The magnetic section of the Bilbao Crystallographic Server -2nd Tutorial

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This 2nd tutorial includes practical introductory examples of the combined use of the following programs:

k-SUBGROUPSMAG
MAGMODELIZE
MAGNETIC REP
Get_mirreps
MVISUALIZE

For other programs of the magnetic section see the 1st and 3rd tutorials

1. Introduction

In this second tutorial, we shall practice with the tools of the magnetic section of the BCS (k-SUBGROUPSMAG, MAGMODELIZE, MAGNETIC REP, Get_mirreps, MVISUALIZE, etc.), which can be used for modeling a magnetic structure, from some basic experimental information.

As auxiliary program we will also use MAGNEXT, which allows to investigate the plausibility of the possible models according to the systematic absences observed in the magnetic diffraction diagram.

Further information on these programs and the theory behind can be found in [1,2,3]

2. k-SUBGROUPSMAG: Magnetic subgroups consistent with some given propagation vector(s) or a supercell

k-SUBGROUPSMAG can be used to explore ALL possible magnetic symmetries which are consistent with one or more observed propagation vectors. After introducing the space group of the paramagnetic phase (parent space group), the propagation vector(s), and the Wyckoff positions of the magnetic atoms, the program provides all possible symmetries of the magnetic structure, as subgroups of the parent gray group and shows their group-subgroup hierarchy. The conjugacy classes of equivalent subgroups can also be obtained, and the irreps compatible with each symmetry can be retrieved. Also the systematic absences associated with each possible symmetry of the magnetic structure can be obtained.

The possible subgroups provided by the program can be filtered according to different criteria, in particular the condition that the subgroups should correspond to the action of an order parameter transforming according to one (or several) specific irreducible representation(s) of the parent space group.

Through a link with the program MAGMODELIZE, if the parent paramagnetic structure is introduced, models of the magnetic structures can be constructed corresponding to the possible symmetries chosen by the user among the list of subgroups

provided by k-SUBGROUPSMAG. The models can be visualized, and/or exported as magCIF files for further test, refinement or analysis. The magCIF file obtained for each of the alternative magnetic structures can be used for refinement of the model in programs like JANA2006 [3] or FULLPROF [4], or they can be introduced in the program ISODISTORT [5] for mode analysis, or transformed with the structure editor STRCONVERT within the Bilbao server. These magCIF files can also be used for 3D visualization with VESTA[6] or Jmol [7]. A direct link to the tool MVISUALIZE also allows an online visualization with JSmol of the alternative models as they are constructed.

k-SUBGROUPSMAG can also be used in the background by the users of the refinement program GSAS-II [8]. Through a direct online link with k-SUBGROUPSMAG, GSAS-II retrieves the set of possible MSGs that may be relevant for the case under study, and the modelling for each of them is then done directly by GSAS-II.

Example: $Ba_3Nb_2NiO_9$

The paramagnetic structure of $Ba_3Nb_2NiO_9$ (Lufaso, Chem. Mat. 16, 2148 (2004) and Hwang et al., *Phys. Rev. Lett.* (2012) 109, 257205) can be summarized as:
(file: Ba3Nb2NiO9_parent.cif)

Space group: P-3m1 (N. 164)
Lattice parameters: 5.7550, 5.7550, 7.0656 90 90 120
Asymmetric unit:
Ba1 0.33333 0.66667 0.66380
Ba2 0.00000 0.00000 0.00000
Ni1 0.00000 0.00000 0.50000
Nb2 0.33333 0.66667 0.17700
O1 0.50000 0.00000 0.00000
O2 0.16978 0.33960 0.32623
(The small occupancy mixing reported in the older reference is neglected)

Magnetic atom: Ni
Observed propagation vector: (1/3,1/3,1/2)

We will use k-SUBGROUPSMAG, MAGMODELIZE and other programs to explore the possible magnetic orderings compatible with the observed propagation vector. The exploration is done in a hierarchical way starting with those orderings having as much symmetry as possible. Subsequently, the restriction to a single irrep will also be introduced.

2.1 k-SUBGROUPSMAG without irreps

a) Open the main page of k-SUBGROUPSMAG, introduce the number of the space group of the paramagnetic phase and the propagation vector, **and submit with the rest of options in their default values.** A list of 25 possible MSGs are obtained. The Ni atom lies on a special position, and some of the listed symmetries may be irrelevant because they would force a zero magnetic moment on the position of ALL Ni atoms. We shall first drop these irrelevant symmetries.

b) Go back to the main menu and clicking on "Wyckoff" introduce the Wyckoff position 1b occupied by the Ni atoms. This will filter the list of MSGs,

only leaving those that allow non-zero magnetic moments in ALL Ni sites. The list of possible MSGs now reduces to 13, and some of the maximal MSGs are of quite low symmetry (Figure 1).

There are however 4 additional possible MSGs for a magnetic ordering on this site, not shown in the list, which would force SOME of the Ni atoms to have zero magnetic moment. This can be seen by clicking on the button "more options" and then choosing the option: "non-zero magnetic moment allowed at (at least) SOME Wyckoff positions". This will make increase the list to 17 different possible MSGs. But we will first consider that the ordering of all Ni sites is more probable, and we shall stick to the original 13 MSGs shown in Figure 1.

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps	Magnetic structure models (MAGMODELIZE)
1	$P_c\bar{3}1c$ (No. 163.84)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 2 & 0 & 1 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	6=6x1	Conjugacy Class	Get irreps	☐
2	P_c31c (No. 159.64)	$\begin{pmatrix} 1 & 1 & 0 & -2/3 \\ -1 & 2 & 0 & -1/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	12=6x2	Conjugacy Class	Get irreps	☐
3	P_c31m (No. 157.56)	$\begin{pmatrix} 1 & 1 & 0 & -2/3 \\ -1 & 2 & 0 & -1/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	12=6x2	Conjugacy Class	Get irreps	☐
4	P_c312 (No. 149.24)	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 2 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	12=6x2	Conjugacy Class	Get irreps	☐
5	P_c3 (No. 143.3)	$\begin{pmatrix} 2 & -1 & 0 & 1/3 \\ 1 & 1 & 0 & -1/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	24=6x4	Conjugacy Class	Get irreps	☐
6	C_c2/c (No. 15.90)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 3 & 0 & -1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	18=6x3	Conjugacy Class	Get irreps	☐
7	C_c2/m (No. 12.63)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 3 & 0 & -1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	18=6x3	Conjugacy Class	Get irreps	☐
8	C_cc (No. 9.40)	$\begin{pmatrix} 2 & 0 & 0 & 1/5 \\ 1 & 3 & 0 & -2/5 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	36=6x6	Conjugacy Class	Get irreps	☐
9	C_cm (No. 8.35)	$\begin{pmatrix} 2 & 0 & 0 & 1/5 \\ 1 & 3 & 0 & -2/5 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	36=6x6	Conjugacy Class	Get irreps	☐
10	C_c2 (No. 5.16)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 3 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	36=6x6	Conjugacy Class	Get irreps	☐
11	C_c2 (No. 5.16)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 3 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	36=6x6	Conjugacy Class	Get irreps	☐
12	$P_S\bar{1}$ (No. 2.7)	$\begin{pmatrix} 2 & -1 & 0 & -1/2 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$	36=6x6	Conjugacy Class	Get irreps	☐
13	P_S1 (No. 1.3)	$\begin{pmatrix} 2 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	72=6x12	Conjugacy Class	Get irreps	☐

