Tutorial exercises on the use of MAXMAGN and other tools of the Bilbao Crystallographic Server for the analysis of magnetic structures.

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The program MAXMAGN in the Bilbao Crystallographic Server (http://www.cryst.ehu.es) is a computer tool, freely available in the web, which facilitates the systematic use and application of magnetic symmetry in the analysis and determination of commensurate magnetic structures.

It is a known fact that most of the reported magnetic structures are "1-k" magnetic phases, i.e. their magnetic orderings have a single propagation vector. Furthermore, most of them have spin configurations that possess one of the possible maximal magnetic symmetries compatible with its propagation vector. This second property is not well known and its importance and utility has not been yet exploited. The program MAXMAGN makes use of this property in a systematic way by calculating all possible maximal magnetic symmetries and deriving magnetic structural model consistent with them. The assumption of a maximal magnetic symmetry restricts the possible spin arrangements, and limits the number of free parameters or degrees of freedom to be determined experimentally. **In simple cases, these restrictions are equivalent to those obtained applying the representation method, but in general they can be more restrictive.**

The propagation vector of a 1-k magnetic structure can in principle be identified from diffraction experiments. Once this modulation vector is known, the few possible magnetic space groups (i.e. Shubnikov groups) consistent with this vector fulfilling that they have a maximal possible symmetry can be systematically determined. From their knowledge, all possible alternative spin models of maximal symmetry consistent with the observed propagation vector can be derived. This is the main purpose of MAXMAGN. The alternative models provided by the program can then be contrasted with and fitted to the experimental data.

Using as input only the knowledge of the space group of the paramagnetic phase (we shall call it in the following *parent* space group) and the propagation vector **k**, MAXMAGN first provides all possible magnetic space groups of maximal symmetry consistent with this propagation vector. In the following we shall call these groups "*k-maximal magnetic groups*". If a paramagnetic structure is also introduced, the program determines the spin arrangements allowed for each of these possible k-maximal symmetries, and defines their refinable parameters. The output is organized in such a way that the program can be systematically applied to identify and analyse all possible alternative spin models. A CIF-like file can then be obtained for each of the alternative magnetic structures of k-maximal symmetry, which can then be refined in programs like JANA2006 [1] or FULLPROF [2], or they can be introduced in the program ISODISTORT [3] for mode analysis, or transformed with the structure editor STRCONVERT of the Bilbao Crystallographic Server. These CIF-like files can also be used for 3D visualization with VESTA[4] or Jmol [5]. A direct link to the tool MVISUALIZE, also in the Bilbao

crystallographic server also allows an inmediate visualization of each of the alternative models.

The magnetic structure models provided by the program are given by default in a setting as similar as possible to the one of the parent paramagnetic phase (the so-called parent like setting), but they can also be obtained in a standard setting of the magnetic group considered, or alternatively in a setting defined by the user.

If none of the models with k-maximal symmetry are satisfactory, the program can descend to lower symmetries, adding in this controlled way additional degrees of freedom. The program also allows to derive, for a given spin model, all physically equivalent spin arrangements to which the structure can in principle be switched, as they correspond to twin-related or, in general, domain-related spin configurations.

The program MAXMAGN provides an alternative approach to the traditional representation method for the parameterization of magnetic structures, which in most cases is more intuitive and direct. The direct use of magnetic symmetry arguments allows to establish in many cases (when the active irrep is more than one-dimensional) additional constraints fulfilled by the magnetic phase.

In the following, by means of several exercises, we will go step by step, through the different capabilities of the program, using at some points some additional tools of the Bilbao Crystallographic Server. At the end of each example, a comparison with the representation method, i.e an alternative analysis using irreps (irreducible representations) of the parent space group, will also be presented.

Example 1. $CrCl_2$

The paramagnetic structure of $CrCl_2$ can be summarized as (Howard et al., PRB 72, 214114):

Pnnm (#58)

Lattice parameters:
6.8257 6.2139 3.4947
Asymmetric unit:
Cl   0.35860 0.28930 0.00000
Cr 0.00000 0.00000 0.00000

Magnetic atom: Cr

The magnetic phase of this compound is known to have a propagation vector:
k=(0, 1/2, 1/2).

We can use MAXMAGN to explore the possible magnetic orderings of k-maximal symmetry compatible with the observed propagation vector. To have k-maximal symmetry means that the magnetic space group associated with the spin configuration, besides being a subgroup of the grey magnetic group Pnnm1' compatible with the observed propagation vector, fulfills that there exists no other subgroup of Pnnm1' (also compatible with the propagation vector) containing it as a subgroup.

a) Open the main page of MAXMAGN, introduce the number of the space group of the paramagnetic phase and the propagation vector, and submit. Four possible k-maximal magnetic space groups are then listed by the program (Figure 1). Their labels as standard Shubnikov groups (BNS setting) are shown in the first column. Although these labels are equal by pairs, they correspond to different subgroups of Pnnm1', and the second column shows the basis transformations necessary to describe each subgroup in the standard setting (click on the heading "Transformation matrix" to see its definition). This transformation is different for the listed subgroups with the same group-type label. The transformation is given by a 3x3 matrix **P** and a column vector **p**, such that the unit cell basis corresponding to the standard setting a_s, b_s, c_s is given by:

$$\left(\vec{a}_s,\vec{b}_s,\vec{c}_s\right)=\left(\vec{a}_p,\vec{b}_p,\vec{c}_p\right)\cdot P$$

where a_p, b_p, c_p are the unit cell basis of the Pnnm space group, while the origin for the description of the subgroup in the standard setting must also be shifted by **p**, with this vector being given by its components in the parent basis.

It is important to stress that the list only includes one subgroup per conjugate class of subgroups. The other subgroups of each class are physically equivalent and correspond to domain-related configurations.

Maximal magnetic space groups for the space group 58 (*Pnnm*) and the propagation vector k = (0, 1/2, 1/2)

N	Group (BNS)	Transformation matrix	General positions	Systematic absences
1	P_a2_1/c (#14.80) Go to a subgroup	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 2 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show
2	P_a2_1/c (#14.80) Go to a subgroup	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 2 & 0 & 1 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show
3	C_a2/m (#12.64) Go to a subgroup	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ -2 & 0 & 0 & 0 \\ 0 & -2 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show
4	C_a2/m (#12.64) Go to a subgroup	$\begin{pmatrix} 0 & 0 & 1 & 0 \\ -2 & 0 & 0 & 0 \\ 0 & -2 & 0 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	Show	Show

Figure 1: List of distinct k-maximal magnetic space groups for a parent space group Pnnm and a propagation vector (0, 1/2, 1/2), as given by MAXMAGN.

b) Click on the label of the first group for a direct link to MGENPOS with the listing of the Shubnikov group P_a2_1/c (#14.80) in BNS standard setting (see Figure 2). This is a type

IV magnetic space group, with eight distinct representative operations, namely four non-primed operations forming the group P2$_1$/c (#14), plus all these operations multiplied by the "antitranslation" {1'|1/2, 0, 0}. This MGENPOS page has additional links to the OG description of the group, the different possible Wyckoff positions, etc. But this information refers to the standard setting, which requires the use of an oblique cell, and therefore it is far from the description of the structure in the parent Pnnm phase. In general, a description of the magnetic subgroup in a setting as similar as possible to the one used for the parent phase is in practice more useful.

General Positions of the Group P$_a$2$_1$/c (#14.80) [BNS setting]

To display the general positions in the OG setting, please follow this link: P$_{2a}$2$_1$/c (#14.6.91) [Transformation matrix]

Translation lattice generators: (1|1,0,0), (1|0,1,0), (1|0,0,1), (1|0,0,0)

Black-and-white lattice generators: (1|1,0,0), (1|0,1,0), (1|0,0,1), (1'|1/2,0,0)

N	Standard/Default Setting			
	(x,y,z) form	Matrix form	Geom. interp.	Seitz notation
1	x, y, z, +1 m_x,m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	1 +1	{ 1	0 }
2	-x, y+1/2, -z+1/2, +1 -$m_x,m_y,$-m_z	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 1/2 \end{pmatrix}$	2 (0,1/2,0) 0,y,1/4 +1	{ 2$_{010}$	0 1/2 1/2 }
3	-x, -y, -z, +1 m_x,m_y,m_z	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	-1 0,0,0 +1	{ -1	0 }
4	x, -y+1/2, z+1/2, +1 -$m_x,m_y,$-m_z	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	c x,1/4,z +1	{ m$_{010}$	0 1/2 1/2 }
5	x+1/2, y, z, -1 -$m_x,$-$m_y,$-m_z	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}'$	t (1/2,0,0) -1	{ 1'	1/2 0 0 }
6	-x+1/2, y+1/2, -z+1/2, -1 $m_x,$-m_y,m_z	$\begin{pmatrix} -1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 1/2 \end{pmatrix}'$	2 (0,1/2,0) 1/4,y,1/4 -1	{ 2'$_{010}$	1/2 1/2 1/2 }
7	-x+1/2, -y, -z, -1 -$m_x,$-$m_y,$-m_z	$\begin{pmatrix} -1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \end{pmatrix}'$	-1 1/4,0,0 -1	{ -1'	1/2 0 0 }
8	x+1/2, -y+1/2, z+1/2, -1 $m_x,$-m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}'$	n (1/2,0,1/2) x,1/4,z -1	{ m'$_{010}$	1/2 1/2 1/2 }

Go to the list of the Wyckoff Positions of the Group P$_a$2$_1$/c (#14.80)
Go to the Systematic Absences for the Group P$_a$2$_1$/c (#14.80)

Figure 2: List of the 8 representative operations of the magnetic space group P$_a$2$_1$/c (#14.80), as obtained when clicking on the group label in the list shown in Figure 1 (direct link to MGENPOS). Together with the translation lattice these operations span the full group in the setting that we consider as BNS standard.

b) Come back to the main output list shown in Figure 1 and click now on the column headed with "General positions" for the first magnetic subgroup (for the moment we leave unused the optional buttons of the previous two columns). We get then a table which on its left lists the operations of this magnetic space group in its standard setting, and on the right the same corresponding operations but in a setting that we call "parent-like" (see Figure 3). This non-standard setting keeps the origin and also the unit cell orientation of the parent/paramagnetic phase, but multiplying the cell parameters to produce a supercell consistent with the periodicity mantained by the propagation vector.

At the heading of the list one can find the transformation from the parent-like to the standard setting, similarly as we had in the previous table. Note that the listed transformation is however different as it transforms the used "parent-like" basis (and not the parent one) to the standard setting.

