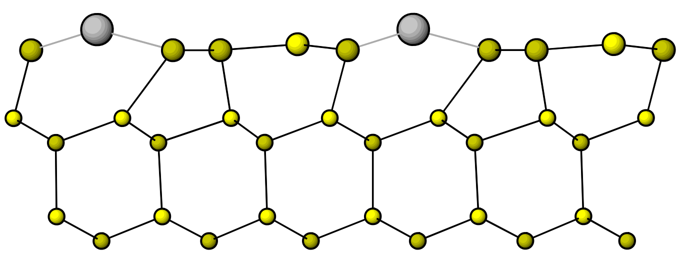
Precession Diffraction: The Philospher's Stone of Electron Crystallography?

Thinking big

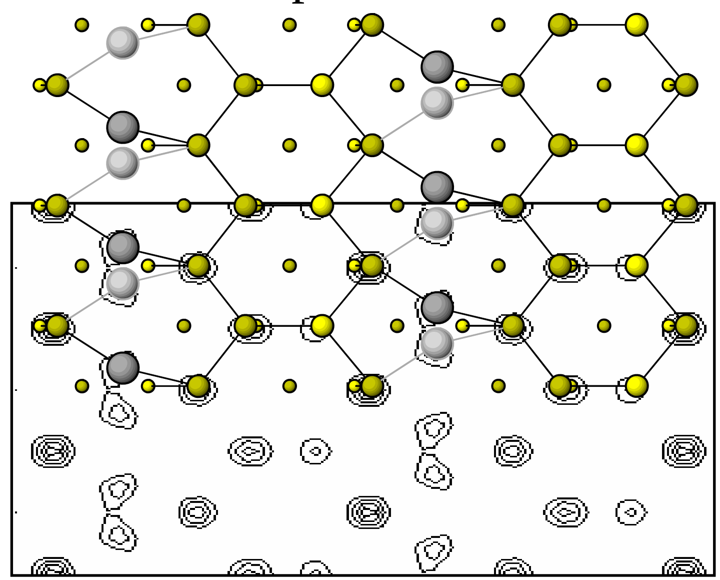
- General *ab-initio* structure determination (nanoparticles, precipitates…) without growing large single crystals
- Without severe dynamical effects, inversion is trivial – very thin samples
- Fundamental problem: dynamical diffraction in general case; no *ab-initio* inversion ***currently*** exists without too much prior knowledge to be more than a demonstration experiment.

It Can Work: Si(111)-(3x1)/Ag Structure

Side view



Top view



Erwin, S. C. Weitering, H. H, PRL 81, 2296 (1998)

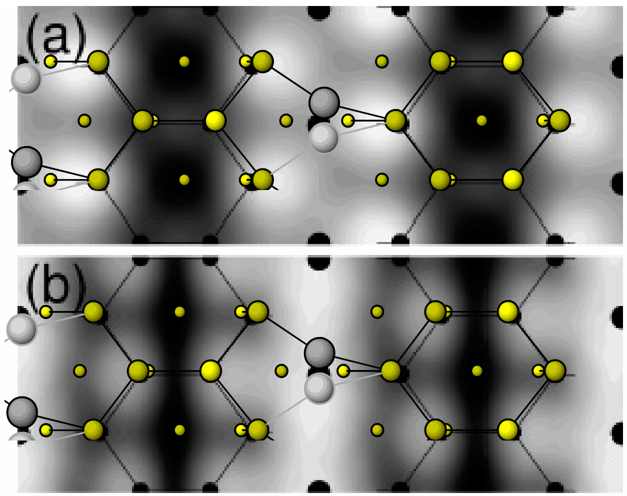
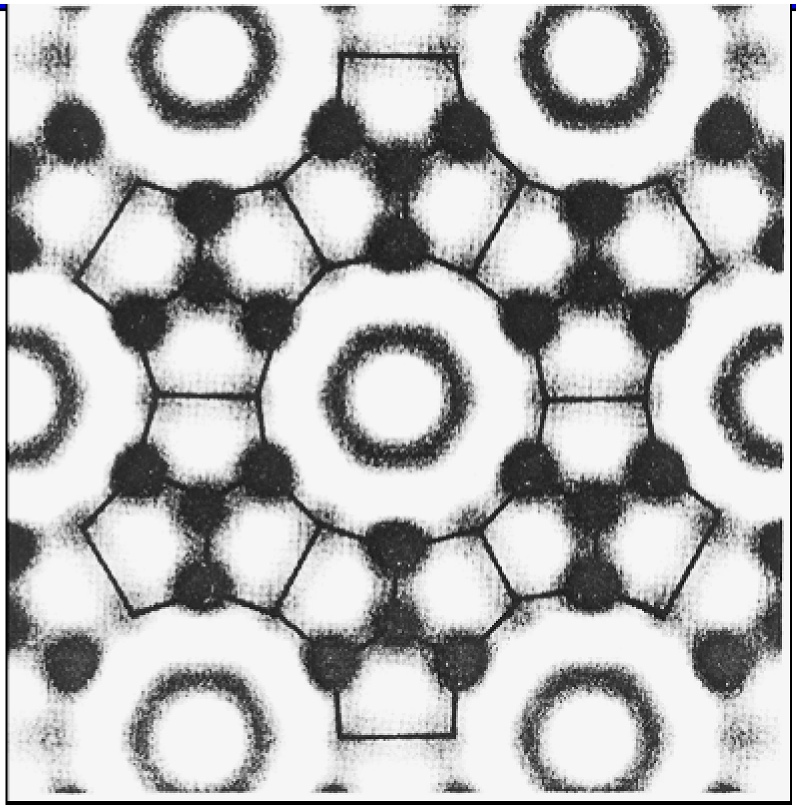


FIG. 4. Simulated STM images for the honeycomb chain-channel model of Li:3 × 1 for (a) filled states and (b) empty states. Black circles indicate the projected positions of Si and Li atoms in the surface layer.

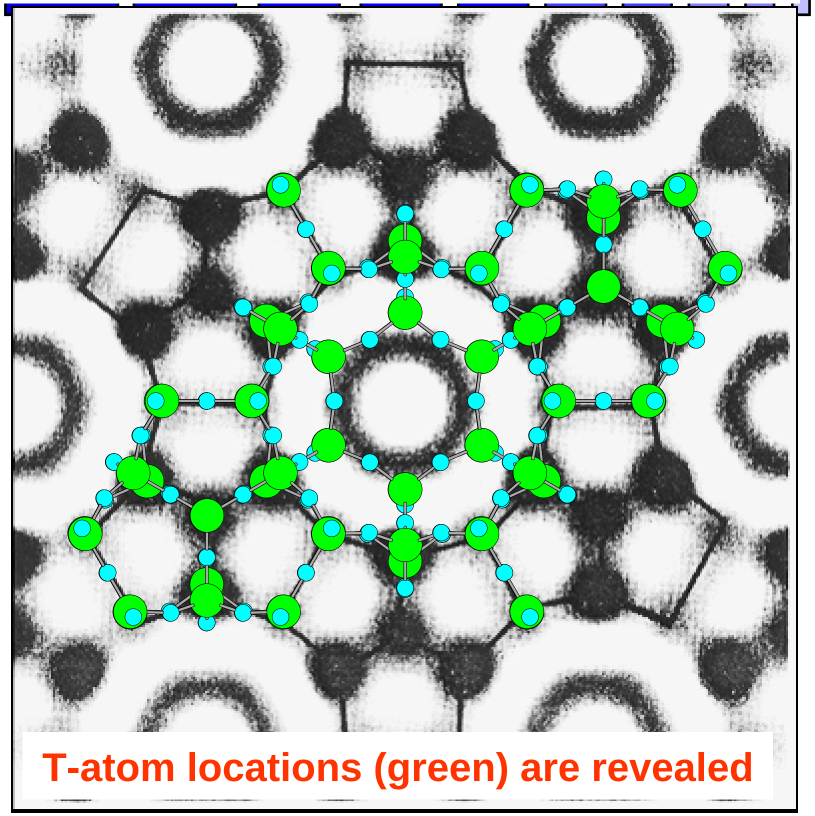
C. Collazo-Davila et al, PRL 80, 1678 (1998)

It can work: bulk

Below: MCM-22 [0001] Projected potential map from electron diffraction intensities and phases from symbolic addition*



Comparison of map with solved structure

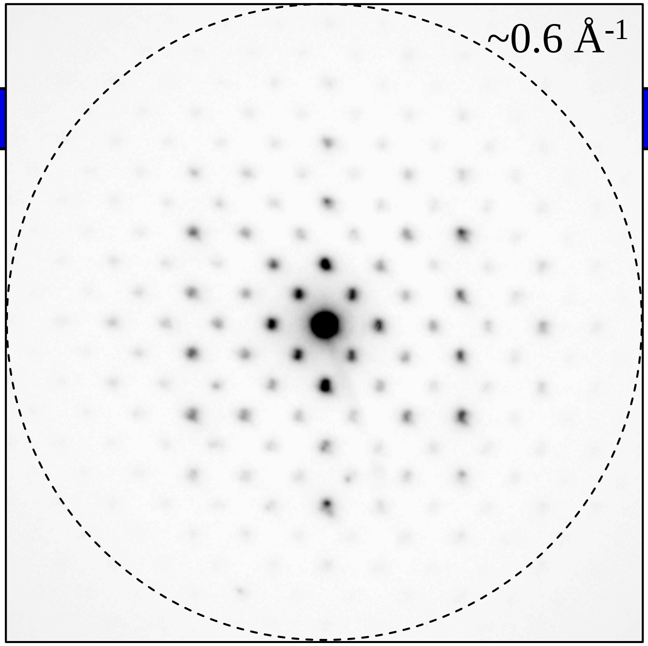


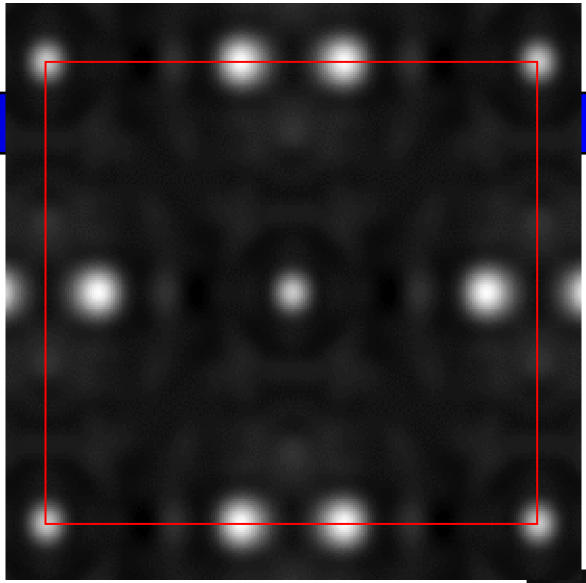
Depends on small thickness (for MCM-22 typical is 100-300 Å). Structure must project well to work in 2D.

*** Nicolopoulos et al, *J. Am. Chem. Soc*. 117 (1995)**

It can fail

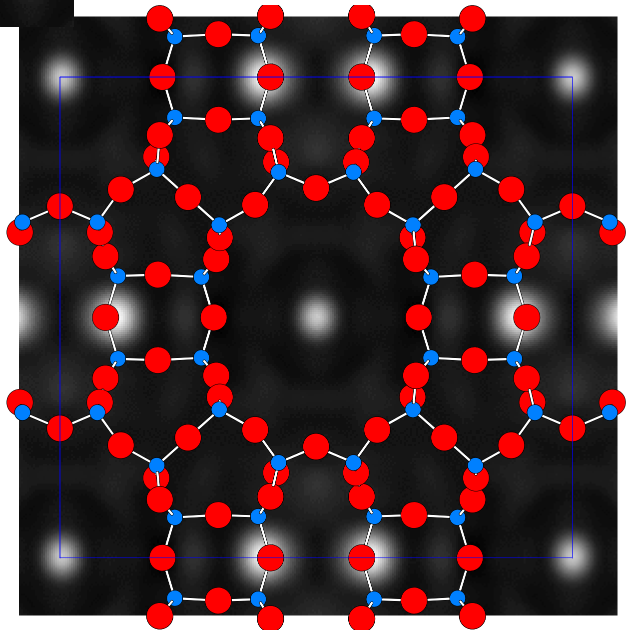
Raw data, Mordenite [001] pattern





Left, Direct Methods solution from fs98, non-precessed

Below, comparison with structure.



Reasons for failure:

Mordenite does not project well

Crystal morphology typically 100 nm or more along [001]

Problems from dynamical effects confirmed with modeled (multislice) data for >300 Å thickness.

Experimental Problems

- Local strain/tilting leads to kinematically forbidden/dynamically allowed spots – well known *coherent* dynamical diffraction effect
- Sometimes thickness is not controlled – results are not very reproducible.
- Often samples are not on zone axis (reduces apparent symmetry)

Theoretical Problems

- Dynamical electron diffraction is “exact”, but in general not analytic; hard to extract trends from numerical calculations!
- Hard to extract from calculations conditions for direct methods to work (beyond 1s model)
- Calculations can be slow

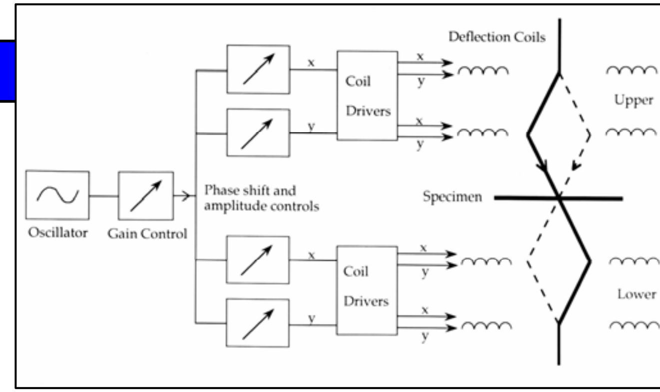
*A*lternative – Electron Precession (1993)

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

R. Vincent, P.A. Midgley

H.H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, UK

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



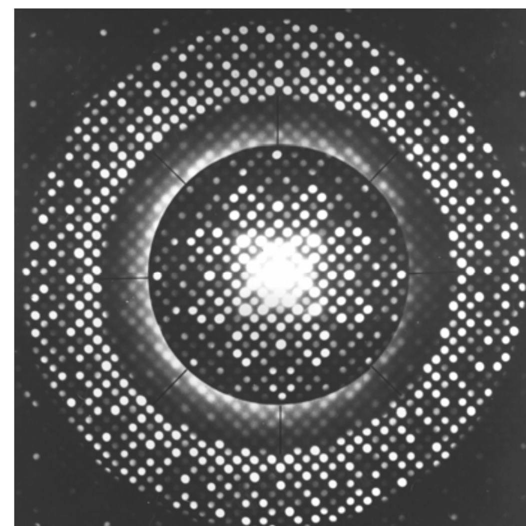
Advantages:

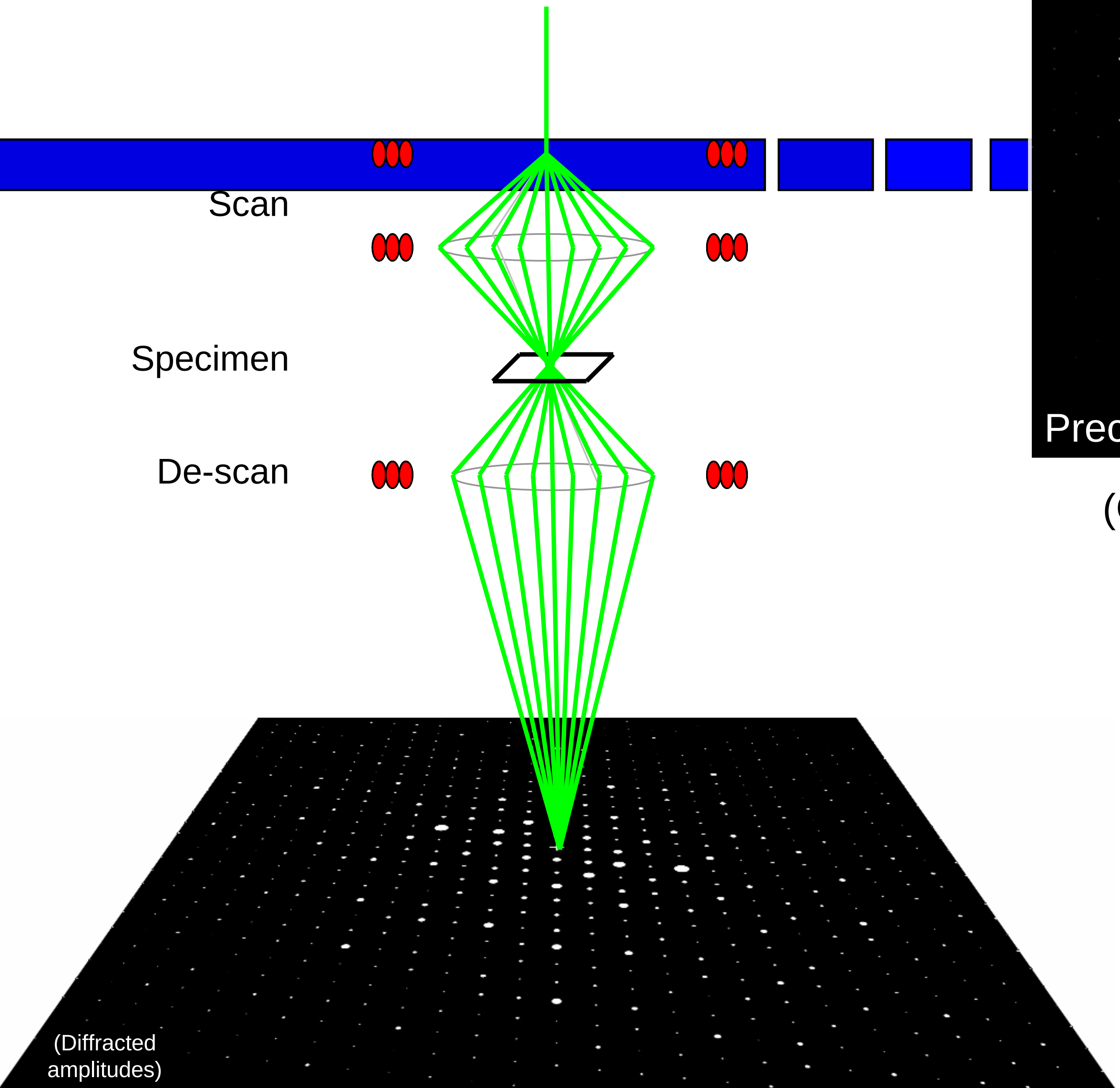
1. PRECESSION → MANY MORE REFLECTIONS INTERCEPTED BY EWALD SPHERE → LARGE DATA SET

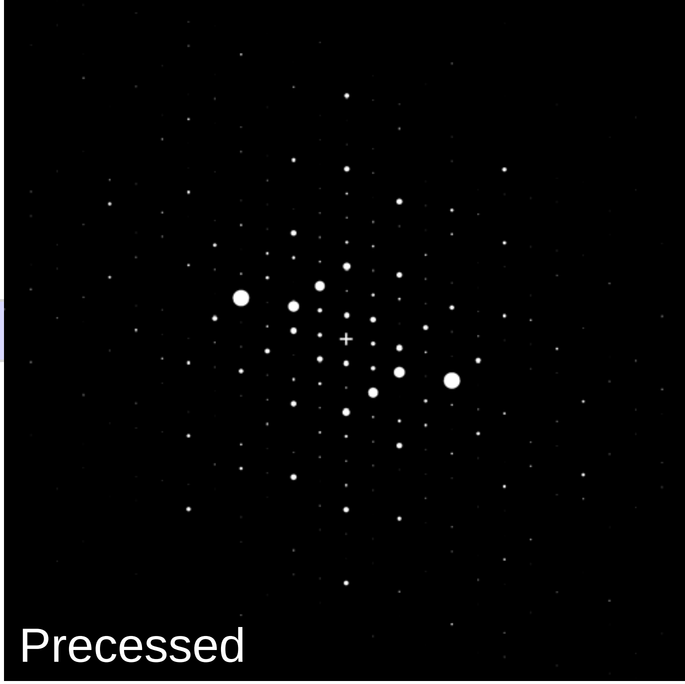
2. DIFFRACTED INTENSITIES DETERMINED BY INTEGRATING THROUGH BRAGG CONDITION → NO BRANCH STRUCTURE
   $\therefore\ I_g \rightarrow |U_g|^2$ (NOT PARTIAL S.F.)

