Abbreviated tutorial exercises on the use of MAXMAGN to determine possible refinable models for a magnetic structure with known propagation vector.

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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, being in most cases 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 exercises we shall focus on the use of MAXMAGN to derive possible spin configurations to be considered as possible models for a magnetic structure of known propagation vector.

Example 1. $CrCl_2$

The structure of $CrCl_2$ in its paramagnetic phase 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, click on the option "structure

data of the paramagnetic phase will be included, 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 first output page lists now four k-maximal subgroups, but two of them are highlighted with a darker background (see Figure 1). They are those that allow a non-zero magnetic moment for at least some of the atoms at the Cr site. The Table includes several columns with information about the subgroups. The last column on the right under the heading "Magnetic structure" is the one to be used to obtain a magnetic structure complying with the listed subgroup.

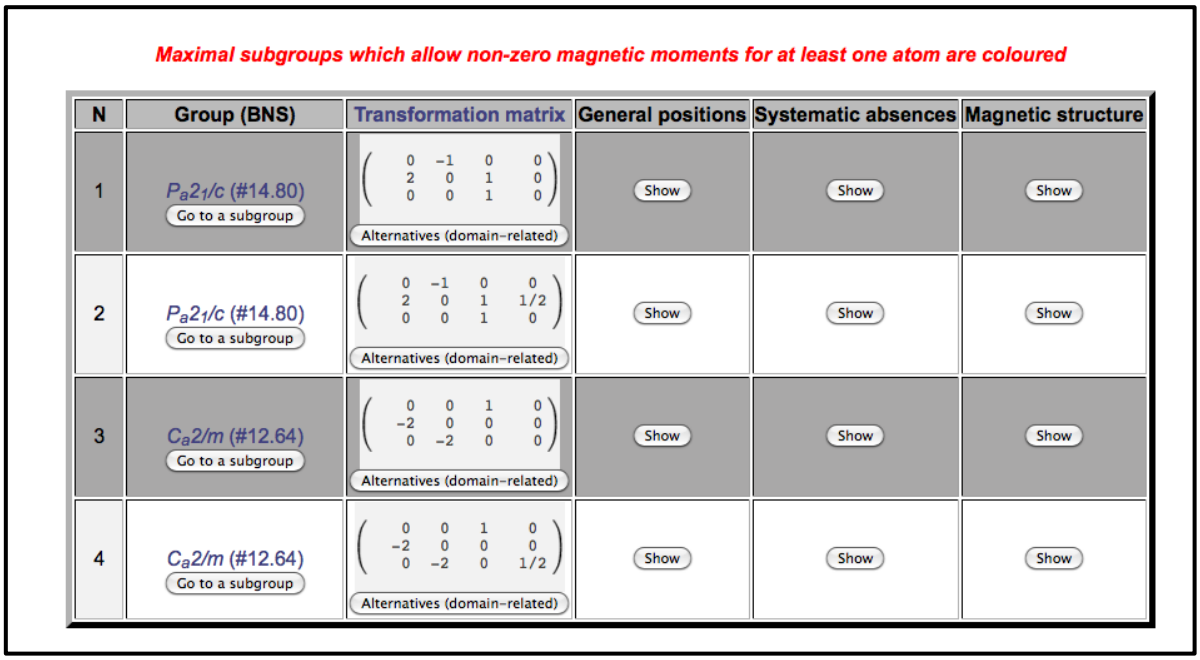


Figure 1: List of distinct k-maximal magnetic space groups for a parent space group Pnnm and a propagation vector (0, 1/2, 1/2), as given by MAXMAGN, after having introduced the paramagnetic structure of $CrCl_2$ in the first input steps. The groups with darker background are the only ones allowing a non-zero average magnetic moment for at least some of the Cr atoms.

b) Click in the "Magnetic structure" column for the second possible group with label C_a2/m (#12.64). The program lists the asymmetric unit of a magnetic structure satisfying this symmetry (see Figure 2). The first column tabulates the atomic positions, where one can see that both Cr and Cl split into two symmetry-independent sites. The magnetic structure is described in a setting that we call "parent-like": (a,2b,2c;0,0,0). 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. 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.

