Accuracy in Powder Diffraction
"Are we there yet?"

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Since APD-III & looking at APD IV Program

- New Standards?

  NIST SRM640d Si

  certified a=0.543 123 nm ± 0.000 008 nm

  NIST SRM660b $La^{11}B_6$ (neutron friendly)

  certified a= 0.415 689 nm ± 0.000 008 nm

  NIST SRM676a Al2O3

  certified crystalline content = 99.02% ± 1.11% (mass fraction)

  certified a=0.475 935 5 nm ± 0.000 008 0 nm

  c=1.299 231 nm ± 0.000 015 nm

  Are all these consistent? Yes, all refer to Cu K_{a1} λ= 0.154 059 29 nm

  More from Jim Cline on these – complex stories

  The new PDF from ICDD

- New Instrumentation?

  11BM – synchrotron high resolution multidetector with focusing; more later

  Other developments (Andy Fitch)

  What do you do with long pulse neutron sources? (Dmitri Argyriou)

  Laboratory instruments – (Pam Whitfield)

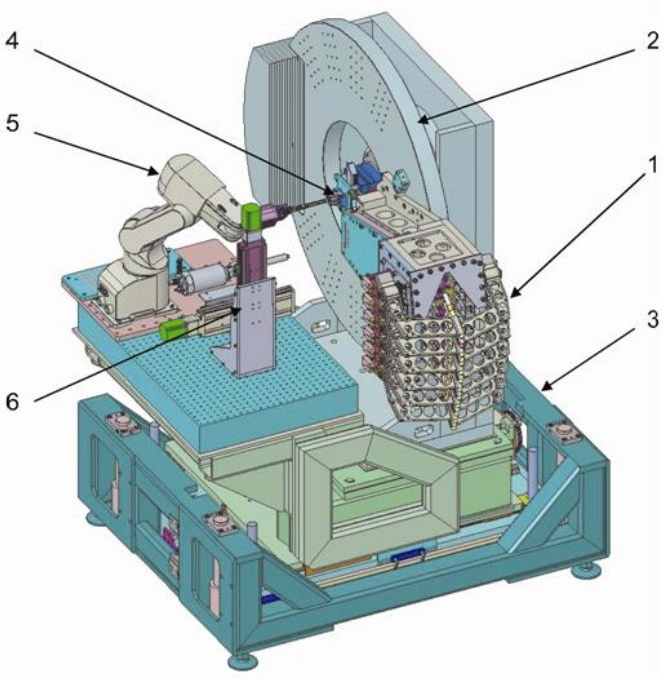
  Detectors & Optics – (Tuesday AM)

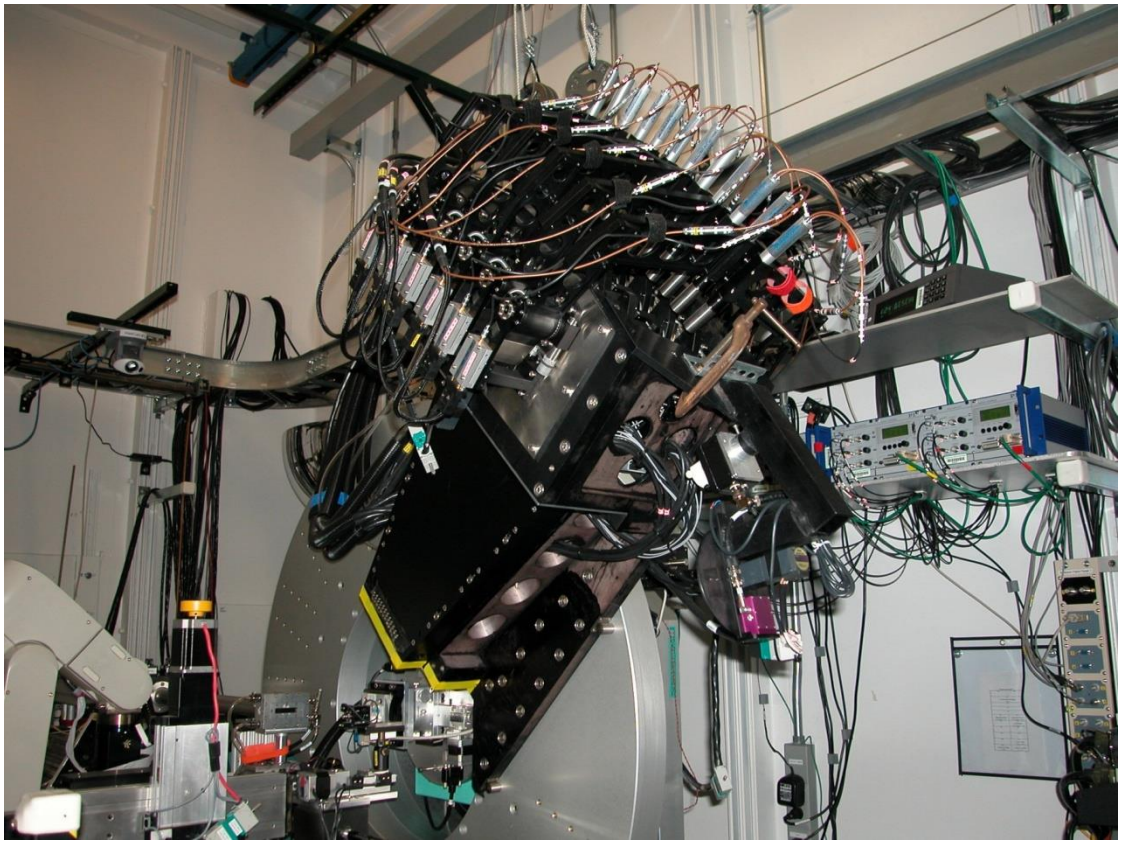
More APD IV Program

- New Software?
  GSAS-II – some surprises & some old sins to be revealed later
  Validation & publication – (Michael Hoyland)
  PDF, MEM, Cluster analysis – (Simon Billinge, Robert Dinnebier, Thomas Degan)
- Old Issues?
  QPA problems (Wednesday)
  Stress/strain line profiles (Thursday)
- New Issues?
  Validation & fraud detection?
- New Experiments?
  Parametric measurements – (John Evans)
  Proteins (Jon Wright) & Pharma materials (MaryJane Tremayne)
  Powder diffraction on Mars! (Dave Bish)

- Now for some stories….

