Symmetry of commensurate magnetic structures: Magnetic space groups

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“It is only slightly overstating the case to say that physics is the study of symmetry”

P. W. Anderson

A symmetry operation in a solid **IS NOT only** a more or less complex transformation leaving the system invariant. **But it must fulfill that the resulting constraints can only be broken through a phase transition.**

A well defined symmetry operation (in a thermodynamic system) must be maintained when scalar fields (temperature, pressure,...) are changed, except if a phase transition takes place.

“**symmetry-forced**” means: “forced for a thermodynamic phase
“**symmetry-allowed**” means: “allowed within a thermodynamic phase”

**Symmetry-dictated properties can be considered symmetry “protected”**
Space Group: Pnma

Lattice parameters:
5.7461 7.6637 5.5333 90.000 90.000 90.000

Atomic positions of asymmetric unit:
La1  0.05130 0.25000 -0.00950
Mn1  0.00000 0.00000 0.50000
O1    0.48490 0.25000 0.07770
O2    0.30850 0.04080 0.72270

Space Group: set of operations \{R|t\}
for all atoms:

\[
\begin{align*}
\text{atom} & \quad \{R|t\} \quad \text{atom'} \\
(x,y,z) & \quad \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = R \begin{bmatrix} x \\ y \\ z \end{bmatrix} + t
\end{align*}
\]

\{R|t\}: R - rotation or rotation+plus inversion
\quad t - translation

\text{LaMnO}_3

\text{Pnma:} 8 related positions for a general position:
\[
\begin{align*}
(x,y,z) & \quad (-x+1/2,-y,z+1/2) & \quad (-x,y+1/2,-z) & \quad (x+1/2,-y+1/2,-z+1/2) = \{2x|\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \\
(-x,-y,-z) & \quad (x+1/2,y,-z+1/2) & \quad (x,-y+1/2,z) & \quad (-x+1/2,y+1/2,z+1/2) = \{m_x|\frac{1}{2} \frac{1}{2} \frac{1}{2}\}
\end{align*}
\]

4 related positions for a special position of type \(x, \frac{1}{4}, z\): \text{special positions are tabulated:}

\[
\begin{align*}
(x,1/4,z) & \quad (-x+1/2,3/4,z+1/2) & \quad (-x,3/4,-z) & \quad (x+1/2,1/4,-z+1/2)
\end{align*}
\]

\text{Wyckoff positions or orbits}
Space Group: Pnma

Lattice parameters: 5.7461 7.6637 5.5333 90.000 90.000 90.000

Atomic positions of asymmetric unit:
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O2   0.30850 0.04080 0.72270

Relations among atoms from the space group:
more than "geometrical", they are "thermodynamic" properties

\[ \text{they may be zero within experimental resolution}
\text{but this is NOT symmetry forced.} \]

La1 \((\approx 0.0 \ 0.25000 \ \approx 0.0)\)

\[ \frac{1}{4} \text{ rigorously fulfilled – if broken, it means a different phase} \]

Whatever microscopic model of atomic forces, if consistently applied, it will yield:
\[ F_y (\text{La1}) = 0.000000 \ (\text{exact!}) \]
Magnetic Symmetry:  
Symmetry is only detected when it does not exist!  
We do not add but substract symmetry operations!

Symmetry operation to be considered: 
(always present in non-magnetic structures but ABSENT in magnetically ordered ones!)

Time inversion/reversal: \{1'|0,0,0\}

- Does not change nuclear variables
- Changes sign of ALL atomic magnetic moments

\[
\{1'|000\} \\
(x,y,z,-m) \Rightarrow (x,y,z,-1)
\]

Magnetic structures only have symmetry operations where time reversal 1’ is combined with other transformations, or is not present at all:
\[
\{1'|t\} = \{1'|0,0,0\} \{1|t\} \\
\{m'| t\} = \{1'|0,0,0\} \{m|t\} \\
\{2'|t\} = \{1'|0,0,0\}\{2|t\} \\
\{3^+|t\} = \{1'|0,0,0\}\{3^+|t\}, \text{ etc.}
\]

But \{1'|0,0,0\} alone is never a symmetry operation of a magn. struct.
All NON-magnetic structures have time inversion symmetry!

If all atomic magnetic moments are zero, time inversion is a (trivial) symmetry operation of the structure:

Actual symmetry of the non-magnetic phase:

\[ Pnma1' = Pnma + \{1'|000\} \times Pnma \]  
(grey group)

16 operations:

\[
\begin{align*}
(x,y,z,+1) & \quad (-x+1/2,-y,z+1/2,+1) & \quad (-x,y+1/2,-z,+1) & \quad (x+1/2,-y+1/2,-z+1/2,+1) \\
(-x,-y,-z,+1) & \quad (x+1/2,y,-z+1/2,+1) & \quad (x,-y+1/2,z,+1) & \quad (-x+1/2,y+1/2,z+1/2,+1) \\
(x,y,-z,-1) & \quad (-x+1/2,-y,z+1/2,-1) & \quad (-x,y+1/2,-z,-1) & \quad (x+1/2,-y+1/2,-z+1/2,-1) \\
(-x,-y,+z,-1) & \quad (x+1/2,y,-z+1/2,-1) & \quad (x,-y+1/2,z,-1) & \quad (-x+1/2,y+1/2,z+1/2,-1)
\end{align*}
\]

Notation:

\[
\begin{align*}
(x+1/2,-y+1/2,-z+1/2,+1) &= \{2x|\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \\
(x+1/2,-y+1/2,-z+1/2,-1) &= \{2x'|\frac{1}{2} \frac{1}{2} \frac{1}{2}\} \\
\{R|t\} & \quad \{R',\theta|t\} & \quad \theta=1 & \quad \theta=-1
\end{align*}
\]
A symmetry operation fulfills:

- the operation belongs to the set of transformations that keep the energy invariant: rotations, translations, space inversion, time reversal.
- the system is undistinguishable after the transformation.

