Summer School on Mathematical Crystallography

3-7 June 2019, Nancy (France)

International Union of CrystallographyCommision on Mathematical and Theoretical Crystallography

IUCr MaThCryst CRM² Cristallographie, Résonance Magnétique et Modélisations AFC C2MP métropole GrandNancy

CRYSTAL-STRUCTURE RELATIONS

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Karlsruher Institut für Technologie

CRYSTAL-STRUCTURE RELATIONSHIPS

Structure relations

Symmetry relations between crystal structures

Structural pseudosymmetry

www.cryst.ehu.es

FCT/ZTF

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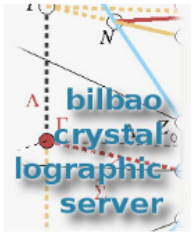

Bilbao Crystallographic Server in forthcoming schools and workshops

News:

- **New Article in Acta Cryst. A** 05/2019: Gallego *et al.* "Automatic calculation of symmetry-adapted tensors in magnetic and non-magnetic materials: a new tool of the Bilbao Crystallographic Server." *Acta Cryst.* (2019) **A75**, 438-447.
- **New Article in Nature** 03/2019: Vergniory *et al.* "A complete catalogue of high-quality topological materials" *Nature* (2019). **566**, 480-485.
- **Updated versions of TENSOR and MTENSOR** 03/2019: The programs give the general expression of tensor properties for a given point group and magnetic point group, respectively..

- 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
- Double point and space groups

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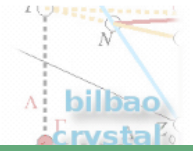

Space-group symmetry

Magnetic Symmetry and Applications

Structure Utilities

CELLTRAN	Transform Unit Cells
STRAIN	Strain Tensor Calculation
WPASSIGN	Assignment of Wyckoff Positions
TRANSTRU	Transform structures.
SETSTRU	Alternative Settings for a given Crystal Structure
EQUIVSTRU	Equivalent Descriptions for a given Crystal Structure
STRCONVERT	Convert & Edit Structure Data (supports the CIF, mCIF, VESTA, VASP formats -- with magnetic information where available)
VISUALIZE	Visualize structures using Jmol
COMPSTRU	Comparison of Crystal Structures with the same Symmetry
STRUCTURE RELATIONS	Evaluation of structure relationships [transformation matrix] between group-subgroup related phases
PSEUDOLATTICE	Pseudosymmetry of a lattice and compatible supergroups

complete catalogue of high-quality topological materials" *Nature* (2019). 566, 480-485.

- Updated versions of TENSOR and MTENSOR 03/2019: The programs give the general expression of tensor properties for a given point group and magnetic point group, respectively..

Raman and Hyper-Raman scattering

Point-group symmetry

Plane-group symmetry

Double point and space groups

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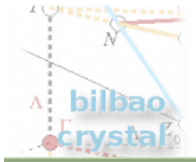

Space-group symmetry

Magnetic Symmetry and Applications

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

Bil
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News

438-447.

- **New Article in Nature** 03/2019: Vergniory *et al.* "A complete catalogue of high-quality topological materials" *Nature* (2019). 566, 480-485.
- **Updated versions of TENSOR and MTENSOR** 03/2019: The programs give the general expression of tensor properties for a given point group and magnetic point group, respectively..

Structure Databases

Raman and Hyper-Raman scattering

Point-group symmetry

Plane-group symmetry

Double point and space groups

CRYSTAL-STRUCTURE RELATIONSHIP

You can access to the material of the workshop by:

http://www.cryst.ehu.es/resources/nancy2019/

You can need to download:

- StructureRelations.txt

STRUCTURE RELATIONS

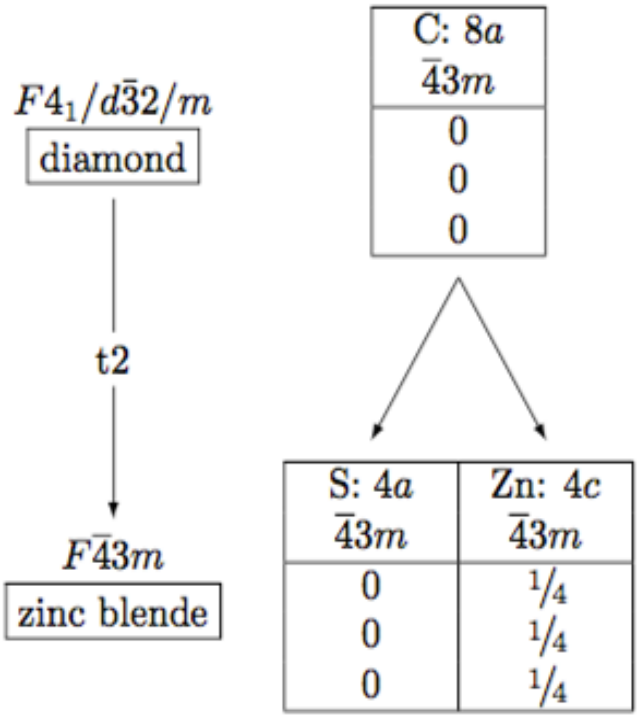
CRYSTAL-STRUCTURE RELATIONSHIP

Structure relations

Symmetry relations using crystallographic group-subgroup relations is a vaulable tool in crystal chemistry and physics.