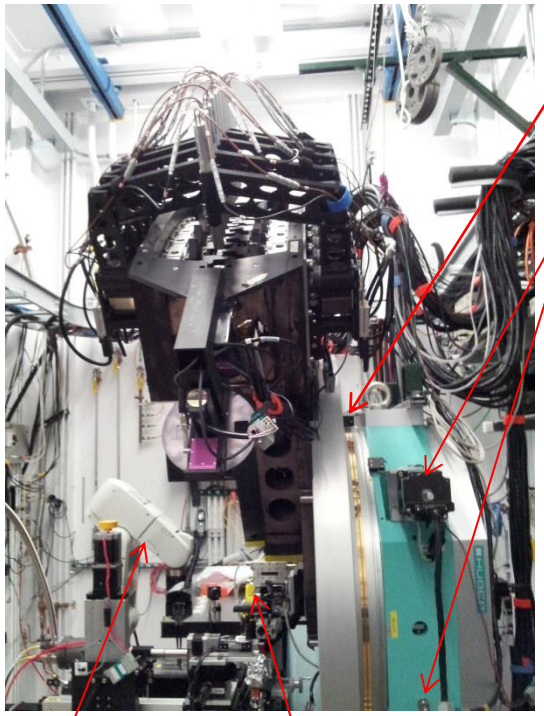
11BM High resolution powder diffractometer at APS