Selected magnetic space group: 3- C_a2/m (#12.64)

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, -2c, a** ; 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_1 Cr 0.00000 0.00000 0.00000	(0,0,0 | 0,0,m_z) (0,0,1/2 | 0,0,-m_z) (0,1/2,0 | 0,0,-m_z) (0,1/2,1/2 | 0,0,m_z)	4	(0,0,M_z)	M_z = 0.0000
	Cr1_2 Cr 0.50000 0.25000 0.25000	(1/2,1/4,1/4 | m_x,m_y,0) (1/2,1/4,3/4 | -m_x,-m_y,0) (1/2,3/4,1/4 | -m_x,-m_y,0) (1/2,3/4,3/4 | m_x,m_y,0)	4	(M_x,M_y,0)	M_x = 0.0000 M_y = 0.0000
2	Cl1_1 Cl 0.35860 0.14465 0.00000	(x,y,0 | 0,0,m_z) (-x,-y,0 | 0,0,m_z) (x,y,1/2 | 0,0,-m_z) (-x,-y,1/2 | 0,0,-m_z) (x,y+1/2,0 | 0,0,-m_z) (-x,-y+1/2,0 | 0,0,-m_z) (x,y+1/2,1/2 | 0,0,m_z) (-x,-y+1/2,1/2 | 0,0,m_z)	8	-	-
	Cl1_2 Cl 0.14140 0.39465 0.25000	(-x+1/2,y+1/4,1/4 | m_x,m_y,0) (x+1/2,-y+1/4,1/4 | m_x,m_y,0) (-x+1/2,y+1/4,3/4 | -m_x,-m_y,0) (x+1/2,-y+1/4,3/4 | -m_x,-m_y,0) (-x+1/2,y+3/4,1/4 | -m_x,-m_y,0) (x+1/2,-y+3/4,1/4 | -m_x,-m_y,0) (-x+1/2,y+3/4,3/4 | m_x,m_y,0) (x+1/2,-y+3/4,3/4 |	8	-	-

Figure 2: Atomic positions and magnetic moments of the asymmetric unit for the subgroup of type C_a2/m (#12.64) listed N. 3 in Figure 1, 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.

c) 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 sites do not split (see Figure 3). 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 equally from one position to another). 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 3, 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 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 | m_x,m_y,m_z) (1/2,1/4,1/4 | m_x,-m_y,-m_z) (0,0,1/2 | -m_x,-m_y,-m_z) (1/2,1/4,3/4 | -m_x,m_y,m_z) (0,1/2,0 | -m_x,-m_y,-m_z) (1/2,3/4,1/4 | -m_x,m_y,m_z) (0,1/2,1/2 | m_x,m_y,m_z) (1/2,3/4,3/4 | m_x,-m_y,-m_z)	8	(M_x,M_y,M_z)	M_x = 0.0000 M_y = 0.0000 M_z = 0.0000
2	Cl1 Cl 0.35860 0.14465 0.00000	(x,y,0 | m_x,m_y,m_z) (-x,-y,0 | m_x,m_y,m_z) (-x+1/2,y+1/4,1/4 | m_x,-m_y,-m_z) (x+1/2,-y+1/4,1/4 | m_x,-m_y,-m_z) (x,y,1/2 | -m_x,-m_y,-m_z) (-x,-y,1/2 | -m_x,-m_y,-m_z) (-x+1/2,y+1/4,3/4 | -m_x,m_y,m_z) (x+1/2,-y+1/4,3/4 | -m_x,m_y,m_z) (x,y+1/2,0 | -m_x,-m_y,-m_z) (-x,-y+1/2,0 | -m_x,-m_y,-m_z) (-x+1/2,y+3/4,1/4 | -m_x,m_y,m_z) (x+1/2,-y+3/4,1/4 | -m_x,m_y,m_z) (x,y+1/2,1/2 | m_x,m_y,m_z) (-x,-y+1/2,1/2 | m_x,m_y,m_z) (-x+1/2,y+3/4,3/4 | m_x,-m_y,-m_z) (x+1/2,-y+3/4,3/4 | m_x,-m_y,-m_z)	16	-	-

Figure 3: 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 1, 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.

d) 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 4). There are four centering translations and antitranslations including the identity, plus four rotational or roto-inversion operations. These operations fully define the position and magnetic moment relations of all atoms within the defined unit cell (a,2b,2c) with those listed in the mCIF as independent asymmetric unit.

```
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 4: 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).

e) 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 5). 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 4). 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 5: 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.

f) Load the mCIF file in the VESTA program to visualize the model. Something similar to the representation shown in Figure 6 can be obtained.

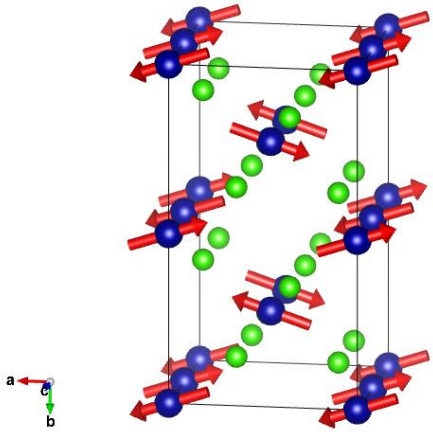


Figure 6: Magnetic ordering in $CrCl_2$ according to the magnetic space group P_a2_1/c (#14.80) listed in Figure 1, and using the parent-like setting (a,2b,2c;0,0,0), having arbitrarily restricted the spins to the plane xy. The figure has been obtained following the steps indicated above. A twin-related equivalent configuration can be obtained following the same procedure but choosing a conjugate subgroup through the option "alternative (domain-related)" on the screen shown in Figure 1. (see the more extended tutorial for details).