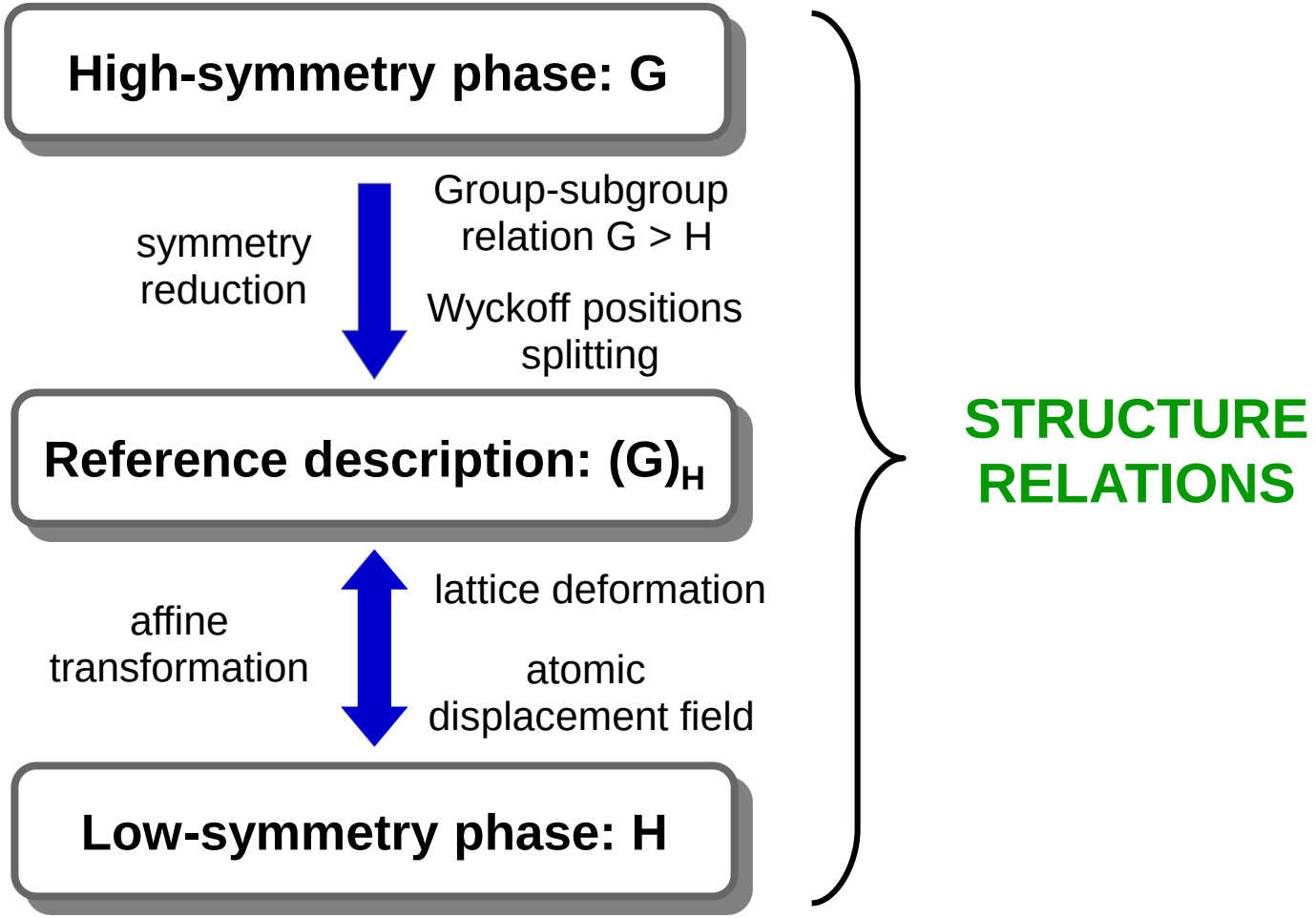
Applications

- Family trees of group-subgroup relations (Bärnighausen tree)
- Twinned crystals and antiphase domains
- Phase transitions
- Prediction of crystal-structure types



Structure relations

Structural Relationship between two structures with group-subgroup related symmetry groups **G > H**



Structure relations

High symmetry structure

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data
[CIF format]

Examinar... No se ha seleccionado ningún archivo.

BCS Format

```
# Space Group ITA number
221
# Lattice parameters
4.006 4.006 4.006 90 90 90
# Number of independent atoms in the asymmetric unit
3
# [atom type] [number] [WP] [x] [y] [z]
Ba   1 1a 0.0 0.0 0.0
Ti   1 1b 0.5 0.5 0.5
O    1 3c 0.5 0.0 0.5
```

Low symmetry structure:

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data
[CIF format]

Examinar... No se ha seleccionado ningún archivo.

BCS Format

```
# Space Group ITA number
38
# Lattice parameters
3.9828 5.6745 5.6916 90 90 90
# Number of independent atoms in the asymmetric unit
4
# [atom type] [number] [WP] [x] [y] [z]
Ba   1 2a 0.0 0.0 0
Ti   1 2b 0.5 0.0 0.5170
O    1 2a 0.0 0.0 0.4890
O    2 4e 0.5 0.2561 0.2343
```

Calculation parameters:

Enter the allowed tolerance (a b c α β γ): .2 .2 .3 2 2 2

Enter the maximum distance allowed between the paired atoms: 1.5 Å

One or both of the structures are given in a non-standard setting? ◉ No | ○ Yes

Calculation method:

◉ The group-subgroup transformation matrices are automatically fetched from the database.

