From mCIF to refinement: Using the Bilbao Crystallographic Server and fullprof to refine Cr_2WO_6 data
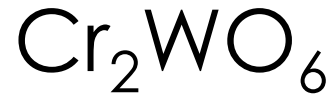
Stuart Calder

**Magnetic Structure Determination
from Neutron Diffraction Data
October 21-23, 2019**

U.S. DEPARTMENT OF ENERGY

Cr_2WO_6

- There is a Cr_2WO_6 example (data/notes) using representation analysis (SARAh/Basirep) and magnetic matrices (Fullprof).

- We will start from the same .cif file used in the other examples and use the same neutron data set. The k-vector has been previously found using k-search (see other Cr_2WO_6 example in this workshop).

- This example will use the Bilbao server and follow these steps:
  - Step 1: create an mcif file with MAXMAGN on the Bilbao Crystallographic Server.
  - Step 2: convert that mcif file into a .pcr file using mCIF2PCR.
  - Step 3: use the created .pcr file to fit the neutron data using Fullprof to determined the magnetic structure.

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Step 1: Creating mCIF file

- Go to Bilboa server: http://www.cryst.ehu.es/
- Select "Magnetic Symmetry and Applications" to open the drop-down menu

Step 1: Creating mCIF file

- Then select "MAXMAGN"

Step 1: Creating mCIF file

- **[1]** Need to have a propagation vector. This can be determined using k-search in fullprof (see other example for Cr_2WO_6). For Cr_2WO_6 it is (0,0,0).

- **[2]** Input the space group number of the crystal structure [136] (or choose from a list of all space groups)- *Note: if you have a cif file this step is not necessary.*

- **[3]** Check the box "Structure data of the paramagnetic phase will be included". This allows you to input a .cif file.

MAXMAGN: Maximal magnetic space groups for a given a propagation vector and resulting magnetic structural models

Step 1: Creating mCIF file

- Choose .cif file (crystal structure only).
  The one for this example is "Cr2WO6.cif"

- Then upload the file.

- If you don't have a cif file then have to fill out the details in "Option 2"

Parent paramagnetic structure cif file

Option 1: Please submit a structure file (CIF format):

Choose File | Cr2WO6.cif | Upload the file
Note: The space group of the cif file will supersede any previous one.

Option 2: Specify structure data by hand:

Space Group: 136 ($P4_2/mnm$)

Lattice parameters (Angstroms and degrees):
a=b=_____ c=_____ alpha=90 beta=90 gamma=90

Number of unique atomic positions: _____

Submit

Step 1: Creating mCIF file

- The paramagnetic phase information is displayed.
  - Select the magnetic atom(s). This case is Cr only.
  - Push Submit. This may take a few minutes to run the calculations.....

Parent phase structure data: Magnetic Atoms

Parent space group: 136 ($P4_2/mnm$)
Lattice parameters (Angstroms and degrees): a=4.57100, b=4.57100, c=8.85300, alpha=90., beta=90., gamma=90.

Atoms: Please select the magnetic ones

N	Atom name	Atom type	Wyckoff Position	Coordinates	Magnetic?
1	W1	W	2a	0.00000 0.00000 0.00000	☐
2	Cr1	Cr	4e	0.00000 0.00000 0.33300	☑
3	O1	O	4f	0.30800 0.30800 0.00000	☐
4	O2	O	8j	0.30800 0.30800 0.33300	☐

Submit

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Step 1: Creating mCIF file

- The possible magnetic space groups are displayed in grey

- To view magnetic structure and export mcif file click on "Show" in last column.

- We will choose the final allowed magnetic structure (#58.395) for this example, but all should be checked to ensure the final model is correct or to determine equivalent solutions.

Maximal magnetic space groups for the parent space group 136 ($P4_2/mnm$) and the propagation vector k = (0, 0, 0)

Maximal subgroups which allow non-zero magnetic moments for at least one atom are coloured

Step 1: Creating mCIF file

- **[1]** The red values under "Magnetic moment" show allowed spin directions. In this case the spins can only be along x or y.

- Try value along x.

- **[2]** Then click "Export to MCIF" file/Visualize

Magnetic Structure

Selected magnetic space group: 12- *Pn'nm* (#58.395)

Setting of the parent group

Parent space group 136 (*P4₂/mnm*)

Lattice parameters: a=4.57100, b=4.57100, c=8.85300, alpha=90., beta=90., gamma=90.

[Go to setting standard (**a, b, c** ; 0, 0, 0)]
[Go to an alternative setting]

2

Export data to MCIF file/Visualize | Go to a subgroup

Atomic positions, Wyckoff positions and Magnetic Moments

N	Atom	New WP	Multiplicity	Magnetic moment	Values of M_x, M_y, M_z
1	W1 W 0.00000 0.00000 0.00000	$(0,0,0 \mid 0,0,0)$ $(1/2,1/2,1/2 \mid 0,0,0)$	2	-	-
2	Cr1 Cr 0.00000 0.00000 0.33300	$(0,0,z \mid m_x,m_y,0)$ $(1/2,1/2,z+1/2 \mid -m_x,m_y,0)$ $(1/2,1/2,-z+1/2 \mid m_x,-m_y,0)$ $(0,0,-z \mid -m_x,-m_y,0)$	4	$(M_x,M_y,0)$	$M_x = 1$ $M_y = 0.00000$
3	O1 O 0.30800 0.30800 0.00000	$(x,x,0 \mid 0,0,m_z)$ $(-x,-x,0 \mid 0,0,-m_z)$ $(-x+1/2,x+1/2,1/2 \mid 0,0,m_z)$ $(x+1/2,-x+1/2,1/2 \mid 0,0,-m_z)$	4	-	-
4	O2 O 0.30800 0.30800 0.33300	$(x,x,z \mid m_x,m_y,m_z)$ $(-x,-x,z \mid m_x,m_y,-m_z)$ $(-x+1/2,x+1/2,z+1/2 \mid -m_x,m_y,m_z)$ $(x+1/2,-x+1/2,z+1/2 \mid -m_x,m_y,-m_z)$ $(-x+1/2,x+1/2,-z+1/2 \mid m_x,-m_y,m_z)$ $(x+1/2,-x+1/2,-z+1/2 \mid m_x,-m_y,-m_z)$ $(x,x,-z \mid -m_x,-m_y,m_z)$ $(-x,-x,-z \mid -m_x,-m_y,-m_z)$	8	-	-

1

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Step 1: Creating mCIF file

- The mcif file is displayed.