Figure 1. List provided by k-SUBGROUPSMAG of all possible magnetic symmetries of a magnetic ordering for a paramagnetic structure with space group *P-3m1* and propagation vector (1/3,1/3,1/2), if the magnetic atom is at the Wyckoff position *1b*, and with the additional condition that ALL magnetic atoms should be allowed to have non-zero magnetic moments. Only one subgroup per conjugacy class is shown. By clicking on the button "conjugacy class" a list of all distinct subgroups belonging to the conjugacy class is shown. The button "Get irreps" is a direct link to the program Get_mirreps, which allows to obtain all the irreps of the parent space group that are compatible with the listed subgroup of the gray parent group. The last column allows to choose those symmetries that one wants to transmit to MAGMODELIZE for further analysis of the corresponding magnetic structure models (as you will see in the steps below).

Each subgroup is defined by the MSG type indicated in the second column with its BNS symbol and its BNS numerical label, and by the transformation to the standard

setting of this MSG, indicated in the third column. This transformation is fundamental to define unambiguously the subgroup. As it happens here, different subgroups can be of the same MSG type, and can only be distinguished by the transformation to standard, which is necessarily different.

The transformation (**P**,**p**) listed for each subgroup, where **P** is a 3x3 matrix and **p** = (p_1, p_2, p_3) a column vector, indicates in each case a choice of unit cell and origin, for which the subgroup adquires the standard setting of the corresponding magnetic space group (MSG) given by the MSG label, i.e. the symmetry operations of the subgroup would take when described using this unit cell and origin, the form used for this MSG in the listings taken as standard (you can use MGENPOS to see these listings). The transformation (**P**,**p**) is defined with respect to the unit cell ($\mathbf{a}_p$,$\mathbf{b}_p$,$\mathbf{c}_p$) and origin $\mathbf{O}_p$ of the parent space group, in the following form:

$$(\mathbf{a}^s,\mathbf{b}^s,\mathbf{c}^s)= (\mathbf{a}_p,\mathbf{b}_p,\mathbf{c}_p).\mathbf{P} \quad , \quad \mathbf{O}^s = \mathbf{O}_p + p_1\,\mathbf{a}_p + p_2\,\mathbf{b}_p + p_3\,\mathbf{c}_p$$

where ($\mathbf{a}^s$,$\mathbf{b}^s$,$\mathbf{c}^s$) and $\mathbf{O}^s$ are the unit cell vectors and origin for a standard setting of the MSG.

*Note that we are using the convention of the International Tables for Crystallography and the transformed basis vectors are the **columns** of the matrix. It is important to be aware of this convention when comparing with other programs (like ISODISTORT), where the **rows** of the matrix are the transformed basis vectors.*

c) Click on the button "Get subgroup-graph" in the output page showing the list of Figure 1. The hierarchical group-subgroup graph of the 13 possible MSGs, as subgroups of the gray symmetry group *P-3m11'* of the paramagnetic phase, is then obtained (Figure 2):

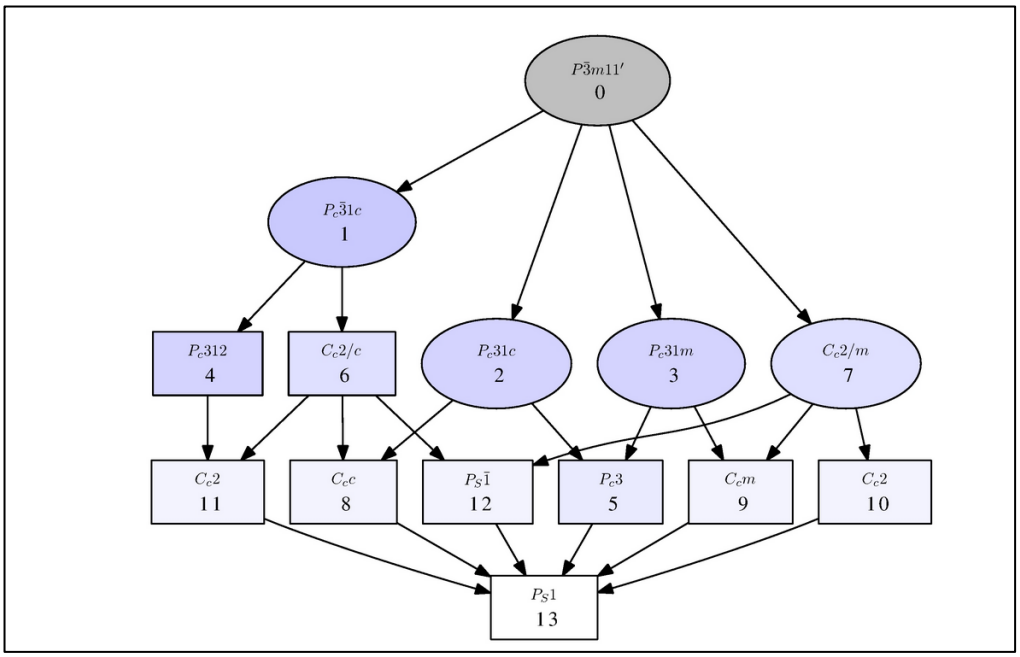


Figure 2. Group-subgroup hierarchical graph of the MSGs listed in Figure 1, all of them subgroups of the parent MSG *P-3m11'*.

Figure 2 shows that the subgroup conjugacy classes numbered 1, 2, 3 and 7 are maximal under these conditions (we called them *k-maximal* subgroups) and they are the first candidates to explore in an eventual fit of experimental diffraction data or in a DFT calculation, as empirically we know that symmetry tends to be kept as high as possible. Two of these four possible k-maximal symmetries are polar along the trigonal axis, and therefore correspond to a magnetic phase bound to have some magnetically induced electric polarization (type II multiferroic). In fact, the structure published for $Ba_3Nb_2NiO_9$ (magndata #1.13) corresponds to one of these polar k-maximal subgroups, namely P_c31c.

d) Go back to the output page with the list shown in Figure 1, and in the last column entitled "magnetic structure models" check the boxes corresponding the mentioned k-maximal subgroups numbered 1 ,2 ,3 and 7; and also at the bottom of the page, check "include structure data of the parent phase", and submit to MAGMODELIZE. A first input page appears to introduce the structure of the paramagnetic phase. Submit the cif file of the parent structure of $Ba_3Nb_2NiO_9$: Ba3Nb2NiO9_parent.cif, or introduce it by hand using the data of the structure listed above. In the next page, check the Ni atom as the only magnetic atom and submit. The resulting output page is partially reproduced in Figure 3.