○ User defined group-subgroup transformation matrix : a,b,c;0,0,0

STRUCTURE RELATIONS

http://www.cryst.ehu.es/cryst/rel.html

$BaTiO_3$

Structure relations

Pm-3m high-symmetry phase

$$(\mathbf{P},p)=\begin{pmatrix} 0 & 1 & 1 & 0.00510 \\ 0 & -1 & 1 & 0.00510 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

Symmetry controlled mapping

(High-symmetry phase)$_{Amm2}$

Global distortion

Lattice deformation
Atomic displacement field

Amm2 low-symmetry phase

High Symmetry Structure

```
221
4.006 4.006 4.006 90 90 90
3
Ba      1    1a     0.000000 0.000000 0.000000
Ti      1    1b     0.500000 0.500000 0.500000
O       1    3c     0.500000 0.000000 0.500000
```

```
038
4.006000 5.665339 5.665339 90.000000 90.000000 90.000000
4
Ba      1       2a      0.000000        0.000000        0.994920
Ti      1       2b      0.500000        0.000000        0.494920
O       1       4e      0.500000        0.250000        0.244920
O       12      2a      0.000000        0.000000        0.494920
```

Low Symmetry Structure

```
38
3.9828 5.6745 5.6916 90 90 90
4
Ba      1    2a     0.000000 0.000000 0.000000
Ti      1    2b     0.500000 0.000000 0.517000
O       1    2a     0.000000 0.000000 0.489000
O       2    4e     0.500000 0.256100 0.234300
```

Structure relations

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
2a	(0,0,z)	Ba1	0.0000	0.0000	-0.0051	0.0289
2b	(1/2,0,z)	Ti1	0.0000	0.0000	-0.0221	0.1257
2a	(0,0,z)	O12	0.0000	0.0000	0.0059	0.0337
4e	(1/2,y,z)	O1	0.0000	-0.0061	0.0106	0.0697

High Symmetry Structure

```
221
4.006 4.006 4.006 90 90 90
3
Ba      1    1a     0.000000 0.000000 0.000000
Ti      1    1b     0.500000 0.500000 0.500000
O       1    3c     0.500000 0.000000 0.500000
```

```
038
4.006000 5.665339 5.665339 90.000000 90.000000 90.000000
4
Ba      1       2a      0.000000        0.000000        0.994920
Ti      1       2b      0.500000        0.000000        0.494920
O       1       4e      0.500000        0.250000        0.244920
O       12      2a      0.000000        0.000000        0.494920
```

Evaluation of the Global Distortion

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0025	0.1257	0.0655	0.035

Low Symmetry Structure

```
38
3.9828 5.6745 5.6916 90 90 90
4
Ba      1    2a     0.000000 0.000000 0.000000
Ti      1    2b     0.500000 0.000000 0.517000
O       1    2a     0.000000 0.000000 0.489000
O       2    4e     0.500000 0.256100 0.234300
```

Exercise 3.5

Cristobalite phase transitions

At low temperatures, the space-group symmetry of cristobalite is given by the space group is $P4_12_12$ (92) with lattice parameters $a = 4.9586\mathring{A}$, $c = 6.9074\mathring{A}$. The four silicon atoms are located in Wyckoff position $4(a)..2$ with the coordinates $x, x, 0; -x, -x, 1/2; 1/2 - x, 1/2 + x, 1/4; 1/2 + x, 1/2 - x, 3/4$, $x = 0.3028$. During the phase transition, the tetragonal structure is transformed into a cubic one with space group $Fd\bar{3}m(227)$, $a = 7.147A$. It is listed in the space-group tables with two different origins.

1. If Origin choice 2 setting is used (with point symmetry $\bar{3}m$ at the origin), then the silicon atoms occupy the position $8(a)$ $\bar{4}3m$ with the coordinates 1/8, 1/8, 1/8; 7/8, 3/8, 3/8 and those related by the face - centring translations. Describe the structural distortion from the cubic to the tetragonal phase by the determination of (i) the displacements if the Si atoms in relative and absolute units, and (ii) the lattice distortion accompanying the transition.
2. Repeat the calculations for the characterization of the phase transition using the *Origin-choice 1* description of the high-symmetry phase (*cf. Exercise Data* file for the structure data).

Exercise 3.6

Lead phosphate phase transition

(a) Lead phosphate $Pb_3(PO_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R\bar{3}m$ (No.166) to a ferroelastic phase of symmetry $C2/c$ (No.15). Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server*:

(a) characterize the symmetry reduction between the high- and low-symmetry phases (index and transformation matrix);

(b) describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.

SYMMETRY RELATIONS BETWEEN CRYSTAL STRUCTURES

BÄRNIGHAUSEN TREES

Symmetry relations between crystal structures

Bärnighausen Trees: Pyrite Structural Family

Aristotype

Basic structure

$P2_1/a\,\bar{3}$

FeS_2

Fe:4*a* $\bar{3}$	S:8*c* 3
0	0.384 [0.616]
0	0.384 [0.616]
0	0.384 [0.616]

t2

$P2_13$

NiAsS

Ni:4*a* 3	S:4*a* 3	As:4*a* 3
−0.006	0.385	0.618
−0.006	0.385	0.618
−0.006	0.385	0.618

t3

Hettotypes

Derivatie structures

$P2_1/b\,2_1/c\,2_1/a$

PdS_2

Pd:4*a* $\bar{1}$	S:8*c* 1
0	0.393 [0.607]
0	0.388 [0.612]
0	0.425 [0.575]

t2

$-\frac{1}{4}, 0, 0$

$x+\frac{1}{4}, y, z$

$Pbc2_1$

CoAsS

Co:4*a* 1	S:4*a* 1	As:4*a* 1
0.259	0.631	0.869
−0.005	0.383	0.619
0	0.380	0.617

lattice parameters in pm:

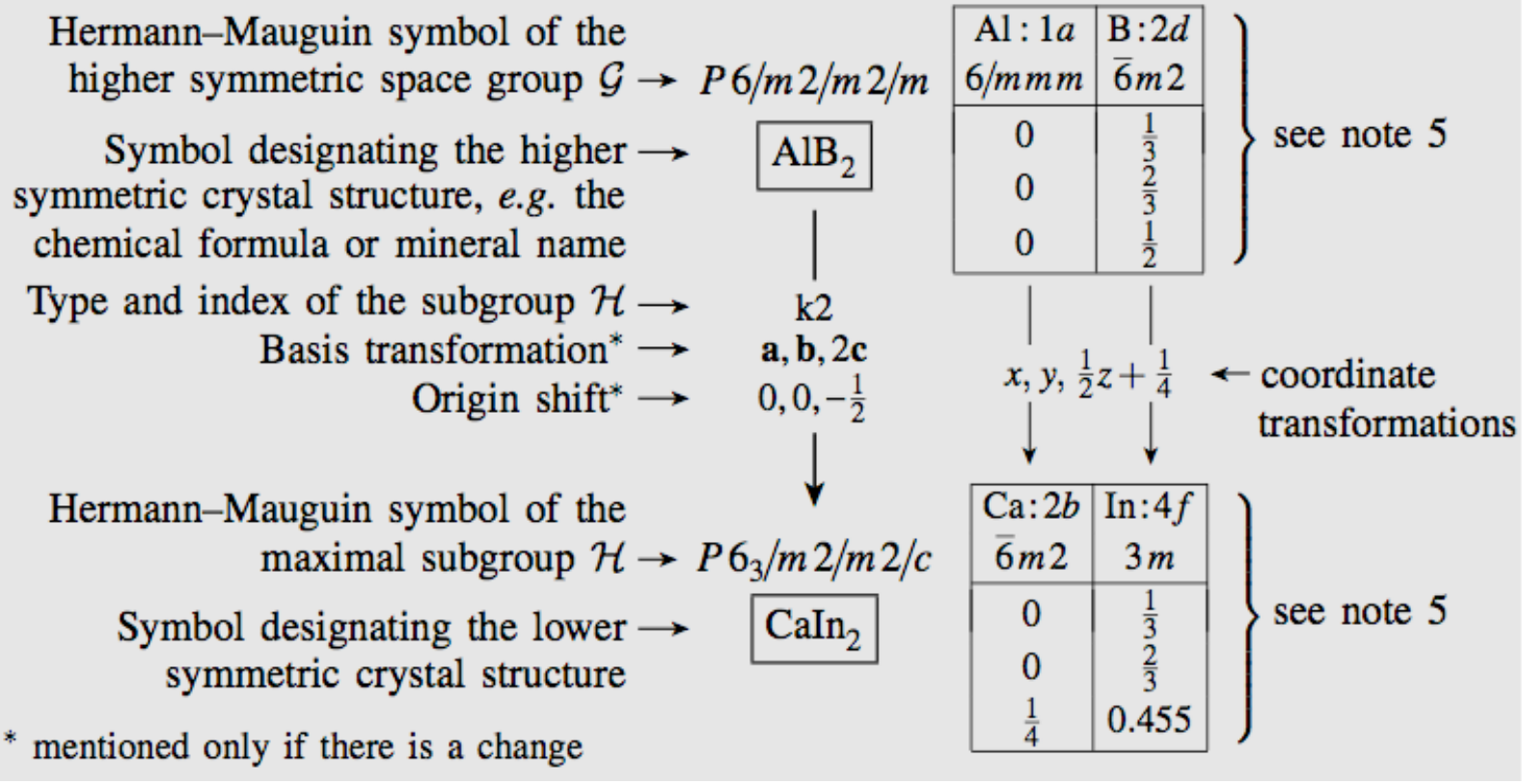
	a	*b*	*c*	references
FeS_2	541.8	541.8	541.8	[80]
NiAsS	568.9	568.9	568.9	[107]
PdS_2	546.0	554.1	753.1	[108]
CoAsS	558.9	558.3	558.1	[109]

