

# Tutorial: $\text{LiFeAs}_2\text{O}_7$

## *Magnetic Structure Determination: Incommensurate Magnetic Structure of the compound $\text{LiFeAs}_2\text{O}_7$*

The powder diffraction data of  $\text{LiFeAs}_2\text{O}_7$  were collected at ILL on the diffractometers D1B (old D1B) with  $\lambda=2.52$  Å and D1A with  $\lambda=1.901$  Å. The space group is non-centrosymmetric C2; the monoclinic cell parameters are  $a \approx 6.679$  Å,  $b \approx 8.286$  Å,  $c \approx 4.743$  Å and  $\beta \approx 103.95^\circ$  at RT. The structural parameters could be obtained from the provided input CIF file **LiFeAs2O7.cif**. The purpose of the tutorial is to solve and refine the incommensurate magnetic structure of this compound using different methods existing in FullProf

### Provided data

In the directory **LiFeAs2O7**, there are the following directories:

**D1B:** Contains the data collected on D1B. The numbered files correspond to the raw data collected as a function of temperature in the range 2.6K-98.6K with relatively low statistics, used only for visualizing the patterns. We have prepared a special file, **scaled\_ParaD1B.xys**, in the paramagnetic state at an approximate temperature of 55K (just above the Néel temperature) to be compared with the high statistics of the pattern, **LFA143\_2K.dat**, taken at 2.6 K. It contains also the instrumental resolution function file **D1B.irf**.

**RT-D1A:** Contains the D1A data taken at room temperature in a file called **LiFeAs2O7\_D1A.dat**, which is in the format corresponding to **Ins=5**. In that directory, there are PCR files ready for refinement. There is also an instrumental resolution function file called **D1A.irf**.

**Search\_Solution:** Contains the D1A data taken at room temperature in a file called **LiFeAs2O7\_D1A.dat**, which is in the format corresponding to **Ins=5**. In that directory, there are PCR files ready for refinement.

**BasIreps:** Contains the files for using BasIreps and several PCR files using different ways of working with FullProf for refining the magnetic structure that are ready for refinement.

**ISODISTORT:** Contains the files for working with the mCIF files generated by ISODISTORT using the formalism of magnetic superspace groups (MSSGs). It contains also PCR files that are ready and adapted to the data of D1B at 2K.

All the provided PCR files are in a state close to convergence for all cases. For starting the tutorial, the user should create a working directory for starting the resolution of the magnetic structure. In that working directory, the user should create from the scratch the PCR files for exploring the possible solutions. Let us call this directory **Working**.

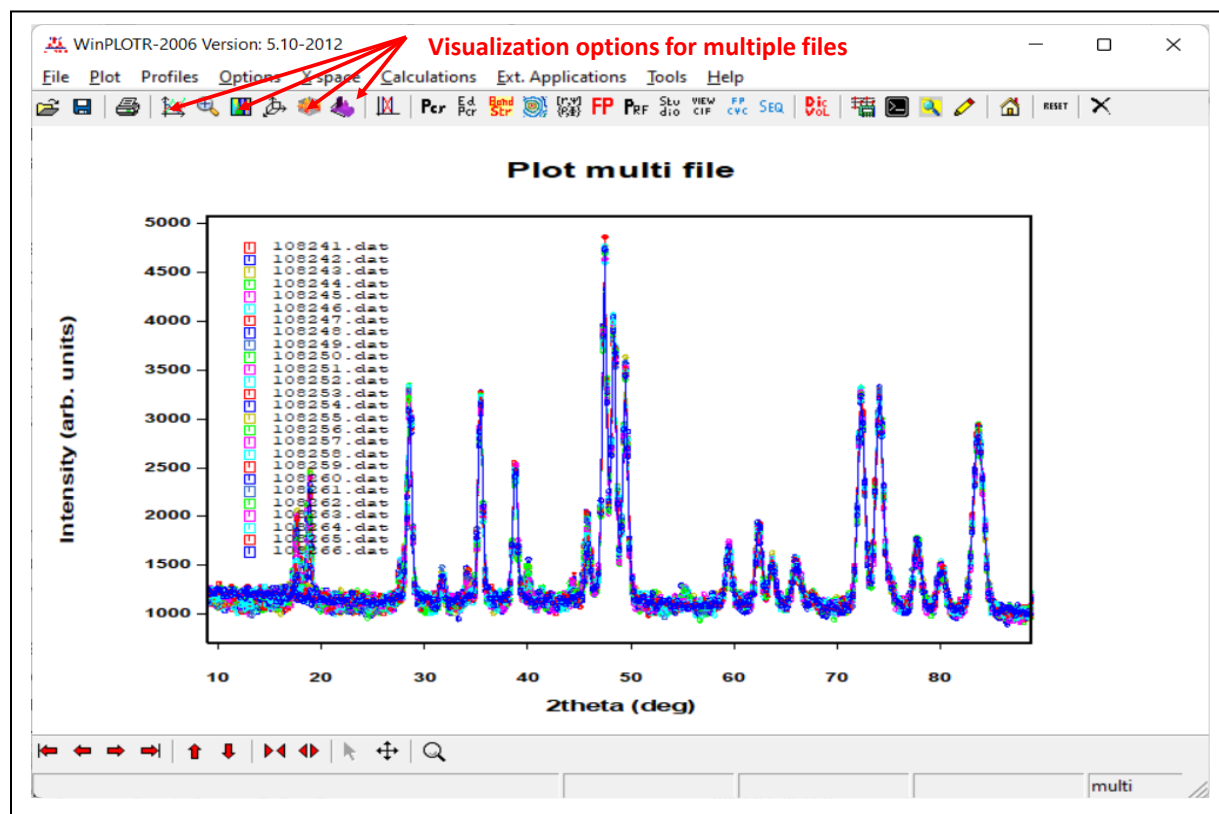
### Introduction

The magnetic structure of this compound has been studied in 2013, before the superspace formalism was implemented in FullProf. The article published in Physical Review B 88 (2013) is provided in the file **PhysRevB.88.214433-LiFeAs2O7.pdf**. The reader interested in the physics of this compound should read carefully the paper.

We shall study the different ways existing in FullProf to refine the magnetic structure of this compound.

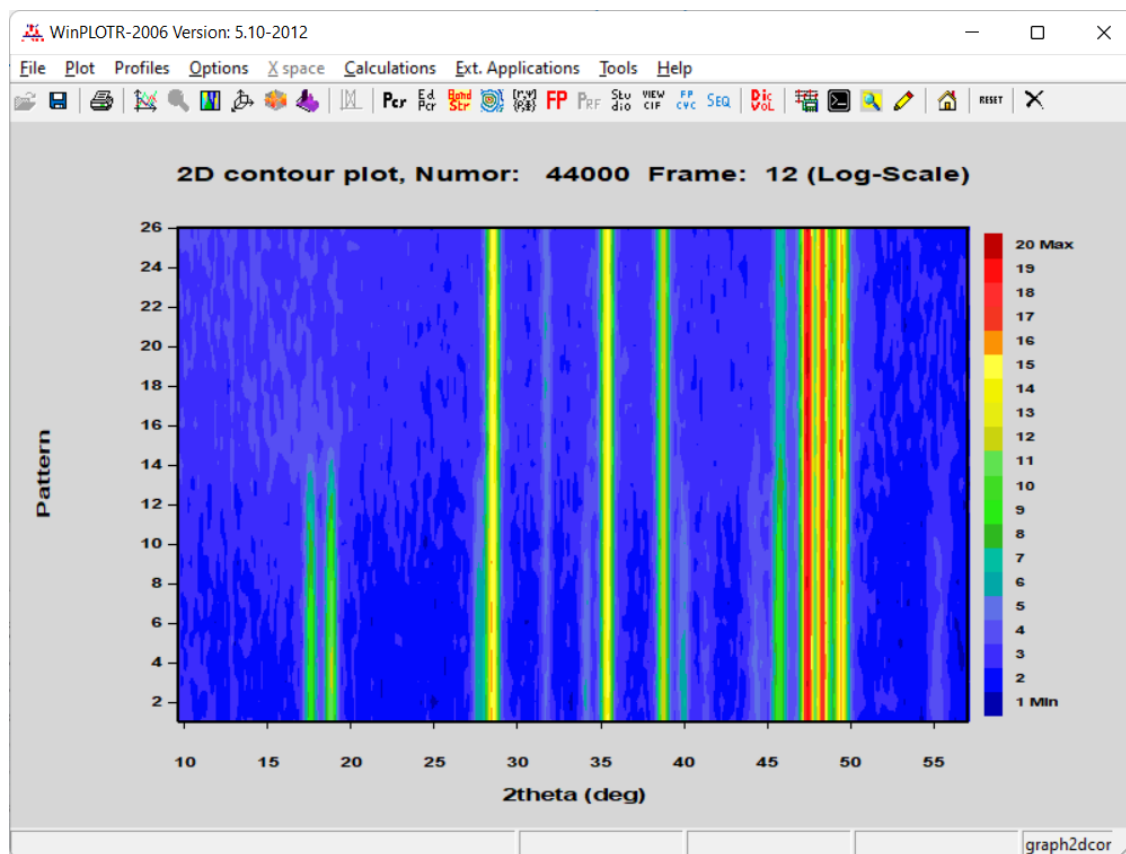
Before starting to do the work, you can explore the data files of D1B to see how the magnetic order appears as a function of temperature. For instance, you may go to the directory **D1B** with the toolbar and open the WinPLOTR-2006 program.

Go to the menu **File > Open Buffer file (\*.buf)** and select the file **ramp.buf**. You will see something similar to the following annotated picture:

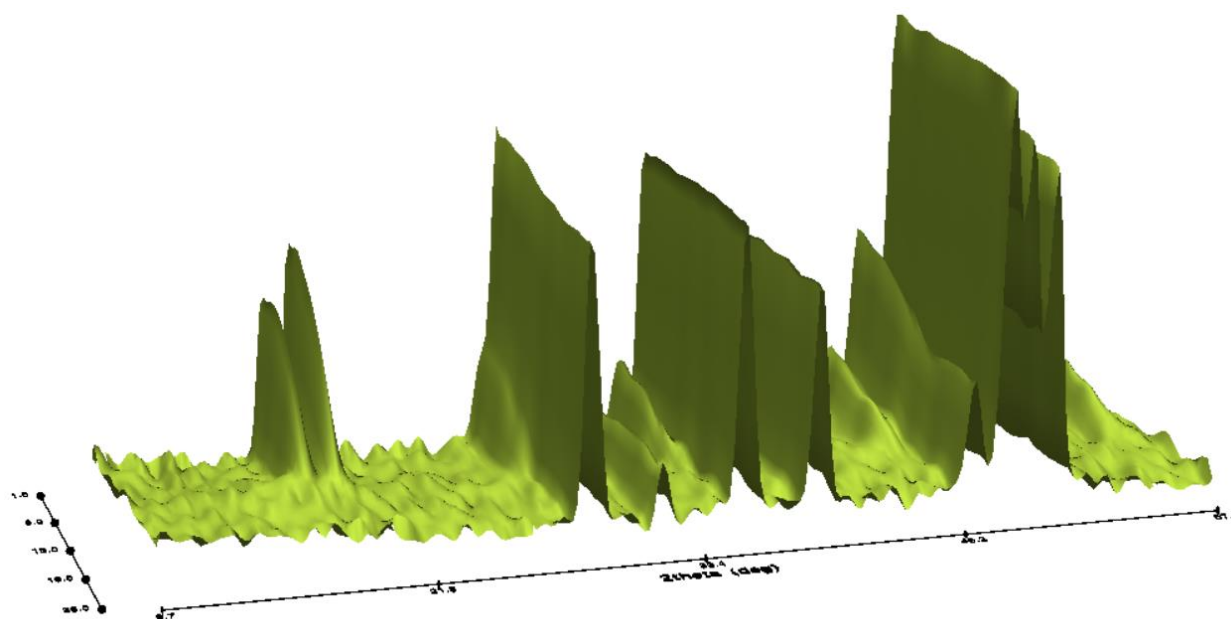


You can use the zoom and the different visualization options existing in WinPLOTR-2006 to appreciate how the magnetic ordering is established as a function of temperature. This particular data collection was taken, after the high statistic data collection, on heating from 2.6 K up to around 100K with a linear increase of the temperature of about 1.3K/minute and continuously recording the diffraction pattern that was saved each 3 minutes.

A contour plot of the whole heating-experiment in logarithmic scale can be seen in the following figure:



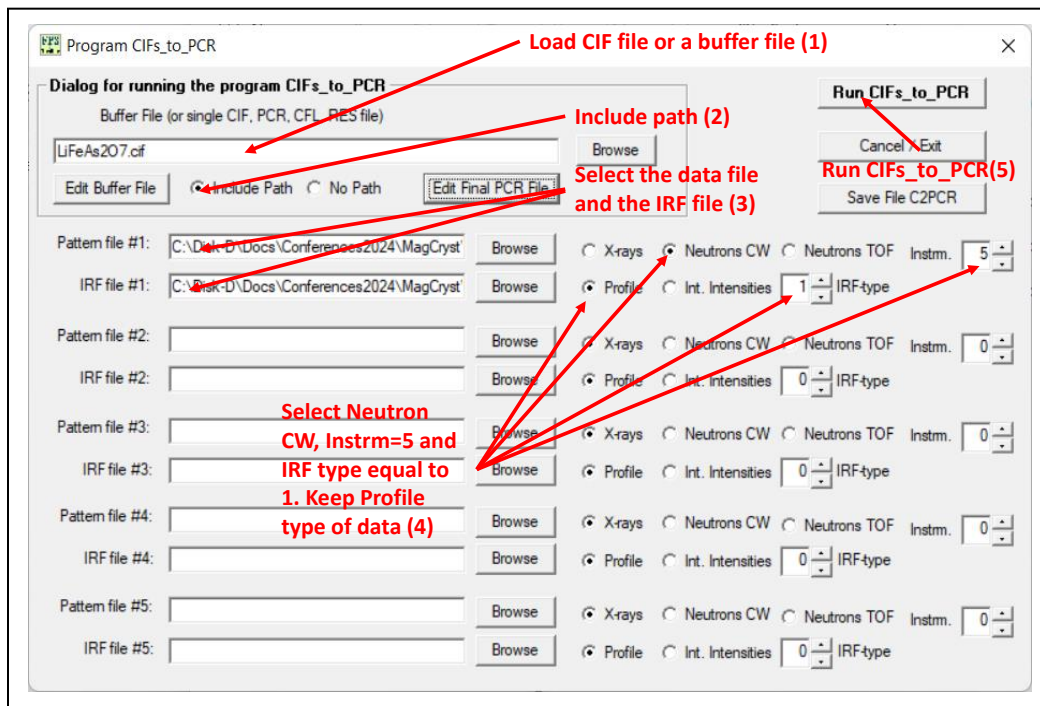
In 3D:



Refinement of the  $\text{LiFeAs}_2\text{O}_7$  crystal structure at RT

The data taken on D1A at room temperature (in the paramagnetic state) can be used to determine precisely the crystal structure and specially the positions of the  $\text{Li}^{+1}$  ions. For that, it is possible to start without the Li positions and see in the difference Fourier map where they are. We shall not do this in the present tutorial and we assume the full structure with Lithium included.

The user should be able to prepare a PCR file template (using EdPCR) from the CIF file **LiFeAs2O7.cif**.



