OAK RIDGE National Laboratory

Magnetic Structure Workshop

# Single crystal neutron diffraction

Huibo Cao

Neutron Scattering Division, ORNL

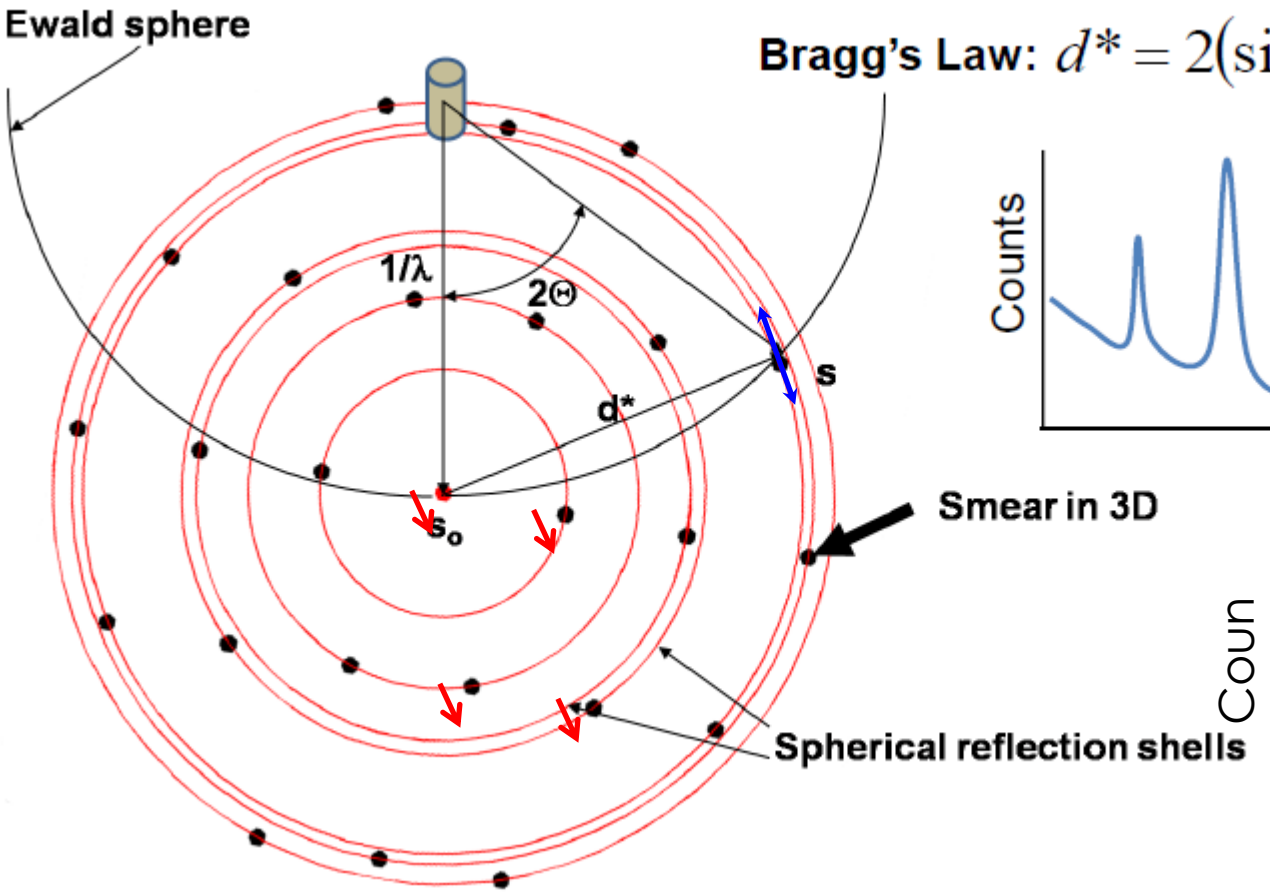
Oak Ridge National Laboratory

ORNL is managed by UT-Battelle, LLC for the US Department of Energy

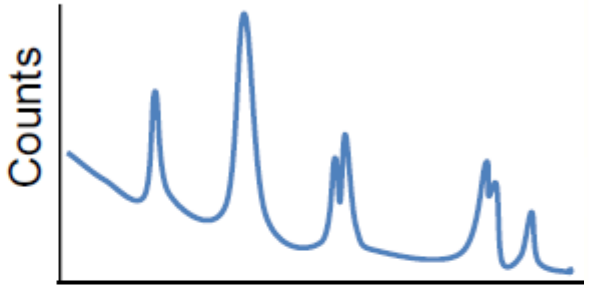
U.S. DEPARTMENT OF ENERGY

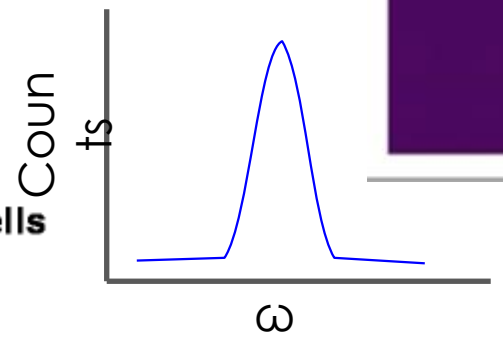
Oct. 3- Oct.7, 2022

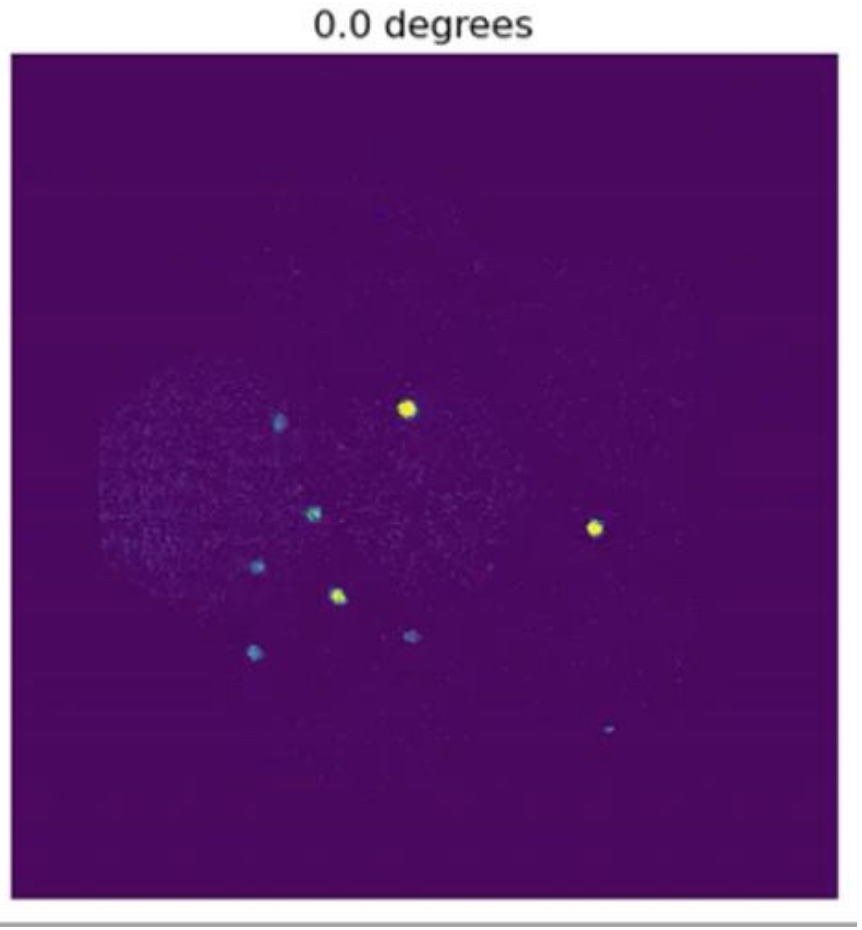
# Single Crystal Diffraction




Bragg's Law: $d^* = 2(\sin\theta)/\lambda$




Propagation vector ***k***?

# Single Crystal Diffraction

**Advantage:**

- More detailed information by measuring well separated Bragg peaks in 3D reciprocal space — **Magnetic form factors**
- **Less samples – mg VS g**
- Larger molecules and unit cells ---- **complex magnetic structures**
- **Less neutron absorption** due to small size, no isotope needed, such as for H, Li, even Eu, Sm, et. al. neutron "block" elements. Intensities corrected by applying the proper absorption correction, like the single crystal X-ray
- **Unambiguously determine the k-vector** –superlattice or satellite peaks (commensurate and incommensurate), dimensionality of scattering (rods, planes, etc.)

**Disadvantage:**

- Need to grow a single crystal
- Data collection can be more time consuming
- Extinction, domain, twining

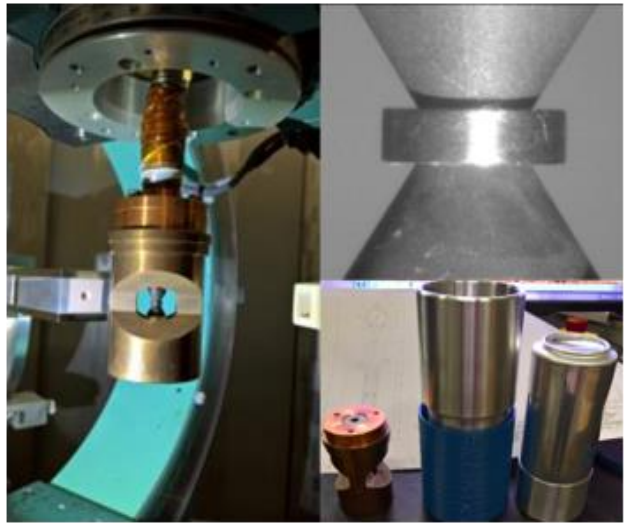
**Always GOOD to combine both X-ray/neutron powder and single crystal diffraction!**

# DEMAND instrument (multi-modes)

1) four-circle mode

2) two-axis mode

Extreme sample environment

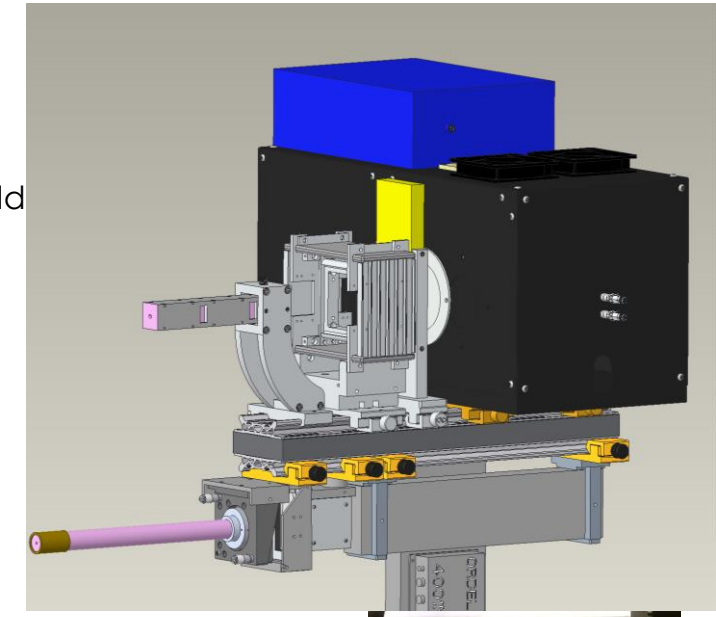


Ultra-low temperature
***T* ~ 0.05 to 700 K**

High magnetic field
***H* ~ -6 to 6 T (vertical)**

High pressure
***P* ~ 0 to 10 GPa**

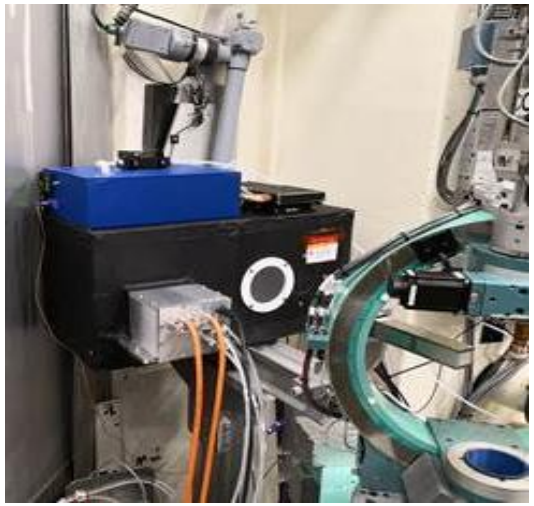
Electric field
***E* ~ 0-$10^4$ voltage/cm**

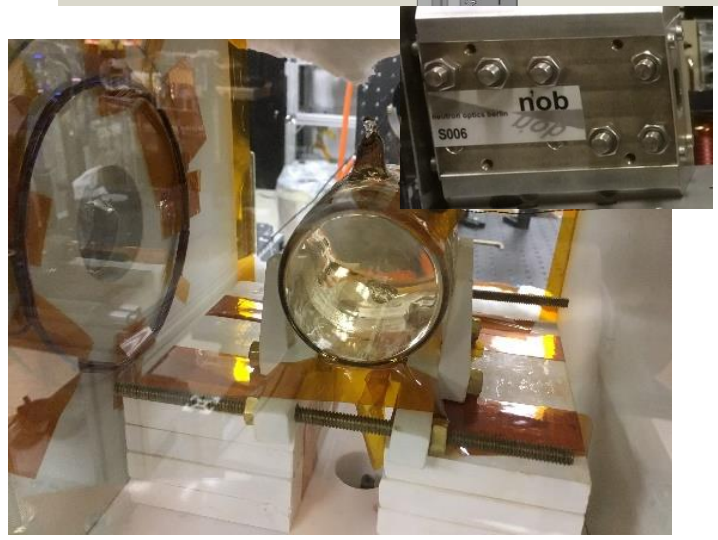


Large area detector $50^0$ (hori) x $50^0$(vert), 3(1) columns position-sensitive but magnetic field insensitive

Beam:
a) High Flux: 2.2 x $10^7$ n/$cm^2$s
b) High Resolution: δd/d =δQ/Q~0.2%

i) Unpolarized neutrons
ii) Polarized neutrons by S-bender SM and He-3 polarizer





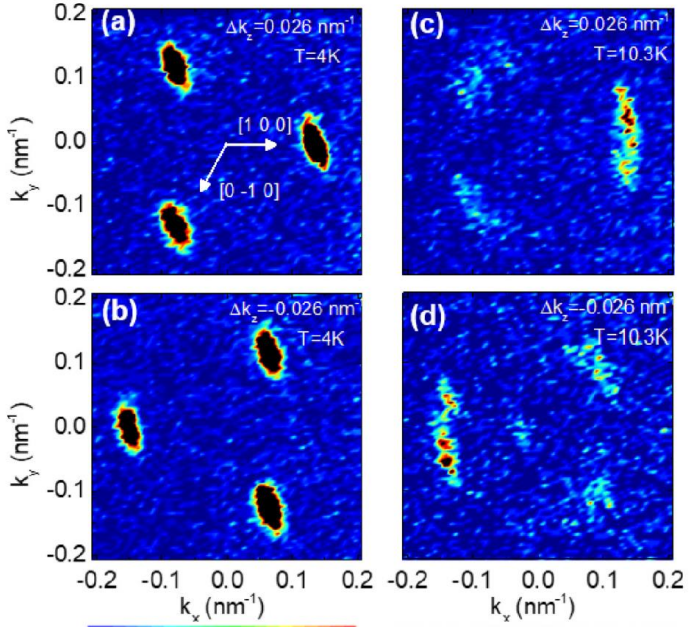



OAK RIDGE National Laboratory

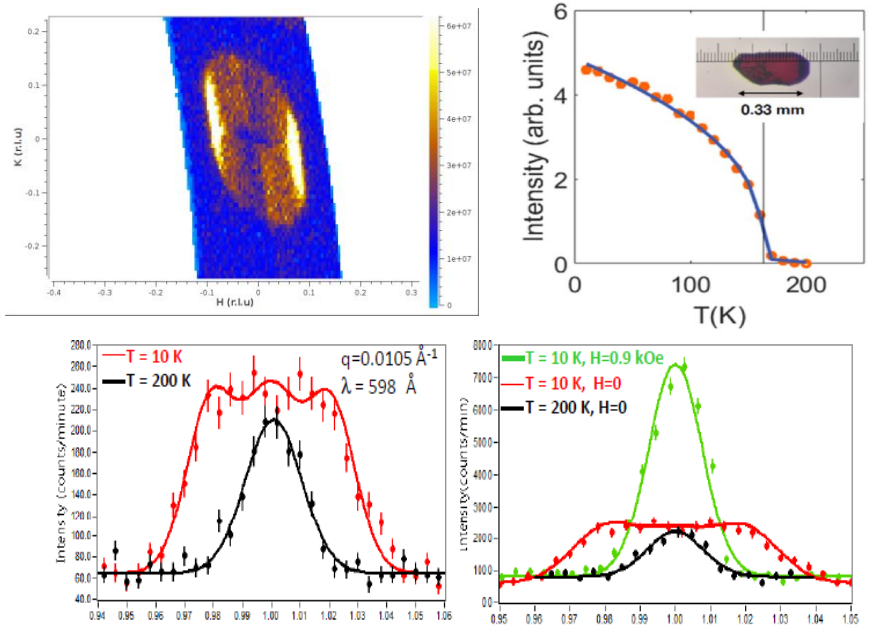
Cao H.B., Chakoumakos B.C., Andrews K.M., Wu Y., Riedel R.A., Hodges J.P., Zhou W., Gregory R., Haberl B., Molaison J.J., Lynn G.W., "DEMAND, a Dimensional Extreme Magnetic Neutron Diffractometer at the High Flux Isotope Reactor", *Crystals*, **9,** 1, 5 (2019).

# Capabilities of DEMAND at HB-3A HFIR

- Complex magnetism and structure
- New materials and phenomena
- Order parameter and phase transitions
- Long/short range magnetic order, local magnetic susceptibility magnetic anisotropy
- Extreme condition tuning

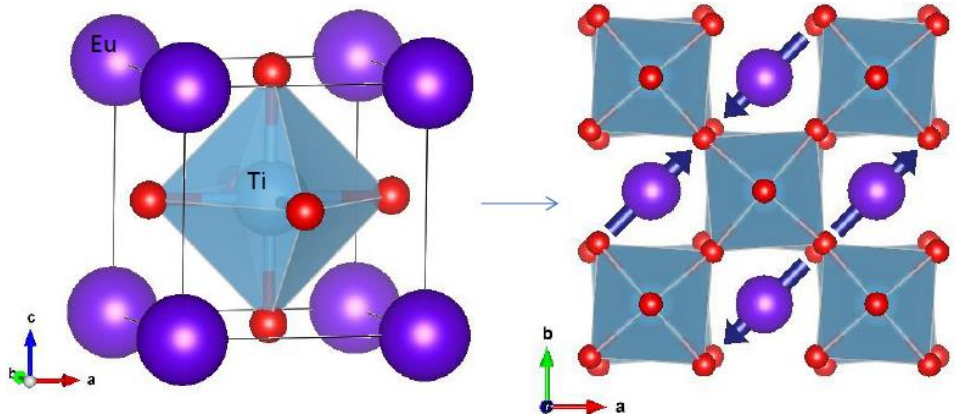


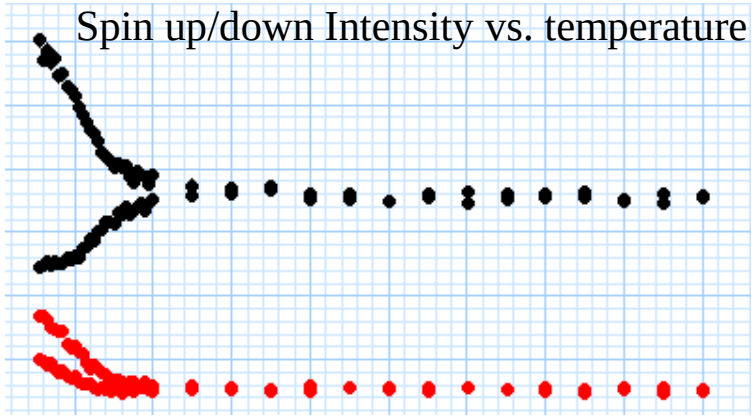

*Physical Review Materials* , **4,** 064419 (2020).

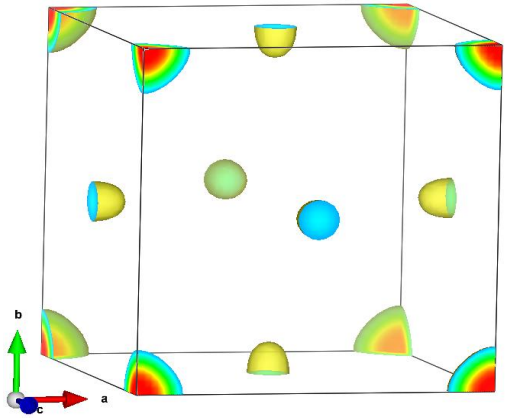



*Physical Review B,* **101,** 184417 (2020).

## Polarized neutron diffraction



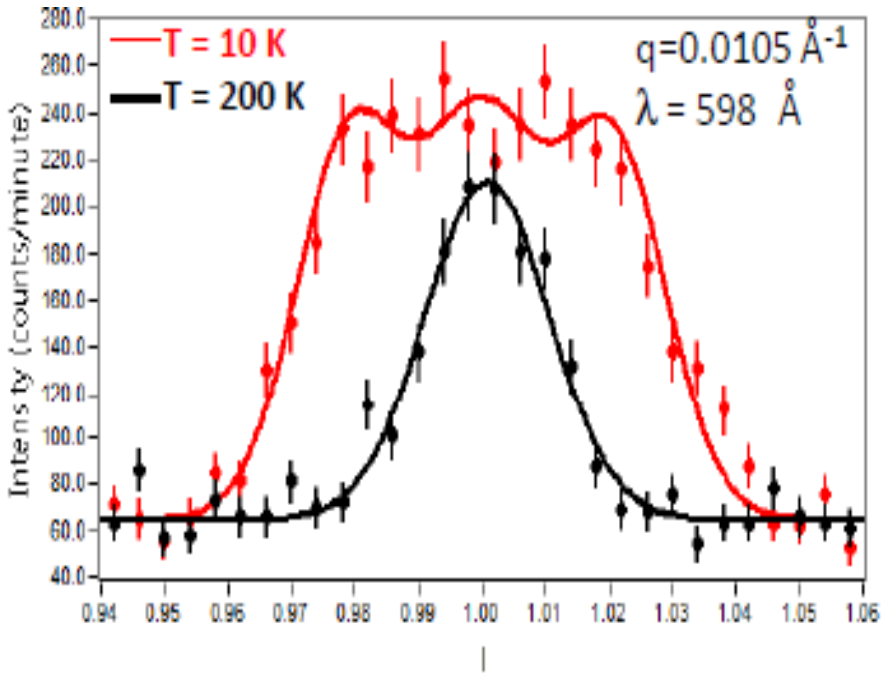



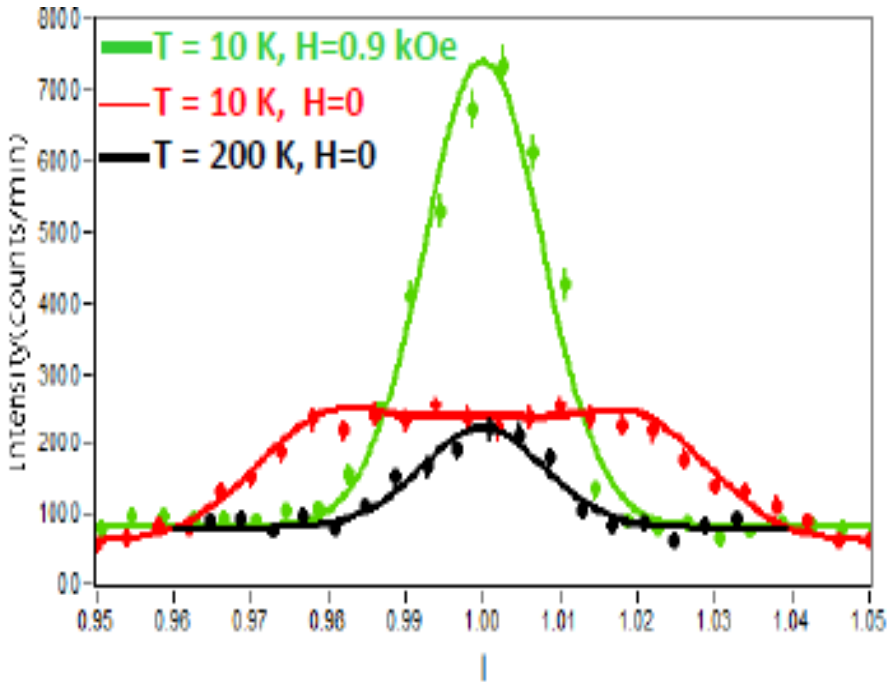



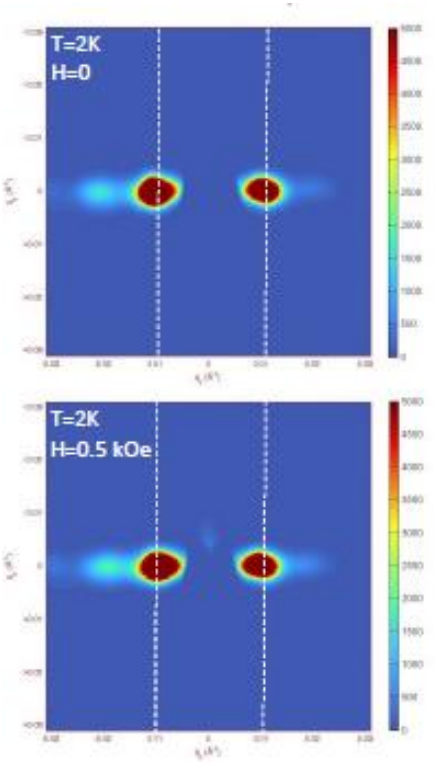
Weak ferromagnetism, local magnetic susceptibility, and magnetization density map

# Single Crystal Diffraction

## High Q-resolution



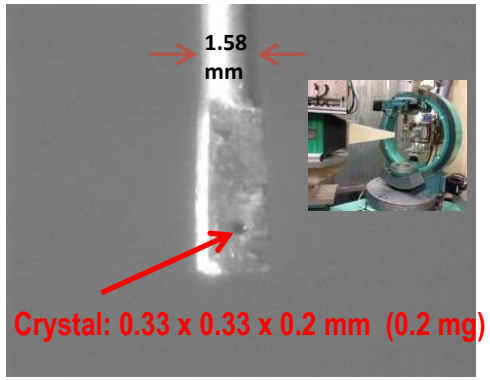



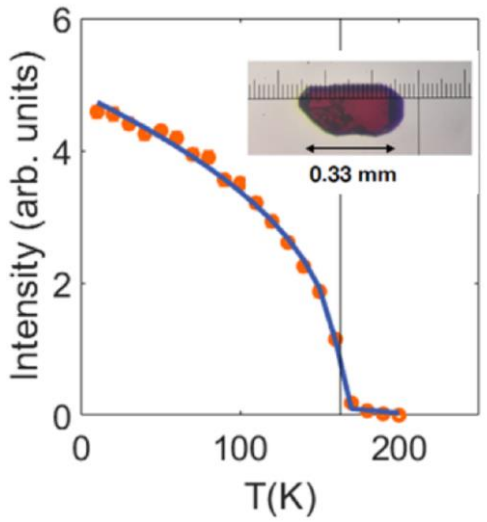




Thermal neutrons ==========Cold neutrons==========➔ SANS

# Single Crystal Diffraction

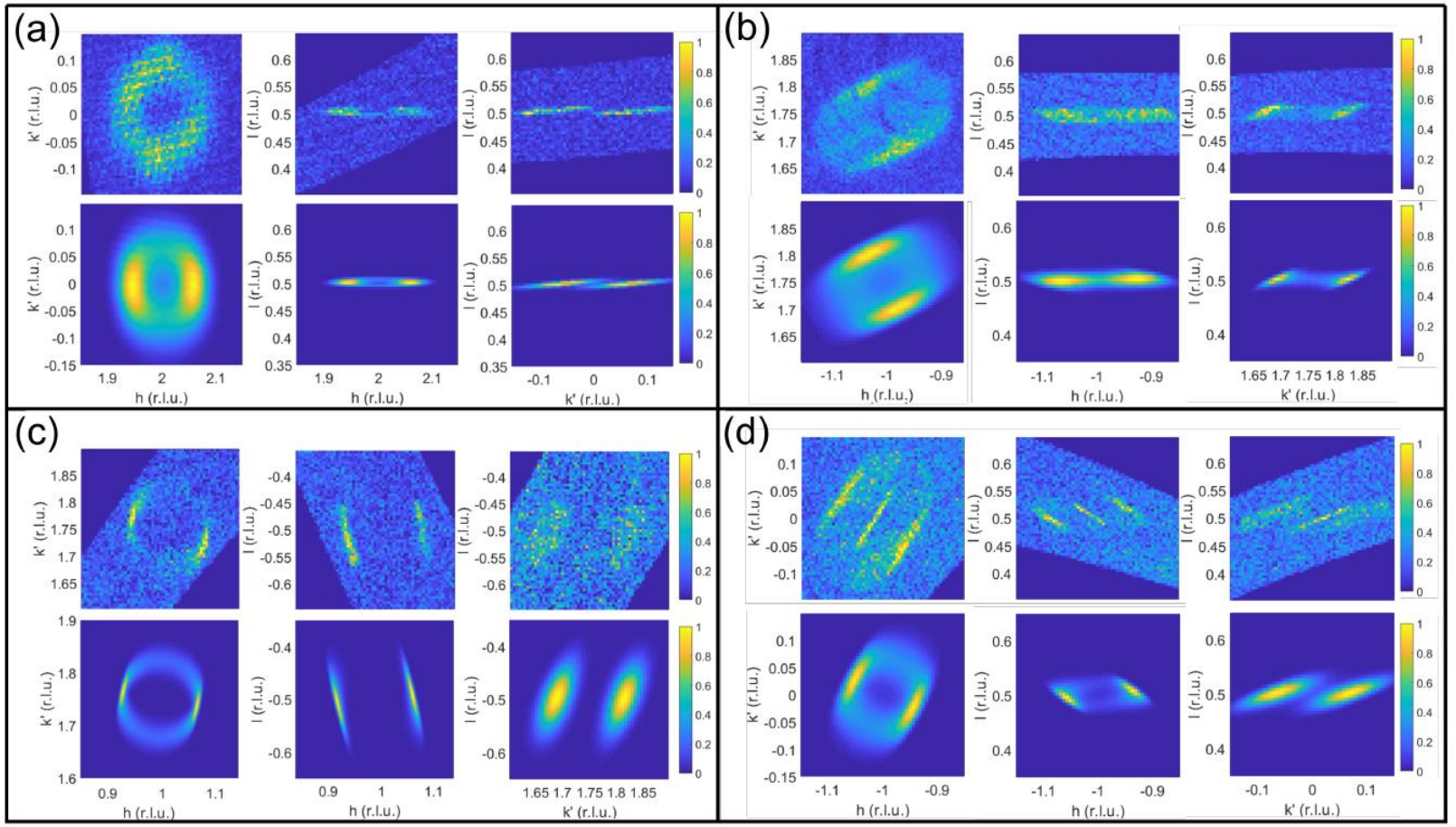
## High flux




Partial antiferromagnetic helical order in single-crystal $Fe_3PO_4O_3$

C. L. Sarkis, M. J. Tarne, J. R. Neilson, H. B. Cao, E. Coldren, M. P. Gelfand, and K. A. Ross
Phys. Rev. B **101**, 184417 – Published 18 May 2020






OAK RIDGE National Laboratory

# Single Crystal Diffraction

Lattice parameters
***k-vector***

↓

Data collection

↓

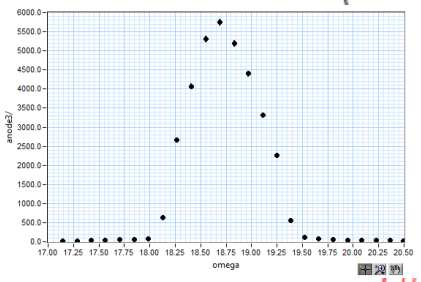
Integration
Lorentz correction
Absorption correction

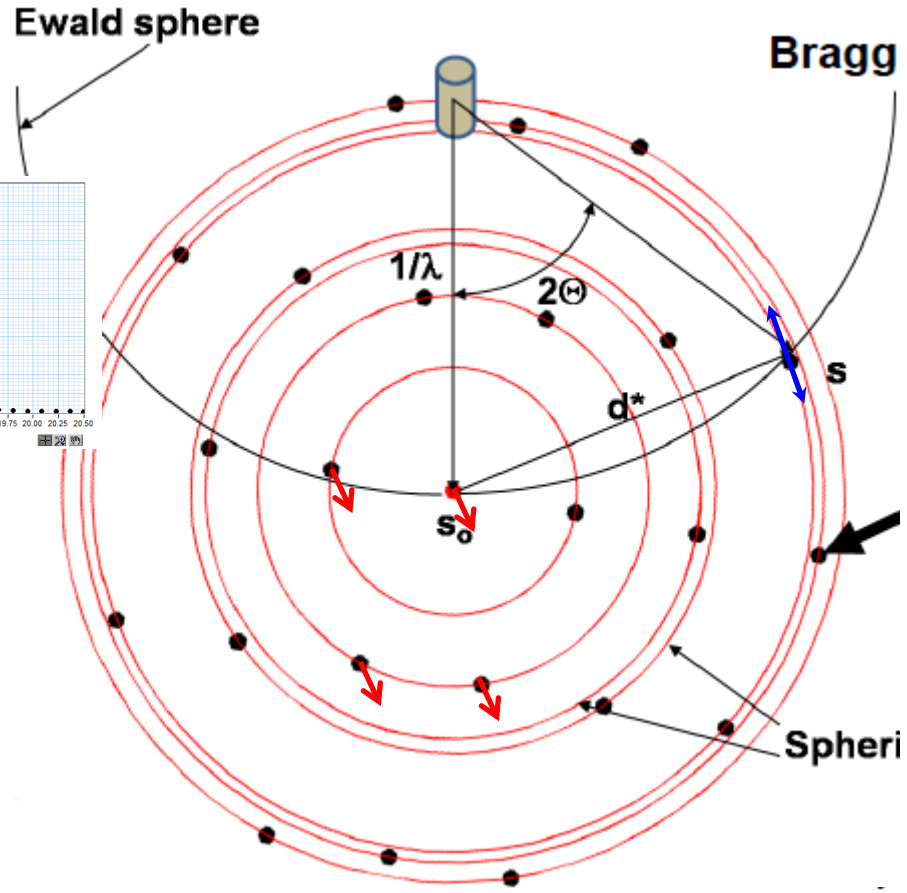
↓

Corrected Integrated Intensities
$h \quad k \quad l \quad Int_{corr} (\propto F^2) \quad \sigma$