U. Mueller, Gargnano 2008

Bärninghausen Trees

Module design of crystal symmetry relations

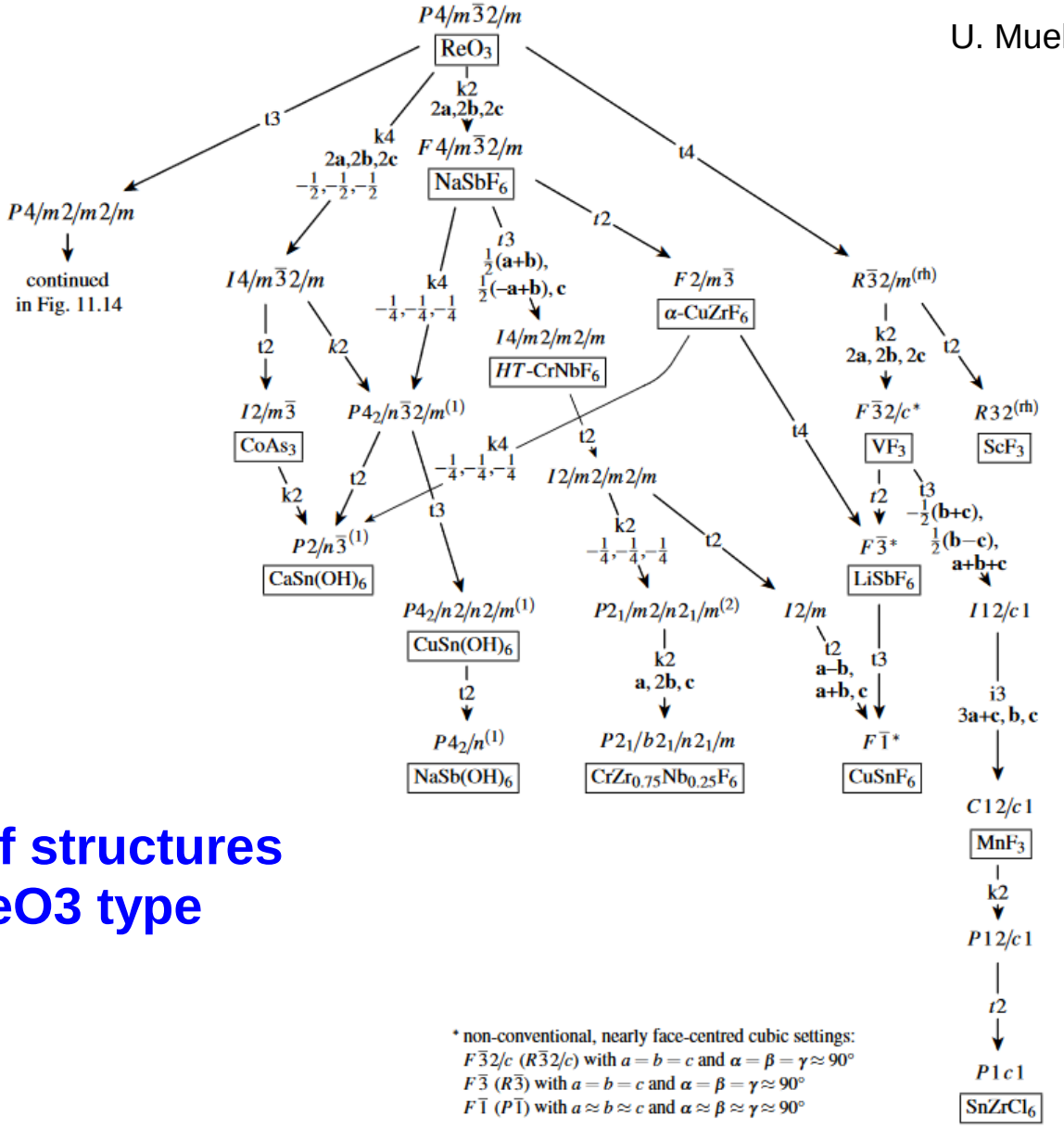
Scheme of the general formulation of the smallest step of symmetry reduction connecting two related crystal structures



