System Design and Verification
of the Precession Electron Diffraction Technique

Christopher S. Own

Thesis defense · 2005.07.13

Acknowledgements

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  - Marks Group
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Overview

I. Background
  - Motivation
  - Precession Electron Diffraction (PED)

II. System Design
  - Instrumentation

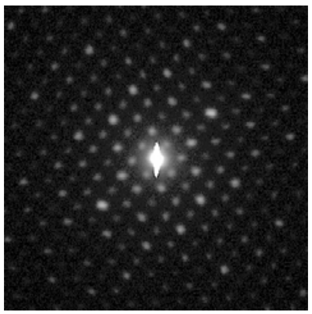
III. Verification
  - Simulation
  - Theoretical models

IV. Examples

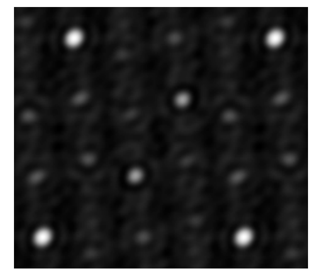
V. Conclusions / Future Work

I. Background

Motivation:
Routine Structural Crystallography



Diffraction Intensities → ***Direct Methods*** → Starting structure model



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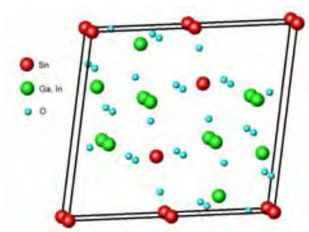
Refinement → **True Structure**



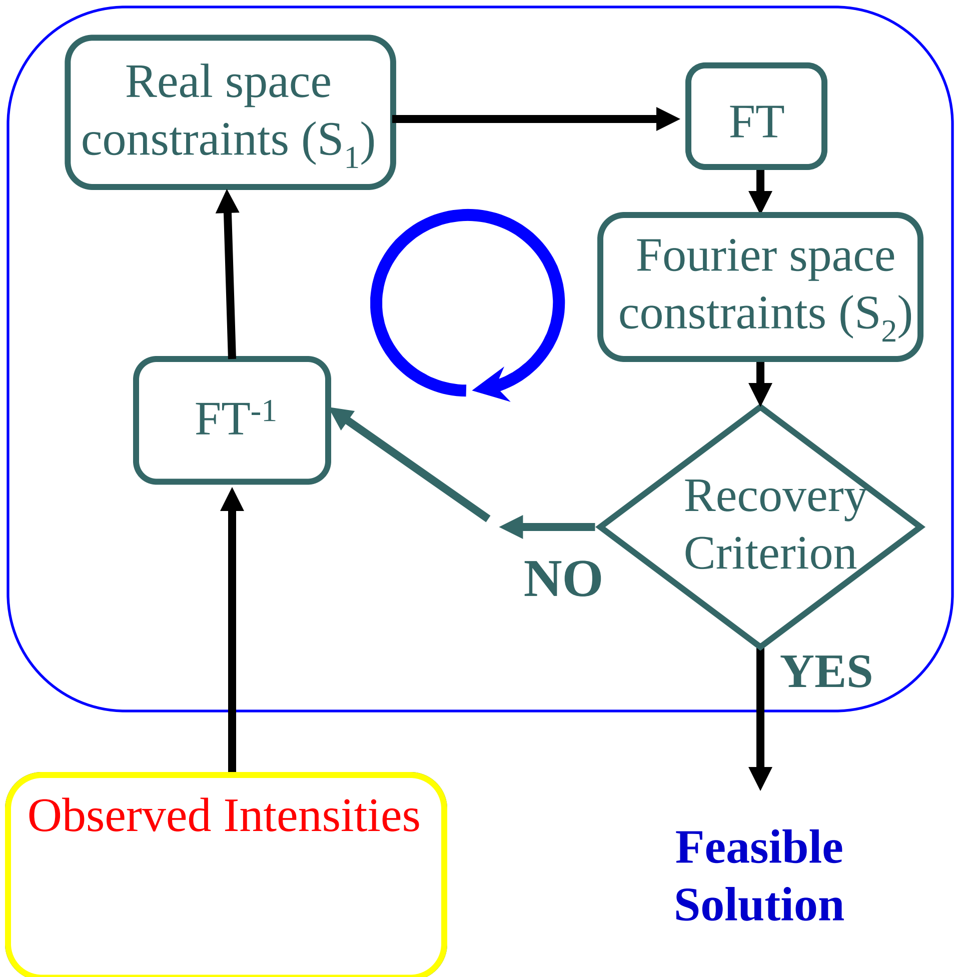
Direct Methods (DM)

- In diffraction experiment we measure intensities
  - (phase information lost)

$$\Phi(k) = F(k)\exp(-i\phi(k))$$

$$I(k) = |F(k)|^2$$

- Recover phases to generate feasible scattering potential maps
- ***Need good intensities to recover correct phases***
  - Else get false structure!



Motivation (cont'd)

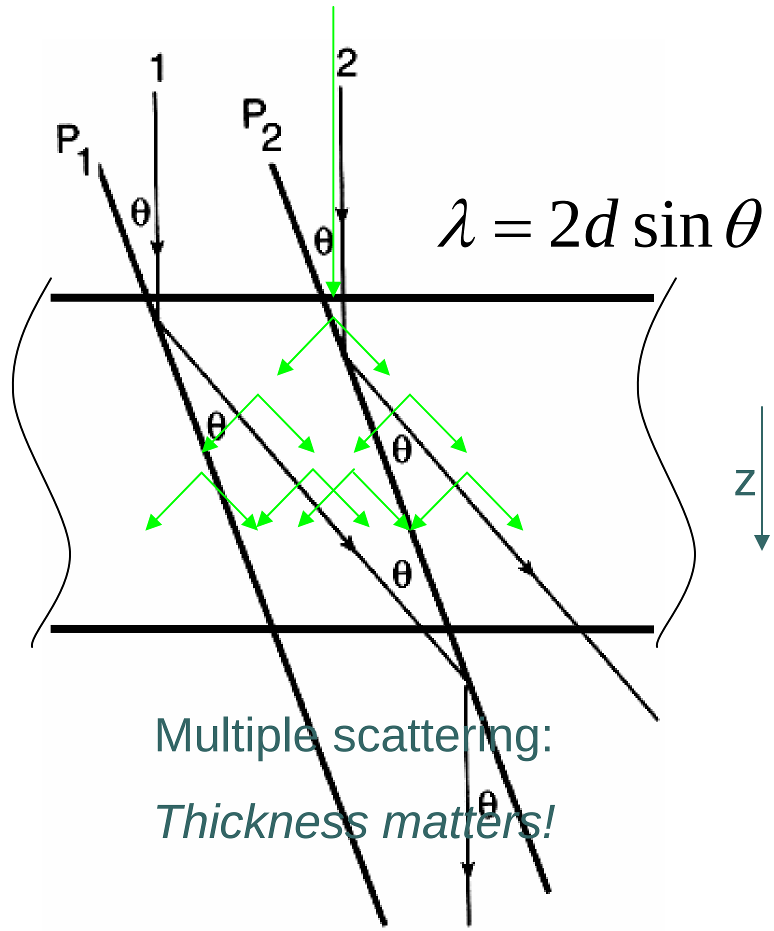
- The crystallography workhorse: X-ray diffraction
  - Limitations for nanoscale characterization:
    - Too low S/N for small crystals, need synchrotron
    - Synchrotron: Cost / time restriction
    - Ring overlap (powder)
    - No imaging
- Solution: Electron Diffraction (ED)
  - Simultaneous imaging/diffraction
  - EDX, EFTEM, etc…
  - Readily available / inexpensive

Problem: Multiple Scattering

- Terminology:
  X-rays: ***Kinematical***
  Electrons: ***Dynamical***

- Direct Methods requires good quality intensities (<15% error)

- ED is often too dynamical:
  - Want kinematical, but even thin specimens dynamical
    - Ultra-thin specimens impossible to make (except surfaces)
  - Error can be 1,000's of %!
    - Hindered routine electron crystallography.



$$\lambda = 2d \sin\theta$$

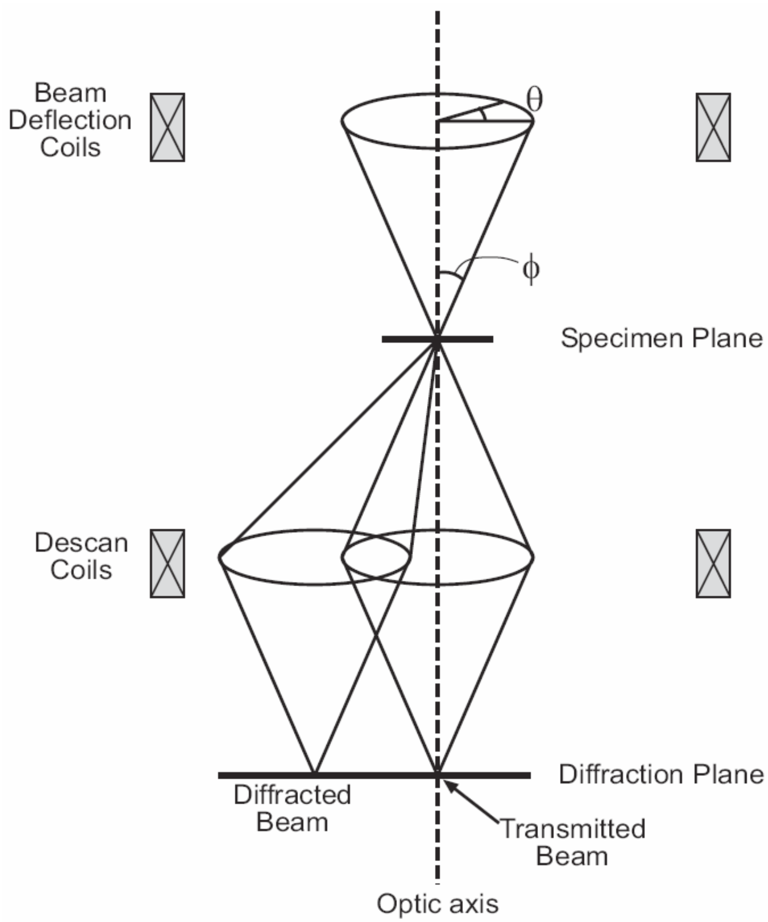
Multiple scattering:

Thickness matters!

Electron Direct Methods can work!

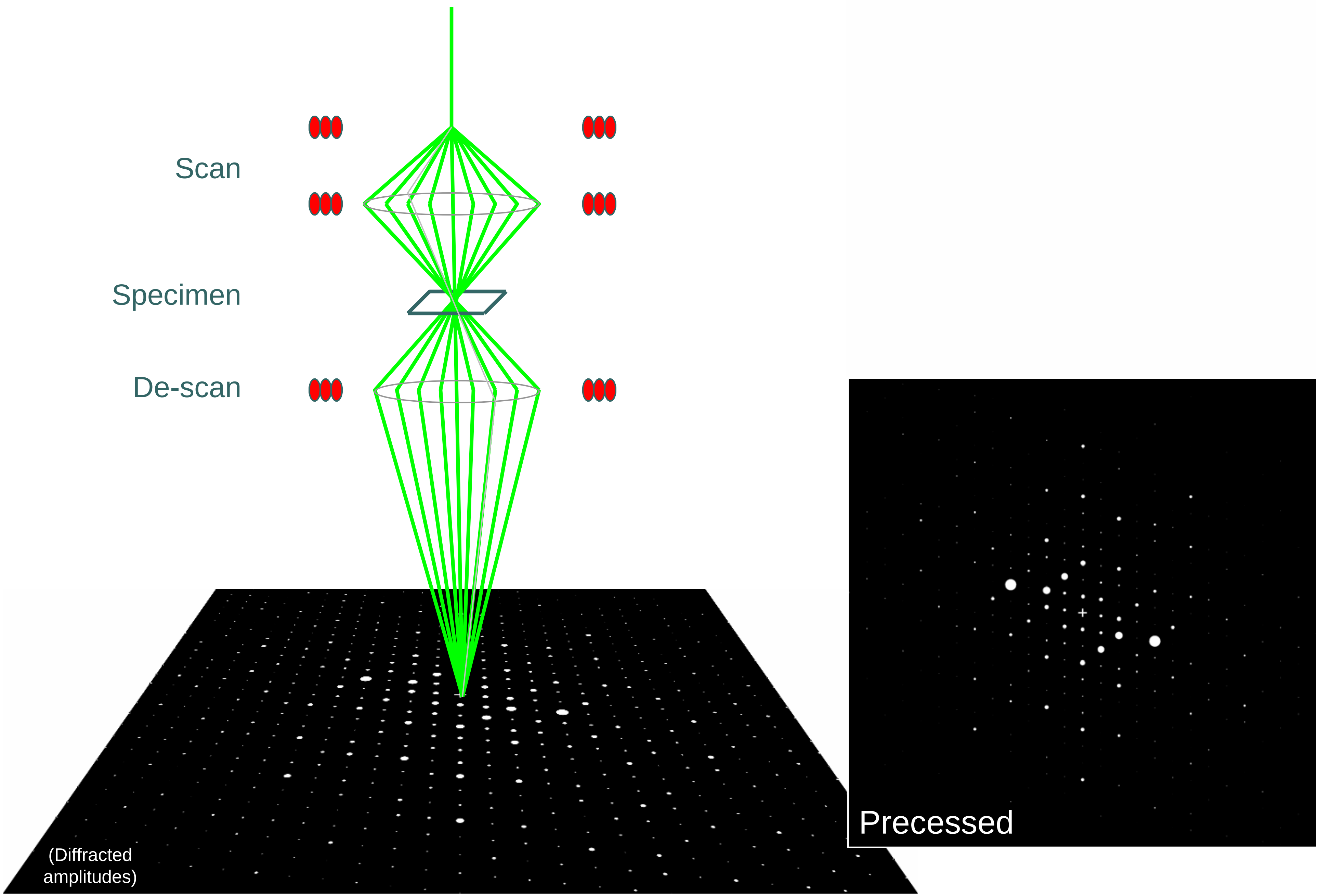
- Data can be kinematical
  - Thin specimens (surfaces)
- Some dynamical data can work
  - Channeling (good projection)
    - Phase relationships preserved *statistically*
  - Pseudo-kinematical EDM
    - Also called intensity mapping
    - *Assumes* deviation from kinematical
    - Intensity relationships preserved
      - Powder, texture patterns ⇨ *Precession*

Vincent-Midgley Precession Technique (PED)†

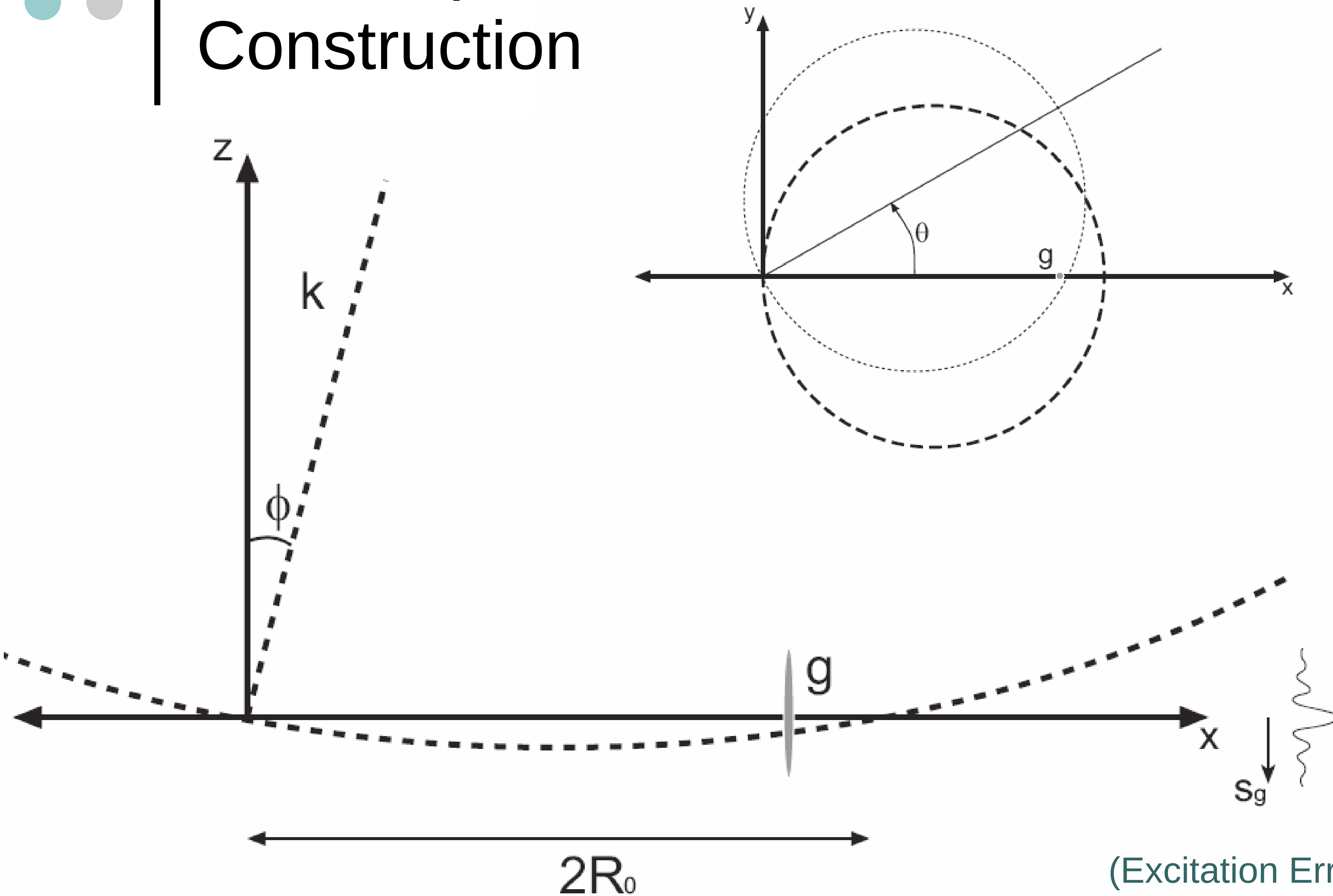


- In theory:
  - Reduces multiple scattering (always off-zone)
    - Lower sensitivity to thickness
  - Reduces sensitivity to misorientation
  - "Quasi-kinematical" intensities result
    - May need correction factors (requires known structure factors)

(Vincent & Midgley, Ultramicroscopy 1994.)