N	Group (BNS)	Transformation matrix	General positions	Properties	Magnetic structure
1	P_c-31c (#163.84) Go to a subgroup	$\begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 2 & 0 & 1 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
2	P_c31c (#159.64) Go to a subgroup	$\begin{pmatrix} 1 & 1 & 0 & 7/3 \\ -1 & 2 & 0 & 8/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
3	P_c31m (#157.56) Go to a subgroup	$\begin{pmatrix} 1 & 1 & 0 & 7/3 \\ -1 & 2 & 0 & 8/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
4	C_c2/m (#12.63) Go to a subgroup	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 3 & 0 & 5/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show

Figure 3. Output page of MAGMODELIZE for the four subgroups of maximal symmetry introduced directly from k-SUBGROUPSMAG.

The second symmetry in the list is the one that is realized in the structure reported for $Ba_3Nb_2NiO_9$ and we will explore it first, but of course when investigating an unknown structure we would go through all the listed subgroups and check which one fits better our data.

e) Construct the magnetic structure corresponding to the second subgroup on the list reproduced in Fig. 3, namely the one of type *P_c31c*, by clicking on "show" in the last column. The resulting output page (Figure 4) shows that the Ni site remains unsplit, with a single symmetry-independent atom.

The unit cell and origin used by default for the description of the structure (what we call "parent-like" setting) is indicated at the heading of the output reproduced in Figure 4, giving its relation with the parent unit cell. This setting

(generally non-standard for the MSG) keeps the origin and also the unit cell orientation of the parent/paramagnetic phase, but if necessary, multiplies the cell parameters to produce a supercell consistent with the periodicity kept by the propagation vector. At the heading of the list one can also find the transformation from the parent unit cell and origin to the standard setting of the MSG, and one can change the description to this setting, or to any arbitrary (but consistent) basis chosen by the user. The output includes a list of the atoms of an asymmetric unit (second column), the corresponding orbit of symmetry related atoms within the defined unit cell (third column), the number of atoms of each orbit (fourth column), the symmetry constraints of the magnetic moments for the representative magnetic atoms in the asymmetric unit (fifth column), and a window to introduce by hand any value for the free components of the magnetic moments (sixth column). One can see in this output, partially reproduced in Figure 4 that the Ni spin has two free parameters, with the spin direction of the independent Ni atom on the xy plane being symmetry dictated, but having an additional free z component. Let us assume for the moment that this z spin component is zero.

Magnetic Structure

Selected magnetic space group: 2- P_c31c (#159.64)

Setting parent-like (**3a, 3b, 2c** ; 0, 0, 0)

Parent space group 164 (*P*-3*m*1)

Lattice parameters: a=17.26500, b=17.26500, c=14.13120, alpha=90.00, beta=90.00, gamma=120.00

[Go to setting standard (**a-b, a+2b, 2c** ; 7/3, 8/3, 0)]
[Go to an alternative setting]

Export data to MCIF file/Visualize | Go to a subgroup

Atomic positions, Wyckoff positions and Magnetic Moments

2	Ba2 Ba 0.00000 0.00000 0.00000	(1/3,1/3,0 | $-m_y,m_y,m_z$) (1/3,1/3,1/2 | $m_y,-m_y,-m_z$) (1/3,2/3,0 | $2m_y,m_y,m_z$) (1/3,2/3,1/2 | $-2m_y,-m_y,-m_z$) (2/3,0,0 | $-m_y,m_y,m_z$) (2/3,0,1/2 | $m_y,-m_y,-m_z$) (2/3,1/3,0 | $2m_y,m_y,m_z$) (2/3,1/3,1/2 | $-2m_y,-m_y,-m_z$) (2/3,2/3,0 | $-m_y,-2m_y,m_z$) (2/3,2/3,1/2 | $m_y,2m_y,-m_z$)	18	-	-
3	Ni1 Ni 0.00000 0.00000 0.25000	(0,0,1/4 | $2m_y,m_y,m_z$) (0,0,3/4 | $-2m_y,-m_y,-m_z$) (0,1/3,1/4 | $-m_y,-2m_y,m_z$) (0,1/3,3/4 | $m_y,2m_y,-m_z$) (0,2/3,1/4 | $-m_y,m_y,m_z$) (0,2/3,3/4 | $m_y,-m_y,-m_z$) (1/3,0,1/4 | $-m_y,-2m_y,m_z$) (1/3,0,3/4 | $m_y,2m_y,-m_z$) (1/3,1/3,1/4 | $-m_y,m_y,m_z$) (1/3,1/3,3/4 | $m_y,-m_y,-m_z$) (1/3,2/3,1/4 | $2m_y,m_y,m_z$) (1/3,2/3,3/4 | $-2m_y,-m_y,-m_z$) (2/3,0,1/4 | $-m_y,m_y,m_z$) (2/3,0,3/4 | $m_y,-m_y,-m_z$) (2/3,1/3,1/4 | $2m_y,m_y,m_z$) (2/3,1/3,3/4 | $-2m_y,-m_y,-m_z$) (2/3,2/3,1/4 | $-m_y,-2m_y,m_z$) (2/3,2/3,3/4 | $m_y,2m_y,-m_z$)	18	$(2M_y,M_y,M_z)$	M_y = 0.00000 M_z = 0.00000

Figure 4. Partial view of the output of MAGMODELIZE describing the magnetic structure under the subgroup of type P_c31c listed in Figure 10, as obtained when clicking in the column "Magnetic structure". The table indicates the positions and moments corresponding to all atoms that are symmetry related with the one listed as representative in the asymmetric unit (all described in the parent-like setting described in the text). The number of symmetry related atoms within the used unit cell (multiplicity) is given in the fourth column. The fifth column indicates the symmetry restrictions on the value of the components of the magnetic moment for the representative magnetic atom listed in the second colum (if any), while the last column on the right allows to introduce specific values for the symmetry-free moment components.

f) Write a non-zero arbitrary value of 1 (Bohr magnetons) for the y component of the Ni magnetic moment, and keep m_z zero. Click then on "Export data to MCIF file/Visualize". A magCIF file of the model is then created, which is shown on a non-editable window. Save the magCIF file by clicking on "bcs_file.mcif", giving it an appropriate name, say P_c3c1.mcif. Inspect the text of the magCIF file and locate the place where the transformation to the standard setting from the one used in the file is indicated. You can see that this transformation is:

(1/3**a**-1/3**b**, 1/3**a**+2/3**b**, **c**; 7/9, 8/9, 0)

Compare with the transformation to standard given in the output page obtained in step d) (see Figure 3). Why are they different? What is the relation between the two transformations?

g) Click on the button "submit to MVISUALIZE" to visualize the structure online with JSmol, using the MVISUALIZE tool. This transmits the magCIF directly to the program MVISUALIZE. On the next webpage that appears, use the button "toggle parent cell" to visualize simultaneously the parent unit cell, and the one that is being used in the description given in the magCIF file. (Figure 5).