General positions of the magnetic space group P_a2_1/c (#14.80) in the parent-like setting (a, 2b, 2c; 0, 0, 0)

Transformation matrix:

$$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 1/2 & 0 \\ 0 & 0 & 1/2 & 0 \end{pmatrix}$$

General positions

[Get symmetry cards (parent-like setting (a, 2b, 2c; 0, 0, 0)) in plain text format]

N	Standard setting			Parent-like setting (a, 2b, 2c; 0, 0, 0)		
	(x,y,z) form	Matrix form	Seitz notation	(x,y,z) form	Matrix form	Seitz notation
1	x,y,z,+1 m_x,m_y,m_z	$\begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&1&0 \end{pmatrix}$	(1|0,0,0)	x,y,z,+1 m_x,m_y,m_z	$\begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&1&0 \end{pmatrix}$	(1|0,0,0)
2	-x,-y,-z,+1 m_x,m_y,m_z	$\begin{pmatrix} -1&0&0&0 \\ 0&-1&0&0 \\ 0&0&-1&0 \end{pmatrix}$	(-1|0,0,0)	-x,-y,-z,+1 m_x,m_y,m_z	$\begin{pmatrix} -1&0&0&0 \\ 0&-1&0&0 \\ 0&0&-1&0 \end{pmatrix}$	(-1|0,0,0)
3	x,-y-1/2,z+1/2,+1 $-m_x,m_y,-m_z$	$\begin{pmatrix} 1&0&0&0 \\ 0&-1&0&-1/2 \\ 0&0&1&1/2 \end{pmatrix}$	$(m_y\|0,-1/2,1/2)$	-x+1/2,y+1/4,z+1/4,+1 $m_x,-m_y,-m_z$	$\begin{pmatrix} -1&0&0&1/2 \\ 0&1&0&1/4 \\ 0&0&1&1/4 \end{pmatrix}$	$(m_x\|1/2,1/4,1/4)$
4	-x,y-1/2,-z+1/2,+1 $-m_x,m_y,-m_z$	$\begin{pmatrix} -1&0&0&0 \\ 0&1&0&-1/2 \\ 0&0&-1&1/2 \end{pmatrix}$	$(2_y\|0,-1/2,1/2)$	x+1/2,-y+1/4,-z+1/4,+1 $m_x,-m_y,-m_z$	$\begin{pmatrix} 1&0&0&1/2 \\ 0&-1&0&1/4 \\ 0&0&-1&1/4 \end{pmatrix}$	$(2_x\|1/2,1/4,1/4)$
5	x,y,z+1,+1 m_x,m_y,m_z	$\begin{pmatrix} 1&0&0&0 \\ 0&1&0&0 \\ 0&0&1&1 \end{pmatrix}$	(1|0,0,1)	x,y+1/2,z+1/2,+1 m_x,m_y,m_z	$\begin{pmatrix} 1&0&0&0 \\ 0&1&0&1/2 \\ 0&0&1&1/2 \end{pmatrix}$	(1|0,1/2,1/2)

Figure 3: List of the representative operations (incomplete) of the magnetic space group P_a2_1/c (#14.80), as obtained when clicking on the column "General positions" of the initial list of MAXMAGN shown in Figure 1. The operations on the right are described in the so-called parent-like setting indicated on the heading of the table, which keeps the crystallographic directions of the parent phase, and introduces a supercell consistent with the propagation vector.

As k=(0,1/2,1/2) in this example, the parent like setting is (a,2b,2c;0,0,0), and a centering {1|0, 1/2, 1/2} is obliged as the lattice translation **b**+**c** is mantained by a spin wave with wave vector (0,1/2,1/2). You can localize this operation in the list. One can also see that this magnetic group maintains the inversion center at the origin, as it keeps the inversion operation {-1|0, 0, 0}, while the monoclinic axis that is maintained is along the x direction in the Pnnm setting.

c) Come back to the main ouput list shown in Figure 1 and click on the fourth column (headed with "General positions") for the second group in the list, which has the same label P_a2_1/c (#14.80). One can see that this second subgroup maintains the inversion operation {-1|0, 1/2, 0} (i.e. {-1|0, 1, 0} in the parent Pnnm setting), but the inversion at the origin {-1|0, 0, 0} is not present. This means that an ordering according to this second subgroup breaks the inversion center at the origin, while it keeps the inversion center that is located at the point (0,1/2,0) in the Pnnm1' grey group. Note that this alternative subgroup of Pnnm1', despite being the same type of magnetic space group

and therefore having the same label as group type as the first one in the list, is NOT equivalent and it is therefore listed as a distinct possible k-maximal magnetic symmetry.

d) Come back to the main output list shown in Figure 1, and click on the fourth column (headed with "General positions") to get the information on the third subgroup of type C_a2/m (#12.64). One can see that in this case the standard setting of the magnetic space group only differs from the parent-like one, by a permutation of the axes. The monoclinic axis of this subgroup is along the z direction of the Pnnm setting. A comparison with the fourth group of the same type shows that, as in the previous pair of subgroups of the same type, they maintain different alternative inversion centers from the parent phase.

e) The symmetry hierarchy can be further explored using the program k-SUBGROUPSMAG. By introducing as parent space group Pnnm1', the propagation vector and, as end subgroup P_s-1, i.e. one restricted to the presence of the space inversion operation and the antitranslation forced by the propagation vector, one obtains a hierarchical graph of the subgroups consistent with the propagation vector (0,1/2,1/2), as shown in Figure 4.
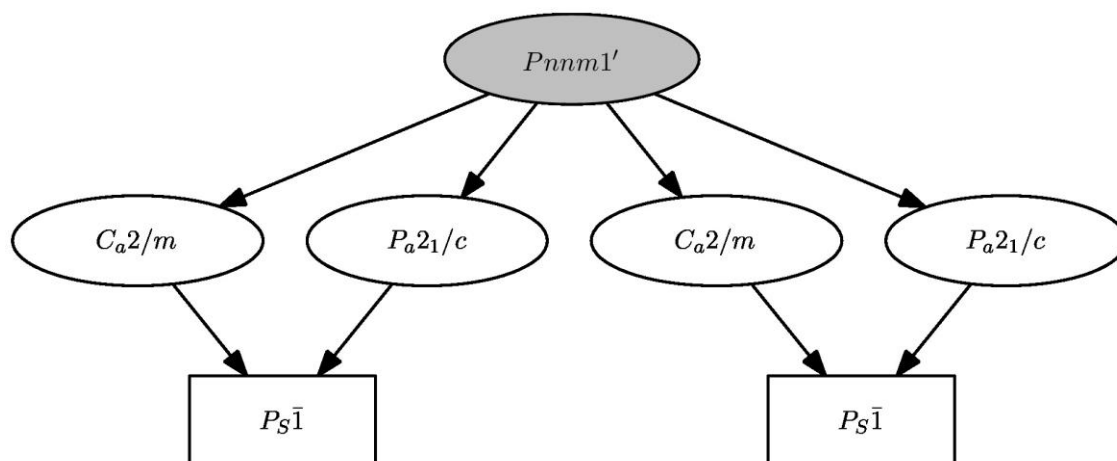
Figure 4: Graph (obtained with k-SUBGROUPSMAG) of all possible magnetic symmetries for a magnetic ordering with a paramagnetic structure with space group Pnnm and a propagation vector (0 1/2 1/2), assuming that at least space inversion is also maintained. Only the BNS label of the corresponding group type is indicated. The k-maximal magnetic groups are highlighted with elliptical frames. Only one subgroup per conjugate class is shown. The two Ps-1 space groups differ in the location of the inversion center. Only one of the two allows a non-zero magnetic moment at the origin, namely the one with the inversion center at the origin (where the Cr magnetic atom lies).

In this example, non-polarized magnetic neutron diffraction is not subject to any specific systematic absence for any of the two possible subgroups. We leave therefore unchecked the fifth column in the first output page headed with "systematic absences", which is a link to the tool MAGNEXT, also available in the Bilbao server, for the calculation of the systematic absences for non-polarized magnetic diffraction. We will see the usefulness of this option in other examples.

f) Come back now to the first input page of MAXMAGN with the main menu, click on the option "structure data of the paramagnetic phase will be included", keeping the space group and propagation vector, and submit. In the next pages introduce the structural data of $CrCl_2$ listed above (either uploading a cif file or by hand), indicating that the Cr atom is magnetic. The structure data of the paramagnetic phase must be described

in the standard setting of the space group of the paramagnetic phase (to work in a non-standard setting, click on the option "Non-conventional setting"; thus, the space group of the paramagnetic phase will be obtained from the symmetry operations present at the cif file). The first output page lists now the same four k-maximal subgroups, but two of them are highlighted with a darker background (see Figure 5). These latter are those that allow a non-zero magnetic moment for at least some of the atoms at the Cr site. The Table includes now an additional column on the right under the heading "Magnetic structure".

Figure 5: List of distinct k-maximal magnetic space groups for a parent space group Pnnm and a propagation vector (0, 1/2, 1/2), as given by MAXMAGN, after having introduced the paramagnetic structure of CrCl$_2$ in the first input steps. The groups with darker background are the only ones allowing a non-zero average magnetic moment for at least some of the Cr atoms.

g) Click in the "Magnetic structure" column for the second possible group with label C$_a$2/m (#12.64). The program lists the asymmetric unit of a magnetic structure satisfying this symmetry (see Figure 6). The first column tabulates the atomic positions, where one can see that both Cr and Cl split into two symmetry-independent sites. The second column indicates the complete orbit for each independent atom for each independent site (Wyckoff orbit), including the magnetic moment relations. Multiplicity and symmetry restrictions on the magnetic moment of each site are shown in the following columns, while on the final column, for magnetic atoms, a menu allows to give specific values to the allowed moment components along the crystallographic axes (units assumed: bohr magnetons). One can see that the two independent Cr sites must necessarily have their moment along different directions. Thus, this symmetry does not allow a collinear ordering.

Figure 6: Atomic positions and magnetic moments of the asymmetric unit for the subgroup of type C_a2/m (#12.64) listed N. 3 in Figure 5, as obtained when clicking in the column "Magnetic structure". The table indicates the Wyckoff orbit of 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). 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 atom listed in the second column, while the last column on the right allows to introduce specific values for the symmetry free moment components.

h) Come back to the previous output page and explore the other alternative maximal symmetry P_a2_1/c (#14.80). In this case, both Cr and Cl site do not split (see Figure 7). The direction of the magnetic moment of the Cr atom is not restricted by symmetry, but its Wyckoff orbit shows that a collinear ordering can occur if the moments are restricted on the plane yz or along x (component m_x has a different set of sign changes through the orbit than the components m_y and m_z, which change sign from one position to another in the orbit in the same form). In accordance with the models reported for this structure, let us assume that the moments lie on the xy plane. According to the listing in Figure 7, this implies a non-collinear model if both components m_x and m_y are non-zero. Introduce some non-zero values for the Mx and My components of Cr, say 3 and 1. Using the appropriate button obtain and save a mCIF file (a CIF-like file) of the resulting magnetic structure. The page showing the mCIF file to be saved has also a button that is a direct link to the tool MVISUALIZE in the Bilbao crystallographic server and allows an inmediate 3D visualization of the chosen magnetic model.

