AIC Commission on Crystallographic Teaching

AIC International Crystallography School 2019

CRYSTALLOGRAPHIC INFORMATION FIESTA

www.cristallografia.org/aicschool2019

30 August
3 September
2019
Naples, Italy

BILBAO CRYSTALLOGRAPHIC SERVER II

STRUCTURE TOOLS

Mois I. Aroyo
Universidad del Pais Vasco, Bilbao, Spain

Structure Databases

FCT/ZTF

bilbao crystallographic server

News:

- **New Article in Nature**
  07/2017: Bradlyn *et al.* "Topological quantum chemistry" *Nature* (2017). **547**, 298-305.
- **New program: BANDREP**
  04/2017: Band representations and Elementary Band representations of Double Space Groups.
- **New section: Double point and space groups**
  - **New program: DGENPOS**
    04/2017: General positions of Double Space Groups
  - **New program: REPRESENTATIONS DPG**
    04/2017: Irreducible representations of the Double Point Groups
  - **New program: REPRESENTATIONS DSG**
    04/2017: Irre
    the Double S
  - **New prog**
    04/2017: Site
    representatic
    Groups
  - **New prog**
    04/2017: Cor
    between the
    of Double Sp

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Space-group symmetry

Magnetic Symmetry and Applications

Group-Subgroup Relations of Space Groups

Representations and Applications

Solid State Theory Applications

Structure Utilities

Structure Databases

B-IncStrDB — The Bilbao Incommensurate Crystal Structure Database

MAGNDATA — A collection of magnetic structures with transportable cif-type files

Raman and Hyper-Raman scattering

Point-group symmetry

Plane-group symmetry

Tutorials

Material used in workshops and schools

Archive

B-IncStrDB

The Bilbao Incommensurate Structures Database

This database is dedicated to incommensurate modulated and composite structures. Commensurate structures described in the superspace formalism are also included.

The database currently hosts 134 entries (of which 24 are composites). (Show all entries)

You can search through these entries using the search form. You can also validate your structures in CIF format, and/or submit them to the database.

This initial database includes mainly structures published in Acta Crystallographica since the search engine at Chester allowed us a rapid collection of the papers.

Some structural parameters have been modified to fulfill the recommendations of the IUCr (for instance thermal displacement parameters in Beta form are not allowed) and to get a unified description of the modulations which permits an easy and safe manipulation of the stored data.
In general the structures are described using the superspace formalism. Modulations can be parameterized according to the different functions in use.

The structural data is saved in CIF format based on the CIF core dictionary and on the the CIF dictionary for modulated structures, plus some extensions, if required.

Apart from the web interface form, CIF files can also be used for importing data to the database.

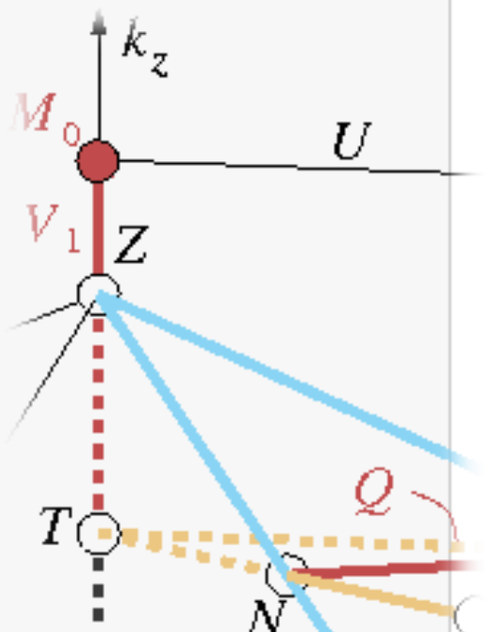
The stored CIFs have been checked for consistency and typos. However, errors due to a bad interpretation of the published data or undetected typographic mistakes may still be there.

Authors are strongly encouraged to revise their data

Please send your comments about this site to: cryst@wm.lc.ehu.es

The Bilbao Incommensurate Structures Database is maintained by the Condensed Matter Physics Group at the Basque University.

Its aim is to provide an easily accessed interface to the incommensurate structures including the modulated structures and composites.



Username/ email:

Password:

Remember me

Login

[Create a new account]

[Forgot your password?]

Most recently added
The Z' = 12 superstructure of Λ-cobalt(III) sepulchrate trinitrate governed by C--H...O hydrogen bonds
Dey, Somnath; Sch"onleber, Andreas; Mondal, Swastik; Prathapa, Siriyara Jagannatha; van Smaalen, Sander; Larsen, Finn
Krebs Acta Crystallographica Section B

Quick Links
Search
Add a new entry
CIF Validator

Bilbao Incommensurate Structures Database

B-IncStrDB

Entries | About Us | Users | Search

BaMn210_MOD

Chemical Properties

Structural Formula Sum: Ba1 F4 Mn1 [Help]
Weight: 268.3 Daltons [Help]

Crystallographic Properties

Exp. Crystal Type of Struc.: mod [Help]
a: 6.01 Å [Help]
b: 30.32(6) Å [Help]
c: 8.44(2) Å [Help]
α: 90 ° [Help]
β: 90 ° [Help]
γ: 90 ° [Help]
Volume: 1538(5) Å^3 [Help]
Crystal System: monoclinic [Help]
Space Group Name (H-M): A 2_1 1 1 [Help]

Symmetry operations of the space group [Help]

Space Group Name: X21(α00)0 [Help]
Number of Formula Units: 8 [Help]

Experimental Data

Absorption_coeff_μ: 6.698 &mm; [Help]
Intensity Measure Temperature: 210 K [Help]
Radiation Type: Mo Kα [Help]
Radiation Wavelength: 0.71069 Å [Help]
Radiation source: X-ray tube [Help]
Max Order of Satellite Reflections: 2 [Help]

View Entry **Date of entry :** 08/11/2010

Incommensurate modulated structure of $BaMnF_4$ with monoclinic symmetry at 100 and 210K.

Sciau, Ph.; Lapasset, J.; Grebille, D.; Berar, J.F. *Acta Cryst. B* **44** 108 - 116 (1988)

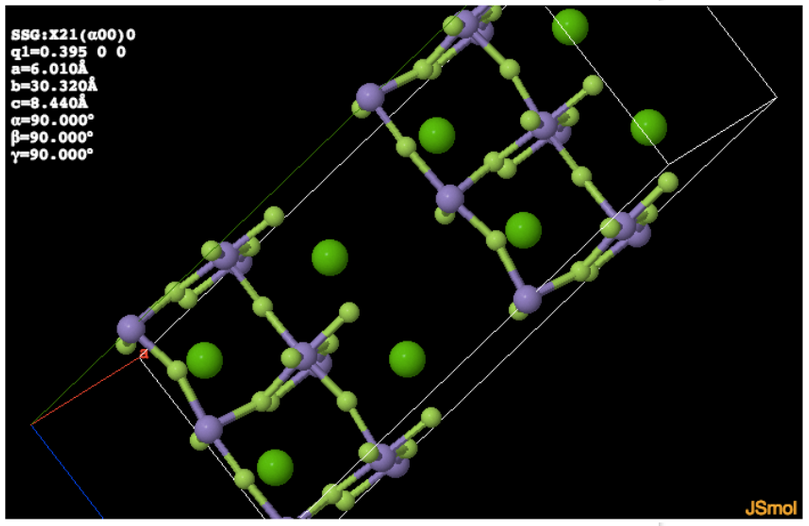
[B-IncStrDB ID: 202EZImNU]

Submitted by : System [B-IncStrDB] CIF File

Find reference: Acta Cryst. B **Volume** 44 **Page** 108 find

CIF core dictionary

CIF dictionary for modulate structures



JSMol interactive visualization

(**Robert M. Hanson**, Northfield, MN)

Refinement Properties

Modulation function desc.: Displacive modulation:Fou
Structure factors calc. details: Gaussian integration
# of observed reflections: 3844 [Help]
Residual factor for the observed refins.: 0.0561 [Help]
Refinement Special Details:
Anisotropic temperature factors refined for reflections wi
WARNING: The published thermal displacement parame
converted to Uiso.

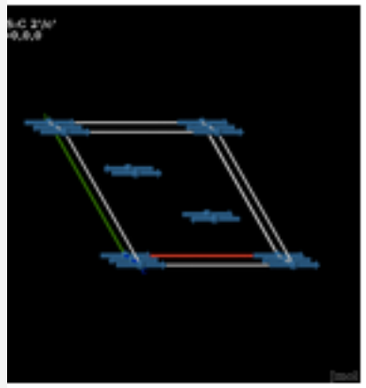
Diffraction Data

Intensity Measure Temperature: 210 K [Help]
Radiation source: X-ray tube [Help]
Radiation Wavelength: 0.71069 Å [Help]

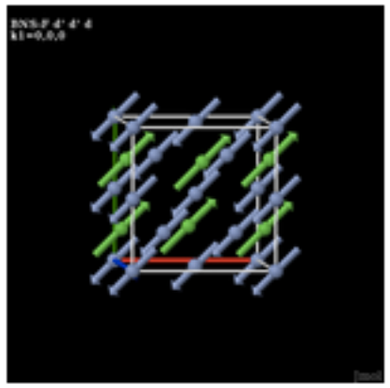
MAGNDATA: collection of magnetic structures

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

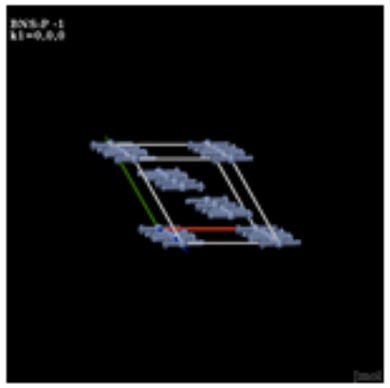
A database of more than 400 published commensurate and incommensurate magnetic structures can be found here. The structures are described using magnetic symmetry (Shubnikov magnetic space groups) in the BNS setting for commensurate structures, and magnetic superspace groups for incommensurate structures. Symmetry is applied both for magnetic moments and atomic positions. The information provided is sufficient to define unambiguously the positions and magnetic moments (if any) of all atoms in the structure. A non-standard setting consistent with the setting of the paramagnetic phase is often used (this setting does not necessarily coincide with the one used in the original reference). A c
downloaded. mcif files
ISODISTORT, VESTA
ISOCIF can be used t
standard setting, as re
for visualization of a s
available. Any entry ca
StrConvert for editing,
files, etc. The magnet
entry can also be 3D



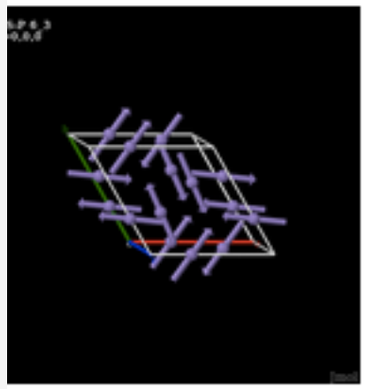
0.3 Ca_3LiOsO_6

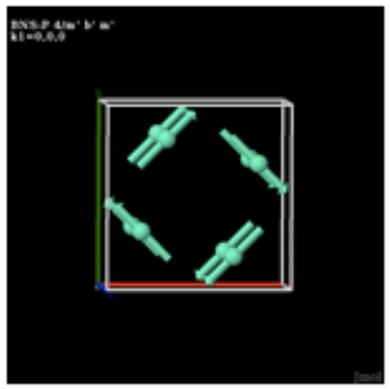


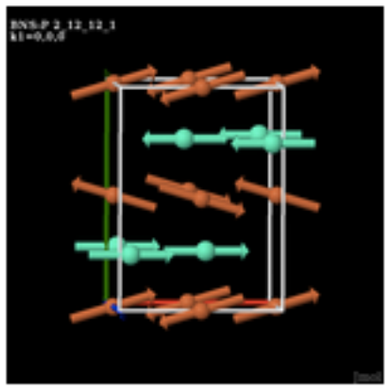
0.4 $NiCr_2O_4$



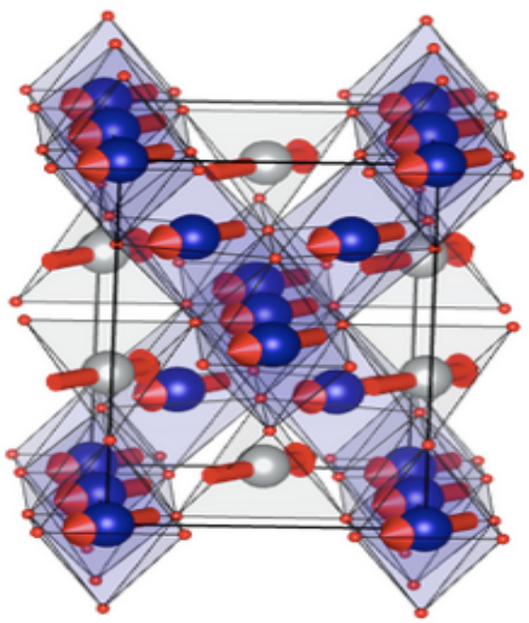
0.5 Cr_2S_3







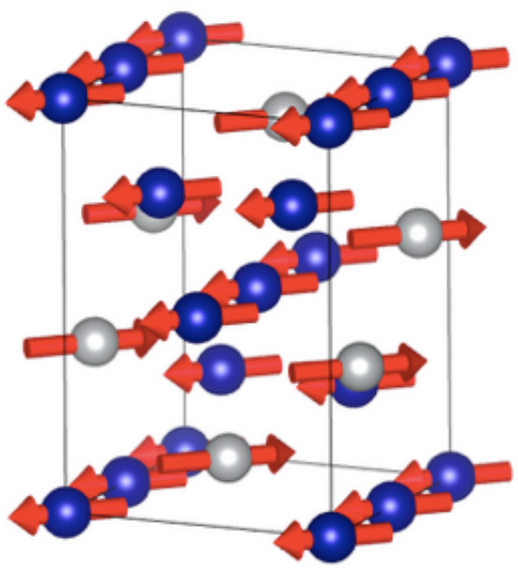
MAGNDATA: A Collection of magnetic structures with portable cif-type file