Symmetry operations in commensurate magnetic crystals:

magnetic space group: \( \{ \{ R_i \mid t_i \} , \{ R'_j \mid t_j \} \} \)

or \( \{ \{ R_i , \theta \mid t_i \} \} \)

\( \theta = +1 \) without time reversal
\( \theta = -1 \) with time reversal
For space operations, the magnetic moments transform as pseudovectors or axial vectors:

\[ T_{\text{axial}}(R) = \det[R] \mathbf{R} \]
Phase Transition / Symmetry break

A magnetic structure is always a “distorted” structure:
It differs from a configuration of higher symmetry by the presence of the ordered atomic magnetic moments (other small distortions may also be significant).

A commensurate magnetic phase represents a symmetry break with respect to a non-magnetic phase (paramagnetic):
Its symmetry is a subgroup of the one of the non-magnetic configuration

\[ G_1' \rightarrow \Omega \quad \Omega \text{ subgroup of } G_1' \]

\( G_1' \) contains the time reversal operation \( \{1'|0 0 0\} \):
\[ G_1' = G + \{1'|0 0 0\} \quad G: \text{ space group} \]
\[ G_1': \text{ grey magnetic group} \]

\( \Omega \) DOES NOT contain the time reversal operation \( \{1'|0 0 0\} \)
magnetic ordering breaks symmetry of time inversion

Magnetic ordered phases:

Time inversion $\{1'|0 0 0\}$ is NOT a symmetry operation of a magnetic phase

LaMnO$_3$

$\text{Pnma1'}$

$\text{Pn'ma'}$

\begin{align*}
(x,y,z,+1) & \rightarrow (-x+1/2,-y,z+1/2,+1) \\
(-x,-y,-z,+1) & \rightarrow (x+1/2,y,-z+1/2,+1) \\
(x,y,z,-1) & \rightarrow (-x+1/2,-y,z+1/2,-1) \\
(-x,-y,-z,-1) & \rightarrow (x+1/2,y,-z+1/2,-1)
\end{align*}
Possible symmetries for a k=0 magnetic ordering:

Possible maximal symmetries for a k=0 magnetic ordering:
How to describe a magnetic structure in a crystallographic unambiguous form

**Magnetic space Group:**
Pn'ma'

**Lattice parameters:**
5.7461 7.6637 5.5333 90.000 90.000 90.000

**Atomic positions of asymmetric unit:**
La1 0.05130 0.25000 -0.00950
Mn1 0.00000 0.00000 0.50000
O1 0.48490 0.25000 0.07770
O2 0.30850 0.04080 0.72270

**Magnetic moments of the asymmetric unit (μB):**
Mn1 3.87 0.0 0.0

For all atoms:

\[
\begin{align*}
\begin{bmatrix} x' \\
y' \\
z' \\
\end{bmatrix} &= \mathbf{R} \begin{bmatrix} x \\
y \\
z \\
\end{bmatrix} + \mathbf{t} \\
\begin{bmatrix} mx' \\
my' \\
mz' \\
\end{bmatrix} &= -\det(\mathbf{R}) \mathbf{R} \begin{bmatrix} mx \\
my \\
mz \\
\end{bmatrix}
\end{align*}
\]

θ = -1 if time inversion
### General Positions of the Group Pn’ma’ (#62.448)

For this space group, BNS and OG settings coincide. Its label in the OG setting is given as: Pn’ma’ (#62.8.509)

<table>
<thead>
<tr>
<th>N</th>
<th>(x, y, z) form</th>
<th>Matrix form</th>
<th>Geom. interp.</th>
<th>Seltz notation</th>
</tr>
</thead>
</table>
| 1 | x, y, z, +1          | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\] | 1 +1          | \{1 | 0\}        |
| 2 | -x, y+1/2, -z, +1    | \[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1 \\
\end{pmatrix}
\] | 2 (0,1/2,0)0,y,0 +1 | \{2010 | 0 1/2 0\} |
| 3 | -x, -y, -z, +1       | \[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 \\
\end{pmatrix}
\] | -1 0,0,0 +1    | \{-1 | 0\}     |
| 4 | x, -y+1/2, z, +1     | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\] | m_x,1/4,z +1 | \{m010 | 0 1/2 0\} |
| 5 | x+1/2, -y+1/2, -z+1/2, -1 | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1 \\
\end{pmatrix}
\] | 2 (1/2,0,0)x,1/4,y,1/4 -1 | \{2\'000 | 1/2 2 1/2\} |
| 6 | -x+1/2, -y, z+1/2, -1 | \[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\] | 2 (0,0,1/2)1/4,0,z -1   | \{2\'001 | 1/2 0 1/2\} |
| 7 | -x+1/2, y+1/2, z+1/2, -1 | \[
\begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{pmatrix}
\] | n (0,1/2,1/2)1/4,y,z -1 | \{m\'000 | 1/2 1/2 1/2\} |
| 8 | x+1/2, y, -z+1/2, -1  | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -1 \\
\end{pmatrix}
\] | a x,y,1/4 -1  | \{m\'001 | 1/2 0 1/2\} |

