9-9:50 am I. Symmetry based modeling and description of magnetic structures. The magCIF file format. An overview.

- 10 min coffee break

10-10:50 am II. Magnetic space groups (Shubnikov groups) (50 mins)

- 10 min coffee break

11-12:15 am III. Hands-on demonstration of some Bilbao Crystallographic Server tools I: MAGNEXT, MAXMAGN, MTENSOR, k-SUBGROUPSMAG, MVISUALIZE

http://www.cryst.ehu.es/resources/ORNL2016/

ZTF-FCT
Zientzia eta Teknologia Fakultatea
Facultad de Ciencia y Tecnología

eman ta zabal zazu
Universidad del País Vasco
Euskal Herriko Unibertsitatea

Magnetic Crystallograhy:
Symmetry based modeling and description of magnetic structures

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BILBAO, SPAIN

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

P. W. Anderson

Science, New Series, Vol. 177, No. 4047 (Aug. 4, 1972), 393-396.

Acknowledgements:

The past and present team in Bilbao of the…

bilbao crystallographic server

[The crystallographic site at the Condensed Matter Physics Dept. of the University of the Basque Country]

present:

- M. I. Aroyo
- E. Tasci
- G. de la Flor
- S. V. Gallego
- L. Elcoro
- G. Madariaga

past:

- D. Orobengoa
- C. Capillas
- E. Kroumova
- S. Ivantchev

- J.L. Ribeiro (Braga, Portugal)
- H. Stokes & B. Campbell (Provo, USA) – program ISODISTORT
- V. Petricek (Prague) - program JANA2006
- J. Rodriguez-Carvajal (Grenoble) program FullProf
- K. Momma (Tsukuba) program VESTA
- R. Hanson (Northfield, USA) program Jmol

Symmetry-Based Computational Tools for Magnetic Crystallography

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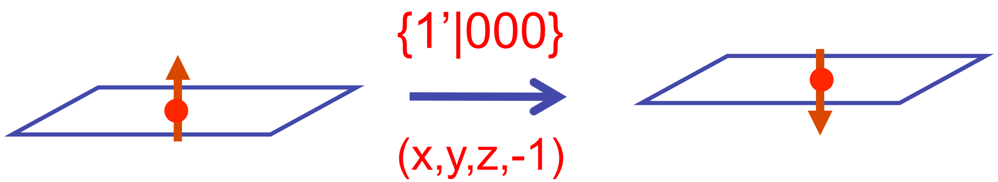
Annu. Rev. Mater. Res. 2015. 45:217–48

Symmetry is only detected when it does not exist!

Magnetic Symmetry: *We do not add but SUBSTRACT symmetry operations !*

Symmetry operation to be considered: Time inversion/reversal: {1'|0,0,0}
(always present in non-magnetic structures but ABSENT in magnetically ordered ones!)
- 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, 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}$\{3^{+}|t\}$, etc.

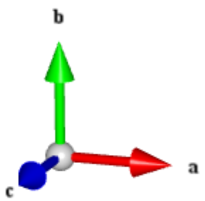
But **{1'|0,0,0}** alone is never a symmetry operation of a magn. struct.

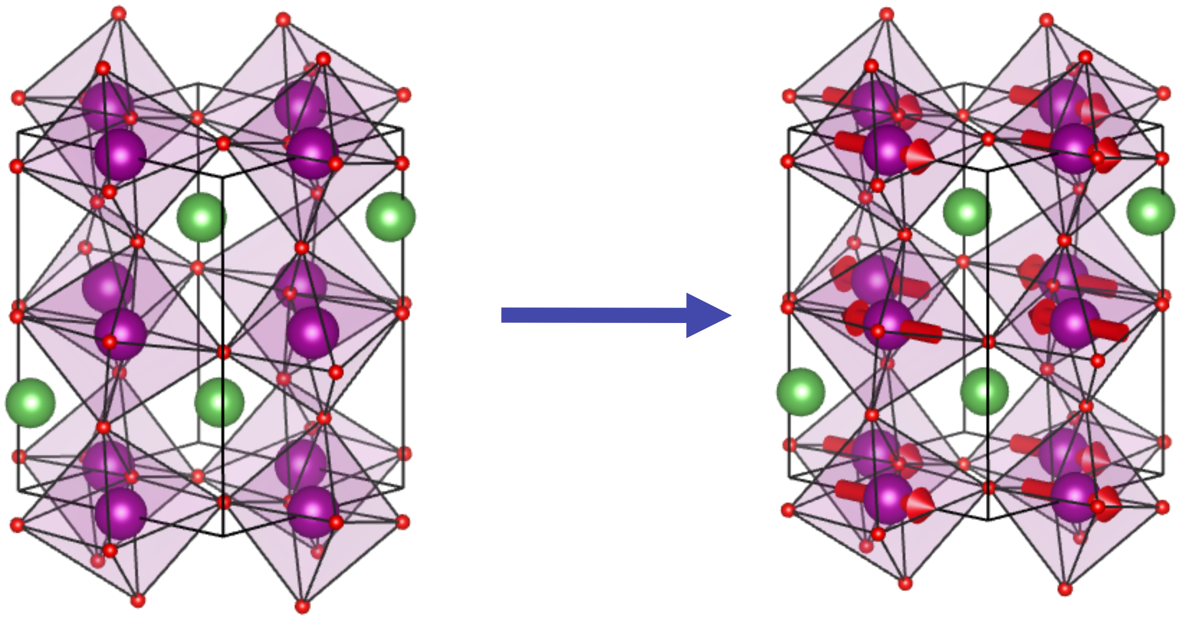
magnetic ordering: a symmetry breaking process

Magnetically ordered phases:

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

$LaMnO_3$

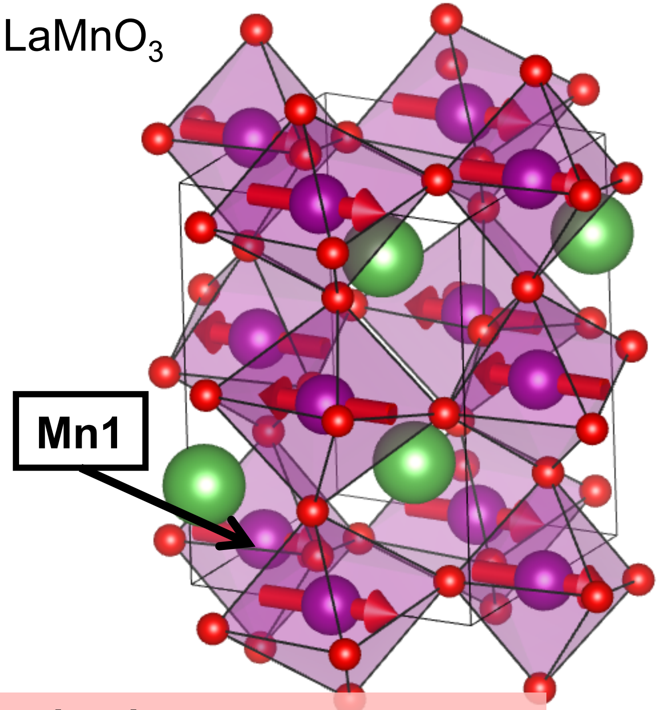




Pnma1' ***Pn'ma'***

(x,y,z,+1)	~~(-x+1/2,-y,z+1/2,+1)~~	(-x,y+1/2,-z,+1)	~~(x+1/2,-y+1/2,-z+1/2,+1)~~
(-x,-y,-z,+1)	~~(x+1/2,y,-z+1/2,+1)~~	(x,-y+1/2,z,+1)	~~(-x+1/2,y+1/2,z+1/2,+1)~~
~~(x,y,z,-1)~~	(-x+1/2,-y,z+1/2,-1)	~~(-x,y+1/2,-z,-1)~~	(x+1/2,-y+1/2,-z+1/2,-1)
~~(-x,-y,-z,-1)~~	(x+1/2,y,-z+1/2,-1)	~~(x,-y+1/2,z,-1)~~	(-x+1/2,y+1/2,z+1/2,-1)

Description of a magnetic structure in a crystallographic 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):

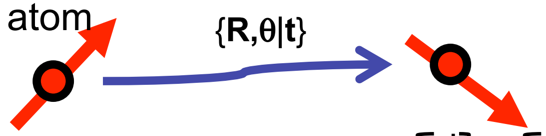
Mn1 3.87 0.0 0.0

Pn' ma' :

1 x,y,z,+1
2 -x,y+1/2,-z,+1
3 -x,-y,-z,+1
4 x,-y+1/2,z,+1
5 x+1/2,-y+1/2,-z+1/2,-1
6 -x+1/2,-y,z+1/2,-1
7 -x+1/2,y+1/2,z+1/2,-1
8 x+1/2,y,-z+1/2,-1

Symmetry operations are relevant both for positions and moments

for all atoms:



(x,y,z) →
$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \mathbf{R} \begin{bmatrix} x \\ y \\ z \end{bmatrix} + \mathbf{t}$$

(for positions: the same as with Pnma)

(mx,my,mz) →
$$\begin{bmatrix} mx' \\ my' \\ mz' \end{bmatrix} = \theta \det(\mathbf{R})\, \mathbf{R} \begin{bmatrix} mx \\ my \\ mz \end{bmatrix}$$

θ=-1 if time inversion

Wyckoff positions in a magnetic structure…

Magn. Space Group:
Pn'ma'

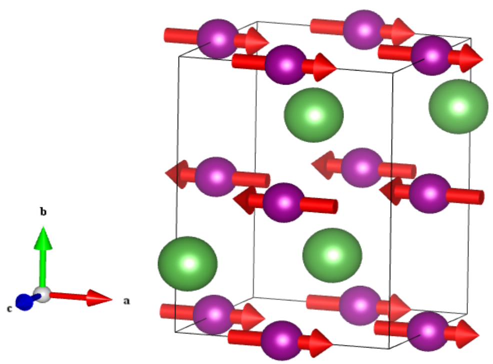
$LaMnO_3$

Multiplicity	Wyckoff letter	Coordinates	
8	d	$(x,y,z \mid m_x,m_y,m_z)$	$(x+1/2,-y+1/2,-z+1/2 \mid -m_x,m_y,m_z)$
		$(-x,y+1/2,-z \mid -m_x,m_y,-m_z)$	$(-x+1/2,-y,z+1/2 \mid m_x,m_y,-m_z)$
		$(-x,-y,-z \mid m_x,m_y,m_z)$	$(-x+1/2,y+1/2,z+1/2 \mid -m_x,m_y,m_z)$
		$(x,-y+1/2,z \mid -m_x,m_y,-m_z)$	$(x+1/2,y,-z+1/2 \mid m_x,m_y,-m_z)$
4	c	$(x,1/4,z \mid 0,m_y,0)$	$(x+1/2,1/4,-z+1/2 \mid 0,m_y,0)$
		$(-x,3/4,-z \mid 0,m_y,0)$	$(-x+1/2,3/4,z+1/2 \mid 0,m_y,0)$
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	$(0,0,0 \mid m_x,m_y,m_z)$	$(1/2,1/2,1/2 \mid -m_x,m_y,m_z)$
		$(0,1/2,0 \mid -m_x,m_y,-m_z)$	$(1/2,0,1/2 \mid m_x,m_y,-m_z)$

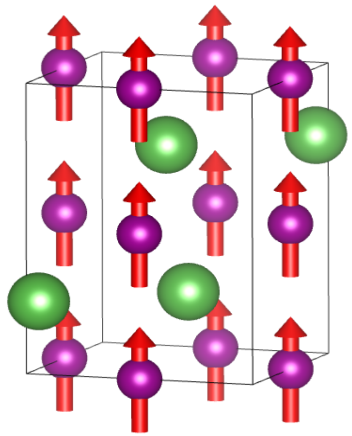
Output of MWYCKPOS in BCS

La (4c)

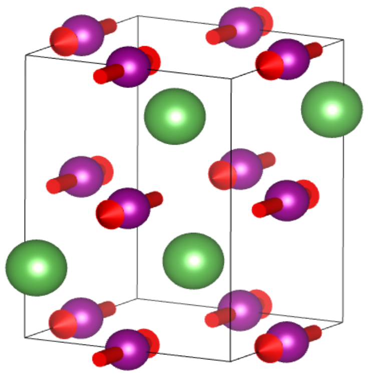
Mn (4b)



mode along x (A_x)



mode along y (F_y)
weak ferromagnet



mode along z (G_z)

magCIF

a CIF-type file format to communicate magnetic structures

(developed by the Commission on magnetic structures of the IUCr)

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, FullProf, VESTA, Jmol, etc.

It includes incommensurate structures

```
_space_group.magn_number_BNS    31.129
_space_group.magn_name_BNS      "P_b m n 2_1"
_space_group.magn_point_group "mm21'"
_space_group.magn_point_group_number "7.2.21"
_cell_length_a                  11.67080
_cell_length_b                  7.36060
_cell_length_c                  5.25720
_cell_angle_alpha               90.00
_cell_angle_beta                90.00
_cell_angle_gamma               90.00

loop_
_space_group_symop.magn_id
_space_group_symop.magn_operation_xyz
_space_group_symop.magn_operation_mxmymz
1 x,y,z,+1 mx,my,mz
2 -x+3/4,-y,z+1/2,+1 -mx,-my,mz
3 x,-y+1/2,z,+1 -mx,my,-mz
4 -x+3/4,y+1/2,z+1/2,+1 mx,-my,-mz

loop_
_space_group_symop.magn_centering_id
_space_group_symop.magn_centering_xyz
_space_group_symop.magn_centering_mxmymz
1 x,y,z,+1 mx,my,mz
2 x+1/2,y,z,-1 -mx,-my,-mz

loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
Ho Ho 0.04195 0.25000 0.98250 1
Ho_1 Ho 0.95805 0.75000 0.01750 1
Mn Mn 0.00000 0.00000 0.50000 1
O1 O 0.23110 0.25000 0.11130 1
O1_1 O 0.7689 0.75000 0.88870 1
O2 O 0.16405 0.05340 0.70130 1
O2_1 O 0.83595 0.55340 0.29870 1

loop_
_atom_site_moment_label
_atom_site_moment_crystalaxis_x
_atom_site_moment_crystalaxis_y
_atom_site_moment_crystalaxis_z
Mn 3.87 0.0 0.0
```

MAGNETIC SYMMETRY IS A “WELL DEFINED” SYMMETRY

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 within a thermodynamic phase”

Symmetry-dictated properties can be considered symmetry “protected”

BEWARE:

Other “extended” symmetries proposed from time to time in the literature do not fullfill this condition! ….

