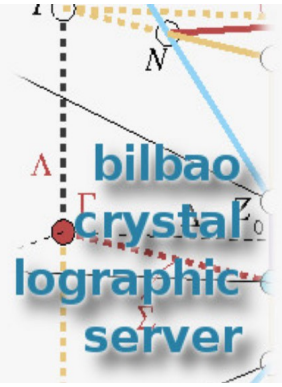
Crystallography Online: Workshop on the use and applications of the structural tools of the Bilbao Crystallographic Server

20-21 August 2018

ECM31
31st European Crystallographic Meeting

Satellite Meeting
31st European Crystallographic Meeting
Oviedo



STRUCTURAL PSEUDOSYMMETRY

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ECM31-Oviedo Satellite

Crystallography online: workshop on the use and applications of the structural tools of the Bilbao Crystallographic Server

20-21 August 2018

News:

- **New program: mCIF2PCR**
  01/2018: Transformation from mCIF to PCR format. The PCR file can be used as input for FullProf.
- **New Article**
  11/2017: Elcoro *et al.* "Double crystallographic groups and their representations on the Bilbao Crystallographic Server" *J. App. Crys.* (2017). **50**, 1457-1477.
- **New Article in Nature**
  07/2017: Bradlyn *et al.* "Topological quantum chemistry" *Nature* (2017).

- Space-group symmetry
- Magnetic Symmetry and Applications
- Group-Subgroup Relations of Space Groups
- Representations and Applications
- Solid State Theory Applications
- Structure Utilities
- Subperiodic Groups: Layer, Rod and Frieze Groups
- Structure Databases
- Raman and Hyper-Raman scattering
- Point-group symmetry
- Plane-group symmetry

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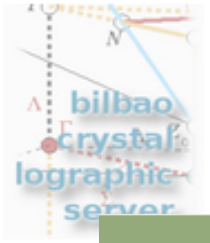
Space-group symmetry

Magnetic Symmetry and Applications



ECM31-Ovie

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Solid State Theory Applications

NEUTRON	Neutron Scattering Selection Rules
SYMMODES	Primary and Secondary Modes for a Group - Subgroup pair
AMPLIMODES	Symmetry Mode Analysis
PSEUDO	Pseudosymmetry Search in a Structure
DOPE	Degree of Pseudosymmetry Estimation
TRANPATH	Transition Paths (Group not subgroup relations)
TENSOR ⚠	Symmetry-adapted form of crystal tensors

News:

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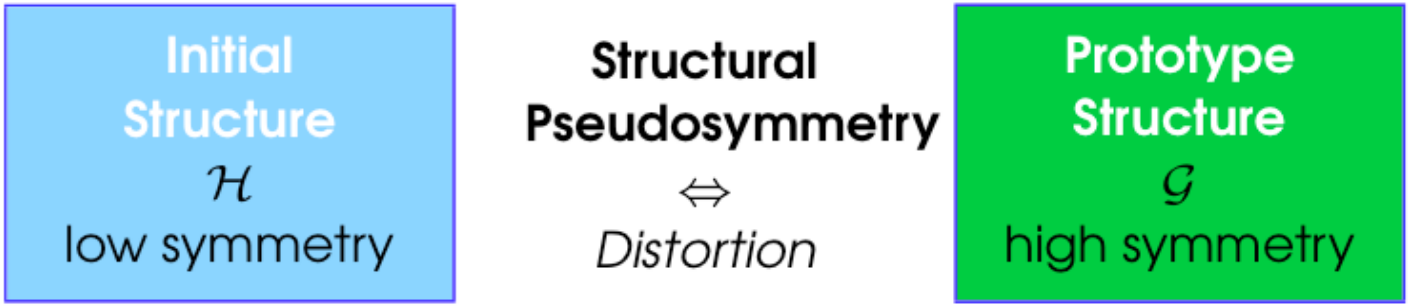
Raman and Hyper-Raman scattering

Point-group symmetry

Plane-group symmetry

Pseudosymmetry search



Search for a structure of space-group symmetry G supergroup of H, such that:

structure		structure		small (symmetry-breaking) distortion
H	=	**G**	+	
r_i		r_i^0		u_i

If the distortion is small enough, it can indicate a symmetry change at high temperature