Selected magnetic space group: 1- P_a2_1/c (#14.80)

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

Lattice parameters: a=6.82570, b=12.42780, c=6.98940, alpha=90.00, beta=90.00, gamma=90.00

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

(Export data to MCIF file) (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	Cr1 Cr 0.00000 0.00000 0.00000	$(0,0,0 \mid m_x,m_y,m_z)$ $(1/2,1/4,1/4 \mid m_x,-m_y,-m_z)$ $(0,0,1/2 \mid -m_x,-m_y,-m_z)$ $(1/2,1/4,3/4 \mid -m_x,m_y,m_z)$ $(0,1/2,0 \mid -m_x,-m_y,-m_z)$ $(1/2,3/4,1/4 \mid -m_x,m_y,m_z)$ $(0,1/2,1/2 \mid m_x,m_y,m_z)$ $(1/2,3/4,3/4 \mid m_x,-m_y,-m_z)$	8	(M_x,M_y,M_z)	$M_x =$ [0.00000] $M_y =$ [0.00000] $M_z =$ [0.00000]
2	Cl1 Cl 0.35860 0.14465 0.00000	$(x,y,0 \mid m_x,m_y,m_z)$ $(-x,-y,0 \mid m_x,m_y,m_z)$ $(-x+1/2,y+1/4,1/4 \mid m_x,-m_y,-m_z)$ $(x+1/2,-y+1/4,1/4 \mid m_x,-m_y,-m_z)$ $(x,y,1/2 \mid -m_x,-m_y,-m_z)$ $(-x,-y,1/2 \mid -m_x,-m_y,-m_z)$ $(-x+1/2,y+1/4,3/4 \mid -m_x,m_y,m_z)$ $(x+1/2,-y+1/4,3/4 \mid -m_x,m_y,m_z)$ $(x,y+1/2,0 \mid -m_x,-m_y,-m_z)$ $(-x,-y+1/2,0 \mid -m_x,-m_y,-m_z)$ $(-x+1/2,y+3/4,1/4 \mid -m_x,m_y,m_z)$ $(x+1/2,-y+3/4,1/4 \mid -m_x,m_y,m_z)$ $(x,y+1/2,1/2 \mid m_x,m_y,m_z)$ $(-x,-y+1/2,1/2 \mid m_x,m_y,m_z)$ $(-x+1/2,y+3/4,3/4 \mid m_x,-m_y,-m_z)$ $(x+1/2,-y+3/4,3/4 \mid m_x,-m_y,-m_z)$	16	-	-

Figure 7: Atomic positions and magnetic moments of the asymmetric unit for the subgroup of type P_a2_1/c (#14.80) listed N. 1 in Figure 5, as obtained when clicking in the column "Magnetic structure". The table indicates the Wyckoff orbit of 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). 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 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.

i) Open the mCIF file as a text file and observe the listing of the symmetry operations. The centering and "anti-centering translations" are listed separately (see Figure 8). There are four centering translations and antitranslations including the identity, plus four rotational or roto-inversion operations. The 16 operations that were listed in a previous output page are the result of multiplying these 4 "rotational" or "roto-inversion" operations by the 4 possible translational or "anti-translational" operations.

```
loop_
_space_group_symop.magn_id
_space_group_symop.magn_operation_xyz
_space_group_symop.magn_operation_mxmymz
1 x,y,z,+1 mx,my,mz
2 x+1/2,-y+1/4,-z+1/4,+1 mx,-my,-mz
3 -x,-y,-z,+1 mx,my,mz
4 -x+1/2,y+1/4,z+1/4,+1 mx,-my,-mz

loop_
_space_group_symop.magn_centering_id
_space_group_symop.magn_centering_xyz
_space_group_symop.magn_centering_mxmymz
1 x,y,z,+1 mx,my,mz
2 x,y+1/2,z+1/2,+1 mx,my,mz
3 x,y+1/2,z,-1 -mx,-my,-mz
4 x,y,z+1/2,-1 -mx,-my,-mz
```

Figure 8: Part of the mCIF file for the P_a2_1/c (#14.80) model of $CrCl_2$ that contains the information on the magnetic space group in the used parent-like setting (a,2b,2c;0,0,0).

j) At the end of the mCIF file observe the listed atomic positions and moments of the asymmetric unit. To be noted that the file only includes the magnetic moment components (along the crystallographic axes) of a single Cr atom (see Figure 9). The values of the rest of Cr atoms in the unit cell are unambiguously determined by the application of the operations of the defined magnetic space group (see Figure 8). It is important to stress that not only the magnetic moments but also the positions of all atoms in the unit cell are obtained by the application of the magnetic symmetry operations to the asymmetric unit listed in the mCIF file.

```
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
Cr Cr  0.00000 0.00000 0.00000
Cl Cl  0.35860 0.14465 0.00000

loop_
_atom_site_moment_label
_atom_site_moment_crystalaxis_x
_atom_site_moment_crystalaxis_y
_atom_site_moment_crystalaxis_z
Cr 3.00000 1.00000 0.00000
```

Figure 9: Part of the mCIF file for the P_a2_1/c (#14.80) model of $CrCl_2$ that contains the information on the atomic positions and magnetic moments of the asymmetric unit.

The obtained mCIF file can be read by the refinement programs JANA2006 or FULLPROF, and if diffraction data were available could be used as a starting symmetry-constrained model to be refined. One must stress in this case that care should be taken that the diffraction data is indexed consistently with the parent-like unit cell that is being employed to describe the structure. The mCIF file obtained from MAXMAGN can also be

read by VESTA or Jmol for visualization purposes, and it can also be employed with ISODISTORT to analyse the model in terms of irrep modes. The tool MVISUALIZE in the Bilbao Crystallographic Server can also read these files, and provides an inmediate 3D visualization with Jmol without the need of any program installation.

k) Load the mCIF file in the VESTA program to visualize the model. Something similar to the representation shown in Figure 10(a) can be obtained.
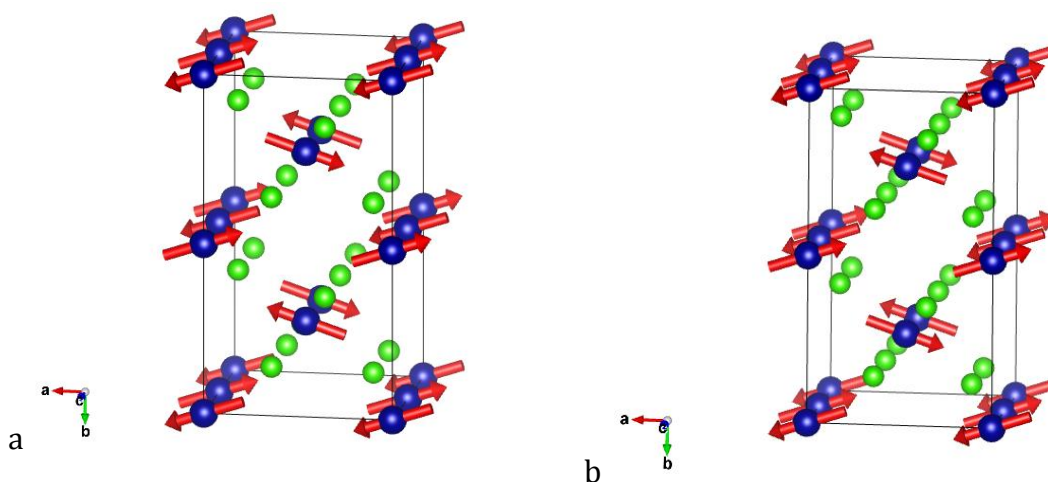

Figure 10: (a) Magnetic ordering in $CrCl_2$ according to the magnetic space group P_a2_1/c (#14.80) using the parent-like setting (a,2b,2c;0,0,0), and having arbitrarily restricted the spins to the plane xy. (b) Magnetic ordering equivalent to the one in (a) corresponding to a twin-related configuration. Its symmetry is given by a magnetic subgroup conjugate to the one associated with the structure in (a). The two arrangements are related for instance by the lost operation $\{2_z'|0, 0, 0\}$ that is present in the paramagnetic phase.

l) Go back to the main output page and click on "alternatives (domain-related)" for the same group. The program prompts then a page with the list of distinct subgroups belonging to the same conjugation class (see Figure 11). One can see that there is an alternative subgroup which is conjugate to the one chosen by the program. This conjugate subgroup will correspond to a physically equivalent configuration that is domain-related with the first one (the one chosen by the program). By clicking "choose" on this second magnetic space group we change the choice of subgroup of type P_a2_1/c (#14.80) to this second one. We obtain then, following the same procedure as above, a magnetic configuration different from the one in Figure 4(a), but equivalent. It corresponds to its transformation by one of the lost operations belonging to the parent grey group. The result to be obtained is shown in Figure 4(b). One can see there that the individual local couplings of FM or AFM type between neighbouring specific sites should not be considered as an absolute part of the magnetic structural model, as they depend on which of the two equivalent descriptions is chosen.

Conjugated (domain-related) subgroups and alternative transformations to standard setting

Selected magnetic space group: 1- P_a2_1/c (#14.80)

Conjugated (domain-related) subgroups

N	Transformation matrix:	Alternative matrices	Choose matrix
1	$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 2 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	Show	Choose
2	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -2 & 0 & -1 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	Show	Choose

Figure 11: Listing of the two subgroups of type P_a2_1/c (#14.80) of the group Pnnm1' that form a conjugation class, and could describe a magnetic ordering with propagation vector (0, 1/2, 1/2) of maximal symmetry in $CrCl_2$. The first subgroup is the one chosen by default by MAXMAGN, while the second one corresponds to a domain-related physically equivalent configuration. The user can change the choice of the representative subgroup, and therefore the chosen configuration, by clicking on the button of the last column. The 3x3 matrix and column vector listed indicates the transformation of each subgroup to the standard setting of the group type, and defines unambiguously each subgroup.

m) Come back to the main output page of the magnetic structure under the group P_a2_1/c (#14.80) described in the parent-like setting (Figure 7), after <u>having switched back to the default choice of the subgroup,</u> and click on the button "use an alternative setting". An mCIF with a description using a smaller unit cell that avoids the centering {1|0, 1/2, 1/2} can be obtained with this option (see Figure 12). The cost is having an oblique unit cell with respect to the Pnnm setting. This description is specially appropiate for ab-initio calculations, as it uses a minimal unit cell. To do that introduce as desired basis transformation from the parent: (a,b+c,-b+c;0,0,0). The input matrix follows the same rule as in other cases, i.e. each matrix column represents a transformed basis vector. The output provided for this user-defined setting is more limited than for the default choice, but the corresponding mCIF file can be equally produced. Introduce arbitrary values for the moment components, similar to those in the previous setting. Taking into account the basis transformation, the moment chosen previously would be (3, 0 .5, 0.5) in this new basis. Download the corresponding mCIF file, and visualize it with VESTA (see Figure 13) or MVISUALIZE.

