

## The magnetic structure of $\text{HoMnO}_3$ . Tutorial example on the use of MAXMAGN and other tools of the Bilbao Crystallographic Server for the analysis of magnetic structures.

J.M. Perez-Mato<sup>1</sup>, S. V. Gallego<sup>1</sup>, L. Elcoro<sup>1</sup>, E. Tasci<sup>2</sup>, G. de la Flor<sup>1</sup> and M.I. Aroyo<sup>1</sup>

<sup>1</sup> Depto. Física de la Materia Condensada, Fac. de Ciencia y Tecnología, Universidad del País Vasco, UPV/EHU, Apdo. 644, Bilbao, Spain.

<sup>2</sup> Department of Physics Engineering, Hacettepe University, 06800 Ankara, Turkey.

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 “1k” magnetic phases, i.e. their magnetic ordering has 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. The importance and utility of this tendency of the magnetic phases to minimize the symmetry break and maximize the resulting symmetry has not been fully considered and 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 1k magnetic structure can in principle be identified from diffraction experiments. Once this modulation wave vector is known, the possible magnetic space groups (i.e. Shubnikov groups) consistent with this vector and 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  $\mathbf{k}$ , 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 magCIF 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 magCIF 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 allows an immediate visualization of each of the alternative models with JSmol.

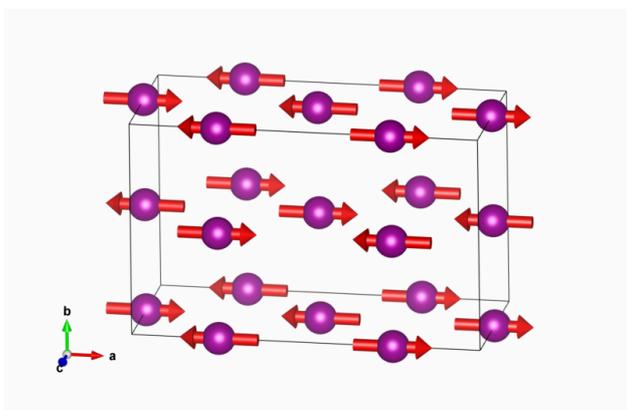
The magnetic structure models provided by the program are given by default in a setting as similar as possible to the one of the parent paramagnetic phase (the so-called parent-like setting), but they can also be obtained in a standard setting of the magnetic group considered, or alternatively in a setting 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, corresponding to twin-related or, in general, domain-related spin configurations. However, for lower symmetries than the k-maximal ones, the alternative more flexible and powerful program k-SUBGROUPSMAG in combination with MAGMODELIZE is recommended (see the tutorial of this alternative program).**

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 an example, 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.

**Example: Orthorhombic HoMnO<sub>3</sub>** (see magndata #1.20)  
(file: HoMnO3\_parent.cif)



**Figure 1:** Magnetic structure of HoMnO<sub>3</sub> (only Mn atoms) according to (Muñoz, A. et al., *Inorg. Chem.* (2001) **40** 1020 - 1028), with magnetic space group (MSG)  $P_{bmn}2_1(-b, a, c; 1/8, 1/4, 0)$  (magndata #1.20).

The paramagnetic structure of HoMnO<sub>3</sub> 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 90 90 90

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

The magnetic phase of this compound has a propagation vector  $\mathbf{k}=(1/2, 0, 0)$  and its antiferromagnetic magnetic order induces a switchable electric polarization, being therefore a multiferroic in the broad sense used nowadays, with magnetically induced ferroelectricity.

We can use MAXMAGN to explore all 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, as it happens.

