Skoltech

LOMONOSOV MOSCOW STATE UNIVERSITY

Elettra Sincrotrone Trieste

RSF Russian Science Foundation

Crystallography and Crystal Chemistry
VIII International School-Conference of Young Scientists 2023

Software and approaches in structural refinement for battery materials

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PhD in **Chemistry**

Center for **Energy Science** and **Technology**

Skoltech, Moscow, Russian Federation

November 10th, 2023

A quick look back

J. Appl. Cryst. (1969). **2**, 65

A Profile Refinement Method for Nuclear and Magnetic Structures

BY H. M. RIETVELD

Reactor Centrum Nederland, Petten (N.H.), The Netherlands

(*Received* 29 *November* 1968)

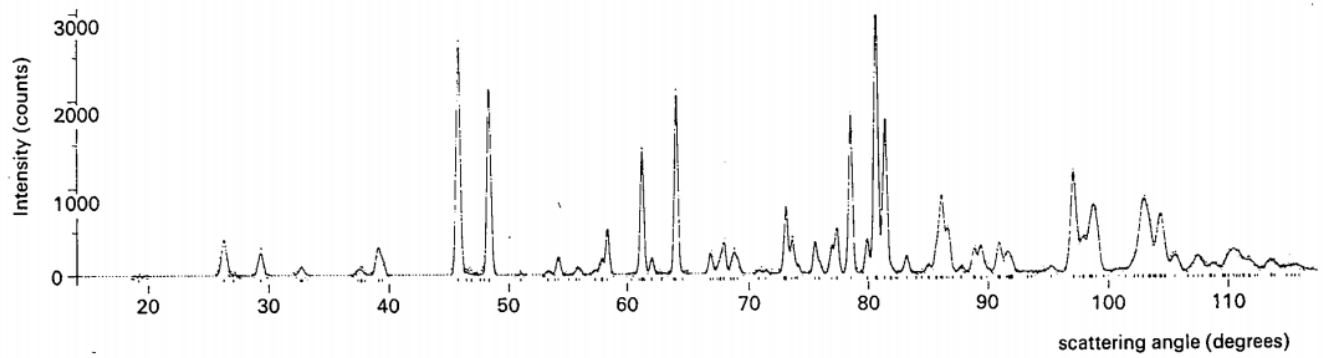


Fig. 5. Neutron powder diffraction diagram of Sr_2UO_5 measured at $\lambda = 2{\cdot}565$ Å; —— calculated profile, ... measured profile.

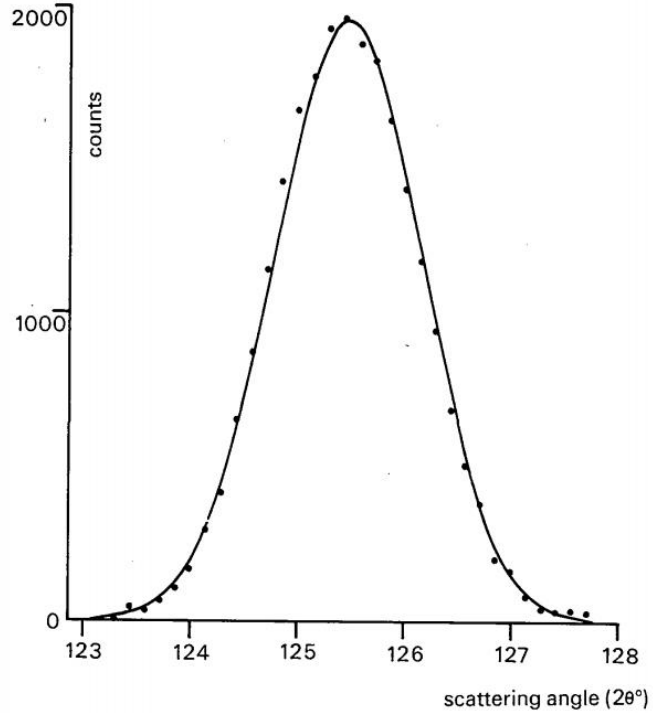


Fig. 1. Comparison of a measured diffraction peak, ..., with a calculated Gaussian peak profile, ——.

