Representation analysis vs. Magnetic Symmetry

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A symmetry operation in a solid **IS NOT** only a more or less complex transformation leaving the solid 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 : "**phase-forced**"
"**symmetry-allowed**” means : "**phase-allowed**"

**symmetry-forced properties can be considered symmetry “protected”**
“It is only slightly overstating the case to say that physics is the study of symmetry”

P. W. Anderson

This magnetic order splits the U atoms into two types

This phase allows that the two U atoms have different non-related moments

There is NO symmetry reason to expect that the orientation of the moments of the two atoms have the very specific relation assumed in the model: it is not symmetry "protected"

This orientation is not expected to be special (extremal) in the energy map
**Ba$_3$Nb$_2$NiO$_9$**  
*PRL.* (2012) 109 257205

Paramagnetic symmetry: P-3m1 1’  
\[ \mathbf{k} = (1/3,1/3,1/2) \]

Magnetic phase symmetry: $P_c 31c$

Moment orientation on the plane xy is “symmetry-protected”

Moment along z symmetry allowed, but negligible

Point group symmetry break: -3m $\rightarrow$ 3m

<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>
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</table>

Polar symmetry: 
It allows a non-zero induced ferroelectric polarization along z
CrN  *Phys Rev* (1960) 117 929

Paramagnetic symmetry: Fm-3m1'

\[ \mathbf{k} = (1/2, 1/2, 0) \]

Magnetic phase symmetry: \( P_{\text{anma}} \)

**Magndata 1.28**

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colinear structure – “symmetry protected”

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NO: This symmetry allows a FM component on the plane perp. to the monoclinic axis

Magnetic space group of magnetic phase: C2′/c′ (monoclinic axis along x)

Collinear (symmetry-forced) phase?:

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

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

The 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

\[ G \rightarrow F \]  

\( G \) contains the time reversal operation \( \{1'|0 \ 0 \ 0\} \): 

\[ G = Go + \{1'|0 \ 0 \ 0\} Go \] 

\( Go \): space group 

\( G = Go1' \) grey magnetic group 

\( F \) does not contain the time reversal operation \( \{1'|0 \ 0 \ 0\} \)
Magnetic Symmetry:

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

Time inversion/reversal: 1’

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

Magnetic structures only have symmetry operations where time reversal 1’ is combined with other transformations:

\{1'|t\} = 1' \{1|t\}
\{m'| t\} = 1' \{m'|t\}
\{2'|t\} = 1'\{2|t\}
\{3^+|t\} = 1'\{3^+|t\}, etc. But never 1’ alone …..
\( \text{Ca}_3\text{LiOsO}_6 \) (Calder et al PRB 2012)

Paramagnetic phase (magnetic) space group: \textbf{R-3c1’}

symmetry group : \( k=(0,0,0) \)

\textbf{C2’/c’} (monoclinic axis along \( x_H \))

\( R \) centring translations conserved:

- \( x,y,z,+1 \) \( \{1|000\} \)
- \( x+2/3,y+1/3,z+1/3,+1 \) \( \{1| 2/3 \ 1/3 \ 1/3 \} \)
- \( x+1/3,y+2/3,z+2/3,+1 \) \( \{1| 1/3 \ 2/3 \ 2/3 \} \)

- \( x-y,-y,-z+1/2,-1 \) \( \{2’_x|00\frac{1}{2}\} \)
- \( -x,-y,-z,+1 \) \( \{-1|000\} \)
- \( -x+y,y,z+1/2,-1 \) \( \{m’_x|00\frac{1}{2}\} \)

Operations lost:

- \( \{2_x|00\frac{1}{2}\} \)
- \( \{-1'|000\} \)
- \( \{m_x|00\frac{1}{2}\} \)

Plus all 3-fold rotations, 2-fold operations and glide planes for directions \( y \) and \( xy \), with and without time reversal.
Phase Transition / Symmetry break / Order Parameter

High symmetry group $G_01' = \{g_i\}$

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 $n \times n$ 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)

Group-subgroup relation:

$G \rightarrow F$

F: isotropy subgroup

Second-order phase transition / Symmetry break / Order Parameter

Key concept of a symmetry break

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

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

High symmetry

Low symmetry

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

$g$ belongs to $F$

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

g does not belong to $F$: $\overrightarrow{Q'}$ equivalent
but distinguishable state (domain)
In general, they are NOT equivalent: an active irrep may give place to several alternative magnetic symmetries.