Comparison with the representation method:
Any arbitrary spin configuration in $CrCl_2$ can be associated with a single irrep, and therefore in this case the traditional representation method 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 only possible irrep (i.e. a specific linear combination of the irrep 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. (see extended tutorial for more details).

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, 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.

Example 2. Orthorhombic $HoMnO_3$ (see MAGNDATA #1.20)

The structure of the paramagnetic phase of $HoMnO_3$ can be summarized as follows (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 7).

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

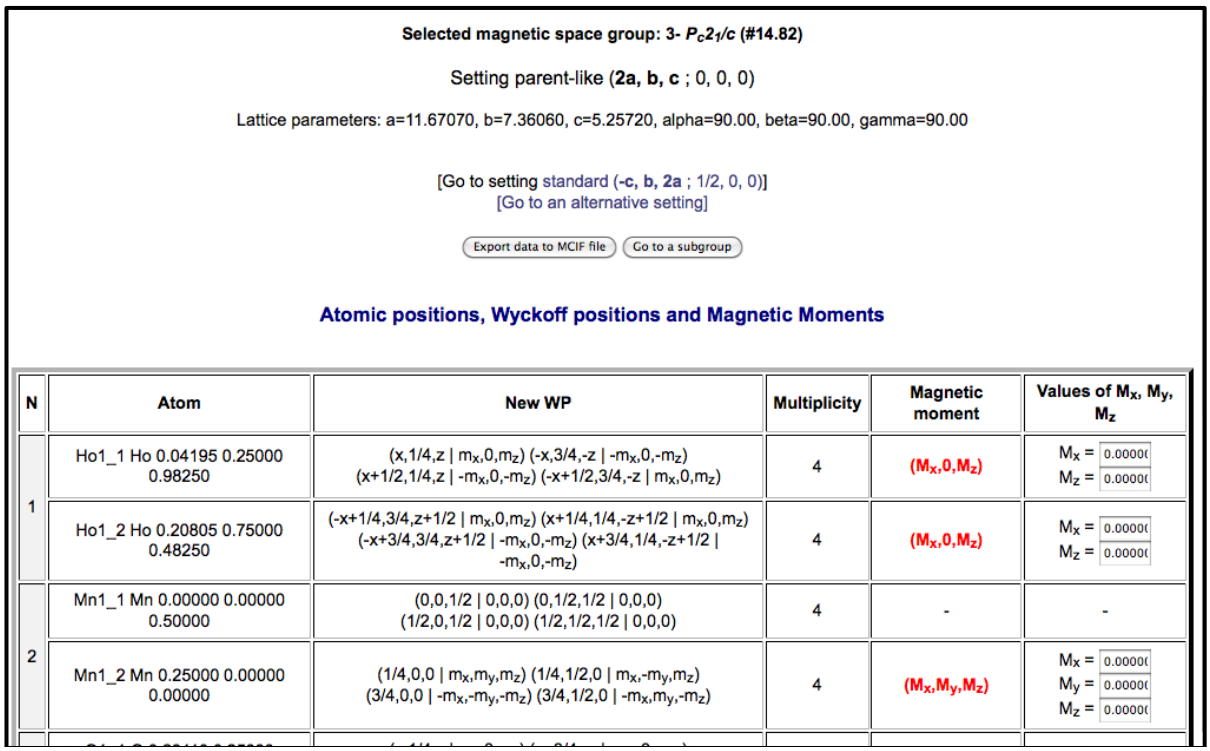
N	Group (BNS)	Transformation matrix	General positions	Systematic absences	Magnetic structure
1	$P_a na2_1$ (#33.149) Go to a subgroup	$\begin{pmatrix} 2 & 0 & 0 & 3/4 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
2	$P_b mn2_1$ (#31.129) Go to a subgroup	$\begin{pmatrix} 0 & 2 & 0 & 3/4 \\ -1 & 0 & 0 & 1/4 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	Show	Show	Show
3	P_c2_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_a2_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 7: 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 $\exp(i2\pi\mathbf{k}.\mathbf{L})= 1$, but having also as "antitranslations" (i.e. translations combined with time reversal) parent lattice translations satisfying $\exp(i2\pi\mathbf{k}.\mathbf{L})= -1$. 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_c2_1/c(#14.82) and P_a2_1/m(#11.55) require that a half of the Mn atoms remain disordered with null magnetic moment (see Figure 8). 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.