**a) Introduce in MAXMAGN the propagation vector and the structural data of the parent structure of HoMnO<sub>3</sub>**, 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 2)

## Maximal magnetic space groups for the parent space group 62 ( $Pnma$ ) and the propagation vector $\mathbf{k} = (1/2, 0, 0)$

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

N	Group (BNS)	Transformation matrix	General positions	Properties	Magnetic structure
1	$P_a n a 2_1$ (#33.149) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 2 & 0 & 0 & 7/4 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences MAGNEXT Tensor properties MTENSOR	<a href="#">Show</a>
2	$P_b m n 2_1$ (#31.129) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 0 & 2 & 0 & 7/4 \\ -1 & 0 & 0 & 1/4 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences MAGNEXT Tensor properties MTENSOR	<a href="#">Show</a>
3	$P_c 2_1/c$ (#14.82) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 0 & 0 & -2 & 1/2 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences MAGNEXT Tensor properties MTENSOR	<a href="#">Show</a>
4	$P_a 2_1/m$ (#11.55) <a href="#">Go to a subgroup</a>	$\begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$ Alternatives (domain-related)	<a href="#">Show</a>	Systematic absences MAGNEXT Tensor properties MTENSOR	<a href="#">Show</a>

**Figure 2:** List of distinct  $\mathbf{k}$ -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  $\text{HoMnO}_3$  in the first input steps. The groups have all darker background indicating that all of them allow a non-zero average magnetic moment for at least some of the Mn or Ho atoms. This means that for this structure, any of the four alternative maximal symmetries are possible.

This list includes a representative of all the classes of magnetic subgroups equivalent by conjugation with respect to 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  $\mathbf{k}$ . The space groups are determined by mathematically searching among the subgroups of the grey group. 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 cannot describe the symmetry of a magnetic phase.

The transformation  $(\mathbf{P}, \mathbf{p})$  listed for each subgroup, where  $\mathbf{P}$  is a  $3 \times 3$  matrix and  $\mathbf{p} = (p_1, p_2, p_3)$  a column vector, indicates in each case a choice of unit cell and origin, for which the subgroup acquires the standard setting of the corresponding magnetic space group (MSG) given by the used MSG label, i.e. the symmetry operations of the subgroup would take, when described using this unit cell and origin, the form used for this MSG in the listings available in internet (ISOTROPY webpage or Bilbao Crystallographic Server) and taken as standard. The transformation  $(\mathbf{P}, \mathbf{p})$  is defined with respect to the unit cell  $(\mathbf{a}_p, \mathbf{b}_p, \mathbf{c}_p)$  and origin  $\mathbf{O}_p$  of the parent space group, in the following form:

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

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

**b) Explore the list of four possible models of maximal symmetry by clicking on the last column headed with "magnetic structure".** Start with the monoclinic centrosymmetric symmetry  $P_c2_1/c$  (#14.82). The program lists the asymmetric unit of a magnetic structure whose symmetry is given by this subgroup (see Figure 3). The unit cell and origin used by default, what we call "parent-like" setting, is indicated at the heading of the list:  $(2\mathbf{a}, \mathbf{b}, \mathbf{c}; 0, 0, 0)$ . This setting (generally non-standard) 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 maintained by the propagation vector. At the heading of the list one can also find the transformation from the parent unit cell and origin to the standard setting, and one can change the description to this setting, or to any consistent arbitrary basis chosen by the user.

The first column in the list tabulates the atomic positions, where one can see that both Ho and Mn atoms 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 one of the two independent Mn sites must necessarily have null magnetic moment. Thus, this symmetry does not allow a full magnetic ordering of the Mn atoms.

Check that the other possible k-maximal monoclinic subgroup of type  $P_a2_1/m$  (#11.55) also requires that a half of the Mn atoms remain disordered with null magnetic moment, while this does not happen for the orthorhombic subgroups. This means that a fully ordered magnetic arrangement of all the Mn atoms of maximal symmetry can only be achieved under the non-centrosymmetric symmetries  $P_a n a 2_1$  (#33.149) or  $P_b m n 2_1$  (#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 (with ferroelectricity along c), if all magnetic Mn atoms order and the phase symmetry is maximal. One can check which of the four possible listed maximal symmetries support a non-zero polarization by clicking on the corresponding link to MTENSOR in the initial output list (Figure 2), and inspecting with this program the symmetry adapted form of an electrical polarization for each symmetry.