⬇

phase transition

Pseudosymmetry search

Applications

Prediction of phase transitions

Search for **new ferroic materials**
- ferroelectrics
- ferroelastics

Prediction of the symmetry and structure of some other phase of a material

Detection of **false symmetry assignments** (overlooked symmetry)

Space-group determination of theoretically determined structure (e.g. *ab initio* calculations)

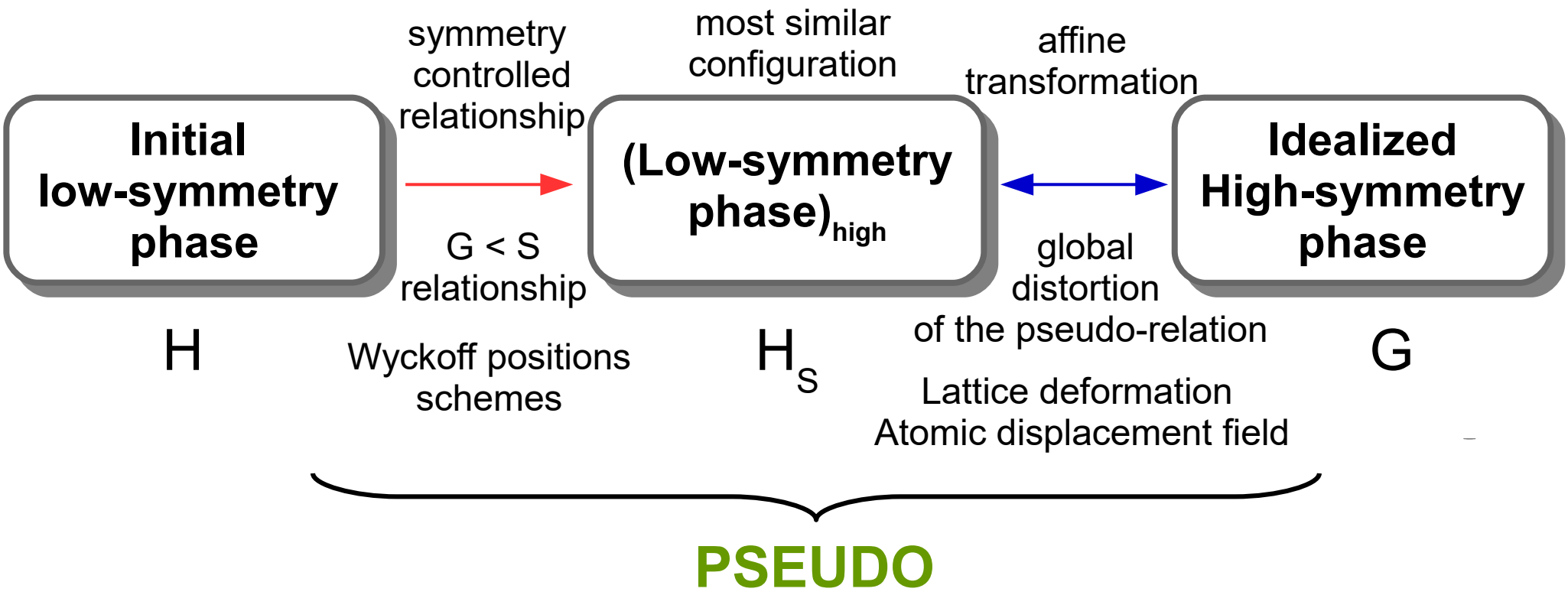
Determination of an optimised virtual parent structure (paraphase)