### Step 1, creation of the PCR file from a previous existing CIF file:

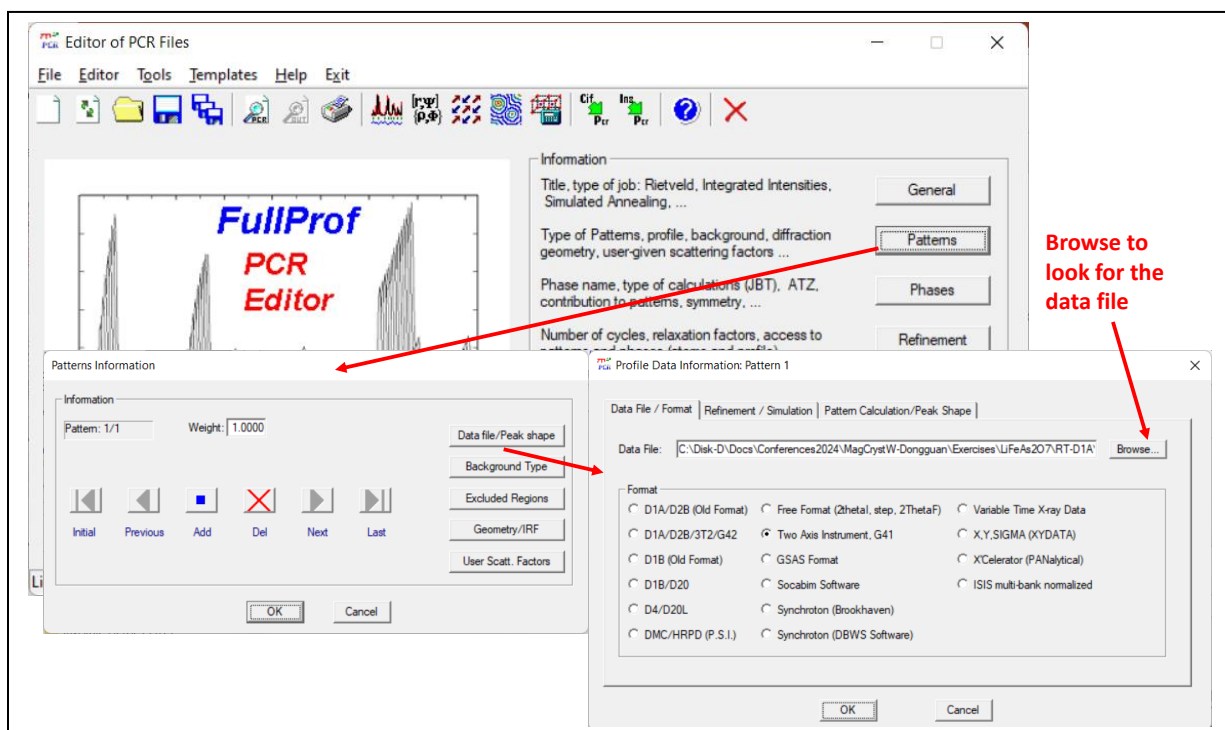
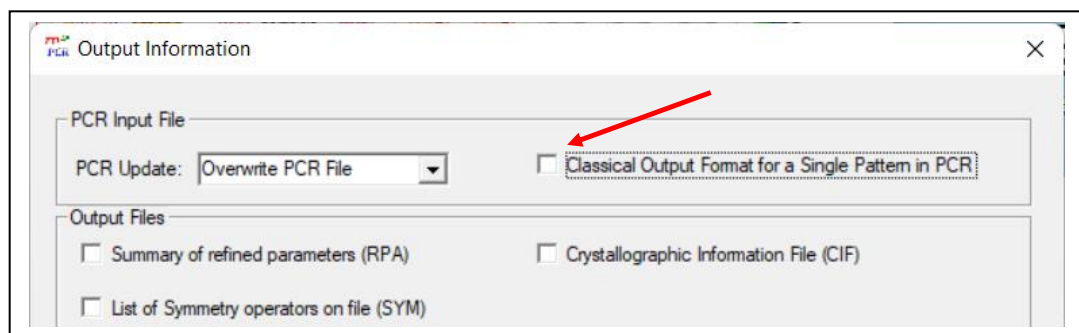
Copy the above CIF file into the directory **Working**. Open the toolbar of the FullProf Suite and select the directory **Working**. Open the menu **Tools** and select **Cifs\_to\_PCR**. The dialog above opens. The following actions should be performed: Load the CIF file clicking on Browse button. Check-in **Include Path**. Load the pattern data file (Look for the file **LiFeAs207\_D1A.dat** that must be in the **RT-D1A** directory). Load the IRF file that is in the same directory

Once the above steps are done, check-in the radio button: **Neutrons CW** and select the value 5 for the box **Instrm**. When everything is done just click on the button: **Run Cifs\_to\_PCR**. You can edit the final PCR file to have a look and change whatever you want (number of cycles, refinement codes, etc.). You can exit the dialog by pushing the button **Cancel/Exit**.

When there is only a single pattern, the generated PCR file does not contain the name of the data file. For changing that, use EdPCR. Load the recently created PCR file into the Toolbar and invoke EdPCR. Click on the button **Output** and in the following dialog uncheck the box

**Classical Output Format for a Single Pattern in PCR**. Click on OK button and save the PCR file from EdPCR. Now within EdPCR click on:

## Patterns > Data file/Peak shape



After selecting the data file, click on OK buttons and save the PCR file. In the latest version of **CIFs\_to\_PCR**, when the data file is in a different directory than that of the PCR files the program creates directly the good multi-pattern format.

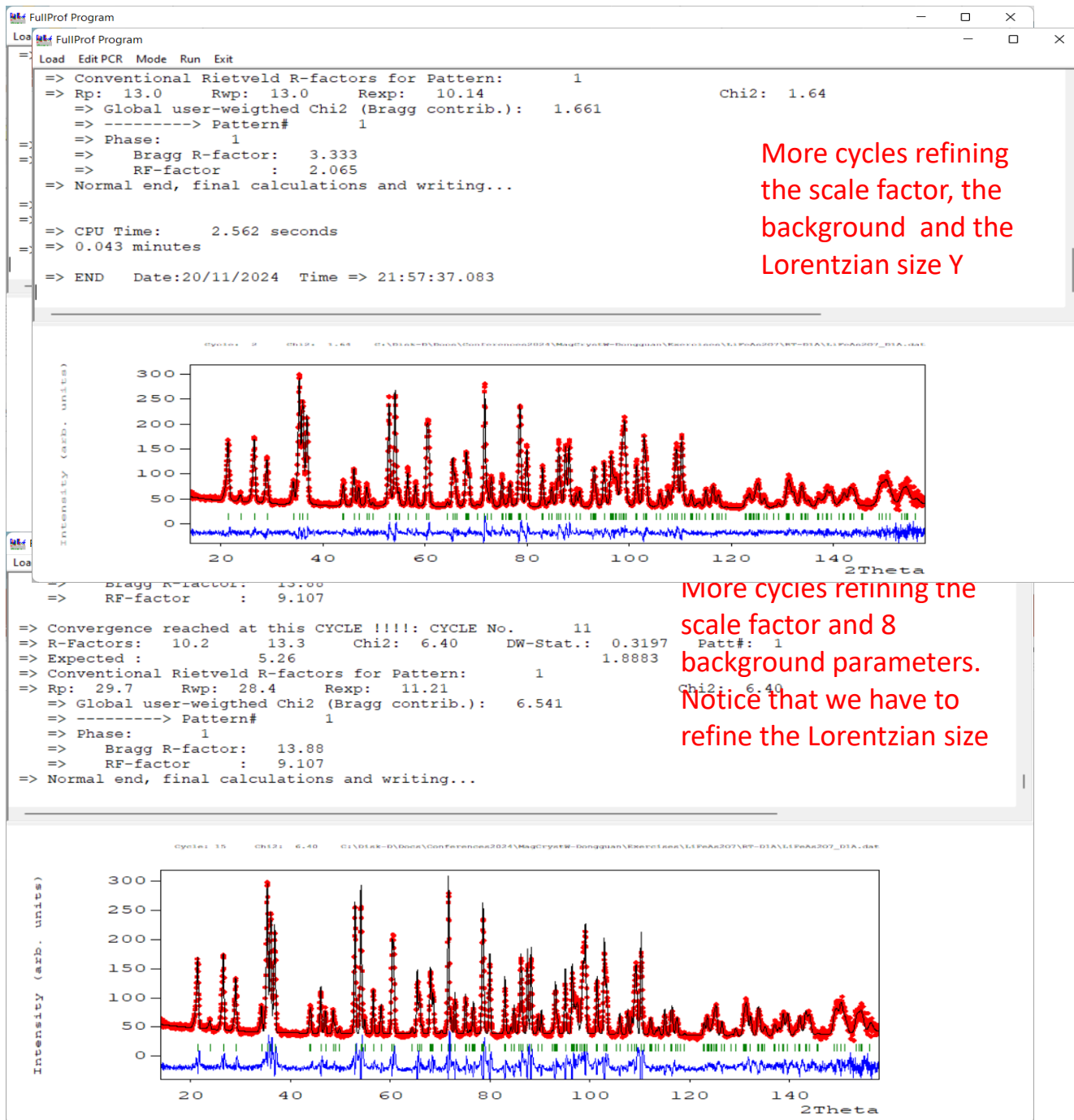
Before starting refinements, put Rpa=-1 to automatically generate a CIF file, modify the number of cycles and select the excluded regions (in our case 1: 0.00 to 14.00, 2: 160.00 to 189.00)



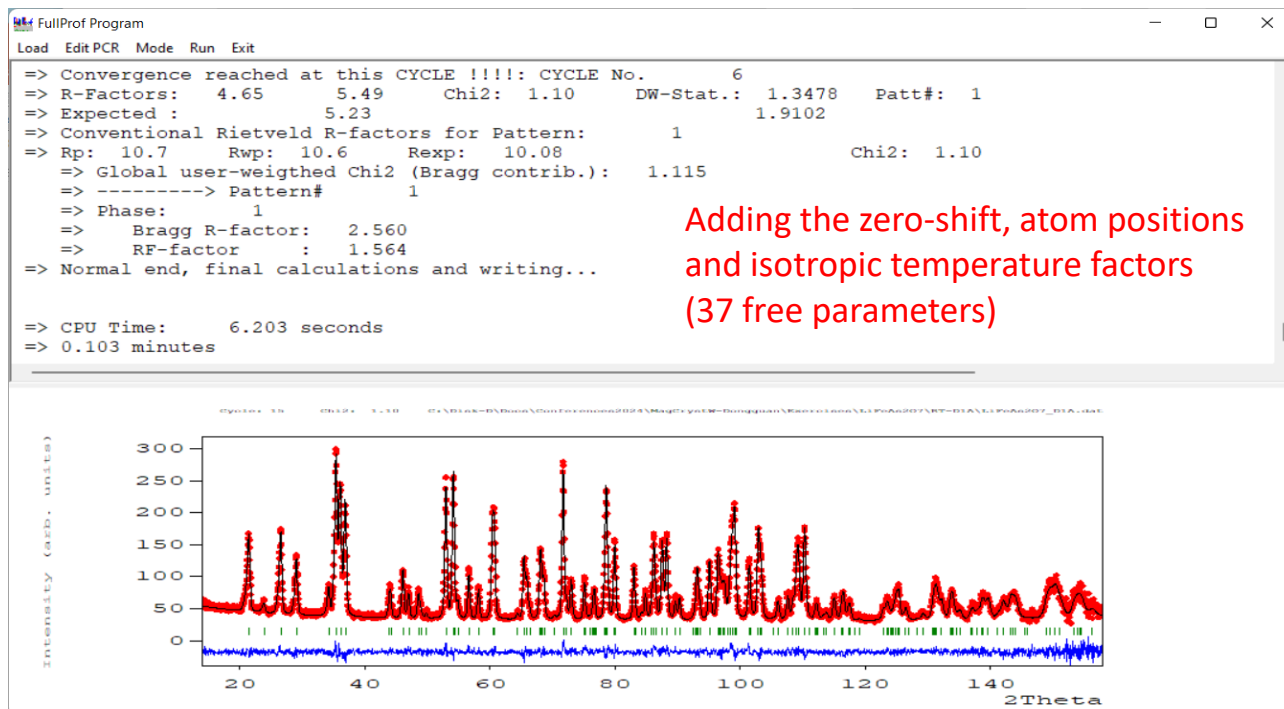


parameter in each refinement cycle. From the toolbar with the **LiFeAs207.pcr** file loaded, click on the button of FullProf for running the program. We should obtain something similar to the following images:

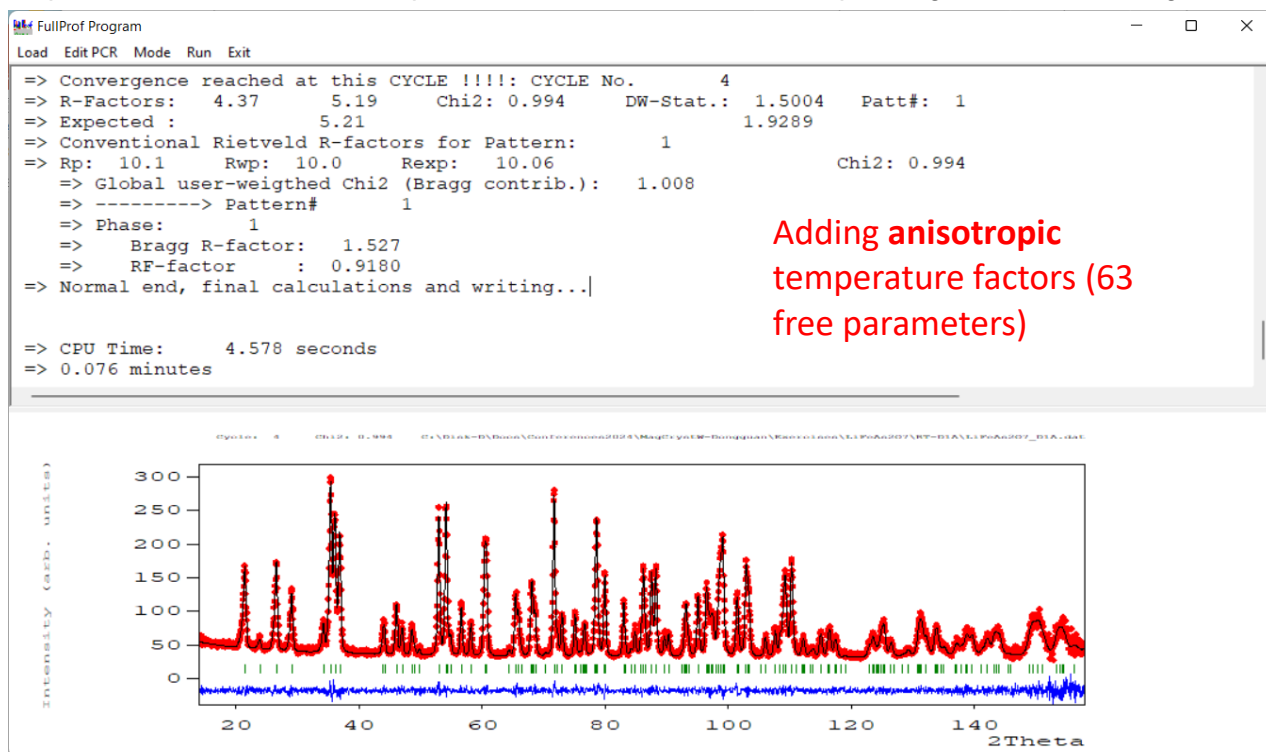
If we put the starting value of  $Y=0.05$  and refine it, we arrive to the following situation (notice that all structural parameters, cell parameters and zero-shift are still fixed)



From that point, we can refine the zero-shift (putting 1.0 below the value) and all structural parameters by using the command: **VARY xyz b cell**, that may be put in the title of the phase or in the **COMMANDS - END\_COMMANDS** section (just below the title of the phase). The program attributes codewords to all structural parameters taking into account the symmetry of the atomic sites.



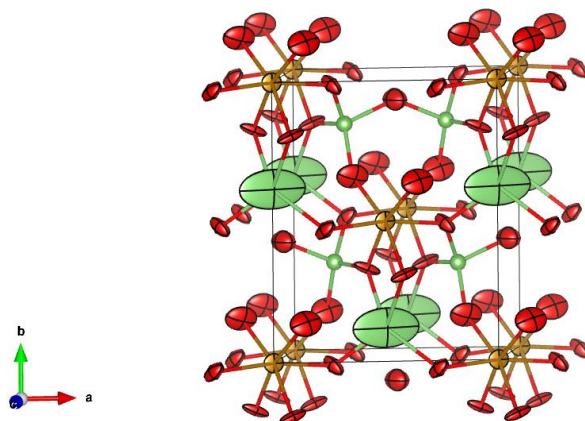
We can stop here, but we can also try to refine the anisotropic temperature factors. For doing that we can save the PCR file with another name (for instance LiFeAs2O7\_aniso.pcr) and put a “-2” in the position **N<sub>t</sub>** of each atom. The program automatically convert the isotropic temperature factor B to anisotropic betas and attribute the corresponding codewords taking into





account the site symmetry of the atom. You will see that the “-2” are automatically converted to “2” indicating an anisotropic refinement. We can see that probably some refined anisotropic temperature factors give rise to non-sense values, in such a case you can turn-back the atom to isotropic removing “2” and the two lines of the beta-parameters and codes. This happened for the As atom and the final result after anisotropic refinement appears as:

The picture of the obtained crystal structure appears as



## Step 2, apply the results from D1A to the paramagnetic state using the data of D1B:

Save the PCR file (with isotropic B's) of D1A with another name, for instance **paraD1B.pcr**, to prepare it for analysing the data of D1B. We have to select the name of the data file that should correspond to something like “... **LiFeAs2O7\D1B\scaled\_ParaD1B.xys**”. We have to change the **Ins** parameter to 10 and the name of the IRF file to that of **D1B.irf**. Having a look with WinPLOTR-2006 to the data file **scaled\_ParaD1B.xys** we can modify the excluded regions. We have also change to  $\mu R=0.2$  because the wavelength is different. We have to fix the structural parameters and refine the scale factor and a few background parameters (previous deleting the existing values).