Selected magnetic space group: 3- P_c2_1/c (#14.82)

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

Lattice parameters: a=11.67070, b=7.36060, c=5.25720, alpha=90.00, beta=90.00, gamma=90.00

[Go to setting standard (**-c, b, 2a** ; 1/2, 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	Ho1_1 Ho 0.04195 0.25000 0.98250	(x,1/4,z | m_x,0,m_z) (-x,3/4,-z | -m_x,0,-m_z) (x+1/2,1/4,z | -m_x,0,-m_z) (-x+1/2,3/4,-z | m_x,0,m_z)	4	(M_x,0,M_z)	M_x = 0.0000 M_z = 0.0000
	Ho1_2 Ho 0.20805 0.75000 0.48250	(-x+1/4,3/4,z+1/2 | m_x,0,m_z) (x+1/4,1/4,-z+1/2 | m_x,0,m_z) (-x+3/4,3/4,z+1/2 | -m_x,0,-m_z) (x+3/4,1/4,-z+1/2 | -m_x,0,-m_z)	4	(M_x,0,M_z)	M_x = 0.0000 M_z = 0.0000
2	Mn1_1 Mn 0.00000 0.00000 0.50000	(0,0,1/2 | 0,0,0) (0,1/2,1/2 | 0,0,0) (1/2,0,1/2 | 0,0,0) (1/2,1/2,1/2 | 0,0,0)	4	-	-
	Mn1_2 Mn 0.25000 0.00000 0.00000	(1/4,0,0 | m_x,m_y,m_z) (1/4,1/2,0 | m_x,-m_y,m_z) (3/4,0,0 | -m_x,-m_y,-m_z) (3/4,1/2,0 | -m_x,m_y,-m_z)	4	(M_x,M_y,M_z)	M_x = 0.0000 M_y = 0.0000 M_z = 0.0000

Figure 8: 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 7, 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) 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 (see Figure 9). The experimental diffraction data indicates that the Mn spins are essentially collinear along the x direction. Therefore introduce only 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.

Selected magnetic space group: 1- $P_a na2_1$ (#33.149)

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

Lattice parameters: a=11.67070, b=7.36060, c=5.25720, alpha=90.00, beta=90.00, gamma=90.00

[Go to setting standard (**2a, b, c** ; 3/4, 1/2, 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	Ho1_1 Ho 0.04195 0.25000 0.98250	(x,1/4,z | m_x,0,m_z) (-x+1/4,3/4,z+1/2 | m_x,0,-m_z) (x+1/2,1/4,z | -m_x,0,-m_z) (-x+3/4,3/4,z+1/2 | -m_x,0,m_z)	4	(M_x,0,M_z)	M_x = 0.0000 M_z = 0.0000
	Ho1_2 Ho 0.95805 0.75000 0.01750	(-x,3/4,-z | m_x,0,m_z) (x+1/4,1/4,-z+1/2 | m_x,0,-m_z) (-x+1/2,3/4,-z | -m_x,0,-m_z) (x+3/4,1/4,-z+1/2 | -m_x,0,m_z)	4	(M_x,0,M_z)	M_x = 0.0000 M_z = 0.0000
2	Mn1 Mn 0.00000 0.00000 0.50000	(0,0,1/2 | m_x,m_y,m_z) (1/4,0,0 | m_x,m_y,-m_z) (0,1/2,1/2 | m_x,-m_y,m_z) (1/4,1/2,0 | m_x,-m_y,-m_z) (1/2,0,1/2 | -m_x,m_y,-m_z) (3/4,0,0 | -m_x,-m_y,m_z) (1/2,1/2,1/2 | -m_x,m_y,-m_z) (3/4,1/2,0 | -m_x,m_y,m_z)	8	(M_x,M_y,M_z)	M_x = 0.0000 M_y = 0.0000 M_z = 0.0000
3	O1_1 O 0.23110 0.25000 0.11130	(x,1/4,z | m_x,0,m_z) (-x+1/4,3/4,z+1/2 | m_x,0,-m_z) (x+1/2,1/4,z | -m_x,0,-m_z) (-x+3/4,3/4,z+1/2 | -m_x,0,m_z)	4	-	-
	O1_2 O 0.76890 0.75000 0.88870	(-x,3/4,-z | m_x,0,m_z) (x+1/4,1/4,-z+1/2 | m_x,0,-m_z) (-x+1/2,3/4,-z | -m_x,0,-m_z) (x+3/4,1/4,-z+1/2 | -m_x,0,m_z)	4	-	-

Figure 9: 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 7, 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 magnetic sites indicates that the magnetic moment at this site is symmetry-forced to be zero.

