

Tutorial on Magnetic Structure Determination and Refinement using Neutron Powder Diffraction and FULLPROF

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Introduction

This document is a simple tutorial for using FULLPROF as a tool for determining magnetic structures using neutron powder diffraction (NPD). The user of this document should know the basic facts of magnetism and magnetic structures. It is supposed a good knowledge of crystallography and some practice and basic knowledge of the structure of a PCR file (the input control file needed for running FULLPROF). Magnetic symmetry considerations will not be treated in detail here (it is assumed that the user has some knowledge on that subject); however, the available document: *Symmetry and Magnetic Structures*, by J. Rodríguez-Carvajal and F. Bourée, that will be published in the Editions de Physique, treats largely the subject from the point of view of the representation theory. This document will be referenced hereafter as SMS. Some parts of the SMS text and the examples treated there have been taken for the present tutorial. A summary of the most important parts of SMS for this tutorial is given in the appendix of this document. In FullProf there are many ways of writing PCR files for treating magnetic structures; in this document we describe only the simplest ones.

Determination of magnetic structures using the programs of the FULLPROF SUITE

The procedure for determining a magnetic structure using powder diffraction is relatively simple. It can be summarised as follows:

- 1:** Collect a NPD of the sample in the paramagnetic state ($T > T_N$ or T_C). Refine the crystal structure using the collected data and get all the relevant structural and profile parameters. Use FULLPROF and WINPLOTR for doing this task.
- 2:** Collect a NPD below the ordering temperature. Normally additional magnetic peaks appear in the diffraction pattern. It is important to make a refinement by fixing all the structural parameters, without putting a magnetic model in the PCR file, in order to see clearly the magnetic contributions to the diffraction pattern. Get the peak positions of the additional peaks using WINPLOTR-2006 and save them in a format adequate to the program K-SEARCH.
- 3:** Determine the propagation vector(s) of the magnetic structure (See appendix for a summary of the formalism of propagation vectors) by using the program K-SEARCH or by trial and error with an additional phase in the PCR file treated in Le Bail Fit (LBF) mode (no magnetic model). If there are no additional peaks and only an additional contribution to the nuclear peaks is observed, the magnetic structure has as propagation vector $\mathbf{k} = (0, 0, 0)$.
- 4:** Once the propagation vector is determined, use the program BASIREPS in order to get the basis vectors of the irreducible representations (*irreps*) of the propagation vector group ($G_{\mathbf{k}}$).

see SMS or the appendix for more details). With the help of this program one can determine the Shubnikov group and the appropriate magnetic symmetry operators, or, alternatively, use directly the basis vectors of the *irreps*.

5: Solve the magnetic structure by using the symmetry information obtained in step 4 using trial and error methods (5-1) or the simulated annealing (SAnn) procedure (5-2) implemented in FULLPROF.

5-1: In the first case one has to modify the PCR file used in step 2 by adding an additional magnetic phase by putting $J_{bt}=1$ (magnetic phase with Fourier coefficients/magnetic moments referred to the unitary basis along the unit cell axes), $I_{rf}=-1$ (only satellites will be generated). The best way to create such additional magnetic phase is to copy it from an already existing PCR file similar to that of the current case and modify it using the symmetry information obtained in step 4. Run FULLPROF fixing nearly all parameters, except the magnetic moments or the coefficients of the basis functions, and check in the plots if the calculated magnetic peaks have intensities close to the observed ones. If not, change the magnetic model (use another representation or other magnetic symmetry operators) and try again. In some cases this is enough to solve the magnetic structure. In case this does not work use the method described in 5-2.

5-2: In the second case one has to modify the PCR file used in step 2 by adding an additional phase in LBF mode (as for one of the options in step 3). This additional phase has no atoms and we have to put $J_{bt}=2$, $I_{rf}=-1$ and $J_{view}=11$. The nuclear phase has to be treated with fixed scale factor and structural parameters. This allows getting the purely magnetic reflections in a separate file that can be used by FULLPROF in SAnn mode. This method will be explained later in detail.

6: Refine the magnetic using the Rietveld method implemented in FULLPROF. Once the magnetic model gives a calculated powder diffraction pattern close enough to the observed one, we start the refinement phase. If we use the trial and error method (5-1) the refinement step is just the continuation of the previous step. If the simulated annealing method (5-2) was used we have to translate the final solution stored in an automatically generated PCR file to the file for treating directly the powder diffraction profile.

The different steps described above and their order may be changed slightly depending on the previous knowledge the user has on the sample. We will illustrate these steps with a very simple case that may be useful for beginners in magnetic structure determination. We provide together with this document the data files of this example as well as other data files and PCR files corresponding to the examples treated in the SMS document.

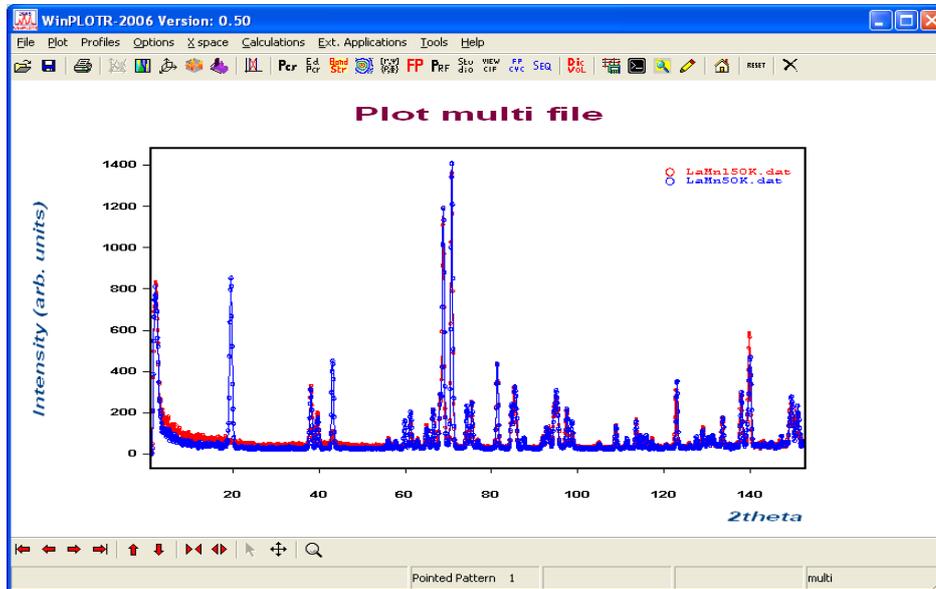
Determination of the magnetic structure of LaMnO₃.

Step 1:

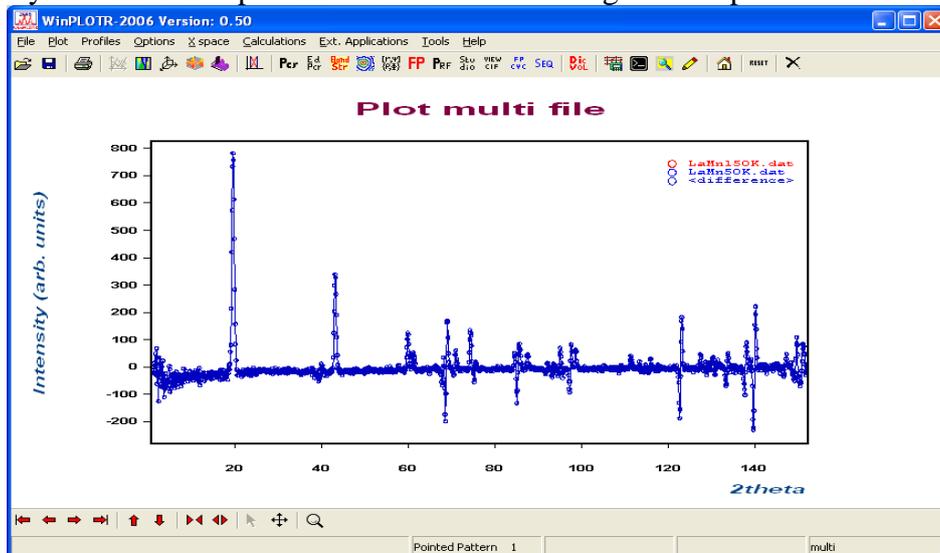
We provide two powder diffraction patterns of LaMnO₃ (F. Moussa, M. Hennion, J. Rodríguez-Carvajal, L. Pinsard and A. Revcolevschi, *Physical Review B* **54** (21), 15149 (1996)) taken at the LLB diffractometer G4.2 with $\lambda=2.59$ Å. The space group is $G=Pbnm$, the cell parameters are $a\approx 5.53$ Å, $b\approx 5.75$ Å and $c\approx 7.68$ Å 150K (paramagnetic phase, $T_N\approx 140$ K). The format of the data corresponds to $I_{ns}=6$ in FULLPROF. The pattern

corresponding to the magnetically ordered phase has been taken at 50K in the same conditions as that of the paramagnetic phase.

In addition to the data, we provide also a complete PCR file well adapted for refining the crystal structure of LaMnO_3 at 150K. The user can open the two diffraction patterns using WINPLOTR-2006 for a comparison. In the figure below we show the plot with the two patterns:

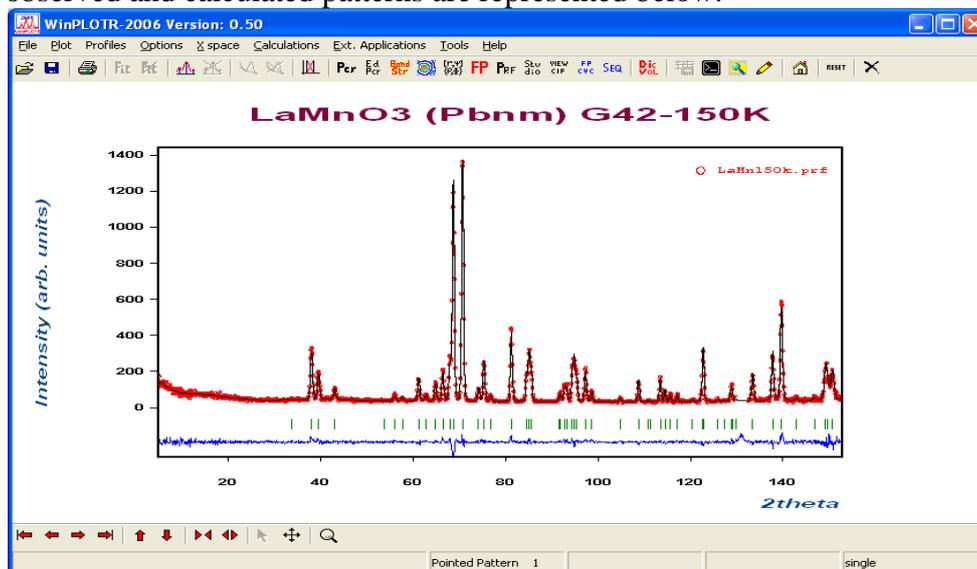


The pattern in blue corresponds to the magnetically ordered phase and one can see the appearance of strong peaks in the low angle part (15-70 degrees in 2θ). The strong peak at very low angle corresponds to the tail of the primary beam and the beam-stop. Using the menu: **Calculations** → **Difference** taking as profile A that of 50K and profile B that of 150 K we can represent the difference pattern alone by selecting the menu: **Profile** → **Show** and then selecting only the difference pattern. We obtain something like the pattern shown below:



One can see the prominent magnetic peaks and oscillating features due to thermal expansion and the consequent difference in cell parameters. It is also important to remark that the background of the 50K-150K difference pattern is negative. This is due to the diminution of the paramagnetic scattering. Notice also that the red curve in the first figure is above the blue one and the effect is more prominent at low angles.

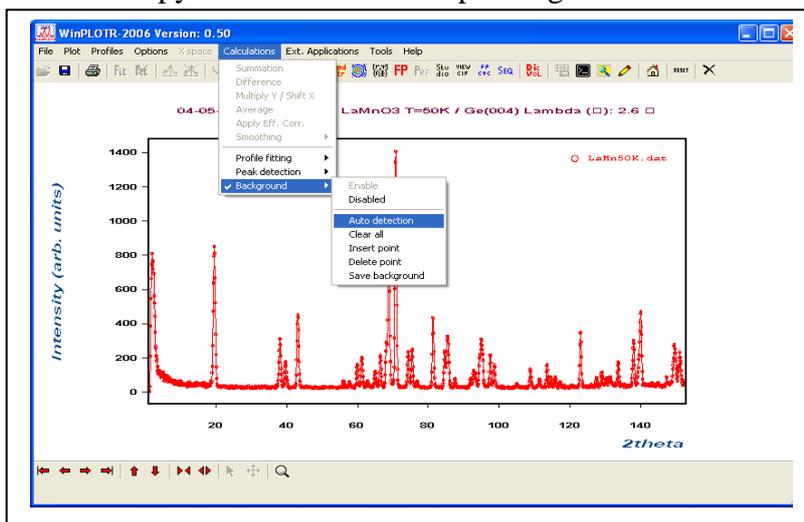
For completing the step 1 of the procedure the refinement of the crystal structure of LaMnO_3 can be done with the provided PCR file called `LaMn150k.pcr`. This is done straightforwardly by running FULLPROF from the TOOLBAR or directly from WINPLOTR-2006. The observed and calculated patterns are represented below:



Notice that we have excluded one region in which appears a broad peak from the sample environment.

Step 2:

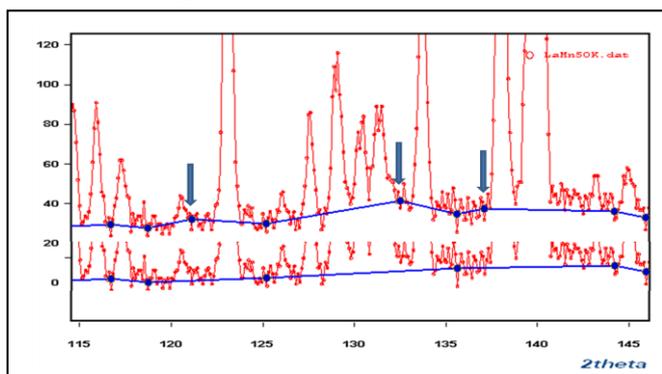
Now we copy the PCR file corresponding to 150K into another PCR file that we shall call `test-a.pcr`.