PHYSICAL REVIEW B VOLUME 12, NUMBER 11 1 DECEMBER 1975

Magnetic ordering in $CsCoBr_3$

Phys. Rev. B 12 (1975)

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(Received 31 March 1975)

The magnetic ordering in $CsCoBr_3$ has been studied by neutron diffraction, on both powder and single-crystal specimens, and by specific-heat and magnetic-susceptibility measurements. This compound has the hexagonal $CsNiCl_3$ type of structure, and the susceptibility shows characteristic one-dimensional behavior, while the specific heat indicates that three-dimensional ordering occurs at about 28°K. The neutron single-crystal study shows that between T_N and 14°K the magnetic structure is consistent with the orthorhombic space group $Cmc2_1$, with one-third of the antiferromagnetic cobalt chains being disordered and the other two-thirds antiferromagnetically coupled in the basal plane. Between 4 and 10°K the structure may be described by the space group $Cm'c2_1$, and is similar to the collinear arrangement reported for $CsCoCl_3$ and $RbCoBr_3$ but with a small canting of about 10°. The transformation from one structure to the other in the region of 10–14°K can be explained equally well by either the formation of an intermediate phase of lower symmetry or by a discontinous process in which the two phases coexist. The powder data temperature phase compatible with the space $C_pm'c2_1'$, consistent with nearest-neighbor interactions in the basal plane.

Use of magnetic space groups (Shubnikov groups) widely extended in the 60s-70s

Phys. Rev. B 6, 2669 (1972)

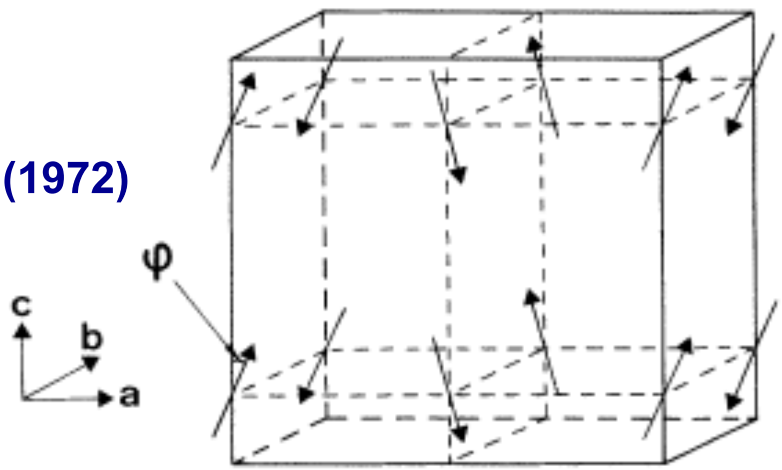


FIG. 1. Arrangement of the magnetic moments according to the magnetic space group $P_{2b}cca'$. All spins are in the *ac* plane.

Representation analysis is introduced as a "superior" alternative to magnetic symmetry groups, and it can also deal with incommensurate structures.

(1968)

Acta Cryst. (1968). A**24**, 217

Representation Analysis of Magnetic Structures

BY E. F. BERTAUT

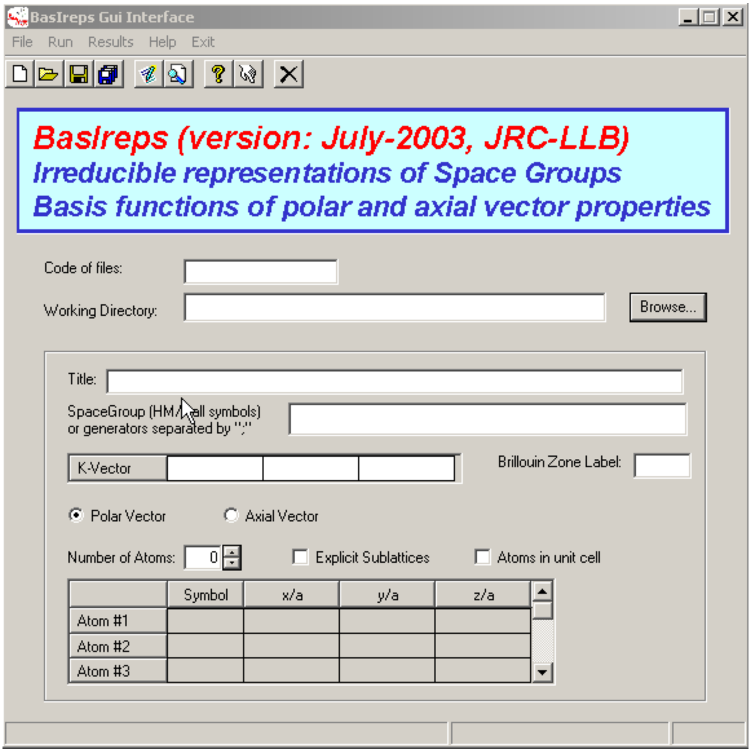
Abstract:

In the analysis of spin structures a 'natural' point of view looks for the set of symmetry operations which leave the magnetic structure invariant and has led to the development of magnetic or Shubnikov groups. A second point of view presented here simply asks for the transformation properties of a magnetic structure under the classical symmetry operations of the 230 conventional space groups and allows one to assign irreducible representations of the actual space group to all known magnetic structures. The superiority of representation theory over symmetry invariance under Shubnikov groups is already demonstrated by the fact proven here that the only invariant magnetic structures describable by magnetic groups belong to real one-dimensional representations of the 230 space groups. Representation theory on the other hand is richer because the number of representations is infinite, *i.e.* it can deal not only with magnetic structures belonging to one-dimensional real representations, but also with those belonging to one-dimensional complex and even to two-dimensional and three-dimensional representations associated with any **k** vector in or on the first Brillouin zone.

We generate from the transformation matrices of the spins a representation Γ of the space group

It includes incommensurate magnetic structures…

computer programs for representation analysis soon available:



Basireps(FullProf) from J. Rodriguez-Carvajal

SARA*h* Representational Analysis -
Performs the calculations of Representational Analysis. These allow the determination of atomic displacements or magnetic structures that can accompany a second-order phase transition. Output files includes a tailored summary with cut-and-paste tables written in LaTeX. (Win9x, 2000, Vista and Windows 7) [1]

SARAh from A.S. Wills

For many good reasons the representation approach became the most used method of analysis. But with a "collateral damage": many magnetic structures were determined and reported without identifying its magnetic symmetry not even its point-group symmetry.

The belief that representation method was a full alternative to the magnetic symmetry groups is not due to Bertaut….

Acta Cryst. (1968) A24, 217

E. F. BERTAUT 229

this will impose less stringent conditions on the coef-ficients in the Hamiltonian.

7. Magnetoelectricity

The reader may get the impression that the author is hostile to the use of magnetic groups. In fact the author is only defending representation theory. The main objection of the reader might be that in the abstract sense magnetic and space groups are isomorphous* so that a structure belonging to a representation of a space group G (even when the representation is not one-dimensional real) also belongs to a representation of the isomorphous Shubnikov group G'. This is perfectly correct, but still means that we would abandon symmetry invariance in favour of representation theory.

Can we ignore magnetic groups entirely? The answer is no, not only in microscopic, say atomic systems† (Dimmock & Wheeler, 1962) but also macroscopically when a magnetic system is coupled with other forms of energy.

A specific example is magnetoelectricity.‡ Here the

What is the problem of using “only” irreps?

i) Degrees of freedom of a magn. phase are constrained by its symmetry group: this can imply stronger restrictions than the irrep assignment, but it can also allow secondary degrees of freedom not described by this irrep.

ii) Physical properties, couplings are constrained by the symmetry of the phase:

for instance in multiferroics:

magnetoelectric, magnetoelastic, twinning, switching properties, etc. are governed by the magnetic point group in relation with the parent point group (ferroic species)

The magnetic symmetry group of an incommensurate phase is a magnetic superspace group…with a well defined **magnetic point group**

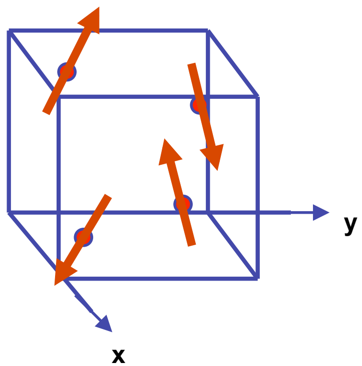
Representation analysis vs magnetic space groupsc

In simple cases (one dimen. irreps) both symmetry descriptions are equivalent

Example: nuclear space group C222, magnetic ordering with k=0

C2221' —irrep B_2→ **C2' 22'**

B_2 spin ordering mode on C222 nuclear structure:



magnetic space group: C2' 22'

(better label for irrep: mB_2)

time reversal

Character Table

D_2(222)	#	1	2_z	2_y	2_x	functions	θ	
A	Γ_1	1	1	1	1	x^2,y^2,z^2	-1	C222
B_1	Γ_3	1	1	-1	-1	z,xy,J_z	-1	C2' 2' 2
B_2	Γ_2	1	-1	1	-1	y,xz,J_y	-1	C2' 22'
B_3	Γ_4	1	-1	-1	1	x,yz,J_x	-1	C22'2'

mB_2 irrep == C2' 22' symmetry

BUT Full equivalence ONLY for 1-dim irreps

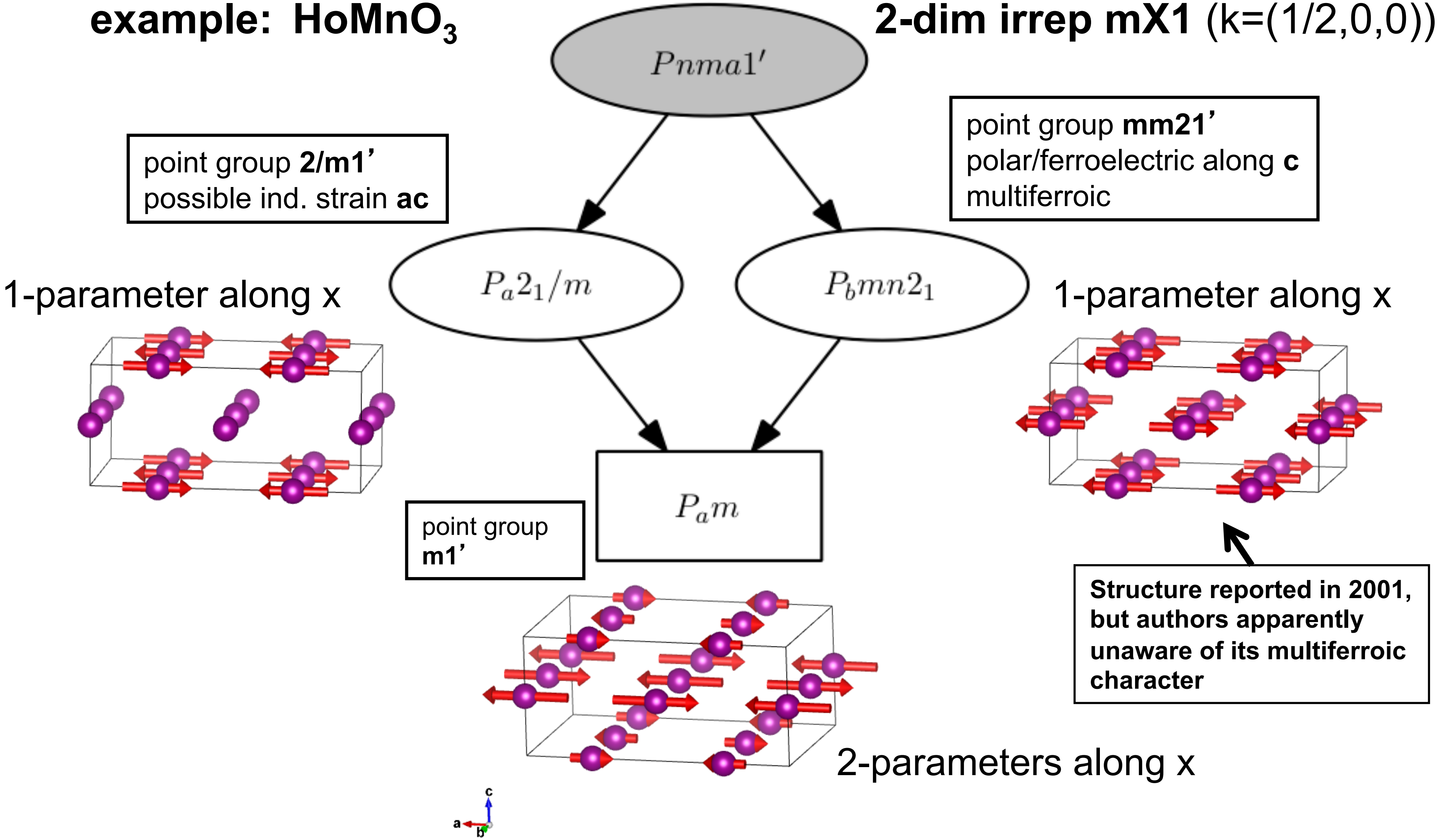
Representation analysis vs magnetic space groups