Scan
Specimen
De-scan
(Diffracted
amplitudes)
Processed

Ewald Sphere Construction



(Excitation Error)

Problems and Questions

- Previous studies:
  - R-factors ~ 0.3-0.4†

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

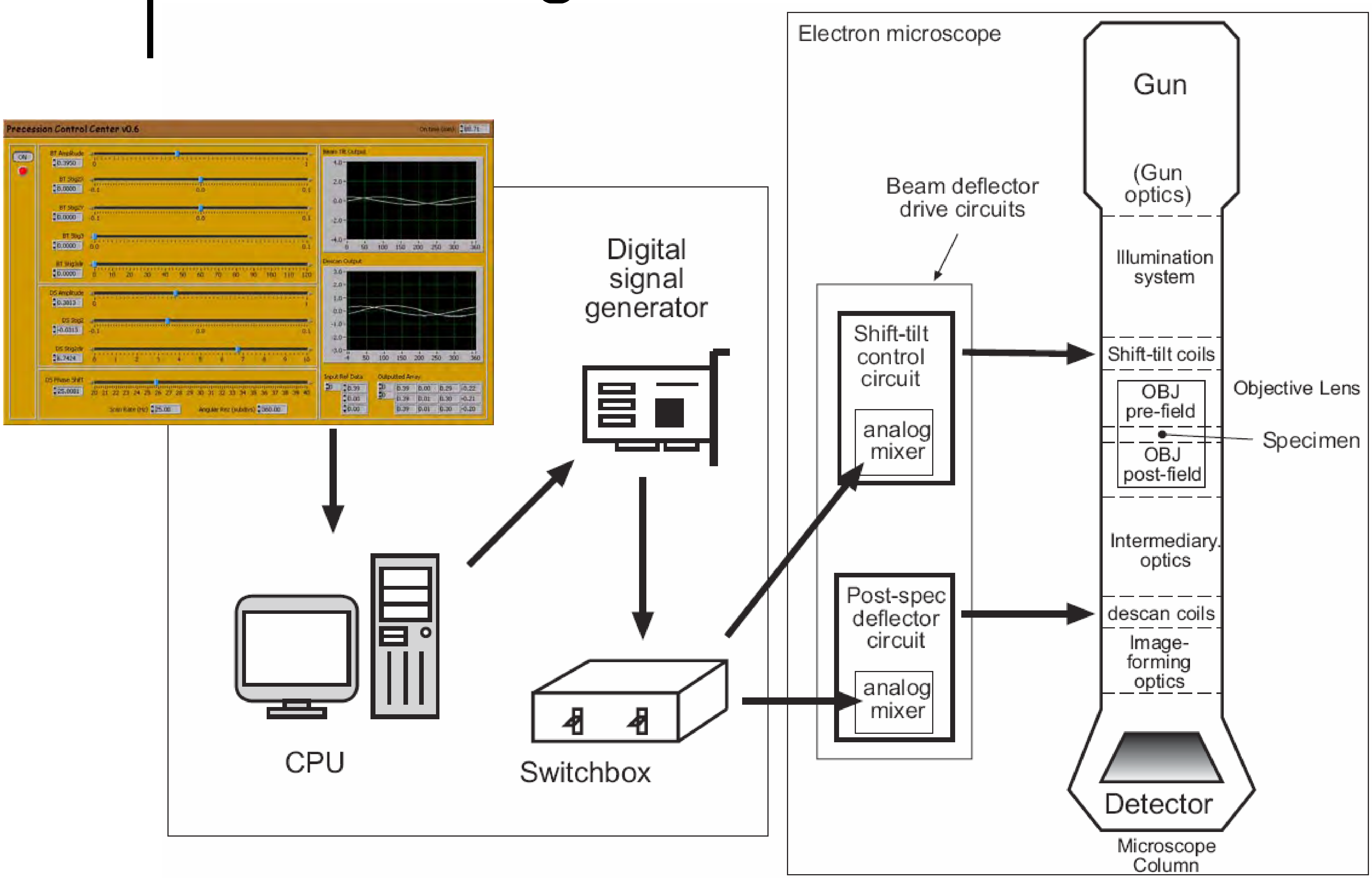
- Precession was not well-understood
  - Can one just use intensities?
  - How to use correction factors if F_g not known?
    - Are they correct?
    - Is geometry-only valid?
  - Our early experiments gave mixed results too

- *Why didn't it work?*
- *How can we make it work?*

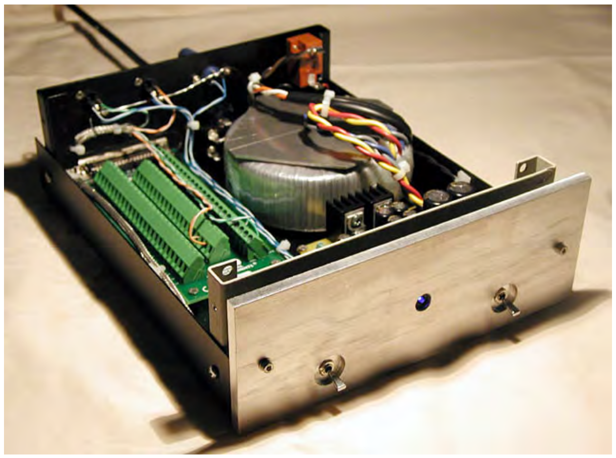
II. System Design

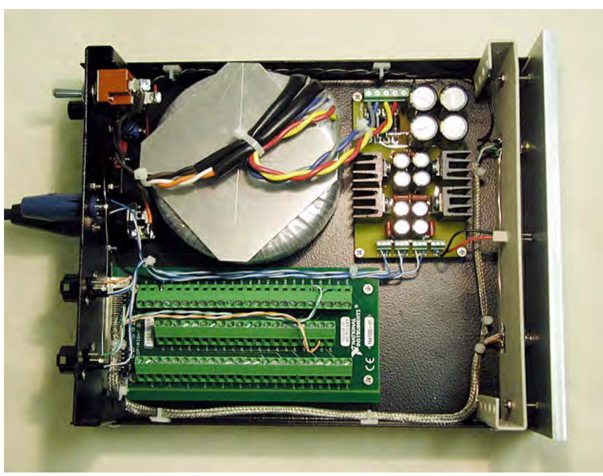
The Design

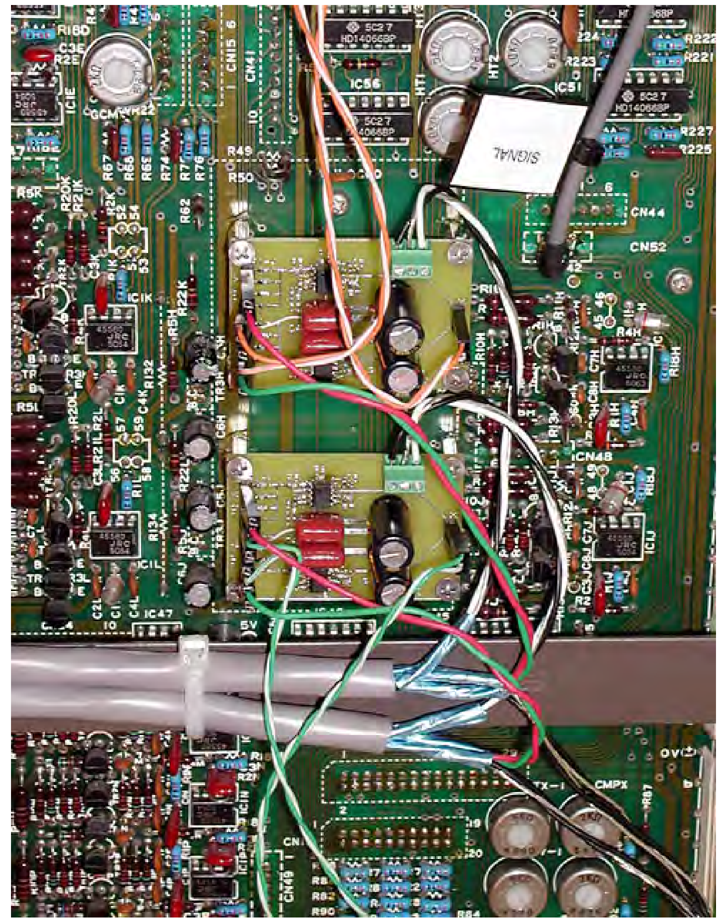
US patent application:
"A hollow-cone electron diffraction system".
Application serial number 60/531,641, Dec 2004.



Generation II hardware







Optical Aberration Compensation

$$x_1 = A_1 \cdot \cos\theta \qquad x_2 = s \cdot \cos\theta$$

$$y_1 = A_1 \cdot \sin\theta \qquad y_2 = -s \cdot \sin\theta$$

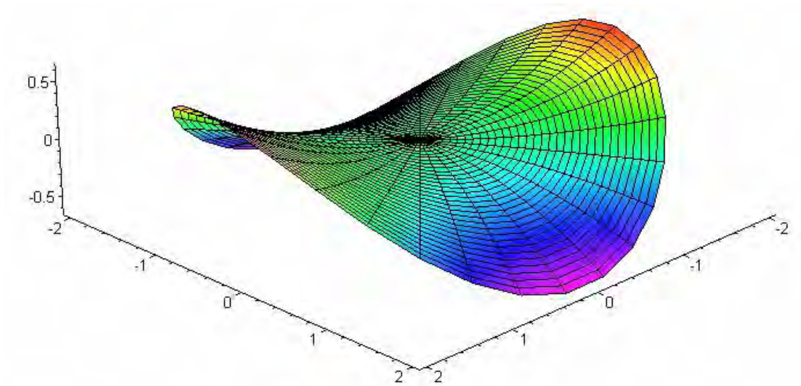
$$x_3 = [A_3 \cdot \cos(3 \cdot (\theta + \phi_3))] \cdot \cos\theta$$

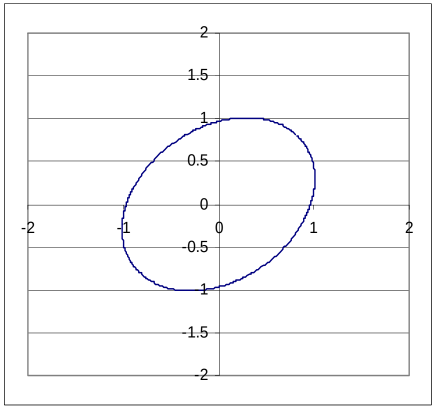
$$y_3 = [A_3 \cdot \cos(3 \cdot (\theta + \phi_3))] \cdot \sin\theta$$

For forming fine probe

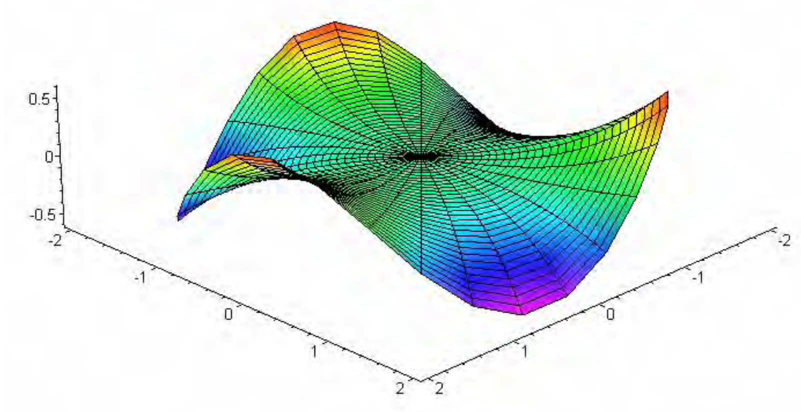
$$x_{out} = [(x_1 + x_2) \cdot \cos\phi_2 + (y_1 + y_2) \cdot \sin\phi_2] + x_3$$

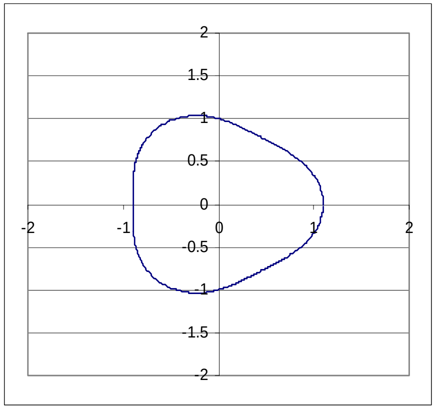
$$y_{out} = [-(x_1 + x_2) \cdot \sin\phi_2 + (y_1 + y_2) \cdot \cos\phi_2] + y_3$$





2-fold 45° rotation





3-fold, no rotation

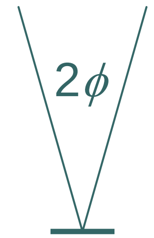
III. Verification

Section Outline:

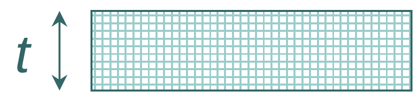
- Investigate models
  - Multislice simulation
  - Comparison of correction factors (old and new)
- Compare to experimental data
- Suggested approach for novel structures

Simulation parameters

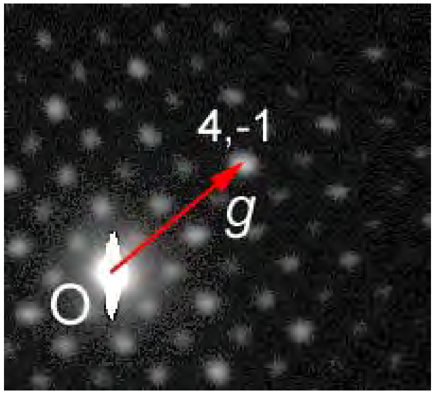
- ϕ = cone semi-angle
  - 0 – 50 mrad typical



