

Example: $\text{Cs}_2\text{FeCl}_5\cdot\text{D}_2\text{O}$

Refinement of Nuclear and Magnetic Structures on Single Crystal using FullProf

$\text{Cs}_2\text{FeCl}_5\cdot\text{D}_2\text{O}$

Single crystal data collected at D9 diffractometer (ILL) with $\lambda=0.841 \text{ \AA}$

Additional powder data collected at D1B diffractometer (ILL) with $\lambda=2.52 \text{ \AA}$ to determine the magnetic propagation vector.

The space group at low temperature is $I2/c$ (a non-standard setting of $C2/c$, used for practical reasons). The cell parameters at 20K (paramagnetic phase, $T_N \approx 6.5\text{K}$) are $a \approx 17.05 \text{ \AA}$, $b \approx 7.352 \text{ \AA}$, $c \approx 16.136 \text{ \AA}$, $\beta \approx 89.95^\circ$.

The structural parameters are provided in the CIF file obtained from X-ray diffraction structural determination.

A detailed explanation of this example can be consulted on DOI: 10.1103/PhysRevB.96.104428

This tutorial is divided in two parts:

A) **Nuclear structure.** From a partially known structure (determined by X-rays) + single crystal neutron diffraction data:

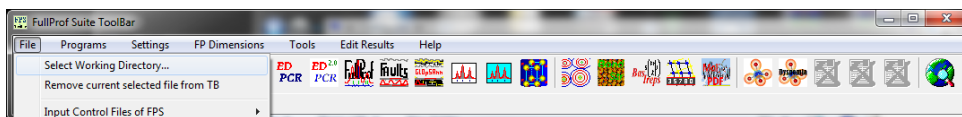
- Create a PCR file with the structural information using Edit PCR
- Refine the positions of the light atoms which were not localized by X-ray diffraction

B) **Magnetic structure.** (Powder + single crystal neutron diffraction data)

- Use k-search and powder diffraction data to determine the magnetic propagation vector
- Use BasIreps to determine the possible magnetic models (magnetic structures)
- 3) Use single crystal data to refine the different magnetic models.
 - Plot the results

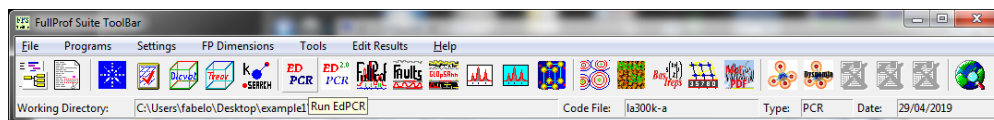
A) **Nuclear structure**

- 1) **Create a working directory** (don't use space or special characters in the path).
 - a. Copy in this folder all the input files.
- 2) **Create an initial PCR file.**
 - a. Open the FullProf toolbar (clicking on the desktop icon)
 - b. Select the working directory. "file > Select working directory..."

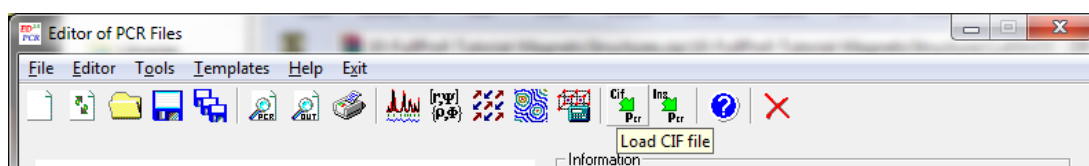


c. Locate the working directory and click on OK.

d. Click on the EdPCR icon, in the FP toolbar.

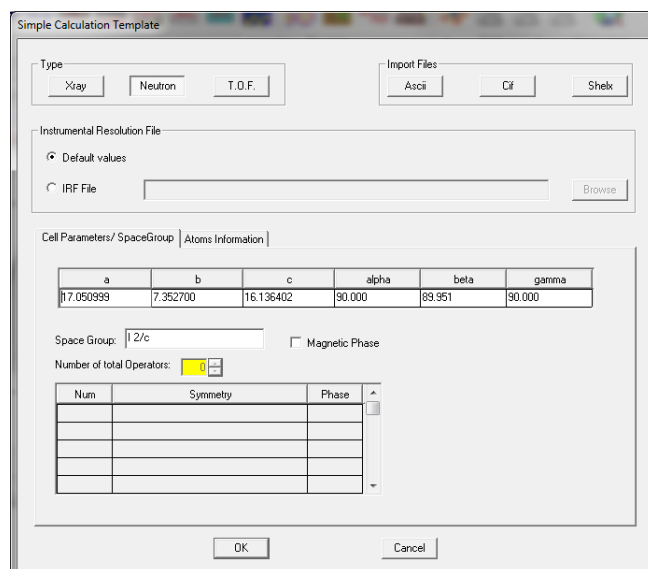


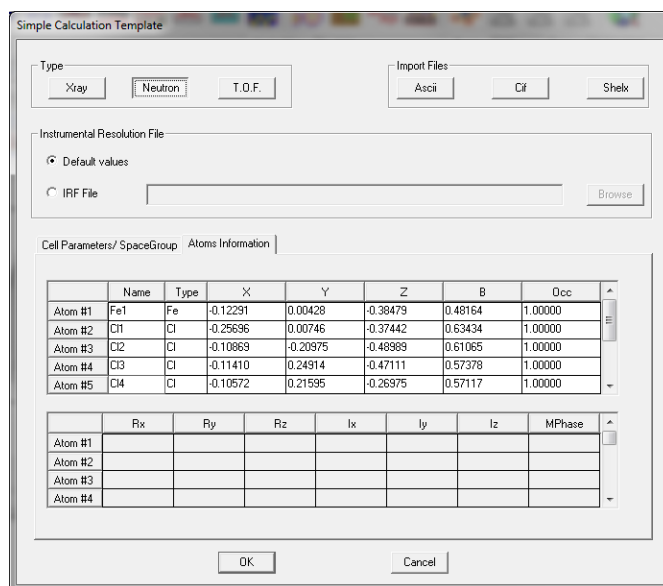
e. Click on the cif_to_pcr icon in the EdPCR.



f. Select the .cif file (RX.cif)

g. Select Neutron as source type, check that the unit cell and the space group correspond with the provided at the beginning of this file. Check in the “atoms information” windows that all is consistent with the provided CIF file. Check that the occupation is correctly imported from the CIF file. Click on OK to exit.



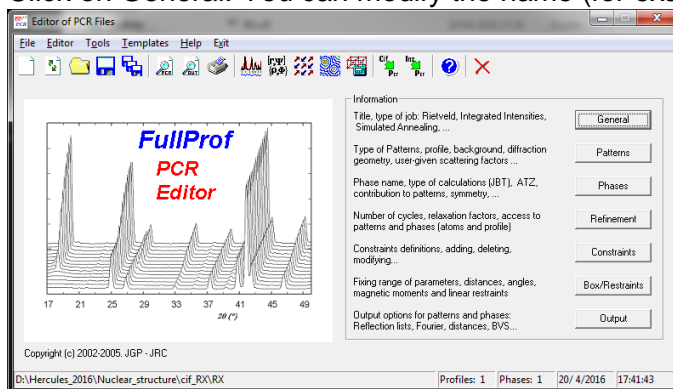


- h. Save the PCR file ("Save as"). Rename the file with an intuitive name (in our case it could be "nuclear.pcr").

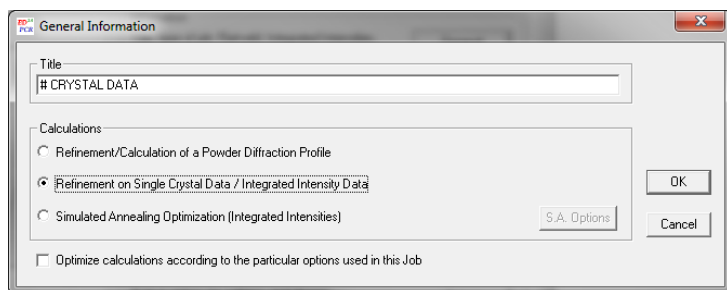
With these simple steps, you have already created an initial PCR file. The current PCR file corresponds by default to a powder pattern calculation with a wavelength of 1.54 Å and generic instrument resolution parameters. In the next step we are going to modify all these parameters using the program EdPCR. Advanced users can modify these parameters directly editing the PCR file in plain text. A powerful text editor is highly recommended, we are going to use Notepad ++ which is freely distributed (<https://notepad-plus-plus.org/download/v7.6.6.html>).