Go to the list of the Wyckoff Positions of the Group Pn’ma’ (#62.448)
Go to the Systematic Absences for the Group Pn’ma’ (#62.448)
Parameters to describe a magnetic structure...

Space Group: \( \text{Pn'ma'} \)

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Coordinates</th>
</tr>
</thead>
</table>
| 8            | d              | \( (x,y,z \mid m_x^*,m_y^*,m_z^*) \) \( (x+1/2,-y+1/2,z+1/2 \mid -m_x^*,m_y^*,m_z^*) \) \( (-x+y+1/2,-z \mid -m_x^*,m_y^*,m_z^*) \) \( (-x+y+1/2,-z \mid m_x^*,m_y^*,m_z^*) \) |}
| 4            | c              | \( (x,1/4,z \mid 0,m_y^* \mid 0) \) \( (x+1/2,1/4,-z+1/2 \mid 0,m_y^* \mid 0) \) \( (-x,3/4,-z \mid 0,m_y^* \mid 0) \) \( (-x+1/2,3/4,z+1/2 \mid 0,m_y^* \mid 0) \) |}
| 4            | b              | \( (0,0,1/2 \mid m_x^*,m_y^*,m_z^*) \) \( (1/2,1/2,0 \mid -m_x^*,m_y^*,m_z^*) \) \( (0,1/2,1/2 \mid -m_x^*,m_y^*,m_z^*) \) \( (1/2,0,0 \mid m_x^*,m_y^*,m_z^*) \) |}
| 4            | a              | \( (0,0 \mid m_x^*,m_y^*,m_z^*) \) \( (1/2,1/2,1/2 \mid -m_x^*,m_y^*,m_z^*) \) \( (0,1/2,0 \mid -m_x^*,m_y^*,m_z^*) \) \( (1/2,0,1/2 \mid m_x^*,m_y^*,m_z^*) \) |}

Output of MWYCKPOS in BCS

La

Mn

mode along x

mode along y weak ferromagnet

mode along z
**Parameters to describe a magnetic structure...**

**Space Group:**
Pn'ma'

<table>
<thead>
<tr>
<th>Multiplicity</th>
<th>Wyckoff letter</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>d</td>
<td>( (x,y,z)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-x,y+1/2,z )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-x,y,z )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>((x,-y+1/2,z) )</td>
</tr>
</tbody>
</table>

**Magnetic moments of the asymmetric unit (µB):**

- **La**
- **Mn**

Why only x-component?:

exchange interaction \( S_i \cdot S_j \) is dominant!

Parameters to describe a magnetic structure...

Mode along x

Mode along y

Weak ferromagnet

Mode along z

Exchange \( S_i \cdot S_j \) is isotropic!
only depends on the relative orientations

The MSG and non-collinearity results from weak crystal anisotropy (x-easy axis)
Description in terms of irrep modes

Pn’ma’ $\rightarrow$ mB$_{2g}$

(Irrep = irreducible representation)

<table>
<thead>
<tr>
<th>Character Table</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{2h}$ (mmm)</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>$mA_g$</td>
</tr>
<tr>
<td>$mB_{1g}$</td>
</tr>
<tr>
<td>$mB_{2g}$</td>
</tr>
<tr>
<td>$mB_{3g}$</td>
</tr>
<tr>
<td>$mA_u$</td>
</tr>
<tr>
<td>$mB_{1u}$</td>
</tr>
<tr>
<td>$mB_{2u}$</td>
</tr>
<tr>
<td>$mB_{3u}$</td>
</tr>
</tbody>
</table>

One $mB_{2g}$ spin mode
(or basis function)
Build up the model of the magnetic structure of LaMnO$_3$ using STRCONVERT (exercise 1)

1. Upload the cif file of LaMnO$_3$ in STRCONVERT. Change to magnetic option. Transform to P1 to produce the whole set of atomic positions within the unit cell. Introduce magnetic moments along x of the four Mn atoms: 1,-1,-1,1. Use findsym to find the MSG, and the description using this MSG. Visualize the magnetic structure with Jmol. Introduce a non-zero component my at the single symmetry-independent Mn atom, and transform again to P1 to observe that the resulting my values for 4 Mn atoms within the unit cell have the same sign (expected weak FM along y). Create an mcif file of the structure with STRCONVERT, open it with a text editor and localize the different data items: unit cell, atomic positions, symmetry operations. Download the mcif file in VESTA and visualize with this tool. (file required: 1.LaMnO3_parent.cif)
Structure Data Converter & Editor

Please submit a structure file:
Browse... No file selected. Upload the file

[Supported file formats: CIF, mCIF, VESTA, VASP]

Symmetry
Magnetic Space Group # (BNS): 31.129 (P_bmn2_1) Type: IV

Lattice Parameters
a: 11.670 Å   b: 7.360 Å   c: 5.257 Å
α: 90.00°   β: 90.00°   γ: 90.00°

Symmetry Operations [Show/Hide]

Recognized formats:
1. x,y,z mx,my,mz +1
   x,y,z mx,my,mz +1
   x,y,z
   x,y,z +1
   1 'x, y, z'
   1 x,y,z

Update the symmetry operators with the above Apply

Symmetry operations have been parsed from the file/form Populate with operators from database
### Atomic Positions & Magnetic Moments

Switch to the treatment of the vectors as: displacements ‡ Go!

