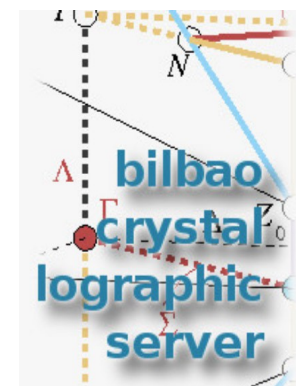


Crystallography Online: Workshop on the use and applications of the structural tools of the Bilbao Crystallographic Server

20-21 August 2018



Satellite Meeting
31st European Crystallographic Meeting
Oviedo



CRYSTAL-STRUCTURE RELATIONSHIP BILBAO CRYSTALLOGRAPHYC SERVER

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CRYSTAL-STRUCTURE RELATIONSHIP

Structure relations

Symmetry relations between crystal structures



www.cryst.ehu.es



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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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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

Point-group symmetry

Plane-group symmetry

ECM:

Crys
works
applicat
to
Crys

20

News:

• New

01/20

mCIF

• New

11/20

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).

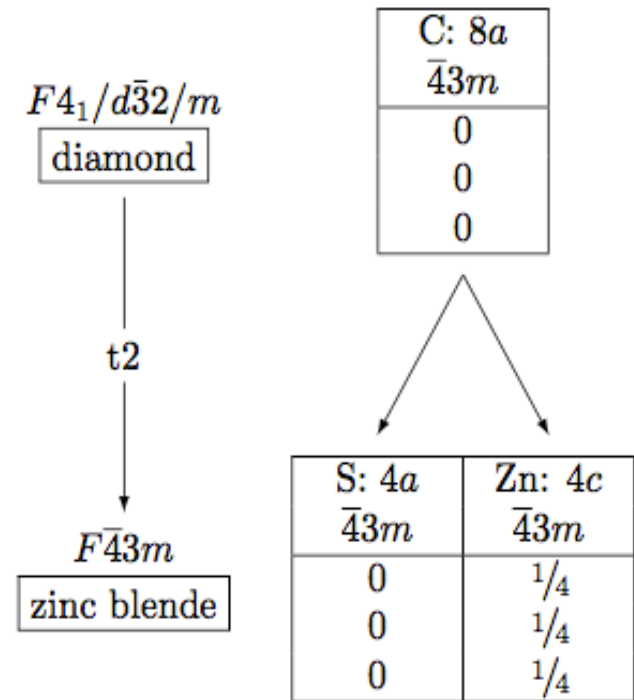


Structure relations

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

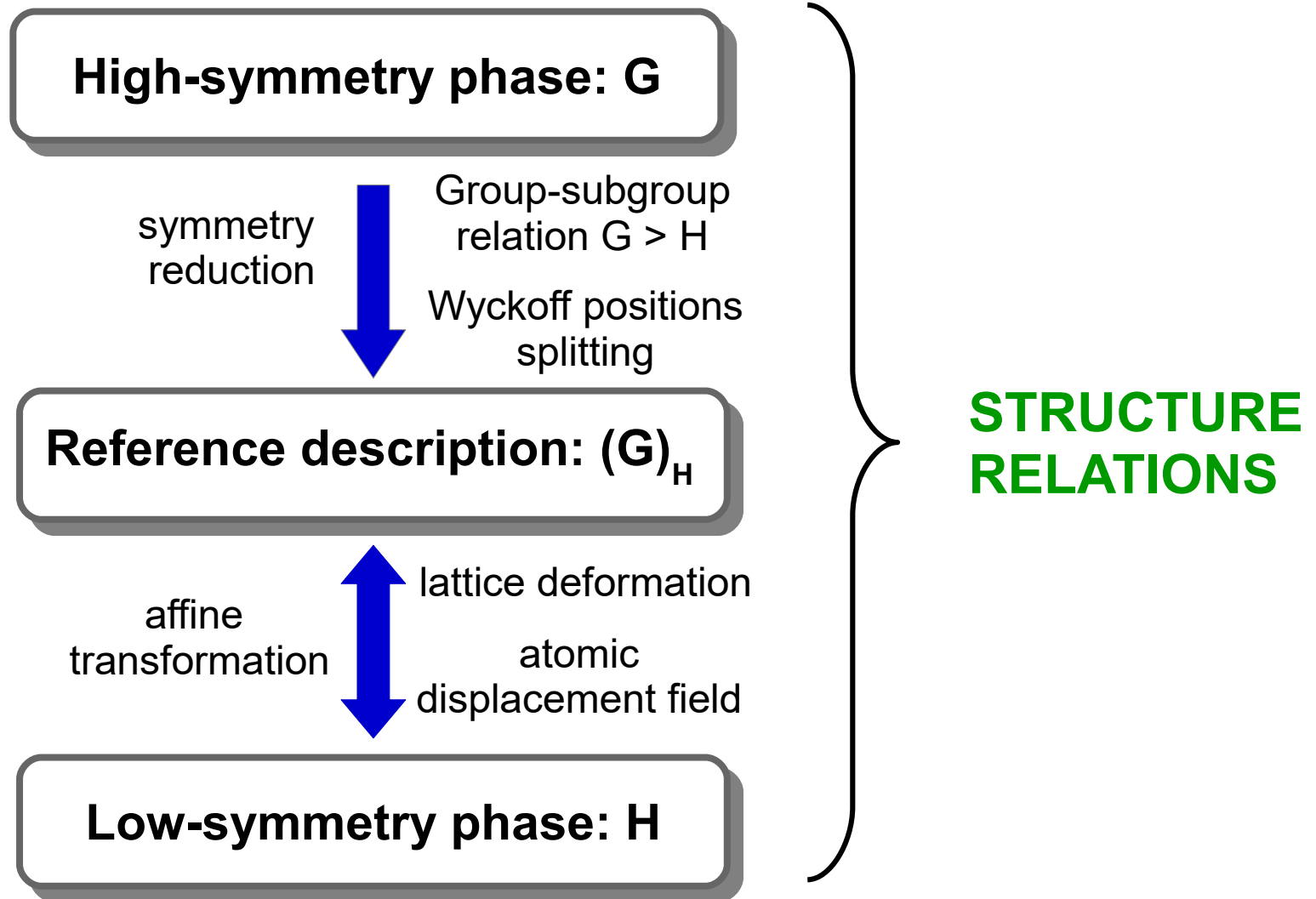
Applications:

- 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 $\mathbf{G} > \mathbf{H}$



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.

```
# 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
```

BCS Format

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.

```
# 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
```

BCS Format

STRUCTURE RELATIONS

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

Calculation parameters:

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

Enter the maximum distance allowed between the paired atoms: 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**:



Structure relations

Pm-3m high-symmetry phase

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

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)	$d_{\text{av.}}$ (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 2.1

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 $a = 4.9586\text{\AA}$, $c = 6.9074\text{\AA}$. 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 $Fd\bar{3}m(227)$, $a = 7.147\text{\AA}$. 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 2.1(1)