↓

Structure solution



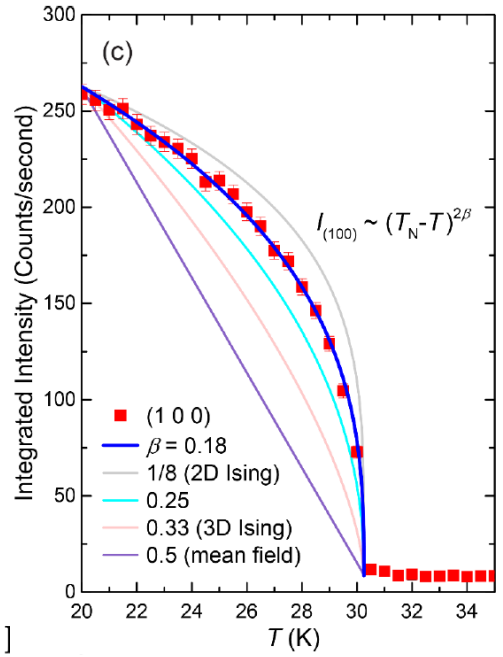

**10 reflections for each refining parameter**
Fixed lattice parameters used in data analysis

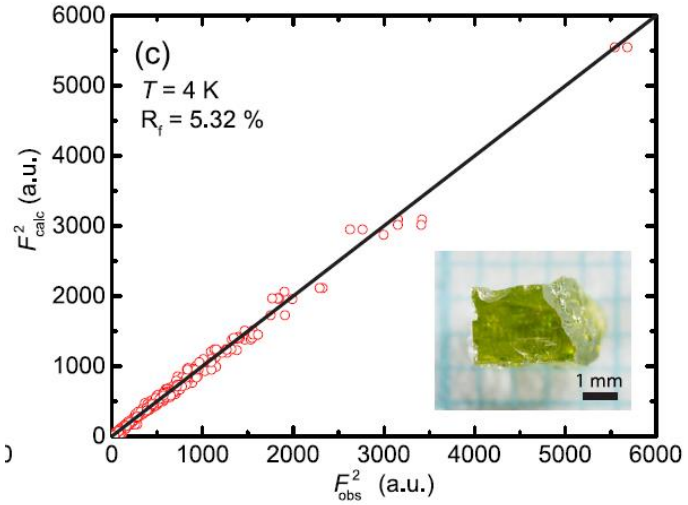
# Single Crystal Diffraction

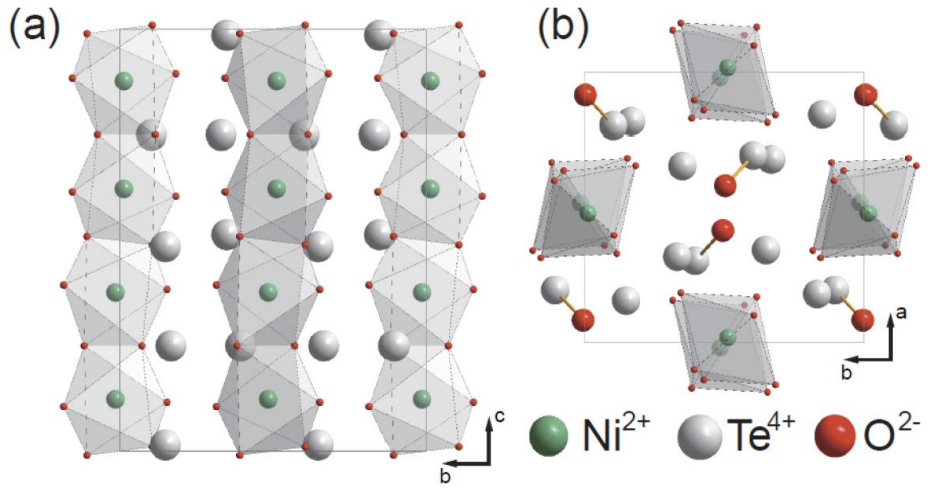
Use the magnetic symmetry with Bilbao crystallographic server

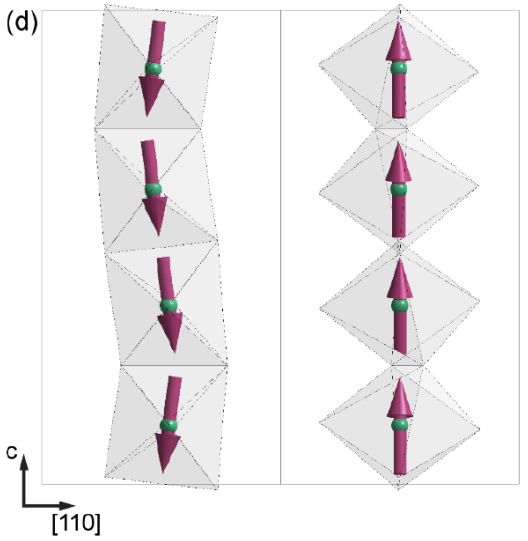
$NiTe_2O_5$ https://www.youtube.com/watch?v=mBEiDP-Rz8s PhysRevB.100.144441.pdf

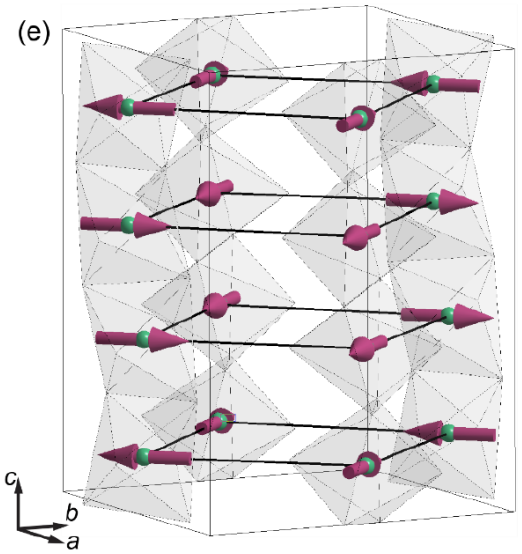
| | |
|---|---|
| Structure | Orthorhombic |
| Space group | *Pbnm* |
| *a* (Å) | 8.4418 |
| *b* (Å) | 8.8663 |
| *c* (Å) | 12.1203 |



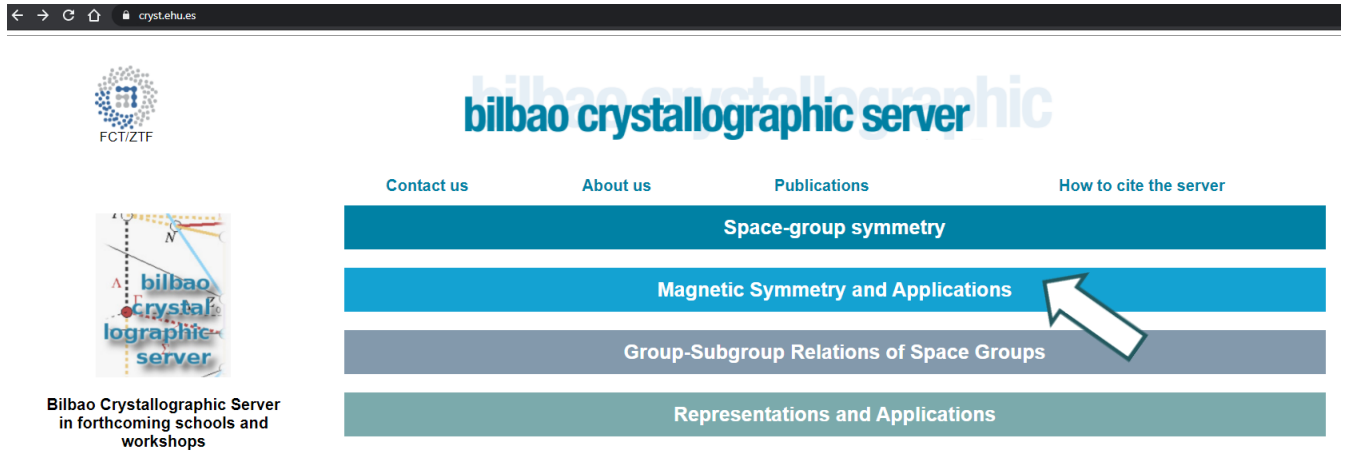



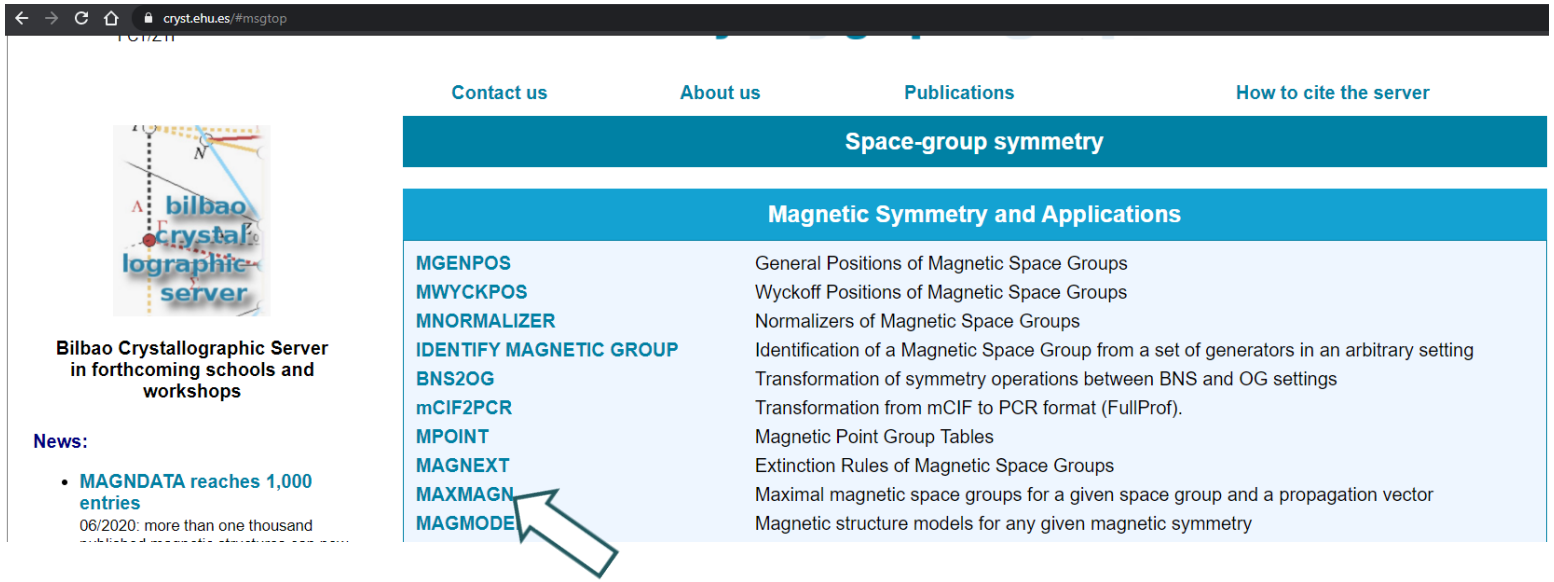



# Single crystal diffraction example $NiTe_2O_5$



# Single crystal diffraction example $NiTe_2O_5$

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

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

MAXMAGN provides the possible magnetic space groups that can be assigned to a 1-k commensurate magnetic phase assuming that the magnetic symmetry is a maximal one. The space group of the paramagnetic phase (parent group) and the observed propagation vector are required as input. Optionally, the parent paramagnetic structure can be introduced (by hand or by a cif file). In this latter case the program provides the constrains for the different possible symmetries and cif-like files can be produced. These files permit the different alternative models to be analyzed, refined, shown graphically, transported to ab-initio codes etc., with programs as ISODISTORT, JANA2006, StrConvert, VESTA, etc. These cif-like files

2

☑ *Structure data of the paramagnetic phase will be included* ☐ *Non-conventional setting*

Please, enter the label of the space group of the paramagnetic phase (parent group) 1 *Pnma* choose it 62

Please, enter the propagation vector k: $k_x$ 0 $k_y$ 0 $k_z$ 0

3

Submit

4

**Parent paramagnetic structure cif file**

1

**Option 1: Please subm structure file (CIF format):**

Choose File No file chosen 2 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: *Pnma* (No. 62)

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

Number of unique atomic positions:

Submit

NiTe2O5_powder X-ray.cif

# Single crystal diffraction example $NiTe_2O_5$

## Parent phase structure data: Magnetic Atoms

Parent space group: *Pnma* (No. 62)
Lattice parameters (Angstroms and degrees): a=8.86640, b=12.12040, c=8.44180, alpha=90.000, beta=90.000, gamma=90.000

**Atoms: Please select the magnetic ones**

| N | Atom name | Atom type | Wyckoff Position | Coordinates | Magnetic? |
|---|---|---|---|---|---|
| 1 | Te1 | Te | 8d | 0.85150 0.48630 0.15960 | ☐ |
| 2 | Te2 | Te | 4c | 0.10630 0.25000 0.19650 | ☐ |
| 3 | Te3 | Te | 4c | 0.33470 0.25000 0.68170 | ☐ |
| 4 | Ni1 | Ni | 8d | 0.51680 0.12270 0.98460 | ☑ |
| 5 | O1 | O | 4c | 0.12570 0.25000 0.66770 | ☐ |
| 6 | O2 | O | 4c | 0.45830 0.25000 0.12450 | ☐ |
| 7 | O3 | O | 8d | 0.48600 0.13540 0.40880 | ☐ |
| 8 | O4 | O | 8d | 0.68770 0.10950 0.14060 | ☐ |
| 9 | O5 | O | 8d | 0.38430 0.48520 0.11530 | ☐ |
| 10 | O6 | O | 8d | 0.34410 0.12770 0.82250 | ☐ |

1

Submit

2

OAK RIDGE National Laboratory

# Single crystal diffraction example $NiTe_2O_5$

**Maximal magnetic space groups for the parent space group *Pnma* (No. 62) and the propagation vector k = (0, 0, 0)**

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

| N | Group (BNS) | Transformation matrix | General positions | Properties | Magnetic structure |
|---|---|---|---|---|---|
| 1 | *Pn'm'a'* (#62.449) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show |
| 2 | *Pn'ma'* (#62.448) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show |
| 3 | *Pnm'a'* (#62.447) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show |
| 4 | *Pn'm'a* (#62.446) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show |
| 5 | *Pnma'* (#62.445) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show |
| 6 | *Pnm'a* (#62.444) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show |
| 7 | *Pn'ma* (#62.443) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show |
| 8 | *Pnma* (#62.441) Go to a subgroup | $\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related) | Show | *Systematic absences* MAGNEXT *Tensor properties* MTENSOR | Show **1** |

Try all possible magnetic symmetries, sometimes need to go lower symmetries for a solution. Here I pick the "*Pnma*" as the right option since I have tried all of them.

# Single crystal diffraction example $NiTe_2O_5$

## Magnetic Structure

**Selected magnetic space group: 8- *Pnma* (#62.441)**

Setting of the parent group

Parent space group *Pnma* (No. 62)

Lattice parameters: a=8.86640, b=12.12040, c=8.44180, alpha=90.000, beta=90.000, gamma=90.000

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

1

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 | Te1 Te 0.85150 0.48630 0.15960 | (x,y,z \| $m_x$,$m_y$,$m_z$) (-x+1/2,-y,z+1/2 \| -$m_x$,-$m_y$,$m_z$) (-x,y+1/2,-z \| -$m_x$,$m_y$,-$m_z$) (x+1/2,-y+1/2,-z+1/2 \| $m_x$,-$m_y$,-$m_z$) (-x,-y,-z \| $m_x$,$m_y$,$m_z$) (x+1/2,y,-z+1/2 \| -$m_x$,$m_y$,$m_z$) (x,-y+1/2,z \| -$m_x$,$m_y$,-$m_z$) (-x+1/2,y+1/2,z+1/2 \| $m_x$,-$m_y$,-$m_z$) | 8 | - | - |
| 2 | Te2 Te 0.10630 0.25000 0.19650 | (x,1/4,z \| 0,$m_y$,0) (-x+1/2,3/4,z+1/2 \| 0,-$m_y$,0) (-x,3/4,-z \| 0,$m_y$,0) (x+1/2,1/4,-z+1/2 \| 0,-$m_y$,0) | 4 | - | - |
| 3 | Te3 Te 0.33470 0.25000 0.68170 | (x,1/4,z \| 0,$m_y$,0) (-x+1/2,3/4,z+1/2 \| 0,-$m_y$,0) (-x,3/4,-z \| 0,$m_y$,0) (x+1/2,1/4,-z+1/2 \| 0,-$m_y$,0) | 4 | - | - |
| 4 | Ni1 Ni 0.51680 0.12270 0.98460 | (x,y,z \| $m_x$,$m_y$,$m_z$) (-x+1/2,-y,z+1/2 \| -$m_x$,-$m_y$,$m_z$) (-x,y+1/2,-z \| -$m_x$,$m_y$,-$m_z$) (x+1/2,-y+1/2,-z+1/2 \| $m_x$,-$m_y$,-$m_z$) (-x,-y,-z \| $m_x$,$m_y$,$m_z$) (x+1/2,y,-z+1/2 \| -$m_x$,$m_y$,$m_z$) (x,-y+1/2,z \| -$m_x$,$m_y$,-$m_z$) (-x+1/2,y+1/2,z+1/2 \| $m_x$,-$m_y$,-$m_z$) | 8 | ($M_x$,$M_y$,$M_z$) | $M_x$ = 1, $M_y$ = 1, $M_z$ = 1 |
| 5 | O1 O 0.12570 0.25000 0.66770 | (x,1/4,z \| 0,$m_y$,0) (-x+1/2,3/4,z+1/2 \| 0,-$m_y$,0) (-x,3/4,-z \| 0,$m_y$,0) (x+1/2,1/4,-z+1/2 \| 0,-$m_y$,0) | 4 | - | - |
| 6 | O2 O 0.45830 0.25000 0.12450 | (x,1/4,z \| 0,$m_y$,0) (-x+1/2,3/4,z+1/2 \| 0,-$m_y$,0) (-x,3/4,-z \| 0,$m_y$,0) (x+1/2,1/4,-z+1/2 \| 0,-$m_y$,0) | 4 | - | - |
| 7 | O3 O 0.48600 0.13540 0.40880 | (x,y,z \| $m_x$,$m_y$,$m_z$) (-x+1/2,-y,z+1/2 \| -$m_x$,-$m_y$,$m_z$) (-x,y+1/2,-z \| -$m_x$,$m_y$,-$m_z$) (x+1/2,-y+1/2,-z+1/2 \| $m_x$,-$m_y$,-$m_z$) (-x,-y,-z \| $m_x$,$m_y$,$m_z$) (x+1/2,y,-z+1/2 \| -$m_x$,$m_y$,$m_z$) (x,-y+1/2,z \| -$m_x$,$m_y$,-$m_z$) (-x+1/2,y+1/2,z+1/2 \| $m_x$,-$m_y$,-$m_z$) | 8 | - | - |
| 8 | O4 O 0.68770 0.10950 0.14060 | (x,y,z \| $m_x$,$m_y$,$m_z$) (-x+1/2,-y,z+1/2 \| -$m_x$,-$m_y$,$m_z$) (-x,y+1/2,-z \| -$m_x$,$m_y$,-$m_z$) (x+1/2,-y+1/2,-z+1/2 \| $m_x$,-$m_y$,-$m_z$) (-x,-y,-z \| $m_x$,$m_y$,$m_z$) (x+1/2,y,-z+1/2 \| -$m_x$,$m_y$,$m_z$) (x,-y+1/2,z \| -$m_x$,$m_y$,-$m_z$) (-x+1/2,y+1/2,z+1/2 \| $m_x$,-$m_y$,-$m_z$) | 8 | - | - |
| 9 | O5 O 0.38430 0.48520 0.11530 | (x,y,z \| $m_x$,$m_y$,$m_z$) (-x+1/2,-y,z+1/2 \| -$m_x$,-$m_y$,$m_z$) (-x,y+1/2,-z \| -$m_x$,$m_y$,-$m_z$) (x+1/2,-y+1/2,-z+1/2 \| $m_x$,-$m_y$,-$m_z$) (-x,-y,-z \| $m_x$,$m_y$,$m_z$) (x+1/2,y,-z+1/2 \| -$m_x$,$m_y$,$m_z$) (x,-y+1/2,z \| -$m_x$,$m_y$,-$m_z$) (-x+1/2,y+1/2,z+1/2 \| $m_x$,-$m_y$,-$m_z$) | 8 | - | - |
| 10 | O6 O 0.34410 0.12770 0.82250 | (x,y,z \| $m_x$,$m_y$,$m_z$) (-x+1/2,-y,z+1/2 \| -$m_x$,-$m_y$,$m_z$) (-x,y+1/2,-z \| -$m_x$,$m_y$,-$m_z$) (x+1/2,-y+1/2,-z+1/2 \| $m_x$,-$m_y$,-$m_z$) (-x,-y,-z \| $m_x$,$m_y$,$m_z$) (x+1/2,y,-z+1/2 \| -$m_x$,$m_y$,$m_z$) (x,-y+1/2,z \| -$m_x$,$m_y$,-$m_z$) (-x+1/2,y+1/2,z+1/2 \| $m_x$,-$m_y$,-$m_z$) | 8 | - | - |

2

1

### mCIF file of the structure

**Submit this mcif file to MVISUALIZE for 3D visualization of the structure using Jmol:** Submit to MVISUALIZE

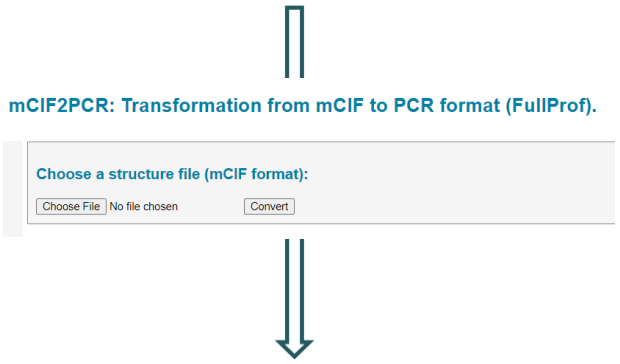
**Download mCIF file:** bcs_file.mcif

*[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: 27/09/2020 07:02:10
# NiTe2O5_powder X-ray.cif

data_5yOhtAoR
_audit_creation_date              2020-09-27
_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
_irrep_small_dimension
_irrep_direction_type
_irrep_action
_irrep_modes_number
_irrep_presence
?  ?  ?  ?  ?  ?  ?

_exptl_crystal_magnetic_properties_details
;
;

_active_magnetic_irreps_details
;
k-maximal magnetic symmetry
;

