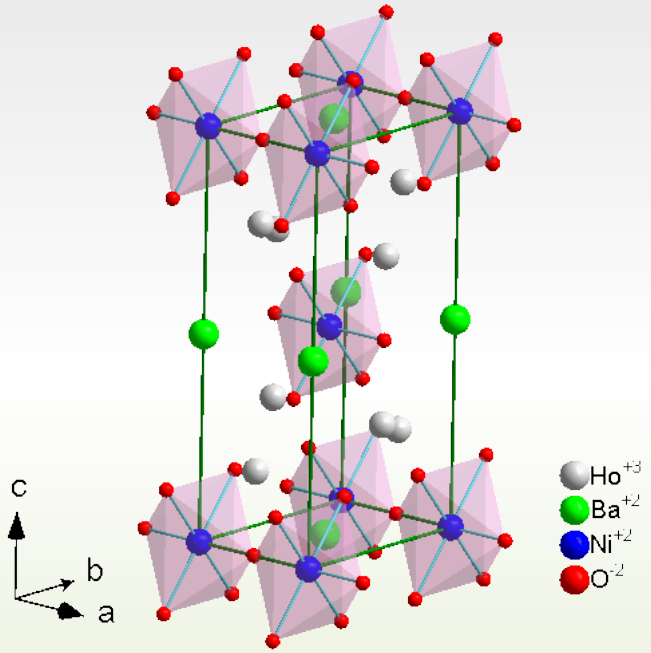
# Magnetic structure determination of $Ho_2BaNiO_5$ using FullProf Suite and SARAh

**$Ho_2BaNiO_5$**

Orthorhombic ( Space group: *Immm)*
*a=3.764 A, b=5.761 A, c,=11.336 A)*

$NiO_6$ octahedra form chains along the a-axis.

3D Antiferromagnetic ordering at $T_N$ ~ 53 K

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EDP Sciences


**Neutron diffraction study of the magnetic ordering in the series $R_2BaNiO_5$ (R = Rare Earth)**

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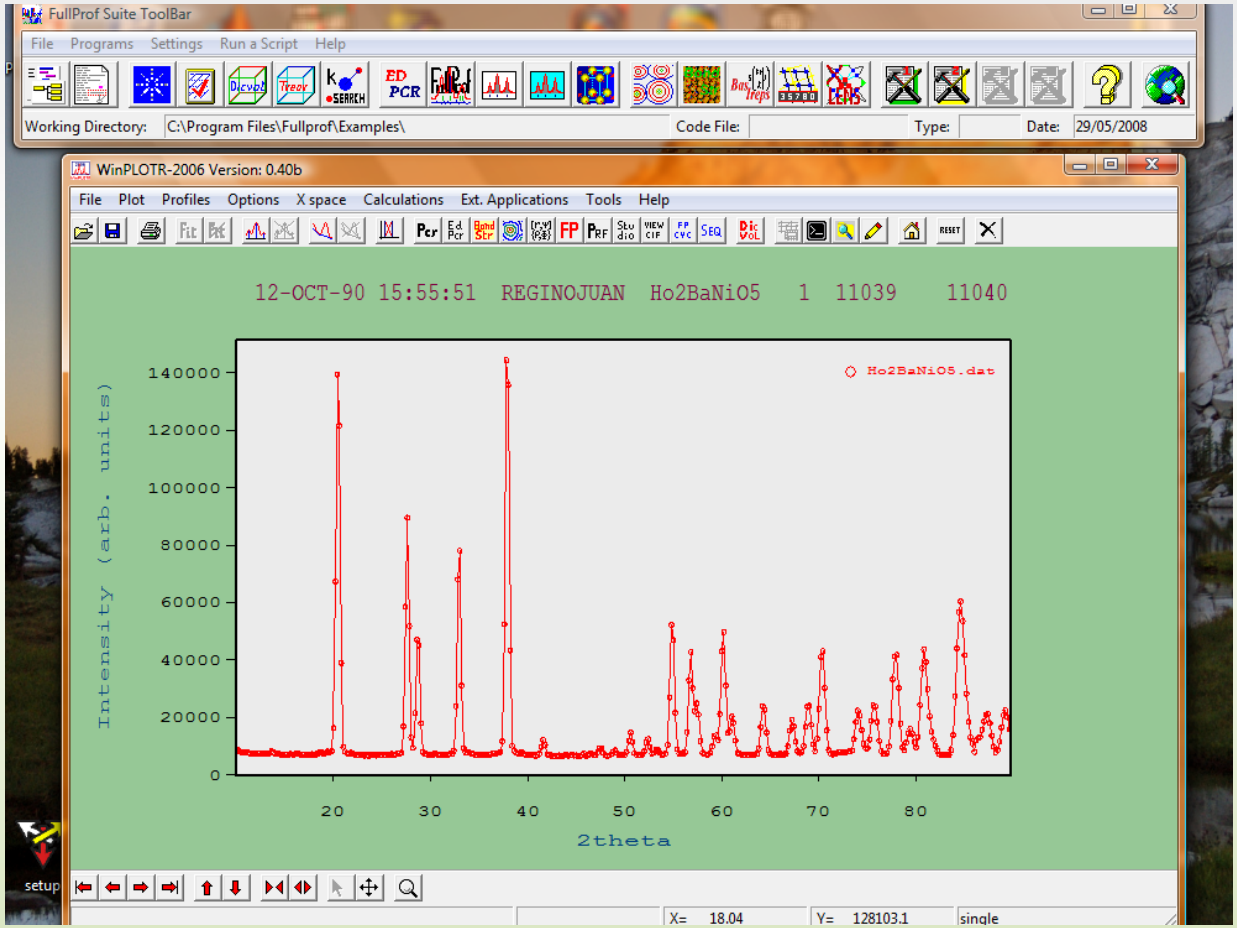
| Atom | Wyck. | Site | x/a | y/b | z/c |
|---|---|---|---|---|---|
| Ho | 4j | mm2 | 1/2 | 0 | 0.2025(4) |
| Ni | 2a | mmm | 0 | 0 | 0 |

## STARTING INFORMATION

- Neutron powder diffraction data collected at D1B –ILL at 1.5 K using λ = 2.524 Å (File : Ho2BaNiO5.dat )
- Instrument resolution file: ( d1b_ill.irf )
- Crystal structure known ( File: Ho2BaNiO5.cif )



# STEPS FOR MAGNETIC STRUCTURE DETERMINATION

✓ refining the crystal structure for the paramagnetic state ($T > T_N$ or $T_C$)
→ **obtain all the relevant structural and profile parameters**

✓ preparing a PCR file and performing a refinement of the low temperature data ($T < T_N$) with fixed structural parameters (without a magnetic model )
→ **identify the magnetic contribution to the diffraction pattern**

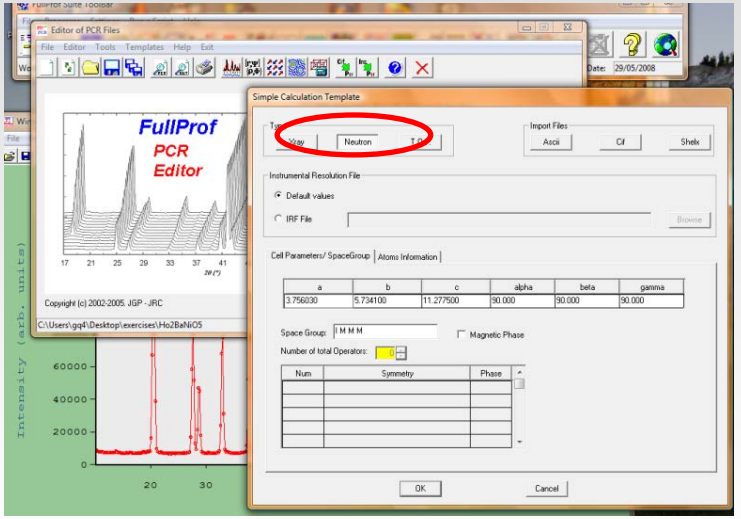
✓ indexing the magnetic reflections
→ **use *k-search* to determine the propagation vector(s) $k_m$**

✓ Performing symmetry analysis (propagation vector, space group, atomic position)
→ **use *BasIreps* or *SARAh* to get IRs and Basis vectors**

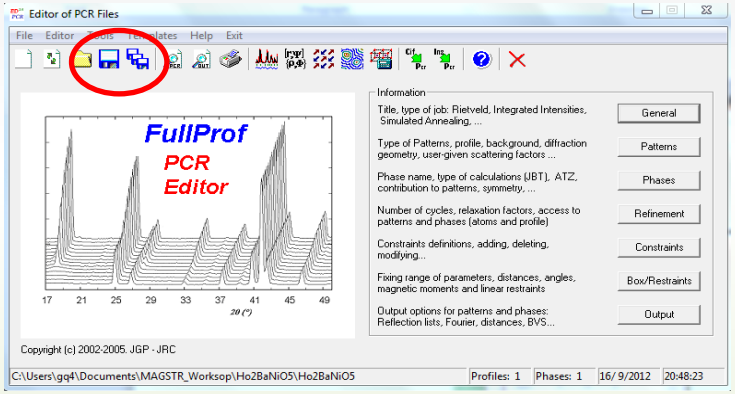
✓ Adding the magnetic phase to the PCR file (using the symmetry information) and **solve the magnetic structure using trial and error methods**