In this example, non-polarized magnetic neutron diffraction is not subject to any specific systematic absence distinguishing the four possible subgroups. We keep therefore unchecked the button entitled "systematic absences", which is a link to the tool MAGNEXT, also available in the Bilbao Crystallographic Server, for the calculation of the systematic absences of non-polarized magnetic diffraction. This option is however very useful in other cases to distinguish the diffraction signatures of different possible symmetries.

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

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

Parent space group 62 ( $Pnma$ )

Lattice parameters: a=11.67080, 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]

**Atomic positions, Wyckoff positions and Magnetic Moments**

N	Atom	New WP	Multiplicity	Magnetic moment	Values of $M_x, M_y, M_z$
1	Ho_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	( $M_x, 0, M_z$ )	$M_x = 0.00000$ $M_z = 0.00000$
	Ho_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	( $M_x, 0, M_z$ )	$M_x = 0.00000$ $M_z = 0.00000$
2	Mn_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	(0, 0, 0)	-
	Mn_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	( $M_x, M_y, M_z$ )	$M_x = 0.00000$ $M_y = 0.00000$ $M_z = 0.00000$

**Figure 3:** Atomic positions and magnetic moments (partial) of the asymmetric unit of  $\text{HoMnO}_3$  for the subgroup of  $Pnma1'$  of type  $P_c2_1/c$  (#14.82), listed N. 3 in Figure 2, as obtained when clicking in the column "Magnetic structure". The table indicates the positions and moments which correspond to all atoms that are symmetry related with the one listed as representative in the asymmetric unit, all described in the parent-like setting (see text). The number of symmetry related atoms within the used unit cell (multiplicity) is given in the fourth column. The fifth column indicates the symmetry restrictions on the value of the components of the magnetic moment for the representative magnetic atom listed in the second column (if any), while the last column on the right allows to introduce specific values for the symmetry-free moment components. One can see that both the Ho and Mn split into two independent sites.

**c) For the subgroup of type  $P_c2_1/c$  (#14.82) in the list provided by the program (Figure 2), click on the option "go to a subgroup" and in the following menu choose as generators of the chosen lower 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 group still requires that some Mn atoms remain disordered with null magnetic moment. A similar situation happens if you descend from the other monoclinic subgroup and also try to keep the inversion center. We can therefore predict that whatever is the magnetic ordering of  $\text{HoMnO}_3$  with propagation vector  $(1/2, 0, 0)$ , if it involves all the Mn atoms, it must necessarily break the centrosymmetry of the structure, and magnetic order of all Mn sites is bound to yield a polar structure and as a consequence, if the system is an insulator, a magnetically induced electric polarization with ferroelectric properties can be expected.**

**d) Construct a magnetic structure complying with the maximal symmetry  $Pnna2_1$  (#33.149).** Notice that in this case the difference between the standard setting and the parent-like one is only an origin shift. The experimental diffraction data indicates that the Mn spins are essentially collinear along the x direction (weakness of reflections with diffraction vectors with the a direction or close to it). Therefore, introduce a non-zero value for the  $m_x$  component of the Mn independent atom. This restricts the model to a collinear ordering, although, as

shown in the list, both polar symmetries allow an arbitrary direction for the Mn moment, that would produce a non-collinear arrangement. 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 allow their independent refinement. A symmetry-consistent crosscheck of their possible deviation from the *Pnma* relations due to magnetostructural couplings is therefore possible.