12 Multidetector/analyzers
Each individually tunable

11BM close ups

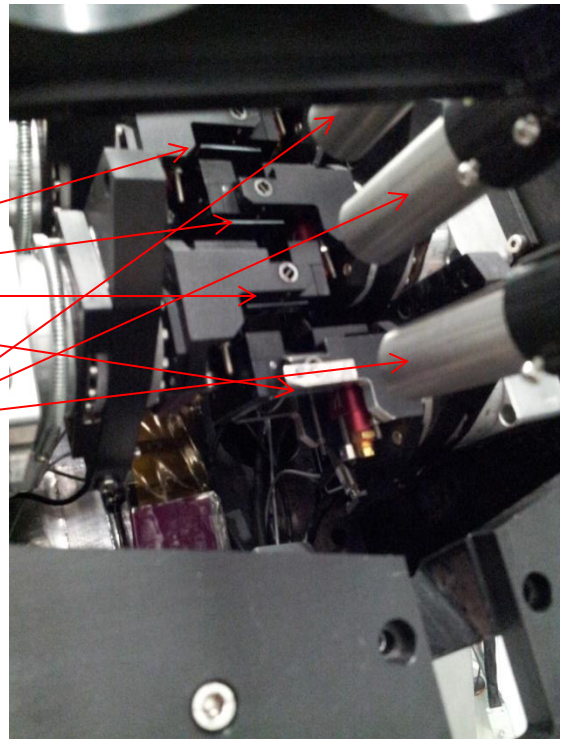


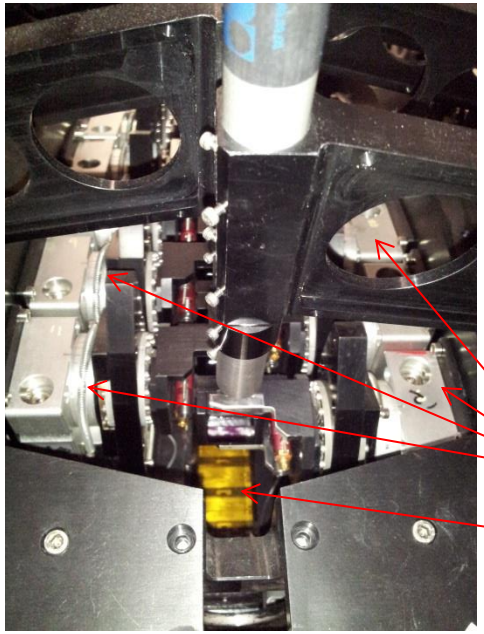
Heidenhain strip & read head

2Θ motor & thumb screw

Si 111 crystals

$LaCl_3$ scintillator detectors



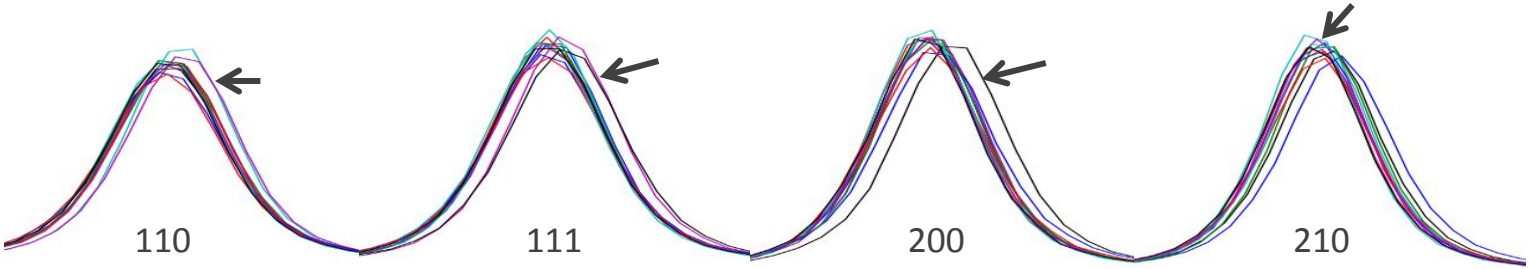


Robot
Sample position

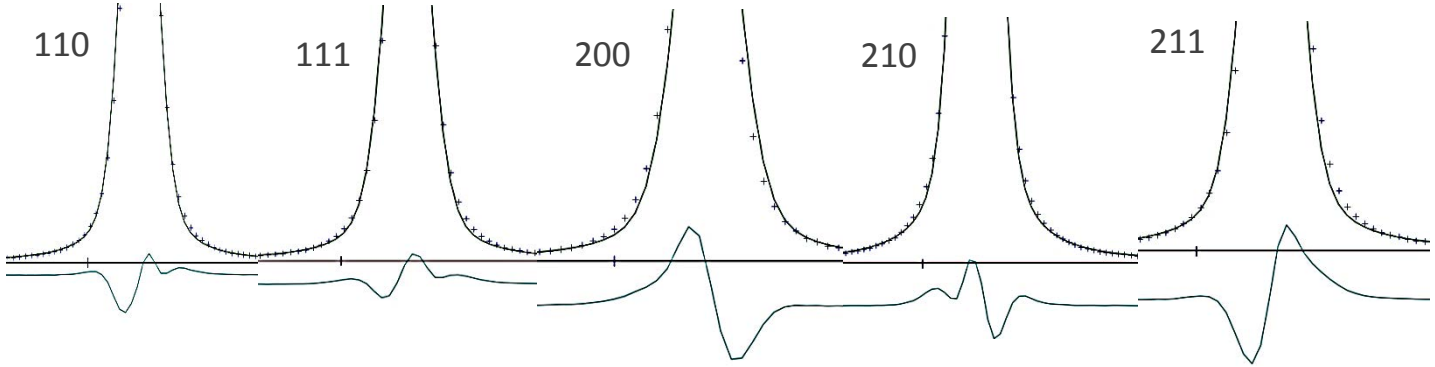
Analyzer Ω drives; left & right
Kapton cover & upstream slits

11BM at APS – high resolution focusing data processing:

- 12 powder patterns; ~2° offset; normal continuous scan data collection
  - Calibration: Si/Al_2O_3 mixture of SRMs
  - 12 pattern Rietveld refinement: Zero, λ, (U, V, W, etc. Al_2O_3 a & c as well)
  - Interpolate to common 2Θ scale & merge LaB_6 data: use λ_{avg}

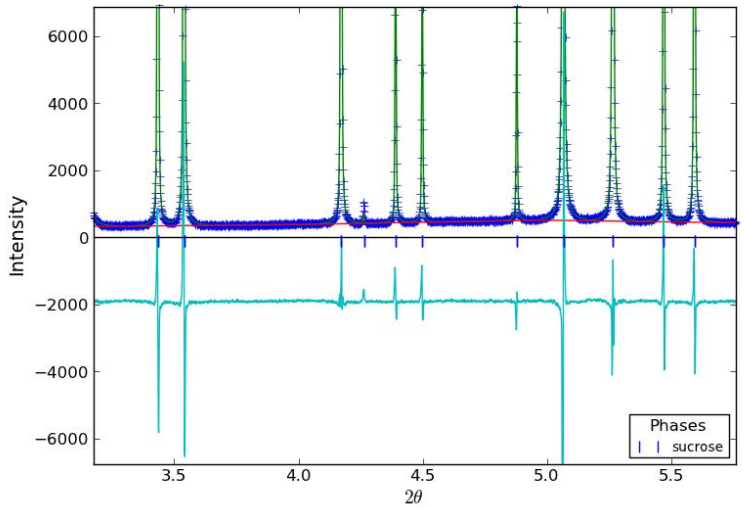


  - Remaining mismatches: different detectors at different angles!
  - Rietveld refinement: residual peak displacements: R_{wp} 9.346%



Sucrose test case – grind under org. solvent can also use 10X powdered sugar as is

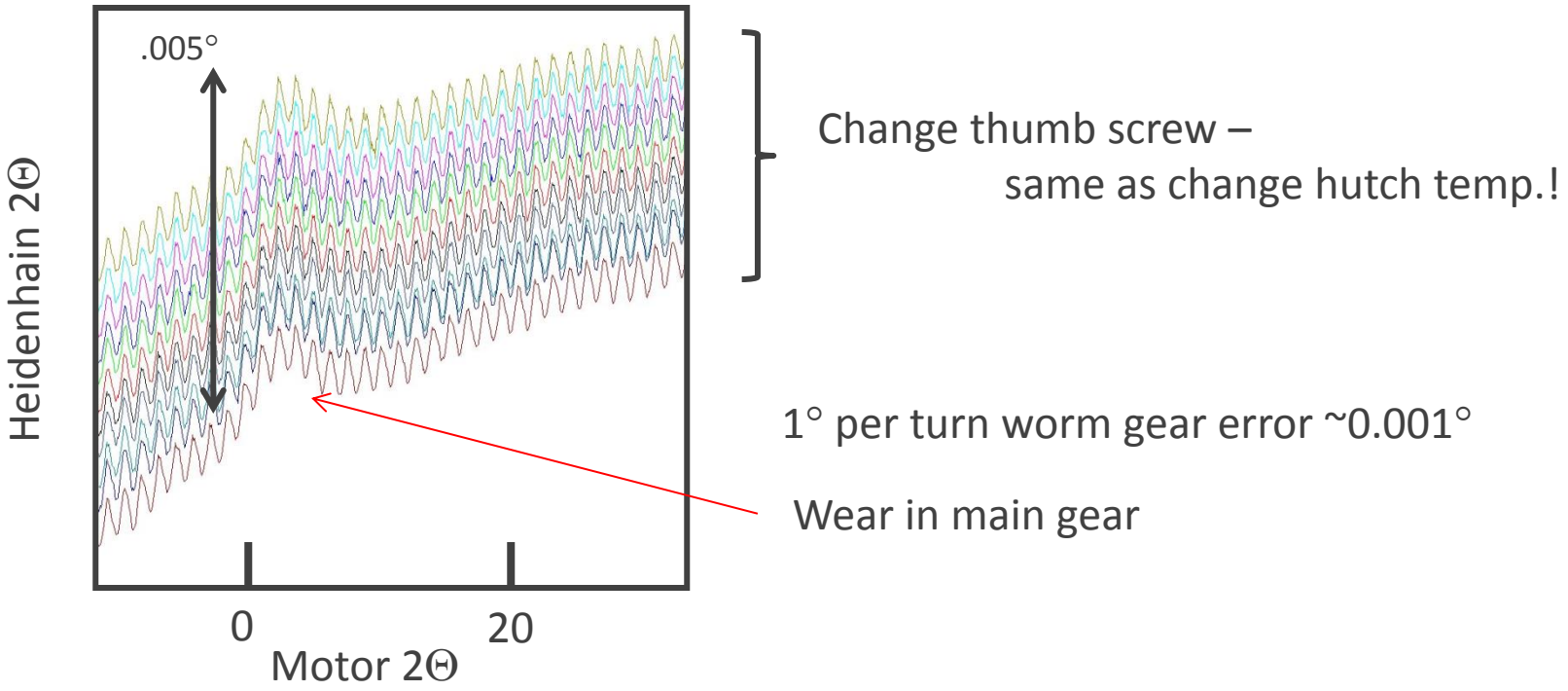
- Rietveld refinement (d_{min} ~1Å) R_{wp} 8.919% for 115 parm/22385 obs peak position mismatches