- **[1]** This can be downloaded by clicking on "bcs_file.mcif"

- **[2]** Magnetic structure can also be visualized by clicking "Submit to MVISUALIZE"

mCIF file of the structure

2

Submit this mcif file to MVISUALIZE for 3D visualization of the estructure using Jmol | Submit to MVISUALIZE

1

Download mCIF file: bcs_file.mcif

[The preview text below is non-editable, only copy-allowed]

```
#\#CIF_2.0
# Created by the Bilbao Crystallographic Server
# http://www.cryst.ehu.es
# Date: 19/06/2018 04:11:35
# Cr2WO6.cif

data_5yOhtAoR
_audit_creation_date            2018-06-19
_audit_creation_method          "Bilbao Crystallographic Server"

_citation_journal_abbrev        ?
_citation_journal_volume        ?
_citation_page_first            ?
_citation_page_last             ?
_citation_article_id            ?
_citation_year                  ?
_citation_DOI                   ?

loop_
_citation_author_name
?

_atomic_positions_source_database_code_ICSD  ?
_atomic_positions_source_other               ?

_transition_temperature  ?
_experiment_temperature  ?

loop_
_irrep_id
_irrep_dimension
```

Step 1: Creating mCIF file

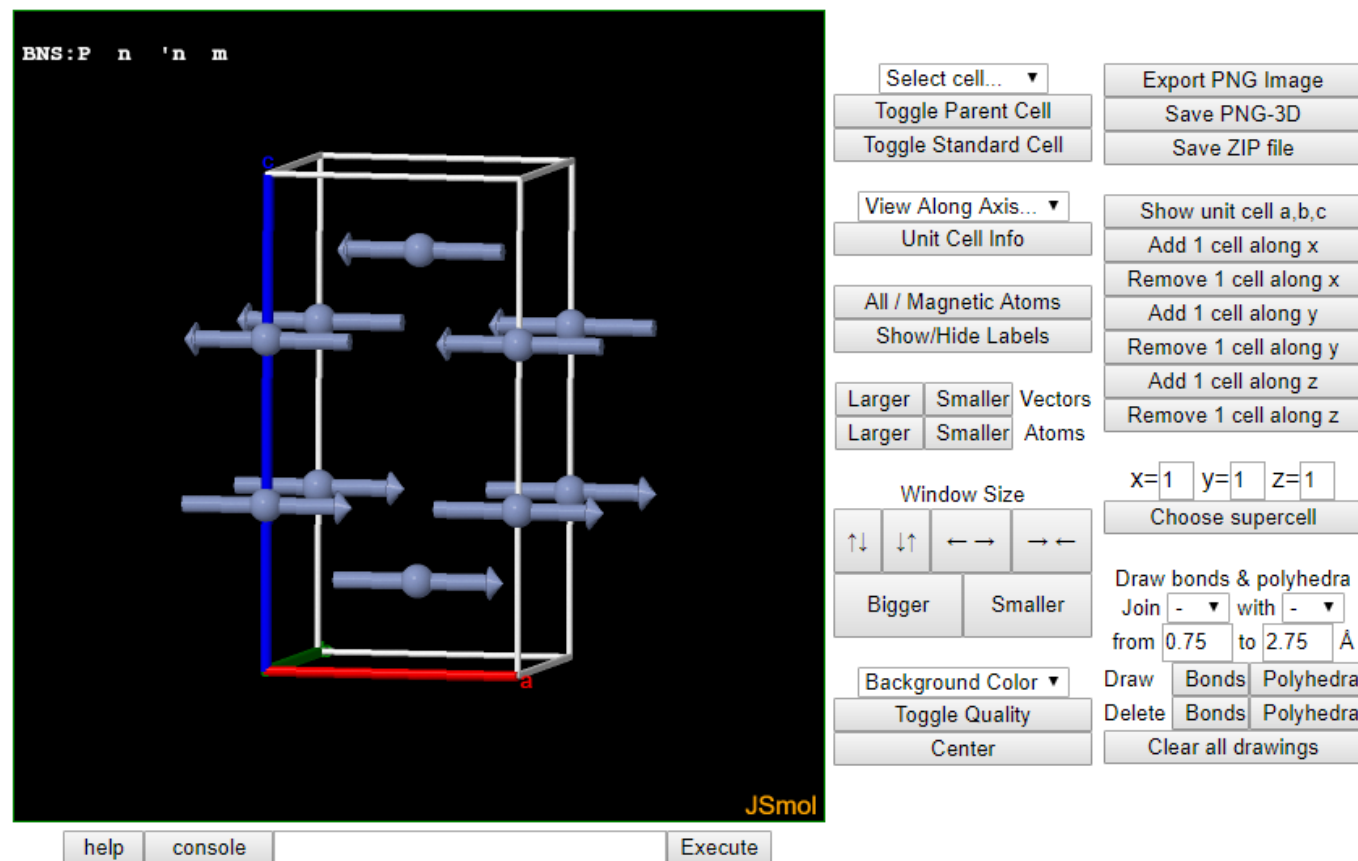- MVISUALIZE lets you quickly check magnetic structure.

- But we will use the downloaded mcif to fit data using fullprof.

  We now need to go to Step 2

Step 2: Creating a pcr from an mcif file

- Go back to the main page on server and open mCIF2PCR

Step 2: Creating a pcr from an mcif file

mCIF2PCR: Transformation from mCIF to PCR format (FullProf).

mCIF_to_PCR

Given a magCIF file, it produces a PCR template that can be used as input for FullProf (the program mCIF_to_PCR (FullProf) is used). By default the provided PCR file is intended for a simulation. The file can be then modified by hand for a refinement of the model.