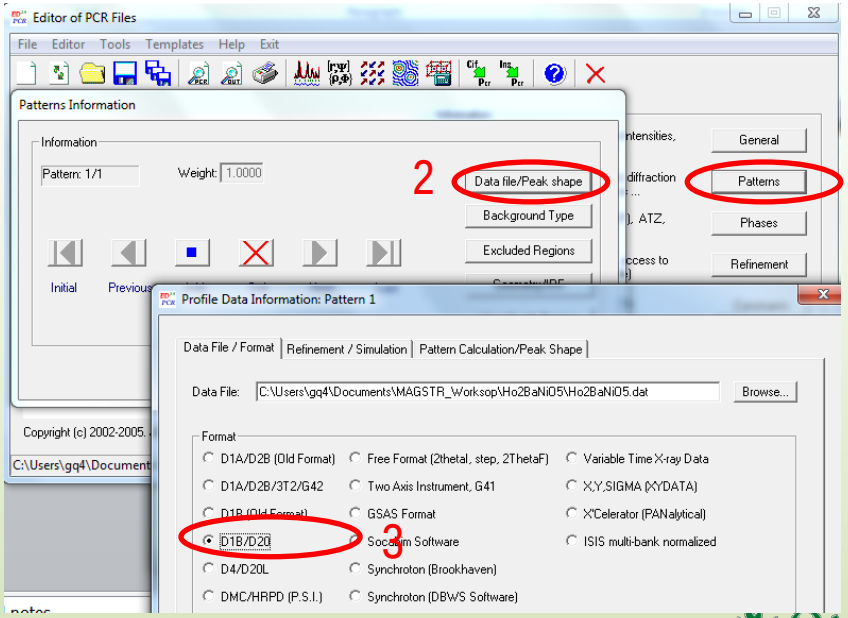
✓ **Magnetic structure model visualization using FpStudio program**

- use **EdPCR** to create the input file for FullProf (*.PCR)



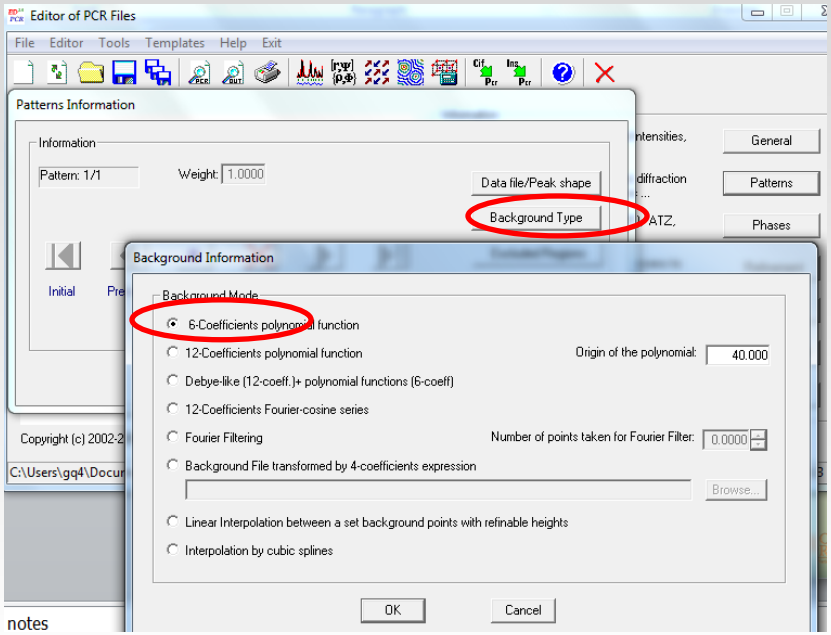

- import the crystallographic information by clicking on “CIF to PCR”
- in the new window, select the “Neutron” tab for the type of calculations
- use the “Browse” button to upload the instrument resolution file “IRF” (d1b_ill.irf)

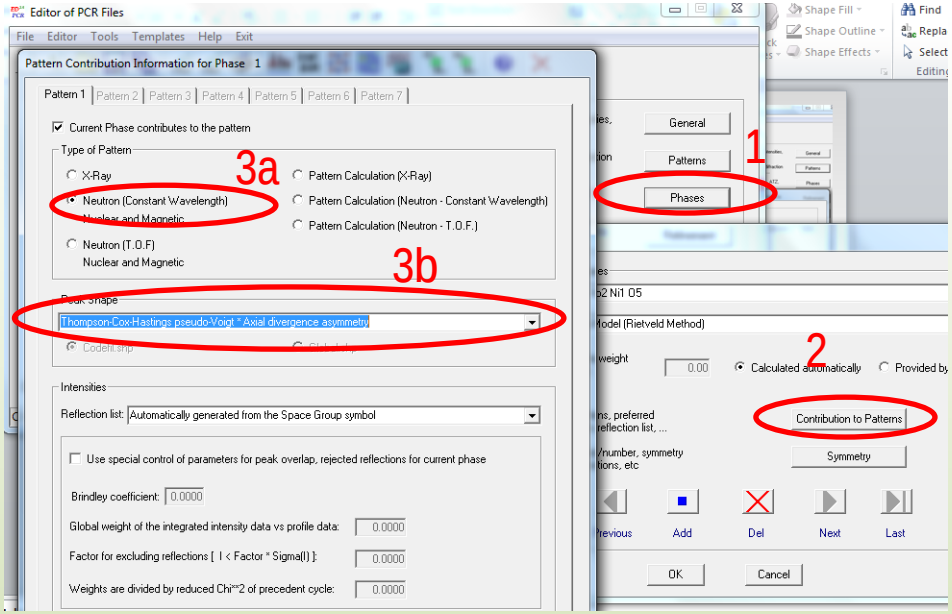



- save the PCR file by clicking the “Save” button
- open the “Patterns” tab (1) and then the “Data file/ peak shape” (2) and select the “D1B/D20” for the data file format (3)

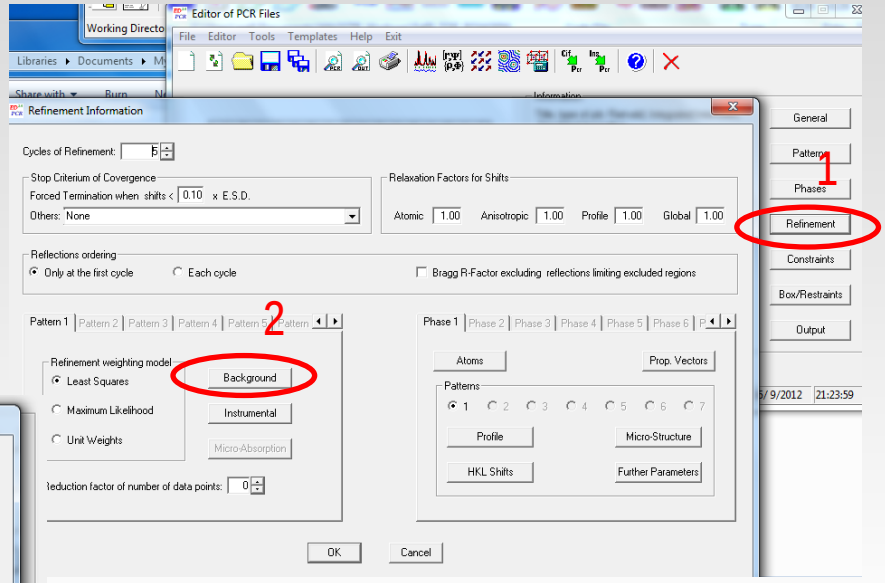
- "Refinement/Simulation" tab, make sure that "Neutron-CW" option is selected, wavelength is "**User defined**" $\lambda_1=\lambda_2=2.524$Å
- "pattern calculation" the "Thompson-Cox-Hastings pseudo-Voigt" peak shape is chosen
- For the background information, select the "6-coefficients polynomial function"