- Pawley refinement (d_{min} ~1Å) R_{wp} 6.712% same position mismatches
- Charge flipping trials ~50% successful

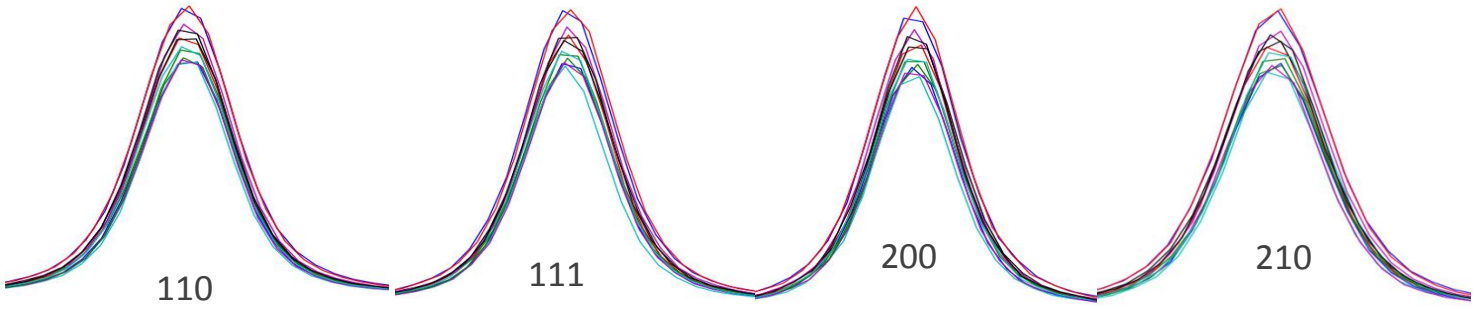
Investigation -

- Use Heidenhain in 0.01° 2Θ step scan; record motor & Heidenhain positions

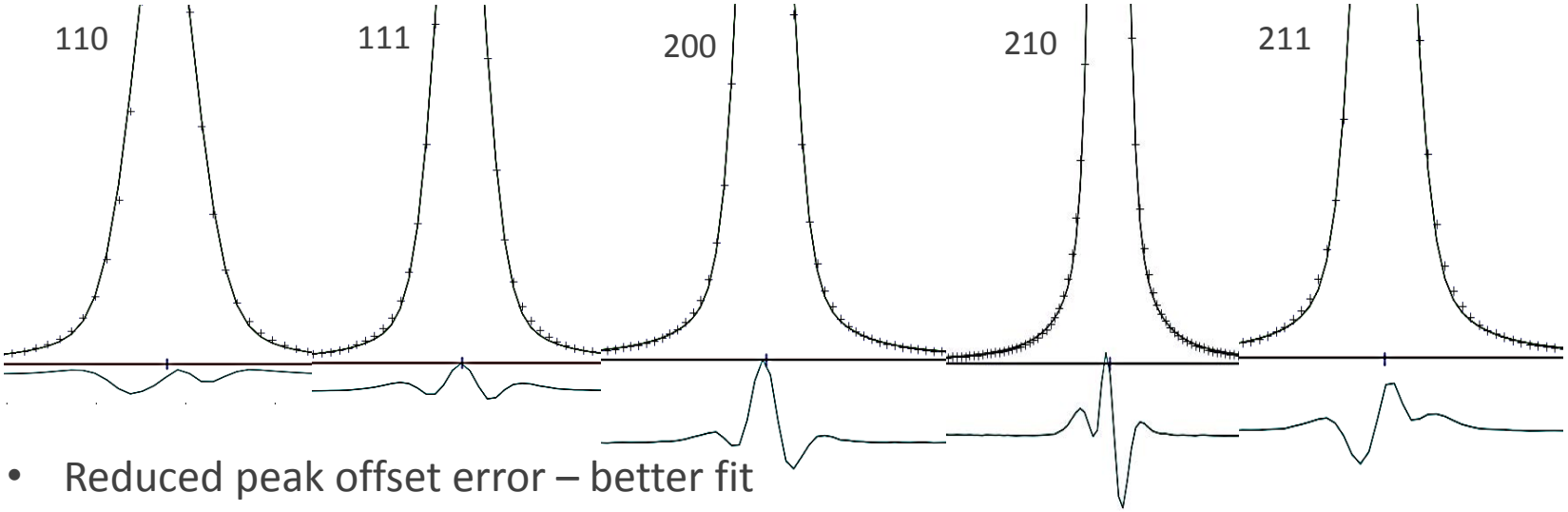


- Solution: Use Heidenhain curve to interpolate 2Θ for each of 12 detectors; then apply 2°+Zero offset, interpolate again from calibration result & then merge
- Calibration data must be corrected before fitting!