Before running FULLPROF, edit this file and fix all parameters, taking the precaution of incrementing arbitrarily the Chi-square value in order to oblige the program to save the PCR file event if the refinement (in fact a comparing calculation) goes worse. Another important point is that the background has changed; we can use WinPLOTR-2006 to select manually or automatically a

background for the pattern at 50K as shown in the figure. If one uses the automatic mode

(Auto detection) as shown in the figure, a series of background points are automatically generated. An inspection is needed in order to eliminate some of the points by selecting the appropriate option in the **Calculations** → **Background** → **Delete point** menu. In the following figure we show the aspect of the background after



eliminating the points marked with arrows.

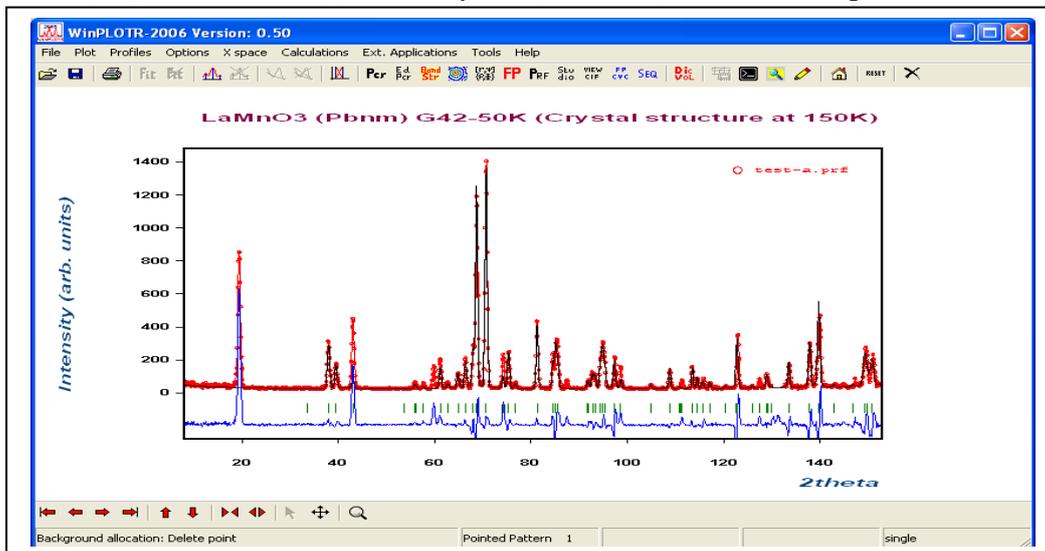
We save the background points in a file by selecting **Calculations**→ **Background**→ **Save background** menu. A file is created and from it the background can be pasted in the PCR file replacing the background refined at 150K. Below we show the aspect of the PCR file in which important points of the header part are emphasised.

```

COMM LaMnO3 (Pbnm) G42-50K (Crystal structure at 150K)
! Current global Chi2 (Bragg contrib.) = 999999.844
! Files => DAT-file: LaMn50k.dat, PCR-file: test-a
!Job  Npr  Nph  Nba  Nex  Nsc  Nor  Dum  Iwg  Ilo  Ias  Res  Ste  Nre  Cry  Uni  Cor  Opt  Aut
      1   7   1  30   3   0   1   0   0   0   0   0   0   0   0   0   0   0
!
!Ipr Ppl  Ioc  Mat  Pcr  Ls1  Ls2  Ls3  NLI  Prf  Ins  Rpa  Sym  Hkl  Fou  Sho  Ana
      0   0   1   0   1   0   4   0   0   1   6   0   0   0   0   0   0
! Lambda1 Lambda2  Ratio  Bkpos  Wdt  Cthm  muR  AsyLim  Rpolarz  2nd-muR->Patt# 1
      2.597000 2.597000 0.00000 90.00  8.0  0.00  0.65  180.00  0.00  0.00
!
!NCY  Eps  R_at  R_an  R_pr  R_gl  Thmin  Step  Thmax  PSD  Sent0
      15  0.10  1.00  1.00  1.00  1.00  1.0000  0.100000  152.9000  0.000  0.000
!
!2Theta/TOF/E(Kev)  Background  for Pattern# 1
      8.30000 47.0000
      11.90000 40.0000
      17.10000 34.0000
.....
!
! Excluded regions (LowT HighT) for Pattern# 1
      -10.00 8.20
      130.30 132.00
      160.00 180.00
!
!
      0  !Number of refined parameters
!
! Zero  Code  SyCos  Code  SySin  Code  Lambda  Code MORE ->Patt# 1
      0.10323 51.0 0.00000 0.0 0.00000 0.0 0.000000 0.00 0
.....

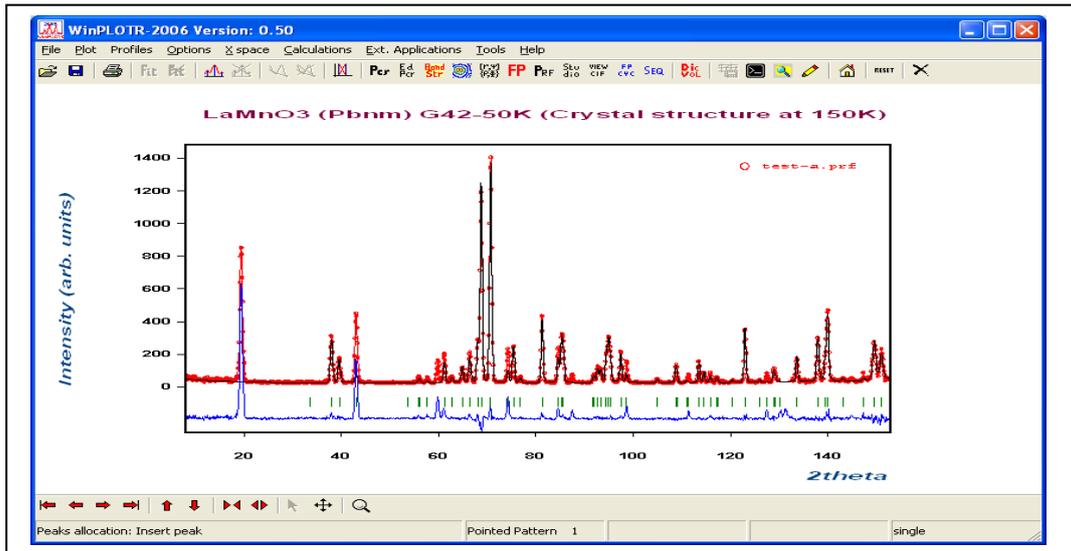
```

Notice that we use the profile function $N_{pr}=7$, we have changed the number of background points ($N_{ba}=30$), we use the March-Dollase model for preferred orientation ($N_{or}=1$), option to re-write the PCR file on output ($P_{cr}=1$), the data format adequate for G4.2 ($I_{ns}=6$), an effective absorption coefficient ($\mu_R=0.65$), the asymmetry correction is applied everywhere ($A_{syLim}=180.0$), fifteen cycles ($N_{CY}=15$) and we have put $A_{ut}=0$ in order to

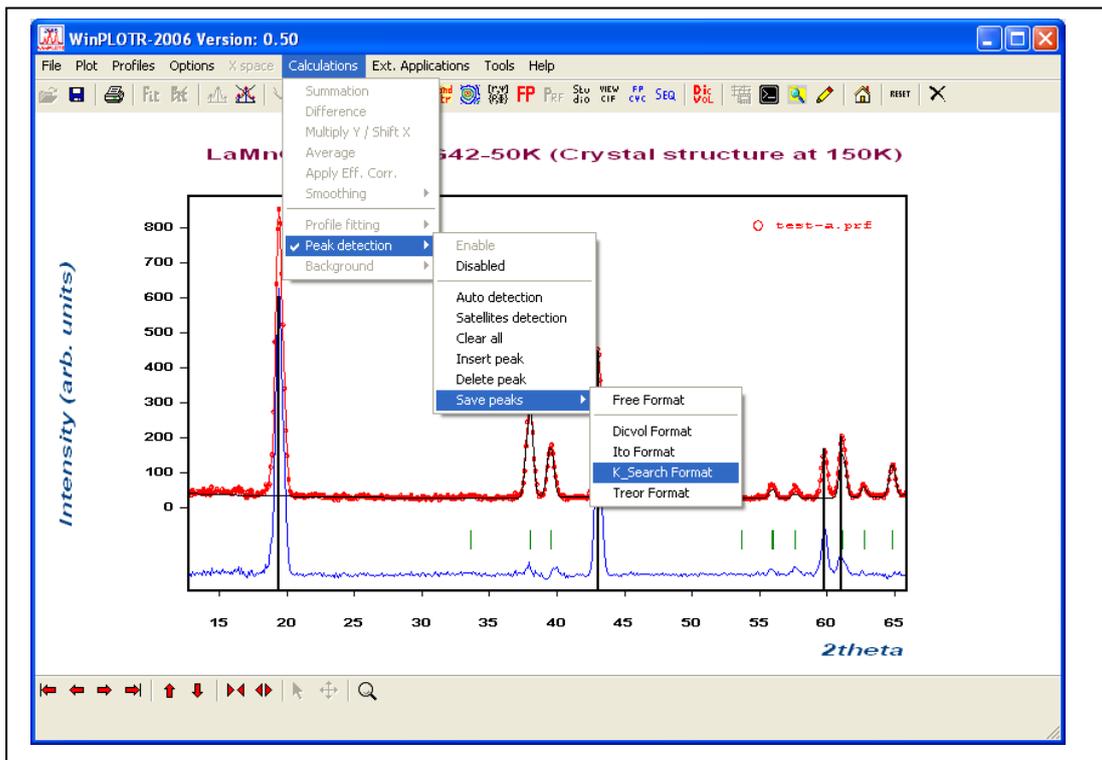


fix all parameter by putting the number of refined parameters equal to zero.

Doing all the above things and running FULLPROF we obtain a plot similar to that shown in the figure. If we refine only the cell parameters we obtain a much better agreement. We can see better the magnetic peaks as shown below after refining only the cell parameters.



Using this last plot we can select the magnetic peak positions at low angles. It is better to use a refined plot because the selection of magnetic peaks gives automatically corrected positions (zero shifts not needed). Few magnetic peaks are necessary to search the propagation vector for commensurate structures. In the following figure we show that we have selected the four most prominent peaks at low angles and we want to save them in a file with the format needed



by the program K-SEARCH.

After selection the menu option **Calculations** → **Peak detection** → **Save peaks** → **K_Search Format** the program opens a dialog in which the user can select the appropriate options. We

must start considering only the special k-vectors option and go for incommensurate structures if the case we are unable to find a solution.

Step 3:

Having a look into the previous figure, we see that some magnetic peaks seem to appear on top of nuclear peaks. This is an indication that the propagation vector may be $\mathbf{k}=\mathbf{0}$. If we run the program K-SEARCH just after saving the file `k-search.sat`, in which the selected (or

```

C:\WINDOWS\system32\cmd.exe
*****
*          PROGRAM K_SEARCH          *
*****
<J.R.C. ILL-January 2009>

=> The expected maximum R-factor for a solution is:    3.0957
=> Writing partial results ...

=> Testing 90 internal k-vectors
Solution:      1 k =(< 0.0000 0.0000 0.0000>) R-F:    0.6691
Solution:      2 k =(< 0.0000 0.2500 0.0000>) R-F:    0.6703
Solution:      3 k =(< 0.0000 0.2500 0.1250>) R-F:    1.7378
Solution:      4 k =(< 0.2500 0.2500 0.1250>) R-F:    0.7093
=> Special k-vector solutions found!

=> List of the best 10 solutions for 4 satellites

      Kx          Ky          Kz          R-factor
0.000000  0.000000  0.000000  0.669077
0.000000  0.250000  0.000000  0.670317
0.250000  0.250000  0.125000  0.709284
0.000000  0.250000  0.125000  1.737757

=> A probable solution is the special kvector ks =(< 0.0000 0.0000 0.0000>)
=> The corresponding R-factor is:    0.6691

```

automatically detected satellite) peaks are saved, a window opens showing the solutions found by the program. Do not forget to select the console window and press the *enter* key (\downarrow) to close it if we want to re-run the program.

In our case is clear that the $\mathbf{k} = (0, 0, 0)$ solution is the best. This can be verified by repeating the final part of the step 2 in which we select more peaks at higher angles. Sometimes a better R-factor is found for a wrong solution when the number of peaks is small. For instance, a small shift in positioning one of the four peaks would give the solution $\mathbf{k}=(0, \frac{1}{4}, 0)$, with a better R-factor. This has always to be checked by using more peaks or by doing a LBF generating the satellites.