Pseudosymmetry search

Initial structure of space-group symmetry H

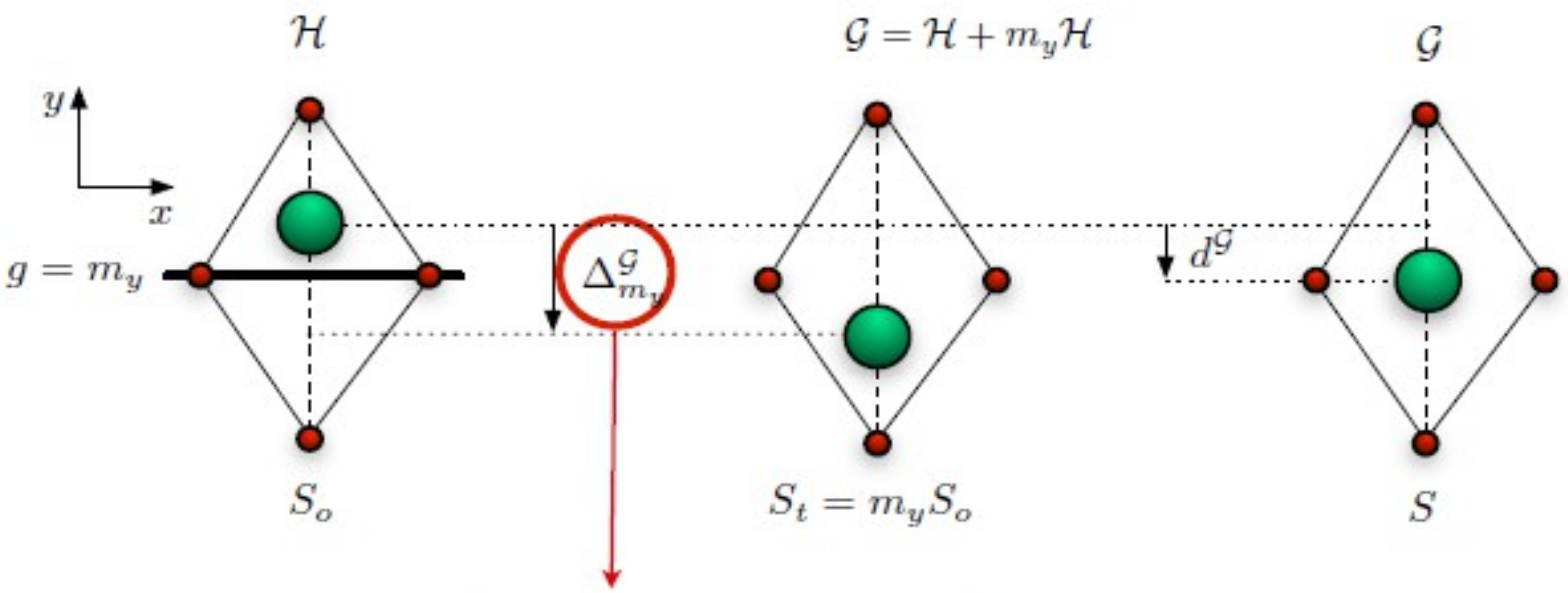
search for a structure of

Space-group symmetry G>Hsuch that the initial structure can be described by the high-symmetry structure with tolerably small distortion



Pseudosymmetry search

Atomic displacements method

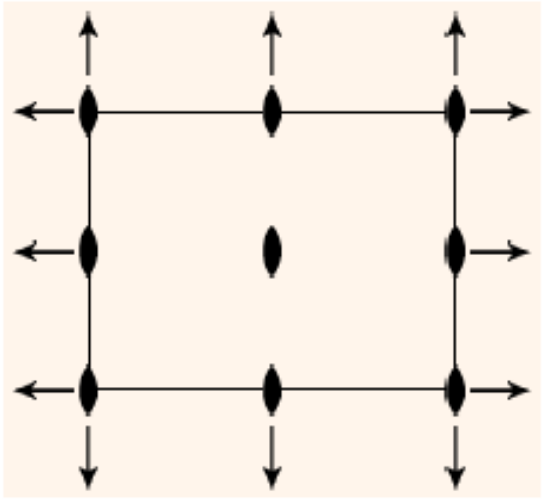


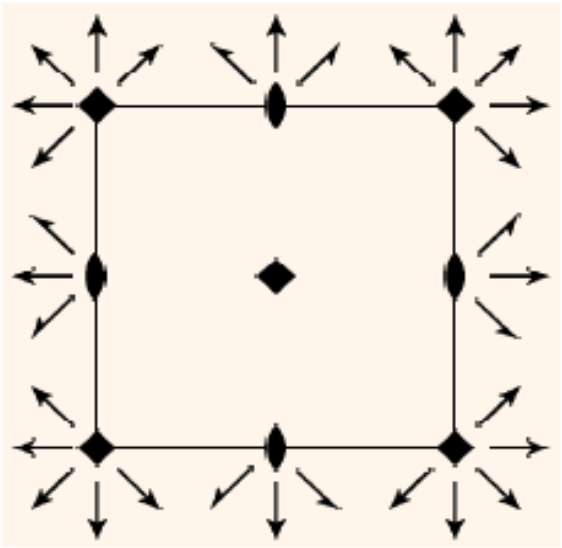
The high symmetry phase is described by a **supergroup** of the initial space group.