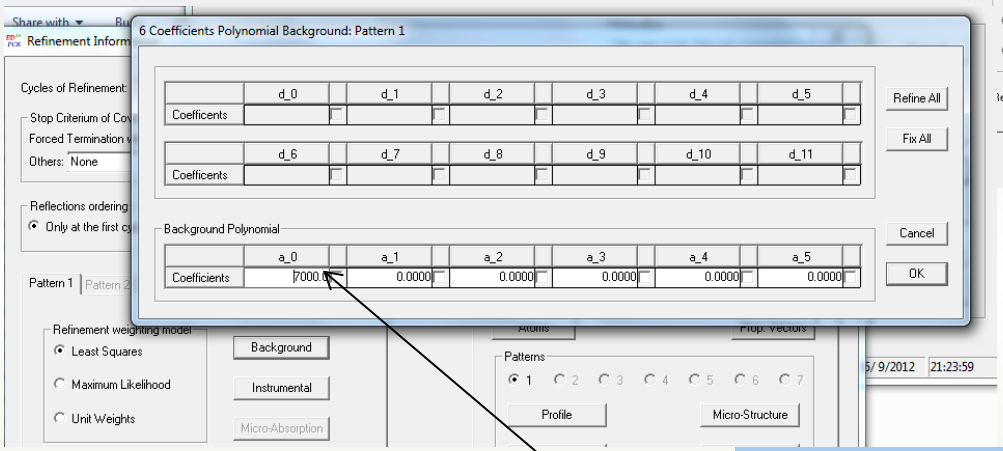


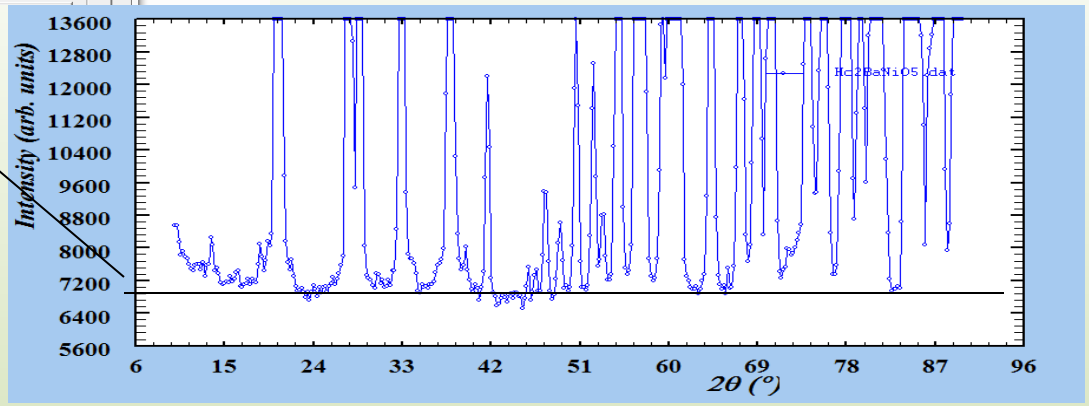




- From the main window of EdPcr, open the "Phases" tab (1) and then click on the "Contribution to patterns" (2) and then select the "current phase contributes to the pattern" & "neutron (constant wavelength)" (3a) and "Thompson-Cox-Hastings pseudo-Voigt" for the peak shape (3b), Reflection list : "Automatically generated from space group"

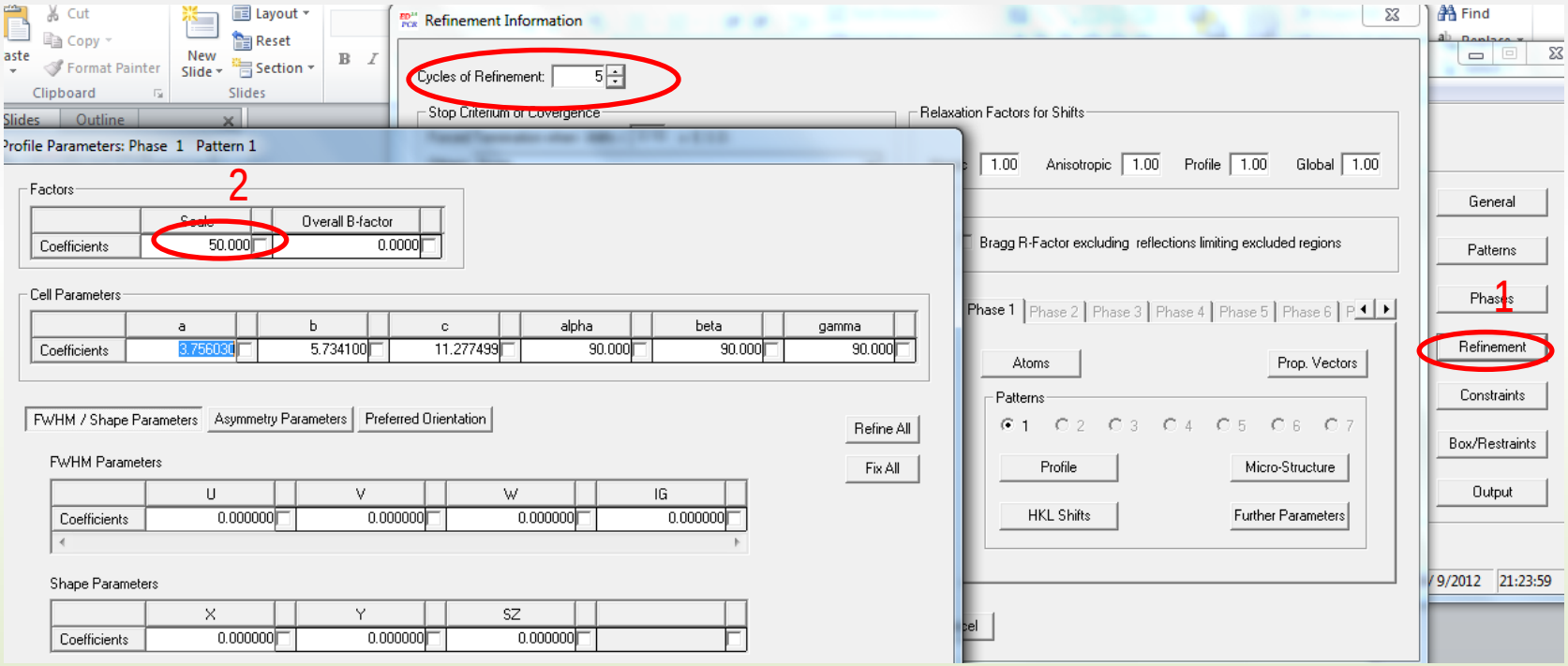
- Open the “Refinement” (1) and then the “Background” and add value for the “a_o” coefficient ( ~7000, read from the data file) that will give a first flat approximation for the background