3. REDUCES NON-SYSTEMATIC DYNAMICAL EFFECTS

4. FOCUSSED PROBE → HIGH SPATIAL RESOLUTION (~0·1 μm)





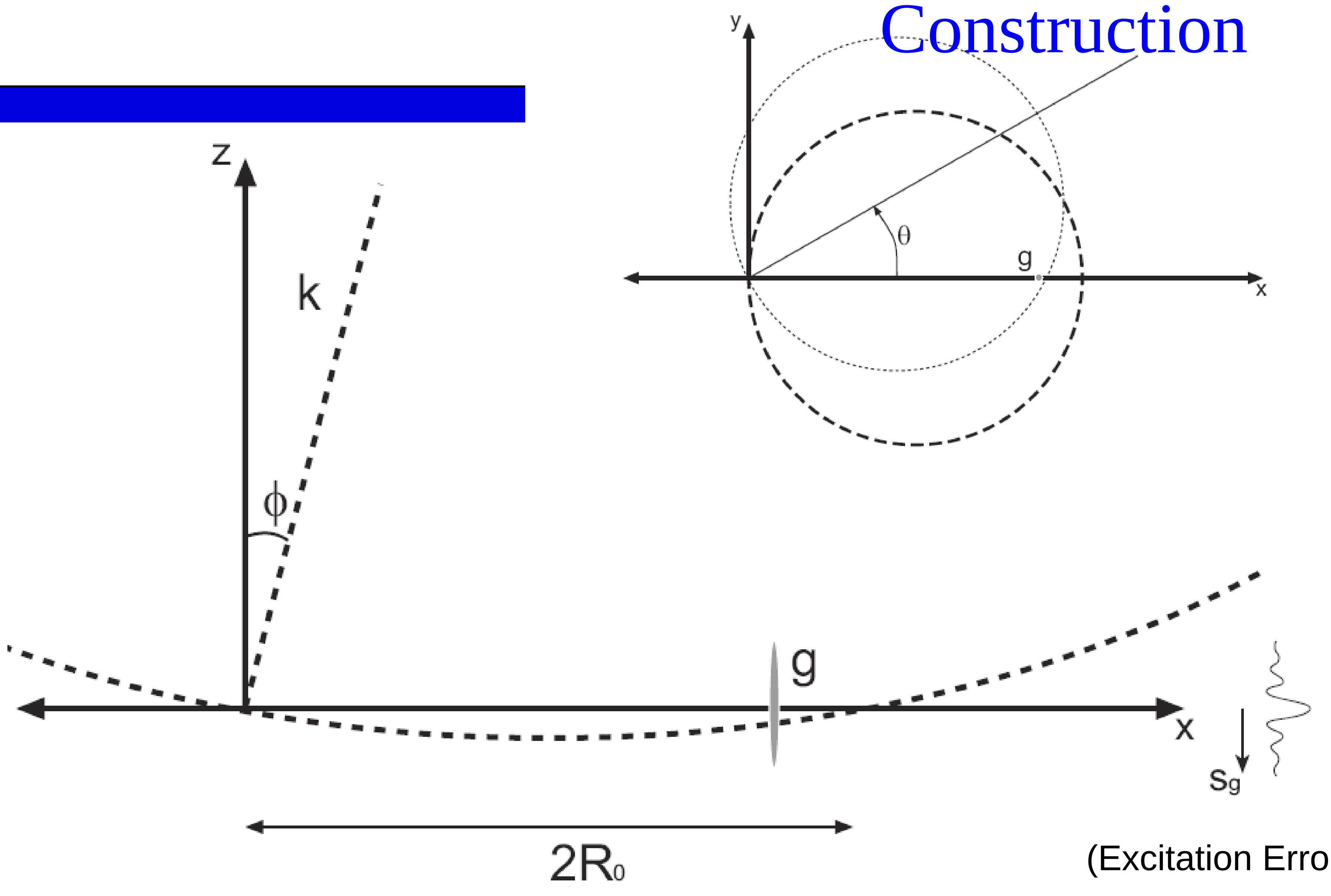


$(Ga,In)_2SnO_5$ Intensities

412Å crystal thickness

Conventional
Precessional
Precession…
Diffraction Pattern

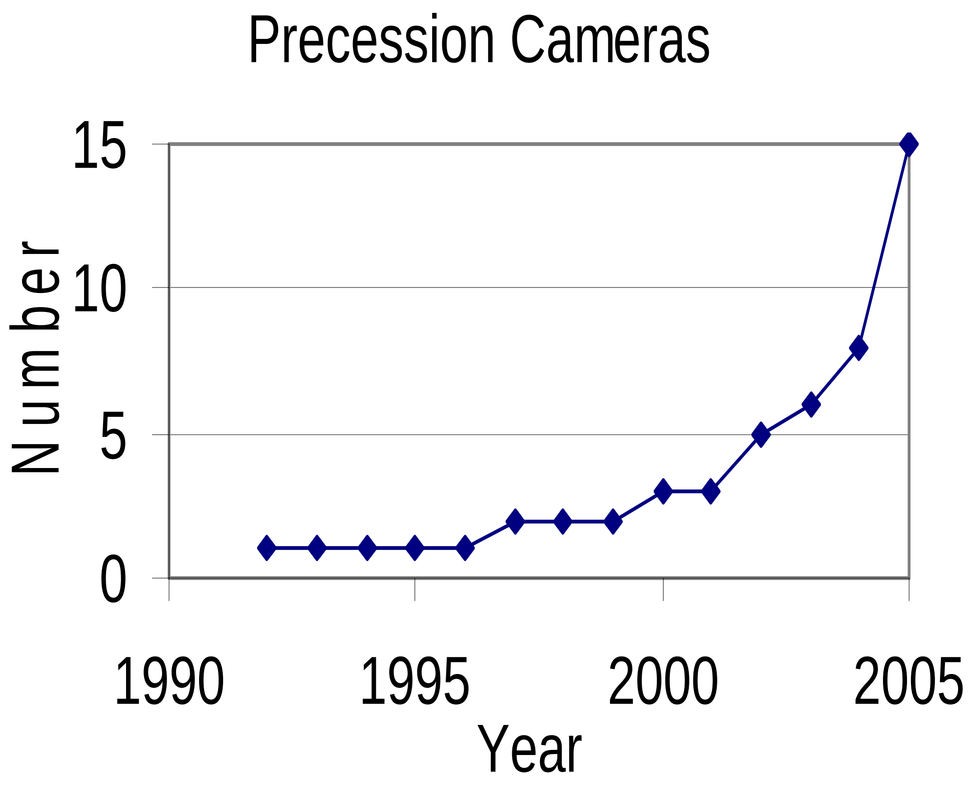
Ewald Sphere Construction



(Excitation Error)

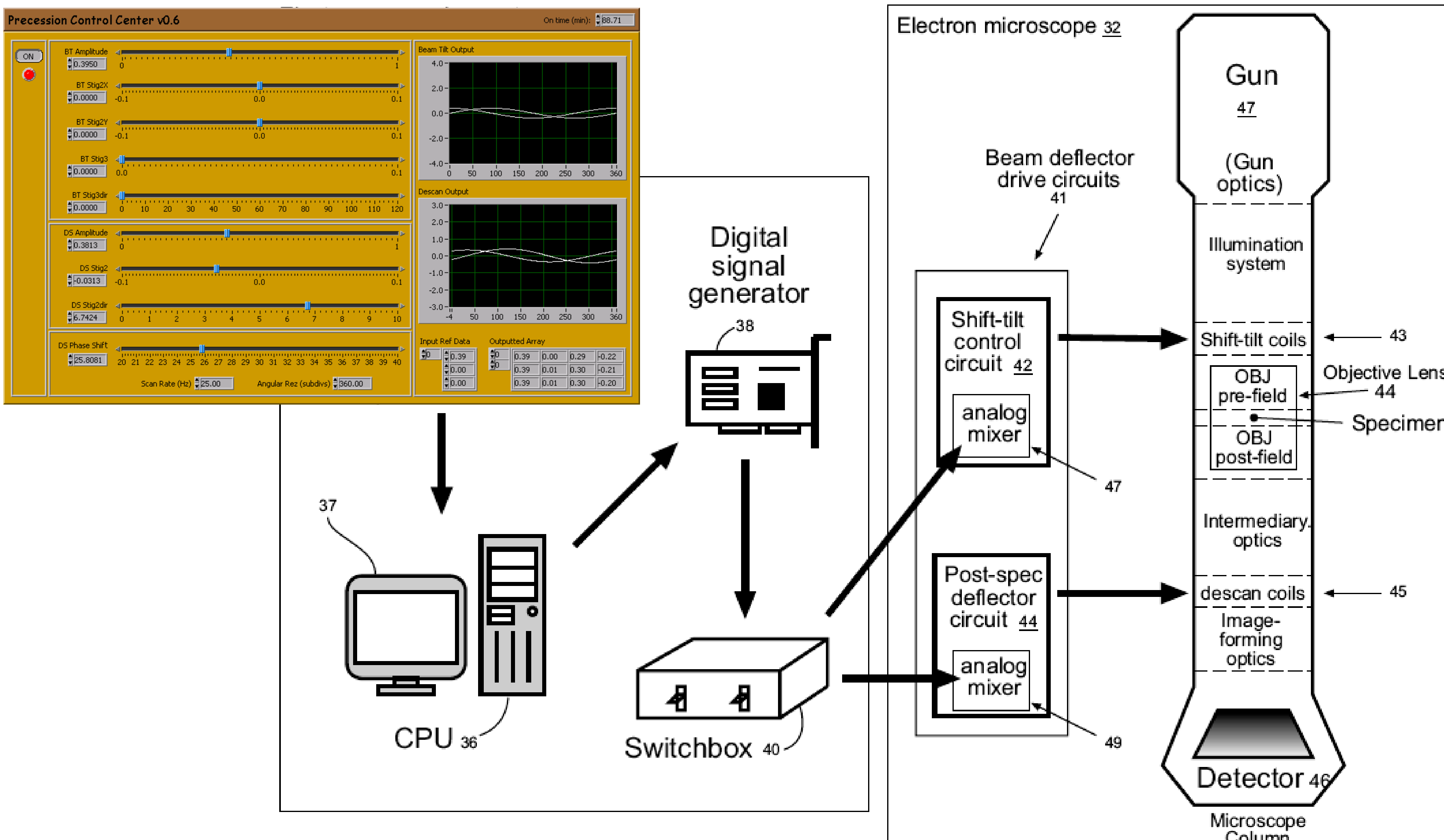
Precession Camera to date

- 1992: Vincent-Midgley
- 1997: Gjonnes
- 2000: NU1 (C.S.Own, undergrad thesis)
- 2002: Gemmini, NU2 (UOP)
- 2003: Castel
- 2004: NU3 (UOP), Spinning Star (Exxon)
- 2005: NU4 (NU & UIUC), SS (5)

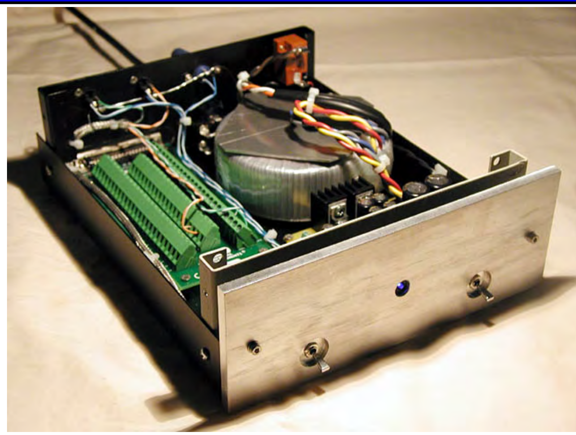


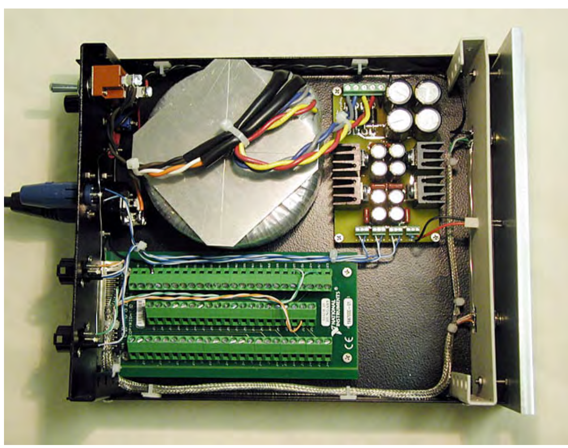
Precession System

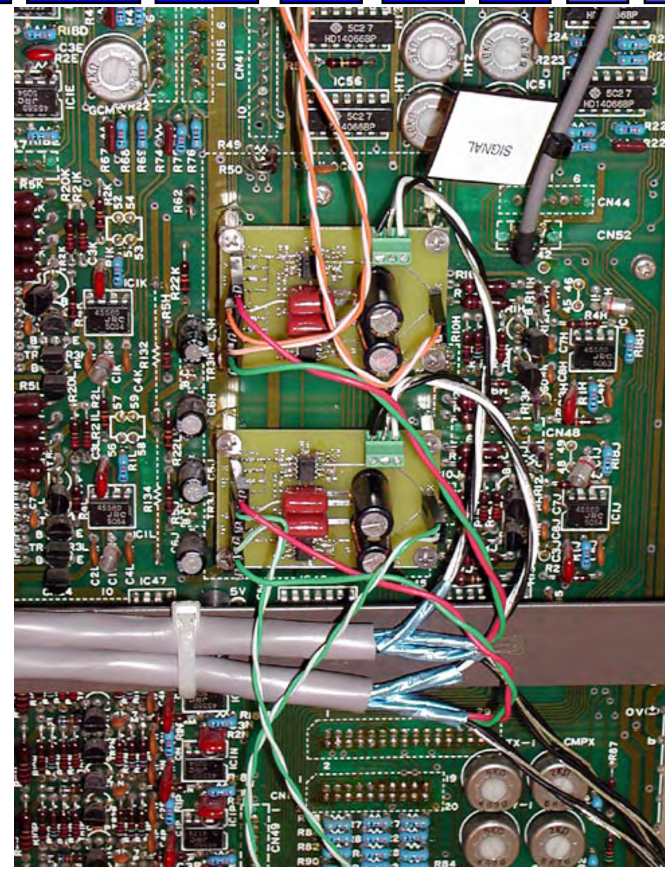
US patent application:
***"A hollow-cone electron diffraction system"*.**
Application serial number 60/531,641, Dec 2004.