α -Cristobalite \rightarrow β -Cristobalite

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=44094		Details	Bonds	Pattern	Structure	Jmol	CC=44095		Details	Bonds	Pattern	Structure	Jmol
Title	First-principles study of crystalline silica.						Title	First-principles study of crystalline silica.					
Authors	Feng Liu;Garofalini, H.;King-Smith, D.;Vanderbilt, D.						Authors	Feng Liu;Garofalini, H.;King-Smith, D.;Vanderbilt, D.					
Reference	Physical Review, Serie 3. B - Condensed Matter (1994) 49 , 12528-12534 Link XRef SCOPUS SCIRUS Google Also: Phase Transition (1992) 38 , 127-220						Reference	Physical Review, Serie 3. B - Condensed Matter (1994) 49 , 12528-12534 Link XRef SCOPUS SCIRUS Google Also: Phase Transition (1992) 38 , 127-220					
Compound	Si O2 - [Cristobalite alpha] Silicon oxide - HT [AX2] [tP12] [b a] [TeO2(alpha)]						Compound	Si O2 - [Cristobalite beta] Silicon oxide - HT [AX2] [cF24] [h a] []					
Cell	4.9586, 4.9586, 6.9074, 90., 90., 90. P41212 (92) V=169.84						Cell	7.147, 7.147, 7.147, 90., 90., 90. FD3-MS (227) V=365.07					
Remarks	MIN =Cristobalite alpha : PDC =01-089-3434 : PDF =39-1425 : THE TYP =TeO2(alpha) : XDS At least one temperature factor missing in the paper. No R value given in the paper. Metastable up to 500 K (2nd ref. , Tomaszewski), above Fd3-m						Remarks	MIN =Cristobalite beta : PDC =01-089-3435 : PDF =4-359 : THE XDS At least one temperature factor missing in the paper. The coordinates are those given in the paper but the atomic distances do not agree with those calculated during testing.The coordinates are probably correct. No R value given in the paper. Metastable above 500 K (2nd ref. , Tomaszewski), stable above 1743 K					
Atom (site) Oxid.		x, y, z, B, Occupancy					Atom (site) Oxid.		x, y, z, B, Occupancy				
Si1	(4a)	4	0.3028	0.3028	0	0 1	Si1	(8a)	4	0	0	0	0 1
O1	(8b)	-2	0.2383	0.1093	0.1816	0 1	O1	(96h)	-2	0.125	0.081	0.169	0 0.1667

Origin choice 2:

Si 8a $1/8, 1/8, 1/8$ $7/8, 3/8, 3/8$

Exercise 2.2 (a)

Lead phosphate phase transition

- (a) Lead phosphate $\text{Pb}_3(\text{PO}_4)_2$ 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.



Exercise 2.2 (b)

