Representation analysis vs. Magnetic Groups

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Phase Transition / Symmetry break / Order Parameter

High symmetry group $G_0' = \{g_i\}$

Key concept of a symmetry break: order parameter

Distortion in the structure

$\vec{Q} = Q_1 \vec{d}_1 + \ldots + Q_n \vec{d}_n$

Distortion after application of $g_i$

$\vec{Q}' = Q'_1 \vec{d}_1 + \ldots + Q'_n \vec{d}_n$

Irreducible representation of $G$ (irrep) (matrices)

$T(g) \vec{Q} = \vec{Q}'$

$T(g)$: one nxn matrix for each operation $g$ of $G$

distortions: Vectors in a multidimensional space
Phase Transition / Symmetry break / Order Parameter

High symmetry group $G = \{g\}$

Irreducible representation of $G$ (irrep) (matrices)

T(g) $\vec{Q} = \vec{Q}$

T(g) $\vec{Q} = \vec{Q}' \neq \vec{Q}$

g belongs to $F$

g does not belong to $F$: $\vec{Q}'$ equivalent but distinguishable state (domain)

Key concept of a symmetry break

Order parameter $Q = (Q_1, Q_2) = \rho (a_1, a_2)$

$\ a_1^2 + a_2^2 = 1$

High symmetry group F: isotropy subgroup

For special directions of $Q$, $F$ of higher symmetry: epikernels

For general direction of $Q$, the lowest $F$: kernel

amplitude
Invariance equation:

\[ T[(\mathbf{R}, \theta|\mathbf{t})] = \begin{pmatrix} a & b \\ \vdots & \vdots \\ a & b \end{pmatrix} \]

\((\mathbf{R}, \theta|\mathbf{t})\) is a nxn matrix of irrep.

isotropy subgroups:

epikernels of the irrep, depending on the direction (a,a,...), (a,0,...), etc...

kernel of the irrep: operations represented by the unit matrix. MSG kept by any direction (a,b,...)
Single irrep assignment vs. magnetic space groups (MSG) in commensurate structures. Cases

1) 1-dim. irrep: irrep and MSG assignment are equivalent for defining the constraints on the atomic magn. moments
Description in terms of irreps

\[ Pn'ma' \text{ === one irrep} \]  
(Irrep = irreducible representation)

<table>
<thead>
<tr>
<th>Character Table</th>
<th>#</th>
<th>(2_z)</th>
<th>(2_y)</th>
<th>(2_x)</th>
<th>(-1)</th>
<th>(m_z)</th>
<th>(m_y)</th>
<th>(m_x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pnma)</td>
<td>(\Gamma_1^+)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(Pn'm'a)</td>
<td>(\Gamma_3^+)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(Pn'ma')</td>
<td>(\Gamma_2^+)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(Pnm'a)</td>
<td>(\Gamma_4^+)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>(Pn'm'a')</td>
<td>(\Gamma_1^-)</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(Pn'ma')</td>
<td>(\Gamma_3^-)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(Pnm'a)</td>
<td>(\Gamma_2^-)</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(Pn'ma)</td>
<td>(\Gamma_4^-)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ k=0 \quad 2_z, 2_y, 2_x, -1', m_z, m_y, m_x \]

\[ 1, -1, 1, -1, 1, -1, 1 \]
Example: parent space group Pnma (Pnma1')

\[ k=0 \quad 8 \text{ possible irreps, all 1-dim} \]

One to one correspondence between each irrep and one MSG
Maximal magnetic space groups for the parent space group 62 (Pnma) and the propagation vector \( k = (0, 0, 0) \)

Only non-zero moments for the MSGs associated with the irreps present in the magnetic representation