A quick look back

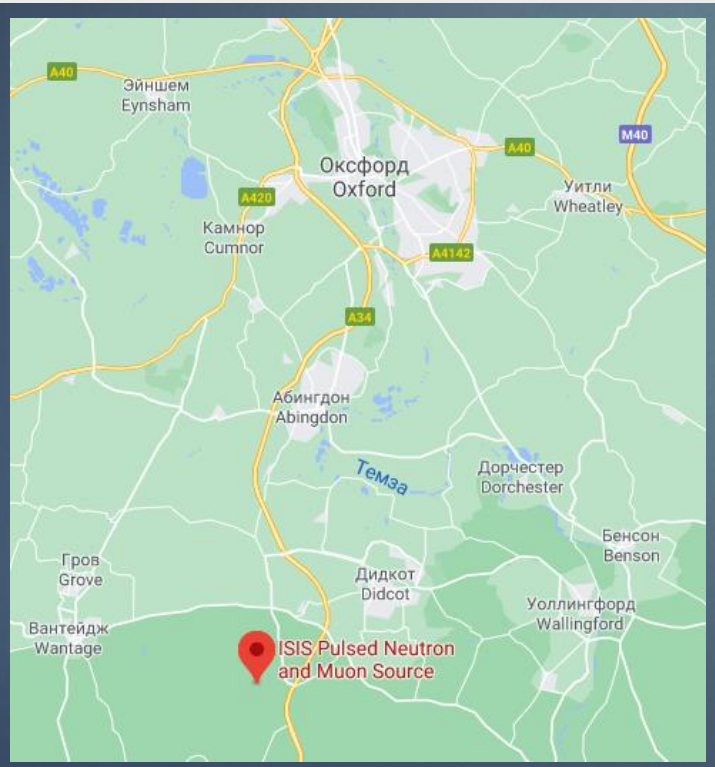
Electrologica X-8

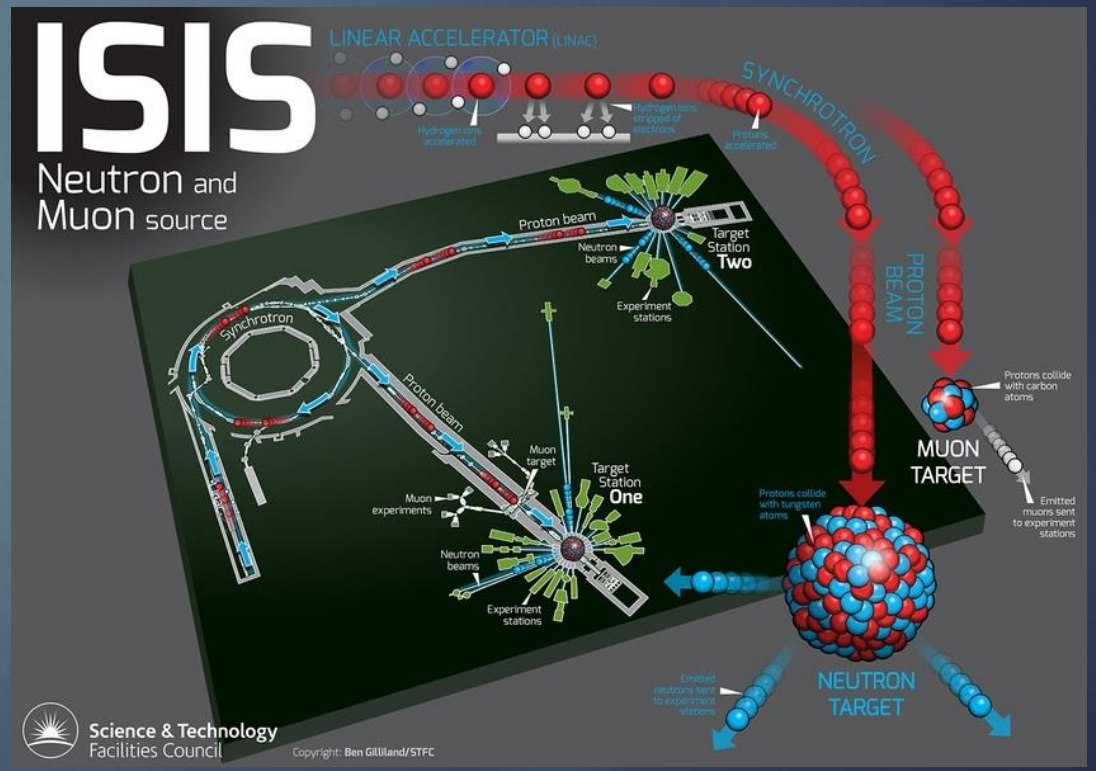
A quick look back

Corpus ID: 60486565

The Cambridge Crystallography Subroutine Library. Extended Mark 2 users manual

P. Brown, J. C. Matthewman · Published 1981 · Computer Science

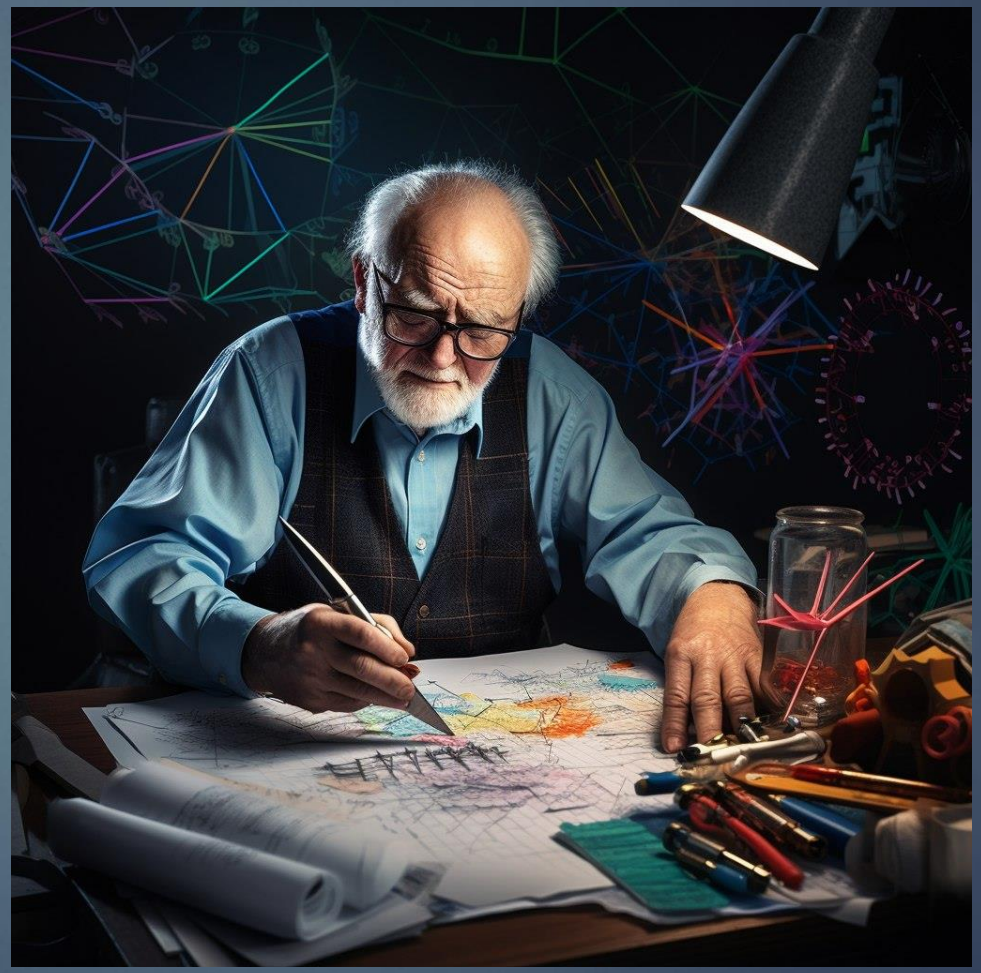




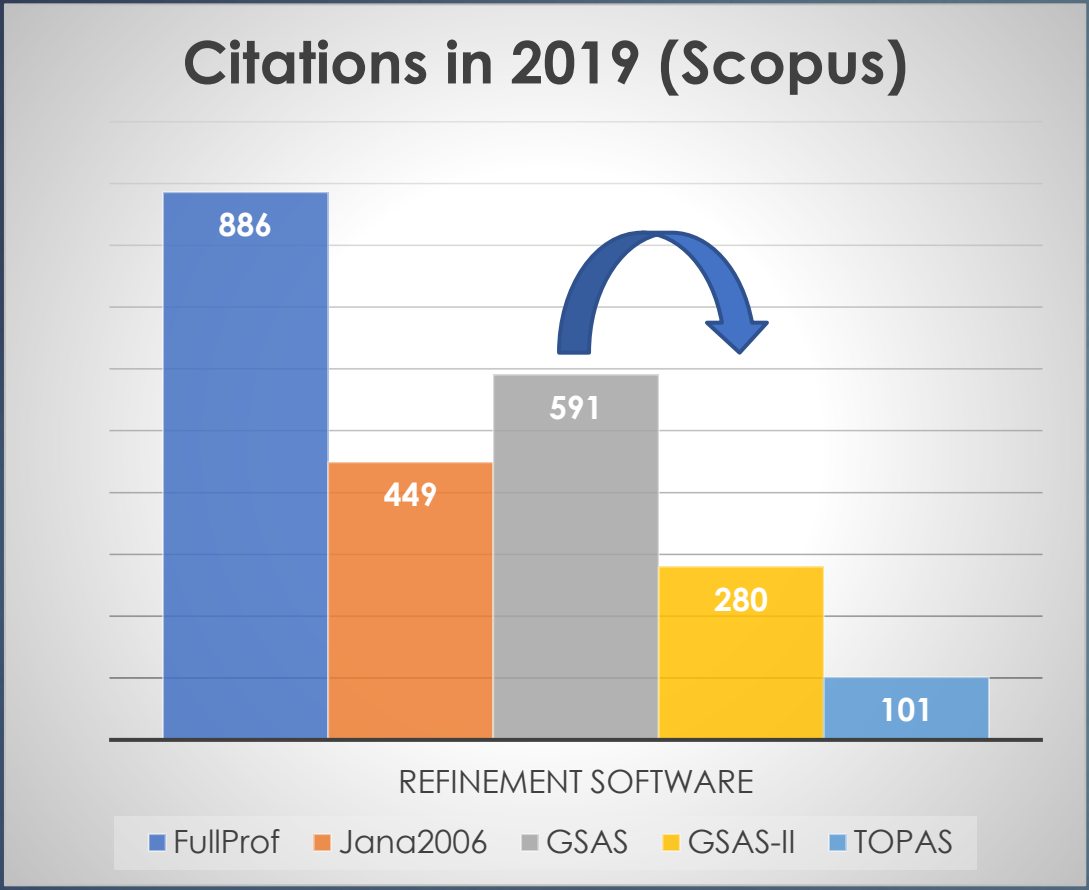
Refinement the way just like elders did

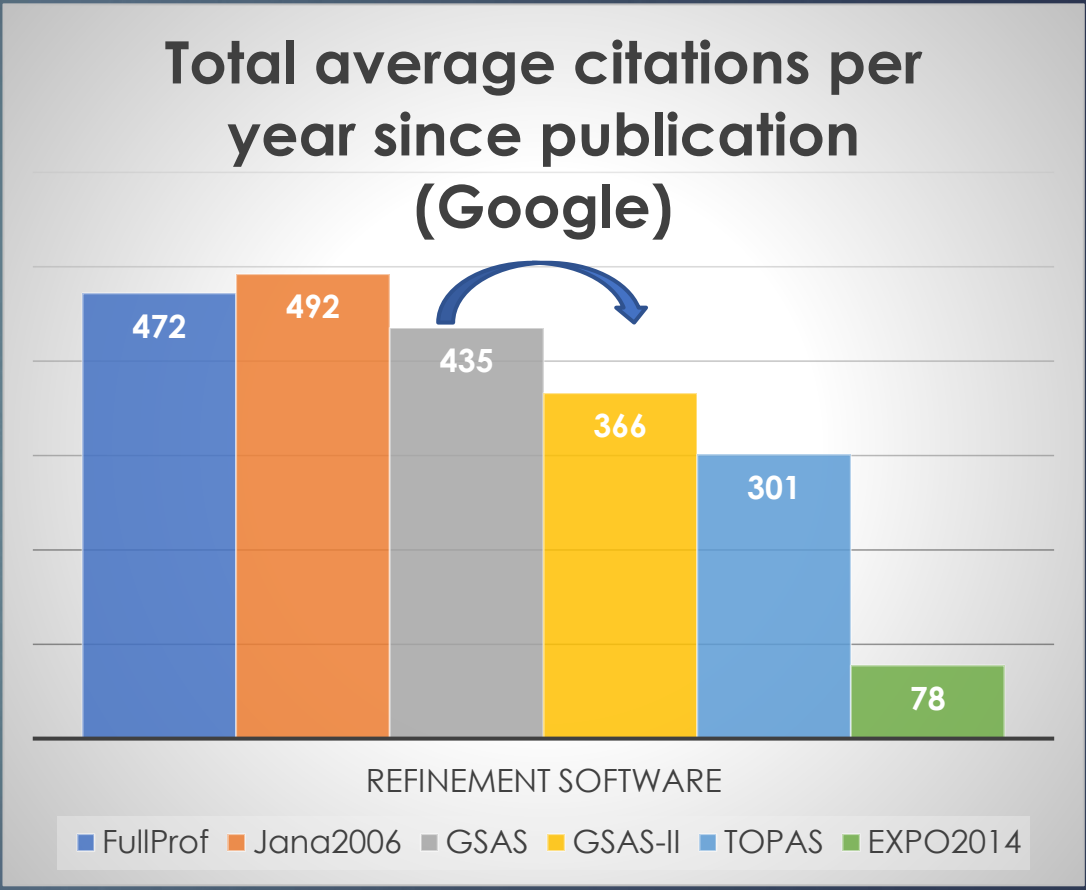
You will need:

- Nicely printed graph,
- Scissors,
- Scales,
- Keen eye,
- Steady hands.



What are the options today?*





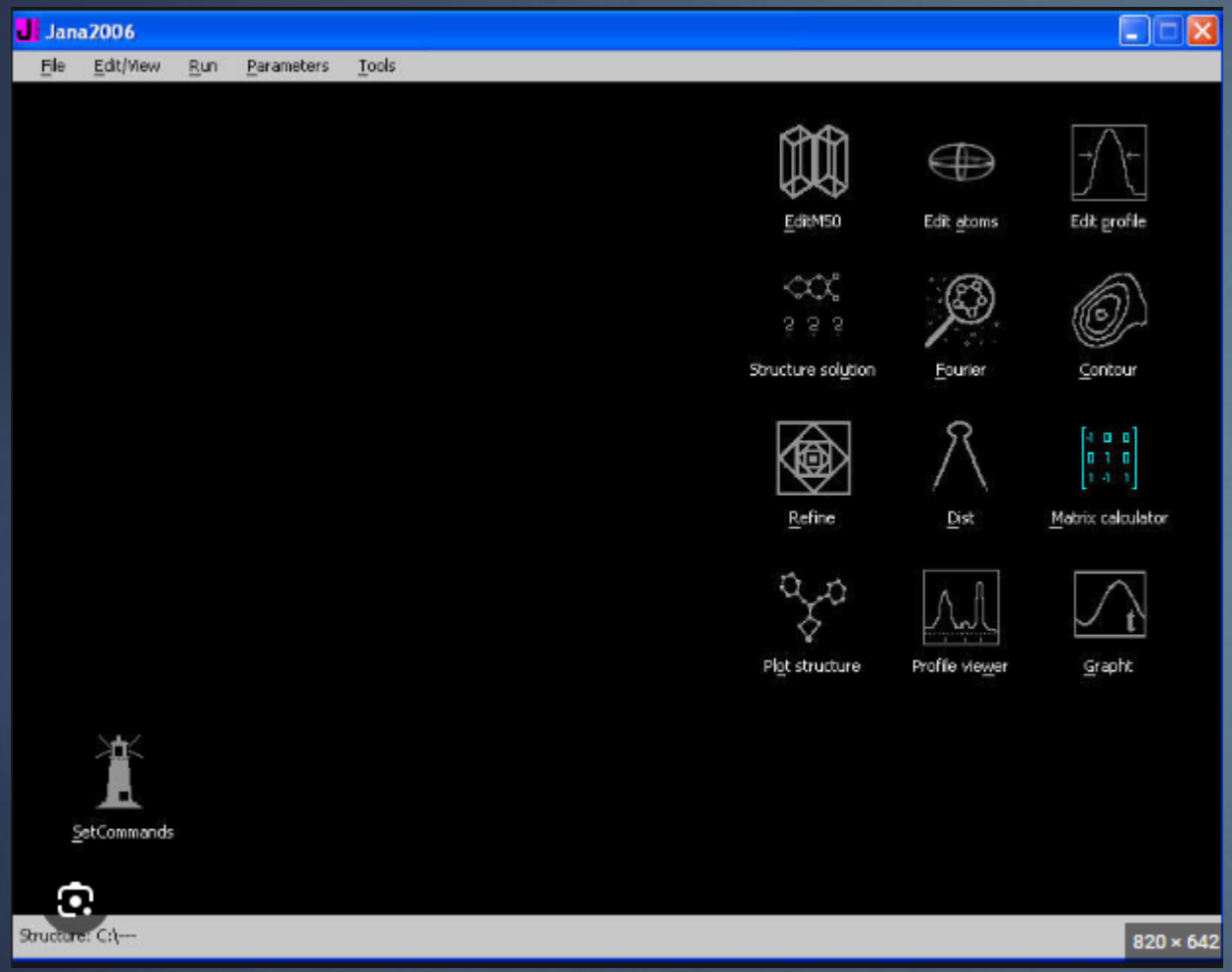
*Disclaimer: there are more

Jana2006 (V. Petříček, M. Dušek and L. Palatinus)
Institute of Physics, Academy of Sciences of the Czech Republic

- Capabilities
  - Rietveld/Pawley refinement (magnetic structures) (XRD, ND, TOF)
  - **Modulated structures refinement**
  - Fourier mapping
  - Charge flipping
  - Monte Carlo / Simulated annealing
  - Strain/size analysis
  - Indexing
  - Stacking faults
  - Small-Angle scattering
  - Single-Crystal refinement

- Reliable
- Rather Simple
- Easy to link to externals
- Wide tutorial base
- **Free**