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

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

- \( \text{R-3c1}' \) (2-dim irrep)
- \( \text{C2/c} \) (coincident)
- \( \text{C2'}/\text{c'} \) (2-dim irrep)

Especial directions 1:

- \( \text{P-1} \)

Especial directions 2:

- \( \text{C2/c} \)

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

2x2 matrix of irrep \( \text{mGM3}^+ \)

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

| irrep mGM3+           | \{1|000\} | \{-1|000\} | \{3+|000\} | \{-3+|000\} | \{3-|000\} | \{-3-|000\} | \{2_x|001/2\} | \{m_x|001/2\} | \{2_y|001/2\} | \{m_y|001/2\} | \{2_{xy}|001/2\} | \{m_{xy}|001/2\} |
|-----------------------|----------|----------|----------|----------|----------|----------|---------------|-------------|---------------|-------------|---------------|---------------|---------------|
| \(w^1\) 0 0 1        | 1 0      | w 0      | w* 0     | 0 w*     | 0 w       | 0 1       | \(2^x x|000\) | m_x|001/2 | \(2^y y|000\) | m_y|001/2 | \(2^x_{xy}|000\) | m_{xy}|001/2 |
| All lattice translations: | \{1'|000\} | \{-1'|000\} | \{3'+|000\} | \{-3'+|000\} | \{3'-|000\} | \{-3'-|000\} | \{2'_{xy}|001/2\} | m_{xy}|001/2 | \{2'_{y}|001/2\} | m_{y}|001/2 | \{2'_{xy}|001/2\} | m_{xy}|001/2 |
| \{1|T\}               | 1 0      | -w 0     | -w* 0    | 0 -w*    | 0 -w      | 0 -1      | \(-1 0\)     | \(-1 0\)    | \(-1 0\)     | \(-1 0\)    | \(-1 0\)     | \(-1 0\)     |

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

For any \(\alpha\) - symmetry operations \{1|000\} and \{-1|000\} plus the lattice

If \(\alpha=0,\pi\) \(\{2_{xy}|000\}\) and \(m_{xy}|000\)

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 \(m_y|000\)

\(C2/c\)

If \(\alpha=\pi/2, -\pi/2\) \(\{2'_{xy}|000\}\) and \(m'_{xy}|001/2\)

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 \(m'_{y}|000\)

\(C2'/c'\)
Basirreps output

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

--- 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 Sk(j) of the atoms non-related by lattice translations are the following:

SYMM \(x,y,z\) \(\begin{array}{c|c|c|c|c}\) Atom: Os\(_1\) & 0.0000 & 0.0000 & 0.0000
Sk(1): \((u+p,0,0) + i.(-r_0.u+r_0.p,-r_1.u+r_1.p,0)\)

SYMM \(y,x,-z+1/2\) \(\begin{array}{c|c|c|c|c}\) Atom: Os\(_2\) & 0.0000 & 0.0000 & 0.5000
Sk(2): \((0,v+w,0) + i.(r_1.v-r_1.w,r_0.v-r_0.w,0)\)

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

\(r_0 = 0.57735 \quad r_1 = 1.154700\)
Sarah output  
Transformation to basis functions

\[ m\text{GM3}^+ \text{ irrep} \]

<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>
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<th>IR # 6, BASIS VECTOR:</th>
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<td>ATOM 2:</td>
<td>((0, 6, 0, 0) + i(0, 0, 0, 0))</td>
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<td>ATOM 2:</td>
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</table>

4 basis functions: 4 parameters
In general, 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...