U. Mueller, Gargnano 2008

Bärninghausen Trees

U. Mueller, Gargnano 2008

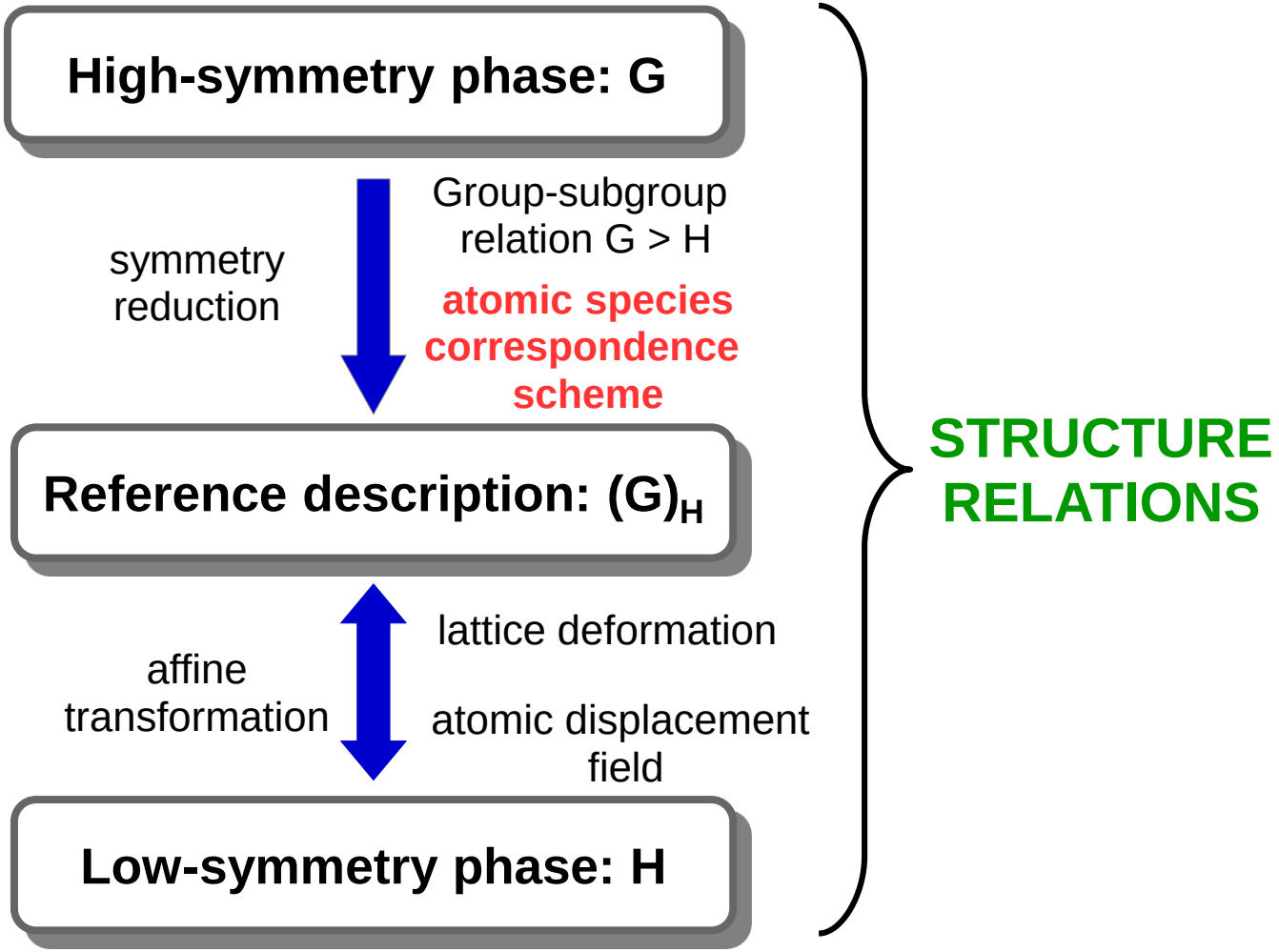


The family of structures of the ReO3 type

* non-conventional, nearly face-centred cubic settings:
$F\bar{3}2/c$ ($R\bar{3}2/c$) with $a = b = c$ and $\alpha = \beta = \gamma \approx 90°$
$F\bar{3}$ ($R\bar{3}$) with $a = b = c$ and $\alpha = \beta = \gamma \approx 90°$
$F\bar{1}$ ($P\bar{1}$) with $a \approx b \approx c$ and $\alpha \approx \beta \approx \gamma \approx 90°$

Symmetry relations between crystal structures

Structural Relationship between two structures with group-subgroup related symmetry groups **G > H**



Symmetry relations between crystal structures

High symmetry structure

Enter the formula units in the **high symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data
[CIF format]
Examinar... No se ha seleccionado ningún archivo.

BCS Format

```
221
3.007 3.007 3.007 90. 90. 90.
3
Al   1    48n 0.170000     0.290000     0.470000
```

Low symmetry structure:

Enter the formula units in the **low symmetry structure**
(Leave blank for auto-detection via the volume information)

Structure Data
[CIF format]
Examinar... No se ha seleccionado ningún archivo.

BCS Format

```
099
4.252540 4.252540 3.00700          000 90.000000 90.
15
Fe   1    8g   0.910000     0.380000     0.170000
Fe   1_2  8g   0.620000     0.090000     0.830000
Fe   1_3  8g   0.440000     0.730000     0.470000
Fe   1_4  8g   0.270000     0.560000     0.530000
Fe   1_5  8g   0.650000     0.820000     0.290000
Fe   1_6  8g   0.820000     0.650000     0.710000
Fe   1_7  8g   0.410000     0.880000     0.170000
Fe   1_8  8g   0.120000     0.590000     0.830000
Fe   1_9  8g   0.940000     0.230000     0.470000
Fe   1_10    8g   0.770000     0.060000     0.530000
Fe   1_11    8g   0.150000     0.320000     0.290000
Fe   1_12    8g   0.320000     0.150000     0.710000
```

Different atomic species

Calculation parameters:

Enter the allowed tolerance (a b c α β γ): 2 2 2 2 2 2

Enter the maximum distance allowed between the paired atoms: 1.5 Å

One or both of the structures are given in a non-standard setting? ◉ No | ○ Yes

Calculation method:

◉ The group-subgroup transformation matrices are automatically fetched from the database.

○ User defined group-subgroup transformation matrix : a,b,c;0,0,0

Species Matching:

☐ Force a species match even if the two structures contain the same types of elements

Exercise 3.8

Hettotype of CsCl structure

Show that the crystal structure of CoU maybe interpreted as a slightly distorted CsCl (or b-brass, CuZn)-type structure. Using the structural data in the Exercise Data file, characterize the structural relationship between the CuZn structure and CoU structure.

#CuZn (CsCl type): Pm-3m
221
2.959 2.959 2.959 90. 90. 90.
2
Cu 1 1a 0.0 0.0 0.0
Zn 1 1b 0.5 0.5 0.5

#CoU type:$I2_13$
199
6.3557 6.3557 6.3557 90. 90. 90.
2
Co 1 8a 0.2940 0.2940 0.2940
U 1 8a 0.0347 0.0347 0.0347

Exercise 3.9

HT-quartz and LT-quartz

(a) Upon heating above 573 ºC the LT-quartz transforms to its HT form. Set up the corresponding Bärnighausen tree that describes the symmetry relations between the two quartz forms. Which additional degree of freedom are present in the lower symmetry form? (The crystal structures of HT-quartz and LT-quartz can be found in the ExerciseData file.)

(b) Consider the structure data of $AlPO_4$ listed in the ExerciseData file. Describe its structural relationship to quartz and construct the corresponding Bärnighausen tree.

Hint:

In order to find the structural relationship between quartz and $AlPO_4$ consider the splitting of Si positions into two: one for Al and one for P.