New merge result on LaB_6



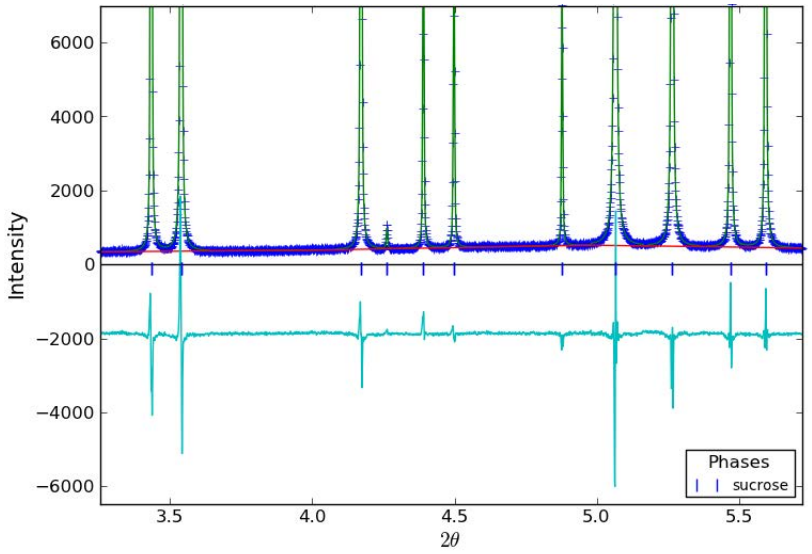
- Much tighter merge – no mismatches
- Rietveld refinement R_{wp} 7.461% (cf. 9.346% w/o correction)



- Reduced peak offset error – better fit

Effect on sucrose data

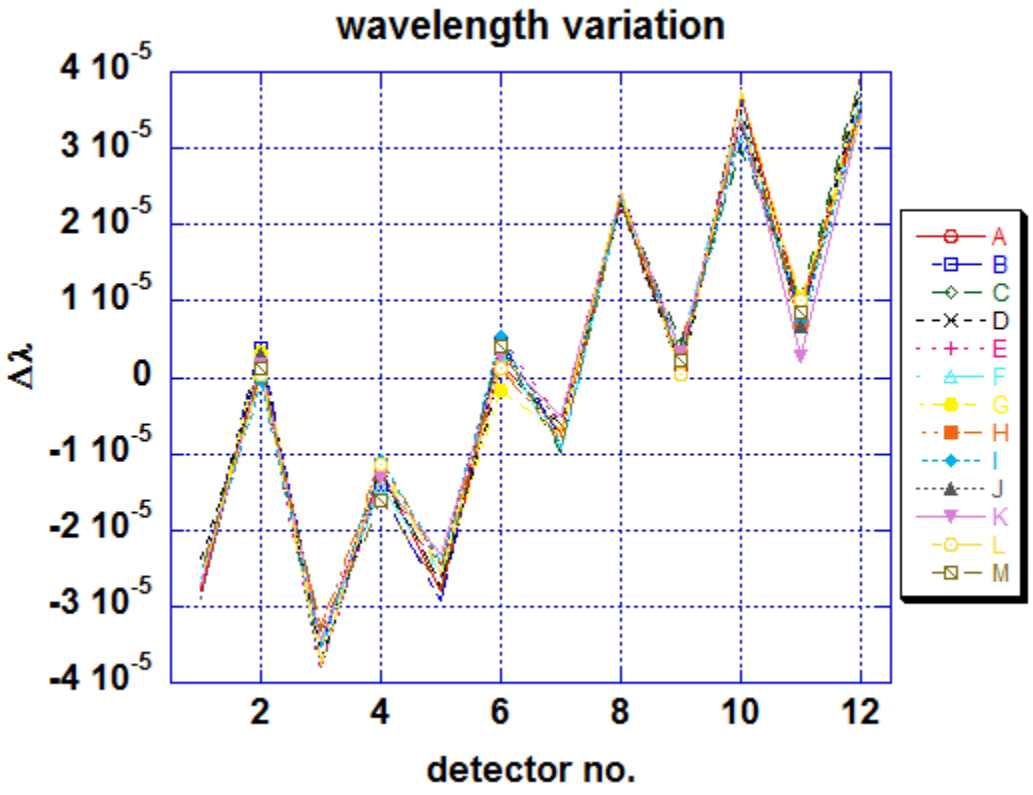
- Rietveld refinement (d_{min} ~1Å) R_{wp} 7.126% (cf ~9%)
  less peak mismatches (but still some)



- Pawley refinement (d_{min} ~1Å) R_{wp} 4.969%
  smaller mismatches, but still there
- Charge flipping trials no better (actually worse, go figure!)

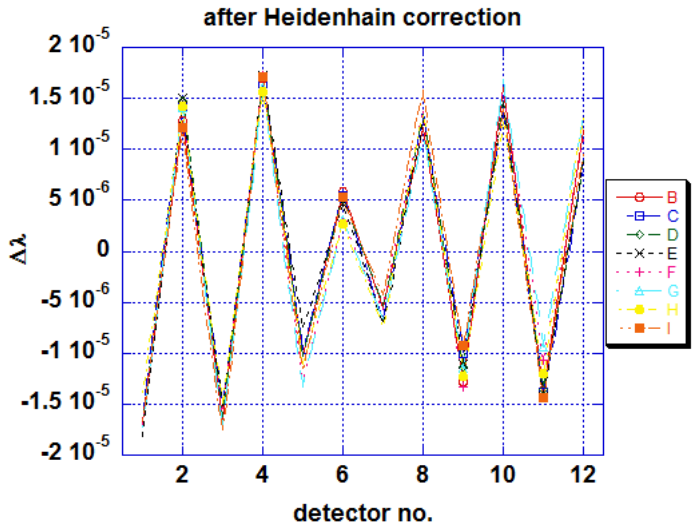
Remaining 11BM mystery

- Calibration: Rietveld refine λ, Z for each detector from Si/Al_2O_3 scan.
- Result – λ depends on detector (no matter what we do!)
- Δλ – few eV effect at 30keV



Things tried:

- Shift beam up/down
- Tuning analyzer xtals
  last tilt L/R
- Not temperature
  Δλ 10x too big
- 2Θ corr. did have an effect!