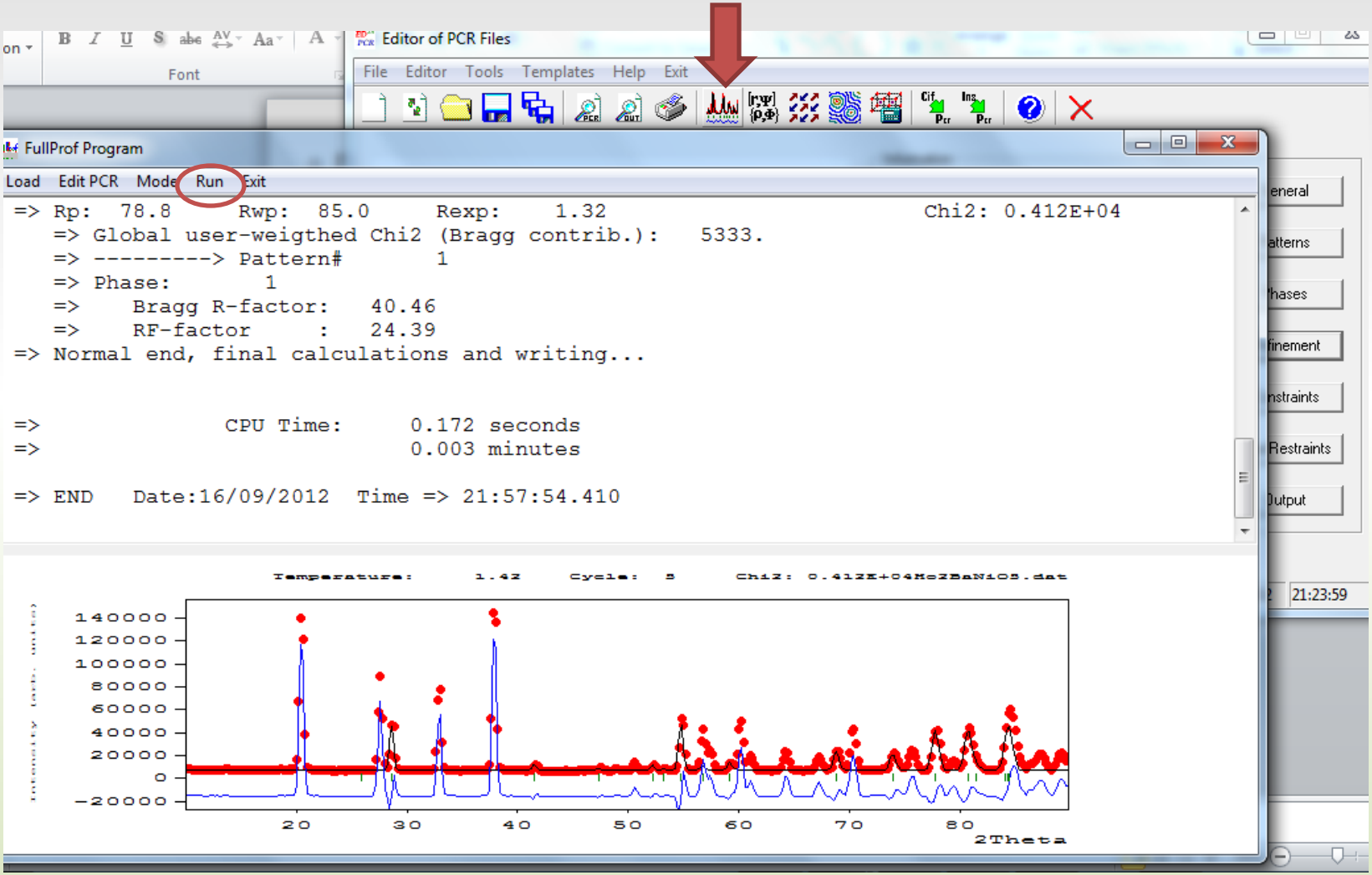



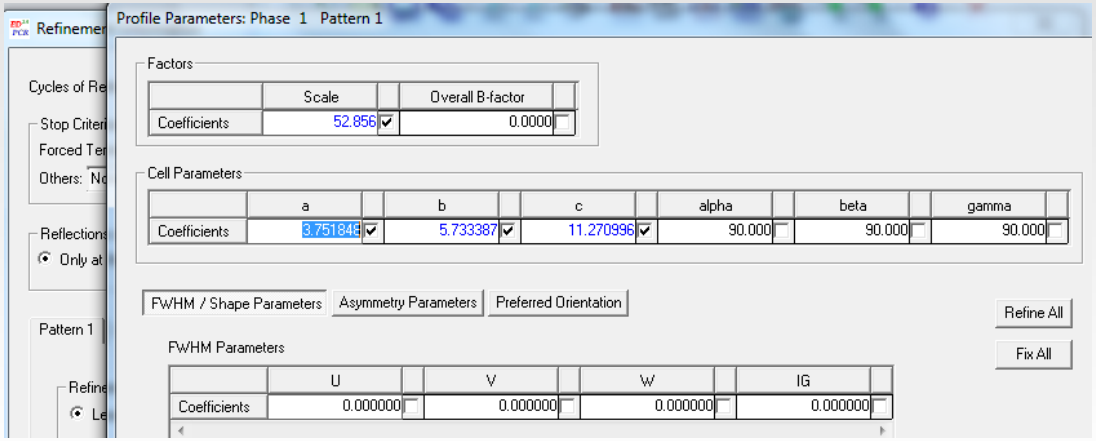
- From the same “Refinement” window (1) , click on the “Profile” tab and and set a number for the “Scale factor” (~ 50 for this example). The number of “cycles of refinement” can also be increased at this time
- save the PCR file by clicking the “Save” button, every time a change has been made



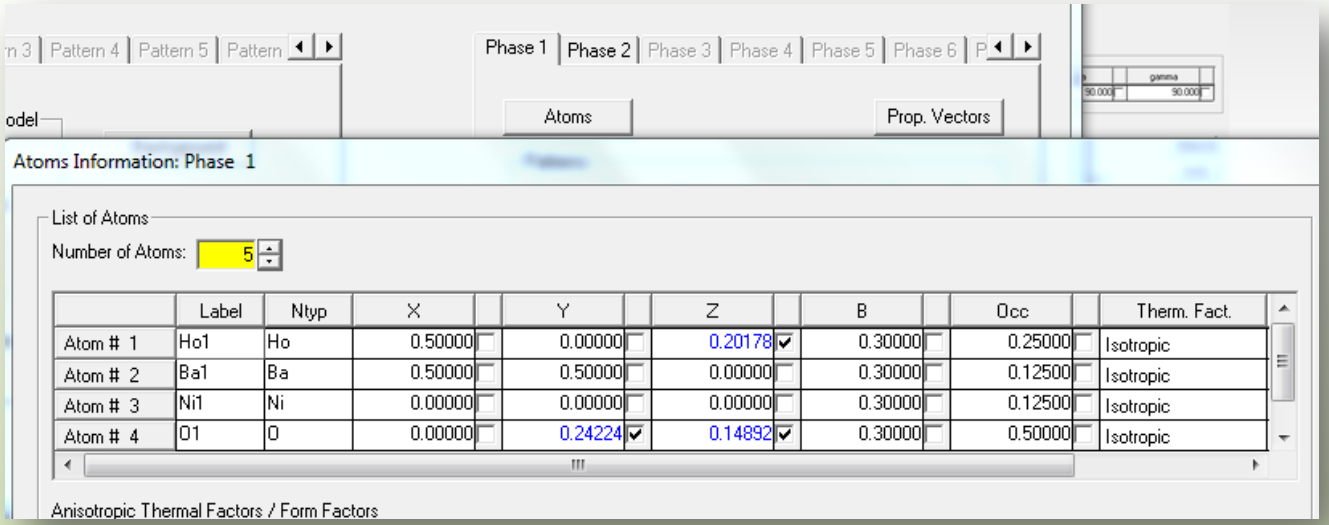
- Run the Fullprof program by click on button indicated below. All the parameters are fixed at this time.

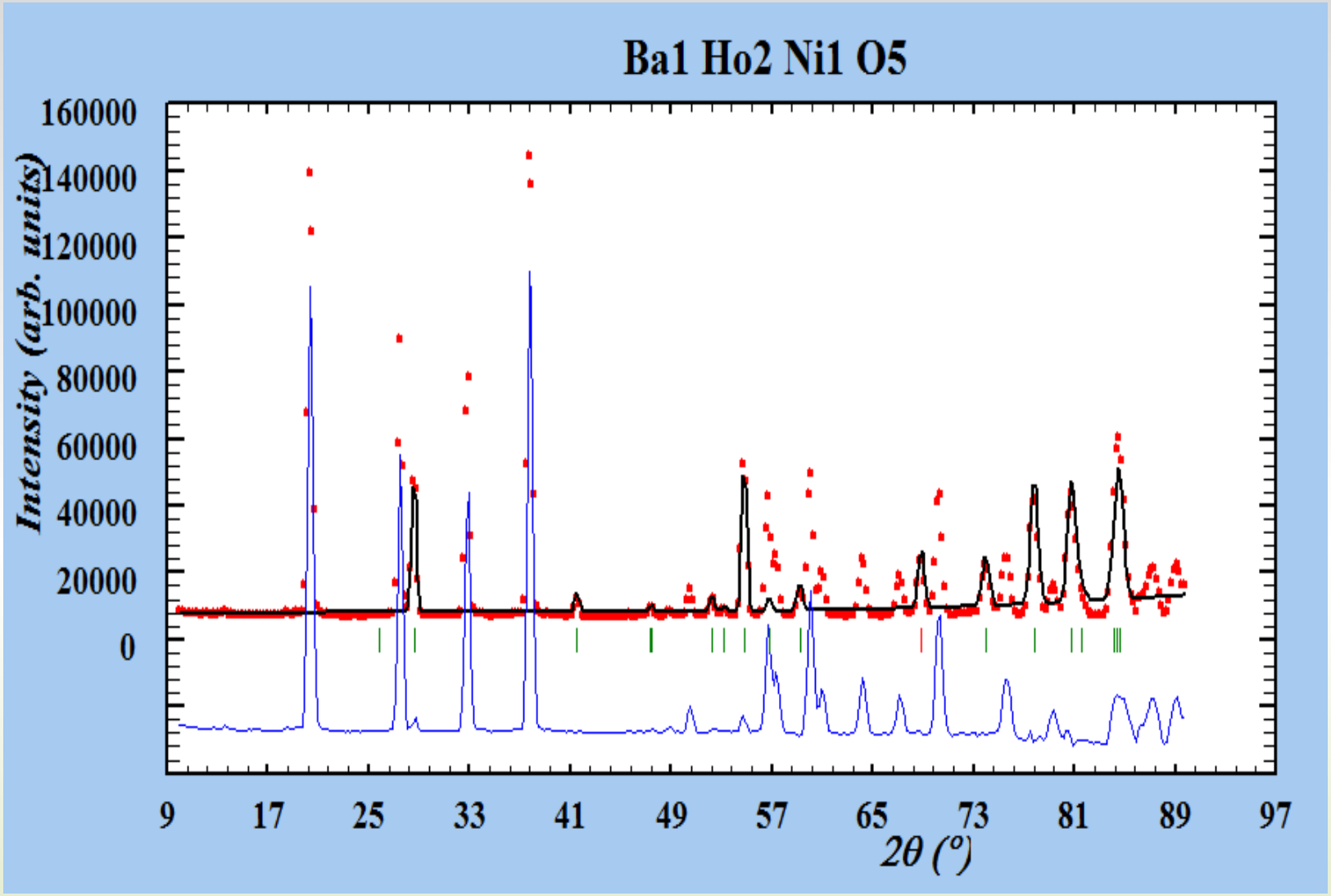


- ✓ You can run the refinement again by allowing the scale factor, lattice parameters, some of the background coefficients and the 2theta zero to vary
- ✓ Refined parameters appear in blue or red (with additional constraints)




- ✓ Atomic parameters (fractional atomic positions, thermal factors, occupation) can be accessed through Refinement ➔ Phase # tab ➔ Atoms

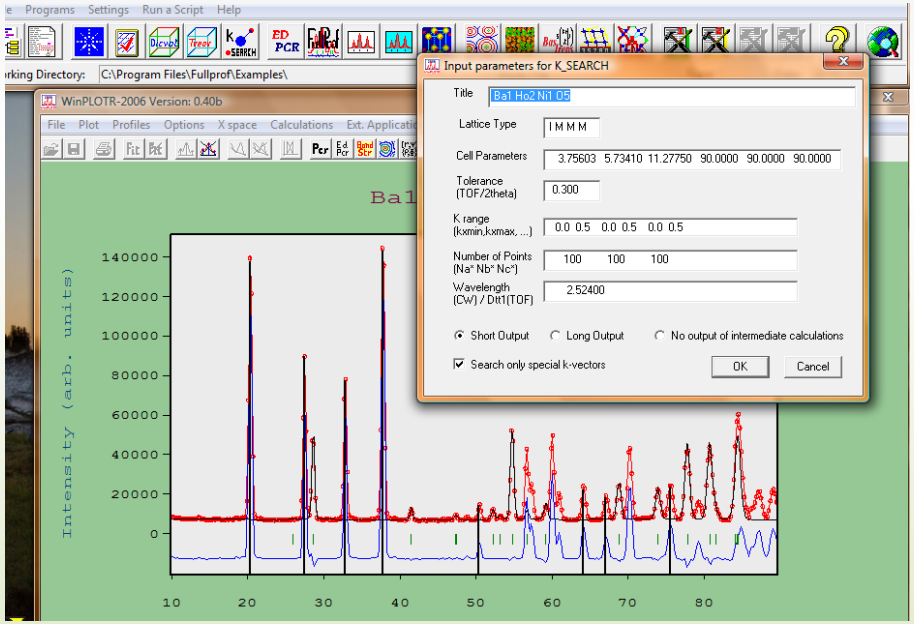





- ✓ Open the PRF file (Rietveld plot) by using the Winplotr program. The result will look something similar to the figure above
- ✓ The reflections that are left unindexed are all magnetic in origin