3) Modify the PCR file according to the current example.

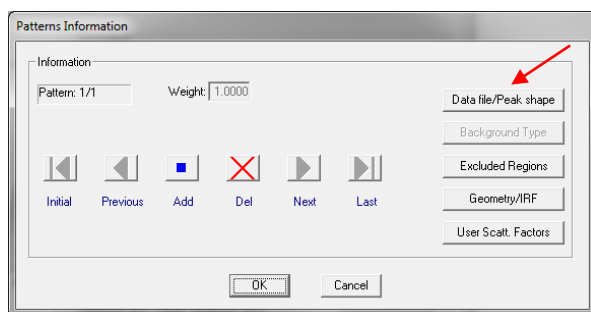
- a. Click on General. You can modify the name (for example "Cs2FeCl5-nuclear").



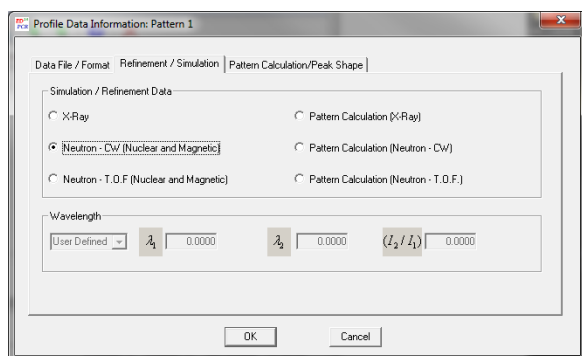
- b. In "Calculations", select "Refinement on Single Crystal Data / Integrated Intensity Data" and click on OK.



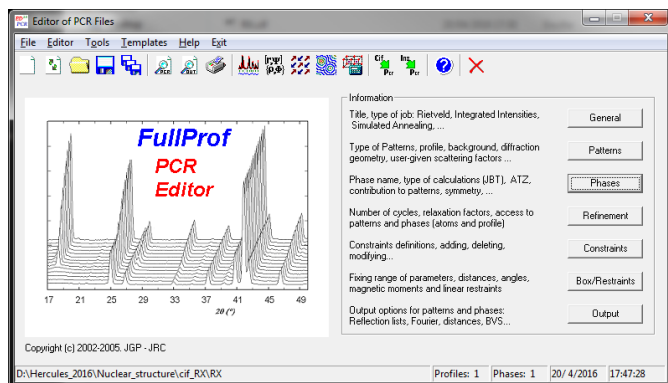
c. Click on “Patterns” > Data file/Peak shape



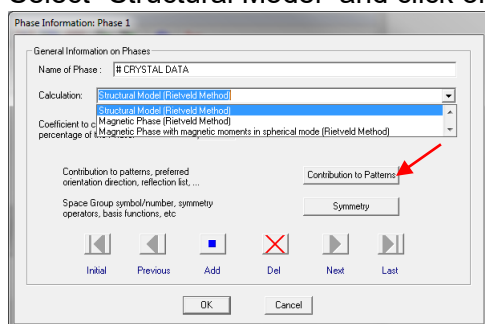
d. In the “Refinement/Simulation” tab, select “Neutron Constant Wavelength (Nuclear and Magnetic)” and click “ok”



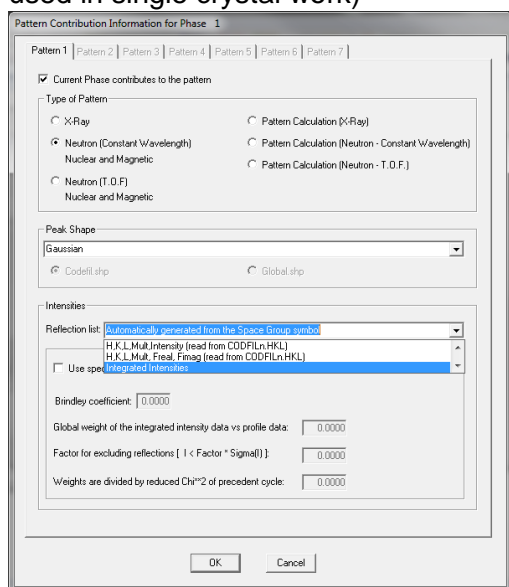
e. Click on “Phases”



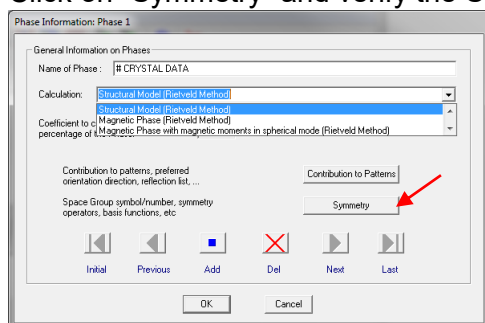
- f. Select “Structural Model” and click on “Contribution to Patterns”

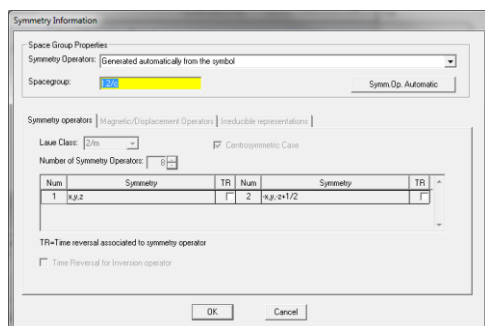


- g. Select again “Neutron Constant Wavelength (Nuclear and Magnetic)”. Under “Intensities”, select “Integrated intensities” and click “ok” (N.B. The peak shape is not used in single crystal work)

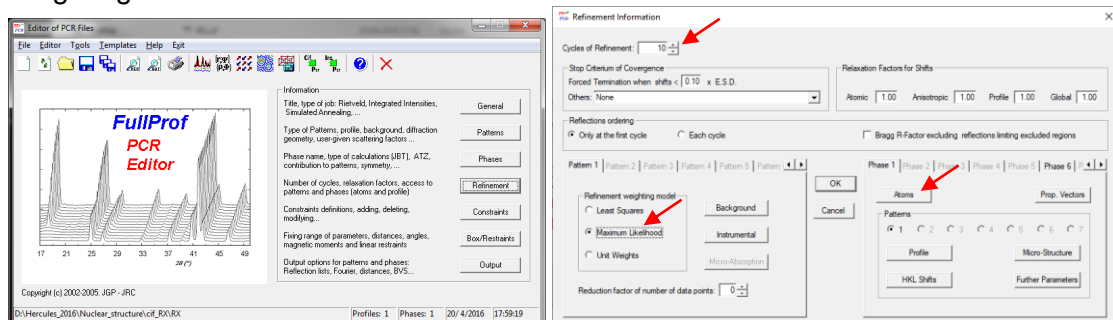


- h. Click on “Symmetry” and verify the Space Group

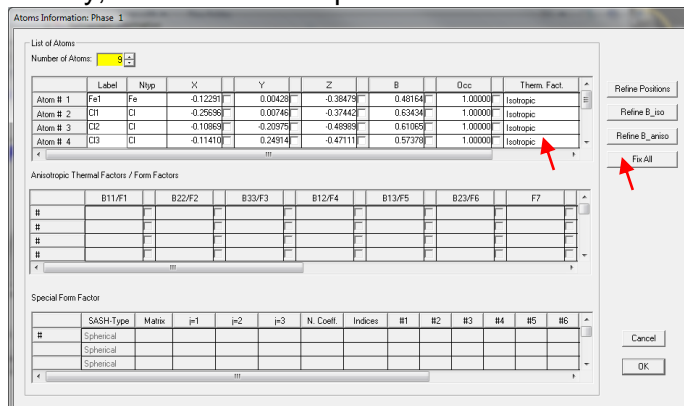




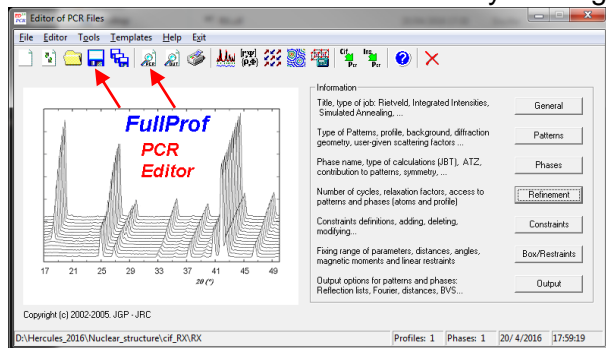
- i. Click on “Refinement”, set the cycles of refinement to ~10 and the Refinement weighting model to the second one. Then click on “Atoms”



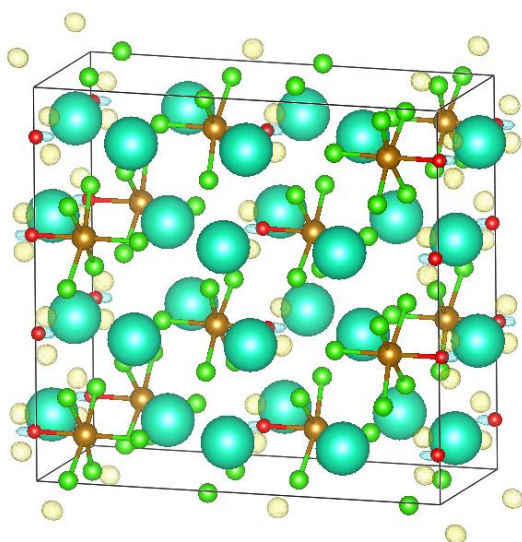
- j. Initially, we will let all the parameters fixed and the thermal parameters isotropic.