Choose a structure file (mCIF format):

Choose File   bcs_file_21132.mcif   Convert

1   **2**

- **[1]** Choose the mcif we just created through maxmagn

- **[2]** Click convert

The file has been successfully converted.

Click to download it

- This will convert the file and "Click to download it" will download the .pcr file

- We will use this .pcr file in Step 3. Put it in the same folder as the data file "Cr2WO6_T4K.dat"

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Step 3: Refining the magnetic structure with Fullprof

- Pcr file created contains a single phase with crystal structure and magnetic ions.

- The pcr file calculates the pattern based on default values.

- We need to change the defaults in the .pcr file in the same way done for the examples created from a .cif file.

- To do this we work down the Tabs in the GUI (General/Patterns/Phases/Refinement) and/or edit the text file.

- The values will depend on the instrument the data was collected on.
  - This case is for HB-2A at HFIR measured with the 2.41 A wavelength.

Step 3: Refining the magnetic structure with Fullprof

- Select the format of the data file Fullprof should refine.

- Patterns → Data file/Peak Shape → X,Y,SIGMA (XYDATA)
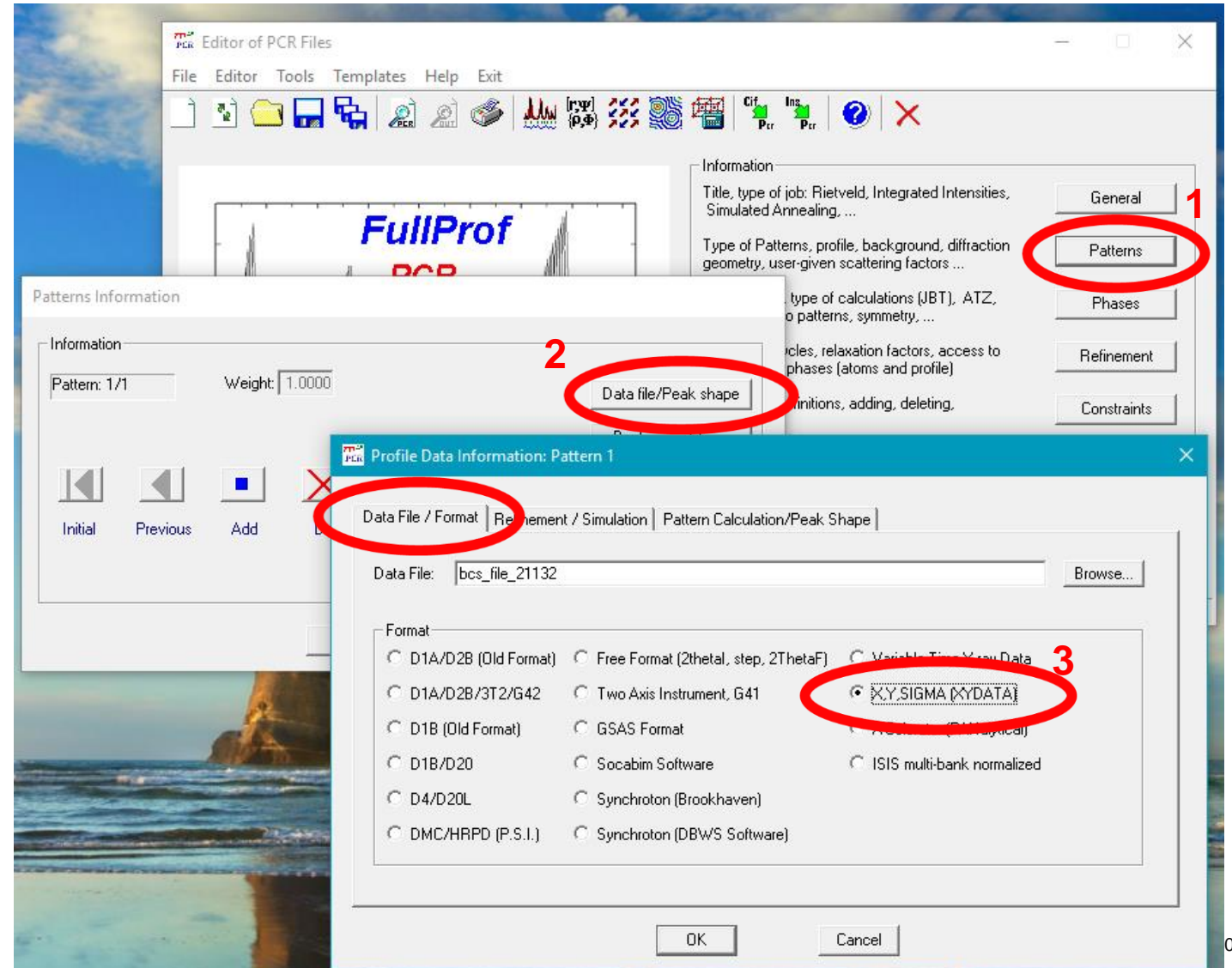
Step 3: Refining the magnetic structure with Fullprof

