The Nature of Precession Electron Diffraction Data

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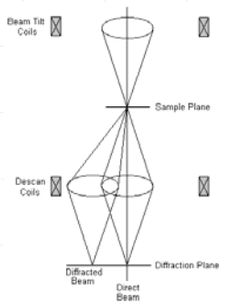
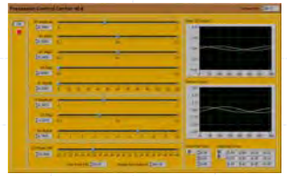


†(Vincent & Midgley. (1994) Ultramicroscopy. **53**, 271.)

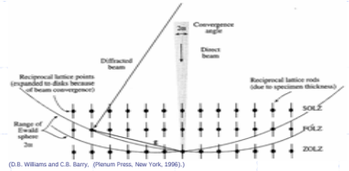
- Vincent-Midgley Precession technique†:
  - Hollow-cone diffraction
  - An innovative tool for structural crystallography
  - Non-systematic dynamical effects reduced
  - Claim is that F_{prec} is pseudo-kinematical
- Precession should improve data quality:
  - Avoids exact Bragg condition
  - Lowers probability for dynamical coupling
- Major questions:
  - Does it improve electron diffraction data?
  - If so, how?
  - How do you prepare precession data for use in direct methods?

2nd Generation Precession Instrument: On JEOL 2000FX

- Fast operation to >1KHz
- Distortion corrections:
  - Software includes 2- and 3-fold objective pre-field compensations
- Preserves normal scope operation
- ***Portable***
  - PC-based front end
  - Ultra-flexible



- Improvements (1st generation = Hitachi H-9000)
  - Better probe localization
  - Quick sample transfer
  - Larger range of tilts
  - DP acquisition via CCD



(D.B. Williams and C.B. Barry. (Plenum Press, New York, 1996).)

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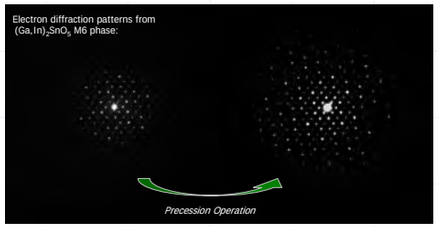
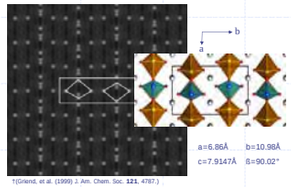


- Effects of precession:
  - Expands dataset out to large **g**
  - Integrates non-systematic dynamical effects
  - Can provide 3-D data with one experiment
  - In theory, makes dataset more kinematical

Precession amplitude ≈ Kinematical amplitude?

- $La_4Cu_3MoO_{12}$: a novel cuprate
  - Previously solved using x-ray data.†
- Potential map: Direct Methods using precession ***intensities*** (F_{hkl}^2). ‡
  - Amplitudes yield poor solution
  - Intensities yield better solution (right)
  - La atoms missing in map: evidence of remaining dynamical character.

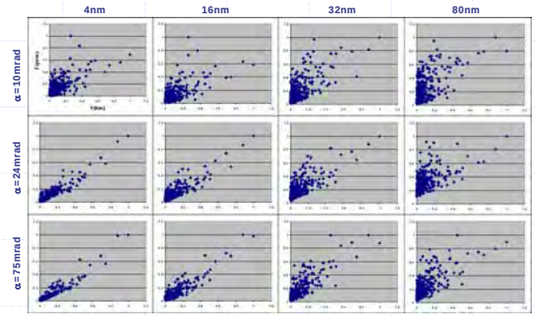


†(Grend, et al. (1999) J. Am. Chem. Soc. **121**, 4787.)
‡Note: intensities acquired using 1st generation instrument.)

Why did intensities work better?

Precession Multislice: $(Ga,In)_2SnO_5$ Model System

- F_{prec}-F_{kin} plots show correlation between precession and kinematical
  - Ideal for Direct Methods if dataset follows line defined by $F_{prec}=F_{kin}$

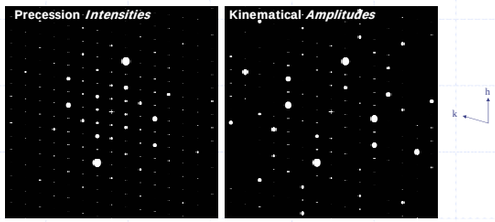


- ⇧ thickness: ⇧ non-linearity of precession data
- ⇧ angle: dataset remains linear through more thickness
- Important feature: offset of low **g**
  - As ℓ increases, precession emphasizes weaker reflections
  - Large error of low **g** prevents straightforward structure solution
  - Can be linearized by a) using F_{prec}^2or b) subtracting **g**-dependent offset term
- 2-beam integration describes only a small set of precession conditions

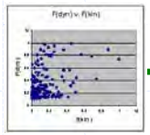
- Good precession data incorporates:
  - Large tilt angle
  - Small-to-moderate thickness
  - Low aberrations

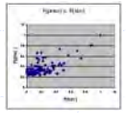
If above conditions are met, truly pseudo-kinematical amplitudes are obtainable.

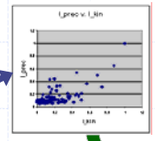
Precession In Action: Example Structure Solution

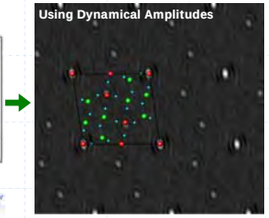


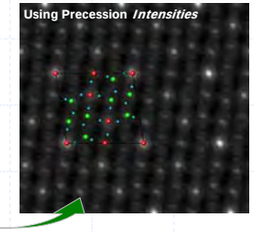
- $(Ga,In)_2SnO_5$
  - Previously solved via electron and neutron diffraction†
- Dynamical and Precession:
  - 2 sets of intensities from same sample area
- Specimen moderately thick: exhibits offset
  - Can exclude low-order g
  - Use intensities
- I_{prec}–derived structure map
  - Relative intensities incorrect, but locates all cation positions
  - Banding is due to under-estimated <030> reflection
  - Very good starting point for structure refinement











†(Sinkler, et al. (1999) J. Am. Chem. Soc. **121**, 4787.)
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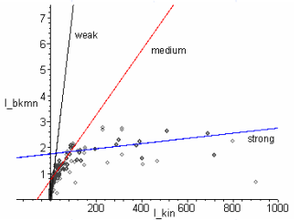
2-beam theory:

- Vincent & Midgley (1994): an integration of Blackman formula
  - Commonly accepted approximation for precession (below form is for SA precession):†

†(Vincent & Midgley. (1994) Ultramicroscopy. **53**, 271.)

$$\frac{Idyn}{Ikin} = \sqrt{1-\frac{g}{2R_0}} \cdot \frac{1}{A_{hkl}} \int_0^{A_{hkl}} J_0(2x)dx$$



- I_{bkmn} v. I_{kin} plot behaves similarly to y=√x.
  - This suggests that (in this case):

$$F_{hkl} \approx c \cdot (F_{prec})^2$$

- Ways to improve data:
  - Using powers of F_{hkl} one can linearize precession dataset
    - Suggested by Dorset (1995) for conventional on-zone dynamical data
  - By excluding weak reflections, can increase probability of finding basic structure
    - Intensity ordering of strong reflections *must* be preserved

Caveat: under what conditions can you do this?