Figure 12: Menu to introduce an alternative user-chosen setting (unit cell) to describe the magnetic structure, once one of the possible k-maximal magnetic symmetries has been chosen. The unit cell introduced must be consistent with the periodicity of the magnetic ordering, and this is cross-checked by the program.
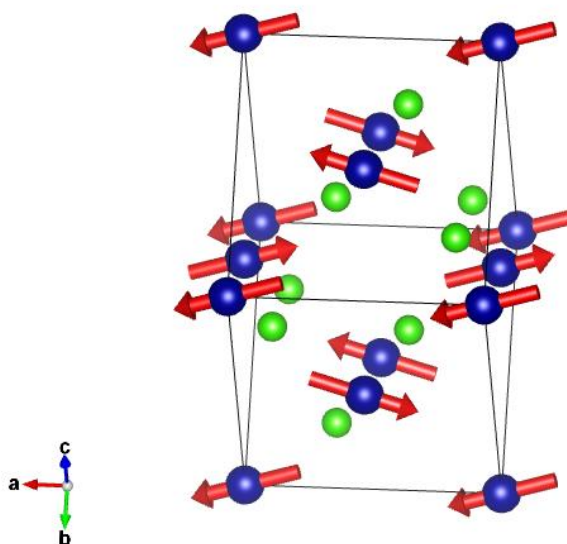

Figure 13: Magnetic structure as in Figure 10(a), using a primitive unit cell basis related with the parent unit cell by (a,b+c,-b+c;0,0,0).

n) Open the tool STRCONVERT at the Bilbao crystallographic server and introduce the mCIF file. This tool allows various editing and save operations of the information of the mCIF. Here we apply the button "Transform the structure to P1 setting" to obtain a listing of all the atoms in the unit cell with their magnetic moments (see Figure 14). This can be specially useful for an ab-initio calculation using a code that works without symmetry and requires the information on all atoms in a primitive unit cell. The orbit of magnetic atoms in the primitive cell used is reduced to four atoms. The first two Cr atoms, Cr1_1 and Cr1_2, are those in the Pnnm unit cell at the origin and at (1/2, 1/2, 1/2) transformed to the new basis, while the two additional ones are those related by a translation **c** of the parent unit cell. The latter have therefore opposite moments as obliged for a magnetic ordering with a propagation vector (0, 1/2, 1/2). Therefore the specific features that define this model with k-maximal magnetic symmetry reduce to the

moment relation (mx, -my, -mz) of Cr1_2 with respect to the moment (mx, my, mz) of Cr1_1, the remaining relations being obliged by the value of the propagation vector.

Symmetry

Magnetic Space Group # (BNS): 1.1   (P1)   *Type: I*

Lattice Parameters

a: 6.8257 Å   b: 7.1292 Å   c: 7.1292 Å

α 121.29(°   β: 90.000°   γ: 90.000°

Symmetry Operations [Show/Hide]

Atomic Positions & Magnetic Moments
Switch to the treatment of the vectors as: [displacements ▴] (Go!)

Label	Element	x	y	z	Occ.	m_x	m_y	m_z
☐ Cr1_1	Cr	0.00000	0.00000	0.00000	1.00000	3.000	0.500	−0.500
☐ Cr1_2	Cr	0.50000	0.50000	0.00000	1.00000	3.000	−0.500	0.500
☐ Cr1_3	Cr	0.00000	0.50000	0.50000	1.00000	−3.000	−0.500	0.500
☐ Cr1_4	Cr	0.50000	0.00000	0.50000	1.00000	−3.000	0.500	−0.500
☐ Cl1_1	Cl	0.35860	0.14465	0.85535	1.00000	0.000	0.000	0.000
☐ Cl1_2	Cl	0.85860	0.35535	0.14465	1.00000	0.000	0.000	0.000
☐ Cl1_3	Cl	0.64140	0.85535	0.14465	1.00000	0.000	0.000	0.000

Figure 14: Main menu page (partial) of STRCONVERT after introducing the mCIF file of the magnetic model of k-maximal symmetry using a setting (a, b+c,-b+c;0,0,0) with respect to the parent Pnnm, and after having clicked "Transform the structure to P1 setting". The program lists positions and magnetic moments of all atoms in the unit cell.

p) Obtain the equivalent domain-related configuration described in the same primitive magnetic unit cell following the same steps as above. Use then STRCONVERT again to list all atoms in the unit cell:

Label	Element	x	y	z	Occ.	m_x	m_y	m_z
☐ Cr1_1	Cr	0.00000	0.00000	0.00000	1.00000	3.000	0.500	−0.500
☐ Cr1_2	Cr	0.50000	0.00000	0.50000	1.00000	3.000	−0.500	0.500
☐ Cr1_3	Cr	0.00000	0.50000	0.50000	1.00000	−3.000	−0.500	0.500
☐ Cr1_4	Cr	0.50000	0.50000	0.00000	1.00000	−3.000	0.500	−0.500

Figure 15: Main menu page (partial) of STRCONVERT after introducing the mCIF file of the alternative domain-related magnetic model of k-maximal symmetry using a setting (a, b+c,-b+c;0,0,0) with respect to the parent Pnnm, and after having clicked "Transform the structure to P1 setting". The program lists positions and magnetic moments of all atoms in the unit cell, which can be compared with those in Figure 14.

In Figure 15, the atom listed as Cr1_4 is the one listed as Cr1_2 in the previous model. The relation of the moment of this atom with the one of Cr1_1 is now (-mx, my, mz), i.e. just the opposite spin coupling, although it describes a fully equivalent spin configuration. This means that if the spin configuration were a collinear arrangement restricted along x or on the plane yz, individual local FM or AFM couplings between neighbouring atoms have no absolute meaning as description of the spin configuration.

Epilogue to this first example: The case of $CrCl_2$ was considered by Izyumov et al. in their book "Neutron Diffraction of Magnetic Materials" [6] as a paradigmatic example, which according to these authors demonstrated the insufficiency of the magnetic space groups to describe the spin correlations occuring in many magnetic structures. This reference assumed that the magnetic structure of $CrCl_2$ is a collinear arrangement on the plane xy, with the moments of the Cr atoms at the origin and at (1/2, 1/2, 1/2) being equal and opposite. From the considerations above, it is clear that the model considered in this reference is incompatible with any of the two possible k-maximal symmetries, and its symmetry is limited to its common subgroup P_s-1 (see Figure 4), where the two Cr sites would be symmetry independent. Therefore the opposite values of the moments in the two Cr sites, which were assumed in that model, would be an important constraint satisfied by this magnetic phase that was not explained by its magnetic symmetry. A revision of the original reports on the magnetic structure of $CrCl_2$ shows however that the collinear model on the xy plane assumed by Izyumov et al. has not very solid ground. The experimental data presented in these old publications are extremely poor and their fit to more symmetrical configurations did not seem to have been checked. Furthermore, some recent unpublished ab-initio calculations and new refinements using the scarce poor data available in the literature indicate that the monoclinic arrangement of k-maximal symmetry discussed above is probably a more appropiate model for the magnetic phase of this compound.

Comparison with the representation method:
The little group of the propagation vector (0, 1/2, 1/2) is the full group Pnnm. As can be seen using REPRES (in the Bilbao crystallographic server) there are two 2-dim irreps of Pnnm for this wave vector: T1+ and T1- (T is the standard label for the vector (0, 1/2, 1/2) in the Brillouin zone). Therefore, for the grey group Pnnm1' there are two analogous irreps: mT1+ and mT1- , which can be relevant for a magnetic ordering (the symbol m is used to distinguish irreps odd for time reversal from even ones). The magnetic representation for this wave vector and limited to the magnetic moments of the Cr atoms is however restricted to the irrep mT1+, contained three times (see for instance the results using Basireps of the FullProf suite [2]):

$$M_{repr} = 3 \; mT1+$$

This means that any arbitrary spin configuration with a propagation vector (0, 1/2, 1/2) transforms according to the irrep mT1+, and can therefore be described in terms of 6 basis functions associated with this irrep. In other words, the assumption of the magnetic ordering complying with a single irrep does not introduce any constraint, and the representation method is of no use in this example. This should be compared with the constraints introduced by the assumption of one of the two possible k-maximal magnetic groups discussed above, where the number of free parameters describing the spin configuration is limited to three in both cases.

We can use ISOCIF and ISODISTORT [3] to perform the mode decomposition of the monoclinic model of k-maximal symmetry P_a21/c (#14.80) represented in Figure 10(a). ISOCIF should be used to

transform the mCIF produced above in step h) into a standard setting. This mCIF file in standard setting can be then uploaded in ISODISTORT (method 4) as the distorted structure to be decomposed into symmetry modes with respect to the Pnnm structure, which should have been uploaded previously as parent structure. The mode decomposition provided by ISODISTORT shows that the spin configuration corresponds as expected to mT1+, but restricted to a special direction in the representation space corresponding to the k-maximal symmetry discussed above, which is listed here as a so-called isotropy subgroup of the irrep mT1+. The number of listed basis modes complying with this specific symmetry is only three, as expected from the description done above using directly the magnetic space group.

Summarizing, any arbitrary spin configuration in CrCl$_2$ can be associated with the irrep mT1+, and therefore in this case the representation method in its traditional form is of no use. A spin ordering restricted to have one of the k-maximal magnetic symmetries discussed above corresponds to the choice of a special direction of higher symmetry within the mT1+ representation (i.e. a specific linear combination of the three pairs of mT1+ basis functions), so that the number of free parameters in the possible combination of basis modes is restricted from 6 to 3. To assign a k-maximal magnetic group is therefore NOT equivalent to the assignment of an irrep, and introduces additional constraints.

Example 2.   Orthorhombic HoMnO$_3$ (see MAGNDATA #1.20)

The paramagnetic structure of HoMnO$_3$ can be summarized as (Muñoz, A. et al., *Inorg. Chem.* (2001) **40** 1020 - 1028):

Space group: Pnma (#62)
Lattice parameters:
5.83536 7.36060 5.25722

Asymmetric unit:
Ho1 - 0.08390 0.25000 0.98250
Mn1 - 0.00000 0.00000 0.50000
O1 - 0.46220 0.25000 0.11130
O2 - 0.32810 0.05340 0.70130

Magnetic atoms: Ho1, Mn1

   The magnetic phase of this compound is known to have a propagation vector k=(1/2, 0, 0) and its antiferromagnetic magnetic order induces a switchable electric polarization, being therefore a multiferroic in the broad sense that is presently employed.

We can use MAXMAGN to explore the possible magnetic orderings of k-maximal symmetry with this propagation vector, to demonstrate that the parent space group and the propagation vector is sufficient information to predict that this system, if fully magnetically ordered, has a great probability of being multiferroic.

a) Introduce in MAXMAGN the propagation vector and the structural data of the parent structure of HoMnO$_3$, either using the data above or with the corresponding CIF file, indicating the magnetic character of Mn and Ho. A list of four possible k-maximal magnetic space groups are obtained (see Figure 16)

N	Group (BNS)	Transformation matrix	General positions	Systematic absences	Magnetic structure
1	*P$_a$na2$_1$* (#33.149) Go to a subgroup	$\begin{pmatrix} 2 & 0 & 0 & 3/4 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
2	*P$_b$mn2$_1$* (#31.129) Go to a subgroup	$\begin{pmatrix} 0 & 2 & 0 & 3/4 \\ -1 & 0 & 0 & 1/4 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
3	*P$_c$2$_1$/c* (#14.82) Go to a subgroup	$\begin{pmatrix} 0 & 0 & 2 & 1/2 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
4	*P$_a$2$_1$/m* (#11.55) Go to a subgroup	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show

Figure 16: List of distinct k-maximal magnetic space groups for a parent space group Pnma and a propagation vector (1/2, 0, 0), as given by MAXMAGN, after having introduced the paramagnetic structure of HoMnO$_3$ in the first input steps. The groups with darker background are those allowing a non-zero average magnetic moment for at least some of the Mn or Ho atoms. In this case, the four alternative symmetries are possible.

