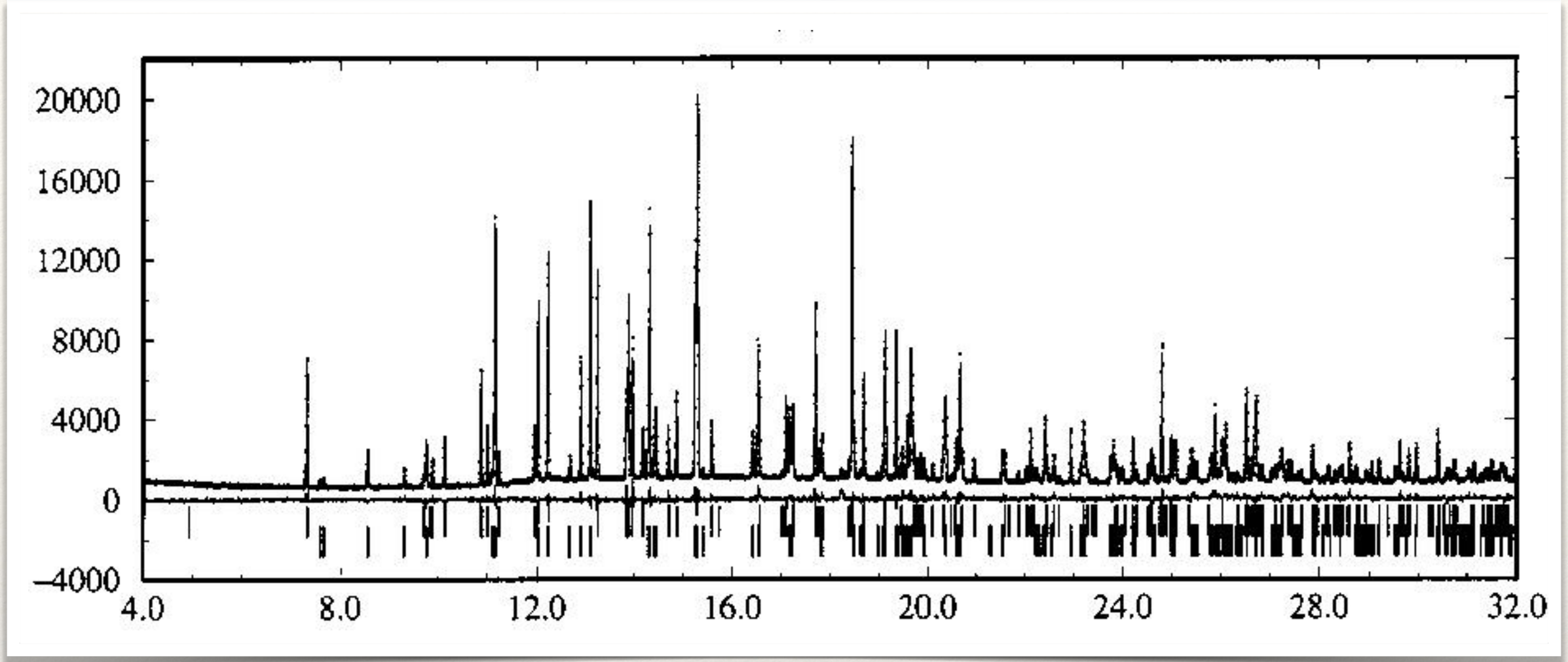

FPSchool

Indexing powder diffraction patterns

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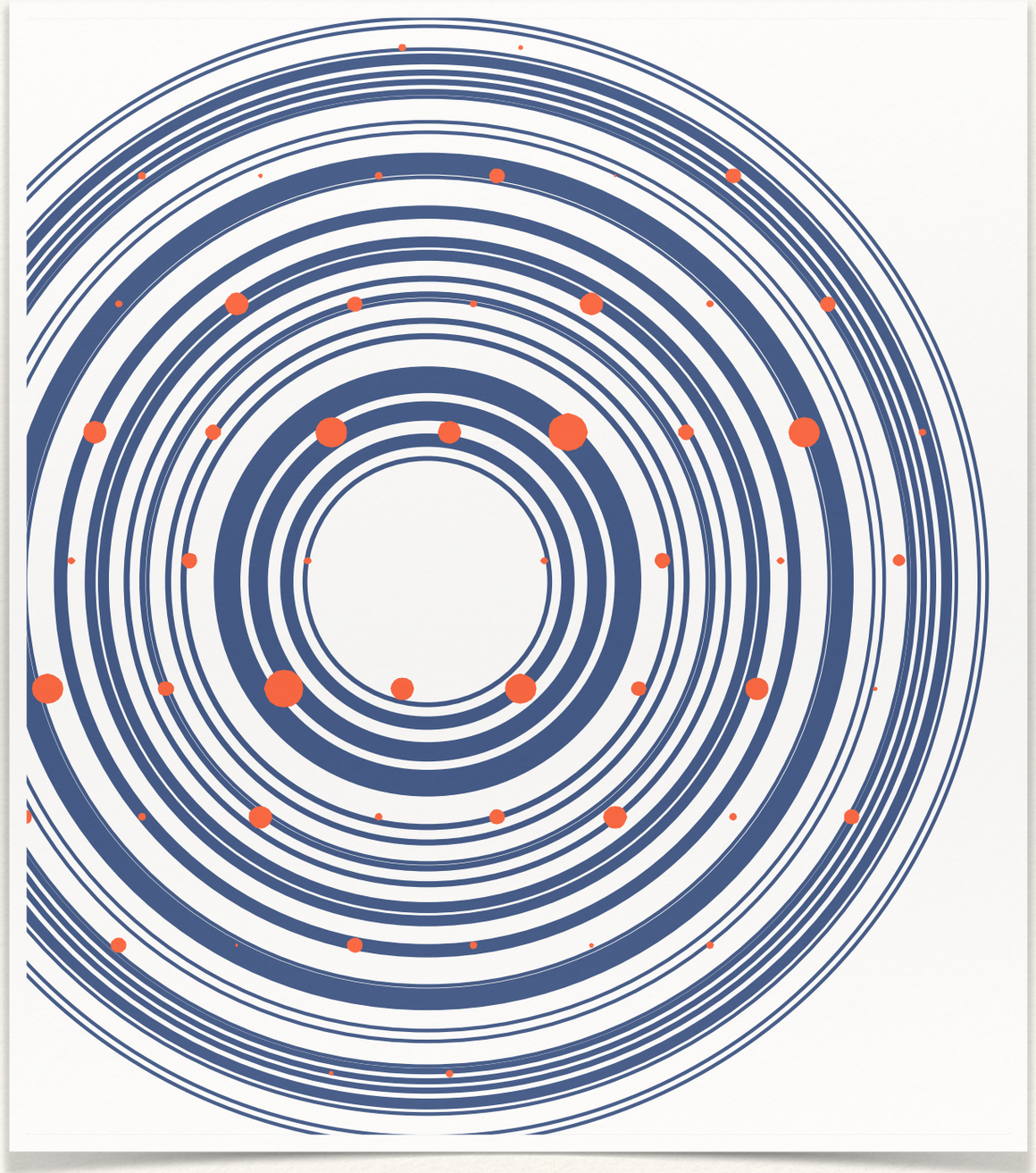
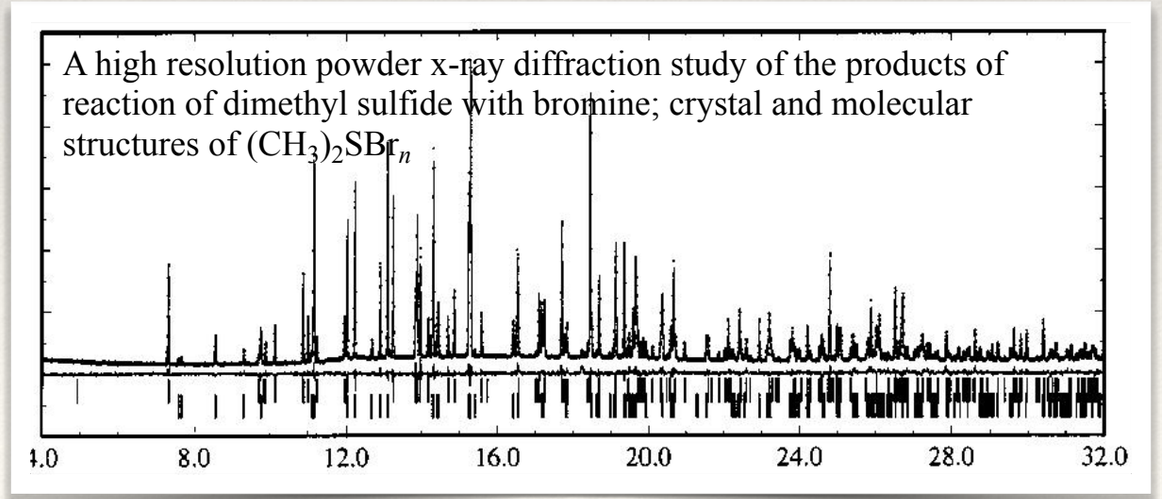
The indexing problem

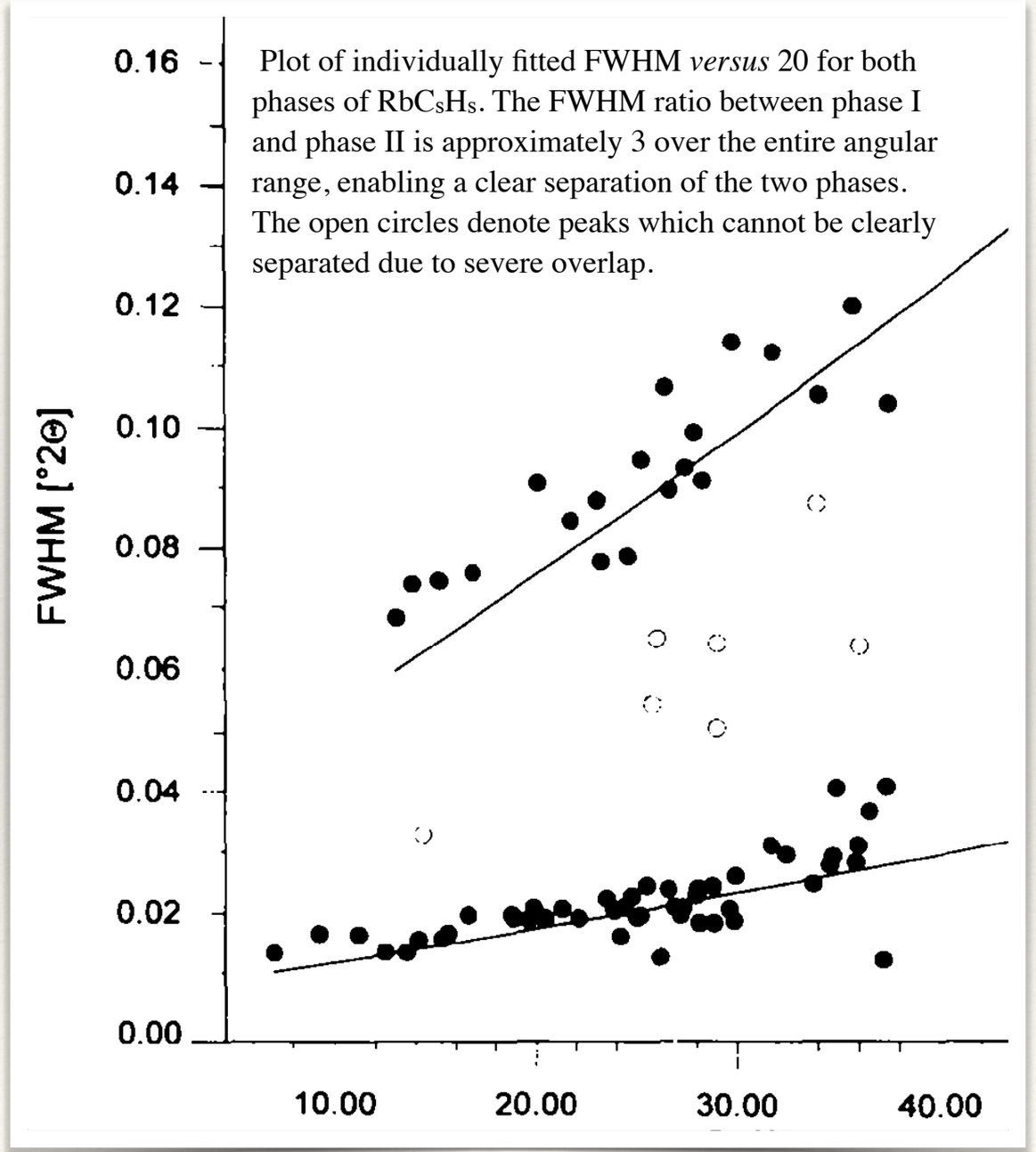
- Single Crystal:
  - Unit cell and symmetry unambiguous
  - Each reflection: correct Miller indices *hkl*
  - Diffracted intensity (structure amplitude $|F|_{hkl}$) accurate
- Powder:
  - **nothing** of all this known …
  - Informations in a powder pattern:
    - Peak positions as function of unit cell dimensions
    - Peak shapes
    - Integrated intensities