_parent_space_group.name_H-M_alt  'P  n  m  a'
_parent_space_group.IT_number                    062
_parent_space_group.transform_Pp_abc  'a,b,c;0,0,0'
```

# Single crystal diffraction example $NiTe_2O_5$

bcs_file_23269.mcif

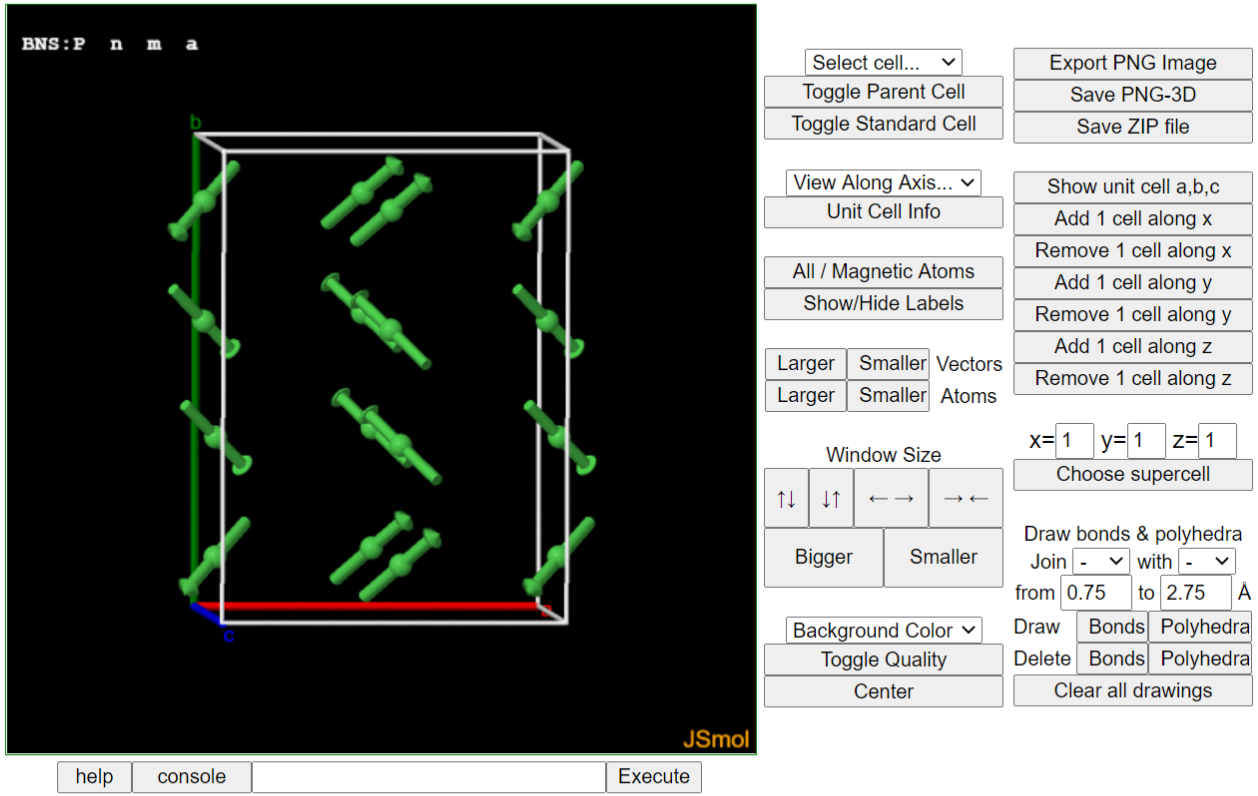



bcs_file_23269.pcr

## MVISUALIZE: 3D Visualization of magnetic structures with Jmol

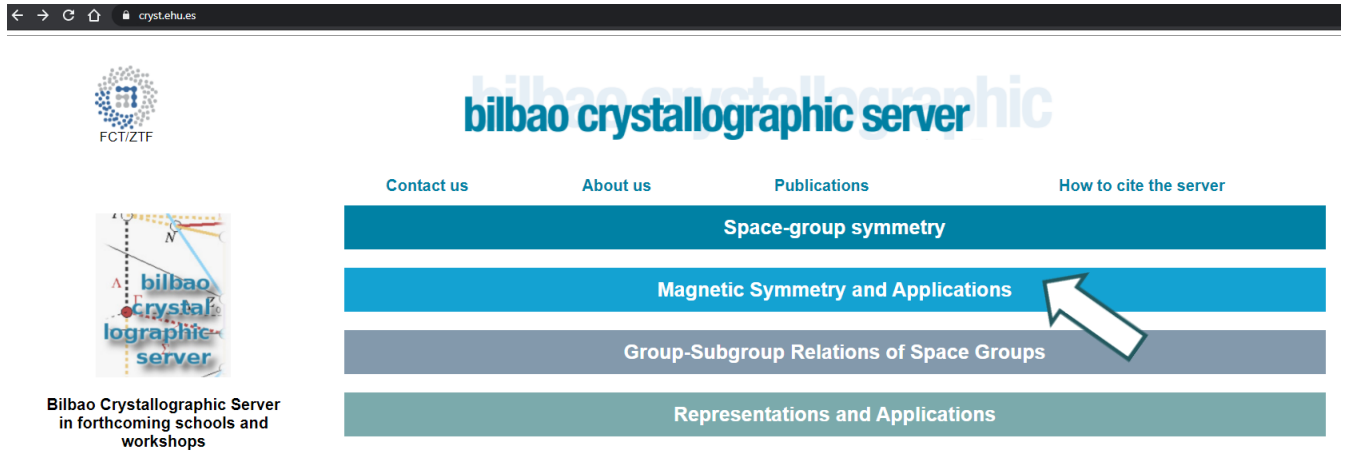
MVISUALIZE Main Page

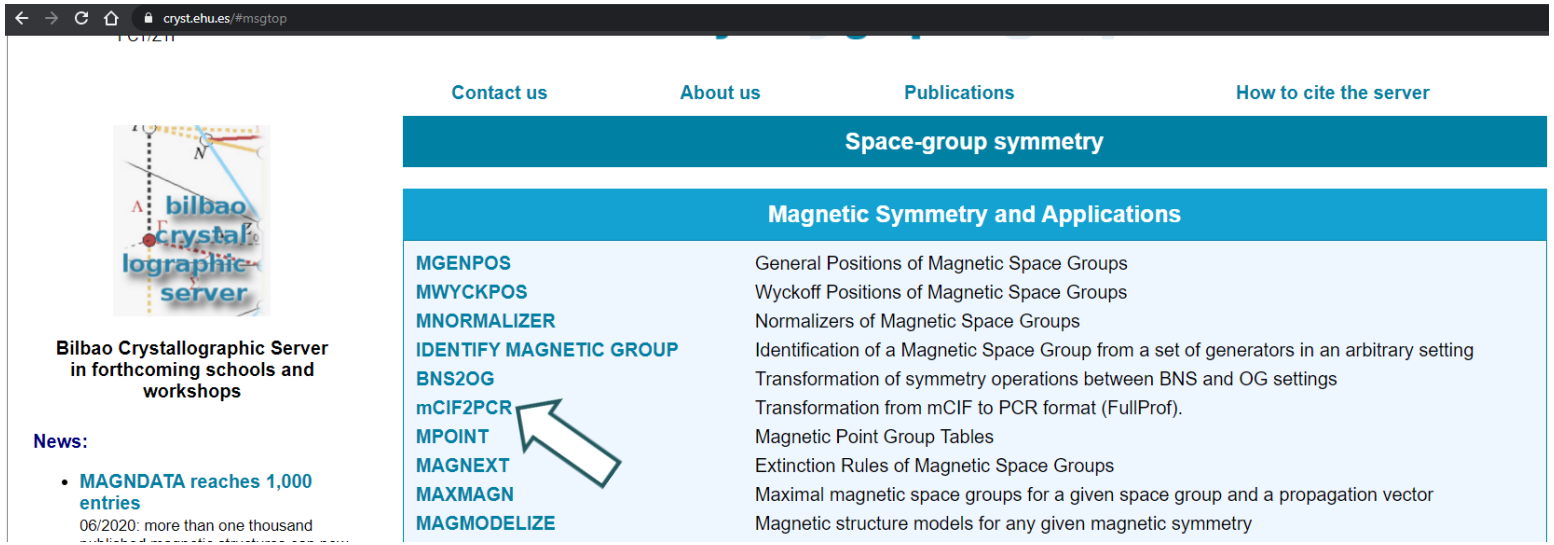
Show/Hide File



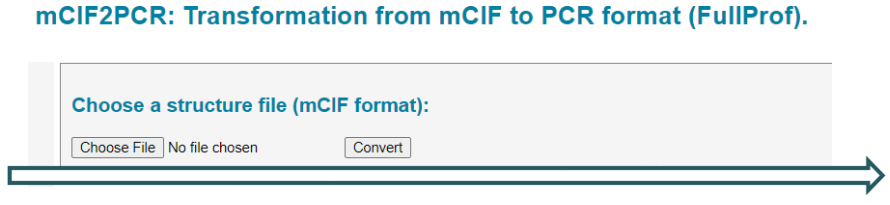

***Note:*** *If the application stops working right or any malfunction is observed, it is probably a temporal problem due to the cache memory of your browser. Clear your web browser cache to solve it. If you still observe any malfunction, write an e-mail to cryst@wm.lc.ehu.es explaining the problem in detail.*

# Single crystal diffraction example $NiTe_2O_5$




bcs_file_23269.mcif

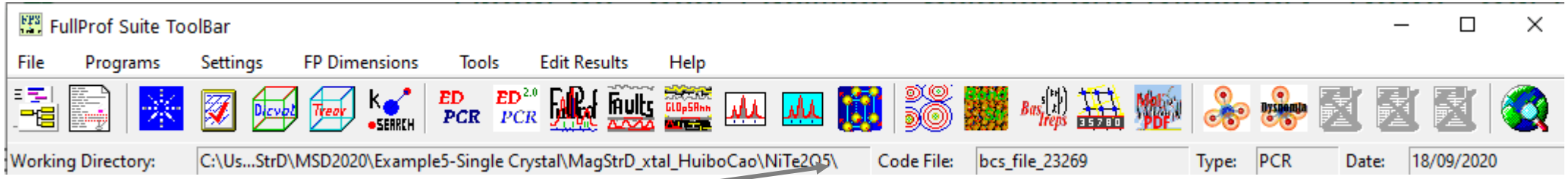



bcs_file_23269.pcr



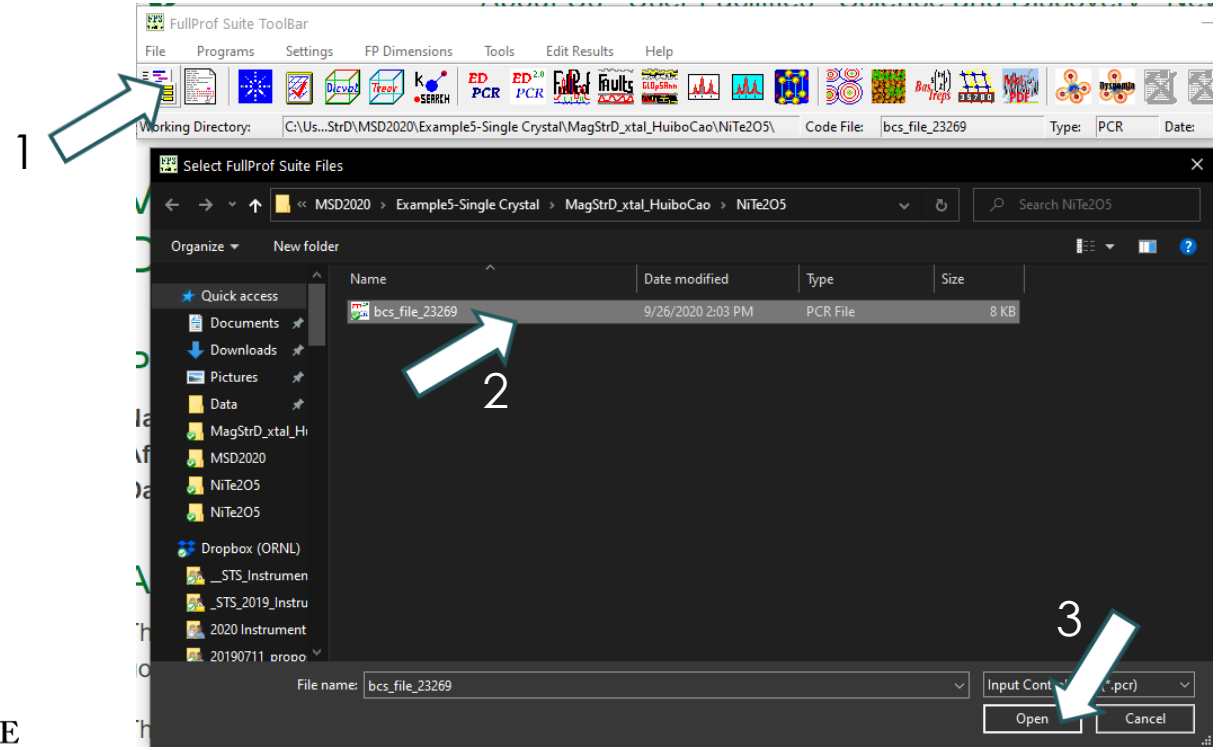
OAK RIDGE National Laboratory

# Single crystal diffraction example $NiTe_2O_5$

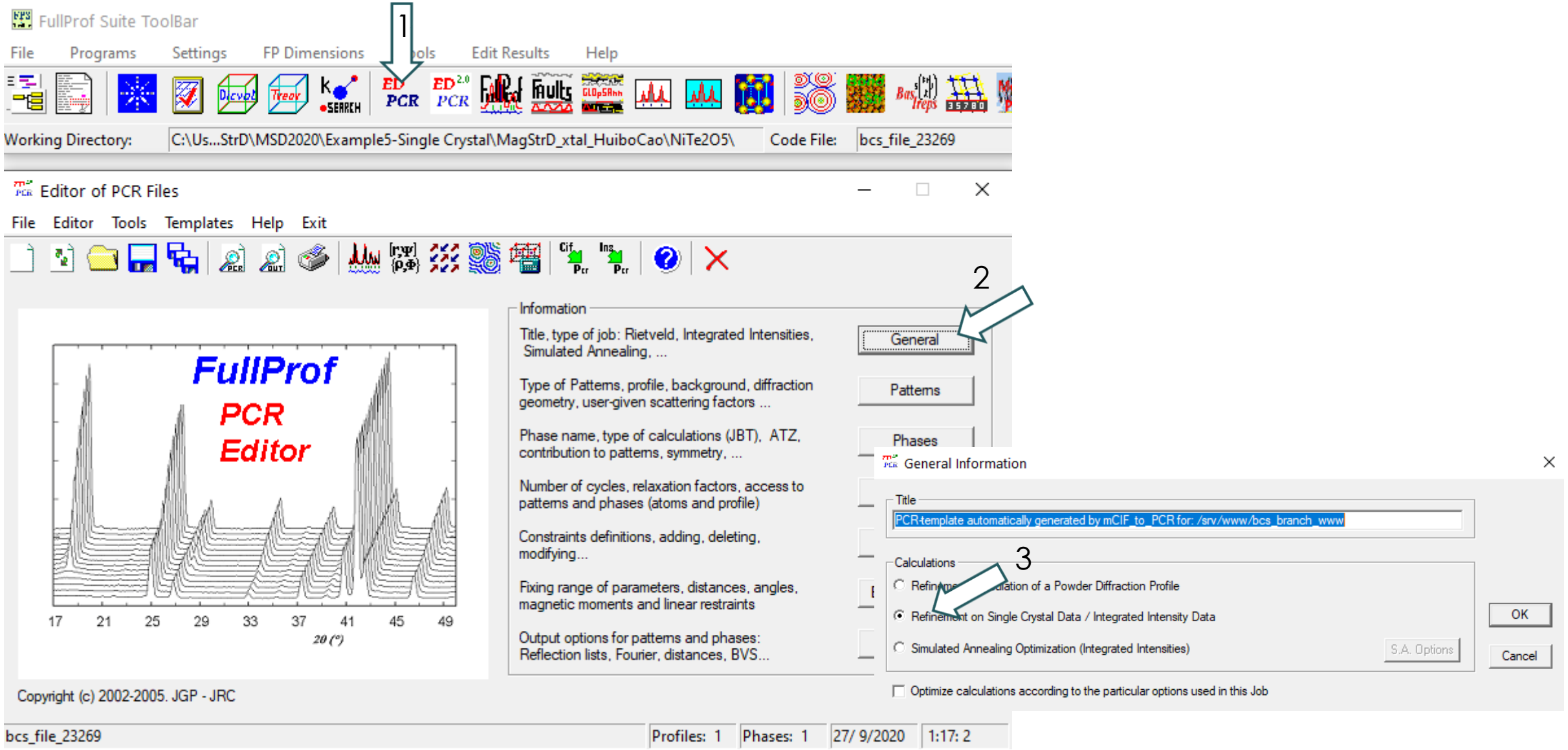



bcs_file_23269.pcr

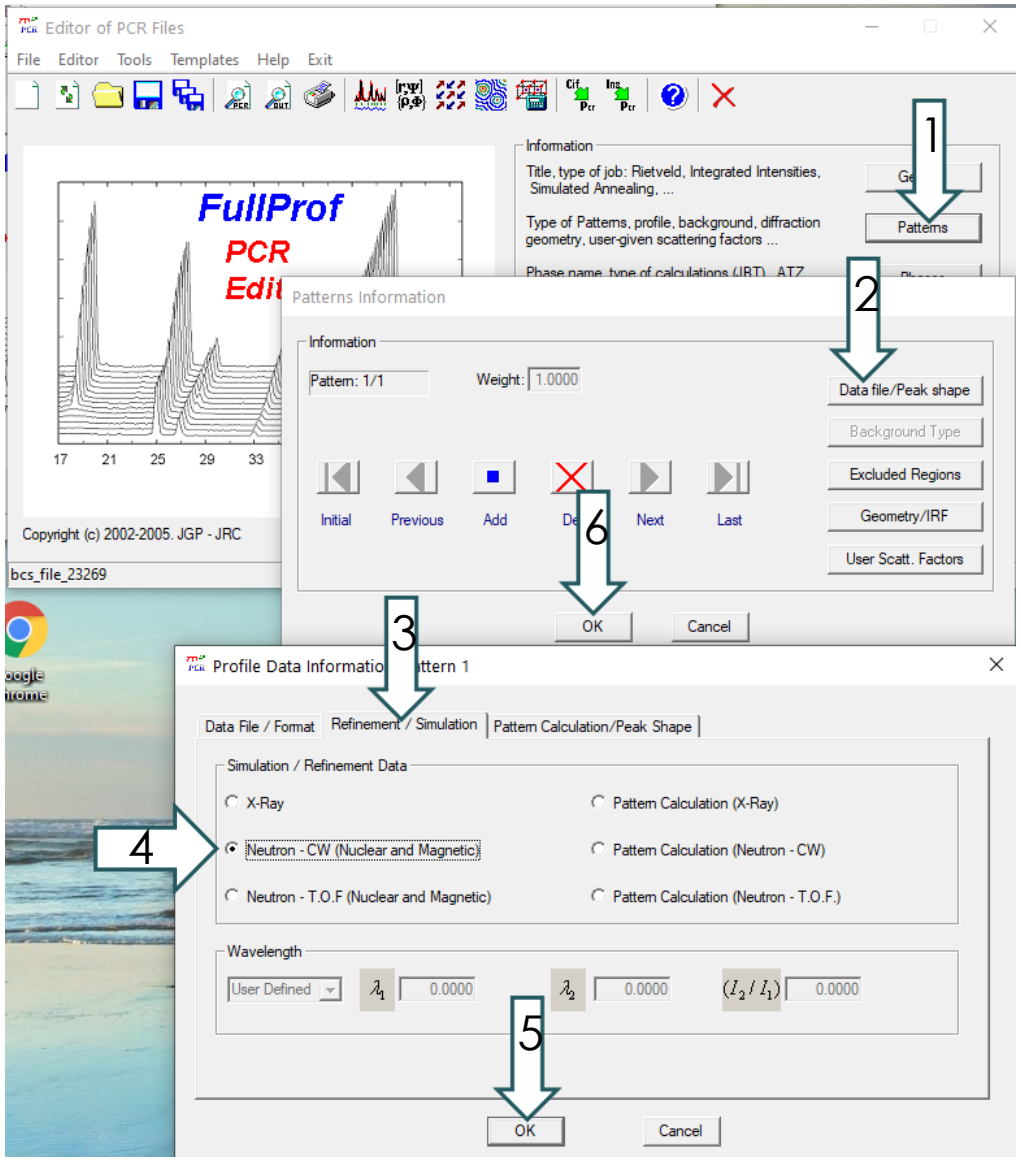
Copy the created pcr to the folder with the data file (.int), then select the bcs_file_23269.pcr

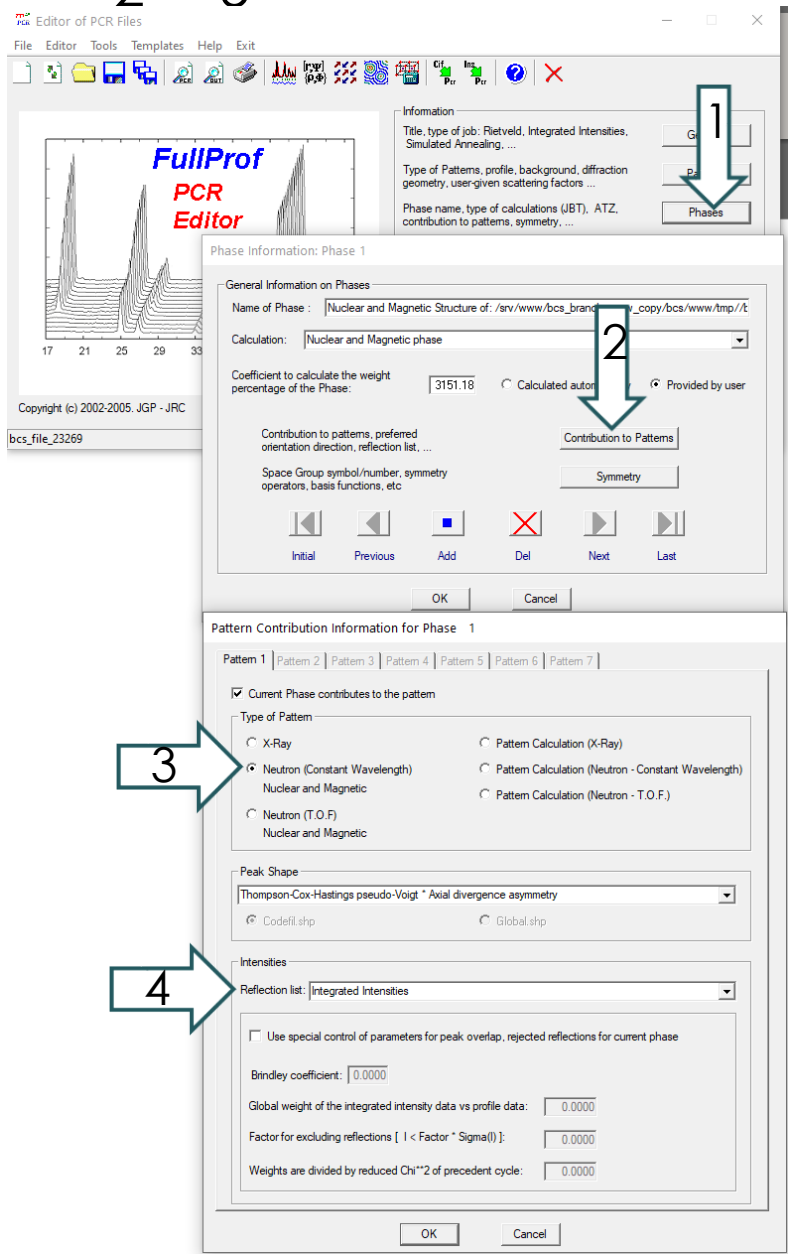


# Single crystal diffraction example $NiTe_2O_5$



# Single crystal diffraction example $NiTe_2O_5$

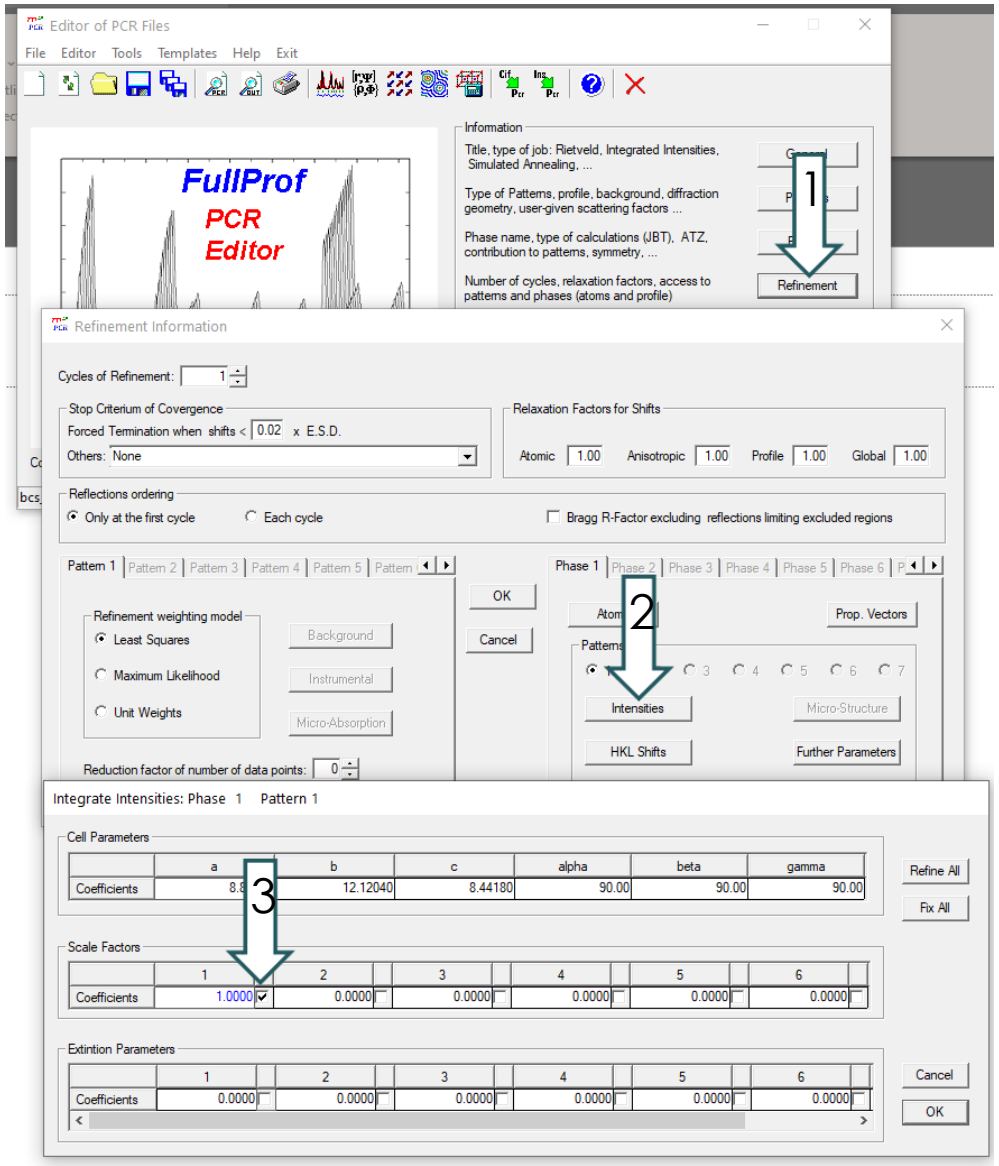


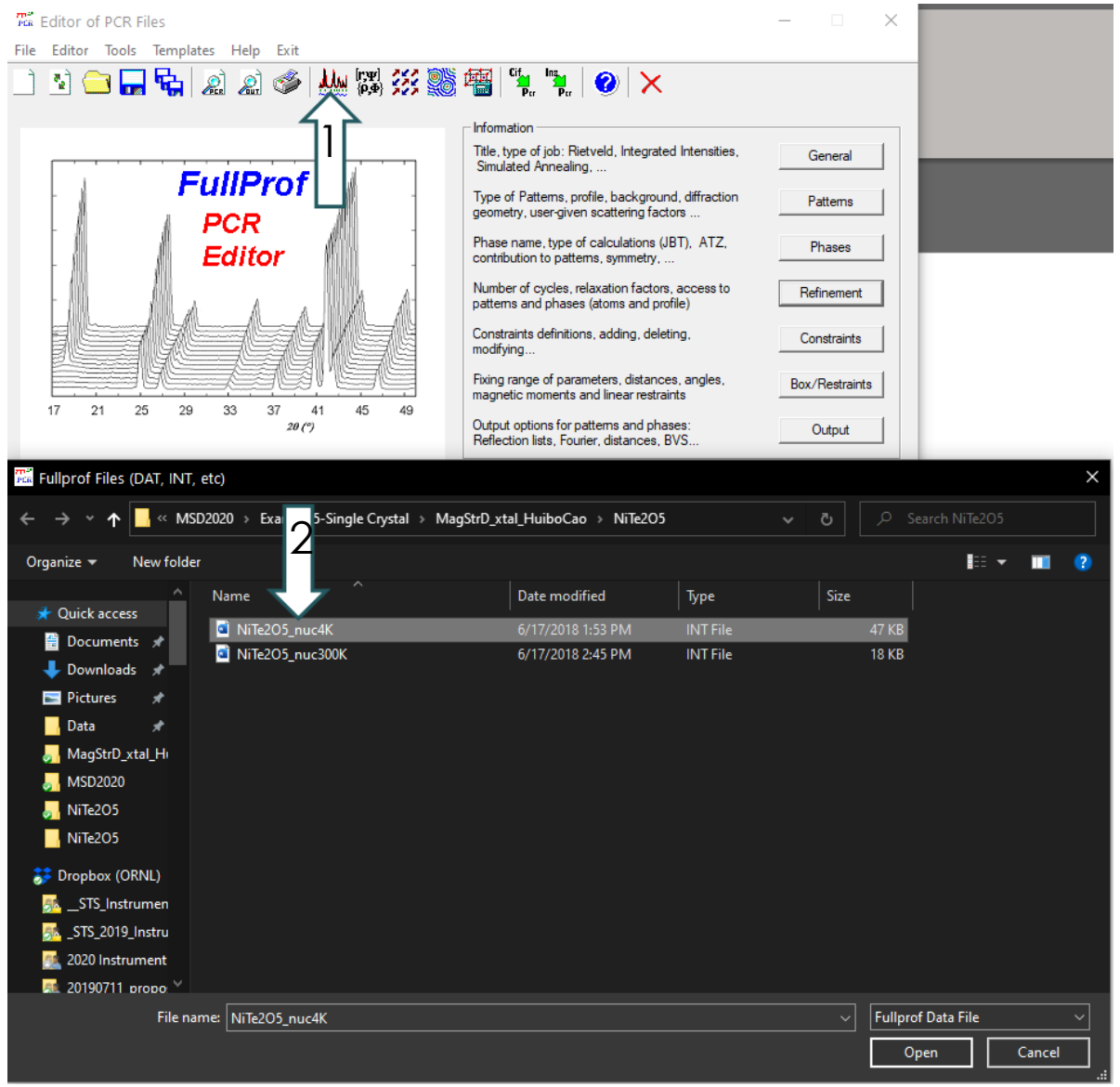






OAK RIDGE National Laboratory

# Single crystal diffraction example $NiTe_2O_5$






OAK RIDGE National Laboratory

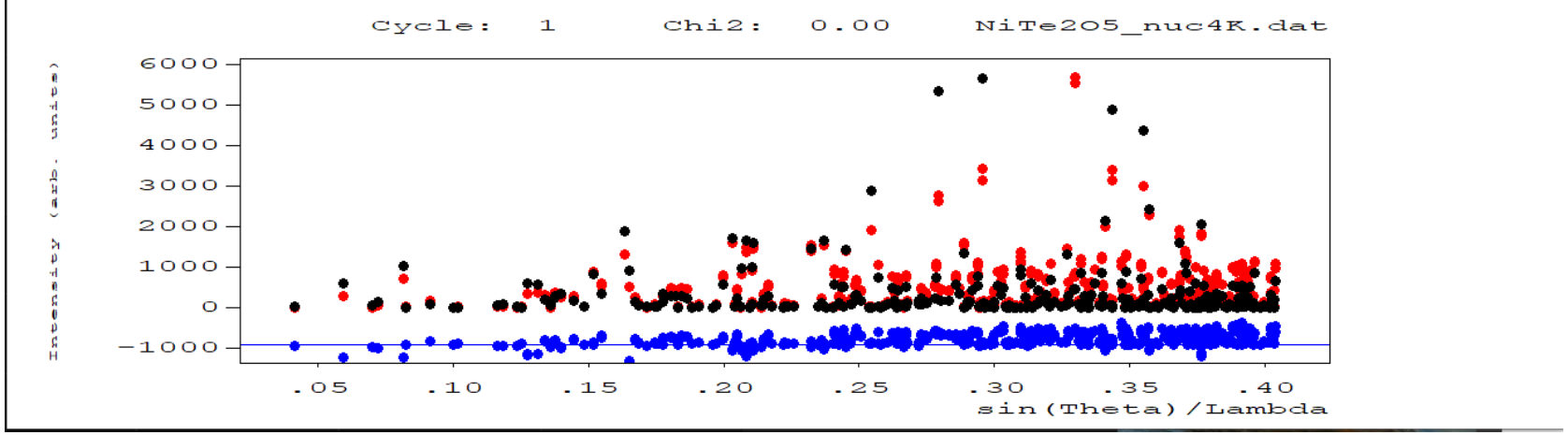
# Single crystal diffraction example $NiTe_2O_5$

"Run" the refinement and then "Exit"

FullProf Program

Load Edit PCR Mode Run Exit

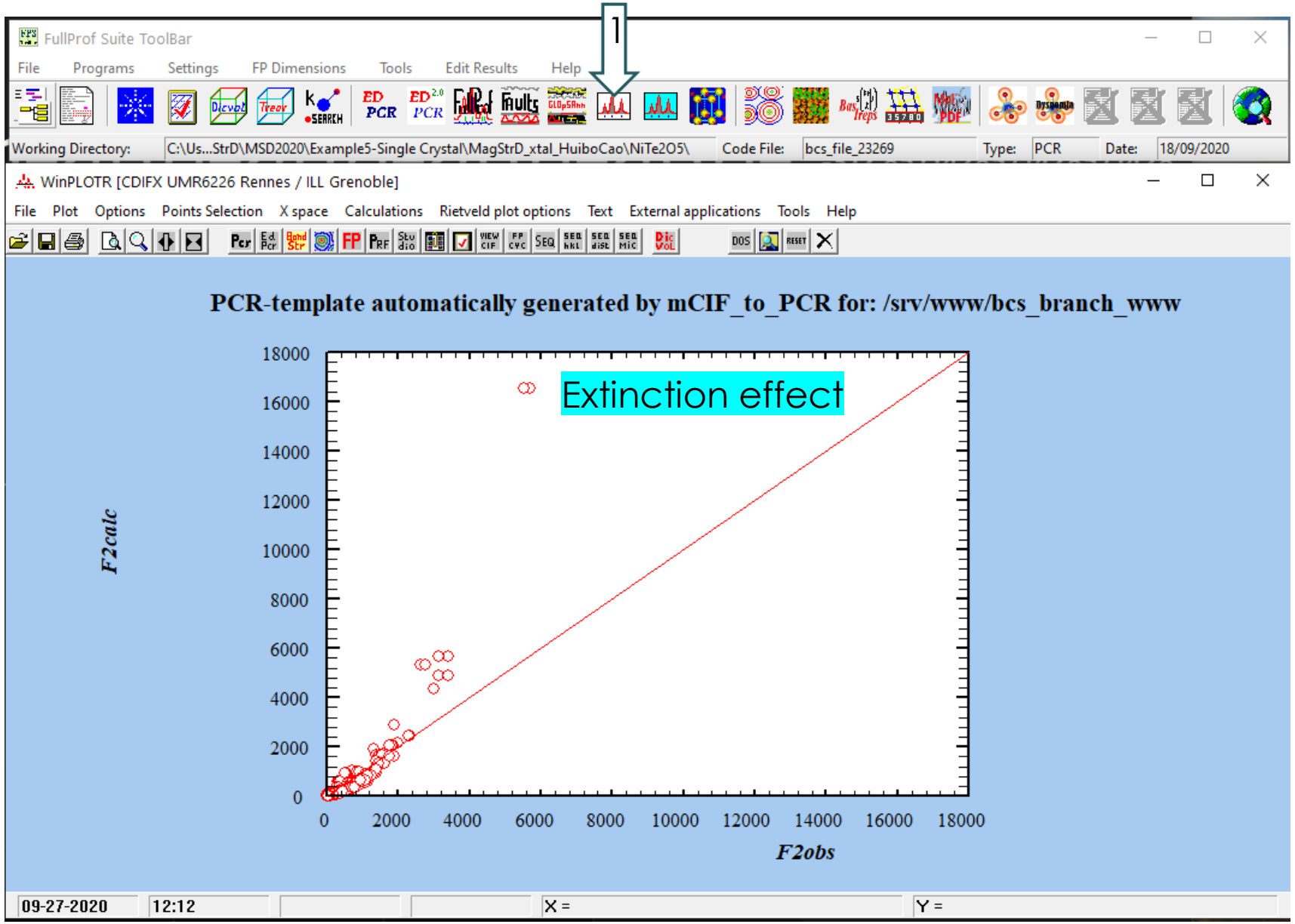
```
=> Solving L.S. equations...
=> Writing results for cycle       1
   => Global user-weigthed Chi2 (Bragg contrib.):   517.3
   => ---------> Pattern#       1
   => Phase:       1
   =>    RF2 -factor :   48.54
   =>    RF2w-factor :   59.63
   =>    RF  -factor :   28.01
   =>    Chi2(Intens):   367.6
   =>  N_eff Reflect.:     582 and    0.000     * sigma < Int
=> Conv. not yet reached -> [Max] Shift(  Scale1)/(eps*Sigma)= -333.52 abs> 1
=> Normal end, final calculations and writing...
=> Contribution to Yi for phase:       1


=> CPU Time:     0.992 seconds
=> 0.017 minutes

=> END   Date:27/09/2020  Time => 12:08:34.631
```



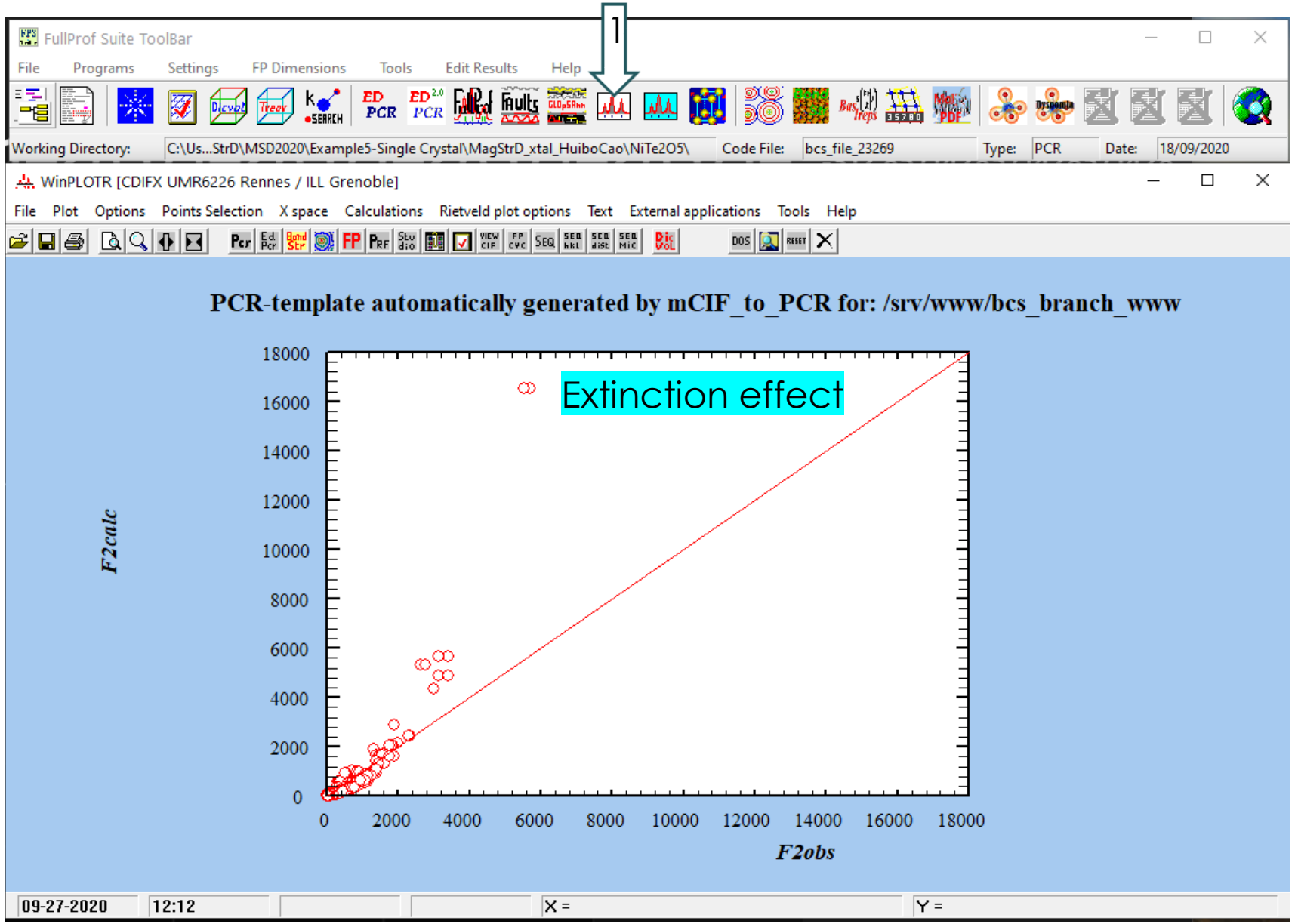



OAK RIDGE National Laboratory

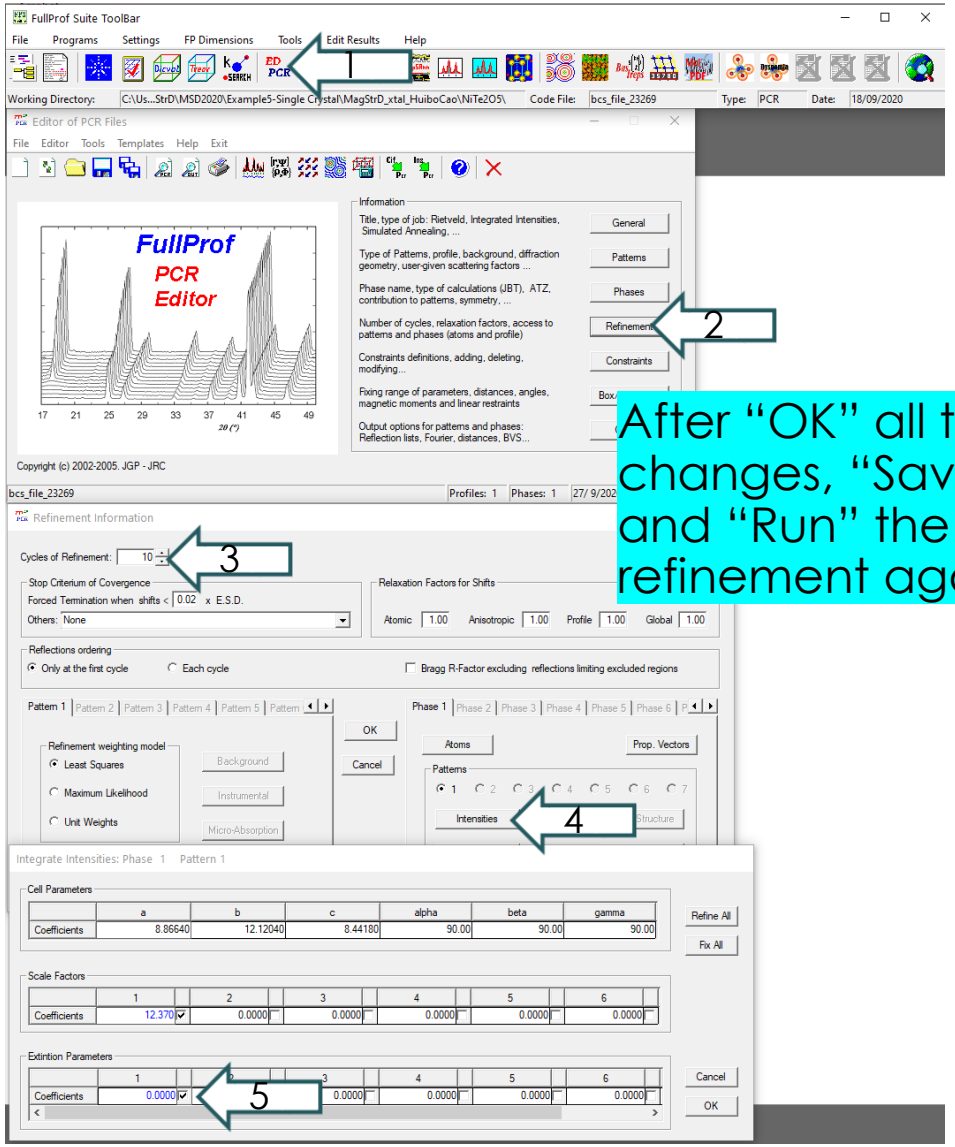
# Single crystal diffraction example $NiTe_2O_5$



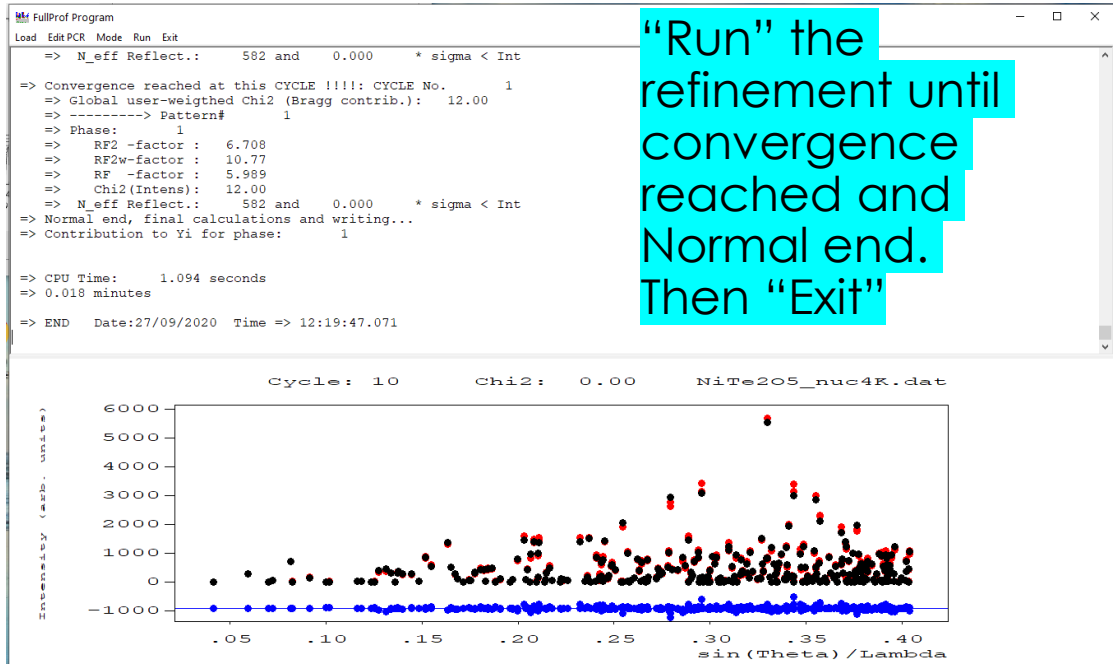
# Single crystal diffraction example $NiTe_2O_5$



# Single crystal diffraction example $NiTe_2O_5$

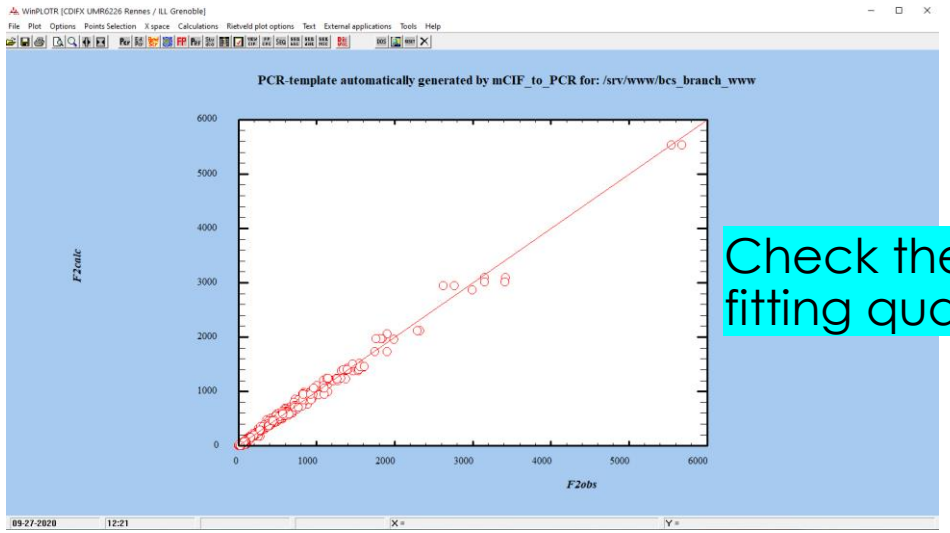



After "OK" all the changes, "Save" and "Run" the refinement again



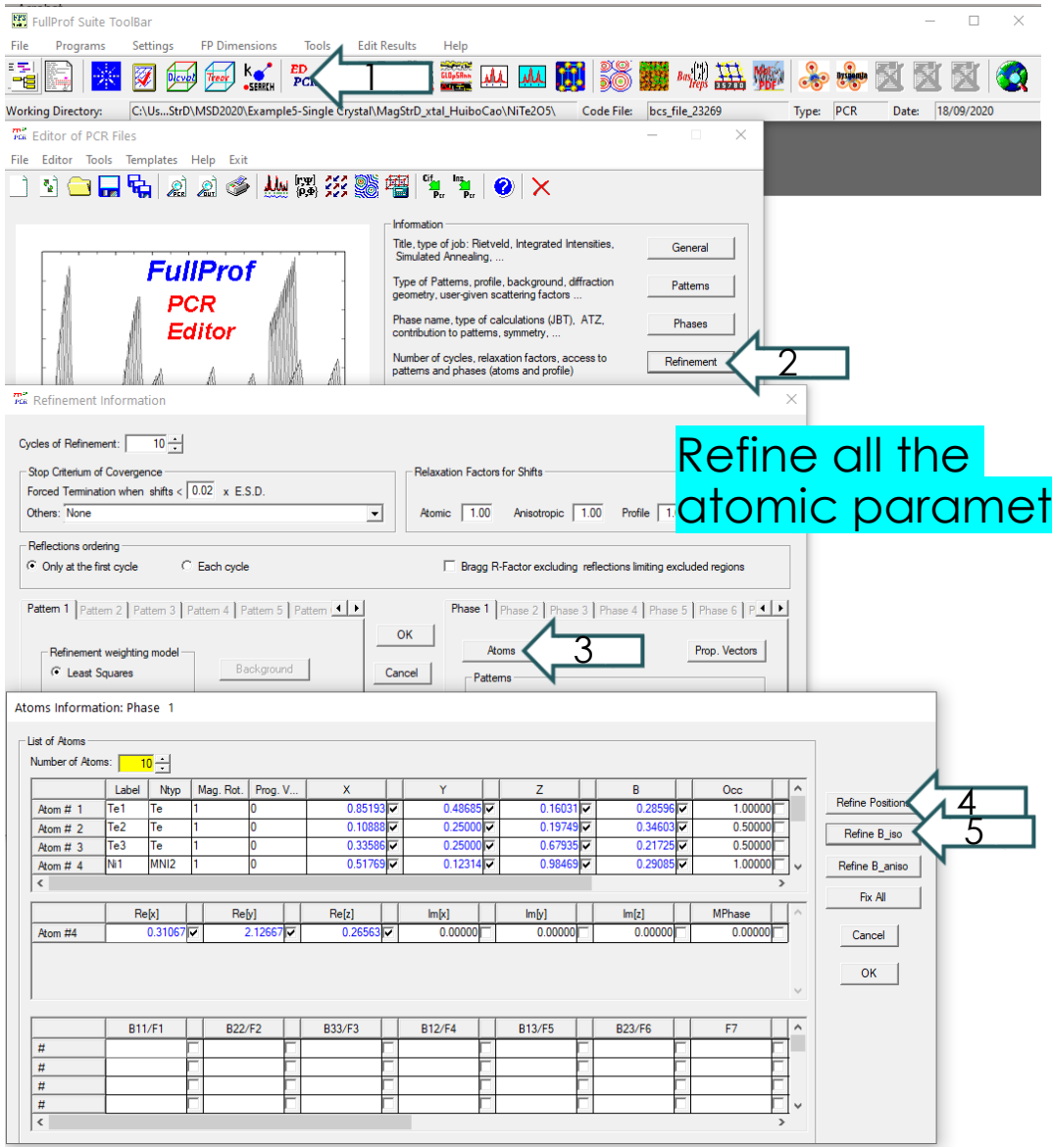

"Run" the refinement until convergence reached and Normal end. Then "Exit"



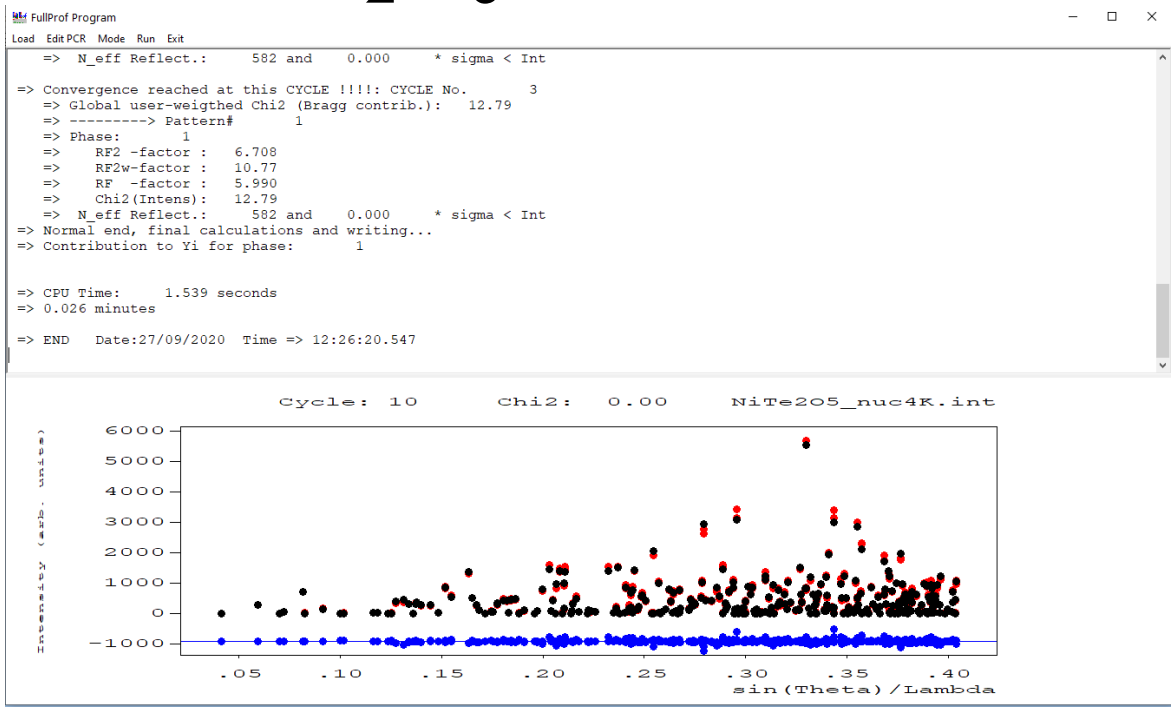



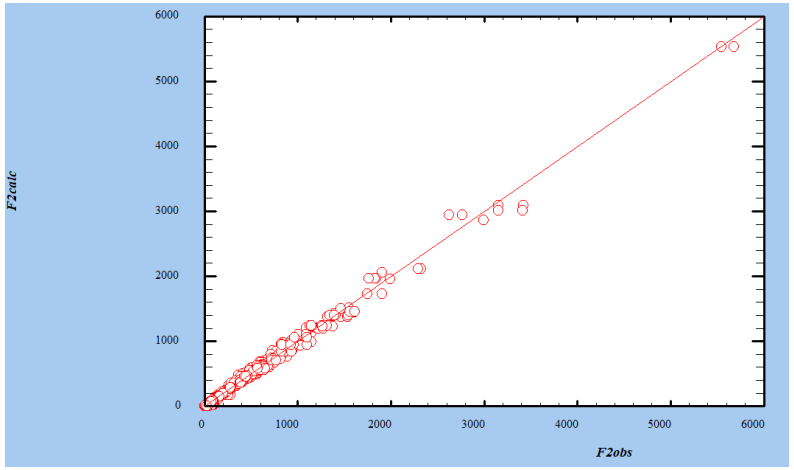

Check the fitting quality

# Single crystal diffraction example $NiTe_2O_5$




Refine all the atomic parameters

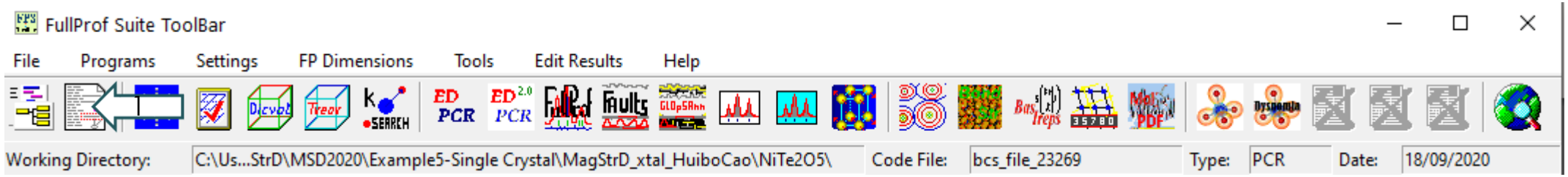





OAK RIDGE National Laboratory

# Single crystal diffraction example $NiTe_2O_5$