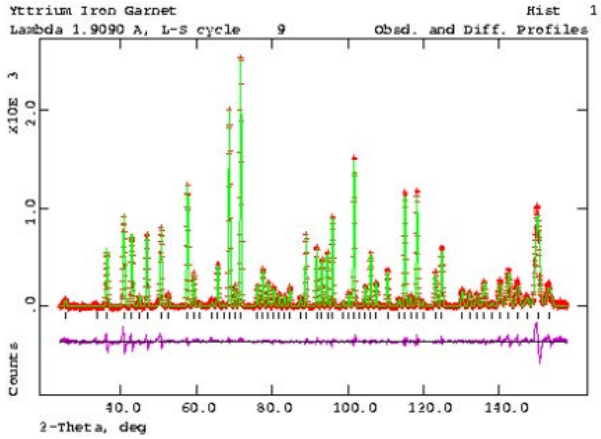


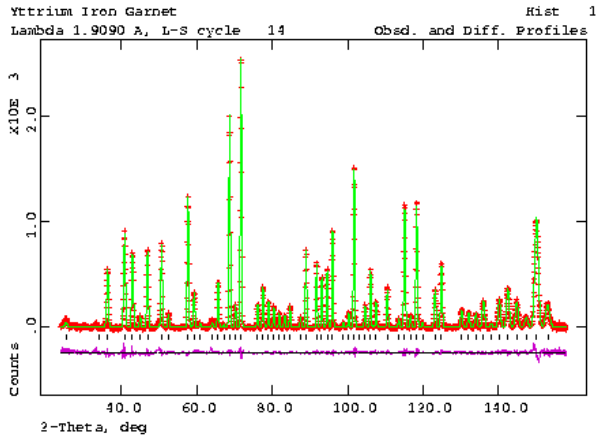
- Can't ignore! Else poor merge from λ dispersion!

Software: Garnet exercise in GSAS-II

After refine of atom x, Uiso & frac

R_{wp} ~7%





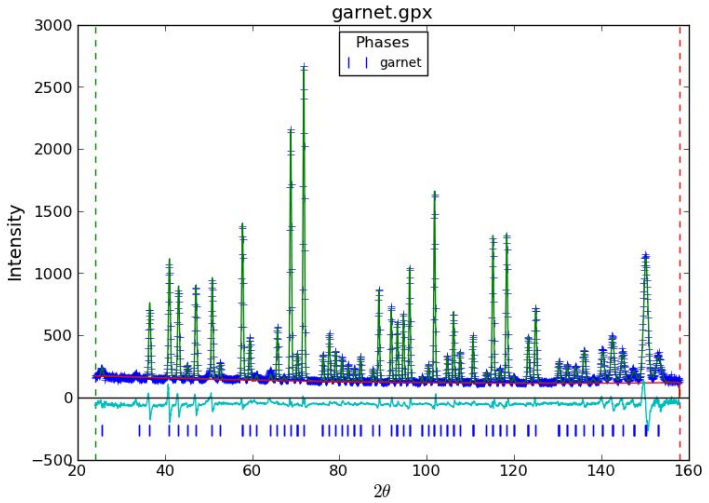
GSAS-II same result

The old GSAS garnet exercise – last step: refine U, V, W & asym to get R_{wp} from ~7% to 5% with profile fxn #2 – C.J. Howard Simpson's rule integration

GSAS-II peak shape function:

Finger, Cox & Jephcoat/van Laar & Yelon

No effect from refining SH/L – the asymmetry coeff.!



So what is it?

D1a at ILL; circa 1980

Does detector bank pivot about sample center?

A squashed germanium [551] monochromator is

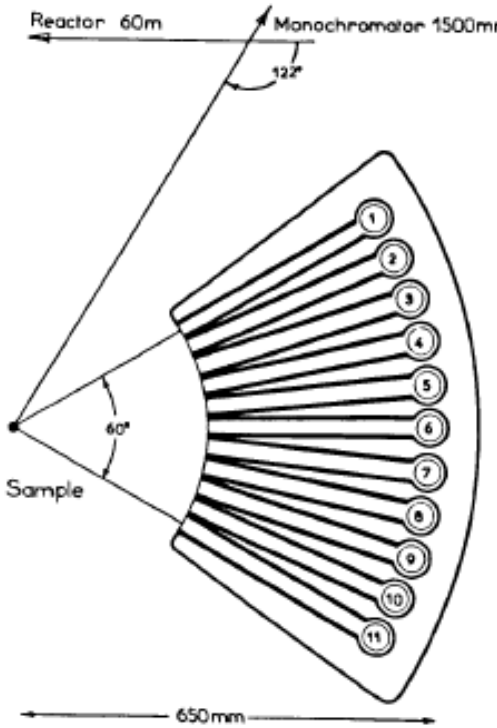


Fig. 1. Schematic diagram of the D1A multicollimator diffractometer. The large monochromator take-off angle means that the diffraction pattern is focussed for the parallel geometry shown ($2\theta = 122°$). The counter bank can be swept through 0° to $2\theta = 160°$ for the highest angle counter, usually in steps of 0.05°.

GSAS-II “sample” displacement parameters

Δx, Δy displacement; ⊥ & || to beam all in scattering plane

$$\Delta(2\Theta) = \frac{0.09}{\pi R}[\Delta x \cos 2\Theta + \Delta y \ \sin 2\Theta]$$ R in mm → Δx, Δy in μm

D1a; R = 650mm; GSAS-II refine Δx, Δy

1.75mm & -2.24mm; R_{wp} 4.87%

(better than old GSAS!)