Jana2006


Jana2006
File
Edit/View
Run
Parameters
Tools
EditM50
Edit atoms
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Fourier
Contour
Refine
Dist
Matrix calculator
Plot structure
Profile viewer
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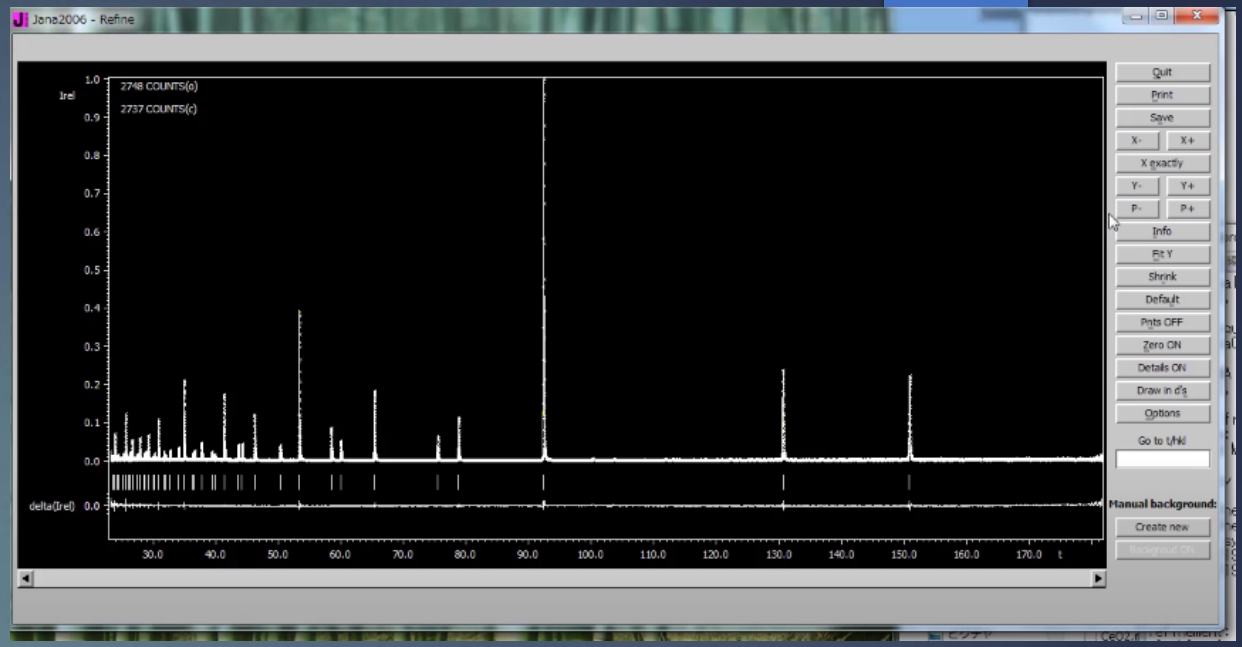
Jana2006 - Refine
2748 COUNTS(o)
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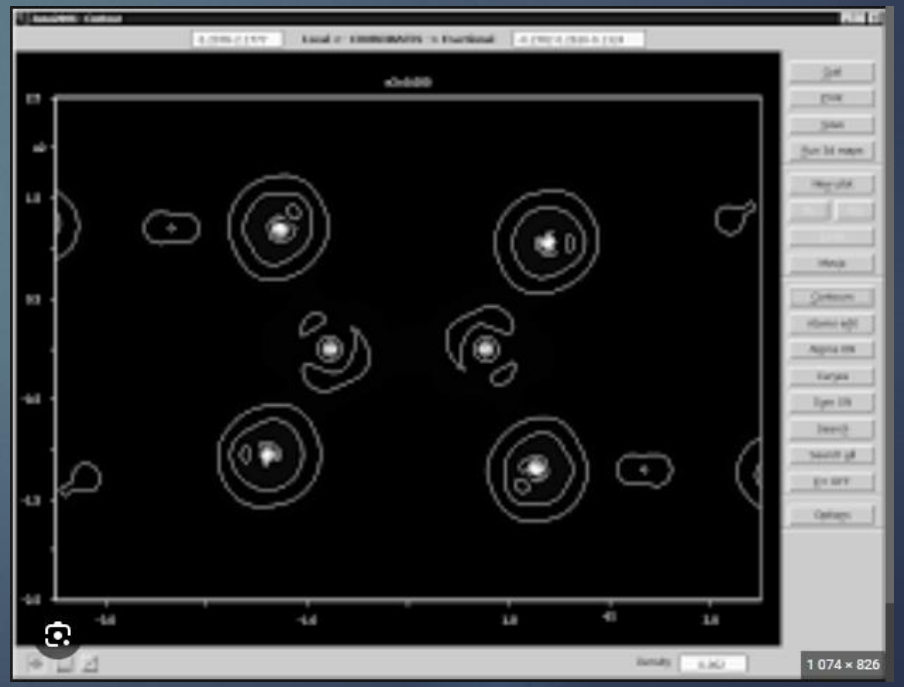
Create new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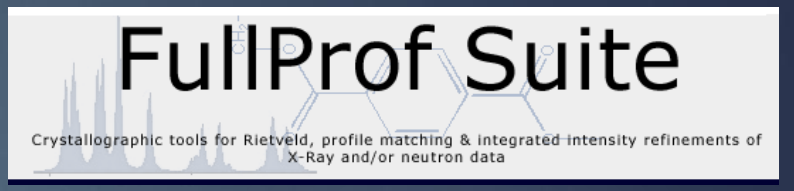
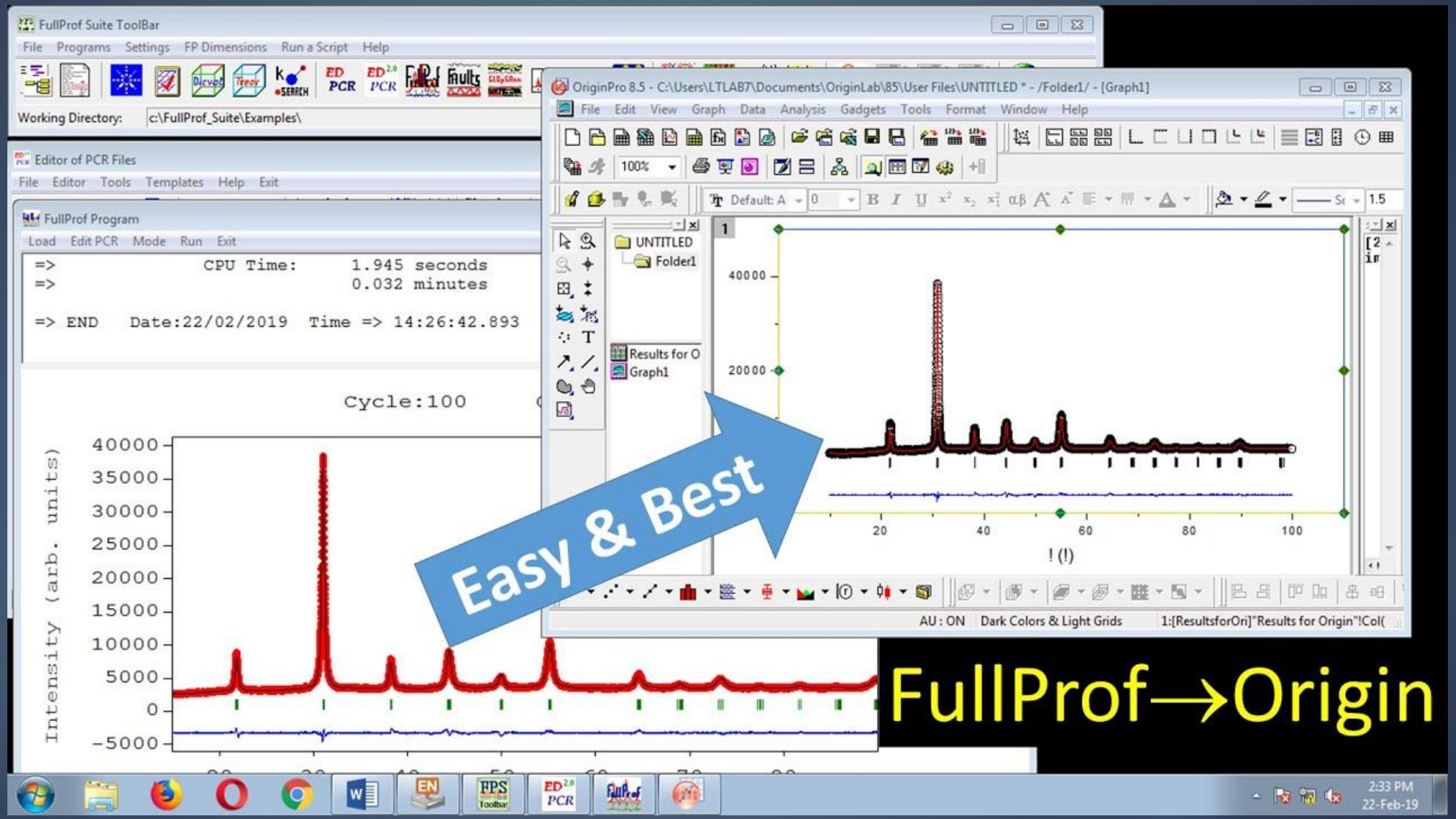
FullProf (J. Rodriguez-Carvajal)
ESRF France



- Capabilities
  - Rietveld/Pawley refinement (magnetic structures) (XRD, ND, TOF)
  - **Magnetic structure refinement**
  - Fourier mapping
  - Charge flipping
  - Monte Carlo / Simulated annealing
  - Strain/size analysis
  - Indexing
  - Stacking faults
  - Small-Angle scattering
  - Single-Crystal refinement

- Well-established
- OriginPro integration
- **Free**

FullProf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FullProf Program
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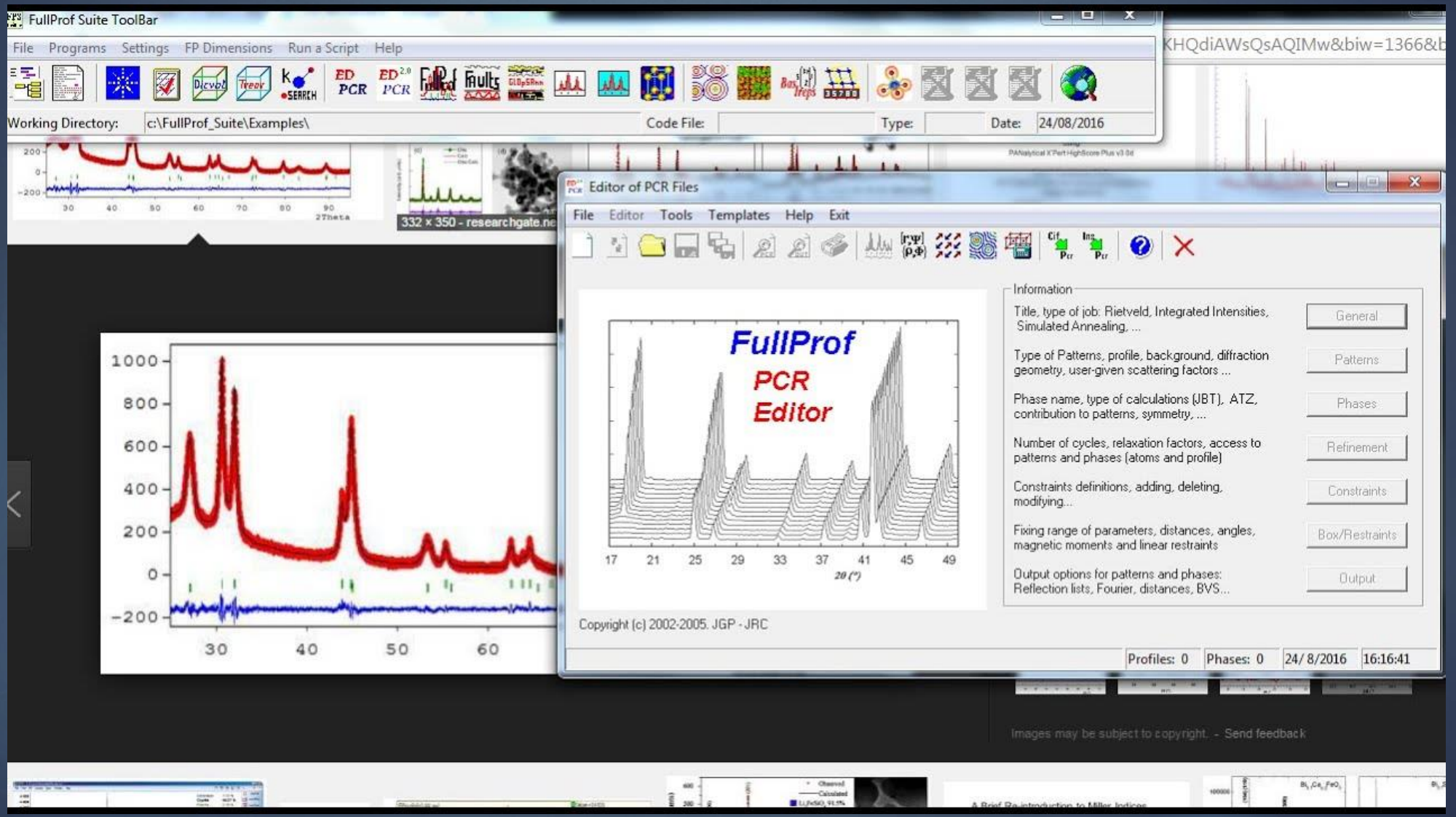
FullProf


FullProf Suite ToolBar
File Programs Settings FP Dimensions Run a Script Help
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Code File:
Type:
Date: 24/08/2016
Editor of PCR Files
File Editor Tools Templates Help Exit
FullProf
PCR
Editor
Information
Title, type of job: Rietveld, Integrated Intensities, Simulated Annealing, ...
General
Type of Patterns, profile, background, diffraction geometry, user-given scattering factors ...
Patterns
Phase name, type of calculations (JBT), ATZ, contribution to patterns, symmetry, ...
Phases
Number of cycles, relaxation factors, access to patterns and phases (atoms and profile)
Refinement
Constraints definitions, adding, deleting, modifying...
Constraints
Fixing range of parameters, distances, angles, magnetic moments and linear restraints
Box/Restraints
Output options for patterns and phases: Reflection lists, Fourier, distances, BVS...
Output
Copyright (c) 2002-2005. JGP - JRC
Profiles: 0
Phases: 0
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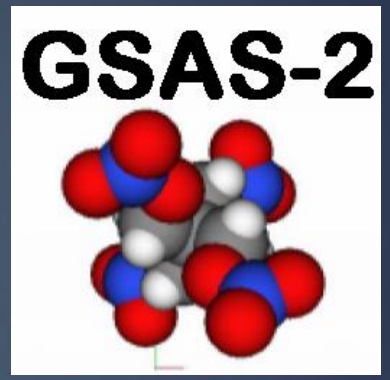
16:16:41
2Theta
2θ (°)

GSAS-II (R. Von-Dreele and B. Toby) Argonne National Laboratory, US

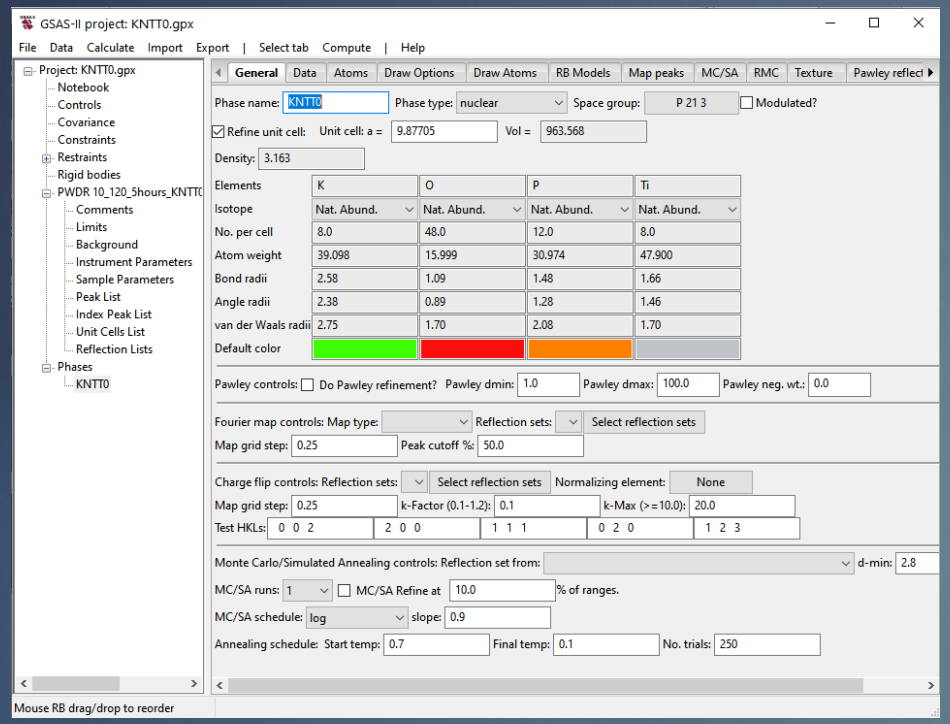
- Capabilities
  - Rietveld/Pawley refinement (magnetic structures) (XRD, ND, TOF)
  - Fourier mapping
  - Charge flipping
  - Monte Carlo / Simulated annealing
  - Strain/size analysis
  - Sequential refinement
  - Indexing
  - Combined refinement
  - Stacking faults
  - 2D image data processing
  - Small-Angle scattering
  - Single-Crystal refinement