```
Te3     Te          1  0    0.33585   0.25000   0.67935   0.21603   0.50000     0     0  #
                              131.00      0.00    151.00    201.00      0.00
Ni1     MNI2        1  0    0.51769   0.12313   0.98469   0.28998   1.00000     1     0  #
                              161.00    171.00    181.00    231.00      0.00
      0.31025   2.12711    0.26565   0.00000   0.00000   0.00000   0.00000 <-MagPar
        31.00     21.00      11.00      0.00      0.00      0.00      0.00
O1      O           1  0    0.12318   0.25000   0.65558   0.49032   0.50000     0     0  #
                              191.00      0.00    211.00    371.00      0.00
O2      O           1  0    0.46745   0.25000   0.13392   0.36884   0.50000     0     0  #
                              221.00      0.00    241.00    381.00      0.00
O3      O           1  0    0.49227   0.12742   0.40601   0.54906   1.00000     0     0  #
                              251.00    261.00    271.00    391.00      0.00
O4      O           1  0    0.69194   0.11397   0.14618   0.45197   1.00000     0     0  #
                              281.00    291.00    301.00    401.00      0.00
O5      O           1  0    0.38275   0.48647   0.12018   0.47116   1.00000     0     0  #
                              311.00    321.00    331.00    411.00      0.00
O6      O           1  0    0.34572   0.12987   0.81991   0.64499   1.00000     0     0  #
                              341.00    351.00    361.00    421.00      0.00
!-------> Scale, Extinction and  Cell Parameters for Pattern #  1
!  Scale Factors
!    Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
   55.74       0.000       0.000       0.000       0.000       0.000
        41.00        0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7   Ext-Model
  32.50       0.000       0.000       0.000       0.000       0.000       0.000       1
       61.00        0.00        0.00        0.00        0.00        0.00        0.00
!      a           b           c         alpha       beta        gamma      #Cell Info
   8.866400   12.120400   8.441799   90.000000   90.000000   90.000000   #
    0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
! x-Lambda/2  +          Not yet used parameters
      0.00     0.00000     0.00000     0.00000     0.00000
         1           0           0           0           0
!  2Th1/TOF1   2Th2/TOF2  Pattern to plot
       2.000     130.000       1
```

2

```
! x-Lambda/2  +          Not yet used parameters
     0.01158     0.00000     0.00000     0.00000     0.00000
       51.00        0.00        0.00        0.00        0.00
```

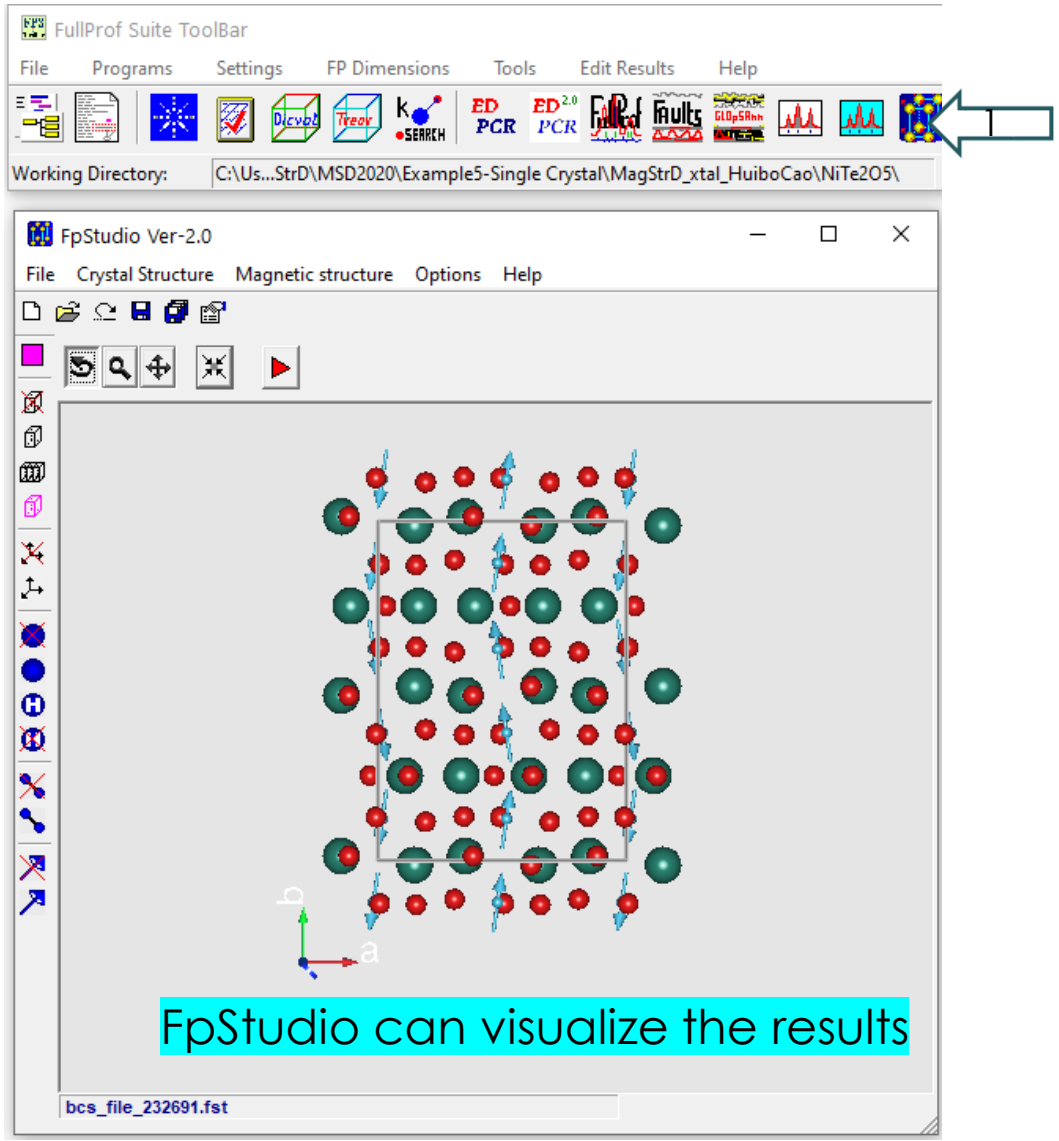
Open the .pcr file in a text editor, flag Lambda/2 (half lambda contamination) on by change the "code" "0" to "1". Then do the refinement again

# Single crystal diffraction example $NiTe_2O_5$

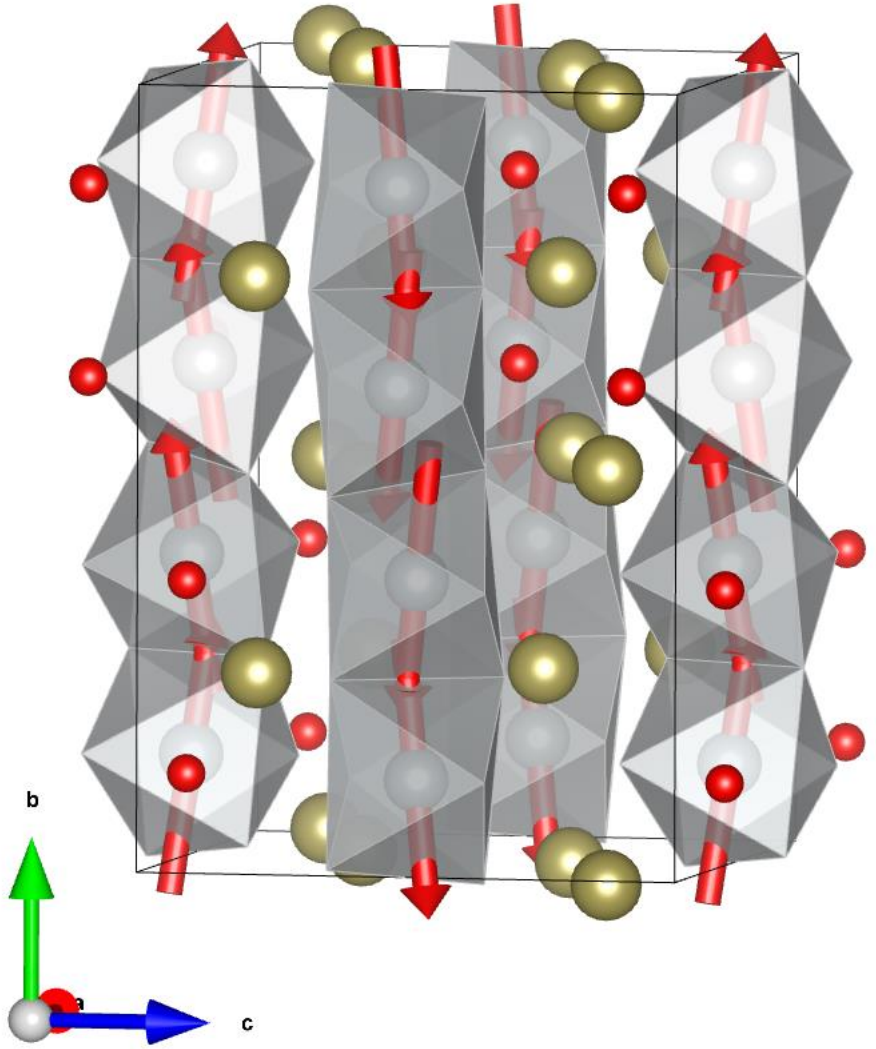
Open the .sum file generated from the refinement to see the refined atomic and ordered moment parameters. The parameters can be found in the .cif and the .mcif files too.

```
=>  No. of reflections for pattern#:   1:   582


==> ATOM PARAMETERS:

 Name       x      sx        y      sy        z      sz        B    sB    occ.  socc.  Mult
Te1     0.85193(  37)  0.48684(  22)  0.16031(  35)  0.285( 85)  1.000(   0)     8
Te2     0.10888(  53)  0.25000(   0)  0.19749(  47)  0.345(112)  0.500(   0)     4
Te3     0.33585(  51)  0.25000(   0)  0.67935(  47)  0.216(109)  0.500(   0)     4
Ni1     0.51769(  21)  0.12313(  14)  0.98469(  19)  0.290( 69)  1.000(   0)     8
O1      0.12318(  53)  0.25000(   0)  0.65558(  51)  0.490(109)  0.500(   0)     4
O2      0.46745(  54)  0.25000(   0)  0.13392(  51)  0.369(107)  0.500(   0)     4
O3      0.49227(  40)  0.12742(  24)  0.40601(  37)  0.549( 92)  1.000(   0)     8
O4      0.69194(  37)  0.11397(  22)  0.14618(  39)  0.452( 89)  1.000(   0)     8
O5      0.38275(  37)  0.48647(  22)  0.12018(  37)  0.471( 81)  1.000(   0)     8
O6      0.34572(  39)  0.12987(  23)  0.81991(  37)  0.645( 85)  1.000(   0)     8

==> MAGNETIC MOMENT PARAMETERS:

 Name      Mx    sMx     My     sMy     Mz     sMz        M     sM      MPhas    sMPhas