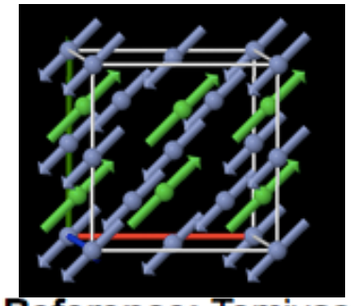
Magnetic structure with all atoms

supported by:
ISODISTORT, VESTA,
JMol, JANA2006,
FullProf

JSMol interactive visualization
(**Robert M. Hanson**, Northfield, MN)



Magnetic structure with only magnetic atoms



NiCr2O4 (#0.4)

MAGNDATA:
collection of magnetic structures

Reference: Tomiyasu, K. et al., *J. Phys. Soc Jpn* (2004) **73** 2539 - ?
Atomic positions from: ICSD #280061

Parent space group (paramagnetic phase): $I4_1/amd$ (#141)
Propagation vector: k1 (0, 0, 0)

Transition Temperature: 74 K

Lattice parameters of the magnetic unit cell:
5.81020 5.81020 8.48060 90.00 90.00 90.00
Transformation from parent structure: (**a**,**b**,**c**;0,0,0)
[View matrix form]

BNS Magnetic Space Group: Fd'd'd (#70.530) (non-standard)
[View symmetry operations]
Transformation to a standard setting: (**-a+b**,**c**,**a+b**;1/2,1,1/2)
[View matrix form]
Systematic absences for this Magnetic Space Group via MAGNEXT

Magnetic Point Group: m'm'm (8.4.27)
[View symmetry operations]
Symmetry-adapted form of material tensors via MTENSOR

$I4_1/amd\,I'$

k=(0,0,0) — **k** maximal symmetry

Fd'd'd
(**-a+b**, **c**,**a+b**;1/2,1,1/2)

Active Irreps: Irrep decomposition

label	dim. full irrep	dim. small irrep	direction	action
mGM5+	2	2	special	primary

Positions and magnetic moments of symmetry independent atoms:
*From now on, magnetic atoms are in boldface and colored in **red**. Magnetic moments are expressed in units of μB*

[Show only magnetic atoms]
[Show all the atoms]
Go to standard | Change setting | Domain-related equivalent descriptions

Label	Atom type	x	y	z	Multiplicity	Symmetry constraints on M	M_x	M_y	M_z	|M|
Ni1	Ni	0.00000	0.25000	0.37500	4	$m_x,m_x,0$	1.16	1.16	0.0	1.64
Cr1	Cr	0.00000	0.00000	0.00000	8	m_x,m_y,m_z	-0.99	-0.99	0.0	1.40

Problem: Material tensors for systems of point-group symmetry **TENSOR**

For the symmetry-adapted form of magnetic crystal tensors see MTENSOR

Tensor calculation for Point Groups

TENSOR provides the symmetry-adapted form of tensor properties for any point (or space) group. On the one hand, a point or space group must be selected, either in standard setting or in a non-standard setting defined by means of a transformation matrix to the standard setting or a set of generators of the point group. On the other hand, a tensor must be defined by the user or selected from the lists of known equilibrium, optical and transport tensors, gathered from scientific literature. If a standard point or space group is defined and a known tensor is selected from the lists the program will obtain the required tensor from and internal database; otherwise, the tensor is calculated live. The working setting is defined by the rules explained here. Live calculation of tensors may take too much time and even exceed the time limit, giving an empty result, if high-rank tensors, a lot of symmetry elements and/or rare settings are introduced.

Additionally, TENSOR allows the introduction of a space group and a subgroup in order to derive the symmetry-adapted form of tensor properties for all the corresponding domain-related equivalent structures.

Further information can be found here

Introduce a parent space group and a subgroup and calculate tensors of the resulting domain-rela

Please, enter a point group by one of these ways:

Choose a point group:

Point or Space Group number: Please, enter the label of the group or choose it

Non-conventional setting

Introduce a point group by hand:

Please, choose a tensor by one of these ways:

Choose a tensor from the lists

Show symmetry-adapted tensors for all the point groups in standard sett

(this overrides previous choices)

EQUILIBRIUM TENSORS

OPTICAL TENSORS

TRANSPORT TENSORS

Equilibrium, optical, transport material tensors of rank ≤ 8

Symmetry-adapted tensor forms for symmetry-related domain states

Example: TENSOR

Magnetoelectric tensor

Information about the selected tensor

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

Group 6/m' (#23.4.85)

α^T_{ij}	j=1	j=2	j=3
i=1	α^T_{11}	α^T_{12}	0
i=2	$-\alpha^T_{12}$	α^T_{11}	0
i=3	0	0	α^T_{33}

Number of independent coefficients: 3

Group 622 (#24.1.87)

α^T_{ij}	j=1	j=2	j=3
i=1	α^T_{11}	0	0
i=2	0	α^T_{11}	0
i=3	0	0	α^T_{33}

Number of independent coefficients: 2

Group 62'2' (#24.4.90)

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

Number of independent coefficients: 1

Group 6mm (#25.1.91)

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

Number of independent coefficients: 1

Group 6m'm' (#25.4.94)

α^T_{ij}	j=1	j=2	j=3
i=1	α^T_{11}	0	0
i=2	0	α^T_{11}	0
i=3	0	0	α^T_{33}

Number of independent coefficients: 2

Group -6'm'2 (#26.3.97)

α^T_{ij}	j=1	j=2	j=3
i=1	α^T_{11}	0	0
i=2	0	α^T_{11}	0
i=3	0	0	α^T_{33}

Number of independent coefficients: 2

Group -6'm2' (#26.4.98)

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

Number of independent coefficients: 1

Group 6/m'mm (#27.3.102)

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

Number of independent coefficients: 1

STRUCTURE UTILITIES

FCT/ZTF

bilbao crystallographic server

News:

- **New Article in Nature**
  07/2017: Bradlyn *et al.* "Topological quantum chemistry" *Nature* (2017). **547**, 298-305.
- **New program: BANDREP**
  04/2017: Band representations and Elementary Band representations of Double Space Groups.
- **New section: Double point and space gro**
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Space-group symmetry

Magnetic Symmetry and Applications

Group-Subgroup Relations of Space Groups

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
VISUALIZE	Visualize structures using Jmol
COMPSTRU	Comparison of Similar Structures with the same Symmetry
STRUCTURE RELATIONS	Finds the transformation matrix that relates the two given group-subgroup related structures within a tolerance.

Tutorials

Material used in workshops and schools

Archive

Plane-group symmetry

Double point and space groups

Bilbao Crystallographic Server

Problem: *ITA* SETTINGS **STRUCTURE** DESCRIPTIONS **SETSTRU**

ITA-settings for the space group C2/c (No.15)

initial setting structure description

$X_f=(P,p)^{-1}X_i$

final setting structure description

Choose the initial and final space groups symbols

ın matrices must be read by columns. **P** is the transformation from standard to non·

$$(a, b, c)_n = (a, b, c)_s P$$

Initial	Final	Setting	P	P^{-1}
○	○	*C* 1 2/*c* 1	a,b,c	a,b,c
○	○	*A* 1 2/*n* 1	-a-c,b,a	c,b,-a-c
○	○	*I* 1 2/*a* 1	c,b,-a-c	-a-c,b,a
○	○	*A* 1 2/*a* 1	c,-b,a	c,-b,a
○	○	*C* 1 2/*n* 1	a,-b,-a-c	a,-b,a-c
○	○	*I* 1 2/*c* 1	-a-c,-b,c	-a-c,-b,c
○	○	*A* 1 1 2/*a*	c,a,b	b,c,a
○	○	*B* 1 1 2/*n*	a,-a-c,b	a,c,-a-b
○	○	*I* 1 1 2/*b*	-a-c,c,b	-a-b,c,b
○	○	*B* 1 1 2/*b*	a,c,-b	a,-c,b
○	○	*A* 1 1 2/*n*	-a-c,a,-b	b,-c,-a-b
○	○	*I* 1 1 2/*a*	c,-a-c,-b	-a-b,-c,a
○	○	*B* 2/*b* 1 1	b,c,a	c,a,b

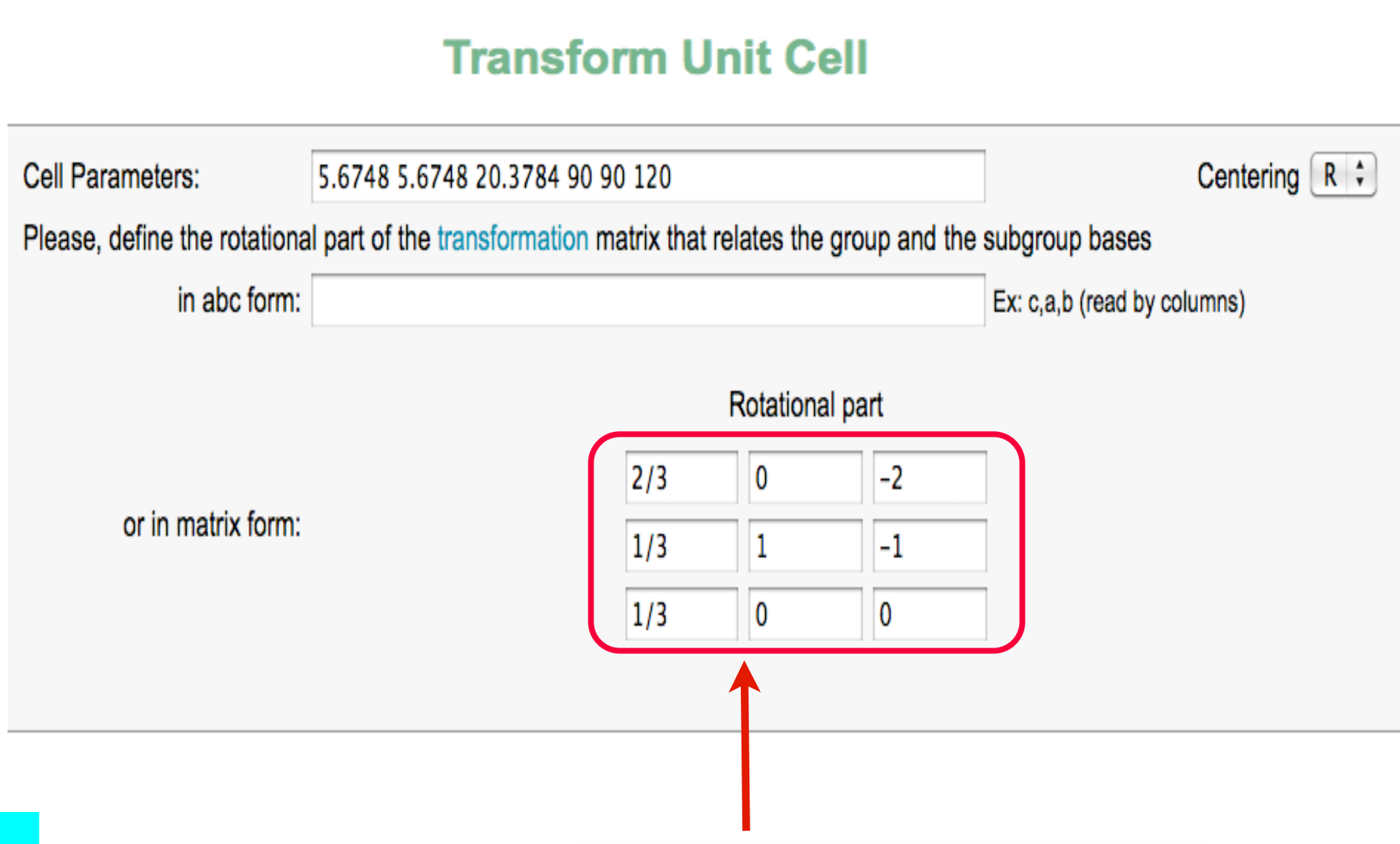
Bilbao Crystallographic Server

Problem: UNIT CELL TRANSFORMATION **CELLTRAN**

lattice parameters hexagonal cell

$G' = P^T G P$

lattice parameters monoclinic cell



(P,p) Transformation matrix

Bilbao Crystallographic Server

Problem: STRUCTURE TRANSFORMATION **TRANSTRU**

Transform Structure

TRANSTRU can transform a structure in two ways:

- To a lower symmetry space group. The transformed structure is given in the low symmetry space group basis, taking care of all possible splittings of the Wyckoff positions.
- With an arbitrary matrix. The structure, including the cell parameters and the atoms in the unit cell, is transformed with an arbitrary matrix introduced by the user.

Only the default choice for the conventional setting of the space groups is used.

Structure Data [in CIF format] — Examinar...