1. Good sample – preferably single-phase

- Indexing of multi-phase powder patterns is ***not*** trivial:
  - Dinnebier et al., *Acta Cryst.* **B53** (1997) 153-158.
  - Vaughan et al., *J. Chem. Soc., Dalton Trans.* (1999) 79–84.





2. Choose the best technique

1. Good sample — preferably single-phase
2. Best quality powder pattern
   - Best technique: sorry to say, but HiRes XRD helps
   - Trickbox: differential thermal expansion
   - Well-known zero-shift ($2\Theta_0$)
     - more serious than statistical error of same magnitude
     - $\sigma(2\Theta) < 0.02^{o}$

Conventional lab. x-rays	*High resolution lab. x-rays*	*Synchrotron x-rays*	*Low-resolution neutrons*	*High resolution neutrons*
fair	√	√	*poor*	√

3. ≥ 20 accurate low angle peak positions

1. Good sample — preferably single-phase
2. Best quality powder pattern
   - Best technique: High Resolution XRD
   - Well-known zero-shift ($2\Theta_0$)
3. Determine at least 20 accurate low-angle peak positions
   - Synchrotron XRD w/ parallel geometry → high resolution monochromators
   - Include weak lines

- Deduce likely space groups from peaks present and those systematically absent

Indexing in reciprocal space

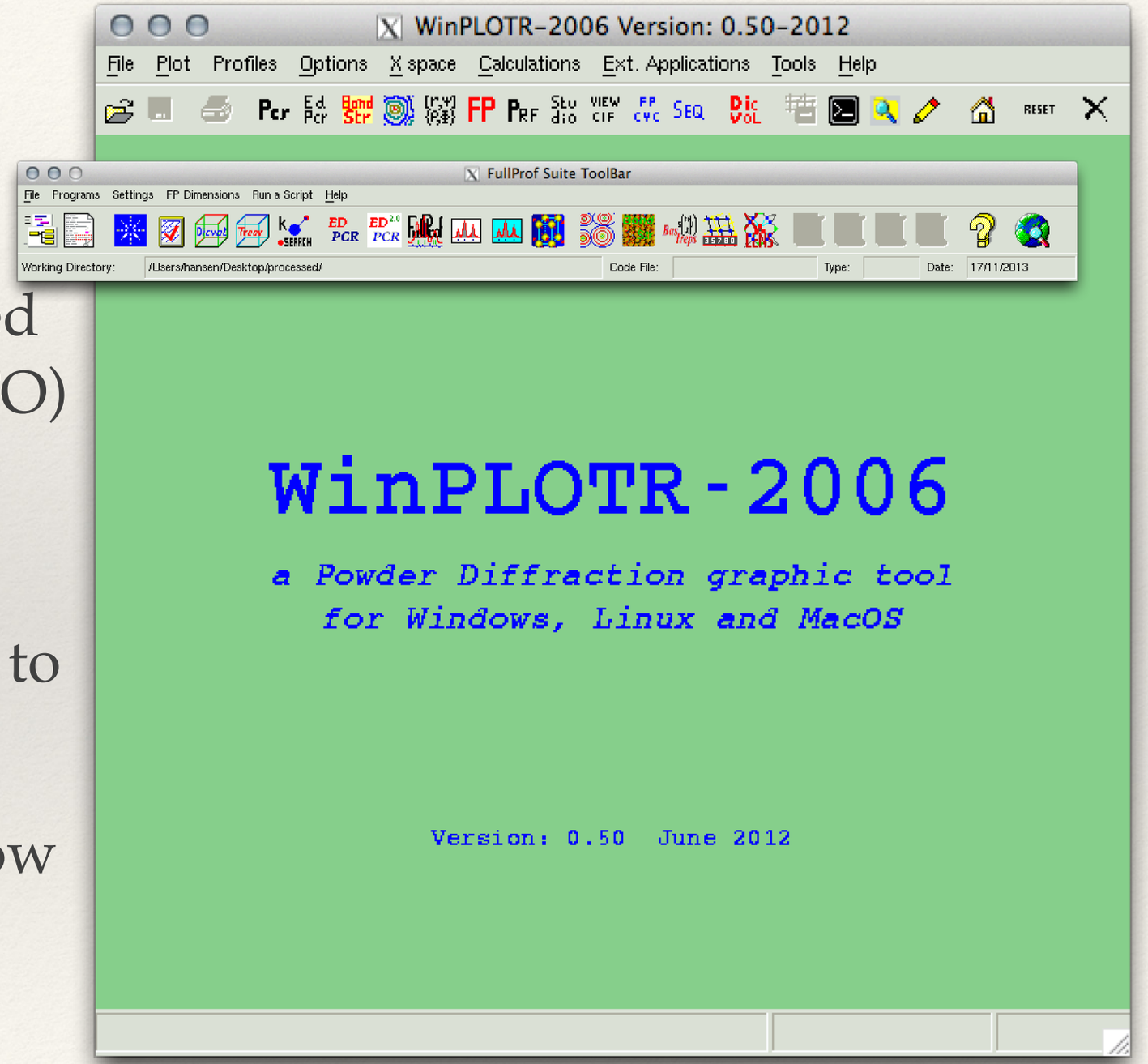
- Bragg's law: $n\lambda = 2d \sin\theta \Rightarrow 1/d^2 = (2\sin\theta/\lambda)^2$
- d-spacing: $\mathbf{d} = h\mathbf{a} + k\mathbf{b} + l\mathbf{c} \Rightarrow$
  - $1/d^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + kl \cdot 2b^*c^* \cdot \cos\alpha^* + hl \cdot 2b^*c^* \cdot \cos\beta^* + hk \cdot 2b^*c^* \cdot \cos\gamma^*$
  - $Q(hkl) = h^2A + k^2B + l^2C + klD + hlE + hlF$ with $Q = 1/d^2$
  - Goal: Finding the six constants A … F …