Ni1      0.310( 57)   2.127( 35)   0.266( 42)    2.1660( 367)    0.0000(   0)
```

# Single crystal diffraction example $NiTe_2O_5$



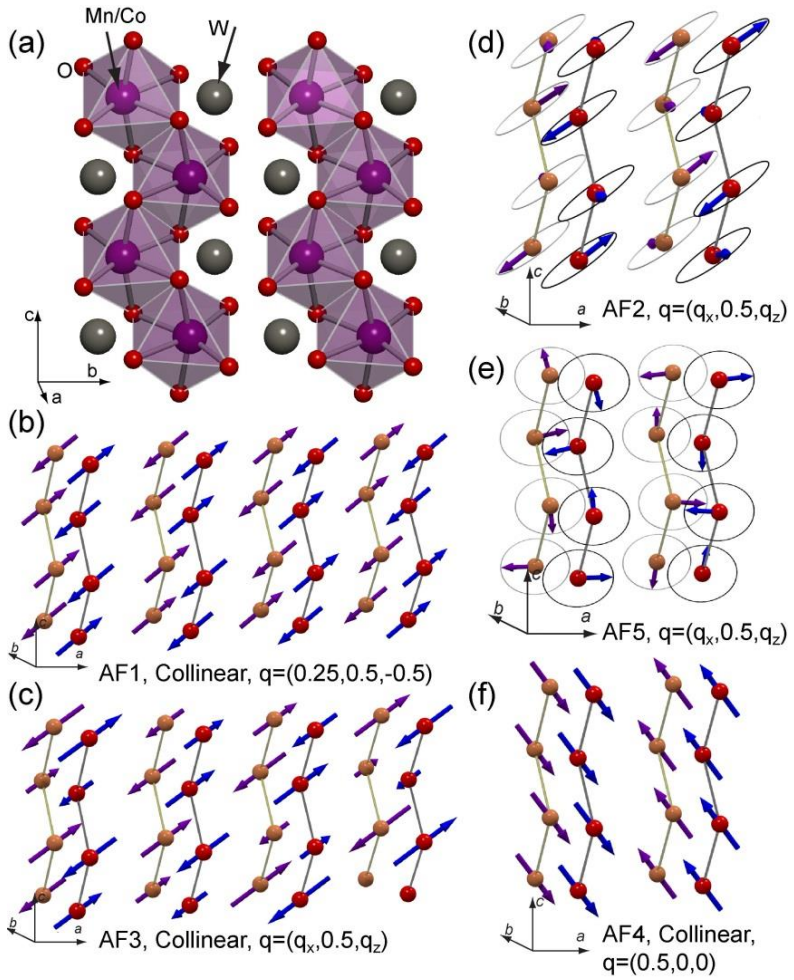

FpStudio can visualize the results



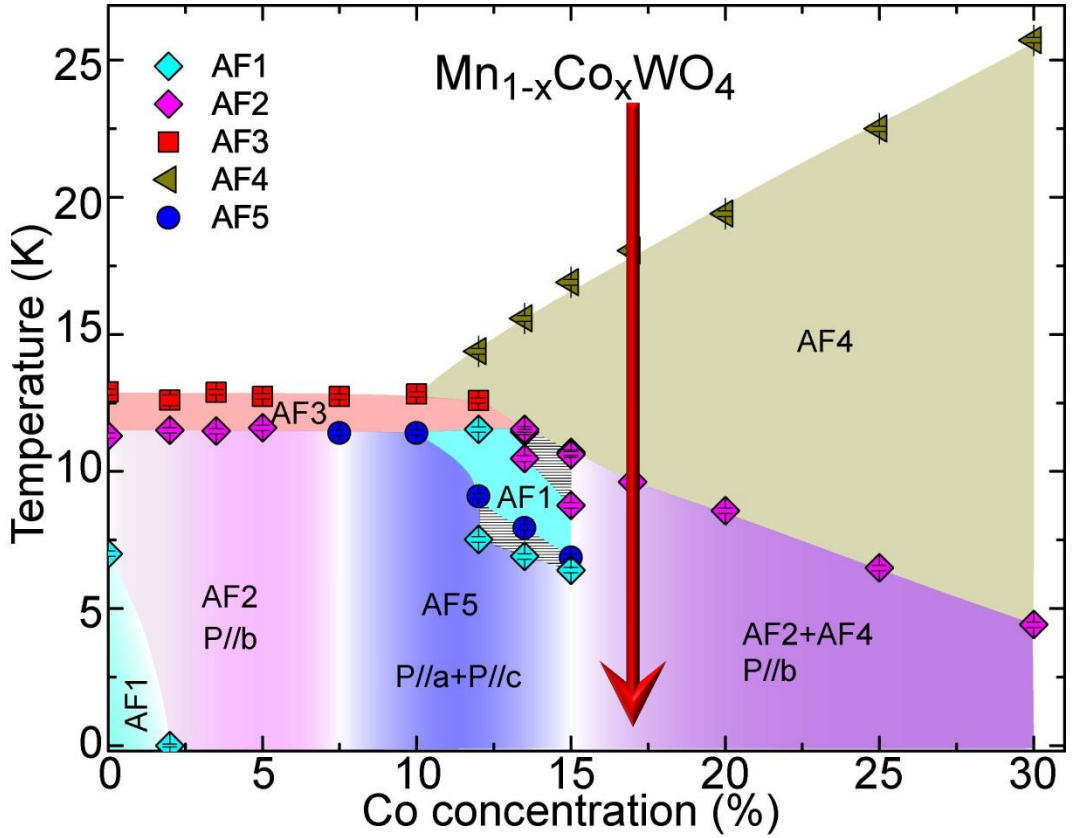

Vesta is another software can read the .mcif or .vesta file generated from FP refinement

# Single crystal diffraction **Magnetic Structures in $Mn_{1-x}Co_xWO_4$**

Phase with both Commensurate AF and Incommensurate AF is selected: 17% Co-doping $MnWO_4$



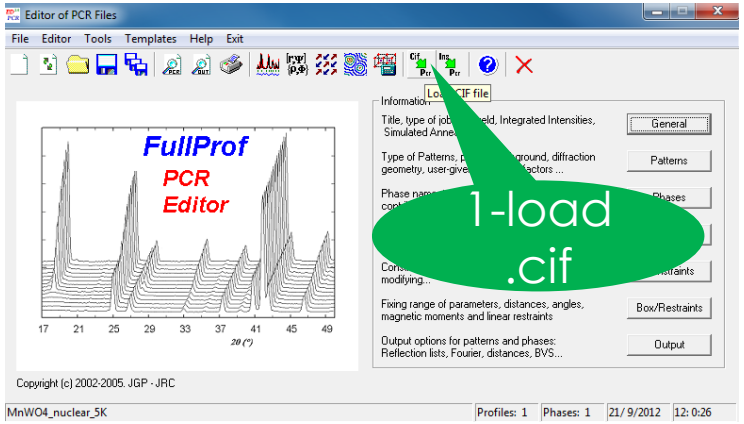

Feng Ye et al., Phys. Rev. B (2012)

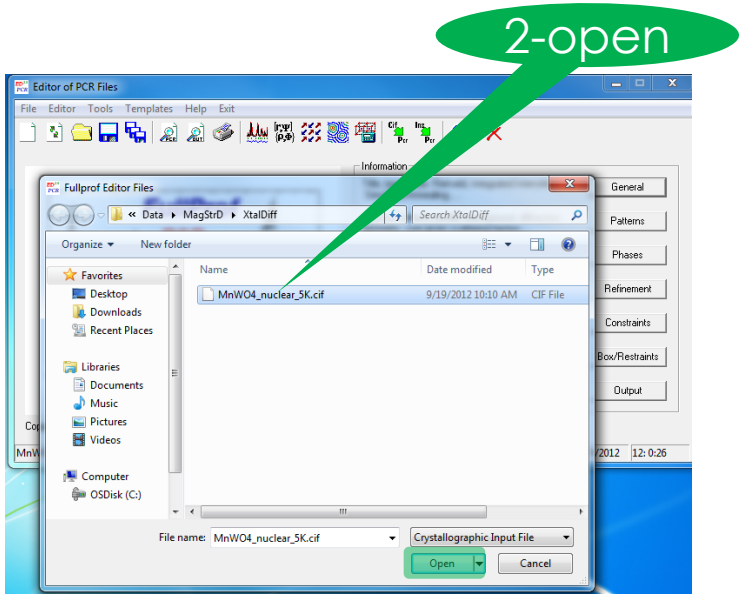


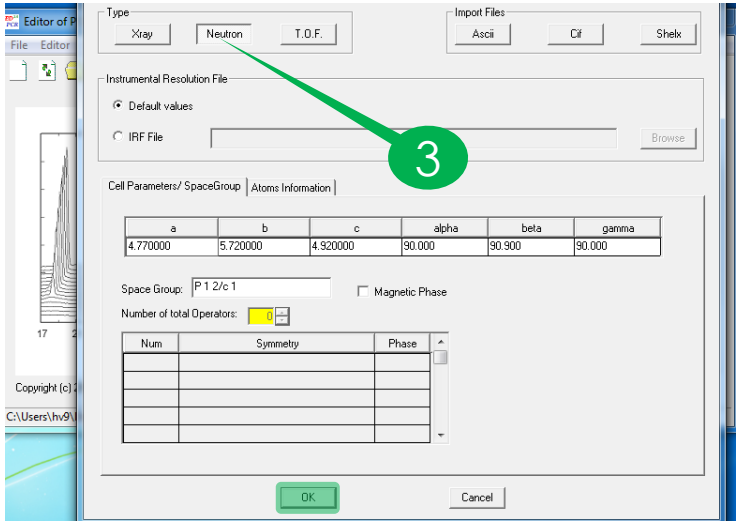

*P* 1 2/*c* 1 ***a***=4.77 Å ***b***=5.72 Å ***c***=4.92 Å **β**=90.9°

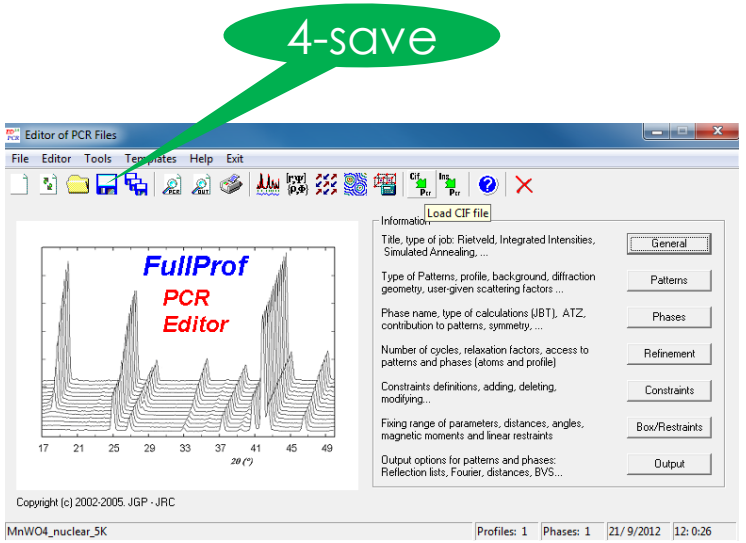
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Create .pcr file from .cif file



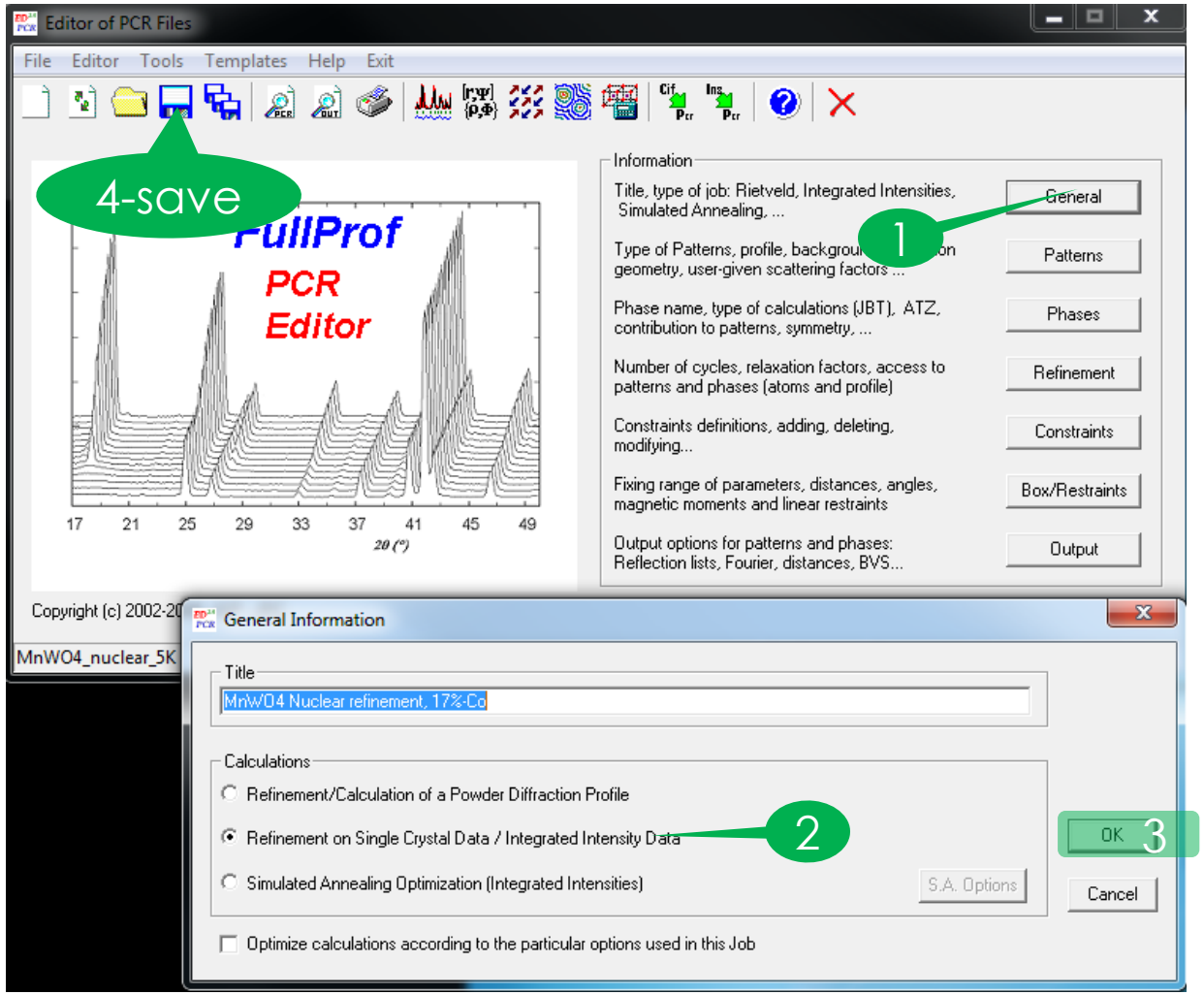






OAK RIDGE National Laboratory

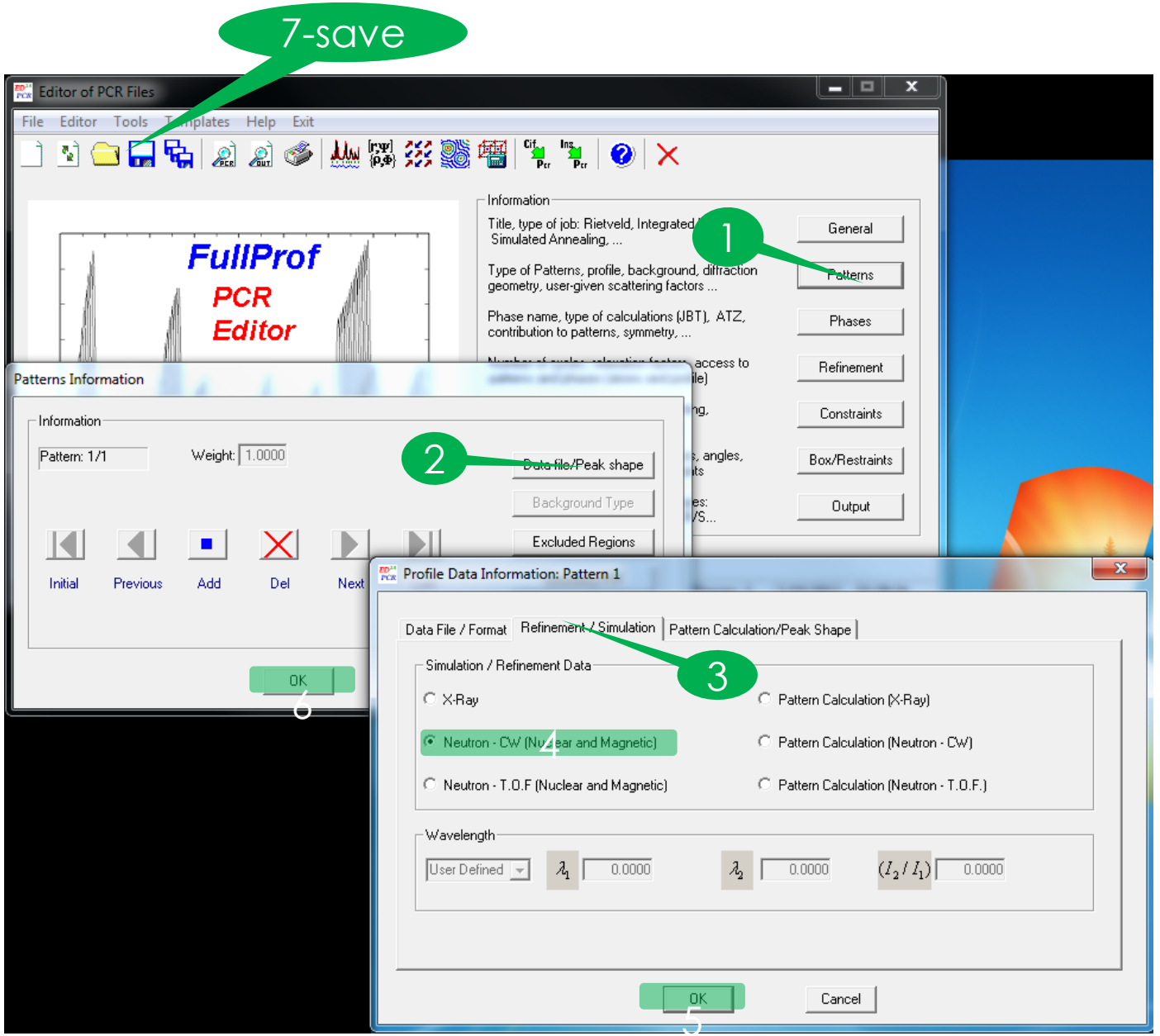
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## General-TAB



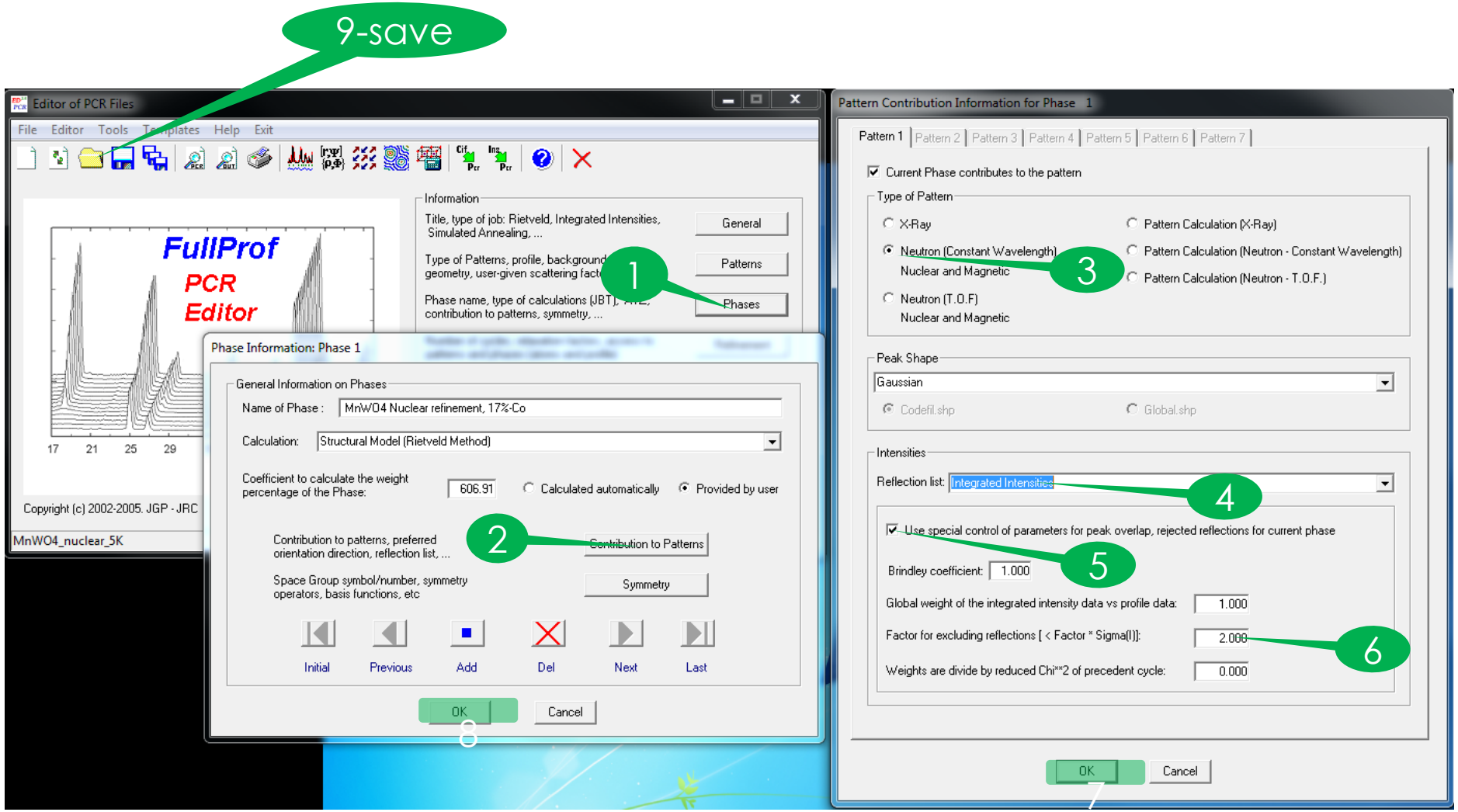
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Pattern



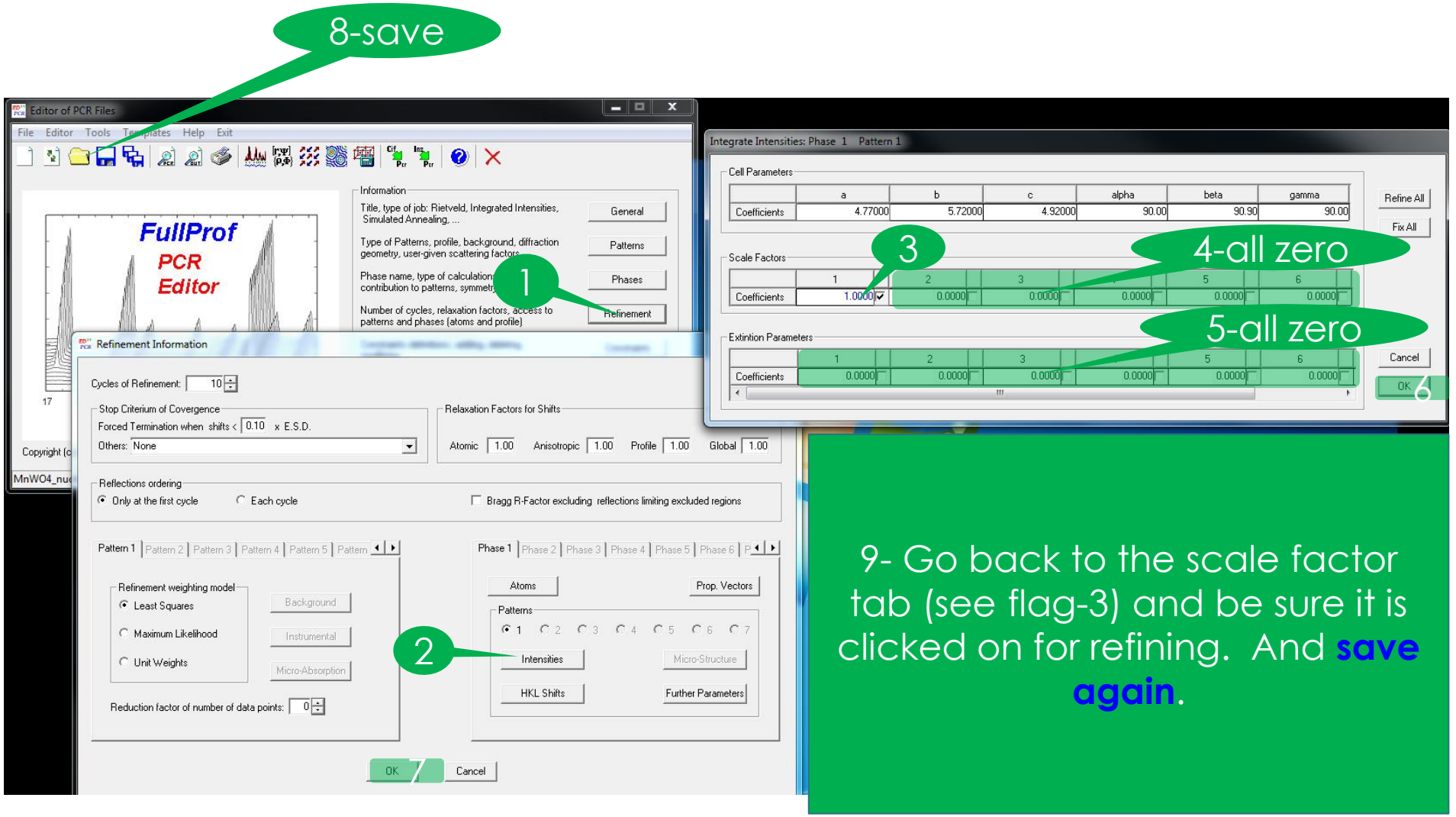
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Phase



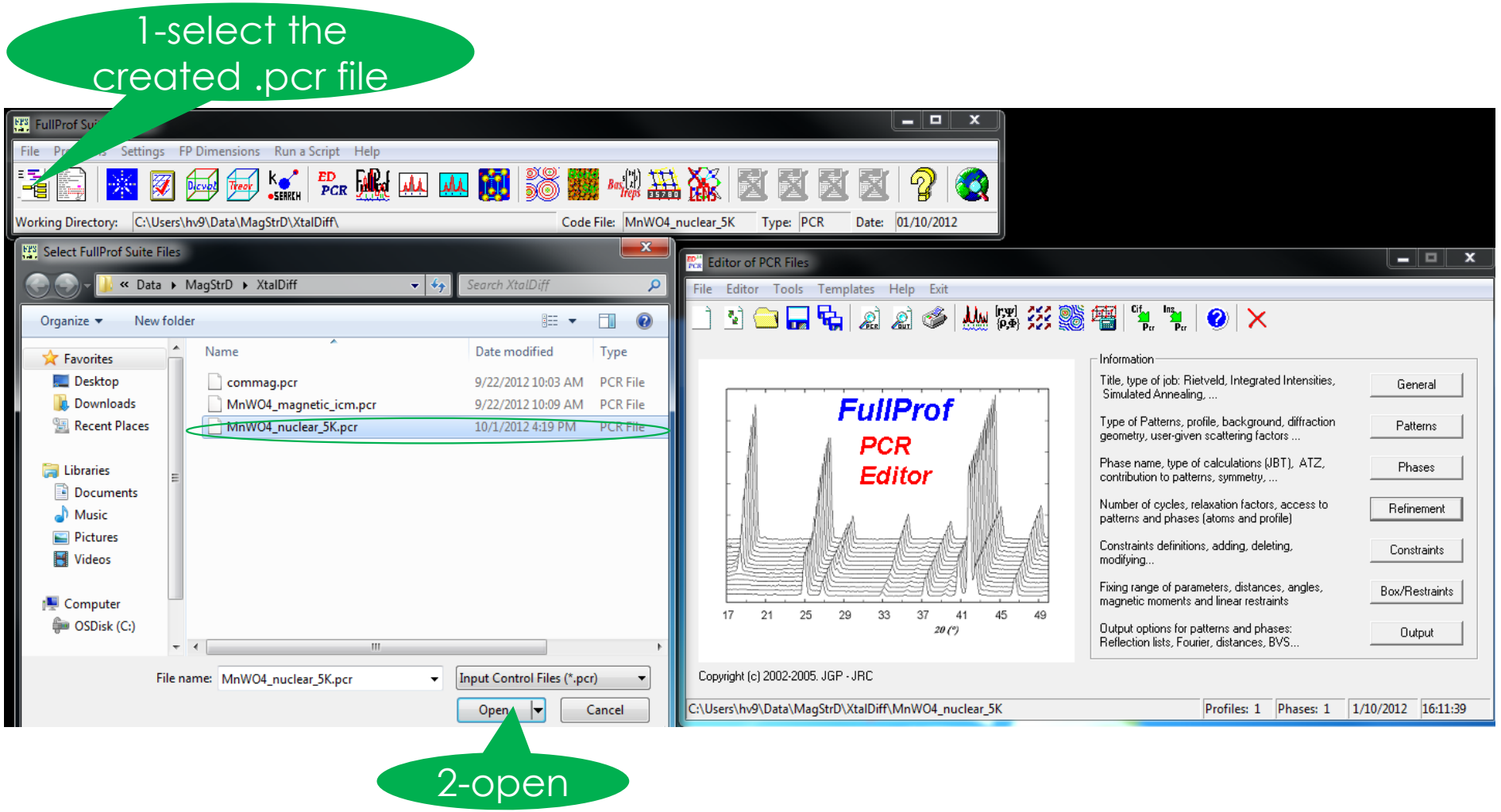
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine



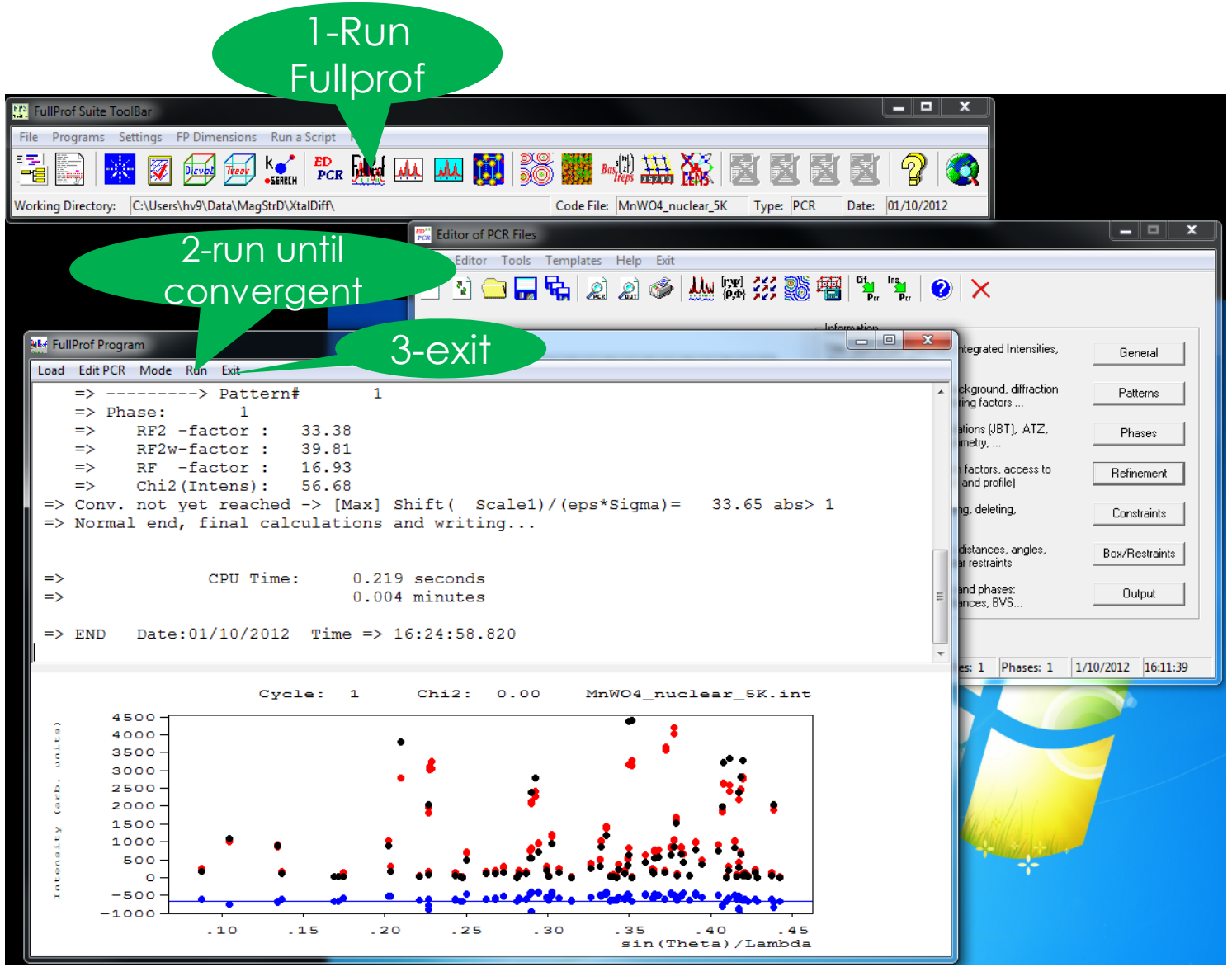
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine



# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine

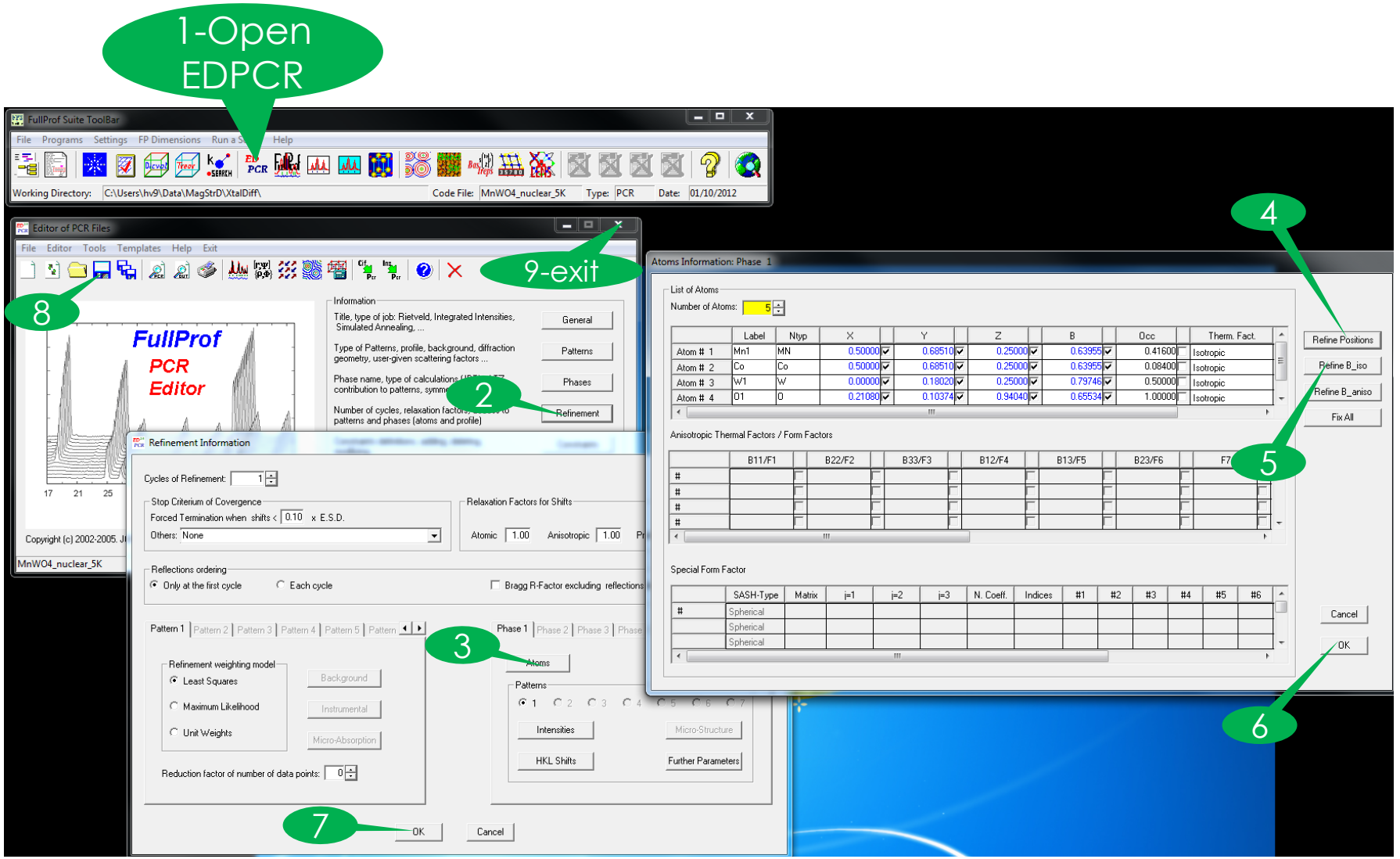





OAK RIDGE National Laboratory

# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine

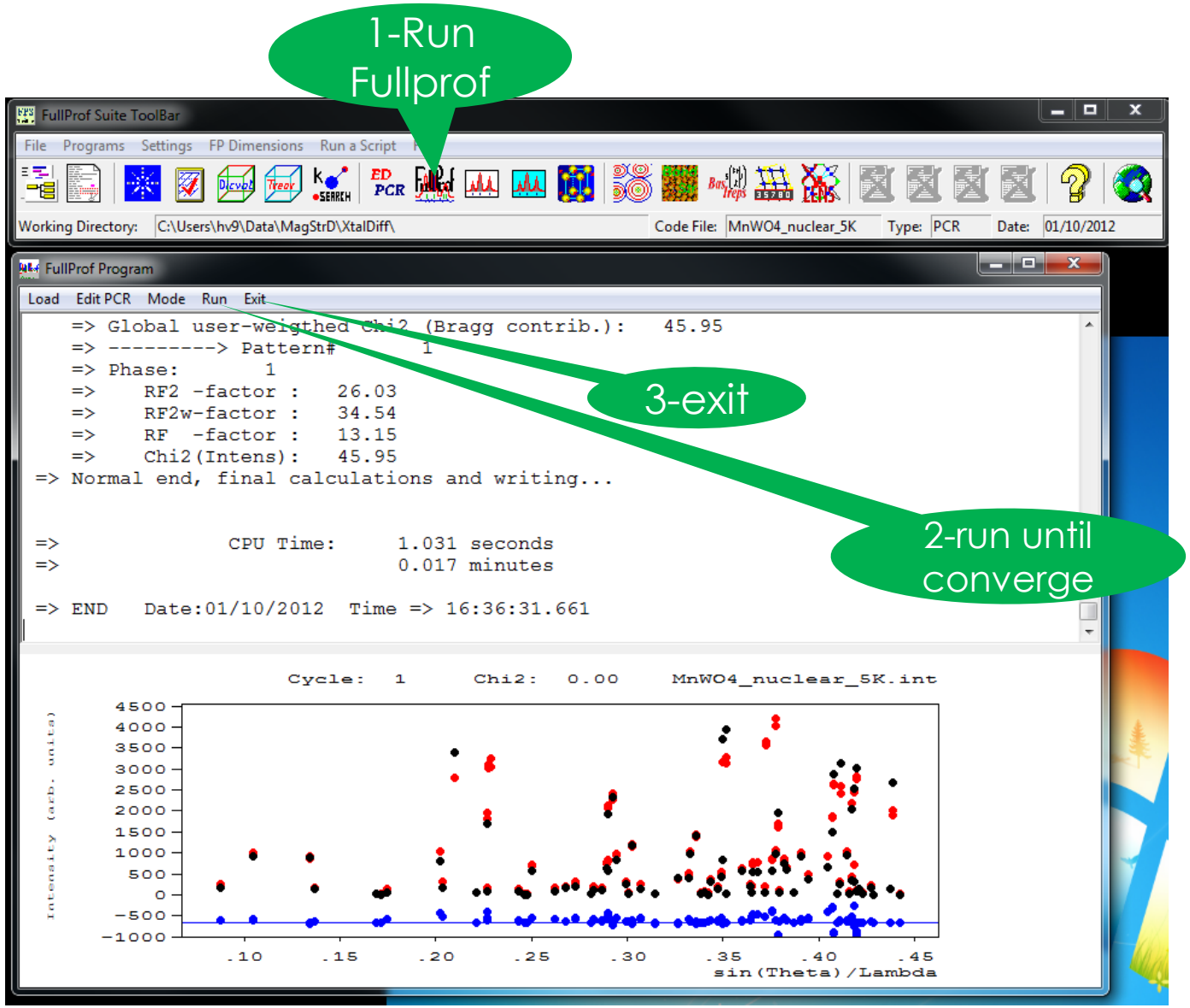





OAK RIDGE National Laboratory

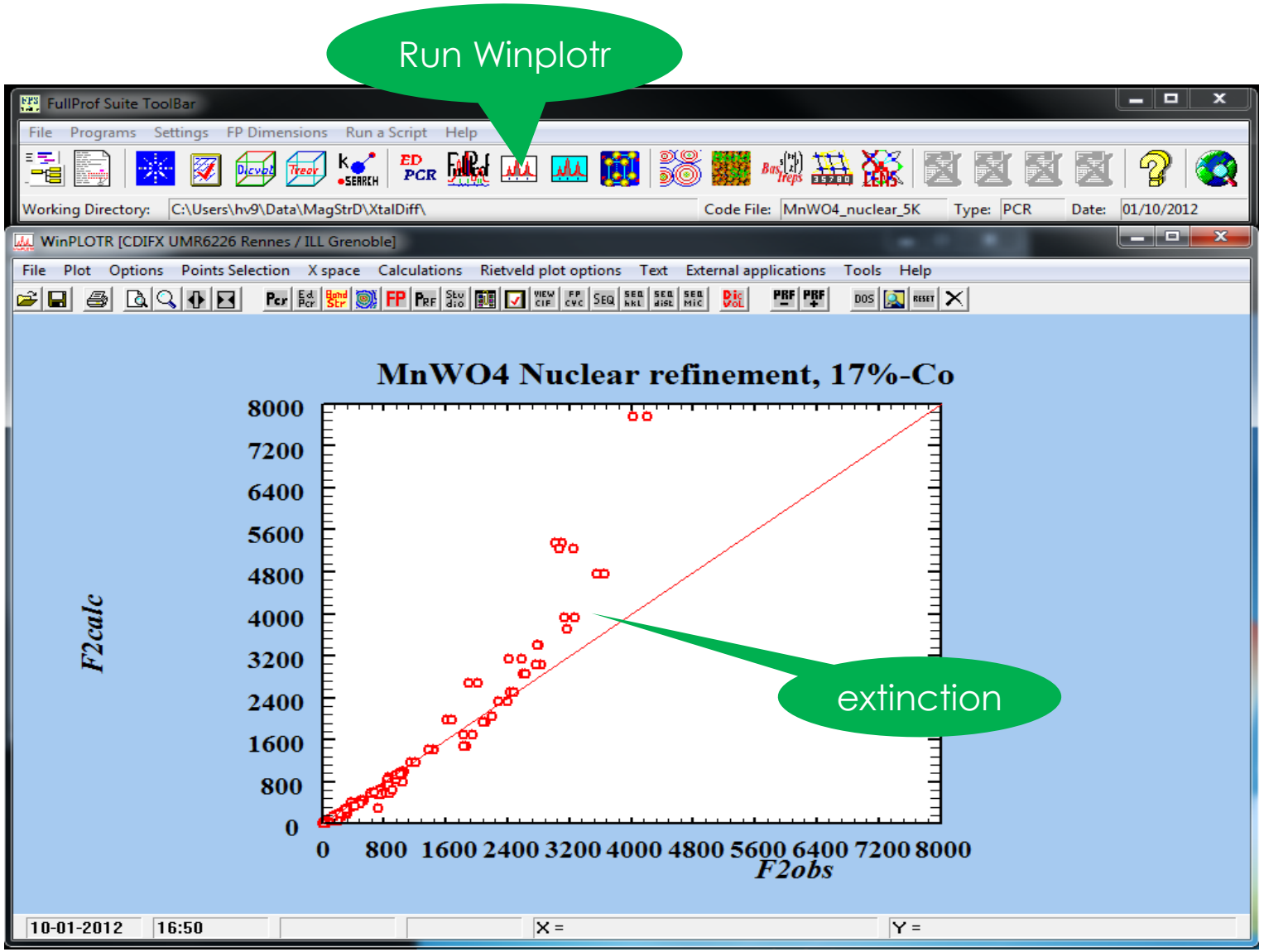
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine



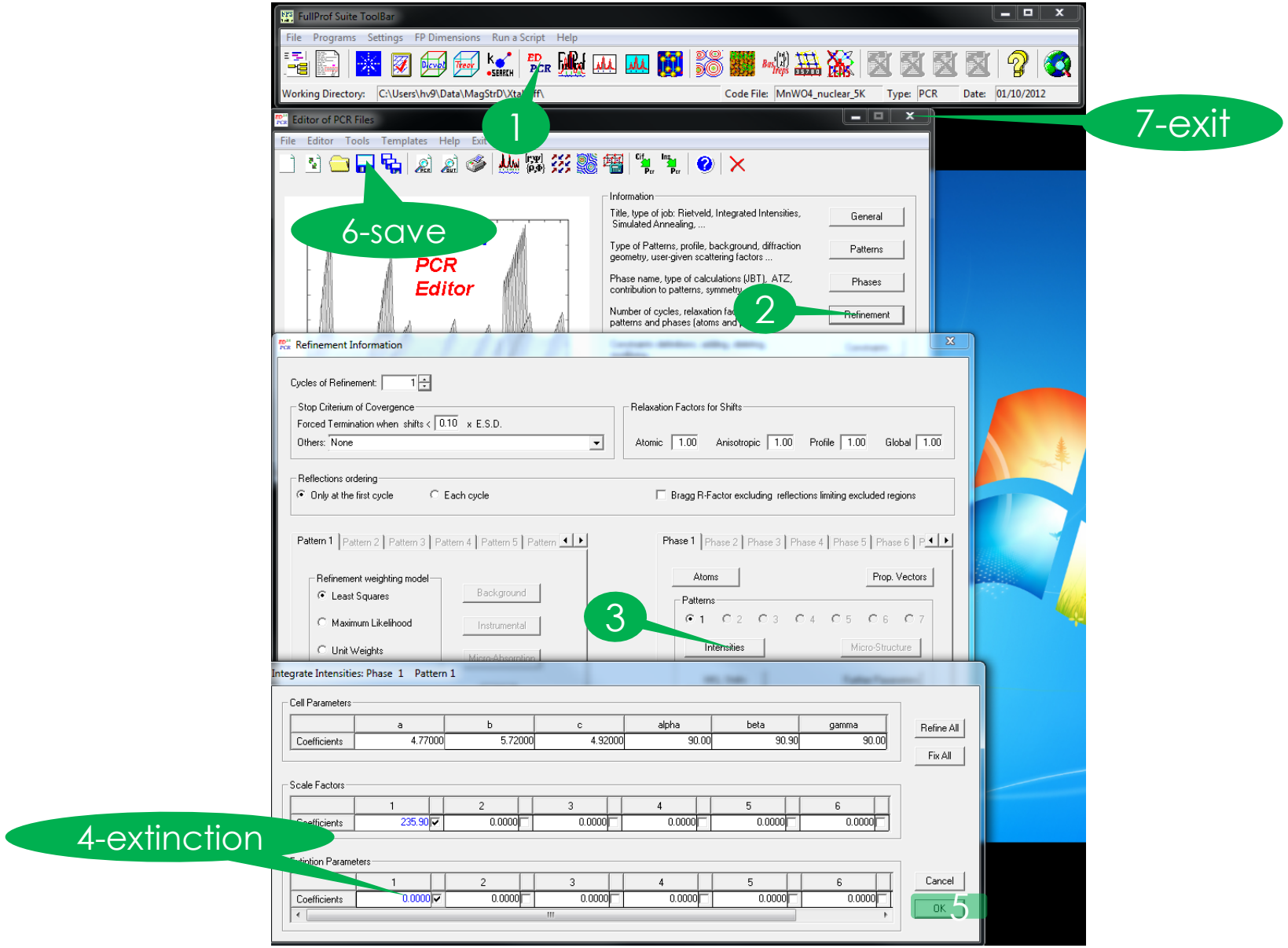
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine



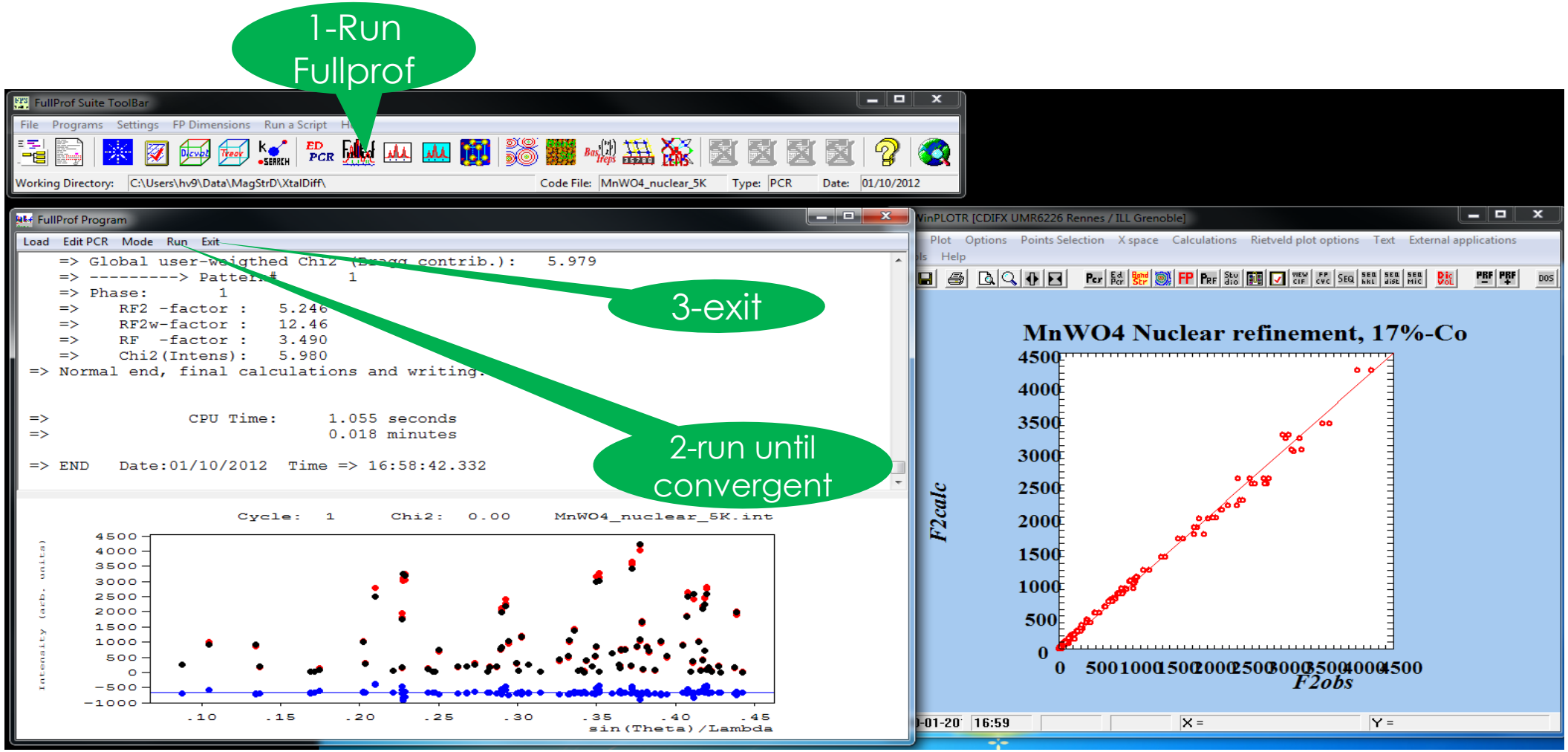
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine



# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine



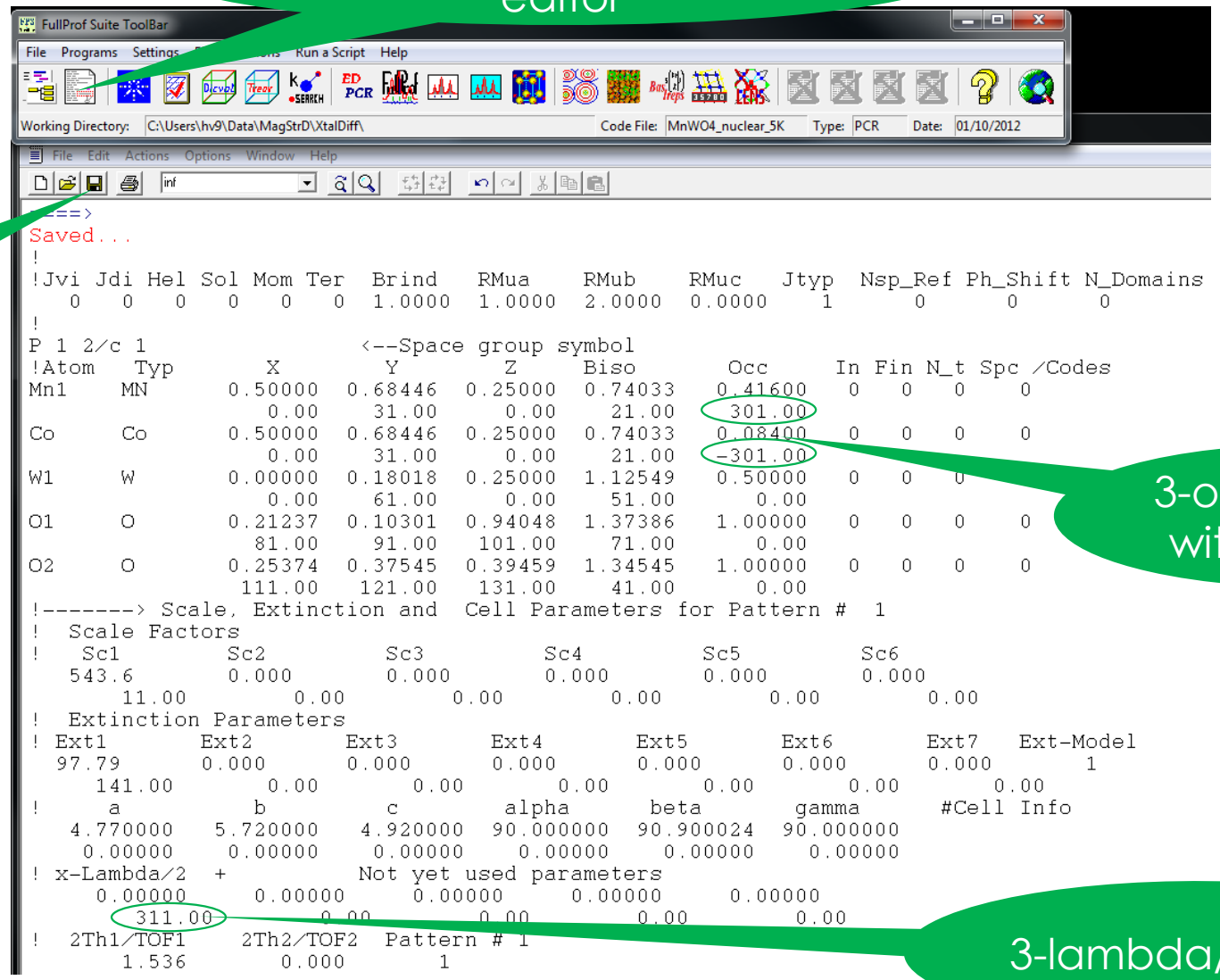



OAK RIDGE National Laboratory

# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine

1-Open .pcr file in text editor



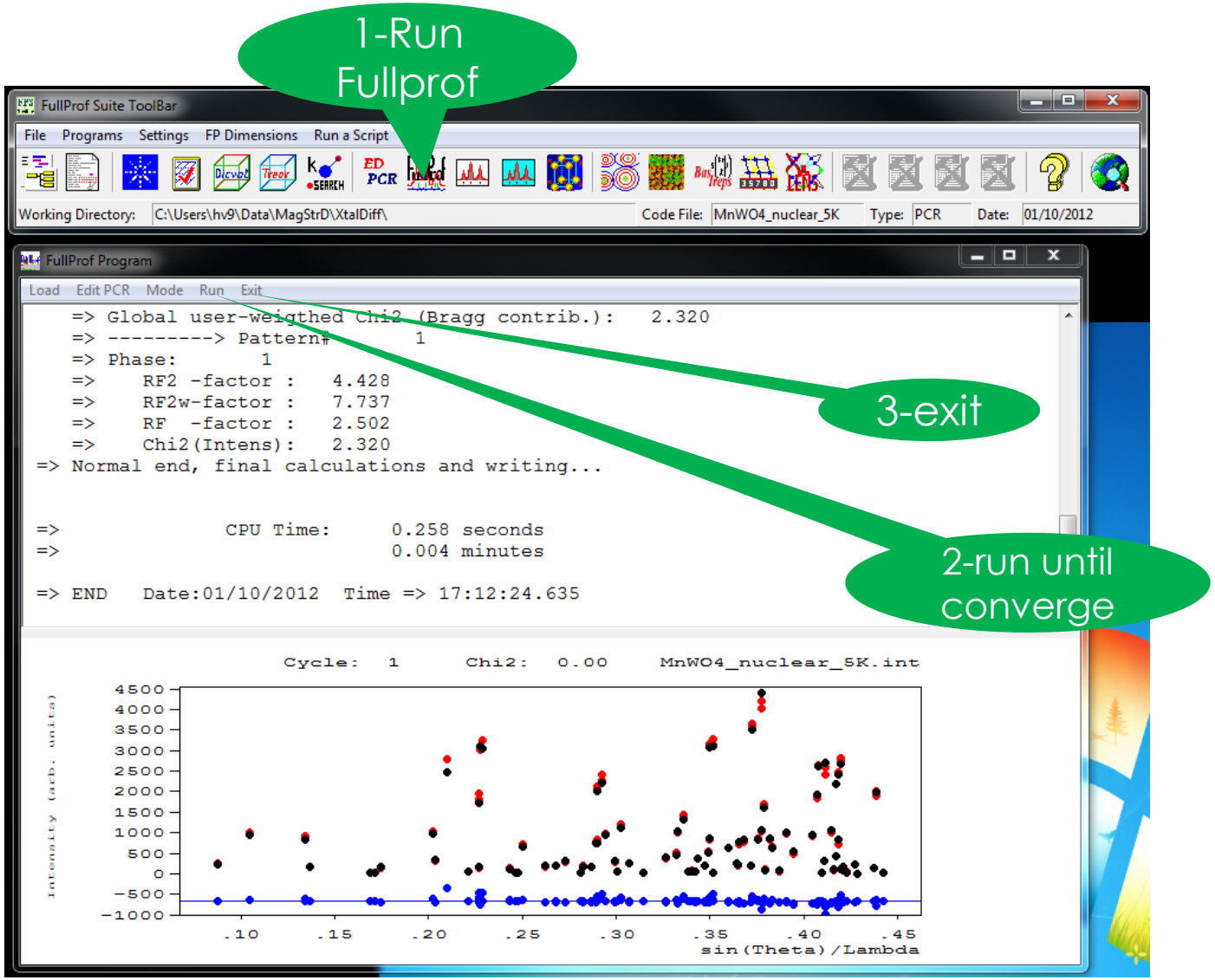

4-Save & exit

3-occup. refine with constrain

3-lambda/2 refine

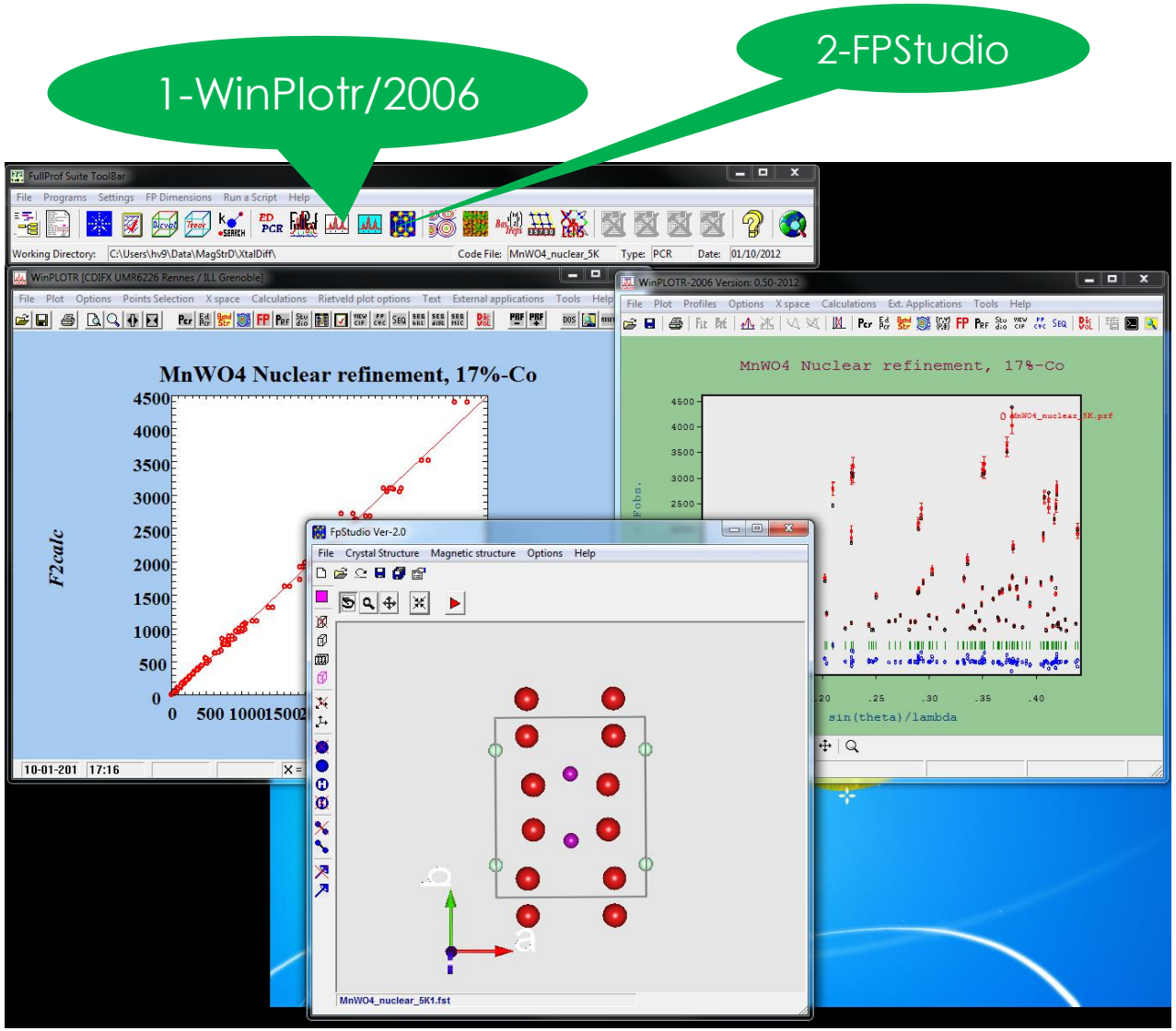
# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

## Refine



# Nuclear structure of $Mn_{1-x}Co_xWO_4$ refined by FullProf

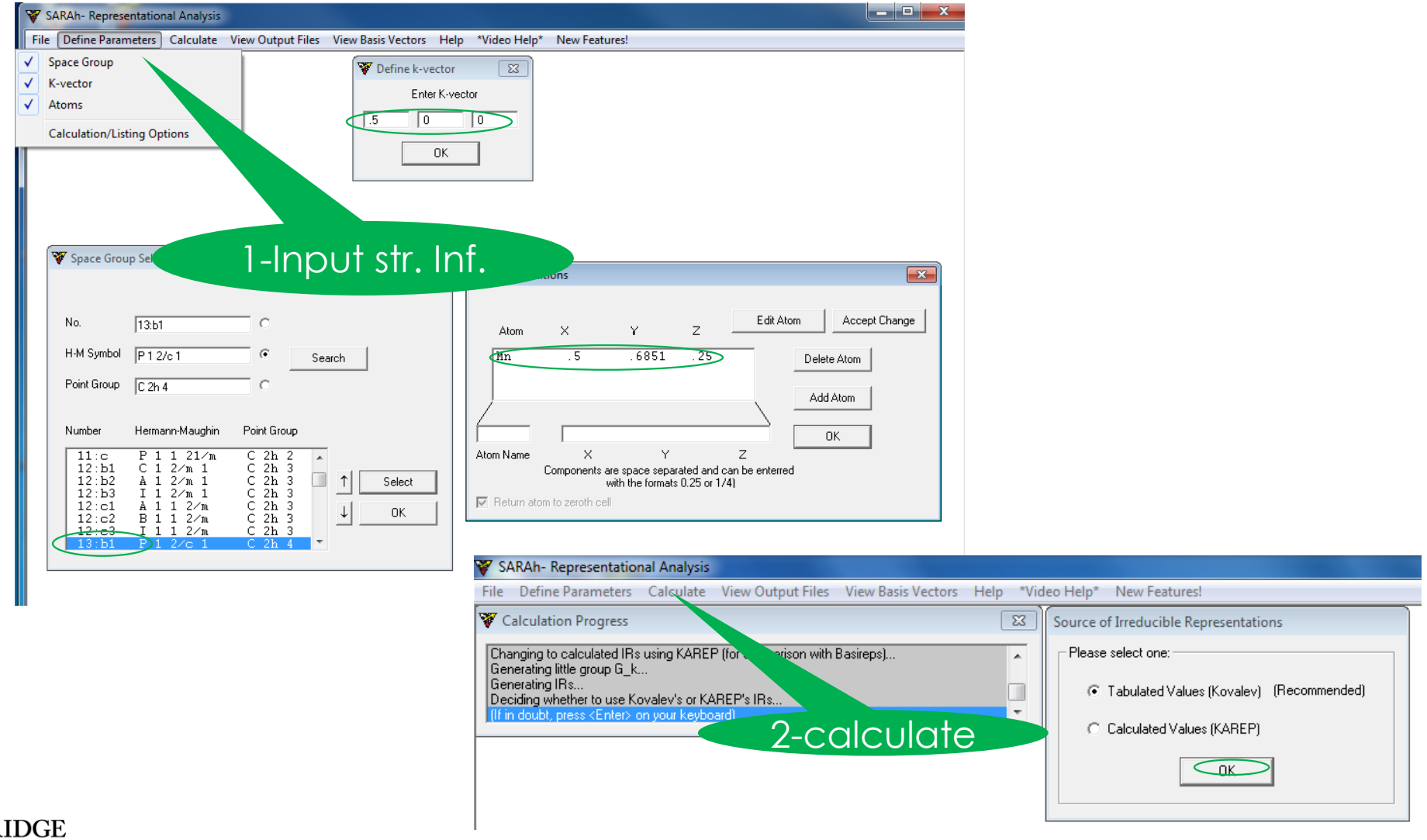
## Refine




can be refined, such as "anisotropic extinction model" and "anisotropic displacements", which depends on your physics and the number of reflections. Here it is good enough for the magnetic structure

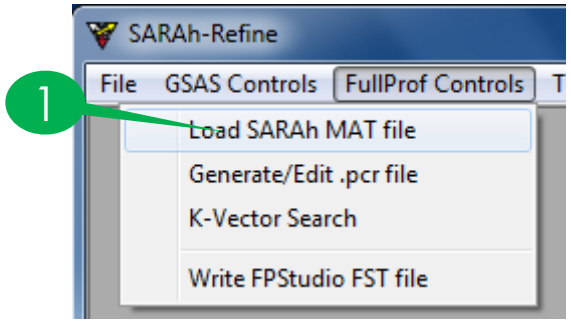
# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

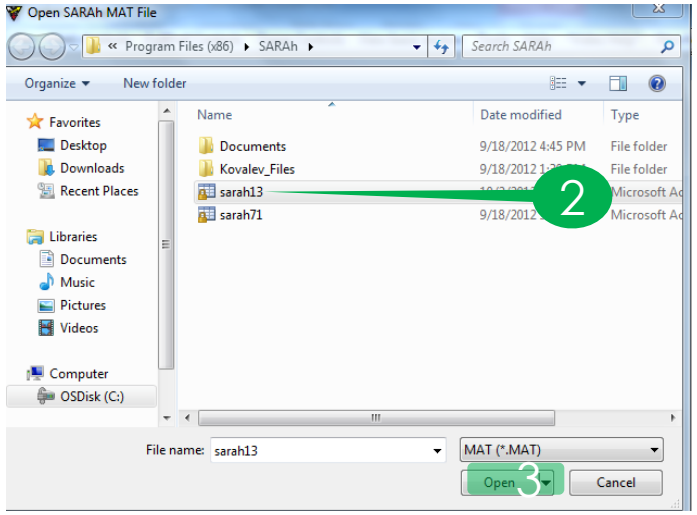
## Create the magnetic phase using SARAh-Representation Analysis

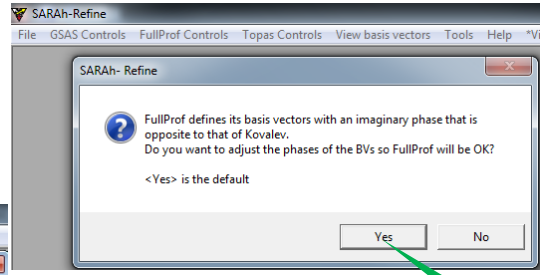


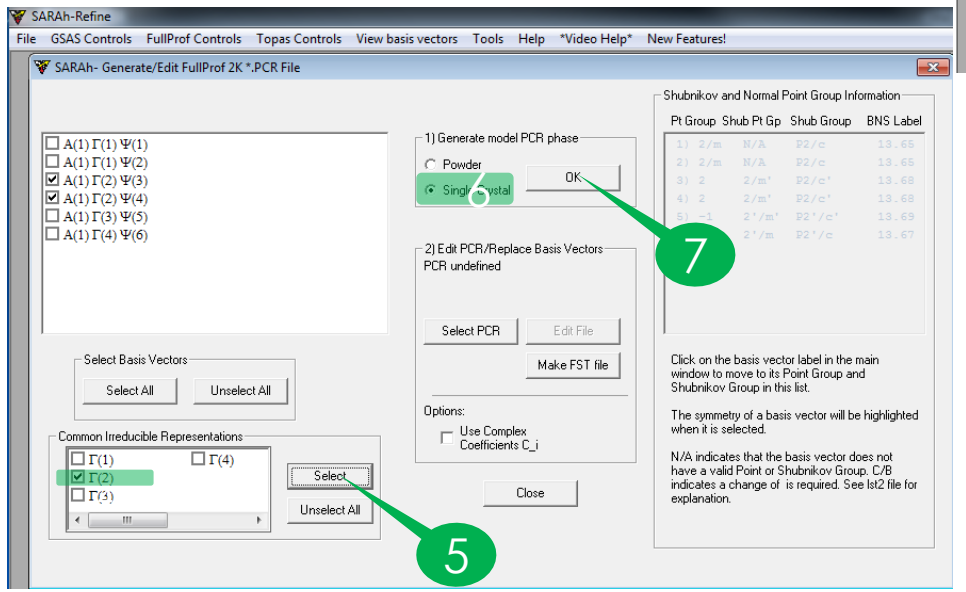
# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Create the magnetic phase using SARAh-Refine




Generate magnetic phase in sarah13.pcr
We will create the magnetic phase .pcr file from nuclear structure .pcr by inserting the sarah13.pcr

# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Create the magnetic .pcr