- k. Click “ok” twice to go back to the main window and save the modified PCR file. You can visualize the PCR file in text format by clicking in the corresponding icon.



- b. Open Vesta and plot the structure and the difference Fourier map



View of the initial crystal structure model together with the difference Fourier Map (positive density in yellow and negative density in blue)

The bond can be edited in Vesta in the Edit menu > Bond

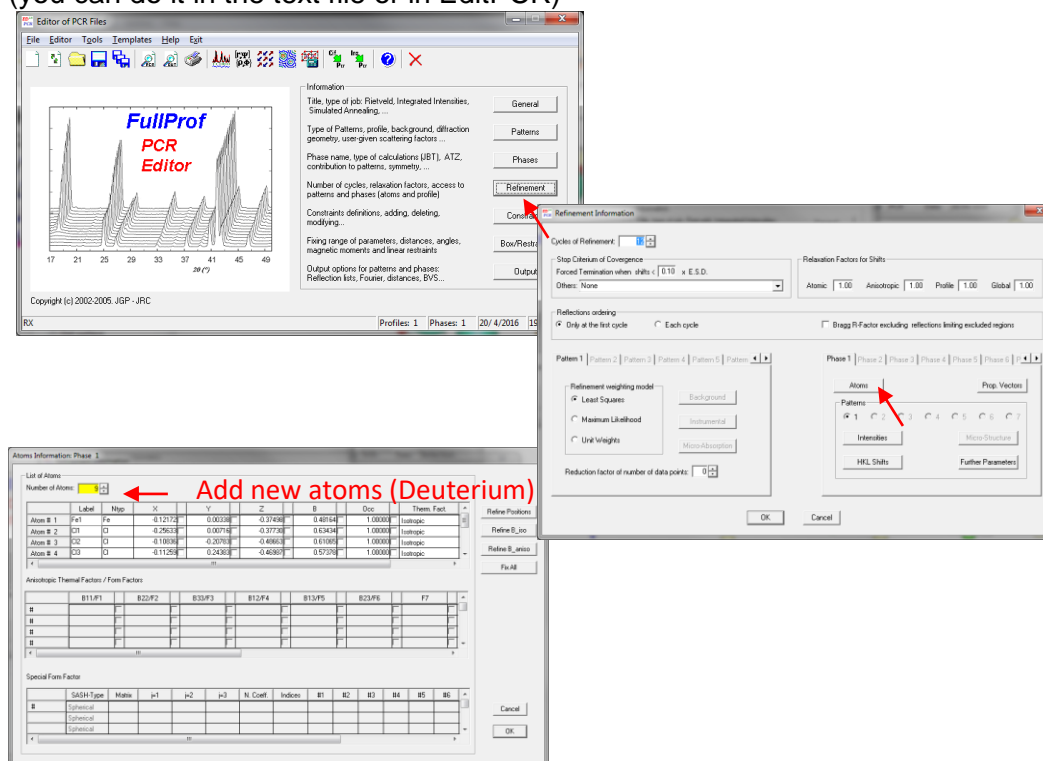
The limits in the density map can be modified in Vesta in Properties > Isosurfaces > Levels

- c. Open the file filename.pks. This file contains the x,y,z coordinates and density obtained from the Fourier map

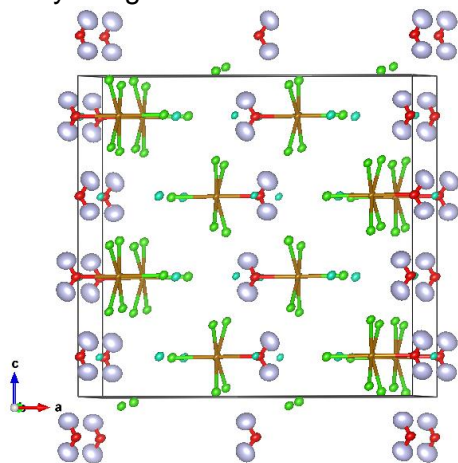
Number of Peaks = 9

Peak	x/a	y/b	z/c	Occ	Density
Pk_1	0.0319	0.0412	0.5774	1.0000	1.0963
Pk_2	0.0335	0.0445	0.6725	1.0000	1.0189
Pk_3	0.0291	0.0025	0.6229	1.0000	-0.4879
Pk_4	0.2471	0.0280	0.1373	1.0000	-0.2784
Pk_5	0.1061	0.2229	0.0220	1.0000	-0.2451
Pk_6	0.1132	0.2177	0.2395	1.0000	-0.2217
Pk_7	0.1221	0.4962	0.8764	1.0000	-0.2263
Pk_8	0.0113	0.0286	0.8297	1.0000	-0.2225
Pk_9	0.1295	0.2526	0.4651	1.0000	-0.1975

- d. Based on the densities from the .pks file, include the missing atoms in the initial model (you can do it in the text file or in EditPCR)



- e. By plotting the structure, verify that the new atoms are in the good positions. Now the fit should be close to the experimental data.
- f. Refine the scale factor
- g. Refine the x y z coordinates of the different atoms
- h. Refine the isotropic thermal parameters of the different atoms
- i. Refine the extinction parameter (this is very a sensitive parameter, if problems you can fix all the other parameters before refining this one)
- j. Transform the isotropic displacement into anisotropic starting from heavy atoms and then following with the light ones
- k. Verify the goodness of fit and check the crystal structure plotting it in Vesta



The final model should be similar to this. The thermal parameters are represented at 99 % of probability.

The sample was measured at 20K, which explains the small size of the ellipsoids.

B) Magnetic structure

Determination of the magnetic propagation vector:

Single crystal:

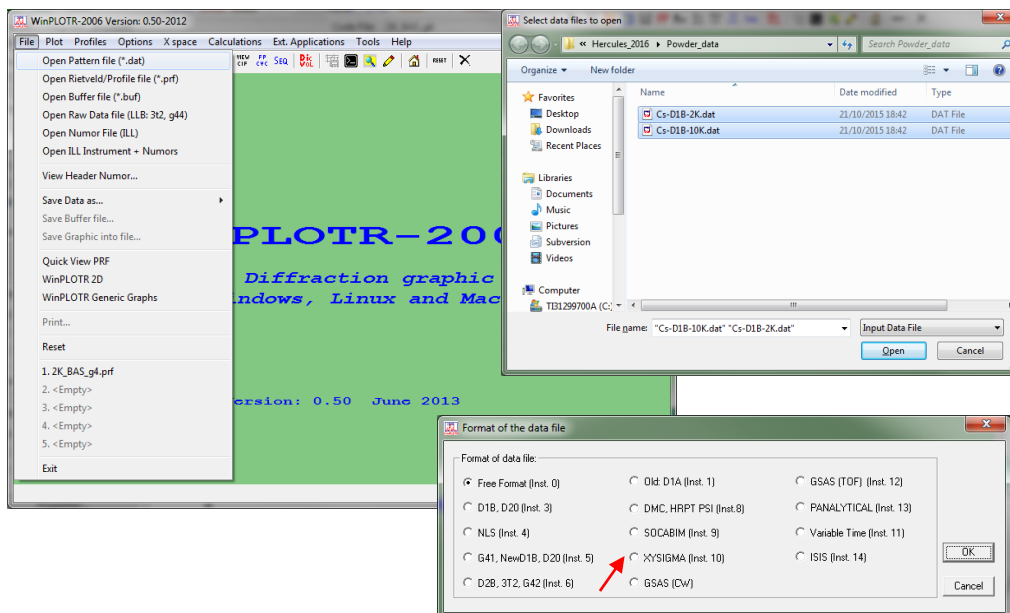
- Explore the reciprocal space in order to find new reflections (magnetic reflections)
- Index the new reflections to obtain a compatible propagation vector
- Measure a full set of magnetic reflections