**Selected magnetic space group: 1- *P<sub>a</sub>na2<sub>1</sub>* (#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]

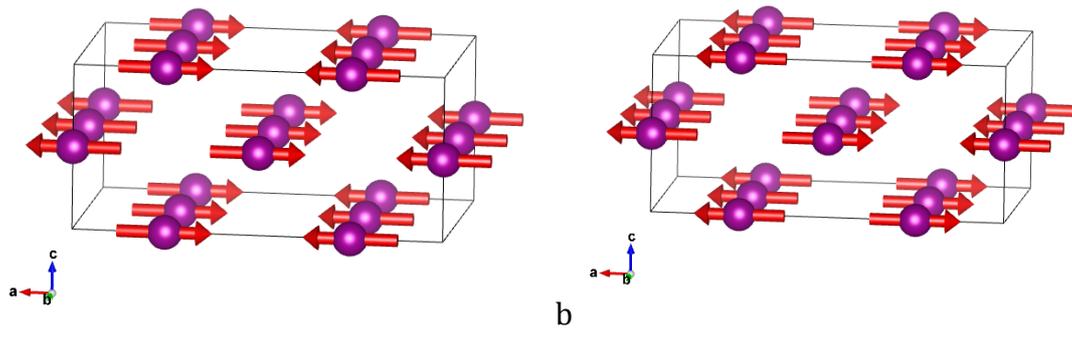
Export data to MCIF file    Go to a subgroup

**Atomic positions, Wyckoff positions and Magnetic Moments**

N	Atom	New WP	Multiplicity	Magnetic moment	Values of M <sub>x</sub> , M <sub>y</sub> , M <sub>z</sub>
1	Ho1_1 Ho 0.04195 0.25000 0.98250	(x, 1/4, z   m <sub>x</sub> , 0, m <sub>z</sub> ) (-x+1/4, 3/4, z+1/2   m <sub>x</sub> , 0, -m <sub>z</sub> ) (x+1/2, 1/4, z   -m <sub>x</sub> , 0, -m <sub>z</sub> ) (-x+3/4, 3/4, z+1/2   -m <sub>x</sub> , 0, m <sub>z</sub> )	4	(M <sub>x</sub> , 0, M <sub>z</sub> )	M <sub>x</sub> = 0.00000 M <sub>z</sub> = 0.00000
	Ho1_2 Ho 0.95805 0.75000 0.01750	(-x, 3/4, -z   m <sub>x</sub> , 0, m <sub>z</sub> ) (x+1/4, 1/4, -z+1/2   m <sub>x</sub> , 0, -m <sub>z</sub> ) (-x+1/2, 3/4, -z   -m <sub>x</sub> , 0, -m <sub>z</sub> ) (x+3/4, 1/4, -z+1/2   -m <sub>x</sub> , 0, m <sub>z</sub> )	4	(M <sub>x</sub> , 0, M <sub>z</sub> )	M <sub>x</sub> = 0.00000 M <sub>z</sub> = 0.00000
2	Mn1 Mn 0.00000 0.00000 0.50000	(0, 0, 1/2   m <sub>x</sub> , m <sub>y</sub> , m <sub>z</sub> ) (1/4, 0, 0   m <sub>x</sub> , m <sub>y</sub> , -m <sub>z</sub> ) (0, 1/2, 1/2   m <sub>x</sub> , -m <sub>y</sub> , m <sub>z</sub> ) (1/4, 1/2, 0   m <sub>x</sub> , -m <sub>y</sub> , -m <sub>z</sub> ) (1/2, 0, 1/2   -m <sub>x</sub> , -m <sub>y</sub> , -m <sub>z</sub> ) (3/4, 0, 0   -m <sub>x</sub> , -m <sub>y</sub> , m <sub>z</sub> ) (1/2, 1/2, 1/2   -m <sub>x</sub> , m <sub>y</sub> , -m <sub>z</sub> ) (3/4, 1/2, 0   -m <sub>x</sub> , m <sub>y</sub> , m <sub>z</sub> )	8	(M <sub>x</sub> , M <sub>y</sub> , M <sub>z</sub> )	M <sub>x</sub> = 0.00000 M <sub>y</sub> = 0.00000 M <sub>z</sub> = 0.00000
3	O1_1 O 0.23110 0.25000 0.11130	(x, 1/4, z   m <sub>x</sub> , 0, m <sub>z</sub> ) (-x+1/4, 3/4, z+1/2   m <sub>x</sub> , 0, -m <sub>z</sub> ) (x+1/2, 1/4, z   -m <sub>x</sub> , 0, -m <sub>z</sub> ) (-x+3/4, 3/4, z+1/2   -m <sub>x</sub> , 0, m <sub>z</sub> )	4	-	-
	O1_2 O 0.76890 0.75000 0.88870	(-x, 3/4, -z   m <sub>x</sub> , 0, m <sub>z</sub> ) (x+1/4, 1/4, -z+1/2   m <sub>x</sub> , 0, -m <sub>z</sub> ) (-x+1/2, 3/4, -z   -m <sub>x</sub> , 0, -m <sub>z</sub> ) (x+3/4, 1/4, -z+1/2   -m <sub>x</sub> , 0, m <sub>z</sub> )	4	-	-