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

High Symmetry Structure

```
166
5.6748 5.6748 20.3784 90 90 120
5
Pb      1       3a      0.000000        0.000000        0.000000
Pb      2       6c      0.000000        0.000000        0.207100
PV      3       6c      0.000000        0.000000        0.388400
O       4       6c      0.000000        0.000000        0.324000
O       5       18i     0.842400        0.157600        0.430100
```

asymmetric unit

default settings

Transform structure to a subgroup basis

Transform structure with an arbitrary matrix

Show

subgroup basis

arbitrary transformation

Bilbao Crystallographic Server

Example **TRANSTRU**: $Pb_3(VO_4)_2$

Description
R-3m (166)

Validity (P,p)

WP splittings

Description
$P2_1/c$ (14)

(P,p)

Structure

```
166
5.6748 5.6748 20.3784 90 90 120
5
Pb      1       3a      0.000000        0.000000        0.000000
Pb      2       6c      0.000000        0.000000        0.207100
PV      3       6c      0.000000        0.000000        0.388400
O       4       6c      0.000000        0.000000        0.324000
O       5       18h     0.842400        0.157600        0.430100
```

Low symmetry Space Group: 14

Transformation Matrix:

In matrix form:

Rotational part			Origin Shift
2/3	0	-2	0
1/3	1	-1	0
1/3	0	0	0

EXERCISES

Problem 2.1

Structure 1: Space group *I*4$_1$/*amd* (141) a=6.60 $\mathring{A}$ c=5.88 $\mathring{A}$
origin choice 1 at $\bar{4}m2$

Structure 2: Space group *I*4$_1$/*amd* (141) a=6.616 $\mathring{A}$ c=6.015 $\mathring{A}$
origin choice 2 at $2/m$ at 0,-1/4,1/8 from $\bar{4}m2$

Compare the two structure descriptions and check if they belong to the same structure type.

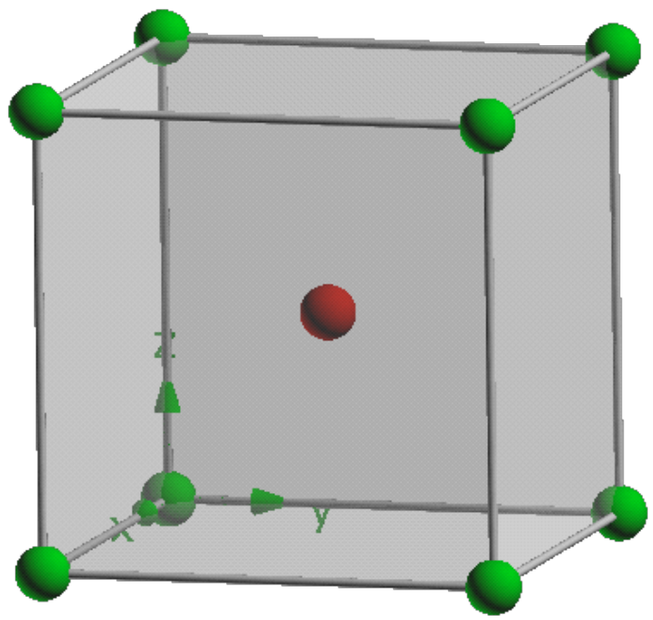
Hint: *In order to compare the different data, the parameters of Structure 1 are to be transformed to 'origin at center 2/m', i. e. ORIGIN CHOICE 2.*

$$O(2)=O(1)+p, \quad p=0,-1/4,1/8$$

Use the tool SETSTRU

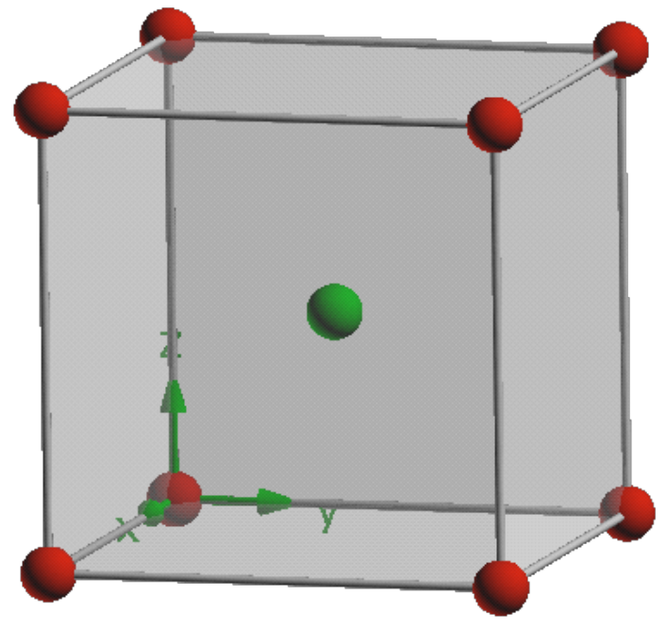
Problem: EQUIVALENT DESCRIPTIONS

EQUIVSTRU



CsCl

Pm-3*m* (221)



1a (0,0,0) ⟶ 1b (1/2,1/2,1/2)

1b (1/2,1/2,1/2) ⟶ 1a (0,0,0)

How to find all possible equivalent descriptions of a crystal structure?

Example CsCl: **EQUIVSTRU**

Equivalent Descriptions of Crystal Structures

Equivalent Structures

Given a space group IT*A* number, the cell parameters (separated with spaces) and the atom positions, the program EQUIVSTRU transforms the corresponding structure with the elements of the euclidean normalizer of the space group. All the transformed structures are equivalent symmetry descriptions of the given initial structure. The atom positions are identified generating the Wyckoff sets.

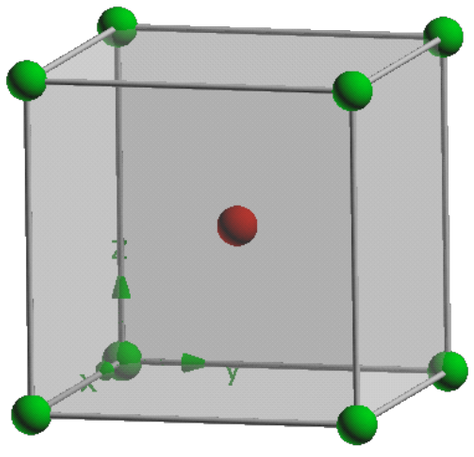
Structure Data
[in CIF format]

Examinar...

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

Structure

```
#Exercise 3.2a(CsCl)
# Space Group ITA number
221
# Lattice parameters
4.12599 4.12599 4.12599 90.0 90.0 90.0
# Number of independent atoms in the asymmetric unit
2
# [atom type] [number] [WP] [x] [y] [z]
Cl     1    1a     0.000000 0.000000 0.000000
Cs     1    1b     0.500000 0.500000 0.500000
```



Structure number 1

Normalizer coset representative: x,y,z

Transformed unit cell:

4.1260 4.1260 4.1260 90.00 90.00 90.00

Transformed structure:

AT.	WP	SS	Representative	Atomic orbit
Cl1	1a (0,0,0)	m-3m	(0.000000,0.000000,0.000000)	(0.000000,0.000000,0.000000)
Cs1	1b (1/2,1/2,1/2)	m-3m	(0.500000,0.500000,0.500000)	(0.500000,0.500000,0.500000)

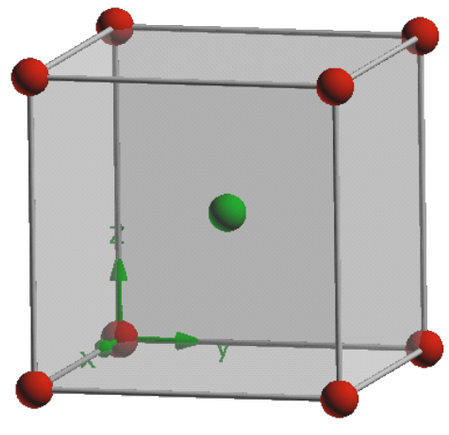
Structure number 2

Normalizer coset representative: x+1/2,y+1/2,z+1/2

Transformed unit cell:

4.1260 4.1260 4.1260 90.00 90.00 90.00

Transformed structure:



AT.	WP	SS	Representative	Atomic orbit
Cl1	1b (1/2,1/2,1/2)	m-3m	(0.500000,0.500000,0.500000)	(0.500000,0.500000,0.500000)
Cs1	1a (0,0,0)	m-3m	(0.000000,0.000000,0.000000)	(0.000000,0.000000,0.000000)

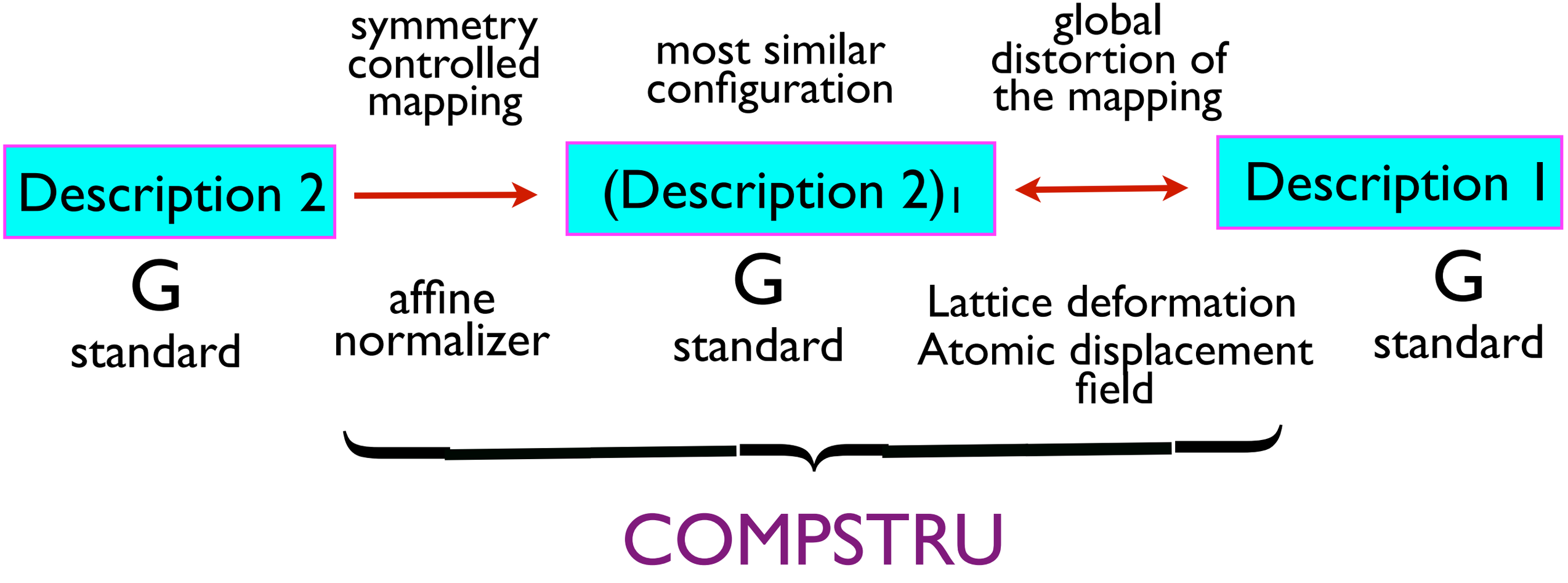
Different descriptions of the same structure

COMPSTRU

PROBLEM:

Two descriptions of the same structure with respect to the same space group, specified by unit-cell parameters and atomic coordinates data.

Search for a mapping of the two descriptions such that the global distortion accompanying the mapping is tolerably small.



Problem: **Similarity of the descriptions**

Description 1
a_1, b_1, c_1
(x_1, y_1, z_1)

How to measure the ***similarity*** between two descriptions ?

Description 2
a_2, b_2, c_2
(x_2, y_2, z_2)

degree of lattice distortion

$$S = \frac{1}{3}\sqrt{\sum_i \eta_i^2}$$

η_i-eigenvalues of the Lagrangian strain tensor

average atomic displacements

$$d_{av} = \frac{1}{n}\sum_i m_i u_i$$

u_i-atomic displacements

maximal atomic displacements

maximal displacements of the paired atoms

Problem: **Similarity of the descriptions**

Description 1
a_1, b_1, c_1
(x_1, y_1, z_1)

How to measure the ***similarity*** between two descriptions ?

Description 2
a_2, b_2, c_2
(x_2, y_2, z_2)

Bergerhoff *et al.* *Acta Cryst.*(1999), **B**55, 147

structural descriptor

$$\Delta = [\sqrt{2}\Delta(c) + 1]\Delta(d) - 1$$

$$\sum_i m[(x_i - y_i)^2]^{\frac{1}{2}} / \sum m$$

weighted mean difference between atomic coordinates

$$[(b_1/a_1)(c_1/a_1)]/[(b_2/a_2)(c_2/a_2)]$$

relation between axial ratios

Problem: COMPARISON OF STRUCTURES **COMPSTRU**

Comparison of crystal structures of the same symmetry

structure 1

default settings

structure 2

tolerances

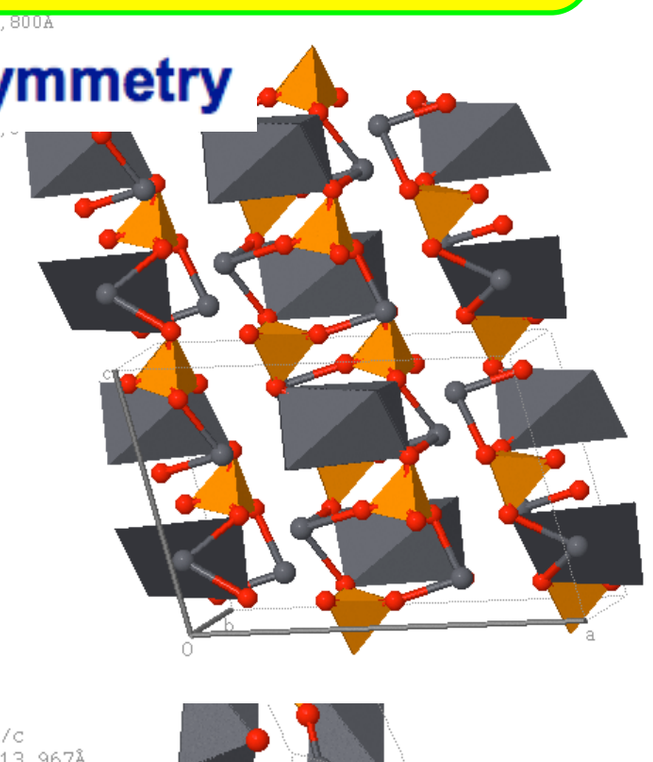
Structure Data
[in CIF format]

Examinar...