```
!
!NCY  Eps  R_at  R_an  R_pr  R_gl      Thmin       Step       Thmax    PSD    Sent0
  1  0.10  1.00  1.00  1.00  1.00       1.5360   0.000000      0.0000   0.000   0.000
!
!
     16    !Number of refined parameters
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:      4.43
!-------------------------------------------------------------------------------
 MnWO4 Nuclear refinement, 17%-Co
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth        ATZ    Nvk Npr More
   5   0   0 0.0 0.0 1.0   0   4   0   0   0        606.914   0   0   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind    RMua     RMub     RMuc    Jtyp  Nsp_Ref Ph_Shift N_Domains
   0   0   0   0   0   0  1.0000  1.0000   2.0000   0.0000     1       0       0       0
!
P 1 2/c 1                 <--Space group symbol
!Atom   Typ        X         Y         Z        Biso       Occ      In Fin N_t Spc /Codes
Mn1     MN       0.50000   0.68491   0.25000   0.63149   0.41661    0   0   0     0
                   0.00     31.00      0.00     21.00     161.00
Co      Co       0.50000   0.68491   0.25000   0.63149   0.08339    0   0   0     0
                   0.00     31.00      0.00     21.00    -161.00
W1      W        0.00000   0.18007   0.25000   0.76064   0.50000    0   0   0     0
                   0.00     61.00      0.00     51.00       0.00
O1      O        0.21097   0.10361   0.94038   0.66934   1.00000    0   0   0     0
                  81.00     91.00    101.00     71.00       0.00
O2      O        0.25098   0.37544   0.39396   0.72572   1.00000    0   0   0     0
                 111.00    121.00    131.00     41.00       0.00
!-------> Scale, Extinction and  Cell Parameters for Pattern #  1
!  Scale Factors
!   Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
   455.1       0.000       0.000       0.000       0.000       0.000
    11.00        0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7   Ext-Model
  78.96       0.000       0.000       0.000       0.000       0.000       0.000       1
   141.00        0.00        0.00        0.00        0.00        0.00        0.00
!     a           b           c        alpha       beta        gamma       #Cell Info
  4.770000    5.720000    4.920000   90.000000   90.900024   90.000000
   0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
! x-Lambda/2  +          Not yet used parameters
   0.02137     0.00000     0.00000     0.00000     0.00000
   151.00        0.00        0.00        0.00        0.00
!  2Th1/TOF1   2Th2/TOF2  Pattern # 1
     1.536       0.000       1
```

```
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     1.00
!-------------------------------------------------------------------------------
Magnetic Phase
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   4  -2   0   0        0.00   1   0   0
!
P -1                      <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
    2     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
!
SYMM X, Y, Z
BASR        2        0        0        0        0        2
BASI        0        0        0        0        0        0
SYMM -X+1, -Y+1, -Z+1
BASR        2        0        0        0        0        2
BASI        0        0        0        0        0        0
!
!Atom Typ  Mag Vek    X       Y       Z       Biso    Occ      C1       C2       C3
!     C4       C5       C6       C7       C8       C9       MagPh
MN1  MMN3  1   0     .50000   .68510   .25000  .30000 1.00000   0.000    0.000    0.000
                    0.00     0.00     0.00     0.00     0.00     0.00     0.00
   0.000    0.000    0.000    0.000    0.000    0.000    .00000
   0.00     0.00     0.00     0.00     0.00     0.00
!  Scale Factors
!  Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
  100.0       0.000       0.000       0.000       0.000       0.000
    .00         0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
!    Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7
     0.000       0.000       0.000       0.000       0.000       0.000       0.000
      0.00        0.00        0.00        0.00        0.00        0.00        0.00
!     a           b           c        alpha       beta        gamma
273
 1   1  1  90  90  90
   0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
!  Not yet used parameters
 0.00000 0.00000 0.00000 0.00000 0.00000
   0.00    0.00    0.00    0.00    0.00
! Propagation vectors:
    .5000000    .0000000    .0000000          Propagation Vector  1
   0.000000    0.000000    0.000000
```

all-zero

all-zero

all-zero

sarah13.pcr → insert/replace → MnWO4_nuclear_5K.pcr → Save as → commag.pcr

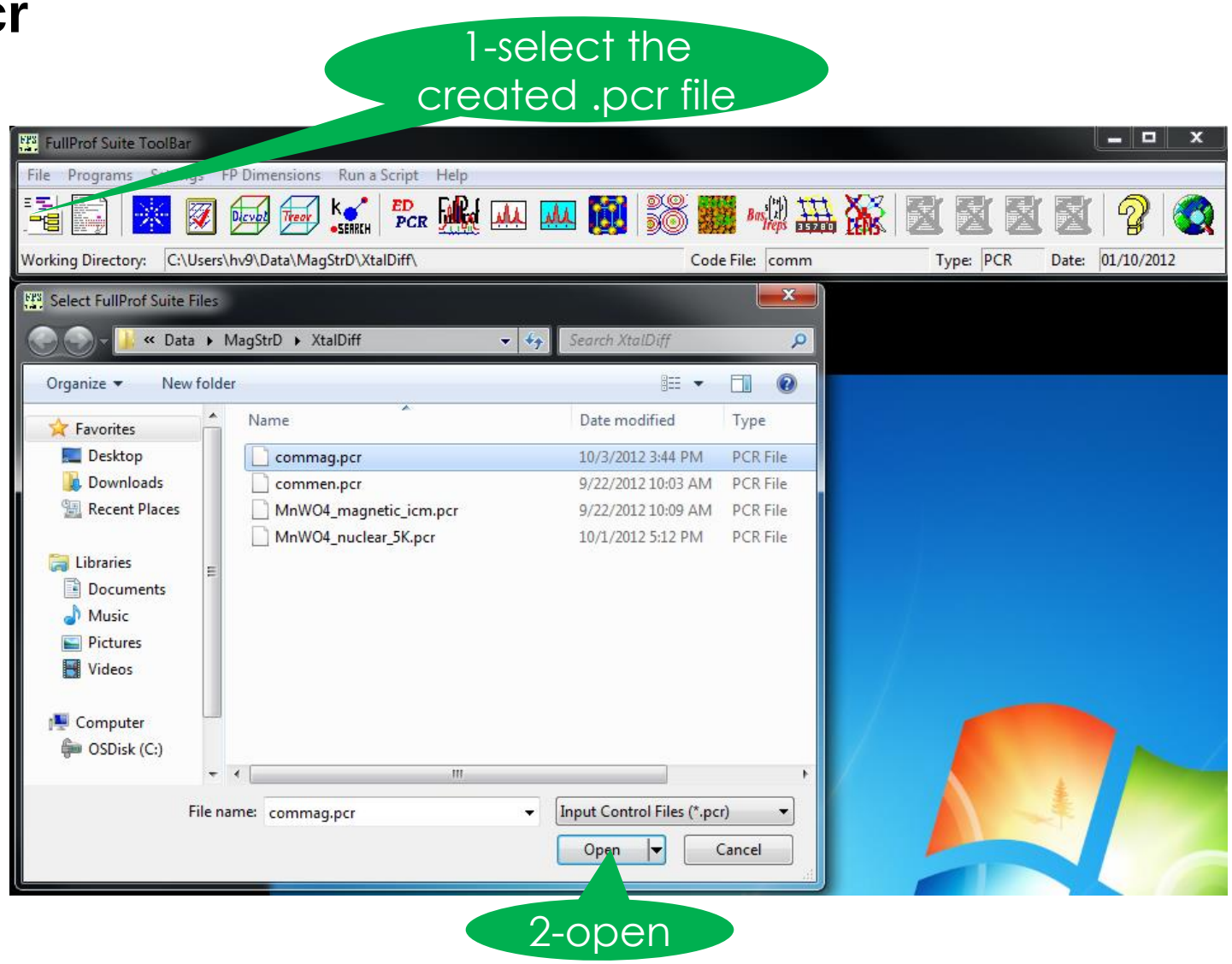
# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Commag.pcr

```
Saved...
COMM MnWO4 commensurate magnetic structure refinement, 17%-Co
! Current global Chi2 (Bragg contrib.) =      2.320
! Files => DAT-file: MnWO4_nuclear_5K.int,  PCR-file: MnWO4_nuclear_5K
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   0   1   0   0   0   0   0   0   0   0   0   0   0   1   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   0   3   0   0   0   0   0   0   0
!
!NCY  Eps  R_at  R_an  R_pr  R_gl      Thmin       Step       Thmax    PSD    Sent0
  1  0.10  1.00  1.00  1.00  1.00      1.5360   0.000000     0.0000   0.000   0.000
!
!
     16    !Number of refined parameters
!-------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     4.43
!-------------------------------------------------------------------------------
 MnWO4 Nuclear refinement, 17%-Co
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth     ATZ   Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   4  -2   0   0       0.00  1   0   0
!
P -1                        <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
     2     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
!
SYMM X, Y, Z
BASR        2       0       0       0       2
BASI        0       0       0       0       0
SYMM -X+1, -Y+1, -Z+1
BASR        2       0       0       0       2
BASI        0       0       0       0       0
!
!Atom Typ  Mag Vek    X       Y       Z       Biso    Occ      C1       C2       C3
!     C4      C5      C6      C7      C8      C9      MagPh
MN1  MMN3  1   0     .50000  .68510  .25000 .30000 1.00000    0.000    0.000    0.000
                    0.00     0.00     0.00     0.00     0.00     0.00     0.00     0.00
   0.000    0.000    0.000    0.000    0.000    0.000    .00000
    0.00     0.00     0.00     0.00     0.00     0.00     0.00
!-------> Scale, Extinction and  Cell Parameters for Pattern #  1
!  Scale Factors
!   Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
   455.1        0.000       0.000       0.000       0.000       0.000
      0        0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7   Ext-Model
  78.96       0.000       0.000       0.000       0.000       0.000       0.000       1
     0        0.00        0.00        0.00        0.00        0.00        0.00
!      a           b           c          alpha       beta        gamma       #Cell Info
   4.770000    5.720000    4.920000   90.000000   90.900024   90.000000
    0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
! x-Lambda/2  +          Not yet used parameters
     0.02137     0.00000     0.00000     0.00000     0.00000
     0        0.00        0.00        0.00        0.00
! Propagation vectors:
    .5000000    .0000000    .0000000          Propagation Vector  1
   0.000000    0.000000    0.000000
!  2Th1/TOF1    2Th2/TOF2  Pattern # 1
      1.536       0.000       1
```

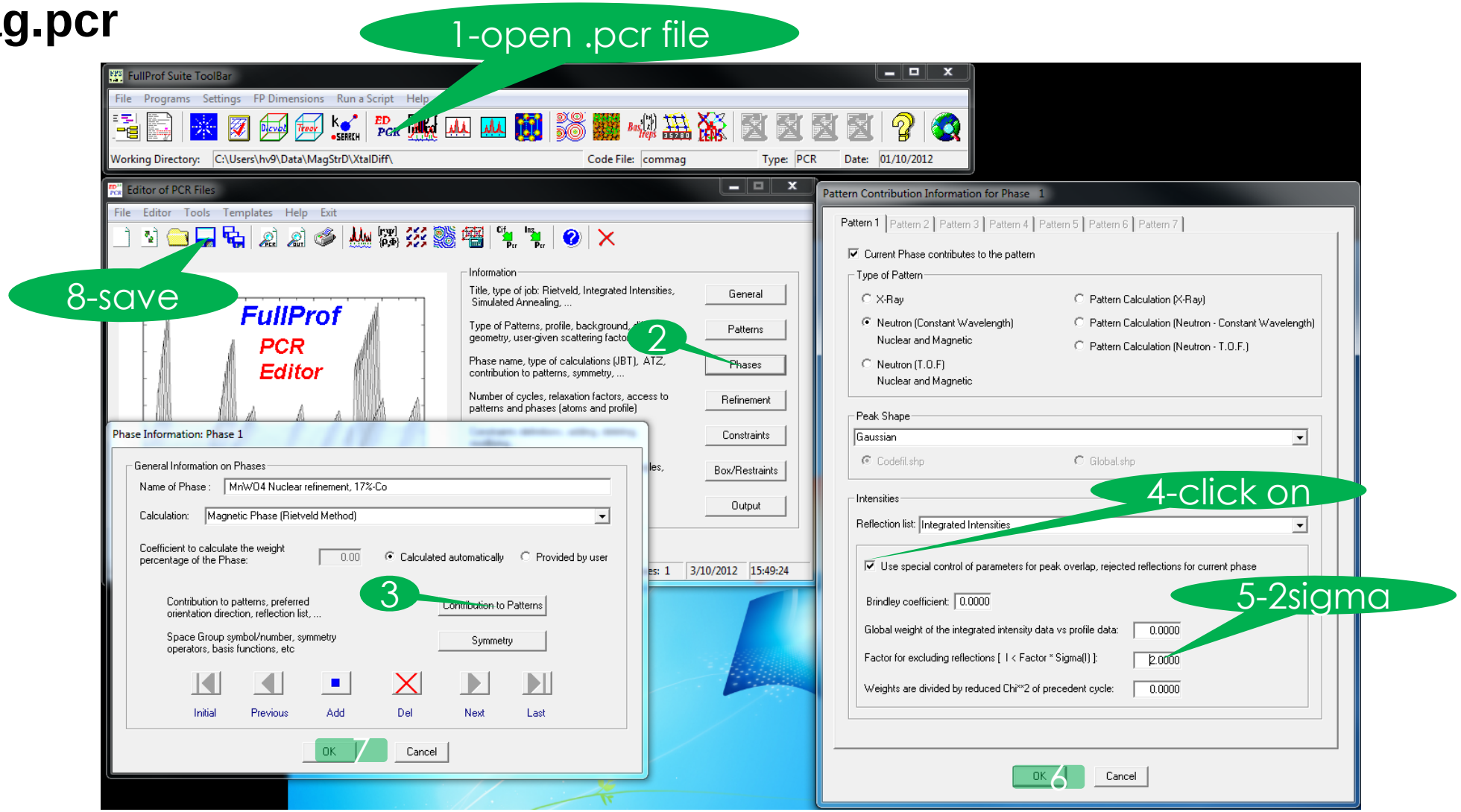
# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Commag.pcr



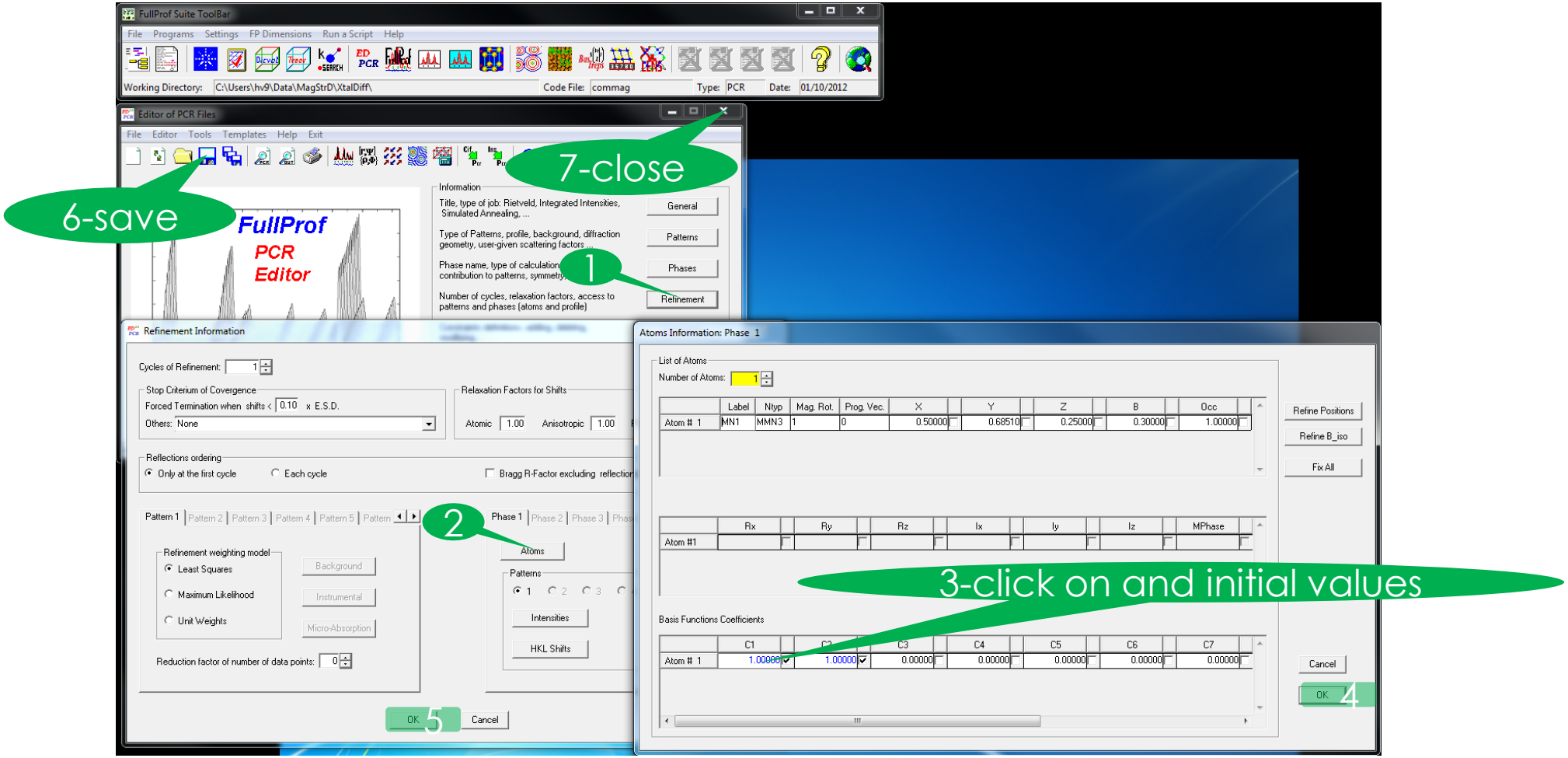
# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Commag.pcr



# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Commag.pcr

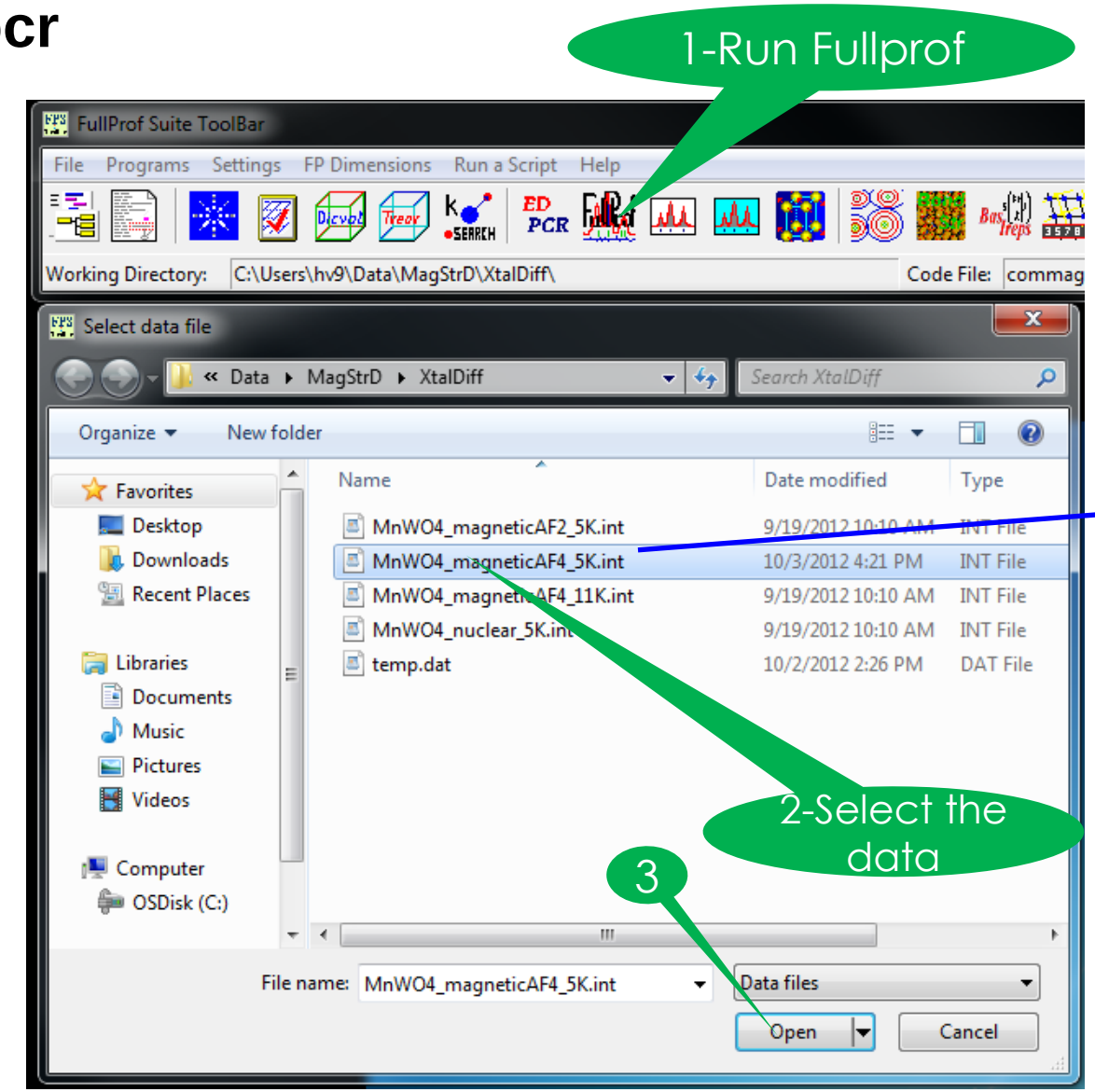





OAK RIDGE National Laboratory

# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

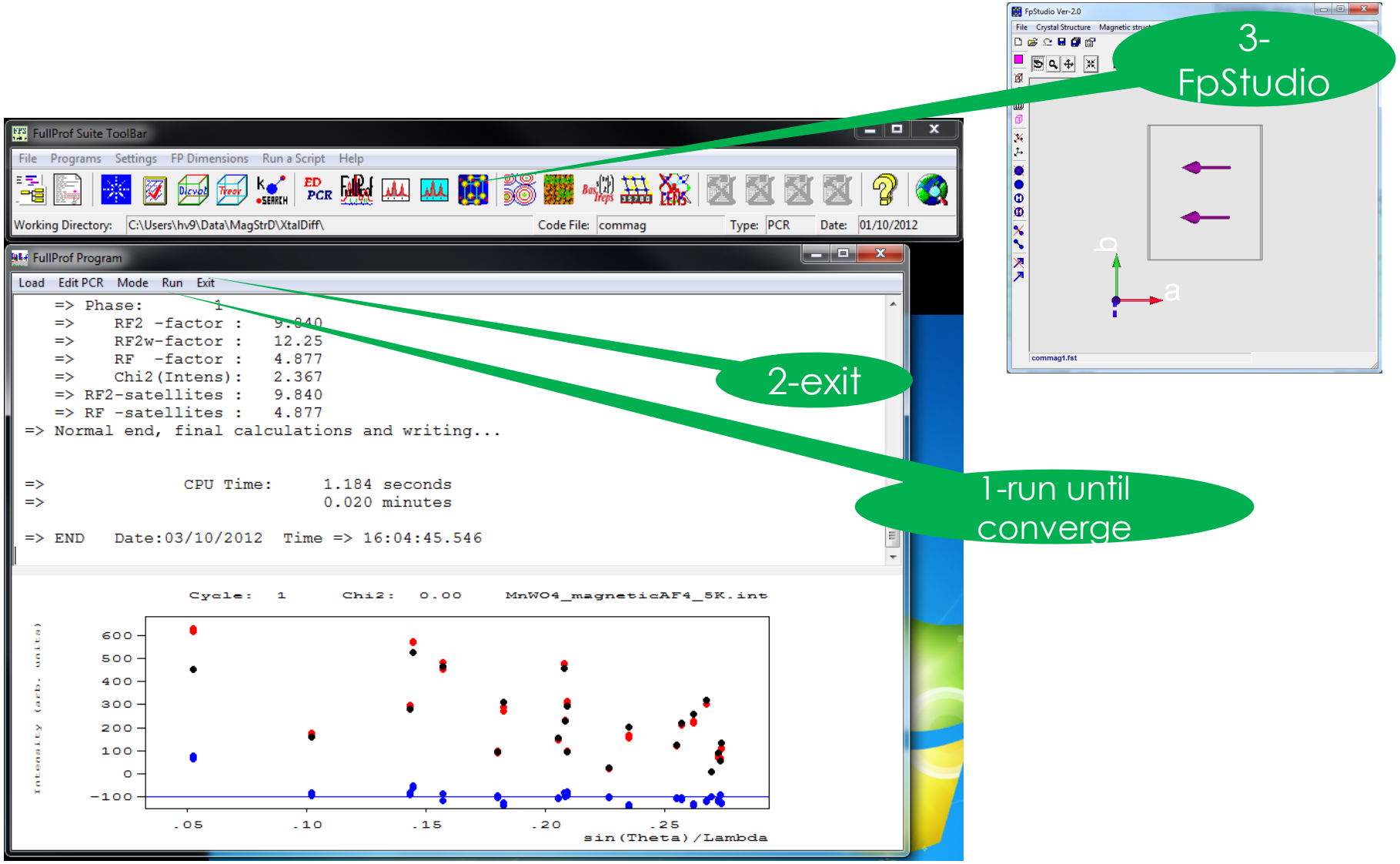
## Commag.pcr