<table>
<thead>
<tr>
<th>Label</th>
<th>Element</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
<th>m&lt;sub&gt;x&lt;/sub&gt;</th>
<th>m&lt;sub&gt;y&lt;/sub&gt;</th>
<th>m&lt;sub&gt;z&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho</td>
<td>Ho</td>
<td>0.04195</td>
<td>0.25000</td>
<td>0.98250</td>
<td>1.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Ho_1</td>
<td>Ho</td>
<td>0.95805</td>
<td>0.75000</td>
<td>0.01750</td>
<td>1.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.50000</td>
<td>1.00000</td>
<td>3.87000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>O1</td>
<td>O</td>
<td>0.23110</td>
<td>0.25000</td>
<td>0.11130</td>
<td>1.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>O1_1</td>
<td>O</td>
<td>0.76890</td>
<td>0.75000</td>
<td>0.88870</td>
<td>1.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>O2</td>
<td>O</td>
<td>0.16405</td>
<td>0.05340</td>
<td>0.70130</td>
<td>1.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>O2_1</td>
<td>O</td>
<td>0.83595</td>
<td>0.55340</td>
<td>0.29870</td>
<td>1.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
</tbody>
</table>

**Longest Arrow size:** 1.314

[for VESTA format export: Å (Default: min(a,b,c)/4)]

[for Jmol visualize: a proportional coefficient]
a CIF-type file can be produced:

These files permit the different alternative models to be analyzed, refined, shown graphically, transported to ab-initio codes etc., with programs as ISODISTORT, JANA2006, STRCONVERT, etc. A controlled descent to lower symmetries is also possible.
### General Positions of the Group Pn'ma' (#62.448)

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</tr>
</thead>
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<tr>
<td>1</td>
<td>x, y, z, +1 mₓ,mᵧ,mz</td>
<td>(1 0 0 0 0 1 0 0 0)</td>
<td>1 +1</td>
<td>{ 1</td>
</tr>
<tr>
<td>2</td>
<td>-x, y+1/2, -z, +1 mₓ,mᵧ,mz</td>
<td>(-1 0 0 0 0 1 0 1/2 0)</td>
<td>2 {0,1/2,0}y,0,+1</td>
<td>{ 2</td>
</tr>
<tr>
<td>3</td>
<td>-x+1/2, -y, -z, +1 mₓ,mᵧ,mz</td>
<td>(-1 0 0 0 0 -1 0 0 1)</td>
<td>-1,0,0,+1</td>
<td>{-1</td>
</tr>
<tr>
<td>4</td>
<td>x, -y+1/2, z, +1 mₓ,mᵧ,mz</td>
<td>(1 0 0 0 0 -1 0 0 1)</td>
<td>mₓ,1/4,z,+1</td>
<td>{ m</td>
</tr>
<tr>
<td>5</td>
<td>x+1/2, -y+1/2, -z+1/2, -1 mₓ,mᵧ,mz</td>
<td>(1 0 0 0 0 1/2 -1 0 1/2)</td>
<td>2 {1/2,0,0}x,1/4,1/4,-1</td>
<td>{ 2'</td>
</tr>
<tr>
<td>6</td>
<td>x+1/2, -y, z+1/2, -1 mₓ,mᵧ,mz</td>
<td>(-1 0 0 0 0 1/2 -1 0 0)</td>
<td>2 {0,0,1/2}1/4,0,z,-1</td>
<td>{ 2</td>
</tr>
<tr>
<td>7</td>
<td>x+1/2, y+1/2, z+1/2, -1 mₓ,mᵧ,mz</td>
<td>(-1 0 0 0 0 1/2 0 1 0)</td>
<td>n {0,1/2,1/2}1/4,y,z,-1</td>
<td>{ m'</td>
</tr>
<tr>
<td>8</td>
<td>x+1/2, y, -z+1/2, -1 mₓ,mᵧ,mz</td>
<td>(1 0 0 0 0 1/2 0 0 -1)</td>
<td>a,x,y,1/4,-1</td>
<td>{ m'</td>
</tr>
</tbody>
</table>

Magnetic point group: m’mm’

Pn’ma’ = P12₁/m1 + {2’₁₀₀|1/2,1/2,1/2} P12₁/m1
Types of magnetic space groups:

(for a commensurate magnetic structure resulting from a paramagnetic phase having a grey magnetic group $G_1'$)

Time inversion $\{1' | 0 0 0\}$ is NOT a symmetry operation of magnetic structure, but combined with a translation it can be...