# ➢ INDEX THE MAGNETIC REFLECTIONS USING THE k-search program

- open the PRF file using WinPlotr-2006 program and select the un-indexed reflections to create the input file for "k-search" program. For doing this, in the menu of winplotr click on "Calculations"- "peak detection"-"enable" . After enabling, go again to "Calculations"- "peak detection" and "insert peak". After selecting the magnetic peaks, go to "save peaks" to save them as "K-search format"



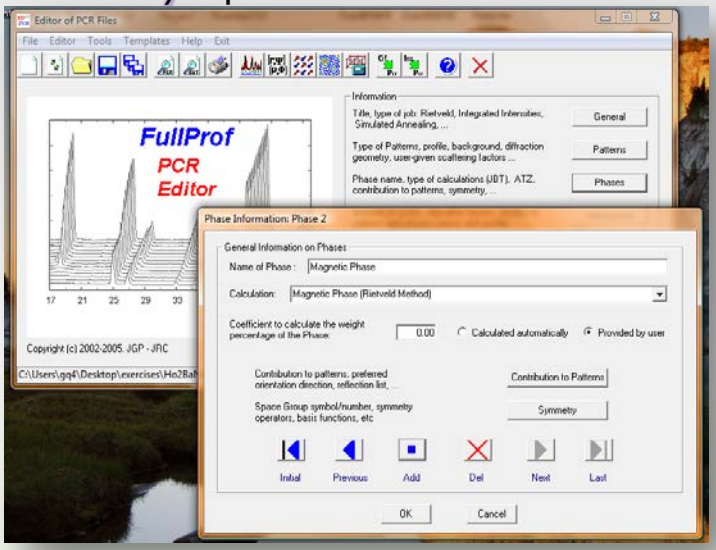

- run "k-search" program to find the propagation vector and see the results listed in the file "k_search.kup"

```
=> List of satellites (hkl)+(Kx,Ky,Kz) for the best solution:

          Kx=0.5000     Ky=0.0000     Kz=0.5000

   H  K  L   n      D*(cal)      D*(obs)     2Th(cal)     2Th(obs)  2Th(obs-cal)
  ---------------------------------------------------------------------------
   1  0  1   1       0.1403       0.1398      20.3982      20.3261      -0.0721
   1  0 -1   1       0.1882       0.1880      27.4762      27.4512      -0.0250
   1  1  0   1       0.2238       0.2237      32.8159      32.7950      -0.0209
   1  1  2   1       0.2566       0.2564      37.7840      37.7571      -0.0269
   1  0 -3   1       0.3377       0.3371      50.4500      50.3532      -0.0968
   1  0  5   1       0.4206       0.4205      64.1262      64.0944      -0.0318
  -1  1  0   1       0.4380       0.4375      67.1170      67.0208      -0.0962
   1  2 -3   1       0.4855       0.4854      75.5671      75.5454      -0.0217

=>  Best R-factor:  0.9461 %  for propagation vector:
                              k  =  ( 0.5000  0.0000  0.5000)
```

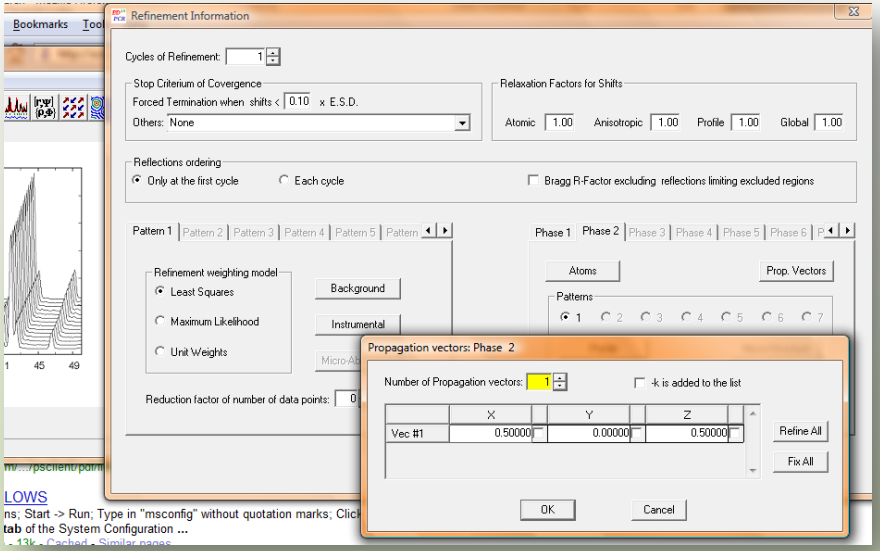
for the $Ho_2BaNiO_5$ → $k_m$= (0.5, 0, 0.5)

# ➢ ADDING THE MAGNETIC PHASE AS A SECOND PHASE TO THE PCR

✓ use PCR Editor to introduce the magnetic phase as a second phase. Go to the "Phases" tab and click on the "Add" button. You can name (ex. *magphase*) the new phase as you wish, and in the "calculation" tab select the "Magnetic phase (Rietveld Method)" option.



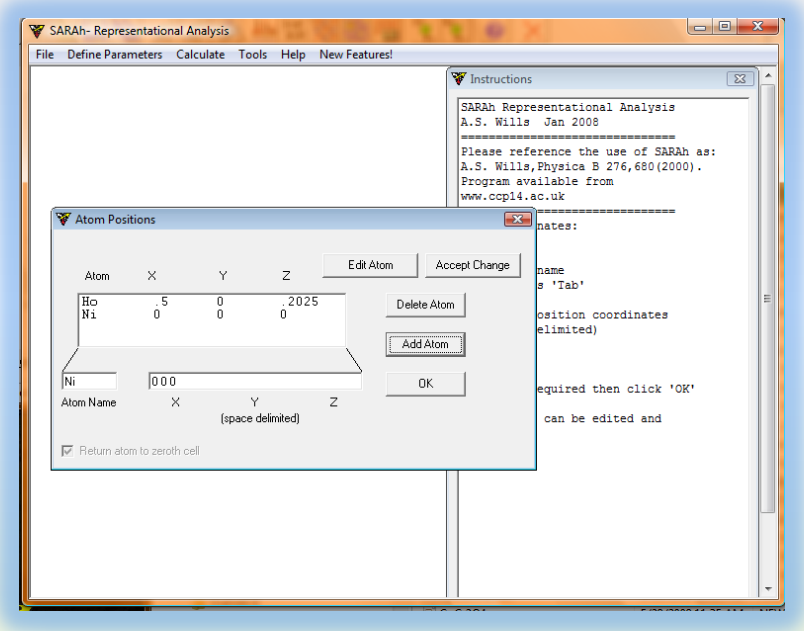

✓ the propagation vector for the magnetic phase needs to be added into the PCR file. For doing that, you need to click on "Refinement" button and then select the "Phase 2" and "Prop. Vectors"

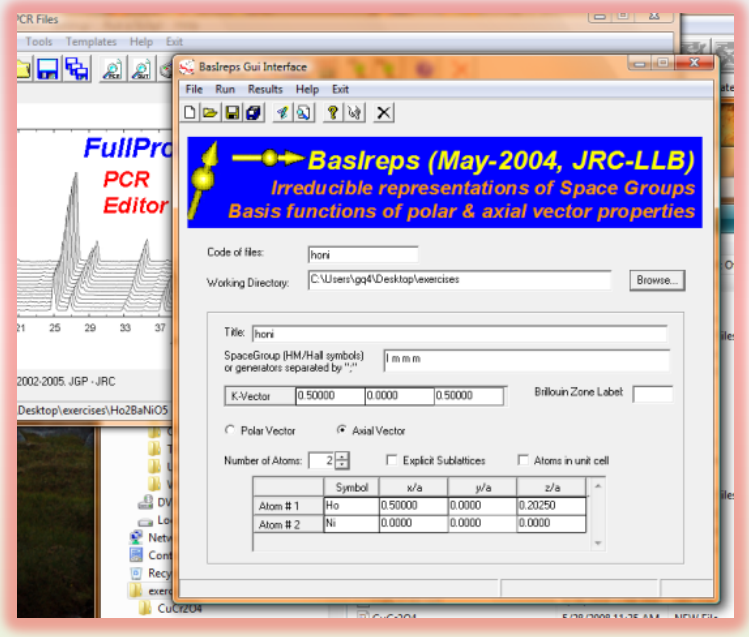



✓ you can also open the PCR file using your default text editor at this time and verify that the second phase has been successfully added . Don't worry about the symmetry at this time.

# PERFORM SYMMETRY ANALYSIS

- ✓ use the SARAh program or **BasIreps** to generate the Irreducible representations and basis vectors associated with $k_m$= (0.5, 0, 0.5). Both programs require as an input the $k_m$ vector, space group and atom positions of the magnetic ion.