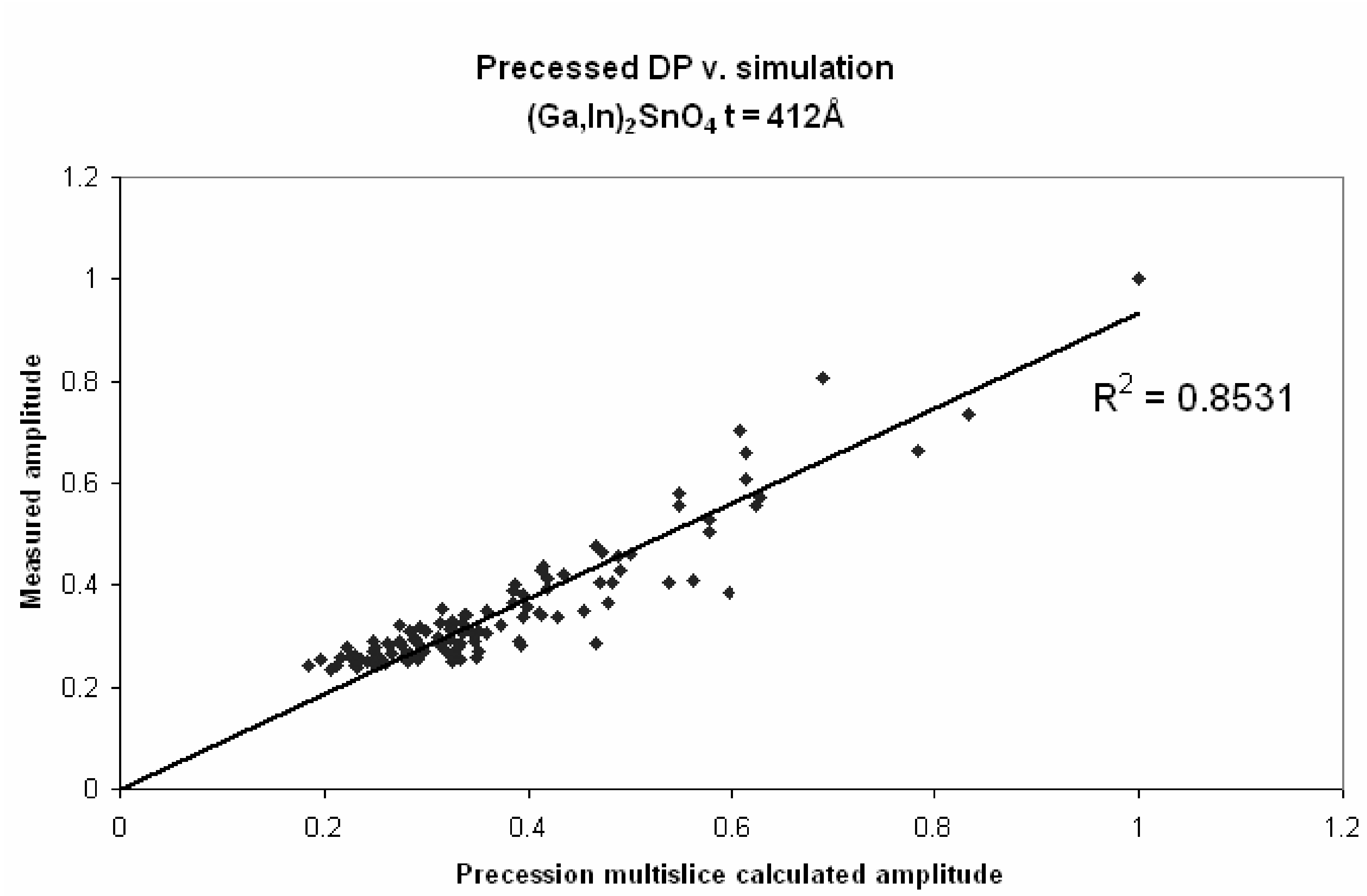
- *t* = thickness
  - ~20 – 50 nm typical
  - Explore: 4 – 150 nm



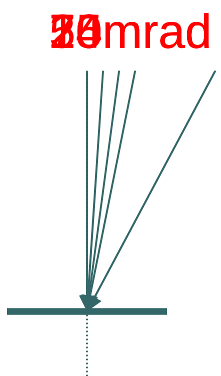
- ***g*** = reflection vector
  - |*g*| = 0.25 – 1 $Å^{-1}$ are structure-defining

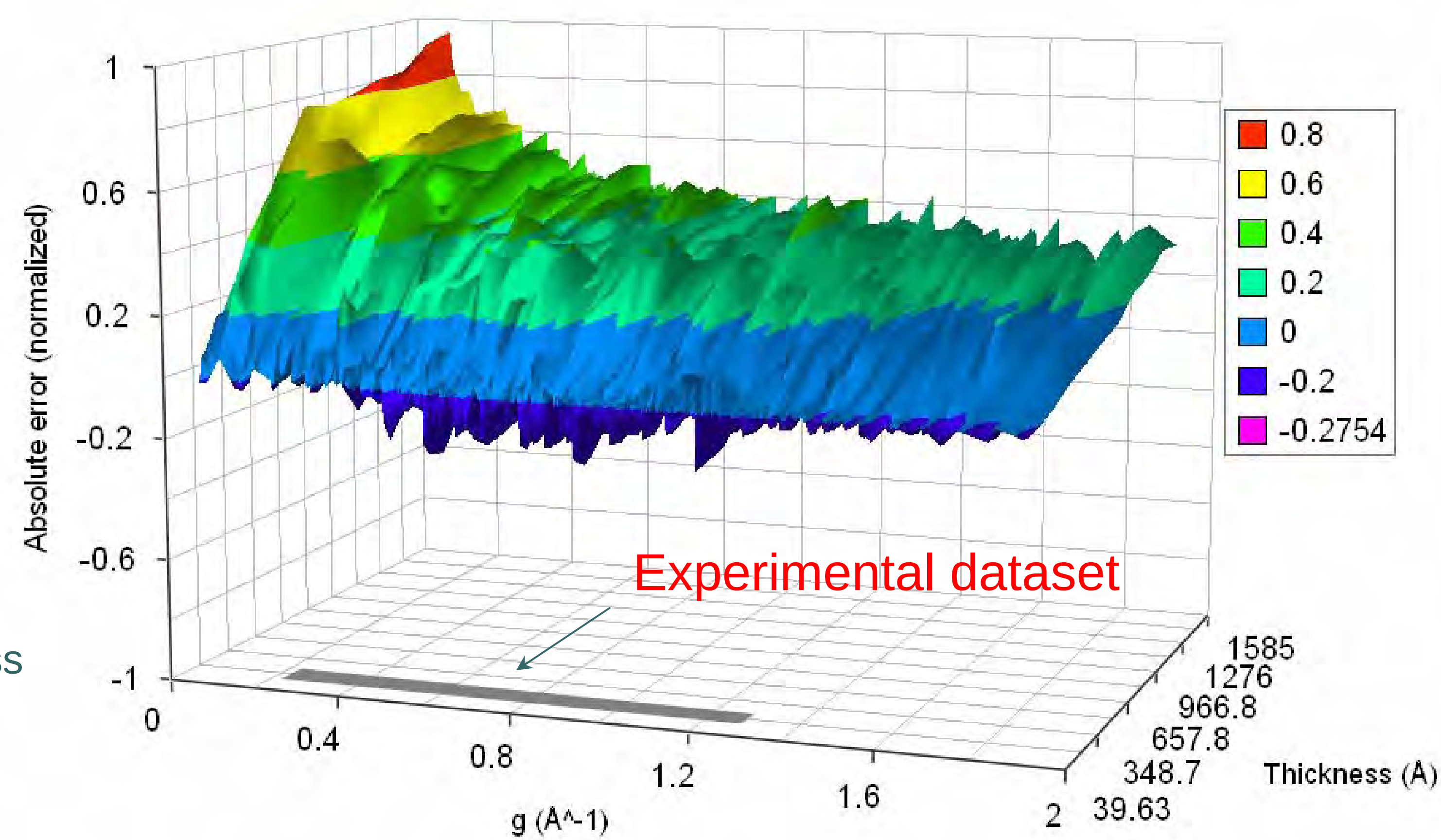


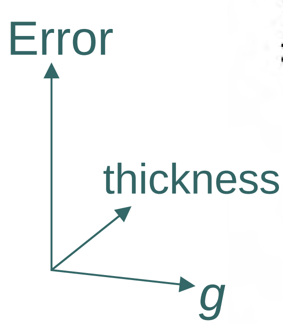
Multislice Simulation:
A Correct Model



Error analysis:
$F_{sim}(t) - F_{kin}$ (normalized)

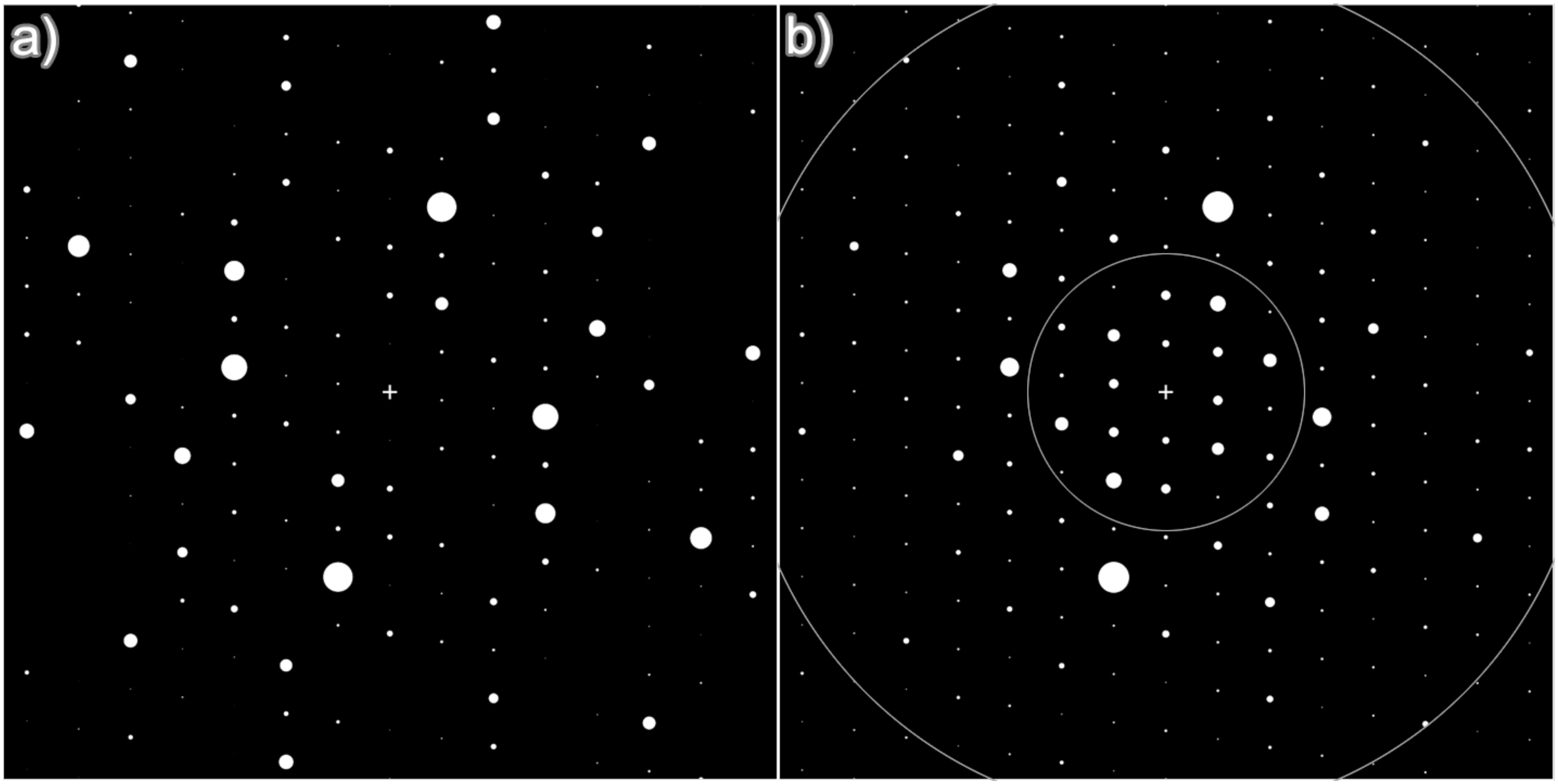






(Own, Sinkler, & Marks, in preparation.)

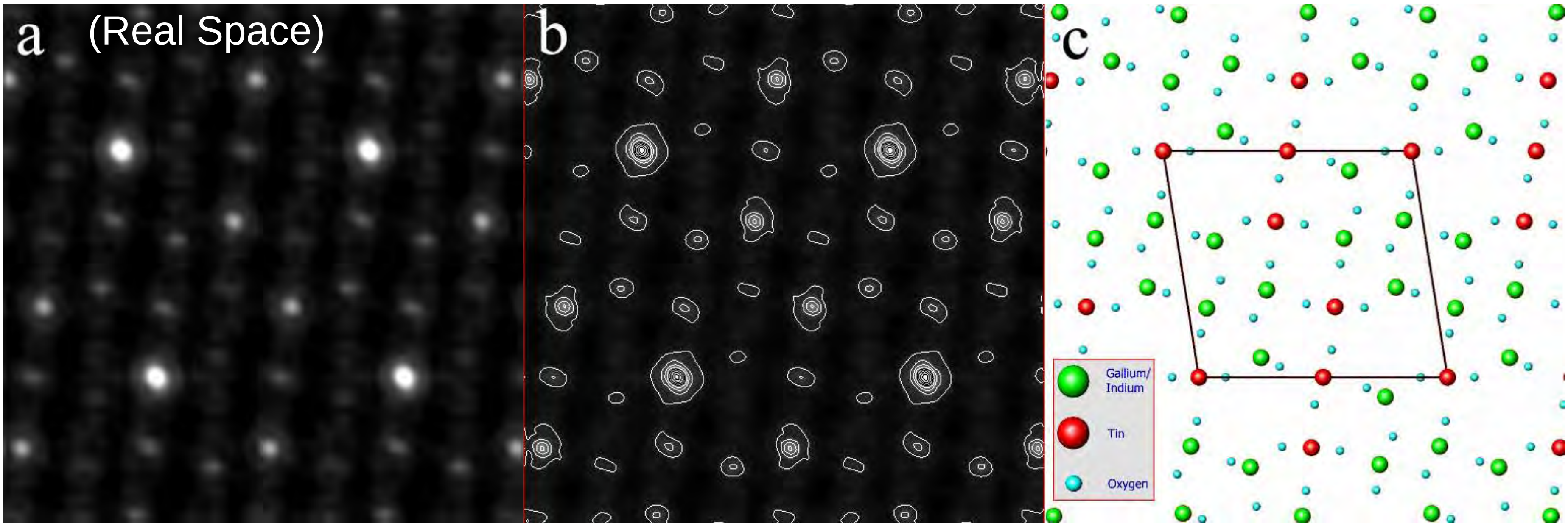
$(Ga,In)_2SnO_4$ data



Kinematical Amplitudes

Precession Intensities

$(Ga,In)_2SnO_4$ precession data: High-pass filtered amplitudes



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

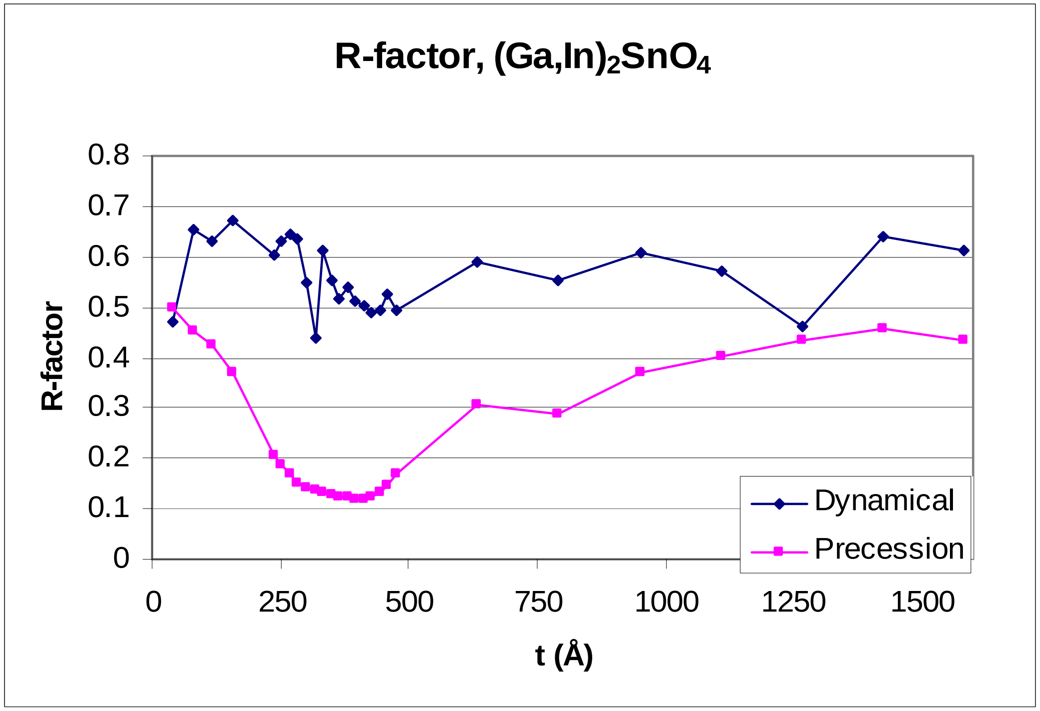
$\Delta R_{mean} <$ **4 pm**

(Sinkler, et al. J. Solid State Chem, 1998.
Own, Sinkler, & Marks, in press.)