Let us describe how to introduce an additional phase using the LBF method. We can make a copy of the file `test-a.pcr` into the file `test-b.pcr`, edit this last file and add a new phase. For doing that we change the number of phase to two ($N_{ph}=2$) and we duplicate the complete description of the phase block (including the profile parameters). After that, in the phase 2 we change eventually the name, we remove the atoms and we put $J_{bt}=2$, $I_{rf}=-1$ and $N_{vk}=1$, we have to add the propagation vector in the appropriate place. The aspect of the important parts of the PCR file is shown below:

```

COMM LaMnO3 (Pbnm) G42-50K (Crystal structure at 150K + Le Bail Fit)
! Current global Chi2 (Bragg contrib.) =    23.81
! Files => DAT-file: LaMn50K.dat, PCR-file: test-b
!Job Npr Nph Nba Nex Nsc Nor Dum Iwg Ilo Ias Res Ste Nre Cry Uni Cor Opt Aut
  1   7   2   30   3   0   1   0   0   0   0   0   0   0   0   0   0   0   0   0
.....
      0      !Number of refined parameters

```

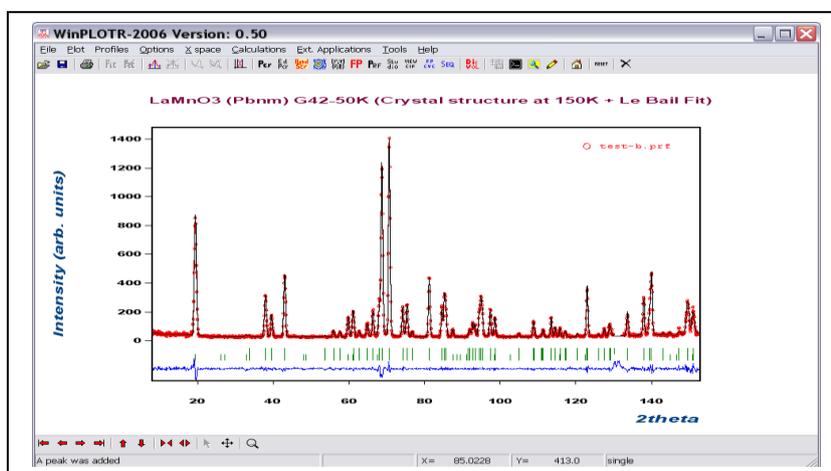
Notice that we have put $Aut=0$ because we will fix all parameters before starting the LBF run.

```

.....
!
!      a          b          c          alpha      beta      gamma      #Cell Info
!      5.536947   5.749676   7.668954   90.000000   90.000000   90.000000
!      21.000000   31.000000   11.000000   0.000000   0.000000   0.000000
! Pref1 Pref2  Asy1    Asy2    Asy3    Asy4    S_L    D_L
! 1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.03500 0.02200
!      0.00      0.00      0.00      0.00      0.00      0.00      0.00      0.00
!-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern# 1: 16.76
!-----
LaMnO3 (Magnetic contribution, without model)
!
! Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
! 0 0 0 0.0 0.0 1.0 2 -1 0 0 0 967.367 1 7 1
!
! Jvi Jdi Hel Sol Mom Ter Brind RMua RMub RMuc Jtyp Nsp_Ref Ph_Shift N_Domains
! 11 0 0 0 0 0 1.0000 0.0000 0.0000 0.0000 1 0 0 0
!
P -1 <--Space group symbol for hkl generation
!-----> Profile Parameters for Pattern # 1
! Scale Shapel Bov Str1 Str2 Str3 Strain-Model
! 2.9309 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0
! 0.00000 0.000 0.000 0.000 0.000 0.000 0.000
! U V W X Y GauSiz LorSiz Size-Model
! 0.076688 -0.277607 0.397605 0.048728 0.000000 0.000000 0.000000 0
! 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
! a b c alpha beta gamma #Cell Info
! 5.536947 5.749676 7.668954 90.000000 90.000000 90.000000
! 21.000000 31.000000 11.000000 0.000000 0.000000 0.000000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
! 1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.03500 0.02200
! 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! Propagation vectors:
! 0.0000000 0.0000000 0.0000000 Propagation Vector 1
! 0.0000000 0.0000000 0.0000000
! 2Th1/TOF1 2Th2/TOF2 Pattern # 1
! 8.200 152.900 1

```

We have removed the atoms and selected the LBF ($Jbt=2$) with generation of satellites ($Irf=-1$). $Nvk=1$ tells the program that we have a single propagation vector that is given after the line in which we have the preferred orientation parameters. Notice that we have put also $More=1$ in order to introduce the new line starting with Jvi . The value $Jvi=11$ tells the program that it has to generate a list of integrated intensities grouped into clusters that can be treated again by FULLPROF when using the SAnn mode. The rest of the values in the line are not important except $Jtyp$ that should be equal to 1 (neutrons). The program handles directly the values if we provide only the first item $Jvi=11$. Notice that the



space group used is “P -1”, this is because the symbol is used for generating the fundamental reflections and then the satellites (that in this case coincide) and no symmetry is assumed because we do not know yet the magnetic structure. Running FULLPROF with the above file one obtains after refining the cell parameters and the FWHM parameters, a plot of

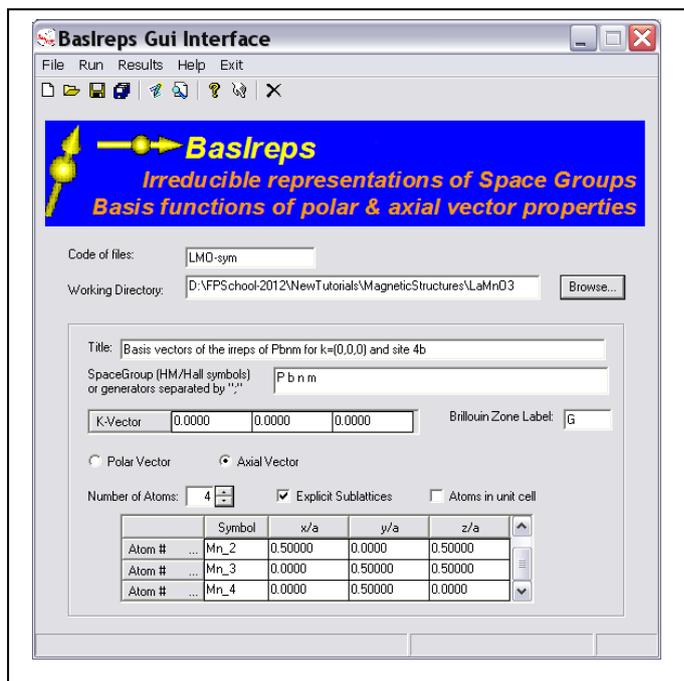
the observed and calculated patterns similar to that shown in the figure above. The program has produced several files containing intensities, in particular the file called `test-b2_cltr.int`, containing exclusively the magnetic contribution with reflections re-grouped when forming part of a cluster. The header of the file is written below:

```
!Phase No:2 LaMnO3 (Magnetic contribution) Overlapped reflections re-grouped-> Obs = j LP F^2
(4i4,2f16.5,i4,3f14.4)
2.59700 0 2 0.6500
1
1 0.00000 0.00000 0.00000
0 0 1 1 572.19104 7.06131 2 0.0000 0.0000 19.4976
0 1 0 1 2.70224 1.51152 2 0.0000 0.0000 26.1057
1 0 0 1 1.81073 1.31823 2 0.0000 0.0000 27.1281
0 -1 1 1 -1.00000 0.78080 2 0.0000 0.0000 32.7923
0 1 1 1 11.07332 1.10422 2 0.0000 0.0000 32.7923
-1 0 1 1 -1.00000 0.52146 2 0.0000 0.0000 33.6286
1 0 1 1 8.85244 0.73746 2 0.0000 0.0000 33.6286
1 -1 0 1 -1.00000 0.16060 2 0.0000 0.0000 38.0035
1 1 0 1 21.08212 0.22712 2 0.0000 0.0000 38.0035
```

The first line contains a title, the second the format in which the data have to be read, the third line contains the wavelength. The 0 indicates that we have squared structure factors (in fact intensities for powders), the 2 indicates that we have powder data and then the observations contain the product of the multiplicity, Lorentz factor and the square of the structure factor. The fourth line contains the number of propagation vectors (one in this case), the fifth line contains the ordinal number of the propagation vector and their components. The rest of the lines are the *hkl* indices of the parent reflection and the number in the list of the propagation vector, the integrated intensity, a pseudo-sigma, the multiplicity, non-used values and the 2theta angle of the reflection. The file may be used for doing a SAnn job for determining the magnetic structure.

Step 4:

As the propagation vector is $\mathbf{k} = (0, 0, 0)$, the magnetic unit cell is identical to the nuclear cell. The Mn atoms are in the Wyckoff position *4b*: $1(1/2,0,0)$, $2(1/2,0,1/2)$, $3(0,1/2,1/2)$ and $4(0,1/2,0)$, with four sublattices. The whole symmetry analysis may be performed by hand or by using one of the available computing programs doing the work automatically. We use



hereafter the program BASIREPS [11]. The formulas described in the appendix corresponding to the section "Representation analysis for Magnetic Structures" are programmed in BASIREPS and the user can simply use it with a minimal knowledge of group theory.

The input for BASIREPS is very simple and normally only the first representative of the Wyckoff site is needed. In this particular case we want a well defined order of the atoms of the different sublattices of the *4b* site. The input is shown in the dialog of the GUI for BASIREPS. Notice that the name of the atoms when the **Explicit Sublattices** check box is marked are

given with an underscore and a number. This is a constraint of the program. If we do not use this option we have to provide only the first representative atom of the full site. The program generates the sublattices by applying the symmetry operators of the space group but the order may be different from that of interest to the user. If the check box **Atoms in unit cell** is marked, the program applies the appropriate lattice translations for obtaining positive fractional coordinates of the atoms of all generated sublattices.

The propagation vector is invariant, so $\mathbf{G}_k = \mathbf{G} = Pbnm$. The list of the irreducible representations (all of them of dimension 1) is given in Table 1, in which $p=1/2$. This table has been prepared from the output of BASIREPS.

Table 1: Irreducible representations of $\mathbf{G}_k = \mathbf{G} = Pbnm$.

Irreps	{1}	{2 _z 00p}	{2 _x pp0}	{2 _y ppp}	{-1}	m={m _z 00p}	b={m _x pp0}	n={m _y ppp}	SG
Γ_1 :	1	1	1	1	1	1	1	1	<i>Pbnm</i>
Γ_2 :	1	1	1	1	-1	-1	-1	-1	<i>Pb'n'm'</i>
Γ_3 :	1	1	-1	-1	1	1	-1	-1	<i>Pb'n'm</i>
Γ_4 :	1	1	-1	-1	-1	-1	1	1	<i>Pbnm'</i>
Γ_5 :	1	-1	1	-1	1	-1	1	-1	<i>Pbn'm'</i>
Γ_6 :	1	-1	1	-1	-1	1	-1	1	<i>Pb'nm</i>
Γ_7 :	1	-1	-1	1	1	-1	-1	1	<i>Pb'nm'</i>
Γ_8 :	1	-1	-1	1	-1	1	1	-1	<i>Pbn'm</i>

We have provided the symbol of the Shubnikov group (SG) corresponding to each irreducible representation in the last column of the table. All *irreps* are real, so we have a perfect correspondence between *irreps* and Shubnikov groups.

We do not give here the matrices of the magnetic representation Γ_m , of dimension $3 \times p_j = 3 \times 4 = 12$, because it can be easily deduced by hand or from the information given in the output file of BASIREPS (we give the details in the Appendix B). Γ_m has the characters: $\chi(\Gamma_m - 4b) = (12, 0, 0, 0, 12, 0, 0, 0)$ and decomposes (see equations 14 in the Appendix A) in terms of the *irreps* of the previous table as follows:

$$\Gamma_m(4b) = 3\Gamma_1 \oplus 3\Gamma_3 \oplus 3\Gamma_5 \oplus 3\Gamma_7$$

This means that if a single *irrep* defines the magnetic structure we have only three free parameters: $n_f = n_v \times \dim(\Gamma_v) = 3 \times 1 = 3$, which is well below the 12 components of magnetic moments in the primitive cell. The calculation of the basis vectors applying the formula (17) in the appendix A is done by BASIREPS. Here we reproduce the (simplified) output of the calculation for the *irrep* Γ_3 corresponding to the experimental magnetic structure:

```

+++++
Basis functions of Representation IRrep( 3) of dimension 1 contained 3 times in GAMMA
+++++
      SYMM  x, y, z      -x+1, -y, z+1/2      -x+1/2, y+1/2, -z+1/2      x-1/2, -y+1/2, -z
      Atoms:      Mn_1      Mn_2      Mn_3      Mn_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)

      SYMM  x, y, z      Atom: Mn_1      0.5000  0.0000  0.0000
      Sk(1): (u, v, w)
      SYMM  -x+1, -y, z+1/2      Atom: Mn_2      0.5000  0.0000  0.5000
      Sk(2): (-u, -v, w)
      SYMM  -x+1/2, y+1/2, -z+1/2      Atom: Mn_3      0.0000  0.5000  0.5000
      Sk(3): (u, -v, w)
      SYMM  x-1/2, -y+1/2, -z      Atom: Mn_4      0.0000  0.5000  0.0000
      Sk(4): (-u, v, w)

```

The fact that only four *irreps* contribute to the magnetic representation is due to the fact that the Wyckoff position (4b) contains a centre of symmetry and the *irreps* with $\chi(\bar{1})=-1$ are not allowed. In other terms, time inversion cannot be mixed with the centre of symmetry in this case because the atoms in that position would have a zero magnetic moment. The point group $\bar{1}$ is not admissible.

The interpretation of the above table in terms of the mathematical expressions given in the appendix is as follows (the indices $n\lambda$ are combined in a single integer index):

Example 1: the atomic component of the basis vector (BsV) 1 for atom Mn₂ of representation Γ_3 for propagation vector (000) is: $\mathbf{S}_{n\lambda}^{k\nu}(js) = \mathbf{S}_1^{(000)3} Mn_2 = (-1, 0, 0)$

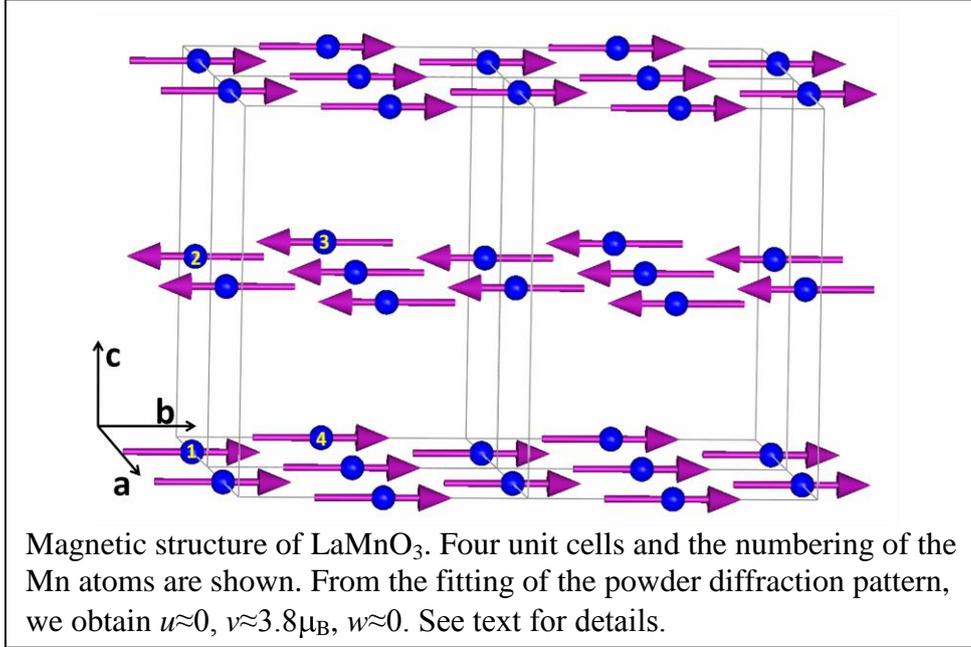
Example 2: The atomic component of the basis vector 2 for atom Mn₃ of representation Γ_3 for propagation vector (000) is: $\mathbf{S}_{n\lambda}^{k\nu}(js) = \mathbf{S}_2^{(000)3} Mn_3 = (0, -1, 0)$