- ✓ for this example we will use the program SARAh. See the software's website for the tutorial on how to run the program. The program generates a summary file containing the basis vectors components for the two magnetic ions. The file is located in SARAh program's folder.

- ✓ The result of the symmetry analysis is also summarized in a TEX file, in Sarah directory, as shown in this capture:

**Ho**

| IR | BV | Atom | BV components | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $m_{\parallel a}$ | $m_{\parallel b}$ | $m_{\parallel c}$ | $im_{\parallel a}$ | $im_{\parallel b}$ | $im_{\parallel c}$ |
| $\Gamma_1$ | $\psi_1$ | 1 | 0 | 4 | 0 | 0 | 0 | 0 |
| | | 2 | 0 | 4 | 0 | 0 | 0 | 0 |
| $\Gamma_2$ | $\psi_2$ | 1 | 4 | 0 | 0 | 0 | 0 | 0 |
| | | 2 | -4 | 0 | 0 | 0 | 0 | 0 |
| | $\psi_3$ | 1 | 0 | 0 | 4 | 0 | 0 | 0 |
| | | 2 | 0 | 0 | -4 | 0 | 0 | 0 |
| $\Gamma_3$ | $\psi_4$ | 1 | 4 | 0 | 0 | 0 | 0 | 0 |
| | | 2 | 4 | 0 | 0 | 0 | 0 | 0 |
| | $\psi_5$ | 1 | 0 | 0 | 4 | 0 | 0 | 0 |
| | | 2 | 0 | 0 | 4 | 0 | 0 | 0 |
| $\Gamma_4$ | $\psi_6$ | 1 | 0 | 4 | 0 | 0 | 0 | 0 |
| | | 2 | 0 | -4 | 0 | 0 | 0 | 0 |

Table 1: Basis vectors for the space group I m m m with $\mathbf{k}_{-55} = (.5,\ 0,\ .5)$.The decomposition of the magnetic representation for the $Ho$ site $(.5,\ 0,\ .2025)$ is $\Gamma_{Mag} = 1\Gamma_1^1 + 2\Gamma_2^1 + 2\Gamma_3^1 + 1\Gamma_4^1$. The atoms of the nonprimitive basis are defined according to 1: $(.5,\ 0,\ .2025)$, 2: $(.5,\ 0,\ .7975)$.

**Ni**

| IR | BV | Atom | BV components | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $m_{\parallel a}$ | $m_{\parallel b}$ | $m_{\parallel c}$ | $im_{\parallel a}$ | $im_{\parallel b}$ | $im_{\parallel c}$ |
| $\Gamma_1$ | $\psi_1$ | 1 | 0 | 4 | 0 | 0 | 0 | 0 |
| $\Gamma_3$ | $\psi_2$ | 1 | 4 | 0 | 0 | 0 | 0 | 0 |
| | $\psi_3$ | 1 | 0 | 0 | 4 | 0 | 0 | 0 |

Table 2: Basis vectors for the space group I m m m with $\mathbf{k}_{-55} = (.5,\ 0,\ .5)$.The decomposition of the magnetic representation for the $Ni$ site $(0,\ 0,\ 0)$ is $\Gamma_{Mag} = 1\Gamma_1^1 + 0\Gamma_2^1 + 2\Gamma_3^1 + 0\Gamma_4^1$. The atom of the primitive basis is defined according to 1: $(0,\ 0,\ 0)$.

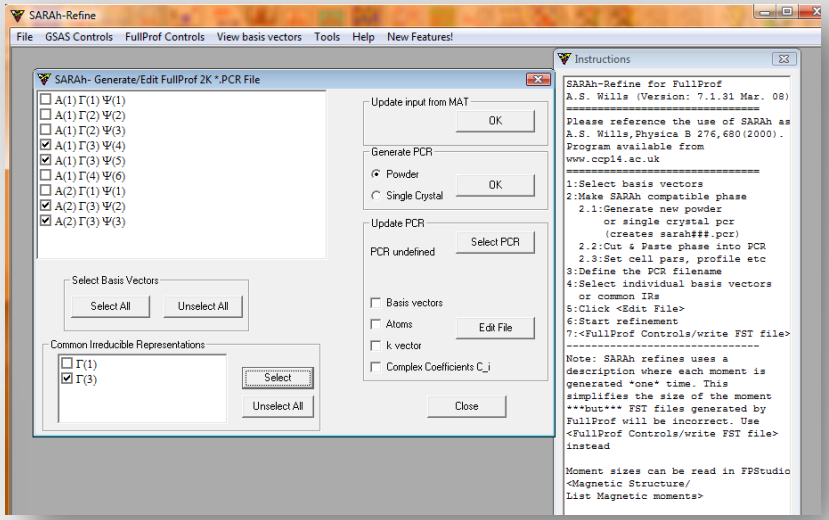
$\Gamma_1$ constraints moments to lie along the *b-axis*

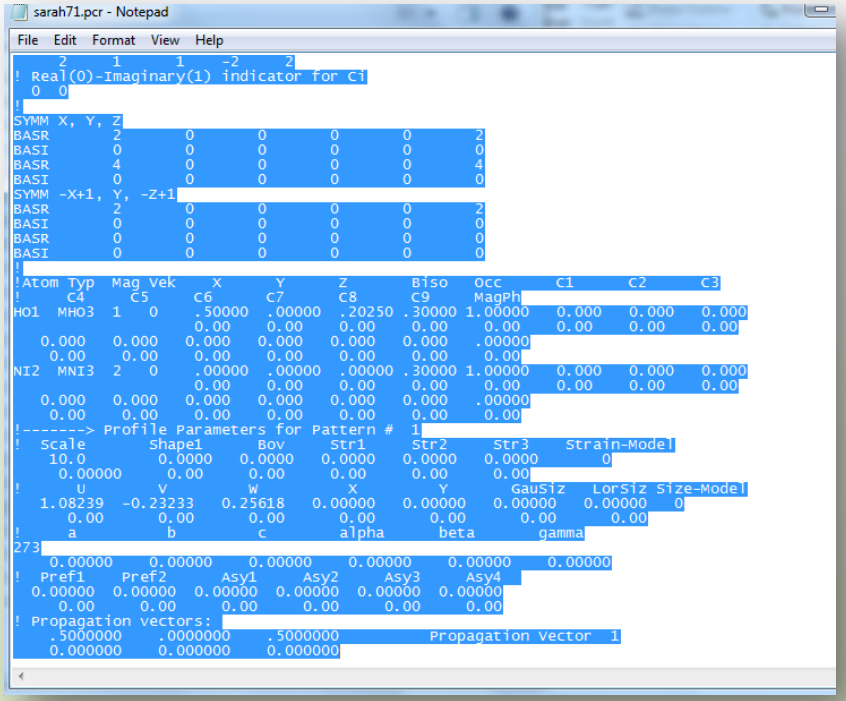
$\Gamma_3$ constraints moments to lie in the *ac-plane*

- ✓ If the two sites (Ni and Ho) order according to the same representation only the representations 1 and 3 are allowed.

- ✓ **"SARAh Refine"** program can be used to generate the magnetic phase for the PCR (FullProf) format (see Sarah manual for more details). In our case , it will generate the file "sarah71.pcr"

- ✓ You'll need to select the basis vectors corresponding to one of the two common Irreducible Representations (gamma3 or Γ3 in our case).



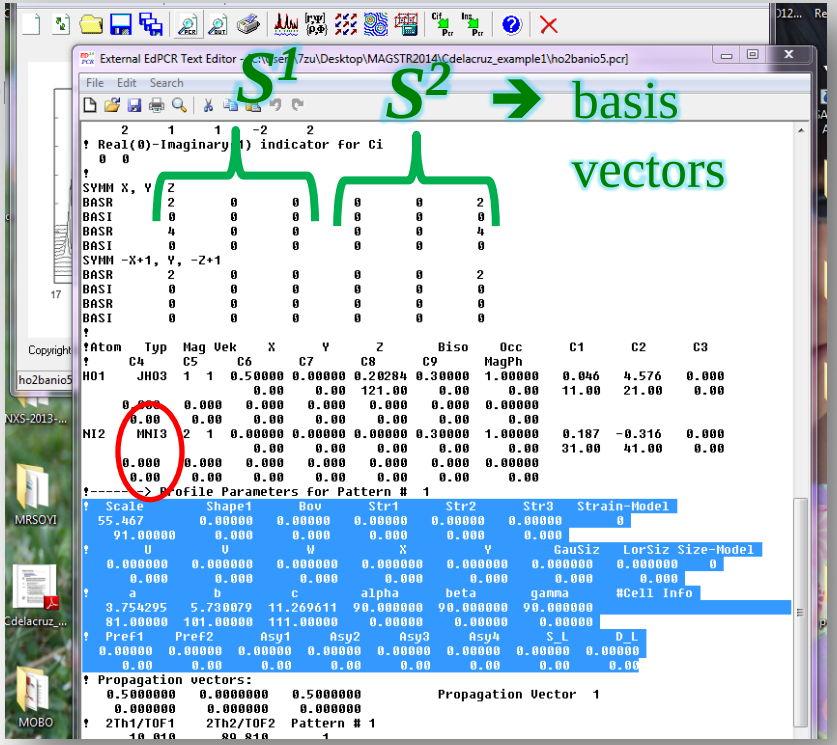



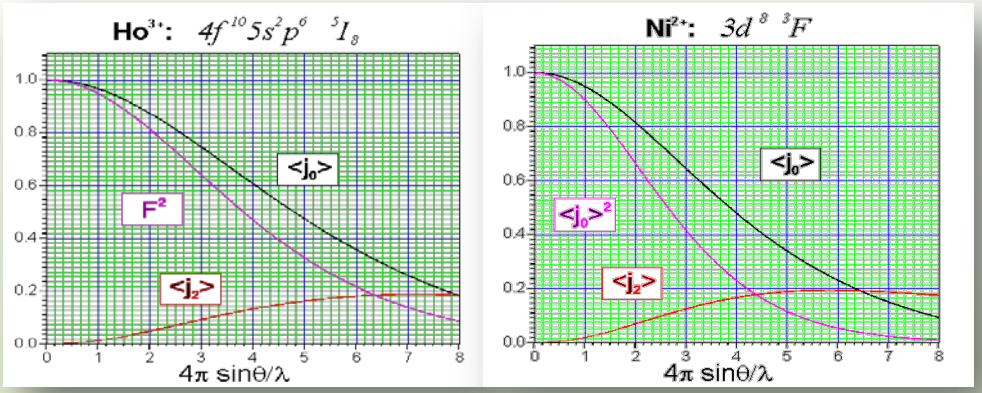

- ✓ Note that the selected model Γ3 constraints the magnetic moments of Ho and Ni to lie in the *ac*-plane