For multidim. irreps: several MSGs are possible for the same irrep

Representation analysis vs magnetic space groups

For multidim. irreps: several MSGs are possible for the same irrep

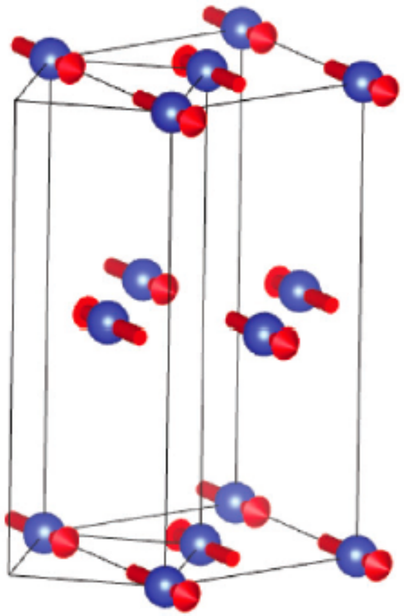
example: $HoMnO_3$ **2-dim irrep mX1** (k=(1/2,0,0))



The same spin arrangement can produce different MSGs (and different ferroic properties) *(The non magnetic atoms are also important for the magnetic symmetry!)*

Pr_2CuO_4

I4/mmm, k=(1/2,1/2,0)



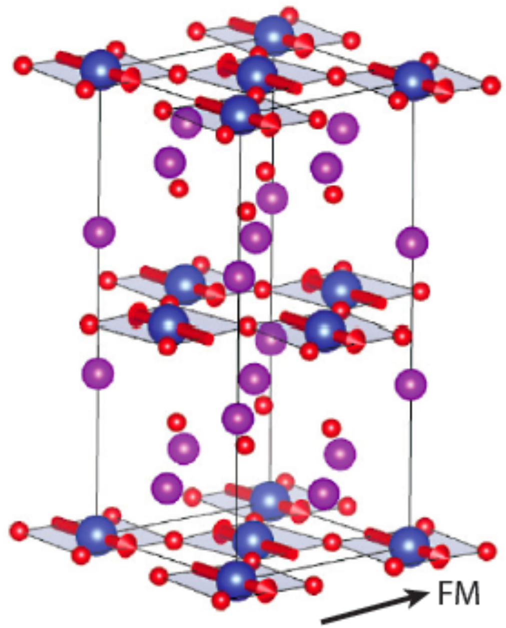
C_Accm

(**c**, **a** – **b**, **a** + **b**; 1/4, 3/4, 1/4)

Point group: mmm1'

Gd_2CuO_4

Cmce, k=(0,0,0)



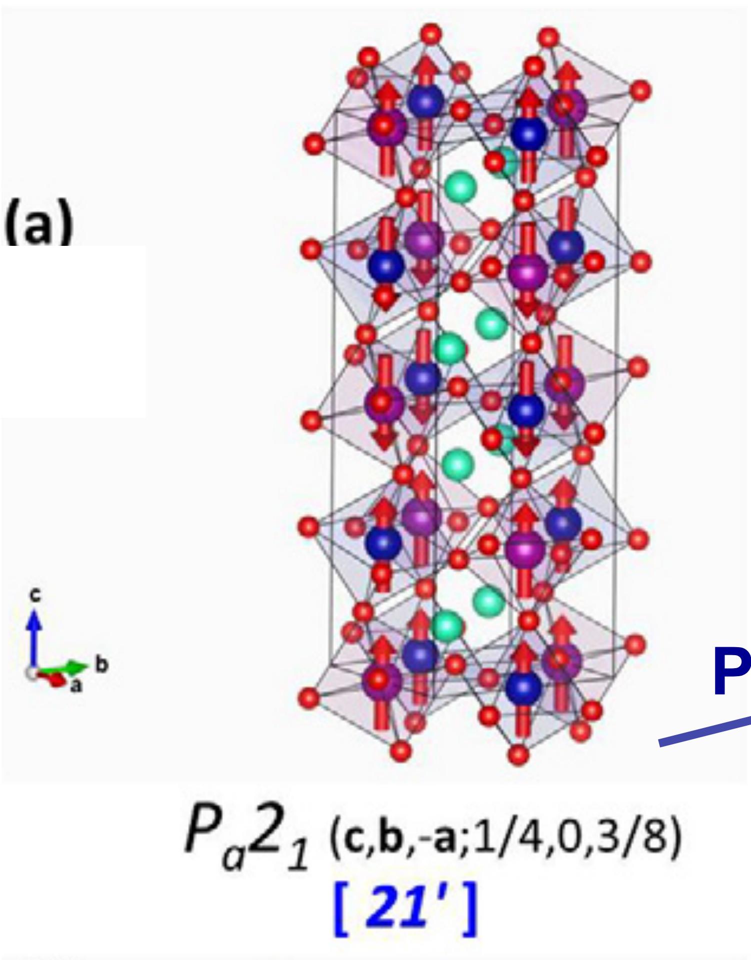
Cm'ca'

(**c**, **a** – **b**, **a** + **b**; 0, 0, 0)

Point group: m'mm'

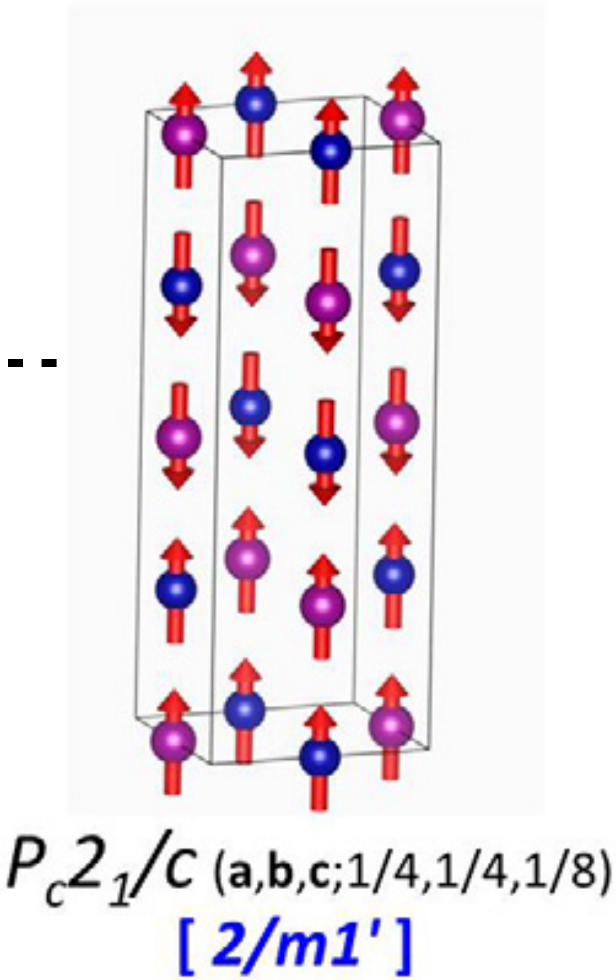
(weak ferromagnetism)

Polar magnetic symmetry of Lu_2MnCoO_6 due to the non-magnetic atoms:



P_y

chains + + - -



Polar symmetry when non-magnetic atoms are considered.

Non-polar symmetry without non-magnetic atoms !

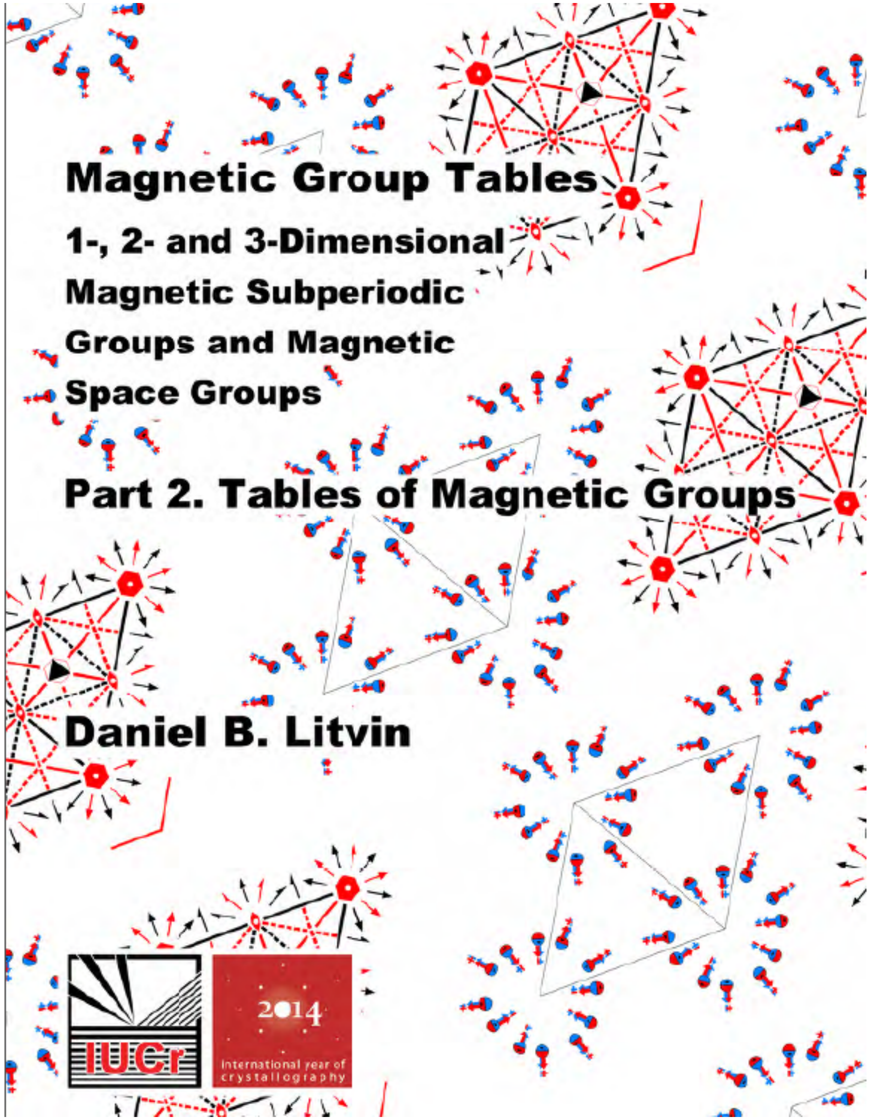
The polar direction is NOT along the chains!

Towards the systematic application of Magnetic Symmetry….

Acta Cryst. A (2008)

Daniel T. Litvin

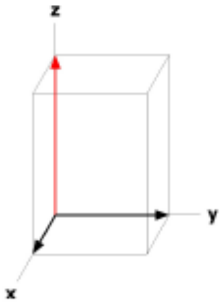
http://www.iucr.org/books



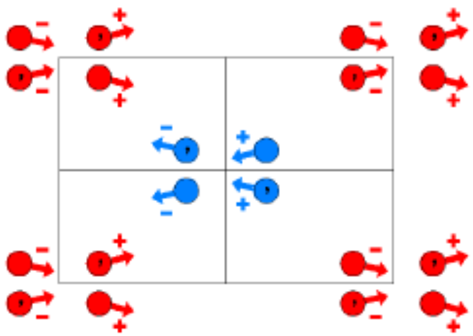
Towards the systematic application of Magnetic Symmetry….

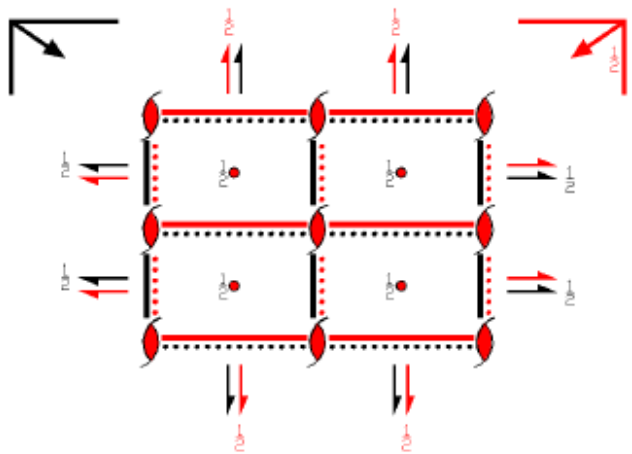
D.T. Litvin Tables of the 1651 MAGNETIC SPACE GROUPS (MSGs)

2008



$P_{2c}m'mn$	mmm1'	Orthorhombic
59.9.486	$P_{2c}2_1/m'2_1'/m2'/n$	





Origin at m'm2'/n at 1/4,1/4,0 from $\bar{1}'$

Asymmetric unit $0 \le x \le 1/2$; $0 \le y \le 1/2$; $0 \le z \le 1/2$

Symmetry Operations

For (0,0,0) + set

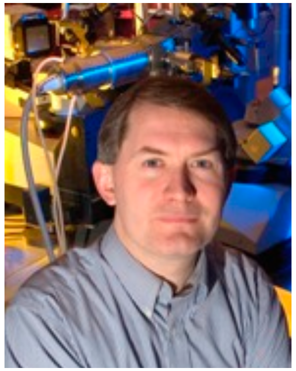
(1) 1 (1|0,0,0)	(2) 2' 0,0,z (2_z|0,0,0)'	(3) 2' (0,1/2,0) 1/4,y,0 (2_y|1/2,1/2,0)'	(4) 2 (1/2,0,0) x,1/4,0 (2_x|1/2,1/2,0)
(5) $\bar{1}'$ 1/4,1/4,0 ($\bar{1}$|1/2,1/2,0)'	(6) n (1/2,1/2,0) x,y,0 (m_z|1/2,1/2,0)	(7) m x,0,z (m_y|0,0,0)	(8) m' 0,y,z (m_x|0,0,0)'

For (0,0,1)' + set

(1) t' (0,0,1) (1|0,0,1)'	(2) 2 (0,0,1) 0,0,z (2_z|0,0,1)	(3) 2 (0,1/2,0) 1/4,y,1/2 (2_y|1/2,1/2,1)	(4) 2' (1/2,0,0) x,1/4,1/2 (2_x|1/2,1/2,1)'
(5) $\bar{1}$ 1/4,1/4,1/2 ($\bar{1}$|1/2,1/2,1)	(6) n' (1/2,1/2,0) x,y,1/2 (m_z|1/2,1/2,1)'	(7) c' (0,0,1) x,0,z (m_y|0,0,1)'	(8) c (0,0,1) 0,y,z (m_x|0,0,1)

Towards the systematic application of Magnetic Symmetry….