- Patterns → Data file/Peak Shape →Refinement/Simulation

- **[3]** Select Neutron – CW

- **[4]** Change wavelength to user defined and 2.41 A

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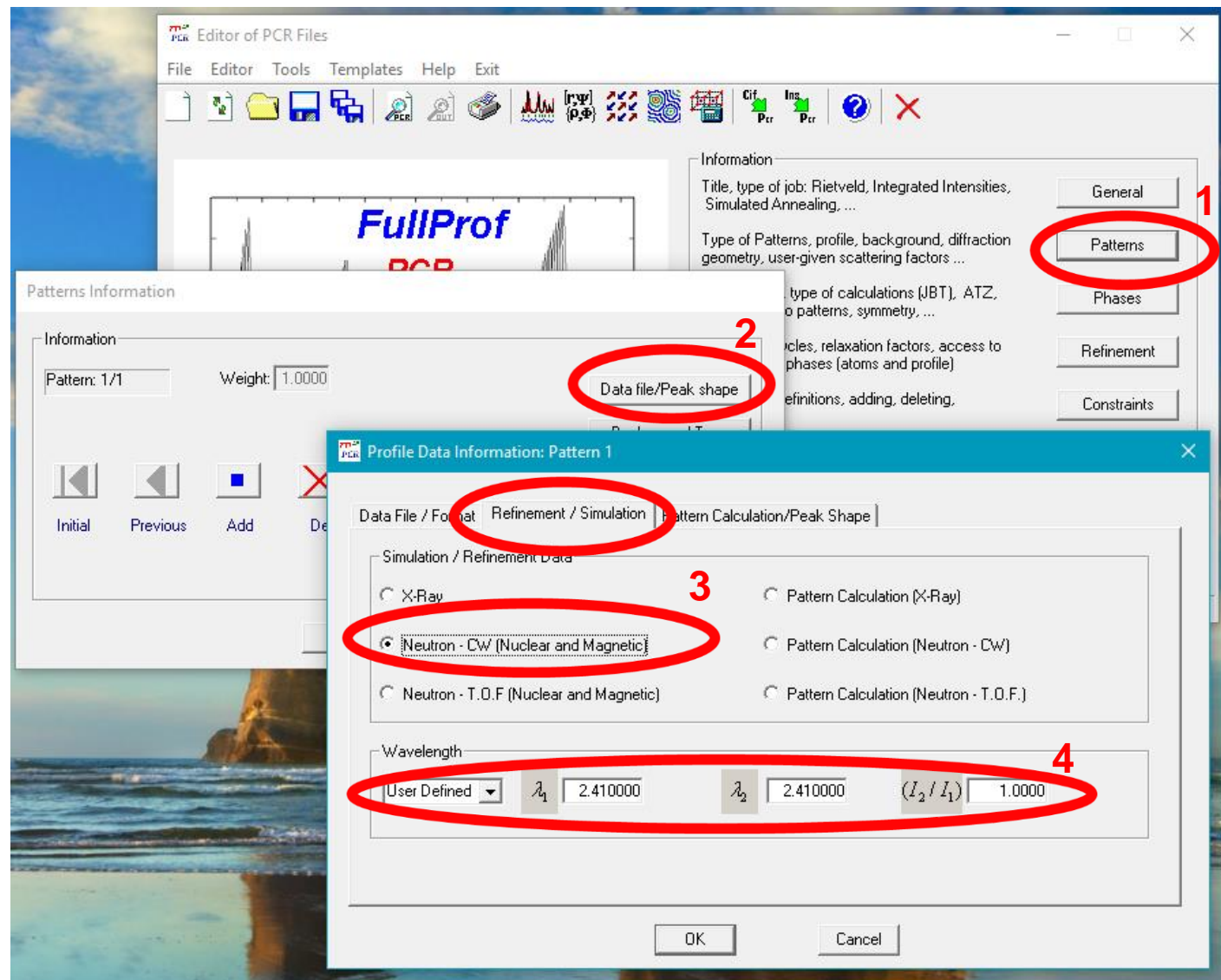
Step 3: Refining the magnetic structure with Fullprof

- Patterns→ Background Type →6-coefficient
- Select background type

...nation Workshop, ORNL 2019
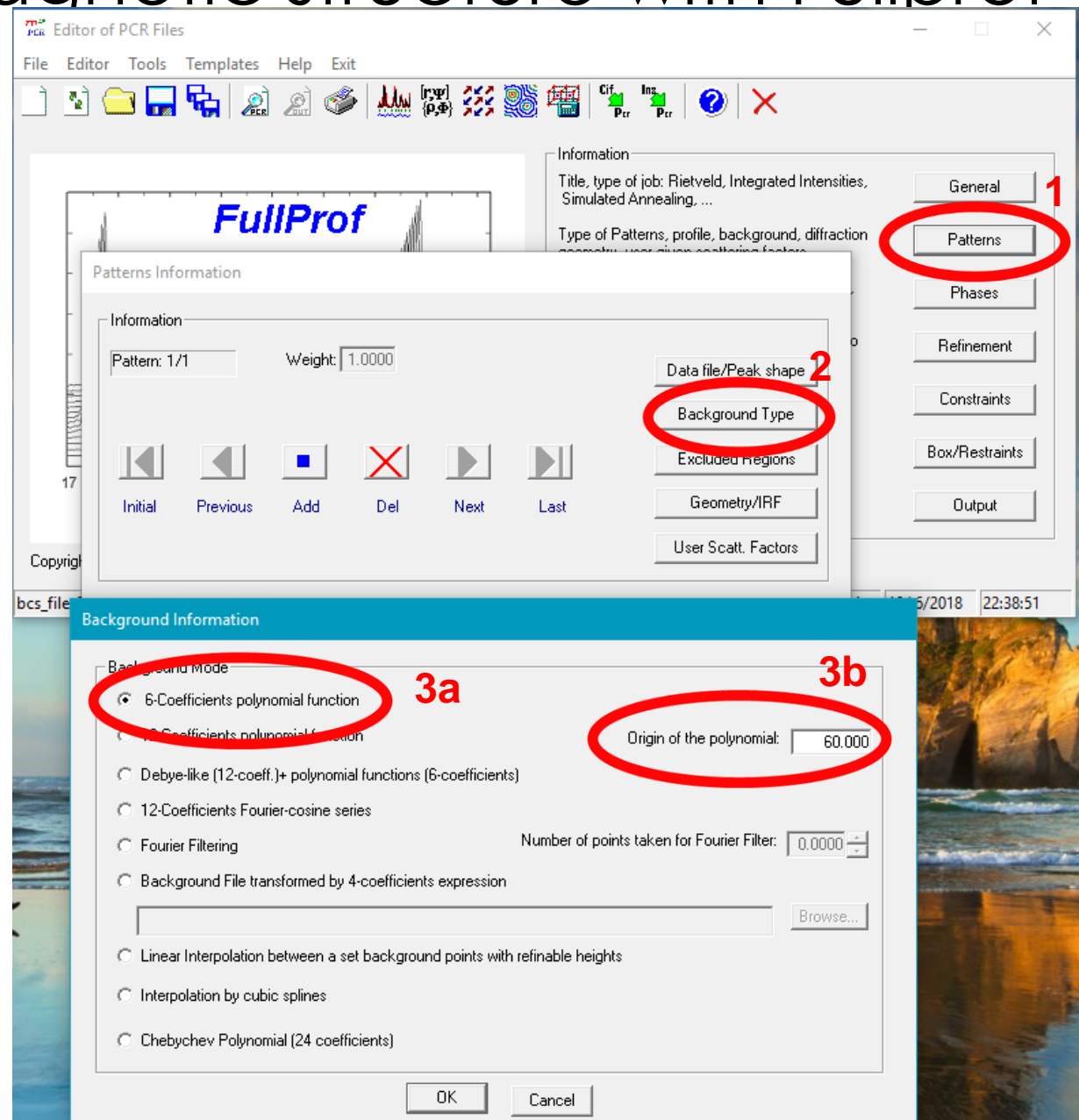
Step 3: Refining the magnetic structure with Fullprof

