The magnetic section of the Bilbao Crystallographic Server - 3rd Tutorial

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This 3rd tutorial includes practical introductory examples of the following programs:

k-SUBGROUPSMAG & MAGMODELIZE (applied to a multi-k structure)**:** Section 2
MAGNDATA: Section 3
BNS2OG: Section 4

For other programs of the magnetic section see the 1st and 2nd tutorials

1. Introduction

In this third tutorial, we shall continue practicing with k-SUBGROUPSMAG, MAGMODELIZE and other programs in the Bilbao Crystallographic Server, which can be used for modeling a magnetic structure from some basic experimental information. We will consider a more complex structure with a multi-k spin arrangement. 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].

We will also explore some of the features and search options available in the database of magnetic structures MAGNDATA. Detailed information on this program can be found in [4,5].

Finally we will use the program BNS2OG with a specific MSG, which will show the relation between these two different forms to describe the symmetry of a commensurate magnetic structure.

2. k-SUBGROUPSMAG AND MAGMODELIZE applied to a multi-k structure.

k-SUBGROUPSMAG combined with MAGMODELIZE can be used to explore and enumerate all possible single-k and multi-k magnetic structures for a set of observed propagation vectors. We will apply it to the following example:

Example: Nd_2CuO_4 (magndata entry #2.6)
[Skanthakumar, S. et al., *PHYSICAL REVIEW B* (1993) **47** 6173 - 6176]
The paramagnetic structure of Nd_2CuO_4 can be summarized as (icsd 202885, Gopalakrishnan et al., Mat. Res. Bull. 24, 321-330 (1989)):

Space group: I4/mmm (N. 139)
Lattice parameters: 3.9385, 3.9385, 12.1465   90 90 90
Asymmetric unit:
Cu1 - 0.00000 0.00000 0.00000
Nd1 - 0.00000 0.00000 0.35150
O1 - 0.00000 0.50000 0.00000
O2 - 0.00000 0.50000 0.25000

(the attached file: Nd_2CuO_4_parent.cif can be used to introduce this structure in MAGMODELIZE)

This structure is reported to have a multi-k magnetic phase with the Cu atoms magnetically ordered according to two propagation vectors which are symmetry related by the parent symmetry:

k1= (1/2,1/2,0)
k2= (1/2,-1/2,0)

2.1 Modeling with one single propagation vector *(if you are already familiar with the use of k-SUBGROUPSMAG with a single k-vector, and you want to go quick to 2k models, skip these first steps and go directly to section 2.2)*

a) Introduce in the input page of k-SUBGROUPSMAG the parent space group number and the propagation vector (1/2,1/2,0). Introduce the Wyckoff position of the Cu atom as the only magnetic atom, and submit. The program then lists all possible subgroups (actually a representative for each possible conjugacy class of physically equivalent subgroups) that allow non-zero magnetic moments in all Cu sites. The number of possible symmetries is 7, and it does not increase if, clicking on "more options", the condition is relaxed to all symmetries allowing non-zero magnetic moments at SOME sites, instead of ALL. This means we have absolutely ALL possible magnetic symmetries for a magnetic ordering with the propagation vector introduced in the input and the magnetic moments in the Cu site.

b) Go back to the input page and check the condition: "Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter)". The list of possible subgroups is then reduced to three (Figure 1). These are the possible MSGs resulting from a transition with a single primary irrep .

Subgroups of the paramagnetic space group :	I4/mmm1' (N. 139)
Lowest magnetic space group to consider:	P1 (N. 1.1)
Magnetic propagation wave-vectors	(1/2,1/2,0)
Wyckoff positions occupied by the magnetic atoms	2a:(0,0,0)
Only subgroups compatible with a Landau-type transition	

List of subgroups that can be the result of a Landau-type transition

Get the subgroup-graph   More options

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps	Magnetic structure models (MAGMODELIZE)
1	C_Accm (No. 66.500)	$\begin{pmatrix} 0 & -1 & 1 & -1/4 \\ 0 & 1 & 1 & 1/4 \\ -1 & 0 & 0 & 1/4 \end{pmatrix}$	4=2x2	Conjugacy Class	Get irreps	☑
2	C_Amca (No. 64.480)	$\begin{pmatrix} 1 & 0 & -1 & 0 \\ -1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$	4=2x2	Conjugacy Class	Get irreps	☑
3	C_Amca (No. 64.480)	$\begin{pmatrix} 0 & -1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$	4=2x2	Conjugacy Class	Get irreps	☑

Select/Deselect all subgroups
☑ Include structure data of the parent phase

Submit selected subgroups to MAGMODELIZE: Submit
Hint: Submit many subgroups to MAGMODELIZE, when the 'include structure' option is selected, may take too long

Figure 1: Possible subgroups of *I4/mmm1'*, which can result from a magnetic ordering on the atomic site 2a, with (1/2,1/2,0) as single propagation vector, and according to a single irrep (Landau-type phase transition).

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 is the case here, different subgroups can be of the same MSG type and therefore they have the same MSG symbol. They can only be distinguished by the transformation to standard, which is necessarily different.

The transformation $(\mathbf{P},\mathbf{p})$ listed for each subgroup, where $\mathbf{P}$ is a 3x3 matrix and $\mathbf{p} = (p_1, p_2, p_3)$ a column vector, indicates in each case a choice of unit cell and origin, for which the subgroup adquires the standard setting of the magnetic space group (MSG) type specified by the MSG label. This means that the symmetry operations of the subgroup would take when described using this unit cell and origin, the form used for this MSG type in the listings taken as standard. The transformation $(\mathbf{P},\mathbf{p})$ 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 of a standard setting of the MSG. This means that the columns of the 3x3 matrix are the transformed unit cell vectors.

c) Go back to the input page and uncheck the Landau condition used in the previous step, and check instead the condition: "Only maximal subgroups". Observe that the list of subgroups provided by the program is just the same that in the previous step: In general, k-maximal subgroups always fulfill the Landau condition, but the reverse, which is also fulfilled here, is in general not true.