Powder:

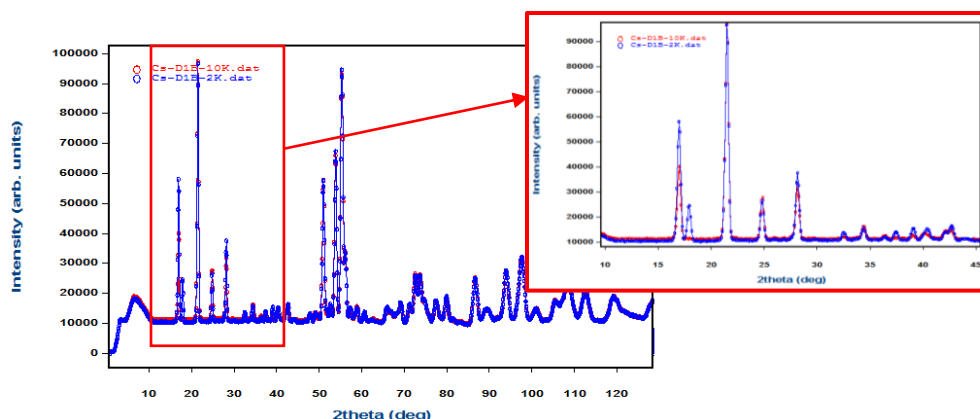
- Compare patterns in paramagnetic phase and ordered phase
- Select the positions of the magnetic reflections
- Index the possible propagation vector using K_search program (included in FP)

Exercise:

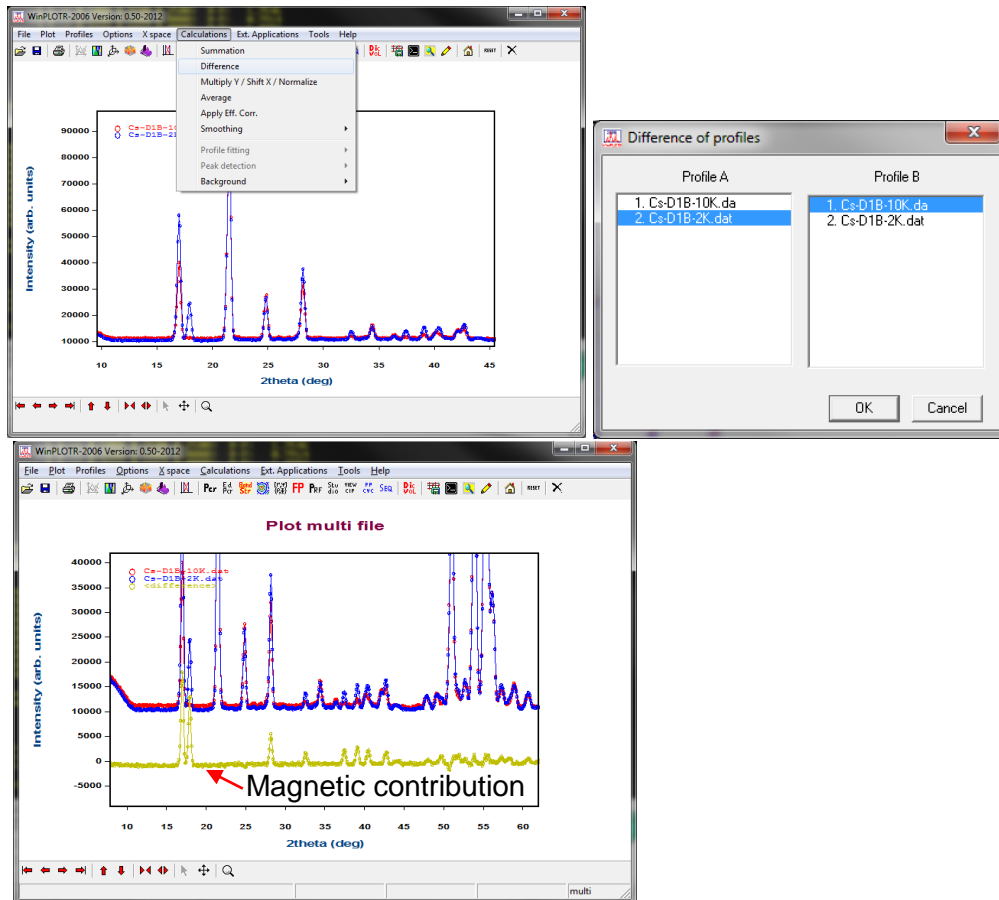
- 1) Use K_search and powder diffraction data to determine the magnetic propagation vector
 - a. Open the powder patterns in WinPLOTR-2006 (both the paramagnetic and ordered phases). The format is XYSigma.



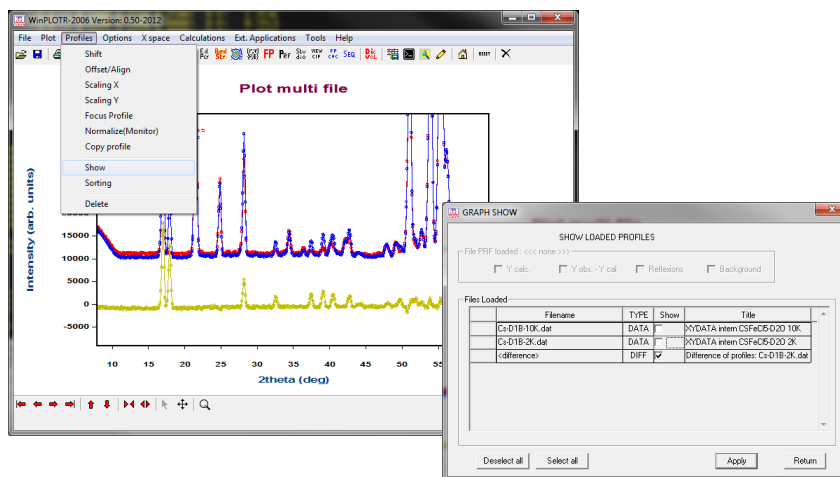
- b. Compare both patterns. The magnetic reflections are expected at low Q.

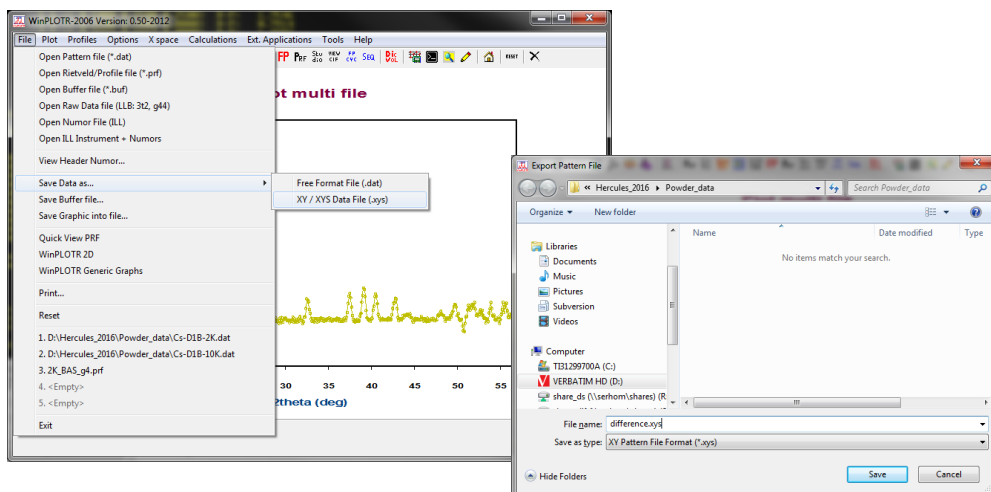


c. The difference between both patterns will show the magnetic contribution (Calculations > Difference)