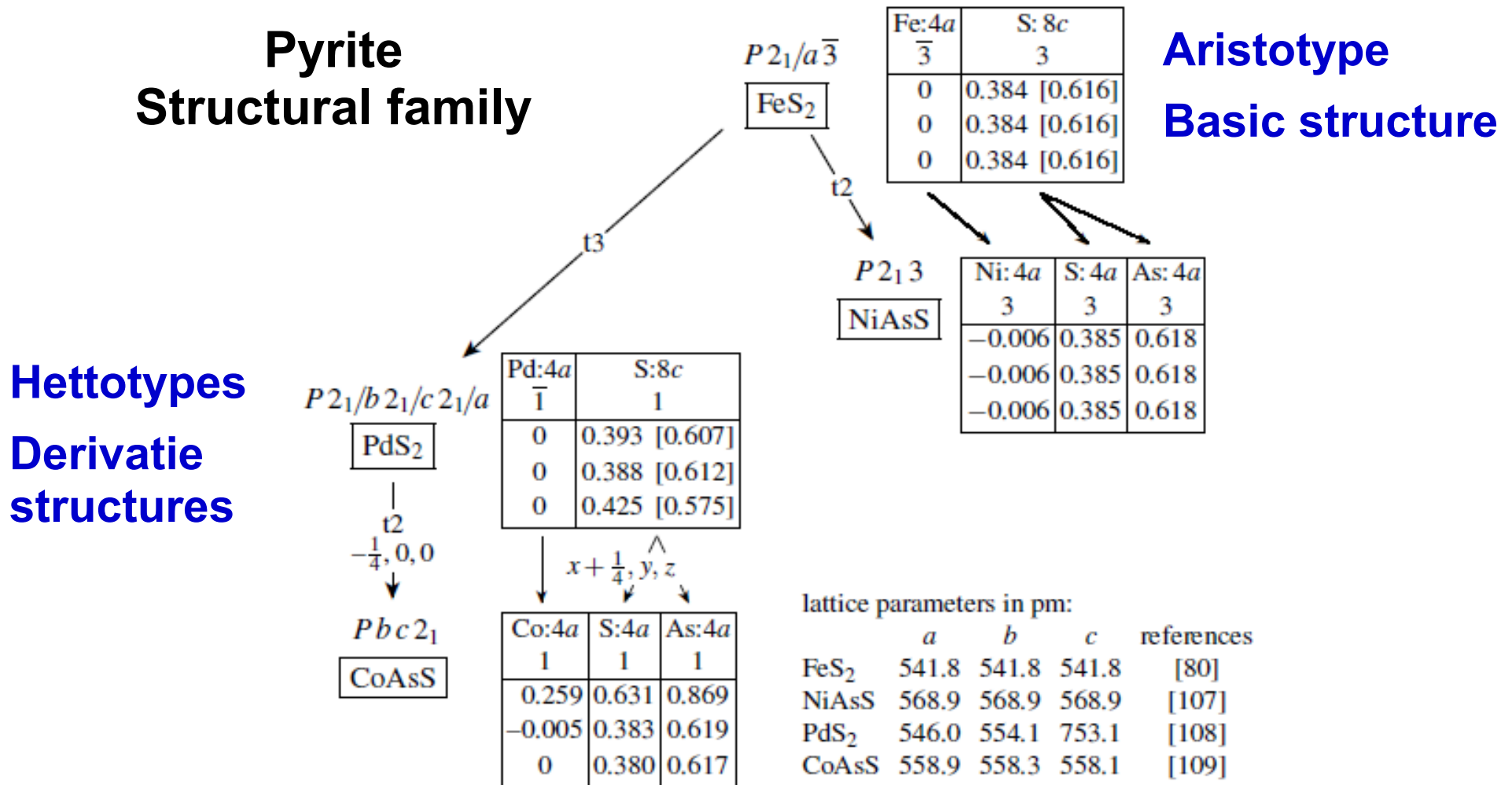
Lead vanadate phase transition

- (b) Lead phosphate-vanadate $\text{Pb}_3(\text{PVO}_4)_2$ shows a phase transition from a paraelastic high-temperature phase with symmetry $R\bar{3}m$ (No.166) to a ferroelastic phase of symmetry $P2_1/c$ (No.14). Using the structure data given in the *ExerciseData* file and the tools of the *Bilbao Crystallographic Server* 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