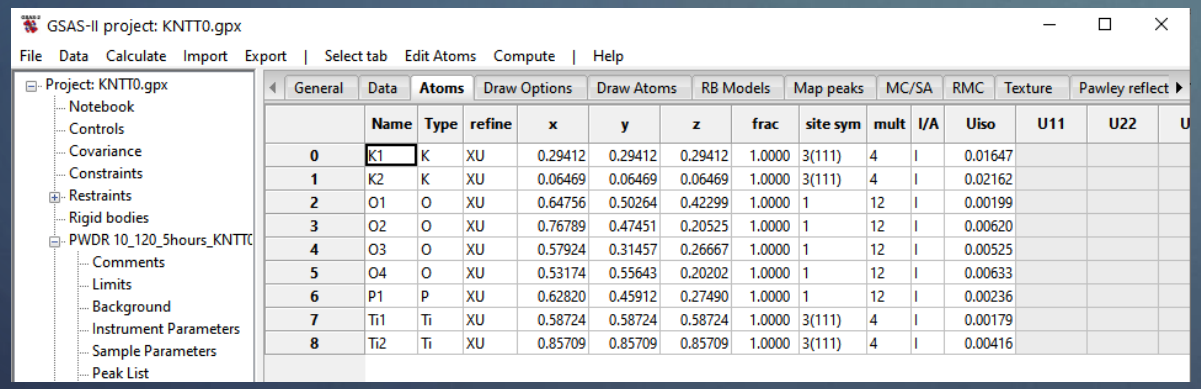
- Stable
- Reliable
- Quick
- Simple
- Easy import/export
- **Free**

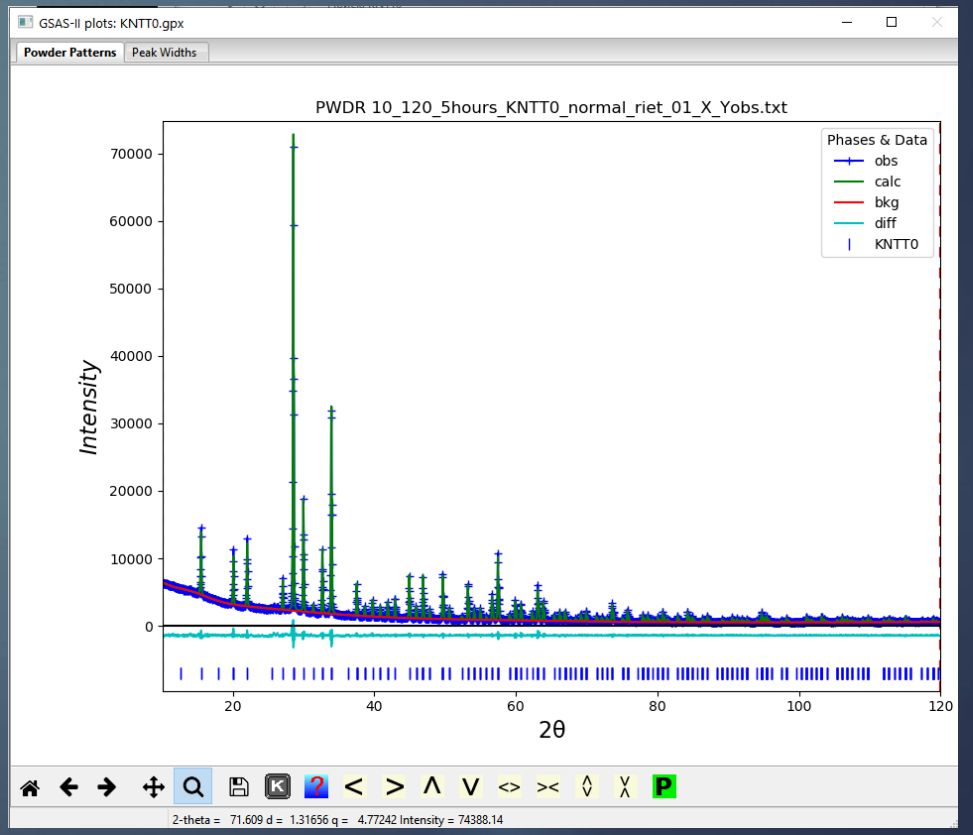
Argonne NATIONAL LABORATORY

GSAS-II

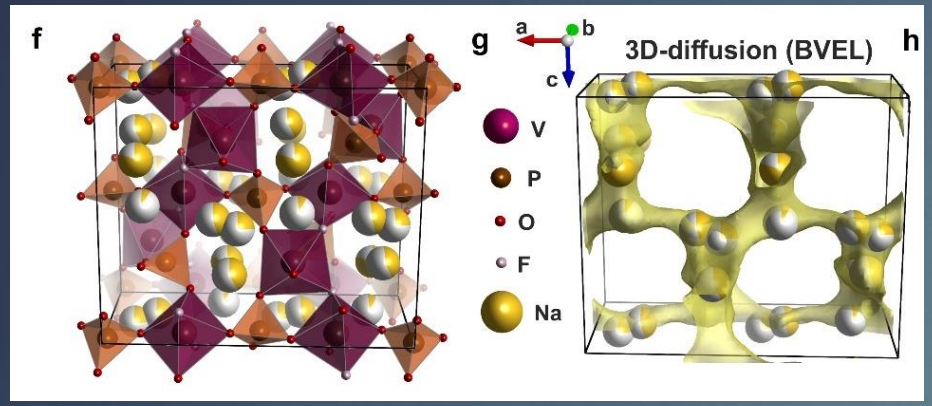


- 50 variables
- 4189 observations
- ~2.5 seconds per cycle

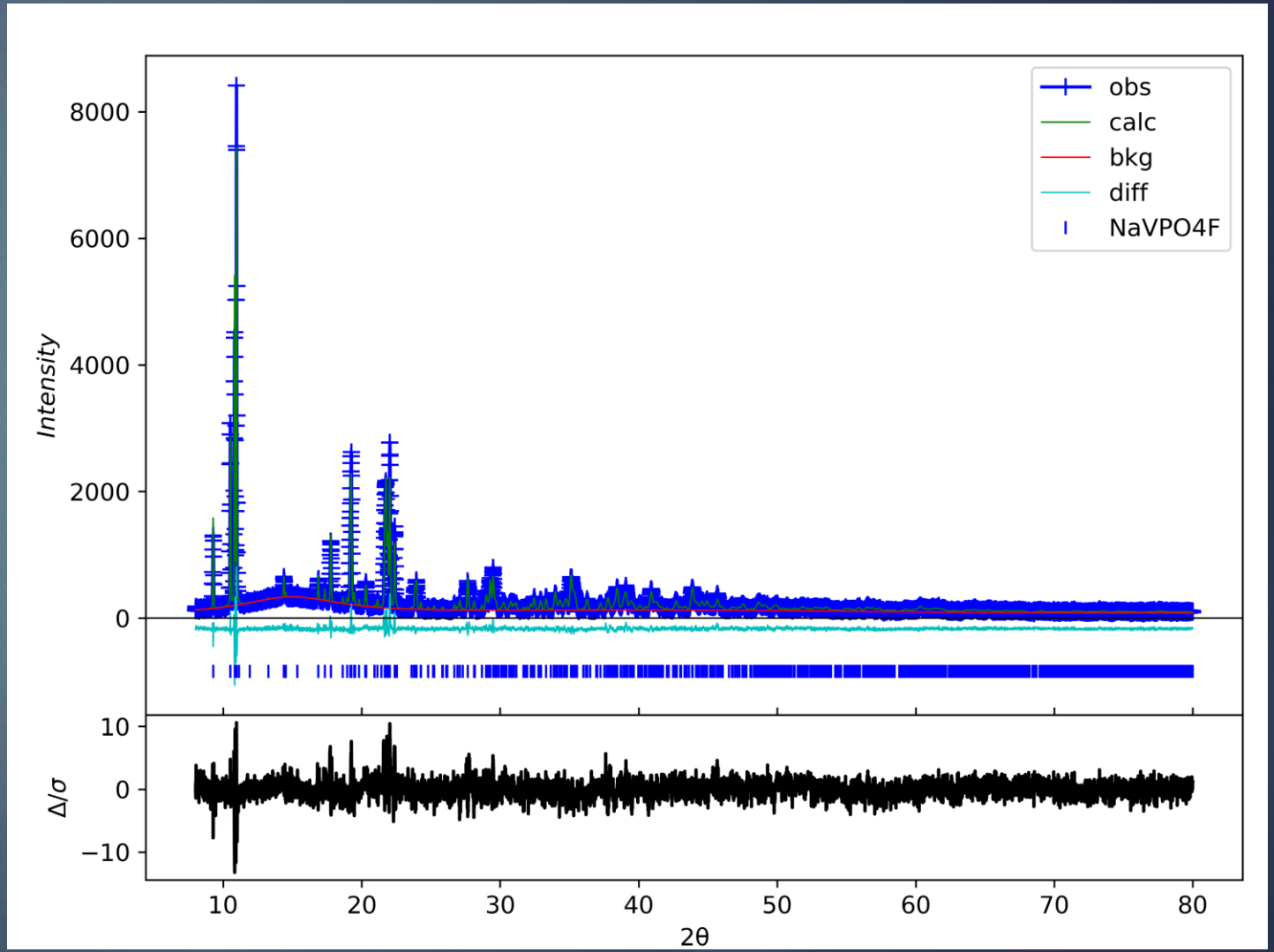




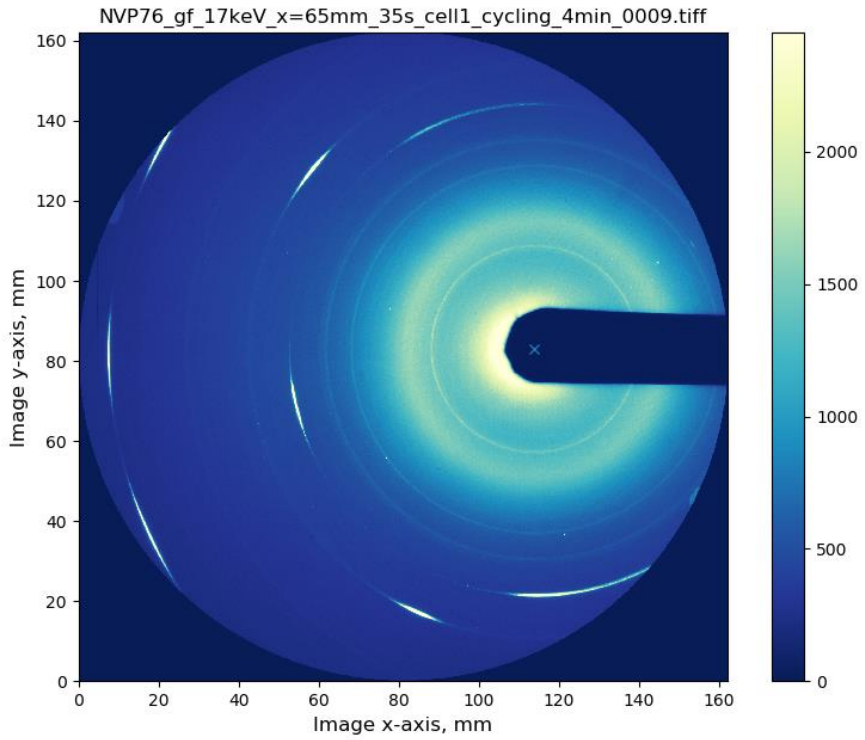
GSAS-II: Rietveld refinement

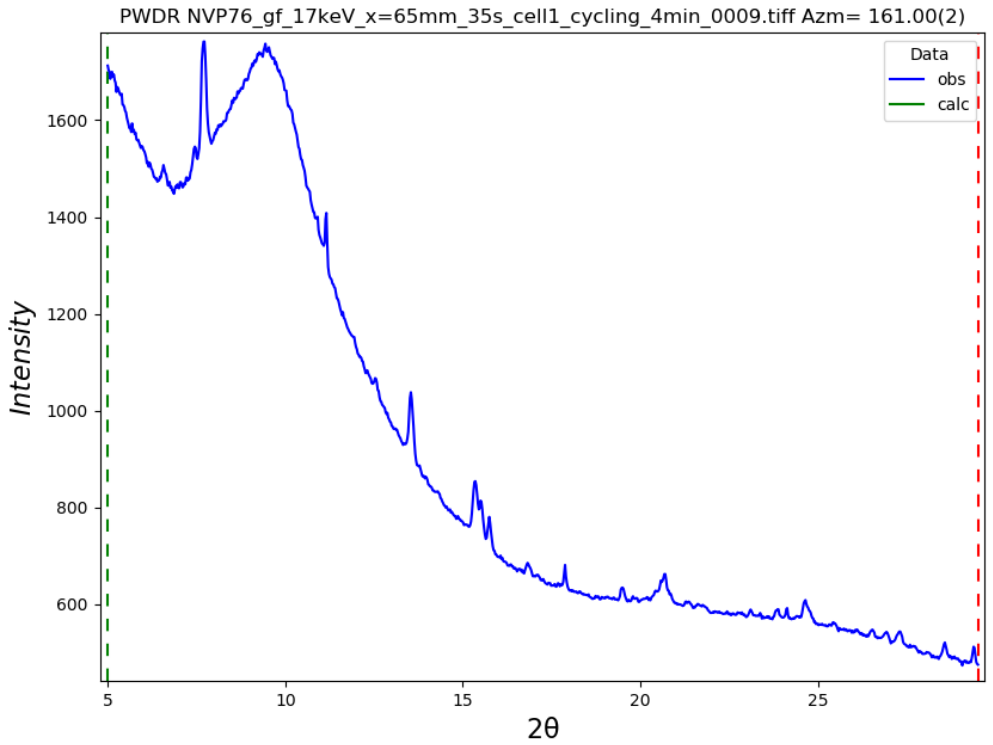


Real-life case: refinement of synchrotron data (Elettra)