It should be noticed that this list is comprehensive in the sense that it includes a representative of all the classes of magnetic subgroups equivalent by conjugation with respect the parent space group. The list therefore encompasses all possible non domain-equivalent magnetic symmetries, which are consistent with the observed magnetic propagation vector, and have no supergroup (magnetic group) above them that also fulfils this condition. The determination of this list only requires the knowledge of the parent space group and the propagation vector **k**. The space groups are determined by mathematically searching among the subgroups of the grey group *Pnma1'* of the parent phase all maximal subgroups which have as Bravais magnetic lattice the one defined by the vector **k**, i.e. the sub-lattice of the parent lattice formed by the parent lattice translations **L** that satisfy exp(i2π**k.L**)= 1, but having also as "antitranslations" (i.e. translations combined with time reversal) parent lattice translations satisfying exp(i2π**k.L**)= -1. The condition of the subgroups being maximal is considered in an extended form, disregarding intermediate subgroups of type II (grey groups), as by definition they contain the time reversal operation and therefore they cannot describe the symmetry of a magnetic phase.

b) Explore the listed four possible models of maximal symmetry by clicking on the last column headed with "magnetic structure". Check first that the models with monoclinic centrosymmetric symmetry P$_c$2$_1$/c(#14.82) and P$_a$2$_1$/m(#11.55) require that a half of the Mn atoms remain disordered with null magnetic moment. This means that a fully ordered magnetic arrangement of the Mn of maximal symmetry under the observed propagation can only be achieved under the non-centrosymmetric symmetries P$_a$na2$_1$ (#33.149) or P$_b$mn2$_1$ (#31.129). The point symmetry in both cases is the grey polar point

group mm21'. As shown by the listed transformation matrices, in both cases the polar axis is along the c axis of the Pnma setting. A multiferroic character of the magnetic phase should therefore be expected if all magnetic Mn atoms order and the phase symmetry is maximal. The polar direction is also predicted to be along the c axis.

Figure 17: Atomic positions and magnetic moments (partial) of the asymmetric unit of $HoMnO_3$ for the subgroup of Pnma1' of type P_c2_1/c (#14.82), listed N. 3 in Figure 16, as obtained when clicking in the column "Magnetic structure". The table indicates the Wyckoff orbit of 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). 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 column (if any), while the last column on the right allows to introduce specific values for the symmetry-free moment components. Both the Ho and Mn split into two independent sites. The bar in the fifth column for some of the magnetic sites indicates that the magnetic moment at this site is symmetry-forced to be zero.

c) Using the program k-SUBGROUPSMAG construct the graph of all magnetic subgroups (conjugate classes) consistent with the observed propagation vector, and check that apart from the monoclinic k-maximal subgroups there is only a third possible centrosymmetric symmetry, namely a subgroup of type P_s-1, which is a common subgroup of the two centrosymmetric monoclinic groups of maximal symmetry (see Figure 18). Check the operations belonging to this subgroup using the options of k-SUBGROUPSMAG.
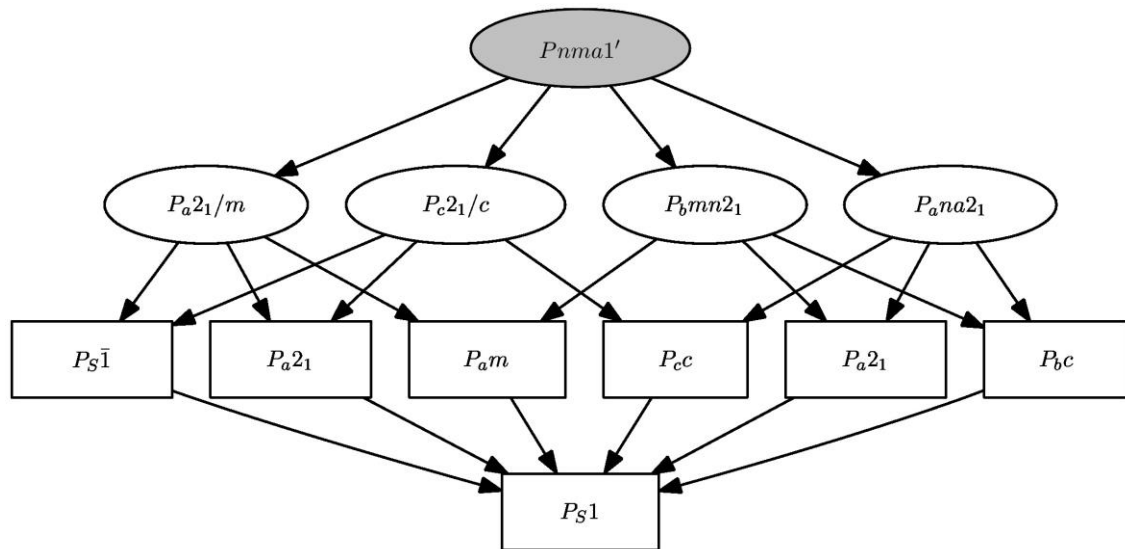
Figure 18: Graph (obtained with k-SUBGROUPSMAG) of all possible magnetic symmetries for a magnetic ordering with a paramagnetic structure with space group Pnma and a propagation vector (1/2 0 0). Only the BNS label of the corresponding group type is indicated. The k-maximal magnetic groups are highlighted with elliptical frames. Only one subgroup per conjugate class is shown. Except for the two monoclinic k-maximal subgroups and its common subgroup P_s-1, all other possible symmetries are polar and allow an induced electric polarization. The three non-polar subgroups are not possible for a full magnetic ordering of $HoMnO_3$, as they require that some Mn sites remain with zero moment.

d) Click on the option "go to a subgroup" for the subgroup of Pnma1' of type P_c2_1/c (#14.82), listed N. 3 in Figure 16, and in the following menu choose as generators of the chosen subgroup the inversion operation {-1|0, 0, 0} and the anti-translation {1'|1/2, 0, 0}. Submit this subgroup and check in the output that by this means the subgroup P_s-1 has been chosen. Click on the option "magnetic structure" of the next output page, and observe in the next output that a magnetic structure subject to this minimal centrosymmetric symmetry still requires that some Mn atoms remain disordered with moment zero. You can therefore predict that whatever is the magnetic ordering of $HoMnO_3$ with propagation vector (1/2,0,0), if it involves all Mn atoms it must necessarily break the centrosymmetry of the structure, and the system is bound to have (if the system is an insulator) a magnetically induced electric polarization with ferroelectric properties.

e) Construct a magnetic structure complying with the maximal symmetry P_ana2_1 (#33.149) following the same procedure as in the example 1. Notice that in this case the difference between the standard setting and the parent-like is only an origin shift. The experimental diffraction data indicates that the Mn spins are essentially collinear along the x direction. Therefore introduce a non-zero value for the Mx component of the Mn independent atom, although as shown in the listing both polar symmetries allow an arbitrary direction for the Mn moment, that would have non-collinear character. Keep disordered the moment of the Ho atoms maintaining at zero their symmetry-allowed x and z components. Notice that this symmetry break splits into two the Ho site and the two oxygen sites of the parent structure. This means that many additional structural degrees of freedom are in principle triggered by the magnetic ordering and they can be taken into account in a controlled and systematic way, if the magnetostructural coupling is sufficiently strong to be detectable, using the magnetic space group for defining the constraints on the atomic positions. The atomic positions listed for the split atomic sites of the asymmetric unit satisfy among them the relations coming from the Pnma

symmetry, but their separate listing within the new asymmetric unit would allows their independent refinement. A symmetry-consistent crosscheck of their possible deviation from the Pnma relations due magnetostructural couplings is therefore possible.

Figure 19: Atomic positions and magnetic moments (partial) of the asymmetric unit of HoMnO$_3$ for the subgroup of Pnma1' of type P$_a$na2$_1$ (#33.149), listed N. 1 in Figure 16, as obtained when clicking in the column "Magnetic structure". The table indicates the Wyckoff orbit of 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). 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 moment components of the representative magnetic atom listed in the second column (if any), while the last column on the right allows to introduce specific values for its symmetry-free moment components. The Ho split into two independent sites, while the Mn remains a single independent site. The bar in the fifth column for some of the <u>magnetic</u> sites indicates that the magnetic moment at this site is symmetry-forced to be zero.

f) Produce an mCIF file of the P$_a$na2$_1$ (#33.149) model and visualize it with VESTA or Jmol. If only the magnetic atoms are visualized, it will be something similar to Figure 20(a).
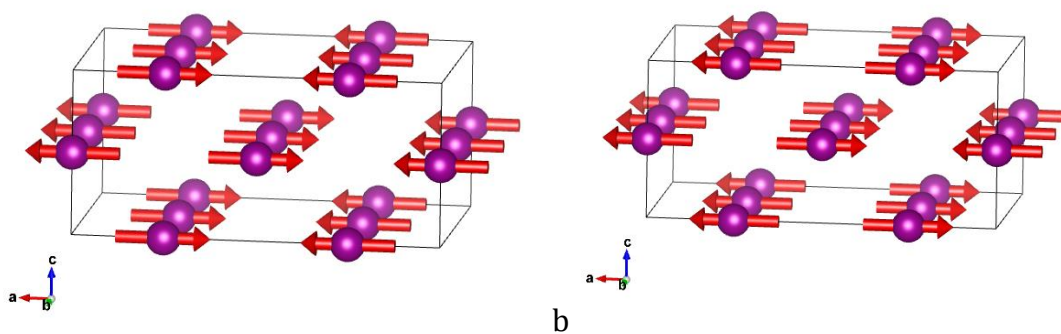
a

b

Figure 20: (a) Possible k-maximal magnetic ordering for HoMnO$_3$ according to the magnetic space group P$_a$na2$_1$(#33.149) using the parent-like setting (2a,b,c;0,0,0), and having restricted the spins along x. (b) Magnetic ordering equivalent to the one in (a) corresponding to a twin-related configuration. Its symmetry is given by a magnetic subgroup conjugate to the one associated with the structure in (a). The two arrangements are related for instance by the lost inversion operation {-1|0, 0, 0} present in the paramagnetic phase. This operation also switches the polarity and therefore the two magnetic configurations have opposite magnetically induced polarizations along the c direction.

g) Come back to the main output list of k-maximal magnetic groups and click for "alternatives (domain related)" of the listed group P$_a$na2$_1$(#33.149) to change to the second conjugate subgroup of this type. Follow then the same procedure as before and obtain the mCIF file of the corresponding magnetic arrangement. It is shown in Figure 20(b). This arrangement is twin related with the previous one. The lost inversion operation for instance transforms one into the other. The two configurations are physically equivalent and correspond to domains having opposite magnetically induced electric polarizations along c.

h) Come back to the main output list of k-maximal magnetic groups (Figure 16) and follow the same procedure for the second possible polar group P$_b$mn2$_1$ (#31.129). Notice in the output that in this phase if there is some magnetic ordering of the Ho atoms it can only happen along the b axis.