d) Obtain and save 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 9.

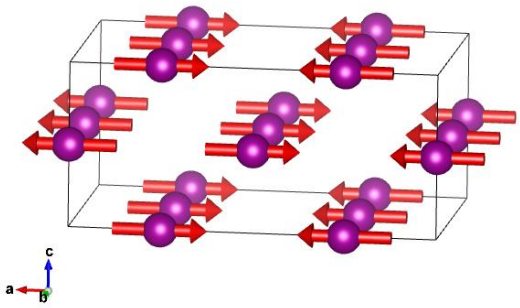


Figure 10: Possible k-maximal magnetic ordering for $HoMnO_3$ according to the magnetic space group P_ana2_1(#33.149) using the parent-like setting (2a,b,c;0,0,0), and having restricted the spins along x. An equivalent magnetic ordering twin-related by the lost inversion operation and with opposite polarity can be obtained by choosing the conjugate subgroup with the option "Alternative (domain-related)" on the screen shown in Figure 7.

e) Come back to the main output list of k-maximal magnetic groups (Figure 7) and follow the same procedure for the second possible polar group P_bmn2_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.

Selected magnetic space group: 2- *P_bmn2_1* (#31.129)

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

Lattice parameters: a=11.67070, b=7.36060, c=5.25720, alpha=90.00, beta=90.00, gamma=90.00

[Go to setting standard (**-b, 2a, c** ; 3/4, 1/4, 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	Ho1_1 Ho 0.04195 0.25000 0.98250	(x,1/4,z | 0,m_y,0) (-x+1/4,3/4,z+1/2 | 0,m_y,0) (x+1/2,1/4,z | 0,-m_y,0) (-x+3/4,3/4,z+1/2 | 0,-m_y,0)	4	(0,M_y,0)	M_y = 0.0000
	Ho1_2 Ho 0.95805 0.75000 0.01750	(-x,3/4,-z | 0,m_y,0) (x+1/4,1/4,-z+1/2 | 0,m_y,0) (-x+1/2,3/4,-z | 0,-m_y,0) (x+3/4,1/4,-z+1/2 | 0,-m_y,0)	4	(0,M_y,0)	M_y = 0.0000
2	Mn1 Mn 0.00000 0.00000 0.50000	(0,0,1/2 | m_x,m_y,m_z) (1/4,0,0 | m_x,m_y,-m_z) (0,1/2,1/2 | -m_x,m_y,-m_z) (1/4,1/2,0 | -m_x,m_y,m_z) (1/2,0,1/2 | -m_x,-m_y,-m_z) (3/4,0,0 | -m_x,-m_y,m_z) (1/2,1/2,1/2 | m_x,-m_y,m_z) (3/4,1/2,0 | m_x,-m_y,-m_z)	8	(M_x,M_y,M_z)	M_x = 0.0000 M_y = 0.0000 M_z = 0.0000
3	O1_1 O 0.23110 0.25000 0.11130	(x,1/4,z | 0,m_y,0) (-x+1/4,3/4,z+1/2 | 0,m_y,0) (x+1/2,1/4,z | 0,-m_y,0) (-x+3/4,3/4,z+1/2 | 0,-m_y,0)	4	-	-
	O1_2 O 0.76890 0.75000 0.88870	(-x,3/4,-z | 0,m_y,0) (x+1/4,1/4,-z+1/2 | 0,m_y,0) (-x+1/2,3/4,-z | 0,-m_y,0) (x+3/4,1/4,-z+1/2 | 0,-m_y,0)	4	-	-
4	O2_1 O 0.16405 0.05340 0.70130	(x,y,z | m_x,m_y,m_z) (-x+1/4,-y,z+1/2 | m_x,m_y,-m_z) (x,-y+1/2,z | -m_x,m_y,-m_z) (-x+1/4,y+1/2,z+1/2 | -m_x,m_y,m_z) (x+1/2,y,z | -m_x,-m_y,-m_z) (-x+3/4,-y,z+1/2 | -m_x,-m_y,m_z) (x+1/2,-y+1/2,z | m_x,-m_y,m_z) (-x+3/4,y+1/2,z+1/2 | m_x,-m_y,-m_z)	8	-	-
	O2_2 O 0.83595 0.55340 0.29870	(-x,y+1/2,-z | m_x,m_y,m_z) (x+1/4,-y+1/2,-z+1/2 | m_x,m_y,-m_z) (-x,-y,-z | -m_x,m_y,-m_z) (x+1/4,y,-z+1/2 | -m_x,m_y,m_z) (-x+1/2,y+1/2,-z | -m_x,-m_y,-m_z) (x+3/4,-y+1/2,-z+1/2 | -m_x,-m_y,m_z) (-x+1/2,-y,-z | m_x,-m_y,m_z) (x+3/4,y,-z+1/2 | m_x,-m_y,-m_z)	8	-	-

Figure 11: Atomic positions and magnetic moments (partial) of the asymmetric unit of $HoMnO_3$ for the subgroup of Pnma1' of type P_bmn2_1 (#31.129), listed N. 2 in Figure 7, 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.