GSAS-II: 2D integration





Integration

GSAS-II: sequential refinement

Operando data processing

File Data Calculate Import Export | Columns/Rows Pseudo Vars Parametric Fit Seq Export | Help

- PWDR NVO44_pp_17keV_
- Phases
  - NaVPO4O
  - Sequential results

	No.	Use	Rwp	$\Delta\chi^2$ (%)	0::a	0::b	0::c	0::Vol	:*:Scale
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0001_mccd_A182.fxye Bank 1	0	☑	1.646	0.03441	12.71165	6.29707	10.60430	848.833	1.38387
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0002_mccd_A182.fxye Bank 1	1	☑	1.631	-0.03114	12.71326	6.29758	10.60679	849.210	1.38889
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0003_mccd_A182.fxye Bank 1	2	☑	1.632	0.03624	12.71267	6.29848	10.60556	849.192	1.37282
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0004_mccd_A182.fxye Bank 1	3	☑	1.605	0.09778	12.70801	6.29767	10.60079	848.391	1.36416
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0005_mccd_A182.fxye Bank 1	4	☑	1.633	0.05971	12.70778	6.29681	10.60198	848.354	1.41886
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0006_mccd_A182.fxye Bank 1	5	☑	1.620	-0.07627	12.70155	6.29650	10.59744	847.533	1.40277
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0007_mccd_A182.fxye Bank 1	6	☑	1.620	0.00458	12.70059	6.29751	10.59555	847.455	1.41119
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0008_mccd_A182.fxye Bank 1	7	☑	1.609	-0.08063	12.69641	6.29314	10.59569	846.600	1.41083
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0009_mccd_A182.fxye Bank 1	8	☑	4.469	-0.06099	12.68734	6.29080	10.58025	844.448	1.31111
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0010_mccd_A182.fxye Bank 1	9	☑	1.583	0.05825	12.69314	6.28560	10.60000	845.710	1.42267
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0011_mccd_A182.fxye Bank 1	10	☑	1.581	0.01577	12.69896	6.28204	10.60278	845.840	1.32732
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0012_mccd_A182.fxye Bank 1	11	☑	1.588	-0.11884	12.69667	6.27738	10.60602	845.319	1.36950
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NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0014_mccd_A182.fxye Bank 1	13	☑	1.588	-0.07454	12.69800	6.26594	10.61002	844.186	1.33812
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0015_mccd_A182.fxye Bank 1	14	☑	1.571	0.13419	12.69610	6.25856	10.60999	843.063	1.41862
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0016_mccd_A182.fxye Bank 1	15	☑	1.564	0.06156	12.69140	6.25551	10.61272	842.556	1.35540
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0017_mccd_A182.fxye Bank 1	16	☑	1.639	0.09152	12.68631	6.25276	10.61649	842.147	1.32481
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NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0021_mccd_A182.fxye Bank 1	20	☑	1.553	-0.15096	12.67360	6.24276	10.62008	840.242	1.34953
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NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0026_mccd_A182.fxye Bank 1	25	☑	1.513	0.05393	12.65654	6.22754	10.62746	837.647	1.36172
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0027_mccd_A182.fxye Bank 1	26	☑	1.519	0.08939	12.65467	6.22655	10.62744	837.389	1.38533
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NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0032_mccd_A182.fxye Bank 1	31	☑	1.631	-0.15331	12.64219	6.22280	10.63195	836.413	1.34877
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0033_mccd_A182.fxye Bank 1	32	☑	1.695	0.06348	12.63780	6.22147	10.63421	836.122	1.32938
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NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0037_mccd_A182.fxye Bank 1	36	☑	1.656	0.04444	12.62593	6.21780	10.63485	834.895	1.24025
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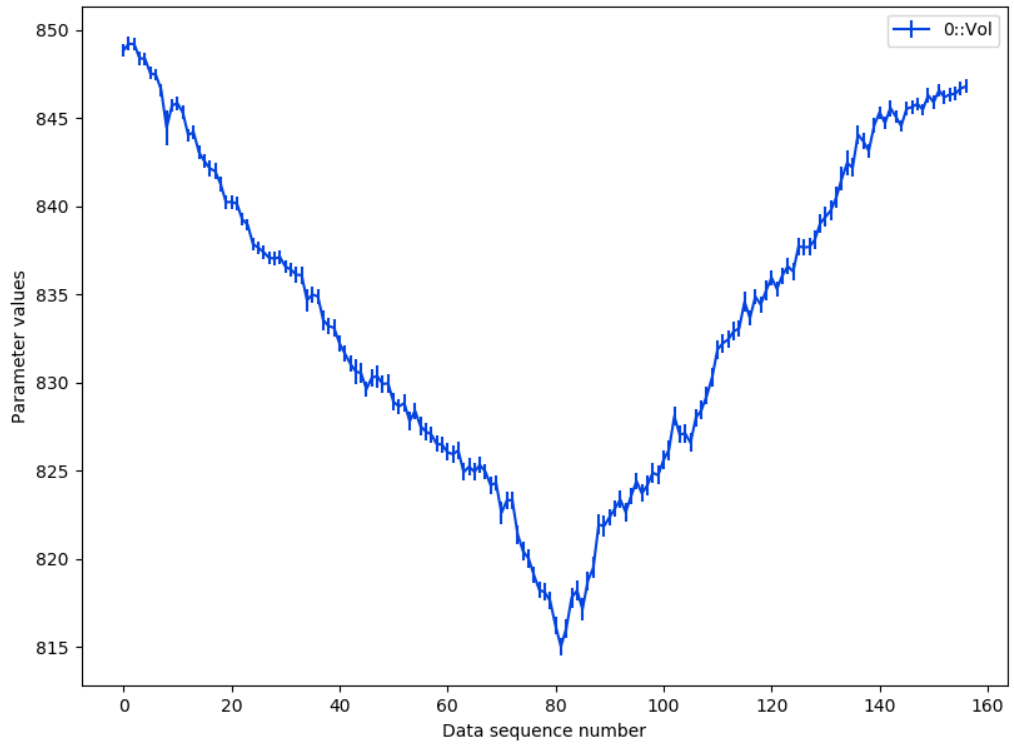
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0039_mccd_A182.fxye Bank 1	38	☑	1.620	0.03796	12.61940	6.21212	10.62861	833.211	1.23680
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0040_mccd_A182.fxye Bank 1	39	☑	1.664	-0.05032	12.61837	6.21044	10.63106	833.110	1.17901
NVO44_pp_17keV_x=65mm_30s_cell1_cycling_3min_0041_mccd_A182.fxye Bank 1	40	☑	1.671	0.06106	12.61708	6.20558	10.62929	832.234	1.25821

Mouse RB drag/drop to reorder

Select column to export; Double click on column to plot data; on row for Covariance

Powder Patterns | Sequential refinement | Covariance

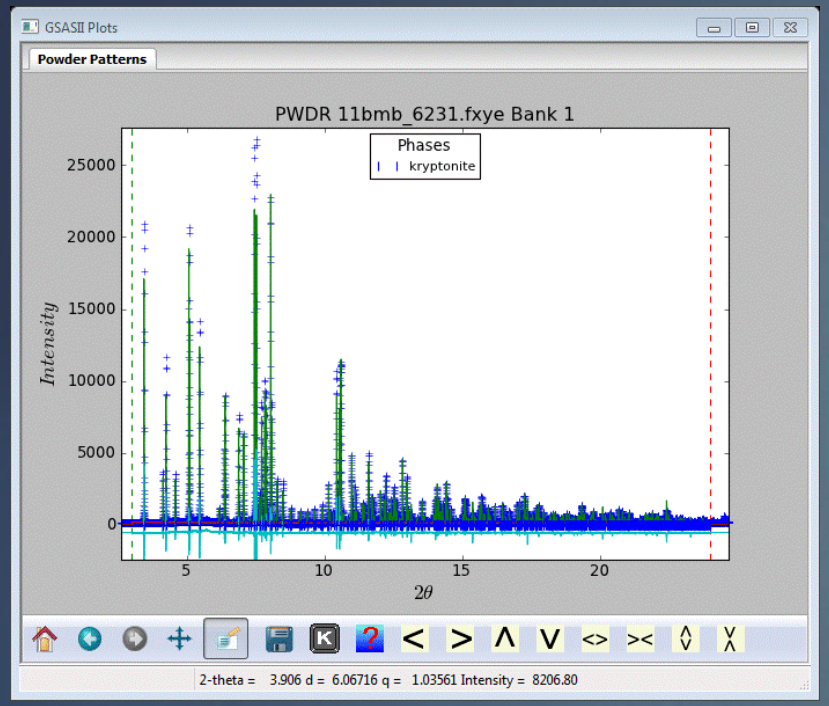


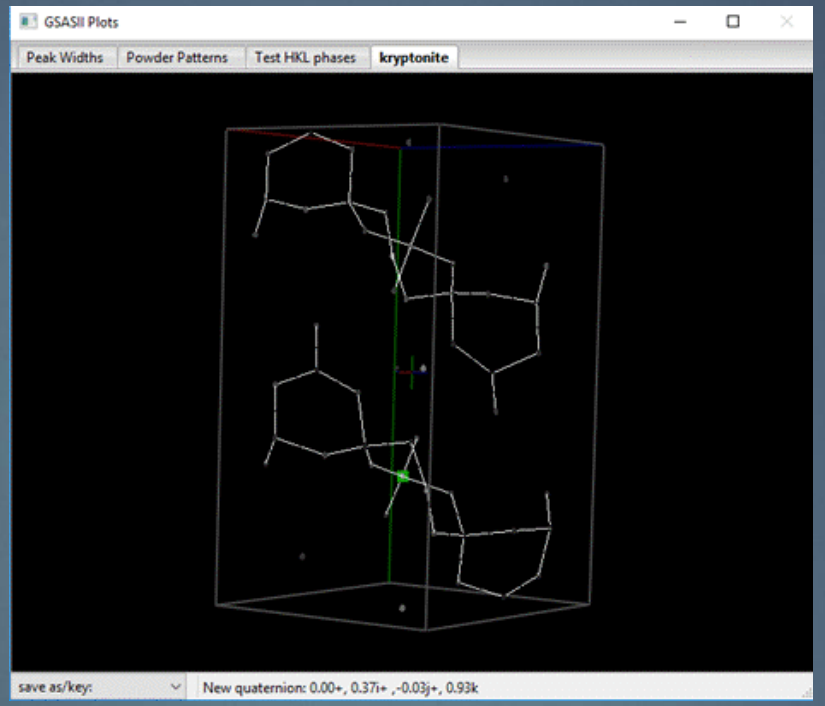
press L to toggle lines, S to select X axis, T to change titles (reselect column to show?)

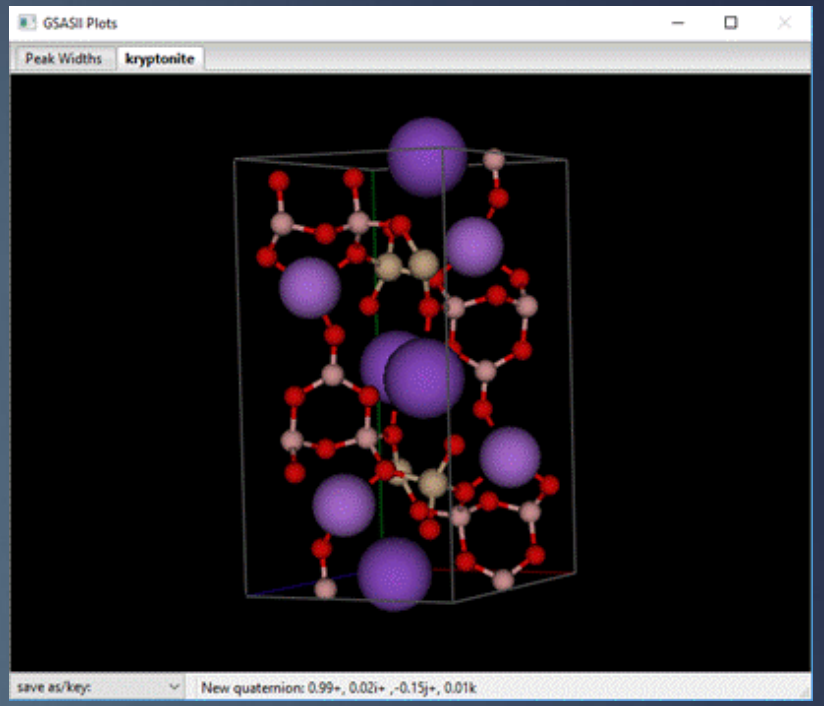
156 powder histograms dataset
~ 15 min for the whole run