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

Structure 1

```
15
13.800 5.691 9.420 90.0 102.3 90.0
7
Pb     1    4e     0.0000 0.2910 0.2500
Pb     2    8f     0.3170 0.3090 0.3520
P      1    8f     0.5990 0.2410 0.4470
O      1    8f     0.6430 0.0300 0.3920
O      2    8f     0.6340 0.4640 0.3740
O      3    8f     0.6420 0.2800 0.6120
O      4    8f     0.4910 0.2220 0.4200
```



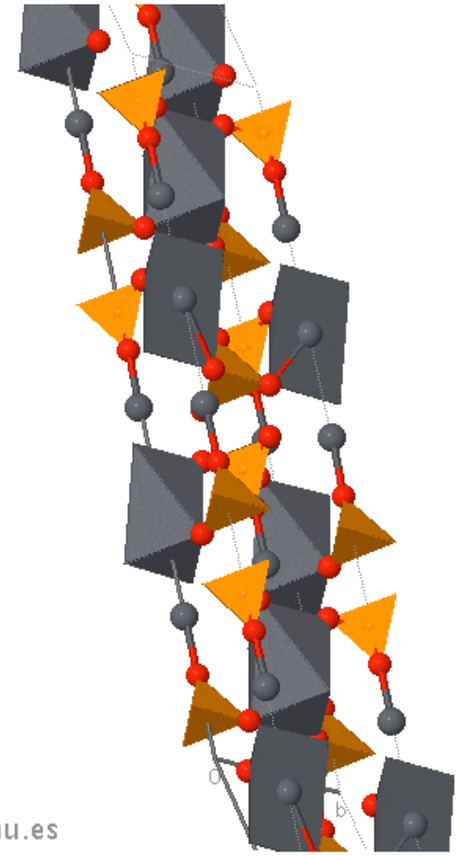
Structure Data
[in CIF format]

Examinar...

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

Structure 2

```
15
13.967 5.560 40.778 90.0 166.713 90.0
7
Pb   1    4e   0.0000   0.0000   0.7500
Pb   2    8f   0.0000   0.0000   0.8563
P    1    8f   0.0000   0.0000   0.9511
O    1    8f   0.0000   0.0000   0.9145
O    2    8f   0.2715   0.7285   0.8885
O    3    8f   0.9570   0.5000   0.1170
O    4    8f   0.7285   0.2715   0.6115
```



Enter the maximum distance allowed between the paired atoms: 1 Å

Enter the allowed tolerance (a b c α β γ): .5 .5 .5 5 5 5

.cryst.ehu.es

Example COMPSTRU: $Pb_3(PO_4)_2$

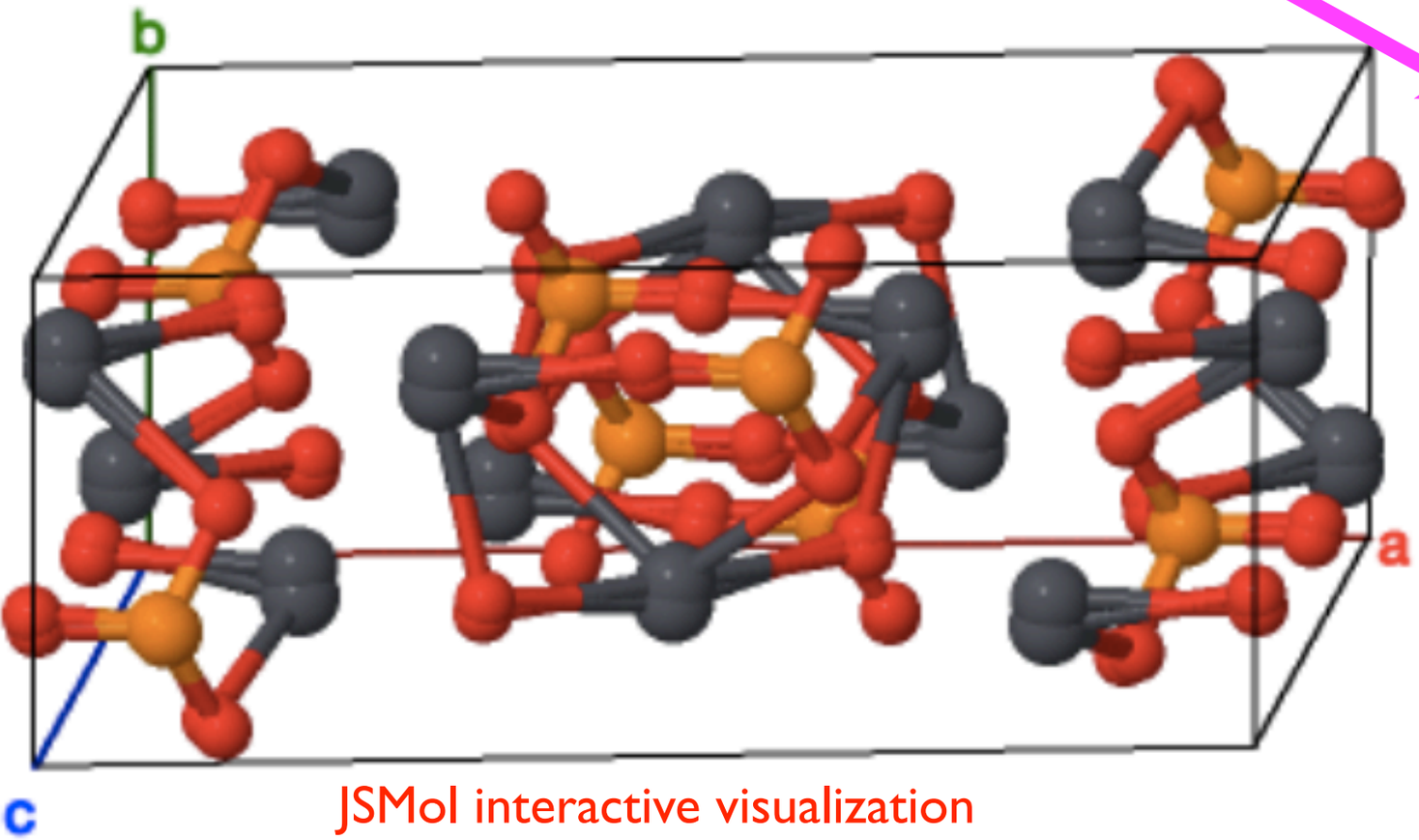
Structure #1

```
15
13.800 5.691 9.420 90.0 102.3 90.0
7
Pb     1    4e     0.0000 0.2910 0.2500
Pb     2    8f     0.3170 0.3090 0.3520
P      1    8f     0.5990 0.2410 0.4470
O      1    8f     0.6430 0.0300 0.3920
O      2    8f     0.6340 0.4640 0.3740
O      3    8f     0.6420 0.2800 0.6120
O      4    8f     0.4910 0.2220 0.4200
```

Structure #2

```
15
13.967 5.560 40.778 90.0 166.713 90.0
7
Pb   1    4e   0.0000   0.0000   0.7500
Pb   2    8f   0.0000   0.0000   0.8563
P    1    8f   0.0000   0.0000   0.9511
O    1    8f   0.0000   0.0000   0.9145
O    2    8f   0.2715   0.7285   0.8885
O    3    8f   0.9570   0.5000   0.1170
O    4    8f   0.7285   0.2715   0.6115
```

affine + Euclidean normalizers



JSMol interactive visualization

(**Robert M. Hanson**, Northfield, MN)

Most similar configuration to Structure #1

```
015
13.967000 5.560000 9.630055 90.000000 103.295059 90.000000
7
Pb      1       4e      0.000000        0.250000        0.250000
Pb      2       8f      0.318900        0.250000        0.356300
P       1       8f      0.603300        0.250000        0.451100
O       1       8f      0.493500        0.250000        0.414500
O       2       8f      0.644000        0.478500        0.388500
O       3       8f      0.644000        0.250000        0.617000
O       4       8f      0.644000        0.021500        0.388500
```

Evaluation of the structure similarity

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0116	0.3386	0.1430	0.066

structural descriptor $\Delta = 0.066$

Problem: COMPARISON OF STRUCTURE DESCRIPTIONS **COMPSTRU**

Problem 2.2

In ICSD can be found several structure data sets of ε-Fe_2O_3, all of them of symmetry $Pna2_1$(No.33). Compare the following two descriptions and check if they belong to the same structure type.

Problem 2.2

ICSD data for ε-Fe_2O_3,

ICSD for WWW

Details of the selected entries

Print **2** entries selected.

CC=Collection Code: [AB2X4]=ANX Form: [cF56]=Pearson: [e d a]=Wyckoff Symbol: [Al2MgO4]=Structure Type:

******Click the ANX, Pearson or Wyckoff Symbol to find structures with that symbol***.***

CC=173024 Details Bonds Pattern Structure Jmol

Title	High- and low-temperature crystal and magnetic structure of epsilon-Fe2 O3 and their correlation to its magnetic properties.
Authors	Gich, M.;Frontera, C.;Roig, A.;Taboada, E.;Molins, E.;Rechenberg, H.R.;Ardisson, J.D.;Macedo, W.A.A.;Ritter, C.;Hardy, V.;Sort, J.;Skumryev, V.;Nogues, J.
Reference	Chemistry of Materials (2007) **18**, 3889-3897 **Link XRef SCOPUS SCIRUS Google**
Compound	**Fe2 O3** - Iron(III) oxide - epsilon **[A2X3] [oP40] [a10] [AlFeO3]**
Cell	5.0885(5), 8.7802(14), 9.4709(13), 90., 90., 90. **PNA21 (33)** V=423.14
Remarks	R=0.013300 : NDP RVP SNP TEM =200 : TYP =AlFeO3 : XDP MAG At least one temperature factor missing in the paper.

Atom	(site)	Oxid.	x, y, z, B, Occupancy				
O1	(4a)	-2	0.978(2)	0.3282(15)	0.4314(11)	0	1
O2	(4a)	-2	0.515(2)	0.4907(17)	0.4187(16)	0	1
O3	(4a)	-2	0.650(3)	0.9979(13)	0.1883(9)	0	1
O4	(4a)	-2	0.160(3)	0.1637(15)	0.1956(7)	0	1
O5	(4a)	-2	0.841(3)	0.1680(15)	0.6669(7)	0	1
O6	(4a)	-2	0.527(2)	0.1637(19)	0.9362(9)	0	1
Fe1	(4a)	3	0.1928(11)	0.1506(6)	0.5807(3)	0	1
Fe2	(4a)	3	0.6826(6)	0.0291(3)	0.7897(5)	0	1
Fe3	(4a)	3	0.1858(10)	0.1519(6)	0	0	1
Fe4	(4a)	3	0.8104(7)	0.1580(4)	0.3071(3)	0	1

CC=415250 Details Bonds Pattern Structure Jn

Title	Synthesis and structural analysis of epsilon-(Fe2 O3).
Authors	Kelm, K.;Mader, W.
Reference	Zeitschrift fuer Anorganische und Allgemeine Chemie (2005) **631**, 2383-2389 **Link XRef SCOPUS SCIRUS Google**
Compound	**Fe2 O3** - Diiron(III) oxide - epsilon **[A2X3] [oP40] [a10] [AlFeO3]**
Cell	5.0715(2), 8.7359(4), 9.4178(4), 90, 90, 90 **PNA21 (33)** V=417.24
Remarks	R=0.039000 : TYP =AlFeO3 : XDP RVP

Atom	(site)	Oxid.	x, y, z, B, Occupancy				
Fe1	(4a)	3	0.6768(9)	0.8427(5)	0.0000000	0.050(2)	1.00000
Fe2	(4a)	3	0.204(1)	0.3509(8)	0.7726(9)	0.063(3)	1.00000
Fe3	(4a)	3	0.807(1)	0.6605(8)	0.693(1)	0.069(2)	1.00000
Fe4	(4a)	3	0.6852(9)	0.4634(5)	0.983(2)	0.046(1)	1.00000
O1	(4a)	-2	0.337(2)	0.853(2)	0.887(1)	0.0063326	1.00000
O2	(4a)	-2	0.019(3)	0.474(2)	0.610(2)	0.0063326	1.00000
O3	(4a)	-2	0.453(3)	0.677(2)	0.651(2)	0.0063326	1.00000
O4	(4a)	-2	0.527(3)	0.669(2)	0.100(1)	0.0063326	1.00000
O5	(4a)	-2	0.868(3)	0.334(2)	0.863(1)	0.0063326	1.00000
O6	(4a)	-2	0.336(3)	0.513(1)	0.891(1)	0.0063326	1.00000

Problem: Isoconfigurational Structure Types **COMPSTRU**

Lima-de Faria *et al.* *Acta Cryst.*(1990), **A**46, 1

Isopointal structure types

Space group

Wyckoff position sequence

Pearson symbol

(crystal system, centring type, total number of atoms in the unit cell)

Allmann, Hinek. *Acta Cryst.*(2007), **A**63, 412

Inorganic Crystal Structure Database (2009)
http://icsdweb.fiz-karlsruhe.de

isoconfigurational structure types?