Example 3: the full basis vector 2 for representation Γ_3 and propagation vector (000) for the whole set of atoms is:

$$BsV(2,1:4) \rightarrow \Psi_{n\lambda}^{k\nu} = \Psi_2^{(000)3} = \overbrace{(0, 1, 0)}^1, \overbrace{(0, -1, 0)}^2, \overbrace{(0, -1, 0)}^3, \overbrace{(0, 1, 0)}^4$$

If we call u, v, w the three free mixing coefficients (in our case they are real numbers because $\mathbf{k}=0$), the magnetic structure can be globally described by the global Fourier coefficient (it coincides with the whole set of magnetic moments):

$$\mathbf{m}_{[1,2,3,4]} = \mathbf{S}_{[k]} = \sum_{n\lambda} C_{n\lambda}^{k\nu} \Psi_{n\lambda}^{k\nu} = u\Psi_1^{k\nu} + v\Psi_2^{k\nu} + w\Psi_3^{k\nu}$$



The individual magnetic moments of the four atoms are:

$$Sk(1) \rightarrow \mathbf{m}_1 = \mathbf{S}_{k1} = \sum_{n\lambda} C_{n\lambda}^{k\nu} \mathbf{S}_{n\lambda}^{k\nu}(1) = (u, v, w); \quad Sk(2) \rightarrow \mathbf{m}_2 = \mathbf{S}_{k2} = \sum_{n\lambda} C_{n\lambda}^{k\nu} \mathbf{S}_{n\lambda}^{k\nu}(2) = (-u, -v, w)$$

$$Sk(3) \rightarrow \mathbf{m}_3 = \mathbf{S}_{k3} = \sum_{n\lambda} C_{n\lambda}^{k\nu} \mathbf{S}_{n\lambda}^{k\nu}(3) = (u, -v, w); \quad Sk(4) \rightarrow \mathbf{m}_4 = \mathbf{S}_{k4} = \sum_{n\lambda} C_{n\lambda}^{k\nu} \mathbf{S}_{n\lambda}^{k\nu}(4) = (-u, v, w)$$

A very common notation in the literature is that of sequence of signs $G(+,-,+,-)$, $A(+,-,-,+)$, $F(+,+,+,+)$ and $C(+,+,-,-)$, called *modes* by Bertaut [6,7,8,9]. For the current *irrep* Γ_3 (Shubnikov group $Pb'n'm$) the label for the magnetic structure in terms of these modes is: (G_x, A_y, F_z) .

The structure is antiferromagnetic with a very weak ferromagnetic component (only seen by macroscopic magnetisation measurements) along c and formed by ferromagnetic planes stacked antiferromagnetically along c . This is the so called A-type AF structure in literature about perovskites. The structure is shown in the above Figure.

If we list the four magnetic moments (identical to Fourier coefficients in this case) as:

$$1(u,v,w); \quad 2(-u,-v,w); \quad 3(u,-v,w); \quad 4(-u,v,w)$$

together with the symmetry operators that pass from atom 1 to 1, 2, 3, 4, respectively:

$$1(x,y,z):1; \quad 2(-x+1,-y,z+1/2):2_{1z}; \quad 3(-x+1/2,y+1/2,-z+1/2):2_{1y}; \quad 4(x-1/2,-y+1/2,-z):2_{1x}$$

we can see that the rotational parts of the symmetry operators correspond to the action of the elements: $1, 2_z, 2_y$ and 2_x respectively. We can interpret the symbols (u, v, w) as matrices corresponding to the transformation of the magnetic moment of the atom 1 to the magnetic moments of the atoms 1,2,3,4. As binary axes are proper rotations, we can see that the matrices correspond to the symmetry operators: $1, 2_z, 2'_y$ and $2'_x$ respectively. Time inversion is then associated with the symmetry operators 2_{1y} and 2_{1x} as required by the Shubnikov group $Pb'n'm$ (see the characters of the *irrep* Γ_3 for operators $\{2_x|1/2^1/2^0\}$ and $\{2_y|1/2^1/2^1/2\}$ in Table 1).

Step 5:

In the case of LaMnO_3 , a simple trial and error method, using the symmetry information of the step 4, provides the correct magnetic model. As we have anticipated, the correct solution corresponds to the *irrep* Γ_3 for representation, to arrive to this conclusion we have to test, at this stage, the different representations using reasonable values of the magnetic moments. Let us summarise the list of basis vectors and Fourier coefficients for the four possible *irreps* in the case of LaMnO_3 adapted from the output of BASIREPS.

```

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

```

	SYMM	x, y, z	-x+1, -y, z+1/2	-x+1/2, y+1/2, -z+1/2	x-1/2, -y+1/2, -z											
	Atoms:	Mn_1	Mn_2	Mn_3	Mn_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)

SYMM	x, y, z	Sk(1):	(u, v, w)
SYMM	-x+1, -y, z+1/2	Sk(2):	(-u, -v, w)
SYMM	-x+1/2, y+1/2, -z+1/2	Sk(3):	(-u, v, -w)
SYMM	x-1/2, -y+1/2, -z	Sk(4):	(u, -v, -w)

```

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

```

	SYMM	x, y, z	-x+1, -y, z+1/2	-x+1/2, y+1/2, -z+1/2	x-1/2, -y+1/2, -z											
	Atoms:	Mn_1	Mn_2	Mn_3	Mn_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)

SYMM	x, y, z	Sk(1):	(u, v, w)
SYMM	-x+1, -y, z+1/2	Sk(2):	(-u, -v, w)
SYMM	-x+1/2, y+1/2, -z+1/2	Sk(3):	(u, -v, w)
SYMM	x-1/2, -y+1/2, -z	Sk(4):	(-u, v, w)

```

+++++
=> Basis functions of Representation IRrep( 5) of dimension 1 contained 3 times in GAMMA
+++++

      SYMM  x,y,z      -x+1,-y,z+1/2      -x+1/2,y+1/2,-z+1/2      x-1/2,-y+1/2,-z
Atoms:      Mn_1      Mn_2      Mn_3      Mn_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)

      SYMM x,y,z      Sk(1): (u, v, w)
      SYMM -x+1,-y,z+1/2      Sk(2): (u, v,-w)
      SYMM -x+1/2,y+1/2,-z+1/2      Sk(3): (u,-v, w)
      SYMM x-1/2,-y+1/2,-z      Sk(4): (u,-v,-w)

+++++
=> Basis functions of Representation IRrep( 7) of dimension 1 contained 3 times in GAMMA
+++++

      SYMM  x,y,z      -x+1,-y,z+1/2      -x+1/2,y+1/2,-z+1/2      x-1/2,-y+1/2,-z
Atoms:      Mn_1      Mn_2      Mn_3      Mn_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)

      SYMM x,y,z      Sk(1): (u, v, w)
      SYMM -x+1,-y,z+1/2      Sk(2): (u, v,-w)
      SYMM -x+1/2,y+1/2,-z+1/2      Sk(3): (-u, v,-w)
      SYMM x-1/2,-y+1/2,-z      Sk(4): (-u, v, w)

```

For treating magnetic structures in FULLPROF there are several ways. Let us start by describing the most important points for constructing a PCR file in which we want to introduce the calculation of the magnetic contribution to a powder diffraction pattern.

A magnetic structure phase requires describing only the magnetic atoms in the unit cell. So we can start making a copy of the crystallographic structural phase and removing the non-magnetic atoms. We have to put $Jbt=1$ or $Jbt=-1$ to tell the program that what we are describing is a magnetic structure and to make calculations of magnetic structure factors and magnetic intensities. The negative value indicates that we will use spherical description of the Fourier components of magnetic moments. As stated above $Irf=-1$ is necessary to instruct the program to generate only the magnetic satellites for the magnetic contribution. If the propagation vector is $\mathbf{k}=(0, 0, 0)$ this is not necessary and we can put $Irf=0$ and $Nvk=0$. We have to put also $Isy=-1$ or $Isy=-2$ for telling the program that we will read symmetry instructions ($Isy=-1$) or directly the component of the basis vectors of the *irreps* ($Isy=-2$). The symbol of the space group that we need to provide in the magnetic phase is not used for generating atoms. It is only used for generating magnetic reflections, so, in the absence of the knowledge of the magnetic symmetry it is safe to use the symbol "L -1" where L is the lattice symbol: P, A, B, C, I, F or R. The program generates at the end a shorter list of magnetic reflections with the proper multiplicity that can be re-used for reading the indices (using $Irf=1$) instead of re-generating the reflections for each run if we do not change the magnetic model. After the symbol of the space group for generating reflections if we have to provide the number ($Nsym$) of symmetry operators (SYMM), if the magnetic structure is centrosymmetric ($Cen=2$) or not ($Cen=1$), the Laue class number ($Laue$) and the number ($MagMat$) of different sets of magnetic operators (MSYM).

After providing this information we have to introduce the magnetic atoms lines in which the magnetic form factor symbol, following immediately after the label of the atom, has to be given. For transition metals the name identifying the magnetic form factor is given as symbol: MCSV, CS is the chemical symbol and V is a number corresponding to the valence of the magnetic ion. For rare earths the symbol is JCSV to instruct the program to use the dipolar

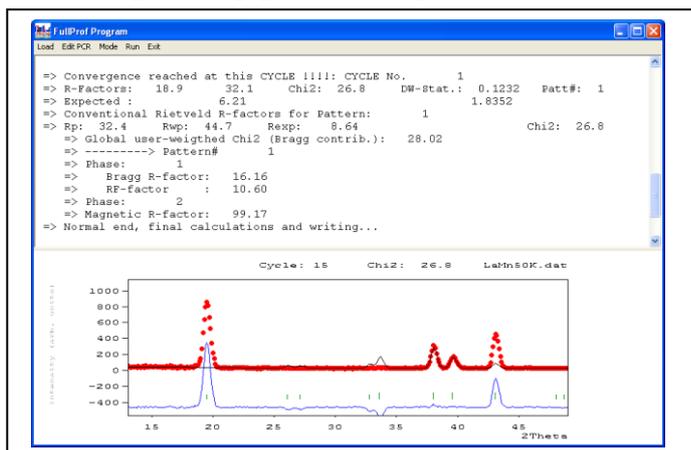
approximation for the form factor. The real part of the Fourier coefficients of magnetic moments (here equivalent to magnetic moments, see equation (6) in appendix A) are provided after the coordinates, isotropic temperature factor and occupation factor. The line of refinement codes is given just below. The imaginary components as well as an eventual magnetic phase related to the site (none of them necessary when $\mathbf{k}=1/2\mathbf{H}$) are provided in an additional line followed by another line with the refinement codes.

We reproduce below the magnetic part of the PCR file corresponding to the first *irrep* calculated by BASIREPS, using magnetic symmetry operators.

```

!-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern# 1: 99.17
!-----
LaMnO3 (Magnetic contribution) irrep1
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
 1 0 0 0.0 0.0 1.0 1 -1 -1 0 0 967.367 1 7 0
!
P -1 <--Space group symbol for hkl generation
!Nsym Cen Laue MagMat
 4 2 3 1
!
SYMM x,y,z
MSYM u,v,w, 0.0
SYMM -x+1,-y,z+1/2
MSYM -u,-v,w, 0.0
SYMM -x+1/2,y+1/2,-z+1/2
MSYM -u,v,-w, 0.0
SYMM x-1/2,-y+1/2,-z
MSYM u,-v,-w, 0.0
!
!Atom Typ Mag Vek X Y Z Biso Occ Rx Ry Rz
! Ix Iy Iz beta11 beta22 beta33 MagPh
Mn MMN3 1 0 0.50000 0.00000 0.00000 0.46901 0.50000 0.143 2.000 1.012
 0.000 0.000 0.000 0.000 0.000 0.000 0.00000
 0.00 0.00 0.00 0.00 0.00 0.00 0.00
!-----> Profile Parameters for Pattern # 1
! Scale Shape1 Bov Str1 Str2 Str3 Strain-Model
 2.9309 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0
 0.00000 0.000 0.000 0.000 0.000 0.000 0.000
! U V W X Y GauSiz LorSiz Size-Model
 0.089148 -0.323950 0.426334 0.054033 0.000000 0.000000 0.000000 0
 0.000 0.000 0.000 0.000 0.000 0.000 0.000
! a b c alpha beta gamma #Cell Info
 5.536546 5.749394 7.668513 90.000000 90.000000 90.000000
 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
! Pref1 Pref2 Asy1 Asy2 Asy3 Asy4 S_L D_L
 1.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.03500 0.02200
 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
! Propagation vectors:
 0.000000 0.000000 0.000000 Propagation Vector 1
 0.000000 0.000000 0.000000
! 2Th1/TOF1 2Th2/TOF2 Pattern # 1
 8.200 152.900 1

```



If we run FULLPROF fixing all parameters and putting arbitrary magnetic symmetry operators as in the present example, we see that the agreement is very poor, and the most important is that the strongest reflection (001) is calculated with zero intensity. This is because the first *irrep* corresponds to the Shubnikov group *Pbnm* that has (001) as a forbidden reflection.

If we try to refine the magnetic

moment a divergence condition will appear at some cycle.