N	Group (BNS)	Transformation matrix	General positions	Properties	Magnetic structure
1	C_Accm (#66.500) Go to a subgroup	$\begin{pmatrix} 0 & -1 & 1 & 7/4 \\ 0 & 1 & 1 & 1/4 \\ -1 & 0 & 0 & 1/4 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
2	C_Amca (#64.480) Go to a subgroup	$\begin{pmatrix} 1 & 0 & -1 & 0 \\ -1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show
3	C_Amca (#64.480) Go to a subgroup	$\begin{pmatrix} 0 & -1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences MAGNEXT Tensor properties MTENSOR	Show

Figure 2: Partial view of the output page of MAGMODELIZE for the three subgroups in Figure 1, introduced directly from k-SUBGROUPSMAG.

d) Check the three subgroups in the last column of the output list shown in Figure 1, check "include structure data of the parent phase" at the bottom of the page, and submit to MAGMODELIZE. Upload then the CIF file of the parent structure of Nd_2CuO_4 (Nd_2CuO_4_parent.cif) when required, and check the Cu site as magnetic in the corresponding input page. Then submit. The resulting output is partially shown in Figure 2.

e) Use the buttons in the last column of the output shown in Figure 2 to produce magCIF files of the three possible models and visualize them, introducing an arbitrary value for the spin modulus in the intermediate output page that appears with a menu to introduce by hand the magnetic moments of the only symmetry independent Cu in the asymmetric unit. (similar procedure to what we did in tutorial B for another case (Figure 3).
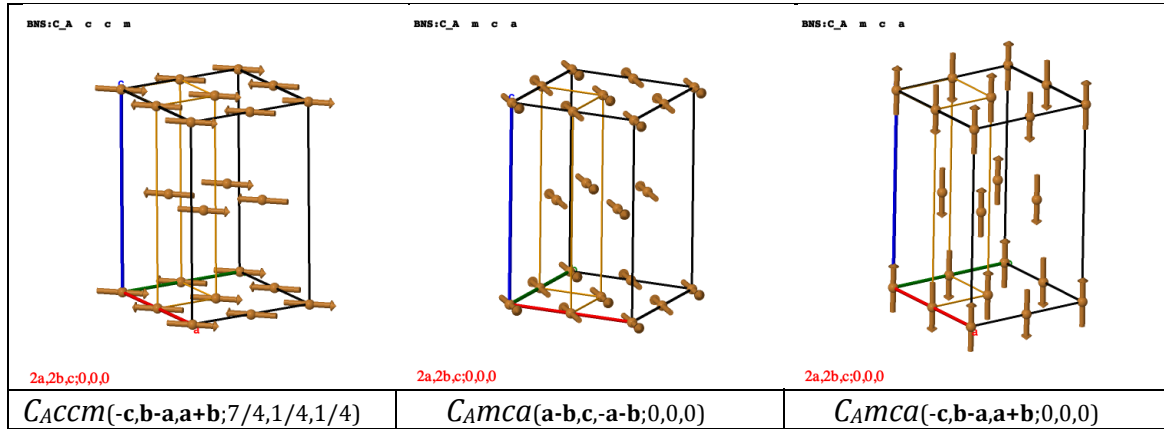

$C_A ccm$(-**c**,**b**-**a**,**a**+**b**;7/4,1/4,1/4)	$C_A mca$(**a**-**b**,**c**,-**a**-**b**;0,0,0)	$C_A mca$(-**c**,**b**-**a**,**a**+**b**;0,0,0)

Figure 3: Models (only Cu atoms) obtained with MAGMODELIZE for the three subgroups in Figure 2, corresponding to 1k magnetic structures.

2.2 Modeling with two propagation vectors

In the previous steps we have assumed that the magnetic structure is a single-k structure. However the wave vector (1/2,1/2,0) has a symmetry related one: (1/2,-1/2,0) through the symmetry operations of the parent group. We say then that the wave vectors *star* has two vectors. In most experimental cases, specially with powder diffraction, it may be impossible to distinguish if a magnetic structure ofthis type involves a single one or the two propagation vectors. In the absence of a significant magnetostriction, both wave vectors have the same modulus, and will overlap in the powder diffraction. In the case of single crystal diffraction, the distinction between the diffraction diagram of a 2k-structure or a multi-domain 1k-structure with appropriate domain populations can also be problematic.

In any case, even if the distinction between a 1k model and a 2k model may be experimentally impossible, it seems important to determine and fully define the two competing models, which fit equally well the experimental data, not taking for granted the one that is simpler to determine. In our particular example, the single crystal data under magnetic field favored the 2k structure model, but in general, if multi-k models are possible, they are in principle plausible alternatives to a single-k model. This is what we will do now for our particular example.

f) Come back to an empty input page of k_SUBGROUPSMAG, write the parent space group number. Introduce the propagation wave vector (1/2,1/2,0) and click on the option "show the independent vectors of the star". Check the two vectors of the star that are then shown by the program. Introduce the Wyckoff position of the Cu atom, and submit. By default, the program lists only

the possible subgroups, which allow a non-zero magnetic moment in ALL Cu atoms (17 conjugacy classes of subgroups). But this time we shall consider all possible symmetries, including those that force a null spin at some Cu sites.

g) Click on "more options" in the output page obtained in f), choose "Non-zero magnetic moment allowed (*at least*) at some Wyckoff positions" and submit. The list of possible subgroups increases to 18, and six of them are "k-maximal" (Figure 4).
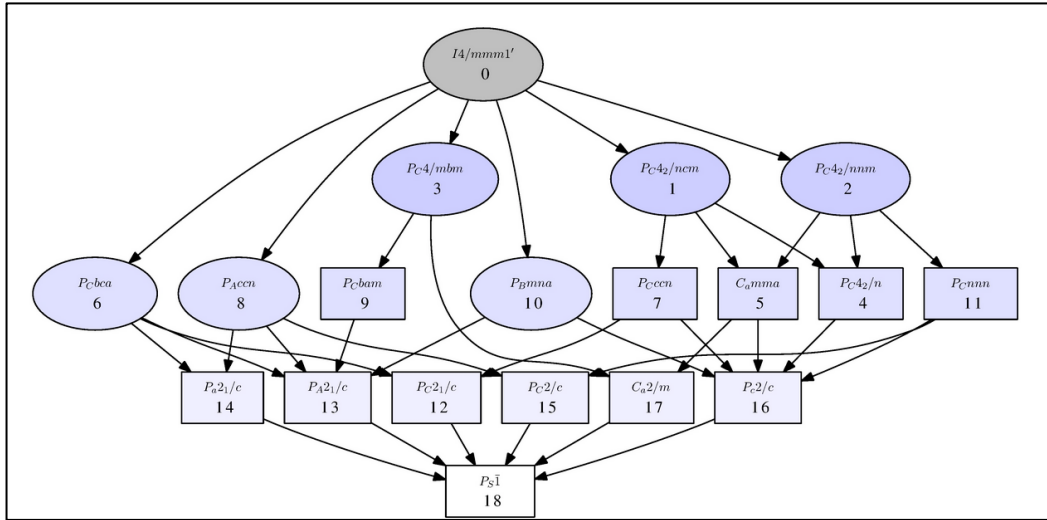

Figure 4. All possible MSGs that can be realized in a structure with parent space group *I4/mmm*, by a 2k magnetic ordering with propagation vectors (1/2,1/2,0) and (1/2,-1/2,0), and with the magnetic atom at the site 2a (0,0,0).

h) Go back to the input page and on the option "choose irreps" click on "representations". the irrep decomposition of the magnetic representation for the site 2a calculated through a direct link with the program MAGNETIC REP. is then shown, and a menu to choose one or more of the possible irreps is provided (Figure 5). We could start now to choose one by one the three possible irreps and obtain the possible symmetries for each of the irreps, as we did in the second tutorial. But the program has a simpler way to filter all the possible symmetries that can be attained through the activity of single irrep, in accordance with the Landau assumption. This can be done with the "Landau-type" filter, as we did above for the 1k structures.