<table>
<thead>
<tr>
<th>N</th>
<th>Group (BNS)</th>
<th>Transformation matrix</th>
<th>General positions</th>
<th>Systematic absences</th>
<th>Magnetic structure</th>
</tr>
</thead>
</table>
| 1  | \( Pn'm'a' \) (#62.449) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |
| 2  | \( Pn'm'a' \) (#62.448) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |
| 3  | \( Pn'm'a' \) (#62.447) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |
| 4  | \( Pn'm'a' \) (#62.446) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |
| 5  | \( Pnma' \) (#62.445) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |
| 6  | \( Pn'm'a' \) (#62.444) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |
| 7  | \( Pn'm'a' \) (#62.443) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |
| 8  | \( Pnma \) (#62.441) | \[
\begin{pmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1 \\
\end{pmatrix}
\] | Show | Show | Show |

mGM4+
mGM3+
mGM2+
mGM1+
Filter in \textit{k-SUBGROUPSMAG} restricting to one or more irreps

\textbf{Space group of the paramagnetic phase: }Pnma (No. 62)
\textbf{Choose the irreducible representation(s) for each propagation vector}

If no Wyckoff position has been given, a general position will be assumed

\textbf{Non bolded irreps are incompatible with the given Wyckoff positions}
\textbf{Bolded irreps} are compatible with at least one given Wyckoff position
\textbf{Red colored irreps} are compatible with all the Wyckoff positions given

\textbf{Possible magnetic irreducible representations}

\textbf{Propagation wave-vector(s)}
\textbf{GM:}(0,0,0)

\textbf{Decomposition of the magnetic representation(s) into irreps.}
\textbf{4b:}(0,0,1/2)

\[ \rightarrow \quad 3 \times \text{mGM}+1(1) \oplus 3 \times \text{mGM}2+1(1) \oplus 3 \times \text{mGM}3+1(1) \oplus 3 \times \text{mGM}4+1(1) \]

\textbf{Choose the representation(s)}
\begin{tabular}{l}
\textbf{Irreps:} & \text{mGM}1+1(1) & \text{mGM}2+1(1) & \text{mGM}3+1(1) & \text{mGM}4+1(1) & \text{mGM}1-1 & \text{mGM}2-1 & \text{mGM}3-1 & \text{mGM}4-1 \\
\end{tabular}

Submit
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>$(x,y,z \mid m_x,m_y,m_z)$ $(x+1/2,-y+1/2,-z+1/2 \mid -m_x,m_y,m_z)$ $(-x,y+1/2,-z \mid -m_x,m_y,-m_z)$ $(-x+1/2,-y,z+1/2 \mid m_x,m_y,-m_z)$ $(-x,-y,-z \mid m_x,m_y,m_z)$ $(-x+1/2,y+1/2,z+1/2 \mid -m_x,m_y,m_z)$ $(x,-y+1/2,z \mid -m_x,m_y,-m_z)$ $(x+1/2,y,-z+1/2 \mid m_x,m_y,-m_z)$</td>
</tr>
<tr>
<td>4</td>
<td>c</td>
<td>$(x,1/4,z \mid 0,m_y,0)$ $(x+1/2,1/4,-z+1/2 \mid 0,m_y,0)$ $(-x,3/4,-z \mid 0,m_y,0)$ $(-x+1/2,3/4,z+1/2 \mid 0,m_y,0)$</td>
</tr>
<tr>
<td>4</td>
<td>b</td>
<td>$(0,0,1/2 \mid m_x,m_y,m_z)$ $(1/2,1/2,0 \mid -m_x,m_y,m_z)$ $(0,1/2,1/2 \mid -m_x,m_y,-m_z)$ $(1/2,0,0 \mid m_x,m_y,-m_z)$</td>
</tr>
<tr>
<td>4</td>
<td>a</td>
<td>$(0,0,0 \mid m_x,m_y,m_z)$ $(1/2,1/2,1/2 \mid -m_x,m_y,m_z)$ $(0,1/2,0 \mid -m_x,m_y,-m_z)$ $(1/2,0,1/2 \mid m_x,m_y,-m_z)$</td>
</tr>
</tbody>
</table>

irrep basis spin modes equivalent to Wyckoff position constraints

$A_x$ mode along $x$

$F_y$ mode along $y$ weak ferromagnet

$G_z$ mode along $z$
Single irrep assignment vs. magnetic space groups (MSG) in commensurate structures. Cases

1) 1-dim. irrep: irrep and MSG assignment are equivalent for spin relations.