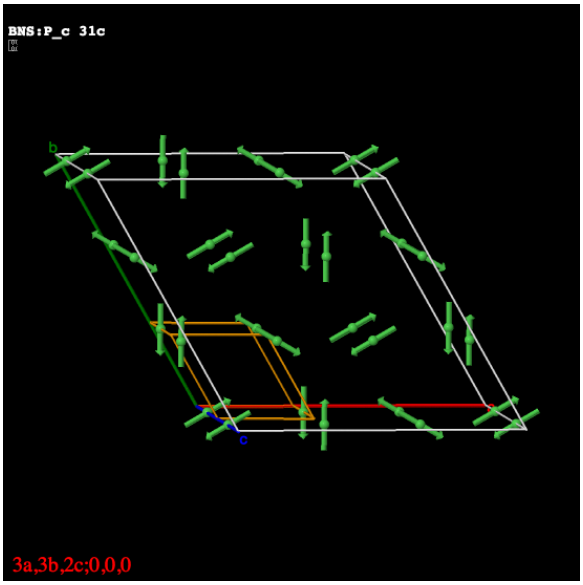


Figure 5. Representation of the magnetic structure with symmetry P_c31c (**a**-**b**, **a**+2**b**, **c**; 7/3,8/3,0) assuming a null value of the allowed z-component of the Ni spin, as obtained with MVISUALIZE, and showing both the parent unit cell and the one of the *parent-like* setting used.

h) Use the button "toggle standard" to visualize the standard unit cell proposed by the transformation indicated in the magCIF file. (Figure 6).

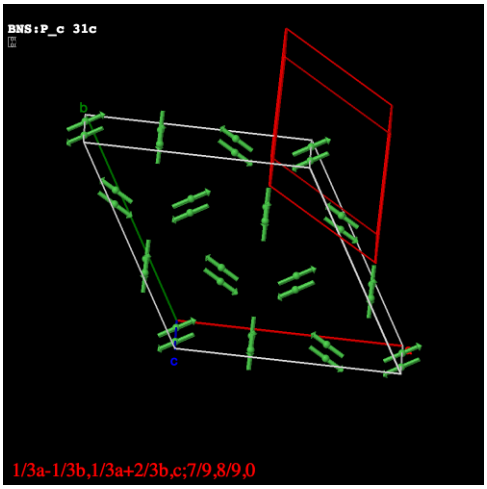


Figure 6. Representation of the magnetic structure with symmetry P_c31c as obtained with MVISUALIZE, and showing both the standard unit cell indicated in the magCIF file and the one of the *parent-like* setting used.

i) In the button-menu entitled "select cell", select "standard cell" to visualize the structure using the standard unit cell proposed in the magCIF file (Figure 7). Explore the buttons that the page offers to control, edit, export, etc. the image. A complementary window to introduce any Jmol command is also available. In addition, by right-clicking on the graphic window, a detailed Jmol menu is unfolded, and in particular a console can be opened to manipulate the image.

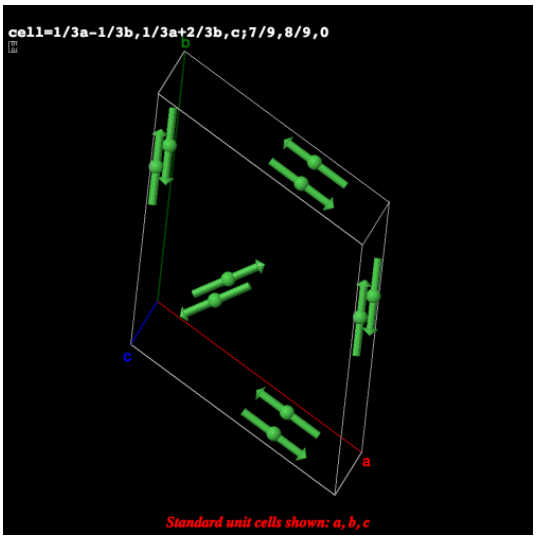
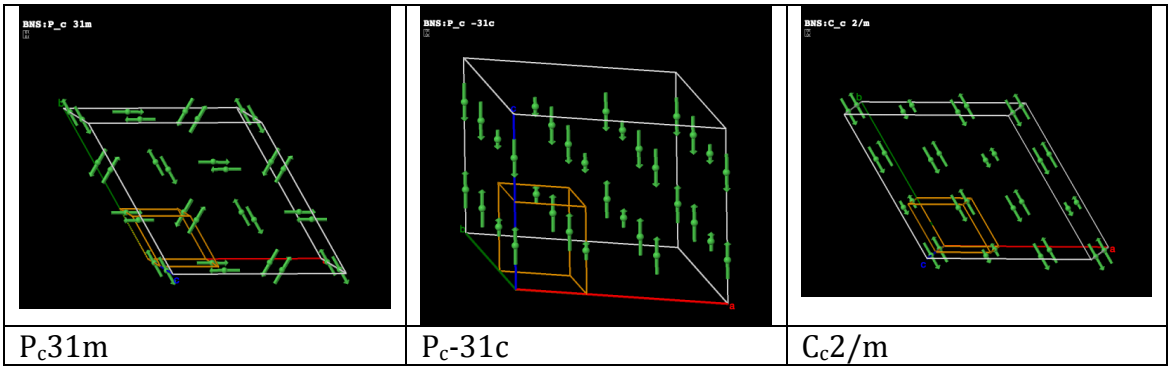


Figure 7. Representation of the magnetic structure with symmetry P_c31c as obtained with MVISUALIZE, using the standard unit cell indicated in the magCIF file.

j) Do analogous steps to e), f) and g) for the other three subgroups in the list of Figure 3 to obtain magCIF files of the corresponding magnetic structures and visualize them either with the direct link to MVISUALIZE, or loading the corresponding magCIF files in Jmol or VESTA. (Figure 8)



P_c31m	P_c-31c	C_c2/m

Figure 8. Scheme of the magnetic structures with the indicated maximal symmetries listed in Figure 3, as obtained with MVISUALIZE using the corresponding magCIF files created with MAGMODELIZE. For the case of *P_c-31c* and *C_c2/m*, the Ni site splits into two symmetry independent sites, each with a single free parameter, and they have been given arbitrary different values to distinguish the two sites. In the case of *P_c31m*, the single Ni site has only one free parameter, with no z spin component allowed.

k) Go back to the output page of MAGMODELIZE with the four subgroups of maximal symmetry, which was obtained in step d) and is shown in Figure 3, and investigate the systematic absences for the four symmetries, using the direct link to MAGNEXT.

When inspecting the output of this program for each subgroup one must take into account that the used (h,k,l) indexing corresponds to the supercell with which the magnetic structure is being described. On Figure 9, a partial view of the output of MAGNEXT for the second subgroup in the list (*P_c31c*) is shown. One can see that that all reflections of type (0,0,l) will be absent. Notice that the absence of the reflections on the c direction, however, should not be taken as a general indication that the moments are along this direction.