```
Saved...
Single crystal data of MnWO4-17pCo (hb3a)
! Data format
(4i5,2f8.2,i4,3f8.2)
!Wavelength Itypdata Ipow(n)
1.53600   0    0
! The number of propagation vectors
1
! nv    k-vector
1 0.5 0 0
!   h    k    l    nv  F^2      sigma(F^2)  code
   -3   -0   -0    1  220.77    24.02    1
   -2   -0   -1    1    6.77    28.95    1
   -2   -0   -0    1  483.14    26.21    1
   -2   -0    1    1    4.23     3.34    1
   -2   -0    2    1    0.00     0.00    1
   -2    1   -2    1   67.54     8.40    1
   -2    1   -1    1  476.88    23.83    1
   -2    1   -0    1   88.78     8.86    1
   -2    1    1    1  148.23    10.55    1
   -2    1    2    1    8.79     1.74    1
   -2    2   -1    1  211.75    31.62    1
   -2    2   -0    1  167.75    12.99    1
   -2    2    1    1  120.06    13.22    1
   -1   -0   -0    1  630.71    34.79    1
   -1   -0    1    1    0.00     0.00    1
   -1   -0    2    1  100.72     9.14    1
   -1    1   -1    1  575.06    41.47    1
   -1    1   -0    1  177.01    11.62    1
   -1    1    1    1  296.13    17.86    1
   -1    1    2    1   21.93     8.54    1
   -1    2   -2    1  110.18    17.98    1
   -1    2   -1    1  315.65    32.47    1
   -1    2   -0    1  272.73    16.39    1
   -1    2    1    1  229.09    25.01    1
   -1    2    2    1   79.71    12.33    1
   -1    3   -0    1  302.73    21.20    1
   -0    0   -2    1   99.62    10.96    1
   -0    0   -1    1    0.00     0.00    1
   -0    0   -0    1  615.47    37.11    1
   -0    1   -2    1   26.86     7.11    1
   -0    1   -1    1  288.24    19.69    1
   -0    1   -0    1  163.86    12.48    1
   -0    1    1    1  568.64    40.37    1
   -0    2   -2    1   70.87    16.70    1
   -0    2   -1    1  234.70    27.29    1
   -0    2   -0    1  289.51    15.90    1
   -0    2    1    1  306.09    32.96    1
   -0    2    2    1  105.75    18.82    1
   -0    3   -0    1  302.12    18.40    1
    1    0   -2    1    7.58    19.89    1
    1    0   -1    1    3.09     3.09    1
    1    0   -0    1  452.89    28.44    1
    1    0    1    1    0.00     0.00    1
    1    1   -2    1    2.77     7.06    1
    1    1   -1    1  151.09    12.34    1
    1    1   -0    1   97.32    10.11    1
    1    1    1    1  474.56    23.26    1
    1    1    2    1   61.17     8.99    1
    1    2   -1    1  123.40    14.72    1
    1    2   -0    1  156.49    13.42    1
    1    2    1    1  218.98    29.27    1
    2    0   -0    1  229.92    26.76    1
```

# Commensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Commag.pcr



# Incommensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## Commag.pcr

```
COMM MnWO4 commensurate magnetic structure refinement, 17%-Co
! Current global Chi2 (Bragg contrib.) =       2.364
! Files => DAT-file: MnWO4_magneticAF4_5K.int,  PCR-file: commag
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   0   1   0   0   0   0   0   0   0   0   0   0   1   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   3   0   0   0   0   0   0   0   0
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin       Step       Thmax    PSD    Sent0
  1  0.10  1.00  1.00  1.00  1.00      1.5360   0.000000     0.0000   0.000   0.000
!
!
      2    !Number of refined parameters
!------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     9.81
!------------------------------------------------------------------------------
 MnWO4 Nuclear refinement, 17%-Co
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   4  -2   0   0         0.000   1   0   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind    RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift N_Domains
   0   0   0   0   0   0  1.0000  1.0000  2.0000  0.0000    1       0       0       0
!
P -1                    <--Space group symbol for hkl generation
! Nsym   Cen  Laue Ireps N_Bas
    2     1     1    -1     2
! Real(0)-Imaginary(1) indicator for Ci
  0  0
!
SYMM X, Y, Z
BASR       2       0       0       0       0       2
BASI       0       0       0       0       0       0
SYMM -X+1, -Y+1, -Z+1
BASR       2       0       0       0       0       2
BASI       0       0       0       0       0       0
!
!Atom   Typ  Mag Vek    X       Y       Z       Biso    Occ      C1       C2       C3
!     C4      C5      C6      C7      C8      C9      MagPh
MN1    MMN3  1  0  0.50000 0.68510 0.25000 0.30000  1.00000  -0.996    1.360    0.000
                     0.00    0.00    0.00    0.00     0.00    11.00    21.00     0.00
      0.000   0.000   0.000   0.000   0.000   0.000  0.00000
       0.00    0.00    0.00    0.00    0.00    0.00     0.00
!-------> Scale, Extinction and  Cell Parameters for Pattern #  1
!  Scale Factors
!    Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
   455.1         0.000       0.000       0.000       0.000       0.000
         0.00        0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7   Ext-Model
  78.96        0.000       0.000       0.000       0.000       0.000       0.000      1
        0.00        0.00        0.00        0.00        0.00        0.00        0.00
!     a           b           c         alpha       beta        gamma       #Cell Info
   4.770000    5.720000    4.920000   90.000000   90.900224   90.000000
    0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
! x-Lambda/2  +           Not yet used parameters
     0.02137     0.00000     0.00000     0.00000     0.00000
        0.00        0.00        0.00        0.00        0.00
! Propagation vectors:
   0.5000000   0.0000000   0.0000000                Propagation Vector  1
    0.000000    0.000000    0.000000
!  2Th1/TOF1    2Th2/TOF2   Pattern # 1
      1.536        0.000        1
```

## sarah13.pcr

**Generated with k= (0.217  0  -0.46)**