Generation II hardware







Electron Precession: A Guide for Implementation, C.S. Own, L.D. Marks, and Wharton Sinkler, Reviews of Scientific Instrumentation, 76, 33703 (2005)

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**

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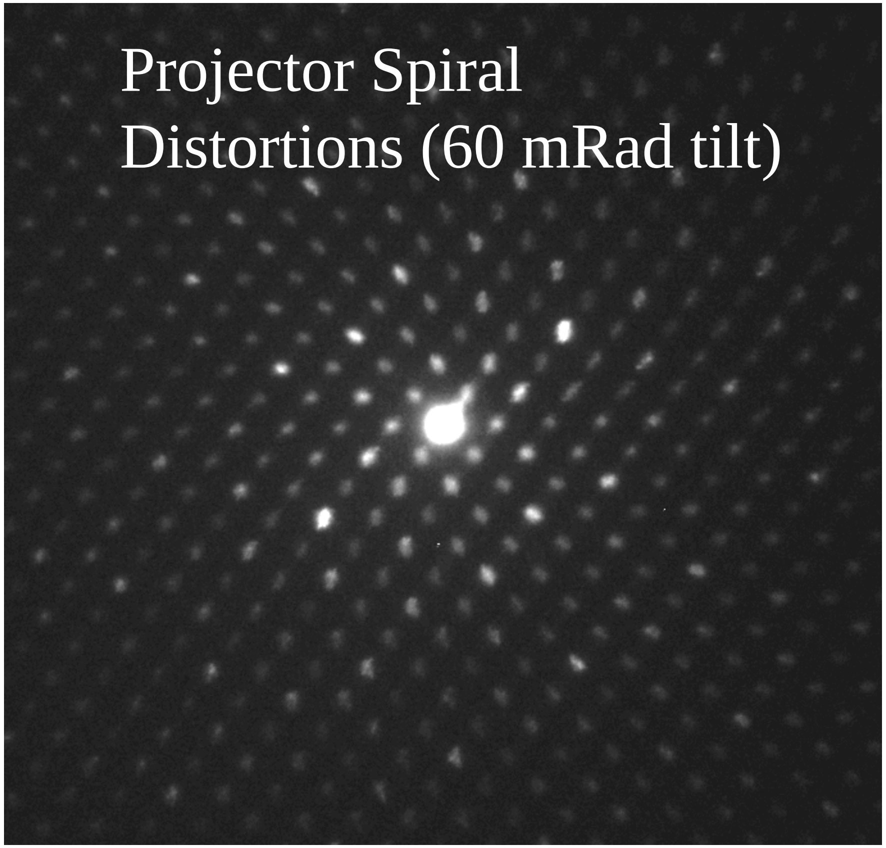
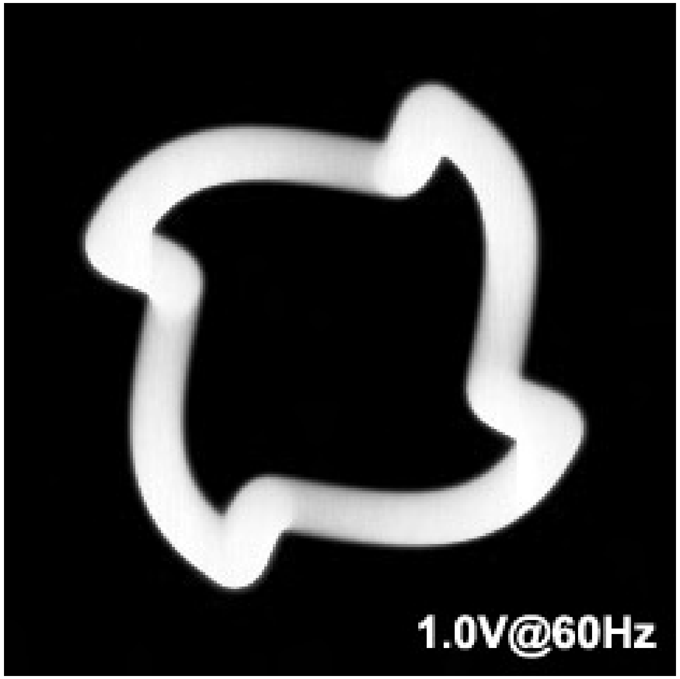
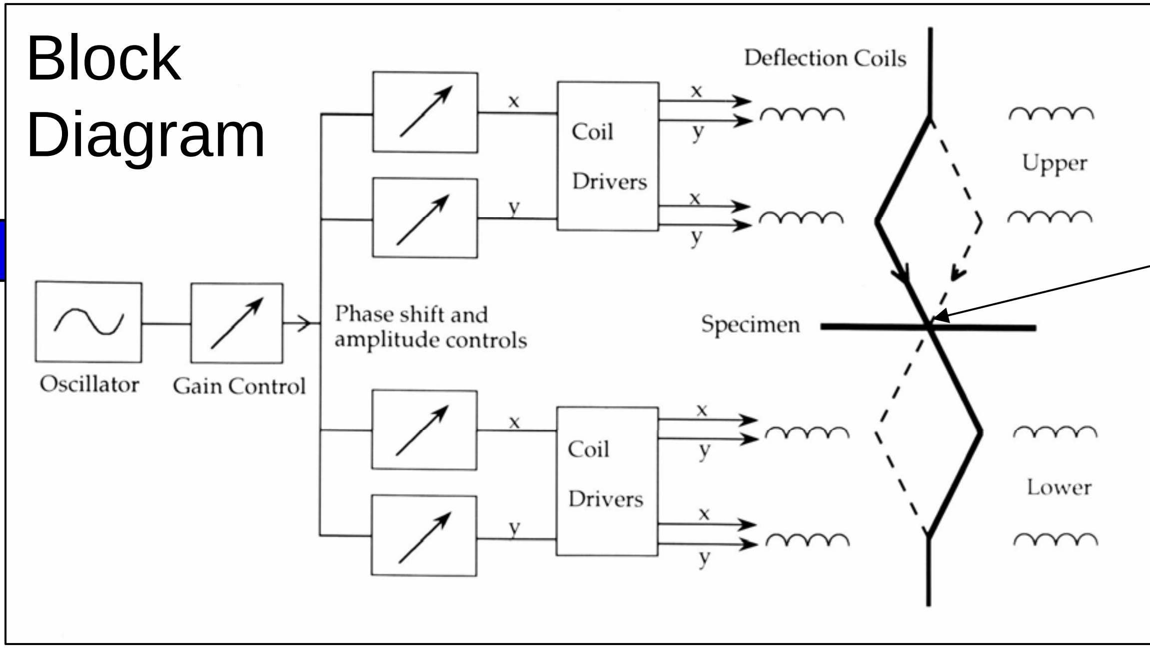
Some Practical Issues

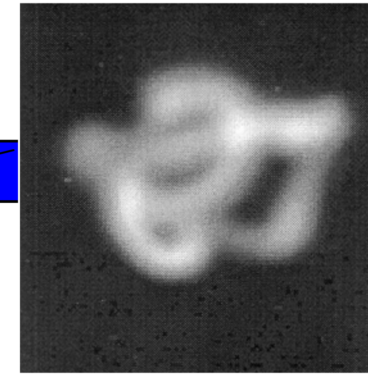




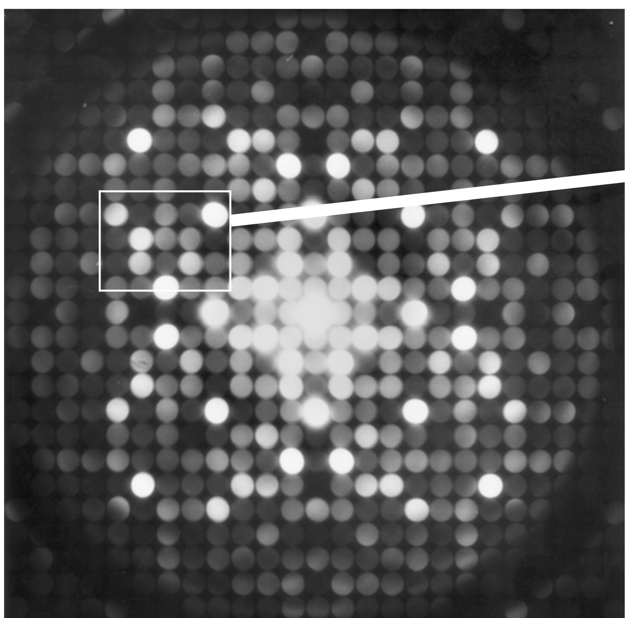
Bi-polar push-pull circuit
(H9000)

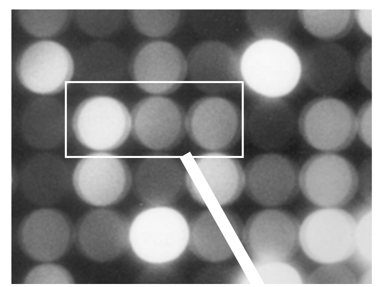
Block Diagram

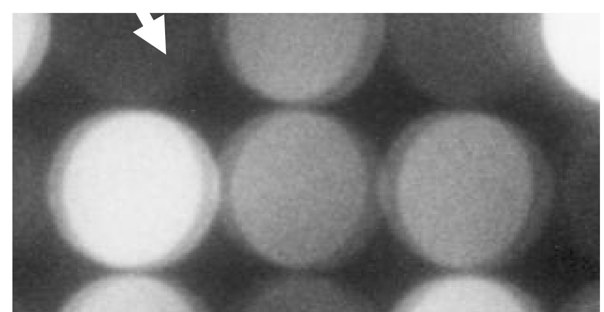




‘Aberrations’

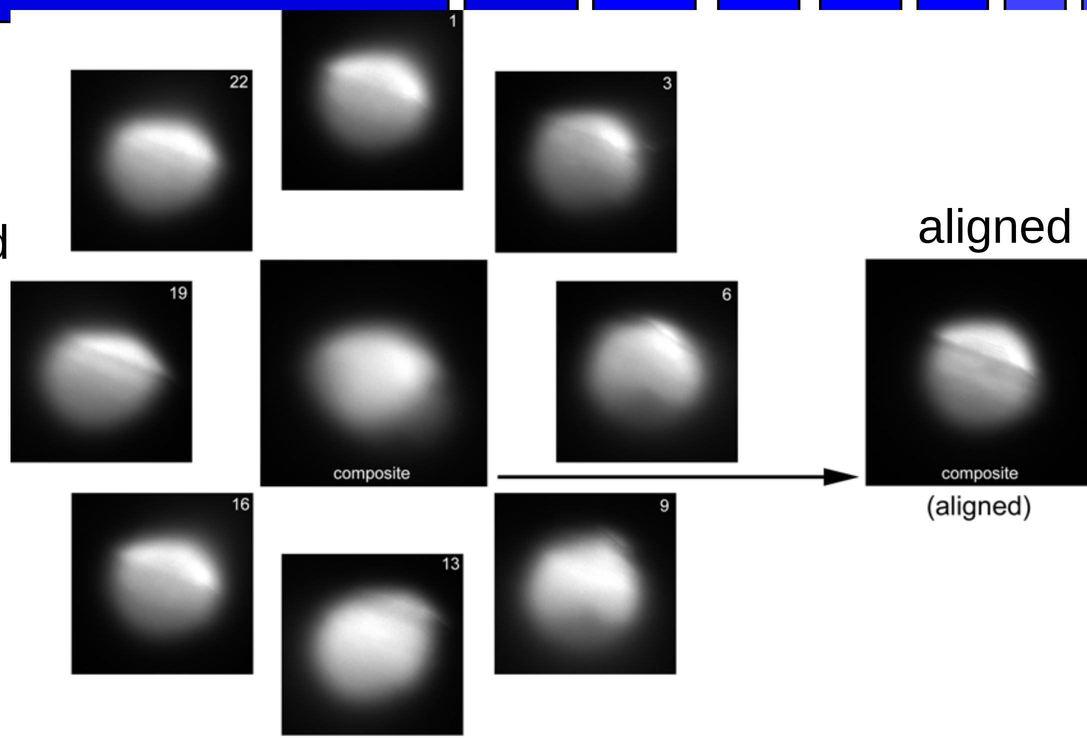






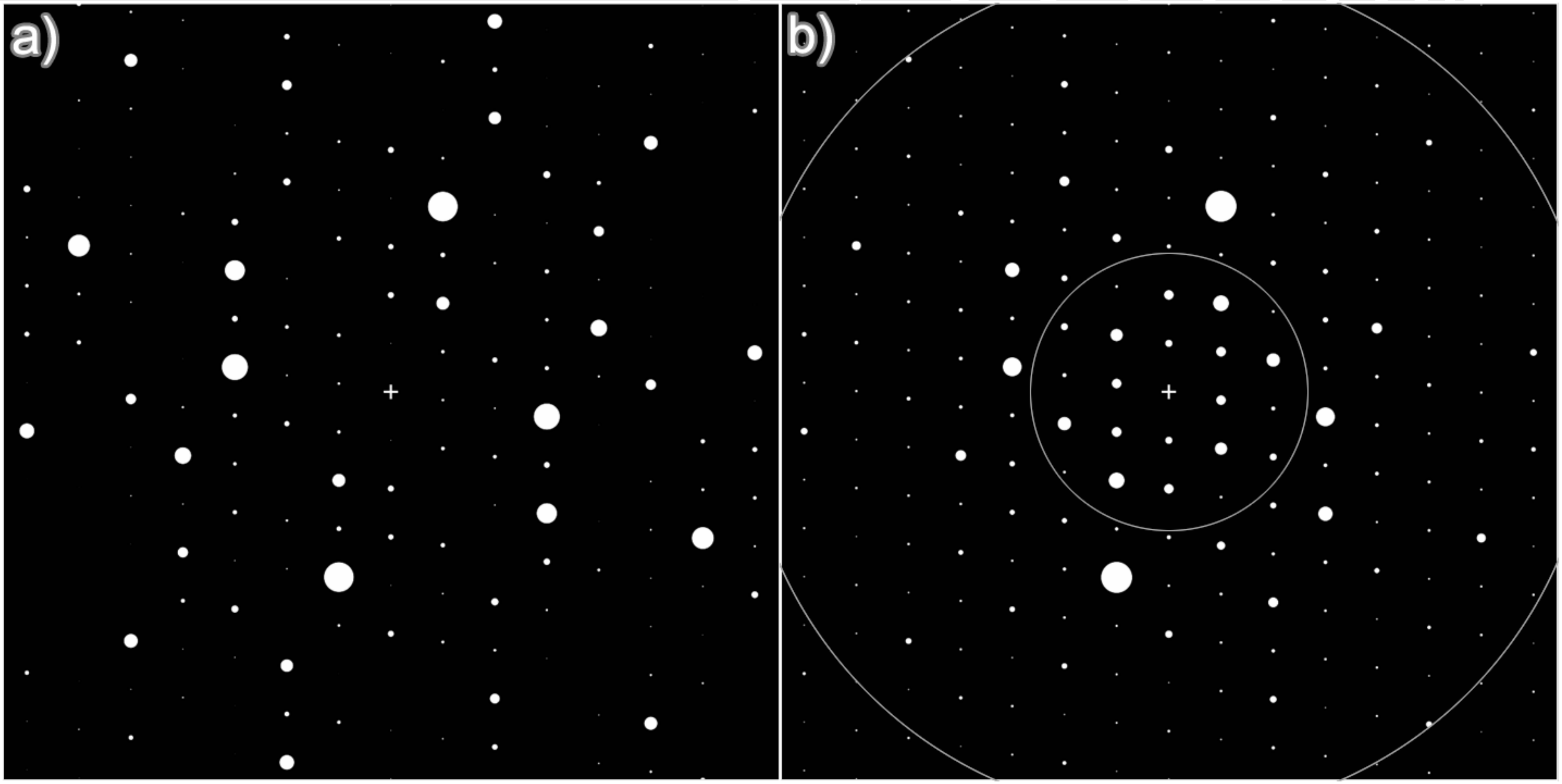
Demonstrate Probe wandering
50nm probe @ α~25mRad (NU2)

Slightly misaligned



- Each image from montage is from a different tilt
- The location in real space deviates by ~10-15nm in the slightly misaligned condition
- Meticulous alignment suppresses the deviation but cannot remove it
- Smallest probe (NU3) ~ 20nm

Qualitative Comparison:
$(Ga,In)_2SnO_4$ (a known structure)

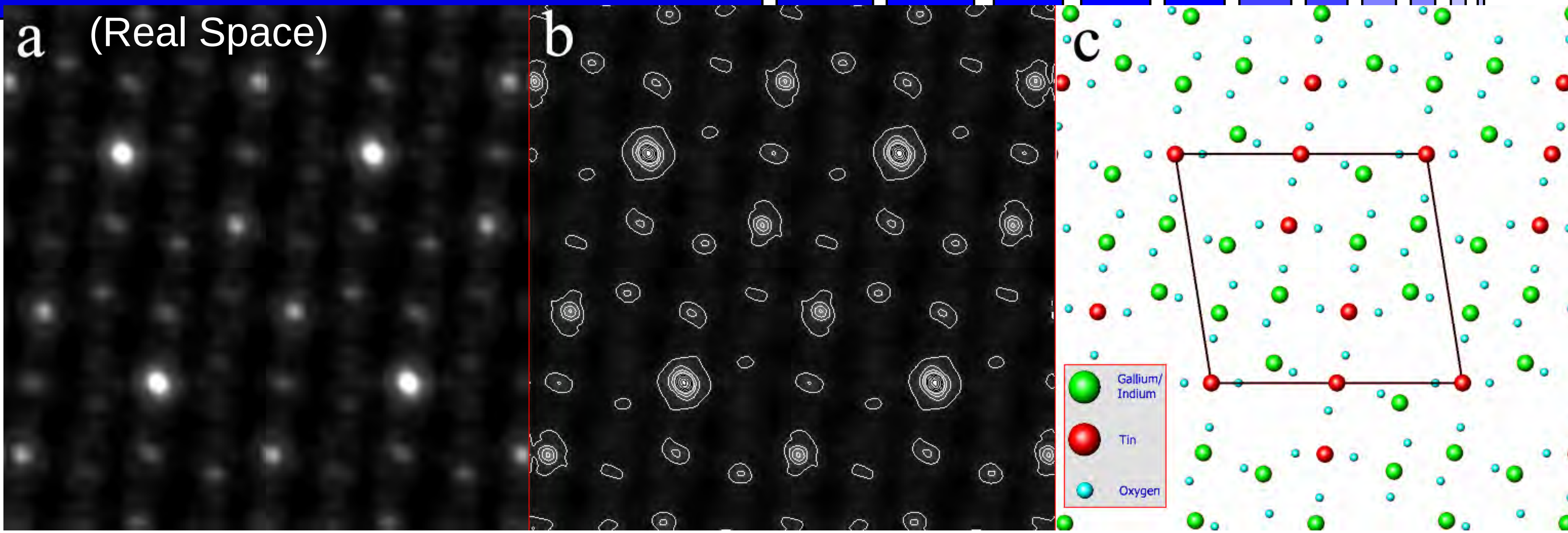


Kinematical (reference)

Precession pattern (experiment)
ϕ = 24mrad

$(Ga,In)_2SnO_4$ precession data:

Direct methods solution (EDM)



	ΔR (Å)
Sn1	0.00E+00
Sn2	0.00E+00
Sn3	6.55E-03
In/Ga1	5.17E-02
In/Ga2	2.37E-03
Ga1	6.85E-02
Ga2	1.22E-01

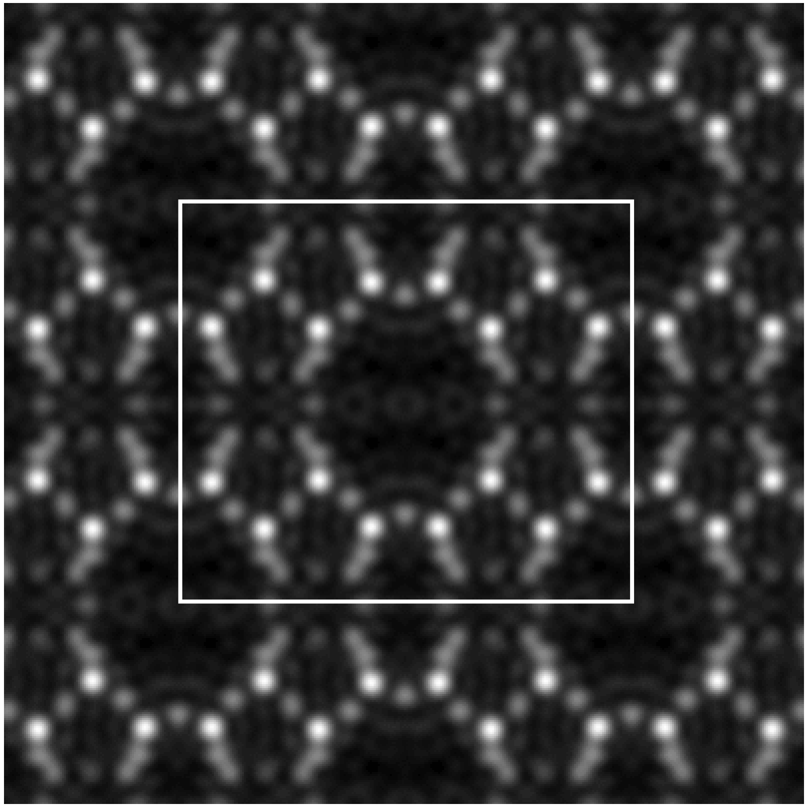
Displacement ($R_{neutron} - R_{precession}$):

$\Delta R_{mean} < \mathbf{4*10^{-2}}$ **Å**

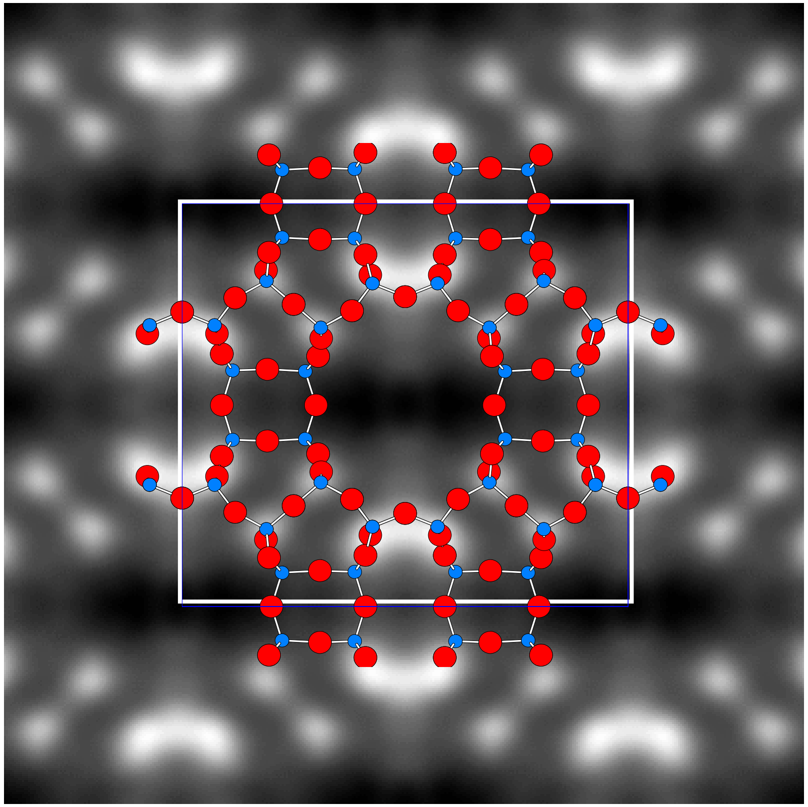
(Sinkler, et al. J. Solid State Chem, 1998).