Systematic Absences of the magnetic space group *P_c31c* (#159.64) in the setting (3a, 3b, 2c; 0, 0, 0) of the parent space group *P*-3*m*1 (No. 164)

Values of h, k, l: **h integer, k integer, l integer**

Warning: h, k, l are referred to the parent-like setting

Systematic absences for general reflections (produced by centrings):

Diffraction vector type: **(h k l)** -> Systematic absence: **l = 2n or h + 2k /= 3n**

Systematic absences for special reflections:

Diffraction vector type: **(0 0 l)** -> Systematic absence: **l any**

```
For  l = 1 :      I = 0       F = (0,0,Fz)
```

[Show form of structure factor for every type of reflection]

Figure 9. Output of MAGNEXT for the subgroup of type *P_c31c* when introduced directly with the optional button available in the ouput of k-SUBGROUPSMAG (Figure 3).

Comparing with analogous outputs for the other three subgroups, you can check that this systematic absence happens for the first three subgroups in the list, while it does not exist in the monoclinic subgroup of type C_c2/m. This means that the observation of reflections of type (0,0,l) would allow to discard these three trigonal subgroups, and we would only be left with the monoclinic one as possible k-maximal symmetry.

The systematic absence for general reflections (h,k,l), which is listed for all the subgroups, is trivial in the sense that it is equivalent to the presence of the propagation vector (1/3,1/3,1/2), if the reflections were indexed using the parent unit cell. Here, the reciprocal unit cell of the supercell (3a,3b,2c) is being used for the indexing, and then self-consistently, the MSG associated with the structure introduces this general systematic absence, which reduces the reflections to those that can be explained with the mentioned propagation vector.

l) Click on "Show form of structure factor for every type of reflection" at the bottom of the output reproduced in Figure 9. Inspecting the resulting output, derive that if the magnetic moments in the structure lie on the xy plane with no component along z, then all reflections of type (h,-h,0), (h,0,0) and (0,k,0) should be absent (a structure factor component can only be non-zero if there are spins in the structure with some non-zero component in this direction, and you have to consider that the diffraction vectors are expressed with respect to the reciprocal unit cell, while the structure factor is expressed in the direct space unit cell basis) .

m) Load the magCIF file corresponding to the subgroup of type *P_c31c* saved in step f) in the program VESTA. Go in this program to Edit -> Edit Data -> Structure Parameters. In the menu of symmetry independent atoms, delete all atoms except the magnetic Ni site -> OK.
Then Edit -> Vectors -> Click on the list Ni site and on the listed vector, and click on "set". This will recover the correct assignment of the vector describing the spin of the Ni site, which has been lost through the deleting of the preceding atoms. You can save the image that you have obtained for instance as .png using File -> Export Raster Image. Compare the view of the structure that you have obtained with the one that is available in MAGNDATA for the reported structure and it is reproduced in Figure 10. The arrangement is different, but **is it equivalent?**

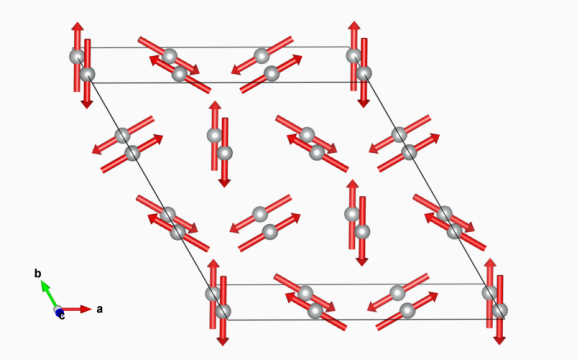


Figure 10: Magnetic structure of $Ba_3Nb_2NiO_9$ (only Ni atoms), according to Hwang et al., *Phys. Rev. Lett.* (2012) 109, 257205 (MAGNDATA #1.13).

n) Come back to the listing of subgroups that you obtained in step b) and is reproduced in Figure 1 and inspect the subgroup index of the relevant subgroup for your structure. This index is listed as 6x2. This means that the lattice and the point group are decreased by a factor 6 and 2 in the magnetic ordering, respectively, such that the number of operations in the subgroup is 12 times smaller. This means that we should expect 12 different domains, i.e. 12 different but equivalent arrangement of the structure, obtained by applying to the structure 12 lost symmetry operations. Those obtained by just applying time reversal, i.e. by flipping all spins, are trivial, and therefore we are left with 6 different distinct forms to describe the structure, which are equivalent.

The final question in the previous step is then to decide if the spin arrangement shown in Figure 5, and the one in Figure 10 are domain-related and therefore equivalent. One can intuitively be convinced that it is the case, but one should do it rigorously (in many cases, arrangements that look similar are not equivalent!). A rigorous verification is done by just checking that the two structures can be related by a lost operation of the parent group.

For this kind of problems we can use MVISUALIZE as a standalone program to enumerate and construct all distinct equivalent domain-related forms of describing the structure. We shall do this in the following steps.

o) Go to the program MVISUALIZE and upload the magCIF file saved in step f) corresponding to the subgroup *P_c31c*, and shown in Figure 5. The program then shows a page with an image of the uploaded structure. **On the left click on the button "domain-related equivalent structures"**. The resulting output page shows at the bottom the list of 6 possible domain-related equivalent structures (Figure 11). For each structure a lost operation (coset representative) is given. This operation relates the domain-related structure of this row with the first one in the list, which is the one of the input magCIF file. The six additional trivial domain-related structures, obtained by the application of time reversal (spin flip) to those listed, are not included in this list.

Domain-related equivalent structures: coset representatives and conjugated subgroups

The transformation matrices of the table are from the parent space group to the standard setting of the listed magnetic space groups
The coset representatives used to derive the domain-related equivalent structures are expressed in the setting of the parent group

N	Coset representatives		Transformation matrix	Magnetic Structure
	(x,y,z) form	Seitz notation		
1	x,y,z,+1	{ 1 | 0 }	$\begin{pmatrix} 1 & 1 & 0 & 7/3 \\ -1 & 2 & 0 & 8/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	Show
2	x+1,y,z,+1	{ 1 | 1 0 0 }	$\begin{pmatrix} 1 & 1 & 0 & 1/3 \\ -1 & 2 & 0 & 8/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	Show
3	x+1,y+1,z,+1	{ 1 | 1 1 0 }	$\begin{pmatrix} 1 & 1 & 0 & 1/3 \\ -1 & 2 & 0 & 2/3 \\ 0 & 0 & 2 & 0 \end{pmatrix}$	Show
4	y,x,-z,+1	{ 2_{110} | 0 }	$\begin{pmatrix} -1 & 2 & 0 & 8/3 \\ 1 & 1 & 0 & 7/3 \\ 0 & 0 & -2 & 0 \end{pmatrix}$	Show
5	x-y,-y,-z,+1	{ 2_{100} | 0 }	$\begin{pmatrix} 2 & -1 & 0 & 8/3 \\ 1 & -2 & 0 & 1/3 \\ 0 & 0 & -2 & 0 \end{pmatrix}$	Show
6	-x,-x+y,-z,+1	{ 2_{010} | 0 }	$\begin{pmatrix} -1 & -1 & 0 & 2/3 \\ -2 & 1 & 0 & 1/3 \\ 0 & 0 & -2 & 0 \end{pmatrix}$	Show