The modified PCR file, **paraD1B.pcr**, should be similar to this one (we have highlighted in red the changes with respect to the corresponding file for D1A) :

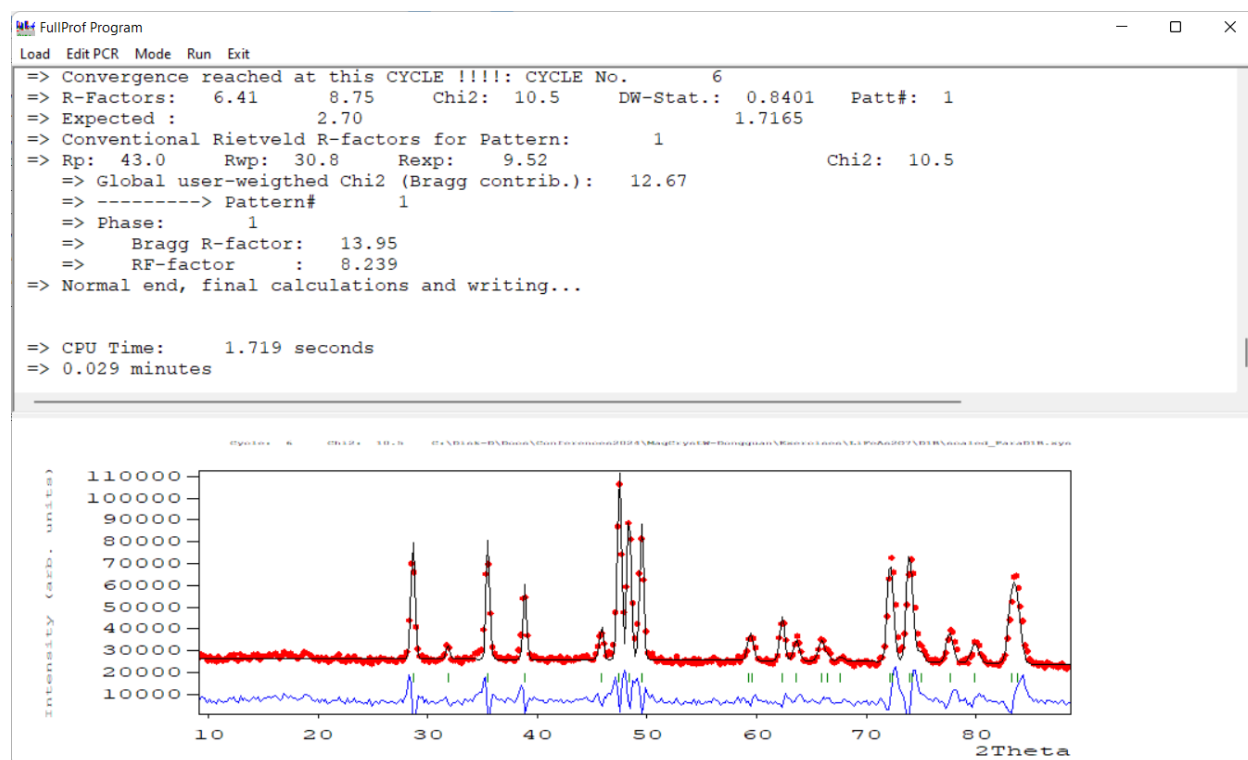
```
Phases extracted from file: LiFeAs2O7.cif => Paramagnetic data at 55K on D1B
! Current global Chi2 (Bragg contrib.) = 999991.097
NPATT 1 1 <- Flags for patterns (1:refined, 0: excluded)
W_PAT 1.000
!Nph Dum Ias Nre Cry Opt Aut
1 0 0 0 0 0 1
!Job Npr Nba Nex Nsc Nor Iwg Ilo Res Ste Uni Cor Anm Int
1 7 -5 2 0 1 0 0 1 0 0 0 0 0 0 !-> Patt#: 1
!
!File names of data(patterns) files
C:\Disk-D\Docs\Conferences2024\MagCrystW-Dongguan\Exercises\LiFeAs2O7\D1B\scaled_ParaD1B.xys
!
! Resolution file for Pattern# 1
C:\Disk-D\Docs\Conferences2024\MagCrystW-Dongguan\Exercises\LiFeAs2O7\D1B\D1B.irf
!Mat Pcr NLI Rpa Sym Sho
0 1 0 -1 0 0
!Ipr Ppl Ioc Ls1 Ls2 Ls3 Prf Ins Hkl Fou Ana
0 0 1 0 4 0 3 10 0 0 0 0 !-> Patt#: 1
!
! Lambda1 Lambda2 Ratio Bkpos Wdt Cthm muR AsyLim Rpolarz 2nd-muR -> Patt#1
2.520 2.520 0.00000 40.000 15.000 0.0000 0.2000 180.00 0.0000 0.0000
!
```

```

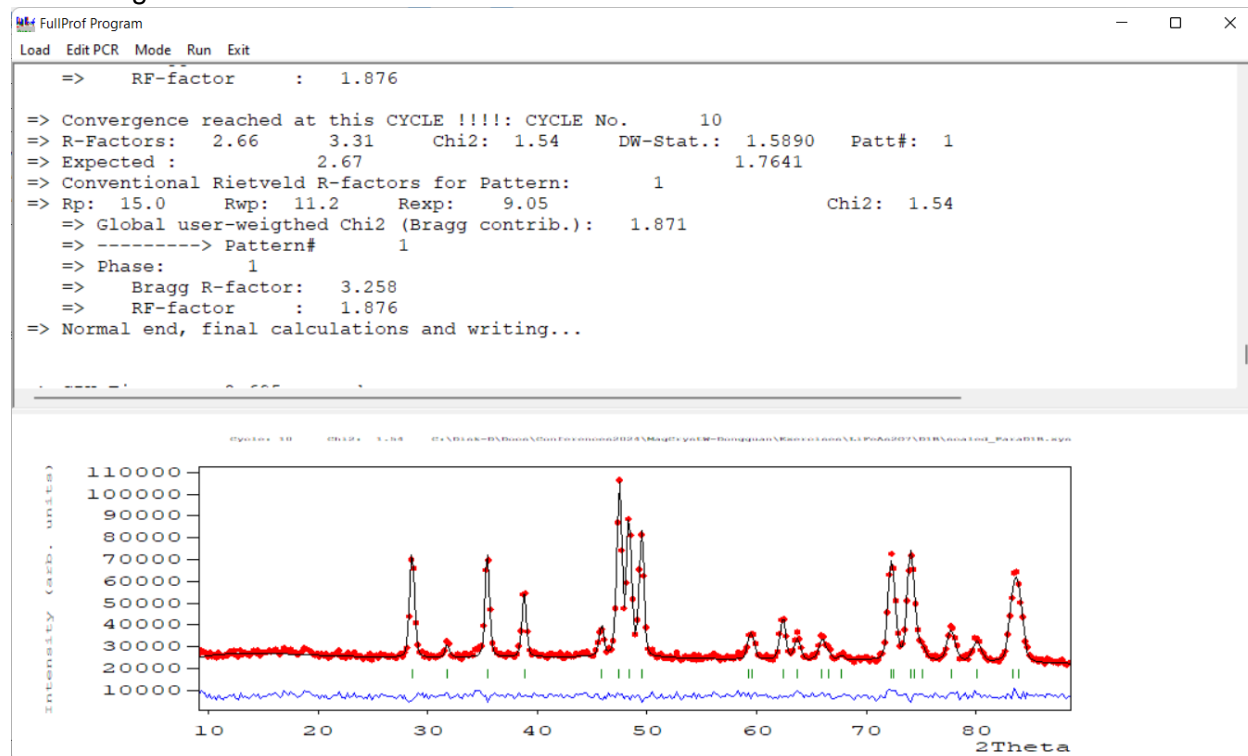
!NCY Eps R_at R_an R_pr R_gl
15 0.10 1.00 1.00 1.00 1.00
! Thmin Step Thmax PSD Sent0 -> Patt#: 1
1.0000 0.050000 157.9500 0.000 0.000
!
! Excluded regions (LowT HighT) for Pattern# 1
0.00 9.00
88.70 180.00
!
39 !Number of refined parameters
!
! Zero Code SyCos Code SySin Code Lambda Code MORE ->Patt# 1
0.01785 131.0 0.00000 0.0 0.00000 0.0 0.000000 0.00 0
!
! Background coefficients/codes for Pattern# 1 (Chebychev polynomials, up to 24 coeff)
26044.070 1.525 10.707 -0.698
1 1 1 1
0 0.0
0.00 0.00
0.000 0.000 0.000 0.000 0.000 0.000
0.00 0.00 0.00 0.00 0.00 0.00
0.000 0.000 0.000 0.000 0.000 0.000
0.00 0.00 0.00 0.00 0.00 0.00
!-----
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 2.4494
!-----
LiFeAs2O7.cif FIX xyz b cell
!
!Nat Dis Ang Jbt Isy Str Furth ATZ Nvk More
7 0 0 0 0 0 0 649.2540 0 0
!Contributions (0/1) of this phase to the 1 patterns
1
!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern# 1
0 7 1 0 0
! Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
0.000 0.000 1.000 1.000 0.000 0.000 0.000
!
C 2 <--Space group symbol
!Atom Typ X Y Z Biso Occ In Fin N_t Spc /Codes
As As 0.78243 0.32819 0.59117 0.50870 1.00000 0 0 0 0
381.00 371.00 361.00 331.00 0.00
Fe Fe 0.00000 -0.00928 0.00000 0.50564 0.50000 0 0 0 0
0.00 321.00 0.00 201.00 0.00
O1 O 0.74915 0.47209 0.82357 0.62967 1.00000 0 0 0 0
301.00 291.00 281.00 191.00 0.00
O2 O 0.83204 0.14716 0.74627 1.33512 1.00000 0 0 0 0
271.00 261.00 251.00 181.00 0.00
O3 O 0.61016 0.30838 0.27753 0.43086 1.00000 0 0 0 0
241.00 231.00 221.00 171.00 0.00
O4 O 0.00000 0.40528 0.50000 1.11777 0.50000 0 0 0 0
0.00 211.00 0.00 161.00 0.00
Li Li 0.00000 0.60862 0.00000 3.40647 0.50000 0 0 0 0
0.00 311.00 0.00 151.00 0.00
!-----> Profile Parameters for Pattern # 1 ----> Phase # 1
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
80.3481091 0.00000 0.00000 0.00000 0.00000 0.00000 0
1.00000 0.000 0.000 0.000 0.000 0.000
! U V W X Y GauSiz LorSiz Size-Model
0.000000 0.000000 0.000000 0.000000 0.0000 0.000000 0.000000 0
0.00 0.00 0.00 0.00 0.00 0.00 0.00
! a b c alpha beta gamma # Cell Info
6.678764 8.285525 4.742907 90.000000 103.949829 90.000000
391.00000 351.00000 341.00000 0.00000 141.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! 2Th1/TOF1 2Th2/TOF2 Pattern to plot
9.000 89. 1

```

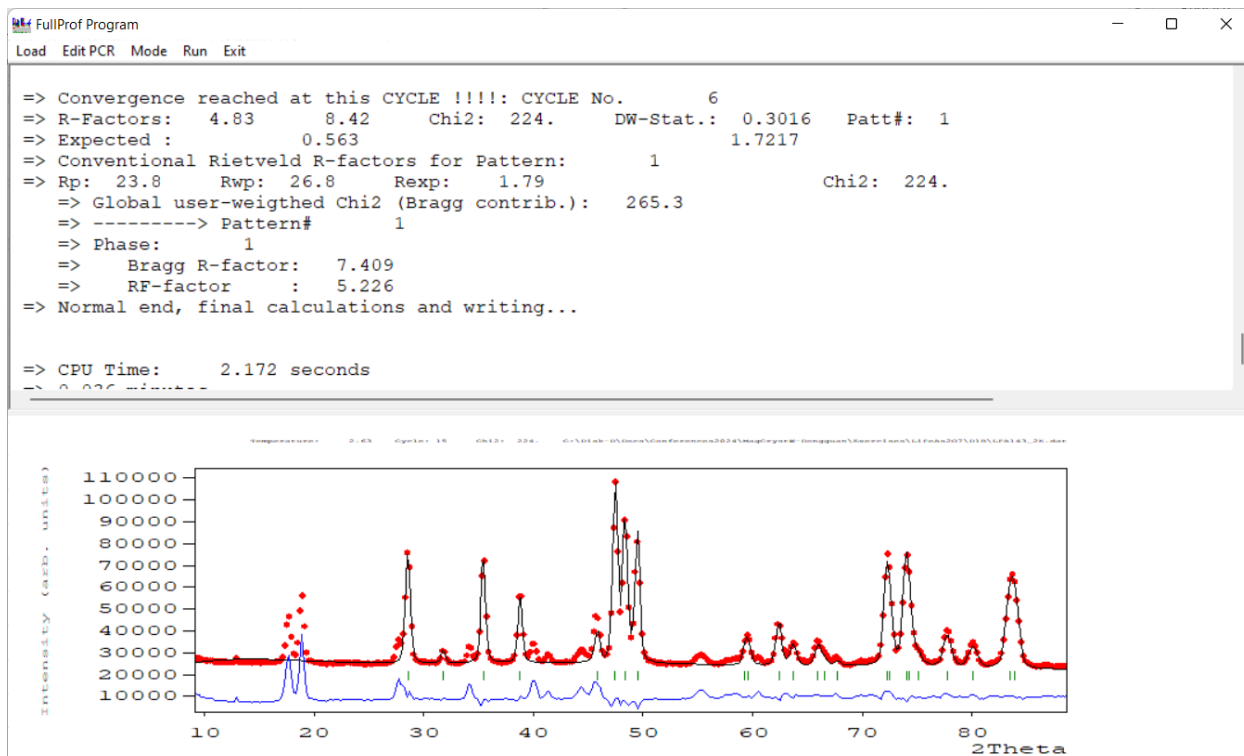
After running this file, we obtain something like:



Now we can add the cell parameters, the Y-size parameter and few more background points. Then we get:

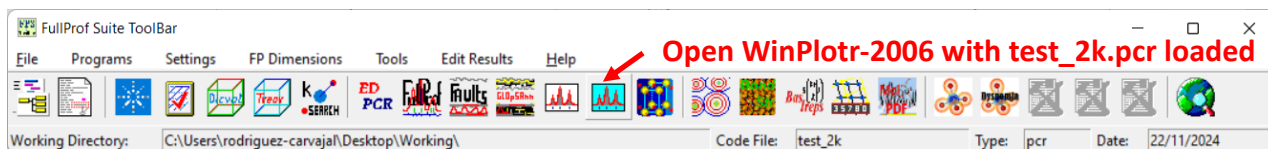


Now, we can save the file **paraD1B.pcr** with another name to be run with the high statistics file taken at 2.6K. Let us call it **test\_2k.pcr**. We have to fix all background parameters and change the name of the **Ins** parameter to **Ins =3** and the data file to **LFA143\_2K.dat**. Load the saved file **test\_2k.pcr** into the toolbar. If we run FullProf from the toolbar, we obtain something similar to this:

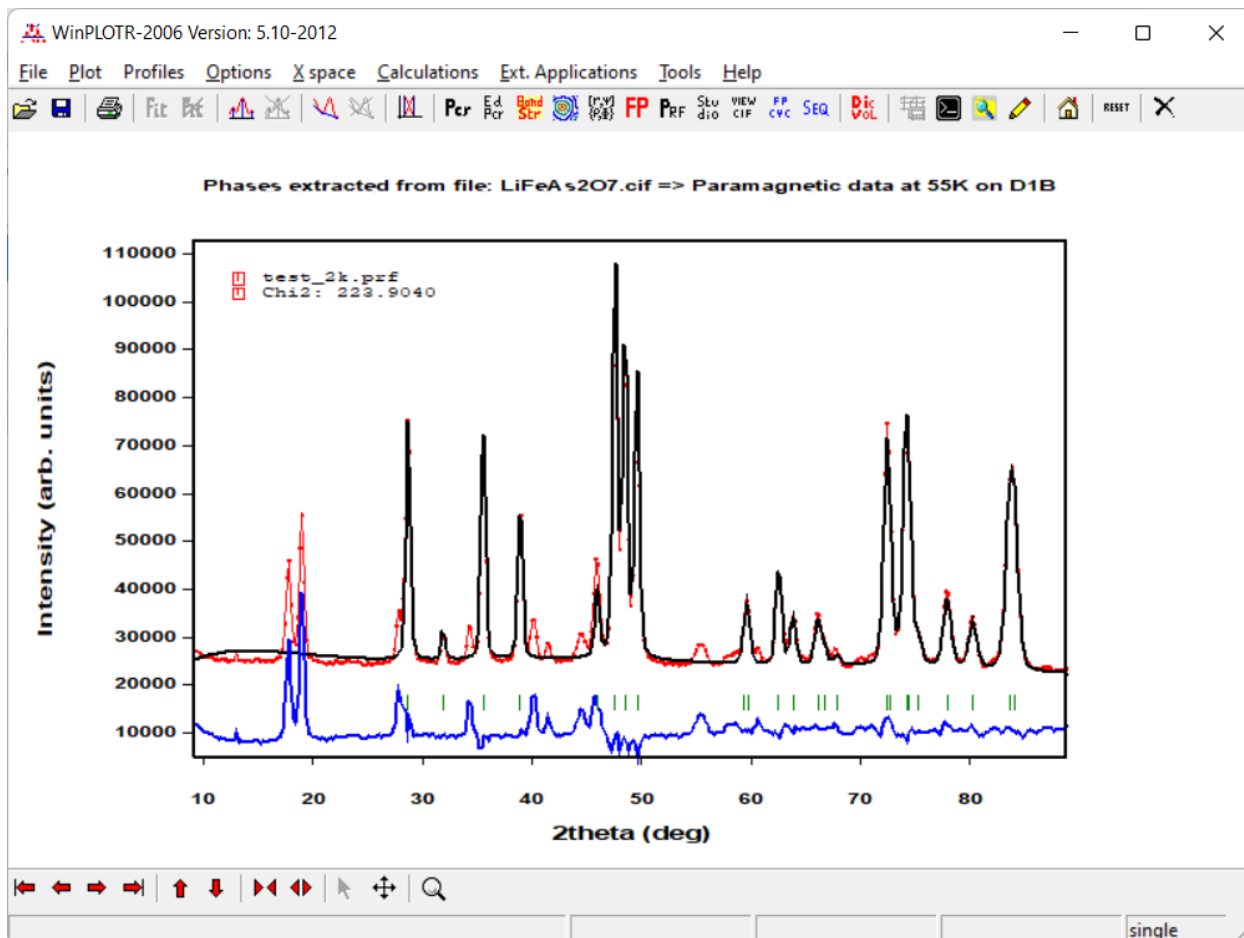


We see in the difference pattern the appearance of the magnetic peaks. These have to be studied in order to get the propagation vector characterizing the magnetic order of this compound. This will be done in the following step

**Step 3 Determination of the k-vector:** With the file `test_2k.pcr` loaded in the toolbar, invoke the program WinPLOTR-2006. This will automatically visualize the file `test_2k.prf` that contains all the needed information to prepare a file for the program `k_Search`.