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<td>(m_x, m_y, m_z)</td>
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3 parameters
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)
- mGM3+, special combination of irrep basis modes) (special direction of the OP)
- mGM2+, FM spins along z
  - 1 parameter (mz)
- mGM2+, FM spins along z
  - 2 parameters (mx,my)
Representation analysis vs magnetic space groups

- R-3c1'
- C2/c1'
- R-3c'
- C2'/c'

GM3+, displacive modes (magneto-structural coupling)

mGM2+, FM spins along z
mGM3+, special combination of irrep basis modes
(special direction of the OP)

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

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

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

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<tr>
<th>atom</th>
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A more complex example: HoMnO$_3$ (Muñoz et al. Inorg. Chem. 2001)

$G_p = Pnma$

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

diffraction peaks:

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

1' belongs to the point group of the magnetic phase!!
Why the (magnetic) order parameter usually takes “special” directions of higher symmetry in the irreps space?

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

\(Q_i\) : Symmetry-breaking coordinates

Symmetry-forced extrema
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.
1) Extended small irrep = 1-dim: irrep and MSG assignment are equivalent for spin relations for 1k magn. structure.

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

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

ErAuGe

Paramagnetic symmetry: $P6_3mc1'$

Irreps $mT_i$

Irrep star: 3 $k$

Dim. extended small irrep: 1

Dim. full irrep: 3

One to one correspondence MSG : irrep

MSG type/label may equal, but they are different subgroups of parent one (distinguishable by the matrix relating their standard settings with the one of the parent)
Single irrep assignment vs. magnetic space groups (MSG) in commensurate structures. Cases

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2) N dim. irrep, N>1: several MSG (isotropy subgroups) are possible for the same irrep. The assignment of a MSG restricts the magnetic configuration beyond the restrictions coming from the irrep.
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   case 2.1: The MSG symmetry 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.
2) N dim. irrep, N>1: several MSG (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 symmetry only allows a spin ordering according to a single irrep

Paramagnetic symmetry: Fm-3m1'
\[ k = (1/2, 1/2, 0) \quad \text{star: 12 ks} \]
small irrep: 1 dim  extended small irrep (k,-k: 2 dim)

Magnetic phase symmetry: \( P_{anma} \)

\[ M_{\text{representation}} = mSM2 + mSM3 + mSM4 \]
Space group: Pnma
propagation vector \( k = (1/2 \ 0 \ 0) \) (point \( X \))
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case 2.1: The MSG symmetry 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 MSG symmetry allows the presence of other secondary irreps. Other irrep arrangements are compatible with the MSG. (for simple propagation vectors (2k=reciprocal lattice) not frequent)
Space group: R-3c
propagation vector $k=(0\ 0\ 0)$ (GM point)
Why an MSG may allow the presence of secondary irreps?

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

All irreps compatible with MSG are allowed…. 

One can always find a symmetry-consistent microscopic mechanism explaining its existence as induced effect (for instance, Dzyaloshinski-Moriya….)
\( \text{Ca}_3\text{LiOsO}_6 \) (Calder et al PRB 2012)

**Paramagnetic symmetry:** R-3c1 1’

**Magnetic group magnetic phase:**

**C2'/'c’** (monoclinic axis along x)

**Collinear (symmetry-forced) phase?**:

**NO:** This symmetry allows a FE component on the plane perp. to the monoclinic axis

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>2.0000</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.
Symmetry-allowed coupling inducing weak FM along z (mGM2+)

\[ \mathbf{Q} = (S, S^*) \]

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

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

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

Allowed energetical coupling terms:

\[ S_1: \text{mGM1+} \]
\[ (S^3 + S^*3)S_1 \approx \rho^3 \cos (3\alpha) \]
\[ \text{S}_1 \approx \rho^3 \cos (3\alpha) \]

\[ S_2: \text{mGM2+} \]
\[ (S^3 - S^*3)S_2 \approx \rho^3 \sin (3\alpha) \]
\[ \text{S}_2 \approx \rho^3 \sin (3\alpha) \]

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

**C2/c:** \[ S_1 \alpha \rho^3, \quad S_2 = 0 \]
\[ \alpha = n\pi/3 \quad \text{mGM1+} \]
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 (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 symmetry 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. (for simple propagation vectors (2k=reciprocal lattice) not frequent)
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(for simple propagation vectors (2k=reciprocal lattice) not frequent)

Exceptionally: two different irreps may have the same MSG as isotropy subgroup....
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
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