Figure 11. Partial output of MVISUALIZE when using the option "domain-related equivalent decriptions" for the structure construted in step f) and shown in Figure 5 . The six equivalent domain-related structures are listed together with an operation that transforms it into the input one (the first one).

p) Click on "show" for the 3rd case in the list shown in Figure 11. The resulting output page shows the structure related with the first one by the application of the lost lattice translation (1,1,0). The output allows to download a magCIF of this equivalent transformed structure, visualize it, transform it to the standard setting, change it to any setting, etc.

q) Click on "Visualize" on the output page obtained in the previous step and compare the view of the structure with the one that is available in MAGNDATA for the reported structure and reproduced in figure 10. Check that they are the same structure. Note that this identification of the MSG of the structure means that the symmetry of the structure reported for $Ba_3Nb_2NiO_9$ has a free z component for the moment of the symmetry independent Ni atom. This means that in this phase a spin canting along z is possible.

(If you have been very quick with the previous steps, you can try to imagine and/or produce using this program the images of the other four possible domain equivalent descriptions of the structure. Otherwise, go to the next step).

2.2. k-SUBGROUPSMAG with irreps

Up to now we have only made use of the condition that the MSG describing the symmetry of the magnetic structure should be a subgroup of the gray group *P-3m11'*, and must be consistent with the observation of (1/3,1/3,1/2) as single propagation vector. We have shown that for this example the structure that has been reported can be obtained by just looking at the four possible models of

maximal symmetry, which are compatible with the observed propagation vector (k-maximal subgroups). We have also obtained that this experimental structure can have a canting of the spins along the z direction, as it is perfectly compatible with its MSG.

But k-SUBGROUPSMAG can also introduce the additional filter that the investigated symmetry break should be the result of a spin arrangement according to one (or more) specific irrep(s). We will continue practicing these options with the same example.

r) Go back to the main input page of k-SUBGROUPSMAG obtained in step b) and in the option "choose irreps" click on "representations". The program provides then an output page with the irrep decomposition of the magnetic representation for the Wyckoff site *1b* (Figure 12) (it uses the result of the output of the program MAGNETIC REP, also in the Bilbao server, which can be used as a standalone program for decomposing the magnetic representation into irreps for any paramagnetic parent group and any Wyckoff position)

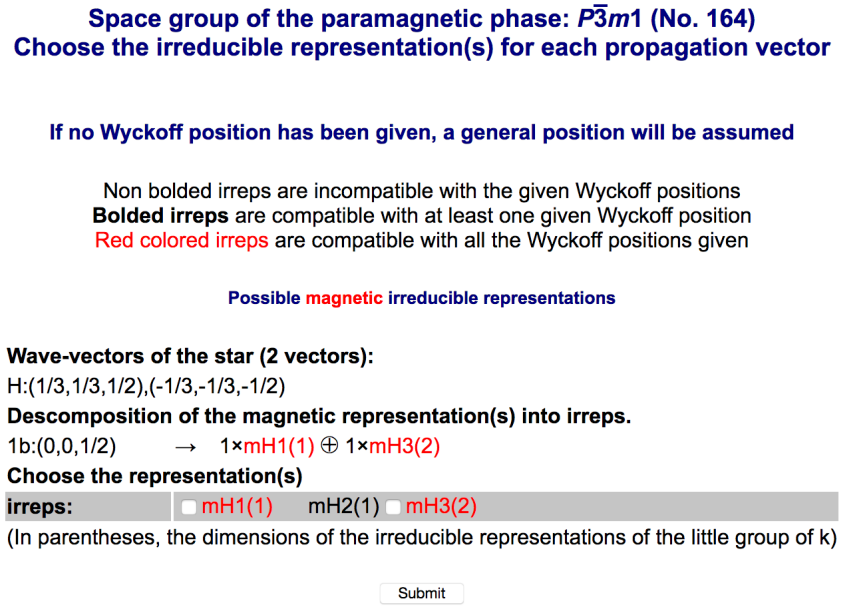


Figure 12. Irrep decomposition of the magnetic representation for the propagation vector (1/3,1/3,1/2) and the site *1b*, as given by k-SUBGROUPSMAG. The number in parenthesis after each irrep indicate the dimension of the small irrep. As the irrep star has two vectors, a factor 2 relates the dimension of each irrep with that of the corresponding small irrep.

The irrep labels in this output are those used in the ISOTROPY webpage, and one can always inspect their matrix form by going to the program REPRESENTATIONS SG (or also the program REPRES) in the section "Representations and Applications" of the Bilbao Crystallographic Server, taking into account that the symbol *m* in the irrep label only indicates that the irrep is odd for time reversal. One can see in the output shown in Figure 12 that there are two possible irreps for the magnetic ordering of the Ni site.

s) Check irrep mH1 and submit to include in the input the condition of the magnetic ordering being according to this irrep. Submit the new input page.

The list and graph of possible MSGs for this irrep can then be obtained with only three possible symmetries (Figures 13).

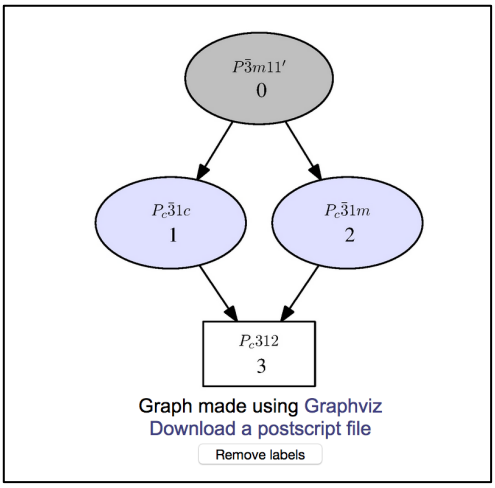


Figure 13. Graph of the possible MSGs that can be realized by a magnetic ordering according to the 2-dim irrep mH1.

The two epikernels of mH1, of type P_c-*31c* and P_c-*31m*, shown in Figure 13 are two of the six k-maximal subgroups in the list of 25 subgroups that were obtained above in step a). The second one, P_c-*31m*, forces a cero magnetic moment at some of the Ni sites. This is the reason why this subgroup did not appear in step b).