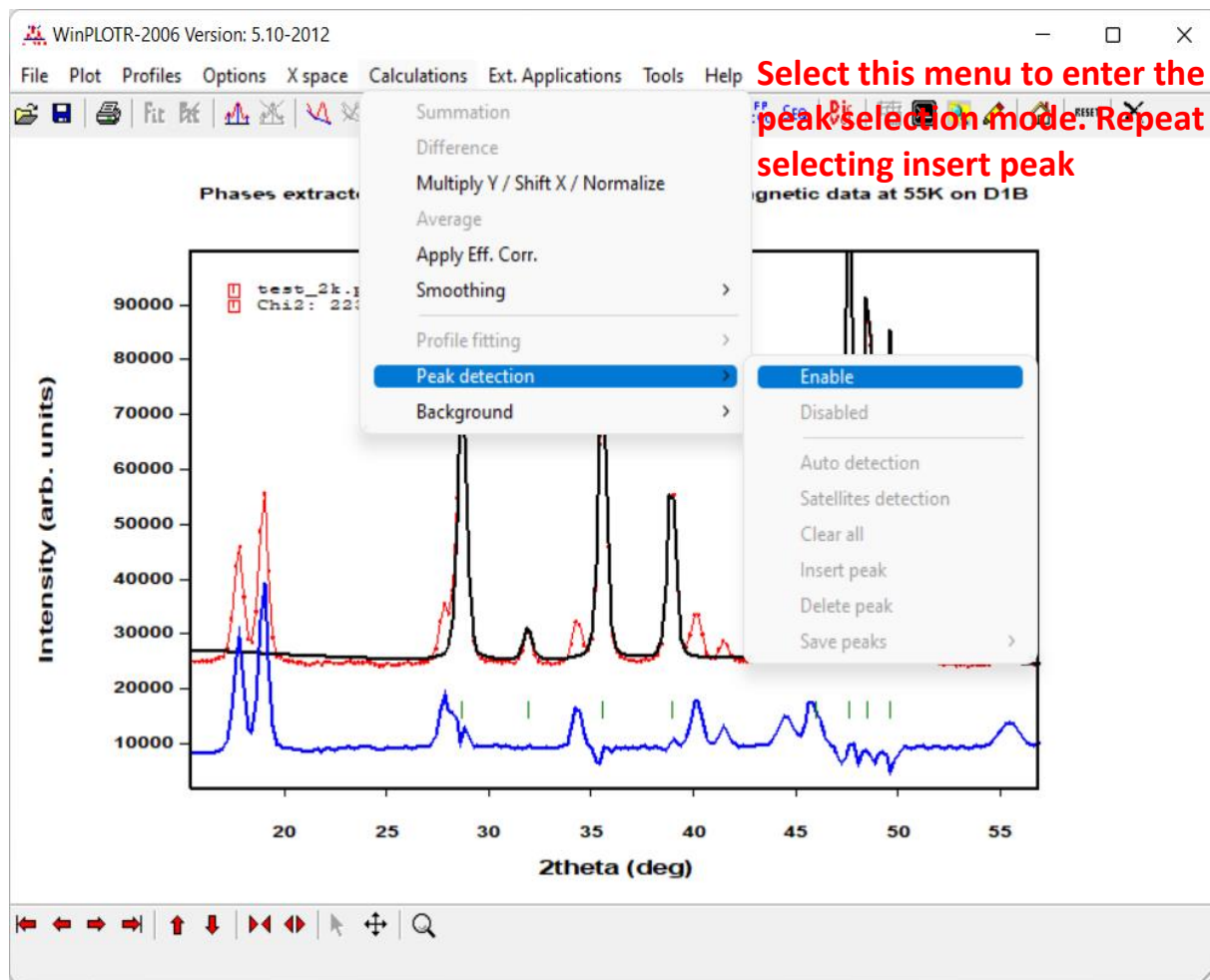
We obtain a picture similar to that:



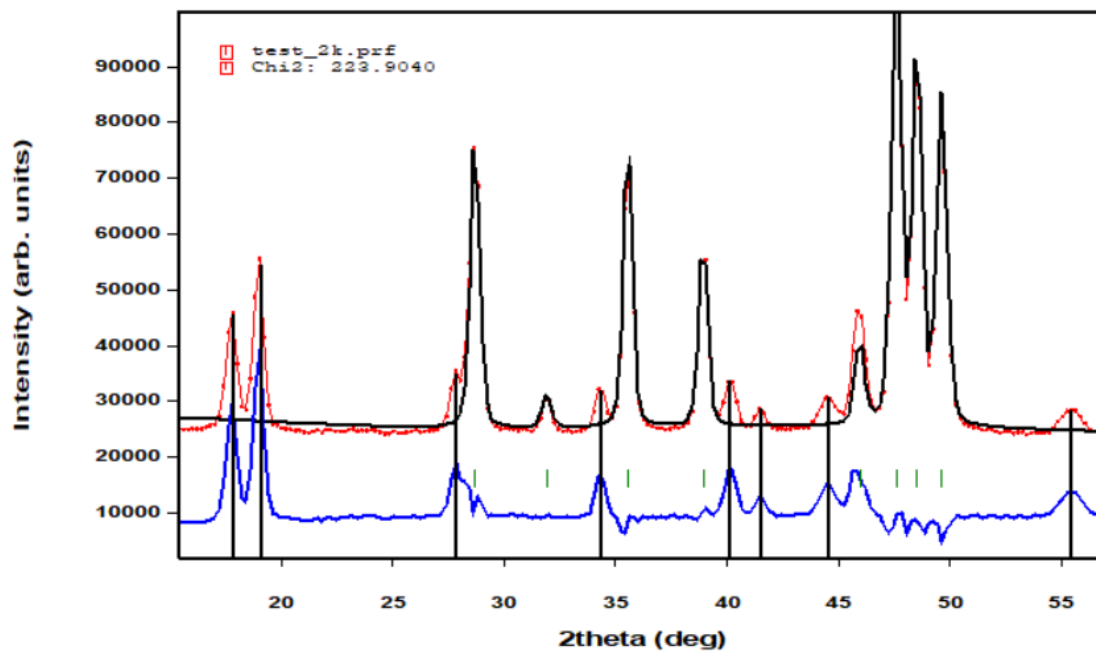
We see that the background is not the same as that at 55K because the paramagnetic diffuse scattering has now been merged into magnetic Bragg peaks. We can modify that introducing manually point-by-point background positions to be interpolated for doing a more realistic fit of the background, however this is not important for selecting the magnetic peak positions from WinPLOTR-2006. For doing that make the following:

- Make a zoom of the area between 15 and 57 degrees in 2-theta.
- Then go to the **Calculations** menu to activate the **Peak detection** and select **Enable**.
- Repeat now the procedure but now select **Insert peak** now select
- Move the mouse to the peak positions of the magnetic reflections that are those not fitted by the calculated pattern. With the mouse left button click on the top of each peak positions. Avoid those peaks too close to nuclear peaks.
- The selected peak will be corrected from the zero-shift because the PRF file incorporates that in the 2-Theta positions.

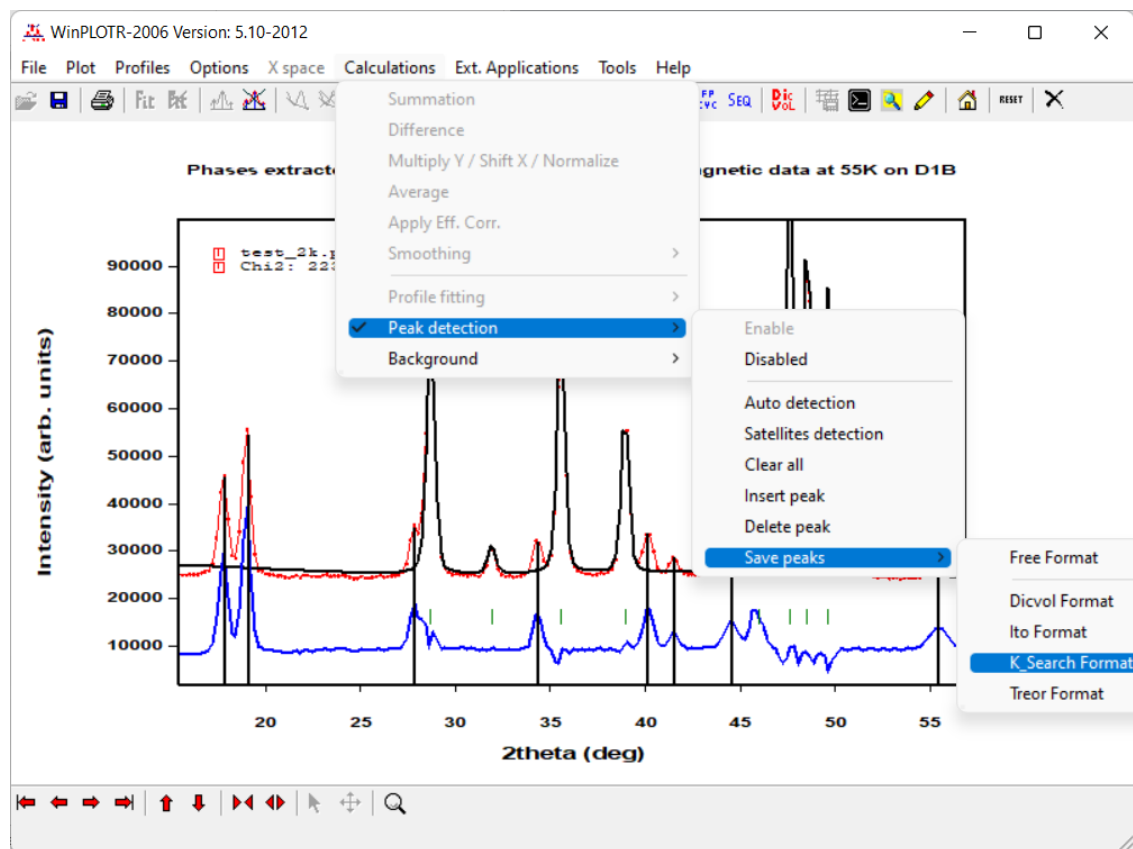




After selecting the peaks, you should have an image of the pattern like this:



Once the peak are selected, one has to save them in a particular format for using the program K\_Search. In the **Calculation > Peak detection** menu select **Save peaks > K\_Search format**.



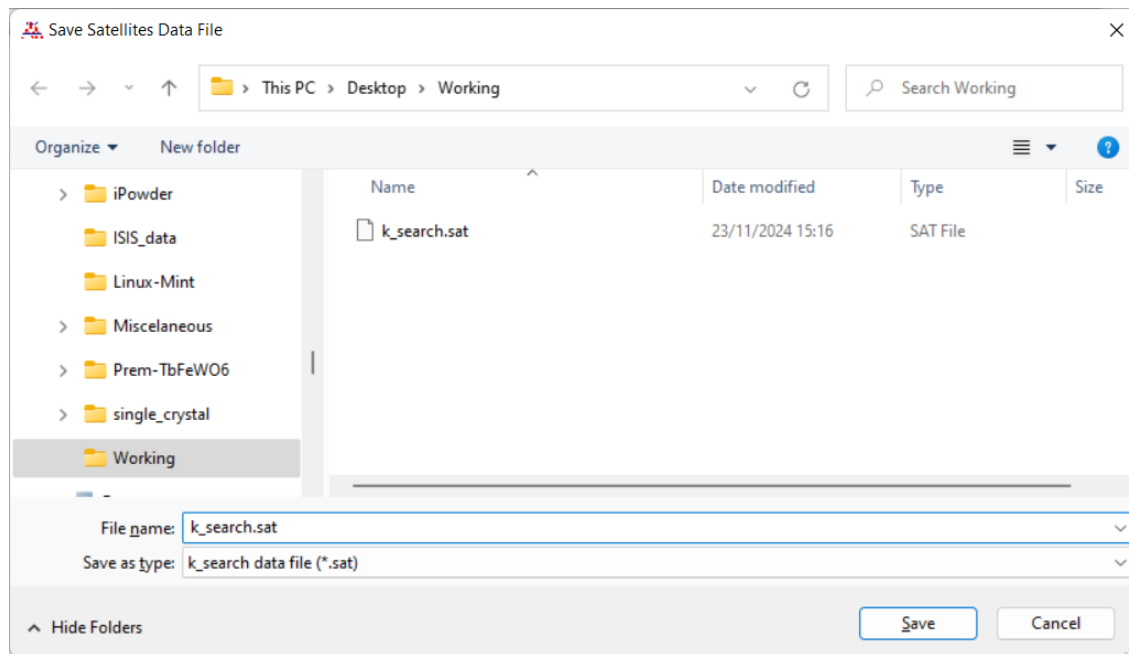
The following dialog appear for giving the conditions to run K\_Search.

The screenshot shows the 'Input parameters for K\_SEARCH' dialog box. The 'Title' field contains 'Phases extracted from file: LiFeAs207.cif => Pa'. The 'Lattice Type' is set to 'C 2'. The 'Cell Parameters' are '6.65335 8.25405 4.72377 90'. The 'Tolerance (TOF/2theta)' is '0.300'. The 'K range (kxmin,kxmax,...)' is '0.0 0.5 0.0 0.5 0.0 0.5'. The 'Number of Points (Na\* Nb\* Nc\*)' are '100 100 100'. The 'Wavelength (CW) / Dtt1(TOF)' is '2.52000'. The 'Short Output' radio button is selected. The 'Search only special k-vectors' checkbox is checked. Red arrows point to the 'K range' field and the 'Search only special k-vectors' checkbox. Red text explains that the limits should be modified for a C-centered cell and that the checkbox should be unchecked to search for general k-vectors.

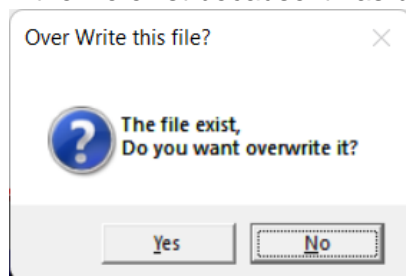
**Modify the limits because it is a C-centered cell and it may have components higher than 1/2. For instance: 0 1 0 0.5 0 1**

**Uncheck this box to search for general k-vectors**

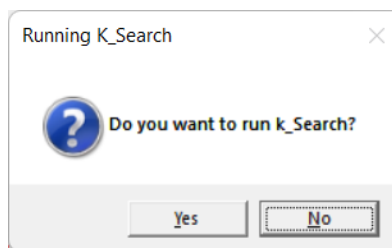
When clicking on OK, the program proposes to save a K-Search input file with the name **k\_search.sat**



If the file exist because it has been created before, you will get a small dialog,



You may say “yes” and the program proposes to you the possibility to run k\_Search



You should say also yes! Then a terminal opens in which the program k\_Search will be working.

```

C:\WINDOWS\SYSTEM32\cmd.exe
>> End special k-vectors test ... continuing with general k-vectors
>> Total number of points in the grid : 2060451
71.19% S: 100 k =( 0.7150 0.0100 0.1550) R-F: 1.3295 R-best: 1.5325
72.22% S: 200 k =( 0.7250 0.0160 0.1600) R-F: 3.6704 R-best: 1.0356

>> List of the best incommensurate 10 solutions for 8 satellites

      Kx      Ky      Kz      R-factor
0.715000  0.014000  0.155000  1.035631
0.715000  0.012000  0.155000  1.051651
0.715000  0.016000  0.155000  1.123046
0.715000  0.018000  0.155000  1.275483
0.715000  0.010000  0.155000  1.329459
0.720000  0.016000  0.155000  1.410066
0.720000  0.018000  0.155000  1.414602
0.715000  0.020000  0.155000  1.436355
0.720000  0.014000  0.155000  1.459657
0.720000  0.020000  0.155000  1.508208

>> Powder diffraction may give wrong results even if the R-factors for the solutions are "good"
The best way to verify the solutions is to perform a full profile fitting and look for mismatches

Total CPU-Time

      CPU-seconds:      0.39
      CPU-minutes:      0.01
      CPU-hours   :      0.00

>> Press <enter> to finish

```

Notice that the  $k_y$ -value is quite small and probably it may be taken as zero. You may try to limit the variation of the k-components according to this starting solution, by saving again the peaks from WinPLOTR-2006 and changing the conditions for searching. Keep in mind that the value is not too precise and can be later on refined.