Classic indexing software

- ITO
  - J.W. Visser, *J. Appl. Cryst.* **2** (1969) 89.
  - Good for unit cells of compounds in low symmetry
- TREOR
  - P.E. Werner, *Z. Krist.* **120** (1964) 375.
  - Trial- and error method, seperately for cubic, hexagonal, tetragonal, orthorhombic, monoclinic and triclinic systems
- DICVOL
  - D. Louër, *J. Appl. Cryst.* **18** (1972) 271. A. Boultif, D. Louër, *J. Appl. Cryst.* **37** (2004) 724.
  - Successive dichotomy method, originally not for monoclinic and triclinic lattices.

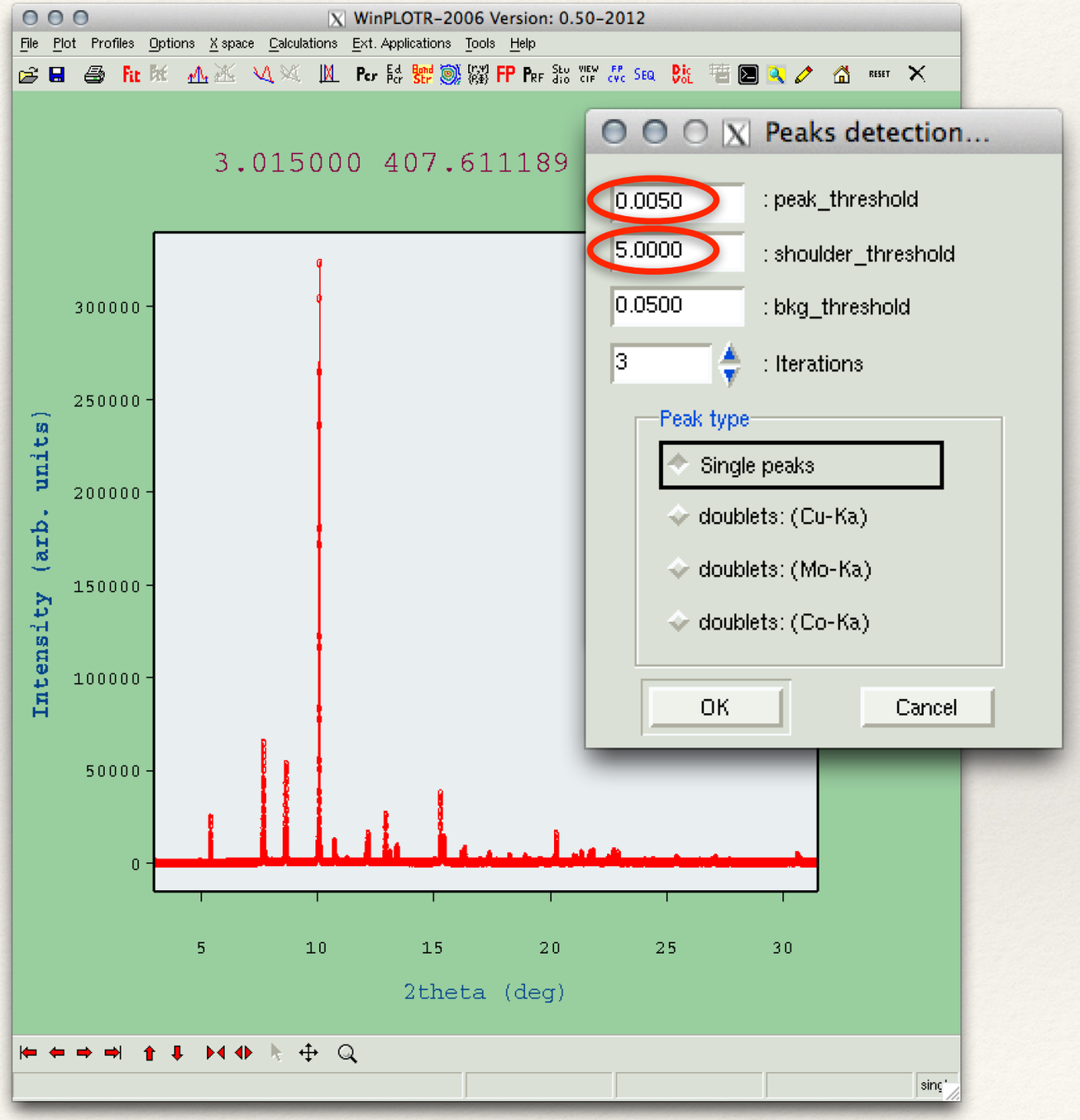
Implementation in FullProf suite

- WinPlotR (2006) allows convenient peak extraction
- These peaks can be redirected to DICVOL or TREOR (or ITO) The result of indexing is redirected into an pcr file
- This file permits a Le Bail fit to check the solution
- The extracted intensities allow for a space group determination