**Figure 4:** Atomic positions and magnetic moments (partial) of the asymmetric unit of HoMnO<sub>3</sub> for the subgroup of *Pnma*1' of type *P<sub>a</sub>na2<sub>1</sub>* (#33.149), listed N. 1 in Figure 2, 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. One can see that the Ho split into two independent sites, while the Mn remains a single independent site, but it becomes a general position of the MSG, with free position coordinates.

**e) Produce a magCIF file of the *P<sub>a</sub>na2<sub>1</sub>* (#33.149) model and visualize it with VESTA or Jmol.** If only the magnetic atoms are visualized, it will be something similar to Figure 5(a).



**Figure 5:** (a) Possible k-maximal magnetic ordering for HoMnO<sub>3</sub> according to the magnetic space group  $P_{ana}2_1$ (#33.149) using the parent-like setting  $(2a,b,c;0,0,0)$ , and having restricted the spins along  $a$ . (b) Magnetic ordering equivalent to the one in (a) corresponding to a twin-related configuration. Its symmetry is given by a 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.

**f) Come back to the main output list of k-maximal magnetic groups and click on "alternatives (domain related)" of the listed group  $P_{ana}2_1$ (#33.149) to change to the second conjugate subgroup of this type. Follow then the same procedure as before and obtain the magCIF file of the corresponding magnetic arrangement. It is shown in Figure 5(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  $c$ .**

**g) Come back to the main output list of k-maximal magnetic groups (Figure 2) and follow the same procedure for the second possible polar group  $P_{bmn}2_1$  (#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 6)**

Selected magnetic space group:  $2-P_6mn2_1$  (#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]

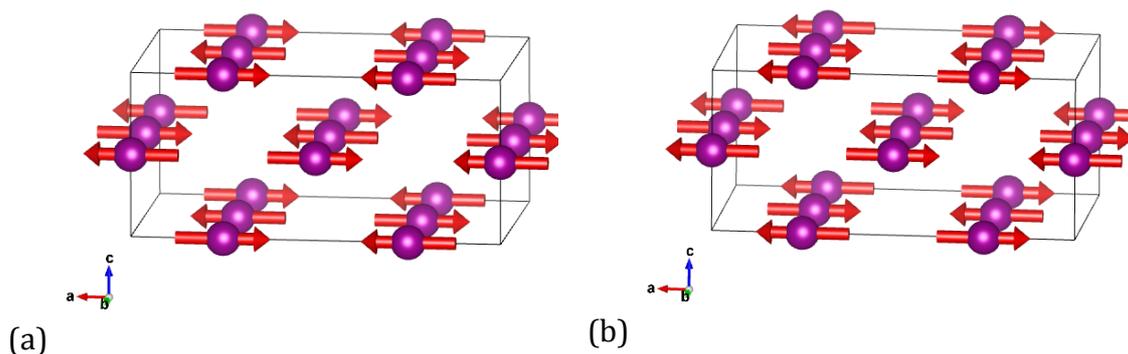
Export data to MCIF file    Go to a subgroup