- ✓ Open the PCR file generated by Sarah ("sarah71.pcr"), copy the entire content of the file and PASTE it over the section of the second phase of your Ho2BaNiO5 PCR file.

- ✓ once the magnetic phase is defined into your PCR file, examine the profile parameter section; you'll need to set the profile parameters for the magnetic phase (phase 2) the same as you have in the structural phase (phase 1). Copy/paste that section from the phase1 to the phase 2. Make sure that you are not removing the line defining the propagation vector, at the end of the phase 2 section.

- ✓ note that the scale factor and the lattice parameters of the structural and magnetic phase need to be constrained to have the same values in both the nuclear and magnetic phases.




$$\mathbf{S}_{kjs} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{k\,\nu}_{n\lambda}(js)$$

**Fourier coefficient for calculation of $m_{ljs}$ at each site**

$$\mathbf{S_k} = C_1 S^1 + C_2 S^2$$

$$\langle j_0(\sigma) \rangle + \left(1 - \frac{3}{2}\right) \langle j_2(\sigma) \rangle$$

International Tables of Crystallography, Volume C, ed. by AJC Wilson, Kluwer Ac. Pub., 1998, p. 513

- ✓ make sure that the correct parameters for the magnetic scattering form factors are used **JHO3** for the magnetic rare earth $Ho^{3+}$ and **MNI3** for the transition metal ion $Ni^{3+}$

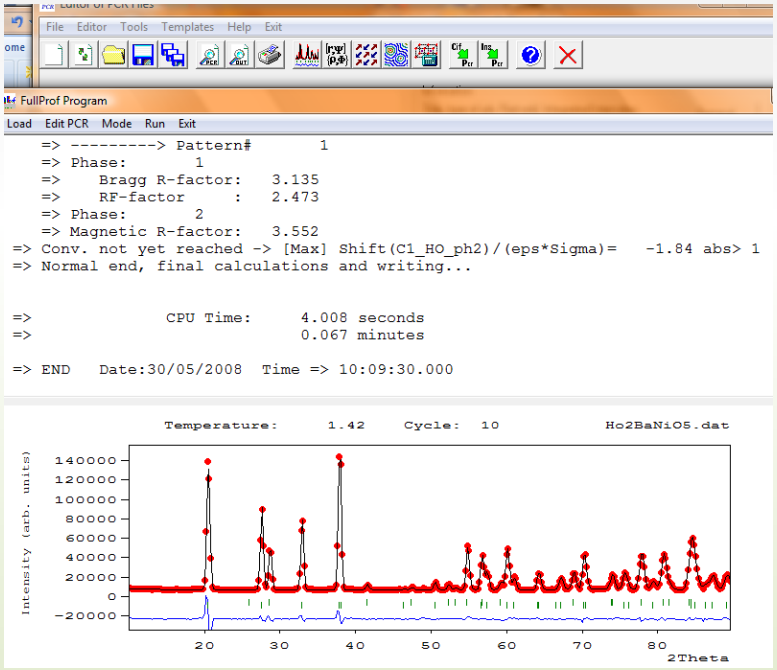
# MAGNETIC STRUCTURE REFINEMENT

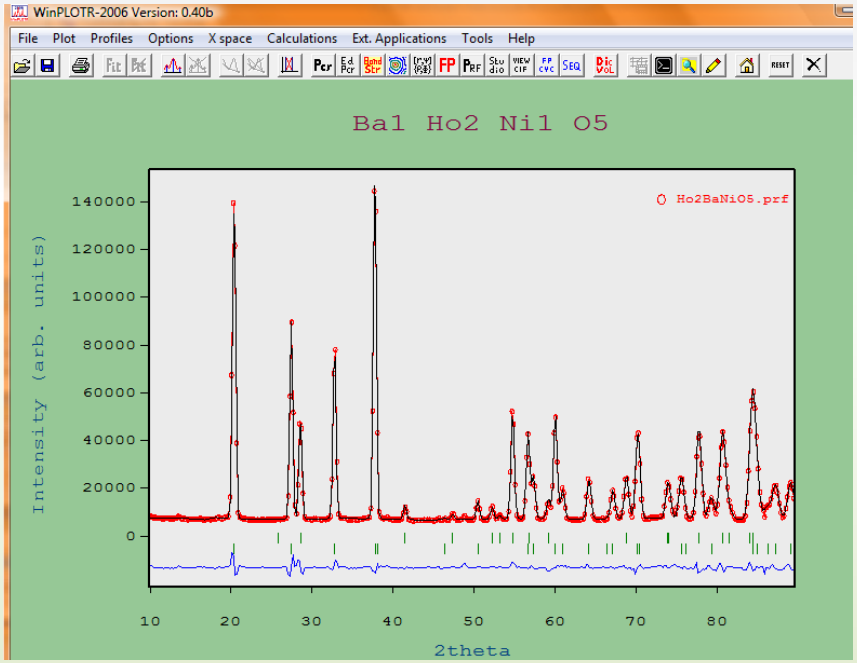
- ✓ select the basis vector coefficients C1 and C2 for the two independent magnetic ions (Ho and Ni) to be refined

Basis Functions Coefficients

| | C1 | | C2 | | C3 | | C4 | |
|---|---|---|---|---|---|---|---|---|
| Atom # 1 | 2.00000 | ✓ | 2.00000 | ✓ | 0.00000 | | 0.00000 | |
| Atom # 2 | 0.12300 | ✓ | 0.18300 | ✓ | 0.00000 | | 0.00000 | |

- ✓ run the refinement using the FullProf program
- ✓ start to refine additional parameters (profile, lattice …) to obtain a good quality fit.



# MAGNETIC MOMENT DETERMINATION

✓ Check the output file (*.out) from FullProf. Verify that the magnetic structure model and the magnitude of the Ho and Ni moments are meaningful

External EdPCR Text Editor - [C:\Users\7zu\Desktop\MAGSTR2014\Cdelacruz_example1\Ho2BaNiO5.out]

File Edit Search

```
---------------------------------------------------------------------------------------
=> Phase  2 Name: Magnetic Phase
---------------------------------------------------------------------------------------
=> New parameters, shifts, and standard deviations

Atom        x       dx      sx       y       dy      sy       z       dz      sz       B       dB      sB      occ.

HO1      0.50000 0.00000 0.00000  0.00000 0.00000 0.00000  0.20250 0.00000 0.00000  0.30000 0.00000 0.00000  1.00000
NI2      0.00000 0.00000 0.00000  0.00000 0.00000 0.00000  0.00000 0.00000 0.00000  0.30000 0.00000 0.00000  1.00000

=>   Coefficients of basis vectors, shifts, and standard deviations:
Atom         C1        dC1       sC1        C2        dC2       sC2        C3        dC3       sC3
             C4        dC4       sC4        C5        dC5       sC5        C6        dC6       sC6
             C7        dC7       sC7        C8        dC8       sC8        C9        dC9       sC9
          MPhas     dMPhas    sMPhas

  HO1     0.089718  0.000000  0.065527  9.029646  0.000000  0.054908  0.000000  0.000000  0.000000
          0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
          0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
          0.000000  0.000000  0.000000
  NI2     0.765226  0.000000  0.125650 -1.242781  0.000000  0.050806  0.000000  0.000000  0.000000
          0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
          0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000  0.000000
          0.000000  0.000000  0.000000
```

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The moment $\boldsymbol{m}_{ljs}$ is calculated from the refined values of the Fourier components $\boldsymbol{S}_{kjs}$

$$\mathbf{m}_{ljs} = \sum_{\{k\}} \mathbf{S}_{kjs} exp\{-2\pi i \mathbf{k}\mathbf{R}_l\}$$

$$\mathbf{S}_{kjs} = \sum_{n\lambda} C^{\nu}_{n\lambda} \mathbf{S}^{k\nu}_{n\lambda}(js)$$