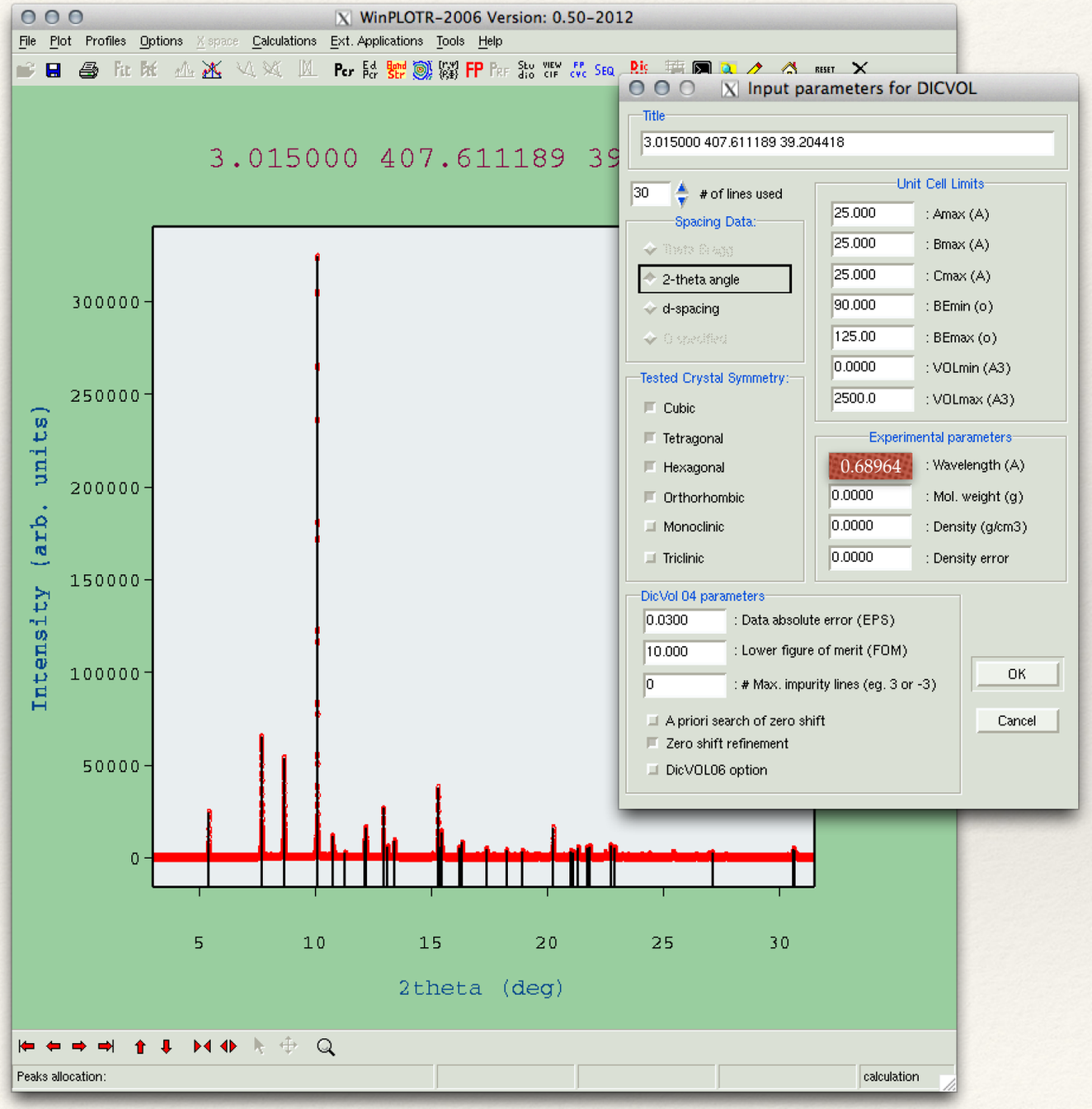
WinPlotR-2006: Peak search

- Calculations → Peak detection → Enable
- Calculations → Peak detection → Auto detection
- Calculations → Peak detection → Insert / Delete peak