It includes the case of 1k-structures with $k \neq 0$ and $-k$ equivalent to $k$, and the small irrep active being 1-dim.
1k magn. structure with -k equiv. to k and small irrep 1-dim: MSG and irrep assignment equivalent for spin constraints

ErAuGe

Paramagnetic symmetry: $P6_3mc1'$

$k = (1/2, 0, 0)$ (point M in the BZ)

Magnetic phase symmetry: $P_{Cna21}$ (#33.154)

<table>
<thead>
<tr>
<th>Label</th>
<th>Atom type</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Symmetry constraints on M</th>
<th>$M_x$</th>
<th>$M_y$</th>
<th>$M_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er1</td>
<td>Er</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.25</td>
<td>$2m_y, m_y, m_z$</td>
<td>0.0</td>
<td>0.0</td>
<td>8.8</td>
</tr>
</tbody>
</table>

irrep star: 3 k
dim. extended small irrep: 1

dim. full irrep: 3

Irreps $mM_i$

One to one correspondence MSG : irrep

However it is convenient to know that the magnetic point group is $mm21'$ ....

and the effective space group for atomic positions in case of magnetostructural non-negligible effects is: $Cmc2_1$ ....
Single irrep assignment vs. magnetic space groups (MSG) in commensurate structures. Cases

1) 1-dim. irrep: irrep and MSG assignment are equivalent for spin relations.

2) N dim. irrep, N>1: several MSG (epikernels or isotropy subgroups of the irrep) are possible for the same irrep. The MSG depends on the way the spin basis functions are combined. The assignment of a MSG restricts the magnetic configuration beyond the restrictions coming from the irrep.
Single irrep assignment vs. magnetic space groups (MSG) in commensurate structures. Cases

1) 1-dim. irrep: irrep and MSG assignment are equivalent for spin relations.

2) N dim. irrep, N>1: several MSG (epikernels or isotropy subgroups of the irrep) are possible for the same irrep. The assignment of a MSG restricts the magnetic configuration beyond the restrictions coming from the irrep.

  case 2.1: The MSG is a k-maximal subgroup: it only allows a spin ordering according to a single irrep (further restricted to fulfill the MSG constraints). No other irrep arrangements are compatible with the MSG.
Parent space group: 

$P4_2/mnm$ (N. 136)

Propagation vector: 
k = (0,0,0)

Magnetic site: 
Cr 4e (0,0,z)

File: 6.Cr2WO6_parent.cif
K-SUBGROUPS

SMAG: maximal subgroups
Maximal magnetic space groups for the parent space group 136 (P4_2/mnm) and the propagation vector \( k = (0, 0, 0) \)

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

<table>
<thead>
<tr>
<th>N</th>
<th>Group (BNS)</th>
<th>Transformation matrix</th>
<th>General positions</th>
<th>Properties</th>
<th>Magnetic structure</th>
</tr>
</thead>
</table>
| 1 | P4_2/mnm' (#136.503) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 2 | P4_2/mnm' (#136.502) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 3 | P4_2/mnm' (#136.501) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 4 | P4_2/mnm' (#136.500) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 5 | P4_2/mnm' (#136.499) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 6 | P4_2/mnm' (#136.496) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 7 | P4_2/mnm' (#136.497) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 8 | P4_2/mnm' (#136.495) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 9 | Cmm'm' (#65.486) | \[
\begin{pmatrix}
1 & 1 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 10 | Cmm'm' (#65.483) | \[
\begin{pmatrix}
1 & 1 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
| 11 | Pmm'm' (#65.388) | \[
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\] | Alternatives (domain-related) | Systematic absences | Tensor properties |
Magnetic site splits into two independent sites

Two spin parameters to be fit

Cr1_1 (mx,-mx,0)
Cr1_2 (mx',-mx',0)
Only ONE independent magnetic site. But two independent spin components. Spin canting symmetry allowed

Two spin parameters to be fit
Irrep mGM5+:

2 d.f.
2 basis f.