$$\mathcal{G} = \mathcal{H} + g_2\mathcal{H} + \cdots + g_m\mathcal{H}$$

Minimal supergroups

Supergroups of space groups





H < G is called a minimal supergroup of H if there exists no intermediate group Z for which H < Z < G

$$\mathcal{H} = \mathrm{P222}$$

$$\mathcal{G} = \mathrm{P422}$$

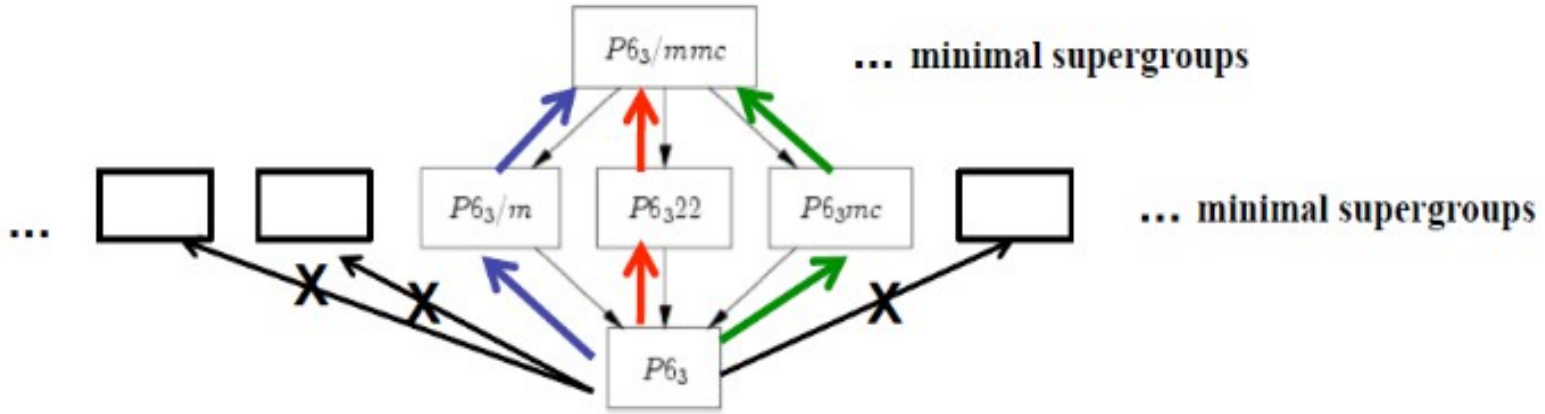
$$\mathrm{P422} = \mathrm{P222} + (4|\omega)\mathrm{P222}$$

	4 en	ω	$\mathcal{G}$
4_z	$(0,0,0)$	$(0,0,0)$	$(P422)_1$
4_y	$(0,0,0)$	$(0,0,0)$	$(P422)_2$
4_x	$(0,0,0)$	$(0,0,0)$	$(P422)_3$
4_z	$(\frac{1}{2},0,0)$	$(\frac{1}{2},\frac{1}{2},0)$	$(P422)'_1$
4_y	$(\frac{1}{2},0,0)$	$(\frac{1}{2},0,\frac{1}{2})$	$(P422)'_2$
4_x	$(0,\frac{1}{2},0)$	$(0,\frac{1}{2},\frac{1}{2})$	$(P422)'_3$

Pseudosymmetry search

Any group – supergroup relation can be represented by a chain of minimal supergroups

$$\mathcal{G} > \mathcal{H} \rightarrow \mathcal{G} > \ldots > Z_2 > Z_1 > \mathcal{H}$$



Stepwise detection of pseudosymmetry for successive minimal supergroups

If a structure of symmetry H is pseudosymmetric for a supergroup G, it will be pseudosymmetric for all intermediate subgroups Z_i

Pseudosymmetry search

PSEUDO: http://www.cryst.ehu.es/cryst/pseudosymmetry.html

Formulae

Structure data
[in CIF format]

Examinar... No se ha seleccionado ningún archivo.