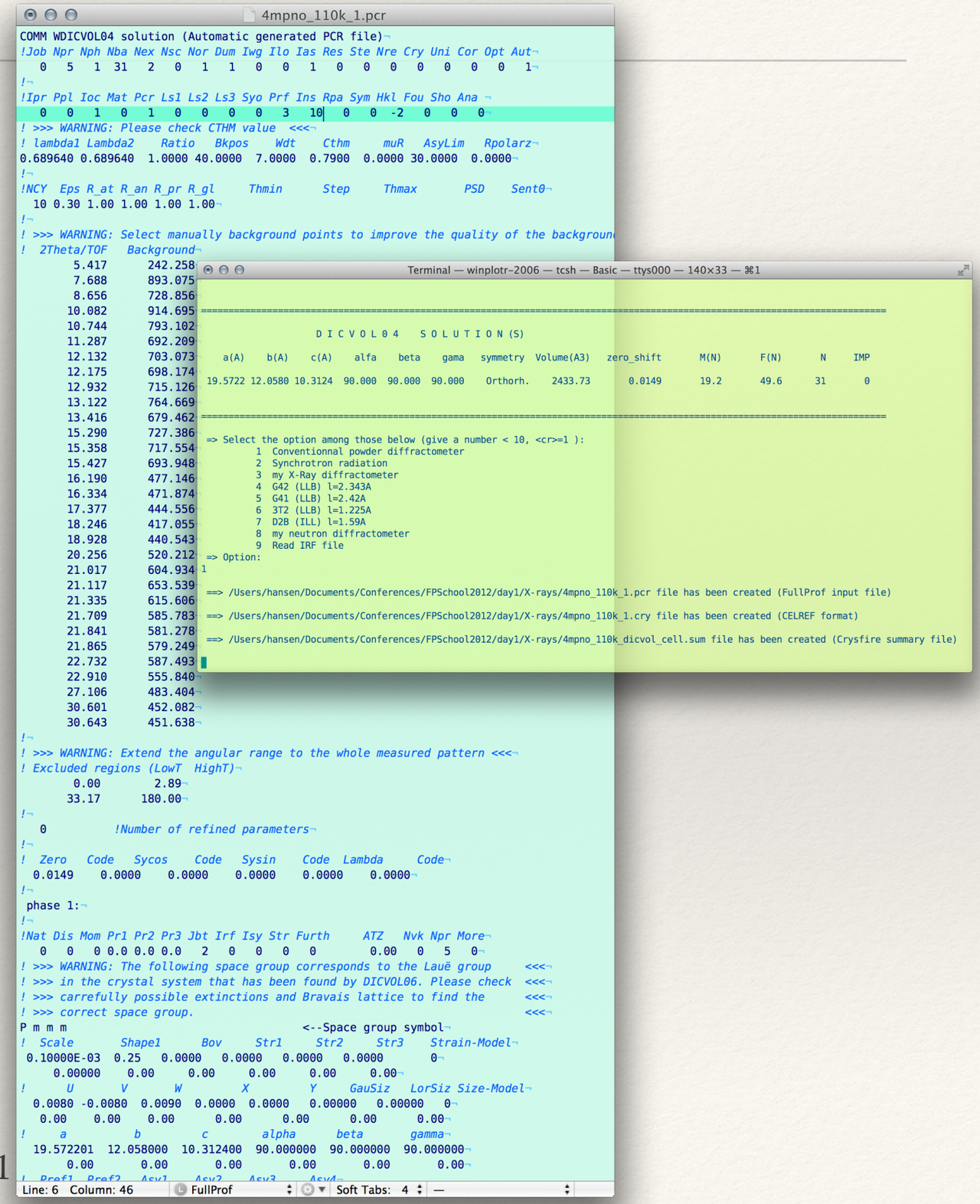
WinPlotR-2006: Save peaks

- Calculations → Save peaks→ Dicvol Format
  - Change options, give wavelength
- Run Dicvol …