(Own, Sinkler, & Marks, submitted.)

Mordenite, kind-of solves

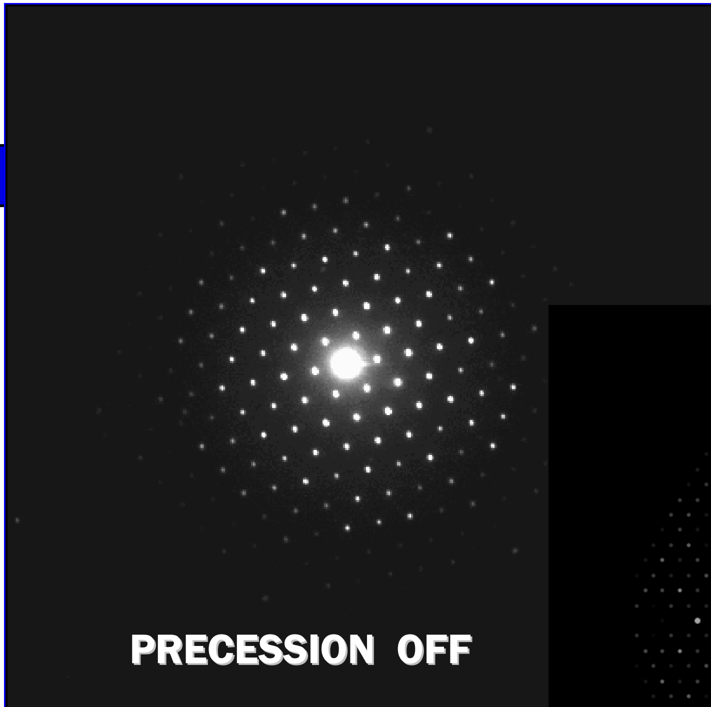


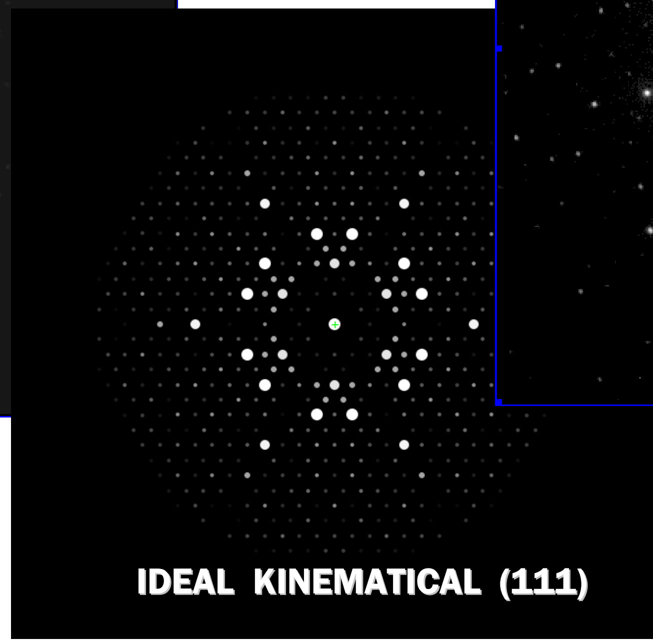
From modeled kinematical data



8th ranked solution, from raw precession data

APPLICATION : FIND TRUE CRYSTAL SYMMETRY





UVAROVITE (111)

Courtesy M.Gemmi
Univ of Milano

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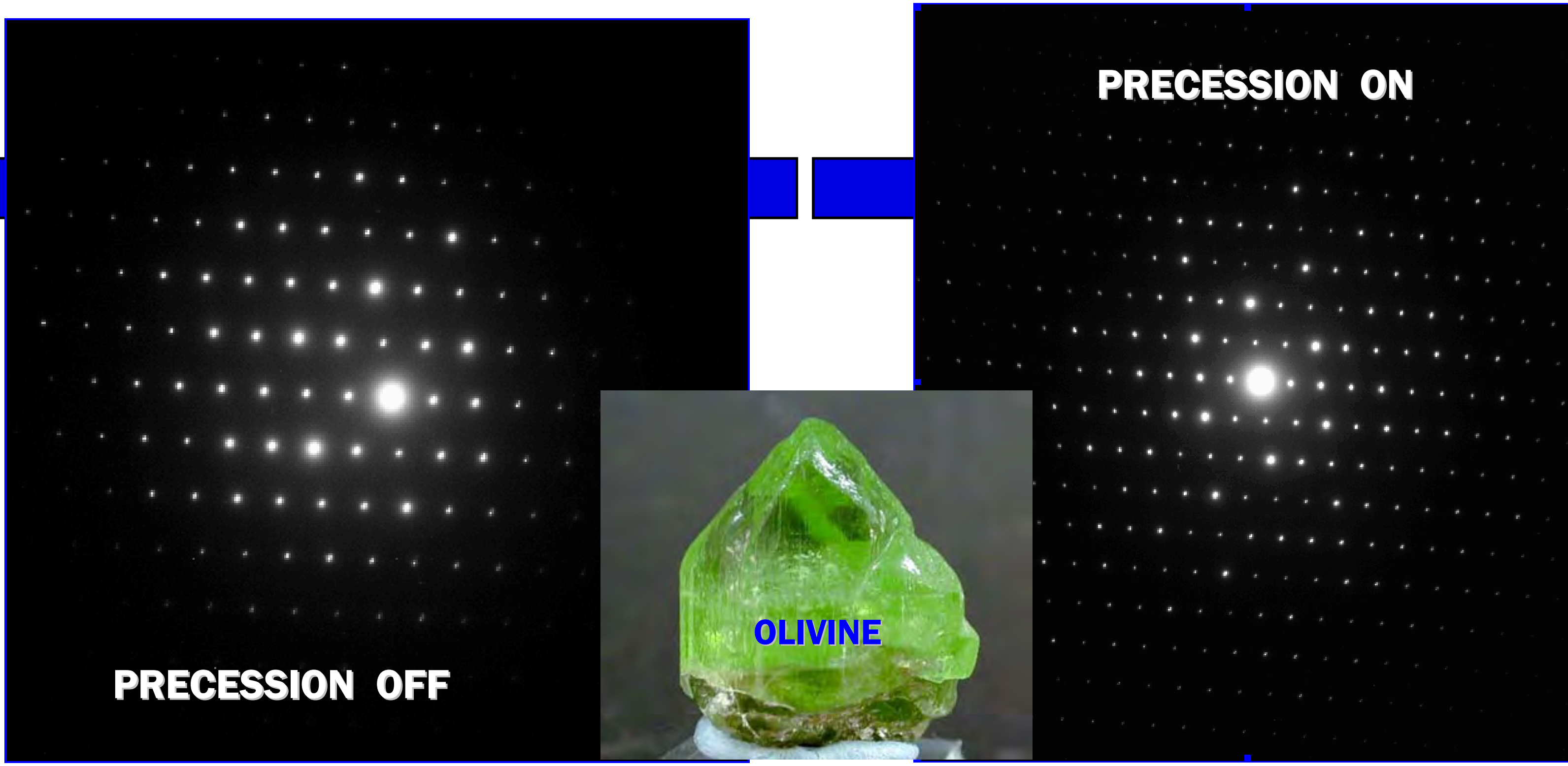
APPLICATION : PERFECT CRYSTAL ORIENTATION



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.

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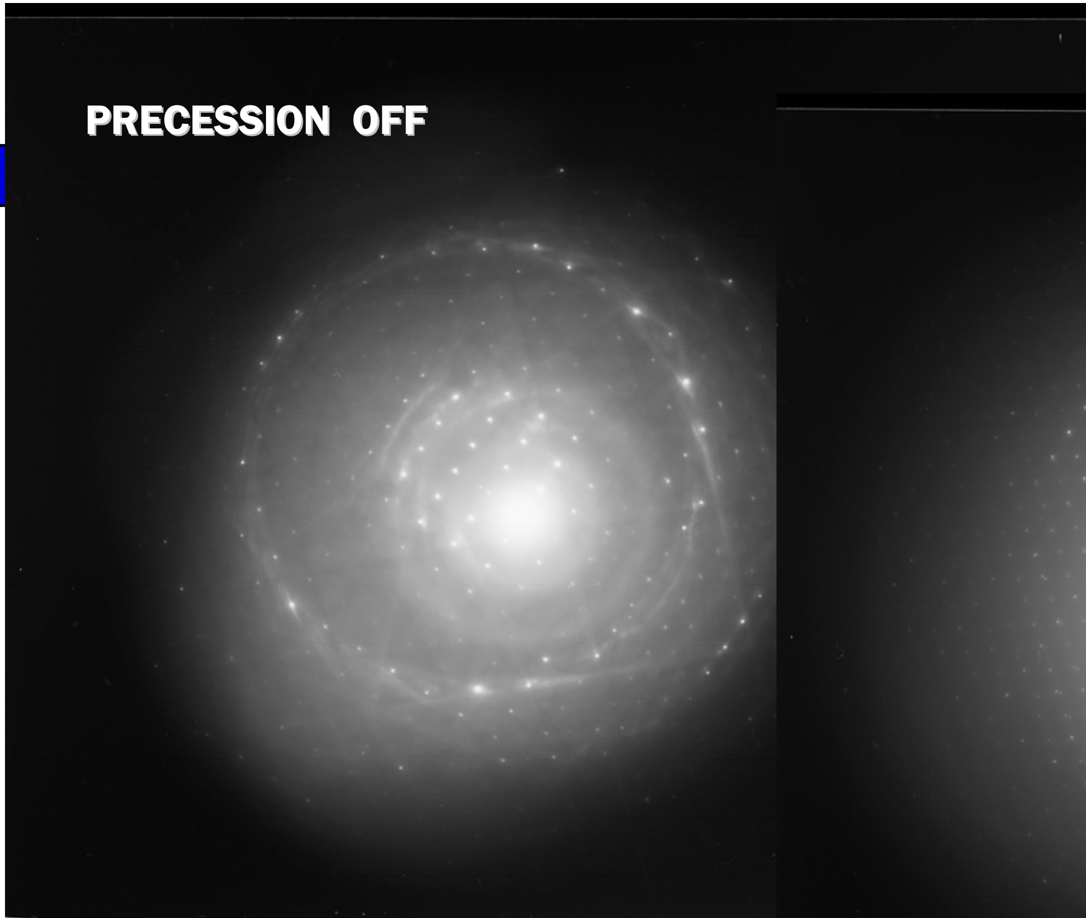
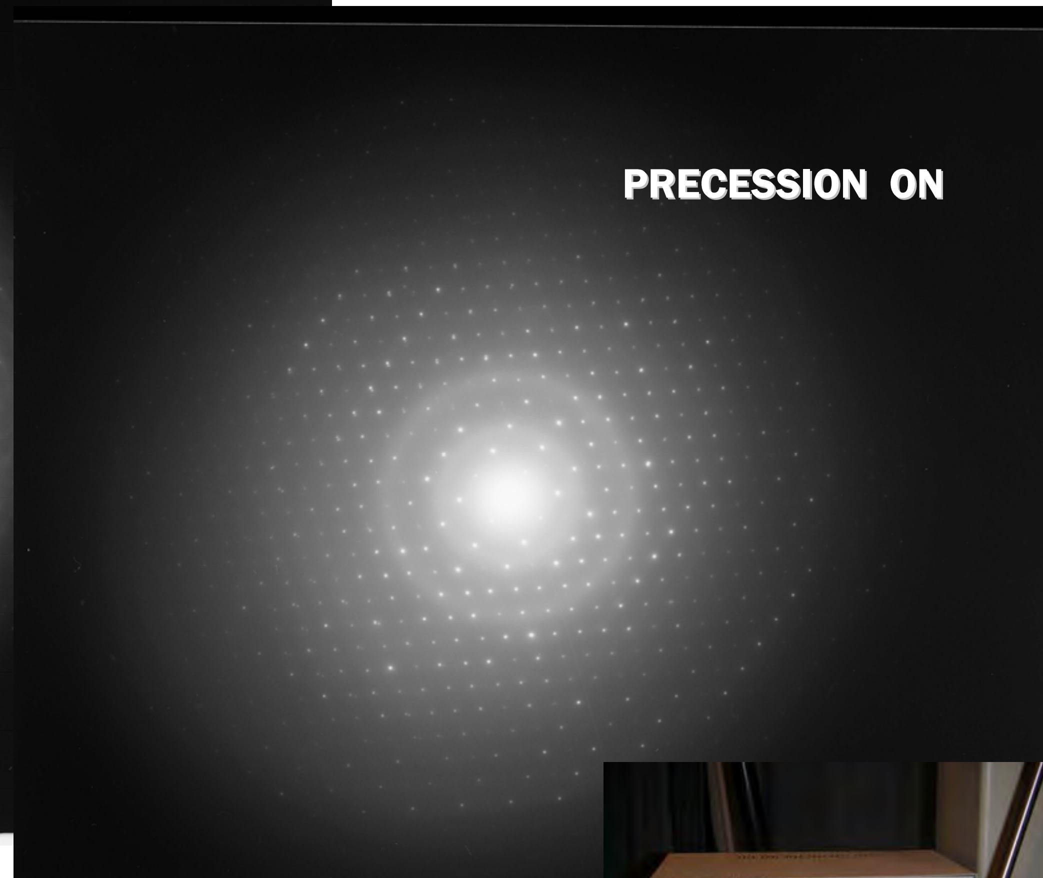
Courtesy X.Zou, S.Hovmoller Univ Stockholm

APPLICATION : PERFECT CRYSTAL ORIENTATION

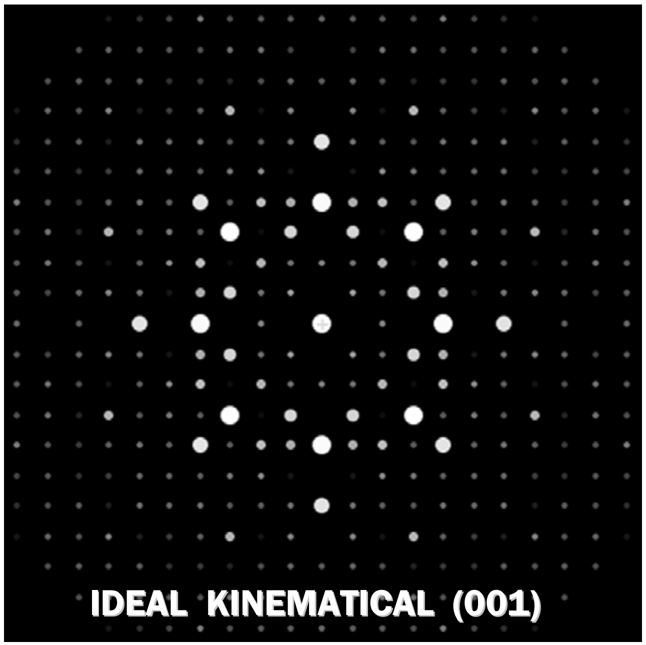


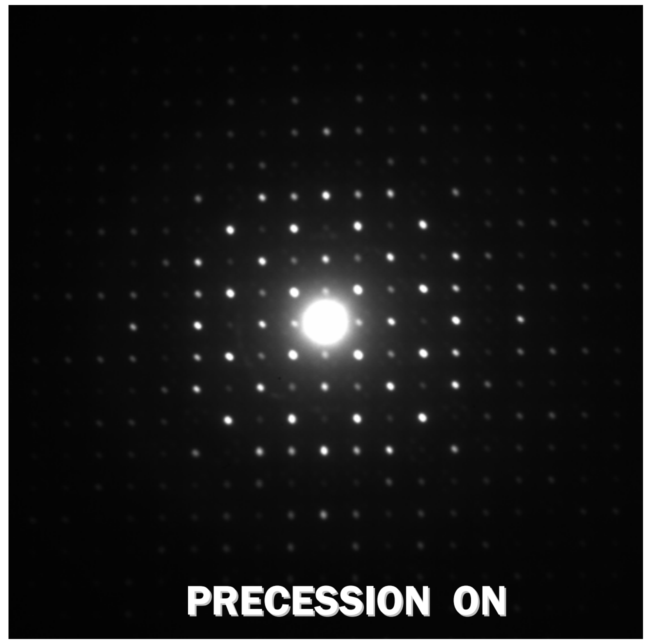


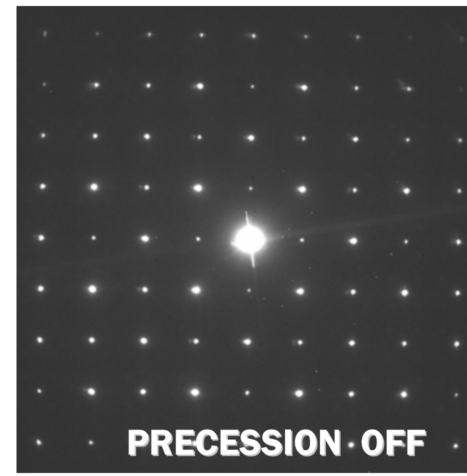
Precession is not sensible to small variation of thickness and (or) misorientation; in this example $NdAl_3(BO_3)_4$ crystal alhough is far from zone axis orientation, after precession is on show similar pattern to a nearby zone axis oriented crystal.