H. T. Stokes



B. J. Campbell

1. Computer readable listings of MSGs (Shubnikov groups)
2. Extension of some of the programs of the ISOTROPY suite to magnetic systems (combined application of irreps and magnetic symmetry groups)

http://stokes.byu.edu/iso/isotropy.php

ISOTROPY Software Suite

Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell, Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84606, USA, stokesh@byu.edu

Description: The ISOTROPY software suite is a collection of software which applies group theoretical methods to the analysis of phase transitions in crystalline solids.
How to cite: ISOTROPY Software Suite, iso.byu.edu.

References and Resources

Isotropy subgroups and distortions

- ISODISTORT: Explore and visualize distortions of crystalline structures. Possible distortions include atomic displacements, atomic ordering, strain, and magnetic moments.
- ISOSUBGROUP: Coming soon!
- ISOTROPY: Interactive program using command lines to explore isotropy subgroups and their associated distortions.
- SMODES: Find the displacement modes in a crystal which brings the dynamical matrix to block-diagonal form, with the smallest possible blocks.
- FROZSL: Calculate phonon frequencies and displacement modes using the method of frozen phonons.

Space groups and irreducible representations

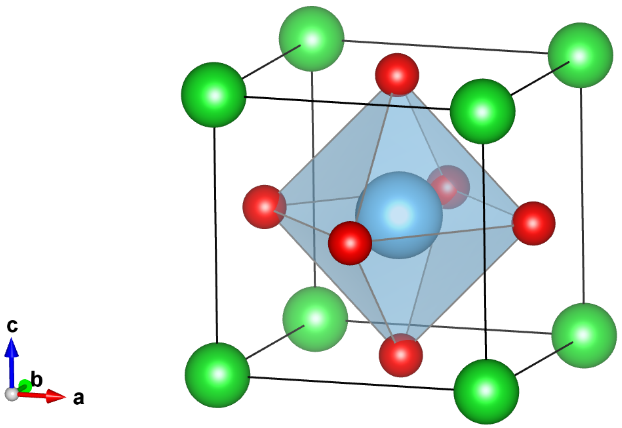
- ISOCIF: Create or modify CIF files.
- FINDSYM: Identify the space group of a crystal, given the positions of the atoms in a unit cell.
- **New!** ISO-IR: Tables of Irreducible Representations. The 2011 version of IR matrices.

Magnetic symmetry application tools and databases in the Bilbao Crystallographic Server

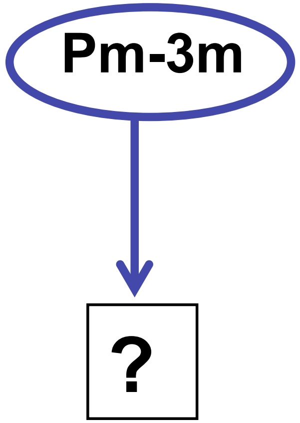
Magnetic Symmetry and Applications	
MGENPOS	General Positions of Magnetic Space Groups
MWYCKPOS	Wyckoff Positions of Magnetic Space Groups
MAGNEXT	Extinction Rules of Magnetic Space Groups
IDENTIFY MAGNETIC GROUP	Identification of a Magnetic Space Group from a set of generators in an arbitrary setting
MPOINT ⚠	Magnetic Point Group Tables
MAXMAGN	Maximal magnetic space groups for a given a propagation vector and resulting magnetic structural models
MAGMODELIZE	Magnetic structure models for any given magnetic symmetry
k-SUBGROUPSMAG	Magnetic subgroups consistent with some given propagation vector(s) or a supercell
MAGNDATA ⚠	A collection of magnetic structures with transportable cif-type files
MVISUALIZE ⚠	3D Visualization of magnetic structures with Jmol
MTENSOR ⚠	Symmetry-adapted form of magnetic crystal tensors

main developers:
Samuel V. Gallego, Luis Elcoro, Emre S. Tasci, Mois. I. Aroyo, J. Manuel Perez-Mato

Possible distorted structures/phases of $BaTiO_3$ with k=(0,0,0) ?

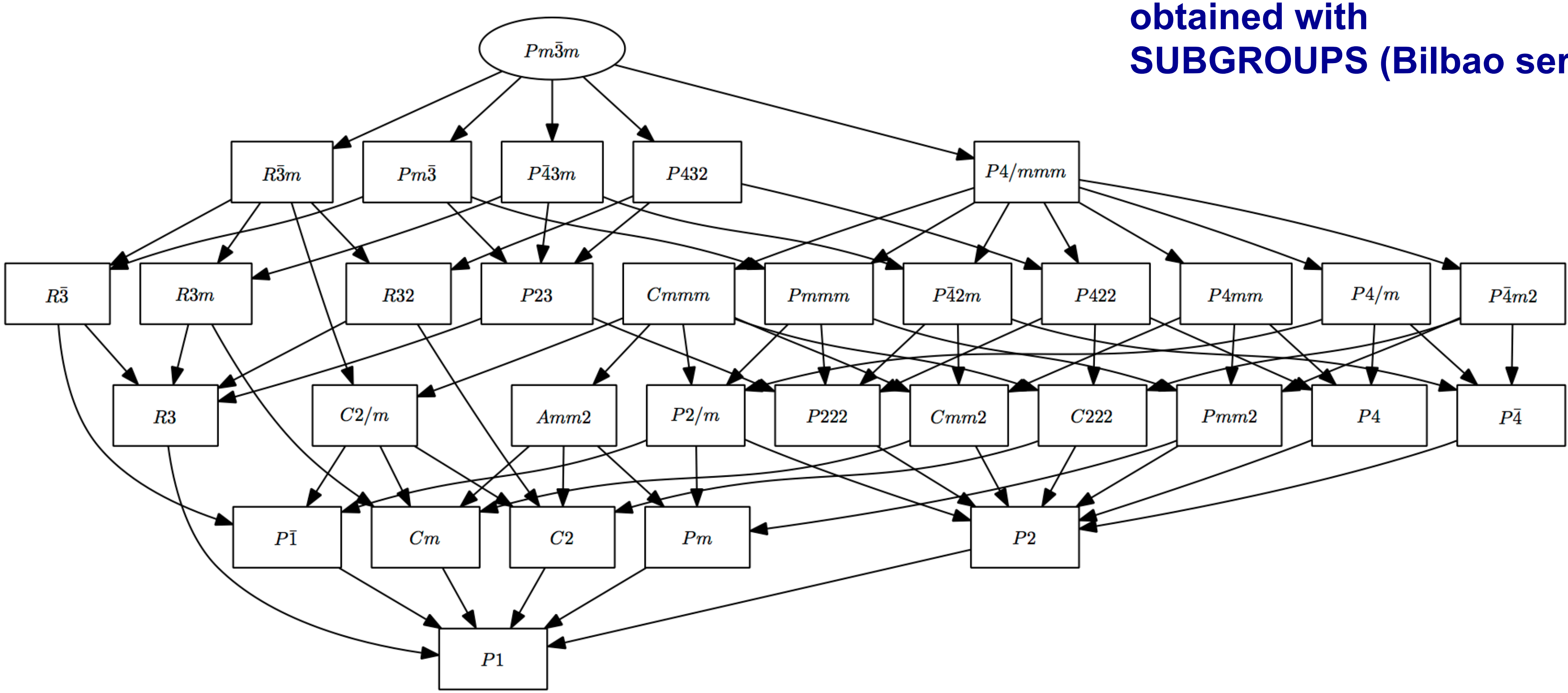


$BaTiO_3$

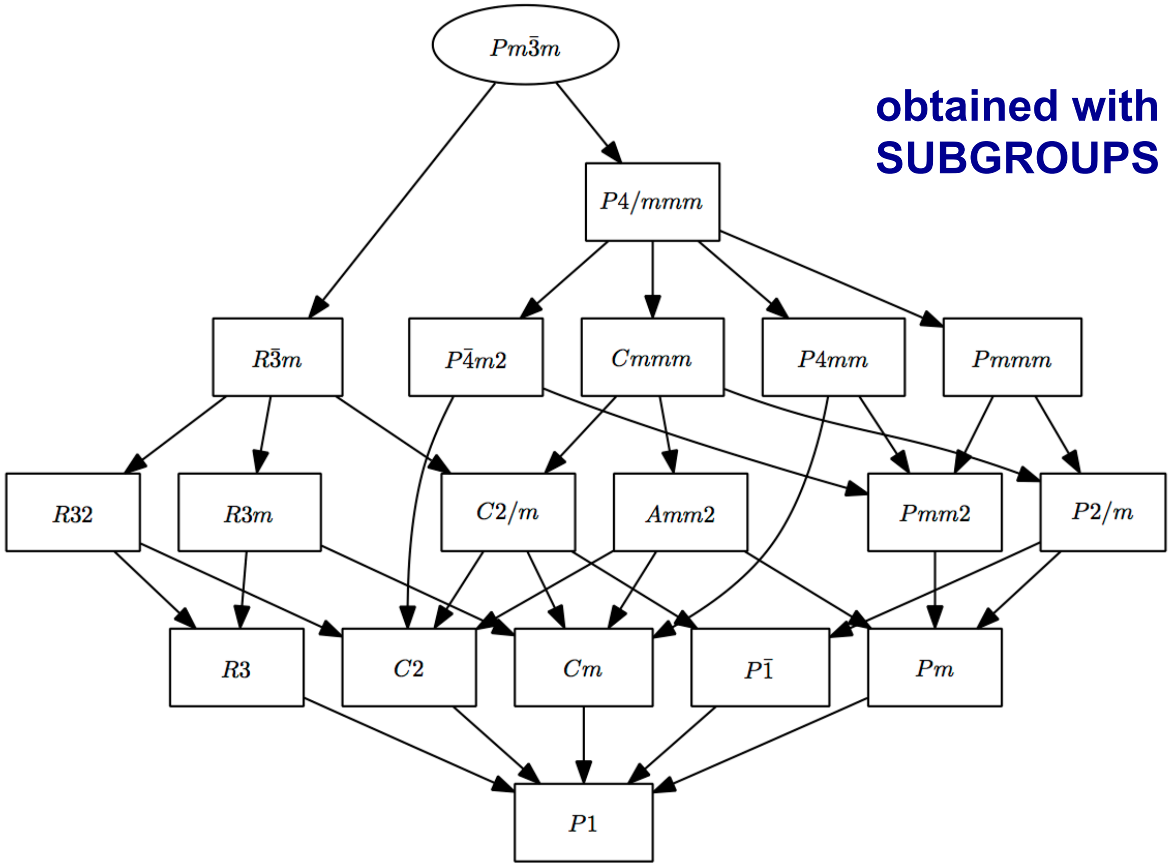


Subgroups of cubic Pm-3m without multiplication of the unit cell (k=0):

obtained with SUBGROUPS (Bilbao server)



Subgroups of cubic Pm-3m without multiplication of the unit cell (k=0) which are possible for atomic positions at 1a,1b and 3c :

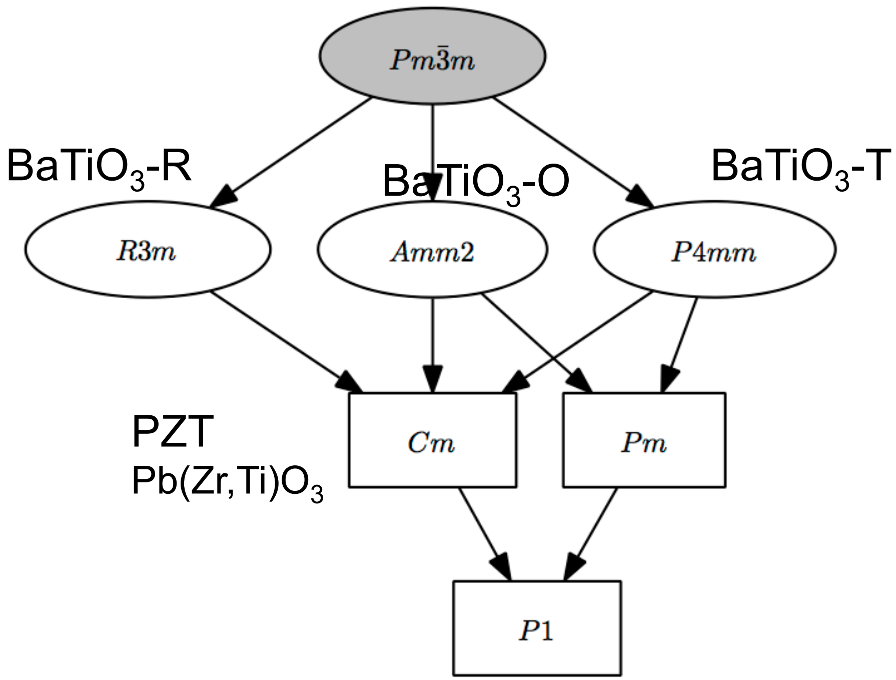


obtained with SUBGROUPS (Blibao server)