STRUCTURAL PSEUDOSYMMETRY

Pseudosymmetry search

Initial Structure $\mathcal{H}$ low symmetry	Structural Pseudosymmetry $\Leftrightarrow$ *Distortion*	Prototype Structure $\mathcal{G}$ high symmetry

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

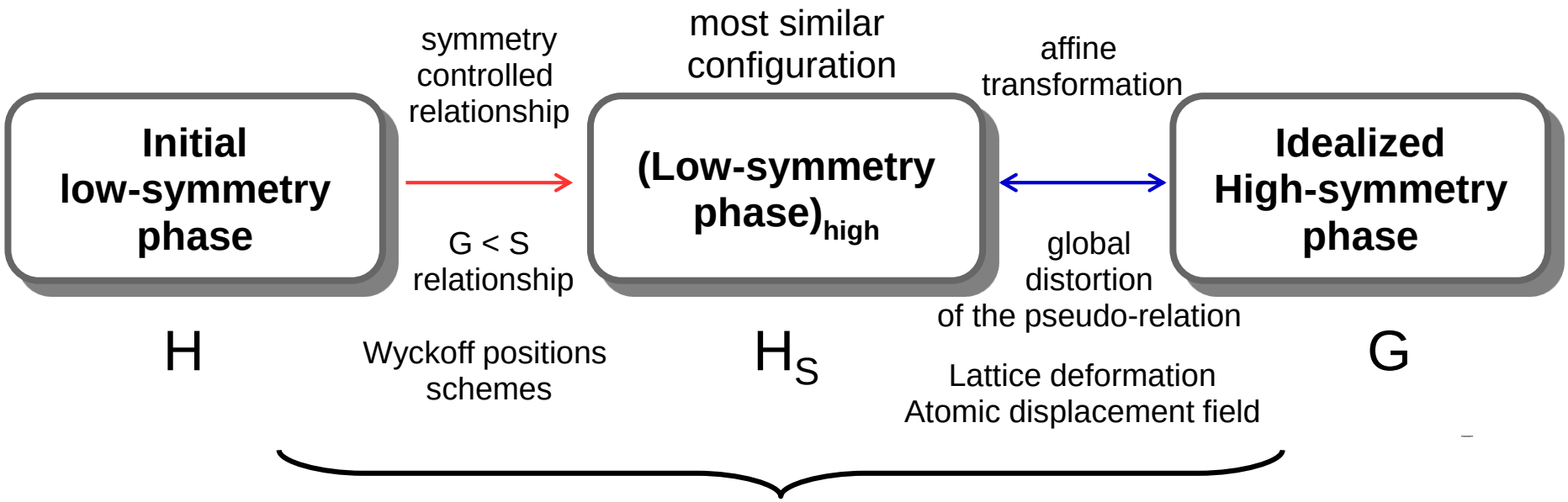
- ✓ Prediction of phase
- ✓ Search for new ferroic materials
- ✓ Prediction of the symmetry and structure of some other phase of a material
- ✓ Detection of false symmetry assignment (overlooked symmetry)
- ✓ Space-group determination of theoretical determined structure (e.g. ab initio calculations)
- ✓ Determination of an optimised virtual parent structure (paraphrase)

Pseudosymmetry search

Initial structure of space-group symmetry H

search for a structure of

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

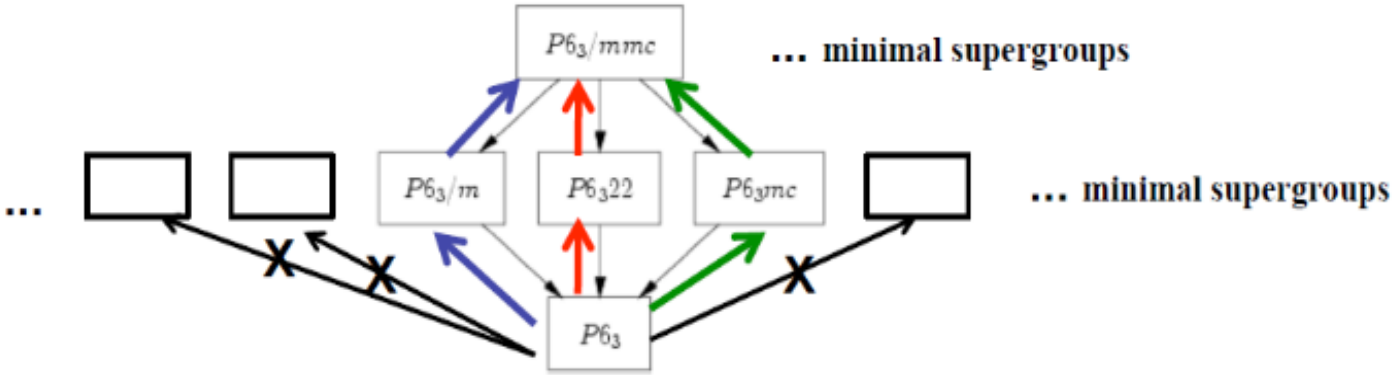


Capillas et al. Z. Kristallogr. 226 (2011)

Pseudosymmetry search

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

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



The search for pseudosymmetry can be performed as a 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

Capillas et al. Z. Kristallogr. 226 (2011)

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

Search of maximal pseudosymmetry stepwise

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

Search among supergroups with fixed k-index

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

Search of pseudosymmetry for a specific supergroup

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 3.11

Analyse the structural pseudosymmetry of Pb_2MgWO_6

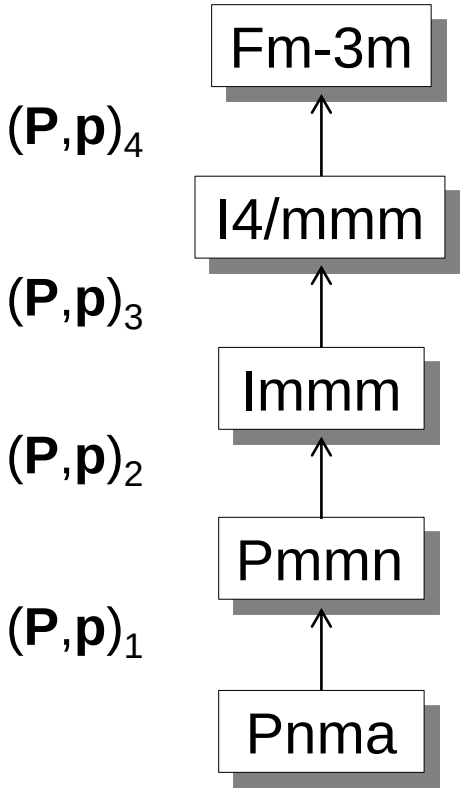
Option 1: Search of maximal pseudosymmetry stepwise ‘climbing’ via minimal supergroups