- Make phase contribute to refinement.

- **[1]** Phases➔ **[2]** Contribution to Patterns➔ **[3]** Neutron (constant wavelength)

- Peak shape should be "Thompson-Cox…."
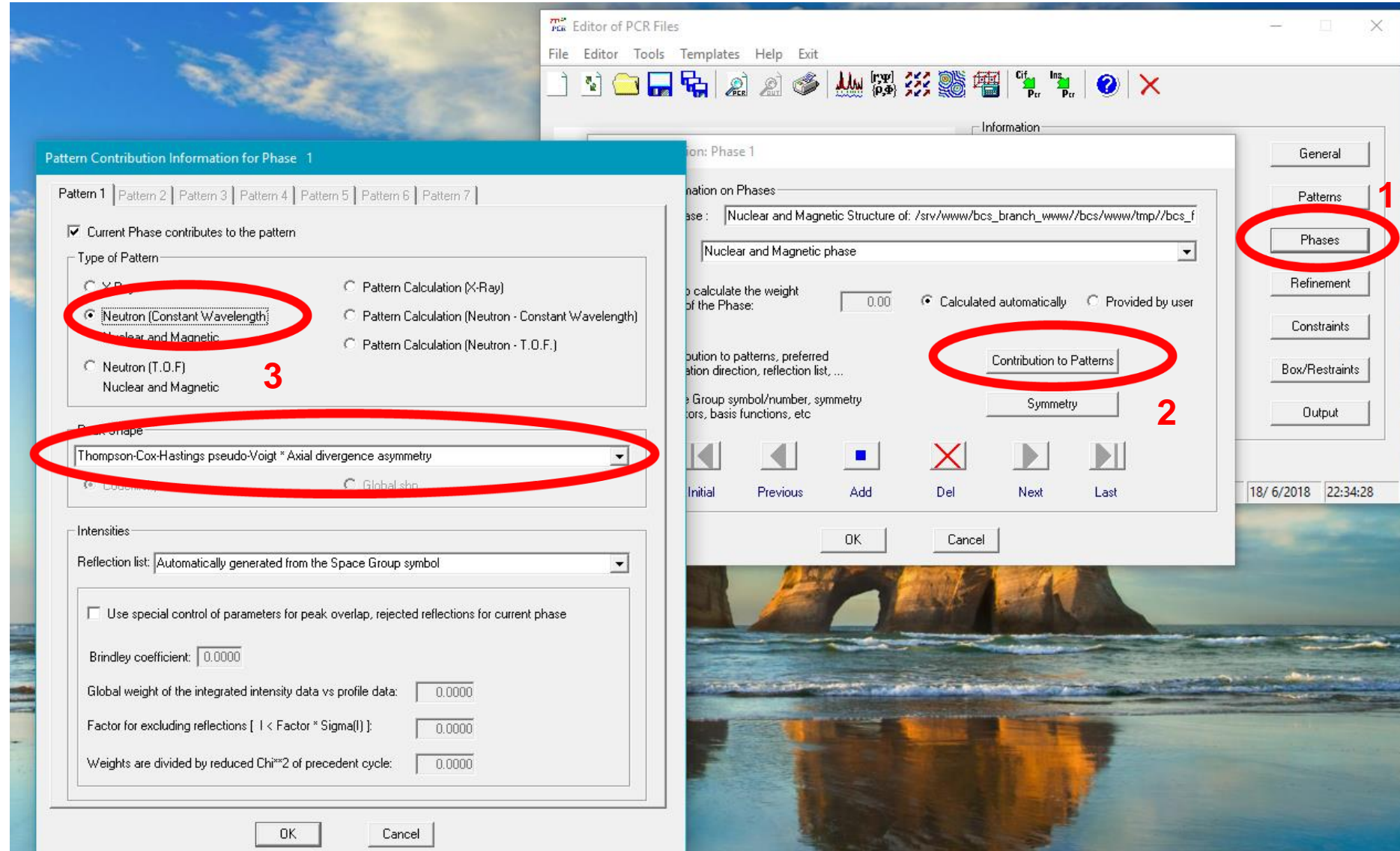
Step 3: Refining the magnetic structure with Fullprof

- Setting starting values for refinements
- Starting background values

Step 3: Refining the magnetic structure with Fullprof

- Instrumental zero value.

