Electron Precession for Routine Crystallography

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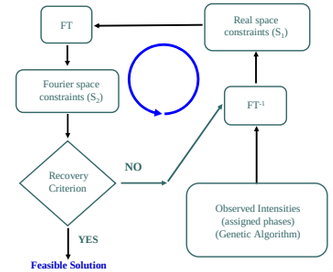
< Direct Methods (DM) >

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

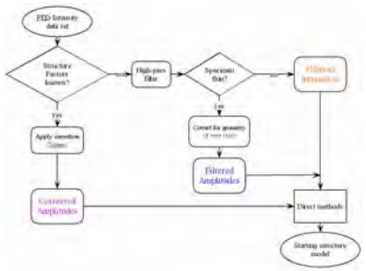
$$S.F. = F(k)\exp(-i\phi(k))$$

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

- If the phases were known:
  - Generate scattering potential maps
- For atomic structures, phase information is encoded within intensities
  - Requires **< 10-20%** RMS intensity error in order to work

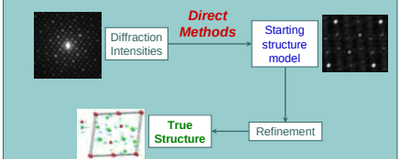


< PED Solution Flow Diagram>



< Introduction >

- The difficult step in structure determination is obtaining a good starting structure



  - If starting structure is close, refinement to true structure is accurate and reliable
  - Direct methods (phase recovery) is the key step but requires good intensities (see box)
- Traditionally, use X-rays (e.g., synchrotron):
  - Very kinematical (single scattering)
  - DM works well with kinematical data
- Transmission electron diffraction is better for many nanomaterials problems:
  - Fine probe (0.5Å-50nm)
  - Multiple data collection in one instrument
    - Chemical information (EELS, EDX)
    - Imaging and diffraction
  - *In-situ* capabilities
  - TEM is widely available and can be less expensive
- However, electron diffraction data is strongly distorted by dynamical (multiple) scattering:
  - Intensity oscillates with specimen thickness
  - Phase inversion on dynamical intensities is not usually successful
  - *A priori* information needed
    - Structure solutions to date using TEM usually need combination of multiple techniques
    - ***Time and $$$***
- The solution:
  - **Precession Electron Diffraction (PED)**

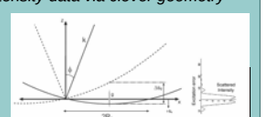
< References >

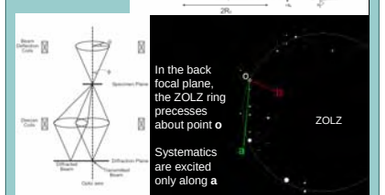
1. Vincent & Midgely, Ultramic. 1994.
2. Gjonnes, Ultramic. 1997.
3. Sinkler, et al. J. Solid State Chem. 1998.
4. Gemmi, et al. Acta Cryst. 1998.
5. Gjonnes, et al. Acta Cryst 1998a.
6. Gjonnes, et al. Acta Crysta 1998b.
7. Blackman, Proc. Roy. Soc. 1939.
8. Own, Subramanian, & Marks, Mic. & Microanal. 2004.
9. Own & Marks. US Patent application # 60/531,641. Dec 2004.
10. Own & Marks, Rev. Sci. Instr. 2005
11. Own, Sinkler & Marks, Ultramic. in press.

< P.E.D.[1] >

- Conical beam rock/de-rock via deflectors
  - Avoids most multiple scattering – Usually only one strong beam excited at once.
  - An effective integration over excitation error
    - Like powder diffraction or texture patterns
  - Insensitive to tilt misorientation
  - *Better intensity data via clever geometry*

Note: All results shown use parallel beam.

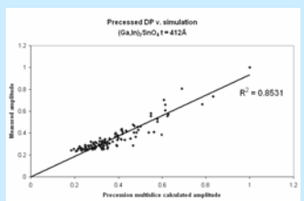




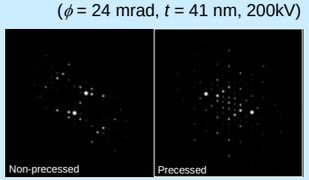
- Instrumentation[10]
  - PED mode retrofittable onto most any TEM
  - We have developed optical aberration compensations and rapid alignment[9]
  - The key variables[8,10]:
    - Tilt angle ϕ
    - Thickness t
    - Spatial frequency of reflection $|g|$
- Questions:
  1. Why were literature results inconsistent?[4-6]
  2. What is the true nature of the data?
  3. Do correction factors need to be applied, how and when should we apply them?

< Result 1: Precession Multislice >

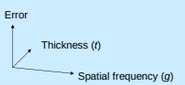
I. Precession multislice is the correct model for precession:



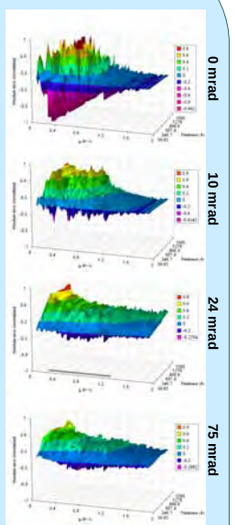
Simulated patterns show improved intensity ordering.
(ϕ = 24 mrad, t = 41 nm, 200kV)