We give again the relevant part of the PCR file, now corresponding to the *irrep* Γ_7 . The other parts are identical to the previous PCR file

```

. . . . .
!
SYMM x,y,z
MSYM u,v,w, 0.0
SYMM -x+1,-y,z+1/2
MSYM u, v,-w, 0.0
SYMM -x+1/2,y+1/2,-z+1/2
MSYM -u, v,-w, 0.0
SYMM x-1/2,-y+1/2,-z
MSYM -u, v, w, 0.0
!
!Atom Typ Mag Vek X Y Z Biso Occ Rx Ry Rz
! Ix Iy Iz beta11 beta22 beta33 MagPh
Mn MMN3 1 0 0.50000 0.00000 0.00000 0.46901 0.50000 0.143 2.000 1.012
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
. . . . .

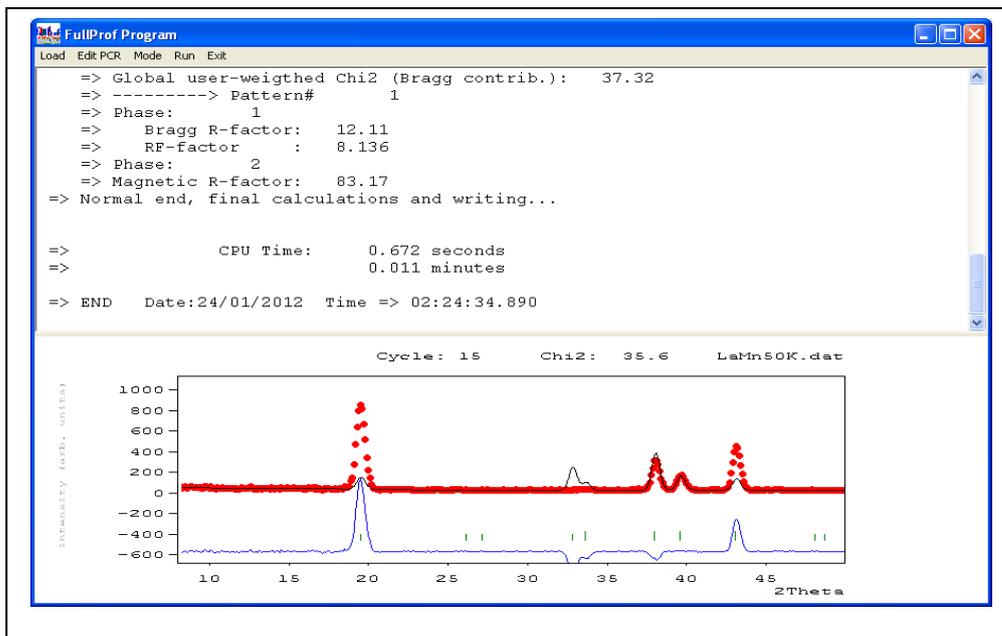
```

If we test the representation 7 corresponding to the Shubnikov group $Pb'nm'$ we obtain also a very bad result without calculated intensity for the most prominent magnetic reflection (001). A similar result is observed for *irrep* Γ_5 . Only when we use the *irrep* Γ_3 , corresponding to the Shubnikov group $Pb'n'm$, the result indicates that we can start to refine.

```

. . . . .
!
SYMM x,y,z
MSYM u, v, w, 0.0
SYMM -x+1,-y,z+1/2
MSYM -u, -v, w, 0.0
SYMM -x+1/2,y+1/2,-z+1/2
MSYM u, -v, w, 0.0
SYMM x-1/2,-y+1/2,-z
MSYM -u, v, w, 0.0
!
!Atom Typ Mag Vek X Y Z Biso Occ Rx Ry Rz
! Ix Iy Iz beta11 beta22 beta33 MagPh
Mn MMN3 1 0 0.50000 0.00000 0.00000 0.46901 0.50000 2.442 1.424 1.947
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00
. . . . .

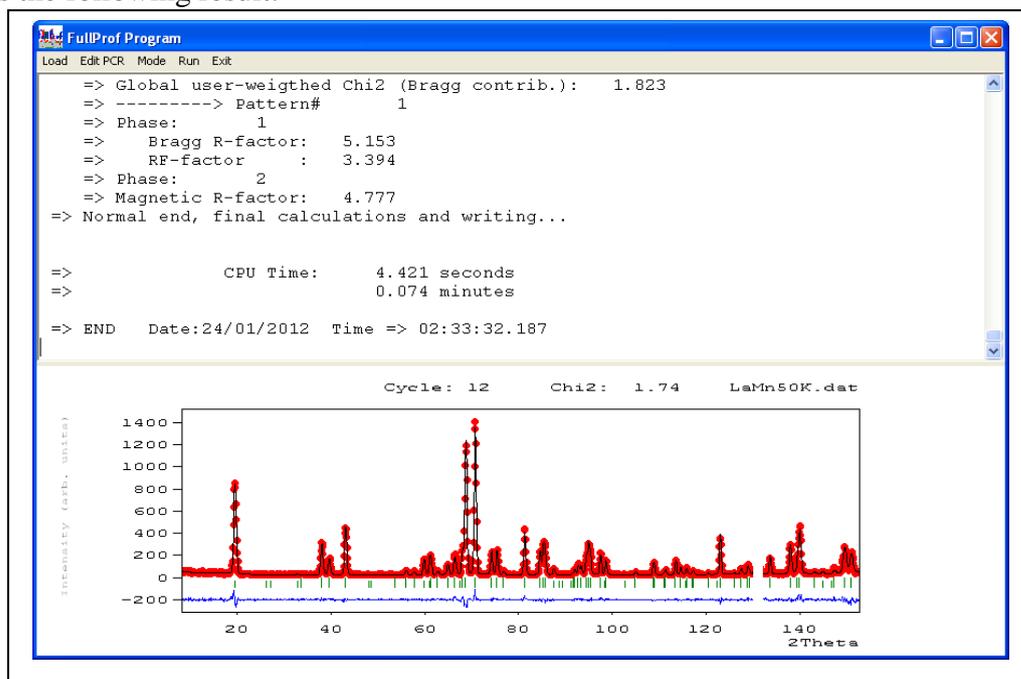
```



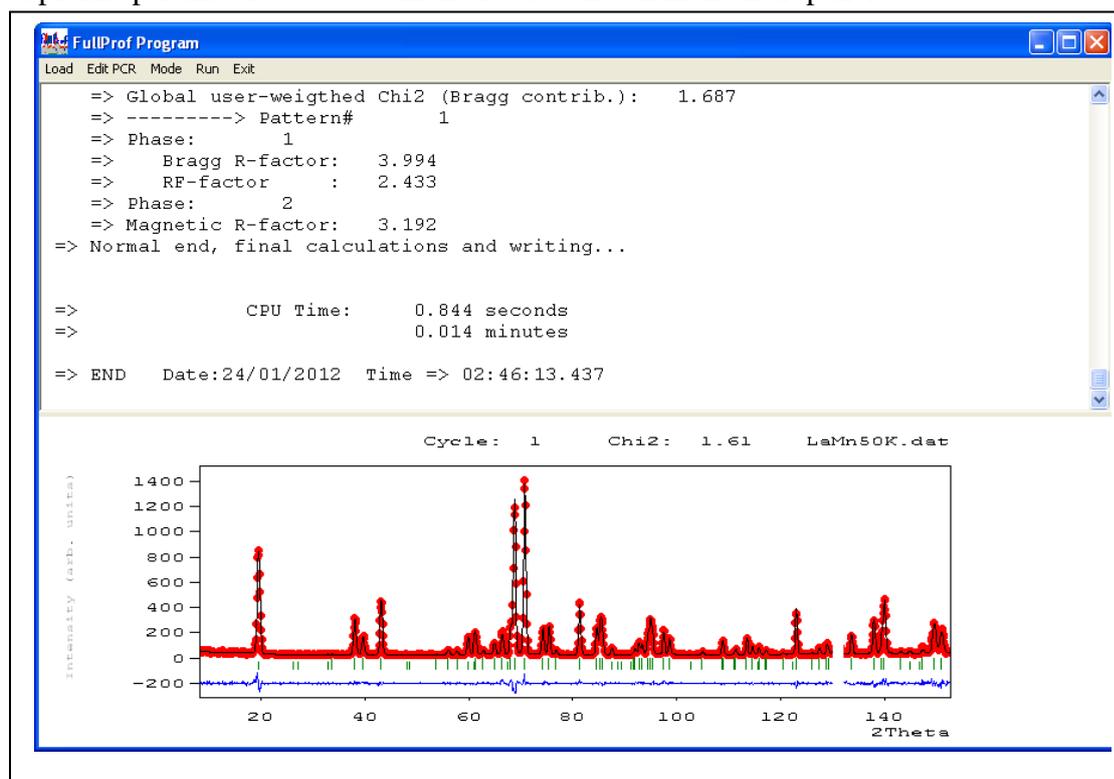
If we run FULLPROF fixing all parameters and putting arbitrary magnetic symmetry operators as in the example above, we see that there is now a non null intensity calculated below the (001) magnetic reflection.

Starting from these values and refining only the magnetic moments (putting 1.0 1.0 1.0 as refinement codes as we assume that $A_{\text{ut}}=1$), we can see that the program is able to refine correctly the magnetic structure.

The run of the program in the conditions defined above converges at the cycle number 12 and gives the following result:



At this stage we can refine all structural parameters, the background, the unit cell and the rest of profile parameters. We obtain the results shown in the next panel:



Instead of using $J_{bt}=1$ (components along the unitary vectors along the crystallographic basis \mathbf{a} , \mathbf{b} , \mathbf{c}) we can use spherical components by putting $J_{bt}=-1$. The relevant part of the PCR file has the following aspect for the case of the *irrep* Γ_3 corresponding to the correct solution. In read we have emphasised the variables that have changed with respect to the option $J_{bt}=1$.

```

!-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern# 1: 3.19
!-----
LaMnO3 (Magnetic contribution) irrep 3 Pb'n'm
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
1 0 0 0.0 0.0 1.0 -1 -1 -1 0 0 967.367 1 7 0
!
P -1 <--Space group symbol for hkl generation
!Nsym Cen Laue MagMat
4 2 1 1
!
SYMM x,y,z
MSYM u, v, w, 0.0
SYMM -x+1,-y,z+1/2
MSYM -u, -v, w, 0.0
SYMM -x+1/2,y+1/2,-z+1/2
MSYM u, -v, w, 0.0
SYMM x-1/2,-y+1/2,-z
MSYM -u, v, w, 0.0
!
!Atom Typ Mag Vek X Y Z Biso Occ Rm Rphi Rtheta
!Im Iphi Itheta beta11 beta22 beta33 MagPh
Mn MMN3 1 0 0.50000 0.00000 0.00000 0.56838 0.50000 3.874 85.965 101.814
0.00 0.00 0.00 101.00 0.00 141.00 151.00 161.00
0.000 0.000 0.000 0.000 0.000 0.000 0.000000
0.00 0.00 0.00 0.00 0.00 0.00 0.00
!-----> Profile Parameters for Pattern # 1
. . . . .

```

The other possibility to describe the magnetic structure in FULLPROF is to use directly the file produced by BASIREPS with extension *.fp, in our case LMO-sym.fp (see the input of BASIREPS given previously). The header and the *irrep* Γ_3 part of this file are shown below.

```

-----
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
-> Mn_1 : 0.5000 0.0000 0.0000 : (x,y,z) + ( 0 , 0 , 0 )
-> Mn_2 : 0.5000 0.0000 0.5000 : (-x,-y,z+1/2) + ( 1 , 0 , 0 )
-> Mn_3 : 0.0000 0.5000 0.5000 : (-x+1/2,y+1/2,-z+1/2) + ( 0 , 0 , 0 )
-> Mn_4 : 0.0000 0.5000 0.0000 : (x+1/2,-y+1/2,-z) + (-1 , 0 , 0 )
. . . . .
=> Basis functions of Representation IRrep( 3) of dimension 1 contained 3 times in GAMMA
Representation number : 3 for Site: 1
Number of basis functions: 3
----- Block-of-lines for PCR start just below this line
P -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
BASR 0 0 0 0 0 0 0 0 0
SYMM -x+1,-y,z+1/2
BASR -1 0 0 0 -1 0 0 0 1
BASR 0 0 0 0 0 0 0 0 0
SYMM -x+1/2,y+1/2,-z+1/2
BASR 1 0 0 0 -1 0 0 0 1
BASR 0 0 0 0 0 0 0 0 0
SYMM x-1/2,-y+1/2,-z
BASR -1 0 0 0 1 0 0 0 1
BASR 0 0 0 0 0 0 0 0 0
----- End-of-block of lines for PCR

```

In red we have emphasised the part we have to paste in the PCR file to work with FULLPROF using directly the basis vectors. The final PCR file using this option (`Isy=-2`) is written below:

```

-----
! Data for PHASE number: 2 ==> Current R_Bragg for Pattern# 1: 3.18
-----
LaMnO3 (Magnetic contribution) irrep 3 Pb'n'm
!
!Nat Dis Mom Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth ATZ Nvk Npr More
1 0 0 0.0 0.0 1.0 1 -1 -2 0 0 967.367 1 7 0
!
P -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+1,-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+1/2,y+1/2,-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-1/2,-y+1/2,-z
BASR -1 0 0 0 1 0 0 0 1
BASI 0 0 0 0 0 0 0 0 0
!
!Atom Typ Mag Vek X Y Z Biso Occ C1 C2 C3
! C4 C5 C6 C7 C8 C9 MagPh
Mn MMN3 1 0 0.50000 0.00000 0.00000 0.56878 1.00000 0.269 3.783 0.794
0.000 0.000 0.000 0.000 0.000 101.00 0.00 141.00 151.00 161.00
0.000 0.000 0.000 0.000 0.000 0.000 0.00000
0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00

```

Notice that in this case, as `Cen=1` was given in the `LMO-sym.fp` file; we have put the occupation equal to 1.0 because we are using just four symmetry operators. This is needed if we want to use the same scale factor for the nuclear and magnetic part.

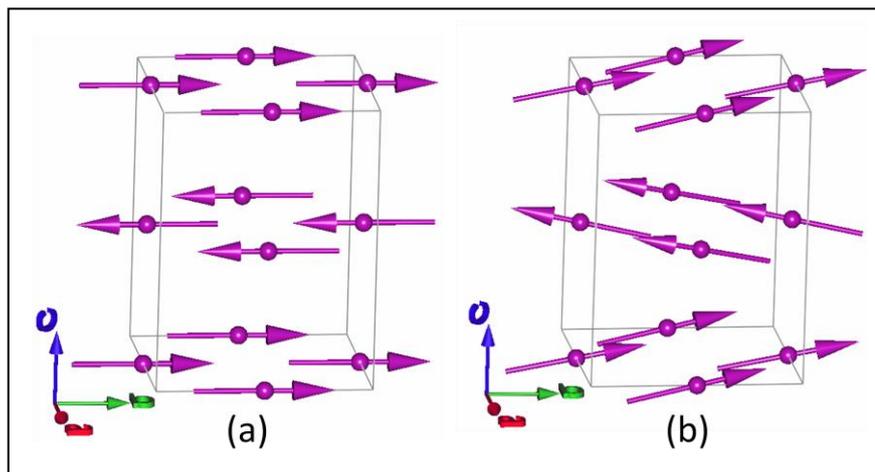
In the conventional crystallographic description the general multiplicity of the space group *Pbnm* is 8 and the multiplicity of the special Mn position (4*b*) is four, so the occupation was $n/M = 4/8 = 0.5$ in the nuclear part. In the magnetic part we are using just four symmetry operators so the occupation is 1.0.

If we put `Cen=2` this implies that we use not only the four symmetry operators given explicitly in the file but we add four other symmetry operators obtained from those given multiplied by an inversion operator and in that case we have also to put $n/M = 0.5$ as we did in the other examples of the PCR file for refining the magnetic structure.