```
!------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:     1.00
!------------------------------------------------------------------------------
Magnetic Phase
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   4  -2   0   0         0.00  -1   0   0
!
P -1                    <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
    2     1     1    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
!
SYMM X, Y, Z
BASR       1       0       0       0       1       0       0       0       1
BASI       0       0       0       0       0       0       0       0       0
SYMM X, -Y+1, Z+1/2
BASR    .125       0       0       0    -.125      0       0       0    .125
BASI    .992       0       0       0    -.992      0       0       0    .992
!
!Atom Typ  Mag Vek    X       Y       Z       Biso    Occ      C1       C2       C3
!     C4      C5      C6      C7      C8      C9      MagPh
MN1  MMN3  1   0    .50000  .68510  .25000 .30000 1.00000   0.000    0.000    0.000
                    0.00    0.00    0.00    0.00    0.00    0.00     0.00     0.00
   0.000   0.000   0.000   0.000   0.000   0.000   .00000
    0.00    0.00    0.00    0.00    0.00    0.00    0.00
!  Scale Factors
!   Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
  100.0         0.000       0.000       0.000       0.000       0.000
     .00         0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
!    Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7
     0.000       0.000       0.000       0.000       0.000       0.000       0.000
      0.00        0.00        0.00        0.00        0.00        0.00        0.00
!     a           b           c         alpha       beta        gamma
273
 1  1  1   90  90  90
    0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
!  Not yet used parameters
 0.00000 0.00000 0.00000 0.00000 0.00000
    0.00    0.00    0.00    0.00    0.00
! Propagation vectors:
    .2170000    .5000000   -.4600000                Propagation Vector  1
    0.000000    0.000000    0.000000
```

Save as **incommag.pcr**

# Incommensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## incommag.pcr

3-Save & exit

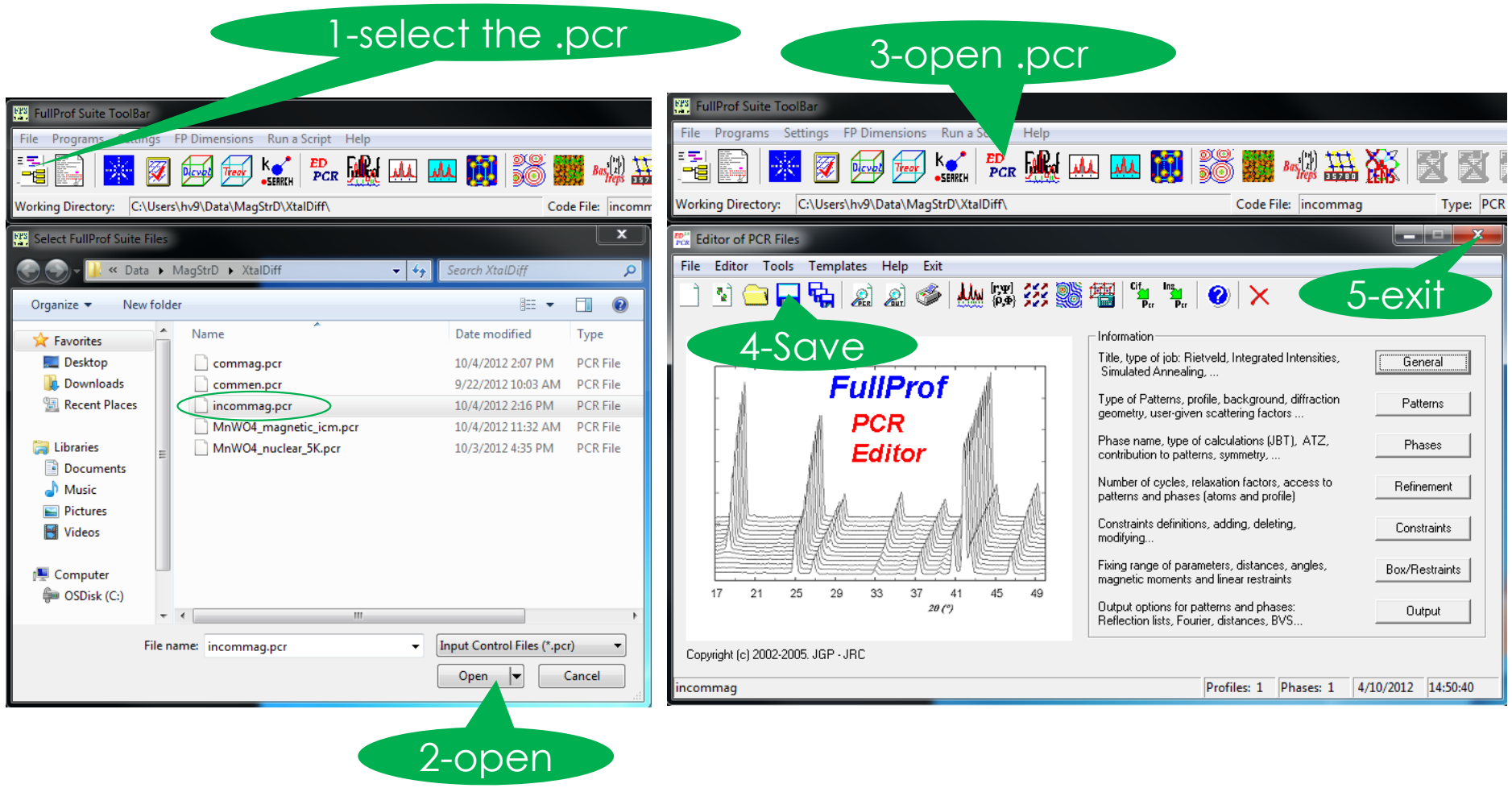
```
COMM MnWO4 commensurate magnetic structure refinement, 17%-Co
! Current global Chi2 (Bragg contrib.) =      2.364
! Files => DAT-file: MnWO4_magneticAF4_5K.int,  PCR-file: commag
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
   1   0   1   0   0   0   0   0   0   0   0   0   0   1   0   0   0   1
!
!Ipr Ppl Ioc Mat Pcr Ls1 Ls2 Ls3 NLI Prf Ins Rpa Sym Hkl Fou Sho Ana
   0   0   1   0   1   0   4   0   0   3   0   0   0   0   0   0   0
!
!NCY  Eps  R_at  R_an  R_pr  R_gl     Thmin      Step       Thmax    PSD    Sent0
  1  0.10  1.00  1.00  1.00  1.00      1.5360   0.000000     0.0000   0.000   0.000
!
!
      2    !Number of refined parameters
!------------------------------------------------------------------------------
!  Data for PHASE number:   1  ==> Current R_Bragg for Pattern#  1:      9.81
!------------------------------------------------------------------------------
 MnWO4 Nuclear refinement, 17%-Co
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth       ATZ    Nvk Npr More
   1   0   0 0.0 0.0 1.0   1   4  -2   0   0         0.000   1   0   1
!
!Jvi Jdi Hel Sol Mom Ter  Brind   RMua    RMub    RMuc   Jtyp  Nsp_Ref Ph_Shift N_Domains
   0   0   0   0   0   0  1.0000  1.0000  2.0000  0.0000    1       0       0       0
!
P -1                        <--Space group symbol
! Nsym   Cen  Laue Ireps N_Bas
    2     1     1    -1     3
! Real(0)-Imaginary(1) indicator for Ci
  0  0  0
!
SYMM X, Y, Z
BASR       1       0       0       0       0       0       0       0       1
BASI       0       0       0       0       1       0       0       0       0
SYMM X, -Y+1, Z+1/2
BASR    .125       0       0       0    -.992       0       0       0    .125
BASI    .992       0       0       0    -.125       0       0       0    .992
!
!Atom   Typ  Mag Vek    X       Y       Z       Biso    Occ      C1       C2       C3
!     C4       C5       C6       C7       C8       C9       MagPh
MN1    MMN3  1  0  0.50000 0.68510 0.25000 0.30000  1.00000  -0.996   1.360    0.000
                     0.00     0.00     0.00     0.00     0.00    11.00    21.00    1.00
     0.000    0.000    0.000    0.000    0.000    0.000  0.00000
       0.00     0.00     0.00     0.00     0.00     0.00     0.00
!-------> Scale, Extinction and  Cell Parameters for Pattern #  1
!  Scale Factors
!   Sc1         Sc2         Sc3         Sc4         Sc5         Sc6
   455.1        0.000       0.000       0.000       0.000       0.000
         0.00        0.00        0.00        0.00        0.00        0.00
!  Extinction Parameters
! Ext1        Ext2        Ext3        Ext4        Ext5        Ext6        Ext7   Ext-Model
  78.96       0.000       0.000       0.000       0.000       0.000       0.000       1
        0.00        0.00        0.00        0.00        0.00        0.00        0.00
!     a           b           c         alpha       beta        gamma       #Cell Info
   4.770000    5.720000    4.920000  90.000000  90.900024  90.000000
    0.00000     0.00000     0.00000     0.00000     0.00000     0.00000
! x-Lambda/2  +          Not yet used parameters
     0.02137     0.00000     0.00000     0.00000     0.00000
       0.00        0.00        0.00        0.00        0.00
! Propagation vectors:
     .2170000    .5000000   -.4600000          Propagation Vector  1
    0.000000    0.000000    0.000000
!  2Th1/TOF1   2Th2/TOF2  Pattern # 1
      1.536       0.000       1
```

1-use unique axis b as imaginary component

2-refine C3

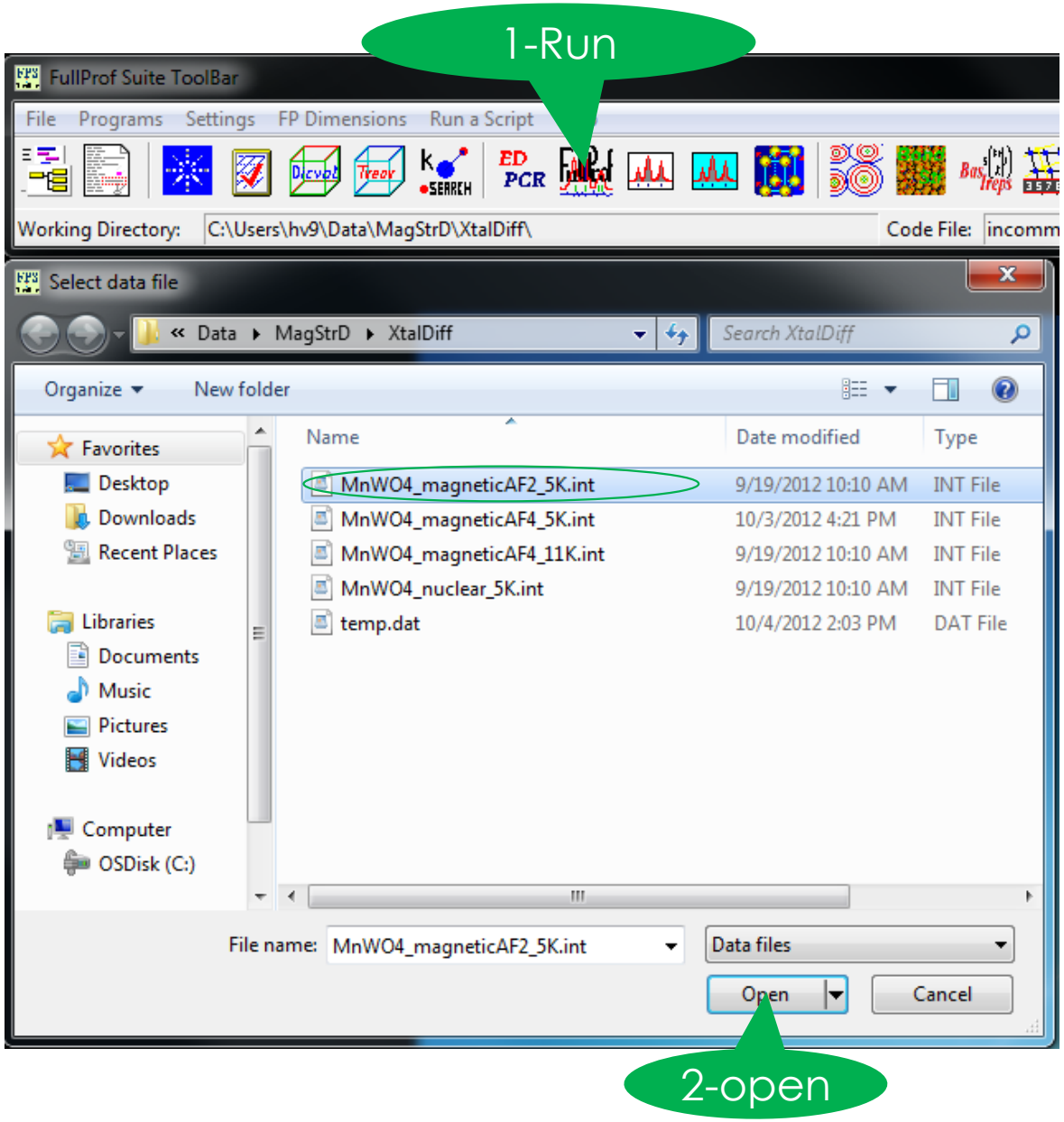
# Incommensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## incommag.pcr



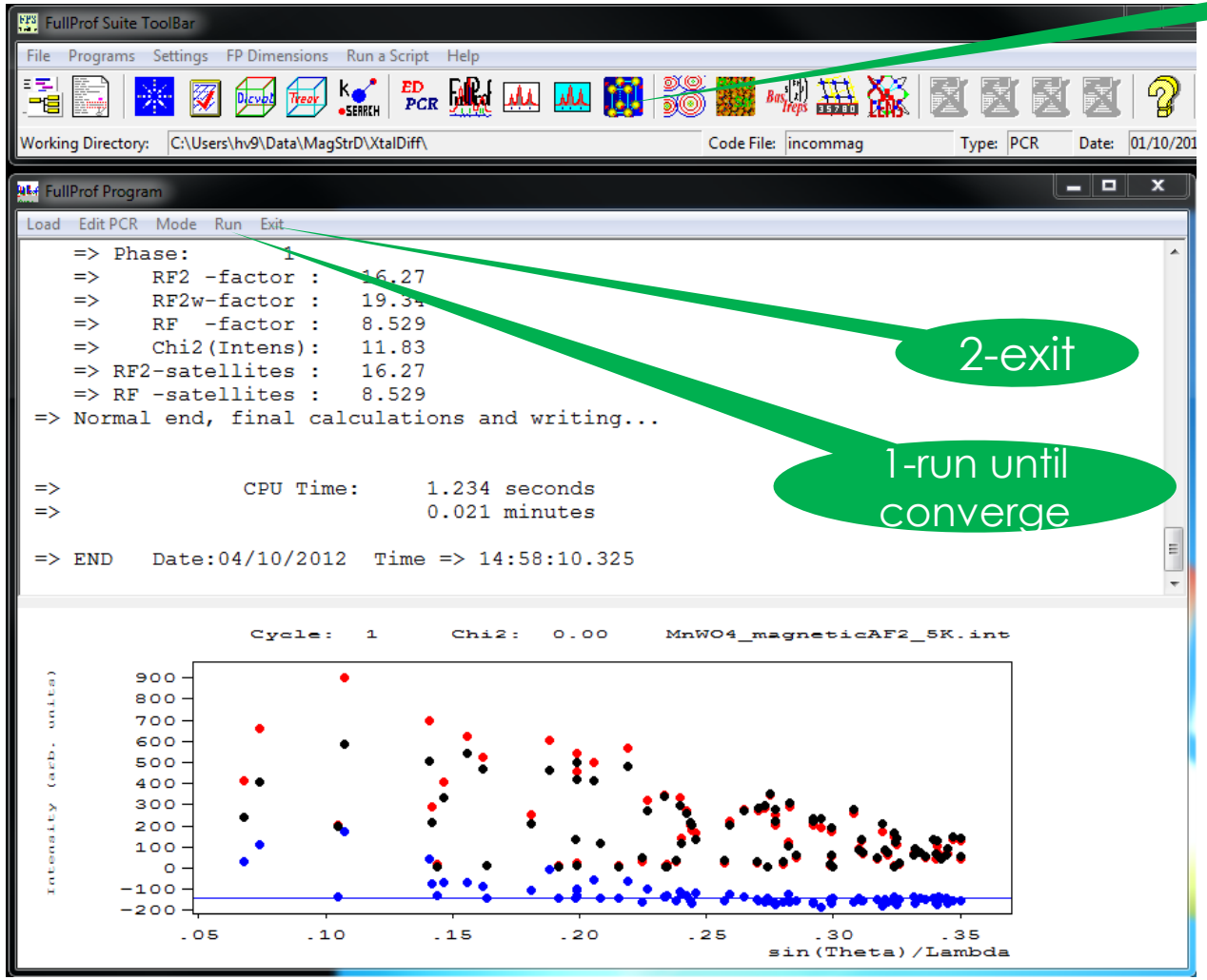
# Incommensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

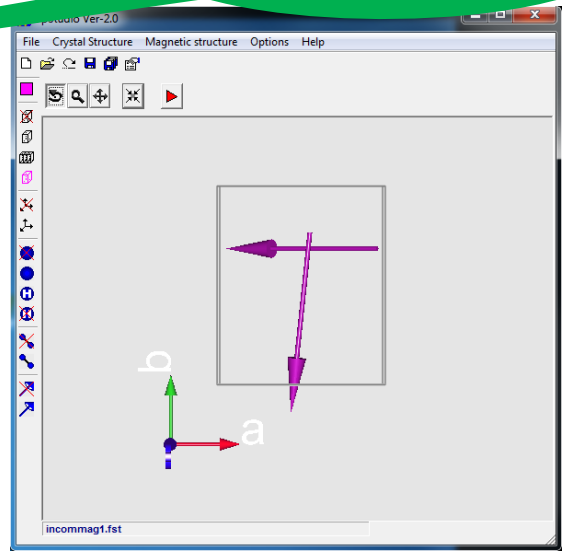
**incommag.pcr**



# Incommensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

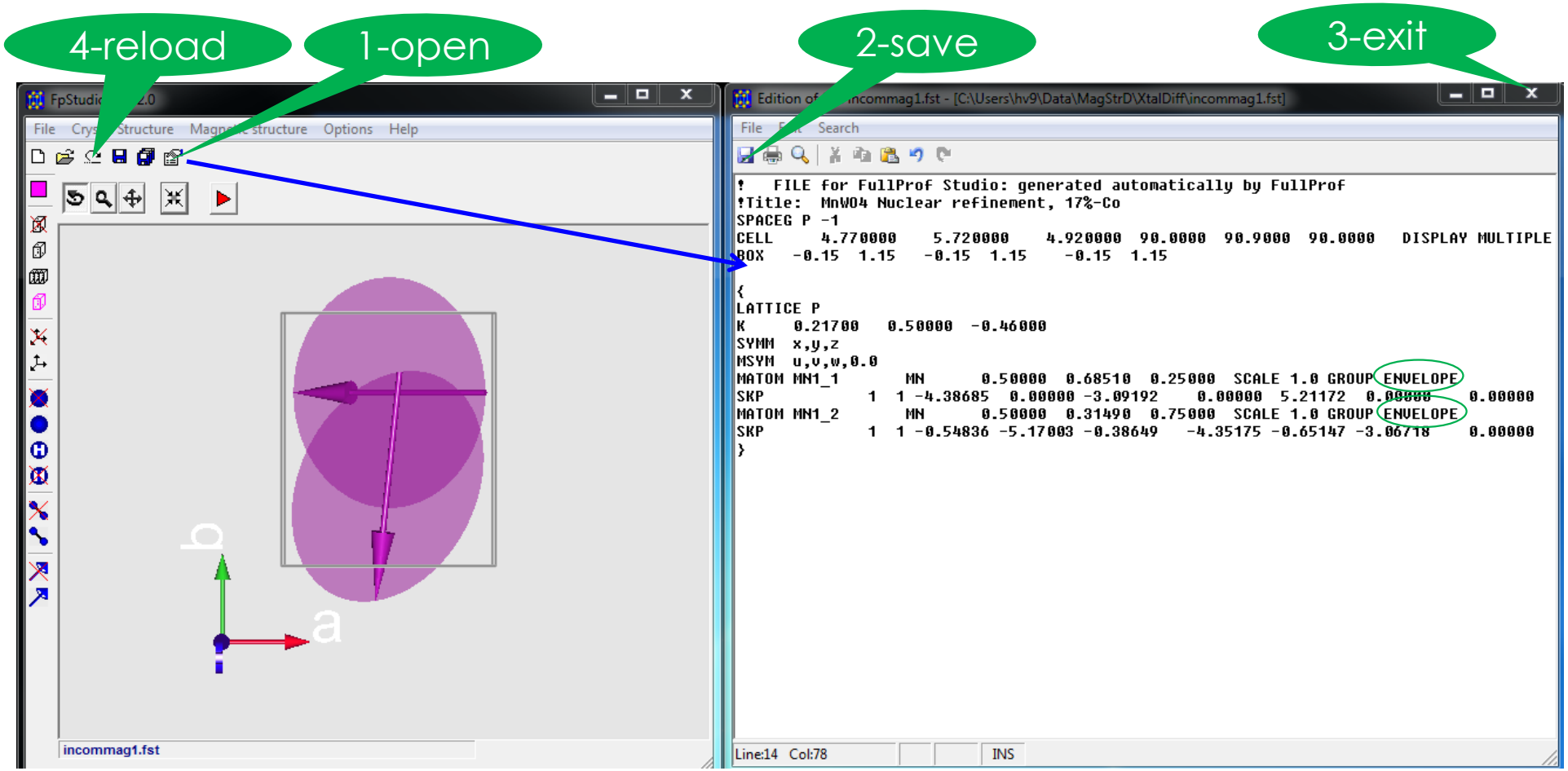
## incommag.pcr



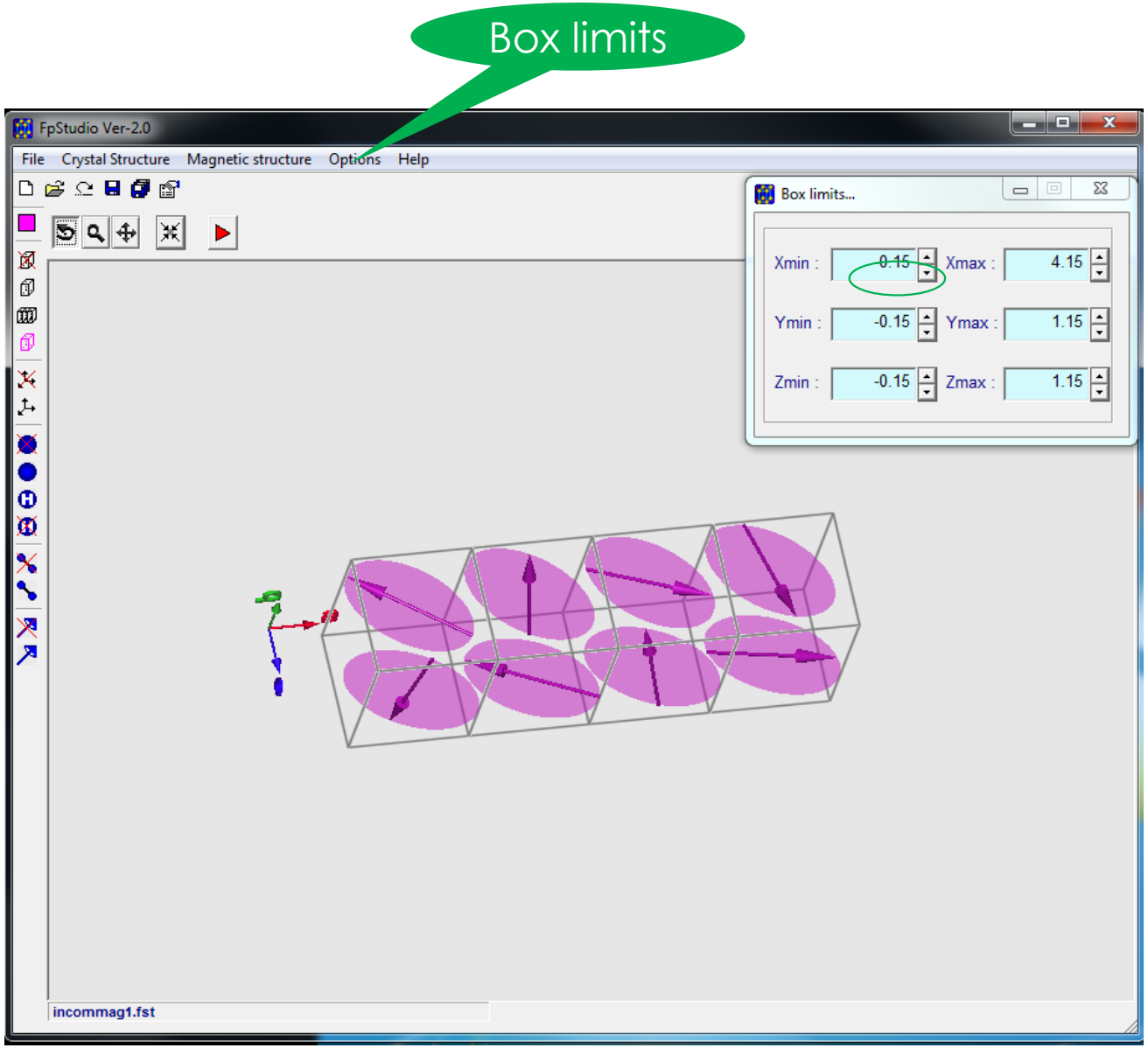
# Incommensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

## incommag.fst



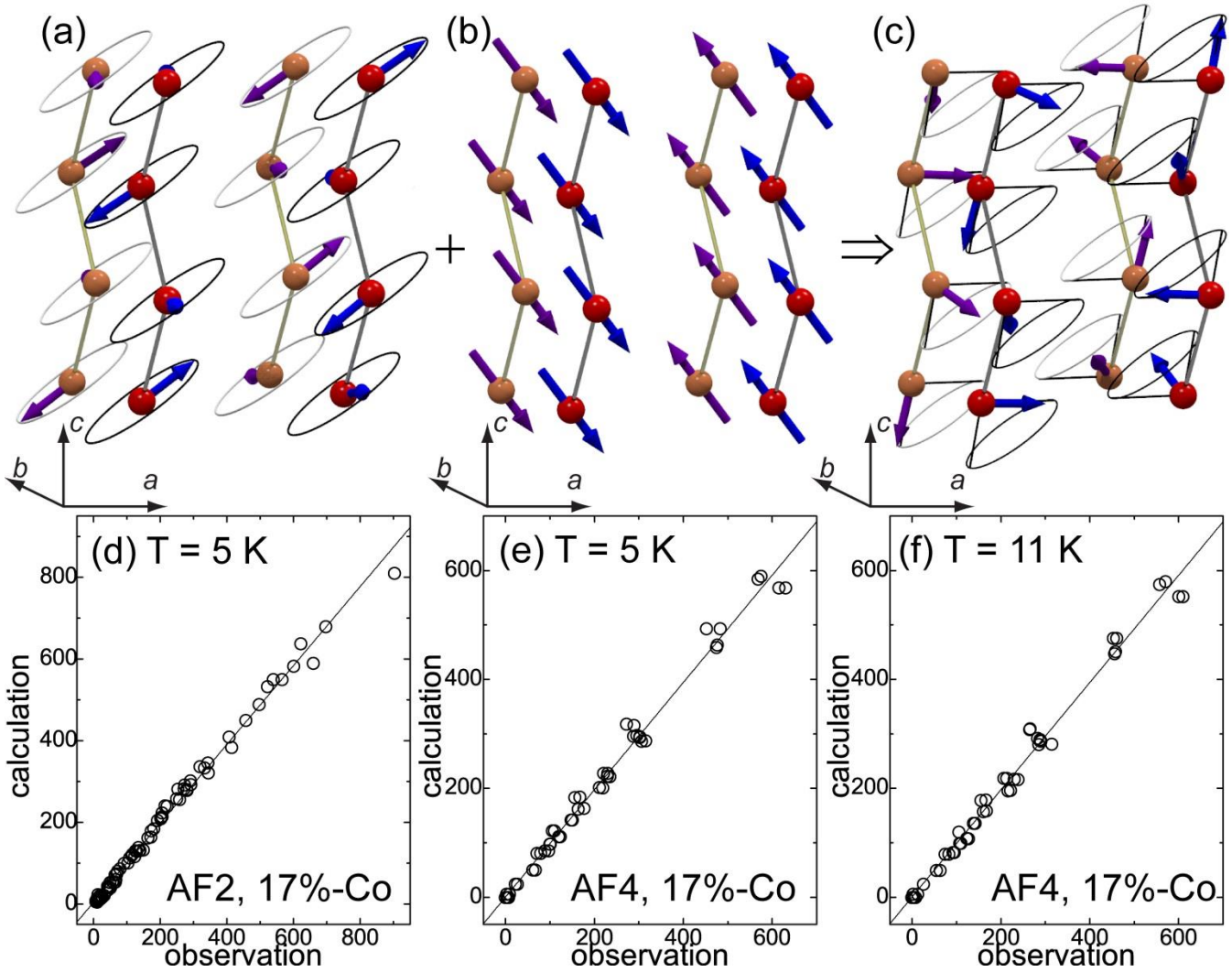
# Incommensurate magnetic structure of $Mn_{1-x}Co_xWO_4$

**incommag.fst**



# What is the magnetic structure at 5 K?

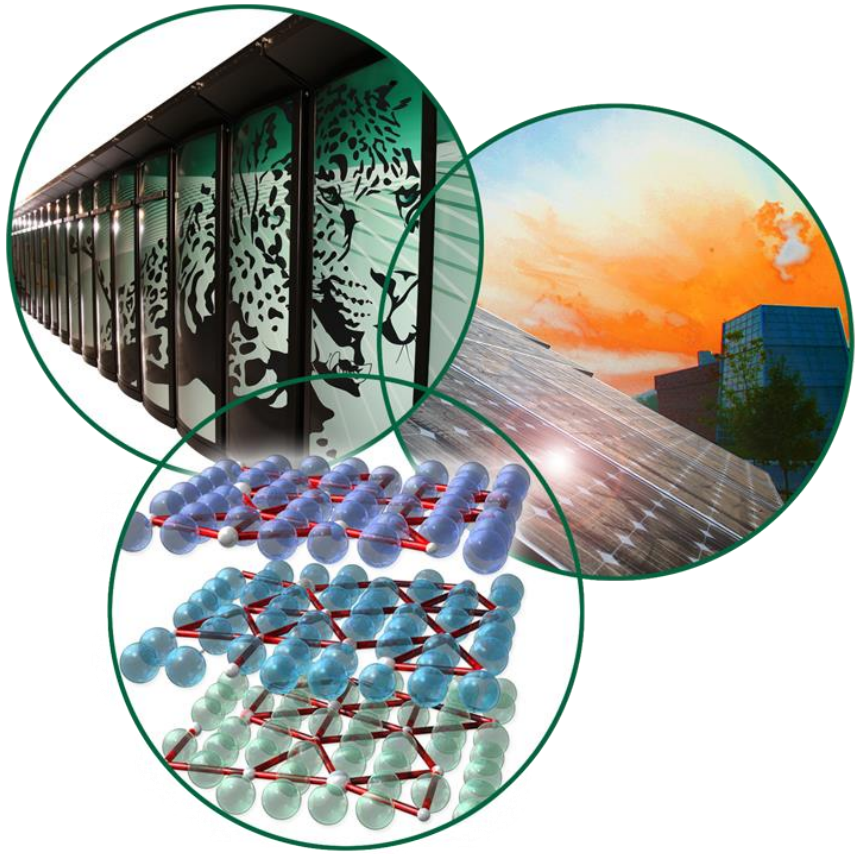
Combine two magnetic structures together



# Atomic displacements and thermal motion in triphylite - lithiophilite, $Li(Fe,Mn)PO_4$ solid solution


**Huibo Cao**
**Bryan Chakoumakos**

**Neutron Scattering Science Division**
**Oak Ridge National Laboratory**
**Oak Ridge, Tennessee**



OAK RIDGE National Laboratory

U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

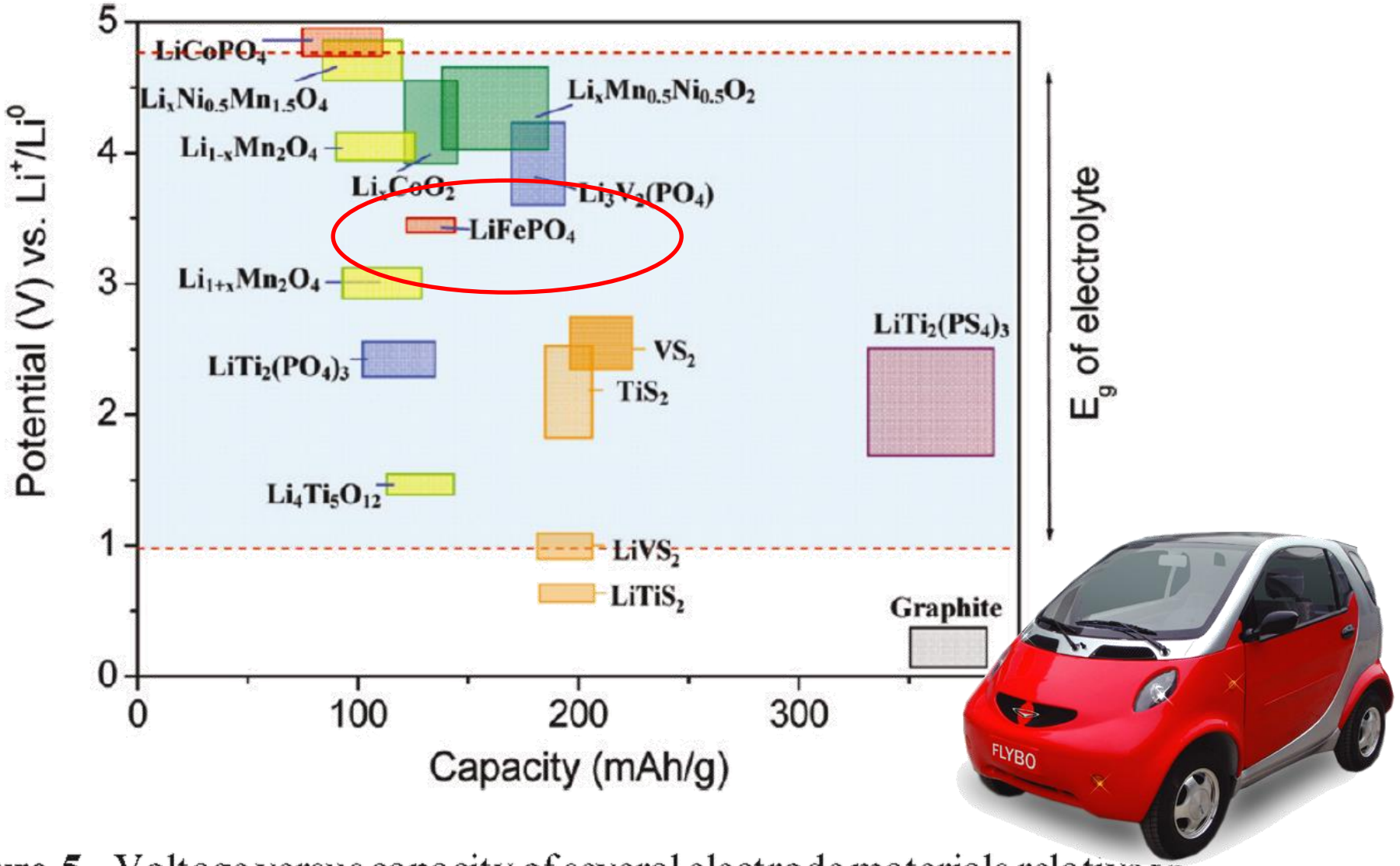
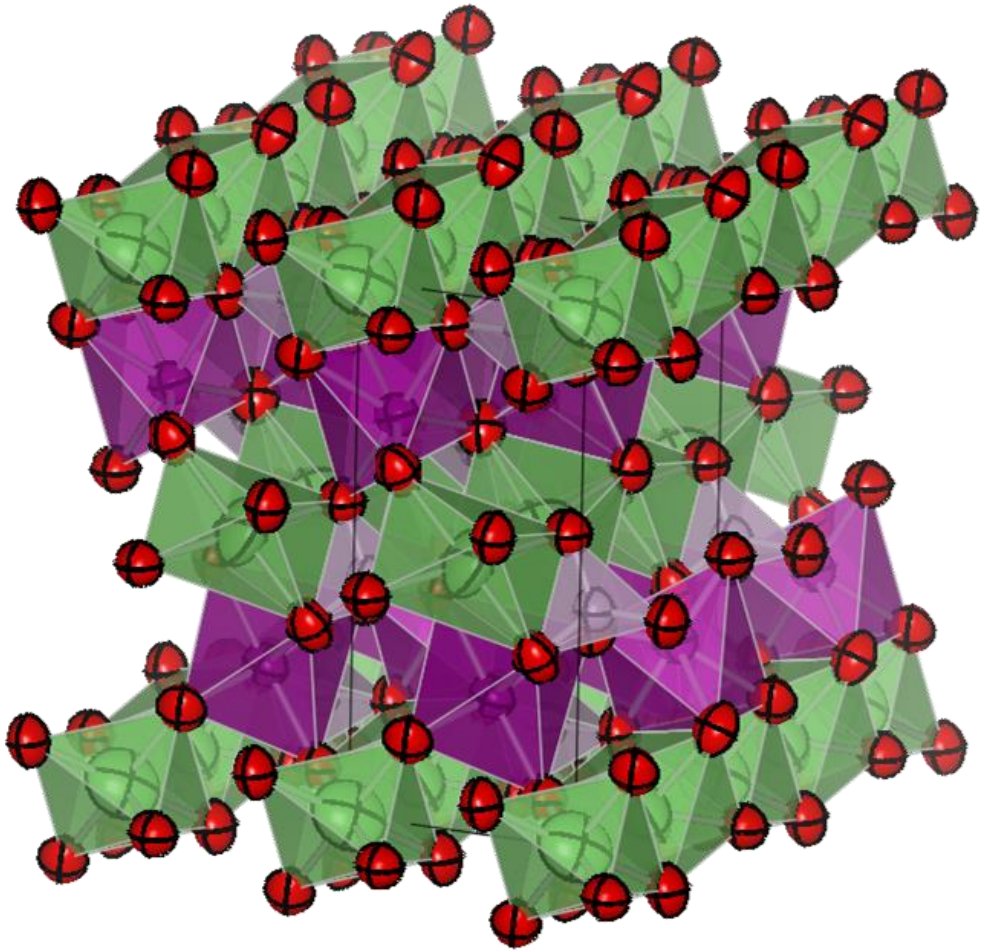
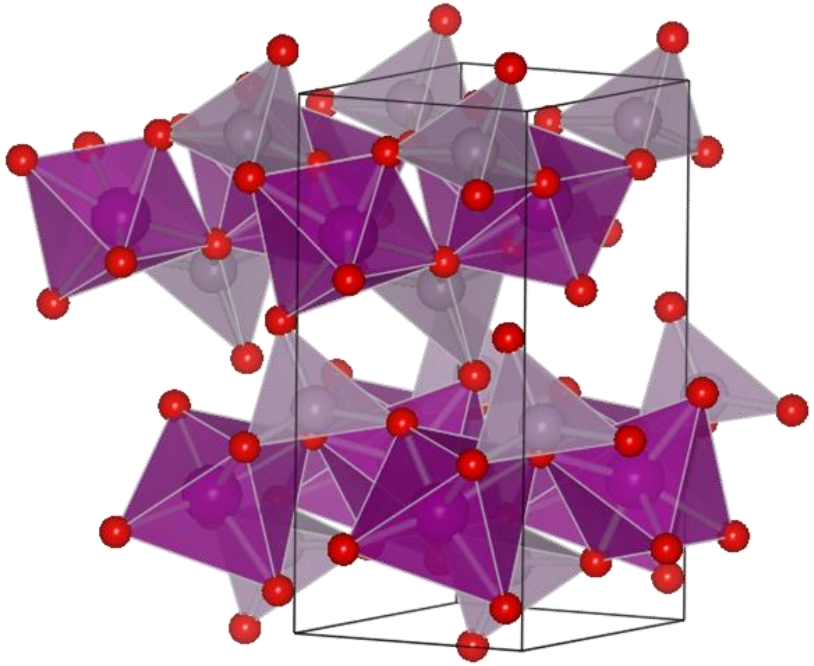



**Figure 5.** Voltage versus capacity of several electrode materials relative to the window of the electrolyte 1 M $LiPF_6$ in EC/DEC (1:1).

**(Goodenough and Kim 2010)**

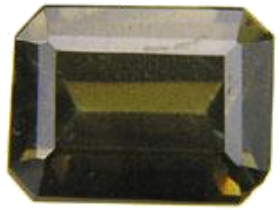


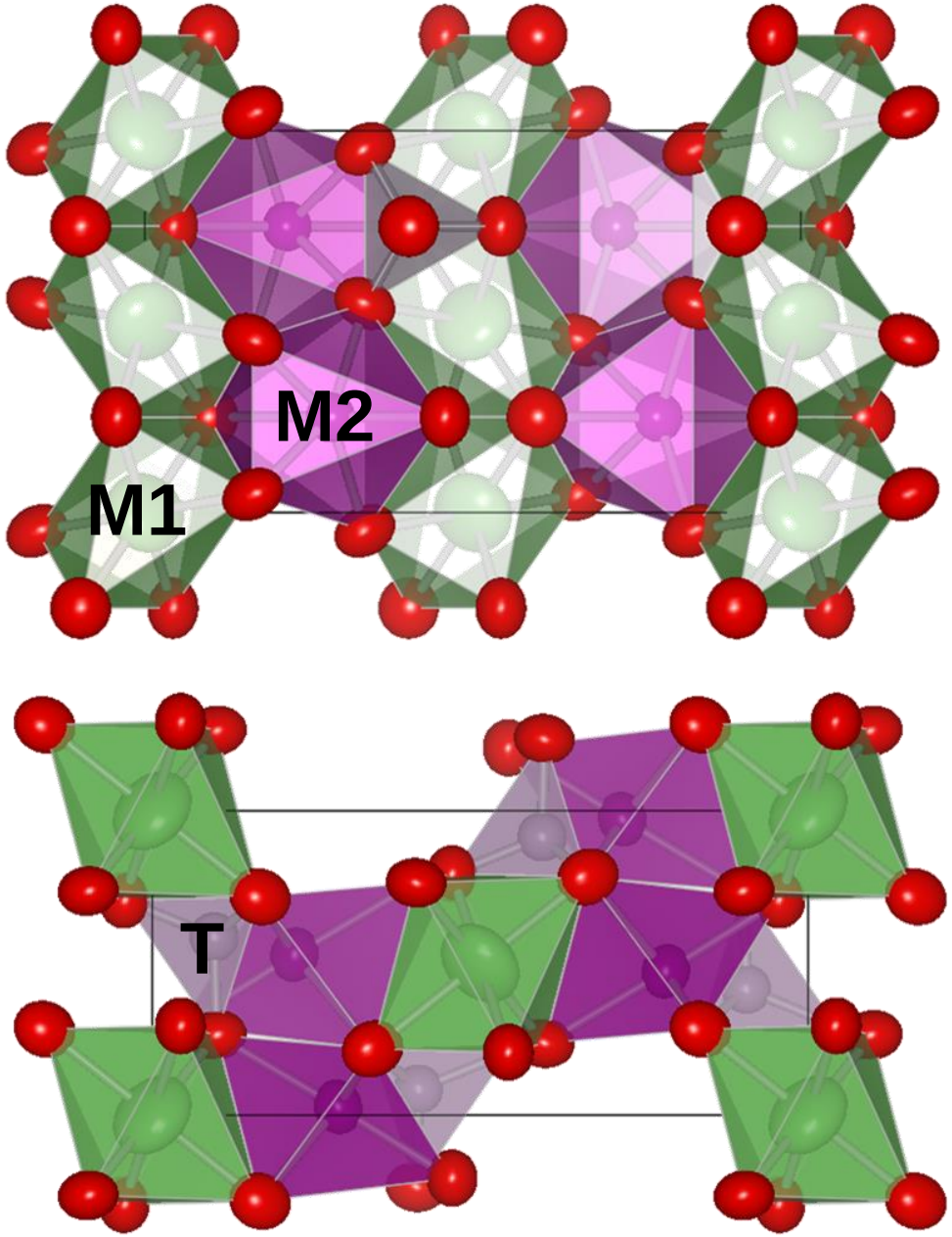
$LiFe^{2+}PO_4$



$Fe^{3+}PO_4$
Delacourt et al. (2005)

**Triphylite – lithiophilite ($LiFePO_4$ – $LiMnPO_4$) occurs naturally as large crystals in granitic pegmatites, which are noted for their giant crystal textures.**






# Olivine Structure-Type $M1M2TX_4$

## *Pnma*

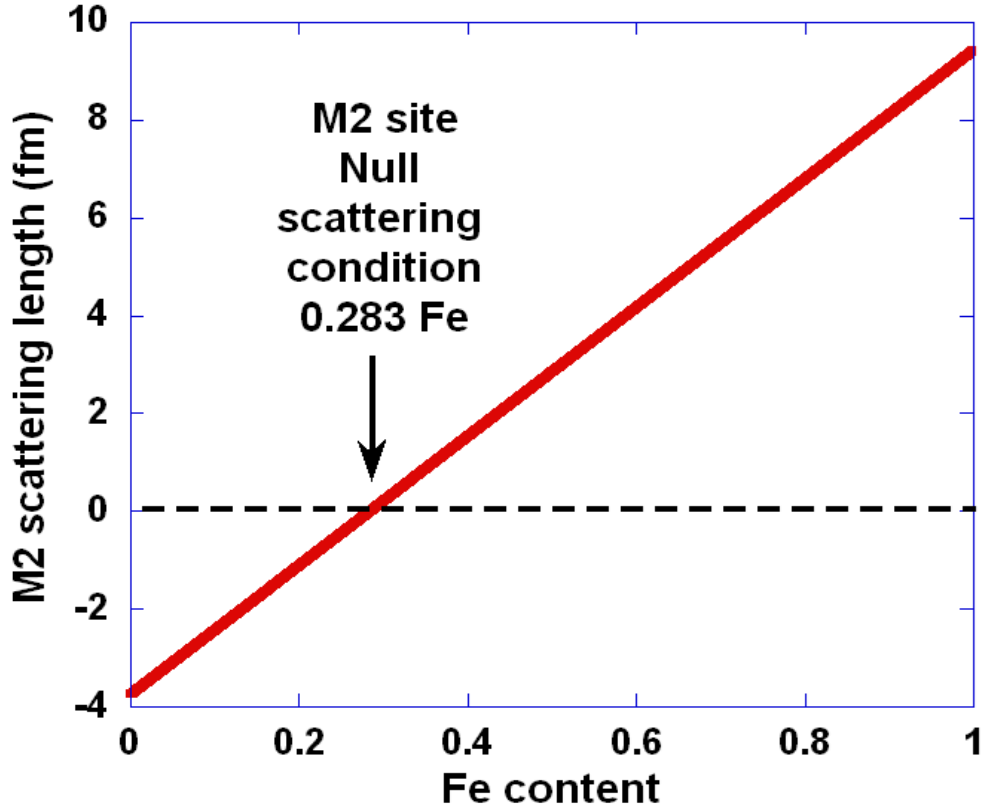
| atom | site | | position | | | *ADP* |
|---|---|---|---|---|---|---|
| M1 | 4*a* | -1 | 0 | 0 | 0 | *U* |
| M2 | 4*c* | .*m*. | *x* | ¼ | *z* | *U* |
| T | 4*c* | .*m*. | *x* | ¼ | *z* | *U* |
| X1 | 4*c* | .*m*. | *x* | ¼ | *z* | *U* |
| X2 | 4*c* | .*m*. | *x* | ¼ | *z* | *U* |
| X3 | 8*d* | 1 | *x* | *y* | *z* | *U* |

**Structural parameters:**
**20 isotropic**
**43 anisotropic**

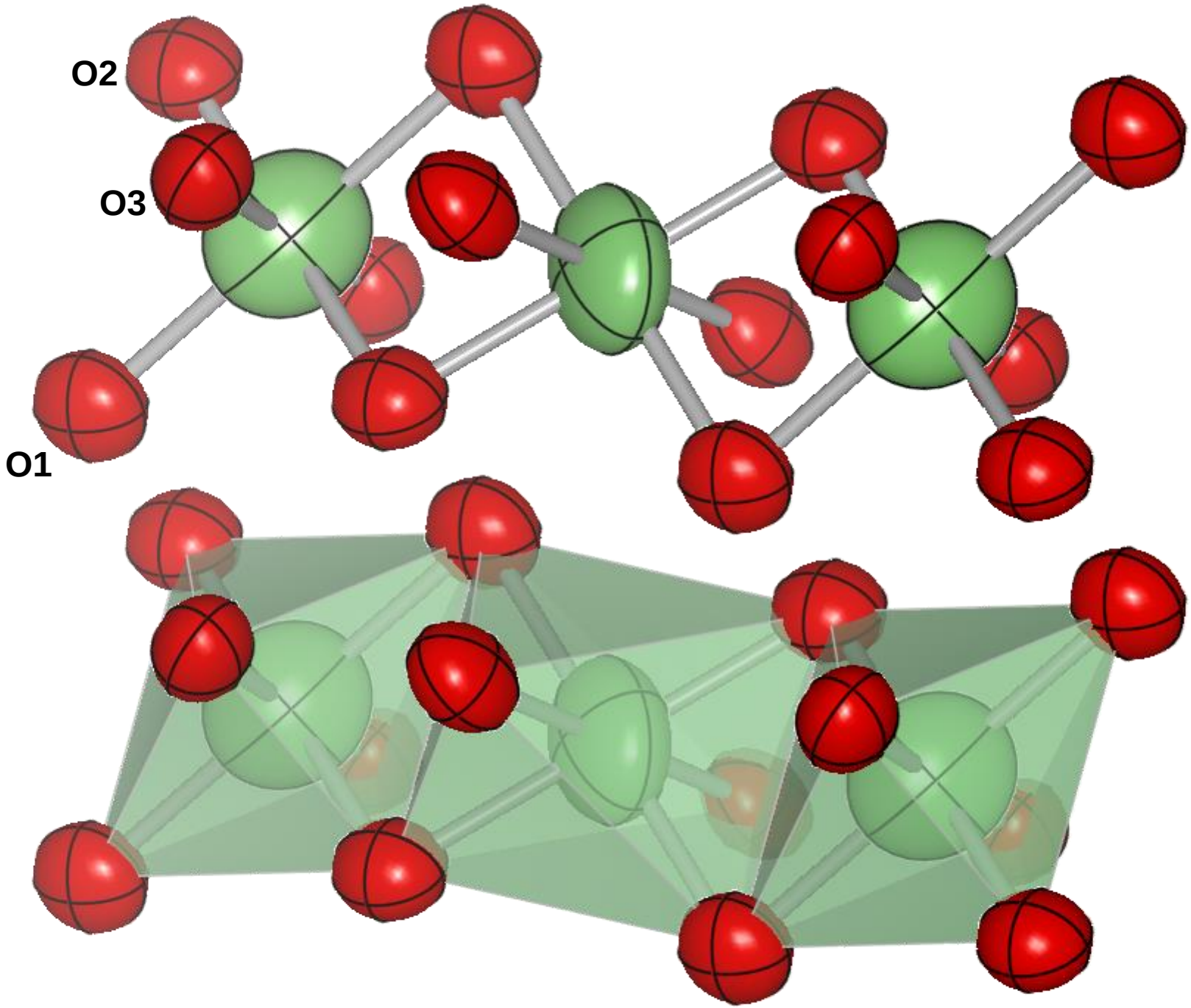
# Neutron diffraction refinement details

## Scattering Lengths

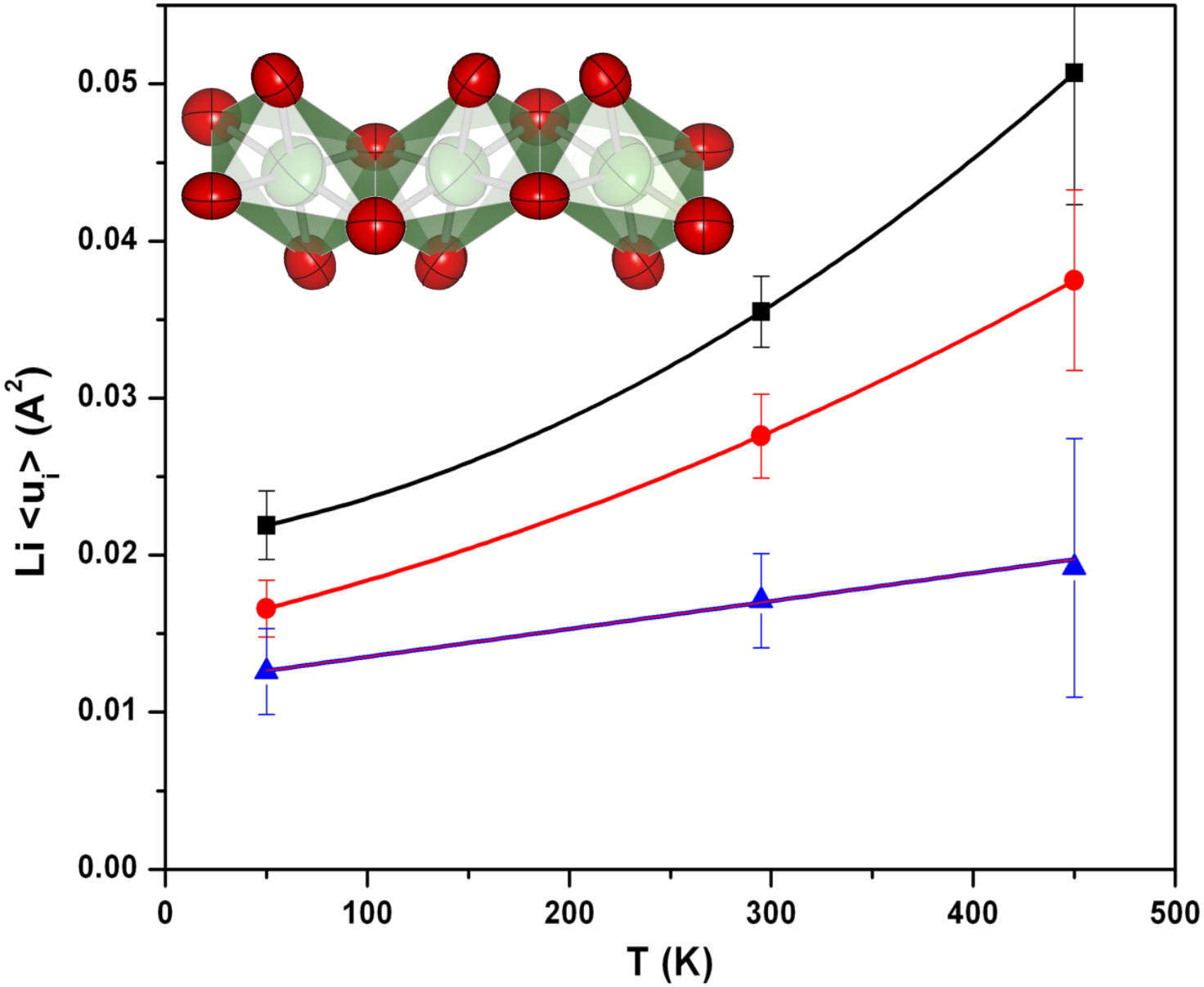
| | |
|---|---|
| Li | -1.90 fm |
| Mn | -3.73 fm |
| Fe | 9.45 fm |
| O | 5.803 fm |



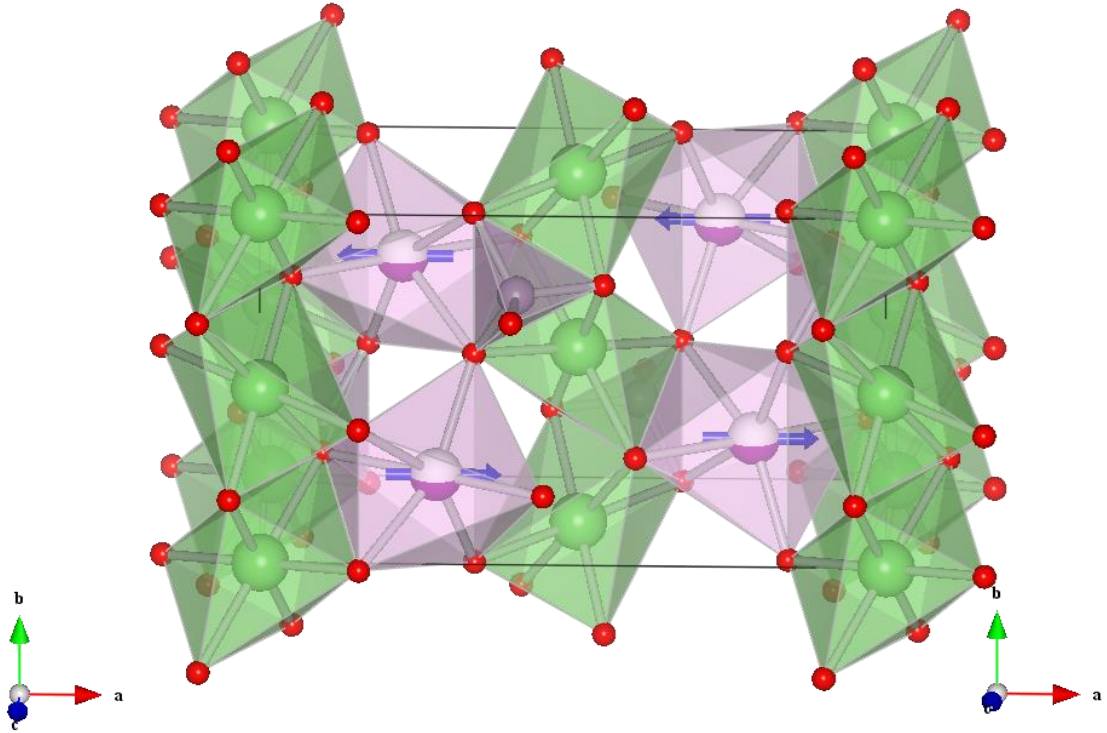

- We need to measure about 450 unique reflections to get a good refinement, i.e., data to parameter ratio ~ 10:1.
- Orthorhombic symmetry allows us to collect one octant of the full sphere of reflections.

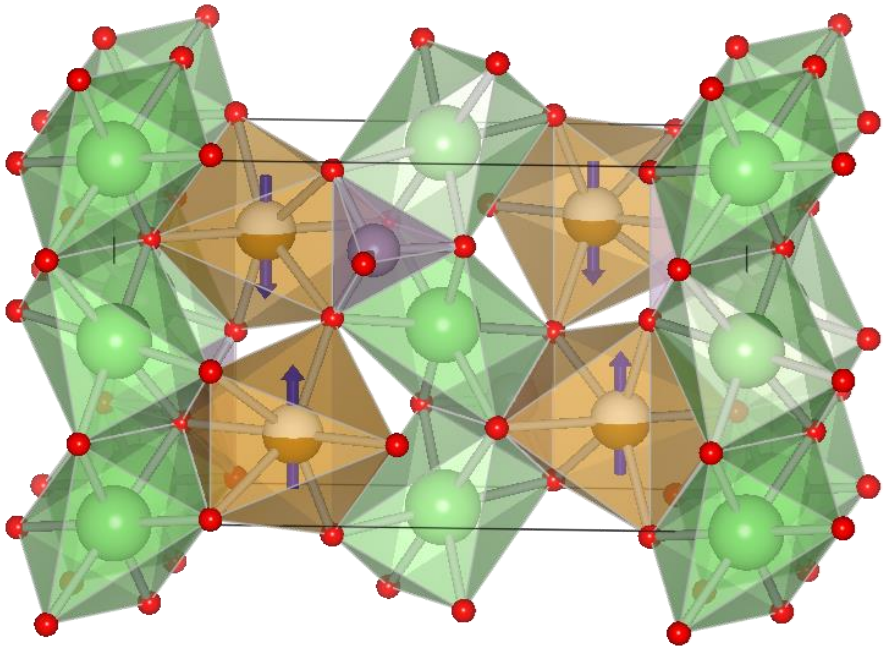

O2
O3
O1

# Principal Mean Square Atomic Displacements for Li in Triphylite $Li(Fe_{0.04}Mn_{0.96})PO_4$



# Magnetic Structures



**Lithiophilite $LiMnPO_4$**
**$T_N$ = 34 K**
**$M$ = 4.3 $\mu_B$**
**along a axis**
**Collinear antiferromagnetic**
**Li et al.**
***Phys. Rev. B* (2009), 79, 144410.**

**Triphylite $LiFePO_4$**
**$T_N$ = 52 K**
**$M$ = 4.6 $\mu_B$**
**along b axis**
**Collinear antiferromagnet**
**Santoro and Newnham,**
***Acta Cryst.* (1967) 22, 344.**

# Single crystal diffraction

**Thanks !**

**Questions to caoh@ornl.gov**