Figure 5. Irrep decomposition of the magnetic representation for the site 2a for the wave vectors (1/2,1/2,0) and (-1/2,1/2,0). The parenthesis behind each irrep label indicates the dimension of the small irrep.

i) Do not use the menu shown in Figure 5. Instead, go back to the main input page of the program and check "Show only subgroups that can be the result of a Landau-type transition (single irrep order parameter)". The list is then reduced to 5 subgroups. But again here, the list refers to symmetries that allow non-zero magnetic moment in ALL magnetic sites.

j) Click on the button "more options", choose the second option: "Non-zero magnetic moments allowed (*at least*) at SOME Wyckoff positions", and submit. The list is now increased to 6 subgroups (Figure 6).

N	Group Symbol	Transformation matrix	Group-Subgroup index	Other members of the Conjugacy Class	irreps	Magnetic structure models (MAGMODELIZE)
1	P_C4_2/ncm (No. 138.529)	$\begin{pmatrix} 1 & -1 & 0 & 1/2 \\ 1 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	4=4x1	Conjugacy Class	Get irreps	☐
2	P_C4_2/nnm (No. 134.481)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	4=4x1	Conjugacy Class	Get irreps	☐
3	P_C4/mbm (No. 127.397)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	4=4x1	Conjugacy Class	Get irreps	☐
4	P_Cccn (No. 56.375)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	☐
5	P_Cbam (No. 55.363)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	☐
6	P_Cnnn (No. 48.263)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	8=4x2	Conjugacy Class	Get irreps	☐

Figure 6. Partial ouput with the list of the possible subgroups of *I4/mmm1'*, which can result from a magnetic ordering on the atomic site 2a, with the two symmetry related wavevectors (1/2,1/2,0) and (1/2,-1/2,0) as propagation vectors, and with a single irrep for the primary order parameter (Landau-type phase transition).

k) Inspect the group-subgroup hierarchy of the groups in Figure 6 by clicking on the button: "Get the subgroup-graph" (Figure 7).
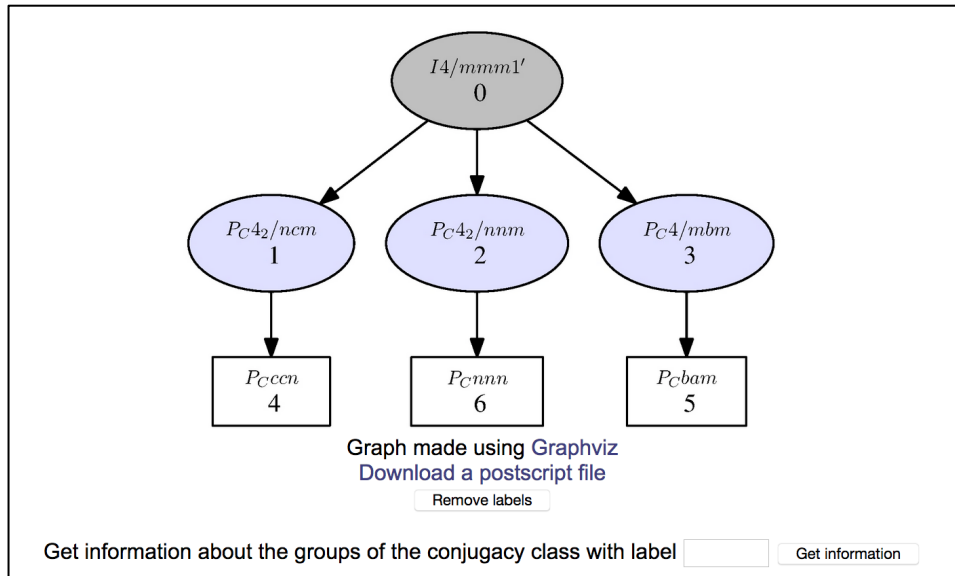
Figure 7. Group-subgroup graph of the subgroups shown in Figure 6.

l) By clicking on the button: "Get irreps" in the listing reproduced in Figure 6, inspect the magnetic irreps which are compatible for the subgroups of type P_C4_2/nnm and P_Cnnn, which are group-subgroup related. Verify that the symmetry break into these subgroups, which are group-subgroup related, is produced by the same irrep, namely mX4+ (*the calculation by Get_mirreps for this case will take some time!*). The resulting outputs for the two subgroups show that while in the higher subgroup the direction within mX4+ is (a,-a), meaning that the two spin waves with different propagation vectors combine with equal amplitudes, in the lower group, the irrep direction is represented by (a,b) (Figure 8), meaning that the spin waves of the two propagation vectors have different amplitudes.

Group→subgroup	Transformation matrix
$I4/mmm1'$ (N. 139.532)→P_Cnnn (N. 48.263)	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$

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)	$I4/mmm1'$ (No. 139.532) a,b,c;0,0,0	matrices of the irreps
	GM_4^+: (a)	$Fmmm1'$ (No. 69.522) a+b,-a+b,c;0,0,0	
X: (1/2,1/2,0)(1/2,1/2,1)	mX_4^+: (a,b)	P_Cnnn (No. 48.263) a+b,-a+b,c;0,0,0	matrices of the irreps
M: (1,1,1)	M_2^+: (a)	$P4_2/mmc1'$ (No. 131.436) a,b,c;0,1/2,0	matrices of the irreps
	M_3^+: (a)	$P4/mnc1'$ (No. 128.400) a,b,c;0,0,0	

Figure 8. Irreps, OP directions and isotropy subgroups compatible with the subgroup of I4/mmm1' of type P_Cnnn as obtained with the button "Get irreps" in the subgroup list.

The possible MSGs resulting from the presence of only one of the two mX4+ spin waves, corresponding to the special directions (a,0) or (0,a) within the irrep, are not present in the list shown in Figure 6. These directions mean that only one of the two wave vectors has a spin wave with non-zero amplitude. They are therefore associated with single k magnetic structures, and the program is only listing the symmetries correspondings to spin arrangements where the two propagation vectors are involved, as demanded in the input. The subgroup corresponding to a mX4+ order parameter with direction (a,0) and a single propagation vector must be one of those obtained in step b). Which one? You can get the answer using the button "Get irreps" in the listing obtained in step b).

m) Go back to the listing of subgroups shown in Figure 6 and check in the last column the three tetragonal MSGs of maximal symmetry at the head of the list, check also "include structure data of the parent phase" at the bottom of the list and submit to MAGMODELIZE to construct the structure models consistent with these three symmetries. In the next page upload the CIF file of the parent phase of Nd_2CuO_4 (Nd2CuO4_parent.cif). Choose Cu as magnetic and submit. The resulting output is partially shown in Figure 9.