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

Global error metric: R_1

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



- Broad clear global minimum
- R-factor = 0.118
  - Experiment matches simulated known structure
  - Compare to > 0.3 from previous precession studies (unrefined!)

- Accurate thickness determination:
  - **Average *t* ~ 41nm** (very thick crystal for studying this material)

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

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

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

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

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

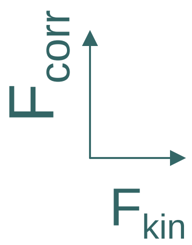
An approximation

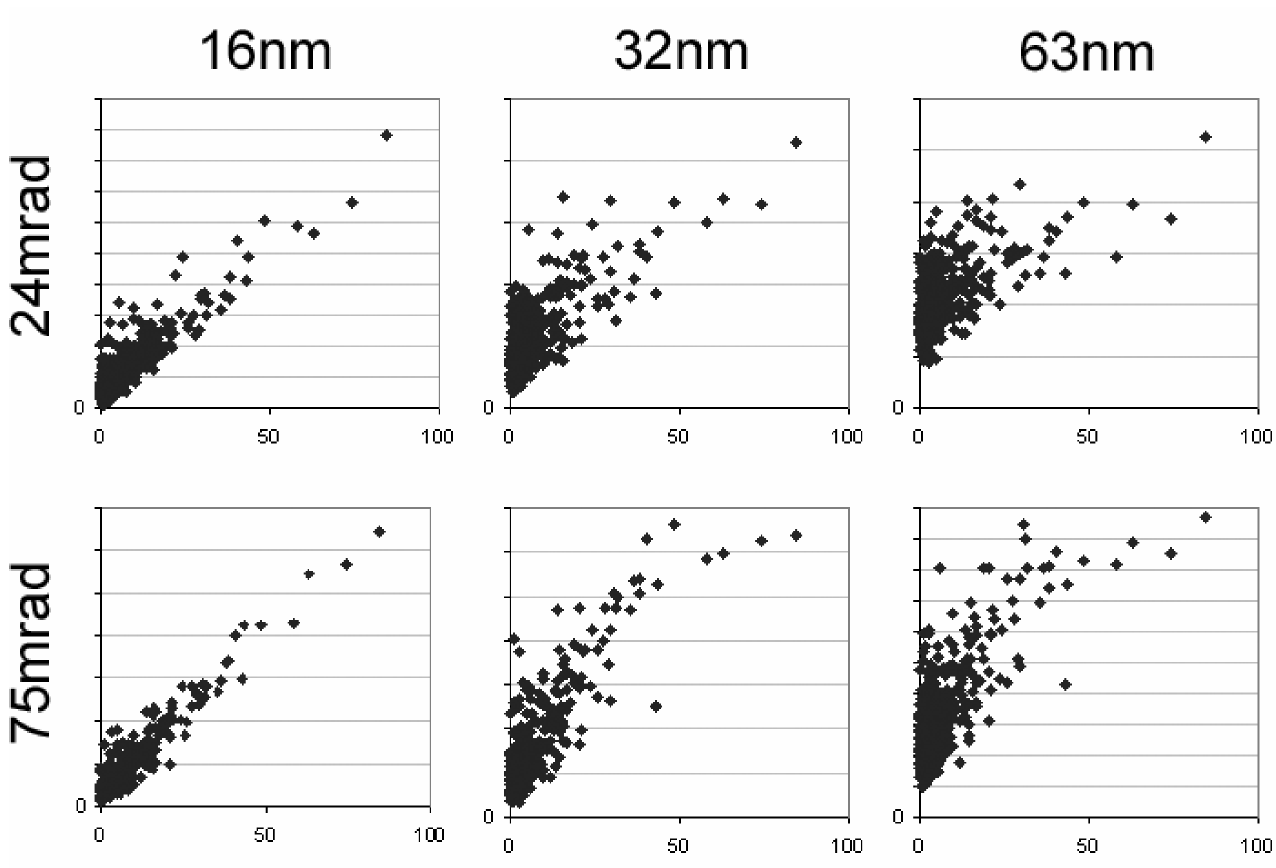
Geometry correction

Dynamical correction

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

Lorentz-only correction:
Geometry information is insufficient





Need structure factors to apply the correction!

New Dynamical Two-beam Correction Factor

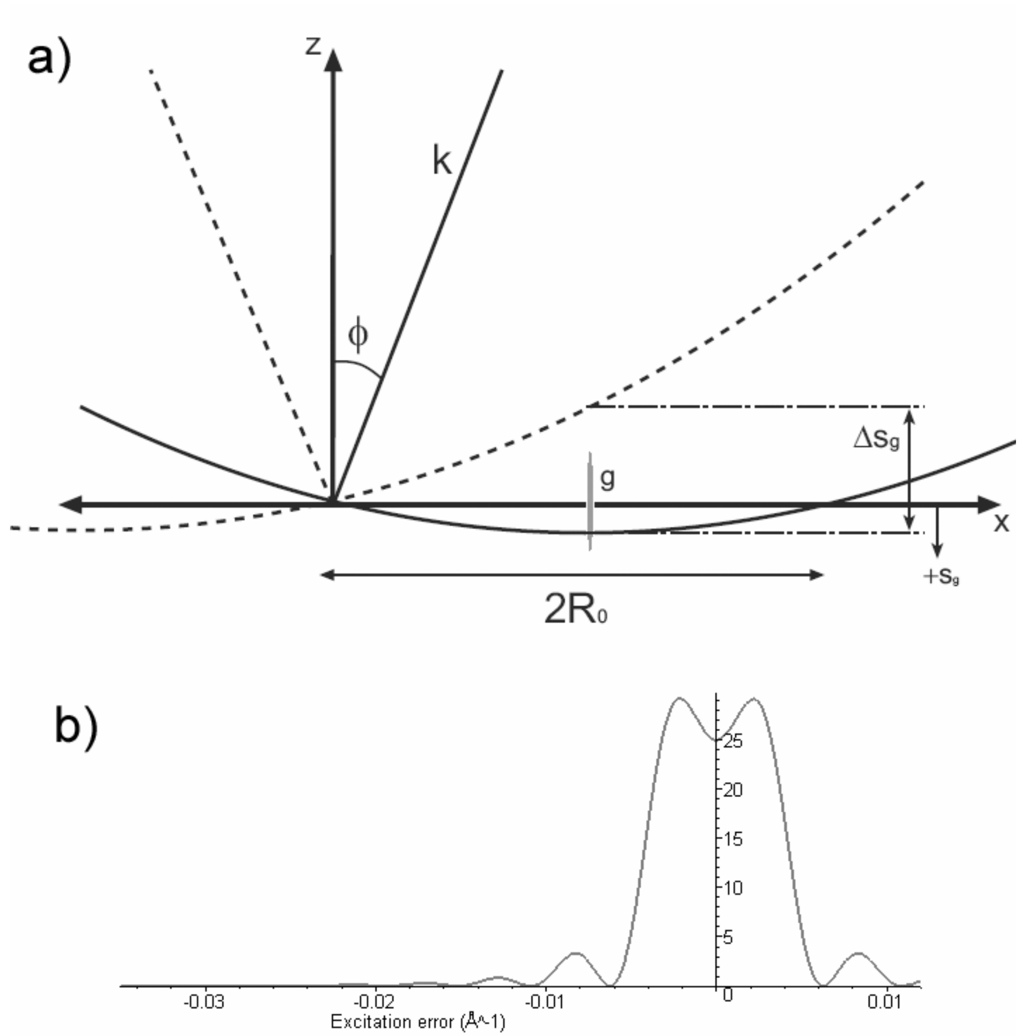
$$C_{2beam}(g,t,\phi) = F_g^{\ 2}\left(\frac{1}{\xi_g^{\ 2}}\int_0^{2\pi}\frac{\sin^2(\pi t s_{eff})}{(s_{eff})^2}d\theta\right)^{-1}$$

- Sinc function altered by ξ_g
- A function of structure factor F_g
  - Some F_g must be known to use!

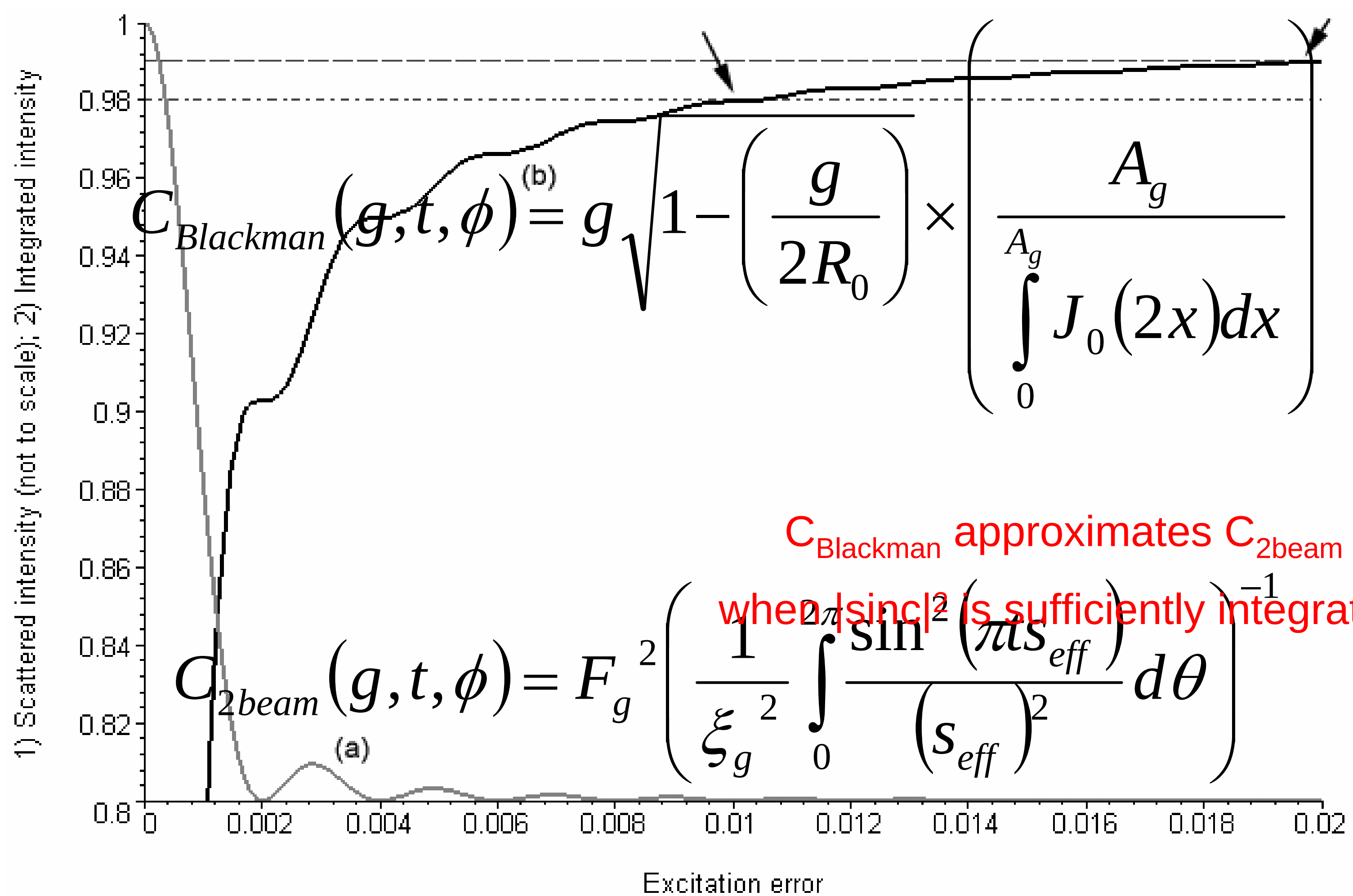
$$s_{eff} = \sqrt{s^2 + \frac{1}{\xi_g^{\ 2}}}$$

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

t = 20 nm, ξ_g = 25 nm



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

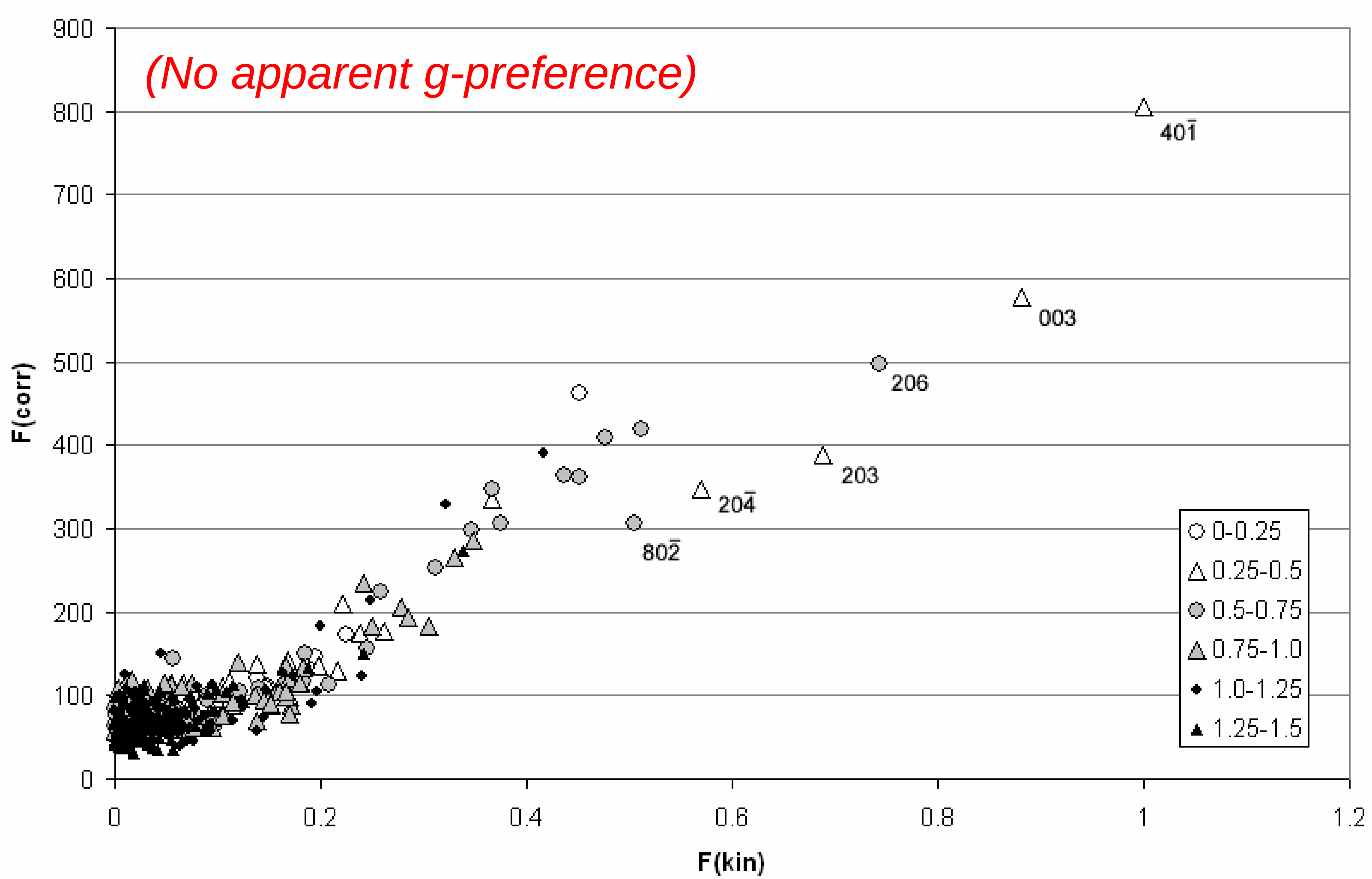


$$C_{Blackman}(g,t,\phi) = g\sqrt{1-\left(\frac{g}{2R_0}\right)} \times \left(\frac{A_g}{\int_0^{A_g} J_0(2x)dx}\right)$$