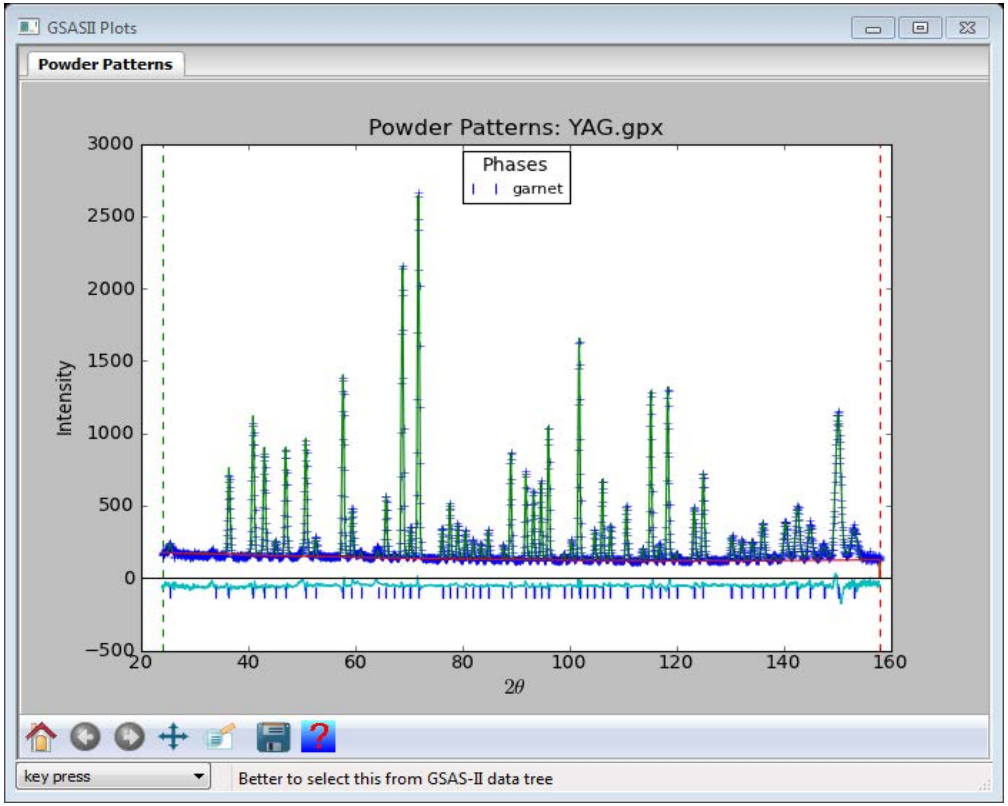
Within reason – detector bank twisted a bit?

Sample displaced in cryostat?

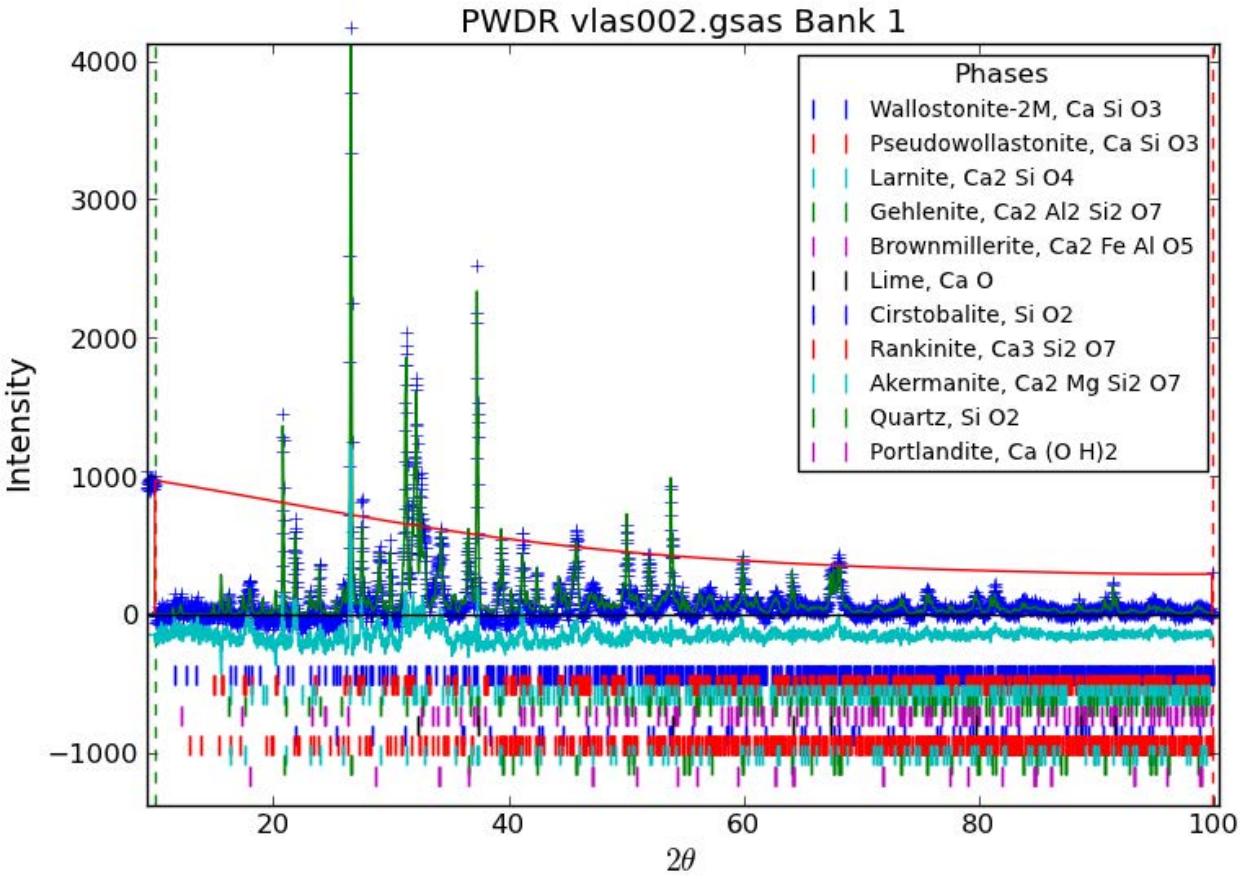
Sample absorption effect?

Not asymmetry!