Precession on akermanite

[001]







$Ca_2MgSi_2O_7$ Tetragonal

a= 0.7835 nm C= 0.501 nm

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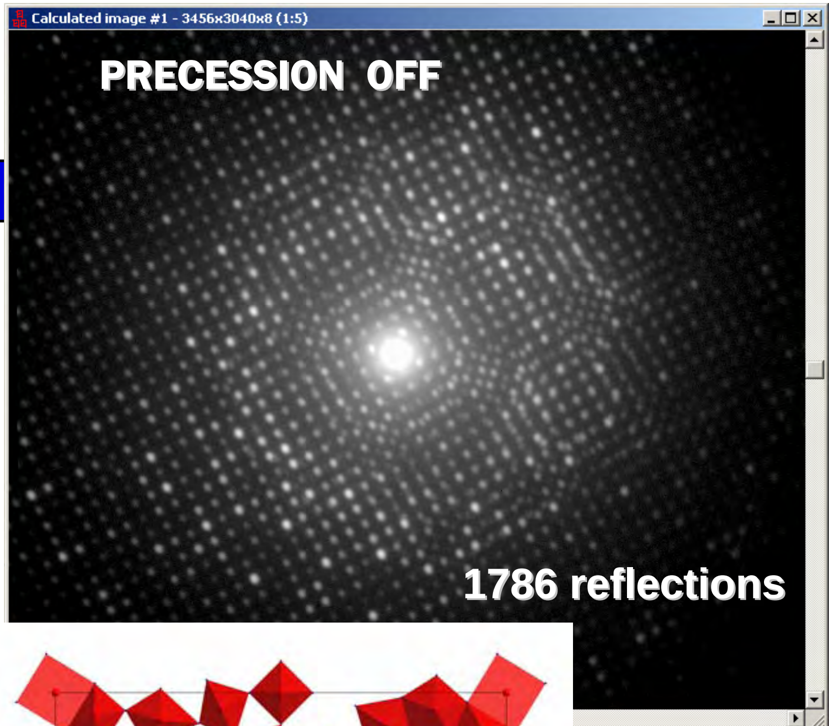
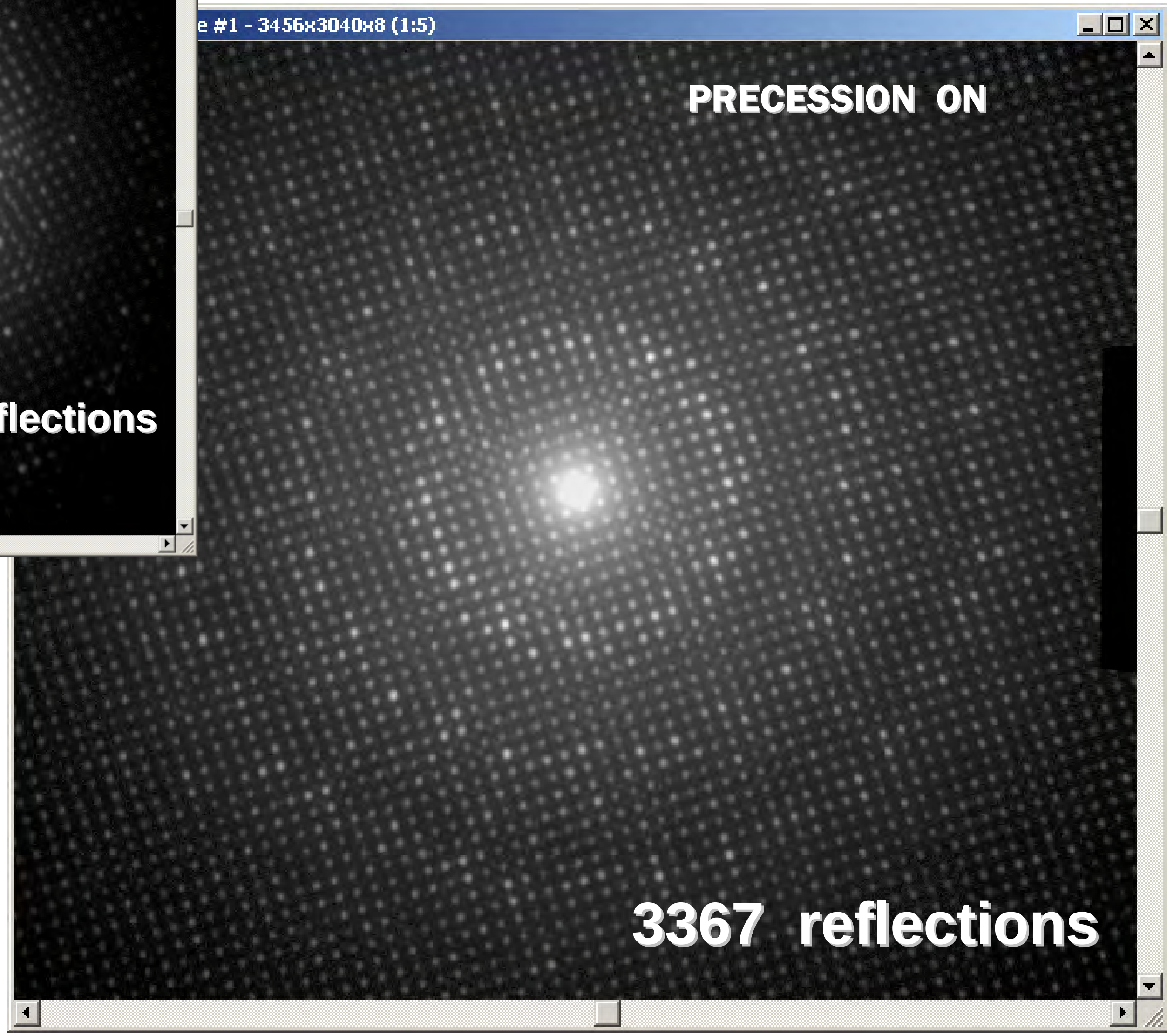
Courtesy M.Gemmi Univ of Milano

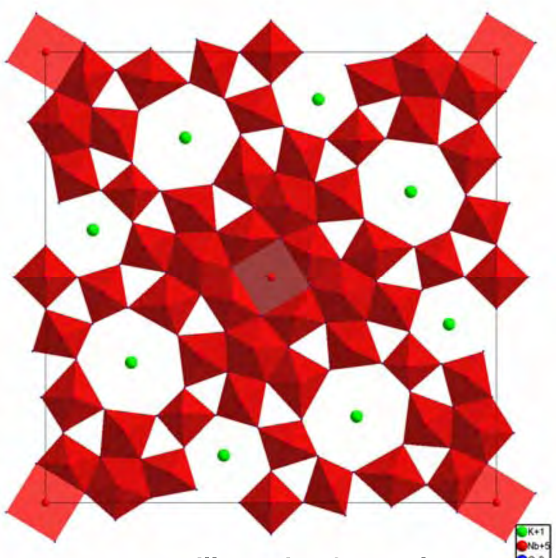
AUTOMATIC DETERMINATION OF CRYSTAL SYMMETRY

KNb_7O_{18} TETRAGONAL

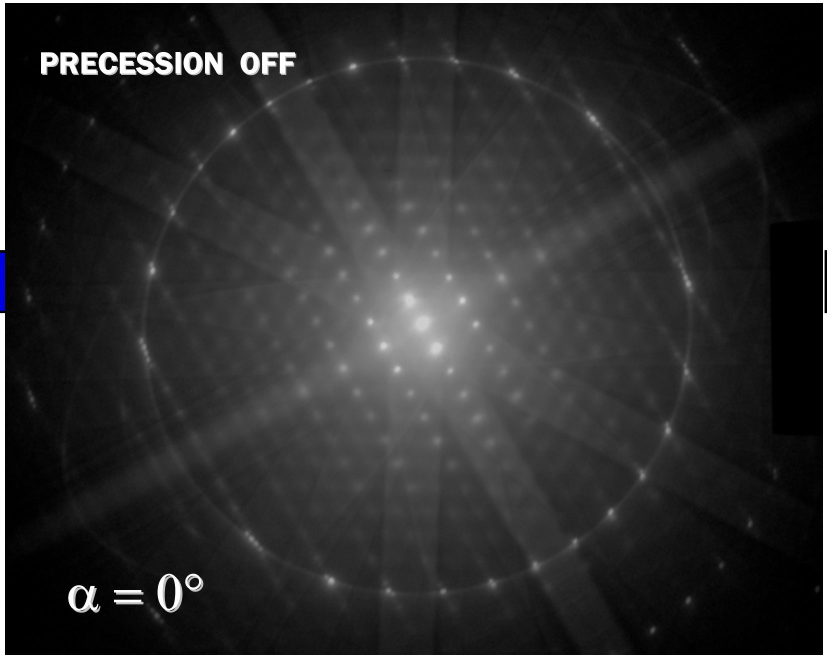
a = b = 2.749 nm c= 0.394 nm

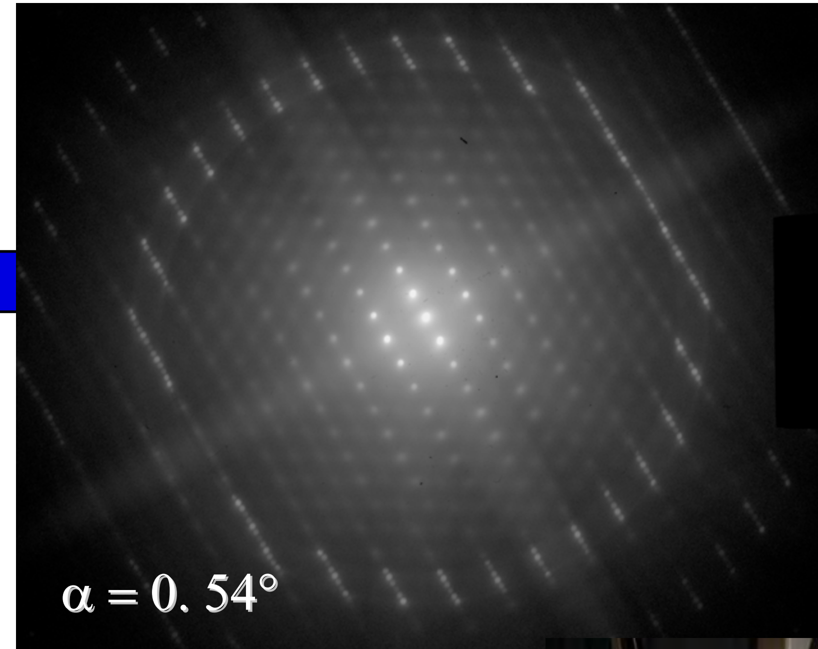






Courtesy J.Portillo Univ of Barcelona
T. Weirich Univ Aachen Germany





SiC 4H hexagonal P6_3mc

In this application example by varying precession angle symmetry of FOLZ becomes more and more visible ;

it is then straightforward space and point group symmetry determination of crystal (without use of convergent beam)

Courtesy JP Mornirolli Univ of Lille France

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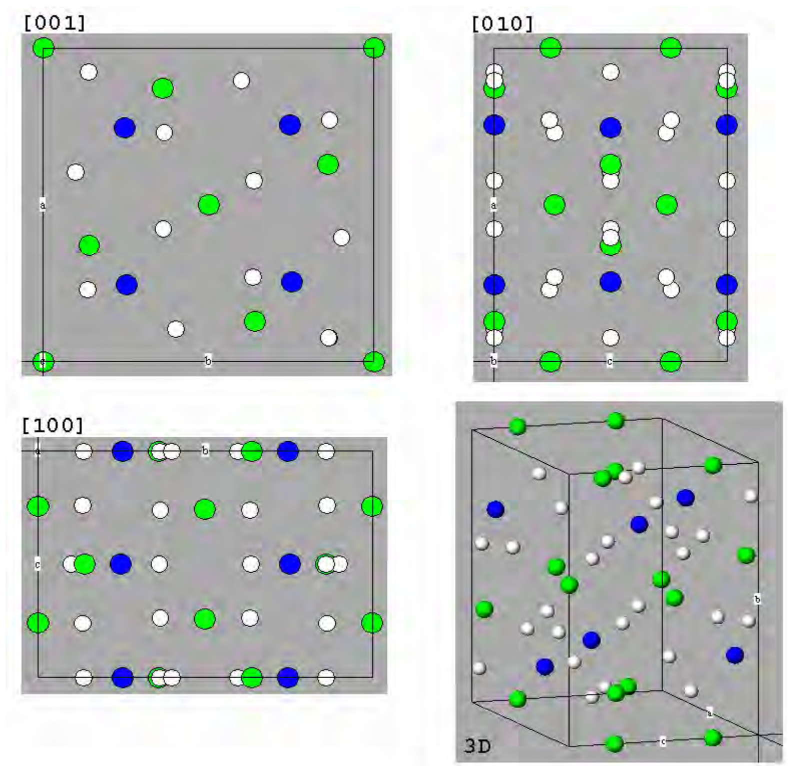
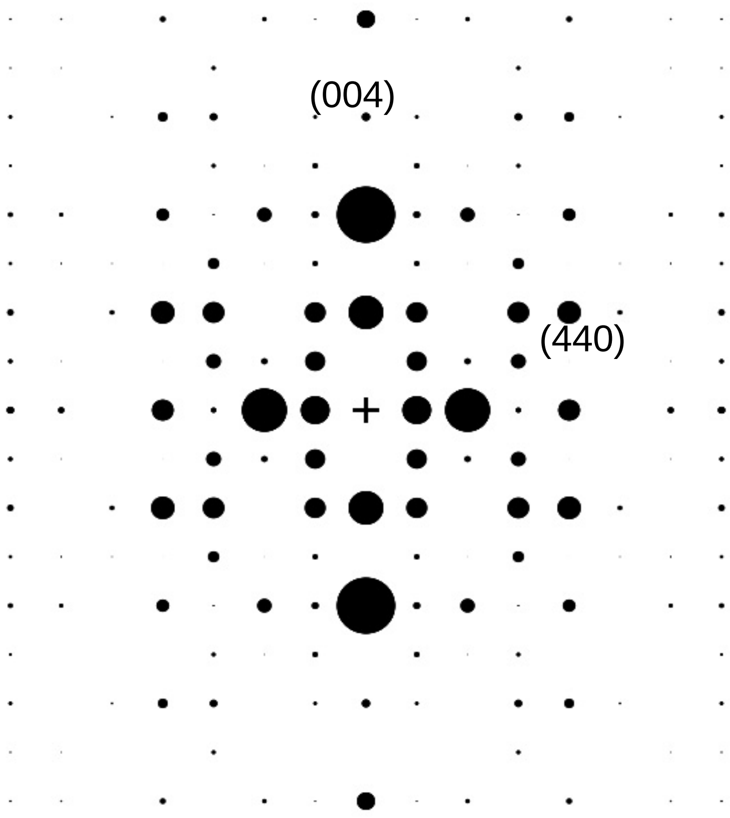
Test Case: Andalusite

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



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

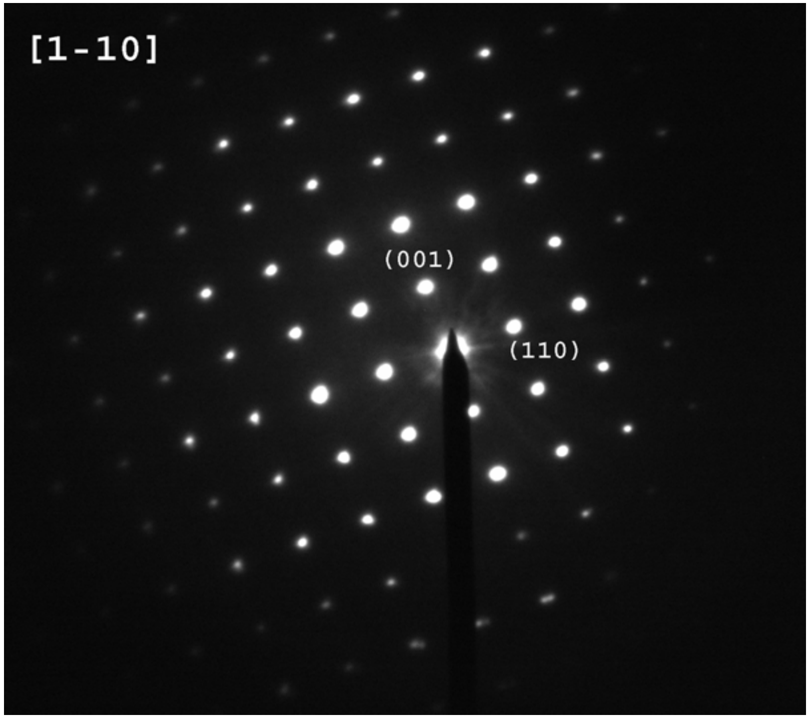
Kinematical Simulation [1$\bar{1}$0]