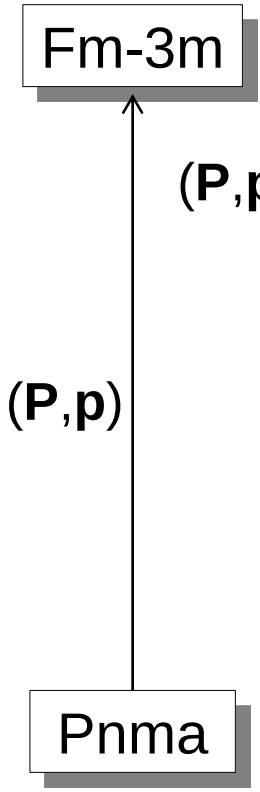
```
#Exercise 2.4.10:Pb2MgWO6:Pseudo1
# Space Group ITA number
62
# Lattice parameters
11.4059 7.9440 5.6866 90.00 90.00 90.00
# Number of independent atoms in the asymmetric unit
8
# [atom type] [number] [WP] [x] [y] [z]
Pb    1   8d    0.1422 0.0032 0.7804
Mg    1   4c    0.3772 0.25 0.7519
W     1   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
```

Exercise 3.11 (ii)

Analyse the structural pseudosymmetry of Pb_2MgWO_6

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





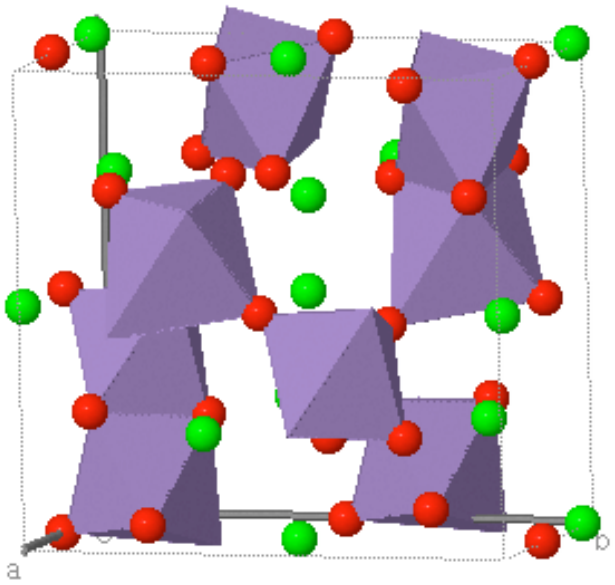
$(\mathbf{P},\mathbf{p})=(\mathbf{P},\mathbf{p})_1(\mathbf{P},\mathbf{p})_2(P,p)_3(P,p)_4$

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

Exercise 3.12

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°

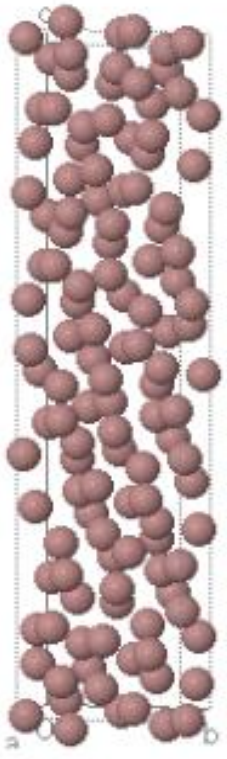


Exercise 3.13

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°



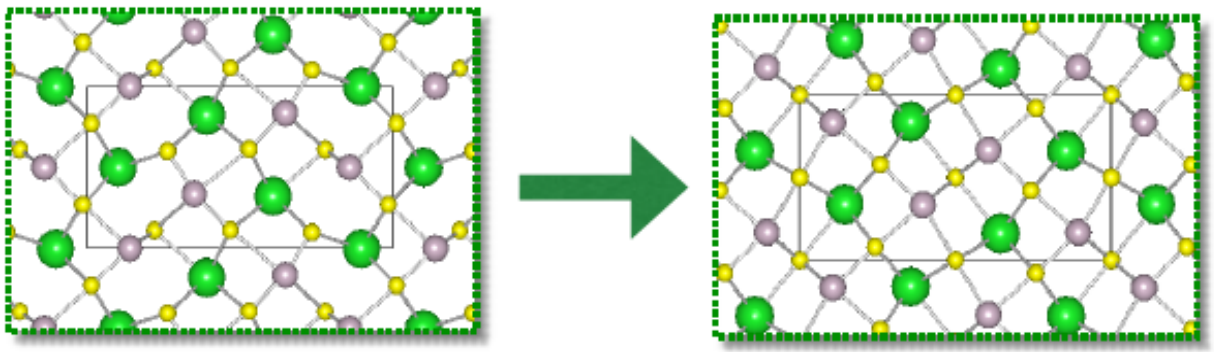
Hint: As a first step check the structural pseudosymmetry with respect to an isomorphic supergroup of index 13, specified by the transformation matrix: **a**,**b**,13**c**, i.e. first apply Option 3 of PSEUDO

SERCH FOR FERROELECTRIC MATERIALS

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: 0.4

grid for optimization

Exercise 3.15

Non-polar phases of $NaSb_3F_{10}$

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, $P6_3/mmc$.