**Input parameters for K\_SEARCH**

Title: Phases extracted from file: L

Lattice Type: C 2

Cell Parameters: 6.65335 8.25405 4.72377 90.0000 103.9656 90.0000

Tolerance (TOF/2theta): 0.300

Krange (kxmin,kxmax,...): 0.5 0.8 0.0 0.05 0.0 0.5

Number of Points (Na\* Nb\* Nc\*): 400 100 400

Wavelength (CW) / Dtt1(TOF): 2.52000

☒ Short Output ☐ Long Output ☐ No output of intermediate calculations

☐ Search only special k-vectors

OK Cancel

**We have increased the grid in the a\*c\* plane and also diminish the interval for searching**

Now clicking again, we obtain

```
C:\WINDOWS\SYSTEM32\cmd.exe
75.94% S: 22600 k =( 0.7280 0.0260 0.1538) R-F: 3.5499 R-best: 0.6823
76.13% S: 22700 k =( 0.7287 0.0135 0.1538) R-F: 3.3590 R-best: 0.6823
76.38% S: 22800 k =( 0.7295 0.0150 0.1538) R-F: 3.3323 R-best: 0.6823
88.73% S: 22900 k =( 0.7663 0.0405 0.1587) R-F: 4.1079 R-best: 0.6823

=> List of the best incommensurate 10 solutions for 8 satellites

      Kx      Ky      Kz      R-factor
0.716750  0.013500  0.153750  0.682318
0.716000  0.013500  0.153750  0.693271
0.716000  0.013000  0.153750  0.694730
0.716750  0.014000  0.153750  0.715755
0.716000  0.014000  0.153750  0.735982
0.716750  0.013000  0.153750  0.750735
0.717500  0.014000  0.153750  0.752583
0.716000  0.012500  0.153750  0.758041
0.716750  0.014500  0.153750  0.759857
0.716000  0.014500  0.153750  0.778663

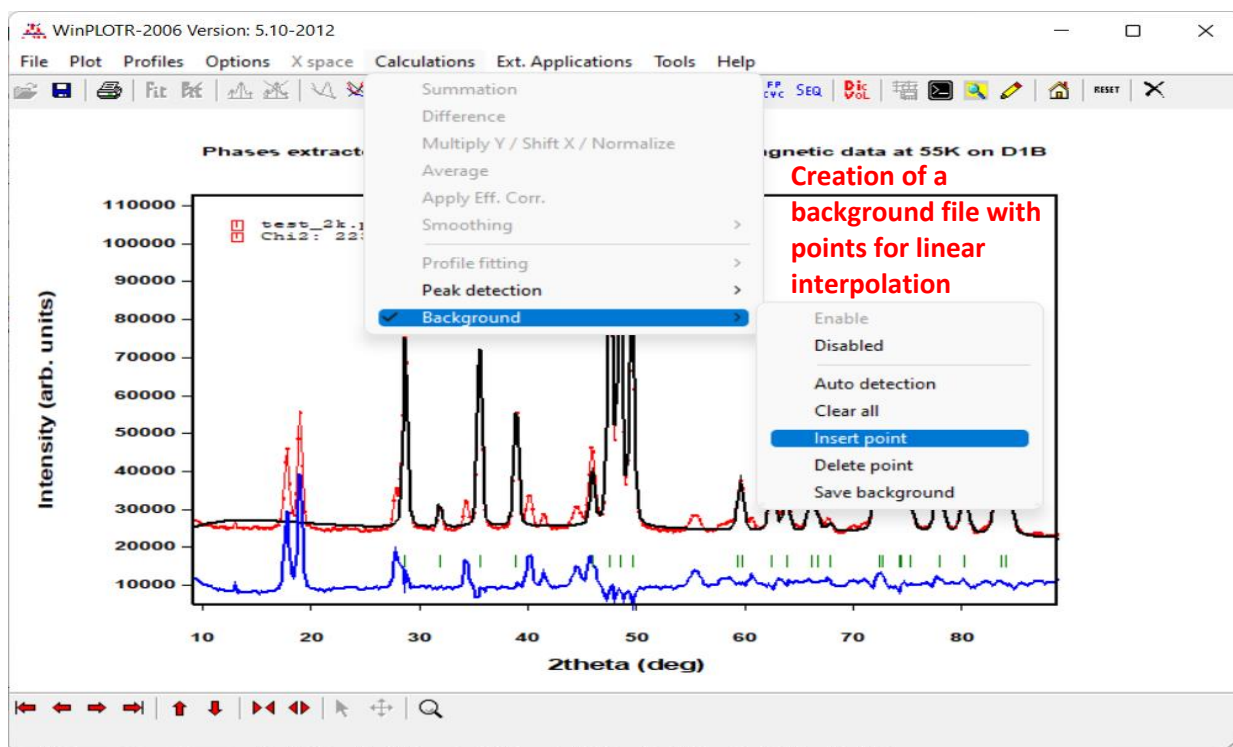
=> Powder diffraction may give wrong results even if the R-factors for the solutions are "good"
    The best way to verify the solutions is to perform a full profile fitting and look for mismatches

      Total CPU-Time

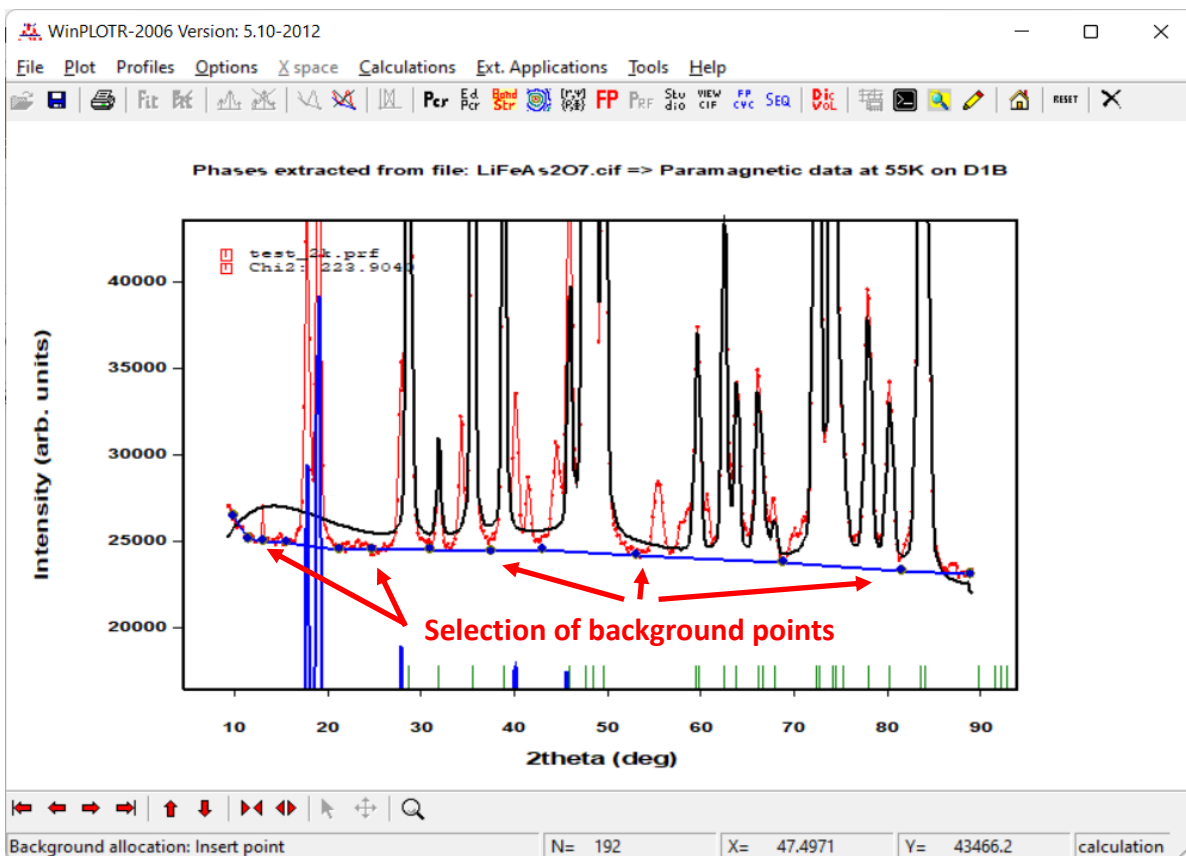
      CPU-seconds:      3.22
      CPU-minutes:      0.05
      CPU-hours   :      0.00

=> Press <enter> to finish
```

We can try to test the propagation vector  $\mathbf{k}=(0.716, 0, 0.154)$  by introducing an additional phase in the previous PCR file in which we can change the background to a fixed list of points for linear interpolation. For doing that, we can continue with WinPLOTR-2006 in which the PRF file **test\_2k.prf** is loaded. We have to disable the **Peak detection** mode and enable the **Background > Insert point** menu, as shown in the following figure:



The cursor of the mouse changes to a cross and the user can select the background points as shown in the following figure:

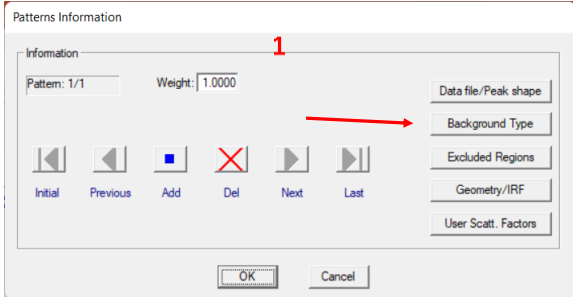


Once the points have been selected, they can be saved in a file (normally called **background.bgr**) that can be incorporated easily into the PCR file using EdPCR.

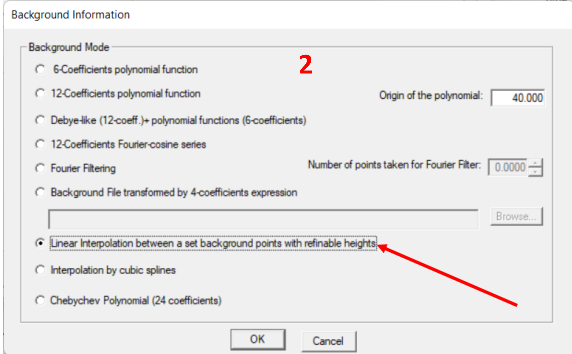


To incorporate the background into the PCR file this is the sequence to follow:

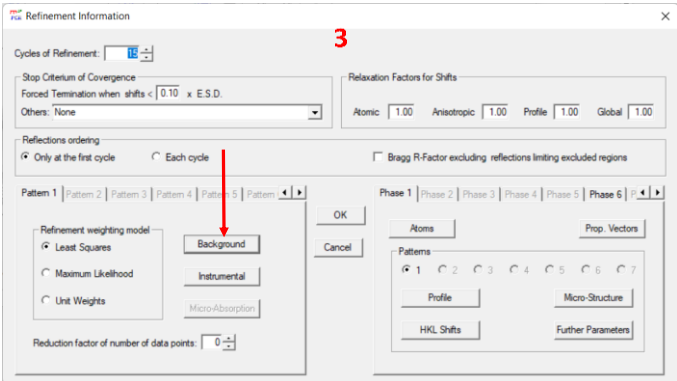
**From the button Patterns**



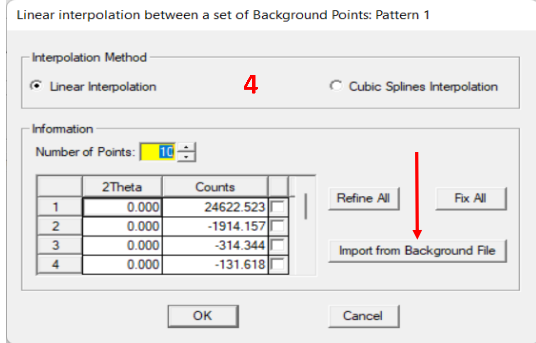
**Background Information**



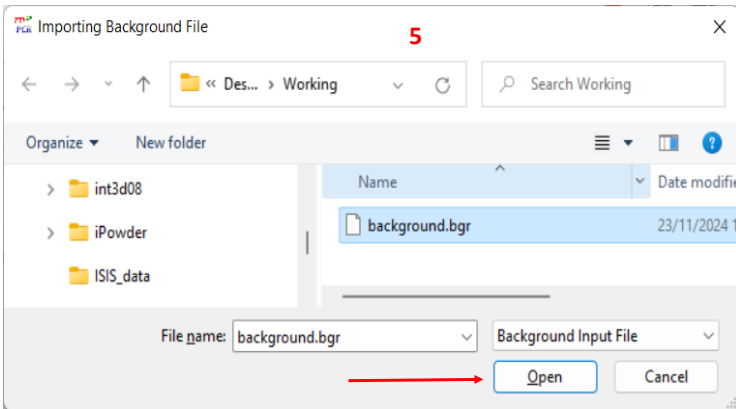
**From the button Refinement**



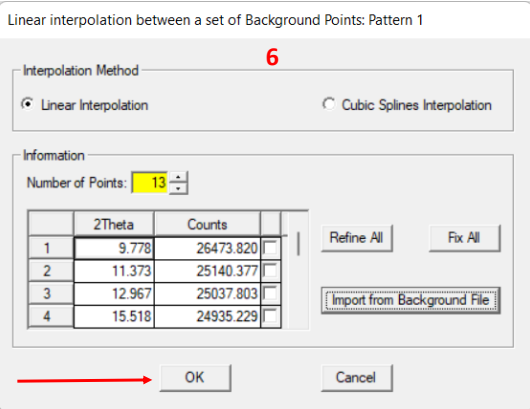
**Linear interpolation between a set of Background Points: Pattern 1**



**Importing Background File**



**Linear interpolation between a set of Background Points: Pattern 1**



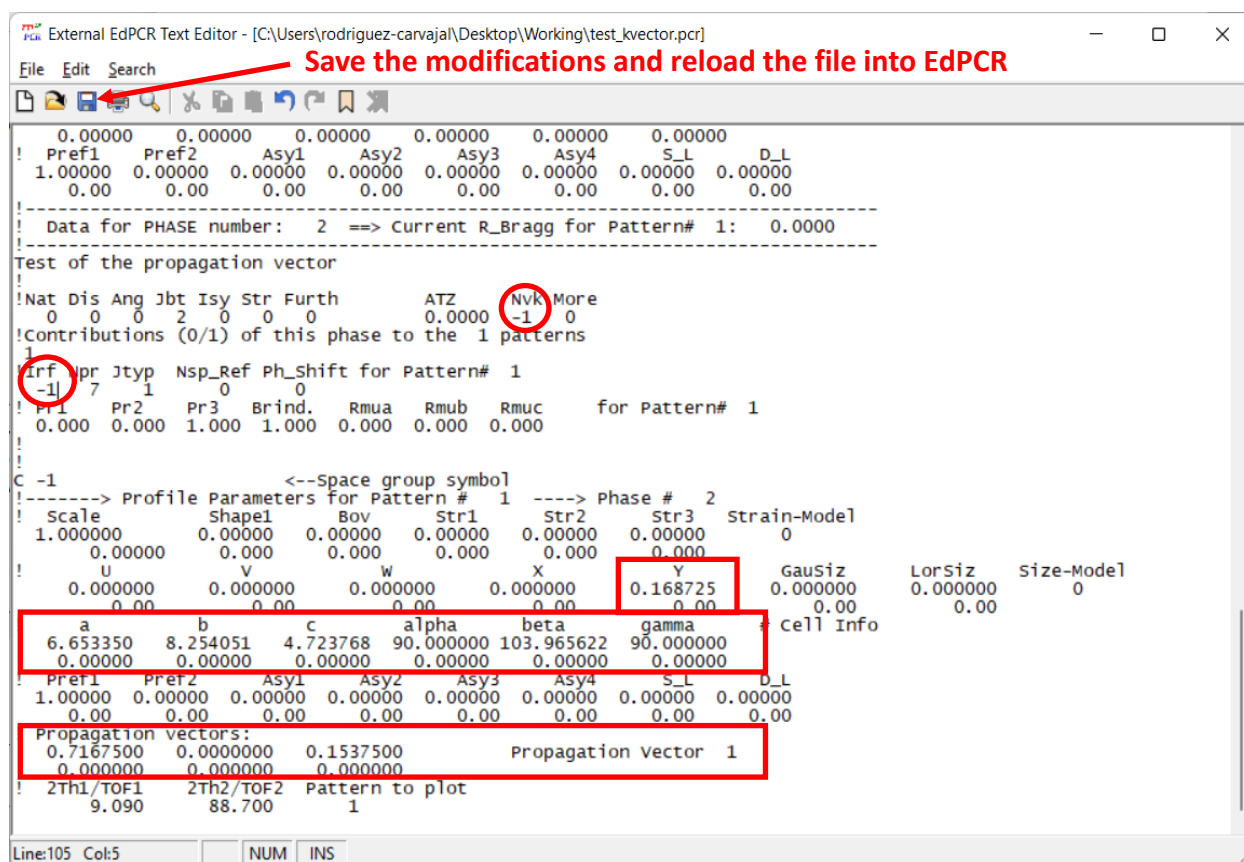
Sequence for importing a background file into a previously existing PCR file

After importing the background file, you can save the new PCR file with a new name. We shall call this new PCR file **test\_kvector.pcr**.