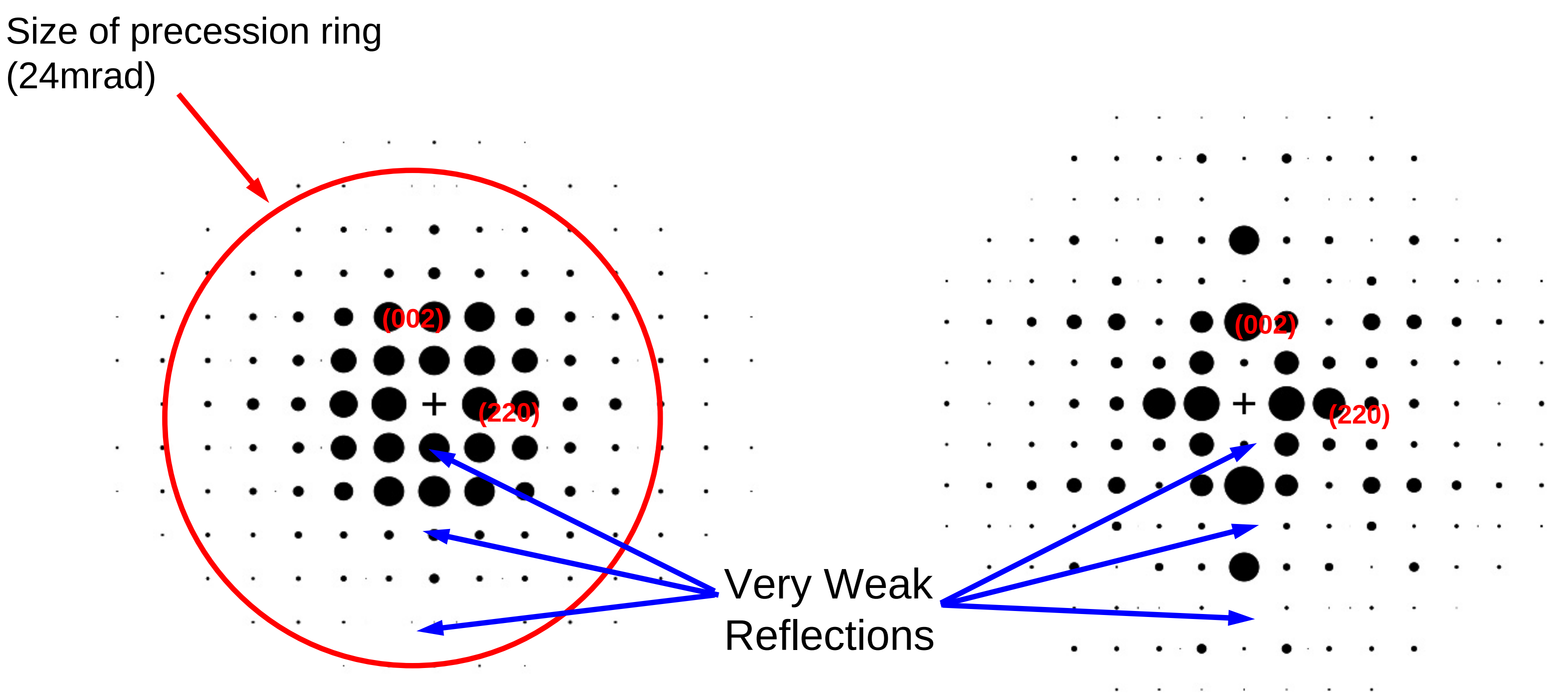
- Computed using WebEMAPS
- Note: lots of weak reflections
- p2mm Symmetry
- Diameter →Intensity

Initial Measurement with 8100

- Exhibited a very strong (001) spot(s), kinematically weak
- Check CCD calibration
  - Computed: 36 μm/pix
  - S.Y. Li: 6.8 μm/pix
- Go to UOP and do some precession

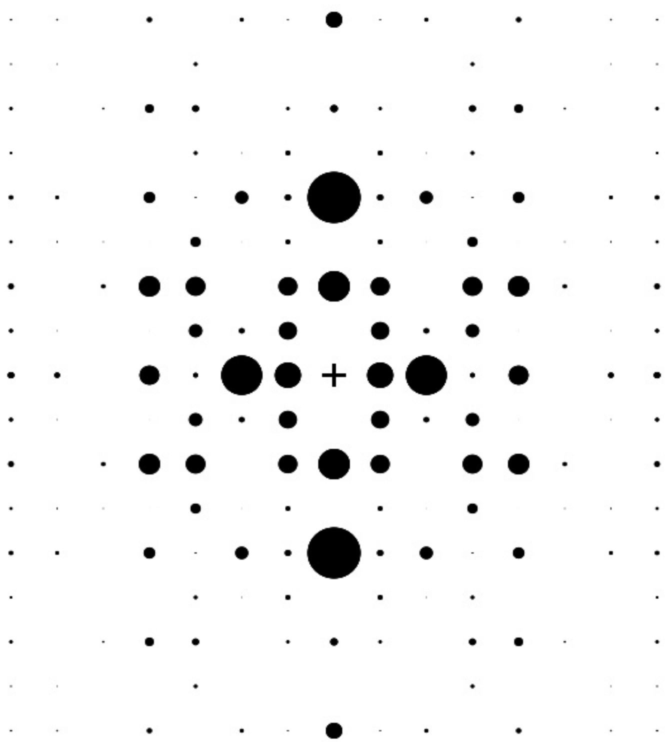


Measured DP $[1\bar{1}0]$

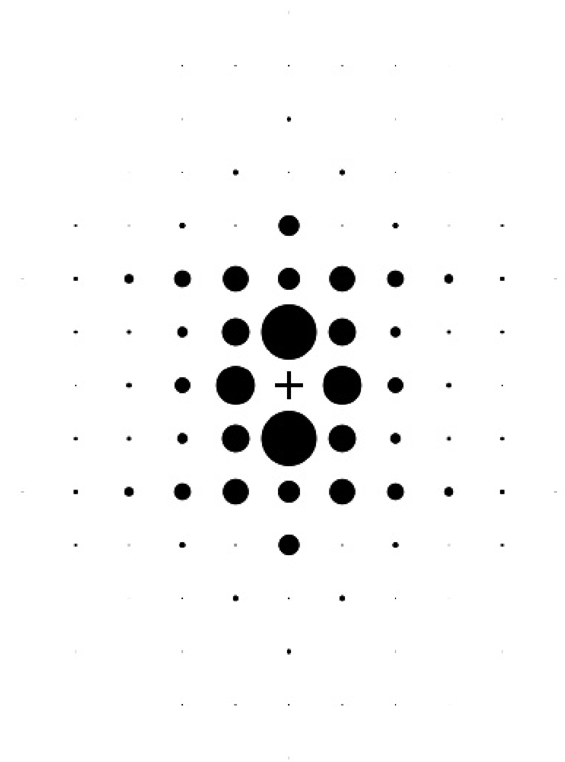


- DPs measured with EDM (p2mm) and plotted in Semper
- Precession angle rather low (24 mrad)
- What is the effect of increasing the angle?

Comparison of Kinematical vs. Precession Simulations



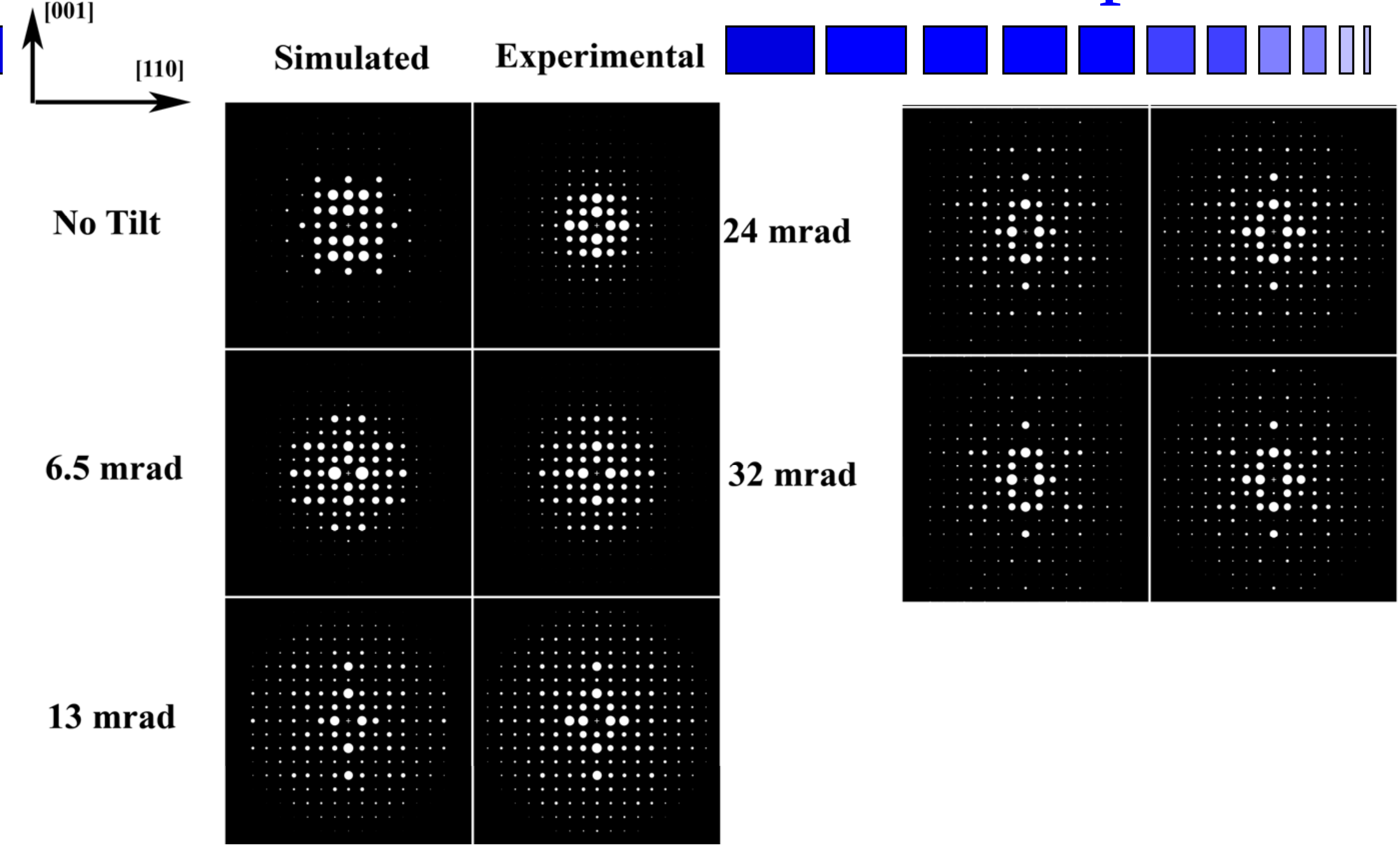
Kinematical



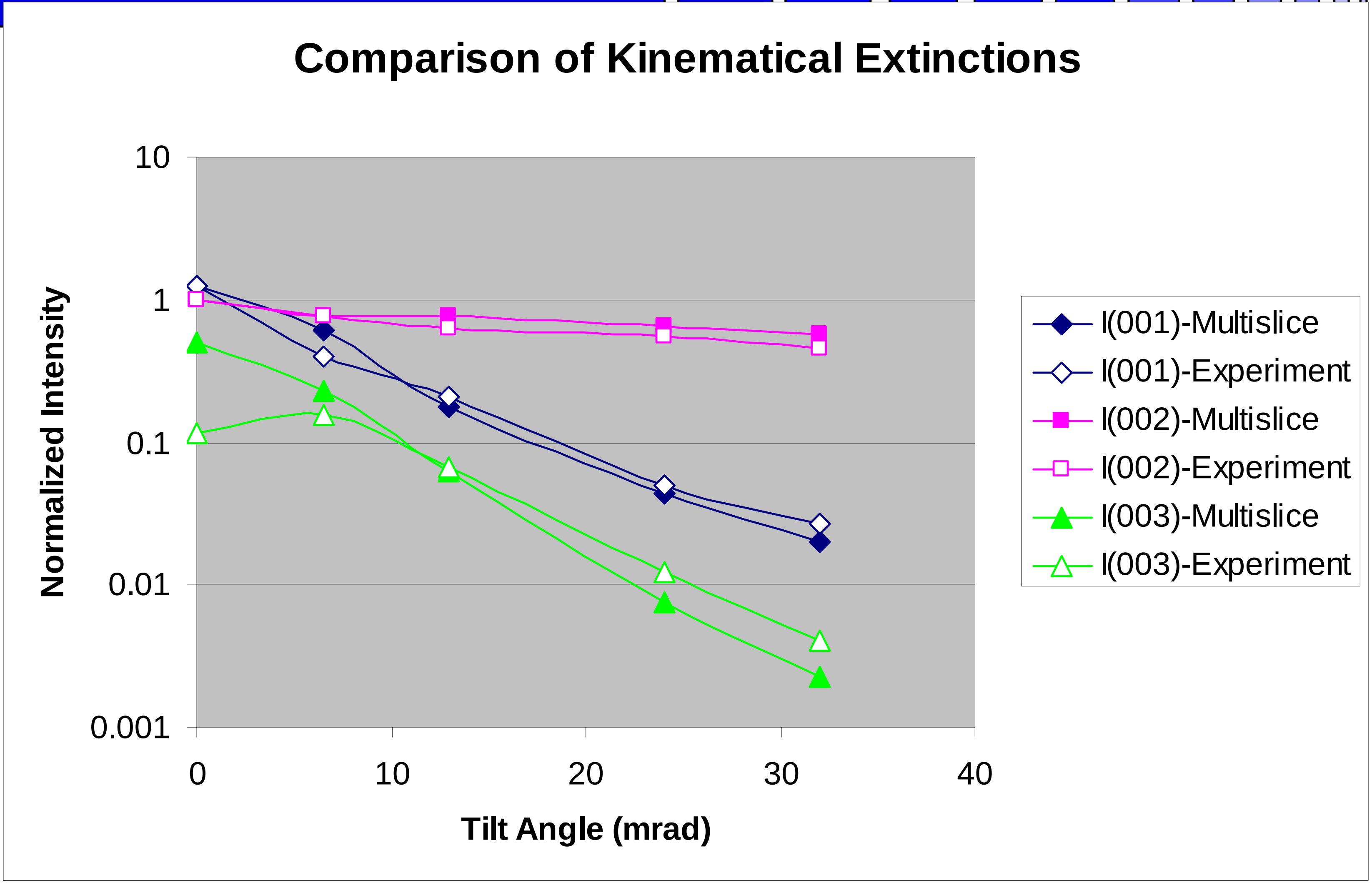
Full Dynamical mrad

Problem(?) with precession simulation: Weak thickness dependance of the result…sample thickness not well known (300A used)

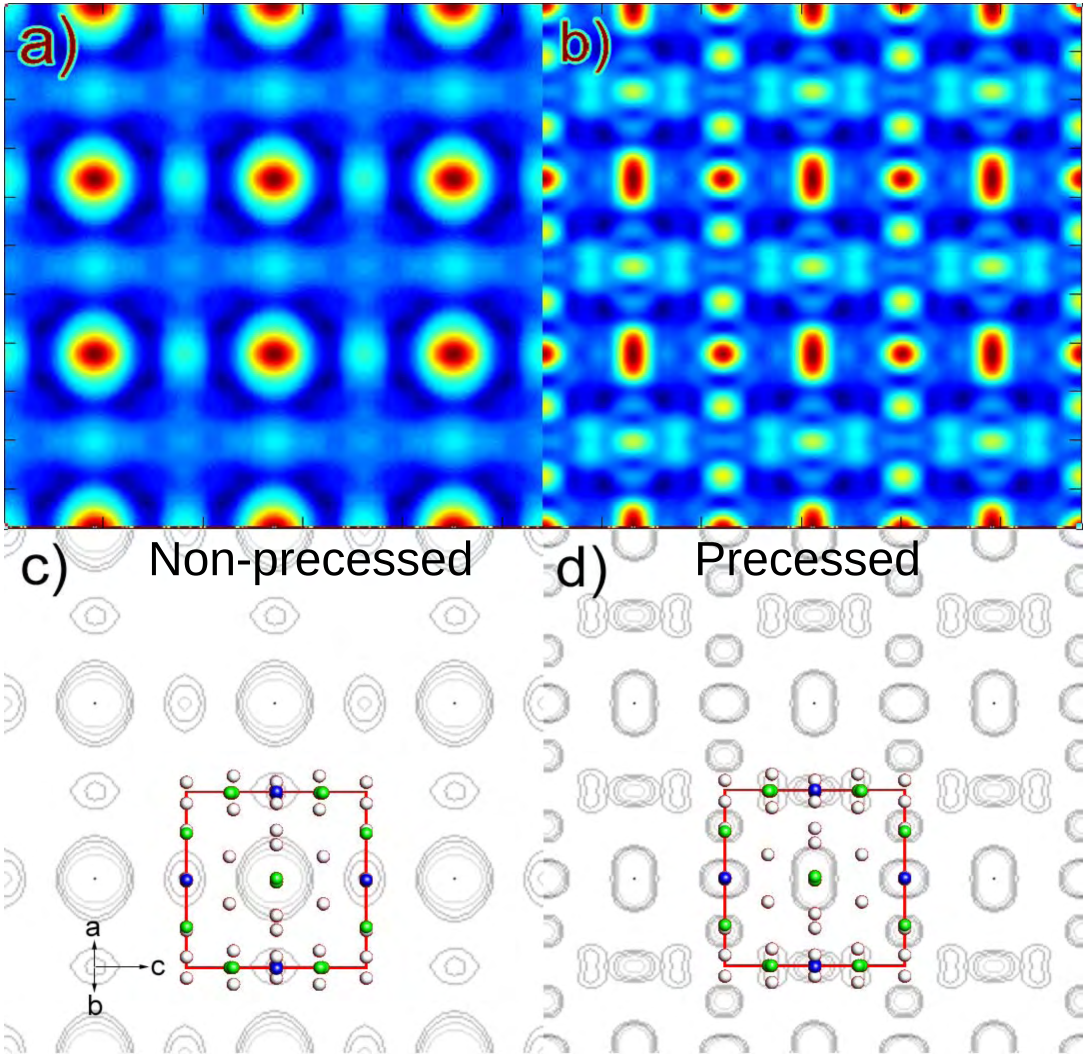
Comparison


[001]
[110]
Simulated
Experimental
No Tilt
6.5 mrad
13 mrad
24 mrad
32 mrad

Numbers


Comparison of Kinematical Extinctions
Normalized Intensity
10
1
0.1
0.01
0.001
0
10
20
30
40
Tilt Angle (mrad)
I(001)-Multislice
I(001)-Experiment
I(002)-Multislice
I(002)-Experiment
I(003)-Multislice
I(003)-Experiment

Electron Direct Methods Potential Maps [110]



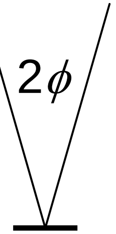
Problems and Questions

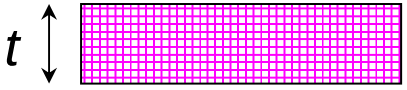
- Previous studies:
  - R-factors ~ 0.3-0.4†
- Precession was not well-understood
  - Can one just use intensities?
  - Correction terms ?
    - Are they correct?
    - Is geometry-only (Lorentz correction) valid?
  - Our early experiments (2000) gave mixed results too
- *Why didn't it work?*
- *How can we make it work?*

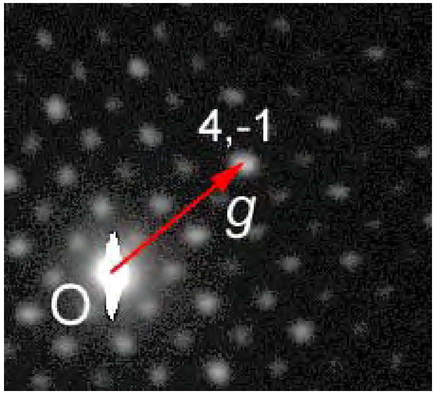
†(J. Gjonnes, et al., Acta Cryst A, 1998.
K. Gjonnes, et al., Acta Cryst A, 1998.
M. Gemmi, et al., Acta Cryst A, 2003.)