- We know this from nuclear refinement done in previous example in this school.
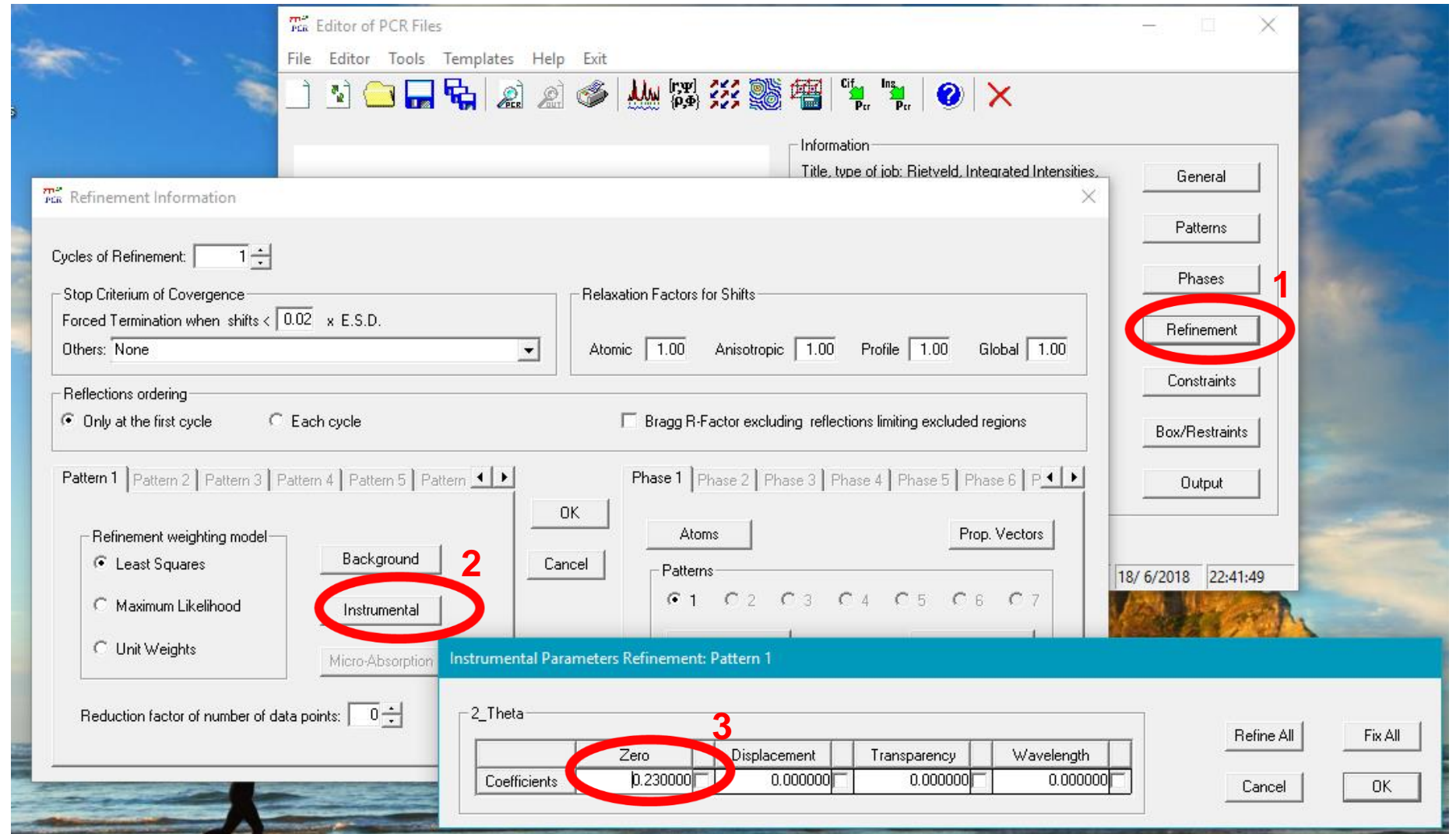
Step 3: Refining the magnetic structure with Fullprof

- Update "Scale" and "Profile" parameters U,V,W,X to those shown

Step 3: Refining the magnetic structure with Fullprof

- In "Refinement " → "atoms" input thermal parameters (0.3). [1,2,3]

- Note that Re(x) and Re(y) are set to refine.

- This is a default in files from mcif to pcr that we will turn off in next slide.

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Step 3: Refining the magnetic structure with Fullprof

- Open pcr text file.

- Delete "VARY mxmymz" to turn off automatically refining moments.

- Turn off the refinement labels 11.0 and 21.0.

Delete this to stop auto refinements of moments

Step 3: Refining the magnetic structure with Fullprof

- Change to values circled to set up pcr file for refinement of crystal structure only first.

- **[1]** NCY → number of refinement cycles

- **[2]** Refine background

- **[3]** Make values under MCR2 zero to add no moment (only crystal structure)