HINT: [The option for a given filename is preferential]

CIFs file

Initial Structure (LS)

```
99
3.999 3.999 4.02 90 90 90
4
Ba 1 - 0.000000 0.000000 0.000000
Ti 2 - 0.500000 0.500000 0.420000
O  3 - 0.500000 0.500000 0.03
O  4 - 0.500000 0.000000 0.58
```

BCS format

PSEUDO Is not applicable to structures with order-disorder features in their distortion

Pseudosymmetry search

Option 1

Select supergroups type for pseudosymmetry search.

- (•) Minimal supergroups — [ ] [Show only indices in supergroups table]
- ( ) Supergroups with k-index — i_k: 1
- ( ) Specify supergroup transformation — G: 221

	Linear part			Origin Shift
Transf. Matrix (in option 3 only)	1	0	0	0
	0	1	0	0
	0	0	1	0

- ( ) ⚠ For monoclinic and triclinic structures: previous check of lattice pseudosymmetry — **Ang. Tol (in degrees)** 5 [*]

[*] Only for triclinics and monoclinics.

Enter the tolerance (maximum allowed distance) for pseudosymmetry search.

Maximum Δ: 2

Tolerance [Å]

Pseudosymmetry search

Option 2

Select supergroups type for pseudosymmetry search.

- (•) Minimal supergroups — [ ] [Show only indices in supergroups table]
- ( ) Supergroups with k-index — i_k: 1
- ( ) Specify supergroup transformation — G: 221

	Linear part			Origin Shift
Transf. Matrix (in option 3 only)	1	0	0	0
	0	1	0	0
	0	0	1	0

- ( ) ⚠ For monoclinic and triclinic structures: previous check of lattice pseudosymmetry — **Ang. Tol (in degrees)** 5 [*]

[*] Only for triclinics and monoclinics.

Enter the tolerance (maximum allowed distance) for pseudosymmetry search.

Maximum Δ: 2

Tolerance [Å]

Pseudosymmetry search

Option 3

Select supergroups type for pseudosymmetry search.

- (•) Minimal supergroups — [ ] [Show only indices in supergroups table]
- ( ) Supergroups with k-index — i_k: 1
- ( ) Specify supergroup transformation — G: 221

Transf. Matrix (in option 3 only)

	Linear part			Origin Shift
	1	0	0	0
	0	1	0	0
	0	0	1	0

- ( ) ⚠ For monoclinic and triclinic structures: previous check of lattice pseudosymmetry — **Ang. Tol (in degrees)** 5 [*]

[*] Only for triclinics and monoclinics.

Enter the tolerance (maximum allowed distance) for pseudosymmetry search.

Maximum Δ: 2

Tolerance [Å]

Pseudosymmetry search

Select supergroups type for pseudosymmetry search.

- (•) Minimal supergroups — [ ] [Show only indices in supergroups table]
- ( ) Supergroups with k-index — i_k: 1
- ( ) Specify supergroup transformation — G: 221

Transf. Matrix (in option 3 only)

	Linear part			Origin Shift
	1	0	0	0
	0	1	0	0
	0	0	1	0

Option 4

( ) ⚠ For monoclinic and triclinic structures: previous check of lattice pseudosymmetry — **Ang. Tol (in degrees)** 5 [*]

New Version Coming Soon

[*] Only for triclinics and monoclinics.

Enter the tolerance (maximum allowed distance) for pseudosymmetry search.