II. Amplitude Error plots

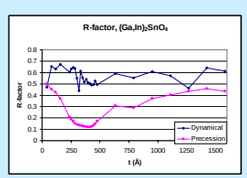


- How to read these plots:
  - ±0.4 on plot corresponds to ±16% intensity error
  - Bumpiness means data is dynamical
    - *t*-axis: pendellosung oscillations
    - *g*-axis: dynamical exchange between neighboring beams
- Trends as ϕ (prec. angle) ⇧
  - Larger ϕ decreases error
  - Negative error disappears
    - After critical angle (~20mrad), errors become small
  - Primary errors are near transmitted beam
    - Systematics, diffuse scattering
    - In regime **< 0.25 Å^{-1}**
  - Smaller thicknesses have low error
    - Will solve well with DM without correction factors
    - Larger thicknesses need correction



III. *R*-factor (for unrefined solution)[11]

- Broad clear global minimum: R_1 ~ 0.118
  - Experiment matches simulated known structure
  - Compare to R_1 ~ 0.3-0.45 from previous precession studies after refinement (this is unrefined!)
- Accurate thickness determination:
  - **Average *t* ~ 41nm** (ordinarily intractable by DM)



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

< Result 2: Correction Factors >

I. Previous corr. factor (an approx.)[2,7]

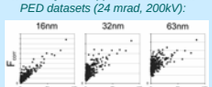
- Integral over all space (like powder diff.)

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

Geometry correction term — Dynamical correction term

An *a priori* correction: Geometry-only (no dynamical)

Geometry term applied to calculated PED datasets (24 mrad, 200kV):



Result: Does not work! Need dynamical term (requires knowledge of structure factors)

II. New, more exact corr. factor

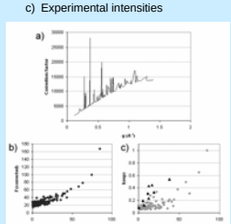
- Exact integral over scattered intensity
  - Sinc function altered by ξ_g (2-beam)
  - A function of structure factor F_g
    - Some F_g must be known to use it!
  - $C_{Blackman}$ converges to this for large t

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

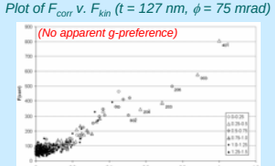
$$s_{eff} = \sqrt{s^2 + \frac{1}{\xi_g^2}} \qquad \xi_g = \frac{\pi V_c \cos\theta_B}{\lambda F_g}$$

C_{2beam} applied to GITO system:

a) Correction factor v. |g|
b) Corrected multislice amplitudes
c) Experimental intensities



Correction factor applied to simulated data
Plot of F_{corr} v. F_{kin} (t = 127 nm, ϕ = 75 mrad)



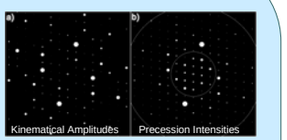
Result:

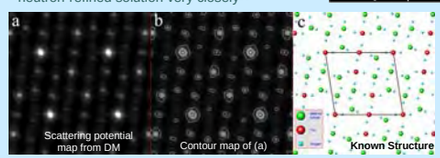
- An exact integration of two-beam approximates PED well
- Consider the bessel integral limits
  - Precession *intensity* approximates true amplitude for large A_g.

< Result 3: Examples >

I. (Ga,In)$_2$SnO$_4$ [010][3]

- Using intensities (F_g^2) w/ DM
  - No filtering, all cation peaks found
- Displacement: $R_{neutron} - R_{precession}$
  - Average ΔR less than **4 pm!**
  - PED solution (unrefined) matches neutron-refined solution very closely[11]



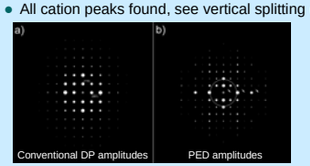


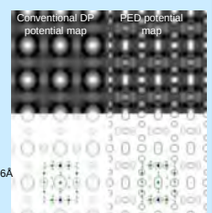
Atom position deviations (unrefined v. refined):

	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

II. Al_2SiO_5 [110] (andalusite)

- Using amplitudes, high-pass filtering
  - Forbiddens disappear in PED pattern
  - All cation peaks found, see vertical splitting (O features)

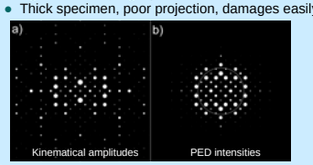


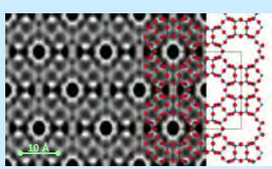


a = 7.79Å
c = 5.56Å
b = 7.90Å

III. $Al_8Si_{40}O_{96}$ [001] (mordenite)

- Using intensities, high-pass filtering
  - Thick specimen, poor projection, damages easily

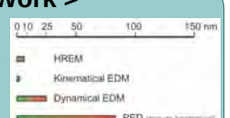




Solution was hard to find (above is a babinet soln.); large temp-factors and large open framework give poor projection. This is challenging for PED, but solvable.

< Conclusions / Future Work >

- Now we have better understanding of PED
  - Reduces overall error, errors @ low-index reflections
  - Precession extends usable thickness > 50 nm
  - Correction factor must include dynamical
    - 2-beam w/ exact integration limits is a sufficient model
  - Must exceed critical angle (ϕ > 20 mrad)
- Structure maps from good PED expt.
  - DM maps with well-defined peaks
  - See cations, don't see light atoms
  - Can process much thicker specimens



Future Work

1. More structures
   - Repertoire of solved structures
2. Aberration corrected precession
   - Fine probe, fancy scanning configuration
   - Can avoid multi-beam excitation, also data mining
3. A general correction factor (iterative)
   - For thick specimens

For more information, see http://www.numis.northwestern.edu/Research/Current/precession.shtml