- **[4]** Refine scale, **[5]** a,b,c lattice constants

- Set peak profile values for **[6]** U,V,W,X and **[7]** S_L, D_L. Do not refine these yet since lattice constants may be off (i.e. peak positions not correct).
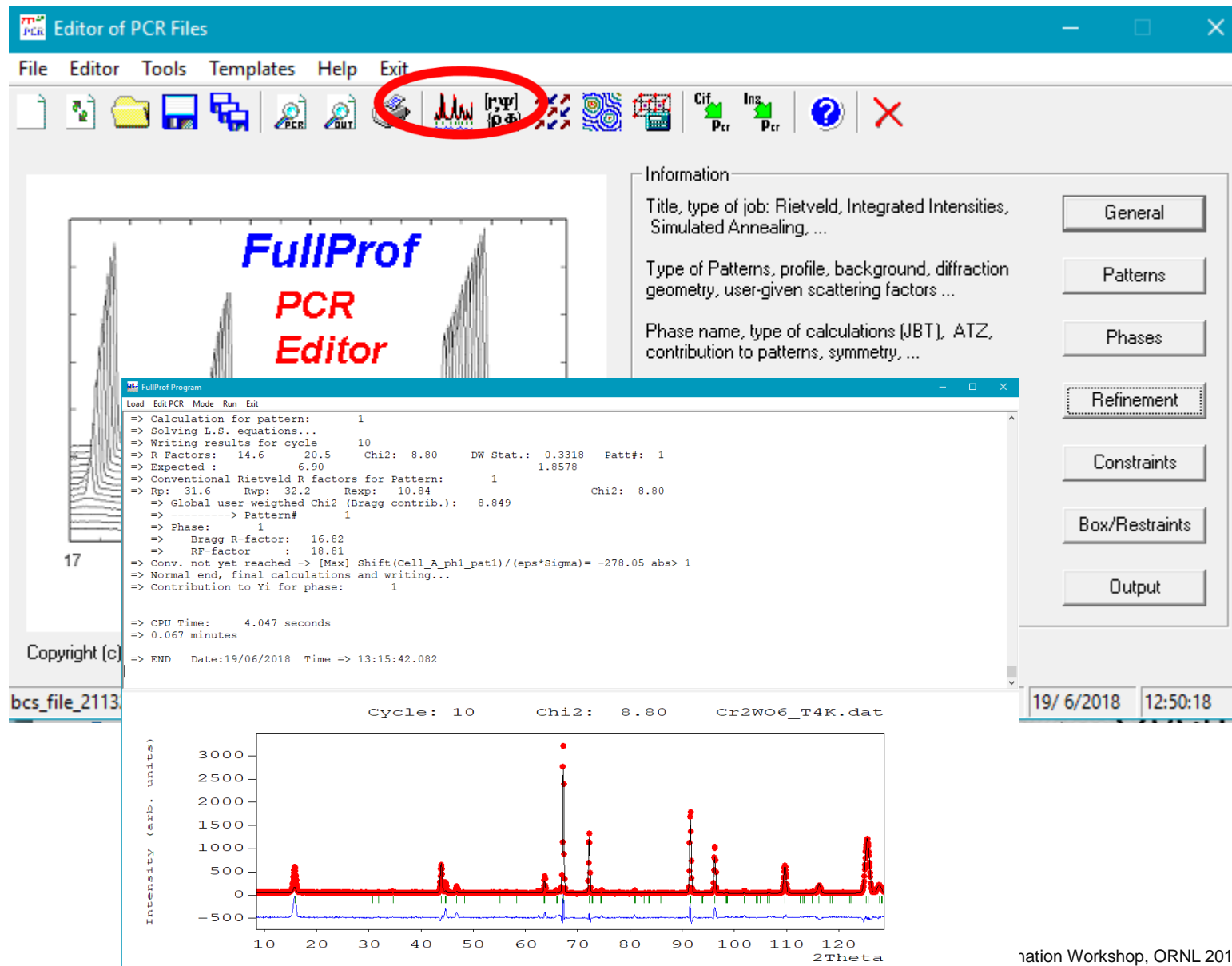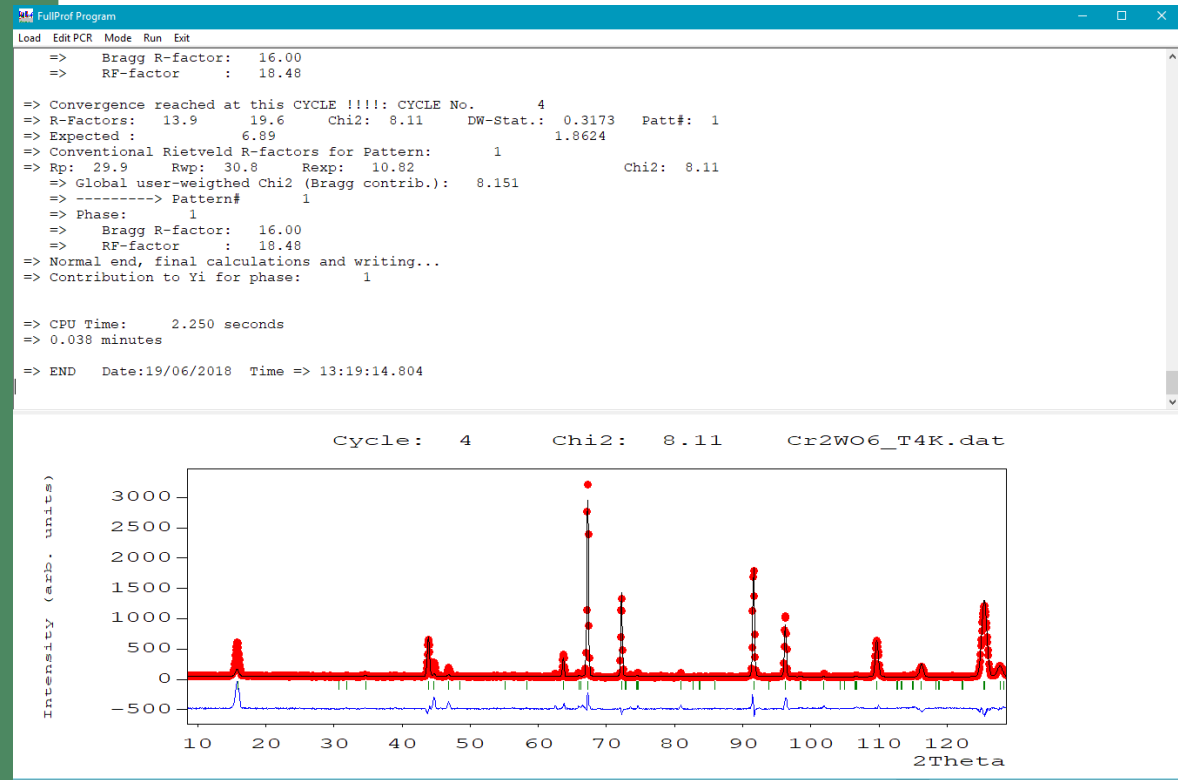
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Step 3: Refining the magnetic structure with Fullprof

- Run the refinement.

- Select the "Cr2WO6_T4K.dat" neutron data file.

- Refinement captures most of the data well.