Maximum Δ: 2

Tolerance [Å]

Exercise 2.4

Analyse the structural pseudosymmetry of Pb_2MgWO_6

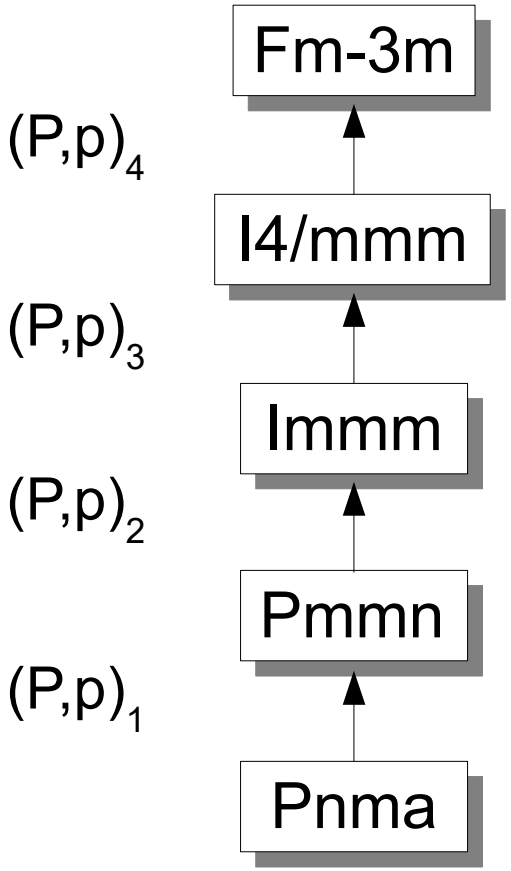
Option 1: Search of maximal pseudosymmetry stepwise ‘climbing’ via minimal supergroups

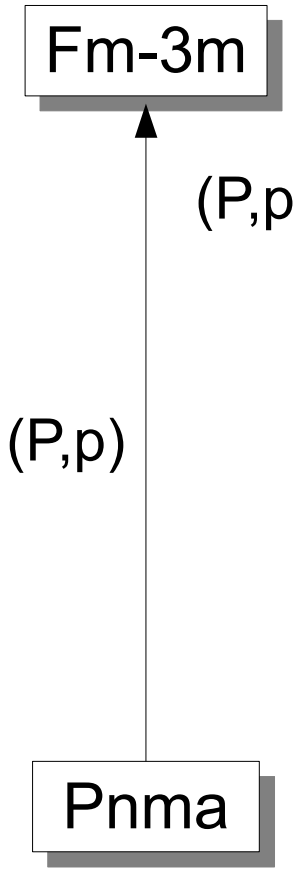
```
#Exercise 2.4.10:Pb2MgWO6:Pseudo1
# Space Group ITA number
62
# Lattice parameters
11.4059 7.9440 5.6866 90.00 90.00 90.00
# Number of independent atoms in the asymmetric unit
8
# [atom type] [number] [WP] [x] [y] [z]
Pb    1   8d    0.1422 0.0032 0.7804
Mg   1   4c    0.3772 0.25 0.7519
W     1   4c    0.1161 0.25 0.2577
O     1   8d    0.1314 0.4907 0.2365
O     2   4c    0.0027 0.25 0.0133
O     3   4c    0.0103 0.25 0.4991
O     4   4c    0.237 0.25 -0.0153
O     5   4c    0.2491 0.25 0.4745
```

EXCERCISE – Exercise 2.4 (ii)

Analyse the structural pseudosymmetry of Pb_2MgWO_6

Option 3: Search of structural pseudosymmetry with respect to specific supergroup