Multislice simulation parameters

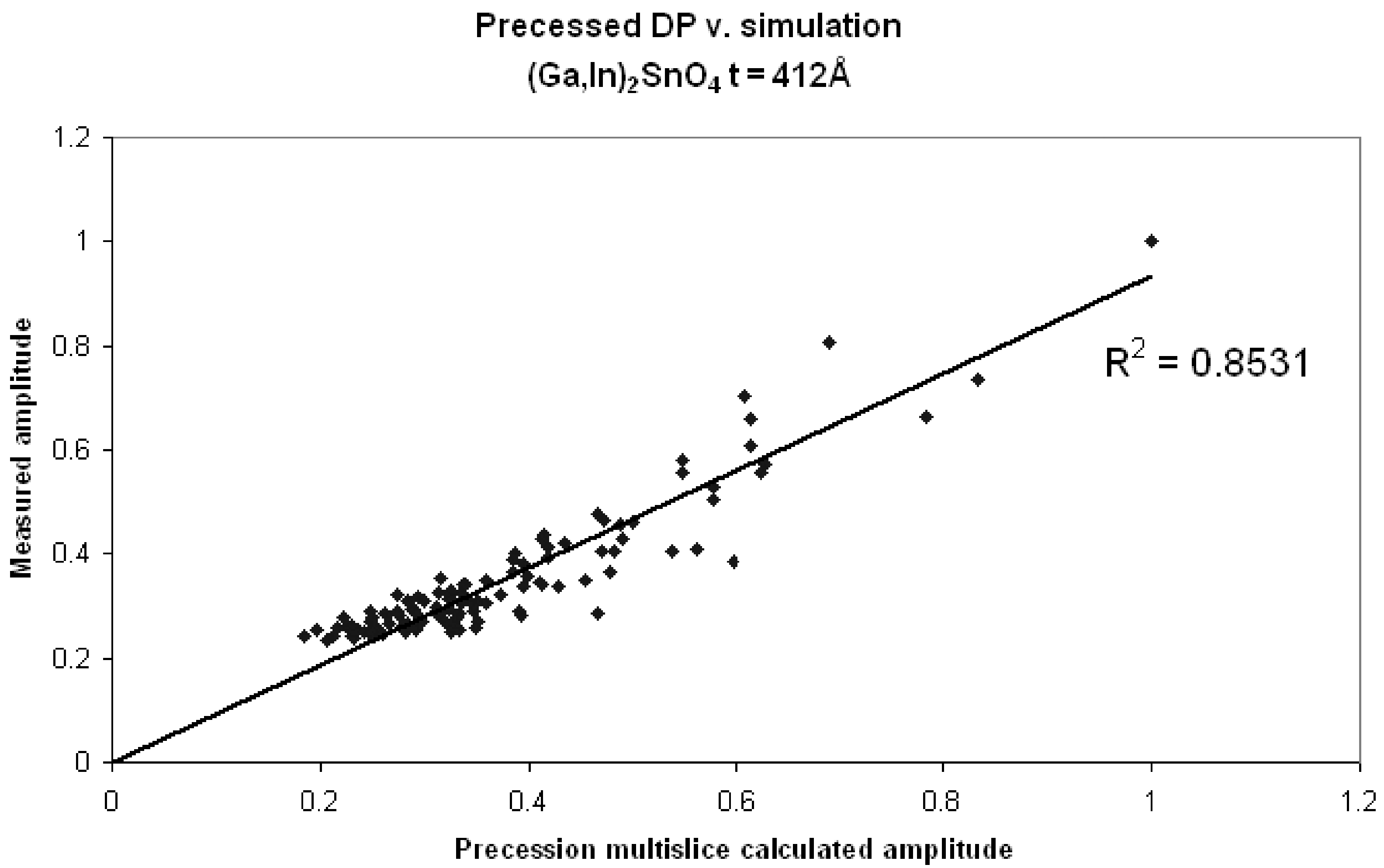
- "Conventional" multislice (NUMIS code)
- Integrate over different incident directions 100-1000 tilts
- ϕ = cone semi-angle
  - 0 – 50 mrad typical
- t = thickness
  - ~20 – 50 nm typical
  - Explore: 4 – 150 nm
- ***g*** = reflection vector
  - $|g| = 0.25 – 1$ Å^{-1} are structure-defining





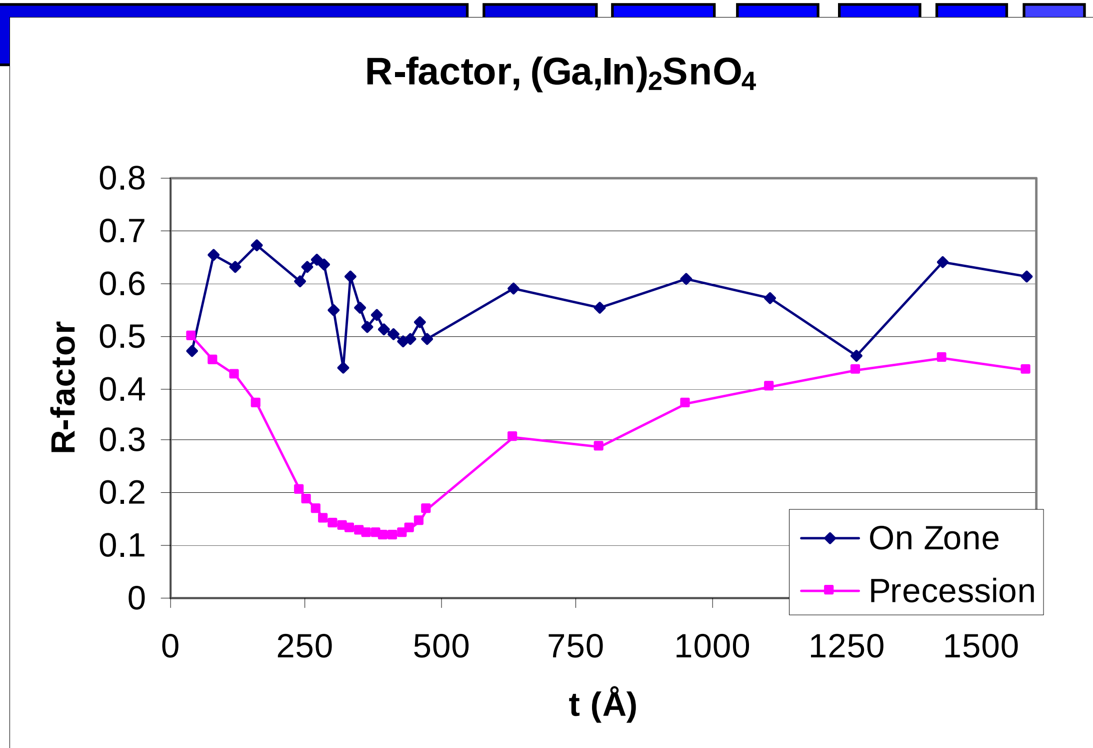


Multislice Simulation: good agreement with experiment



Global error metric: R_1

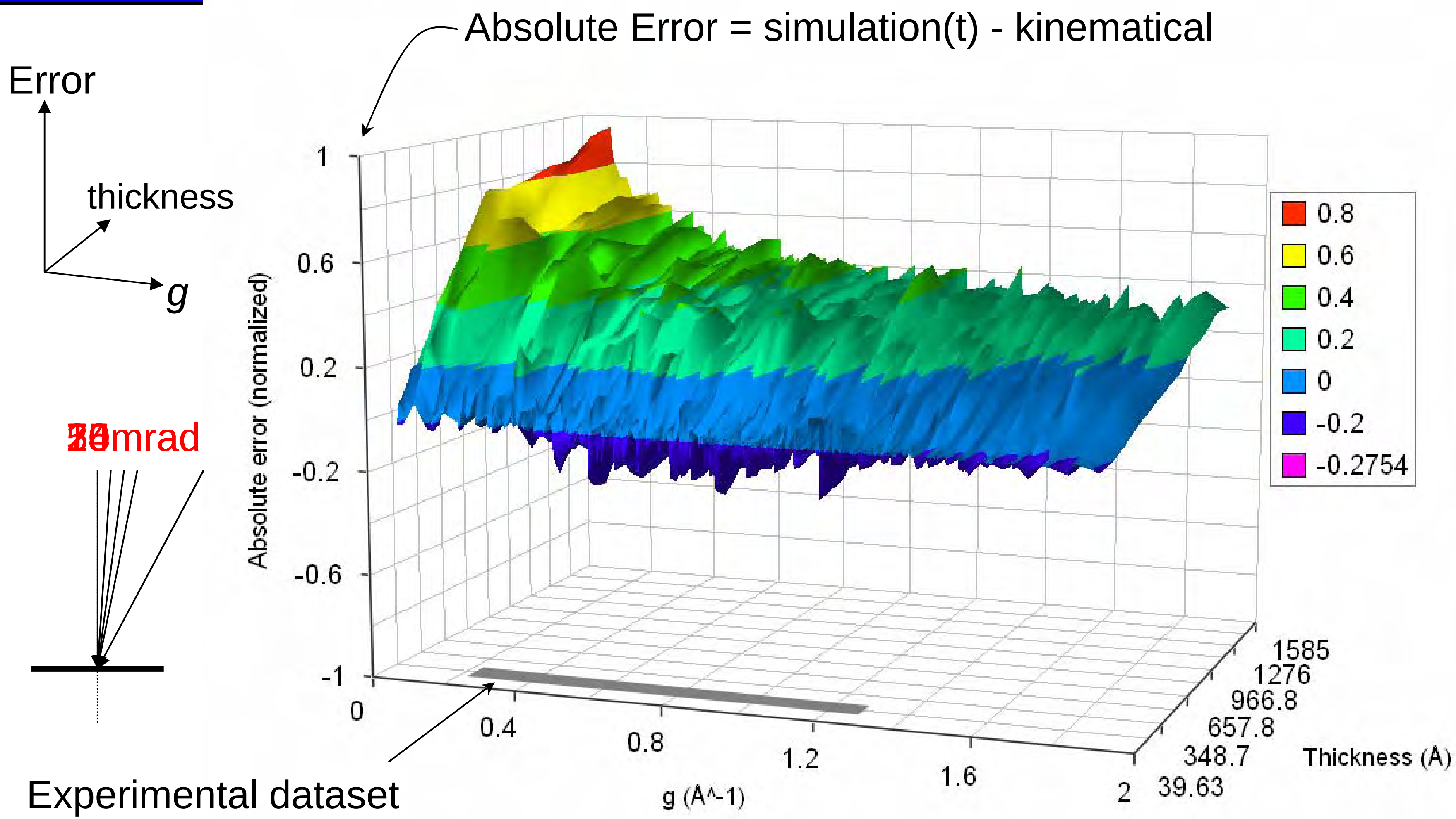
$$R_1 = \frac{\sum \left| F_{exp} - F_{sim} \right|}{\sum F_{exp}}$$



- 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

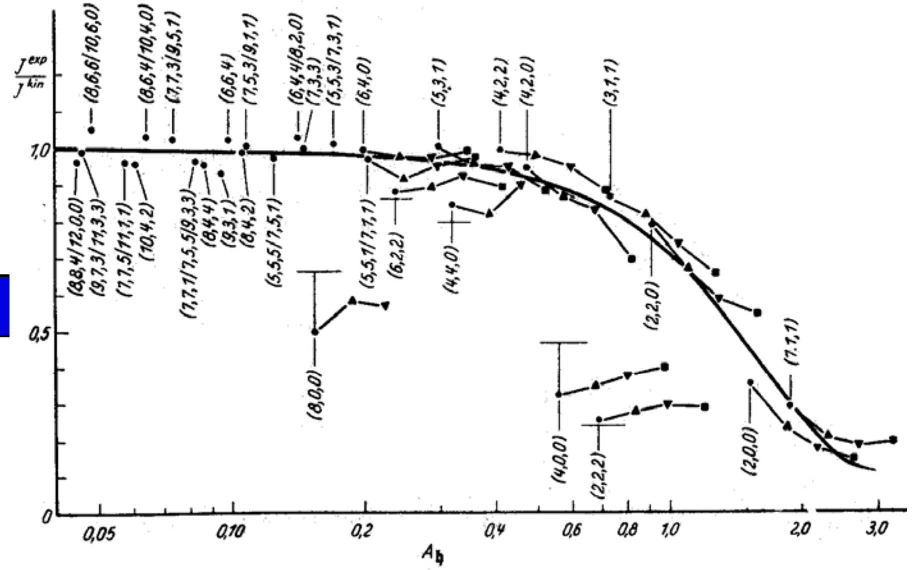


(Own, Sinkler, & Marks, in preparation.)

Dynamical two-beams corrections

For polycrystal it is necessary to integrate on various angles of incidence beam:

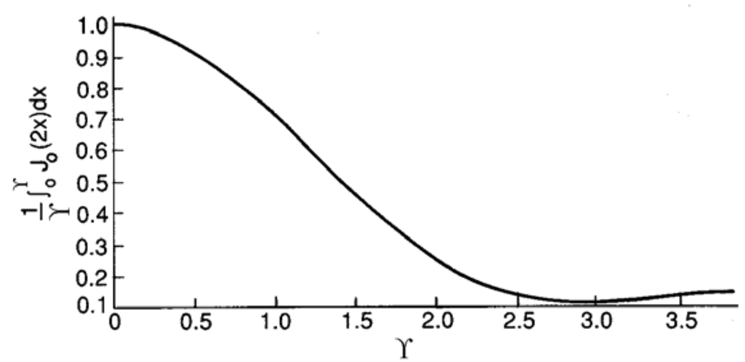
$$\int_{-\infty}^{\infty} \frac{\sin^2[A(1+w^2)^{1/2}]}{1+w^2}\,dw = \pi A \int_0^A J_0(2x)\,dx$$



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].)

$$\mathbf{I^{o}_{hkl} / I^{c}_{hkl} = (\Upsilon)^{-1} \int_0^{\Upsilon} J_o(2x)\,dx = D_{hkl}(\Upsilon)}$$

$$\mathbf{I^{o}_{hkl} / I^{c}_{hkl} \rightarrow D^{o}_{hkl}(\Upsilon) \rightarrow t_{hkl} \rightarrow t_{av} \rightarrow}$$
$$\mathbf{\rightarrow D^{av}_{hkl}(\Upsilon) \rightarrow I^{o,corr}_{hkl} / I^{c}_{hkl} \rightarrow I^{o,corr}_{hkl}}$$



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

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t > 50 nm: needs correction
How to use PED intensities

- Treat like powder diffraction
  - Apply Lorentz-type dynamical correction factor to get true intensity:†

$$I_g^{true} \approx I_g^{corrected} = C_{Blackman} \times I_g^{\exp}$$

$$C_{Blackman}(g,t,\phi) = g\sqrt{1-\left(\frac{g}{2R_0}\right)} \times \left(\frac{A_g}{\int_0^{A_g} J_0(2x)\,dx}\right)$$