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

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

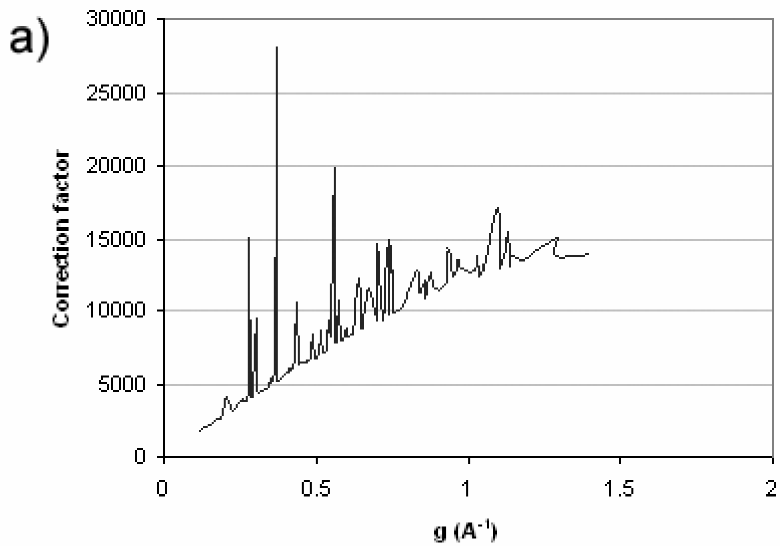
C_{2beam} correction:
t = 127 nm, ϕ = 75 mrad



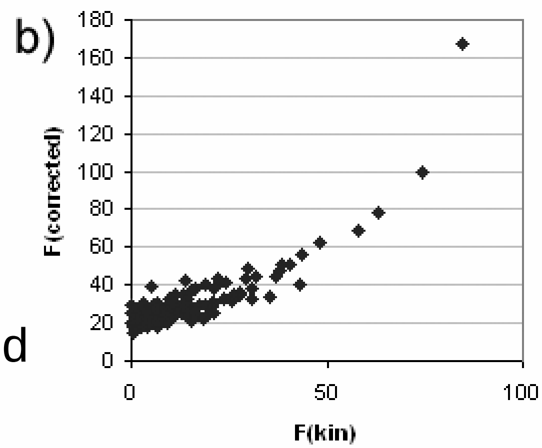
a priori correction: GITO (41 nm)

Consider the limits of the Blackman formula

Correction factor

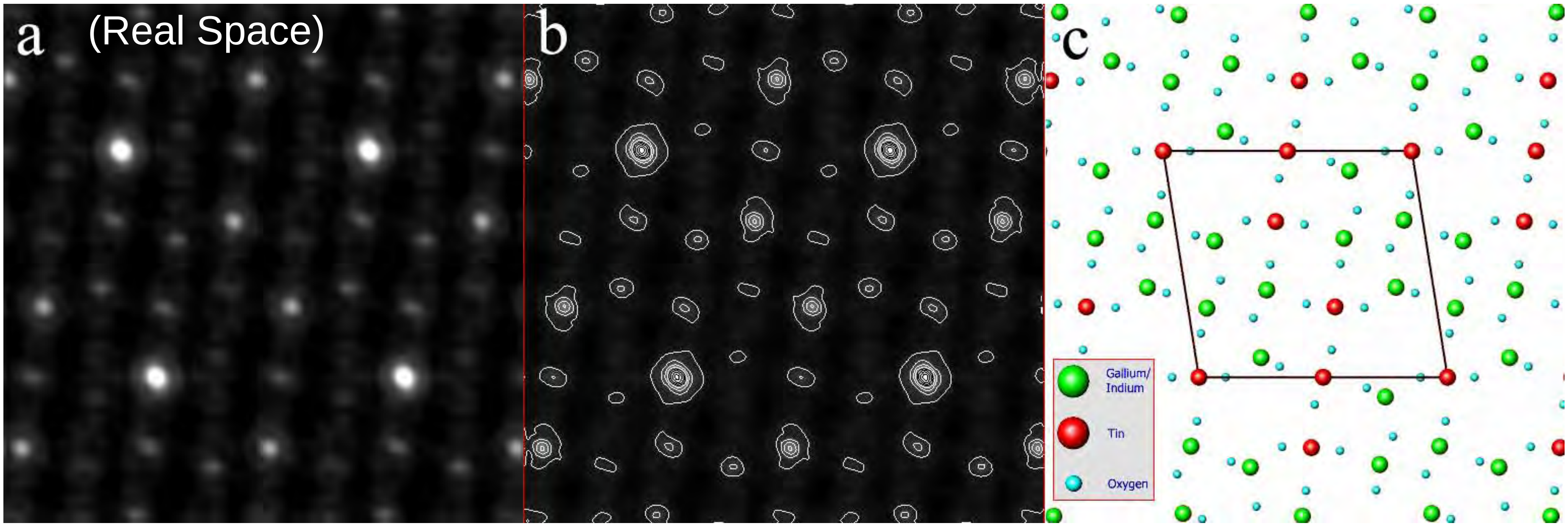


Corrected



Try GITO

Using intensities (F_g^2) w/ DM



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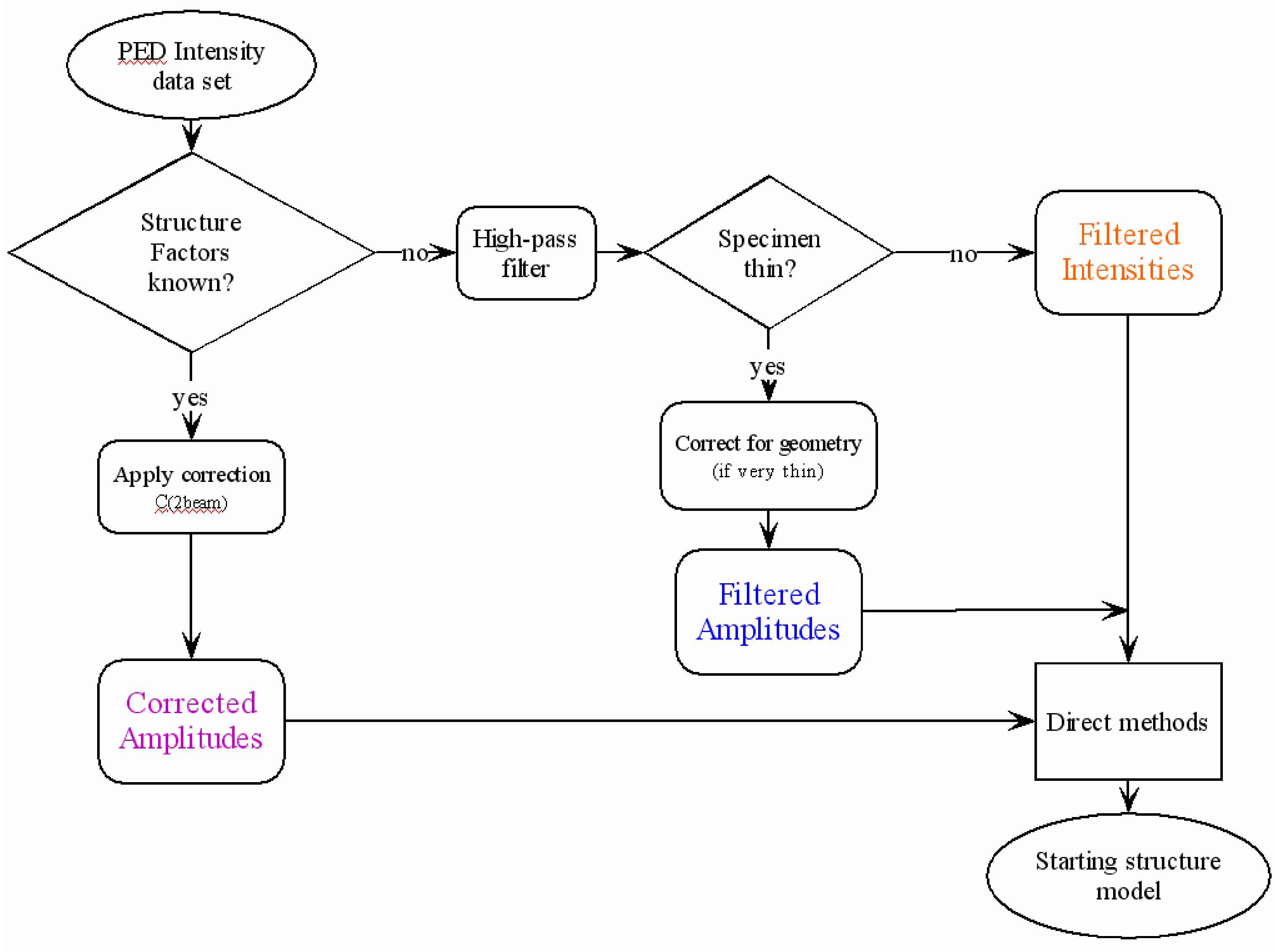
Displacement ($R_{neutron} - R_{precession}$):

ΔR_{mean} < **4 pm**

(Sinkler, et al. J. Solid State Chem, 1998.
Own, Sinkler, & Marks, in press.)

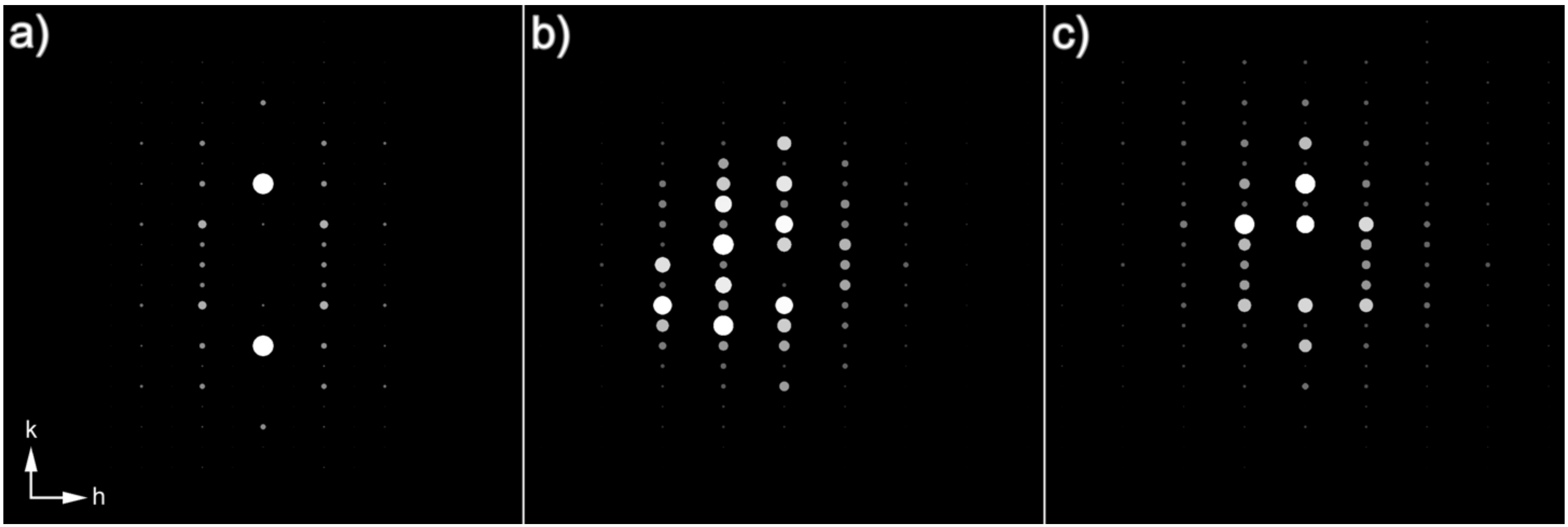
Suggested PED flowchart



IV. Examples

1. $La_4Cu_3MoO_{12}$
2. $Al_8Si_{40}O_{96}$
3. Al_2SiO_5

$La_4Cu_3MoO_{12}$ [001]
Intensities comparison



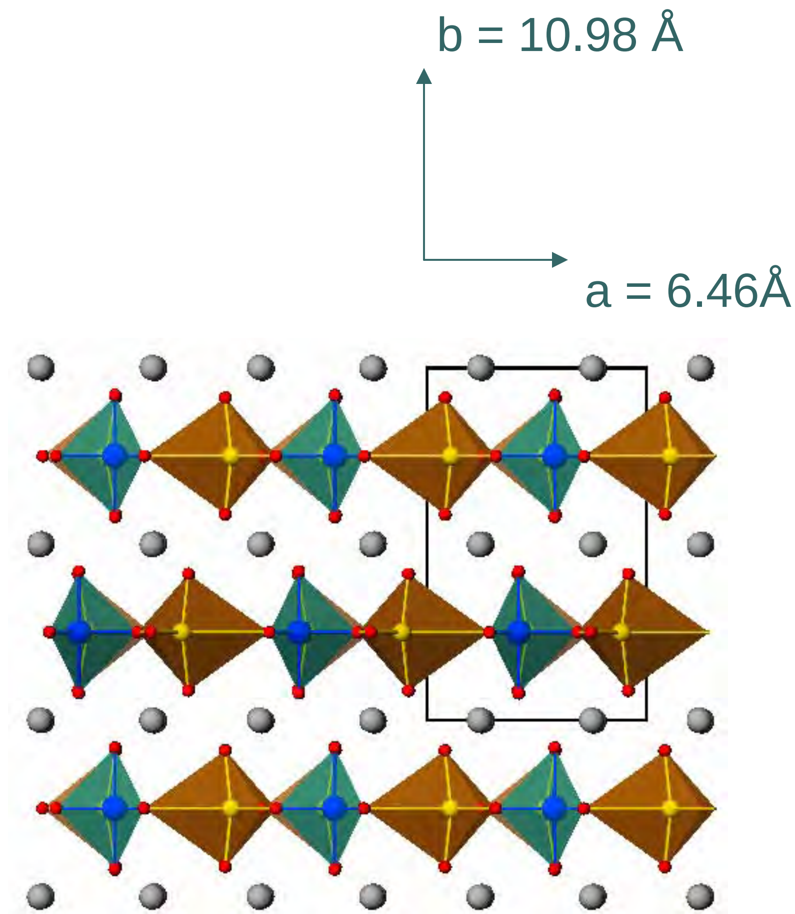
Kinematical Intensities

Conventional Diffraction Intensities

PED intensities

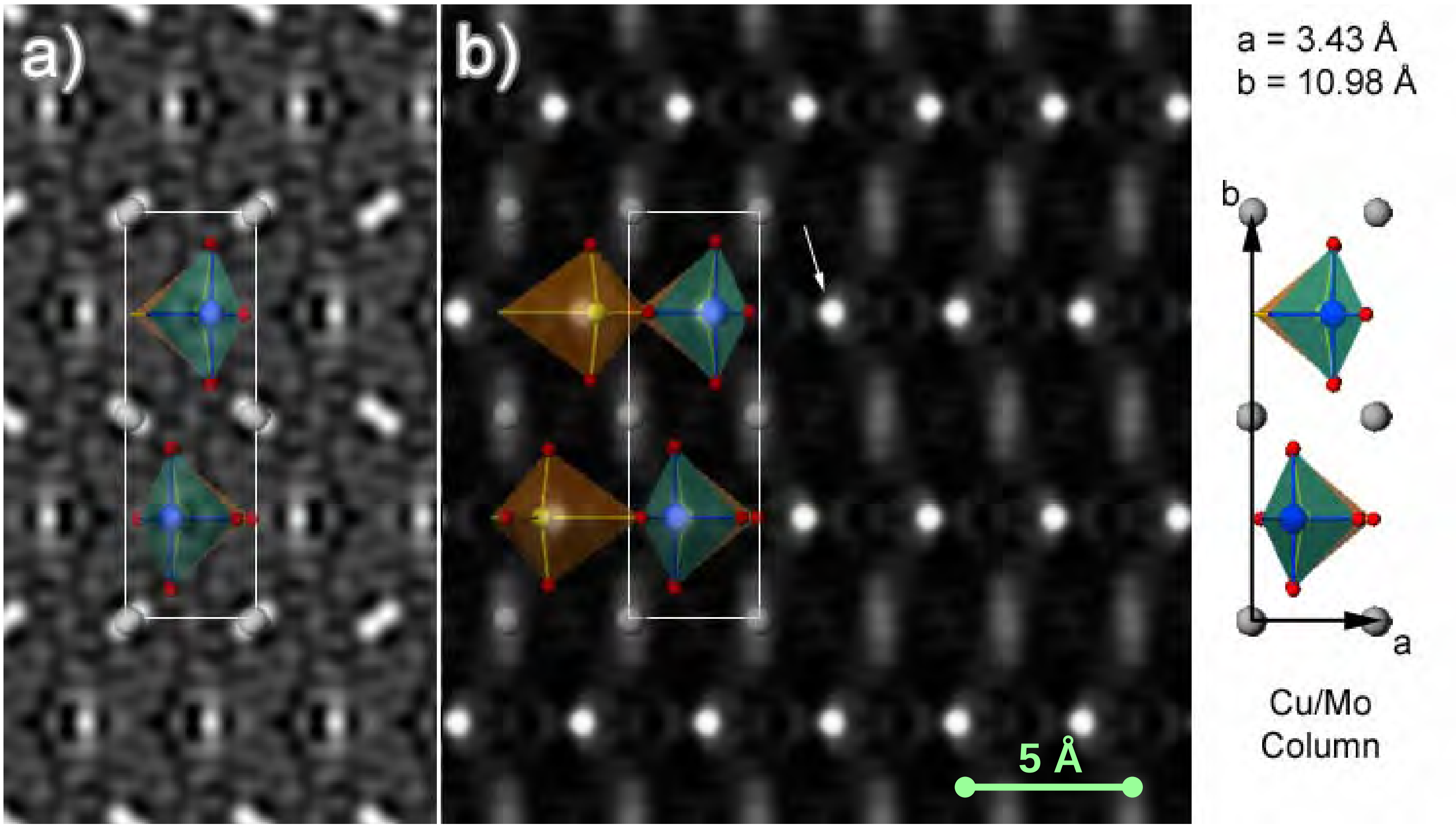
Proposed structure: highly ordered

- Homeotype of $YAlO_3$
  - Rare earth hexagonal phase
- Frustrated structure: doubling of cell along *a-axis*†
  - Maintains stoichiometry
- Better R-factor if twinning model introduced in refinement



†(Griend et al., JACS 1999.)