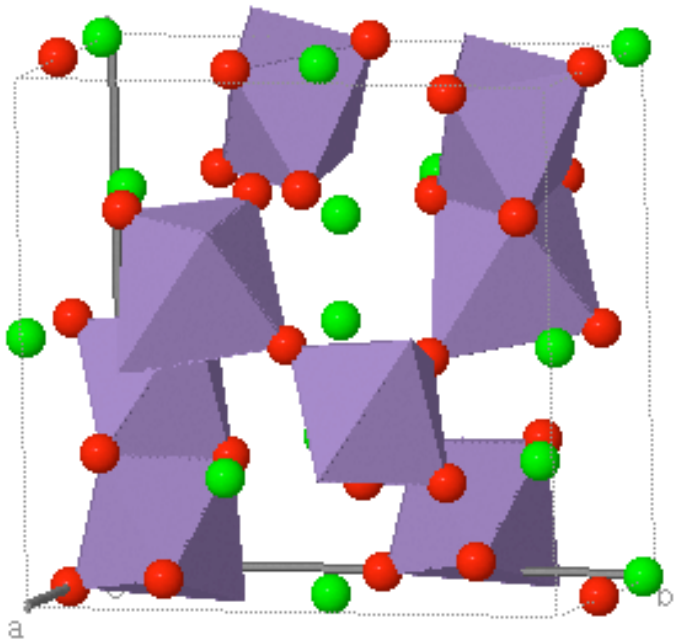
$(P,p)=(P,p)_1(P,p)_2(P,p)_3(P,p)_4$

P=a-b,c,-1/2a-1/2b
p=1/2,1/4,1/4

Exercise 2.5

Analyse the structural pseudosymmetry of the virtual structure of $C222_1$ (No. 20) symmetry stepwise, *i.e.* via the minimal supergroup Option 1 of PSEUDO. Compare the results if different minimal-supergroup paths are followed.

C222_1
a=5,444Å
b=9,412Å
c=9,063Å
α=90,0°
β=90,0°
γ=90,0°

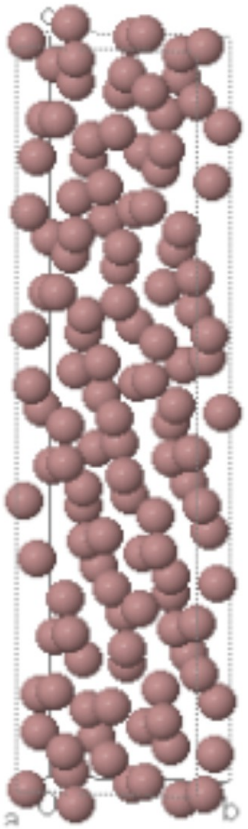


Exercise 2.6

Ga under pressure

Analyse the structural pseudosymmetry of the orthorhombic phase Ga-II of Ga under pressure. (For the structure data, see the Structure Data file.)

C222_1
a=5,976Å
b=8,576Å
c=35,758Å
α=90,0°
β=90,0°
γ=90,0°

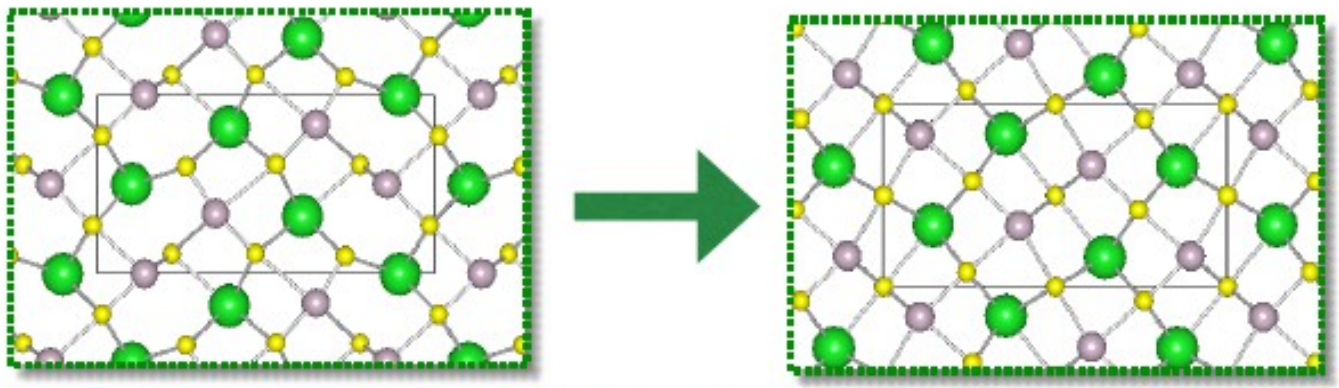


Hint: As a first step check the structural pseudosymmetry with respect to an isomorphic supergroup of index 13, specified by the transformation matrix: a,b,13c, i.e. first apply Option 3 of PSEUDO

Search for ferroelectrics

Two necessary conditions for a structure to be ferroelectric:

- Polar symmetry group (it should allow non-zero polarization)
- Pseudosymmetry with respect to a non-polar symmetry group (the polar distortion should be small and “multistable”)



Search for ferroelectrics

Select minimal supergroups of space group *P4mm* (99)