Isoconfigurational structure types

Isopointal

similar

Crystallographic orbits

Geometrical interrelationships

Composition type (ANX formula)

Range of c/a ratio

β-range

Atomic coordinates

Chemical properties

Isoconfigurational (configurationally isotypic) Structure Types

PROBLEM:

Consider two isopointal structures specified by their space-group symmetry, unit-cell parameters and atomic coordinates data.

We search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.

symmetry controlled mapping

most similar configuration

global distortion of the mapping

Structure 2 → (Structure 2)$_I$ ↔ Structure I

G
standard

atomic species correspondence scheme

G
standard

Lattice deformation
Atomic displacement field

G
standard

COMPSTRU

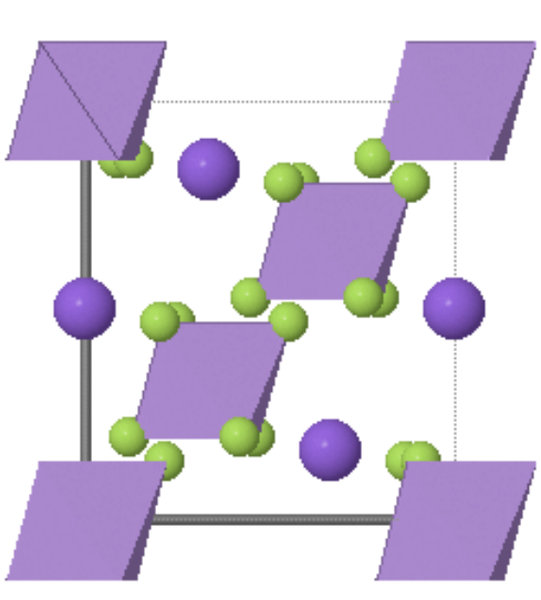
Problem: Isoconfigurational StructureTypes **COMPSTRU**

EXERCISES

Problem 2.3

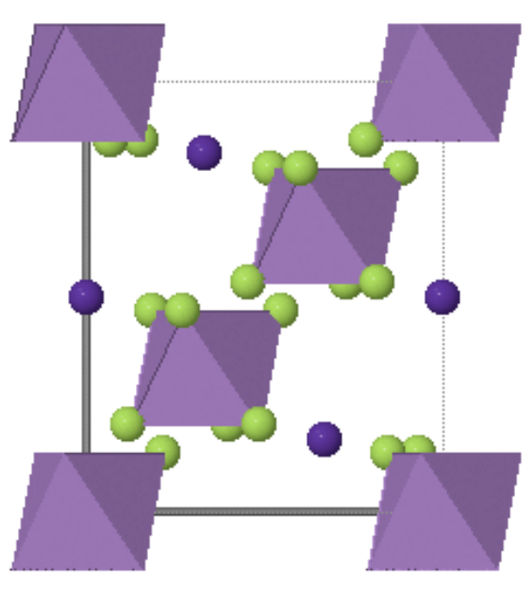
Do these compounds belong to the
same structure type ?

$KAsF_6$



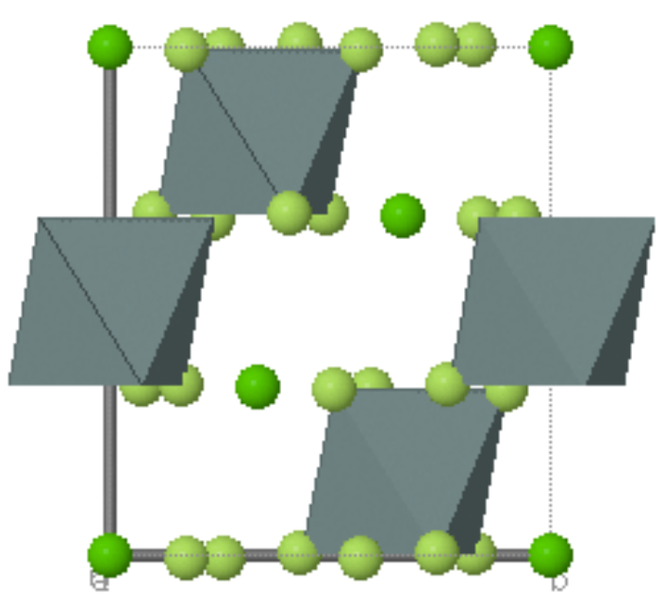
```
148
7.3480 7.3480 7.2740 90.00 90.00 120.00
3
K     1   3b    0.333333 0.666666 0.166666
As    1   3a    0 0 0
F     1   18f   0.1292 0.2165 0.1381
```

$BaIrF_6$



```
148
7.3965 7.3965 7.2826 90.00 90.00 120.00
3
Ba    1   3b    0.333333 0.666666 0.166666
Ir    1   3a    0 0 0
F     1   18f   0.0729 0.2325 0.1640
```

$BaSnF_6$



```
148
7.4279 7.4279 7.4180 90.00 90.00 120.00
3
Sn    1   3b    0 0 0.5
Ba    1   3a    0 0 0
F     1   18f   0.2586 0.8262 0.0047
```

Koch, Fischer. *MathCryst Satell.*, ECM22, Budapest 2004

Example: STRUCTURE TYPES **COMPSTRU**

STUDY OF THE FAMILY **ABF6**

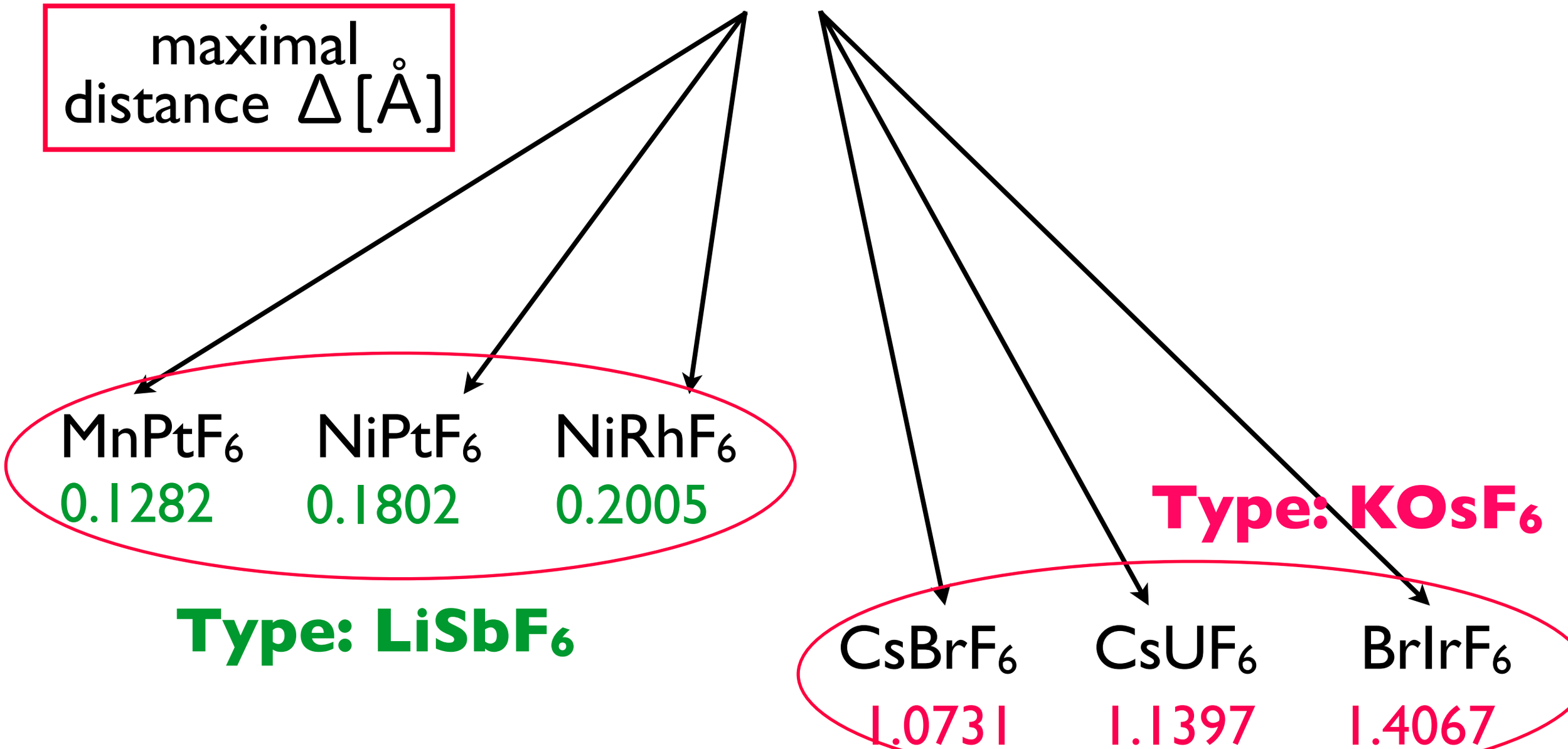
KCrF6	LiNbF6	VNbF6	HgRhF6	MgPbF6	InAsF6
RbCrF6	LiRuF6	CoZrF6	NiRhF6	ZnPbF6	CsNbF6
KAsF6	LiRhF6	PdPtF6	CaCrF6	NiPbF6	HgCrF6
RuAsF6	LiTaF6	FeNbF6	MgCrF6	MgPdF6	CoSnF6
CsAsF6	LiOsF6	CaSnF6	CdCrF6	CaPdF6	CsNbF6
RbSbF6	LiIrF6	FeZrF6	MnSnF6	ZnPdF6	MnPtF6
BaSnF6	LiPtF6	CuZrF6	FeSnF6	CdPdF6	CdRhF6
CsBrF6	LiAuF6	CaPtF6	ZnSnF6	LiSbF6	NaBiF6
CsSbF6	NiPtF6	ZnPtF6	NiSnF6	BaIrF6	TlAsF6
CsBiF6	CdPtF6	CoPtF6	CuSnF6	RbBiF6	
CsUF6	LiPF6	MgRhF6	CdSnF6	KRhF6	
KOsF6	LiAsF6	CaRhF6	CdTiF6	CsReF6	
NaCrF6	PdZrF6	ZnRhF6	LiBiF6	KPF6	

Example: STRUCTURE TYPES COMPSTRU

STUDY OF THE FAMILY **ABF6**

Reference structure:
$CaCrF_6$

maximal distance Δ [Å]



SOLID-STATE APPLICATIONS

FCT/ZTF

bilbao crystallographic server

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Space-group symmetry

Magnetic Symmetry and Applications

Group-Subgroup Relations of Space Groups

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

Point-group symmetry

ECM31-Oviedo Satellite

Crystallography online: work
use and applications of the st
of the Bilbao Crystallograp

20-21 August 201

News:

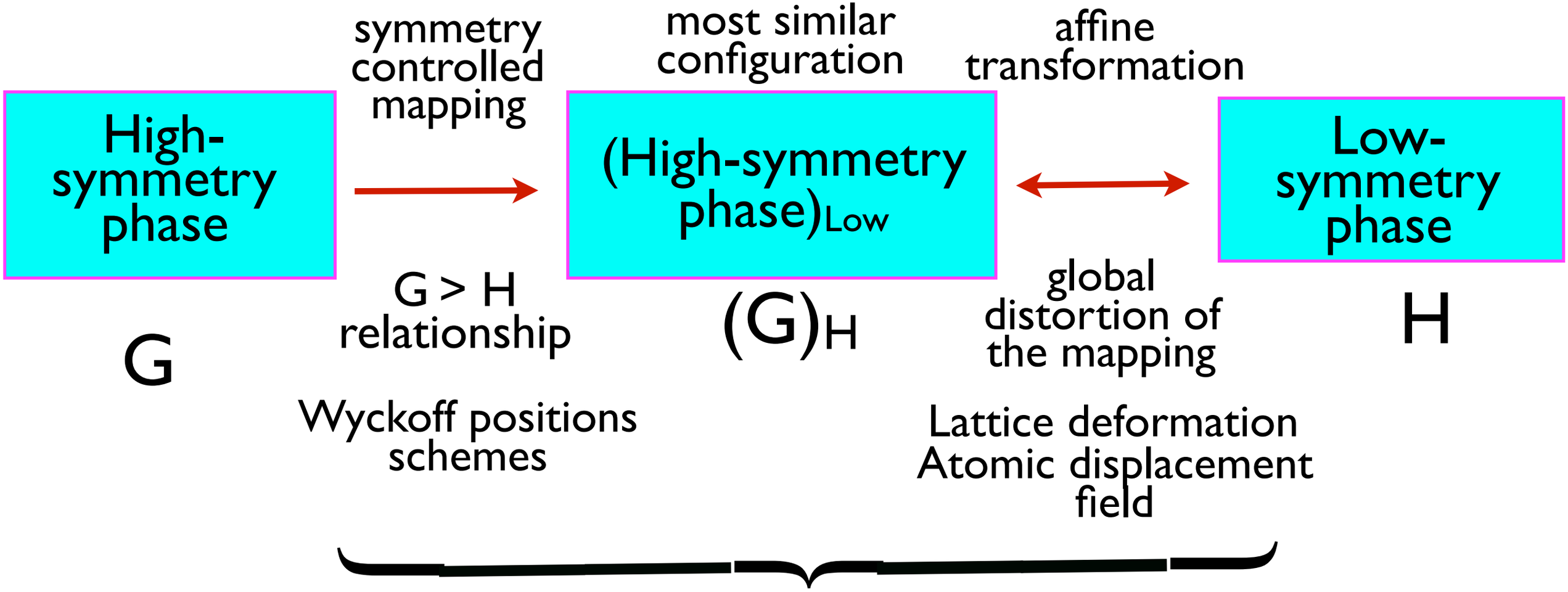
- **New Article in Nature**
  07/2017: Bradlyn *et al.* "Topolog
  chemistry" *Nature* (2017). **547**,
- **New program: BANDRE**
  04/2017: Band representations
  Band representations of Double
- **New section: Double poi**
  groups
  - **New program: DGENPOS**
    04/2017: General positions of Double Space Groups
  - **New program: REPRESENTATIONS DPG**

Structure Relationships

PROBLEM:

Consider two phases of the same compound (specified by their unit-cell parameters and atomic coordinates) with group-subgroup related symmetry groups G>H

Search for a mapping of the two structures such that the global distortion accompanying the mapping is tolerably small.