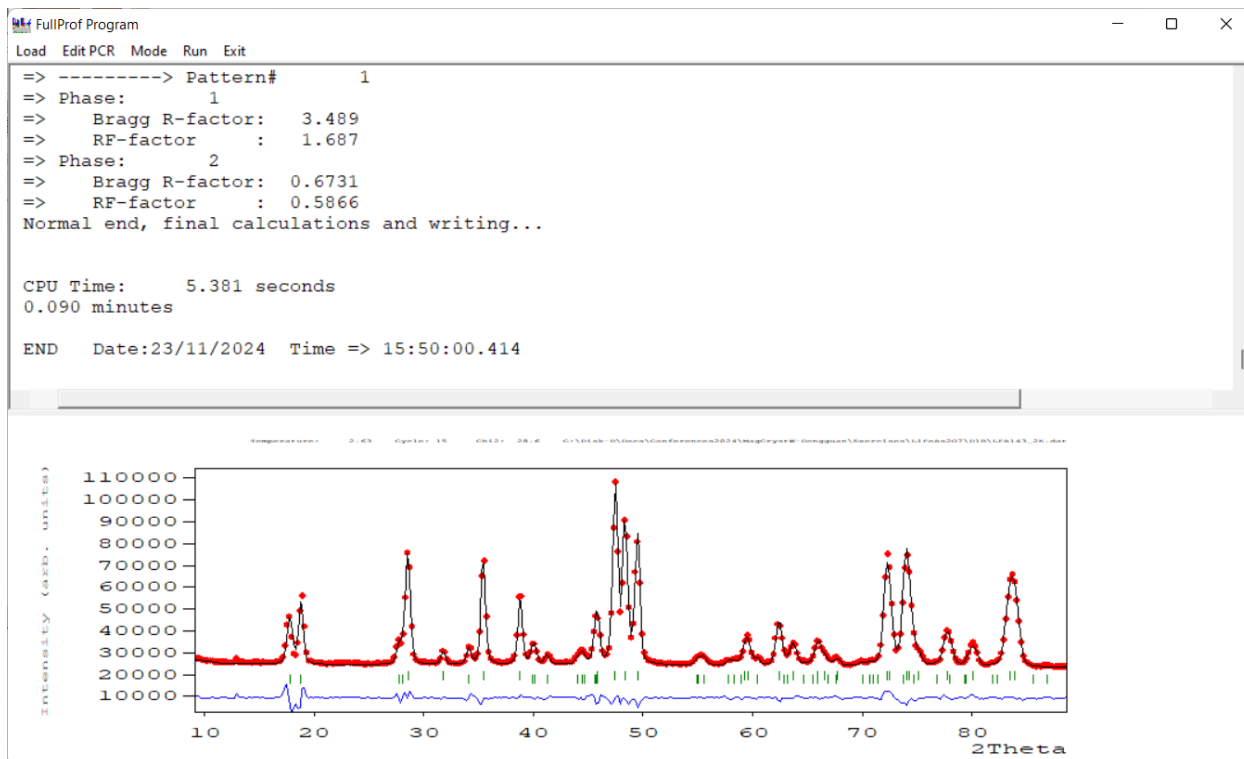
An experienced user can add manually a new phase into the freshly created PCR file; however, EdPCR can be used to add a new phase that will be in Le Bail fit mode. This will allow to test and refine the components of the k-vector at 2.6K. For doing that with EdPCR, you should click on the **Phases** button that opens a dialog in which you should press the button **Add**. In the same dialog, you can add a new title for the new phase (for instance “Refinement of k- vector”). In the **Calculation** box select the item: **“Profile Matching with constant scale factor”**. Clicking on the **Contribution to Patterns** button a new dialog opens and you have to check the box **“Current Phase contributes to the pattern”**, select the **“Neutron (Constant Wavelength)”** radio button. In the **Peak Shape** box select the item **“Thompson-Cox-Hastings pseudo-Voigt \* Axial divergence asymmetry”** and in **Reflection list**: select

**“Automatically generated from the Space Group symbol”**. Click on OK and then click on the button **Symmetry** and a new dialog opens. Select the option **Symmetry operators**: **“Generated automatically from the symbol”** and enter **“C -1”** as space group symbol for generating reflections without putting any symmetry except the centring conditions. After clicking successively in **OK** buttons, save the intermediate file **test\_kvector.pcr**. Once the file saved, you can have a look into it using the internal editor of EdPCR by selecting in the general menu: **Editor > Input Control File (.PCR)**. This will open the file in the internal editor. You may find that the cell parameters of the new phase are equal to zero and there is no propagation vector. You can use the internal editor to copy and paste the cell parameters of the phase 1 in to the corresponding place of the phase 2, the same for the Y-size parameter, add **Nvk=-1**, and put **Irf=-1** to tell the program to generate only satellites of the nuclear reflections. Finally, you can insert the propagation vector, so the aspect of the new added phase in the PCR file should be similar to the image shown below:

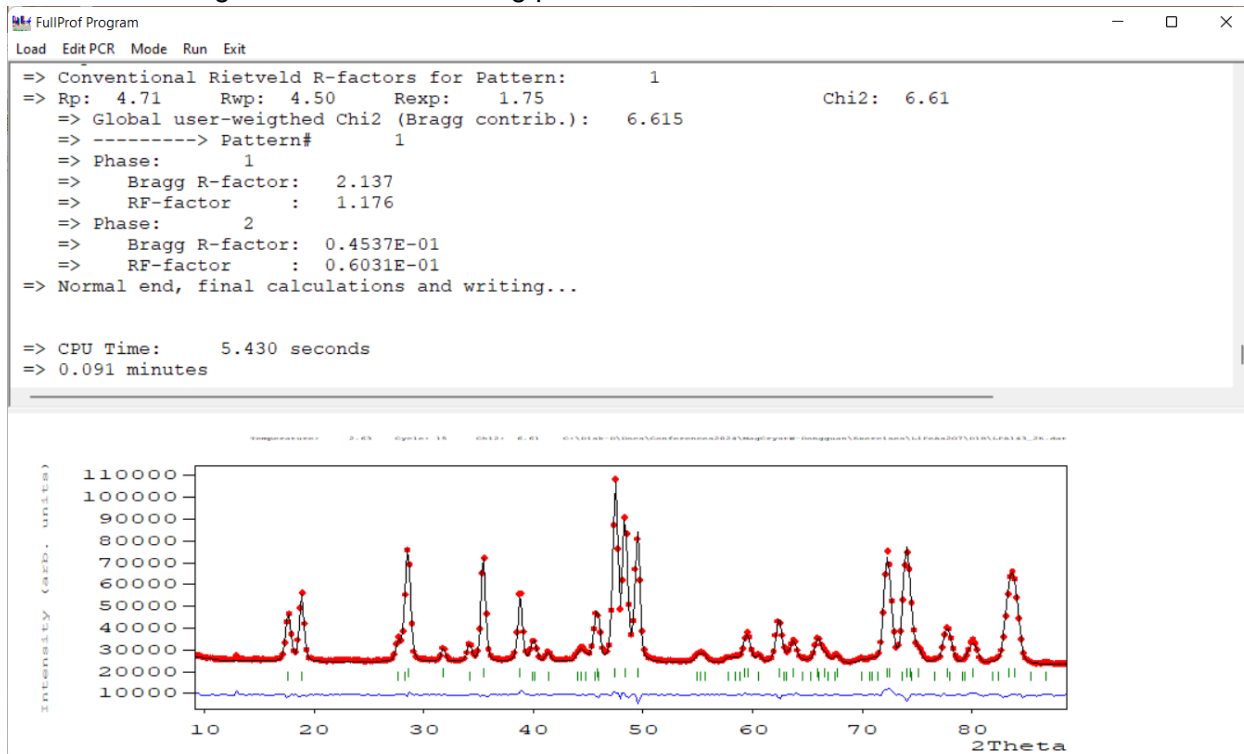
After having prepared the file, fix all kind of parameters by using EdPCR or directly removing the codewords existing in the original PCR file. Load the new file **test\_kvector.pcr** into the



toolbar and run FullProf. The Le Bail fit starts (even if you have fixed all parameters, the integrated intensities are estimated and changed at each refinement cycle) and you may run several time the same job. After closing the windows running FullProf, you can reload the resulting PCR file into EdPCR or in your favourite editor. You will see that **Irf** has changed from the value -1 to the value 2. This is because the first time you run the Le Bail fit the program uses only the generated satellites and in the subsequent runs the program will read (**Irf =2**) the reflection indices and their intensity from the file **test\_kvector1.hkl** that will be updated each time we run a Le Bail fit. You obtain something similar to the following figure without varying the parameters.



You can now refine the cell parameters and Y-size parameters of the two phases constraining them to be the same, the components of the propagation vector, the zero shift, etc. You will obtain something similar to the following picture:



At the end you have verified that the propagation vector with  $k_y=0$  is very well refined.

## Determination of the magnetic structure of $\text{LiFeAs}_2\text{O}_7$

Once the propagation vector is known, we can start to look for possible magnetic structures explaining the observed intensities. We shall use two approaches for that task. First, we will use

Baslreps for obtaining the basis vectors of the irreducible representations (*irreps*) of the propagation vector group and, second, we will use ISODISTORT for generating magnetic CIF files implementing the Magnetic Super Space Groups (MSSG) that can be converted to PCR files using the utility `mCIF_to_PCR`.

### Use of Baslreps

In the toolbar, clicking on the button of Baslreps opens a dialog that you should fill with the appropriate values:

Baslreps Gui Interface

File Run Results Help Exit

Code of files:

Working Directory:

Title:

SpaceGroup (HM/Hall symbols) or generators separated by ",":

K-Vector:    Brillouin Zone Label:

☐ Polar Vector ☒ Axial Vector ☐ Full Physically Irreps (PIR) ☐ Extended Little Group (PIR)

Number of Atoms:  ☐ Explicit Sublattices ☐ Atoms in unit cell

Atom #	Symbol	x/a	y/a	z/a
...	Fe	0.0000	0.0000	0.0000

☒ Short Output

When running the program the files `LiFeAs.bsr` and `LiFeAs.fp` are generated. This is a case especially simple because there is a single atom in a primitive cell and a single *irrep* of the propagation vector group (little group), which has only the identity as symmetry operator. The *irrep* of  $G_k=C1$  is one-dimensional. Of course, we have to consider the extended little group that coincides with the full space group because the symmetry operator  $\{2_y|000\}$  transform  $\mathbf{k}$  into  $-\mathbf{k}$ . For that, rename the code of files (instead of `LiFeAs`, write `LiFeAs-Ext`) and you have to check the box **“Extended Little Group (PIR)”**.

You will see that that the only difference is that now the *irrep* of the full space group is two-dimensional. However, the basis vectors of the single Fe atom are the same. The resulting Fourier coefficient of the single Fe atom is  $\mathbf{S}_k(\text{Fe})=(u, v, w)$  with  $u, v, w$  complex coefficients, so the magnetic structure has apparently no constraint and six degrees of freedom. Baslreps does not make a systematic analysis of the isotropy subgroups, however the coefficients of the resulting Fourier coefficients can be selected and constraints can be applied. A way to explore the possible constraints introduced by the preservation of the binary axis is to use Baslreps for a

single atom in a general position. In such a case, the two Fe atoms related by the binary axis  $\{2_y|000\}$  (Fe1 at x,y,z and Fe2 at -x,y,-z) have Fourier coefficients of the form:

$\mathbf{S}_k(\text{Fe1})=(u + p, v + q, w + r)$  and  $\mathbf{S}_k(\text{Fe2})=(-u + p, v - q, -w + r)$ , see the output file **LiFeAs-Est.bsr**.

If we select the u, v and w as real numbers and p, q, r as purely imaginary we can re-write the Fourier coefficients as  $\mathbf{S}_k(\text{Fe1})=(u + i p, v + i q, w + i r)$  and  $\mathbf{S}_k(\text{Fe2})=(-u + i p, v - i q, -w + i r)$ . If we force the position of the Fe atom to be confined at the origin then  $\mathbf{S}_k(\text{Fe1})= \mathbf{S}_k(\text{Fe2})$  and this implies  $u=0, w=0$  and  $q=0$  so the Fourier coefficient of the Fe-atom at the origin has the form  $\mathbf{S}_k(\text{Fe})=(i p, v, i r)$  with only 3 degrees of freedom. The other option is to consider that the binary axis is lost and the general Fourier coefficient is of the form:  $\mathbf{S}_k(\text{Fe})=(u + i p, v + i q, w + i r)$  with six degrees of freedom, which is the lowest symmetry.

For testing the most symmetric model  $\mathbf{S}_k(\text{Fe})=(i p, v, i r)$ , one can use EdPCR and transform the **test\_kvector.pcr** file in another PCR file, that we call here **mag\_model\_a.pcr**.

The steps to prepare a file for the refinement of this model using EdPCR are the following

**Step 1: Phase Information: Phase 2**

General Information on Phases

1 **Change the name of the phase**

2 **Select Magnetic Phase**

Calculation: [Magnetic Phase (Rietveld Method)]

Coefficient to calculate the weight percentage of the Phase: 0.00

Contribution to patterns, preferred orientation direction, reflection list, ...

Space Group symbol/number, symmetry operators, basis functions, etc.

Initial Previous Add Del Next Last

OK Cancel

**Step 2: Pattern Contribution Information for Phase 2**

Pattern 1 | Pattern 2 | Pattern 3 | Pattern 4 | Pattern 5 | Pattern 6 | Pattern 7

2 **Select Satellite reflections**

☒ Current Phase contributes to the pattern

Type of Pattern

☐ X-Ray

☒ Neutron (Constant Wavelength) Nuclear and Magnetic

☐ Neutron (T.O.F.) Nuclear and Magnetic

Peak Shape

Thompson-Cox-Hastings pseudo-Voigt \* Axial divergence asymmetry

☒ Codefill.shp

Intensities

Reflection list: [Satellite reflections are generated automatically from Space group symbol]

☐ Use special control of parameters for peak overlap, rejected reflections for current phase

Brindley coefficient: 0.0000

Global weight of the integrated intensity data vs profile data: 0.0000

Factor for excluding reflections [  $1 < \text{Factor} * \text{Sigma}(I)$  ]: 0.0000

Weights are divided by reduced  $\chi^2$  of precedent cycle: 0.0000

OK Cancel

**Step 3: Symmetry Information**

Space Group Properties

Symmetry Operators: [Basis functions of the irreducible representations of the propagation vector group]

Spacegroup: **C-1**

Symmetry operators | Magnetic/Displacement Operators | Irreducible representations

Laue Class: -1

Number of Symmetry Operators: 1

Centrosymmetric Case

Num	Symmetry	TR
1	x,y,z	

TR=Time reversal associated to symmetry operator

☐ Time Reversal for Inversion operator

OK Cancel

**Step 4: Symmetry Information (Detailed)**

Space Group Properties

Symmetry Operators: [Basis functions of the irreducible representations of the propagation vector group]

Spacegroup: **C-1**

Symmetry operators | Magnetic/Displacement Operators | Irreducible representations

Number of Atomic basis functions: 3

Number of Irreducible Representations: 1

Complex basis functions

Num	Coefficient Ci Type
1	Imaginary
2	Real
3	Imaginary

Num	Expression
Real 1	100 010 001
Imag	

**Enter the basis vectors from the output of Baslreps**

**Select the kind of coefficients**

OK Cancel



After clicking on OK buttons save the provisory PCR file. We have now introduced the atoms of this second phase. From the **Refinement** button of EdPCR, select Phase 2, and start to introduce the different items:

Atoms Information: Phase 2

List of Atoms  
Number of Atoms:

Atom #	Label	Ntyp	Mag. Rot.	Prog. Vec.	X	Y	Z	B	Occ
Atom # 1	Fe	MFE3	1	0	0.00000	0.00000	0.00000	0.50564	1.00000

**Enter the atom symbol, magnetic scattering factor, positions, etc.**

Atom #1	Rx	Ry	Rz	lx	ly	lz	MPhase

**Put reasonable values for starting C1, C2, C3**

Basis Functions Coefficients

Atom #	C1	C2	C3	C4	C5	C6	C7
Atom # 1	2.00000	4.00000	3.0	0.00000	0.00000	0.00000	0.00000

Buttons: Refine Positions, Refine B\_iso, Fix All, Cancel, OK

Click on OK buttons and save the new PCR file. The aspect of the second (magnetic) phase of this file after saving it and running FullProf to refine the C-coefficients is the following