N	Group (BNS)	Transformation matrix	General positions	Properties	Magnetic structure
1	P_C4_2/ncm (#138.529) [Go to a subgroup]	$\begin{pmatrix} 1 & -1 & 0 & 1/2 \\ 1 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences [MAGNEXT] Tensor properties [MTENSOR]	Show
2	P_C4_2/nnm (#134.481) [Go to a subgroup]	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences [MAGNEXT] Tensor properties [MTENSOR]	Show
3	P_C4/mbm (#127.397) [Go to a subgroup]	$\begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Systematic absences [MAGNEXT] Tensor properties [MTENSOR]	Show

Figure 9. Partial output of MAGMODELIZE for the three chosen subgroups, with the different options.

n) Click on the last column for the first MSG.

Selected magnetic space group: 1- P_C4_2/ncm (#138.529)

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

Parent space group 139 (*I4/mmm*)

Lattice parameters: a=7.87700, b=7.87700, c=12.14650, alpha=90.00, beta=90.00, gamma=90.00

[Go to setting standard (**a+b, -a+b, c** ; 1/2, 1/2, 0)]
[Go to an alternative setting]

Export data to MCIF file/Visualize   Go to a subgroup

Atomic positions, Wyckoff positions and Magnetic Moments

N	Atom	New WP	Multiplicity	Magnetic moment	Values of M_x, M_y, M_z
1	Nd1 Nd 0.00000 0.00000 0.35150	(0,0,z | 0,m_y,0) (0,0,-z | 0,m_y,0) (1/4,1/4,z+1/2 | m_y,0,0) (1/4,1/4,-z+1/2 | m_y,0,0) (0,1/2,z | 0,-m_y,0) (0,1/2,-z | 0,-m_y,0) (1/4,3/4,z+1/2 | -m_y,0,0) (1/4,3/4,-z+1/2 | -m_y,0,0) (1/2,0,z | 0,-m_y,0) (1/2,0,-z | 0,-m_y,0) (3/4,1/4,z+1/2 | -m_y,0,0) (3/4,1/4,-z+1/2 | -m_y,0,0) (1/2,1/2,z | 0,m_y,0) (1/2,1/2,-z | 0,m_y,0) (3/4,3/4,z+1/2 | m_y,0,0) (3/4,3/4,-z+1/2 | m_y,0,0)	16	-	-
2	Cu1 Cu 0.00000 0.00000 0.00000	(0,0,0 | 0,m_y,0) (1/4,1/4,1/2 | m_y,0,0) (0,1/2,0 | 0,-m_y,0) (1/4,3/4,1/2 | -m_y,0,0) (1/2,0,0 | 0,-m_y,0) (3/4,1/4,1/2 | -m_y,0,0) (1/2,1/2,0 | 0,m_y,0) (3/4,3/4,1/2 | m_y,0,0)	8	**(0,M_y,0)**	M_y = 0.00000

Figure 10. Magnetic structure (partial view) under the constraints of the subgroup P_C4_2/ncm (a+b,-a+b,c; ½, ½, 0), as obtained when clicking on "show" in the last column. 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 (see 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.

The unit cell and origin used by default (what we call "parent-like" setting) is indicated at the heading of the list reproduced in Figure 10, giving its relation with respect to the parent unit cell. This setting (generally non-standard) 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 vectors. 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 consistent arbitrary basis chosen by the user. The output, which is partially reproduced in Figure 10, 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 a value to the free components of the magnetic moments (sixth column).

o) Introduce an arbitrary value, say 1 (Bohr magnetons), for the component m_y of Cu1 and click on "Export 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 under an appropriate name by clicking on the link "bcs_file.mcif" . This magCIF

file can then be visualized in a standalone version of VESTA or Jmol, or it can be introduced for refinement in JANA2006 or FullProf.

p) Click on the button "submit to MVISUALIZE" to visualize the structure online with JSmol, using the MVISUALIZE tool. (Figure 11)
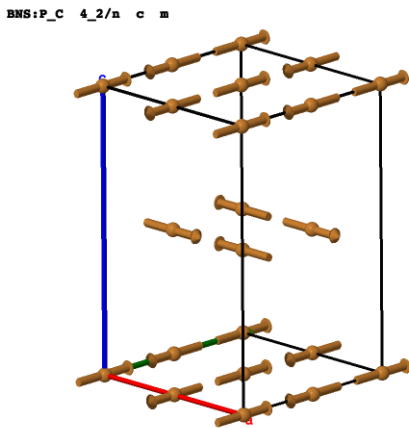

BNS:P_C 4_2/n c m

Figure 11. Scheme of the 2k magnetic structure of Nd_2CuO_4 (only Cu atoms), if the MSG were the subgroup P_C4_2/ncm (a+b,-a+b,c; ½, ½, 0), as given by the visualization tool of MAGMODELIZE.

q) Upload the magCIF file saved in step o), corresponding to the structure shown in Figure 11, in the program MVISUALIZE. On the left, click on "domain-related equivalent descriptions". The resulting output page shows at the bottom the list of possible domain-related equivalent structures (Figure 12). For each structure a lost operation (coset representative) is given. This operation relates the domain-related structure represented in this row with the first one in the list, which is the one of the input magCIF file. The list shows that there are only two non-trivial possible domain-related equivalent descriptions of the structure. The second one is related by the lost centering translation (1/2,1/2,1/2). The additional trivial equivalent domains related by time reversal (spin flip) are not included in the 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 }	$\begin{pmatrix} 1 & -1 & 0 & 1/2 \\ 1 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	Show
2	x+1/2,y+1/2,z+1/2,+1	{ 1 | 1/2 1/2 1/2 }	$\begin{pmatrix} 1 & -1 & 0 & 1 \\ 1 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	Show

Figure 12. List of subgroups within the chosen conjugacy class

r) Click on "show" for the 2nd case in the list shown in Figure 12. The resulting output page shows the structure obtained by the application of the lost lattice translation (1/2,1/2,1/2). The output page allows to download a magCIF of this

equivalent structure, visualize it, transform it to the standard setting, change it to any setting, etc.

s) Click on "Visualize" on the output page obtained in the previous step. (Figure 13) This spin arrangement is physically equivalent to the one obtained previously and shown in Figure 11. From the output of MVISUALIZE shown in Figure 12, we know that there is no other possible description of the structure.
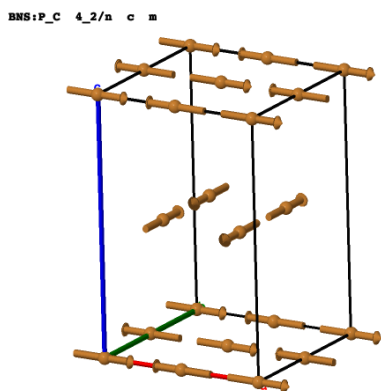