Cristobalite phase transition

STRUCTURE RELATIONS

Fd-3m High-symmetry phase

$$(P,p)=\begin{pmatrix} 1/2 & 1/2 & 0 & 5/8 \\ -1/2 & 1/2 & 0 & 3/8 \\ 0 & 0 & 1 & 3/8 \end{pmatrix}$$

Symmetry-controlled mapping

(High-symmetry phase)$_{P41212}$

Global distortion

Lattice deformation
Atomic displacement field

$P4_12_12$ Low-symmetry phase

High Symmetry Structure

```
227
7.147 7.147 7.147 90 90 90
1
Si     1    8a     0.125000 0.125000 0.125000
```

Description of the High Symmetry Structure in the most similar configuration to the Low Symmetry Structure

```
092
5.053692 5.053692 7.147000 90.000000 90.000000 90.000000
1
Si      1       4a      0.250000        0.250000        0.000000
```

Evaluation of the Global Distortion

S	$d_{max.}$ (Å)	$d_{av.}$ (Å)	Δ
0.0149	0.3774	0.7548	0.122

Low Symmetry Structure

```
92
4.9586 4.9586 6.9074 90 90 90
1
Si     1    4a     0.302800 0.302800 0.000000
```

Problem 2.4

Lead phosphate phase transition

Lead phosphate $Pb_3(PO_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry *R-3m* (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:*

(i)characterize the symmetry reduction between the high- and low-symmetry phases (index, graph of maximal subgroups, etc.);

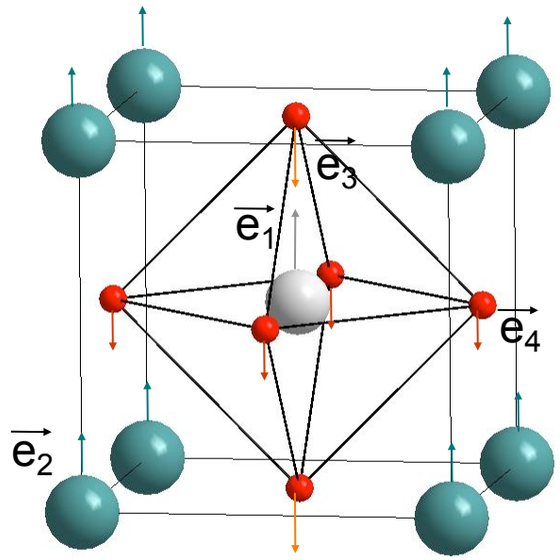
(ii)describe the structural distortion from the rhombohedral to the monoclinic phase by the evaluation of the lattice strain and the atomic displacements accompanying the phase transition.

Problem: SYMMETRY-MODE ANALYSIS

AMPLIMODES

Distorted Structure H = **High-Symmetry Structure G** + **"frozen" modes**

distortion mode = Amplitude x polarization vector



Description of a "mode":

$\vec{u}(\text{atoms}) = Q\ \vec{e}$

amplitude — polarization vector

$\mathbf{e} = (\vec{e}_1, \vec{e}_2, \vec{e}_3, \vec{e}_4)$

normalization: (within a unit cell) $|\vec{e}_1|^2 + |\vec{e}_2|^2 + |\vec{e}_3|^2 + 2|\vec{e}_4|^2 = 1$

comparison of amplitudes of different "frozen" distortion modes

AMPLIMODES calculates the amplitudes and polarization vectors of all distortion modes with different symmetries (irreps) frozen in a distorted structure.

Phase transitions in $SrBi_2Ta_2O_9$ (SBT)

AMPLIMODES

Initial data:

$\mathcal{G}$ — *I*4/*mmm* (139)

Sr: 2a
Ta: 4e
Bi: 4e
O1: 2b
O2: 4e
O3: 4d
O4: 8g

High-temperature prototype

Group-theoretical analysis

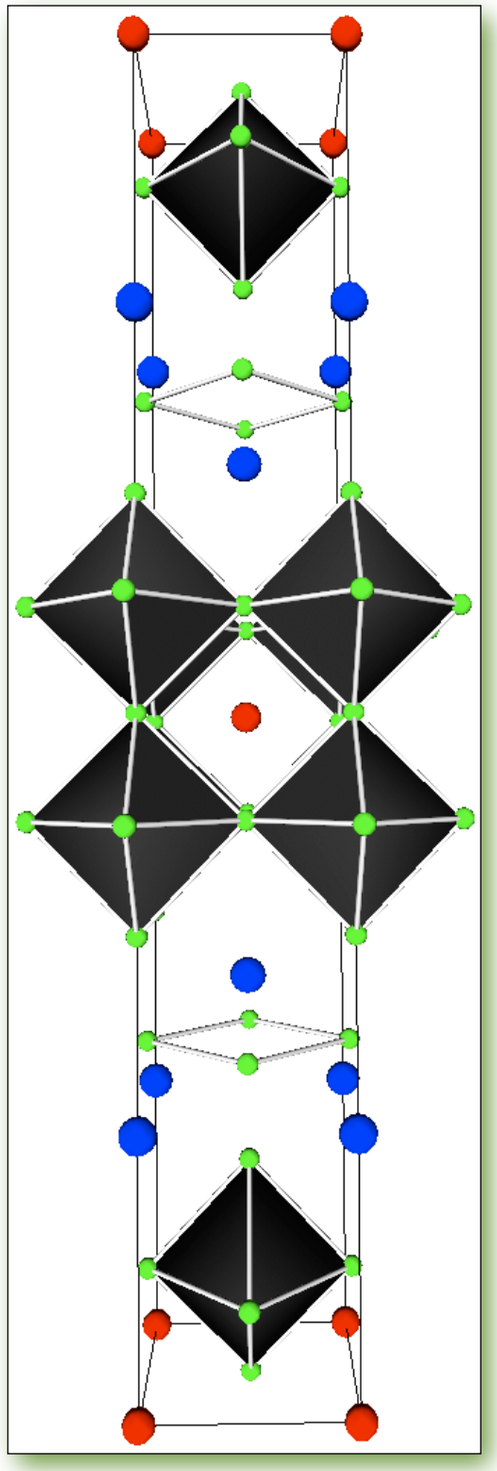
(P,p)=

$$\begin{pmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

[i]=[8]

$\mathcal{H}$ — $Cmc2_1$ (36)

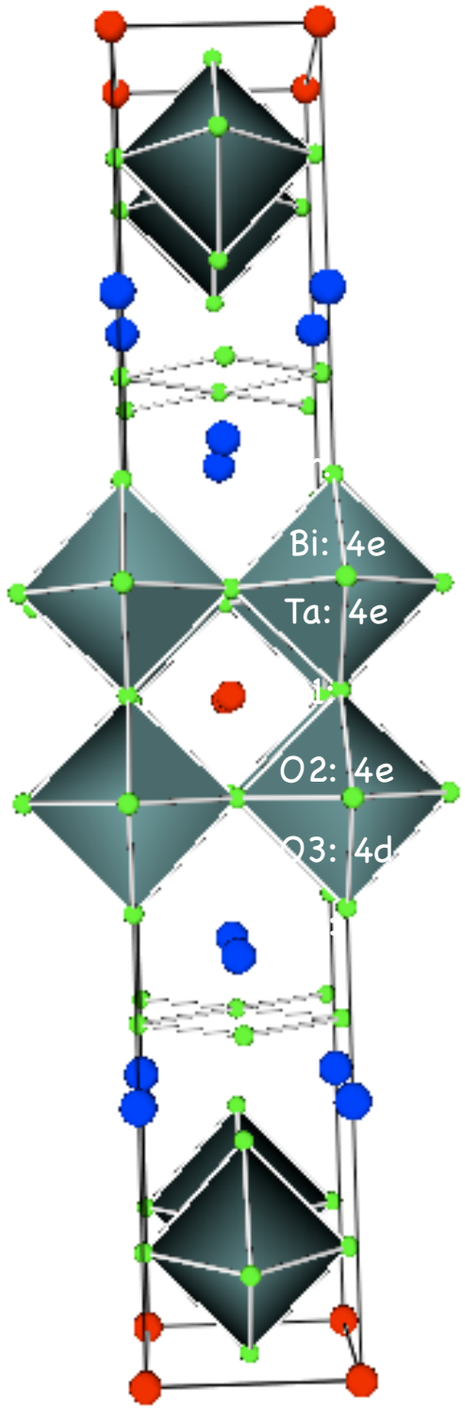
Low-temperature ferroelectric



AMPLIMODES

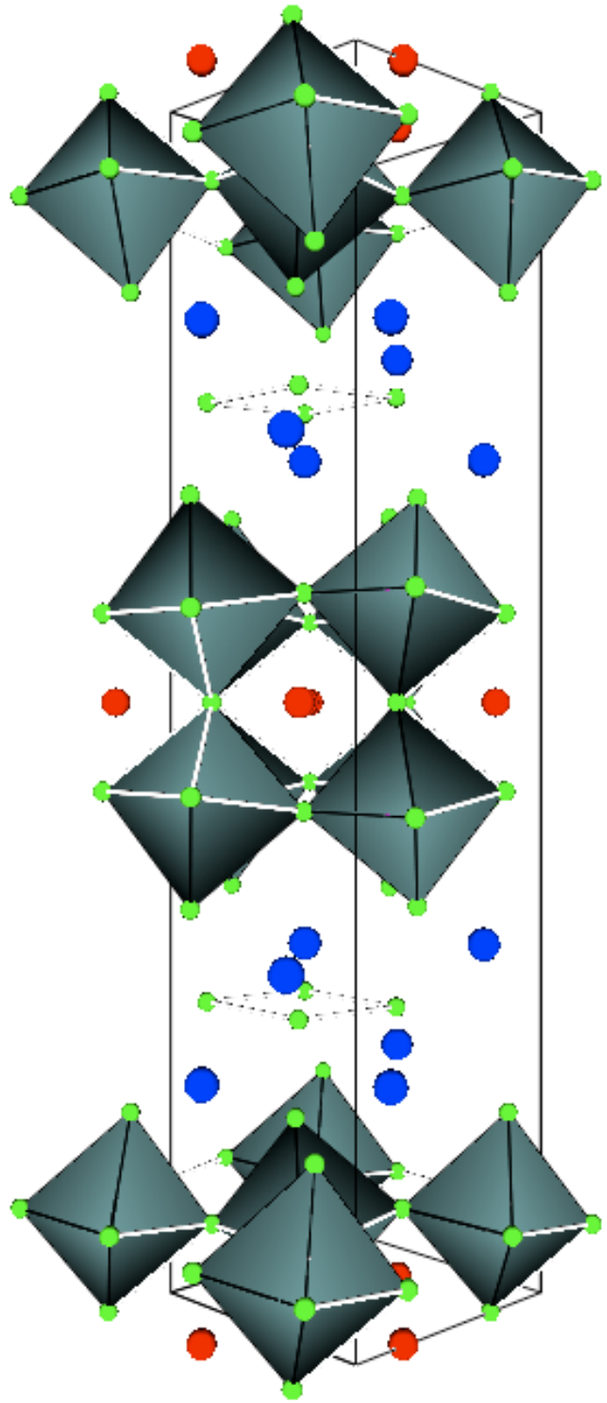
Example: $SrBi_2Ta_2O_9$ (SBT)

$$(\mathbf{a},\mathbf{b},\mathbf{c})_{\mathcal{H}} = (\mathbf{a},\mathbf{b},\mathbf{c})_{\mathcal{G}} \begin{pmatrix} 0 & 1 & 1 \\ 0 & -1 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$



I4/mmm (139) → $Cmc2_1$ (36)