f) Restrict again the model to have the moments along the x axis and obtain the corresponding mCIF file. It is depicted in Figure 12. 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.

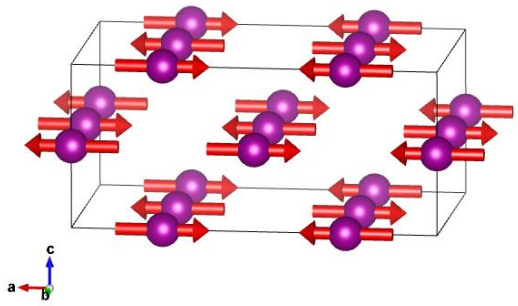


Figure 12: Possible k-maximal magnetic ordering for $HoMnO_3$ according to the magnetic space group P_bmn2_1 (#31.129), using the parent-like setting (2a,b,c;0,0,0), and having restricted the spins along x. This is the magnetic arrangement that has been reported for this compound (Muñoz, A. et al., *Inorg. Chem.* (2001) **40** 1020 - 1028. See entry 1.20 of MAGNDATA). An equivalent magnetic ordering twin-related by the lost inversion operation and with opposite polarity can be obtained by choosing the conjugate subgroup with the option "Alternative (domain-related)" on the screen shown in Figure 7.

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).

Comparison with the representation method:
The spin ordering in $HoMnO_3$ complies with one of the k-maximal magnetic symmetries discussed above, namely P_bmn2_1 (#31.129), and it corresponds to the choice of a special direction of higher symmetry within the space of an irrep, so that the number of free symmetry-adapted basis modes is restricted from 6 to 3. To assign this k-maximal magnetic group is therefore NOT equivalent to the assignment of the irrep. It introduces additional constraints (see extended tutorial for more details).

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

The structure of the paramagnetic phase 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 the mentioned 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 13). 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*-3*m*) 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 13: 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) 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 14) 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.

Magnetic Structure

Selected magnetic space group: 4- *R_I-3m* (#166.102)

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

		(1/3,2/3,z+5/6 | 0,0,0) (1/3,2/3,-z+5/6 | 0,0,0)			
3	Fe1 Fe 0.50000 0.00000 0.25000	(1/2,0,1/4 | m_x,0,0) (0,1/2,1/4 | 0,m_x,0) (1/2,1/2,1/4 | -m_x,-m_x,0) (1/6,1/3,5/12 | -m_x,0,0) (2/3,5/6,5/12 | 0,-m_x,0) (1/6,5/6,5/12 | m_x,m_x,0) (5/6,2/3,1/12 | -m_x,0,0) (1/3,1/6,1/12 | 0,-m_x,0) (5/6,1/6,1/12 | m_x,m_x,0) (1/2,0,3/4 | -m_x,0,0) (0,1/2,3/4 | 0,-m_x,0) (1/2,1/2,3/4 | m_x,m_x,0) (1/6,1/3,11/12 | m_x,0,0) (2/3,5/6,11/12 | 0,m_x,0) (1/6,5/6,11/12 | -m_x,-m_x,0) (5/6,2/3,7/12 | m_x,0,0) (1/3,1/6,7/12 | 0,m_x,0) (5/6,1/6,7/12 | -m_x,-m_x,0)	18	(M_x,0,0)	M_x = 0.0000
		(0,0,z | 0,0,0) (0,0,-z | 0,0,0)			

Figure 14: 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 13, 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.

c) 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 15).