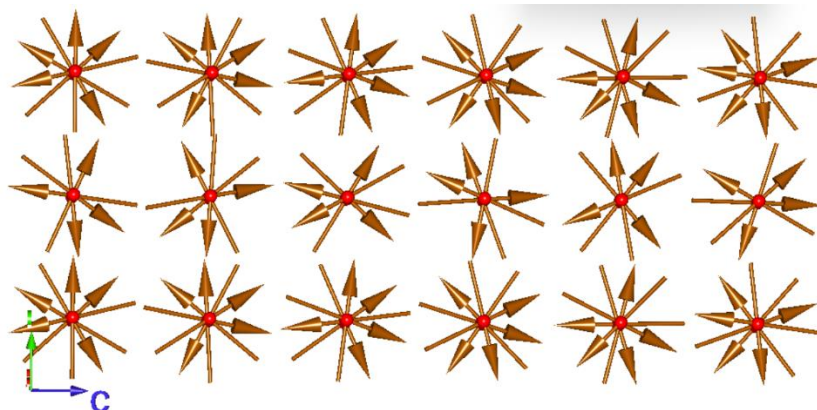
```

Magnetic model (ip,v,ir)
!
!Nat Dis Ang Jbt Isy Str Furth      ATZ      Nvk More
! 1 0 0 1 -2 0 0      55.8470 -1 0
!Contributions (0/1) of this phase to the 1 patterns
!
!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern# 1
! -1 7 1 0 0
! Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
! 0.000 0.000 1.000 1.000 0.000 0.000 0.000
!
!
!C -1      <--Space group symbol for hkl generation
! Nsym cen Laue Ireps N_Bas
! 1 1 1 3
! Real(0)-Imaginary(1) indicator for ci
! 1 0 1
!
!SYMM x,y,z
BASR 1 0 0 0 1 0 0 0 1
!
!Atom Typ Mag Vek X Y Z Biso Occ C1 C2 C3
!C4 C5 C6 C7 C8 C9 MagPh
Fe MFE3 1 0 0.00000 0.00000 0.00000 0.50564 1.00000 2.094 4.082 4.543
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 111.00 121.00 131.00
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
!
!-----> Profile Parameters for Pattern # 1 -----> Phase # 2
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
! 229.8259 0.00000 -0.31999 0.00000 0.00000 0.00000 0
! 21.00000 0.000 101.000 0.000 0.000 0.000
!
! U V W X Y GauSiz Lorziz Size-Model
! 0.000000 0.000000 0.000000 0.000000 0.150115 0.000000 0.000000 0
! 0.00 0.00 0.00 0.00 0.00 91.00 0.00 0.00
!
! a b c alpha beta gamma # Cell Info
! 6.653615 8.255447 4.726791 90.000000 103.984558 90.000000
! 51.00000 61.00000 71.00000 0.00000 81.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
! 1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
!
! Propagation vectors:
! 0.7092559 0.0000000 0.1546032 Propagation Vector 1
! 31.000000 0.000000 41.000000

```

At starting, we have put arbitrary numbers (in Bohr magnetons) of the order of 2 to 4 as the initial values of the C-coefficients. After few cycles, we obtain something like this.





We can use, instead of basis vectors, direct complex Fourier coefficients and refine their components. This corresponds to the following flags in the PCR file: **Jbt=1** and **Isy=-1**. The relevant parts of the PCR for this kind of refinement is shown below.

```

Data for PHASE number: 2 ==> Current R_Bragg for Pattern# 1: 4.6929
LiFeAs207 D1B 2K
!Nat Dis Ang Jbt Isy Str Furth ATZ Nvk More
1 0 0 1 -1 0 0 55.8470 -1 0
!Contributions (0/1) of this phase to the 1 patterns
!Irf Jtyp Nsp_Ref Ph_Shift for Pattern# 1
-1 7 1 0 0
Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
0.000 0.000 1.000 1.000 0.000 0.000 0.000
C -1 <--Space group symbol for hkl generation
!Nsym Cen Laue MagMat
1 1 1 1
SYMM x,y,z
MSYM u,v,w,0.0
!Atom Typ Mag Vek X Y Z Biso Occ Rx Ry Rz # ENVELOP
Fe MPF3 1 0 0.00000 0.00000 0.00000 0.00000 1.00000 0.000 4.122 0.000
0.00 0.00 0.00 0.00 0.00 0.00 0.00
2.090 0.000 4.542 0.000 0.000 0.000 0.000000
211.00 0.00 141.00 0.00 0.00 0.00 0.00
!-----> Profile Parameters for Pattern # 1 -----> Phase # 2
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
230.1580 0.00000 0.21549 0.00000 0.00000 0.00000 0
11.00000 0.000 131.000 0.000 0.000 0.000
! U V W X Y Gausiz Lorsiz Size-Model
0.000000 0.000000 0.000000 0.000000 0.154258 0.000000 0.000000 0
0.00 0.00 0.00 0.00 71.00 0.00 0.00
! a b c alpha beta gamma # Cell Info
6.653628 8.255591 4.726836 90.000000 103.985405 90.000000
101.00000 111.00000 91.00000 0.00000 121.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! Propagation vectors:
0.7089851 0.0000000 0.1547081 Propagation Vector 1
61.000000 0.000000 51.000000

```

**Standard Fourier coefficients of magnetic moments**

**Only satellites are generated**

**No symmetry, just C-centering**

**Expression of Fourier coefficients:**  

$$S_k = 1/2 \{ (R_x, R_y, R_z) + i (I_x, I_y, I_z) \}$$

A complete PCR file, using this approach, with the name **LiFeAs-JBT1.pcr** is provided in the Baslreps directory.

We can see that the  $R_y$  and  $I_z$  parameters are quite close (they correspond to the coefficients C2 and C3 in the basis function description); if we include the constraint  $R_y=I_z$  we obtain a helix with circular envelope.

We can do a refinement making equal the two values and using the same codeword. This reduces the number of free parameters of the magnetic structure to two. This gives rise to a

slightly worse refinement. We can try to test the lowest symmetry option using especial kind of refinement using other options in FullProf.

## Use of special incommensurate models in real space

### Conical uniaxial structures

In FullProf, it is possible to use directly special magnetic models adapted to work in real space using geometrical concepts of angles and real magnetic moments. In particular if we use the value  $Jbt=5$ , the used model correspond to a general conical structure in which we provide the value of the modulus of the magnetic moment, the semi-angle of the cone and the two angles for orienting the axis of the cone with respect to the lattice. The format of the file is similar to the case of using Fourier coefficients

```

LiFeAs2O7 D1B 2K
!
!Nat Dis Ang Jbt Isy Str Furth ATZ Nvk More
1 0 0 5 -1 0 0 0.0000 -1 0
!Contributions (0/1) of this phase to the 1 patterns
1
!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern# 1
-1 7 1 0 0
!Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
0.000 0.000 1.000 1.000 0.000 0.000 0.000
!
!
C -1 <---Space group symbol for hkl generation
!Nsym Cen Laue MagMat
1 1 1 1
!
SYMM x,y,z
MSYM u,v,w,0.0
!
!Atom Typ Mag Vek X Y Z Biso Occ Mom Phic Phase # ENVELOP
! Phi & Theta of Cone-axis unused params
Fe MFE3 1 0 0.00000 0.00000 0.00000 0.00000 1.00000 4.311 90.000 0.000
0.00 0.00 0.00 0.00 0.00 0.00 0.00
202.562 80.015 0.000 0.000 0.000 0.000 0.00000
141.00 131.00 0.00 0.00 0.00 0.00 0.00

```

Here we use a single value for the magnetic moment  $Mom=4.311 \mu_B$ , half the angle of the cone equal to 90 degrees because there is no ferromagnetic component (pure helix). The orientation of the cone axis is referred to a Cartesian system for which:  $x//a$ ;  $z$  is along  $c^*$ ; and  $y$  is within the  $ab$ -plane. The model correspond to a pure helical structure with circular envelope (constant magnetic moment) but with the plane of helix departing slightly from the perpendicular to the  $a$ - $c$  plane of the monoclinic unit cell.

We have provided the file **LiAsFe-JBT5.pcr** in the Baslreps directory to check this refinement. We can see that using three parameters we improve a little bit the refinement using the basis functions or the Fourier coefficients.

### Helical multi-axial structures

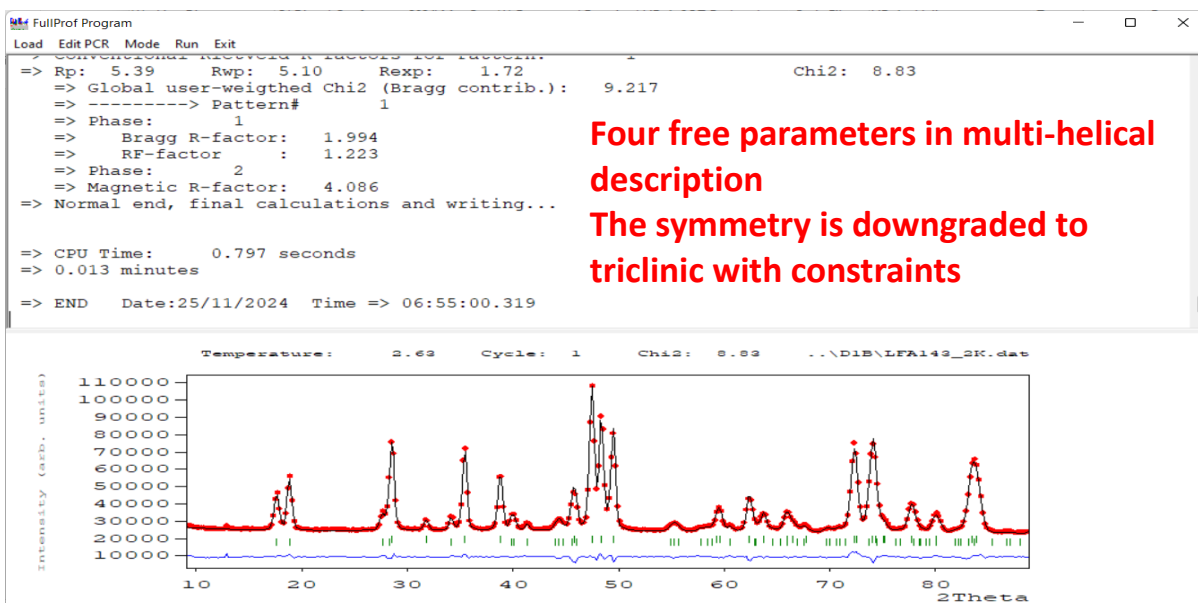
There is still another way of working with special cases in FullProf. This is the case when we want to model multiaxial structures. For accessing this kind of model, one has to use  $More=1$  and add a line in the PCR the keyword **Hel** should be put equal to two. For details about this option, the user can consult the document **fp2k.inf** that is accessible from the toolbar **Help > Manuals > News ...> FullProf**. The user should search for the note of 9 October 2004 where everything is explained in detail.

The relevant part of the PCR file looks like this:

```
LiFeAs2O7 D1B 2K
!
!Nat Dis Ang Jbt Isy Str Furth ATZ NVK More
1 0 0 -1 -1 0 0 55.8470 -1 1
!Jvi Jdi Hel Sp Mom Ter N_Domains
0 0 2 0 0 0 0
!Contributions (0/1) of this phase to the 1 patterns
1
!Irf Npr Jtyp Nsp_Ref Ph_Shift for Pattern# 1
-1 7 1 0 0
! Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
0.000 0.000 1.000 1.000 0.000 0.000 0.000
!
!
C -1 <---Space group symbol for hkl generation
!Nsym Cen Laue MagMat
1 1 1 1
!
SYMM x,y,z
MSYM u,v,w,0.0
!
!Atom Typ Mag Vek X Y Z Biso Occ Mr Mi Chi
! Phi Theta unused beta11 beta22 beta33 MagPh
Fe MFE3 1 0 0.00000 0.00000 0.00000 0.00000 1.00000 4.351 4.351 0.000
16.437 283.296 0.000 0.000 0.000 0.000 0.00000 31.00 31.00 0.00
141.00 131.00 0.00 0.00 0.00 0.00 0.00
```

We obtain the same refinement as with Jbt=5 with three free parameters.

We have provided the file **LiAsFe-Helix.pcr** in the Baslreps directory to check this kind of refinement. We can see that using four parameters we improve a little bit the refinement using the basis functions or the Fourier coefficients.



### Use of ISODISTORT

To perform a full symmetry analysis of the magnetic structure of  $\text{LiFeAs}_2\text{O}_7$ , the best is to use the concept of magnetic superspace group (MSSG). Here we will learn how to use this formalism within FullProf with the help of the web-based program ISODISTORT. At variance with Baslreps, ISODISTORT perform a full analysis of the isotropy subgroups applying the concept of order parameter direction in the representation space that allows a systematic classification of the possible MSSG for high dimensional representations. In the case of an incommensurate structure, because we should use at least the extended little group to combine  $\mathbf{k}$  and  $-\mathbf{k}$ , the dimension of the relevant *irreps* is at least two. The symmetry operators preserved in the high dimensional MSSG are those that are kept invariant. The abstract space in which the matrices



of the representation act is formed by vectors  $\eta$  of the same dimension. An isotropy subgroup  $I_{\eta}^{\nu}(G)$  is formed by the operators that leave invariant a particular order parameter vector for the *irrep*  $\nu$ .

$$I_{\eta}^{\nu}(G) = \{ g \in G \mid \Gamma^{\nu}(g)\eta = \eta \}$$

The systematic study of the isotropy subgroups is not implemented in Baslreps, but you can use the ISOTROPY software suite to do the work.

The order parameter in two dimension may be of the form (a, 0), (a, a) and (a, b). Looking at the output of Baslreps, we see that the single representation of the extended little group for  $\mathbf{k}=(\alpha,0,\gamma)$  in the space group C2 has the following matrices:

$$\{1|000\} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \{2_y|000\} \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We can see that the order parameter (a, 0) is preserved by the two operators, (a, a) is not preserved, and in this particular case is similar to (a, b) that are only preserved by the identity. This means that there exist only two MSSG for this particular case. We can verify this using ISODISTORT.

Go to the ISODISTORT web site and do the following:

## ISODISTORT

Version 6.12.1, Oct 2023

Harold T. Stokes, Branton J. Campbell, and Dorian M. Hatch, Department of Physics and Astronomy, Brigham Young University, Provo, Utah, 84602, USA, branton\_campbell@byu.edu

**Description:** ISODISTORT is a user-friendly internet-based tool for exploring the structural distortion modes of crystalline materials induced by irreducible representations of the parent space-group symmetry. The stand-alone ISOVIZ application further allows one to visualize and interactively manipulate the modes generated in ISODISTORT.

**NOTE:** Interactive visualizations must now be saved to disk and opened with the standalone ISOVIZ application.

[Help, Tutorials, Version History](#)

[Legacy copy of ISODISTORT version 5.6.1, August 2013](#)

Begin by entering the structure of parent phase: ?

[Get started quickly with a cubic perovskite parent.](#)

Import parent structure from a CIF structure file:   No file selected.

If you don't have a parent CIF, create one using [ISOCIF](#).

**Click here to navigate in**

Begin by entering the structure of parent phase: ?

[Get started quickly with a cubic perovskite parent.](#)

Import parent structure from a CIF structure file:   LiFeAs2O7.cif

**ISODISTORT: search**

Space Group: 5 C2 C2-3. Lattice parameters: a= 6.67924, b= 8.28621, c= 4.74327, alpha= 90.00000, beta= 103.94960, 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  
As 4c (x,y,z), x=-0.21780, y= 0.33730, z=-0.40910, Fe 2a (0,y,0), y= 0.00000, O1 4c (x,y,z), x=-0.25060, y= 0.48110, z=-0.17640, O2 4c (x,y,z), x=-0.16880, y= 0.15680, z=-0.25330, O3 4c (x,y,z), x=-0.38990, y= 0.31760, z= 0.27780, O4 2b (0,y,1/2), y= 0.41460, Li 2a (0,y,0), y=-0.36310  
Include dispersive ALL, magnetic Fe distortions

Types of distortions to be considered  ?

strain: ☐

Displacive: all ☐ none ☐ As ☒ Fe ☒ O ☒ Li ☒

Occupational: all ☐ none ☐ As ☐ Fe ☐ O ☐ Li ☐

Magnetic: all ☐ none ☐ As ☐ Fe ☒ O ☐ Li ☐

Rotational: all ☐ none ☐ As ☐ Fe ☐ O ☐ Li ☐

**Put Fe atom as magnetic and remove the strain**

Important: You must click on Change to implement any changes in the above type of distortions to be considered.

## Method 2: General method - search over specific k points

?

**Select the B point of the Brillouin Zone**

Specify k point: B, k1 (a,0,g) a= 0.7094 b= g= 0.1542 # of independent incommensurate modulations= 1

Change number of superposed IRs: 1  ?

**Fill the values of the propagation vector components and put 1 for a single independent incommensurate modulation**

Important: You must click on Change to implement any changes in the number of superposed IRs.