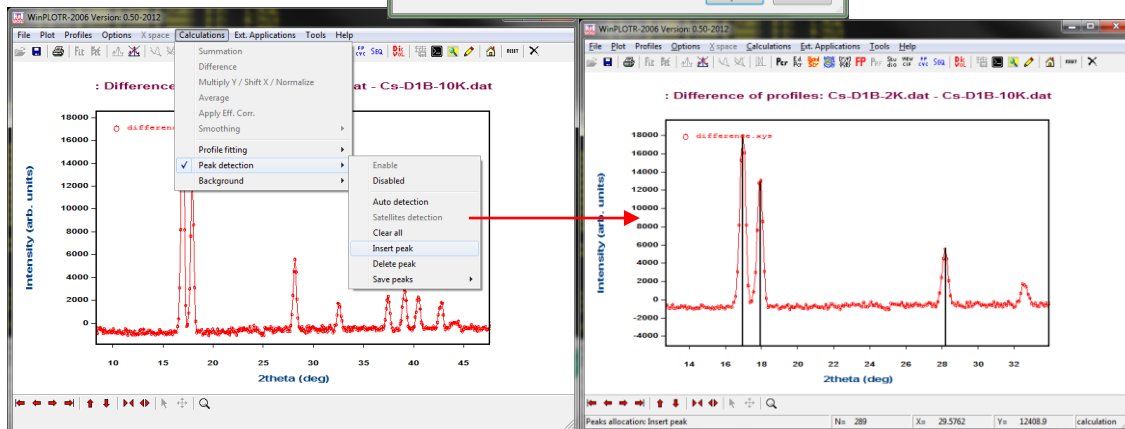
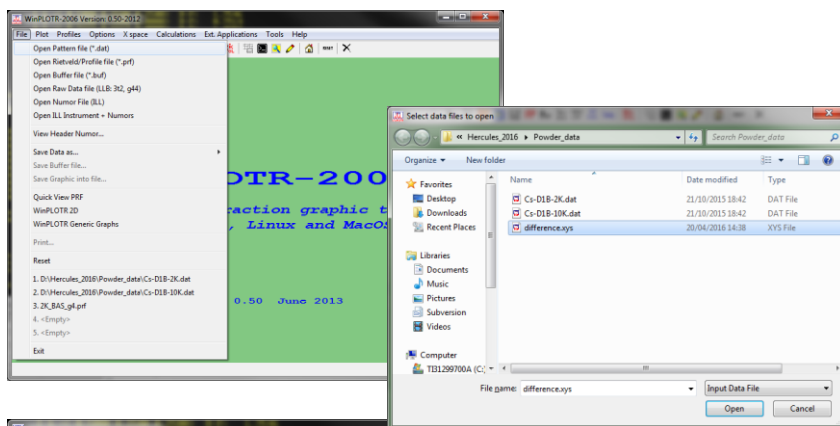


d. Show only the difference pattern and save it (in .xys format).

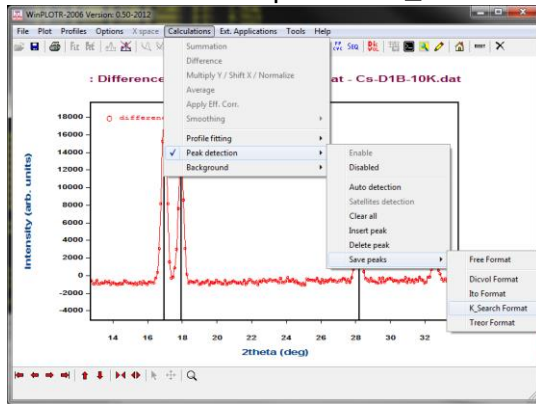




e. Open again the difference pattern and select the magnetic peaks: Calculation > Peak detection/Enable, and then again Calculation > Insert peak

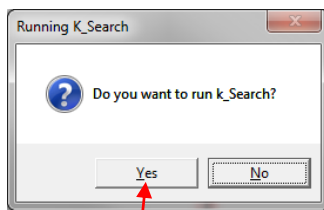


f. Save the selected peaks in k_search format



g. Fill the boxes with the crystallographic information: Data collected at D1B diffractometer (ILL) with $\lambda=2.52$ Å; monoclinic space group $I2/c$ ($I\ 1\ 2/c\ 1$); cell parameters $a=17.05$ Å, $b=7.352$ Å, $c=16.136$ Å, $\beta=89.95^\circ$.

h. Run k_search



The most probable propagation vector is $k = (0,0,0)$

(The complete output can be revised in the k-search.kup file)

```
C:\windows\system32\cmd.exe

=> Testing 90 internal k-vectors
Solution: 1 k = (0.0000 0.0000 0.0000) R-F: 0.7219
Solution: 2 k = (0.5000 0.2500 0.2500) R-F: 1.9505
Solution: 3 k = (0.2500 0.2500 0.5000) R-F: 2.5186
Solution: 4 k = (0.0000 0.2500 0.5000) R-F: 4.0177
Solution: 5 k = (0.2500 0.5000 0.0000) R-F: 1.2080
Solution: 6 k = (0.3333 0.6667 0.0000) R-F: 1.6825
Solution: 7 k = (0.6667 0.3333 0.0000) R-F: 1.6825
Solution: 8 k = (0.0000 0.2500 0.1250) R-F: 1.4520
Solution: 9 k = (0.1250 0.2500 0.1250) R-F: 1.3641
Solution: 10 k = (0.1250 0.1250 0.5000) R-F: 2.1988
Solution: 11 k = (0.3333 0.5000 0.5000) R-F: 1.7270

=> Special k-vector solutions found!

=> List of the best 10 solutions for 4 satellites

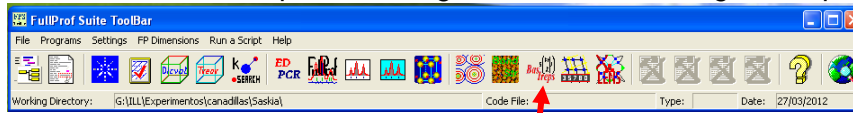
Ks      K0      K2      R-factor
0.000000 0.000000 0.000000 0.721939
0.250000 0.500000 0.000000 1.288044
0.125000 0.250000 0.125000 1.364122
0.000000 0.250000 0.125000 1.452034
0.333330 0.666670 0.000000 1.682457
0.666670 0.333330 0.000000 1.682401
0.333330 0.500000 0.500000 1.727259
0.500000 0.250000 0.250000 1.958502
0.125000 0.125000 0.500000 2.198813
0.250000 0.250000 0.500000 2.518606

=> A probable solution is the special k-vector ks = (0.0000 0.0000 0.0000)
=> The corresponding R-factor is: 0.7219

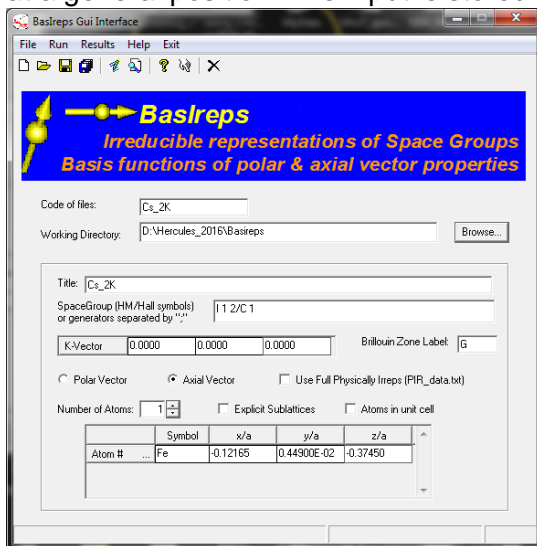
Total CPU-Time
CPU-seconds: 0.83
CPU-minutes: 0.00
CPU-hours : 0.00

=> Press <enter> to finish
```

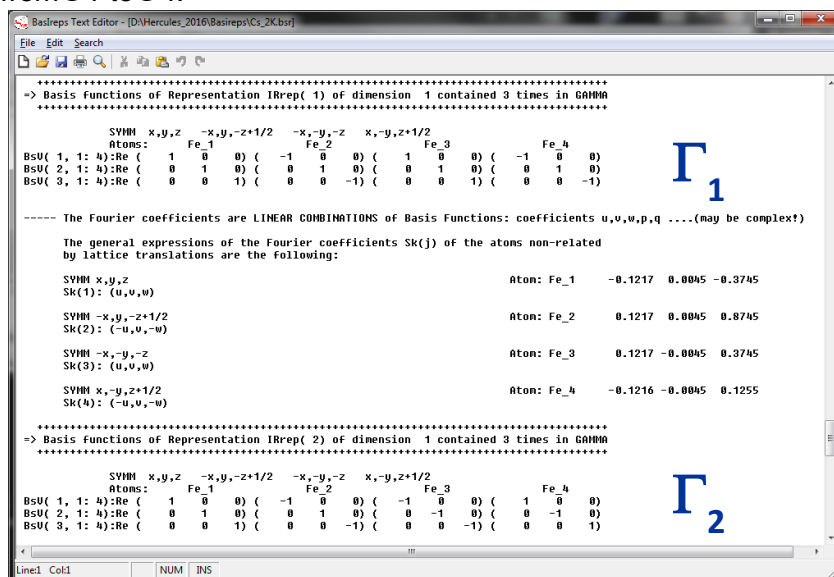
2) Determination of the possible magnetic structures using Baslreps



- a. For the Irreps calculation we are going to use Baslreps program. Click on the Baslreps icon on the FP tool bar. Fill the information required: code of file, the working directory, the nuclear space group and the propagation vector (in this case $\mathbf{k}=0$). Remember that magnetic moments are axial vectors. The number of magnetic atoms within the unit cell can be provided explicitly or the program can calculate the different orbits using the space group symmetry. In this case the space group is $I12/c1$ and the magnetic atoms is Fe atom at a general position. The input is stored in the .smb file.