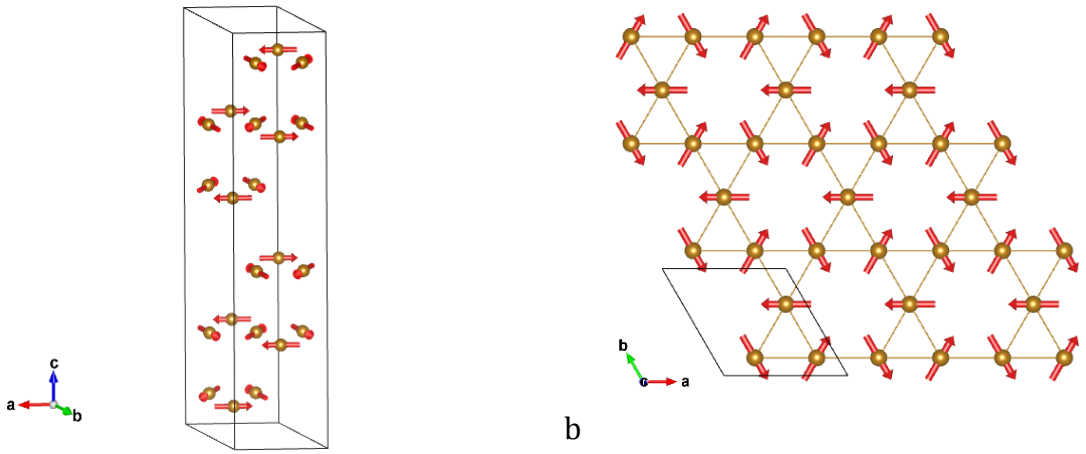
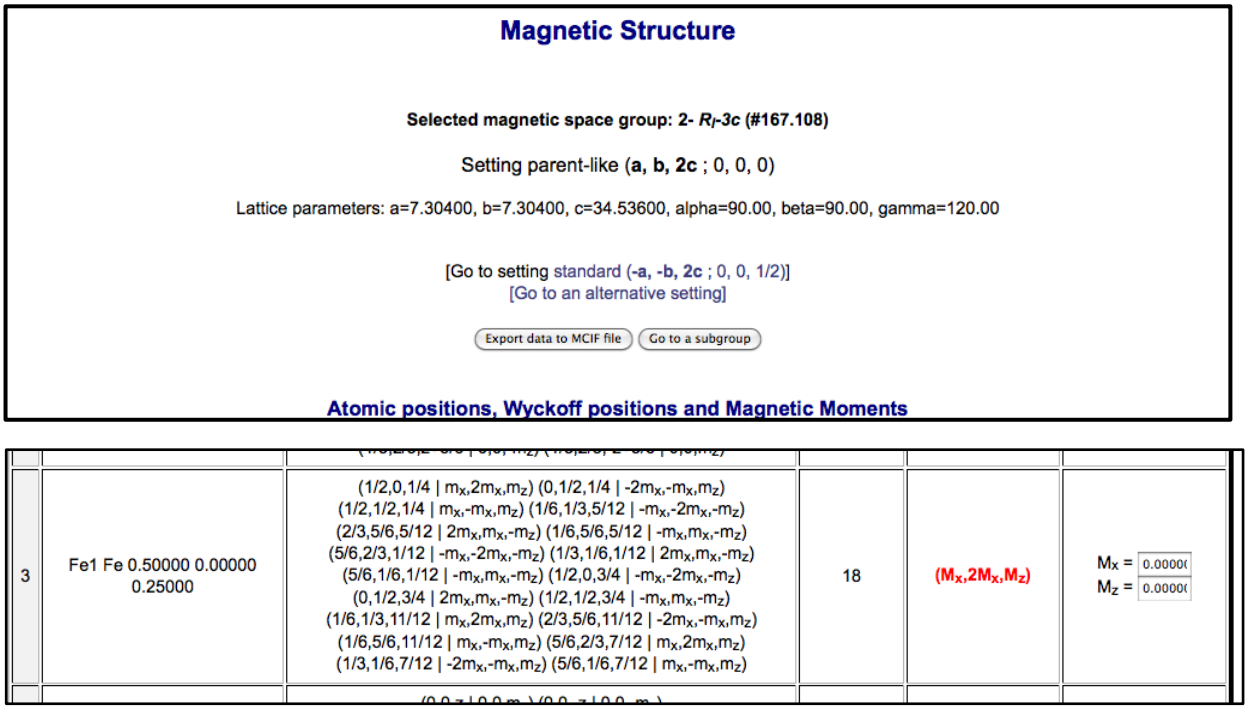


Figure 15: Possible magnetic ordering with k-maximal symmetry for $KFe_3(OH)_6(SO_4)_2$ according to the magnetic space group R_I-3m (#166.102) using the parent-like setting (a,b,2c;0,0,0). The Fe magnetic moment is only scale free. (a) Arrangement of Fe spins within a unit cell. (b) view of one of the layers on the xy plane showing the Kagome lattice of Fe atoms.

d) 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 16) 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 also a component along the z axis is allowed.