NB: Also effective in v. high resolution synchrotron Debye-Scherrer patterns (e.g. 11BM) Δx ~10μm for R~1000mm



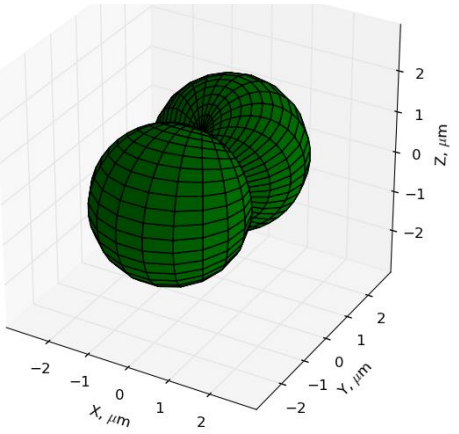
GSAS-II & QPA: The 9 phase limit is gone!



11 phase quantitative phase determination in GSAS-II (thx: Jim Kaduk)

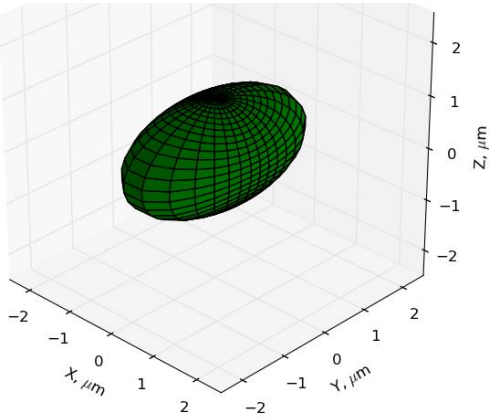
Software – An old error comes to light

- Aim of new GSAS-II development – graphical display of all results
- Anisotropic size & µstrain
- Old GSAS equation:
  e.g. $X + X_e \cos\phi$



- What!

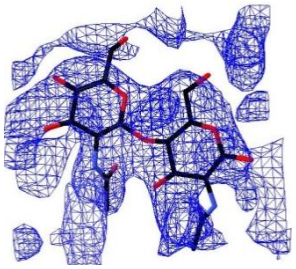
- New GSAS-II equation:
  $S = {S_i S_a} / {\sqrt{(S_i \cos\phi)^2 + (S_a \sin\phi)^2}}$
  (crystallite size or µstrain)

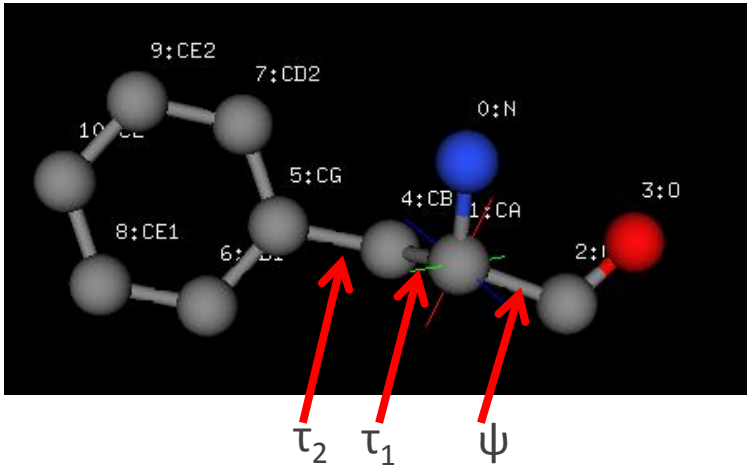


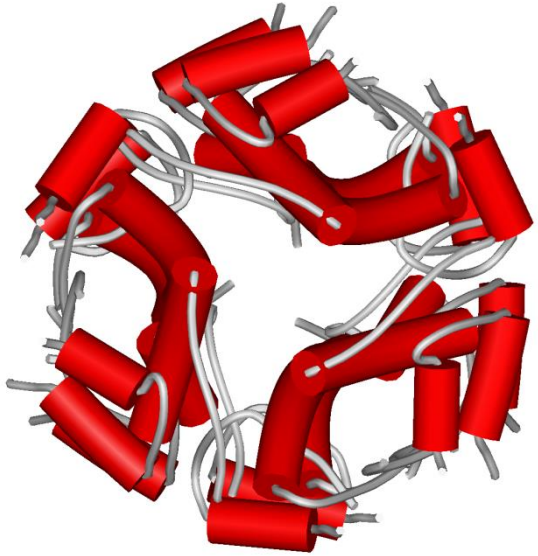
- A 25yr old error!

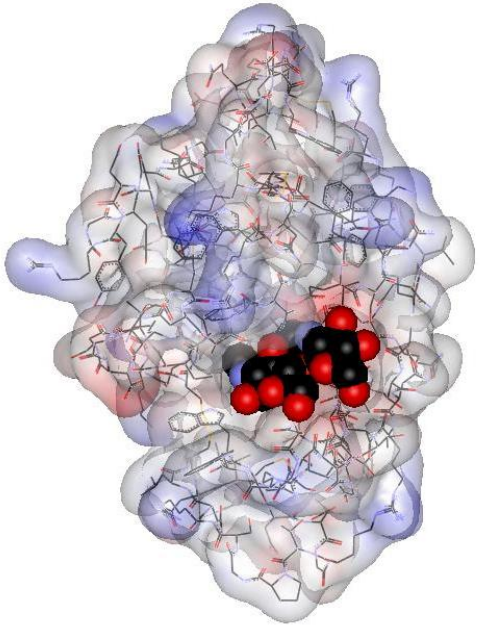
Protein polycrystallography

- Started ~APD III
- 1st Refined structure – metmyoglobin
- 1st Solved structure - Zn insulin from grinding single xtals; 102 residues
  R3 unit cell a=81.276Å,c=73.037Å – double c-axis: >1600 atoms
  Good backbone but poor side chains
- 1st Bound molecules – NAG, etc. on lysozyme from maps
- Multidata refinements
- Rigid bodies – 6 parm & torsions vs 3X no.atoms









- Computing – 1hr/cycle! →5min or less (soon to be in GSAS-II)

Conclusion

- So: “Are we there Yet?”
- New instrumentation – find new APD issues & fix them
- New software – fix old errors & find new opportunities
- Thanks!