$NaVOHPO_4$ vs. Na

GSAS-II: charge flipping





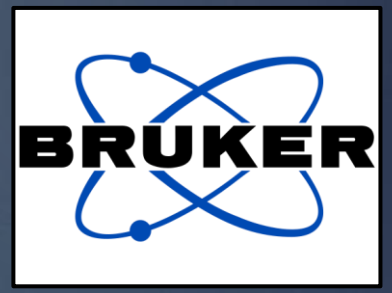


Generation of electron density map

Identification of the atoms and refinement

Tutorial: subversion.xray.aps.anl.gov/pyGSAS/Tutorials/CFjadarite

Topas Bruker/Academic (A. Coelho and J. Evans), BRUKER



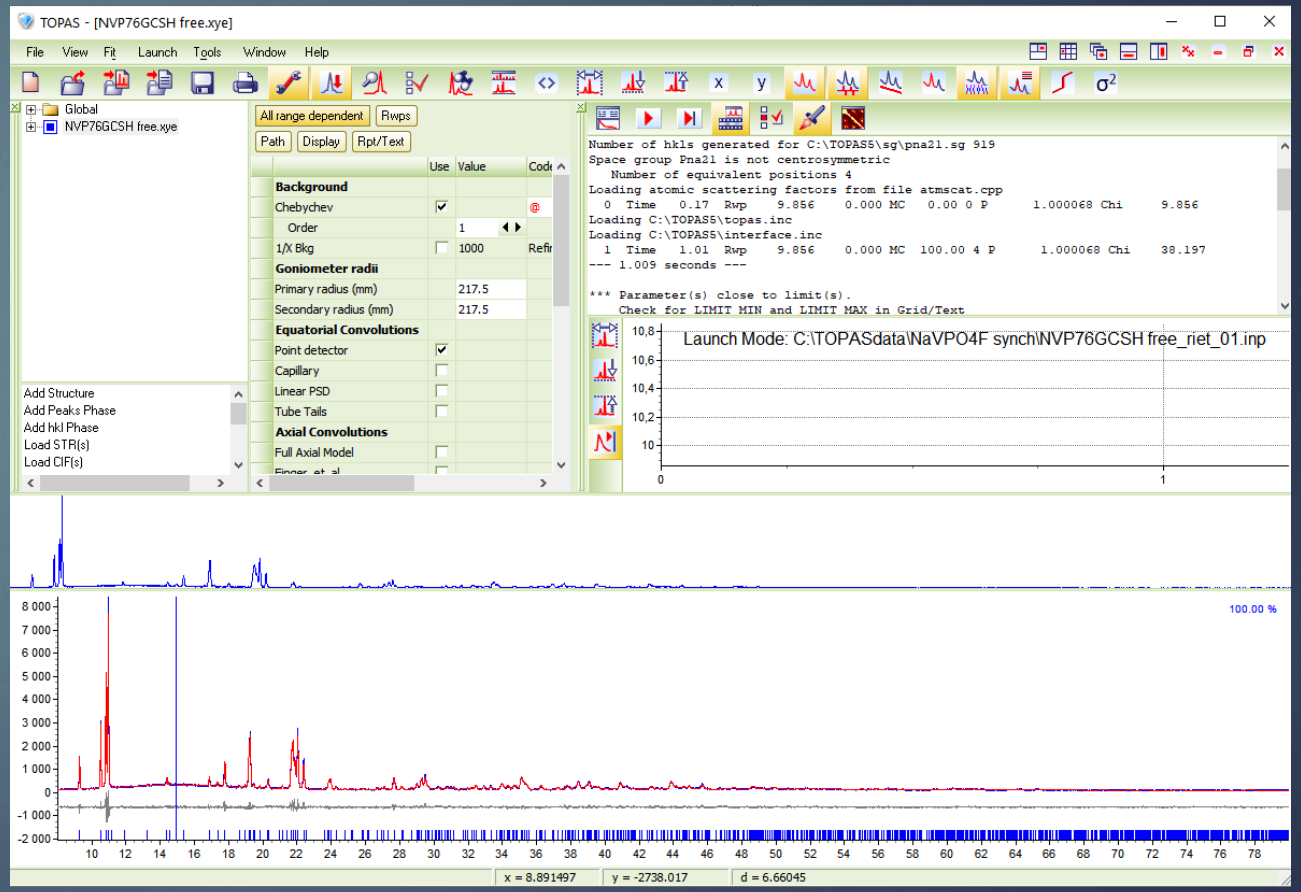
- Capabilities
  - Rietveld/Pawley refinement (magnetic structures) (XRD, ND, TOF)
  - Fourier mapping
  - Charge flipping
  - Monte Carlo / Simulated annealing
  - Strain/size analysis
  - Sequential refinement
  - Indexing
  - Combined refinement
  - Stacking faults
  - Parametric refinement
  - Small-Angle scattering
  - Single-Crystal refinement
  - Pair Distribution Function
  - Fundamental approach/ W/K_b contamination/tube tails
  - Cloud computing using Amazon Web Services

- Stable
- Reliable
- Very Fast!
- Large data processing
- Customizable
- Programmable

TOPAS (in combination with jEdit)

```
/* Rietveld refinement comprising two phases */
xdd File_Name.xy
    CuKa5(0.001)  ' Five emission profile lines
    Radius(217.5)
    LP_Factor(26.4)
    Full_Axial_Model(12, 15, 12, 2.3, 2.3)
    Slit_Width(0.1)
    Divergence(1)
    Zero_Error(@, 0)
    bkg @ 0 0 0 0 0 0
    STR(R-3C, "Corundum Al2O3")
        Trigonal(@ 4.759, @ 12.992)
        site Al              z @ 0.3521 occ Al+3 1 beq @ 0.3
        site O  x @ 0.3062 z 0.25      occ O-2  1 beq @ 0.3
        scale @ 0.001
        CS_L(@, 100)
        r_bragg 0
    STR(Fm-3m, Fluorite)
        Cubic(@ 5.464)
        site Ca                        occ Ca 1 beq @ 0.5
        site F  x 0.25  y 0.25 z 0.25 occ F  1 beq @ 0.5
        scale @ 0.001
        CS_L(@, 100)
        r_bragg 0
```

Figure 1
TOPAS example input file written in the INP script comprising readable text. Keywords in green, macros in blue, refined parameters in red, comments in purple.



A. Coelho, TOPAS and TOPAS-Academic: an optimization program integrating computer algebra and crystallographic objects written in C++, J. Appl. Cryst. (2018). 51

TOPAS (in combination with jEdit)

```
/* Rietveld refinement comprising two phases */
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   bkg @ 0 0 0 0 0 0
   STR(R-3C, "Corundum Al2O3")
      Trigonal(@ 4.759, @ 12.992)
      site Al            z @ 0.3521 occ Al+3 1 beq @ 0.3
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      scale @ 0.001
      CS_L(@, 100)
      r_bragg 0
   STR(Fm-3m, Fluorite)
      Cubic(@ 5.464)
      site Ca                       occ Ca 1 beq @ 0.5
      site F  x 0.25  y 0.25 z 0.25 occ F  1 beq @ 0.5
      scale @ 0.001
      CS_L(@, 100)
      r_bragg 0
```
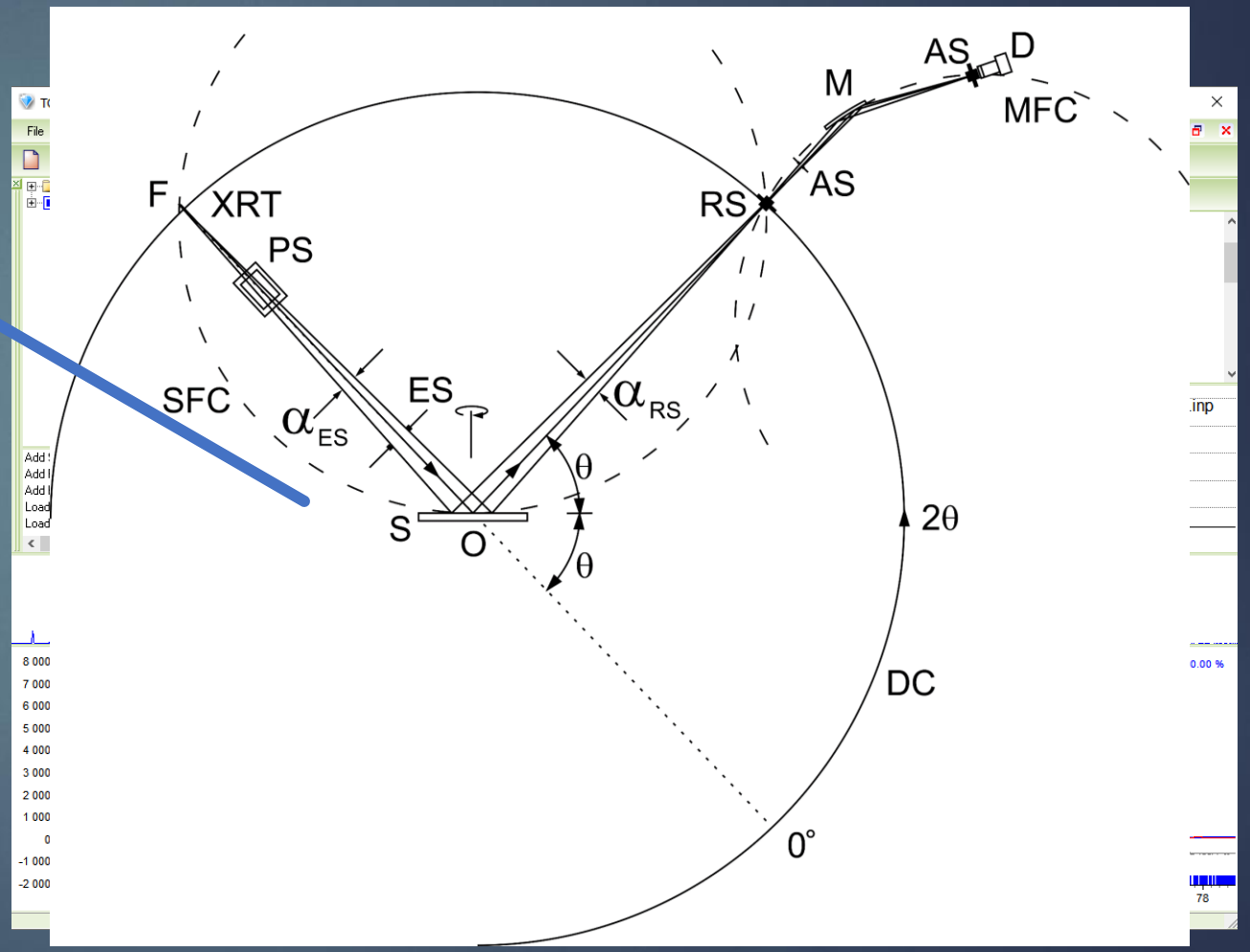
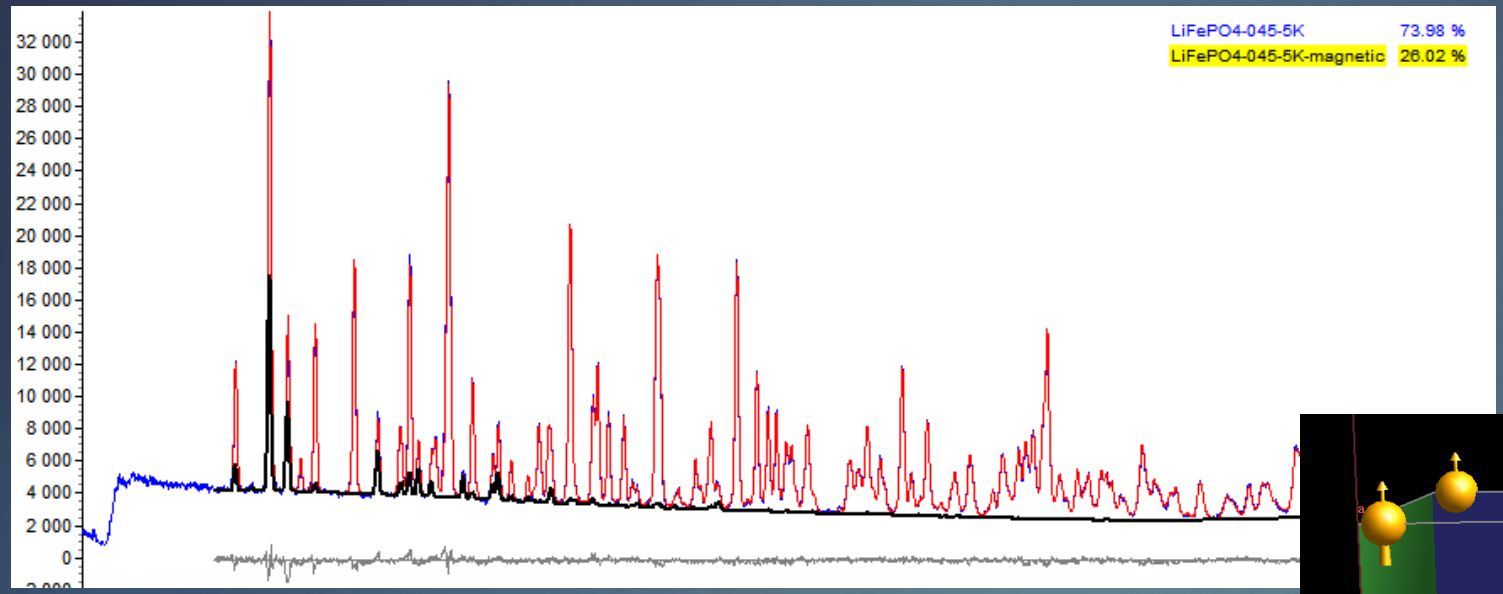

Figure 1
TOPAS example input file written in the INP script comprising readable text. Keywords in green, macros in blue, refined parameters in red, comments in purple.