A word of caution is obliged here: magnetic structures with some fraction of the magnetic sites having zero average magnetic moments are less common, and therefore one may consider them less probable to be realized, but there is no reason to discard them beforehand, and magnetic structures of this type are also reported (see for instance the structure of $Gd_2Ti_2O_7$ (magndata #1.56)).

t) Come back to the output page with the irrep decomposition of the magnetic representation and check irrep mH3, instead of mH1. Submit to produce a new input page with this second irrep. Submit the new input page. The list and graph of possible MSGs that can be realized by a magnetic ordering according to this irrep is then obtained. The large dimension of this irrep makes that the number of possible distinct magnetic symmetries quite large, namely 14, with 13 distinct irrep epikernels and the kernel. Six of the epikernels are maximal. Some of these maximal subgroups split the *1b* site, with some of the resulting split sites being symmetry forced to have zero spin. These groups can be filtered and discarded using the option that appears clicking the "more options" button and then applying the option that limits the list of subgroups to those allowing non-zero magnetic moment in ALL sites (Figure 14). The number of possible MSGs reduces then to 11, and the number of maximal epikernels to 4.

One of the maximal epikernels of mH3 is the subgroup P_c*31c*, which is the symmetry of the reported structure of $Ba_3Nb_2NiO_9$ (MAGNDATA #1.13). Hence, mH3 can be considered the active irrep for the magnetic ordering of this compound. This irrep describes the transformation properties of the 4-dim primary order parameter responsible of this phase.

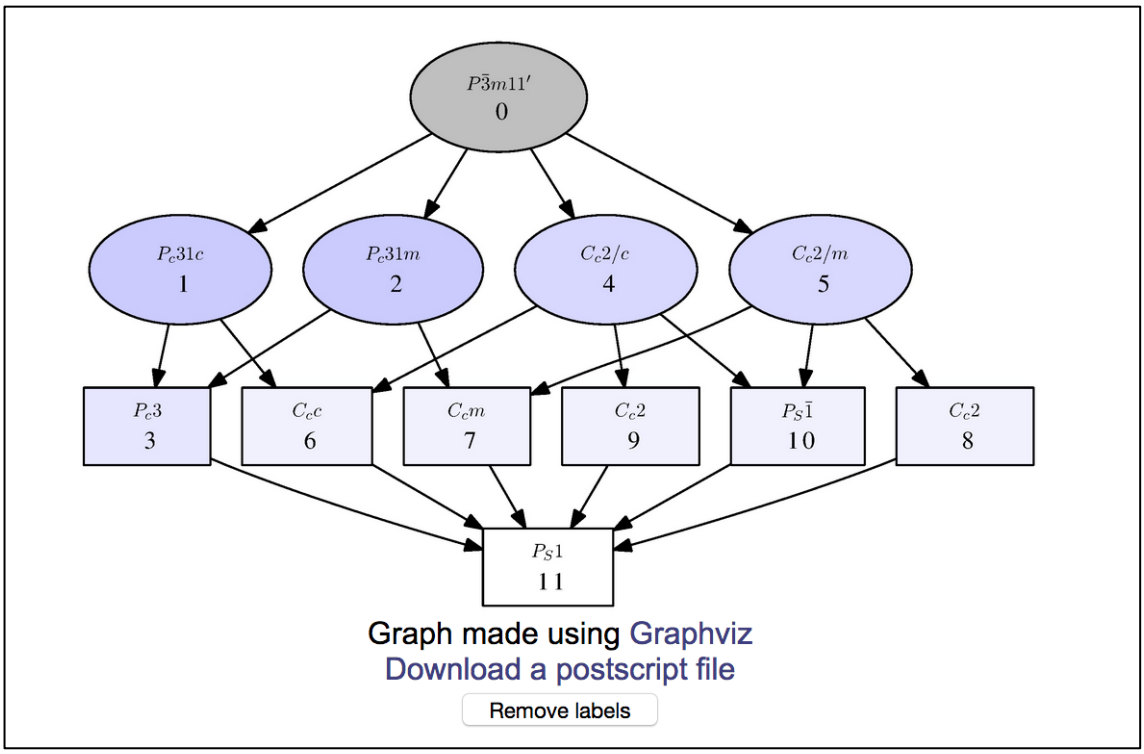


Figure 14. Graph of the possible MSGs that can be realized by a magnetic ordering according to the 4-dim irrep mH3, with the additional restriction that the MSG should allow non-zero magnetic moments at ALL sites derived from the Wyckoff positions *1b* of the parent space group *P-3m1*.

Three of these maximal epikernels can be identified with three k-maximal MSGs obtained in step c) shown in Figure 2. But the additional fourth maximal epikernel in Figure 12, of type *C_c2/c*, is not a k-maximal subgroup. This means that there must be at least a MSG consistent with the propagation vector, allowing magnetic order at all Ni sites, which is a supergroup of this group of type C_c2/c. This supergroup can be easily seen on Figure 2: it is the subgroup *P_c-31c*, which has been already investigated in step j).

v) Check the button "Get irreps" for the subgroup of type C_c2/c in the listing of subgroups corresponding to Figure 14. The program then links directly to the standalone program Get_mirreps, which provides for the pair parent group-magnetic subgroup, the list of compatible irreps, and for each of them the required irrep direction, and the corresponding isotropy subgroup. The resulting output (Figure 15) shows that not only irrep mH3, but also the irrep mH1 is also compatible with the group *C_c2/c*.

List of physically irreducible representations and order parameters between a parent group and a given subgroup.

Input data

Group→subgroup	Transformation matrix
$P\bar{3}m11'$ (N. 164.86)→C_c2/c (N. 15.90)	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 1 & 3 & 0 & -1/2 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$

Representations and order parameters

Show the graph of isotropy subgroups

k-vectors	irreps and order parameters	isotropy subgroup transformation matrix	link to the irreps
GM: **(0,0,0)**	GM_1^+: (a)	$P\bar{3}m11'$ (No. 164.86) a,b,c;0,0,0	matrices of the irreps
	GM_3^+: (a,-(√3 a))	$C2/m1'$ (No. 12.59) 2a+b,b,c;0,0,0	
K: **(1/3,1/3,0)**	K_1: (a,√3 a)	$P\bar{3}1m1'$ (No. 162.74) 2a+b,-a+b,c;1,0,0	matrices of the irreps
	K_3: (a,0,√3 a,0)	$C2/m1'$ (No. 12.59) 2a+b,3b,c;0,-1/2,0	
A: **(0,0,1/2)**	mA_1^-: (a)	$P_c\bar{3}c1$ (No. 165.96) a,b,2c;0,0,1/2	matrices of the irreps
	mA_3^-: (a,√3 a)	C_c2/c (No. 15.90) 2a+b,b,2c;0,0,1/2	
H: **(1/3,1/3,1/2)**	mH_1: (a,-(a/√3))	$P_c\bar{3}1c$ (No. 163.84) a-b,a+2b,2c;0,1,1/2	matrices of the irreps
	mH_3: (a,0,-(a/√3),0)	C_c2/c (No. 15.90) 2a+b,3b,2c;0,-1/2,1/2	

Figure 15. Output of the program Get_mirreps obtained by clicking on the button "Get irreps" for the epikernel of mH3 of type C_c2/c.