F subgroup of $G$

$F \leq G$

magn. space group:

$F$

magn. point groups:

$P_F$

nuclear space group:

$F$

Types of magnetic space groups:

- **Type I**
  - some may allow ferromagnetic order
  - $F$
  - $P_F$

- **Type III**
  - some may allow ferromagnetic order
  - $F + \{R'|t\}F$
  - $P_F + R'P_F$
  - $F + \{R|t\}F = H$

- **Type IV**
  - antiferromagnetic order
  - (ferromagnetism not allowed)
  - $F + \{1'|t\}F$
  - $P_F + 1' P_F$
  - $F + \{1|t\}F = H$

**antitranslation / anticentering**

(Type II are the grey groups …..)
Type of MSG depends on the propagation vector of the magnetic ordering:

- Most magn. orderings are 1k-magnetic structures.
- 1k-magnetic structures: moment changes from one unit cell to another according to a single wave vector or propagation vector \( \mathbf{k} \).
- Phase factor for unit cell \( \mathbf{T} \): \( \exp(-i2\pi\mathbf{k}.\mathbf{T}) \)
- The lattice translations such that \( \exp(-i2\pi\mathbf{k}.\mathbf{T})=1 \) define the lattice maintained by of the magnetic structure.
- The lattice translations such that \( \exp(-i2\pi\mathbf{k}.\mathbf{T})=-1 \), are kept as antitranslations (type IV MSG). Only occur if \( nk=\text{recipr. lattice vector with } n=\text{even} \)

![Diagram showing multiple k structures](image)

Multiple k structures: analogous situation ...
### General Positions of the Group $P_{bmn2_1}$ (#31.129) [BNS setting]

To display the general positions in the OG setting, please follow this link: $P_{2bm2_1}$ (#31.6.217) [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: $(1|1,0,0), (1|0,1,0), (1|0,0,1), (1'|0,1/2,0)$

<table>
<thead>
<tr>
<th>N</th>
<th>(x,y,z) form</th>
<th>Matrix form</th>
<th>Geom. interp.</th>
<th>Seltz notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$x, y, z, +1$</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>$1 \ +1$</td>
<td>${1</td>
</tr>
<tr>
<td>2</td>
<td>$-x+1/2, -y, z+1/2, +1$</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 &amp; 1/2 \ 0 &amp; -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 &amp; 1/2 \end{pmatrix}$</td>
<td>$2 \ (0,0,1/2) \ 1/4,0,z +1$</td>
<td>${2_001</td>
</tr>
<tr>
<td>3</td>
<td>$-x, y, z, +1$</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>$m \ 0,y,z +1$</td>
<td>${m_{100}</td>
</tr>
<tr>
<td>4</td>
<td>$x+1/2, -y, z+1/2, +1$</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 &amp; 1/2 \ 0 &amp; -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 &amp; 1/2 \end{pmatrix}$</td>
<td>$n \ (1/2,0,1/2) \ x,0,z +1$</td>
<td>${m_{010}</td>
</tr>
<tr>
<td>5</td>
<td>$x, y+1/2, z, -1$</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 &amp; 1/2 \ 0 &amp; 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>$t \ (0,1/2,0) \ -1$</td>
<td>${1'</td>
</tr>
<tr>
<td>6</td>
<td>$-x+1/2, -y+1/2, z+1/2, -1$</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 &amp; 1/2 \ 0 &amp; -1 &amp; 0 &amp; 1/2 \ 0 &amp; 0 &amp; 1 &amp; 1/2 \end{pmatrix}$</td>
<td>$2 \ (0,0,1/2) \ 1/4,1/4,z +1$</td>
<td>${2'001</td>
</tr>
<tr>
<td>7</td>
<td>$-x, y+1/2, z, -1$</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 &amp; 1/2 \ 0 &amp; 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>$b \ 0,y,z -1$</td>
<td>${m'_{100}</td>
</tr>
<tr>
<td>8</td>
<td>$x+1/2, -y+1/2, z+1/2, -1$</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 &amp; 1/2 \ 0 &amp; -1 &amp; 0 &amp; 1/2 \ 0 &amp; 0 &amp; 1 &amp; 1/2 \end{pmatrix}$</td>
<td>$n \ (1/2,0,1/2) \ x,1/4,z -1$</td>
<td>${m'_{010}</td>
</tr>
</tbody>
</table>

$P_{bmn2_1} = Pmn2_1 + \{1'|0,1/2,0\} Pmn2_1$
Tables of magnetic space groups ("standard" settings)

1.- E-book: D.B. Litvin: "Magnetic space groups" (Electronic Book)


(listing using only OG setting)

2.- Computer readable listing:

   **ISOTROPY webpage:** http://stokes.byu.edu/iso/magnetic.spacegroups.html

   H.T. Stokes and B.J. Campbell

   (listing using BNS and OG settings)

3.- **Bilbao crystallographic server** (www.cryst.ehu.es)

   (listings using BNS and OG settings)

Here we will always use BNS settings for the MSGs
Magnetic symmetry tools and applications in the BCS:

<table>
<thead>
<tr>
<th>Tool</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGENPOS</td>
<td>General Positions of Magnetic Space Groups</td>
</tr>
<tr>
<td>MWYCKPOS</td>
<td>Wyckoff Positions of Magnetic Space Groups</td>
</tr>
<tr>
<td>MAGNEXT</td>
<td>Extinction Rules of Magnetic Space Groups</td>
</tr>
<tr>
<td>IDENTIFY MAGNETIC GROUP</td>
<td>Identification of a Magnetic Space Group from a set of generators in an arbitrary setting</td>
</tr>
<tr>
<td>MAXMAGN</td>
<td>Maximal magnetic space groups for a given a propagation vector and resulting magnetic structural models</td>
</tr>
<tr>
<td>MAGMODELLIZE</td>
<td>Magnetic structure models for any given magnetic symmetry</td>
</tr>
<tr>
<td>k-SUBGROUPSMAG</td>
<td>Magnetic subgroups consistent with some given propagation vector(s) or a supercell</td>
</tr>
<tr>
<td>MAGNDATA</td>
<td>A collection of magnetic structures with transportable cif-type files</td>
</tr>
<tr>
<td>MVISUALIZE</td>
<td>3D Visualization of magnetic structures with Jmol</td>
</tr>
</tbody>
</table>
Obtain all possible magnetic symmetries for a magnetic phase with propagation vector \((1/2,0,0)\) and parent space group \(Pnma\) (exercise 2)

2. Using \(k\)-SUBGROUPMSMAG obtain the \(k\)-maximal subgroups for the parent space group \(Pnma\) for a propagation vector \(k=(1/2,0,0)\).
Possible magnetic symmetries for a magnetic phase with propagation vector \((1/2,0,0)\) and parent space group \(\text{Pnma}\)

Symmetry operation \(\{1'\}|1/2,0,0\) is present in any case: all MSGs are type IV

\[
\exp(i2\pi \mathbf{k} \cdot \mathbf{a}) = -1
\]

\((\text{magnetic cell} = (2a_p, b_p, c_p))\)
HoMnO$_3$  An Inevitable multiferroic...

parent space group: Pnma, k=(1/2,0,0)

graphic models are depicted assuming collinearity along x (my and mz are symmetry allowed)

Structure reported in 2001, but authors unaware of its multiferroic character
Why the (magnetic) order parameter usually takes “special” directions of higher symmetry in the irrep space?

Domains/variants: symmetry related configurations around a higher-symmetry configuration

$Q_i$ : Symmetry-breaking coordinates

Symmetry-forced extrema
\[ \text{HoMnO}_3 \]

**unit cell:** \(2a_p, b_p, c_p\)

**Magnetic space group:** \(P_{bmn2_1} (31.129)\)

to transform to conventional setting :
\((-b, a, c; 3/8,1/4,0)\)

| WP | + (1'|1/2 0 0) |
|----|---------------|
| 8b | \((x, y, z \mid m_x, m_y, m_z), (-x+1/4, -y, z+1/2 \mid -m_x, -m_y, m_z), (x, -y+1/2, z \mid -m_x, m_y, -m_z), (-x+1/4, y+1/2, z+1/2 \mid m_x, -m_y, -m_z)\) |
| 4a | \((x, 1/4, z \mid 0, m_y, 0), (-x+1/4, 3/4, z+1/2 \mid 0, -m_y, 0)\) |

**Equivalent to the use of space group \(Pnm2_1(31)\) with half cell along \(a\):**

**Atomic positions of asymmetric unit:**

\[
\begin{align*}
\text{Ho1} & \quad 4a \quad 0.04195 \quad 0.25000 \quad 0.98250 \\
\text{Ho2} & \quad 4a \quad 0.95805 \quad 0.75000 \quad 0.01750 \\
\text{Mn1} & \quad 8b \quad 0.00000 \quad 0.00000 \quad 0.50000 \\
\text{O1} & \quad 4a \quad 0.23110 \quad 0.25000 \quad 0.11130 \\
\text{O12} & \quad 4a \quad 0.76890 \quad 0.75000 \quad 0.88870 \\
\text{O2} & \quad 8b \quad 0.16405 \quad 0.05340 \quad 0.70130 \\
\text{O22} & \quad 8b \quad 0.83595 \quad 0.55340 \quad 0.29870 \\
\end{align*}
\]

**Magnetic moments of the asymmetric unit (\(\mu_B\)):**

\[
\begin{align*}
\text{Mn1} & \quad 3.87 \quad \approx 0.0 \quad \approx 0.0 \\
\end{align*}
\]

**General position:**
\(x, y, z\) not restricted by symmetry!

**Magnetic Point Group:** \(mm21'\)

Split independent positions in the lower symmetry

zero values are not symmetry “protected”
Check the symmetry restrictions on the Mn and Ho spins resulting from the symmetry of the magnetic phase of HoMnO$_3$. (exercise 3)