$$A_g = \frac{\pi t}{\xi_g^{\,2}}$$

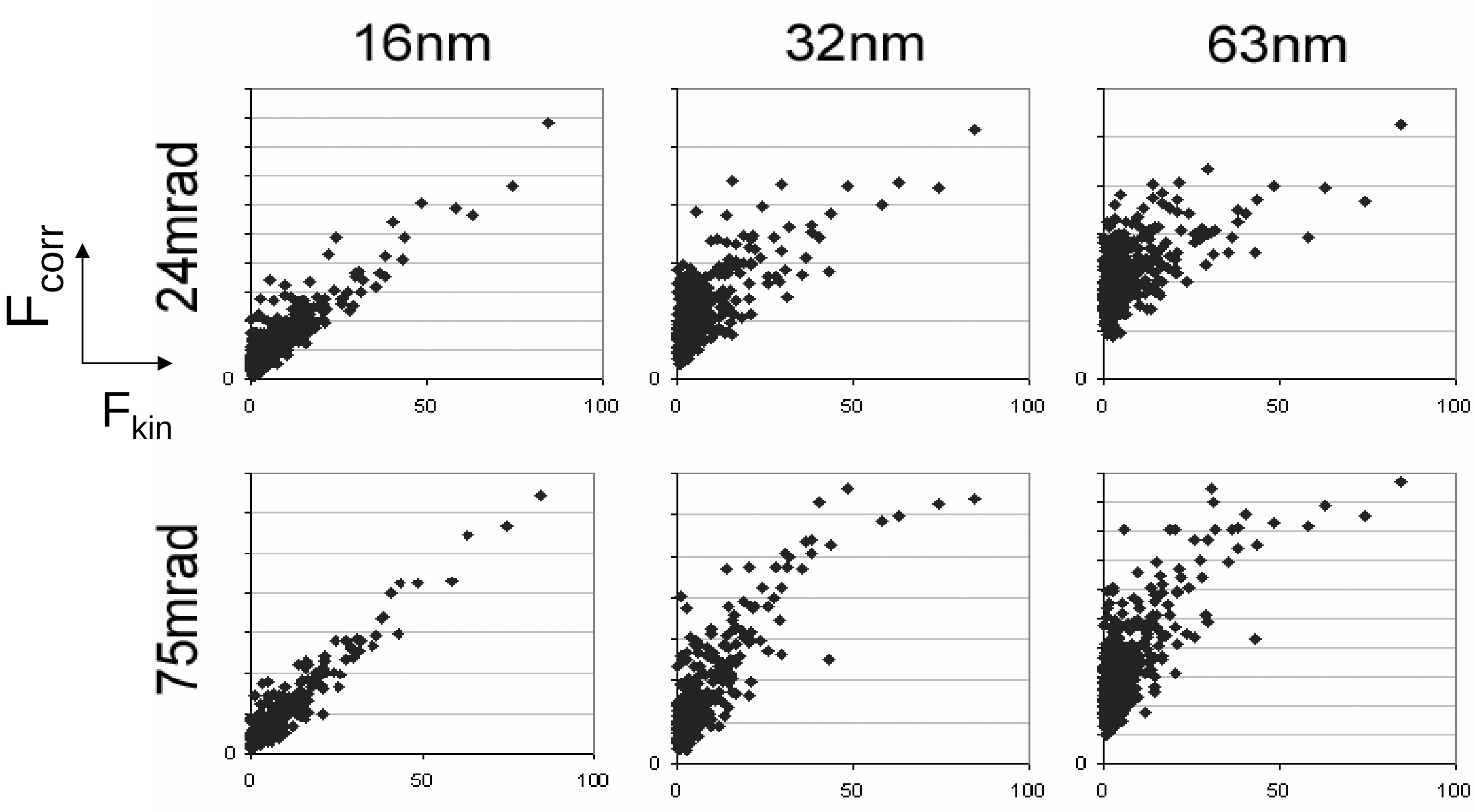
Geometry correction

Dynamical correction

An approximation

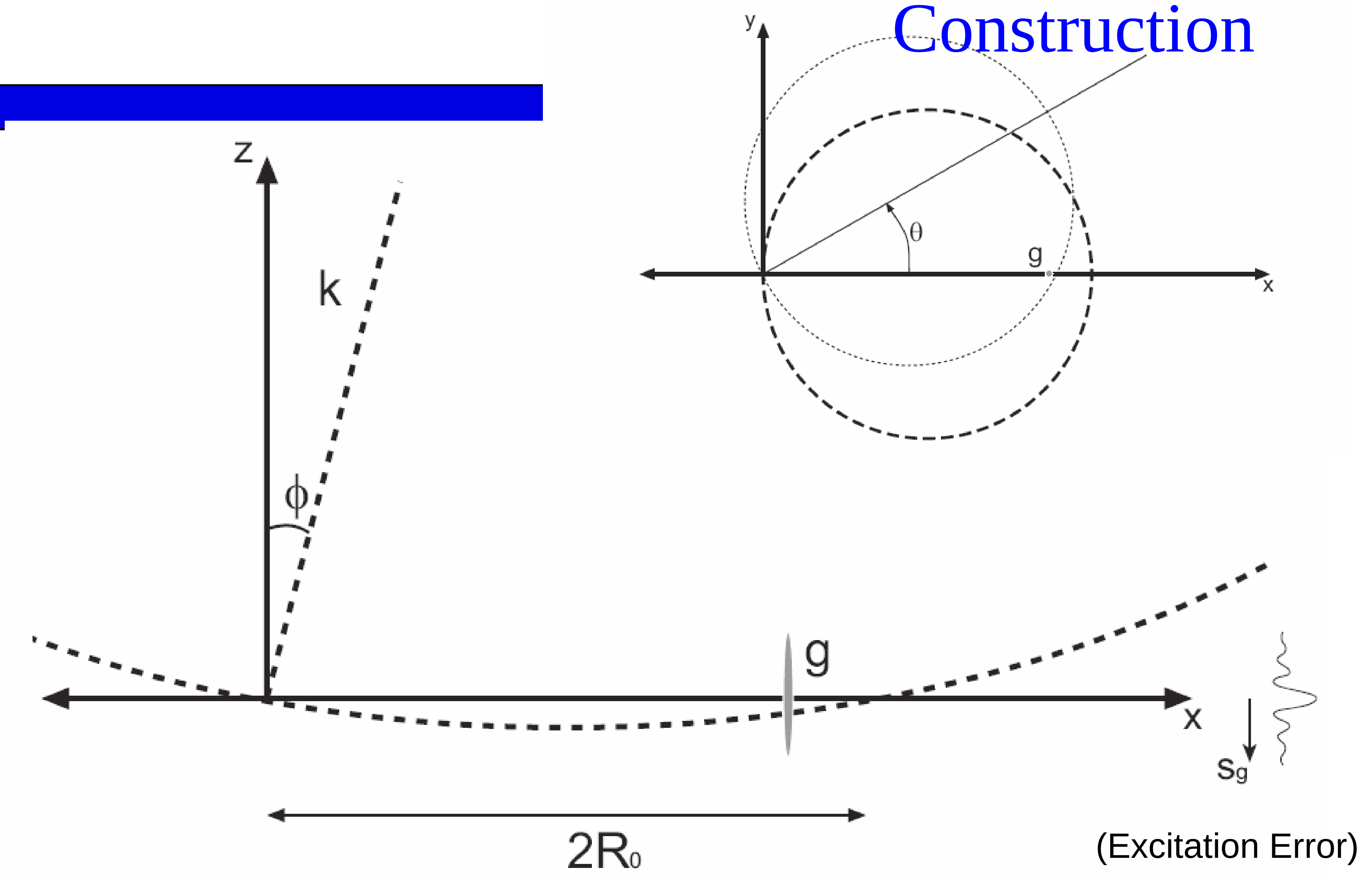
†(K. Gjønnes, Ultramic, 1997.
M. Blackman, Proc. Roy. Soc., 1939.)

Lorentz-only correction:
Geometry information is insufficient



Need structure factors to apply the correction!

Ewald Sphere Construction



New Dynamical Two-beam Correction Factor

$$C_{2beam}(g,t,\phi) = F_g^{\ 2}\left(\frac{1}{\xi_g^{\ 2}}\int_0^{2\pi}\frac{\sin^2(\pi t s_{eff})}{(s_{eff})^2}\,d\theta\right)^{-1}$$

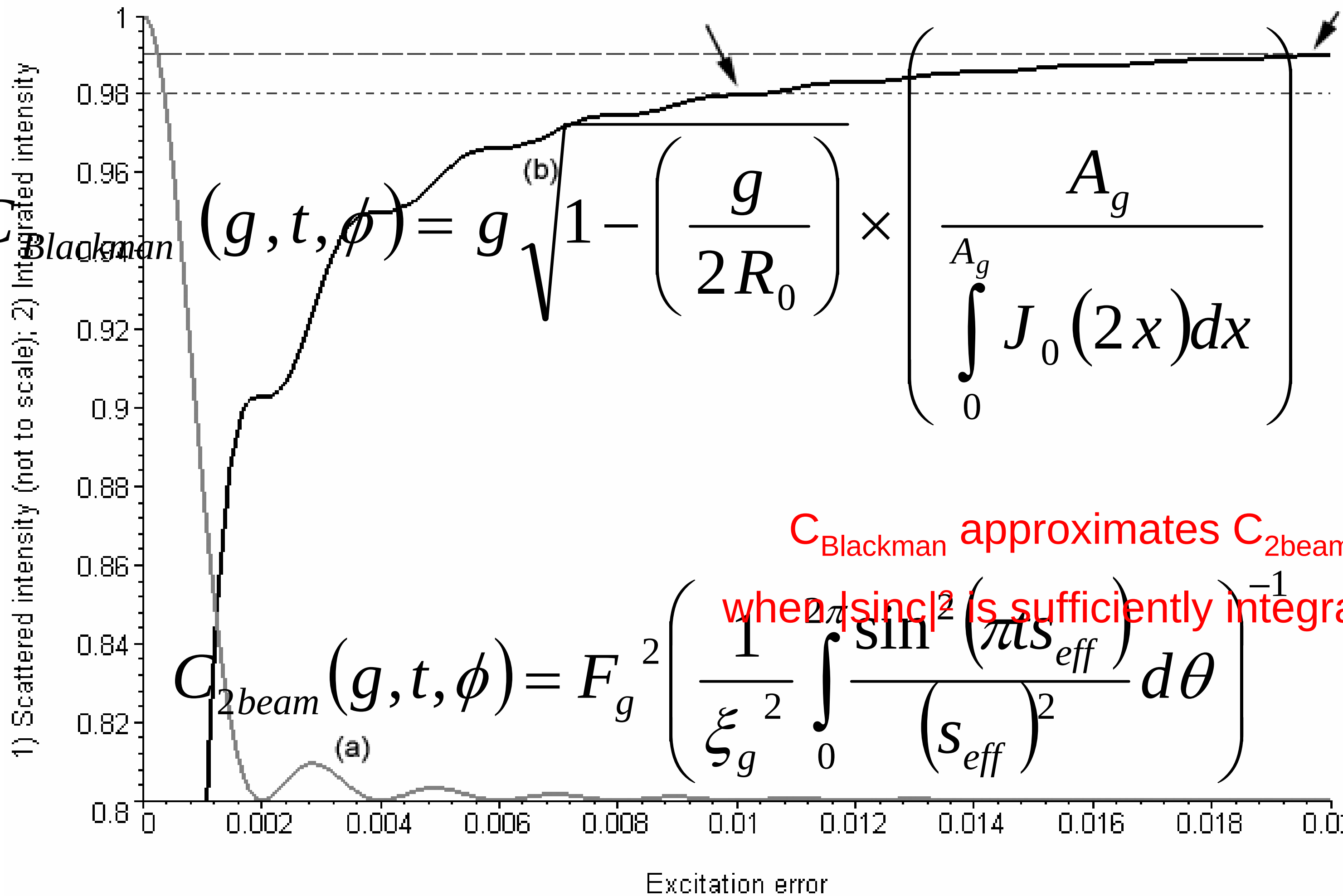
- Sinc function altered by ξ_g

$$s_{eff} = \sqrt{s^2 + \frac{1}{\xi_g^{\ 2}}}$$

- A function of structure factor F_g
  - Some F_g must be known to use!

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

$C_{Blackman}$ v. C_{2beam}



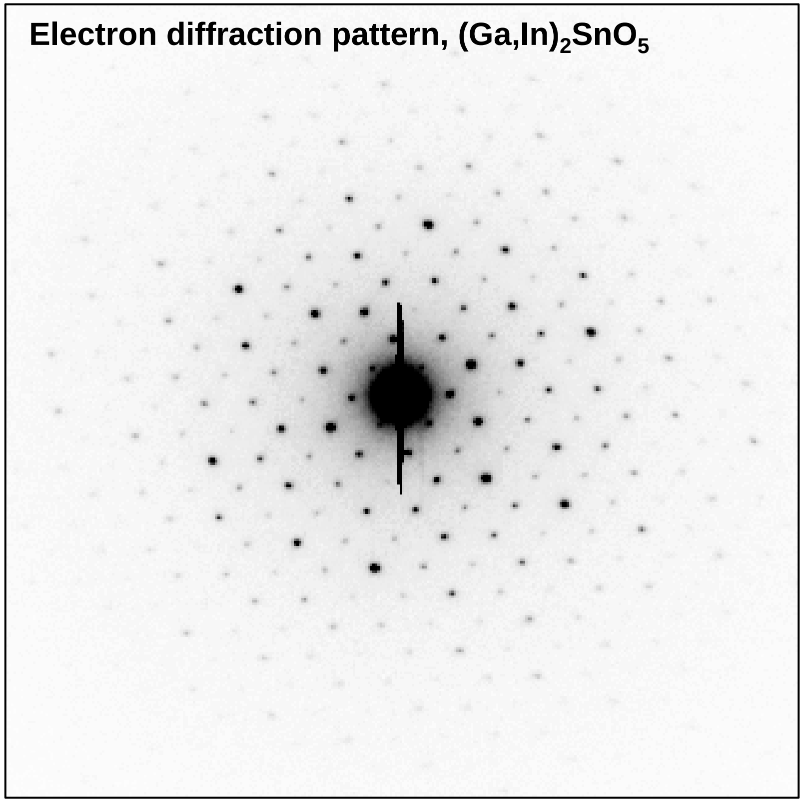
$$C_{Blackman}(g,t,\phi) = g\sqrt{1-\left(\frac{g}{2R_0}\right)} \times \left(\frac{A_g}{\int_0^{A_g} J_0(2x)\,dx}\right)$$

$$C_{2beam}(g,t,\phi) = F_g^{\;2}\left(\frac{1}{\xi_g^{\;2}}\int_0^{2\pi}\frac{\sin^2(\pi s_{eff})}{(s_{eff})^2}\,d\theta\right)^{-1}$$

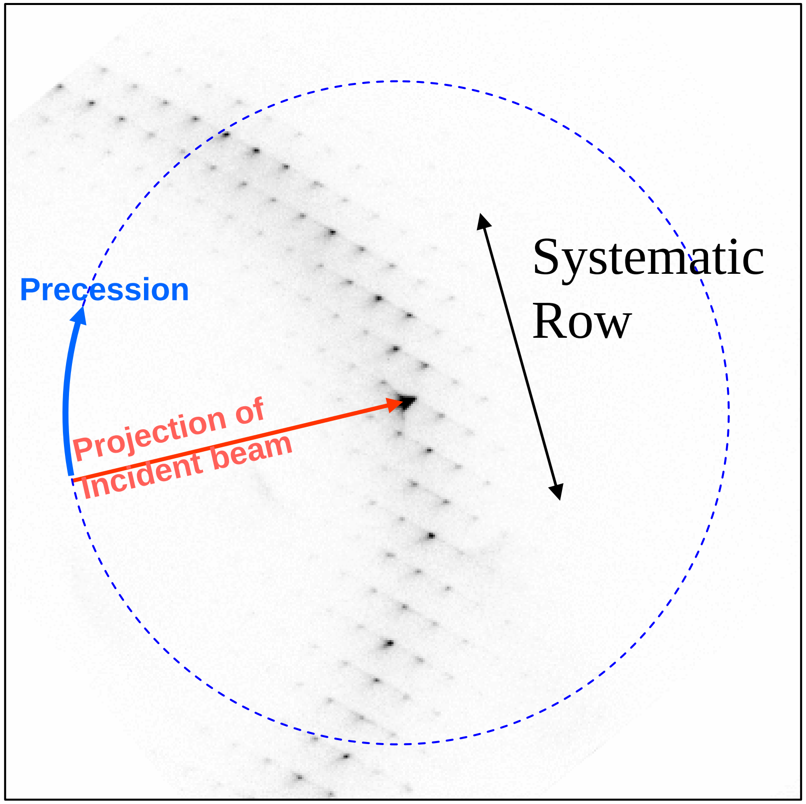
$C_{Blackman}$ approximates C_{2beam} when $|\mathrm{sinc}|^2$ is sufficiently integrated

Approximate model: quasi-systematic row

Many-beam zone axis condition, strongly dynamical.



Large beam tilt; weakens dynamical effects.

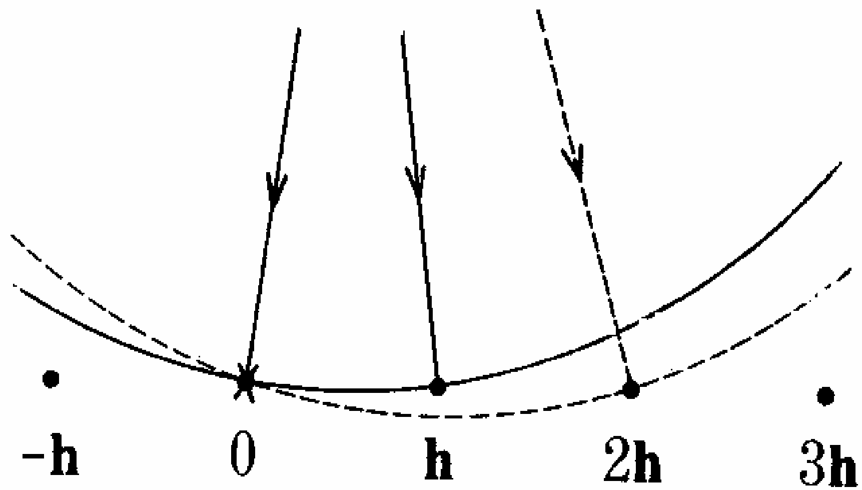


Dynamical corrections by Bethe potentials

- **Two-beam scattering with accounting for weak reflexions. «Bethe potentials» - modified potentials in many beam theory:** $U_{0,h} = v_h - \sum_g [v_g v_{h-g}/(\kappa^2 - k_g^2)]$;

$$v_g/(\kappa^2 - k_g^2) << 1 \ ; \ v_{h-g}/(\kappa^2 - k_g^2) << 1$$

When the Bragg conditions for one reflection is satisfied, the other reflections of "systematic set" always have the same "excitation errors"



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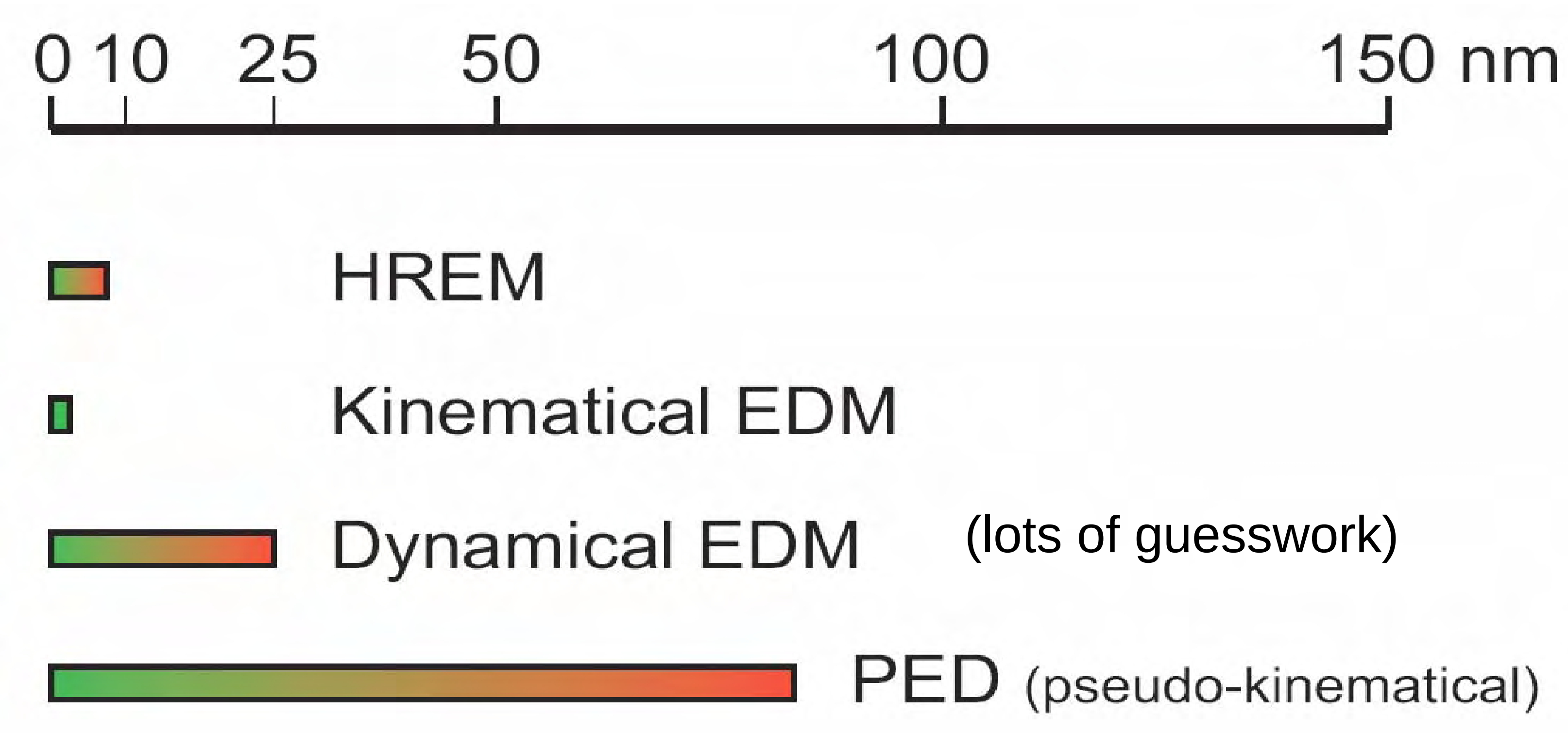
Application: Thickness ranges



Summary

- Perhaps the Philosophers Stone…
  - Easy to implement (semi-commercial)
  - Much better than other electron diffraction techniques in most cases
  - Much, much easier to interpret
  - Amenable to direct methods analysis
- Not the end of the story….