As the magnetic representation of site *1b* for the observed propagation vector decomposes in the form (Figure 12):

$$1\ \mathrm{mH1(1)} + 1\ \mathrm{mH3(2)}$$

and the output reproduced in Figure 15 indicates a fixed direction within both irrep spaces, a spin arrangement complying with the subgroup C_c2/c, will have a single degree of freedom corresponding to each irrep. mH3 is the primary irrep for this symmetry, and the four irrep spin basis functions must be combined in a specific form to produce this symmetry, leaving a single amplitude to fit. But this MSG allows a second degree of freedom with the same propagation vector according to mH1, as secondary irrep. The output in Figure 15 shows also that irreps for the wave vector A: (0,0,1/2), are also symmetry compatible. This wave vector is in fact associated with the third harmonic of the primary spin wave with propagation vector (1/3,1/3,1/2). This means that secondary irreps corresponding to a third harmonic (label A for the irreps) can be the symmetry of additional coupled secondary spin waves in the C_c2/c structure.

w) Go to the main menu of the magnetic section of the BCS, and click on the program MAGNETIC REP at the end of the list, and on the appearing menu, introduce the parent space group of our case: 164, and the propagation vector: (0,0,½) corresponding to the point A. In the next input page choose the

Wyckoff position of Ni. The program then provides the irrep decomposition of the magnetic representation for this Wyckoff position and the wave vector A (0,0,1/2):

1 mA1-(1) + 1 mA3-(2).

The output also indicates that the irrep star has only one vector, and therefore the dimensions in parenthesis are the dimensions of the full irreps. Taking into account the output reproduced in Figure 15, this means that a structure according to the subgroup C_c2/c will have 2 additional secondary parameters in their spin arrangement corresponding to the irreps mA1- and mA3-, which are allowed as third harmonics of the primary mH3 spin ordering. The total number of spin degrees of freedom is therefore 4, corresponding to four different irreps, and only one of them corresponds to the primary 4-dim irrep mH3.

x) Submit to MAGMODELIZE the subgroup C_c2/c in the list of subgroups corresponding to Figure 14, using the option at the bottom of the list, and introducing when required the parent structure of $Ba_3Nb_2NiO_9$, as done in step d) and f) for other symmetries.

Check that the structure has indeed four free parameters for the spins. The Ni site having split into two independent sites with four free components (Figure 16). In general, if we give to these four independent spin parameters arbitrary values we are describing a structure where spin modes corresponding to the four irreps mentioned above will be present. How can one correlate these four parameters so that the resulting structure only involves the primary irrep mH3 and only a single parameter is free? This (unfortunately) is not provided by MAGMODELIZE, which only produces the magnetic structure model under this MSG with the four free parameters as spin components of the symmetry independent sites. The decomposition of the four degrees of freedom in terms of four spin basis functions, adapted to the four irreps, can be done using ISODISTORT [5].

3	Ni1_1 Ni 0.00000 0.00000 0.25000	(0,0,1/4 | $2m_y,m_y,m_z$) (0,0,3/4 | $-2m_y,-m_y,-m_z$) (0,2/3,1/4 | $2m_y,m_y,m_z$) (0,2/3,3/4 | $-2m_y,-m_y,-m_z$) (1/3,1/3,1/4 | $2m_y,m_y,m_z$) (1/3,1/3,3/4 | $-2m_y,-m_y,-m_z$) (1/3,2/3,1/4 | $2m_y,m_y,m_z$) (1/3,2/3,3/4 | $-2m_y,-m_y,-m_z$) (2/3,0,1/4 | $2m_y,m_y,m_z$) (2/3,0,3/4 | $-2m_y,-m_y,-m_z$) (2/3,1/3,1/4 | $2m_y,m_y,m_z$) (2/3,1/3,3/4 | $-2m_y,-m_y,-m_z$)	12	$(2M_y,M_y,M_z)$	M_y = 0.00000 M_z = 0.00000
	Ni1_2 Ni 0.00000 0.33333 0.25000	(0,1/3,1/4 | $2m_y,m_y,m_z$) (0,1/3,3/4 | $-2m_y,-m_y,-m_z$) (1/3,0,1/4 | $2m_y,m_y,m_z$) (1/3,0,3/4 | $-2m_y,-m_y,-m_z$) (2/3,2/3,1/4 | $2m_y,m_y,m_z$) (2/3,2/3,3/4 | $-2m_y,-m_y,-m_z$)	6	$(2M_y,M_y,M_z)$	M_y = 0.00000 M_z = 0.00000
		(1/9,2/9,z | m_x,m_y,m_z) (2/9,1/9,-z | $-m_x,-m_y,-m_z$) (1/9,2/9,z+1/2 | $-m_x,-m_y,-m_z$) (2/9,1/9,-z+1/2 | m_x,m_y,m_z)			

Figure 16. Partial view of the output of MAGMODELIZE for the epikernel of mH3 of type C_c2/c, as obtained when clicking in the column "Magnetic structure". One can see that the Ni atoms split into two independent sites and four free parameters exist. An arbitrary set of values for the four symmetry independent moment components implies however an uncontrolled combination of spin modes corresponding to four different irreps (see text).

This is an example of the need of including both MSG and irreps constraints if one wants to refine the structure in a controlled way: if only the traditional representation method is employed and the refinement is restricted to the mH3 irrep, there will be four free parameters to refine as there are four independent spin basis functions for this irrep, and the symmetry of the spin arrangement for

an arbitrary combination of these four basis functions to be refined would be the minimal symmetry allowed by this irrep, i.e. the irrep kernel P_s1 (see Figure 14), while if the structure is refined only using the crystallographic constraints of the subgroup of type C_c2/c, then again we have four free parameters to refine, but they represent uncontrolled combinations of spin modes corresponding to the irreps mH3, mH1, mA1- and mA3-.

If one wants to refine the structure under the condition that its symmetry is C_c2/c and in addition that the magnetic ordering is restricted to the primary irrep mH3, and therefore with a single parameter to refine, then one needs to consider BOTH the symmetry constraints coming from the MSG and the additional restrictions coming from the irrep mH3, restricted to the appropriate direction to be compatible with the mentioned subgroup.

y) Click on the button "Get irreps" for the subgroup of type P_c31c in the listing of subgroups corresponding to Figure 14. From the resulting output and the previous decompositions of the magnetic representation discussed in the previous steps, derive that the magnetic structure will have two degrees of freedom for the spin, and one of them corresponds to the secondary irrep mA1-. By looking at the structure model corresponding to the subgroup of type *Pc-31c*, which was obtained in step j) and the ouput of Get_mirreps for it, derive that the decomposition of these two degrees of freedom into mH3 and mA1- components is quite trivial: the xy spin correlated components of the independent Ni site corresponds to the primary mH3 arrangement, restricted to the subgroup of type *Pc31c*, while the symmetry-allowed z component correspons to the secondary irrep mA1-, which is a third harmonic, which can appear through high order couplings.

z) If you still have the mood for doing something else: go back to the output page of MAGMODELIZE with the four subgroups of maximal symmetry, which was obtained in step d) and is shown in Figure 3, and investigate the differences on tensor properties for these four k-maximal symmetries, using the direct link to MTENSOR [9].

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