Figure 21: Atomic positions and magnetic moments (partial) of the asymmetric unit of HoMnO$_3$ for the subgroup of Pnma1' of type P$_b$mn2$_1$ (#31.129), listed N. 2 in Figure 16, as obtained when clicking in the column "Magnetic structure". The table indicates the Wyckoff orbit of 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). 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 moment components of the representative magnetic atom listed in the second column (if any), while the last column on the right allows to introduce specific values for its symmetry-free moment components. The Ho splits into two independent sites, while the Mn remains a single independent site. The bar in the fifth column for some of the <u>magnetic</u> sites indicates that the magnetic moment at this site is symmetry-forced to be zero.

i) Restrict again the model to have the moments along the x axis and obtain the corresponding mCIF files for the two twin related configurations. They are depicted in Figure 22. This is actually the model that has been reported for HoMnO$_3$ (see MAGNDATA 1.20). Note that the symmetry allows canting of the spins along the y and z directions, which would break the perfect collinearity, while keeping the symmetry.
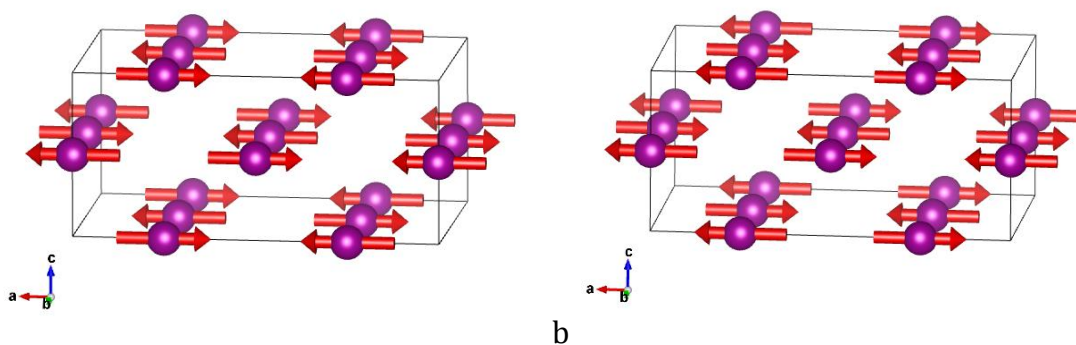
a

b

Figure 22: (a) Possible k-maximal magnetic ordering for $HoMnO_3$ according to the magnetic space group P_bmn2_1 (#31.129), using the parent-like setting (2a,b,c;0,0,0), and having restricted the spins along x. (b) Magnetic ordering equivalent to the one in (a) corresponding to a twin-related configuration. Its symmetry is given by a magnetic subgroup conjugate to the one associated with the structure in (a). The two arrangements are related for instance by the lost inversion operation {-1|0, 0, 0} present in the paramagnetic phase. The inversion also switches the polarity and therefore the two magnetic configurations will have opposite values for the magnetically induced polarization along the c direction. This is the magnetic arrangement that has been reported for this compound (Muñoz, A. et al., *Inorg. Chem.* (2001) **40** 1020 - 1028. See entry 1.20 of MAGNDATA).

We have seen above that the atomic positions become split because of the symmetry break, and the symmetry relations that they have to fullfill rigorously in the magnetic phase are described by the same symmetry operations that are valid for the magnetic moments, which are listed in the mCIF file. The presence or not of time reversal in these symmetry operations is irrelevant for the atomic positions, which are then subject to the constrains of an *effective* space group obtained by disregarding the presence of time reversal in the operations. This effective space group is the one used for the labelling of the magnetic space group in the OG description. Thus, in our case, the group P_bmn2_1 (#31.129) in BNS notation is the group $P_{2b}m'n2_1'$ (#31.7.218) and in this case the effective space group for the atomic positions (and eletron density) is of the same type as the one used for the BNS notation, namely the space group $Pmn2_1$(#31).

j) Come back to the main list of k maximal groups (Figure 16) and click on the column "general positions" for the group P_bmn2_1 (#31.129) (previously switch back the group to its default choice) in order to see the symmetry operations of the group in the parent-like setting, and derive the effective space group for the atomic positions in this setting :

Parent-like setting (2a, b, c; 0, 0, 0)		
(x,y,z) form	**Matrix form**	**Seitz notation**
x,y,z,+1 m_x,m_y,m_z	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	$\{1\,\|\,0\}$
-x+3/4,-y,z+1/2,+1 $-m_x,-m_y,m_z$	$\begin{pmatrix} -1 & 0 & 0 & 3/4 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	$\{2_{001}\,\|\,3/4\ 0\ 1/2\}$
x,-y+1/2,z,+1 $-m_x,m_y,-m_z$	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	$\{m_{010}\,\|\,0\ 1/2\ 0\}$
-x+3/4,y+1/2,z+1/2,+1 $m_x,-m_y,-m_z$	$\begin{pmatrix} -1 & 0 & 0 & 3/4 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	$\{m_{100}\,\|\,3/4\ 1/2\ 1/2\}$
x+1/2,y,z,-1 $-m_x,-m_y,-m_z$	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}'$	$\{1'\,\|\,1/2\ 0\ 0\}$
-x+1/4,-y,z+1/2,-1 $m_x,m_y,-m_z$	$\begin{pmatrix} -1 & 0 & 0 & 1/4 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}'$	$\{2'_{001}\,\|\,1/4\ 0\ 1/2\}$
x+1/2,-y+1/2,z,-1 $m_x,-m_y,m_z$	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}'$	$\{m'_{010}\,\|\,1/2\ 1/2\ 0\}$
-x+1/4,y+1/2,z+1/2,-1 $-m_x,m_y,m_z$	$\begin{pmatrix} -1 & 0 & 0 & 1/4 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}'$	$\{m'_{100}\,\|\,1/4\ 1/2\ 1/2\}$

Figure 23: General positions or representative symmetry operations of the subgroup of Pnma1' of type P_bmn2_1 (#31.129), listed N. 2 in Figure 16, in the parent-like setting (2a,b,c;0,0,0), as obtained when clicking in the column "general positions".

One can see that the primitive unit cell of the effective lattice for the non-magnetic degrees of freedom is half the size of the magnetic unit cell, since for the non-magnetic degrees of freedom the operation $\{1'\|1/2\ 0\ 0\}$ is fully equivalent to a centering translation $\{1\|1/2\ 0\ 0\}$. The effective space group is then given by the operations: $\{1\|\ 0\ 0\ 0\}$, $\{2_{001}\|3/4\ 0\ 1/2\}$, $\{m_{010}\|\ 0\ 1/2\ 0\}$, $\{m_{100}\|3/4\ 1/2\ 1/2\}$, plus the centering translation $\{1\|1/2\ 0\ 0\}$. Therefore, the effective primitive unit cell for the atomic positions remains the parent unit cell (a,b,c;0,0,0). If we use this parent basis for the atomic positions instead of the parent-like one, the operations of the effective space group constraining the atomic positions is then given by the operations:

$\{1\|\ 0\ 0\ 0\}$, $\{2_{001}\|\ 1/2\ 0\ 1/2\}$, $\{m_{010}\|\ 0\ 1/2\ 0\}$, $\{m_{100}\|\ 1/2\ 1/2\ 1/2\}$ or

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

This is indeed a space group of type $Pmn2_1$ (#31) in a non-standard setting. The standard setting can be reached with the transformation (-b, a, c; 1/4, 1/4, 0) (you can check it using IDENTIFY GROUP in the Bilbao Crystallographic Server).

Comparison with the representation method:
The little group of the propagation vector (1/2, 0, 0) is the full group Pnma. As can be seen using REPRES (in the Bilbao crystallographic server) there are two 2-dim irreps of Pnma for this wave vector: X1 and X2 (X is the standard label for the vector (0, 1/2, 1/2) in the Brillouin one). Therefore, for the grey group Pnma1' there are two analogous irreps: mX1 and mX2 , which can be relevant for a magnetic ordering (the symbol m is used to distinguish irreps odd for time reversal from even ones). The magnetic representation for this wave vector and limited to the spins of the Mn atoms decomposes into these irreps in the following form (see for instance the results using Basireps of the FullProf suite [2]):

$M_{repr} = 3\ mX1 + 3\ mX2$

Therefore, the assumption of the magnetic ordering complying with one of the two single irreps reduces the numbers of degrees of freedom of the spin configuration from 12 to 6, i.e. there are 6 independent spin basis functions to be considered, and therefore 6 refinable parameters when describing a spin configuration of the Mn atoms complying with one of the two irreps. This should be compared with the constraints introduced by the assumption of one of the four possible k-maximal magnetic groups discussed above, where the number of free refinable parameters describing the spin configuration is limited to three in any of the four cases. Using ISODISTORT as in the previous example one can check that the k-maximal subgroups $P_b mn2_1$ and $P_a 2_1/m$ correspond to spin configurations according to the irrep mX1, but restricted within a special "direction" in the representation space. This means that the mX1 basis functions must be combined in a specific form such that the number of free parameters reduces from 6 to 3. $P_b mn2_1$ and $P_a 2_1/m$ are so-called isotropy subgroups (or epikernels) of the irrep mX1. Similarly, $P_a na2_1$ and $P_c 2_1/c$ are isotropy subgroups (epikernels) of the irrep mX2 and the restriction of the configuration to one of these alternative symmetries reduces the number of effective basis functions from 6 to 3.

Summarizing, the spin ordering in $HoMnO_3$ complies with one of the k-maximal magnetic symmetries discussed above, namely $P_b mn21$ (#31.129), and it corresponds to the choice of a special direction of higher symmetry within the space of mX1 distortions, so that the number of free symmetry-adapted basis modes is restricted from 6 to 3. To assign this k-maximal magnetic group is NOT equivalent to the assignment of the irrep mX1. It introduces additional constraints.

Example 3: $KFe_3(OH)_6(SO_4)_2$ (MAGNDATA #1.25)

The paramagnetic structure of this compound can be found in the Inorganic Crystal Structure Database (ICSD, #34344):

Space group R-3m (#166)

Lattice parameters:
7.30400 7.30400 34.53600 90.00 90.00 120.00

Asymmetric unit:
Fe 1 - 0.5 0.0 0.5
K 1 - 0.00000 0.00000 0.00000
O 1 - 0.00000 0.00000 0.39340
O 2 - 0.21800 -0.21800 -0.05430
O 3 - 0.12470 -0.12470 0.13510

S 1 - 0.00000 0.00000 0.30840

Magnetic atom: Fe

The magnetic phase of this compound is known to have a propagation vector k=(0, 0, 3/2).