Figure 13. Scheme of the 2k magnetic structure (only Cu atoms) of Nd_2CuO_4 if the MSG were P_C4_2/ncm (a+b,-a+b,c; 0, 0, 0). This is physically equivalent to the one of Figure 11, and corresponds to a domain-related configuration.

t) Go back to the listing reproduced in Figure 6, and do similar steps for the two other maximal MSGs in the list to obtain the corresponding magnetic structure models. (If a long time has passed since the creation of this list with MAGMODELIZE, you may have to repeat the process of creating this list, to avoid errors). Obtain magCIF files for each model and figures for the domain-related descriptions.

v) Using the direct link to MAGNEXT for each subgroup in the list shown in Figure 9, which of the three models can be discarded if diffraction peaks of type (h,-h,0) or (h,h,0) are observed?

w) Go to MAGNDATA and inspect the entry 2.6 which describes the 2k magnetic structure reported for Nd_2CuO_4. Identify which of the three possible 2k models of maximal symmetry that you have investigated corresponds to the reported structure (disregard the symmetry identification that is already present in the database and just compare visually the structures: the original publication reporting the structure did not use magnetic symmetry and just depicted graphically the proposed structure).

3. EXPLORING AND SEARCHING IN MAGNDATA

MAGNDATA is a collection of more than 1,000 published commensurate and incommensurate magnetic structures [4,5]. The description of each structure makes full use of magnetic symmetry: magnetic space groups (MSGs) in a BNS setting for commensurate structures, and magnetic superspace groups (MSSGs), with the basic cell in a BNS setting, for incommensurate structures. The same magnetic symmetry-group operations are applied to both the magnetic moments and the atomic positions (the time-reversal part of an operation has no impact on atom positions).

The information provided for each structure is sufficient to define unambiguously the positions and magnetic moments (if non-zero) of the atoms in the structure. A non-standard MSG setting that matches that of the paramagnetic phase is often used; this setting does not necessarily coincide with the one used in the original reference.

Each MAGNDATA entry can be downloaded in either magCIF or VESTA format. The reading of magCIF files is supported by ISOCIF and FINDSYM, VESTA, Jmol, JANA2006, FullProf, GSAS-II, etc. ISOCIF can also be used to transform a magCIF file with a non-standard setting into a standard setting. The VESTA files provided allow the visualization of a single magnetic unit cell. Any downloaded entry can be subsequently uploaded into STRCONVERT (another tool of the Bilbao Crystallographic Server) for editing, visualization, format conversion, etc. MAGNDATA also allows one to directly 3D visualize each magnetic structure in Jmol via the web interface.

We will show here with some examples some of the features of this small database, and in particular the type of searches that can be done.

3.1. Fully equivalent descriptions of a magnetic structure

Sometimes it is not obvious to obtain all equivalent forms to describe a magnetic structure. Often several models may fit equally well the experimental data, and it is not obvious if they are really different models, which cannot be distinguished or they are equivalent descriptions of the structure. In this program, there is an option to enumerate all possible equivalent descriptions.

a) Go to the main page of MAGNDATA and the window "Element search" write the elements: Ce In, and and click on "Search". On the resulting list, click on the entry corresponding to CeNIn, in the second column of the listing. A page with detailed information on the magnetic structure published for this compound is shown.

At the top of the page the possibility of downloading a magCIF file of the structure is given, and you can visualize it also online with JSmol. Below, all the information regarding the unit cell, MSG, atomic positions, magnetic moments of the asymmetric unit, etc., which allows to construct unambiguously the magnetic structure are given. But here we are interested on possible different forms of describing the same structure. We can see that in the present description the Ce single site of the parent structure has split into two symmetry-independent sites, with their magnetic moments having perpendicular directions.

b) Click on the button: "domain-related equivalent descriptions". The upper part of the output summarizes again the magnetic structure being considered. In

the lower part (Figure 3.1), the set of distinct non-trivial domains are listed, indicating a lost symmetry operation, which transforms this domain-related structure with the original one. The trivial domains corresponding to the action of spin reversal are not listed, and those, which imply rotations of the magnetic structure in space are included, but they have a white background at the top for each MSG and they are of no interest for our purpose, as they correspond to trivial rotations of the structure.

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 }	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 1/2 \end{pmatrix}$	Show
2	x,z+1,-y+1,+1	{ 4^-_{100} | 0 1 1 }		Show
3	z,x,y,+1	{ 3^+_{111} | 0 }	$\begin{pmatrix} -1 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \\ 1 & 1 & 0 & 1/2 \end{pmatrix}$	Show
4	-y+1,x,z+1,+1	{ 4^+_{001} | 1 0 1 }		Show
5	y,z+1,x,+1	{ 3^-_{111} | 0 1 0 }	$\begin{pmatrix} 1 & 1 & 0 & 1/2 \\ -1 & 1 & 0 & 3/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	Show
6	z+1,-y,x,+1	{ 2_{101} | 1 0 0 }		Show

Figure 3.1

According to this output, 12 distinct types of domains are expected for this structure, but for us only the second one in the list is of interest, because the corresponding structure is described with the same MSG as the original structure that we have introduced, and will therefore only differ in the values of the magnetic moments (and the atomic positions, in the rare case that these may have suffered some kind of displacive distortion, due to some magneto-structural coupling).

c) Click on "show" for the second domain in the list shown in Figure 3.1

An output page with the corresponding equivalent structure is shown. It has a window where the corresponding magCIF file is shown in a non-editable form, which can be downloaded by clicking on "bcs_file.mcif", and also can be directly visualized.
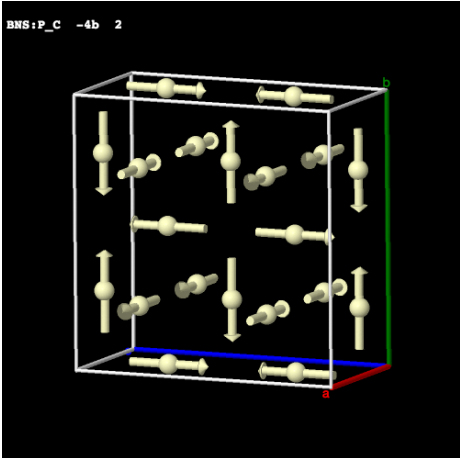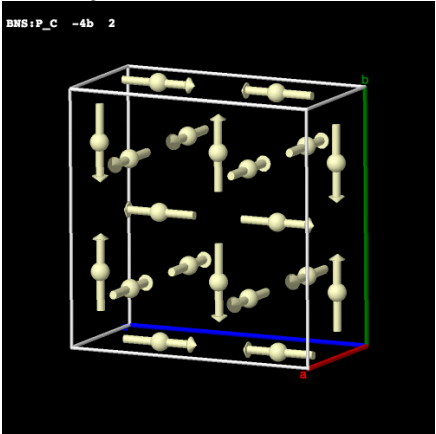

Figure 3.2: The two domain-related equivalent descriptions of the magnetic structure of CeNIn (only Ce atoms).