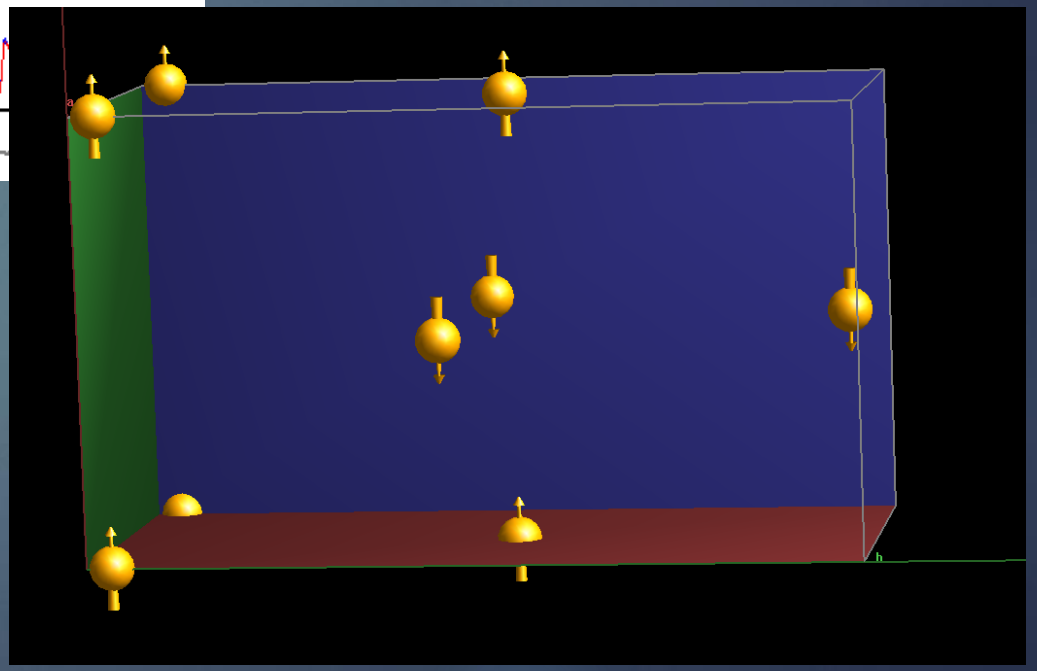
Fundamental approach to diffraction profile description



A. Coelho, TOPAS and TOPAS-Academic: an optimization program integrating computer algebra and crystallographic objects written in C++, J. Appl. Cryst. (2018). 51

TOPAS: Magnetic Structure Refinement





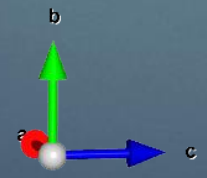
$LiFePO_4$ at 5K

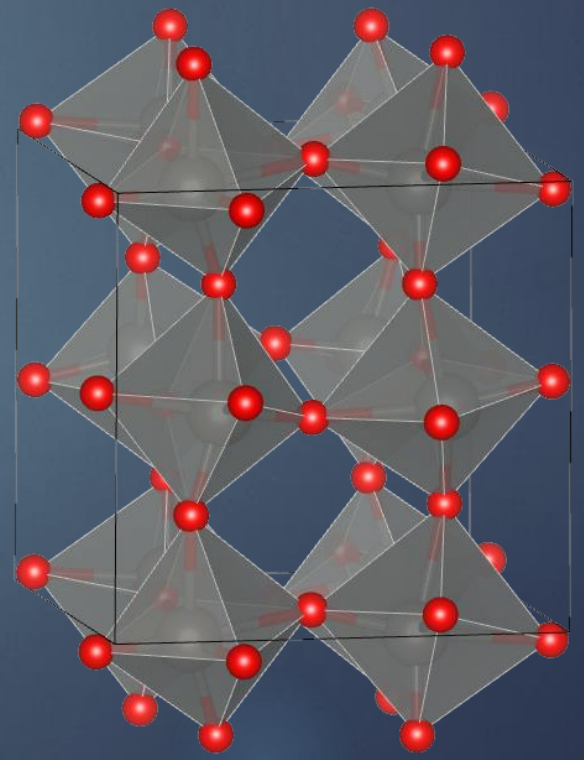
TOPAS: Symmetry mode refinement

ISODISTORT: distortion

Space Group: 221 Pm-3m Oh-1, Lattice parameters: a=3.76000, b=3.76000, c=3.76000, alpha=90.00000, beta=90.00000, gamma=90.00000
Default space-group preferences: monoclinic axes a(b)c, monoclinic cell choice 1, orthorhombic axes abc, origin choice 2, hexagonal axes, SSG standard setting
W 1a (0,0,0), O 3d (1/2,0,0)
Include strain, displacive ALL distortions
Reading CIF file...
Done.

Life example
WO_3 refinement
demo





TOPAS: Exhaustive Symmetry Search

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
pubs.acs.org/JACS

An Exhaustive Symmetry Approach to Structure Determination: Phase Transitions in $Bi_2Sn_2O_7$

James W. Lewis,[†] Julia L. Payne,[†] Ivana Radosavljevic Evans,[†] Harold T. Stokes,[‡] Branton J. Campbell,[‡] and John S. O. Evans*[,†]

[†]Department of Chemistry, University Science Site, Durham University, South Road, Durham DH1 3LE, United Kingdom
[‡]Department of Physics & Astronomy, Brigham Young University, Provo, Utah 84602, United States

DOI: 10.1021/jacs.6b04947

Automatic search over 547 intermediate subgroups

Assisted with ISODISTORT

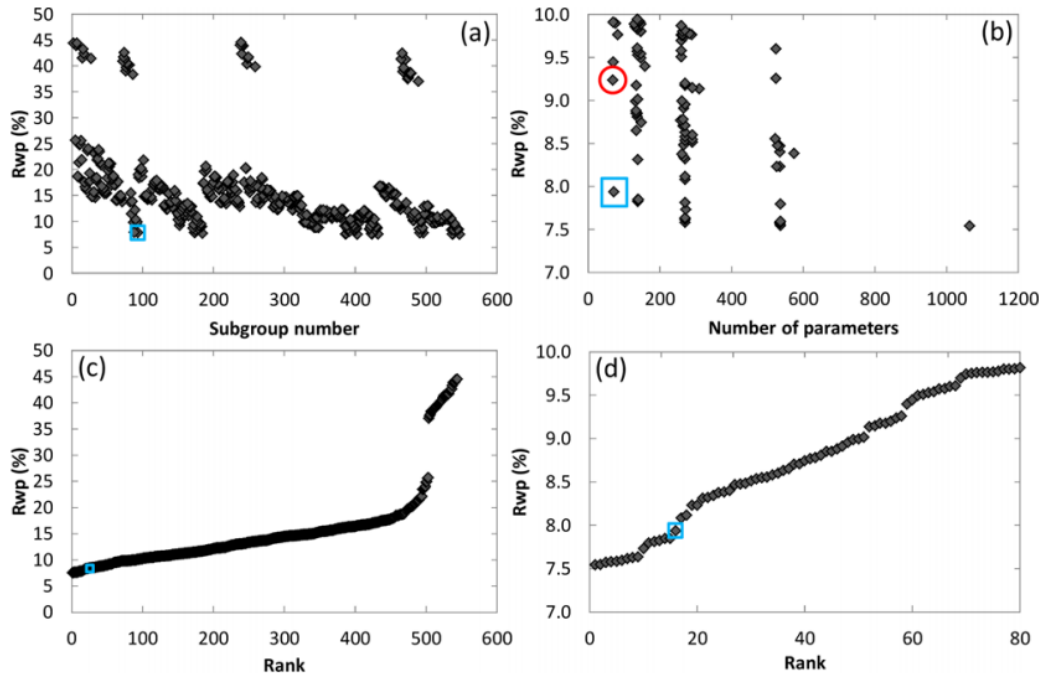


Figure 5. Final R_{wp} values from refinements of the 547 candidate models for α-$Bi_2Sn_2O_7$ against ~293 K X-ray and neutron diffraction data. Individual panels are α-phase equivalents to those in Figure 4. Candidate #152 (our best β-structure model) is marked with a red circle, and candidate #88 (our best α-structure model) is marked with a blue square.

https://community.dur.ac.uk/john.evans/topas_workshop/tutorial_exhaustive_symmetry.htm

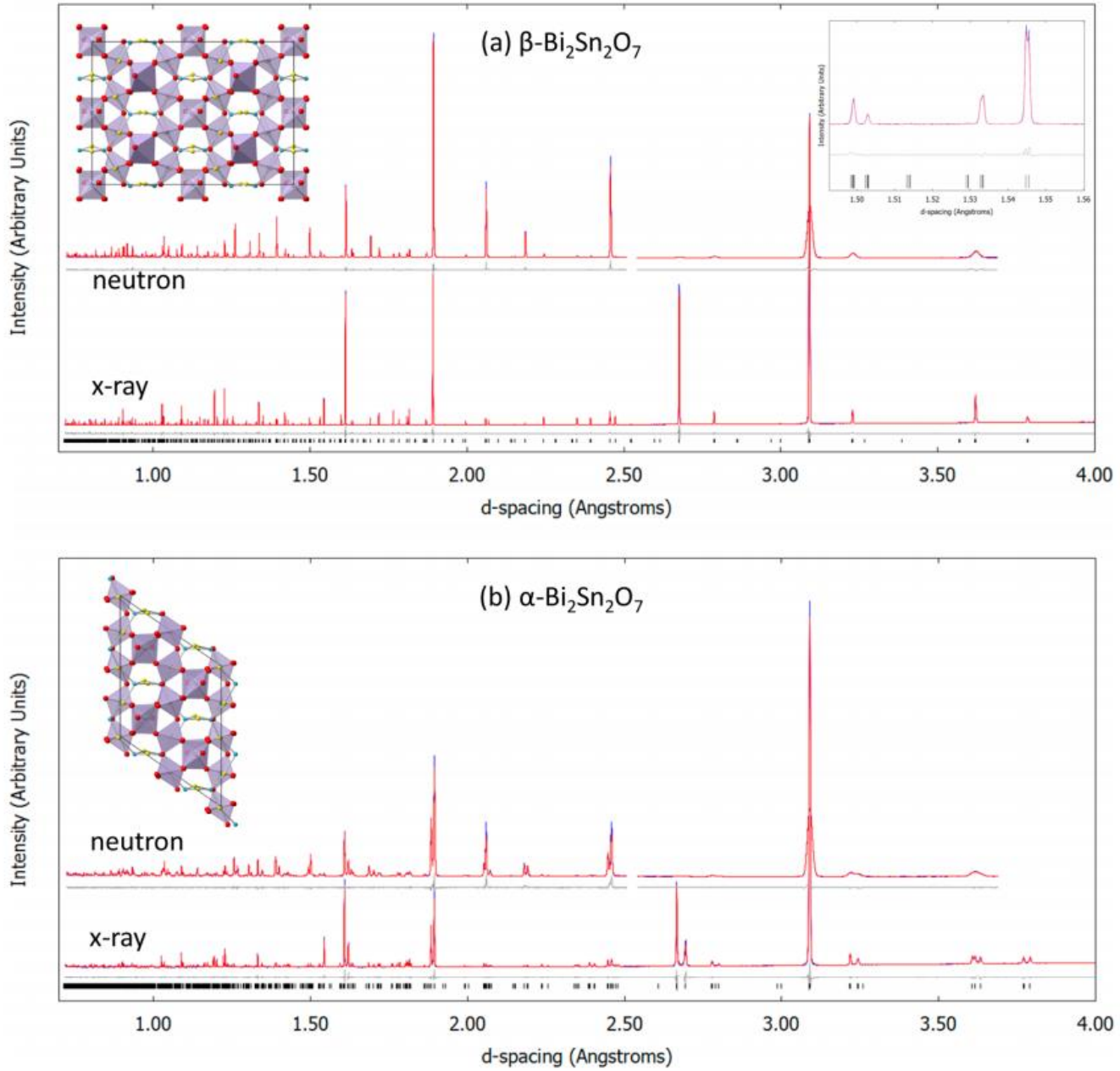
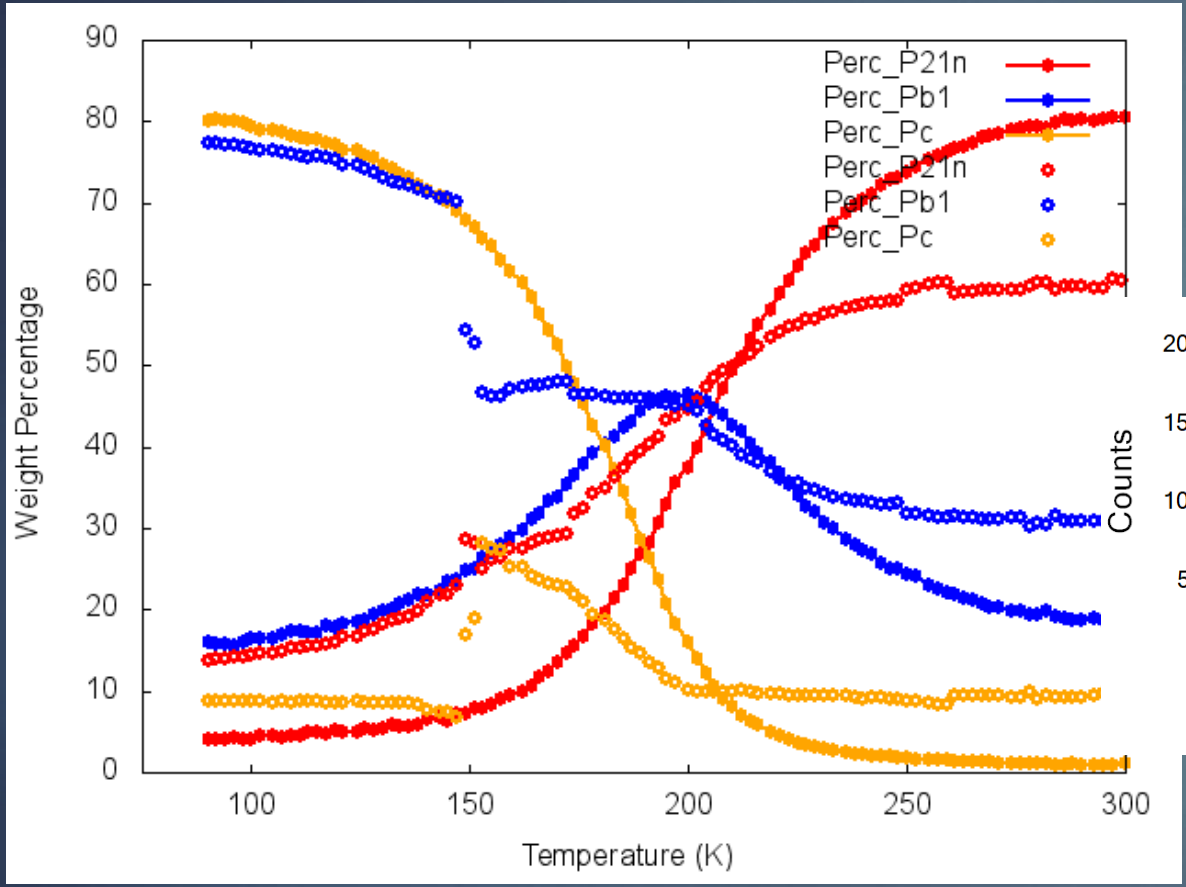
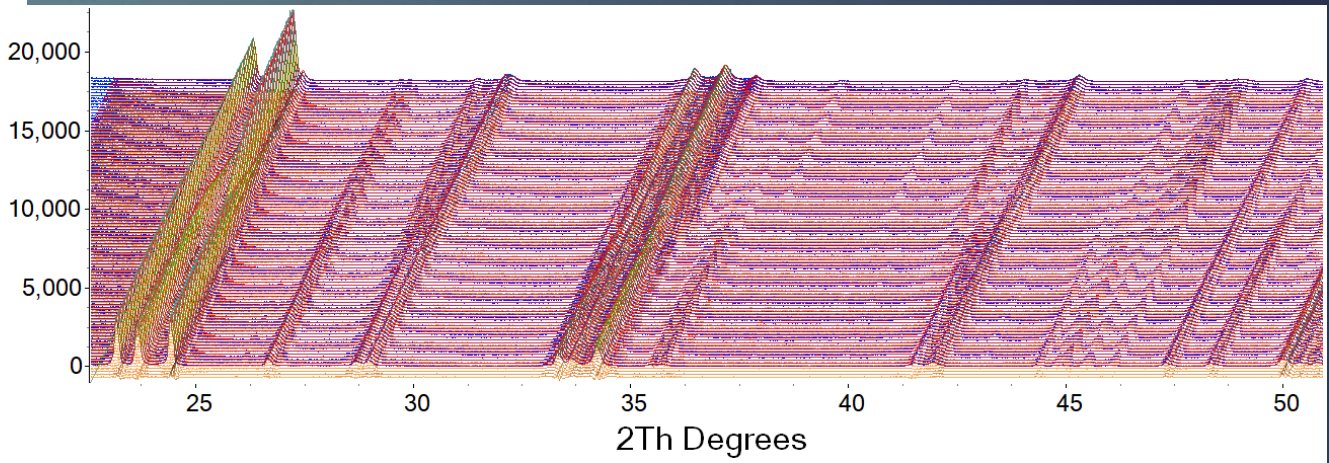