The Fe atoms in this compound lie on layers forming 2D Kagome lattices, and their spin arrangement was studied by Inami, T. et al., *J. of Magn. and Magn. Mat.* (1998) 177, 752 (see MAGNDATA #1.25). In this reference no symmetry arguments were applied and the model proposed was found, according to the authors, by checking 24 different alternative possible configurations. The exercise below with MAXMAGN shows however that there are only two configurations of highest symmetry which should be first considered as being the most probable, and in fact, the model proposed by this experimental study is one them.

a) Introduce the data in MAXMAGN using the cif file or the listing above, and flag Fe as magnetic. Four possible k-maximal magnetic symmetries are listed as possible, from which two of them allow a non-zero magnetic moment of the Fe site (see Figure 24). Check that there are no twin-related configurations described by alternative conjugate groups, by clicking on "alternative (domain-related)".

Maximal magnetic space groups for the space group 166 (R-3m) and the propagation vector k = (0, 0, 3/2)

Maximal subgroups which allow non-zero magnetic moments for at least one atom are coloured

N	Group (BNS)	Transformation matrix	General positions	Systematic absences	Magnetic structure
1	R$_I$-3c (#167.108) Go to a subgroup	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
2	R$_I$-3c (#167.108) Go to a subgroup	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
3	R$_I$-3m (#166.102) Go to a subgroup	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 2 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
4	R$_I$-3m (#166.102) Go to a subgroup	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 2 & 1/2 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show

Figure 24: List of distinct k-maximal magnetic space groups for a parent space group R-3m and a propagation vector (0, 0, 3/2), as given by MAXMAGN, after having introduced the paramagnetic structure of $KFe_3(OH)_6(SO_4)_2$ in the first input steps. The groups with darker background are those allowing a non-zero average magnetic moment for at least some of the Fe atoms. Only two of the symmetries are therefore possible for the magnetic Fe ordering.

b) Click on the fifth column to see the systematic absences of any of the two allowed groups (they are the same):

Magnetic diffraction Systematic Absences for the given Magnetic Space Group:

(in the BNS basis of the input)

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

Systematic absences for general reflections (produced by centrings):

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

Systematic absences for special reflections:

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

For l = 3 :   I = 0   F = (0,0,Fz)

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

Figure 25: Systematic absences for the k-maximal subgroup of type R_I-3c, listed N. 2 in Figure 24, as given by MAXMAGN, after having clicked on the column headed with "systematic absences".

To understand the listing of systematic absences obtained (see Figure 25) one has to take into account that the used (h,k,l) indices correspond to the parent-like basis (a, b, 2c). Firstly, the absences for any reflection (h,k,l) are given. On one hand, the centering translation {1| 1/3 2/3 1/3 } yields the extinction for h+2k+l different from a multiple of 3. Secondly, the antitranslation {1'|0,0,1/2} forces the absence of **magnetic** diffraction for *l* even.

If one transforms the (h,k,l) indexation into a description in terms of the propagation vector k=3/2**c***, the meaning of these absences becomes rather simple:

$$H = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m\vec{k} = h\vec{a}^* + k\vec{b}^* + \left(2l_0 + 3m\right)\left(\frac{\vec{c}^*}{2}\right)$$

The *l* index is therefore $2l_0+3m$, with l_0 being the index of a neighboring reflection associated with non-magnetic diffraction index in the parent basis. Therefore, the systematic absence for *l* even just means that second order magnetic reflections with m=2 are forbidden, and therefore magnetic and non-magnetic diffraction reflections do not overlap. This is a general property of all magnetic space groups of type IV, i.e. those that have antitranslations. The other systematic absence is a signature of the *R* centering.

On the other hand, the specific absence of all magnetic reflections of type (0,0,*l*) is much more specific. It is related with the existence of the three-fold symmetry in the magnetic group. The breaking of this extinction would imply that the symmetry of the ordering is necessarily lower, having broken the three-fold rotation symmetry.

c) Come back to the main list of k-maximal groups (Figure 24) and using the button in the last column for the group R_I-3m (#166.102) obtain a magnetic structure complying with this symmetry. The listing obtained (see Figure 26) shows that the moment of the representative Fe site in the asymmetric unit is forced to lie along the (1,0,0) direction. Note that the parent-like setting used is (a,b,2c;0,0,0), and if it were fitted to a diffraction pattern, the diffraction data should indexed consistently with this magnetic unit cell.

Figure 26: Atomic positions and magnetic moments (partial, only Fe site shown) of the asymmetric unit of $KFe_3(OH)_6(SO_4)_2$ for the subgroup of type R_I-3m (#166.102), listed N. 4 in Figure 24, as obtained when clicking in the column "Magnetic structure". The table indicates the Wyckoff orbit of 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). 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 moment components of the representative magnetic atom, while the last column on the right allows to introduce specific values for its symmetry-free moment components.

d) Assign an arbitrary initial value to the component Mx of Fe, and save the resulting mCIF file. This file could be introduced for a refinement of the model in the refinement programs JANA2006 or FULLPROF, if diffraction data were available, of it could be subject to an irrep mode analysis with ISODISTORT. We only use it here for the visualization of the model with VESTA or Jmol (see Figure 27).
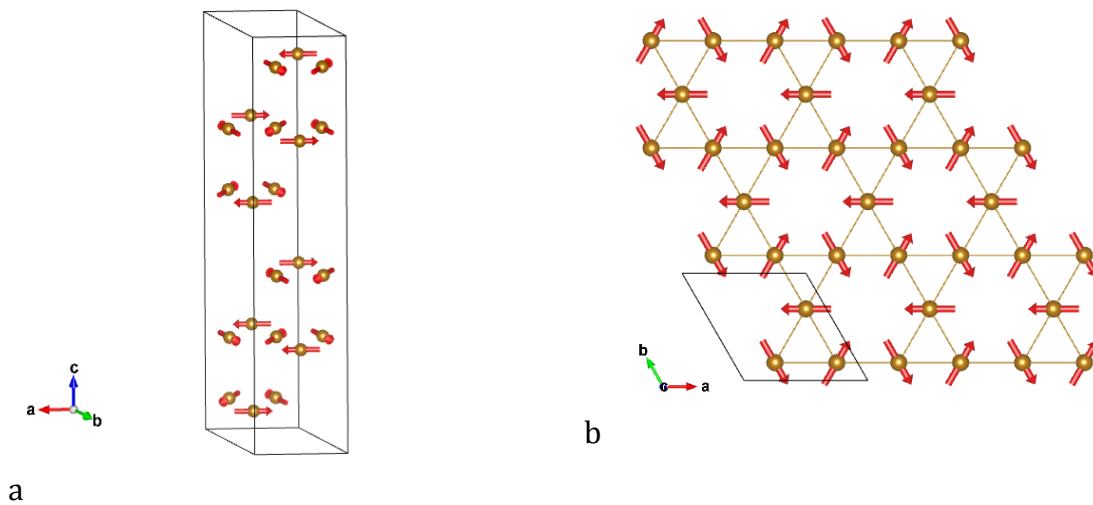
a

b

Figure 27: Possible magnetic ordering with k-maximal symmetry for $KFe_3(OH)_6(SO_4)_2$ according to the magnetic space group R_I-3m (#166.102) using the parent-like setting (a,b,2c;0,0,0). The Fe magnetic moment is only scale free. (a) Arrangement of Fe spins within a unit cell. (b) view of one of the layers on the xy plane showing the Kagome lattice of Fe atoms.

e) Come back to the main list of k-maximal groups and using the button in the last column for the group R_I-3c (#167.108) obtain a magnetic structure complying with this symmetry. The listing obtained (see Figure 28) shows that the moment of the representative Fe site in the asymmetric unit is forced to have its component on the plane xy along the (1,2,0) direction, but a component along the z axis is allowed.

Magnetic Structure

Selected magnetic space group: 2- R_I-3c (#167.108)

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

Lattice parameters: a=7.30400, b=7.30400, c=34.53600, alpha=90.00, beta=90.00, gamma=120.00

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

(Export data to MCIF file) (Go to a subgroup)

Atomic positions, Wyckoff positions and Magnetic Moments

| 3 | Fe1 Fe 0.50000 0.00000 0.25000 | (1/2,0,1/4 \| $m_x,2m_x,m_z$) (0,1/2,1/4 \| $-2m_x,-m_x,m_z$) (1/2,1/2,1/4 \| $m_x,-m_x,m_z$) (1/6,1/3,5/12 \| $-m_x,-2m_x,-m_z$) (2/3,5/6,5/12 \| $2m_x,m_x,-m_z$) (1/6,5/6,5/12 \| $-m_x,m_x,-m_z$) (5/6,2/3,1/12 \| $-m_x,-2m_x,-m_z$) (1/3,1/6,1/12 \| $2m_x,m_x,-m_z$) (5/6,1/6,1/12 \| $-m_x,m_x,-m_z$) (1/2,0,3/4 \| $-m_x,-2m_x,-m_z$) (0,1/2,3/4 \| $2m_x,m_x,-m_z$) (1/2,1/2,3/4 \| $-m_x,m_x,-m_z$) (1/6,1/3,11/12 \| $m_x,2m_x,m_z$) (2/3,5/6,11/12 \| $-2m_x,-m_x,m_z$) (1/6,5/6,11/12 \| $m_x,-m_x,m_z$) (5/6,2/3,7/12 \| $m_x,2m_x,m_z$) (1/3,1/6,7/12 \| $-2m_x,-m_x,m_z$) (5/6,1/6,7/12 \| $m_x,-m_x,m_z$) | 18 | $(M_x,2M_x,M_z)$ | M_x = 0.00000 M_z = 0.00000 |

Figure 28: Atomic positions and magnetic moments (partial, only Fe site shown) of the asymmetric unit of $KFe_3(OH)_6(SO_4)_2$ for the subgroup of type R_I-3c (#167.108), listed N. 2 in Figure 24, as obtained when

clicking in the column "Magnetic structure". The table indicates the Wyckoff orbit of 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). 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 moment components of the representative magnetic atom, while the last column on the right allows to introduce specific values for its symmetry-free moment components.