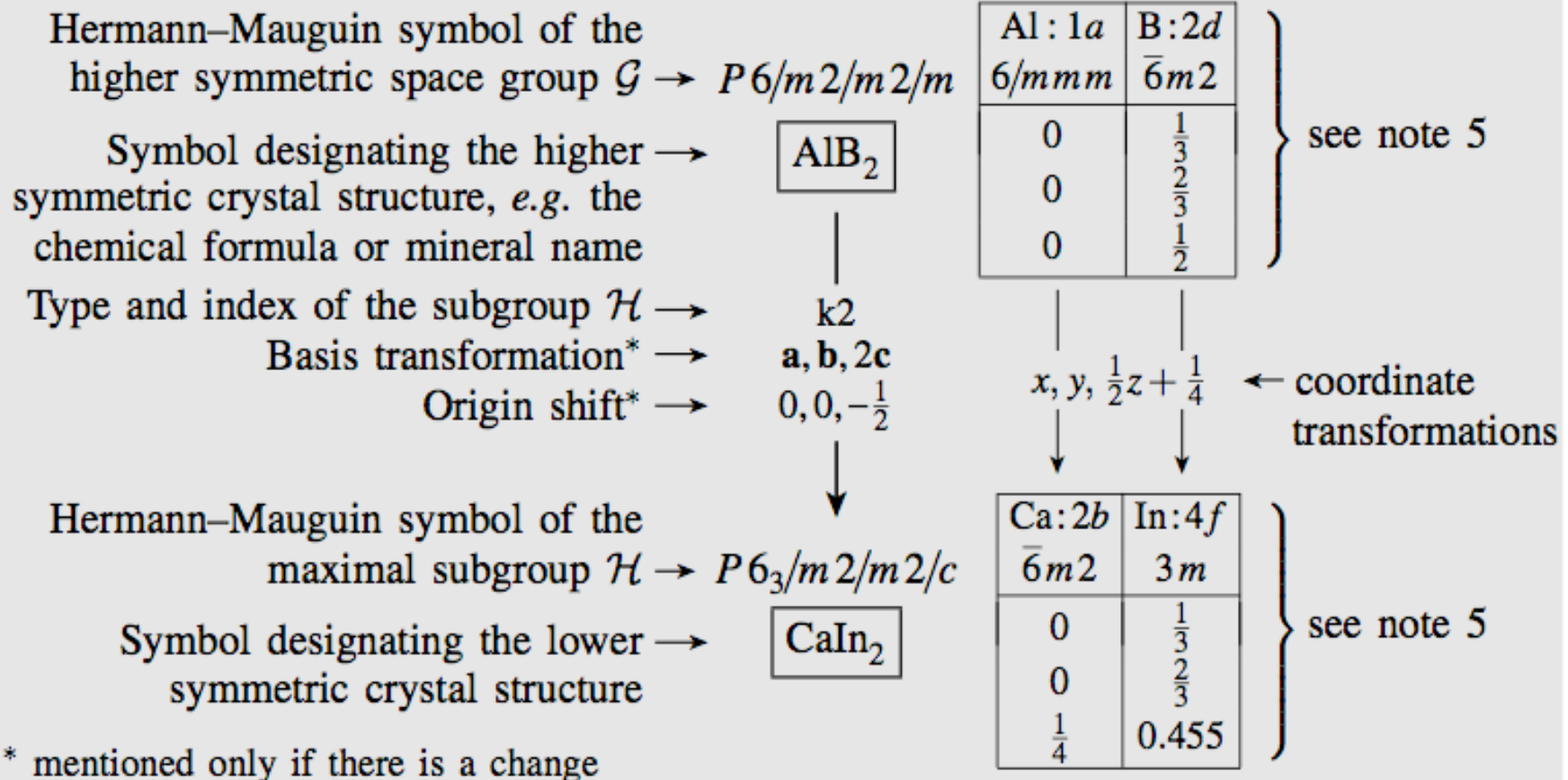
Bärnighausen Trees



Bärninghausen Trees