By just looking at the view of new spin arrangement, or by just inspecting the list of positions and magnetic moments of the asymmetric unit of the transformed structure, one can see that this structure just differs from the original one, by having the magnetic moment of Ce1_1 with the opposite value. This means that the relative signs of the moments of Ce1_1 and Ce1_2 are arbitrary, both possibilities representing physically equivalent orderings, which will equally fit its powder diffraction diagram.

Note that the proposed model includes equal modulus for the spins of the two symmetry independent Ce atoms, and this is not symmetry forced.

3.2. Weak ferromagnets

Antiferromagnetic (AFM) phases with a weak ferromagnetic (FM) component can be of special interest because the magnetic ordering can be directly coupled with an external magnetic field through this weak FM canting. This weak FM is often so small that may be negligible in diffraction experiments, and therefore it is usually reported as having a null value in the determination of the magnetic structure.

Using symmetry alone, we can however predict which magnetic structures are to be expected to have some FM component, however small, because it is allowed by their MSG.

d) Click on "Advanced Search and Statistics" at the heading of the main page of MAGNDATA or of the page with the entry of the preceding steps.
A page is then shown with a full list of the structures in the database, and basic information for each structure.

e) Click on the headings of the columns, which are in blue color, in order to see that you could order the structures according to the parent space group, the MSG or the magnetic point group.

f) Go to the search menu at the top of the page and on the properties filters choose "ferromagnetic", and click on "search" button. The list is reduced to about 150 structures. All of them have a MSG allowing some FM component. Some of them are actually ferrimagnetic, or even ferromagnets. Note for instance the entry #1.1.10 at the end, which is a conical incommensurate structure, which will certainly have a large FM component. We are however, interested in materials where the FM component, even if not being the magnetic order parameter, it transforms according to the same irrep as the AFM order parameter, and therefore can be strongly coupled with it.

g) In the "Class" filter at the top, uncheck all classes except class "0", and in the irreducible representations put "NO" for number of primary irreps >1.
This limits the search to those commensurate structures where there is a single order parameter with null propagation vector (the same as for a FM ordering), but the list still includes more than 100 structures.

h) Include now the filter "multidimensional small irrep": "yes". This limits the lists to order parameters, which are multidimensional, which is the typical situation in the first reported classical weak ferromagnets. The list is now reduced to about 40 structures. It includes well studied weak FM, like $MnCO_3$ (#0.115), $CoCO_3$ (#0.114), $NiCO_3$ (#0.113), $FeBO_3$ (#0.112), $Ba_2CoGe_2O_7$ (#0.56). But the list also includes structures, which are ferrimagnetic, and even ferromagnetic and would have to be discarded by hand.

i) Open for instance the entry #0.157 corresponding to $Yb_2Sn_2O_7$, and click on "show all magnetic atoms in unit cell and their moment relations", in order to see the strong FM component along z, all spins of all atoms being aligned in this direction. (Figure 3.3). This is clearly a ferromagnet along z, with some perpendiculat AFM canting.

Label	Atom type	x	y	z	Multiplicity	Symmetry constraints on M	M_x	M_y	M_z	|M|
Yb1	Yb	0.50000	0.50000	0.50000	16	m_x,m_x,m_z	-0.13(1)	-0.13(1)	1.03(1)	1.05

[Show all magnetic atoms in unit cell and their moment relations]

Positions and magnetic moments of all atoms in unit cell, with magnetic moment relations explicitly given:

Set of atoms in the unit cell related by symmetry with the magnetic atom Yb1:

Atom	x	y	z	Symmetry constraints on M	M_x	M_y	M_z
1	0.50000	0.50000	0.50000	m_x,m_x,m_z	-0.13000	-0.13000	1.03000
2	0.75000	0.00000	0.25000	$m_x,-m_x,m_z$	-0.13000	0.13000	1.03000
3	0.50000	0.25000	0.25000	$-m_x,m_x,m_z$	0.13000	-0.13000	1.03000
4	0.75000	0.75000	0.50000	$-m_x,-m_x,m_z$	0.13000	0.13000	1.03000
(0,1/2,1/2) + set click here to show and hide							
5	0.50000	0.00000	0.00000	m_x,m_x,m_z	-0.13000	-0.13000	1.03000
6	0.75000	0.50000	0.75000	$m_x,-m_x,m_z$	-0.13000	0.13000	1.03000
7	0.50000	0.75000	0.75000	$-m_x,m_x,m_z$	0.13000	-0.13000	1.03000
8	0.75000	0.25000	0.00000	$-m_x,-m_x,m_z$	0.13000	0.13000	1.03000
(1/2,0,1/2) + set click here to show and hide							
(1/2,1/2,0) + set click here to show and hide							

Figure 3.3

3.3. Proper ferrotoroidics

j) Go back to the first input page of MAGNDATA, click on "Advanced Search and Statistics", in the resulting page on the search menu, at the top, go to "Non-zero tensors" and in the first box, unfold the list of tensors and choose: "Magnetoelectric tensor α_ij (direct effect)". Click on "Search". A list of more than 100 structures, which are expected to have linear magnetoelectric properties, is then shown at the bottom of the output page.

k) Go back to the search menu at the top and add in "Non-zero tensors" in the second box, as additional filter with "OR": "Polar toroidal moment" (the tensors are roughly alphabetically ordered in the unfolded list, but this one is at the bottom, ordered by "toroidal"). Click again on "Search". Verify that the resulting list of structures is just the same as the one obtained in step j). This is a

general property: all symmetries allowing a non-zero toroidal moment, also allow linear magnetoelectricity.

l) Change the "OR" by "AND" in the condition for the two non-zero tensors. The list is now reduced, but more than 80 structures are still listed. These are all structures, with a magnetic ordering, which can result in a non-zero (polar) toroidal moment.

m) Open the entry of one of the structures in the list, for instance the case #0.14 (Gd_5Ge_4) and click on the button: *Symmetry-adapted form of material tensors via MTENSOR".* On the MTENSOR menu that appears, open "EQUILIBRIUM TENSORS", choose "Magnetoelectric tensor α_ij (direct effect)", and click on "Get results". Save the form of the output magnetoelectric tensor.

n) Do the same as in step m), but now for a structure, which appears in the full list of magnetoelectric structures, but it is not on the list of structures with non-zero toroidal moment, for instance the entry #0.26 (TmAgGe).
   Compare the form of the magnetoelectric tensor of this material (with symmetry-forced zero toroidal moment), with the magnetoelectric tensor obtained in the previous step, for a structure with symmetry allowed non-zero toroidal moment. One can then observe a general property: magnetoelectric materials not supporting a toroidal moment have necessarily a symmetric magnetoelectric tensor.
   We are only interested in "proper" ferrotoroidic materials, where the toroidal moment is not only allowed to have non-zero values, but it can be considered the order parameter of the transition. Therefore the toroidal moment must have the symmetry properties of the primary irrep of the magnetic transition [6]. If we select the structures where the irrep associated with the symmetry break is the same as the irrep associated with the (polar) toroidal moment, then we are are just selecting all structures that can be considered either "proper" or "pseudo-proper" ferrotoroidic, with the transformation properties of the toroidal moment being equal to those of the order parameter. All structures with a single magnetic irrep active with null propagation vector, and with no secondary irrep allowed, fulfill this symmetry condition: the magnetic irrep associated with order parameter is the only possible one, and therefore must also be the one of associated with the symmetry-allowed non-zero toroidal moment.