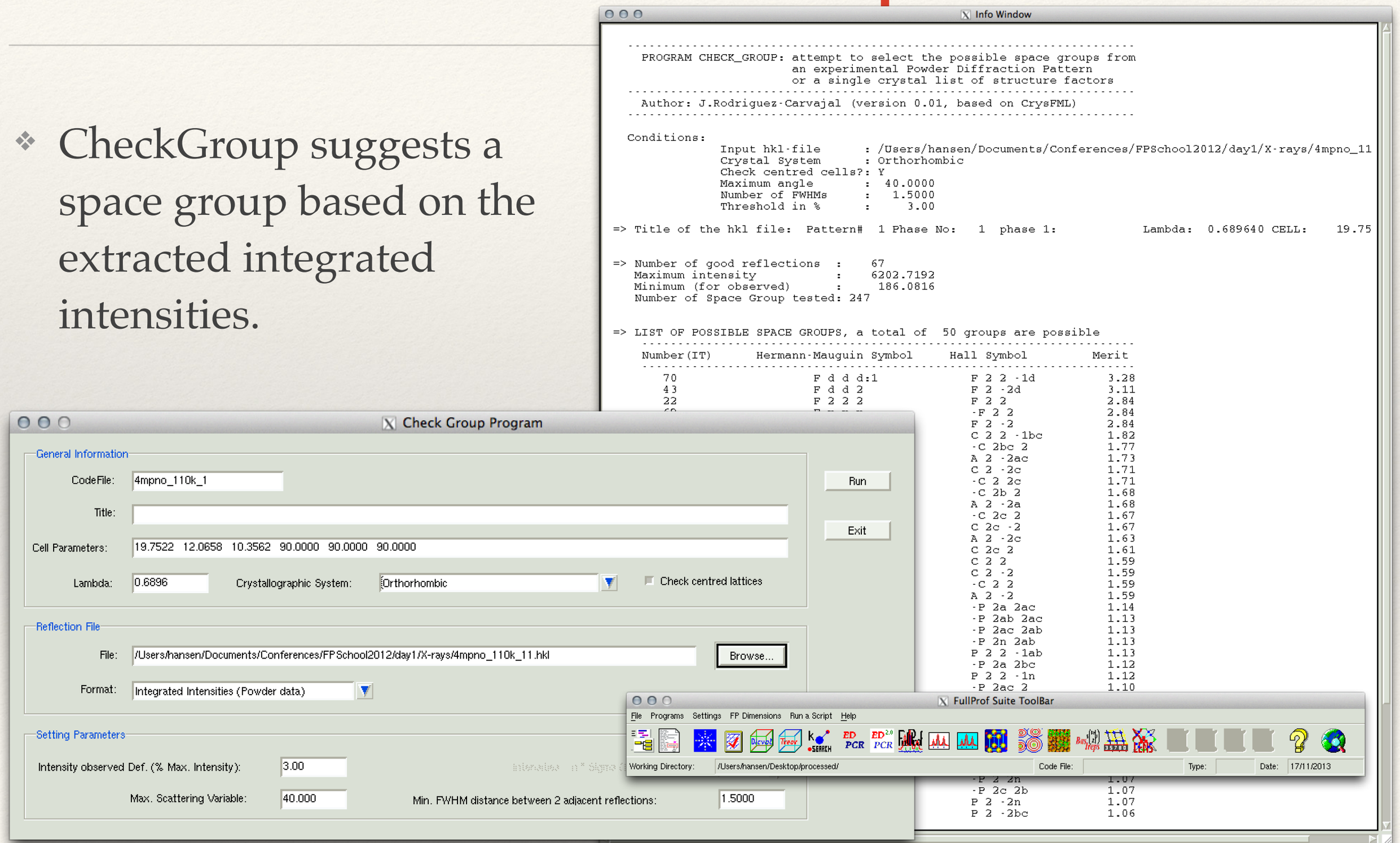
Le Bail fit with DICVOL solution

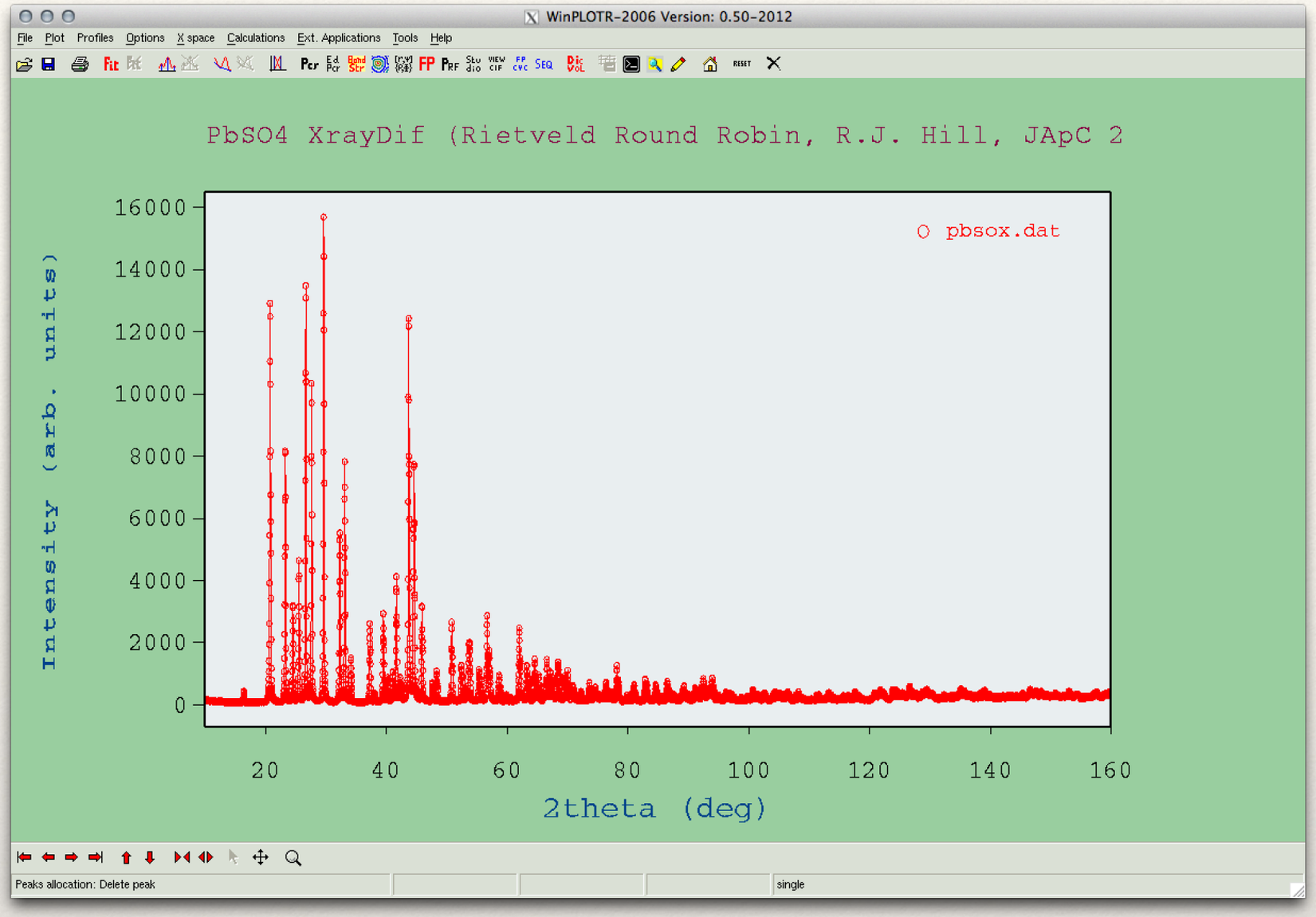
- The PCR file is automatically generated.
  - Minor editing: wavelength, Instrument format, peak profile
- Running FullProf with it will do a Le Bail fit (further refinements on peak-shape parameters, zero shift and lattice parameters are possible)
  - U,V,W,X,Y
  - zero-shift, lattice constants