- b. The list of the irreducible representations (all of them of dimension 1) can be consulted on the extended output of Baslreps (*.bsr). There are 4 possible magnetic representations, from Γ_1 to Γ_4 .



- c. Baslreps gives also an output (*.fp) with a block for each IR, ready to be copied and pasted into the PCR file. The different models should be tested against the experimental data

```
-----
Output of BasIREPS for FullProf
-----
The group of lines starting with the symbol of space groups and
finishing with the last keyword BASI, may be pasted into the PCR file

      X      Y      Z      for site: 1
-> Fe_1   :  -0.1217  0.0045 -0.3745  : (x,y,z)
-> Fe_2   :   0.1217  0.0045  0.8745  : (-x,y,-z+1/2)
-> Fe_3   :   0.1217 -0.0045  0.3745  : (-x,-y,-z)
-> Fe_4   :  -0.1216 -0.0045  0.1255  : (x,-y,z+1/2)

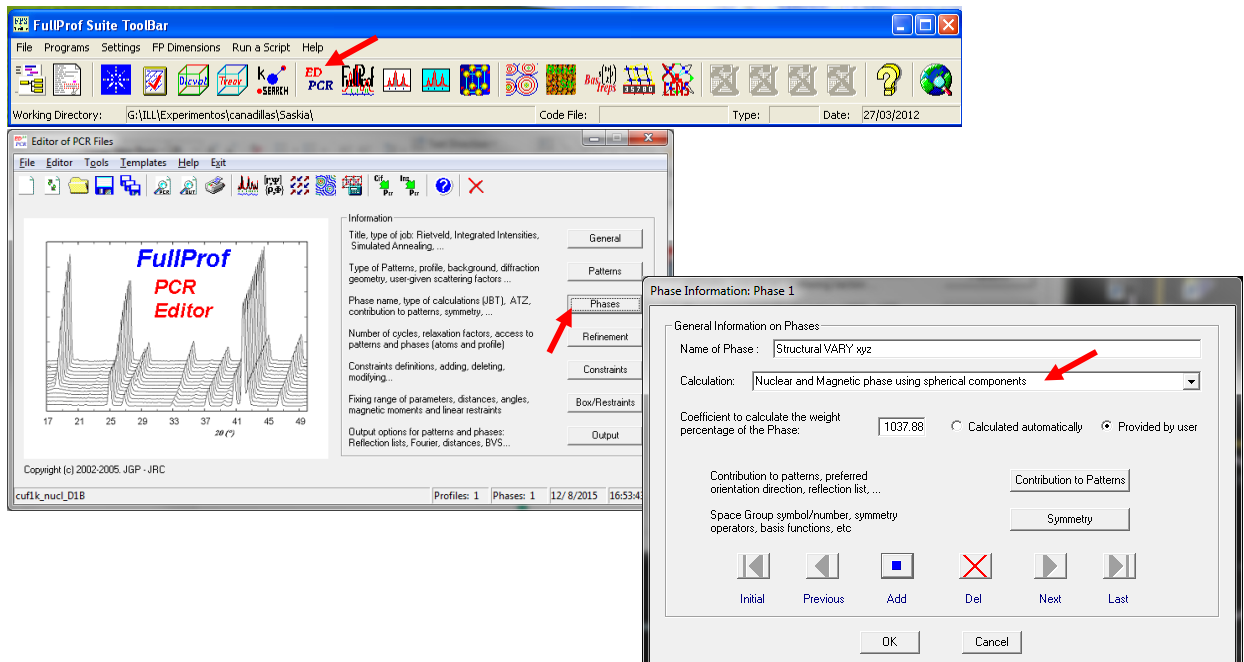
=> Basis functions of Representation IRrep( 1) of dimension 1 contained 3 times in GAMMA
Representation number : 1 for Site: 1
Number of basis functions: 3

----- Block-of-lines for PCR start just below this line
I -1                                     <--Space group symbol for hkl generation
! Nsym   Cen   Laue Ireps N_Bas
   4       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,-z+1/2
BASR -1  0  0  0  1  0  0  0 -1
BASI  0  0  0  0  0  0  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,z+1/2
BASR -1  0  0  0  1  0  0  0 -1
BASI  0  0  0  0  0  0  0  0  0
----- End-of-block of lines for PCR

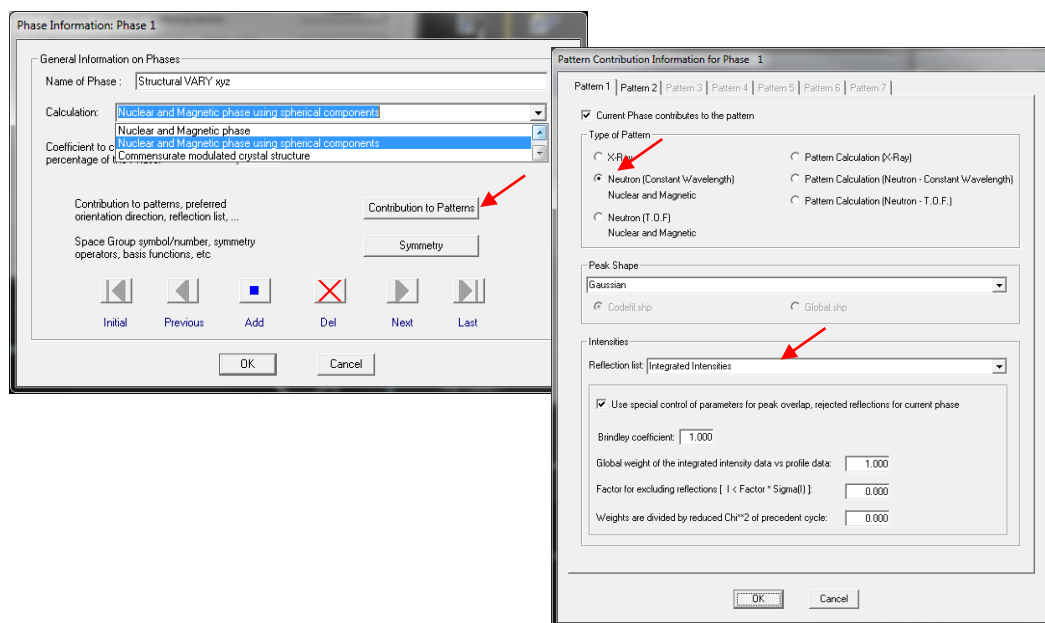
=> Basis functions of Representation IRrep( 2) of dimension 1 contained 3 times in GAMMA
Representation number : 1 for Site: 1
-----
```

3) Use of single crystal data to determine the magnetic structure

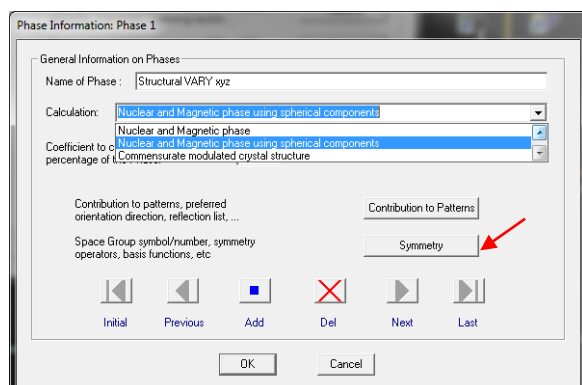
- a. Modify the previous nuclear PCR file into a nuclear+ magnetic one (Jbt=10): Open EdPCR, and under “Phases”, select “Nuclear and magnetic phase using spherical components” for the type of calculation



b. In “Contribution to Patterns” select again “Neutron Constant Wavelength (Nuclear and Magnetic)”. Under “Intensities”, select “Integrated intensities” and click “ok” (The peak shape is not used in single crystal work)



c. Back in the “Phase information” window, go to “Symmetry”.