Once we have refined the data we can use FULLPROF STUDIO for visualising the crystal and magnetic structure. A plot of the magnetic structure together with the crystal structure can be obtained by putting the keyword “magph2” (or in general “magphn” without quotes, being *n* the number of the magnetic phase) in the same line in which appears the name of the crystallographic phase. This tells the program that the phase number 2 corresponds to the magnetic structure related to the nuclear one.

Another point that is important to consider is the reliability of the obtained magnetic parameters with neutron powder diffraction. The *irrep* Γ_3 implies a ferromagnetic component along the *c*-axis, this means that the intensity contribution is on top of non-forbidden nuclear reflections. The refinement of that component has a tendency to give a higher value than that really occurring in the sample. The reason is that small errors in the nuclear structure or in

absorption correction are compensated by changing the value of the ferromagnetic component. In the following picture we can see the magnetic structure with fixed to zero x and z components (a), corresponding to the mode $(0, A_y, 0)$ and with all parameters free (b), corresponding to the mode (G_x, A_y, F_z) .



The agreement factors are practically the same, so we cannot determine precisely the value of the ferromagnetic component. The following panel compares the results obtained with the two refinements.

Name	Mx	sMx	My	sMy	Mz	sMz	M	sM	Chi2	R-Mag
Mn	0.000 (0)		3.755 (22)		0.000 (0)		3.7555 (221)		1.73	3.04
Mn	0.268 (94)		3.783 (22)		0.794 (69)		3.8743 (298)		1.69	3.19

We can see that the improvement of the Chi-square by introducing the two additional magnetic parameters is really marginal and the magnetic R-Bragg factor is slightly better for the case in which we have put the constraints of zero components along x and z.

The ferromagnetic component obtained using macroscopic measurements can be much better determined than with NPD. To get reliable weak ferromagnetic components with NPD we have to obtain very good statistics in the paramagnetic phase as well as in the ordered state and work on the difference diagram.

The example we have treated here is very simple but it is useful for beginners. In more complicated cases it may be necessary to use the SAnn option in FULLPROF in order to determine the magnetic structure *ab initio*. The problem of creating a PCR file adapted for SAnn has been treated in two other documents: the tutorial on Y_2O_3 and the tutorial on symmetry modes). The method is completely equivalent, the only thing that changes in the PCR file is just the description of the magnetic structure using $J_{bt}=1$ or $J_{bt}=-1$. Another important point is that the scale factor should be kept constant and equal to the scale factor obtained for the nuclear structure; otherwise the magnetic moment amplitudes cannot be properly determined.

Together with this document we give the data files and PCR files containing the nuclear structure of the Ho_2BaNiO_5 and that of $DyMn_6Ge_6$ that are treated from the point of view of the symmetry in the SMS document. With the experience gained in doing this exercise the reader should be able to solve and refine the magnetic structures of these two last compounds.

Appendix A: Magnetic structures

Basic descriptions of magnetic structures

The magnetic structures are commonly represented as a set of arrows, associated to the magnetic atoms, with magnitudes and orientations characteristics of the particular magnetic structure. For considering symmetry properties we have to suppose that each arrow is in fact a current loop, the direction of which determines the orientation of the arrow by the right-hand rule of electromagnetism.

There are essentially two ways of describing magnetic structures. The most close to conventional crystallography is the use of magnetic space groups (Shubnikov groups) and the other way is the formalism of propagation vectors used together with the representation analysis. A third way that combines the two others is the approach of Superspace Magnetic Groups that will not be treated here.

Shubnikov groups: To study the invariance of magnetic configurations we have to introduce a new operator that is usually called “spin reversal” or “time reversal”. This operator is acting on magnetic moments that are “classical axial vectors”. The action consists of changing the sense of the current loop (proportional to the product of a charge by a velocity vector), so that the orientation of the magnetic moment is reversed. We note this operator as $1'$ and it acts only on the magnetic moments/spins not on the atom positions: $1' \cdot \mathbf{m} = -\mathbf{m}$.

The spin reversal operator cannot be contained in the set of symmetry operators that leave invariant a magnetically ordered system, however it is contained in the paramagnetic state of a magnetic system. This gives immediately the so called “paramagnetic space groups” that are obtained by adding $1'$ to the set of symmetry elements of the space group. The notation of the paramagnetic space groups is identical to that of crystallographic groups with the $1'$ symbol added (e.g. $P6mm1'$). In magnetically ordered systems the spin reversal operator can be combined with a conventional symmetry operator. The operator is called “primed” to indicate that we have to invert the spin after applying the “non-primed” operator to the spin.

The symmetry operators we have to consider for exploring the invariance of spin configurations are then formed by the usual operators considered in crystallography together with these same operators followed by the spin reversal.

Mathematically the action of whatever kind of symmetry operator, which can be represented by an orthogonal matrix in the appropriate reference frame, on an axial vector is identical to that on a polar vector except that we have to multiply by the determinant of the matrix. Moreover if we consider a “primed” element we have to multiply again by -1 all the components of the resulting vector. In summary a general operator $g = \{h | \mathbf{t}_h + \mathbf{n}\}$ acting on an atom \mathbf{r}_j in the cell at the origin (zero-cell) having a magnetic moment \mathbf{m}_j is transformed as follows:

Position:

$$\mathbf{r}_j' = g \mathbf{r}_j = \{h | \mathbf{t}_h + \mathbf{n}\} \mathbf{r}_j = h \mathbf{r}_j + \mathbf{t}_h + \mathbf{n} = \mathbf{r}_i + \mathbf{a}_{gj} \quad (1)$$

Magnetic moment:

$$\mathbf{m}_j' = g \mathbf{m}_j = \det(h) \delta h \mathbf{m}_j \quad (2)$$

The transformed atom position \mathbf{r}_j' is translationally equivalent to the atom labelled “ i ” in the zero-cell. The vector \mathbf{a}_{gj} is a lattice vector depending on the initial atom j and the operator g . It is called “returning vector” because its opposite is the vector we need to apply on the transformed atom to put it back in the zero-cell.

The corresponding magnetic moment is transformed using only the rotational part of the operator and the resulting vector is multiplied by the determinant and the “signature” (δ) of the operator. The signature is $\delta=1$ for unprimed elements and $\delta=-1$ for primed elements.

In a magnetically ordered system the operator g is a symmetry operator if it is a symmetry operator of the space group and if $\mathbf{m}_j'=\mathbf{m}_i$.

Whatever crystallographic magnetic group, \mathbf{M} , can be obtained as a subgroup of the exterior direct product of $\mathbf{R} = \{1, 1'\}$ by the crystallographic group \mathbf{G} : $\mathbf{M} \subset \mathbf{G} \otimes \mathbf{R}$. The group \mathbf{G} is always a magnetic group (called “colourless”). The paramagnetic (“grey”) groups of the form $\mathbf{P}=\mathbf{G}+\mathbf{G}1'$ are also magnetic groups. The fact that the product of two primed elements must be an unprimed element gives the fundamental lemma for constructing the rest of magnetic groups (“black-white” groups): *the magnetic groups derived from the crystallographic group \mathbf{G} can be constructed considering the index 2 subgroups \mathbf{H} of \mathbf{G} as constituting the unprimed elements and the rest of operators, $\mathbf{G} - \mathbf{H}$, those that are multiplied by the time reversal operator.*

One obtains a total of 1651 types of Shubnikov groups. Among the 1651 magnetic space groups, considering \mathbf{G} as a space group type, 230 are of the form $\mathbf{M}_0=\mathbf{G}$ (called also “monochrome”), 230 of the form $\mathbf{P}=\mathbf{G}+\mathbf{G}1'$ (paramagnetic or “grey” groups) and 1191 of the form $\mathbf{M}=\mathbf{H}+(\mathbf{G}-\mathbf{H})1'$ (“black-white” groups). Among the black-white groups there are 674 in which the subgroup $\mathbf{H} \subset \mathbf{G}$ is an equi-translation group: \mathbf{H} has the same translation group as \mathbf{G} (first kind, BW1). The rest of black-white groups, 517, are equi-class group (second kind, BW2). In this last family the translation subgroup contains “anti-translations” (pure translations associated with the spin reversal operator). The two notations for describing magnetic space groups existing in the literature are due to Belov-Neronova-Smirnova (BNS) [1] and to Opechowski-Guccione (OG) [2]. Both notations are identical for the major part of magnetic space groups except for the second kind black-white magnetic space groups. Recently a list of all magnetic space groups, in a similar form as that of the ITA for crystallographic groups, has been published [4] using the OG notation. A re-interpretation of [4] in terms of the BNS notation has also been published [5].

The formalism of propagation vectors: If we disregard, for the moment, the symmetry properties, except the translation subgroup of the space group, of the magnetic moment configuration whatever class of magnetic structure can be represented by the Fourier series:

$$\mathbf{m}_{lj} = \sum_{\mathbf{k}} \mathbf{S}_{\mathbf{k}j} \exp(-2\pi i \mathbf{k} \mathbf{R}_l) \quad (3)$$

This defines the magnetic moment of the atom numbered j in the unit cell having as origin the lattice vector \mathbf{R}_l (the atom at $\mathbf{R}_{lj} = \mathbf{R}_l + \mathbf{r}_j$). The \mathbf{k} vectors are defined in reciprocal space and are called propagation vectors of the magnetic structure. For the description of magnetic structures they can be restricted to the first Brillouin zone (BZ). Notice that a Fourier series is nothing else than a development of a function in terms of Bloch functions.

The Fourier coefficients $\mathbf{S}_{\mathbf{k}j}$ are, in general, complex vectors and must verify the equality $\mathbf{S}_{\mathbf{k}j} = \mathbf{S}_{-\mathbf{k}j}^*$ to make the sum result a real vector. In practice, most of the magnetic structures can be describe by a small number (1 to 3) of propagation vectors.

Let us describe general types of magnetic structures of increasing degree of complexity, using the formalism of propagation vectors through the expression (3).

a) The simplest types of magnetic structures existing in complex crystals have a single null propagation vector at the centre of the BZ: $\mathbf{k} = (0, 0, 0) = \mathbf{0}$. The Fourier coefficients should be real and can be identified to the magnetic moments directly:

$$\mathbf{m}_{lj} = \mathbf{S}_{0j} \exp(-2\pi i \mathbf{0} \mathbf{R}_l) = \mathbf{S}_{0j} = \mathbf{m}_{0j} \quad (4)$$

This expression tells us that the orientation and magnitudes of the magnetic moments in whatever cell of the crystal are identical to those of the zero-cell. The translational symmetry of the magnetic structure is identical to that of the crystal structure: the magnetic unit cell is the same as the chemical cell. This class of magnetic structures may be ferromagnetic, ferrimagnetic or antiferromagnetic, collinear or non-collinear. The propagation vector at the centre of the BZ does not mean that the magnetic structure is ferromagnetic. This is only true for Bravais lattices (a single magnetic atom per primitive cell). This kind of magnetic structure can be described by one of the 230 monochrome or the 674 black-white first kind (BW1) magnetic space groups.

b) The next class of magnetic structures corresponds also to a single propagation vector, in this case of the form: $\mathbf{k} = 1/2\mathbf{H}$, where \mathbf{H} is a reciprocal lattice vector. The propagation vectors of this kind correspond to high symmetry points of the surface of the BZ (Lifchitz points). In this case we have:

$$\mathbf{m}_{lj} = \mathbf{S}_{kj} \exp(-2\pi i \mathbf{k} \mathbf{R}_l) = \mathbf{S}_{kj} \exp(-\pi i \mathbf{H} \mathbf{R}_l) = \mathbf{S}_{kj} (-1)^{\mathbf{H} \mathbf{R}_l} = \mathbf{S}_{kj} (-1)^{n_l} = \mathbf{m}_{0j} (-1)^{n_l} \quad (5)$$

This expression tells us that the orientation and magnitudes of the magnetic moments in whatever cell of the crystal are either identical or opposite to those of the zero-cell. The translational symmetry is lower than that of the chemical cell. The magnetic cell can easily be deduced from the particular values of the propagation vector (see [15] for a classification of magnetic lattices in terms of propagation vectors). The magnetic structures of this kind are necessarily antiferromagnetic and can be described by one of the 517 black-white second kind (BW2) magnetic space groups.

c) This is the general case, where the \mathbf{k} -vector is not a special vector as in the two previous types. For these cases there is no Shubnikov group, in three dimensions, that can describe the symmetry properties of such spin configuration. The general expression of the Fourier coefficient for the atom j is explicitly given by:

$$\mathbf{S}_{kj} = \frac{1}{2} \{ \vec{R}_{kj} + i \vec{I}_{kj} \} \exp(-2\pi i \phi_{kj}) = \frac{1}{2} \{ R_{kj}^x \mathbf{e}_1 + R_{kj}^y \mathbf{e}_2 + R_{kj}^z \mathbf{e}_3 + i(I_{kj}^x \mathbf{e}_1 + I_{kj}^y \mathbf{e}_2 + I_{kj}^z \mathbf{e}_3) \} \exp(-2\pi i \phi_{kj}) \quad (6)$$

Only six real parameters define the \mathbf{S}_{kj} vectors, so the phase factor ϕ_{kj} is not generally needed, but it is convenient to use it when particular relations or constraints between real and imaginary vectors, $(\vec{R}_{kj}, \vec{I}_{kj})$, are given. The calculation of the magnetic moment of the atom j in the unit cell of index l , should be performed by using the formula (3) that may be also written in this case as:

$$\mathbf{m}_{lj} = \sum_{(\mathbf{k})} \{ \vec{R}_{kj} \cos 2\pi[\mathbf{k} \mathbf{R}_l + \phi_{kj}] + \vec{I}_{kj} \sin 2\pi[\mathbf{k} \mathbf{R}_l + \phi_{kj}] \} \quad (3')$$

where the sum is now extended to half the number of propagation vectors, i.e. over the total number of pairs $(\mathbf{k}, -\mathbf{k})$.

If the magnetic structure represents a *helical* order the Fourier coefficients are of the form:

$$\mathbf{S}_{kj} = \frac{1}{2} \{m_{1j} \mathbf{u}_j + i m_{2j} \mathbf{v}_j\} \exp(-2\pi i \phi_{kj}), \quad \text{with } |\mathbf{u}_j| = |\mathbf{v}_j| = 1, \quad \mathbf{u}_j \cdot \mathbf{v}_j = 0 \quad (7)$$

where \mathbf{u}_j and \mathbf{v}_j are orthogonal unit vectors.