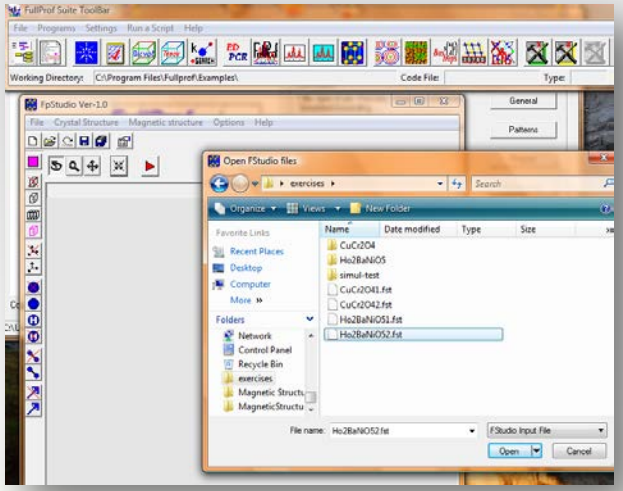
**Ho:** Mx = 0.09(6) $\mu_B$ ; Mz = 9.03(5) $\mu_B$

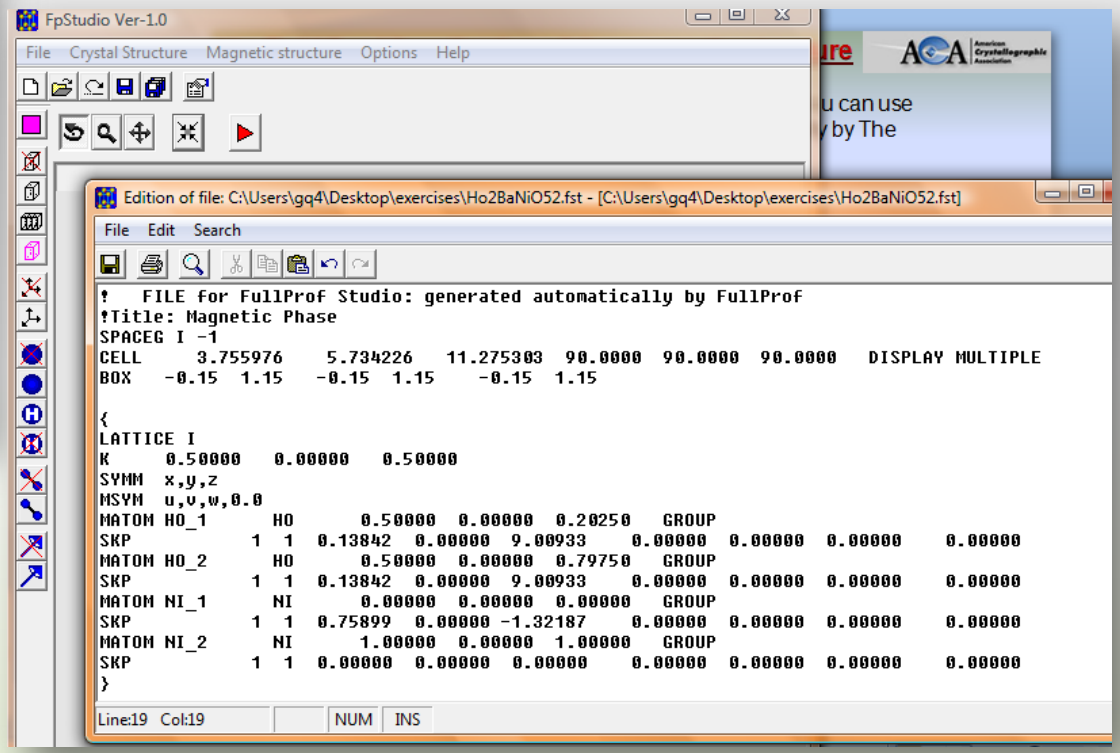
**Ni :** Mx = 0.77(12) $\mu_B$ ; Mz = -1.24(5) $\mu_B$

the moment of Ho is nearly parallel to the c-axis and the Ni-moment is canted by ~ 29 deg with respect to the c-axis

# VISUALIZATION OF THE MAGNETIC STRUCTURE

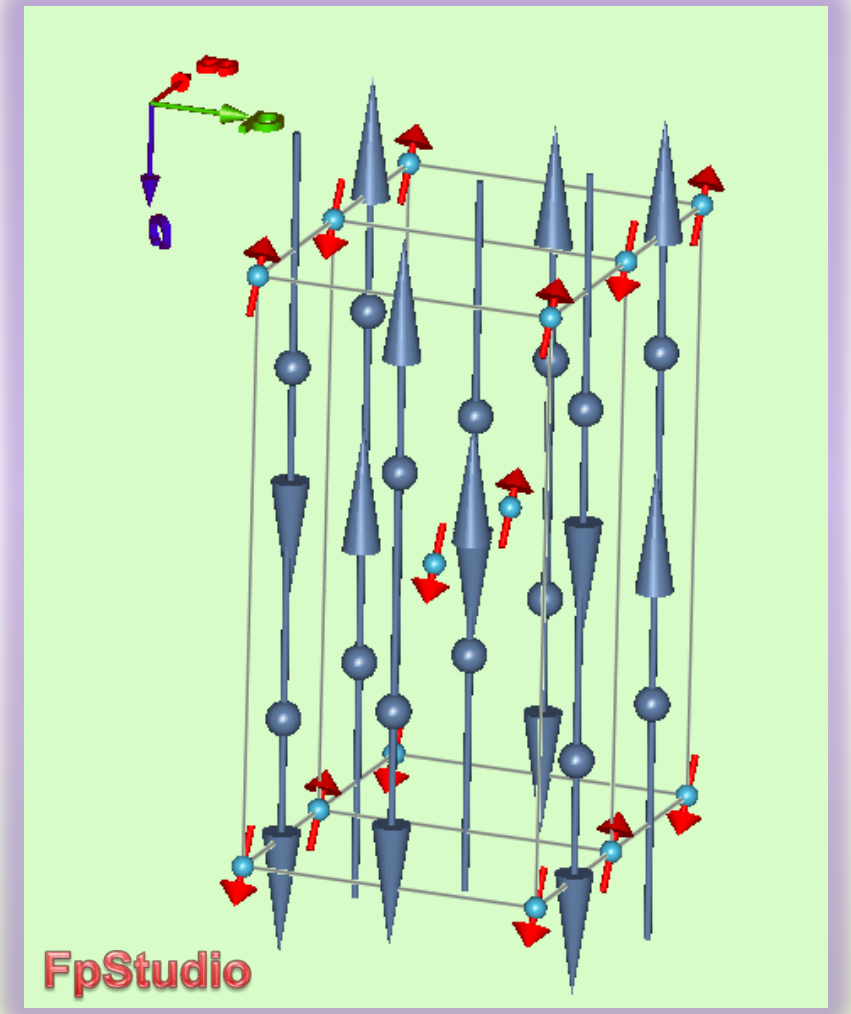
- ✓ to visualize the determined magnetic structure you can use **FpStudio** program. It reads *.fst files, generated automatically by The Fullprof or SARAh






- ✓ FpStudio uses Fourier coefficients notation (u,v,w). You can edit the input file if necessary..

# CONGRATULATIONS ! Here is your magnetic structure




- ✓ To see list of magnetic moments at each site:
  Magnetic structure ➔ List magnetic moments

Ho

Atom : HO1_1 HO

| x | y | z | Translation | k | MSYM | m(a) | m(b) | m(c) | Mtot |
|---|---|---|---|---|---|---|---|---|---|
| 0.500 | 0.000 | 0.203 | ( 0, 0, 0) | 1 | 1 | 0.090 | 0.000 | 9.030 | |
| | | | | | | 0.090 | 0.000 | 9.030 | 9.030 |
| | | | ( 0, 1, 0) | 1 | 1 | 0.090 | 0.000 | 9.030 | |
| | | | | | | 0.090 | 0.000 | 9.030 | 9.030 |
| 0.000 | 0.500 | 0.703 | ( 0, 0, 0) | 1 | 1 | 0.090 | 0.000 | 9.030 | |
| | | | | | | 0.090 | 0.000 | 9.030 | 9.030 |
| | | | ( 1, 0, 0) | 1 | 1 | -0.090 | 0.000 | -9.030 | |

Ni

Atom : NI2_1 NI

| x | y | z | Translation | k | MSYM | m(a) | m(b) | m(c) | Mtot |
|---|---|---|---|---|---|---|---|---|---|
| 0.000 | 0.000 | 0.000 | ( 0, 0, 0) | 1 | 1 | 0.765 | 0.000 | -1.243 | |
| | | | | | | 0.765 | 0.000 | -1.243 | 1.459 |
| | | | ( 0, 0, 1) | 1 | 1 | -0.765 | 0.000 | 1.243 | |
| | | | | | | -0.765 | 0.000 | 1.243 | 1.459 |
| | | | ( 0, 1, 0) | 1 | 1 | 0.765 | 0.000 | -1.243 | |
| | | | | | | 0.765 | 0.000 | -1.243 | 1.459 |
| | | | ( 0, 1, 1) | 1 | 1 | -0.765 | 0.000 | 1.243 | |
| | | | | | | -0.765 | 0.000 | 1.243 | 1.459 |
| | | | ( 1, 0, 0) | 1 | 1 | -0.765 | 0.000 | 1.243 | |
| | | | | | | -0.765 | 0.000 | 1.243 | 1.459 |
| | | | ( 1, 0, 1) | 1 | 1 | 0.765 | 0.000 | -1.243 | |