Step 3: Refining the magnetic structure with Fullprof

- **[1]** Select the U,V,W,X to refine
- This improves refinement and leads to convergence.


```
!-------------------------------------------------------------------
! Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:    0.00
!-------------------------------------------------------------------
Nuclear and Magnetic Structure of: /srv/www/bcs_branch_www//bcs/www/tmp//bcs_fil
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
   4   0   0 0.0 0.0 1.0  10   0   2   0   0      767.677    0   7   0
!
Pn'nm  number:58.395       <--Magnetic Space group symbol (BNS symbol & number)
Transform to standard:
Parent Space Group:        IT_number:  136
Transform from Parent:
! Nsym   Cen  N_Clat N_Ant
    8     0     0     0
!
! Symmetry operators
  1 x,y,z,+1
  2 -x,-y,-z,-1
  3 x,y,-z,+1
  4 -x,-y,z,-1
  5 -x+1/2,y+1/2,-z+1/2,-1
  6 x+1/2,-y+1/2,-z+1/2,+1
  7 x+1/2,-y+1/2,z+1/2,+1
  8 -x+1/2,y+1/2,z+1/2,-1
!
!Atom   Typ     Mag Vek      X         Y         Z        Biso      Occ     N_type  Spc/Fftype
!        Rx       Ry        Rz        Ix        Iy        Iz      MagPh  / Line below:Codes
!        beta11   beta22    beta33    beta12    beta13    beta23  / Line below:Codes
W1     W       1  0     0.00000   0.00000   0.00000   0.30000   0.25000    0    0 #
                       0.00      0.00      0.00      0.00      0.00
Cr1    MCR2    1  0     0.00000   0.00000   0.33300   0.30000   0.50000    1    0 #
                       0.00      0.00      0.00      0.00      0.00
       1.00000  0.00000   0.00000   0.00000   0.00000   0.00000   0.00000 <-MagPar
             0    0.00      0.00      0.00      0.00      0.00      0.00
O1     O       1  0     0.30800   0.30800   0.00000   0.30000   0.50000    0    0 #
                       0.00      0.00      0.00      0.00      0.00
O2     O       1  0     0.30800   0.30800   0.33300   0.30000   1.00000    0    0 #
                       0.00      0.00      0.00      0.00      0.00
!-------> Profile Parameters for Pattern #  1
! Scale       Shape1     Bov      Str1      Str2      Str3    Strain-Model
  1.5720      0.00000    0.00000   0.00000   0.00000   0.00000    0
    31.00000    0.000      0.00      0.000     0.000     0.000
     U         V         W         X          Y         GauSiz   LorSiz Size-Model
  0.440000  -0.700000  0.350000  0.040000   0.000000  0.000000  0.000000    0
     1         1         1         1         0.000     0.000     0.000
!      a         b         c       alpha      beta      gamma     #Cell Info
  4.582274  4.586748  8.856397  90.000000  90.000000  90.000000   #
  61.00000  31.00000  51.00000   0.00000    0.00000    0.00000
! Pref1     Pref2     Asy1      Asy2      Asy3      Asy4      S_L       D_L
  1.00000   0.00000   0.00000   0.00000   0.00000   0.00000   0.03300   0.03300
  0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00
! 2Th1/TOF1   2Th2/TOF2  Pattern to plot
    8.500      128.694        1
```

FullProf Program

Load Edit PCR Mode Run Exit

```
=>    Bragg R-factor:   16.00
=>    RF-factor    :   18.48
=> Convergence reached at this CYCLE !!!!: CYCLE No.     4
=> R-Factors:  13.9     19.6    Chi2:  8.11    DW-Stat.:  0.3173   Patt#: 1
=> Expected :       6.89                         1.8624
=> Conventional Rietveld R-factors for Pattern:    1
=> Rp: 29.9    Rwp: 30.8    Rexp:  10.82              Chi2:  8.11
   => Global user-weigthed Chi2 (Bragg contrib.):   8.151
   => ---------> Pattern#     1
   => Phase:    1
   =>    Bragg R-factor:   16.00
   =>    RF-factor    :   18.48
=> Normal end, final calculations and writing...
=> Contribution to Yi for phase:     1

=> CPU Time:    2.250 seconds
=> 0.038 minutes

=> END   Date:19/06/2018  Time => 13:19:14.804
```

Cycle: 4   Chi2:   8.11   Cr2WO6_T4K.dat

Step 3: Refining the magnetic structure with Fullprof

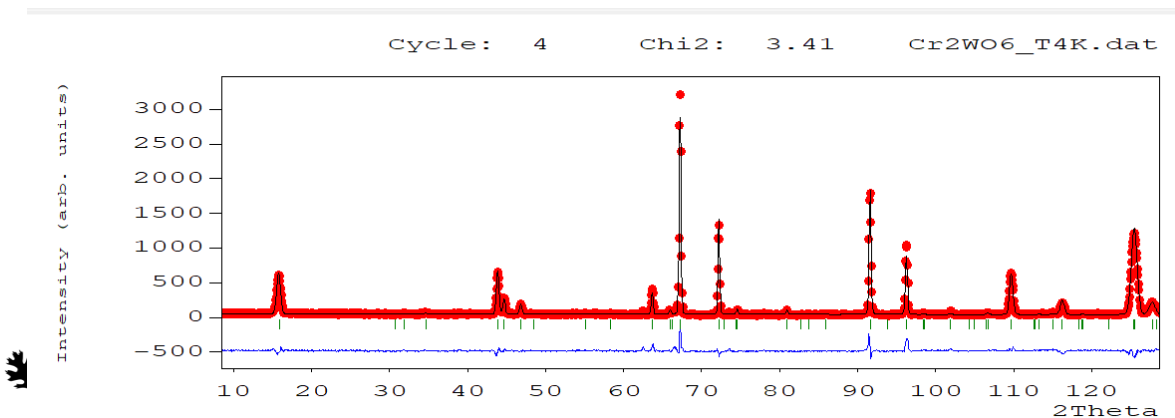- **[1]** Can now select the magnetic moment to refine. (Either in GUI or text file)

- All peaks now fit well.

Step 3: Refining the magnetic structure with Fullprof

- Check magnetic structure in .fst file

- Check moment size is reasonable (~2μ_B/Cr)

- Refinement can be further improved by altering the thermal parameters, asymmetry, more background, atomic positions, zero, etc.