Representation analysis for magnetic structures

In the most general case the expression (3) can be written with an additional index as:

$$\mathbf{m}_{ljs} = \sum_{\{\mathbf{k}\}} \mathbf{S}_{kj_s} \exp\{-2\pi i \mathbf{k} \mathbf{R}_l\} \quad (8)$$

l : index of a direct lattice point (origin of an arbitrary unit cell)

j : index for a Wyckoff site (orbit)

s : index of a sublattice of the j site

The Fourier coefficients verify: $\mathbf{S}_{kj_s} = \mathbf{S}^*_{-\mathbf{k}j_s}$ (9)

The group $\mathbf{G}_{\mathbf{k}}$ is formed by the set of symmetry operators that leave invariant the propagation vector: $\mathbf{G}_{\mathbf{k}} = \{g \in \mathbf{G} \mid g\mathbf{k} = \mathbf{k} + \mathbf{H}, \mathbf{H} \in \mathbf{L}^*\}$, where \mathbf{L}^* is the crystallographic reciprocal lattice.

One can generate a reducible representation of $\mathbf{G}_{\mathbf{k}}$ by considering the complex working space spanned by all the components of \mathbf{S}_{kj_s} .

As the atoms belonging to different sites do not mix under the symmetry operators, we can treat separately the different sites. For us the index j is then fixed and the index s varies from 1 to p_j . For

The working complex space for site j has dimension $n_j = 3 \times p_j$ is then spanned by unit vectors $\{\boldsymbol{\epsilon}_{s\alpha}^{kj}\}$ ($\alpha = 1, 2, 3$ –or x, y, z and $s = 1 \dots p_j$) represented as column vectors (with a single index n) with zeroes except for $n = \alpha + 3(s-1)$. The vectors $\{\boldsymbol{\epsilon}_{s\alpha}^{kj}\}$ are formed by direct sums (juxtaposition) of 3D unit vectors $\mathbf{u}_{s\alpha}^{kj}$.

$$\boldsymbol{\epsilon}_{s\alpha}^{kj} = \sum_{\oplus s=1, p_j} \mathbf{u}_{s\alpha}^{kj} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 0 \\ 1 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ 0 \\ 0 \end{pmatrix} \begin{matrix} x, 1 \\ y, 1 \\ \vdots \\ z, s-1 \\ x, s \\ y, s \\ z, s \\ \vdots \\ \vdots \\ \vdots \\ y, p_j \\ z, p_j \end{matrix} \rightarrow \boldsymbol{\epsilon}_{11}^{kj} = \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix} \quad \boldsymbol{\epsilon}_{12}^{kj} = \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \\ 0 \end{pmatrix} \quad \boldsymbol{\epsilon}_{23}^{kj} = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ 0 \\ 0 \end{pmatrix} \dots \rightarrow (\boldsymbol{\epsilon}_{s\alpha}^{kj})_n = \delta_{n, \alpha + 3(s-1)} \quad (10)$$

The vectors $\{\boldsymbol{\epsilon}_{s\alpha}^{kj}\}$ may be considered as the columns of the unit matrix of dimension $n_j \times n_j = 9p_j^2$:

$$\{\boldsymbol{\epsilon}_{11}^{\mathbf{k}j} \quad \boldsymbol{\epsilon}_{12}^{\mathbf{k}j} \quad \boldsymbol{\epsilon}_{13}^{\mathbf{k}j} \quad \dots \quad \boldsymbol{\epsilon}_{p_j 2}^{\mathbf{k}j} \quad \boldsymbol{\epsilon}_{p_j 3}^{\mathbf{k}j}\} = \begin{pmatrix} 1 & 0 & 0 & \dots & \dots & 0 & 0 \\ 0 & 1 & 0 & \dots & \dots & 0 & 0 \\ 0 & 0 & 1 & \dots & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & \dots & 1 & 0 \\ 0 & 0 & 0 & \dots & \dots & 0 & 1 \end{pmatrix}$$

$$\Phi_{s\alpha}^{\mathbf{k}j} = \sum_{\oplus l} \boldsymbol{\epsilon}_{s\alpha}^{\mathbf{k}j} \exp(-2\pi i \mathbf{k} \mathbf{R}_l) \rightarrow \begin{pmatrix} 0 \\ \vdots \\ 0 \\ 0 \\ \vdots \\ 0 \\ \vdots \\ \vdots \\ \exp(-2\pi i \mathbf{k} \mathbf{R}_l) \\ \vdots \\ \vdots \\ \vdots \end{pmatrix} \begin{matrix} \mathbf{R}_0 \\ \\ \mathbf{R}_1 \\ \\ \vdots \\ \\ \mathbf{R}_l \\ \\ \vdots \\ \\ \vdots \end{matrix} \rightarrow (\Phi_{s\alpha}^{\mathbf{k}j})_n = e^{-2\pi i \mathbf{k} \mathbf{R}_l} \delta_{n, \alpha + 3(s-1) + 3lp_j} \quad (11)$$

If one applies the symmetry operators of $\mathbf{G}_{\mathbf{k}}$ to the vectors $\{\boldsymbol{\epsilon}_{s\alpha}^{\mathbf{k}j}\}$ taking into account that they are axial vectors we obtain another vector (after correcting for the Bloch phase factor if the operator moves the atom outside the reference zero-cell) of the same basis.

The matrices $\Gamma_{\beta q, \alpha s}^{\mathbf{k}j}(g)$ of dimension $n_j \times n_j$ corresponding to the different operators constitute what is called the ‘‘Magnetic Representation’’ for the site j and propagation vector \mathbf{k} .

The action of the operator $O(g)$, corresponding to the symmetry operator g , on the vector $\{\boldsymbol{\epsilon}_{s\alpha}^{\mathbf{k}j}\}$ can be described as follows: applying a symmetry operator to the vector position and the unit spin associated to the atom js along the α -axis, changes the index js to jq and reorient the spin according to the nature of the operator $g = \{h | \mathbf{t}_h\}$ for axial vectors.

$$\boldsymbol{\epsilon}_{s\alpha}^{\mathbf{k}j} = \sum_{\oplus s} \mathbf{u}_{s\alpha}^{\mathbf{k}j} \quad 3D \rightarrow (\mathbf{u}_{s\alpha}^{\mathbf{k}j})_n = \delta_{n, \alpha}; \quad 3p_j D \rightarrow (\boldsymbol{\epsilon}_{s\alpha}^{\mathbf{k}j})_n = \delta_{n, \alpha + 3(s-1)}$$

$$\Phi_{s\alpha}^{\mathbf{k}j} = \sum_{\oplus l} \boldsymbol{\epsilon}_{s\alpha}^{\mathbf{k}j} \exp(-2\pi i \mathbf{k} \mathbf{R}_l) \quad 3Np_j D \rightarrow (\Phi_{s\alpha}^{\mathbf{k}j})_n = e^{-2\pi i \mathbf{k} \mathbf{R}_l} \delta_{n, \alpha + 3(s-1) + 3lp_j} \quad (12)$$

The operator g acting on atom positions permute the numbering of the atoms belonging to a same site and provide a returning vector \mathbf{a}_{gs}^j , that must appear in a phase factor when working with Bloch functions, when the transformed atom is outside the zero-cell.

$$O(g)\boldsymbol{\epsilon}_{s\alpha}^{\mathbf{k}j} = \sum_{q\beta} \Gamma_{q\beta, s\alpha}^{\mathbf{k}j}(g)\boldsymbol{\epsilon}_{q\beta}^{\mathbf{k}j} = \sum_{q\beta} e^{2\pi i \mathbf{k} \cdot \mathbf{a}_{gs}^j} \det(h) h_{\beta\alpha} \delta_{s, gq}^j \boldsymbol{\epsilon}_{q\beta}^{\mathbf{k}j}$$

The explicit components of the magnetic representation are:

$$\begin{aligned}
\Gamma_{Perm} &\rightarrow P_{q,s}^{kj}(g) = e^{2\pi i \mathbf{k} \mathbf{a}_{gs}^j} \delta_{q,gs} \\
\Gamma_{Axial} &\rightarrow V_{\beta\alpha}(g) = \det(h) h_{\beta\alpha} \\
\Gamma_{Mag} = \Gamma_{Perm} \otimes \Gamma_{Axial} &\rightarrow \Gamma_{\beta q, \alpha s}^{kj}(g) = e^{2\pi i \mathbf{k} \mathbf{a}_{gs}^j} \det(h) h_{\beta\alpha} \delta_{q,gs}
\end{aligned} \tag{13}$$

The δ symbol has value equal to 1 when the operator g transforms the atom s into the atom q , and zero otherwise.

The decomposition of the magnetic representation in terms of irreducible representations of the group of the propagation vector can be obtained using the following formulae:

$$\begin{aligned}
\Gamma_{Mag} &= \sum_{\oplus \nu} n_{\nu} \Gamma^{\nu} = n_1 \Gamma^1 \oplus n_2 \Gamma^2 \oplus n_3 \Gamma^3 \dots \oplus n_m \Gamma^m \\
n_{\nu} &= \frac{1}{n(\mathbf{G}_{0\mathbf{k}})} \sum_{g \in \mathbf{G}_{0\mathbf{k}}} \chi_{Mag}(g) \chi^{*\nu}(g)
\end{aligned} \tag{14}$$

Projection operators and basis vectors of irreducible representations of $\mathbf{G}_{\mathbf{k}}$

The basis functions of the *irreps* of $\mathbf{G}_{\mathbf{k}}$ can be calculated using the projection operator formula particularised for the explicit expression of $O(g)$ acting on the vectors $\{\mathbf{e}_{\alpha s}^{kj}\}$. The explicit formula giving the n_j -dimensional basis vectors of the representation Γ^{ν} for site j is the following:

$$\begin{aligned}
\psi_{\lambda}^{k\nu}(j) &= \frac{1}{n(\mathbf{G}_{0\mathbf{k}})} \sum_{g \in \mathbf{G}_{0\mathbf{k}}} \Gamma_{\lambda[\mu]}^{*\nu}(g) O(g) \mathbf{e}_{s\alpha}^{kj} \quad (\lambda = 1, \dots, l_{\nu}) \\
\psi_{\lambda}^{k\nu}(j) &= \frac{1}{n(\mathbf{G}_{0\mathbf{k}})} \sum_{g \in \mathbf{G}_{0\mathbf{k}}} \Gamma_{\lambda[\mu]}^{*\nu}(g) \sum_{q\beta} \exp(2\pi i \mathbf{k} \mathbf{a}_{gs}^j) \det(h) h_{\beta\alpha} \delta_{s,gq}^j \mathbf{e}_{q\beta}^{kj}
\end{aligned} \tag{15}$$

It is convenient to use, instead of the basis vectors for the whole set of magnetic atoms in the primitive cell, the so called *atomic components* of the basis vectors, which are normal 3D constant vectors attached to individual atoms:

$$\psi_{\lambda}^{k\nu}(j) = \sum_{\oplus, s=1, \dots, p_j} \mathbf{S}_{\lambda}^{k\nu}(js) \tag{16}$$

The explicit expression for the atomic components of the basis functions is:

$$\mathbf{S}_{\lambda}^{k\nu}(js) \propto \sum_{g \in \mathbf{G}_{0\mathbf{k}}} \Gamma_{\lambda[\mu]}^{*\nu}(g) e^{2\pi i \mathbf{k} \mathbf{a}_{gs}^j} \det(h) \delta_{s,g[q]}^j \begin{pmatrix} h_{1\alpha} \\ h_{2\alpha} \\ h_{3\alpha} \end{pmatrix} \tag{17}$$

A general magnetic structure can be described by a Fourier series as (3) where the index j was for a generic magnetic atom irrespective of symmetry. The Fourier series can be rewritten using the notation used in the present section, simply by changing the index j for the double index js . The fundamental hypothesis of the symmetry analysis, when working with magnetic structures, is that the Fourier coefficients \mathbf{S}_{kj_s} that describe magnetic structures with propagation vector \mathbf{k} must be a linear combination of the basis functions (atomic components) of the $\mathbf{G}_{\mathbf{k}}$ irreducible representations.

$$\mathbf{S}_{\mathbf{k}j_s} = \sum_{n\lambda} C_{n\lambda}^{\mathbf{k}\nu} \mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(j_s) \quad (18)$$

where ν labels the active irreducible representation, Γ^ν , of the propagation vector group $\mathbf{G}_{\mathbf{k}}$, λ labels the component corresponding to the dimension of the representation Γ^ν , n is an additional index (with respect to expression (18)) running between one and the number of times ($n=1\dots n_\nu$) the representation Γ^ν is contained in the global magnetic representation Γ_{Mag} . The quantities $\mathbf{S}_{n\lambda}^{\mathbf{k}\nu}(j_s)$ are constant vectors, in general complex, obtained by the application of the projection operator formula to axial unit vectors along the directions of the unit cell axes attached to the positions j_s . In the case the representation analysis is fully used, the mixing coefficients $C_{n\lambda}^{\mathbf{k}\nu}$ are the free parameters of the magnetic structure and usually the total number is lower than the number of Fourier components of each magnetic atom in the unit cell. If we add a sum over representations, the expression (18) gives the most general case; in practice one has to assume additional constraints because the number of mixing coefficients may be too high.

The number of free coefficients to describe a magnetic structure corresponding to a single representation of $\mathbf{G}_{\mathbf{k}}$ is related to the number of independent basis vectors $n_f \propto n_\nu \times \dim(\Gamma^\nu)$. In the general case the basis functions can be complex vectors as well as the coefficients $C_{n\lambda}^{\mathbf{k}\nu}$, the condition $\mathbf{S}_{\mathbf{k}j_s} = \mathbf{S}_{-\mathbf{k}j_s}^*$ assures the reality of the magnetic moments. The effective number of free parameters depends on some additional assumptions related to the consideration of the star of the wave vector. Let us consider only a single wave vector and the representations of $\mathbf{G}_{\mathbf{k}}$. In such a case, the analysis is successful when the number of free parameters is lower than $6p_j$ in the case of \mathbf{k} not equivalent to $-\mathbf{k}$ or $3p_j$ in case of real Fourier coefficients. In summary, the group theory, considering only $\mathbf{G}_{\mathbf{k}}$, is useful when:

$$n_f = 2 n_\nu \times \dim(\Gamma^\nu) < 6 p_j \quad (\text{for } \mathbf{k} \text{ non equivalent to } -\mathbf{k}) \quad (19)$$

$$n_f = n_\nu \times \dim(\Gamma^\nu) < 3 p_j \quad (\text{for } \mathbf{k} \text{ equivalent to } -\mathbf{k}) \quad (19')$$

The factor 2 comes from the fact that, in general, the coefficients may be complex (modulus and phase). When the constraints introduced by symmetry analysis are not enough to simplify the problem and tackle successfully the experimental data, one has to consider other kind of restrictions imposed by the previous knowledge of the physics of the system. The most common constraint, based on physical grounds, is that the magnetic moment of the different atoms belonging to a same crystallographic site should have the same modulus, at least for commensurate magnetic structures.