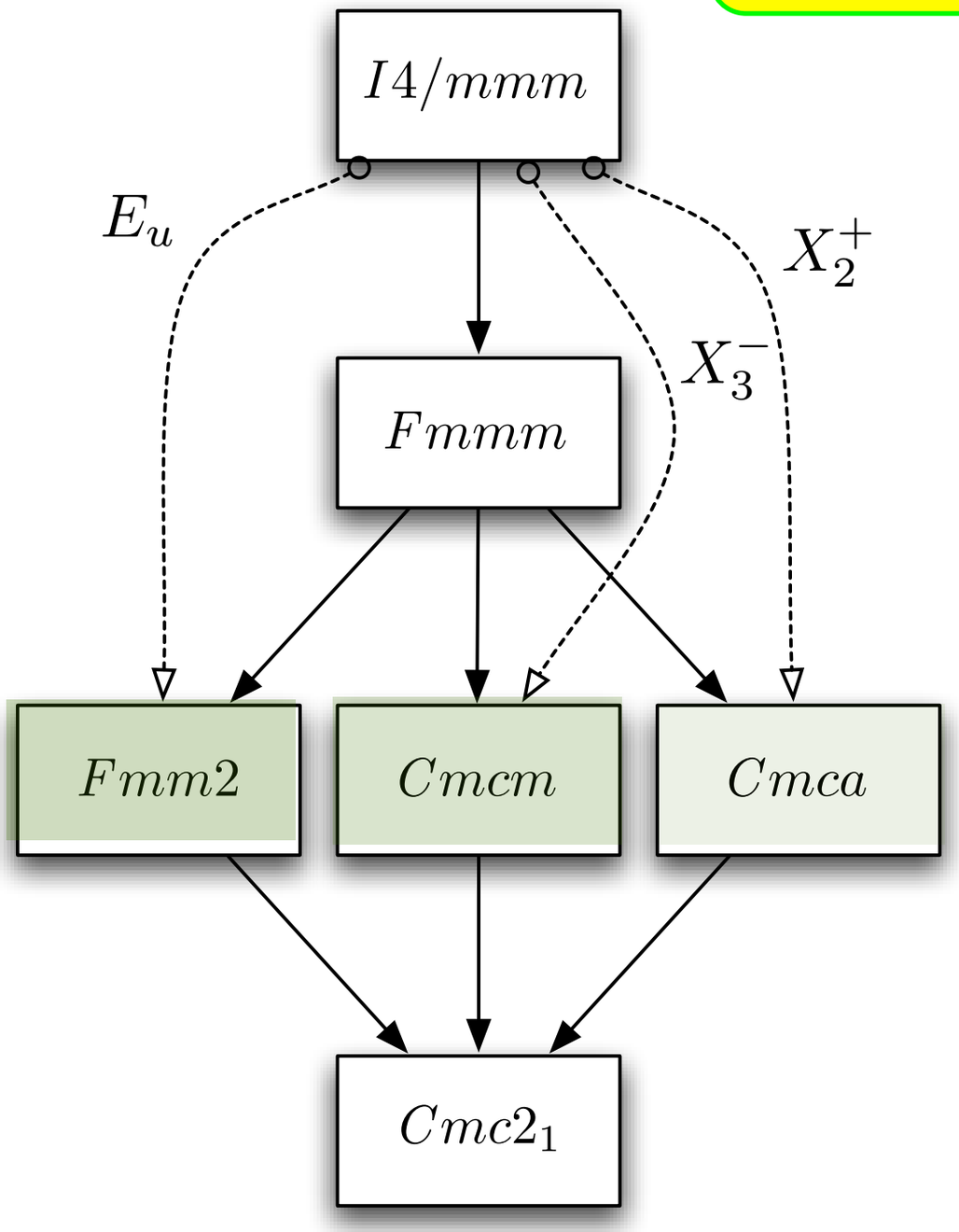
Sr: 2a	⟷	Sr: 4a
Ta: 4e	⟷	Ta: 8b
Bi: 4e	⟷	Bi: 8b
O1: 2b	⟷	O1: 4a
O2: 4e	⟷	O2: 8b
O3: 4d	⟷	O3: 8b
O4: 8g	⟷	O4: 8b
	⟷	O5: 8b



Structural data ⟶ Global distortion

Example: $SrBi_2Ta_2O_9$ (SBT)

AMPLIMODES

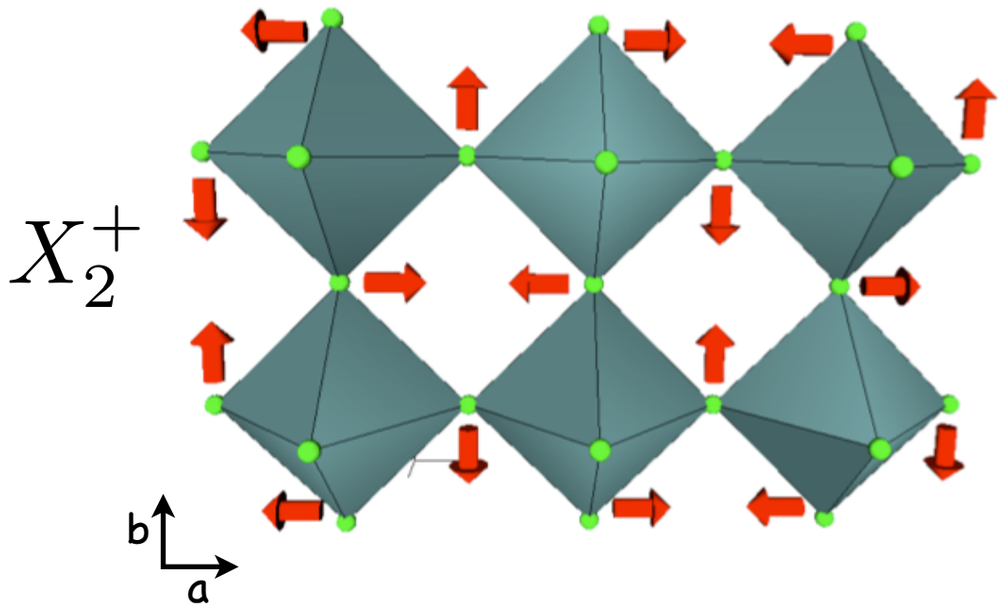


At least two modes for breaking the symmetry to $Cmc2_1$

Coupled order parameters

$$\begin{cases} E_u \\ X_3^- \\ X_2^+ \end{cases}$$

Three types of contributions to the global distortion



$$\{\text{Distortion}\} = Q_{E_u}(E_u) + Q_{X_2^+}(X_2^+) + Q_{X_3^-}(X_3^-)$$

0.6134 Å 0.2603 Å 0.8970 Å

Problem: PSEUDOSYMMETRY SEARCH

PSEUDO

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 H	=	Structure G	+	small (symmetry-breaking) distortion

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

↓

phase transition

Applications: **PSEUDO**

Prediction of phase transitions

Search for ferroic materials
-new ferroelectrics
-new 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)

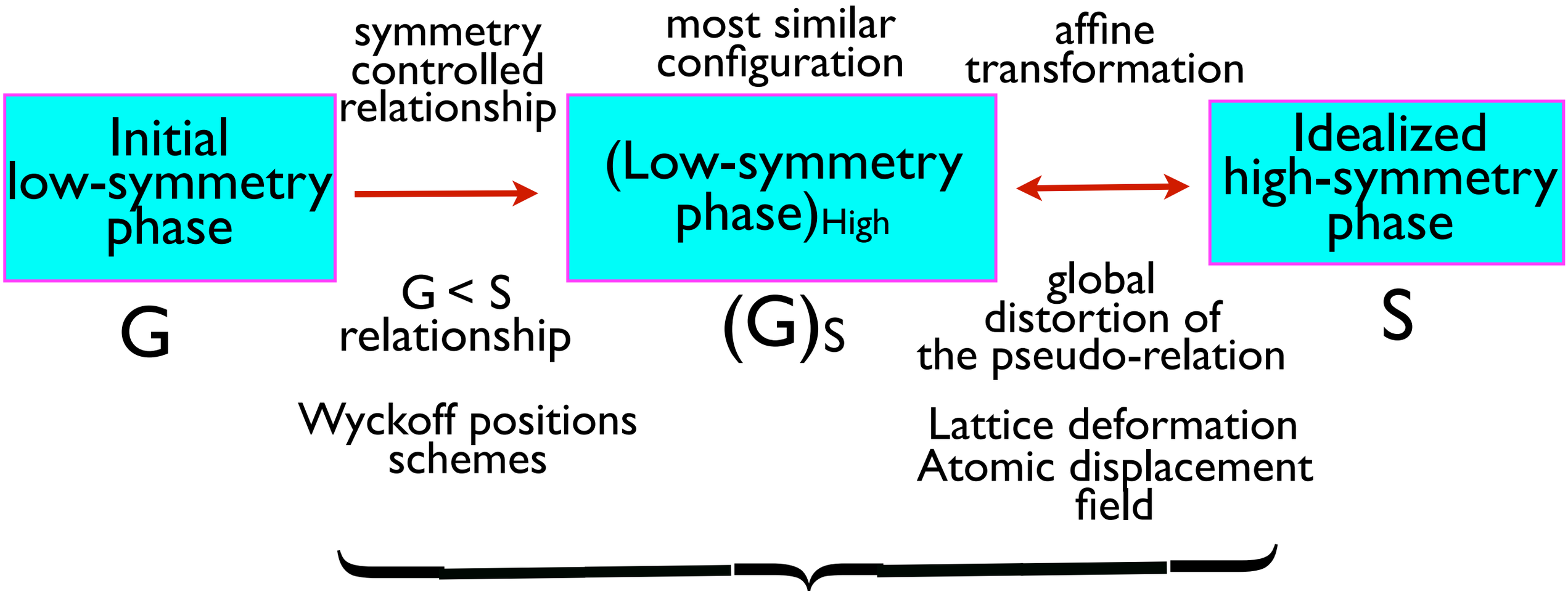
Determination of an optimised virtual parent structure (paraphase)

Structural Pseudosymmetry

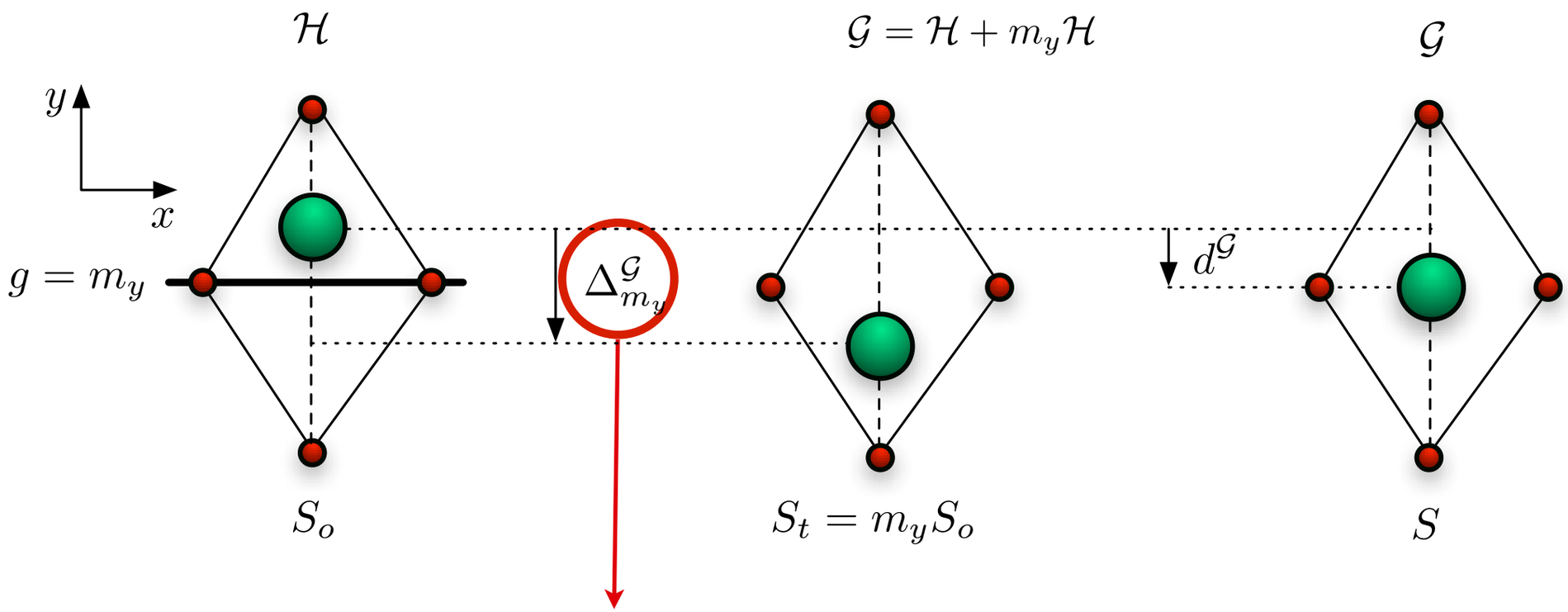
PROBLEM:

Given the initial structure specified by space-group symmetry G its unit-cell parameters and atomic coordinates

Search for a structure of space-group symmetry S>G such that the initial structure can be described by the high-symmetry structure with tolerably small distortion



PSEUDO: ATOMIC DISPLACEMENTS METHOD



Maximal distance between all compatible atom pairings

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

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

EXERCISES

Problem 2.5 (i)

Analyse the structural pseudosymmetry of Pb_2MgWO_6

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

```
#(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
```