d. We will use the information obtained from Basireps (here below) to fill the different fields in the “Symmetry Information” window

```

SYMM -x,y,-z+1/2                      Atom: Fe_2    0.1
Sk(2): (u,-v,w)

SYMM -x,-y,-z                          Atom: Fe_3    0.1
Sk(3): (u,v,w)

SYMM x,-y,z+1/2                        Atom: Fe_4   -0.1
Sk(4): (u,-v,w)

+++++
=> Basis functions of Representation IRrep( 4) of dimension 1 contained 3 times in GAMMA
+++++

      SYMM  x,y,z    -x,y,-z+1/2    -x,-y,-z    x,-y,z+1/2
Atoms:  Fe_1      Fe_2      Fe_3      Fe_4
BsV( 1, 1: 4):Re ( 1  0  0) ( 1  0  0) ( -1  0  0) ( -1  0  0)
BsV( 2, 1: 4):Re ( 0  1  0) ( 0 -1  0) (  0 -1  0) (  0  1  0)
BsV( 3, 1: 4):Re ( 0  0  1) ( 0  0  1) (  0  0 -1) (  0  0 -1)

----- The Fourier coefficients are LINEAR COMBINATIONS of Basis Functions: coefficients u,v,w

The general expressions of the Fourier coefficients Sk(j) of the atoms non-related
by lattice translations are the following:

SYMM x,y,z                      Atom: Fe_1   -0.1
Sk(1): (u,v,w)

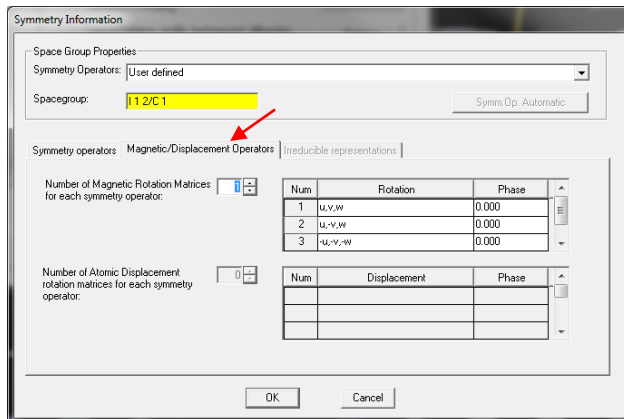
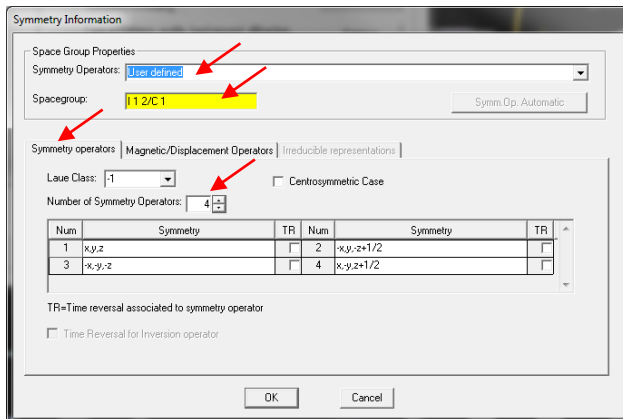
SYMM -x,y,-z+1/2                Atom: Fe_2    0.1
Sk(2): (u,-v,w)

SYMM -x,-y,-z                   Atom: Fe_3    0.1
Sk(3): (-u,-v,-w)

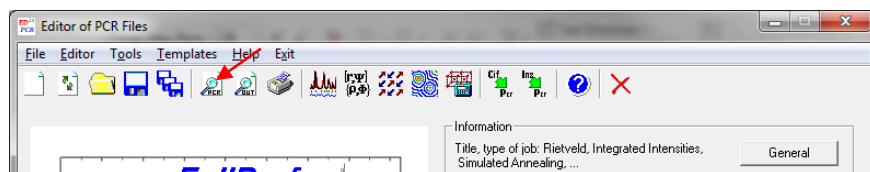
SYMM x,-y,z+1/2                 Atom: Fe_4   -0.1
Sk(4): (-u,v,-w)

```

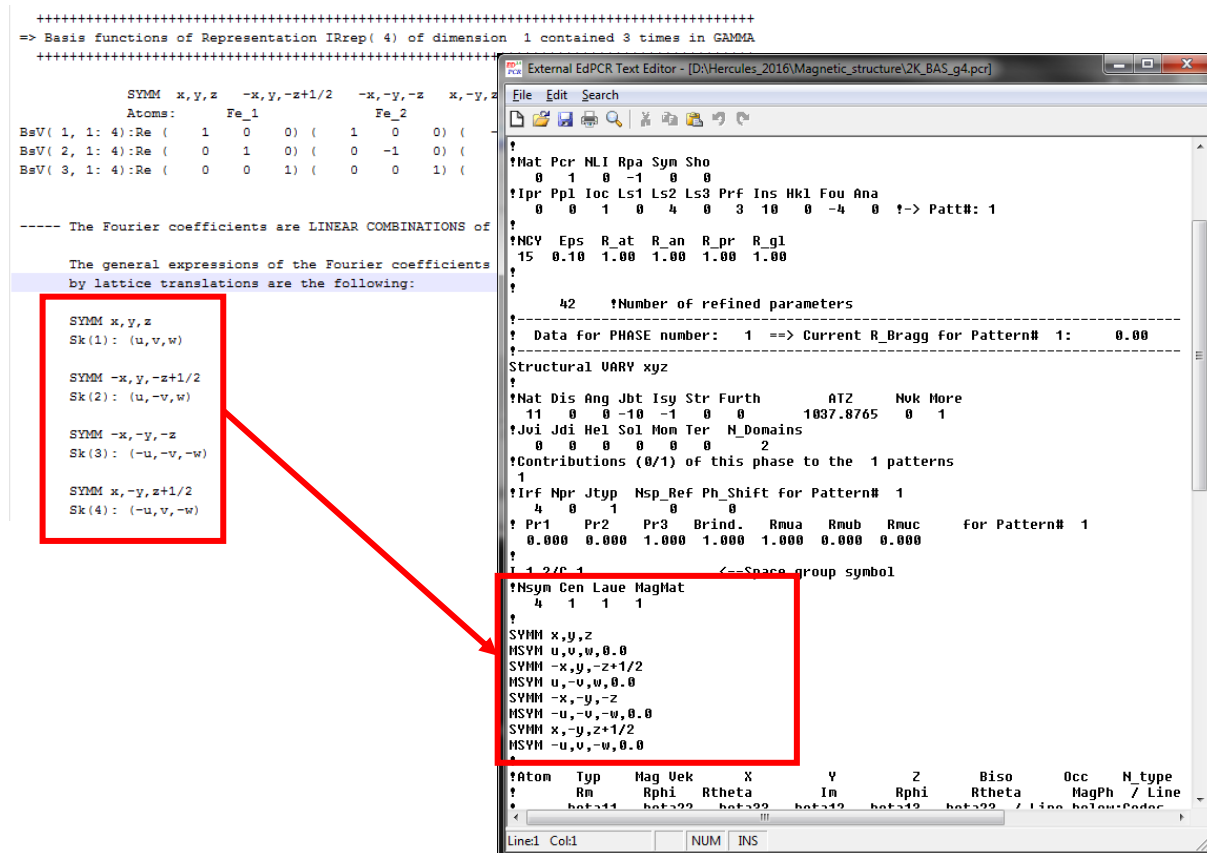
e. In the “Symmetry Information” window the Symmetry Operators will be “User defined”. The (nuclear) Space Group is $I 1 2/c 1$. The symmetry operators are 4 and can be taken from the Basireps output.