\( P4_2/mnm1' \)

2 d.f.
2 basis f.

\( Cmm'm' \)

2 d.f.
2 basis f.

\( Pnn'm' \)

4 degrees of freed.
4 basis functions

\( P2'/m' \)

Irrep mGM5-:

2 d.f.
2 basis f.

\( P4_2/mnm1' \)

2 d.f.
2 basis f.

\( Cm'mm \)

2 d.f.
2 basis f.

\( Pn'n'm \)

4 degrees of freed.
4 basis functions

\( P2'/m \)

Invariance equation:

\[
T[(R, \theta|t)] \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}
\]

2x2 matrix of irrep

\( (R, \theta|t) \) is conserved by the magnetic arrangement

possible MSGs depending on the direction of the order parameter \((a,b)\)
Invariance equation:

\[ T[(R, \theta|t)] \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix} \]

\( (R, \theta|t) \) is conserved by the magnetic arrangement

**isotropy subgroups:**

epikernels of the irrep, depending on the direction (a,a), (a,0), etc...

kernel of the irrep: operations represented by the unit matrix. MSG kept by any direction (a,b)
Programs that determine the epikernels and kernel of any irrep, and produce magnetic structural models complying with them.

Program for mode analysis:
ISODISTORT
http://stokes.byu.edu/iso/isotropy.php  Stokes & Campbell, Provo

Both programs also support incommensurate cases, deriving epikernels and kernel of the irreps in the form of MSSGs, and corresponding magnetic models

Program for structure refinement:
http://jana.fzu.cz/  V. Petricek, Prague

diffraction peaks:

 propagation vector $k=(1/2 \ 0 \ 0)$ : point X

symmetry operation kept: \( \{1'|1/2 \ 0 \ 0\} \)

$1'$ belongs to the point group of the magnetic phase
Space group: Pnma
propagation vector \( k = (1/2 \ 0 \ 0) \) (point X)
Single irrep assignment vs. magnetic space groups (MSG) in commensurate structures. Cases

1) 1-dim. irrep: irrep and MSG assignment are equivalent for spin relations.

2) N dim. irrep, N>1: several MSG (epikernels or isotropy subgroups) are possible for the same irrep. The assignment of a MSG restricts the magnetic configuration beyond the restrictions coming from the irrep.

   case 2.1: The MSG is a k-maximal subgroup: it only allows a spin ordering according to a single irrep (further restricted to fulfill the MSG constraints). No other irrep arrangements are compatible with the MSG.

   case 2.2: The MSG is \textbf{NOT} a k-maximal subgroup: it allows the presence of other irreps (secondary). Other irreps are compatible with the MSG. (for simple propagation vectors (2k=reciprocal lattice) not frequent)
NiO

Parent space group: \textbf{Fm-3m}

\textbf{k} = (1/2, 1/2, 1/2) – point L in the BZ

\textbf{MSG}: \textbf{C}_c2/c

\textbf{M}_{\text{Ni}} = m(1,1,-2)

(a/4 + b/4 - c/2, a/4 - b/4, -a/2 - b/2; 0, 0, 0)
NiO parent space group: Fm-3m

\[ \mathbf{k} = (1/2, 1/2, 1/2) \] – point L in the BZ

Ni site 4a \((0,0,0)\)

little group of \(\mathbf{k}\): R-3m

\[ M_{\text{rep}} = mL^{2+} + mL^{3+} \]

1-dim 2-dim

Relation between the irrep description and the one using a MSG in the case NiO (exercise 13)