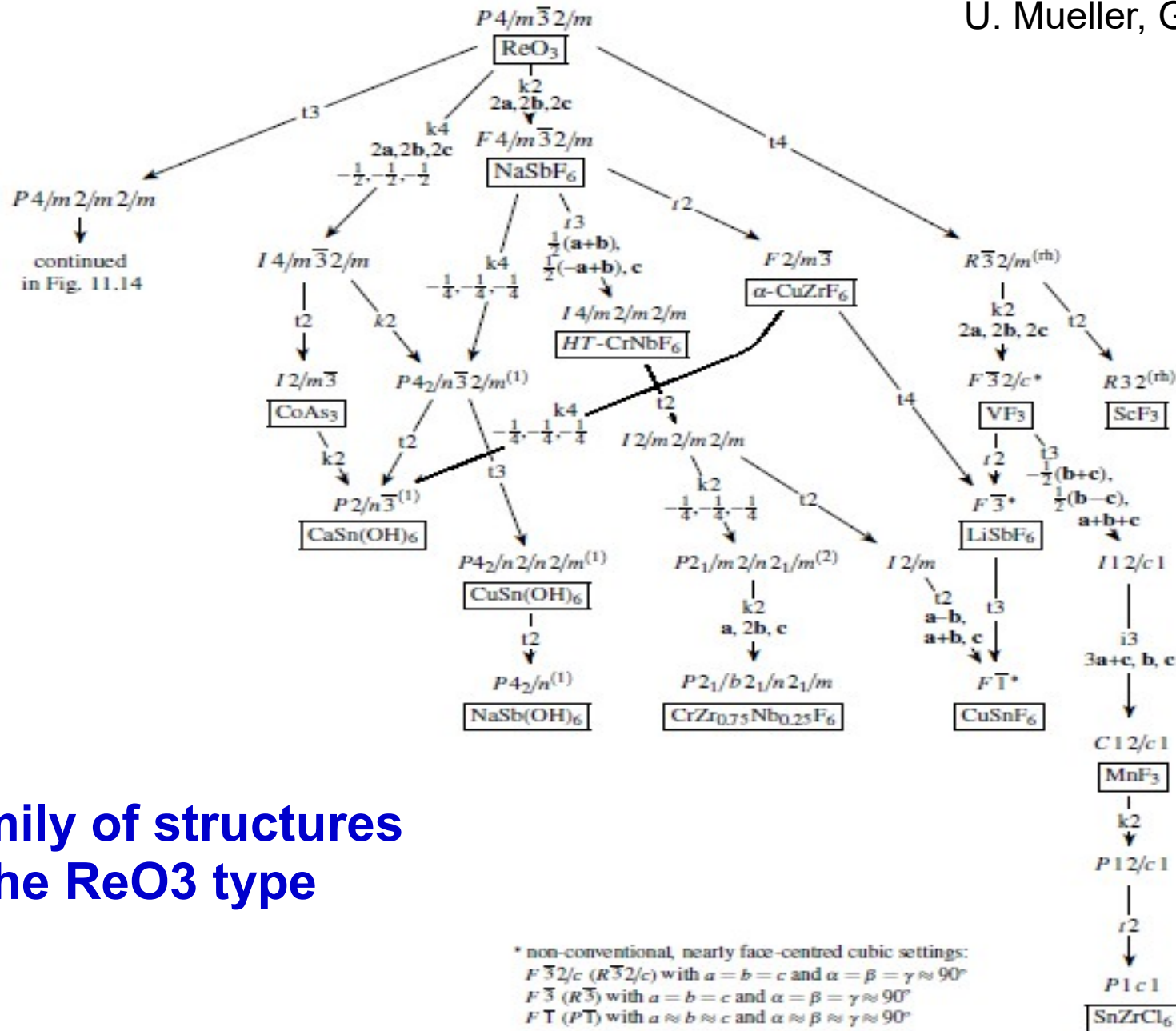
Module design of crystal symmetry relations