PED solutions: disorder

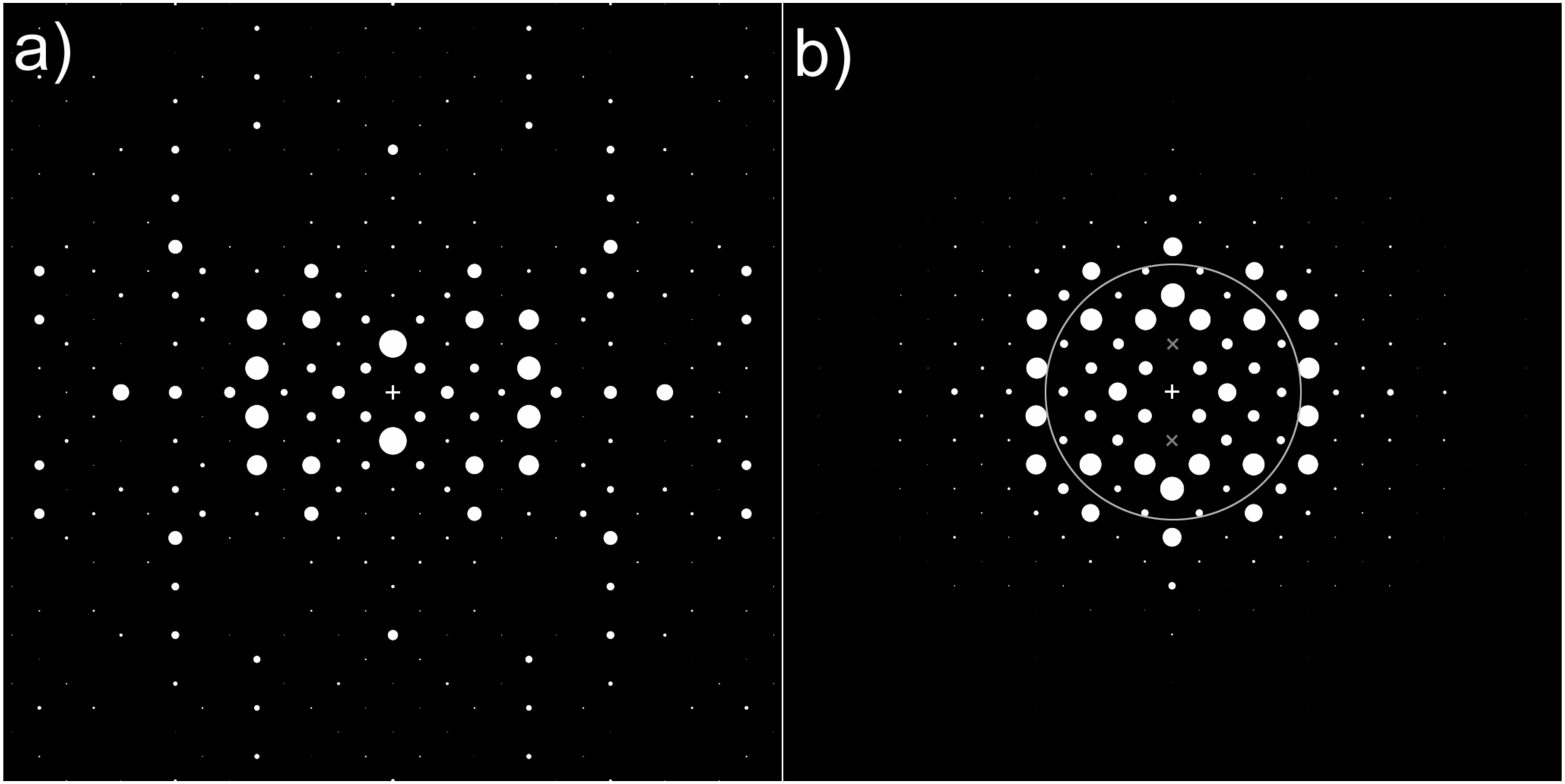


Amplitude solution
(high-pass filtered)

Intensity solution
(high-pass filtered)

$Al_8Si_{40}O_{96}$ [001] (Mordenite):

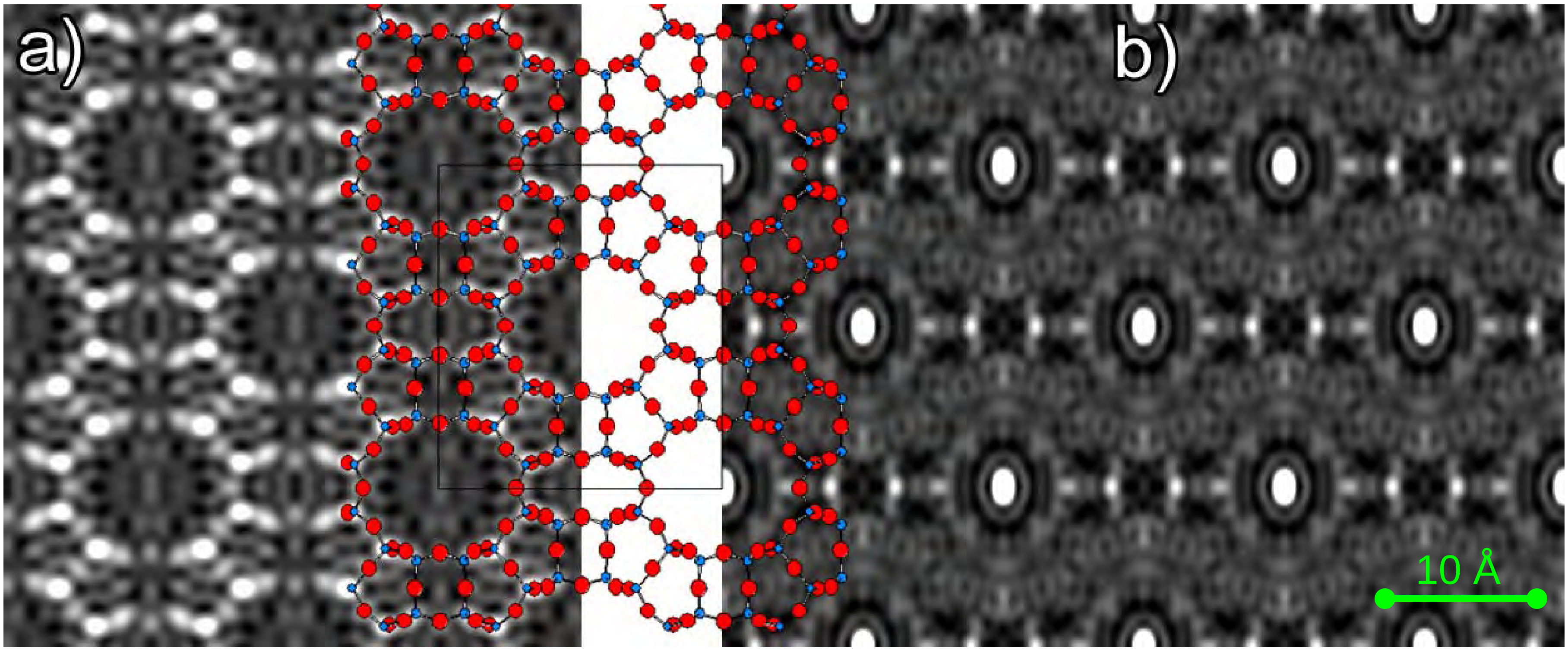
Thick (50 nm), poor projection characteristics



Kinematical amplitudes

PED intensities

Preliminary solution
Amplitudes, high-pass filtered

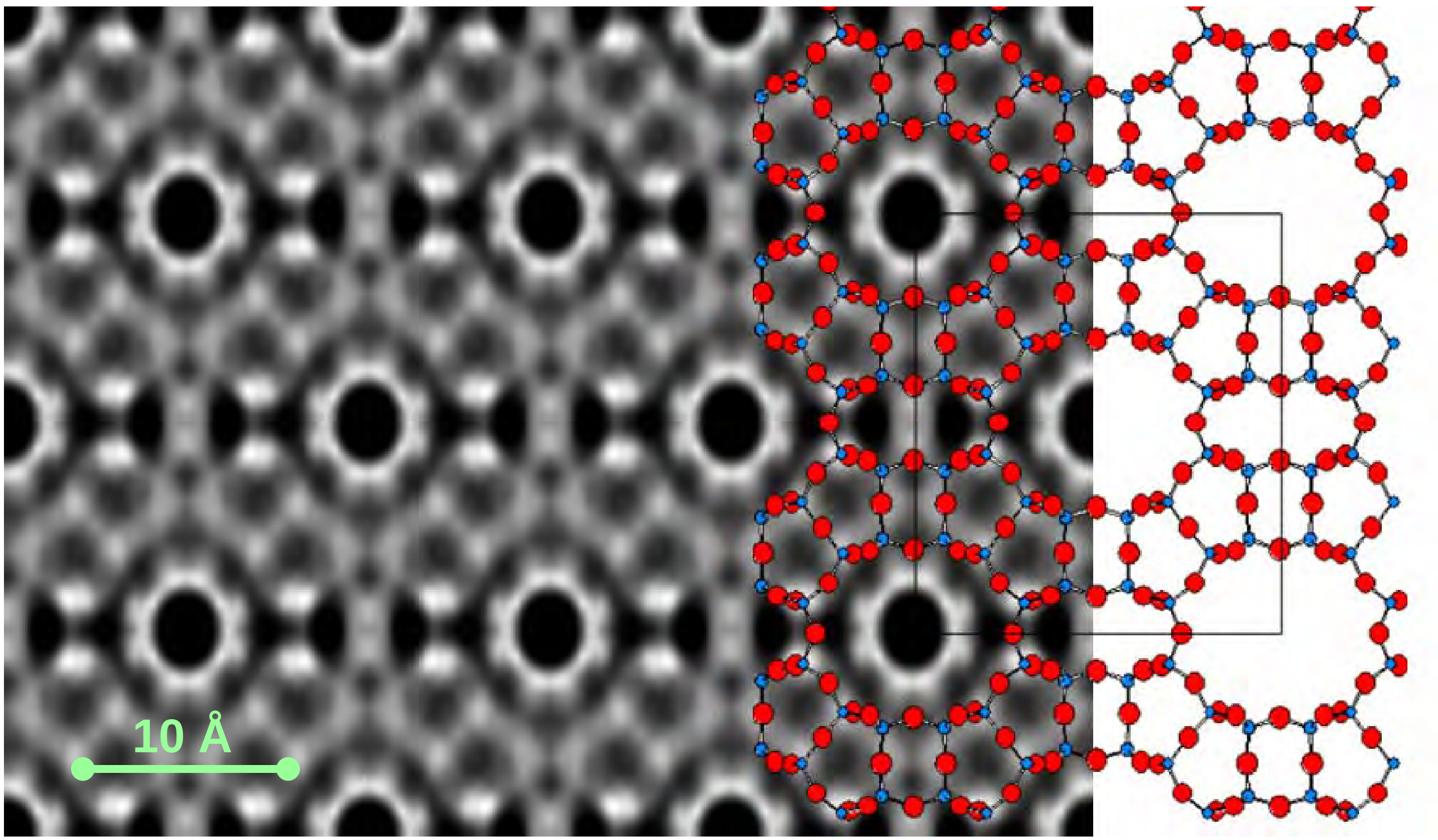


Kinematical Solution
($1Å^{-1}$ resolution)

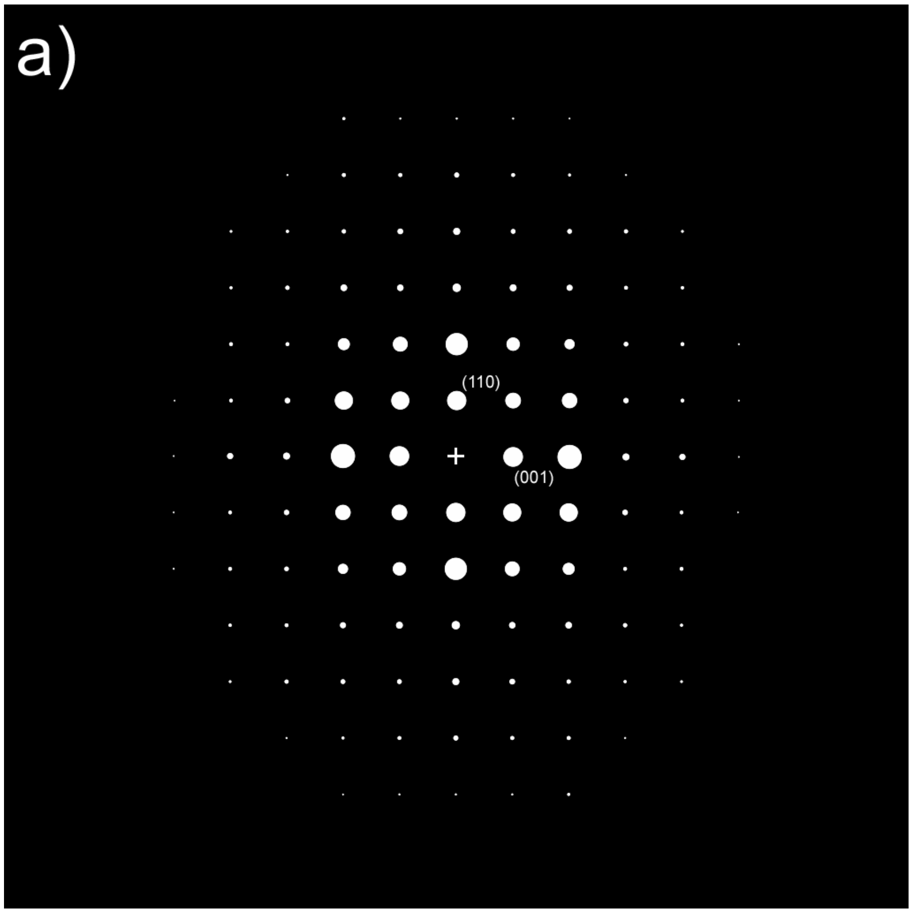
PED Amplitudes
Solution

Babinet solution

High-pass filtered intensities



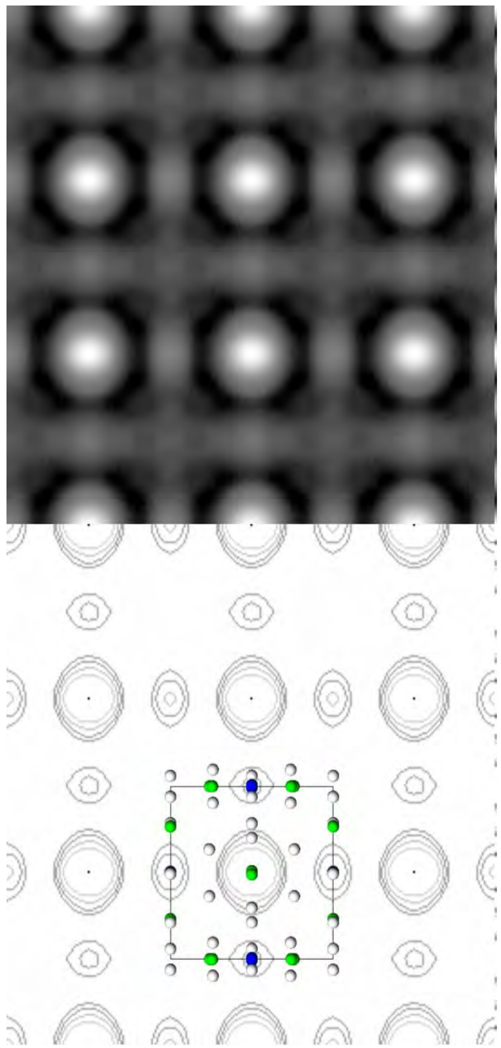
Al_2SiO_5 [1$\underline{1}$0] (Andalusite)