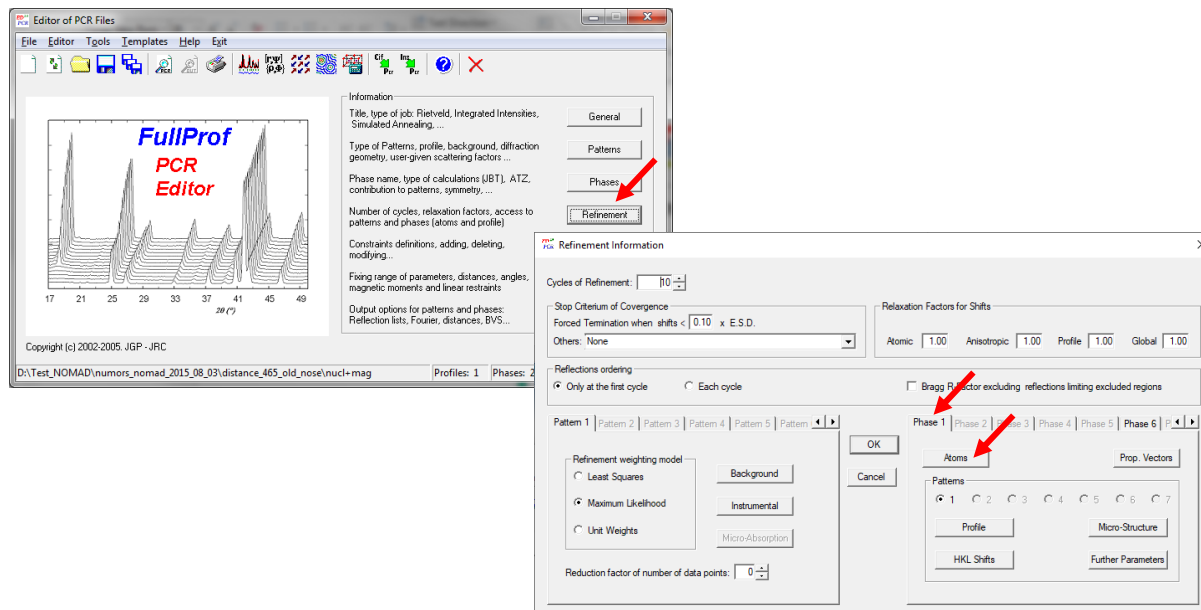
f. After filling all the information, save and open the pcr file using a text editor or clicking in the corresponding icon.



Now we have a PCR file with the magnetic symmetries included



f. The next step is to **include the information related with the magnetic atoms** into the PCR file. You will need to click on “Refinement” and modify the atoms information (Phase 1)



g. In the “Atoms Information” window:

- Transform first the B factors to isotropic and fix them.
- The Fe atom must be Ntyp: MFE3, i.e. M (magnetic) FE (iron) 3 (charge 3+).
- Mag.Rot. is the magnetic symmetry operator. If there is more than one magnetic site, the magnetic symmetry operators can be different for each site.
- Prog V. is a label for the propagation vector. Fullprof can work with more than one propagation vector. In the present case with $\mathbf{k} = (0, 0, 0)$ this label should be zero.
- The coefficients Re[m], Re[Phi] and Re[theta] are the adjustable parameters of the magnetic structure using spherical components

Atoms Information: Phase 1

List of Atoms
Number of Atoms: 11

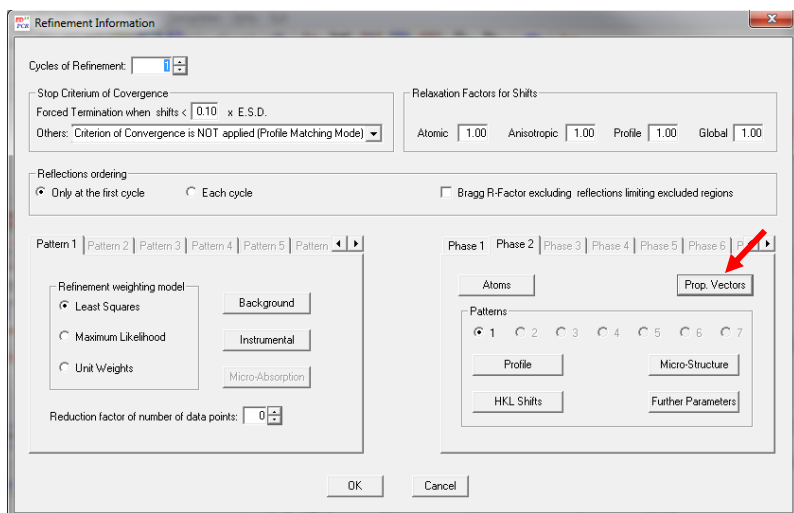
	Label	Ntyp	Mag. Rot.	Prog. V.	X	Y	Z	B	Occ
Atom # 1	Fe1	MFE3	1	0	-0.12168	0.00449	-0.37450	0.10459	1.00000
Atom # 2	Cl1	Cl	0	0	-0.25607	0.00604	-0.37763	0.24047	1.00000
Atom # 3	Cl2	Cl	0	0	-0.10881	-0.21214	-0.48595	0.39906	1.00000
Atom # 4	Cl3	Cl	0	0	-0.11238	0.24386	-0.47132	0.21842	1.00000

	Re[m]	Re[Phi]	Re[Theta]	Im[m]	Im[Phi]	Im[Theta]	MPhase
Atom #1	-4.38966	90.00000	90.00000	0.00000	0.00000	0.00000	0.00000

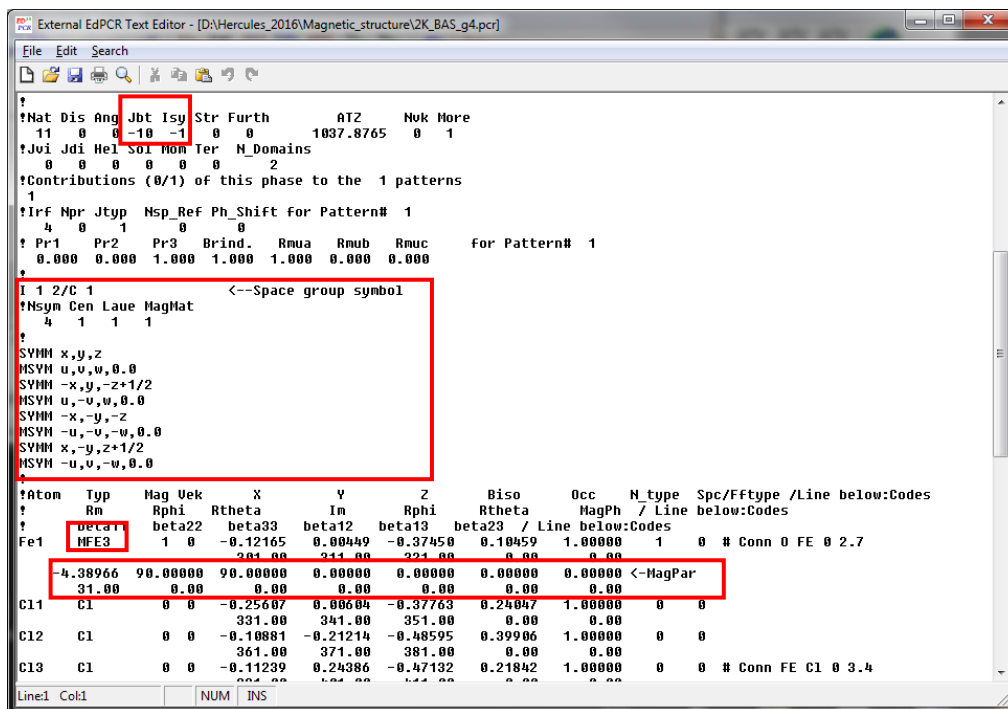
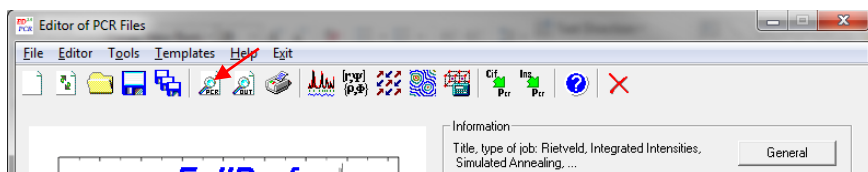
	B11	B11/F1	B22	B11/F1	B33	B11/F1	B12	B11/F1	E
Atom #10	0.00109		0.01187		0.00206		-0.00110		
Atom #11	0.00225		0.01195		0.00154		0.00021		

Buttons: Refine Positions, Refine B_iso, Refine B_aniso, Fix All, Cancel, OK

h. If the magnetic propagation vector was different from $\mathbf{k} = (0, 0, 0)$, it could be included in the PCR by clicking in "Prop. Vectors"



i. Save and open the pcr file using a text editor or clicking in the corresponding icon. The parts corresponding to the magnetic structure are highlighted below



[illegible]