Magnetic Structure

Selected magnetic space group: 2- *R*$_I$-3*c* (#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]

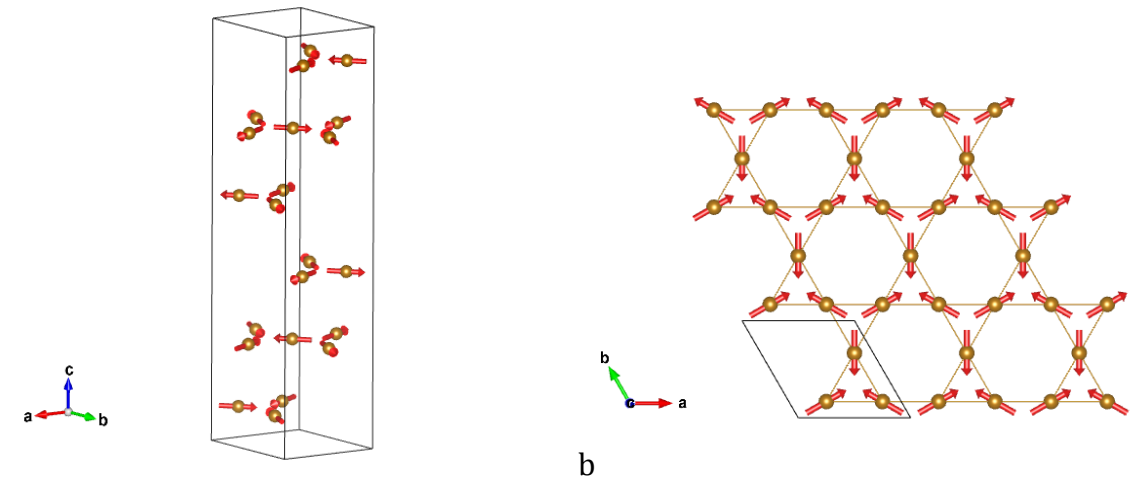
Export data to MCIF file | Go to a subgroup

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 = 0.0000 M_z = 0.0000

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 13, 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 16). 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 16: 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:
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, and macroscopic properties (subject to the associated point group symmetry -3m1'). See extended tutorial for more details.

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

The structure of the paramagnetic phase is given by

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

unit cell parameter:
7.7197 5.2402 10.8706 90.000 108.991 90.000

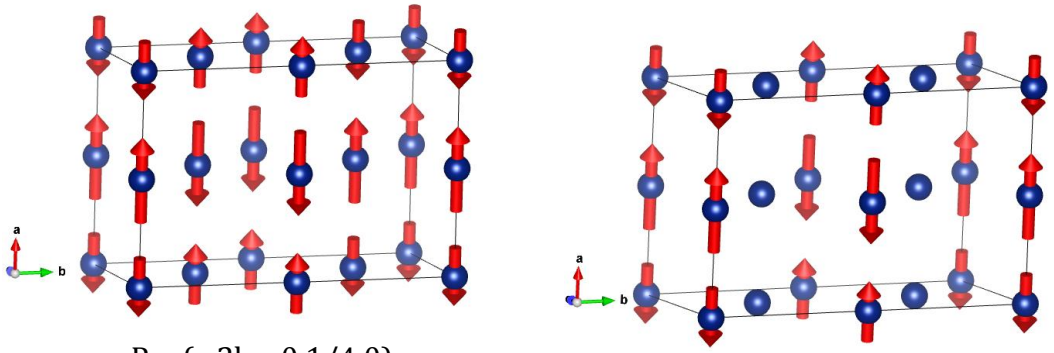
F1 - 0.04480 0.15100 0.16290
F2 - -0.10830 0.29780 -0.07580
F3 - 0.25140 0.16200 0.00310
F4 - 0.61790 0.21920 0.13470
F5 - 0.49180 0.24420 -0.12280
Mn1 - 0.00000 0.00000 0.00000
Mn2 - 0.50000 0.00000 0.00000
Na1 - 0.15350 -0.01070 0.36470
Na2 - 0.34410 0.44390 0.17996

(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 Figure 17. 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_bc (a,2b,c;0 1/4 0)

P_s-1 (a,-c,2b;0 0 0)

Figure 17: Magnetic moment arrangements assumed along x for the Mn atoms of Na_2MnF_5 subject to each of the two possible non-equivalent magnetic space groups of k-maximal symmetry. Symmetry independent Mn atoms are distinguished by arbitrary different moment values. Half of the Mn moments must remain disordered in the centrosymmetric arrangement. The two twin-related configurations for each group type related by the lost binary rotation can be obtained using the "Alternative (domain-related)" option.

Comparison with the representation method:

This is a similar case to that of example 1. Any arbitrary spin configuration in Na_2MnF_5 with the observed propagation vector can be associated with a single irrep, 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 only possible irrep (i.e. a specific linear combination of the six pairs of irrep 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. (see extended tutorial for more details).

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