o) In the "Class" filter, at the top, uncheck all classes except class "0" (propagation vector=0), and in the irreducible representations put "NO" for number of primary irreps >1. Put also "NO" on "Secondary irreps allowed?". You will obtain a list of more than 50 structures, which can be considered proper or pseudo-proper "ferrotoroidics" having a single irrep compatible with the magnetic ordering. The toroidal moment may be large or small, but if different from zero, all the distinct domains of the structure will be distinguishable by their different value/orientation of their toroidal moments. Even if the toroidal moment is strictly zero (due to some particular orientation of the spins) this spin arrangement will be linearly coupled with the toroidal conjugate field **E** x **H**, and domain switching with this field will be possible.

p) Verify that wellknown ferrotoroidics like LiCoPO$_4$, LiFeSi$_2$O$_6$, etc. [7] are on the list obtained.

3.4. Conflicting Models

q) Go back to the main page of MAGNDATA and submit an "Element search" with the element Eu. Two of the structures that are then listed correspond to the same compound EuZrO$_3$ (#0.146 nd #0.147). **Open the two entries and compare the two structures.**
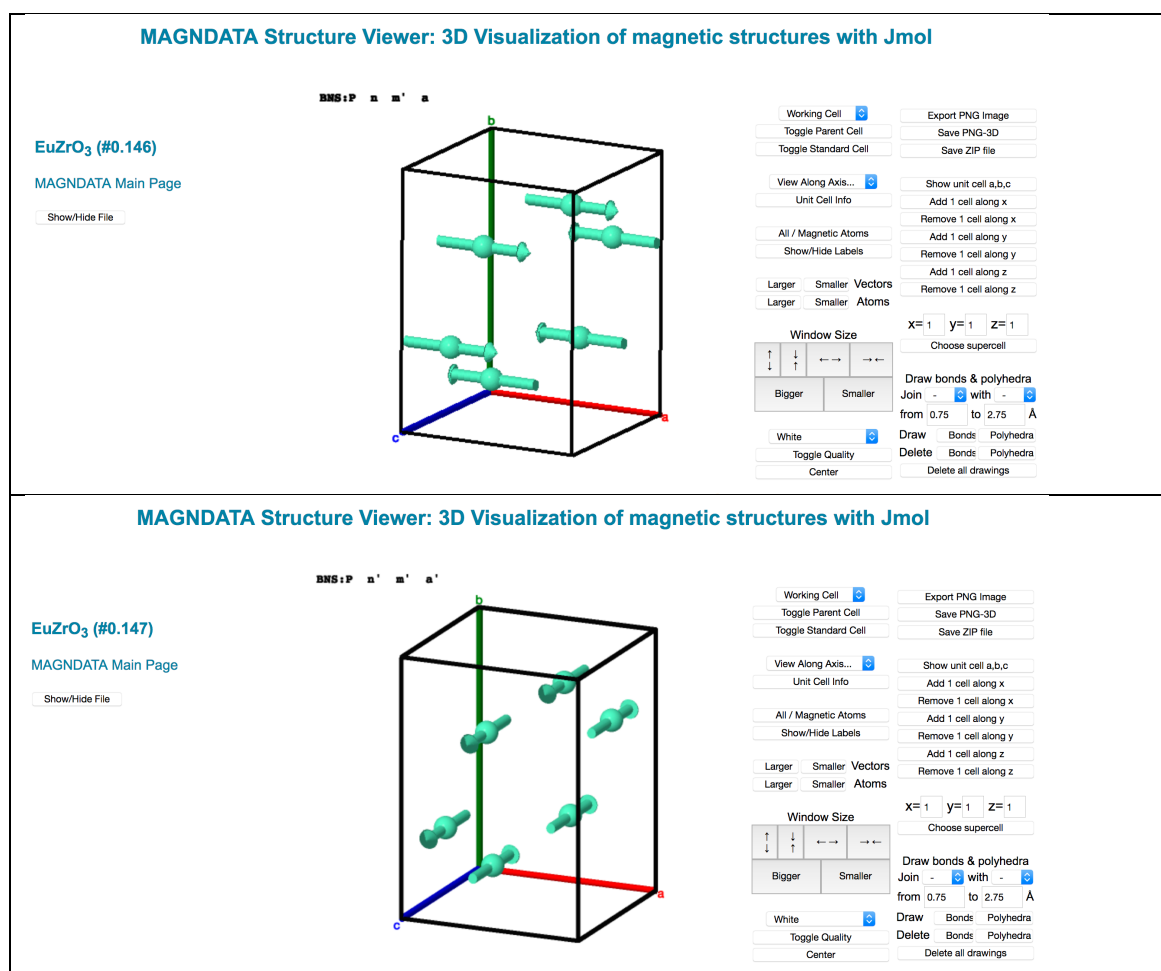

Figure 3.4

Although it is the same collinear spin arrangement, the easy axis that is proposed is different. This results into different MSGs for the two structures (Figure 3.4). It may be difficult experimentally to determine unambiguously the direction of the easy axis, specially in pseudotetragonal structures, as this one, so it is not strange that these two different models have been proposed. We can try to see if there are however some properties that would distinguish the two structures.

r) Go back to the pages of the two structures in MAGNDATA and click on: "*Systematic absences for this Magnetic Space Group via MAGNEXT*". Compare

the results. Could some systematic absence be used as signature of one or the other model?

s) Go back to the entries of the two structures and click on *"Symmetry-adapted form of material tensors via MTENSOR"*. Click on "Equilibrium Tensors" and in the list of tensors that unfolds choose "Magnetoelectric tensor α_{ij} (direct effect)", and click at the bottom on "Get results". Compare the form of the magnetoelectric tensor for the two structures. Which type of single crystal magnetoelectric experiment could help to decide which is the correct structure?

4. The BNS2OG program

This program can be used to obtain the OG description of a MSG, if introduced in the BNS form (non-standard, in general), and vice versa.

a) Open MAGNDATA, at the top in "Enter the label of the structure", write 1.34 and submit. The page for the entry #1.34 (HoAuGe) appears**. At the top click on the button "submit to STRCONVERT".** The menu page of STRCONVERT appears with the magnetic structure of HoAuGe downloaded. Below the heading: "Symmetry operations" the operations of the MSG are listed in a window. Copy this list, for a future "paste", as input in the BNS2OG program.

b) Open the BNS2OG program and click on the "BNS" button to indicate you are going to introduce the generators of a MSG in a BNS setting. An input window appears.

c) Paste in the available window the list of symmetry operations that was copied in step a) and submit. The program then identifies the MSG group type in the BNS and the OG notation, and indicates transformations to the BNS standard setting, and to the OG standard setting of the MSG. Verify that the identified MSG type and the transformation to standard BNS agrees with the information given in MAGNDATA for this MSG in the corresponding entry from where it has been taken.