3. Upload the mcif file of HoMnO$_3$ in STRCONVERT. Introduce a non-zero spin component of Ho along x or along z, and try to obtain all the atomic positions and moments within the unit cell by transforming to trivial symmetry P1. Check that the program in both cases (for Ho moment along x or z) gives and error/warning: this means that if the Ho atoms are magnetically ordered in this phase, their magnetic moments can only be directed along b. Come back to the description using the MSG using the back button of the browser and introduce now a non-zero spin component for the Ho atoms along b and transform again to P1 to observe the resulting values for the symmetry-related Ho atoms within the unit cell. Come back to the description using the MSG, and visualize the magnetic structure with Jmol and/or VESTA. Using MVISUALIZE observe the differences between the parent unit cell, the standard unit cell and the unit cell actually used in the description. (file required: 2.HoMnO3.mcif)
Check the symmetry operations present in the magnetic structure of HoMnO$_3$. (exercise 4)

4. Upload the mcif file of HoMnO$_3$ in STRCONVERT. Among the listed symmetry operations identify the anticentering operation \( \{1'|1/2,0,0\} \). Identify also in the list the operations \( \{2_z|3/4,0,1/2\} \) and \( \{2_z'|1/4,0,1/2\} \). Copy/paste the list of symmetry operations and introduce them in the program “IDENTIFY MAGNETIC GROUP” and check the MSG of the structure. (file required: 2.HoMnO3.mcif)
Subgroup of Pnma1’ in a basis: 2a_p, b_p, c_p

1 x,y,z,+1
2 -x+3/4,-y,z+1/2,+1
3 x,-y+1/2,z,+1
4 -x+3/4,y+1/2,z+1/2,+1

centering and “anticentering” translations:
1 x,y,z,+1
2 x+1/2,y,z,-1

Pnma1' = P_a nm2_1 + (1'|000)P_a nm2_1 +(-1|000) P_a nm2_1 + (-1'|000) P_a nm2_1

It is the MSG P_b mn2_1 (31.129) in a non-standard basis
Transformation to its standard setting: (-b, a, c; 3/8,1/4,0)
Effect of the magnetic ordering on the nuclear/lattice structure:

- case 1: no symmetry break for “nuclear structure”

\[
P_{2/m} \rightarrow P_{c2/m}
\]

for the nuclear/lattice structure:

\[
P_{2/m} \rightarrow P_{2/m}
\]

- case 2: symmetry break for “nuclear structure”

\[
P_{nma} \rightarrow P_{mn2_1} (-b_p, a_p, c_p; 1/4,1/4,0)
\]
Von Neumann principle:

- all variables/parameters/degrees of freedom compatible with the symmetry can be present in the total distortion

- Tensor crystal properties are constrained by the point group symmetry of the crystal.

- Reversely: any tensor property allowed by the point group symmetry can exist (large or small, but not forced to be zero)
### Table 1.7. Heesch–Shubnikov Point Groups of Crystals Which May Exhibit Ferromagnetism and Ferroelectricity

(Ascher, 1970) (from 122 point groups)

<table>
<thead>
<tr>
<th>Point group</th>
<th>M and P</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, m′m′2, 3, 3m′, 4, 4m′m′, 6, 6m′m′m′</td>
<td>M</td>
</tr>
<tr>
<td>m′m′2′</td>
<td>M</td>
</tr>
<tr>
<td>2′</td>
<td>M ⊥ z  \ P</td>
</tr>
<tr>
<td>m</td>
<td>M</td>
</tr>
<tr>
<td>m′</td>
<td>M ⊥ z  \ P ⊥ z</td>
</tr>
<tr>
<td>1</td>
<td>No restriction</td>
</tr>
</tbody>
</table>

A. P. Cracknell, "Magnetism in crystalline materials" 1975
Symmetry-constrained tensor properties:

<table>
<thead>
<tr>
<th>Magnetic point group</th>
<th>$Q_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 1'</td>
<td>$\begin{bmatrix} Q_{11} &amp; Q_{12} &amp; Q_{13} \ Q_{21} &amp; Q_{22} &amp; Q_{23} \ Q_{31} &amp; Q_{32} &amp; Q_{33} \end{bmatrix}$</td>
</tr>
<tr>
<td>2, m', 2/m'</td>
<td>$\begin{bmatrix} Q_{11} &amp; Q_{12} &amp; 0 \ Q_{21} &amp; Q_{22} &amp; 0 \ 0 &amp; 0 &amp; Q_{33} \end{bmatrix}$</td>
</tr>
<tr>
<td>2', m, 2'/m</td>
<td>$\begin{bmatrix} 0 &amp; 0 &amp; Q_{13} \ 0 &amp; 0 &amp; Q_{23} \ Q_{31} &amp; Q_{32} &amp; 0 \end{bmatrix}$</td>
</tr>
<tr>
<td>222, m'm'2, m'm'm'</td>
<td>$\begin{bmatrix} Q_{11} &amp; 0 &amp; 0 \ 0 &amp; Q_{22} &amp; 0 \ 0 &amp; 0 &amp; Q_{33} \end{bmatrix}$</td>
</tr>
<tr>
<td>22'2', mm2, (m'm2'), m'mm</td>
<td>$\begin{bmatrix} 0 &amp; Q_{12} &amp; 0 \ Q_{21} &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 0 \end{bmatrix}$</td>
</tr>
<tr>
<td>4, 4', 4/m', 3, 3', 6, 6', 6/m'</td>
<td>$\begin{bmatrix} Q_{11} &amp; Q_{12} &amp; 0 \ -Q_{12} &amp; Q_{11} &amp; 0 \ 0 &amp; 0 &amp; Q_{33} \end{bmatrix}$</td>
</tr>
</tbody>
</table>