Use k-SUBGROUPPSMAG to obtain for the possible active irreps the possible resulting magnetic symmetries.
\[ M_{\text{rep}}(\text{site } 4a) = mL^2 + mL^3 \]

- 1-dim
- 2-dim

Diagram:
- Magnetic site 4a
- \( mL^2 \)
- \( mL^3 \) (a,a)
- \( mL^3 \) (a,0)
- \( mL^3 \) (a,b)
- \( \text{C}_2/c \)
- \( \text{C}_2/m \)
- \( P_{\bar{S}\bar{I}} \)
**NiO**  
parent space group: Fm-3m  
\[ k = (1/2,1/2,1/2) \] – point L in the BZ  
little group of \( k \): R-3m  
\[ M_{\text{rep}} = m\text{L}^2+ + m\text{L}^3+ \]  
1-dim 2-dim

**Table 5**  Epikernels and kernels of some magnetic irreps of \( Fm\bar{3}m' \) at the L point of the Brillouin zone

<table>
<thead>
<tr>
<th>Irrep</th>
<th>Order parameter direction</th>
<th>Magnetic space group</th>
<th>Transformation to standard</th>
<th>Spin degrees of freedom</th>
<th>Ni spin basis modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL2+</td>
<td>(a)</td>
<td>( R_{f}\bar{3}c ) (#167.108)</td>
<td>((-a_p/2 + c_p/2, b_p/2 - c_p/2, -2a_p - 2b_p - 2c_p; 0, 0, 0))</td>
<td>1</td>
<td>(1, 1, 1)</td>
</tr>
<tr>
<td></td>
<td>(a, 0)</td>
<td>( C_{2/c} ) (#12.63)</td>
<td>((a_p/2 + b_p/2 - c, a_p/2 - b_p/2, -a_p - b_p; 0, 0, 0))</td>
<td>1</td>
<td>(1, -1, 0)</td>
</tr>
<tr>
<td>mL3+</td>
<td>(a, a)</td>
<td>( C_{2/c} ) (#15.90)</td>
<td>((a_p/2 + b_p/2 - c, a_p/2 - b_p/2, -a_p - b_p; 0, 0, 0))</td>
<td>1</td>
<td>(1, 1, -2)</td>
</tr>
<tr>
<td></td>
<td>(a, b)</td>
<td>( P_{\bar{S}1} ) (#7.28)</td>
<td>((-b_p/2 + c_p/2, a_p/2 - b_p/2, a_p + c_p; 0, 0, 0))</td>
<td>2</td>
<td>(1, -1, 0)</td>
</tr>
</tbody>
</table>
Possible alternative model for NiO of maximal symmetry for the same irrep mL3+ (exercise 14)

Using k-SUBGROUPSMAG and MAGMODELIZE obtain an mcif file of the alternative model for NiO with symmetry $C_{c2/m}$, which can result if the irrep mL3+ is the active one and visualize it. (file required: 6.NiO_parent.cif).
\[ \text{Ca}_3\text{LiOsO}_6 \]

(Calder et al PRB 2012)

**Paramagnetic symmetry:** R-3c1 1’

**Magnetic space group of magnetic phase:**

\[ \mathbf{C2’/c’} \quad (\text{monoclinic axis along x}) \]

Predicted to be weak ferromagnet along \( z \) and along \((1,2,0)_H\) (perp. to the monoclinic axes)

<table>
<thead>
<tr>
<th>Label</th>
<th>Atom type</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Symmetry constraints on M</th>
<th>( M_x )</th>
<th>( M_y )</th>
<th>( M_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>Os</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>( m_x, m_y, m_z )</td>
<td>2.2000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