$BaTiO_3$

The next step is to select the supergroups which the pseudosymmetry should be searched for. Each supergroup in the table can be selected by marking the corresponding che

Select/Unselect all: ☐

No. #	Select	HM Symb.	IT Numb.	Index	Index i_k	Transformation (P,p)	Transformed Cell	Wyckoff Positions Splitting Consideration
1	☐	*P4mm*	099	2	2	**a,b,2c** ; 0,0,2t	3.9990 3.9990 2.0100 90.00 90.00 90.00	This transformation is invalid under Wyckoff Splitting criteria. Details..
2	☐	*P4mm*	099	2	2	**a-b,a+b,c** ; 0,0,t	2.8277 2.8277 4.0200 90.00 90.00 90.00	This transformation is invalid under Wyckoff Splitting criteria. Details..
3	☐	*P4mm*	099	3	3	**a,b,3c** ; 0,0,3t	3.9990 3.9990 1.3400 90.00 90.00 90.00 Lattice parameters don't comply [Threshold: 0.5Å for a,b,c ; 10° for α,β,γ & lengths must be >2.0Å]	This transformation is invalid under Wyckoff Splitting criteria. Details..
4	☐	*P4mm*	099	5	5	**a,b,5c** ; 0,0,5t	3.9990 3.9990 0.8040 90.00 90.00 90.00 Lattice parameters don't comply [Threshold: 0.5Å for a,b,c ; 10° for α,β,γ & lengths must be >2.0Å]	This transformation is invalid under Wyckoff Splitting criteria. Details..
5	☐	*P4mm*	099	7	7	**a,b,7c** ; 0,0,7t	3.9990 3.9990 0.5743 90.00 90.00 90.00 Lattice parameters don't comply [Threshold: 0.5Å for a,b,c ; 10° for α,β,γ & lengths must be >2.0Å]	This transformation is invalid under Wyckoff Splitting criteria. Details..
6	☐	*P4mm*	099	9	9	**a,b,9c** ; 0,0,9t	3.9990 3.9990 0.4467 90.00 90.00 90.00 Lattice parameters don't comply [Threshold: 0.5Å for a,b,c ; 10° for α,β,γ & lengths must be >2.0Å]	This transformation is invalid under Wyckoff Splitting criteria. Details..
7	☐	*P4mm*	099	9	9	**3a,3b,c** ; 0,0,t	1.3330 1.3330 4.0200 90.00 90.00 90.00 Lattice parameters don't comply [Threshold: 0.5Å for a,b,c ; 10° for α,β,γ & lengths must be >2.0Å]	This transformation is invalid under Wyckoff Splitting criteria. Details..
8	☐	*I4mm*	107	2	2	**a,b,c** ; 0,0,t	3.9990 3.9990 4.0200 90.00 90.00 90.00	This transformation is invalid under Wyckoff Splitting criteria. Details..
9	☑	*P4/mmm*	123	2	1	**a,b,c** ; 0,0,t	3.9990 3.9990 4.0200 90.00 90.00 90.00	This transformation is valid under Wyckoff Splitting conditions. Details..
10	☐	*P4/nmm*	129	2	1	**a,b,c** ; 1/4,1/4,t	3.9990 3.9990 4.0200 90.00 90.00 90.00	This transformation is invalid under Wyckoff Splitting criteria. Details..

HINT: The initial structure is polar, which means that, in general, an origin shift will be necessary to minimize the displacements between the initial polar structure and the hypothetical idealized parent one. Please insert a minimum grid for the optimization (in Angstroms)

grid for optimization

Grid: 0.4

Exercise 2.7

The compound $NaSb_3F_{10}$ whose room-temperature phase is polar, space group $P6_3$, has been predicted to be ferroelectric. (For the structure data, see the Structure Data file.) The symmetries $P6_322$ and $P6_3/mmc$ had been proposed for two successive non-polar phases at high temperature.

Applying the pseudosymmetry approach confirm the predictions for the non-polar phases of $NaSb_3F_{10}$. Show that apart from $P6_322$, there are two more appropriate candidates for the intermediate phases between the polar phase $P6_3$ and the non-polar one of maximal symmetry, $P6_3/mmc$.