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



Bärninghausen Trees

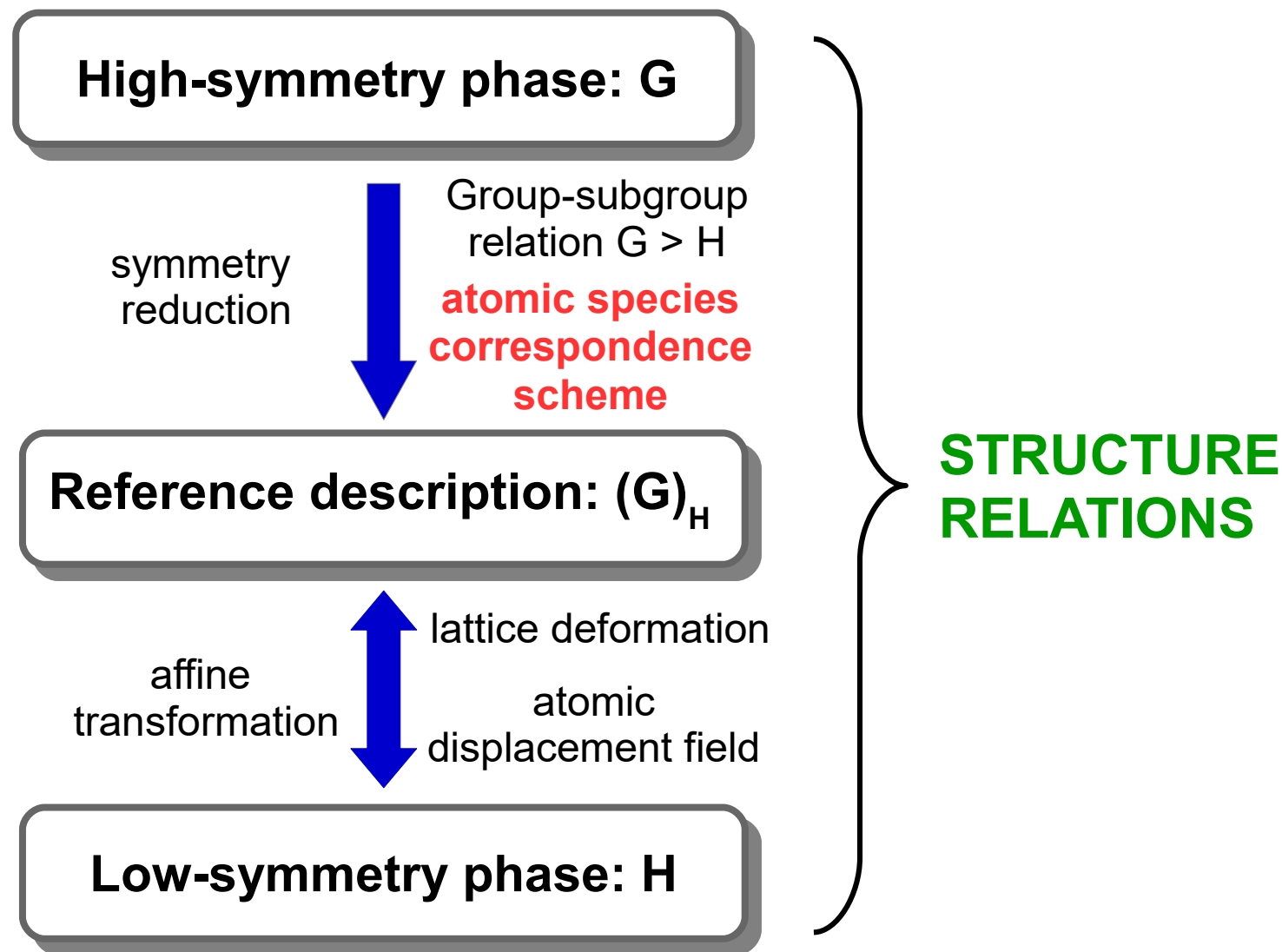
U. Mueller, Gargnano 2008



The family of structures
of the ReO3 type

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
```

Different atomic species

Calculation parameters:

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

Enter the maximum distance allowed between the paired atoms: Å

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

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 3.007000 0.000000 90.000000 90.000000
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
```

Calculation method:

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

User defined group-subgroup **transformation matrix**:

Species Matching:

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



Exercise 2.3

Hettotype of CsCl structure

Show that the crystal structure of CoU maybe interpreted as a slightly distorted CsCl (or β -brass, CuZn)-type structure. Using the structural data in the Exercise Data 1e, characterize the structural relationship between the CoU structure and CsCl structure.

```
#CuZn (CsCl type): P432  
221  
2.959 2.959 2.959 90. 90. 90.  
2  
Cu 1 1a 0 0 0  
Zn 1 1b 0.5 0.5 0.5
```

```
#CoU type:I213  
199  
6.3557 6.3557 6.3557 90. 90. 90.  
2  
Co 1 8a 0.294 0.294 0.294  
U 1 8a 0.0347 0.0347 0.0347
```