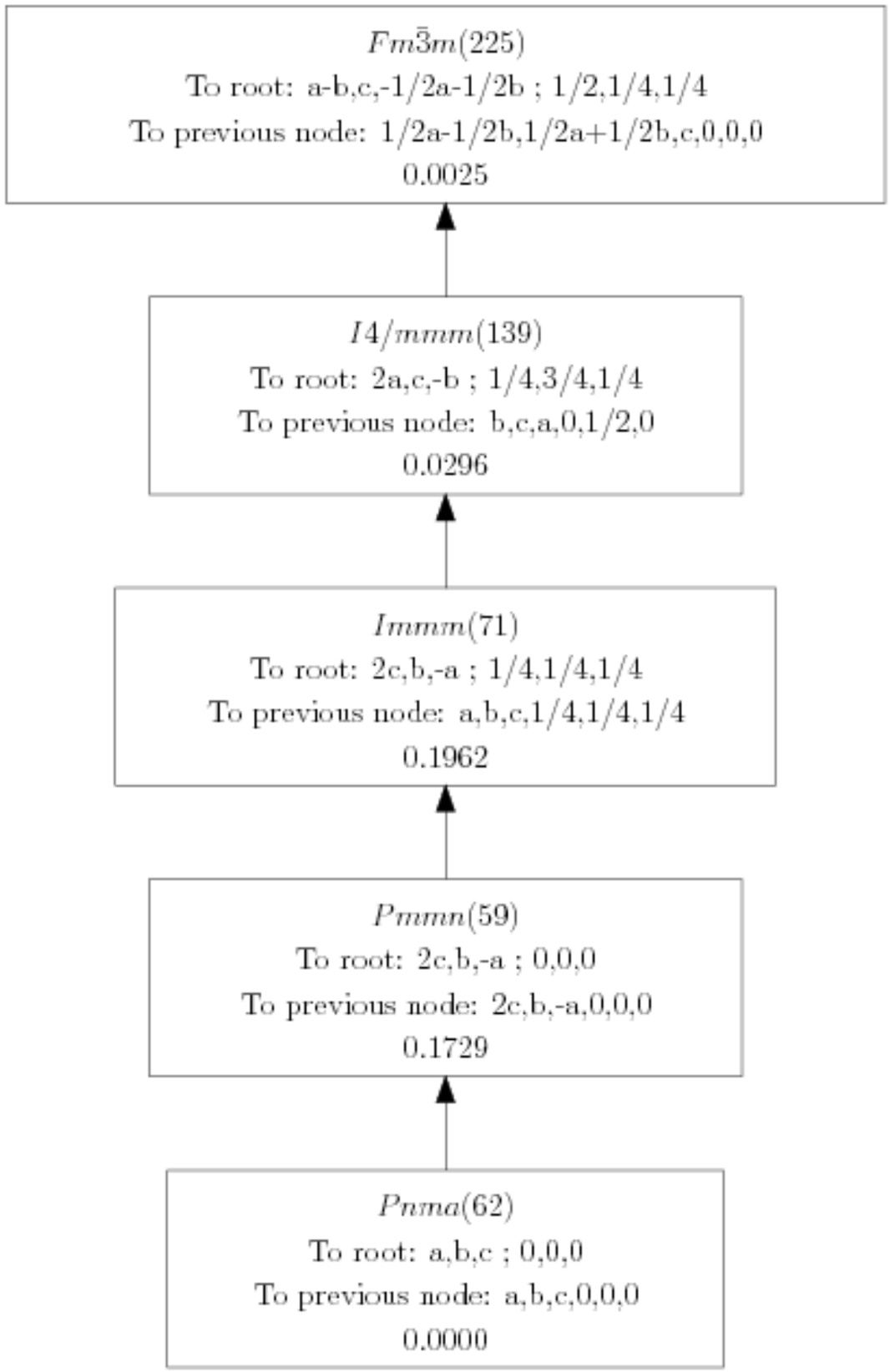
Structural pseudosymmetry of Pb_2MgWO_6

Graph of minimal supergroups

each step is characterized by:

-transformation matrices $(P,p)_i$

-maximal displacements

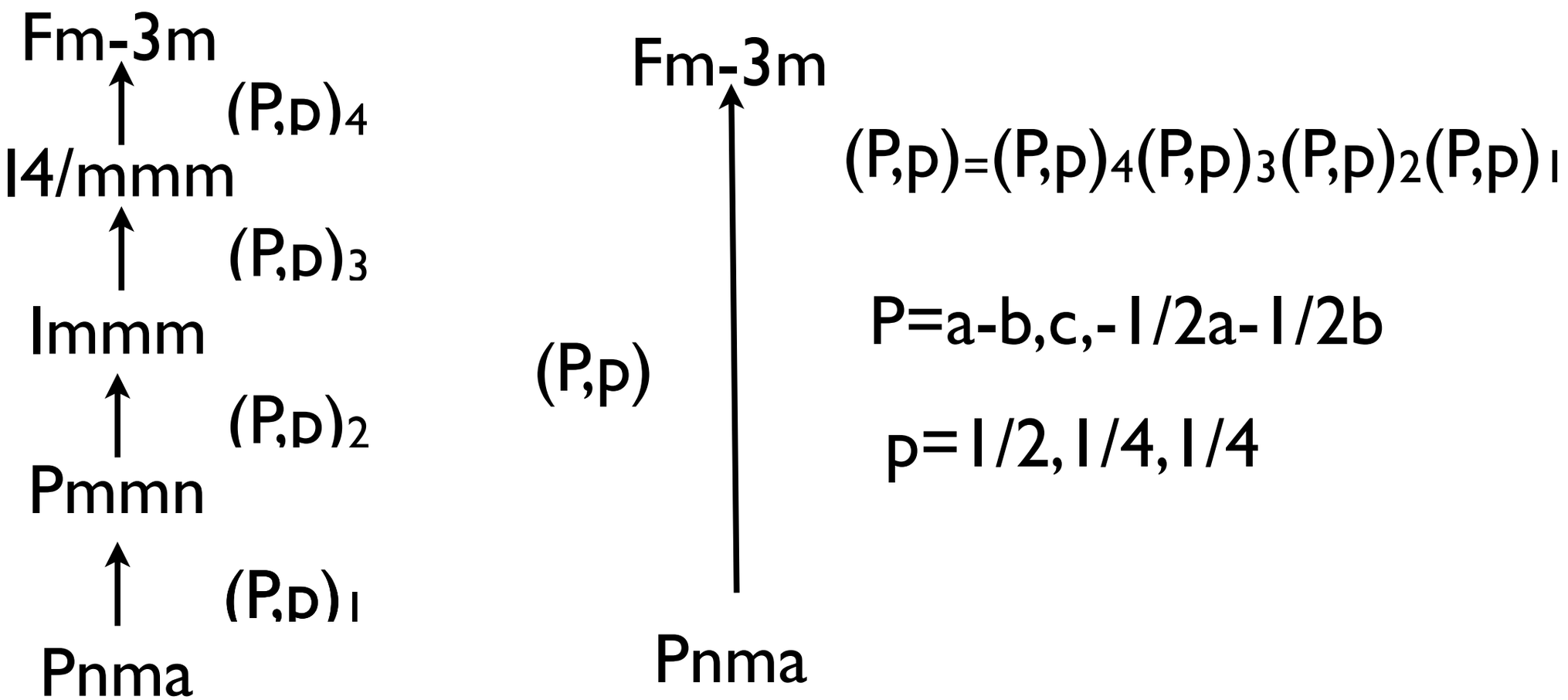


EXERCISES

Problem 2.5 (ii)

Analyse the structural pseudosymmetry of Pb_2MgWO_6

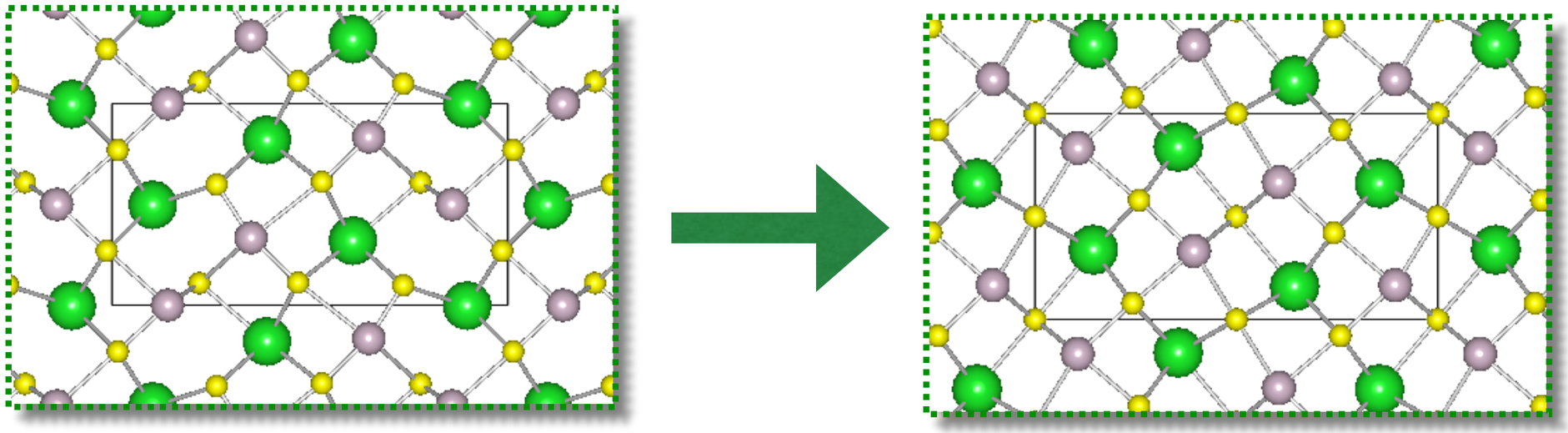
Option 3: Search of structural pseudosymmetry with respect to specific supergroup



Problem: Search for ferroelectrics (as pseudosymmetric structures)

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”)



$Pna2_1$ $BaHgS_2$ Pbam

(max. displacement 0.49 A)

Problem: Prediction of *Pna2₁* ferroelectrics

PSEUDO

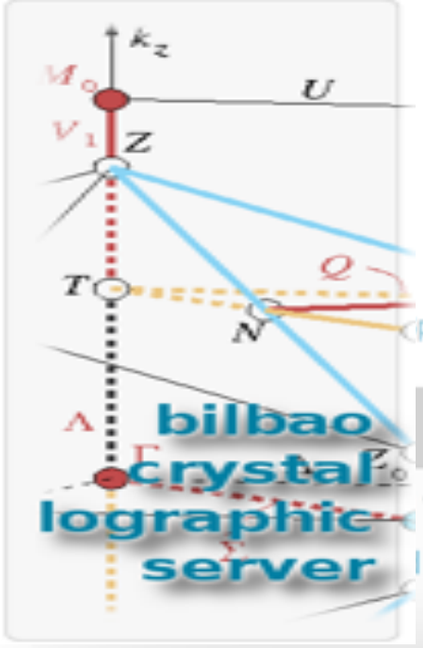
ICSD (Inorganic Crystal Structure Database)

	Binary	Ternary	Quaternary	Total
Entries	39	202	223	464
Compounds	26	125	161	312
Pseudo. Entries	20	100	40	160
Pseudo. Compounds	12	66	36	114
Overlooked Sym.	7	30	9	46
Known Ferro.	1	14	4	19
Candidates?	1	13	4	18

Problem 2.6

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, $P6_3/mmc$.



bilbao crystallographic server

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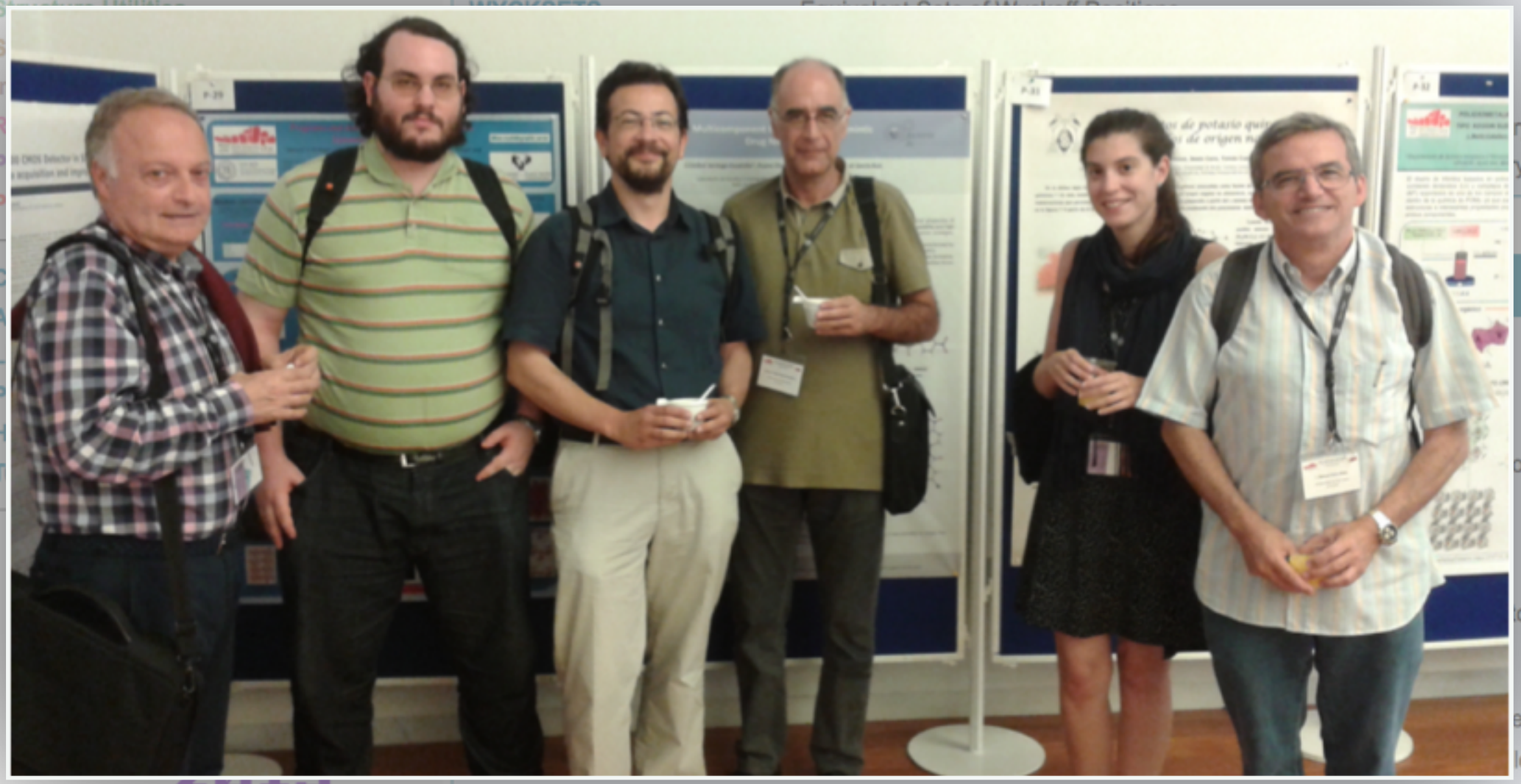

http://www.cryst.ehu.es