But the most important information is at the bottom of the output page. First the BNS operations are listed separating centering and anticentering operations from the rest, and below this first information, the essential output of the program can be found, namely, the description of the MSG which has been introduced, but in an OG form, which in general is non-standard. The OG unit cell that the program proposes tries to be similar to the BNS basis that is being used.

The OG model is given in the following form:

i) A transformation from the BNS unit cell of the input MSG to a OG unit cell is proposed. (Figure 3.5)

Transformation matrix from the input BNS to the proposed OG

$$\begin{pmatrix} 1/2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$
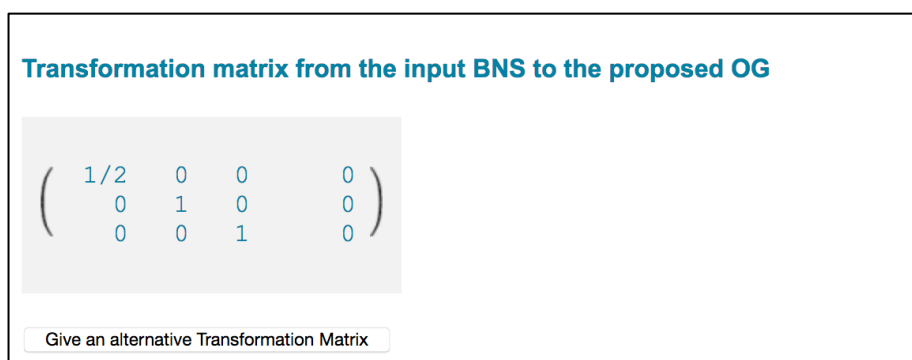
Give an alternative Transformation Matrix

Figure 3.5

This transformation is not unique, and you can introduce alternative ones, which will be accepted as long as they are mathematically possible. The basis transformation proposed by the program is the one shown in Figure 3.5. But by clicking on the button "Give an alternative transformation matrix" you can change it. For instance, you can add an origin shift (0,0,1/2).

ii) The list of OG symmetry operations are then given for the proposed new OG unit cell and origin, with the set of translations and antitranslations separated.

iii) The list of OG symmetry operations is again listed in the form required by the magCIF format: with the black&white lattice defined by means of the so-called OG wavevector k, a vector such that the factor exp(i**k**.**T**) is either +1 or -1 for any lattice translation **T** defined by the OG unit cell and its centerings (Figure 3.5), those lattice translations with factor -1 being the antitranslations.

Alternative description in the OG setting (see the help for an explanation)

General positions, (0,0,0)+set

x,y,z,1
-x,-x+y,1/2+z,-1
-x,-y,1/2+z,1
x,x-y,z,-1

Centering operations of the OG lattice
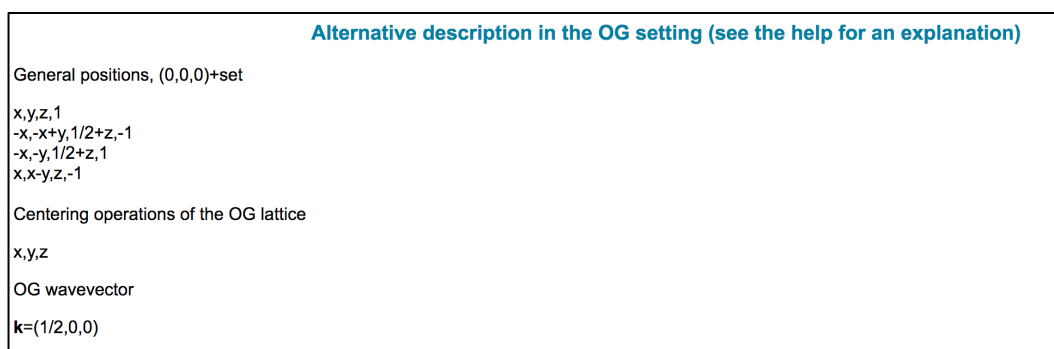
x,y,z

OG wavevector

k=(1/2,0,0)

Figure 3.5

d) Go back to the entry 1.34 of MAGNDATA, and compare the OG unit cell proposed by the program with the unit cell of the parent phase. Also compare the OG wavevector with the experimental propagation vector.

e) Do the same steps a) to e) for the MSG of the entry #1.176.

f) Compare the OG unit cell proposed by the program with the parent unit cell of the structure. Why are they different in this case?

g) Compare the OG wavevector with the experimental propagation vector. Why are they different in this case? What is the relation between the two vectors?

REFERENCES

[1] J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, and M.I. Aroyo, "*Symmetry-based computational tools for Magnetic Crystallography*", *Annu. Rev. Mater. Res.* (2015), **45**:13.1-13.32.

[2] S. V. Gallego, E. S. Tasci, G. de la Flor, J. M. Perez-Mato and M. I. Aroyo, "*Magnetic symmetry in the Bilbao Crystallographic Server: a computer program to provide systematic absences of magnetic neutron diffraction*", *J. Appl. Cryst.* (2012). **45**, 1236-1247.

[3] S. V. Gallego, J. Etxebarria, L. Elcoro, E.S. Tasci and J.M. Perez-Mato, "*Automatic calculation of symmetry-adapted tensors in magnetic and non-magnetic materials: A new tool of the Bilbao Crystallographic Server*", Acta Cryst. A (2019) 75, 438-447.

[4] S. V. Gallego, J. M. Perez-Mato, L. Elcoro, E. S. Tasci, R.M. Hanson, K. Momma, M. I. Aroyo and G. Madariaga, "*MAGNDATA: towards a database of magnetic structures. I. The commensurate case*", J. Appl. Cryst. (2016). **49**, 1750-1776.

[5] S.V. Gallego, J.M. Perez-Mato, L. Elcoro, E.S. Tasci, R.M. Hanson, M.I. Aroyo and G. Madariaga, "*MAGNDATA: towards a database of magnetic structures. II. The incommensurate case*", J. Appl. Cryst. (2016). **49**, 1941-1956.

[6] N.A. Spaldin, M. Fiebig, M. Mostovoy, "*The toroidal moment in condensed-matter physics and its relation to the magnetoelectric effect*", J. Phys. Condens. Matter 20 (43) (2008) 434203.

[7] S. Gnewuch, E. E. Rodriguez, "*The fourth ferroic order: Current status on ferrotoroidic materials*", J. Solid State Chem. 271 (2019) 175-190.