They can be non-zero. They are symmetry-forced to be equal for all atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Symmetry constraints on M</th>
<th>( M_x )</th>
<th>( M_y )</th>
<th>( M_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.3333</td>
<td>( m_x, m_y, m_z )</td>
<td>2.2000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>2</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.6667</td>
<td>( m_x, m_y, m_z )</td>
<td>2.2000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>3</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>( m_x, m_y, m_z )</td>
<td>2.2000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>4</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.5000</td>
<td>( -m_x + m_y, m_y, m_z )</td>
<td>-2.2000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>5</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.1667</td>
<td>( -m_x + m_y, m_y, m_z )</td>
<td>-2.2000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>6</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.8333</td>
<td>( -m_x + m_y, m_y, m_z )</td>
<td>-2.2000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
Our example: \( \text{Ca}_3\text{LiOsO}_6 \)

Isotropy subgroups (kernel and epikernels) of \( \text{mGM3}^+ \):

- **irrep \( \text{mGM3}^+ \) (2-dim irrep)**:
  - \( R-3c1' \)

- **Especial directions 1**: \( C2/c \)

- **Especial directions 2**: \( C2'/c' \)

Specific combinations of the irrep basis modes (from Basirreps, for instance)

Invariance equation:

\[
T[(R, \theta|t)] \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}
\]

\( (R, \theta|t) \) is conserved by the magnetic arrangement

- **kernel**: common to any \( \text{mGM3}^+ \) ordering

**Isotropy subgroups (kernel and epikernels) are derived by programs as**: ISODISTORT or JANA2006
Possible different magnetic space groups for the same irrep

For any phase \( \alpha \) of the order parameter \( Q \), symmetry operations \{1|000\} and \{-1|000\} plus the lattice are conserved:

- If \( \alpha = 0, \pi \) \( \{2_x|000\} \) and \( \{m_x|000\} \)
- If \( \alpha = 2\pi/3, -2\pi/6 \) \( \{2_x|000\} \) and \( \{m_x|000\} \)
- If \( \alpha = -2\pi/3, 2\pi/6 \) \( \{2_y|000\} \) and \( \{m_y|000\} \)
- If \( \alpha = \pi/2, -\pi/2 \) \( \{2_{xy}|000\} \) and \( \{m_{xy}|000\} \)
- If \( \alpha = -5\pi/6, \pi/6 \) \( \{2_x|000\} \) and \( \{m_x|000\} \)
- If \( \alpha = -\pi/6, 5\pi/6 \) \( \{2_y|000\} \) and \( \{m_y|000\} \)

For any phase \( \alpha \) of the order parameter \( Q \). symmetry operations \{1|000\} and \{-1|000\} plus the lattice are conserved

\( Q = (S, S^*) \quad Q = \rho e^{i\alpha} \)

\( C2/c \quad C2'/c' \)
Basirreps output

Magnetic representation: \( \text{mGM1}^+ + \text{mGM2}^+ + 2\text{mGM3}^+ \)

\[
\begin{align*}
\text{SYM} & \quad x, y, z \\
\text{Atoms} & \quad \text{Atoms}\text{ 0s}_1 & \quad \text{Atoms}\text{ 0s}_2
\end{align*}
\]

\begin{align*}
\text{BsU( 1, 1: 2)}: & \quad \text{Re} (1.00 0.00 0.00) (0.00 0.00 0.00) \\
& \quad \text{Im} (-0.50 -1.15 0.00) (0.00 0.00 0.00) \\
\text{BsU( 2, 1: 2)}: & \quad \text{Re} (0.00 0.00 0.00) (0.00 0.00 0.00) \\
& \quad \text{Im} (0.50 1.15 0.00) (1.15 0.50 0.00) \\
\text{BsU( 3, 1: 2)}: & \quad \text{Re} (0.00 0.00 0.00) (0.00 0.00 0.00) \\
& \quad \text{Im} (0.50 -1.15 0.00) (-1.15 0.50 0.00) \\
\text{BsU( 4, 1: 2)}: & \quad \text{Re} (1.00 0.00 0.00) (0.00 0.00 0.00) \\
& \quad \text{Im} (0.50 1.15 0.00) (0.00 0.00 0.00)
\end{align*}

The Fourier coefficients are LINEAR COMBINATIONS of Basis Functions: coefficients u,v,w,p,q ...(may be complex!)