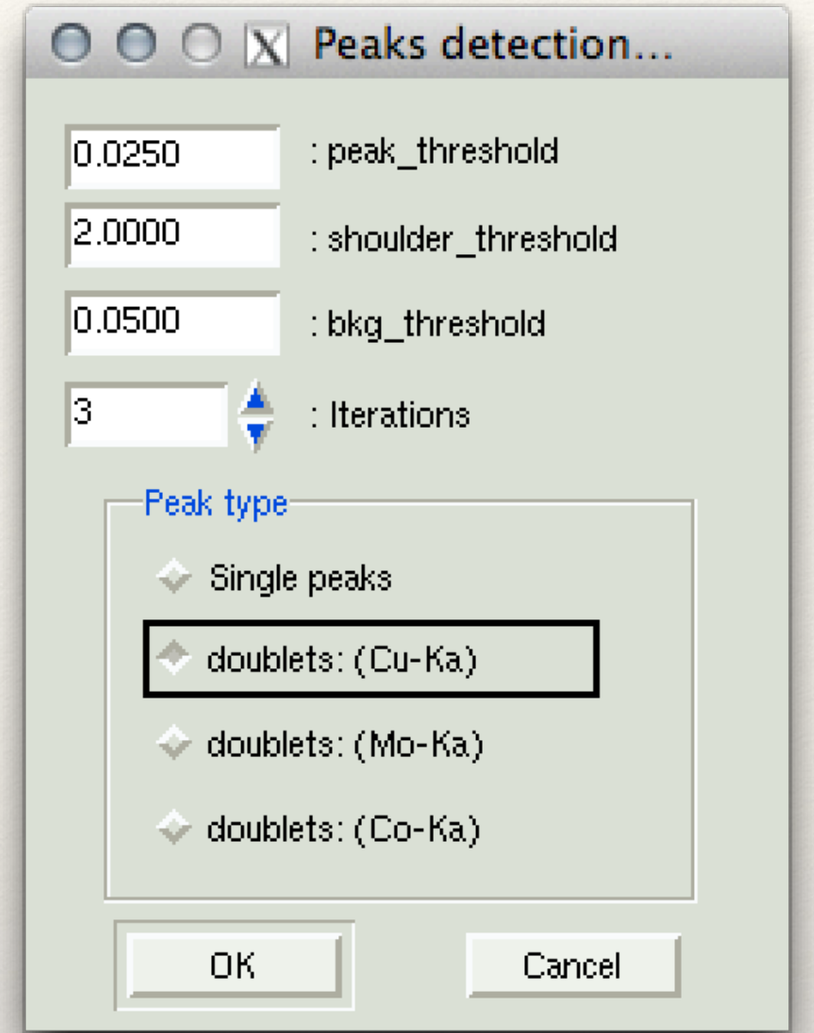


CheckGroup

- CheckGroup suggests a space group based on the extracted integrated intensities.



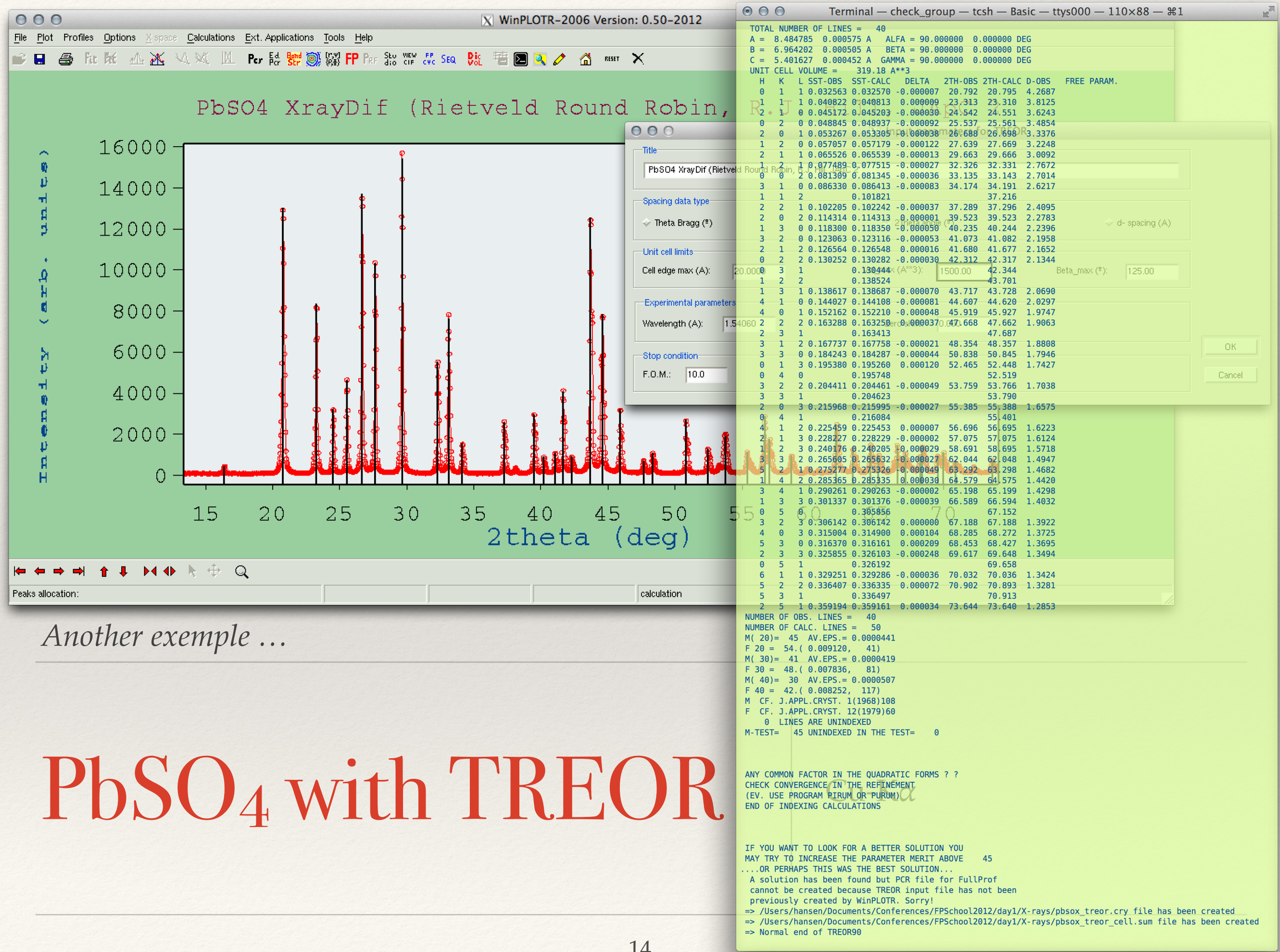




Another exemple …

$PbSO_4$ with TREOR

Cu-Kα



Another exemple …

$PbSO_4$ with TREOR