f) Assuming that the plane xy is the easy plane for the magnetic ordering, assign an arbitrary initial value to the Mx of Fe, keeping zero the Mz component, and save the resulting mCIF file. This mCIF file could then be introduced for a refinement of the model in the programs JANA2006 or FULLPROF, if diffraction data were available, or it could subject to an irrep mode analysis with ISODISTORT. We only use it here for the visualization of the model with VESTA or Jmol (see Figure 29). This is in fact the model proposed by Inami, T. et al., *J. of Magn. and Magn. Mat.* (1998) 177, 752 (see MAGNDATA #1.25) after checking 24 different configurations.
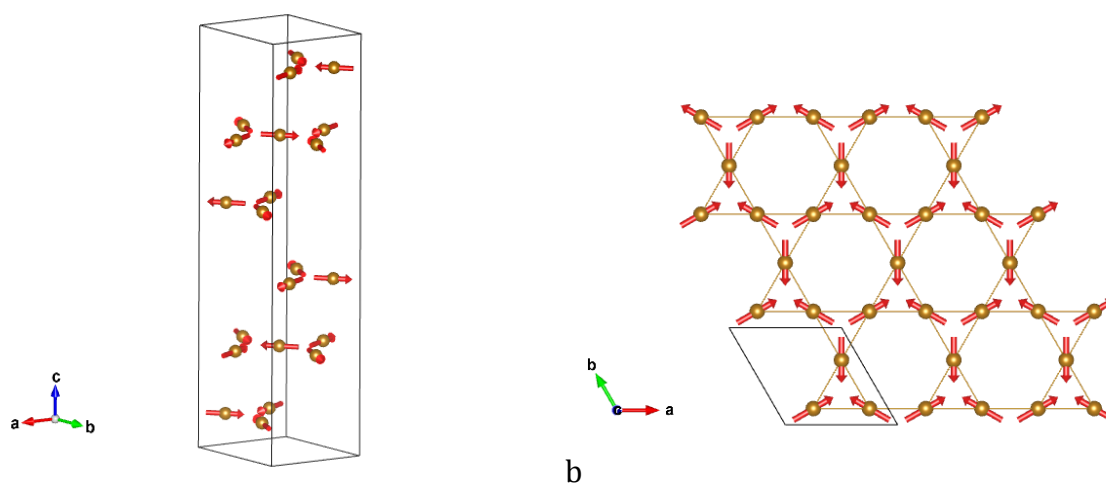

a

b

Figure 29: Possible magnetic ordering with k-maximal magnetic symmetry for $KFe_3(OH)_6(SO_4)_2$ according to the magnetic space group R_I-3c (#167.108), described in the parent-like setting (a,b,2c;0,0,0). A symmetry allowed z-component of the spins is not included. (a) Arrangement of Fe spins within a magnetic unit cell. (b) view of one of the layers on the xy plane showing the Kagome lattice of Fe atoms.

Comparison with the representation method:
The little group of the propagation vector (0, 0, 3/2) is the full group R-3m. As can be seen using REPRES (in the Bilbao crystallographic server) there are six irreps of R-3m for this wave vector. Therefore, for the grey group R-3m1' there are six analogous irreps which can be relevant for a magnetic ordering, i.e. which are odd for time reversal, namely the 1-dim irreps mT1+, mT2+, mT1-,mT2- and the 2-dim irreps mT3+ and mT3- (the symbol m is used to indicate that they are odd for time reversal). The so-called magnetic representation for this wave vector and limited to the spins of the Fe atoms decomposes into irreps in the following form (see for instance the results using Basireps of the FullProf suite [2]):

$$M_{repr} = 2\ mT1\text{-} + mT2\text{-} + 3\ mT3\text{-}$$

In contrast with the multidimensional irreps, which were relevant in the previous examples, for a 1-dim irrep there is a one to one correspondence between the irrep and a magnetic space group. Thus, in this example the assumption of a magnetic ordering complying with one of the two 1-dim irreps is equivalent to the assigning of a specific magnetic space group. The magnetic symmetry associated with a magnetic distortion according to either mT1- or mT2- is in fact given by the group R_I-3c (#167.108) or R_I-3m (#166.102), respectively, which are the k-maximal magnetic space groups

discussed above. This is a general property: magnetic space groups associated with magnetic orderings complying with a single 1-dim irrep are k-maximal in the sense used here. In the present case the magnetic ordering corresponds to the 1-dim irrep mT1-.

Summarizing, in contrast to the previous examples, to say that the magnetic phase of $KFe_3(OH)_6(SO_4)_2$ has symmetry R_I-3c (#167.108) or that it complies with the irrep mT1- of R-3m are equivalent statements in what concerns the resulting constraints for the atomic magnetic moments. One should however consider that the magnetic symmetry assignment includes additional information, as it also comprehends the constraints on all degrees of freedom of the material, including non-magnetic ones, macroscopic properties (subject to the associated point group symmetry -3m1') and the knowledge of symmetry-related systematic absence rules in unpolarized neutron magnetic diffraction patterns (see program MAGNEXT in the Bilbao Crystallographic Server).

Example 4: Na_2MnF_5 (MAGNDATA #1.55) (Nuñez, P. et al., *Solid State Commun.* (1994) **92** , 601)

Paramagnetic structure

Space Group: $P2_1/c$ (#14)

unit cell parameter:
7.7197 5.2402 10.8706 90.000 108.991 90.000

F1 - 0.04480 0.15100 0.16290
F2 - -0.10830 0.29780 -0.07580
F3 - 0.25140 0.16200 0.00310
F4 - 0.61790 0.21920 0.13470
F5 - 0.49180 0.24420 -0.12280
Mn1 - 0.00000 0.00000 0.00000
Mn2 - 0.50000 0.00000 0.00000
Na1 - 0.15350 -0.01070 0.36470
Na2 - 0.34410 0.44390 0.17996

(or a similar model from ICSD #61206)

Magnetic atoms: Mn1, Mn2

Propagation vector (0, 1/2, 0)

Following a similar procedure as in previous examples, and assuming that the moments are oriented along the x direction obtain the two possible magnetic structural models of k-maximal symmetry represented in its two twinned forms in Figure 30. The magnetic ordering reported by Nuñez et al. is in fact the one having the monoclinic symmetry P_bc, with the additional restriction of making equal the moment moduli of the two independent Mn sites, and the moments restricted along the x axis. This magnetic ordering breaks the centrosymmetry of the paramagnetic phase, the symmetry being polar.

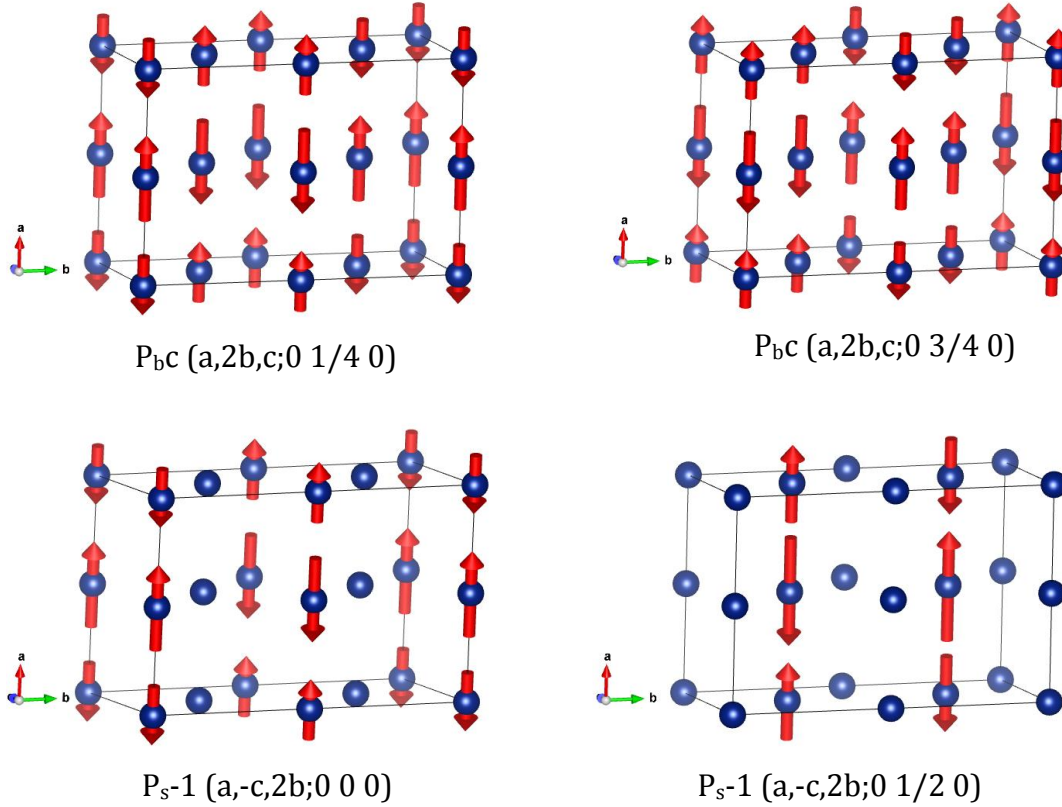Derive from the output of MAXMAGN that non-collinear AFM cantings along y and z are allowed in this phase.

P$_b$c (a,2b,c;0 1/4 0)

P$_b$c (a,2b,c;0 3/4 0)

P$_s$-1 (a,-c,2b;0 0 0)

P$_s$-1 (a,-c,2b;0 1/2 0)

Figure 30: Magnetic moment arrangements assumed along x for the Mn atoms of Na$_2$MnF$_5$ subject to each of the possible magnetic space groups of maximal symmetry. Symmetry independent Mn atoms are distinguished by arbitrary different moment values. Half of the Mn moments must remain disordered in the centrosymmetric arrangements. The two twin-related configurations for each group type are related by the lost binary rotation. Additional trivial twinned configurations are obtained by switching all magnetic moments (time reversal operation).

Comparison with the representation method:
This is a similar case to that of example 1. The assumption of a single irrep active does not constraint the spin configuration as the magnetic representation of the two Mn atoms only includes a single irrep. The little group of the propagation vector (0, 1/2, 0) is the full group P2$_1$/c. As can be seen using REPRES (in the Bilbao crystallographic server) there is only one 2-dim irrep of P2$_1$/c for this wave vector: Z1 (Z is the standard label for the vector (0, 1/2, 0) in the Brillouin one). Therefore, for the grey group P2$_1$/c1' there is one analogous irrep: mZ1, which can be relevant for a magnetic ordering (the symbol m is used to distinguish irreps that are odd for time reversal from even ones). The magnetic representation for this wave vector and the magnetic moments of the two independent Mn atoms can only contain this irrep (see for instance the results using Basireps of the FullProf suite [2]):

$$M_{repr} = 6 \ mZ1$$

This means that any arbitrary spin configuration with a propagation vector (0, 1/2, 0) transforms according to the irrep mZ1, and can be described in terms of 12 basis functions associated with this irrep. In other words, the assumption of the magnetic ordering complying with a single irrep does

not introduce any constraint, and the representation method is of no use for this case. This should be compared with the constraints introduced by the assumption of one of the two possible k-maximal magnetic groups discussed above, where the number of free parameters describing the spin configuration is limited to six in both cases.

Summarizing, any arbitrary spin configuration in Na_2MnF_5 with the observed propagation vector can be associated with the irrep mZ1, and therefore in this case the representation method in its traditional form is of no use. A spin ordering restricted to have one of the k-maximal magnetic symmetries shown above corresponds (see example 1) to the choice of a special direction of higher symmetry within the mZ1 representation (i.e. a specific linear combination of the six pairs of mZ1 basis functions), so that the number of free parameters in the possible combination of basis modes is restricted from 12 to 6. Hence, to assign a k-maximal magnetic group is NOT equivalent to the assignment of an irrep, and introduces additional constraints.

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