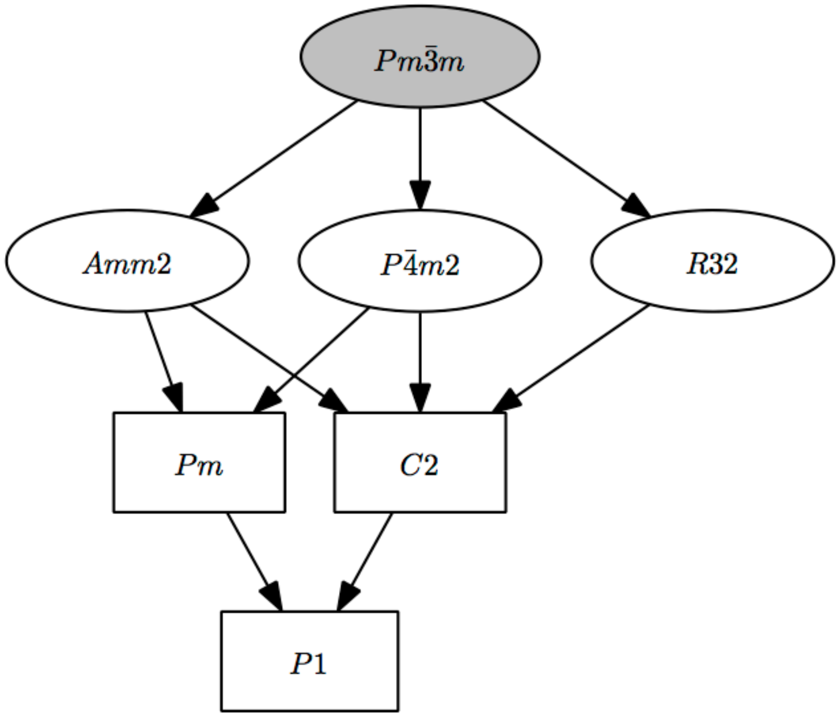
Subgroups of cubic Pm-3m without multiplication of the unit cell (k=0) which are possible for atomic positions at 1a,1b and 3c depending on the irrep of the order parameter:

Irrep **GM4-:**

obtained with SUBGROUPS (Bilbao server)

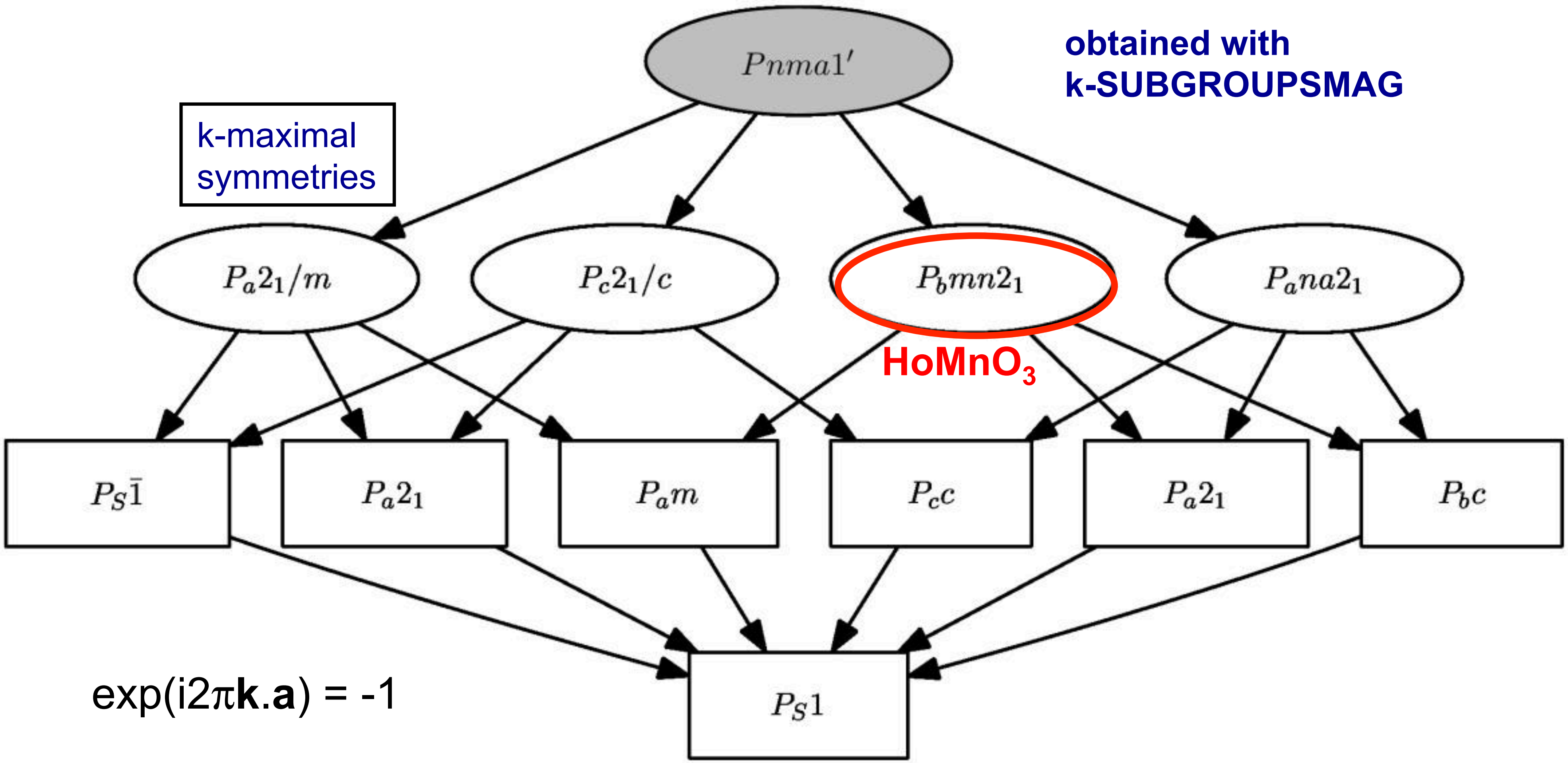


Irrep **GM5-:**



Possible magnetic symmetries for a magnetic phase with propagation vector (1/2,0,0) and parent space group Pnma

(a maximal symmetry compatible with the k-vector is often realized)



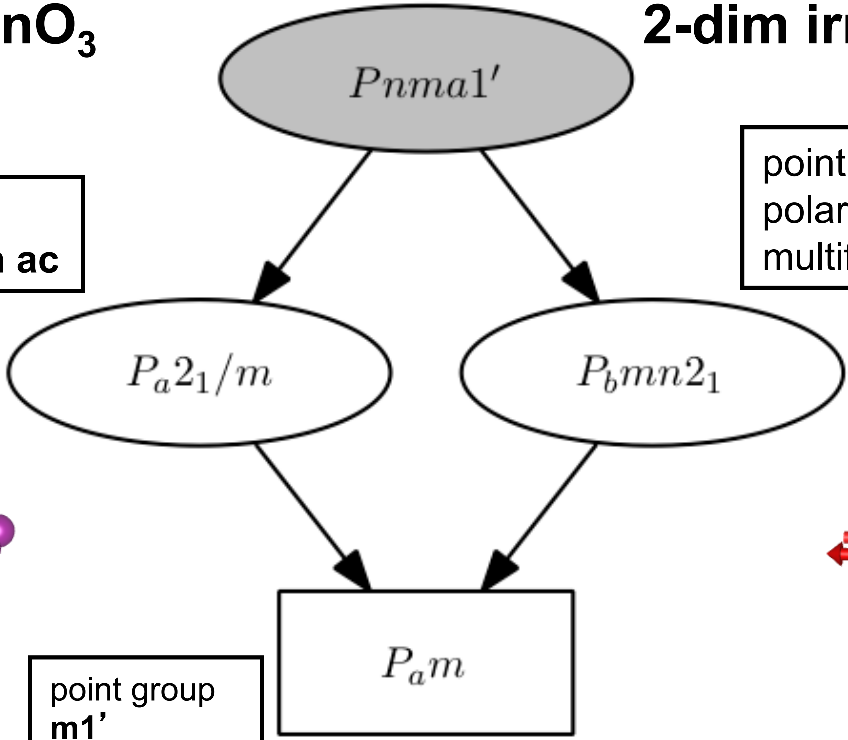
Symmetry operation {1'|1/2,0,0} is present in any case
(magnetic cell= $(2\mathbf{a}_p,\mathbf{b}_p,\mathbf{c}_p)$)

Representation analysis vs magnetic space groupsc

For multidim. irreps: several MSGs are possible for the same irrep

example: $HoMnO_3$

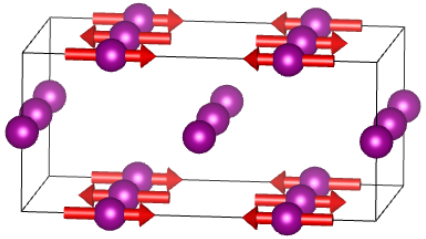
2-dim irrep mX1 (k=(1/2,0,0))



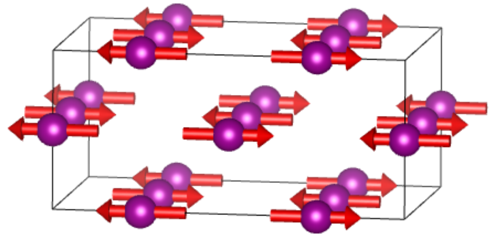
point group **2/m1'**
possible ind. strain **ac**

point group **mm21'**
polar/ferroelectric along **c**
multiferroic

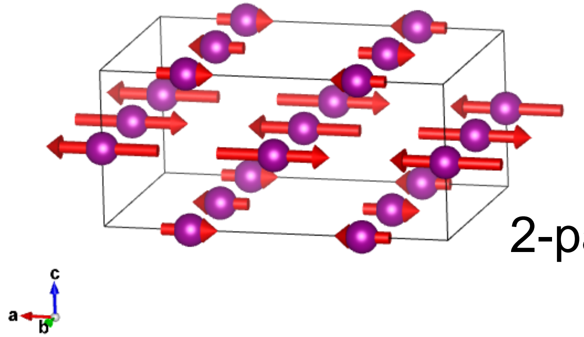
1-parameter along x



1-parameter along x

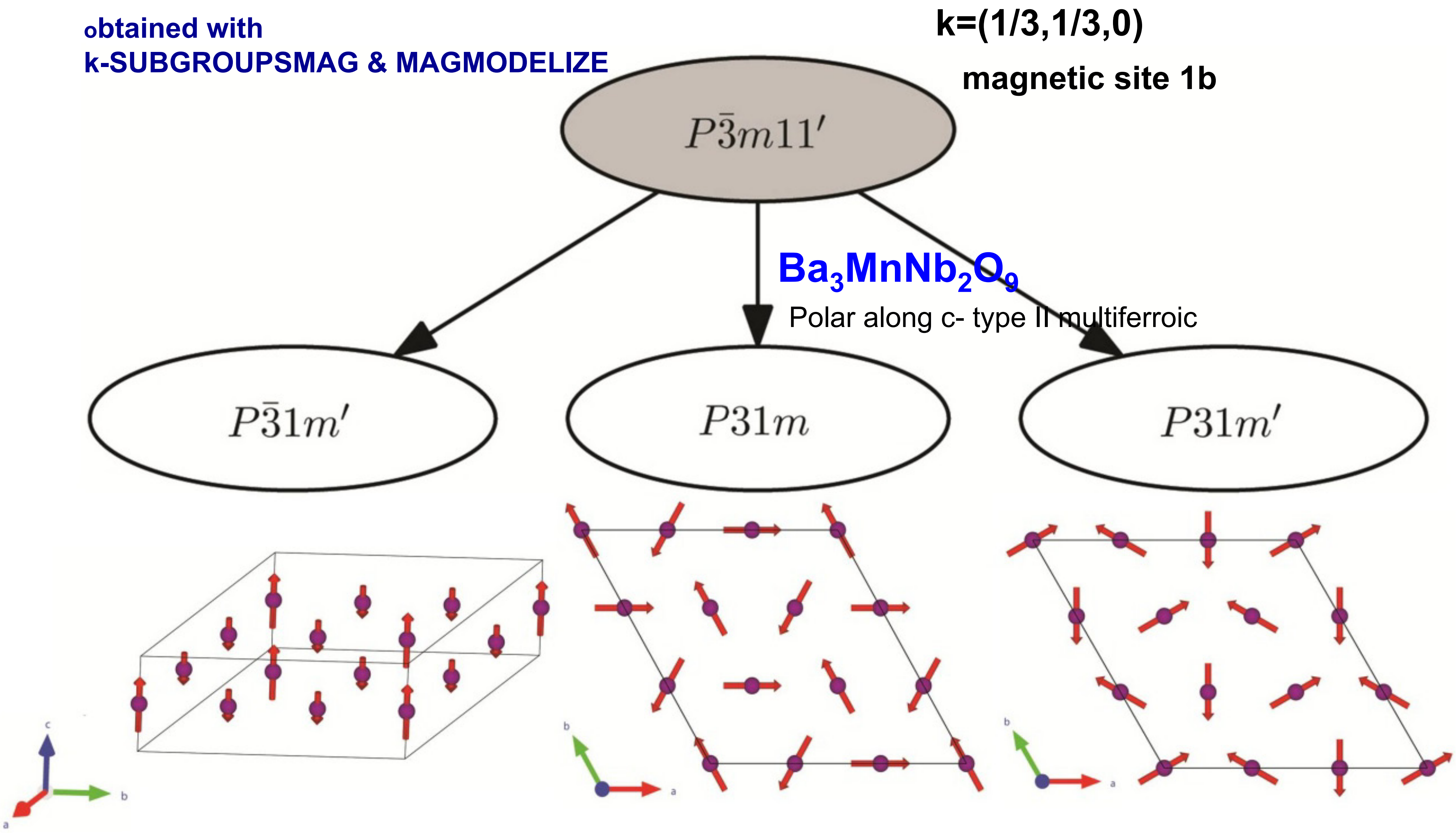


point group
m1'