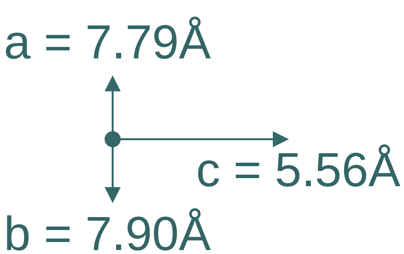


Conventional diffraction amplitudes

Andalusite [1$\bar{1}$0] solution

Non-precessed



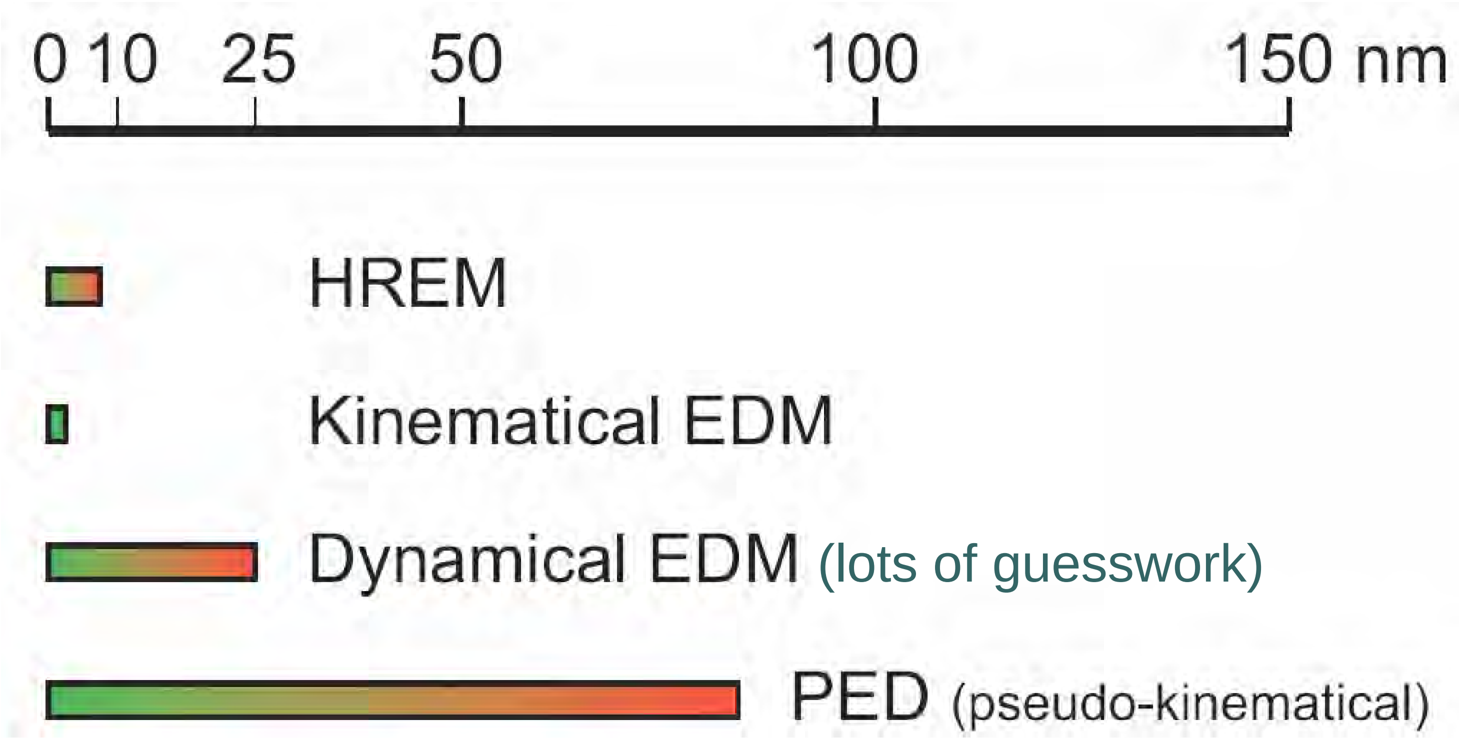


V. Conclusions & Future Work

Conclusions

- Now have a better understanding of Precession
  - Reduces overall error
  - Errors at low *g*
  - Precession extends the usable thickness to ~ 50 nm
  - Correction factor must include dynamical type
- Good PED experiment characteristics:
  - DM maps with well-defined peaks
  - See cations, don’t see light atoms
- Methods for *a priori* bulk electron crystallography

Summary: Thickness ranges



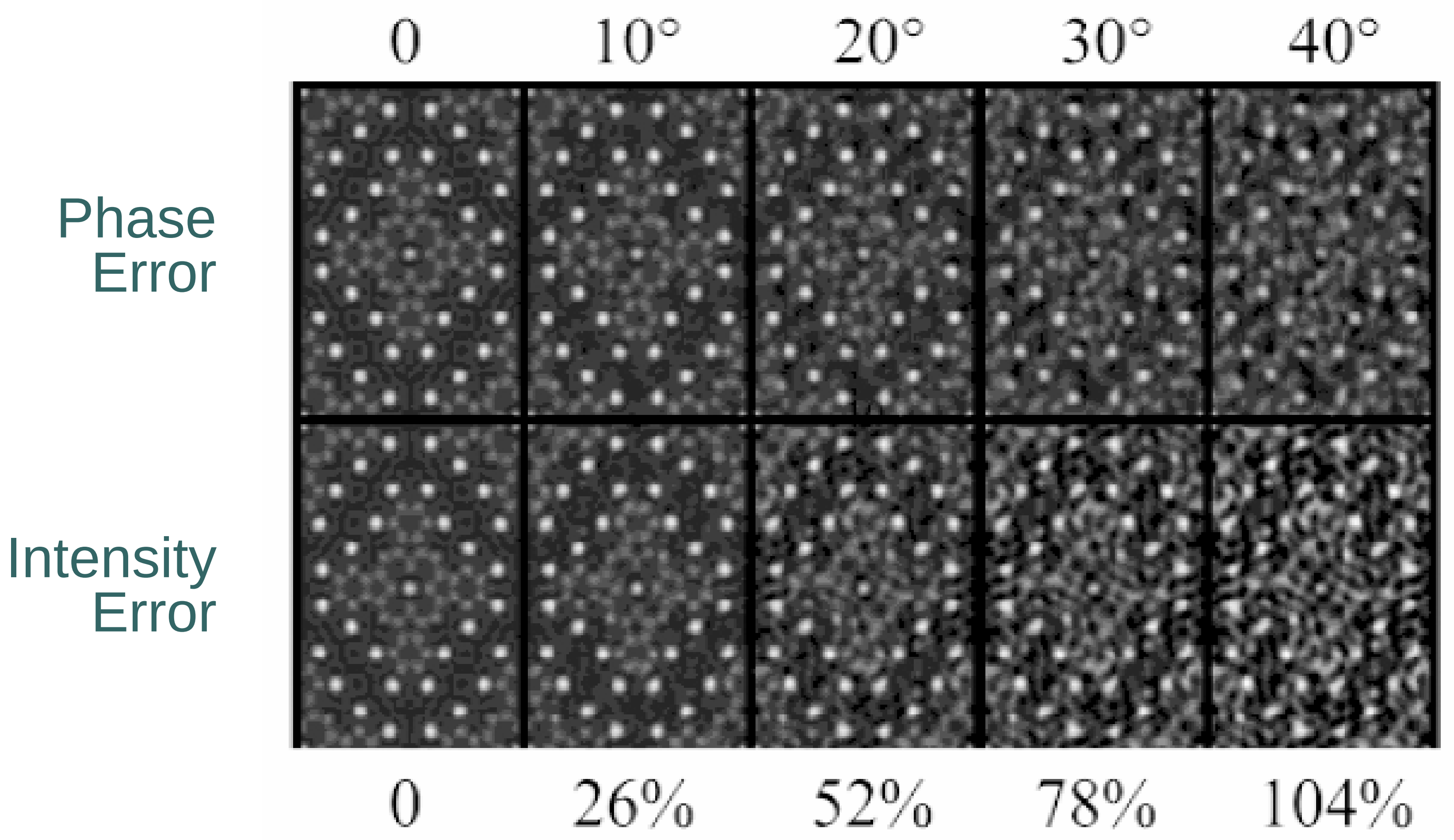
Future Work

1. More structures
   - Repertoire of solved structures
2. Aberration corrected precession
   - Test high angles experimentally
   - Fancy scanning configuration
     - Can avoid multi-beam excitation
     - Data mining
3. A general correction factor (iterative)
   - For thick specimens

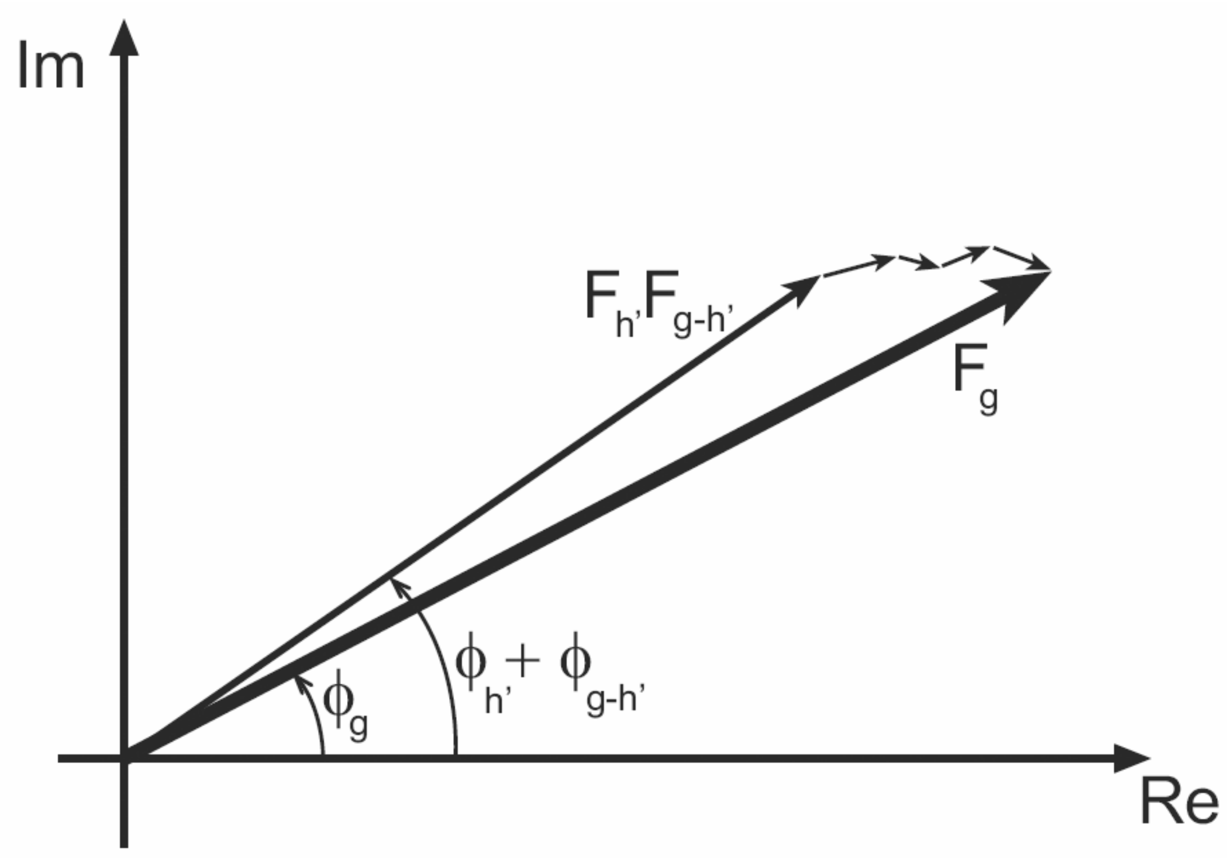
Thank you!

Questions…

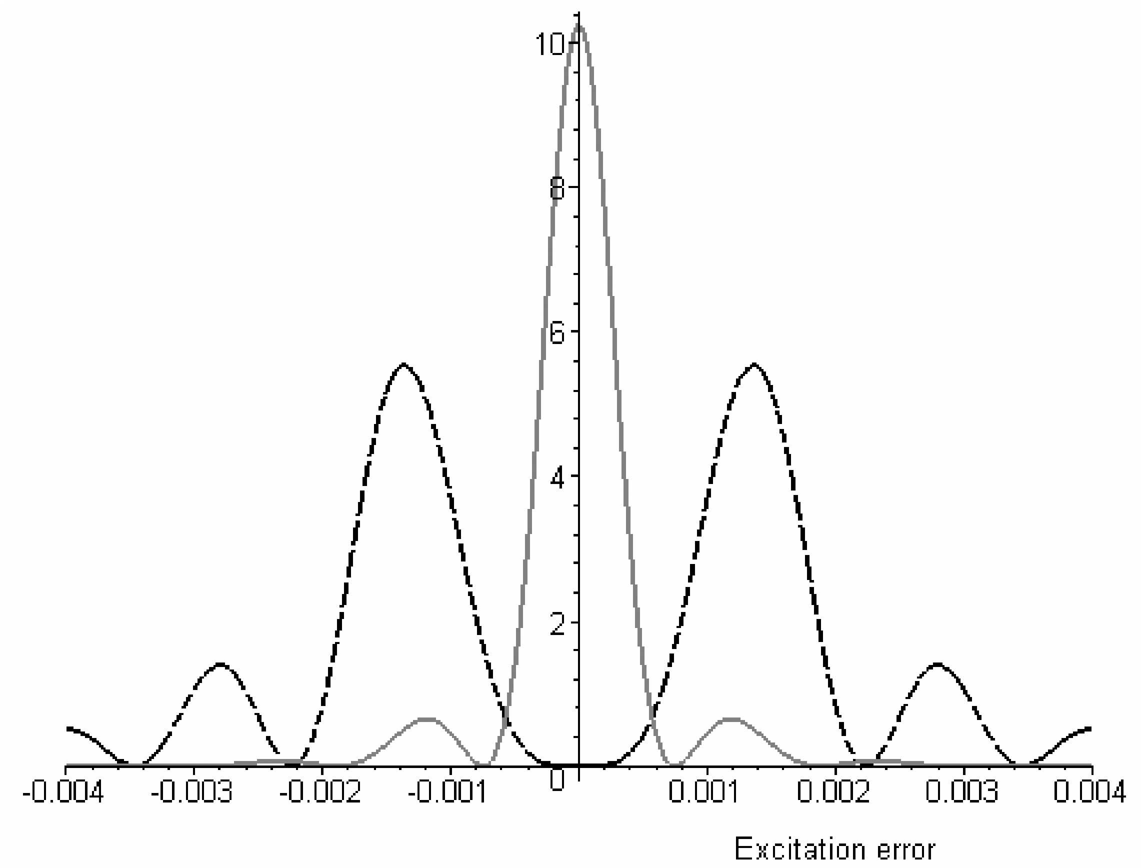
Intensity v. phase error



Triplets



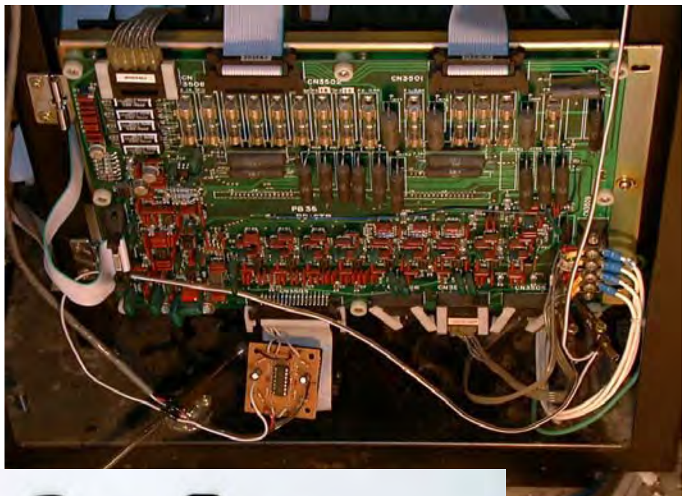
Thicker specimens: Two-beam Dynamical Coupling