**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 <sub>y</sub> ,0) (-x+1/4,3/4,z+1/2   0,m <sub>y</sub> ,0) (x+1/2,1/4,z   0,-m <sub>y</sub> ,0) (-x+3/4,3/4,z+1/2   0,-m <sub>y</sub> ,0)	4	(0,M <sub>y</sub> ,0)	M <sub>y</sub> = <input type="text" value="0.00001"/>
	Ho1_2 Ho 0.95805 0.75000 0.01750	(-x,3/4,-z   0,m <sub>y</sub> ,0) (x+1/4,1/4,-z+1/2   0,m <sub>y</sub> ,0) (-x+1/2,3/4,-z   0,-m <sub>y</sub> ,0) (x+3/4,1/4,-z+1/2   0,-m <sub>y</sub> ,0)	4	(0,M <sub>y</sub> ,0)	M <sub>y</sub> = <input type="text" value="0.00001"/>
2	Mn1 Mn 0.00000 0.00000 0.50000	(0,0,1/2   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (1/4,0,0   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (0,1/2,1/2   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (1/4,1/2,0   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (1/2,0,1/2   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (3/4,0,0   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (1/2,1/2,1/2   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (3/4,1/2,0   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> )	8	(M <sub>x</sub> ,M <sub>y</sub> ,M <sub>z</sub> )	M <sub>x</sub> = <input type="text" value="0.00001"/> M <sub>y</sub> = <input type="text" value="0.00001"/> M <sub>z</sub> = <input type="text" value="0.00001"/>
3	O1_1 O 0.23110 0.25000 0.11130	(x,1/4,z   0,m <sub>y</sub> ,0) (-x+1/4,3/4,z+1/2   0,m <sub>y</sub> ,0) (x+1/2,1/4,z   0,-m <sub>y</sub> ,0) (-x+3/4,3/4,z+1/2   0,-m <sub>y</sub> ,0)	4	-	-
	O1_2 O 0.76890 0.75000 0.88870	(-x,3/4,-z   0,m <sub>y</sub> ,0) (x+1/4,1/4,-z+1/2   0,m <sub>y</sub> ,0) (-x+1/2,3/4,-z   0,-m <sub>y</sub> ,0) (x+3/4,1/4,-z+1/2   0,-m <sub>y</sub> ,0)	4	-	-
4	O2_1 O 0.16405 0.05340 0.70130	(x,y,z   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (-x+1/4,-y,z+1/2   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (x,-y+1/2,z   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (-x+1/4,y+1/2,z+1/2   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (x+1/2,y,z   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (-x+3/4,-y,z+1/2   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (x+1/2,-y+1/2,z   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (-x+3/4,y+1/2,z+1/2   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> )	8	-	-
	O2_2 O 0.83595 0.55340 0.29870	(-x,y+1/2,-z   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (x+1/4,-y+1/2,-z+1/2   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (-x,-y,-z   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (x+1/4,y,-z+1/2   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (-x+1/2,y+1/2,-z   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (x+3/4,-y+1/2,-z+1/2   -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (-x+1/2,-y,-z   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> ) (x+3/4,y,-z+1/2   m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub> )	8	-	-

**Figure 6:** Atomic positions and magnetic moments (partial) of the asymmetric unit of  $\text{HoMnO}_3$  for the subgroup of  $Pnma1'$  of type  $P_6mn2_1$  (#31.129), listed N. 2 in Figure 2, 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. One can see that the Ho split into two independent sites, while the Mn remains a single independent site, but it becomes a general position with its three coordinates free.