A. P. Cracknell,
B. "Magnetism in crystalline materials" 1975
Ferroic properties

HoMnO$_3$

param. phase  antiferrom. phase

$\text{Pnma } 1' \rightarrow \text{P}_{\text{a}nm21}$

index 4  $\rightarrow$  4 total number of domains

point groups

$\text{mmm } 1' \rightarrow \text{mm21}'$

index 2  $\rightarrow$  2 ferroic domains

Secondary symmetry-allowed effect: spontaneous polarization: $P_z$

$\text{Pnma1'} = \text{P}_{\text{an}m21} + (1'|000)\text{P}_{\text{an}m21} + (-1|000)\text{P}_{\text{an}m21} + (-1'|000)\text{P}_{\text{an}m21}$

generators of the four domain configurations:

$\{g_n\} = \{(1|000), (-1|000), (1'|000), (-1'|000)\}$

domains: equivalent energy minima

$(S_1, S_2) = (S, 0)$  $P_z$  $(S_1, S_2) = (0, S)$

Their MSG are equivalent, but not equal in general
The importance of non-magnetic atoms:

The same spin arrangement can produce different MSGs (and different ferroic properties) depending on the symmetry of the parent structure.

$l4/mmm, \mathbf{k}=(1/2,1/2,0)$

$Cmce, \mathbf{k}=(0,0,0)$

$I-42m, \mathbf{k}=(1/2,1/2,0)$

$\text{Pr}_2\text{CuO}_4$

$\text{Gd}_2\text{CuO}_4$

Hypothetical spin configuration on a structure of type $\text{GaMnSe}_4$
Diffraction symmetry (non-polarized)

Non-polarized magnetic diffraction at diffraction vector $H$ is proportional to the component of $F_M(H)$ perpendicular to $H$

$$H = ha^* + kb^* + lc^* = (h,k,l)$$

Consequences of a symmetry operation $\{R, \theta | t\}$:

non-magnetic: $F(H) = e^{i2\pi H \cdot t} F(H.R)$  \hspace{1cm} \text{Intensity}(H.R) = \text{Intensity}(H)$

magnetic: $F_M(H) = \theta \det(R) e^{i2\pi H \cdot t} R \cdot F_M(H.R)$ \hspace{1cm} \text{Intensity}(H.R) = \text{Intensity}(H)$

$$H.t = ht_1 + kt_2 + lt_3$$
$$H.R = (h,k,l) \cdot R$$
Diffraction symmetry (non-polarized) and systematic absences

\[ H = ha^* + kb^* + lc^* \quad = \quad (h,k,l) \]

Extinction rules: (“trivial” cases)

\{1'|0 0 0 \}  
(non-magnetic structures)

\[ F(H) = e^{i2\pi H.t} F(H.R) \quad \rightarrow \quad F(H) = F(H) \]

\[ F_M(H) = \theta \det(R) e^{i2\pi H.t} R. F_M(H.R) \quad \rightarrow \quad F_M(H) = - F_M(H) \]

\{1'|0 0 1/2 \}  
(type IV MSG)

\[ F(H) = e^{i\pi l} F(H) \quad \text{Nuclear diffraction: absent } l = \text{ odd} \]

\[ F_M(H) = - e^{i\pi l} F_M(H) \quad \text{Magnetic diffraction: absent } l = \text{ even} \]
Diffraction symmetry (non-polarized) and systematic absences

\[ H = h a^* + k b^* + l c^* = (h, k, l) \]

Extinction rules:

\[ \{2_z \mid 0 \ 0 \ 0 \} \]

- **H**(0,0,\( l \))
- **H.2z** = **H**

\[ F(H) = e^{i2 \pi H.t} F(H) \rightarrow F(H) = F(H) \]

Absence for all (0,0,\( l \))

\[ \{2_z \mid 0 \ 0 \ \frac{1}{2} \} \]

- **H**(0,0,\( l \))
- **H.2z** = **H**

\[ F(H) = e^{i2 \pi H.t} F(H) \rightarrow F(H) = e^{i \pi l} F(H) \rightarrow \]

Absence for \( l \)=odd

\[ F_M(H) = \theta \ det(2_z) \ e^{i2 \pi H.t} 2_z \cdot F_M(H) \rightarrow F_M(H) = e^{i \pi l} 2_z \cdot F_M(H) \]

Absence for **H** presence

Systematic absences for \( \{2'_{ \frac{1}{2}} \mid 0 \ 0 \ \frac{1}{2} \} \)?
**Ba}_5\text{Co}_5\text{ClO}_{13}**

nuclear/positional reflection condition:
\[(2h,-h,l) \quad l=2n\]

**Magnetic diffraction:**
Reflection \((2, -1, 3)\) pure magnetic
\[(2h,-h,l)\]

\(\text{P}_{6_3}'/\text{m'm'c} (194.268):\) absent \(l\) even
present \(l\) odd

\(\text{P}_{6_3}/\text{m'm'c} (194.270):\) absent \(l\) odd

*(spins are symmetry restricted to be along \(c\) in both groups)*
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