2-parameters along x

Structure reported in 2001, but authors apparently unaware of its multiferroic character



obtained with
k-SUBGROUPSMAG & MAGMODELIZE
k=(1/3,1/3,0)
magnetic site 1b
$P\bar{3}m11'$
$Ba_3MnNb_2O_9$
Polar along c- type II multiferroic
$P\bar{3}1m'$
$P31m$
$P31m'$

$Sr_2F_2Fe_2OS_2$

Parent: I4/mmm1'

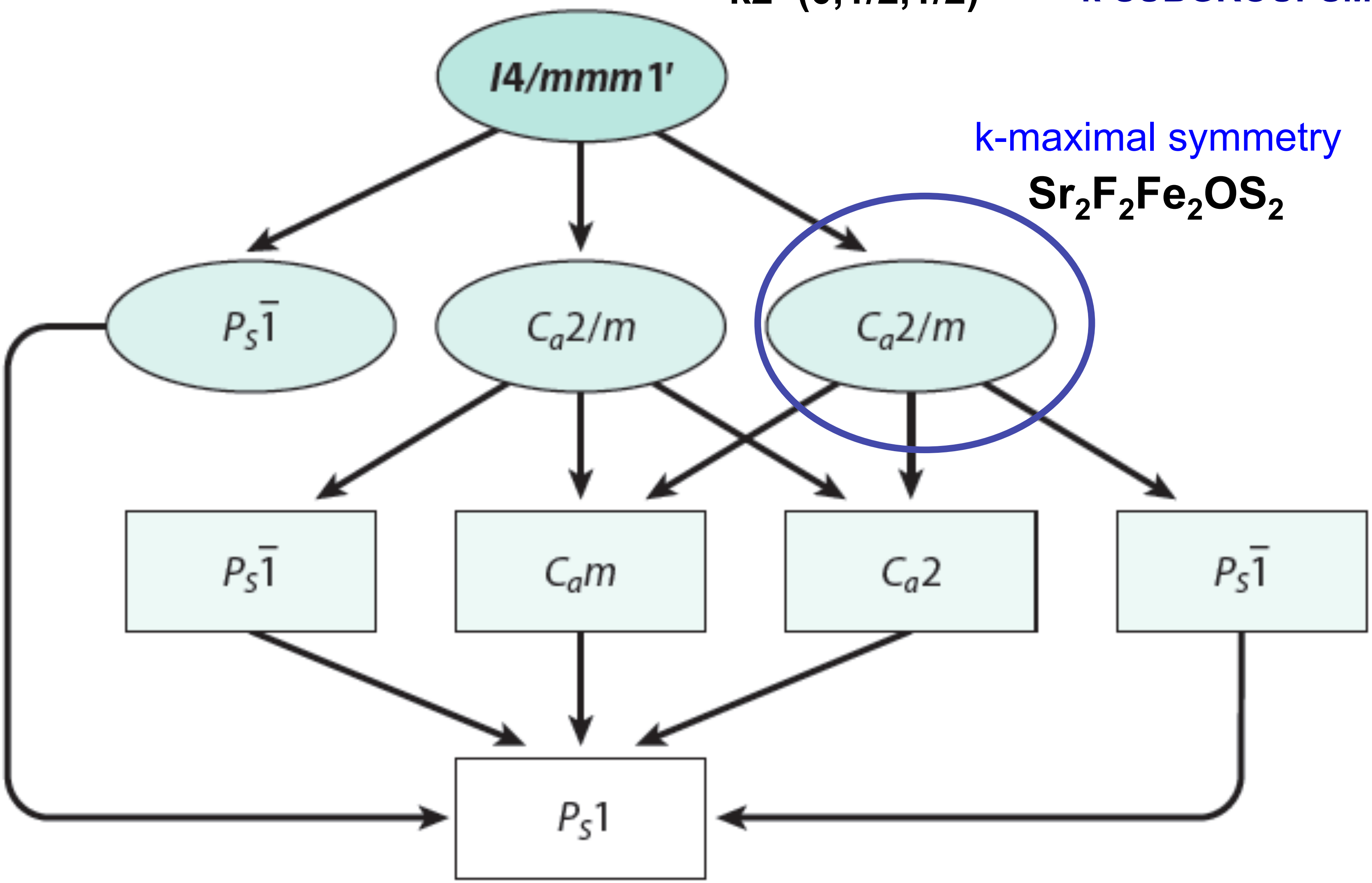
2k magnetic structure

k1=(-1/2,0,1/2)
k2=(0,1/2,1/2)

2k magnetic structure

k1=(-1/2,0,1/2)
k2=(0,1/2,1/2)

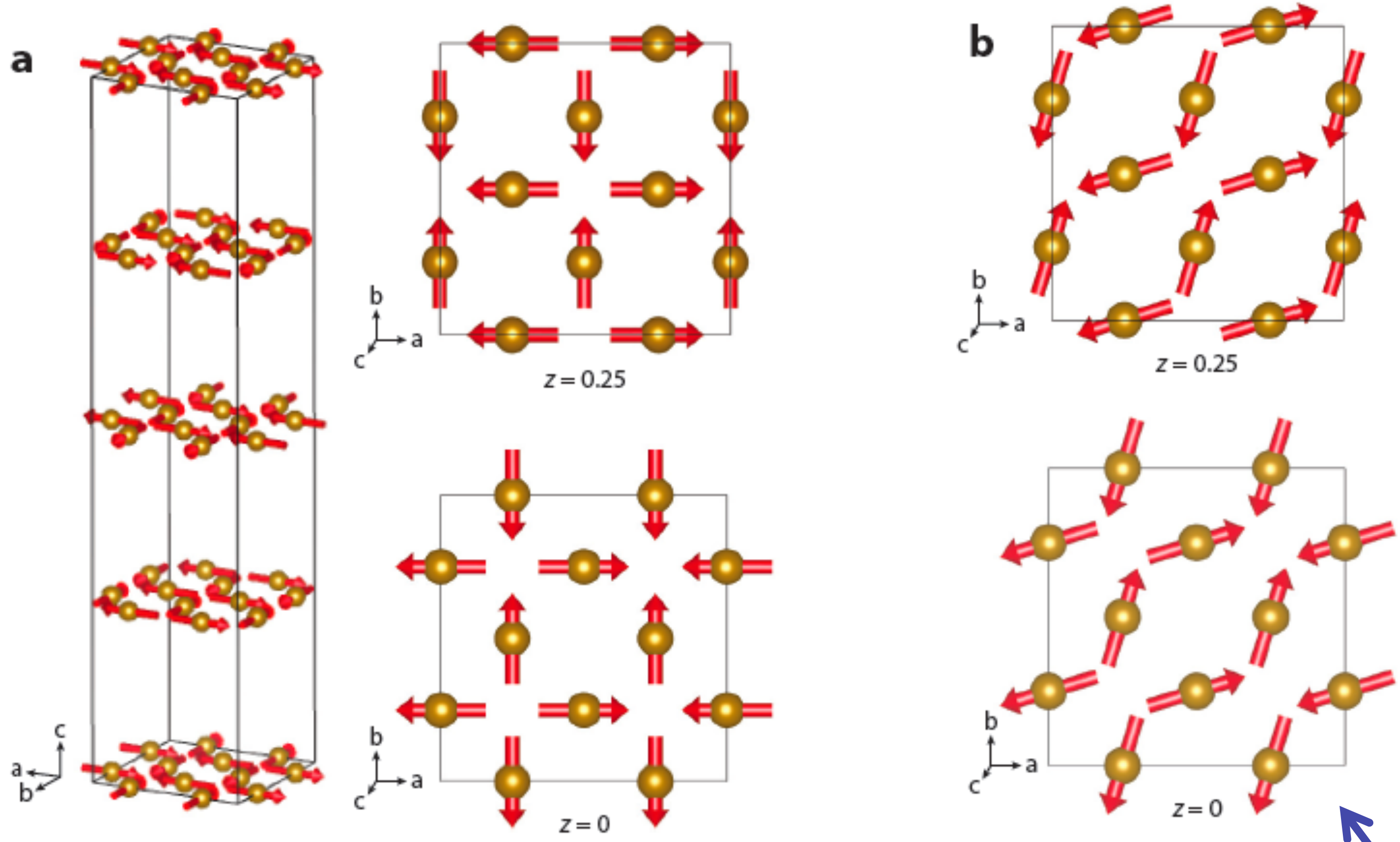
obtained with
k-SUBGROUPSMAG



$Sr_2F_2Fe_2OS_2$

2k magnetic structure

I4/mmm1' -> C_a2/m **k1=(-1/2,0,1/2)** **k2=(0,1/2,1/2)**



Zhao et al., *Phys Rev B (R)* (2013)

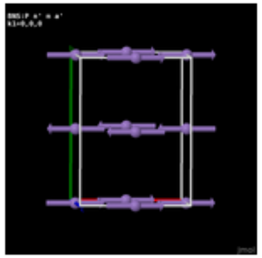
symmetry allowed by the MSG
but it is a different irrep!

MAGNDATA: A Collection of magnetic structures with portable cif-type files

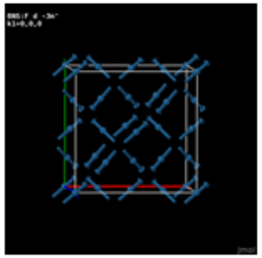
Element search (separate with space or comma): ⊙AND ○OR Search

312 structures found

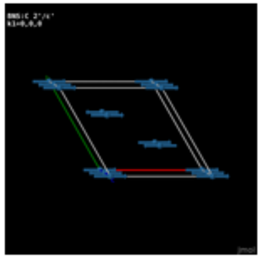
Zero propagation vector



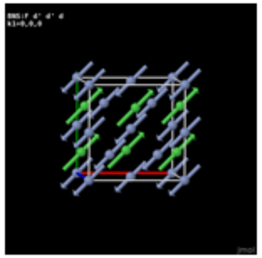
0.1 $LaMnO_3$



0.2 $Cd_2Os_2O_7$



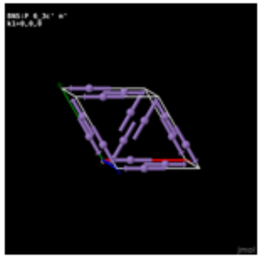
0.3 Ca_3LiOsO_6



0.4 $NiCr_2O_4$

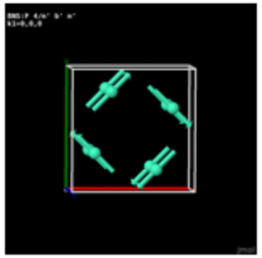
0.5 Cr_2S_3

0.6 $YMnO_3$

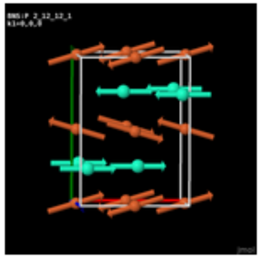


0.7 $ScMnO_3$

0.8 $ScMnO_3$



0.9 GdB_4

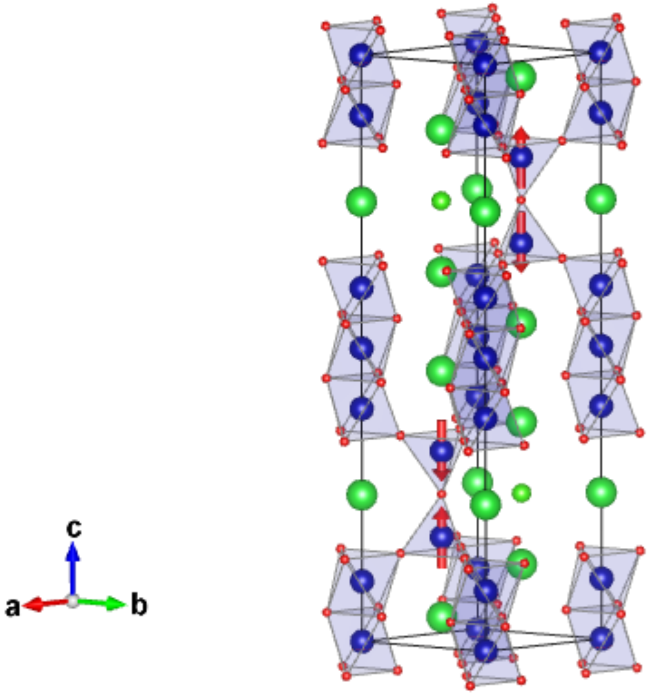


0.10 $DyFeO_3$

$Sr_2F_2Fe_2OS_2$ (MAGNDATA #2.2)

Magnetic Space Groups	
MGENPOS	General Positions of Magnetic Space Groups
MWYCKPOS	Wyckoff Positions of Magnetic Space Groups
MAGNEXT	Extinction Rules of Magnetic Space Groups