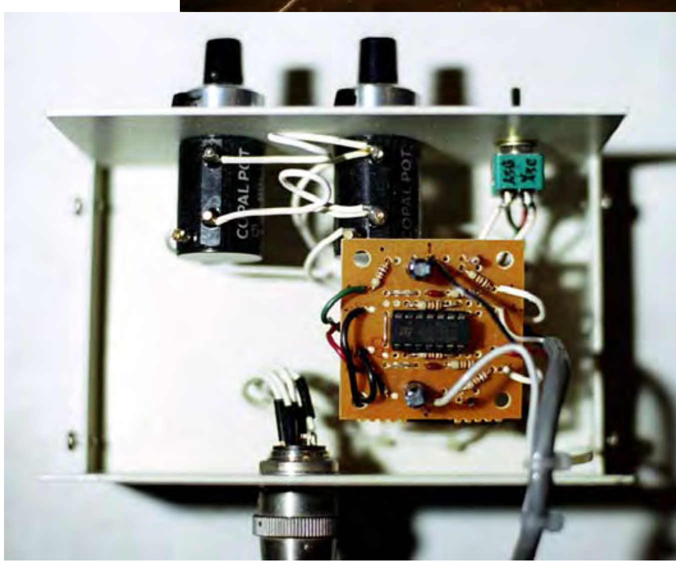


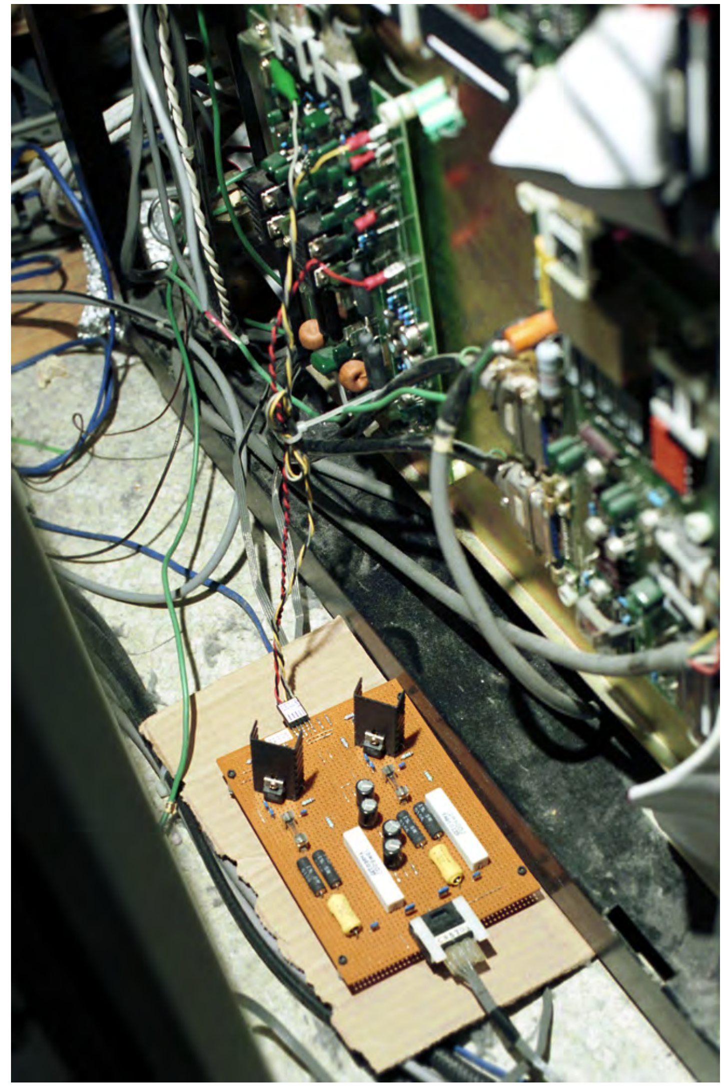
Design features

- Improvements upon previous implementations
  - Versatile: digital signal generation
  - Live settings update
  - 1KHz operating bandwidth
  - Forms fine spots for reliable measurement
  - 2-fold and 3-fold aberration compensations
    - Able to form fine probe (< 25 nm)
  - Rapid alignment (15 min)

Generation I Hardware

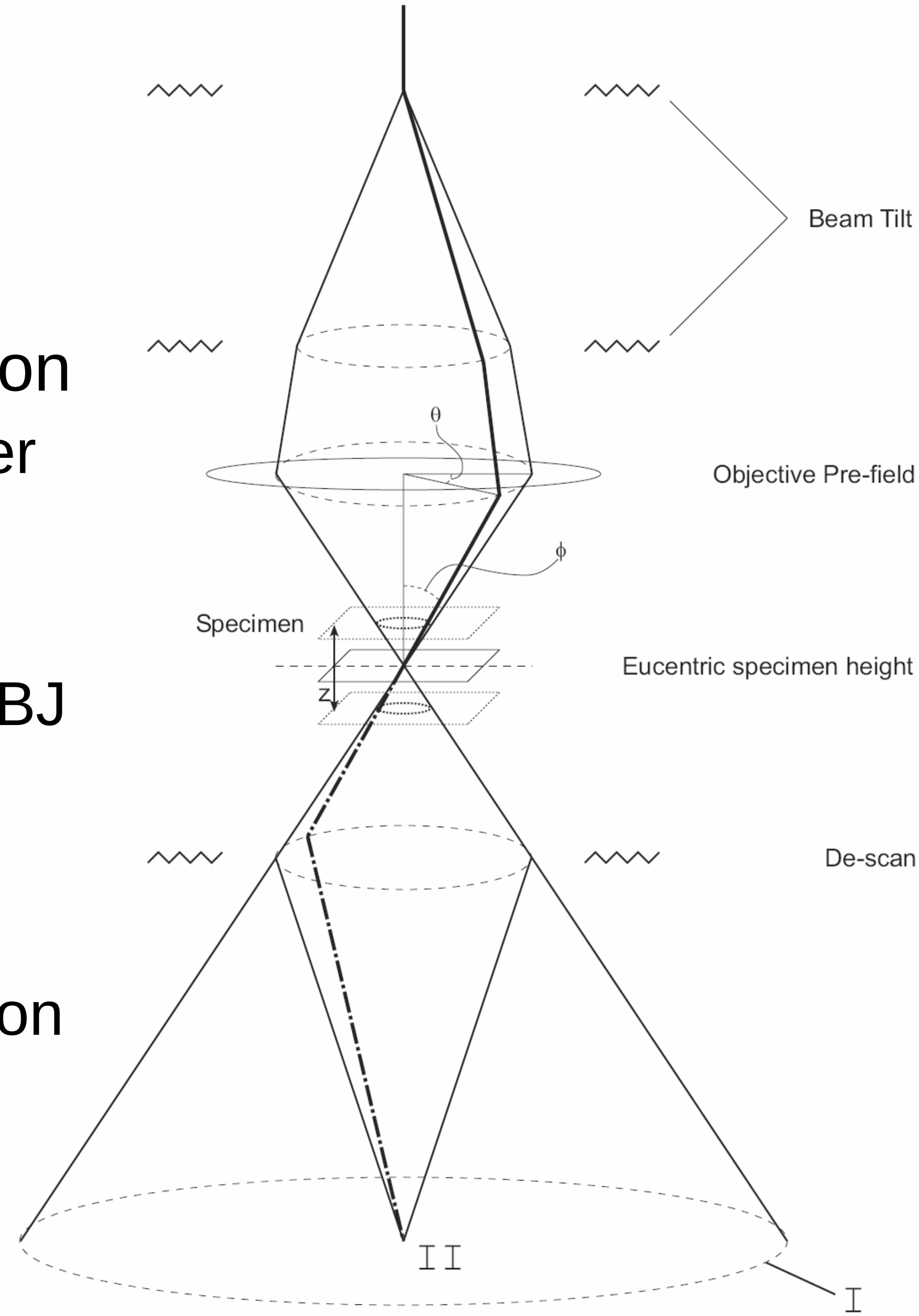






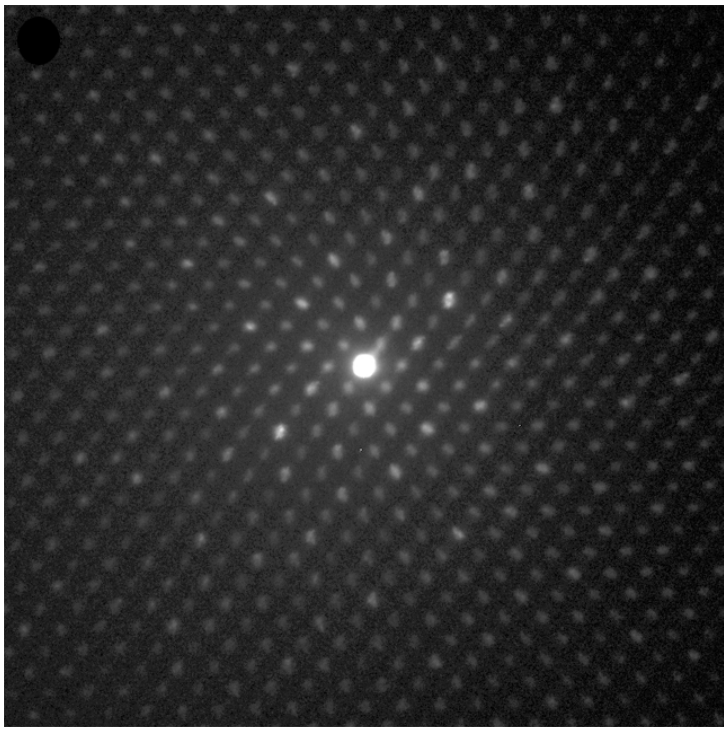
Alignment Detail

- Parallel illumination
  - Small condenser
  - Fine probe
- Specimen height
  - Meet optimal OBJ excitation
- Distortion compensations
  - Probe localization <50nm

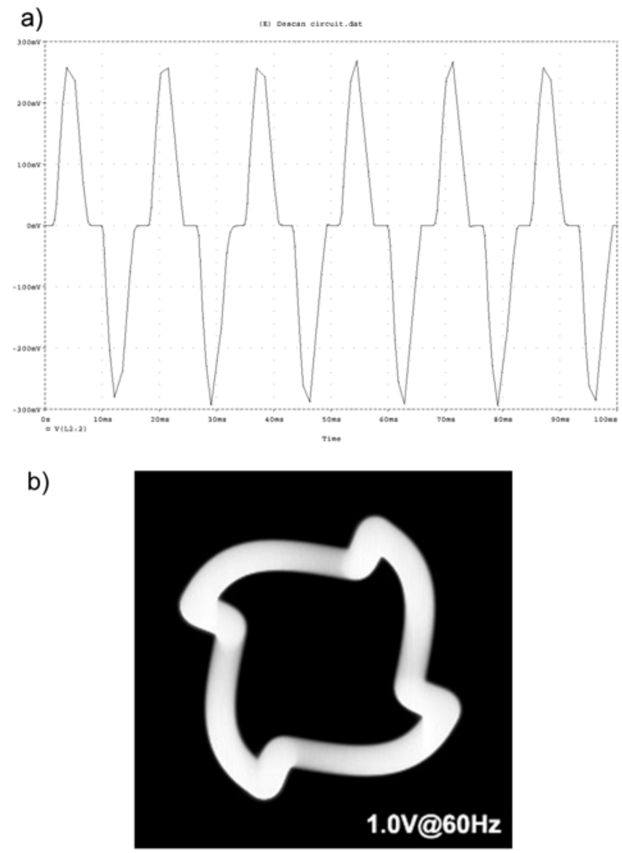


(C.S. Own & L.D. Marks, Rev. Sci. Instr. 2005.)

Teething problems

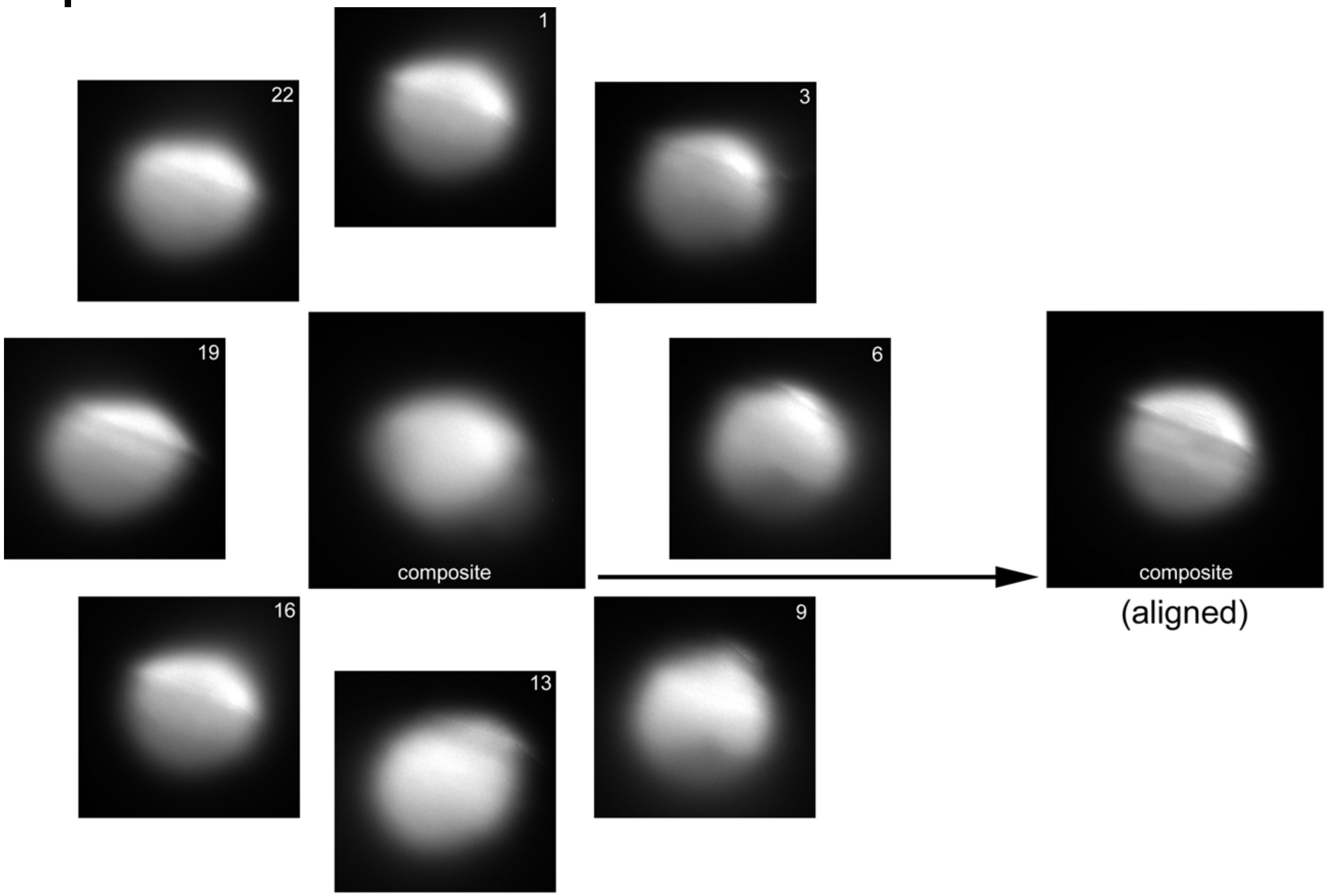


Projector Lens Spiral
Distortion



Crossover Distortion

Alignment example



(aligned)