Instead of using directly the mixing coefficients for describing a magnetic structure, one can use a more traditional crystallographic approach in some cases. The Fourier component \mathbf{k} of the magnetic moment of atom j_1 , which transforms to the atom j_s when the symmetry operator $g_s = \{h|\mathbf{t}\}_s$ of $\mathbf{G}_{\mathbf{k}}$ is applied ($\mathbf{r}_{j_s}^i = g_s \mathbf{r}_{j_1}^i = h_s \mathbf{r}_{j_1}^i + \mathbf{t}_s$), is transformed as:

$$\mathbf{S}_{\mathbf{k}j_s} = M_{j_s} \mathbf{S}_{\mathbf{k}j_1} \exp\{-2\pi i \phi_{\mathbf{k}j_s}\} \quad (20)$$

The matrices M_{j_s} and phases $\phi_{\mathbf{k}j_s}$ can be deduced from the relations between the Fourier coefficients and atomic basis functions (18). The matrices M_{j_s} correspond, in the case of commensurate magnetic structures, to the rotational parts of the magnetic Shubnikov group acting on magnetic moments.

How we get information about magnetic structures: magnetic neutron scattering

The intensity of magnetic Bragg peaks due to neutron scattering by magnetically ordered systems can be calculated in a similar way as for X-rays or nuclear neutron scattering. The most important difference is that the scattering amplitude is not a scalar variable.

The scattering amplitude vector, for a single atom with atomic moment \mathbf{m} , is given by:

$$\mathbf{a}(\mathbf{Q}) = pf(Q)\mathbf{m}_\perp = \frac{1}{2}r_e\gamma f(Q)\left(\mathbf{m} - \frac{\mathbf{Q}(\mathbf{m}\cdot\mathbf{Q})}{Q^2}\right) = \frac{1}{2Q^2}r_e\gamma f(Q)(\mathbf{Q}\times\mathbf{m}\times\mathbf{Q}) \quad (21)$$

The constant $p = r_e \gamma/2 = 0.2695$ allows the conversion of the magnetic moments, given in Bohr magnetons to scattering lengths units of 10^{-12} cm. The other constants appearing in formula (21) are: the classical radius of the electron $r_e = e^2 / mc^2 = 2.81776 \times 10^{-13}$ cm and the magnetic moment of the neutron in nuclear magnetons $\gamma (=1.9132)$. The function $f(Q)$ is the atomic magnetic form-factor (Fourier transform of the unpaired electron density, normalized as $f(0) = 1$, assumed to be spherical hereafter), and \mathbf{m}_\perp is the perpendicular component of the atomic moment to the scattering vector $\mathbf{Q} = 2\pi\mathbf{s}$. Only the perpendicular component of \mathbf{m} contributes to the magnetic scattering of neutrons by matter. The vectorial character of the interaction allows determining the magnetic moment direction with respect to the crystal lattice.

For a single crystal with a magnetic structure described by the formula (3), the magnetic intensity is practically zero in the whole reciprocal space except at positions given by:

$$\mathbf{s} = \mathbf{h} = \mathbf{H} + \mathbf{k} \quad (22)$$

Magnetic diffraction appears like a filter. Each satellite is decoupled of the rest of satellites, so if there are different propagation vectors \mathbf{k} there is no interference between them, so there is always a phase factor between the Fourier coefficients $\mathbf{S}_\mathbf{k}$ corresponding to different propagation vectors that is not accessible by diffraction methods unless a crystal structure distortion is coupled with the magnetic ordering. Only when $\mathbf{k} = \mathbf{0}$ there is a magnetic contribution in top of the nuclear reflections.

For a particular magnetic reflection the magnetic structure factor of the unit cell is:

$$\mathbf{M}(\mathbf{h}) = \mathbf{M}_\mathbf{h} = p \sum_j f_j(h) \mathbf{S}_{\mathbf{k}_j} e^{2\pi i \mathbf{h} \cdot \mathbf{r}_j} = p \sum_j f_j(|\mathbf{H} + \mathbf{k}|) \mathbf{S}_{\mathbf{k}_j} e^{2\pi i (\mathbf{H} + \mathbf{k}) \cdot \mathbf{r}_j} \quad (23)$$

The intensity of a magnetic Bragg reflection is proportional to the square of the magnetic interaction vector:

$$\mathbf{M}_{\perp\mathbf{h}} = \frac{1}{h^2} \mathbf{h} \times \mathbf{M}_\mathbf{h} \times \mathbf{h} = \mathbf{e} \times \mathbf{M}_\mathbf{h} \times \mathbf{e} = \mathbf{M}_\mathbf{h} - (\mathbf{e} \cdot \mathbf{M}_\mathbf{h}) \mathbf{e} \quad (24)$$

where \mathbf{e} is the unit vector along the scattering vector $\mathbf{h} = \mathbf{H} + \mathbf{k}$. In the case of a propagation vector $\mathbf{k} = \mathbf{0}$ the intensity of a Bragg reflection for non polarised neutrons is given by:

$$I_\mathbf{h} = N_\mathbf{h} N_\mathbf{h}^* + \mathbf{M}_{\perp\mathbf{h}} \cdot \mathbf{M}_{\perp\mathbf{h}}^* \quad (25)$$

where $N_{\mathbf{h}} = F(\mathbf{h})$ is the nuclear structure factor, otherwise only the second term (pure magnetic scattering) of the sum contributes to the intensity of reflection \mathbf{h} .

Appendix B: Explicit calculations of the decomposition of the magnetic representation in the case of LaMnO_3 and the basis vectors of *irrep*

The matrices of the magnetic representation of dimension $3 \times 4 = 12$ can be obtained by the direct product of the permutation (dimension 4) and the axial (dimension 3) representations. The axial representation is formed by the rotational part of the coset representatives of $\mathbf{G}_{\mathbf{k}}$ multiplied by the determinant. The axial representation is then:

$$\begin{aligned}
 1 &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & 2_{1z} &\rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & 2_{1x} &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & 2_{1y} &\rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
 -1 &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & m &\rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & b &\rightarrow \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & n &\rightarrow \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}
 \end{aligned}$$

The characters of these matrices are: $\chi_v(1)=3$, $\chi_v(2_{1z}) = -1$, $\chi_v(2_{1x}) = -1$, $\chi_v(2_{1y}) = -1$, $\chi_v(-1)=3$, $\chi_v(m) = -1$, $\chi_v(b) = -1$, $\chi_v(n) = -1$

The permutation representation does not contain phase factors because the propagation vector is zero. The matrices can be obtained just looking at the transformations of the following numbers representing the atoms of the Wyckoff site $4b$ (the character of the permutation matrices are also given).

Op.	Atom: 1	2	3	4	Character
1	1	2	3	4	4
2_{1z}	2	1	4	3	0
2_{1x}	4	3	2	1	0
2_{1y}	3	4	1	2	0
-1	1	2	3	4	4
m	2	1	4	3	0
b	4	3	2	1	0
n	3	4	1	2	0

One can see that the four last operators produce the same permutations of the atoms as that of the first four operators. This is a characteristic of this special position. As an example the matrices of the permutation representation corresponding to the operators 2_{1x} and m are:

$$2_{1x} \rightarrow P(2_{1x}) = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad m \rightarrow P(m) = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

The magnetic representation can be obtained just by direct product of the axial and permutation representations. In general we do not need the explicit writing of these matrices because we are mostly interested in the decomposition of the magnetic representation in terms of the *irreps* of \mathbf{G}_k and for that we need only the characters of this representation, that can be easily obtained as the product of the characters of the axial representation and those of the permutation representation. These characters are:

Characters	1	2_{1z}	2_{1x}	2_{1y}	-1	m	b	n
$\Gamma(\text{Axial})$	3	-1	-1	-1	3	-1	-1	-1
$\Gamma(\text{Perm})$	4	0	0	0	4	0	0	0
$\Gamma(\text{Mag})$	12	0	0	0	12	0	0	0

As an example the complete magnetic matrix of the above two operators are:

$$\Gamma_{Mag}(2_{1x}) = \begin{pmatrix} 0 & 0 & 0 & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\ 0 & 0 & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & 0 \\ 0 & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & 0 & 0 \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & 0 & 0 & 0 \end{pmatrix}$$

$$\Gamma_{Mag} = \sum_{\oplus \nu} n_{\nu} \Gamma^{\nu} = 3\Gamma^1 \oplus 3\Gamma^3 \oplus 3\Gamma^5 \oplus 3\Gamma^7$$

It is easy to see that the only irreducible representations that are contained in the magnetic representation are those having the character equal to 1 for the inversion centre. These are called *gerade* or even representations (in some notations a subscript g is added to the symbol of the representation). The decomposition shows that we have to get three basis vectors for each representation. This coincides also with the number of free parameters of the different magnetic structures.

The final step is the calculation of the basis vectors of each irreducible representation contained in Γ_{Mag} . This can be done applying the projection operator formulae (15-17). For representations of dimension 1 the projection operator formula can be simplified replacing the matrix elements by the characters:

$$\Psi^{k\nu} = \frac{1}{n(\mathbf{G}_{0\mathbf{k}})} \sum_{g \in \mathbf{G}_{0\mathbf{k}}} \chi^{*\nu}(g) O(g) \boldsymbol{\varepsilon}^{kj}$$

$$\Psi_1^{k1} = \frac{1}{n(\mathbf{G}_{0\mathbf{k}})} \sum_{g \in \mathbf{G}_{0\mathbf{k}}} \chi^{*1}(g) O(g) \boldsymbol{\varepsilon}_{1x} = \frac{1}{8} (1 \cdot \boldsymbol{\varepsilon}_{1x} - 1 \cdot \boldsymbol{\varepsilon}_{2x} + 1 \cdot \boldsymbol{\varepsilon}_{4x} - 1 \cdot \boldsymbol{\varepsilon}_{3x} + 1 \cdot \boldsymbol{\varepsilon}_{1x} - 1 \cdot \boldsymbol{\varepsilon}_{2x} + 1 \cdot \boldsymbol{\varepsilon}_{4x} - 1 \cdot \boldsymbol{\varepsilon}_{3x})$$

$$\Psi_1^{k1} = \frac{1}{4} (\boldsymbol{\varepsilon}_{1x} - \boldsymbol{\varepsilon}_{2x} - \boldsymbol{\varepsilon}_{3x} + \boldsymbol{\varepsilon}_{4x}) = \frac{1}{4} (1, 0, 0; -1, 0, 0; -1, 0, 0; 1, 0, 0)$$

$$\Psi_2^{k1} = \frac{1}{4} (\boldsymbol{\varepsilon}_{1y} - \boldsymbol{\varepsilon}_{2y} + \boldsymbol{\varepsilon}_{3y} + \boldsymbol{\varepsilon}_{4y}) = \frac{1}{4} (0, 1, 0; 0, -1, 0; 0, 1, 0; 0, -1, 0)$$

$$\Psi_3^{k1} = \frac{1}{4} (\boldsymbol{\varepsilon}_{1z} + \boldsymbol{\varepsilon}_{2z} - \boldsymbol{\varepsilon}_{3z} - \boldsymbol{\varepsilon}_{4z}) = \frac{1}{4} (0, 0, 1; 0, 0, 1; 0, 0, -1; 0, 0, -1)$$

In our case the atomic component of the basis vectors can be written in a more simplified form: we can drop the indices \mathbf{k}, j, λ and μ , moreover no phase factor with returning vectors appear because $\mathbf{k} = (0, 0, 0)$ so that the expression (13) reduces to

$$\mathbf{S}^{\nu} s \propto \sum_{g \in \mathbf{G}_{0\mathbf{k}}} \chi^{*\nu}(g) \det(h) \delta_{s, g[q]} \begin{pmatrix} h_{1\alpha} \\ h_{2\alpha} \\ h_{3\alpha} \end{pmatrix}$$

If we calculate the atomic components applying directly the above formula for each sublattice ($s=1, 2, 3, 4$) and for each component ($\alpha=x, y, z$) we obtain the 3D-vectors separated by “;” in the complete basis functions. As an example let us calculate some of them taking into account that the δ -symbol selects only the operators that leave the starting atom s invariant. For the first atom only the identity and the inversion centre have to be taken into account if we take $q=1$ as starting atom:

$$\begin{aligned}
\mathbf{S}_1^1 \cdot 1 &\propto \sum_{g \in \mathbf{G}_{0k}} \chi^{*1}(g) \det(h) \delta_{1,g[1]} \begin{pmatrix} h_{1x} \\ h_{2x} \\ h_{3x} \end{pmatrix} = 1 \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} + 1 \cdot \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \propto \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \\
\mathbf{S}_2^1 \cdot 1 &\propto \sum_{g \in \mathbf{G}_{0k}} \chi^{*1}(g) \det(h) \delta_{1,g[1]} \begin{pmatrix} h_{1y} \\ h_{2y} \\ h_{3y} \end{pmatrix} \propto \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}; & \quad \mathbf{S}_3^1 \cdot 1 &\propto \sum_{g \in \mathbf{G}_{0k}} \chi^{*1}(g) \det(h) \delta_{s,g[1]} \begin{pmatrix} h_{1z} \\ h_{2z} \\ h_{3z} \end{pmatrix} \propto \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \\
\mathbf{S}_1^1 \cdot 2 &\propto \sum_{g \in \mathbf{G}_{0k}} \chi^{*1}(g) \det(h) \delta_{2,g[1]} \begin{pmatrix} h_{1x} \\ h_{2x} \\ h_{3x} \end{pmatrix} = \chi^{*1}(2_{1z}) \cdot \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix} + \chi^{*1}(m) \cdot \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix} \propto \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix} \\
\mathbf{S}_2^1 \cdot 2 &\propto \sum_{g \in \mathbf{G}_{0k}} \chi^{*1}(g) \det(h) \delta_{2,g[1]} \begin{pmatrix} h_{1y} \\ h_{2y} \\ h_{3y} \end{pmatrix} \propto \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix}; & \quad \mathbf{S}_3^1 \cdot 2 &\propto \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}
\end{aligned}$$

We see that the atomic components calculated, using the direct formula, correspond well to the 3D vectors embedded as part of the row used for the complete basis functions. The calculation by hand using the explicit formula is probably not as intuitive as the use of the projection operator directly but it is quite convenient for automatic calculations using computer programs.

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