$Ba_5Co_5ClO_{13}$



nuclear/positional reflection condition:

(2h,-h,l) l=2n

(magnetic sites: 2a, 4e, 4f. all $(0,0,m_z)$)

Magnetic diffraction:

Reflection (2, -1, 3) **pure magnetic**

(2h,-h,l)

$P6_3'/m'm'c$ (194.268): absent l even
present l odd

$P6_3/m'm'c$ (194.270): absent l odd

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

obtained with **MTENSOR**

Symmetry-adapted form of the Magnetoelectric tensor α^T_{ij} (inverse effect)

- 2 nd rank Magnetoelectric tensor α^T_{ij} (inverse effect)
- Transforms like **aeV²**
- Axial tensor which inverts under time-reversal symmetry operation
- Constitutive equation: $\mathbf{P_i=\alpha^t_{ij}H_j}$
- Relates Magnetic field **H** with Polarization **P**

3m

α^t_{ij}		j		
		1	2	3
i	1	0	α^t_{12}	0
	2	$-\alpha^t_{12}$	0	0
	3	0	0	0

3m1'

α^t_{ij}		j		
		1	2	3
i	1	0	0	0
	2	0	0	0
	3	0	0	0

IOP Publishing Journal of Physics: Condens
J. Phys.: Condens. Matter **28** (2016) 286001 (15pp) doi:10.1088/0953-8984/28/2

Symmetry conditions for type II multiferroicity in commensurate magnetic structures

J M Perez-Mato[1], S V Gallego[1], L Elcoro[1], E Tasci[2] and M I Aroyo[1]

[1] Departamento de Fisica de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Apartado 644, 48080 Bilbao, Spain
[2] Department of Physics, Middle East Technical University, 06800 Ankara, Turkey

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Abstract

Type II multiferroics are magnetically ordered phases that exhibit ferroelectricity as a magnetic induced effect. We show that in *single-k* magnetic phases the presence in the paramagnetic phase of non-symmorphic symmetry combined with some specific type of magnetic propagation vector can be sufficient for the occurrence of this type of multiferroic behaviour. Other symmetry scenarios especially favourable for spin driven multiferroicity are also presented. We review and classify known type II multiferroics under this viewpoint. In addition, some other magnetic phases which due to their symmetry properties can exhibit type II multiferroicity are pointed out.

What about incommensurate structures?

Symmetry of Incommensurate Crystal Phases. I. Commensurate Basic Structures

BY A. JANNER AND T. JANSSEN


9. Magnetic superspace groups

As shown by Overhauser (1962, 1968), the ground state of an electron gas in a crystal does not necessarily have a uniform spin and charge distribution, but may show charge-density waves (CDW) and/or spin-density waves (SDW). We have already seen that CDW's may lead to an incommensurate crystal phase. The same can occur in magnetic crystals through SDW's. Actually, incommensurability was discovered first in

Acta Cryst. (1980). A **36**, 399–408 **1980**

10. Magnetic superspace-group symmetry of Cr

In the AF_2 phase $\mathbf{S}(\mathbf{k})$ is parallel to the z axis and left invariant [according to (72)] by $(4_z, 1)$ and $(m_x, 1)'$. Again, if the phase relation (84) holds, then it is also left invariant by $(m_z, \bar{1})$. In this case the magnetic superspace group for the AF_2 phase is

$$M_{AF_2} = P^{I}{}^{P}_{b}{}^{4/}_{1}{}^{m}_{\bar{1}}{}^{m'}_{1}{}^{m'}_{1}. \qquad (86)$$

2014 IUCr Ewald Prize to Janner and Janssen

Aloysio Janner and T. W. J. M. (Ted) Janssen, Emeriti Professors at U. of Nijmegen, The Netherlands, have been awarded the tenth Ewald Prize, 'for the development of superspace crystallography and its application to the analysis of aperiodic crystals'. The award will be presented on August 5, 2014, at the opening ceremony of the IUCr congress in Montreal, Canada.

First fundamental steps towards the combined application of magnetic superspace symmetry and representation analysis in incommensurate magnetic structures :

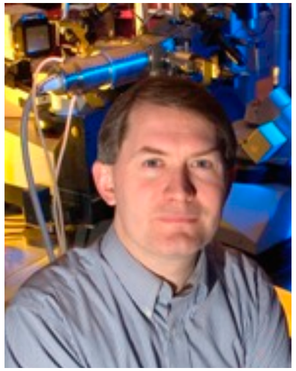
Acta Cryst. A (2010)

Magnetic space and superspace groups, representation analysis: competing or friendly concepts?

Václav Petříček,* Jiří Fuksa and Michal Dušek

2. JANA2006 is extended to allow refinement of magnetic structures both commensurate and incommensurate, using magnetic space and superspace groups

First fundamental steps towards the combined application of magnetic superspace symmetry and representation analysis in incommensurate magnetic structures :



H. T. Stokes B. J. Campbell

1. Extension of some of the programs of the ISOTROPY suite to magnetic systems including incommensurate structures and magnetic superspace groups.

http://stokes.byu.edu/iso/isotropy.php

ISOTROPY Software Suite

Harold T. Stokes, Dorian M. Hatch, and Branton J. Campbell, Department of Physics and Astronomy, Brigham Young University, Provo, Utah 84606, USA, stokesh@byu.edu

Description: The ISOTROPY software suite is a collection of software which applies group theoretical methods to the analysis of phase transitions in crystalline solids.
How to cite: ISOTROPY Software Suite, iso.byu.edu.

References and Resources

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Space groups and irreducible representations

- ISOCIF: Create or modify CIF files.
- FINDSYM: Identify the space group of a crystal, given the positions of the atoms in a unit cell.
- **New!** ISO-IR: Tables of Irreducible Representations. The 2011 version of IR matrices.
- ISO-MAG: Tables of magnetic space groups, both in human-readable and computer-readable forms.

J. Phys.: Condens. Matter 24 (2012) 163201 (20pp) doi:10.1088/0953-8984/24/16/163201

TOPICAL REVIEW

Magnetic superspace groups and symmetry constraints in incommensurate magnetic phases

J M Perez-Mato[1], J L Ribeiro[2], V Petricek[3] and M I Aroyo[1]

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[2] Centro de Física da Universidade do Minho, P-4710-057 Braga, Portugal
[3] Institute of Physics, Academy of Sciences of the Czech Republic v.v.i., Na Slovance 2, CZ-18221 Praha 8, Czech Republic

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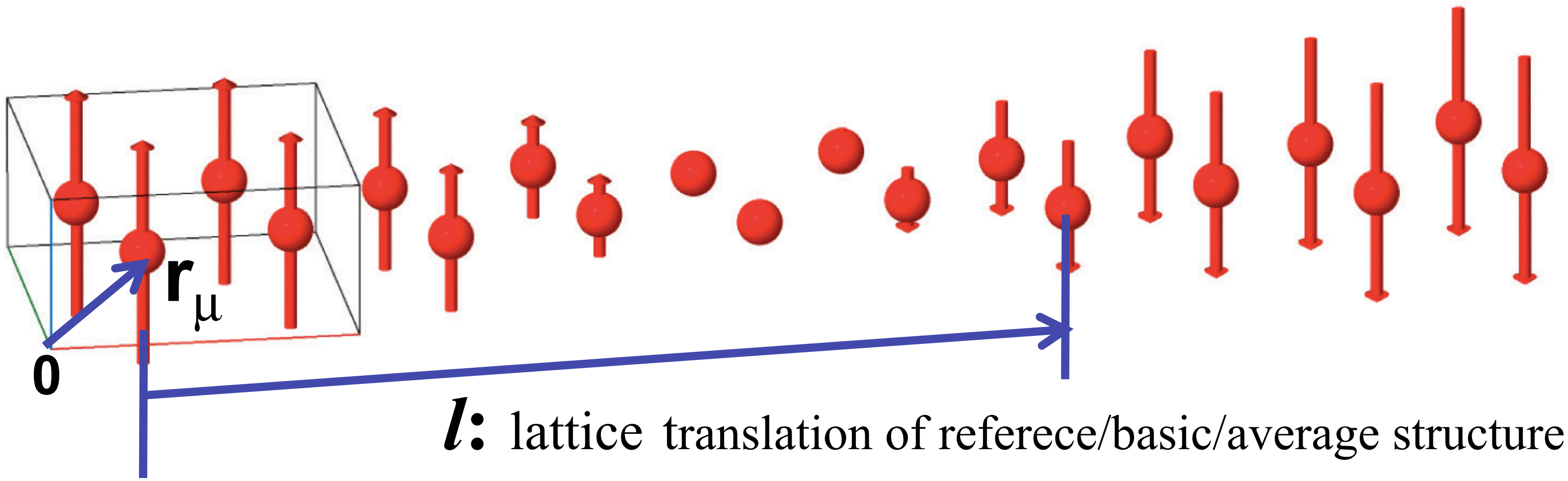
Published 26 March 2012
Online at stacks.iop.org/JPhysCM/24/163201

Abstract

Superspace symmetry has been for many years the standard approach for the analysis of non-magnetic modulated crystals because of its robust and efficient treatment of the structural constraints present in incommensurate phases. For incommensurate magnetic phases, this generalized symmetry formalism can play a similar role. In this context we review from a practical viewpoint the superspace formalism particularized to magnetic incommensurate phases. We analyse in detail the relation between the description using superspace symmetry

Incommensurate modulated structures



Harmonic Modulation with propagation vector k of "quantity" A of atom μ:

$$A(\boldsymbol{l},\mu)= A_{\mu}\, e^{-i2\pi \mathbf{k}.(\boldsymbol{l}+\mathbf{r}\mu)} + A^{*}_{\mu}\, e^{i2\pi \mathbf{k}.(\boldsymbol{l}+\mathbf{r}\mu)}$$

How do we describe a modulated structure without periodicity?

Simplest case: single-k modulated structures

(One incommensurate propagation vector k (and its opposite **-k**!) **:**

Incommensurate Structure	**=**	**Basic (periodic) structure + set of atomic modulation functions $A_\mu(x_4)$**

general anharmonic case

μ= 1,…,n atoms in unit cell of basic structure

$$A(\boldsymbol{l},\mu) = \sum_n A_{\mu,n}\, e^{-i2\pi n\mathbf{k}.(\boldsymbol{l}+\mathbf{r}_\mu)} + A^*_{\mu,n} e^{i2\pi n\mathbf{k}.(\boldsymbol{l}+\mathbf{r}_\mu)}$$

$$A_\mu(x4) = \sum_n A_{\mu,n}\, e^{i2\pi n x4} + A^*_{\mu,n} e^{-i2\pi n x4}$$

A global shift of the modulation functions along x_4 keeps the energy invariant

$$A(\boldsymbol{l},\mu) = A_\mu(x4 = \mathbf{k}.(\boldsymbol{l}+\mathbf{r}_\mu))$$

$$A_\mu(x_4) = A_{\mu 0} + \sum_{n=1,\dots} A_{\mu,ns}\sin(2\pi n x_4) + A_{\mu,nc}\cos(2\pi n x_4)$$

SYMMETRY OF INCOMMENSURATE PHASES

(Phase) global shift of all modulations along x_4 is energy invariant!

Symmetry operations in 1k incommensurate crystals:

sym. operations: space group operations
+ phase shifts of all modulations along x_4

magnetic superspace group: $\{ \{\mathbf{R}_i | \mathbf{t}_i , \tau_i\} , \{\mathbf{R'}_j|\mathbf{t}_j , \tau_j\} \}$

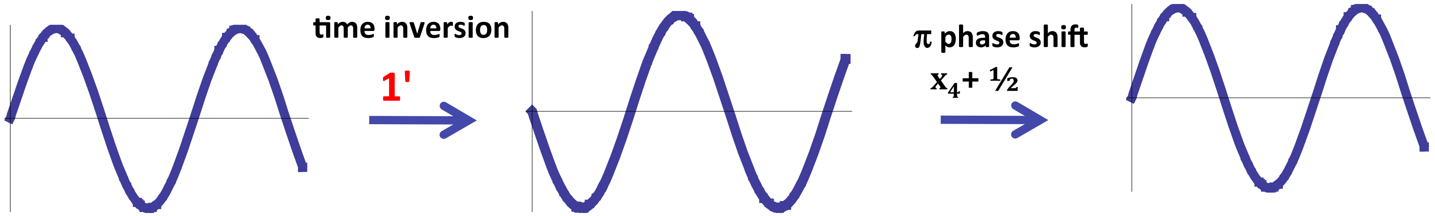
magnetic point group: set of all roto-inversion and roto-inversion+time inversion operations **{R, R'}** in its magnetic **superspace group!**

Incommensurate magnetic structures have an unambiguous magnetic point group symmetry

A simple general but <u>very important</u> "Theorem":

(1'| 0 0 0 ½)   is a superspace symmetry operation of any single-k INC magnetic modulation.