The general expressions of the Fourier coefficients \( \text{Sk}(j) \) of the atoms non-related by lattice translations are the following:

\[
\begin{align*}
\text{SYM} & \quad x, y, z \\
\text{Sk}(1): & \quad (u+p,0,0)+i.(-r_0.u+r_0.p,-r_1.u+r_1.p,0) \\
\text{SYM} & \quad y, x, -z+1/2 \\
\text{Sk}(2): & \quad (0,u+v,0)+i.(r_1.v-r_1.w,r_0.v-r_0.w,0)
\end{align*}
\]

Values of real constants \( r_0,r_1,... \)

\[
\begin{align*}
\text{r0} = & \quad 0.57735 & \text{r1} = & \quad 1.15470
\end{align*}
\]
Sarah output  Transformation to basis functions

mGM3$^+$ irrep

<table>
<thead>
<tr>
<th>IR # 6, BASIS VECTOR: #</th>
<th>1 (ABSOLUTE NUMBER:# 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATOM 1:</td>
<td>(6 0 0 0) + i(0 0 0 0)</td>
</tr>
<tr>
<td>ATOM 2:</td>
<td>(0 0 0 0) + i(0 0 0 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IR # 6, BASIS VECTOR: #</th>
<th>2 (ABSOLUTE NUMBER:# 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATOM 1:</td>
<td>(0 0 0 0) + i(0 0 0 0)</td>
</tr>
<tr>
<td>ATOM 2:</td>
<td>(0 6 0 0) + i(0 0 0 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IR # 6, BASIS VECTOR: #</th>
<th>3 (ABSOLUTE NUMBER:# 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATOM 1:</td>
<td>(0 0 0 0) + i(0 0 0 0)</td>
</tr>
<tr>
<td>ATOM 2:</td>
<td>(6.928 3.464 0 0) + i(0 0 0 0)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IR # 6, BASIS VECTOR: #</th>
<th>4 (ABSOLUTE NUMBER:# 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ATOM 1:</td>
<td>(-3.464-6.928 0 0) + i(0 0 0 0)</td>
</tr>
<tr>
<td>ATOM 2:</td>
<td>(0 0 0 0) + i(0 0 0 0)</td>
</tr>
</tbody>
</table>

4 basis functions: 4 parameters
For multidimensional irreps, assigning an irrep is NOT equivalent to the assigning of a magnetic space group:

Our example: \( \text{Ca}_3\text{LiOsO}_6 \)

Magnetic symmetry is MORE restrictive than assigning an irrep…

<table>
<thead>
<tr>
<th>Label</th>
<th>Atom type</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>Symmetry constraints on ( M )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>Os</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>( m_x, m_y, m_z )</td>
</tr>
</tbody>
</table>

3 parameters
Space group: R-3c
propagation vector $k = (0\ 0\ 0)$ (GM point)
Magnetic symmetry is MORE restrictive than assigning an irrep...

BUT also LESS restrictive than assigning an irrep !:

Irrep mGM3+ restricts the spins to the xy plane (R-setting), but the magnetic group C2′/c′ allows a FM component along z.

GM3+, displacive modes (magneto-structural coupling) (strain)

C2/c1′  R-3c1′

mGM2+, FM spins along z
1 parameter (mz)

C2′/c′  R-3c′

mGM3+, special combination of irrep basis modes)
(special direction of the OP)
2 parameters (mx,my)
R-3c1', C2/c1', R-3c', C2'/c', mGM3+, special combination of irrep basis modes

mGM2+, FM spins along z

mGM3+, displacive modes (magneto-structural coupling)

C2'/c' symmetry: mGM3+ distortion restricted to C2'/c' symmetry: (2 parameters)

mGM2+ distortion (R-3c' symmetry): (1 parameter)