**After clicking on OK we have the following dialog**

## ISODISTORT: irreducible representation

Space Group: 5 C2 C2-3, Lattice parameters: a= 6.67924, b= 8.28621, c= 4.74327, alpha= 90.00000, beta= 103.94960, 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  
 As 4c (x,y,z), x=-0.21780, y= 0.33730, z=-0.40910, Fe 2a (0,y,0), y= 0.00000, O1 4c (x,y,z), x=-0.25060, y= 0.48110, z=-0.17640, O2 4c (x,y,z), x=-0.16880, y= 0.15680, z=-0.25330, O3 4c (x,y,z), x=-0.38990, y= 0.31760, z= 0.27780, O4 2b (0,y,1/2), y= 0.41460, Li 2a (0,y,0), y=-0.38310  
 Include displacive ALL, magnetic Fe distortions  
 k point: B, k1 (a,0,g), a=0.70940, g=0.15420 (1 incommensurate modulation/1 arm)

Choose an IR and OPD (optional):

IR:  OPD:

Select the magnetic *irrep* mB1

After clicking on OK we have the following dialog

## ISODISTORT: order parameter direction

Space Group: 5 C2 C2-3, Lattice parameters: a= 6.67924, b= 8.28621, c= 4.74327, alpha= 90.00000, beta= 103.94960, 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  
 As 4c (x,y,z), x=-0.21780, y= 0.33730, z=-0.40910, Fe 2a (0,y,0), y= 0.00000, O1 4c (x,y,z), x=-0.25060, y= 0.48110, z=-0.17640, O2 4c (x,y,z), x=-0.16880, y= 0.15680, z=-0.25330, O3 4c (x,y,z), x=-0.38990, y= 0.31760, z= 0.27780, O4 2b (0,y,1/2), y= 0.41460, Li 2a (0,y,0), y=-0.38310  
 Include displacive ALL, magnetic Fe distortions  
 k point: B, k1 (a,0,g), a=0.70940, g=0.15420 (1 incommensurate modulation/1 arm)  
 IR: mB1, mk1t1

Finish selecting the distortion mode by choosing an order parameter direction ?

- ☒ P (a,0) 5.1.4.1.m14.2 B2.1'(a,b,0)0s, basis={ (1,0,0,0), (0,0,1,0), (0,-1,0,0), (0,0,0,1) }, origin=(0,0,0,0), s=1, i=1, k-active= (0.70940,0,0.15420)  
☐ C\* (a,b) 1.1.1.1.m2.2 P1.1'(a,b,g)0s, basis={ (0,0,1,0), (1/2,1/2,0,0), (-1/2,1/2,0,0), (0,0,0,1) }, origin=(0,0,0,0), s=1, i=2, k-active= (0.70940,0,0.15420)

\*Though only one order parameter was requested, this isotropy subgroup requires the superposition of two or more order parameters with the same OPD form but different branch-amplitude ratios, and hence different modulation phases. This situation does not arise at commensurate k points.

We see that, as discussed before only two possibilities appears. ISODISTORT uses a standard setting for the MSGs and MSSGs. Usually we are interested in preserving the paramagnetic setting for the unit cell. The notation in this case of the MSSG is: C2.1'(a,0,g)0s instead of B2.1'(a,b,0)0s. After clicking on OK we get the dialog:

## ISODISTORT: distortion

Space Group: 5 C2 C2-3, Lattice parameters: a= 6.67924, b= 8.28621, c= 4.74327, alpha= 90.00000, beta= 103.94960, 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  
 As 4c (x,y,z), x=-0.21780, y= 0.33730, z=-0.40910, Fe 2a (0,y,0), y= 0.00000, O1 4c (x,y,z), x=-0.25060, y= 0.48110, z=-0.17640, O2 4c (x,y,z), x=-0.16880, y= 0.15680, z=-0.25330, O3 4c (x,y,z), x=-0.38990, y= 0.31760, z= 0.27780, O4 2b (0,y,1/2), y= 0.41460, Li 2a (0,y,0), y=-0.38310  
 Include displacive ALL, magnetic Fe distortions  
 k point: B, k1 (a,0,g), a=0.70940, g=0.15420 (1 incommensurate modulation/1 arm)

IR: mB1, mk1t1

☒ P (a,0) 5.1.4.1.m14.2 B2.1'(a,b,0)0s, basis={ (1,0,0,0), (0,0,1,0), (0,-1,0,0), (0,0,0,1) }, origin=(0,0,0,0), s=1, i=1, k-active= (0.70940,0,0.15420)

Lattice parameters of undistorted supercell: a=6.67924, b=4.74327, c=8.28621, alpha=90.00000, beta=90.00000, gamma=103.94960

☐ Save interactive distortion ? ☒ CIF file ? ☐ Distortion file ? ☐ Domains ? ☐ Modes details ☐ Complete modes details ? ☐ IR matrices

We have to select the generation of a CIF file, but we have to fill the following dialog in order to have an mCIF file in the setting of the parent paramagnetic structure.

☒ Use alternate (possibly nonstandard) setting in CIF, Topas, Fullprof, or modes details output (matrix  $S^{-1}$ )

Relative to ☒ parent ☐ subgroup

Basis vectors of subgroup lattice (rational numbers):

$$a'_{s1} = \boxed{1} a_{s1} + \boxed{0} a_{s2} + \boxed{0} a_{s3} + \boxed{0} a_{s4}$$

$$a'_{s2} = \boxed{0} a_{s1} + \boxed{1} a_{s2} + \boxed{0} a_{s3} + \boxed{0} a_{s4}$$

$$a'_{s3} = \boxed{0} a_{s1} + \boxed{0} a_{s2} + \boxed{1} a_{s3} + \boxed{0} a_{s4}$$

$$a'_{s4} = \boxed{1} a_{s4}$$

Origin of subgroup (either rational or decimal numbers):

$$r' = \boxed{0} a_{s1} + \boxed{0} a_{s2} + \boxed{0} a_{s3} + \boxed{0} a_{s4}$$

Check this box for preserving the parent setting  
Change to (0 0 0 0) to preserve the origin

Once this has been done, click on OK the program will indicate you to save the file **subgroup.cif**. You can change the name at the same time of saving the file. It is recommended (mostly when you have many possibilities) to use the name containing the order parameter, the space group symbol and numbers as indicated in a red box in the previous dialog. In our case we will use **P(a,0)5.1.4.1.m14.2\_B2.1'(a,b,0)0s.mcif** (eliminate the spaces or replace them by an underscore, replace symbols not allowed by the operating system, etc.)

The downloaded mCIF file can be transformed to a PCR file using the utility **mCIF\_to\_PCR** accessible from the toolbar. If you want to use an existing PCR and transform it, you should use the utility from the command line. Let us use the previously existing **paraD1B.pcr** to be modified for MSSG use. For that, you should open a terminal in your working directory, where the mCIF file has been downloaded, and write as indicated below

```
C:\WINDOWS\SYSTEM32\cmd.exe
22/11/2024 08:19      5,686 Test.pcr
23/11/2024 13:53      5,096 test_2k.pcr
24/11/2024 15:34      6,825 test_kvector.pcr
       7 File(s)      41,364 bytes
       0 Dir(s)  219,411,279,872 bytes free

C:\Users\rodriguez-carvajal\Desktop\Working>mCIF_to_PCR P(a,0)5.1.4.1.m14.2_B2.1'(a,b,0)0s.mcif paraD1B.pcr 1
```

You just write the name of the utility followed by the full name of the mCIF file, the name of the PCR file to be changed (**paraD1B.pcr**) and the number of the phase that has to be replaced (1). Pressing <Enter> in the keyboard and the program runs showing some information in the screen and at the end you should press another time in <Enter>. Now the PCR **paraD1B\_mod.pcr** has been created and it is ready to make a refinement. The resulting PCR file cannot be edited by EdPCR because MSSGs are not implemented in this GUI, so the user is obliged to edit the file in a text editor. We need to change the generated title and we have to change another time the name of the data file to **LFA143\_2K.dat**, as well as **Ins=3**. Unfortunately, the present version of **mCIF\_to\_PCR** is only adapted for the classical single pattern format of the PCR file, so we have to modify this part of the generated PCR file by hand.

Let us have a look into the generated PCR file after being modified by hand.

```

LiFeAs207.cif => MSSG at T=2.6K: Nuc&Mag. Structure -> P(a,0)5.1.4.1.m14.2_B2.1'(a,b,0)0s.mcif
! Current global Chi2 (Bragg contrib.) = 999991.838
NPATT 1 1 <- Flags for patterns (1:refined, 0: excluded)
W PAT 1.000
!Nph Dum Ias Nre Cry Opt Aut
1 0 0 0 0 0 0 1
!Job Npr Nba Nex Nsc Nor Iwg Ilo Res Ste Uni Cor Anm Int
1 7 -5 2 0 1 0 0 1 0 0 0 0 0 0 !-> Patt#: 1
!
!File names of data(patterns) files
C:\Disk-D\Docs\Conferences2024\MagCrystW-Dongguan\Exercises\LiFeAs207\D1B\scaled_ParaD1B.xys
!
! Resolution file for Pattern# 1
C:\Disk-D\Docs\Conferences2024\MagCrystW-Dongguan\Exercises\LiFeAs207\D1B\D1B.irf
!Mat Pcr NLI Rpa Sym Sho
0 1 0 -1 0 0
!Ipr Ppl Ioc Ls1 Ls2 Ls3 Prf Ins HKL Fou Ana
0 0 1 0 4 0 3 0 0 0 0 !-> Patt#: 1
!
! Lambda1 Lambda2 Ratio Bkpos Wdt Cthm muR AsyLim Rpolarz 2nd-muR -> Patt# 1
2.520000 2.520000 0.00000 40.000 15.000 0.0000 0.2000 180.00 0.0000 0.0000
.
.....

!-----
! Data for PHASE number: 1 ==> Current R_Bragg for Pattern# 1: 2.4766 Magnetic R-Factor: 4.3664
!-----
Nuclear and Magnetic Structure of: P(a,0)5.1.4.1.m14.2_B2.1'(a,b,0)0s VARY mymymz McosMsin
!
!Nat Dis Ang Jbt Isy Str Furth ATZ Nvk More
7 0 0 7 2 0 0 81.1568 1 0
!Contributions (0/1) of this phase to the 1 patterns
1
!Irf Npr Jtyp Nsp Ref Ph Shift for Pattern# 1
0 7 1 0 0
! Pr1 Pr2 Pr3 Brind. Rmua Rmub Rmuc for Pattern# 1
0.000 0.000 1.000 1.000 0.000 0.000 0.000
!
B2.1'(a,b,0)0s 5.1.4.1.m14.2 <--Magnetic Super Space group symbol (name & number)
Transform to standard: a1,a3,-a2,a4;0,0,0
Parent Space Group: IT number: 0
Transform from Parent:
! Generators
Genr x,y,z,t,1
Genr -x,y,-z,-t,1
Genr x,y,z,t+1/2,-1
Genr -x,y,-z,-t+1/2,-1
Genr x+1/2,y+1/2,z,t,1
Genr -x+1/2,y+1/2,-z,-t,1
Genr x+1/2,y+1/2,z,t+1/2,-1
Genr -x+1/2,y+1/2,-z,-t+1/2,-1
N qc 1
Q coeff
1

```

Change the title  
Change the value of Chi2

Change the name of the file to  
LFA143\_2K.dat

Change the type of format

MSSG option

Instead of the full list of operators one can select a series of generators

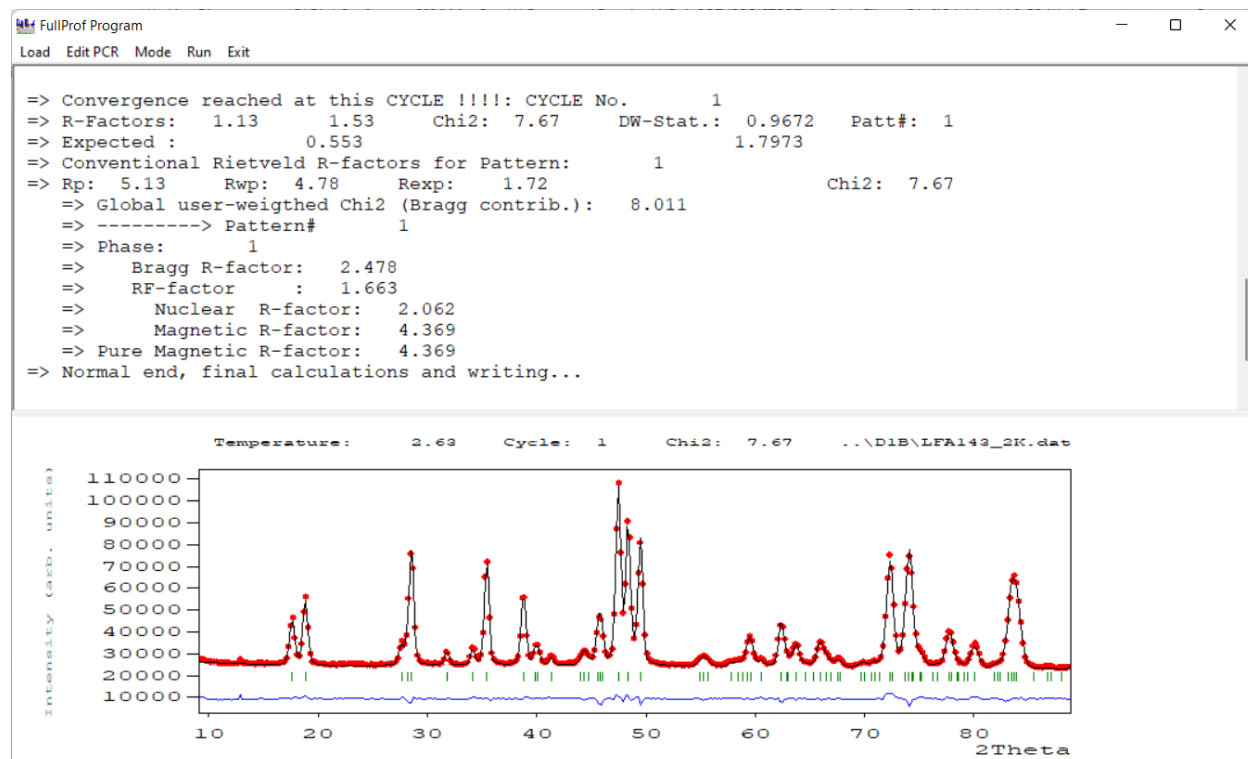
Q-coefficients, control the harmonics

```

! Atom Typ Max_Qcoeff X Y Z Bis0 Msinx Msinz Occ N_type Spc / Line below:Codes
! Mcosx Mcosy Mcosz Msinx Msinz Msinz / Line below:Codes
! beta11 beta22 beta33 beta12 beta13 beta23 / Line below:Codes
As_1 As 0 0.28220 0.83730 0.59090 0.00000 0.50000 0 0 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
Fe_1 MFE2 1 0.00000 0.00000 0.00000 0.00000 0.25000 1 0 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
MagM0-Moment: 0.00000 0.00000 0.00000 <- Homogeneous magnetic moment
0.00000 0.00000 0.00000
Mcos-Msin-1: 0.00000 4.27396 0.00000 2.25919 0.00000 4.58660 <-Amplitudes Modulated moments
0.00000 181.00000 0.00000 121.00000 0.00000 111.00000
O1_1 O 0 0.24940 -0.01890 0.82360 0.00000 0.50000 0 0 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
O2_1 O 0 0.33120 0.65680 0.74670 0.00000 0.50000 0 0 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
O3_1 O 0 0.11010 0.81760 0.27780 0.00000 0.50000 0 0 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
O4_1 O 0 0.00000 0.41460 0.50000 0.00000 0.25000 0 0 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
Li_1 Li 0 0.00000 0.61690 0.00000 0.00000 0.25000 0 0 #
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
!-----> Profile Parameters for Pattern # 1 -----> Phase # 1
! Scale Shape1 Boy Str1 Str2 Str3 Strain-Model
226.5582 0.00000 0.09666 0.00000 0.00000 0.00000 0
11.00000 0.000 51.000 0.000 0.000 0.000
! U V W X Y GauSiz LorSiz Size-Model
0.000000 0.000000 0.000000 0.000000 0.153160 0.000000 0.000000 0
0.00 0.00 0.00 0.00 211.00 0.00 0.00
! a b c alpha beta gamma # Cell Info
6.653615 8.255688 4.726988 90.000000 103.986748 90.000000 # MULTCELL 14 1 18
61.00000 41.00000 31.00000 0.00000 21.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! Propagation vectors:
0.7091331 0.0000000 0.1546126 1 1.0000 <-- Propagation Vector, nharm, sintl lim 1
201.000000 0.000000 191.000000

```

When running FullProf with this file you obtain something like this:



We can see that the refinement is similar to those we have performed using other methods. The program generates a series of files, and in particular, mCIF files that can be submitted to the MAGNDATA system at the Bilbao Crystallographic Server (BCS). Normally there is a mCIF file containing all the symmetry information needed to describe the magnetic structure. The name of this file is

composed by the code of the PCR file followed by “\_ssgn.mcif”, where “n” is a number equal to the number of the phase treated with an MSSG. This file can be submitted to MVISUALIZE at the BCS for a rapid visualization of the magnetic structure.

The other mCIF file is formed by the code of the PCR file followed “n.mcif”. This is a P1 description of the magnetic structure. This file can be submitted to VESTA for visualization; however, one has to be careful with atoms outside, or in de boundaries of the provided supercell in the instruction “MULTCELL na nb nc” in the PCR file. Those atoms are wrong ...

The picture of the magnetic structure can be displayed using a supercell in VESTA.