Invariance of (sinusoidal) irrep magnetic modulations for (1'| 0 0 0 ½):



1' belongs to the symmetry point group of ANY single-k INC phase (grey point group)

Consequences of (1'| 0 0 0 ½) :

$$A_{\mu}(x_4 + ½) = 1' A_{\mu}(x_4)$$

Magnetic modulations

modulation of magnetic moments

$$M_{\mu}(x_4 + ½) = - M_{\mu}(x_4)$$

odd-harmonics : 1k, 3k ,5k ...

modulation of atomic displac.

$$u_{\mu}(x_4 + ½) = u_{\mu}(x_4)$$

even-harmonics : 2k, 4k ...

structural modulations

Symmetry relations between the atomic modulations

Example: inversion in an incommensurate 1-k magnetic structure:

(x y z) atom 1 —(**-1**|000)→ (-x -y -z) atom 2

(**-1**|000,0): **-x1 –x2 –x3 –x4 +1** → **$\mathbf{M}_2(-x_4) = \mathbf{M}_1(x_4)$**

modulation of magnetic moments

If atom 1= atom 2: (atom 1 lies on the inversion center)

$\mathbf{M}_1(-x_4) = \mathbf{M}_1(x_4)$

$$M_{1\alpha}(x_4) = M_{1\alpha,0} + M_{1\alpha,nc}\cos(2\pi x_4)$$

α= ***x, y, z***

only cosine terms

collinear

Two Possible Maximal Symmetries for α-Li_2IrO_3 :

It can be obtained with ISODISTORT or with JANA:

C2/m1'

k=(0.32,0,0)
BZ sym. plane B

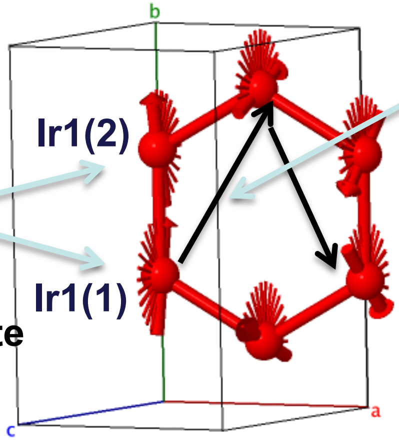
irrep mB1 → *C2/m1'(α0γ)00s*

irrep mB2 → *C2/m1'(α0γ)0ss*

Point group: 2/m1'
no chiral twinning!

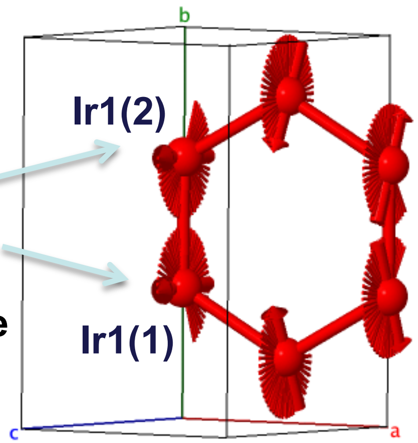
[α-Li_2IrO_3 (# 1.1.41)]

Symmetry Related:
{-1|010,0}
{m_y|010,0}
imply opposite chiralities



C -centering lattice translations: spin relations dictated by propagation vector k

Symmetry related:
{-1|010,0}
{m_y|010,1/2}
imply opposite chiralities



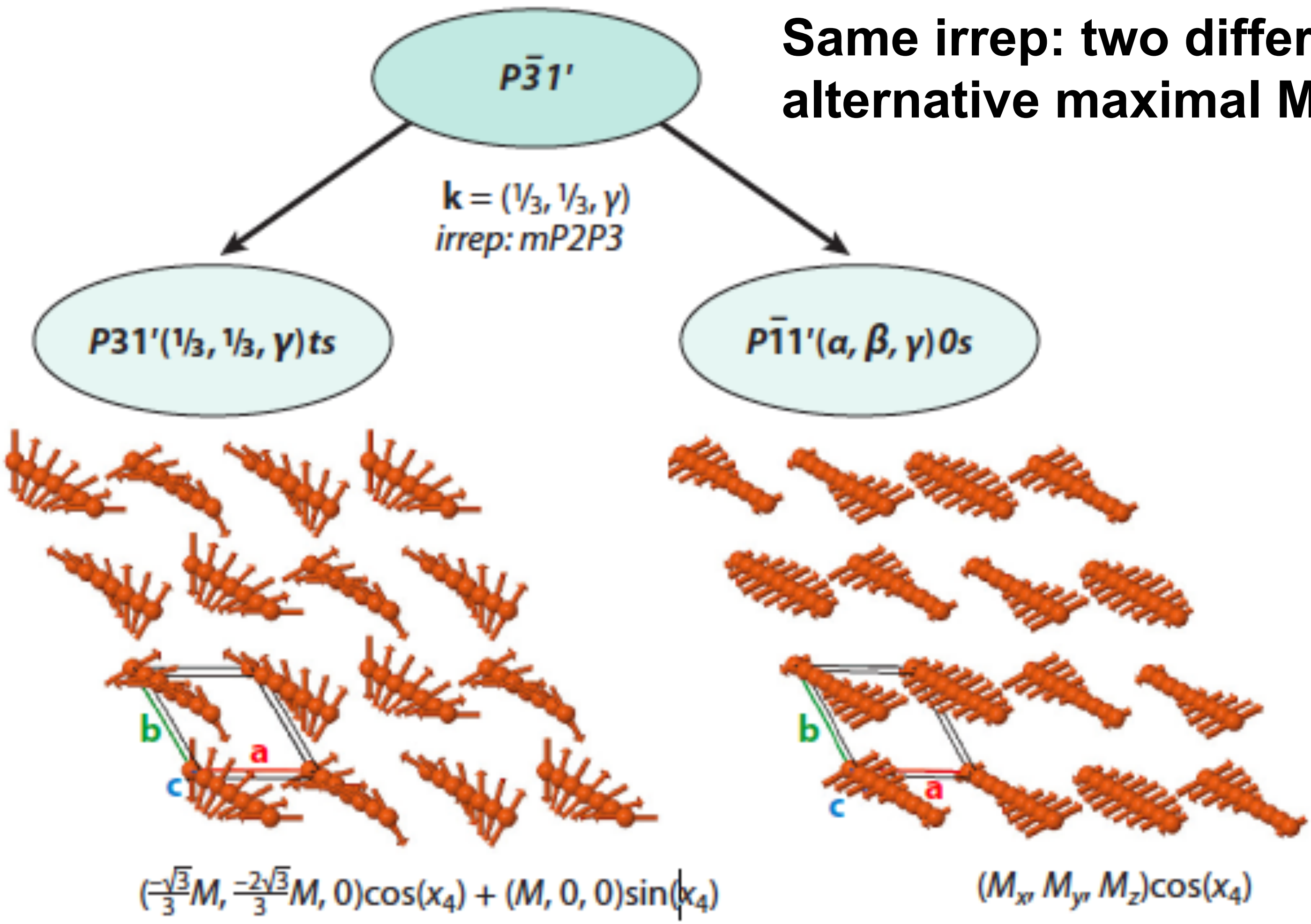
Ir1(1): $M(x_4)$ = (0,my,0) cos($2\pi x_4$) + (mx,0,mz) sin($2\pi x_4$)

Ir1(1): $M(x_4)$ = (mx,0,mz) cos($2\pi x_4$) + (0,my,0) sin($2\pi x_4$)

3 parameters

Representation analysis vs magnetic space groupsc

Same irrep: two different alternative maximal MSSGs



Possible MSSGs for a given irrep are derived by ISODISTORT and by JANA2006

Description of an incommensurate structure using superspace symmetry: $RbFe(MoO_4)_2$

magndata 1.1.2

Basic unitcell:
(not necessarily the paramgn one).

5.5955(6), 5.5955(6), 7.4377(7)
90, 90, 120

Propagation (wave) vector:

1 0.333333 0.333333 0.458

Superspace group: P31'(1/3,1/3,g)ts

x1,x2,x3,x4 ,+1
-x2,x1-x2,x3,-x2+x4+1/3,+1
-x1+x2,-x1,x3,-x1+x4+2/3, +1
x1,x2,x3,x4+1/2, -1
-x2,x1-x2,x3,-x2+x4+5/6,-1
-x1+x2,-x1,x3,-x1+x4+1/6,-1

Asymmetric unit (positions):

Rb1 Rb 0.00000 0.00000 0.50000
Fe1 Fe 0.00000 0.00000 0.50000
Mo1 Mo 0.333333 0.666667 0.234(3)
Mo2 Mo -0.333333 -0.666667 -0.234(3)
O1 O 0.333333 0.666667 0.463(6)
O2 O -0.333333 -0.666667 -0.463(6)
O3 O 0.103(4) -0.218(3) 0.158(4)
O4 O -0.103(4) 0.218(3) -0.158(4)

Asymmetric unit (moments):

Fe1 0 0 0

Asymmetric unit (moment modulations):

			cosine	sine
Fe1	x	1	-3.9/√3	3.9(5)
Fe1	y	1	-3.9*2/√3	0

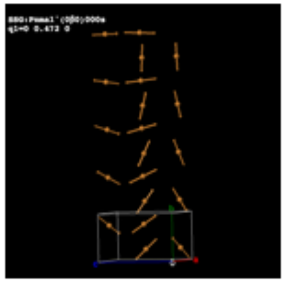
Asymmetric unit (position modulations): ???
They may exist! (subject to the same superspace group)

information portable through a magCIF file

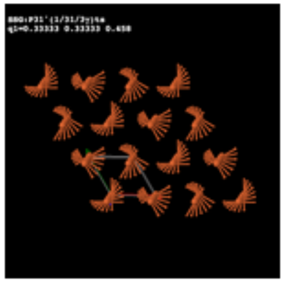
MAGNDATA

INCOMMENSURATE STRUCTURES

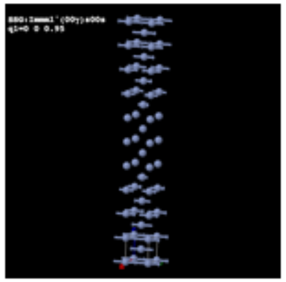
One propagation vector



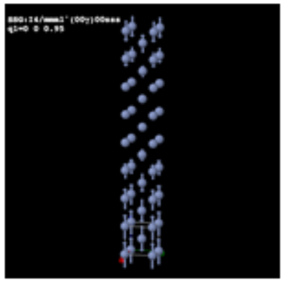
1.1.1 Cs_2CuCl_4



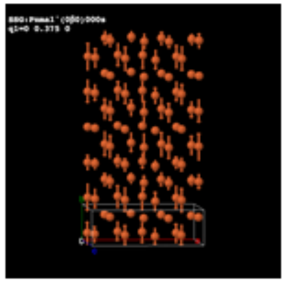
1.1.2 $RbFe(MoO_4)_2$



1.1.3 Cr

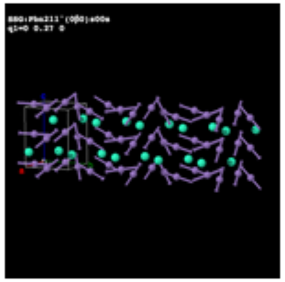


1.1.4 Cr

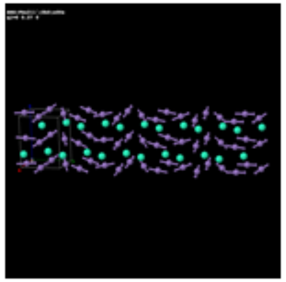


1.1.5 $CaFe_4As_3$

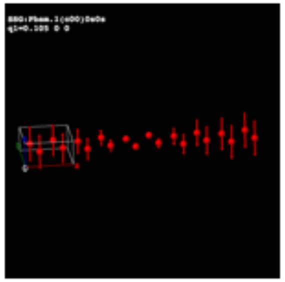
1.1.6 $TbMnO_3$



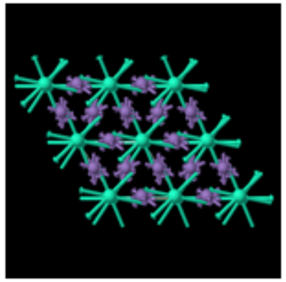
1.1.7 $TbMnO_3$



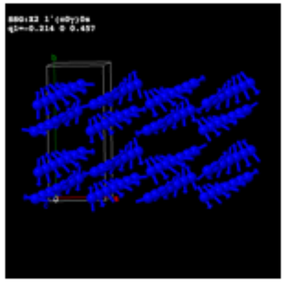
1.1.8 $TbMnO_3$



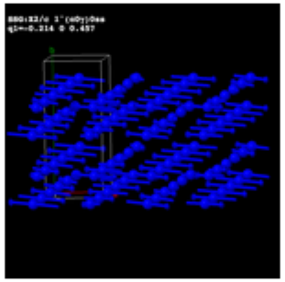
1.1.9 Ce_2Pd_2Sn



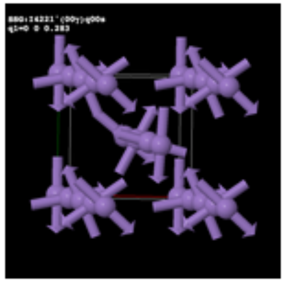
1.1.10 $DyMn_6Ge_6$



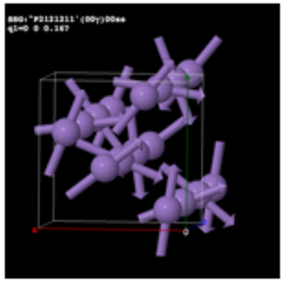
1.1.11 $MnWO_4$



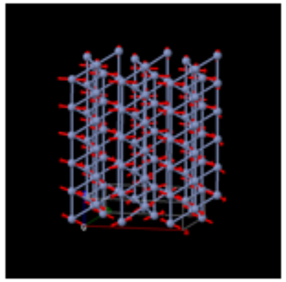
1.1.12 $MnWO_4$



1.1.13 $MnAu_2$



1.1.14 MnGe



1.1.15 $CaCr_2O_4$

Conclusions:

- **Properties of magnetic phases are constrained by their magnetic symmetry: a 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 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, and there are now free computer tools for that!**

The future of Magnetic Crystallography is clearly an unified approach of symmetry invariance and representations

(borrowed from a recent presentation of Juan Rodriguez-Carvajal (ILL))

Magnetic symmetry groups

A related workshop is taking place in december :