C2'/c' symmetry (all compatible irreps allowed)

The same symmetry change as in classical weak ferromagnets NiCO₃, CoCO₃, MnCO₃

<table>
<thead>
<tr>
<th>atom</th>
<th>x, y, z</th>
<th>moment restrictions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>0,0,0</td>
<td>mx, my, 0</td>
</tr>
</tbody>
</table>

<table>
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<tr>
<th>atom</th>
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<th>moment restrictions</th>
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<tr>
<td>Os</td>
<td>0,0,0</td>
<td>0,0, mz</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Label</th>
<th>Atom type</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Symmetry constraints on M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Os</td>
<td>Os</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>mₓ, mᵧ, mž</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mₓ</th>
<th>Mᵧ</th>
<th>Mₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.20000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
</tbody>
</table>
Why an MSG may allow the presence of secondary irreps?

….because the symmetry of the primary magnetic ordering allows adequate couplings which can induce their appearance without any additional symmetry break.

No need to make a book keeping of these possible couplings… The MSG does it for us!:

All irrep modes compatible with the MSG have adequate couplings with the primary order parameter to allow their non-zero value.

One can always find a symmetry-consistent microscopic mechanism explaining its existence as an induced effect (Dzyaloshinski-Moriya…)
Symmetry-allowed coupling inducing weak FM along z (mGM2+)

\[ Q = (S, S^*) \]

\[ S = \rho e^{i\alpha} \]

\[ (S^3 + S^*) \]

\[ (S^3 - S^*) \]

\[ (S^3 + S^*) \]

\[ (S^3 - S^*) \]

Allowed energetical coupling terms:

\[ S_1: mGM1+ \]
\[ (S^3 + S^*) S_1 \approx \rho^3 \cos (3\alpha) S_1 \]
\[ S_2: mGM2+ \]
\[ (S^3 - S^*) S_2 \approx \rho^3 \sin (3\alpha) S_2 \]

\[ C2'/c': \]
\[ S_1 = 0, S_2 \alpha \rho^3 \]
\[ \alpha = n\pi/3 + \pi/2 \]
\[ mGM2+ \]
\[ S_2 = \text{FM component along } z \]

\[ C2/c: \]
\[ S_1 \alpha \rho^3, S_2 = 0 \]
\[ \alpha = n\pi/3 \]
\[ mGM1+ \]
Single irrep assignment vs. magnetic space groups (MSG) in commensurate structures. Cases

1) 1-dim. irrep: irrep and MSG assignment are equivalent for spin relations.

2) N dim. irrep, N>1: several MSG (epikernels or isotropy subgroups) are possible for the same irrep. The assignment of a MSG restricts the magnetic configuration beyond the restrictions coming from the irrep.

   case 2.1: The MSG is a k-maximal subgroup: it only allows a spin ordering according to a single irrep (further restricted to fulfill the MSG relations). No other irrep arrangements are compatible with the MSG.

   case 2.2: The symmetry allows the presence of other secondary irreps. Other irrep arrangements are compatible with the MSG.

   Exceptionally: two different irreps may have the same MSG as epikernel....
Conclusions:

• Properties of magnetic phases are constrained by their magnetic symmetry: a magnetic space group (if commensurate) or superspace group (if incommensurate)

• Whatever method one has employed to determine a magnetic structure, the final model should include its magnetic symmetry.

• Representation analysis of magnetic structures is NOT in general equivalent to the use of magnetic symmetry (i.e. to give an irrep is not equivalent to give the magnetic space (superspace) group of the system)

• The best approach: to combine both representation analysis and magnetic symmetry
Acknowledgements:

The past and present team in Bilbao of the...

**present:**
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- E. Tasci
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- S. V. Gallego
- L. Elcoro
- G. Madariaga

**past:**
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- C. Capillas
- E. Kroumova
- S. Ivantchev

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