**h) Restrict again the model to have the moments along the x axis and obtain the corresponding magCIF files for the two twin related configurations.** They are depicted in Figure 7. This is actually the model that has been reported for  $\text{HoMnO}_3$  (see MAGNDATA entry #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 7:** (a) Possible k-maximal magnetic ordering for HoMnO<sub>3</sub> 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 due to the symmetry break, and the symmetry relations that they have to fulfill rigorously in the magnetic phase are described by the same symmetry operations that are valid for the magnetic moments, which are listed in the magCIF file. The presence or not of time reversal in these symmetry operations is irrelevant for the atomic positions, which are then subject to the constraints 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 electron density) is of the same type as the one used for the BNS notation, namely the space group  $Pmn2_1$ (N. 31).

**i) Come back to the main list of k maximal groups (Figure 2) 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 <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub>	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	{ 1   0 }
-x+3/4,-y,z+1/2,+1 -m <sub>x</sub> ,-m <sub>y</sub> ,m <sub>z</sub>	$\begin{pmatrix} -1 & 0 & 0 & 3/4 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	{ 2 <sub>001</sub>   3/4 0 1/2 }
x,-y+1/2,z,+1 -m <sub>x</sub> ,m <sub>y</sub> ,-m <sub>z</sub>	$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	{ m <sub>010</sub>   0 1/2 0 }
-x+3/4,y+1/2,z+1/2,+1 m <sub>x</sub> ,-m <sub>y</sub> ,-m <sub>z</sub>	$\begin{pmatrix} -1 & 0 & 0 & 3/4 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	{ m <sub>100</sub>   3/4 1/2 1/2 }
x+1/2,y,z,-1 -m <sub>x</sub> ,-m <sub>y</sub> ,-m <sub>z</sub>	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	{ 1'   1/2 0 0 }
-x+1/4,-y,z+1/2,-1 m <sub>x</sub> ,m <sub>y</sub> ,-m <sub>z</sub>	$\begin{pmatrix} -1 & 0 & 0 & 1/4 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	{ 2' <sub>001</sub>   1/4 0 1/2 }
x+1/2,-y+1/2,z,-1 m <sub>x</sub> ,-m <sub>y</sub> ,m <sub>z</sub>	$\begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	{ m' <sub>010</sub>   1/2 1/2 0 }
-x+1/4,y+1/2,z+1/2,-1 -m <sub>x</sub> ,m <sub>y</sub> ,m <sub>z</sub>	$\begin{pmatrix} -1 & 0 & 0 & 1/4 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 1 & 1/2 \end{pmatrix}$	{ m' <sub>100</sub>   1/4 1/2 1/2 }

**Figure 8:** General positions or representative symmetry operations of the subgroup of  $Pnma1'$  of type  $P_bmn2_1$  (#31.129), listed N. 2 in Figure 2, in the parent-like setting (2a,b,c;0,0,0), as obtained when clicking in the column "general positions".

Get the list of symmetry operations reproduced in Figure 8 in a text format using the option at the heading of the list. Introduce them by means of a copy/paste in the input window of the program IDENTIFY GROUP (available in the section "Space group symmetry" of the Bilbao Crystallographic Server) and transform them into ordinary space group operations by deleting the  $\pm 1$  symbols and the numeric labels of the operations. The program will then identify the space group as of type  $Pmn2_1$  (N.31) in a non-standard setting, with the transformation to standard setting:  $(\mathbf{b}, -1/2\mathbf{a}, \mathbf{c}; 1/8, 1/4, 0)$ . Thus, the primitive unit cell of the effective lattice for the non-magnetic degrees of freedom is half the size of the magnetic unit cell along  $\mathbf{a}$ . Why?

## REFERENCES

- [1] [jana.fzu.cz/](http://jana.fzu.cz/)
- [2] [www.ill.eu/sites/fullprof/](http://www.ill.eu/sites/fullprof/)
- [3] [iso.byu.edu](http://iso.byu.edu)
- [4] [jp-minerals.org/vesta/](http://jp-minerals.org/vesta/)
- [5] [jmol.sourceforge.net/](http://jmol.sourceforge.net/)