Figure 6. Final Rietveld fits for (a) β-$Bi_2Sn_2O_7$ and (b) α-$Bi_2Sn_2O_7$ models. Neutron data have been scaled and offset vertically for plotting. Neutron data for d > 2.5 Å are from the lower resolution 90° data bank. Inset to (a) shows X-ray fit in the region of the (4 8 0) and (0 8 8) reflections at $d \approx$ 1.55 Å, which would be unsplit for a metrically cubic cell. Structure insets are views down [0 1 0], key as in Figure 1.

TOPAS: Parametric refinement





G.W. Graham and J. Evans, Parametric Rietveld refinement, J. Appl. Cryst. (2007). 40, 87–95

TOPAS: Parametric refinement

ZrP_2O_7

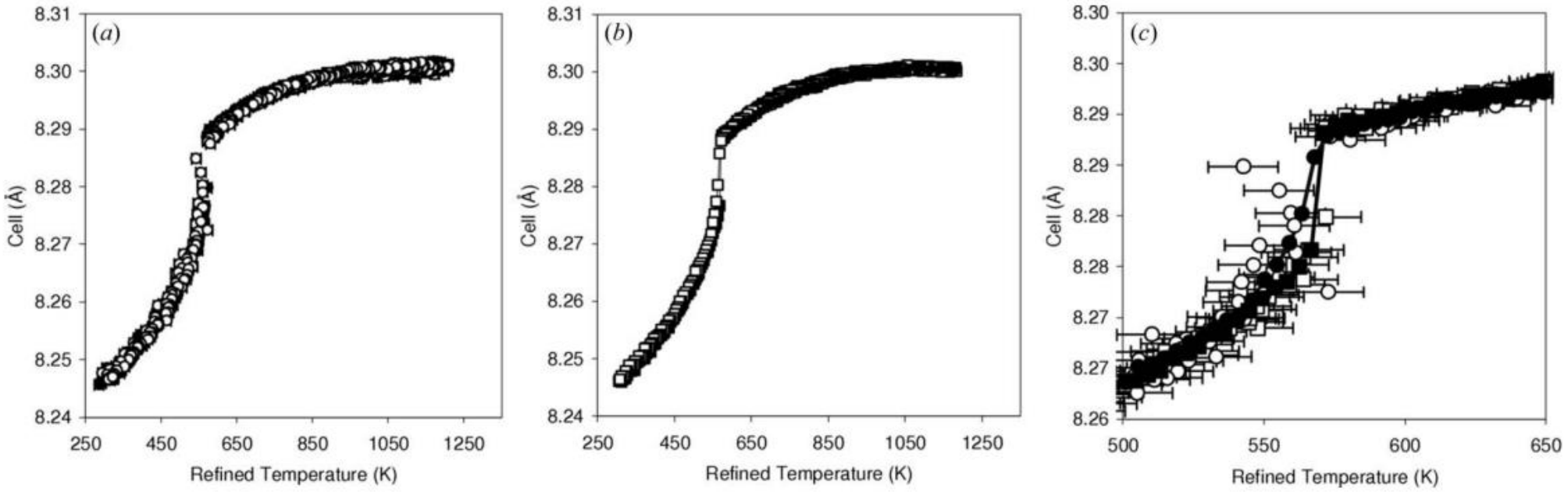
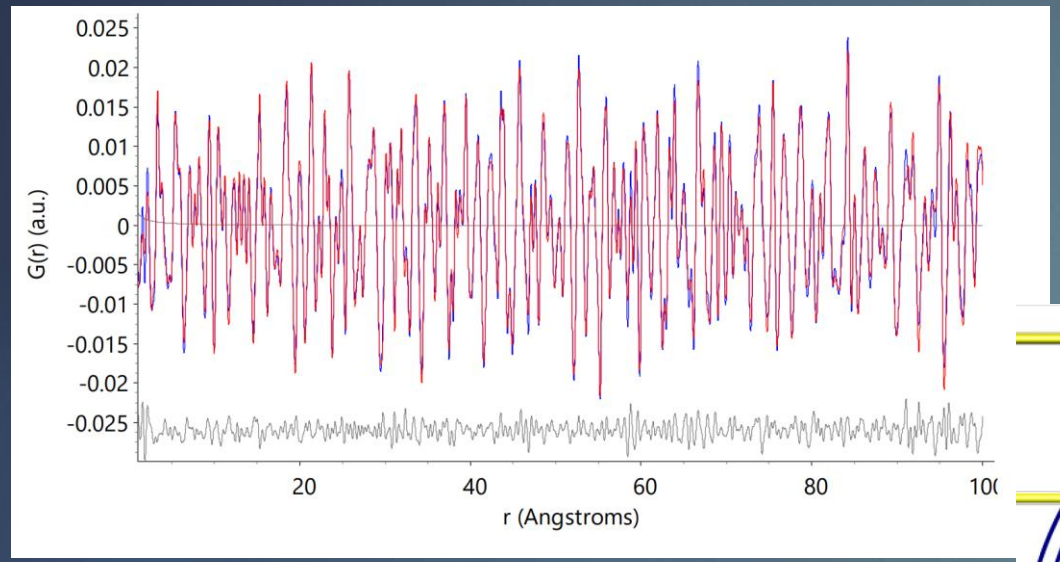
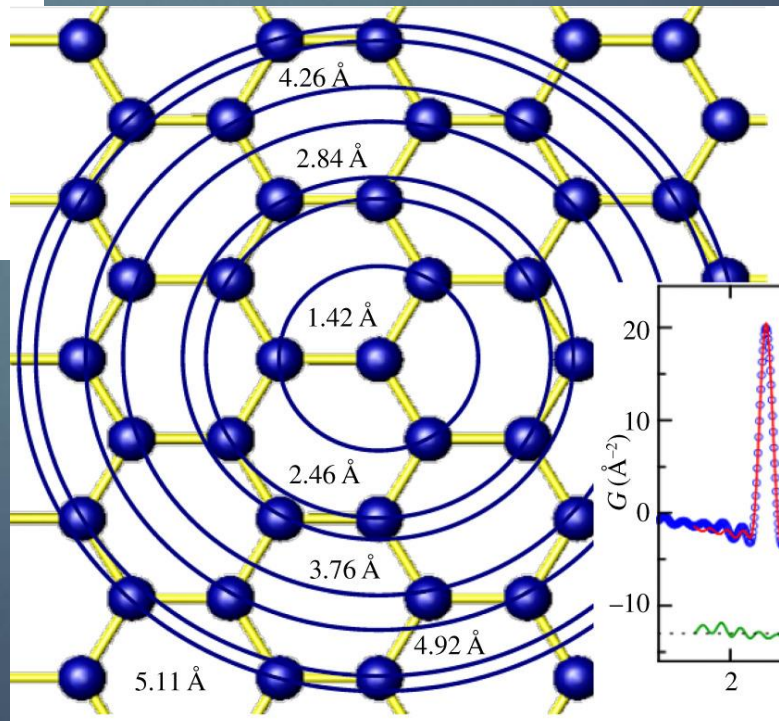


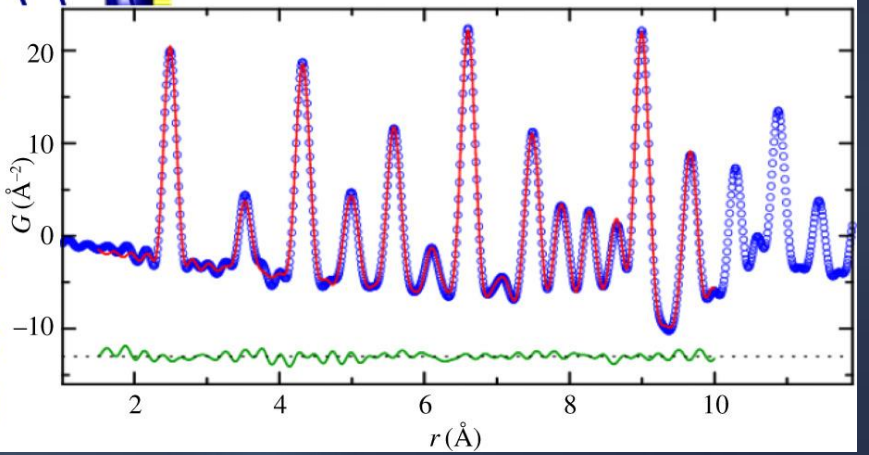
Figure 8
Cell parameters from (*a*) independent and (*b*) parametric fitting of 871 and 435 data sets; closed points, warming; open points, cooling. (*c*) The region close to the phase transition. Data taken on warming are represented by squares; cooling data by circles; open symbols represent independent fitting; closed symbols represent parametric fitting.

TOPAS: Pair Distribution Function





pair distribution function (PDF) gives the probability of finding an atom at a distance 'r' from a given atom.



Conclusions

A ZOO of software

Refinement schools

The Power of Habits

APPROACHES ARE LIMITED BY ONLY YOUR IMAGINATION

And by a bit of a knowledge on how to use tools…

Thx!